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Development of Novel Synthetic Methods and Reaction Media for Selective Functionalization of Fullerenes

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January 2013

Department of Applied Chemistry

Graduate School of Engineering

Osaka University

Development of Novel Synthetic Methods and Reaction Media for Selective Functionalization of Fullerenes 2013 Toshiki Na

Development of Novel Synthetic Methods and Reaction Media for Selective Functionalization of Fullerenes

（フラーレンの選択的官能化を指向した新規官能化法および反応媒体の開発）

2013

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Preface

The studies presented in this thesis were conducted under the supervision by Professor Dr. Satoshi Minakata, Department of Applied Chemistry, Graduate School of Engineering, Osaka University during 2007-2013.

The objects of this thesis are development of novel methodologies and reaction media for selective functionalization of fullerenes. The author hopes that the fundamental work described in this thesis contributes to further development of synthetic methods in fullerene chemistry, functional material, and other related fields of chemistry.

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Contents

Chapter 1 Highly Selective Synthesis of Azafulleroids and Aziridinofullerenes Utilizing *N,N*-Dihaloamide Reagents

Chapter 2 Selective Diels-Alder Reaction of C_{60} and 1,3-Dienes in MCM-41 as A Reaction Medium

Chapter 3 Encapsulation of C_{60} into Functionalized γ-Cyclodextrin and the Reaction Behavior of the Complex

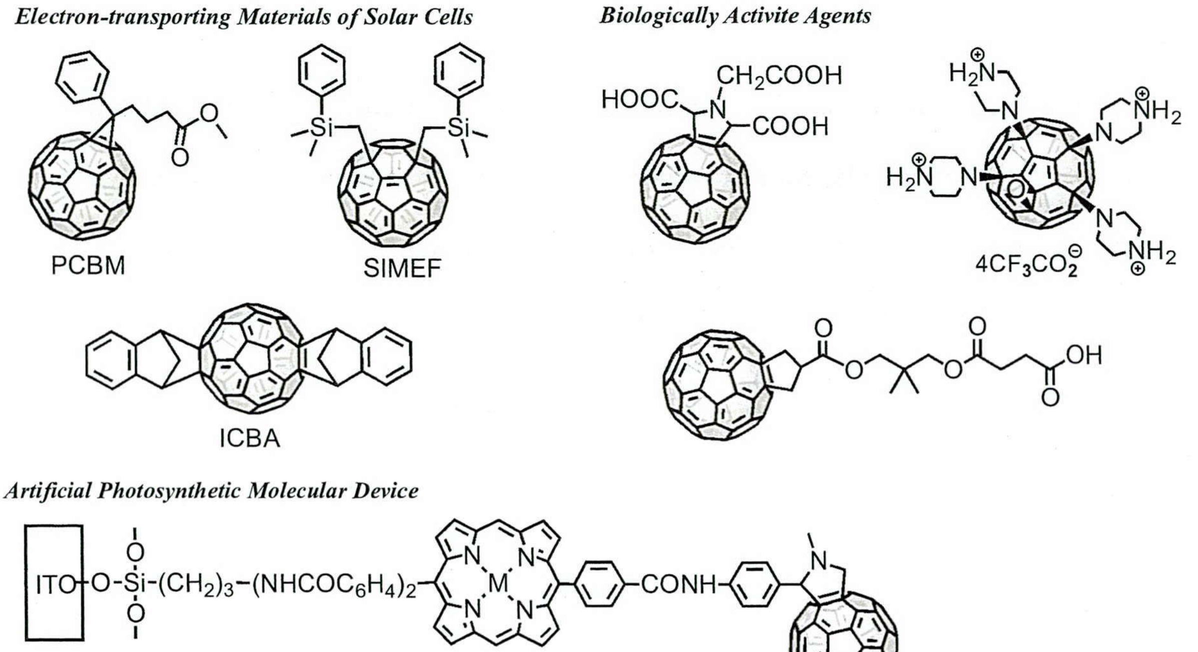
General Introduction

1. Fullerenes

Fullerenes, which have closed-cage shapes, consist of only sp^2-hybridized carbon atoms, and constitute the third allotrope of carbon besides diamond and graphite. C_{60} is the most stable, abundant, and representative molecule of fullerene family. The existence and unique soccer ball-like structure with spherical I_h-symmetry of C_{60} were firstly predicted by Osawa in 1970,[1a,b] although it was 15 years later that its existence was certainly proven by Curl, Kroto, and Smalley.[1c] Since the discovery of C_{60}, extensive studies on functionalization of C_{60} and C_{60} derivatives as materials have been reported due to their fascinating physical and chemical properties.[2]

2. A Variety of Functionalized C_{60}

A number of functionalized C_{60} have been synthesized and applied to a variety of fields, because of the unique chemical and electronic properties of C_{60}. For example, Wudl *et al.* have developed [6,6]-phenyl-C_{61}-butylic acid methyl ester (PCBM). Since this compound was revealed to have high electron-transporting ability, it is applicable to bulk heterojunction (BHJ) solar cells as an electron-transporting material (Figure 1).[3] Li *et al.* as well as Nakamura and Matsuo's groups devised more efficient photovoltaic devices based on C_{60} derivatives (ICBA[4f] and SIMEF[4g], respectively). Other many groups also have been engaged in creating superior fullerene-based materials that show the higher power conversion efficiencies (PCEs).[4] Fukuzumi *et al.* reported artificial photosynthetic molecular devices based on C_{60}–porphyrin dyad.[5] Furthermore, some C_{60} derivatives have been designed for potential biological usage such as gene delivering agents and HIVP inhibitors.[6] Hence, from the view points of the exploration of C_{60}-based functional materials, the development of novel synthetic methods for functionalization of C_{60} is of significant importance.



Electron-transporting Materials of Solar Cells

Biologically Activite Agents

Artificial Photosynthetic Molecular Device

Figure 1. Examples of functionalized fullerene derivatives and their applications.

3. Chemical Reactivity and Reactions of C_{60}

In addition to the pyramidalization of carbon atoms of C_{60} that confers excess strain on the molecule, triply-degenerated and energetically-low LUMOs are responsible for the high reactivity toward various nucleophilic reagents. In a sense, therefore, the chemical reactivity of C_{60} is similar to that of electron-deficient olefins.[7] Utilizing this unique reactivity of C_{60}, methods to functionalize C_{60} have been widely investigated (Figure 2)[8]: C_{60} undergoes the [4 + 2] Diels-Alder, [3 + 2] 1,3-dipolar, and [2 + 2] cycloaddition reactions as well as nucleophilic and radical addition reactions. Meanwhile, in the presence of Lewis acid, electrophilic addition reactions, exemplified with the Friedel-Crafts reaction, proceed through the intermediacy of fullerene cation. Furthermore, some addition reactions catalyzed by transition metals have been developed, allowing for the direct introduction of aryl, allyl, and alkynyl groups to C_{60}.[8c]

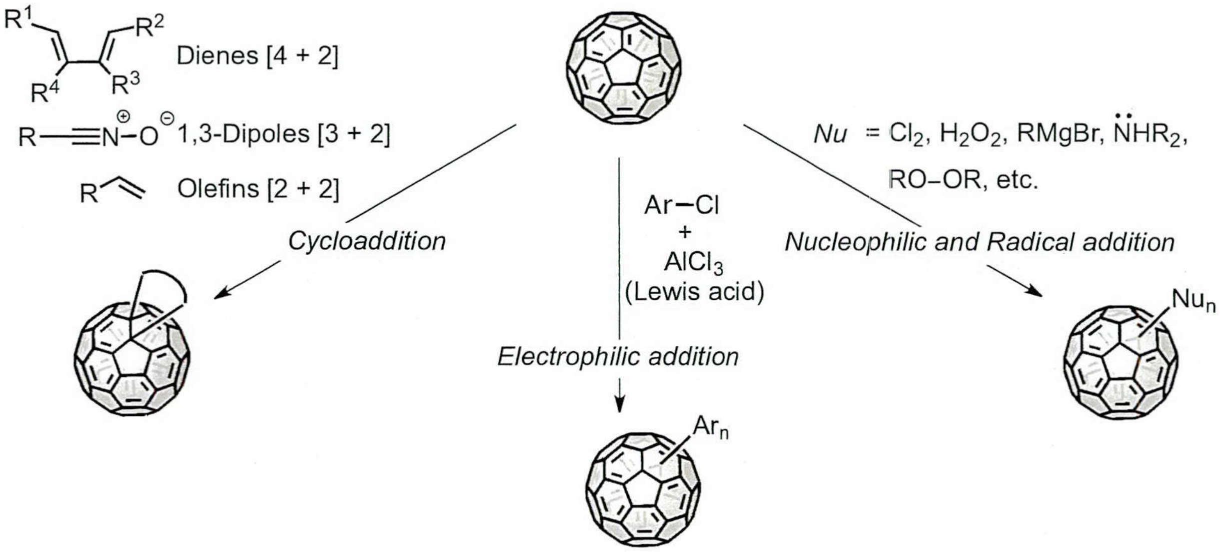


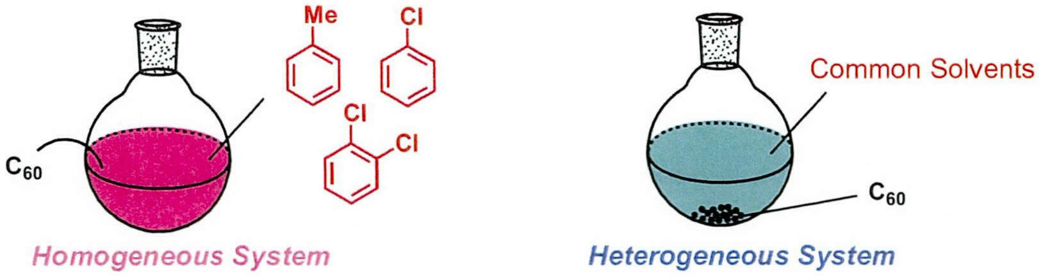
Figure 2. Representative addition reactions of C_{60}.

4. Problems in Functionalization of C_{60}

Although various methods to synthesize C_{60} derivatives have been reported, there still remain some problems in functionalization of C_{60} that are the case with higher fullerenes. The representative ones are solubility and selectivity as described below.

4-1. Solubility

In general, organic synthetic reactions are conducted in a homogeneous system. However, solvents that dissolve C_{60} are limited to arenes such as 1,2-dichlorobenzene, chlorobenzene, toluene, and benzene. C_{60} is sparingly soluble in common solvents such as chloroform, *n*-hexane, ethanol, and acetonitrile due to the highly symmetric structure and its tendency to aggregation (Figure 3).[9] The limitation in choosing solvents restrict applicable reagents, thereby leading to a major obstacle to develop new efficient functionalization methods of fullerenes.



Arenes	(mg/mL)
1,2-dichlorobenzene	27.0
chlorobenzene	7.0
toluene	2.8
benzene	1.7

Common Solvents	(mg/mL)
chloroform	0.160
n-hexane	0.043
ethanol	0.001
acetonitrile	0.000

Figure 3. Homogeneous (left) and heterogeneous (right) systems of C_{60} and its solubility in organic solvents.

So far, several research groups revealed that complexation of C_{60} is one of the efficient methods for the improvement of the apparent solubility in various solvents. For example, the use of the detergent Tween-20, phospholipids, micelles, liposomes, vesicles, or polyvinylpyrrolidone improved the apparent solubility of C_{60} in polar solvents such as water, alcohol, and DMSO, by including C_{60} into their hydrophobic phase.[10] Furthermore, Fujita *et al.* utilized the coronene-containing supramolecular complex as a pseudo-solvent, which enhanced the apparent solubility of C_{60} in toluene by ~30 times compered to the bare C_{60} (Figure 4).[11]

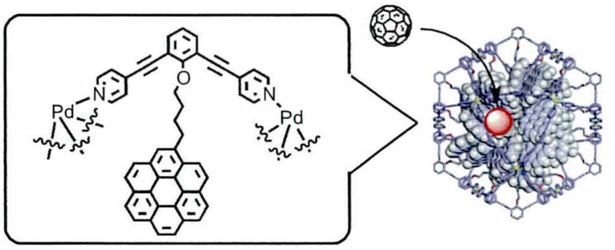


Figure 4. Enhancement of the apparent solubility of C_{60} by forming supramolar inclusion complex.

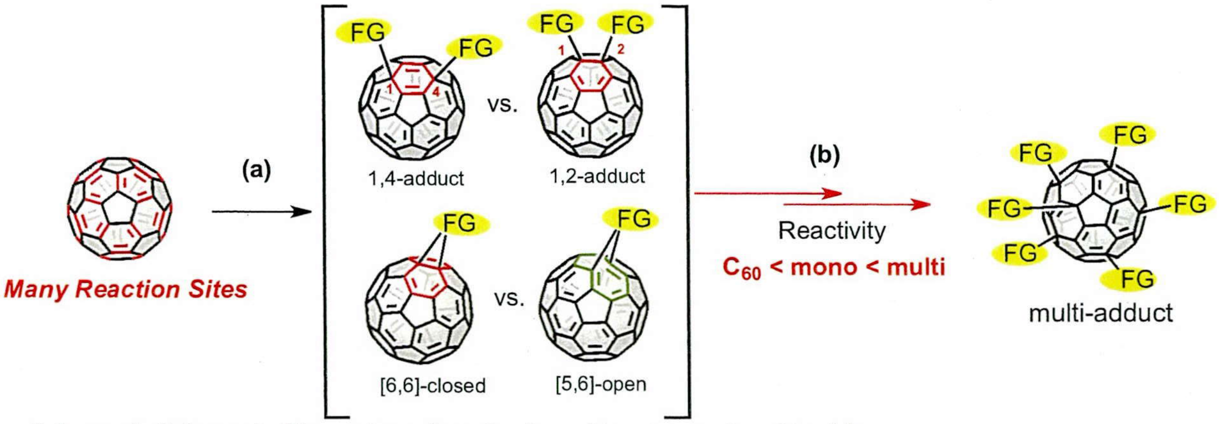
The spramolecular procedures described above raised the apparent solubility of C_{60}, but have not been utilized for reaction of C_{60}. Considering the homogeneous character of the complexation status, efficient derivatization of C_{60} in C_{60}-insoluble media would be feasible by developing novel reaction media for C_{60}.

4-2. Selectivity (Control of Reactivity and Reaction Sites)

Even though some reactions in homogeneous system proceed smoothly and efficiently, there still remains another significant problem in functionalization of C_{60}: the control of isomeric selectivity and multiplicity of reaction.

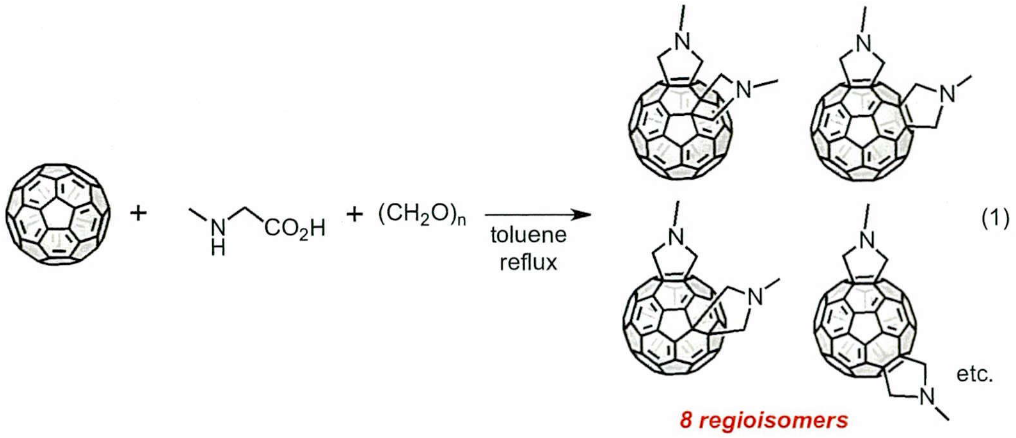
Since C_{60} has chemically equivalent 30 reaction sites, the reactions of C_{60} would afford several isomers (step **a** in Scheme 1).[8a,12] For example, the difference in the positions to which functional groups add, results in the formation of regioisomers (*e.g.* 1,2-adduct vs. 1,4-adduct). Moreover, functionalized C_{60} would have a couple of types of constitutional isomers such as C_2-symmetric [6,6]-closed and C_s-symmetric [5,6]-open structures. These isomers are quite difficult to separate from their reaction mixture.

In addition, as C_{60} derivatives possessing some special functional groups have higher reactivity than that of the pristine C_{60}, these situations are prone to yield multi-adducts (step **b** in Scheme 1). Therefore, the introduction of desired number of functional groups is a challenging task.



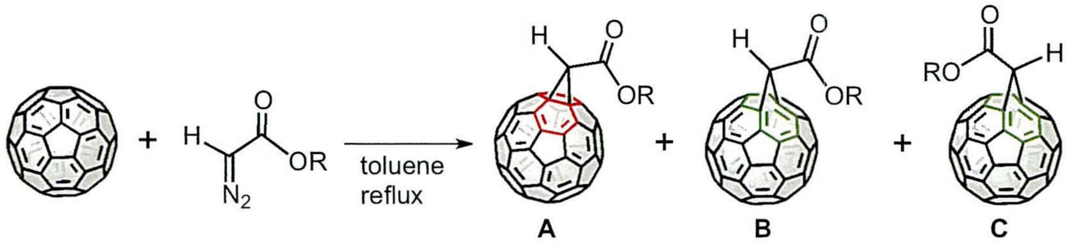
Scheme 1. Schematic illustration of production of isomers and multi-adducts.

In the case of formation of bis-adducts in the [n + 2] (n = 2☐4) type cycloaddition reactions of C_{60}, a mixture of some regioisomers is generally formed.[13] As shown in equation 1, the Prato reaction gives eight regioisomers of bis-adducts.[14] Because of the difficulty in separation of these regioisomers, an expensive Buckyprep column[15] is required to purify them with HPLC treatment.



(1)

Meanwhile, Diederich *et al.* reported that the cycloaddition of C_{60} with diazoacetate produced two constitutional isomers ([6,6]-closed **A** and [5,6]-open **B**) along with the diastereomer of **B** (**C**, Eq. 2).[16]



(2)

Both examples described above give multi-adducts in addition to mono-adducts. It is, therefore, desired to develop C_{60} reaction methods to control of the degree of reaction multiplicity as well as selective production of regio- or structural isomers.

5. Synopsis of this thesis

Although various methods to synthesize C_{60} derivatives have been reported, a little is known for the fundamental methodologies that concurrently resolve the problems described so far on the functionalization of C_{60}.

The present thesis has been conducted to develop two types of different approaches for selective synthesis of functionalized C_{60} derivatives. One utilizes the combination of radicophilicity of C_{60} and electrophilic nature of *N*-sulfonyl radicals, which are readily generated from *N*-halogenated compounds. Controlling the reactivity and the rate of radical generation leads to suppression of over reactions (Figure 5a). The other includes the use of novel reaction media, which not only dissolve C_{60} but also control the reaction-sites in functionalization of C_{60} (Figure 5b). This thesis consists of general introduction, three chapters, and conclusion.

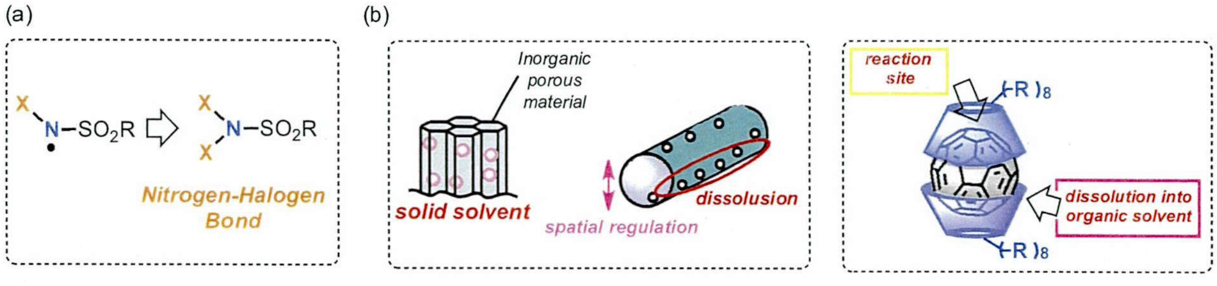


Figure 5. Strategy for development of selective functionalization of C_{60} utilizing (a) electrophilic radicals and (b) novel reaction media.

In Chapter 1, selective and direct syntheses of two constitutional isomers of iminofullerenes from C_{60} utilizing *N,N*-dihaloamides as an N_1 unit under mild conditions. The obtained iminofullerenes were evaluatedas electron-transporting material in photovoltaic cells.

In Chapter 2, the selective mono-adduct formation in Diels-Alder reaction of C_{60} and dienes in mesoporous silica as reaction media is described.

In Chapter 3, the encapsulation of C_{60} into lipophilic γ-cyclodextrin, and the selective introduction of a functional group to C_{60} and the fabrication of a thin-film utilizing the synthesized inclusion complex is described. Furthermore, selective extraction of C_{60} from fullerite (a 1:1 mixture of C_{60} and C_{70}) utilizing size selective complexation of cyclodextrin is mentioned.

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13. See Figure S1; The two groups are located in the same hemisphere (*cis*) or in opposite hemisphere (*trans*) of the C_{60} cage. There are another types of reaction sites, which is termed *equatorial* (e_{face}) or simply *e* (e_{edge}). Furthermore, *cis-3*, *trans-3*, and *trans-2* addition patterns are inherently chiral and represent stereogenic units (^{f,s}A or ^{f,s}C).

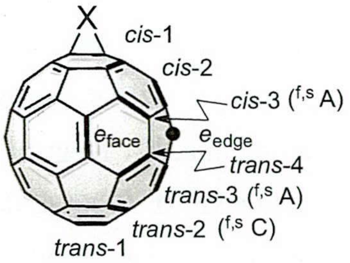

Figure S1. The possible C_{60} bis-adduct isomers

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Chapter 1

Highly Selective Synthesis of Azafulleroids and Aziridinofullerenes Utilizing *N,N*-Dihaloamide Reagents

1-1. Introduction

As mentioned in the general introduction, a number of synthetic methods of fullerene derivatives have been reported.[1] Nevertheless, some problems still remain – namely, the difficulty in synthesis of mono-functionalized C_{60} derivatives. Chapter 1 describes development of the method to induce mono-adduct selective syntheses of iminofullerenes by suppressing formation of multi-adducts. The present method selectively affords two isomers of iminofullerenes.

Iminofullerenes having nitrogen-bridged fullerene cage structures constitute a large family of functionalized fullerenes. They exclusively exist as either of two isolable isomers: [5,6]-open cluster architecture with 60 π-electron system (aza[60]fulleroids) or [6,6]-closed with 58 π-electron system (aziridino[60]fullerenes, Figure 1).[1a]

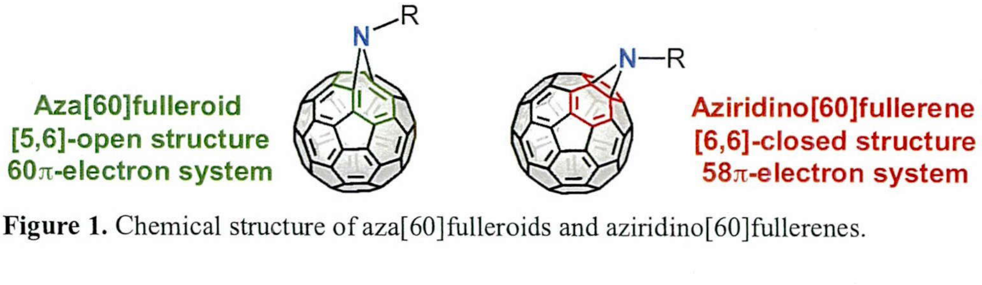
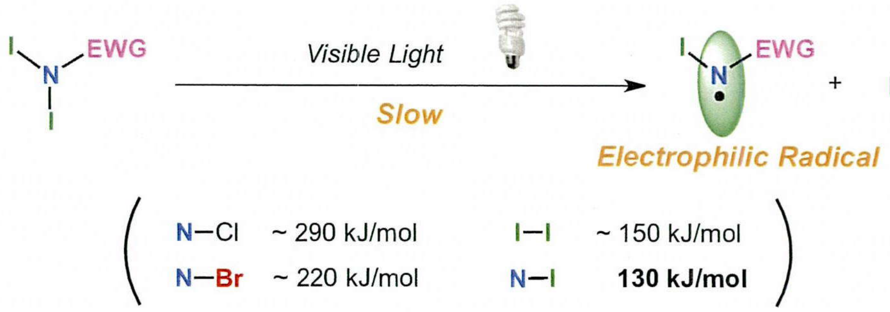


Figure 1. Chemical structure of aza[60]fulleroids and aziridino[60]fullerenes.

They serve not only as the key synthetic precursors to heterofullerenes[2] but also as promising new candidates for n-type (electron-transporting) semiconducting materials due to their high electron-transfer abilities. For example, Wudl and Heeger recently have reported the performance of n-channel organic field-effect transistors (OFETs) and bulk heterojunction (BHJ) solar cells based on iminofullerenes.[3] The conjugated polymer that possessing an azafulleroid moiety functions as a dopant of poly(vinylphenylene), (PPV)-based organic light-emitting diodes (OLEDs).[4] Meanwhile, aziridinofullerenes bearing long alkyl-chains on the nitrogen formed self-assembled bilayer membranes.[5] The most widely used synthetic method for iminofullerenes thus far involves the reaction of C_{60} with organoazides.[6] Representative protocol involves 1,3-dipolar [3+2] cycloaddition of organoazides with C_{60}, followed by thermal extrusion of N_2[6p] from the intermediately formed [6,6] triazolines,[6c] leading to [5,6]-open azafulleroids as a major product together with [6,6]-closed aziridinofullerenes as a minor product. Conventional methods aforementioned require highly toxic and explosive organoazides and high reaction temperatures, and the isomeric ratio of the forming iminofullerenes strongly depends on the nature of substituents on the nitrogen atom. Moreover, not only mono-adduct but also multiadducts are yielded. In this context, recently, some groups have developed such synthetic methods for iminofullerenes without utilizing organoazides.[7-10] Akasaka and co-workers have reported the [2+1] cycloaddition of C_{60} with nitrene generated by photolysis of readily prepared *N*-*p*-toluenesulfonylsulfilimine, to give *N*-tosylaziridinofullerene in a selective manner.[7] Iminophenyliodinanes (RN=IPh) also have emerged as alternative candidates for the synthesis of iminofullerenes. The group led by Gan reported the aziridination reaction of C_{60} utilizing alkyl-substituted iminoiodinane (R = CH_2CO_2Me), which was generated in situ from glycine ester with hypervalent iodine reagent and I_2,[8] whereas the Itami group developed the Cu-catalyzed variant using TsN=IPh to prepare

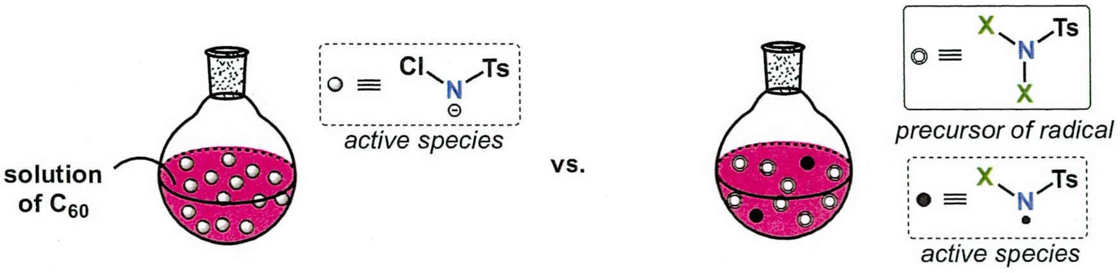
N-*p*-tosylaziridinofullerene in sufficient chemical yield.[9] As part of our efforts aimed at developing chemical modification reactions of C_{60}, our group has previously developed an ionic aziridination of C_{60} utilizing chloramine salts as an N_1 unit through addition-cyclization pathway, exclusively providing [6,6]-closed aziridinofullerenes.[10] At the same time, a unique rearrangement of aziridinofullerenes to azafulleroids catalyzed by a chloramine salt in the presence of MS4A was reported, albeit not a straightforward route to azafulleroids. However, chloramine salts, which are unstable and difficult to isolate, and reflux conditions are indispensable in this method. Although the reaction produced iminofullerenes with high selectivity, chemical yield was still low.

In order to conduct the reaction under mild conditions and suppress the production of multi-adducts, I focused attention on radical species, which is more reactive toward fullerenes than anion species. *N*-haloganeted reagents as precursors for the generation of *N*-centered radical species would be useful for selective functionalization of C_{60}. The bond dissociation energy of nitrogen–iodine bond is the lowest among nitrogen–halogen bonds such as N–Cl and N–Br, and even lower than of that iodine–iodine bond (Scheme 1). For this reason, the generation of *N*-centered radical through homolytic cleavage of nitrogen-halogen bond under mild conditions would be feasible.



Scheme 1. The generation of amidyl radical under the illumination of fluoroscent lamp

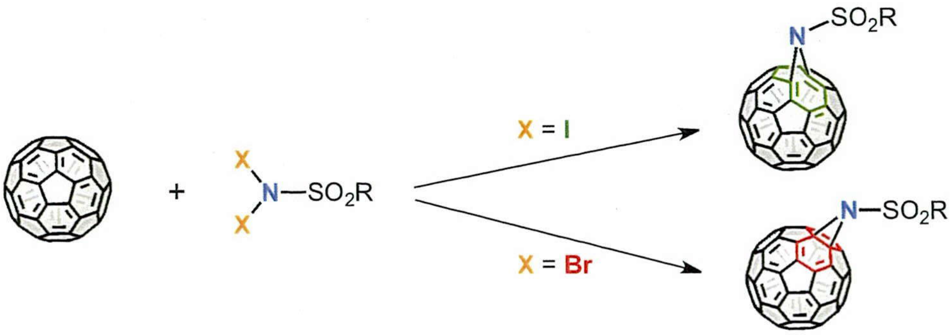
Since the rate of radical generation would be relatively slow under the illumination of a visible light, the ration of the amounts of C_{60} against the radical species is so huge that multi-addition would be suppressed (Figure 2). The use of the radical species bearing an electron-withdrawing group might control the reactivity toward C_{60} and hamper the over reactions. I envisioned that these ideas described above lead to the improvement of chemical yields of desired products by the suppression of multi-adducts formation under the mild conditions.



Leading to Selective Functionalization

Figure 2. Strategy for the suppression of multi-addition reactions on functionalization of C_{60}.

During the course of investigations, it was found that the difference of halogen on the nitrogen atom gives azafulleroids or aziridinofullerenes as a sole product (Scheme 2).



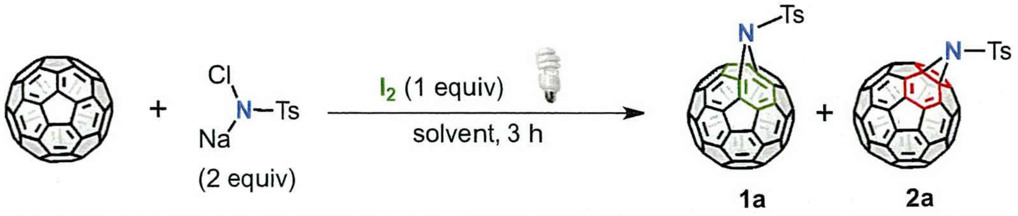
Scheme 2. Selective synthesis of iminofullerenes

Results and Discussion

1-2. Reaction of C_{60} and Chloramine-T in the Presence of Iodine

Our group reported the treatment of chloramine-T with iodine would generate *N*-iodosulfonamide (it still remains unclear whether it exists as *N*-chloro-*N*-iodo or *N*,*N*-diiodo form).[11] Making the use of *N*-iodinated reagent as a radical precursor, preliminary reactions were conducted (Table 1). The treatment of C_{60} with two equivalents of *N*-chloro-*N*-sodio-*p*-toluenesulfonamide (chloramine-T) and an equimolar amount of I_2 in toluene at room temperature gave exclusively [5,6]-open azafulleroid **1a** as a major product together with trace amounts of [6,6]-closed aziridinofullerene **2a**, combined yield of the products being 12% with the isomeric ratio of 97:3 (Table 1, entry 1). Notably, compared to the results our group has previously reported, in which the reaction of C_{60} with an ammonium chloramine salt exclusively gave aziridinofullerenes **2a**,[10] the sense of the isomeric product was completely inversed in this reaction. The unexpected result prompted us to further explore the unique reaction, and as the results of the survey of reaction conditions other than reagents (entries 2–8). Although chlorobenzene and 1,1,2,2-tetrachloroethane were not effective solvents in terms of chemical yields, the reactions exclusively afforded azafulleroid **1a** (entries 2 and 3). Use of decalin as a solvent did not give any iminofullerenes (entry 4). The employment of *o*-dichlorobenzene (*o*-DCB) gave **1a** as the sole product with 100% "selectivity"[12] (entry 5). The prolonged reaction time resulted in decrease in selectivity, probably because of production of multi-adducts (entries 5 and 6). At the higher temperature, both chemical yield and selectivity lowered (entry 7). A stoichiometric amount of Aliquat®336 as a phase-transfer agent was added, providing **1a** in high chemical yield (42%) without any formation of **2a**, although the selectivity is decreased to moderate (entry 8).

Table 1. Optimization of reaction conditions on selective synthesis of azafulleroids



entry	solvent	temp. (°C)	yield (%)[a,b]	ratio (**1a** : **2a**)[c]
1	toluene	rt	12 (97)	97 : 3
2	chlorobenzene	rt	13 (98)	98 : 2
3	1,1,2,2-tetrachloroethane	rt	21 (74)	95 : 5
4	decalin	rt	0 (-)	–
5	*o*-DCB	rt	21 (100)	100 : 0
6[d]	*o*-DCB	rt	40 (73)	100 : 0
7	*o*-DCB	80	30 (66)	97 : 3
8[e]	*o*-DCB	rt	42 (64)	100 : 0

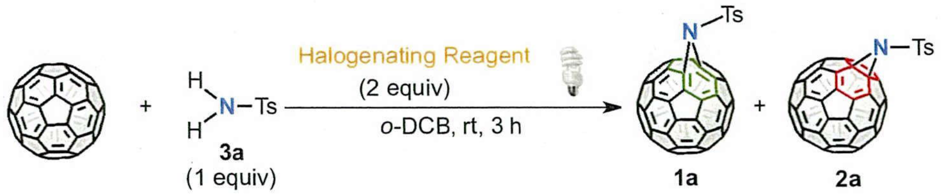
[a] Combined yield of **1** and **2**. [b] The values in the parentheses indicate selectivity of products.
[c] Determined by ^{1}H NMR. [d] Reaction time: 24 h. [e] Two equivalents of Aliquat®336 was added.

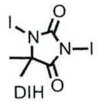
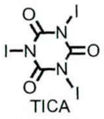
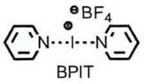
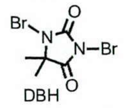
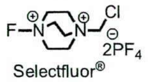
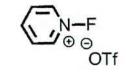
1-3. Synthesis of Iminofullerenes from C_{60} and Sulfonamide Using Halogenating Reagents

As shown in Table 1, it was implied that *N*,*N*-dihaloamide should play the key role in the unique selective reaction. Meanwhile, our group revealed *N*,*N*-diiodocarboxamides were prepared by the treatment of the corresponding amide and *t*-BuOI generated from *t*-BuOCl and sodium iodide *in situ*.[13] In light of the fact that sulfonamides have two acidic hydrogens exchangeable with halogens, I envisioned that the concomitant use of sulfonamides with an appropriate halogenating reagent would generate dihalosulfonamides *in situ*. Furthermore, sulfonamides are readily available compared to the corresponding chloramine salts, and thus the use of them is desirable from the viewpoint of synthetic versatility and product diversity. In this regard, I scrutinized electrophilic halogenating reagents in the reaction of C_{60} with *N*-toluenesulfonamide (**3a**) at room temperature (Table 2). At first, the treatment of C_{60}, *N*-tosylamide and *t*-BuOI as an iodonium source gave only **1a**, albeit low chemical yield (16%)

with moderate selectivity (53%) (entry 1). On the other hand, the use of commonly available chlorinating reagents such as *t*-BuOCl and *N*-succinimide (NCS) failed to give **1a** and **2a**, only to recover unreacted C_{60} quantitatively (entries 2 and 3). Iodinating reagents composed of diatomic interhalogen molecules (I_2, IBr, ICl) were also found ineffective for the reaction (entries 4–6). In the case of ICl, the recovery of C_{60} was moderate probably due to the production of $C_{60}Cl_n$ instead of formation of iminofullerenes.[14] I was delighted to find that the employment of *N*-iodosuccinimide (NIS) provided **1a** in high chemical yield (52%) with perfect selectivity and isomeric ratio, whereas the elongation of reaction time (24 h) not only resulted in slightly lower yield (45%) of products with moderate selectivity (57%) but also caused the formation of trace amounts of aziridinofullerene **2a** (entries 7 and 8). Benzene-fused variants of NIS (*N*-iodophthalimide: NIPI,[15] and *N*-iodosaccharin: NISac[16]) and hydantoin-based bifunctional reagent (DIH[17]) also exclusively afforded **1a** in high yield, although selectivities were inferior to that of NIS (entries 9, 11, and 13). The improvements of the selectivities using these reagents were observed when the reaction time was shortened to 1.5 h at the expense of slight decrease in chemical yields (entries 10, 12, and 14). Ternary iodinating reagent (triiodoisocyanuric acid: TICA[18]) did not improve the efficiency of the reaction (entry 15). The use of highly electrophilic iodonium reagent (bis(pyridine)iodonium tetrafluoroborate: BPIT[19]) resulted in lower chemical yield and isomeric ratio (entry 16). The concomitant use of hypervalent iodine reagent with I_2, which has emerged as a representative non-metal oxidant, gave **1a** in good yield, indicating the involvement of nitrogen-center radical (entry 17).[20] To my surprise, the reaction using *N*-bromosuccinimide (NBS) for 24 h produced only aziridinofullerene **2a** without the formation of **1a**, although both of chemical yield and selectivity were quite low (entry 18). This encouraged me to further exploit the reaction systems, because the result indicated that switching isomeric products would be feasible only by changing the applied halogenating reagents. No product formation was observed when Br_2 and AcOBr were employed, although slight amounts of C_{60} were consumed (entries 19 and 20). Brominated counterparts of NIPI, NISac, and DIH (NBPI,[21] NBSac,[22] and DBH,[23] respectively) were examined for the synthesis of **2a** (entries 21–23) from analogical reasoning of the successful results for the selective synthesis of azafulleroid **1a**. At this point, DBH was found to be the best reagent to give **2a** in terms of chemical yield (entry 23), although the improved method is discussed afterward (*vide infra*). Fluoronium (F^+) sources such as Selectfluor® and *N*-fluoropyridinium triflate were ineffective for the reaction (entries 24 and 25).

Table 2. Effect of halogenating reagent on the production of iminofullerenes[a]



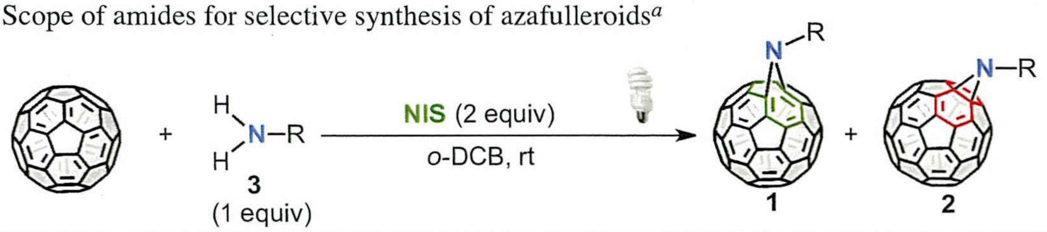
entry	halogenating reagent	yield (%)[b]	ratio (**1a** : **2a**)[c]
1	*t*BuOI	16 (53)	100 : 0
2	*t*BuOCl	0 (-)	-
3	NCS	0 (-)	-
4	I_2	0 (-)	-
5	IBr	0 (-)	-
6	ICl	0 (-)	-
7	**NIS**	**52 (100)**	**100: 0**
8[d]	NIS	45 (57)	100 : 0
9	 NIPI	52 (72)	100 : 0
10[e]		36 (100)	100 : 0
11	 NIsac	45 (63)	100 : 0
12[e]		25 (96)	100 : 0
13[f]	 DIH	45 (61)	100 : 0
14[e,f]		41 (77)	100 : 0
15[g]	 TICA	45 (63)	100 : 0
16	 BPIT	25 (96)	100 : 0
17	$PhI(OAc)_2/I_2$	40 (64)	100 : 0
18[d]	**NBS**	**6 (13)**	**0 : 100**
19[d]	Br_2	0 (-)	-
20[h]	AcOBr	0 (-)	-
21[d]	 NBPI	0 (-)	0 : 100
22[h]	 NBsac	5 (12)	0 : 100
23[d]	 DBH	9 (23)	0 : 100
24	 Selectfluor®	0 (-)	-
25	 OTf	0 (-)	-

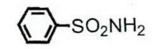
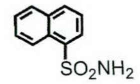
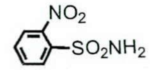
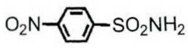
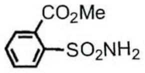
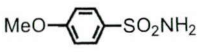
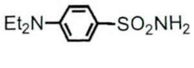
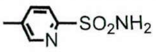
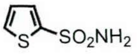
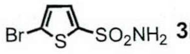
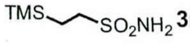
[a] Reaction conditions: C_{60} (0.05 mmol), halogenating reagent (0.1 mmol), and **3a** (0.05 mmol) in *o*-DCB (25 mL) at room temperature for 3 h. [b] Combined isolated yields of **1a** and **2a**; The values in parentheses indicate selectivity of products. [c] Determined by ^1H NMR. [d] Reaction time: 24 h. [e] Reaction time: 1.5 h. [f] One equivalent of DIH (0.05 mmol) was employed. [g] A 0.66 equivalent (0.033 mmol) of TICA was employed. [h] Reaction time: 12 h.

1-4. Selective Synthesis of Azafulleroids Using Iodinating Reagens

For selective synthesis of azafulleroid **1a**, NIS was found to be the best reagent among tested, in terms of chemical yield and selectivity. Thus, having established the reaction conditions for selective synthesis of azafulleroid **1a**, a wide range of sulfonamides was applied to the optimal reaction conditions to verify the versatility of the synthetic method (Table 3). The reaction with benzenesulfonamide (**3b**) with NIS proceeded efficiently to give the corresponding azafulleroid **1b** as the sole product in high yield with excellent selectivity (entry 1). Although the reaction with 1-naphthalenesulfonamide (**3c**) required a rather long reaction time of 72 h, azafulleroid **1c** was exclusively formed in good yield with moderate selectivity (entry 2). Electron-withdrawing substituents on the benzene ring (**3d–f**) did not significantly affect the chemical yield, selectivity, and isomeric ratio, although the reaction time strongly depended on the amides (entries 3–5). It should be noted that sulfonamides bearing an electron-donating group such as OMe (**3g**) and NEt_2 (**3h**) underwent the desired reaction without being iodinated at all,[24] leading to the corresponding azafulleroid **1g** and **1h** in 53% and 25% yield, respectively (entries 6 and 7). In the case of the reaction with **3h**, the use of 1 equivalent of alternative iodinating reagent DIH improved the chemical yield up to 36% (entry 8). Six- and five-membered heteroarene-substituted sulfonamides **3i–3k** were also found applicable to the reaction conditions (entries 9–11). Specifically, bromothiophene-substituted azafulleroid **1k** would be intriguing molecule (entry 11), since it could serve as a versatile building block for donor-accept (D-A) fullerene dyads, which could be applicable to photosynthesis systems or single-molecule organic solar cells (SMOCs).[25] Furthermore, [60]fullerene was successfully transformed into alkylsulfone-substituted azafulleroids **1l** and **1m** by the reaction with simple alkylsulfonamides **3l** and **3m**, respectively, in high yields (entries 12 and 13). It is worthy noting that the Me_3Si group was compatible with the concomitant use of electrophilic iodinating reagent to provide the corresponding azafulleroid **1n** (entry 14). In addition to a wide variety of sulfonamides, phosphoric amides such as **3o** and **3p** were also applicable to the reaction conditions to give the unfamiliar phosphoric-substituted azafulleroids **1o** and **1p** as the single isomeric products in good yields (entries 15 and 16). In all cases, unreacted C_{60} was easily separated from the resulting iminofullerenes by column chromatography on silica gel and reusable. The structure of all azafulleroids synthesized were identified by standard spectroscopic technique such as ^{1}H-, ^{13}C-NMR, IR, UV/vis spectroscopy, and FAB-MS.[26] The ^{13}C NMR spectra of **1** showed 32 signals ranging from 130 to 150 ppm assignable to sp^2 carbons of the C_{60} skeleton, thereby supporting the C_s symmetry of the [5,6]-open structure.[6e]

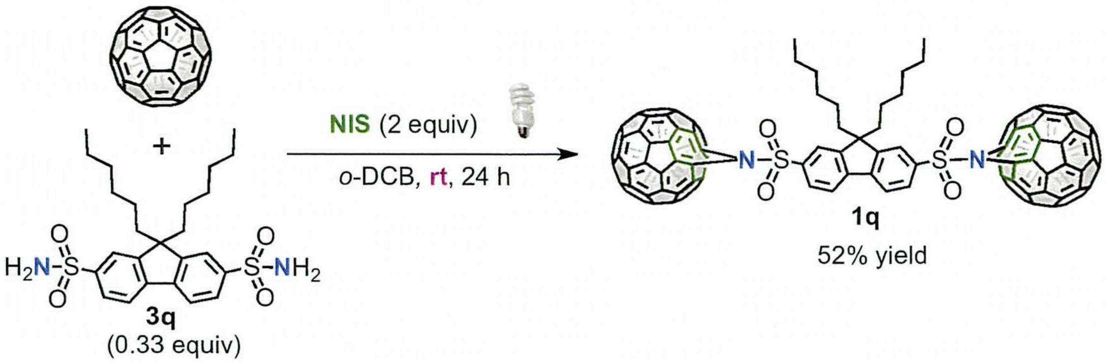
Table 3. Scope of amides for selective synthesis of azafulleroids[a]



entry	RNH$_2$		time (h)	yield (%)[b]	ratio (1a : 2a)[c]
1		3b	7	54 (96)	100 : 0
2		3c	72	43 (60)	95 : 5
3		3d	12	44 (92)	100 : 0
4		3e	24	50 (100)	100 : 0
5		3f	72	41 (88)	95 : 5
6		3g	30	53 (81)	95 : 5
7		3h	24	25 (96)	100 : 0
8[d]			36	36 (82)	100 : 0
9[e]		3i	6	62 (98)	100 : 0
10[d,f]		3j	24	40 (75)	100 : 0
11[e]		3k	36	29 (91)	100 : 0
12	Me–SO$_2$NH$_2$	3l	20	60 (84)	98 : 2
13	nBu–SO$_2$NH$_2$	3m	22	46 (85)	95 : 5
14[f]		3n	6	35 (67)	100 : 0
15	Ph$_2$P(O)NH$_2$	3o	12	43 (86)	100 : 0
16[f]	(EtO)$_2$P(O)NH$_2$	3p	12	24 (65)	100 : 0

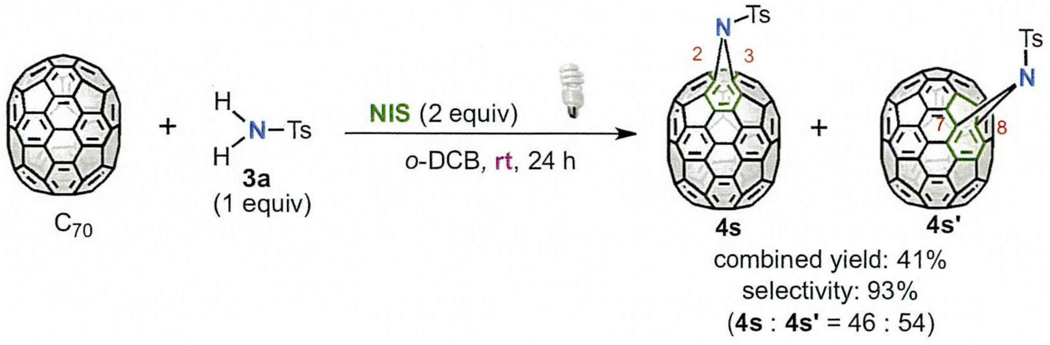
[a] Reaction conditions: C_{60} (0.05 mmol), NIS (0.1 mmol), and **3** (0.05 mmol) in *o*-DCB (25 mL) at room temperature for the time indicated. [b] Combined isolated yields of **1** and **2**; The values in parentheses indicate selectivity of products. [c] Determined by ^{1}H NMR. [d] One equivalent of DIH (0.05 mmol) was employed. [e] Three equivalents of NIS (0.05 mmol) were employed. [f] Reaction was conducted at 0 °C.

Notably, the treatment of C_{60} with NIS and bis(sulfonamide) **3q** bearing a fluorene moiety, exclusively provided A-D-A dumbbell-shaped azafulleroid **1q** as the single isomer in high yield (Eq. 1).[27]



(1)

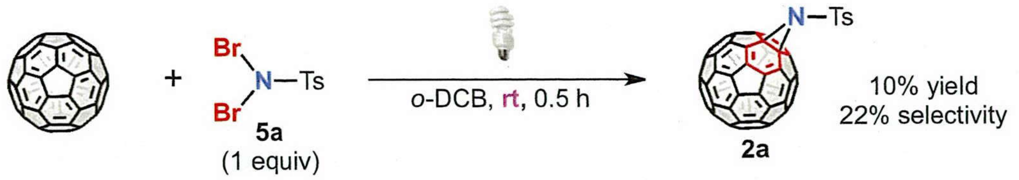
Furthermore, the selective functionalization reaction was successfully applied to C_{70} to give aza[70]fulleroids[6a,b] as a mixture of regioisomers **4s** ([2,3]-open) and **4s**□ ([7,8]-open) in 41% combined yield (Eq. 2). Although the control of the regioselectivity was difficult in this case, it is worth noting that the chemical yield was much improved compared to the result that utilizes organoazides.[6a]



(2)

1-5. Selective Synthesis of Aziridinofullerenes Using *N,N*-Dibromosulfonamides

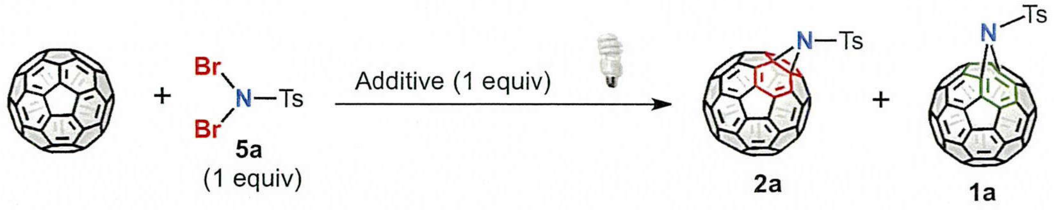
Having established the selective synthetic method for azafulleroids, I turned my attention to the development of selective synthesis of aziridinofullerenes, which would serve as a complementary method to the sulfonamides/NIS system. In light of the fact that the reaction of C_{60} with some brominating reagents such as NBS, NBSac, and DBH exclusively provided aziridinofullerene **2a** instead of azafulleroid **1a**, (*e.g.*, see entries 18, 22, and 23 in Table 2), I assumed that *N*,*N*-dibromosulfonamide $TsNBr_2$ would be the key chemical species in the reaction. To attest the hypothesis, the reaction of C_{60} using *N*,*N*-dibromosulfonamide **5a**, which was readily prepared by treating amide **3a** with Br_2 and NaOH or by chloramine-T with Br_2 in water,[28] was conducted. As anticipated, aziridinofullerene **2a** was produced as the sole product in 10 % yield without the formation of azafulleroid **1a**, albeit low selectivity (Eq. 3).



(3)

Meanwhile, Kovacia *et al.* reported that the treatment of *N*,*N*-dichloro-p-toluenesulfonamide and $CuBr_2$ afforded *N*,*N*-dibromoamide through radicalic halogen exchange reaction.[29] Because of enhancement of generating efficiency of a similar amidyl radical species to my systems, I hypothesized the addition of metal halides improve the efficiency of generation of radical species from *N*,*N*-dibromosulfonamides. In order to improve the chemical yield of **2a** and selectivity, the reaction parameters of solvent, reaction time, reaction temperature, and additive were screened (Table 4). I was delighted to find the addition of an equimolar amount of metal salts enhanced the reaction efficiency, while organic salt was ineffective for the reaction (entries 1–6). Among the salts examined, NaI was found to be the most effective (entry 2). The choice of the organic solvents had significant influences not only on the chemical yield but also on the isomeric ratio of **2a**/**1a**, although the appropriate explanation for the solvent effect remains unclear at this point (entries 7–9). The fact that the use of toluene, which is sufficient solvent for dissolution of fullerene, failed to consume C_{60} might suggest the involvement of radical species in the reaction pathway. The prolonged reaction time to 60 min resulted in the decrease in chemical yield as well as in selectivity, which is probably attributable to the formation of multi-adducts as reaction proceeds (entry 2 vs 10). The reaction at higher temperature of 60 °C did not improve the chemical yield and the selectivity (entry 11). In sharp contrast, the reaction at lower temperature of 0 °C was beneficial in terms of good chemical yield and selectivity, probably due to the suppression of further reactions such as multi-addition (entry 12). At last, the reaction at 0 °C for 50 min was found to give **2a** in the exclusive manner of 41% yield with 74% selectivity, which result is one of the most efficient values for the preparation of [6,6]-closed *N*-Ts aziridinofullerene **2a** starting from C_{60} under the mild conditions.[14]

Table 4. Optimization study for selective synthesis of aziridinofullerene **2a**[a]

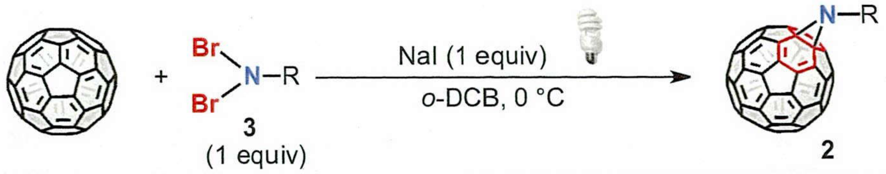


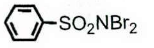
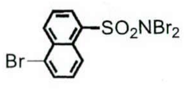
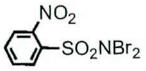
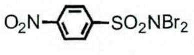
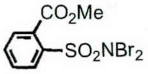
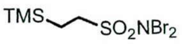
entry	solvent	time (min)	temp. (°C)	additive	yield (%)[b]	ratio (**2a** : **1a**)[c]
1	*o*-DCB	30	rt	NaBr	13 (33)	100 : 0
2	*o*-DCB	30	rt	NaI	31 (94)	100 : 0
3	*o*-DCB	30	rt	LiI	8 (32)	100 : 0
4	*o*-DCB	30	rt	KI	21 (66)	100 : 0
5	*o*-DCB	30	rt	CuI	13 (33)	100 : 0
6	*o*-DCB	30	rt	*n*-Bu_4NI	0 (-)	-
7	$Cl_2CHCHCl_2$	30	rt	NaI	3 (18)	78 : 22
8	chlorobenzene	30	rt	NaI	8 (18)	56 : 44
9	toluene	30	rt	NaI	0 (-)	-
10	*o*-DCB	60	rt	NaI	27 (69)	100 : 0
11	*o*-DCB	30	60	NaI	7 (15)	100 : 0
12	*o*-DCB	30	0	NaI	24 (100)	100 : 0
13	***o*-DCB**	**50**	**0**	**NaI**	**41 (74)**	**100 : 0**

[a] Reaction conditions: C_{60} (0.05 mmol), **5a** (0.1 mmol), and additive (0.05 mmol) in solvent (25 mL) at the reaction temperature for the time indicated. [b] Combined isolated yield of **2a** and **1a**; the values in parentheses indicate selectivity of products. [c] Determined by ^1H NMR.

To test the versatility of the method, I examined the substrate scope of the reaction (Table 5). The corresponding *N,N*-dibromo sulfonamides **5** were prepared according to the reported methods.[28] Electronically neutral and deficient dibromoamides were applicable to the reaction, to provide the corresponding aziridinofullerenes **2b**, **2r**, **2d**–**2f** as the sole product in good yield in all cases (entries 1–5). Alkyl substituent on sulfonyl group did not affect the efficiency of the reaction (entries 6 and 7). In all cases, no formation of azafulleroid was observed. All aziridinofullerenes **2** were characterized in the similar way to azafulleroids.[26] Especially, ^{13}C NMR measurements were useful for identification of their structural symmetry. The existence of 15 signals in the region of 130–150 ppm indicated the C_{2v} symmetric structure of [6,6]-closed mono-adduct. At the same time, the peak at around 80 ppm gave the strong evidence for the presence of sp^3-hybridized carbon on the fullerene sphere.[30] Also, UV-vis spectra of **2** showed characteristic absorption at around 420 nm, indicating the [6,6]-closed structure (*vide infra*).

Table 5. Scope of *N*,*N*-dibromoamides for selective synthesis of aziridinofullerenes[a]

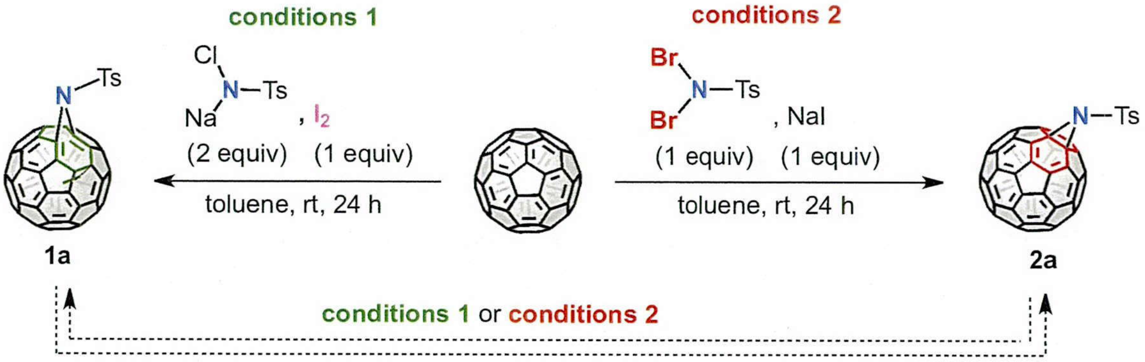


entry	RNBr$_2$		time (h)	yield (%)[b]
1		**5b**	0.75	54 (96)
2		**5r**	0.5	43 (60)
3		**5d**	6	44 (92)
4		**5e**	1	50 (100)
5		**5f**	2	41 (88)
6	Me–SO$_2$NBr$_2$	**5l**	1	60 (84)
7		**5n**	2	35 (67)

[a] Reaction conditions: C_{60} (0.05 mmol), **5** (0.05 mmol), and NaI (0.05 mmol) in *o*-DCB (25 mL) at 0 °C for the time indicated. [b] Isolated yield; the values in parentheses indicate selectivity of products. [c] The reaction was carried out at room temperature.

1-6. Investigation on Reaction Pathway, Reactive Species, and Mechanism

On the basis of the fact that the isomeric mixtures of iminofullerenes were formed in some cases (*e.g.*, see entry 1 in Table 1 and entries 7 and 8 in Table 4), isomerization routes between azafulleroid and aziridinofullerene were taken into consideration. Isolated **1a** and **2a** were separately subjected to the reaction conditions that produced each isomer: **1a** was treated with two equivalents of I_2 and *N*-chloro-*N*-sodio-sulfonamide in toluene at room temperature; **2a** was treated with an equimolar mixture of NaI and DBT in chlorobenzene (Scheme 3). As results, no isomerization was observed in both cases. These results are consistent with the facts that isomerization between *N*-tosyl iminofullerenes **1a** and **2a** requires photochemical- (from **1a** to **2a**)[6a] and thermal-stimuli (from **2a** to **1a**),[7b] although the easiness to isomerize of other iminofullerenes would strongly depend on their *N*-substituents.[31] Thus, iminofullerenes **1a** and **2a** would be formed directly from C_{60} independently in both cases, not by way of isomerization pathways.



Scheme 3. Investigation of isomerization pathway between azafulleroids and aziridinofullerenes

Regarding the reactive species in the selective reactions, the involvement of *N*,*N*-dihalosulfonamides or related species should be considered. Our group has previously reported that *tert*-butyl hypoiodite (*t*-BuOI) is a powerful iodinating reagent for the compounds having acidic hydrogens such as carboxamides[13d] or *N*-alkeylsulfonamides.[13f] It is reasonable to speculate that proton exchange with iodine is rather favored process, since the acidity of N–H of arylsulfonamides is much higher than that of arylcarboxamides (*e.g.*, pK_a of $PhSO_2NH_2$ and $PhC(O)NH_2$ in DMSO is 16.1 and 23.3, respectively).[32] In fact, when sulfonamide **3a** was treated with two equivalents of *t*-BuOI in CD_3CN at room temperature, the broad singlet signal at around 5.6 ppm on the ^{1}H NMR chart attributable to N–H completely disappeared (Figure 3b and c) and an aromatic signal at 7.74 ppm shifted to 7.82 ppm, indicating the formation of diiodoamide **A** or its oligomeric species such as $[TsN]_3I_4$.[33] Subsequent treatment of the resulting solution with C_{60} in *o*-DCB afforded azafulleroid **1a** as the sole product in 30% yield with moderate selectivity (Figure 3a).

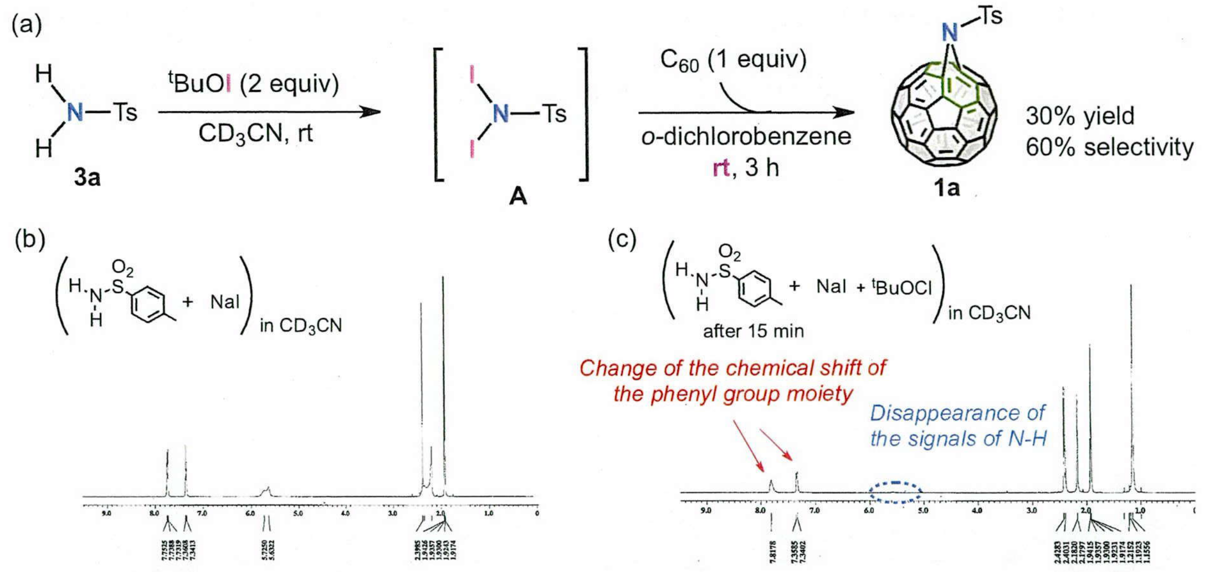
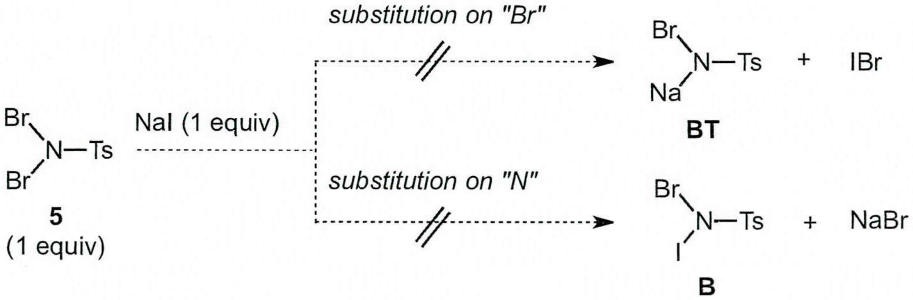


Figure 3. (a) Preperation of *N,N*-dihaloamide **A** and its reaction with C_{60}. (b) ^{1}H NMR spectra of **3a** (0.015 mmol) and NaI (0.03 mmol) in CD_3CN (0.7 mL) at room temperature; (c) after treated with 0.03 mmol of *t*-BuOI.

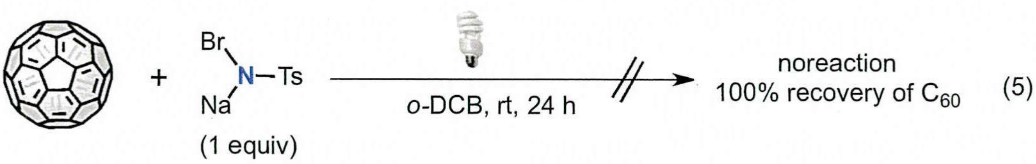
Furthermore, the reaction of C_{60} with *p*-NO_2–$C_6H_4SO_2$–NI_2 (*p*-$NsNI_2$), which was readily prepared through halogen exchange of *p*-$NsBr_2$ with I_2 and isolable compound,[33] provided the *p*-Ns-substituted azafulleroid **1e** in 26% yield with 65% selectivity (Eq. 4). The lines of evidence would support that *N,N*-diiodosulfonamide **A** or its oligomeric complex $[TsN]_3I_4$ are the active species in the selective formation of azafulleroids.[34]

Regarding aziridinofullerene synthesis, although structure-defined *N*,*N*-dibromosulfonamides were employed to the reaction, the involvement of *N*-bromo-*N*-sodio tosylamide (bromamine-T: **BT**) or halogen exchanged *N*-bromo-*N*-iodo-tosylamide **B** that could generate through S_N2 reaction at Br and N center by I^-, respectively, should be taken into consideration under the optimal conditions (Scheme 4).



Scheme 4. Exclusion of the possibilities of the involvement of other species

The possibilities of the involvement of both **BT** and **B** were excluded by the following experiments: (1) the treatment of C_{60} with **BT**, which can be readily prepared from chloramine-T and Br_2,[35] did not give any iminofullerene products only to recover unreacted C_{60} quantitatively (Eq. 5); (2) no liberation of IBr was observed by UV-vis spectroscopic study (Figure 4);



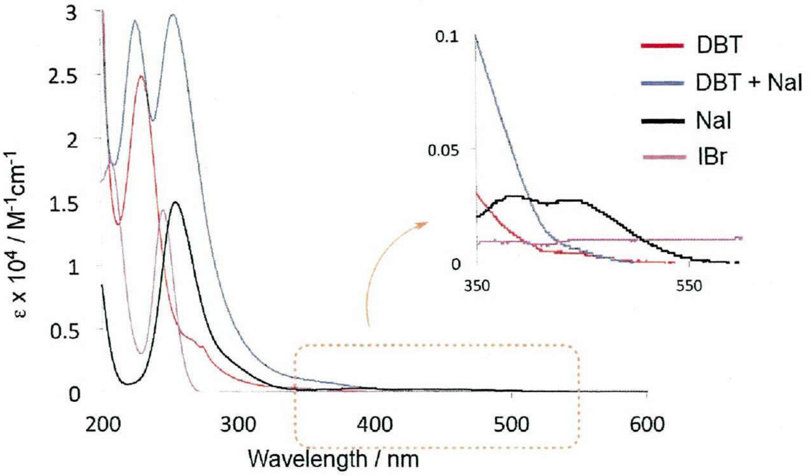
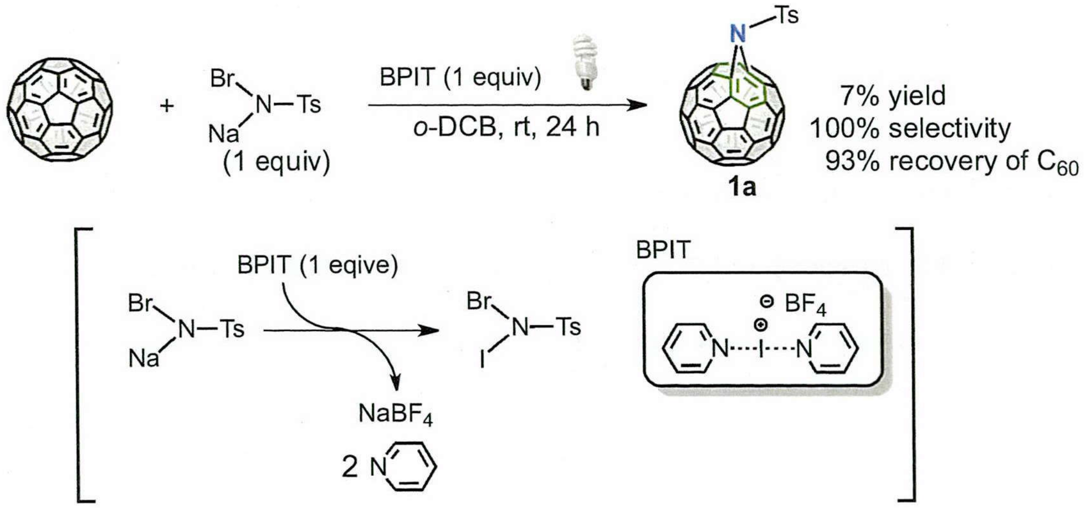


Figure 4. UV-vis spectra of *N,N*-dibromo-*p*-toluenesulfonamide (DBT), NaI, and an equimolar mixture of DBT and NaI, together with IBr spectrum for comparison. The spectra were measured at room temperature in MeCN solutions (1.0 x 10^{-4} M) with the scanning range starting from 200 to 600 nm.

(3) the reaction of C_{60} with mixed dihaloamide **B**, generated separately by the treatment of **BT** with I^+ equivalent BPIT, provided azafulleroid **1a** instead of aziridinofullerene **2a** in 7% yield (Scheme 5).

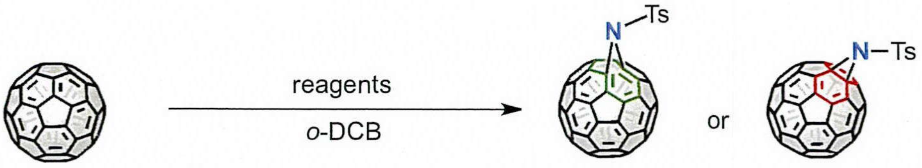


Scheme 5. The reaction of C_{60} with *N*-bromo-*N*-iodo-*p*-toluenesulfonamide in the presence of BPIT.

Although the detail of the exact species still remain uncertain at present, I proposed that iodide attack on the positive bromine to form pseudo-polyhalide complex $[TsN(Br)Br–I]^-Na^+$,[36] which should weaken N–Br bond enough to cleavage either homolytically or heterolytically.

It would be interesting to note that the reaction using $TsNX_2$ (X = Br, I) with C_{60} required the presence of laboratory light for the efficient reaction progression (Table 6). When the reaction was conducted under dark, chemical yields of iminofullerenes were remarkably decreased (entries 2 and 5) compared to the results obtained under the presence of ambient light (entries 1 and 4). Furthermore, the addition of stoichiometric amounts of Galvinoxyl, a representative free radical inhibitor, suppressed the reaction completely with quantitative recovery of C_{60} in both cases (entries 3 and 6).[37] These results implied the involvement of radical species in both selective reactions.

Table 6. Reaction of C_{60} with $TsNX_2$ in the presence / absence of ambient light



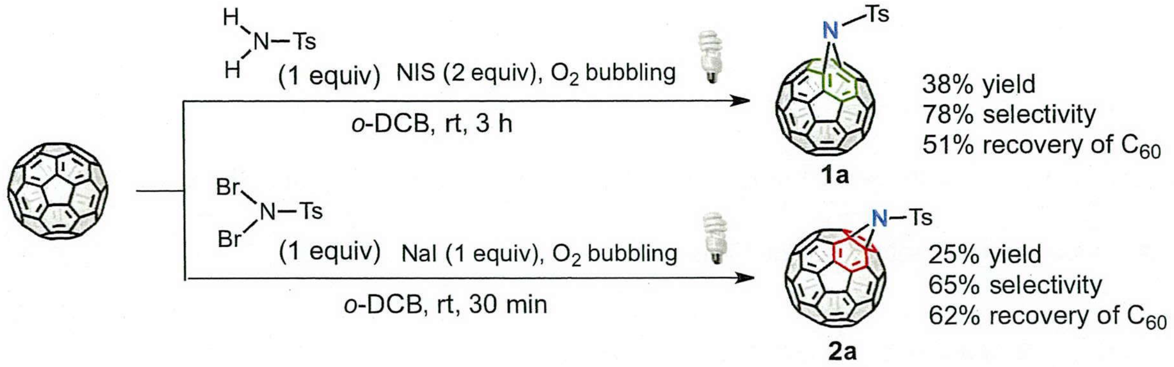
1a 2a

entry[a]	reagents (equiv)	dark or 💡	product	yield (%)[b]	recovery of C_{60} (%)
1	$TsNH_2$ (1)/NIS (2)	💡	**1a**	52 (100)	48
2		dark	**1a**	9 (100)	91
3	addition of Galvinoxyl (2)	💡	**1a**	0 (-)	100
4	$TsNBr_2$ (1)/NaI (1)	💡	**2a**	41 (74)	44
5		dark	**2a**	18 (86)	79
6	addition of Galvinoxyl (2)	💡	**2a**	0 (-)	96

[a] Reaction conditions; 3 h, rt (entries 1-3) or 50 min, 0 °C (entries 4-6). [b] The values in parentheses indicate selectivity of products.

In order to obtain further insights in the character of radical species, several experiments were conducted. The O_2 bubbling over the reaction of C_{60} with $TsNX_2$ (X = Br, I) did not retard the reaction efficiency (Eq. 6), excluding the involvement of the excited triplet state of C_{60} ($^3C_{60}$*), which is highly susceptible to O_2 and should be easily quenched.[38] Furthermore, the

UV-vis-NIR spectroscopic analysis of the mixture of $TsNX_2$ and C_{60} in *o*-dichlorobenzene did not show any absorption bands ranging from 850 nm to 1150 nm characteristic to fullerene radical anion ($C_{60}^{\bullet-}$) (Figure 5).[39] These results suggest that the electron transfer from dihalosulfonamide to $^3C_{60}^*$ to generate fullerene anion $C_{60}^{\bullet-}$ less likely occurred in the reaction systems.



(6)

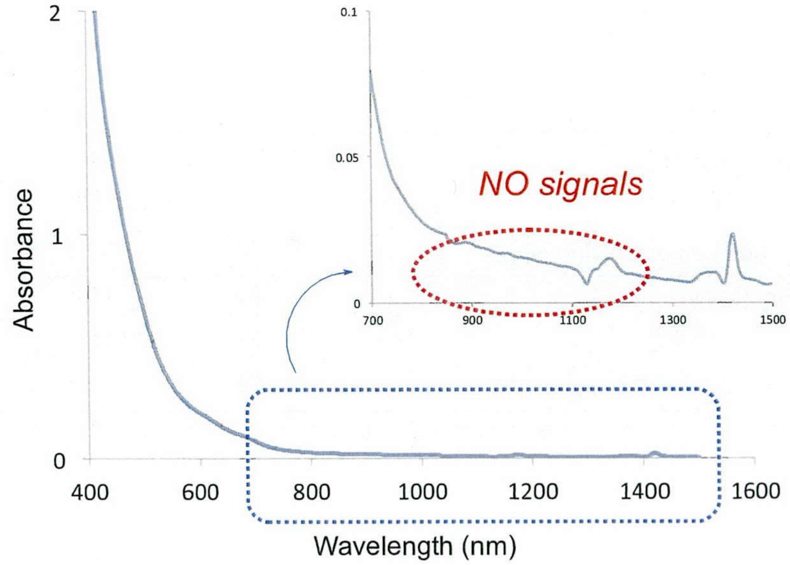
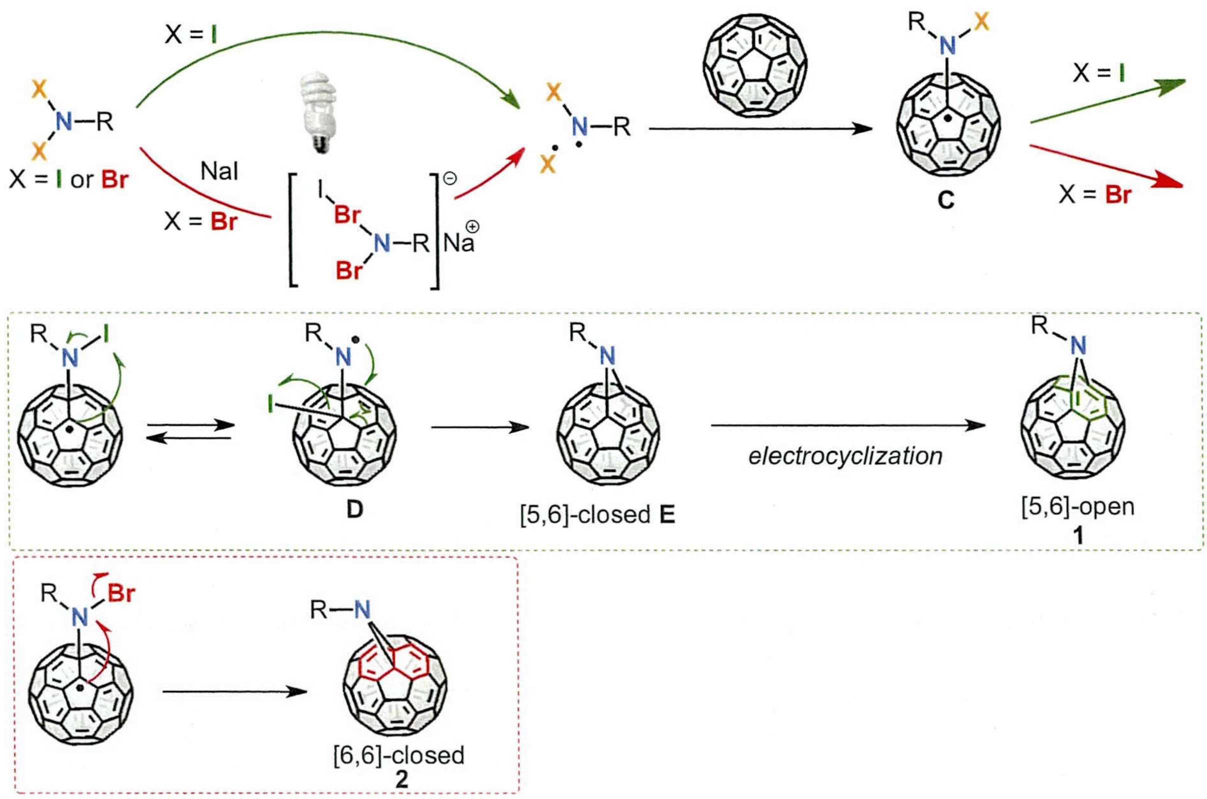


Figure 5. NIR spectra of a mixture of C_{60}, *p*-toluenesulfonamide, and *t*-BuOI in *o*-DCB/MeCN at room temperature.

On the basis of the experimental results, I proposed a plausible reaction mechanism in Scheme 6. The first step would involve the homolytic cleavage of N–X bond of RSO_2NX_2 to generate amidyl radical $RSO_2(X)N•$,[40] which process should be promoted by visible light.[41] In light of the quite small value of the bond dissociation energy (BDE) for N–I bond (130 kJ/mol),[42] the assumption would be reasonable. As for the homolytic fission of slightly stronger N–Br bond (BDE ~ 220 kJ/mol), the addition of NaI should play an important role in this step as discussed in the previous sections. The possibilities are that I^- coordinate to Br to form $[TsN(Br)Br–I]^-Na^+$, facilitating the fission of weaken N–Br bond, or that I^- function as an electron reductant to form Ts(Br)N• and Br^-.[29] The resulting amidyl radical would react with C_{60} to generate fullerene radical **C**. Since the highest spin density of mono-adduct fullerene radicals reportedly localize on the adjacent carbon to substituent on the [6,6] junction,[43] it should be reasonable that the further reaction proceed from this position. When the nitrogen is substituted with a considerably bulky and soft atom, iodine, the radical would attack to iodine atom rather than to sterically congested nitrogen atom, giving *N*-centered radical with 1,2-substituent on fullerene cage **D**. The subsequent intramolecular cyclization at [5,6]-junction with the liberation of I• should provide [5,6]-closed iminofullerene **E**, and the spontaneous electro-cyclization would provide [5,6]-open azafulleroid **1**. On the other hand, when halogen is bromine, which has more electron-negative and smaller size than iodine, the fullerene radical would directly attack on nitrogen, leading to [6,6]-closed aziridinofullerene **2**.



Scheme 6. Plausible reaction mechanism

1-7. Physicochemical Properties of the Products

With a series of iminofullerenes **1** and **2** in hand, various properties of them were investigated to asses the products as candidates for n-type semiconducting materials.

Absorption spectra of the dilute CH_2Cl_2 solution of iminofullerenes were measured at the concentration of 10^{-5} M. Representative spectra are shown in Figure 6.[44] As reported in the literature, all the azafulleroids **1** showed distinct absorption at around 330 nm and broad peak centered at around 550 nm, which are characteristic to [5,6]-open aza[60]fulleroids (Figure 1). It should be worth noting that azafulleroids bearing NEt_2 (**1h**) and $P(O)(OEt)_2$ (**1p**) groups exhibited broadening of the 330 nm peak and slight red-shift of the absorption edge, suggesting the existence of weak donor-acceptor interaction in these compounds. Dumbbell-shaped azafulleroid **1q** showed enhanced absorption coefficient due to the doubled number of fullerene moiety per a molecule. As for aziridino[60]fullerenes **2**, diagnostic peaks at around 420 nm, which are characteristic to 1,2-adduct at [6,6]-junction, were identified in all cases. In this case, no significant change in the shape of absorption spectra and absorption edges were observed.

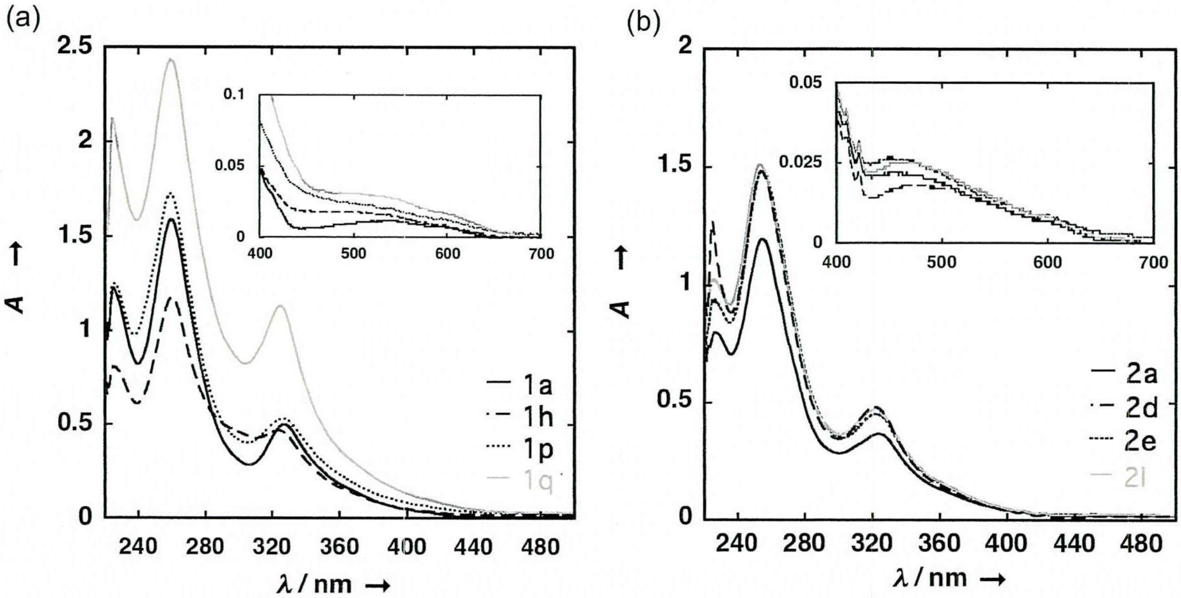


Figure 6. UV-vis absorption spectra of CH_2Cl_2 solutions of (a) azafulleroids **1a**, **1h**, **1p**, **1q** and (b) aziridinofullerenes **2a**, **2d**, **2e**, **2l**.

With the aim at applying the synthesized iminofullerenes to n-type semiconducting materials in photovoltaic devices, solubility, thermal stability, and the electrochemical properties of the products were investigated (Table 7). Solubility is a quite important factor to realize solution-processed fabrication of organic optoelectronic devices.[45] The solubility of iminofullerenes was found to strongly depend on the substituent nature of amide group. Specifically, *p*-nitrophenylsulfonyl- (**1e**), thienylsulfonyl- (**1j**, **1k**), and (trimethylsilyl)ethylsulfonyl-substituted (**1n**) azafulleroids exhibited sufficient solubility over 1.1 wt% in toluene, which is over 3 times higher than that of pristine C_{60} (*ca.* 0.32 wt%).[46] Thermogravimetric analysis (TGA) of the iminofullerenes revealed that azafulleroids **1** are rather thermally-stable (T_d > 230 °C) while the T_d of aziridinofullerenes **2** varied, ranging from as low as 135 °C (**2n**) to as high as 336 °C (**2f**). To evaluate the electrochemical behavior and estimate the LUMOs, cyclic voltammetry (CV) of iminofullerenes was conducted. While many of the azafulleroids **1** showed a quasi-reversible reduction peak at around –0.9 V against Fc/Fc$^+$ redox potential, a few samples such as PhSO$_2$-sbustituted azafulleroid **1b** or *n*-BuSO$_2$-substituted **1m** did not exhibited any reversibility in reduction cycle. Aziridinofullerenes **2** were less stable to electrochemical reduction in homogeneous solution than azafulleroids, leading to difficulty in determining the half-wave potential $^{red}E_{1/2}$ for the first reduction. These results made remarkable contrast to the aza-analogues of PC$_{61}$BM (APCBMs) developed by Wudl, which showed clear reversible electrochemical reduction peaks.[3] The difference in the behavior for electrochemical reduction could be ascribed to the existence of strongly electron-accepting sulfonyl moiety, which would function as a good electron acceptor and immediately degrade from the R$_2$N•SO$_2^-$, which should make the analysis of the results difficult.[47] Therefore, the LUMOs were estimated from the reduction potential onsets (Table 7) together with those of C$_{60}$ and PC$_{61}$BM for comparison. All the iminofullerenes showed the lower LUMOs than those of C$_{60}$ (–3.80 eV) and PC$_{61}$BM (–3.72 eV). These results made a contrast with APCBMs,[3] which exhibited slightly higher LUMOs than that of PC$_{61}$BM but higher than C$_{60}$, probably due to the existence of strong electron-withdrawing sulfonyl group in **1** and **2** leading to lowering the LUMOs through inductive effect.

Table 7. Summary of properties of azafulleroids and aziridinofullerenes

compd.	solubility (wt%,rt)	T_d (°C)^a	$_{red}E^1$ (V)^b	LUMO (eV)^c	compd.	solubility (wt%,rt)	T_d (°C)^a	$_{red}E^1$ (V)^b	LUMO (eV)^c
C_{60}	0.32		1.010	3.80	**1m**	<0.10	331	0.914	3.89
PCBM	1.10		1.074	3.72	**1n**	>1.10	310	0.938	3.86
1a	0.33	326	0.927	3.87	**1o**	<0.10	354	0.974	3.83
1b	0.29	358	0.905	3.89	**1p**	0.50	265	0.959	3.84
1c	0.51	328	0.937	3.86	**1q**	0.08	329	0.860	3.94
1d	0.76	237	0.909	3.89	**2a**	0.76	248	0.933	3.88
1e	>1.10	301	0.846	3.95	**2b**	0.57	268	0.906	3.89
1f	0.16	318	0.927	3.87	**2d**	0.69	241	0.914	3.89
1g	0.50	313	0.913	3.89	**2e**	0.76	158	0.865	3.94
1h	0.29	242	0.938	3.86	**2f**	0.12	336	0.923	3.88
1i	0.57	301	0.910	3.87	**2l**	0.57	217	0.917	3.88
1j	>1.10	266	0.912	3.89	**2n**	0.76	135	0.944	3.86
1k	>1.10	260	0.898	3.90	**2r**	0.19	193	0.860	3.94
1l	0.38	334	0.907	3.89					

[a] The degradation temperature at 5% of weight loss inder N_2 flow. [b] Measured in a mixed solvent of *o*-DCB/CH_3CN (4:1) using *n*-Bu_4NPF_6 as an electrolyte at room temperature at the scan rate of 0.1 V/s; the values in the colum are the onset potencials of the 1st reduction peak versus Fc/Fc^+ (Fc=ferrocene). [c] Estimated from the following equation: LUMO = (4.8 $+_{red}E_1$) eV.

1-8. Application to Photovoltaic Cells

Based on the basic information of the physical and chemical properties, photovoltaic cells containing iminofullerenes as an electron-transporting material were fabricated. The iminofullerene samples for the application were chosen according to the criterion of the solubility being higher than that of C_{60} (0.32 wt% in toluene) for the purpose of solution processing of n-type material. The configuration of the device was based on simple p-n heterojunction structure as shown in Figure 7a. Molybdenum trioxide (MoO_3) was deposited on indium tin oxide (ITO) electrode as an intermediate layer.[48] Tetravalent oxometal titanyl phthalocyanine (TiOPc) was fabricated by a vacuumdeposition technique on this intermediate layer to act as a hole-transporting layer.[49] The electron-transporting layer was deposited by spin-coating with a solution of iminofullerene **1** or **2** in chlorobenzene (0.5 wt%), followed by annealing at 120 °C for 5 min under an inert atmosphere. The successive deposition of a buffer layer of bathocuproine (BCP), which would form an Ohmic contact between an Al electrode and an electron-transporting layer to facilitate smooth electron-transfer from iminofullerenes to Al,[50] was conducted by vacuum deposition. A representative current density–voltage (*J*-*V*) curve of the device based on azafulleroid **1g** under dark and under AM 1.5G illumination is shown in Figure 7b.[51] The distinct photocurrent generation under light illumination clearly demonstrated that the azafulleroid **1g** functioned as an electron-transporting materials.

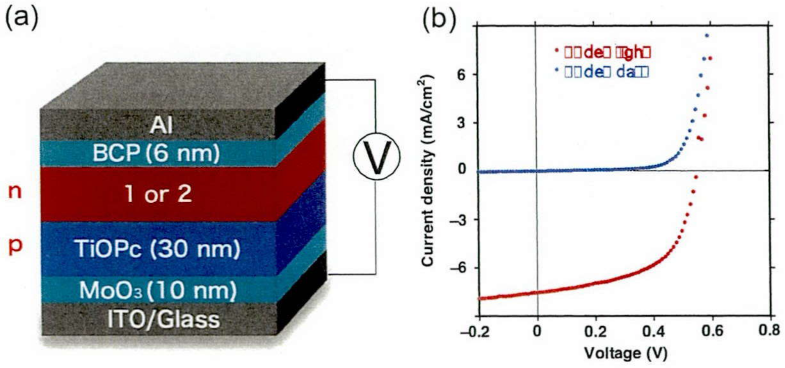


Figure 7. (a) Device architecture of the p-n heterojunction photovoltaic device containing an iminofullerene **1** or **2**; (b) Current density–voltage characteristic of the device using **1g** under dark (circle plot) and under illumination of AM 1.5 G, 100 mW/cm^2 (triangle plot).

The parameters of device performances of the voltaic devices, i.e., open circuit voltage (V_{OC}), short circuit current density (J_{SC}), fill factor (*FF*), and power conversion efficiency (PCE), are summarized in Table 8 with those of $PC_{61}BM$-based device for comparison. Among the devices fabricated, the devices using **1j**, **4a** (and **4a'**), and **2b** did not provide sufficient curves to be assessed. For all devices, V_{OC} were lower than that of the device with $PC_{61}BM$ (0.73), reflecting the lower LUMOs compared to $PC_{61}BM$, although the precise correlation between LUMOs and V_{OC} were not attained.[52] Power conversion efficiencies (PCEs) of the devices exceeded 1.0%. Notably, the devices using **1a**, **1g**, and **2a** showed higher PCEs than that of $PC_{61}BM$-based device (2.05%). Although it could be hard to compare with the performances of BHJ solar cells composed of other soluble fullerene-based materials, these results shown here would demonstrate the high potential of the iminofullerenes as electron-transporting materials.

Table 8. Summary of performances of PVCs under AM 1.5 G illumination

compnd.	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
PCBM	0.73	6.2	45	2.05
1a	0.53	8.1	53	**2.29**
1e	0.44	7.8	56	1.94
1n	0.55	7.6	47	2.00
1g	0.55	7.5	57	**2.35**
1p	0.50	6.2	43	1.33
2a	0.58	7.7	49	**2.19**
2e	0.51	5.8	45	1.34
2n	0.61	5.8	46	1.61

1-9. Conclusion

The author has developed highly selective synthetic methods for azafulleroids and aziridinofullerenes under the mild conditions utilizing easily handling *N,N*-dihaloamides as the key chemical species. The reactions tolerated various functionalities of amides and allowed for obtaining isomeric iminofullerenes in high yields. Furthermore, I have demonstrated that the iminofullerenes synthesized here were found to be utilized as good electron-transporting materials in p-n heterojunction photovoltaic devices.

1-10. Experimental Section

General experimental methods

All reactions were carried out under an atmosphere of nitrogen. Dehydrated *o*-dichlorobenzene was used as received. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd). Analytical thin-layer chromatography (TLC) was performed on precoated silica gel glass plates (silica gel 60 F_{254}, 0.25 mm thickness, Merck Ltd). Infrared spectra and near infrared spectra were acquired on a JASCO FT/IR-410 or SHIMAZU FTIA-8400S and JASCO V-670. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^{1}H NMR, 270 MHz; ^{13}C NMR, 68 MHz), JMTC-400/54/SS (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) and Varian Unity-INOVA 600 (^{1}H NMR, 600 MHz; ^{13}C NMR, 150 MHz) using tetramethylsilane as an internal standard. UV/Vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer. FAB-Mass spectra were measured with a JEOL TMS-700 spectrometer. High resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. Cyclic voltammetry (CV) was performed with ALS-600 (BAS Inc.) system. All measurements were carried out in a one-comportment cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and Ag/Ag^+ reference electrode. The CV measurements were performed in a *o*-DCB/MeCN (4/1 v/v) solution containing tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte at room temperature at the scanning rate of 0.1 V/s. All potentials were corrected against Fc/Fc^+. Thermogravimetric analysis (TGA) was performed with TG/DTA-7200 (SII) system. Samples were (*ca.* 7 mg) placed in a Pt pan and ramped at 10 °C/min under N_2 flow. The fluorescent lamp (5316 HL) is available for purchase at HITACH, Ltd.

Typical procedure for the synthesis of azafulleroids using chloramine-T and iodine

Iodine (12.7 mg, 0.05 mmol) was added to a *o*-DCB (25 mL) solution of fullerene (36 mg, 0.05 mmol) and chloramine-T (0.1 mmol). The resulting mixture was allowed to stir at room temperature for indicated time. After completion of the reaction, the mixture was passed through a short column on a silica gel pad (3 g), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

Typical procedure for the synthesis of azafulleroid using amides and N-iodosuccinimide

N-Iodosuccinimide (22.5 mg, 0.1 mmol) was added to a *o*-DCB (25 mL) solution of fullerene (36 mg, 0.05 mmol) and amide (0.05 mmol). The resulting mixture was allowed to stir at room temperature for indicated time. After completion of the reaction, the mixture was passed through a short column on a silica gel pad (3 g), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

Spectra data of azafulleroids **1a**,[6a] **1b**,[10b] **1g**,[6a] and **1l**[6a] were identical with those in the literature.

1,6-*N*-(1-naphthalenesulfonyl)aza[60]fulleroid (1c)

black solid; FT-IR (KBr) cm^{-1} 3434, 1509, 1338, 1164, 1134, 766; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.61-7.70 (m, 2H), 7.71-7.77 (m, 1H), 7.98 (d, 1H, *J* = 7.6 Hz), 8.19 (d, 1H, *J* = 8.1 Hz), 8.57 (dd, 1H, *J* = 1.4 Hz, 7.6 Hz), 8.88 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 125.2, 127.3, 128.8, 128.9, 129.1, 131.8, 133.50, 133.54, 134.3, 134.9, 135.99, 136.03, 137.9, 138.4, 138.5, 138.7, 139.8, 140.06, 140.14, 141.7, 141.8, 142.7, 142.9, 143.0, 143.1, 143.3, 143.5, 143.69, 143.71, 143.09, 144.0, 144.08, 144.14, 144.2, 144.3, 144.4, 144.7, 147.3, 147.9; UV-vis (CH_2Cl_2) λ_{max} nm 224, 258, 322; FAB-MS *m/z* 925 $[M]^+$; HR-MS: calcd for ($C_{70}H_7NO_2S$): 925.0234, found: 925.0197; R_f = 0.34 (toluene/hexane = 1/1)

1,6-*N*-(2-nitrobenzenesulfonyl)aza[60]fulleroid (1d)

black solid; FT-IR (KBr) cm^{-1} 3435, 2923, 1637, 1543, 1381, 1174, 1124; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.80-7.84 (m, 3H), 8.33-8.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 124.6, 131.2 (2C), 131.6, 131.9, 132.3, 134.4, 134.6, 135.7, 137.7, 138.2, 139.5, 139.9 (2C), 141.5 (2C), 142.4, 142.5, 142.7, 142.8, 143.1, 143.2, 143.4, 143.56, 143.64, 143.9, 144.0 (2C), 144.1, 144.4, 146.9, 147.7; UV-vis (CH_2Cl_2) λ_{max} nm 224, 257, 324; FAB-MS *m/z* 920 [M]$^{+}$; HR-MS: calcd for ($C_{66}H_4N_2O_4S$): 919.9892, found: 919.9894; R_f = 0.13 (toluene/hexane = 1/1)

1,6-*N*-(4-nitrobenzenesulfonyl)aza[60]fulleroid (1e)

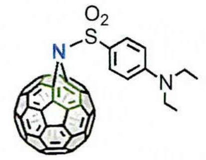
black solid; FT-IR (KBr) cm^{-1} 3446, 2924, 1529, 1346, 1173, 1086, 854, 744, 615; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.41 (m, 4H); ^{13}C NMR ($CDCl_3$:CS_2 = 2:1, 68 MHz) δ 124.2, 124.6, 127.4, 129.5, 129.7, 130.2, 131.6, 132.4, 134.5, 134.7, 137.5, 138.2, 138.3, 139.8, 140.0, 141.3, 141.5, 142.3, 142.4, 142.7, 142.9, 143.1, 143.3, 143.5, 143.7, 143.8, 143.86, 143.94, 143.98 (2C), 144.04 (2C), 144.3, 144.7, 146.9, 148.6, 150.3; UV-vis (CH_2Cl_2) λ_{max} nm 225, 257, 324; FAB-MS *m/z* 920 [M]$^{+}$; HR-MS: calcd for ($C_{66}H_4N_2O_4S$): 919.9892, found: 919.9908; R_f = 0.25 (toluene/hexane = 1/1)

1,6-*N*-(2-carboxymethylbenzenesulfonyl)aza[60]fulleroid (1f)

black solid; FT-IR (KBr) cm^{-1} 3446, 2923, 1738, 1429, 1365, 1292, 1257, 1172, 1115, 1059; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.66-7.75 (m, 3H), 8.27-8.30 (m, 1H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 53.34, 129.2, 130.0, 132.7, 133.4, 133.6, 134.7, 135.6, 136.4, 137.6, 137.8, 138.2, 138.3, 139.1, 139.3, 139.5, 140.0, 141.49, 141.54, 142.4, 142.6, 142.8, 142.9, 143.1, 143.3, 143.5, 143.6, 143.7, 143.90, 143.93, 143.99, 144.024, 144.1, 144.5, 147.0, 147.8, 167.1; UV-vis (CH_2Cl_2) λ_{max} nm 225, 258, 324;

FAB-MS *m/z* 934 ($[M]^{+}$+1); HR-MS: calcd for ($C_{68}H_7NO_4S$): 933.0096, found: 933.0121; R_f = 0.25 (toluene)

1,6-*N*-(4-*N'*,*N'*-diethylaminobenzenesulfonyl)aza[60]fulleroid (1h)

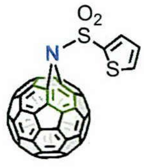


black solid; FT-IR (KBr) cm^{-1} 3422, 1589, 1509, 1150, 1092, 638, 526; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.20 (t, 6H, *J* = 7.3 Hz), 3.43 (d 2H *J* = 7.3 Hz), 6.66 (d, 2H, *J* = 8.9 Hz), 7.92 (d, 2H, *J* = 8.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 12.3, 44.8, 110.5, 121.1, 122.2, 131.6, 135.0, 135.1, 135.6, 137.4, 138.2, 138.3, 138.7, 139.7, 139.9, 140.0, 141.7 (2C), 142.7, 142.8, 142.96, 143.03, 143.2, 143.4, 143.6, 143.7, 143.8, 143.95, 143.97, 144.1, 144.18, 142.02, 144.22, 144.24, 144.7, 147.5, 148.2, 151.6; UV-vis (CH_2Cl_2) λ_{max} nm 224, 258, 320; FAB-MS *m/z* 947 ($[M]^{+}$+1); HR-MS: calcd for ($C_{70}H_{14}N_2O_2S$) $[M]^{+}$: 946.0776, found: 946.0754; R_f = 0.4 (toluene)

1,6-*N*-(5-methyl-2-pyridinesulfonyl)aza[60]fulleroid (1i)

black solid; FT-IR (KBr) cm^{-1} 3450, 2920, 2345, 1439, 1367, 1175, 731, 668, 526; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.49 (s, 3H), 7.78 (dd, 1H, *J* = 1.9, 7.8 Hz), 8.17 (d, 1H, *J* = 7.8 Hz), 8.62 (d, 1H, *J* = 1.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 18.78, 123.8, 132.7, 134.8, 135.8, 138.0, 138.26, 138.34, 138.4, 138.5, 138.6, 139.2, 139.7, 140.1, 141.73, 141.75, 142.7, 143.0, 143.1, 143.3, 143.5, 143.7, 143.8, 143.9, 144.0, 144.1, 144.15, 144.19, 144.21, 144.23, 144.25, 144.6, 144.9, 147.4, 148.9, 151.0, 153.6; UV-vis (CH_2Cl_2) λ_{max} nm 224, 258, 324; FAB-MS *m/z* 890 ($[M]^{+}$); HR-MS: calcd for ($C_{61}H_3NO_2S$): 890.0150, found: 890.0173; R_f = 0.13 (toluene)

1,6-*N*-(2-thiophenesulfonyl)aza[60]fulleroid (1j)

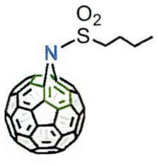


black solid; FT-IR (KBr) cm^{-1} 3259, 2922, 1637, 1375, 1340, 1322, 1165, 1090; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.19 (dd, 1H, *J* = 2.4, 4.9 Hz), 7.76 (d, 1H, *J* = 4.9 Hz), 7.95 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 127.8, 132.3, 132.9, 133.7, 134.4, 134.7, 134.8, 134.9, 135.6, 137.8, 138.2, 138.5, 139.3, 139.6, 140.0, 141.4, 141.5, 142.4, 142.5, 142.8, 143.1, 143.3, 143.5, 143.7, 143.8, 143.95, 144.04, 144.3, 144.6 (2C), 145.7, 146.0, 147.1, 148.8; UV-vis (CH$_2$Cl$_2$) λ_{max} nm 225, 256, 325; FAB-MS *m/z* 882 ([M]$^+$+1); HR-MS: calcd for (C$_{64}$H$_3$NO$_2$S$_2$): 880.9605, found: 880.9596; R$_f$ = 0.25 (toluene/hexane = 1/1)

1,6-*N*-(5-bromo-2-thiophenesulfonyl)aza[60]fulleroid (1k)

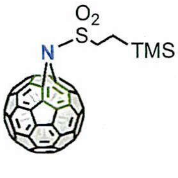
black solid; FT-IR (KBr) cm^{-1} 3448, 2924, 1637, 1375, 1165, 1088, 802, 609; ^{1}H NMR (CDCl$_3$:CS$_2$= 2:1, 270 MHz) δ 7.13 (d, 1H, *J* = 3.8 Hz), 7.67 (d, 1H, *J* = 3.8 Hz); ^{13}C NMR (CDCl$_3$:CS$_2$ = 2:1, 68 MHz) δ 122.7, 130.7, 132.4, 134.7, 134.8, 135.3, 137.7, 138.2, 138.5, 139.7, 140.0, 141.4, 141.5, 142.4, 142.5, 142.79 (2C), 142.82, 142.9, 143.1, 143.3, 143.51, 143.54, 143.7, 143.8, 143.9, 143.97, 143.98, 144.01, 144.04 (2C), 144.3, 144.6, 147.1; UV-vis (CH$_2$Cl$_2$) λ_{max} nm 224, 257, 324; FAB-MS *m/z* 960 ([M]$^+$+1); HR-MS: calcd for (C$_{64}$H$_2$BrNO$_2$S$_2$): 958.8710, found: 958.8740; R$_f$ = 0.25 (toluene/hexane = 1/1)

1,6-*N*-(1-butylsulfonyl)aza[60]fulleroid (1m)



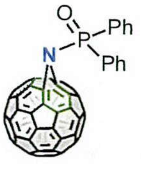
black solid; FT-IR (KBr) cm^{-1} 3446, 2924, 2360, 1637, 1153, 1116; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.03 (t, 3H, *J* = 7.3 Hz), 1.58 (m, 2H), 2.03 (m, 2H), 3.50 (m, 2H); ^{13}C NMR (CDCl$_3$:CS$_2$ = 2:1, 125 MHz) δ 13.7, 21.7, 25.7, 54.4, 133.8, 134.9, 136.1, 137.9, 138.6, 138.7, 139.8, 140.1, 140.2, 141.7, 141.8, 142.6, 142.8, 142.9, 143.0, 143.1, 143.3, 143.5, 143.6, 143.8, 144.0, 144.05, 144.09, 144.12, 144.13, 144.21, 144.24, 144.4, 144.6, 147.1, 147.4; UV-vis (CH_2Cl_2) λ_{max} nm 225, 258, 324; FAB-MS *m/z* 856 ($[M]^+$+1); HR-MS: calcd for ($C_{64}H_9NO_2S$): 855.0354, found: 855.0383; R_f = 0.25 (toluene/hexane = 1/1)

1,6-*N*-{(2-trimethylsilyl)ethanesulfonyl}aza[60]fulleroid (1n)



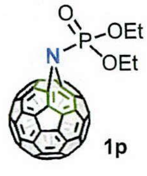
black solid; FT-IR (KBr) cm^{-1} 3429, 1654, 1354, 1153, 833; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.13 (s, 9H), 1.27-1.34 (m, 2H), 3.42-3.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ -1.85, 10.6, 51.3, 133.7, 134.8, 135.9, 137.7, 138.4, 138.55, 138.61, 139.7, 139.9, 140.0, 141.5, 141.6, 142.45 (2C), 142.67, 142.74, 142.9, 143.1, 143.3, 143.4, 143.7, 143.8, 143.88, 143.92, 143.96, 144.01, 144.04, 144.2, 144.4, 147.0, 147.1; UV-vis (CH_2Cl_2) λ_{max} nm 224, 257, 324; FAB-MS *m/z* 900 ($[M]^+$+1); HR-MS: calcd for ($C_{65}H_{13}NO_2SSi$): 899.0436, found: 899.0452; R_f = 0.25 (toluene/hexane = 1/1)

1,6-*N*-(diphenylphosphino)aza[60]fulleroid (1o)



black solid; FT-IR (KBr) cm^{-1} 3446, 2929, 1654, 1623, 1434, 1116, 729; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.26-8.34 (m, 4H), 7.56-7.60 (m, 6H); ^{13}C NMR ($CDCl_3$:CS_2= 2:1, 125 MHz) δ 128.6, 128.7, 128.9, 130.5, 132.6, 132.8, 133.0, 133.8, 134.6, 135.0, 136.3, 136.6, 137.2, 137.4, 138.0, 138.4, 138.9, 140.0, 141.1, 142.1, 142.6, 142.7, 142.8, 142.9, 143.1, 143.4, 143.5, 143.6, 143.7, 143.8, 143.88, 143.94, 144.1, 144.3, 144.5, 145.8, 147.2; UV-vis (CH_2Cl_2) λ_{max} nm 224, 258, 321; FAB-MS *m/z* 936 ($[M]^+$+1); HR-MS: calcd for ($C_{72}H_{10}NOP$): 935.0500, found: 935.0527; R_f = 0.40 (toluene/ethyl acetate = 8/2)

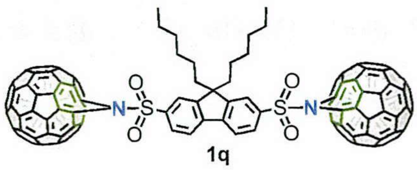
1,6-*N*-(diethoxyphosphino)aza[60]fulleroid (1p)



1p

black solid; FT-IR (KBr) cm^{-1} 3448, 2924, 1637, 1051; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.46-1.59 (m, 6H), 4.39-4.52 (m, 4H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 16.4, 64.5, 134.1, 134.15, 134.21, 136.59, 136.63, 137.48, 137.52, 138.26, 138.29, 138.9, 139.6, 141.1, 141.7, 142.6, 142.7, 142.8, 143.0, 143.2 (2C), 143.3, 143.5, 143.70 (2C), 143.74 (2C), 143.8, 143.9, 144.0, 144.1, 144.2, 144.6, 146.27, 146.33, 147.2; UV-vis (CH_2Cl_2) λ_{max} nm 225, 260, 324; FAB-MS *m/z* 872 ([M]$^+$+1); HR-MS: calcd for ($C_{67}H_7NO_2S$) [M]$^+$: 871.0398, found: 871.0386; R_f = 0.50 (toluene/ethyl acetate = 8/2)

Bisadduct (1q)



1q

black solid; FT-IR (KBr) cm^{-1} 3007, 2927, 1442, 1301, 1056, 983, 912, 860, 771, 752, 729; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.78 (t, 6H, *J* = 6.8 Hz), 1.01 (m, 16H), 2.00 (m, 4H), 7.93 (d, 2H, *J* = 1.0, 8.1 Hz), 8.16 (d, 2H, *J* = 1.0 Hz), 8.24 (dd, 2H, *J* = 1.0, 8.1 Hz); ^{13}C NMR ($CDCl_3$:CS_2 = 2:1, 125 MHz) δ 14.1, 22.9, 24.2, 30.1, 31.7, 39.4, 56.3, 121.7, 124.2, 127.7, 128.2, 128.9, 129.0, 130.5, 133.2, 134.90, 134.94, 137.7, 137.8, 138.0, 138.2, 138.6, 139.0, 139.8, 140.2, 141.6, 141.7, 142.59, 142.62, 143.0, 143.1, 143.3, 143.6, 143.8, 143.9, 144.0, 144.1, 144.21, 144.25, 144.3, 144.4, 144.9, 147.3, 149.1, 153.2; UV-vis (CH_2Cl_2) λ_{max} nm 224, 257, 321; FAB-MS *m/z* 1929 ([M]$^+$+1); HR-MS: calcd for ($C_{145}H_{32}N_2O_4S_2$) [M]$^+$: 1928.1803, found: 1928.1817; R_f = 0.25 (toluene)

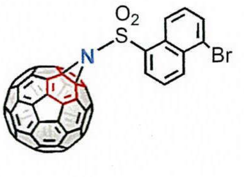
Selective Synthesis of Aziridinofullerenes

Typical procedure for the synthesis of aziridinofullerenes using N,N-dibromoamides and NaI

Sodium iodide (7.5 mg, 0.05 mmol) was added to a *o*-DCB (25 mL) solution of fullerene (36 mg, 0.05 mmol) and *N,N*-dibromoamide (0.05 mmol). The mixture was allowed to stir at room temperature for indicated time. The solution was passed through a short column on a silica gel pad (3 g), and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel.

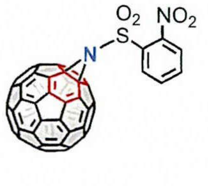
Spectra data of **2a**,[6a] **2b**,[10b] **2g**,[6a] and **2l**[10b] were identical with those in the literature.

1,2-*N*-(6-bromo-1-naphthalenesulfonyl)aziridino[60]fullerene (2r)



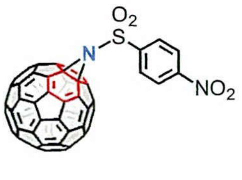
black solid; FT-IR (KBr) cm^{-1} 1350, 1167, 1138, 994, 785, 615, 525; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.72 (dd, 1H, *J* = 7.3, 8.6 Hz), 7.86 (t, 1H, *J* = 7.8, 8.6 Hz), 8.04 (d, 1H, *J* = 7.3 Hz), 8.71 (d, 1H, *J* = 7.8 Hz), 8.78 (d, 1H, *J* = 8.6 Hz), 9.30 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 79.8, 123.8, 124.9, 125.5, 129.0, 130.0, 131.0, 131.5, 132.7, 134.4, 135.0, 140.8, 141.1, 141.7, 141.9, 142.8, 142.92, 142.95, 143.69, 143.71, 143.9, 144.3, 144.89, 144.94, 144.98, 145.1; UV-vis (CH_2Cl_2) λ_{max} nm 224, 251, 317; FAB-MS *m/z* 1005 ($[M]^+$+1); HR-MS: calcd for ($C_{70}H_6BrNO_2S$) $[M]^+$: 1002.9303, found: 1002.9309; R_f = 0.13 (toluene/hexane = 1/1)

1,2-*N*-(2-nitrobenzenesulfonyl)aziridino[60]fullerene (2d)



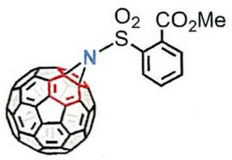
black solid; FT-IR (KBr) cm^{-1} 3434, 1539, 1363, 1169, 1121, 526; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.96-8.02 (m, 2H), 8.12-8.15 (m, 1H), 8.61-8.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 80.6, 125.7, 131.1, 133.2, 134.1, 134.8, 140.8 (2C), 141.2, 142.1, 142.3, 142.8, 143.1, 143.2, 143.3, 143.6, 144.0, 144.5, 144.6, 145.2, 145.3, 145.4, 147.4; UV-vis (CH_2Cl_2) λ_{max} nm 316, 253, 224; FAB-MS *m/z* 921 ($[M]^+$+1); HR-MS: calcd for ($C_{66}H_4N_2O_4S$): 919.9892, found: 919.9927; R_f = 0.38 (toluene/hexane = 1/1)

1,2-*N*-(4-nitrobenzenesulfonyl)aziridino[60]fullerene (2e)



black solid; FT-IR (KBr) cm^{-1} 3450, 2923, 2854, 2362, 1596, 1355, 1169, 671, 621; ^1H NMR ($CDCl_3$:CS_2 = 2:1, 270 MHz) δ 8.56 (s, 4H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 79.4, 124.8, 128.1, 128.9, 129.6, 141.0, 141.2, 141.7, 142.1, 142.4, 143.1, 143.76, 143.84, 143.9, 144.0, 144.5, 145.1, 145.2, 145.3, 151.0; UV-vis (CH_2Cl_2) λ_{max} nm 224, 253, 316; FAB-MS *m/z* 921 ($[M]^+$+1); HR-MS: calcd for ($C_{66}H_4N_2O_4S$) $[M]^+$: 919.9892, found: 919.9898; R_f = 0.43 (toluene/hexane = 1/1)

1,2-*N*-(2-carboxymethylbenzenesulfonyl)aziridino[60]fullerene (2f)



black solid; FT-IR (KBr) cm^{-1} 1735, 1169, 1081, 526; ^1H NMR ($CDCl_3$, 270 MHz) δ 4.07 (s, 3H), 7.82-7.85 (m, 2H), 7.92-7.96 (m, 1H), 8.52-8.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 53.67, 80.9, 129.85, 130.28, 131.6, 132.5, 133.8, 138.5, 140.6, 140.9, 142.0, 142.1, 143.0, 143.1, 143.9, 144.0, 144.4, 144.5, 144.99, 145.04, 145.1, 145.2, 166.8; UV-vis (CH_2Cl_2) λ_{max} nm 224, 252, 317; FAB-MS *m/z* 934 ($[M]^+$+1); HR-MS: calcd for ($C_{68}H_7NO_4S$): 933.0096, found: 933.0125; R_f = 0.1 (toluene/hexane = 1/1)

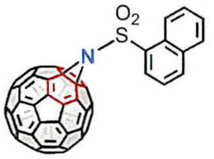
1,2-*N*-{(2-trimethylsilyl)ethanesulfonyl}aziridino[60]fullerene (2n)

black solid; FT-IR (KBr) cm^{-1} 1349, 1151, 816, 754, 525; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.22 (s, 9H), 1.52-1.59 (m, 2H), 3.71-3.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -1.8, 10.3, 52.9, 79.4, 141.0, 141.1, 142.0, 142.2, 142.9, 143.1, 143.17, 143.19, 143.5, 144.0, 144.3, 144.6, 145.1, 145.16, 145.24, 145.4; UV-vis

(CH_2Cl_2) λ_{max} nm 224, 252, 317; FAB-MS *m/z* 900 ($[M]^+$+1); HR-MS: calcd for ($C_{65}H_{13}NO_2SSi$): 899.0436, found: 899.0431; R_f = 0.38 (toluene/hexane = 1/1)

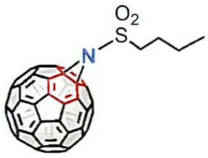
* **2c** and **2m** were obtained in the selective synthesis of azafulleroids as a minor product.

1,2-*N*-(1-naphthalenesulfonyl)aziridino[60]fullerene (2c)



black solid; FT-IR (KBr) cm^{-1} 2956, 2312, 1338, 1163, 1134, 798, 765, 738; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.71-7.78 (m, 2H), 7.86-7.92 (m, 1H), 8.10 (d, 1H *J* = 18.0 Hz), 8.30 (d, 1H, *J* = 18.0 Hz), 8.65 (d, 1H, *J* = 16.8, 3.0 Hz), 9.28 (d, 1H, *J* = 19.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 80.1, 124.4, 125.2, 127.5, 128.9, 129.1, 129.2, 130.5, 134.1, 134.5, 136.2, 141.0, 141.3, 142.0, 142.2, 142.9, 143.17, 143.21, 143.3, 143.96, 144.02, 144.3, 144.6, 145.1, 145.16, 145.24, 145.4; UV-vis (CH_2Cl_2) λ_{max} nm 222, 252, 318, 417; FAB-MS *m/z* 925 $[M]^+$; HR-MS: calcd for ($C_{64}H_9NO_2S$): 925.0197, found: 925.0202; R_f = 0.45 (toluene/hexane = 1/1)

1,2-*N*-(*n*-butanesulfonyl)aziridino[60]fullerene (2m)

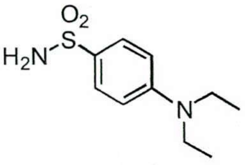


black solid; FT-IR (KBr) cm^{-1} 2985, 2922, 1463, 1425, 1344, 1151, 819, 729; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.10 (t, *J* = 7.2 Hz, 3H), 1.73 (q, *J* = 7.2 Hz, 2H), 2.29-2.34 (m, 2H), 3.78-3.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 13.7, 21.7, 25.6, 55.8, 79.3, 141.0, 141.1, 142.0, 142.9, 143.17, 143.20, 143.3, 143.96, 144.0, 144.3, 144.6, 145.13, 145.17, 145.24, 145.4; UV-vis (CH_2Cl_2) λ_{max} nm 224, 252, 318, 417; FAB-MS *m/z* 855 $[M]^+$; HR-MS: calcd for ($C_{64}H_9NO_2S$): 855.0354, found: 855.0323; R_f = 0.31 (toluene/hexane = 1/1)

Preparation of sulfonamides

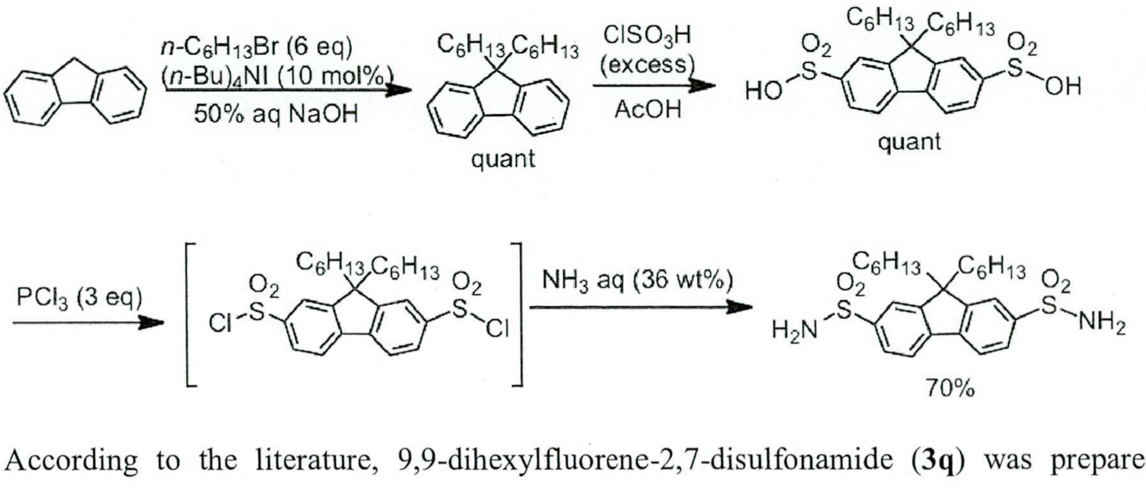
1-naphthalenesulfonamide (**3c**),[53] 1-butanesulfonamide (**3m**),[54] and 2-(trimethylsilyl)ethanesulfonamide (**3n**)[55] were prepared according to the procedure in the literatures and identified by ^{1}H NMR, ^{13}C NMR, IR, MASS, HR-MASS spectroscopy.

4-(*N,N*-diethylamino)benzenesulfonamide (3h)[56]



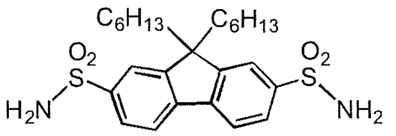
Prepared by the procedure described in ref. 61. colorless solid; 82% yield; mp. 131.6-133.3 °C; IR (KBr, cm^{-1}) 1597, 1514, 1311, 1147, 812; ^{1}H NMR (CD_3CN, 270 MHz) δ 1.14 (t, *J* = 7.0 Hz, 6H), 3.41 (q, *J* = 14.0 Hz, 4H), 5.33 (s, br, 2H), 6.71 (d, *J* = 9.2 Hz, 2H), 7.59 (d, *J* = 9.2, 2H); ^{13}C NMR (CD_3CN, 100 MHz) δ 12.5, 45.1, 111.2, 128.9, 128.9, 151.3; MS (CI, isobutane): *m/z* (relative intensity, %) 229 ($[M+H]^+$, 100); HRMS (CI, isobutane): *m/z* Calcd for $C_{10}H_{17}N_2O_2S$ (M+H) 229.1011, found 229.1013.

Preparation of 9,9-dihexylfluorene-2,7-disulfonamide (3q)[57]



According to the literature, 9,9-dihexylfluorene-2,7-disulfonamide (**3q**) was prepared and identified by ^{1}H NMR, ^{13}C NMR, MASS and HR-MASS spectroscopy.

9,9-dihexylfluorene-2,7-disulfonamide (3q)



Colorless solid; 70% yield; mp. 165.4-167.0 °C; IR (KBr, cm^{-1}) 2927, 2854, 1319, 1151, 817; ^1H NMR (CD_3CN, 600 MHz) δ 0.51 (m, 2H), 0.73-0.75 (m, 3H), 1.00-1.09 (m, 6H), 2.10 (m, 2H), 7.90 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.93 (d, *J* = 1.8 Hz, 2H), 7.99 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (CD_3CN, 150 MHz) δ 14.2, 23.1, 24.5, 30.1, 32.1, 40.2, 57.1, 121.9, 122.1, 126.5, 144.12, 144.13, 153.2; FAB-MS *m/z* 492 ($[M]^+$); HR-MS: calcd for ($C_{25}H_{36}N_2O_4S_2$): 492.2116, found: 492.2101.

Preparation of *N,N*-dibromosulfonamides

General procedure for the preparation of N,N-dibromosulfonamides[28]

Sulfonamide (0.06 mol) was dissolved in a solution of NaOH (0.03 mol, 1.2 g) in water (25 mL) at room temperature. Then bromine (2.17 mL) was added dropwise with vigorous stirring. The resulting precipitate was filtered and washed with cold water to give *N,N*-dibromosulfonamide as yellow solid.

N,N-dibromo-*p*-toluenesulfonamide (**5a**),[58] *N,N*-dibromobenzenesulfonamide (**5b**),[59] *N,N*-dibromo-2-acetylbenzenesulfonamide (**5f**),[60] and *N,N*-dibromo-2-(trimetylsilyl)ethanesulfonamide (**5n**)[61] were prepared according to the procedure in the literatures. These sulfonamides were identified by ^1H NMR, ^{13}C NMR, IR, MASS, HR-MASS spectroscopy.

N,N-dibromo-5-bromonaphthalenesulfonamide (5r)

Yellow solid; 67% yield; mp. 162 °C (decomp); IR (KBr, cm^{-1}) 1576, 1343, 1138, 998, 900, 780; ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.55 (dd, 1H, *J* = 8.1, 7.3 Hz), 7.74 (dd, 1H, *J* = 8.9, 7.3 Hz), 7.79 (d, 1H, *J* = 7.3 Hz), 8.51 (d, 1H, *J* = 8.9 Hz), 8.59 (d, 1H, *J* = 7.3 Hz), 8.73 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR (CDCl$_3$, 68 MHz) δ 123.5, 125.2, 125.3, 125.4, 129.1, 130.8, 131.7, 135.2, 136.2; EI *m/z* 443 ([M]$^+$+1); HR-MS: calcd for ($C_{10}H_6Br_3NO_2S$) [M]$^+$: 440.7669, found: 440.7649.

In order to determine the chemical structure of **5r**, dibromoamide **5r** was reduced to 5-bromonaphthalenesulfonamide by the following procedure, and the position of Br group was assigned by 2D NMR measurement of the sulfonamide (see the Figure S1).

A suspension of *N,N*-dibromosulfonamide **5r** (442 mg, 1 mmol) was stirred in 1M HCl aq (10 mL) for 10 min, extracted with ethyl acetate (10 mL×3), then dried over Na_2SO_4. The organic phase was concentrated under reduced pressure to give 5-bromonaphtalenesulfonamide quantatively.

Colorless solid; mp. 204-206 °C; IR (KBr, cm^{-1}) 3344, 3244, 1558, 1327, 1132, 997, 916, 781; ^{1}H NMR (CD$_3$CN, 600 MHz) δ 5.92 (s, br, 2H), 7.59 (dd, 1H, *J* = 7.8, 8.4 Hz), 7.73 (dd, 1H, *J* = 7.8, 8.4 Hz), 7.79, 7.99 (d, 1H, *J* = 7.2 Hz), 8.30 (dd, 1H, *J* = 6.0, 7.2 Hz), 8.53 (d, 1H, *J* = 8.4 Hz), 8.67 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR (CD$_3$CN, 150 MHz) δ 124.0, 125.8, 127.0, 129.16, 129.21, 130.0, 132.1, 133.15, 133.22, 139.9; EI *m/z* 285 ([M] 100); HR-MS: calcd for ($C_{10}H_8BrNO_2S$) : 284.9459 , found: 284.9462.

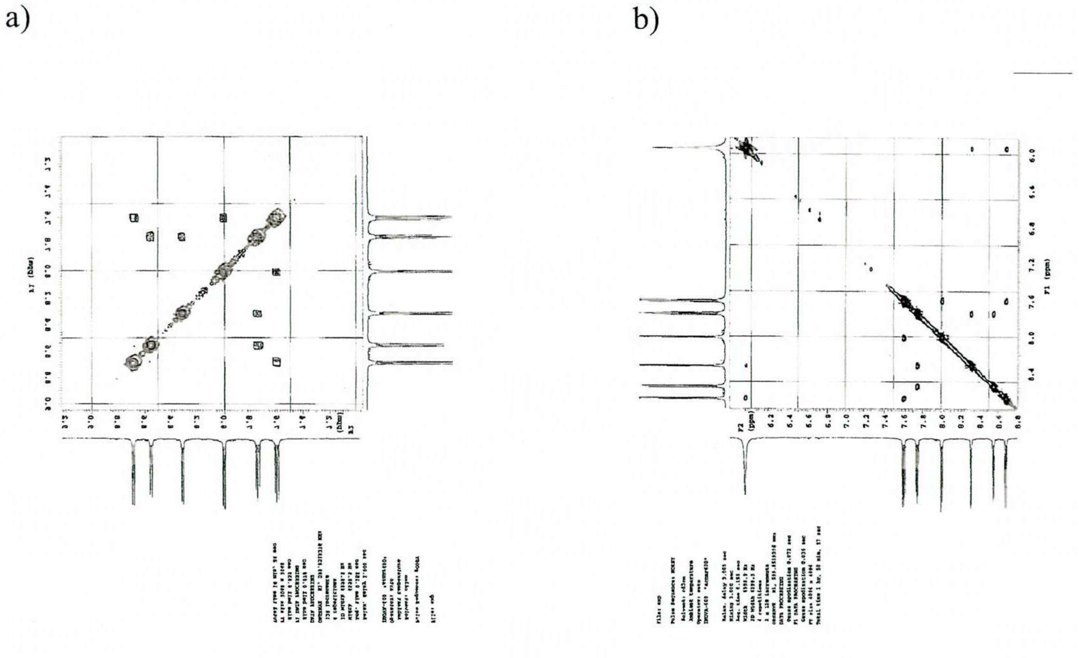


Figure S1. 2D NMR spectra of 5-bromonaphthalenesulfonamide a) H-H COSY b) H-H NOESY.

***N,N*-dibromo-2-nitrobenzenesulfonamide (5d)**

Yellow solid; 71% yield; mp. 136 °C (decomp.); IR (KBr, cm^{-1}) 3369, 3261, 1530, 1361, 1336, 1159, 1128, 785; ^{1}H NMR (CD_3CN, 270 MHz) δ 7.65-7.79 (m, 3H), 8.49 (dd, 1H, $J = 6.8, 2.7$ Hz); ^{13}C NMR (CD_3CN, 150 MHz) δ 124.7, 130.4, 132.4, 132.6, 134.9, 149.8; EI *m/z* 360 ($[M]^+ + 1$); HR-MS: calcd for ($C_6H_4Br_2N_2O_4S$): 357.8259, found: 357.8269.

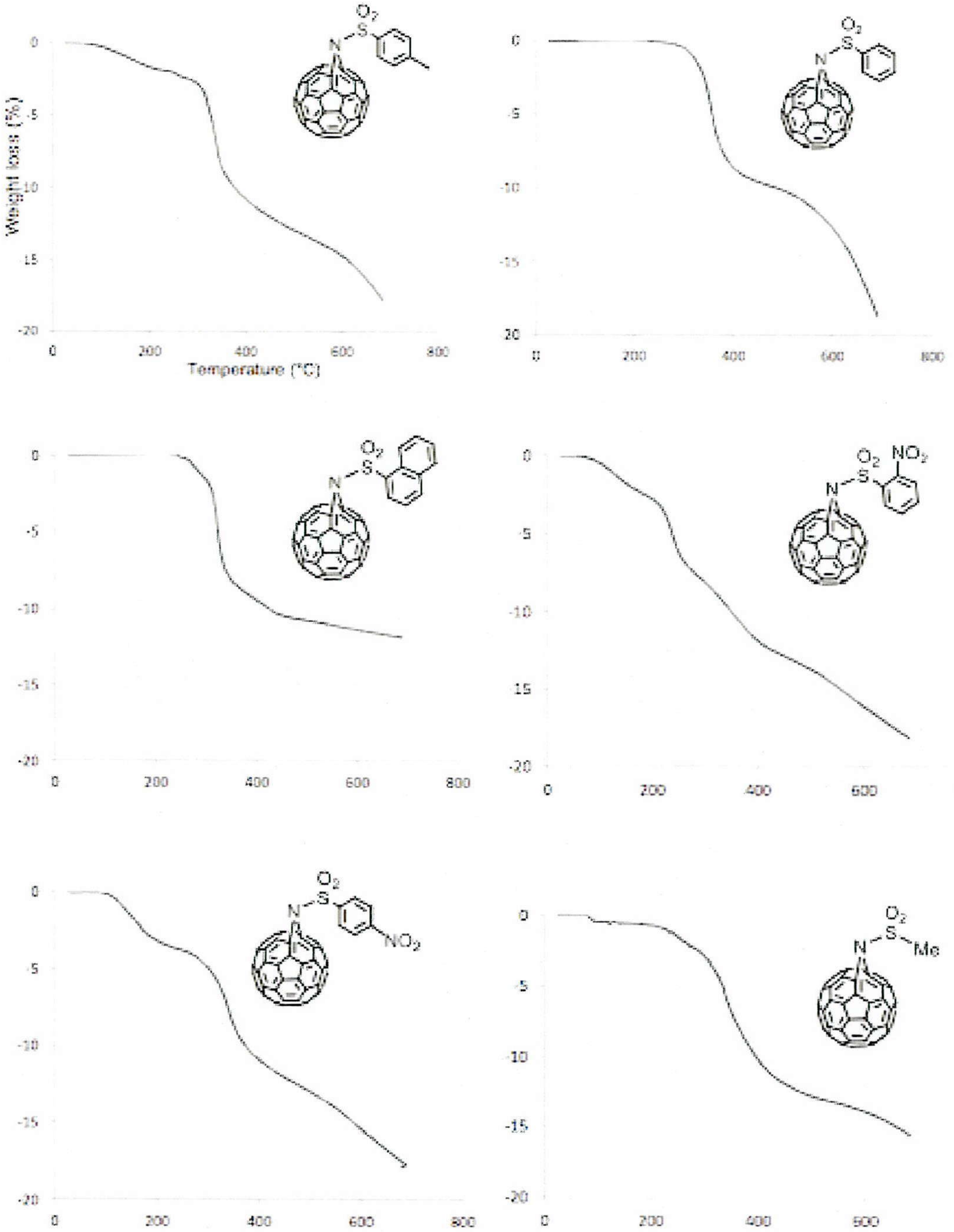
***N,N*-dibromo-4-nitrobenzenesulfonamide (5e)**

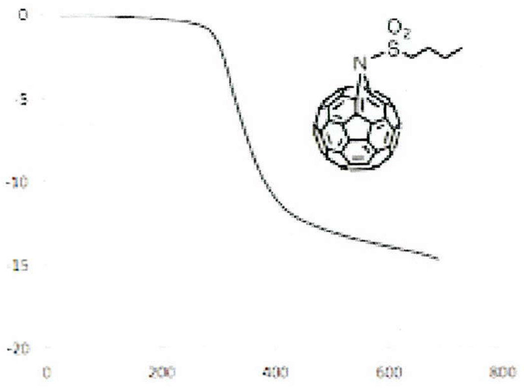
Yellow solid; 93% yield; mp. 142 °C (decomp.); IR (KBr, cm^{-1}) 3332, 3248, 1610, 1566, 1344, 1311, 1159, 1091, 826, 738; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.34 (d, 2H, $J = 8.4$ Hz), 8.49 (d, 2H, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 124.1, 124.9, 127.9, 132.5; EI *m/z* 360 ($[M]^+ + 1$); HR-MS: calcd for ($C_6H_4Br_2N_2O_4S$): 357.8259, found: 357.8261.

_N,N_-dibromomethanesulfonamide (5l)

Yellow solid; 38% yield; mp. 113 °C (decomp); IR (KBr, cm^{-1}) 3010, 2927, 1311, 1149, 964, 768; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 32.3; EI *m/z* 253 ($[M]^{+}$+1); HR-MS: calcd for ($CH_3Br_2NO_2S$): 250.8251, found: 250.8249.

Figure S2. TGA profiles of azafulleroids and aziridinofullerenes measured under nitrogen flow from 40 to 700 °C at the ramp rate of 10 °C/min.

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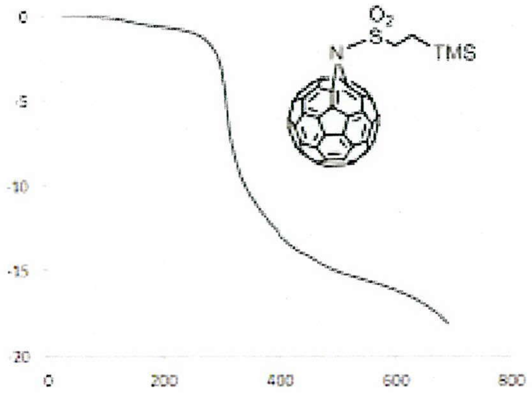
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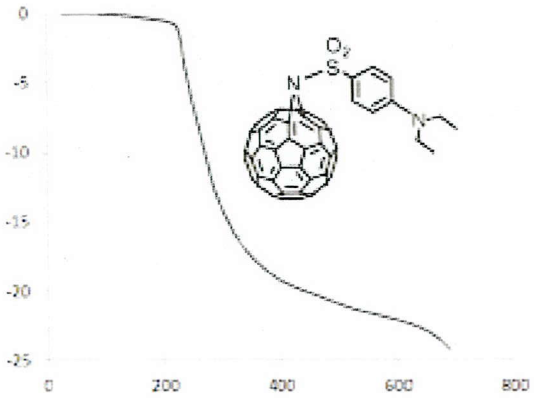
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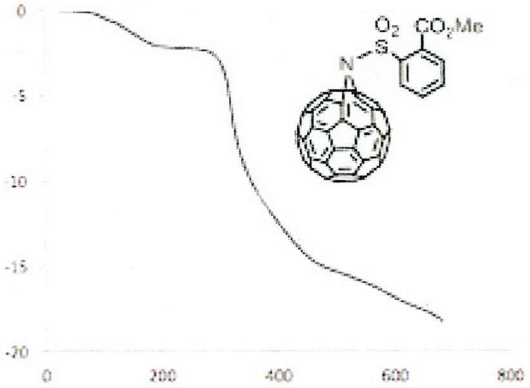
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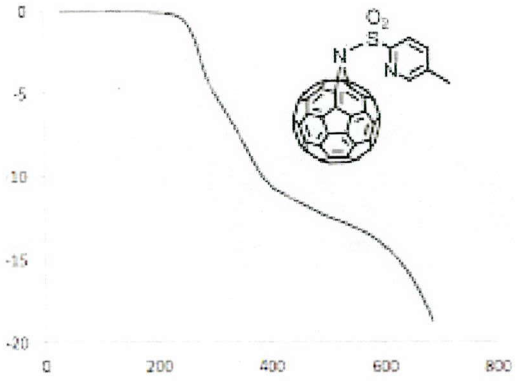
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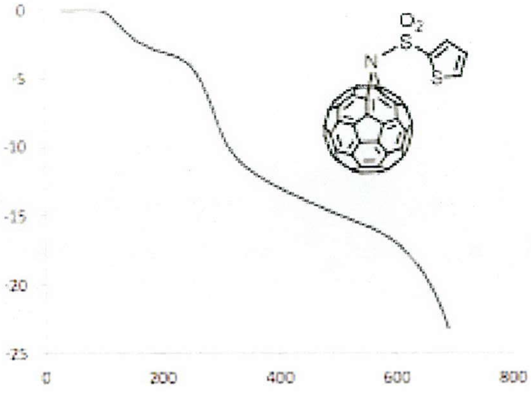
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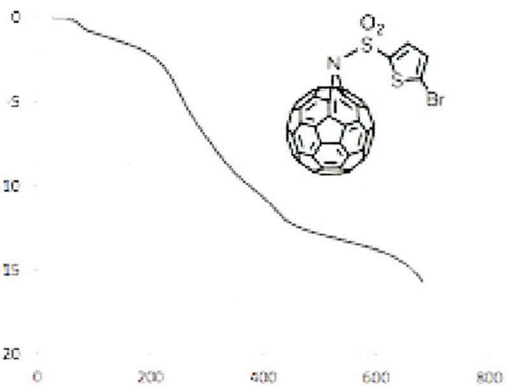
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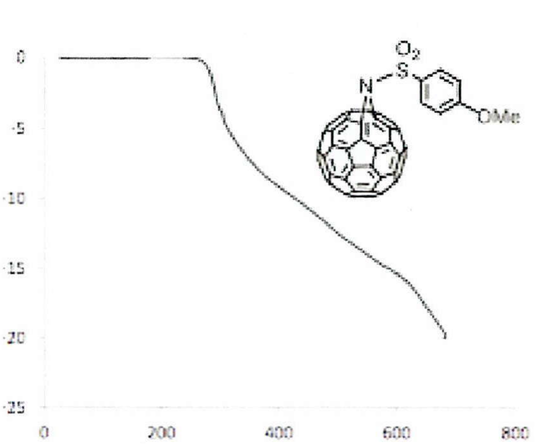
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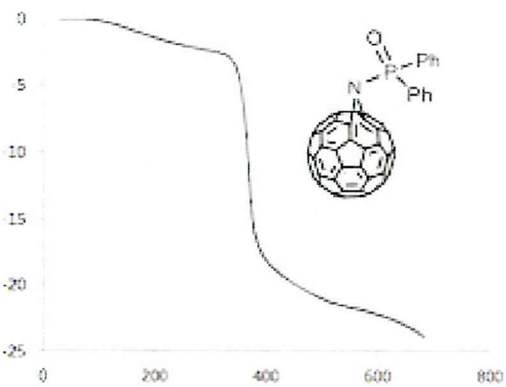
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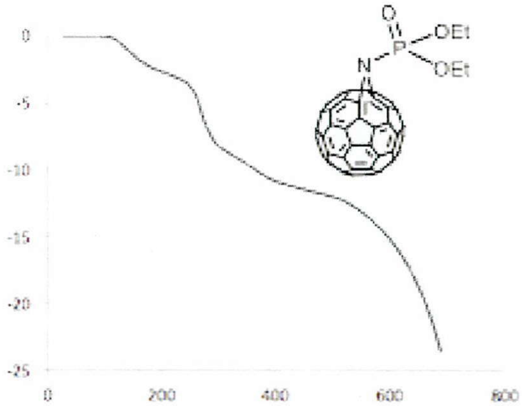
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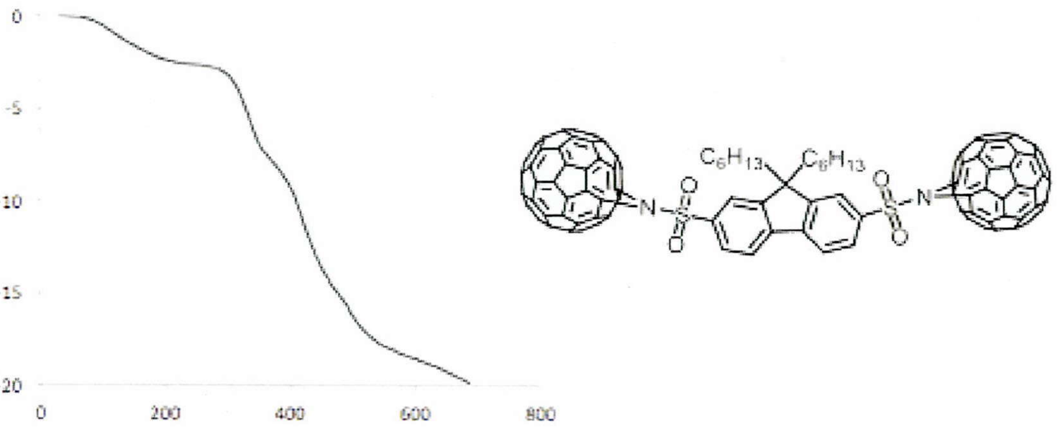
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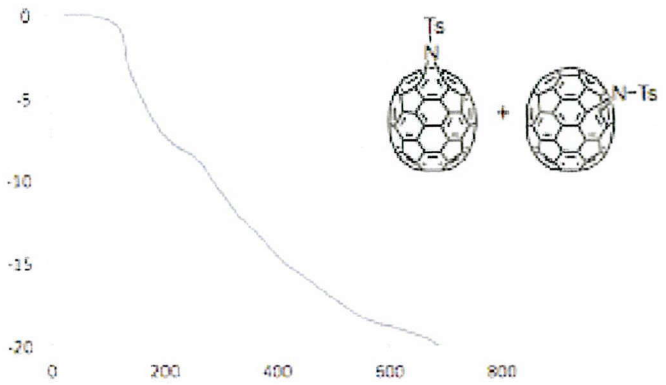
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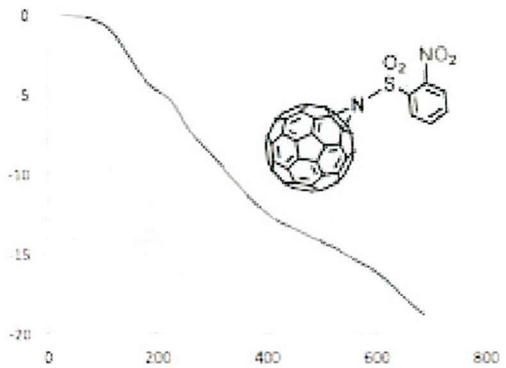
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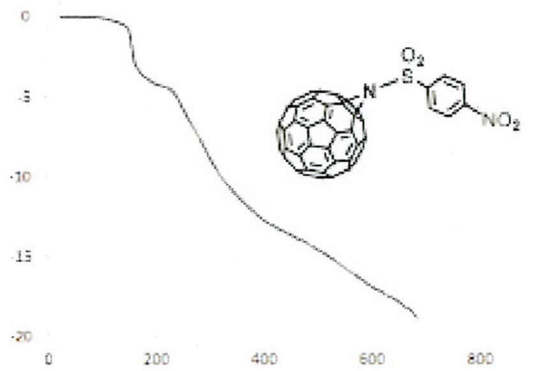
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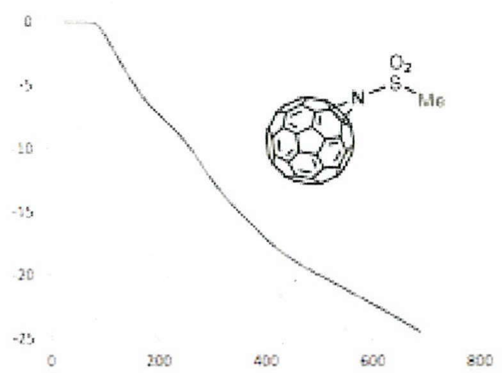
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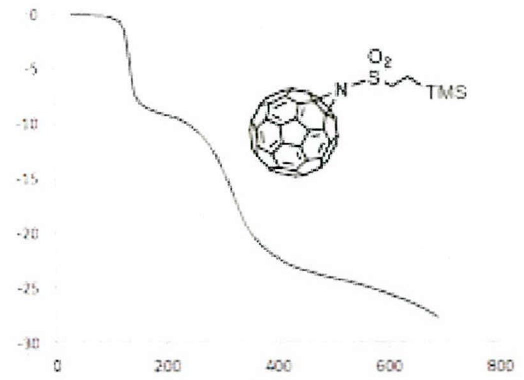
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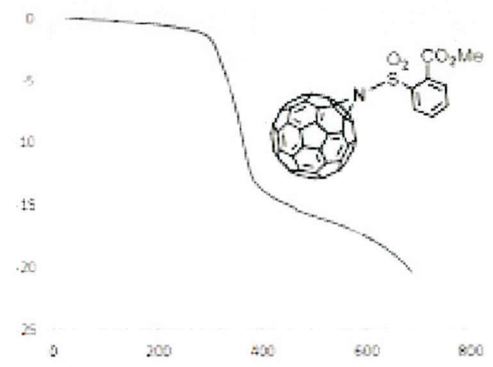
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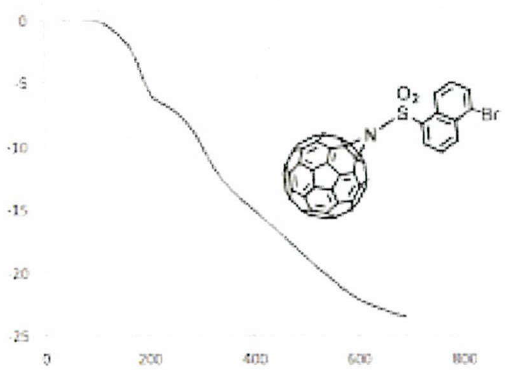
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N
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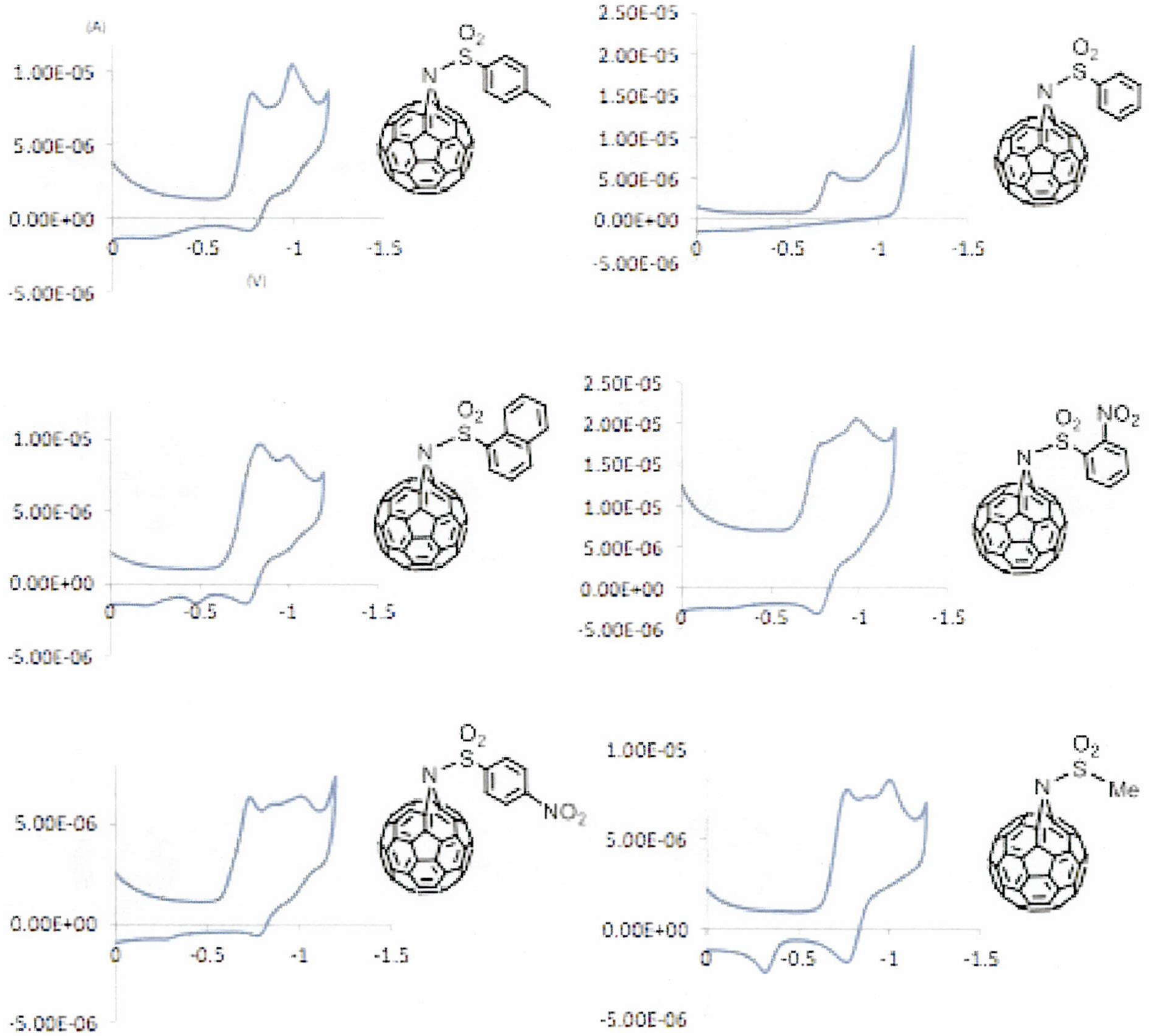
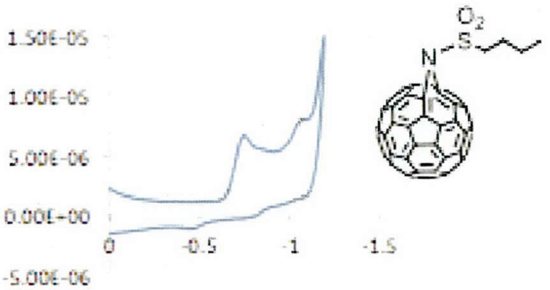
Br

Figure S2. Cyclic voltammograms of azafulleroids and aziridinofullerenes. Measurement was performed at room temperature in *o*-DCB/MeCN (4:1 v/v) solutions (1.0 □10^{-5} M) containing 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte and with a glassy carbon as the working electrode. The counter electrode was a Pt wire, and an Ag wire was used as the reference electrode. The scan rate was 100 mV. The values for ${}^{red}E_{onset}$ in V versus Fc/Fc^{+} (Fc = ferrocene)

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0.00E+00
-5.00E-06
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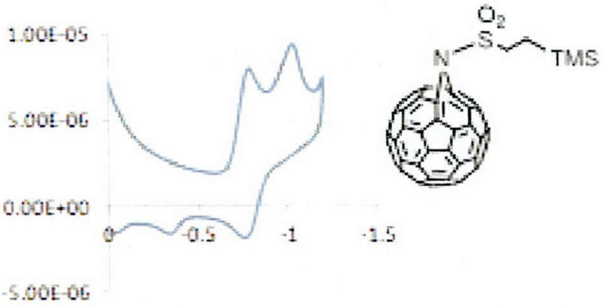
-0.5
-1
-1.5
O2
N
S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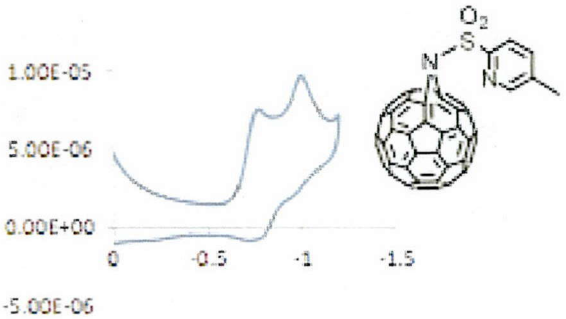
O2
N
S
TMS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-1
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O2
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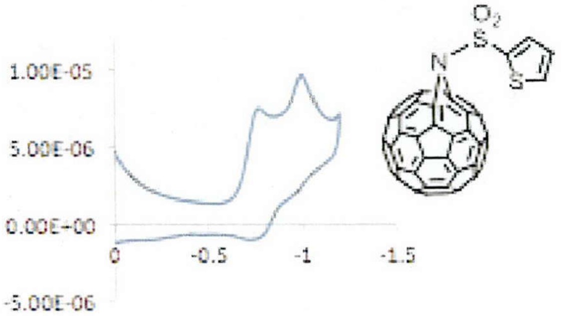
S
N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O2
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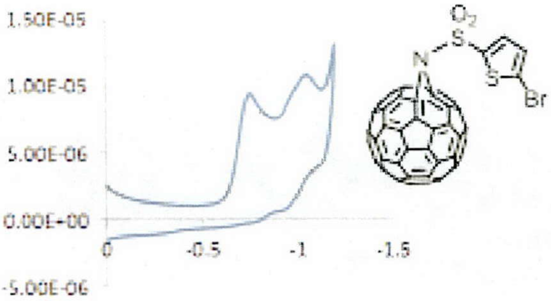
S
S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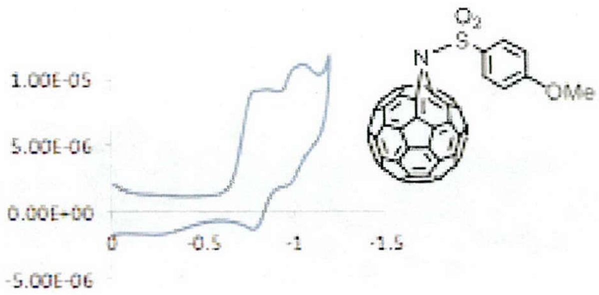
-1
-1.5
O2
N
S
S
Br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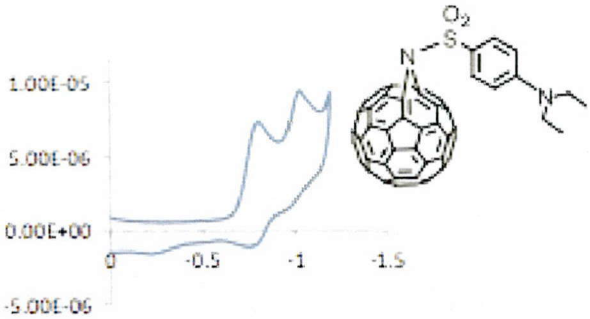
-5.00E-06
0
-0.5
-1
-1.5
O2
N
S
OMe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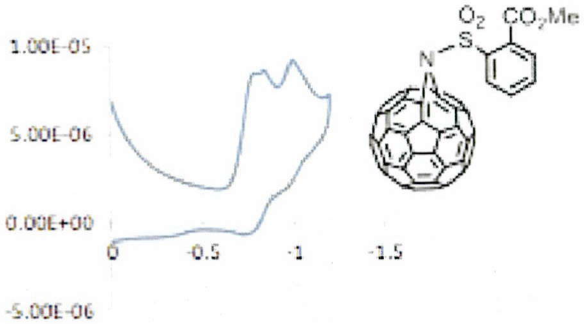
-1
-1.5
O2
N
S
N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-1
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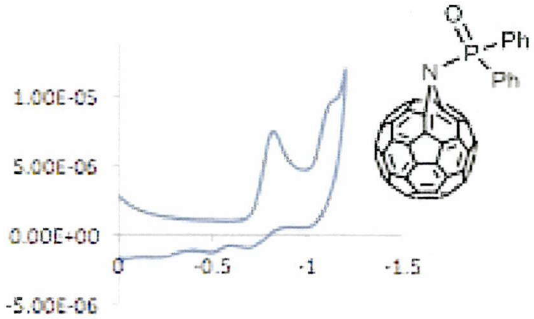
O2
CO2Me
N
S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-1.5
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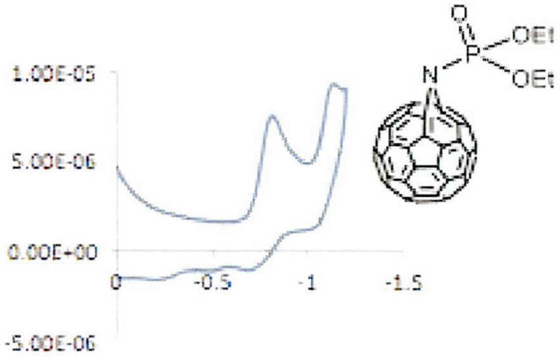
P
Ph
Ph
N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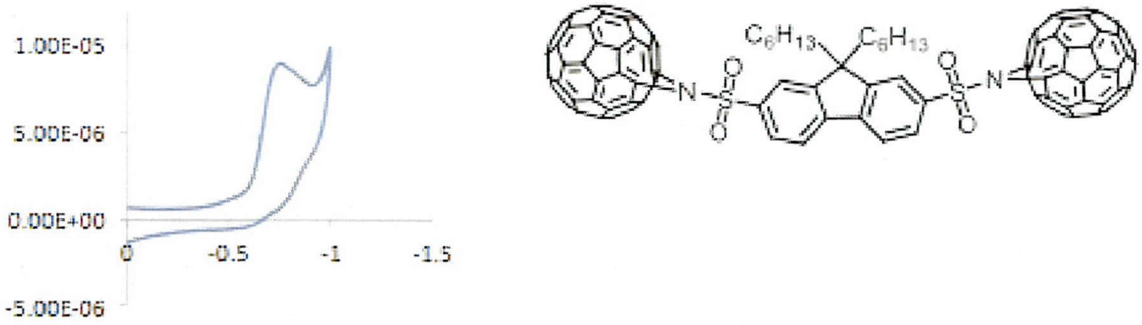
P
OEt
OEt
N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-5.00E-06
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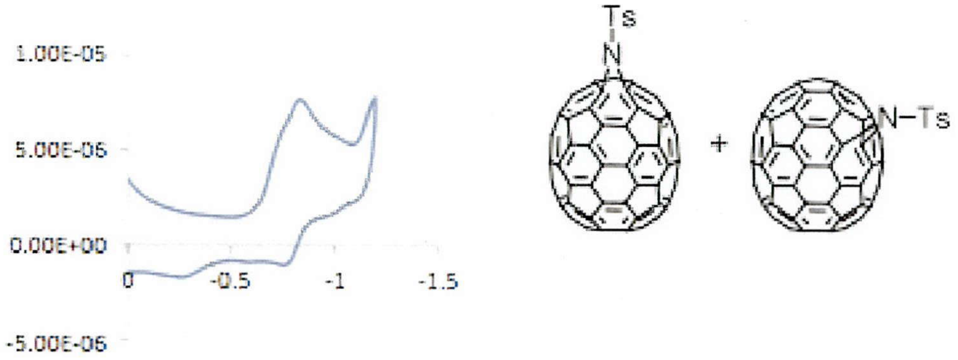
-1
-1.5
C6H13
C6H13
N
S
O
O
S
O
O
N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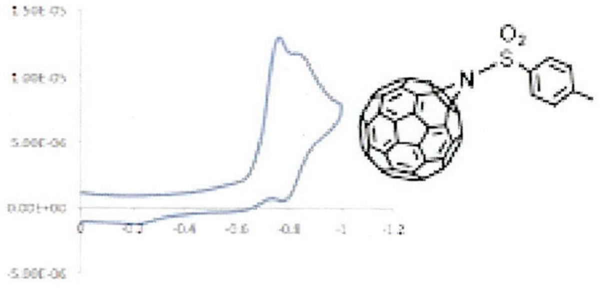
-0.5
-1
-1.5
Ts
N
+
N–Ts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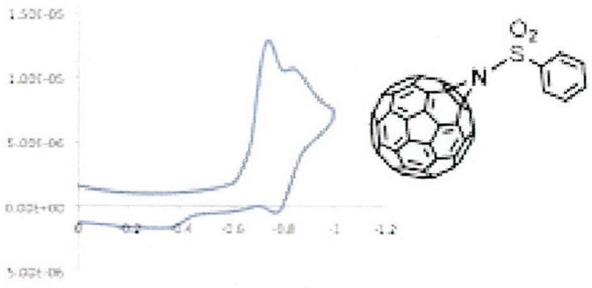
-0.4
-0.6
-0.8
-1
-1.2
O2
S
N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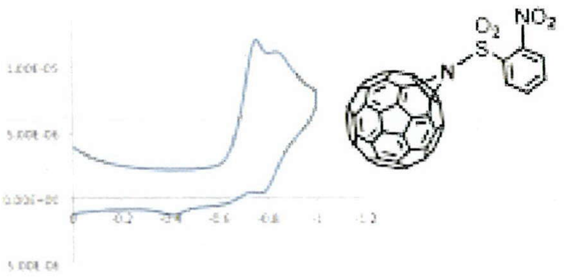
-0.8
-1
-1.2
O2
S
N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-0.2
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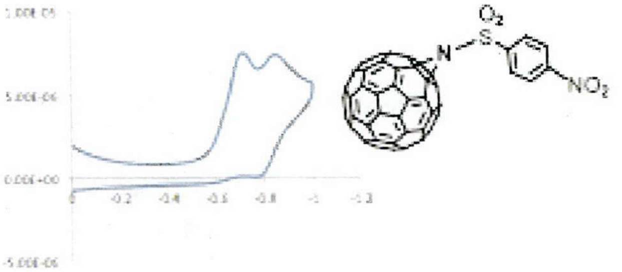
-0.8
-1
-1.2
O2
NO2
N
S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-5.00E-06
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
O2
N
S
NO2


1.00E-05
5.00E-06
0.00E+00
-5.00E-06
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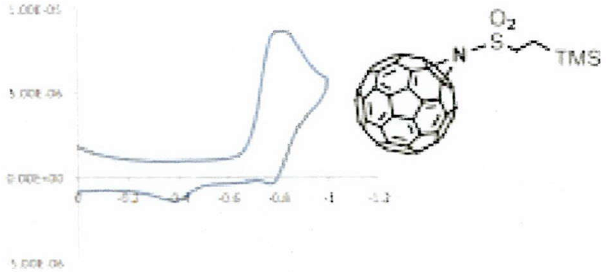
-0.2
-0.4
-0.6
-0.8
-1
-1.2
O2
N
S
Me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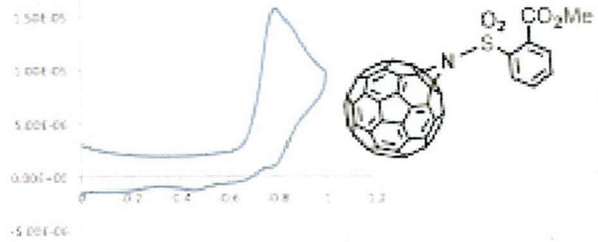
0
-0.2
-0.4
-0.6
-0.8
-1
-1.2
O2
N
S
TMS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0.00E+00
-5.00E-06
0
0.2
0.4
0.6
0.8
1
1.2
O2
CO2Me
N
S

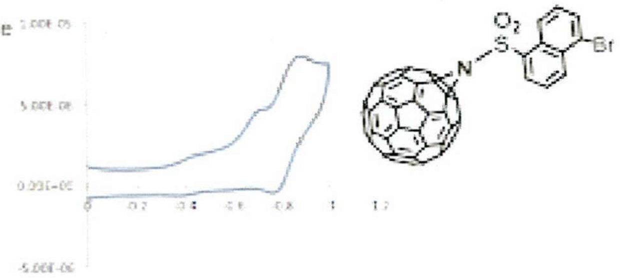
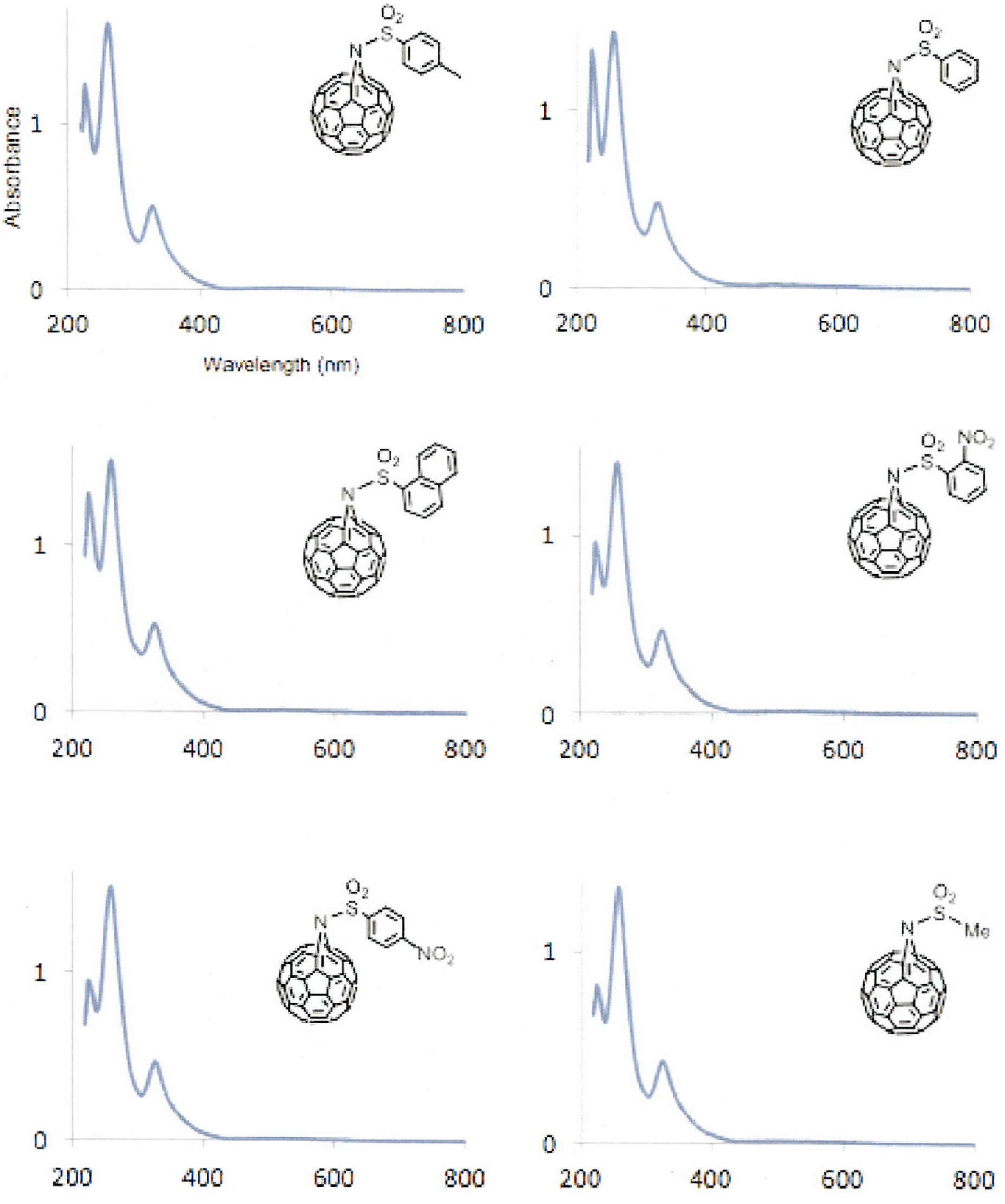
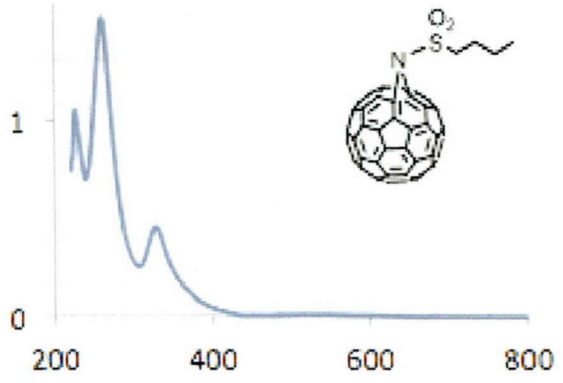
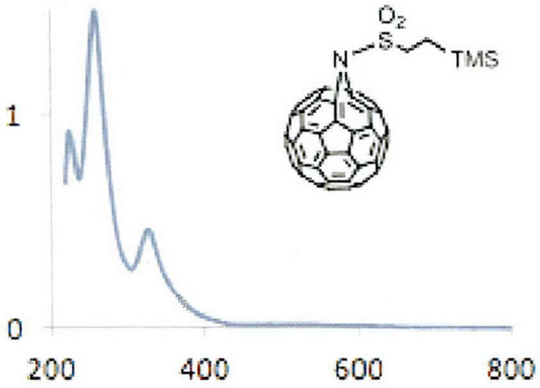

1.00E-05
5.00E-06
0.00E+00
-5.00E-06
0
0.2
0.4
0.6
0.8
1
1.2
O2
N
S
Br

Figure S3. UV-vis spectra of CH_2Cl_2 solutions (1.0×10^{-5} M) of azafulleroids and aziridinofullerenes measured at room temperature with the scanning range starting from 200 to 800 nm.

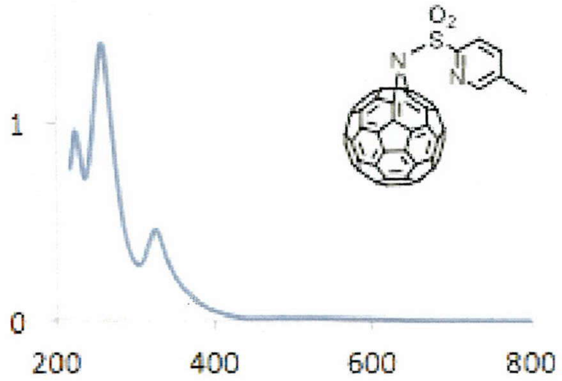




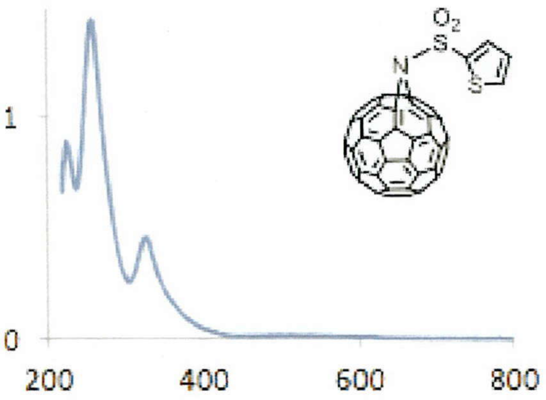
N
S
O2
1
0
200
400
600
800



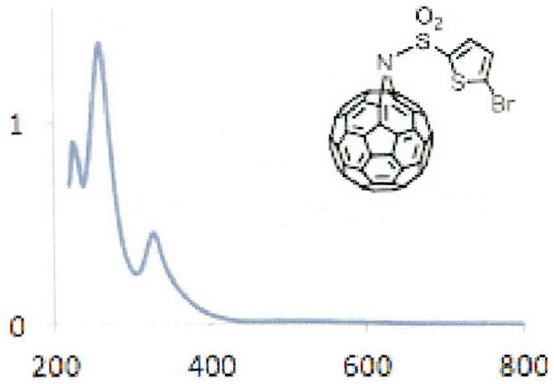
N
S
O2
TMS
1
0
200
400
600
800



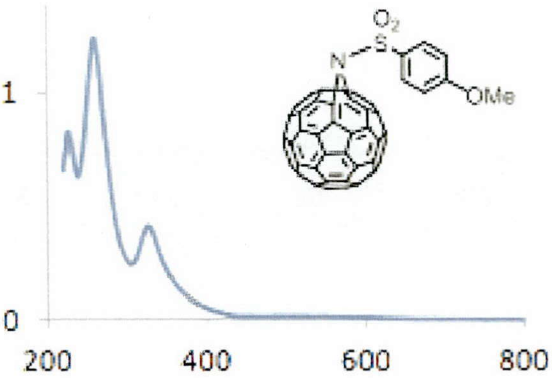
N
S
O2
N
1
0
200
400
600
800



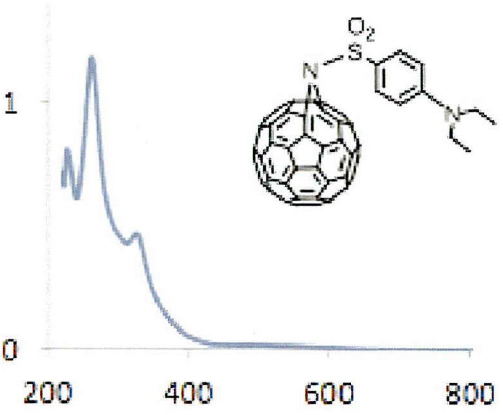
N
S
O2
S
1
0
200
400
600
800

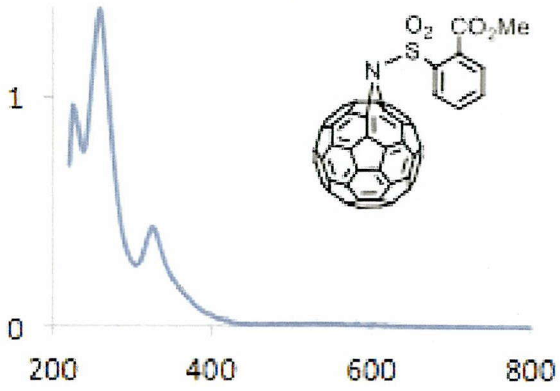


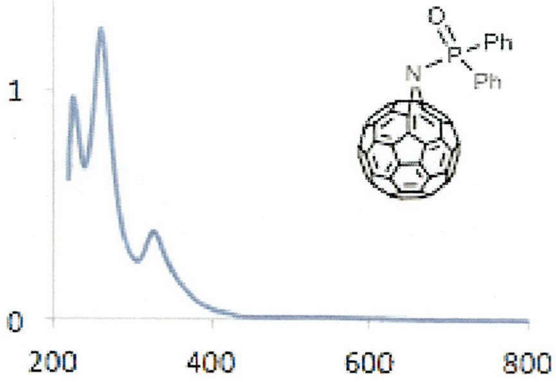
N
S
O2
S
Br
1
0
200
400
600
800

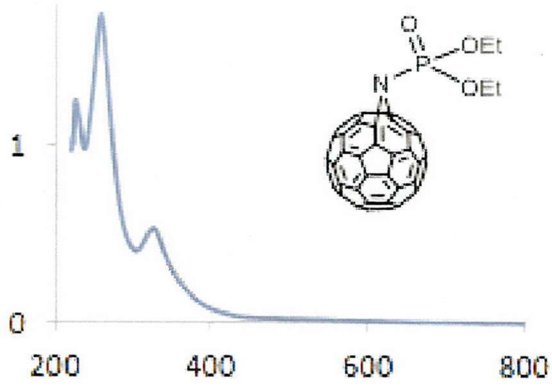


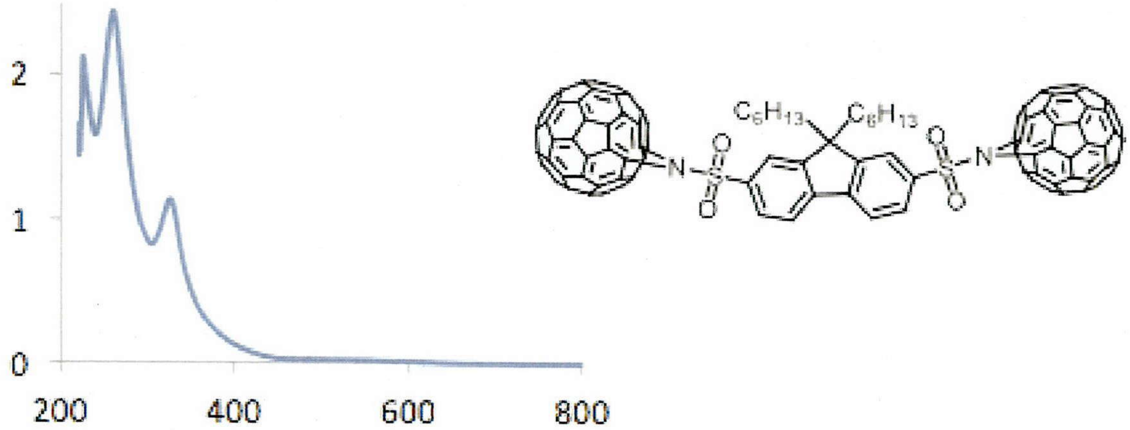
N
S
O2
OMe
1
0
200
400
600
800

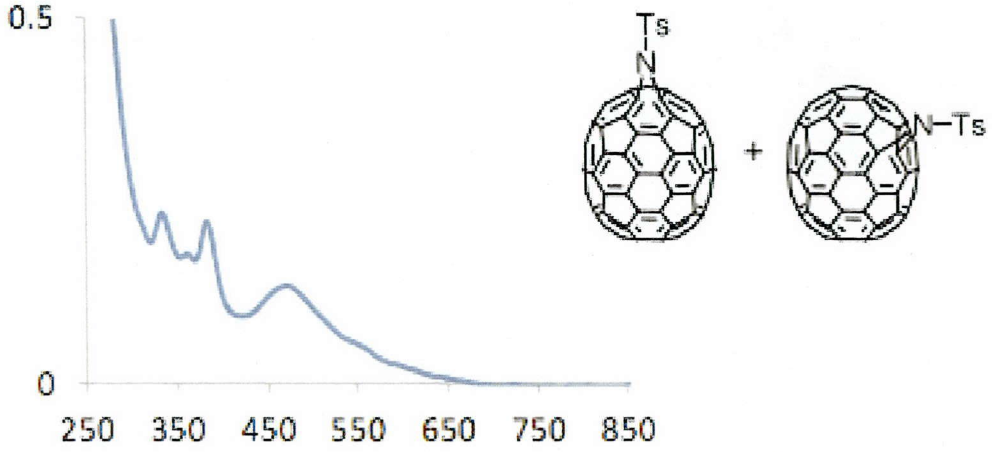

1
0
200
400
600
800
O2
N
S
N

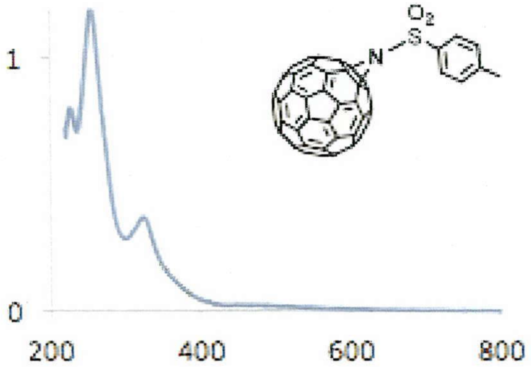

1
0
200
400
600
800
O2
CO2Me
N
S

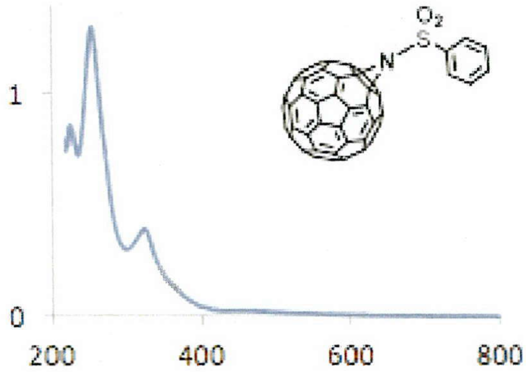

1
0
200
400
600
800
O
P
Ph
Ph
N

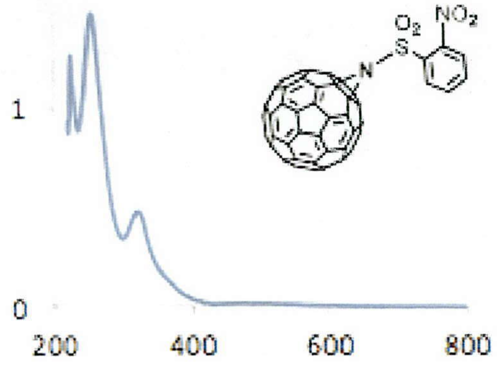

1
0
200
400
600
800
O
P
OEt
OEt
N

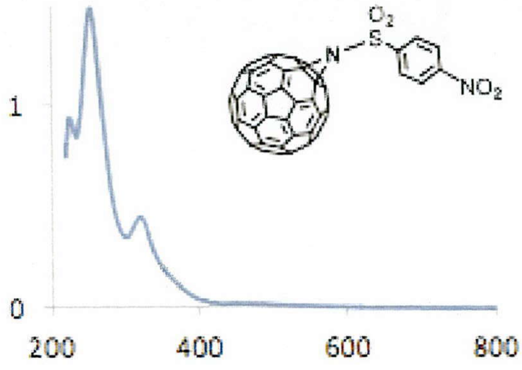

2
1
0
200
400
600
800
C6H13
C6H13
N
S
O
O
S
O
O
N

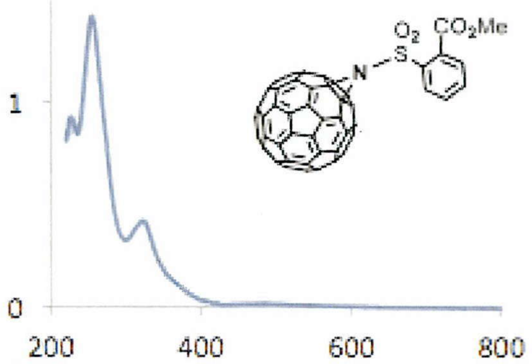

0.5
0
250
350
450
550
650
750
850
Ts
N
+
N–Ts

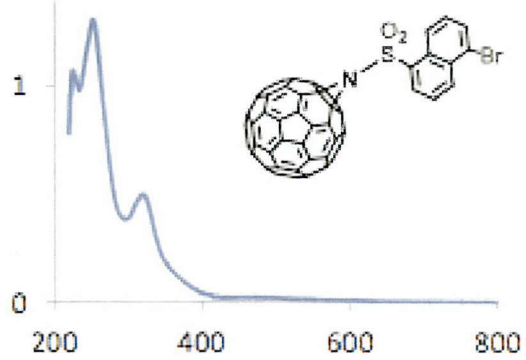

1
0
200
400
600
800
O2
S
N

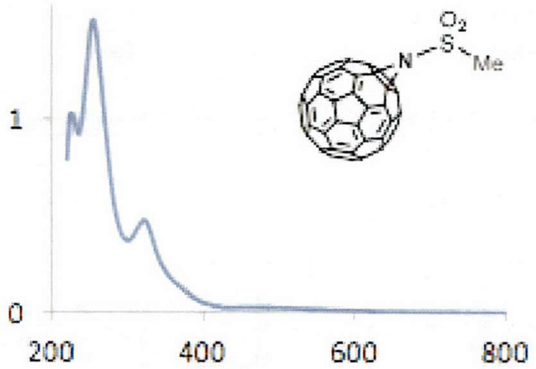

1
0
200
400
600
800
O2
S
N


1
0
200
400
600
800
O2
NO2
S
N


1
0
200
400
600
800
O2
S
N
NO2


O2
CO2Me
S
N
1
0
200
400
600
800


O2
S
Br
N
1
0
200
400
600
800


O2
S
Me
N
1
0
200
400
600
800

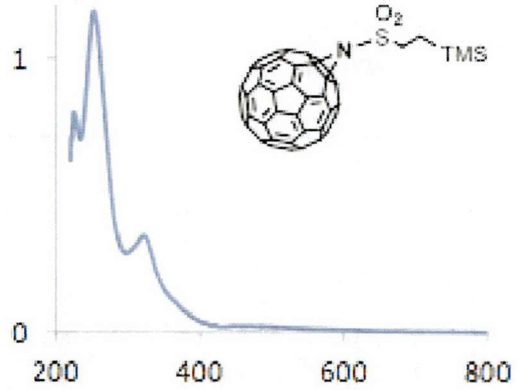
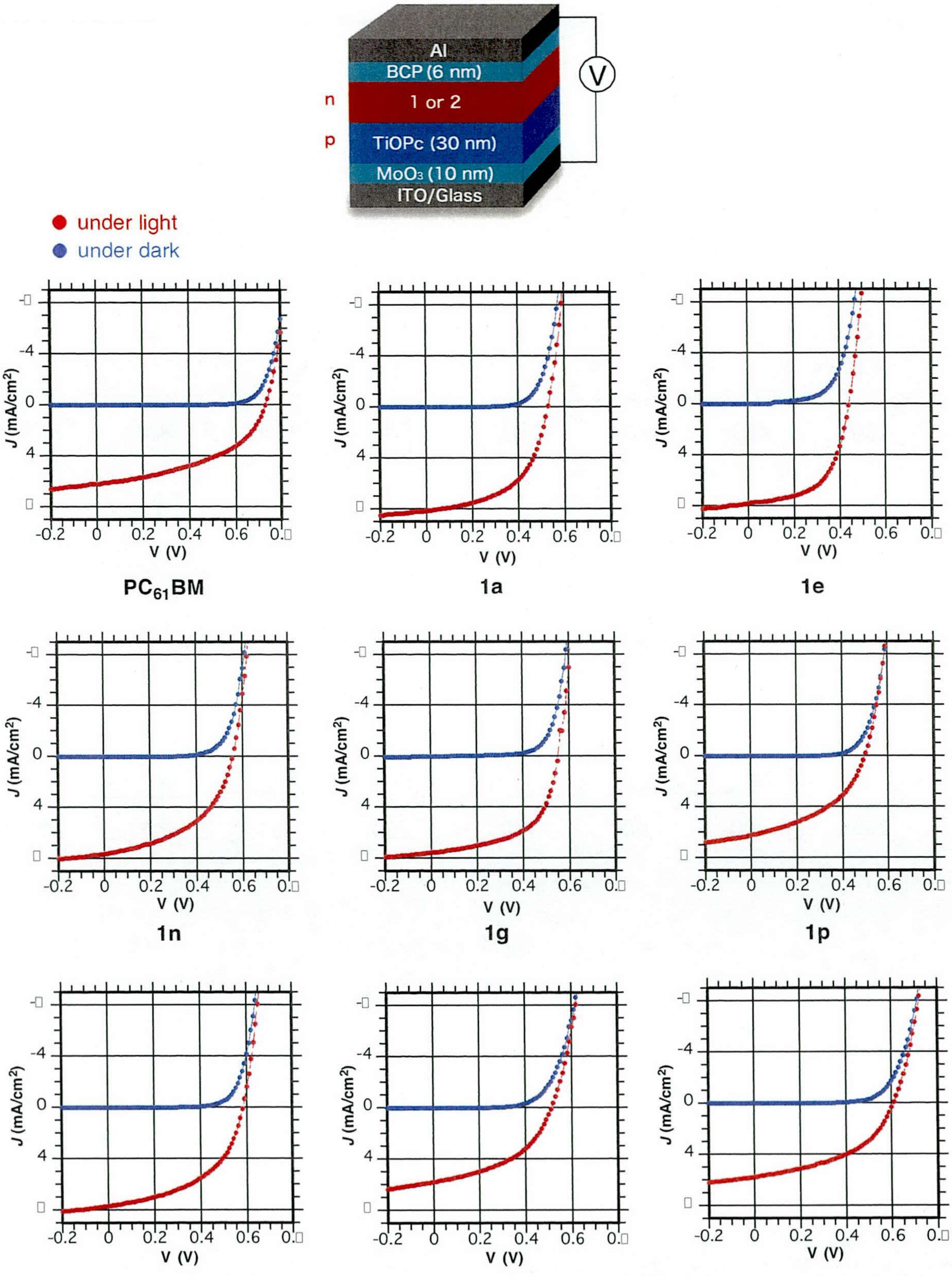

O2
S
TMS
N
1
0
200
400
600
800

Figure S4. *J*-*V* curve plots of photovoltaic cells based on **1** and **2**.



PC$_{61}$BM **1a** **1e**

1n **1g** **1p**

2a **2e** **2n**

1-11. References and Notes

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Chapter 2

Selective Diels-Alder reaction of C_{60} and 1,3-Dienes in MCM-41 as A Reaction Medium

2-1. Introduction

In order to resolve the problem of low solubility of C_{60}, periodic mesoporous silica, MCM-41 was utilized as the novel reaction medium. MCM-41 has been used in the field of organic synthesis over the past two decades because of their unique chemical and structural characteristics.[1] There are three main applications of such materials in organic synthesis. First, MCM-41 is applied to the synthesis of polymers as a directing template by taking advantage of their unique pore shapes.[2] Second is as heterogeneous catalysts. For example, unmodified mesoporous silica gels have the potential to function as an acid catalyst.[3] Immobilization of the internal surface of silicas with organic bases,[4] metal ions,[5] transition metal complexes[6] or nanoparticles[7] can also act as heterogeneous catalysts for organic transformations. Moreover, metal oxides embedded into the silica intrasurface catalyzes epoxydation of olefins.[8] Lastly, various organic compounds as well as proteins are incorporated into its pores.[9,10] By utilizing the feature that MCM-41 incorporates organic molecules into its pore, our group reported that C_{60} was efficiently included into the pore of MCM-41 (C_{60}@MCM-41) by solvophobic process, with C_{60} being despersed at molecular level in the intenal surface of MCM-41.[11]

From the fact that C_{60} was homogeneously distributed, I made a hypothesis that the mesoporous silica can be regarded as a potential solvent for reactions of C_{60}. The use of MCM-41 as a reaction medium for C_{60} would enable us to conduct organic reactions without the use of external media. In other words, various organic reactions can proceed in C_{60}-insoluble media (Figure 1). Furthermore, by making use of spacial regulation of its pores, selective production of C_{60} derivatives that are functionalized with number-defined functionalities could be feasible. In order to better understand this process, the Diels-Alder reaction of C_{60} with conjugated dienes was examined as a model reaction.

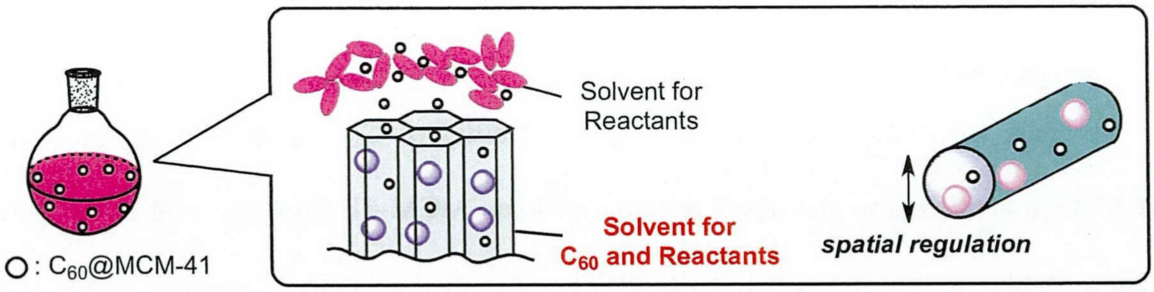
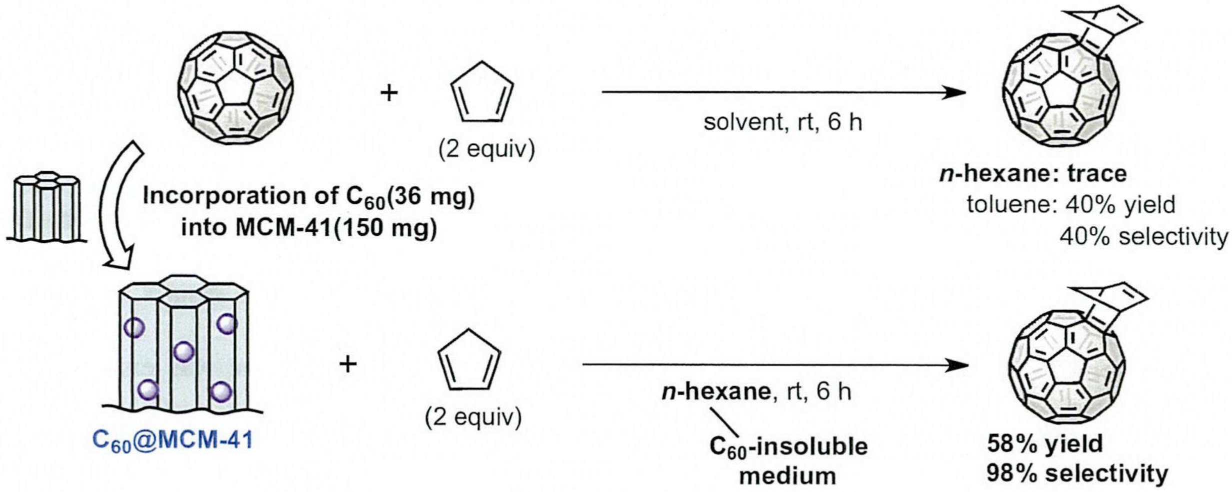


Figure 1. Strategy for use of MCM-41 as a reaction medium for C_{60}.

Results and Discussion

2-2. The Diels-Alder Reaction of C_{60}@MCM-41 and Cyclopentadiene

The reaction of C_{60} with cyclopentadiene in *n*-hexane at room temperature for 6 h gave only a trace amount of the adduct, because C_{60} is sparingly soluble in *n*-hexane (Scheme 1).[12] The use of toluene, a solvent for both C_{60} and cyclopentadiene, afforded the cycloadduct, but the yields (selectivity: 40%, absolute yield: 40%) were quite low because of yielding multi-adducts. Meanwhile, when C_{60} (36 mg, 0.05 mmol) included into MCM-41 (diameter: 3.0 nm, 150 mg) was treated with two equivalents of cyclopentadiene under the same conditions, the cycloadduct was obtained in 58% absolute yield (98% selectivity, based on converted C_{60}).



Scheme 1. The Diels-Alder Reaction of C_{60} included into MCM-41 with cyclopentadiene

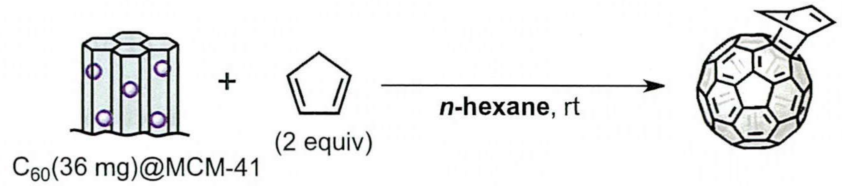
X-ray diffraction (XRD) indicated C_{60} was completely included into MCM-41 in the reaction system. Furthermore, because C_{60} in MCM-41 was not transferred to *n*-hexane from its pores. These facts would indicate that the Diels-Alder reaction took place on interface of

MCM-41. To obtain the further insight, I scrutinized the effect of the reacction time and the amount of MCM-41.

2-3. The effect of reaction time and the amount of MCM-41 on Diels-Alder Reaction

The yields (selectivity and chemical yield) could not be improved the chemical yield when the reaction time was shortened to 1 h or extended beyond 6 h (Table 1, entries 2 and 3). In the case of entry 2, multi-adducts were yielded, then selectivity was decreased. The excellent selectivity induced using MCM-41 compared with that in toluene appears to be dependent on specific size of the microcavity of the mesoporous silica. The effect of the concentration of C_{60} in MCM-41 was investigated by increasing the amount of MCM-41 used in the reaction. An increase in the amount of MCM-41 used induced a decrease in both chemical yield and selectivity (entry 4). In this case, the concentration of C_{60} in MCM-41 is half the amount used in the case of entry 1. The amount of C_{60} per unit volume should be half and the concentration of cyclopentadiene is the same, thus the reaction shown in entry 4 resulted in the formation of multi-adducts as shown in Figure 2. In order to confirm this conclusion, the use of two-fold volume of *n*-hexane led to almost the same results as reported for Scheme 1 (entry 5). The effect of the concentration of cyclopentadiene was examined by changing the volume of *n*-hexane. Reducing the volume of *n*-hexane accelerated the reaction (entry 1 vs. 6). Diluting the cyclopentadiene solution gave excellent selectivity, but the reaction was very slow (entry 1 vs. 7). The concentration of C_{60} into MCM-41 and cyclopentadiene in *n*-hexane affected the Diels-Alder reaction in a manner similar to that observed for a reaction in a homogeneous solution. These findings clearly indicate that mesoporous silica, MCM-41, can function as reaction media for Diels-Alder reactions of C_{60}.

Table 1. The Diels-Alder reaction of C_{60}@MCM-41 with cyclopentadiene



entry	**MCM-41 (mg)**	time (h)	yield (%)	selectivity (%)
1	150	6	58	98
2	150	1	28	98
3	150	12	48	60
4	300	6	41	68
5[a]	300	6	51	91
6[b]	150	1	40	93
7[a]	150	1	18	100

[a] Two-fold volume of *n*-hexane was used. [b] A half volume of *n*-hexane was used.

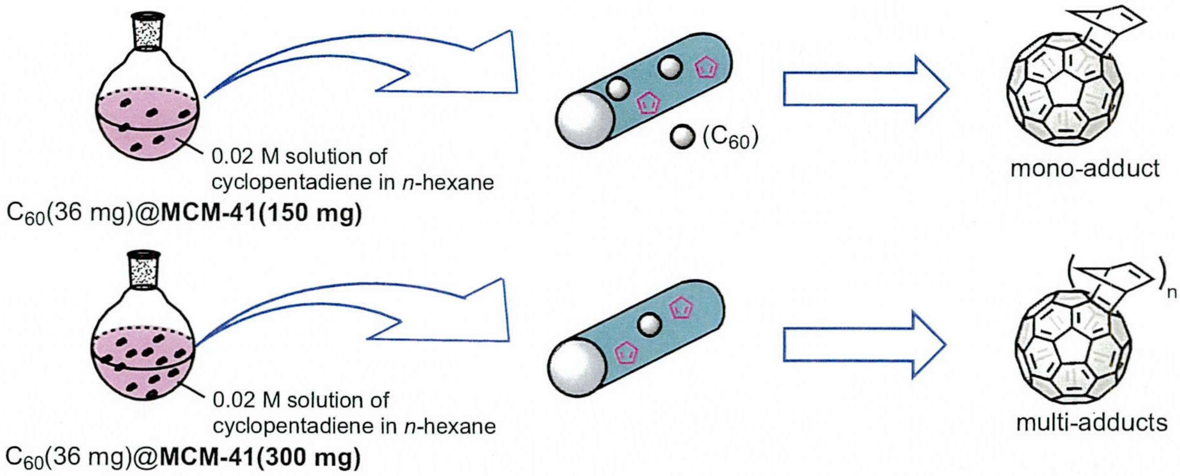


Figure 2. Schematic illustration of the amount of C_{60} per unit volume of MCM-41.

2-4. Kinetic Study of The Diels-Alder Reaction of C_{60}@MCM-41 and Cyclopentadiene

In order to collect compelling evidence in favor of reaction media like homogeneous system, the reaction rate of the Diels-Alder reaction of C_{60}@MCM-41 with cyclopentadiene was determined by monitoring the decrease in C_{60} under pseudo-first-order conditions,[13] using a large excess of the diene with respect to C_{60}. The plots of $\ln([C_{60}]_0/[C_{60}])$ vs. reaction time (Figure. 3) showed that the reaction shows first-order linearity ($R^2>0.94$), and the rate constant

(k_{obs}) was determined to be 4.2 x 10^{-2}(s^{-1}) at 300 K. The reaction of C_{60} with cyclopentadiene in the absence of MCM-41 under the same conditions resulted in 88% of the C_{60} being recovered. These results strongly support the conclusion that MCM-41 as reaction media on the Diels-Alder reaction acted in a manner similar to homogeneous system.

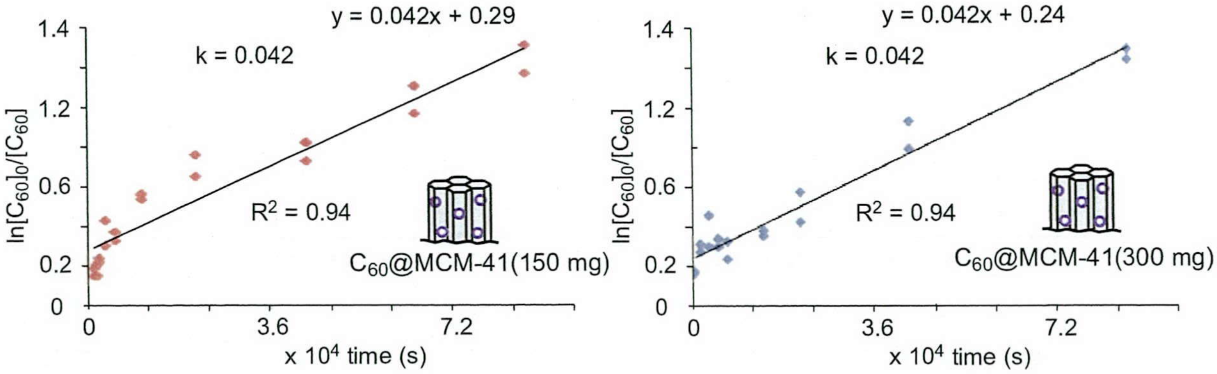


Figure 3. Kinetic study of the Diels-Alder reaction of C_{60} with cyclopentadiene.

2-5. The Effect of Pore Size on The Diels-Alder Reaction

To investigate effect of pore size on the Diels-Alder reaction, typical MCM-41 materials (diameter: 1.7 nm and 4.1 nm)[14] and typical silicas (BW-300 purchased from Fuji Silysia Co., average diameter: 6 nm, and Silica gel 100 purchased from MERK CO., average diameter: 10 nm) having micro-, meso- and macropores were used for the reaction. Since C_{60}, when incorporated into MCM-41 would interact with the internal surface, the amount of C_{60} incorporated would depend on the specific surface area. Considering the results for MCM-41 (3.0 nm, 1450 m^2g^{-1}), C_{60} (*ca.* 72 mg) would be predicted to be included into MCM-41 (1.7 nm, 1070 m^2g^{-1}) (100 mg). Unexpectedly, as shown Figure 4a, only 10 mg of C_{60} was incorporated into MCM-41 (1.7 nm) (150 mg). The other three silica's XRD were indicated that C_{60} was included into each silica (Figure 4b, c, and d). This result indicates that the diameter of MCM-41 (1.7 nm) is too narrow to include C_{60}.

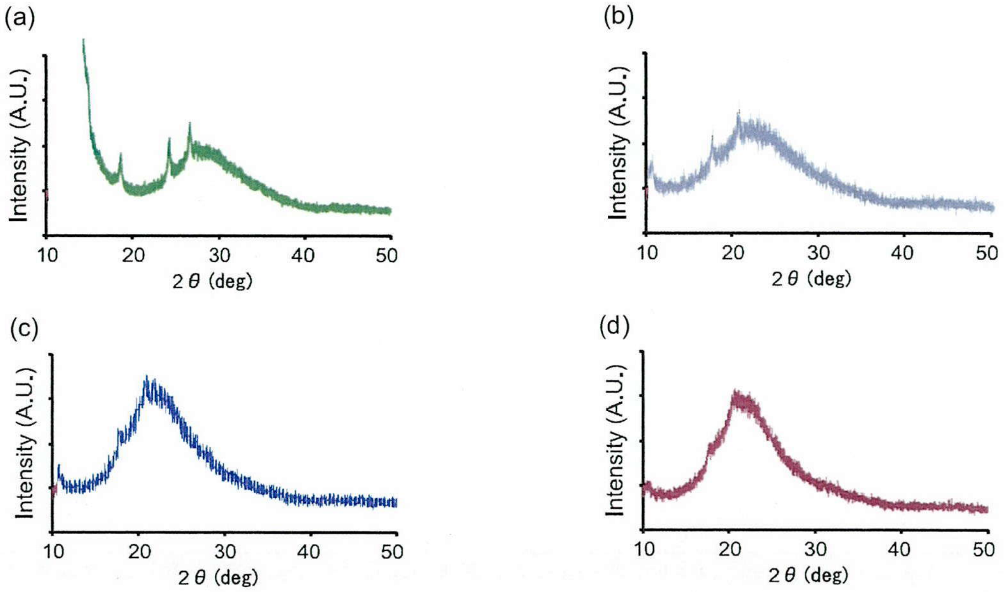
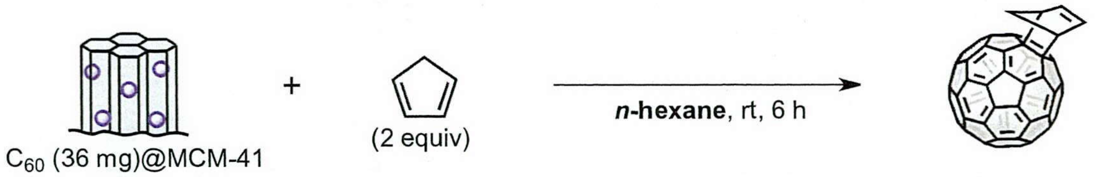


Figure 4. XRD patterns of the composites derived from C_{60} and (a) MCM-41 (1.7 nm), (b) MCM-41 (4.1 nm), (c) BW-300, (d) Silicagel 100.

The composites were employed in the Diels-Alder reaction of C_{60} with cyclopentadiene. When C_{60}(10 mg)@MCM-41(100 mg, 1.7 nm) was treated with two equivalents of cyclopentadiene in *n*-hexane (0.02 M), the efficiency (absolute yield: 8%) and selectivity (36%) were considerably lower than the corresponding values found for MCM-41 (3.0 nm) (Table 2, entry 1 vs. 2). This result suggests that the cyclopentadiene could not react efficiently with the C_{60} in the pore because the interspace between C_{60} and the inner wall of silica is too narrow. The low selectivity can be attributed to the fact that the C_{60} located at the site of the opening of the cavity mainly reacted with cyclopentadiene. On the other hand, use of MCM-41 having bigger pore size (4.1 nm) led to decrease the selectivity (entry 2 vs. 3). Because of the loss of the spatial regulation derived from large pore size, multi-adducts would be produced.

Table 2. The effect of pore size of MCM-41 on the Diels-Alder reaction

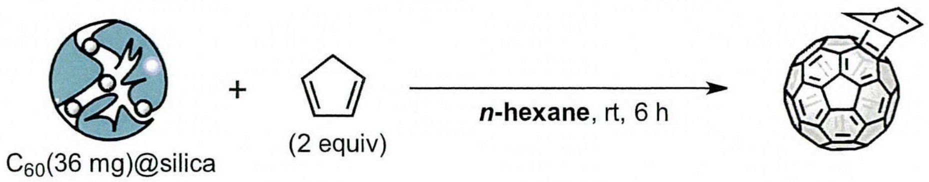


entry	amount of MCM-41 (mg)	pore size (nm)	surface area (m^2/g)	yield (%)^a
1^b	100	1.7	1450	8 (36)
2	150	3.0	1226	58 (98)
3	500	4.1	1050	46 (84)

^{a} The values in parentheses indicate selectivity of products. ^{b} 10 mg of C_{60} was incoporated.

In the case of both BW-300 and Silica gel 100 with various pore sizes, the yields for the reaction (46% yield, 74% selectivity, and 45% yield, 76% selectivity) were also lower than those for MCM-41 (3.0 nm) (Table 3). The microporous material that included C_{60} would inhibit the access of cyclopentadiene because the space available for the reaction is too narrow. When C_{60} is incorporated into a macroporous moiety it would react with more cyclopentadiene molecules, leading to the formation of multiadducts because space was available (over reaction), leading to multiadducts.

Table 3. The Diels-Alder reaction of C_{60}@silicas with cyclopentadiene

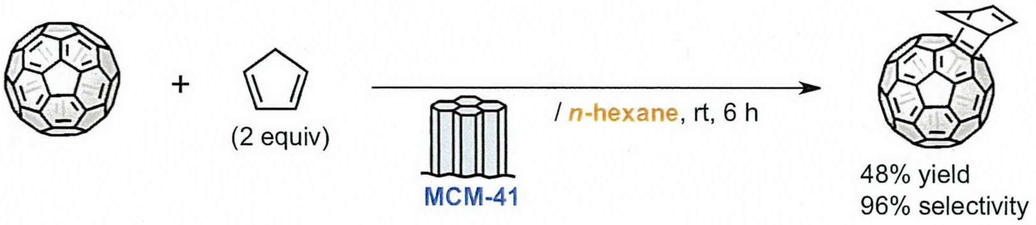


silica (mg)	pore size (nm)	surface area (m^2/g)	yield (%)^a
BW-300^b (400)	6^c	456	46 (74)
Silicagel 100^d (580)	10^c	319	45 (76)
MCM-41 (150)	3	1226	58 (98)

^{a} The values in parentheses indicate selectivity of products. ^{b} Fuji Silysia Co. ^{c} Average pore size. ^{d} MERCK Co.

2-6. The Diels-Alder Reaction of C_{60} with Cyclopentadiene without Inclusion Process

Without the use of C_{60}@MCM-41, when C_{60} and cyclopentadiene in the presence of MCM-41 was stirred at room temperature for 6 hours in *n*-hexane, the monoadduct was produced in 48% yield (96% selectivity) (Eq. 1).



(1)

Since the reaction was very slow in the absence of MCM-41, it is likely that the C_{60} was incorporated into MCM-41 under these conditions. An XRD of the composite **A** derived from MCM-41 (150 mg) and C_{60} (36 mg) after stirring for 6 hours in *n*-hexane is shown (Figure 5a and b) as a blue line. A control sample was prepared by grinding a mixture of C_{60} and MCM-41 in a mortar and the XRD pattern of this composite is shown as a red line. A comparison of the composite **A** with the control sample suggests that simply stirring the components in *n*-hexane would permit the C_{60} to be partially incorporated into the MCM-41. Our group reported that the curve in differential thermal analysis (DTA) measurements for MCM-41 including C_{60} (C_{60}@MCM-41) was very sharp – in the temperature range of 420-570 °C, indicating that C_{60} had been incorporated into MCM-41 and was homogeneously distributed. The peak temperature and the shape of curve for the composite **A** stirred in *n*-hexane are almost the same as that for C_{60}@MCM-41 reprted previously (Figure 5c).[11] This result also supports the conclusion that C_{60} is incorporated into MCM-41 by simply stirring these compounds in *n*-hexane. This provides further support for the Diels-Alder reaction proceeding in MCM-41.

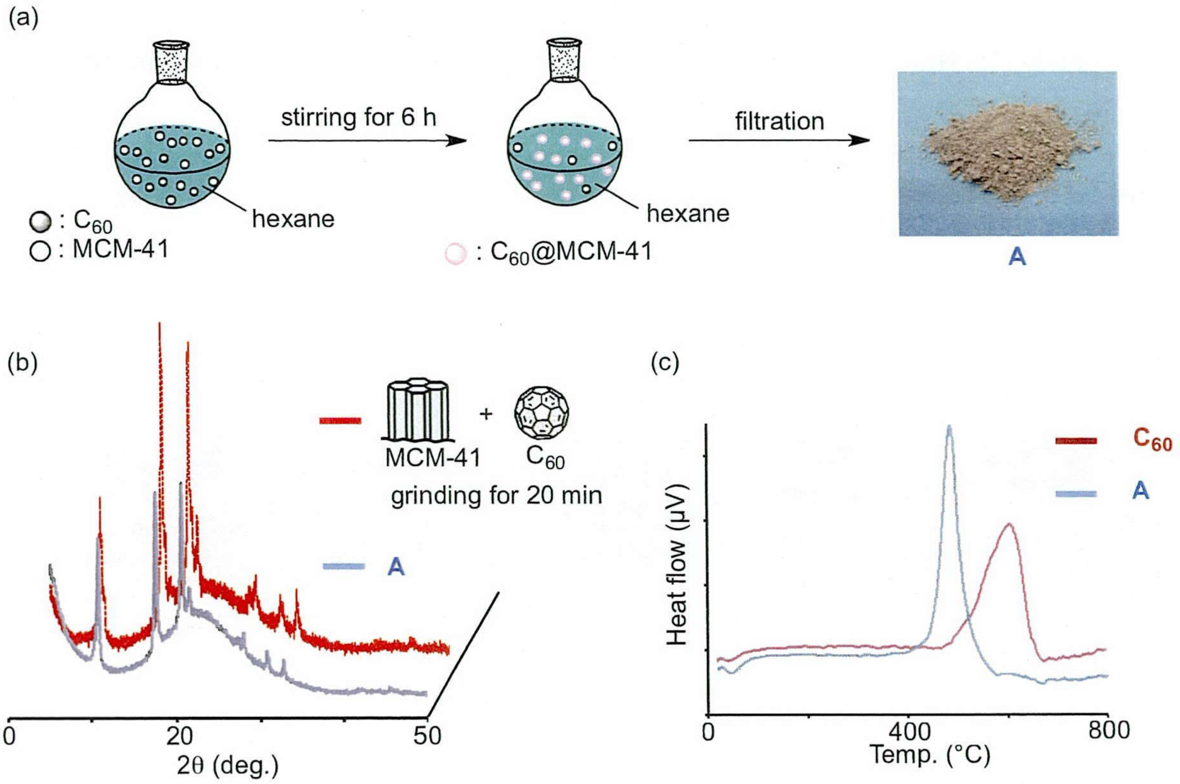


Figure 5. (a) Schematic illustration of preparation of the composite **A**. (b) Comparison of XRD patterns between the composite **A** and the sample grinded C_{60} and MCM-41. (c) DTA profile of the composite **A** and bulk C_{60}.

2-7. Conclusion

In summary, a new organic reaction in a periodic mesoporous material is described; the Diels-Alder reaction of C_{60} with cyclopentadiene was used as a model reaction. The inorganic material was found to function as a reaction medium for selective functionalization of C_{60} utilizing its unique spatial reguration. The presented system has possibilities to apply to other organic reactions, since it represents a new organic reaction medium that has wide potential for use in organic synthesis.

2-8. Experimental Section

General experimental methods

All reactions were carried out under an atmosphere of nitrogen. *n*-Hexane was freshly distilled over sodium-benzophenone kethyl under dry nitrogen. Products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Co.). Analytical thin-layer chromatography was performed on precoated silica gel glass plates (silica gel 60 F_{254}, 0.25 mm thickness) (Merck Co.). Infrared spectra were obtained on a JASCO FT/IR-410 infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (^1H NMR, 270 MHz; ^{13}C NMR, 68 MHz) using tetramethylsilane as an internal standard. UV/Vis spectra were performed on a Shimadzu UV-265 spectrophotometer. X-ray powder diffraction (XRD) patterns were measured on a Rigaku RINTO 2500 with Cu-Ka radiation (50kV, 200 mA) in the 2θ range from 10° to 50°. Differential thermal analyses (DTA) were carried out (DTA-60H, Shimazu) in a synthetic air atmosphere (heating rate of 10 °C/min). FAB-Mass spectra were measured with a JEOL TMS-700 spectrometer. High resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer.

Preparation of C_{60}@MCM-41[11]

MCM-41 (150 mg) was added to a solution of C_{60} (36 mg, 0.5 mmol) in toluene (50 mL), and the solvent was evaporated to dryness using a rotary evaporator. The addition of chloroform to the residue, followed by evaporation of the solvent, yielded a gray colored solid.

Experimental procedure for the reaction of C_{60}@MCM-41 with cyclopentadiene

Cyclopentadiene (0.1 mmol) was added to a suspention of C_{60}@MCM-41 (prepared from C_{60} (36 mg, 0.05 mmol) and MCM-41 (150 mg)) in *n*-hexane (5.0 mL). The mixture was allowed to stir at room temperature for 6 hours under an atomosphere of nitrogen. The resulting suspension was filtered through Celite to remove excess cyclopentadiene followed by washing with toluene, giving a mixture of cycloadducts and unreacted C_{60}. After concentration of the solution, the residue was purified by column chromatography on silica gel (eluent: toluene / hexane = 1 / 20) to afford 22.8 mg (58%) of monoadduct and C_{60} (recovery: 14.7 mg, 41%)

1,2-{[1',4']epicyclopent-2'-eno}-[60]fullerene[15]

black solid ; FT-IR (KBr) 725, 790, 1099, 1184, 1259, 1326, 1637, 2921 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 2.52 (m, 1H), 3.44 (m, 1H), 4.50 (m, 2H), 7.07 (m, 2H); ^{13}C NMR ($CDCl_3$:CS_2= 2:1, 68 MHz) δ28.15, 81.26, 84.66, 139.94, 141.08, 142.24, 142.29, 142.80, 143.15, 143.16, 143.78, 144.03, 144.08, 144.54, 144.56, 144.78, 144.81, 145.13, 145.21, 154.84; UV-Vis (CH_2Cl_2) λ_{max} 361, 328, 256, 223 nm; FAB-MS *m/z* 786 ([M]$^+$+1); HR-MS: calcd for ($C_{65}H_6$): 786.0470, found: 786.0480.

2-9. References and Notes

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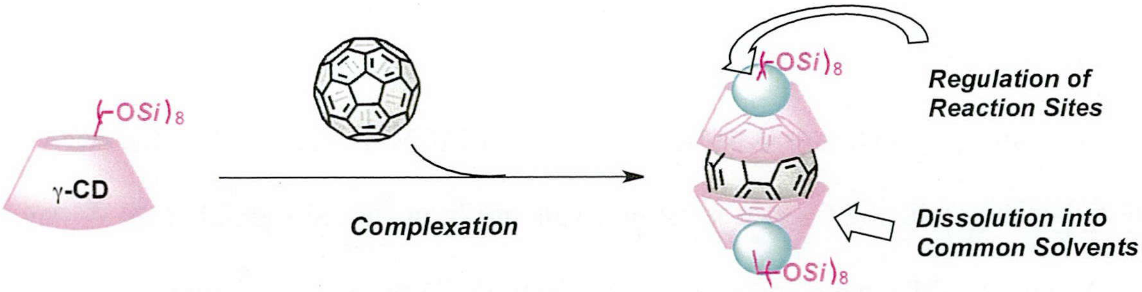
Chapter 3

Encapsulation of C_{60} into Functionalized γ-Cyclodextrin and the Reaction Behavior of the Complex

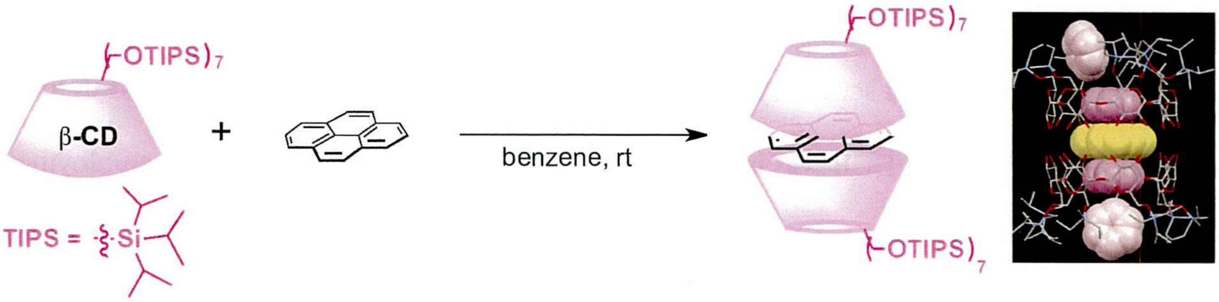
3-1. Introduction

In this Chapter, an alternative methodology for selective functionalization of C_{60} is proposedusing γ-cyclodextrin derivatives in place of MCM-41 described in Chapter 2. Host-guest chemistry utilizing C_{60} as a guest molecule has been studied soon after the discovery of C_{60}.[1] Among the fullerene complexes, γ-cyclodextrin(CD)-bicapped C_{60} complex [(γ-CD)$_2$·C_{60}] has been extensively studied, because of its unique property of high solubility in water.[2] The main driving force of the complexation is hydrophobic interactions between the fullerene sphere and the γ-CD cavity, along with the presence of an appropriate diameter of the cavity (7.5–8.3 Å) and the truncated cone shape of γ-CD.[3] Due to its hydrophilic nature, the complex [(γ-CD)$_2$·C_{60}] is intrinsically insoluble in nonpolar and weakly polar organic solvents.[4] Contrary to a great number of studies using [(γ-CD)$_2$·C_{60}] and their derivatives,[5] the organic solvent-soluble counterparts, to the best of my knowledge, have not yet been reported to date. Since pristine C_{60} is only soluble in nonpolar and weakly polar organic solvents such as toluene (2.8 mg/mL), 1,2-dichlorobenzene (27 mg/mL), and tetrachloroethane (5.3 mg/mL) as mentioned general introduction,[6] efficient chemical functionalization of C_{60} in organic solution phase has been severely hampered.[7] Taking these backgrounds into account, the creation of organic solvent-soluble γ-CD-bicapped C_{60} inclusion complexes would not only be an intriguing research subject but also a promising approach for enhancing the concentration of C_{60} in organic solvents, thus thereby leading to the improvement of efficiencies of conventional chemical reactions of C_{60} in organic phase. In addition to this potential feature, the complexation could offer an option to regulate the reaction sites of C_{60} by covering a large part of the surface with two hoop-shaped architectures.[8] leading to selective functionalization of C_{60} (Scheme 1).



Scheme 1. Strategy for using C_{60}/γ-cyclodextrin derivatives complex

Recently, Kida and Akashi have found that heptakis(6-*O*-trisorganosilyl)-β-cyclodextrins (Si-β-CDs) effectively form inclusion complexes of pyrene[9a] and chlorinated benzenes[9b] in nonpolar organic solvents such as benzene and cyclohexane (Scheme 2).



Scheme 2. Encapsulation of π-conjugated molecules into triisopropylsilyl-β-cyclodextrin

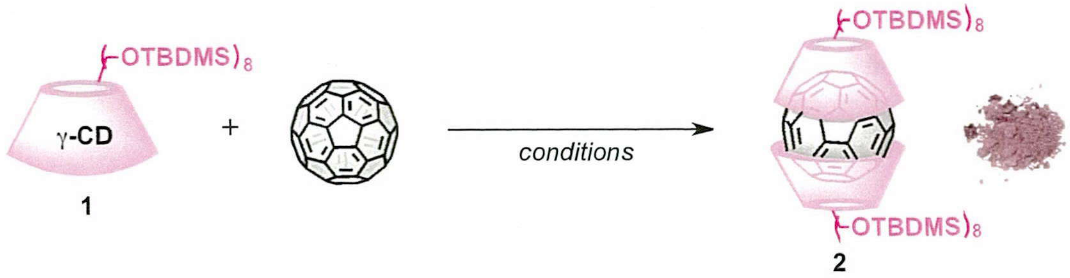
Inspired by their pioneering findings, An attempt was made to let C_{60} serve as a guest molecule for organosilylated-CDs (Si-CDs). Described in this Chapter is, the preparation, isolation, and characterization of an organosilylated γ-CD (Si-γ-CD)-bicapped C_{60} complex, which is highly soluble to nonpolar and weakly polar organic solvents. Furthermore, making use of its unique features, selective chemical functionalization of C_{60}, separation of C_{60} from fullerite (a mixture of C_{60} and C_{70}), and solution-processed fabrication of a thin-film of the complex were demonstrated.

Results and Discussion

3-2. Synthesis and Charactalization of Bicapped Complex between C_{60} and TBDMS-γ-Cyclodextrin

Octakis(6-*O*-*t*BuMe$_2$Si)-γ-CD (TBDMS-γ-CD, **1**) was chosen as a host molecule and prepared according to the literature procedure.[10] At the outset, C_{60} was treated with 2 equivalents of **1** in toluene under reflux for 48 h. After the reaction mixture was allowed to cool to room temperature, the resulting purple precipitates were collected. To our delight, the characterization of the solids by the combination of several spectroscopic methods such as Mass, NMR, UV/Vis, and circular dichroism (CD) spectra together with elemental analysis confirmed the formation of the desired bicapped inclusion complex [(TBDMS-γ-CD)$_2$·C_{60}] **2** in as good as 77% yield (Table 1, entry 1). Highly encouraged by the result, a series of conditions for the complexation was scrutinized. The shortening of reaction time (24 h) resulted in lower yield (entry 2). Use of *o*-DCB was not effective for the synthesis of **2**, whereas the employment of benzene yielded the desired inclusion complex (entries 3-5). As a result, the use of excess amounts of C_{60} in toluene under reflux gave the corresponding inclusion complex **2** in 95% isolation yield (entry 6). In sharp contrast, no trace amounts of the complexes were detected at room temperature, suggesting that the complexation is entropy-driven (entry 7). Although the complexation of C_{70} with TBDMS-γ-CD was attempted under the optimized conditions for C_{60}, no complexes were formed, indicative of the feasibility of selective separation of C_{60} from C_{70} based on the large difference in the affinities toward **1** (*vide infra*).

Table 1. Survey of optimal conditions for the preparation of **2**



entry	**1** (equiv)	solvent	temp. (°C)	time (h)	yield (%)[a]
1	(2.0)	toluene	111	48	77
2	(2.0)	toluene	111	24	44
3	(2.0)	*o*-dichlorobenzene	111	24	20
4	(2.0)	*o*-dichlorobenzene	180	24	24
5	(2.0)	benzene	80	24	41
6	(1.0)	toluene	111	48	95
7	(1.0)	toluene	rt	24	0

[a] The values based on **1**.

As characterization, MALDI-TOF spectroscopic analysis of **2** showed three distinct peaks at *m*/*z* = 5138, 4418, and 2929, which are assignable to the molecular ions of complex **2**, the dimer of **1**, and **1**$\cdot C_{60}$ [1:1] complex, respectively (Figure 1), supporting the formation of the complex **2**.

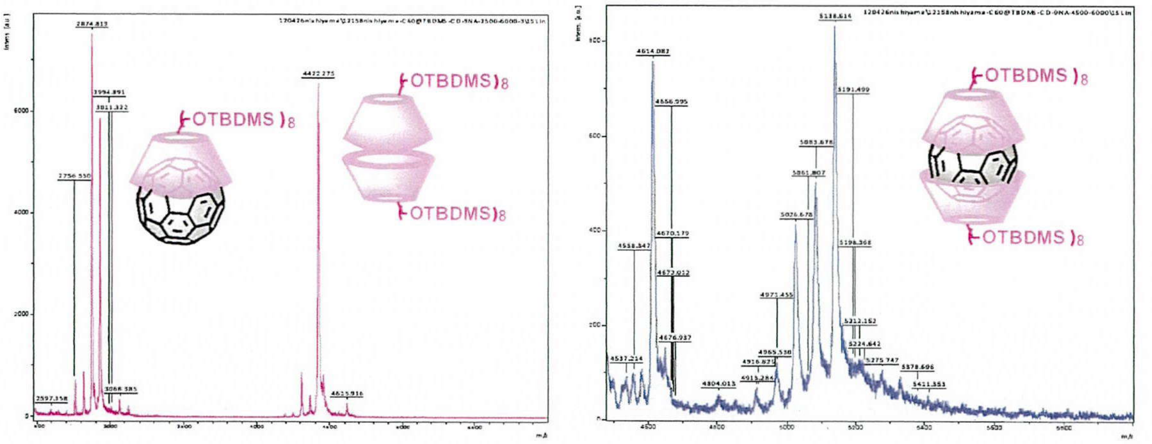


Figure 1. MALDI-TOF Mass spectra of **2.**

The supramolecular interactions between TBDMS-γ-CD and C_{60} were evidenced by ^1H NMR analysis. Figure 2 shows the ^1H NMR spectra of a $CDCl_3$ solution of TBDMS-γ-CD (Figure 2a) and its inclusion complex **2** (Figure 2b) recorded at room temperature. Both of the two broad singlet signals of **1** at 6.86 and 5.32 ppm, which are attributable to alcoholic protons H^1 and H^2, respectively, shifted to the higher field regime (6.53 and 5.05 ppm, respectively), while the signal of H^3 (δ 4.00 ppm) shifted to the lower field (δ 4.24 ppm). This behavior is consistent with that observed with water-soluble $(\gamma\text{-CD})_2\cdot C_{60}$ complex, probably due to the result of charge-transfer interactions as suggested by Yoshida et al.[2a]

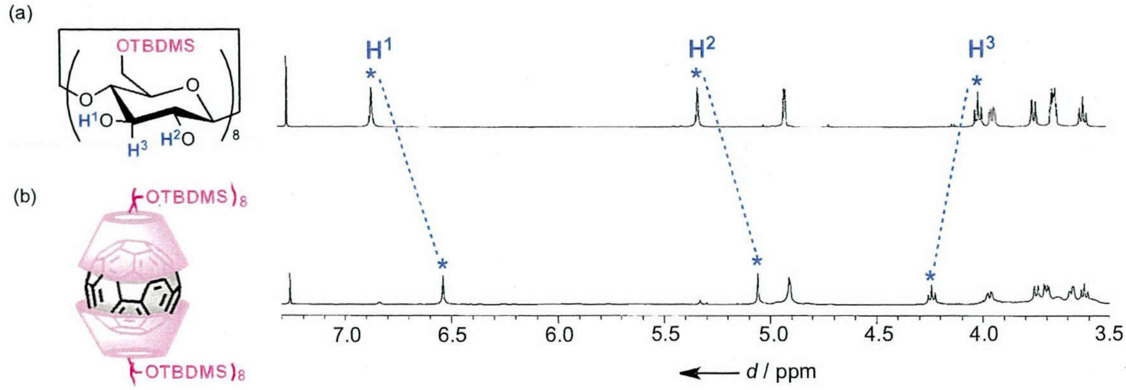


Figure 2. ^{1}H NMR spectra of $CDCl_3$ solution of (a) TBDMS-γ-CD **1**; (b) complex **2** at room temperature.

The observation of the only one set of the peaks ascribed to **2** indicates the slow dissociation process relative to the NMR time-scale at room temperature. To determine the stoichiometry of the components of complex **2**, the Job plots experiment was conducted (Figure 3). ^{1}H NMR spectra were measured at 100 °C in toluene-d_8 with keeping the total concentration of TBDMS-γ-CD and C_{60} constant (6.66 mM). Relative concentrations of [(TBDMS-γ-CD)$_2$·C_{60}], which were estimated from the integration of OH^1 signals, were plotted against ([TBDMS-γ-CD]/[TBDMS-γ-CD]+[C_{60}]). From this result, the 2:1 stoichiometry of **2** was unambiguously confirmed.

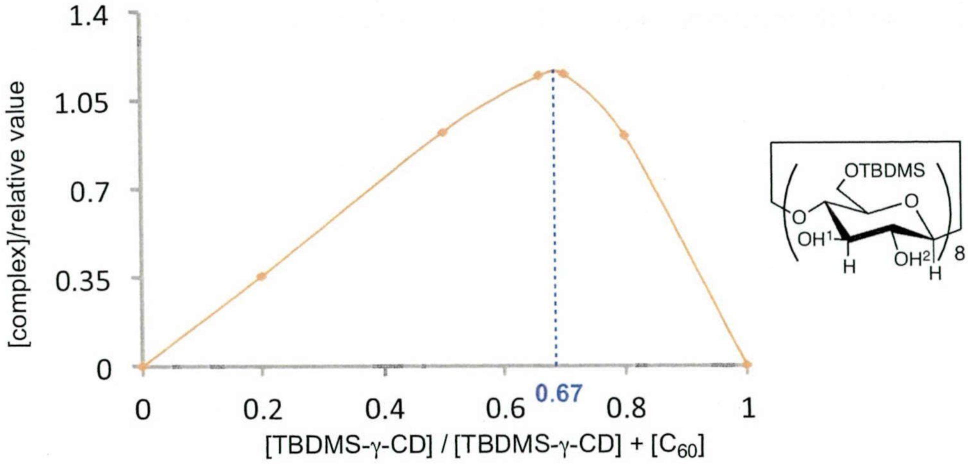


Figure 3. The Job plots for the formation of **2** from C_{60} and TBDMS-γ-CD **1**.

The circular dichroism spectrum of cyclohexane solution of **2** clearly evidenced the presence of chirality in the complex, confirming the inclusion of C_{60} into the host cavity (Figure 4a). Furthermore, supramolecular interactions between C_{60} and TBDMS-γ-CDs were again evidenced by UV/Vis spectra (Figure 4b) where a slight red-shift of the absorption band at around 410 nm was observed, attributable to the charge-transfer interactions between C_{60} and the cavity of the organosilylated γ-CDs.

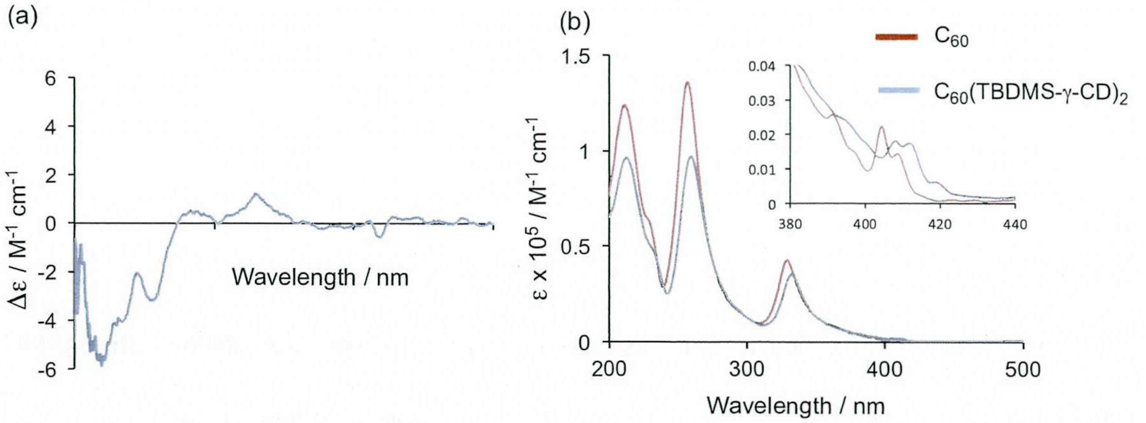


Figure 4. (a) CD spectrum of cyclohexane solution (1 x 10^{-5} M) of $[(\text{TBDMS-}\gamma\text{-CD})_2 \cdot C_{60}]$ complex **2** recorded at 25 °C; (b) UV/Vis spectra of cyclohexane solutions (1 x 10^{-5} M) of C_{60} (red line) and **2** (blue line) recorded at 25 °C.

For further evidence of the inclusion was confirmed by X-ray diffraction (XRD) analysis of the complex **2**,[5g,11] where none of the characteristic peaks that are assignable to C_{60} (2θ = 11.0, 17.5, and 21.7°) or TBDMS-γ-CD (halo peaks at 2θ= 21.7 and 22°) were observed (Figure 5).

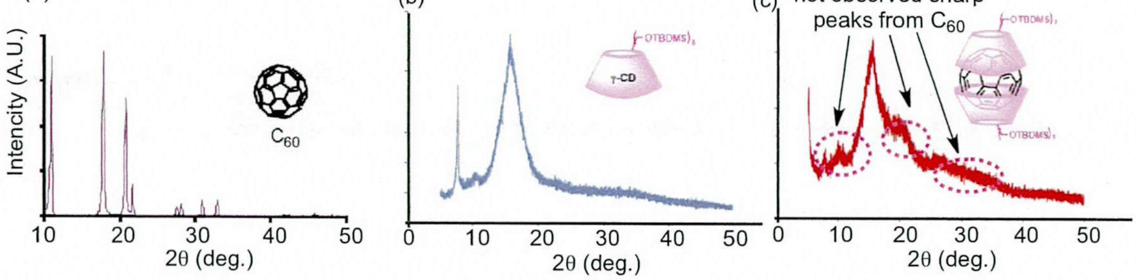
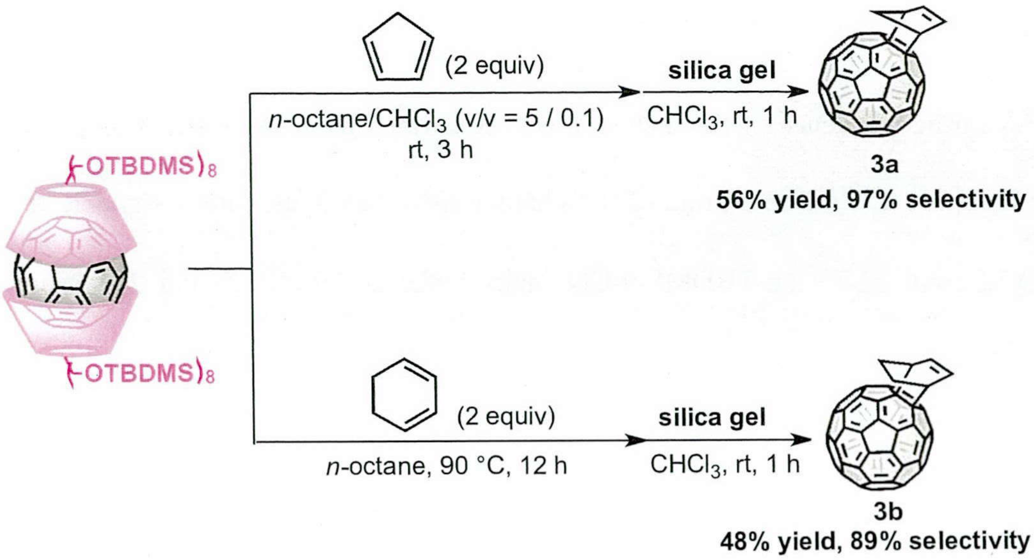


Figure 5. Powder X-ray diffraction patterns of (a) C_{60}, (b) TBDMS-γ-CD, and (c) **2**.

3-3. Reaction of C_{60} / TBDMS-γ-CD Inclusion Complex with Conjugated Dienes

As a proof of our concept, the formal Diels-Alder reaction of C_{60} with dienes in nonpolar organic solvents, which poorly dissolve pristine C_{60} was conducted (Scheme 3). It should be noted that the decomplexation of complex **2** was easily performed by the treatment of silica gel and quantitative C_{60} and TBDMS-γ-CD were easily isolated by column chromatography with chloroform as an eluent. Although the reaction conditions are not optimized, I was delighted to find that the reaction of **2** with cyclopentadiene and cyclohexadiene in *n*-octane smoothly proceeded, and the treatment of the crude mixture with silica gel to remove TBDMS-γ-CD, giving rise to mono-adducts **3a** and **3b** in good yields with high selectivities in both cases.[12] In sharp contrast, the reactions of the pristine C_{60} with the dienes under the same conditions resulted in miserable outcomes (**3a**: 8% yield with 40% selectivity; **3b**: 8% yield with 36% selectivity). These results clearly demonstrate the validity of our concept of utilizing silylated γ-CD as an auxiliary group to solubilize C_{60} as well as to control the reaction sites.



Scheme 3. The formal Diels-Alder reaction of C_{60} with diene using complex **2**

3-4. Survey of the Solubility of (TBDMS-γ-CD)$_2$·C_{60} to Various Solvents

One of the distinctive features of the complex **2** is its high solubility in nonpolar and weakly polar organic solvents, leading to the drastic enhancement of the apparent solubilities of C_{60} as I hypothesized. The apparent solubilities of C_{60} were calculated from the content of C_{60} in the saturated solutions of complex **2** and expressed as bar charts along with the solubilities of pristine C_{60} for comparison (Figure 6).[6] The complex **2** was found to be highly soluble in nonpolar and weakly polar organic solvents such as $CHCl_3$ (269.9 mg/mL), CH_2Cl_2 (419.8 mg/mL), 1,1,2,2-tetrachloroethane (TCE, 449.2 mg/mL), *n*-hexane (78.7 mg/mL), as well as toluene (249.7 mg/mL) and 1,2-dichlorobenzene (1,2-DCB, 710.7 mg/mL), while the solubilities in highly polar solvents were quite low. Notably, the apparent solubility of C_{60} in $CHCl_3$ using the inclusion complex **2** was enhanced by 226 times over that of pristine C_{60} (for the detail values, see ref. 13, Table S1).

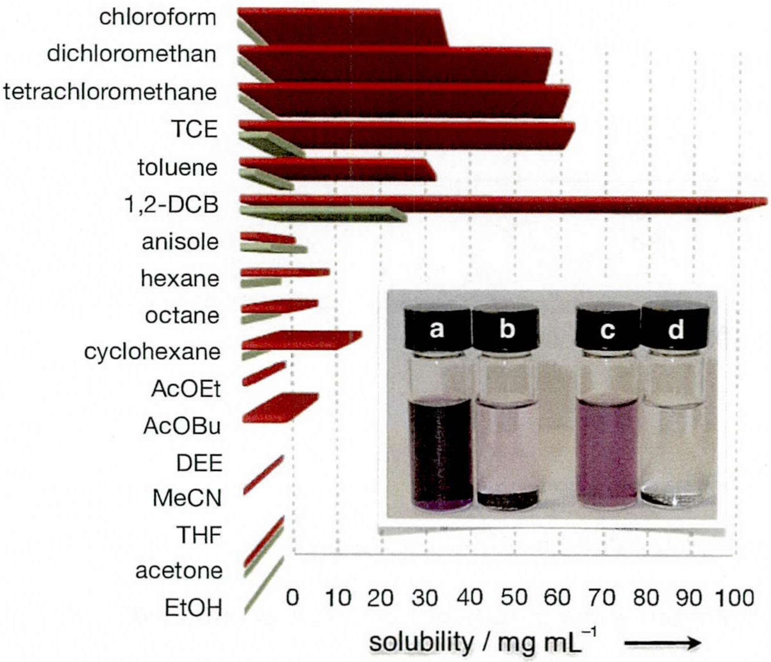
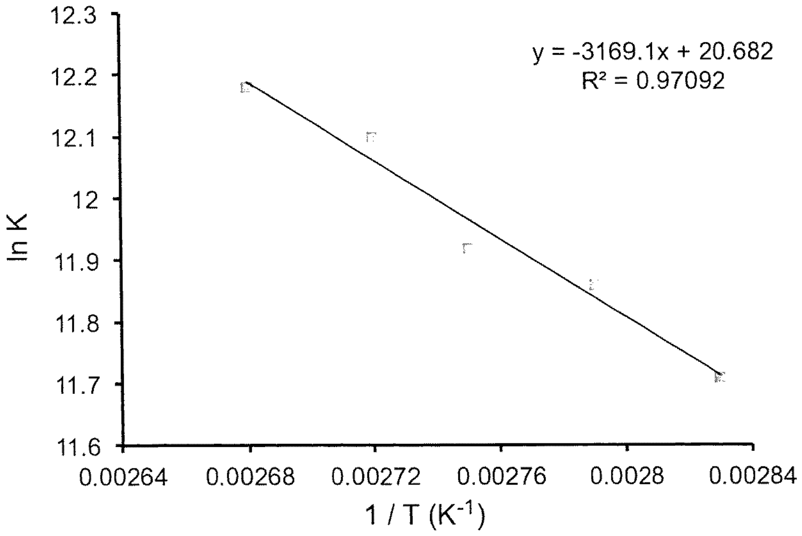


Figure 6. Apparent solubilities of C_{60} calculated from the solubilities of (TBDMS-γ-CD)$_2$·C_{60} complex **2** (red bars) along with the reported solubilities of pristine C_{60} (green bars, ref. 6). The inserted photograph shows (a) a chloroform solution of **2** (257 mg in 3 mL); (b) C_{60} in chloroform (36 mg in 3 mL); (c) a hexane solution of **2** (30.8 mg in 3 mL); (d) C_{60} in hexane (36 mg in 3 mL).

3-5. Estimation of the Assosiation Constants and Thermodynamic Paramerters

For an understanding of the complexation process, thermodynamic parameters of the complexation of C_{60} with **1** were estimated from the van't Hoff plot obtained by ^1H NMR titration (Figure 7). As a result, it was revealed that the complexation is entropy-driven ($\Delta H = +26$ kJ/mol; $\Delta S = +0.17$ kJ/mol), which is consistent with the observation that the complex **2** was formed only when heated. A factor that contributes to the positive entropy could be the release of water molecules from the cavity of the γ-CD.[3b]



$$\Delta G = \Delta H - T\Delta S$$
$$-RT\ln K = \Delta H - T\Delta S$$
$$\ln K = -\Delta H/RT + \Delta S/R$$

$$\Delta H = +26 \text{ kJ/mol}$$
$$\Delta S = +0.17 \text{ kJ/mol}$$

Figure 7. The van't Hoff plots for the estimation of thermodynamic parameters of the complexation process between C_{60} and TBDMS-γ-CD in toluene-d_8.

The association constants of the complexation processes K_1 and K_2 in toluene at 100 °C, which are expressed by the equations 1 and 2, respectively, were determined to be 177 ± 8 (M^{-1}) and $6.8 \times 10^3 \pm 700$ (M^{-1}), respectively, by UV/Vis titration technique (Figure 8).[1a,14] Accordingly, the equilibrium constant (K, Eq 3) for the formation of inclusion complex **2** from C_{60} and TBDMS-γ-CD **1** is calculated to be $1.2 \times 10^6 \pm 5600$ (M^{-2}). Although it would be difficult to simply compare the equilibrium constant *K* with those of the reported fullerene inclusion complexes, the *K* for the formation of **2** can be classified in relatively high values.[1]

$$\text{TBDMS-}\gamma\text{-CD} + C_{60} \underset{}{\overset{K_1}{\rightleftharpoons}} \text{TBDMS-}\gamma\text{-CD}\cdot C_{60} \qquad (1)$$

$$\text{TBDMS-}\gamma\text{-CD}\cdot C_{60} + \text{TBDMS-}\gamma\text{-CD} \overset{K_2}{\rightleftharpoons} (\text{TBDMS-}\gamma\text{-CD})_2\cdot C_{60} \qquad (2)$$

$$2\ \text{TBDMS-}\gamma\text{-CD} + C_{60} \overset{K}{\rightleftharpoons} (\text{TBDMS-}\gamma\text{-CD})_2\cdot C_{60} \qquad (3)$$

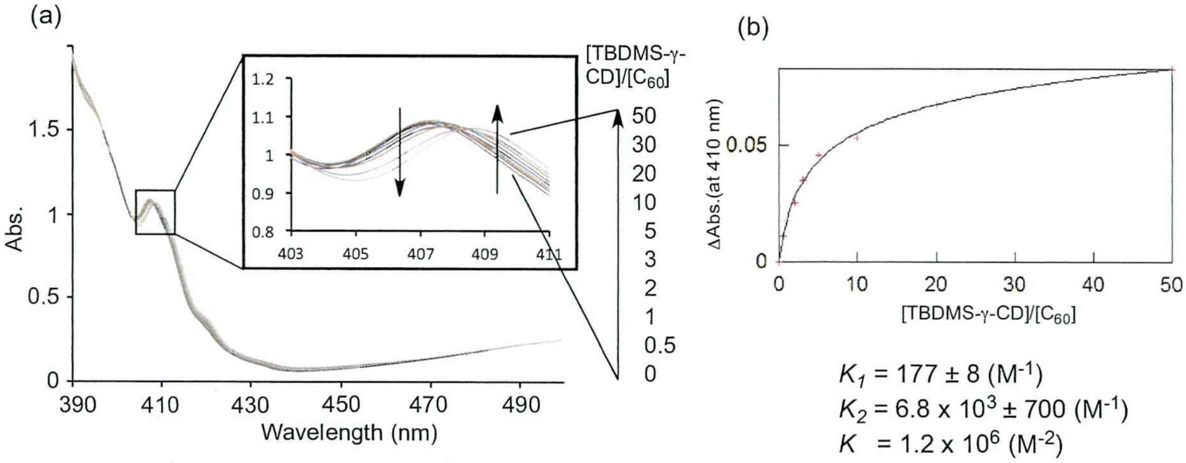
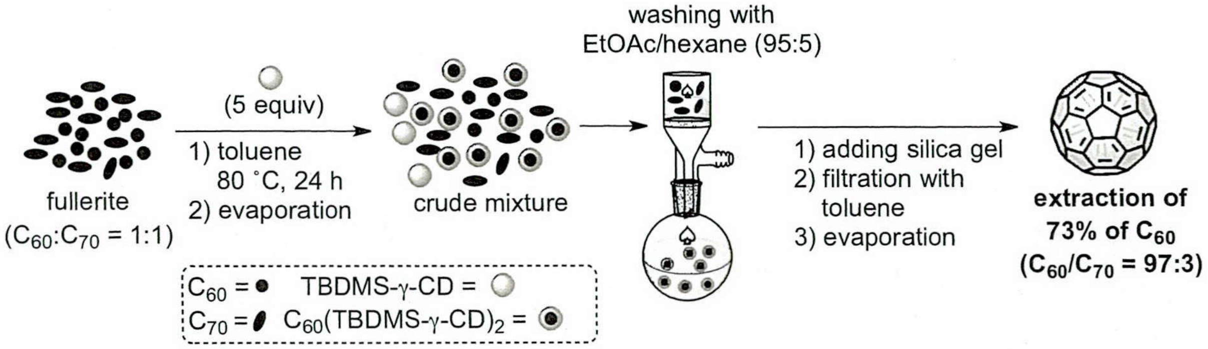


Figure 8. (a) UV/Vis absorption spectra changes of a toluene solution of C_{60} (4.0×10^{-4} M) in the presence of various amounts of TBDMS-γ-CD; (b) UV/Vis titration plots at 410 nm for complexation between C_{60} and TBDMS-γ-CD in toluene at 100 °C ($[C_{60}] = 4.0 \times 10^{-4}$ M).

3-6. Selective Extraction of C_{60} from Fullerite Utilizing Size Selective Complexation

Focusing on its high affinity of the TBDMS-γ-CD toward C_{60} and the easily implementable isolation process, the separation of C_{60} from an equimolar mixture of C_{60} and C_{70} (fullerite) utilizing the selective complexation phenomena, was demonstrated.[15] Scheme 4 illustrates the procedures: 1) a toluene solution of the mixture of fullerite and **1** (5 equiv) was heated at 80 °C for 24 h, followed by evaporating the solvent to give a solid mixture; 2) the solid was washed with EtOAc/*n*-hexane (95:5) on a Celite-pad to elute inclusion complex **2**, while the remaining fullerenes were precipitated; 3) silica gel was added to the filtrate to remove TBDMS-γ-CD, followed by filtration of the mixture by washing with toluene and the evaporation of the mixture to extract C_{60} in a good fraction of recovery (73% of the starting C_{60}) with the ratio of C_{60}/C_{70} being 97:3,[16] which result is comparable to those obtained with calixarene-based fullerene receptors.[11]



Scheme 4. An illustlative flow chart of the procedures for separation of C_{60} from fllerite

3-7. Solution-processed Fabrication of Thin-Film of C_{60}(TBDMS-γ-CD)$_2$

Moreover, to further probe the potentials of the highly soluble inclusion complex, the fabrication of the complex using a solution-process was demonstrated. The thin-film was fabricated on the Si substrate by spin-coating a chlorobenzene solution of **2** (10 wt%) at the 1200 rpm for 60 seconds and dried at 70°C for 10 min (for the detail conditions, see ref. 17). The morphology analysis with atomic force microscope (AFM) clearly confirmed that the thin-film is smooth and flat without any formation of the aggregates of C_{60} (Figure 9a and b). On the other hand, spin-coating a solution of chlorobnzene solution of C_{60} without complexation with TBDMS-γ-CD on the Si substrate result in the aggregation of C_{60} (Figure 9c). These results suggested that encapsulation of C_{60} into TBDMS-γ-CD prevented the aggregation of the guest molecule, C_{60}.

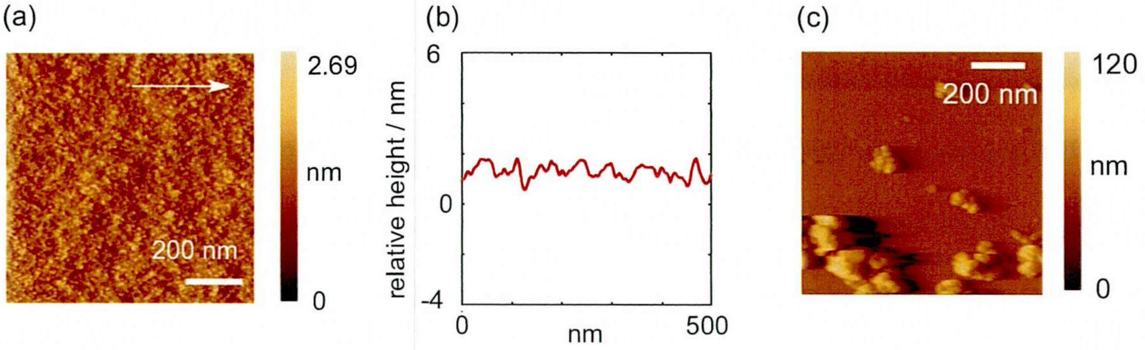


Figure 9. (a) AFM image (1 x 1 μm) and (b) the cross-section profile of the thin-film of inclusion complex **2** fabricated on the Si substrate. (c) AFM image (1 x 1 μm) of C_{60} fabricated with the same procedures.

3-8. Conclusion

In conclusion, I have prepared, isolated, and characterized an organic solvent-soluble inclusion complex of [60]fullerene utilizing organosilylated γ-cyclodextrin for the first time. The complexation was found to be entropy-driven. Furthermore, I have shown some new prospective aspects of the unique complex. Especially, the selective Diels-Alder reaction, based on the control of reaction sites of C_{60} by covering with the surface of C_{60}, took place.

3-9. Experimental Section

General experimental methods

All reactions were carried out under an atmosphere of nitrogen. *n*-Alkanes were freshly distilled over sodium/benzophenone ketyl under dry nitrogen. Diels-Alder products were purified by chromatography on silica gel BW-300 (Fuji Silysia Chemical Ltd). Analytical thin-layer chromatography (TLC) was performed on pre-coated silica gel glass plates (silica gel 60 F_{254}, 0.25 mm thickness, Merck Ltd). Infrared spectra were acquired on a SHIMAZU FTIA-8400S. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-INOVA 600 (^{1}H NMR, 600 MHz; ^{13}C NMR, 150 MHz) using tetramethylsilane as an internal standard. UV-Vis spectra were recorded on a Shimadzu UV-2550, JASCO V-650, and UV-550 spectrophotometers. Circular dichroism spectra were recorded on a JASCO 720 WI. X-ray powder diffraction (XRD) patterns were measured on a Rigaku RINTO 2500 with Cu-Ka radiation (50 kV, 200 mA) in the 2θ range from 10° to 50°. FAB-Mass spectra were measured with a JEOL TMS-700 spectrometer. High-resolution mass spectra were obtained on a JEOL JMS-DX303HF mass spectrometer. MALDI-TOF mass spectra were measured with a BRUKER DALTONICS autoflex II using a sample of a 4:1 mixture of matrix (9-nitroanthracene, 10 mg/mL chloroform solution) and C_{60}@TBDMS-γ-CD (5 mg/mL chloroform solution). Elemental analysis performed at the Analytical Center, Faculty of Engineering, Osaka University. High performance liquid chromatography (HPLC) was performed using an LC system equipped with Buckyprep column (ϕ 20 x 250) and UV detector (SHIMAZU RID-10A).

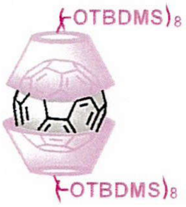
Synthesis of TBDMS-γ-CD (1)

TBDMS-γ-CD (**1**) was prepared according to the procedure in the literature and identified using ^{1}H NMR, ^{13}C NMR, IR, MASS, HR-MASS spectroscopy.[10]

Preparation of inclusion complex 2 [(TBDMS-γ-CD)$_2$·C$_{60}$]

To a solution of C_{60} (0.025 mmol) in toluene (15 mL), TBDMS-γ-CD was added. The resulting mixture was allowed to stir under indicated conditions. After completion of the reaction, solvent was evaporated under reduced pressure. Ethyl acetate was added to the residue, and the suspension was filtered. The residue was washed with *n*-hexane, and the filtrate was evaporated under reduced pressure to give a crude product, which was further washed with ethanol and acetone. The solid was dried under vacuum to give pure complex **2**.

[(TBDMS-γ-CD)$_2$·C$_{60}$] (2)



The title complex was purified by recrystallization from $CHCl_3$/benzene (5:1). Yield: 95%, purple solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.54 (s, *OH*), 5.06 (s, *OH*), 4.91 (d, 16H, J = 4.2 Hz), 4.24 (t, 16H, J = 9.0 Hz), 3.97 (d, 16H, J = 10.8 Hz), 3.75 (d, 16H, J = 10.8 Hz), 3.70 (dd, 16H, J = 4.2 Hz, 9.3 Hz), 3.58 (d, 16H, J = 10.8 Hz), 3.52 (t, 16H, J = 9.3 Hz), 0.87 (s, 144H), 0.036 (s, 48H), 0.024 (s, 48H); ^{13}C NMR (150 MHz, $CDCl_3$): d 143.1, 102.5, 82.5, 73.7, 73.1, 73.0, 61.9, 25.9, 18.3, –5.0, –5.2; IR (ATR): *n* 3383, 2931, 1628, 1462, 1253, 1157, 1084, 1038, 961, 880, 691, 529 cm^{-1}; UV/Vis (cyclohexane, 1.0 × 10^{-5} M) λ_{max} 213, 260, 332, 411 nm; MS (MALDI-TOF) *m/z*: 5138 [(TBDMS-γ-CD)$_2$·C$_{60}$], 4418 [(TBDMS-γ-CD)$_2$], 2929 [(TBDMS-γ-CD)·C$_{60}$]; Anal. Calcd for $C_{252}H_{384}O_{80}Si_{16}$: C, 58.85; H, 7.53. Found: C, 58.60: H, 7.84.

Experimental procedure for UV/Vis titration

A toluene solution of C_{60} (3.0 mL, 4.0 × 10^{-4} M) was titrated with host molecule (ranging from 2.0 × 10^{-4} to 2.0 × 10^{-2} M) at 100 °C. The titration plots (changes in the UV absorption intensity of C_{60} against the host concentration) were analyzed by a non-linear least-squares curve fitting method to extract the association constants (K_1 and K_2).

Separation of C_{60} from fullerite

To the equimolar mixture of C_{60} and C_{70} (fullerite) in toluene (3.33 mM), was added TBDMS-γ-CD (3.0 equiv) in nitrogen atmosphere. The mixture was stirred at 80 °C for 24 hours and cooled to room temperature. The solution was concentrated under vacuum to obtain the crude product. A mixed solvent of ethyl acetate and *n*-hexane (95/5) was added to the mixture, and the resulting suspension was filtered on a Celite-pad. The filtrate was evaporated under reduced pressure to give a solid. To the solid, $CHCl_3$ and silica gel were added in order to implement the decomplexation process.The resulting suspension was filtered on a silica gel pad to remove TBDMS-γ-CD, and the residue on the pad was washed with toluene. The evaporation of the filtrate gave [60]fullerene, which was then subjected to HPLC analysis using pyrene as an internal standard (eluent: toluene). The analysis revealed that the ratio of C_{60}/C_{70} was 97:3 with the recovery fraction of C_{60} being 73%.

The formal Diels-Alder reaction of C_{60} using the complex 2

Diene was added to a solution of complex **2** (0.05 mmol) in *n*-hexane (5.0 mL). The mixture was allowed to stir at room temperature for indicated time in the manuscript under an atmosphere of nitrogen. The resulting solution was evaporated under reduced pressure. The residue was dissolved in $CHCl_3$, and silica gel (BW-300) was added to the solution. The suspension was stirred for 1 h, filtered on a Celite-pad to remove TBDMS-γ-CD, then followed by washing with toluene to give a mixture of cycloadducts and unreacted C_{60}. After concentration of the solution, the crude product was purified by column chromatography on silica gel (eluent: toluene/hexane = 1/20). Spectroscopic data of **3a** and **3b** were identical with those reported in the literatures.[18]

3-10. References and Notes

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12. “Selectivity” is defined as the following equation: selectivity = [chemical yield of product]/[conversion of C_{60}] ×100.

Table S1. The solubilities of C_{60} to various solvents.

solvent	**2** (mg/mL)^a	pristine C_{60}	solvent	**2** (mg/mL)^a	pristine C_{60}
$CHCl_3$	269.9 (36.2)	0.16^b	cyclohexane	127.5 (17.1)	0.036^b
CH_2Cl_2	419.8 (56.2)	0.26^b	ethyl acetate	5.7 (0.8)	-
tetrachloromethane	441.9 (59.3)	0.32^b	*n*-butyl acetate	58.5 (7.8)	-
1,1,2,2-TCE	449.2 (60.2)	5.3^b	DEE	decomp. (-)	-
toluene	249.7 (33.4)	2.8^b	MeCN	0.4 (0.1)	0.0^b
1,2-DCB	710.7 (95.3)	27^b	THF	decomp (-)	-
anisole	22.8 (3.1)	5.6^b	acetone	0.7 (0.1)	0.001^b
hexane	78.7 (10.5)	0.043^b	EtOH	0.0 (-)	0.001^b
octane	59.2 (7.9)	0.025^c			

^{a} The values in parentheses indicate the content of C_{60}.
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16. The C_{60}/C_{70} ratio was determined by HPLC analysis using pyrene as an internal standard.

17. The procedure for fabrication of a thin-film: A silicon wafer (N(100) OSAKA Titanium technologies Co., Ltd.) was first cleaned with detergent, sonicated in acetone and isopropyl alcohol, and subsequently dried in an oven overnight. The complex **2** was spin-coated (1200 rpm over 60 s) from a chlorobenzene solution (10 wt%, after passing 0.45 μm filter). The substrate was dried for 10 min at 70 °C in air.

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Conclusion

The present thesis deals with the development of novel synthetic methods and reaction media for selective functionalization of C_{60}. The results obtained through the studies described in this thesis are summarized as follows:

Chapter 1 described the development of a novel method for highly selective syntheses of azafulleroids and aziridinofullerenes using *N,N*-dihaloamides through radicalic pathways. The method would successfully reduce the formation of multi-adducts. The isomeric iminofullerenes were found switchable only by changing the *N,N*-dihaloamides applied. Furthermore, synthesized iminofullerenes potentials as electron-transporting materials use was demonstrated by applying to p-n junction type solar cells.

In Chapter 2, employing of mesoporous silica gel, MCM-41, as a novel reaction medium in order to overcome the problems of low solubility of C_{60} to common solvents was described. By utilizing inclusion phenomena of C_{60} into mesopores of MCM-41, the selective mono-adduct formation in Diels-Alder reaction of C_{60} with 1,3-dienes was realized in this C_{60}-insolble media. The pore size of MCM-41 drastically affected the efficiency of the Diels-Alder reaction, and MCM-41 was shown to have a couple of abilities of a reaction medium and reaction control by its spatial regulation.

Chapter 3 described that supramolecular inclusion complex of C_{60} with organosilylated γ-CD was utilized for dissolution in some organic solvents and control of reaction sites for selective functionalization of C_{60}. Unambiguously identified inclusion complex of C_{60} with TBDMS-γ-CD (stoichiometry: 1:2) showed high solubility in nonpolar and weakly polar solvents, in which C_{60} is poorly soluble. The Diels-Alder reaction with 1,3-dienes preceded to perform selective production of mono-adduct in pristine C_{60}-insoluble solvent, probably due to the regulation of reaction sites of C_{60} by covering a large part of the surface. Furthermore, by utilization of size selective complexation of TBDMS-γ-CD, the selective separation of C_{60} from fullerite was also attained. The high solubility of the bicapped fullerene complex was applicable in fabrication of a thin-film.

List of Publications

The content of this thesis has been published in the following papers.

1) The Diels-Alder Reaction of C_{60} and Cyclopentadiene in Mesoporous Silica as a Reaction Medium
Satoshi Minakata, Toshiki Nagamachi, Kazuhisa Nakayama, Takeyuki Suzuki, Takanori, Tanaka
Chem. Commun. **2011**, 47, 6338-6340.

2) Selective Functionalization of Fullerenes with *N,N*-Dihalosulfonamides as an N_1 Unit: Versatile Syntheses of Aza[60]fulleroids and Aziridino[60]fullerenes and Their Application to Photovoltaic Cells
Toshiki Nagamachi, Youhei Takeda, Kazuhisa Nakayama, Satoshi, Minakata
Chem. Eur. J. **2012**, *18*, 12035-12045.

3) An Inclusion Complex of C_{60} with Organosilylated γ-Cyclodextrin: Drastic Enhancement of Apparent Solubility of C_{60} in Nonpolar and Weakly Polar Organic Solvents
Youhei Takeda, Toshiki Nagamachi, Katsuaki Nishikori, Satoshi Minakata
Asian J. Org. Chem. **2013**, *2*, 69.

List of Supplementary Publications

1) The Ionic Introduction of an N_1 Unit to C_{60} and a Unique Rearrangement of Aziridinofullerene
Satoshi Minakata, Ryoji Tsuruoka, Toshiki Nagamachi, Mitsuo Komatsu
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Youhei Takeda, Satoru Enokijima, Toshiki Nagamachi, Kazuhisa Nakayama, Satoshi Minakata
Asian J. Org. Chem. **2013**, *2*, 91.

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Toshiki Nagamachi

Development of Novel Synthetic Methods and Reaction Media for Selective Functionalization of Fullerenes 2013 Yoshiki Na