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Doctoral Dissertation

Synthesis and Function of Supramolecular Frameworks Constructed from Metalloporphyrin Complexes Bearing Pyrenylphenyl Moieties

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January 2026

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General Introduction

1. Solid-state materialization of molecules

Functional molecules possess a designability and tunability of their electronic states based on their chemical structures, making them highly useful building blocks for the construction of functional materials. In general, the solid state materials offer superior safety, stability, and ease of handling compared with the corresponding solution state. Because of these advantages, a wide variety of solid-state materialization strategies for utilizing functional molecules have been extensively investigated. Representative approaches of them include thin-film formation techniques, immobilization in polymers, immobilization on silica- and carbon-based materials, and crystallization (Fig. 1). Because the functions of molecule-based solid materials depend not only on the intrinsic chemical structures of the constituent molecules but also strongly on their aggregation states and arrangements in the solid state, the establishment of methodologies for precisely controlling these assemblies is of critical importance. In the following sections, each of these approaches is outlined.

1.1 Thin-film formation techniques

Thin-film formation techniques represent an important materials-processing strategy that enables the direct application of functional molecules to devices (Fig. 1a). Representative methods include vacuum deposition,^[1] spin coating,^[2,3] inkjet printing,^[4,5] and the Langmuir–Blodgett technique.^[6,7] These techniques enable control over film thickness, molecular orientation, and composition. In particular, they are indispensable in the fields of organic electronics and photonics devices.^[8,9] In addition, the drop-casting method is frequently employed for the fabrication of electrode catalysts.^[10]

1.2 Immobilization in polymers

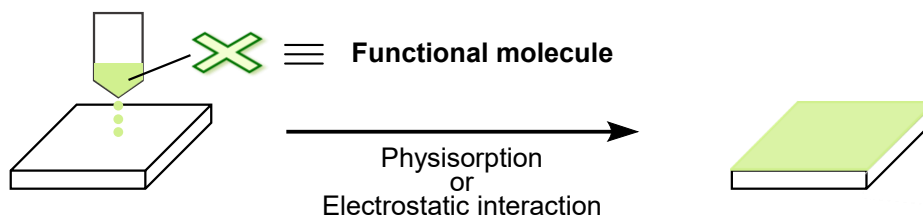
Polymerization, in which functional molecules are chemically incorporated into polymer backbones,^[11–13] as well as approaches that disperse functional molecules within polymer matrices,^[14] are useful strategies for realizing solid materials with excellent processability and mechanical flexibility (Fig. 1b). Owing in particular to their superior film-forming ability and mechanical robustness, these materials have been actively explored for applications in luminescent materials, sensors, and optical devices.^[15–17] Moreover, these strategies offer high molecular design flexibility, enabling precise control over the concentration of functional molecules and systematic tuning of material properties through copolymerization.

1.3 Immobilization on silica- and carbon-based materials

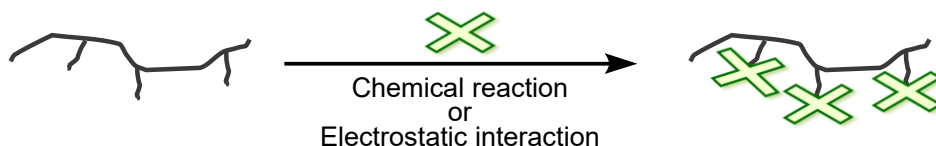
Silica- and carbon-based materials have been extensively investigated as catalyst supports because silica offers high robustness and a large surface area, while carbon materials provide excellent electrical conductivity together with large surface areas (Fig. 1c).^[10,18–22] Silica supports enable

covalent immobilization via surface silanol groups, thereby suppressing leaching of the immobilized molecules and affording high structural stability. Carbon-based materials play an important role in applications such as electrode catalysts and electrochemical reactions, as they allow efficient electron transfer through the support and facilitate electronic interactions with molecular catalysts.

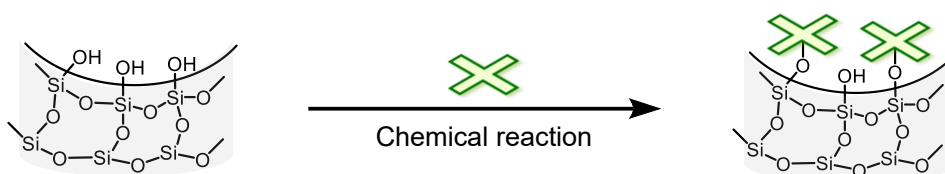
(a) *Thin-film formation techniques*



(b) *Immobilization in polymer*



(c) *Immobilization on silica-based materials*



(d) *Immobilization on carbon-based materials*

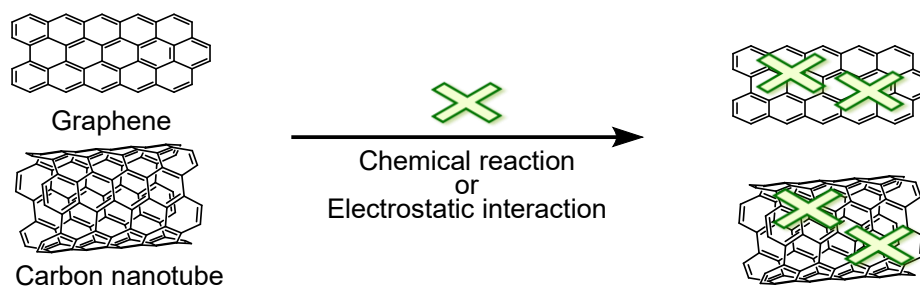


Fig. 1. Schematic illustration of methods for the solid-state materialization of functional molecules: (a) thin-film formation techniques, (b) immobilization in polymers, (c) immobilization on silica-based materials, and (d) immobilization on carbon-based materials.

1.4 Crystallization

Crystallization represents one of the most fundamental yet powerful approaches for solid-state materialization of functional molecules.^[23] The properties of crystalline solid is largely affected by their crystal structure. Indeed, in molecule-based crystals, it is well established that the strength and anisotropy of intermolecular interactions critically influence mechanical responses such as elasticity, plasticity, and brittleness.^[24] On the other hand, because molecular assemblies in crystals are stabilized by a variety of intermolecular interactions, it is not straight forward to predict their crystal structure or properties solely from the chemical structure of molecules. Therefore, significant efforts have been devoted to controlling crystal structures in order to establish clear structure–property relationships. One of approach is crystal engineering.^[23,25] It has introduced the concept of the supramolecular synthon to predict the afforded crystal structure (Fig. 2). Supramolecular synthon is a structural unit constructed from known or deliberately designed intermolecular interactions, providing a rational basis not only for directing crystal structures but also for designing mechanical properties through the modulation of interaction strength and directionality. The other approach is the construction of molecule-based porous crystalline materials. The representative example is metal–organic frameworks (MOFs) reported by R. Robson *et al.*,^[26] S. Kitagawa *et al.*,^[27] and O. M. Yaghi *et al.*^[28] It possess higher-order architectures and functionalities distinct from conventional molecular crystals. These discoveries triggered rapid advances in methodologies for developing other molecule-based porous materials, as discussed in the following section.

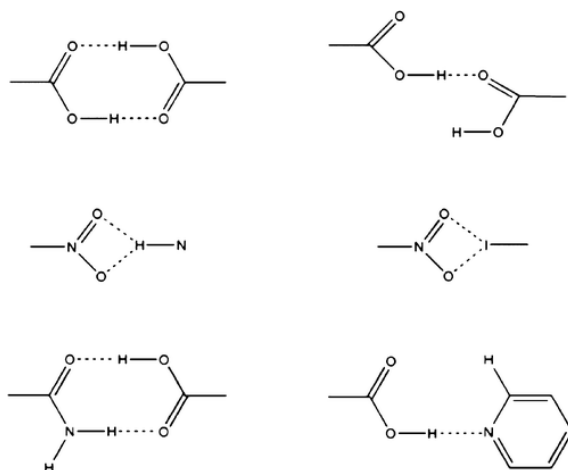


Fig. 2. Representative supramolecular synthons.^[23] Reprinted with permission from G. R. Desiraju, *J. Am. Chem. Soc.* **2013**, *135*, 9952–9967. <https://doi.org/10.1021/ja403264c>. Copyright 2013 American Chemical Society.

2. Molecule-based porous materials

Molecule-based porous materials formed via self-assembly, in which molecules spontaneously organize into ordered structures, have attracted rapidly increasing attention in recent years. Because these materials are constructed from molecularly designed building units, they enable advanced materials design in terms of chemical structural diversity, the facile incorporation of functionalities, and the predictability of the resulting structures.

Representative classes of molecule-based porous materials include metal–organic frameworks (MOFs), constructed through metal–coordination bonds^[29–31]; covalent organic frameworks (COFs), constructed through covalent bonds^[32–34]; and hydrogen-bonded organic frameworks (HOFs), constructed through hydrogen-bonds (Fig. 3).^[35] More recently, molecule-based porous materials constructed through non-covalent interactions such as halogen-bonded organic frameworks (XOFs),^[36] supramolecular organic frameworks (SOFs),^[37–39] and van der Waals open frameworks (WaaFs),^[40] have been developed, further expanding the conceptual scope of molecular porous materials.

All these materials are molecule-based porous materials assembled from molecular units and have several key advantages, including well-defined pore structure, high crystallinity, structural diversity, and the ability to precisely incorporate functional sites. Owing to these features, extensive research has been devoted to their applications in areas such as gas adsorption and separation, which requires large specific surface areas and ordered pore structures,^[41–43] and catalytic reactions, in which confined reaction environments within the pores can be effectively exploited.^[44–46]

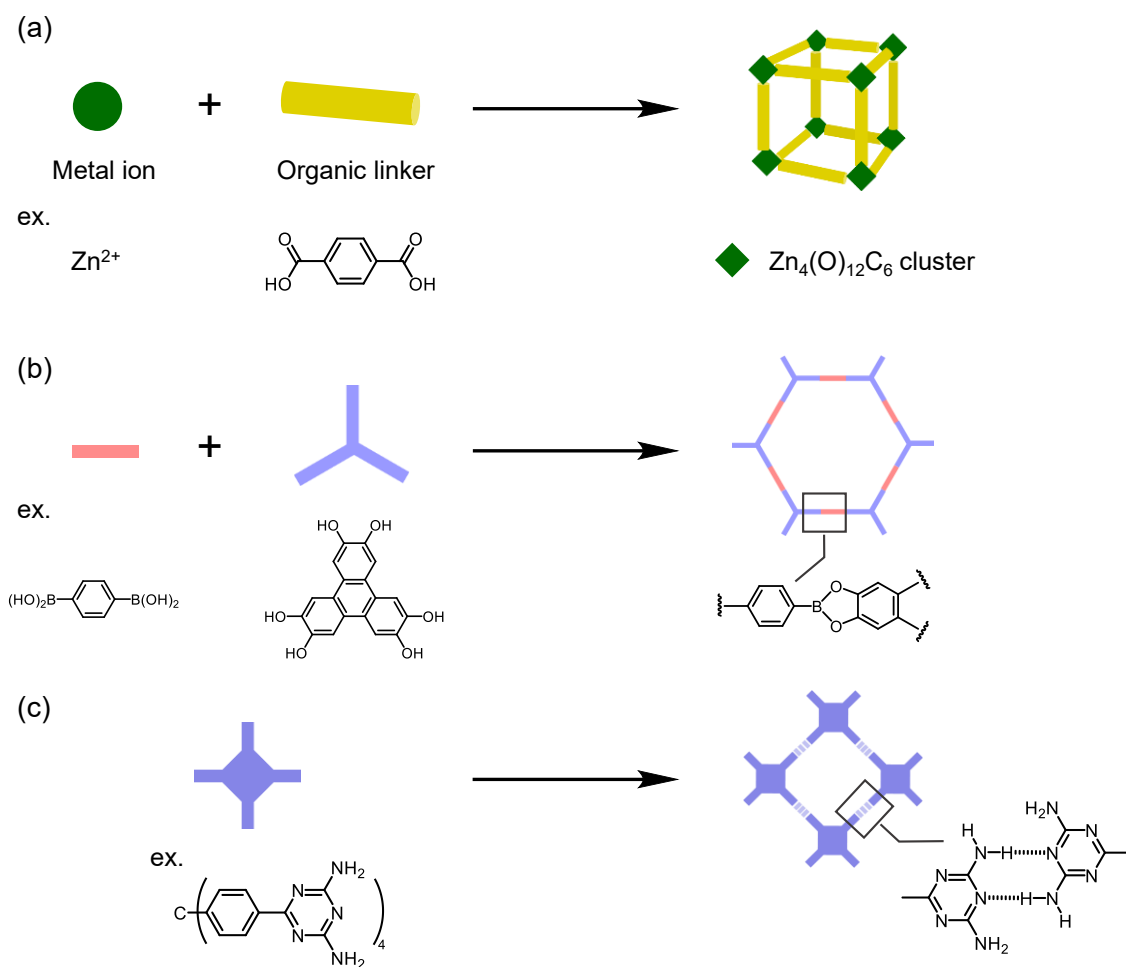


Fig. 3. Schematic illustration of the synthesis of (a) MOFs, (b) COFs, and (c) HOFs.

3. Introduction of catalytically active sites as functional moieties

To impart advanced functionalities to molecule-based porous materials, the strategic introduction of catalytically active sites as functional sites within the pore structure is of critical importance. Molecule-based porous materials, particularly MOFs, possess structural units that are clearly defined at the molecular level, providing a high degree of design flexibility for catalytically active sites. This feature enables the enhancement of reactivity, selectivity, and stability by exploiting reaction environments that are distinct from those in homogeneous molecular catalysts.^[47] For example, Lin *et al.* reported that by stabilizing Rh- and Ir-phosphine complexes and suppressing disproportionation reactions, the resulting systems exhibited higher turnover numbers in hydrogenation and hydrosilylation reactions than their homogeneous counterparts.^[48] Cui *et al.* synthesized isostructural family of chiral porous MTV-MOFs by controlling incorporation of one, two, or three different enantiopure metallosalen-based linkers and demonstrated that adjacent metallosalen units enable cooperative activation, resulting in higher efficiency and enantioselectivity than the sum of the individual components.^[49] Therefore, the introduction of catalytically active sites into crystalline porous materials is considered to be an effective strategy that directly enables the development of new catalytic materials. In this section, representative strategies for introducing catalytically active sites are outlined, including:

- (1) the utilization of functionalized organic linkers;
- (2) the utilization of specific secondary building units (SBUs); and
- (3) post-synthetic modification (PSM).

3.1 The utilization of functionalized organic linkers

One of the key features of molecule-based porous materials is the ability to directly incorporate molecular units known as homogeneous catalysts into the framework as organic linkers. Owing to their high degree of molecular design flexibility, organic linkers enable the introduction of a wide variety of catalytically active sites into MOFs, including those for oxidation catalysis,^[50] reduction catalysis,^[51] and photocatalysis.^[52] Representative example of such functional linkers is salen-based linkers (Fig. 4).^[53,54] By integrating these functional linkers into the framework, the catalytic functions established in homogeneous systems can be effectively transplanted into the pore environment of MOFs.

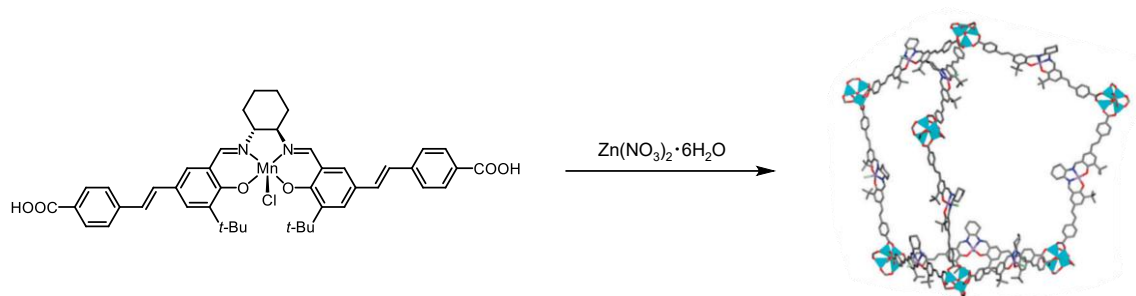


Fig. 4. MOFs utilizing salen-based linker.^[54]

3.2 The utilization of specific SBUs

Secondary building units (SBUs) are characteristic structural motifs of MOFs and play a crucial role not only in constructing the framework structure but also in serving as catalytically active sites.^[29,31] Representative SBUs that fulfill these roles include paddlewheel-type dinuclear metal clusters ($[M_2(O_2CR)_4]$),^[55] and trigonal prismatic metal clusters ($[M_3O(O_2CR)_6]$),^[56] and octahedral hexanuclear Zr clusters $[Zr_6O_4(OH)_4(COO)_{12}]$ ^[57,58] (Fig. 5). In these SBUs, solvent molecules or weakly coordinated ligands located at axial or terminal positions can be removed through activation treatments, resulting in the formation of open metal sites (OMSs). These OMSs function as Lewis acidic sites or adsorption sites, thereby playing a key role in catalytic reactions and molecular adsorption.

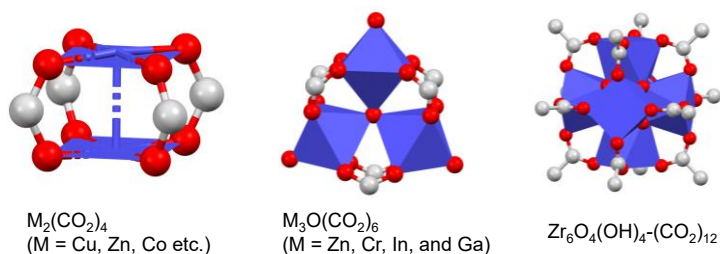


Fig. 5. The representative SBUs serves as catalytically active sites. C = grey, O = red, polyhedral and metal ions = blue.

3.3 Post-synthetic modification (PSM)

PSM is a versatile approach that enables chemical functionalization while preserving the preassembled framework structure, making it particularly compatible with the high structural stability of MOFs.^[59] In the following, representative PSM strategies for introducing catalytically active sites are outlined.

3.3.1 Post-synthetic metalation

Post-synthetic metalation enables the selective introduction of metal ions into preorganized chelating sites within organic linkers, thereby allowing the construction of active centers analogous to those in homogeneous catalysts within the pore structures of MOFs. Representative examples are porphyrin-, salen-, and BINAP-based MOFs (Fig. 6).^[60,61] Furthermore, the use of linkers bearing chelating functional groups, such as bipyridine,^[62,63] phenanthroline,^[63,64] and terpyridine,^[65] enables the precise introduction of transition-metal ions, thereby facilitating the rational design of catalytically active sites tailored to specific catalytic reactions.

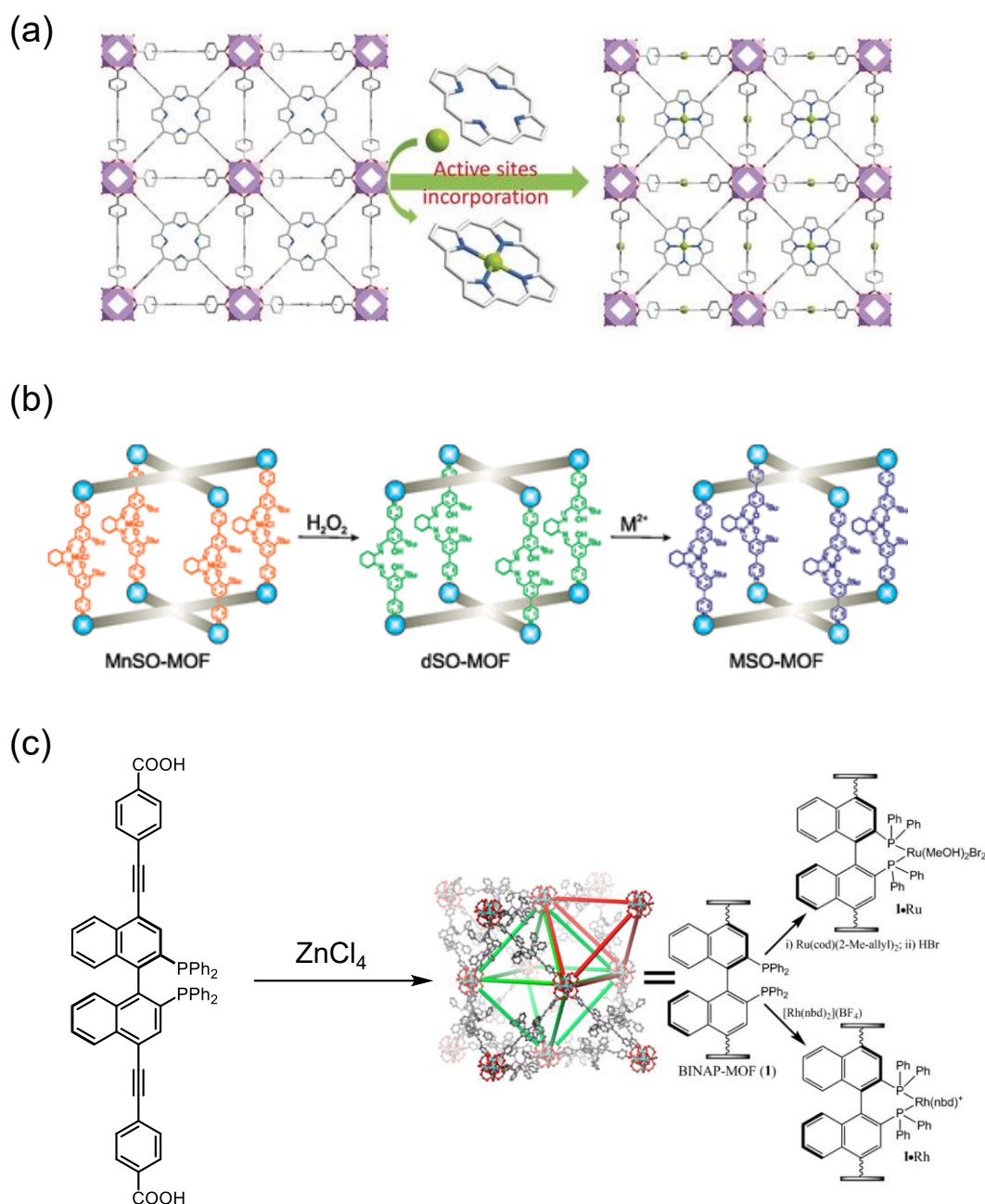


Fig. 6. (a) Post-synthetic metalation of porphyrin-MOF.^[66] Adapted with permission from Ref. 66. © Wiley-VCH GmbH. (b) Post-synthetic metalation of salen-MOF.^[67] Reprinted with permission from A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp, S. T. Nguyen, *J. Am. Chem. Soc.* **2011**, *133*, 13252–13255. <https://pubs.acs.org/doi/10.1021/ja204820d>. Copyright 2011 American Chemical Society. (c) Post-synthetic metalation of BINAP-based MOF.^[68] Adapted with permission from G. R. Desiraju, *J. Am. Chem. Soc.* **2013**, *135*, 9952–9967. <https://doi.org/10.1021/ja403264c>. Copyright 2013 American Chemical Society.

3.3.2 Metal ion exchange of SBUs

Metal ion exchange is a strategy for replacing the metal centers in the SBUs of MOFs with different metal ions while preserving the overall crystal structure. SBUs that are particularly susceptible to metal ion exchange include those that (i) can generate OMSs,^[69–71] (ii) contain terminally coordinated solvent molecules,^[72–75] or (iii) possess metal sites with sufficient flexibility to adopt coordination numbers higher than those suggested by crystallographic analysis (Fig. 7).^[76–80]

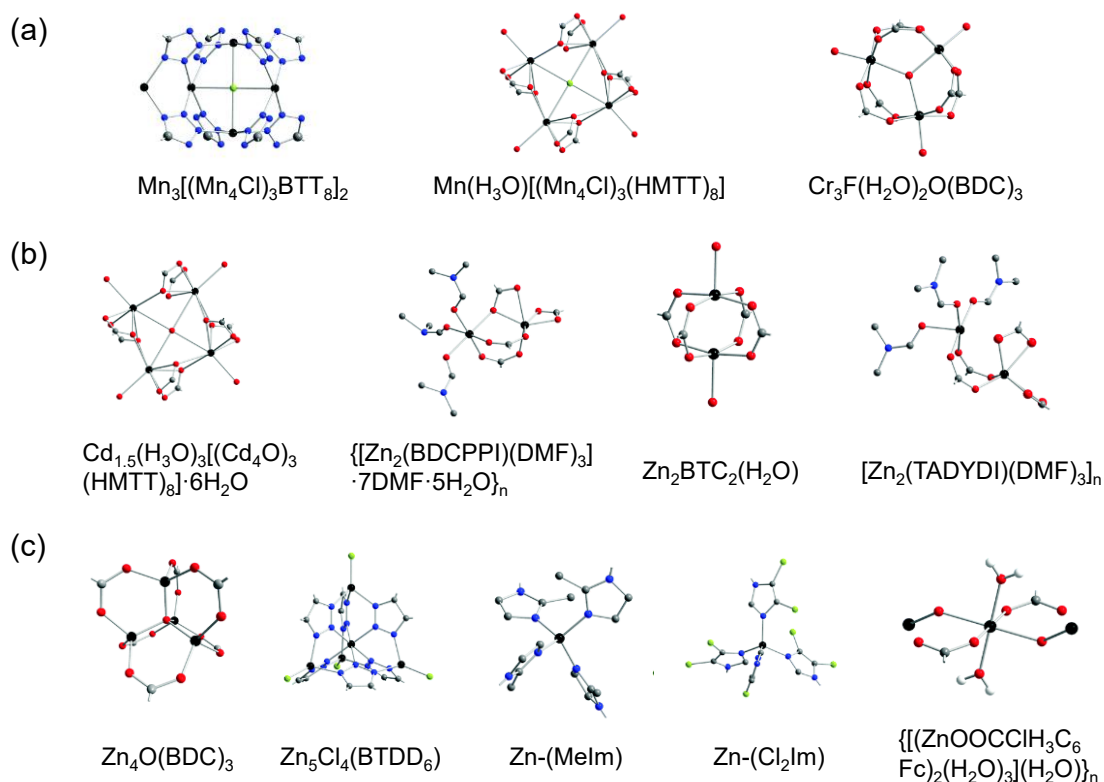


Fig. 7. The known examples of MOF SBUs that undergo cation exchange: SBU (a) that can generate OMSs, (b) contain terminally coordinated solvent molecules, and (c) possess metal sites with sufficient flexibility to adopt coordination numbers higher than those suggested by crystallographic analysis. C = grey, N = blue, O = red, Cl = green, and metal = black. Adapted from Ref. 60 from the Royal Society of Chemistry.

3.3.3 Ligand exchange

Ligand exchange with exogenous molecules bearing functional groups represents an effective strategy for enhancing the chemical and physical properties of MOFs. For example, the SBUs of carboxylate-based MOFs can undergo ligand exchange to introduce functional groups such as amino, azido, and formyl groups (Fig. 8).^[81] Furthermore, the introduced functional groups can be subsequently modified with bulky dyes or quenchers, enabling additional functionalization. In other cases, metal complexes bearing carboxylate groups can be directly incorporated into MOFs through ligand exchange, providing another versatile route for introducing functional molecular units (Fig. 9).^[82,83]

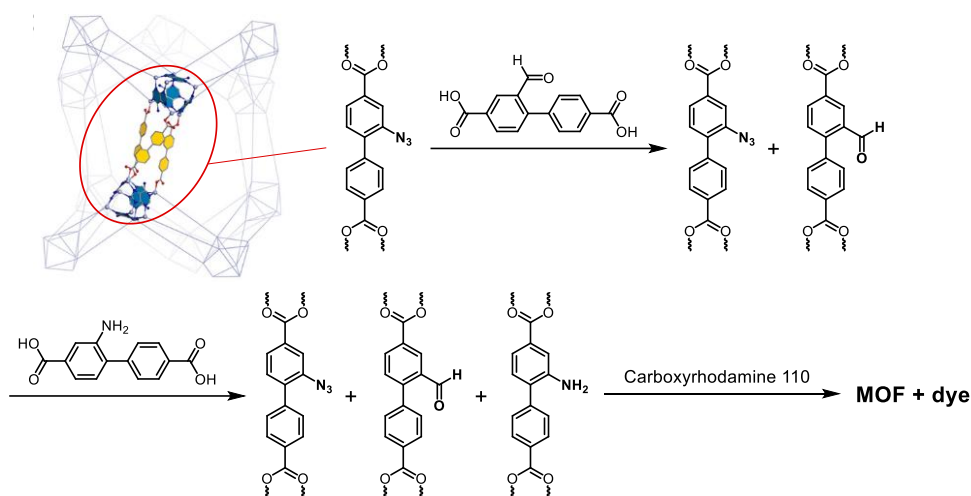


Fig. 8. Sequential post-synthetic ligand exchange, followed by post-synthetic modification with a dye.^[81]

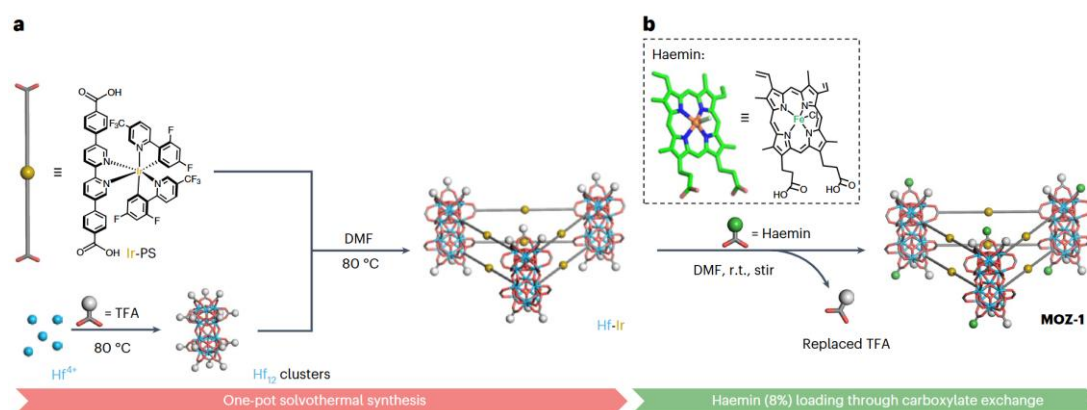


Fig. 9. (a) Hf-Ir monolayer was synthesized through a one-pot solvothermal synthesis to interlink Hf₁₂ secondary building units with Ir-PS. (b) MOZ-1 was synthesized through post-synthetic modification of Hf-Ir monolayer with haemin, wherein weakly coordinated TFA is replaced through carboxylate exchange. r.t., room temperature. Adapted with permission from Ref. 83. © Springer Nature.

Challenges of introduction of catalytically active sites into MOFs

As described above, although these strategies have enabled the introduction of a wide variety of catalytically active sites into MOFs, fundamental challenges remain. Because MOFs are assembled through coordination bonds, substitution-labile sites may become coordinatively saturated by coordination to organic linkers, which can lead to the loss of catalytic function. To overcome this drawback, as discussed above, strategies such as the incorporation of catalytically active sites into organic linkers or the utilization of open metal sites (OMSs) have been explored; however, these approaches inherently restrict the types of catalytically active sites that can be accommodated. Moreover, PSM methods raise additional concerns, as they often lead to non-uniform local structures, thereby limiting structural homogeneity and complicating the precise establishment of structure–activity correlations. Therefore, the development of methodologies for achieving uniform catalytically active sites and the advancement of analytical techniques for the precise determination of local structures are essential challenges for future research.

4. Supramolecular framework catalyst

As an effective solution to the challenges described above, our research group has pioneered a novel design concept referred to as supramolecular framework catalysts, which enables the introduction of catalytically active sites into molecule-based porous materials. In this approach, metal complexes bearing non-covalent interaction sites are designed and synthesized as molecular modules, and their crystallization leads to the formation of ordered porous frameworks through self-assembly driven by non-covalent interactions (Fig. 10).^[84–89]

In contrast to MOFs, in which the construction of framework structure is driven by coordination bonds, the non-covalent interactions employed in this strategy do not compete with metal–ligand coordination at the catalytic centers. Consequently, the coordination environment and electronic structure of the metal complex catalysts are not perturbed, allowing porous frameworks to be constructed without compromising catalytic reactivity. This design principle enables the realization of porous crystalline porous materials that retain catalytically active sites, thereby addressing key challenges associated with conventional strategies for introduction of catalytically active site.

Indeed, our group has demonstrated that supramolecular framework catalysts constructed using this approach exhibit excellent catalytic performance in reactions such as hydrogen evolution^[86,87] and CO₂ reduction,^[88,89] providing the effectiveness of this design concept. Nevertheless, reports on supramolecular framework catalysts remain limited, and further efforts toward material development and functional expansion are required to generalize this strategy and explore its full potential.

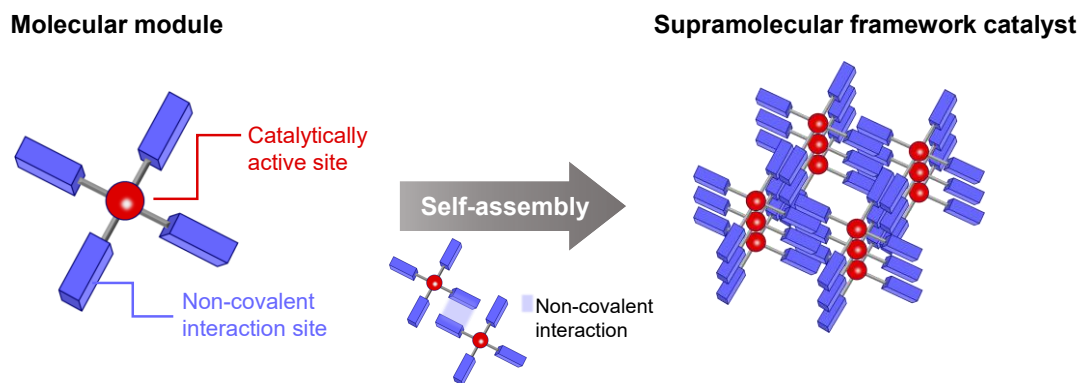


Fig.10. Schematic illustration of the synthesis of supramolecular framework catalyst.

5. Aim and survey of this thesis

The aim of this thesis is to establish a design principle for supramolecular framework catalysts and to demonstrate the effectiveness of this concept through applications to both catalysis and luminescent materials. This study focuses on metal porphyrin complexes, which possess high symmetry and well-defined electronic structures, and designs molecular modules bearing pyrenylphenyl moieties capable of engaging in π - π and CH- π interactions, thereby enabling the formation of ordered supramolecular frameworks with controlled functionality.

This thesis consists of three chapters.

Chapter 1 describes the development of a Ru(II)-porphyrin-based supramolecular framework catalyst for styrene epoxidation via oxygen atom transfer (OAT) reactions (Fig. 11a). Self-assembly of a pyrenylphenyl-functionalized Ru-porphyrin complex affords a crystalline porous framework that preserves the coordination environment of the Ru catalytic center. The resulting heterogeneous catalyst exhibits higher catalytic activity, enhanced durability, recyclability, and size-selective behavior compared to the corresponding homogeneous system, demonstrating that heterogenization via supramolecular framework formation is an effective strategy for improving Ru-porphyrin catalysis.

Chapter 2 focuses on the development of a more sustainable oxidation system by replacing the precious-metal center with an earth-abundant manganese ion (Fig. 11b). A Mn(III)-porphyrin-based supramolecular framework catalyst was constructed and applied to Mukaiyama-type aerobic epoxidation using molecular oxygen as the oxidant. The Mn-porphyrin framework exhibits significantly higher catalytic activity than the previously developed Ru-based system and surpasses other reported molecule-based porous crystalline frameworks incorporating earth-abundant metals in terms of turnover frequency and production rate. This chapter highlights the potential of supramolecular frameworks for integrating high catalytic efficiency with sustainability.

Chapter 3 extends the supramolecular framework concept from catalysis to solid-state luminescent materials (Fig. 11c). An Ir(III)-porphyrin-based supramolecular framework was synthesized in which emissive centers are spatially isolated within a well-defined crystalline lattice. This spatial isolation effectively suppresses intermolecular interactions and energetic disorder, resulting in near-infrared phosphorescence with a significantly narrower full width at half maximum compared to an amorphous counterpart. These results demonstrate that supramolecular frameworks provide a powerful platform for controlling photophysical properties through precise molecular assembly.

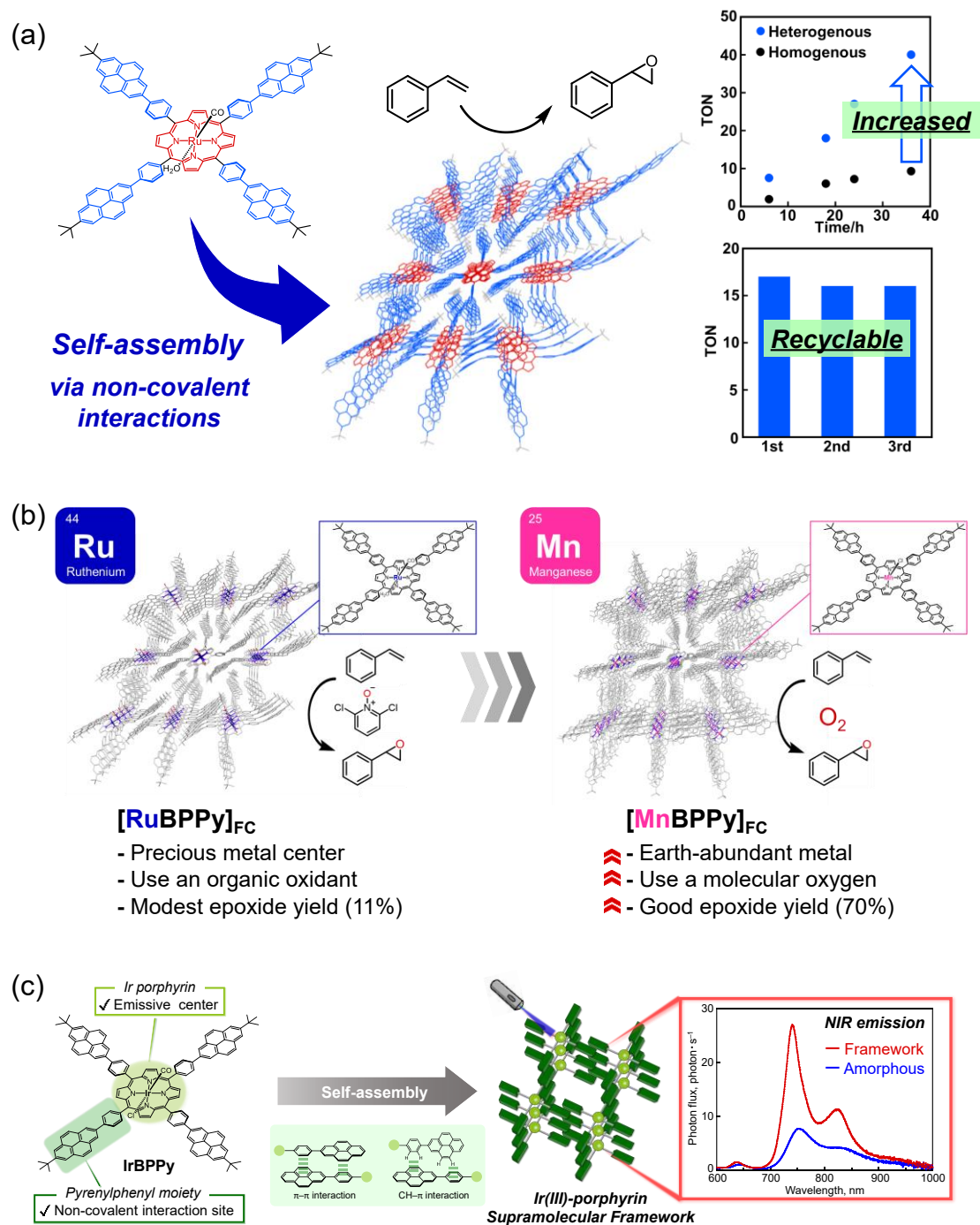


Fig. 11. The schematic illustration of achievements in (a) chapter 1, (b) chapter 2, and (c) chapter 3.

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Chapter 1

Development of a Ru–porphyrin-based supramolecular framework catalyst for styrene epoxidation

Introduction

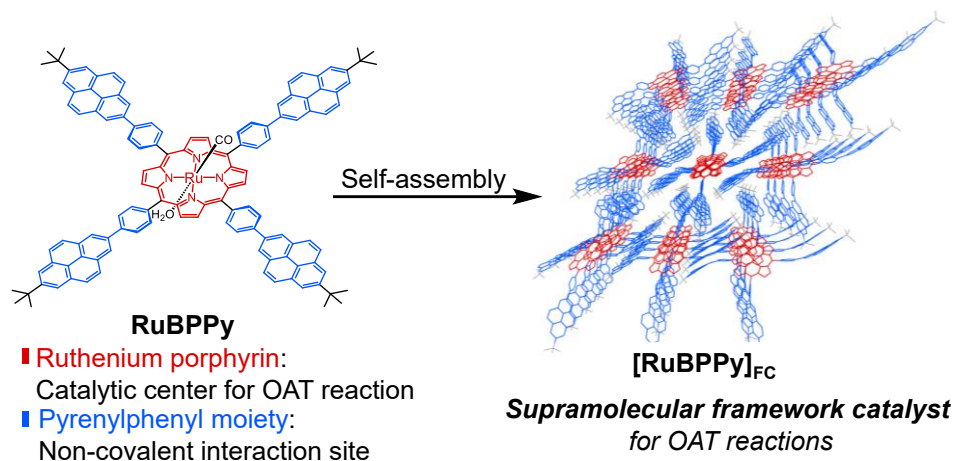
Catalysts for oxygen atom transfer (OAT) reactions have recently gained significant attention in both synthetic and biological systems.^[1–3] These reactions, with metal-oxo species comprising the key active species, facilitate the conversion of hydrocarbons into alcohols and epoxides, which are valuable raw materials for chemical products.^[1] In nature, Fe–porphyrins in cytochrome P450 enzymes are capable of catalysing a variety of OAT reactions under mild conditions via Fe-oxo intermediates.^[2] Inspired by this natural system, metalloporphyrins have been studied and applied as catalysts for OAT reactions over the past half century.^[4] Among them, Ru–porphyrins have received considerable attention because of the rich coordination and redox chemistry of Ru as well as its close periodic relationship with the biologically significant metal iron.^[5]

In the catalytic oxidation reaction of Ru–porphyrins, Ru–oxo porphyrin complexes show three different oxidation states with $[\text{Ru}^{\text{VI}}(\text{por})(\text{O})_2]$,^[6] $[\text{Ru}^{\text{V}}(\text{por})(\text{O})(\text{L})]$,^[7] and $[\text{Ru}^{\text{IV}}(\text{por})(\text{O})(\text{L})]$ ^[8] (por = porphyrin in general, L = monodentate ligand) as active species that can oxidize a wide variety of organic substrates, particularly various alkenes, benzylic hydrocarbons, and arenes.^[9] Notably, Ru–porphyrins can be activated by mild oxidants such as heteroaromatic *N*-oxides.^[6d] Due to these unique properties, Ru–porphyrins exhibit high potential as catalysts for OAT reactions; the literature contains several examples of Ru–porphyrins that function as catalysts for OAT reactions.^[9]

The heterogenization of Ru–porphyrins could improve their catalytic performance. To date, there are many reports on the synthesis of molecule-based heterogeneous-framework catalysts by the self-assembly of metal complexes through coordination bonds (forming metal–organic frameworks (MOFs))^[10–12] or non-covalent interactions.^[13,14] These framework catalysts generally show unique features derived from the catalytic centres immobilized in their structures and a heterogeneous porous nature. Thus, catalytic materials enabling the accumulation of substrates, a high reaction selectivity and recyclable properties can be synthesized. However, the literature contains very few reports on molecule-based heterogeneous framework catalysts containing Ru–porphyrins.^[15] Furthermore, to the best of our knowledge, no Ru–porphyrin-based heterogeneous framework catalysts for OAT reactions are reported to date.

Herein, I report the development of a new Ru–porphyrin-based supramolecular-framework catalyst containing non-covalent interactions for styrene epoxidation. A Ru(II)–porphyrin complex with pyrenylphenyl moieties at the *meso*-position, aquacarbonyl{5,10,15,20-tetrakis(4-(7-*tert*-butyl)-pyrene-2-yl)phenyl}porphyrinato}ruthenium(II) (**RuBPPy**), was used as the building unit of the

catalyst. **RuBPPy** contains two key features: a Ru-based catalytic centre for the OAT reaction and pyrene moieties as non-covalent interaction sites (Scheme 1). The self-assembly of **RuBPPy** via non-covalent interactions results in the supramolecular framework catalyst, **[RuBPPy]_{FC}**, which shows excellent OAT catalysis.

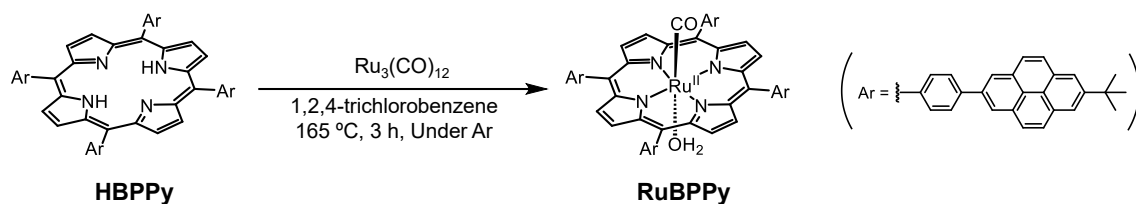


Scheme 1. Schematics of the structure and features of the new Ru-porphyrin complex (**RuBPPy**) developed in this work and the supramolecular framework (**[RuBPPy]_{FC}**) construction strategy.

Results and discussion

Synthesis and characterization of RuBPPy

For the synthesis of **RuBPPy**, the free base porphyrin 5,10,15,20-tetrakis(4-(7-tert-butyl)pyrene-2-yl)phenyl porphyrin (**HBPPy**), which was synthesised according to a previously reported procedure,^[13d] was reacted with $\text{Ru}_3(\text{CO})_{12}$ for 3 h in 1,2,4-trichlorobenzene at 165 °C under argon (Scheme 2).^[7d] The formation of **RuBPPy** was confirmed by NMR spectroscopy, UV-vis spectroscopy, and elemental analysis.



Scheme 2. Synthetic scheme for **RuBPPy**.

The UV-vis absorption spectrum of **RuBPPy** exhibited bands attributed to pyrene moieties at 313, 326, and 342 nm, a Soret band at 418 nm, and Q-bands at 532 and 566 nm (Fig. 1). Compared with the spectrum of **HBPPy**, a blue shift of the Soret band and reduction in the number of Q-bands were observed in the spectrum of **RuBPPy**, confirming Ru-ion insertion into the porphyrin ring of **RuBPPy**. The cyclic voltammogram of **RuBPPy** in a tetra-*n*-butyl ammonium perchlorate (TBAP)/*o*-dichlorobenzene solution (0.1 M) indicated one reversible oxidation and one reversible reduction wave at 0.30 and -2.19 V (vs. Fc/Fc⁺), respectively (Fig. 2), corresponding to porphyrin-centred redox, as reported in the literature.^[16]

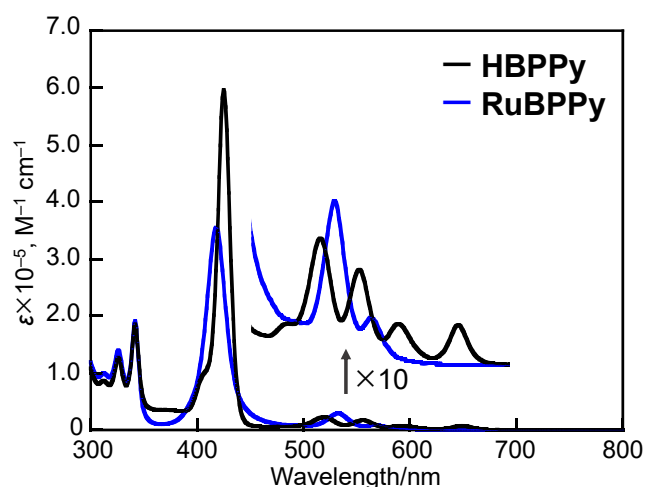


Fig. 1. UV-vis absorption spectra of **HBPPy** and **RuBPPy** in CHCl₃.

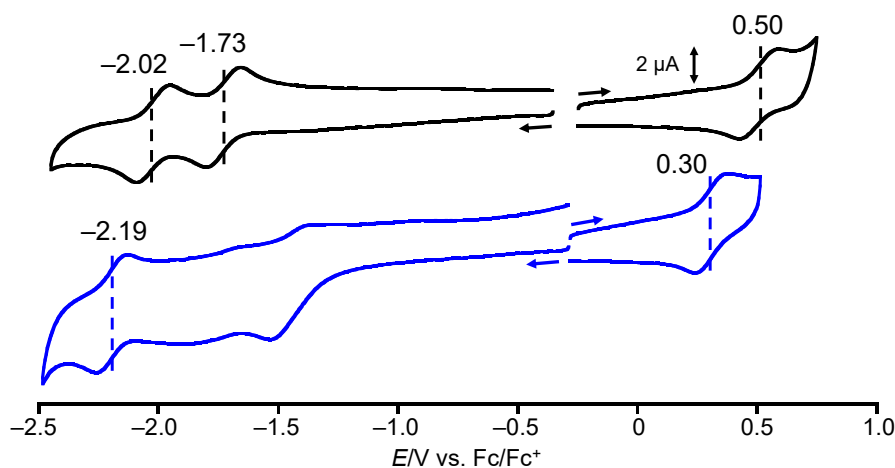


Fig. 2. Cyclic voltammograms of **HBPPy** (0.2 mM, black) and **RuBPPy** (0.2 mM, blue) in *o*-DCB with TBAP (0.1 M) under Ar. WE: GC, RE: Ag/Ag⁺, CE: Pt wire, Scan rate: 100 mV s⁻¹.

Synthesis and characterization of [RuBPPy]_{FC}

Subsequently, the formation of a framework catalyst via the self-assembly of **RuBPPy** was investigated. To produce single crystals of as-synthesized **RuBPPy** (i.e., [RuBPPy]_{as-syn}, Figs. 3 and 4 and Table 1, the description of the crystal structure), an **RuBPPy** solution in a mixed solvent comprising chloroform and acetonitrile (2:1) was gradually evaporated. The removal of residual solution from the crystals of [RuBPPy]_{as-syn} and drying at 25 °C *in vacuo* afforded dried crystals ([RuBPPy]_{FC}). The single-crystal X-ray diffraction (SC-XRD) analysis of [RuBPPy]_{FC} indicated that self-assembled **RuBPPy** comprised the supramolecular framework of [RuBPPy]_{FC} in the triclinic system with the *P*-1 space group. Fig. 5a and Table 2 contain an Oak Ridge Thermal Ellipsoid Program (ORTEP) drawing and summary of the crystallographic data of [RuBPPy]_{FC}, respectively. The Ru–N distance (2.046(3)–2.057(3) Å) in the synthesized crystals lies within the normal range of Ru–N distances in similar porphyrin-based Ru(II) compounds (Table 3).^[6f,6g,17] Moreover, the coordination of carbon monoxide and water molecules at the axial positions indicates the presence of an Ru(II) centre in the system.^[6f,6g]

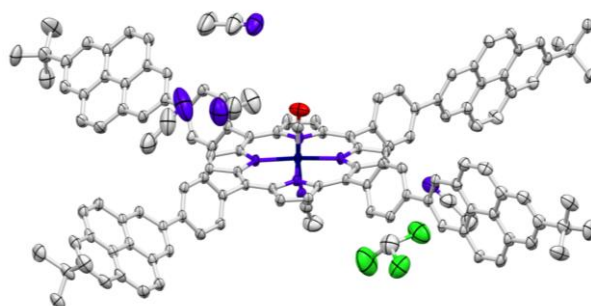


Fig. 3. An ORTEP drawing of [RuBPPy]_{as-syn} (50% probability ellipsoids). Hydrogen atoms and disordered atoms are omitted for clarity. C = gray, N = blue, O = red, and Ru = dark blue.

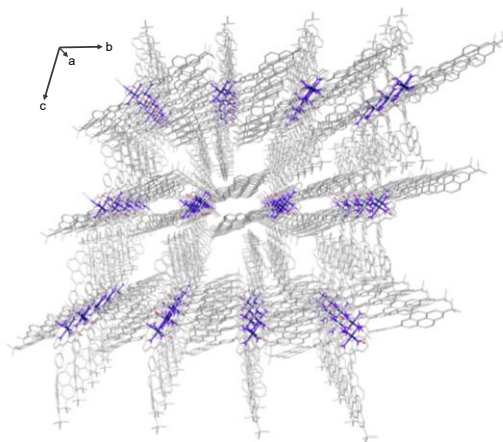


Fig. 4. Packing structure of [RuBPPy]_{as-syn}. Crystal solvents are omitted for clarify.

Table 1. Summary of crystallographic data for **[RuBPPy]_{as-syn}**.

formula	C ₁₃₆ H ₁₀₈ Cl ₃ N ₉ ORu
formula weight	2091.73
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> , Å	15.3821(2)
<i>b</i> , Å	16.7184(4)
<i>c</i> , Å	23.3719(3)
<i>α</i> , deg	102.612(2)
<i>β</i> , deg	104.1350(10)
<i>γ</i> , deg	93.6510(10)
<i>V</i> , Å ³	5644.16(18)
<i>Z</i>	2
ρ_{calc} , g/cm ³	1.231
<i>F</i> (000)	2180.0
MoK α , cm ⁻¹	0.71073
<i>T</i> , K	123
2 θ_{max} , deg	62.618
reflns measd	95711
uniq reflns	30950
<i>R</i> (int)	0.0455
data/restraints/params	30950/0/1399
<i>R</i> ₁	0.0820
w <i>R</i> ₂	0.2286
<i>GOF</i>	1.054

Table 2. Summary of crystallographic data for [RuBPPy]_{FC}.

formula	C ₁₂₅ H ₉₂ N ₄ O ₂ Ru
formula weight	1783.09
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> , Å	7.8860(6)
<i>b</i> , Å	16.7298(10)
<i>c</i> , Å	19.9827(10)
<i>α</i> , deg	112.717(5)
<i>β</i> , deg	94.736(5)
<i>γ</i> , deg	95.806(5)
<i>V</i> , Å ³	2398.0(3)
<i>Z</i>	1
ρ_{calc} , g/cm ³	1.235
<i>F</i> (000)	930.0
MoK α , cm ⁻¹	0.71073
<i>T</i> , K	123
2 θ_{max} , deg	50.106
reflns measd	26456
uniq reflns	8493
<i>R</i> (int)	0.1580
data/restraints/params	8493/25/604
<i>R</i> ₁	0.0638
w <i>R</i> ₂	0.1149
<i>GOF</i>	0.948

Table 3. Summary of the averaged Ru–N bond distances^a of Ru–porphyrins.

Complex	Averaged Ru–N bond distance ^b /Å	Reference
[RuBPPy]_{as-syn}	2.054(3)	This work
[RuBPPy]_{FC}	2.052(3)	This work
[Ru(II)(TPP)(CO)(H ₂ O)] ^c	2.045(3)	[6f]
[Ru(II)(TPP)(CO)(EtOH)]	2.049(5)	[17a]
[Ru(II)(F ₂₀ -TPP)(CO)(H ₂ O)] ^d	2.055(3)	[6g]
[Ru(II)(TMTTP)(CO)(H ₂ O)] ^e	2.070(4)	[17b]
[Ru(III)(TPP)(OEt)(EtOH)]	2.040(6)	[18]
[Ru(III)(2,6-Cl ₂ TPP)(Ph)(OEt ₂)] ^f	2.031(4)	[7d]
[Ru(III)(2,6-Cl ₂ TPP)(Ph)(H ₂ O)]	2.034(14)	[7d]
[Ru(III)(2,6-Cl ₂ TPP)(Cl)(THF)]	2.041(4)	[7d]
[Ru(IV)(TMP)(Cl) ₂] ^{g, h}	2.024(9), 2.034(6)	[19]
[Ru(IV)(2,6-Cl ₂ TPP)(Cl) ₂]	2.040(7)	[19]

^aThe distances between Ru atom and N atom of porphyrin ring, ^bThe distance with standard deviation, ^cTPP = tetraphenylporphyrinato dianion, ^dF₂₀-TPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato dianion, ^eTMTTP = 1,3,5,7-tetramethyl-2,4,6,8-tetraterphenylporphyrinato dianion, ^f2,6-Cl₂TPP = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato dianion, ^gTMP = *meso*-tetramesitylporphyrinato dianion. ^hThere are two types of independent molecules in the unit cell.

Notably, the packing structure of the crystal comprises a 1D columnar structure stabilised by CH– π interactions between the pyrenylphenyl rings along the *a* axis (Fig. 5b), which is further stabilised by π – π interactions between the pyrenyl and phenyl moieties (Fig. 5c), resulting in the formation of a porous framework structure (Fig. 6). Considering the van der Waals radii of the constituent atoms, the size of the pore entrance is estimated to be $4.8 \times 2.8 \text{ \AA}^2$. Therefore, pyrenylphenyl moieties contribute towards the formation and maintenance of the supramolecular framework structure of **[RuBPPy]_{FC}**, even after the removal of guest solvent molecules.

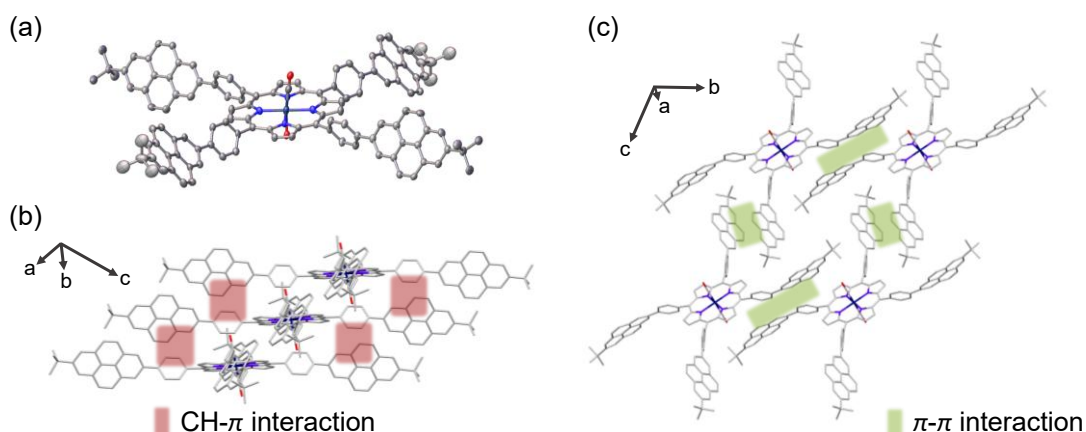


Fig. 5. (a) An ORTEP drawing of **RuBPPy** (50% probability ellipsoids). Hydrogen atoms and disordered atoms are omitted for clarity. C = gray, N = blue, O = red, and Ru = dark blue. (b) 1D columnar structure of **[RuBPPy]_{FC}**. (c) Intercolumnar interactions observed in **[RuBPPy]_{FC}**.

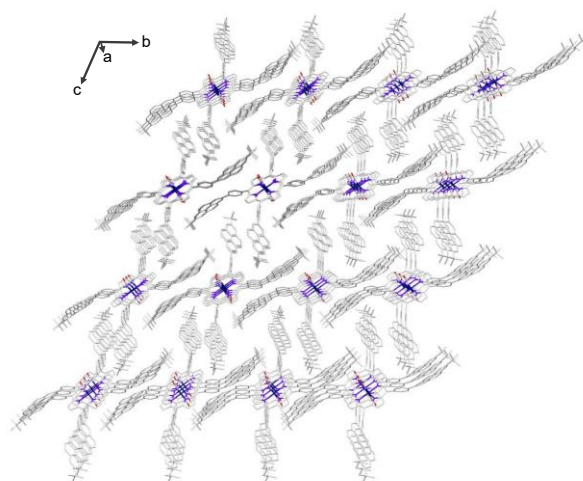


Fig. 6. Packing structure of **[RuBPPy]_{FC}**.

The diffuse reflectance spectrum of **[RuBPPy]_{FC}** contained characteristic absorption bands at 328 and 343 nm corresponding to pyrene moieties, a Soret band at 421 nm, and Q-bands at 537 and 572 nm attributed to the Ru-porphyrin moiety (Fig. 7a), similar to the absorption bands of **RuBPPy** in the solution state (*vide supra*). The FT-IR spectrum of **[RuBPPy]_{FC}** contained the characteristic carbonyl stretching band of the coordinated axial ligand at 1949 cm⁻¹ and a sharp band corresponding to the rocking vibration of the pyrrole units of the porphyrin ring at 1006 cm⁻¹ (Fig. 8), indicating the formation of the Ru(II) state.^[20]

The experimental powder X-ray diffraction (PXRD) pattern and simulated spectrum constructed using single-crystal diffraction data were consistent, confirming the phase purity of **[RuBPPy]_{FC}** (Fig. 7b). This framework is stable in cyclohexane, hexane, acetonitrile and mixed solvents (Fig. 9). The CO₂ adsorption isotherm was measured at 195 K to investigate the porosity of **[RuBPPy]_{FC}** (Fig. 7c). The maximum uptake was 71 cm³ g⁻¹, which is comparable to some previously reported porphyrin-based supramolecular frameworks.^[13d,21] The Brunauer-Emmett-Teller (BET) surface area was estimated to be 206 m² g⁻¹. The thermogravimetric analysis (TGA) of the sample (dried at 80 °C for 30 min *in vacuo*) within 25–600 °C under N₂ flow with a heating rate of 2 °C min⁻¹ was used to investigate the thermal stability of **[RuBPPy]_{FC}** (Fig. 7d). **[RuBPPy]_{FC}** showed a weight loss of 2.0% within 60–135 °C corresponding to the release of H₂O molecules. Subsequently, the TGA curve showed a relatively stable plateau up to 260 °C, followed by the decomposition of the framework. Therefore, **[RuBPPy]_{FC}** comprises a porous molecule-based supramolecular framework that shows thermal stability up to 260 °C, retaining the characteristics of the mononuclear complex **RuBPPy**.

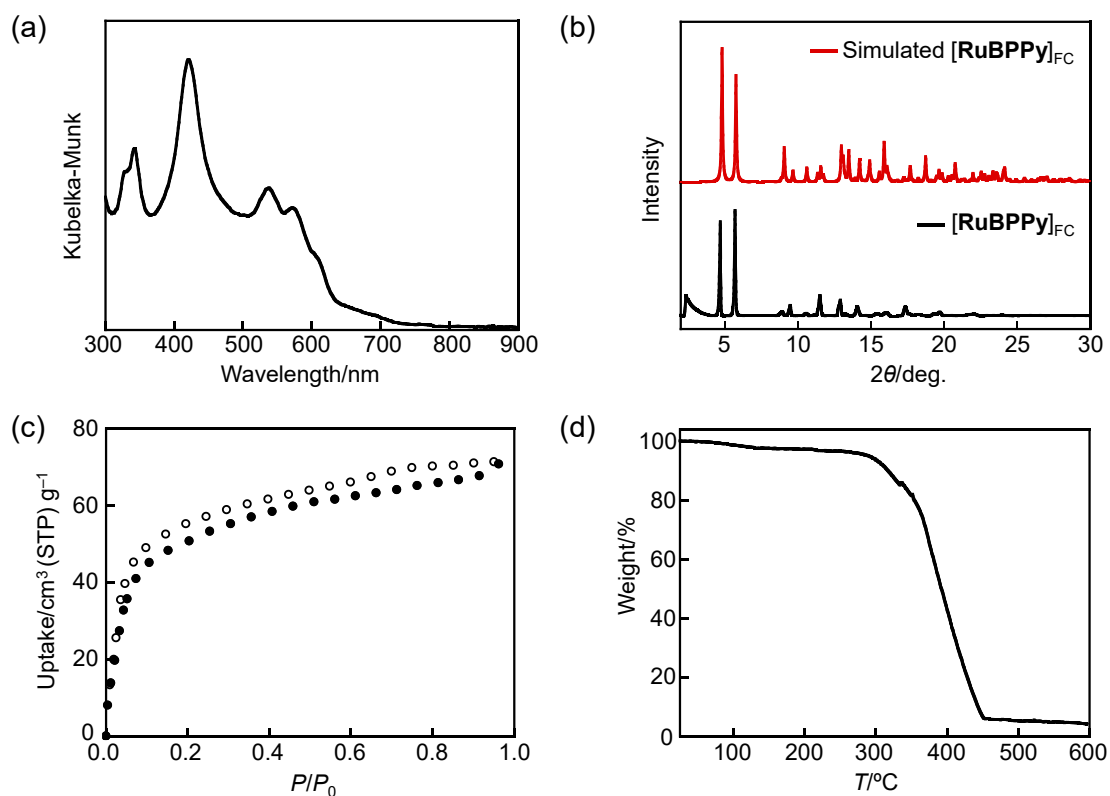


Fig. 7. (a) Diffuse-reflectance UV-vis spectrum of $[\text{RuBPPy}]_{\text{FC}}$. (b) Experimental and simulated PXRD patterns for $[\text{RuBPPy}]_{\text{FC}}$. (c) Adsorption and desorption isotherms of CO_2 for $[\text{RuBPPy}]_{\text{FC}}$ at 195 K. (d) TGA curve of $[\text{RuBPPy}]_{\text{FC}}$ within 25–600 °C under N_2 .

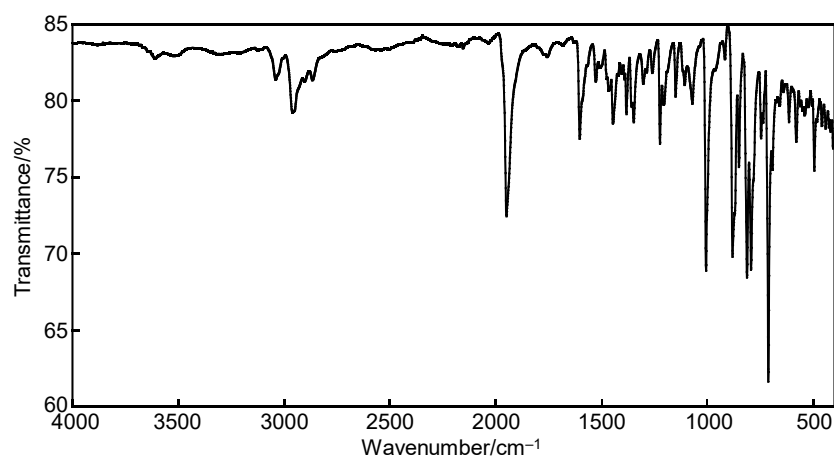


Fig. 8. FT-IR spectrum of $[\text{RuBPPy}]_{\text{FC}}$.

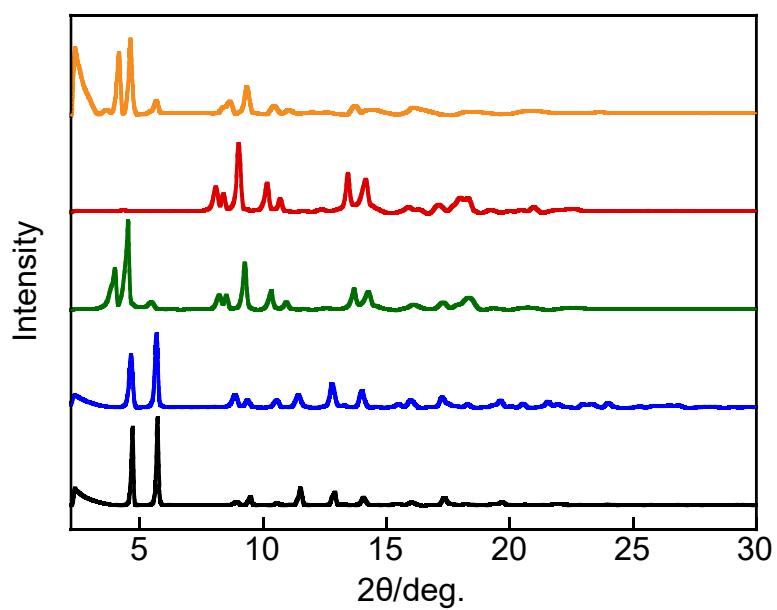


Fig. 9. PXRD patterns for $[\text{RuBPPy}]_{\text{FC}}$ (black), after soaking in acetonitrile (blue), hexane (green), cyclohexane (red) and 5.0% benzene in cyclohexane (orange) for 2 h and drying.

Epoxidation of styrene

Next, the activity of the crystalline solid, **[RuBPPy]_{FC}** in the catalytic epoxidation of styrene was examined. Styrene epoxidation under heterogeneous conditions by **[RuBPPy]_{FC}** was carried out in a mixed solvent comprising benzene (5.0%) in cyclohexane with the mild oxidant 2,6-dichloropyridine *N*-oxide at 20 °C for 18 h in an argon atmosphere under Xe-lamp photoirradiation (400 nm ≤ λ, 300 W). Photoirradiation was used for the decarbonylation of the Ru-centre.^[22] GC-FID analysis after the reaction showed that the **[RuBPPy]_{FC}**-catalysed epoxidation of styrene generated styrene oxide with a turnover number (TON) of 19 without overoxidation (Table 4, Entry 1). The porphyrin skeleton is maintained in the post catalyst (Fig. 10a) and no increase of TON was observed in the filtrate from which the catalyst was removed (Fig. 10b). Control experiments conducted in the absence of **[RuBPPy]_{FC}**, the oxidant, or photoirradiation resulted in no epoxide production, confirming the necessity of all these elements in the target reaction (Table 4, Entry 2-4). No oxidized products were obtained under conditions in which O₂ or H₂O₂ was used instead of 2,6-dichloropyridine *N*-oxide. The catalytic activity with *p*-substituted styrene was investigated and the TON with non-substituted styrene was the highest in this system (Table 5). This trend is distinct from that of previously reported systems,^[6h,7d,19] in which styrene derivatives with electron-donating groups exhibited higher activities. This difference in reactivity can be attributed to the effects of the pore structure of the catalyst.

Table 4. Epoxidation of styrene with 2,6-dichloropyridine *N*-oxide and **[RuBPPy]_{FC}**.^a

Entry	Deviation from standard conditions	TON ^b
1	None	19 ± 0.8 ^c
2	No catalyst	0
3	No oxidant	0
4	No light	0

^aStandard reaction conditions: **[RuBPPy]_{FC}** = 0.14 μmol, [2,6-dichloropyridine *N*-oxide] = 7.0 mM (100 equiv.), [styrene] = 43 mM (620 equiv.) in 5.0% benzene in cyclohexane (2.0 mL) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (400 nm ≤ λ, 300 W). ^bDetermined by GC–FID based on the **[RuBPPy]_{FC}**. ^cAverage value over 3 runs with standard deviation.

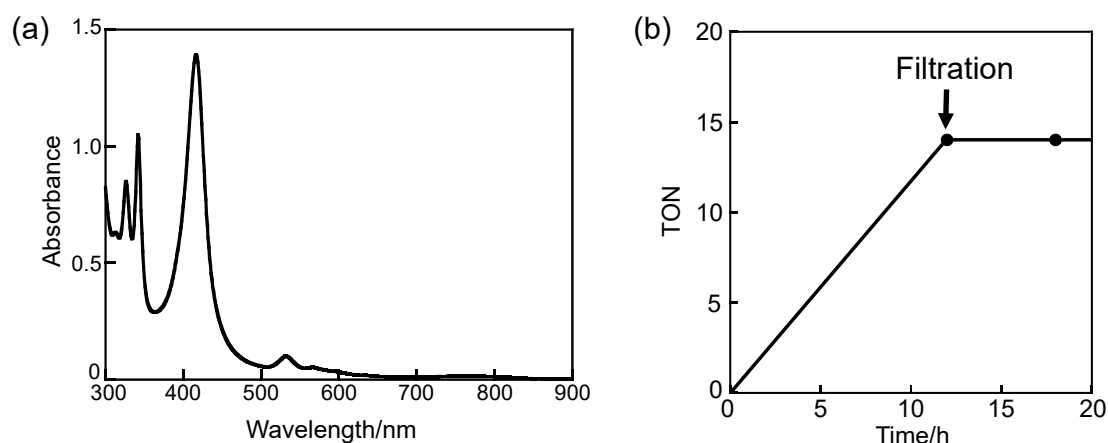


Fig. 10. (a) A UV-vis spectrum of the post catalyst dissolved in CHCl_3 after the epoxidation reaction of styrene for 18 h. (b) The catalytic activity of epoxidation in the presence of the catalyst for 12 h and of the filtrate (in the absence of the catalyst) for an additional 6 h.

Table 5. Epoxidation of styrene derivatives.

Entry	R	TON
1	H	$19 \pm 0.8^{a,b}$
2	Cl	7.2^c
3	Me	18^c
4	OMe	15^c

$[\text{RuBPPy}]_{\text{FC}} = 0.14 \text{ } \mu\text{mol}$, $[\text{2,6-dichloropyridine } N\text{-oxide}] = 7.0 \text{ mM}$ (100 equiv.), $[\text{substance}] = 43 \text{ mM}$ (620 equiv.) in 5.0% benzene in cyclohexane (2.0 mL) at $20 \text{ }^\circ\text{C}$ for 18 h under argon under visible light irradiation from a Xe lamp ($400 \text{ nm} \leq \lambda$, 300 W). ^aDetermined by GC-FID based on the $[\text{RuBPPy}]_{\text{FC}}$, ^bAveraged value over 3 runs with standard deviation, ^cDetermined by ^1H NMR using 1,1,2,2-tetrachloroethane as an internal standard based on the $[\text{RuBPPy}]_{\text{FC}}$.

I have investigated the catalytic activity of styrene epoxidation upon different light wavelength. In this experiment, special attention has been paid to clarify the role of pyrene unit. As the pyrene units can absorb the light shorter than ca. 450 nm (Fig. 11), I have used the following conditions in these experiments; (a) $400\text{ nm} \leq \lambda$ (standard condition), (b) $400\text{ nm} \leq \lambda \leq 455\text{ nm}$ (where the absorption bands of the pyrene unit and the Soret band of the porphyrin moiety exist), and (c) $455\text{ nm} \leq \lambda$ (where no absorption bands of the pyrene unit exists). As a result, almost no light wavelength dependence on the TON values was confirmed as shown in Table 6. The result suggests that the excitation of the porphyrin unit is essential for the catalysis. These catalytic epoxidation results indicate that styrene is oxidised by Ru-oxo species generated via the reaction of the photochemically decarbonylated Ru(II) centre with 2,6-dichloropyridine *N*-oxide.^[23]

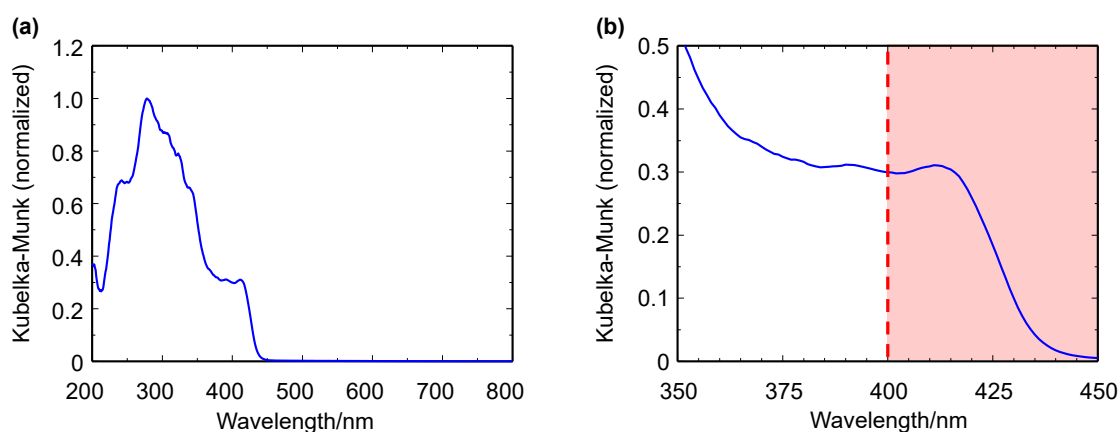


Fig. 11. (a) A diffuse-reflectance UV-vis spectrum of 4-(7-(tert-butyl)pyren-2-yl)benzaldehyde, and (b) an enlarged figure of (a). These figures are reproduced with the permission from ref. 13e.

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Table 6. Epoxidation of styrene upon different light wavelength.

Entry	Wavelength	TON ^a
1	$400\text{ nm} \leq \lambda$	19 ± 0.8^b
2	$400\text{ nm} \leq \lambda \leq 455\text{ nm}$	23
3	$455\text{ nm} \leq \lambda$	19

[RuBPPy]_{FC} = 0.14 μmol , [2,6-dichloropyridine *N*-oxide] = 7.0 mM (100 equiv.), [styrene] = 43 mM (620 equiv.) in 5.0% benzene in cyclohexane (2.0 m) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (300 W). ^aDetermined by GC–FID based on the [RuBPPy]_{FC}, ^bAveraged value over 3 runs with standard deviation.

Subsequently, the effect of the framework structure of the catalyst on its activity was investigated by comparing the activity of **RuBPPy** (homogeneous state) with that of heterogeneous **[RuBPPy]_{FC}**. The time course of the reaction in Fig. 12a indicates that the TON increases linearly for a significant duration; moreover, the TON in the heterogeneous system is approximately four times higher than that in the homogenous system. In addition, the TON reached 134 after 96 h under the optimized conditions: **[RuBPPy]_{FC}** = 0.14 μ mol, [2,6-dichloropyridine *N*-oxide] = 28 mM (400 equiv.), [styrene] = 86 mM (1240 equiv.) in 5.0% benzene/cyclohexane (2.0 mL) at 20 °C under argon under visible light irradiation from a Xe lamp (400 nm $\leq \lambda$, 300 W). Recycling tests were used to investigate the recyclability of the catalytic system. After catalysing styrene epoxidation for 18 h, **[RuBPPy]_{FC}** was filtered, washed several times with acetonitrile, and dried at 70 °C for 30 min *in vacuo*. This powder was used to catalyse epoxidation in the subsequent reaction cycle. Fig. 12b shows that the catalytic activity was maintained for three cycles. Therefore, **[RuBPPy]_{FC}** shows efficient catalysis, durability, and recyclability, confirming the high performance of heterogeneous Ru–porphyrin catalytic systems.

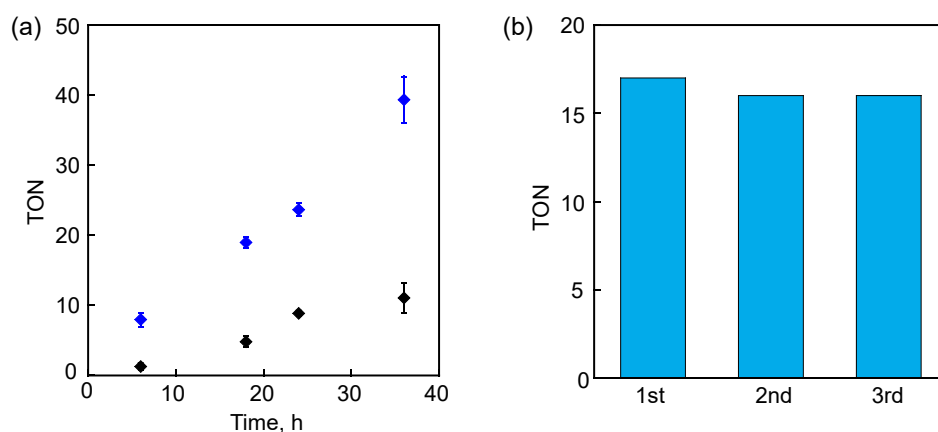
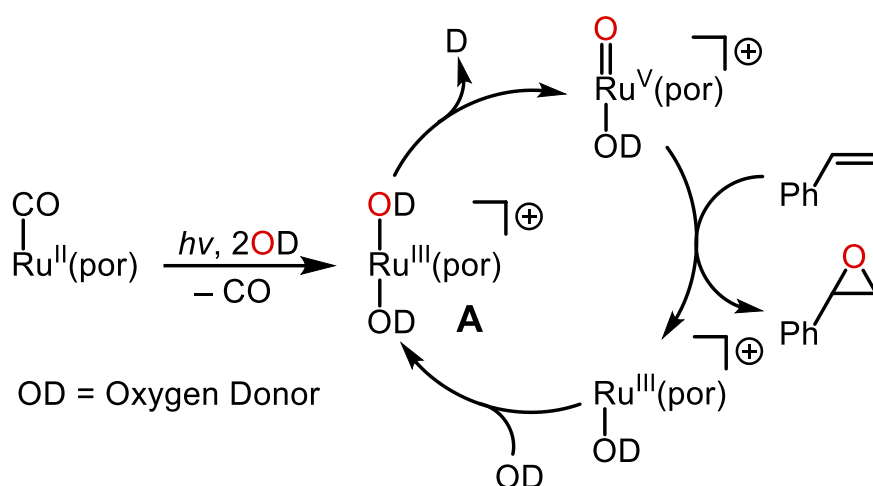


Fig. 12 (a) Time course of the TON for styrene epoxidation by **[RuBPPy]_{FC}** in a heterogeneous system containing a mixed solvent (cyclohexane/benzene) (blue) and by **RuBPPy** in a homogenous system containing benzene (black). All the other reaction conditions are the same as those listed in Table 4. (b) Recyclability tests of **[RuBPPy]_{FC}** for 18 h over three cycles.

A possible reaction mechanism for the epoxidation mediated by **[RuBPPy]_{FC}** is proposed (Scheme 3). Initially, the reaction of Ru complex with an oxygen donor (OD), 2,6-dichloropyridine *N*-oxide, under the photoirradiated condition affords the one-electron oxidized complex with two OD ligands (**A** in Scheme 3) as a key intermediate. The fact that the reaction did not proceed under dark condition (Entry 4 in Table 4) and the previous report^[6d] support that photo-induce decarbonylation is required for the catalysis. Subsequently, Ru(V)-oxo species forms and the formed species reacts with styrene to generate a product and Ru(III)-OD complex. Further reaction of the complex with OD affords **A** to close the catalytic cycle. Note that the Ru(II)-porphyrin carbonyl is known to undergo epoxidation reaction with a Ru(V)/Ru(III) catalytic cycle in the presence of 2,6-dichloropyridine *N*-oxide as an oxidant.^[23]



Scheme 3. Proposed mechanism of styrene epoxidation with Ru(II)-porphyrin carbonyl complex and 2,6-dichloropyridine *N*-oxide.

Conclusion

In conclusion, the new microporous supramolecular framework catalyst (**[RuBPPy]_{FC}**) synthesised in this study via the self-assembly of Ru(II) porphyrins through non-covalent interactions between the pyrenylphenyl moieties at *meso*-positions of the porphyrin ring exhibits a highly ordered structure with micropores, as confirmed by SC-XRD and gas adsorption measurements. **[RuBPPy]_{FC}** catalyses the epoxidation of styrene in a heterogeneous system more efficiently than in a homogenous system with long-term stability. Notably, the heterogeneous nature of the framework catalyst affords reusability with almost no decrease in catalytic activity. These results suggest that heterogenization of molecular catalysts via self-assembly could be an effective strategy for enhancing catalytic performance. This is the first example of a Ru(II)–porphyrin-based framework catalyst exhibiting catalytic activity in the OAT reaction. The results presented herein offer a novel strategy for the construction of molecular heterogeneous catalytic systems for OAT reactions.

Experimental section

General procedures

Pyrrole, sodium borohydride, 1-methyl-2-pyrrolidone (NMP) and Triruthenium dodecacarbonyl ($\text{Ru}_3\text{CO}_{12}$) were purchased from Sigma-Aldrich Co., LLC. *p*-formylphenylboronic acid, tripotassium phosphate bis(triphenylphosphine)palladium(II) dichloride, diethyl ether, ferrocene, trifluoroacetic acid (TFA), 1,2,4-trichlorobenzene, hydrogen peroxide, sodium carbonate, sodium sulfate, hexane, cyclohexane, benzene and Chloroform- d_1 (CDCl_3) were purchased from Wako Pure Chemical Industries, Ltd. Methanol, chloroform (CHCl_3), tetrahydrofuran (THF), *o*-dichlorobenzene (*o*-DCB), acetonitrile (MeCN), ethanol and acetone were purchased from Kanto Chemical Co., Inc. 2-bromo-7-tert-butylpyrene, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) and 2,6-dichloropyridine were purchased from Tokyo Chemical Industry Co., Ltd. All solvents and reagents are of the highest quality available and used as received. NMR spectra were collected at room temperature on a JEOL JNM-ECS400 spectrometer. Elemental analysis was performed on a J-SCIENCE LAB MICRO CORDER JM10 elemental analyzer. UV-visible spectra were recorded on a Shimadzu UV-3600 UV-vis-near-IR spectrophotometer. Diffuse-reflectance UV-visible spectrum was recorded on a Shimadzu UV-3600i Plus UV-vis-NIR spectrophotometer. A white standard of BaSO_4 was used as the reference for diffuse-reflectance spectroscopic measurements. FT-IR spectrum was recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer. Powder X-ray diffraction data were collected on a Rigaku MiniFlex600. The CO_2 adsorption isotherms at 195 K were measured using a BELSORP-max volumetric adsorption analyzer from MicrotracBEL Corp. The temperature was adjusted using a cryostatic temperature controller from ULVAC CRYOGENICS INC. The sample was dried under a dynamic vacuum at 373 K for 16 h prior to the measurement.

Synthesis

Synthesis of 4-(7-(tert-butyl)pyren-2-yl)benzaldehyde

4-(7-(tert-butyl)pyren-2-yl)benzaldehyde was synthesized as previously reported.^[13d] ¹H-NMR (400 MHz, CDCl₃) δ = 10.13 (s, 1H), 8.40 (s, 2H), 8.25 (s, 2H), 8.11 (s, 4H), 8.06 (s, 4H), 1.60 (s, 9H) ppm.

Synthesis of 5,10,15,20-tetrakis(4-(7-tert-butyl)pyren-2-yl)phenylporphyrin (HBPPy)

HBPPy was synthesized as previously reported.^[13e] ¹H-NMR (400 MHz, CDCl₃) δ = 9.10 (s, 8H), 8.74 (s, 8H), 8.48 (d, J = 8.0 Hz, 8H), 8.34 (d, J = 7.6 Hz, 8H), 8.29 (s, 8H), 8.25 (d, J = 9.2 Hz, 8H), 8.17 (d, J = 8.8 Hz, 8H), 1.63 (s, 36H), -2.55 (s, 2H) ppm. λ_{max} (CHCl₃)/nm 312 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 8600), 326 (13000), 342 (19000), 425 (600000), 519 (22000), 556 (17000), 593 (7500), 649 (7300).

Synthesis of aquacarbonyl{5,10,15,20-tetrakis(4-(7-tert-butyl)pyrene-2-yl)phenyl}porphyrinato}-ruthenium(II) (RuBPPy)

RuBPPy was synthesized by modifying a previous report.^[7d] A 50-mL schlenk was charged with 1,2,4-trichlorobenzene (10 mL), followed by degassing with argon for 15 min. After that, **HBPPy** (78.6 mg) was added to the degassed solution under argon. The reaction system was then purged continuously with argon and heated to 165 °C. 5 portions of Ru₃(CO)₁₂ (15.7 mg each, total 78.6 mg) were added to the reaction mixture (protected with argon flow) at a 15-minute interval. After the addition of the final portion, the mixture was allowed to stir for an extra 1 h. The reaction mixture was then cooled to room temperature and filtered to remove unreacted Ru₃(CO)₁₂. The filtrate was purified through silica gel column chromatography with CHCl₃. The eluent containing 1,2,4-trichlorobenzene was obtained and concentrated under vacuum. The red precipitate was obtained by pureeing the solution into MeCN (300 mL) and filtration. Recrystallization by the slow evaporation using an evaporator (40 °C, 285 hpa) of a mixed solvent of chloroform and acetonitrile (2:1) gave the dark red solid (52 mg, 60%). ¹H-NMR (400 MHz, CDCl₃) δ = 8.95 (s, 8H), 8.74 (s, 8H), 8.37-8.50 (m, 8H), 8.30-8.37 (m, 8H), 8.29 (s, 8H), 8.20-8.27 (m, 8H), 8.11-8.20 (d, J = 8.8 Hz, 8H), 1.63 (s, 36H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 149.36, 144.38, 141.70, 140.73, 138.32, 134.70, 132.18, 131.75, 131.18, 128.27, 127.67, 126.36, 124.21, 123.87, 123.02, 122.65, 121.91, 35.46, 32.13 ppm. Elemental analysis Calcd. for C₁₂₅H₉₄N₄O₂Ru · H₂O (**RuBPPy** · H₂O): C, 83.26%; H, 5.37%; N, 3.11%. Found: C, 83.08%; H, 5.44%; N, 3.20%. λ_{max} (CHCl₃)/nm 312 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 9900), 326 (14000), 342 (19000), 418 (350000), 532 (29000), 566 (8800).

Synthesis of 2,6-dichloropyridine *N*-oxide

2,6-dichloropyridine *N*-oxide was synthesized as previously reported.^[24] ¹H NMR (400 MHz, CDCl₃): δ = 7.12 (t, J = 8.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H) ppm.

Electrochemical measurement

Cyclic voltammetry was performed with a Bio-Logic-Science Instruments potentiostat interfaced to a computer with SP-50 software, at room temperature under Ar using a one-compartment cell with a standard three-electrode configuration, which consisted of a glassy carbon disk (diameter 3 mm, BAS Inc.), a Ag/Ag⁺ couple, and a platinum wire as the working, reference and auxiliary electrodes, respectively. The working electrode was treated between scans using polishing with 0.05 μm alumina paste (BAS Inc.) and washing with purified H₂O. Ferrocene was used as an internal standard, and all potentials reported within this work are referenced to the ferrocenium/ferrocene couple at 0 V.

Single-crystal X-ray structural analysis

Single crystal X-ray diffraction data were collected on a Synergy Custom system CCD Plate equipped with confocal monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) coated with Paratone-N (Hampton Research Corp., Aliso Viejo, CA, USA). Data was processed using CrysAlisPro system software.^[25] The structures were solved by a dual-space algorithm using SHELXT program^[26] through the Olex2 interface.^[27] All non-hydrogen atoms were refined anisotropically using a least-squares method, and hydrogen atoms were fixed at calculated positions and refined using a riding model. SHELXL-2014/7 was used for structure refinement.^[28] Full-matrix least-squares refinements on F^2 based on unique reflections with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ($I > 2.00 \sigma(I)$) and $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ were performed. *PLATON-SQUEEZE*^[29] was performed for **[RuBPPy]_{as-syn}** and, 121 electrons were found per unit cell. This is consistent with the presence of one CHCl₃ molecule per asymmetric unit which accounts for 116 electrons per unit cell. Mercury 4.2.0 was used for visualization and analysis of the structure. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 2368114 for **[RuBPPy]_{FC}** and 2368115 for **[RuBPPy]_{as-syn}**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Photochemical epoxidation of styrene

For the typical run, 5.0% benzene in cyclohexane (2.0 mL) solution containing 43 mM styrene was added to **[RuBPPy]_{FC}** (260 µg, 0.14 µmol) and 2,6-dichloropyridine *N*-oxide (2.30 mg, 14 µmol) in 9 mL glass vial in a glove box. The vial was sealed, and the solution was sonicated for 1 minute. Then, the solution was irradiated with a 300 W Xe lamp equipped with a 400 nm long pass filter (Edmund Industrial Optics) to produce the light in the range of $400\text{ nm} \leq \lambda$ at 20 °C in a custom-made aluminium box with the cooling system (Fig. 13). After stopping the reaction, 1.0 µL chlorobenzene was added as the internal standard and **[RuBPPy]_{FC}** was filtered. The filtrate was used for quantification of the amount of styrene oxide by a Shimadzu GC–2014 with a FID detector equipped with a capillary column (Rtx®-1701). Calibration curves were obtained by sampling known amounts of styrene oxide. In these experiments, the mixed solvent, 5.0% benzene in cyclohexane, was used due to following three reasons; (1) the dielectric constants of these solvents are similar with each other (2.3 for benzene and 2.0 for cyclohexane), (2) **[RuBPPy]_{FC}** is insoluble and can disperse well in cyclohexane, and (3) the oxidant, 2,6-dichloropyridine *N*-oxide, is soluble in benzene and less soluble in cyclohexane.

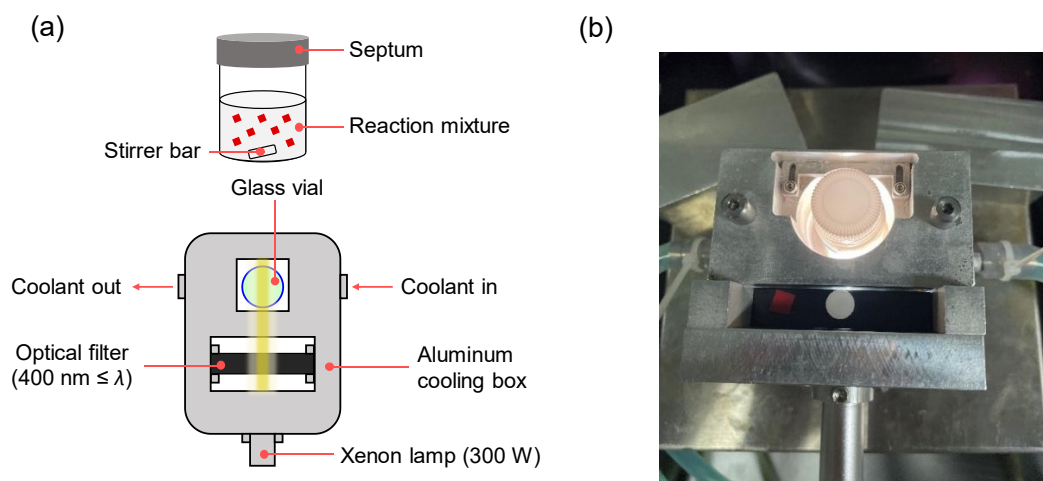


Fig. 13. Custom-made photoreactor. Schematic illustration (a) and a photograph (b) are shown. The coolant was set to 20 °C to maintain a constant sample temperature during measurement.

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Chapter 2

Mn–porphyrin-based supramolecular framework catalyst for Mukaiyama-type epoxidation

Introduction

Epoxidation reactions play a vital role in the chemical industry owing to the extensive utilization of epoxides in polymers, pharmaceuticals, and agrochemicals.^[1–3] In general, two categories of catalysts facilitate epoxidation reactions: heterogeneous and molecule-based homogeneous catalysts. Heterogeneous catalysts offer advantages such as high durability and recyclability.^[4,5] On the other hand, molecule-based homogeneous catalysts allow for the fine-tuning of reactivity and selectivity through structural modifications at the molecular level.^[6–8] Consequently, molecule-based heterogeneous catalysts present a compelling option as they allow the integration of both heterogeneous and molecule-based homogeneous catalysts.

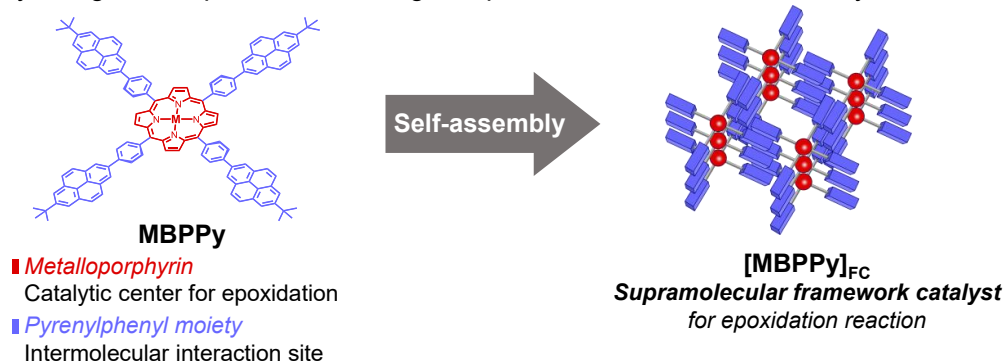
In this context, the use of porous crystalline frameworks constructed from metal complex-based catalysts is a promising approach for developing molecule-based heterogeneous catalysts, as seen in metal–organic frameworks (MOFs)^[9–11] and covalent organic frameworks (COFs).^[12–14] These materials offer precisely tuned reactivity and selectivity derived from well-defined molecular catalytic centers and durability and recyclability owing to their heterogeneous nature. Furthermore, their porous structure aids in substrate accumulation and enhancing reaction rates, and the immobilization of catalytic centers in the structure helps prevent deactivation. Thus far, various types of porous crystalline frameworks for epoxidation reactions have been extensively researched, showing enhanced catalytic activity, size selectivity, durability, and recyclability compared to homogeneous counterparts.^[15–17] Common oxidants for epoxidation reactions using porous crystalline frameworks include iodosylbenzene and *tert*-butyl hydroperoxide, which generate harmful organic waste. From both environmental and economic standpoints, utilizing molecular oxygen (O₂) under ambient conditions is highly promising due to its low cost, abundance, and production of only water as a byproduct.^[18] To utilize O₂ as an oxygen source, a Mukaiyama-type catalytic epoxidation system that combines a metal complex with an aldehyde as a co-reductant is an attractive approach.^[19,20] In addition, to enhance the sustainability of these oxidation systems, utilization of earth-abundant transition metals like Fe, Mn, and Cu as catalytic centers is desirable. While aerobic epoxidation systems based on MOFs and COFs incorporating these metal ions under mild conditions have been documented,^[21–31] further enhancements in catalytic efficiency are necessary. Thus, developing porous crystalline frameworks with earth-abundant metal centers for highly efficient aerobic epoxidation under mild conditions remains a challenge.

Recently, we developed a novel Ru–porphyrin-based supramolecular framework catalyst for

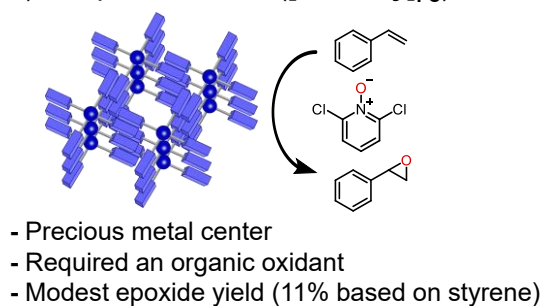
styrene epoxidation, utilizing our original concept of constructing a porous crystalline framework (Figs. 1a and 1b).^[32] This concept involves the formation of a supramolecular framework catalyst through the self-assembly of discrete catalyst modules, that have a metal-complex catalytic center and specific intermolecular interaction sites.^[33–38] This material retains catalytically active metal centers and enables the expression of catalytic functions utilizing its inherent porosity. The self-assembly of a catalyst module, a Ru(II)–porphyrin complex with pyrenylphenyl moieties at the *meso*-positions, aquacarbonyl{5,10,15,20-tetrakis(4-(7-*tert*-butyl)pyrene-2-yl)phenyl} porphyrinato} ruthenium(II) (**RuBPPy**), produced a Ru–porphyrin-based supramolecular framework catalyst, **[RuBPPy]_{FC}**. Evaluation of the catalytic activity revealed that **[RuBPPy]_{FC}** catalyzes the epoxidation of styrene more efficiently in a heterogeneous system compared to a homogenous system, demonstrating long-term stability and recyclability. However, this system poses challenges for sustainable chemistry due to its reliance on a precious metal center, the need for an organic oxidant, and its modest catalytic activity.

In this work, I report the development of a new Mn–porphyrin-based supramolecular framework catalyst with intermolecular interactions for Mukaiyama-type alkene epoxidation using O₂ as an oxidant under ambient conditions (Fig. 1c). Manganese is a promising catalytic center due to its abundance, low toxicity, and capacity to generate reactive Mn-oxo species for epoxidation reactions.^[39] Moreover, Mn–porphyrins are highly effective catalytic centers for aerobic epoxidation reactions within the metalloporphyrin family.^[40,41] Therefore, I utilized a Mn(III)–porphyrin complex with pyrenylphenyl moieties at the *meso*-position, chloro{(5,10,15,20-tetrakis(4-(7-*tert*-butyl)pyrene-2-yl)phenyl)porphyrinato} manganese (III) (**MnBPPy**) as a catalyst module. The self-assembly of **MnBPPy** through intermolecular interactions produced the supramolecular framework catalyst (**[MnBPPy]_{FC}**). **[MnBPPy]_{FC}** exhibited superior performance in the Mukaiyama-type epoxidation of styrene using isobutyraldehyde (IBA) as a co-reductant, achieving a higher yield of styrene oxide compared to its Ru-based counterpart, **[RuBPPy]_{FC}**. This Mn–porphyrin-based supramolecular framework showcased enhanced catalytic activity and improved sustainability by incorporating an earth-abundant metal center and utilizing O₂ as a green oxidant, surpassing the catalytic efficiency of the previously reported **[RuBPPy]_{FC}**. Moreover, the turnover frequency (TOF) and production rate of **[MnBPPy]_{FC}** surpassed those of other relevant porous crystalline frameworks incorporating earth-abundant metals documented to date.

a) Key design concept of constructing a supramolecular framework catalyst



b) Our previous work ([RuBPPy]_{FC})



c) This work ([MnBPPy]_{FC})

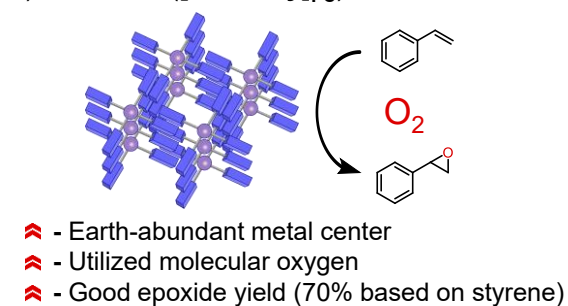
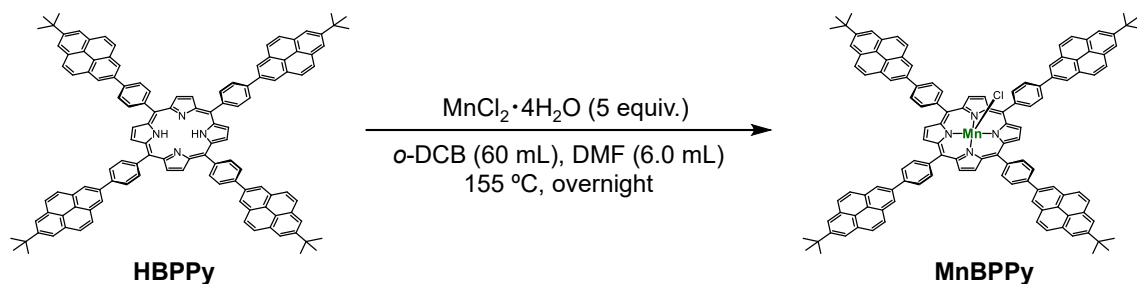


Fig. 1 (a) Key design concept of constructing a supramolecular framework catalyst, (b) our previous work, and (c) this work.

Results and discussion

Synthesis and characterization of MnBPPy

For the synthesis of **MnBPPy**, the free-base porphyrin 5,10,15,20-tetrakis(4-(7-tert-butyl)pyrene-2-yl)phenyl porphyrin (**HBPPy**), synthesized following a previously reported procedure,^[34] reacted with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in a mixture of *o*-dichlorobenzene (*o*-DCB) and *N,N*-dimethylformamide (DMF) at 155 °C overnight (Scheme 1). Formation of **MnBPPy** was confirmed by ultraviolet–visible (UV–vis) absorption spectroscopy (Fig. 2). The UV–vis absorption spectrum of **MnBPPy** displayed π – π^* transition bands corresponding to the pyrene moieties at 312, 327, and 342 nm,^[34] a Soret band corresponding to the porphyrin moiety at 481 nm, and Q-bands corresponding to the porphyrin moiety at 586 and 624 nm. A red shift of the Soret band and a decrease in the number of Q-bands in the **MnBPPy** spectrum compared to **HBPPy** indicated Mn-ion insertion into the porphyrin ring. Elemental analysis validated product. These results indicated that **MnBPPy** was successfully synthesized.



Scheme 1. Synthetic scheme for **MnBPPy**.

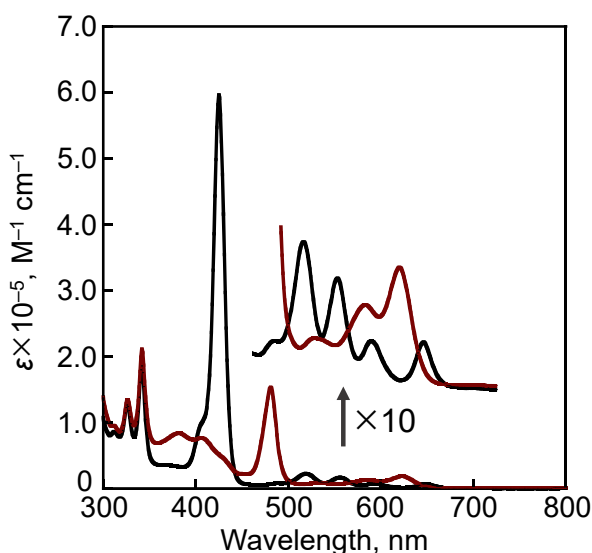


Fig. 2. UV–vis absorption spectra of **HBPPy** (black) and **MnBPPy** (green) in CHCl_3 .

Synthesis and characterization of [MnBPPy]_{FC}

Subsequently, I investigated the formation of a supramolecular framework catalyst via the self-assembly of **MnBPPy**. Single crystals suitable for single-crystal X-ray diffraction (SC-XRD) analysis were obtained by diffusing acetonitrile (MeCN) into an *o*-DCB solution of **MnBPPy**. The SC-XRD analysis revealed that the self-assembled **MnBPPy** formed a supramolecular framework in a triclinic system with the *P*-1 space group. Fig. 3a and Table 1 feature an Oak Ridge Thermal Ellipsoid Program (ORTEP) drawing and a summary of the crystallographic data of [MnBPPy]_{FC}, respectively. The packing structure of [MnBPPy]_{FC} consists of a 1D columnar structure stabilized by CH– π interactions between the pyrenylphenyl rings along the *a* axis (Fig. 3b). Additionally, CH– π interactions between the pyrenylphenyl moieties further stabilize the structure (Fig. 3c), leading to the creation of a porous framework (Fig. 3d). The interactions along the *a* axis in [MnBPPy]_{FC} resemble those in a previously reported Ru–porphyrin-based supramolecular framework ([RuBPPy]_{FC}),³² while the interactions in the *b,c* plane are different: CH– π interactions were observed in [MnBPPy]_{FC}, while π – π interactions were observed in [RuBPPy]_{FC}. Based on the van der Waals radii of the atoms involved, the estimated pore entrance size is $5.82 \times 3.55 \text{ \AA}^2$ for [MnBPPy]_{FC}, which is larger than that of [RuBPPy]_{FC} ($4.8 \times 2.8 \text{ \AA}^2$). In addition, the accessibility of styrene and IBA to the pore channels was evaluated by comparing the pore size with their molecular sizes estimated from quantum chemical calculations (Fig. 4). The comparable dimensions indicate that both molecules can diffuse into the channel (Fig. 5). These findings highlight the utility of pyrenylphenyl moieties in constructing supramolecular framework structures.

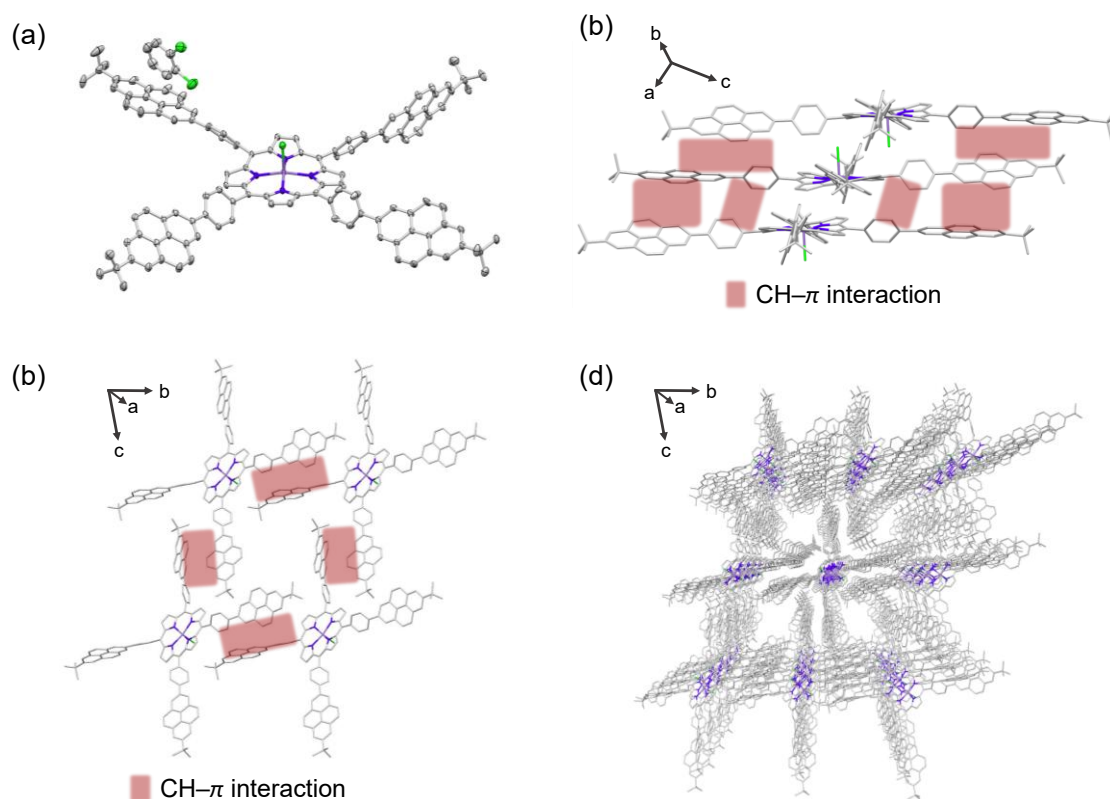


Fig. 3. (a) An ORTEP drawing of **MnBPPy** (50% probability ellipsoids). Hydrogen atoms and disordered atoms are omitted for clarity. Carbon is represented in gray, nitrogen in blue, oxygen in red, manganese in purple, and chlorine in green. (b) 1D columnar structure of **[MnBPPy]_{FC}** along the *a* axis. (c) Intercolumnar interactions observed in **[MnBPPy]_{FC}** along the *b* and *c* axes. (d) Packing structure of **[MnBPPy]_{FC}**. Crystal solvents are omitted for clarify in (b–d).

Table 1. Summary of crystallographic data for [MnBPPy]_{FC}.

formula	C ₁₃₀ H ₉₆ Cl ₃ N ₄ Mn
formula weight	1875.39
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> , Å	13.2456(2)
<i>b</i> , Å	18.5816(4)
<i>c</i> , Å	21.7249(3)
<i>α</i> , deg	105.068(2)
<i>β</i> , deg	90.5710(10)
<i>γ</i> , deg	95.392(2)
<i>V</i> , Å ³	5131.76(16)
<i>Z</i>	2
ρ_{calc} , g/cm ³	1.214
<i>F</i> (000)	1960.0
MoK α , cm ⁻¹	0.71073
<i>T</i> , K	123
2 θ_{max} , deg	62.666
reflns measd	85186
uniq reflns	28014
<i>R</i> (int)	0.0600
data/restraints/params	28014/22/1285
<i>R</i> ₁	0.0714
w <i>R</i> ₂	0.1894
<i>GOF</i>	1.043

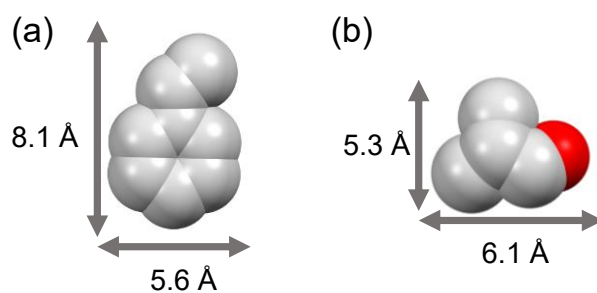


Fig. 4. Molecular size of (a) styrene and (b) IBA estimated based on their van der Waals radii using quantum chemical calculations.

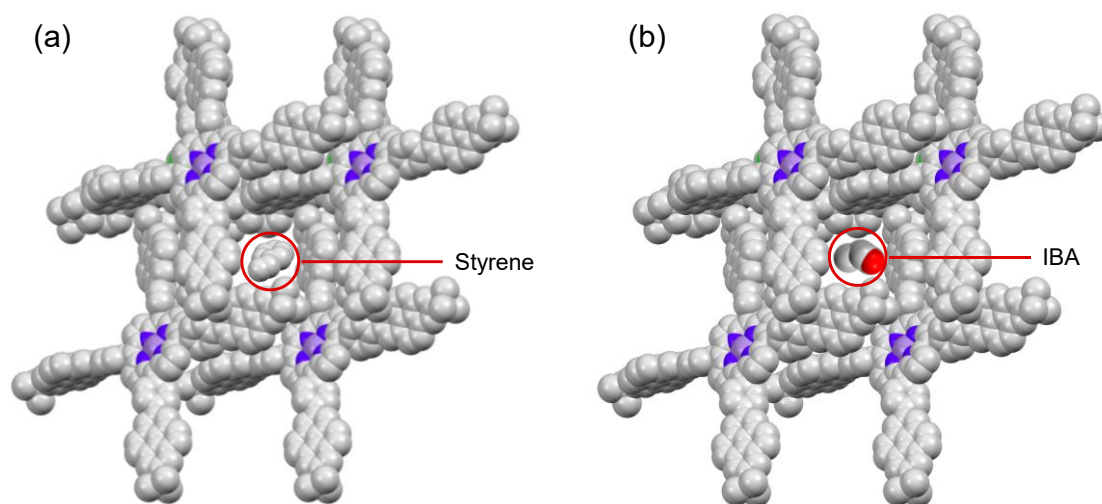


Fig. 5. Illustration of the pore structure and the inclusion of (a) styrene and (b) IBA.

To acquire a bulk sample of $[\text{MnBPPy}]_{\text{FC}}$, a solution of MnBPPy in a mixed solvent comprising chloroform (CHCl_3) and MeCN (2:1, v/v) was gradually evaporated. The resulting precipitate underwent filtration and vacuum drying at 70 °C for 1 h to yield the crystalline solid. The powder X-ray diffraction (PXRD) pattern of $[\text{MnBPPy}]_{\text{FC}}$ closely matched the simulated pattern calculated using SC-XRD data of $[\text{MnBPPy}]_{\text{FC}}$. It showed the three strong peaks assigned as the diffraction from (001), (010) and (01-1) respectively at 4° – 7° (Fig. 6, black), which were shifted slightly compared with simulated peaks calculated using single-crystal diffraction data of $[\text{MnBPPy}]_{\text{FC}}$ (Fig. 6, blue). Tuning the cell parameter of single-crystal diffraction data (b ; 18.5816 $\rightarrow$ 17.71, c ; 21.7249 $\rightarrow$ 21.18, α ; 105.068 $\rightarrow$ 101.7) gave the pattern that matched the experimental pattern (Fig. 6, red and Table 2). The pore size was also reduced from 5.82 Å $\times$ 3.55 Å to 5.75 Å $\times$ 3.38 Å. These changes are considered to be due to the removal of crystal solvents. This observation is supported also by the elemental analysis and thermogravimetric analysis (TGA). The elemental analysis of $[\text{MnBPPy}]_{\text{FC}}$ indicated a match between the experimental result and $\text{MnBPPy} \cdot 3\text{H}_2\text{O}$, suggesting the absence of crystal solvents such as CHCl_3 and MeCN in $[\text{MnBPPy}]_{\text{FC}}$. TGA of $[\text{MnBPPy}]_{\text{FC}}$ revealed no significant weight loss associated with the removal of guest molecules (Fig. 7). These findings suggest that $[\text{MnBPPy}]_{\text{FC}}$ maintained its framework structure upon guest-molecule removal.

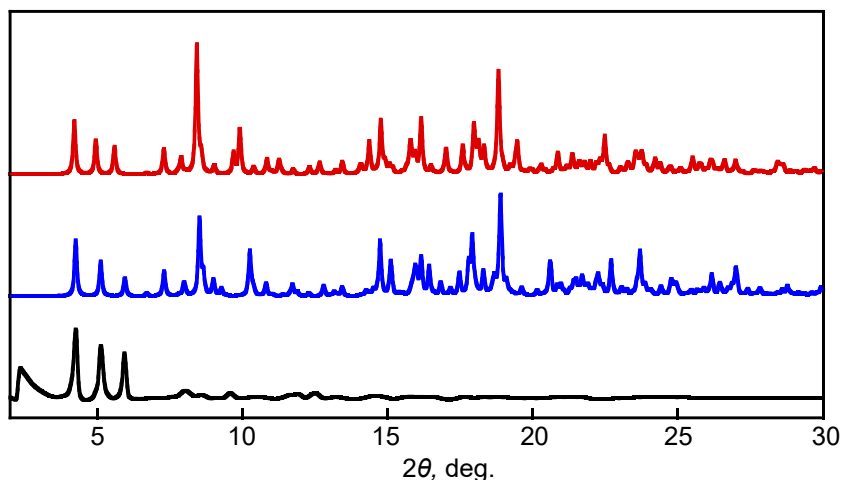


Fig. 6. Experimental (black), simulated PXRD patterns from crystal structure (red) and modified pattern from the simulated pattern (blue) for $[\text{MnBPPy}]_{\text{FC}}$.

Table 2. Summary of cell parameters and Miller index of the crystalline powder, $[\text{MnBPPy}]_{\text{FC}}$ (Exp.), the single crystal (Sim.) and modified crystal structure from $[\text{MnBPPy}]_{\text{FC}}$ (Modified).

	a	b	c	α	β	γ	(001)	(010)	(01-1)
Exp.							4.26	5.12	5.95
Sim.	13.2456	18.5816	21.7249	105.068	90.571	95.932	4.20	4.95	5.59
Modified	13.2456	17.71	21.18	101.7	90.571	95.932	4.26	5.12	5.95

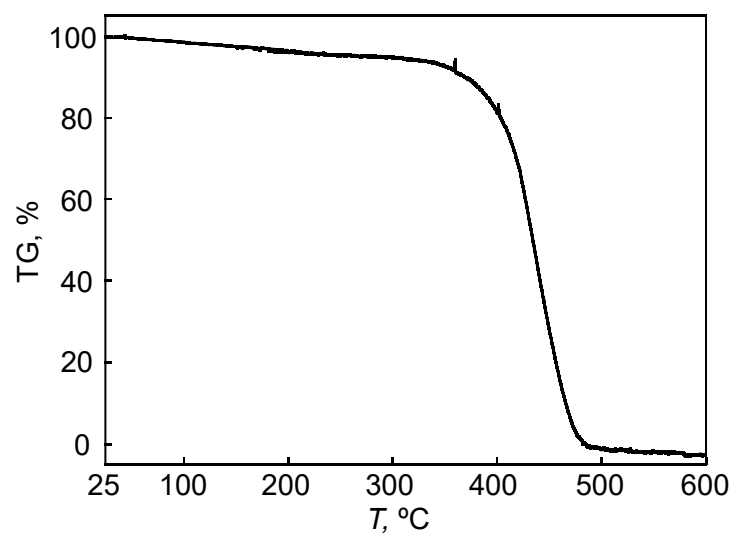


Fig. 7. TGA curve of [MnBPPy]_{FC} within 25–600 °C under N₂.

Further characterization of **[MnBPPy]_{FC}** was carried out using diffuse reflectance spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, and TGA. The diffuse reflectance spectrum of **[MnBPPy]_{FC}** contained characteristic absorption bands at 344 nm corresponding to the pyrene moieties, a Soret band at 486 nm, and Q-bands at 595 and 641 nm associated with the Mn–porphyrin moiety (Fig. 8), similar to the absorption bands of **MnBPPy** in the solution state (*vide supra*). The FT-IR spectrum of **[MnBPPy]_{FC}** displays a Mn–N vibration band at 1006 cm⁻¹ (Fig. 9).^[42] The TGA of the sample (dried at 70 °C for 1 h *in vacuo*) within 25–600 °C under N₂ flow with a heating rate of 2 °C min⁻¹ was used to investigate the thermal stability of **[MnBPPy]_{FC}**, exhibiting that **[MnBPPy]_{FC}** can be thermally stable up to 300 °C (Fig. 7). This framework is more thermally stable than **[RuBPPy]_{FC}**, which only remains stable up to 260 °C.^[32]

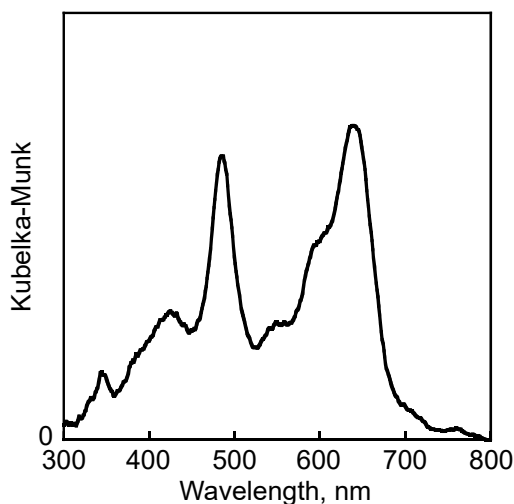


Fig. 8. Diffuse-reflectance UV–vis spectrum of **[MnBPPy]_{FC}**.

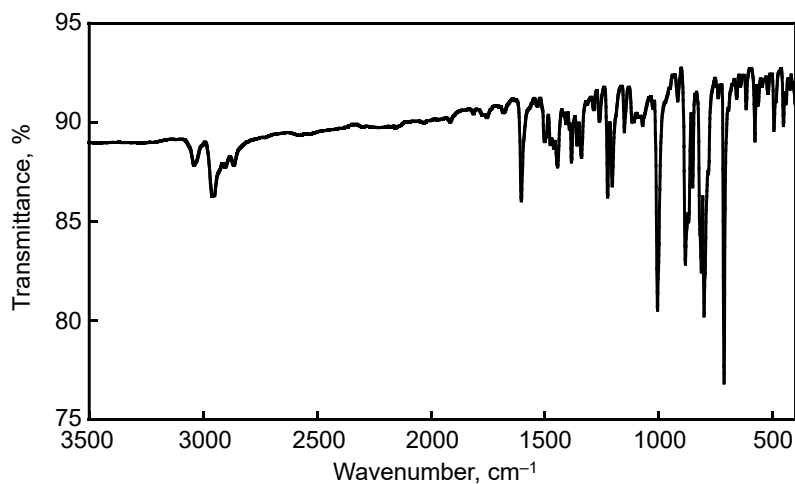


Fig. 9. FT-IR spectrum of **[MnBPPy]_{FC}**.

Mukaiyama-type epoxidation

The catalytic activity of the porous crystalline framework, **[MnBPPy]_{FC}**, in the Mukaiyama-type aerobic epoxidation of styrene was investigated. The optimization of reaction conditions was carried out for the Mukaiyama-type epoxidation of styrene using **[MnBPPy]_{FC}** as a heterogeneous catalyst. Reactions were performed in MeCN (5.0 mL) in the presence of styrene and IBA under O₂ using a balloon. First, reaction temperature was examined. Interestingly, the epoxide yield obtained at room temperature was higher than that at 60 °C (Table 3). The effects of the amounts of IBA, styrene, and the catalyst were also investigated. A large amount of IBA (4.0 mmol) was necessary for the reaction to proceed (Entries 1–3 in Table 4). Increasing the amount of styrene from 0.20 mmol to 1.0 mmol led to a higher epoxide yield (Entry 4 in Table 4). Moreover, increasing the catalyst loading from 0.10 mol% to 0.50 mol% further improved the epoxide yield. (Entry 5 in Table 4). Therefore, the optimal conditions for the epoxidation of styrene were determined to be room temperature, 1.0 mmol of styrene, 4.0 mmol of IBA, and 0.50 mol% of **[MnBPPy]_{FC}**.

Table 3. Investigation of reaction temperature for the epoxidation of styrene with O₂ and IBA in the presence of **[MnBPPy]_{FC}**.^a

Entry	Temperature, °C	Yield, %
1	RT	33
2	60	17

^aStandard reaction conditions: **[MnBPPy]_{FC}** (0.10 μmol), styrene (2.0 mmol), and IBA (5.0 mmol) in MeCN (5.0 mL) for 5 h under O₂ using a balloon. The product was identified by GC-FID. ^b5h

Table 4. Optimization of reaction conditions for the epoxidation of styrene with O₂ and IBA in the presence of [MnBPPy]_{FC}.^a

[MnBPPy]_{FC} IBA MeCN, O₂, 6 h				
Entry	IBA, mmol	Styrene, mmol	Catalyst loading, μmol	Yield, %
1	0.50	0.20	0.10	n.d.
2	1.25	0.50	0.10	n.d.
3	4.0	0.20	0.10	21
4	4.0	1.0	0.10	51
5 ^b	4.0	1.0	0.50	54

^aStandard reaction conditions: [MnBPPy]_{FC}, styrene, and IBA in MeCN (5.0 mL) at room temperature for 6 h under O₂ using a balloon. The product was identified by GC-FID. ^b5h

In the optimized condition, the aerobic oxidation of styrene afforded styrene oxide as the main product in 70% yield and benzaldehyde as a side product in 3.3% yield after 5 h (Entry 1 in Table 5, and Fig. 10). Other byproducts such as acetophenone and styrene glycol were not detected by ^1H NMR and GC-FID analysis. Control experiments performed in the absence of $[\text{MnBPPy}]_{\text{FC}}$ or IBA did not produce the epoxide (Entries 2 and 3 in Table 5). Similarly, conducting the reaction under an Ar atmosphere resulted in no epoxide formation (Entry 4 in Table 5). These results confirmed the necessity of all these elements in the target reaction. To confirm whether $[\text{MnBPPy}]_{\text{FC}}$ operated in the solid state, the reaction mixture was stirred in the presence of $[\text{MnBPPy}]_{\text{FC}}$, styrene, and IBA in MeCN for 2 h under an Ar atmosphere. The reaction mixture was then filtered, and the reaction was conducted under O_2 . Almost no catalyst was eluted from the UV-vis absorption spectrum (Fig. 11), and the filtrate produced no products. In addition, I conducted an ICP-AES measurement of post-reaction filtrate under the standard condition, and the amount of Mn species leached into the solution was found to be small (1.6 %). These results indicated that the catalytic activity originated from the solid-state catalyst. A recycling experiment was performed to evaluate the recyclability of $[\text{MnBPPy}]_{\text{FC}}$. After the aerobic epoxidation of styrene under standard conditions, the catalyst was recovered by filtration, washed with MeCN, and dried under vacuum at 70°C for 1 h. The recovered catalyst was reused under identical conditions, affording styrene oxide in a yield comparable to that obtained in the first cycle (Entries 5 and 6 in Table 5). These results demonstrate the recyclability and stability of $[\text{MnBPPy}]_{\text{FC}}$ as a heterogeneous catalyst.

Table 5. Epoxidation of styrene with O_2 and IBA in the presence of $[\text{MnBPPy}]_{\text{FC}}$.^a

Entry	Deviation from standard conditions	Yield, %
1	None	70
2	No $[\text{MnBPPy}]_{\text{FC}}$	0
3	No IBA	0
4	Under Ar	0
5	$[\text{MnBPPy}]_{\text{FC}}$	65 ^b
6	$[\text{MnBPPy}]_{\text{FC}}$	65 ^c
7	$[\text{RuBPPy}]_{\text{FC}}$ instead of $[\text{MnBPPy}]_{\text{FC}}$	2.5

^aStandard reaction conditions: $[\text{MnBPPy}]_{\text{FC}}$ (0.50 μmol), styrene (1.0 mmol), and IBA (4.0 mmol) in MeCN (5.0 mL) at room temperature for 5 h under O_2 using a balloon. The products were identified by ^1H NMR spectroscopy with 1,1,2,2-tetrachloroethane as the internal standard. ^bfirst cycle. ^csecond cycle.

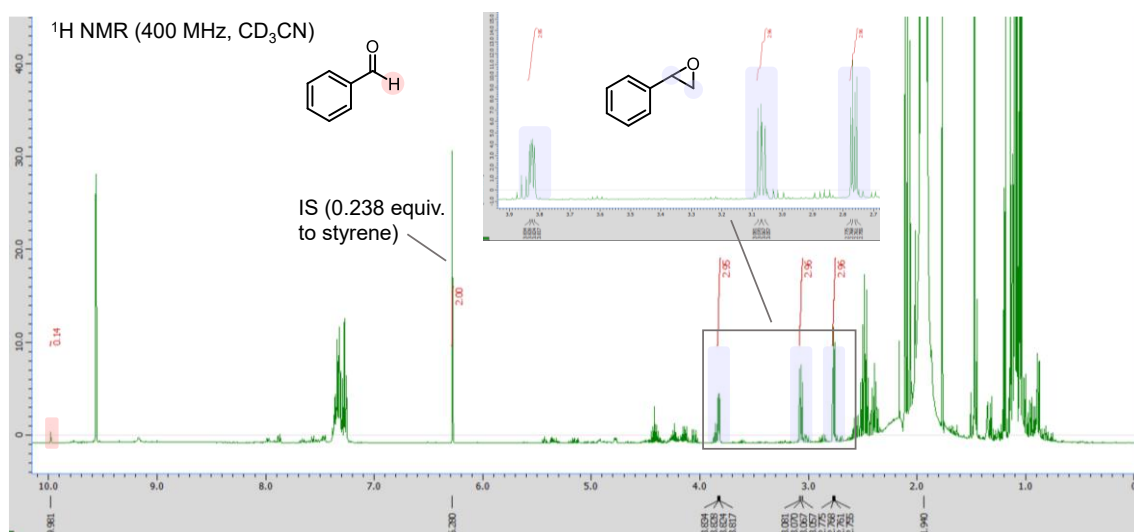


Fig. 10. ¹H NMR chart of epoxidation of styrene with O₂ and IBA in the presence of [MnBPPy]_{FC}.

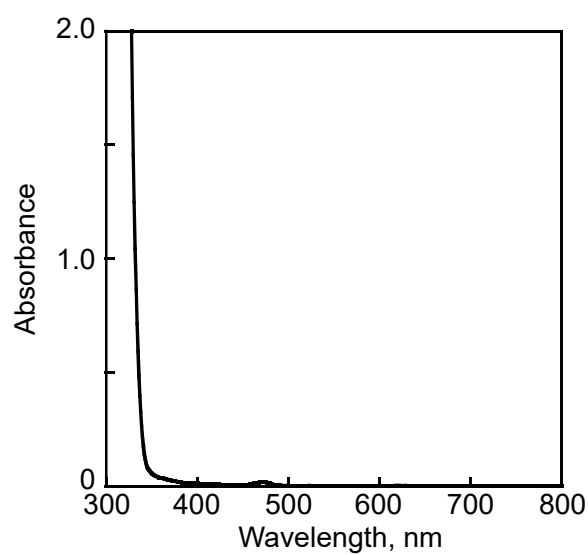
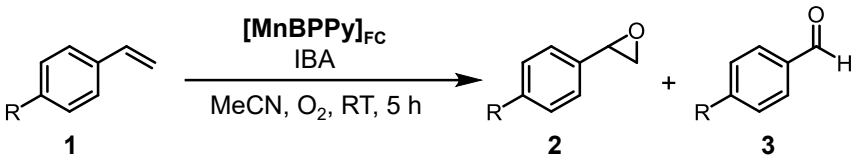


Fig. 11. UV-vis spectrum of the filtrate of reaction mixture stirred for 2 h under Ar.

To evaluate the substrate scope, the catalytic activities of *p*-substituted styrenes, *p*-chlorostyrene, and *p*-methylstyrene were investigated (Entries 2 and 3 in Table 6, and Figs. 12 and 13). The yield of *p*-chlorostyrene oxide was lower than that of non-substituted styrene because of the electrophilicity of the chloro-substituent, and the yield of *p*-methylstyrene oxide was comparable to that of non-substituted styrene oxide. Styrene derivatives bearing bulkier substituents, 4-*tert*-butylstyrene and *p*-phenylstyrene were also examined, and no inhibition of the reaction was observed even with substrates with bulky substituents (Entries 4 and 5 in Table 6, and Figs. 14 and 15).

Table 6. Epoxidation of styrene derivatives.

			
Entry	R	Yield of 2 , %	Yield of 3 , %
1	H	70	3.3
2	Cl	57	0.99
3	Me	73	3.0
4 ^b	^t Bu	77	3.0
5 ^b	Ph	86	5.2

Standard reaction conditions: **[MnBPPy]_{FC}** (0.50 μmol), styrene (1.0 mmol), and IBA (4.0 mmol) in MeCN (5.0 mL) at room temperature for 5 h under O₂ using a balloon. Products were determined by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

^b**[MnBPPy]_{FC}** (0.10 μmol).

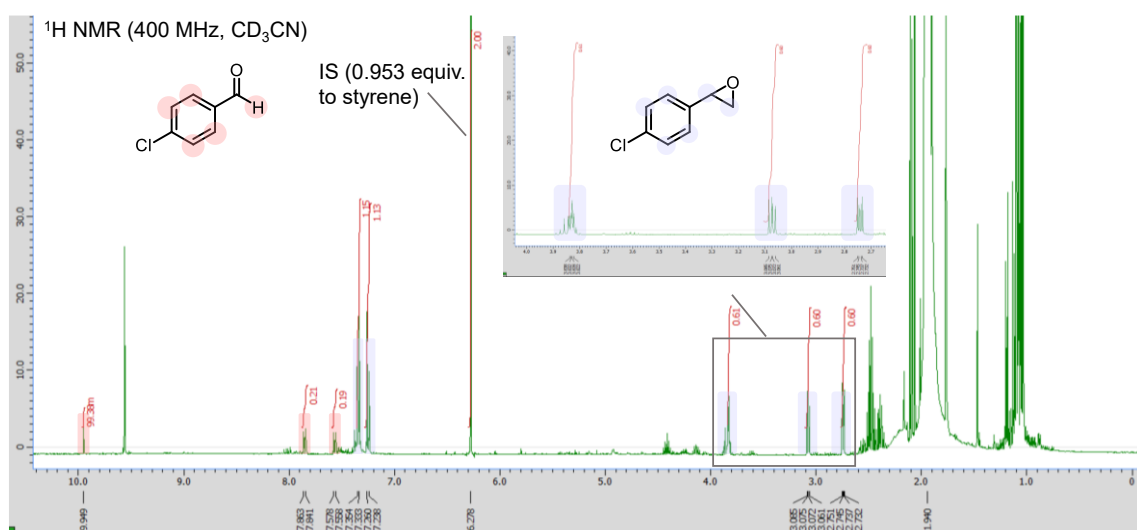


Fig. 12. ¹H NMR chart of Mukaiyama-type epoxidation of *p*-chlorostyrene with [MnBPPy]_{FC}.

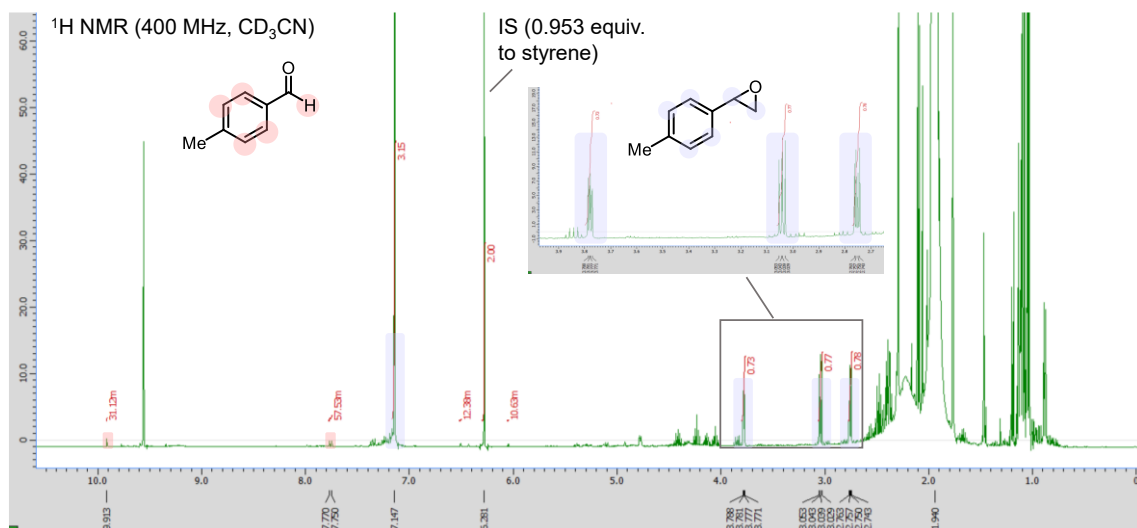
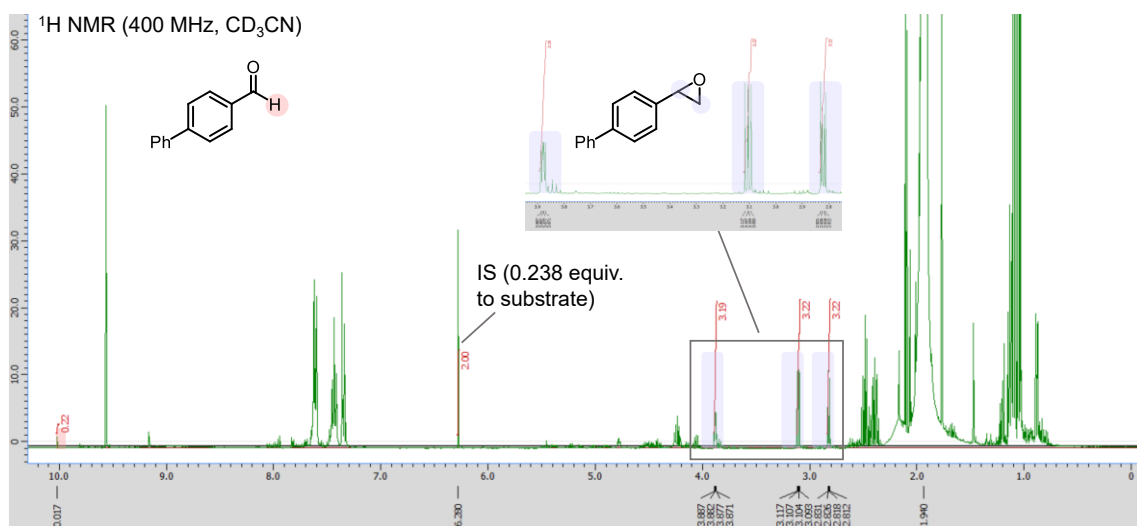
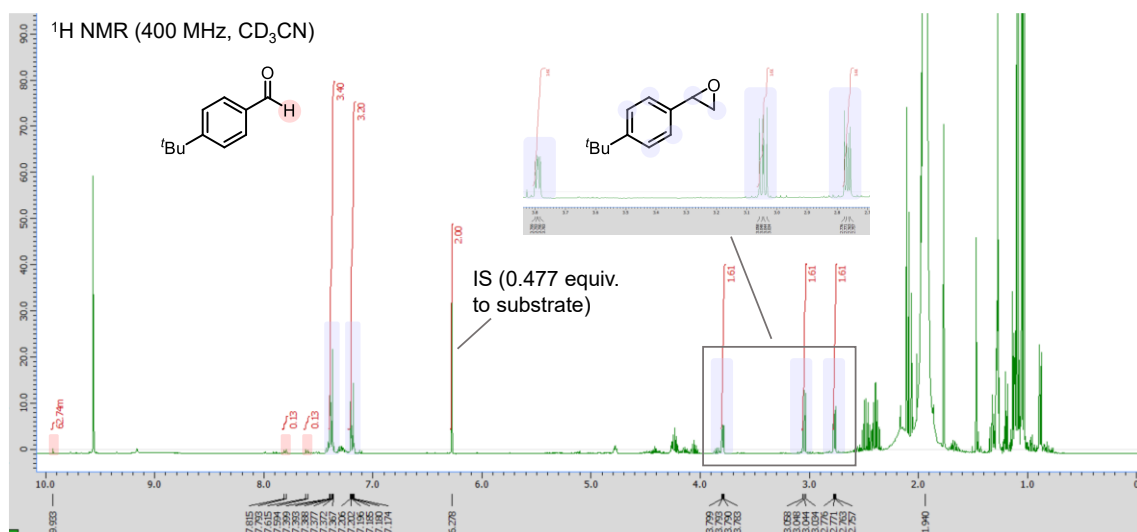


Fig. 13. ¹H NMR chart of Mukaiyama-type epoxidation of *p*-methylstyrene with [MnBPPy]_{FC}.



Mechanistic studies

Several attempts were made to unveil the reaction mechanism of our system. First, time-course analysis the reaction showed that the induction period was observed during the first 1 h of the reaction (Fig. 16). Similar results were also observed for Mukaiyama-type epoxidation reaction promoted by Mn-based complexes.^[43]

Subsequently, the possible contributions of homogeneous and heterogeneous pathways were examined. The ICP-AES measurements were conducted, and the amount of Mn species leached into the solution was found to be small (1.6 %), although the contribution of the dissolved molecules as a homogeneous catalyst cannot be quantified. Mukaiyama-type epoxidation reactions are known to proceed via two proposed pathways involving either Mn–oxo species or acylperoxy radicals as the active intermediates.^[43,44] Therefore, to explain the observed reactivity, I considered four plausible pathways involving the following active species: (i) heterogeneous Mn–oxo species, (ii) heterogeneous acylperoxy radical, (iii) homogeneous Mn–oxo species, and (iv) homogeneous acylperoxy radical.

Based on the experimental results obtained in this study, I attempted to discuss the plausible reaction mechanism. However, for the following reasons, I was unable to draw a definitive conclusion as to which of the above pathways (i–iv) is dominant. First, because a slight leaching of Mn species was detected, it is difficult to determine the relative contributions of homogeneous and heterogeneous catalysts in the reaction. Furthermore, the Hammett analysis was performed. The analysis gave a reaction constant (ρ) of -0.66 (Fig. 17). This value is intermediate between those obtained for the epoxidation of *p*-X-styrenes with MnTPPCl in the presence of IBA and O₂ ($\rho = -0.55$) and in the absence of the complex ($\rho = -0.73$).^[44] This result suggests both Mn–oxo complexes and acylperoxy radicals are involved the reaction, while the fact that the filtrate exhibited continued reactivity in the filtration test indicates that radical intermediates may also participate (Fig. 18).

In addition, the results of diastereoselectivities of the epoxidation of *cis*-olefins with our epoxidation system did not allow us to conclusively determine whether the active species is a Mn–oxo complex or an acylperoxy radical (Table 7, Figs.19 and 20).^[45,46] It should also be noted that previous reports on Mukaiyama-type epoxidation systems have pointed out the intrinsic difficulty in distinguishing between mechanisms involving Mn–oxo and radical pathways.^[43,44] For these reasons, determining a single dominant pathway for the present system is challenging at this stage. Future studies, including operando spectroscopic measurements, are planned to obtain deeper mechanistic insight.

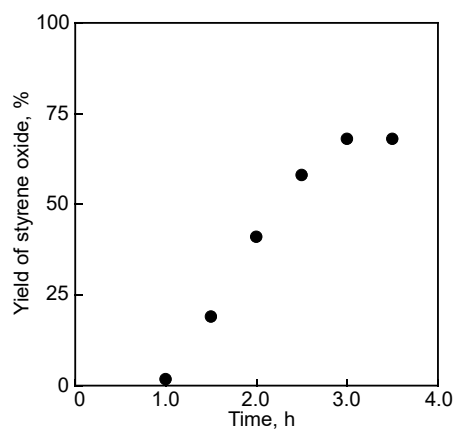


Fig. 16. Time course of epoxidation styrene with O₂ and IBA in the presence of [MnBPPy]_{FC}.

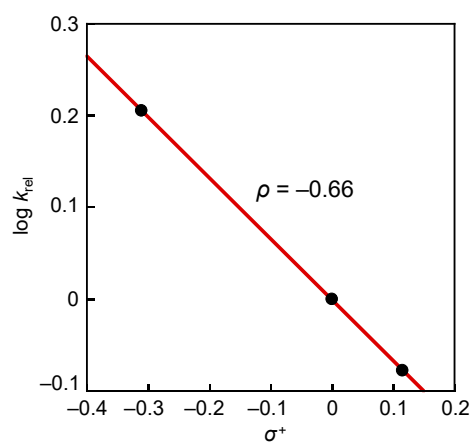


Fig. 17. Hammett plot for the relative rates of disappearance of *para*-substituted styrenes in the epoxidation of styrene with O₂ and IBA in the presence of [MnBPPy]_{FC}.

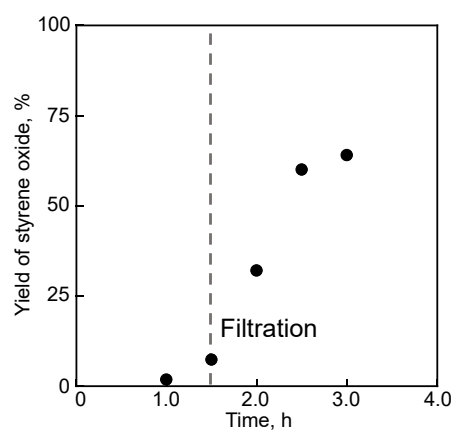


Fig. 18. Filtration test of epoxidation styrene with O₂ and IBA in the presence of [MnBPPy]_{FC}.

Table 7. Epoxidation of *cis*-alkenes with O₂ and IBA in the presence of [MnBPPy]_{FC}.^a

$ \begin{array}{c} \text{R}_1 \text{---} \text{CH} = \text{CH} \text{---} \text{R}_2 \\ \xrightarrow[\text{MeCN, O}_2, \text{RT, 5 h}]{\text{[MnBPPy]}_{\text{FC}}, \text{IBA}} \end{array} \rightarrow \begin{array}{c} \text{R}_1 \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{R}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array} + \begin{array}{c} \text{R}_1 \text{---} \text{CH} \text{---} \text{CH} \text{---} \text{R}_2 \\ \diagdown \quad \diagup \\ \text{O} \quad \text{O} \end{array} $				
$ \begin{array}{l} \text{1a: R}_1 = \text{Ph, R}_2 = \text{Me} \\ \text{1b: R}_1 = \text{Me, R}_2 = \text{n-Pr} \end{array} $				
$ \begin{array}{c} \text{cis-2} \qquad \qquad \text{trans-2} \end{array} $				
Substrate	Yield, %			
	<i>cis</i> -2	<i>trans</i> -2	Conv. of 1	<i>cis</i> -2: <i>trans</i> -2
1a	11	82	96	1.0 : 7.6
1b	31	34	73	1.0 : 1.1

^aStandard reaction conditions: [MnBPPy]_{FC} (0.50 μmol), *cis*-alkene (1.0 mmol), and IBA (4.0 mmol) in MeCN (5.0 mL) at room temperature for 5 h under O₂ using a balloon. The products were identified by ¹H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

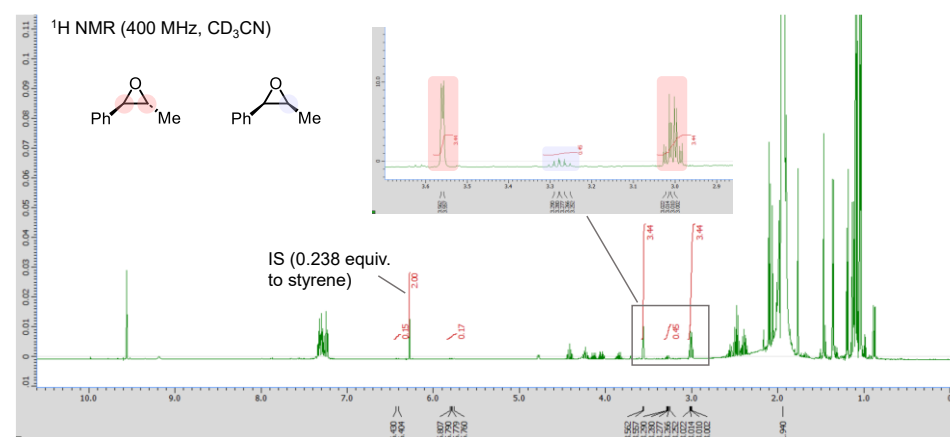


Fig. 19. ¹H NMR chart of Mukaiyama-type epoxidation of *cis*-β-methylstyrene with [MnBPPy]_{FC}.

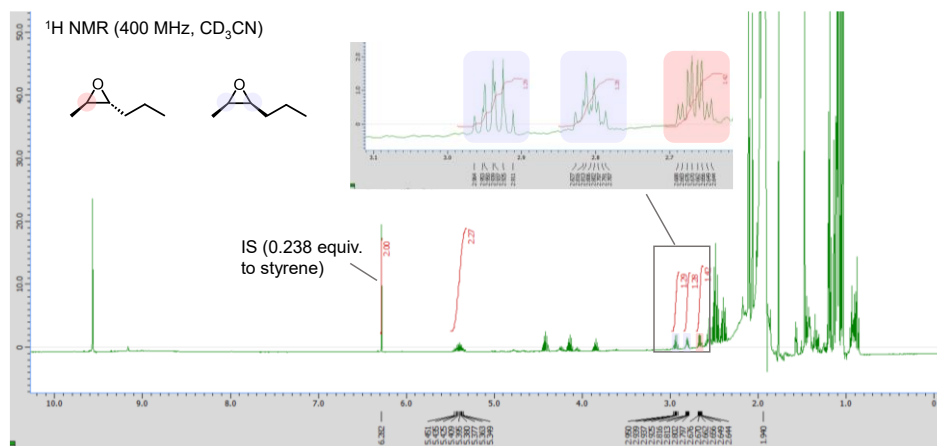


Fig. 20. ¹H NMR chart of Mukaiyama-type epoxidation of *cis*-2-hexene with [MnBPPy]_{FC}.

Comparison of catalytic activity with previous works

The catalytic activity of **[MnBPPy]_{FC}** for Mukaiyama-type epoxidation using was compared with previously reported systems, including our prior research and other molecule-based porous crystalline frameworks with earth-abundant metals. Specifically, **[MnBPPy]_{FC}** achieved a 70% yield of styrene oxide in the Mukaiyama-type epoxidation of styrene, surpassing the yield obtained with the Ru(II)–porphyrin-based supramolecular framework catalyst **[RuBPPy]_{FC}** (2.5%, Entry 2 in Table 8). It also outperformed the previously reported **[RuBPPy]_{FC}** epoxidation system combined with 2,6-dichloropyridine *N*-oxide, which yielded only 11% (Entry 3 in Table 8).^[32]

Beyond the **[RuBPPy]_{FC}**, **[MnBPPy]_{FC}** showed a TOF of 280 h^{−1} and a production rate of 160 mmol g^{−1} h^{−1} for styrene oxide through Mukaiyama-type epoxidation under mild conditions, surpassing all reported molecule-based porous crystalline solids with earth-abundant metal centers (Entries 2–9 in Table 9).^[47–50] Additionally, in the Mukaiyama-type epoxidation of other alkenes under mild conditions, **[MnBPPy]_{FC}** demonstrated the highest TOF and production rate among the catalysts (Entries 10–18, Table 9).^[51–57] These results collectively establish that **[MnBPPy]_{FC}** represents one of the most efficient porous crystalline frameworks for the Mukaiyama-type epoxidation of alkenes, particularly in systems incorporating earth-abundant metal centers.

Table 8. Comparison of catalytic activity of **[MnBPPy]_{FC}** with **[RuBPPy]_{FC}**.^a

Entry	Catalyst	Oxidant	Epoxide yield, %
1 ^a	[MnBPPy]_{FC}	O ₂	70
2 ^a	[RuBPPy]_{FC}	O ₂	2.5
3 ^b	[RuBPPy]_{FC}	2,6-dichloropyridine <i>N</i> -oxide	11

^aReaction conditions: Catalyst (0.50 μmol), styrene (1.0 mmol), and IBA (4.0 mmol) in MeCN (5.0 mL) at room temperature for 5 h under O₂ using a balloon. ^bReaction conditions: **[RuBPPy]_{FC}** (0.14 μmol), styrene (0.086 mmol), and 2,6-dichloropyridine *N*-oxide (0.014 mmol) in 5.0% benzene in cyclohexane (2.0 mL) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (400 nm ≤ λ, 300 W).

Table 9. Molecule-based porous crystalline solids featuring earth-abundant metal centers for Mukaiyama-type epoxidation of alkene under mild conditions.^a

Entry	Catalyst	Metal center	Substrate	TOF ^b , h ⁻¹	Production rate ^c , mmol g ⁻¹ h ⁻¹	Ref.
1	[MnBPPy] _{fc}	Mn	Styrene	280	160	This work
2	Zr-TCPP(Mn)	Mn	Styrene	53	— ^d	[47]
3	MOF-525-Mn	Mn	Styrene	— ^d	130	[48]
4	IRMOF-3[Mn]	Mn	Styrene	— ^d	4.7	[49]
5	Zr-TCPP(Fe)	Fe	Styrene	63	— ^d	[47]
6	MOF-253	Fe	Styrene	6.7	38	[50]
7	Zr-TCPP(Ni)	Ni	Styrene	18	— ^d	[47]
8	Zr-TCPP(Cu)	Cu	Styrene	30	— ^d	[47]
9	Zr-TCPP(Zn)	Zn	Styrene	8	— ^d	[47]
10	CuCl ₂ -UiO-67-BPY	Cu	Cyclohexene	25	— ^d	[51]
11	Ti ₈ -Cu ₂	Cu	Cyclohexene	21	6.1	[52]
12	Cu ²⁺ @COMOC-4	Cu	Cyclohexene	22	23	[53]
13	CuBDC	Cu	Cyclooctene	0.17	17	[54]
14	Cu-BTC	Cu	Cyclooctene	11	— ^d	[55]
15	MIL-101-SO ₃ @Cu-1	Cu	Cyclooctene	25	— ^d	[56]
16	Cu-MOF-1	Cu	Cyclooctene	— ^d	9.8	[57]
17	Cu-MOF-2	Cu	Cyclooctene	— ^d	9.8	[57]
18	Cu-MOF-3	Cu	Cyclooctene	— ^d	9.0	[57]

^aMolecule-based porous crystalline solids featuring earth-abundant metal centers (M = Mn, Fe, Ni, Zn, Cu) for Mukaiyama-type epoxidation under mild conditions are selected. Mild conditions are defined as below 40 °C and under O₂ at ambient pressure in this study. ^bTOF calculated by TON versus reaction time. ^cProduction rate calculated by amount of epoxide production versus amount of catalyst and reaction time. ^dCould not be calculated due to lack of information.

Conclusion

In conclusion, I developed a novel Mn–porphyrin-based supramolecular framework catalyst (**[MnBPPy]_{FC}**) for Mukaiyama-type aerobic epoxidation by self-assembling a pyrenylphenyl-functionalized Mn(III)–porphyrin complex via intermolecular interactions. Single crystal structural analysis of **[MnBPPy]_{FC}** revealed a porous framework structure formed by CH– π interactions between pyrenylphenyl moieties at *meso*-positions of the porphyrin ring. The porous crystalline framework, **[MnBPPy]_{FC}**, demonstrated excellent catalytic performance in the Mukaiyama-type epoxidation of styrene using O₂ and IBA, yielding 70% styrene oxide, significantly higher than with a previously reported Ru–porphyrin-based supramolecular framework catalyst (**[RuBPPy]_{FC}**). Furthermore, the TOF and production rate of **[MnBPPy]_{FC}** for styrene oxide in aerobic epoxidation under mild conditions exceeded those of previously reported porous crystalline frameworks with earth-abundant metals. These results highlight the effectiveness of recyclable porous crystalline frameworks created with molecular precision through intermolecular interactions. This study not only broadens the design approach for molecule-based heterogeneous catalysts but also advances sustainable oxidation chemistry by incorporating non-precious metals and environmentally friendly oxidants.

Experimental section

General procedures

Manganese(II) chloride tetrahydrate, DMF, hexane and chloroform-D (CDCl_3) were purchased from Wako Pure Chemical Industries, Ltd. Methanol, CHCl_3 , tetrahydrofuran (THF), *o*-DCB, and MeCN were purchased from Kanto Chemical Co., Inc. Styrene, *p*-chlorostyrene, *p*-methylstyrene, 4-*tert*-butylstyrene, *p*-phenylstyrene, *cis*- β -methylstyrene, *cis*-2-hexene, IBA, and acetonitrile-D (CD_3CN) were purchased from Tokyo Chemical Industry Co., Ltd. The free-base porphyrin, 5,10,15,20-tetrakis(4-(7-*tert*-butyl)pyren-2-yl)phenyl)porphyrin (**HBPPy**), and aquacarbonyl{5,10,15,20-tetrakis(4-(7-*tert*-butyl)pyrene-2-yl)phenyl) porphyrinato}-ruthenium(II) (**RuBPPy**) were synthesized as previously reported.^[32,34] All solvents and reagents were of high quality and used as received. NMR spectra were recorded at room temperature using a JEOL JNM-ECS400 spectrometer. Elemental analysis was conducted with a J-SCIENCE LAB MICRO CORDER JM10 elemental analyzer. UV-vis spectra and diffuse reflectance UV-vis spectra were measured using a Shimadzu UV-3600i Plus UV-vis-NIR spectrophotometer. A white standard of BaSO_4 served as the reference for diffuse reflectance spectroscopic measurements. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. PXRD data were collected with a Rigaku MiniFlex600 diffractometer. ICP-AES data was obtained with an ICPS-7510.

Synthesis of chloro{(5,10,15,20-tetrakis(4-(7-*tert*-butyl)-pyrene-2-yl)phenyl)-porphyrinato} manganese (III) (**MnBPPy**)

A solution of manganese(II) chloride tetrahydrate (18.1 mg, 0.91 mmol) in DMF (6 mL) was added to a solution of **HBPPy** (148 mg, 0.090 mmol) in *o*-DCB (60 mL). The mixture was heated at 155 °C overnight. The resulting mixture was poured into hexane (450 mL), and the precipitate was washed with MeCN and water to afford the desired product. Recrystallization in a mixed solvent of CHCl_3 (200 mL) and MeCN (80 mL) (2:1) by slow evaporation using reduced pressure (330 to 300 hPa) over several hours produced a dark-green solid (20 mg, 64% yield). Elemental analysis Calcd. for $\text{C}_{124}\text{H}_{92}\text{N}_4\text{ClMn} \cdot 3\text{H}_2\text{O}$ (**MnBPPy**· $3\text{H}_2\text{O}$): C, 83.55%; H, 5.54%; N, 3.14%. Found: C, 83.45%; H, 5.57%; N, 3.12%. UV-vis (in CHCl_3 , λ_{max} , nm): 312 (ϵ , $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 9300), 327 (13000), 342 (15000), 382 (8300), 406 (7600), 481 (210000), 586 (1300), 624 (1800).

Single-crystal X-ray structural analysis

Single crystal X-ray diffraction data were collected on a Synergy Custom system CCD Plate equipped with confocal monochromated Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) coated with Paraffin Liquid, High viscosity type (nacalai tesque). Data was processed using CrysAlisPro system software.^[58] The structures were solved by a dual-space algorithm using SHELXT program^[59] through the Olex2 interface.^[60] All non-hydrogen atoms were refined anisotropically using a least-squares method, and

hydrogen atoms were fixed at calculated positions and refined using a riding model. SHELXL-2014/7 was used for structure refinement.^[61] Full-matrix least-squares refinements on F^2 based on unique reflections with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ($I > 2.00 \sigma(I)$) and $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ were performed. *PLATON-SQUEEZE*^[62] was performed for **[MnBPPy]_{FC}** and, 135 electrons were found per unit cell. This is consistent with the presence of one *o*-dichlorobenzene molecule unit cell which accounts for 148 electrons per unit cell. Mercury 4.2.0 was used for visualization and analysis of the structure. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 2470143 for **[MnBPPy]_{FC}**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Mukaiyama-type epoxidation of alkenes

After 15 min of O₂ bubbling, alkenes (1.0 mmol) and IBA (4.0 mmol) were added to the catalyst dispersion (**[MnBPPy]_{FC}** = 0.50 μmol, MeCN = 5.0 mL). The reaction mixture was stirred at room temperature under O₂ using a balloon. Following the reaction, 1,1,2,2-tetrachloroethane was included as an internal standard, and the product yield was determined by ¹H NMR.

Recycle experiments

After 15 min of O₂ bubbling, alkenes (1.0 mmol) and IBA (4.0 mmol) were added to the catalyst dispersion (**[MnBPPy]_{FC}** = 0.50 μmol, MeCN = 5.0 mL). The reaction mixture was stirred for 5 h at room temperature under O₂ using a balloon. Following the reaction, 1,1,2,2-tetrachloroethane was included as an internal standard, and the product yield was determined by ¹H NMR. After the reaction, **[MnBPPy]_{FC}** was filtered, washed several times with acetonitrile, and dried at 70 °C for 1 h *in vacuo*. The filter paper containing **[MnBPPy]_{FC}** and MeCN (5.0 mL) were placed in a vial, and the catalyst dispersion was prepared by sonication for 15 min. After removing the filter paper, the reaction was carried out under the same procedure using the resulting catalyst dispersion.

Time-course analysis

After 15 min of O₂ bubbling, alkenes (1.0 mmol) and IBA (4.0 mmol) were added to the catalyst dispersion (**[MnBPPy]_{FC}** = 0.50 μmol, MeCN = 5.0 mL). The reaction mixture was stirred at room temperature under O₂ using a balloon. An aliquot of the reaction mixture was withdrawn by a syringe at each time point, added to a CD₃CN solution containing 1,1,2,2-tetrachloroethane as an internal standard, and the product yield was determined by ¹H NMR.

Hammett analysis

After 15 min of O₂ bubbling, styrene (0.50 mmol), substituted styrene (0.50 mmol) and IBA (4 mmol) were added to the catalyst dispersion (**[MnBPPy]_{FC}** = 0.50 μmol, MeCN = 5.0 mL). The reaction

mixture was stirred for 2 h at room temperature under O₂ using a balloon. Following the reaction, 1,1,2,2-tetrachloroethane was included as an internal standard, and the product yield was determined by ¹H NMR. The relative rates k_{rel} were determined by the Equation (1) in which Y_f and Y_i are the final and initial quantities of substituted styrene; H_f and H_i are the final and initial quantities of styrene.

$$k_{\text{rel}} = k_Y / k_H = \log(Y_f / Y_i) / \log(H_f / H_i) \quad (1)$$

The Hammett analysis gave a reaction constant (ρ) of -0.66 (Fig. S16). This value is intermediate between those obtained for the epoxidation of *p*-X-styrenes with MnTPPCl in the presence of IBA and O₂ ($\rho = -0.55$) and in the absence of the complex ($\rho = -0.73$),^[44] suggesting both Mn-oxo complexes and acylperoxy radicals are involved the reaction.

Filtration test

After 15 min of O₂ bubbling, alkenes (1.0 mmol) and IBA (4.0 mmol) were added to the catalyst dispersion ([MnBPPy]_{FC} = 0.50 μmol, MeCN = 5.0 mL). The reaction mixture was stirred for 1.5 h at room temperature under O₂ using a balloon. The mixture was then filtered, and the reaction continued with the filtrate after bubbling O₂ for 15 minutes. An aliquot of the reaction mixture was withdrawn by syringe at each time point, added to a CD₃CN solution containing 1,1,2,2-tetrachloroethane as an internal standard, and the product yield was determined by ¹H NMR.

Investigation of diastereoselectivity in the epoxidation of *cis*-alkenes

After 15 min of O₂ bubbling, *cis*-alkenes (1.0 mmol) and IBA (4.0 mmol) were added to the catalyst dispersion ([MnBPPy]_{FC} = 0.50 μmol, MeCN = 5.0 mL). The reaction mixture was stirred at room temperature under O₂ using a balloon. Following the reaction, 1,1,2,2-tetrachloroethane was included as an internal standard, and the product yield was determined by ¹H NMR.

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Chapter 3

Synthesis and photophysical properties of an Ir(III)–porphyrin-based supramolecular framework

Introduction

Solid-state molecular luminescent materials have attracted considerable attention because they provide stable and processable platforms for sensing, imaging, and optoelectronic applications.^[1–4] Among their various characteristics, narrowband emission is especially appealing due to its potential to enable high-resolution imaging and ultrahigh-definition display technologies.^[5–7] In the solid state, luminescence behavior is strongly governed by the molecular packing arrangement. When emissive molecules aggregate randomly or in a densely packed fashion, the emission band often becomes broadened and weakened (Fig. 1a).^[8,9] These effects arise from various excited-state interactions, including vibronic coupling, π – π stacking, excimer formation, and intermolecular charge-transfer processes, all of which facilitate undesired energy-dissipation pathways and reduce the spectral sharpness.^[10–12] Spatial isolation of emissive centers is a particularly promising concept to suppress such intermolecular interactions because it directly minimizes the influence of intermolecular interactions and can therefore yield intrinsically sharper emission bands (Fig. 1b).^[13,14] For example, emissive molecules bearing sterically demanding substituents that suppress intermolecular aggregation have been shown to exhibit sharper emission bands.^[15–18] In this context of isolating emissive centers, the supramolecular frameworks developed in our group offer a fundamentally different and highly attractive design approach.^[19–26] These frameworks are molecule-based porous materials constructed through the self-assembly of metal complexes via non-covalent interactions. They possess well-defined structures that spatially isolate substitutionally active metal centers. I have employed these frameworks as heterogeneous catalysts by leveraging their distinctive structural features and intrinsic porosity.^[21–26] However, the application of this supramolecular framework concept to luminescent materials has not yet been explored.

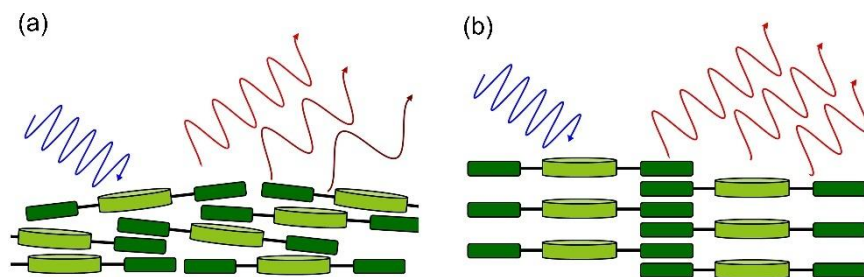
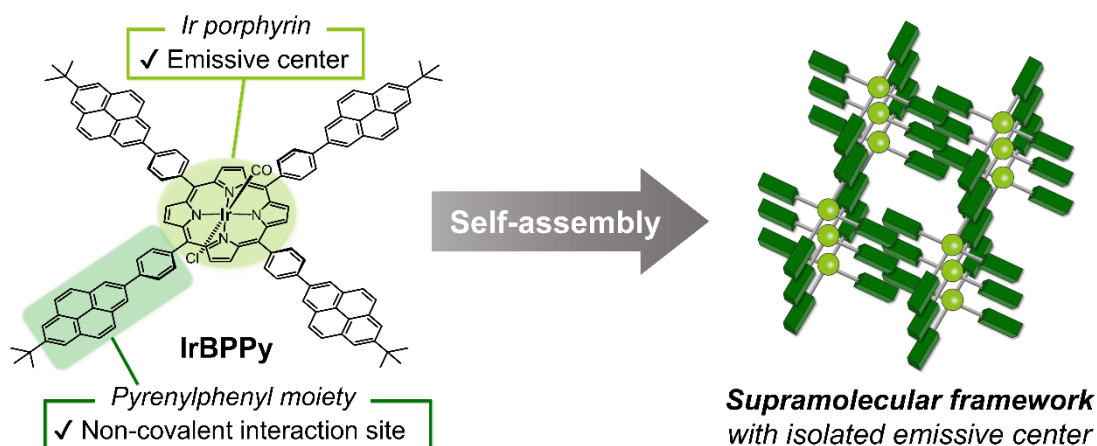


Fig. 1. Luminescence behavior in the solid state of emissive molecules in (a) a randomly aggregated state and (b) an ordered isolated state.

Herein, I report the development of a new type of luminescent material based on a supramolecular framework constructed through non-covalent interactions. The key to this design is the use of an Ir(III)–porphyrin complex as the molecular building unit. Ir(III)–porphyrin complexes exhibit unique photophysical features, especially strong phosphorescence at room temperature.^[27–31] Despite their intriguing luminescent properties, studies on Ir(III)–porphyrin complexes in the solid state remain limited.^[30,32] This is presumably due to the strong influence of π -stacking on their luminescence properties.^[33,34] Our strategy involves designing an Ir(III)–porphyrin complex bearing pyrenylphenyl moieties as non-covalent interaction sites that promote self-assembly, thereby forming an ordered framework structure (Scheme 1). The resulting supramolecular framework successfully integrates isolated emissive Ir–porphyrin units within an extended crystalline structure and exhibits a narrower full width at half maximum (FWHM) of the emission bands compared to its amorphous counterpart, demonstrating that isolation of emission center within a supramolecular framework is effective.

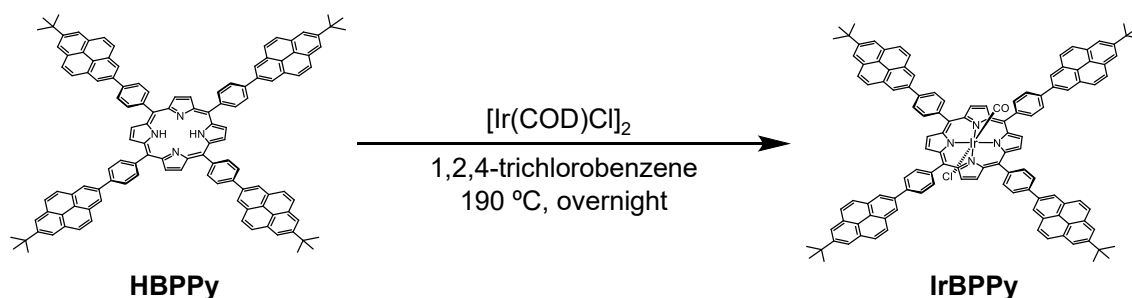


Scheme 1. Schematics of the structure and features of the new Ir(III)-porphyrin complex (**IrBPPy**) developed in this work and supramolecular framework construction strategy.

Results and discussion

Synthesis and characterization of IrBPPy

For the synthesis of **IrBPPy**, the free-base porphyrin 5,10,15,20-tetrakis(4-(7-tert-butyl)pyrene-2-yl)phenyl porphyrin (**HBPPy**), was first synthesized by following a previously reported procedure.^[23] **HBPPy** was then reacted with $[\text{Ir}(\text{COD})\text{Cl}]_2$ in 1,2,4-trichlorobenzene at 190 °C overnight, based on a modified literature method (Scheme 2).^[35] The formation of **IrBPPy** was confirmed by ^1H NMR spectroscopy, UV-vis absorption spectroscopy, and elemental analysis. The ^1H NMR spectrum of **IrBPPy** showed the disappearance of the characteristic peak of internal proton of the porphyrin ring, which was observed at $\delta = -2.55$ ppm for **HBPPy** (Fig. 2). The UV-vis absorption spectrum of **IrBPPy** exhibited absorption bands attributed to pyrene moieties at 312, 326, and 342 nm, and those attributed to the Ir-porphyrin moiety (a Soret band at 426 nm and Q-bands at 534 and 570 nm) (Fig. 3). Compared with the UV-vis absorption spectrum of **HBPPy**, (Soret: 425 nm; Q bands 519, 556, 593, and 649 nm), the red shifts of the both Soret and Q-bands were observed. In addition, the reduction in the number of Q-bands, arising from the degeneracy of the electronic states under a higher symmetry coordination, was observed in the spectrum of **IrBPPy**.³⁶ These spectral features indicate the insertion of an Ir-ion into the porphyrin ring.



Scheme 2. Synthetic scheme for **IrBPPy**.

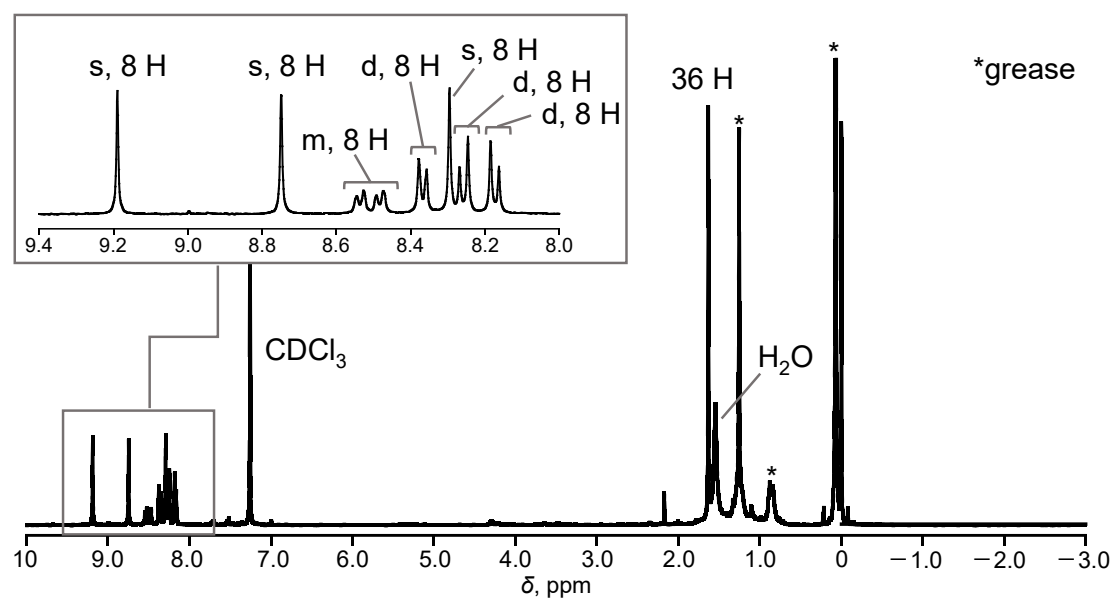


Fig. 2. ^1H NMR spectra of **IrBPPy** in CDCl_3 (400 MHz).

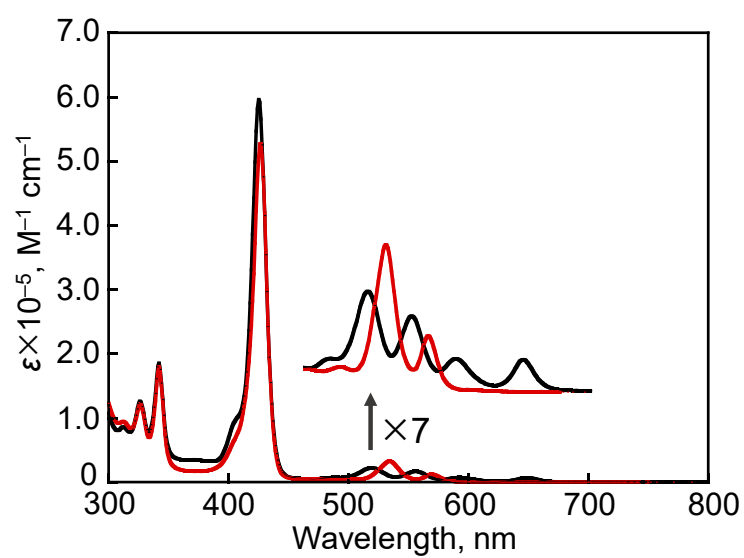


Fig. 3. UV-vis absorption spectra of **HBPPy** (black) and **IrBPPy** (red) in CHCl_3 .

Synthesis and characterization of [IrBPPy]_F

Subsequently, the formation of a supramolecular framework via the self-assembly of **IrBPPy** was investigated. Single crystals suitable for single-crystal X-ray diffraction (SC-XRD) analysis were obtained by slow vapor diffusion of pentane into an *o*-dichlorobenzene solution of **IrBPPy** at room temperature. The SC-XRD analysis revealed that self-assembled **IrBPPy** comprised the framework structure ([**IrBPPy**]_F) in the triclinic system with the *P*-1 space group. Fig. 4a and Table 1 contain an Oak Ridge Thermal Ellipsoid Program (ORTEP) drawing and summary of the crystallographic data of [**IrBPPy**]_F, respectively. In this structure, carbon monoxide and chloride coordinated as axial ligands of the Ir center are disordered into two distinct sites (occupancies 0.73442 and 0.26558). The Ir–carbon distances are 1.882 (8) Å (major) and 2.030 (3) Å (minor) and the Ir–Cl distances are 2.3275 (15) Å (major) and 2.229 (4) Å (minor). These distances are comparable to those observed in Ir(III) porphyrin carbonyl chloride.^[37,38] The average Ir–N bond distance 2.048 (1) Å lies in the normal range of Ir–N distances observed for the previously reported Ir(III)-porphyrin complexes.^[37–41] Based on these results, the oxidation state of iridium was determined to be +3. Notably, the packing structure of the crystal comprises planes stabilised by π – π and CH– π interactions between the pyrenylphenyl moieties along the *b* and *c* axes (Fig. 4b), which is further stabilised by CH– π interactions between phenyl and pyrenyl moieties along the *a* axis (Fig. 4c), resulting in the formation of a porous framework structure with AB stacking (Figs. 4d–f). Considering the van der Waals radii of the constituent atoms, the size of the pore entrance is estimated to be 7.3×7.0 Å². *o*-Dichlorobenzene molecules were observed as crystal solvents within the pores. It should be noted that the distance between the iridium centers is 9.438 (4) Å, suggesting the isolation of porphyrin unit.

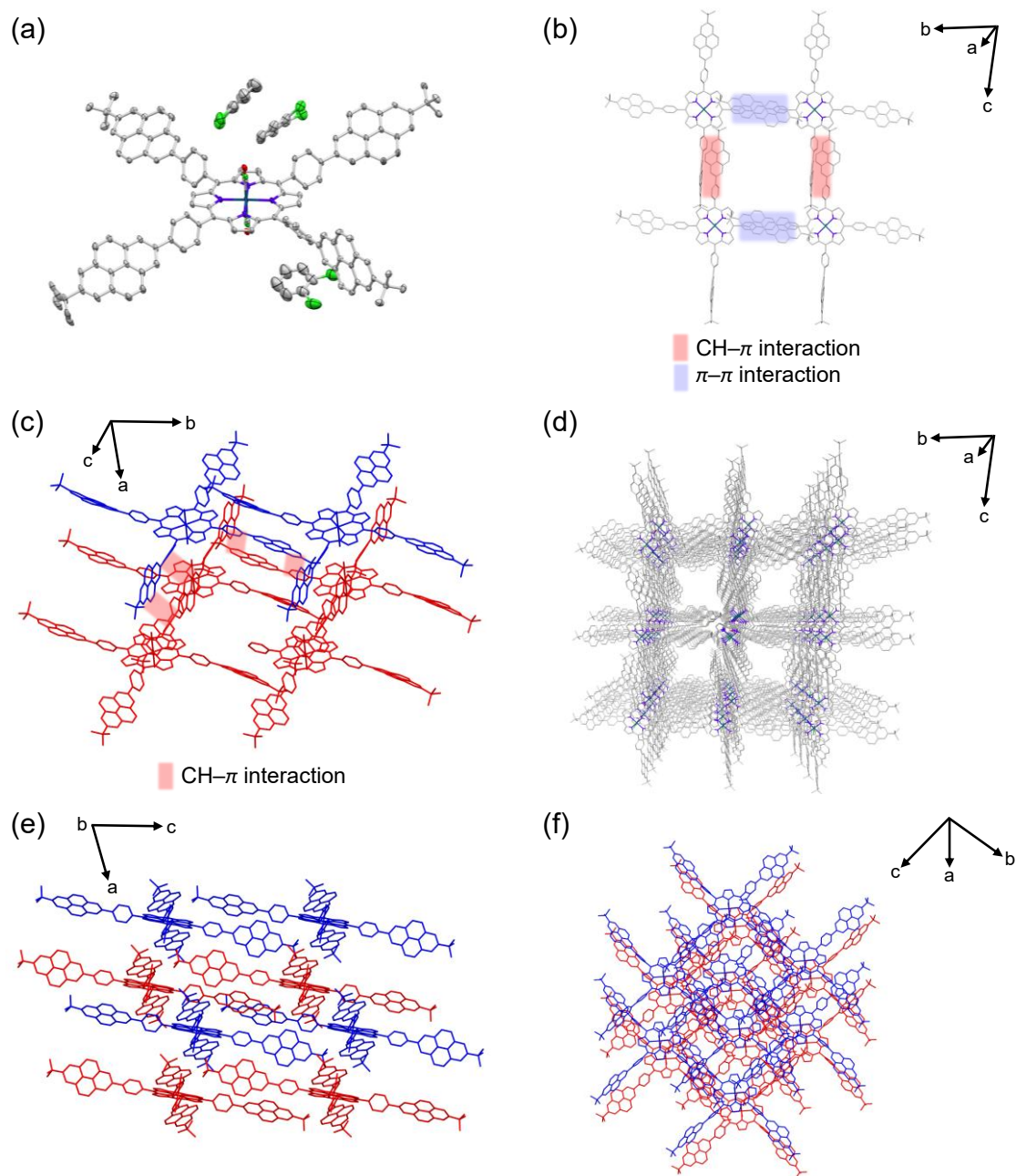


Fig. 4. (a) An ORTEP drawing of **IrBPPy** (50% probability ellipsoids). Hydrogen atoms and disordered atoms are omitted for clarity. Carbon is represented in gray, nitrogen in blue, oxygen in red, iridium in dark blue, and chlorine in green. (b) The planes stabilised by the pyrenylphenyl moieties along the b and c axes. (c) AB stacking structure along the a axis. (d) Packing structure of $[\text{IrBPPy}]\text{F}$. Packing structure viewed (e) along the b axis and (f) from a perspective view. Crystal solvents are omitted for clarify. Crystal solvents are omitted for clarify in (b–f).

Table 1. Summary of crystallographic data for [IrBPPy]_F.

formula	C ₁₄₃ H ₁₀₄ Cl ₇ IrN ₄ O
formula weight	2334.65
crystal system	Triclinic
space group	<i>P</i> -1
<i>a</i> , Å	15.7690(2)
<i>b</i> , Å	20.9372(5)
<i>c</i> , Å	21.8348(4)
<i>α</i> , deg	83.773(2)
<i>β</i> , deg	74.5170(10)
<i>γ</i> , deg	83.929(2)
<i>V</i> , Å ³	6884.1(2)
<i>Z</i>	2
ρ_{calc} , g/cm ³	1.126
<i>F</i> (000)	2388.0
MoK α , cm ⁻¹	0.71073
<i>T</i> , K	123
2 θ_{max} , deg	56
reflns measd	108490
uniq reflns	33062
<i>R</i> (int)	0.0370
data/restraints/params	33062/388/1445
<i>R</i> ₁	0.0476
w <i>R</i> ₂	0.1352
<i>GOF</i>	1.069

To confirm stability of framework structure of $[\text{IrBPPy}]_{\text{F}}$ after removing crystal solvent, powder X-ray diffraction (PXRD) of the dried crystalline solid was performed. The experimental PXRD pattern was similar to the simulated pattern calculated from the SC-XRD data (Fig. 5). Therefore, $[\text{IrBPPy}]_{\text{F}}$ is considered to maintain its framework structure after removing crystal solvents. The results of SC-XRD and PXRD analyses thus confirm the successful synthesis of the desired material incorporating isolated emissive centers.

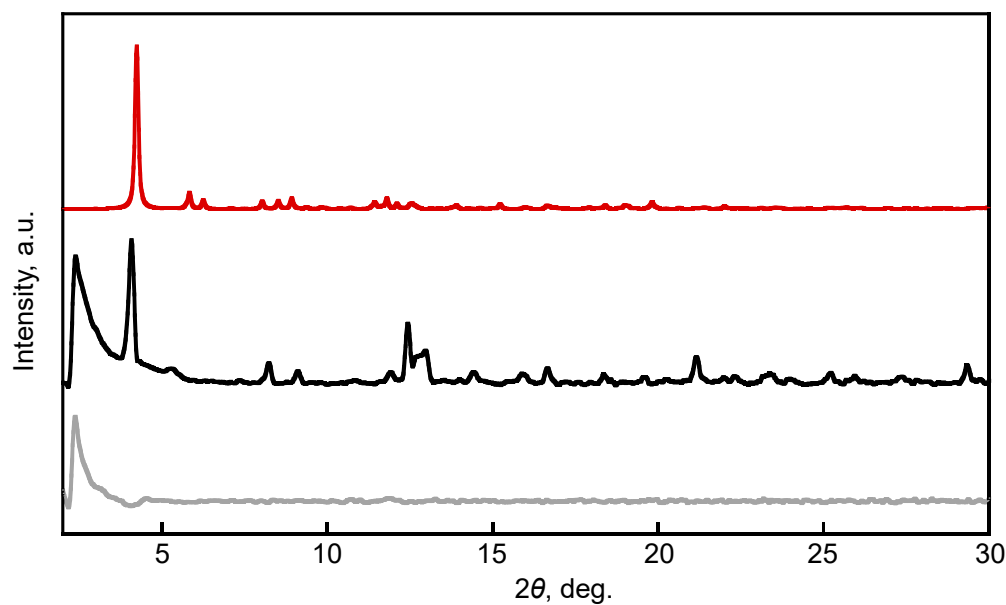


Fig. 5. Experimental PXRD patterns of $[\text{IrBPPy}]_{\text{F}}$ (black) and $[\text{IrBPPy}]_{\text{A}}$ (gray), and the simulated PXRD pattern calculated from the SC-XRD data (red).

Further characterization of **[IrBPPy]_F** was carried out using Fourier-transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA). The FT-IR spectrum of **[IrBPPy]_F** contained the characteristic carbonyl stretching band of the coordinated axial ligand at 2042 cm⁻¹ (Fig. 6a).^[39,42,43] The oxidation-state marker band of **[IrBPPy]_F**, which corresponds to the rocking vibration of the pyrrole units of the porphyrin ring, was observed as a sharp band at 1015 cm⁻¹, and the wavenumber of the band is comparable to that of a previously reported Ir(III) porphyrin carbonyl chloride complex (1017–1026 cm⁻¹).^[29] This result also confirms the iridium(III)-oxidation state of the complex. The TGA of the dried sample of **[IrBPPy]_F** (dried at 80 °C for 1 h *in vacuo*) was measured within 25–600 °C under N₂ flow with a heating rate of 2 °C min⁻¹ to investigate the thermal stability of **[IrBPPy]_F**. The TGA curve exhibited no significant weight loss up to 270 °C (Fig. 6b), indicating the high thermal stability of **[IrBPPy]_F**. At higher temperatures, an exothermic event was observed in the DTA profile, which is associated with thermal decomposition accompanied by combustion of the organic porphyrin skeleton.

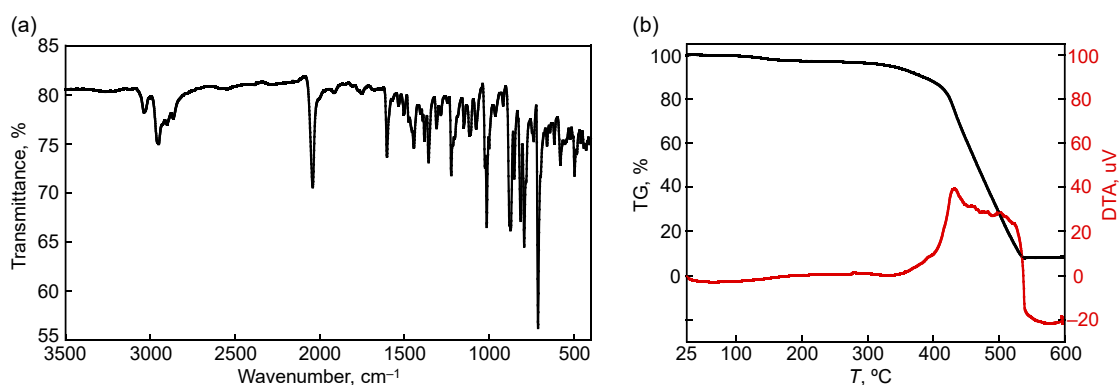


Fig. 6. (a) FT-IR spectrum of **[IrBPPy]_F**. (b) TGA and DTA curve of **[IrBPPy]_F** within 25–600 °C under N₂.

Investigation of photophysical properties of [IrBPPy]_F

The photophysical properties of [IrBPPy]_F were investigated. The diffuse reflectance spectrum of [IrBPPy]_F contained characteristic absorption bands at 325 and 342 nm corresponding to pyrene moieties, a Soret band at 428 nm, and Q-bands at 539 and 578 nm attributed to the Ir-porphyrin moiety (Fig. 7a), similar to the absorption bands of IrBPPy in the solution state (*vide supra*). Subsequently, the photoluminescent properties of [IrBPPy]_F were investigated. Upon photoexcitation of the Soret band at 428 nm using a 405 nm laser diode, [IrBPPy]_F exhibits two NIR emission peaks at 740 and 823 nm at room temperature (Fig. 7b, red line). Similar peaks were observed for Ir(III)-porphyrin complexes in previous reports and assigned as the phosphorescence.^[27–31] To clarify the effect of the framework structure on its photophysical properties, we also attempted to measure the emission spectra of IrBPPy in the solution state by varying both the concentration and the solvent; however, no detectable photoluminescence was observed under any of the examined conditions using a conventional commercial photoluminescence spectrometer. Accordingly, an amorphous solid of IrBPPy ([IrBPPy]_A) was prepared as a comparative compound by evaporation of a chloroform solution of IrBPPy (for details of the preparation of the amorphous sample, see the Experimental section). The PXRD patterns of [IrBPPy]_A did not exhibit any significant diffraction peaks, confirming its amorphous (Fig. 5, gray line). The FT-IR spectrum of [IrBPPy]_A exhibits a characteristic carbonyl stretching band of the coordinated axial ligand at 2042 cm⁻¹ and an oxidation-state marker band at 1016 cm⁻¹ (Fig. 8a). These bands are essentially identical to those observed for [IrBPPy]_F, indicating that the electronic state and coordination environment of the Ir(III)-porphyrin center are nearly identical in the crystalline and amorphous states. The TGA curve of [IrBPPy]_A indicates thermal stability up to 203 °C, which is lower than that of [IrBPPy]_F (Fig. 8b). This reduced thermal stability is attributed to the inhomogeneous molecular arrangement in the amorphous state. Upon photoexcitation of [IrBPPy]_A with the same conditions, [IrBPPy]_A exhibits a broader emission peak at 751 nm with a shoulder at 826 nm (Fig. 7b, blue line). The sharpness of the NIR emission peaks of [IrBPPy]_F and [IrBPPy]_A with λ_{max} spanning from 740 to 832 nm were analyzed by determining their FWHM (Figs. 7c, 7d, and Table 2). As a result, the FWHM of the peaks for [IrBPPy]_F (85 meV at 740 nm and 821 nm) was found to be narrower than that of [IrBPPy]_A (105 meV at 751 nm and 826 nm). The broadening can be caused by the inhomogeneous environments around the luminescent center. Thus, various intermolecular interactions and vibronic couplings in the amorphous state can be suppressed by the framework structure. These results suggest that isolation of the emission center within the framework contributes to the sharp emission peak.

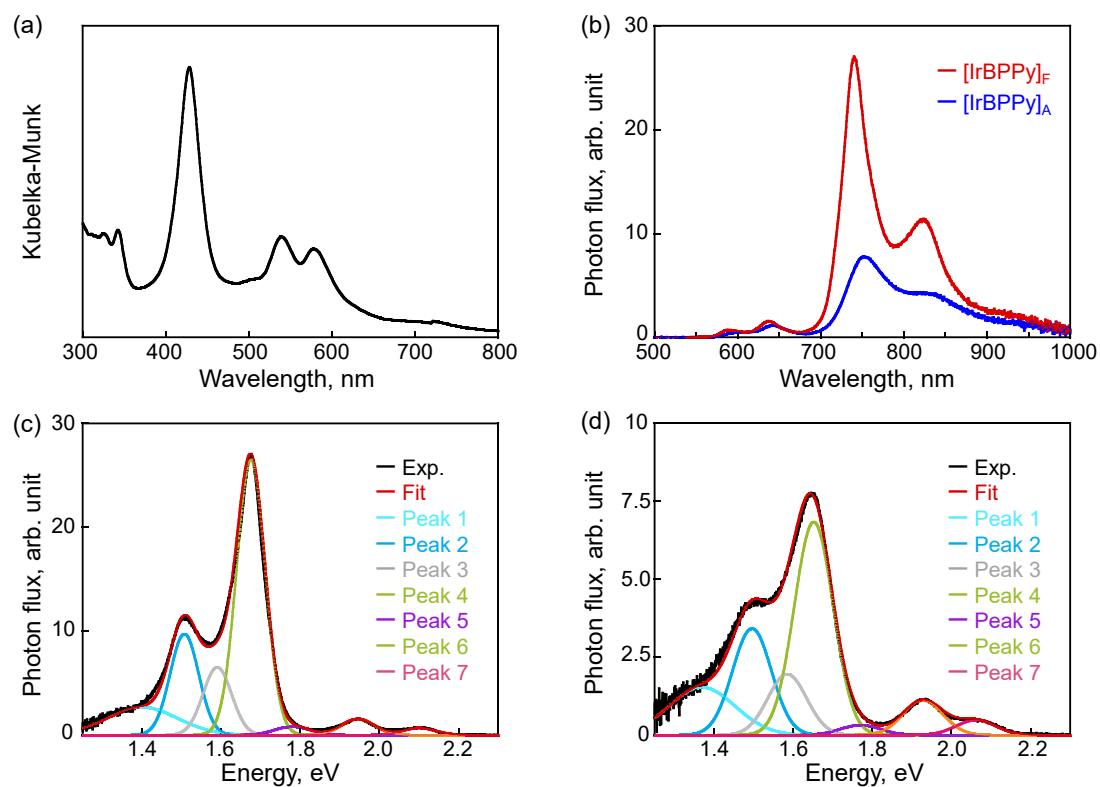


Fig. 7. (a) Diffuse reflectance spectrum of **[IrBPPy]_F** (b) Emission spectrum of **[IrBPPy]_F** (red) and **[IrBPPy]_A** (blue). (c) Peak deconvolution of emission bands of **[IrBPPy]_F** and (d) **[IrBPPy]_A**.

Table 2. FWHM of the deconvoluted Gaussian peaks.

	[IrBPPy]_F		[IrBPPy]_A	
	Wavenumber, cm ⁻¹	FWHM, meV	Wavenumber, cm ⁻¹	FWHM, meV
Peak 1	11290	211	11050	197
Peak 2	12160	85	12070	115
Peak 3	12820	85	12870	115
Peak 4	13510	85	13320	115
Peak 5	14360	105	14280	118
Peak 6	15690	97	15550	118
Peak 7	16940	97	16630	118

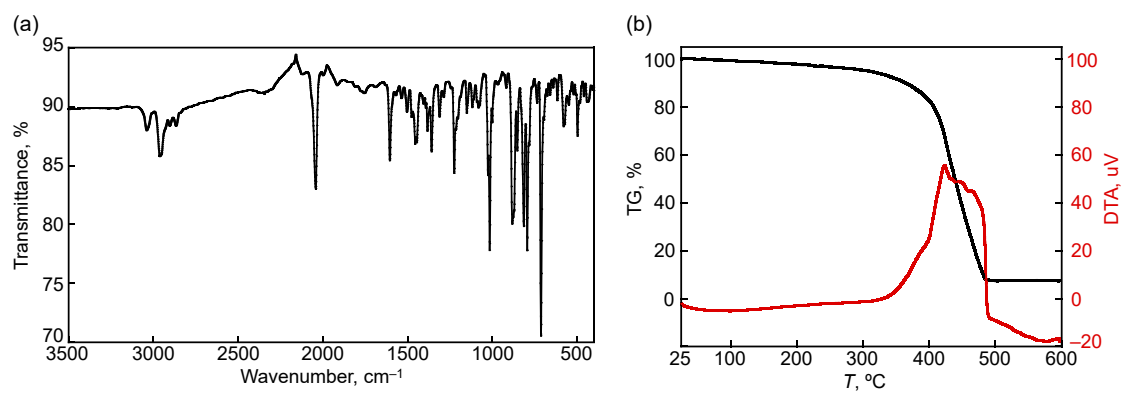


Fig. 8. (a) FT-IR spectrum of **[IrBPPy]_F**. (b) TGA and DTA curve of **[IrBPPy]_F** within 25–600 °C under N₂.

Conclusion

In conclusion, I synthesized a novel Ir(III)–porphyrin-based supramolecular framework via self-assembly of Ir(III) porphyrins through non-covalent interactions between the pyrenylphenyl moieties at *meso*-positions of the porphyrin ring. SC-XRD analysis revealed that the framework is stabilized by multiple π – π and CH– π interactions, leading to a well-isolated emission center. The resulting crystalline solid, **[IrBPPy]_F** shows distinct NIR phosphorescence bands at 739 and 823 nm. The narrower FWHM of **[IrBPPy]_F** compared to its amorphous counterpart, **[IrBPPy]_A**, indicates that the ordered structure effectively isolates the emissive Ir–porphyrin centers. Although several Ir(III)–porphyrin-based MOFs have been reported as catalysts,^[32,43–49] studies on their luminescent properties remain scarce.^[32] This work represents a rare example investigating the luminescence of an Ir(III)–porphyrin-based porous crystalline framework. These findings demonstrate that the rational design of supramolecular frameworks constructed from emissive molecular complexes bearing non-covalent interaction sites enables them to serve as powerful platforms for controlling photophysical behavior of molecules in the solid state.

Experimental section

General procedures

Hexane, pentane and chloroform-D (CDCl_3), liquid paraffin were purchased from FUJIFILM Wako Pure Chemical Co. Chloroform (CHCl_3), *o*-dichlorobenzene, and MeCN were purchased from Kanto Chemical Co., Inc. $[\text{Ir}(\text{COD})\text{Cl}]_2$, 1,2,4-trichlorobenzene were purchased from Tokyo Chemical Industry Co., Ltd. All solvents and reagents were of high quality and used as received. The free-base porphyrin, 5,10,15,20-tetrakis(4-(7-*tert*-butyl)pyren-2-yl)phenyl)porphyrin (**HBPPy**) was synthesized as previously reported.^[24] An amorphous solid of **IrBPPy** was prepared by evaporation of the CHCl_3 solution of **IrBPPy** and drying the afforded solid *in vacuo* at 80 °C. NMR spectra were recorded at room temperature using a JEOL JNM-ECS400 spectrometer. Elemental analysis was conducted with a J-SCIENCE LAB MICRO CORDER JM10 elemental analyzer. UV-vis spectra and diffuse reflectance UV-vis spectrum was recorded using a Shimadzu UV-3600i Plus UV-vis-NIR spectrophotometer. A white standard of BaSO_4 served as the reference for diffuse reflectance spectroscopic measurements. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer. PXRD data were collected with a Rigaku MiniFlex600 diffractometer. Thermogravimetric (TG) analyses were performed under a N_2 atmosphere with a flow rate of 40 mL min^{-1} at a heating rate of 2 °C min^{-1} using a Shimadzu DTG-60. PL spectra were recorded at room temperature in a spectrometer (TFCAM-7000F, Lambda Vision) using a 405 nm laser diode (PL255, THORLABS).

Synthesis of chloro{5,10,15,20-tetrakis(4-(7-*tert*-butyl)pyrene-2-yl)phenyl)-porphyrinato}-carbonyliridium(III) (**IrBPPy**)

HBPPy (20 μmol) and $[\text{Ir}(\text{COD})\text{Cl}]_2$ (1.5 eq.) in 1,2,4-trichlorobenzene (14 mL) was stirred at 190 °C overnight. The precipitate was removed by filtration. The filtrate was purified by flash column chromatography over silica gel using chloroform as eluent. The eluent containing 1,2,4-trichlorobenzene was obtained and concentrated under vacuum. The red precipitate was obtained by dripping the solution into hexane (400 mL) and filtration. Recrystallization by slow vapor diffusion of pentane into an *o*-dichlorobenzene solution of **IrBPPy** at room temperature gave the dark red solid (19 mg, 49%). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 9.19 (s, 8H), 8.75 (s, 8H), 8.47-8.55 (m, 8H), 8.37 (d, J = 7.6 Hz, 8H), 8.30 (s, 8H), 8.26 (d, J = 9.2 Hz, 8 H), 8.17 (d, J = 9.2 Hz, 8H), 1.63 (s, 36H) ppm. Elemental analysis Calcd. for $\text{C}_{125}\text{H}_{92}\text{N}_4\text{Ir}_1\text{O}_1\text{Cl}_1 \cdot 1.5\text{H}_2\text{O}$ (**IrBPPy** $\cdot$ 1.5 H_2O): C, 78.16%; H, 4.99%; N, 2.92%. Found: C, 78.19%; H, 5.12%; N, 2.92%. λ_{max} (CHCl_3)/nm 312 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 96000), 326 (120000), 342 (180000), 426 (540000), 534 (34000), 570 (13000).

Preparation of a supramolecular framework ([IrBPPy]_F) and an amorphous solid ([IrBPPy]_A)

The crystalline solid was obtained by recrystallization via slow vapor diffusion of pentane into an *o*-dichlorobenzene solution of **IrBPPy** at room temperature. The resulting solid was then dried at 80 °C *in vacuo* for 1 h to afford [IrBPPy]_F. [IrBPPy]_A was prepared by evaporation of the CHCl₃ solution of **IrBPPy** and drying the resulting solid *in vacuo* at 80 °C for 1 h.

Single-crystal X-ray structural analysis

Single crystal X-ray diffraction data were collected on a Synergy Custom system CCD Plate equipped with confocal monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) coated with liquid paraffin. Data was processed using CrysAlisPro system software.^[50] The structures were solved by a dual-space algorithm using SHELXT program^[51] through the Olex2 interface.^[52] All non-hydrogen atoms were refined anisotropically using a least-squares method, and hydrogen atoms were fixed at calculated positions and refined using a riding model. SHELXL–2014/7 was used for structure refinement.^[53] Full-matrix least-squares refinements on F^2 based on unique reflections with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ ($I > 2.00 \sigma(I)$) and $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ were performed. A solvent mask^[54] was calculated, and 562 electrons were found in a volume of 3104 Å³ in 1 void per unit cell. Mercury 4.2.0 was used for visualization and analysis of the structure. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 2502547 for **IrBPPy**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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Concluding remarks

In this doctoral dissertation, supramolecular frameworks constructed from metal porphyrin complexes bearing pyrenylphenyl moieties were developed, and their functionalities were systematically explored in the contexts of catalysis and luminescence. In the Ru(II)- and Mn(III)-porphyrin-based supramolecular frameworks, self-assembly driven by non-covalent interactions enabled the construction of molecule-based porous materials while preserving the intrinsic coordination environments and reactivity of the metal centers. As a result, these materials exhibited enhanced catalytic performance, durability, recyclability, and size-selective behavior compared to their homogeneous counterparts.

In particular, the Mn-porphyrin supramolecular framework catalyst demonstrated outstanding performance in Mukaiyama-type aerobic epoxidation under mild conditions by combining an earth-abundant metal center with molecular oxygen as a green oxidant. Its catalytic activity, turnover frequency, and production rate exceeded those of previously reported molecule-based porous crystalline frameworks incorporating earth-abundant metals, underscoring the effectiveness of supramolecular framework formation as a strategy for sustainable oxidation catalysis.

Furthermore, the Ir(III)-porphyrin-based supramolecular framework successfully extended this design concept to luminescent materials. Spatial isolation of emissive Ir-porphyrin units within an ordered crystalline framework suppressed intermolecular interactions and energetic disorder, resulting in significantly narrowed near-infrared emission bands compared to an amorphous solid. This finding establishes supramolecular frameworks as a promising platform not only for heterogeneous catalysis but also for the rational design of narrowband luminescent materials.

Overall, the results presented in this thesis clearly demonstrate that supramolecular framework construction based on non-covalent interactions provides an effective materialization strategy that reconciles molecular-level design with precise control over assembly states. The design principles established herein are broadly applicable to a wide range of molecule-based functional materials, including catalysts, luminescent materials, and potentially systems for separation, sensing, and energy conversion, thereby offering a fundamental guideline for the future development of molecular solid-state materials.

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List of publications

Chapter 1

1. Development of a Ru–porphyrin-based supramolecular framework catalyst for styrene epoxidation
A. Yoneda, T. Watanabe, K. Kosugi, T. Takahara, S. Kusaka, R. Matsuda, Y. Saga, T. Kambe, M. Kondo, S. Masaoka, *Chem. Commun.* **2024**, 60, 13939.

Chapter 2

2. Mn–porphyrin-based supramolecular framework catalyst for Mukaiyama-type epoxidation
A. Yoneda, M. A. D. O. Yau, K. Kosugi, T. Kambe, M. Kondo, S. Masaoka, *Coord. Chem. Res.* **2025**, 2, 100017.

Chapter 3

3. Synthesis and photophysical properties of an Ir–porphyrin-based supramolecular framework
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Other publications

1. Redox-active tin(ii) complexes with sterically demanding *o*-phenylenediamido ligands and their reactivity with organic azides

H. Sugimoto, **A. Yoneda**, M. Yano, K. Sato, Y. Shiota, M. Miyanishi, K. Yoshizawa and S. Itoh, *Dalton Trans.* **2025**, 54, 5025.