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Conference paper

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Closed-shell and open-shell dual nature of singlet diradical compounds

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Abstract: Unlike triplet diradicals, singlet diradicals can vary in diradical character from 0 % to 100 % depending on linker units that allow two formally unpaired electrons to couple covalently. In principle, the electronic structure of singlet diradicals can be described as a quantum superposition of closed-shell and open-shell structures. This means that, depending on the external environment, singlet diradicals can behave as either closed-shell or open-shell species. This paper summarizes our progress in understanding the electronic structure of π-conjugated singlet diradical molecules in terms of closed-shell and open-shell dual nature. We first discuss the coexistence of intra- and intermolecular covalent bonding interactions in the π-dimer of a singlet diradical molecule. The intra- and intermolecular coupling of two formally unpaired electrons are related to closed-shell and open-shell nature of singlet diradical, respectively. Then we demonstrate the coexistence of the covalent bonding interactions in the one-dimensional stack of singlet diradical molecules having different diradical character. The relative strength of the interactions is varied with the magnitude of singlet diradical index y_0. Finally, we show the dual reactivity of a singlet diradical molecule, which undergoes rapid [4 + 2] and [4 + 4] cycloaddition reactions in the dark at room temperature. Closed-shell and open-shell nature endow the singlet diradical molecule with the reaction manner as diene and diradical species, respectively.

Keywords: π-dimer; closed-shell and open-shell dual nature; coexistence of covalent bonding interaction; cycloaddition reaction; diradicaloid; ICPOC-25; one-dimensional stack; singlet diradical.

Introduction

Polycyclic aromatic compounds with singlet diradical character have attracted much attention because of their unique physical properties and reactivity [1–4]. Many chemists have prepared and characterized singlet diradical compounds, including bisphenalenyls [5–16], diindenoarenes [17–51], zethrenes [52–70], cethrenes [71–73], acenes [74–83], heteroacenes [84–87], periacenes [88–104], and so on. A series of studies on singlet diradical compounds have revealed that diradicaloid species possess common phenomenological feature such as low-energy absorption bands, weak double-excitation absorption bands, NMR signal broadening, thermally activated ESR signals, two-photon absorption, and ambipolar field effect transistor (FET) properties. The electronic structure of singlet diradicals can be described as a resonance hybrid of closed-shell forms and open-shell diradical forms, especially appreciable contribution of the open-shell character to the ground state brings the unique phenomena of singlet diradicals.

The resonance hybrid, that is, quantum superposition, would lead to a duality of closed-shell and open-shell nature in behaviors of singlet diradicals. Such a dual nature has been exemplified by rapid [4 + 2] and [4 + 4] self-dimerization of *o*-quinodimethane under dark condition at low temperature [105–110]. This paper focuses on our

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studies on singlet diradical compounds in terms of duality of interactions, that is, intra- and intermolecular covalent bonding interactions.

Coexistence of intra- and intermolecular covalent bonding interactions

Coexistence in a dimer of a singlet diradical molecule

The compound **1** contains a thienoquinoid scaffold, which possesses diradicaloid character due to the recovery of thiophene aromaticity in the diradical canonical forms. As for **1**, the delocalization of unpaired electrons on phenalenyl rings affords the stabilization of diradical structures, leading to appreciable singlet diradical character (Fig. 1). Actually, a broken symmetry UB3LYP calculation shows the singlet diradical index (y_0) of 72 %.

X-ray crystallographic analysis of **1** revealed that **1** adopts a dimeric form with a short π–π separation distance of ~3.1 Å in the center of the molecule, as shown in Fig. 2A, B [6]. The distance is much shorter than the sum of the van der Waals radii of carbon atoms (3.4 Å), implying an attractive interaction between molecules. Because **1** has no strong electron-withdrawing or electron-donating groups and its dipole moment (0.81 Debye) is not very large, it is unlikely that the electrostatic interaction is the dominant factor in the short proximity distance. The attractive interaction in the dimer would be an intermolecular covalent bonding interaction, which originate from the double excitation configuration ${}^1\Phi_{\mathrm{H,H}\rightarrow\mathrm{L,L}}$, that is, a singlet diradical contribution. Based on the broken symmetry UB3LYP calculation of **1**, the occupation numbers of HOMO and LUMO are 1.3 and 0.7, respectively. In this case, an LUMO–LUMO interaction will lead to a stabilization of the system, because a newly formed 'LUMO' of the dimer, which is more stabilized than the original LUMO, can accommodate 1.4 electron (Fig. 2C). In addition, an HOMO–HOMO interaction seems likely to contribute the stabilization of the system, because a newly formed 'HOMO' of the dimer contains only 0.6 electrons, which results in the suppression of a four-electron repulsion that is generally derived from the interaction between fully occupied orbitals. In other words, substantial diradical character of **1**, which is a partial decoupling of an electron–electron pair within a molecule, allows for a covalent bonding interaction between molecules. In the dimeric pair of **1**, coexistence of intra- and intermolecular covalent bonding interactions would be established (Fig. 2D).

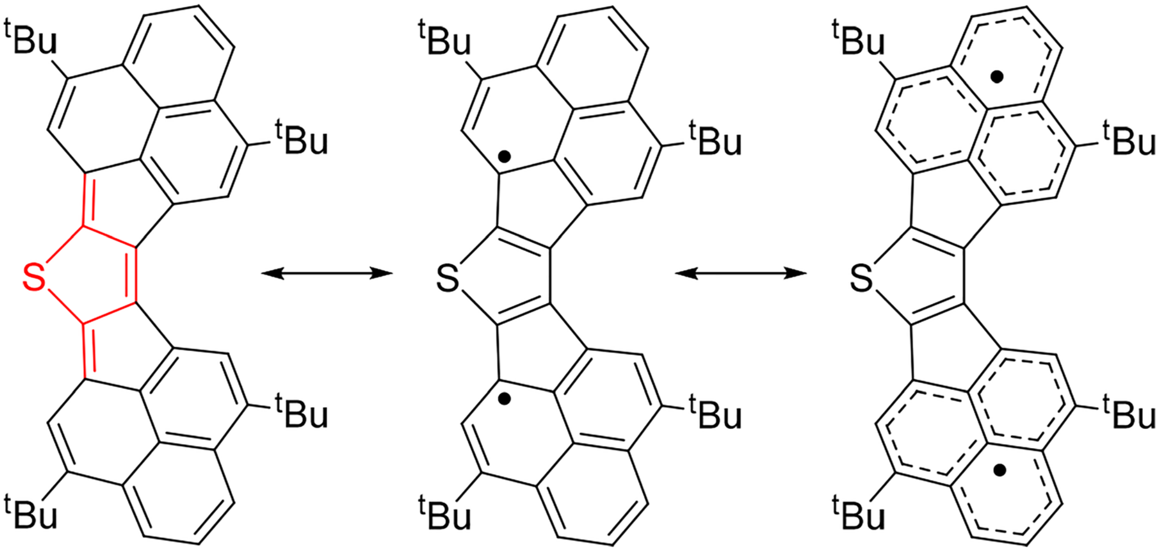

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Fig. 1: Resonance formula of singlet diradical **1**. A thienoquinoid scaffold is shown in red.

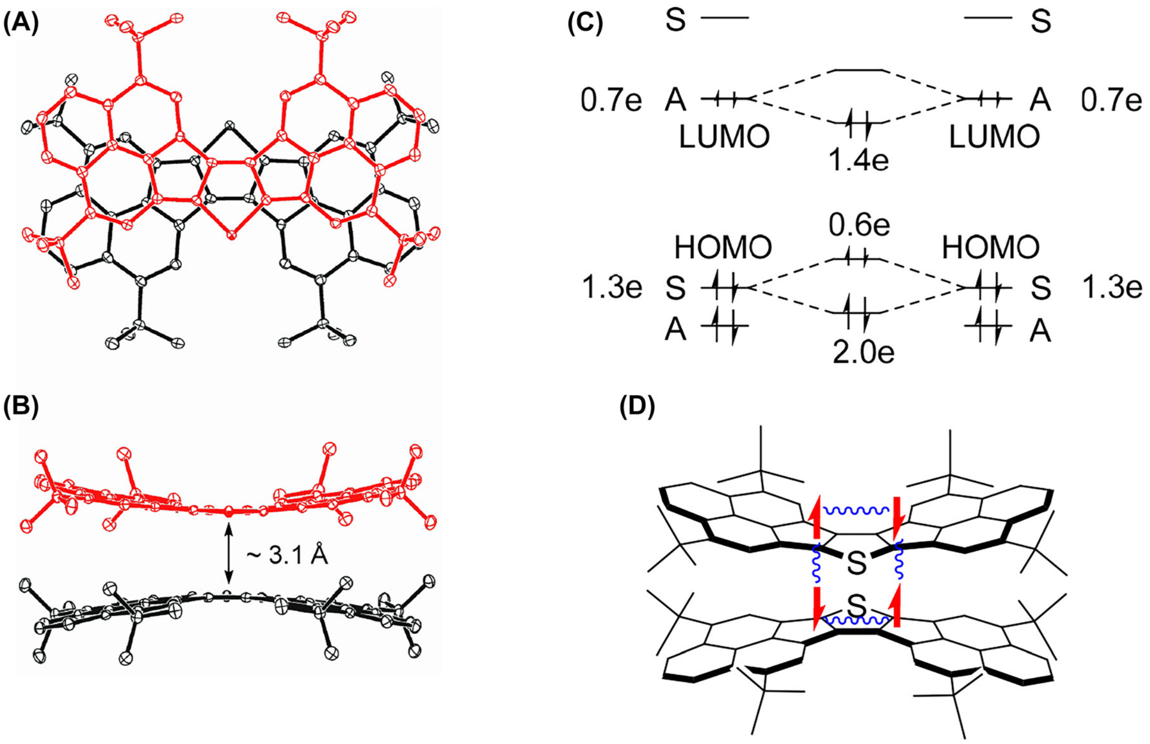


Fig. 2: Spin–spin interaction of the dimer of **1**. (A) Top view and (B) side view of a dimeric pair of **1** (CCDC-237621). Hydrogen atoms are omitted for clarity. (C) Schematic drawing of the molecular orbital interaction of the dimeric **1** with diradical contribution through the double excitation configuration $^1\Phi_{\mathrm{H,H}\rightarrow\mathrm{L,L}}$. 'S' and 'A' denote the symmetry of the molecular orbitals. (D) Covalent bonding interaction (blue wavy lines) between unpaired electrons in the dimeric pair of **1**.

Coexistence in a one-dimensional chain of singlet diradical molecules

The compound **2** is a singlet diradical molecule, in which *p*-quinodimethane is embedded in the center of the molecule. Similar to the diradicaloid **1**, the closed-shell Kekulé form of **2** also resonates well with the diradical form **2′** by virtue of aromatic sextet formation, and then, the unpaired electrons emerging on the terminal carbons of the *p*-quinodimethane moiety can delocalize over the phenalenyl rings (**2″**), as shown in Fig. 3A. Highly delocalized spin structure of **2** is supported by a broken symmetry UB3LYP calculation (Fig. 3B) that shows the diradical index y_0 of 37 %.

The diphenyl derivative (**3**, Fig. 4A) of **2** has been prepared by a multi-step synthesis from commercially available acenaphthene [7]. X-ray crystallographic analysis of a single crystal of **3** revealed that **3** forms a one-dimensional (1D) stack with superimposed phenalenyl rings. The π–π separation distance (R, the averaged distance of close contacts between the α-carbon atoms and between the central carbon atoms) between the overlapping phenalenyls is 3.137 Å (Fig. 4B), which is much shorter than the sum of the van der Waals radius of carbon atoms. The short contact is ascribable to an intermolecular covalent bonding interaction of two unpaired electrons formally appearing on the phenalenyl rings. The coexistence of intra- and intermolecular covalent bonding interactions in the 1D chain is confirmed by a substantially large red shift of an HOMO–LUMO absorption band. A dilute CH_2Cl_2 solution of **3** shows an intense HOMO–LUMO absorption band at 746 nm, whereas the solid **3** shows a lowest energy band at 1440 nm. In the 1D stack, a covalent bonding interaction works between the molecules as well as within the molecule, and the coexistence of the interactions causes electron delocalization over the 1D stack, resulting in the large red shift of 6600 cm^{-1}. Based on the valence bond model, the coexistence can be described by the resonance hybrid of intramolecular (form **A** in Fig. 4C) and intermolecular (form **B**) covalent bonding interactions. The strength of the covalent bonding interactions was

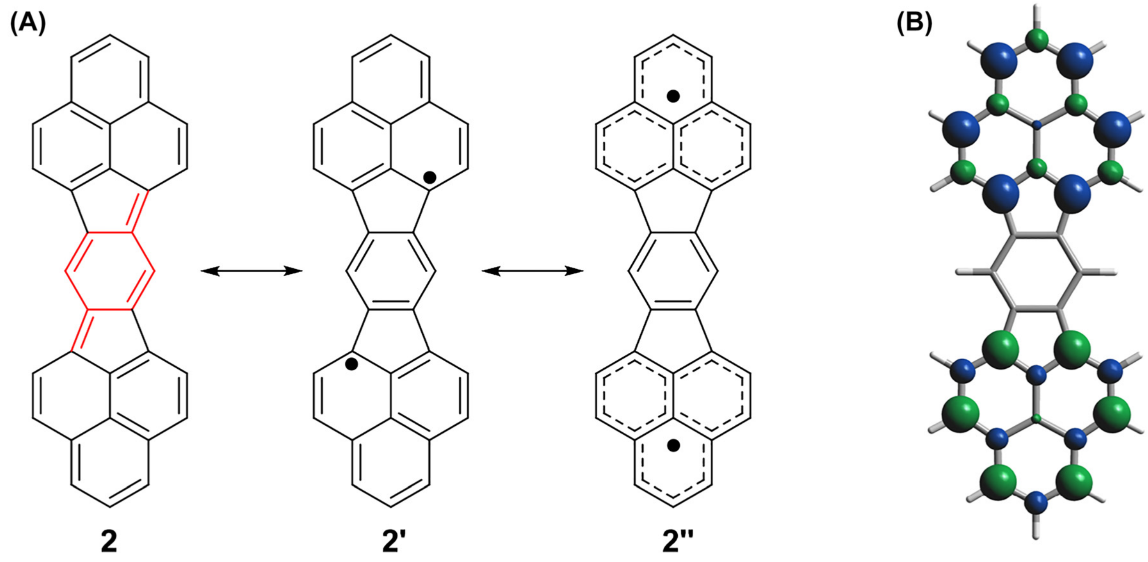


Fig. 3: Electronic structure of **2**. (A) Resonance formula of singlet diradical **2**. The *p*-quinodimethane scaffold is shown in red. (B) Spin density map of **2** (UB3LYP/6-31G**).

quantum-chemically estimated by Huang and Kertesz [10]. They interpret the electronic structure of the 1D chain using an alternating Heisenberg chain model, and interestingly, demonstrate that the *inter*molecular interaction ($2J/k_b = -3300$ K) is stronger than the *intra*molecular one ($2J/k_b = -2200$ K). These concomitant interactions in the 1D chain confers an electroconductive property to the solid of **3**. The electroconductivity of a compressed pellet of **3** at room temperature is 1.0×10^{-5} S cm^{-1} with an activation energy of 0.3 eV at 200–300 K. It is noted that the conductivity is obtained in a single component state, not a charge transfer complex or salt, and is substantially large among structurally well-defined hydrocarbon molecules. Thin-film properties and ambipolar transport are also investigated. The organic field-effect transistors (OFETs) based on **3** exhibits ambipolar transport with balanced hole and electron mobilities in the order of 10^{-3} cm^2 V^{-1} s^{-1} [111].

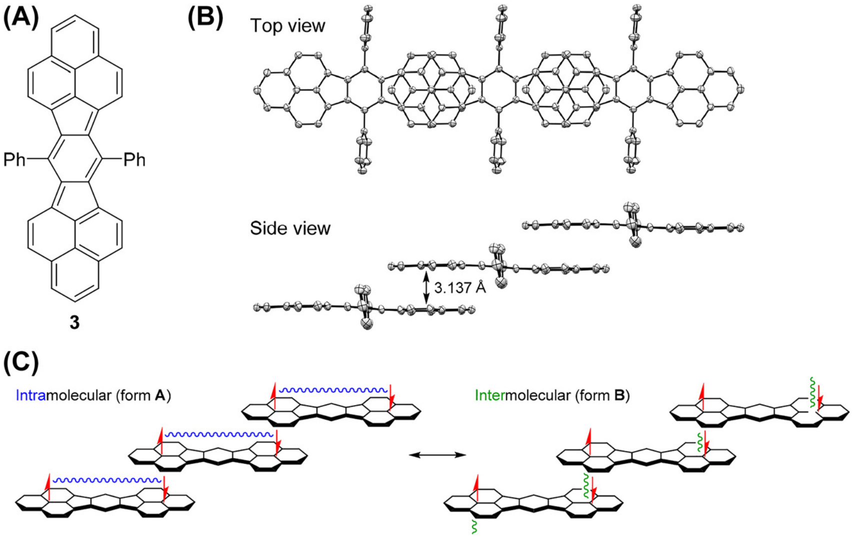


Fig. 4: Spin–spin interaction of the one-dimensional (1D) stack of **3**. (A) Structure of **3**. (B) X-ray crystallographic structure of the 1D stack of **3** (CCDC-275077). Hydrogen atoms are omitted for clarity. (C) Resonance formula for describing the electronic structure of the 1D stack of **3**. Blue and green wavy lines represent intra- and intermolecular covalent bonding interactions, respectively.

By changing the interplanar distance *R* between overlapping phenalenyl rings, the strength of intra- and intermolecular interactions of the 1D chain can be adjusted. The dimethyl derivative **4** (Fig. 5A) yield single crystals, which incorporate various kinds of recrystallization solvents (benzene, toluene, and chlorobenzene) [11]. X-ray measurements show that at 200 K the crystal containing benzene molecules has the shortest interplanar distance (R = 3.160 A, see Table 1). At the same temperature, crystals containing chlorobenzene (PhCl) show a longer interplanar distance (R = 3.225 A), indicating that the separation distance also changes as the measurement temperature is changed. In an extreme case, crystals containing toluene showed $R = \infty$, that is, no overlap of the phenalenyl rings. Table 1 shows that there is a strong correlation between the separation distance *R* and the length of the linker bond (*L*) connecting the phenalenyl ring and the central benzene ring. As the overlapping phenalenyl rings get closer together, the bond ***a*** becomes longer. Because the length of ***a*** is related to the strength of the intramolecular covalent bond interaction, the longer ***a*** means the weaker intramolecular interaction. As the covalent bonding interaction becomes stronger between molecules (form **B** in Fig. 4C), the intramolecular interaction becomes weaker (form **B**). In other words, there is a trade-off between the strength of intramolecular and intermolecular interactions (Fig. 5B). The optical spectra are also affected by the separation distance *R*. The reflection spectra of a single crystal of **4**/PhCl show a blue-shift of the lowest energy band upon cooling. This means that the stronger the intermolecular interaction, the wider the gap between the valence band and the conduction band. In principle, when alternating electron–electron interactions are equal, the band gap vanishes. The wider gap observed at low temperatures in **4**/PhCl suggests that the contribution of form **B** in the 1D stack of **4** is larger than that of form **A**, consistent with the theoretical result given by Huang and Kertesz (see above). It is also noteworthy that there is no abrupt change in the *π*–*π* separation distance, bond length, or optical bands when the temperature is varied. This means that the 1D chain of **4** does not undergo a phase transition in the temperature range of 100 K–300 K.

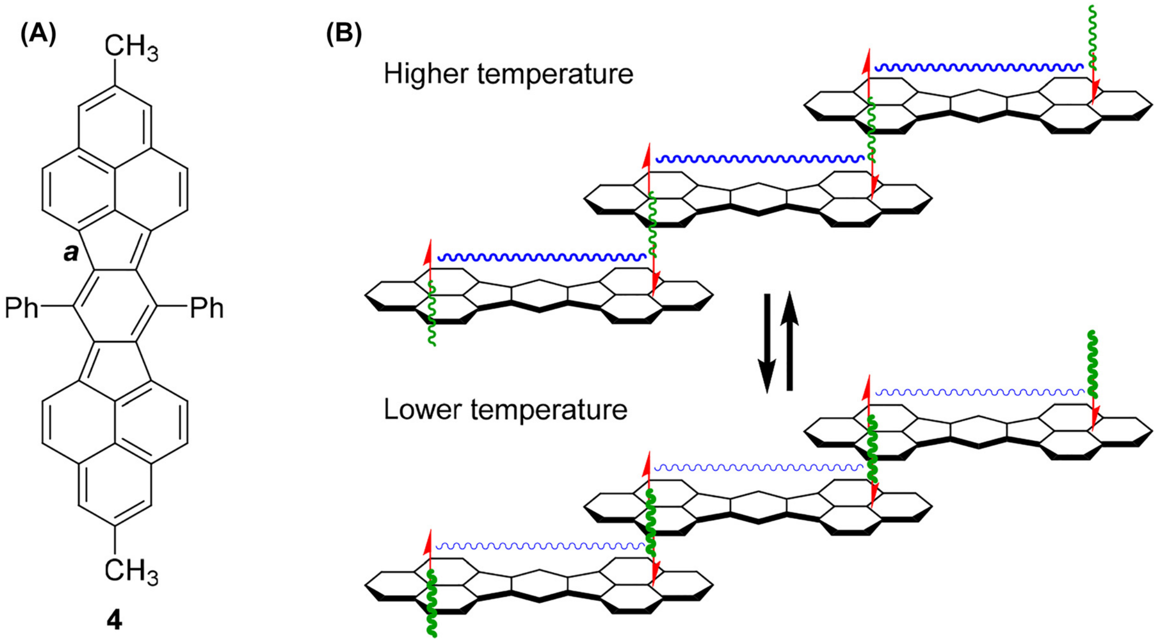


Fig. 5: Spin–spin interaction of the 1D stack of **4**. (A) Structure of **4**. (B) Temperature changes in the strength of intramolecular (blue wavy lines) and intermolecular (green wavy lines) interactions.

Table 1: The π–π separation distances (R) between overlapping phenalenyl rings and the lengths (L) of the bond $\boldsymbol{a}$, in the crystals of **4**.

Solvates	Benzene	PhCl	PhCl	PhCl	Toluene
T/K[a]	200	100	200	300	200
R/Å	3.160	3.208	3.225	3.279	n.d.[b]
L/Å[c]	1.476(2)	1.472(2)	1.469(2)	1.465(3)	1.457(2)

[a]X-ray measurement temperatures. [b]No overlap was observed. [c]Mean values.

Appearance of coexistence in a one-dimensional chain of a singlet diradical molecule

[5]Cumulene-linked bisphenalenyl (**5**) also forms a 1D stack in solid state (Fig. 6) [16]. However, the averaged π–π separation distance (R) between the overlapping phenalenyl rings is 3.379 Å at 250 K, which is much longer than that of **3** and **4**. The wider separation is a consequence of a weaker intermolecular covalent bonding interaction originating from smaller diradical character of **5**. The diradical index y_0 of **5** is estimated to be 17 % by a broken symmetry UB3LYP/6-31G** calculation. The overlapping motif of phenalenyl rings at 250 K is close to a ring-over-bond fashion, which deviates from the ideal overlap pattern found in π-dimers of phenalenyl radicals (Fig. 7). In the π-dimers of phenalenyl radicals, a perfect SOMO–SOMO overlap is obtained. With decreasing temperature, the π–π separation distance of **5** becomes shorter, and at the same time, the overlapping motif approaches the ideal one. As a result, the intermolecular covalent bonding interaction becomes stronger at lower temperatures. Considering the close relationship between intra- and intermolecular interactions, the covalent bonding interaction within the molecule would become weaker upon cooling. Variable temperature Raman measurements support these changes. The frequency of the Raman peak attributed to the symmetrical stretching of the cumulene chain in solution is identical to that observed in the crystalline state (ν = 2156 cm^{-1}) at room temperature. This coincidence implies that the electronic state of **5** in the 1D chain does not differ significantly from that of the discrete molecule, indicating a negligible covalent bonding interaction between molecules. At 200 K, a small new band is observed at ca. 2120 cm^{-1} along with the original intense band. With further decreasing temperature (100 K and 5 K), the lower energy band becomes more intense. According to DFT calculations, this lower energy band arises from enhanced diradical electronic structure. These findings can be explained by the following model (Fig. 8). At room temperature, the covalent bonding interaction is limited to within a molecule. The electronic structure of the 1D chain is almost identical to that of a discrete molecule. At low temperatures, phenalenyl rings come close to each other and seeks for an intermolecular covalent bonding, and then, domains, in which intra- and intermolecular interactions coexist, begin to appear in the 1D chain. By using a molecule with small diradical character, we could find the onset of the coexistence of intra- and intermolecular covalent bonding interactions in the 1D chain (that is, alternating antiferromagnetic Heisenberg liner chain) of diradicaloid compounds.

Intermolecular-biased coexistence in a one-dimensional chain of singlet diradical molecules

Naphthoquinoid- and anthraquinoid-embedded bisphenalenyl molecules have significantly large diradical character [9, 12, 14]. Broken symmetry UB3LYP calculations shows y_0 of 56 % and 62 % for **6** and **7**, respectively. Both diradicaloids also give rise to slip-stacking 1D-chains similar to **3** and **4**, in which phenalenyl rings are perfectly overlapped in an ideal manner (Fig. 9). The interplanar distance of the superimposed phenalenyl rings are 3.170 Å and 3.122 Å for **6** and 7, respectively, which are much shorter than the van der Waals contact of carbon atoms. In solution state, **6** and **7** exhibit HOMO–LUMO absorption bands in near infrared (NIR) region (867 nm for **6**, 984 nm for 7). These absorption bands are located in lower energy region than that of **3** and **4**, due to larger diradical character, that is, smaller HOMO–LUMO gaps. The HOMO–LUMO absorption bands of **6** and **7** in solid state are also observed in NIR region. The solid state bands are shifted to lower energy region relative to

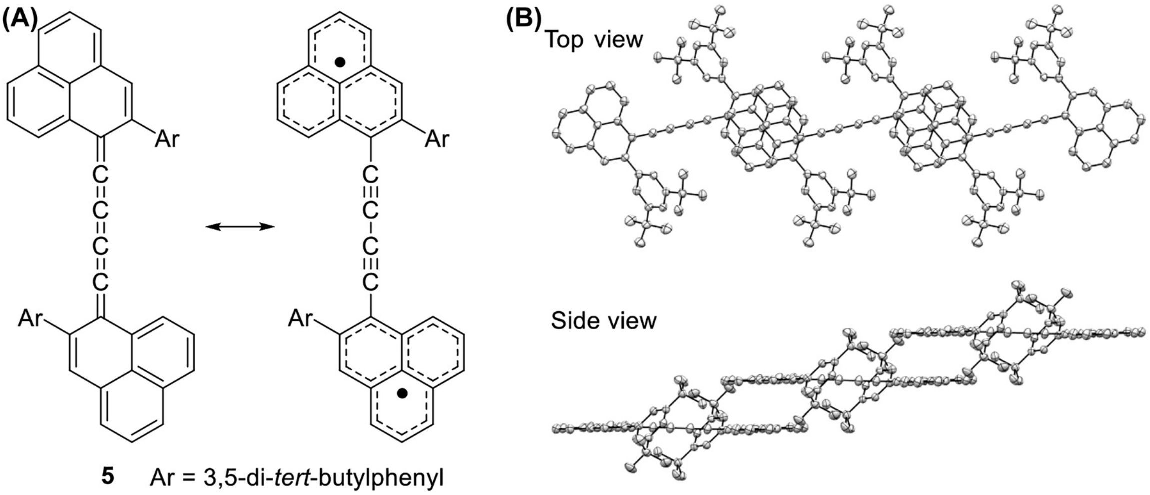


Fig. 6: Structure of **5**. (A) Resonance formula of **5**. (B) X-ray crystallographic structure of the 1D stack of **5** (CCDC-2061476, 2061477, 2061478). Hydrogen atoms are omitted for clarity.

the solution HOMO–LUMO bands owing to the coexistence of intra- and intermolecular covalent bonding interactions in the 1D stacks. However, as shown in Fig. 9C, the solid state NIR bands are observed in *higher* energy region with increasing singlet diradical character: 1440 nm for **3**, 1280 nm for **6**, and 1025 nm for 7. These higher energy shifts are derived from off-balanced relationship between intra- and intermolecular interactions. As the intramolecular interaction becomes weaker (that is, larger diradical character), the intermolecular interaction stronger. Actually, the polarized reflection spectrum measured on the (0 1 0) surface of a single crystal reveals that in the 1D chain of 7, the intermolecular interaction is much stronger than the intramolecular interaction.

Dual nature in cycloaddition reactions

Sigmarene **8**, which is *o*-quinodimethane-embedded bisphenalenyl, has substantial diradical character (y_0 = 44 %, broken symmetry UB3LYP/6-31G**). Although unpaired electrons are delocalized over the whole of the molecule, the highest spin density is found at the exo-methylene carbon atoms of the *o*-quinodimethane moiety (Fig. 10A). The dihydro precursor of the tetra-substituted derivative **9** has been prepared by a multi-step synthesis from 5-bromo-1-naphthaldehyde [112]. Dehydrogenation of this precursor with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) yields **9** as a reactive intermediate, which immediately self-dimerizes to give the doubly σ-bonded compound **10**. The two sigmarene subunits are linked by two σ-bonds at the carbon atoms having the highest spin density (Fig. 10B).

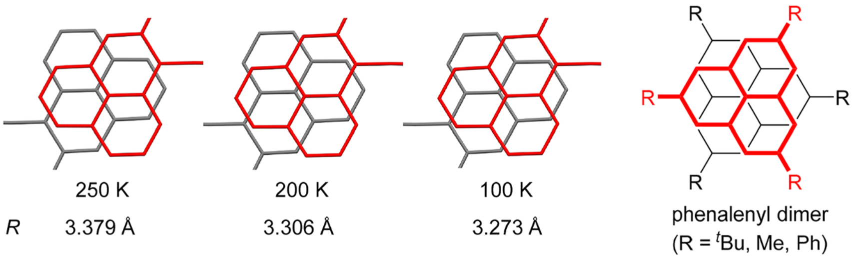


Fig. 7: Temperature dependence of the stacking motif of phenalenyl rings in the 1D chain of **5**.

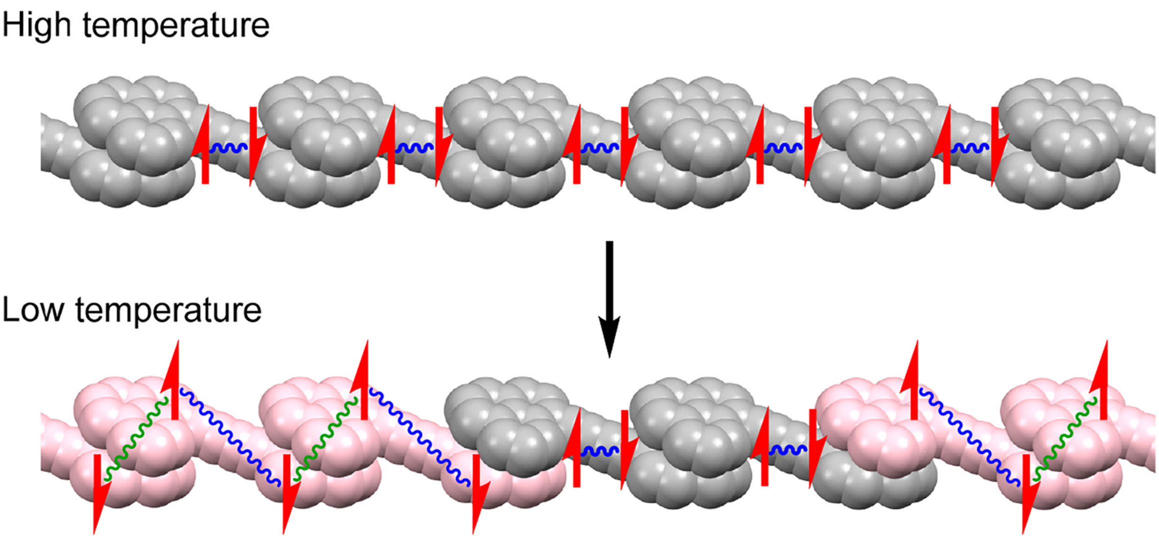


Fig. 8: Temperature dependence of spin-pairing mode in the 1D chain of **5**. Blue and green wavy lines represent intra- and intermolecular covalent bonding interactions, respectively.

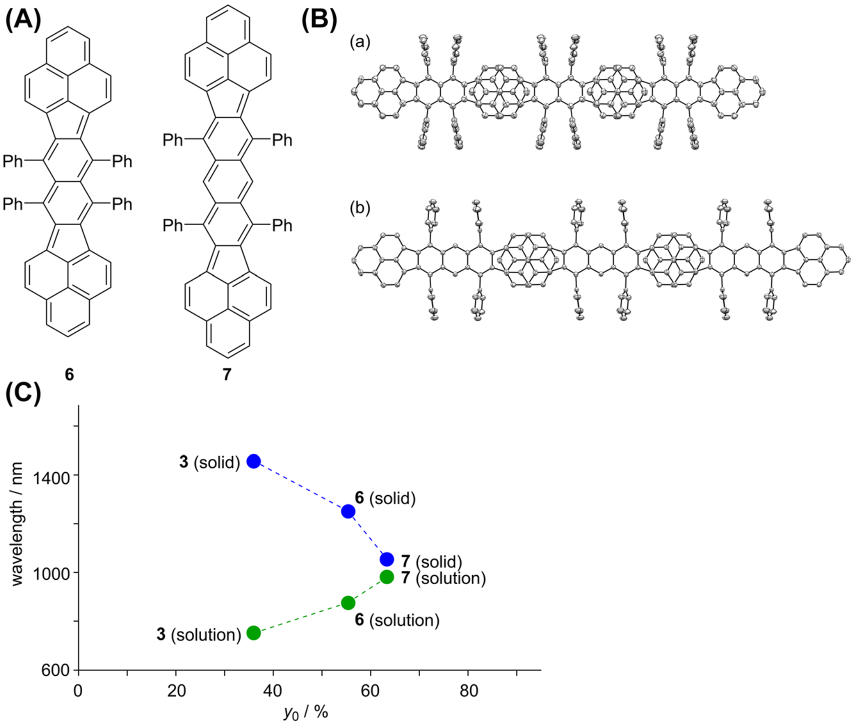
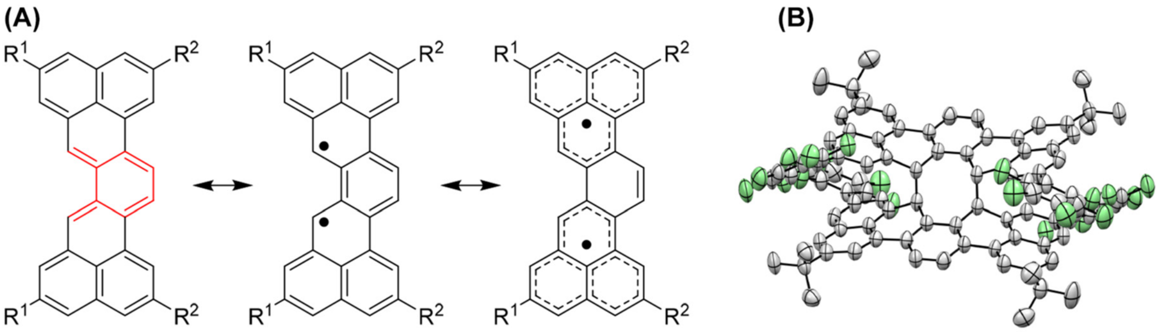


Fig. 9: Properties of **6** and **7**. (A) Structures of **6** and **7**. (B) X-ray crystallographic structures of the 1D stacks of (a) **6** (CCDC-822581) and (b) **7** (CCDC-871897). Hydrogen atoms are omitted for clarity. (C) The wavelength of the lowest energy absorption bands in solution (green) and solid (blue) states for **3**, **6**, and **7**, as a function of the singlet diradical index y_0.

The dimer **10** dissociates slightly to a monomeric species in solution at room temperature, and the reverse reaction proceeds extremely fast. The enthalpy and entropy changes associated with the dissociation reaction are determined by variable temperature UV–vis absorption measurements to be 84 ± 1 kJ mol^{-1} and



8, $R^1 = R^2 = H$
9, $R^1 = C_6F_5$, $R^2 = {}^tBu$,

10

Fig. 10: Structure of sigmarene. (A) Resonance formula of sigmarene **8** and **9**. The *o*-quinodimethane scaffold is shown in red. (B) X-ray crystallographic structure of **10** (CCDC-1974033). Hydrogen atoms are omitted for clarity.

147 ± 3 J mol^{-1} K^{-1}, respectively. Laser flash photolysis (LFP) measurements reveal that the rate constant for the dimerization reaction is 17,600 ± 300 M^{-1} s^{-1} at 294 K, and the activation enthalpy and entropy of the dimerization reaction are only 26 ± 1 kJ mol^{-1} and −78 ± 5 J mol^{-1} K^{-1}, respectively. It is noteworthy that the self-dimerization reaction occurs very rapidly even under dark conditions and at room temperature although a [4 + 4] cycloaddition reaction is thermally forbidden in the framework of the orbital symmetry rule. Furthermore, the monomer **9** is also found to undergo concerted [4 + 2] cycloaddition with fumaronitrile at room temperature in the dark, giving rise to a single stereoisomer **11**. Detailed analysis of the reaction mechanism by DFT calculations ((U)ωB97XD/6-31G**) reveals that the [4 + 4] self-dimerization reaction proceeds in a stepwise manner, whereas the [4 + 2] cycloaddition reaction prefers a concerted process. Thus, diradicaloid **9** exhibits the behavior of both a normal diene species and a diradical species. The reactivity of **9** represents the duality of the closed-shell and open-shell electronic structure of singlet diradicals (Fig. 11).

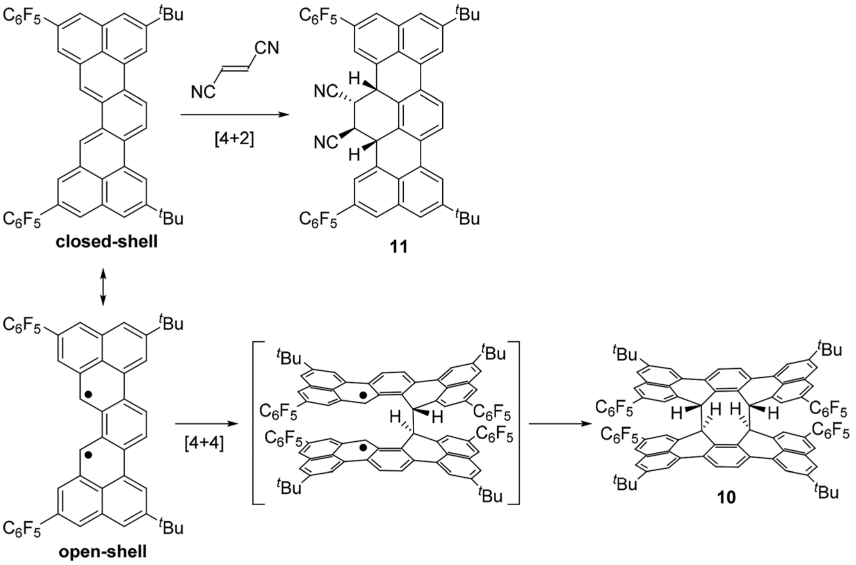


Fig. 11: Dual nature of the reactivity of **9**.

Conclusion

By investigating the behavior of singlet diradical compounds, we could determine the characteristic properties of weakly coupled electron pairs. It was found that singlet diradicals seek for a covalent bonding even between molecules due to partial dissociation of the electron pair within a molecule. Furthermore, we also demonstrated that singlet diradicals show the coexistence of intra- and intermolecular covalent bonding interactions in molecular aggregates such as dimers and one-dimensional stacks. Another prominent feature is the duality of the reactivity. Singlet diradical species were found to behave as either closed-shell or open-shell, depending on the reaction partner. We believe that these unique properties of singlet diradical compounds will expand the possibilities of π-conjugated molecular systems and lead to the development of new organic electronic materials and reaction catalysts.

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