Dual Association Modes of the 2,5,8-Tris(pentafluorophenyl)phenalenyl Radical

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Dual association modes of 2,5,8-tris(pentafluorophenyl)phenalenyl radical

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Dedicated to Professor Ichiro Murata on the occasion of his 85th birthday.

Abstract: 2,5,8-tris(pentafluorophenyl)phenalenyl radical was obtained by a straightforward synthesis in 11 steps from 2,7-dibromonaphthalene. This radical crystallized in a σ-dimer form from an acetonitrile solution and in a π-stack form from a melted liquid. The π-stack is not confined to dimerization but is extended to a one-dimensional (1D) uniform stack with an interplanar distance of 3.503 Å. This unique duality in association mode comes from thermodynamic stability of phenalenyl.

Introduction

Most organic free radicals are short-lived species and rapidly decompose through dimerization, together with disproportionation, oxidization and hydrogen abstraction. Although σ-bond formations have long been considered the most natural phenomena of dimerization, this point of view started to change, after the isolation of π-dimers of tetracyanoethylene (TCNE) radical anion [1] and 2,5,8-tri-*tert*-butyl phenalenyl (**1b**).[2] This new mode of dimerization invokes the term "multicenter bonding [3] (pancake bonding) [4]" for the description of the structure, which is characterized by attractive interactions derived from a covalent bonding interaction of two unpaired electrons as well as a dispersion force.

Phenalenyl is a hydrocarbon radical that is thermodynamically stabilized by the delocalization of an unpaired electron over six equivalent carbon atoms. However, the parent phenalenyl (**1a**) has not been isolated yet in a pure form because of its kinetic instability. It is believed that **1a** forms a σ-bond (2e/2c bonding) to give a σ-dimer, by spectroscopic [5] and product analyses.[6] On the other hand, the introduction of *tert*-butyl groups at 2,5,8-positions (**1b**) leads to another dimerization mode, π-dimer,[2,7] where unpaired electrons couple covalently by 2,000 K [8] through a twelve-center SOMO–SOMO overlap (2e/12c bonding). Thus, phenalenyl is a peculiar radical that shows the bimodal (σ and π) in dimerization.[9] This raises questions about that chemical modification on phenalenyl can lead to other association modes, which is associated with exploring the chemical bonding interactions of organic radicals.

1a: R = H
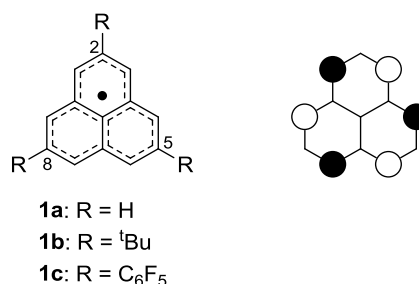**1b**: R = ^{t}Bu
1c: R = C$_6$F$_5$

Figure 1. (Left) Structure of phenalenyls (**1a–c**) and (right) SOMO of phenalenyl.

Here we report the synthesis and association modes of a new phenalenyl radical having three pentafluorophenyl (C$_6$F$_5$) groups at 2,5,8-positions (**1c**). In the solid state, **1c** shows both σ and π modes, which are confirmed by X-ray crystallographic analysis. The π mode is not confined to dimerization but is extended to a one-dimensional (1D) stack, where a relatively wide half-filled band is formally formed through a consecutive multicenter bonding interaction. The C$_6$F$_5$ groups of **1c** effectively suppress an excessive contact between

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spin-bearing moieties, resulting in a uniform stack of the radical at temperatures down to 10 K.

Results and Discussion

Synthesis and Characterization of σ-Dimer of 1c

The C_6F_5 substituents are attached at the carbon atoms that are a node of the SOMO as shown in Figure 1, and therefore, the SOMO never distributes on the C_6F_5 groups. Scheme 1 shows the synthetic route to **1c**. The target radical **1c** was synthesized from 2,7-dibromonaphthalene **2** in 11 steps. Two C_6F_5 groups were introduced by Suzuki–Miyaura coupling. After formylation, the aldehyde **3** was converted to unsaturated ester **4** by Horner–Emmons reaction. The ester **6**, obtained by hydrogenation of **5** in ambient pressure, was hydrolyzed in basic condition. The Friedel–Crafts cyclization at low temperature of the acid chloride derived from **7** gave phenalanone **8**, and third pentafluorophenyl group was introduced by nucleophilic aromatic substitution. The key precursor, phenalene **11**, was obtained by the reduction of **9** and subsequent dehydration.
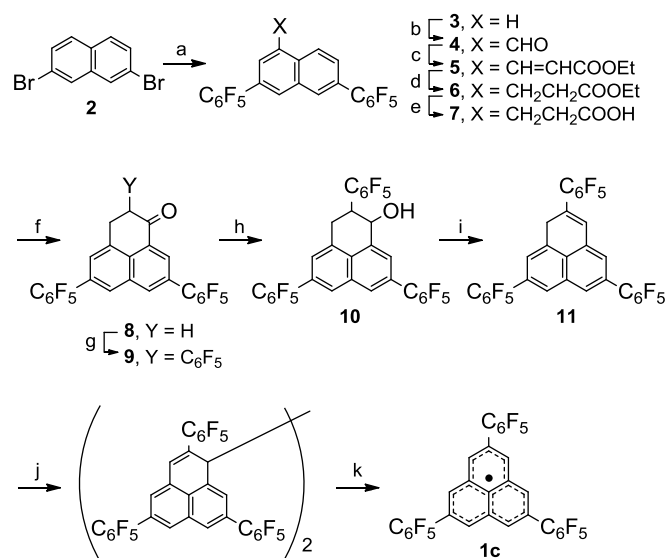
Scheme 1. Synthetic route to 1c. a) $C_6F_5B(OH)_2$, $Pd_2(dba)_3$, $^tBu_3P$, CsF, Ag_2O, DMF, 100 °C, 52%; b) $CHCl_2OCH_3$, $AlCl_3$, CH_2Cl_2, −78 to −40 °C, 81%; c) $(EtO)_2POCH_2COOEt$, NaH, THF, rt, quant.; d) H_2, Pd-C, CH_2Cl_2, EtOH, rt, quant.; e) NaOH aq., THF, 50 °C, quant.; f) (1) $(COCl)_2$, (2) $AlCl_3$, CH_2Cl_2, −78 to −40 °C, 86%; g) C_6F_6, NaH, THF, 65 °C, 60%; h) $NaBH_4$, CH_2Cl_2, EtOH, rt, 81%; i) p-TsOH, toluene, 120 °C, 93%; j) DDQ, toluene, 80 °C, 90%; k) Melting at 300 °C and then cooling in a degassed tube.

Treatment of **11** with dichlorodicyano-p-benzoquinone (DDQ) gave colorless crystals, which were identified as a σ-dimer of **1c** by X-ray crystallographic analysis (Figure 2). It is notable that this X-ray analysis is the first structural characterization of a σ-dimer of electronically-unperturbed phenalenyl. The σ-dimer features a long σ-bond (1.636(7) Å) connecting two phenalenyl rings, implying the weakness of the σ-bond. Indeed, a toluene solution of the σ-dimer at room temperature showed a well-resolved multiline ESR spectrum corresponding to **1c**, and therefore, **1c** and its σ-dimer exist as an equilibrium mixture in the solution state. The ESR signals decreased in the intensity with decreasing temperature and almost disappeared at 230 K. The enthalpy and entropy changes for σ-dimerization of **1c** were determined to be −64.0 kJ mol^{-1} and −135 J K^{-1} mol^{-1}, respectively, by variable temperature ESR measurements (Figure S1).

The enthalpy change of **1c** is found to be larger than that of the parent phenalenyl radical (−41 kJ mol^{-1}),[10] indicating higher propensity of **1c** to σ-dimerization. This is probably due to a face-to-face attractive interaction between the C_6F_5 group and the phenalenyl ring. Figure 3 shows the observed and simulated ESR spectra of **1c** along with the proton and fluorine hyperfine coupling constants (HFCCs). The spin density map shown in Figure 3d indicates that an unpaired electron mostly resides on the phenalenyl ring while the C_6F_5 groups bear quite small spin densities.
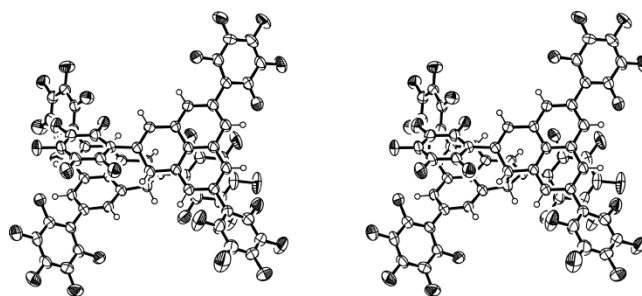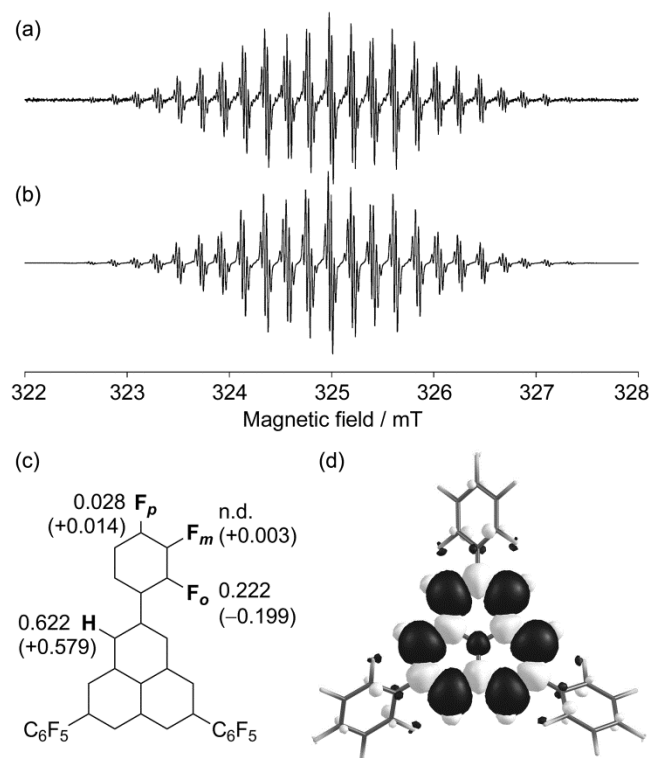
Figure 2. The ORTEP drawing (stereo view) of the σ-dimer of **1c** with thermal ellipsoids at 50 % probability.

Figure 3. a) Observed ($g = 2.0027$, at room temperature) and b) simulated ESR spectra of **1c**; c) Determined HFCCs (in mT) of **1c**. HFCC of *meta*-fluorine (F_m) could not be determined. In parentheses, HFCCs calculated with a UBLYP/6-31G**//UB3LYP/6-31G** method are shown; d) Spin density map calculated with a UBLYP/6-31G**//UB3LYP/6-31G** method. Black and white surfaces represent α and β spin densities drawn at 0.0005 e/au^3 level, respectively.

^{1}H NMR spectrum of the σ-dimer in CDCl$_3$ showed six singlet peaks at 298 K (Figure 4). The signals were relatively broad, while upon cooling line sharpening was observed (Figure S2). No peak corresponding to a π-dimer was observed in the temperature range of 233 − 298 K. The σ-dimer of phenalenyl potentially has three stereoisomers, *RS* (meso) and *RR/SS* (chiral) at the σ-bonded carbons,

2

as shown in Figure 5. The X-ray structure of the σ-dimer of **1c** suggests that the species observed in the ^{1}H NMR spectrum is a racemic mixture of the *RR* and *SS* isomers.
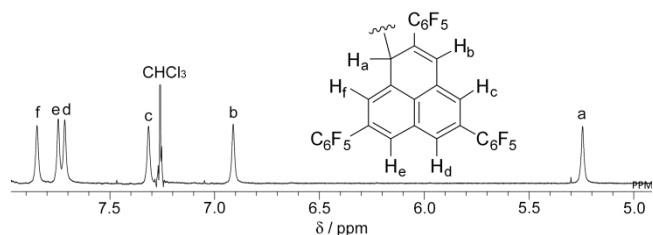

Figure 4. ^{1}H-NMR spectrum (500 MHz) of **1c** in CDCl$_3$ (5 mM) at 298 K. Assignment of the signals are based on NOESY and COSY measurements (Figure S3).
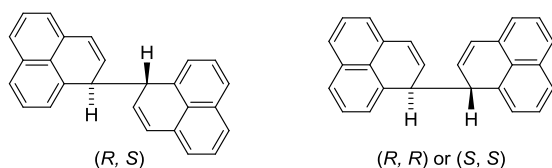

Figure 5. Stereoisomers of the σ-dimer of phenalenyl. (Left) *meso*- and (right) chiral form. For the chiral form, one of the enantiomers is shown.

Preparation and Characterization of 1D Uniform π-Stack of 1c

Heating at 573 K of a powdered σ-dimer in a sealed degassed tube resulted in melting accompanied by a color change from colorless to purple, and subsequent cooling the purple liquid gave dark purple needles suitable for X-ray crystallographic analysis. The X-ray measurement at 10 K showed the distinctive feature that the radical **1c** forms a 1D chain with an equidistant stack (3.6467(4) Å) of the molecule, as shown in Figure 6. [11] In the 1D chain, **1c** adapts an eclipsed stacking motif (that is, fully superimposed stacking motif), in contrast to a staggered stacking motif (that is, 60° rotated stacking motif) found in 2,5,8-tri-*tert*-butyl phenalenyl dimer.[2] Each 1D chain is surrounded by six adjacent chains (Figure 6c) and the linking between the chains would be derived from a weak C–H•••F–C hydrogen bonding interaction.[12] The C$_6$F$_5$ groups serve as buffers to keep neighboring radical moieties apart, and consequently, magnetic interactions between the chains would remain minimal. The extended Hückel molecular orbital (EHMO) band structure calculation [13] supports this idea, because the calculation on the crystal structure gave a relatively large dispersion for SOMO bands along the stacking axis (*a*-axis), while no dispersion perpendicular to the stacking axis (Figure S4).

A 1D chain of organic radicals is prone to the first-order spin-Peierls transition,[14] which is intrinsic lattice instability (that is, dimerization) in spin-1/2 antiferromagnetic Heisenberg chains. The high tolerance of **1c** to the first-order spin-Peierls transition relies on two structural factors of the C$_6$F$_5$ substituent groups; a slipped stacking arrangement (Figure 7b) and a twisted conformation with respect to the phenalenyl ring (Figure 7c). Polyfluorinated phenyl rings prefer a slipped face-to-face overlap,[15] in which an attractive force (electrostatic and dispersion) and a repulsive force (exchange repulsion) are well balanced.[16] The C$_6$F$_5$ groups of **1c** also stack in a slipped manner in the 1D chain and the interplanar distances (*d'* in Figure 7c) between the C$_6$F$_5$ groups are quite short; 3.223, 3.241, and 3.291 Å (3.252 Å on average). The C$_6$F$_5$ groups are twisted by 33.25,

38.70, and 42.44° (38.13° on average) with respect to the phenalenyl ring due to the steric repulsion between *ortho*-fluorine atoms and hydrogen atoms. As shown in Figure 7d, in case of the slipped stacking of the C$_6$F$_5$ groups, the interplanar distance (*d* in Figure 7c) between the phenalenyl rings is identical to *d'* when the C$_6$F$_5$ group adopts a parallel conformation, while twisting the C$_6$F$_5$ group leads to *d* > *d'* under the condition of the same *d'*. The interplay of the C$_6$F$_5$ groups between the slipped stacking and the twisted conformation suppresses an excessive contact between phenalenyl rings. As a result, the phenalenyl rings uniformly stack with the interplanar distance (*d*) of 3.503 Å in a space surrounded by three closely stacked C$_6$F$_5$ columns. Thus, three C$_6$F$_5$ groups attached to the phenalenyl ring play a crucial role to control the structure of the 1D chain.
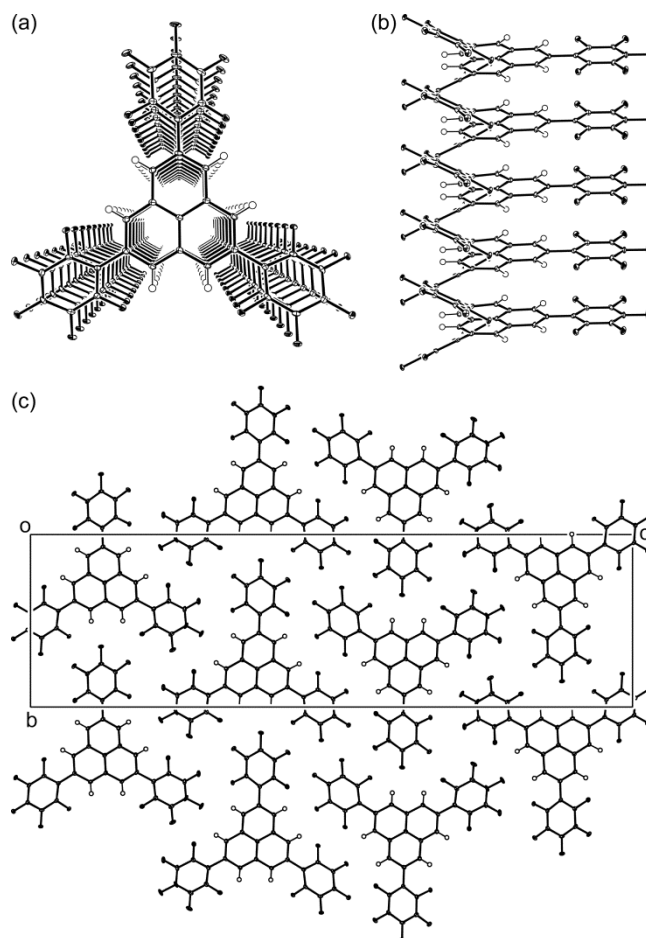

Figure 6. a) Top view and b) side view of the 1D chain of **1c**; c) Packing diagram of **1c** in the (1 0 0) plane (*bc*-plane). All the molecules are crystallographically equivalent and stack along the [1 0 0] direction (*a*-axis).

In the 1D chain, the SOMO of **1c** almost perfectly overlaps between neighboring molecules. This large SOMO−SOMO overlap suggests that the electronic structure of the 1D chain can be described by a delocalized electron band based on a consecutive multicenter covalent bonding interaction. Indeed the powder of **1c** showed a new intense absorption band at 777 nm that was not found in the monomer spectrum (Figure S5). The EHMO (single zeta basis set) calculation gives a half-filled band with a relatively large bandwidth of 0.29 eV in the stacking direction, as mentioned above, suggesting a potential metallic behavior. The electrical conductivity of a compressed pellet of the purple **1c** was measured by a two-probe method. However, room temperature conductivity was less than 10^{-10} S cm^{-1}. A widely

accepted criterion for a metallic behavior is a U/W value < 1, where U is on-site Coulomb repulsion energy and W is bandwidth. We obtained U of 1.66 eV and W of 0.29 eV from the cyclic voltammetry (Figure S6) and the EHMO band calculation, respectively. Due to a large U/W value **1c** becomes a Mott–Hubbard insulator.
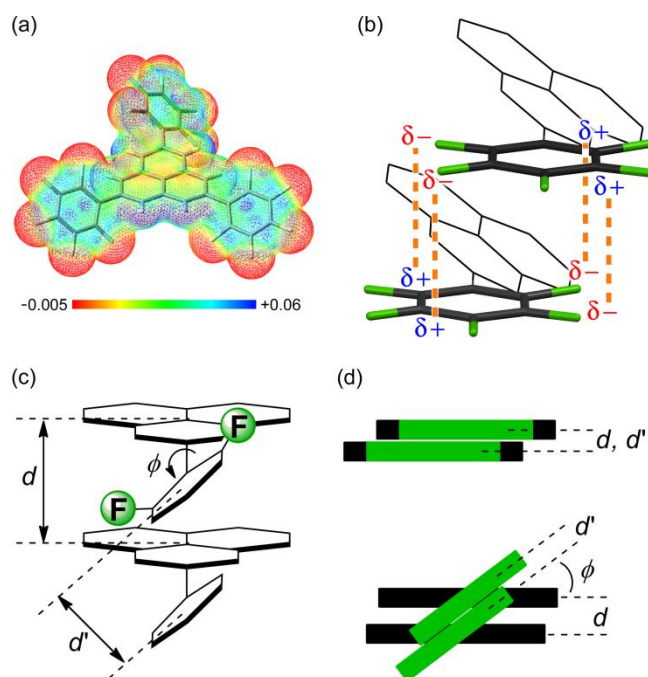

Figure 7. a) Electrostatic potential map of **1c** calculated at the UB3LYP/6-31G** level; b) Electrostatic interaction (orange dashed lines) between C_6F_5 groups in the 1D chain of **1c**. Some C_6F_5 groups and hydrogen atoms are omitted for clarity; c) Interplanar distances between phenalenyl rings (d) and between C_6F_5 groups (d') in the 1D chain. ϕ is the twist angle of the C_6F_5 group; d) Schematic drawings of side views of the stack of **1c** with different ϕs. Green and black lines represent C_6F_5 groups and phenalenyl rings, respectively. (upper) Parallel and (lower) twisted conformations of C_6F_5 rings.

Magnetic Property of the 1D π-Stack

The magnetic property of the purple **1c** was measured by a SQUID magnetometer at 2–380 K. The magnetic susceptibility (χ) vs. T plot is shown in Figure 8. The χ values exhibit a continuous decrease upon cooling from 380 K followed by a minimum at 70 K. Below 70 K, the χ values rapidly increases with decreasing temperature, which is presumably due to the presence of paramagnetic impurities or chain breaks induced by defects. We tried to fit the χ curve to a uniform antiferromagnetic spin-1/2 Heisenberg chain model (namely, a Bonner−Fisher model)[17] modified with inter-chain magnetic interactions (zJ') in the framework of the mean-field approximation [18] and with a finite chain model developed by Mila et al. [19] for the treatment of paramagnetic species. Actually, the best fit was obtained with the following parameters; $J/k_B = -279$ K,[20] $zJ'/k_B = +908$ K, N_0 (the average length of the finite chain) = 10.8 (the fitted curve is shown in Figure S7). However, we found that the inter-chain magnetic interaction (zJ') is unrealistically large because each 1D radical chain is well separated by the C_6F_5 groups that have quite small spin densities. We suspected that the 1D chain in fact might consist of π-stacks with alternating large and small spacing because the χ curve could also be fitted by adopting an alternating antiferromagnetic spin-1/2 Heisenberg chain model [21] with parameters of $J_1 = -327$ K, $J_2 = -147$ K, and ρ (a defect concentration) = 4.0% (Figure S8). However, we could not find any evidence of π-stack dimerization from X-ray diffuse scattering patterns (Figure S9).

For understanding the magnetic behavior, further analyses should be made with the aid of calorimetric measurements [22] and quantum mechanical calculations, because second-order or higher-order phase transitions might take place in the 1D chain.
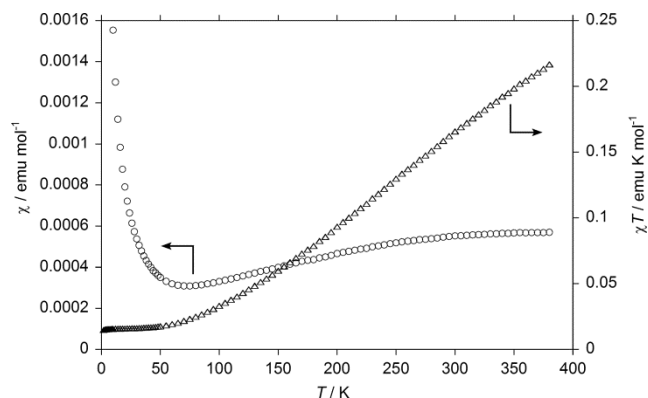

Figure 8. Temperature dependence of χ and χT measured on powdered **1c** at 1 T. Open circles and open triangles correspond to measured χ and χT, respectively.

Conclusion

In conclusion, a pentafluorophenyl-substituted phenalenyl radical showed the bimodal (σ and π) in association mode. For the π mode, a consecutive multicenter bonding interaction leads to electron delocalization in a 1D uniform stack of the radical and a covalent bonding interaction comes to ca. 600 K (= $2|J|/k_B$). High thermodynamic stability of phenalenyl diminishes the stability of a σ-dimer, while its planar structure gives adequate stabilization to π-associations due to a multicenter bonding interaction, resulting in a small energy difference between σ and π-modes. This implies that chemical modification of phenalenyl gives an opportunity for a variety of associations (for instance, π-trimer), which will open up new avenues for fundamental understanding of chemical bonds and magnetic material use. The work based on this idea is currently in progress in our laboratories.

Experimental Section

2,7-Bis(perfluorophenyl)naphthalene (3)

A 100 mL round bottom flask was charged with 2,7-dibromonaphthalene **2** (0.90 g, 3.1 mmol), pentafluorophenylboronic acid (1.7 g, 7.8 mmol) , silver(I) oxide (0.88 g, 3.8 mmol) , cesium fluoride (1.3 g, 8.8 mmol) , and DMF (30 mL) under nitrogen atmosphere. To the reaction mixture was added tris(dibenzylideneacetone)dipalladium (0.15 g, 0.17 mmol) and a solution of tri-*tert*-butylphosphine in hexane (0.35 M, 1.1 mL) . The reaction mixture was heated at 90 ℃ for 7 days. The resulting mixture was cooled to room temperature and precipitate was filtered out. The filtrate was extracted with dichloromethane. The organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (hexane) to give a **3** as a colorless solid (0.75 g, 52%). mp 147–148 ℃; R_f = 0.33 (hexane); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.98 (s, 2H), 7.68–7.56 (m, 2H); IR (KBr) ν = 1526 (s), 1515 (m), 1493 (s), 1408 (w), 1340 (w), 1067 (m), 998 (s), 957 (w), 913 (m), 847 cm^{-1} (m); EI-MS *m/z* 460 (M$^+$); Anal. Calcd for C$_{22}$H$_6$F$_{10}$: C, 57.41; H, 1.31. Found: C, 57.15; H, 1.45.

3,6-bis(perfluorophenyl)-1-naphthaldehyde (4)

Dichloromethyl methyl ether was added to a solution of **3** (0.50 g, 1.1 mmol) in dichloromethane (50 mL) at –78 ℃ under nitrogen atmosphere. To the solution was added aluminium chloride (0.54 g, 4.0 mmol). The reaction mixture was warmed gradually to – 40 ℃ and stirred for 3 h. The reaction was quenched with hydrochloric acid and extracted with dichloromethane. The organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (dichloromethane/hexane 1:1) to give **4** as a colorless solid (0.43 g, 81%). mp 172–173 ℃; R_f = 0.59 (dichloromethane/hexane 1:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 10.46 (s, 1H), 9.42 (d, *J* = 8.8 Hz, 1H), 8.24 (s, 1H), 8.11– 8.09 (m, 1H), 8.08 (s, 1H), 8.03–7.78 (m, 1H); IR (KBr) ν = 1703 (s), 1651 (w), 1526 (s), 1513 (m), 1493 (s), 1081 (s), 1056 (w), 996 (m), 971 (m), 940 (w), 840 cm^{-1} (m); EI-MS *m/z* 488 (M$^+$); Anal. Calcd for C$_{23}$H$_6$F$_{10}$O: C, 56.58; H, 1.24. Found: C, 56.49; H, 1.47.

(*E*)-Ethyl 3-(3,6-bis(pentafluorophenyl)naphthalen-1-yl)acrylate (5)

A 100 mL round bottom flask was charged with 60% sodium hydride (60 mg, 1.6 mmol) and THF (15 mL) under nitrogen atmosphere. To the suspension was added triethyl phosphonoacetate (0.31 mL, 1.6 mmol) and stirred for 10 min. The solution of **4** (0.64 g, 1.3 mmol) in THF (35 mL) was added to the reaction mixture and stirred at room temperature for 45 min. The reaction was quenched with aqueous ammonium chloride and extracted with ether. The organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (dichloromethane/hexane 1:1) to give **5** as a colorless solid (0.73 g, 99%). mp 134–135 ℃; R_f = 0.48 (dichloromethane/hexane 1:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.51 (d, *J* = 15.9 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 8.02 (s, 2H), 7.82 (s, 1H), 6.57 (d, *J* = 15.6 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); IR (KBr) ν = 3083 (w), 2989 (w), 2906 (w), 1730 (s), 1651 (m), 1637 (m), 1524 (s), 1496 (s), 1445 (w), 1369 (m), 1314 (m), 1267 (m), 1181 (m), 1086 (m), 1071 (m), 1046 (m), 993 (s), 979 (s), 908 (w), 871 (w), 835 cm^{-1} (m); EI-MS *m/z* 558 (M$^+$); Anal. Calcd for C$_{27}$H$_{12}$F$_{10}$O$_2$: C, 58.08; H, 2.17. Found: C, 57.98; H, 2.25.

Ethyl 3-(3,6-bis(pentafluorophenyl)naphthalen-1-yl)propanoate (6)

A solution of **5** (0.73 g, 1.3 mmol) in a mixed solvent of dichloromethane (6 mL) and ethanol (60 mL) was hydrogenated over 10% Pd/C (80 mg) under hydrogen atmosphere for 3 h at room temperature. Pd/C was filtered out and the filtrate was evaporated. The residue was purified by column chromatography on silica gel (dichloromethane/hexane 1:1) to give **6** as a colorless solid (0.72 g, 99%). R_f = 0.48 (dichloromethane/hexane 1:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.20 (d, *J* = 8.8 Hz, 1H), 7.99 (s, 1H), 7.87 (s, 1H), 7.47 (d, *J* = 1.2 Hz, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.51 (t, *J* = 8.2 Hz, 2H), 2.81 (t, *J* = 7.2 Hz, 2H); IR (KBr) ν = 2986 (w), 1735 (m), 1651 (w), 1524 (s), 1494 (s), 1179 (w), 1081 (m), 992 (s), 971 (w), 911 (w), 833 cm^{-1} (m); HRMS (ESI, positive): m/z Calcd for C$_{27}$H$_{14}$O$_2$F$_{10}$: 560.0829 [M$^+$]; found: 560.0836.

3-(3,6-Bis(pentafluorophenyl)naphthalen-1-yl)propionic acid (7)

10% aqueous sodium hydroxide (25 mL) was added to a solution of **6** (0.72 g, 1.3 mmol) in THF (40 mL). The reaction mixture was heated at 50 ℃ and stirred for 24 h. The reaction was acidified with hydrochloric acid and extracted with ether. The organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. The filtrate was evaporated to give **7** as a colorless solid (0.69 g, 100%). mp 196–197 ℃; R_f = 0.36 (ethyl acetate/hexane 1:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.20 (d, *J* = 9.0 Hz, 1H), 8.00 (s, 1H), 7.88 (s, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.48 (s, 1H), 3.52 (t, *J* = 8.1 Hz, 2H), 2.89 (t, *J* = 8.1 Hz, 2H); IR (KBr) ν = 3099 (br), 1721 (m), 1651 (w), 1524 (s), 1496 (s), 1178 (w), 1088 (m), 1065 (m), 991 (m), 918 (w), 829 cm^{-1} (m); EI-MS *m/z* 532 (M$^+$); Anal. Calcd for C$_{25}$H$_{10}$F$_{10}$O$_2$: C, 56.41; H, 1.89. Found: C, 56.63; H, 2.18.

5,8-Bis(pentafluorophenyl)-2,3-dihydro-1*H*-phenalen-1-one (8)

A solution of **7** (0.69 g, 1.3 mmol) in oxalyl chloride (30 mL) was heated at 60 ℃ for 14 h. After removal of excess oxalyl chloride under reduced pressure, the residue was dissolved in dichloromethane (40 mL), and then to the solution cooled to –78 ℃ aluminium chloride (1.0 g, 7.5 mmol) was added. The reaction mixture was warmed to – 40 ℃ and stirred for 3 h. The reaction was quenched with hydrochloric acid and extracted with dichloromethane. The organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (dichloromethane/hexane 1:1) to give **8** as a colorless solid (0.60 g, 92%). mp 178–179 ℃; R_f = 0.32 (dichloromethane/hexane 1:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.29 (d, *J* = 1.6 Hz, 1H), 8.21 (d, *J* = 1.2 Hz, 1H), 7.95 (s, 1H), 7.57 (d, *J* = 1.2 Hz, 1H), 3.55 (t, *J* = 7.0 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 2H); IR (KBr) ν = 2967 (w), 1702 (m), 1651 (w), 1524 (s), 1495 (s), 1436 (w), 1416 (w), 1336 (m), 1135 (w), 1092 (m), 1078 (w), 1085 (w), 988 (m), 913 cm^{-1} (w); EI-MS *m/z* 514 (M$^+$); Anal. Calcd for C$_{25}$H$_8$F$_{10}$O: C, 58.38; H, 1.58. Found: C, 58.16; H, 1.67.

2,5,8-Tris(pentafluorophenyl)-2,3-dihydro-1*H*-phenalen-1-one (9)

A 50 mL round bottom flask was charged with **8** (0.60 g, 1.2 mmol), 60% sodium hydride (1.0 g, 25 mmol) and hexafluorobenzene (3.0 mL, 25 mmol) under nitrogen atmosphere. To the suspension THF (40 mL) was added and heated at 60 ℃ for 1 h. After cooling, the reaction was quenched with water and extracted with ether. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (dichloromethane/hexane 1:2) and recrystallized from ethanol to give **9** as a colorless solid (0.48 g, 60%). mp 212.5–213.9 ℃; R_f = 0.62 (dichloromethane:hexane = 1:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.37 (d, *J* = 1.6 Hz, 1H), 8.28 (s, 1H), 8.02 (s, 1H), 7.60 (s, 1H), 4.75 (dd, *J* = 13.8 Hz, 6.4 Hz, 1H), 4.02 (t, *J* = 14.7 Hz, 1H), 3.63 (dd, *J* = 15.9 Hz, 5.7 Hz, 1H); IR (KBr) ν = 2932 (w), 1710 (m), 1655 (w), 1524 (s), 1496 (s), 1441 (w), 1415 (w), 1306 (w), 1249 (w), 1117 (m), 1087 (m), 1074 (m), 1054 (w), 1006 (m), 987 (m), 953 (m), 917 cm^{-1} (w); EI-MS *m/z* 680 (M$^+$); Anal. Calcd for C$_{31}$H$_7$F$_{15}$O: C, 54.73; H, 1.04. Found: C, 54.75; H, 0.86.

2,5,8-Tris(pentafluorophenyl)-2,3-dihydro-1*H*-phenalen-1-ol (diastereomer mixture) (10)

Sodium borohydride (32 mg, 0.84 mmol) was added to a solution of **9** (0.48 g, 0.70 mmol) in dichloromethane (10 mL) and ethanol (10 mL) under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with aqueous ammonium chloride and extracted with dichloromethane. The organic layer was washed with water and brine, and dried over anhydrous sodium sulfate. The filtrate was evaporated and the residue was purified by column chromatography on hydrous (6%) silica gel (dichloromethane/hexane 1:1) to give **10** as a pale yellow powder (0.39 g, 81%). R_f = 0.42 (dichloromethane/hexane 1:1). ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.02 (s, 1H), 7.95 (s, 1H), 7.91-7.89 (m, 3H), 7.60 (s, 1H), 7.49 (s, 1H), 7.38 (s, 1H), 7.18-7.16 (m, 2H), 5.56 (d, *J* = 9.3 Hz, 1H), 5.12 (s, 1H), 4.37 (t, *J* = 14.7 Hz, 1H), 3.94-3.74 (m, 3H), 3.35-3.27 (m, 2H); IR (KBr) ν = 3435 (br), 2936 (w), 1654 (w), 1524 (s), 1496 (s), 1441 (w), 1415 (w), 1386 (w), 1316 (w), 1098 (w), 1053 (m), 989 (s), 955 (m), 945 cm^{-1} (w); HRMS (ESI, positive): m/z Calcd for C$_{31}$H$_9$OF$_{15}$: 682.0431 [M$^+$]; found: 682.0417.

2,5,8-Tris(pentafluorophenyl)-1*H*-phenalene (11)

p-Toluenesulfonic acid monohydrate (3 mg, 0.016 mmol) was added to a solution of diastereomer mixture of **10** (32 mg, 0.047 mmol) in toluene (7 mL) and heated at 120 ℃ for 40 min under nitrogen atmosphere. The reaction mixture was cooled at 0 ℃ and then the solution diluted with hexane (28 mL) was filtered rapidly on hydrous (6%) silica gel to give **11** as a colorless powder (29 mg, 93%). R_f = 0.81 (dichloromethane/hexane 1:2). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.74 (s, 2H), 7.39 (s, 1H), 7.19 (s, 1H), 6.82 (s, 1H), 4.38 (s, 2H); IR (KBr) ν = 1650 (w), 1602 (w), 1579 (w), 1523 (s), 1491 (s), 1421 (w), 1385 (w), 1318 (w), 1115 (w), 1093 (w), 1055 (w), 992 (s), 942 (w), 907 (w), 814 cm^{-1} (w); EI-MS *m/z* 664 (M$^+$); Anal. Calcd for C$_{31}$H$_7$F$_{15}$: C, 56.04; H, 1.06. Found: C, 56.09; H, 0.93.

Tris(pentafluorophenyl)phenalenyl σ-dimer (σ-dimer of 1c)

A solution of **11** (57 mg, 0.086 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (11 mg, 0.048 mmol) in toluene (11 mL) was heated at 80 ℃ for 30 min under nitrogen atmosphere. After cooled in an ice bath, the solution was diluted with hexane (15 mL) and filtered rapidly on hydrous (6%) silica gel to give a σ-dimer of **1c** as a pale yellow solid (54 mg, 90%). R_f = 0.78 (dichloromethane:hexane = 1:1); IR (KBr) ν = 1652 (w), 1523 (s), 1494 (s), 1442 (w), 1409 (w), 1387 (w), 1318 (m), 1115 (w), 1091 (m), 1063 (m), 1023 (w), 990 (s), 948 (m), 909 (m), 814 cm^{-1} (m); EI-MS *m/z* 663 (M$^+$/2).

2,5,8-Tris(pentafluorophenyl)phenalenyl (1c)

A quartz tube (8 mm ϕ) was charged with powdered σ-dimer of **1c** and was sealed under reduced pressure (~10^{-3} Pa). The tube was heated by a heat gun until the powdered sample melted. The gradual cooling at room temperature gave dark purple needles of **1c**.

Acknowledgements

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Entry for the Table of Contents (Please choose one layout only)

Dual association modes

Ar = C_6F_5

σ-mode   π-mode

Pentafluorophenyl-substituted phenalenyl radical is isolated. In the solid state this radical shows dual association modes; σ-dimer and one-dimensional uniform π-stack.