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Aryl−Perfluoroaryl Substituted Tetracene: Induction of Face-to-Face $\pi-\pi$ Stacking and Enhancement of Charge Carrier Properties

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S Supporting Information

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Control of molecular ordering and packing of π-conjugated molecules in the solid state in order to enhance their charge transport properties is critical for organic electronics.[1] For instance, the use of bulky substituents to control the packing density of π-conjugated compounds is an effective means of tuning the electronic interaction between molecules. This has been demonstrated with bulky trialkylsilylethynyl-substituted pentacenes, end-group-substituted oligothiophenes, halogenated perylene diimide derivatives, and so on.[2] These approaches to crystal engineering have resulted in high-performance organic field-effect transistors (OFETs).

Herein we report an efficient method for control of molecular packing, as illustrated in Figure 1. We chose a simple tetracene core substituted with aryl (Ar) and perfluoroaryl (FAr) groups at the 5- and 11-positions as a demonstration of concept (Figure 1a). Regarding our molecular design, we hypothesized that the Ar and FAr substituents would induce not only an Ar−FAr interaction[3] (face-to-face stacking, Figure 1b) but also a supporting C−H···F interaction (short lateral distance, Figure 1b,c) between neighboring molecules.[4] Thus, it can be expected that such "strong, complementary" interactions will lead to a well-defined $\pi-\pi$ stacking structure of charge transporting units (Figure 1c). We also disclose the photoconductivity and charge carrier mobility of the compound to discuss the validity of the concept.

In detail, phenyl and perfluorophenyl substituents were selected for the following reasons: (1) Quadrupole moment: Because phenyl and perfluorophenyl groups each have a large, permanent quadrupole moment with similar magnitude and opposite sign,[5] the quadrupole moments are expected to effectively offset each other; thus, these groups do not interrupt charge transport and can serve as charge transport units. (2) Electronic effect: Despite acene−FAr bonds being twisted because of steric hindrance, an electron-deficient FAr substituent on an electron-rich acene should slightly decrease the HOMO and LUMO energies, thus improving chemical stability. To this end, we synthesized 5-perfluorophenyl-11-phenyltetracene (FPPT), together with 5,11-diphenyltetracene (PPT) as a reference compound for comparison (Scheme 1).

FPPT was synthesized in three steps starting from commercially available tetracene, as shown in Scheme 1. Dibromination of tetracene was performed using a previously reported method.[6] The Suzuki−Miyaura coupling reaction[7] of sterically hindered 5,11-dibromotetracene with phenylboronic acid was successfully carried out using tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), bis(2-diphenylphosphinophenyl)ether (DPEphos), and K_2CO_3 in a mixture of toluene and ethanol to obtain monosubstituted 5-bromo-11-phenyltetracene (BrPT) in 57% yield, together with PPT in 18% yield. The perfluorophenyl group was introduced by perfluoroarylation[8] of BrPT to afford the target compound (FPPT) in 78% yield. FPPT showed good solubility in most chlorinated organic solvents as well as in THF and toluene, which makes it a promising candidate for solution-processable devices.

The cyclic voltammograms of FPPT and PPT in dichloromethane showed reversible one-electron reduction and one-electron oxidation (Table S1 and Figure S1 in the Supporting Information). The half-wave potentials for reversible oxidation and reduction of FPPT were found to be 0.18 and 0.15 V higher than those of PPT, respectively. These observations were in good agreement with the results from DFT calculation (Figure S2 in the Supporting Information). These results suggest that both the oxidized and reduced species of these compounds are stable in solution and that one perfluorophenyl group could successfully lower the HOMO and LUMO levels.

Stability under ambient conditions is also an important criterion for organic semiconductors. We evaluated the stability of FPPT by UV−vis spectroscopy in chloroform, under white-light illumination in air (Figures S3 and S4 in the Supporting Information). FPPT was found to have the highest stability among investigated compounds: its half-life was six-, six-, and twofold longer than that of PPT, rubrene, and tetracene, respectively. This observation indicates that the electron-withdrawing perfluorophenyl group is a useful moiety for improving the oxidative stability of organic semiconducting materials. In addition, FPPT was thermally stable up to 300 °C in nitrogen

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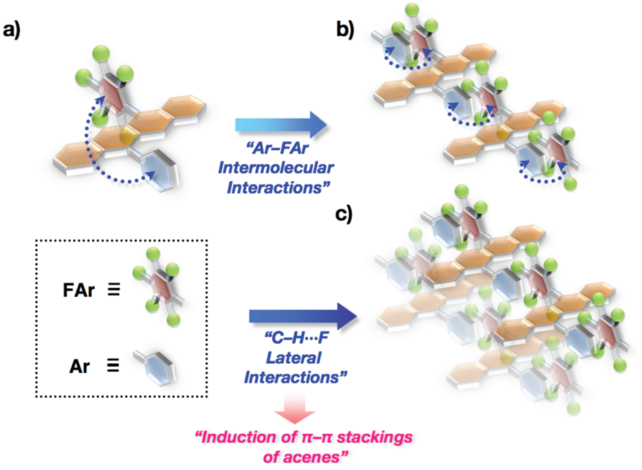
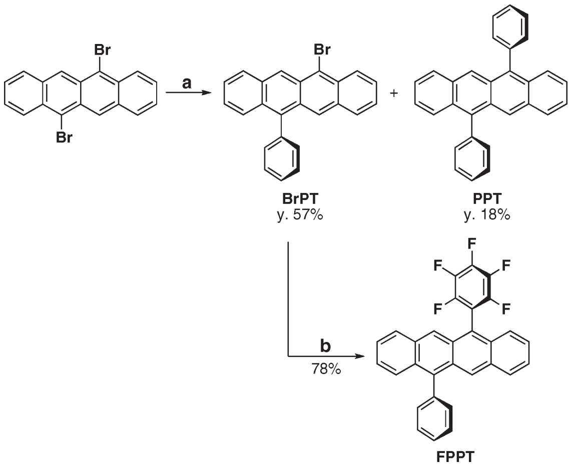


Figure 1. Molecular design and concept for the enhancement of $\pi-\pi$ stacking between neighboring charge transporting units by the introduction of Ar and FAr substituents.

Scheme 1. Synthesis of FPPT[a]



[a] Reagents and Conditions: (a) Phenylboronic acid, $Pd_2(dba)_3$, DPE-phos, 2 M K_2CO_3 aq, toluene−EtOH, 95 °C, 4.5 h, 57%. (b) Pentafluorobenzene, $Pd(OAc)_2$, S-Phos, K_2CO_3, ^{i}PrOAc, 80 °C, 43 h, 78%.

(Figure S5 in the Supporting Information) and tolerated vacuum deposition in our test.

To reveal the intermolecular interactions, we performed single-crystal X-ray structure analyses of FPPT and PPT (Figures 2 and S6−S11 in the Supporting Information). In the molecular structure of FPPT, the tetracene core has an almost flat configuration with an interplanar angle of 0.25° between the mean planes of rings B and C (Figure 2a). The dihedral angles between the tetracene core and substituents were roughly perpendicular (Figure 2a). There are three types of intermolecular interactions. One type is the Ar−FAr interaction (Figure 2b) in the face-to-face stacking mode of phenyl and perfluorophenyl groups with an interplanar distance of 3.37 Å, a similar value to that reported for benzene-d_6 and perfluorobenzene (3.36 Å).[9] The second is the C−H···F interactions, seen in the following short contacts: C−H1···F1, C−H2···F2, and C−H3···F3, as shown in Figure 2b,c. In particular, C−H1···F1 exhibits the shortest distance of 2.40 Å, which might be critical to forming this packing structure.[4,10] The third involves close $\pi-\pi$ interorbital interaction between the tetracene cores. The interplanar distance between tetracene cores ranged from 3.30 to 3.35 Å, shorter than the sum of the C···C van der Waals radii (3.40 Å) (Figure 2d). Therefore, efficient charge transport can be expected from the strong electronic coupling between the adjacent molecules (Figure 2e). On the other hand, $\pi-\pi$ stacking of the tetracene core of PPT was not observed (Supporting Information). Only the C−H···π interaction can be seen in the single-crystal structure. These data indicate that the Ar and FAr groups play an essential role in the molecular ordering in the single crystal.

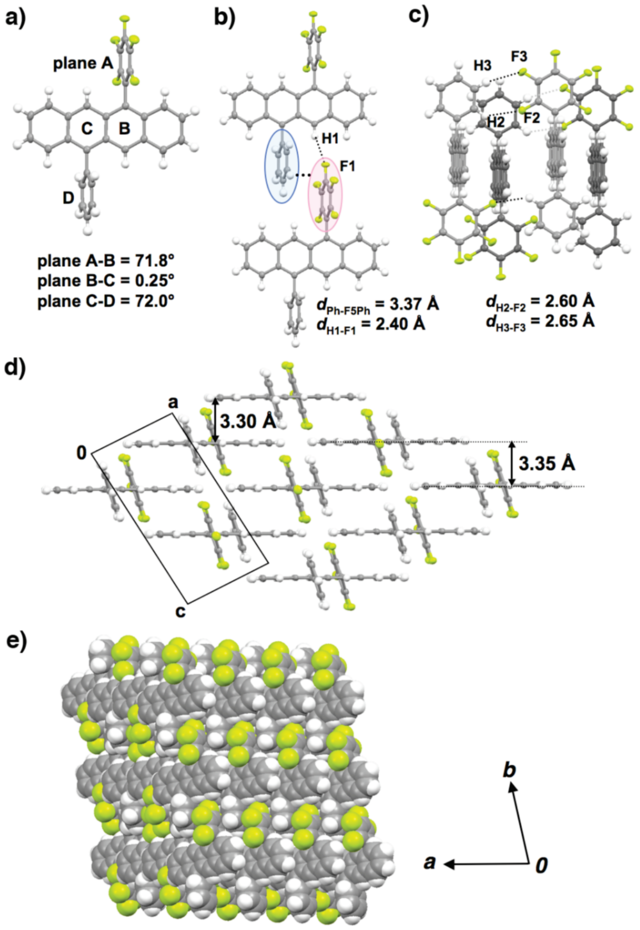


Figure 2. Crystal structure of FPPT. (a) Molecular structure with dihedral angles between planes A, B, C, and D. (b) Two-site intermolecular interactions (Ar−FAr interaction and C−H···F interaction). (c) C−H···F interactions between substituents. (d) Distance between tetracene units. (e) CPK model of the packing structure.

As judged from the X-ray structure data, the molecular packing structure of FPPT should be highly beneficial to charge transport properties because the system has a well-ordered face-to-face $\pi-\pi$ stacking structure, which can create effective electronic overlap of the π-orbitals. To measure the conductive properties of FPPT, we carried out flash-photolysis time-resolved microwave conductivity (FP-TRMC) measurements, which can be used to predict the nanometer-scale conductivity of charge carriers generated by laser pulse irradiation under a low-frequency microwave electric field.[11] Figure 3a,b shows the photoconductivity ($\phi\Sigma\mu$)[12] and its peak value for microcrystalline samples of

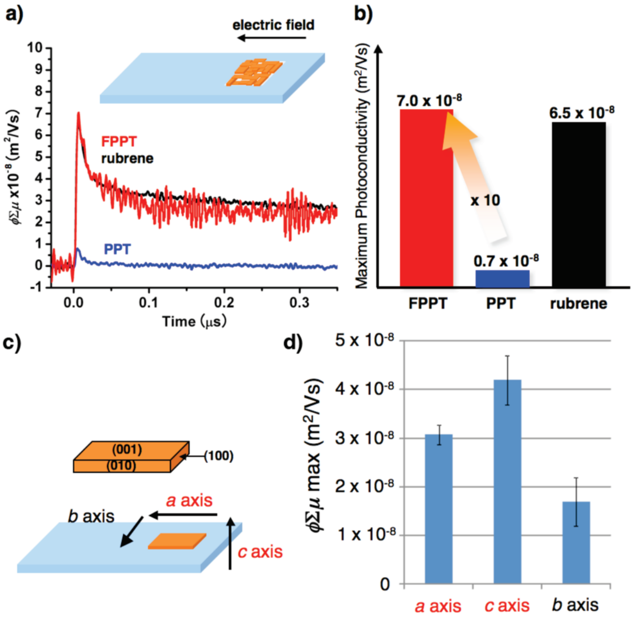


Figure 3. Photoconductivity of FPPT. (a) Transient photoconductivity for FPPT, PPT, and rubrene (red, blue, and black lines, respectively) microcrystals. (b) Comparison of maximum photoconductivity. (c) Crystal axes and indices for axis-dependent photoconductive measurement on a FPPT single crystal. (d) Result of the anisotropic photoconductivity.

FPPT, PPT, and rubrene. Rubrene is an appropriate material for comparison because it has the same tetracene core with phenyl substituents and was reported to have the highest hole mobility among organic single-crystal FETs.[13] Notably, FPPT exhibited the same order of photoconductivity and kinetics behavior as rubrene, and both have considerably higher photoconductivity than PPT.

We next investigated the anisotropic charge transport properties of a FPPT single crystal. The overlapping π-orbitals of the tetracene cores are aligned face-to-face along the *a* and *c* axes (see Figure 2d,e). The microwave electric field was applied parallel (*a* and *b* axes) and perpendicular (*c* axis) to the quartz plate (Figure 3c) to evaluate photoconductivity for each axis. Peak conductivity was found to be ca. twofold larger in the *a* and *c* axes than in the *b* axis. These results suggest that suitable molecular arrangement will provide the charge carrier pathway for good mobility in future works.

Finally, we evaluated thin-film charge transport properties and investigated thin-film morphologies to discuss the effects of Ar and FAr groups. Perfluoroaryl- or perfluoroalkyl-containing organic thin-film transistors (OTFTs) have been paid much attention.[14] OTFTs based on FPPT and PPT were fabricated in a top-contact, bottom-gate configuration. Notably, FPPT was found to exhibit an average hole mobility that reached 4.2 × 10^{-2} cm^2/(V s) with an on/off ratio greater than 10^5 on an *n*-octadecyltrimethoxysilane (OTS)-treated SiO_2 substrate (Table S2 and Figure S12 in the Supporting Information).[15] Under the same conditions, however, PPT exhibited values smaller by 2 orders of magnitude (3.1 × 10^{-4} cm^2/(V s)).[15] These results were supported by AFM images of thin films of FPPT and PPT, which displayed smooth two-dimensional and bumpy three-dimensional crystal growth, respectively (Figures S13−16 in the Supporting Information). The results suggest that the interactions between Ar and FAr play an effective role in controlling the thin-film morphology, as well as in enhancing the charge carrier mobility.

In conclusion, we have demonstrated that the introduction of Ar and FAr groups as substituents onto tetracene at the 5- and 11-positions induced a well-defined, close face-to-face stacking of the tetracene cores. This approach is promising for inducing π−π stacking among charge transport units. Additionally, the proposed synthetic methodology can be easily used to prepare other organic semiconducting cores starting from the corresponding dibromo compounds. Photoconductivity and OTFT measurements clearly demonstrated that the proposed system can control the molecular packing as well as the film morphology, resulting in enhanced charge transport properties. Further investigations on the synthesis of new derivatives as well as OFET measurements on single-crystal FETs are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information. Supporting Information with detailed synthetic procedures, electrochemical and thermal data, stability test data, theoretical calculations, and thin-film morphology and crystallinity data for FPPT and PPT (PDF). X-ray crystal structure data for FPPT and PPT are also included (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) In the case of FPPT and PPT devices, the two-dimensional crystalline thin films were occasionally observed on the vapor-treated OTS, leading to the high mobilities, whereas the 3D polycrystalline thin-film growth was observed more frequently on most other substrates, resulting in low mobilities.