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A pro-aromatic bisphenaleno-thieno[3,2-b]thiophene (BPT-TIPS) was synthesized and compared with an anti-aromatic bisindenothieno[3,2-b]thiophene (S2-TIPS). BPT-TIPS showed larger diradical character, stronger absorption, longer excited state lifetime and better redox amphotericity than S2-TIPS.

Quinoidal n-conjugated molecules have recently attracted increasing interest due to their unique physical properties (low band gap and open-shell diradical character) and potential applications for field-effect transistors (FETs), non-linear optics, and spin-based electronics. For this reason, various quinoidal polycyclic aromatic hydrocarbons (PAHs) and their thiophene-based analogues have been synthesized and some of them have been successfully applied in ambipolar or n-channel FETs. In terms of such promising applications, fundamental understanding of how the fusion mode and the aromaticity/anti-aromaticity/pro-aromaticity affect the ground state electronic structure and consequently the physical properties is important. Recently, our group and Haley’s group independently reported the synthesis and properties of a series of quinoidal bisindenothieno-[n]thioacenocenes (Sn-TIPS) (n = 1-4), which can be regarded as an anti-aromatic system containing an annulene framework with 4n π-electrons (Fig. 1). These molecules also displayed small to moderate diradical character in the ground state due to the recovery of the aromaticity of the central thioacene moiety in the diradical form (Fig. 1). Analogues of this system are the bisphenaleno-thioacenocenes in which the two indeno-units are replaced by two phenaleno-moieties, and the resulting quinoidal system is now pro-aromatic and an open-shell diradical resonance form can be drawn (Fig. 1). A comparison between these two systems will provide insights into the correlations between the aromaticity, the ground state electronic structures, and the physical properties. Therefore, in this work, a pro-aromatic bisphenaleno-thieno[3,2-b]thiophene (BPT-TIPS) was synthesized and its ground state and physical properties were compared with its anti-aromatic counterpart, a bisindenothieno[3,2-b]thiophene (S2-TIPS) (Fig. 1). Our studies clearly show their distinctively different ground-state electronic structures and physical properties. Moreover, ordered 3D packing structure was observed in single crystals, qualifying BPT-TIPS as a new high performance semiconductor.

The key intermediate for the synthesis of BPT-TIPS was a α,α-di-ester substituted thiieno[3,2-b]thiophene (TT) (2), which was obtained by regio-selective lithiation of 2,3,5,6-tetramethylthiophene (TT) (1) followed by quenching with methyl cyanide (Scheme 1). Suzuki coupling between 2 and 2-methylpyridine-1-yl)boronic acid gave 3 in 55% yield. Hydrolysis of 3 followed by acidification gave the diacid 4 in almost quantitative yield, which was converted into the corresponding carboxylic acid chloride with thionyl chloride in dry CH2Cl2. Subsequent double Friedel–Crafts acylation with AlCl3 afforded the desired diketone 5 in 85% yield. Finally, addition of triisopropylsilyl ethynyl lithium to the diketone 5

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4. Electronic Supplementary Information (ESI) available: Synthetic procedures and structural characterization data; additional physical characterization data; DFT calculations details. See DOI: 10.1039/x0xx00000x

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**Fig. 1.** Structures of anti-aromatic bisindenothieno-thioacenocene Sn-TIPS (n = 1-4) and pro-aromatic bisphenaleno-thieno[3,2-b]thiophene BPT-TIPS.

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and reduction of the intermediate diols by SnCl₂ gave the targeted compound **BPT-TIPS** in 45% yield.

**Scheme 1. Synthetic route of BPT-TIPS:** (a) i) n-BuLi, THF, -78 °C, 1 h; ii) NC-COOME, -78 °C – r.t., overnight; (b) (2-methylnaphthalen-1-yl)boronic acid (4 equiv.), Pd(PPh₃)₃Cl₂, toluene/EtOH/H₂O (3:1:1), one drop aliquot 336, reflux, overnight; (c) i) NaOH, MeOH/THF (1:1), reflux overnight; ii) 10% HCl (aq.); (d) i) SOCl₂, dry CH₂Cl₂, reflux; ii) AlCl₃, dry CH₂Cl₂, 0 °C - r.t., overnight; (e) i) trisopropylsilyl ethyl lithium, THF, 0 °C – r.t.; ii) SnCl₂, toluene, r.t., 12 h.

**BPT-TIPS** exhibits good solubility and stability, displaying a blue colour in CH₂Cl₂, while **S2-TIPS** exhibits a deep green colour (Fig. 2a). Additionally, **BPT-TIPS** shows a well-resolved absorption spectrum in CH₂Cl₂ with an intense \( \pi \)-band at 682 nm (log \( \varepsilon \) = 5.03; \( \varepsilon \): molar extinction coefficient in M⁻¹ cm⁻¹), which is commonly observed in many closed-shell PAsHs such as acenes⁶ and closed-shell quinoid compounds such as heptazethrene.⁷ Therefore, this observation indicates that **BPT-TIPS** likely has a closed-shell electronic structure in the ground state. **S2-TIPS** exhibits a very different absorption spectrum with a broad the-longest-wavelength absorption band centered at 606 nm with much weaker intensity than that of **BPT-TIPS**, in accordance with its aromatic character. Femtosecond transient absorption (TA) measurement was conducted to explore the excited-state dynamics of **BPT-TIPS** in toluene. The TA spectra exhibit ground-state bleach signal around 690 nm and a broad weak excited-state absorption band in 450-600 nm region (Fig. S1 in ESf). The single excited-state lifetime (\( \tau_1 \)) was estimated to be 5.3 ns, which is much longer than that of the anti-aromatic **S2-TIPS** (\( \tau_1 \) = 1.1 ps, \( \tau_2 \) = 10 ps).⁸ Moreover, two-photon absorption (TPA) measurements were also conducted for **BPT-TIPS** in toluene by the Z-scan technique in the NIR region from 1300 to 1500 nm (Fig. S2 in ESf) and a maximum TPA cross section value (\( \sigma^{(2)}_{\text{max}} \)) of 620 GM (\( \lambda_{\text{exc}} \) = 1400 nm) was obtained, which is slightly higher than that for **S2-TIPS** (\( \sigma^{(2)}_{\text{max}} \) = 520 GM, \( \lambda_{\text{exc}} \) = 1400 nm) under the same condition.⁹

**BPT-TIPS** displays excellent amphoteric redox behavior with two reversible oxidation waves (\( E_{1/2}^{\text{ox}} \) = -0.03, +0.44 V vs Fc⁺/Fc) and two reversible reduction waves (\( E_{1/2}^{\text{red}} \) = -1.73, -1.38 V vs Fc⁺/Fc) (Fig. 2b). The HOMO and LUMO energy levels were estimated to be -4.65 eV and -3.46 eV from the onset of the first oxidation and reduction wave, respectively. While the anti-aromatic **S2-TIPS** which has a HOMO/LUMO level of -5.35/-3.75 eV (\( E_{\text{g}} \) = 1.60 eV) is easily reduced but hard to be oxidized, the pro-aromatic **BPT-TIPS** can be easily oxidized and reduced to the corresponding radical cations/anions and dications/dianions, respectively. Such difference can be explained by the aromatic nature of both the cationic and anionic forms of **BPT-TIPS**, but for **S2-TIPS** its cationic forms are unstable due to the anti-aromatic nature of the cyclopentadieny1 cation while its anionic forms are stable due to the aromatic character of the cyclopentadienyl anion.

The broken symmetry DFT calculation (UCAM-B3LYP/6-31G*) predicted that **BPT-TIPS** has an open-shell single diradical ground state, but with a small diradical character (\( \gamma \) = 18.6%) and a large singlet-triplet energy gap (\( E_{\text{ST}} \) = -13.3 kcal/mol). Such a small diradical character was not observed experimentally, and **BPT-TIPS** showed sharp NMR spectra even at elevated temperatures and was found ESR silent, suggesting a more closed-shell configuration of the ground state. With the same computation method, **S2-TIPS** was predicted to be a typical closed-shell system with a negligible diradical character. X-ray crystallographic analysis of **BPT-TIPS** (at 100 K) further elaborated their ground-state geometry (Fig. 3).¹ The molecule is distorted from planarity due to the repulsion between the methyl groups and the TT unit (Fig. 3a). Large bond length alternation was found in the central TT-quinoledimethene moiety of both **BPT-TIPS** (Fig. 3b) and **S2-TIPS** indicating that closed-shell quinoid form contributes most to the ground-state structure in both cases. However, NICS(1)zz calculations distinguished their different electronic structures. For **BPT-TIPS**, the NICS(1)zz values for the central two rings A and B are negative but much less negative than the outmost two rings C and D, indicating a small aromatic character of the rings A and B which can be correlated with its intrinsic pro-aromaticity. In contrast, the central two rings A and B in **S2-TIPS** possess positive NICS(1)zz values, implying a typical anti-aromatic character. **BPT-TIPS** can be also regarded as an isoelectronic structure of an octazethrene analogue (OZ-TIPS),¹ which has a larger diradical character due to the larger resonance energy of naphthalene spacer than thieno[3,2-b]acene.

Molecules of **BPT-TIPS** are packed into a 1D infinite head-to-tail chain with a short average \( \pi \)-stacking distance of 3.34 Å (Fig. 3c). The top view shows that the stacking is through phenalenyl-phenalenyl interaction, which is similar to the multi-center covalent bonding in the biphenalenyls,¹² but the distance is in the typical \( \pi \)-\( \pi \) stacking distance range (3.3-3.6 Å). Spin density distribution of the singlet diradical of **BPT-TIPS** shows that the spins are easily distributed along the whole \( \pi \)-conjugated framework (Fig. S3 in ESf), which thus explains the
decreased covalent character of the phenalenyl-phenalenyl interactions. The 1D polymer chains are then further stacked into a compact 3D network (side view, Fig. 3c), which is desirable for efficient charge transport.

Bottom-gate, top-contact FETs were thus fabricated and used to evaluate the charge transporting properties of BPT-TIPS in both drop-casted and spin-coated thin films (ESI†). All the devices exhibited p-type operation with well-defined saturation behavior in nitrogen (Fig. S4 in ESI†). An average field effect hole mobility of 0.14 cm²V⁻¹s⁻¹ with a threshold voltage (Vth) of 4 V and a current on/off ratio of 10⁴ were measured for the spin-coated thin films on OTS modified substrates (Table S2 in ESI†). When processed with drop casting method, large crystal domain was acquired, and as a result, the hole mobility was improved to 0.26 cm²V⁻¹s⁻¹ almost without shifting the Vth. The different performance can be further correlated with the small surface roughness of the drop-casted thin films as revealed by optical microscope and atom force microscope measurements (Fig. S5-7 in ESI†). The XRD data in both drop-casted and spin-coated thin films indicate that the BPT-TIPS molecule has a similar layer-like packing to that of its single crystal (Fig. S8-9 in ESI†). Under similar processing conditions, the thin films of S2-TIPS showed much lower field-effect hole mobility (0.016 cm²V⁻¹s⁻¹), which presumably can be ascribed to its separated columnar superstructure observed in the single crystals.⁵⁰

In summary, we demonstrate that the quinoidal BPT-TIPS has distintively different ground-state electronic structure and physical properties from its analogue S2-TIPS, which can be correlated with their respective pro-aromatic and anti-aromatic character. Our studies indicate that a pro-aromatic system exhibits a larger diradical character, stronger absorption, longer excited state lifetime and better redox amphotericity than its anti-aromatic counterpart, which is important for future molecular design. The 3D ordered packing structure of this type of diradicaloid molecule led to a relatively high charge carrier mobility, which also paved the way to design materials for spin-dependent charge transport studies in next stage.

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Notes and references
† Crystallographic data for BPT-TIPS: C₅₂H₄₀S₄Si₄. M = 799.25, monoclinic, a = 17.7574(16) Å, b = 14.7085(14) Å, c = 17.0416(15) Å, β = 90°, β = 90.251(5)°, γ = 90°, V = 4451.0(7) Å³, T = 100(2) K, space group P 21/c, Z = 4, CuKα radiation λ = 1.54178 Å, R₁ = 0.0770 (I > 2σ(I)), wR²(F) = 0.2043 (I > 2σ(I)); R₁ = 0.1048 (all data), wR²(F) = 0.2471 (all data). CCDC No: 1055932


