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Functionalized oligothiophene-based heterocyclic aromatic fluorescent compounds with various donor–acceptor spacers and adjustable electronic properties: a theoretical and experimental perspective

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ABSTRACT

Syntheses, characterizations, optical, electrochemical, and thermal properties of a family of linear oligothiophene-based heterocyclic aromatic fluorescent compounds are described herein. They all have effective π-conjugated systems with D−π−D or A−π−A structures as well as different bromo, thiocyno, formyl, and triphenylamino tails. X-ray single-crystal structure of 2TPA2T methanol semisolvate reveals a trans configuration with different dihedral angles between adjacent aromatic heterocycles. Theoretical and experimental studies have been made to reveal the differences from related compounds with adjustable electronic properties. The influences of introducing different D/A functionalized tails on the band-gap convergence have also been discussed, where the convergence behavior corrected via the thienyl ring coefficient (\( \text{corr} \)) shows better correlation of linear fitting based on the extrapolation of HOMO–LUMO gaps at the B3LYP/6-31G* level.

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1. Introduction

Research on the π-functional materials, such as thiophene-based and fluorene-based molecules and polymers, has been attracting considerable interests in view of their wide applications on organic semiconducting materials and electronic devices, such as dye-sensitized solar cells (DSSCs), organic solar cells (OSCs), as well as dye-sensitized solar cells (DSSCs), organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), chemosensors, biosensors, and electrochemical devices. In particular, linear conjugated oligomers share many of the properties of conjugated polymers with certain advantages including their well-defined chemical structures, monodispersity, better solubility, easier purification, fewer defects, and the possibility to introduce versatile functionalities. However, rational design and synthesis of extended heterocyclic aromatic systems for constructing high-performance electronic materials are still very important and challenging issues.

Limited by the tremendous gap that still exists between the structures and the properties, these problems have not been completely solved. Up till now, many theoretical and experimental efforts have been made on the studies of a variety of linear conjugated oligomers. From the basic research perspective, exploration of the convergence behavior of the HOMO–LUMO gaps at the B3LYP/6-31G* level.

...
other hand, the introduction of a functional terminal group\textsuperscript{14} into oligothiophenes provides an opportunity for incorporating the \pi-conjugated system covalently into a more complex system. For example, \pi-conjugated oligomers, based on benzothiadiazole and thiophene, increasing and decreasing the donor and acceptor strengths, are reported for nonlinear optics and near-IR emission by the Reynolds’ group.\textsuperscript{15} For many applications, such as OLEDs and photovoltaics, the HOMO–LUMO gap is critical to an optimized device because it determines the color of the light emitted for an OLED or the monochromatic incident photon-to-electron conversion efficiency for a photovoltaic device.

Taking all the above-mentioned factors into consideration, it is believed that the linear oligothiophene-based heterocyclic aromatic fluorescent compounds, bearing delocalized \pi-systems, versatile D–A hybrids, and functionalized terminal groups, are good candidates for the investigations on the design and synthesis of \pi-conjugated oligomers from a theoretical and experimental perspective. In our previous work, a family of 1,10-phenanthroline- and bithiazole-based heterocyclic aromatic compounds with terminal thienyl, imidazolyl, pyridyl groups has been described.\textsuperscript{16} Furthermore, temperature-dependent semiconducting and photo-responsive properties of self-assembled nanocomposite films and nanodevices fabricated from these compounds and their metal complexes have been explored.\textsuperscript{17} Herein we have extended our work on the oligothiophene-centered semiconducting and fluorescent systems where terminal bromo, thiocyanato, formyl, and triphenylamino groups are successfully introduced (Scheme 1). The syntheses and full characterizations of this family of linear heterocyclic aromatic compounds with various electron-donating and electron-withdrawing tails have been described, and the aim of combining various donor and acceptor substituents into molecules is to finely tune their electronic structures and compare their spectroscopic, electrochemical, and thermal properties.

\begin{equation}
\text{Scheme 1. Synthetic route of oligothiophene-based heterocyclic aromatic fluorescent compounds.}
\end{equation}

All these obtained linear heterocyclic aromatic compounds promote us to further explore possible rules between their structures and properties, for example, the relationship between the number of aromatic heterocycles and the electronic and fluorescent spectra, band-gap alterations, the limitation of solubility of compounds, which is also influenced by the substituent effects. So theoretical and experimental studies have been made to reveal the differences from 42 related compounds (Scheme 2) with adjustable electronic properties, where the influences of introducing seven types of functionalized terminals (i.e., proton, bromo, imidazolyl, pyridyl, thiocyanato, formyl, and triphenylamino groups) and the number of aromatic heterocycles (\(n=1\)–6) on the convergence behavior of HOMO–LUMO gaps have been included. It is found that convergence behavior corrected via the thienyl ring coefficient (\(\eta_{corr}\)) shows better correlation of linear fitting, which is based on the extrapolation of HOMO–LUMO gaps at the B3LYP/6-31G* level.

2. Results and discussion

2.1. Syntheses and spectral characterizations

As shown in Scheme 2, 42 model compounds were involved in the systematic comparisons for a theoretical and experimental perspective in terms of band-gap engineering. Among them, 31 of them are known compounds including 7 new compounds in this work and the other 11 compounds are unreported. Our synthetic strategy was based on the routes shown in Scheme 1, in which the starting materials 3,3’-dimethyl-2,2’:5’,2”-terthiophene (3T-Me) and 3,3’’-dimethyl-2,2’:5’,2’’:5’,2”’-quaterthiophene (4T-Me) were prepared according to our previously reported approaches.\textsuperscript{10c} All the target compounds were prepared by carbon–carbon (C–C) bond and/or carbon–nitrogen (C–N) bond cross-coupling reactions. The combination of different cross-coupling methods, such as Kumada–Corriu, Suzuki–Miyaura, Ullmann reactions, have been carried out to optimize the experimental conditions in order to prepare the linear \pi-conjugated compounds with high yields. As can been seen in Figs. S1–9, all the heterocyclic aromatic compounds have been characterized by \(^1\)H, \(^13\)C NMR, and EI-TOF-MS spectra, and the results clearly demonstrate the formation of expected compounds.
In comparison with the oligothiophenes bearing no substituent, we have previously demonstrated that the introduction of a \( \beta \)-methyl group to the thiophene ring can effectively increase the solubility of resulting compounds in organic solvents without impacting the molecular planarity and electronic structure, which facilitates the related C–C bond and C–N bond cross-coupling reactions and improves the final yields.16c In this work, \( \beta \)-methyl-thiophene extended quaterthiophene compounds \( 6T\text{-Me} \) and \( Br5T\text{-Me} \) were firstly prepared in one-pot reaction (63.7 and 8.5%) by the treatment of Grignard reagents obtained from corresponding oligothiophene-based bromides and magnesium turnings with a \([\text{NiCl}_2(\text{dppp})]\) catalyst in dry THF. It is worth mentioning that \( Br5T\text{-Me} \) has been further confirmed by the \( ^1\text{H} \rightarrow ^1\text{H} \) correlation spectroscopy (COSY) NMR shown in Fig. S15c.

As anticipated, triphenylamino-terminated compounds \( 2\text{TPA}_2\text{T-Me} \), \( 2\text{TPA}_3\text{T-Me} \), and \( 2\text{TPA}_4\text{T-Me} \) were synthesized with satisfactory yields in the presence of a \([\text{Pd}(\text{PPh}_3)_4]\) catalyst by using a strong cross-coupling reagent, i.e., 4-(diphenylamino)phenylboronic acid. Furthermore, the resultant yields for \( 2\text{TPA}_2\text{T-Me} \), \( 2\text{TPA}_3\text{T-Me} \), and \( 2\text{TPA}_4\text{T-Me} \) can be improved by using \( \text{Cs}_2\text{CO}_3 \) instead of \( \text{Na}_2\text{CO}_3 \) as a base. As shown in Scheme 1, formyl terminated quaterthiophene compound \( 2\text{CHO}_4\text{T-Me} \) was also firstly prepared by the classical Vilsmeier–Haack reaction in a yield of 71.3%, in which the mono-formyl compound \( \text{CHO}_4\text{T-Me} \) was carefully separated as a by-product in a yield of 3.8% by silica gel column chromatography.

As illustrated in Fig. 1, all new compounds show characteristic absorptions at 350–432 nm in their electronic spectra.
corresponding to the $\pi-\pi^*$ transitions within the conjugated system of the whole aromatic heterocycles. As expected, the maximum absorption wavelengths are shifted to lower energy bands when the number of aromatic heterocycles is increased, which are comparable with those in oligothiophene compounds. Moreover, it is noted that this family of linear heterocyclic aromatic compounds are fluorescence active, and compound BrST-Me shows a yellow-green fluorescence peak at 485 nm and a UV–vis absorption peak at 395 nm ($\lambda_{\text{vis}}=16,300$) simultaneously. Similar bathochromic shifts have been found in the fluorescence emission spectra of compounds 2SCN4T-Me, 2SCN9T-Bu, 2TPA2T, 2TPA3T-Me, and 2TPA4T-Me when the number of aromatic heterocycles (namely delocalized $\pi$-systems) is increased. In contrast, compounds CHO4T-Me and 2CHO4T-Me have the poor intensity of fluorescence emission because of the fluorescence quenching of formyl group. Compared with the 1,10-phenanthroline-based aromatic heterocyclic compounds showing blue fluorescence emissions, obvious red-shifts are observed for these oligothiophene-based compounds especially for those pyridyl and triphenylamino-terminated terthiophene systems. As shown in Fig. 3, TGA of oligothiophene-based compounds indicates that they can keep unchangeable structure of oligothiophene-based compounds have been checked herein in thermal stability compared with corresponding terthiophene-based counterparts. In contrast, the $T_{d10}$ values for compounds 2TPA4T-Me, 2Br6T-Me, 2CHO4T-Me, and 2SCN4T-Me are found to be in the range 217–289 °C, indicative of lower thermal stability.

2.4. Electrochemical properties

The electrochemical behavior of heterocyclic aromatic compounds was examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in their 1.0 M CH$_2$Cl$_2$ solutions containing 0.1 M TBAClO$_4$ as the supporting electrolyte at different scan rates (10, 20, 50, 80, 100 mV s$^{-1}$) in Fig. 4. All potentials reported herein were calibrated with the ferrocene/ferrocenium couple (Fc$^+/Fc$) as internal standard. Oxidation onset potentials ($E_{\text{onset}}^+$) as well as HOMO/LUMO energy levels were determined by a combined analysis of the CV, DPV and absorption data are summarized in Table 1. The onset oxidation was measured relative to the Fc$^+/Fc$ couple for which an energy level of $-5.10$ eV versus vacuum was assumed. As depicted in Fig. 4 and SI11, TPA-terminated oligothiophenes show reversible and well-defined redox response in the CV measurements. The onset oxidation potentials ($E_{\text{onset}}^+$) of these compounds were determined to be 0.05 V for 2TPA4T-Me, 0.08 V for 2TPA3T-Me, and 0.14 V for 2TPA2T. In general, the HOMO of D–A oligomer is determined by the HOMO of the donor unit, while the LUMO of D–A oligomer is controlled by the LUMO of acceptor unit. As can be seen in Fig. 4, one or two oxidation waves have been observed for all compounds, and the reduction potentials as well as the measured currents are found to be dependent on their molecular structures. The first oxidation wave can be attributed to the formation of cation-radical species and the second one is ascribed to the successive oxidation of cation-radical to its corresponding dication, which have been observed previously in other oligothiophene systems.

2.5. Density function theory (DFT) computations

DFT calculations are carried out with the Gaussian 03, Revision C02 programs, using the B3LYP method and 6–31G* basis set. The fixed atom coordinates of 42 oligothiophene-based compounds, based on the structural parameters determined by the
Fig. 4. CV (a, b, c, d) and DPV (e, f) for heterocyclic aromatic compounds in CH₂Cl₂ (1.0 × 10⁻³ M) containing 0.10 M of TBAClO₄ under argon. The different scanning rate: 10, 20, 50, 80, 100 mV/s (a) 2TPA₂T; (b) 2TPA₃T-Me; (c) 2TPA₄T-Me versus Fc⁺/Fc.

Table 1
UV–vis absorption and fluorescence emission data, optical, electrochemistry, and calculated HOMO–LUMO energy gaps (E_g) for related heterocyclic aromatic compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>UV–vis λmax [nm (eV)]</th>
<th>ϵ (L mol⁻¹ cm⁻¹)</th>
<th>E_{opt} (eV)</th>
<th>E_{calc} (eV)</th>
<th>Fluorescence λ_max (nm)</th>
<th>T_d (°C)</th>
<th>E_{HOMO} (eV)</th>
<th>E_{LUMO} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2TPA₂T</td>
<td>409 (3.03)</td>
<td>3200</td>
<td>2.61</td>
<td>3.40</td>
<td>482</td>
<td>412</td>
<td>0.14</td>
<td>-5.24</td>
</tr>
<tr>
<td>2TPA₃T-Me</td>
<td>414 (2.99)</td>
<td>44,500</td>
<td>2.54</td>
<td>3.07</td>
<td>508</td>
<td>398</td>
<td>0.08</td>
<td>-5.18</td>
</tr>
<tr>
<td>2Im₆T-Me</td>
<td>357 (3.47)</td>
<td>47,700</td>
<td>2.96</td>
<td>3.45</td>
<td>460</td>
<td>335</td>
<td>0.35</td>
<td>-5.45</td>
</tr>
<tr>
<td>2Py₄T-Me</td>
<td>399 (3.11)</td>
<td>45,800</td>
<td>2.66</td>
<td>2.99</td>
<td>506</td>
<td>273</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2TPA₄T-Me</td>
<td>430 (2.88)</td>
<td>30,600</td>
<td>2.46</td>
<td>2.83</td>
<td>525</td>
<td>271</td>
<td>0.05</td>
<td>-5.15</td>
</tr>
<tr>
<td>2Im₆T-Me</td>
<td>389 (3.19)</td>
<td>57,700</td>
<td>2.73</td>
<td>3.02</td>
<td>452</td>
<td>358</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2Py₄T-Me</td>
<td>420 (2.95)</td>
<td>27,800</td>
<td>2.54</td>
<td>2.80</td>
<td>533</td>
<td>451</td>
<td>0.30</td>
<td>-5.40</td>
</tr>
<tr>
<td>2CHO₄T-Me</td>
<td>419 (2.96)</td>
<td>5100</td>
<td>2.47</td>
<td>2.78</td>
<td>454</td>
<td>217</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CHO₄T-Me</td>
<td>410 (3.02)</td>
<td>27,100</td>
<td>2.54</td>
<td>2.83</td>
<td>584</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2Br₆T-Me</td>
<td>384 (3.23)</td>
<td>32,700</td>
<td>2.79</td>
<td>3.21</td>
<td>482</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2SCN₄T-Me</td>
<td>390 (3.18)</td>
<td>3580</td>
<td>2.71</td>
<td>2.97</td>
<td>468</td>
<td>289</td>
<td>0.55</td>
<td>-5.65</td>
</tr>
<tr>
<td>2SCN₉T-Bu</td>
<td>432 (2.87)</td>
<td>62,900</td>
<td>2.39</td>
<td>2.50</td>
<td>547</td>
<td>—</td>
<td>0.14</td>
<td>-5.24</td>
</tr>
<tr>
<td>Br₅T-Me</td>
<td>395 (3.14)</td>
<td>16,300</td>
<td>2.64</td>
<td>2.83</td>
<td>485</td>
<td>278</td>
<td>0.25</td>
<td>-5.35</td>
</tr>
<tr>
<td>6T-Me</td>
<td>411 (3.02)</td>
<td>6060</td>
<td>2.57</td>
<td>2.67</td>
<td>503</td>
<td>417</td>
<td>0.18</td>
<td>-5.28</td>
</tr>
<tr>
<td>2Br₆T-Me</td>
<td>392 (3.16)</td>
<td>22,000</td>
<td>2.74</td>
<td>2.61</td>
<td>513</td>
<td>220</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

1. Optical band gap determined from the UV–vis absorptions in their methanol solutions.
2. The geometries are calculated by B3LYP method and 6-31G* basis set.
3. 10% Weight-loss temperature.
4. Oxidation onset potentials determined from DPV versus Fc⁺/Fc.
5. Calculated from E_{HOMO} = (E_{onset} + 5.10).
6. Calculated from E_{LUMO} = E_{HOMO} + E_{opt}.
X-ray diffraction method and fully optimization, are used for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap calculations (Table 1). The resultant HOMO–LUMO gaps for TPA-extended compounds 2TPA2T, 2TPA3T-Me, and 2TPA4T-Me are 3.40, 3.07, and 2.83 eV, respectively, which are analogous to their UV–vis absorption peaks.

According to the DPV measurements, the corresponding oxidation potentials for four quaterthiophene-based derivatives 2SCN4T-Me, 2Py4T-Me, 2TPA4T-Me, and 6T-Me were determined to be 0.55, 0.30, 0.05, and 0.18 V, respectively (Table 1, Fig. 4e and f). Further analyses of the frontier orbitals reveal that the introduction of electron-donating groups raises the HOMO energy levels, while the introduction of electron-withdrawing groups lowers the LUMO energy levels, which will greatly decrease the HOMO–LUMO gaps of resultant compounds. It is noted that there is an almost linear relationship between the experimentally determined (CV and UV–vis absorption spectra) and the theoretically calculated energy levels for the HOMOs and LUMOs of these triphenylamino- and thiocyano-terminated oligothiophene hybrids (Figs. 5 and 6). This relationship demonstrates that, despite the uncertainty in the calculated absolute values, theoretical calculations can serve as a useful tool to predict and guide the synthesis of future oligomer and polymer materials at least in some cases.

To make further comparisons of the HOMO–LUMO gaps from a theoretical and experimental perspective, the extrapolation for a series of π-conjugated oligothiophenes at the B3LYP/6-31G* level was carried out. However, the theoretical prediction is not accurate in accordance with the experimental results. To solve this problem, Zade et al.10 used the correction index method where the relationship between the first adiabatic ionization potential of oligothiophenes and chain length correlates linearly with an empirically obtained value of 1/(n0.75). The same correction strategy has been used herein, but a new thienyl ring coefficient (n corr) has been introduced (Eq. 1) to correct the effective number of oligothiophene (n eff) according to Kuhn’s equation23 (see SI) due to the presence of different terminal groups. So the n eff coefficient includes the contribution of different terminal groups in our...
offers us opportunity to evaluate the effects of different D

To improve our ways of working and reduce the re-

search time.

Based upon the above-mentioned electronic spectra, electro-

chemistry, and DFT computational data, systematic comparisons in

terms of the band-gap engineering show that the energy discrep-

ancy between the HOMO and LUMO decreases as the length of

conjugation increases. However, when the number of monomer

units exceeds a certain value at which the effective conjugation

length is saturated, the band gap starts to level off. Therefore, un-
limited extension of the conjugation length results only in a limited

reduction of the band gap. Moreover, incorporation of the electron-

donating or electron-withdrawing substituents directly into the

aromatic unit in the main chain represents another effective way to

finely tune the electronic structure by perturbing the molecular

orbi

tals through either inductive or mesomeric effects. We think

our effects on studying the functionalized oligothiophene-based

heterocyclic aromatic fluorescent compounds with various D–A

spacers and adjustable electronic properties can provide a theo-

retical screening approach for the discovery of novel organic

semiconductor cores and terminals before conventional chemical

synthesis.

3. Conclusions

Following the idea of introducing specific organic D–A hybrids

to promote the direct electronic separation and transportation and

retaining the effective and linear delocalized π systems simulta-

neously, a series of line

longer than 2 nm (2TPA2T, 2TPA3T-Me, 2TPA4T-Me, 2C9T-Me, 2C9T-Bu,

2CHO4T-Me, CHO4T-Me, 6T-Me, Br5T, and 2Br6T) have been re-

ported in this work. Synthetic, structural, thermal, computational,

and spectral comparisons have been carried out for these mono-

and bi-functional thiophene/thiocyanato/triarylamine/formyl

extended oligothiophene compounds with different number of

aromatic heterocycles in order to reveal the differences between

cross-coupling approaches and experimental conditions on the

C–C bond and C=N bond formation, molecular conformation, and
dihedral angles between neighboring heterocycles, band gaps and
energy levels, electronic, fluorescent, and electrochemistry spectra
of related compounds. X-ray single-crystal structure of 2TPA2T
methanol semisolvate reveals a trans configuration with different
dihedral angles between adjacent aromatic heterocycles. Com-

pounds 2TPA2T, 2Py4T-Me, and 6T-Me show excellent perfor-
mance in the thermal stability, which suggests that they may be

good candidates for the device fabrication.
A theoretical and experimental perspective has been carried out for this family of linear oligothiophene-based heterocyclic aromatic fluorescent compounds, which have effective π-conjugated systems with D–π–D or A–π–A structures and different terminal groups namely, bromo, imidazolyl, pyridyl, thiocyanato, formyl, and triphenylamino tails. The influences of introducing different D–A functionalized tails on the band-gap convergence have also been discussed, where the convergence behavior corrected via the thienyl ring coefficient shows better correlation of linear fitting based on the extrapolation of HOMO–LUMO gaps. As we know, designing better organic optoelectronic materials requires a comprehensive understanding of the electronic structure. A theoretical screening and optimizing approach can help us find novel organic semiconductors as soon and as effectively as possible prior to the chemical synthesis. We hope this study can provide some useful information on the general rules between structures and properties. Further studies are being undertaken on the field-effect, light-emitting, photoresponsive, and photovoltaic properties of these linear aromatic hetercycle-based nanowires, nanocomposite films, and nanodevices.

4. Experimental section

4.1. General

All melting points were measured without any corrections. Unless otherwise specified, solvent of analytical grade was purchased directly from commercial sources and used without any further purification. Tetrahydrofuran (THF) was freshly distilled from the sodium/benzophenone mixture prior to use. Anhydrous solvents were drawn into syringes under the flow of dry N2 gas and directly transferred into the reaction flasks to avoid contamination. Column chromatography was carried out on silica gel (300–400 mesh) and analytical thin-layer chromatography (TLC) was performed on glass plates of silica gel GF-254 with detection by UV. Standard techniques for synthesis were carried out under argon atmosphere. Heterocyclic aromatic compounds 3,3'-dimethyl-2,2'-dithienyldi(3T-Me), 5,5''-dibromo-3,3''-dimethyl-2,2''-dithienyldi(2TPA2T-Me), 3,3''-dimethyl-2,2'',5,5''-quaterthiophene (4T-Me), and 5,5''-dibromo-3,3''-dimethyl-2,2''-5,5''-quaterthiophene (2BrT-4T-Me) were prepared from 2,5-dibromo-3,3'-terthiophene (2TPA2T-Me) via literature methods.

4.2. Syntheses and characterizations of heterocyclic aromatic compounds

4.2.1. 2TPA2T. A mixture of 2BrT (0.32 g, 1.00 mmol), 4-(diphenylamino)phénylboronic acid (1.16 g, 4.00 mmol), cesium carbonate (1.30 g, 4.00 mmol), [Pd(PPh3)4] (0.06 g, 0.05 mmol), toluene (20 mL), and water (5 mL) was degassed for 0.5 h and heated to reflux for 40 h under argon atmosphere. The mixture was then allowed to cool to the room temperature and extracted with chloroform. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. The filtrate was evaporated, and the residue was purified by column chromatography over silica gel using hexane and dichloromethane (1:1) as eluent to give 0.57 g (88.1%) of 2TPA2T as a yellow solid. The yellow single crystals of 2TPA2T suitable for X-ray diffraction measurement were grown and isolated from DMF by slow evaporation in air at room temperature for 2 weeks. Melting point: >300 °C. Anal. Calcd for [C43H29N2S2]: C, 61.05; H, 4.03%; Found: C, 61.05; H, 4.03%

4.2.2. 2TPA3T-Me. The synthesis of 2TPA3T-Me was similar to that described for 2TPA2T. Yield: 75.3% (0.64 g) as a red solid. Melting point: 219–221 °C. Anal. Calcd for [C46H26N2S3]: C, 76.74; H, 4.77; N, 3.31%. Found: C, 76.52; H, 4.93; N, 3.15%. Main FTIR absorptions (KBr pellets, cm⁻¹): 3451 (b), 2365 (m), 1587 (s), 1499 (vs), 1480 (m), 1375 (s), 1273 (m), 1175 (m), 1087 (m), 1025 (m), 813 (s), 749 (m), 695 (m), 599 (w). 1H NMR (500 MHz, CDCl3): δ: 7.45 (d, J = 8.0 Hz, ph), 7.29 (t, 8H, ph), 7.14 (d, J = 8.0 Hz, ph), 7.11 (m, 4H, thio), 7.05 (m, 8H, ph), 2.43 (s, 6H, CH3). 13C NMR (125 MHz, CDCl3) δ: 146.7, 141.4, 134.7, 129.3, 128.1, 122.8, 122.7, 15.9. El-TOF-MS (m/z): calc'd for [C46H32N2S3]: 652.2 (100.0%), 653.2 (49.9%). Found: 652.0 (100.0%), 653.0 (11.6%).

4.2.3. 2TPA4T-Me. The synthesis of 2TPA4T-Me was similar to that described for 2TPA2T. Yield: 75.3% (0.64 g) as a red solid. Melting point: 219–221 °C. Anal. Calcd for [C49H30N2S4]: C, 76.74; H, 4.77; N, 3.31%. Found: C, 76.52; H, 4.93; N, 3.15%. Main FTIR absorptions (KBr pellets, cm⁻¹): 3451 (b), 2365 (m), 1587 (s), 1499 (vs), 1480 (m), 1375 (s), 1273 (m), 1175 (m), 1087 (m), 1025 (m), 813 (s), 749 (m), 695 (m), 599 (w). 1H NMR (500 MHz, CDCl3): δ: 7.45 (d, J = 8.6 Hz, ph), 7.27 (t, 8H, ph), 7.14 (d, J = 7.65 Hz, ph–thio), 7.05 (m, 10H, ph–thio), 2.44 (s, 6H, CH3). 13C NMR (125 MHz, CDCl3) δ: 147.4, 141.5, 135.0, 129.3, 125.6, 124.6, 124.3, 124.1, 123.9, 123.5, 123.2, 122.8, 15.9. EI-TOF-MS (m/z): calc'd for [C49H32N2S4]: 844.2 (100.0%), 845.2 (62.1%), 846.2 (19.1%). Found: 844.2 (100.0%), 845.2 (32.4%), 846.2 (8.9%).

4.2.4. 6T-Me and Br5T-Me. Activated Mg turning (1.04 g, 42.95 mmol) in 20 mL of anhydrous THF and a catalytic amount of dry N2 gas was added to a solution of 2-bromo-3-methylthiophene (2.5 mL, 22.20 mmol) in 10 mL of anhydrous THF was slowly dropped into the reaction mixture. Once the vigorous reaction had started, the rest of the 2-bromo-3-methylthiophene solution was started, the rest of the 2-bromo-3-methylthiophene solution was added dropwise to keep the mixture refluxing over reaction mixture was allowed to proceed for 2 h at the room temperature and cullated into an ice-cooled solution of 2Br4T-Me (2.58 g, 5.00 mmol) and [Ni(dppp)Cl2] (0.11 g, 0.20 mmol) in dry THF (40 mL). After being stirred for 2 h at the room temperature, the reaction mixture was refluxed for another 12 h and then cooled to the room temperature. The reaction mixture was quenched with saturated NH4Cl aqueous solution, extracted thoroughly with chloroform (CHCl3) until no more products could be detected by TLC, washed with brine. The resulting organic layer was dried over anhydrous sodium sulfate and filtered. Compounds 6T-Me and Br5T-Me were purified by silica gel column chromatography employing CHCl3 solution to give red solid in yields of 1.75 g (63.7%) for 6T-Me and 0.23 g (8.5%) for Br5T-Me, respectively. Compound 6T-Me: Melting point: >300 °C. Anal. Calcd for [C50H38N2S3]: C, 78.70; H, 4.21%; Found: C, 78.70; H, 4.21%

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Compound Br5T-Me: Melting point: >300 °C. Anal. Calcld for [C23H17BrS5]: C, 51.77; H, 3.21%. Found: C, 51.55; H, 3.43%. Main FTIR absorptions (KBr pellets, cm⁻¹): 3409 (b), 2922 (s), 2362 (w), 1730 (m), 1448 (s), 1062 (s), 788 (s), 710 (m), 618 (m).¹H NMR (500 MHz, CDCl₃) δ: 7.14 (d, 2H, J = 3.4 Hz, thio), 7.12 (d, 1H, J = 3.0 Hz, thio), 7.07 (d, 1H, J = 2.8 Hz, thio), 6.99 (d, 1H, J = 2.8 Hz, thio), 6.93 (s, 1H, thio), 6.88 (d, 1H, J = 4.9 Hz, thio), 6.86 (s, 1H, thio), 2.43 (d, 6H, J = 4.9 Hz, CH₃).¹³C NMR (125 MHz, CDCl₃) δ: 137.1, 135.7, 134.5, 134.2, 134.0, 131.6, 130.4, 129.7, 126.5, 129.4, 123.8, 123.3, 110.1, 15.7, 15.5, 15.4. EI-TOF-MS (m/z): calculated for [C₂₃H₁₇BrS₅]⁺: 533.9 (100.0%), 531.9 (82.7%), 534.9 (28.5%), 532.9 (20.7%). Found: 533.9 (100.0%), 531.9 (97.2%), 534.9 (75.5%), 532.9 (96.6%).

2. 2Br6T-Me. In the absence of light, NBS (0.39 g, 2.20 mmol) was dissolved in DMF (5 mL) and injected into a solution of 6T-Me (0.55 g, 1.00 mmol) in DMF (20 mL) at 40 °C under argon atmosphere. The mixture was stirred for 4 h at 60 °C and then cooled to the room temperature. Water (50 mL) was added into the mixture, and the crude yellow solid was precipitated, filtered, and rinsed with a 50% ethanol/water solution. The desired compound 2Br6T-Me was purified by silica gel column chromatography (CHCl₃) to give red solid in yields of 0.67 g (94.3%). Melting point: >300 °C. Anal. Calcld for [C₂₀H₁₂N₂S₆]: C, 50.82; H, 2.56; N, 5.93%. Found: C, 50.64; H, 2.82; N, 5.75%. Main FTIR absorptions (KBr pellets, cm⁻¹): 3449 (b), 2359 (m), 2152 (m), 1644 (s), 1582 (m), 1438 (s), 1400 (m), 1099 (s), 986 (m), 855 (m), 780 (s).¹H NMR (500 MHz, CDCl₃) δ: 7.22 (s, 1H, CHO), 7.18 (d, 1H, J = 3.6 Hz, thio), 7.18 (d, 2H, J = 3.9 Hz, thio), 6.87 (d, 4H, J = 9.4 Hz, thio), 2.43 (s, 6H, CH₃).¹³C NMR (125 MHz, CDCl₃) δ: 182.4, 141.5, 140.4, 139.7, 139.1, 136.6, 135.8, 134.7, 134.4, 134.1, 131.6, 131.3, 130.8, 134.7, 134.4, 134.1, 131.6, 128.1, 126.2, 124.6, 124.1, 123.7, 29.7, 15.9, 15.5. EI-TOF-MS (m/z): calculated for [C₂₈H₂₀Br₂S₆]⁻: 1410.0 (100.0%), 1405.2 (25.1%). Found: 1413.9 (100.0%), 1414.9 (14.6%). Compound CHO4T-Me: Melting point: 170–172 °C. Anal. Calcld for [C₂₈H₂₄O₄S₄]: C, 59.03; H, 3.65%. Found: C, 58.85; H, 3.38%. Main FTIR absorptions (KBr pellets, cm⁻¹): 3446 (b), 1708 (m), 1657 (s), 1446 (m), 1377 (m), 1238 (m), 1184 (m), 1079 (w), 858 (w), 789 (m), 679 (w), 471 (w).¹H NMR (500 MHz, CDCl₃) δ: 9.82 (s, 1H, CHO), 7.55 (s, 1H, thio), 7.25 (d, 1H, J = 4.1 Hz, thio), 7.18 (m, 3H, thio), 7.07 (d, 1H, J = 3.6 Hz, thio), 6.91 (d, 1H, J = 5.0 Hz, thio), 2.49 (s, 3H, CH₃), 2.44 (s, 3H, CH₃).¹³C NMR (125 MHz, CDCl₃) δ: 182.4, 141.5, 140.4, 139.7, 139.1, 136.6, 135.8, 134.7, 134.4, 134.1, 131.6, 128.1, 126.2, 124.6, 124.1, 123.7, 29.7, 15.9, 15.5. EI-TOF-MS (m/z): calculated for [C₂₂H₁₄O₂S₄]⁻: 386.6. Found: 386.0.

4.3. X-ray data collection and structural determination

Single-crystal sample of 2TPAZT methanol semisolvate was covered with glue and mounted on a glass fiber and then used for data collection. Crystallographic data were collected on a Bruker SMART 1K CCD diffractometer, using graphite mono-chromated Mo Kα radiation (λ = 0.71073 Å). The crystal system was determined by Laue symmetry and the space group was assigned on the basis of systematic absences using XPREP.¹⁴ Absorption corrections were performed to all data and the structure was solved by direct methods and refined by full-matrix least-squares method on F² by using the SHELXTL-PC software package. All non-H atoms were anisotropically refined and all hydrogen atoms were inserted in the calculated positions assigned fixed isotropic thermal parameters and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details, and refinement results is listed in Table S11, whereas bond distances and angles are given in Table S12.

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Supplementary data

Tables of the crystal data, experimental details and refinement results, selected bond lengths and angles, figures of r–r stacking interactions, DFT computational details, ¹H, ¹³C, ²⁴⁷H COSY NMR and EI-TOF-MS spectra, and electrochemistry diagrams for related compounds are included. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.06.087.

References and notes
