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Stable thiophene-based pure blue fluorescent molecules were successfully synthesized via a Pd-catalyzed Sonogashira coupling reaction of 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene with phenylacetylenes. The structures of these symmetrical compounds, including dithieno[3,2-b:2',3'-d]thiophene (DTT) as the π-center and various donor (D) groups, were determined on the basis of NMR spectral data, elemental analysis, and X-ray crystallography. The electronic properties of the D-π-D compounds also were investigated by spectroscopic methods such as UV-vis absorption spectroscopy and fluorescence emission spectroscopy guided by density functional theory (DFT) calculations (B3LYP/6-31G*). Additionally, the photo-properties were examined, which highlighted their potential application as blue-emitting materials in organic light-emitting diodes (OLEDs).

Introduction

Considerable attention has been paid to the development of oligothiophenes for use in organic solar cells, π-conjugated conducting polymers, high-performance organic field-effect transistors (OFET), and organic light-emitting materials. Generally, one of the strategies for fine-tuning the HOMOLUMO gap involves the utilization of extended thiophene subunits and particularly those rigid structures possessing an extended π-conjugation in the ground state, such as thienothiophenes (TTs) and dithienothiophenes (DTTs). Thiophenes can be obtained from thienoacenes that are effective for increasing the intermolecular interactions and adjusting the band gap of organic materials in the solid state. Dithieno[3,2-b:2',3'-d]thiophene (DTT) contains three annulated thiophene rings, which is one of the six isomers of DTTs with unique electronic properties due to their planar conjugated, sulfur-rich, and highly thermal stable structure.

The first synthesis and spectroscopic assignments of DTT were reported in 1971. The fused structure of DTT can promote π-stacking which is predicted to be a favourable motif for high charge transport in devices. This approach can help to create materials with low-energy electronic transitions based on donor-acceptor interactions. In this context, Kim and Navarette designed and synthesized a series of D-π-D and D-π-A type molecules base on the DTT unit for nonlinear optical materials. They also provided some desirable strategies to access further materials with this type of motif. This goal can be achieved by extending the degree of π conjugation within the materials, which affords smaller band gaps. Thus, there is substantial interest in the synthesis and photo-physical properties of new families of planar structures with π-conjugated pure-blue light-emitting molecules. Specifically, 6-bis(arylethynyl) substituted DTT derivatives are of interest. In these compounds, the π-functionalized phenylacetylene groups were successfully introduced into the thiophene core at the 2,6-positions to afford planar conjugated structures by employing a modified Sonogashira coupling reaction. The introduction of the phenylacetylene groups is expected to extend the conjugation of the thiophene chromophore. This results in a shift of the wavelength of absorption and fluorescence emission into the pure blue visible region of the electromagnetic spectrum and an improvement of the fluorescence quantum yields. In this paper, we report the synthesis of four types of dithienothiophene derivatives that combine the high hole mobility function of diarylethynyl substituents with the high efficiency and hole-injection ability of dithienothiophene as the conjugation core. This was achieved by using a Pd-catalysed Sonogashira coupling reaction (Scheme 1). In addition, the synthesis of four D-π-D chromophores starting from dithieno[3,2-b:2',3'-d]thiophene is also described.

Moreover, the photo-physical properties of these compounds are examined in solution through spectroscopic techniques, and this is supported with density functional theory (DFT) calculations.

Results and discussion

Synthesis and characterization

2,6-Dibromodithieno[3,2-b:2',3'-d]thiophene 1 was prepared by brominating dithieno[3,2-b:2',3'-d]thiophene (DTT) with N-bromosuccinimide (NBS) in acetic acid at room temperature for 2 h according to the previously reported procedure. The Pd-catalysed Sonogashira cross-coupling reactions were carried out between the 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene 1 and the phenylacetylenes under modified reaction conditions to afford the target 2,6-bis(arylethynyl)-substituted dithieno[3,2-b:2',3'-d]thiophenes 2a–d in moderate yield (Scheme 1).

The structures of these novel planar π-conjugated compounds 2a–d were fully characterized on the basis of 1H-NMR, 13C-NMR spectra, mass spectrometry and elemental analysis. 1H-NMR spectral data (300 MHz, CDCl3) for 2 show a singlet for the 3, 5-positions at δ = 7.46 ppm (2a), δ = 7.43 ppm (2b), δ = 7.41 ppm (2c) and δ = 7.36 ppm (2d), which are slightly downfield shifted from the dithieno[3,2-b:2',3'-d]thiophene 1 (δ = 7.27 ppm) and 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene 2
Simultaneously, the structures of 2a–d were further established on the basis of the base peak molecular ion at m/z[M⁺] 369.00 for 2a, 508.11 for 2b, 456.04 for 2c and 482.13 for 2d in their mass spectra. All results were consistent with the proposed structures. These four bis(arylethynyl)-functionalized dithieno[3,2-b:2′,3′-d]thiophenes 2a–d are very stable solids with colours from orange to red that can be kept in air for prolonged period of times at room temperature. All compounds have good solubility in all the common organic solvents including hexane, with melting points from 153 °C to over 255 °C. A single crystal of 2c, suitable for X-ray diffraction studies, was obtained by slow evaporation of solvents from a mixture of CH₂Cl₂ and hexane (3:2) at room temperature. From the X-ray diffraction studies, the extended π-conjugation of the dithieno[3,2-b:2′,3′-d]thiophene derivative 2c (Figure 1a) was revealed which lies on a mirror plane. From the packing pattern, a supramolecular network was constructed via a number of complicated intermolecular interactions. As a representative example, there are S1···S2 interactions at 3.408 Å giving rise to chains parallel to the c axis (Figure 1b). These chains then stack parallel to the b axis, and no significant π-π stacking interactions between the pyrene rings were observed. However, there are two different kinds of interactions based on the planar π-conjugated thiophene and C₆ aromatic ring, namely: 1) a C–H···π interaction of the donor group with the C₆ aromatic ring (blue pane), where the C–H···π distance is 2.704 Å; and 2) an S···π interaction of the S atom with the thiophene ring of the neighbouring molecules (dark blue pane) at a distance of 3.241 Å (Figure 1c). These intermolecular interactions lead to the three-dimensional framework (Figure 1d).

**Photo-physical properties**

The UV-vis absorption and fluorescence spectra of these four types of 2,6-bis(arylethynyl)-substituted dithieno[3,2-b:2′,3′-d]thiophenes 2a–d were measured in dilute dichloromethane and the optical data is summarized in Table 1. Compared with the value for the parent compound DTT at 291 nm, the maximum absorption wavelength of the D-π-D DTT derivatives 2 is observed more than ca. 95 nm red-shifted to 386 (2a), 390 (2b), 392 (2c), and 415 (2d), respectively. As expected, the molecular geometries of the D-π-D structures have a great influence on the optical properties due to the intramolecular charge transfer (ICT). On the other hand, for the UV-vis absorption spectra of the 2a–c, the profiles of these spectra are almost identical and the absorption bands were observed in the range of 340–430 nm (Figure 2a), which showed a large number of transition bands.

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<tr>
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<tr>
<td>2a</td>
<td>386</td>
<td>412 (386)</td>
<td>35</td>
<td>0.41</td>
</tr>
<tr>
<td>2b</td>
<td>390</td>
<td>424 (388)</td>
<td>34</td>
<td>0.47</td>
</tr>
<tr>
<td>2c</td>
<td>392</td>
<td>429 (389)</td>
<td>37</td>
<td>0.48</td>
</tr>
<tr>
<td>2d</td>
<td>415</td>
<td>484 (413)</td>
<td>69</td>
<td>0.57</td>
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DTT 291 374 (372) 83 0.01

All measurements were performed under degassed conditions. a 10⁻⁶ M in CH₂Cl₂, λₑₐ is the absorption band appearing at the longest wavelength. b 10⁻⁶ M in CH₂Cl₂, λₑₐ is the fluorescence band appearing at the shortest wavelength. c Absolute quantum yield in CH₂Cl₂ at ~ 10⁻⁶ M.

The fluorescence spectra of 2a–c exhibited a sharp peak at λₑₐ max = 412, 424, and 429 nm with a shoulder, respectively. The emission spectrum of 2d displays a single broad peak at 484 nm, which indicates that the emission occurs from the lowest excited state with the largest oscillator strength. With the increase of the π-conjugation, a gradual bathochromic shift in the λₑₐ max is clearly observed in the order of 2a < 2b < 2c < 2d, implying that the energy gap between the ground and the excited states would decrease in this order. In this process, the ICT plays an important role in lowering the energy gap. 18

Figure 3 shows the the fluorescence emission spectra of compound 2b for the concentration effect in dichloromethane at
room temperature. With increasing concentration of 2b from 1.0 × 10⁻⁶ M (line 1) to 1.0 × 10⁻³ M (line 9), the corresponding emission at 429 nm was observed for the monomer unit, and the intensity of this emission band gradually increased. The reason is for the sterically hindered substituents of the two bulky tert-butyl groups on the benzene rings at the 2, 6-positions in 2b which plays a very important role for inhibiting the close face-to-face \( \pi-\pi \) stacking interaction between the neighboring DTT units, which is consistent with the crystallographic results of 2c. In order to obtain more insight into of the photophysical properties of these new coplaner-shaped conjugation

![Figure 4](image)

**Figure 4.** (a), (b) Normalised fluorescence spectra and Lippert-Mataga plots of compound 2d recorded in (A) 1, 4-dioxane, (B) Cyclohexane, (C) THF, (D) CH₂Cl₂, and (E) DMF at 25 °C.

compounds, the normalized absorption spectra and the emission spectra of compound 2d in various solvent systems are determined and the optical data are summarized in Table 2. It is well-known that solvatochromic effects is not only depend on molecular structure, but also depend on the nature of the chromophore, as well as the solvents. Each monomer shows a slight solvatochromism in the absorption spectra and emission spectra. For 2d, a change of solvent from nonpolar cyclohexane to polar DMF caused only a very slight, positive, bathochromic shift with the \( \pi-\pi^* \) absorption band from 410 to 415 nm. On the other hand, in the case of the emission spectrum of 2d, we observed a substantial positive bathochromism with a peak around 446 nm in cyclohexane, while we observed a broad and red-shifted emission with only one peak at 515 nm in the highly polar solvent, DMF (Figure 4).

Such large Stokes’ shift observed for 2d in polar solvents which may result from the difference of the dipole moments between the delocalized ground state and the highly localized excited one. The highly localized excited state must come from between the delocalized ground state and the highly localized butyl groups on the benzene rings at the 2, 6-positions in molecular structure, but also depend on the nature of the properties of these new coplaner-shaped conjugation

\[
\Delta v = 2 \Delta \mu_{eg}^2 \Delta f / h c a^3 + \text{const},
\]

\[
\Delta f = [(e - 1) / (2e + 1)] - [(n^2 - 1) / (2n^2 + 1)]
\]

**Table 2.** Optical absorption and emission spectroscopic data for 2d in various solvents at room temperature.*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>Absorption * ( \lambda_{\text{abs}} ) [nm]</th>
<th>Fluorescence * ( \lambda_{\text{max}} ) [nm]</th>
<th>( \Phi_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 4-dioxane</td>
<td>386</td>
<td>412 (386)</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>390</td>
<td>424 (388)</td>
<td>0.47</td>
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<tr>
<td>THF</td>
<td>392</td>
<td>429 (389)</td>
<td>0.48</td>
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\( \Phi_e \) = Absolute quantum yield in CH₂Cl₂ at \( ~ \times 10^{-6} \) M.

Where \( \Delta v \) and \( \Delta \mu_{eg} \) are Stokes’ shift and the difference in the dipole moment between the excited and ground states, respectively; \( \Delta f \) is the orientation polarizability; \( h \) is Planck’s constant; \( c \) is the velocity of light; \( a \) is the Onsager radius around a fluorophore; \( \varepsilon \) is the dielectric constant; \( n \) is refractive index. To calculate \( \Delta \mu_{eg} \), the Stokes’ shifts for 2d were plotted against the \( \Delta f \) values in the various solvents of 1,4-dioxane, Cyclohexane, THF, CH₂Cl₂ and DMF (Figure 4). According to the Lippert–Mataga equation, the \( \Delta \mu_{eg} \) value for 2d was estimated to be ca. 30 D (from the slope), meaning that the dipole moment of 2d drastically changed from the ground to the excited states. On the basis of the large \( \Delta \mu_{eg} \) value and the DFT analysis for the ground states, one might suppose that charge separation can exist only in the excited states of the donor-modified \( \pi \)-extended dithienothiophene. The Lippert–Mataga plot for the various solvents used in this study also gave a relatively good correlation between the Stokes’ shifts of 2d and their \( \Delta f \) values. The thiophene core in 2d can behave as an acceptor moiety against the dimethylamino groups to increase the fluorescence solvatochromic probability based on ICT mechanism. As expected, the findings obtained from UV/vis and fluorescence spectra and Lippert–Mataga analysis imply that the charge separation arises in the excited states of the donor-modified 2d.

**Quantum chemistry calculations**

To reinforce the ICT mechanism, DFT calculations for 2 were performed to understand the electronic structures of the D-\( \pi \)-D compounds at the B3LYP/6-31G(d) level. In particular, the effect of the introduction of donor moieties onto the \( \pi \)-extended DTT. The optimized molecular geometries and frontier molecular orbitals of the four DTT-based derivatives for the DTT core are illustrated in Figure 5. In this model, obviously, the HOMOs of the compounds 2 are almost spread over the entire molecular skeleton, while the LUMOs are mostly distributed over the \( \pi \)-center, including the DTT core and the side triple bonds onto the DTT unit. Compared with the DTT unit, the separated LUMOs resulted from the electron-donating nature of the phenyl groups. The gradually increasing HOMO energy levels were delocalized onto the backbone.

\[ \begin{array}{cccc}
\text{CH}_2\text{Cl}_2 & 415 & 484 (413) & 0.57 \\
\text{DMF} & 291 & 374 (372) & 0.01 \\
\end{array} \]

\( ^{a} \) All measurements were performed under degassed conditions. \( ^{b} \) \( \times 10^{-6} \) M in CH₂Cl₂, \( \lambda_{\text{abs}} \) is the absorption band appearing at the longest wavelength. \( ^{c} \) \( \times 10^{-6} \) M in CH₂Cl₂, \( \lambda_{\text{abs}} \) is the fluorescence band appearing at the shortest wavelength. \( ^{d} \) Wavelength of excitation. \( ^{e} \) Absolute quantum yield in CH₂Cl₂ at \( ~ \times 10^{-6} \) M.
implying that the π-electrons were delocalized by the introduction of the conjugated side chain. The resulting extension of the side chain conjugation decreased the bandgap of the DTT derivatives resulting in the improved absorption of light at longer wavelengths and which are consistent with the photophysical properties results.

Conclusions

In conclusion, the modified Sonogashira cross-coupling reaction of the dibrominated DTT 1 with various kinds of phenylacetylenes produced at 100 °C for 48 h, and a new series of well-defined, DTT-based derivatives 2 with planer π-extended conjugated structures were obtained by this strategy. Upon construction of the D-π-D structures by additional p-substituted phenylethynyl in DTT, the HOMO-LUMO gap was diminished by an increase in the HOMO orbital energy and decrease in the LUMO orbital energy, which exhibited remarkable intermolecular charge-transfer (ICT). The results were verified through inspecting the absorption and emission spectra of compounds 2, for which obvious red-shift was observed. These D-π-D chromophores emitted bright blue-fluorescence and have good solubility in common organic solvents. Hence, they are promising as blue organic light-emitting materials for the fabrication of OLED devices, and further detailed investigations aimed at developing this applied research are currently ongoing in our group.

Experimental

1H and 13C NMR spectra were recorded at 300 MHz and 75 MHz on a Nicolet Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me4Si as an internal reference. Mass spectra were obtained on a Nicolet Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed by Yanaco MT-5. UV-vis spectra were recorded on a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer. Emission spectra were performed in a semimicro fluorescence cell (Hellma®; 104F-QS, 10 x 4 mm, 1400 µL) with a Varian Cary Eclipse spectrophotometer. Gas–liquid chromatograph (GLC) analyses were performed by Shimadzu gas chromatograph, GC-14A; silicone OV-1, 2 m; programmed temperature rise, 12 °C min⁻¹; carrier gas nitrogen, 25 mL min⁻¹.

Synthesis of 2,6-bis(phenylethynyl)dithieno[3,2-b:2',3'-d]thiophene (2a)

2,6-Dibromodithieno[3,2-b:2',3'-d]thiophene (1) (150 mg, 0.424 mmol), phenylacetylene (0.15 mL, 1.37 mmol), Pd(PPh₃)₄ (30 mg, 0.043 mmol), PPh₃ (22.3 mg, 0.086 mmol), Et₃N (7.5 mL), CuI (20 mg, 0.106 mmol) and DMF (7.5 mL) were mixed together and heated at 100 °C for 78 h in a Schlenk tube equipped with a magnetic stirring bar and a reflux condenser under N₂ atmosphere. The reaction was quenched with saturated solution of ammonium chloride (30 mL) and extracted with CHCl₃ (100 mL) three times. Then, the combined organic phase was washed with brine, and dried over MgSO₄. Evaporation of the solvent under vacuum resulted in a solid residue. The residue was adsorbed in silica gel (Wako gel, C-300) and purified by column chromatography using hexane as eluent and recrystallization from hexane to afford the desired compound 2a as yellow prisms (40 mg, 24%); m.p. 153 °C; δH (CDCl₃) 7.36–7.39 (6H, m, Ar-H), 7.46 (2H, s, Ar-H) and 7.54–7.56 (4H, m, Ar-H); δC (CDCl₃) 83.05, 95.02, 122.55, 124.27, 125.15, 128.46, 128.74, 131.48, 141.75, 170.61; m/z 369.0 (M⁺) (Found: C, 72.41; H, 3.08%). C₂₄H₁₂S₃ (369.55) requires C, 72.69; H, 3.05%.

Synthesis of 2,6-bis(4-tert-butylphenylethynyl)dithieno[3,2-b:2',3'-d]thiophene (2b)

Similarly, 2,6-bis(4-tert-butylphenylethynyl)dithieno[3,2-b:2',3'-d]thiophene (2b) was obtained in 20% yield as yellow needles (hexane); m.p. 187 °C; δH (CDCl₃) 1.33 (18H, s, t-Bu), 7.39 (4H, d, J = 8.4 Hz, Ar-H), 7.43 (2H, s, Ar-H) and 7.48 (4H, d, J = 8.4 Hz, Ar-H); δC (CDCl₃) 29.71, 40.17, 109.161, 111.81, 124.01, 128.73 and 150.4; m/z 508.11 (M⁺) (Found: C, 73.86; H, 5.43%). C₃₂H₁₄S₃ (508.76) requires C, 72.69; H, 5.55%.

Synthesis of 2,6-bis(3-methoxyphenylethynyl)dithieno[3,2-b:2',3'-d]thiophene (2c)

Similarly, 2,6-bis(3-methoxyphenylethynyl)dithieno[3,2-b:2',3'-d]thiophene (2c) was obtained in 18% yield as yellow needles (hexane); m.p. 157 °C; δH (CDCl₃) 3.84 (6H, s, OMe), 6.90 (4H, d, J = 8.8 Hz, Ar-H), 7.41 (2H, s, Ar-H) and 7.48 (4H, d, J = 8.8 Hz, Ar-H); δC (CDCl₃) 55.35, 81.83, 95.04, 114.16, 114.64, 124.58, 124.67, 131.09, 133.05, 141.50 and 160.05; m/z 456.04 (M⁺) (Found: C, 68.04; H, 3.54%). C₂₆H₁₆S₃ (456.60) requires C, 68.39; H, 3.53%.

Synthesis of 2,6-bis(dimethylamino)phenylethynyl)dithieno[3,2-b:2',3'-d]thiophene (2d)

Similarly, 2,6-bis(dimethylamino)phenylethynyl)dithieno[3,2-b:2',3'-d]thiophene (2d) was obtained in 5% yield as reddish-brown prisms (CHCl₃); m.p. 255 °C; δH (CDCl₃) 3.01 (12H, s, Me), 6.67 (4H, d, J = 8.8 Hz, Ar-H), 7.36 (2H, s, Ar-H) and 7.41 (4H, d, J = 8.8 Hz, Ar-H) and 7.41 (4H, d, J = 8.8 Hz, Ar-H).
Hz, Ar-H); δc (CDCl3) 29.71, 40.17, 109.16, 111.81, 124.01, 132.73 and 150.39; m/z 482.13 (M+) (Found: C, 67.54; H, 4.54%). C28H22S3 (482.69) requires C, 67.67; H, 4.59%.

**Single-crystal X-ray diffraction measurements**

A suitable single crystal (0.96 × 0.24 × 0.03 mm³) was taken up and mounted on a Bruker APEX 2 CCD diffractometer equipped with fine-focus MoKα (λ = 0.71073 Å) sealed tube radiation source for 2c. Detailed crystallographic data for 2c: C2H3O2S5, M = 456.57, orthorhombic, Pmc21, a = 50.00818(10), b = 7.3183(3), c = 5.9542(2) Å, V = 2178.9 (14) Å³, Z = 4, Δf = 1.392 g/cm³, T = 150(2) K, yellow lat; 9611 reflections measured of which 2715 were independent; data corrected for absorption on the basis of symmetry equivalent and repeated data (min and max transmission factors: 0.723 0.989) and Lp absorption on the basis of symmetry equivalent and repeated data.

**Notes and references**


Scheme 1. Synthesis of 2,6-bis(arylethynyl) substituted DTT derivatives 2.

Figure 1. (a) Crystal structure of 2c; (b), (c) detailed interactions between the neighbouring DTT molecules; (d) an overall view of the stacking of the self-assembly along the c axis.