Photochromic oligothienoacene derivatives with photo-switchable luminescene properties and computational studies†

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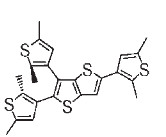
Photochromic thieno[3,2-*b*]thiophenes and dithieno[3,2-*b*:2′,3′-*d*]-thiophene with photo-switchable luminescence properties have been synthesized using a Suzuki cross-coupling reaction; their electronic structures, and photochromic and luminescence behaviour have also been studied.

Oligothienoacene derivatives have recently received increasing attention as they have been shown to display photoluminescence,[1] electroluminescence,[1b,d] non-linear optical,[2] and field-effect transistor properties;[1a,3] all of which are important properties for the fabrication of organic optoelectronic devices. With the well-known and attractive photochromic behaviour of diarylethenes[1f,4] and our recent interest in the design and synthesis of diarylethene-functionalized ligands,[5] we believe that incorporation of the diarylethene moiety into the oligothienoacene core would generate molecular materials with photoswitchable functional properties, which could be brought about by the reversible photochromic reactions.[6] Previously, we reported the synthesis of diarylethene-containing 1,10-phenanthroline[5a–d] through the Suzuki cross-coupling reactions of 5,6-dibromo-1,10-phenanthroline with thienylboronic acids. Using the same synthetic strategy, photochromic diarylethene-containing thieno[3,2-*b*]thiophenes and dithieno[3,2-*b*:2′,3′-*d*]thiophene were synthesized through the coupling of 2-methylthien-3-yl derivatives into the oligothienoacene core and their photophysical and photochromic properties were studied.



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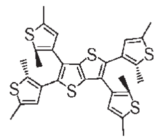

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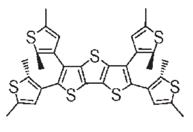

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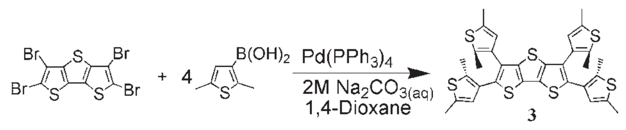
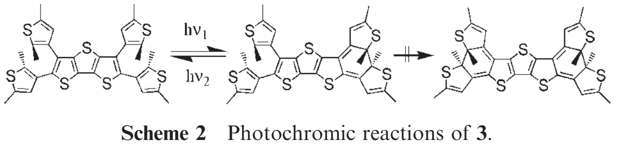
Due to the lack of efficient synthetic methodologies for oligothienoacenes, the uses of these systems were limited. Different synthetic methodologies for these fused thiophene systems have been recently reviewed.[7] Using the synthetic routes developed by Iddon and coworkers[8] as well as Frey, Holmes and coworkers,[9] the bromo-derivatives of thieno[3,2-*b*]thiophene and dithieno[3,2-*b*:2′,3′-*d*]thiophene were prepared. Subsequent Suzuki cross-coupling reactions of these bromo-derivatives with an excess of 2-methylthien-3-yl boronic acid using $Pd(PPh_3)_4$ as catalyst in a mixture of aqueous Na_2CO_3 (2 M) and 1,4-dioxane under reflux conditions (Scheme 1) gave target compounds **1–3** in moderate yield.



Scheme 1 Synthetic route for **3**.

Compounds **1–3** have been characterized by ^{1}H NMR, EI-MS and gave satisfactory elemental analyses.§ Unlike the commonly encountered poor processability of the fused thiophene systems, compounds **1–3** have good solubility in common organic solvents, which is attributed to the presence of the solubilizing 2,5-dimethylthiophene substituents. The compounds all dissolved in benzene to give colorless solutions, with intense absorption bands at *ca.* 330 nm for **1** and **2** and at *ca.* 350 nm for **3**, corresponding to the $\pi \rightarrow \pi^*$ transitions of the fused thiophene rings mixed with that of the dimethylthiophene moieties. The lower absorption energy for **3** compared to that of **1** and **2** is in line with the more extended π-conjugation for dithienothiophene compared to thienothiophene.[1c,10] On excitation with $\lambda \leq 370$ nm, compounds **1–3** displayed intense luminescence with $\lambda_{em} \approx 405$ nm for **1** and **2** [**1**, $\tau_o < 1$ ns, $\phi_{em}(\lambda_{ex}$ 330 nm$) = 0.10$; **2**, $\tau_o < 1$ ns, $\phi_{em}(\lambda_{ex}$ 330 nm$) = 0.06$] and $\lambda_{em} \approx 420$ nm for **3** [$\tau_o < 1$ ns, $\phi_{em}(\lambda_{ex}$ 330 nm$) = 0.14$], derived from the thienothiophene and dithienothiophene moieties, respectively. The red shift in the emission maximum for **3** compared to that for **1** and **2** is also supportive of the assignment. The exceptionally short emission lifetime in the sub-nano-second range is suggestive of a fluorescence origin.

On UV excitation into the absorption bands ($\lambda \leq 370$ nm for **1** and **2**, and $\lambda \leq 392$ nm for **3**), all compounds in benzene solution displayed photochromism and became purplish red in colour with the evolution of an intense absorption band at *ca.* 380 nm in the UV region and a moderately intense absorption band at *ca.* 560 nm in the visible region, typical of absorptions of the closed form.[4–6] However, for compounds **2** and **3**, which consist of two diarylethene moieties, photocyclization could only take place at one of the diarylethene moieties even upon prolonged irradiation (Scheme 2). This could be reflected in



Scheme 2 Photochromic reactions of **3**.

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† Electronic supplementary information (ESI) available: Experimental procedures and the computational details of 1–3. See DOI: 10.1039/b810585e

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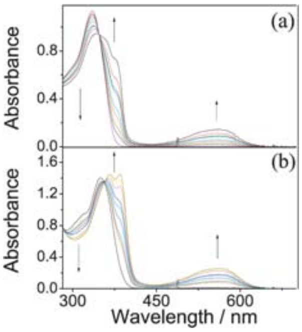

Fig. 1 UV-Vis absorption spectral changes of (a) **1** (4.32×10^{-5} M) and (b) **3** (4.22×10^{-5} M) in benzene solution upon excitation at 326 nm.

the ^{1}H NMR spectra as well as the observation of the very well-defined isosbestic point and the close resemblance of the UV-Vis absorption spectral changes of **2** and **3** compared to that of **1** on UV excitation (Fig. 1). Similar inactivity of the second photocyclization has also been reported for molecules containing two diarylethene moieties.[11] This may be attributed to the presence of the lower-lying excited state in the 8a,8b-dimethyl-1,8-dithia-*as*-indacene moiety (closed form moiety), which quenched the reactive excited state *via* an effective intramolecular pathway. On excitation into the absorption of the closed forms **1′–3′** at 500–610 nm, the absorption bands of the closed form decreased in intensity, indicative of the regeneration of the open forms **1–3** as a result of the photochromic backward reaction. The quantum yield for both processes have been determined (Table 1). Similar to other diarylethenes,[4–6] the quantum yields for the photocyclization (0.24–0.35)[12] are much higher compared to that for the photocycloreversion (0.04–0.08).

Apart from the changes in the absorption properties, the emission intensities of **1–3** were found to drop significantly on conversion to the closed forms **1′–3′** (Fig. 2). Similarly, the decrease in the emission intensity on conversion to the closed forms **1′–3′** may be attributed to the quenching of the emissive excited state by the lower-lying excited state of the closed form moiety. This is in agreement with the rationale for the inactivity of the second photocyclization reaction.

Table 1 A summary of the photochemical quantum yields of **1–3** in benzene solution at 298 K

	Photocyclization, ϕ_{326}	Photocycloreversion, ϕ_{502}
1	0.32	0.08
2	0.36	0.06
3	0.24	0.04

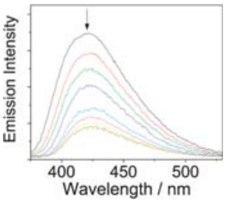

Fig. 2 Emission spectral changes of **3** in benzene solution upon excitation at the isosbestic point (λ_{ex} = 356 nm).

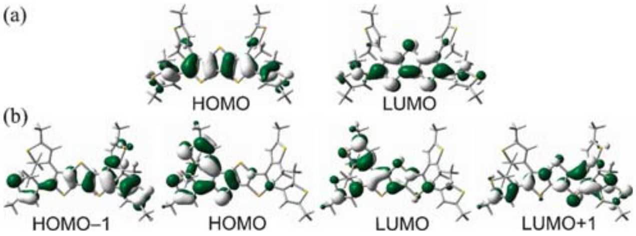

Fig. 3 Spatial plots (isovalue = 0.03) of selected TDDFT/CPCM frontier molecular orbitals of (a) **3** and (b) **3′**.

In order to gain further insight into the nature of the electronic absorption and emission properties of this class of compounds, DFT, TDDFT, HF and CIS calculations[13] were performed to study the electronic structures of the ground and excited states for **1–3** and **1′–3′**. To reduce the computational cost, only the photochemically active antiparallel conformation in the open forms (Fig. S1†) were considered. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the open forms **1–3** are mainly contributed from the respective π and π* orbitals of the oligothienoacene core, mixed slightly with the π and π* orbitals of the peripheral thiophene rings. However, for the closed forms **1′–3′**, the HOMO and LUMO consist of the π and π* orbitals localized on the condensed thiophene moiety, respectively. Fig. 3 shows the spatial plots of selected frontier molecular orbitals of **3** and **3′**. The orbital energies of the HOMO and LUMO are listed in Table 2. The smaller HOMO–LUMO gap in **3** compared to that of **1** and **2** is consistent with the observation in the UV-Vis absorption spectra. In addition, a significant decrease in HOMO–LUMO energy gap is found in **1′–3′**, relative to the corresponding **1–3** as a more extended π-conjugation in the condensed thiophene moiety leads to the increase in energy of π and decrease in energy of π* orbitals (See Table 2).

Selected singlet–singlet transitions of **1–3** and **1′–3′** are listed in Table S1† and Table S2,† respectively. The spectral assignment is based on the correlation of the experimental band maxima with the calculated excitation wavelengths of the transitions with significant oscillator strengths (*f*). The absorption bands are computed at 336 nm (f = 0.881) for **1**, 334 nm (f = 0.654) for **2** and 353 nm for **3** (f = 0.970). This transition mainly corresponds to an excitation from HOMO to LUMO, which can be assigned as the π–π* transition of oligothienoacene core, slightly mixed with π–π* transition of the peripheral thiophene rings. These calculated wavelengths are in excellent agreement with the λ_{max} in the major electronic absorption bands (334 nm for **1**, 332 nm for **2**, and 350 nm for **3**).

Two singlet excited states in the closed forms **1′–3′**, S_1 and S_3, with the calculated excitation wavelengths that compare well with the λ_{max} in the high- and low-energy absorption bands, were observed in the electronic absorption spectra in **1′–3′** (378 and 560 nm for **1′**, 370 and 560 nm for **2′**, and 386 and 564 nm for **3′**). The calculated excitation wavelengths for the S_1 excited state are

Table 2 The TDDFT/CPCM orbital energies of **1–3** and **1′–3′**

	Open form			Closed form		
	1	**2**	**3**	**1′**	**2′**	**3′**
LUMO	−1.12	−1.09	−1.27	−1.91	−1.89	−1.97
HOMO	−5.45	−5.45	−5.41	−4.59	−4.59	−4.62
$\Delta E_{\text{HOMO–LUMO}}$	−4.33	−4.36	−4.15	−2.68	−2.70	−2.65

computed at 585 ($f = 0.187$) for **1′**, 582 ($f = 0.189$) for **2′**, and 589 nm ($f = 0.224$) for **3′**, mainly consisting of an excitation from HOMO to LUMO, and can be assigned as the IL π–π* transition of the condensed thiophene moiety. The S_3 state of the closed forms is mainly composed of two excitations, HOMO−1 → LUMO and HOMO → LUMO+1 (Table S2†), which is computed at 377 ($f = 1.025$) for **1′**, 378 ($f = 0.776$) for **2′**, and 392 nm ($f = 1.067$) for **3′**. In view of the topologies of the MOs involved in the excitation with the largest transition coefficient (HOMO−1 → LUMO), the high-energy absorption band in **1′–3′** can be attributed to the π–π* transitions from the orbital concentrated on peripheral thiophene(s) and the oligothienoacene core to the orbital concentrated on the condensed thiophene moiety (see Fig. 3) with charge transfer character, mixed with the π–π* transitions from the condensed thiophene moiety.

The optimized structures of the S_1 state of the open forms **1–3** and selected changes in the structural parameters relative to that of the corresponding ground state optimized at the HF level of theory are shown in Fig. S2.† The major geometrical changes in the excited states occur mainly in the oligothienoacene core, in which the C=C bond distances are lengthened whereas the C–C bond distances are shortened. The feature is understandable, as the excitation involves population of the LUMO which contains quinoid character. On the basis of these S_1 optimized geometries, the emission energies of the open forms **1–3** are computed using TDDFT/CPCM at the PBE1PBE level of theory. The emission energy is computed at 394 nm for **1**, 386 nm for **2** and 400 nm for **3**. Although the calculated emission energies are all slightly blue-shifted when compared to the λ_{em} in the emission spectra (400 nm for **1**, 405 nm for **2** and 420 nm for **3**), a red shift in the emission energy for **3** relative to **1** and **2** is reproduced and in line with the experiment.

In summary, a series of photochromic diarylethene-containing fused thiophenes has been synthesized and their photophysical and photochromic properties studied. The photoluminescence properties of these compounds were successfully modulated using the photochromic reactions. The electronic structures as well as the nature of the absorption and emission properties of this class of compounds have been studied by theoretical calculations. Extension of this work towards the fabrication of photoswitchable field effect transistors using these compounds is now in progress.

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Notes and references

§ Characterization of **1**. Found: C, 61.20; H, 4.85. Calc. for $C_{24}H_{22}S_5$: C, 61.23; H, 4.71%. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ 2.11 (3H, s, Me), 2.13 (3H, s, Me), 2.16 (6H, s, Me), 2.21 (3H, s, Me), 2.34 (3H, s, Me), 6.80 (1H, s, thienyl proton), 6.86 (1H, s, thienyl proton), 6.92 (1H, s, thienyl proton), 7.06 (1H, s, thienothienyl proton); *m*/*z* (EI) 470 (100%) [M$^+$].

Characterization of **2**. Found: C, 61.96; H, 4.92. Calc. for $C_{30}H_{28}S_6$: C, 62.02; H, 4.86%. ^{1}H NMR (400 MHz; C_6D_6; Me_4Si): δ 2.10 (6H, s, 2-Me), 2.14 (6H, s, 2-Me), 2.18 (6H, s, 5-Me), 2.20 (6H, s, 5-Me), 6.76 (2H, s, thienyl proton), 6.98 (2H, s, thienyl proton); *m*/*z* (EI) 580 (100%) [M$^+$].

Characterization of **3**. Found: C, 60.47; H, 4.55. Calc. for $C_{32}H_{28}S_7$: C, 60.34; H, 4.43%. ^{1}H NMR (400 MHz; C_6D_6; Me_4Si): δ 2.09 (6H, s, 2-Me), 2.11 (6H, s, 2-Me), 2.14 (6H, s, 5-Me), 2.20 (6H, s, 5-Me), 6.74 (2H, s, thienyl proton), 6.90 (2H, s, thienyl proton); *m*/*z* (EI) 636 (100%) [M$^+$].

1 (*a*) X. C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat and R. H. Friend, *J. Am. Chem. Soc.*, 1998, **120**, 2206; (*b*) F. Osterod, L. Peters, A. Kraft, T. Sano, J. J. Morrison, N. Feeder and A. B. Holmes, *J. Mater. Chem.*, 2001, **11**, 1625; (*c*) X. Zhang and A. J. Matzger, *J. Org. Chem.*, 2003, **68**, 9813; (*d*) M. Mazzeo, V. Vitale, F. D. Sala, M. Anni, G. Barbarella, L. Favaretto, G. Sotgiu, R. Cingolani and G. Gigli, *Adv. Mater.*, 2005, **17**, 34; (*e*) P. Bäuerle, M. Ammann, M. Wilde, G. Götz, E. Mena-Osteritz, A. Rang and C. A. Schalley, *Angew. Chem., Int. Ed.*, 2007, **46**, 363; (*f*) X. Li and H. Tian, *Tetrahedron Lett.*, 2005, **46**, 5409.

2 (*a*) M. Blenkle, P. Boldt, C. Bräeuchle, W. Grahn, I. Ledoux, H. Nerenz, S. Stadler, J. Wichern and J. Zyss, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1377; (*b*) O. K. Kim, A. Fort, M. Barzoukas, M. Blanchard-Desce and J. M. Lehn, *J. Mater. Chem.*, 1999, **9**, 2227; (*c*) J. Casado, V. Hernandez, O. K. Kim, J. M. Lehn, J. T. Lopez Navarrete, S. Delgado Ledesma, R. Ponce Ortiz, M. C. Ruiz Delgado, Y. Vida and E. Periz-Inestrosa, *Chem.–Eur. J.*, 2004, **10**, 3805.

3 (*a*) J. Cornil, J. P. Calbert, D. Beljonne, R. Silbey and J. L. Brédas, *Adv. Mater.*, 2000, **12**, 978; (*b*) M. D. Iosip, S. Destri, M. Pasini, W. Porzio, K. P. Pernstich and B. Batlogg, *Synth. Met.*, 2004, **146**, 251; (*c*) K. Xiao, Y. Q. Liu, T. Qi, W. Zhang, F. Wang, J. H. Gao, W. F. Qiu, Y. Q. Ma, G. L. Cui, S. Y. Chen, X. W. Zhan, G. Yu, J. G. Qin, W. P. Hu and D. B. Zhu, *J. Am. Chem. Soc.*, 2005, **127**, 13281; (*d*) I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, 2006, **5**, 328.

4 (*a*) M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985; (*b*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (*c*) M. M. Krayushuin, *Chem. Heterocycl. Compd.*, 2001, **37**, 15; (*d*) K. Matsuda and M. Irie, *J. Photochem. Photobiol., C*, 2004, **5**, 169; (*e*) H. Tian and S. J. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85; (*f*) Y. Feng, Y. Yan, S. Wang, W. Zhu, S. Qian and H. Tian, *J. Mater. Chem.*, 2006, **16**, 3685.

5 (*a*) V. W. W. Yam, C. C. Ko and N. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 12734; (*b*) C. C. Ko, W. M. Kwok, V. W. W. Yam and D. L. Phillips, *Chem.–Eur. J.*, 2006, **12**, 5840; (*c*) T.-W. Ngan, C.-C. Ko, N. Zhu and V. W.-W. Yam, *Inorg. Chem.*, 2007, **46**, 1144; (*d*) J. K.-W. Lee, C.-C. Ko, K. M.-C. Wong and V. W.-W. Yam, *Organometallics*, 2007, **26**, 12; (*e*) P. H.-M. Lee, C.-C. Ko, N. Zhu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2007, **129**, 6058.

6 (*a*) F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327; (*b*) P. Belser, L. De Cola, F. Hartl, V. Adamo, B. Bozic, Y. Chriqui, V. M. Iyer, R. T. F. Jukes, J. Küni, M. Querol, S. Roma and N. Salluce, *Adv. Funct. Mater.*, 2006, **16**, 195.

7 (*a*) A. Comel, G. Sommen and G. Kirsch, *Mini-Rev. Org. Chem.*, 2004, **1**, 367; (*b*) T. Ozturk, E. Ertas and O. Mert, *Tetrahedron*, 2005, **61**, 11055.

8 L. S. Fuller, B. Iddon MP and K. A. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1999, 1273.

9 J. Frey, A. D. Bond and A. B. Holmes, *Chem. Commun.*, 2002, 2424.

10 M. Catellani, R. Lazzaroni, S. Luzzati and J.-L. Brédas, *Synth. Met.*, 1999, **101**, 175.

11 (*a*) K. Higashiguchi, K. Matsuda, M. Matsuo, T. Yamada and M. Irie, *J. Photochem. Photobiol., A*, 2002, **152**, 141; (*b*) K. Higashiguchi, K. Matsuda and M. Irie, *Angew. Chem., Int. Ed.*, 2003, **42**, 3537; (*c*) K. Higashiguchi, K. Matsuda, N. Tanifuji and M. Irie, *J. Am. Chem. Soc.*, 2005, **127**, 8922.

12 The quantum yields have not been corrected to the active antiparallel conformation as the two forms are readily inter-converted and are in dynamic equilibrium at room temperature.

13 See supplementary information for the computational details.