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Tetrahedron Letters 47 (2006) 4961–4964

Tetrahedron Letters

Donor–acceptor molecules containing thiophene chromophore: synthesis, spectroscopic study and electrogenerated chemiluminescence

Xichuan Yang,[a,*] Xiao Jiang,[a] Changzhi Zhao,[b] Ruikui Chen,[a]
Peng Qin[a] and Licheng Sun[a,c,*]

[a] *State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology(DUT), 158 Zhongshan Road, 116012 Dalian, PR China*
[b] *College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, 53 Zhengzhou Road, 266042 Qingdao, PR China*
[c] *Department of Chemistry, Organic Chemistry, Royal Institute of Technology(KTH), Teknikringen 30, 10044 Stockholm, Sweden*

Received 27 February 2006; revised 24 April 2006; accepted 25 April 2006
Available online 26 May 2006

Abstract—Donor–acceptor molecules containing thiophene chromophore with remarkably large Stokes shift (>210 nm) have been found to exhibit strong and stable ECL emission via the singlet excited state without the addition of any co-reactant or a second compound.

It is well known that electrogenerated chemiluminescence (ECL) has been developed as an important and valuable detecting technique in analytical chemistry. A series of studies on ECL has been conducted in recent years. Several review articles including different aspects of ECL have also been published.[1a–d] During the past two decades, most attention has been paid to the ECL reaction based on the ruthenium polypyridine complexes, especially $\mathrm{Ru(bpy)_3^{2+}}$ and its derivatives, which have shown broad applications.[1e–k] Many studies in this field have been carried out by Bard and co-workers. By comparison, however, organic molecules capable of generating ECL have been reported relatively infrequently. There are a number of reports on the photophysics of the donor–acceptor π-conjugated (D–π–A) systems, but only a few studies have been reported on the generation of ECL through the direct attachment of a donor to an acceptor.[2] As examples, Bard and co-workers reported detail studies on the ECL of the D–π–A molecule (BPQ–PTZ).[3a] Recently, Ho and co-workers have also reported the ECL of a series of D–π–A compounds.[4]

In this letter, we report the synthesis and photophysical properties of a series of new multifunctional organic fluorescent molecules, **1**–**5**, with 1,2,2,4-tetramethyl-1,2,3,4-tetrahydroquinolin-6-yl, *N*,*N*-dimethylamino or

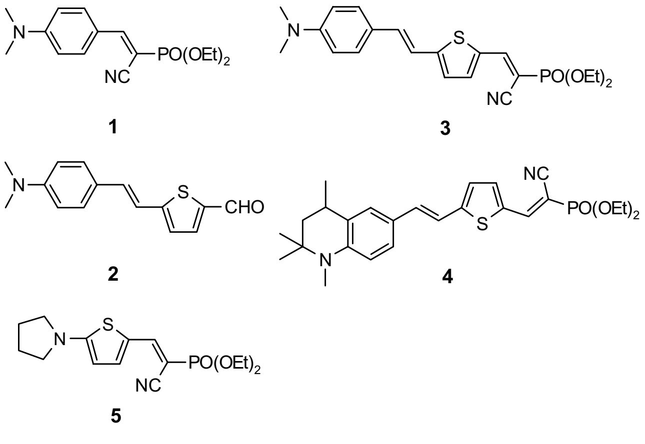

Figure 1. The Structures of D–π–A Molecules **1**–**5**.

Keywords: D–π–A; Thiophene; Electrogenerated chemiluminescence (ECL); Twist intramolecular charge transfer (TICT).

[*] Corresponding authors. Tel.: +86 411 88993886; fax: +86 411 83702185 (X.Y.); tel.: +46 8 7908127; fax: +46 8 7912333 (L.S.); e-mail addresses: yangxc@dlut.edu.cn; lichengs@kth.se

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doi:10.1016/j.tetlet.2006.04.154

Table 1. Photophysical Characters of Compounds **1**–**5** in CH_3OH

Compound	λ_{abs} (nm)	λ_{em} (nm)	$\Delta\lambda_{st}$ (nm)	E_g(eV)
1	408	464	56	2.73
2	433	651	218	2.39
3	487	710	223	2.10
4	507	734	227	1.97
5	444	485	41	2.58

pyrrolidine as the donor moiety, a thienylvinyl unit as the bridge, and diethyl cyanomethylphosphonate as the acceptor moiety (Fig. 1). These molecules exhibit chemiluminescence on a platinum electrode, with Ag/Ag^+ as reference electrode in CH_2Cl_2, when an electronic-pulse was applied on the electrodes. In addition, a twist intramolecular charge transfer (TICT) fluorescence with relatively larger Stokes shift (>210 nm) was also observed, indicating the potential applications of these molecules as fluorescence sensors, polarity sensors, etc.[5]

The D–π–A molecules **1**–**5** are prepared according to a general synthetic procedure. Reaction of 4-*N*,*N*-dimethylamino-benzaldehyde with diethyl 2-thienylmethylphosphonate in the presence of *t*-BuOK via Horner–Emmons Witting conditions leads to the formation of compound (*E*)-1-(4-*N*,*N*-dimethylaminophenyl)-2-(2-thienyl)ethylene. This compound was formylated in the unsubstituted 5-position of the thiophene ring in the presence of *n*-BuLi by Vilsmeier reaction to give compound **2**. Compound **3** was prepared by Knoevenagel condensation of **2** with diethyl cyanomethylphosphonate in the presence of piperidine. Compound **4** was prepared by a similar procedure to **3**. Other compounds were obtained according to the above corresponding method.

The absorption and emission maxima of compounds **1**–**5** in CH_3OH are listed in Table 1. The absorption spectrum of **3** has a large red shift (more than 80 nm) and a broad absorption band in comparison with **1**, see Figure 2a, due to the presence of a thiophene chromophore and the existence of the twist intramolecular charge transfer (TICT) states of **3**.[4a] For a similar reason, compound **4** exhibits an even larger red shift. Both compounds **3** and **4** have the same electron-acceptor group. The larger red shift of **4** than **3** is most likely attributable to the difference in their electron donor parts. The ring structure at the end of the electron-donating group in **4** avoids free rotation about the N–C bond forming a rigid planar configuration, while **3** has the possibility for free rotation. Compared to **1**, the λ_{max} of **5** is obviously red shifted due to the effective delocalization of π-electrons in the presence of the thiophene chromophore (Table 1). Furthermore, the energy gap, E_g (Table 1), between the LUMO and the HOMO of these molecules was decreases with the increasing strength of the D–π–A system.

It is noteworthy to mention that remarkably large Stokes shifts (>210 nm) were observed for compounds **2**, **3**, and **4** (see Fig. 2b and Table 1). This also strongly suggests the possible occurrence of a TICT state from the donor moiety to the acceptor unit in these molecules.[3,4a,6]

The redox potentials of compounds **1**–**5** are summarized in Table 2, and the cyclic voltammograms of compounds **1** and **3** in CH_2Cl_2 are shown in Figure 3. The CV of compound **3** exhibited a reversible and an irreversible one-electron oxidation wave, and a quasi-reversible

Table 2. Electrochemical data (vs SCE), fluorescent and ECL characters of compounds **1**–**5** in CH_2Cl_2

Compound	$E_{pa}(1)$ (V)[a]	E_{pc} (V)	λ_{em} (nm)	λ_{ECL} (nm)	$-\Delta H^\circ_{ann}$ (eV)[b]	E_s (eV)
1	1.07	−1.90	453	—	—	—
2	0.66	−1.74	584	572	2.24	2.12
3	0.66	−1.46	657	630	1.96	1.89
4	0.55	−1.46	687	654	1.85	1.80
5	0.86	−1.94	481	500	2.64	2.58

[a] Only the first oxidation potentials are listed in Table 2.

[b] $-\Delta H^{o}_{ann}/\text{eV} = E_{pa}(1) - E_{pc}(1) - 0.16\text{eV}$.[7]

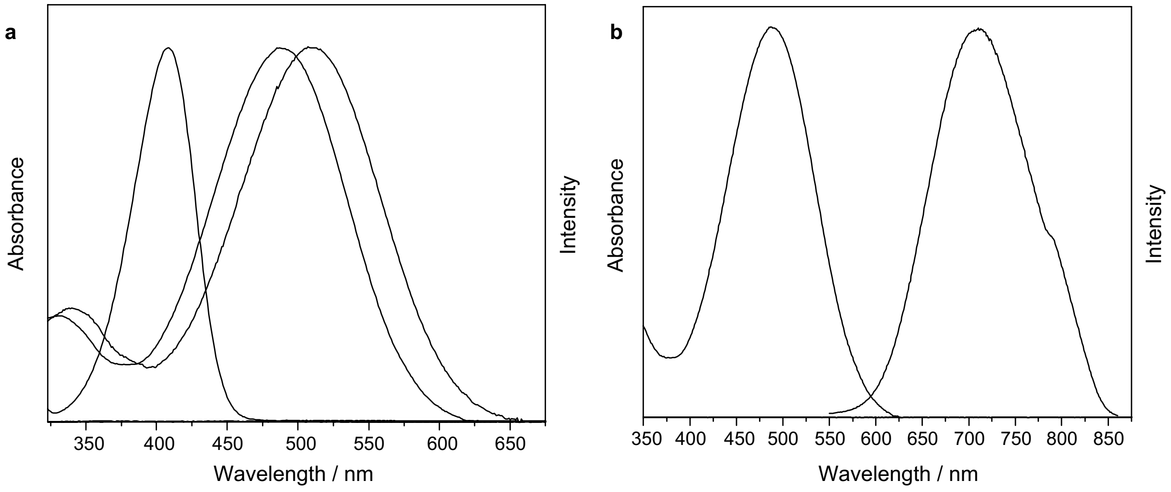

Figure 2. (a) Optical absorption of **1** (left curve), **3** (middle curve) and **4** (right curve) in CH_3OH. (b) Absorption (left curve) and fluorescence (right curve) spectra of **3** in CH_3OH.

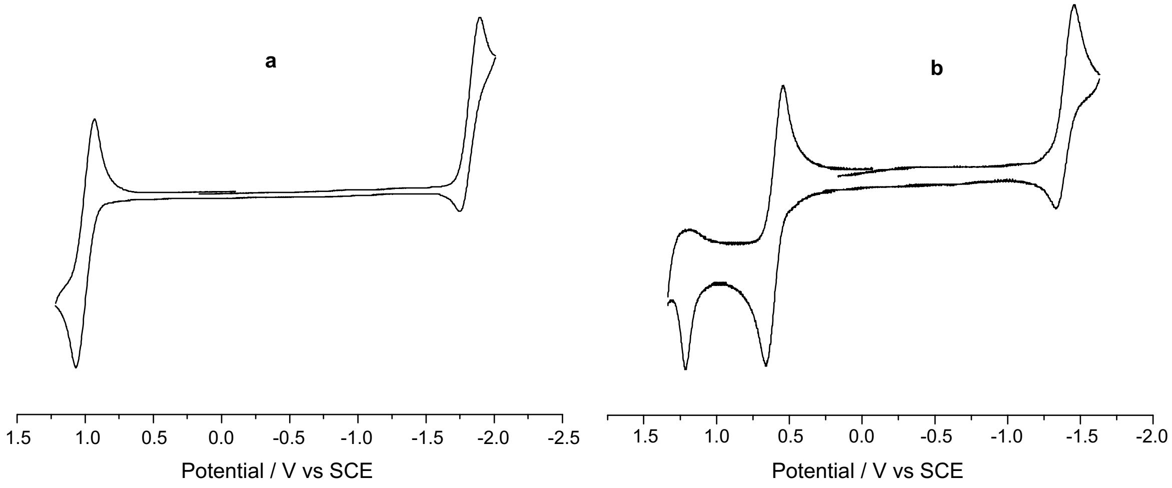

Figure 3. Cyclic voltammograms of **1** (a) and **3** (b) with sample concentration of 10^{-3} M containing 50 mM $TBAPF_6$ as the supporting electrolyte in CH_2Cl_2 using a platinum electrode as a working electrode and Ag/Ag^+ as reference electrode, scan rate $100\ mV\,s^{-1}$.

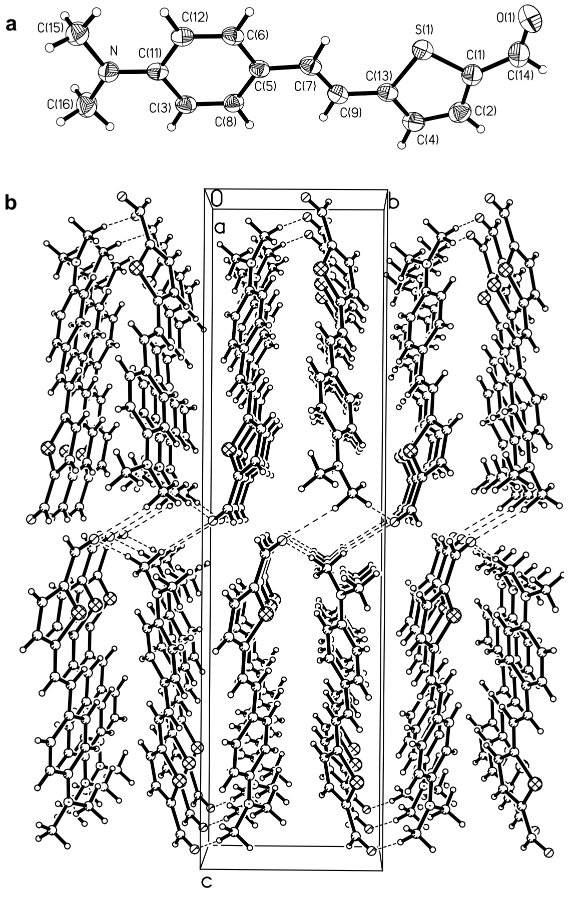

Figure 4. X-ray crystal structure (a) and crystal packing diagram (b) of compound **2** with thermal ellipsoid set at 30% probability.

one-electron reduction wave. The CV of compound **2** is very similar to that of **3**. When comparing the E_{pc} values of **2** and **3**, it is evident that the reduction potential of **2** is more negative than that of **3** (Table 2). This indicates that the reduction of **3** is easier than **2** due to the introduction of a strong electron-withdrawing group.

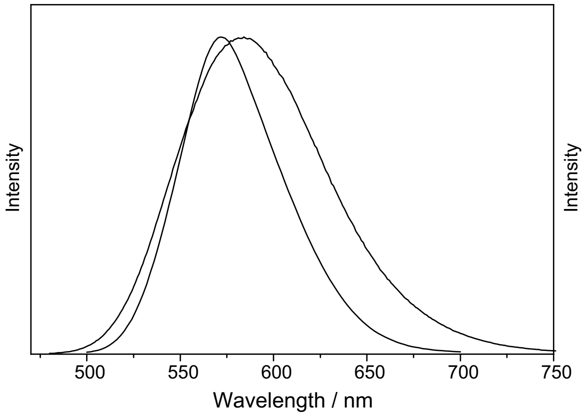

Figure 5. ECL (left curve) and fluorescence (right curve) spectra of 10^{-3} M solution of **2** in CH_2Cl_2 containing 50 mM $TBAPF_6$ as an electrolyte. The potential was stepped up from −1.8 to +1.2 V pulse for 0.5 s.

The X-ray crystal structure of compound **2** (Fig. 4) shows that the molecule has a planar structure, indicating an effective conjugation through the molecular axis.[8] From the crystal packing diagram, it was found that the inter-planar distance between the two parallel benzene or thiophene planes of adjacent molecules was 2.63 Å, which is within the range of a typical π–π interaction.[4d,9]

In our electrochemical study, the first oxidation and first reduction processes in these molecules are chemically reversible in the cyclic voltammograms. So the electrogenerated radical ions are stable, and therefore an efficient ECL could occur as a result of ion annihilation.[4b] Figure 5 shows the ECL spectrum of compound **2** in CH_2Cl_2 containing 50 mM $TBAPF_6$ as an electrolyte. The ECL maxima for compounds **1**–**5** are summarized in Table 2. Compounds **2**, **3**, **4** and **5** exhibit ECL character, while **1** does not. The ECL emission maximum of **2** is blue-shifted in comparison with the fluorescence emission maximum in the same solvent. This may be attributed to the π–π interaction between the two parallel molecules in solution (Fig. 4b). This type of interaction formation may cause the ECL emission to be blue-shifted when compared with the photoluminescence values previously reported.[4c]

The ECL maximum of **2** in CH_2Cl_2 is close to the photoluminescence maximum, and only blue shifted by ca. 12 nm (Fig. 5). The narrow emission band of ECL, and the absence of a relatively large shift for the ECL maximum compared to those of photoluminescence, excludes the possibility of excimer formation (E-route) during the ion annihilation process.[4b,10] More importantly, the ECL intensity is not increased when the fluorophore concentration is increased. Thus, we can safely conclude that there is no excimer formation during the ECL process. By comparison, the fluorescence spectrum of **2** was recorded in CH_2Cl_2 in the same concentration (10^{-3} M) as used for the ECL measurements. We found that the photoluminescence maximum is invariable as compared to that at 10^{-5} M concentration, although with drastically reduced intensity. Therefore, it can be considered that the ECL emissive species is different from that of the photoluminescent species, and the ECL emission is from an aggregate which is formed via the π–π interaction of two adjacent parallel molecules.[11a]

The ECL emission of compounds **1**–**5** involve TICT states,[11b] and the blue shift can be explained as above. Compounds **1** and **5** have simple and similar molecular structure; however, an ECL emission was observed for **5** but not for **1**. In addition to the delocalization of π-electrons mentioned above for compound **5**, under electrochemistry conditions, the charge separation is more accessible due to the introduction of thiophene ring. Here, the positive and negative charges are effectively separated which allows for a longer life time. Thus, ECL emission could be easily produced via the annihilation reaction of a radical anion and a radical cation.[12] In this case, the energy provided by the radical ions is sufficient enough to populate the singlet excited state. When the ECL is produced via the S-route, the following equation must be satisfied:[12]

$$-\Delta H^{\circ}_{\mathrm{ann}} \geqslant E_{\mathrm{s}} \tag{1}$$

where $-\Delta H^{\circ}_{\mathrm{ann}}$ is the annihilation reaction enthalpy and E_{s} is the energy for the first excited singlet generation state.

As seen from Table 2, the energy provided by the ion-annihilation reaction is larger than that required for the direct production of the singlet state, hence it is enough to produce a singlet state directly. Furthermore, in these energy sufficient systems, all the stable ECL spectra can be observed via the S-route without the addition of any co-reactant or a second compound.

Acknowledgements

Financial support of this work from the following sources is gratefully acknowledged: China Natural Science Foundation (Grant 20128005), the Ministry of Science and Technology (MOST) (Grant 2001CCA02500), the Ministry of Education (MOE) and the Swedish Energy Agency and the Swedish Research Council.

References and notes

1. (a) Kulmala, S.; Suomi, J. *Anal. Chim. Acta* **2003**, *500*, 21–69; (b) Richter, M. M. *Chem. Rev.* **2004**, *104*, 3003–3036; (c) Fähnrich, K. A.; Pravda, M.; Guilbault, G. G. *Talanta* **2001**, *54*, 531–559; (d) Knight, A. W. *Trends Anal. Chem.* **1999**, *18*, 47–62; (e) White, H. S.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 6891–6895; (f) Ege, D.; Becker, W. G.; Bard, A. J. *Anal. Chem.* **1984**, *56*, 2413–2417; (g) Zu, Y.; Bard, A. J. *Anal. Chem.* **2000**, *72*, 3223–3232; (h) Miao, W.; Bard, A. J. *Anal. Chem.* **2004**, *76*, 7109–7113; (i) Yin, X.-B.; Dong, S.; Wang, E. *Trends Anal. Chem.* **2004**, *23*, 432–441; (j) Choi, H. N.; Cho, S.-H.; Lee, W.-Y. *Anal. Chem.* **2003**, *75*, 4250–4256; (k) Honda, K.; Yoshimura, M.; Rao, T. N.; Fujishima, A. *J. Phys. Chem. B* **2003**, *107*, 1653–1663.
2. (a) Kapturkiewicz, A.; Grabowski, Z. R.; Jasny, J. *J. Electroanal. Chem.* **1990**, *279*, 55–65; (b) Kapturkiewicz, A.; Herbich, J.; Nowacki, J. *Chem. Phys. Lett.* **1997**, *275*, 355–362.
3. (a) Lai, R. Y.; Fabrizio, E. F.; Lu, L.; Jenekhe, S. A.; Bard, A. J. *J. Am.Chem. Soc.* **2001**, *123*, 9112–9118; (b) Lai, R. Y.; Kong, X.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 12631–12639.
4. (a) Chen, C.-Y.; Ho, J.-H.; Wang, S.-L.; Ho, T.-I. *Photochem. Photobiol.Sci.* **2003**, *2*, 1232–1236; (b) Wong, K.-T.; Hung, T.-H.; Chao, T.-C.; Ho, T.-I. *Tetrahedron Lett.* **2005**, *46*, 855–858; (c) Ho, T.-I.; Elangovan, A.; Hsu, H.-Y.; Yang, S.-W. *J. Phys. Chem. B* **2005**, *109*, 8626–8633; (d) Elangovan, A.; Kao, K.-M.; Yang, S.-W.; Chen, Y.-L.; Ho, T.-I.; Su, Y. O. *J. Org. Chem.* **2005**, *70*, 4460–4469.
5. (a) Lobo, B. C.; Abelt, C. J. *J. Phys. Chem. A* **2003**, *107*, 10938–10943; (b) Sumalekshmy, S.; Gopidas, K. R. *J. Phys. Chem. B* **2004**, *108*, 3705–3712.
6. (a) Mehlhorn, A.; Schwenzer, B.; Schwetlick, K. *Tetrahedron* **1977**, *33*, 1489–1491; (b) Yang, J.-S.; Liau, K.-L.; Wang, C.-M.; Hwang, C.-Y. *J. Am. Chem. Soc* **2004**, *126*, 12325–12335.
7. Faulkner, L. R.; Tachikawa, H.; Bard, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 691–699.
8. Crystal structure data for **2**: $C_{14}H_{15}NOS$, $M_r = 257.34$, orthorhombic, space group: $P2_12_12_1$, $a = 6.1356(4)$, $b = 7.6377(5)$, $c = 28.6163(18)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1341.01(15)$ Å^3, $Z = 4$, $F(000) = 544$, $D_c = 1.275$ g cm^{-3}, $R = 0.0465$, $R_w = 0.1175$.CCDC-278807 contains the supplementary crystallographic data for this letter. These data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).
9. Coates, G. W.; Dunn, A. R.; Henling, L. M.; Ziller, J. W.; Lobkovsky, E. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 3641–3649.
10. Prieto, I.; Teetsov, J.; Fox, M. A.; Bout, D. A. V.; Bard, A. J. *J. Phys. Chem. A* **2001**, *105*, 520–523.
11. (a) Elangovan, A.; Chiu, H.-H.; Yang, S.-W.; Ho, T.-I. *Org. Biomol. Chem.* **2004**, *2*, 3113–3118; (b) Elangovan, A.; Yang, S.-W.; Lin, J.-H.; Kao, K.-M.; Ho, T.-I. *Org. Biomol. Chem.* **2004**, *2*, 1597–1602.
12. Fungo, F.; Wong, K.-T.; Ku, S.-Y.; Hung, Y.-Y.; Bard, A. J. *J. Phys. Chem. B* **2005**, *109*, 3984–3989.