ORGANIC LETTERS

2002
Vol. 4, No. 11
1891−1894

Preparation of 4,4-Diaryl-2-(tricyanoethenyl)dithienosiloles and Vapor-Chromic Behavior of the Film

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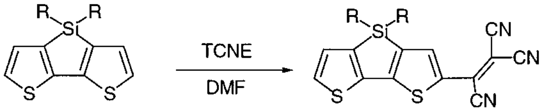
Received March 18, 2002

ABSTRACT



Reactions of 4,4-diphenyl- and 4,4-di(*p*-tolyl)dithienosilole with tetracyanoethene (TCNE) in DMF gave coupling products 4,4-diphenyl- and 4,4-di(*p*-tolyl)-2-(tricycanoethenyl)dithienosilole (1a and 1b) in good yield. The films of 1b exhibited vapor-chromism, and the color of the film changed from red to blue-purple upon exposure to the vapor of organic solvents such as ethanol, methanol, acetonitrile, ethyl acetate, acetone, and hexane. The color reverted to the original red upon contact with chloroform vapor, indicating that this process is reversible.

The silole (silacyclopentadiene) ring has been extensively studied as a novel conjugated system, in which the σ^*-orbital of the silole silicon atom may effectively interact with the π^*-orbital of the butadiene fragment, leading to the low-lying LUMO.[1] In particular, since Tamao et al. reported that 2,5-bis(pyrrol-2-yl)silole derivatives exhibit highly electron-transporting properties, applicable to electron-transport in electroluminescent (EL) devices,[2] many papers concerning the functionalities of silole-containing compounds and polymers have been published.[3]

Recently, we synthesized dithienosiloles (DTSs), in which a bithiophene system is bridged intramolecularly by a silylene unit at the β,β'-position forming a silole ring.[4] Interestingly, DTSs show highly electron-transporting properties, and the devices with a structure of ITO/TPD/Alq/DTS/Mg−Ag, where TPD, Alq, and DTS are the hole-transport, emitter, and electron-transport, respectively, emit strong electroluminescence (EL).[5] In these compounds, the nature of substituents on the thiophene α-carbons markedly affects the electronic states, and introduction of electron-withdrawing groups lowers the LUMO energy level.[6] In fact, the

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(1) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693.

(2) (a) Tamao, K.; Ohno, S.; Yamaguchi, S. *Chem. Commun.* **1996**, 1873. (b) Tamao, K.; Uchida, M.; Izumikawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *116*, 11974. (c)

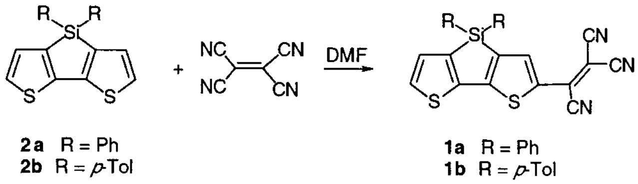
(3) For recent works, see: (a) Uchida, M.; Izumizawa, T.; Nakano, T.; Yamaguchi, S.; Tamao, K. *Chem. Mater.* **2001**, *13*, 2680. (b) Luo, J.; Xie, Z.; Lam, W. Y.; Cheng, L.; Chen, H.; Qiu, C.; Kwok, H. S.; Zhan, X.; Liu, Y.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2001**, 1740. (c) Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem. Lett.* **2001**, 98. (d) Tamao, K.; Yamaguchi, S. *J. Organomet. Chem.* **2000**, *611*, 5. (e) Adachi, A.; Yasuda, H.; Sanji, T.; Sakurai, H.; Okita, K. *J. Luminescence* **2000**, *87−9*, 1174. (f) Lee, Y.; Sadki, S.; Tsuie, B.; Reynolds, J. R. *Chem. Mater.* **2001**, *13*, 2234.

(4) (a) Ohshita, J.; Nodono, M.; Watanabe, T.; Ueno, Y.; Kunai, A.; Harima, Y.; Yamashita, K.; Ishikawa, M. *J. Organomet. Chem.* **1998**, *553*, 487. (b) Adachi, A.; Ohshita, J.; Kunai, A.; Okita, K.; Kido, J. *Chem. Lett.* **1998**, 1233. (c) Ohshita, J.; Nodono, M.; Kai, H.; Watanabe, T.; Kunai, A.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Okita, K.; Harima, Y.; Yamashita, K.; Ishikawa, M. *Organometallics* **1999**, *18*, 1453. (d) Adachi, A.; Ohshita, J.; Kunai, A.; Okita, K. *Jpn. J. Appl. Phys.* **1999**, *38*, 2148. (e) Ohshita, J.; Kai, H.; Sumida, T.; Kunai, A.; Adachi, A.; Sakamaki, K.; Okita, K. *J. Organomet. Chem.* **2002**, *642*, 137.

(5) ITO = indium tin oxide, TPD = *N,N'*-diphenyl-*N,N'*-di(*m*-tolyl)-1,1-biphenyl-4,4′-diamine, Alq = tris(8-quinolinolato)aluminum(III).

10.1021/ol025889y CCC: $22.00

Scheme 1



maximum luminance of 16 000 cd/m^2 among the DTS-based devices was obtained when a film of DTS bearing electron-withdrawing pyridyl groups at the α-carbons of the thiophene rings was employed as the electron-transport. On the contrary, introduction of electron-donating thienyl groups at the same positions of DTS significantly suppresses the electron-transporting properties.

To obtain DTS-based materials with higher electron-transporting properties, we synthesized DTSs bearing a strongly electron-withdrawing tricyanoethenyl group.[7] Although attempted building of an efficient EL device based on the present tricyanoethenyl-substituted DTS was unsuccessful, we found that the vapor-deposited film exhibited unique vapor-chromic behavior.

Tricyanoethenyl-substituted DTSs (**1a**,**b**) were obtained in 85% and 87% yields, respectively, from the reactions of 2,6-unsubstituted DTSs (**2a**,**b**) with excess tetracyanoethene (TCNE) in DMF as shown in Scheme 1.[8] Compounds **1a**,**b** are deep red metallic colored crystals and melt at high temperatures without decomposition. They are soluble in common organic solvents and can be fabricated to clear films by vapor deposition or spin-coating of the solutions.

Table 1. Optical and Electrochemical Properties of Compounds **1a**,**b**, **2a**,**b**, and **3**

	absorpn[a]			emissn[a]	peak potential[b] (V vs Ag$^+$/Ag)	
compd	λ_{max} (nm)	$\epsilon \times 10^{-3}$	λ_{edge} (eV)	λ_{max} (nm)	oxidn	redcn
1a	512	32	2.1	574	1.20	−0.80
1b	513	33	2.1	575	1.21	−0.79
2a	356	6.1	3.2	420	0.87	nd[c]
2b	358	7.9	3.1	420	0.98	nd[c]
3	484	30	2.2	563	1.30	−0.78

[a] In THF. [b] Determined by CV in acetonitrile containing 100 mM of LiClO$_4$ as the supporting electrolyte and 2 mM of the substrate at the scan rate of 100 mV/s. [c] Not detected.

Table 1 summarizes the optical and electrochemical properties of **1a**,**b**, in comparison with those of the parent DTSs **2a**,**b** and 5-(tricyanoethenyl)-2,2′-bithiophene (**3**). Compound **3** was prepared in 50% yield from the reaction of 2,2′-bithiophene with TCNE, similarly to **1a**,**b**.[9] As shown in Table 1, the absorption and emission maxima of **1a**,**b** were markedly red-shifted from those of **2a**,**b** by about 150 nm. The absorption edges of **1a**,**b** were also red-shifted from those of **2a**,**b** by about 1 eV. The cyclic voltammograms (CVs) of **1a**,**b** measured in acetonitrile showed irreversible oxidation peaks at about 1.2 V vs Ag$^+$/Ag, which are shifted positively from those observed for **2a**,**b**. These results seem to indicate the smaller band-gap energies as well as the lower energy level of HOMOs for **1a**,**b** as compared with those of **2a**,**b**. This is suggestive of the lower-lying LUMOs of **1a**,**b** than those of **2a**,**b**, in accordance with the fact that the CVs of **1a**,**b** revealed the cathodic reduction peak at ca. −0.8 V vs Ag/Ag$^+$, while **2a**,**b** are inactive in the reductive mode in the range down to −2.0 V. When compared with **3**, the absorption maxima and edges of **1a**,**b** were red-shifted by about 30 nm and 0.1 eV, respectively. The reduction peak of **1a**,**b** in the CVs appeared at essentially the same potential as those of **3**, while the electrochemical oxidation took place at lower energy, indicating that the HOMOs of **1a**,**b** are at higher energies relative to that of **3**, being primarily responsible for the red-shifts in the absorption maxima.

Interestingly, the emission maxima of **1a**,**b** and **3** moved to higher energies, by 10, 15, and 8 nm, respectively, when the solvent was changed from THF to less polar diethyl ether. This is in contrast to **2a**,**b** whose emission spectra exhibited no clear solvent dependence. The wavelengths of UV absorption maxima were also affected by the solvent polarity, but much less sensitively, and the same change of the solvent led to blue-shifts by less than 2 nm. In ethyl acetate, the spectra revealed the absorption and emission maxima at almost the same energies as those in THF, except for the emission spectrum of **3**, which showed the maximum at 478 nm, 6 nm blue shifted from that in THF.

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(6) Ohshita, J.; Kai, H.; Takata, A.; Iida, T.; Kunai, A.; Ohta, N.; Komaguchi, K.; Shiotani, M.; Adachi, A.; Sakamaki, K.; Okita, K. *Organometallics* **2001**, *20*, 4800.

(7) Synthesis of compounds having a tricyanoethenylthiophene unit and their utilities such as for nonlinear optical materials have been studied. For example, see: (a) Rao, V. P.; Jen, A. K−Y.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 1118. (b) de Lucas, A. I.; Martin, N.; de Miguel, P.; Seoane, C.; Albert, A.; Cano, F. H. *J. Mater. Chem.* **1995**, *5*, 1141. (c) Bu, X. R.; Li, H.; Van Derveer, D.; Mintz, E. A. *Tetrahedron Lett.* **1996**, *37*, 7331. (d) Eckert, K.; Schroder, A.; Hartmann, H. *Eur. J. Org. Chem.* **2000**, 1327. (e) Lee, J. S.; Kim, K. *J. Heterocycl. Chem.* **2000**, *37*, 363.

(8) **Illustrative procedure for the preparation of 1a and 1b:** To a solution of 0.100 g (0.290 mmol) of **2a** in 1 mL of DMF was added at room temperature 0.185 g (1.44 mmol) of TCNE, and the solution was stirred for 5 h at room temperature. The resulting mixture was poured into water and extracted with ethyl acetate. The extracts were combined and dried over MgSO$_4$. After evaporation of the solvent, the residue was chromatographed (silica gel, ethyl acetate/*n*-hexane = 1/10) to give crude solids. The crude solids were crystallized from a mixed solvent of ethyl acetate/*n*-hexane =1/2 to give 0.11 g (85%) of **1a** as dark red crystals: mp 255.0−255.5 °C; *m/z* 447 [M$^+$]; ^{1}H NMR (δ in CDCl$_3$) 7.38 (d, 1H, J = 4.7 Hz, thiophene ring H), 7.41 (t, 4H, J = 7.4 Hz, *m*-Ph), 7.50 (tt, 2H, J = 7.4, 1.7 Hz, *p*-Ph), 7.59 (m, 4H, *o*-Ph), 7.70 (d, 1H, J = 4.7 Hz, thiophene ring H), 8.13 (s, 1H, thiophene ring H); ^{13}C NMR (δ in CDCl$_3$) 112.43, 112.92, 113.01, 128.67, 131.00, 131.35, 131.92, 134.03, 135.32, 135.97, 143.22, 143.69, 147.79, 148.60, 164.85; ^{29}Si NMR (δ in CDCl$_3$) −20.22. Anal. Calcd for $C_{25}H_{13}N_3S_2Si$: C, 67.08; H, 2.93; N, 9.39. Found: C, 67.07; H, 3.01; N, 9.48. Compound **1b** was obtained in a fashion similar to that above as dark red crystals: mp 255.5−256.5 °C, *m/z* 475 [M$^+$]; ^{1}H NMR (δ in CDCl$_3$) 2.37 (s, 6H, CH$_3$), 7.22 (d, 4H, J = 8.0 Hz, Ph), 7.35 (d, 1H, J = 4.7 Hz, thiophene ring H), 7.47 (d, 4H, J = 8.0 Hz, Ph), 7.68 (d, 1H, J = 4.7 Hz, thiophene ring H), 8.10 (s, 1H, thiophene ring H); ^{13}C NMR (δ in CDCl$_3$) 21.64, 112.50, 112.97, 113.02, 125.05, 129.47, 131.00, 131.87, 133.92, 135.35, 135.93, 141.68, 143.33, 144.22, 147.61, 149.24, 164.90; ^{29}Si NMR (δ in CDCl$_3$) −20.20. Anal. Calcd for $C_{27}H_{17}N_3S_2Si$: C, 68.18; H, 3.60; N, 8.83. Found: C, 68.02; H, 3.60; N, 8.62.

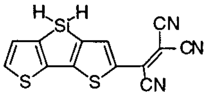
(9) Data for **3**: red crystals; mp 205−206 °C; *m/z* 267 [M$^+$]; ^{1}H NMR (δ in CDCl$_3$) 7.15 (dd, 1H, J = 4.8, 4.0 Hz), 7.37 (d, 1H, J = 4.4 Hz), 7.53 (br, 2H), 8.00 (d, 1H, J = 4.4 Hz); ^{13}C NMR (δ in CDCl$_3$) 111.99, 112.31, 112.64, 128.68, 129.22, 130.24, 131.97, 132.14, 134.47, 141.40, 152.32. Anal. Calcd for $C_{13}H_5N_3S_2$: C, 58.41; H, 1.89; N, 15.72. Found: C, 58.46; H, 1.87; N, 15.70.

Table 2. Relative HOMO and LUMO Energy Levels (eV) for Compounds **1c**, **2c**, and **3**, Derived from MO Calculations at the HF/6-31G Level

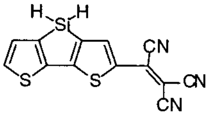
compd	HOMO	LUMO	compd	HOMO	LUMO
1c-1	−8.51	−0.66	**3−1**	−8.81	−0.57
1c-2	−8.49	−0.58	**3−2**	−8.56	−0.59
			3−3	−8.64	−0.64
2c[a]	−7.88	1.75	**3−4**	−8.60	−0.62

[a] Reference 4c.

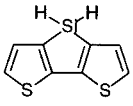
Table 2 summarizes the results of the ab initio molecular orbital (MO) calculations on the model compounds **1c**, **2c**, and **3** at the level of HF/6-31G.[10] All of the possible two and four planar conformers, with respect to the rotation around the single bonds between the π-systems, were found to be stable with the energy minimum, for **1c** and **3**, respectively. However, the conformation does not significantly affect the HOMO and LUMO energy levels and the orbital profiles. As shown in Table 2, both of the HOMOs and LUMOs of **1c** were calculated to be at lower energy levels than those of **2c**. In addition, **1c** has higher-lying HOMOs relative to **3**, although the LUMOs of **1c** and **3** are almost at the same level. These are in good agreement with the optical and electrochemical data obtained for the actual compounds described as above.



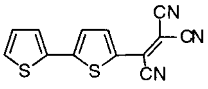
1c-1



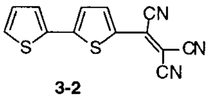
1c-2



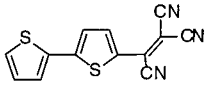
2c



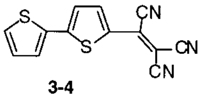
3-1



3-2



3-3



3-4

The HOMOs and LUMOs of the conformers of **1c** derived from the calculations spread over the whole of the molecule. The LUMOs, however, are more localized on the tricyanoethenyl unit rather than on the DTS ring, while the HOMOs are mainly composed of the DTS π-orbital. Probably, the tricyanoethenyl unit in **1c** plays a major role as the electron-withdrawing group to lower both the LUMO and HOMO energy levels, relative to **2c**. On the other hand, the resonance effect of the tricyanoethenyl group, which would raise the HOMO level, seems to be too small to compensate for the inductive effect. This rather localized orbital profile also suggests that the charge displacement is involved in the excited states to some extent, in accordance with the solvent-dependence of the emission spectra of **1a**,**b**. Since similar orbital localization is observed for the HOMOs and LUMOs of **3**, the presence of the silole ring in **1c** may affect only the HOMO obviously to raise the level relative to that of **3**.

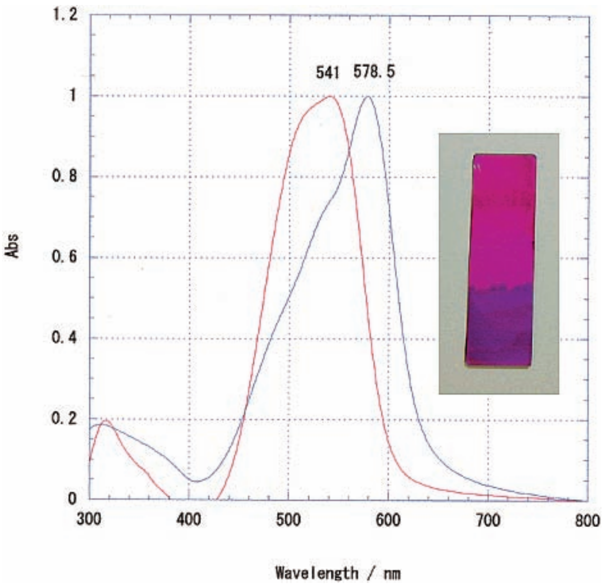


Figure 1. UV spectra of a vapor-deposited film of **1b** on a quartz plate (red line) before and (blue line) after a short contact with ethanol vapor. Inset is a photo of the film, of which the bottom half was treated with ethanol.

The low-lying LUMOs of **1a**,**b** as estimated by the optical and electrochemical properties, as well as the MO calculations, prompted us to examine them as the electron-transport for the multilayer EL device system. However, the device with a structure of ITO/TPD (40 nm)/Alq (50 nm)/**1b** (10−20 nm)/Mg−Ag did not emit any luminance, and no current was detected up to an applied voltage of 20 V.

To our surprise, the vapor-deposited film of **1b** exhibited vapor-chromic behavior and the λ_{max} moved from 541 to 579 nm, accompanied by a color change from red to blue-purple upon exposure to ethanol vapor, as shown in Figure 1. A similar change was observed when the film was dipped in liquid ethanol for a short period of time. The color remained unchanged after several months without exposure to ethanol, and the color reverted to the original red after a short contact with chloroform vapor, indicating that this process is reversible. When the blue-purple film was dissolved in $CDCl_3$ and the solution was analyzed by ^1H NMR, a spectrum consistent with that of **1b** was obtained, indicating that no corresponding chemical reactions occurred with the color change. The ^1H NMR spectrum showed also the absence of a detectable amount of ethanol in the film. Although we have no clear data to understand the mechanism of the vapor-chromism, the X-ray diffraction measurements of the film showed that the strong peak at 14.67 Å of the original film moved to 14.72 Å, after contact with the ethanol vapor. Presumably, some changes in the solid-state structure were involved. In contrast to this, compound **3** gave no clear films by either vapor deposition or spin-coating

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(10) *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA.

of the solution, but always afforded cloudy light red films and the contact of the films with ethanol led to no color changes.

Similar quick color and UV spectral changes occurred when the films of **1b** were exposed to other polar organic solvents, such as methanol (λ_{max} of the film after the contact = 579 nm), acetonitrile (580 nm), ethyl acetate (582 nm), and acetone (582 nm). A contact with hexane also caused a similar color change of the film, but much less sensitively. The absorption maximum of the film of **1b** moved to 574 nm after exposure to hexane vapor for 1 min. Exposure of the film to steam led to no color and spectral changes.

In conclusion, a novel tricyanoethenyl-DTS system that may be potentially important as a new donor−acceptor type chromophore has been developed.[11] Studies to extend this system to the new functionality materials are underway.

Acknowledgment. This work was supported in part by the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grant-in-Aid for Scientific Research, No. 13029080), and NEDO (Project No. 01A26005a). We thank Sankyo Kasei Co. Ltd. and Mitsubishi Chemical Corporation Fund for financial support. We also thank Prof. K. Inumaru and Prof. S. Yamanaka (Hiroshima University) for the measurements of X-ray diffraction of the film of **1b**.

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(11) For recent synthesis of bithiophene-based donor−acceptor type chromophores, see: Hartmann, H.; Eckert, K.; Schröder, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 556.