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PREPARATION AND OPTICAL PROPERTIES OF DITHIENOSILOLE-ARYLPHOSPHINE ALTERNATE OLIGOMERS

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Abstract Dithienosilole-arylphosphine alternate oligomers were prepared by the Stille coupling reactions of bis(tributylstannyl)dithienosilole with bis(4-bromophenyl)phenylphosphine and -phosphine oxide. The resulting oligomers are dark orange solids, and they can be spincoated to thin films on substrates. They are emissive in solutions as well as in films.

Keywords Emission; oligomer; phosphine; phosphine oxide; silole; thiophene

INTRODUCTION

Silole-containing π -conjugated systems have been extensively studied as active components for organic electronic devices, such as organic light emitting diodes (OLEDs), organic thin film transistors (OTFT), organic photovoltaic cells (OPV), and organic sensors,¹ since applications of silole derivatives to OLEDs as electron-transporting materials were demonstrated by Tamao et al.² The excellent electron-transporting properties of siloles are ascribed to the interaction between the silicon σ^* - and the butadiene π^* -orbital ($\sigma^* - \pi^*$ conjugation),^{1–3} which lowers the LUMO energy level to enhance the electron affinity.

Previously, we reported the synthesis of dithienosiloles (DTSs) with a silole ring fused to a bithiophene unit.⁴ This system exhibits extended conjugation compared with that of silole-free bithiophene, attributable not only to the coplanarity of the two thiophene rings fixed by the tricyclic system, but also to the $\sigma^* - \pi^*$ conjugation, and it has been demonstrated by us and other research groups that DTS-based compounds are applicable to OLEDs, OTFTs, and OPVs.^{1a,5} Recently, we found that DTS derivatives with arylphosphine substituents show excellent photoluminescence (PL) properties (Chart 1).⁶

Interestingly, these compounds exhibit efficient blue-green PL, even in the solid states with the maximum quantum yield of $\varphi = 0.79$ for compound **1a**. This is presumably due to the packing in the solid states, which suppresses the rotation with respect to the

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1a R = Ph, X = Ione pair

$$\lambda_{max} = 380 \text{ nm}, \lambda_{em} = 465 (464) \text{ nm}, \Phi = 0.22 (0.79)$$

1b R = Ph, X = O
 $\lambda_{max} = 361 \text{ nm}, \lambda_{em} = 422 (434) \text{ nm}, \Phi = 0.85 (0.41)$
1c R = Ph, X = S
 $\lambda_{max} = 369 \text{ nm}, \lambda_{em} = 433 (442) \text{ nm}, \Phi = 0.13 (0.47)$
2b R = Nap, X = O
 $\lambda_{max} = 363 \text{ nm}, \lambda_{em} = 425 (434) \text{ nm}, \Phi = 0.71 (0.43)$

Chart 1 Structures of emissive DTSs. UV absorption and emission maxima, and quantum yields in $CHCl_3$ (data in solid).

C-P and C-Si bonds to decrease the probabilities of nonradiative decay from the excited states of these compounds. It was also demonstrated that vapor-deposited films of these DTS-phosphine compounds are usable as emissive layers in multilayered OLEDs. In the hope of obtaining solution processable DTS-based materials with efficient PL properties, we prepared oligomers composed of an alternate arrangement of DTS and arylphosphine units.

RESULTS AND DISCUSSION

First, we examined the reactions of dilithiodithienosilole and dichlorophenylphosphine as shown in Equation (1). However, all attempts to prepare the expected product with a DTS-P alternate structure were unsuccessful, and a viscous oil with the molecular weight less than $M_w = 1000$ was always obtained under various reaction conditions.



This is probably due to the steric hindrance for the P-C bond formation, and we introduced phenylene spacers in this system, as oligomers 3a and 3b in



DITHIENOSILOLE-ARYLPHOSPHINE OLIGOMERS

Oligomer	Yield/%	$M_{\rm w} \left(M_{\rm w} / M_{\rm n} \right)$	UV abs λ_{max}/nm		PL $\lambda_{\rm em}/{\rm nm} (\varphi/\%)^b$	
			in CHCl ₃	film	in CHCl ₃	film
3a	46	2800 (1.2)	416	420	513 (16)	560 (6)
3b	31	2500 (1.2)	418	433	491 (36)	609 (8)

Table 1 Properties of oligomers 3a and 3b^a

^aAfter reprecipitation from chloroform-hexane.

^bExcited at the absorption maximum.

Equation (2). Stille coupling reactions of bis(tributylstannyl)dithienosilole 4 with bis-(4-bromophenyl)phenylphosphine and -phosphine oxide (5a and 5b) in toluene at the reflux temperature afforded the oligomers, after reprecipitation of the organic products from chloroform-hexane.

The yields, molecular weights, and optical properties of **3a** and **3b** are summarized in Table 1. The oligomer structures were verified by spectroscopic analysis. ¹H NMR spectra of these oligomers reveal only broad signals, but the integration ratios are almost consistent with the expected structures. They are dark orange solids and do not melt up to 300° C, and are soluble in common organic solvents, such as THF and chloroform, but insoluble in hexane and ethanol. As expected, the oligomers can be processed to thin solid films by spin-coating and drop-cast on substrates, such as glass and quartz plates.

Absorption and emission spectra of oligomer **3a** in chloroform reveal the maxima, slightly red-shifted from those of diphenyldithienosilole **6** by 7 and 18 nm,⁷ respectively (Chart 2), indicating the effects of the phosphine linkage on the conjugation in **3a**. Similar red-shifts were reported for the introduction of phosphine substituents on a DTS ring.⁶ However, the red-shifts of **3a** from **6** are much smaller than those of **1a** from **7** (Chart 2), which are 24 and 45 nm for absorption and emission, respectively. It is likely that the degree of n- π interaction between the phosphine and π -conjugated unit is reduced by expansion of the π -conjugation.



Chart 2 DTS derivatives with their absorption and emission maxima in CHCl₃.

Phosphine oxide **3b** shows absorption and emission spectra similar to **3a** in chloroform, as depicted in Figures 1a and 1b, again indicating reduced $n-\pi$ interaction in these oligomers. In their films, however, oligomer **3b** exhibits a remarkably red-shifted band compared to **3a** by about 50 nm, as can be seen in Figure 1c. The reason for the red-shift is unclear, but the existence of polar phosphine oxide groups in **3b** may facilitate the intermolecular interaction of **3b**. The emission quantum yields of the present oligomers were



Figure 1 (a) UV absorption and (b) emission spectra of **3a** and **3b** in CHCl₃. (c) Emission spectra of spin-coated films of **3a** and **3b** on quartz plates.

determined in solutions as well as in spin-coated films, as listed in Table 1. It is noteworthy that these oligomers show efficient orange emission even in films.

In conclusion, we prepared DTS-arylphosphine alternate oligomers by the Stille coupling reactions, which are emissive in solutions as well as in films. Although the PL quantum yields of the films of **3a** and **3b** are lower than those of **1a** and **1b**, the good film forming properties clearly suggest their potential applications to OLEDs. Studies on the applications of the present oligomers to OLED and the preparation of other oligomeric or polymeric DTS-arylphosphine compounds are in progress.

EXPERIMENTAL

General Procedure and Materials

Toluene was distilled from sodium and stored over activated molecular sieves before use. Monomers **4**⁸ and **5a**⁹ were prepared as reported in the literature. Mass spectra were measured on a Shimadzu QP5050A spectrometer. NMR spectra were recorded on a JEOL LA-400 spectrometer. UV and emission spectra were measured on Shimadzu UV-3150 and RF-5000 spectrophotometers, respectively. Emission quantum yields were determined in an integration sphere attached by a Hamamatsu Photonics C7473 Multi-Channel Analyzer.

Preparation of Monomer 5b¹⁰

To an aqueous solution of hydrogen peroxide (10.5 mL, 30%), a solution of **5a** in chloroform (50 mL) was added slowly at room temperature, and the resulting mixture was stirred for 2 h. To this, water (20 mL) was added, and the organic layer was separated. The aqueous layer was extracted with chloroform, and the organic layer and the extracts were combined then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a silica gel column eluting with hexane/ethyl acetate = 1/2 to give the title compound as a colorless solid. MS *m*/z 434 (M⁺ for ⁷⁹Br). ¹H NMR (400 MHz in CDCl₃): δ = 7.48–7.64 (m). ¹³C NMR (100 MHz in CDCl₃): δ = 127.44 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 12.3 Hz), 131.10 (d, *J* = 104.3 Hz), 131.91 (d, *J* = 10.0 Hz), 131.92 (d, *J* = 12.8 Hz), 132.40 (d, *J* = 2.8 Hz), 133.49 (d, *J* = 10.6 Hz); one carbon is missing due to overlapping with other signals. HR-mass calcd. for C₁₈H₁₄Br₂OP: 434.91435; found: 434.91434.

Preparation of Oligomers 3a and 3b

A mixture of **4** (208 mg, 0.20 mmol), **5a** (84 mg, 0.20 mmol), PdCl₂(PPh₃)₂ (8 mg 0.01 mmol), CuI (2 mg, 0.01 mmol), and toluene (10 mL) was heated to reflux for 48 h under dry nitrogen. After filtration of the resulting precipitates, the solvent was evaporated. Reprecipitation of the residue from chloroform-hexane gave oligomer **3a** as a dark red solid, mp >300°C. GPC $M_w = 2800$, $M_w/M_n = 1.2$. ¹H NMR (400 MHz in CDCl₃): $\delta = 0.76-0.95$ (m, 6H, CH₂CH₂CH₂CH₃), 1.22–1.40 (m, 4H, CH₂CH₂CH₂CH₃), 1.49–1.67 (br m, 4H, CH₂CH₂CH₂CH₃), 2.53–2.64 (m, 4H, CH₂CH₂CH₂CH₃), 7.11–7.69 (m, 23H, ring protons). ¹³C NMR (100 MHz in CDCl₃): $\delta = 13.91$, 22.35, 33.42, 35.82, 128.46, 128.55, 128.62, 128.74, 131.94, 132.06, 133.53, 133.65, 135.42, 135.44, no other signals were observed probably due to overlapping with major peaks. HR-MS calcd for C₁₈H₁₄Br₂OP: 434.91435; found: 434.91434.

Polymer **3b** was obtained in a manner similar to that above, 31% yield, mp >300°C. GPC: $M_w = 2500$, $M_w/M_n = 1.2$. ¹H NMR (400 MHz in CDCl₃): $\delta = 0.76-1.00$ (m, 6H, CH₂CH₂CH₂CH₂CH₃), 1.26-1.41 (m, 4H, CH₂CH₂CH₂CH₃), 1.49-1.67 (br m, 4H, CH₂CH₂CH₂CH₂CH₃), 2.59 (t, 4H, J = 7.9 Hz, CH₂CH₂CH₂CH₂CH₃), 7.14-7.33 (m, 6H, thiophene and benzene ring protons), 7.43-7.74 (m, 17H, benzene ring protons). ¹³C NMR (100 MHz in CDCl₃): $\delta = 13.91$, 22.34, 33.41, 35.75, 128.54, 133.49, 133.65, 135.42, no other signals were observed probably due to overlapping with major peaks.

REFERENCES

- (a) Wang, M.; Zhang, G.; Zhang, D.; Zhu, D.; Tang, B. Z. J. Mater. Chem. 2010, 20, 1858–1867;
 (b) Chen, J.; Cao, Y. Macromol. Rapid Commun. 2007, 28, 1714–1742;
 (c) Yamaguchi, S.; Tamao, K. Chem. Lett. 2005, 34, 2–7.
- Tamao, K.; Uchida, M.; Izumikawa, T.; Furukawa, K.; Yamaguchi, S. J. Am. Chem. Soc. 1996, 118, 11974–11975.
- 3. Yamaguchi, S.; Tamao, K. J. Chem. Soc., Dalton Trans. 1998, 3693–3702.
- (a) Ohshita, J.; Nodono, M.; Watanabe, T.; Ueno, Y.; Kunai, A.; Harima, Y.; Yamashita, K.; Ishikawa, M. J. Organomet. Chem. 1998, 553, 487–491; (b) 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, 1453–1459.
- 5. Ohshita, J. Macromol. Chem. Phys. 2009, 210, 1360-1370.
- 6. Ohshita, J.; Kurushima, Y.; Lee, K.-H.; Ooyama, Y.; Harima, Y. Organometallics 2007, 26, 6591–6595.
- 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, 4800–4805.
- Ohshita, J.; Kimura, K.; Lee, K.-H.; Kunai, A.; Kwak, Y.-W.; Son, E.-C. J. Polym. Sci. A, Polym. Chem. 2007, 45, 4588–4596.
- Rancurel, C.; Heise, H.; Koehler, G. H.; Schatzschneider, U.; Rentschler, E.; Vidal-Gancedo, J.; Veciana, J.; Sutter, J.-P. J. Phys. Chem. A 2004, 108, 5903–5914.
- 10. Hu, Y.; Chen, W.; Xu, L.; Xiao, J. Organometallics 2001, 20, 3206-3208.

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