ORGANIC
LETTERS

2007
Vol. 9, No. 18
3611−3614

Synthesis and Photophysical Properties of Phosphole-Cored Dendrimers

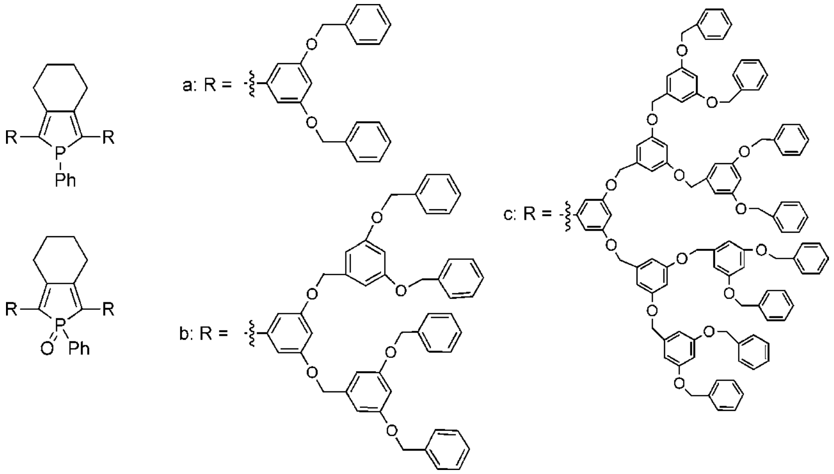
Takanobu Sanji,* Kentaro Shiraishi, and Masato Tanaka*

*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259-R1-13,
Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

sanji@res.titech.ac.jp; m.tanaka@res.titech.ac.jp

Received July 9, 2007

ABSTRACT



Phosphole-cored dendrimers having poly(benzyl ether) units through the third generation have been synthesized. The dendrimers display intense blue photoluminescence, the quantum yield increasing with the increasing generation of the dendron units. The optical properties are easily tuned by oxidation of the phosphorus atom of the phosphole ring.

Over the past decades, the design and synthesis of novel π-conjugated systems have been active areas of research because of their applications as optoelectronic materials, such as organic thin film transistors and organic electroluminescent (EL) devices. Among a variety of π-conjugated systems, π-conjugated molecules containing the main group element have attracted considerable interest recently.[1] This is because the orbital interaction of the main group element moiety plays an intriguing role in the π-conjugated framework. In this context, phosphacyclopentadiene, phosphole, is an interesting building block for the construction of conjugated systems, where an interaction between the butadiene π^* orbital and the low-lying σ^*(P−R) orbital takes place in the ring.[2] Phosphole also possesses a central phosphorus atom, which retains a versatile reactivity. This offers the possibility of tuning the electronic properties of the materials by simple chemical modifications, such as oxidation. Several reports have addressed the synthesis of phospholes with a variety of substituent groups[3−5] and phosphole-based polymers.[6,7] Réau and co-workers very recently demonstrated light-emitting behavior in phospholes and their sulfide derivatives.[8]

---

(1) (a) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578. (b) Hissler, M.; Dyer, P. W.; Réau, R. *Coord. Chem. Rev.* **2003**, *244*. 1. (c) Mathey, F. *Acc. Chem. Res.* **2004**, *37*, 954. (d) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2. (e) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681.

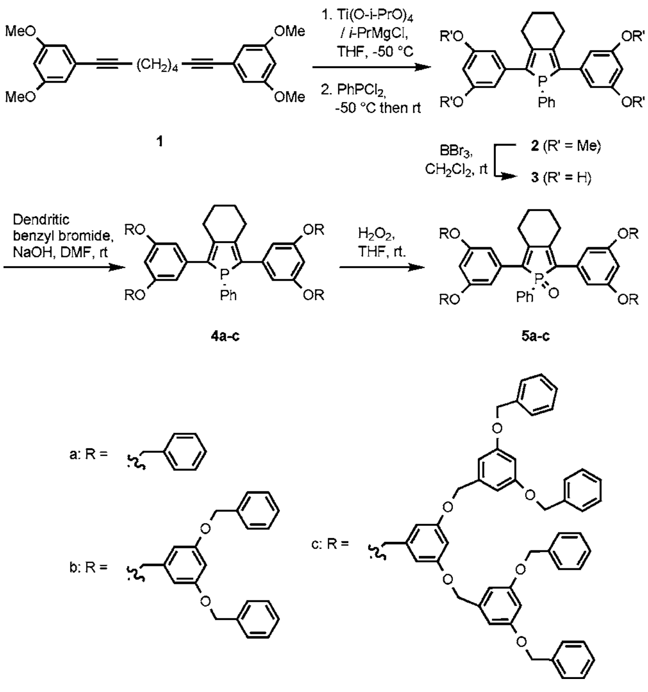
(2) (a) Delaere, D.; Dransfeld, A.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Org. Chem.* **2000**, *65*, 2631. (b) Nyulaszi, L. *Chem. Rev.* **2001**, *101*, 1229. (c) Delaere, D.; Nguyen, M. T.; Vanquickenborne, L. G. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1522. (d) Delaere, D.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Organomet. Chem.* **2002**, *643*, 194. (e) Ma, J.; Li, S.; Jiang, Y. *Macromolecules* **2002**, *35*, 1109. (f) Delaere, D.; Nguyen, M. T.; Vanquickenborne, L. G. *J. Phys. Chem. A* **2003**, *107*, 838.

(3) Deschamps, E.; Ricard, L.; Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1158.

10.1021/ol701606t CCC: $37.00

We designed dendrimers with phosphole at the core. Dendrimers are a class of highly ordered, three-dimensional, tree-like macromolecules that are potential building blocks for the construction of functional materials.[9,10] In this regard, dendritic macromolecules offer a special opportunity for improvement of photophysical properties. For example, the dendritic framework provides a site-isolation framework for chromophores placed at the core, a light-harvesting antenna, and an energy transfer interaction.[11] In the application to EL devices, it is also important to develop materials with improved stability and an alternative class of materials for solution processing. Recently, several groups have reported dendrimer-based EL devices.[12,13] We show herein the synthesis and photophysical properties of phosphole-cored dendrimers.[14]

Scheme 1



Our synthetic strategy for phosphole-cored dendrimers is based on the convergent method,[15] i.e., by coupling the focal point of the dendrons to the phosphole-core. Scheme 1 shows the synthesis of phosphole-cored dendrimers **4a**−**c**. A Ti(II)-mediated cyclization[16−18] of 1,7-diyne **1** leading to an intermediate titanacyclopentadiene followed by subsequent addition of dichlorophenylphosphine gave phosphole **2** in 83% yield. Deprotection of **2** with boron tribromide afforded phosphole **3** (90% yield), which was treated with dendritic benzyl ether-type bromides to furnished dendrimers **4a**−**c** in moderate yields (44−58%). Although the reactivity of the dendritic bromide became somewhat low as the generation increased, monitoring each reaction by TLC revealed that the starting bromide was consumed nearly completely in a few hours.

Next, we examined oxidation of the phosphorus atom of the phosphole dendrimers because phosphole can be subjected to simple chemical modifications to alter its electronic properties, as mentioned in the introductory section. The reaction of phospholes **4a**−**c** with hydrogen peroxide afforded phosphole oxide-cored dendrimers **5a**−**c** in good yields (70−97%).

The dendrimers **4a**−**c** and **5a**−**c** were fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR, and elemental analyses. In the ^{31}P NMR spectra, the signals assigned to the phosphorus atom on the phosphole and phosphole-oxide ring core were observed at about 13 and 43 ppm, respectively. The elemental

---

(4) (a) Hay, C.; Vilain, D. L.; Deborde, V.; Toupet, L.; Réau, R. *Chem. Commun.* **1999**, 345. (b) Hay, C.; Fischmeister, C.; Hissler, M.; Toupet, L.; Réau, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 1812. (c) Hay, C.; Hissler, M.; Fischmeister, C.; Rault-Berthelot, J.; Toupet, L.; Nyulászi, L.; Réau, R. *Chem. Eur. J.* **2001**, *7*, 4222. (d) Hay, C.; Fave, C.; Hissler, M.; Rault-Berthelot, J.; Réau, R. *Org. Lett.* **2003**, *5*, 3467. (e) Fave, C.; Hissler, M.; Kárpáti, T.; Rault-Berthelot, J.; Deborde, V.; Toupet, L.; Nyulászi, L.; Réau, R. *J. Am. Chem. Soc.* **2004**, *126*, 6058.

(5) (a) Baumgartner, T.; Neumann, T.; Wirges, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6197. (b) Neumann, T.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 495. (c) Baumgartner, T.; Wilk, W. *Org. Lett.* **2006**, *8*, 503. (d) Durben, S.; Dienes, Y.; Baumgartner, T. *Org. Lett.* **2006**, *8*, 5893. (e) Dienes, Y.; Eggenstein, M.; Neumann, T.; Englert, U.; Baumgartner, T. *Dalton Trans.* **2006**, 1424. (f) Matano, Y.; Miyajima, T.; Nakabuchi, T.; Imahori, H.; Ochi, N.; Sakaki, S. *J. Am. Chem. Soc.* **2006**, *128*, 11760.

(6) (a) Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566. (b) Morisaki, Y.; Aiki, Y.; Chujo, Y. *Macromolecules* **2003**, *36*, 2594. (c) Sebastian, M.; Hissler, M.; Fave, C.; Rault-Berthelot, J.; Odin, C.; Réau, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 6152. (d) Morisaki, Y.; Na, H.-S.; Aiki, Y.; Chujo, Y. *Polym. Bull.* **2007**, *58*, 777. (e) Na, H.-S.; Morisaki, Y.; Aiki, Y.; Chujo, Y. *Polym. Bull.* **2007**, *58*, 645.

(7) Our group has reported dibenzophosphole oxide-based polymers: Makioka, Y.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **2004**, *33*, 44.

(8) (a) Fave, C.; Cho, T.-Y.; Hissler, M.; Chen, C.-W.; Luh, T.-Y.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2003**, *125*, 9254. (b) Su, H.-C.; Fadhel, O.; Yang, C.-J.; Cho, T.-Y.; Fave, C.; Hissler, M.; Wu, C.-C.; Réau, R. *J. Am. Chem. Soc.* **2006**, *128*, 983.

(9) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819.

(10) (a) Majoral, J.-P.; Caminade, A.-M. *Chem. Rev.* **1999**, *99*, 845. (b) Caminade, A.-M.; Maraval, A.; Majoral, J.-P. *Eur. J. Inorg. Chem.* **2006**, 887.

(11) (a) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (b) Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1998**, *120*, 10895. (c) Sato, T.; Jing, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658.

(12) (a) Lo, S.-C.; Burn, P. L. *Chem. Rev.* **2007**, *107*, 1097. (b) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701. (c) Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *Adv. Mater.* **2007**, *19*, 1675.

(13) (a) Wang, P.-W.; Liu, Y.-J.; Devadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237. (b) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12385. (c) Lo, S.-C.; Male, N. A. H.; Markham, J. P. J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Samuel, I. D. W. *Adv. Mater.* **2002**, *14*, 975. (d) Markham, J. P. J.; Lo, S.-C.; Magennis, S. W.; Burn, P. L.; Samuel, I. D. W. *Appl. Phys. Lett.* **2002**, *80*, 2645.

(14) Recently, we reported a facile one-pot synthesis and photophysical properties of silole-core dendrimers: (a) Sanji, T.; Ishiwata, H.; Kaizuka, T.; Tanaka, M.; Sakurai, H.; Nagahata, R.; Takeuchi, K. *Chem. Lett.* **2005**, *34*, 1130. (b) Sanji, T.; Ishiwata, H.; Kaizuka, T.; Tanaka, M.; Sakurai, H.; Nagahata, R.; Takeuchi, K. *Can. J. Chem.* **2005**, *83*, 646.

(15) (a) Hawker, C.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. (b) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819.

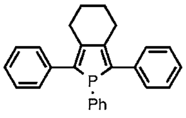
(16) (a) Yamaguchi, S.; Jin, R. Z.; Tamao, K.; Sato, F. *J. Org. Chem.* **1998**, *63*, 10060. (b) Block, E.; Birringer, M.; He, C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1604. (c) Sato, K.; Nishihara, Y.; Huo, S.; Xi, Z.; Takahashi, T. *J. Organomet. Chem.* **2001**, *633*, 18. (d) Suzuki, D.; Tanaka, R.; Urabe, H.; Sato, F. *J. Am. Chem. Soc.* **2002**, *124*, 3518. (e) Tanaka, R.; Hirano, S.; Urabe, H.; Sato, F. *Org. Lett.* **2003**, *5*, 67.

(17) (a) Tomita, I. *Polym. Prepr.* **2004**, *45*, 415. (b) Tomita, I.; Ueda, M. *Macromol. Symp.* **2004**, *209*, 217. (c) Matano, Y.; Miyajima, T.; Nakabuchi, T.; Matsutani, Y.; Imahori, H. *J. Org. Chem.* **2006**, *71*, 5792.

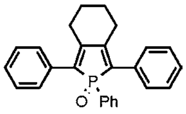
(18) For syntheses of phospholes via a zirconacyclopentadiene route, see: (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Douglas, T.; Theopold, K. H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1367. (c) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

analyses were also satisfactory. All these spectral observations support the structure of the phosphole-cored and phosphole oxide-cored dendrimers.

The photophysical properties of phosphole-cored **4a**−**c** and phosphole oxide-cored dendrimers **5a**−**c** are of interest. The photophysical data in solution, along with those of the parent compounds **4d** and **5d** (see below), are summarized in Table 1 and the absorption and photoemission spectra of **4a**−**d** are shown in Figure 1. In the absorption spectra, the phosphole-cored dendrimers **4a**−**c** display two absorption bands at about 280 and 360 nm, assignable to the benzyl ether-type dendrons and the focal phosphole ring, respectively. The intensity of the absorption of the dendron units increases with the increasing generation of the dendrons, while the intensity and position of absorption of the phosphole ring do not change significantly. When the phosphole ring is excited at 360 nm, **4a**−**c** display an emission at about 470 nm. The excitation spectra, monitored at 470 nm, reproduce the absorption spectra almost perfectly for **4a**−**c**. The quantum yield (Φ_{PL}) increases with the increasing generation of the dendron units, as shown in Table 1. The Φ_{PL} of the parent phosphole **4d** is 12%, but the Φ_{PL} of **4c** is 46%, which is the highest ever reported for 2,5-diaryl-substituted phosphole chromophores in solution.



4d



5d

When the benzyl ether-type dendron unit is excited at 280 nm, the dendrimers also display an emission at around 470 nm from the phosphole ring unit, but no emission from the benzyl ether-type dendron units (310 nm),[11b] indicating that the energy transfer (ET) from the dendron units to the focal phosphole ring occurs within the dendrimers. However, the ET efficiency, estimated by a comparison of the absorption spectrum and the excitation spectrum of the phosphole-cored dendrimers by monitoring the emission of the acceptor,[19] is not high (67% for **4b** and 24% for **4c**) compared with that of the previously reported light-harvesting dendrimers.[11] This is probably because the spectral overlap between donor emission and acceptor absorption necessary for high ET efficiency[20] is small.

Table 1. Photophysical Properties of Phosphole-Cored **4** and Phosphole Oxide-Cored Dendrimers **5**

	in solution[a]				film[b]	
	ABS		EM		ABS	EM
compd	λ_{max}/ nm	ϵ/ $10^4\,cm^{-1}\,M^{-1}$	λ_{PLmax}/ nm[c]	Φ_{PL}[d,e]	λ_{max}/ nm	λ_{PLmax}/ nm[f]
4a	357	12.2	469	0.19	362	489
4b	357	11.5	477	0.37	359	472
4c	357	11.6	476	0.46	358	469
4d	352	10.4	460	0.12	356	492
5a	375	9.2	505	0.0020	379	503
5b	379	9.8	502	0.0062	382	505
5c	379	8.5	501	0.016	389	501
5d	370	8.5	505	0.0012	380	496

[a] In THF. [b] Cast film from a toluene solution on a quartz plate. [c] Excited at ca. 370 nm. [d] Quantum yield. [e] Determined with quinine sulfate as a standard. [f] Excited at ca. 380 nm.

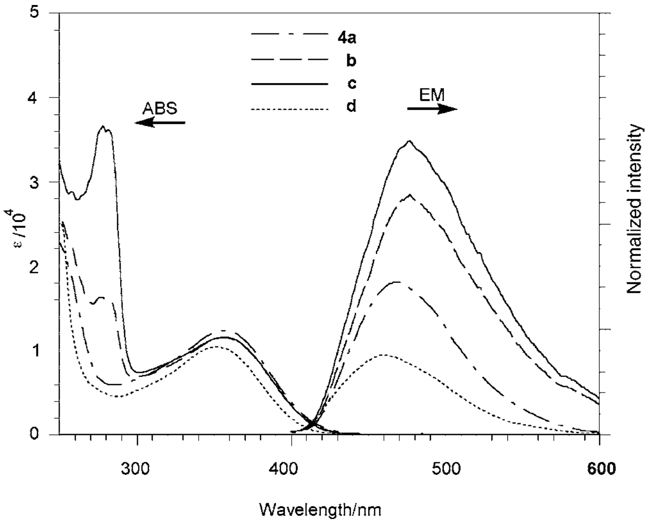


Figure 1. Absorption and photoemission (excited at ca. 370 nm) spectra of **4a**−**d** in THF.

The phosphole oxide-cored dendrimers **5a**−**c** exhibit absorption maxima at about 380 nm, which is red-shifted relative to those of the phosphole-cored dendrimers (Table 1; also see the Supporting Information). In the photoemission spectra, the phosphole oxide-cored dendrimers **5a**−**c** show a significant red shift of about 30 nm and an emission at 500 nm, while the quantum yields drop sharply. These spectral features mean that the optical and electronic properties of the phosphole-cored dendrimers are changed by oxidation of the phosphorus atom of the phosphole ring.

The solid-state behavior will probably increase the feasibility of employing these compounds in electronic devices. The conformal films of **4a**−**d** and **5a**−**d** on a quartz substrate were obtained by casting a toluene solution of the dendrimers. The photophysical data in the solid state are summarized in Table 1. The absorptions are red-shifted to about 360 nm in the film relative to those of the solution absorption spectra. In the emission spectra, the films of **4a**−**c** and **5a**−**c** display an intense blue light emission ($\lambda_{PL,max}$ = 470−490 nm) and a bluish-green emission ($\lambda_{PL,max}$ = 500 nm), respectively.

In summary, we have demonstrated the first example of the synthesis of phosphole-cored and phosphole oxide-cored

---

(19) (a) Gust, D.; Moore, T. A.; Moore, A.; Devadoss, C.; Liddell, P. A.; Hermant, R. M.; Nieman, R. A.; Demanche, L. J.; DeGraziano, J. M.; Gouni, I. *J. Am. Chem. Soc.* **1992**, *114*, 3590. (b) Schulman, S. G. *Molecular Luminescence Spectroscopy: Methods and Applications*; John Wiley & Sons, Inc: New York, 1993; Vol. 3.

(20) Turro, N. J. *Modern Molecular Photochemistry*; University Books: Sausalito, CA, 1991.

dendrimers having poly(benzyl ether) units through the third generation. These dendrimers display an intense blue-green photoluminescence, the quantum yield increasing with the increasing generation of the dendron units. In addition, the optical properties of the phosphole-cored dendrimer are easily tuned by oxidation of the phosphorus atom of the phosphole ring. Further, the conformal films of these dendrimers on a quartz substrate are obtained by casting a toluene solution of the dendrimers and an intense emission is observed. The findings reported herein would be important in view of optoelectronic applications. Further study along this line is currently in progress.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan (No. 16685004).

Supporting Information Available: Experimental procedures and absorption and photoemission spectra of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL701606T