Available online at www.sciencedirect.com

Tetrahedron Letters 46 (2005) 5273–5276

Tetrahedron Letters

Synthesis and photophysical properties of phenothiazine-labeled conjugated dendrimers

Xiao-Hang Zhang,[a] Suk-Ho Choi,[b] Dong Hoon Choi[c] and Kwang-Hyun Ahn[a,*]

[a]*College of Environment and Applied Chemistry, Institute of Natural Science, Kyung Hee University, Yongin City 449-701, South Korea*
[b]*College of Electronics and Information, Institute of Natural Science, Kyung Hee University, Yongin City 449-701, South Korea*
[c]*Department of Chemistry, Korea University, Seoul 136-701, South Korea*

Received 30 April 2005; revised 9 June 2005; accepted 10 June 2005

Abstract—A novel class of conjugated dendrimers bearing phenothiazines as peripheral groups and phenylenevinylene-group as a core has been synthesized through the Wittig–Horner reaction in moderate to good yield.

Conjugated polymers have attracted considerable attention because of their various applications in electronics and optoelectronics such as organic light-emitting diodes (OLEDs)[1] and photovoltaic cells.[2] However, the aggregation of π-conjugated skeleton often results in low quantum efficiency of luminescence.[3] Although, branching of polymers can prevent the close packing of the system, it is prone to lead to poor charge injection and transport.[4] Thus, rather than employing a linear geometry like in polymers, dendrimers based on a self-similar fractal branching geometry are potentially ideal macromolecules to overcome the conflict. In the past decades, efforts have been made to use the conjugated dendrimers as both charge transporting[5] and light-emitting materials.[4,6] Compared with the small organic molecules and polymers used in OLEDs, the dendrimers have a number of advantages such as the ability to spatially control the active components and thus the EL properties, and the ability to promote the durability of devices.

Phenothiazines, a pharmaceutically important class of heterocycles, have been used recently as spectroscopic probes in supramolecular assembly for PET (photoinduced electron transfer) studies[7] and as electron donor components in the materials science due to their low reversible oxidation potentials.[8] For example, donor–acceptor systems with phenothiazine as the electron donor and phenylquinoline group as an electron acceptor provide an approach for the design of new materials exhibiting efficient ECL (eletrogenerated chemluminescence).[9] And, phenothiazine-based conjugated polymers that were used as a light-emitting material have also been reported recently.[10] Since we have been interested in EL materials based on a dendritic structure, we thought that the dendrimer with the phenothiazine group might give improved EL properties compared with the linear conjugated polymer. Thus, herein we report the synthesis and photophysical characterization of a novel class of conjugated dendrimers based on the phenylenevinylene-based core with phenothiazine derivatives as the peripheral group.

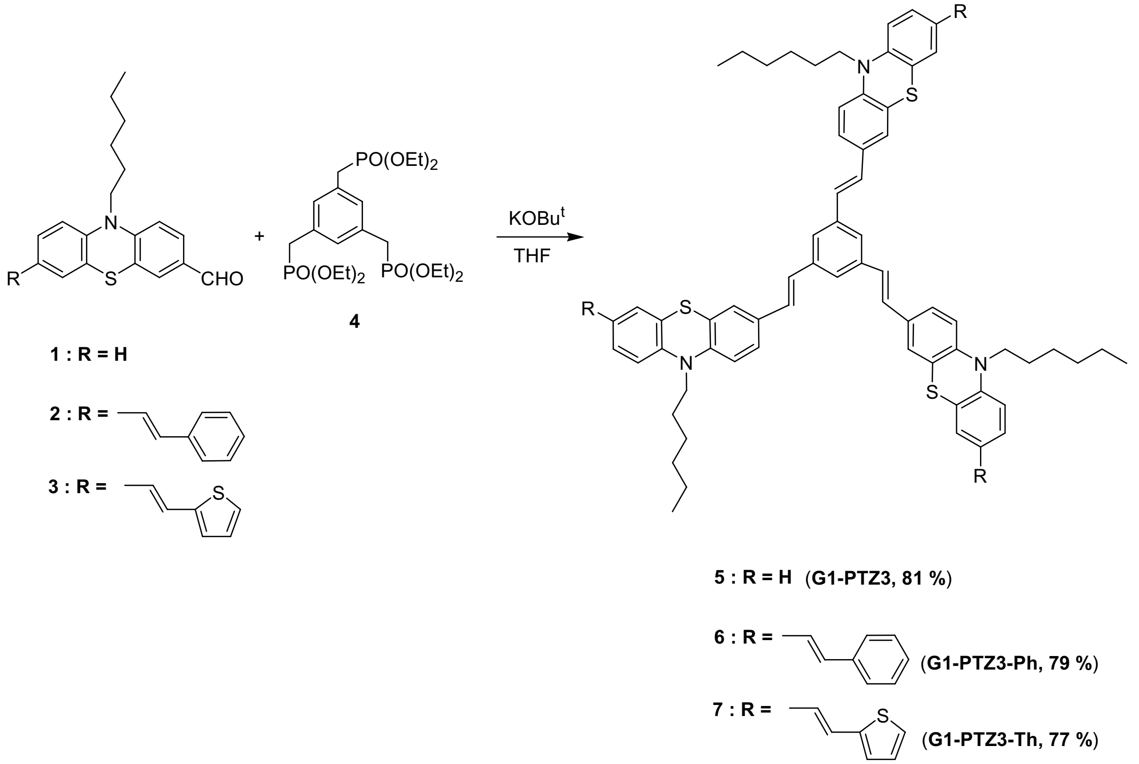
The typical Wittig–Horner reaction between heterocyclic aldehydes, **1**–**3** and the core building block, hexaethyl 1,3,5-benzenetriyltris(methylenephosphonate), **4**[11] was used for the synthesis of the first generation dendrimer, **G1-PTZ3** and its derivatives (Scheme 1). The conjugated aldehyde, **2**, was prepared by palladium-catalyzed Heck reaction[13] of styrene with 7-iodophenothiazine-3-carbaldehyde, **8**, derived from the iodination of 10-*n*-hexyl-10*H*-phenothiazine-3-carbaldehyde, **1**.[12] The thiophene-containing aldehyde, **3** was synthesized from the mono-protected compound, **10** in a two-step procedure such as Wittig–Horner reaction with diethyl thiophen-2-ylmethylphosphonate,[14] followed by

---

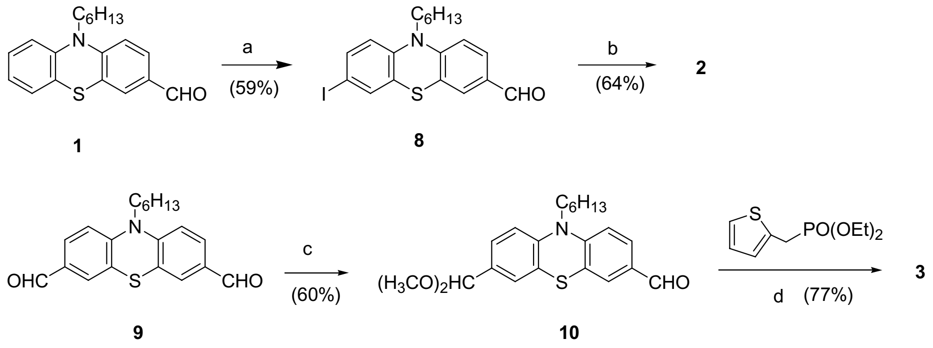
Keywords: Dendrimer; Phenothiazine; OLED; Luminescence.

* Corresponding author. Tel.: +82 312012447; fax: +82 312027337; e-mail: khahn@khu.ac.kr

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.06.051



Scheme 1. Synthesis of the first generation dendrimer and its derivatives.

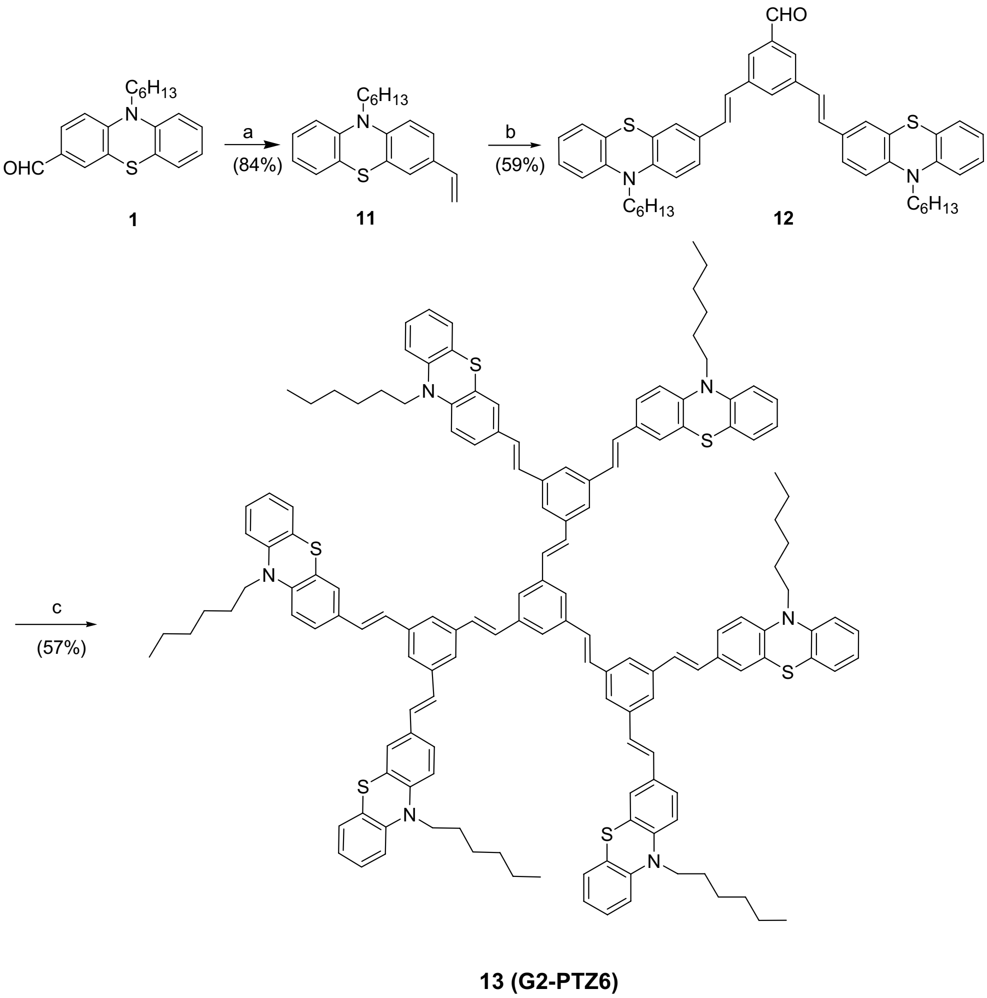


Scheme 2. Reagents and conditions: (a) I_2, H_5IO_6, H_2SO_4, AcOH, H_2O, 80 °C, 6 h; (b) styrene, $Pd(OAc)_2$, K_3PO_4, DMA, 116 °C, 16 h; (c) $CH(OCH_3)_3$, MeOH, DOWEX® 50WX8-100, reflux, overnight; (d) (i) KOBu^t, THF, rt, 2 h; (ii) 2 M HCl, $CHCl_3$, rt, 0.5 h.

deprotection (Scheme 2). The synthesis of second generation dendrimer was started from the Wittig reaction between phenothiazine-3-carbaldehyde, **1** and methyltriphenylphosphonium bromide, which gave the 3-ethenyl-10-*n*-hexyl-10*H*-phenothiazine, **11** in good yield. The intermediate **12**, obtained by the Heck reaction between **11** and 3,5-dibromobenzaldehyde, was coupled with the hexaethyl 1,3,5-benzenetriyltris(methylenephosphonate), **4** to produce **13** (**G2-PTZ6**) in moderate yield (Scheme 3).

These dendrimers, which are soluble in various organic solvents such as chloroform, dichloromethane, 1,2-dichloroethane, and THF, were characterized by standard spectroscopic measurements.[15] The ^{1}H NMR spectra ($CDCl_3$) of **G1-PTZ3** and **G2-PTZ6** showed sharp and well resolved signals at room temperature. On the other hand, the signals of **G1-PTZ3-Ph** and **G1-PTZ3-Th** were broad at room temperature, which might be due to the slow conformational change because of the extended chain length. Broadened signals were also observed in the ^{13}C NMR spectra of these compounds. The coupling constant ($J = 16.2$ Hz) of olefinic protons in the **G1-PTZ3** indicates that Wittig–Horner reaction afforded the pure all-trans isomer, which was further confirmed by the characteristic absorption band of trans double bond at 957 cm^{-1} in IR spectra.[4,16] In addition, all the NMR spectra indicate that the dendrimers adopt highly symmetric conformations in solution.

Absorption and fluorescence spectra of these dendritic molecules are shown in Figure 1. Dendrimer **G1-PTZ3** has a maximum absorption at 379 nm, which is about 57 nm red-shifted to that of 3-ethenyl-10-*n*-hexyl-10*H*-



Scheme 3. Reagents and conditions: (a) Ph_3PCH_3Br, KOBu^t, THF, rt, 2 h; (b) 3,5-dibromobenzaldehyde, $Pd(OAc)_2$, K_3PO_4, DMA, 110 °C, 24 h; (c) **4**, KOBu^t, THF, rt, 3 h.

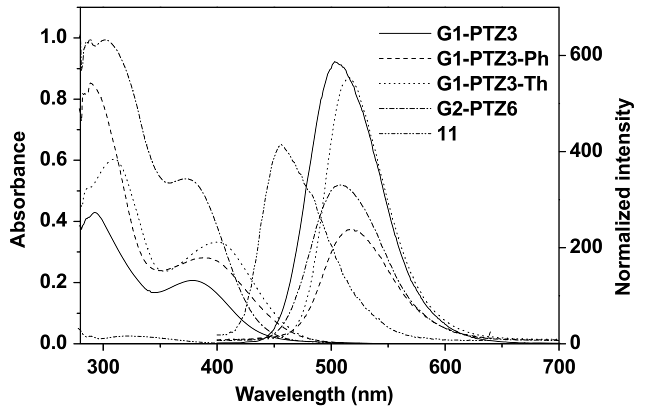


Figure 1. UV–vis (left) and fluorescence (right) spectrum of dendrimers (4×10^{-6} M) in THF.

phenothiazine, **11**. This absorption is also about 30 nm longer than that of phenylenevinylene core, which has a broad absorption band (270–390 nm) with a peak at 350 nm.[5d] The quite large red-shift confirms the effectively elongated π-conjugated dendritic skeleton of the compound with substituents such as phenyl and thiophene ring. In addition, the absorption and fluorescence of all dendrimers show a good correlation to the conjugation length from the core to the periphery with the exception of **G2-PTZ6**, which shows a blue-shifted absorption maximum at 372 nm and a slightly red-shifted emission at 509 nm. These results might be observed because of the increased steric hindrance as the number of generations are increased[6k] (Table 1). The rather large Stokes shift shown by all these dendrimers could be explained based on the more planar conformation of the phenothiazine ring in excited state compared with the ground state.[10]

Table 1. Photophysical data of dendrimers

	λ_{max}/nm ($\varepsilon_{max}/10^{-4}$ M^{-1} cm^{-1})	λ_{em}/nm	Stokes shift/nm	Φ_f[a]
G1-PTZ3	379 (5.18)	503	124	0.083
G1-PTZ3-Ph	388 (7.04)	517	129	0.037
G1-PTZ3-Th	400 (8.31)	515	115	0.048
G2-PTZ6	374 (13.5)	509	135	0.058
11	322 (0.636)	456	134	0.18

[a] 9,10-Diphenylanthracene (DPA) was used as a standard (λ_{exc} = 380 nm; Φ_{dpa} = 0.91 in benzene).

In conclusion, we have synthesized novel dendrimers bearing phenothiazines as peripheral groups and phenylenevinylene-group as a core. We are currently investigating EL properties of these molecules.

Acknowledgments

This work was supported by the Korean Research Foundation (KRF-2003-005-C00002).

References and notes

1. (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539; (b) Braun, D.; Heeger, A. J. *Appl. Phy. Lett.* **1991**, *58*, 1982; (c) Bradley, D. D. C. *Adv. Mater.* **1992**, *4*, 756; (d) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.
2. Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Sciences* **1995**, *270*, 1789.
3. Joswick, M. D.; Cambell, I. H.; Barashkov, N. N.; Ferraris, J. P. *J. Appl. Phys.* **1996**, *80*, 2883.
4. Beavington, R.; Frampton, M. J.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Adv. Funct. Mater.* **2003**, *13*, 211.
5. (a) Bettenhausen, J.; Strohriegl, P. *Adv. Mater.* **1996**, *8*, 507; (b) Miller, L. L.; Duan, R. G.; Tully, D. C.; Tomalia, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 507; (c) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1993**, *65*, 807; (d) Kwon, T. W.; Alam, M. M.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4657; (e) Satoh, N.; Cho, J.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 8104.
6. (a) Pillow, J. N. G.; Halim, M.; Lupton, J. M.; Burn, P. L.; Samuel, I. D. W. *Macromolecules* **1999**, *32*, 5985; (b) Wang, P. W.; Liu, Y. J.; Devadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237; (c) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Adv. Mater.* **1999**, *11*, 371; (d) Lupton, J. M.; Samuel, I. D. W.; Burn, P. L.; Mukamel, S. *J. Chem. Phys.* **2002**, *116*, 455; (e) Lupton, J. M.; Samuel, I. D. W.; Burn, P. L.; Mukamel, S. *J. Phys. Chem. B* **2002**, *106*, 7647; (f) Pogantsch, A.; Wenzl, F. P.; List, E. J. W.; Leising, G.; Grimsdale, A. C.; Müllen, K. *Adv. Mater.* **2002**, *14*, 1061; (g) Markham, J. P. J.; Lo, S.-C.; Magennis, S. W.; Burn, P. L.; Samuel, I. D. W. *Appl. Phys. Lett.* **2002**, *80*, 2645; (h) Ma, D.; Lupton, J. M.; Samuel, I. D. W.; Lo, S.; Burn, P. L. *Appl. Phys. Lett.* **2002**, *81*, 2285; (i) Cao, X.; Zhang, W.; Wang, J.; Zhou, X.; Lu, H.; Pei, J. *J. Am. Chem. Soc.* **2003**, *125*, 12430; (j) Furuta, P.; Brooks, J.; Thompson, M. E.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2003**, *125*, 13165; (k) Hwang, G. T.; Kim, B. H. *Org. Lett.* **2004**, *6*, 2669; (l) Li, J.; Liu, D.; Ma, C.; Lengyel, O.; Lee, C.; Tung, C.; Lee, S. *Adv. Mater.* **2004**, *16*, 1538.
7. (a) Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5378; (b) Jones, W. E., Jr.; Chen, P.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 387.
8. (a) Spreitzer, H.; Daub, J. *Chem. Eur. J.* **1996**, *2*, 1150; (b) Krämer, C. S.; Müller, T. J. J. *Eur. J. Org. Chem.* **2003**, 3534.
9. (a) Lai, R. Y.; Fabrizio, E. F.; Lu, L.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 9112; (b) Lai, R. Y.; Kong, X.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2003**, *125*, 12631.
10. (a) Kong, X.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2003**, *36*, 8992; (b) Hwang, D.; Kim, S.; Park, M.; Lee, J.; Koo, B.; Kang, I.; Kim, S.; Zyung, T. *Chem. Mater.* **2004**, *16*, 1298.
11. Blanchard, P.; Svenstrup, N.; Rault-Berthelot, J.; Riou, A.; Bercher, J. *Eur. J. Org. Chem.* **1998**, 1743.
12. Tosa, M.; Paizs, C.; Majdik, C.; Moldovan, P.; Novak, L.; Kolonits, P.; Szabo, L.; Irimi, F. *J. Mol. Catal. B: Enzym.* **2002**, *17*, 241.
13. Yao, Q.; Kinney, E. P.; Yang, Z. *J. Org. Chem.* **2003**, *68*, 7528.
14. Woo, H. Y.; Shim, H.; Lee, K. *Synth. Met.* **1999**, *101*, 136.
15. The general procedure used for the Wittig–Horner reaction: 592 mg (1.90 mmol) of 10-*n*-hexyl-10*H*-phenothiazine-3-carbaldehyde **1** and 335 mg (0.63 mmol) of **4** were dissolved in 10 ml of dry THF. The resulting solution was added dropwise slowly to 564 mg (5.04 mmol) of $KOBu^t$ in 30 ml of dry THF at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 for 12 h. The reaction was quenched by adding a small amount of saturated aqueous solution of NH_4Cl and extracted with ethyl acetate. The organic phase was dried over $MgSO_4$. Chromatography on silica gel (ethyl acetate/hexane 1:10) gave 525 mg (81%) of product **5** as a yellow solid. Mp 94–96 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, $J = 6.9$ Hz, 9H), 1.30–1.33 (m, 12H), 1.44 (m, 6H), 1.81 (m, 6H), 3.84 (t, $J = 7.2$ Hz, 6H), 6.81–6.97 (m, 12H), 7.04 (d, $J = 16.2$ Hz, 3H), 7.12–7.17 (m, 6H), 7.27–7.31 (m, 6H), 7.44 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.00, 22.58, 26.62, 26.78, 31.43, 47.54, 115.32, 122.40, 123.29, 123.31, 124.20, 124.88, 124.95, 125.89, 126.68, 127.20, 127.39, 127.79, 131.71, 137.98, 144.55, 144.78; HRMS (FAB) *m*/*z* calcd $C_{66}H_{69}N_3S_3$ $(M+H)^+$ 1000.4692, found 1000.4732. The same procedure was used to prepare the dendrimers **6**, **7**, and **13**: Compound **6**: Mp 115–117 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, $J = 6.6$ Hz, 9H), 1.30–1.42 (m, 18H), 1.78 (m, 6H), 3.82 (br s, 6H), 6.78–6.97 (m, 18H), 7.25–7.48 (m, 30H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 26.5, 29.6, 31.4, 47.4, 115.1, 124.0, 124.8, 125.9, 126.3, 127.3, 128.6, 131.8, 137.3, 143.9 (The ^{13}C NMR gives poor resolution, so the number of C bar in the spectra is far less than the theoretical number.); HRMS (FAB) *m*/*z* calcd $C_{90}H_{87}N_3S_3$ $(M+H)^+$ 1306.8689, found 1306.6140. Compound **7**: Mp 127–129 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, $J = 6.6$ Hz, 9H), 1.25–1.40 (m, 18H), 1.76 (m, 6H), 3.74 (br s, 6H), 6.74–7.26 (m, 39H), 7.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.6, 26.5, 29.6, 31.4, 47.5, 115.0, 120.0, 120.2, 123.3, 123.8, 124.1, 124.5, 124.7, 124.8, 125.1, 125.6, 125.9, 126.5, 126.6, 127.5, 128.1, 131.2, 131.6, 137.8, 143.0, 143.8; HRMS (FAB) *m*/*z* calcd $C_{90}H_{87}N_3S_3$ $(M+H)^+$ 1324.9520, found 1324.4833. Compound **13**: Mp 110–112 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, $J = 6.9$ Hz, 18H), 1.27–1.42 (m, 36H), 1.75 (m, 12H), 3.72 (br s, 12H), 6.70 (d, $J = 8.4$ Hz, 6H), 6.79 (d, $J = 8.4$ Hz, 9H), 6.88–6.97 (m, 15H), 7.10–7.15 (m, 18H), 7.18–7.24 (m, 12H), 7.31 (s, 3H), 7.39 (s, 6H), 7.49 (s, 3H); unresolved and broaden ^{13}C NMR spectra; MALDI-TOF MS *m*/*z* calcd $C_{150}H_{150}N_6S_6$ (M^+) 2228.03, found 2228.69.
16. He, F.; Xia, H.; Tang, S.; Duan, Y.; Zeng, M.; Liu, L.; Li, M.; Zhang, H.; Yang, B.; Ma, S.; Liu, S.; Shen, J. *J. Mater. Chem.* **2004**, *14*, 2735.