ORGANIC
LETTERS

2006
Vol. 8, No. 25
5701−5704

Rigid Linear and Star-Shaped π-Conjugated 2,2′:6′,2″-Terpyridine Ligands with Blue Emission

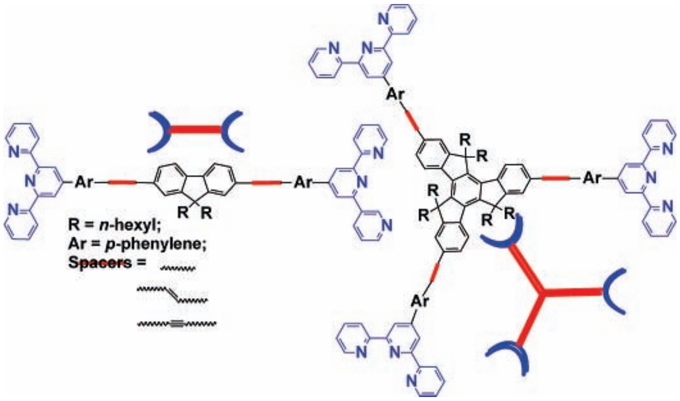
Si-Chun Yuan, Hai-Bo Chen, Yun Zhang, and Jian Pei*

The Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

jianpei@pku.edu.cn

Received August 30, 2006

ABSTRACT



A series of rigid linear and star-shaped π-conjugated 2,2′:6′,2″-terpyridine derivatives with the C–C single-, double-, and triple-bond linkages have been developed through the Suzuki, the Sonogashira, and the Wittig reactions. Such large rigid ligands exhibit strong blue emission in dilute solutions.

Supramolecular chemistry has become one of the most interesting fields in modern chemistry. The design and preparation of new ligands utilizing versatile synthetic strategies accelerates the development of transition-metal complexes in supramolecular structures.[1] The intense interest in polypyridyl ligands and their complexes with transition-metal ions is due especially to their applications as luminescent sensors in molecular biology and medical diagnostics, as photocatalysts, and as active materials in self-assembly, preorganized molecular devices, and photoactive molecular wires.[2] Recently, such complexes have been practical as components of devices in new electroluminescent materials and in information process and storage applications in molecular electronics and photonics.[3]

Among the N-heterocyclic derivatives, 2,2′:6′,2″-terpyridines have a high binding affinity toward transition-metal ions due to $d\pi{-}p\pi^*$ back-bonding of the metal ions to pyridine rings and a chelation effect useful for multinuclear supramolecular construction. π-Conjugated oligomers with substituents at the 4′-position of the 2,2′:6′,2″-terpyridine

---

(1) (a) Lehn, J.-M. *Supramolecular Chemistry, Concept and Perspectives*; VCH: Weinheim, 1995. (b) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689−1746. (c) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892−2926. (d) Newkome, G. R.; Wang, P.; Moorefield, C.; Cho, T. J.; Mohapatra, P. P.; Li, S.; Hwang, S.-H.; Lukoyanova, O.; Echegoyen, L.; Palagallo, J. A.; Lancu, V.; Hla, S.-W. *Science* **2006**, *312*, 1782−1785. (e) Flores-Torres, S.; Hutchison, G. R.; Soltzberg, L. J.; Abruña, H. D. *J. Am. Chem. Soc.* **2006**, *128*, 1513−1522. (f) Bonnet, S.; Collin, J.-P.; Koizumi, M.; Mobian, P.; Sauvage, J.-P. *Adv. Mater.* **2006**, *18*, 1239−1250.

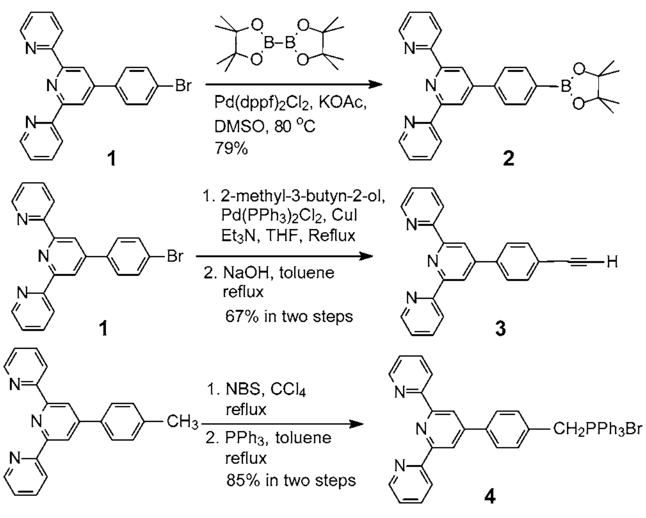
(2) (a) Erkkila, K. E.; Odom, D. T.; Barton, J. K. *Chem. Rev.* **1999**, *99*, 2777−2795. (b) Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1−12. (c) Lainé, P.; Bedioui, F.; Amouyal, E.; Albin, V.; Burruyer-Penaud, F. *Chem.−Eur. J.* **2002**, *8*, 3162−3176. (d) Ott, S.; Kritikos, M.; Åkermark, B.; Sun, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3285−3288. (e) Andres, P. R.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 1043−1068. (f) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373−399. (g) Bianké, G.; Häner, R. *ChemBioChem* **2004**, *5*, 1063−1068. (h) Schmittel, M.; Kalsani, V.; Kishore, R. S. K.; Cölfen, H.; Bats, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 11544−11545. (i) Schmittel, M.; Kalsani, V.; Mal, P.; Bats, J. W. *Inorg. Chem.* **2006**, *45*, 6370−6377. (j) Hwang, S. H.; Moorefield, C. N.; Dai, L.; Newkome, G. R. *Chem. Mater.* **2006**, *18*, 4019−4022.

10.1021/ol0621405 CCC: $33.50

unit exhibit fascinating spectroscopic and redox properties as well as electronic communication between the metal-based units.[4] Their distinct photophysical, electrochemical, and magnetic properties create the potential for designing new functional materials.[2,4] The blue-emitting ligands might be very important as the hosts for photoinduced energy and electron-transfer processes in supramolecular chemistry.[4] However, up to now, there were only a few reports of the synthesis and studies of rigid linear or star-shaped π-conjugated 2,2′:6′,2″-terpyridines.[5] Therefore, their applications have not been investigated as thoroughly as those of 2,2′-bipyridines.[6]

In this contribution, we present the design, synthesis, and photophysical properties of nine novel rigid linear and star-shaped 2,2′:6′,2″-terpyridine derivatives, in which various linkages are employed to fix 2,2′:6′,2″-terpyridine units and conjugated moieties. The introduction of such fluorene and truxene units efficiently improves the solubility and the properties of desired molecules. These building blocks can not only construct linear conjugated metallic wires but also afford the large-sized dendritic complexes, which might be useful to understand the structure−property relationships in supramolecular chemistry and to develop new functionalized materials for optoelectronic devices.

Scheme 1. Synthesis of Three 2,2′:6′,2″-Terpyridine Precursors



The preparation of 4′-(4-bromophenyl)-2,2′:6′,2″-terpyridine **1** followed the typical procedures.[7] We constructed various topic functionalized systems employing versatile synthetic strategies from 4′-aryl-2,2′:6′,2″-terpyridine. Scheme 1 illustrates synthetic approaches to three 2,2′:6′,2″-terpyridine precursors for the Suzuki, the Sonogashira, and the Wittig reactions, respectively. The Miyaura coupling between **1** and bis(pinacolato)diboron with catalyst Pd(pddf)$_2$Cl$_2$ afforded **2** without a homocoupling byproduct.[8] The Sonogashira coupling reaction of **1** with 2-methyl-3-butyn-2-ol catalyzed by Pd(PPh$_3$)$_2$Cl$_2$ revealed an alcohol followed by the deprotection using NaOH to produce ethylene-terminating **3** in 67% yield.[9] We also obtained **4** for the Wittig reaction.[10]

Scheme 2 exhibits the Suzuki coupling to 2,2′:6′,2″-terpyridine derivatives **5a**−**c**, in which a C−C single bond was employed to link conjugated moieties with 2,2′:6′,2″-terpyridine units. The Suzuki coupling of **1** and 9,9-dihexylfluoren-2-ylboronic acid with Pd(PPh$_3$)$_4$ afforded monotopic 2,2′:6′,2″-terpyridine derivative **5a** in 87% yield.[11] Following the same procedures, we also obtained ditopic ligand **5b** in 79% yield. Compound **2** reacted with **8**[12] afforded tritopic ligand **5c**. The Sonogashira route to **6a**−**c** is outlined in Scheme 3. Compound **3** reacted with 9,9-dihexyl-2-bromofluorene, 9,9-dihexyl-2,7-diiodofluorene, and **8** catalyzed by Pd(PPh$_3$)Cl$_2$ produced three ligands **6a**, **6b**, and **6c** in good yields, respectively.[12]

The Wittig reaction of **4** with 9,9-dihexylfluorene-2-carbaldehyde using *t*-BuOK afforded the desired C−C double-bond linkages to produce **7a** in 83% yield as shown in Scheme 4.[13] We also employed the same procedures to produce **7b** and **7c**, respectively. From their NMR spectra,

---

(3) (a) Ziessel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178*−*180*, 1251−1598. (b) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34. (c) Wong, C. T.; Chan, W. K. *Adv. Mater.* **1999**, *11*, 455−459. (d) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219*−*221*, 545−572. (e) Yu, S.-C.; Kwok, C.-C.; Chan, W.-K.; Che, C.-M. *Adv. Mater.* **2003**, *15*, 1643−1647. (f) Flood, A. H.; Stoddart, J. F.; Steuerman, D. W.; Heath, J. R. *Science* **2004**, *306*, 2055−2056. (g) Ciofini, I.; Lainé, P. P.; Bedioui, F.; Adamo, C. *J. Am. Chem. Soc.* **2004**, *126*, 10763−10777. (h) Benniston, A. C.; Harriman, A.; Li, P.; Sams, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 2553−2564. (i) Duprez, V.; Biancardo, M.; Spanggaard, H.; Krebs, F. C. *Macromolecules* **2005**, *38*, 10436−10448. (j) Hagemann, O.; Jørgensen, M.; Krebs, F. C. *J. Org. Chem.* **2006**, *71*, 5546−5559. (k) Benniston, A. C.; Harriman, A.; Li, P.; Patel, P. V.; Sams, C. A. *J. Org. Chem.* **2006**, *71*, 3481−3493.

(4) (a) Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Ssauvage, J.-P.; Sour, A.; Constable, E. C.; Thompson, A. M. W. C. *J. Am. Chem. Soc.* **1994**, *116*, 7692−7699. (b) Barigelletti, F.; Flamigni, L.; Calogero, G.; Hammarström, L.; Sauvage, J.-P.; Coolin, J.-P. *Chem. Commun.* **1998**, 2333−2334. (c) Hissler, M.; El-ghayoury, A.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1717−1720. (d) Bernhard, S.; Goldsmith, J. I.; Takada, K.; Abruña, H. D. *Inorg. Chem.* **2003**, *42*, 4389−4393. (e) Duncan, T. V.; Rubtson, I. V.; Uyela, H. T.; Therien, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 9474−9475. (f) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373−399. (g) Barbieri, A.; Ventura, B.; Barigellitti, F.; de Nicolar, A.; Quesada, M.; Ziessel, R. *Inorg. Chem.* **2004**, *43*, 7359−7368. (h) Duprez, V.; Bianocardo, M.; Spanggaard, H.; Krebs, F. C. *Macromolecules* **2005**, *38*, 10436−10448. (i) Schmittel, M.; Kalsani, V.; Kishore, R. S. K.; Cölfen, H.; Bats, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 11544−11545. (j) Benniston, A. C.; Harriman, A.; Li, P.; Sams, C. A. *J. Am. Chem. Soc.* **2005**, *127*, 2553−2564. (k) Benniston, A. C.; Harriman, A.; Li, P.; Patel, P. V.; Sams, C. A. *J. Org. Chem.* **2006**, *71*, 3481−3493. (l) Torres, S. F.; Hutchison, G. R.; Soltzberg, L. J.; Abruña, H. D. *J. Am. Chem. Soc.* **2006**, *128*, 1513−1522.

(5) (a) Constable, E. C.; Thompson, A. M. W. C. *J. Chem. Soc., Dalton Trans.* **1992**, 3467−3475. (b) Constable, E. C. *Chem. Commun.* **1997**, 1073−1080. (c) Kimura, M.; Hamakawa, T.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *Inorg. Chem.* **2001**, *40*, 4775−4779. (d) Winter, A.; Hummel, J.; Risch, N. *J. Org. Chem.* **2006**, *71*, 4862−4871.

(6) Newkome, G. R.; Patri, A. K.; Holder, E.; Schubert, U. S. *Eur. J. Org. Chem.* **2004**, 235−254.

(7) (a) Kröhnke, F. *Synthesis* **1976**, 1−24. (b) Cave, G. W. V.; Raston, C. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3258−3264.

(8) (a) Aapley, C. J.; Williams, J. A. G. *New J. Chem.* **2001**, *25*, 1136−1147. (b) Goodall, W.; Wild, K.; Arm, K. J.; Williams, J. A. G. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1669−1681.

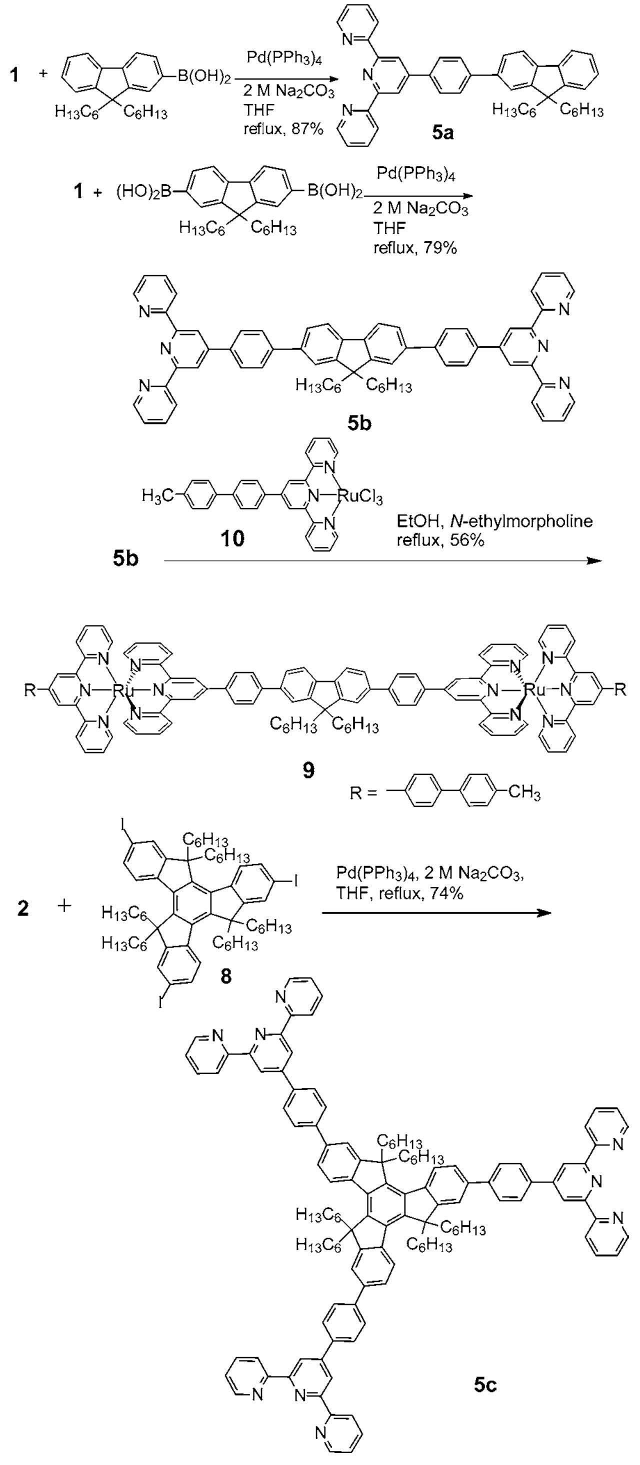
(9) Constable, E. C.; Housecroft, C. E.; Johnston, L. A.; Armspach, D.; Neuburger, M.; Zehnder, M. *Polyhedron* **2001**, *20*, 483−492.

(10) Tessore, F.; Roberto, D.; Ugo, R.; Pizzotti, M.; Quici, S.; Cavazzini, M.; Bruni, S.; De Angelis, F. *Inorg. Chem.* **2005**, *44*, 8967−8978.

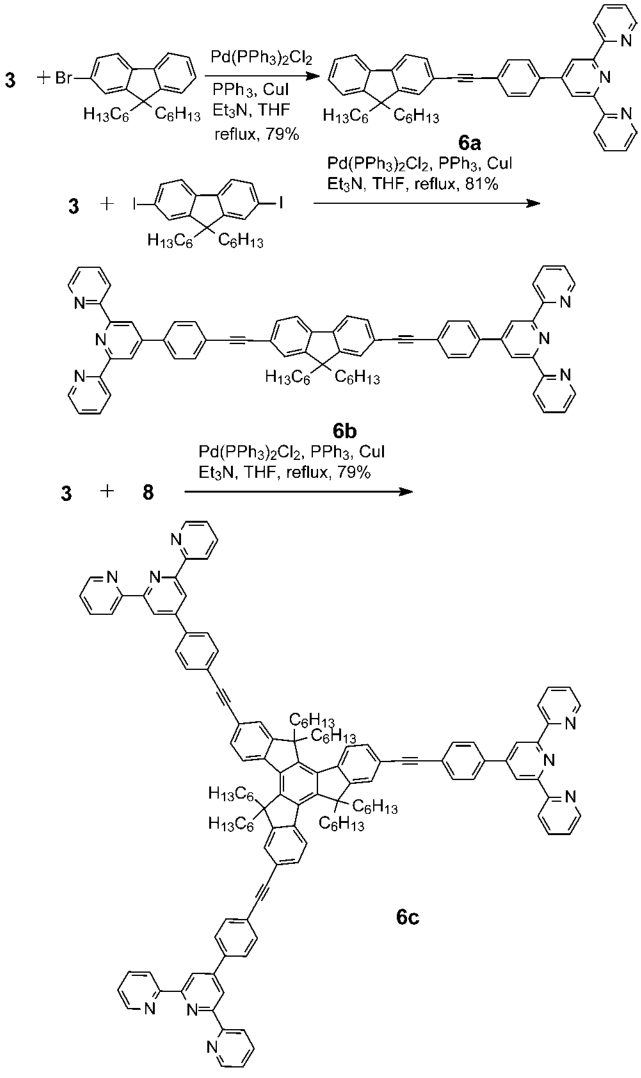
(11) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(12) (a) Cao, X.-Y.; Zi, H.; Zhang, W.; Lu, H.; Pei, J. *J. Org. Chem.* **2005**, *70*, 3645−3653. (b) Ziessel, R. *Synthesis* **1999**, 1839−1865.

Scheme 2. Synthesis of 2,2′:6′,2″-Terpyridine Derivatives



Scheme 3. Synthesis of 2,2′:6′,2″-Terpyridine Derivatives



we observed that all double bonds predominantly existed as the *E*-isomer at room temperature. Finally, compound **5b** reacted with **10**[8a] to produce linear dinuclear ruthenium complex **9** in moderate yield as shown in Scheme 2.

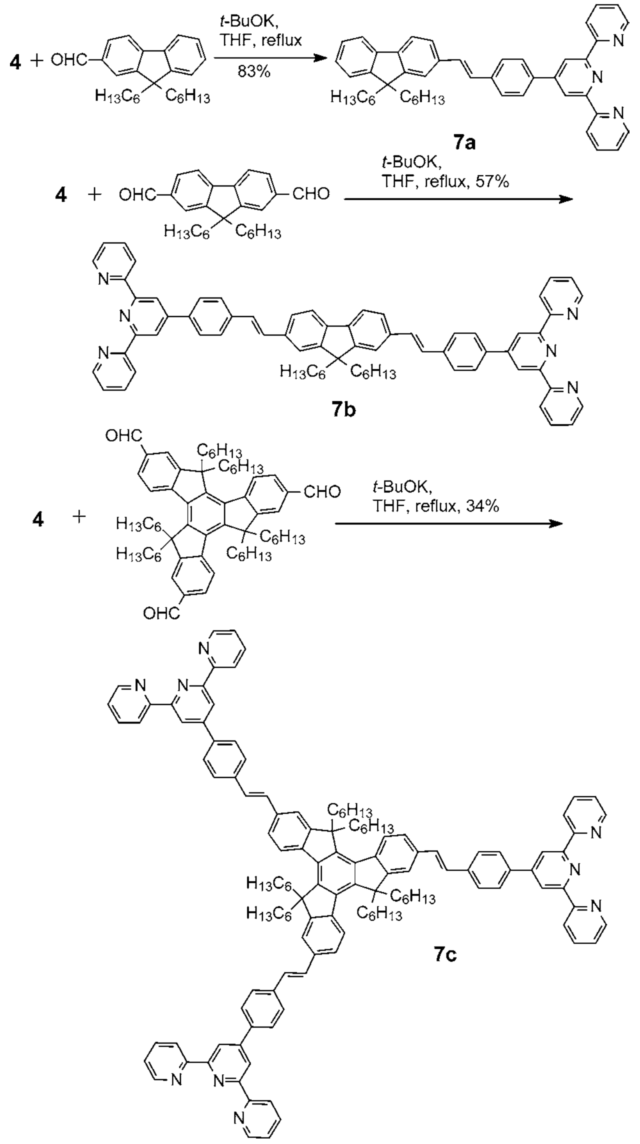
All ligands were readily soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, and THF, which allowed us to conveniently obtain their ^1H and ^{13}C NMR spectra, MALDI-TOF MS, and elemental analysis characterization data to verify the structure and the purity of these ligands (see the Supporting Information).

For their photophysical properties, the absorption and the photoluminescent (PL) spectra of **5a**−**c**, **6a**−**c**, and **7a**−**c** in dilute CH_2Cl_2 solutions were recorded. Their concentration in solutions was ca. 1.0×10^{-6} M. Table 1 summarizes their photophysical properties. Figure 1 illustrates the absorption and emission behaviors of **5b**−**7b** and **5c**−**7c** in solution (the spectra of **5a**−**7a** are shown in the Supporting information). The absorption λ_{max} of **5a** was exhibited at 326 nm. Because of the increase of the effective conjugation length, the absorption of **5b** and **5c** peaked at 349 and 342 nm, respectively, which red shifted about 23 and 16 nm in comparison with that of **5a**. For the absorption λ_{max}, we also observed the red shift of 30 nm for **6b** (367 nm) and of 24 nm for **6c** (351 nm) in comparison with that of **6a** (331 nm), respectively. Similar behaviors were observed from compounds **7a**−**c**. In comparison with 4′-phenyl-2,2′:6′,2″-terpyridine,[5] all six compounds showed an obvious red shift

---

(13) Jiang, Y.; Wang, J.-Y.; Ma, Y.; Cui, Y.-X.; Zhou, Q.-F.; Pei, J. *Org. Lett.* **2006**, *8*, 4287−4290.

Scheme 4. Synthesis of 2,2′:6′,2″-Terpyridine Derivatives



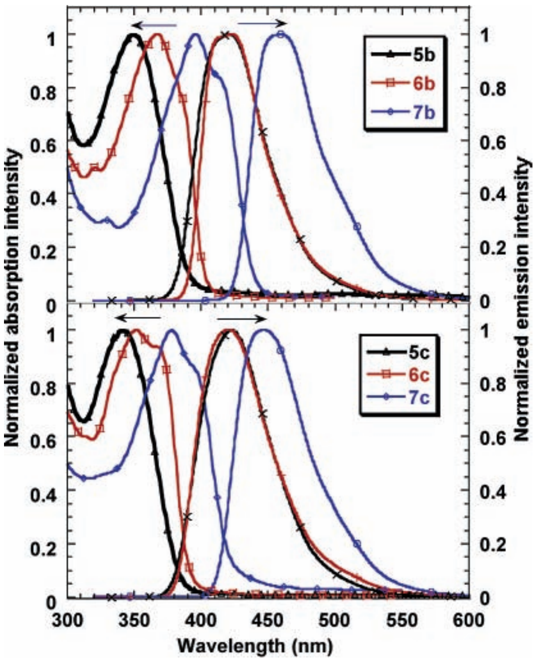


Figure 1. Normalized absorption and emission spectra of **5b**−**7b** and **5c**−**7c** in dilute CH_2Cl_2 solutions. Emission spectra were obtained upon excitation at the absorption maximum.

in their absorption spectra. Moreover, the molar extinction coefficient of these compounds was enhanced up to 10^5 M^{-1} cm^{-1}, which provided us opportunities to prepare new light-harvesting dendritic complexes with high-energy utilization efficiency.

The emission color of these compounds covered the blue range. We observed that the emission λ_{max} of **5b** (421 nm) was close to that of **5c** (422 nm), and the emission λ_{max} of **6b** (424 nm) was almost the same as that of **6c** (423 nm). However, compared with that of **7b** (459 nm), the emission λ_{max} of star-shaped molecule **7c** (446 nm) blue shifted about 13 nm. Such PL behaviors were similar to their absorption features. These investigations demonstrated that the conjugation linkage played an important role in their photophysical properties. We believe that this class of terpyridine derivatives might be extended to emit red emission after perseveringly increasing the effective conjugation length. These compounds can be promising candidates as the host for photoinduced energy and electron transfer within new functional materials.

Table 1. Photophysical Properties of **5a**−**c**, **6a**−**c**, and **7a**−**c** in Solutions

	5a	**5b**	**5c**	**6a**	**6b**	**6c**	**7a**	**7b**	**7c**
λ_{abs} (nm)	326	349	342	337	367	351	363	396	378
λ_{em} (nm)	408	421	422	412	424	423	437	459	446

In conclusion, we have prepared nine linear and star-shaped rigid conjugated 2,2′:6′,2″-terpyridine ligands **5a**−**c**, **6a**−**c**, and **7a**−**c** with various linkages. Such facile synthetic methodology is helpful for us to construct novel dendritic complexes in supramolecular chemistry. The investigation of their photophysical properties indicates that they emit strong blue color in solutions, which provides potential for such materials as the hosts to construct novel functionalized metallic materials for understanding the energy and electron-transfer processes. Combining these star-shaped compounds with diverse metals will also afford us a new platform to develop metallodendrimers.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (NSFC 20425207, 50473016, and 20521202).

Supporting Information Available: Experimental procedures and characterization data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0621405