

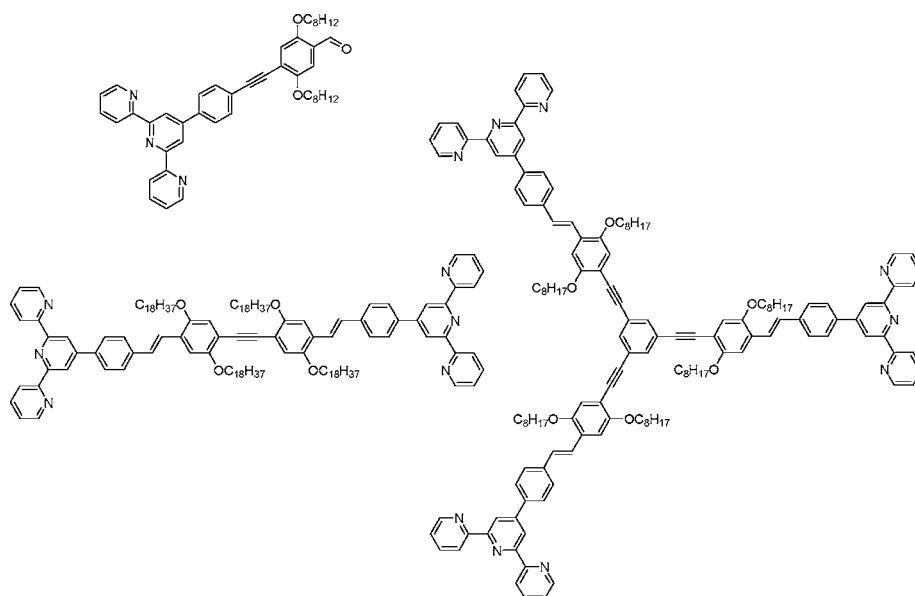
Rigid  $\pi$ -Conjugated Mono-, Bis-, and  
Tris(2,2':6',2''-terpyridines)Andreas Winter,<sup>†</sup> Daniel A. M. Egbe,<sup>†</sup> and Ulrich S. Schubert<sup>\*,†,‡</sup>

Laboratory for Macromolecular Chemistry and Nanoscience, Eindhoven University of  
Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands and  
Center for Nanoscience (CeNS), LMU München, Geschwister-Scholl-Platz 1,  
80333 Munich, Germany

u.s.schubert@tue.nl

Received March 24, 2007

## ABSTRACT



A set of rigid,  $\pi$ -conjugated linear mono- and bisterpyridines and star-shaped tristerpyridines have been synthesized using Pd(0)-catalyzed coupling reactions and the Horner–Wadsworth–Emmons reaction. The terpyridyl ligands obtained feature strong emission in the blue range with high quantum yields in dilute solution and thin films.

Supramolecular chemistry has evolved into one of the most active areas of research in modern chemistry. Both the design and effective preparation of new functional ligands and their incorporation into supramolecular assemblies by transition metal complexation mark the key challenges in this field.<sup>1</sup>

In recent years, oligopyridyl ligands and especially their transition metal complexes have found numerous applications as luminescent sensors in molecular biology and medical diagnostics, in photocatalysis, as active materials in self-assembled molecular devices, and as photoactive molecular

wires.<sup>2</sup> Furthermore, these complexes have been introduced effectively in electroluminescent materials and for storage applications in molecular electronics and photonics.<sup>3</sup>

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

<sup>†</sup> Eindhoven University of Technology.<sup>‡</sup> LMU München.

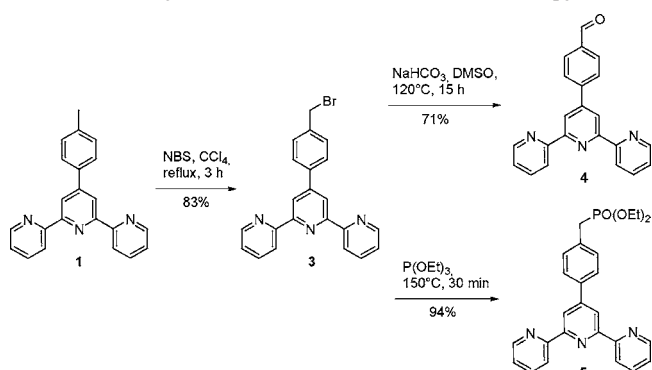
The remarkably high binding affinity toward most transition metal ions by  $d\pi \rightarrow p\pi^*$  bonding, together with their chelation properties, make terpyridines attractive building blocks for the construction of supramolecular assemblies. 2,2':6',2''-Terpyridines bearing  $\pi$ -conjugated substituents at the 4'-position are known to present interesting photophysical and electrochemical properties.<sup>1b,2e,4</sup> The electronic communication between the metal-complexed units of bis- and tristerpyridines is another fascinating feature pointing out their potentials in the design of new functional materials.<sup>2–4</sup> Light-emitting ligands are considered to be important structures as hosts for photoinduced energy and electron transfers in supramolecular chemistry.<sup>4</sup> However, unlike for their 2,2'-bipyridyl counterparts,<sup>5</sup> the applications of  $\pi$ -conjugated terpyridines in these fields have not been elaborated so far and only a few publications deal with the synthesis and properties of rigid-linear or star-shaped derivatives.<sup>6</sup>

In continuation of prior work in the field of terpyridines and their applications in supramolecular chemistry,<sup>1b,c,7</sup> as well on the design of PPV/PPE hybrid polymers,<sup>8</sup> we now present the synthesis and photophysical investigations of new

rigid  $\pi$ -conjugated mono-, bis-, and tris(2,2':6',2''-terpyridines). The structures shown in this contribution bearing various conjugated linkages—including alkene, alkyne, and phenyl moieties—and solubilizing alkoxy chains are promising with respect to the design of new supramolecular assemblies, molecular wires, or dendritic structures.

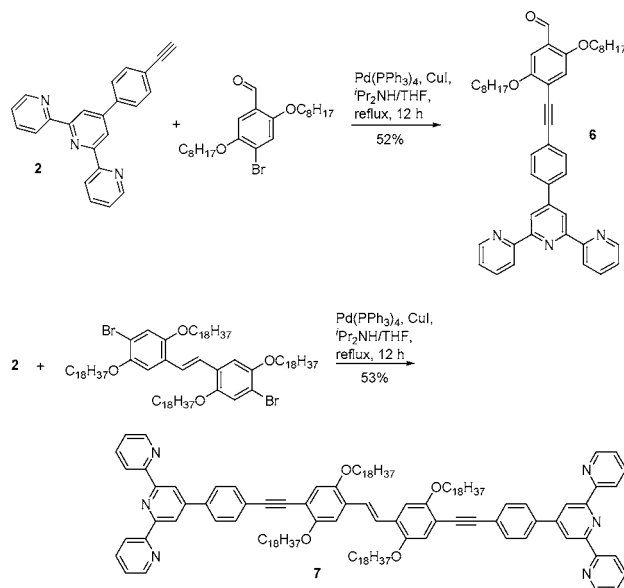
A set of 4'-substituted 2,2':6',2''-terpyridines were chosen as the starting point for the construction of the rigid mono-, bis-, and tristerpyridines via Pd(0)-catalyzed coupling reactions and the Horner–Wadsworth–Emmons reaction (HWE). For this purpose, the Kröhnke-type derivatives **1** and **2** were prepared according to methods published previously.<sup>9</sup> Scheme 1 summarizes the straightforward syntheses of the key substrates **4** and **5** for the HWE reactions.<sup>10</sup>

**Scheme 1.** Synthesis of 4'-Substituted 2,2':6',2''-Terpyridines



The Pd(0)-catalyzed Sonogashira cross-coupling reaction of the ethynyl-functionalized terpyridine **2** (see Supporting Information for details) with bis(alkoxy)-aryl bromides in the presence of  $\text{Pd(PPh}_3)_4/\text{CuI}$  as catalyst directly provided the

**Scheme 2.** Sonogashira Coupling of Ethynyl Terpyridine **2**



(2) (a) Erkkila, K. E.; Odom, D. T.; Barton, J. K. *Chem. Rev.* **1999**, *99*, 2777–2795. (b) Barigeletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1–12. (c) Ott, S.; Kritikos, M.; Åkermar, B.; Sun, L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3285–3288. (d) Andres, P. R.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 1043–1068. (e) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373–399. (f) Bianké, G.; Häner, R. *ChemBioChem* **2004**, *5*, 1063–1068. (g) Schmitt, M.; Kalsani, V.; Mal, P.; Bats, J. W. *Inorg. Chem.* **2006**, *45*, 6370–6377. (h) Hwang, S. H.; Moorefield, C. N.; Dai, L.; Newkome, G. R. *Chem. Mater.* **2006**, *18*, 4019–4022.

(3) (a) Ziesel, R.; Hissler, M.; El-ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *178–180*, 1251–1598. (b) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219–221*, 545–572. (c) Flood, A. H.; Stoddart, J. F.; Steuerman, D. W.; Heath, J. R. *Science* **2004**, *306*, 2055–2056. (d) Ciofini, I.; Lainé, P. P.; Bedioui, F.; Adamo, C. *J. Am. Chem. Soc.* **2004**, *126*, 10763–10777. (e) Duprez, V.; Biancardo, M.; Spanggaard, H.; Krebs, F. C. *Macromolecules* **2005**, *38*, 10436–10448. (f) Hagemann, O.; Jørgensen, M.; Krebs, F. C. *J. Org. Chem.* **2006**, *71*, 5546–5559. (g) Benniston, A.; Harriman, A.; Li, P.; Patel, P. V.; Sams, C. A. *J. Org. Chem.* **2006**, *71*, 3481–3493.

(4) (a) Barigeletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Cargill Thompson, A. M. W. *J. Am. Chem. Soc.* **1994**, *116*, 7692–7699. (b) Barigeletti, F.; Flamigni, L.; Calogero, G.; Hammarström, L.; Sauvage, J.-P.; Collin, J.-P. *Chem. Commun.* **1998**, 2333–2334. (c) Hissler, M.; El-ghayoury, A.; Harriman, A.; Ziesel, 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) Barbieri, A.; Ventura, B.; Barigeletti, F.; de Nicolai, A.; Quesada, M.; Ziesel, R. *Inorg. Chem.* **2004**, *43*, 7359–7368.

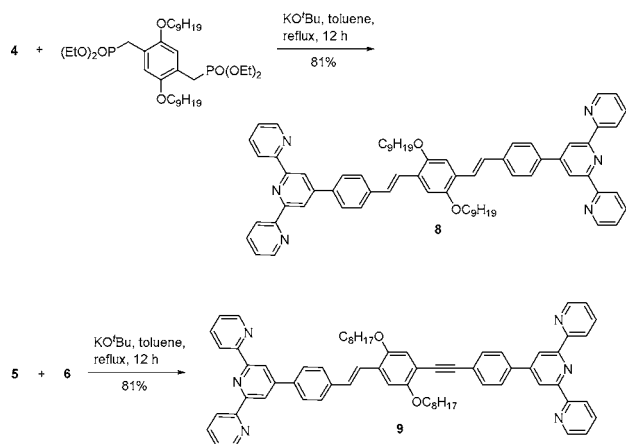
(5) Newkome, G. R.; Patri, A. K.; Holder, E.; Schubert, U. S. *Eur. J. Org. Chem.* **2004**, 235–254.

(6) (a) Chen, Y.-Y.; Tao, Y.-T.; Lin, H.-C. *Macromolecules* **2006**, *39*, 8559–8566. (b) Yuan, S.-C.; Chen, H.-B.; Pei, J. *Org. Lett.* **2006**, *8*, 5701–5704. (c) Winter, A.; Hummel, J.; Risch, N. *J. Org. Chem.* **2006**, *71*, 4862–4871. (d) Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1992**, 3467–3475. (e) Constable, E. C. *Chem. Commun.* **1997**, 1073–1080.

(7) (a) Lohmeijer, B. G. G.; Schubert, U. S. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4016–4027. (b) Hofmeier, H.; Hoogenboom, R.; Wouters, M. E. L.; Schubert, U. S. *J. Am. Chem. Soc.* **2005**, *127*, 2913–2921. (c) Meier, M. A. R.; Wouters, D.; Ott, C.; Guillet, P.; Fustin, C.-A.; Gohy, J.-F.; Schubert, U. S. *Macromolecules* **2006**, *39*, 1569–1576.

(8) (a) Egbe, D. A. M.; Bader, C.; Klemm, E.; Ding, L.; Karasz, F. E.; Grummt, U.-W.; Birckner, E. *Macromolecules* **2003**, *36*, 9303–9312. (b) Ding, L.; Egbe, D. A. M.; Karasz, F. E. *Macromolecules* **2004**, *37*, 6124–6131. (c) Kietzke, T.; Egbe, D. A. M.; Hoerhold, H.-H.; Neher, D. *Macromolecules* **2006**, *39*, 4018–4022. (d) Tekin, E.; Wijlaars Holder, E.; Egbe, D. A. M.; Schubert, U. S. *J. Mater. Chem.* **2006**, *16*, 4294–4298.

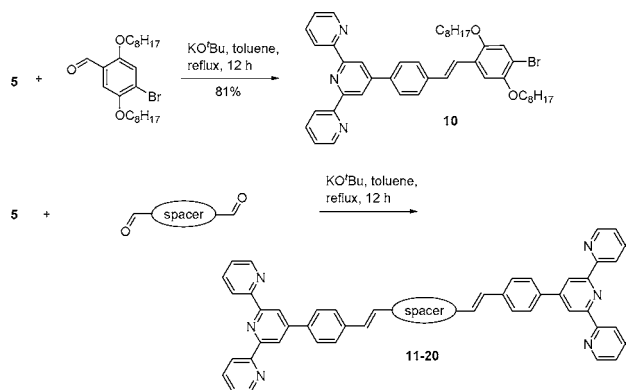
**Scheme 3.** HWE Reaction of the Aldehyde-Functionalized Terpyridines **4** and **6**



corresponding mono- and bisterpyridines (**6** and **7**) in moderate to good yields as depicted in Scheme 2.<sup>6a</sup>

In a second approach, the HWE reaction of terpyridines **4–6** using KOtBu as a base afforded the desired C–C double bonds with high *E*-selectivity, which was proven by <sup>1</sup>H NMR spectroscopy. The general protocol was successfully applied to synthesize the  $\pi$ -conjugated mono- and bisterpyridines **8–16** in yields higher than 80% (Schemes 3 and 4, Table 1).

**Scheme 4.** HWE Reaction of the Phosphonate-Functionalized Terpyridine **5**



In comparison, the Horner–Wadsworth–Emmons reaction was found to be the method of choice for the attachment of  $\pi$ -conjugated spacers to the terpyridine moiety, as the starting materials are easily accessible via known procedures and the yields are significantly higher than for the Pd(0)-catalyzed coupling reactions.

(9) (a) Wang, J.; Hanan, G. S. *Synlett* **2005**, 1251–1254. (b) Smith, C. B.; Raston, C. L.; Sobolev, A. N. *Green Chem.* **2005**, 7, 650–654. (c) Winter, A.; van den Berg, A. M. J.; Hoogenboom, R.; Kickelbick, G.; Schubert, U. S. *Synthesis* **2006**, 2873–2878.

(10) (a) Jørgensen, M.; Krebs, F. C. *J. Org. Chem.* **2005**, 70, 6004–6017. (b) Collin, J.-P.; Heitz, V.; Sauvage, J.-P. *Tetrahedron Lett.* **1991**, 32, 5977–5980.

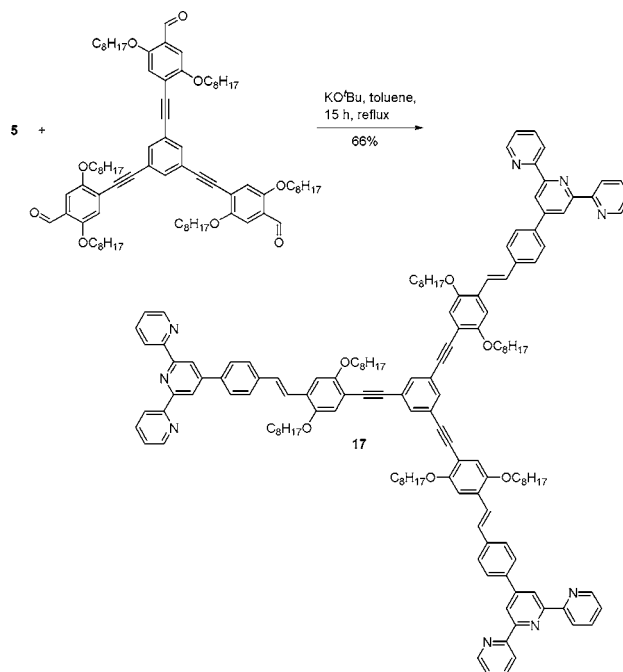
**Table 1.** Overview of the HWE Reaction of Phosphonate-Functionalized Terpyridine **5** with Various Aromatic Dialdehydes

| entry | spacer | yield |
|-------|--------|-------|
| 11    |        | 85%   |
| 12    |        | 83%   |
| 13    |        | 79%   |
| 14    |        | 88%   |
| 15    |        | 91%   |
| 16    |        | 82%   |

Additionally, the method was successfully extended to the synthesis of a star-shaped  $\pi$ -conjugated tristerpyridine **17** (yield 66%) starting from the phosphonate-functionalized terpyridine **5** and an aromatic trialdehyde (Scheme 5).<sup>11</sup>

All terpyridine derivatives shown in this contribution were fully characterized by NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis (see Support-

**Scheme 5.** Synthesis of the Star-Shaped Tristerpyridine **17**



ing Information). Because of the long alkoxy chains, an improved solubility in organic solvents of medium polarity in comparison to unsubstituted analogous substrates was achieved.

The photophysical properties of the  $\pi$ -conjugated terpyridines as summarized in Table 2 were investigated by absorption and emission spectroscopy.

**Table 2.** Photophysical Properties of Terpyridines 6–17

| entry                            | 6   | 7   | 8   | 9   | 10  | 11  |
|----------------------------------|-----|-----|-----|-----|-----|-----|
| $\lambda_{\text{abs}}/\text{nm}$ | 348 | 407 | 417 | 394 | 358 | 414 |
| $\lambda_{\text{em}}/\text{nm}$  | 440 | 478 | 480 | 459 | 437 | 479 |
| $\Phi_{\text{fl}}/\%$            | 28  | 68  | 82  | 81  | 21  | 78  |

| entry                            | 12  | 13  | 14  | 15  | 16  | 17  |
|----------------------------------|-----|-----|-----|-----|-----|-----|
| $\lambda_{\text{abs}}/\text{nm}$ | 392 | 424 | 423 | 419 | 406 | 433 |
| $\lambda_{\text{em}}/\text{nm}$  | 444 | 487 | 471 | 490 | 458 | 461 |
| $\Phi_{\text{fl}}/\%$            | 85  | 54  | 74  | 68  | 60  | 59  |

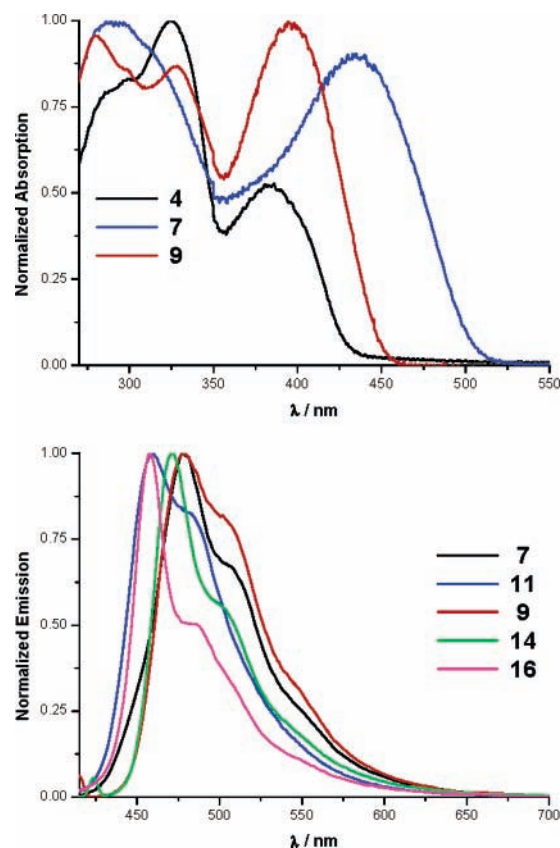
As illustrated in Figure 1, strong absorption around 350 nm was observed for the  $\pi$ -conjugated terpyridines **6** and **10**. With increasing conjugation, a distinct red-shift of the absorption maximum (between 60 and 80 nm), together with a strong increase in the molar extinction coefficient, for all bis- and terterpyridines was found. This effect is most pronounced for the bisterpyridines **13–15** indicating the very high effective conjugation length of these derivatives.

The emission maxima of the terpyridines cover the whole blue range (425–500 nm). In comparison to the terpyridines **6** and **10** and in similarity to their absorption behavior, the emission maximum of the higher conjugated derivatives is also red-shifted. High quantum yields up to 85% were determined. As a result, the conjugated terpyridines shown here might be promising candidates for the design of functional supramolecular materials.

We also compared the emission data obtained for dilute solutions to those of spin-coated thin films. Because of strong  $\pi$ – $\pi$  stacking in the solid state, the emission is quenched significantly. Thin films were obtained by spin-coating the materials onto glass slides. In comparison to the solutions, a red-shifting of the emission maxima of approximately 30 nm with quantum yields of about 25% was observed.

In conclusion, a library of  $\pi$ -conjugated terpyridines with various linkages and geometries have been synthesized.

(11) (a) Weber, E.; Hecker, M.; Koepp, E.; Orlia, W.; Czugler, M.; Csöregi, I. *J. Chem. Soc., Perkin Trans. II* **1988**, 1251–1257. (b) Xu, Z.; Kiang, Y.-H.; Lobkovsky, E. B.; Emmott, N. *J. Am. Chem. Soc.* **2000**, 122, 8376–8391.



**Figure 1.** Normalized absorption (top) and emission spectra (bottom) of terpyridines in dilute  $\text{CHCl}_3$  solution ( $10^{-6}$  mol/L). Emission spectra were obtained upon excitation at the absorption maximum.

These compounds are suitable building blocks for the design of supramolecular assemblies, including block copolymers or chain-extended polymers, by metal complexation. Strong blue emission with high quantum yields has been observed for the solutions and thin films. These properties reveal the potential of these terpyridine systems with respect to potential applications as functional materials.

**Acknowledgment.** Financial support of this work by the Dutch Polymer Institute, the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (VICI award for U.S. Schubert), and the Fonds der Chemischen Industrie is kindly acknowledged.

**Supporting Information Available:** Experimental procedures and characterization data for all compounds shown in this contribution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL0707261