Pergamon

SCIENCE DIRECT®

Tetrahedron Letters 44 (2003) 7711–7714

TETRAHEDRON LETTERS

Redox-switchable π-conjugated systems bearing terminal ruthenium(II) complexes

Xiuliang Shen, Toshiyuki Moriuchi and Toshikazu Hirao*

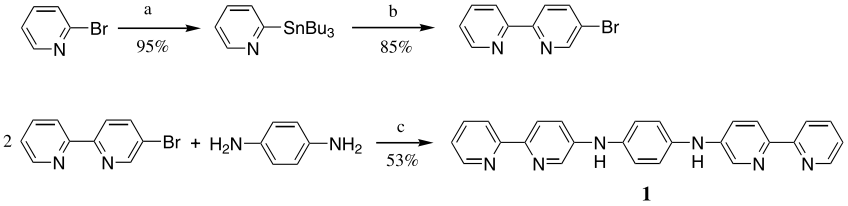
Department of Materials Chemistry, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871, Japan

Received 1 July 2003; revised 27 August 2003; accepted 28 August 2003

Abstract—*p*-Phenylenediamine bearing terminal bipyridyl moieties was synthesized by palladium-catalyzed amination. The corresponding ruthenium(II) complex was formed and characterized, providing a redox-switchable photoinduced electron-transfer system.

π-Conjugated polymers and oligomers have received extensive interest because of the potential application to electronic materials depending on their electrical properties.[1] The redox-active π-conjugated unit of polyanilines and oligoanilines exists in three redox forms, which include the reduced phenylenediamine dianion, the partially reduced semiquinonediimine radical anion, and the oxidized neutral quinonediimine. Coordination of the quinonediimine moiety to transition metals has been demonstrated to afford a multi-redox system.[2] Although polynuclear bipyridyl ruthenium(II) complexes linked by a bridging spacer have been investigated electrochemically and photophysically to provide electronic and photo-active devices,[3] only few cases focused on redox-active bridging spacers.[4] A combination with a redox-active *p*-phenylenediamine function is expected to afford a novel redox-active donor–acceptor system. In a previous paper, two phenylenediamine pendant groups have been incorporated into the bipyridyl ruthenium complex to give a redox-switching system.[5] We herein report the synthesis of a π-conjugated redox-active *p*-phenylenediamine ligand possessing terminal bipyridyl moieties and its complexation to the corresponding dinuclear ruthenium(II) complex.

The π-conjugated *p*-phenylenediamine **1** was prepared as shown in Scheme 1. 5-Bromo-2,2′-bipyridine was produced in good yield by modification of the literature procedure.[6] First, 2-bromopyridine was converted to 2-tributylstannylpyridine. The thus-obtained stannylpyridine underwent Stille-type coupling with 2,5-dibromopyridine to give 5-bromo-2,2′-bipyridine.[7] The phenylenediamine **1** was conveniently synthesized by the $Pd_2(dba)_3$/*S*-BINAP-catalyzed amination of 5-bromo-2,2′-bipyridine with *p*-phenylenediamine.[8] Due to its insolubility, the BOC derivative was used for the purification by silica-gel column chromatography, followed by thermolysis under an inert atmosphere to give pure **1** in 95% yield.[9a]



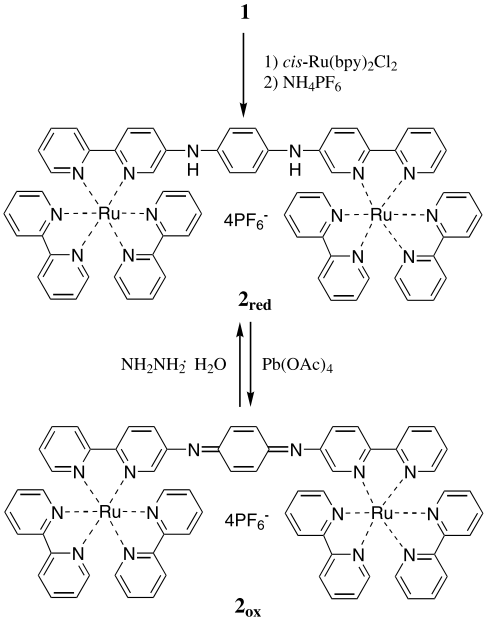
Scheme 1. *Reagents and conditions*: (a) BuLi, THF, hexane, Bu_3SnCl, −78°C; (b) 2,5-dibromopyridine, cat. $Pd(PPh_3)_4$, DMF, 100°C; (c) 4 mol% $Pd_2(dba)_3$, 9 mol% *S*-BINAP, 2.8 equiv. NaO^{t}Bu, toluene, 90°C.

Keywords: π-conjugated ligand; redox-active spacer; bipyridyl ruthenium(II) complex; photoinduced electron transfer.
* Corresponding author. Previous department name: Department of Applied Chemistry, Faculty of Engineering. Tel.: +81-6-6879-7413; fax: +81-6-6879-7415; e-mail: hirao@chem.eng.osaka-u.ac.jp

0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2003.08.102

The complexation of **1** with *cis*-$Ru(bpy)_2Cl_2$ and successive treatment with NH_4PF_6 led to the formation of the dinuclear ruthenium(II) complex $\mathbf{2_{red}}$ (Scheme 2). The redox function of the phenylenediamine moiety was investigated chemically. On treatment with $Pb(OAc)_4$, the complex $\mathbf{2_{red}}$ was readily oxidized to $\mathbf{2_{ox}}$ possessing the quinonediimine moiety. On the other hand, $\mathbf{2_{ox}}$ could be reduced to $\mathbf{2_{red}}$ with $NH_2NH_2{\cdot}H_2O$. These ruthenium complexes, $\mathbf{2_{red}}$ and $\mathbf{2_{ox}}$, were fully characterized by spectral data and elemental analyses.[9b] The ^1H NMR spectrum of $\mathbf{2_{red}}$ at room temperature is shown in Figure 1. A combination with the 2D NMR experiments (HH cosy, HMQC, and HMBC) permitted assignment of all protons. Two singlet protons of **C** at 6.87 and 6.86 ppm suggests a *syn*-conformer as a possible structure in the solution. Furthermore, the 2D-ROESY of $\mathbf{2_{red}}$ in CD_3CN exhibited correlation between the protons at the different aromatic groups (Fig. 1), as exemplified by the correlation between the protons at the 1- or 3-position of **C** and those of the pyridyl protons (at the 3-, 4-, 5- and 6-position of **D**). The MNDO calculation with ROESY-derived distance restraints also suggests a *syn*-conformer of $\mathbf{2_{red}}$.

The redox properties were also studied electrochemically. The ligand **1** in DMF showed two separate oxidation waves at 0.15 and 0.27 V ($E_{1/2}$ versus Fc/Fc^+) assignable to the successive one-electron oxidation processes of the *p*-phenylenediamine moiety. In the case of the complex $\mathbf{2_{red}}$ in CH_2Cl_2, three separate oxidation waves were observed at 0.43, 0.71 and 0.81 V. The two former redox waves are assigned to the successive one-electron oxidation processes of the *p*-phenylenediamine moiety, giving the oxidized species, $\mathbf{2_{red}}^{\bullet+}$ and $\mathbf{2_{ox}}$, as illustrated in Scheme 3. The complexation resulted in anodic shift. The redox behavior of the bipyridyl moieties is almost similar to that of $(bpy)_3Ru(PF_6)_2$ (Table 1).



Scheme 2.

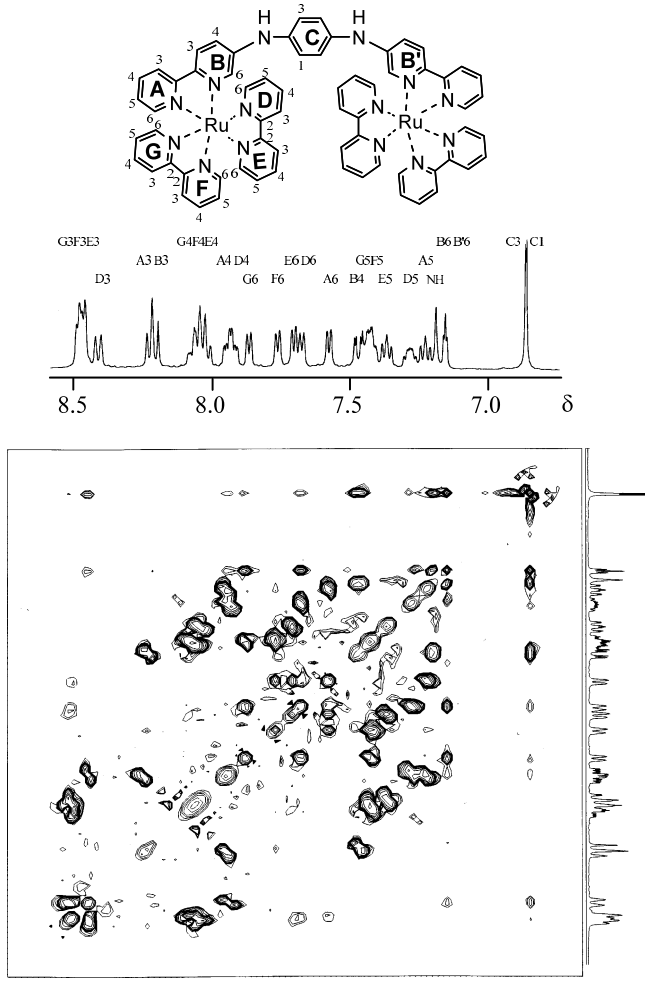
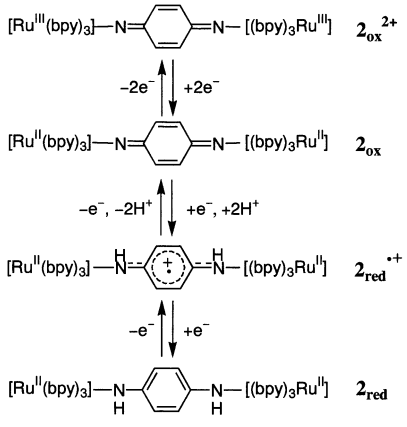


Figure 1. One-dimensional and ROESY ^1H NMR spectra of $\mathbf{2_{red}}$ (CD_3CN, 298 K, 400 MHz).



Scheme 3. Redox processes of $\mathbf{2_{red}}$.

In the emission spectrum of $\mathbf{2_{red}}$ excited at 450 nm in CH_2Cl_2, almost complete quenching was observed (Fig. 2). The quenching of $\mathbf{2_{red}}$ is probably attributed to the photoinduced electron transfer from the *p*-phenylenediamine moiety to the bpy-Ru moieties, wherein the *p*-phenylenediamine moiety serves as an electron

Table 1. Electrochemical data[a] of **1**, $\mathbf{2_{red}}$, $\mathbf{2_{ox}}$ and $(bpy)_3Ru$

Compound	E_{red3}	E_{red2}	E_{red1}	E_{ox1}	E_{ox2}	E_{ox3} ($Ru^{2+/3+}$)
1[b]				0.15	0.27	
$\mathbf{2_{red}}$	−2.33	−2.16	−1.89	0.43	0.71	0.81
$\mathbf{2_{ox}}$	−2.39	−1.98	−0.84			0.81
$(bpy)_3Ru$[c]	−2.18	−1.93	−1.73			0.88

[a] $E_{1/2}$/V (versus Fc/Fc^+); [Compound] = 1.0 mM; Solv. CH_2Cl_2. Recorded with Bu_4NPF_6 as an eletrolyte (0.1 M). Potentials were obtained by cyclic voltammetry with a scan rate of 100 mV s^{-1} under argon.
[b] In DMF.
[c] In MeCN.

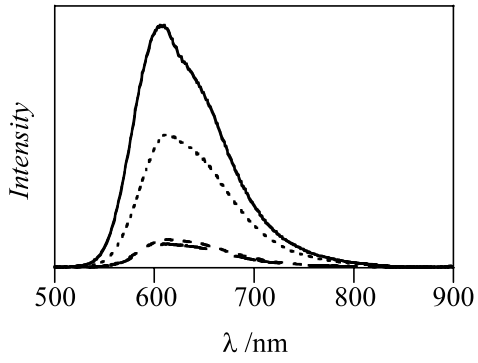


Figure 2. Emission spectra of $\mathbf{2_{red}}$ (---), $\mathbf{2_{ox}}$ (– -), $(bpy)_3Ru$ (—) and $(bpy)_3Ru$ with 1.0 equiv. of **1** (···). Solv. CH_2Cl_2; under argon; 2×10^{-5} M. λ_{ex} = 450 nm.

donor.[5,10] The emission was also quenched in the case of the oxidized form $\mathbf{2_{ox}}$. Based on the reported electron-transfer mechanism of the ruthenium complexes bearing a viologen or benzoquinone moiety,[5,11] this phenomenon might be explained by the photoinduced electron transfer in a direction opposite to that of $\mathbf{2_{red}}$. A much less effective intermolecular quenching of $(bpy)_3Ru(PF_6)_2$ with **1** indicates an intramolecular quenching process for both $\mathbf{2_{red}}$ and $\mathbf{2_{ox}}$.

In conclusion, the *p*-phenylenediamine **1** was demonstrated to serve as a redox-active ligand to afford a novel redox-active dinuclear ruthenium(II) complex, which was oxidized to the quinonediimine derivative for a redox-switchable photoinduced electron-transfer system. Further investigation on the photoinduced electron-transfer mechanism and application to functional materials is now in progress.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 13128206) from the Ministry of Education, Science, and Culture, Japan. Thanks are due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of their facilities.

References

1. (a) MacDiarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphrey, B. D. *Synth. Met*. **1987**, *18*, 393; (b) Salaneck, W. R.; Clark, D. T.; Samuelsen, E. J. *Science and Application of Conductive Polymers*; Adams Hilger: New York, 1990; (c) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc*. **1990**, *112*, 7869; (d) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477; (e) Miller, J. S. *Adv. Mater*. **1993**, *5*, 671; (f) Bloor, D. *Chem. Br*. **1995**, *31*, 385; (g) Jestin, I.; Frère, P.; Blanchard, P.; Roncali, J. *Angew. Chem*. **1998**, *110*, 990; *Angew. Chem., Int. Ed*. **1998**, *37*, 942 and references cited therein. See also the Nobel lectures of Heeger, A. J.; MacDiarmid, A. G.; Shirakawa, H. In *Angew. Chem./Angew. Chem., Int. Ed*. **2001**, *40*, 2575.
2. (a) Moriuchi, T.; Bandoh, S.; Miyaishi, M.; Hirao, T. *Eur. J. Inorg. Chem*. **2001**, 651; (b) Moriuchi, T.; Miyaishi, M.; Hirao, T. *Angew. Chem., Int. Ed*. **2001**, *40*, 3042; (c) Moriuchi, T.; Kamikawa, M.; Bandoh, S.; Hirao, T. *Chem. Commun*. **2002**, 1476; (d) Hirao, T. *Coord. Chem. Rev*. **2002**, *226*, 81; (e) Moriuchi, T.; Shen, X.; Saito, K.; Bandoh, S.; Hirao, T. *Bull. Chem. Soc. Jpn*. **2003**, *76*, 595.
3. For reviews on this subject, see: (a) Balzani, V.; Juris, A.; Venturi, M. *Chem. Rev*. **1996**, *96*, 759; (b) De Cola, L.; Belser, P. *Coord. Chem. Rev*. **1998**, *177*, 301; (c) Belser, P.; Bernhard, S.; Blum, C.; Beyeler, A.; De Cola, L.; Balzani, V. *Coord. Chem. Rev*. **1999**, *190–192*, 155; (d) Brigelletti, F.; Flamigni, L. *Chem. Soc. Rev*. **2000**, *29*, 1.
4. (a) Auburn, P. R.; Lever, A. B. P. *Inorg. Chem*. **1990**, *29*, 2551; (b) Hartl, F.; Snoeck, T. L.; Stufkens, D. J.; Lever, A. B. P. *Inorg. Chem*. **1995**, *34*, 3887; (c) Keyes, T. E.; Forster, R. J.; Jayaweera, P. M.; Coates, C. G.; McGarvey, J. J.; Vos, J. G. *Inorg. Chem*. **1998**, *37*, 5925; (d) Staffilani, M.; Belser, P.; De Cola, L.; Hartl, F. *Eur. J. Inorg. Chem*. **2002**, 335.
5. Hirao, T.; Iida, K. *Chem. Commun*. **2001**, 431.
6. Hunan, G. S.; Schubert, U. S.; Volkmer, D.; Riviere, E.; Lehn, J.-M.; Kyritssakas, N.; Fischer, J. *Can. J. Chem*. **1997**, *75*, 169.
7. 5-Bromo-2,2′-bipyridine was isolated from unreacted materials and organotin by-products by acidification of the reaction mixture and subsequent extraction with CH_2Cl_2. 2-Tributylstannylpyridine, 2,5-dibromopyridine, and tributyltin chloride were extracted into the organic phase, but 5-bromo-2,2′-bipyridine and another by-product, terpyridine (tpy), still remained in the aqueous layer. Addition of $NiCl_2{\cdot}6H_2O$ to the aqueous phase neutralized by 28% ammonia solution, followed by

extraction with CH_2Cl_2 led to the complete separation of 5-bromo-2,2′-bipyridine from tpy. Finally, the product, 5-bromo-2,2′-bipyridine, was purified as a white solid by further sublimation.

8. Sadighi, J. P.; Singer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 4960.
9. (a) **1**: mp 219–220°C (uncorrected). IR (KBr): 3252, 3035, 1597, 1578, 1566, 1541, 1510, 1460, 1330 cm^{-1}. UV–vis (CH_2Cl_2:DMF = 10:1): λ_{max} (log ε) = 350 (4.51) nm. ^1H NMR (DMSO-d_6, 400 MHz): δ 8.58 (d, 2H, J = 4.4 Hz, A6), 8.53 (s, 2H, NH), 8.36 (d, 2H, J = 2.6 Hz, B6), 8.23 (d, 2H, J = 6.6 Hz, A3), 8.22 (d, 2H, J = 8.8 Hz, B3), 7.84 (dd, 2H, J = 6.6, 6.6 Hz, A4), 7.49 (dd, 2H, J = 8.8, 2.6 Hz, B4), 7.30 (dd, 2H, J = 6.6, 4.4 Hz, A5), 7.18 (s, 4H, C1). ^{13}C NMR (DMSO-d_6, 100 MHz): 155.8 (A2), 149.1 (A6), 145.5 (B3), 141.7 (B6), 137.1 (B2), 137.0 (A3), 135.9 (C2), 122.7 (A5), 121.1 (B5), 120.8 (B4), 120.5 (C1), 119.2 (A3) ppm. MS (FAB): m/z = 417 (M^++1). Anal. calcd for $C_{26}H_{20}N_6$: C, 74.98; H, 4.84; N, 20.18. Found: C, 74.90; H, 4.79; N, 20.17; (b) $\mathbf{2_{red}}$: mp 252–253°C (decomp). IR (KBr): 3396, 1598, 1512, 1466, 1446, 1324 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 452 (3.47) nm. ^1H NMR (CD_3CN, 400 MHz): δ 8.50–8.47 (m, 6H, G3, F3, and E3), 8.42 (d, 2H, J = 8.4 Hz, D3), 8.24 (d, 2H, J = 7.3 Hz, A3), 8.22 (d, 2H, J = 9.0 Hz, B3), 8.10–8.01 (m, 6H, G4, F4, and E4), 7.94 (td, 2H, J = 7.9, 1.5 Hz, A4), 7.93 (td, 2H, J = 7.9, 1.5 Hz, D4), 7.87 (d, 2H, J = 5.8 Hz, G6), 7.77 (d, 2H, J = 5.8 Hz, F6), 7.71 (d, 2H, J = 5.1 Hz, E6), 7.68 (d, 2H, J = 5.1 Hz, D6), 7.58 (d, 2H, J = 4.8 Hz, A6), 7.48 (dd, 2H, J = 9.2, 2.6 Hz, B4), 7.46–7.41 (m, 4H, G5, and F5), 7.39–7.36 (m, 2H, E5), 7.31–7.27 (m, 2H, D5), 7.25–7.22 (m, 2H, A5), 7.19 (s, 2H, NH), 7.17 (d, 1H, J = 2.6 Hz, B6), 7.16 (d, 1H, J = 2.6 Hz, B′6), 6.87 (s, 2H, C1 or C3), 6.86 (s, 2H, C3 or C1). ^{13}C NMR (CD_3CN, 100 MHz): 158.4 (A2), 158.1 (D2), 158.0 (E2), 158.0 (G2), 157.9 (F2), 152.7 (E6), 152.7 (F6), 152.6 (D6), 152.5 (G6), 152.0 (A6), 147.2 (B2), 145.6 (B5), 138.7 (G4), 138.7 (E4), 138.7 (F4), 138.5 (A4), 138.5 (D4), 138.1 (B6), 138.0 (B′6), 136.3 (C2), 128.6 (F5), 128.6 (G5), 128.5 (E5), 128.4 (D5), 126.5 (A5), 125.9 (B3), 125.2 (F3), 125.2 (E3), 125.2 (G3), 125.0 (D3), 123.5 (C1 or C3), 123.4 (C3 or C1), 123.0 (A3), 121.8 (B4), 121.8 (B′4) ppm. MS (FAB): m/z = 1678 ($M-PF_6$)$^+$. Anal. calcd for $C_{66}H_{52}N_{14}Ru_2(PF_6)_4 \cdot 0.5H_2O$: C, 43.27; H, 2.92; N, 10.70. Found: C, 42.91; H, 2.91; N, 10.35. $\mathbf{2_{ox}}$: mp 257–258°C (decomp). IR (KBr): 1603, 1585, 1464, 1446, 1314 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 446 (4.65) nm. ^1H NMR (CD_3CN, 400 MHz, *syn* and *anti*-isomers): δ 8.51–8.43 (m, 24H, A3, B3, D3, E3, F3, and G3), 8.09–8.03 (m, 16H, D4, E4, F4, and G4), 7.98 (td, 4H, J = 7.7, 1.5 Hz, A4), 7.88 (d, 4H, J = 5.2 Hz, py6), 7.76 (d, 4H, J = 5.5 Hz, py6), 7.71–7.69 (m, 12H, A6 and py6), 7.54 (dd, 2H, J = 8.4, 1.8 Hz, $B4_{anti}$), 7.47–7.32 (m, 22H, A5, $B4_{syn}$, and py5), 7.27 (d, 2H, J = 1.8 Hz, $B6_{syn}$), 7.21 (d, 2H, J = 1.8 Hz, $B6_{anti}$), 6.98 (d, 2H, J = 2.2 Hz, $phen_{syn}$), 6.89–6.86 (m, 2H, $phen_{anti}$), 6.61–6.57 (m, 4H, $phen_{anti}$ and $phen_{syn}$). ^{13}C NMR (CD_3CN, 100 MHz): 161.2 (C: phen), 158.0–157.9 (D2, E2, F2, and G2), 157.7 (A2), 154.4 ($B2_{anti}$), 154.3 ($B2_{syn}$), 152.8–152.7 (D6, E6, F6, and G6), 152.6 (A6), 149.6 (B5), 144.6 ($B6_{syn}$), 144.0 ($B6_{anti}$), 139.0–138.9 (A4, D4, E4, F4, G4, and $phen_{anti}$), 137.9 ($phen_{syn}$), 130.1 ($B4_{anti}$), 129.7 ($B4_{syn}$), 128.7–128.6 (D5, E5, F5, and G5), 128.1 (A5), 126.8 ($phen_{syn}$), 125.9 ($phen_{anti}$), 125.5 (B3), 125.3–125.2 (D3, E3, F3, and G3), 124.8 (A3) ppm. MS (FAB): m/z = 1676 ($M-PF_6$)$^+$. Anal. calcd for $C_{66}H_{50}N_{14}Ru_2(PF_6)_4 \cdot 3H_2O$: C, 42.27; H, 3.01; N, 10.46. Found: C, 42.12; H, 2.83; N, 10.29.
10. Hirao, T.; Saito, K. *Tetrahedron Lett.* **2000**, *41*, 1413.
11. (a) Yonemoto, E. H.; Riley, R. L.; Kim, Y. I.; Atherton, S. J.; Schmbehl, R. H.; Mallouk, T. E. *J. Am. Chem. Soc.* **1992**, *114*, 8081; (b) Goulle, V.; Harriman, A.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1034.