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A Fused Donor−Acceptor System Based on an Extended Tetrathiafulvalene and a Ruthenium Complex of Dipyridoquinoxaline

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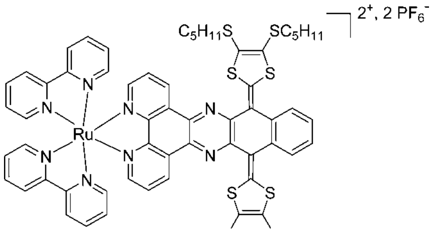
ABSTRACT



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An application of the Horner−Wadsworth−Emmons reaction carried out on a ruthenium compound as the electrophilic precursor is described for the synthesis of fused donor−acceptor system 1 based on an extended tetrathiafulvalene and a ruthenium complex of dipyridoquinoxaline units.

Ruthenium(II) complexes containing aromatic heterocyclic sp^2 nitrogen-donor chelating ligands have been widely studied in the past decades mainly because of their special photophysical, photochemical, and electrochemical properties.[1] Ruthenium polypyridyl complexes are involved in the development of photonic devices[2] and have proven to be the most efficient sensitizers for Grätzel dye-sensitized solar cells to date.[3] Such complexes are also of particular interest for the study of photoinduced energy and electron transfer processes occurring in donor−acceptor systems[4] that mimic structures involved in natural photosynthesis.[5] Another recent promising area of applications concerns biological developments, since ruthenium(II) complexes containing a dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) moiety present high affinity for DNA[6] and can inhibit gene transcription, offering promising properties for the design of DNA markers and agents in photochemotherapy.[7] The association of a ruthenium(II) polypyridyl complex acting as electron acceptor with an electron donor has been less investigated. For

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(1) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277. (b) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759–833. (c) Campagna, S.; Puntoriero, F.; Nastasi, F.; Bergamini, G.; Balzani, V. *Top. Curr. Chem.* **2007**, *280*, 117–214.

(2) Belser, P.; Bernhard, S.; Blum, C.; Beyeler, A.; De Cola, L.; Balzani, V. *Coord. Chem. Rev.* **1999**, *190−192*, 155–169.

(3) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737–740. (b) Grätzel, *Nature* **2001**, *414*, 338–344. (c) Grätzel, M. *Inorg. Chem.* **2005**, *44*, 6841–6851.

(4) De Cola, L.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301–346.

(5) (a) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163–170. (b) Sun, L.; Hammarström, L.; Åkermark, B.; Styring, S. *Chem. Soc. Rev.* **2001**, *30*, 36–49.

(6) (a) Friedman, A. E.; Chambron, J.-C.; Sauvage, J.-P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960–4962. (b) Ortmans, I.; Moucheron, C.; Kirsch-De Mesmaeker, A. *Coord. Chem. Rev.* **1998**, *168*, 233–271. (c) Erkkila, K. E.; Odom, D. T.; Barton, J. K. *Chem. Rev.* **1999**, *99*, 2777–2795. (d) Peng, B.; Chen, X.; Du, K.-J.; Yu, B.-L.; Chao, H.; Ji, L.-N. *Spectrochim. Acta, Part A* **2009**, *174*, 896–901.

(7) Pauly, M.; Kayser, I.; Schmitz, M.; Dicato, M.; Del Guerzo, A.; Kolber, I.; Moucheron, C.; Kirsch-De Mesmaeker, A. *Chem. Commun.* **2002**, *108*, 6–1087.

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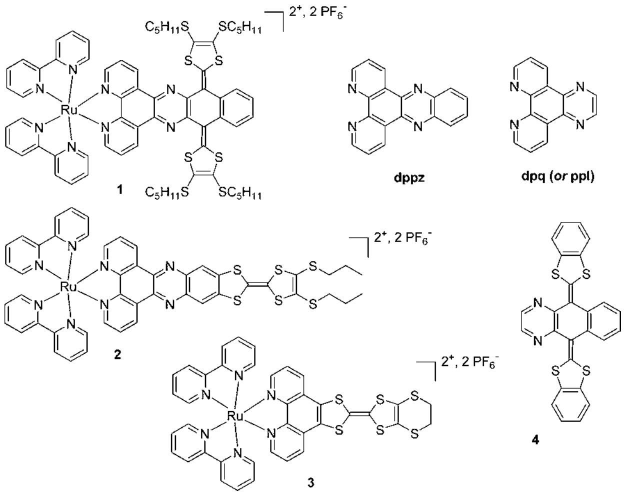
example, ruthenium(II) complexes of dipyrroloylquinoxaline phenanthroline[8] and ferrocene-imidazophenanthroline[9] have been developed as efficient anions chemosensors.

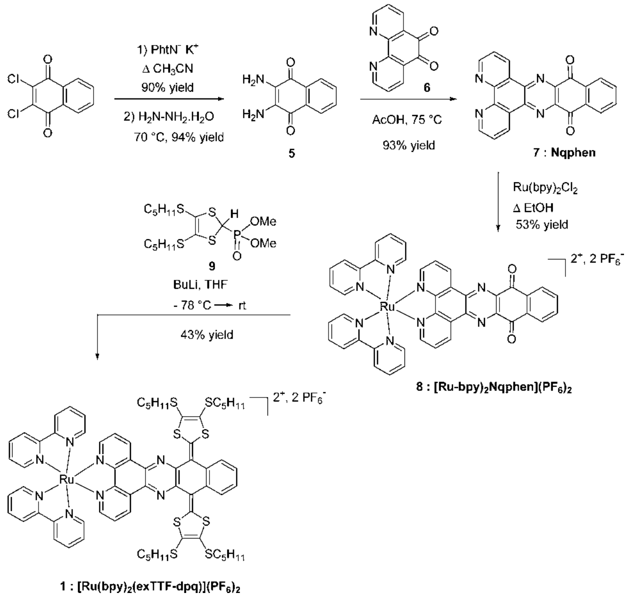
Owing to their unique π-donor properties, tetrathiafulvalene (TTF) and its derivatives have been associated with a large range of electron acceptor units in the search for specific intramolecular electronic interactions.[10] The use of a TTF molecule associating an aromatic heterocyclic sp^2 nitrogen-donor chelating ligand (pyridine, bipyridine, phenanthroline, etc.) has been extensively developed, but corresponding transition metal complexes are still rare.[11] With the aim of developing new systems showing long-lived charge-separated state and photoredox switches, ruthenium(II) complexes of TTF-dppz dyad **2** were synthesized by Liu and co-workers. One of the synthetic approaches involved the condensation of a diamino-functionalized TTF ligand with the phendione ruthenium bipyridyl complex to reach dyad **2** (Scheme 1).[12] Very recently, fused TTF−1,10-phenanthroline and related ruthenium(II) bipyridyl complex **3** were also reported.[13] Tetrathiafulvalenes with extended π-conjugation (exTTF) constitute a well-known class of electron donors.[14] It is well-established that the insertion of a quinodimethane structure into the TTF skeleton enhances the donor ability, since an aromatic ring is formed upon oxidation, thus stabilizing the cationic species. Consequently, *p*-quinodimethane analogues of TTF usually exhibit high π-donating ability, characterized by a one-stage two-electron oxidation process.[15] To our knowledge, an exTTF has never been associated to a heterocyclic sp^2 nitrogen-donor chelating ligand. On this ground, we report here the synthesis and characterizations of the ruthenium(II) complex [Ru(bpy)$_2$(exTTF-dpq)](PF$_6$)$_2$ (**1**) based on the redox-active exTTF and dipyrido[3,2-*f*:2′,3′-*h*]-quinoxaline (dpq) ligand.[16] Compound **4**, described by Yamashita et al. to reach organic field-effect transistors, can be considered as a unique example to date combining an exTTF and a quinoxaline moiety.[17]

Scheme 1. Structures of Complex **1** and Some Related Complexes



First we developed an efficient synthesis of the ligand Nqphen **7**.[18] This key building block was previously prepared in five steps and in an overall 30% yield from 2,3-dichloronaphthoquinone.[19] We performed the synthesis of this ligand in three steps in an overall 79% yield (Scheme 2). Compound **5** was prepared in 85% yield according to a two-step procedure from commercially available 2,3-dichloronaphtoquinone.[20] On the other hand, Phendione **6** was

Scheme 2. Synthesis of the Complex [Ru(bpy)$_2$(exTTF-dpq)](PF$_6$)$_2$ **1**



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[8] Mizuno, T.; Wei, W.-H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1134–1135.

[9] Zapata, F.; Caballero, A.; Espinosa, A.; Tárraga, A.; Molina, P. *J. Org. Chem.* **2008**, *73*, 4034–4044.

[10] (a) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372–1409. (b) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891–4945. (c) Canevet, D.; Sallé, M.; Zhang, G.; Zhang, D.; Zhu, D. *Chem. Commun.* **2009**, 2245–2269.

[11] Lorcy, D.; Bellec, N.; Fourmigué, M.; Avarvari, N. *Coord. Chem. Rev.* **2009**, *253*, 1398–1438.

[12] Goze, C.; Leiggener, C.; Liu, S.-X.; Sanguinet, L.; Levillain, E.; Hauser, A.; Decurtins, S. *ChemPhysChem* **2007**, *8*, 1504–1512.

[13] Keniley, L. K.; Ray, L.; Kovnir, K.; Dellinger, L. A.; Hoyt, J. M.; Shatruk, M. *Inorg. Chem.* **2010**, *49*, 1307–1309.

[14] (a) *TTF Chemistry. Fundamentals and Applications of Tetrathiafulvalene*; Yamada, J., Sugimoto, T., Eds.; Springer Verlag: New Yorker, 2004. (b) Gorgues, A.; Hudhomme, P.; Sallé, M. *Chem. Rev.* **2004**, *104*, 5151–5184. (c) Martín, N.; Sánchez, L.; Herranz, M. A.; Illescas, B.; Guldi, D. M. *Acc. Chem. Res.* **2007**, *40*, 1015–1024. (d) Wenger, S.; Bouit, P.-A.; Chen, Q.; Teuscher, J.; Di Censo, D.; Humphry-Baker, R.; Moser, J.-E.; Delgado, J. L.; Martín, N.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2010**, *132*, 5164–5169.

[15] (a) Yamashita, Y.; Kobayashi, Y.; Miyashi, T. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1052–1053. (b) Bryce, M. R.; Moore, A. J.; Hasan, M.; Ashwell, G. J.; Fraser, A. T.; Clegg, W.; Hursthouse, M. B.; Karaulov, A. I. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1450–1452. (c) Martín, N.; Sánchez, L.; Seoane, C.; Ortí, E.; Viruela, P. M.; Viruela, R. *J. Org. Chem.* **1998**, *63*, 1268–1279.

[16] Dipyrido[3,2-*f*:2′,3′-*h*]-quinoxaline (dpq) is sometimes also referenced as pyrazino[2,3-*f*][1,10]-phenanthroline (ppl): Díaz, R.; Francois, A.; Leiva, A. M.; Loeb, B.; Norambuena, E.; Yaòez, M. *Helv. Chim. Acta* **2006**, *89*, 1220–1230.

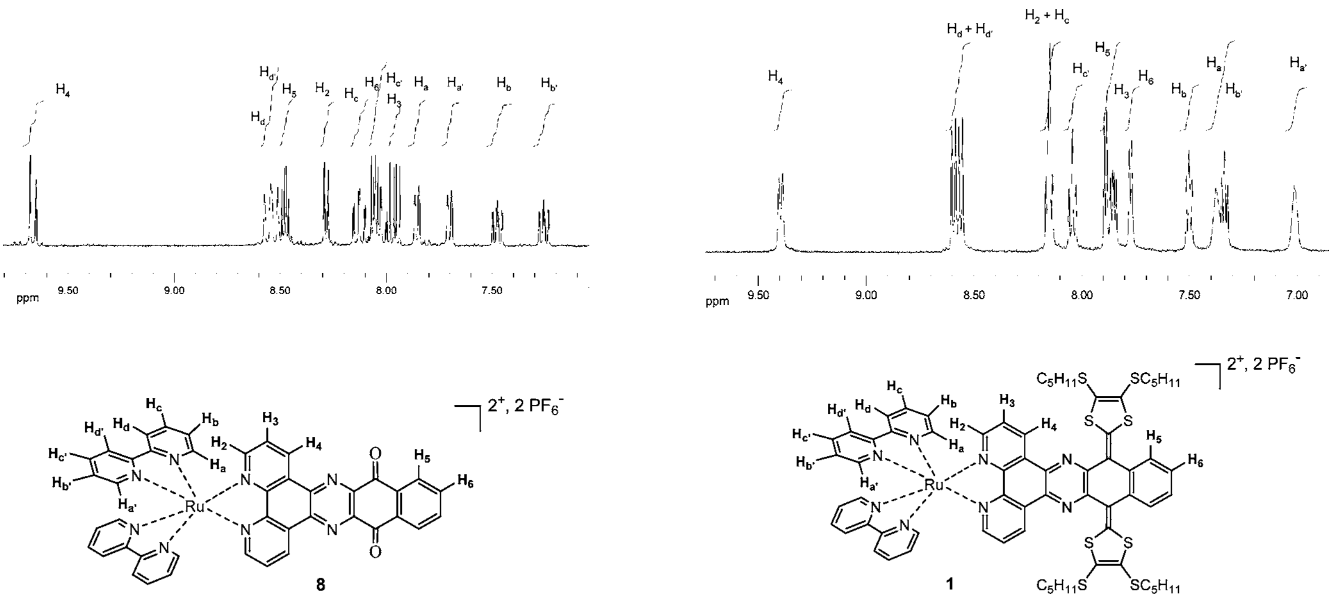

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Figure 1. Aromatic region of the ^{1}H NMR spectra in CD_3CN of ruthenium(II) bipyridyl complexes **1** and **8**.

synthesized according to reported procedure.[21] Nqphen ligand **7** was isolated in 93% yield as a pale greenish powder from condensation of compounds **5** and **6** in glacial acetic acid. It should be noted that complexes (Nqphen)Re(CO)$_3$Cl and (Nqphen)Re(CO)$_3$(OTf) were previously reported in the literature.[19] The ruthenium(II) complex **8** was prepared by reaction of Nqphen **7** with Ru(bpy)$_2$Cl$_2$[22] in refluxing ethanol. Treatment with an aqueous solution of NH_4PF_6 was followed by purification by flash chromatography on deactivated alumina using acetonitrile as the eluent. [Ru(bpy)$_2$Nqphen](PF$_6$)$_2$ **8** was isolated as an ochre powder in 53% yield. The key point of this synthesis corresponds to the Horner−Wadsworth−Emmons (HWE) reaction, which was remarkably carried out on ruthenium compound **8** as the electrophilic precursor. Complex **8** was soluble in acetonitrile, but this solvent was incompatible with HWE reaction conditions using butyllithium. Consequently complex **8** was added as a solid to a large excess of the phosphonate anion generated at −78 °C in tetrahydrofuran from compound **9**.[23] The reaction mixture was allowed to warm to room temperature, and the color of the solution changed from pale yellow to bordeaux around −15 °C. The purification was achieved by chromatography on deactivated alumina. After elution using dichloromethane to remove tetrakis-pentylsulfanylTTF issued from decomposition of phosphonate anion,[24] complex **1** was eluted using dichloromethane/methanol (95/5). Complex **1** was isolated after precipitation as a bordeaux powder in 43% yield.

Assignments of proton signals in the aromatic region were determined for complex **8** by examining $^{1}H-^{1}H$ COSY experiments in CD_3CN (Figure 1). The spectrum shows eight signals identifiable with four protons for each bipyridyl ligand defined as H_a, H_b, H_c, and H_d ($H_{a'}$, $H_{b'}$, $H_{c'}$ and $H_{d'}$, respectively) for the two pyridine moieties. These protons show characteristic chemical shifts with H_d, $H_{d'} > H_c$, $H_{c'} > H_a$, $H_{a'} > H_b$, $H_{b'}$ in agreement with previous observations on ruthenium(II) bipyridyl complex of phenanthroline derivative.[25] By comparison with the spectrum of compound **8**, the ^{1}H NMR spectrum of complex **1** shows an important shielding of protons H_a and $H_{a'}$ (from 7.70 and 7.85 to 7.01 and 7.38 ppm, respectively) associated with the presence of larger and less defined signals, which could result from the interaction between the exTTF donor and the Ru(bpy)$_2$-dpq acceptor. The chemical shift of proton H_4 of the dpq moiety is also significantly upfield-shifted (from 9.66 to 9.39 ppm for complexes **8** and **1**, respectively) as a result of the establishment of intramolecular 1,5-sulfur−nitrogen interactions between the 1,3-dithiole and the pyrazine ring, as already described in the case of compound **4**.[26] The ^{19}F spectrum of complex **1** exhibits

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(17) (a) Yamashita, Y.; Suzuki, T.; Miyashi, T. *Chem. Lett.* **1989**, 1607–1610. (b) Morioka, Y.; Nishida, J.; Fujiwara, E.; Tada, H.; Yamashita, Y. *Chem. Lett.* **2004**, *33*, 1632–1633.

(18) Ligand Nqphen = dipyrido[3,2-*a*:2′,3′-*c*]-benzo[3,4]-phenazine-11,16-quinone.

(19) Díaz, R.; Reyes, O.; Francois, A.; Leiva, A. M.; Loeb, B. *Tetrahedron Lett.* **2001**, *42*, 6463–6467.

(20) Anzenbacher, Jr., P.; Palacios, M. A.; Jursíková, K.; Marquez, M. *Org. Lett.* **2005**, *7*, 5027–5030.

(21) Frey, J.; Kraus, T.; Heitz, V.; Sauvage, J.-P. *Chem.*—*Eur. J.* **2007**, *13*, 7584–7594.

(22) Ru(bpy)$_2$Cl$_2$ was prepared according to literature: Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334–3341.

(23) Hudhomme, P.; Sallé, M.; Gautier, N.; Belyasmine, A.; Gorgues, A. *Arkivoc* **2006**, *4*, 49–72.

(24) Such decomposition of the phosphonate functionality was previously noted to reach stilbene derivatives :Bergmann, E. D.; Solomonovici, A. *Synthesis* **1970**, 183–189.

(25) (a) Ye, B.-H.; Ji, L.-N.; Xue, F.; Mak, T. C. W. *Transition Met. Chem.* **1999**, *24*, 8–12. (b) Chesneau, B.; Passelande, A.; Hudhomme, P. *Org. Lett.* **2009**, *11*, 649–652.

(26) Yamashita, Y.; Tanaka, S.; Imaeda, K.; Inokuchi, H.; Sano, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1132–1133.

characteristic peaks at −72.7 and −74.2 ppm for both PF_6^- anions. MALDI-TOF results are in agreement with the structure of complex **1** with a molecular ion peak at m/z = 1648 presenting an isotopic distribution in agreement with the calculated pattern.

The redox potentials of donor−acceptor system **1** were determined by cyclic voltammetry measurements (Figure 2).

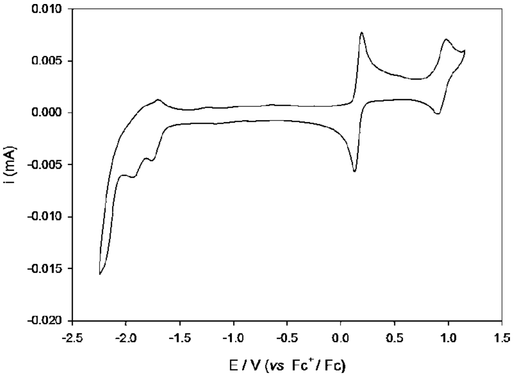

Figure 2. Cyclic voltammogram of complex **1** recorded in a CH_2Cl_2/CH_3CN (9:1) solution (5×10^{-4} M) using Bu_4NPF_6 0.1 M as supporting electrolyte, Pt wires as counter and working electrodes, $Ag/AgNO_3$ as reference electrode, 100 mV/s.

Complex **1** showed the presence of two oxidation waves. The first one ($E_{1/2}^{ox1}$ = +0.16 V vs Fc^+/Fc) corresponds to the reversible two-electron process associated with the formation of the dication $exTTF^{2+}$. This value is in full agreement with that previously observed for compound **4**[17] and p-quinodimethane analogues of TTF.[15]

Moreover, this oxidation potential can be compared with the two reversible oxidation peaks of compound **2** ($E_{1/2}^{ox1}$ = +0.29 V and $E_{1/2}^{ox2}$ = +0.61 V vs Fc^+/Fc, CH_2Cl_2/CH_3CN 5:1) characteristic of the cation radical $TTF^{+\bullet}$ and dication TTF^{2+} species, respectively, thus confirming the higher π-donating ability of exTTF over TTF analogues.

The following reversible one-electron process observed in the cyclic voltammogram of compound **1** corresponds to the $Ru^{II/III}$ redox couple at $E_{1/2}^{ox2}$ = +0.94 V. At negative potentials, two irreversible reduction waves are observed at E_{pc}^{red1} = −1.76 V and E_{pc}^{red2} = −1.94 V, which are assigned to the reduction of the dpq and bpy units, respectively.[12]

The absorption spectra of complexes **1** and **8** were recorded in dichloromethane (Figure 3). Both complexes present an absorption band in the region around 450 nm that can be assigned to a metal to ligand charge transfer (MLCT) transition.[27] By comparison with the spectrum of complex **8**, the broad band centered around 600 nm could be attributed to the intraligand charge-transfer (ILCT) transition with the exTTF acting as the donor and the dpq subunit as the acceptor, in good agreement with a similar band observed for dyad **2**.[12] A detailed investigation of the photophysical properties is in progress.

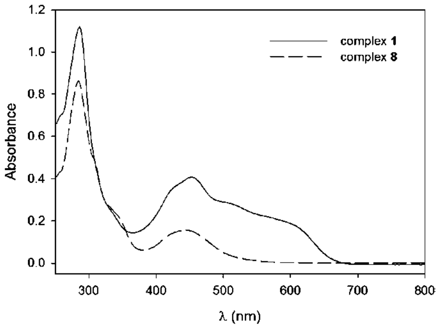

Figure 3. UV−vis spectra of complexes **1** and **8** in CH_2Cl_2 (10^{-5} M).

In conclusion, we report a straightforward and versatile method to prepare a new donor−acceptor dyad incorporating a π-extended TTF and ruthenium(II) bipyridyl complex of dipyridoquinoxaline ligand. This approach appears very promising for the synthesis of different dyads as functionalities can be introduced on the exTTF unit in the last synthetic step.

Acknowledgment. This work was supported by the French National Research Agency in the frame of the program ANR PNANO entitled TTF-based Nanomat.

Supporting Information Available: Synthetic methods and characterizations, supplementary spectroscopic data, and cyclic voltammetric results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) (a) Chambron, J.-C.; Sauvage, J.-P.; Amouyal, E.; Koffi, P. *Nouv. J. Chim.* **1985**, *9*, 527–529. (b) Rillema, D. P.; Blanton, C. B.; Shaver, R. J.; Jackman, D. C.; Boldaji, M.; Bundy, S.; Wor1, L. A.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 1600–1606. (c) Shan, B. Z.; Zhao, Q.; Goswami, N.; Eichhorn, D. M.; Rillema, D. P. *Coord. Chem. Rev.* **2001**, *211*, 117–144.