on the use of the Group 8 metals (the metals of the iron, cobalt, and nickel triads), in which the metal ions are d^6 or d^8. We are interested in incorporating metal–metal quadruple bonds with a $\sigma^2\pi^4\delta^2$ configuration into organic conjugated polymers because the dinuclear center is redox-active and its ease of oxidation can be tuned over a considerable range by the selection of the metal (M = Cr, Mo, W) and the ancillary ligands,[5] even to the point that the M_2 center is more easily oxidized than cesium.[6] The M_2 center may also be brought into conjugation with the π system of the organic polymer through the agency of a carboxylate link.[7] The carboxylate π system couples with both the π system of the polymer backbone and the M_2 δ orbitals. We recently illustrated this by the preparation of some discrete model complexes of the type $[M_2(O_2CR)_4]$, in which R = mono-, bi-, and terthienyl (α,α′) groups.[8]

Herein, we describe our synthesis of oligomeric/polymeric thienyl-based materials incorporating metal–metal quadruple bonds. The general reaction is shown in Equation (1),

$$[M_2(O_2CR)_4] + HOOC\text{-}(Thp)_n\text{-}COOH \xrightarrow[\text{toluene}]{22\,^\circ C}$$
$$[M_2(O_2CR)_2(O_2\text{-}C(Thp)_n\text{-}CO_2)]_m + 2\,RCOOH \qquad (1)$$

although, as noted below, there are important restrictions (Thp = thiophene = $2,5\text{-}C_4H_2S$). Full experimental details are given in the Supporting Information.

To prepare soluble oligomers/polymers of the desired empirical formula, we found it necessary to introduce chain-branching alkyl substituents on both the spectator carboxylate and the thienyl dicarboxylate. Thus far, we have enjoyed most success with 2,4,6-triisopropylbenzoate (2,4,6-iPr$_3$C$_6$H$_2$CO$_2$ = TiPB) as the ancillary ligand. This group has the added advantage that the *trans*-disubstituted product appears to be the preferred thermodynamic product. This is also evident from the preparations of the discrete compounds for molybdenum [Eq. (2)] and for tungsten [Eq. (3)]. For

$$[Mo_2(TiPB)_4] + 2\,HOOC\text{-}(Thp)_n\text{-}R \xrightarrow[\text{toluene}]{22\,^\circ C}$$
$$\textit{trans-}[Mo_2(TiPB)_2(O_2C\text{-}(Thp)_n\text{-}R)_2] + 2\,TiPB\text{-}H \qquad (2)$$

$$[W_2(TiPB)_2(tBuCO_2)_2] + 2\,HOOC\text{-}(Thp)_n\text{-}R \xrightarrow[\text{toluene}]{22\,^\circ C}$$
$$\textit{trans-}[W_2(TiPB)_2(O_2C\text{-}(Thp)_n\text{-}R)_2] + 2\,tBuCOOH \qquad (3)$$

molybdenum, we used the corresponding homoleptic carboxylate $[Mo_2(TiPB)_4]$[9] and for tungsten, the mixed compound $[W_2(TiPB)_2(tBuCO_2)_2]$ as starting materials. Even with the use of only 1 equivalent of the thienyl carboxylic acid, the bis,bis-substituted product $[M_2(TiPB)_{4-x}(O_2C\text{-}(Thp)_n\text{-}R)_x]$ (Thp = $2,4\text{-}C_4H_2S$; $n = 1,2$: R = H; $n = 3$: R = Me) is formed in preference to other combinations.

Only one isomer is observed in solution for these M_2 complexes and, as is shown in Figure 1, steric factors favor the *trans* substitution about the M_2 paddle-wheel core. The twisting of the phenyl rings out of the plane of their attendant carboxylate groups removes $M_2(\delta)$-to-$C_6(\pi)$ conjugation. In the UV/Vis spectrum, the $M_2(\delta)$-to-(aryl carboxylate) transition is very weak in comparison with the $M_2(\delta)$-to-(thienyl carboxylate) transition. As is shown in Figure 2, the $M_2(\delta)$-to-thienyl(π*) transition moves to lower energy as *n* increases
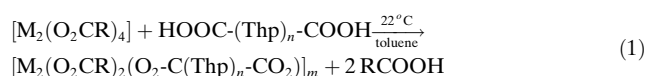
Oligothiophenes Incorporating Metal–Metal Quadruple Bonds**

Malcolm H. Chisholm,* Arthur J. Epstein,*
Judith C. Gallucci, Florian Feil, and Wesley Pirkle

There is considerable interest at this time in inorganic–organic hybrid materials, and metal-containing polymers constitute an important section within this general field. The work of Manners and co-workers[1] with metallocene-derived polymers, Friend, Raithby, and co-workers[2] with metallated polyynes and poly(phenylenvinylene)s, Wolf and co-workers[3] with metallated polythiophenes, and Thompson, Forrest, and co-workers[4] with iridium and platinum complex doped conjugated polymers, represent four prime areas of recent research interest. The majority of efforts thus far have focused
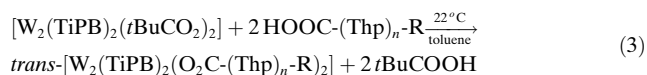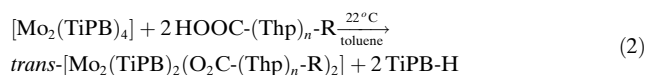
[*] Prof. Dr. M. H. Chisholm, J. C. Gallucci, Dr. F. Feil
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210 (USA)
Fax: (+1) 614-292-0368
E-mail: chisholm@chemistry.ohio-state.edu

Prof. Dr. A. J. Epstein, W. Pirkle
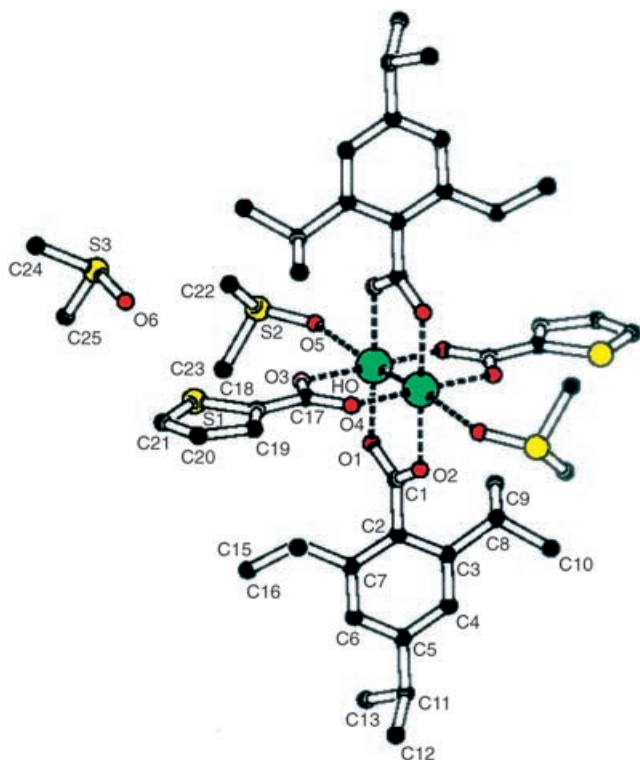Department of Physics, The Ohio State University
Columbus, OH 43210 (USA)

Figure 1. Molecular structure of the centrosymmetric [Mo$_2$(TiPB)$_2$(O$_2$C-Thp-H)$_2$] molecule found in the solid state with two axially coordinating DMSO molecules and one noncoordinating DMSO molecule. The Mo—Mo, Mo—O(TiPB carboxylate), and Mo—O(thiophene carboxylate) interatomic distances are 2.113, 2.111 (av), and 2.110 Å (av), respectively. The dihedral angle between the thienyl ring and its carboxylate group is 0.35° (av).

from 1 to 2 to 3 and is markedly red-shifted and more intense on going from M = Mo to W. The latter is a result of the higher orbital energy of the W$_2$ d electrons and the greater degree of W$_2$(δ)-to-thienyl(π*) overlap.

In reactions of Equation (1), we employed the *n*-hexyl-substituted thienyl dicarboxylic acids (DHTT)H$_2$ (3′,4′-dihexyl-2,2′:5′,2″-terthiophene-5,5″-dicarboxylic acid)[10] and (DHQT)H$_2$ (3″,4″-dihexyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinque-thiophene-5,5⁗-dicarboxylic acid)[11] shown below. Furthermore, an excess of [Mo$_2$(TiPB)$_4$] or [W$_2$(TiPB)$_4$] was used to ensure the total conversion of the dicarboxylic acids. The polymeric materials [M$_2$(TiPB)$_2$(O$_2$C-(Thp)$_n$-CO$_2$)] are formed as flocculent precipitates that are difficult to filter. They are best isolated by centrifugation followed by repeated washings, first with toluene and then hexanes, to remove the

(DHTT)H$_2$

(DHQT)H$_2$
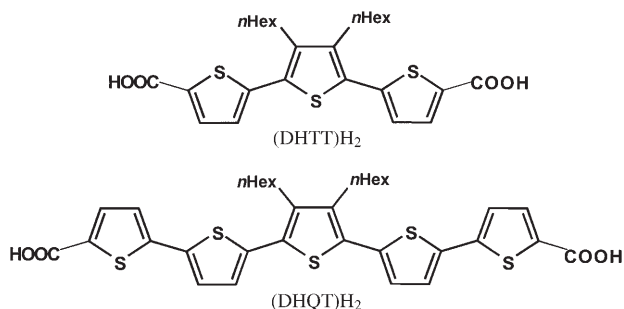
acid TiPB-H and any unreacted monomeric M$_2$ tetracarboxylates. The resulting dried red (M = Mo) or bluish-green (M = W) powders are somewhat soluble in THF and swell to form gels by absorbing approximately 20 times their mass of THF. The ^{1}H NMR spectra of the samples in [D$_8$]THF only show evidence for one type of TiPB and O$_2$C-(Thp)$_n$-CO$_2$ groups. However, the MALDI MS data show molecular ions that correspond to [M$_2$(TiPB)$_2$(O$_2$C-(Thp)$_n$-CO$_2$)]$_2$$^+$ loops, [M$_2$-(TiPB)$_2$(O$_2$C-(Thp)$_n$-CO$_2$)]$_3$$^+$ triangles, and even higher oligomers. These can only arise from a *cis*-substitution pattern at the M$_2$$^{4+}$ center. We propose that this substitution pattern is less common than that of *trans* substitution, but that it is this property, together with some tersubstitution at the Mo$_2$$^{4+}$ center, that facilitates the gel-forming capability of the entangled chains. The system can be described as a dynamic equilibrium of chains, cycles, and cross-linked oligomers/polymers[12] as a result of facile carboxylate-exchange reactions, which are well-documented to be catalyzed by both acid and base (H$^+$, carboxylate).[13] A reasonable estimate of the molecular weight is over 10000 Daltons, or more than 10 repeating units.

The electronic absorption spectra of these oligomers closely resemble those of the model compounds (Figure 2) in that they have well-defined, although broad, absorptions assignable to M$_2$(δ)-to-thienyl(bridge)(π*) and thienyl(π)-to-thienyl(π*) (bridge-to-bridge) transitions. The emission spectra show only the thienyl(π*)-to-M$_2$(δ) transition, as shown in
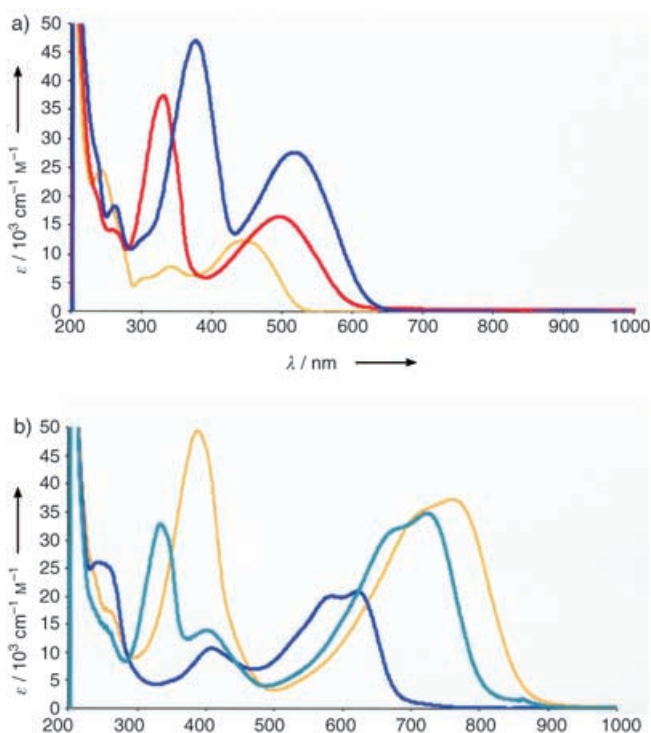

Figure 2. a) Electronic absorption spectra of [Mo$_2$(TiPB)$_2$(O$_2$C-(Thp)-H)$_2$] (yellow), [Mo$_2$(TiPB)$_2$(O$_2$C-(Thp)$_2$-H)$_2$] (red), and [Mo$_2$(TiPB)$_2$(O$_2$C-(Thp)$_3$-Me)$_2$] (blue) in THF at room temperature. b) Electronic absorption spectra of [W$_2$(TiPB)$_2$(O$_2$C-(Thp)-H)$_2$] (blue), [W$_2$(TiPB)$_2$(O$_2$C-(Thp)$_2$-H)$_2$] (green), and [W$_2$(TiPB)$_2$(O$_2$C-(Thp)$_3$-Me)$_2$] (yellow) in THF at room temperature.

Figure 3 for the terthienyl-bridged polymer. These photophysical properties can be described in terms of the Jablonski diagram shown in Figure 4.
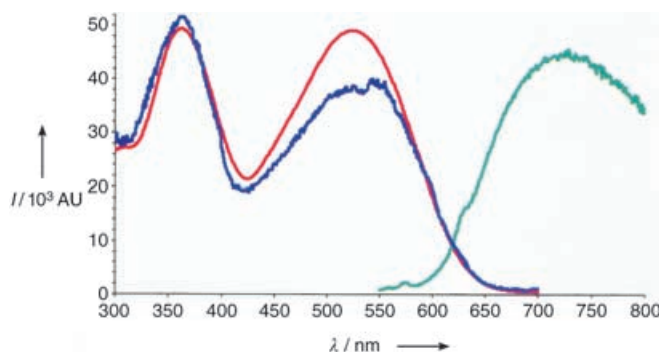

Figure 3. Absorption spectrum (red) of "$Mo_2(TiPB)_2(DHTT)$" in THF at room temperature, and photoluminescence spectrum (green) with excitation at 531 nm. Higher-energy excitation (360 nm) results in a similar spectral profile. The excitation spectrum is shown in blue.
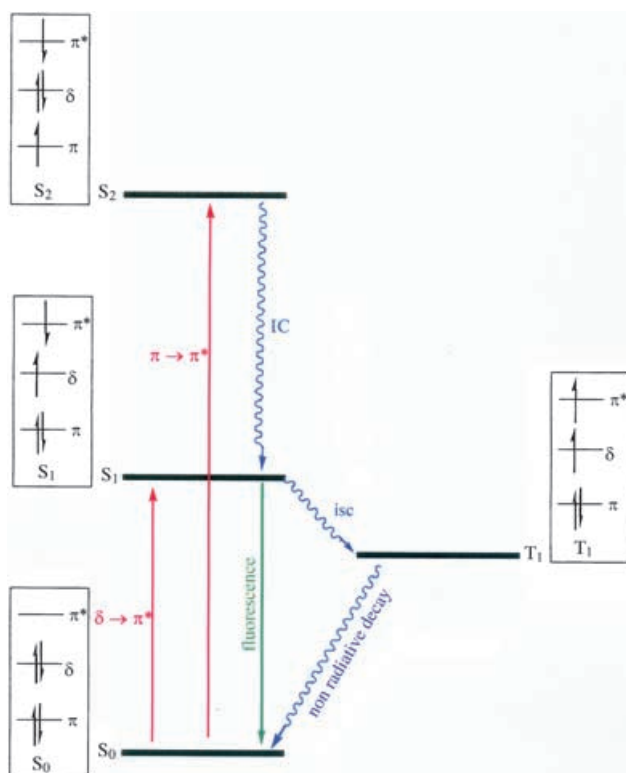

Figure 4. Proposed Jablonski scheme of the absorptions and emission of $[M_2(TiPB)_2(O_2C\text{-}(Thp)_n\text{-}CO_2)]$ oligomers. Absorptions to S_1 and S_2 are observed; emission occurs from S_1 while a nonemissive T_1 state is also observed. IC = internal conversion; ISC = intersystem crossing.

The gels dry to form thin films, and THF solutions can be used to deposit thin films of these metallated oligomers by spin-coating in a dry-box under argon. Deposition on an indium–tin oxide (ITO)-coated glass plate followed by vapor deposition of aluminum or calcium was carried out to make conductivity measurements. As shown in Figure 5, the thin
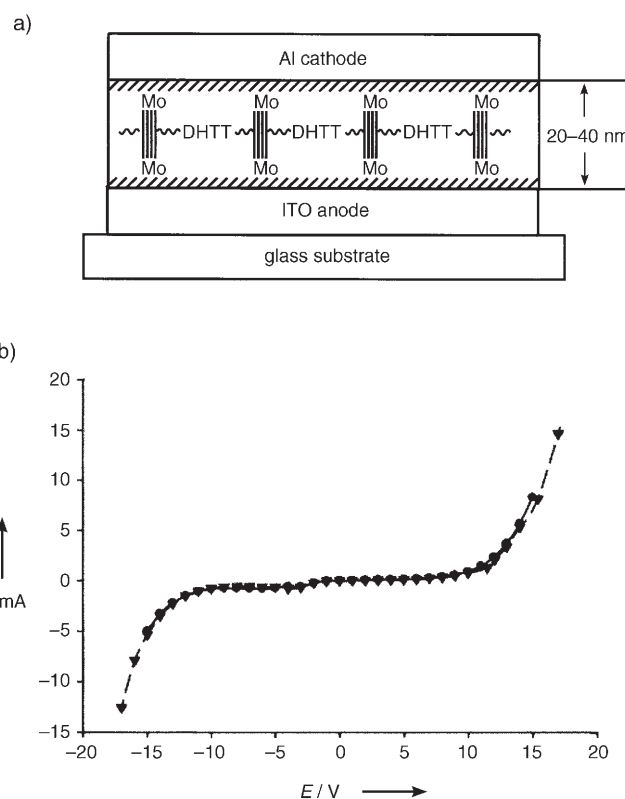
a)

b)

Figure 5. a) Structure of an Al-"$Mo_2(TiPB)_2(DHTT)$"-ITO device; b) current as a function of voltage for the same device (●: *IV* curve from 14 to −14 V; ▼: *IV* curve from 16 to −16 V).

films of the molybdenum terthienyl-bridged material display diode properties, with current being drawn nearly equally in both the forward and reverse bias, reminiscent of interface-controlled symmetrically configured ac-light-emitting (SCALE) devices.[14] Whereas the terthienylmolybdenum-containing films do not show electroluminescence with aluminum, the pentathienyl analogue (derived from $(DHQT)H_2$) does, and both the ter- and pentathienyl-derived thin films show electroluminescence when lower-work-function calcium was used as the cathode (Figure 6). The emission from these films is red-shifted relative to that of the parent
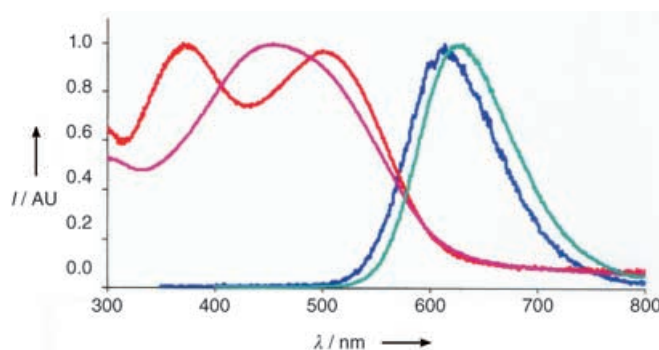

Figure 6. Absorption spectra of an "$Mo_2(TiPB)_2(DHTT)$" thin film (red) and an "$Mo_2(TiPB)_2(DHQT)$" thin film (purple), and electroemission of a Ca-"$Mo_2(TiPB)_2(DHTT)$"-ITO device (blue) and a Ca-"$Mo_2(TiPB)_2(DHQT)$"-ITO device (green).

acids $(DHTT)H_2$ and $(DHQT)H_2$.[15] Furthermore, the electroluminescence spectra display an unusual blue shift relative to the photoluminescence spectra, which suggests the important role of charge trapping in these materials.

In conclusion, we believe that the preliminary findings reported herein indicate that polythiophenes incorporating metal–metal quadruple bonds should have interesting and tunable electronic properties. The M_2 δ electrons lie within the band-gap of the polymer, but are strongly coupled by $M_2(\delta)$-to-$CO_2(\pi)$ conjugation. We anticipate that the electroluminescence for tungsten can be moved into the near-IR region. Further work in this area is in progress.

[1] a) C. Paquet, P. W. Cyr, E. Kumacheva, I. Manners, *Chem. Mater.* **2004**, *16*, 5205; b) I. Manners, *Synthetic Metal-Containing Polymers*, Wiley, New York, **2002**.

[2] a) M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, F. R. Al-Battashi, S. Al-Saadi, B. Ahrens, J. K. Bjernemose, M. F. Mahon, P. R. Raithby, M. Younus, N. Chawdhury, A. Koehler, E. A. Marseglia, E. Tedesco, N. Feeder, S. J. Teat, *Dalton Trans.* **2004**, *15*, 2377; b) M. S. Khan, M. R. A. Al-Mandhary, M. K. Al-Suti, T. C. Corcoran, Y. Al-Mahrooqi, J. P. Attfield, N. Feeder, W. I. F. David, K. Shankland, R. H. Friend, A. Koehler, E. A. Marseglia, E. Tedesco, C. C. Tang, P. R. Raithby, J. C. Collings, K. P. Roscoe, A. S. Batsanov, L. M. Stimson, T. B. Marder, *New J. Chem.* **2003**, *27*, 140.

[3] a) For organometallic and coordination clusters and polymers, see: C. Moorlag, O. Clot, Y. Zhu, M. O. Wolf, *Macromol. Symp.* **2004**, *209*, 133; b) C. Moorlag, O. Clot, M. O. Wolf, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **2004**, *45*, 437; c) T. L. Stott, M. O. Wolf, *Coord. Chem. Rev.* **2003**, *246*, 89.

[4] a) X. Wang, M. R. Andersson, M. E. Thompson, O. Inganas, *Thin Solid Films* **2004**, *468*, 226; b) C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, *Appl. Phys. Lett.* **2001**, *78*, 1622; c) M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 4.

[5] F. A. Cotton, R. A. Walton, *Multiple Bonds Between Metal Atoms*, 2nd ed., Oxford University Press, Oxford, UK, **1994**.

[6] F. A. Cotton, N. E. Gruhn, J. Gu, P. Huang, D. L. Lichtenberger, C. A. Murillo, L. D. Van Dorn, C. C. Wilkinson, *Science* **2002**, *298*, 1971.

[7] M. H. Chisholm, *Dalton Trans.* **2003**, 3941.

[8] M. J. Byrnes, M. H. Chisholm, R. J. H. Clark, J. C. Gallucci, C. M. Hadad, N. J. Patmore, *Inorg. Chem.* **2004**, *43*, 6334.

[9] F. A. Cotton, L. M. Daniels, E. A. Hillard, C. A. Murillo, *Inorg. Chem.* **2001**, *40*, 1639.

[10] M. Belletete, L. Mazerolle, N. Desrosiers, M. Leclerc, G. Durocher, *Macromolecules* **1995**, *28*, 8587.

[11] A. Donat-Bouillud, L. Mazerolle, P. Gagnon, L. Goldenberg, M. C. Petty, M. Leclerc, *Chem. Mater.* **1997**, *9*, 2815.

[12] a) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938; *Angew. Chem. Int. Ed.* **2002**, *41*, 898; Erratum: S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 1528; *Angew. Chem. Int. Ed.* **2002**, *41*, 1460; b) R. E. Furlan, S. Otto, J. K. M. Sanders, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 4801.

[13] M. H. Chisholm, A. M. Macintosh, *J. Chem. Soc. Dalton Trans.* **1999**, 1205.

[14] Y. Z. Wang, D. D. Gebler, L. B. Lin, J. W. Blatchford, S. W. Jessen, H. L. Wang, A. J. Epstein, *Appl. Phys. Lett.* **1996**, *68*, 894.

[15] N. DiCesare, M. Belletete, A. Donat-Bouillud, M. Leclerc, G. Durocher, *J. Lumin.* **1999**, *81*, 111.