Luminescent Unidimensional Organometallic Materials. Structural and Emission Properties of the $\{[Ag(dmb)_2](Y)\}_n$ Polymers (dmb = 1,8-Diisocyano-*p*-menthane; Y = PF_6, BF_4, NO_3)

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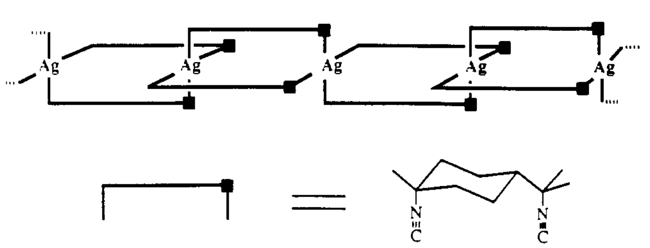
Received March 27, 1992

Macroscopic structural molecular designs for materials useful in microelectronics, nonlinear optics, and other applications have become a current topic of research.[2] The preparation of such materials could be synthetically demanding in some instances, in particular when orientations and distances are critical. In this work we report the preparation and the solid-state properties of unprecedented Ag unidimensional (1-D) polymeric organometallic materials $\{[Ag(dmb)_2](Y)\}_n$[3] (dmb[3] = 1,8-diisocyano-*p*-menthane; Y = PF_6, BF_4, NO_3), which exhibit an appropriate structural backbone for the formation of "molecular wire".[4]

The air- and light-stable $\{[Ag(dmb)_2](Y)\}_n$ compounds (Y = PF_6, BF_4, NO_3) are colorless and insulating polymeric materials.[5] Suitable single crystals (needle shape) for X-ray diffraction studies were obtained for $\{[Ag(dmb)_2](PF_6)\}_n$.[6] The solid-state structure (Figure 1) consists of a 1-D polymer of $Ag(dmb)_2^+$ units where all Ag(I) atoms are tetrahedrally coordinated and doubly bridged with each of the two adjacent Ag neighbors by dmb ligands. Interestingly, the dmb ligands, which adopt the syn configuration, are all unidirectionally oriented head-to-tail (see below). This behavior is unique, since the dmb ligand generally tends to bind to polynuclear complexes in a statistical fashion,[7] and could be associated with intermolecular dmb–dmb steric interactions.



The Ag···Ag distance is 4.964 (1) Å and is comparable to the Ir···Ir separation observed for the encapsulated Ag complex $Ir_2Ag(dmb)_4^{3+}$ (r(Ir···Ir) = 5.284 (2) Å).[7] At this distance, no Ag···Ag interaction is expected in the polymers. The Ag atoms form a zigzag chain (∠Ag···Ag···Ag = 139.15 (4) Å). The poor crystal quality induced large errors on the bond distances and angles (structural data are available in the supplementary material).

The X-ray powder diffraction studies (298 K)[8a] confirm the isostructural nature of the polymers for Y = PF_6 and BF_4.[8b] On the other hand, the polymer with Y = NO_3 is not isostructural with the other two polymers,[8c] presumably due to the nonglobular shape of the NO_3^- anion and the capability of NO_3^- to act as a ligand, inducing stronger Ag^+···Y^- interactions.

The $\{[Ag(dmb)_2](PF_6)\}_n$ polymer in 77 K ethanol solutions exhibits a blue emission (λ_{max} = 385 nm) when irradiated with UV light (λ < 240 nm).[9] The emission lifetime (τ_e) is 1.10 ± 0.02 μs and is much shorter than that measured for the binuclear system $[Ag_2(dmpm)_2](PF_6)_2$ (dmpm = bis(dimethylphosphino)methane) under the same experimental conditions (τ_e = 49.3 ± 0.9 μs),[10] indicated that efficient intramolecular quenching occurs within the polymeric material. This quenching may arise from the presence of the four coordinated isocyanide ligands, but intramolecular energy transfer along the Ag_n zigzag is also possible.[11]

In conclusion, the Ag···Ag separation (~5.0 Å) in these materials is sufficiently large to conceive the possibility of

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(2) (a) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3606. (b) Abrahams, B. F.; Hoskins, B. F.; Liu, J.; Robson, R. *J. Am. Chem. Soc.* **1991**, *113*, 3045. (c) Li, D.; Ratner, M. A.; Marks, T. J.; Zhang, C. H.; Yang, J.; Wong, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7389.

(3) (a) dmb was synthesized according to the procedure reported by: Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530. (b) Details for the preparation and the characterization of the $\{[Ag(dmb)_2](Y)\}_n$ polymers (Y = PF_6, BF_4, NO_3) are provided in the supplementary material.

(4) See for example: Dagami, R. *Chem. Eng. News* **1991**, *69* (May 27), 24.

(5) (a) The polymers are insoluble in nonpolar and weakly polar solvents and water. Saturated solutions are obtained at 60–100 mg/L in polar solvents such as acetone, ethers, and alkyl alcohols. The polymers are, however, soluble in acetonitrile. (b) The solids have resistivities greater than 10^7 Ω.

(6) Crystallographic data acquisition for $\{[Ag(dmb)_2](PF_6)\}_n$: A colorless needle-shaped fibrouslike crystal (0.08 × 0.08 × 0.20 mm) was obtained from slow evaporation of acetonitrile solutions and was mounted on an Enraf-Nonius CAD-4 diffractometer, nearly parallel to the ϕ axis. Diffraction data were collected using graphite-monochromated, Mo Kα radiation (λ = 0.710 73 Å) and the $\omega/2\theta$ scan method at a constant scan rate of 2.7° min^{-1} at 183 K. Crystal data: M = 633.41, orthorhombic, a = 9.303 (3) Å, b = 14.1058 (14) Å, and c = 22.2654 (15) Å, V = 2921.8 (10) $Å^3$, space group $P2_12_12_1$, Z = 4, D_{calc} = 1.440 g cm^{-3}, μ(Mo Kα) = 7.92 cm^{-1}. The lattice parameters were refined from 24 reflections in the range $30° < 2\theta < 40°$; two standard reflections were remeasured every 60 min. A total of 2857 unique reflections were measured, of which 1686 were considered observed with $I_{net} \geq (2.5\sigma)I_{net}$. A spherical absorption correction was applied with minimum and maximum transmission factors of 0.912 and 0.913, respectively. The C, N, and H atoms were refined isotropically whereas Ag, P, and F were refined anisotropically. The hydrogens were all calculated but not refined. The octahedral PF_6 group was refined using a rigid geometry with P–F fixed at 1.58 Å. The final residuals at convergence were R = 0.079 and R_w = 0.068, and GoF = 1.71 ($R = \sum(F_o - F_c)/\sum F_o$, $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, and GoF = $[\sum w(F_o - F_c)^2/(\text{no. of reflns} - \text{no. of params})]^{1/2}$). The maximum- and minimum-density peaks in the final difference Fourier map were 1.09 and −1.09 e $Å^{-3}$, respectively, located in the vicinity of the Ag atom. The structure was solved by direct methods and refined using the NRCVAX system. Weights based on counting statistics were used. Scattering factors were taken from the *International Tables for X-ray Crystallography*. The poor quality of the crystal, which appeared to be fibrous, prevented better refinement, presumably suggesting that the crystal could have been a polysynthetic twin.

(7) Sykes, A.; Mann, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 8252 and references therein.

(8) (a) Details of the X-ray powder diffraction analysis are provided in the supplementary material. (b) The 298 K X-ray powder diffraction analysis for the $[Ag(dmb)_2](Y)$ polymers (Y = PF_6, BF_4) shows that both materials are orthorhombic with a = 9.3, b = 14.1, and c = 22.3 Å for Y = PF_6 (agreement factor is 1.5%) and a = 9.63, b = 13.57, and c = 22.23 Å for Y = BF_4 (agreement factor is 4.0%). (c) Assuming that the a axis (containing the Ag chain) is the same for Y = NO_3 as for Y = PF_6 and BF_4, that the polymers also crystallize as cylinders, packing side by side as in $[Ag(dmb)_2](PF_6)$, and that the packing would be tighter for Y = NO_3, being smaller and planar, then the computed lattice parameters for this polymer would be a = 13.0 Å, b = 9.5 Å, c = 20.5 Å, and β = 95.6° in a monoclinic structure with an agreement factor of 1.6% to the indexation and with 2_1 symmetry according to a unique b axis. This is one possible interpretation of the results; other solutions exist.

(9) (a) The electronic absorption spectrum exhibits a broad band located at 204 nm. This band is assigned to a Ag(I)-localized d → p transition. (b) Perreault, D.; Drouin, M.; Michel, A.; Harvey, P. D. *Inorg. Chem.* **1991**, *30*, 2. (c) The emission spectra for $[Ag(dmb)_2](Y)$ (Y = BF_4, NO_3) have not been investigated.

(10) Harvey, P. D. Unpublished results.

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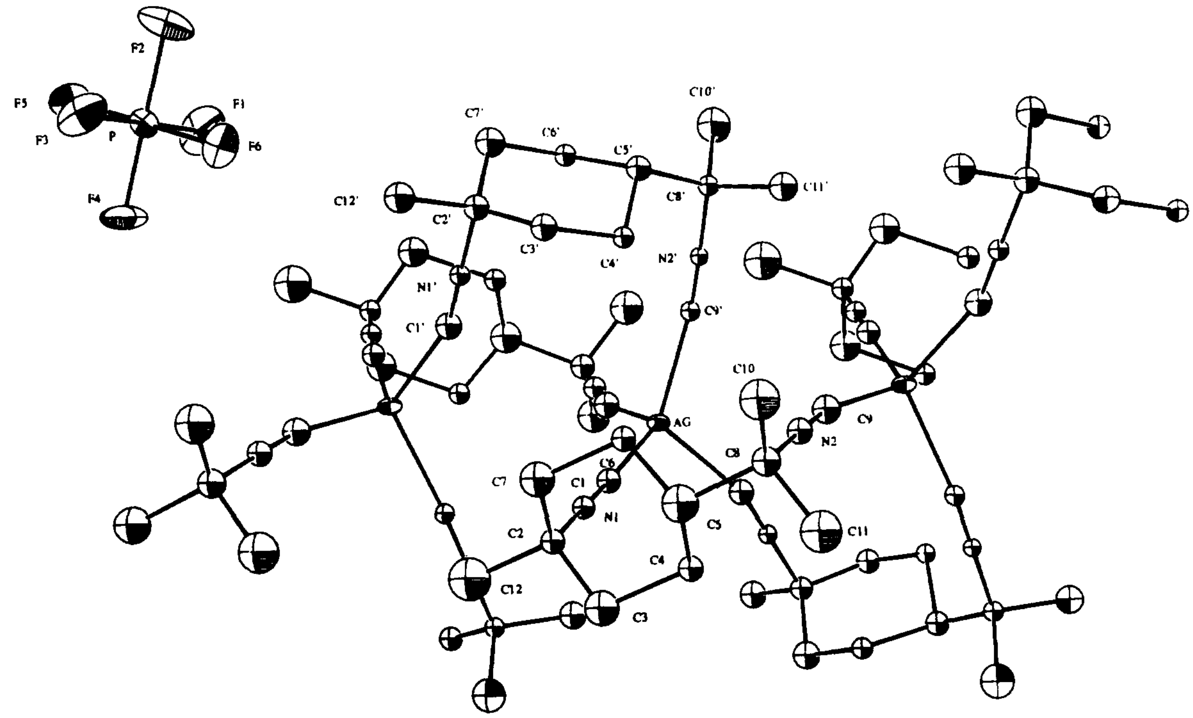

Figure 1. ORTEP drawing of a fragment of the polymer showing 20% probability thermal ellipsoids and the atomic numbering. For clarity, the hydrogen atoms have been omitted and only one PF_6 anion is shown.

encapsulating small monoatomic anions or cations and, hence, of generating chains with relatively close contacts. Partial oxidation of the Ag atoms should then enhance the conductivity of the materials. Work in this area is in progress.

Acknowledgment. We thank the NSERC and FCAR for financial support. D.P. acknowledges the Université de Sherbrooke for a graduate fellowship.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anisotropic thermal parameters, and data collection parameters for $\{[Ag(dmb)_2](PF_6)\}_n$, tables for X-ray powder diffraction, and a textual presentation of the preparation and characterization of the polymers (11 pages). Ordering information is given on any current masthead page.

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(11) 1-D materials generally exhibit energy transfer unidirectionally along the chain. See for example: Knochenmuss, R.; Güdel, H. V. In *Organic and Inorganic Low-Dimensional Crystalline Materials*; Delhaes, P., Drillon, M., Eds.; No. 168, NATO ASI Series B: Physics; Plenum Press: New York, 1987; p 445.