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Photoluminescent supramolecular networks from metal-mediated assembly of polythia conjugated dieneyne

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Received (in Columbia, MO, USA) 2nd January 2003, Accepted 13th March 2003
First published as an Advance Article on the web 31st March 2003

Polythia conjugated dieneyne 1,1,2,5,6,6-hexakis(phenylthio)-1,5-diene-3-yne and its one- and two-dimensional silver(I) coordination polymers, which exhibited fluorescence and redox properties, were prepared and investigated.

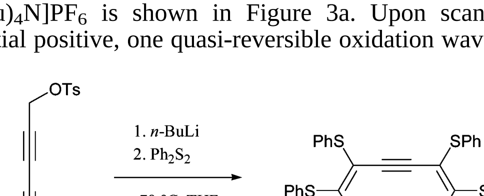
Luminescent polymers have received much attention due to their potential application in emissive devices.[1] Metal-directed assembly has been used to generate coordination polymers based on complexation of transition metals and multifunctional bridging ligands and is one of many useful strategies to design extended frameworks of various topology and dimensionality.[2,3] Ligands with π-conjugated backbones may affect the properties of the resulting polymers by promoting the couplings of metal atoms through delocalized π-electron systems.[4] It has been of interest to use photoactive ligands as building blocks to generate supramolecular polymers.[1,5] We are currently investigating sulfur-containing unsaturated compounds with conjugated π-systems due to their useful electrochemical properties.[6,7] Herein we report the syntheses, structures and electronic properties of a new class of polythia conjugated dieneyne and its silver(I) supramolecular networks.†

The synthesis of **1** was achieved by sequent treatment of 1,6-bis(*p*-toluenesulfonyloxy)-2,4-hexadiyne[8] in THF at −78 °C with 4 equiv. of *n*-BuLi followed by an excess of Ph_2S_2 (Scheme 1). The emission spectrum of **1** is shown in Fig. 1. A strong fluorescence band with $\lambda_{F,max}$ = 492 nm was seen.

The reaction of **1** with $AgCF_3SO_3$ in THF and **1** with $AgNO_3$ in THF/H_2O at rt yielded polymeric coordination complexes **2** and **3**, respectively. A red-shifted fluorescence band ($\lambda_{F,max}$ = 519 nm) relative to that of **1** was observed for polymer **2** (Fig. 2a). In contrast, compound **3** exhibited a slightly blue-shifted emission band at $\lambda_{F,max}$ = 481 nm (Fig. 2b).

The cyclic voltammogram of **1** in CH_2Cl_2 containing 0.1M $[(n\text{-Bu})_4N]PF_6$ is shown in Figure 3a. Upon scanning the potential positive, one quasi-reversible oxidation wave at half-wave potential of +1.00 V *vs.* Ag wire was observed, which is indicative of the formation of π-delocalized radical cations of **1**.[9]

The cyclic voltammogram of **2** in CH_3NO_2 containing 0.1 M $[(n\text{-Bu})_4N]PF_6$ is shown in Fig. 3b. Upon scanning in the positive direction, two oxidation waves were observed; one irreversible wave with a peak potential of 0.30 V *vs.* Ag wire and another reversible wave with a half-wave potential of 0.41 V *vs.* Ag wire. These oxidation potentials of polymeric complex **2** are lower than those ones of ligand **1**.



Scheme 1

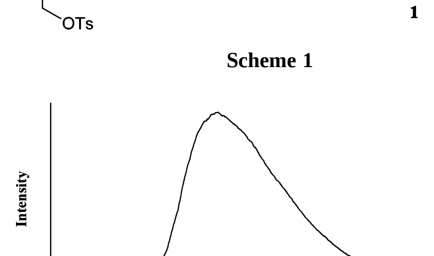


Fig. 1 Solid-state emission spectrum of **1** (λ_{ex} = 400 nm).

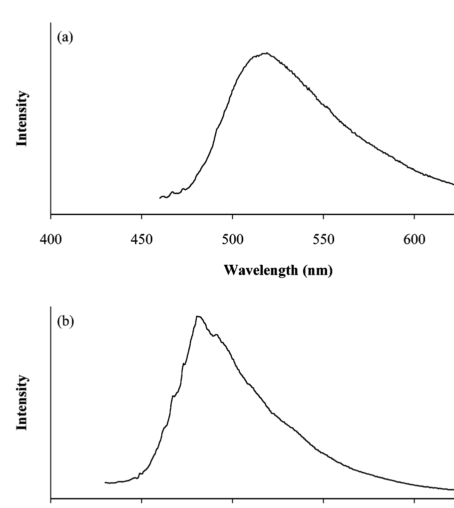


Fig. 2 Solid-state emission spectrum (λ_{ex} = 400 nm) of (a) **2** and (b) **3**.

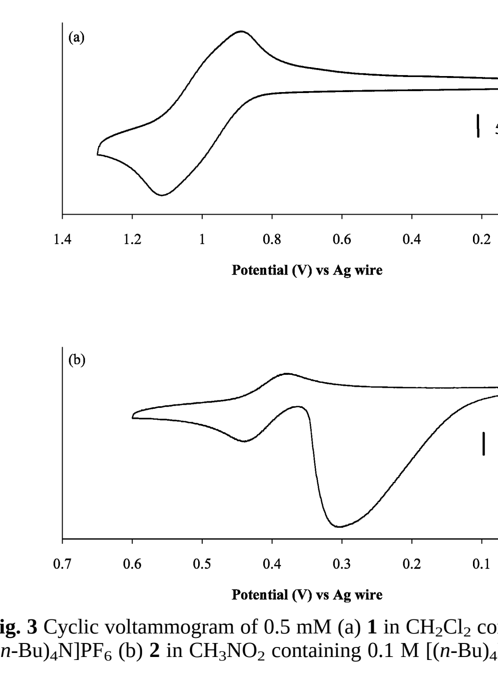
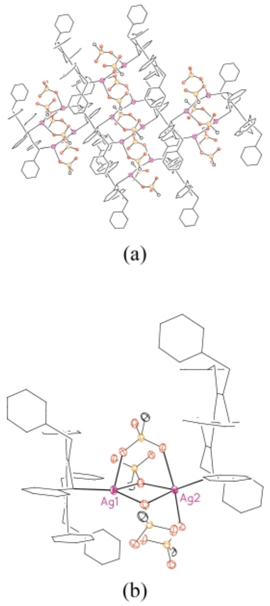


Fig. 3 Cyclic voltammogram of 0.5 mM (a) **1** in CH_2Cl_2 containing 0.1 M $[(n\text{-Bu})_4N]PF_6$ (b) **2** in CH_3NO_2 containing 0.1 M $[(n\text{-Bu})_4N]PF_6$.

DOI: 10.1039/b212789j

The crystal structure of **2** forms a two-dimensional coordination network with layers arranged perpendicular to **c**. Each layer is composed of alternating regions of **1** and $AgCF_3SO_3$ (Fig. 4a).

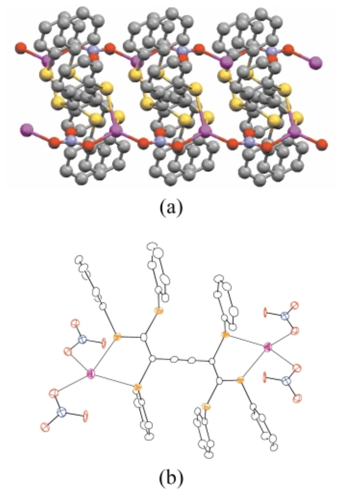
The asymmetric unit of **2** consists of two silver ions, two bridging trifluorosulfonate ligands and half of the thioether ligand **1**, which lies on a crystallographic inversion center at ½, 0, ½. The coordination about the two Ag ions is different. Ag1 is four coordinate while Ag2 is five coordinate (Fig. 4b). The coordination about Ag2 can be described as a distorted trigonal bipyramid. The Ag–O bond lengths range from 2.442(5) to 2.742(6) Å. The Ag2–S bond length is 2.555(2) Å. The tetravalent Ag1 ion has a coordination geometry approximating a trigonal based pyramid. For Ag1, the Ag–O bond lengths range from 2.317(6) to 2.515(5) Å with an Ag–S bond length of 2.452(2) Å. The coordination around Ag1 is essentially the same as that around Ag2 with one of the axial O atoms removed.



(a)

(b)

Fig. 4 (a) A drawing of a layer in **2** (b) a view of the coordination to Ag in **2** (fluorine atoms are omitted for clarity).


(a)

(b)

Fig. 5 (a) View of **3** down the *b*-axis showing the ladder-like structure (b) A view of the coordination to Ag in **3**.

The crystal structure of **3** was found to form a ladder-like one-dimensional polymeric chain extended along **a** (Fig. 5a). Molecules of **1** comprise the rungs of the ladder, while the sides are composed of Ag ions bridged by nitrate ions. As found in **2**, molecules of **1** also lie on crystallographic inversion centers. The silver ion is four-coordinate with distorted tetrahedral AgS_2O_2 coordination with Ag–O bond lengths of 2.397(2) and 2.404(2) Å and Ag–S bond lengths of 2.612(1) and 2.749(1) Å. In contrast to the mode of coordination in **2**, **1** binds to Ag in a bidentate fashion (Fig. 5b) in **3**. The architectures of two-dimensional **2** and one-dimensional **3** indicate that the anions of the silver(I) salts play an important role in the self-assembling process.

In summary, a new type of photofunctional polythioalkene with conjugated backbone has been synthesized and utilized as a building block to generate photoactive one- and two-dimensional supramolecular networks. These fluorescent compounds may have potential application to optoelectronic devices.

We thank the Welch Foundation for financial support of this research.

Notes and references

† Crystal data for **2**: triclinic, space group $P\bar{1}$ (no. 2), $a = 10.4742(3)$, $b = 10.6734(3)$, $c = 13.3298(4)$ Å, $\alpha = 77.106(2)$, $\beta = 77.047(2)$, $\gamma = 88.948(2)°$, $V = 1414.88(7)$ Å^3, $Z = 2$, $D_c = 2.059$ g cm^{-3}, μ(Mo–Kα) = 1.832 mm^{-1}, $T = 153(2)$ K, $\lambda = 0.71073$ Å, 9750 reflections collected, 6446 independent reflections ($R_{int} = 0.0608$), $R_1 = 0.0765$, $wR_2 = 0.1643$ [$I > 2\sigma(I)$].

Crystal data for **3**: $C_{42}H_{30}Ag_2N_2O_6S_6$, $M = 1066.78$, monoclinic, space group $P2_1/n$, $a = 5.6901(1)$, $b = 16.3738(3)$, $c = 21.0277(4)$ Å, $\beta = 93.418(1)°$, $V = 1955.64(6)$ Å^3, $Z = 2$, $D_c = 1.812$ g cm^{-3}, μ(Mo-Kα) = 1.375 mm^{-1}, $T = 153(2)$ K, $\lambda = 0.71073$ Å, 25019 reflections collected, 25019 reflections used in refinement, $R_1 = 0.0692$, $wR_2 = 0.1358$ [$I > 2\sigma(I)$]. The data were corrected for twinning using ROTAX.[10] The twin fraction refined to 0.070(1). CCDC 200585 and 200586. See http://www.rsc.org/suppdata/cc/b2/b212789j/ for crystallographic data in .cif or other electronic format.

1 R. Dobrawa and F. Würthner, *Chem. Commun.*, 2002, 1878; R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121; A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402; J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman and A. Stocking, *Science*, 1996, **273**, 884.

2 M.-C. Brandys and R. J. Puddephatt, *J. Am. Chem. Soc.*, 2002, **124**, 3946; G. D. Munno, M. Julve, F. Nicolo’, F. Lloret, J. Faus, R. Ruiz and E. Sinn, *Angew. Chem., Int. Ed.*, 1993, **32**, 613; B. F. Abrahams, B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1991, **113**, 3606; E. Bosch and C. L. Barnes, *Inorg. Chem.*, 2002, **41**, 2543.

3 M. Oh, G. B. Carpenter and D. A. Sweigart, *Angew. Chem., Int. Ed.*, 2001, **40**, 3191; J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239; S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853.

4 L. F. Szczepura, C. P. Galloway, Y. Zheng, P. Han, A. L. Rheingold, S. R. Wilson and T. B. Rauchfuss, *Angew. Chem. Int. Ed.*, 1995, **34**, 1890.

5 L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071.

6 J. C. Zhong, Y. Misaki, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga and H. Konaka, *Inorg. Chem.*, 2001, **40**, 7096; M. Adam and K. Müllen, *Adv. Mater.*, 1994, **6**, 439.

7 T. Jørgensen, T. K. Hansen and J. Becher, *Chem. Soc. Rev.*, 1994, **23**, 41; M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355.

8 Y. Rubin, S. S. Lin, C. B. Knobler, J. Anthony, A. M. Boldi and F. Diederich, *J. Am. Chem. Soc.*, 1991, **113**, 6943.

9 P. C. B. Page, *Top. Curr. Chem.*, 1999, **205**, 1; H. Tani, Y. Kawada, N. Azuma and N. Ono, *Tetrahedron Lett.*, 1994, **35**, 7051; T. Nabeshima, S. Iwata, N. Furukawa, K. Morihashi and O. Kikuchi, *Chem. Lett.*, 1988, 1325; T. Sugimoto, I. Sugimoto, A. Kawashima, Y. Yamamoto, Y. Misaki and Z.-i. Yoshida, *Heterocycles*, 1987, **25**, 83; D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garrett and N. D. Canfield, *J. Am. Chem. Soc.*, 1971, **93**, 2258.

10 R. I. Cooper, R. O. Gould, S. Parsons and D. J. Watkin, *J. Appl. Cryst.*, 2002, **35**, 168.