Preparation and Characterization of 4-[4-(Dimethylamino)styryl]-1-methylpyridinium Lead Triiodide and its Tribromide Analog

G. C. Papavassiliou, G. A. Mousdis,
and I. B. Koutselas

Theoretical and Physical Chemistry Institute,
National Hellenic Research Foundation,
48, Vassileos Constantinou Ave., Athens 116/35,
Greece

Reprint requests to Prof. G. C. Papavassiliou.
Fax: (301) 7273794

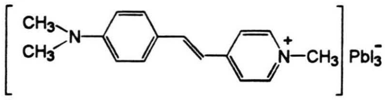
Z. Naturforsch. **56b,** 213–214 (2001);
received November 21, 2000

Organic-Inorganic Hybrids, Low-Dimensional Semiconductors, Optical Properties

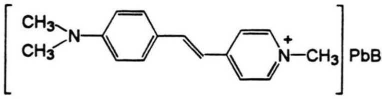
Using 4-[4-(dimethylamino)styryl]-1-methylpyridinium iodide, lead iodide, tetrabutylammonium bromide and lead bromide as starting materials, the title compounds were prepared and characterized analytically and spectroscopically.

Introduction

Organic-inorganic hybrid compounds based on alkyl ammonium, aryl-alkyl ammonium, the corresponding *iso*-thiuronium cations and metal halide anions have been prepared and investigated extensively (see [1–4] and refs therein). In this paper, the preparation and characterization of two organic-inorganic hybrid compounds based on a methyl-pyridinium cation and lead halide anions are reported. These are:



(1)



(2)

In these new compounds, both anion [1–3] and cation [5–8] are photoactive species.

Experimental

trans-4-[4-(Dimethylamino)styryl]-1-methylpyridinium iodide (DSMI) was prepared by the reaction of 4-dimethylamino-benzaldehyde with 1,4-dimethylpyridinium iodide in ethanol at reflux temperature overnight in the presence of piperidine as catalyst [5–6]. The bromide analog (DSMB) was obtained by treating DSMI with NaBr in acetonitrile followed by recrystallization from methanol.

Compound **1** was prepared as follows: A hot solution of DSMI (73.2 mg, 0.2 mmol) and Bu_4NI (300 mg) in CH_3CN (10 ml) was mixed with a hot solution of PbI_2 (92.2 mg, 0.2 mmol) and Bu_4NI (300 mg) in CH_3CN (10 ml). After slow cooling to room temperature a red microcrystalline precipitate was obtained filtered, washed with acetone and air dried; yield 106 mg (64%). Analysis for $C_{16}H_{19}N_2I_3Pb$ (827): calcd. C 23.22, H 2.30, N 3.38, I 46.07; found C 23.32, H 2.20, N 3.35, I 46.22.

Compound **2** was prepared as follows: A hot solution of DSMI (73.2 mg, 0.2 mmol) and Bu_4NBr (161 mg, 0.5 mmol) in CH_3CN (25 ml) was mixed with a hot solution of $PbBr_2$ (73.4 mg, 0.2 mmol) and Bu_4NBr (161 mg, 0.5 mmol) in CH_3CN (25 ml). After slow cooling to room temperature, a precipitate of small brown-golden elongated plates was obtained; it was filtered, washed with acetone and air dried; yield 91 mg (66%). Analysis for $C_{16}H_{19}N_2Br_3Pb$ (686): calcd. C 27.99, H 2.77, N 4.08, Br 34.98; found C 28.12, H 2.87, N 3.93, Br 35.02.

The crystals of the new compounds **1** and **2** were not good enough for X-ray crystal structure determination. Thin deposits of compounds on quartz plates were obtained by rubbing the compounds on the plates. The optical absorption (OA) and photoluminescence (PL) spectra were observed by instrumentation described in [4].

Optical Properties and Discussion

Fig. 1 shows the OA and PL spectra of **1** as well as the OA spectrum of DSMI for comparison. The OA spectrum of **1** exhibits an excitonic peak at 395 nm, due to the PbI_3 network. The stoichiometry of **1** and the position of the excitonic band indicate that the PbI_3 network is either an infinite twin chain of edge-sharing PbI_6 octahedra, as in the case of $[C_{10}H_7CH_2NH_3]PbI_3$ [4b,c], or an infinite chain of face-sharing PbI_6 octahedra, as in the case of $[C_5H_{12}N]PbI_3$ [3,9]. The OA spectrum of **1** exhibits a broad charge-transfer band around 486 nm, and the PL spectrum exhibits a band at 671 nm. The intensities and the shapes of the OA and PL bands do not show considerable differences in comparison to those of DSMI.

Fig. 2 shows the OA and PL spectra of **2** as well as the OA spectrum of DSMB for comparison.

0932–0776/2001/0200–0213 $06.00 © 2001 Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com N

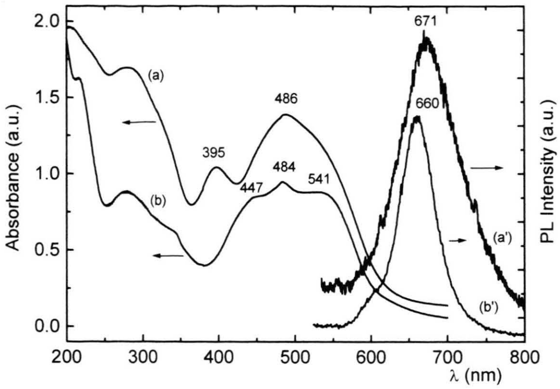


Fig. 1. OA (a, b) and PL (a′, b′) spectra of **1** (a, a′) and DSMI (b, b′). Excitation 450 nm.

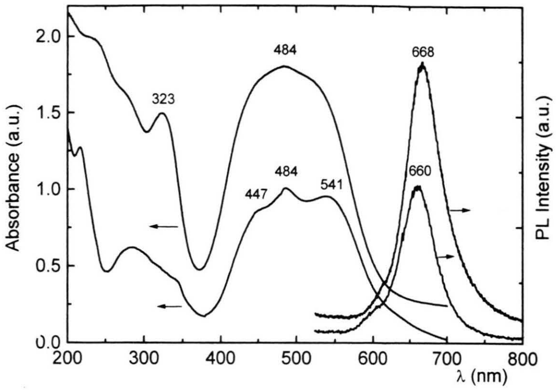


Fig. 2. Same as Fig. 1, but for **2** (a, a′) and DSMB (b, b′).

The spectra are similar to **1** and DSMI, respectively, except that the OA of **2** exhibits an excitonic band at 323 nm, due to the $PbBr_3$ network as in the case of $[C_5H_{12}N]PbBr_3$ [9,10].

In contrast to the PL spectra of $[C_{10}H_7CH_2NH_3]PbI_3$, $[C_{14}H_9CH_2SC(NH_2)_2]_2PbBr_4$ and similar compounds (see [4] and refs therein), the PL spectra of **1** and **2** do not indicate any energy transfer from the excitonic states of the inorganic component to the electronic state of the organic component.

In the region of 400 to 800 nm, the spectra of **1** and **2** are similar to those obtained from intercalated DSMI in mica [8] and MPS_3 (M = Mn, Cd, Zn) [6]. The intercalation compounds in $MnPS_3$ and $CdPS_3$ exhibit nonlinear optical properties [6]. Similar results are expected for **1** and **2**. Moreover, for **1** and **2** it is expected that the incorporation of semiconductor PbX_2 (X = I, Br) into the organic matrix (DSMX) will increase the conductivity. Details on the optical and related properties of **1** and **2** as well as the preparation and the properties of similar organic-inorganic hybrids based on stilbazolium and other chromophores (*e.g.*, those reported in [6]) and metal halides will be reported elsewhere.

---

[1] T. Ishihara, in T. Ogawa, Y. Kanemitsu (eds): Optical Properties of Low-Dimensional Materials, ch. 6, pp. 288–339, World Science, Singapore (1995).
[2] D. B. Mitzi, Progr. Inorg. Chem. **48**, 1 (1999).
[3] G. C. Papavassiliou, Progr. Solid State Chem. **25**, 125 (1997).
[4] a) G. C. Papavassiliou, G. A. Mousdis, I. B. Koutselas, Z. Naturforsch. **56b**, 57 (2001);
b) Adv. Mater. Opt. Electron. **9**, 265 (1999);
c) G. C. Papavassiliou, G. A. Mousdis, C. Raptopoulou, A. Terzis, Z. Naturforsch. **54b**, 1405 (1999).
[5] J. L. R. Wiliams, R. E. Adel, J. M. Carlson, G. A. Reynolds, D. G. Borden, J. A. Ford (Jr.), J. Org. Chem. **28**, 387 (1963).
[6] T. Coradin, R. Clement, P. G. Lacroix, K. Nakatami, Chem. Mater. **8**, 2153 (1996).
[7] D. Gonbeau, T. Coradin, R. Clement, J. Phys. Chem. **103**, 3545 (1999); Ch. F. Zhao, R. Grishi, U. Narang, G. Ruland, P. N. Prasad, J. Phys. Chem. **100**, 4526 (1996); G. Ruland, R. Grishi, P. N. Prasad, J. Am. Chem. Soc. **118**, 2985 (1996); H. Hachisako, T. Yamazaki, H. Ihara, C. Hirayama, K. Yamada, J. Chem. Soc., Perkin Trans. 2, 1681 (1994); Q. Song, C. E. Evans, P. W. Bohn, J. Phys. Chem. **97**, 13736 (1993); M. S. A. Abdel-Mottabel, A. M. Ksheriet, L. F. M. Ismaeiel, F. C. de Schryver, M. A. Vanderauweraer, J. Chem. Soc., Faraday Trans. 2, **85**, 1779 (1989).
[8] J. Kim, M. Lee, J.-H. Yang, J.-H. Choy, J. Phys. Chem. **104**, 1388 (2000).
[9] G. V. Gridunova, E. A. Ziger, V. M. Koshkin, S. V. Linderman, Yu. T. Struchkov, V. E. Shkolover, Phys. Chem. Doclady **278**, 826 (1984).
[10] J. Azuma, K. Tanaka, Int. I. Modern Phys. B, in press (2001).