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Photoproperties of the polymeric $\{[M(dmb)_2]Y\}_n$ materials: photoinduced intrachain energy and intermolecular electron transfers, and design of photovoltaic cells

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Contents

Abstract

This paper describes the structural and electronic spectroscopic properties of polymeric materials of the type $\{[M(dmb)_2]Y\}_n$ ($M = Cu$, Ag; dmb = 1,8-diisocyano-*p*-menthane; $Y = BF_4^-$, NO_3^-, PF_6^-, ClO_4^-). The replacement of Y by TCNQ (tetracyanoquinodimethane anion) leads to electrically insulating materials, which upon doping with neutral TCNQ become conducting. For $M = Cu$, the materials are also photoconducting where a photoinduced electron transfer from the excited CuL_4 center to the neutral TCNQ is demonstrated. Finally, photovoltaic cells have been designed. © 1998 Elsevier Science S.A.

Keywords: Silver; Copper; Polymer; Conducting; TCNQ

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1. Introduction

The bidentate ligand dmb (1,8-diisocyano-*p*-menthane) is capable of bridging transition metals to form bi- [1], tri- [2], tetra- [2,3] and polynuclear complexes [4]. Recently, our group reported the calorimetric and luminescence properties of a series of polymeric materials of the type $\{[M(dmb)_2]Y\}_n$ ($M = Cu$, Ag; $Y = PF_6^-$, BF_4^-, NO_3^-, ClO_4^-, $CH_3CO_2^-$) [5]. The materials exhibit a linear structure where a series of $M(dmb)_2^+$ units are linked together in a double bridging fashion. The M_2 separations are on the order of 5 Å, and the M_3 angle is 140°. The coordination around

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the metal is a distorted tetrahedron where different M–C distances are observed. In solution these materials retain their polymeric structures. By light scattering [5] (LS) and osmometric pressure [3] (OP) measurements, the polymers where M = Cu exhibit a molecular weight on the order of 160 000 (M_w; LS) or 140 000 (M_n; OP). The polymeric chains are on the order of 250 to 300 units long. For the Ag polymers, LS, OP, FT-IR, and spin-lattice ^{13}C NMR measurements indicate that the molecular weights are < 10 000, which indicates that the polymers dissociate in solutions but not completely [3,5]. By differential scanning calorimetry (DSC), the solid materials exhibit a second order phase transition attributable to a glass transition T_g between 35 and 90 °C [5].

2. Results and discussion

The materials are luminescent at 77 K both in the solid state and in solutions with λ_{max} ranging from 520 to 550 nm for M = Cu, and from ~450 to 510 nm for M = Ag [5]. The emission bands are very broad, expanding from 400 to 800 nm, and exhibiting very similar multi-exponential decays, again in both solid state and in solutions. The data compare favorably with that of the monomeric species $[M(CN\text{-}t\text{-}Bu)_4]BF_4$ (M = Cu, Ag), for which the kinetic traces are mono-exponentials, and λ_{emi} ~ 500 nm (M = Cu) and 435 nm (M = Ag, ethanol solutions). By using time-resolved emission spectroscopy, the spectra at short-, medium- and long-delay times have been acquired. Early on both the λ_{emi} and approximate lifetimes are very close to those of the mononuclear species. The relative intensity of the first component is dominant in most cases. At longer delay times, the measured spectra exhibited red-shifted bands. This phenomenon is similar to that of the exciton (energy transfer) well known in organic solids [6,7]. To support this, the polarization ratio (N) of the emission has been measured. In all cases, $N = 1$ indicating that the emission light is completely depolarized. Exciton and energy transfer phenomena depolarize the light. Since the behavior also occurs in very dilute solutions, this energy transfer phenomenon must occur along the polymeric chains.

The metathesis of the counteranions by the anion tetracyanoquino-*p*-dimethane ($TCNQ^-$) produces the dark purple and insulating materials $\{[M(dmb)_2]TCNQ\}_n$ (M = Cu, Ag). The materials are essentially isostructural to that described above based upon X-ray structure determination. However, conducting materials are prepared by dissolving the $\{[M(dmb)_2]TCNQ\}_n$ materials and neutral TCNQ in acetonitrile, and by evaporating the solutions to dryness. These new materials exhibit a quasi-black coloration, or on some occasions the materials have a greyish metallic appearance. Based upon X-ray powder diffraction and IR spectra, the metathesis of the counteranion does not alter the molecular weight of the polymeric materials (i.e. low molecular weight for M = Ag and ~130 000–190 000 for M = Cu). DSC measurements reveal that the materials are still thermoplastic with decreasing T_g. At higher levels of neutral TCNQ, this thermal behavior vanishes. Using the four-point probe, these solid mixtures exhibit conductivity in the semi-conducting range. As a function of TCNQ/TCNQ$^-$ ratio, minima are observed at ~2 where $R=80\ \Omega$ cm (M = Ag) and 1700 Ω cm (M = Cu).

X-ray powder diffraction pattern analysis has shown that the solids consist of a mixture of phases. Some of the phases have been identified as $\{M(dmb)TCNQ\}_n$ neutral TCNQ. A second phase has been isolated and identified as $\{[M(dmb)_2]TCNQ \cdot TCNQ\}_n$ using X-ray powder diffraction, chemical analysis, and ^{1}H NMR spectroscopy. For M = Ag, this second phase exhibits a resistivity of 43 Ω cm at room temperature (pellets), and the resistivity decreases to ~13 Ω cm as the temperature increases to ~75 °C.

While the Ag materials exhibit much better electrical properties than the Cu polymers, the latter are found to be photoconducting (while the Ag ones are not). The rise and the decay in electrical conductivity of pressed pellets during "on/off" experiments slowly expands over a period of 30 min (water cooling jacketed lamp). Typically a disk of 1 mm thickness × 1 cm diameter of a mixture containing $\{[Cu(dmb)_2]TCNQ\}+2TCNQ$ will exhibit an increase of current going from 19 to 23 μA upon broad band irradiation (HgXe medium pressure lamp, 200 W, placed at ~20 cm from the lamp). In order to elucidate the mechanism, a series of experiments has been performed and is now described. The $\{[Cu(dmb)_2]BF_4\}_n$ polymer which is insulating is put in the presence of neutral TCNQ (1:2 ratio) both in the solid state and in ethanol solutions. With time both materials turn blue in the presence of daylight or UV irradiation. The $\{[Ag(dmb)_2]BF_4\}_n$ analogue is inert under the same conditions. By monitoring the reaction by UV–visible spectroscopy, evidence for the formation of TCNQ$^-$ is readily obtained. Further, by monitoring the luminescence spectra and lifetime of the $\{[Cu(dmb)_2]BF_4\}_n$ polymer as a function of added neutral TCNQ, quenching of the emissive excited state of the polymer is observed. We come to the conclusion that the photoprocess is as follows:

$$\{Cu(dmb)_2\}_n^{n+} + h\nu \rightarrow {}^*\{Cu(dmb)_2\}_n^{n+} \quad (1)$$

$$^*\{Cu(dmb)_2\}_n^{n+} + TCNQ \rightarrow \{Cu(dmb)_2\}_n^{(n+1)+} + TCNQ^- \quad (2)$$

For all the TCNQ/TCNQ$^-$ ratios investigated, UV irradiation always increased the conductivity. Excited TCNQ* is not quenched by either $\{[M(dmb)_2]BF_4\}_n$ polymer (M = Cu or Ag).

Photovoltaic cells have been designed using glass supports on which the semiconducting and semi-transparent SnO is deposited at the surface. A thin film of $\{[Cu(dmb)_2]TCNQ\}_n$ TCNQ is subsequently deposited on top from the evaporation of an acetonitrile solution on a rotating stage. Finally, a thin film of Al is vapor deposited on top of the photoconducting film, and the photocurrent was measured between the Al and SnO interface. The photocurrent, as a function of the excitation wavelength and corrected for the lamp, exhibits a maximum at ~475 nm. This apparent maximum is caused in part by the absorption of the glass/SnO section. The photocurrents obtained are modest compared to recent literature data. Further work is in progress, and we propose to replace the neutral TCNQ, which acts as an electron acceptor, with C_{60}.

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