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A novel bithiazole oligomer containing C_{60} and its ferro-complexes: syntheses and magnetic properties

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Abstract

A novel bithiazole oligomer (PCBT) was synthesized from C_{60} and the diazo salt of 2,2′-diamino-4,4′-bithiazole (DABT). Its ferro-complex (PCBT-Fe^{2+}) was prepared from PCBT and $FeSO_4$ in DMSO solution under a purified nitrogen atmosphere. The magnetic behavior of PCBT and PCBT-Fe^{2+} was measured as a function of magnetic field strength (0–60 kOe) at 5 K and as a function of temperature (5–300 K) at a magnetic field strength of 30 kOe. PCBT-Fe^{2+} complex exhibits a hysteresis cycle at 5 K, the observed coercive field (H_C) and remnant magnetization (M_r) are 690 Oe and 0.12 emu/g, respectively. The results show that PCBT is an anti-ferromagnet and its Fe^{2+}-complex is a soft ferromagnet. © 2001 Published by Elsevier Science Ltd.

Keywords: Modified fullerene; Ferro-complex; Magnetic property

Today one of the greatest challenges in the field of magnetic materials research remains the design and preparation of organic ferromagnets [1–8]. Soon after the discovery by Krätschmer et al. [9] of an efficient synthesis route for C_{60}, an organic magnetic material (TDAE-C_{60}) with a Curie temperature of 16.1 K was reported [10]. This discovery sparked a series of investigations aiming to research for new organic magnetic materials based on fullerenes. Many investigations provided a good account of the magnetic properties of such materials [11–14].

In 1998, Hoffmann et al. [15] proposed that polymers built from sulfur, carbon and nitrogen-containing five-membered rings would theoretically display magnetic ordering, but none have yet been obtained. Recently, we reported the synthesis of bithiazole-containing polymeric ferro-complexes and their ferromagnetic properties for the first time [16–18]. Our interest in the bithiazole-based polymers, stems from their potential to bind transition-metal ions as well as the stability of corresponding metal-complexes. In this paper we describe the synthesis of a novel bithiazole oligomer incorporating C_{60} covalently into the main chain and its ferro-complex. Particular attention is paid to the investigation on the magnetic behavior of these materials.

As shown in Scheme 1 (The synthetic routes for PCBT and PCBT-Fe^{2+} complex), the preparation of oligomer (PCBT) was carried out according to the procedure analogous to that reported by Wudl et al. [19]. In our experiment the C_{60} toluene solution was added into a 5 M excess of the diazo salt of 2,2′-diamino-4,4′-bithiazole (DABT) solution at 0–5 °C. The reaction mixture was stirred for 24 h at 0–5 °C and then for 10 h at room temperature. The resulting black precipitate was filtered, then washed successively with water, methanol and ether, and last dried under vacuum at 60 °C for 24 h.[1] The PCBT-Fe^{2+} complex was prepared from PCBT and $FeSO_4$ in DMSO solution at 60 °C under a purified nitrogen atmosphere for two days.[2]

The PCBT and PCBT-Fe^{2+}complex thus obtained was examined by IR spectroscopy together with their precursors (Fig. 1). It can be seen that a typical band pattern appears in the region between 580 and 514 cm^{-1} for PCBT, which is similar to the other fullerene-containing polymer [20]. On the other hand, the splitting in this region is characteristic of a fullerene addition product, which is attributable to the lowering of symmetry. On the basis of the observation, it is possible to say that the parent C_{60} has been substituted with bithiazole units to a certain extent. In comparison with

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[1] The polymer was obtained in 50% yield and insoluble in common organic solvents. Elemental analysis for $[C_{60}(C_6H_2N_2S_2)_2]_n$: Calcd C 82.13%, H 0.38%, N 5.32%; Found C 80.42%, H 0.68%, N 4.98%.

[2] The complex was obtained in 90% yield and insoluble in common organic solvents. Elemental analysis for $[C_{60}(C_6H_2N_2S_2)_2\ (FeSO_4)_{0.8}]_n$: Calcd C 73.62%, H 0.34%, N 4.77%; Found C 71.59%, H 0.61%, N 4.28%, Fe 3.96% (determined by atomic absorption spectrum).

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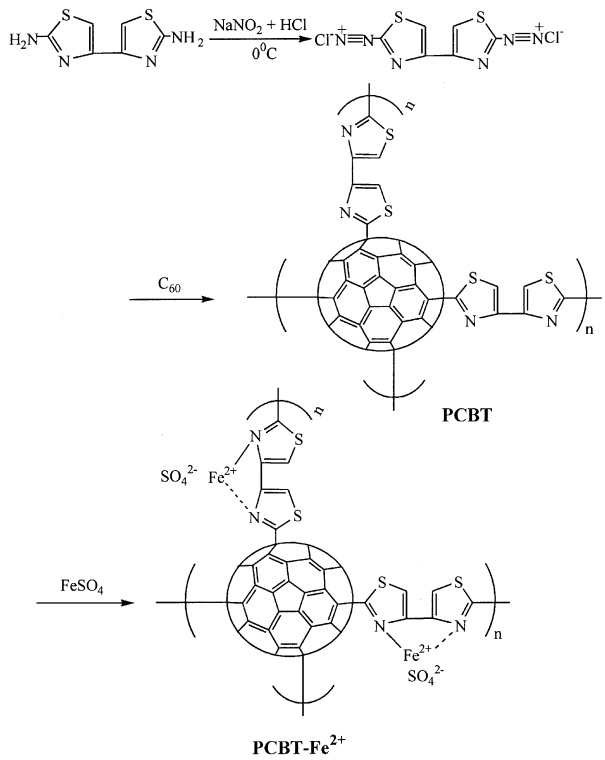

Scheme 1.

its precursors, the IR spectrum of PCBT is simpler due to the rigid chain structure. In addition, it must be noted that there is a significant difference in IR spectra between PCBT and PCBT-Fe^{2+} complex, that is, the peak at 1298 cm^{-1} in PCBT blue-shifted to 1349 cm^{-1} in the case of its Fe^{2+}-complex. The absorption at 1298 cm^{-1} in PCBT might be ascribed to the skeletal vibration, which results from the imino-interchange action of 2-amino-thiazole moiety [21]. However, this imino-interchange exists no longer for PCBT-Fe^{2+} complex. The reasonable explanation is the coordination that took place between the metal ion and

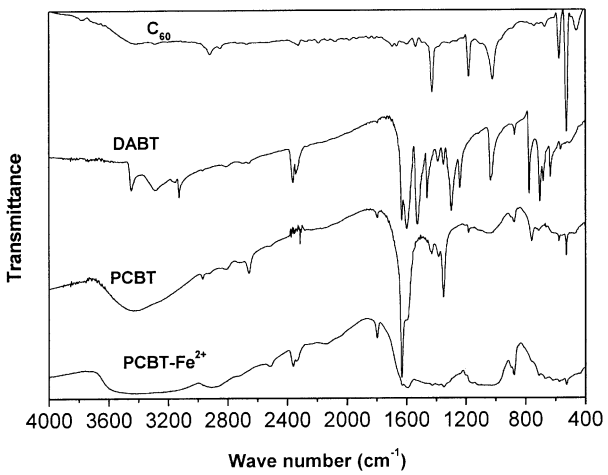

Fig. 1. The IR spectra of C_{60}, DABT, PCBT and PCBT-Fe^{2+} complex.

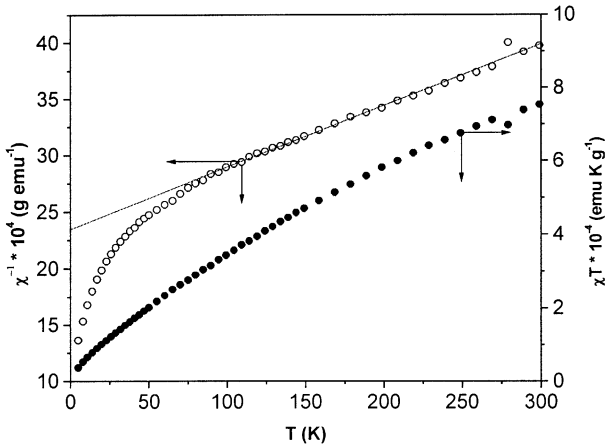

Fig. 2. The product of magnetic susceptibility (χ) and temperature, and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PCBT at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law in the temperature range from 70 to 300 K.

nitrogen atom of bithiazole ring. Furthermore, the peaks assigned to ν_{3a}, ν_{3b}, ν_{3c} and ν_1 of SO_4^{2-} (1116, 1054, 990 and 952 cm^{-1}) suggest that SO_4^{2-} acted as a bidentate ligand via oxygen atoms in the complex [22].

It can be found from Fig. 2 that the magnetic susceptibility (χ) of PCBT follows the Curie–Weiss relationship, $\chi = C/(T - \theta)$, in the temperature range of 300 − 70 K. The negative Curie–Weiss temperature ($\theta = -426.5$) implies the existence of mainly anti-ferromagnetic interaction in this material. However, the magnetic susceptibility of PCBT does not follow the Curie–Weiss law in the temperature range from 5 to 70 K, indicating the presence of exchange interaction at low temperature. At the same time, the curve fashion is different to that of the typical anti-ferromagnet. It is well known that the reciprocal magnetic susceptibility (χ^{-1}) of a typical anti-ferromagnet increases with the temperature decrease under the condition of $T < T_N$. On the contrary, the reciprocal magnetic susceptibility for PCBT decreases sharply with temperature decrease at low temperature range ($T < 50$ K). This phenomenon is a special anti-ferromagnetism, also known as ferrimagnetism [23]. When attempting to fit a straight line to the high temperature data, θ of −426.5 K would be obtained. It is apparent that the θ value of −426.5 K is not the real Curie–Weiss temperature and the paramagnetic model is not adequate for this sample. In fact, the real Curie–Weiss temperature (T_C) should be 0–5 K for PCBT according to the hypothesis proposed by Tebble et al. [23]. In addition, the product of magnetic susceptibility and temperature decreases with a decrease in temperature, which is in accordance with the behavior of an anti-ferromagnet.

In general, materials may exhibit anti-ferromagnetic properties when the interaction distance of unpaired electrons in the components is too near or too far. In order to change PCBT from an anti-ferromagnetic material to a ferromagnet, it is very important to introduce some

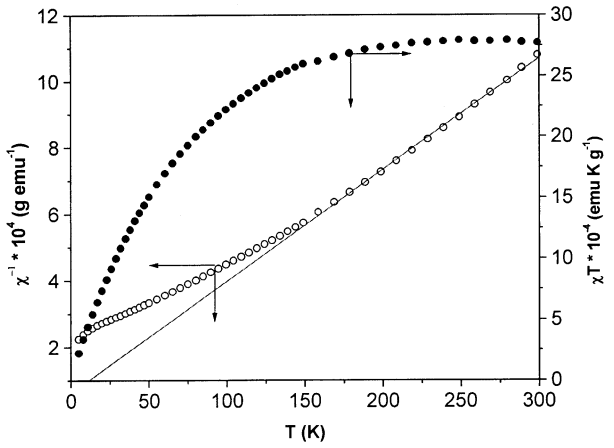

Fig. 3. The product of magnetic susceptibility (χ) and temperature, and reciprocal magnetic susceptibility (χ^{-1}) as a function of temperature (T) for PCBT-Fe^{2+} at an applied magnetic field of 30 kOe. The straight line is a fit to the Curie–Weiss law in the temperature range from 130 to 300 K.

substance with unpaired electrons into the parent compound. Fig. 3 shows that the magnetic susceptibility (χ) of PCBT-Fe^{2+}complex follows the Curie–Weiss relationship in the temperature range of 300–130 K, and the positive Curie–Weiss temperature ($\theta = 10.2$ K) implies the existence of ferromagnetic coupling in the material. The product of magnetic susceptibility and temperature remains constant in the temperature range of 300–130 K. In other words, there is an increase in the magnetic susceptibility of the ferro-complex on decreasing temperature under the present conditions. These results indicate that the PCBT-Fe^{2+}complex has typically ferromagnetic properties.

The further study revealed that the magnetization curve of PCBT-Fe^{2+} as a function of applied field exhibits a hysteresis cycle at low temperature (Fig. 4), which is a characteristic of ferromagnetic interactions. At 5 K, the observed coercive field (H_C) and remnant magnetization (M_r) are 690 Oe and 0.12 emu/g, respectively. From the

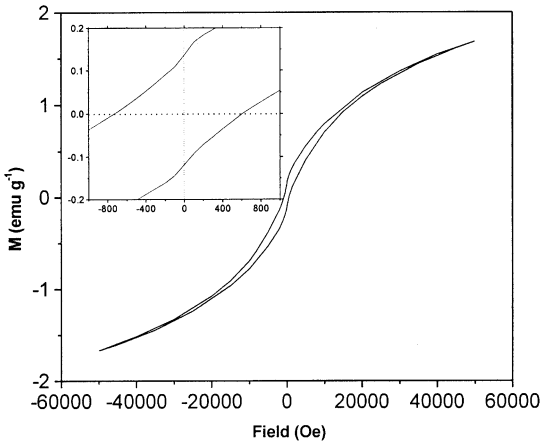

Fig. 4. Magnetic hysteresis loop of PCBT-Fe^{2+} at 5 K. Insert: Expanded view of the region from −900 to 900 Oe.

Table 1
Binding Energies of Fe (2p) Core levels in PCBT-Fe^{2+} and other Fe-containing materials

Materials	Binding energy (eV)		
	Fe $2p_{3/2}$	Fe $2p_{1/2}$	Reference
PCBT-Fe^{2+}	709.1	721.5	This work
Fe	707.3	720.3	[15]
Fe_3O_4	710.8	724.7	[15]
Fe_2O_3	711.6	725.1	[15]

results, we may conclude that the Fe^{2+}-complex is a soft ferromagnet.

We inspected the Fe (2p) core level photoelectron spectra of PCBT-Fe^{2+} in an effort to understand the chemical structure of the iron species in the polymeric complex (Table 1). It was considered that the two peaks near 709.1 and 721.5 eV may be, respectively, related to the binding energies of Fe ($2p_{3/2}$) and Fe ($2p_{1/2}$). In the case of PCBT-Fe^{2+}, the binding energies are not in conformity with those of typical Fe, Fe_3O_4, or Fe_2O_3 reported in the past [24], indicating the absence of these magnetic impurities in the polymeric complex.

In conclusion, a novel bithiazole oligomer containing C_{60} (PCBT) and its ferro-complex were synthesized successfully. An interesting observation on magnetic behavior of these materials is that PCBT is an anti-ferromagnet, but its Fe^{2+}-complex has typically softmagnetic properties.

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