Hybrid Materials

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Synergetic Spin Crossover and Fluorescence in One-Dimensional Hybrid Complexes**

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Abstract: *Hybrid materials integrated with a variety of physical properties, such as spin crossover (SCO) and fluorescence, may show synergetic effects that find applications in many fields. Herein we demonstrate a promising post-synthetic approach to achieve such materials by grafting fluorophores (1-pyrenecarboxaldehyde and Rhodamine B) on one-dimensional SCO Fe^{II} structures. The resulting hybrid materials display expected one-step SCO behavior and fluorescent properties, in particular showing a coupling between the transition temperature of SCO and the temperature where the fluorescent intensity reverses. Consequently, synergetic effect between SCO and fluorescence is incorporated into materials despite different fluorophores. This study provides an effective strategy for the design and development of novel magnetic and optical materials.*

Spin-crossover complexes can undergo magnetic, optical, electrical, and structural variations in response to the changes of external stimuli, such as guest absorption–desorption, pressure, light irradiation, and temperature,[1] thus featuring as one of the most important molecule-based switchable materials. Particularly, some SCO materials may display abrupt spin-state switches accompanied with hysteretic behavior, which endow them with memory effects.[2] These advantages make SCO materials good candidates in fabricating accessories for information processing, sensing, data storage, molecular switches, and displays.[3] To be applicable, a principle that is technologically significant in SCO materials is the possibility of addressing low-spin (LS) and high-spin (HS) states.[4] Thus, the design of a new molecular system combining SCO and other attractive properties, for example, luminescence, that could sense the spin-state transition signal rippling through the molecular system provides an interesting scope for registering the SCO.[5] Such a system would also have potential applications in the fields of drug delivery, biomarkers, and thermometry.[6] To our knowledge, only a handful of attempts have been made to fabricate bifunctional SCO-luminescent materials. For example, Kimizuka et al.[7] reported spin–photon communication systems of lipophilic iron(II)–1,2,4-triazole complexes with 9,10-dimethoxyanthracene-2-sulfonate and 1-pyrenesulfonate anions in which fluorescence characteristics of 1-pyrenesulfonate accumulated on 1D Fe^{II} complex was regulated by self-assembly and dynamic spin conversion. Bousseksou et al.[6] prepared a SCO complex nanomaterial doping with the fluorophore Rhodamine 110, the thermometric properties of which could be modified and controlled. More recently, Garcia et al.[8] reported a dinuclear SCO Fe^{II} complex tagged with a fluorophore that presented intraligand electronic transfer. To search for novel hybrid SCO materials, we herein report two SCO-fluorescent materials that are obtained by a postsynthetic method that involves directly grafting fluorophores 1-pyrenecarboxaldehyde (PCA) and Rhodamine B (RhB), respectively, on the 1D SCO Fe^{II} complex $[Fe(C_2H_4N_4)_3](ClO_4)_2$ (FeL, $C_2H_4N_4$ = 4-NH$_2$-1,2,4-triazole).[9] The corresponding products were assigned to $[Fe(C_2H_4N_4)_{2.56}(C_{19}H_{12}N_4)_{0.44}(ClO_4)_2$ (FeL-PCA, $C_{19}H_{12}N_4$ = L-PCA) and $[Fe(C_2H_4N_4)_{2.71}(C_{30}H_{33}N_6O_2Cl)_{0.29}(ClO_4)_2$ (FeL-RhB, $C_{30}H_{33}N_6O_2Cl$ = L-RhB) (Scheme 1). As expected, they show hysteretic SCO behaviors that are accompanied with fluorescence. More important is that variable temperature fluorimetric and magnetic studies reveal synergetic effects between SCO and fluorescence in both materials.

Samples FeL-PCA and FeL-RhB were prepared from FeL by the condensation reactions of carboxaldehyde group (PCA) and carboxylic acid group (RhB), respectively, with the amino groups on FeL (Scheme 1 and Supporting Information). Elemental analyses indicated that 14.67% and 9.67% 4-amino-1,2,4-triazoles on FeL were grafted with PCA and RhB for FeL-PCA and FeL-RhB, respectively (Supporting Information, Table S1). Thermogravimetric (TG) analyses (Supporting Information, Figure S1) showed a mass loss of nearly 77.40% for FeL at about 425 K, corresponding to the loss of 4-amino-1,2,4-triazoles,[10] whereas the mass losses of approximately 89.50% and 87.70% for FeL-PCA and FeL-RhB, respectively, at 1070 K were increased by 12.13% and 10.34% compared with FeL, which could be assigned to the removal of PCA and RhB on 4-amino-1,2,4-triazoles,[11] in accordance with the EA results. Powder X-ray diffraction (PXRD) studies revealed the intact

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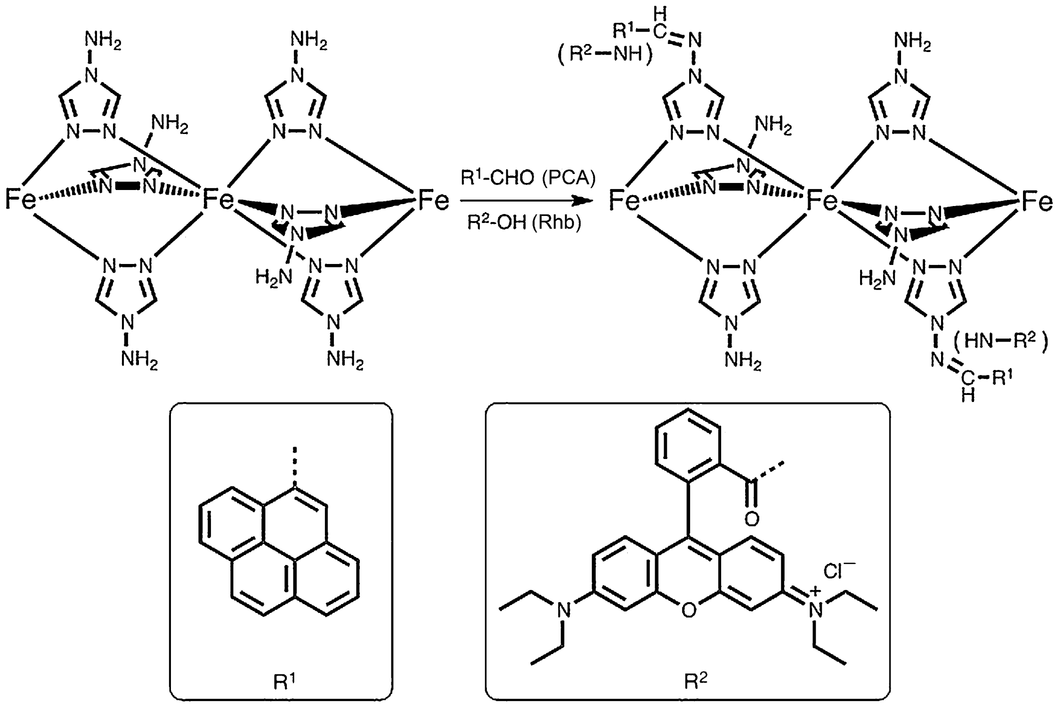

Scheme 1. Preparation of the hybrid materials FeL-PCA and FeL-RhB by grafting fluorophores 1-pyrenecarboxaldehyde (PCA) and Rhodamine B (RhB) on SCO FeL, respectively.

1D structure of FeL during grafting so that the comparison of magnetic and fluorescent properties between FeL-PCA and FeL-RhB were reasonable (Supporting Information, Figure S2).

The fluorescent emission spectra of FeL-PCA and FeL-RhB at room temperature are shown in Figure 1, where PCA, RhB, L-PCA, and L-RhB are also shown for comparison. The fluorophore PCA itself exhibits strong emission between 500 and 700 nm with maximum at 558 nm, whereas L-PCA shows two maximum emissions at 476 and 507 nm, respectively. When PCA is grafted on FeL, the emission of FeL-PCA appears as a broad band maximized at 437 nm. Therefore, obvious blue shifts are presented in the emission spectra of L-PCA and FeL-PCA, that is, 51 nm and 82 nm for L-PCA and 121 nm for FeL-PCA, respectively. Similar phenomena are also observed on L-RhB and FeL-RhB, showing blue shifts of 15 nm for L-RhB and 19 nm for FeL-RhB, respectively. This hypsochromic effect is indicative of the successful graft of PCA (or RhB) on FeL and possible interactions between the magnetic (electronic) properties of FeL and the fluorescent properties of PCA (or RhB).[12]

To establish the interactions between the magnetic (electronic) properties of FeL (see below) and the fluorescent properties of PCA (or RhB) within FeL-PCA (or FeL-RhB), we have investigated the variable-temperature fluorescence of FeL-PCA and FeL-RhB, respectively. As shown in Figure 2 a (see also the Supporting Information, Figure S9), FeL-PCA displayed three fluorescent bands centered at approximately 410 nm, 430 nm, and 620 nm, respectively, at 100 K. Upon increasing the temperature, the emission intensity decreased gradually, as if an expected thermal quenching of fluorescence might occur. However, when the temperature exceeded 200 K, the emission intensity turned up to increase suddenly until 225 K, then the decrease of intensity recovered upon further temperature increasing. These abnormal temperature-dependent fluorescence variations were apparently different from those of L-PCA, which showed a monotonous decrease of emission intensity with increasing temperature (Supporting Information, Figure S10). We realized that the drastic thermal variations of emission intensity happened in the 190–270 K temperature range, which was almost identical to that of the thermally induced spin-state switch of FeL-PCA (see below). The emission intensity of FeL-RhB showed similar temperature-dependent variation trend to that of FeL-PCA, while the inflection points of temperature appeared at 260 K (Figure 2b). As for FeL-RhB, another notable phenomenon was that the strong emission at 659 nm showed a bathochromic shift of 15 nm upon warming, that is, from 659 nm at 130 K to 674 nm at 300 K. More interestingly, a weak emission at 725 nm (at 130 K) decreased along with temperature increasing and simultaneously a new band at 630 nm appeared, showing a remarkable hypsochromic shift of 95 nm. Similar to L-PCA, L-RhB also underwent monotonous decrease of emission intensity upon temperature increasing (Supporting Information, Figure S10). These results provide direct evidence that the changes and shifts of fluorescent emission bands can be attributed to the impact from the SCO Fe^{II} ions, that is, a synergetic fluorescence–SCO effect is present.[8,13] Thus, we can conclude that the fluorophores PCA and RhB display optical properties that are sensitive to and can address the spin states of Fe^{II} ions.

It is well-known that the 1D complex FeL with various anions (Br^-, BF_4^-, ClO_4^-) usually exhibited abrupt spin crossover with hysteresis,[14] and the effects of anions and lattice water molecules on the SCO temperatures were systematically discussed.[14b,15] Typically, the complex FeL with ClO_4^- anions showed SCO with a hysteretic loop of 3 K wide ($T_c\downarrow = 209$ K, $T_c\uparrow = 212$ K).[14b,15] As for our sample (FeL, using ClO_4^- as anions), the as-synthesized 1D complex underwent a one-step, incomplete SCO (Figure 3 inset; Supporting Information, Figure S11), which was characterized by $T_c\downarrow = 189$ K in the cooling mode and $T_c\uparrow = 197$ K in the warming mode, respectively, thus defining an 8 K wide

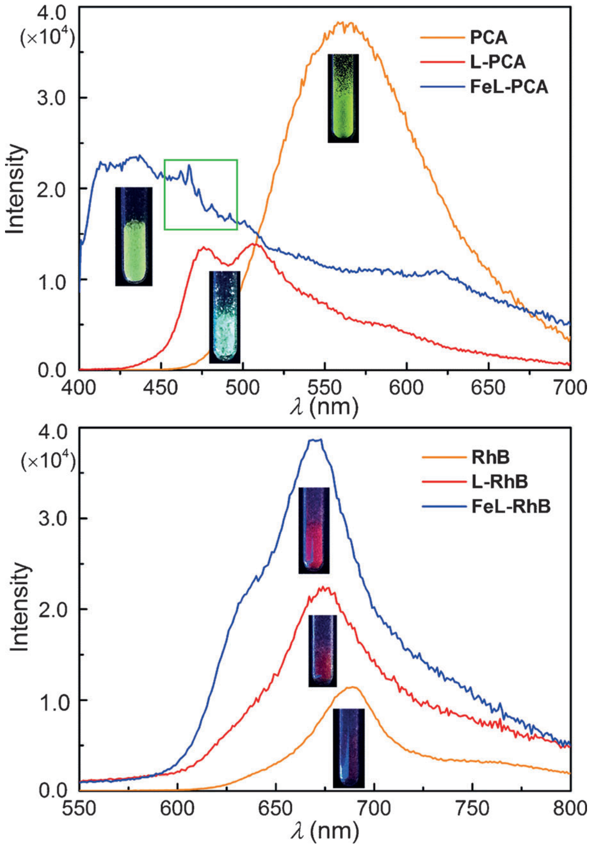

Figure 1. Fluorescence emission spectra at room temperature, excited at 370 nm. L-PCA and L-RhB refer to the products obtained from the direct condensation reactions of 4-amino-1,2,4-triazole (L) with PCA and RhB, respectively. The five sharp peaks marked with green rectangle in FeL-PCA at 450–500 nm in (a) are the emission spectra of the Xe light source (Supporting Information, Figure S8).

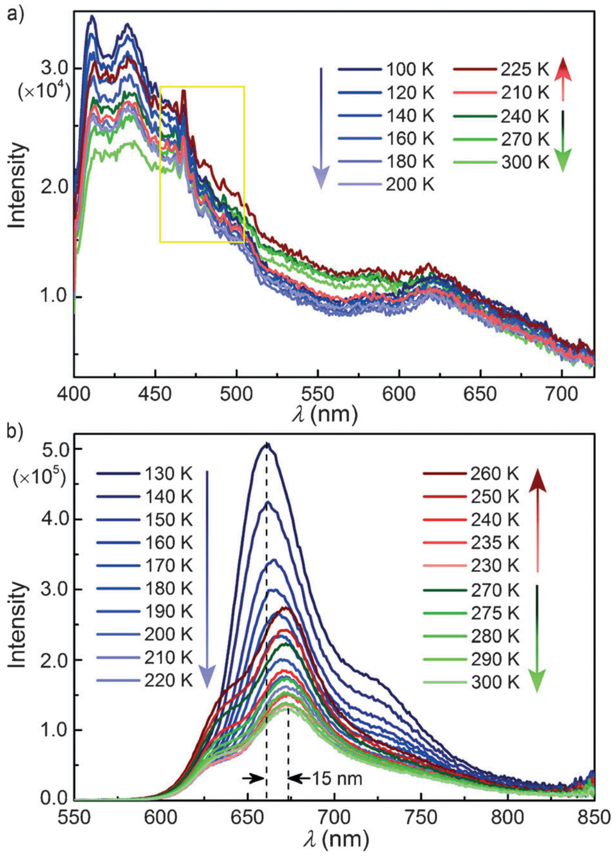

Figure 2. Temperature-dependent emission spectra (warming mode) of FeL-PCA (a) and FeL-RhB (b) excited at 370 nm. The arrow indicates the trend of emission intensity with increasing temperature. The five sharp peaks marked with a yellow rectangle in FeL-PCA at 450–500 nm in (a) are the emission spectra of the Xe light source (Supporting Information, Figure S8).

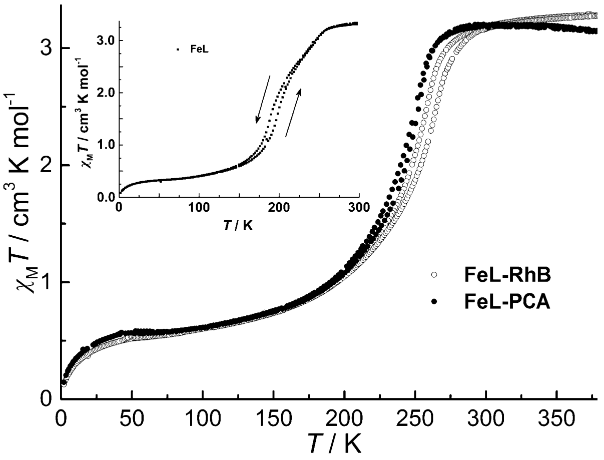

Figure 3. $\chi_M T$ versus T plot of FeL-PCA and FeL-RhB at a sweep rate of 1 K min^{-1} under an applied magnetic field of 5000 Oe. Inset: the magnetic properties of the as-synthesized FeL.

hysteresis loop. As for FeL-PCA and FeL-RhB, their SCO behaviors resembled that of FeL, but showed notable differences in the transition temperature and width of hysteresis (Figure 3). The transition temperatures for FeL-PCA and FeL-Rh were $T_c\downarrow = 220$ K and $T_c\uparrow = 230$ K and $T_c\downarrow = 252$ K and $T_c\uparrow = 263$ K, respectively, giving 10 K and 11 K width of hysteresis loops. The temperatures of the spin transition of FeL-PCA and FeL-RhB were found to be higher than that of FeL,[14b,15] which may be due to the changes of ligand-field strength and intra- and inter-chain interactions that are induced by the graft of fluorophores.

A detailed comparison of the temperature-dependent fluorescence (Figure 2) and magnetic susceptibilities (Figure 3) shows that the SCO of FeL-PCA/FeL-RhB obviously covers the temperature range where the abnormal changes of emission intensity of fluorescence occur, which implies that the increasing of fluorescence may synchronize with the thermally induced SCO.[8,13] To confirm this hypothesis, normalized data of d($\chi_M T$)/dT and emission intensity of fluorescence of FeL-PCA and FeL-RhB in the 100–300 K temperature range (warming mode) are plotted (Figure 4; Supporting Information, Figure S12). Obviously, the SCO of FeL-PCA and FeL-RhB weighed heavily upon the variation tendency of their emission intensity of fluorescence. The critical temperatures obtained from the thermal variation of fluorescence are 225 K and 260 K for FeL-PCA and FeL-RhB, respectively, whereas the SCO temperatures for FeL-

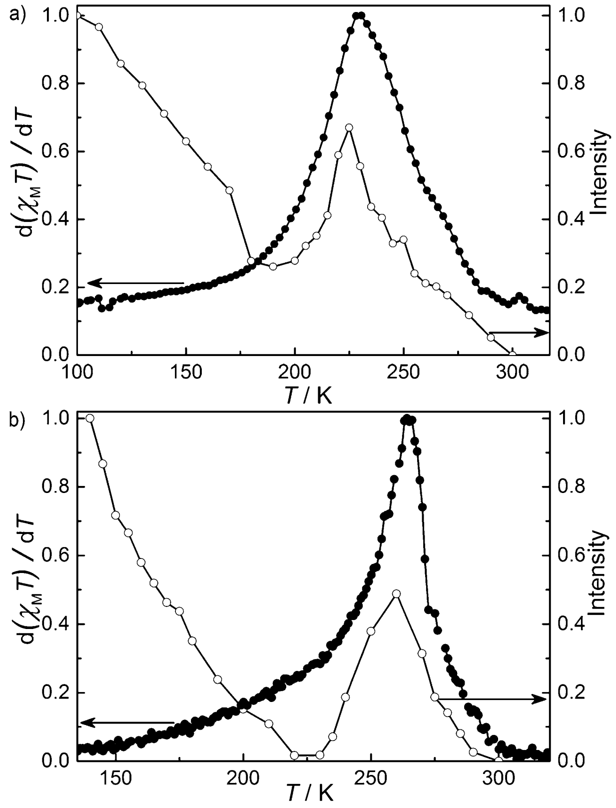

Figure 4. Normalized differential magnetic susceptibilities (d($\chi_M T$)/dT) and the maxima of emission intensity of fluorescence for FeL-PCA (a) and FeL-RhB (b), respectively, in the warming mode.

PCA and FeL-RhB are 230 K and 263 K ($T_c\uparrow$). Therefore, the deviation of critical temperatures between the SCO and fluorescence is less than 5 K, indicating that the fluorescence of grafted PCA or RhB is coupled with the SCO of the 1D structure. A possible mechanism for these two systems is that a reversible electron transfer occurs between the LUMO state of PCA or RhB molecule[16] and the antibonding orbitals (e_g) of Fe^{II} ions, for example, upon warming the LS-to-HS transition leads to the population of the antibonding orbitals and then the electrons on these orbitals are transferred to the LUMO of PCA or RhB, thus causing a sudden increase of fluorescence. Such an electron transfer mechanism is evidenced by the monotonous decreases of emission intensity of L-PCA and L-RhB (warming mode; Supporting Information, Figure S10) without the SCO Fe^{II} centers.

In summary, two hybrid materials have been prepared by post-synthetic grafting the fluorophores PCA and RhB on 1D SCO complex FeL. During this process, the SCO behavior of FeL and optical properties of PCA and RhB are preserved, and most important is that the luminescent properties of the grafted fluorophores can be adjusted by the spin states of FeL because of the synergetic effect between fluorescence and SCO. We believe that the strategy to incorporate luminescence into SCO will open up new avenues for probing and tracking thermosensitive events in multifunctional materials, so there is great potential for exploitation in this area through the synergetic effect of abundant composite molecules with a wide variety of SCO materials.

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