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Encapsulation of a luminescent zinc complex in a nanoporous channel host

Lei Z. Zhang,[b] Ying Xiong,[a] Peng Cheng,*[b] Guo-Qing Tang,*[a] Li-Juan Wang[b] and Dai-Zheng Liao[b]

[a]*Institute of Modern Optics, Nankai University, Tianjin 300071, P. R. China*
[b]*Department of Chemistry, Nankai University, Tianjin 300071, P. R. China*

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A luminescent zinc complex has been encapsulated in the ordered, 3.2 nm wide hexagonal channels of a nanoporous MCM-41 host. A marked 19 nm blue-shift of the major absorption band maximum is found for the zinc complex in ethanol solution relative to the complex loaded in MCM-41, which is correlated with an increased band gap in the former. A 17 nm blue-shift of the emission peak is also observed, which is estimated to be related to the decrease of polarity around the zinc ions.

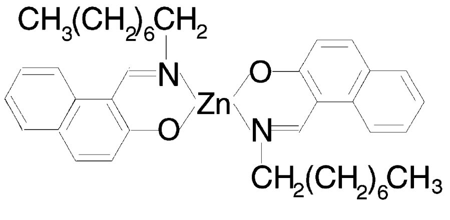
On the basis of the study of semiconductors and metal nanoparticles, many new physical phenomena, such as quantum size effects, have been discovered, and many novel device concepts have been developed.[1,2] Because of the diversity of organic molecules, there is a tendency to extend the research on nanoparticles from metals and semiconductors to the organic field. In the case of organic molecular crystals (OMCs), their electronic and optical properties are fundamentally different from those of inorganic materials, due to weak intermolecular interaction forces of van der Waals type.[3] In recent years, the number of studies of organic nanoparticles has been increasing and most such studies focused on general organic molecules, such as perylene, anthracene and polymers.[4–6] However, reports on nanoparticles of organic chelate compounds are much rarer.

Azomethine–zinc complexes have received considerable recent attention in the study of organic thin-film electroluminescence.[7,8] Since solids with strong blue luminescence could be obtained with these complexes, and they also can be sublimed, electroluminescent (EL) cells containing these complexes could be fabricated. We are interested in the study of the luminescence properties of azomethine–zinc complexes because they are promising key color components required for full-color EL displays as blue luminescent species. It may be possible to confer a greater degree of order on EL processes by utilizing porous, channel-type materials containing light-emitting and electronically interacting guest molecules, since the pathways open for n/p migration–recombination are limited essentially to only one dimension.[9] The discovery of the periodic nanoporous inorganic material known as Mobil Catalytic Material 41 (MCM-41) characterised by large surface areas and narrow pore-size distributions has opened up new opportunities for confining close-packed, functionalised molecules within parallel-aligned porous channels.[10,11] A number of interesting electronic and optical properties have been observed, since the guest molecules themselves are aligned co-parallel within the cavities. For example, stabilization of conducting polyaniline filaments with mobile charge carriers in the aluminosilicate host MCM-41 has been achieved, which represents a step toward the design of nanometer electronic devices.[12]

To understand the luminescent behavior of such host–guest complexation systems is of fundamental and technological importance. We have thus been focusing on the encapsulation of luminescent azomethine–zinc complexes in the nanoporous MCM-41 host which is beneficial for further exploring the probability of fabricating LEDs using electroluminescent nanotube crystals.[9] In this communication, we describe the synthesis of a new zinc complex bis(2-hydroxy-*N*-octylnaphthylideneaminato)zinc(II) monohydrate (Scheme 1), and report its luminescent properties upon loading in MCM-41.[13]

Nanoporous molecular sieve MCM-41 was synthesized according to the literature method.[10] The N_2 adsorption–desorption isotherm for the pure siliceous MCM-41 is apparently a reversible Type IV isotherm.[14] Taking the inflection point at $P/P_0 = 0.35$, we obtain a 3.2 nanometer wide effective mean pore diameter based on the application of the Kelvin equation with a multilayer thickness correlation.[15] Encapsulation of the zinc(II) complex was carried out by stirring a CH_2Cl_2 solution of the complex (5×10^{-4} mol L^{-1}) in the presence of MCM-41 for 4 h at room temperature. The resultant pale yellow powder was filtered off and washed copiously with fresh CH_2Cl_2. Chemical analysis was performed using a ICP 9000 (N + m) spectrometer. The content of the zinc complex in MCM-41 was found to be 2.67 wt%.

The UV–vis absorption spectra of the zinc complex in absolute ethanol (1×10^{-4} mol L^{-1}) (**1**) and of the zinc complex loaded in MCM-41 (**2**) at room temperature are shown in Fig. 1. The ground electronic state of the azomethine ligands is a spin-singlet, and the absorption in Fig. 1 is therefore a spin-allowed singlet–singlet transition. No spectral changes were observed when the concentration of **1** was changed from 1×10^{-4} to 1×10^{-3} mol L^{-1}. Thus it is concluded that **1** can be considered as a dispersed molecular system (*i.e.*, monomers). A remarkable 19 nm blue-shift of the absorption band from 402 nm (3.09 eV) of **2** to 383 nm (3.24 eV) of **1** is observed. While the zinc complexes in ethanol solution show essentially no interactions with each other this would not be so in MCM-41; Coulombic interaction energies between molecules are thus lower in ethanol, leading to a wider



Scheme 1

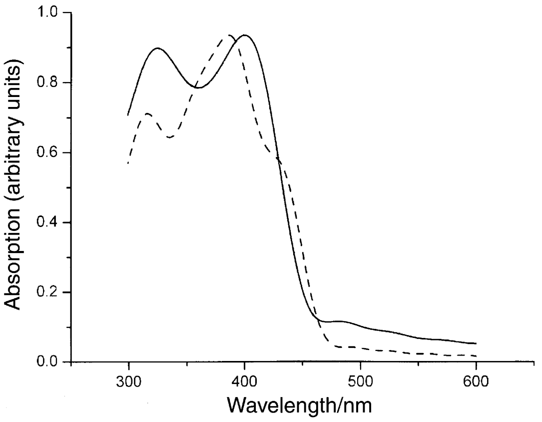


Fig. 1 UV–vis absorption spectra of **1** (dashed line) and **2** (solid line) at room temperature.

band gap. Given that the main contribution to the $S_0 \rightarrow S_1$ transition is due to the HOMO–LUMO transition, the blue-shift of absorption bands can be correlated with an increasing of the HOMO–LUMO band gap in solution. This phenomenon is well in accordance with some recently published papers relating to size effects on the optical properties of organic nanoparticles.[5,6]

The photoluminescence spectra of **1** and **2** excited with 351 nm UV light at room temperature are shown in Fig. 2. In general, emission occurs as a consequence of a non-radiative intramolecular energy transfer from the excited azomethine ligands to the zinc ions, followed by emission from the latter.[16] Thus, the PL emissions in Fig. 2 are assigned to a direct transition from E_1 (the lowest excited state) to E_0 (the ground state) of zinc ions. We postulate that the 17 nm blue-shift of the emission peaks from 471 nm (2.64 eV) of **2** to 454 nm (2.74 eV) of **1** is caused by the decrease of polarity around Zn^{2+} ions since ethanol (C_2H_5OH) is a much less polar medium than MCM-41. As the molecular sieve is not fired again before loading, Si–OH groups cover its intrachannel surface. When the zinc complex is loaded in MCM-41, a larger Stokes shift of zinc ion emission is observed. It is evident from the above measurements that the zinc complexes loading in MCM-41 are nanoparticles.

With the aim to interpret the above experimental data, we suggest an energy state diagram as shown in Fig. 3. The left hand diagram represents the situation for monomers of the zinc complex, whereas the right hand diagram corresponds to nanoparticles of zinc complexes. The emission energy decrease for the latter ($E_1 \rightarrow E_0$) of 0.10 eV is close to the energy difference between the absorption transitions ($S_0 \rightarrow S_1$) of 0.15 eV. The zinc complexes loaded in MCM-41 tend to form nanoparticles without surface passivation (that is, not blocked by chemical capping), which indicates the existence of surface states.[17] It is noteworthy that the blue-shift of the emission peaks is connected with the blue-shift of the absorption bands. For MCM-41 the dimensions of zinc complexes approach those of the nanopores (3.2 nm diameter) and the HOMO–LUMO band gap of the monomeric zinc complexes in ethanol should be larger than that of zinc complexes loaded in MCM-41. Due to this proximity effect , E_1 and E_0 of the zinc ions can be partially degenerated *via* vibronic (vibrational–electronic) coupling between both electronic states, which is consistent with theory.[18]

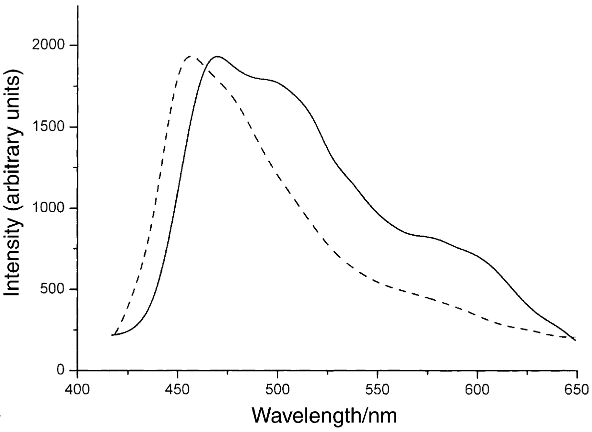


Fig. 2 Photoluminescence spectra of **1** (dashed line) and **2** (solid line) excited with 351 nm UV light at room temperature.

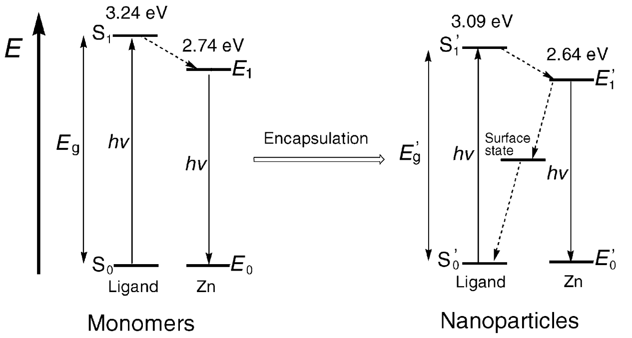


Fig. 3 Proposed energy state diagram for both monomers and nanoparticles of the azomethine–zinc complex. Non-radiative processes are indicated by dashed arrows.

In summary, we have successfully encapsulated a luminescent azomethine–zinc complex in the ordered, 3.2 nm wide hexagonal channels of the nanoporous MCM-41 host. The luminescent behavior of this host–guest complexation system has been studied. An energy state diagram has been proposed for the encapsulation of zinc complexes. The results presented here may prove useful in optoelectronic device applications, such as LEDs using electroluminescent nanotube crystals, and in the study of the fundamental process connecting more conventional classes of materials, *i.e.*, organic molecular crystals.[3,9] Further work is in progress to investigate the photophysics of nanoparticles of organic chelate compounds.

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13 Preparation of the azomethine–zinc complex is as follows: *N*-octylamine (0.258 g, 2.0 mmol) was added dropwise to a solution of 2-hydroxy-1-naphthaldehyde (0.344 g, 2.0 mmol) in boiling absolute ethanol (10 ml). Then, a solution containing $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.219 g, 1.0 mmol) and $CH_3CO_2Na \cdot 3H_2O$ (0.204 g, 1.5 mmol) in H_2O (2 ml) was added to the above boiling mixture. Subsequently, the reaction mixture was refluxed for half an hour and then cooled slowly. Light yellow precipitates were formed, collected by filtration and recrystallized from ethanol. Yield: 0.324 g (0.5 mmol, 50%). $\nu_{C=N}$(KBr)/cm^{-1}: 1614. Calc. for $C_{38}H_{50}N_2O_3Zn$, C, 70.50; H, 7.72; N 4.32. Found C, 70.73; H, 7.56; N, 4.20%.

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17 The quantum yields of the pure zinc complex and the complex loaded in MCM-41 were measured. Significantly, the quantum yield for the former is approximately four times that for the latter. These results indicate that the enhanced radiationless deactivation pathways (*e.g.* fluorescence quenching by a surface state) lead to a reduced emission quantum yield, and are consistent with theory.

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