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Photophysical properties of coumarin derivatives incorporated in MCM-41

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Abstract

Highly ordered MCM-41 has been synthesized and four coumarin derivative dyes were incorporated into it by impregnation method. The absorption and emission spectra of four coumarin derivatives in both toluene and MCM-41 were examined to explore the structural and environmental effects on the optical properties of these dyes. The spectra results indicated that dye molecules existed in monomer form within MCM-41. The maxima of absorption and emissions shifted to red compared with those in toluene due to the strong host–guest interactions. The shifts of emission maxima increased with increasing the volume of the dyes.

Keywords: MCM-41; Coumarin derivatives; Composite materials; Fluorescence; Environment effect; Host–guest interaction

1. Introduction

Incorporation of organic dyes into solid matrix has attracted much attention due to its scientific importance and applications in many areas [1–4]. For example, incorporated chromophores exhibited dramatically increased resistance towards photobleaching [5], which is the main restriction for application of organic dyes.

Incorporation of organic dyes over sol–gels and zeolites has been extensively studied for possible application as sensors [6], solid-state dye lasers [7] and optical switching [8], and reviewed by Schulz-Ekloff [9]. However, sol–gels are found to be unsuitable for the incorporation of dyes due to their broad pore size distribution. On the other hand, the major disadvantage of zeolite for the incorporation of dyes is their small pore size. The discovery of mesoporous molecular sieves [10,11] opened up new possibilities in many areas of chemistry and material science. Among them, the typical MCM-41 possesses well-ordered pore structures with uniform mesopores adjustable from about 1.5 to 10 nm. MCM-41 has a clear advantage over zeolite for incorporation of large organic molecules.

The incorporation of dyes into MCM-41 has been studied in recent years [12–15]. In the majority of these studies, the strong dye/MCM-41 interaction increased the lifetime and lack of aggregation at high concentration of the dye incorporated into the channels of MCM-41 [16]. Last year, Fujiwara reported that Coumarin-modified MCM-41 could realize the photocontrolled reversible release of guest molecules [17,18], which invoked the study on the coumarin dyes in mesoporous molecular sieves.

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Coumarins are the well-known laser dyes for the blue-green spectral region [19]. Among different coumarin dyes, the one having amino substituents at the 7-posotion have found to be of special significance in relation to their laser activity and many other applications. The 7-amino-coumatin dyes undergo substantial change in their dipole moment on excitation from the ground to the excited S_1 state [20,21]. Thus, these molecules are found to be suitable probes in investigating many physical and physiochemical processes in the condensed phase, making use of their fluorescence properties [22,23]. On the other hand, the 7-aminocoumarin dyes are also good electron acceptors [24–26], a number of studies in relation to the electron transfer dynamics used coumarin dyes as the electron acceptors.

The benzopyrylium salt incorporated into mesoporous molecular sieves HMS and MCM-48 have been studied in this laboratory [27,28]. The present work describes the incorporation of four coumarin derivative dyes into MCM-41 by impregnation method from toluene solution. The photophysical properties of the four dyes in MCM-41 are investigated.

2. Experimental section

2.1. Synthesis

MCM-41 was synthesized by hydrothermal method. In a typical synthesis, surfactant cetyltrimethylammonium bromide (CTAB) was dissolved in distilled water and ammonia. Then, tetraethylorthosilicate (TEOS) was dropped into this solution slowly under stirring. The molar composition of the final gel mixture was $1SiO_2$: 0.012 surfactant:$8.6NH_3$:$82H_2O$. After at least 2 h, the gel was transferred into a Teflon-lined autoclave and heated at 393 K for 2 days. The solid products were filtered, washed with distilled water, dried in air and then calcined at 823 K for 5 h in air. The coumarin derivatives were prepared according to literature [20] in our laboratory and recrystallized before use. The molecular structures of these four coumarin derivatives are shown in Scheme 1.

2.2. Incorporation of coumarin derivatives into MCM-41 by impregnation method

One hundred milligrams of calcined MCM-41 molecular sieves were heated at 523 K for 3 h to remove water adsorbed on surface and then allowed to cool to room temperature. Two milliliters of 10^{-3} mol/L toluene solutions of dyes was added under stirring, after 24 h the solids were vacuumed at temperature lower than 373 K to remove toluene. Then the samples were dried at 353 K for characterization.

2.3. Characterization

MCM-41 was characterized by powder X-ray diffraction (XRD) in the low-angle range. XRD measurement was carried out on a Rigaku D/MAX-2550 diffractometer using Cu Kα radiation. Absorption spectra were obtained on a Varian Cary 500. Fluorescence spectra were obtained on a Cary Eclipse fluorescence phospectrometer. All measurements were carried out at room temperature.

Semi-empirical calculations were performed on a windows-based PC using Hyperchem v. 7.0. For these calculations, initial geometry optimization was performed using PM3 parametrization, and then volume calculations were made for the molecules.

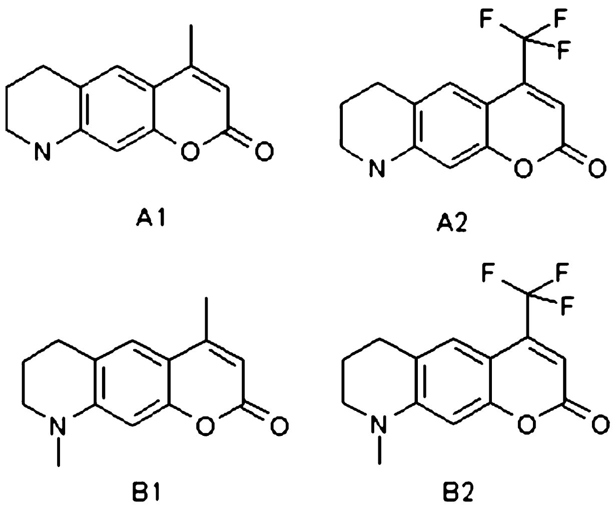
3. Results and discussion

3.1. XRD

Powder XRD pattern of calcined MCM-41 is depicted in Fig. 1, where three reflections are found, corresponding to the (100), (110) and (210) reflections, respectively. All the reflections are indexed based on hexagonal symmetry. These reflections are typical of MCM-41 as described by Kresge et al. [10,11] with highly order.

3.2. Absorption spectra

To understand the effects of dye/MCM-41 interactions on the optical properties, we measured the



Scheme 1. The molecular structures of coumarin derivatives: (A1) 4-methyl-6,7,8,9-tetrahydro-pyrano[3,2-*g*]quinolin-2-one; (A2) 4-trifluoromethyl-6,7,8,9-tetrahydro-pyrano[3,2-*g*]quinolin-2-one; (B1) 4,9-dimethyl-6,7,8,9-tetrahydro-pyrano[3,2-*g*]quinolin-2-one; (B2) 9-methyl-4-trifluoromethyl-6,7,8,9-tetrahydro-pyrano[3,2-*g*]quinolin-2-one.

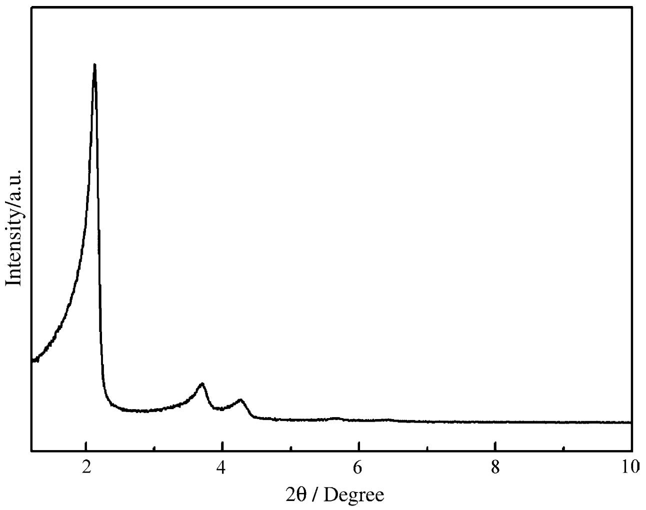


Fig. 1. The powder XRD pattern of calcined MCM-41.

Table 1
The absorption data of four coumarin dyes in toluene and within MCM-41

	λ_{max}, ab (nm)			
Host	A1	A2	B1	B2
Toluene	357	386	362	397
MCM-41	381	409	382	419
Shifts	24	23	20	22

absorption and emission spectra of these four coumarin derivatives in toluene and within MCM-41. Fig. 2 gives the UV–vis spectra of four coumarin dyes in diluted toluene solution and within MCM-41. It can be seen from Fig. 2 that absorptions of four coumarin dyes within MCM-41 resemble to those in toluene, which indicates that the dye molecules exists in a monomer form in MCM-41 due to its high surface area. Compared with absorptions in diluted toluene, the absorptions within MCM-41 show broad structure and shift to red, which shows that strong interactions between four coumarin dyes and MCM-41 exist [29]. The broadness can be explained by the presence of sites with different interaction strengths in MCM-41 that interact with the incorporated dye molecules [30] and also suggests that the dye monomers are distributed at various positions within MCM-41 and experience a range of perturbations [12]. The absorption data of four coumarin dyes in diluted toluene and within MCM-41 are listed in Table 1. It can be known from Table 1 that the absorption maxima of four coumarin dyes within MCM-41 red shift about 22 nm in the range of error compared with those in toluene. This red shift can be explained by the reduction of the HOMO–LUMO band gap. When coumarin dyes are incorporated into MCM-41, the HOMO and LUMO energy levels all increase due to the confinement effect, but the HOMO energy increases more than that of LUMO, so the HOMO–LUMO band gap reduces compared with that in solution [31], resulting in the red shift of absorption spectra.

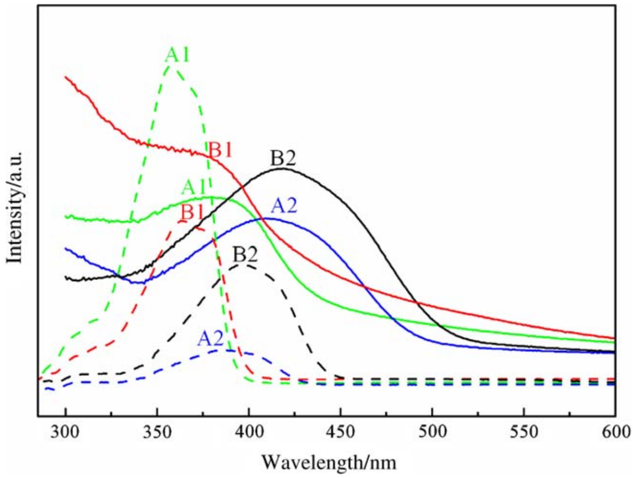


Fig. 2. The absorption spectra of four coumarin derivatives in diluted toluene (dash line) and within MCM-41 (solid line).

3.3. Emission spectra

The emission spectra of four coumarin dyes within MCM-41 and in toluene (10^{-3} mol/L) are shown in Fig. 3. It is clear that the emission shapes of four coumarin dyes within MCM-41 are very similar to those in toluene, but the intensities decreased dramatically. This decrease of emission intensities is due to the relatively strong interaction between dye molecules and MCM-41 [16]. In present study, the carbonyl oxygen atoms of these coumarin dyes and the fluorine atoms at A2 and B2 may H-bonded to silanols groups on the

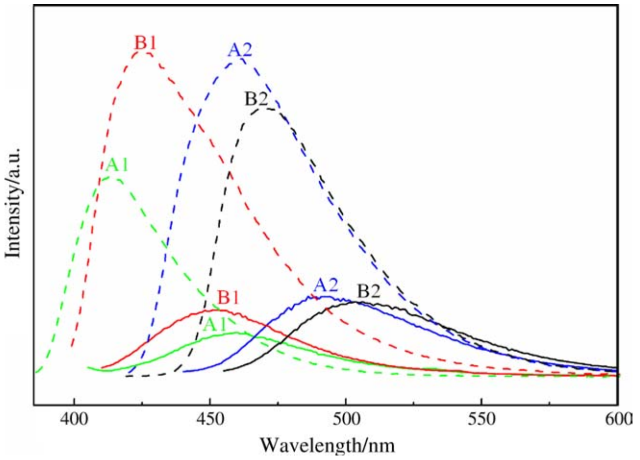


Fig. 3. The emission spectra of four coumarin derivatives in toluene (10^{-3} mol/L, dash line) and within MCM-41 (solid line), excited at respective absorption maxima.

Table 2
The emission data of four coumarin dyes in toluene and within MCM-41

	λ_{max}, em (nm)			
Host	A1	A2	B1	B2
Toluene	409	457	415	461
MCM-41	444	494	454	508
Shifts	35	37	39	47

surface of MCM-41 [32]. These interactions make it possible that energy transfer from the excited state of dyes to MCM-41, thus increase the non-radiated transition of dye-excited state and decrease the fluorescence emission. The emission data of four dyes within MCM-41 and in toluene are listed in Table 2. It can be known from Table 2 that the emissions within MCM-41 shift 35 nm to red for A1 dye, 37 nm for A2 dye, 39 nm for B1 dye and 47 nm for B2 dye compared with those in toluene. These red shifts can be explained partly by the reduction of the HOMO–LUMO band gap [31]; On the other hand, the MCM-41 channels exert influence on the emission of couamrin derivatives within it [33], namely, host–guest interactions that connects to steric effects associated with the pore structure. So this effect enhances with the enlargement of substituent or the volume of organic molecules. The volumes of these four coumarin derivatives computed using Hyperchem software are 644.23, 679.18, 695.58 and 725.67×10^{-3} nm^3 for A1, A2, B1 and B2, respectively. As a result, the red shifts increase with increasing the dye volumes, just as given in Table 2 that the red shifts of emission maxima are in the order of A1 < A2 < B1 < B2.

The four coumarin dyes, especially A2 and B2, have higher light stability, higher light conversion efficiency and wide laser tuning range [34,35]. Incorporation of them into MCM-41 can further tune their emission range, thus these MCM-41/dyes composites exhibit potential application for solid lasers.

4. Conclusions

Highly ordered mesoporous molecular sieves MCM-41 has been synthesized by hydrothermal method. Four coumarin derivatives are incorporated into the channels of MCM-41 by impregnation method. The absorption and emission measurements indicate that the dye molecules exist in monomer form within MCM-41, therefore avoid the aggregation of dyes when applied with high concentration. The emission maxima of these dyes shift to red over 35 nm when incorporated into MCM-41 compared with those in toluene, extending the applicable spectral range of these dyes.

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