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Communications

Microcavity Effect from a Novel Terbium Complex Langmuir–Blodgett Film**

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The use of microcavities as optical resonators has recently been developed as a potential high-density light source for optical communications and color displays. The electromagnetic field of microcavities can be enhanced significantly, and the spontaneous emission of the materials in the cavity can be modified. The fundamental principle of the cavity effect has long been known but novel phenomena in microcavities are still attracting scientists' attention, in terms of both theory and experiments.[1,2] A typical structure of a microcavity is the Fabry–Perot resonator, which comprises a thin layer of emitting material between two mirrors. There are two kinds of common reflective mirrors; namely, dielectric and metal.[3] Emitting materials comprise three main types: semiconductors,[4–6] dyes[7] and polymers.[8–14] However, these materials share one main disadvantage, in that most of them have relatively low fluorescence intensities and broad emission bands.

Fluorescent rare earth complexes have high fluorescence efficiencies, very narrow emission bands and excellent fluorescence monochromaticity.[15,16] In order to get the greatest effect, the optical length of the resonant cavity should be half the emission wavelength, $\lambda/2$. Using standard methods, however, it is quite difficult to precisely control the optical length of the microcavity resonator to fit the narrow emission band. Because of this problem, rare earth complexes are rarely used as microcavity emitting materials.[17] The Langmuir–Blodgett technique, by which the emitting material can be deposited onto substrates layer by layer, offers a better solution to this problem. Recently, we have reported the successful fabrication of a

$\lambda/2$ microcavity with the LB film of a europium complex Eu (NTA)$_4$(HDP) (where NTA and HDP represent β-naphthyltrifluoroacetone and cetylpyridinium anion, respectively). Since the film formation properties of Eu (NTA)$_4$(HDP) are not particularly good, it is necessary to add arachidic acid as a film formation material.[15,18] Here we report the fabrication of a new $\lambda/2$ microcavity, using pure terbium complex [tris (1-phenyl-3-methyl-4-hexadecanoyl-5-pyrazolone)(ethanolyl)terbium, Tb(PMHP)$_3$ (EtOH) (Fig. 1)] as the emitting material, and silver as mirrors. The film formation property of Tb(PMHP)$_3$(EtOH) was greatly enhanced compared to Eu(NTA)$_4$(HDP), and no additional materials were necessary. Changes in the emission spectrum and shortening of the fluorescence lifetime were observed.

The synthesis of the emitting material, Tb(PMHP)$_3$ (EtOH) (abbreviated as TbL$_3$), has been reported elsewhere.[18] The surface pressure (π)–area (A) isotherms of TbL$_3$ are recorded by a NIMA 622 Langmuir trough. Pure water (18.0 ± 0.1 MΩ cm, pH 5.6, 20 °C) was applied as a subphase. A Brewster Angle Microscope (BAM) was also used to monitor the π–A isotherm compressing process at 293 K. Results show that in the solid state region of the isotherm, TbL$_3$ forms a highly uniform and homogeneous Langmuir film at the air/water interface. The recorded isotherms of compression–expansion exhibit strong hysteresis and the two curves form a complete loop. The compression–expansion loop can be repeated at almost the same positions many times.

The TbL$_3$ Langmuir film has excellent transfer properties: The area changes less than one percent when the surface pressure is fixed at 20 mN/m for 20 min. And TbL$_3$ Langmuir film can be transferred onto either hydrophilic or hydrophobic substrates. When deposited onto a hydrophilic quartz substrate, the accumulation could be as many as 100 layers at unit transfer ratio. The excellent transfer properties of this complex make it very good for controlling the optical length of the cavity.

The structure of the microcavity is shown schematically in Figure 1. Silver was chosen for the metal mirrors due to its superb reflectivity, easy evaporating deposition and its ultraviolet transparency at around 320 nm. The thickness of the silver mirror strongly influences its reflectivity and transmissibility.[15] In this work, the thickness of the semi-reflective mirror was 80 nm while the totally reflective mirror was 200 nm thick. The thickness of the semi-reflective mirror was measured by the ultraviolet absorption method at 265 nm. The freshly evaporated semi-reflective silver mirror was fumed in propylmercaptan gas for 24 h at room temperature to obtain a good lipophilic surface. This self-assembled membrane of propylmercaptan molecules im-

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ADVANCED MATERIALS

proves the deposition of the LB film without any change in cavity properties. The TbL₃ Langmuir film was deposited onto the lipophilic pretreated silver film in Y-type through the vertical dipping method, under a surface pressure of 20 mN/m at a dipping speed of 3 mm/min. To vary the cavity optical lengths, the layer number of the Y-type TbL₃ LB film, terminated by the two silver mirrors, was increased from 42 to 86 at two-layer intervals. Since the optical length of the cavity can not be predicted theoretically (because of the microscopic disorder in the molecular orientation and the penetration length in the silver film), the vertical optical lengths of the microcavities were measured by the multibeam reflective interference method (Schimadzu UV-3100 spectrophotometer). The first and the second interference peaks of the cavities were clearly observed in the reflective spectra. This indicates that the microcavities were successfully fabricated. According to the reflectivity of the silver mirrors, the Q-factor was calculated to be 61.
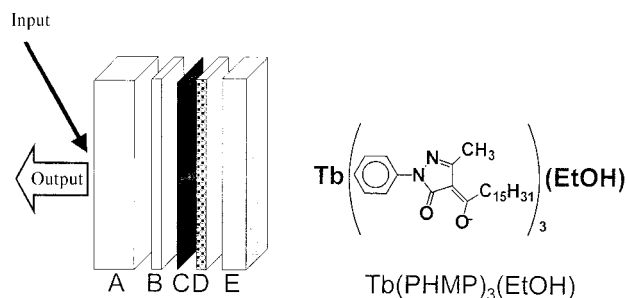

Fig. 1. Schematic structure of the microcavity. A: polished fused quartz substrate, B: semi-reflective silver mirror, C: self-assembled monolayer of propylmercaptan, D: Y-type LB films of TbL₃, E: totally reflective silver mirror.

In our experiment, a 317.5 nm ultraviolet laser was used as the exciting source, while fluorescence intensity and lifetime were measured simultaneously. Figure 2 shows the fluorescence spectrum of the naked LB film of TbL₃. The four characteristic fluorescence emission peaks of Tb^{3+} around 490, 545, 585 and 620 nm correspond to $^5D_4 \rightarrow {}^7F_6$ (induced electric dipole), $^5D_4 \rightarrow {}^7F_5$ (magnetic dipole), $^5D_4 \rightarrow {}^7F_4$ (magnetic dipole) and $^5D_4 \rightarrow {}^7F_3$ (magnetic dipole) transitions, respectively.[16] Our experiments showed that in naked LB films, microcavity and powdery samples, the positions of the emission peaks were almost the same. But microcavities with different optical lengths had different shaped emission spectra compared with those in solid samples (Fig. 2). In one resonant microcavity, some transitions were remarkably enhanced while others were significantly depressed. Compared with the 490 nm emission peak (Fig. 2), the main emission transition ($^5D_4 \rightarrow {}^7F_5$, 545 nm) was strongly increased (approximately 30 times more intense than that of the powdery sample) in the 58 layer microcavity (where twice the vertical optical length was 535 nm), while substantially decreased (as weak as 1/30 of the powder) in the 50 layer microcavity (where twice the vertical optical length was 484 nm). More excitingly, the

two extremely weak transitions around 650 nm ($^5D_4 \rightarrow {}^7F_2$) and 680 nm ($^5D_4 \rightarrow {}^7F_1$) were clearly observed from the thicker microcavity (Figure 2b, line e). The vertical emitting colors from the microcavities could be clearly observed even with the naked eye, varying from blue–green to orange with increasing layer number of the TbL₃ LB film. These phenomena confirm the cavity emission wavelength selectivity (Fig. 2), which makes it possible to use cavity quantum electrodynamics effects to alter spontaneous and stimulated emissions in this novel terbium complex.
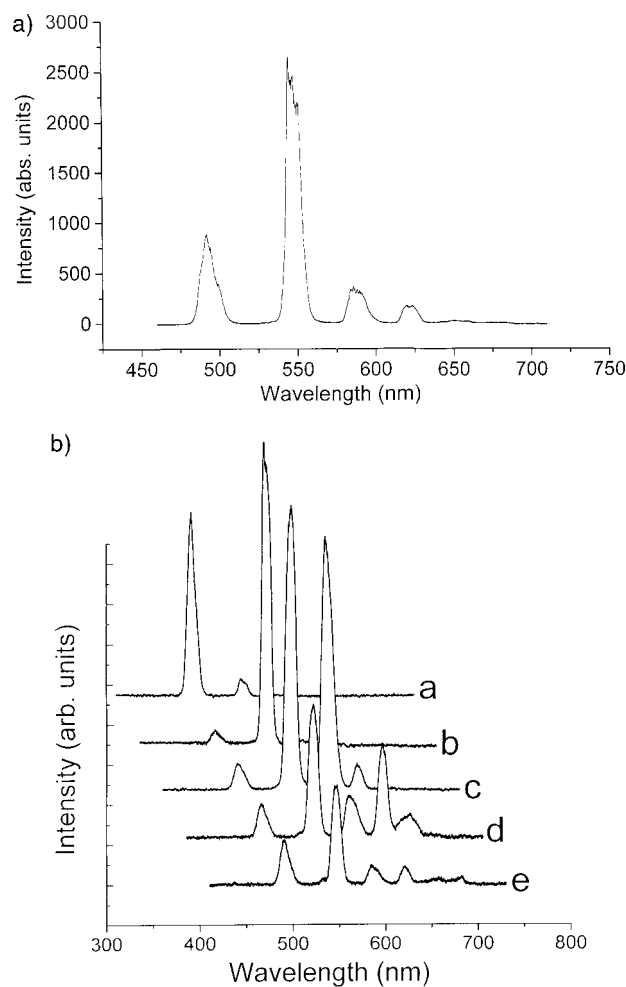

Fig. 2. a) The fluorescence emission spectrum of naked LB film (70 layers) of TbL₃. b) The fluorescence emission spectra of TbL₃ LB film microcavities (a, b, c, d and e correspond to 50, 58, 66, 74 and 82 layers, respectively).

The fluorescence emission decay curves at 545 nm were measured for the powdery complex and microcavities with various optical lengths. All the decay curves were single exponential and the fluorescence lifetimes were obtained through the least squares method. All the lifetime measurements were made under the same conditions. The lifetime of the powdery complex was around 900 μs and those of the microcavities with different optical lengths are shown in Figure 3. Clearly, the optical length of the microcavity

ADVANCED MATERIALS

strongly affects the fluorescence lifetime of the TbL₃ complex. The lifetime was shortest when the cavity optical length was equal to the half-wavelength of the emission peak. This lifetime shortening provides further evidence for the successful fabrication of the resonant microcavity.
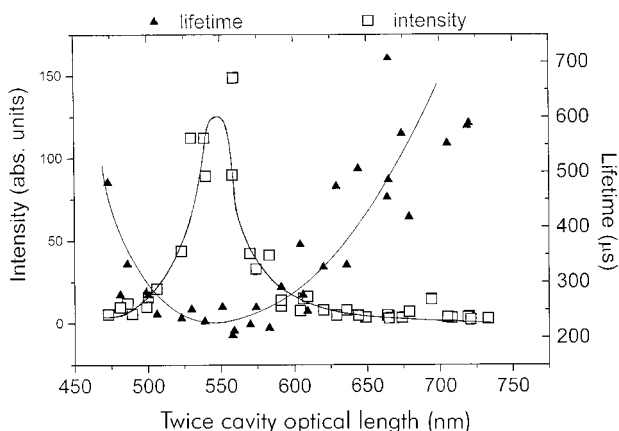

Fig. 3. The relationship between fluorescence (intensity and lifetime) and the cavity optical length for the 545 nm emission.

To understand the incident energy effect, a microcavity with thinner semi-reflective silver mirror (50 nm) was fabricated (Q-factor = 46). Figure 4 shows how the fluorescence intensity and lifetime (at 545 nm) of the TbL₃ complex varied with increasing exciting power. As further confirmation of the microcavity effect, the fluorescence lifetime was shortened sharply with the increase in incident energy. Furthermore, the rapid increase in the fluorescence emission intensity can be viewed as a lasing phenomenon of this microcavity structure resonator. The higher incident energies caused some degradation in emission because of damage to the silver mirrors. This was the first observation in a microcavity using a pure rare earth complex as the emitting material.
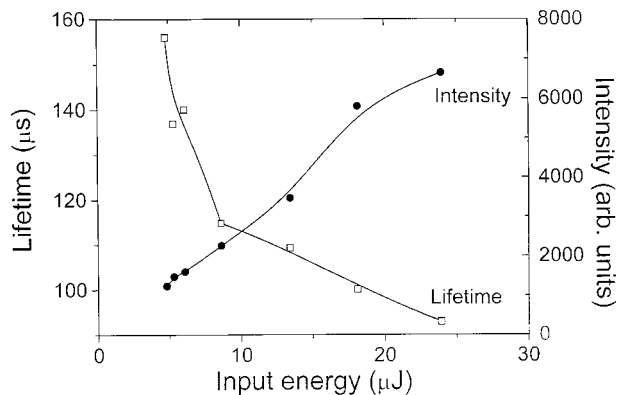

Fig. 4. The relationship between fluorescence (intensity and lifetime) and the excitation pulse energy for the 545 nm emission.

The angular distribution of the microcavity was recorded (the monitoring cone was 18°). When the viewing angle

was shifted from the vertical axis (0°) to 6°, the emission intensity decreased rapidly without any obvious change in the shape of the emission spectra around 545 nm. However, at 20°, the highest position of the emission peak was evidently blue-shifted. This reflects the excellent microcavity emission directionality, an important characteristic of a good microcavity.

In conclusion, a $\lambda/2$ resonant microcavity has been successfully fabricated using just a terbium complex as the emitting material. Two important microcavity effects, fluorescence intensity enhancement and lifetime shortening, have been observed for the first time from a series of resonant microcavities terminated by a pair of silver mirrors. This provides evidence for optically driven microcavities based on rare earth complexes.

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