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Two-dimensional optical waveguiding and luminescence vapochromic properties of 8-hydroxyquinoline zinc (Znq_2) hexagonal microsheets

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Two-dimensional (2D) hexagonal microsheets of 8-hydroxyquinoline zinc (Znq_2) were synthesized readily via a mixed solvent induced self-assembly method. The 2D optical waveguiding properties of the microsheets have been clearly revealed by both fluorescence microscopy and confocal microscopy. In addition, the reversible vapochromic properties of the microsheets have also been demonstrated when the Znq_2 is exposed to HCl and NH_3 vapors.

Organic micro- and nanomaterials have attracted increasing attention due to their potential promising optoelectronic applications, such as field-effect transistors (FETs) transistors (FETs), photodetectors, optical waveguides and chemical chromic sensors.[1] For example, a prototypical green-emitting organic molecule, 9,10-bis(phenylethynyl)anthracene (BPEA) can self-assemble to one-dimensional (1D) microtubes, which can serve as active optical waveguides.[2] To date, most researchers have paid their attention to the optoelectronic properties of 1D organic micro- and nanostructures. The controlled synthesis of 2D organic micro- and nanosheets still remains a great challenge and their optoelectronic performance investigations are fairly scarce. Typically, square organic micro-tiles from hexaphenylsiloles (HPSs) have been used to investigate their optical waveguiding behaviors.[3] Inspired by this success, we investigate whether the controlled synthesis of 2D organic micro- and nanomaterials can be extended to more organic systems, such as metal-organic coordination complexes. On the other hand, luminescence vapochromic materials, as a kind of materials with luminescence changeable ability by vapor stimulating, can be used as sensors for detection air pollution.[4] However, luminescence vapochromic materials based on organic molecules are generally difficult to design and synthesize.[5] Hence, the fabrication of 2D organic micro- and nanosheets with luminescence vapochromic properties is a subject of significant interest in a simple manner.

As a series of typical luminescent metal-organic complexes, metal 8-hydroxyquinoline (Mqn) molecules are particularly attractive in view of their remarkable thermal stability and high fluorescent quantum efficiency.[6] For example, tris-(8-hydroxyquinoline) aluminum (Alq_3) has been widely used in emitting and electron-transporting layer in organic light-emitting diode (OLED) devices.[7] Other Mqn complexes, such as Znq_2, has been demonstrated to exhibit a lower operating voltage as compared to the case of Alq_3 in OLED devices.[8] However, the research reports about Znq_2 micro- and nanostructures have been rare although it may be a promising alternative to Alq_3.[9] Herein, we first report the controlled preparation of 2D hexagonal microsheets of Znq_2 via a facile mixed solvent induced self-assembly method. The remarkable 2D optical waveguiding properties have been clearly demonstrated from fluorescence microscopy results of the hexagonal Znq_2 microsheets. Confocal technique was also used to further explore the detailed optical waveguiding behaviors of the Znq_2 microsheets. Moreover, the 2D microsheets exhibit reversible luminescence vapochromic characteristics. Specifically, the Znq_2 microsheet film undergoes an obvious color change from green to blue when exposed to HCl vapor, while the blue film can also change into yellow when exposed to NH_3 vapor. In addition, the yellow film can recover to original green color after a short heating process.

As shown in Fig. 1, 2D hexagonal microsheets of Znq_2 with well-defined morphologies were successfully prepared via a facile mixed solvent induced self-assembly method. In brief, 3 mL of a stock solution of Znq_2 (20 mM) in DMSO was rapidly injected into 2 mL of a 1:1 (v/v) methanol/H_2O mixture under stirring. After injection, the yellow monomer solution turned into cream-colored colloidal suspension within several seconds and was left undisturbed for 30 min. Typical scanning electron microscopy (SEM) images shown in Fig. 1 a and b reveal clearly that the 2D hexagonal microsheets with a smooth surface have an edge length around ~8 μm and a thickness around 1 μm. A typical TEM image of an individual microsheet is given in Fig. 1c and its corresponding selected area electron diffraction (SAED) pattern is shown in the inset. Combined with the powder X-ray diffraction (XRD) patterns simulated based on the bulk crystals of Znq_2 (Fig. S1 in ESI), it can be concluded that the 2D microsheets have single crystal structures and the growth direction of the microsheets perpendicular to the substrate is [100]. To determine the structural characteristics and intermolecular interactions of Znq_2 microsheets, the equilibrium shape of Znq_2 crystal was simulated by Materials Studio package[10], as showed in Fig. 1d. Based on the simulation results according to BFDH law[11], we can recognize the % total facet area of the (100) face with double multiplicity is 50.66%, much larger than other faces (Tab.S3 in ESI). The large total facet area of (100) and (-100) faces based on the simulation makes the Znq_2 tend to form stable sheet-like structure, which is according with the above-mentioned SEM and TEM results. Besides strong π–π stacking along the [010] direction, we propose that hydrogen-bonding interactions (Fig. S2 in ESI) should be also responsible for the formation of 2D hexagonal microsheets of Znq_2.

As shown in the inset of Fig. 2a, Znq_2/DMSO solution exhibits yellow light, while Znq_2 microsheet suspension shows strong green light upon excitation with a UV lamp. To further examine their optical properties, steady-state spectrum measurements of the monomer solution and microsheets of Znq_2 shown in Fig. 2a were also preformed. The excitation spectrum of the monomer in DMSO presents a characteristic absorption peak at 407 nm. Besides the peak at 407 nm, one can see that another absorption peak of the monomer solution is around 342 nm, compared to the hexagonal microsheets suspension. The emission spectrum of Znq_2 microsheets clearly shows a green emission band at 497 nm when excited by 365 nm. Remarkably, the photoluminescence (PL) of Znq_2 in DMSO is red-shifted from 497 to 565 nm upon excitation by 365 nm, indicating strong polar solvent effects of DMSO[12]. Fig. 2b shows fluorescence microscopy images of the hexagonal Znq_2 microsheets excited with unfocused UV light (330–380 nm). It can be clearly observed that the Znq_2 microsheets exhibit strong green emission, which is consistent with their characteristic PL. Significantly, only the edges of the Znq_2 microsheets exhibit bright emission and the main bodies are nearly nonemissive, suggesting that the Znq_2 microsheets show typical 2D optical waveguides.

To investigate the 2D optical waveguiding behaviors of the Znq_2 microsheets, the spatially resolved PL spectra of a typical microsheet excited by a 408 nm laser were obtained (Fig. 3a). The six edges show brighter green emission than the microsheet surface, revealing that efficient light guiding can occur within 2D microsheets of Znq_2. Fig. 3b shows the collected PL spectra at the midpoint of the right edge by changing the position of the excitation laser beam. It can be clearly noticed that the emission intensity at the midpoint of the edge increases with decreasing the propagation length. A logarithmic scale of the peak intensity of the outputting light for each spectrum in Fig. 3b decays almost linearly with the propagation distance, as depicted in Fig. 3b inset. The average evaluation of the optical loss coefficient was estimated to be 0.022 dB μm^{-1}, which is much lower than that for other organic materials. These results exhibit that the Znq_2 microsheets can serve as an active optical waveguide material due to its smooth surface, high crystallinity and negligible re-absorption. Fig. 3c displays the high-resolution fluorescence spectrum of a mircosheet. It could be implied that the emitted light might be blocked at boundaries by reflection by noting that the strong green out-coupled light from the edges of microsheet shown in Fig. 3a. This kind of reflection leads to the photon confinement in a Znq_2 microsheet, to forming a quasi-whispering-gallery-mode (quasi-WGM) optical resonance cavity.[13] We can calculate the optical path of inner light transport is about 35 μm, nearly 0.4 times of the perimeter of microsheet, by $L = \lambda^2/n\Delta\lambda$, where $\Delta\lambda$ is the wavelength interval between two peaks, λ is the light wavelength, and n (around 1.5) is the refractive index, which providing an evidence that the inner reflection at six edges of the microsheet leads to the quasi-WGM mode in the planar cavity.

It's worth noting that Znq_2 microsheets also have the remarkable characteristic of vapochromic luminescence. Specifically, the Znq_2 microsheet film was first deposited by a simple spin coating method and it emits strong and uniform green luminescence (λ_{em}= 498 nm) when excited by UV light, as shown in the inset of Fig. 4a. Unexpectedly, the green-emitting film can convert to blue light (λ_{em}= 475 nm) upon exposure to saturated HCl vapor for approximately 5 minutes. Meanwhile, we found that the blue-emitting film shows high NH_3 sensitivity and it will be changed into yellow light (λ_{em}= 582 nm) immediately even exposure to trace amount of NH_3 vapor. Moreover, the yellow-emitting film can recover to original green color after a short heating process. Importantly, the Znq_2 microsheet film exhibits reversible vapochromic properties without obvious loss of emission intensity and remains its remarkable gas sensing ability after several stimulus cycles (Fig. 4b and Fig. S5). The luminescence vapochromism mechanism of the Znq_2 microsheet film is believed to originate from the coordination interaction of chlorine ions and NH_3 with zinc (II) center, thereby greatly changing the original coordination structure and crystal configuration of Znq_2 hydrate. A short heating process can drive the gas molecules release to the air and vapochromic Znq_2 film can recover to green color of Znq_2 hydrate,[14] which can be further demonstrated based on the different crystal structures of green-, blue-, and yellow-emitting Znq_2 film, as the XRD patterns shown in Fig. S4. The detail vapochromic study remains to be further carried out to achieve a practical application of gas sensing.

Conclusions

In summary, we have reported the controlled synthesis of two-dimensional (2D) hexagonal microsheets of Znq_2 using a mixed solvent induced self-assembly method. The single-crystalline Znq_2 microsheets exhibit outstanding optical waveguiding behaviors with the lower waveguide loss efficiency. Moreover, Znq_2 microsheets can be regarded as planar optical microcavities in which the crystal edges can confine the emitted photons by reflection. In addition, the Znq_2 microsheet film displays remarkable luminescence vapochromic properties and exhibits good vapochrimism repeatability. Thus, the multifunctional 2D Znq_2 microsheets have a promising application as chemical sensor and active photonic devices.

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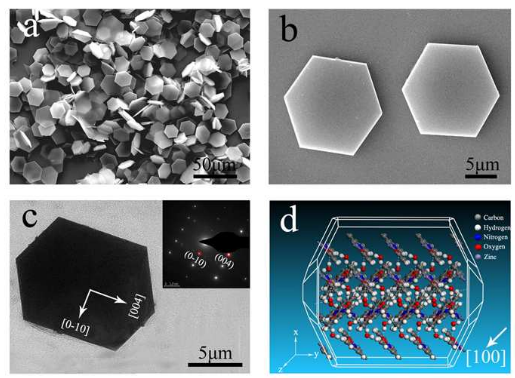

Fig. 1 SEM images of the Znq_2 microsheets at a) low and b) high magnification. c) TEM image of a typical Znq_2 microsheet. Inset shows the corresponding SAED pattern. d) The predicted growth morphology of Znq_2 molecules based on BFDH law.

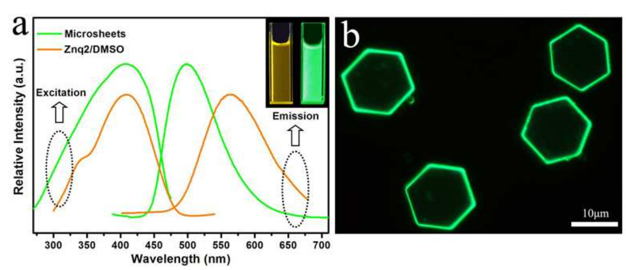

Fig. 2 a) Excitation and emission spectra of Znq_2/DMSO solution (yellow) and Znq_2 microsheets (green). Inset shows the photographs of Znq_2/DMSO solution (left) and Znq_2 microsheet suspension (right) under a UV lamp (365 nm). b) Fluorescence microscopy image of Znq_2 microsheets excited with the unfocused UV light.

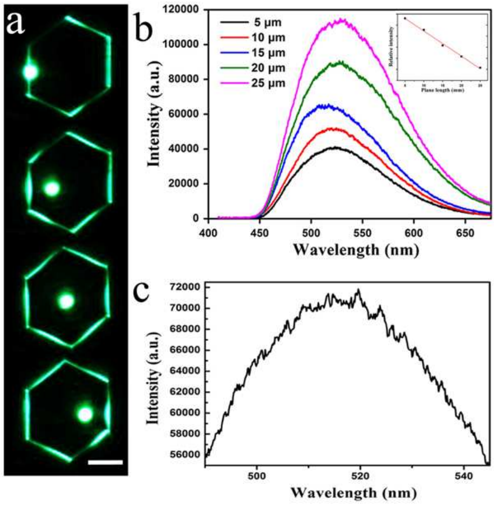

Fig. 3 a) PL images obtained from a single typical Znq_2 microsheet by exciting different positions. The scale bar is 10 µm. b) Spatially resolved PL spectra from the midpoint of the right edge for different separation distances between the excitation spot and midpoint of the right edge shown in (a). Inset shows the logarithmic plots of relative intensities of PL peaks at 520 nm versus distance between excitation and out-coupling spots for the PL spectra. c) Modulated PL spectra of the microsheet.

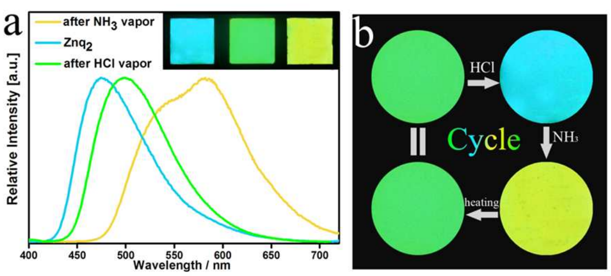

Fig. 4 a) Steady-state emission spectra of Znq_2 microsheets films spin-coated on a quartz substrate (green) and after exposed to HCl (blue) and NH_3 vapors (yellow) upon excitation with 365 nm. Insets show the corresponding photographs under a UV lamp (365 nm). b) The reversible luminescence vapochromic schematic diagram of Znq_2 microsheet films after exposure to HCl and NH_3 vapors.