

Thin film of sulfonated zinc phthalocyanine/layered double hydroxide for achieving multiple quantum well structure and polarized luminescence†

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Ordered thin films based on alternate assembly of zinc phthalocyanine complex and layered double hydroxide monolayers have been fabricated, which exhibit multiple quantum well structure and well-defined polarized luminescence.

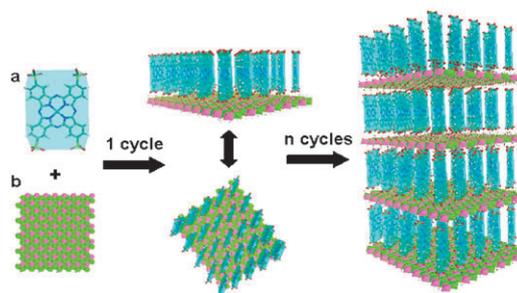
The family of phthalocyanines (Pc) and metal Pc (MPc) have attracted great attention from industry and for fundamental interest, owing to their potential applications in organic optoelectronic devices (such as solar cells¹ and nonlinear optical materials²) based on an excellent two-dimensional 18 π -electron system. Their easily-tunable electronic structure also offers a great opportunity to design and construct diverse supramolecular architectures.³ However, some problems remain unresolved for the Pc-based materials. Firstly, the Pc molecule with a two-dimensional conjugated plane results in the formation of aggregation, which will lead to photoemission red-shifts, broadening and even quenching. Secondly, the low band gap of these materials can induce strong nonradiative relaxation in the excitation process. Thirdly, the interactions between d orbitals of the metals (such as Cu, Co, Ni, Fe) and the frontier orbitals of Pc severely decrease their fluorescent lifetime and efficiency. Therefore, it is still a challenge to further improve the optical properties of Pc-based materials for developing new types of optoelectronic devices.

Layered double hydroxides (LDHs) are a large class of host materials, which can be described by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{z+}A^{n-}_{z/n} \cdot yH_2O$. M^{II} and M^{III} are divalent and trivalent metals respectively; A^{n-} is the anion.⁴ Recently, the delamination of LDHs into single nanosheets and the fabrication of organic-inorganic functional thin films (TFs) have drawn much interest.^{4b,c} Moreover, the orderly assembled thin film systems based on the photoactive anions (PA) and the LDH monolayer also result in one type of novel luminescence materials with the following advantages: (1) the LDH monolayer provides PA with a regular microenvironment to isolate them from each other between adjacent layers and thus reduce the interlayer π - π stacking interaction; (2) the two-dimensional uniform orientation of the guest anions

within the rigid LDH matrix is favorable for the polarized photoemission;^{4d} (3) the energy confined effect of LDH imposing on the PA achieves a new class of organic-inorganic multiple quantum well (MQW) structure with improved stability of the valence electron of the PA.^{4e,f} To date, the MQW structure has only been demonstrated in π -conjugated polymers/LDH films, and whether it can be extended to other PA/LDH systems or not remains unresolved.

The previous reports about the MPc incorporated into LDH systems were mainly concerned with their catalysis properties.^{4h} In this work, ordered MPc-LDH TFs have been constructed based on the anionic zinc tetrasulphophthalocyanine (Scheme 1a, ZnTSPc, with the longest fluorescent lifetimes and higher quantum yields than other MPcs⁵) and exfoliated Mg-Al-LDH monolayers (Scheme 1b) as the basic building blocks, by using the layer-by-layer (LBL) method. The resulting ZnTSPc/LDH TF system presents a long-range ordered structure and well-defined fluorescence with macroscopic luminescence anisotropy. A periodic density functional theoretical (PDM) calculation illustrates that the ZnTSPc/LDH system exhibits MQW structure, which facilitates the enhancement of light-emitting efficiency for photofunctional Pc molecules. The LBL method is a facile approach to design and fabricate novel MPc/LDH light-emitting TFs with polarized luminescence and MQW structures.

UV-vis absorption spectra measurements were employed to monitor the assembly process of the $(ZnTSPc/LDH)_n$ TFs ($n = 4-32$, Fig. 1a). The characteristic absorption bands of ZnTSPc can be observed at 343 (B-band), 688 (Q-band) and 642 nm (vibrational bands associated with the reduction in the symmetry),⁷ whose intensity correlates linearly with the number of bilayer, n (Fig. 1a, inset), demonstrating an ordered



Scheme 1 Assembly process of ZnTSPc/LDH TFs: (a) the chemical formula of ZnTSPc; (b) the representation for the monolayer of Mg-Al-LDH (dark pink: $Al(OH)_6$ octahedra; green: $Mg(OH)_6$ octahedra).

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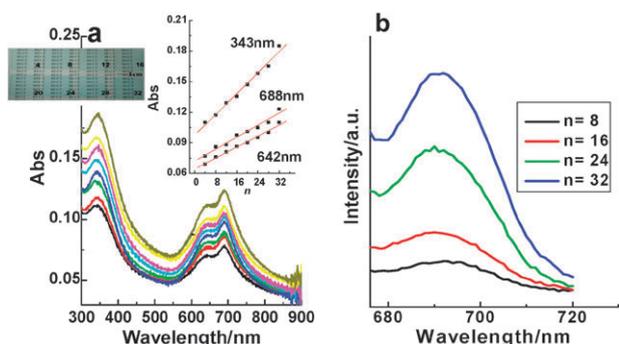


Fig. 1 Optical spectra of $(\text{ZnTSPc/LDH})_n$ ($n = 4\text{--}32$) TFs: (a) UV-vis absorption spectra, (b) photoluminescence spectra. The inset in (a) shows the plots of absorbance at 343, 688 and 642 nm vs. n and the photographs of TFs, respectively.

and regular film growth procedure. The photograph of the TFs under daylight (inset in Fig. 1a) provides a visual verification of the gradual color enhancement upon increasing n . The TFs also exhibit the fluorescence emission at *ca.* 690 nm with enhanced intensity along with n . Compared with the ZnTSPc pristine solution (Fig. S1 in the ESI), no shift in fluorescence emission for the as-prepared TFs with different bilayers was observed, suggesting that the emission of the TFs mainly arises from the monomeric ZnTSPc species throughout the whole assembly process. X-ray diffraction (XRD) patterns (Fig. S2) of the as-prepared TFs show the appearance of a (001) reflection at *ca.* $3.5\text{--}3.6^\circ$, and the peak intensity increases with the increase of bilayer number, indicating that the TFs possess a periodic structure in the normal direction of the film with a period of *ca.* 2.5 nm.

The deposition process of $(\text{ZnTSPc/LDH})_n$ TFs was further monitored by atomic force microscopy and scanning electron microscopy (AFM and SEM) measurements. The surface roughness of the TFs ($n = 8\text{--}32$) ranges from 6.2–13.7 nm (Table S1) obtained by AFM, and the film roughness will not influence the periodic assembly of the ZnTSPc/LDH obviously, as XRD results shown above. The thickness increases linearly from 24 to 83 nm ($n = 8\text{--}32$) from the side-view image of SEM (Fig. S3 and S4), confirming the uniform and periodic structure of the TFs, in agreement with the results revealed by UV-vis and fluorescence spectra described above. A typical top-view SEM image for the

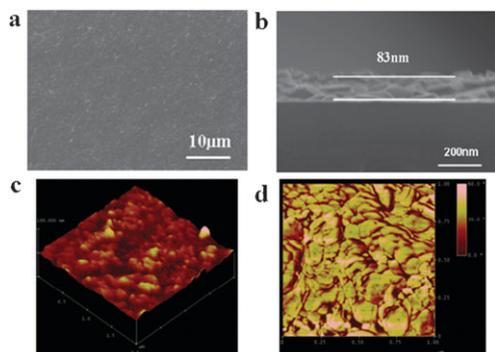


Fig. 2 The morphology of $(\text{ZnTSPc/LDH})_{32}$ TF: (a) top view and (b) side view SEM image; (c) and (d) are the tapping-mode AFM topographic and phase image, respectively.

$(\text{ZnTSPc/LDH})_{32}$ TF (Fig. 2a) shows that the film surface is continuous and homogeneous; moreover, the side view SEM image (Fig. 2b) indicates a thickness of *ca.* 2.6 nm for one bilayer of ZnTSPc/LDH, well consistent with that of XRD observation. The AFM topographical and phase images (Fig. 2c and d) reveal a root-mean square roughness of 13.7 nm, indicating a relatively smooth surface.

The orderly assembled structure of the ZnTSPc/LDH TFs inspired us to exploit their polarized luminescence properties, and the glancing incidence geometry was employed to determine the luminescence anisotropic value r .^{6,8} Compared with ZnTSPc aqueous solution and film samples with low luminescence polarization (Fig. S5), the ZnTSPc/LDH TFs show well-defined photoluminescence between the parallel and perpendicular to the excitation polarized direction (I_{VV} vs. I_{VH}) with the anisotropic value (r) of 0.25–0.28. A typical example for the TFs with 32 bilayers with the I_{VV}/I_{VH} ratio of 2.43 is shown in Fig. 3a. The high r can be attributed to the regular alignment of ZnTSPc anions between LDH monolayers; in addition, the uniform r value ranging from 660–720 nm indicates that polarization scrambling *via* Förster transfer is minimal in the TF.^{4e} Furthermore, the r value is nearly independent of the bilayer number as shown in Fig. 3b. This indicates that the film thickness imposes no obvious influence on macroscopic polarized luminescence of ZnTSPc/LDH TFs throughout the whole assembly process, since the LBL method ensures an ordered assembly of the film.

To obtain the geometric, electronic structure and the energy level of the ZnTSPc/LDH system, a periodic density functional theoretical (PDM) calculation was employed for the idealized model of ZnTSPc/LDH structure (Fig. S6). The calculation results indicate that there is no obvious change in the configuration of the confined ZnTSPc compared with its pristine form. Moreover, the frontier orbital analysis (Fig. 4) shows that the electron density of the highest occupied molecular orbitals (HOMOs) is mainly distributed on the C atoms of the heterocyclic ring and phenyl ring in ZnTSPc, while that of the lowest unoccupied molecular orbitals (LUMOs), comprised of two degeneration orbitals, is mainly located on the C and N atoms in the heterocyclic ring due to the presence of electronic transfer from the C to the neighboring N atoms in the excitation process. The Zn atoms do not participate in the frontier orbitals, which facilitates the improvement of the photostability effectively. Similar results were also obtained for the pristine ZnTSPc and ZnPc system

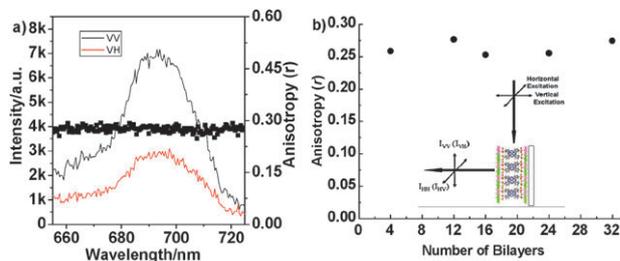


Fig. 3 (a) Polarized fluorescence profiles for the VV, VH modes and anisotropic value (r) for the $(\text{ZnTSPc/LDH})_{32}$ TF; (b) the plot of r averaged in the range 670–710 nm vs. n . The measurement mode with glancing incidence geometry is shown in the inset scheme.

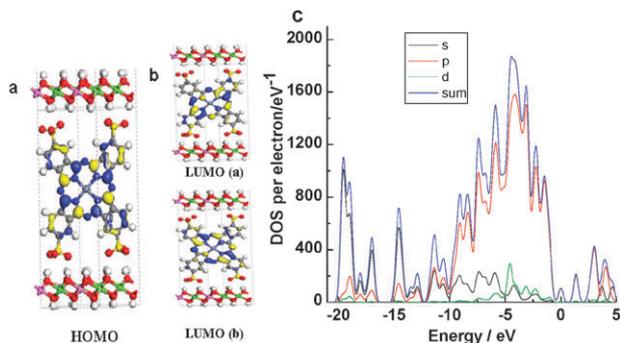


Fig. 4 (a) HOMO and (b) LUMO profiles for the ZnTSPc/LDH system; the two colors denote \pm wave function. (c) TDOS and PDOS for the ZnTSPc/LDH system; the Fermi energy level E_F was set to zero.

(Fig. S7). This indicates that the photo excitation/emission processes for the TFs involve the same mechanism as the free ZnPc-based complex, and no electronic transfer occurs between the LDH and ZnTSPc. The calculations also show that the ZnTSPc/LDH system has a low band gap of *ca.* 1.41 eV at the Γ point (0,0,0) in the first Brillouin Zone (Fig. S8), rather close to that of the pristine ZnTSPc (1.42 eV) and ZnPc (1.45 eV) system (Table S2). Total electronic densities of states (TDOS) and partial electronic densities of states (PDOS) analysis (Fig. 4c, S9, S10) reveal that the O 2p and Mg/Al 3s, H 1s orbitals from the LDH monolayers contribute to the TDOS below and above the HOMO and LUMO, respectively, with a gap of *ca.* 5.7 eV. Around the Fermi level, the TDOS mainly consists of the 2p electrons of conjugated C atoms in ZnTSPc anions. Therefore, the photo excitation process of the ZnTSPc remains practically unchanged upon assembly in the LDH matrix, whereas the Mg–Al–LDH monolayers remain inert. This further indicates that the valence electrons localized in the ZnTSPc are confined within the energy blocking imposed by the LDH monolayers. Therefore, the ZnTSPc/LDH system serves as a multiple quantum well (MQW) structure, which is beneficial to the stabilization of the valence electronic orbital energy for ZnTSPc complex. Although MQW structures have been widely studied in pristine inorganic^{9a} and organic^{9b} systems,^{5d,e} very few observations based on metal complex and inorganic component were reported. The as-fabricated ZnTSPc/LDH TF can be regarded as a new type of hybrid MQW structure, which exhibits host–guest interactions including the electrostatic and/or van der Waals force between two alternate layers.

In summary, ordered (ZnTSPc/LDH)_n TFs were constructed by the use of the LBL technique and show periodic long-range order structure and well-defined photoemission. Polarized luminescence was obtained from this new type of ZnTSPc complex/LDH TFs. A PDFT calculation demonstrates that the ZnTSPc/LDH TF has a low band gap. The light-emitting properties and electronic

structures of the assembled ZnTSPc between the LDH monolayer are nearly invariable compared with its pristine state. No electron delocalization occurs between ZnTSPc and LDH monolayer at the top of the valence band, indicating that the LDH monolayer functions as an energy well layer, which hampers the interlayer interaction of the ZnTSPc. Therefore, the TF can be regarded as a new type of hybrid MQW structure based on metal-complex and inorganic materials. By the combination of experimental and theoretical studies on the ZnTSPc/LDH TFs, a detailed understanding of the geometric and electronic structures of the ZnTSPc chromophore confined between the LDH monolayers was presented. It can be expected that, by designing and tuning the component, diversity and alignment of the light-emitting complex in the energy wells formed by the LDH monolayers, the multi-functional TFs combining the polarized luminescence and MQW structure can be readily extended and applicable to other systems, which have much flexibility and potential applications for the design of various opto-electrical devices.

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