Layer-by-layer assembly of ruthenium(II) complex anion/layered double hydroxide ordered ultrathin films with polarized luminescence[†]

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Ordered ultrathin films of tris(1,10-phenanthroline-4,7-diphenylsulfonate)ruthenium(II) anions and cationic layered double hydroxide monolayers have been fabricated by the layerby-layer assembly technique and show well-defined polarized red luminescence.

Transition-metal-based photoactive complexes (PC) have received a great deal of attention during the last two decades, because their chemical stability and excellent luminescence properties give rise to many possible applications in optoelectronics.¹ Ruthenium-based complexes that feature a metal-to-ligand charge transfer (MLCT) transition mechanism are an important class of such materials, and they have been extensively investigated in solid-state phosphorescent light-emitting devices² and electrochemical cells.³ Generally, oriented photoemissive structures, such as one-dimensional luminescent polymers, show well-polarized luminescence character which can be employed in liquid-crystal displays.⁴ However, except for the recent work of Galyametdinov,⁵ very little attention has been focused on the polarized luminescence characteristics of PC materials, owing to the highly symmetric structure and low luminescence anisotropy of most of these complexes, e.g. the 8-hydroxyquinoline aluminium complex exhibits no polarized emission due to its pseudo-spherical structure.⁶ It is therefore desirable to find ways to develop PC materials with polarized luminescence performance in order to incorporate the advantages of such materials in the next generation of optoelectronic devices.7

Layered double hydroxides (LDHs) are a class of naturally occurring and synthetic materials, which can be described by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{z+}(A^{n-})_{z/n}\cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent metals respectively and A^{n-} is the anion which compensates for the positive charges of the metal hydroxide layers.⁸ LDHs can be exfoliated into positively charged monolayers and assembled in alternation with polyanions *via* a layer-by-layer (LBL) technique, resulting in novel ultrathin films (UTFs).⁹ To the best of our knowledge, however, the assembly of LDH monolayers and small anions has never been reported. This restricts

the available range of LDH-based organic-inorganic hybrid functional UTF materials. Moreover, fabrication of an ordered assembly of such luminescent anions with the layered host structure may offer a new method for constructing films with polarized photoemission, since it should be possible to obtain a uniform and ordered orientation of the guest anions within the rigid LDH matrix.¹⁰ Herein, we demonstrate the fabrication of ordered stacked UTFs, based on a small anionic PC and LDH monolayers as building blocks, by the LBL method. The highly symmetric anion $(D_3 \text{ point group})$, tris(1,10-phenanthroline-4,7-diphenylsulfonate)ruthenium(II) $([Ru(dpds)_3]^{4-}$, Scheme 1a), which has been reported to have the highest photoluminescence quantum yield (36%) of all ruthenium complexes,² was chosen as the light-emitting complex to be assembled with exfoliated Mg-Al-LDH monolayers (Scheme 1b).

The multilayer assembly process (Scheme 1c) of the $(\text{Ru}(\text{dpds})_3/\text{LDH})_n$ (n = 4-32) UTFs deposited on quartz substrates was monitored by UV-visible absorption spectroscopy (Fig. 1a). The intensities of the absorption bands at 196, 287 and 471 nm (resulting from a ${}^{1}\text{E}_{1u}$ transition, a π - π * transition, and an MLCT transition of $[\text{Ru}(\text{dpds})_3]^{4-}$, respectively²) correlate nearly linearly with the number of bilayers n (Fig. 1a, inset), indicative of a stepwise and regular deposition procedure with almost equal amounts of $[\text{Ru}(\text{dpds})_3]^{4-}$ incorporated in each cycle. This was confirmed by the gradual increase in the color intensity of the UTFs with increasing number of bilayers (Fig. 1c). The intensity of the sharp luminescence peak with a maximum at *ca*. 615 nm of the (Ru(dpds)_3/LDH)_n UTFs also displays a monotonic increase with *n*, as shown in Fig. 1b. The luminescence wavelength of



Scheme 1 (a) Structure of $[Ru(dpds)_3]^{4-}$; (b) representation of a monolayer of Mg-Al-LDH (dark pink: Al(OH)₆ octahedra; green: Mg(OH)₆ octahedra); (c) assembly process of $(Ru(dpds)_3/LDH)_n$ UTFs.

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the UTFs with different numbers of bilayers is unshifted from that of the original solution of $[Ru(dpds)_3]^{4-}$ (Fig. S1 in the ESI[†]), which suggests the absence of Ru(dpds)₃ aggregates in the UTFs. X-ray diffraction (XRD) indicates that the UTFs adopt an ordered periodic structure in the direction normal to the substrate with a periodicity of *ca.* 2.44 nm (Fig. S2a, Table S1[†]). This is in agreement with an idealized model of the Ru(dpds)₃/LDH assembled system (Fig. S2b[†]).

The surface morphology and thickness of $(\text{Ru}(\text{dpds})_3/\text{LDH})_n$ UTFs were further investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The top view SEM images (Fig. S3†) of the UTFs show both the homogeneity and the increase of surface coverage with increasing *n*, and a typical SEM image for the $(\text{Ru}(\text{dpds})_3/\text{LDH})_{28}$ UTF is shown in Fig. 2a. The thickness of films with varying numbers of bilayers can be estimated from their side view SEM images



Fig. 1 (a) UV-visible absorption spectra, (b) photoluminescence spectra, and (c) photographs of $(\text{Ru}(\text{dpds})_3/\text{LDH})_n$ (n = 4-32) UTFs. The inset in (a) shows plots of the absorbance at 196, 287 and 471 nm *vs. n.*



Fig. 2 Morphology of $(Ru(dpds)_3/LDH)_{28}$ UTF in (a) top view SEM image, (b) side view SEM image, (c) tapping-mode AFM image, and (d) fluorescence microscope image.

(Fig. S4[†], Fig. 2b). The approximately linear increase in the thickness with *n*, with an average thickness increment of *ca*. 2.1 nm per bilayer cycle (Table S2[†]), consistent with the XRD measurements, confirms that the UTFs have a uniform and periodic layered structure. The AFM topographical image $(2 \ \mu m \times 2 \ \mu m)$ of the $(Ru(dpds)_3/LDH)_{28}$ UTF is shown in Fig. 2c. The value of root-mean-square (rms) roughness for the UTFs increases slowly with the number of deposition cycles (Table S2[†]), from 6.8 nm for 4 bilayers to 10.6 nm for 28 bilayers, indicating that all the films have relatively smooth surfaces. Furthermore, the $(Ru(dpds)_3/LDH)_{28}$ UTF shows a homogeneous bright orange–red color under a fluorescence microscope (Fig. 2d), indicating that the $[Ru(dpds)_3]^{4-}$ chromophore anions are distributed uniformly throughout the UTF.

To further investigate the luminescence properties of the as-prepared UTFs, polarized luminescence measurements (with the glancing incidence geometry as shown in Fig. 3) were employed to measure the luminescence anisotropy value r.¹¹ In contrast to the aqueous solution of $[Ru(dpds)_3]^{4-1}$ which shows essentially no luminescence polarization (r = 0.02), the $(Ru(dpds)_3/LDH)_n$ UTFs showed a well-defined red photoluminescence anisotropy, and a typical example for the film with 28 bilayers is shown in Fig. S5.[†] Values of r in the range 0.20–0.30 were observed when comparing the parallel and perpendicular directions to the excitation polarization (I_{VV} vs. I_{VH}) for the in-plane polarized excitation light. This is slightly less than the highest reported value of 0.4 for a system lacking molecular macroscopic alignment and possessing absorption transition dipoles parallel with the emission one.¹² Moreover, the r value increases systematically upon increasing the number of bilayers from n = 4 to 16 (Fig. 3), indicating the improvement in the macroscopic polarization characteristics and the increase in the extent of orientation of the alignment of $[Ru(dpds)_3]^{4-1}$ between the LDH monolayers.

To better understand the geometric and electronic structures of the Ru(dpds)₃/LDH system, periodic density functional theoretical (DFT) calculations were performed for the idealized model of the Ru(dpds)₃/LDH and the pristine [Ru(dpds)₃]⁴⁻ structure (Fig. S6†). The calculated interlayer



Fig. 3 Plot of luminescence anisotropy values (r) averaged in the range 550–650 nm *vs.* number of bilayers (the measurement mode, with glancing incidence geometry, is shown in the inset scheme).

spacing of the Ru(dpds)₃/LDH system is 2.51 nm, very close to that observed experimentally by XRD and SEM. The most significant change in the geometry of $[Ru(dpds)_3]^{4-}$ upon being assembled with LDH monolayers is that the S-Ru-S angles increase from 71.0° (Fig. S6a⁺) to 110.4° (Fig. S6b⁺), demonstrating that the $[Ru(dpds)_3]^{4-}$ anion undergoes a dramatic reduction in symmetry as a result of the electronic interactions between LDH monolayers and the anions. This may be responsible for the polarized photoemission observed for Ru(dpds)₂/LDH UTFs. Moreover, the frontier orbital analysis shows that for the Ru(dpds)₃/LDH system, the highest occupied molecular orbitals (HOMOs) are only populated on the Ru atom, and the lowest unoccupied molecular orbitals (LUMOs) are mainly distributed on the phenanthroline ring in the dpds anions (Fig. S7c, d[†]). Similar results were also obtained for the pristine $[Ru(dpds)_3]^{4-}$ (Fig. S7a, b⁺). This indicates that the optical excitation/emission processes for the UTFs involve the same MLCT mechanism as the free Ru-based complex. The calculations reveal (Fig. S8[†]) that the Ru(dpds)₃/LDH system has a band gap of 2.14 eV at the Γ point (0,0,0) in the first Brillouin Zone, rather close to that of the pristine $[Ru(dpds)_3]^{4-}$ (2.10 eV). Furthermore, the calculated band gap is close to that of the experimental value for the (Ru(dpds)₃/LDH)₂₈ UTF obtained by cyclic voltammetry measurements (2.21 eV, see Fig. S9[†]). These results confirm that the photoexcitation process of the [Ru(dpds)₃]⁴⁻ remains practically unchanged after intercalation between the LDH monolayers.

In summary, we have demonstrated that the light-emitting complex $[Ru(dpds)_3]^{4-}$ can be co-assembled with LDH monolayers using the LBL technique, resulting in $Ru(dpds)_3/LDH$ UTFs with periodic long-range ordered structures, well-defined red photoluminescence and macroscopic luminescence anisotropy. DFT calculations showed that the interaction of

 $[Ru(dpds)_3]^{4-}$ with the positively charged LDH layers resulted in a major reduction in the symmetry of the anion, which may be responsible for the observed polarized photoluminescence behavior. The light-emitting properties of the Ru(dpds)₃/LDH are nearly identical to those of the pristine $[Ru(dpds)_3]^{4-}$, and this is consistent with calculations showing that the band gaps of Ru(dpds)₃/LDH and [Ru(dpds)₃]⁴⁻ are very similar. This combination of experimental and theoretical studies of Ru(dpds)₃/LDH UTFs involves the first example of the assembly of a photoactive complex and inorganic LDH monolayers, and also provides a detailed understanding of the geometric and electronic structures of the $[Ru(dpds)_3]^{4-}$ chromophore confined between the LDH monolayers. By tuning and controlling the identities of the light-emitting complex and LDH monolayers, it should be possible to fabricate multi-color UTFs using this electrostatic assembly process.

This work therefore opens new ways to design, construct and investigate novel light-emitting UTFs with polarized luminescence which have many potential applications in the design of new opto-electrical devices.

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