

Ordered Poly(*p*-phenylene)/Layered Double Hydroxide Ultrathin Films with Blue Luminescence by Layer-by-Layer Assembly**

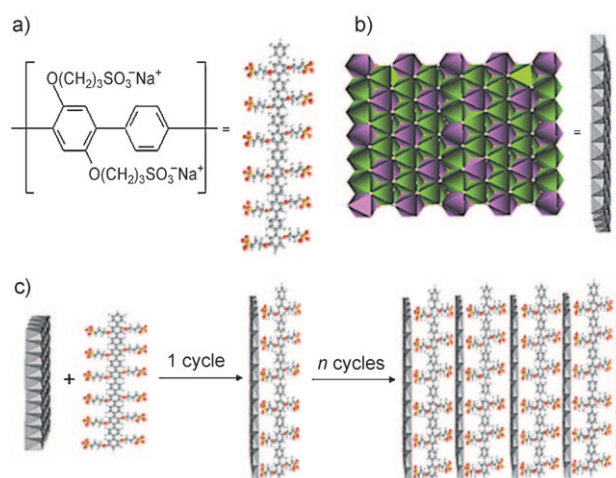
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The π -conjugated polymers (π -CPs), such as poly(*p*-phenylene vinylene) (PPV), poly(*p*-phenylene ethynylene) (PPE), and poly(*p*-phenylene) (PPP), have been received extensive attention recently because of their promising optoelectronic applications in light-emitting diodes (LEDs),^[1] field-effect transistors,^[2] photovoltaic cells,^[3] and bio/chemical sensors.^[4] These luminescent polymers have a rigid-rod chain configuration and intrinsic one-dimensional structural anisotropy, facilitating the preparation of well-oriented thin-film devices with a macroscopic polarized optical effect,^[5] which is used in important applications in optoelectronic devices, such as liquid-crystal displays.^[5a] Key problems, such as fluorescence quenching, short service lifetime, and relatively poor thermal or optical stability, must be resolved when applying the π -CPs that are available to optoelectronic devices, especially for red and blue LEDs. The formation of aggregates in π -CPs can lead to fluorescence red-shifts, broadening, and even quenching owing to the interchain π - π stacking, which is detrimental to their optical applications. Langmuir–Blodgett (LB) films and spin-coating films of PPE, for example, have an undesirable red-shift (or broader emission band) and shorter fluorescence lifetimes, in contrast to their solution counterparts.^[6a] Therefore, much work, including LB techniques and electrostatic layer-by-layer (LBL) assembly by depositing the π -CP with oppositely charged polyelectrolytes, attempts to obtain comparable or superior properties to their solution counterparts.

Layered double hydroxides (LDHs) are one family of pillared solid matrixes that 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 metal ions respectively, and A^{n-} is

the anion compensating for the positive charge of the hydroxide layers.^[7] Recently, some LDHs have been exfoliated into positively charged monolayers, which can be assembled alternately with polyanions into ultrathin films (UTFs) by the LBL technique.^[8] Compared with the flexible chain structure of polyelectrolytes, LDH monolayers are rigid and intralayered crystalline. Therefore, the alternative assembly of π -CPs with rigid LDH monolayers could result in a novel inorganic/organic hybrid UTF, in which the LDH monolayer can provide π -CPs with a more confined and ordered environment for reducing π - π stacking and suppressing the thermal vibration of polymer backbones relating to the nonradiative relaxation of exciting states. Moreover, the existence of inorganic layers may improve the thermal and optical stability of π -CPs.^[7c]

Herein, by using the LBL assembly method, a sulfonated poly(*p*-phenylene) anionic derivate, APPP, was selected to assemble with exfoliated Mg–Al–LDH monolayers (Scheme 1). The components were alternatively deposited



Scheme 1. a) The chemical formula of APPP. b) A representation of one sheet of Mg–Al layered double hydroxide (Mg–Al–LDH; purple: $Al(OH)_6$ octahedra; green: $Mg(OH)_6$ octahedra). c) Assembly process for $(APPP/LDH)_n$ UTF.

to fabricate $(APPP/LDH)_n$ UTF ($n = 3–30$), which has well-defined blue fluorescence and long-range order. This UTF has longer fluorescence lifetimes and a higher photostability for UV irradiation than the comparison sample, APPP/polycation UTF. A periodic density functional theoretical study indicates that the APPP/LDH UTF is a kind of multiple quantum-well structure which confines the valence electrons

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of APPP into the energy wells formed by the inert LDH monolayers.

Figure 1a shows the UV/Vis absorption spectra of (APPP/LDH)_n UTF with various bilayers deposited on quartz substrates. The absorption bands at about 207 nm and 344 nm (¹E_{1u} and π - π^* transition of phenylene^[9]) linearly correlate with the number of bilayers *n* (Figure 1a, inset), indicating a stepwise and regular film deposition procedure. The sharp fluorescence peak at 2.99 eV (415 nm) of (APPP/LDH)_n UTF also increases consistently with *n* (Figure 1b).

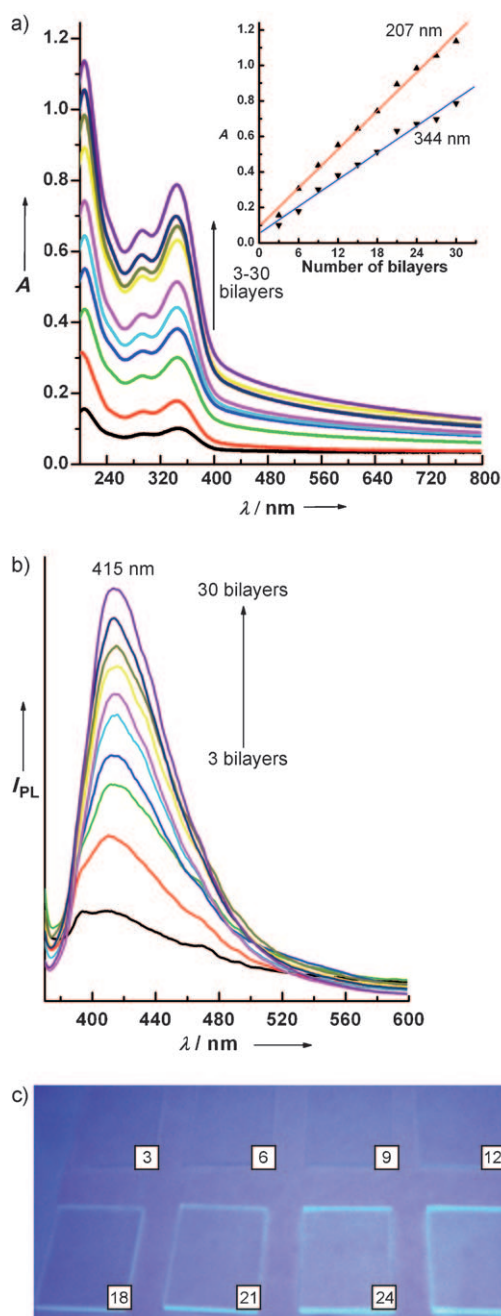


Figure 1. Characterization of (APPP/LDH)_n (*n* = 3–30) UTF: a) UV/Vis absorption spectra, b) fluorescence spectra, and c) photographs under 365 nm UV irradiation at different values of *n*. Inset in (a): absorbance at 207 and 344 nm vs. *n*.

This effect can be visualized by irradiating the thin films with UV light (Figure 1c): the films exhibit uniform bright blue luminescence with increasing intensity from *n* = 3 to 30 bilayers. There is no obvious red or blue shift of the absorption and fluorescence spectra for the as-prepared UTFs with a different number of bilayers, which suggests no formation of APPP aggregates throughout the whole assembly processing. Compared with APPP pristine solution (Supporting Information, Figure S1), the fluorescence peak of the UTF was blue-shifted by about 5 nm, without any obvious broadening. This observation may be related to the fact that the rigid framework of LDH restricts the vibration of polymer backbone owing to non-bonding interactions, as molecular mechanics calculations showed that the non-bonding stabilized energy between LDH layers and APPP is comparable with the vibration energy of free APPP (computational part and FTIR spectra; see the Supporting Information, Figure S2).

A top view of SEM image for (APPP/LDH)₉ UTF (Figure 2a) shows that the film surface is continuous and uniform, with the thickness of 20–23 nm obtained from a side

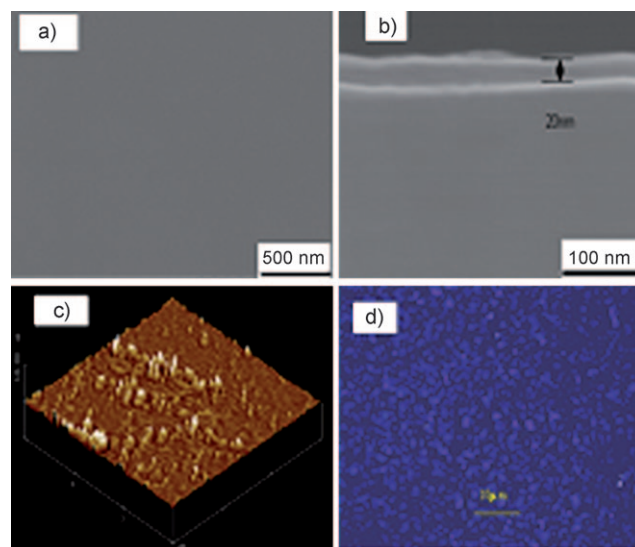


Figure 2. The morphology of (APPP/LDH)₉ UTF: a) top view of SEM image, b) side view of SEM image, c) tapping-mode AFM image, and d) fluorescence microscope image.

view (Figure 2b). The AFM topographical image (3 μm × 3 μm) gives the morphology and roughness information of the UTF; the film surface is very smooth, with a root-mean-square roughness of 5.8 nm. Both the statistical histogram depth and maximal depth obtained from the image are in the range of 21.3–22.3 nm, which is consistent with the thickness estimated by SEM observation. The UTF shows a homogeneous brightness of the dark blue color under the fluorescence microscope (Figure 2d), indicating that the APPP chromophore distributes uniformly throughout the film. Furthermore, the (APPP/LDH)_n UTF deposition and homogeneity were monitored by AFM and SEM (the roughness and thickness information are given in the Supporting

Information, Table S1). The approximately linear increase of the thickness upon increasing bilayer number confirm that the UTF presents a uniform and periodic layered structure, which is in agreement with the behaviors revealed by absorption and fluorescence spectra. Small-angle X-ray diffraction indicates that the UTF is an orderly periodical structure in the normal direction with a period of circa 2 nm (Supporting Information, Figure S3 and Table S2).

The fluorescence lifetime analysis of (APPP/LDH)_n UTF (Supporting Information, Figure S4 and Table S3) reveals that the fluorescence lifetime of (APPP/LDH)_n UTF is prolonged by a factor of nearly 20 (18.63–21.05 ns) compared with the pristine APPP solution (0.88 ns). This remarkable increase can be expected because the rigid LDH monolayers isolate the polymer chains from one another between adjacent layers and thus eliminate the interlayer π – π stacking. Furthermore, the uniform dispersion of the APPP molecules within LDH monolayers avoids the formation of intralayer polymer aggregation, which was confirmed by the polarized fluorescence measurements (Supporting Information, Figure S5). Finally, the APPP molecules are confined within the gallery of the LDH, which can suppress the thermal vibration of the APPP backbones by electrostatic interaction between the sulfonate group in the side chain and the LDH monolayer.

It is instructive to further compare the photophysical properties of APPP/LDH with other APPP/polycation systems. Poly(dimethyldiallylammonium chloride) (PDDA) was chosen as the polycation to alternatively assemble with APPP (Supporting Information, Figure S6). Compared with APPP pristine solution, the maximum emission of APPP/PDDA was red-shifted by circa 8–10 nm, which may be induced by π – π interactions of APPP molecule backbones, as considerable interpenetration between adjacent layers may occur for polyanion/polycation films.^[6b] This result indicates that PDDA could not impose the same isolation effect on APPP as effectively as LDH monolayers. Moreover, the fluorescence lifetimes of (APPP/PDDA)_n films (9.56–14.14 ns; Supporting Information, Table S4) are systematically less than that of (APPP/LDH)_n UTF, indicating that nonradiative relaxation of APPP in excited states could be more effectively suppressed when located between the rigid LDH monolayers. In-situ photoluminescence spectroscopy was performed to investigate the optical stability of two systems. After continuous irradiation with 344 nm UV light for 2 min, the intensity decreases by about 50 % and 30 % for (APPP/PDDA)₂₇ and (APPP/LDH)₂₇, respectively. Moreover, the emission band of (APPP/PDDA)₂₇ broadens to within 400–600 nm after 15 minutes, and the emission light becomes pale (Figure 3a). However, the PL intensity of APPP/LDH decreases gradually in the time range 0–30 min, and the emission light becomes dark blue slightly (Figure 3b), but no obvious band shift was found during the whole process. It can be concluded that APPP/LDH system presents a better UV-light resistance ability than APPP/PDDA.

To better understand the electronic structure of the APPP/LDH system, periodic density functional calculations were performed for the ideal model of the APPP/LDH structure.^[10] Total electronic densities of states (TDOS) and partial electronic densities of states (PDOS) analysis

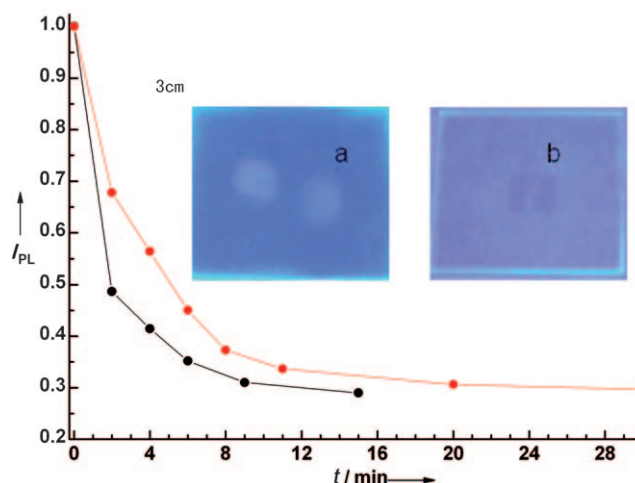


Figure 3. Decay of normalized maximal PL intensity I_{PL} with time, normalized against the initial PL value; $\lambda_{ex} = 365$ nm to probe the UV irradiation resistance ability of (APPP/PDDA)₂₇ (black data points) and (APPP/LDH)₂₇ UTF (red) irradiated under 344 nm UV light. Insets: photographs under UV light of a) (APPP/PDDA)₂₇ and b) (APPP/LDH)₂₇ UTF after the UV resistance experiment was finished.

(Figure 4, and Supporting Information, Figure S7, S8) reveal that the top of the valence band (TVB) and the bottom of the conducting band (BCB) are mainly dominated by the 2p(π)

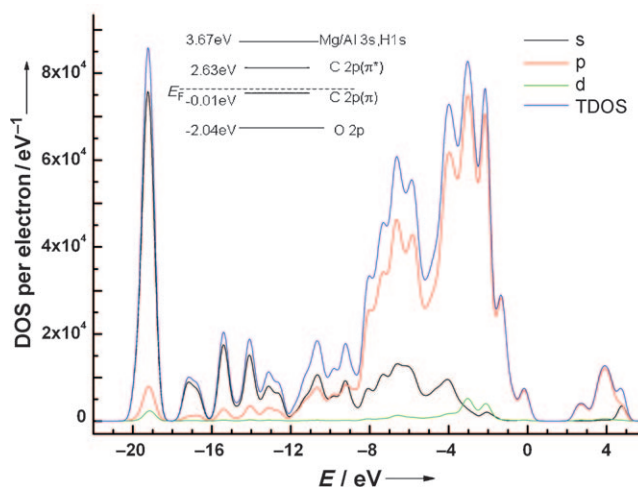


Figure 4. Total and partial electronic density of states (TDOS and PDOS) for the APPP/LDH system. The Fermi energy level E_F was set to zero.

and 2p(π^*) carbon atomic orbitals derived from APPP molecules. Near the Fermi level, the TDOS are mainly contributed by the 2p electrons of carbon atoms in APPP. The O 2p and Mg/Al 3s and the H 1s orbitals from the LDH layers contribute to the TDOS below and above the TVB and BCB, respectively, with a gap of 5.7 eV. Similar results were also gained by frontier orbital analysis (Supporting Information, Figure S9). Therefore, the photoexcitation process mainly occurs in the main chain of APPP, whereas Mg–Al

LDH monolayers remain inert. It thus can be concluded that the APPP/LDH UTF works as a multiple quantum well (MQW) structure for confining the valence electrons localized in the APPP main chains, which facilitates the enhancement of light-emitting efficiency for photoactive polymers, as described above.

In summary, the alternate assembly of APPP with LDH nanosheets results in ordered stacking to form (APPP/LDH)_n UTF with well-defined blue photoluminescence and prolonged fluorescence lifetimes, which confirms that the LDH monolayers improve the luminescence properties of APPP by avoiding the formation of π - π stacking of polymer backbones. Moreover, the existence of LDH monolayer leads to higher UV photostability for the blue luminescence of APPP. Energy band analysis implies that APPP/LDH UTF has small band gap. No electron delocalization occurs between APPP and LDH monolayers at the top of valence band, indicating that the LDH monolayers function as an energy blocking layer that hampers the interlayer interaction of the APPP chains, as in the experimental observation. Therefore, the APPP/LDH UTF can be regarded as a MQW structure. Moreover, it can be expected that, by using the electrostatic assembly process, the diversity of alignment and component of polymer and LDH monolayers can be tuned and controlled to make the as-fabricated UTF have much flexibility and potential for the design of various optoelectrical devices. The LDH energy barrier of the MQW, for example, can be tuned in heights and/or widths by assembling LDH layers with different positive charge density and/or different assembly fashion (LDH monolayer combined with inorganic anions would result in insulating bilayers). Further work is underway with the research on electric characteristics of the UTF.

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