

Organic–inorganic hybrid fluorescent ultrathin films and their sensor application for nitroaromatic explosives

Cite this: *J. Mater. Chem. C*, 2013, **1**, 4128

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The luminescent film materials sensitive to external stimuli are important to develop new types of optical sensors and switches. Herein we report organic–inorganic hybrid ultrathin films (UTFs) with reversible luminescence response to nitroaromatic explosive compounds by the use of layer-by-layer assembly of optical brightener BBU and Mg–Al-layered double hydroxide (LDH) nanosheets. UV-Visible absorption and fluorescence spectroscopy showed an orderly growth of the BBU/LDH films upon increasing the number of deposition cycle. XRD, AFM and SEM measurements indicated that the films feature periodic layered structure with a period of ca. 2 nm as well as uniform surface morphology. The BBU/LDH UTFs exhibit well-defined one/two-photon polarized photoemission with the anisotropy as high as 0.38. Moreover, the UTFs show a fast, selective and reversible luminescence response to different nitroaromatic explosives with the most significant luminescent red-shift occurring for picric acid; in addition, by combining suitable luminescent building blocks, the films can also be extended to other dual-color luminescence systems, which exhibit changes in both luminescence intensity and ratiometric fluorescence upon interaction with explosives, enlightening that these films can serve as new types of selective solid luminescent sensors towards nitroaromatic compounds.

Received 22nd January 2013

Accepted 22nd April 2013

DOI: 10.1039/c3tc30142g

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1 Introduction

Nitroaromatic compounds, such as trinitrotoluene (TNT) and its derivatives, are an important type of industrial materials commonly applied in both environmental, military and forensic science.¹ Most of nitroaromatic compounds degraded from the production of explosives² have detrimental effects on the environment and on human health as toxic and mutagenic substances.³ For example, when explosives are left in the environment for a long period of time, they can change into a variety of degradation products contaminating the soil and groundwater at toxic levels,⁴ which include nitrobenzene (NB), dinitrobenzene (DNB), and trinitrotoluene (TNT).⁵ Therefore, the reliable and selective detection of explosive materials is of critical importance in the fields of chemistry and environmental science.⁶ Recently, the research and development on identifying nitroaromatic compounds have attracted wide attention and application in public security and environmental protection.⁷ However, the detection of nitroaromatic compounds is still challenging due to their relative low vapor pressure and the inherent instability of the parent compounds.

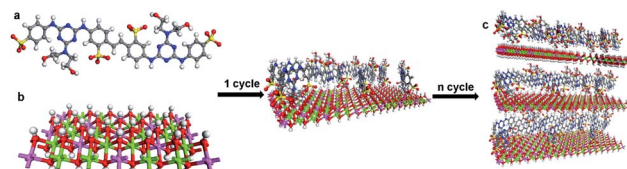
Several analytical techniques have been applied into the detection of nitroaromatic compounds, such as electrochemical method,⁸ chromatography,⁹ infrared spectroscopy,¹⁰ mass spectrometry,¹¹ and so on.¹² However, the relative expensive and complicated manipulation and operation of pre-concentration prior to analysis usually restrict the popularization of these instruments for the recognition of nitroaromatic compounds.¹³ In addition, the sensitivity and selectivity of the explosives still need to be improved to meet the need of practical applications of the instrumentation.¹⁴ Compared with the conventional methods, the optical spectroscopic method, especially fluorescence-based sensor, have currently drawn much attention from both scientific and engineering viewpoints due to their high sensitivity, versatility, rapid response time, and cost-effectiveness.¹⁵ In this sense, organic luminescent molecules have recently become good candidates to detect the nitroaromatic compounds, based on the selective quenching effects of luminescence induced by the nitroaromatic compounds; *e.g.* Zhang and co-workers have reported that a pyrene functionalized fluorescent molecule can be used for the detection of nitroaromatic compounds.^{12e} As we know, most of the reported optical/luminescence materials for detecting nitroaromatic compounds are used in the form of solution or powder systems,¹⁴ while this is unfavorable for their facile manipulation and cycling utility. Moreover, most of the luminescent solution systems can also induce environmental pollution and even operational risk, which is detrimental to human health. Therefore, there continues to be a

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stimulating challenge to develop new types of solid luminescent film systems to meet the need to integrate high selectivity and easy operation for the detection of nitroaromatic compounds.^{16,17}

Layered double hydroxides (LDHs) are a large class of inorganic host materials that can be described by the general formula $[M_{1-x}^{II} M_x^{III} (OH)_2]^{x+} A_{x/n}^{n-} \cdot yH_2O$, where M^{II} and M^{III} are divalent and trivalent metal ions respectively and A^{n-} is the guest anion.¹⁸ LDH materials have attracted recent interest in the areas of catalysis,^{18b} separation process,^{18c} and drug delivery.^{18d} The recent development of techniques for the delamination of LDH microcrystals into nanosheets paves an effective way to fabricate ordered nanostructured thin films.¹⁹ Several examples show that the immobilization of luminescent molecules within a confined LDHs thin film based on host-guest interactions²⁰ exhibited enhanced photoluminescent performance, which is absent in solution and favorable for their practical application as solid luminescent materials. In addition, LDH-based film has an ease in controlling the thickness, structures, and surface morphologies with the aid of layer-by-layer (LBL) assembly. The previous works have mainly studied the structures and static photophysical properties of LDH films,^{19d,f} whereas little attention has been paid on the dynamic and reversible fluorescence response of the films to the analytes, particularly for the toxic nitroaromatic compounds. In addition, from the perspective of the anionic species, although the LBL depositions of LDH and polymers or metal complexes have been well documented, the examples of LBL assembly of LDH nanosheets with small anions are still rarely reported. In this work, we report the fabrication of one new type of organic-inorganic hybrid ultrathin film (UTF) system by use of anionic stilbene derivatives (BBU, Scheme 1a) and Mg-Al-LDH nanosheets (Scheme 1b) as the basic building blocks *via* LBL method. BBU is a well-known optical brightener in the chemical industry; moreover, the stilbene unit in BBU also has attracted much interest because of its excellent optical and electronic properties.²¹ BBU molecule contains four sulfonate and four hydroxyl groups, which facilitate the LBL assembly with LDH nanosheets based on both electrostatic and hydrogen-bond interactions. The resulting BBU/LDH UTFs show long range ordered structures, which also emit uniform polarized one-/two-photon blue luminescence; moreover, it was also found that the luminescence of the UTFs are selectively sensitive to the nitroaromatic compounds solution with different concentrations, particularly in the case of picric acid (PA), which exhibits both luminescence quenching and red-shift emission. Additionally, the repeatability of the UTFs on the detection of nitroaromatic molecules is also investigated. Moreover, the UTF systems with dual-color emission have also been fabricated, which show changes in ratiometric fluorescence upon interaction with explosives. Therefore, this work provides a facile method for the fabrication of UTFs with one-/two-color luminescence by the incorporation of photoactive anions within a two-dimensional LDH inorganic matrix, which can also be applied as a luminescent sensor for the selective detection of nitroaromatic compounds.



Scheme 1 (a) Chemical structure of BBU; (b) the representation of one monolayer of Mg-Al-layered double hydroxide (Mg-Al-LDH) (pink: $Al(OH)_6$ octahedra; green: $Mg(OH)_6$ octahedra); and (c) the assembly process of $(BBU/LDH)_n$ UTFs.

2 Experimental section

2.1 Reagents and materials

Tetrasodium 4,4'-bis[2-di(*b*-hydroxyethyl)amino-4-(4-sulfophenylamino)-s-triazin-6-ylamino] stilbene-2,2'-disulfonate (optical brightener BBU, Scheme 1a) was purchased from Sigma Chemical. Co. Ltd. Sodium poly[2-(3-thienyl) ethoxy-4-butylsulfonate] (PT) was purchased from American Dye Source, Inc. Analytically pure $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and urea were purchased from Beijing Chemical Co. Ltd. and used without further purification.

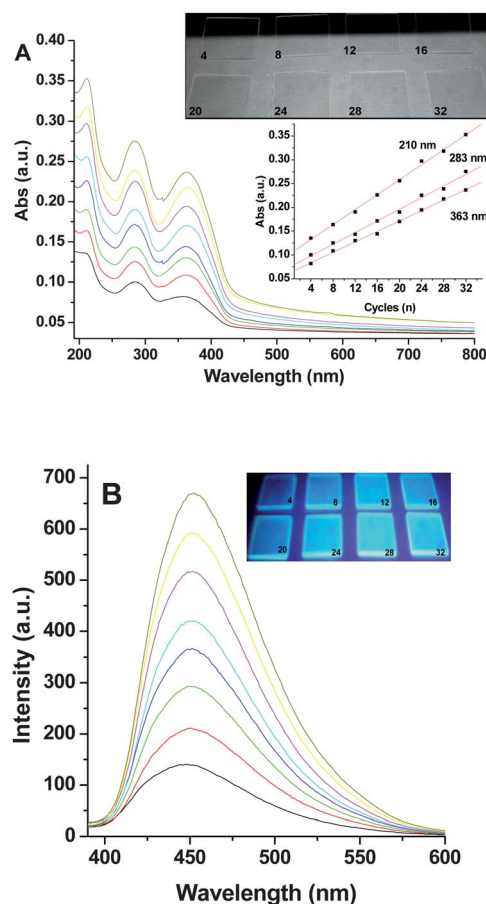
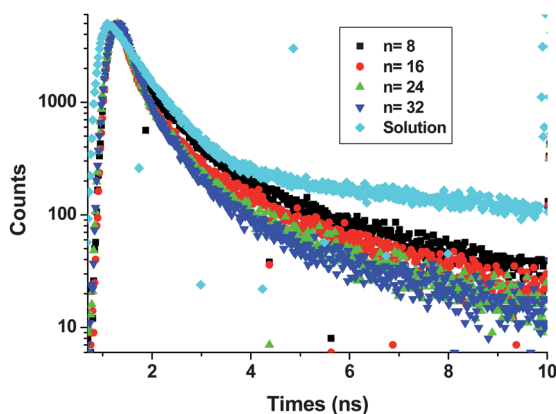


Fig. 1 (a) UV-Visible absorption spectra of the $(BBU/LDH)_n$ ($n = 4-32$) UTFs (the insets show the absorbance at 210, 283, and 363 nm as a function of the bilayer number n) and photographs of UTFs with different n when exposed to the daylight; and (b) fluorescence spectra of the UTFs and photographs of UTFs with different n when exposed to the UV light (365 nm).

Table 1 Photoluminescence quantum yield of (BBU/LDH)_n (n = 8–32) UTFs

Samples	n = 8	n = 16	n = 24	n = 32
PLQY (%)	5.390 ± 0.043	5.024 ± 0.049	4.642 ± 0.020	3.500 ± 0.013
Color coordinates	(0.159, 0.207)	(0.168, 0.203)	(0.158, 0.173)	(0.157, 0.171)

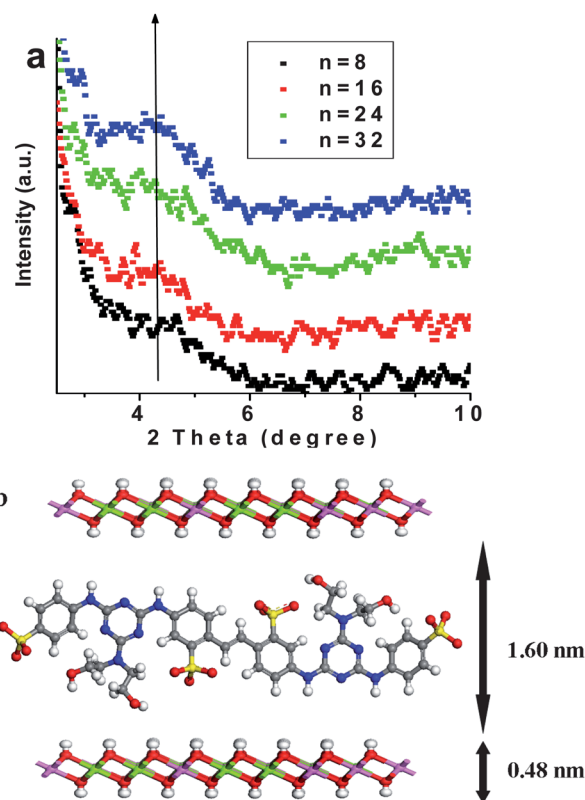
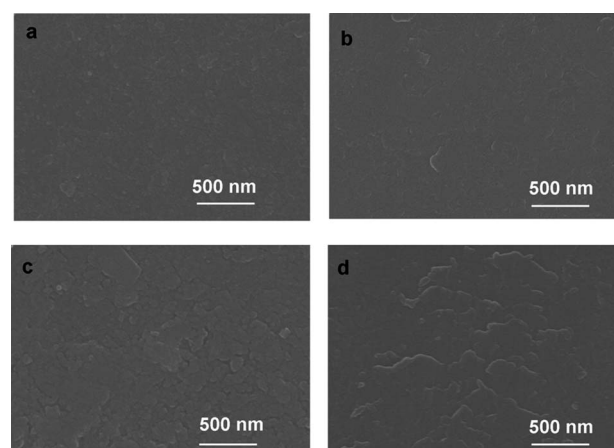
**Fig. 2** The fluorescence decay profiles of (BBU/LDH)_n (n = 4–32) UTFs and solution.**Table 2** Fluorescence decay data of the film samples of BBU/LDH^a

Samples	m	τ _i (ns)	A _i (%)	⟨τ⟩ (ns)	χ ²
n = 8	1	0.58	100.00	0.89	5.771
	2	0.34	48.04		1.461
		1.39	51.96		
n = 16	1	0.52	100.00	0.73	7.488
	2	0.31	62.22		1.683
		1.41	37.78		
n = 24	1	0.55	100.00	0.61	3.420
	2	0.30	63.37		1.487
		1.15	36.63		
n = 32	1	0.44	100.00	0.60	4.661
	2	0.27	62.68		1.681
		1.16	37.32		
Solution	1	0.66	100.00	0.67	1.690
	2	0.26	48.55		1.660
		1.05	51.4		

^a m stands for the mono- or double-exponential fitting of the fluorescence decay curve; τ_i is the fluorescence lifetime, for m = 1, lifetime is τ₁, and for m = 2, two lifetimes are τ₁ and τ₂; A_i stands for the percentage of τ_i. The fitting goodness is indicated by the value of χ². In the double-exponential case, ⟨τ⟩ = A₁τ₁ + A₂τ₂; A₁ + A₂ = 1.

2.2 Fabrication of (BBU/LDH)_n UTFs

The processes of synthesis and exfoliation of Mg–Al–LDH were similar to the procedure described in our previous work.^{19b,c} 0.1 g of Mg–Al–LDH was shaken in 100 cm³ of formamide for 24 h to produce a colloidal suspension of exfoliated Mg–Al–LDH nanosheets. A quartz glass substrate was first cleaned in concentrated NH₃/30% H₂O₂ (7 : 3) solution and then concentrated H₂SO₄ for 30 min in each case. After each step, the quartz substrate was rinsed and washed thoroughly with deionized water. The substrate was dipped in a colloidal suspension (1 g L^{−1}) of LDH

**Fig. 3** (a) Small angle XRD patterns for the (BBU/LDH)_n UTFs with 8, 16, 24, and 32 bilayers and (b) structural model of BBU/LDH.**Fig. 4** SEM images of the (BBU/LDH)_n UTFs in top views for (a) n = 8; (b) n = 16; (c) n = 24; and (d) n = 32.

nanosheets for 10 min followed by thorough washing, and then the substrate was immersed into 100 mL of aqueous BBU solution (5 g L^{−1}) for 10 min. Multilayer films of (BBU/LDH)_n were

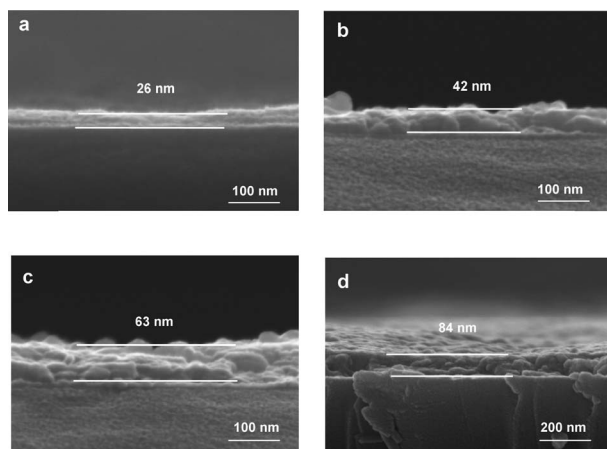


Fig. 5 SEM images of the (BBU/LDH)_n UTFs in side views for (a) $n = 8$; (b) $n = 16$; (c) $n = 24$; and (d) $n = 32$.

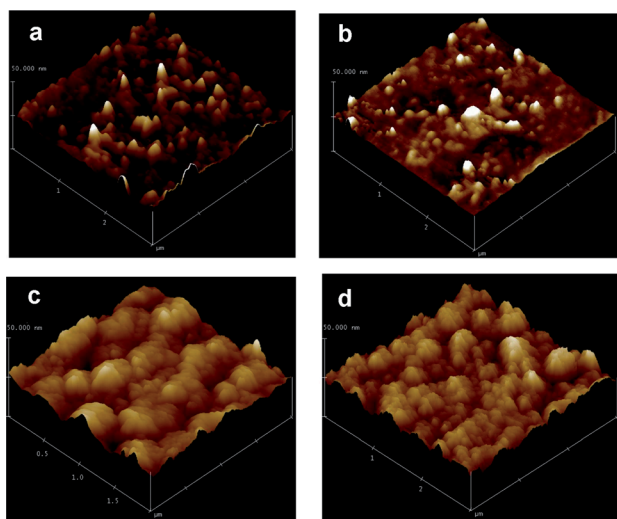


Fig. 6 AFM images of the (BBU/LDH)_n UTFs for (a) $n = 8$; (b) $n = 16$; (c) $n = 24$; and (d) $n = 32$. Their RMS surface roughness values are 3.843, 4.559, 7.072 and 7.474 nm, respectively.

fabricated by alternate deposition of the suspension of LDH nanosheets and the BBU solution for n cycles. The resulting films were dried under a nitrogen gas flow for 2 min at 25 °C. (BBU@PT/LDH)_n was prepared with the same process by the alternate assembly of LDH nanosheet (1 g L^{-1}) and the aqueous solution (100 mL) of mixed BBU (0.5 g) and PT (0.06 g).

2.3 Sample characterization

UV-Visible absorption spectra were collected in the range 190 to 800 nm on a Shimadzu U-3000 spectrophotometer, with a slit width of 1.0 nm. The fluorescence spectra were recorded on a RF-5301PC spectrofluorophotometer with an excitation wavelength of 360 nm. The fluorescence emission spectra were recorded in the range 370–600 nm, and both the excitation and emission slit were set to 3 nm. The detection of the nitroaromatic compounds for the dual-color fluorescence film was performed

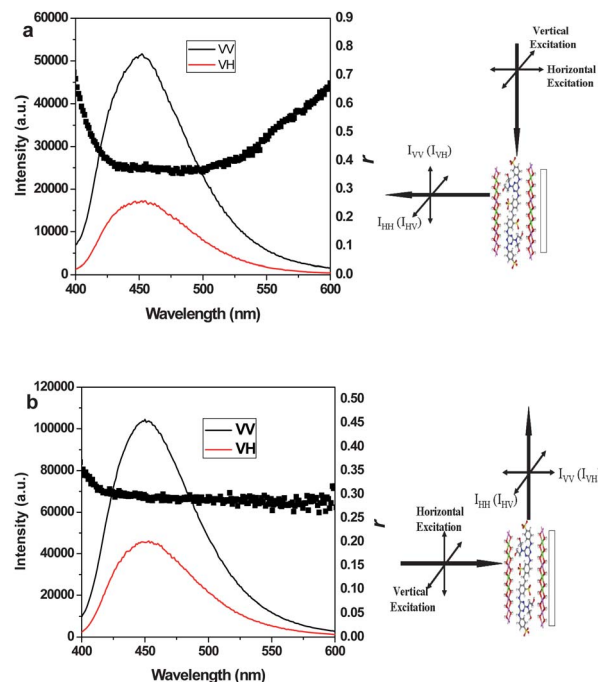


Fig. 7 One-photon polarized fluorescence profiles in the VV, VH modes and anisotropic value (r) for the BBU/LDH with the glancing (a) and vertical (b) incidence geometry of the excitation light (360 nm).

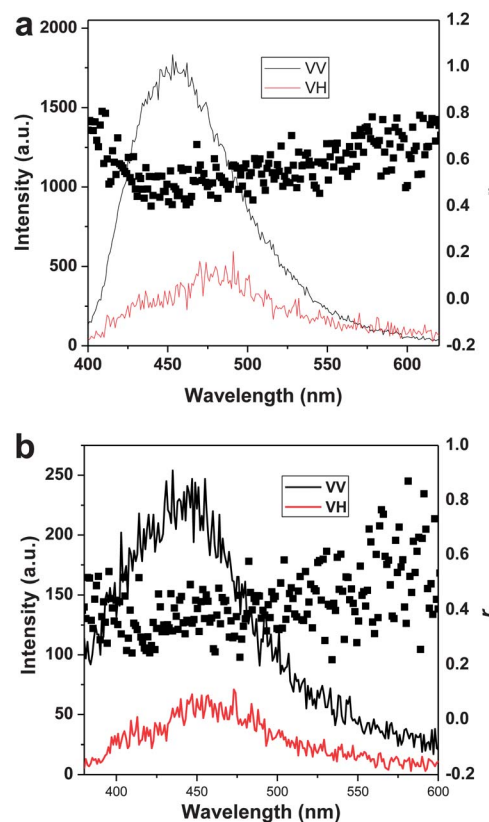


Fig. 8 Two-photon polarized emission fluorescence profiles in the VV, VH modes and anisotropic value (r) for the BBU/LDH with the glancing (a) and vertical (b) incidence geometry of the excitation light (730 nm).

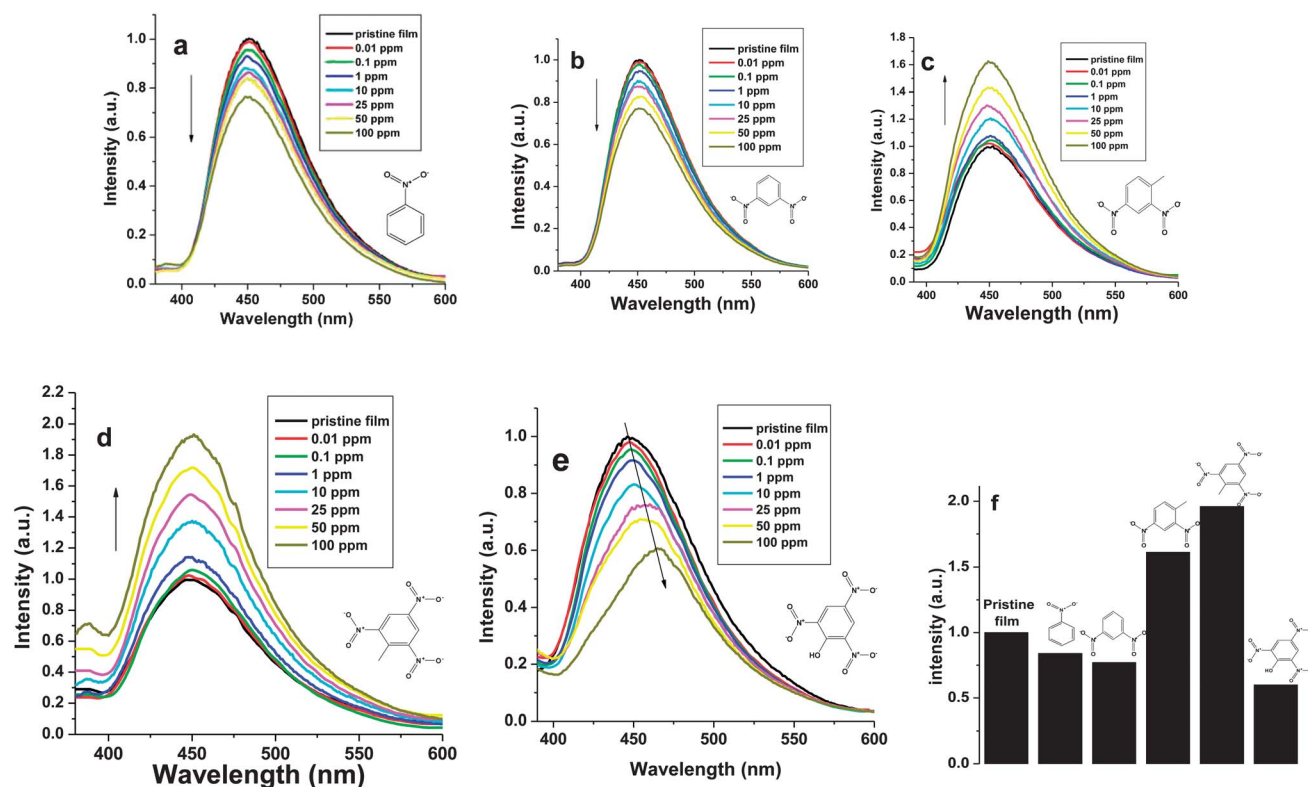


Fig. 9 The luminescent response profiles of the UTF to (a) NB, (b) *m*DNB, (c) DNT, (d) TNT and (e) PA with different concentrations. (f) Comparison of the normalized luminescent intensity of the UTF responding to different nitroaromatic compounds (100 ppm).

on a F-7000 spectrofluorophotometer. Steady-state polarized photoluminescence measurements of BBU/LDH UTFs were recorded with an Edinburgh Instruments FLS 920 spectrofluorimeter. The fluorescence decay profiles were measured by exciting the films at a 372 nm laser in LifeSpec-ps spectrometer, and the fluorescence lifetimes of the total decay were calculated with the F900 Edinburgh instruments software. X-Ray diffraction patterns (XRD) of BBU/LDH UTFs were recorded using a Rigaku 2500VB2+PC diffractometer under the following conditions: 40 kV, 50 mA, Cu K α radiation ($\lambda = 0.154056$ nm) with step-scanning in steps of 0.04° (2θ) in the range 2 to 10° using a count time of 10 s per step. The morphology of the thin films was investigated by using a scanning electron microscope (SEM Hitachi S-3500) equipped with an EDX attachment (EDX Oxford Instruments Isis 300), with an acceleration voltage of 20 kV. The surface roughness was obtained by using atomic force microscopy (AFM) software (Digital Instruments, Version 6.12).

3 Results and discussion

3.1 Fabrication of the BBU/LDH UTFs

Multilayer UTFs were fabricated by alternately dipping a quartz glass slide into a colloidal suspension of LDH nanosheets and an aqueous solution of BBU. The assembly process (Scheme 1c) of the $(\text{BBU/LDH})_n$ ($n = 4$ –32) UTFs deposited on quartz substrates was monitored by UV-visible absorption spectroscopy as shown in Fig. 1a. It can be observed that the intensity of the absorption band at *ca.* 210 ($^1E_{1u}$ transition), 283, and

363 nm (the π – π^* transition of BBU) correlates nearly linearly with the number of bilayers n (Fig. 1a, inset), indicative of a stepwise and regular deposition procedure with almost identical amounts of BBU incorporated in each cycle. Moreover, the photographs of the UTFs under daylight (inset in Fig. 1a) show that the UTFs are highly transparent. In addition, the intensity of the sharp luminescence peak with a maximum at *ca.* 450 nm of the $(\text{BBU/LDH})_n$ UTFs also displays a monotonic increase with n , as shown in Fig. 1b. The thin films under UV light irradiation (the inset of Fig. 1b) also reveal well-defined blue luminescence with enhanced brightness upon increasing n . The fluorescence spectra of the as-prepared UTFs show no obvious red or blue shift relative to that of the pristine BBU solution, suggesting the absence of BBU aggregates in the UTFs throughout the whole assembly process.

3.2 Photoluminescence quantum yield (PLQY) and fluorescence lifetime

To detect the fluorescence efficiency of the UTFs with different bilayers, the measurement on photoluminescence quantum yield (PLQY) was further made, and the values are tabulated in Table 1. It can be observed that the PLQY values of samples decrease slightly from 5.39% to 3.50% along with the increasing n , and such behavior probably related to the increasing self-absorption of the film with high n values; in addition, the color coordinates (Table 1) show that the luminescent colors for the samples are mainly populated within the blue region, and the ordinate has a decreasing trend with increasing n .

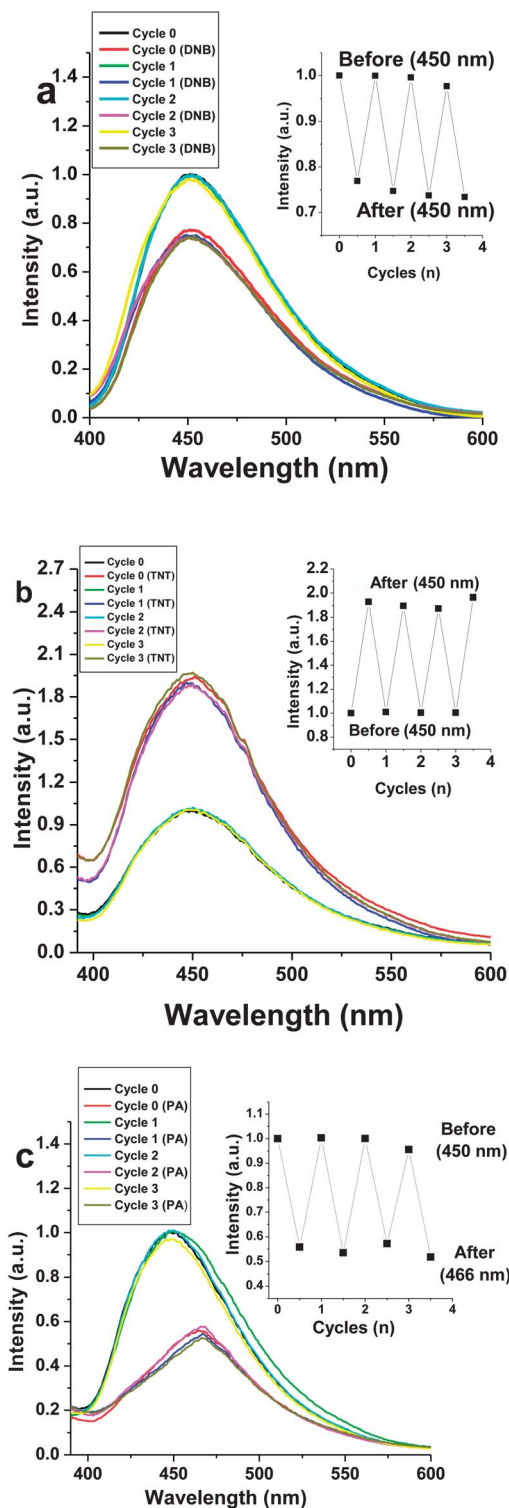


Fig. 10 The fluorescent spectra of the UTF for detecting (a) *m*DNB, (b) TNT, and (c) PA after alternate treatments by nitroaromatic compounds and methanol solutions over four continuous reversible cycles (the inset show the fluorescent intensities over four continuous cycles).

To further obtain insight into the photophysical properties and excited-state information of fluorescence for BBU/LDH, the samples were studied by detecting their fluorescence decays, with excitation and emission wavelength of 372 and 450 nm,

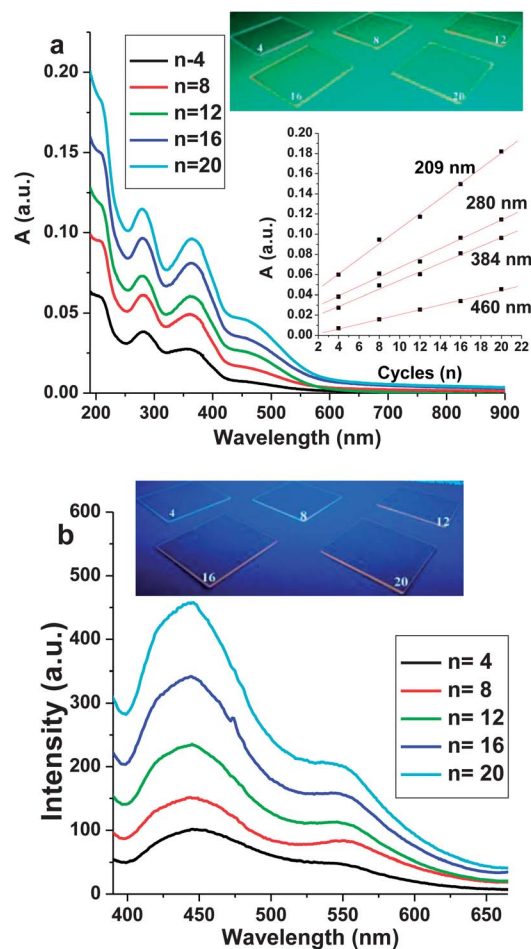


Fig. 11 (a) UV-Visible absorption spectra of the (BBU@PT/LDH)_{*n*} UTFs (the insets show the absorbance at 209, 280, 384 and 460 nm as a function of the bilayer number *n*) and photographs of UTFs with different *n* when exposed to the daylight; and (b) fluorescence spectra of the UTFs and photographs of UTFs with different *n* when exposed to the UV light (365 nm).

respectively. The fluorescence lifetimes were obtained by fitting the decay profiles (Fig. 2) with both one-exponential and double-exponential form respectively, and the results are tabulated in Table 2. In the double-exponential case, the average lifetime, $\langle \tau \rangle$, is also listed in Table 2. Compared with the aqueous solution of BBU (5×10^{-5} mol L⁻¹, *ca.* 0.66 ns for one-exponential τ and 0.67 ns for $\langle \tau \rangle$ in this work), the fluorescence lifetime (0.60–0.89 ns for $\langle \tau \rangle$) of BBU/LDH with a different number of bilayers are compatible with that of the BBU solution. Such behavior indicates that the rigid LDH nanosheets can isolate the main chains of BBU from each other and thus eliminate the interlayer π - π stacking interactions. As well, the decreasing trend of the fluorescence lifetime upon increasing *n* is consistent with that of the PLQY. For the double-exponential fitting cases, the short lifetime (*ca.* 0.26–0.52 ns) listed in Table 2 may correspond to the adsorbed BBU at the surface of LDH nanosheets, while the long lifetime (*ca.* 1.05–1.41 ns) corresponds to the intercalated BBU confined within the gallery of LDH nanosheets, since the intercalated BBU molecule confined between the sheets is more stably immobilized.

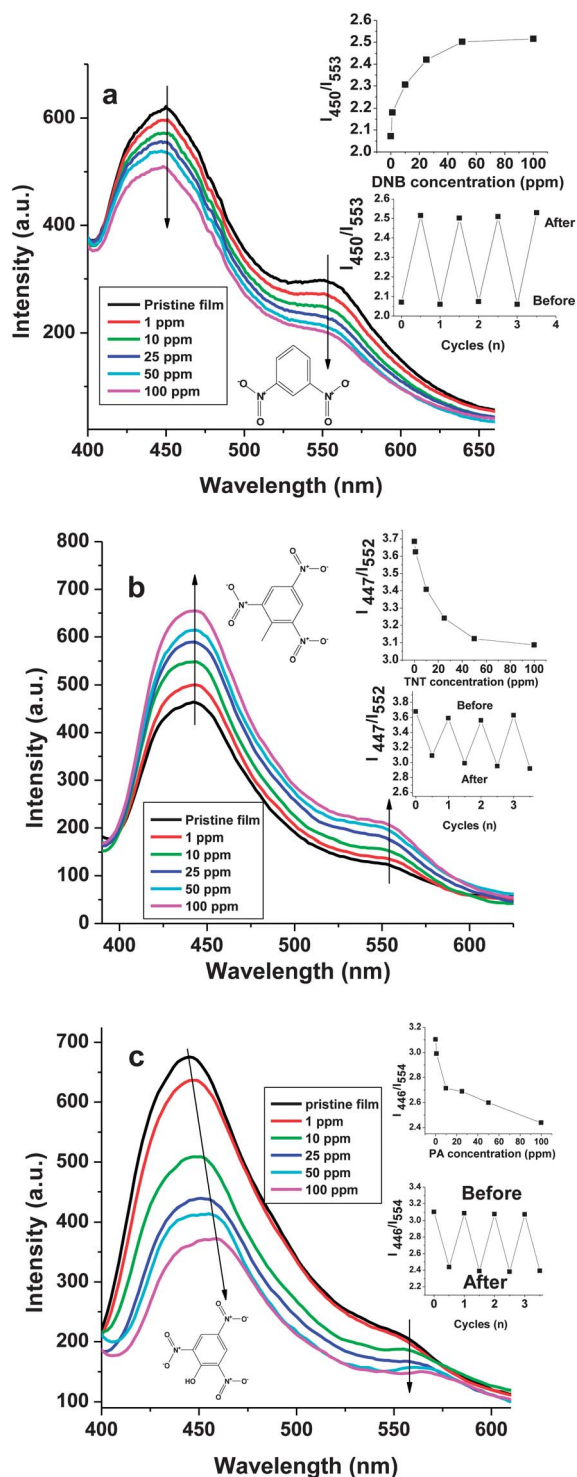


Fig. 12 The luminescent response profiles of the BBU@PT/LDH UTF to (a) *m*DNB ($n = 12$), (b) TNT ($n = 16$), and (c) PA ($n = 20$) with different concentrations. The inset plot shows the change of ratio luminescence between two wavelengths at different concentrations of nitroaromatic compounds, and the reversible ratio-metric fluorescence after alternately treating with nitroaromatic compounds and methanol solutions over four continuous cycles.

3.3 Structure and morphology

Due to the periodic assembly of the UTFs, X-ray diffraction (XRD) was employed to further detect their structure and assembly

process. It can be observed from Fig. 3a that the basal reflections of the as-prepared UTFs with different n appear at *ca.* 4.2° , and the peak intensity increases with the increase of bilayer numbers, indicating that the UTFs possess a periodic long-range ordered structure in the direction normal to the substrate with a period thickness of *ca.* 1.98 nm. This is in agreement with an idealized structural model of the BBU/LDH system in which the BBU anions adopt a parallel arrangement fashion relative to the LDH layers (Fig. 3b). In addition, the absence of the second-order XRD reflection of the UTFs may be attributed to the fact that the order degree of the small anion assembled LDH is relatively lower than that of the polymer/LDH systems, and similar behavior also appears in the anionic complex assembled LDH UTFs.^{19a}

The surface structure and thickness of (BBU/LDH)_{*n*} UTFs were further investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Fig. 4 display the typical top-view SEM images of the (BBU/LDH)_{*n*} UTFs with $n = 8, 16, 24$ and 32 respectively, and it can be observed that the film surface is microscopically continuous and uniform. Furthermore, by observing the side-view SEM images (Fig. 5), the thickness of UTFs with different bilayer numbers can be estimated in the range of 26–84 nm when n increases from 8 to 32. The thickness of the UTFs has a trend of increase nearly linearly as function of the number of deposition cycles, with an average increment of *ca.* 2.6 nm per deposition bilayer number. Based on the thickness values of the UTFs, the height of the interlayer gallery occupied by the BBU anion along the direction normal to the film can be estimated as *ca.* 2.1 nm, since the thickness of one LDH monolayer is *ca.* 0.48 nm. This value is reasonably close to the thickness per bilayer indicated by the XRD results. To further investigate the surface morphology and roughness of the as-prepared UTFs, the deposition process of (BBU/LDH)_{*n*} UTFs was further monitored by atomic force microscopy (AFM). The typical smooth surfaces of the BBU/LDH UTFs ($n = 8$ –32) are observed in Fig. 6, and the values of surface roughness increased slightly upon the increasing n from 3.843 nm ($n = 8$) to 7.474 nm ($n = 32$). The reasons for the increasing surface roughness upon the increasing bilayer number are as follows: firstly, the individual LDH nanosheets within the UTF may be at a different plane, which can result in a local roughness at the junction between the LDH nanosheets; secondly, during the assembly process, the surface coverage cannot reach 100% in each deposition cycle, and the house-of-card structures may also appear for the sample with high bilayer numbers.

3.4 One-photon and two-photon polarized fluorescence of the BBU/LDH film

To further investigate the orderly degree and the microenvironment of BBU within the as-prepared BBU/LDH film, polarized fluorescence measurement was employed to obtain the fluorescence anisotropic value r .²² r can be expressed as the formula:

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (1)$$

where $G = \frac{I_{HV}}{I_{HH}}$, determined from the BBU aqueous solution; I_{VH} stands for the PL intensity obtained with vertical polarized light

excitation and horizontal polarization detection, and I_{VV} , I_{HH} , I_{HV} are defined in a similar way. Two typical measurement setups of polarized fluorescence were employed to determine the fluorescence anisotropic value r . It was observed that, for the in-plane polarized excitation, the BBU/LDH film shows well-defined blue fluorescence anisotropy between the parallel and perpendicular to excitation polarized direction (I_{VV} vs. I_{VH}) with the anisotropic value (r) of *ca.* 0.38 at 450 nm. In addition, the uniform r values in both the polarized excitation and emission spectra indicate that polarization scrambling *via* Förster transfer is minimal in the film, and also confirms the isolated conformation of the BBU anions within the gallery. For the vertical polarized excitation (Fig. 7b), the I_{VV}/I_{VH} ratio is 2.37, lower than that of the horizontal excitation and vertical emission (3.04) by *ca.* 22.0%.

It was noted that the stilbene compound can be a two-photon emissive chromophore, and thus up-conversion polarized fluorescence was further detected by exciting the film at 730 nm. It can be shown that, in both the horizontal (Fig. 8a) and vertical (Fig. 8b) polarized excitation models, the film features well-defined up-conversion polarized emission. The fluorescence anisotropy in both the excitation and emission spectra are close to those excited at 360 nm, and such behavior indicate that fluorescent emission are derived from the process with one-photon and two-photon excited states to the ground state. To the best of our knowledge, anionic chromophore assembled LDH system with the property of up-conversion polarized emission is still rather rare.

3.5 Reversible fluorescence detection of explosive compounds

To investigate the fluorescent response of the UTFs to different nitroaromatic explosive compounds, the luminescence spectra of the (BBU/LDH)₈ UTF were measured after immersing it in different methanol solutions containing five typical nitroaromatic explosives (nitrobenzene (NB), *m*-dinitrobenzene (*m*DNB), 2,4-dinitrotoluene (DNT), trinitrotoluene (TNT), and picric acid (PA)) with varying concentrations (0.01, 0.1, 1, 10, 25, 50, 100 ppm). Fig. 9a and b show the typical PL spectra of the BBU/LDH UTF responding to NB and *m*DNB. It can be observed that the fluorescent intensity of the UTF decreases systematically upon increasing the concentration of explosives. Such behavior can be assigned to the fluorescence quenching of the BBU/LDH upon contacting with the analytes, and similar behavior can also be observed for other powdered chromophores systems.⁷ While upon treated with DNT and TNT solutions, the fluorescence intensity has an increasing trend upon increasing concentration with the TNT being the most significant (shown in Fig. 9c and d). For the PA solutions, the fluorescent position undergoes a remarkable red-shift from 450 to 466 nm accompanied with a decrease in the intensity when increasing the PA concentration (Fig. 9e). The change in the emissive wavelength of the UTF indicates that the BBU/LDH system can be potentially used as a PA fluorescent sensor. Fig. 9f shows the normalized fluorescence intensity of the UTF responding to different nitroaromatic explosive (100 ppm)

solutions, and the selective sensitivity of the fluorescent change of the BBU/LDH UTF to different explosives can be attributed to the different interaction fashions between the explosive molecules and BBU anions within the LDH nanosheets.

Moreover, the recovery and reproducibility of the UTF's fluorescence were also investigated. After the UTF was thoroughly washed with methanol solution for 20 seconds or even heated at 120 °C with an electric dryer to remove the explosives, the fluorescence intensity of UTF can nearly recover to its initial state. Fig. 10 shows the typical examples of the variation of the luminescence intensity dependent on the alternate immersing the UTF in 100 ppm of explosives (*m*DNB, TNT and PA) and methanol solution over four continuous reversible cycles. It can be observed that the BBU/LDH UTF can show a readily reversible photoemission change at least 4 times (Fig. 10, inset), indicating its potential application as luminescence sensor for nitroaromatic compounds.

3.6 Dual-color luminescent film for ratiometric fluorescence detection

Based on the selective detection of explosives for the BBU/LDH UTF, it is possible to further develop other dual-color luminescent systems according to the three-primary-color principle. Blue/orange two-color photoemissive UTFs were constructed by co-assembling BBU@PT units with LDH nanosheets (BBU@PT is the solution of BBU and anionic polythiophene (PT)). The UV-vis spectra of the as-prepared (BBU@PT/LDH)_{*n*} (*n* = 4–20) is shown in Fig. 11a, from which it can be observed that new absorption band belonging to PT appears at *ca.* 460 nm besides those from the BBU (209, 280 and 384 nm). The intensities of characteristic bands exhibit linear relationship with the bilayer numbers, confirming regular assembly of (BBU@PT/LDH)_{*n*} UTFs. The photographs of the UTFs with yellow color under daylight (inset in Fig. 11a) shows the UTFs have high transparency. Fig. 11b shows the PL spectra of the UTFs, which exhibits dual-color luminescence with two main emissive wavelengths located at *ca.* 448 and 550 nm; the intensity of UTFs also displays a monotonic increase with *n*. The thin films under UV light irradiation (the inset of Fig. 11b) also reveal well-defined blue/orange emission with enhanced brightness upon increasing *n*.

The BBU@PT/LDH UTF with different *n* can exhibit dual-color fluorescence response to the nitroaromatic compounds. Herein, taking *m*DNB, TNT and PA with obvious fluorescence change for BBU/LDH as examples, the ratio of the fluorescence intensities at two wavelengths of BBU@PT/LDH (*n* = 12, 16, 20) undergo remarkable changes with different concentration of analytes. Upon treated with *m*DNB, the PL intensity of the (BBU@PT/LDH)₁₂ decreases with the increasing concentration, and the intensity ratio of I_{450}/I_{553} increases from 2.08 to 2.51 upon increasing the concentration from 1 to 100 ppm; the similar decrease in the PL intensity can also be observed when detecting PA by (BBU@PT/LDH)₂₀ (Fig. 12c), while the intensity ratio of I_{446}/I_{554} decreases systematically from 3.10 to 2.44 with increasing concentration from 1 to 100 ppm. For the TNT, the PL intensity (Fig. 12b) and I_{447}/I_{552} value (inset of Fig. 12b) of the (BBU@PT/LDH)₁₆ exhibit increasing and decreasing trends with

the increasing concentration respectively. Based on the selective responses of the change in both the intensity and the intensity ratio with different nitroaromatic molecules, the UTFs may serve as new types of ratiometric luminescent sensors. Moreover, the ratio of the fluorescence intensities for the BBU@PT/LDH between two wavelengths also exhibit reversible transformation by alternately treating with explosives and methanol over four continuous reversible cycles (inset in Fig. 12), confirming that the UTF with dual-color emission could be reused immediately for future practical applications.

4 Conclusion

In summary, (BBU/LDH)_n UTFs have been fabricated by a layer-by-layer assembly technique and show well-defined blue photoluminescence. UV-Visible and fluorescence spectra confirm a stepwise and regular assembled process of the UTFs. SEM and AFM further demonstrate that the UTF surface is microscopically smooth and uniform. The thickness of the UTFs exhibits linear correlation with the bilayer numbers and can be finely controlled in the range of *ca.* 26 to 84 nm. The UTFs show well-defined one-/two-photon polarized fluorescence with anisotropy values of 0.3–0.4. Moreover, the UTFs show selective luminescence response to different nitroaromatic explosives; the luminescence quenching, increase and red-shift of UTFs occur upon treatment with NB and *m*DNB, DNT and TNT, and PA respectively. The luminescence of the UTFs can also be recycled by either eluting with methanol or heat treatment, which guarantee their future practical application. In addition, by combining suitable luminescent building blocks, such as PT, the UTF system is also applicable to other dual-color BBU@PT/LDH systems, which feature changes in both luminescence intensity and ratiometric fluorescence upon interaction with explosives. Therefore, this work not only gives a detailed description of the ordered assembly, regular morphology and down-/up-converted polarized luminescent properties of the photoactive anions confined in LDH nanosheets, but also provides a deep study on the selective detection for nitroaromatic explosives with the aid of reversible luminescence change of UTFs. It can be expected that the (BBU/LDH)_n UTFs could be feasibly applied as a polarized blue luminescent material and sensor film towards nitroaromatic explosives.

Acknowledgements

This work was supported by the National Natural Science Foundation of China, Program for Changjiang Scholars and Innovative Research Team in University (IRT1205), the 973 Program (Grant no.: 2011CBA00504) and 111 Project (Grant no.: B07004). We gratefully acknowledge Prof. David G. Evans and Prof. Xue Duan for their helpful discussions on the fabrication of LDH films.

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