Aggregation-induced emission molecules in layered matrices for two-color luminescence films

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## Experimental

## **Chemicals and Materials**

All reagents were of analytical grade and used without further purification. Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Na<sub>2</sub>CO<sub>3</sub>, NaOH, NaNO<sub>3</sub>, HNO<sub>3</sub>, MgSO<sub>4</sub>, ethanol, petroleum ether, aceton and dichloromethane were purchased from Beijing Chemical Reagent Company (Beijing, China). 9,10-Dibromoanthracene, 4-methoxystryrene, palladium(II) acetate, K<sub>3</sub>PO<sub>4</sub>, boron tribromide, sodium ethoxide (NaOEt) and 1,3-propanesultone were purchased from Alfa Aesar (Ward Hill, MA, USA). The anhydrous N,N-dimethylacetamide (DMAc) was purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Formamide was purchased from Tianjin Fuchen Chemical Reagents Factory (Tianjin, China). Poly(sodium-p-styrenesulfonate) (PSS) was purchased from J&K Chemical Co. (Beijing, China). Water was purified with a Milli-Q purification system (Barnstead, CA, USA).

## Apparatus

Transmission electron microscopy (TEM) photographs were performed on a Tecnai G220

TEM (FEI Company, USA). Atomic force microscopy (AFM) in tapping mode was carried out on a NanoScope IIIa (Digital Instruments Co., Santa Barbara, CA, USA) instrument. Powder Xray diffraction (XRD) measurements were performed on a Bruker (Germany) D8 ADVANCE X-ray diffractometer equipped with graphite-monochromatized Cu/K $\alpha$  radiation ( $\lambda = 1.54$  Å). The patterns of powder were acquired in the  $2\theta$  range of 5–70°. <sup>1</sup>H–nuclear magnetic resonance (1H-NMR) spectra were recorded at room temperature with a 600 MHz Bruker (Germany) spectrometer. Mass spectrum (MS) was carried out with Quattro microtriple quadrupole mass spectrometer (Waters, USA). UV-visible spectra were measured on a USB 4000 miniature fiber optic spectrometer in absorbance mode with a DH-2000 deuterium and tungsten halogen light source (Ocean Optics, Dunedin, FL). Emission fluorescence spectra were obtained using a F-7000 fluorescence spectrophotometer (Hitachi, Japan) at a slit of 5.0 nm with a scanning rate of 1200 nm/min. Steady-state polarized photoluminescence measurement was recorded with an Edinburgh FLS 980 Lifetime and Steady State Spectrometer. The quantum yield values were obtained from the reconvolution fit analysis (Edinburgh F980 analysis software) equipped with an integrating sphere. Fluorescence microscope images were recorded on an Olympus IX71 fluorescence microscope (Olympus, Japan).

## **Procedures**

## Synthesis of 9,10-Bis(4-methoxystyryl)anthracene (1)

9,10-Dibromoanthracene (1.02 g), 4-methoxystryrene (0.96 g),  $K_3PO_4$  (1.92 g) and palladium(II) acetate (60 mg) were added to a 100 mL round-bottom flask equipped with a stir bar, and then dispersed in 30 mL of anhydrous DMAc. The flask containing reaction mixture was placed in an oil bath (110 °C) and stirred for 24 h under N<sub>2</sub> atmosphere. After that, the reaction mixture was cooled to room temperature, and poured into 50 mL water to stop the reaction completely. Then the mixture was extracted with 50 mL dichloromethane for six times. Subsequently, the dichloromethane extracts were washed with saturation salt, dried with MgSO<sub>4</sub>

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2014 and concentrated with a rotary evaporator. Finally, the crude product was chromatographed over silica gel. The column was eluted with a mixture (4:1) of petroleum ether and dichloromethane to yield 1.25 g (94%) of a yellow powder. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta$  (ppm) 8.39-8.41 (m, 4H), 7.79 (d, 2H), 7.63 (d, 4H), 7.45-7.47 (m, 4H), 7.00 (d, 4H), 6.88 (d, 2H), 3.89 (s, 6H).

#### Synthesis of 9,10-Bis(4-hydroxystyryl)anthracene (2)

0.67 g of 1 and 20 mL of anhydrous dichloromethane were added into a 100 mL flask. The mixture was placed into liquid nitrogen-ethanol at -78 °C. A solution of 1.51 g of boron tribromide (6 mmol) in 10 mL anhydrous dichloromethane was added carefully to the mixture while stirring. Then the reaction mixture was stirred overnight and allowed to warm to room temperature slowly. After that, 15 mL water was added carefully to the reaction mixture to make the product and unreacted boron tribromide hydrolyze. The organic phase was separated, dried with MgSO<sub>4</sub> and concentrated with to dryness under vacuum. Finally, the crude product was chromatographed over silica gel. The column was eluted with a mixture (3:1) of petroleum ether and acetone to yield 0.50 g (80%) of a yellow powder. <sup>1</sup>H NMR (DMSO- $d_6$ , 600 MHz):  $\delta$  (ppm) 9.64 (s, 2H), 8.36-8.38 (m, 4H), 7.87 (d, 2H), 7.63 (d, 2H), 7.52-7.54 (m, 4H), 6.85 (d, 4H), 6.80 (d, 2H).

## Synthesis of 9,10-bis[4-(3-sulfonatopropoxyl)-styryl]anthracene sodium salt (3)

0.54 g of 2 and 20 mL of anhydrous ethanol was added into 100 mL flask under nitrogen. Then a solution of NaOEt (0.20 g) in anhydrous ethanol (20 mL) was added by dropwise to the above mixture and stirred for 1 h until the solution color turned to orange-red. After that, 1,3propanesultone (0.37 g) in ethanol (20 mL) was added to the reaction mixture. The mixture was vigorously stirred overnight and a yellow product was precipitated out from the solution. Finally, the product was filtrated and then washed with ethanol and acetone two times to give 0.75 g (82%) of a yellow powder. <sup>1</sup>H NMR (DMSO- $d_6$ , 600 MHz):  $\delta$  (ppm) 8.38 (m, 4H), 7.96 (d, 2H),

#### Synthesis of NO<sub>3</sub>-LDH nanosheets

Typically, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with Mg/Al ratio of 2.0 were dissolved in 60 mL deionized water to give a solution with a total metal cation concentration of 0.045 M. Then urea ([urea]/[NO<sub>3</sub><sup>-</sup>] = 4) was dissolved in the above solution. The mixed solution was heated in 100 mL teflon-lined autoclave at 100 °C for 24 h. After cooling to room temperature, the resulting CO<sub>3</sub>-LDHs were centrifuged, washed with deionized water and dried in a vacuum at 60 °C.

Sencondly, the CO<sub>3</sub>-LDHs (0.3 g) was further treated with 300 mL of an de-CO<sub>2</sub> aqueous solution containing NaNO<sub>3</sub> (0.50 mol) and HNO<sub>3</sub> (0.0015 mol), followed by vigorous stirring for 48 h at 25 °C under N<sub>2</sub> atmosphere. The resulting NO<sub>3</sub>-LDHs were washed with de-CO<sub>2</sub> and deionized water, and then dried in a vacuum at 60 °C.

Finally, 0.1 g of the NO<sub>3</sub>-LDHs was shaken in 100 mL of formamide solution for 48 h to produce a colloidal suspension of exfoliated NO<sub>3</sub>-LDH layers.

## Fabrication of (BSPSA-LDH)<sub>n</sub> and (BSPSA/PSS-LDH)<sub>n</sub> UTFs

The quartz glass substrate was first cleaned in concentrated  $H_2SO_4/30\%$   $H_2O_2$  (7:3) for 30 min. After such procedure, the quartz substrate was rinsed and washed thoroughly with deionized water. The treated substrate was then dipped into a colloidal suspension (1 g/L) of LDH nanosheets for 10 min, followed by dipping in two separate deionized water baths for 2 min each in order to wash thoroughly. Then the substrate was dipped into a BSPSA aqueous solution (0.05 g/L) for 10 min, and the washing procedure of BSPSA was same as that for the LDH layer described above. Multiplayer films of (BSPSA/LDH)<sub>n</sub> were fabricated by depositing alternatively through LDH nanosheets solution and anionic BSPSA solution for n cycles. The

Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2014 resulting films were dried with a nitrogen gas flow at 25 °C.

The fabrication method of the  $(BSPSA/PSS-LDH)_n$  UTFs was similar to  $(BSPSA-LDH)_n$  UTFs, except the preparation of BSPSA/PSS solution, aqueous solutions of BSPSA (0.25 g/L, 4 mL) and PSS (1 g/L, 0.5 mL) were mixed with 15.5 mL of ultrapure water . The electric charge ratio of BSPSA/PSS is nearly 1:1.

# **Supporting Figures**



Fig. S1 XRD patterns of NO<sub>3</sub>-LDH precursors and LDH nanosheets.



**Fig. S2** TEM image of LDH nanosheet (inset: Tyndall light scattering of colloidal solutions of LDH nanosheets.



Fig. S3 Synthetic route of BSPSA.



Fig. S4 Mass spectrum of BSPSA.



Fig. S5 <sup>1</sup>H NMR spectrum of BSPSA.



Fig. S6 Normalized fluorescence spectra of BSPSA/PSS and BSPSA (the BSPSA and PSS

concentration is 0.05 g/L and 0.025 g/L, respectively).



Fig. S7 Polarized photoluminescence profiles in the VV (blue) and VH (red) modes and anisotropic value (r) for (BSPSA/LDH)<sub>5</sub> UTFs. The excitation and emission wavelengths were set at 410 and 545 nm, respectively.



**Fig. S8** UV-vis absorption spectra of the  $(BSPSA-LDH)_n$  UTFs (n = 1-5).



Fig. S9 Normalized fluorescence spectra of  $(BSPSA/PSS-LDH)_n$  UTFs (n = 4-20).



**Fig. S10** Fluorescence microscope images of (A) the (BSPSA-LDH)<sub>5</sub> UTF and (B) the (BSPSA/PSS-LDH)<sub>20</sub> UTF.



**Fig. S11** (A) and (B) show the profile images of the yellow (BSPSA/LDH)<sub>5</sub> UTF and the green (BSPSA-PSS/LDH)<sub>8</sub> UTF, respectively. (C) and (D) show the surface-morphology images of the (BSPSA/LDH)<sub>5</sub> UTF and the (BSPSA-PSS/LDH)<sub>8</sub> UTF, respectively. All images were recorded on an AFM instrument in tapping mode.



**Fig. S12** Normalized luminescence spectra of the pristine BSPSA film in the temperature range 25-85 °C.



**Fig. S13** (A) Normalized fluorescence spectra of the (BSPSA-LDH)<sub>5</sub> UTF when it was dipped in water for several minutes and repeated for 100 cycles; and (B) stored at room temperature for about one month.