ELECTRONIC SUPPLEMENTARY MATERIAL

Intelligent Display Films with Tunable Color Emission Based on a Supermolecular Architecture

Rui Tian, a Ruizheng Liang, a Dongpeng Yan, a Wenyeng Shi, a Xuejiao Yu, a Min Wei, a*
Lin Song Li, b David G. Evans, a and Xue Duan a

a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China. Fax: +86-10-64425385; Tel: +86-10-64412131;
E-mail: weimin@mail.buct.edu.cn
b Key Laboratory for Special Functional Materials, Henan University, Kaifeng 475004, P. R. China
E-mail: lsli@henu.edu.cn

TABLE OF CONTENTS

1. Experimental section
2. Morphology of CdTe QDs
3. UV-vis absorption and fluorescence spectra of Rhodamine 6G, BTBS and CdTe QDs aqueous solution
4. Fabrication of multi-color UTFs
5. Morphological and structural characterization of the multi-color UTFs
6. Stability of the drop-casted film as a comparison sample
7. Fluorescence Lifetime of the mono-color and multi-color UTFs
1. Experimental section

1.1 Materials. 2,2’-(1,2-Ethenediyl) bis[5-[(4-(diethylamino)-6-[2,5-disulfophenyl) amino]-1,3,5-triazin-2-yl]amino] benzene-sulfonicacid] hexasodium salt (BTBS, Scheme 1a) was purchased from Sigma Chemical Co. Ltd. Poly(sodium-p-styrenesulfonate) (PSS, Mw=70000) was purchased from J&K Chemical Co. Ltd. Analytical-grade chemicals including formamide, Mg(NO$_3$)$_2$·6H$_2$O, Al(NO$_3$)$_3$·9H$_2$O, urea, NaNO$_3$ and HNO$_3$ were purchased from Aladdin Chemical Co. Ltd. The deionized and de-CO$_2$ water was used in all the experimental processes.

1.2 Preparation of CdTe QDs. The aqueous synthesis of mercaptosuccinic acid modified CdTe QDs was referred to the reported method.$^1$ In a typical synthesis, 0.985 g (2.35 mmol) of Cd(ClO$_4$)$_2$·6H$_2$O was dissolved in water (125 mL); 0.278 g of mercaptosuccinic acid stabilizer was added under stirring, followed by adjusting the pH value to 11 with addition of a NaOH solution (1.0 M) dropwisely. The solution was transferred into a three-necked flask fitted with a septum valves and was deaerated by N$_2$ bubbling for 30 min. Under stirring, H$_2$Te gas generated by Al$_2$(Te)$_3$ and H$_2$SO$_4$ was purged into the solution together with a slow nitrogen flow, and thus CdTe QD precursor was produced at this stage. The formation and growth of QDs proceeded upon refluxing at 100 °C under open-air conditions with an attached condenser. The fluorescent color of CdTe QDs solution changes from green to red upon increasing refluxing time from 10 min for QD-530 to 2 h for QD-620.

1.3 Fabrication of the multi-color luminescence UTFs. The process of synthesis and exfoliation of MgAl-LDH was similar to the procedure described in our previous work.$^{2-7}$ 0.1 g of MgAl-LDH was shaken in 100 cm$^3$ formamide for 24 h to produce a colloidal suspension of exfoliated MgAl-LDH nanosheets. The quartz glass substrate was cleaned by immersion in concentrated NH$_3$-30% H$_2$O$_2$ (7:3) solution and then concentrated H$_2$SO$_4$ for 30 min in sequence. In order to fabricate the mono-color films, the substrate was dipped in a colloidal suspension (1 g dm$^{-3}$) of LDH nanosheets for 15 min followed by washing thoroughly, and then was immersed into a 20 mL of BTBS aqueous solution (1 g dm$^{-3}$) for another 15 min. Multilayer films of (BTBS/LDH)$_n$ were fabricated by alternate deposition of LDH nanosheets and BTBS anions for $n$ cycles. The (CdTe QDs/LDH)$_n$ UTFs were prepared with a similar LBL method to that of (BTBS/LDH)$_n$ with the QDs concentration of 1 μM. The multi-color luminescence UTFs were fabricated in the same way (Scheme 1). PSS/LDH bilayer (4 bilayers) was assembled between adjacent chromophores to inhibit possible FRET. Finally, the UTFs were rinsed and washed
thoroughly with deionized water and dried in a flow of nitrogen gas.

1.4 Sample Characterization. The UV-vis absorption spectra were collected in the range from 190 to 900 nm on a Shimadzu U-3000 spectrophotometer, with the slit width of 1.0 nm. The fluorescence spectra were performed on a RF-5301PC fluorospectrophotometer with the excitation wavelength of 360 nm. The fluorescence emission spectra range in 380–710 nm, and the excitation and emission slit are set to be 3 and 5 nm, respectively. Photoluminescence quantum yield (PLQY) was measured using a Nanolog FL3-2iHR infrared fluorescence spectrometer equipped with an integrating sphere. Luminescence lifetime measurements were recorded with an Edinburgh Instruments FL 900 fluorimeter. The percentage contribution of each lifetime component to the total decay was calculated with the Edinburgh F900 instruments software. The CIE 1931 color coordinates of the fluorescence were determined using a Photo Research PR-650 SpectraScan colorimeter with the detector vertical to the surface of the UTF. Fluorescence was observed using an OLYMPUS-BX51 fluorescence microscope. The photobleaching was tested by the UV lighting with CHF-XQ 500W. TEM images were recorded on a JEOL JEM-2100 transmission electron microscope with the accelerating voltage of 200 kV. X-ray diffraction patterns (XRD) of the luminescence UTFs were recorded using a Rigaku 2500 VB2+PC diffractometer under the conditions: 40 kV, 50 mA, Cu Kα radiation (λ = 0.154056 nm) with step-scanned in step of 0.04° (2θ) in the range from 0.5 to 8° using a count time of 10 s/step. The morphology of thin films was investigated by using a scanning electron microscope (SEM Hitachi S-3500) equipped with an EDX attachment (EDX Oxford Instrument Isis 300), and the accelerating voltage applied was 20 kV. The surface roughness data were obtained by using the NanoScope IIIa atomic force microscope (AFM) from Veeco Instruments.

2. Morphology of CdTe QDs
Figure S1. TEM images of (A) QD-530 (mean particle size: ~2.5 nm) and (B) QD-620 (mean particle size: ~4.0 nm).  

3. UV-vis absorption and fluorescence spectra of Rhodamine 6G, BTBS and CdTe QDs aqueous solution

![Figure S2](image-url)

Figure S2. UV-vis absorption and fluorescence spectra of (A) Rhodamine 6G, (B) BTBS, (C) QD-530 and (D) QD-620 aqueous solution. The inset shows their photographs under UV-light irradiation.
The fluorescence Quantum Yields (QY) of luminescence materials was determined relative to rhodamine-6G (QY=0.95) using the relation:

\[
QY_x = \frac{A_x n_x^2 F_x}{A_s n_s^2 F_s} QY_s \tag{1}
\]

where \(F_x\) and \(F_s\) are the total integrated fluorescence intensity of the unknown and emission standard, respectively; \(A_x\) and \(A_s\) are the corresponding wavelength-specific absorbance, and \(QY_s\) is the fluorescence quantum yield value for the standard fluorophore. The quantity \((n_x/n_s)^2\) represents the solvent refractive index correction.\(^\text{10}\)

### 4. Fabrication of multi-color UTFs

#### 4.1 (BTBS/LDH)\(_{12}\)(QD-530/LDH)\(_n\) \((n = 0–20)\) UTFs for blue/green luminescence

---

**Figure S3.** UV-vis absorption spectra of the (BTBS/LDH)\(_{12}\)(QD-530/LDH)\(_n\) \((n=0–20)\) UTFs (the inset shows the enlarged absorbance at 500 nm).
Table S2. CIE 1931 color coordinates for the (BTBS/LDH)$_{12}$(QD-530/LDH)$_n$ ($n=0–20$) UTFs as well as the pristine (QD-530/LDH)$_{20}$ UTF

<table>
<thead>
<tr>
<th>$n$ CIE</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
<th>QD-530</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>0.159</td>
<td>0.166</td>
<td>0.176</td>
<td>0.173</td>
<td>0.179</td>
<td>0.182</td>
<td>0.195</td>
<td>0.198</td>
<td>0.201</td>
<td>0.205</td>
<td>0.219</td>
<td>0.228</td>
</tr>
<tr>
<td>$y$</td>
<td>0.108</td>
<td>0.147</td>
<td>0.196</td>
<td>0.223</td>
<td>0.254</td>
<td>0.282</td>
<td>0.303</td>
<td>0.318</td>
<td>0.340</td>
<td>0.359</td>
<td>0.376</td>
<td>0.503</td>
</tr>
</tbody>
</table>

4.2 (BTBS/LDH)$_{12}$(QD620/LDH)$_n$ ($n=0–20$) UTFs for blue/red luminescence

Figure S4. UV-vis absorption spectra of the (BTBS/LDH)$_{12}$(QD-620/LDH)$_n$ ($n=0–20$) UTFs (the inset shows the enlarged absorbance at 600 nm).

Table S3. CIE 1931 color coordinates for the (BTBS/LDH)$_{12}/$(QD-620/LDH)$_n$ ($n=0–20$) UTFs as well as the pristine (QD-620/LDH)$_{20}$ UTF

<table>
<thead>
<tr>
<th>$n$ CIE</th>
<th>0</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
<th>14</th>
<th>16</th>
<th>18</th>
<th>20</th>
<th>QD-620</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>0.159</td>
<td>0.179</td>
<td>0.245</td>
<td>0.282</td>
<td>0.306</td>
<td>0.328</td>
<td>0.397</td>
<td>0.424</td>
<td>0.437</td>
<td>0.453</td>
<td>0.477</td>
<td>0.589</td>
</tr>
<tr>
<td>$y$</td>
<td>0.108</td>
<td>0.123</td>
<td>0.144</td>
<td>0.172</td>
<td>0.177</td>
<td>0.180</td>
<td>0.207</td>
<td>0.220</td>
<td>0.235</td>
<td>0.246</td>
<td>0.255</td>
<td>0.310</td>
</tr>
</tbody>
</table>

4.3 (BTBS/LDH)$_{12}$(QD-530/LDH)$_{16}$(QD-620/LDH)$_n$ ($n=1–12$) UTFs for white luminescence
Figure S5. UV-vis absorption spectra of the (BTBS/LDH)_{12}(QD-530/LDHs)_{16}(QD-620/LDHs)_{n} (n=1–12) UTFs (the inset shows the enlarged absorbance at 500 and 600 nm).

Table S4. CIE 1931 color coordinates for the (BTBS/LDH)_{12}(QD-530/LDH)_{16}(QD-620/LDH)_{n} (n=1-12) UTFs

<table>
<thead>
<tr>
<th>n</th>
<th>CIE</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>y</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|    | 0.228 | 0.239 | 0.240 | 0.256 | 0.283 | 0.317 | 0.322 | 0.363 | 0.374 | 0.386 | 0.396 | 0.407 |
|    | 0.382 | 0.374 | 0.356 | 0.357 | 0.342 | 0.320 | 0.324 | 0.319 | 0.317 | 0.322 | 0.316 | 0.308 |

4.4 Comparison of different fabrication methods

Figure S6. (A) Photographs and (B) fluorescence spectra of the drop-casted film and LBL UTF with similar fluorescence intensity: (a) the aqueous solution for drop-casting, (b) the drop-casted film, (c) the (BTBS/LDH)_{12}(QD-530/LDH)_{16}(QD-620/LDH)_{6} UTF.
5. Morphological and structural characterization of the multi-color UTFs

5.1 Structural characterization of the luminescence UTFs

![Figure S7. XRD patterns of (A) (BTBS/LDHs)
30 UTF, (B) (QD-530/LDHs)
30 UTF, (C) (QD-620/LDHs)
30 UTF.]

Table S5. 2θ degree and d₀₀₁ values of the multi-color UTFs

<table>
<thead>
<tr>
<th>UTFs</th>
<th>2θ(°)</th>
<th>d₀₀₁(Å)</th>
</tr>
</thead>
</table>
| (BTBS/LDHs)
30                      | 5.71  | 1.55    |
| (QD-620/LDHs)
30                     | 1.29  | 6.80    |
| (QD-530/LDHs)
30                   | 1.91  | 4.62    |
| (BTBS/LDHs)
12(QD-620/LDHs)
20       | 1.33  | 6.64    |
| (BTBS/LDHs)
12(QD-530/LDHs)
20     | 1.95  | 4.53    |
| (BTBS/LDHs)
12(QD-530/LDHs)
16(QD-620/LDHs)
12[c] | 1.26[a]/1.9[b] | 4.65[a]/7.01[b] |

[a] Reflection attributed to the (QD-620/LDH) unit.
[b] Reflection attributed to the (QD-530/LDH) unit.
[c] Reflection of the (BTBS/LDH) unit is rather weak which can’t be observed in the diagram.

5.2 Morphological characterization of (BTBS/LDHs)
12(QD-530/LDHs)
ₙ (n=0–20) UTFs

[Images of AFM and TEM images]
**Figure S8.** Morphology of the (BTBS/LDHs)$_{12}$(QD-530/LDHs)$_n$ $(n=0–20)$ UTFs: (A) top-view SEM images, (B) tapping-mode AFM topographical images, (C) side-view SEM images. From 1 to 5: $n=0, 4, 8, 12, 16$, respectively.

**5.3 Morphological characterization of (BTBS/LDHs)$_{12}$(QD-620/LDHs)$_n$ $(n=0–20)$ UTFs**

**Figure S9.** Morphology of the (BTBS/LDHs)$_{12}$(QD-620/LDHs)$_n$ $(n=0–20)$ UTFs: (A) top-view SEM images, (B) tapping-mode AFM topographical images, (C) side-view SEM images. From 1 to 5: $n=0, 4, 8, 12, 16$, respectively.

**5.4 Morphological characterization of (BTBS/LDHs)$_{12}$(QD-530/LDHs)$_{16}$(QD-620/LDHs)$_n$ $(n=0–12)$ UTFs**

**Figure S10.** Morphology of the (BTBS/LDHs)$_{12}$(QD-530/LDHs)$_{16}$(QD-620/LDHs)$_n$ $(n=0–12)$ UTFs: (A) top-view SEM images, (B) tapping-mode AFM topographical images, (C) side-view SEM images. From 1 to 3: $n=0, 4, 8$, respectively.
5.5 The roughness and thickness of multi-color UTFs

Table S6. RMS roughness and thickness parameters for multi-color UTFs with different bilayer number

<table>
<thead>
<tr>
<th>UTFs</th>
<th>n</th>
<th>0</th>
<th>4</th>
<th>8</th>
<th>12</th>
<th>16</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>(BTBS/LDHs)$_{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMS roughness (nm)</td>
<td></td>
<td>2.570</td>
<td>2.954</td>
<td>3.753</td>
<td>4.428</td>
<td>5.069</td>
<td>5.977</td>
</tr>
<tr>
<td>SEM thickness (nm)</td>
<td></td>
<td>~21</td>
<td>~39</td>
<td>~59</td>
<td>~76</td>
<td>~94</td>
<td>~112</td>
</tr>
<tr>
<td>(QD-530/LDHs)$_n$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMS roughness (nm)</td>
<td></td>
<td>2.781</td>
<td>3.131</td>
<td>4.089</td>
<td>4.912</td>
<td>5.564</td>
<td>6.321</td>
</tr>
<tr>
<td>SEM thickness (nm)</td>
<td></td>
<td>~21</td>
<td>~45</td>
<td>~75</td>
<td>~100</td>
<td>~125</td>
<td>~155</td>
</tr>
<tr>
<td>(BTBS/LDHs)$_{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMS roughness (nm)</td>
<td></td>
<td>6.052</td>
<td>7.037</td>
<td>7.601</td>
<td>8.364</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SEM thickness (nm)</td>
<td></td>
<td>~112</td>
<td>~141</td>
<td>~171</td>
<td>~200</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(QD-620/LDHs)$_n$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RMS roughness (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEM thickness (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Stability of the drop-casted film as a comparison sample

Figure S11. (A) Photostability of the drop-casted film upon irradiation by UV light (365 nm) for 300 min; (B) the fluorescence intensity of the drop-casted film (stored at room temperature) recorded weekly in 3 month.
Figure S12. The fluorescence intensity of $(\text{BTBS/LDH})_{12}(\text{QD-530/LDH})_{16}(\text{QD-620/LDH})_7$ UTF in environment with different relative humidity.

7. Fluorescence Lifetime of the mono-color and multi-color UTFs

Table S7. The fluorescence lifetime of mono-color and multi-color UTFs

<table>
<thead>
<tr>
<th>UTFs</th>
<th>t/ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{BTBS/LDH})_{30}$</td>
<td>0.76</td>
</tr>
<tr>
<td>$(\text{QD-530/LDH})_{30}$</td>
<td>6.45</td>
</tr>
<tr>
<td>$(\text{QD-620/LDH})_{30}$</td>
<td>7.77</td>
</tr>
<tr>
<td>$(\text{BTBS/LDH})<em>{12}(\text{QD-530/LDH})</em>{20}$</td>
<td>$440^{[a]}/533^{[b]}$ nm</td>
</tr>
<tr>
<td>$(\text{BTBS/LDH})<em>{12}(\text{QD-620/LDH})</em>{20}$</td>
<td>$440^{[a]}/630^{[c]}$ nm</td>
</tr>
<tr>
<td>$(\text{BTBS/LDH})<em>{12}(\text{QD-530/LDH})</em>{16}(\text{QD-620/LDH})_7$</td>
<td>$440^{[a]}/533^{[b]}/630^{[c]}$ nm</td>
</tr>
</tbody>
</table>

[a] The lifetime of emission at 440 nm.
[b] The lifetime of emission at 533 nm.
[c] The lifetime of emission at 630 nm.

Reference:

2009, **48**, 3073.


