

# Electronic Supplementary Information

## **Encapsulation of perovskite quantum dots into Ln<sup>III</sup>- incorporated polymer matrix to achieve white light emission**

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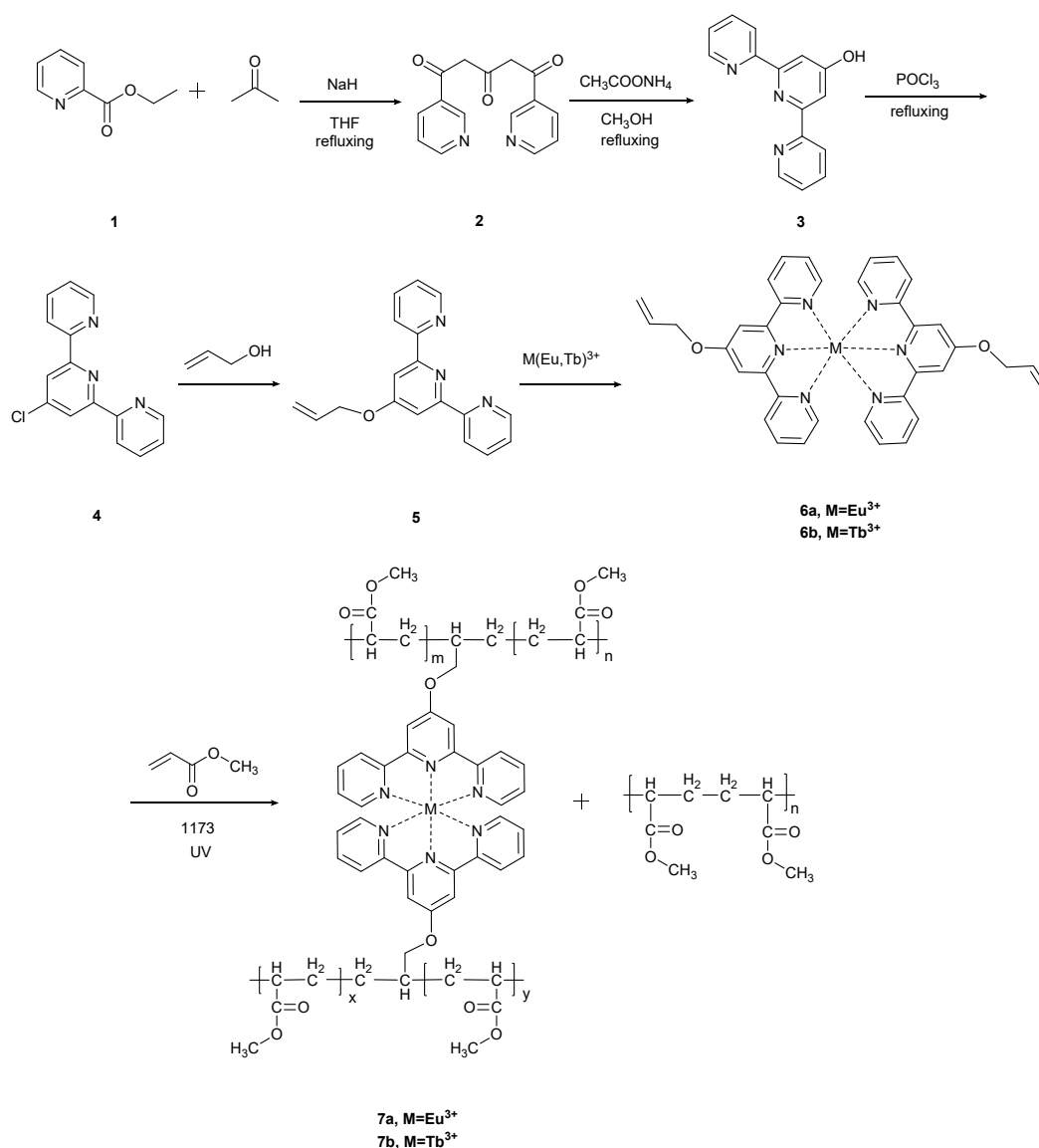
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## Experimental Procedures

### 1.0 Materials

Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , 99.99 %), lead chloride ( $\text{PbCl}_2$ , 99.999%), lead bromide ( $\text{PbBr}_2$ , 99.999%), 1-octadecene (ODE, 90%), oleic acid (OA, AR), oleylamine (OAm, 80%-90%), methyl acrylate (MA, 99%) were purchased from Aladdin; pyridine-2-carboxylic acid ethyl ester, Europium(III) nitrate hexahydrate ( $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.99%), Terbium(III) nitrate hexahydrate ( $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.99%) were purchased from Heowns Biochem Technologies. The chemical reagents were commercially available and directly utilized without further purification.

### 2.0 Methods



Scheme S1. Synthetic route of **7a** and **7b**

### **2.1 Synthesis of 1,5-di(pyridin-3-yl)pentane-1,3,5-trione (2), 4'-hydroxy-2,2':6',2''-terpyridine (3) and 4'-chloro-2,2':6',2''-terpyridine (4)**

Compounds **2-4** were synthesized using a slightly improved literature method.<sup>1</sup>

Compound **3** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.98 (s, 1H), 8.80 (dt, J = 4.9, 1.3 Hz, 2H), 8.00 – 7.85 (m, 4H), 7.44 (ddd, J = 7.3, 4.8, 1.3 Hz, 2H), 7.10 (s, 2H).

Compound **4** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.71 (ddd, J = 4.8, 1.8, 0.9 Hz, 2H), 8.60 (dt, J = 8.0, 1.1 Hz, 2H), 8.49 (s, 2H), 7.87 (td, J = 7.8, 1.8 Hz, 2H), 7.37 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H).

### **2.2 Synthesis of 4'-(allyloxy)-2,2':6',2''-terpyridine (5)**

KOH (0.56 g, 10 mmol) and allyl alcohol (0.116 g, 2 mmol) were added to a 100 mL round bottom flask containing anhydrous dimethyl sulfoxide (10 mL). The reaction mixture was brought to 60 °C and stirred for 0.5 h. Compound **4** (0.54 g, 2 mmol) was added to the reaction system and reacted for 24 h. After cooling to room temperature, the reaction mixture was transferred to a 250 mL two-necked flask, added to water (100 mL), stirred for 6 h and allowed to stand for 10 h. The reaction mixture was filtered, the filter cake was collected and dried to obtain white solid (0.561 g). The crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to give a white solid **5** (0.466 g, 80.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (ddd, J = 4.8, 1.8, 0.9 Hz, 2H), 8.62 (dt, J = 8.0, 1.1 Hz, 2H), 8.04 (s, 2H), 7.85 (td, J = 7.7, 1.8 Hz, 2H), 7.33 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H), 6.11 (ddt, J = 17.2, 10.4, 5.1 Hz, 1H), 5.50 (dq, J = 17.3, 1.6 Hz, 1H), 5.34 (dq, J = 10.6, 1.4 Hz, 1H), 4.80 (dt, J = 5.1, 1.6 Hz, 2H).

### **2.3 Synthesis of Ln<sup>III</sup>-coordinated terpyridyl complex 6a (Eu<sup>III</sup> complex) and 6b (Tb<sup>III</sup> complex)**

Compound **5** (260 mg, 0.9 mmol) was dissolved in 10 mL of anhydrous ethanol. An ethanolic solution of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.1 mol/L, 3 mL) was added to the above system under stirring. The reaction mixture was heated at 70 °C for 10 h, cooled to room temperature and transferred to a beaker containing 100 mL of ether. The above mixture was separated by centrifugation to obtain a white solid **6a** (0.486 g, 73.9%). Compound **6b** was obtained as a white solid (0.407 g, 61.4%) following a similar procedure to the preparation of **6a**.

Compound **6a** HRMS [M + H]<sup>+</sup> calcd for C<sub>36</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>Eu<sup>3+</sup> 732.2245; found: 732.2259;

Compound **6b** HRMS [M + H]<sup>+</sup> calcd for C<sub>36</sub>H<sub>30</sub>N<sub>6</sub>O<sub>2</sub>Tb<sup>3+</sup> 737.0956; found: 737.0934;

### **2.4 Preparation of solution of Ln<sup>III</sup>-incorporated polymer 7a (Eu<sup>III</sup>) and 7b (Tb<sup>III</sup>) in CH<sub>2</sub>Cl<sub>2</sub>**

Compound **6a** (7.32 mg, 0.01 mmol), methyl acrylate (1.722 g, 20 mmol), photoinitiator 1173 (10 μL) and dichloromethane (3 mL) were added to a 10 mL beaker. The resultant mixture was sonicated until all the substances were well dispersed. The reaction mixture was irradiated in a UV dark box for 24 h (λ = 365 nm) to obtain a colorless and viscous solution of polymer **7a** in CH<sub>2</sub>Cl<sub>2</sub>. The solution of Ln<sup>III</sup>-incorporated polymer **7b** in CH<sub>2</sub>Cl<sub>2</sub> was prepared following a similar procedure to the preparation of **7a**.

### **2.5 Preparation of Cs-oleate precursor**

Cs-oleate precursor was prepared according to a reported method developed by Protesescu<sup>2</sup> with some modifications. In brief, Cs<sub>2</sub>CO<sub>3</sub> (0.081 g), OA (0.4 mL) and ODE (4 mL) were loaded into a 3-neck flask. The mixture was degassed and dried under vacuum at 120 °C for 1 h. Then Cs-oleate was obtained after the above mixture reacted completely at 150 °C for 15 min. All above reactions were carried out under Ar.

### **2.6 Synthesis of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> quantum dots**

CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> quantum dots were synthesized according to a reported method developed by Protesescu<sup>2</sup> with some modifications. Briefly, PbCl<sub>2</sub> (69.5 mg 0.25 mmol), PbBr<sub>2</sub> (91.8 mg, 0.25 mmol), OA (1.5 mL), OAm (1.5 mL) and ODE (13 mL) were loaded into a 3-neck flask which was degassed under vacuum at 120 °C for 1 h. Then, under the Ar flow, the temperature of the mixture was raised up to 160 °C and maintained for 15 minutes. After PbX<sub>2</sub> dissolved completely, 1.0 mL of the Cs-oleate solution pre-heated at 120 °C was injected swiftly. After 5 s, the reaction mixture was cooled immediately in an ice-water bath.

### **2.7 Isolation and purification of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> quantum dots**

The above crude solution was centrifuged at 12000 rpm for 10 min and the supernatant was discarded. The obtained precipitate was dispersed in 9 mL of toluene, the resultant mixture centrifuged at 10000 rpm for 10 min and the supernatant discarded. The precipitate was collected and dispersed again in 18 mL of toluene, the resultant mixture centrifuged at 5000 rpm for 5 min and the supernatant collected. Then the toluene solution of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> QDs was obtained.

### **2.8 Preparation of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub>/PMA film**

Methyl acrylate (1.722 g, 20 mmol), photoinitiator 1173 (10 μL) and dichloromethane (3 mL) were added to a 10 mL beaker. The mixture was sonicated until all the substances were well dispersed. The reaction mixture was irradiated in a UV dark box for 24 h (λ = 365 nm) to obtain a colorless and viscous solution of PMA. Then 5 mL of the above obtained PMA solution in CH<sub>2</sub>Cl<sub>2</sub> and 1 mL of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> solution (5 mg/mL) in toluene were mixed together. The above mixed solution (1 mL) was applied dropwise on a glass slide (2 cm × 2 cm), which was allowed to dry slowly in air at room temperature. Uniform CsPbCl<sub>1.5</sub>Br<sub>1.5</sub>/PMA films were then obtained after 24 h.

### **2.9 Preparation of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> QDs film**

The CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> solution (5 mg/mL, 1 mL) in toluene was added to 5 mL of dichloromethane. The above mixed solution (1 mL) was applied dropwise on a glass slide (2 cm × 2 cm), which was allowed to dry slowly in air at room temperature. Uniform CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> QDs films were then obtained after 24 h.

### **2.10 Preparation of white light emission composite film**

The above obtained viscous solution of polymer **7a** in CH<sub>2</sub>Cl<sub>2</sub> (2.9 mL) and **7b** in CH<sub>2</sub>Cl<sub>2</sub> (2.1 mL) and the solution of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> QDs in toluene (5 mg / mL, 1 mL)

were mixed together. 1 mL of the above mixed solution was applied dropwise on a glass slide (2 cm × 2 cm) which was allowed to dry slowly in air at room temperature. Uniform white light emission composite films were then obtained after 24 h.

### **3.0 Characterization**

Powder X-ray diffraction (XRD) patterns were obtained using a Bruker D8-Focus diffractometer with a Cu Ka source. The surface morphology and structure of PQD samples were observed by transmission electron microscopy (TEM, JEM-2100F). The surface morphology and elemental analysis of composite films were performed on a scanning electron microscope (SEM, Hitachi s-4800) equipped with an energy spectrometer. The fourier transform infrared (FTIR) spectrum (sample in the KBr pellet) was recorded on a Bruker Equinox 55 infrared spectrometer. The <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE IIIITM HD 400 MHz NanoBAY. The high resolution mass spectroscopy (HRMS) was recorded on a Bruker 1290UPLC/micrOTOF-QII. The average molecular weights of the polymers were measured by a Viscotek TDA 305 gel permeation chromatograph (GPC). The UV-vis absorbance spectrum was recorded a Shimadzu UV-2600 Spectro-photometer. The photoluminescence (PL) spectra, fluorescence excitation spectra and TR-LTs (Time-resolved Life-times) were recorded using an Edinburgh Instruments FLS1000 spectrophotometer. Absolute photo-luminescent quantum yields (PLQYs) were obtained using an Edinburgh Instruments FLS980 spectrophotometer. The color coordinates of the fluorescence were determined using a PR-650 spectrocolorimeter. Digital images were taken using a mobile phone camera of Oneplus 8T.

#### 4.0 Data Fitting

The lifetimes of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub> QDs, **5**, **6a**, **6b**, **7a** and **7b** were fitted using a bi-exponential decay kinetic:

$$A(t) = A_1 e^{\left(\frac{-t}{\tau_1}\right)} + A_2 e^{\left(\frac{-t}{\tau_2}\right)}$$

And the average PL lifetime ( $\tau_{average}$ ) was calculated based on the following equation:

$$\tau_{average} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

## Supporting Figures

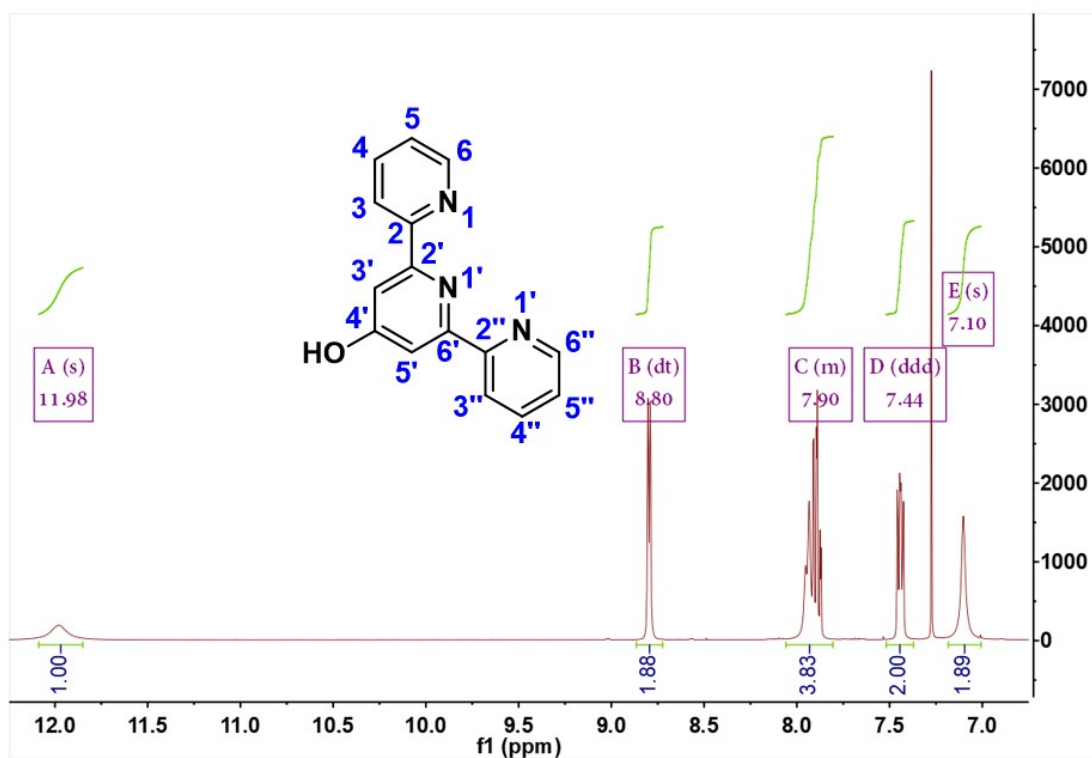


Figure S1. <sup>1</sup>H NMR spectrum of compound 3

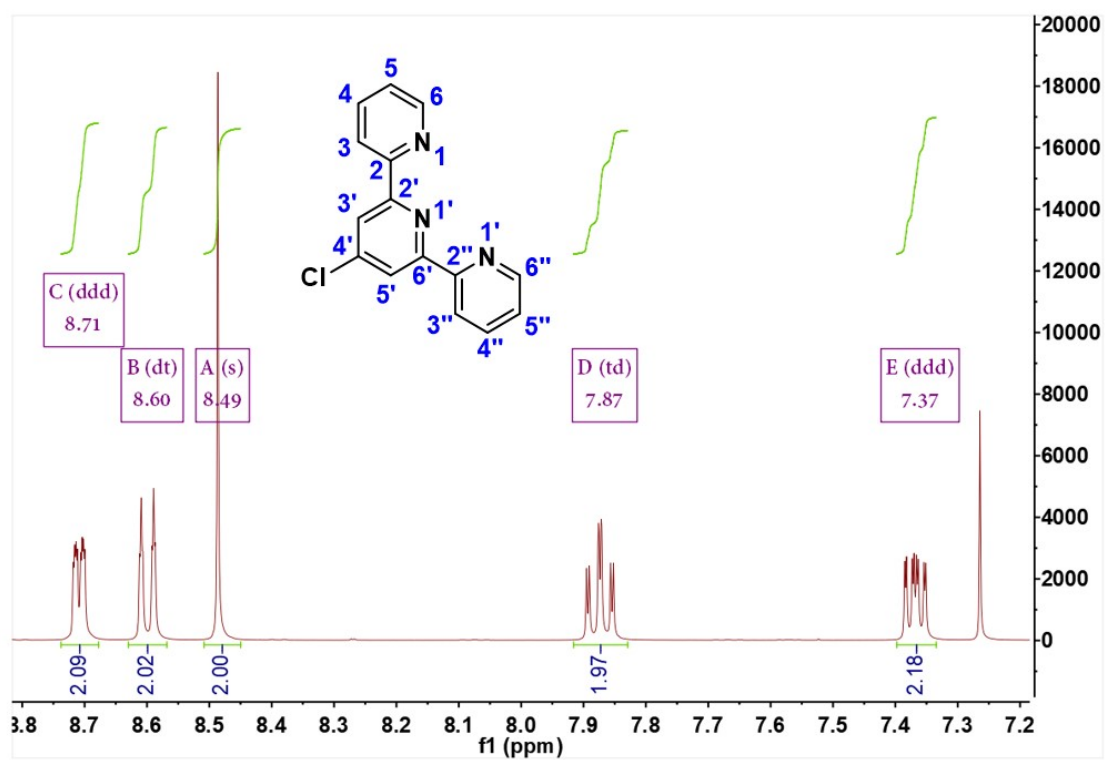


Figure S2. <sup>1</sup>H NMR spectrum of compound 4

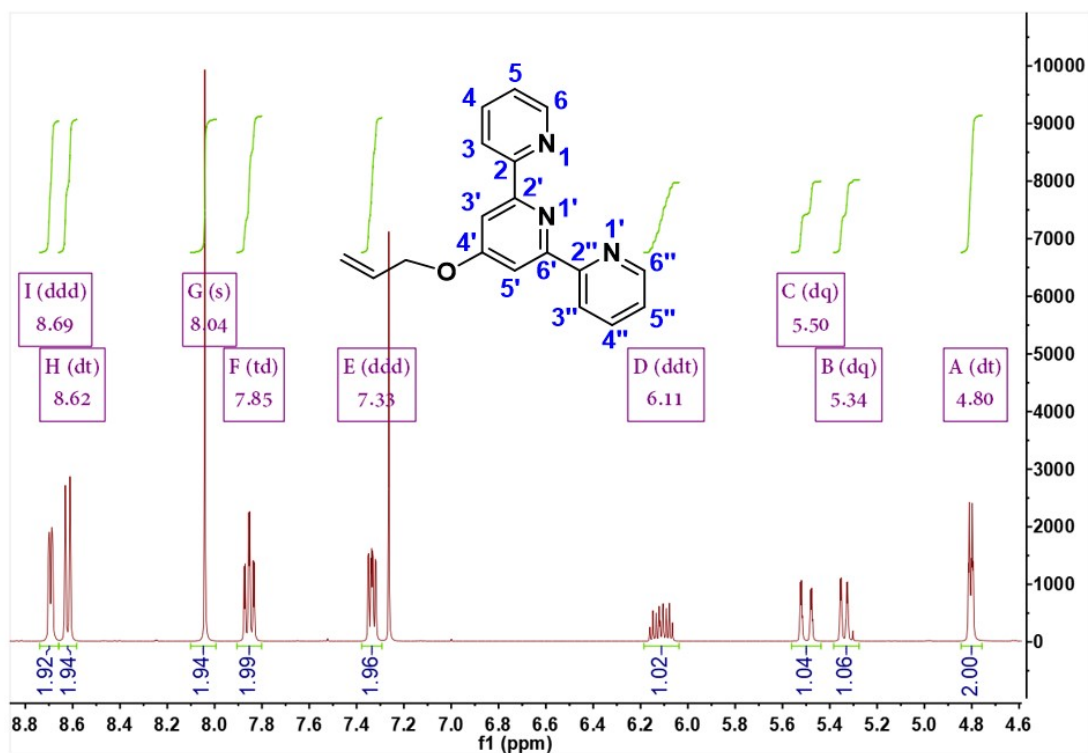


Figure S3. <sup>1</sup>H NMR spectrum of compound 5

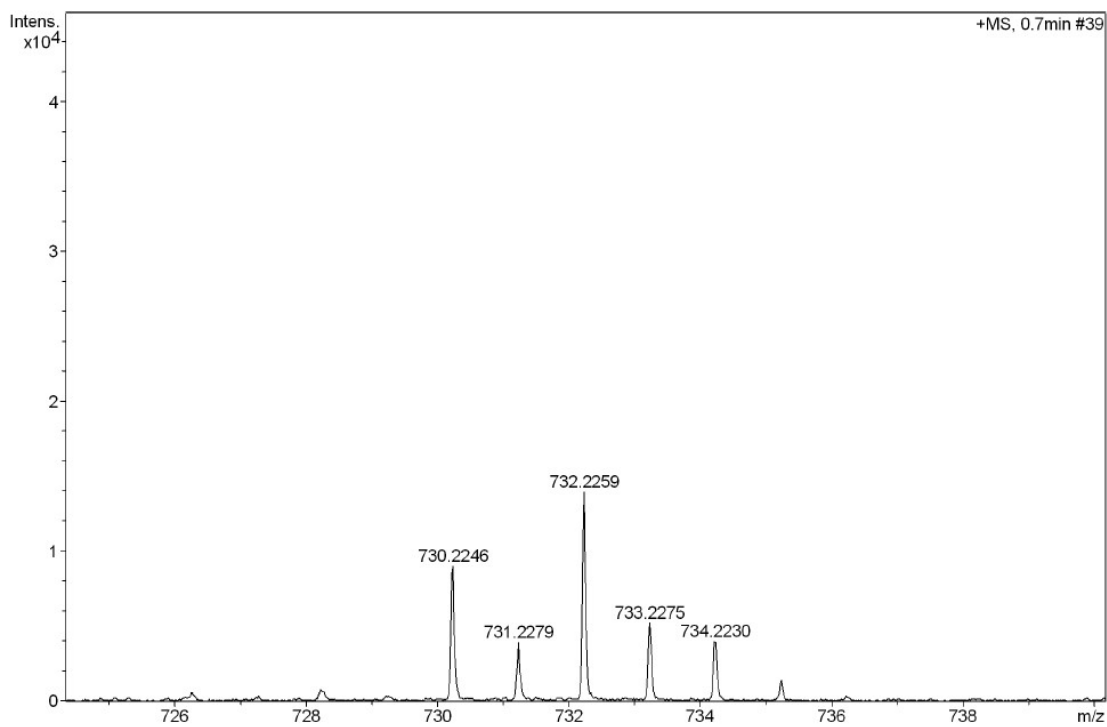
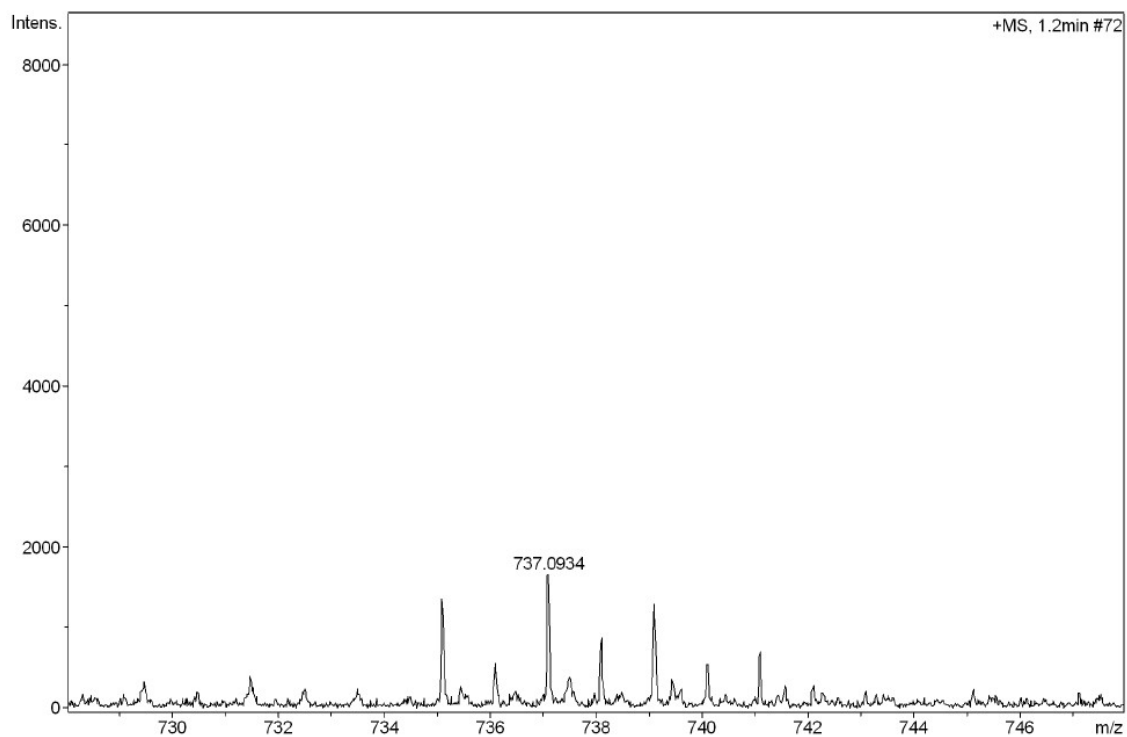
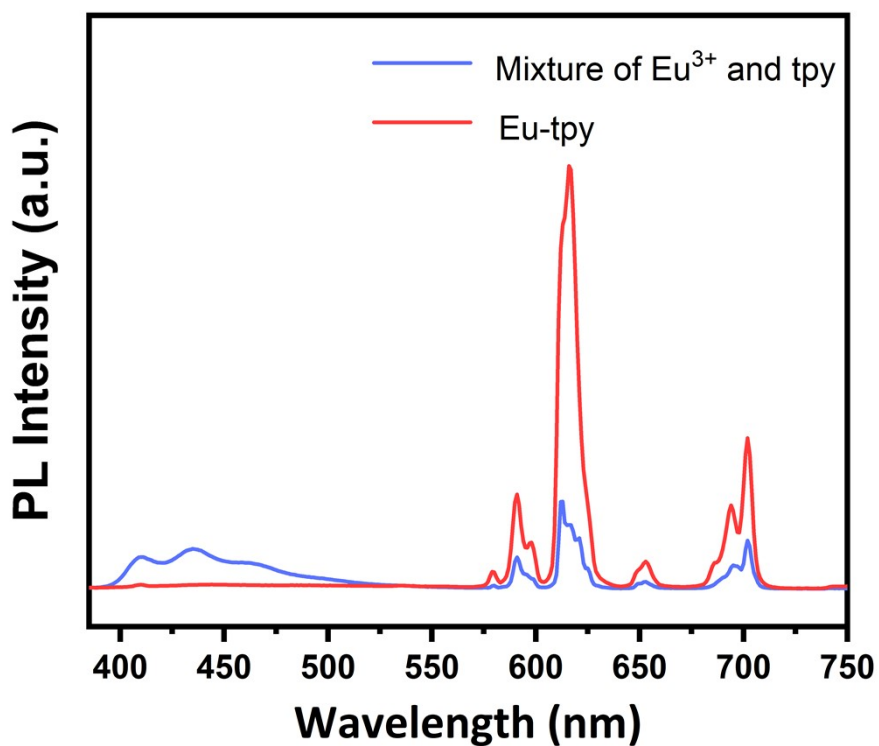


Figure S4. HRMS spectrum of compound 6a





**Figure S5.** HRMS spectrum of compound **6b**



**Figure S6.** Steady-state PL spectra of Eu-tpy and the mixture of Eu<sup>3+</sup> and tpy

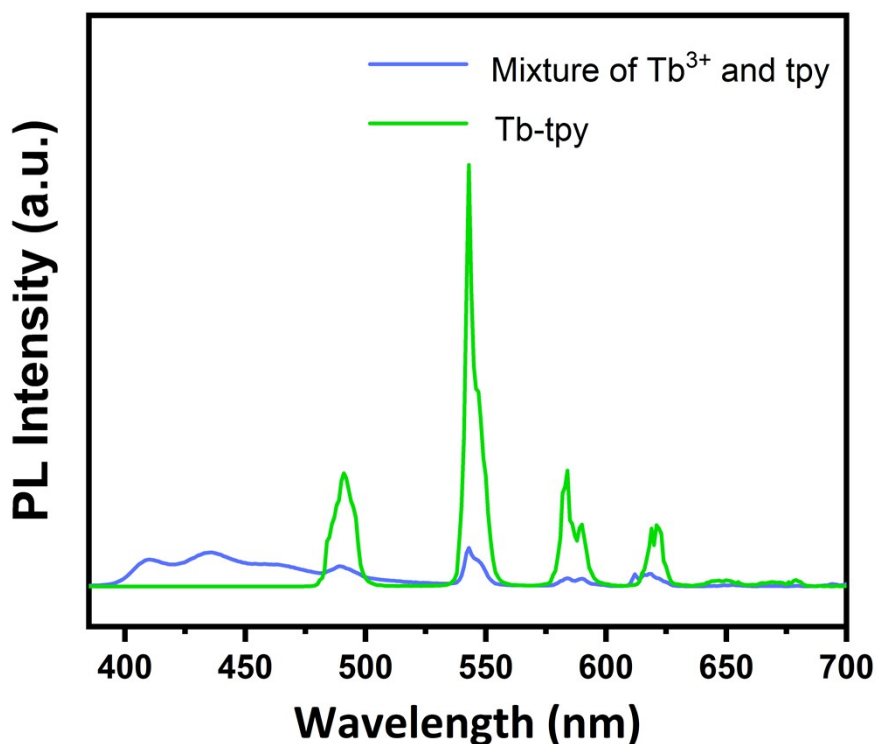


Figure S7. Steady-state PL spectra of Tb-tpy and the mixture of Tb<sup>3+</sup> and tpy

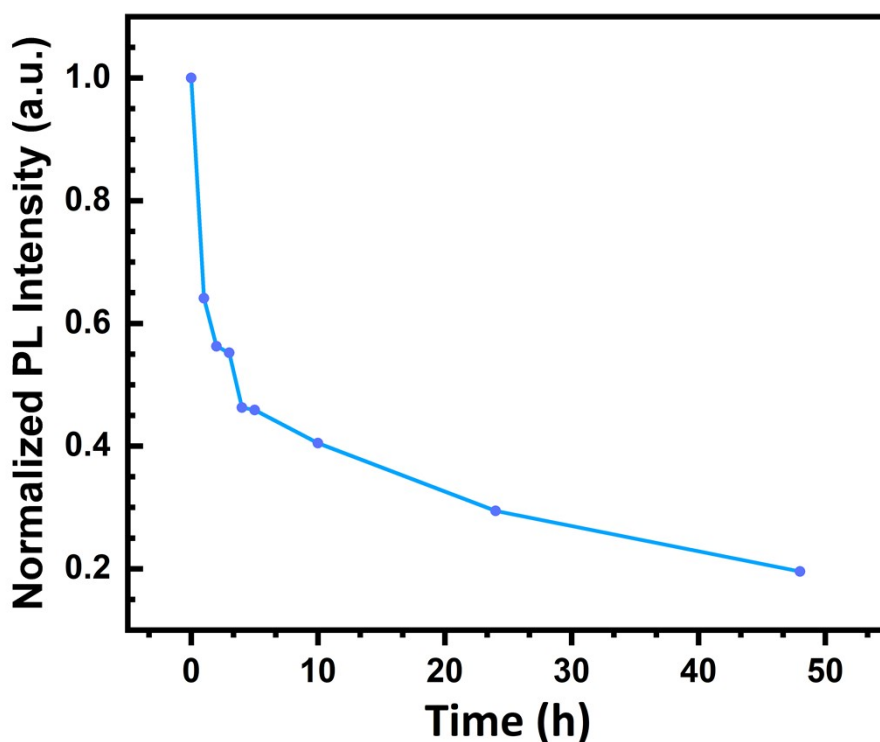


Figure S8. Normalized PL intensity of PQD-B-PMA film stored in water for different periods.

To investigate the water stability of the film, we completely immersed the polymer films with PQDs encapsulated in water and characterized them by the steady-state fluorescence spectra at certain time intervals. The fluorescence intensity variation of

the intrinsic blue emission of the PQDs was recorded to evaluate the water stability of the composite films, as shown in Fig. S8. According to the results, the most significant attenuation of the fluorescence intensity of PQDs was observed in the first hour with the polymer film immersed in water (from 100% to 64.1%). This may be due to the fact that during the encapsulation process the encapsulation matrix solution was mixed with the PQDs solution and then the solvent allowed to evaporate naturally. Inevitably, during this process some PQDs remained on the surface of the polymer film. When the film was immersed in water, the PQDs on the surface were rapidly destroyed, resulting in a significant reduction in the fluorescence intensity. During the second hour, the decay of fluorescence intensity gradually became slow. After 48 hours, the fluorescence intensity of PQDs in the film decayed to 19.6% of the initial value. In contrast, as a control group, the PQD films without polymer encapsulation completely lost their fluorescence emission within a few seconds upon immersing the films in water. Thus, it can be found that the water stability of PQDs can be effectively improved by polymer encapsulation. However, the stability of the films in water is still far from the requirement and much effort should be directed at addressing this issue in the future work.

## Supporting Tables

**Table S1.** GPC data results of **7a**

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	16.457	23.020	25.680
Mn - (Daltons)	217,999	621	31
Mw - (Daltons)	399,567	794	37
Mz - (Daltons)	656,271	1,085	41
Mp - (Daltons)	338,693	528	38
Mw / Mn	1.833	1.280	1.165
Percent Above Mw: 0	100.000	100.000	100.000
Percent Below Mw: 0	0.000	0.000	0.000
Mw 10.0% Low	76,236	345	16
Mw 10.0% High	1.137 e 6	1,963	60
Wt Fr (Peak)	0.147	0.130	0.723
RI Area - (mvml)	115.05	101.10	563.95
UV Area - (mvml)	0.00	0.00	0.00

**Table S2.** GPC data results of **7b**

Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	16.220	23.057	25.657
Mn - (Daltons)	383,624	583	32
Mw - (Daltons)	537,261	674	37
Mz - (Daltons)	721,965	791	42
Mp - (Daltons)	427,734	509	39
Mw / Mn	1.400	1.156	1.167
Percent Above Mw: 0	100.000	100.000	100.000
Percent Below Mw: 0	0.000	0.000	0.000
Mw 10.0% Low	169,333	351	16
Mw 10.0% High	1.220 e 6	1,300	60
Wt Fr (Peak)	0.033	0.125	0.842
RI Area - (mvml)	25.86	98.13	660.04
UV Area - (mvml)	0.00	0.00	0.00

**Table S3.** The PL lifetimes extracted from the original TRPL spectra of **5**, **6a**, **6b**, **7a** and **7b** (at 435 nm).

	<b>5</b>	<b>6a</b>	<b>6b</b>	<b>7a</b>	<b>7b</b>
$\tau_1$ / ns	1.48	1.40	1.42	1.04	1.28
$\tau_2$ / ns	6.68	2.99	3.50	1.58	2.66
$A_1$ / %	93.45	95.24	95.28	47.51	95.10
$A_2$ / %	6.55	4.76	4.72	52.49	4.90
$\tau_{ave}$ / ns	2.73	1.55	1.65	1.38	1.41

**Table S4.** The PL lifetimes extracted from the original TRPL spectra of **6a**, **6b**, **7a** and **7b** at corresponding emission peak energies (**6a** and **7a** at 616 nm, **6b** and **7b** at 543 nm).

	<b>6a</b>	<b>6b</b>	<b>7a</b>	<b>7b</b>
$\tau_1$ / ms	1.39	1.60	1.34	1.44
$\tau_2$ / ms	0	0	0	0
$A_1$ / %	100	100	100	100
$A_2$ / %	0	0	0	0
$\tau_{ave}$ / ms	1.39	1.60	1.34	1.44

**Table S5.** PLQYs of CsPbCl<sub>1.5</sub>Br<sub>1.5</sub>, Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, **6a**, **6b**, **7a**, **7b** and white light composite.

	PLQYs (%)
CsPbCl <sub>1.5</sub> Br <sub>1.5</sub>	52.59
Eu(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	7.21
Tb(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	1.87
<b>6a</b>	32.49
<b>6b</b>	37.44
<b>7a</b>	29.75
<b>7b</b>	24.39
white light composite	18.82

## References

- [1] H. W. Yang, A. Wang, L. Zhang, X. Zhou, G. Yang, Y. Li, Y. Zhang, B. Zhang, J. Song and Y. Feng, *New J. Chem.*, 2017, **41**, 15173-15179.
- [2] L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692-3696.