

## Electronic Supporting Information

### Tunable Electrochemiluminescence from Mixed-Monovalent Cation Perovskite Nanocrystals

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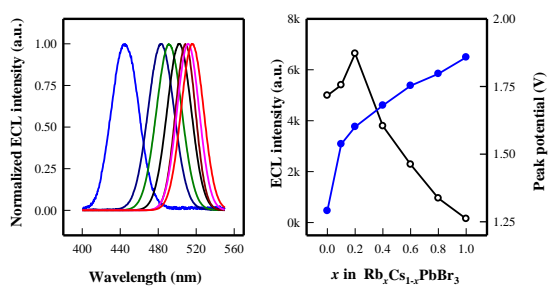
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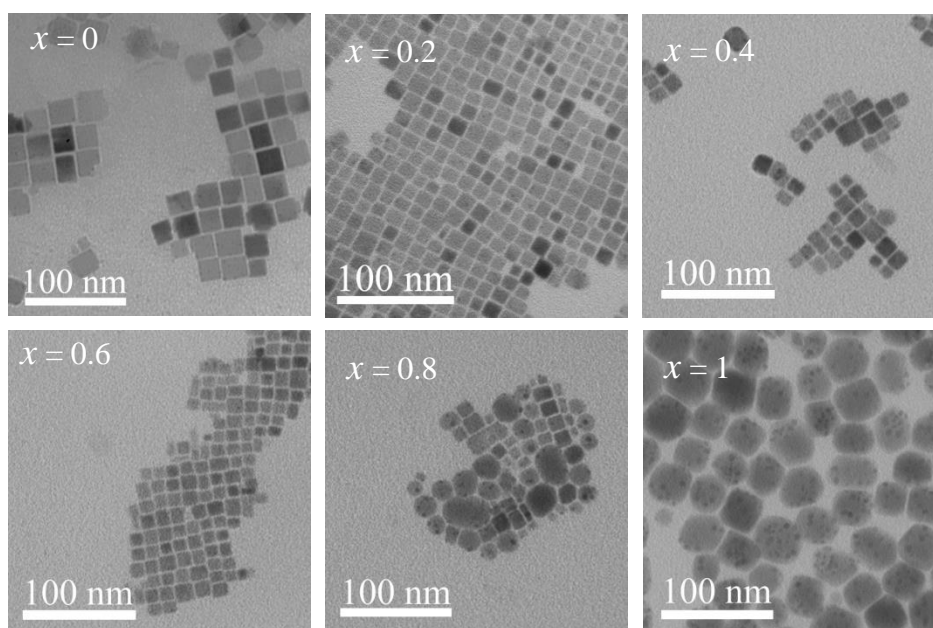
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**Colour graphic:** Dependence of the anodic ECL emission spectra, intensity and peak potential on the  $x$  in  $\text{Rb}_x\text{Cs}_{1-x}\text{PbBr}_3$ .



**Figure S1.** TEM images of  $\text{Rb}_x\text{Cs}_{1-x}\text{PbBr}_3$  NCs

**Table S1.** PL lifetime parameters for CsPbBr<sub>3</sub> NCs and Rb<sub>0.2</sub>Cs<sub>0.8</sub>PbBr<sub>3</sub> NCs.

Samples	$\tau_1$ ns	B <sub>1</sub>	$\tau_2$ ns	B <sub>2</sub>	$\tau^*$ ns
CsPbBr <sub>3</sub>	21.8	2403.6	47.8	596.2	30.9
Rb <sub>0.2</sub> Cs <sub>0.8</sub> PbBr <sub>3</sub>	30.5	2603.4	85.3	395.6	46.8

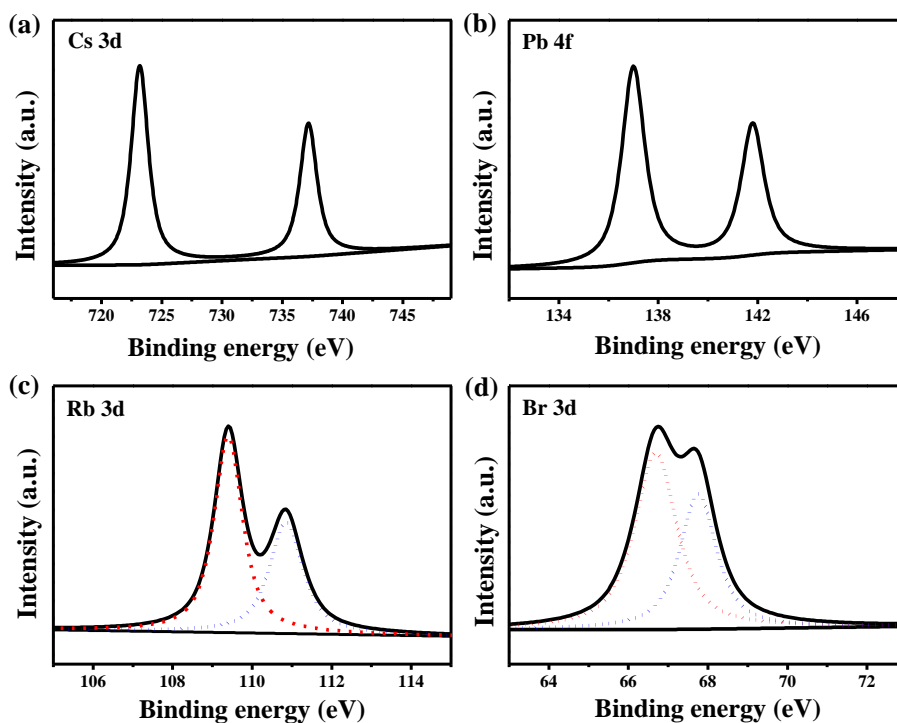
The PL lifetime traces of both CsPbBr<sub>3</sub> NCs and Rb<sub>0.2</sub>Cs<sub>0.8</sub>PbBr<sub>3</sub>NCs could be well fitted with a bi-exponential model by the following equations:

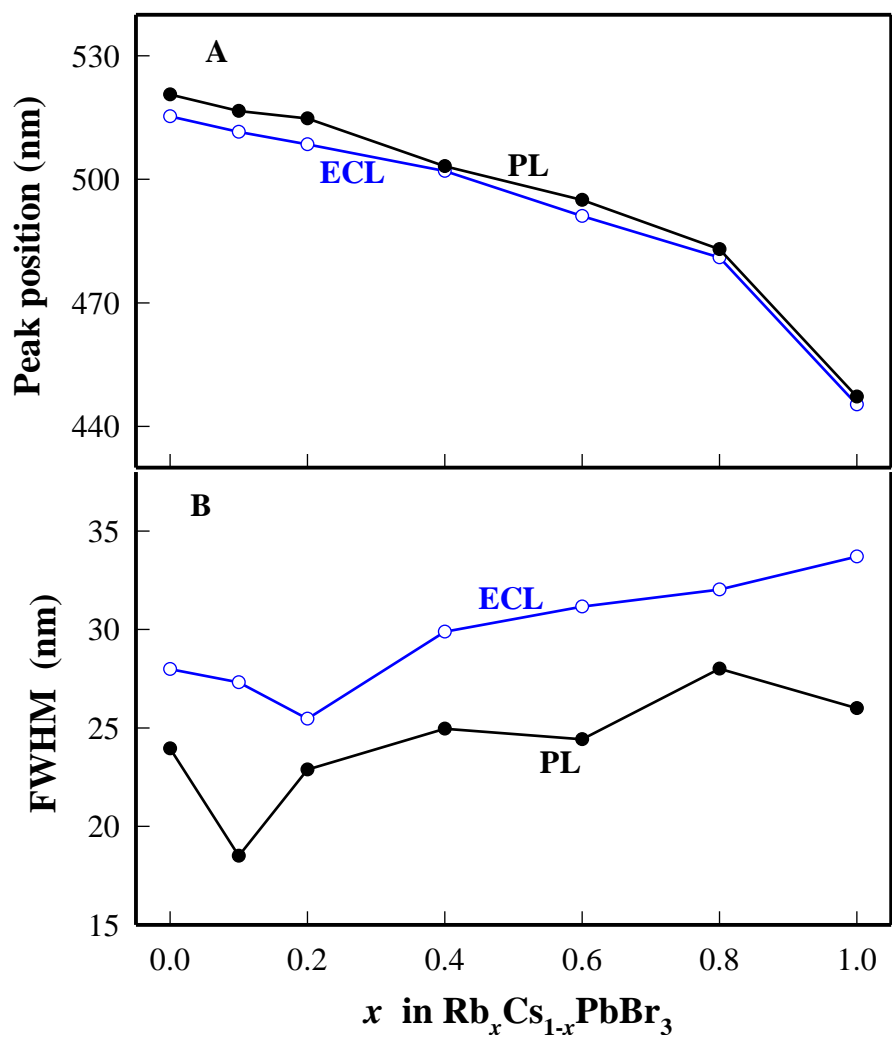
$$I(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$$

Where I is the luminescence intensity; B<sub>1</sub> and B<sub>2</sub> are constants; t is time;  $\tau_1$ ,  $\tau_2$  and  $\tau_3$  are lifetimes for the exponential components.

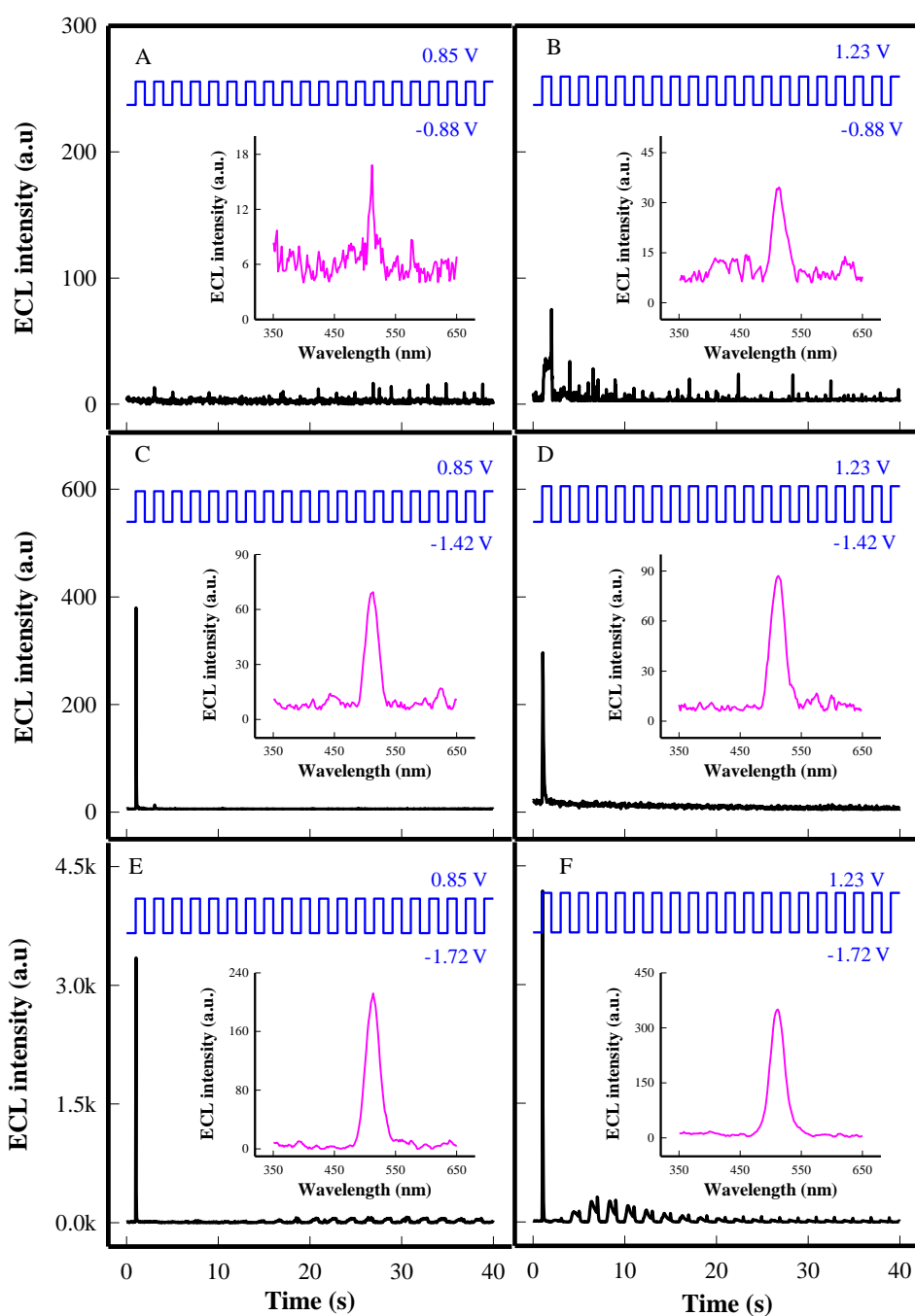
The average lifetime  $\tau^*$  constant is counted by the following equation:

$$\tau^* = (B_1 \tau_1^2 + B_2 \tau_2^2) / (B_1 \tau_1 + B_2 \tau_2)$$

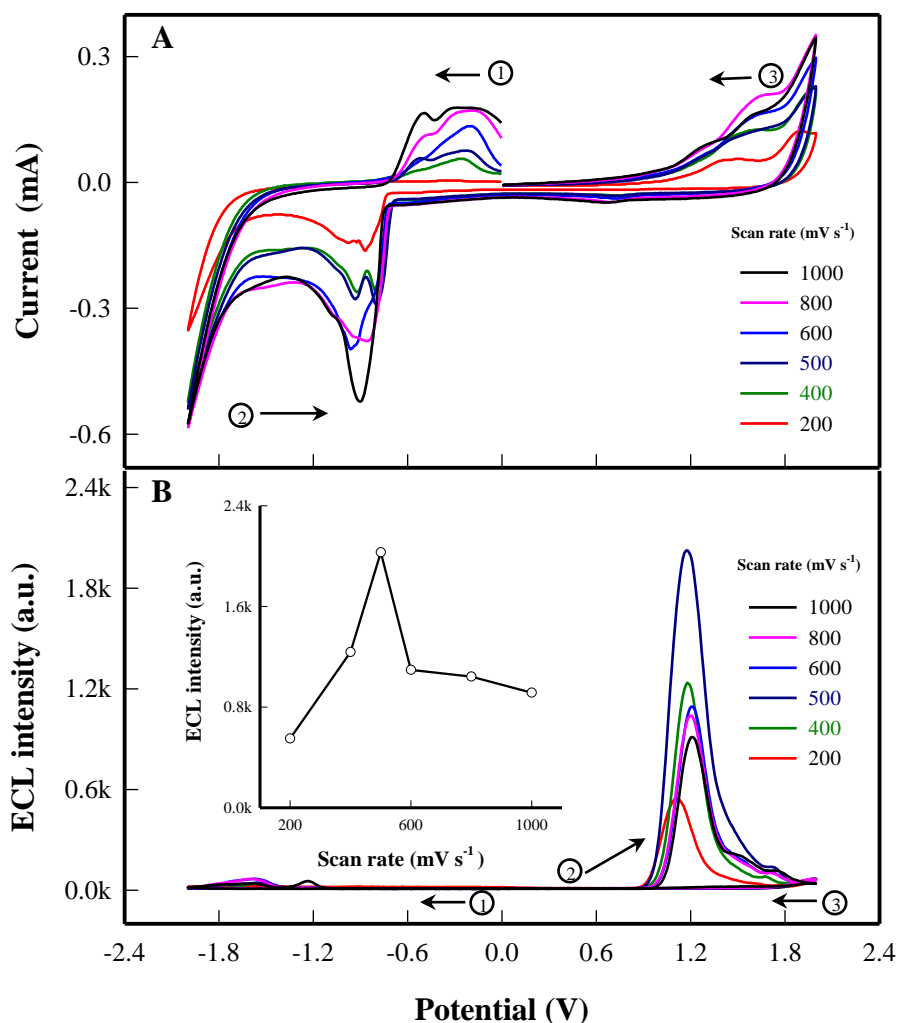
**Figure S2.** High-resolution XPS spectra of (a) Cs 3d<sub>3/2</sub> and 3d<sub>5/2</sub>, (b) Pb 4f<sub>5/2</sub> and 4f<sub>7/2</sub>, (c) Rb 3d<sub>3/2</sub> and 3d<sub>5/2</sub>, (d) Br 3d of the Rb<sub>0.2</sub>Cs<sub>0.8</sub>PbBr<sub>3</sub> NCs.



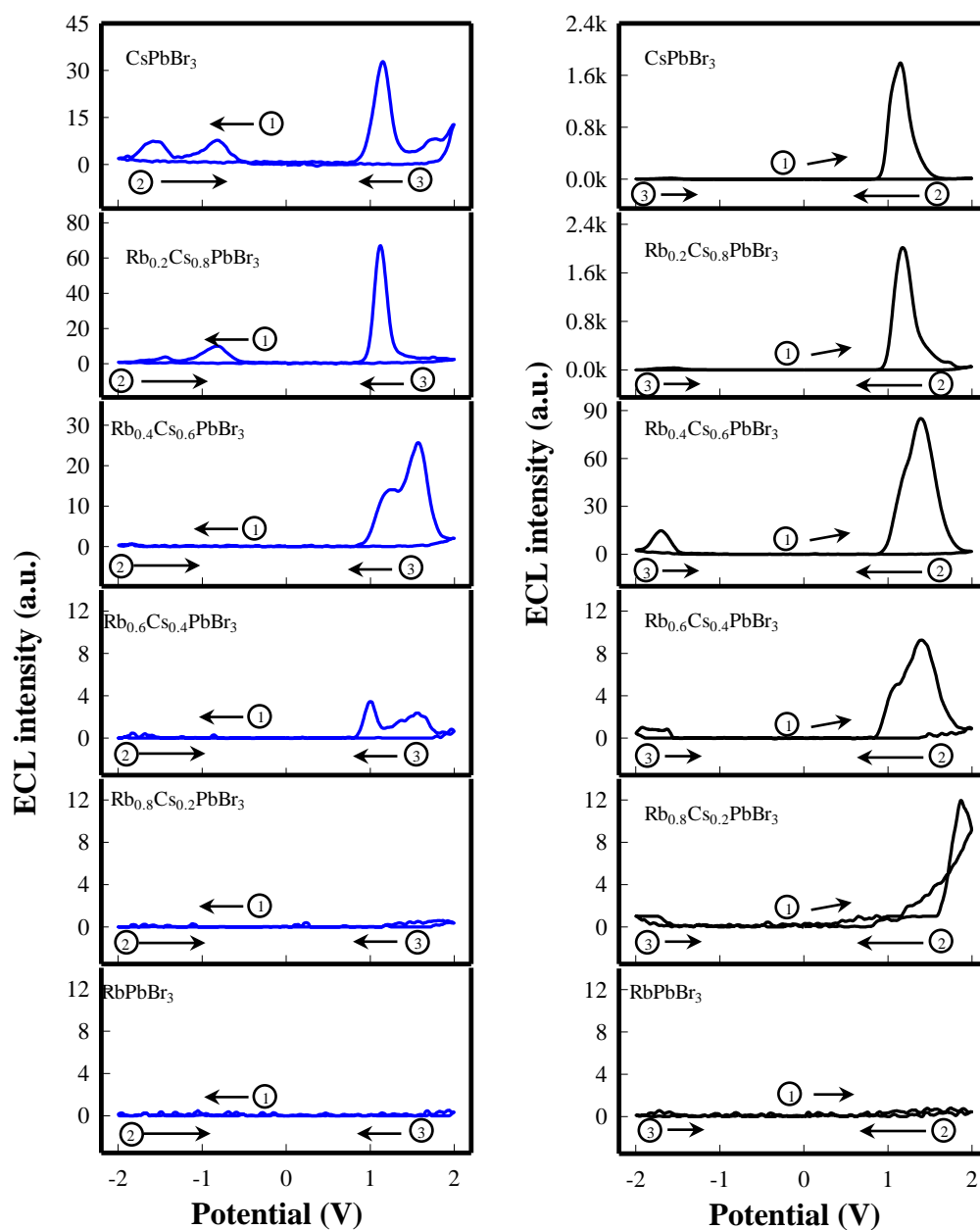
**Figure S3.** Comparison of the influence of  $\text{Rb}^+$  content ( $x$ ) on the tunable anodic ECL peak position (A) and FWHM in PL emission spectra (B) of  $\text{Rb}_x\text{Cs}_{1-x}\text{PbBr}_3$  NCs.



**Figure S4.** Electron injecting initiated ECL transients of CsPbBr<sub>3</sub> NCs|GCE (black line) by stepping the potential between (A) -0.88 V and 0.85 V, (B) -0.88 and 1.23 V, (C) -1.42 V and 0.85 V, (D) -1.42 V and 1.23 V, (E) -1.72 V and 0.85 V, (F) -1.72 V and 1.23 V at 1 Hz for 40 s in air-free dichloromethane containing 0.10 M TBAPF<sub>6</sub>. The blue lines indicate the applied potential steps. Insets: corresponding ECL emission spectra of CsPbBr<sub>3</sub> NCs|GCE (pink line). The exposure time of the CCD was 40 s.



**Figure S5.** (A) CV and (B) potential-ECL profiles of  $\text{Rb}_{0.2}\text{Cs}_{0.8}\text{PbBr}_3$  NCs|GCE in dichloromethane containing 0.1 M  $\text{TBAPF}_6$  by scanning the electrode from  $0 \rightarrow -2.0 \text{ V} \rightarrow 2.0 \text{ V} \rightarrow 0$  at different scan rates. Inset: Anodic ECL intensity at different scanning rates.



**Figure S6.** ECL profiles of  $\text{Rb}_x\text{Cs}_{1-x}\text{PbBr}_3$  NCs/GCE in air-free dichloromethane containing 0.1mM TBAPF<sub>6</sub> with negative (blue lines) or positive (black lines) initial potential scan from 0 V. The scanning rate was 500 mV/s. (The inset arrows indicated the potential scan direction)