

† Discriminatory Fluorescence and FRET in Chiral-Perovskite/RhB system

Materials

Cesium carbonate (Cs_2CO_3 , 99.9%), lead (II) bromide (PbBr_2 , 99%), oleyl amine (OAm, 80%–90%), oleic acid (OAc, 85%), N, N-dimethylformamide (DMF, anhydrous, 99.8%), octadecene (ODE, 90%), *S*- and *R*- α -methylbenzenemethanamine (*S*- and *R*-MBA, 99%), hexane (97%), Rhodamine B (RhB, 99%) were purchased from Shanghai Aladdin Biotechnology. Acetone (AR) and toluene (AR) were purchased from Tianjin Yuanli Chemical Co., Ltd. Methyl acetate (MeOAc, 99%, AR) was purchased from Shanghai Macklin Biochemical Co., Ltd. CdSe/ZnS QDs was purchased from Suzhou Xingshuo Nanotech Co. Ltd. All materials were used as received without further purification.

Experimental Procedure

Synthesis of CsPbBr_3 nanowires (NWs)

Perovskite NWs were synthesized according to the literature.¹ To a solution of ODE (1.25 mL), OAc (0.125 mL), and OAm (0.125 mL), 0.1 mL of Cs-OA precursor (0.102 g of Cs_2CO_3 degassed in 5 mL of ODE and 0.3 mL of OA at 150 °C) and 0.2 mL of PbBr_2 precursor (0.4 M, 147 mg PbBr_2 in 1 mL of DMF) were swiftly injected. After 10 s, 5 mL of acetone was swiftly added to quench the reaction. The NWs was precipitated by centrifugation at 3500 rpm for 5 min and then redispersed in toluene.

Preparation of chiral perovskite nanowires (CPNWs)

A certain amount of chiral ammonium salt methyl acetate solution was added to the initial NWs solution, the molar ratio of the ammonium salt and the initial CsPbBr_3 NWs is 0.2. The mixture was centrifuged for 5 min at 12500 rpm, then the precipitate is collected and dispersed in toluene to obtain the CPNWs.

Preparation of chiral perovskite nanowires and organic molecule hybrid system

The RhB (9.58 mg, 20 μmol) is dissolved in 1 mL acetonitrile, and then the RhB solution with various amounts were added to the chiral CPNWs dispersion in toluene (500 μL) to afford the donor-acceptor mixtures.

Preparation of chiral perovskite nanowires and cadmium selenide quantum dots system

The different volume of CdSe NCs were added to the chiral CPNWs dispersion in toluene (1 mL) to afford the CPNWs donor-CdSe acceptor mixtures for time-resolved fluorescence measurements, and different volume of CdSe NCs were added to the chiral CPNWs dispersion in toluene (500 μ L) to measure the CD and CPL spectra.

Detailed calculation formula for Φ_{ET}

Energy transfer efficiency is typically calculated using the relative fluorescence lifetime (τ) of the donor in the absence and presence of the acceptor.²

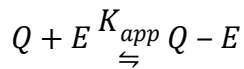
$$\Phi_{ET} = 1 - \tau_{Donor - Acceptor} / \tau_{Donor}$$

where $\tau_{Donor-Acceptor}$ refers to the lifetime of the donor (CPNWs) and acceptor (RhB) mixture; τ_{Donor} is the lifetime in which only the donor exists. The energy transfer efficiency calculated is shown in Fig. S2.

Double reciprocal analysis of K_{app}

Double reciprocal analysis of fluorescence quenching data is carried out to estimate the association between the RhB and CPNWs.^{3,4}

The equilibrium between the quencher (Q) and the emissive species (E) is assumed to involve the formation of a complex, where all species exist in both uncomplexed and complexed states. This equilibrium is governed by an apparent association constant, denoted as K_{app} .⁵



Then, it is assumed that the fluorescence intensity (Φ_f) is considered to be directly proportional to the fluorescence quantum yield (Φ_{PLQY}). This assumption is rational as long as there are no complicating factors such as self-absorption or high scattering, indicated by the low absorbance and low turbidity.⁶

The observed fluorescence quantum yield (or fluorescence intensity, mentioned above), denoted as $\Phi_{f,obs}$, is related to the fluorescence yields of the uncomplexed species (Φ_f^0) and the complexed species (Φ_f') through a degree of association α :

$$\Phi_{f,obs} = (1 - \alpha)\Phi_f^0 + (\alpha)\Phi_f'$$

At relatively high concentrations “ α ” can be equated to $(K_{app}[Q]) / (1 + K_{app}[Q])$, which can be simplified to

$$\frac{1}{\Phi_f^0 - \Phi_{f,obs}} = \frac{1}{\Phi_f^0 - \Phi_f'} + \frac{1}{K_{app}(\Phi_f^0 - \Phi_f')[Q]}$$

the given equation is in the form of $y = mx + b$ represents a linear relationship between the variables y and x . Therefore, if the quencher and emitter form a complex as described by the first equation, suggest that there should be a linear relationship can

be observed for $\frac{1}{\Phi_f^0 - \Phi_{f,obs}}$ graphed vs. $\frac{1}{[Q]}$.

Accordingly, the correlation constant (K_{app}) between CPNWs and RhB is estimated to be $8.1 \times 10^4 \text{ M}^{-1}$ (Fig. S3a). Post a diurnal interval the K_{app} between CPNWs and RhB is determined to be $5.8 \times 10^4 \text{ M}^{-1}$ (Fig. S3b).

Characterizations

Ultraviolet-visible (UV-Vis) absorptions spectroscopy measurements of CPNWs and RhB

The UV-vis absorption spectra were recorded on a MAPADA UV-1800PC spectrometer.

Photoluminescence (PL), PL excitation (PLE) spectroscopy and Time-resolved Photoluminescence (PL Decay) measurements

The PL spectra and PL Decay were recorded by a Horiba Fluorolog system (Horiba-F4600) with an Xe lamp as the excitation source and a Quanta-Phi integrating sphere.

X-ray diffraction (XRD) measurements

The XRD spectra were measured with the XRD Bruker D8-focus with a Cu Ka ($\lambda = 1.5406 \text{ \AA}$) radiation source.

Transmission electron microscopy (TEM) measurements

The TEM images were recorded on a TEM (JEM 2100F) at 200 kV. The samples for measurements were suspended on carbon-coated Cu grids.

Circular dichroism (CD) and circularly polarized light (CPL) measurements

The CD spectra were measured by a Jasco J-1700 CD spectrometer. The CPL spectra were measured on a circularly polarization fluorescence spectrometer (JASCO CPL-200)

Supporting Figures and Tables

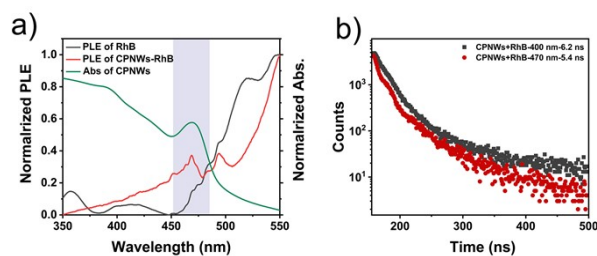


Figure S1. (a) PLE spectra of RhB and CPNWs-RhB mixture, reference absorption spectra of CPNWs; (b) Time-resolved fluorescence spectra of CPNWs-RhB with different excitation wavelengths.

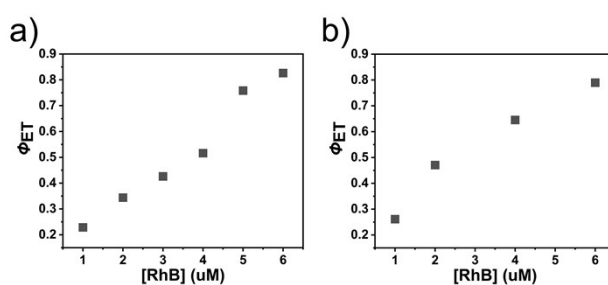


Figure S2. Energy transfer efficiency as a function of RhB concentration obtained by time-resolved fluorescence spectra decay experiments after mixed (a) and aged for one day (b).

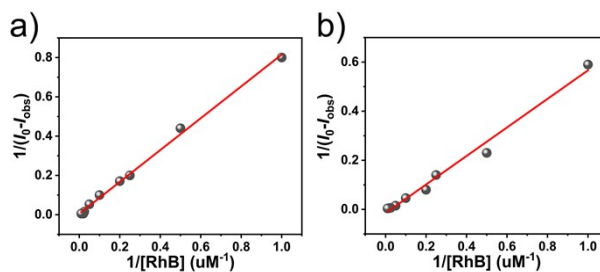


Figure S3. Double-reciprocal analysis of the CPNWs PL quenching data after mixed (a) and aged for one day (b).

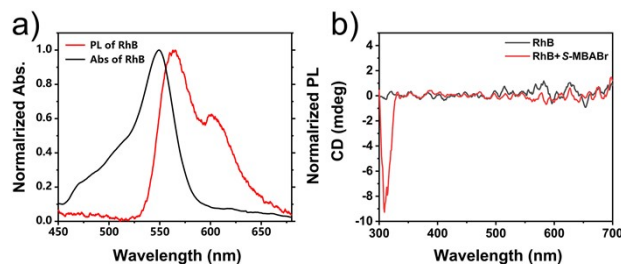


Figure S4. (a) PL spectra and absorption spectra of RhB; (b) CD spectra of RhB and RhB-chiral salts mixture.

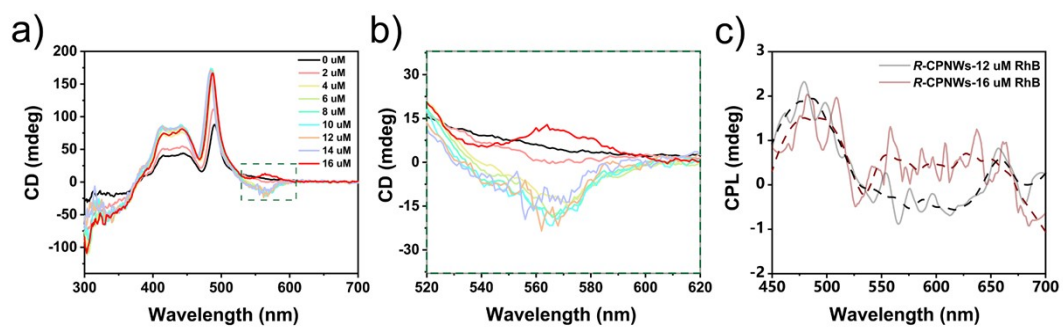


Figure S5. CD spectra of CPNWs with different amount of RhB (a) and enlarged CD spectrum of 520 nm-620 nm (b), CPL spectra of CPNWs with different amount of RhB (c).

Table S1: Fitting parameters of the PL decay of the CPNWs-RhB mixtures monitored at 480 nm.

Sample	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	τ _{avg} (ns)
CPNWs+0 μM RhB	46.67	6.69	53.33	35.60	31.52
CPNWs+0.5 μM RhB	58.46	5.99	41.54	33.84	28.29
CPNWs+1 μM RhB	59.76	5.21	40.24	28.04	23.10
CPNWs+2 μM RhB	57.83	4.42	42.17	25.06	21.04
CPNWs+3 μM RhB	59.60	3.77	40.40	23.76	19.97
CPNWs+4 μM RhB	67.67	2.08	32.33	12.95	10.22
CPNWs+5 μM RhB	26.99	9.77	73.01	1.59	7.27
CPNWs+6 μM RhB	78.01	1.47	21.99	8.56	5.88

Table S2: Fitting parameters of the PL decay of the CPNWs-RhB mixtures after one day monitored at 480 nm.

Sample	A ₁ (%)	τ ₁ (ns)	A ₂ (%)	τ ₂ (ns)	τ _{avg} (ns)
CPNWs+0 μM RhB	19.81	22.53	80.19	6.13	13.93
CPNWs+1 μM RhB	10.28	21.46	89.72	5.92	11.35
CPNWs+2 μM RhB	73.04	4.30	26.96	13.96	9.57
CPNWs+4 μM RhB	22.26	12.40	77.74	2.70	8.21
CPNWs+6 μM RhB	79.92	1.27	20.08	5.77	3.67

TableS3: Fitting parameters of the PL decay of the CPNWs-CdSe mixtures monitored at 480 nm.

Sample	A ₁ (%)	τ_1 (ns)	A ₂ (%)	τ_2 (ns)	τ_{avg} (ns)
CPNWs+0 μ L CdSe	63.65	16.87	36.35	45.66	34.35
CPNWs+20 μ L CdSe	43.63	9.29	56.37	35.88	31.44
CPNWs+40 μ L CdSe	44.01	33.36	55.99	10.12	26.89
CPNWs+80 μ L CdSe	52.52	6.91	47.48	27.20	22.75
CPNWs+120 μ L CdSe	46.16	4.78	53.84	23.43	20.65
CPNWs+160 μ L CdSe	64.47	21.6	35.53	6.15	19.50

Reference

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