## **Electronic Supplementary Information (ESI)**

# Synergistic dye/photocatalyst interconnections for activating efficient light-induced degradation pathways

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**Properties of the selected dyes.** Methylene blue hydrate (MB): a cationic thiazine dye used in the textile, pharmaceutical, paper, dyeing, printing, paint, medical, and food industries; toxic, carcinogenic and non-biodegradable. Rhodamine 6G (Rh6G): a cationic xanthene dye used as a fluorescence tracker in biotechnology applications; toxic if swallowed, may cause an allergic skin reaction, causes serious eye damage, very toxic to aquatic life. Free acid fluorescein (FLU): a neutral xanthene dye used as a fluorescent stain and trace for many living cells and tissue applications; toxic if swallowed; causes serious eye irritation. Rhodamine B (RhB): a cationic xanthene dye used for paper and textile printing, and as a staining fluorescent dye; harmful in contact with eyes, skin, and if swallowed; toxic to aquatic organisms. Eosin B (EoB): an anionic xanthene dye used to detect a wide range of proteins; harmful if swallowed, inhaled, or absorbed through the skin. Erythrosin B (EryB): an anionic xanthene dye used in textile, pharmaceutical, cosmetic and food industries; harmful if swallowed, inhaled, or absorbed through the eyes and skin, while affecting thyroid functions due to presence of iodine in the molecule, when metabolized. Rose Bengal (RB): an anionic xanthene dye used in textile and photochemical industries.; harmful in contact with corneal epithelium and skin.

**Instrumental facilities.** Diffractograms were recorded using a Malvern Panalytical Empyrean  $\alpha$  1 in a powder diffraction mode using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) with a cathode voltage and current of 45 kV and 40 mA, respectively (range: 10-60°, step size: 0.0262°, time per step: 17 s). The diffraction pattern was collected immediately in ambient conditions (T = 22 °C, relative humidity = 30%). The morphology of the powders was acquired by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy using a Zeiss *Sigma 300VP* electron microscope equipped with an Oxford C-MaxN SDD detector with an active area of 20 mm<sup>2</sup>. Perovskite samples were deposited on aluminum stubs and the images were recorded at working distance of 7.5 mm, an acceleration voltage of 15 kV and a magnification of 1000×. The analysis accuracy was checked using the MAC (Micro-Analysis Consultants Ltd) reference materials. The thermogravimetry was carried out using a Q600 TA instrument under a nitrogen flow (40 mL/min) at a temperature scan of 10 °C/min. X-ray photoelectron spectroscopy (XPS) measurements were performed under ultra-high vacuum (UHV) conditions, utilizing the ESCA Model 3000 instrument (Omicron Nanotechnology GmbH). During these measurements, the base pressure was maintained below  $1 \times 10^{-10}$  mbar. A focused monochromatized Al K $\alpha$  radiation (hv = 1486.5 eV) was employed to as an excitation source for XPS. Data acquisition, processing, and analysis were carried out using CasaXPS version 2.3.22 PR1.0. After Shirley background subtraction, peak fitting was conducted, employing an asymmetrical

Gaussian-Lorentzian function component to approximate the line shapes of the fitted components. The calibration was applied to the spectra by setting C Is (C-C) to 284.8 eV. UV-vis absorption spectra were acquired on a Jasco V670 spectrometer operating in transmission mode. The diffuse reflectance spectroscopy measurements of the CsPbBr<sub>3</sub> powder samples were performed using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer, which is equipped with an integrating sphere. Steady-state PL emissions were recorded on a Varian Cary Eclipse instrument. Electrochemical experiments were carried out on a three-electrode Metrohm Autolab PGSTAT 302-N potentiostat in acetonitrile containing 0.10 M n-Bu<sub>4</sub>PF<sub>6</sub> as the supporting electrolyte at a 100 mV/s scan rate. The CsPbBr<sub>3</sub> materials were deposited onto a glassy carbon electrode, while the Ag/Ag<sup>+</sup> quasi-reference electrode was calibrated against ferrocene after each experiment. The reduction potentials of the dyes were measured after their dissolution (concentration:  $1.0 \times 10^{-5}$  M) in acetonitrile. The highresolution electrospray ionization mass spectrometry (HR ESI-MS) analyses were performed using a Bruker microTOF QII mass spectrometer equipped with an electrospray ion source operated in negative ion mode. The sample solutions diluted in methanol were introduced by continuous infusion at a flow rate of 180 µL/min with the aid of a syringe pump. The instrument was operated with endplate offset and capillary voltages set to -500 V (500 V) and -4500 V (3500 V), respectively. The nebulizer pressure was 0.4 bar (N<sub>2</sub>), and the drying gas (N<sub>2</sub>) flow rate was 4.0 L/min. The capillary exit and skimmer voltages were 90 V and 30 V, respectively. The drying gas temperature was set at 180°C. The calibration was carried out with sodium formate. The textural properties of the synthesized materials were analyzed by N2 physisorption at -196 °C using a Quantachrome Autosorb iQ3 gas sorption analyzer. Prior analysis, the samples were degassed under vacuum at 50 °C for 3 h to remove impurities. The total surface area (SBET) was calculated by applied the Brunauer-Emmett-Teller method, instead t-plot method was applied for the pore volume measured at the single point at  $p/p_0=0.95$  from the adsorption isotherm. The Dynamic Light Scattering (DLS) and zeta potential measurements were acquired using Malvern Zetasizer ZS instrument using Zetasizer Software 7.03. Disposable 70-µL UV cuvettes were used for DLS analysis (BRAND #7592 00). Zeta potential was measured in disposable folded capillary cells (Malvern #DTS1070). Powder samples were dispersed in 94% ethanol with the help of a Vortex instrument. We used the following parameters to define the solvent at measurement temperature (25 °C): Dielectric constant 24.3, Viscosity: 1.040 mPa·s, Refractive index 1.361. We used a measurement protocol based on 173° backscattering mode. Two different datasets were measured for DLS. The first set consisted of 6 measurements, each containing  $10 \times 10$  s scans. The second set consisted of 30 measurements, 1 s each. For the zeta potential determination, 3 measurements were performed, each containing 100 scans.



Fig. S1 PL spectrum ( $\lambda_{ex} = 450 \text{ nm}$ ) of the EA-CsPbBr<sub>3</sub> PC dispersed in hexane. Inset: photograph of the corresponding cuvette under UV illumination ( $\lambda_{ex} = 365 \text{ nm}$ ).



Fig. S2 Comparison between the experimental XRD pattern of IPA-CsPbBr<sub>3</sub> and the standard patterns for the cubic, tetragonal, and orthorhombic phases of CsPbBr<sub>3</sub>. The panel on the right shows the data in the  $23-32^{\circ}$  range.



Fig. S3 Comparison between the experimental XRD pattern of IPA-CsPbBr<sub>3</sub> and the standard patterns for the cubic, tetragonal, and orthorhombic phases of CsPbBr<sub>3</sub>. The panel on the right shows the data in the  $23-32^{\circ}$  range.



Fig. S4 Comparison between the experimental XRD pattern of EA-CsPbBr<sub>3</sub> and the standard patterns for the cubic, tetragonal, and orthorhombic phases of CsPbBr<sub>3</sub>. The panel on the right shows the data in the  $23-32^{\circ}$  range.



Fig. S5 Particle size distribution for the EA-CsPbBr<sub>3</sub> sample (30 1-s measurements overlaid).



Fig. S6 Particle size distribution for the ACE-CsPbBr<sub>3</sub> sample (30 1-s measurements overlaid).

### Size Distribution by Volume



Fig. S7 Particle size distribution for the IPA-CsPbBr<sub>3</sub> sample (30 1-s measurements overlaid).

Sample	S <sub>BET</sub>	S <sub>micro</sub>	Pore volume	Pore diameter
	$(m^2 g^{-1})$	$(m^2 g^{-1})$	(m <sup>3</sup> g <sup>-1</sup> )	(nm)
EA-CsPbBr <sub>3</sub>	4.960	0.041	0.045	2.48
IPA-CsPbBr <sub>3</sub>	0.963	n.a.	0.002	2.52
ACE-CsPbBr <sub>3</sub>	0.470	n.a.	0.001	4.07

**Table S1.** Textural properties of the photocatalysts. BET surface area, micropore area, total pore volume, and average pore diameter.  $S_{BET}$ : specific total surface area calculated using the BET.  $S_{micro}$ : specific microporous area calculated using the t-plot.



Fig. S8. SEM image of the microcrystalline EA-CsPbBr<sub>3</sub> powder.



**Fig. S9.** Peak shift in different deconvoluted components of the XPS spectra (Br, Pb and Cs from left to right).

#### Zeta Potential Distribution



Fig. S10 Zeta potential measured for ACE-CsPbBr<sub>3</sub> (3 measurements).



Fig. S11 Zeta potential measured for EA-CsPbBr<sub>3</sub> (3 measurements).

#### Zeta Potential Distribution



Fig. S12 Zeta potential measured for IPA-CsPbBr<sub>3</sub> (3 measurements).



**Fig. S13.** UV/vis absorption spectra at different irradiation times of a) Rh6G and b) FLU in the absence of the EA-CsPbBr<sub>3</sub> PC.



**Fig. S14.** UV/vis absorption spectra at different irradiation times of RhB in the absence of the EA-CsPbBr<sub>3</sub> PC.



**Fig. S15.** UV/vis absorption spectra at different irradiation times of EoB in the absence of the EA-CsPbBr<sub>3</sub> PC.



**Fig. S16.** UV/vis absorption spectra at different irradiation times of EryB in the absence of the EA-CsPbBr<sub>3</sub> PC.



**Fig. S17.** UV/vis absorption spectra at different irradiation times of RB in the absence of the EA-CsPbBr<sub>3</sub> PC.



**Fig. S18.** UV/vis absorption spectra at different irradiation times of EoB in the presence of the EA-CsPbBr<sub>3</sub> PC under anaerobic conditions obtained by removing dioxygen through the Schlenk techniques.



**Fig. S19.** a) UV/vis absorption and corresponding b) PL spectra at different irradiation times of EoB in the presence of the EA-CsPbBr<sub>3</sub> PC upon BQ addition (50 mM) under aerobic conditions.



**Fig. S20.** a) UV/vis absorption and corresponding b) PL spectra at different irradiation times of EoB in the presence of the EA-CsPbBr<sub>3</sub> PC upon BQ addition (50 mM) under anaerobic conditions by removing dioxygen through the Schlenk techniques.



**Fig. S21.** Cyclic voltammograms of EoB and RhB dyes (concentration:  $1.0 \times 10^{-5}$  M) in acetonitrile supported with 0.1 M *n*-Bu<sub>4</sub>PF<sub>6</sub> electrolyte at 100 mV/s on a glassy carbon electrode (GCE). The LUMO energy levels, obtained by measuring the onset potential of the first reduction peak, were calculated according to the following equation:  $E_{LUMO} = -[E_{red} - E_{(Fc/Fc^+)} + 5.10]$  eV. The obtained values were  $E_{LUMO (EoB)} = -3.99$  eV and  $E_{LUMO (RhB)} = -4.31$  eV for EoB and RhB, respectively.



**Fig. S22.** a) UV/vis absorption and corresponding b) PL spectra at different irradiation times of EoB in the presence of the EA-CsPbBr<sub>3</sub> PC upon TEMPO (125 mM) addition after 2 minutes of irradiation. c) PL spectra of EoB before and after the addition of TEMPO (125 mM) in the absence of the EA-CsPbBr<sub>3</sub> PC.



Fig. S23. ESI-MS analysis (upon dilution in methanol) of the reaction mixture (EoB/EA-CsPbBr<sub>3</sub> in ethanol) before the irradiation. The product with m/z = 611.77 is due to an impurity of the substrate.



**ig. S24.** ESI-MS analysis (upon dilution in methanol) of the reaction mixture (EoB/EA-CsPbBr<sub>3</sub> in ethanol) after 6 min irradiation. The product with m/z = 182.82 and m/z = 292.74 can be ascribed to [BrNaBr]<sup>-</sup> and [BrCsBr]<sup>-</sup> adducts. Since these species were not revealed before the irradiation (see Fig. S23), it can be deduced that the bromine atoms are released during the photocatalysis. The second species is attributable to the partial dissolution effect of the bromine excess on the photocatalyst surface, although this interaction does not affect the efficiency and crystalline structure of the catalyst.

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**Fig. S25.** a)-e) UV/vis absorption spectra of the five degradation cycles using the EA-CsPbBr<sub>3</sub> PC for the photocatalytic degradation of EoB.



**Fig. S26.** (left) Diffuse reflectance spectra of the EA-CsPbBr<sub>3</sub> material before and after the EryB photodegradation. (right) The corresponding Kubelka–Munk plots of the reflectance spectra.