

## Supplementary Material (ESI) for Chemical Communications

# Photoelectrochemical Capacitor Using Polyoxometalates Coupled with Semiconductor Nanocrystals as the Photosensitizer

Yuji Akaishi,<sup>\*a</sup> Gimpei Yoshimura,<sup>b</sup> Yui Mokuge,<sup>b</sup> Kona Sumi,<sup>b</sup> Paravee Vas-Ummuay,<sup>c</sup> Yusuke Inomata,<sup>d</sup> and Tetsuya Kida<sup>\*a,d,e</sup>

<sup>a</sup> *Institute of Industrial Nanomaterials (IINa), Kumamoto University, Kumamoto 860–8555, Japan.*

<sup>b</sup> *Department of Materials Science and Applied Chemistry, Graduate School of Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan.*

<sup>c</sup> *Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand.*

<sup>d</sup> *Faculty of Advanced Science and Technology, Kumamoto University, Kumamoto 860-8555, Japan.*

<sup>e</sup> *International Research Organization for Advanced Science and Technology (IROAST), Kumamoto University, Kumamoto 860-8555, Japan.*

\*Author for correspondence and reprint requests;

E-mail address: [tetsuya@kumamoto-u.ac.jp](mailto:tetsuya@kumamoto-u.ac.jp) (T. Kida)

E-mail address: [akaishi@kumamoto-u.ac.jp](mailto:akaishi@kumamoto-u.ac.jp) (Y. Akaishi)

## 1. Experimental details

### 1.1. Chemicals

Cesium carbonate ( $\text{Cs}_2\text{CO}_3$ , anhydrous, 95%), lead acetate trihydrate ( $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ , 99.9%), sodium tungstate(VI) dihydrate (99%), hydrochloric acid (36%), titanium tetraisopropoxide (TTIP, 95%), 1-octadecene (ODE, 95%), oleylamine (OLAM, 95%), oleic acid (OA, 65%), ethanol (99%), acetonitrile ( $\text{CH}_3\text{CN}$ , 99.5%), and toluene (99.5%) were purchased from FUJIFILM Wako Pure Chemical Corporation. Tetrabutylammonium bromide (98%), tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ , 98%), and benzoyl bromide ( $\text{C}_6\text{H}_5\text{COBr}$ , 98%) was purchased from TOKYO CHEMICAL INDUSTRY Co., Ltd. Dichloromethane (99%) was purchased from KANTO CHEMICAL CO., Inc. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 95%) was purchased from Cosmo Bio Co., Ltd. All chemicals were used without further purification.

### 1.2. Synthesis of $\text{CsPbBr}_3/\text{TiO}_2$ nanocomposites

$\text{CsPbBr}_3/\text{TiO}_2$  nanocomposites were synthesized based on the previously reported hot-injection method with slightly modifications.<sup>[1,2]</sup>  $\text{Cs}_2\text{CO}_3$  (16 mg, 0.05 mmol),  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  (76 mg, 0.2 mmol), 0.45 mL of OA, 1 mL of OLAM, and 5 mL of ODE were loaded into a three-neck flask and dried under vacuum for 1 hour at 130 °C. Then, the vacuum atmosphere was switched to an argon atmosphere, and the temperature was increased to 170 °C. At this temperature, 72  $\mu\text{L}$  of benzoyl bromide and 600  $\mu\text{L}$  of TTIP were injected swiftly to the reaction system. The reaction mixture was immediately cooled in an ice-water bath. Finally, 5 mL of toluene was added to the crude solution, and the obtained mixture was centrifuged for 10 min at 4000 rpm. The supernatant was discarded, and the precipitate was redispersed in 10 mL of toluene. The resulting  $\text{CsPbBr}_3/\text{TiO}_2$  nanocomposites were stored in toluene, and they were collected by centrifugation and redispersed in  $\text{CH}_3\text{CN}$  before use.

### 1.3. Synthesis of Tetra-*n*-butylammonium decatungstate (TBADT, $(n\text{Bu}_4\text{N})_4\text{W}_{10}\text{O}_{32}$ )

TBADT was synthesized according to previously reported procedure.<sup>[3]</sup> The product was analyzed on a  $^1\text{H}$  NMR. The resulting TBADT powder was dissolved in  $\text{CH}_3\text{CN}$  before use.

$^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )  $\delta$  (ppm): 0.94 (t,  $J = 8$  Hz, 3H), 1.27–1.36 (m, 2H), 1.53–1.61 (m, 2H), 3.17 (t,  $J = 8$  Hz, 2H)

### 1.4. Material characterization

The morphology of  $\text{CsPbBr}_3/\text{TiO}_2$  nanocomposites was observed by transmission electron microscope (JEM-1400 Plus, JEOL) operated at an accelerating voltage of 80 kV. The crystallinity and crystal structure were determined using X-ray diffraction (XRD, RINT2100, Rigaku) with  $\text{CuK}\alpha$  radiation source in the range of 10–60 degree. The size of TBADT was analyzed with a dynamic light scattering (DLS) spectrophotometer (Zetasizer Nano ZS, Malvern Instruments).  $\zeta$ -potentials of  $\text{CsPbBr}_3/\text{TiO}_2$  nanocomposites in organic solvents were determined with a  $\zeta$ -potential analyzer (Zetasizer Nano ZS, Malvern Instruments) using a “Universal Dip Cell kit” (ZEN 1002, Malvern Instruments). The dip cell was composed of two Pd electrodes with 2 mm spacing and a quartz cuvette.  $^1\text{H}$  NMR spectrum was recorded on an NMR spectrometer (JNM-ECZ400R, JEOL) with tetramethylsilane (TMS) as the internal standard. Attenuated total reflection infrared (ATR-IR) spectrum was measured with an FT-IR spectrometer (Frontier, PerkinElmer). UV–vis absorption spectra were recorded using a spectrophotometer (V-660, JASCO Co.). Photoluminescence (PL) spectra were measured using a fluorescence spectrofluorometer (8300, JASCO Co.). Samples for optical measurements were prepared in quartz cuvettes with a path length of 1 cm. The excitation wavelength was 365 nm.

### 1.5. Photoreduction of TBADT via electron transfer from $\text{CsPbBr}_3/\text{TiO}_2$ nanocomposites

TBADT powder was dissolved in 3 mL of  $\text{CH}_3\text{CN}$  in a quartz cuvette with a path length of 1 cm. The concentration of TBADT in  $\text{CH}_3\text{CN}$  was 0.1 mM, and 20  $\mu\text{L}$  of ethanol was added.  $\text{CsPbBr}_3/\text{TiO}_2$  nanocomposites were dispersed in this solution and its absorbance was set to approximately 1.0 at 500 nm.

Oxygen in the solution was removed by purging with an argon gas for 3 min. The system was irradiated with UV light ( $\lambda = 400$  nm) using a xenon light source (MAX-303, ASAHI SPECTRA) equipped with an optical bandpass filter (HMX0400, ASAHI SPECTRA), or visible light ( $\lambda > 422$  nm) using a xenon lamp (SX-UI301, USHIO) equipped with an optical cut-off filter (LU0422, ASAHI SPECTRA). The intensities of the UV light and visible light sources were 23 and 263 mW, respectively. Changes in the absorbance of TABDT in  $\text{CH}_3\text{CN}$  were monitored during photoreduction. The reaction system was stirred with a magnetic stirring bar in a quartz cuvette to prevent the sedimentation of nanocomposites (Fig. 3a in main text).

### **1.6. Photoenergy charging and discharging using TBADT-CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposite system**

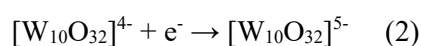
For photoelectrochemical measurements, a two-electrode H-type cell was used, as shown in Fig. 4b. The cell consisted of two compartments separated by a Nafion membrane. A Pt mesh ( $2 \times 2$  cm<sup>2</sup>) was used as the anode, which was soaked in an electrolyte solution containing CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposites, 0.1 mM TBADT, and 0.1 M TBAPF<sub>6</sub> in 15 mL of  $\text{CH}_3\text{CN}$ . Ethanol (1.0 mL) was added as a hole scavenger (electron donor). The cathode made of a Ni mesh ( $2 \times 2$  cm<sup>2</sup>) was immersed in 16 mL of  $\text{CH}_3\text{CN}$  containing 0.1 M TBAPF<sub>6</sub> and 1.0 mM 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). The cathode side was purged with Ar for 10 min to remove oxygen before measurements, while Ar was continuously purged into the anode side to stabilize reduced TBADT<sup>-</sup>. In the electron storage process, the anode containing CsPbBr<sub>3</sub>/TiO<sub>2</sub> and TBADT was irradiated with visible light ( $\lambda > 422$  nm) for 10 min. In this case, the external circuit was switched "off" to prevent electrons captured within the photoreduced TBADT from flowing to the cathode side (open-circuit conditions). In the discharging process, the external circuit was then switched "on", allowing stored electrons to flow into the cathode and reduce TEMPO (short-circuit conditions). The generated current was monitored with a digit multimeter (KEITHLEY 2100 6 1/2, TEKTRONIX INC.) under dark. After 60 min of discharging, the external circuit was switched from "on" to "off" and the same protocol was repeated to examine the cyclability of the charging-discharging processes.

### 1.7. Calculation of the Coulomb efficiency ( $\eta$ ) on TBADT-based photoelectrochemical capacitor

The Coulomb efficiency ( $\eta$ ) on the TBADT-based photoelectrochemical capacitor was calculated using equations (1) according to Faraday's laws of electrolysis:

$$\eta = \frac{Q_D}{n \cdot F} \quad (1)$$

where  $Q_D$  (C) is the total charge,  $n$  (mol) is the molar of TBADT, and  $F$  ( $\text{Cmol}^{-1}$ ) is the Faraday constant. The charging reaction was based on the one-electron reduction reaction of the decatungstate shown in equation (2), and the two-electron reduction reaction was not included.



## 2. Supplementary Figures

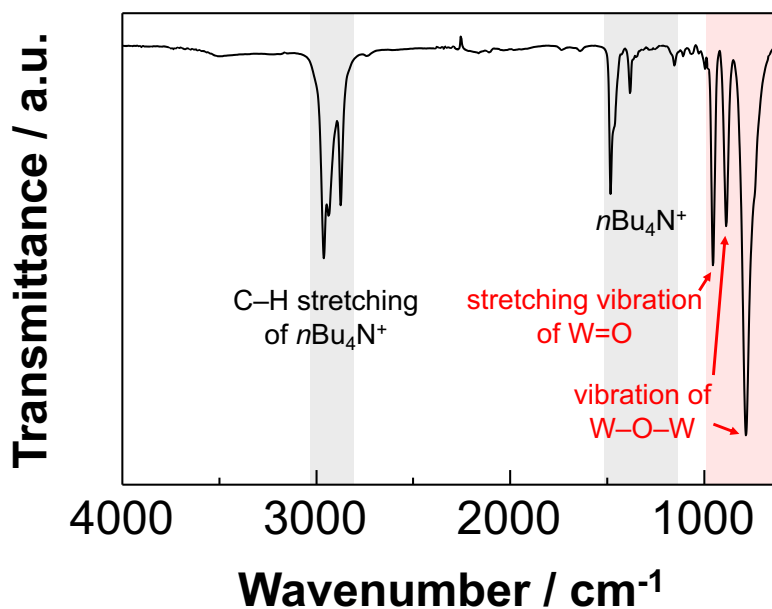
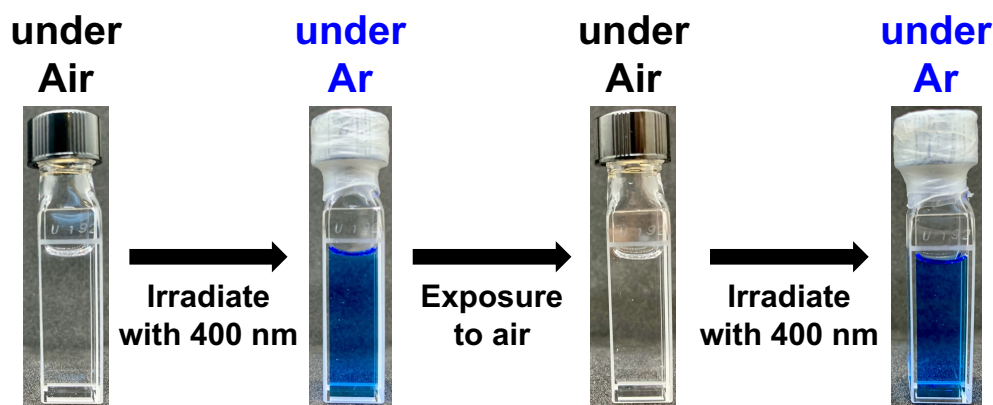
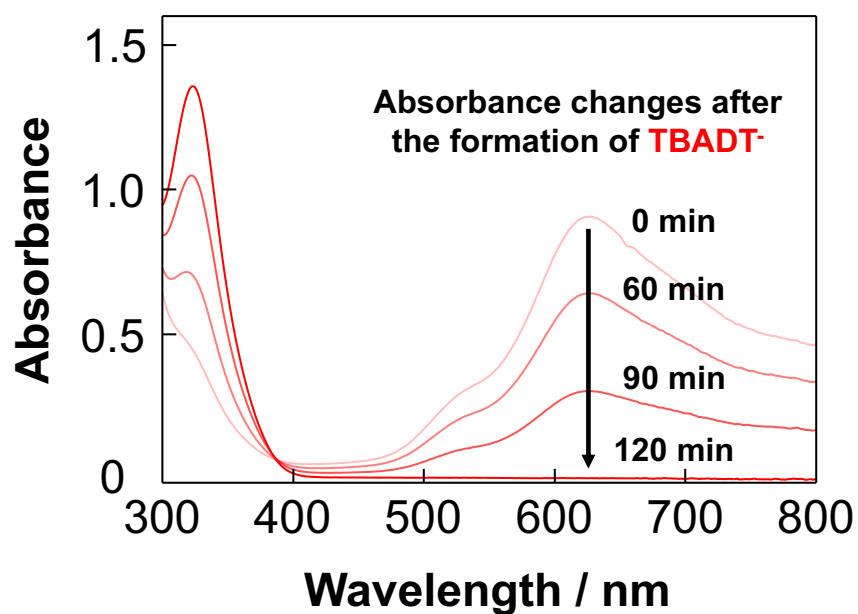


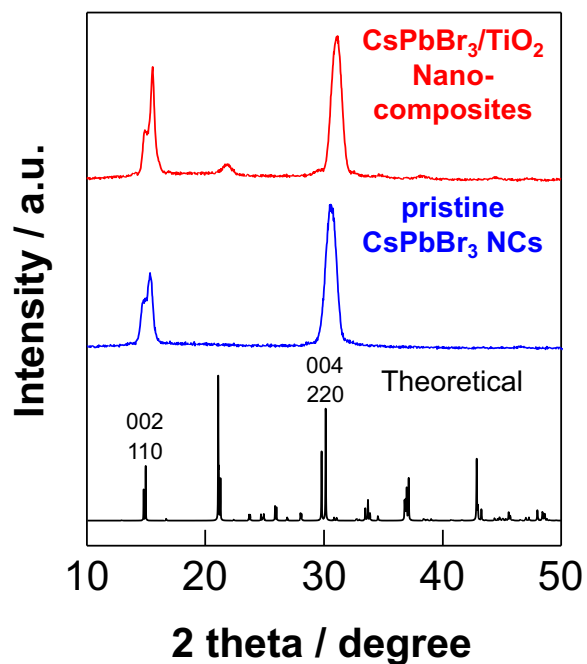
Fig. S1 FT-IR spectrum of synthesized TABDT in the range of 600–4000  $\text{cm}^{-1}$



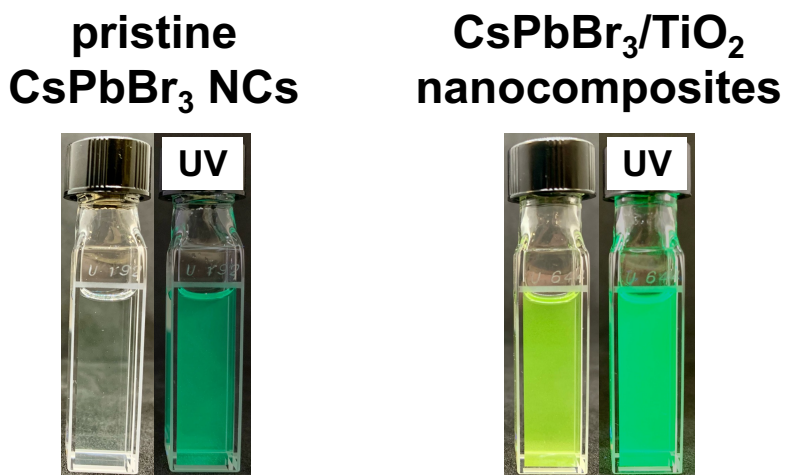
**Fig. S2** Photographs of TBADT solutions in  $\text{CH}_3\text{CN}$  during a cycle of 400 nm light irradiation and air exposure. All solutions contained 0.1 mM TBADT and 0.1 M ethanol.



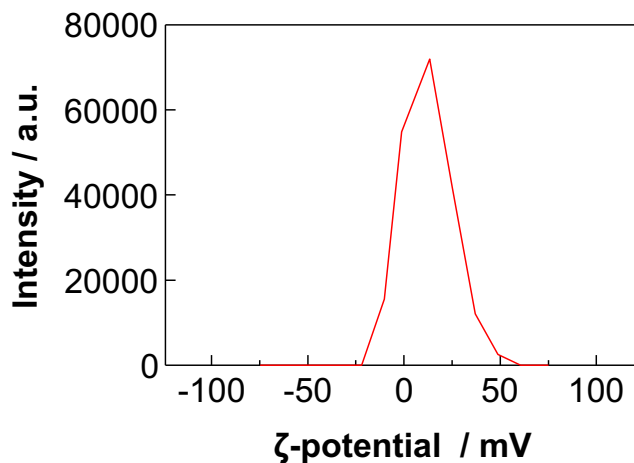
**Fig. S3** Time-dependent UV-vis. absorption spectra of the reduced TABD solution in  $\text{CH}_3\text{CN}$  after irradiation with UV light ( $\lambda = 400$  nm). The solution contained 0.1 mM TBADT and 0.1 M ethanol in the quartz cuvette and was purged with Ar gas before measurement. The cap of the quartz cuvette had two needle marks (inlet and outlet) resulting from the Ar gas purging, which were covered with a double layer of Parafilm M<sup>®</sup>.



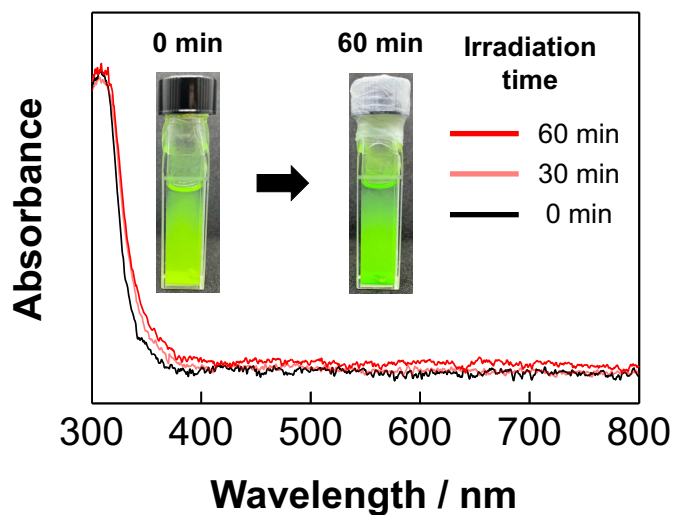
**Fig. S4** XRD patterns of pristine CsPbBr<sub>3</sub> NCs (blue line) and CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposites (red line) and the theoretical pattern of orthorhombic CsPbBr<sub>3</sub> (black line).<sup>[4,5]</sup>



**Fig. S5** Photographs of pristine CsPbBr<sub>3</sub> NCs and CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposites in CH<sub>3</sub>CN under room light or 365 nm UV light. The pristine CsPbBr<sub>3</sub> NCs degraded immediately after they were soaked in CH<sub>3</sub>CN. However, the CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposites were stable in CH<sub>3</sub>CN and emitted bright green light by UV excitation.

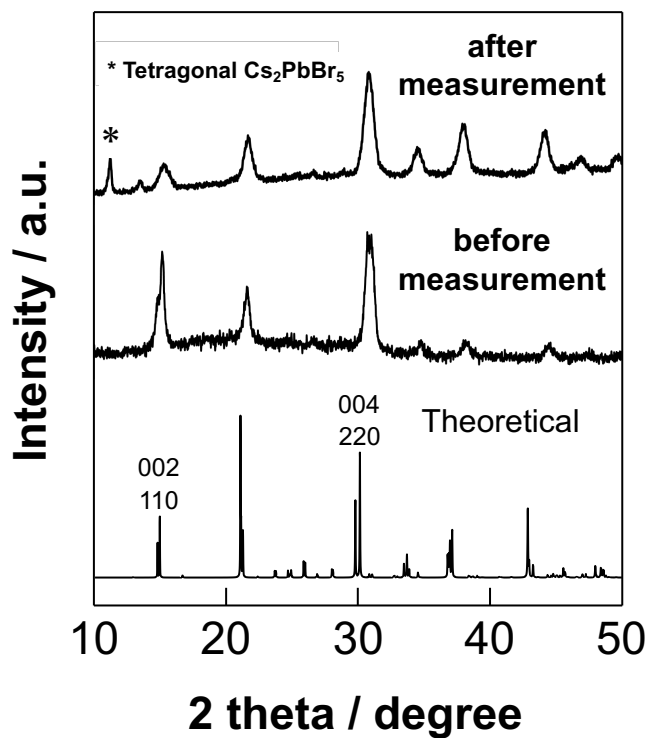


**Fig. S6**  $\zeta$ -potential distribution of CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposites in CH<sub>3</sub>CN. The  $\zeta$ -potential was determined to be +12.5 mV.

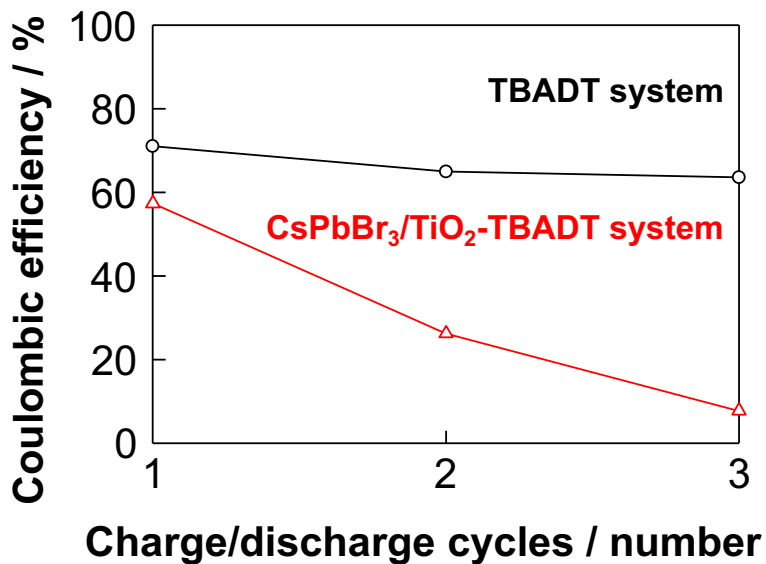


**Fig. S7** UV-vis. absorption spectra of CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposites in CH<sub>3</sub>CN without ethanol under visible light irradiation ( $\lambda > 422$  nm). The system was purged with Ar gas before visible light irradiation. The inset shows photographs of the solution before and after visible light irradiation (precipitates were observed because the stirring was stopped). The color of the precipitate turned only slightly to deep green after 60 min of visible light irradiation.





**Fig. S8** XRD patterns of CsPbBr<sub>3</sub>/TiO<sub>2</sub> nanocomposites before and after photoelectrochemical measurements, and the theoretical pattern of orthorhombic CsPbBr<sub>3</sub>.<sup>[4,5]</sup>



**Fig. S9** Coulombic efficiencies of the discharging process for the TBADT system compared to CsPbBr<sub>3</sub>/TiO<sub>2</sub>-TBADT system. TBADT was charged by monochromic UV light ( $\lambda = 400$  nm), whereas CsPbBr<sub>3</sub>/TiO<sub>2</sub>-TBADT was charged by visible light ( $\lambda > 422$  nm).

## References

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- [5] K. Momma, F. Izumi, *J Appl Crystallogr* **2011**, *44*, 1272.