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Supporting Information for

Hybridizing semiconductor nanocrystals with metal-organic frameworks for visible and near-infrared photon upconversion

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Materials.

All reagents and solvents for synthesis and measurement were used as received without further purification otherwise noted. 4,4'-(anthracene-9,10-diyl)dibenzoic acid (adba) was synthesized according to the reported method.[1]

Characterizations.

^{1}H NMR (300 MHz) spectra were measured on a Bruker DRX-spectrometer using TMS as the internal standard. Elemental analysis was conducted at the Elemental Analysis Center, Kyushu University. MALDI-TOF-MS measurements were carried out by using a BRUKER autoflex III TOF system. Absorption spectra were measured using a HP 8453 spectrophotometer. Photoluminescence measurements were measured on an Edinburgh Instruments FLS980 fluorimeter. Upconverted emission spectra were collected using a Andor iDus DU420A BVF spectroscopy Camera coupled to a spectrograph (ANDOR Shamrock) with external CW excitation at 532 nm and 785 nm. Photoluminescence decays of CdSe/CdS@A-MOF and CdSe/CdS were recorded with a standard time-correlated single photon counting system (Edinburgh Instruments), using excitation at 470 nm. The upconverted emission decay was measured by using a standard time-correlated single photon counting system (HAMAMATSU Quantaurus-Tau C11567-01) using excitation at 531 nm. X-ray powder diffraction (XRPD) analysis was conducted on a Bruker D8 with a copper Kα source. Bright field (BF)-scanning transmission electron microscopy (STEM), high-angle annular dark field (HAADF)-STEM, STEM-energy dispersive X-ray spectrometry (EDX) and high-resolution transmission electron microscopy (HR-TEM) was conducted on a JEOL JEM-ARM200F. The samples for STEM and HR-TEM were prepared by dropping CdSe/CdS@A-MOF or PbS@T-MOF dispersed solutions on carbon-coated Cu grid.

Determination of TTA-UC quantum yield by the relative method.

The upconverted emission quantum efficiency (Φ_{UC}) was determined relative to a standard according to the following equation,

$$\Phi_{UC} = 2\Phi_{std}\left(\frac{N_{std}}{N_{UC}}\right)\left(\frac{I_{UC}}{I_{std}}\right) \qquad \text{(Eq. S1)}$$

where Φ, N and I represent a quantum yield, photon number of excitation light, integrated photon number of emission light. The subscripts *UC* and *std* denote the parameters of the upconversion and standard systems. The emission originated from CdSe/CdS in CdSe/CdS@A-MOF was used as an internal standard whose emission quantum efficiency (Φ_{std}) was determined as 0.01 by using an integrating sphere. Under irradiation of the same position of CdSe/CdS@A-MOF sample with 532 nm CW laser, the upconverted emission and standard emission were detected through 510 nm short pass filter and 600 nm long pass filter, respectively.

Physical properties related to I_{th}

$$I_{th} = (\alpha(E)\Phi_{ET}8\pi D a_0)^{-1}(\tau_{A,T})^{-2} \qquad \text{(Eq. S2)}$$

Where $\alpha(E)$ is the system absorption coefficient, and Φ_{ET} is the triplet energy transfer efficiency from the sensitizer to the emitter, and $\tau_{A,T}$ is the lifetime of the emitter triplet, D is the diffusion constant of emitter triplet and a_0 is the interaction distance of a triplet pair.[2]

Synthesis of CdSe[3,4]

CdO (2 mmol, 0.256 g) was blended with stearic acid (10 mmol, 2.845 g) and 1-octadecene (ODE, 40 mL). The suspension was degassed under vacuum at room temperature and heated at 250 °C under inert atmosphere. The mixture was then degassed at 110 °C for 1 h. Separately, a suspension of Se powder containing Se (2.0 mmol, 58 mg) and ODE (20 mL) was prepared by sonication for 10 min under inert atmosphere. The Se-suspension (5 mL) was injected into the Cd solution which has been heated again to 250 °C. After 10 min, the Se-suspension (1 mL) was further injected into the reaction mixture at 250 °C, and the injection of Se-suspension (0.5 mL) was repeated with an interval of 4 min until the absorption peak of the CdSe nanocrystal reached to about 600 nm. The reaction mixture was cooled down to room temperature. 2.4 mL of octylamine, 48 mL of hexane and 96 mL of methanol were added to the reaction mixture and stirred for 2.5 min at 50 °C. The methanol layer was removed by syringe. This extraction procedure was repeated for four times, while hexane and octylamine were added only for the first and third time. 50 mL of methanol was added to the reaction flask. After centrifugation, the power of CdSe nanocrystal was washed with ethanol and dried under vacuum. From the absorption peak, the diameter of CdSe nanocrystal was estimated as 4.9 nm.[5]

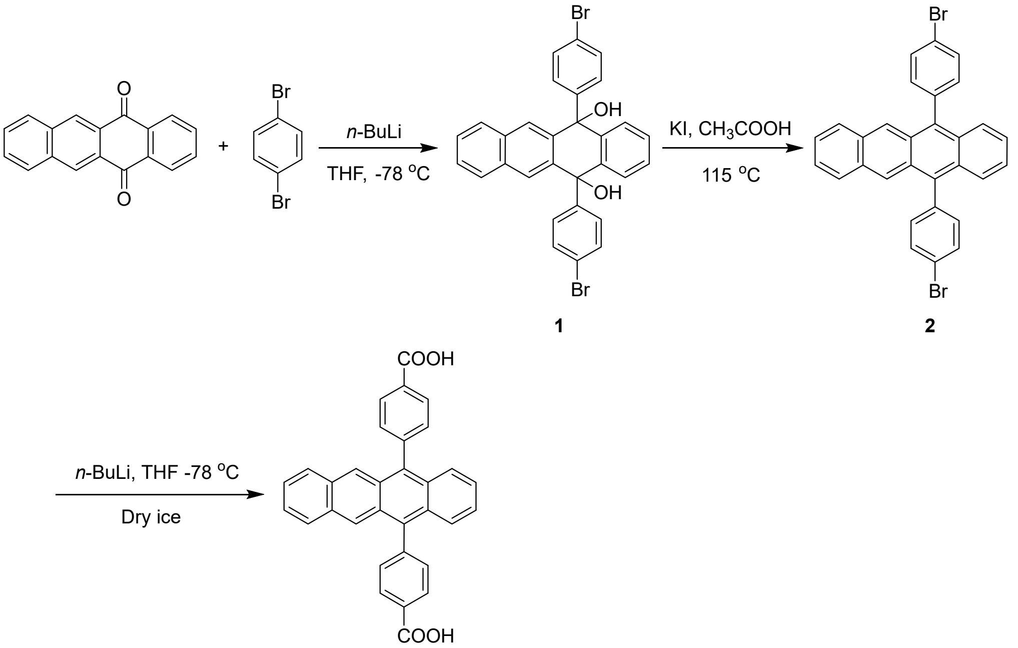
Synthesis of CdSe/CdS[6]

Oleylamine (1.3 mL), ODE (2.7 mL) and CdSe (4.9 nm, 48.5 mg) were added to the reaction flask and degassed at 100 °C under vacuum. Separately, a suspension of S (0.75 mmol, 24 mg) and ODE (5 mL) was prepared under inert atmosphere by sonication for 30 min. A Cd precursor solution was prepared by dissolving cadmium oleate (0.75 mmol, 506 mg) in a mixture of 0.5 mL of oleylamine and 4.5 mL of ODE. The Cd precursor solution (0.84 mL) and the S-Suspension (0.84 mL) were added to the CdSe solution at 100 °C. The reaction mixture was stirred for 20 min at 240 °C for shell growth. After the reaction mixture was cooled down to room temperature, 15 mL of a mixture solution of acetonitrile and chloroform (1:1, v/v) was added into the crude reaction solution to precipitate CdSe/CdS. The mixture was centrifuged, and the precipitate was separated and washed with methanol, a mixed solvent of methanol and hexane (1:2, v/v) and a mixed solvent of methanol, hexane and acetone (1:2:1, v/v). The precipitates were redispersed in toluene and stored as a stock solution in a glove box. By transmission electron microscopy measurements, CdSe/CdS nanocrystal with 5.4 nm in diameter were observed.

Synthesis of CdSe/CdS@A-MOF

Toluene solution of CdSe/CdS (6.8 mg/mL, 50 μL) and Zn(II) acetate dihydrate (31.4 mg, 0.143 mmol) were added into a mixture (4 mL) of diethylformamide (DEF) and toluene (3:1, v/v). The mixed solution was quickly injected into DEF solution (10 mL) containing 4,4'-(anthracene-9,10-diyl)dibenzoic acid (30 mg, 0.072 mmol) at 120 °C. Instantaneously, the reaction mixture was cooled down to room temperature and centrifugated. The obtained precipitates were washed several times with DEF, followed by drying in vacuum at room temperature.

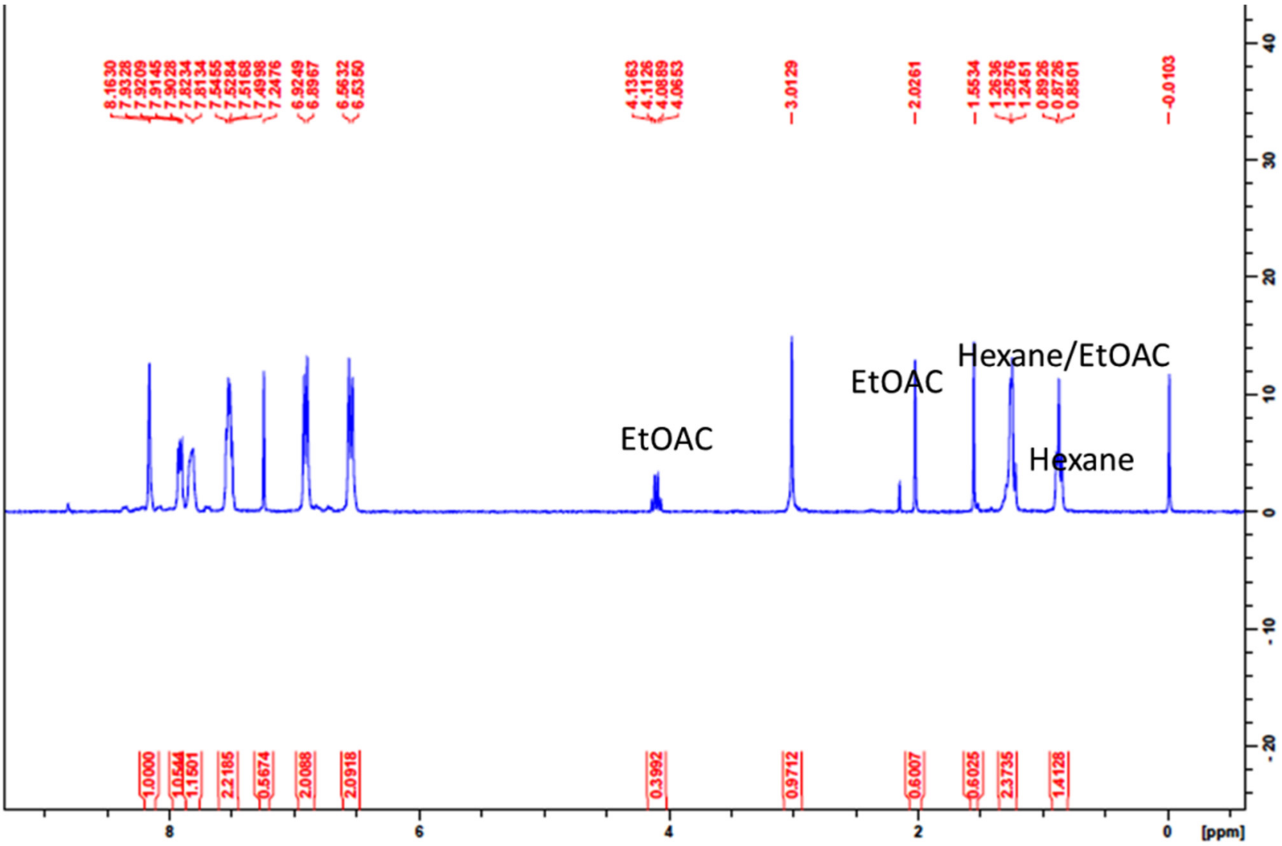
A synthetic scheme of 4,4'-(tetracene-5,12-diyl)dibenzoic acid.



4,4'-(tetracene-5,12-diyl)dibenzoic acid

Synthesis of 1:

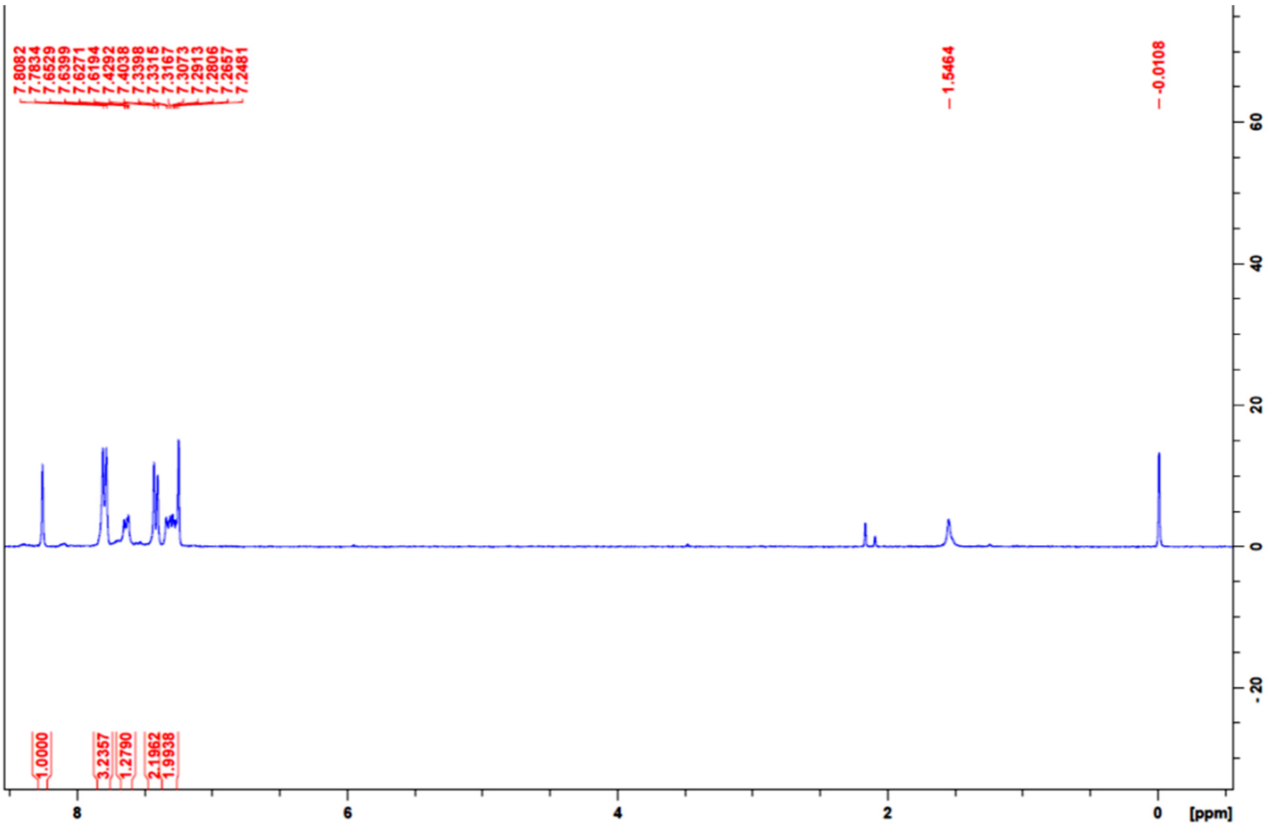
n-BuLi (22.0 mmol, 22.0 mL, 1.0 M in hexanes) was added dropwise to a solution of 1,4-dibromobenzene (10.0 mmol, 2.36 g), dissolved in 20 mL dry THF at -78 °C. The reaction mixture was stirred at -78 °C for 1 hour and then transferred to 5,12-naphthacenequinone (0.73 g, 2.8 mmol), over 15 minutes which was dissolved in 30 mL dry THF cooled to -78 °C. Upon complete transfer, the reaction mixture was stirred for 30 minutes at -78 °C then allowed to warm to room temperature and stirred overnight under nitrogen. The reaction mixture was washed with 10% aqueous HCl and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified via flash chromatography using hexanes and EtOAc (1.5:1, v/v) to yield **1**. Yield: 0.96 g (60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (s, 2H), 7.90-7.93 (m, 2H), 7.81-7.82 (m, 2H), 7.49-7.54 (m, 4H), 6.99 (d, 4H), 6.55 (d, 4H), 3.01 (s, 2H). MALDI-TOF-MS, (dithranol matrix): calculated for $C_{30}H_{20}O_4Br_2$ 569.983; found 571.986 [M^+].



^{1}H NMR spectrum (300 MHz, $CDCl_3$, TMS) of **1**.

Synthesis of 2:

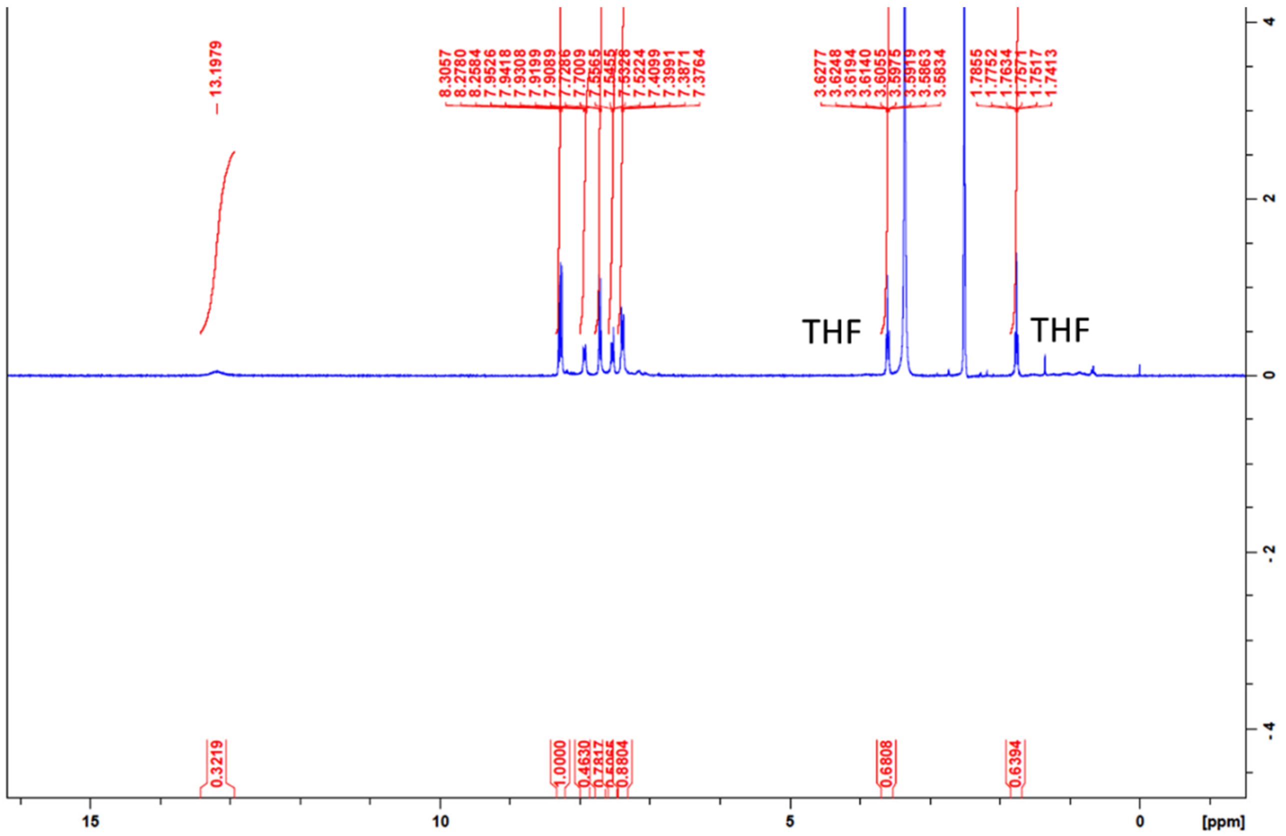
Acetic acid (70 mL) was added to a mixture of **1** (1.94 g, 3.4 mmol) and potassium iodide (2.45 g, 15 mmol) at room temperature. The reaction mixture was then heated to 115 °C for 5 hours. After cooling to room temperature, 300 mL of distilled H_2O was added to the reaction mixture and the resulting orange-red solid was collected via vacuum filtration and washed with distilled H_2O. The crude product was purified by recrystallization from $CHCl_3$/hexanes to yield **2**. Yield 1.64 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 2H), 7.80-7.78 (m, 6H), 7.61-7.65 (m, 2H), 7.34-7.43 (m, 4H), 7.26-7.33 (m, 4H). MALDI-TOF-MS, (dithranol matrix): calculated for $C_{30}H_{18}Br_2$ 535.978; found 537.892 [M$^+$].



^{1}H NMR spectrum (300 MHz, $CDCl_3$, TMS) of **2**.

Synthesis of 4,4'-(tetracene-5,12-diyl)dibenzoic acid:

To a solution of **2** (1.61 g, 3.0 mmol) in 15 mL dry THF cooled to -78 °C, *n*-BuLi (8.0 mmol, 8.0 mL, 1.0 M in hexanes) was added within 15 min. After being stirred at −78 °C for an additional 30 min, solid CO_2 (dry ice) was added and further stirred for 1 hour. The resulting mixture was then allowed to warm up to room temperature. The completion of the reaction was monitored by TLC. The mixture was diluted with 50 mL of ethyl acetate, acidified with dilute hydrochloric acid (aq. 10%) to pH < 4. The compound 4,4'-(tetracene-5,12-diyl)dibenzoic acid is precipitated and filtered off by washing with distilled water. The product recrystallized from THF. Yield 0.77 g (55%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.20 (brs, 2H), 8.26-8.31 (m, 6H), 7.90-7.95 (m, 2H), 7.70-7.73 (m, 4H), 7.52-7.55 (m, 2H), 7.38-7.41 (m, 4H). MALDI-TOF-MS, (dithranol matrix): calculated for $C_{30}H_{20}O_4$ 468.136; found 467.897 [M^+]. Elemental analysis, calculated for $C_{30}H_{20}O_4\cdot$THF: C, 79.98; H, 5.22; found: C, 79.77; H, 5.21.



^{1}H NMR spectrum (300 MHz, DMSO-*d*$_6$, TMS) of 4,4'-(tetracene-5,12-diyl)dibenzoic acid.

Synthesis of T-MOF

To a solution of Zn(II) acetate dihydrate (10.5 mg, 0.048 mmol) in 1 mL of Dimethylformamide (DMF) was quickly added to a DMF solution (2.5 mL) containing 1,4-diazabicyclo[2.2.2]octane (1.9 mg, 0.024 mmol) and 4,4'-(tetracene-5,12-diyl)dibenzoic acid (22.5 mg, 0.048 mmol) at 80 °C. The reaction mixture was cooled down to room temperature and collected by centrifugation. The obtained precipitates were washed several times with DMF, followed by drying in vacuum at room temperature.

Supporting figures:

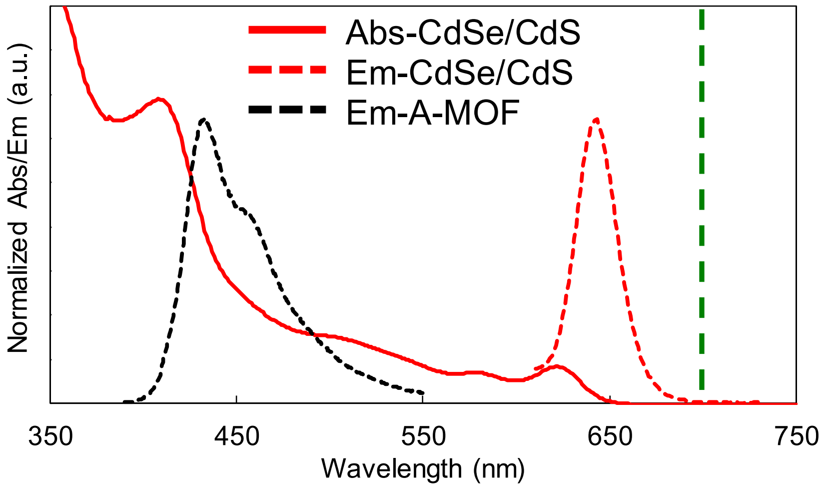


Fig. S1. Normalized absorption and emission (λ_{ex} = 590 nm) spectra of CdSe/CdS in toluene and emission spectrum (λ_{ex} = 370 nm) of A-MOF in the solid state. The green vertical line indicates the triplet state energy level of diphenylanthracene.

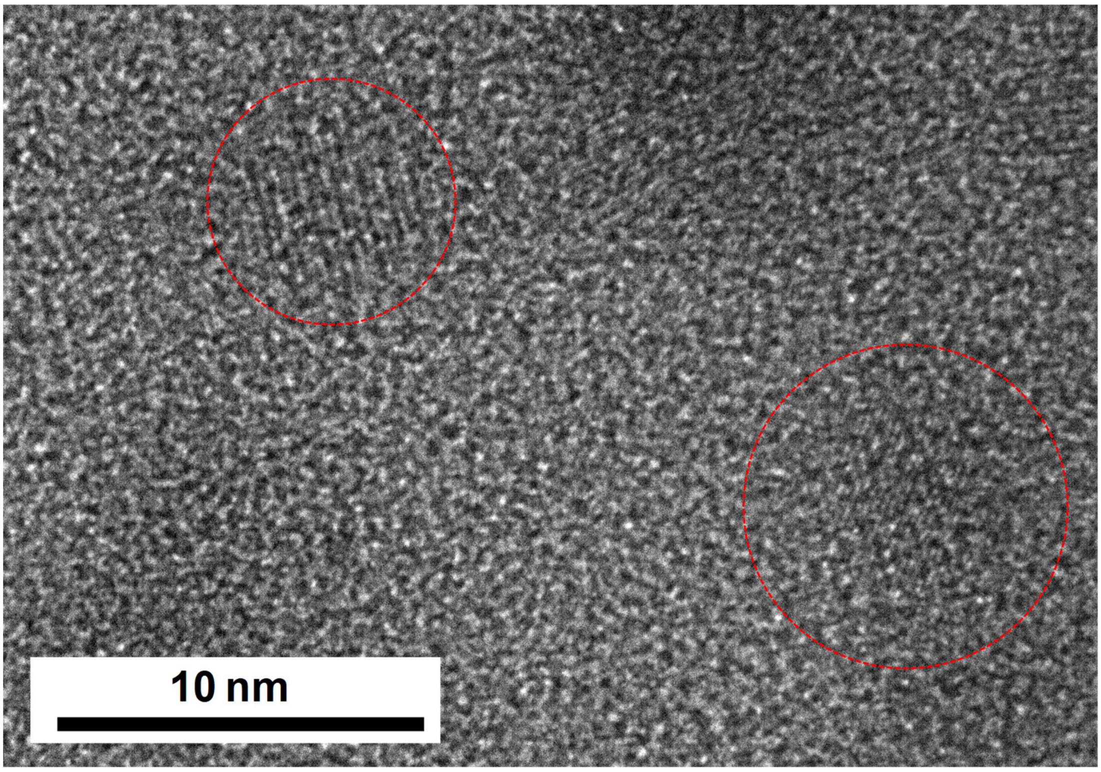


Fig. S2. A HR-TEM image of CdSe/CdS@A-MOF. Lattice fringes of CdSe/CdS nanocrystals were observed.

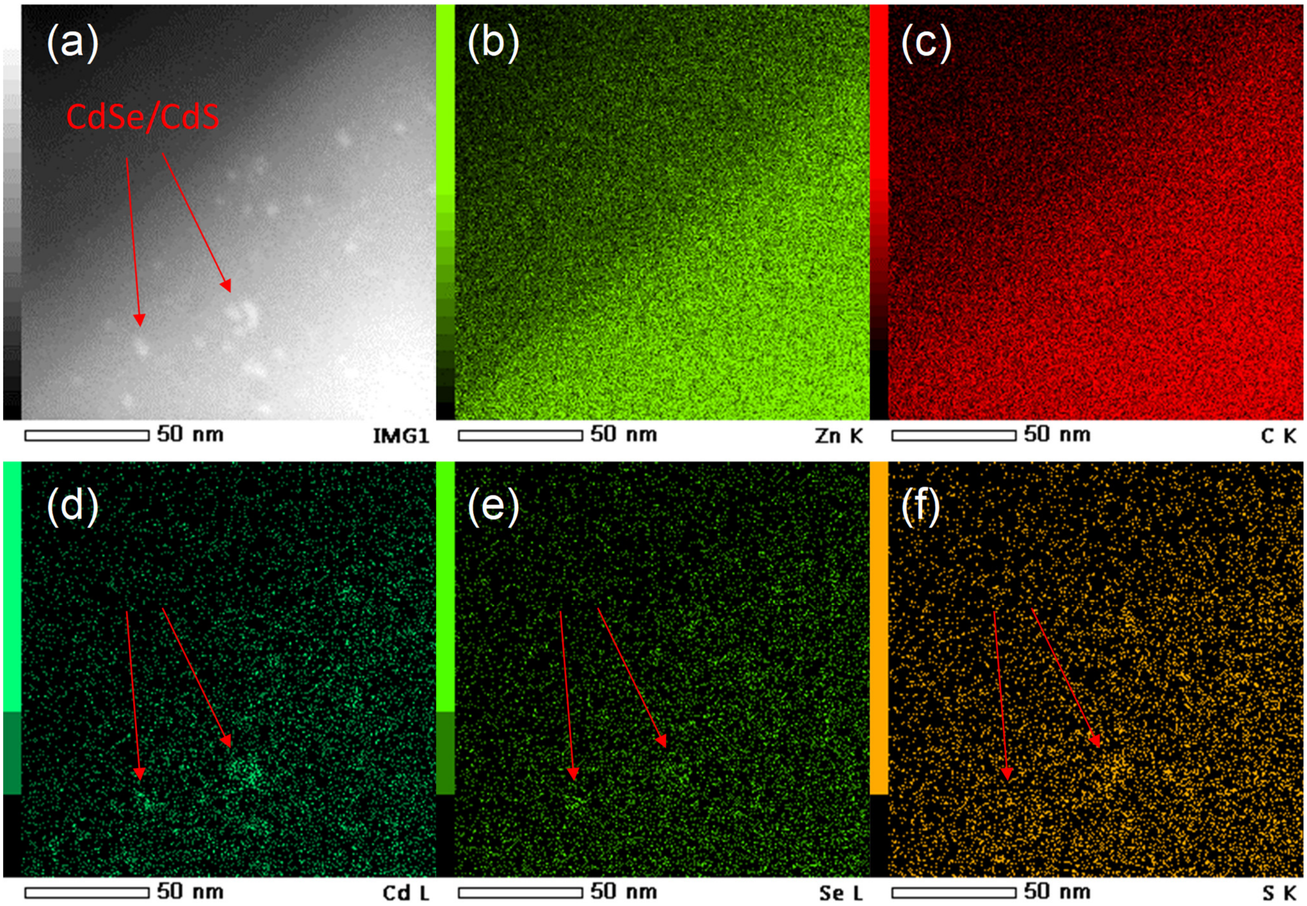


Fig. S3. (a) A HAADF-STEM image and STEM-EDX mapping images for (b) Zn, (c) C, (d) Cd, (e) Se and (f) S atoms of CdSe/CdS@A-MOF.

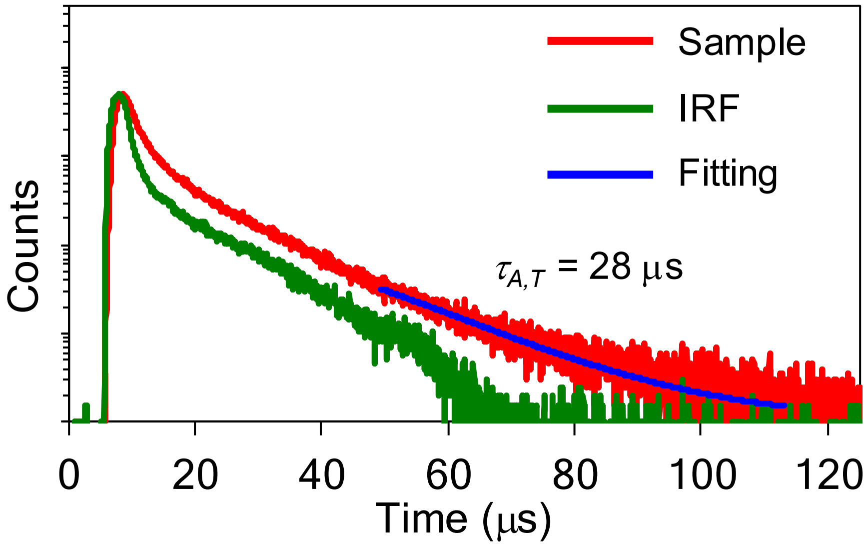


Fig. S4. Time-resolved upconverted emission at 450 nm of CdSe/CdS@A-MOF (λ_{ex} = 531 nm). The fitting curve was obtained by considering the relationship of $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_{A,T})$, where τ_{UC} is UC emission lifetime and $\tau_{A,T}$ is an emitter triplet lifetime.

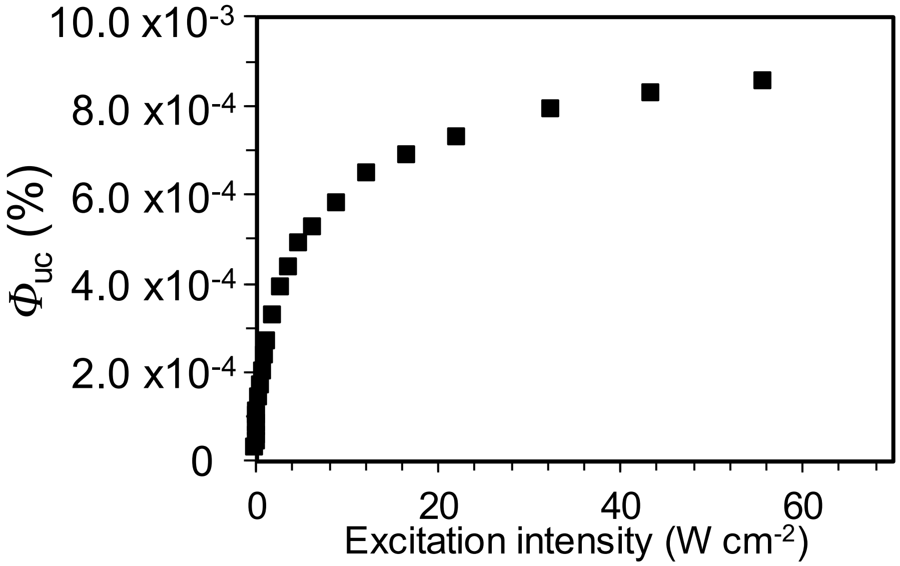


Fig. S5. TTA-UC efficiency Φ_{UC} of CdSe/CdS@A-MOF as a function of excitation intensity of the 532 nm laser.

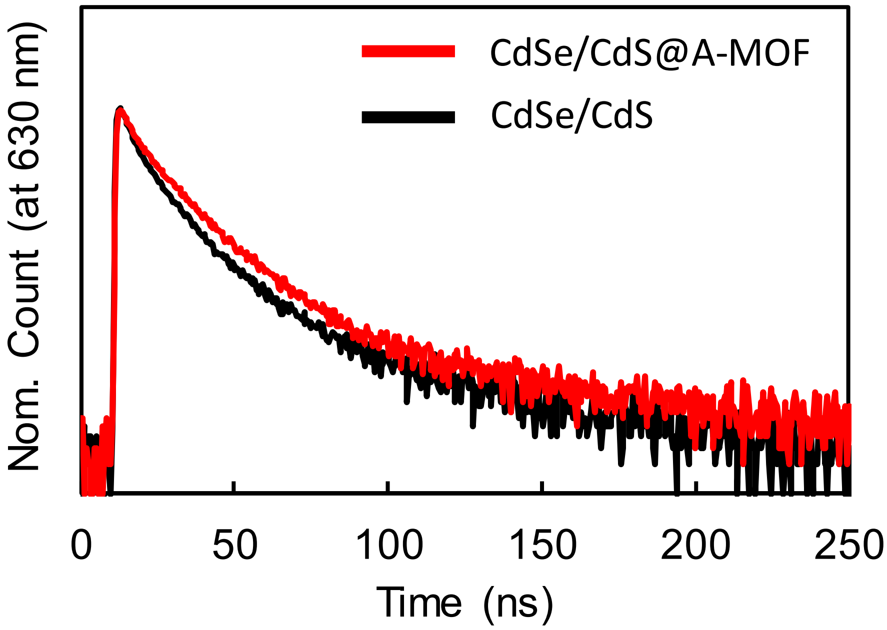


Fig. S6. Emission (630 nm) decays of CdSe/CdS@A-MOF and CdSe/CdS (λ_{ex} = 470 nm).

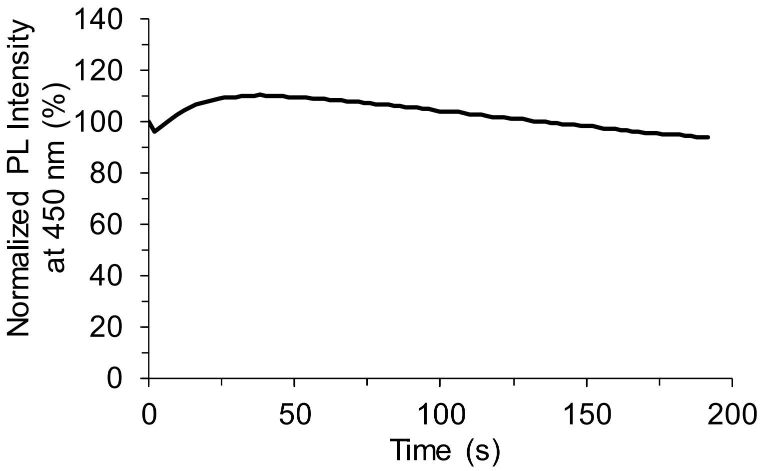


Fig. S7. Time dependence of the upconverted emission intensity at 450 nm of CdSe/CdS@A-MOF (λ_{ex} = 532 nm, laser intensity = 88 W cm^{-2}).

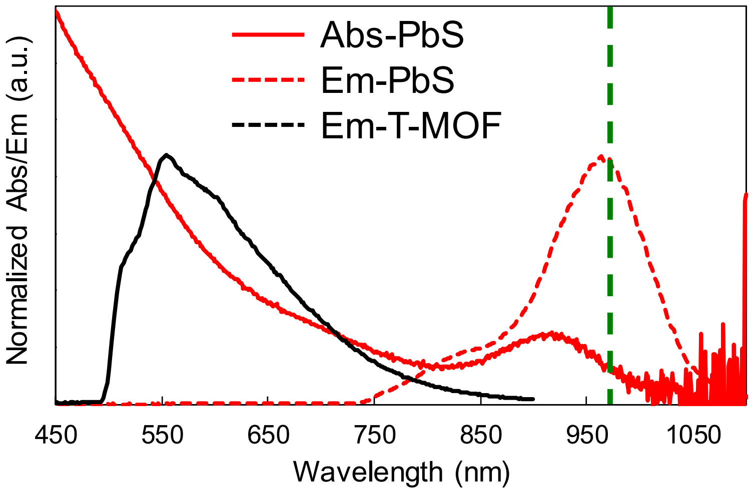


Fig. S8. Normalized absorption and emission (λ_{ex} = 645 nm, 700 nm of long pass filter) spectra of PbS in toluene and emission spectrum (λ_{ex} = 405 nm, 500 nm of long pass filter) of T-MOF in the solid state. The green vertical line indicates the triplet state energy level of tetracene.

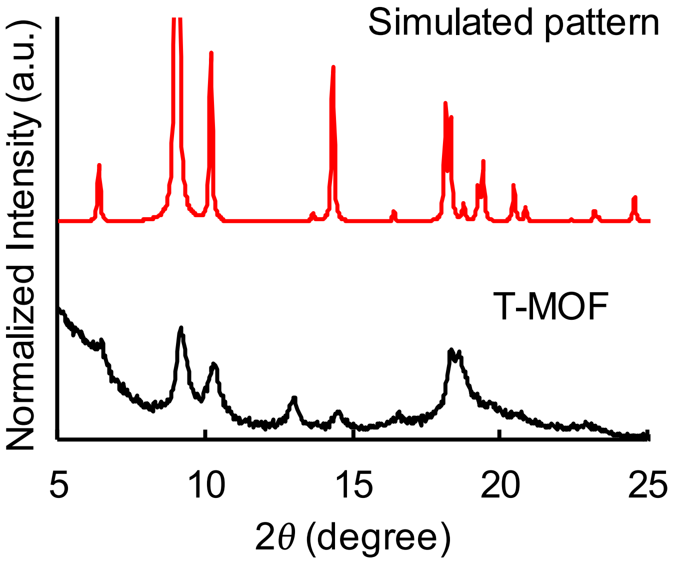


Fig. S9 XRPD patterns of T-MOF (black) and simulated pattern obtained from the single crystal structure of paddlewheel-type diphenylanthracene-based MOF.[1]

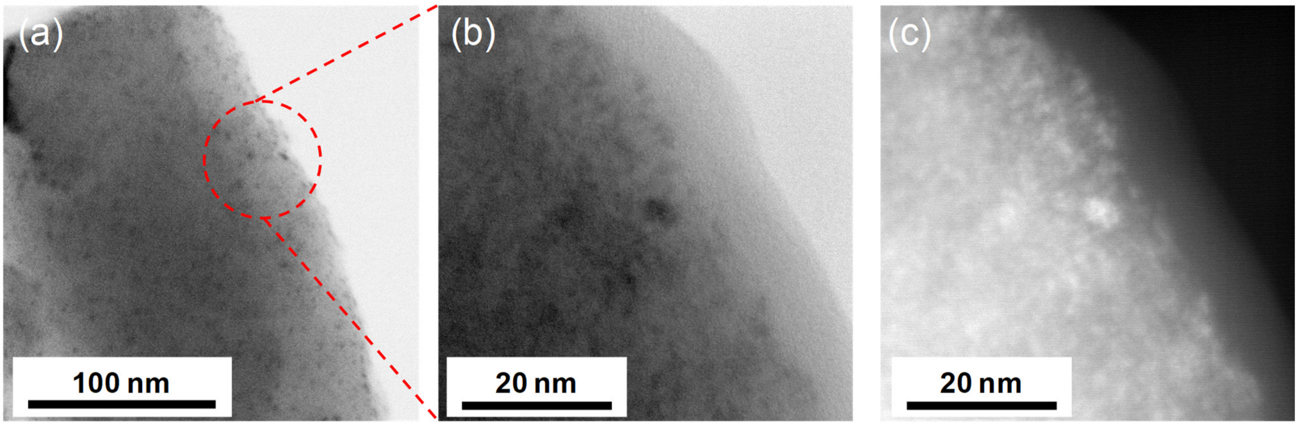


Fig. S10 (a) BF-STEM images of PbS@T-MOF and (b) its enlarged view. (c) A HAADF-STEM image of PbS@T-MOF obtained for the same area of (b).

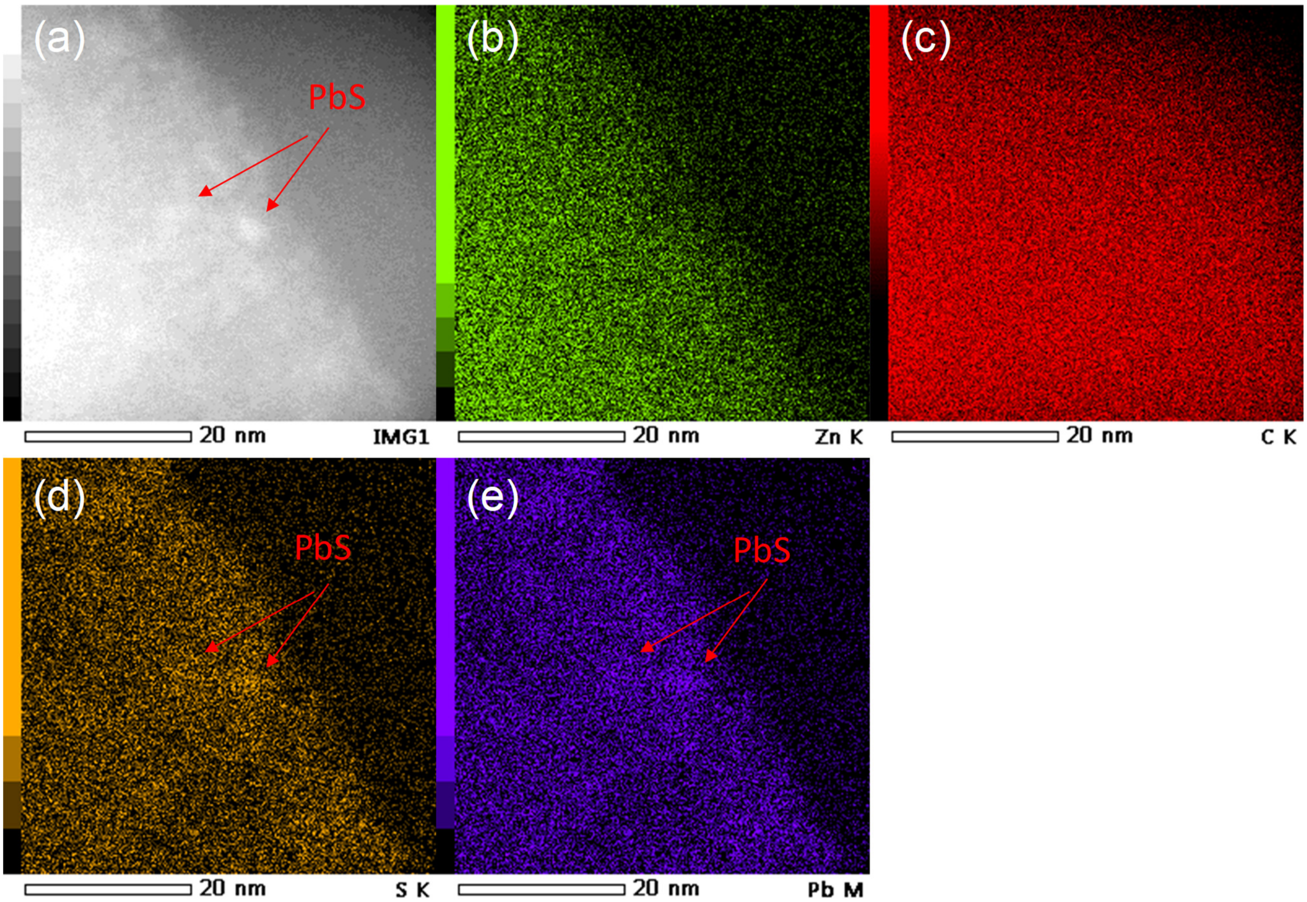


Fig. S11. (a) A HAADF-STEM image and STEM-EDX mapping images for (b) Zn, (c) C, (d) S, and (e) Pb atoms of PbS@T-MOF.

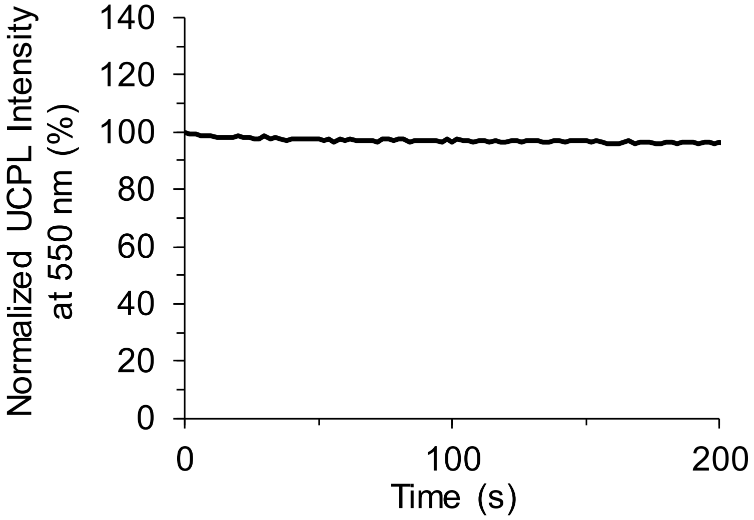


Fig. S12. Time dependence of the upconverted emission intensity at 550 nm of PbS@T-MOF (λ_{ex} = 785 nm, laser intensity = 28W cm^{-2}).

Supporting references:

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