

Supplementary Information

Enhancing Photon Upconversion with Thermally Activated Sensitization and Singlet Energy Collection

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Materials and Instrumentation

Materials

Reagents were purchased from Innochem, Sigma-Aldrich, or J&K Chemical and were used without further purification.

2,5-trimethylsilylethynyl-1,4-hydroquinone and **G2-4Br-OH** were obtained according to the literature procedure.^{1,2}

Cd_{0.5}Zn_{0.5}S was prepared by a precipitate/hydrothermal according to the literature procedure.³

Instrumentation

¹H NMR spectra were recorded with a Bruker Avance P-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Analytical gel permeation chromatography (GPC) was performed using Waters Breeze 2 GPC and calibrated with polystyrene standards. X-ray powder diffraction (XRD) patterns was measured at a scanning rate of 5° min⁻¹ in the 2θ range from 5° to 50° with a Bruker D8 Focus X-ray diffractometer equipped with Cu_{Kα} radiation (λ=1.54050 Å). UV-vis absorption spectrum and emission spectra were recorded by using a Shimadzu UV-2550PC spectrophotometer and a Hitachi F-4600 spectrometer, respectively. The fluorescence lifetimes of the microcrystals were recorded on an Edinburgh FLS1000 spectrometer with a time-correlated single-photon counting (TCSPC) method with excitation at 375 nm by a nanosecond pulse laser (EPL 375). The femtosecond transient absorption data is tested with the Ultrafast HELIOS Fire Systems and analyzed by Surface Explorer. The instrument response function (IRF) is 160 fs.

Upconversion emission spectra and upconversion quantum yields were recorded by using an integrating sphere (Labsphere) combined with a Princeton Instrument Acton SP2500 spectrograph and a SPEC-10 liquid nitrogen-cooled CCD. A 635 nm laser (MRL-III-635Lnm-200mW, Changchun New Industry Optoelectronic Technology Co. LTD) was used as the incident light for upconversion tests.

Preparation of samples for upconversion

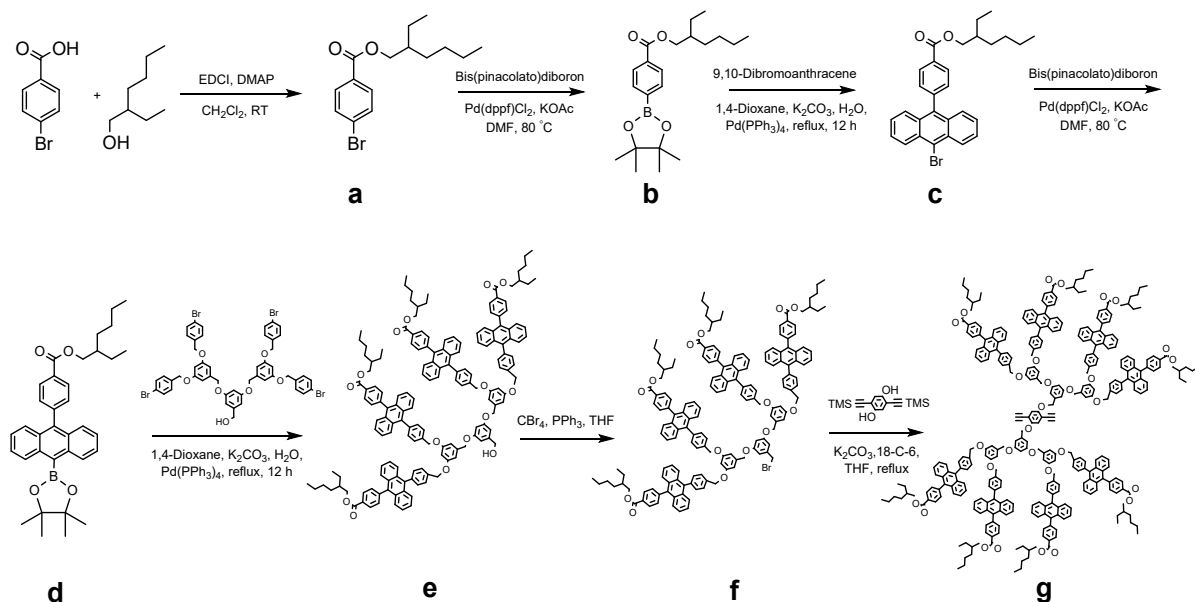
PdTPTBP/DPA or PdTPTBP/DPA/MWDPA microcrystals were prepared by coprecipitation of PdTPTBP and DPA at certain ratios, giving crystalline powders PdTPTBP/DPA/MWDPA. A solution of DPA (30.0 mg), PdTPTBP and MWDPA of corresponding molar ratios in THF (4 mL) was rapidly injected into deionized water (25 mL) under vigorous stirring. After being stirred for 10 min and standing for 24 h at 25 °C, the obtained colloidal solution was subjected to centrifugation at 3000 rpm for 3 min to remove large precipitates. The doped microcrystals were collected by centrifugation at 9000 rpm for 10 min. The microcrystals were dried under vacuum and sealed between two quartz coverslips using epoxy adhesive (Ergo 7300) in a glove box charged with argon.

Preparation of samples for hydrogen photoproduction

All hydrogen photoproduction experiments were performed in oxygen-free conditions. The sacrificial electron donors were Na₂S and Na₂SO₃ in our experiments. TTA upconversion microcrystals, Cd_{0.5}Zn_{0.5}S nanoparticles, Na₂S, and Na₂SO₃ were kept in a glass reactor with 10 mL ultra-pure water and sodium dodecyl sulfate (SDS). Before photogenerated hydrogen, the reaction mixture was purged with nitrogen for 0.5 h to remove dissolved air in the solution, and then methane (5 mL) was injected as an internal standard followed by sonication for 30 min to disperse Cd_{0.5}Zn_{0.5}S. A 10 W LED ($\lambda = 629$ nm) was used as the incident light. The power intensity of incident light was measured by using an Ophir Nova II power meter with a PD300-12W photodetector. The amount of photogenerated hydrogen at various time intervals was analyzed by gas chromatography (GC) using nitrogen carrier gas, molecular sieve 5 Å columns and a TCD detector.

Synthetic Procedures and Characterization

Synthesis of mono-Dendrimer



Scheme S1. Synthesis route of the mono-Dendrimer (g).

2-Ethylhexyl-4-bromobenzoate (a): A solution of dry DCM (200 mL), p-bromobenzoic acid (20.00 g, 99.5 mmol, 1.00 eq.), isooctanol (19.44 g, 149.3 mmol, 1.50 eq.), and DMAP (0.61 g, 5.0 mmol, 0.05 eq.) was stirred for 15 min at 0 °C. EDCI (28.61 g, 149.2 mmol, 1.50 eq.) dissolved in dry DCM (100 mL) was slowly added dropwise to the reaction system at 0 °C. The mixture was warmed to room temperature and stirred under an N₂ atmosphere for 12 hours until the reaction solution changed from white turbid to transparent. The reaction solution was washed with 0.1 M dilute HCl, saturated NaCl solution, and water three times, respectively. The organic phase was collected and dried over MgSO₄ and the solvent was removed under reduced pressure. The crude material was purified by column chromatography eluting with DCM. The title compound was dried under vacuum to give 23.01 g (75%). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 4.30 – 4.18 (m, 2H), 1.77 – 1.65 (m, 1H), 1.49 – 1.28 (m, 8H), 0.92 (dt, J = 13.8, 7.1 Hz, 6H).

2-Ethylhexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (b): The compound

a (4.98 g, 16.0 mmol, 1.00 eq.), bis(pinacolato)diboron (4.47 g, 17.6 mmol, 1.10 eq.), KOAc (4.71 g, 48.1 mmol, 3.00 eq.), Pd(dppf)Cl₂ (0.58 g, 0.8 mmol, 0.05 eq.) and dry DMF (75 mL) were added in the Schlenk bottle under N₂ atmosphere. The mixture was heated to 80 °C and stirred under an N₂ atmosphere for 6 hours. The mixture was filtered through celite and the solvent was removed. The crude material was dissolved in DCM then diluted with water. The layers were separated and the aqueous layer was washed with DCM three times. The organic layer was combined and dried over MgSO₄ and the solvent was removed under reduced pressure. The crude material was purified by column chromatography eluting with DCM/petroleum ether (1:1). The title compound was dried under vacuum to give 5.66 g (98%).

¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 2H), 4.24 (d, *J* = 5.7 Hz, 2H), 1.72 (dd, *J* = 12.1, 5.8 Hz, 1H), 1.36 (s, 12H), 1.32 – 1.25 (m, 8H), 0.95 (dd, *J* = 12.8, 6.1 Hz, 6H).

2-Ethylhexyl-4-(10-bromoanthracen-9-yl) benzoate (c): The compound **b** (1.00 g, 2.78 mmol, 1.00 eq.), 9,10-dibromofluorene (0.93 g, 2.78 mmol, 1.00 eq.), anhydrous K₂CO₃ (1.15 g, 8.34 mmol, 3.00 eq.), Pd(PPh₃)₄ (0.05 g, 0.04 mmol, 0.02 eq.), dioxane (20 mL) and water (4 mL) were added in a Schlenk bottle under N₂ atmosphere. The mixture was heated to 100 °C and stirred under an N₂ atmosphere for 16 hours. The mixture was filtered through celite and the solvent was removed. The crude material was dissolved in DCM then diluted with water. The layers were separated and the aqueous layer was washed with DCM three times. The organic layer was combined and dried over MgSO₄ and the solvent was removed under reduced pressure. The crude material was purified by column chromatography eluting with DCM/petroleum ether (1:1). The title compound was dried under vacuum to give 0.82 g (60%).

¹H NMR (400 MHz, DMSO) δ 8.55 (d, *J* = 8.9 Hz, 2H), 8.22 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.72 (m, 2H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 2.9 Hz, 4H), 4.31 (t, *J* = 5.1 Hz, 2H), 1.79 – 1.71 (m, 1H), 1.47 – 1.30 (m, 8H), 0.93 (dt, *J* = 13.6, 7.0 Hz, 6H).

Boron ester derivative (d): The compound **c** (100.0 mg, 0.21 mmol, 1.00 eq.), bis(pinacolato)diboron (57.2 mg, 0.23 mmol, 1.09 eq.), KOAc (67.7 mg, 0.69 mmol, 3.28 eq.), Pd(dppf)Cl₂ (4.7 mg, 0.006 mmol, 0.03 eq.) and dry DMF (20 mL) were added in a Schlenk

bottle under N₂ atmosphere. The reaction mixture was gradually heated to 80 °C and stirred under an N₂ atmosphere for 6 hours. The reaction mixture diluted with water and the layers were separated. The aqueous layer was washed with DCM three times. The organic layer combined and dried over MgSO₄ and the solvent removed under reduced pressure. The crude material purified by column chromatography eluting with DCM/petroleum ether (1:1). The title compound was dried under vacuum to give 70.6 mg (63%). ¹H NMR (400 MHz, CDCl₃) δ 8.36 (d, *J* = 8.7 Hz, 2H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 4H), 7.25 – 7.14 (m, 2H), 4.26 (s, 2H), 1.71 (dt, *J* = 11.4, 5.7 Hz, 1H), 1.52 (s, 12H), 1.40 (ddd, *J* = 42.0, 23.1, 6.6 Hz, 8H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H).

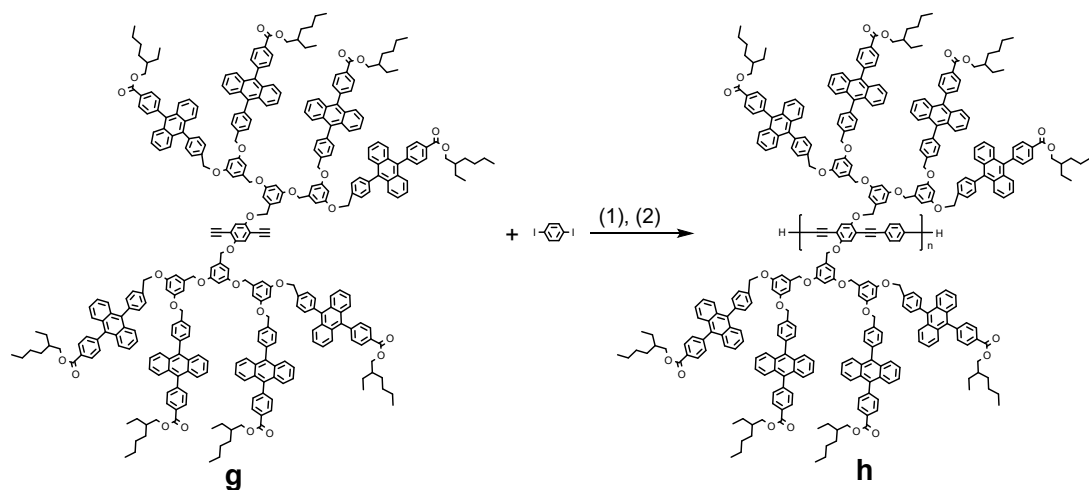
G2-4DPAEH-OH (e): The compound **d** (723.6 mg, 1.35 mmol, 5.00 eq.), G2-4Br-OH (286.0 mg, 0.27 mmol, 1.00 eq.), K₂CO₃ (558.9 mg, 4.05 mmol, 15.00 eq.), Pd(PPh₃)₄ (50.0 mg, 0.04 mmol, 0.14 eq.), dioxane (15 mL) and water (3 mL) were added in a Schlenk bottle under N₂ atmosphere. The reaction mixture was gradually heated to 99 °C and stirred under an N₂ atmosphere for 24 hours. The mixture was filtered through celite and the solvent was removed. The crude material was dissolved in DCM then diluted with water. The layers were separated and the aqueous layer was washed with DCM three times. The organic layer was combined and dried over MgSO₄ and the solvent was removed under reduced pressure. The crude material was purified by column chromatography eluting with DCM. The title compound was dried under vacuum to give 498.0 mg (78%). ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 7.8 Hz, 8H), 7.72 (dd, *J* = 9.8, 5.4 Hz, 16H), 7.62 (dd, *J* = 6.8, 2.8 Hz, 8H), 7.54 (dd, *J* = 17.8, 7.7 Hz, 16H), 7.33 (d, *J* = 2.9 Hz, 8H), 7.32 (d, *J* = 3.0 Hz, 8H), 6.88 (s, 4H), 6.83 (s, 2H), 6.73 (s, 2H), 6.69 (s, 1H), 5.29 (d, *J* = 8.9 Hz, 8H), 5.12 (s, 4H), 4.69 (s, 2H), 4.42 – 4.26 (m, 8H), 1.80 (dt, *J* = 12.0, 6.0 Hz, 4H), 1.60 – 1.33 (m, 32H), 0.97 (dt, *J* = 13.3, 6.9 Hz, 24H).

G2-4DPAEH-Br (f): The compound **e** (500.0 mg, 0.21 mmol, 1.00 eq.), CBr₄ (87.0 mg, 0.26 mmol, 1.24 eq.), PPh₃ (69.0 mg, 0.26 mmol, 1.24 eq.) and a minimum amount of dry tetrahydrofuran were added in a three-necked flask under N₂ atmosphere. The reaction mixture was stirred for 30 min at room temperature and the extent of the reaction was monitored by TLC. The reaction was quenched by adding DCM and water to the reaction mixture. The layers

were separated and the aqueous layer was washed with DCM three times. The organic layer was combined and dried over MgSO₄ and the solvent was removed under reduced pressure. The crude material was purified by column chromatography eluting with DCM. The title compound was dried under vacuum to give 435.3 mg (85%). ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 7.8 Hz, 8H), 7.72 (dd, *J* = 9.8, 5.4 Hz, 16H), 7.62 (dd, *J* = 6.8, 2.8 Hz, 8H), 7.54 (dd, *J* = 17.8, 7.7 Hz, 16H), 7.32 (dd, *J* = 6.7, 3.0 Hz, 16H), 6.88 (s, 4H), 6.83 (s, 2H), 6.73 (s, 2H), 6.69 (s, 1H), 5.29 (d, *J* = 8.9 Hz, 8H), 5.12 (s, 4H), 4.69 (s, 2H), 4.42 – 4.27 (m, 8H), 1.80 (dt, *J* = 12.0, 6.0 Hz, 4H), 1.61 – 1.34 (m, 32H), 1.06 – 0.79 (m, 24H).

mono-Dendrimer (g): The compound **f** (500.0 mg, 0.205 mmol, 2.5 eq.), 2,5-trimethylsilylethynyl-1,4-hydroquinone (24.9 mg, 0.082 mmol, 1.0 eq.), K₂CO₃ (113.2 mg, 0.0820 mmol, 10.0 eq.), 18-C-6 (21.6 mg, 0.082 mmol, 1.0 eq.) and dried THF (10 mL) in a three-neck bottle under N₂ atmosphere. The reaction mixture was gradually heated to reflux and stirred under an N₂ atmosphere for 24 hours. The organic layer was washed with water and DCM collected and dried over MgSO₄. The solvent was removed under reduced pressure and the crude material was purified by column chromatography eluting with THF. GPC isolated gave product **g** about 300 mg (75%). ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 7.8 Hz, 16H), 7.97 – 7.27 (m, 112H), 6.90 – 6.61 (m, 20H), 5.16 (d, *J* = 60.9 Hz, 28H), 4.39 – 4.28 (m, 16H), 3.38 (s, 2H), 1.82 – 1.73 (m, 8H), 1.58 – 1.36 (m, 64H), 0.96 (dt, *J* = 11.7, 6.3 Hz, 48H).

Synthesis of MWDPAs



Scheme S2. Synthesis route of MWDPA. Reagents and conditions: (1) $(\text{Ph}_3\text{P})_4\text{Pd}$, CuI , *iso*- Pr_2NH , THF, 50 °C; (2) $\text{PhC}\equiv\text{CH}$, 50 °C.

The compound **g** (360.1 mg, 0.074 mmol, 1.0 eq.), 1,4-p-diiodobenzene (24.4 mg, 0.074 mmol, 1.0 eq.), a catalytic amount of catalyst $\text{Pd}(\text{PPh}_3)_4$ and CuI , *iPr* $_2\text{NH}$ (2.5 mg, 0.025 mmol, 0.33 eq.) and of anhydrous THF (3 mL) was added in a Schlenk bottle under N_2 atmosphere. The reaction mixture was gradually heated to 50 °C and stirred under an N_2 atmosphere for 24 hours. Then, phenylacetylene (151.1 mg, 1.480 mmol, 20 eq.) and the appropriate amount of $\text{Pd}(\text{PPh}_3)_4$ were added. The reaction mixture was stirred at 50 °C for 12 hours. The solvent was removed under reduced pressure and dissolved in DCM. The solution of crude material was filtered to remove insoluble impurities. The solvent was removed under reduced pressure and the crude material was purified by column chromatography eluting with THF. GPC isolated gave product **g** about 300 mg (83%). ^1H NMR (400 MHz, CDCl_3) δ 8.16 – 7.43 (br, H in DPA), 7.32-6.73 (br, H in dendrimer), 6.87 (br, p-H in inner C_6H_3), 6.82 (br, o-H in inner C_6H_3), 5.06 (br, $\text{Ar-CH}_2\text{-OAr}'$), 4.28 (br, $\text{R-COOCH}_2\text{-R}$), 1.73 (br, R-CH-R_2), 1.54 – 1.35 (br, $\text{R-CH}_2\text{-R}$), 0.91 (br, R-CH_3). GPC analysis (THF, polystyrene standards): $M_w = 16,802$ (average number of repeating units = 3), $M_w/M_n = 1.45$.

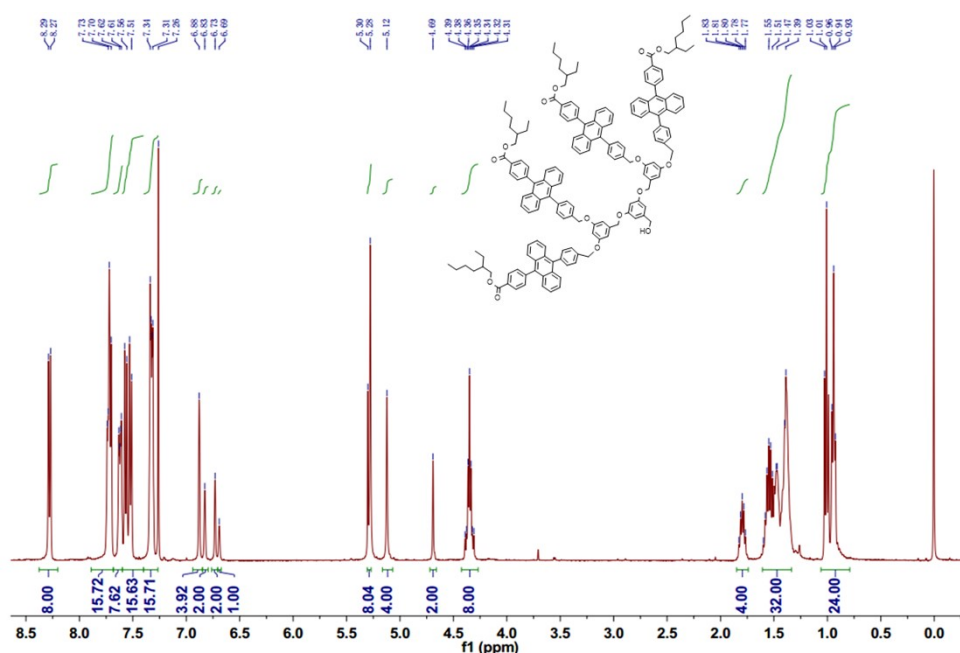


Figure S1. ^1H NMR spectrum of G2-4DPAEH-OH (e).

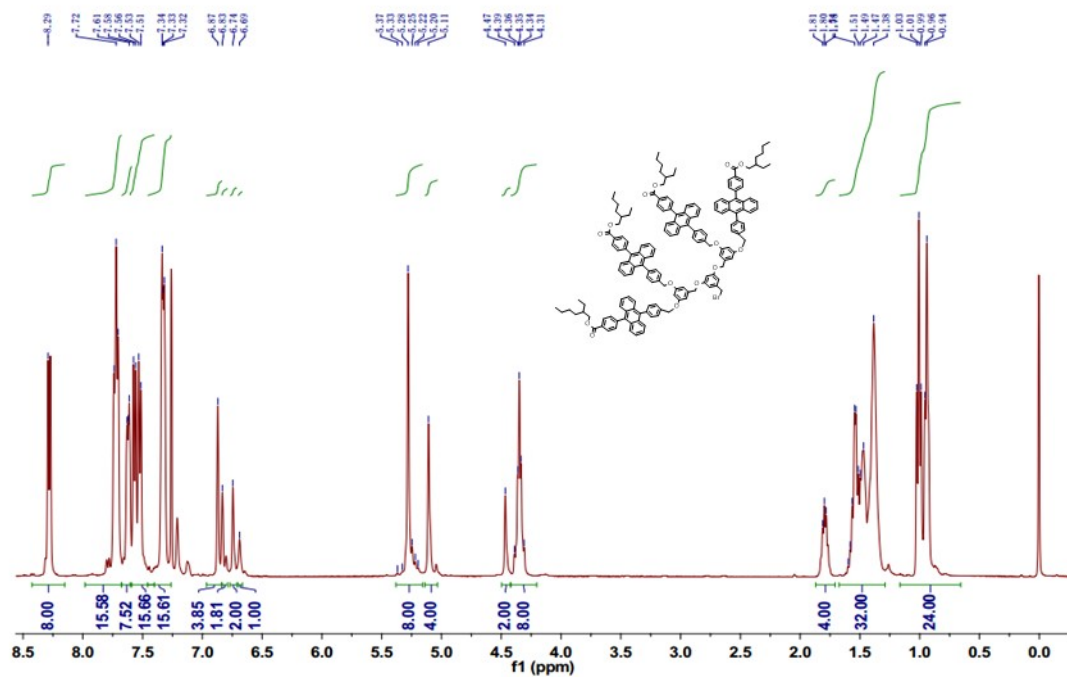


Figure S2. ^1H NMR spectrum of G2-4DPAEH-Br (f).

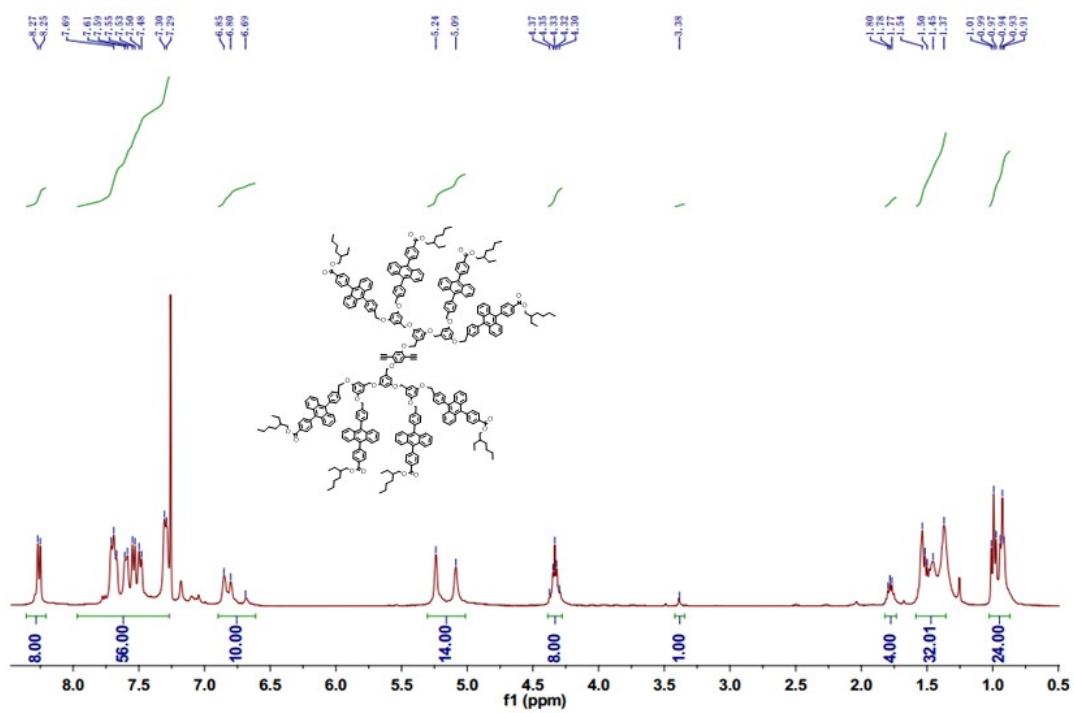


Figure S3. ^1H NMR spectrum of mono-dendrimer (g).

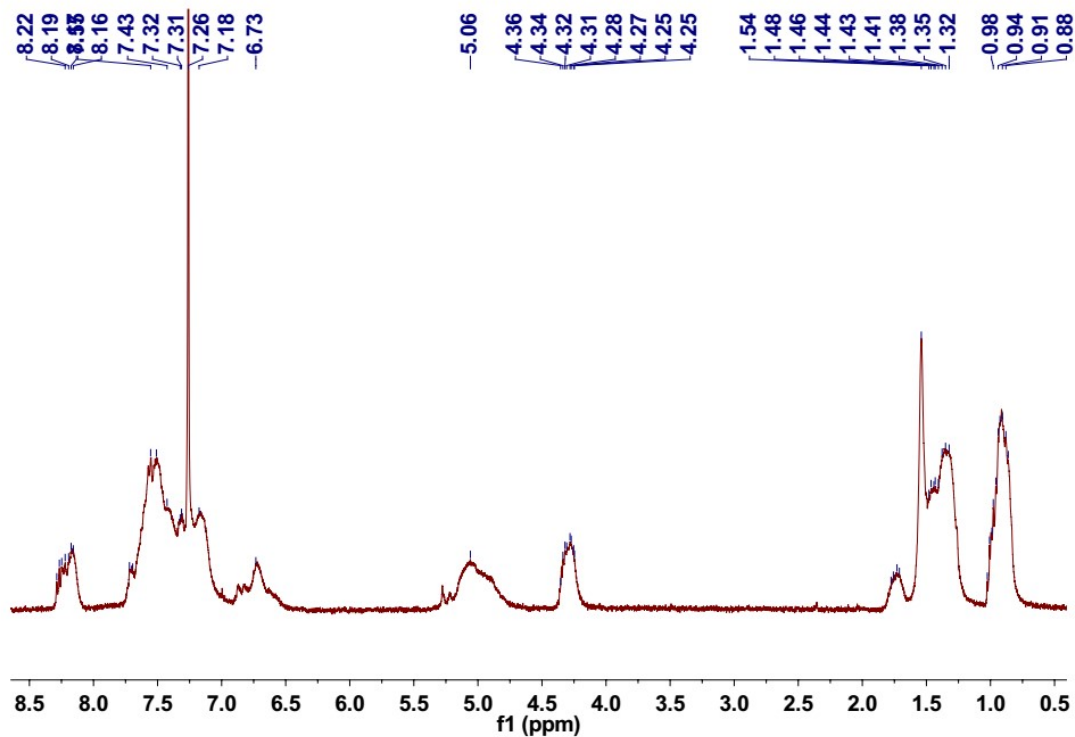


Figure S4. ^1H NMR spectrum of MWDPA.

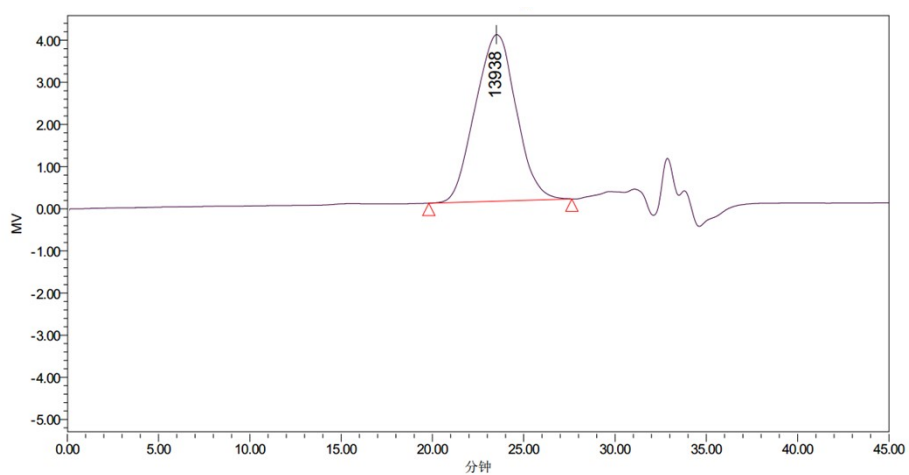


Figure S5. Gel permeation chromatography (GPC) trace of MWDPA.

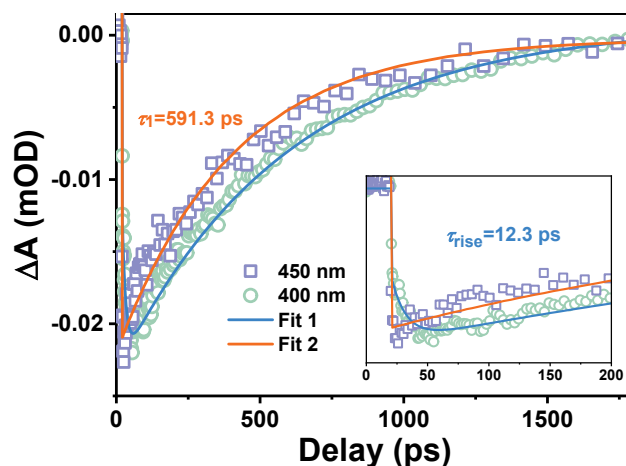


Figure S6. Transient absorption kinetics probed at 500 nm of the stimulated emission from PPE unit of MWDPDA upon excitation with 400 nm (cyan circles) and 450 nm (orange squares) pulses, respectively. Solid lines are the corresponding exponential fits. The inset shows a closer view of the rising region of the stimulated emission from PPE core.

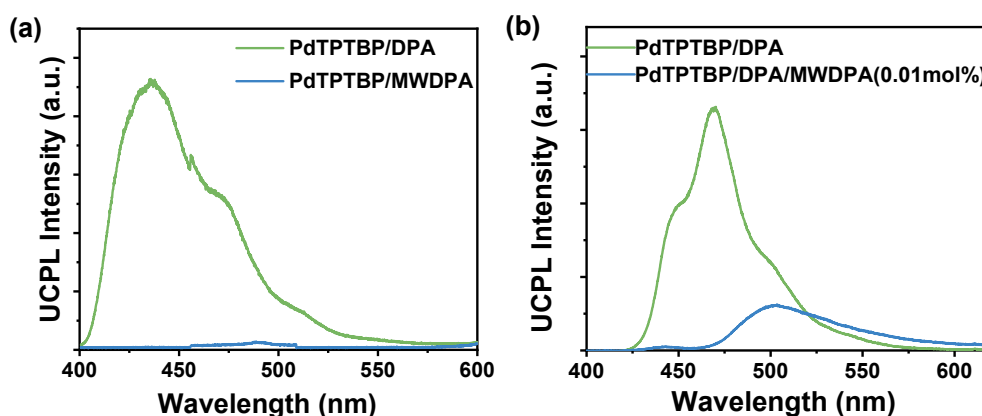


Figure. S7. (a) Upconversion emission spectra of PdTPTBP-DPA and PdTPTBP-MWDPA in toluene. Nominal [DPA] = 4 mM, [PdTPTBP] = 1 μ M. (b) Upconversion emission spectra of PdTPTBP(0.001 mol%)/DPA and PdTPTBP(0.001 mol%)/DPA/MWDPA(0.01 mol%) microcrystals (λ_{ex} = 635 nm, 200 mW/cm²).

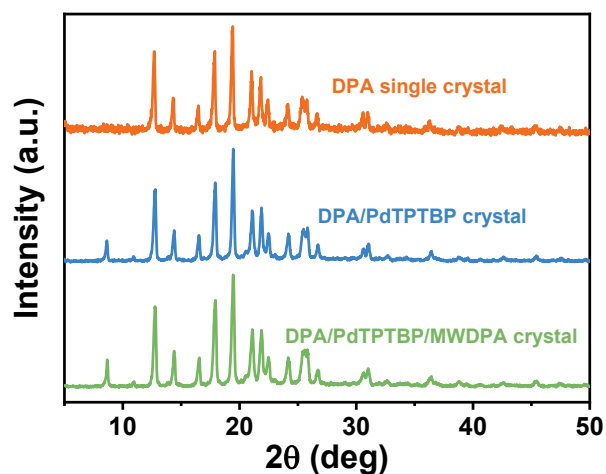


Figure S8. XRD patterns of DPA microcrystal, PdTPTBP(0.001 mol%)/DPA and PdTPTBP(0.001 mol%)/DPA/MWDPA(0.002 mol%) microcrystals.

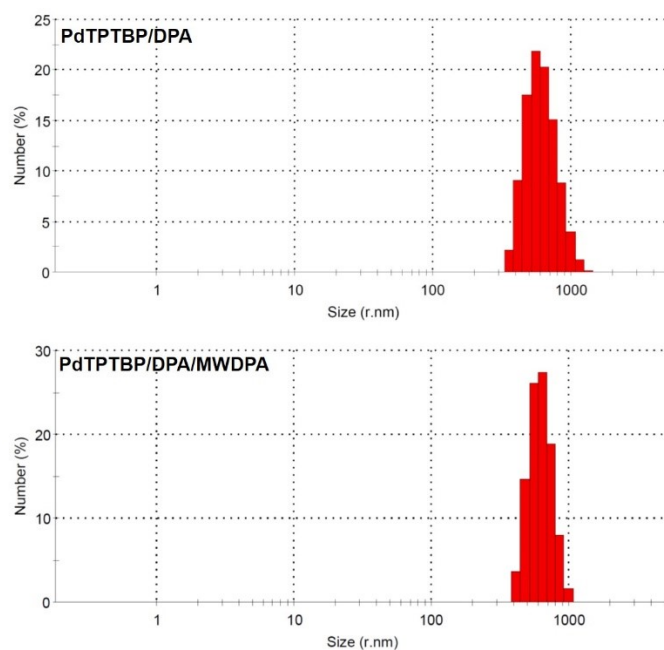


Figure S9. Radius distribution of PdTPTBP(0.001 mol%)/DPA and PdTPTBP(0.001 mol%)/DPA/MWDPA(0.002 mol%) microcrystals obtained by dynamic light scattering.

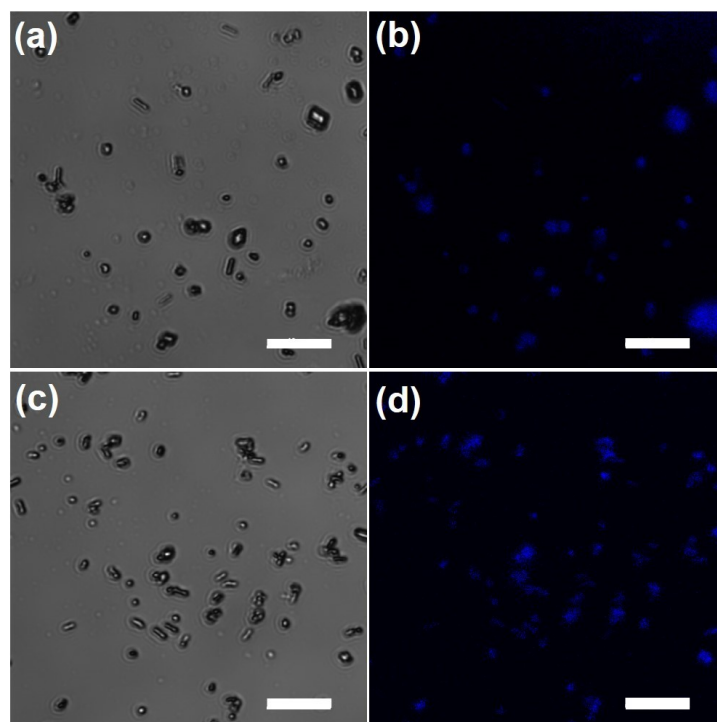


Figure S10. Brightfield (a) and confocal microscopy images (b) of PdTPTBP(0.001 mol%)/DPA microcrystals. Brightfield (c) and upconversion emission images (d) of PdTPTBP(0.001 mol%)/DPA/MWDPA(0.002 mol%) microcrystals. Upconversion emission images were taken with 400–450 nm bandpass filter, under excitation by 635 nm laser. Scale bars = 10 microns.

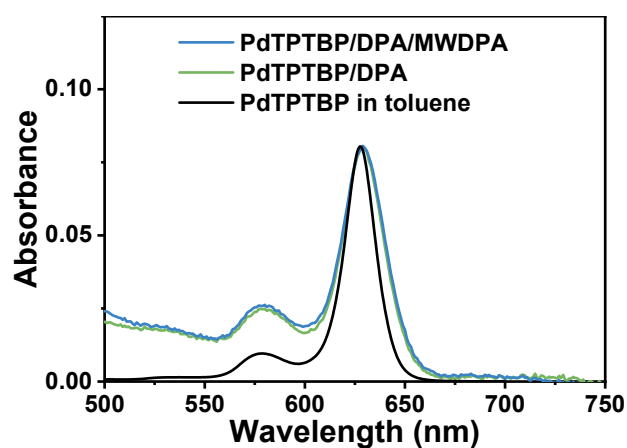


Figure S11. Absorption spectra of photosensitizer PdTPTBP in toluene and UV-Vis diffuse reflectance spectra of PdTPTBP (0.001 mol%) doped in DPA microcrystals and DPA/MWDPA microcrystals.

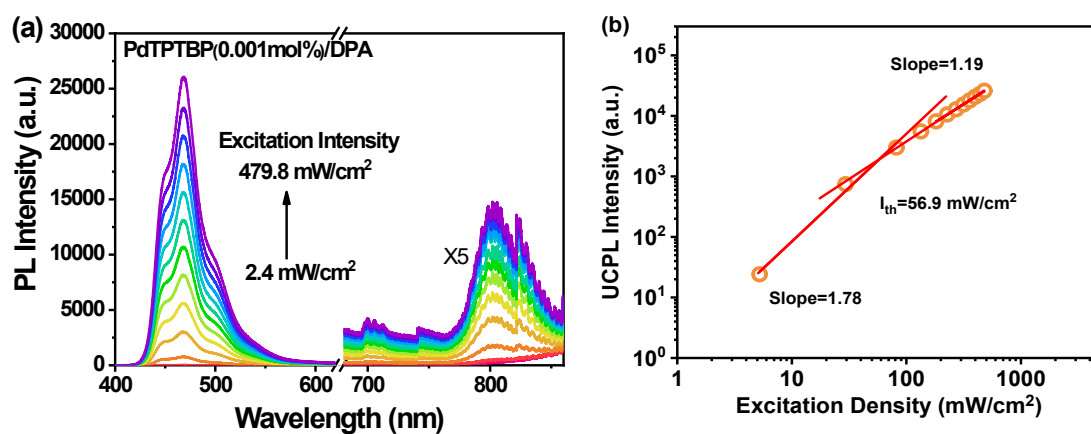


Figure S12. (a) Upconversion luminescence spectra of PdTPTBP(0.001 mol%)/DPA at different excitation light power densities. ($\lambda_{\text{ex}} = 635 \text{ nm}$) (b) A double logarithmic curve of the upconversion luminescence intensity of the PdTPTBP(0.001 mol%)/DPA as a function of excitation light power density.

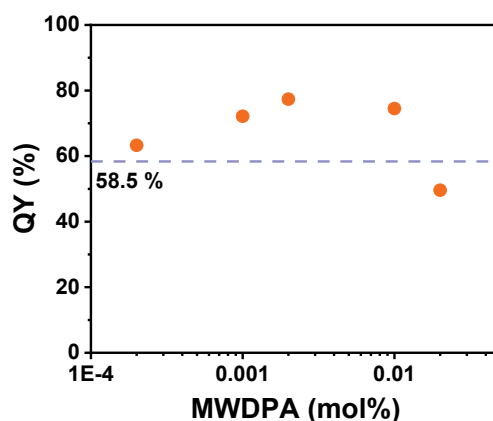


Figure S13. Fluorescence quantum yields of PdTPTBP(0.001 mol%)/DPA/MWDPA microcrystals with various doping content of MWDPA. The dash line indicates the QY value of PdTPTBP(0.001 mol%)/DPA. ($\lambda_{\text{ex}} = 375 \text{ nm}$)

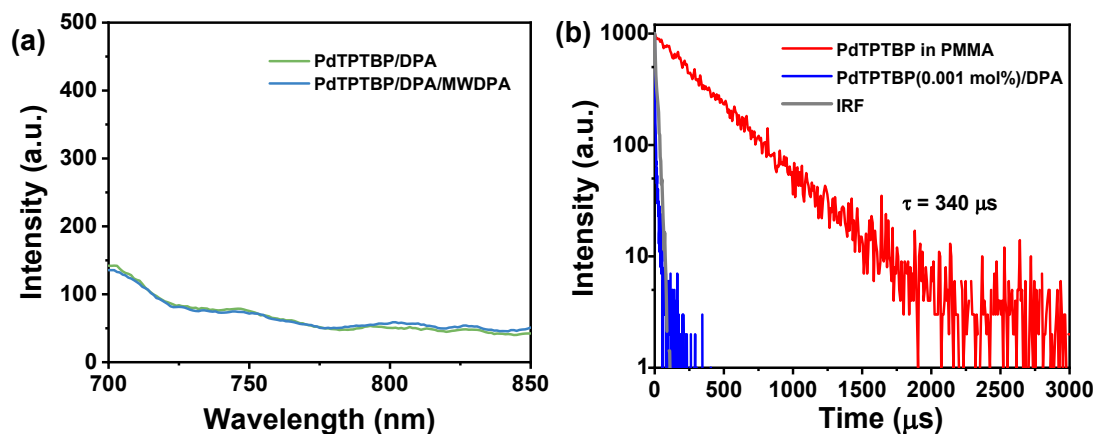


Figure S14. (a) Phosphorescence spectra of PdTPTBP in PdTPTBP(0.001 mol%)/DPA and PdTPTBP(0.001 mol%)/DPA/MWDPA microcrystals. (b) Phosphorescence decays of PdTPTBP in PMMA and PdTPTBP(0.001 mol%)/DPA together with IRF ($\sim 12 \mu\text{s}$). ($\lambda_{\text{ex}} = 635 \text{ nm}$)

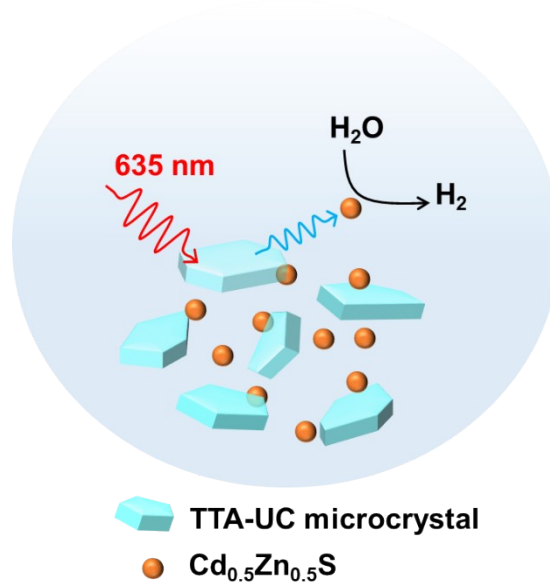


Figure S15. A schematic diagram of the microcrystalline upconversion system doped with molecular wires for photocatalytic hydrogen production.

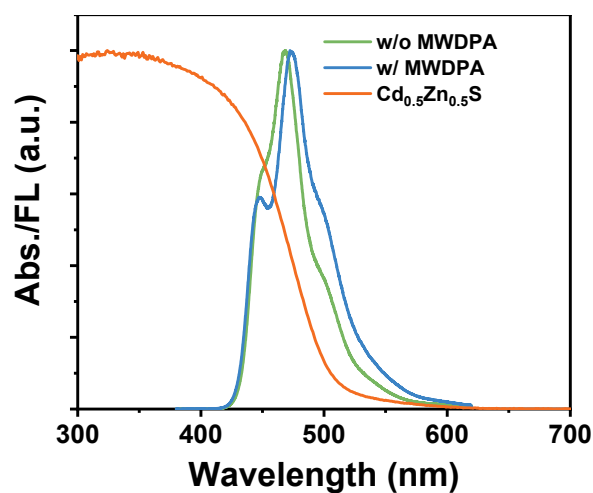


Figure S16. Normalized upconversion luminescence spectra of PdTPTBP(0.001 mol%)/DPA microcrystals with and without MWDPA ($\lambda_{\text{ex}} = 635 \text{ nm}$) and UV-visible diffuse reflection spectrum of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles.

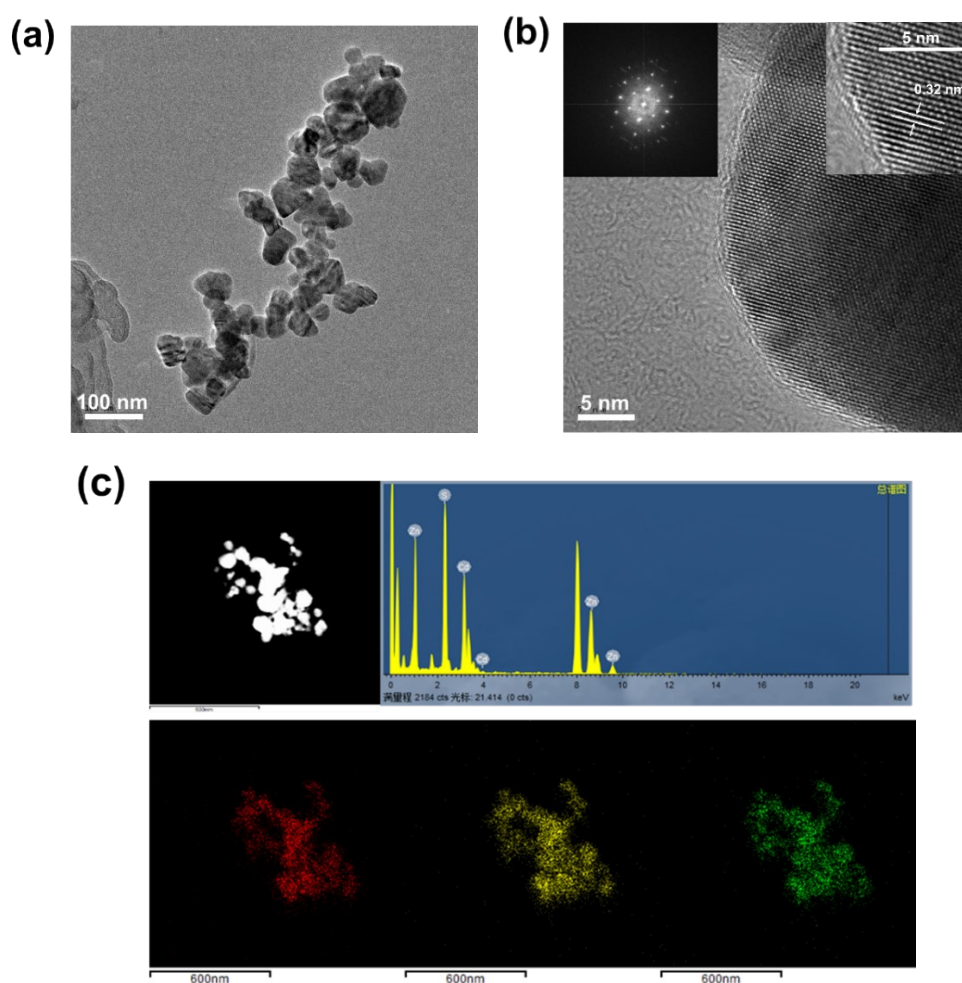


Figure S17. Characterization of the $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles. (a) TEM and (b) high resolution TEM with inset of SAED pattern of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles. (c) EDS mapping of $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}$ nanoparticles.

References

1. Scottwell, S. Ø.; Barnsley, J. E.; McAdam, C. J.; Gordon, K. C.; Crowley, J. D., A ferrocene based switchable molecular folding ruler. *Chem. Commun.* **2017**, 53 (54), 7628-7631.
2. Chen, J.; Li, S.; Zhang, L.; Liu, B.; Han, Y.; Yang, G.; Li, Y., Light-harvesting and photoisomerization in benzophenone and norbornadiene-labeled poly (aryl ether) dendrimers via intramolecular triplet energy transfer. *J. Am. Chem. Soc.* **2005**, 127 (7), 2165-2171.
3. Liu, M.; Wang, L.; Lu, G.; Yao, X.; Guo, L., Twins in Cd_{1-x}Zn_xS solid solution: Highly efficient photocatalyst for hydrogen generation from water. *Energy Environ. Sci.* **2011**, 4 (4), 1372-1378.