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Embedding $CsPbBr_3$ quantum dots into pillar[5]arene-based supramolecular self-assembly for efficient photocatalytic cross-coupling hydrogen evolution reaction

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1. Experimental section

1.1 Materials and physical methods

All the commercial materials and reagents were purchased from Energy Chemical or Aladdin Reagents and used directly as received. All other reagents and solvents were commercially available at analytical grade and were used without further purification. Field-emission scanning electron microscope (FE-SEM, FEI, Sirion 200), transmission electron microscope (TEM, Tecna i-G2-F30 (FEI)), X-ray powder diffraction (XRD, AXS D8-Advanced diffractometer), X-ray photoelectron spectroscopy (XPS, a PHI5702 multifunctional spectrometer), were used to characterize the morphology and composition of the material. UV-vis absorbance measurements were recorded on Shimadzu UV-1750. Photocatalysis was performed using Xenon lamp (HSXF/UV 300), equipped with 400-800 nm filter. Photoluminescence (PL) spectra were acquired on an Edinburgh Instruments FLS920 fluorescence spectrometer. For the measurement of PL lifetime, the used excitation wavelength (λ_{ex}) was 360 nm and the maximum emission wavelength (λ_{em}) was 550 nm. The average lifetime (Ave. τ) is calculated according to $\tau = \tau_1 \cdot I_1 + \tau_2 \cdot I_2 + \tau_3 \cdot I_3$ (τ_i is the lifetime; I_i is the relative intensity). [1, 2] ^{1}H-NMR spectrums were gathered on a JEOL ESC 400 M instrument. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. FT-IR spectra were performed on a Nicolet FT-170SX spectrometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected).

1.2 Energy-transfer efficiency

Energy-transfer efficiency (Φ_{ET}) was calculated from excitation fluorescence spectra through the equation: $\Phi_{ET} = 1 - F_{DA} / F_D$.[1]

Where F_{DA} and F_D are the fluorescence intensities of the emission of $CsPbBr_3$@PTY⊃EYB (donor and acceptor) and $CsPbBr_3$ (donor) respectively, when excited at 360 nm. The energy-transfer efficiency (Φ_{ET}) was calculated as 96.5%

in toluene, measured under the condition of [PTY] = 2×10^{-5} M, [$CsPbBr_3$] =1.25×10^{-4} M, [EYB] = 5×10^{-7} M, and λ_{ex} = 360 nm.

1.3 Fluorescence lifetimes

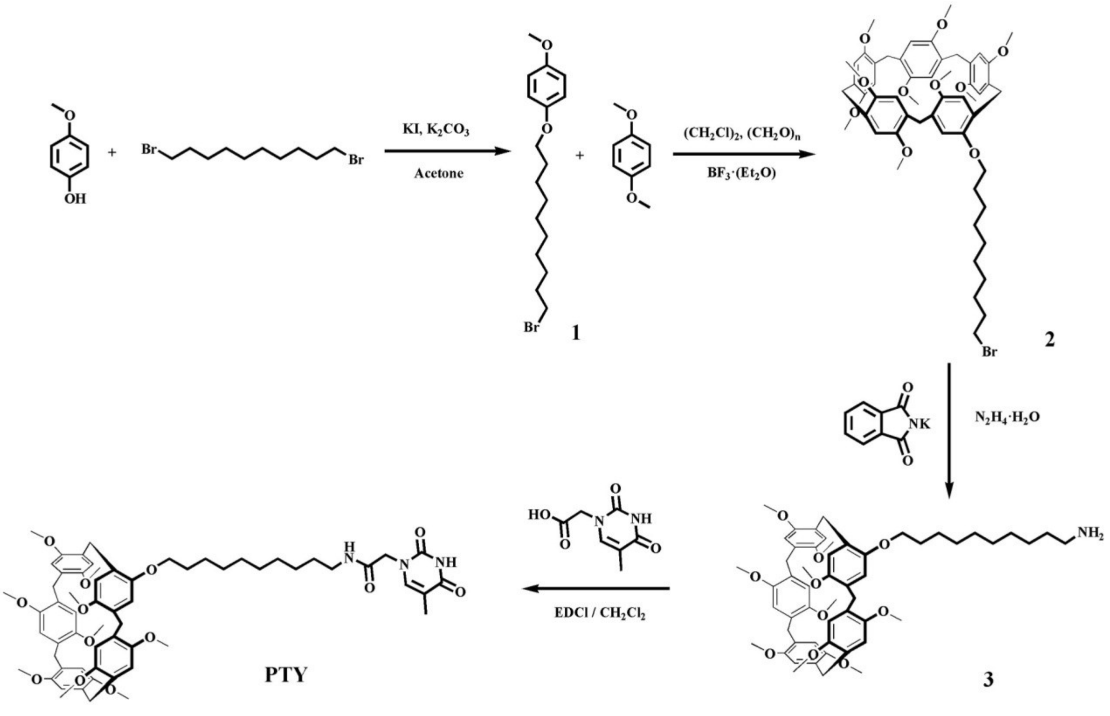
The emission decays of $CsPbBr_3$, $CsPbBr_3$@PTY⊃EYB and EYB in toluene solvent were studied and the decay traces for the samples were well fitted with triple exponential function *Y(t)* based on nonlinear least-squares, using the following expression.[2]

$$Y(t)= B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$$

where B_1, B_2, B_3 are fractional contributions of time-resolved emission decay lifetimes τ_1, τ_2, τ_3 and the average lifetime τ could be concluded from the equation:

$$\langle\tau\rangle = \frac{B_1\tau_1^2+B_2\tau_2^2+B_3\tau_3^2}{B_1\tau_1+B_2\tau_2+B_3\tau_3}$$

2. Synthesis and characterizations of compounds.



Scheme S1. Synthesis of compound PTY.

Synthesis of compound 1.[3] A mixture of 4-methoxyphenol (2.48 g, 20.0 mmol), K_2CO_3 (13.82 g, 100 mmol), KI (3.32 g, 20 mmol), 1,10-dibormodecane (24.01 g, 80 mmol) and acetone (400.0 mL) were added to a 500 mL round-bottom flask under nitrogen atmosphere. The reaction mixture was stirred at 65 ℃ for 72 h. After the solid was filtered off, the solvent was evaporated and the residue was dissolve in CH_2Cl_2. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (V/V = 50:1) as the eluent, compound 1 as white solid (6.53 g, yield 95%) was isolated. Mp: 60-62 ℃. ^1H NMR ($CDCl_3$, 600 MHz), δ/ppm: 6.83 (s, 4H), 3.91-3.89 (t, J = 6.6 Hz, 2H), 3.76 (s, 3H), 3.41-3.39 (t, J = 6.9 Hz, 2H), 1.86-1.82 (m, 2H), 1.77-1.72 (m, 2H), 1.45-1.41 (m, 2H), 1.35-1.30 (m, 10H).

Synthesis of compound 2.[4] 1-(10-bromodecyloxy)-4-methoxybenzene (compound 1) (1.72 g, 5 mmol) was added to a solution of 1,4-dimethoxybenzene (8.29 g, 60 mmol) and paraformaldehyde (3.00 g, 100 mmol) in 1,2-dichloroethane (250 mL), the mixture was stirred at room temperature for 40 min. Then, boron trifluoride diethyl etherate (6 mL, 47.6 mmol) was added to the solution and the mixture was stirred at 30 ℃ for 40 min. After the reaction was finished, the resulting oil was dissolved in CH_2Cl_2 (250 mL) and washed third with H_2O (300 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product. After purification by column chromatography using petroleum ether/ethyl acetate (V/V = 50:1) as the eluent, compound 2 as a white solid (1.67g, yield 35%) was isolated. Mp: 170-172 ℃. ^1H NMR (CDCl3, 600 MHz), δ/ppm: 6.95-6.80 (m, 10H), 3.98-3.96 (t, J = 6.2 Hz, 2H), 3.80-3.70 (m, 37H), 2.93-2.61 (m, 2H), 1.83-1.71 (m, 4H), 1.34-1.31 (m, 2H), 1.25-0.68 (m, 10H). ESI-MS m/z: 2 Calcd for $C_{54}H_{67}BrO_{10}$, 954.3918; Found 954.3923.

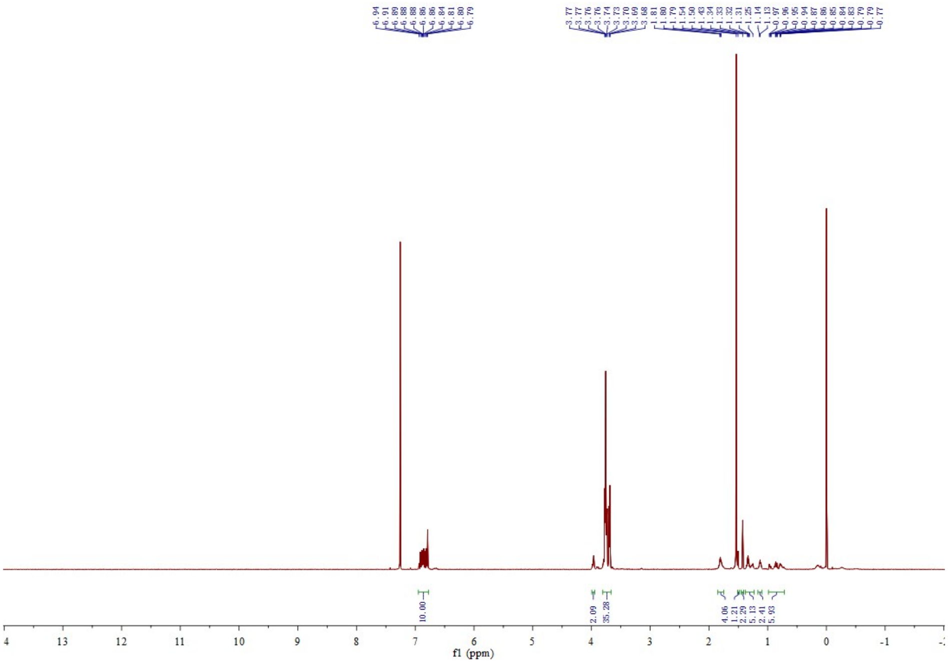


Figure S1. ^{1}H NMR spectrum of 2 in $CDCl_3$.

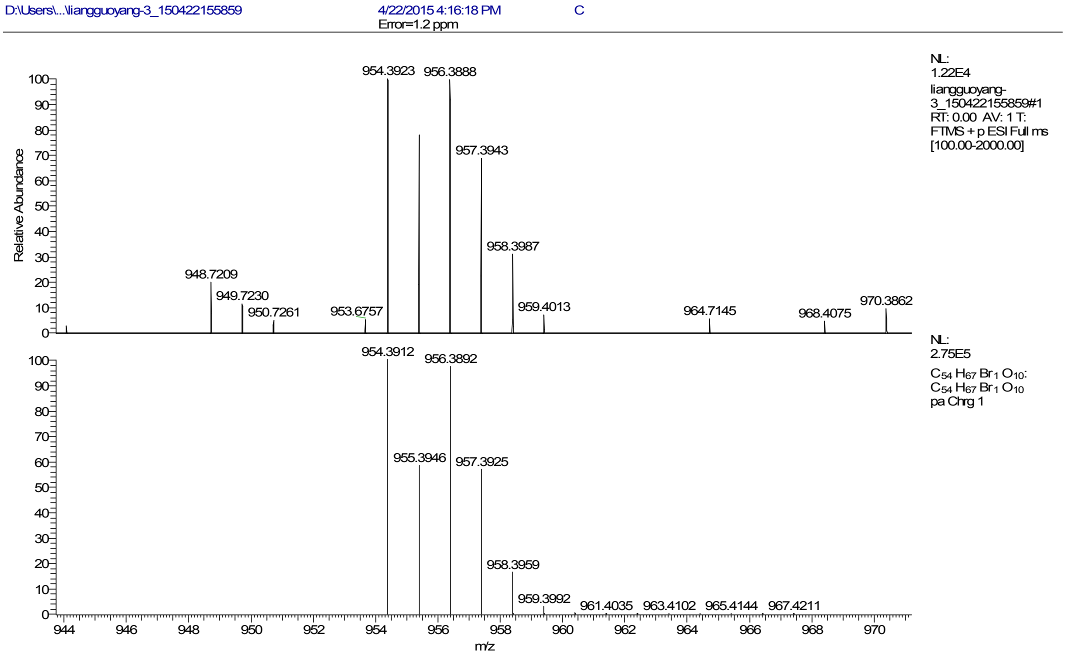


Figure S2. ESI-MS spectrum of **2**.

Synthesis of compound 3. Compound 3 was synthesized by a similar route as Huang's.[5] A mixture of bromo-functionalized pillar[5]arene (compound 2) (0.95 g, 1.0 mmol) and phthalimide potassium (0.21 g, 1.1 mmol) in 30 mL of DMF was stirred at 90 ℃ for 24 h under nitrogen atmosphere. After adding water (100 mL), the resulting precipitates were collected by filtration and dried to give crude product. The crude product was dissolved in THF (30 mL), methanol (3 mL) and hydrazine hydrate (3 mL). After stirred at 50 ℃ for 24 h, the reaction mixture was concentrated by rotary evaporation. The resulting residue was dissolved in CH_2Cl_2 (150 mL) and washed with H_2O (2 × 200 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to afford the crude product, which was isolated by flash column chromatography using dichloromethane/methanol (V/V = 10 : 1). The fractions containing the product were combined and concentrated under vacuum to give compound 3 (0.70 g, yield 65%) as a white solid. Mp: 138-140 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz), δ 7.05 – 6.75 (m, 10H), 3.75 (m, 39H), 1.80 (s, 2H), 1.67 (s, 2H), 1.55 (s, 2H), 1.24 (s, 12H).

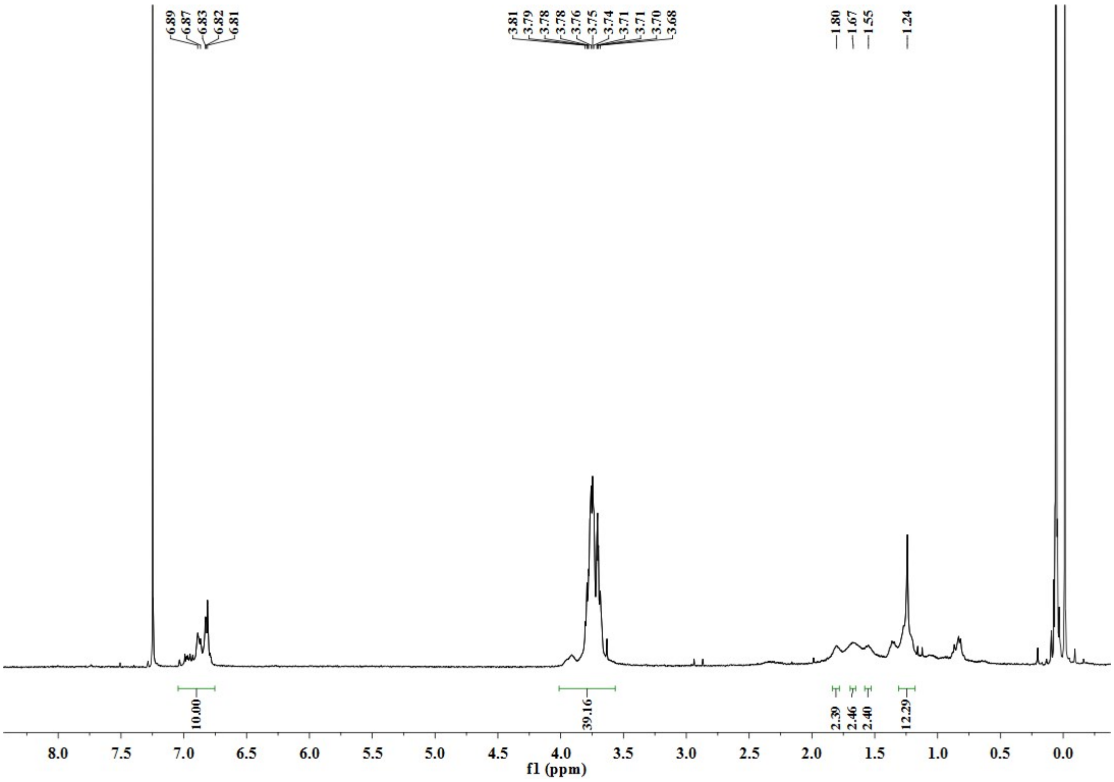


Figure S3. ^{1}H NMR spectrum of 3 in $CDCl_3$.

Synthesis of PTY: 3 (300 mg, 0.34 mmol), thymidine derivative (81 mg, 0.44 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (84 mg, 0.44 mmol), and 4-dimethylaminopyridine (3 mg) were added into dichloromethane (50 mL). Then, the resulting solution was stirred at room temperature for 24 h. The mixture was concentrated at reduced pressure. The crude product was purified by silica column chromatography (dichloromethane/methanol = 30:1) to give a white solid (0.25 g, yield: 70%). ^{1}H NMR (400 MHz) δ 7.09 (s, 1H), 6.86 – 6.74 (m, 10H), 4.30 (s, 2H), 4.21 (t, J = 6.0 Hz, 2H), 3.75 (d, J = 3.9 Hz, 10H), 3.68 (d, J = 12.9, 7.6 Hz, 27H), 2.81 (d, J = 2.6 Hz, 2H), 1.94 (d, J = 6.3 Hz, 3H), 1.82 – 1.63 (m, 4H), 1.56 – 1.47 (m, 3H), 1.41 (t, J = 6.0 Hz, 2H), 1.32 (d, J = 6.3 Hz, 6H), 1.22 (d, J = 3.7 Hz, 3H). ESI-MS m/z: [PTY + H$^+$] Calcd for $C_{61}H_{76}N_3O_{13}$, 1058.53; Found 1058.49.

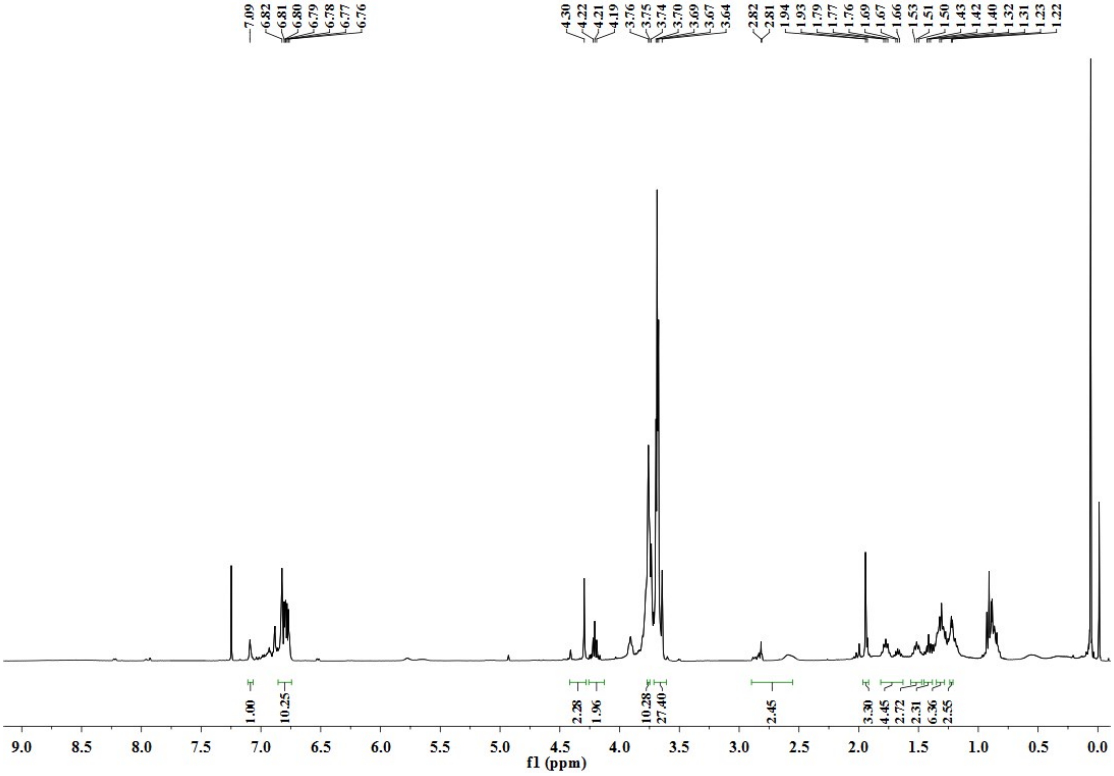


Figure S4. ^{1}H NMR spectrum of compound PTY in $CDCl_3$.

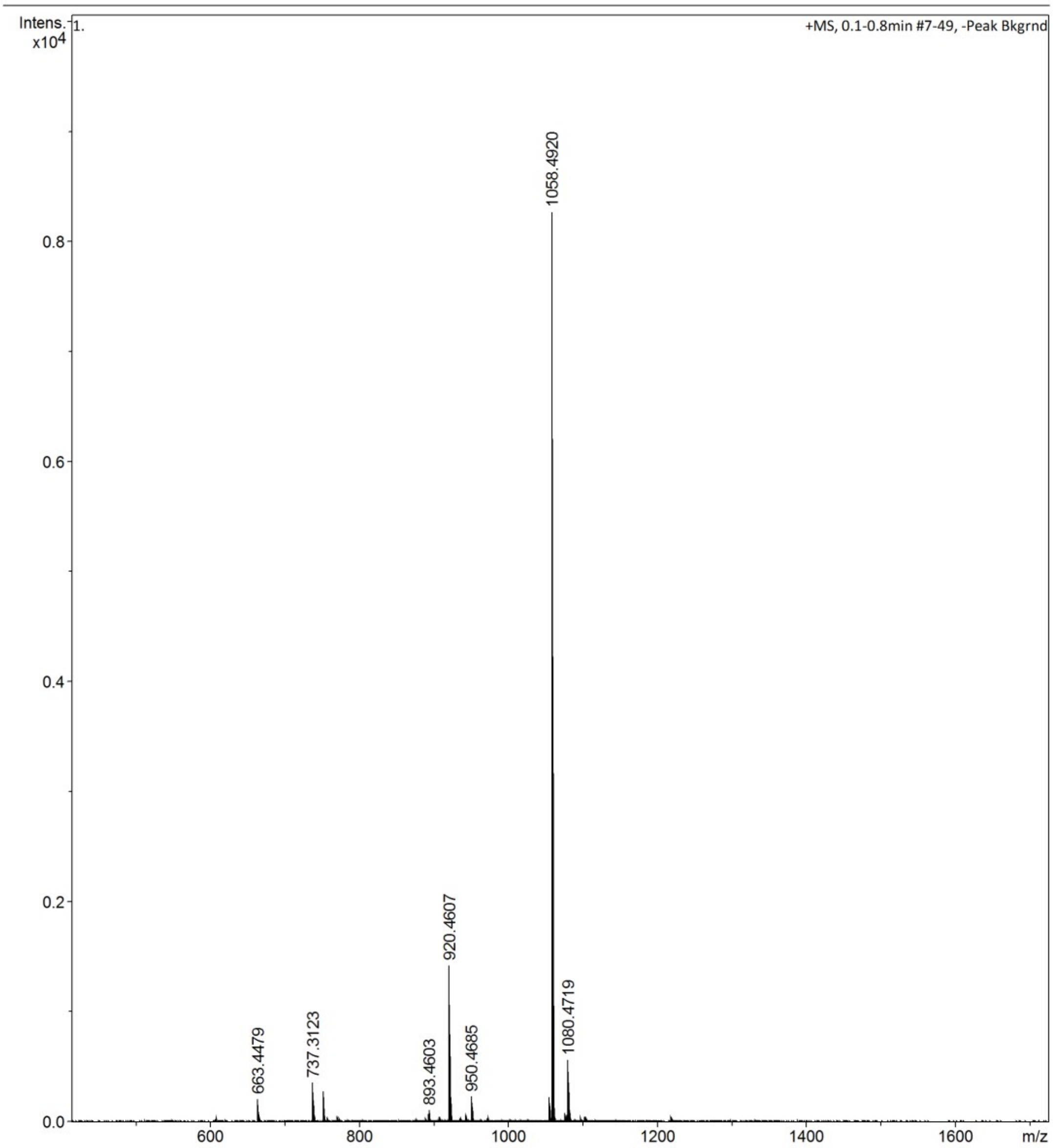
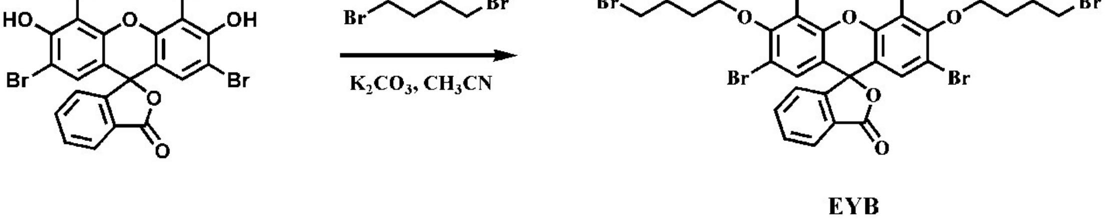


Figure S5. ESI-MS spectrum of PTY.



Scheme S2. Synthesis of compound EYB.

Synthesis of EYB: A mixture of eosin Y (1.30 g, 2.0 mmol), K_2CO_3 (1.38 g, 10 mmol), 1,4-dibormodecane (2.40 g, 8 mmol) and acetonitrile (80.0 mL) were added to a 250 mL round-bottom flask under nitrogen atmosphere. The reaction mixture was stirred at 80 ℃ for 24 h. After the solid was filtered off, the solvent was evaporated and the residue was dissolve in CH_2Cl_2. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (V / V = 20:1) as the eluent, compound EYB as shiny red solid (0.92 g, yield 50%) was isolated. ^{1}H NMR (400 MHz,) δ 8.32 (d, *J* = 7.7, 1.4 Hz, 1H), 7.80 (d, *J* = 19.2, 7.6, 1.4 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.10 (s, 1H), 4.14 (d, *J* = 18.0, 6.1 Hz, 4H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.36 (t, *J* = 6.5 Hz, 2H), 2.26 – 2.17 (m, 2H), 2.08 (d, *J* = 8.7, 5.6 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.72 (d, *J* = 5.4, 3.4 Hz, 2H).

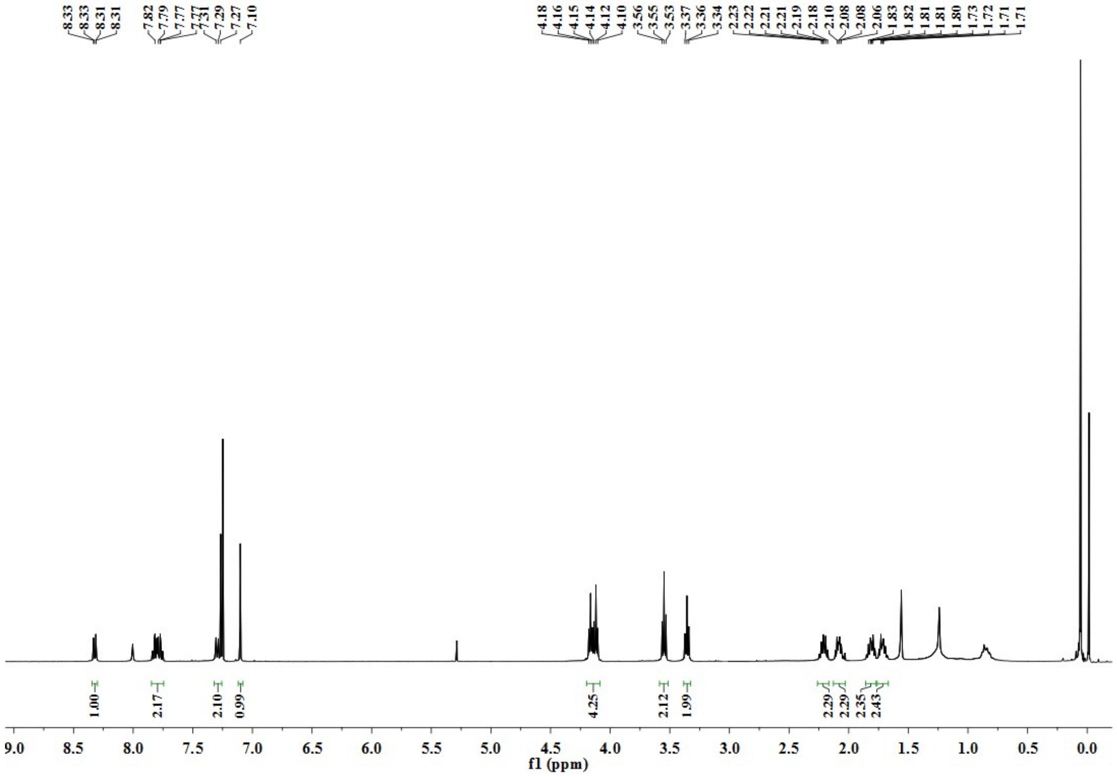


Figure S6. ^{1}H NMR spectrum of compound EYB in $CDCl_3$.

3.^{1}H NMR spectra of PTY, Pb^{2+} and PTY⊃EYB in different concentrations

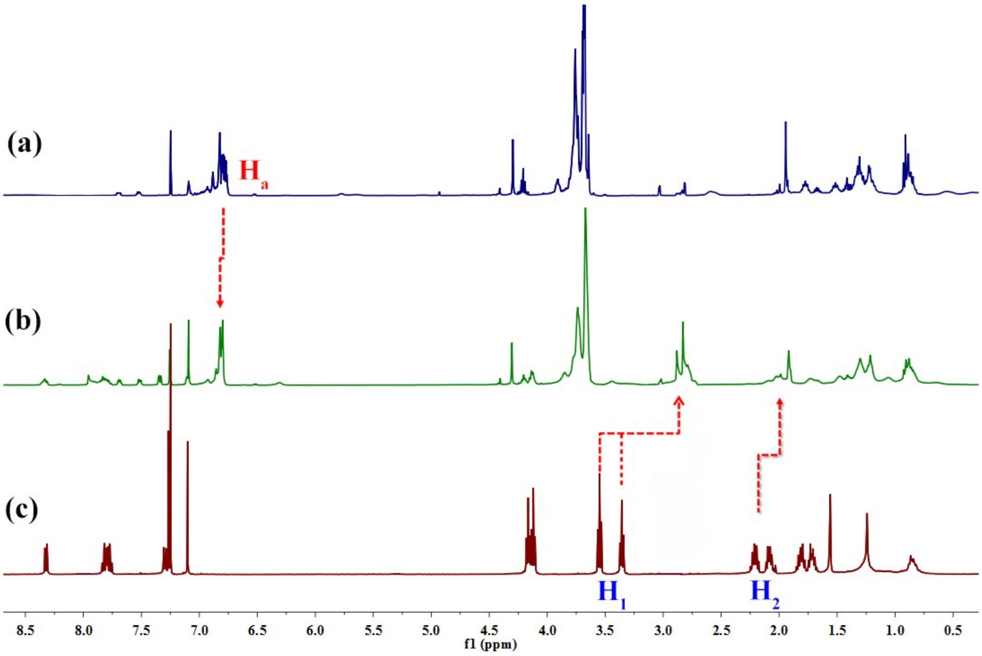


Figure S7. Partial spectra of ^{1}H NMR (400 MHz, CDCl$_3$, 298K) of EYB upon complexation with 2.0 equiv. of PTY (5 mg/mL); (a) PTY; (b) PTY⊃EYB; (c) EYB.

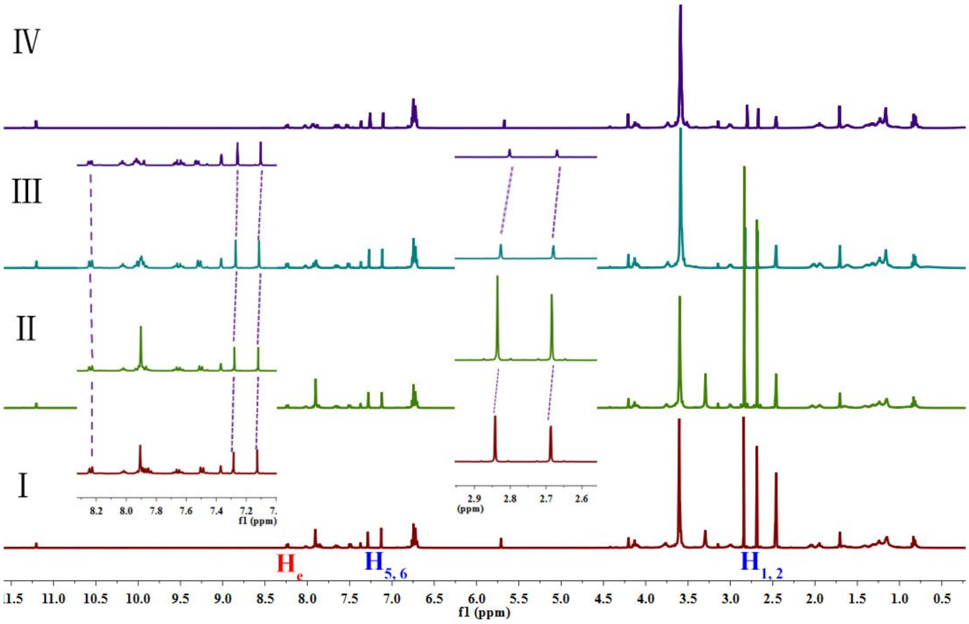


Figure S8. Partial ^{1}H NMR spectra (400 MHz, 298 K) of PTY⊃EYB in DMSO-d_6 at various concentrations: (Ⅰ) 10.0, (Ⅱ) 20.0, (Ⅲ) 40.0, and (Ⅳ) 80.0 mg/mL.

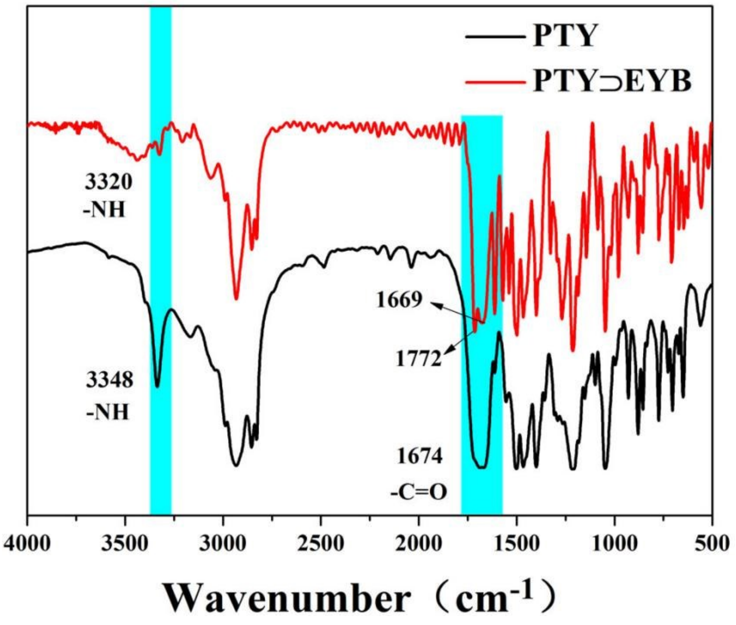


Figure S9. IR spectra of PTY, PTY⊃EYB.

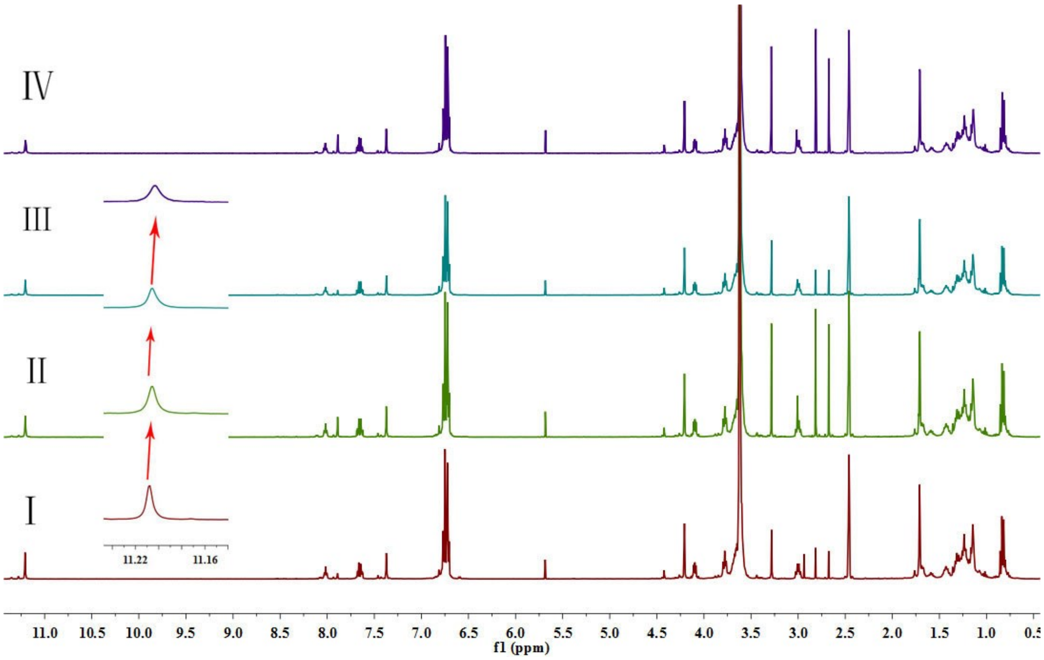


Figure S10. Partial spectra of ^{1}H NMR (DMSO-d_6, 400 MHz, 298 K) titration of PTY with different equivalents of Pb^{2+}: (Ⅰ) 0; (Ⅱ) 0.4; (Ⅲ) 0.8; (Ⅳ) 1.2.

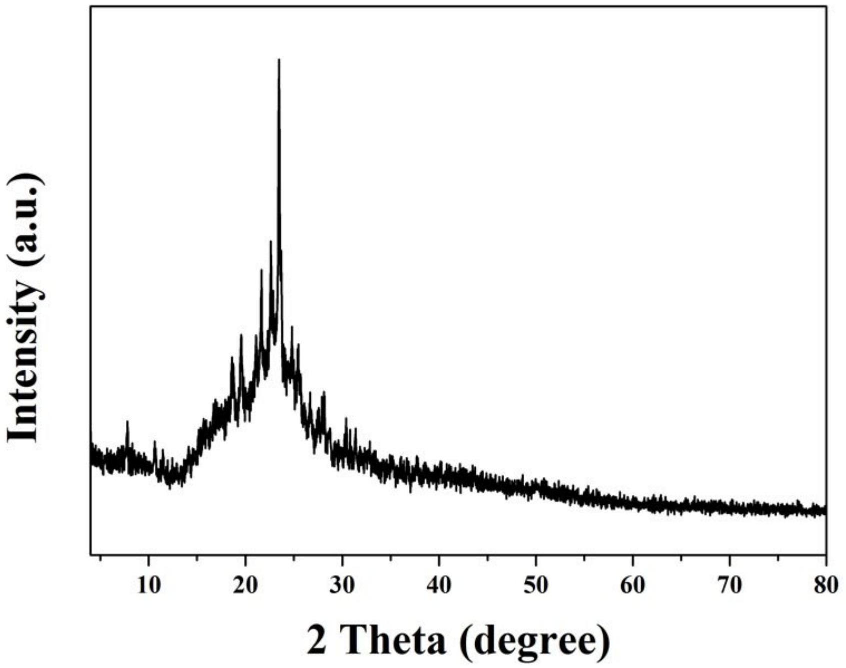


Figure S11. (a) XRD diagrams of PTY⊃EYB.

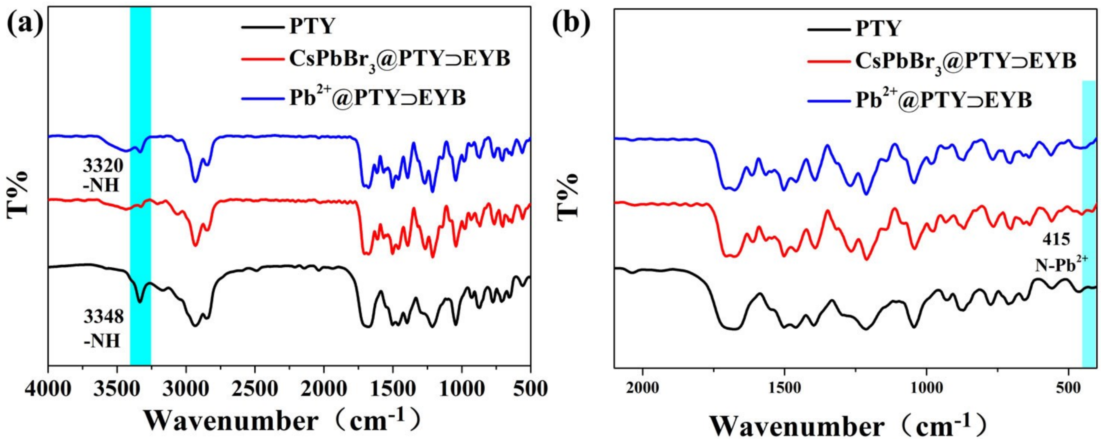


Figure S12. IR spectra of compound PTY, Pb^{2+}@PTY⊃EYB and $CsPbBr_3$@PTY⊃EYB.

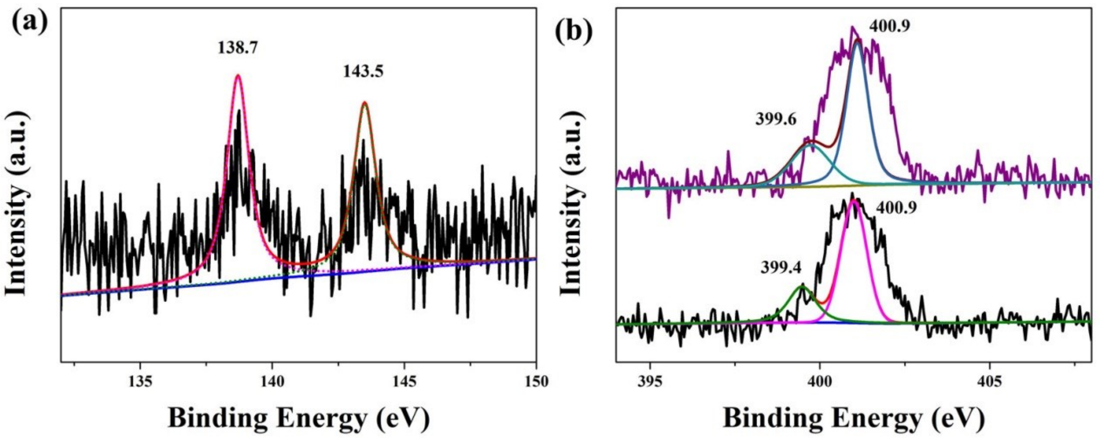


Figure S13. XPS spectra of PTY⊃EYB and Pb^{2+}@PTY⊃EYB: (a) N and (b) Pb.

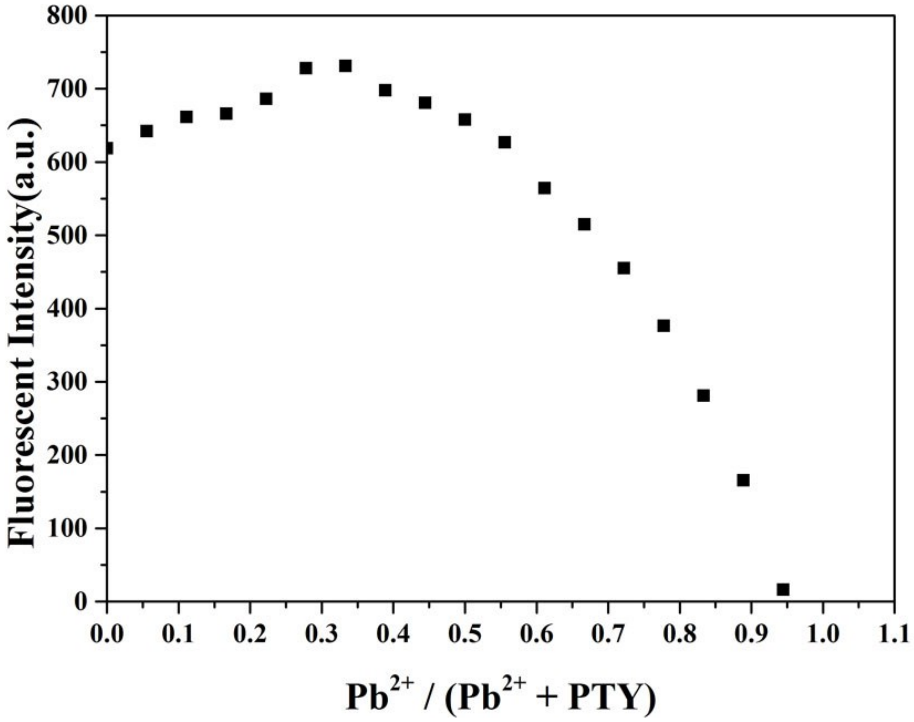


Figure S14. The Job's plot examined between Pb^{2+} and PTY, indicating the 1:2 stoichiometry, which was carried out by fluorescence spectra (λ_{ex} = 360 nm).

4. SEM and TEM images of $CsPbBr_3$@PTY⊃EYB

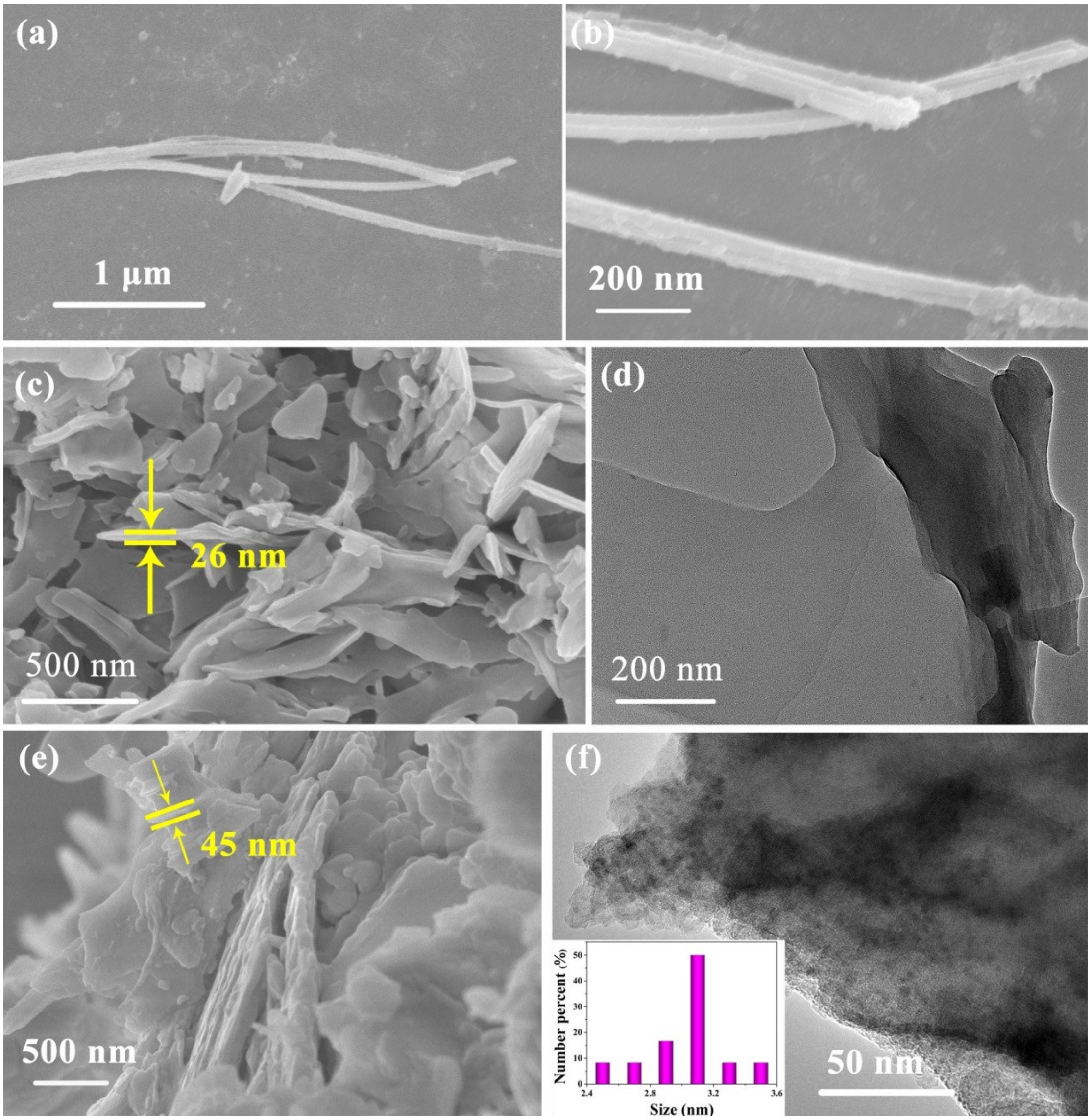


Figure S15. Representative SEM and TEM images showing the morphology of (a) (b) PTY⊃EYB (c) Pb^{2+}@PTY⊃EYB, (e) $CsPbBr_3$@PTY⊃EYB, TEM of (d) Pb^{2+}@PTY⊃EYB, (f) $CsPbBr_3$@PTY⊃EYB.

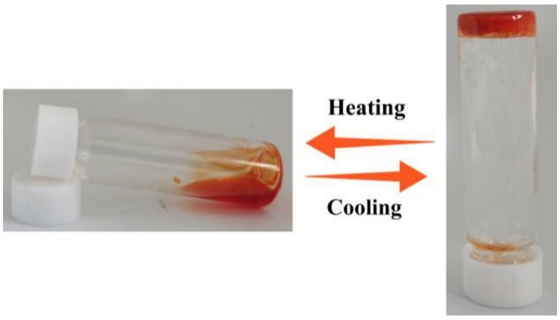


Figure S16. Glue–sol transitions of the supramolecular polymer Pb^{2+}@PTY⊃EYB in isopropanol solution.

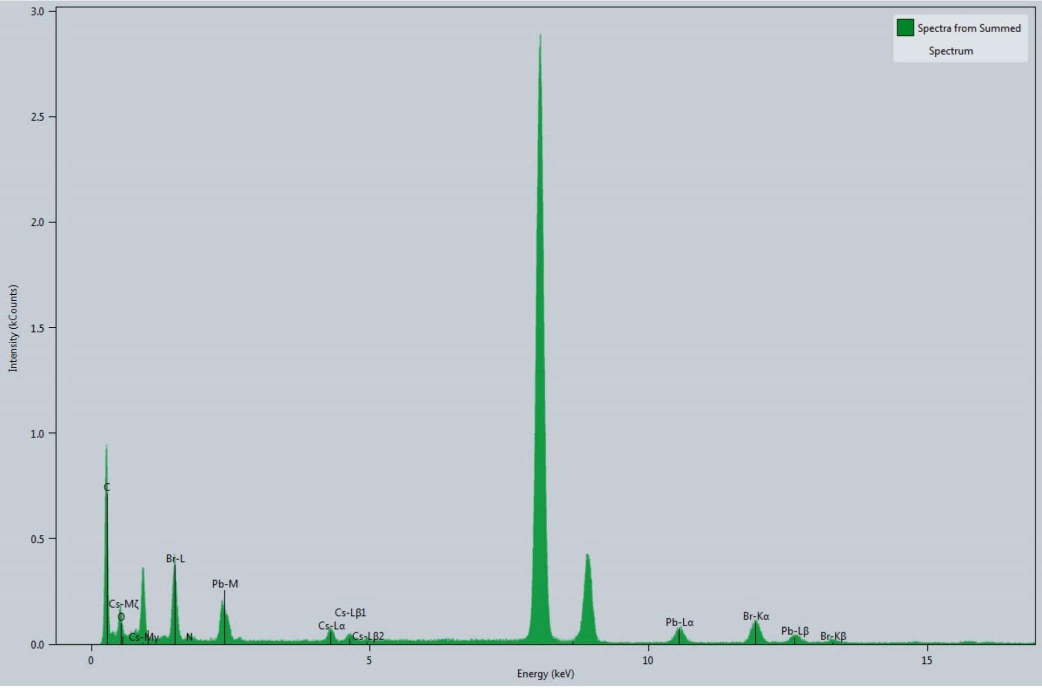


Figure S17. TEM-EDS spectra of $CsPbBr_3$@PTY⊃EYB.

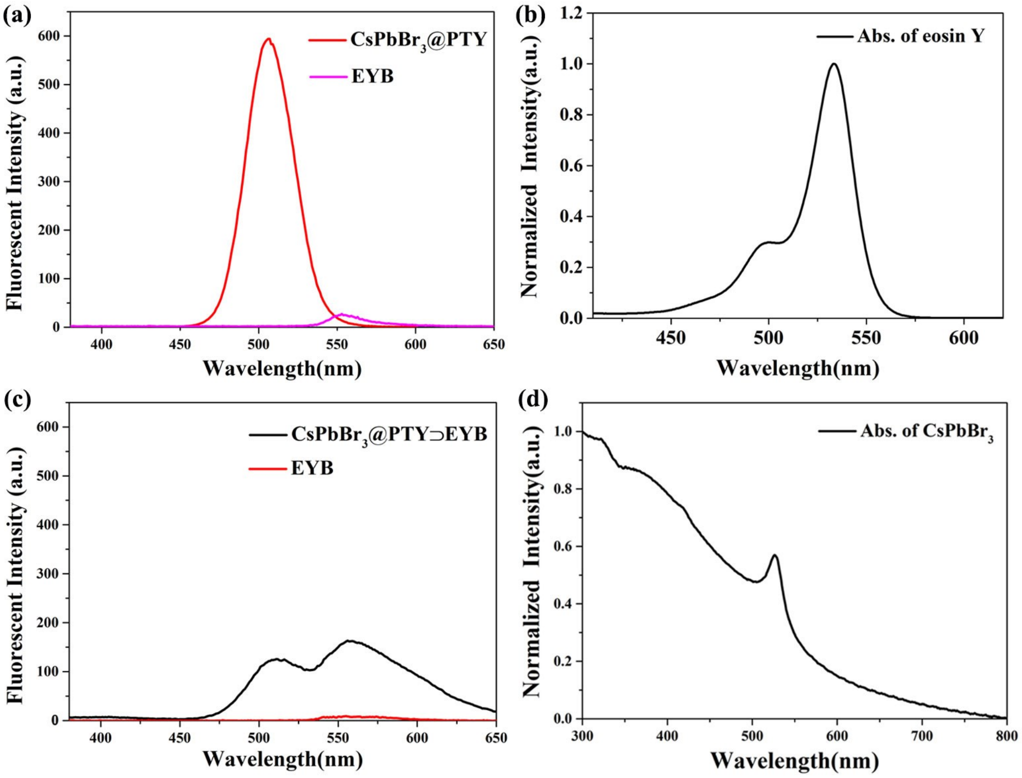


Figure S18. (a) PL emission spectra of CsPbBr$_3$@PTY and EYB upon excitation at 360 nm; (b) UV-vis absorption spectrum of eosin Y. (c) Fluorescence spectra of CsPbBr$_3$@PTY⊃EYB and EYB upon excitation at 360 nm. (d) UV-vis absorption spectrum of CsPbBr$_3$.

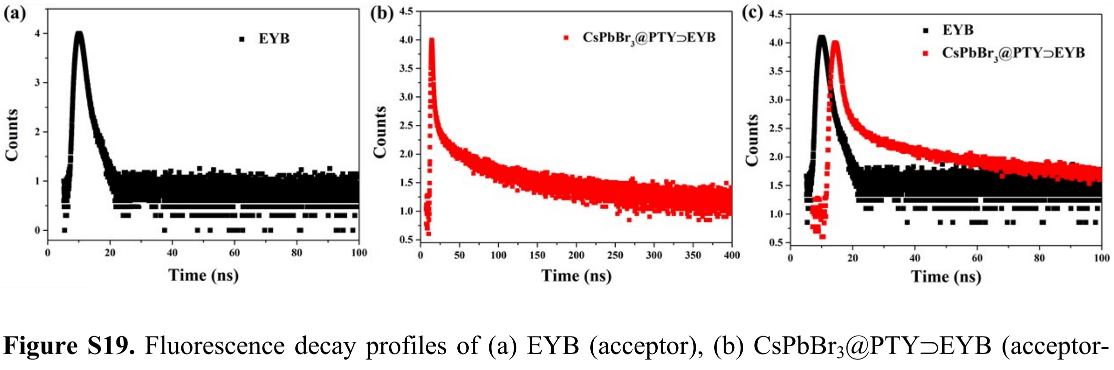


Figure S19. Fluorescence decay profiles of (a) EYB (acceptor), (b) CsPbBr$_3$@PTY⊃EYB (acceptor-donor) and (c) the first 100 ns emission decay of the acceptor and acceptor-donor (λ_{ex}= 515 nm).

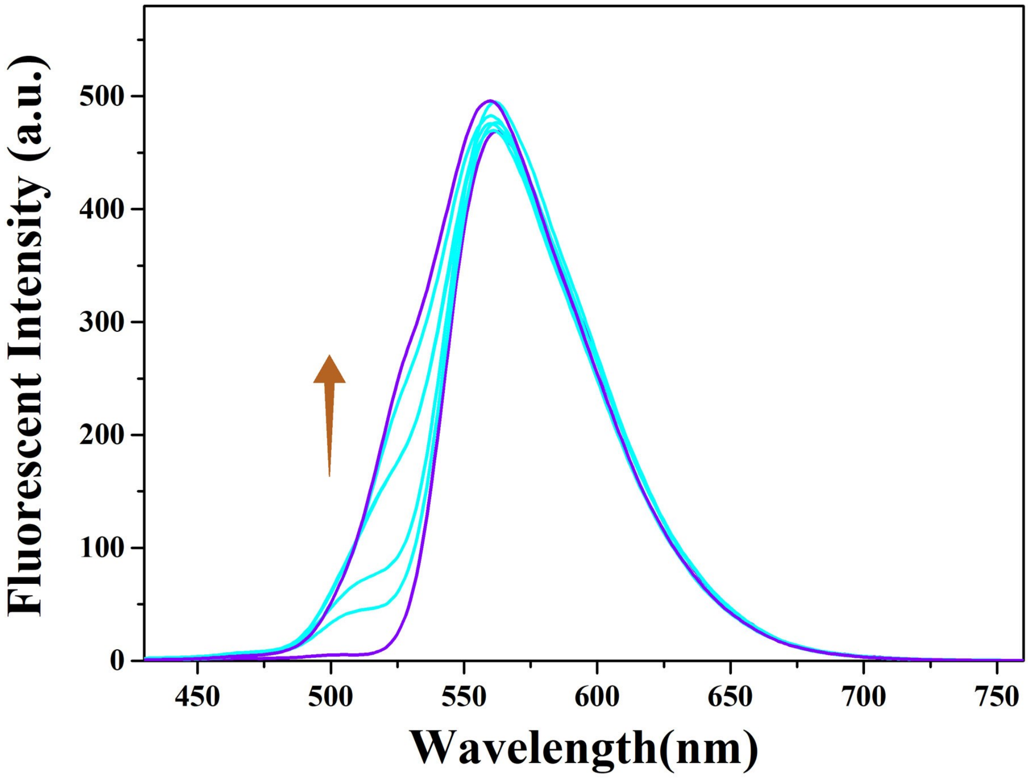


Figure S20. Fluorescence spectra of EYB upon excitation at 515 nm before and after the addition of $CsPbBr_3$@PTY.

Table S1. Multiexponential fit parameters for the decay of photoluminescence lifetime at 360 nm.[2]

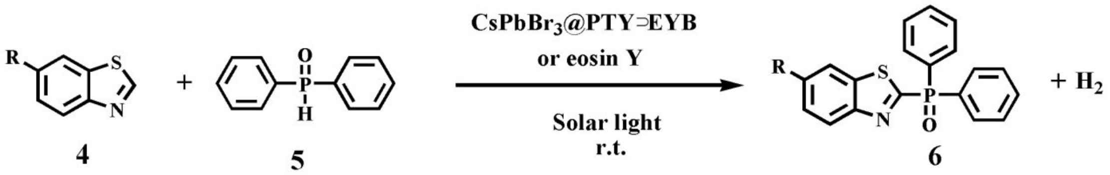
	τ_1(S)	B_1	τ_2(S)	B_2	τ_3(S)	B_3	average lifetime(ns)
$CsPbBr_3$@PTY	12.16	2245.17	62.29	565.29	2.08	6117.36	8.43
$CsPbBr_3$@PTY⊃EYB	9.72	2477.47	39.59	345.17	2.03	6847.97	5.34

Table S2. Multiexponential fit parameters for the decay of photoluminescence lifetime at 515 nm.

	τ_1(S)	B_1	τ_2(S)	B_2	τ_3(S)	B_3	average lifetime(ns)
EYB	0.57	2.87E+07	2.35	876.97	0.57	-2.87E+07	0.57

$CsPbBr_3$@PTY⊃EYB	8.98	396.56	65.23	121.71	9.99	9736.83	2.07

5. Study of the catalytic activities of free eosin Y and the light-harvesting system



Benzothiazole 5 (50 μmol, 1 equiv.), diphenylphosphine oxide 6 (150 μmol, 3 equiv.), eosin Y (5 μmol, 5 mol %) or $CsPbBr_3$@PTY⊃EYB (5 μmol, 5 mol %) were dissolved in $CHCl_3$ (1.5 mL) to a 25 mL Schlenk tube. The mixture was cooled by liquid nitrogen, degassed and purged with nitrogen for six times, and then stirred and irradiated by Xenon lamp (100 mW / cm^2) at room temperature. After that, the organic layer was collected and concentrated after washed with saturated $NaHCO_3$ solution. The product was detected by GC analysis (50 °C 1 min, 15 °C/min, 250 °C) by using standard products as the reference to calculate the conversions and yields of the reaction based on the retention time. The standard product was obtained by column chromatography using petroleum ether/ethyl acetate.

Table S3. Photocatalytic hydrogen evolution reaction

Entry		Catalyst	Light irradiation	Yield [%][a]
1	-H (6a)	$CsPbBr_3$@PTY⊃EYB	12h	83%
2	$-OCH_3$ (6b)	$CsPbBr_3$@PTY⊃EYB	12h	81%
3	$-NH_2$ (6c)	$CsPbBr_3$@PTY⊃EYB	12h	78%
4	$-NO_2$ (6d)	$CsPbBr_3$@PTY⊃EYB	12h	76%

[a] Yield determined by GC using standard products.

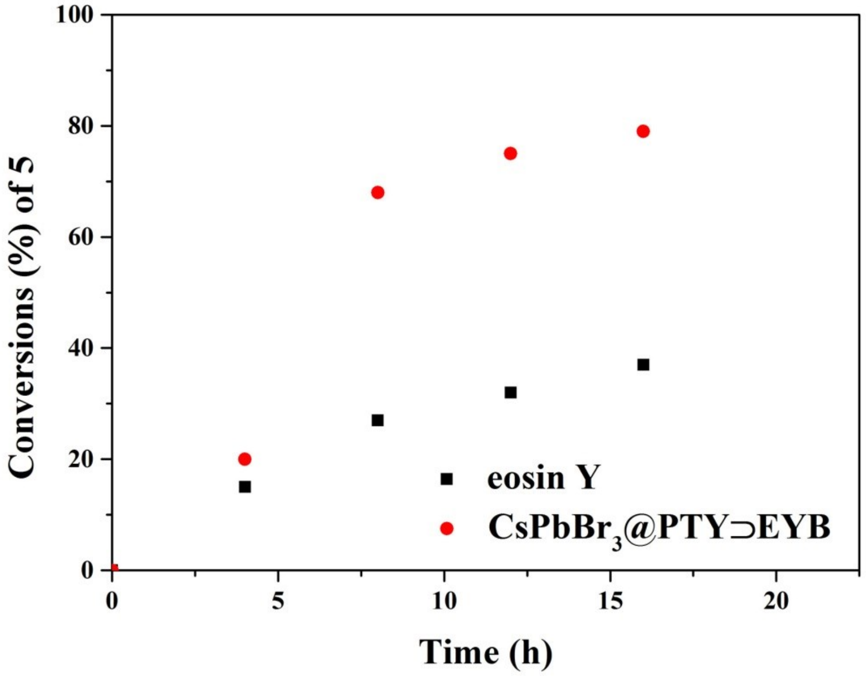


Figure S21. Conversions of 5 versus reaction time.

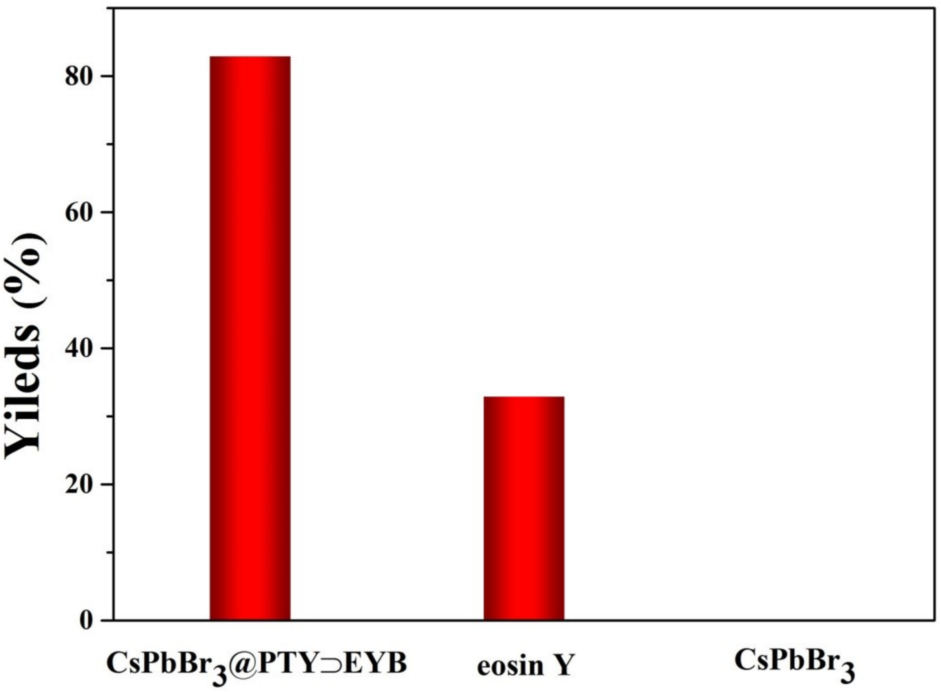


Figure S22. Yields of 6a CsPbBr$_3$@PTY⊃EYB, eosin Y and CsPbBr$_3$ after photochemical reaction 12h.

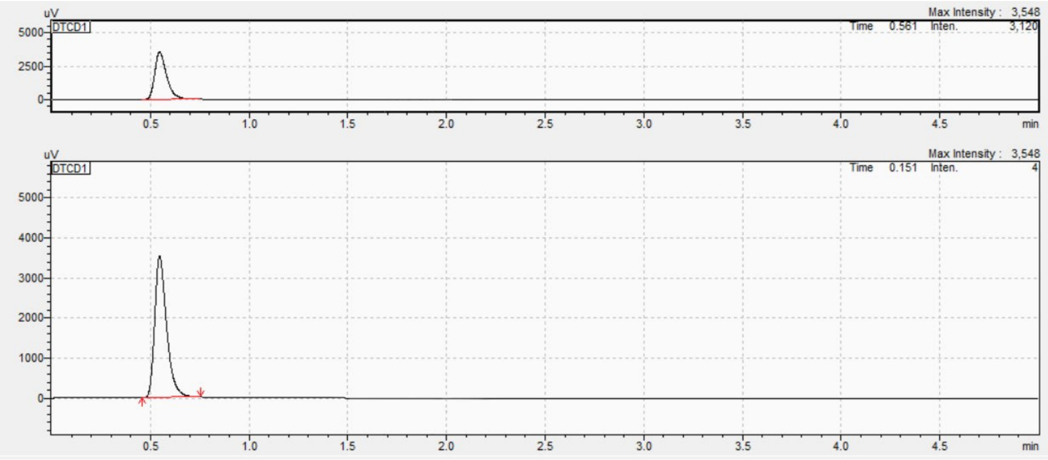


Figure S23. GC spectra of the H_2 using CsPbBr$_3$@PTY⊃EYB as photocatalyst upon irradiation for 24h.

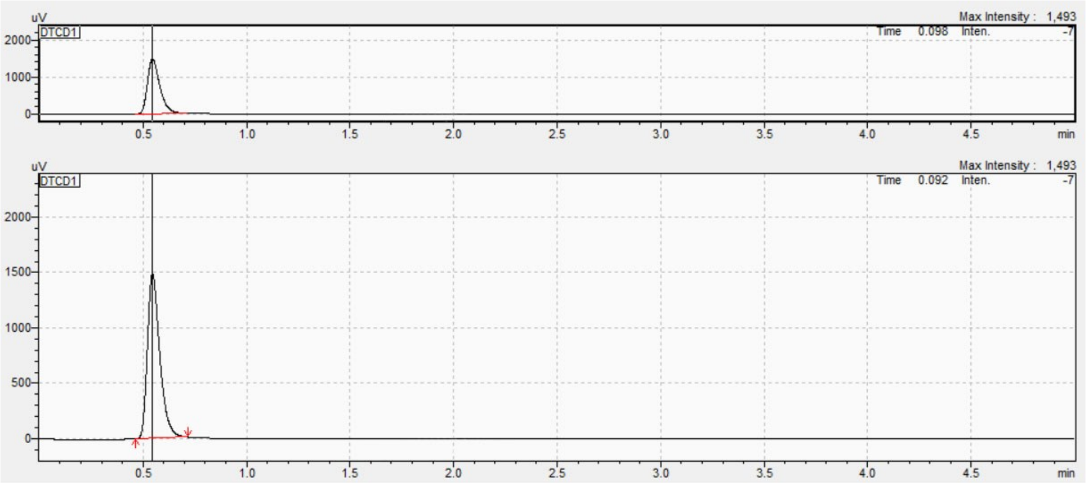


Figure S24. GC spectra of the H_2 using eosin Y as photocatalyst upon irradiation for 24h.

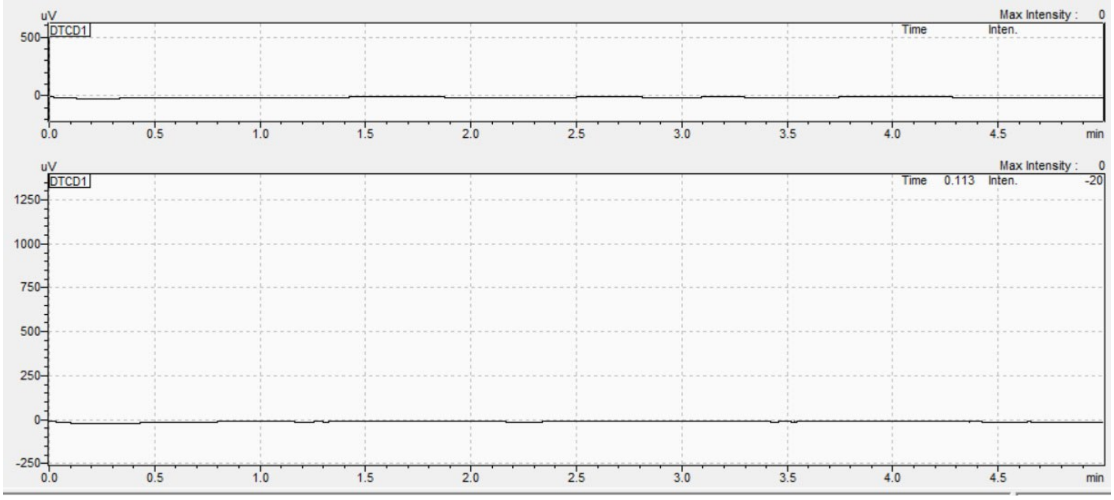


Figure S25. GC spectra of the H_2 using $CsPbBr_3$ as photocatalyst upon irradiation for 24h.

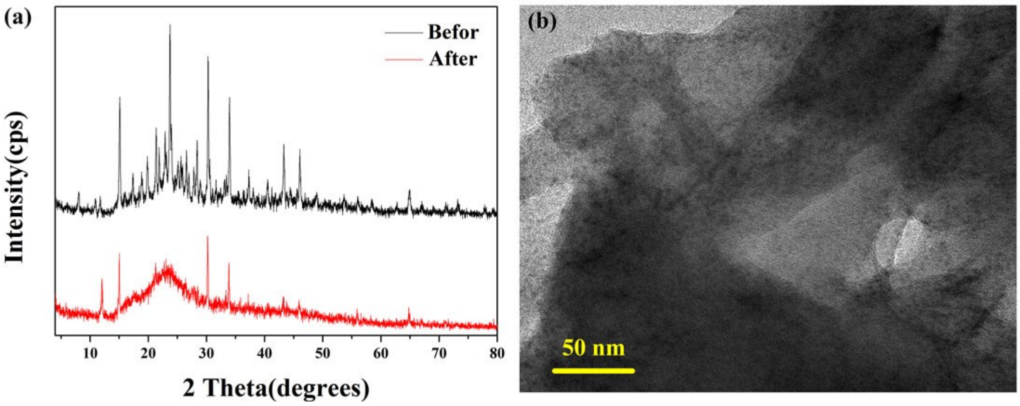
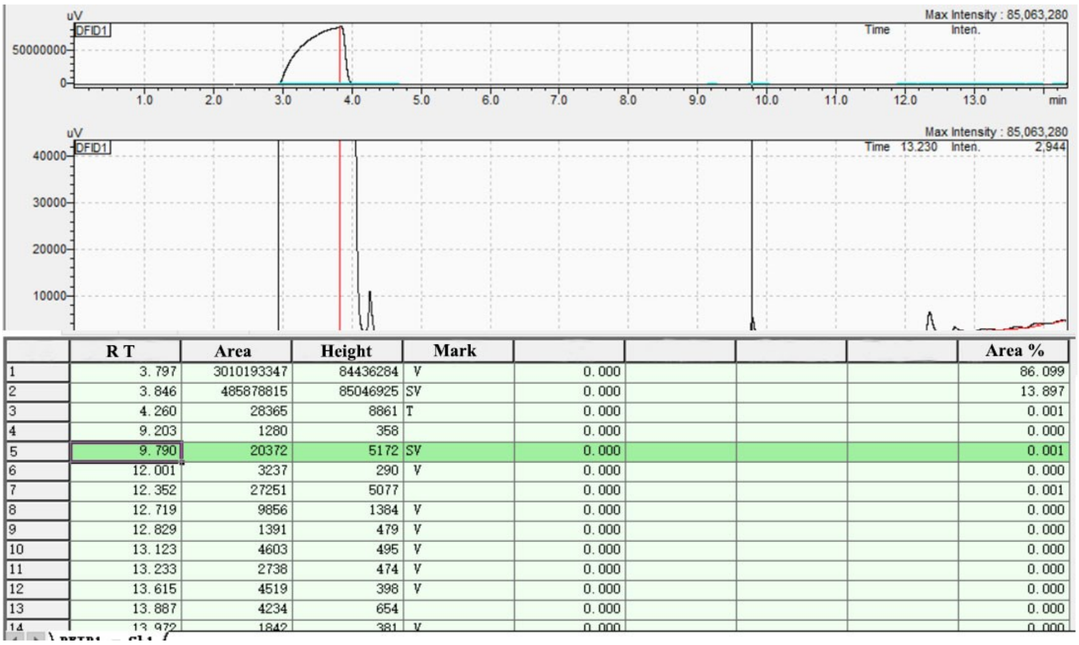


Figure S26. (a) XRD and (b) TEM images of $CsPbBr_3$@PTY⊃EYB after Photochemical reaction 12h.



	R T	Area	Height	Mark					Area %
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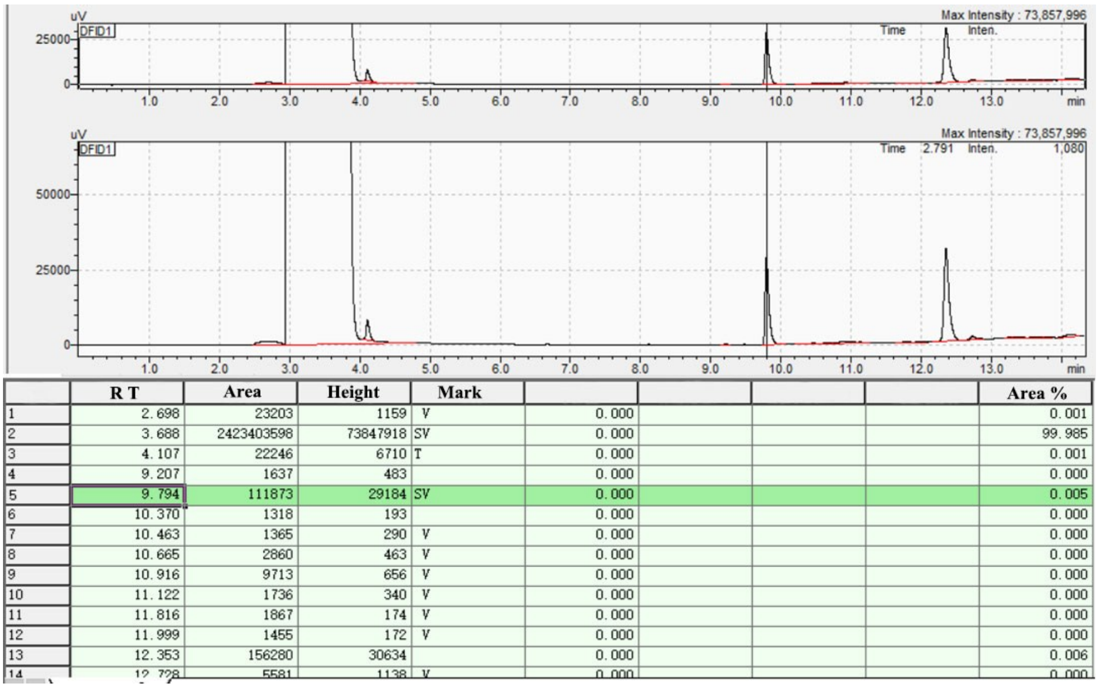
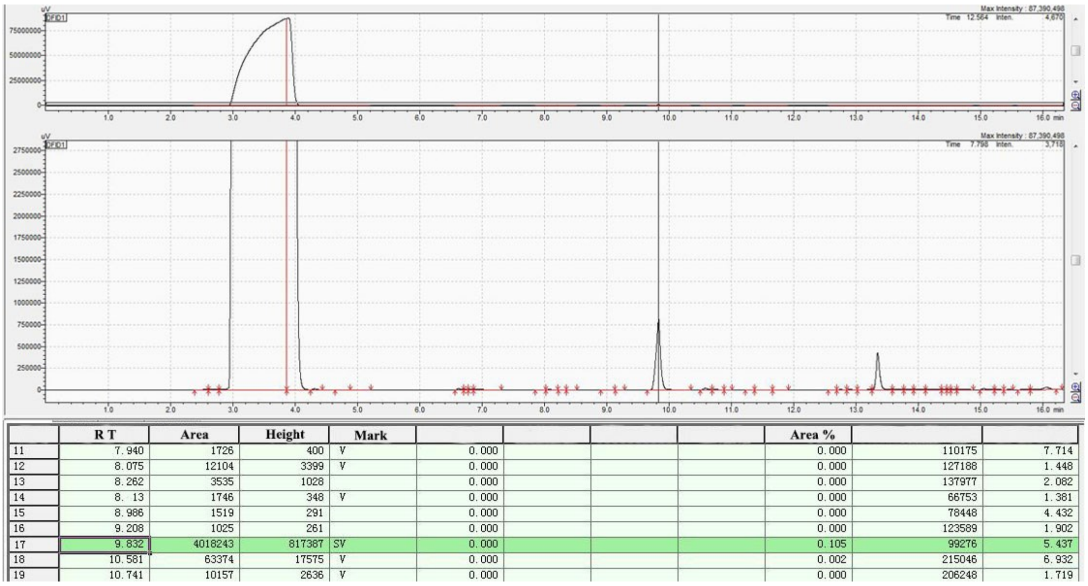
2	3. 846	485878815	85046925	SV	0. 000				13. 897
3	4. 260	28365	8861	T	0. 000				0. 001
4	9. 203	1280	358		0. 000				0. 000
5	9. 790	20372	5172	SV	0. 000				0. 001
6	12. 001	3237	290	V	0. 000				0. 000
7	12. 352	27251	5077		0. 000				0. 001
8	12. 719	9856	1384	V	0. 000				0. 000
9	12. 829	1391	479	V	0. 000				0. 000
10	13. 123	4603	495	V	0. 000				0. 000
11	13. 233	2738	474	V	0. 000				0. 000
12	13. 615	4519	398	V	0. 000				0. 000
13	13. 887	4234	654		0. 000				0. 000
14	13. 972	1842	381	V	0. 000				0. 000

Figure S27. GC spectra of the 6a using CsPbBr$_3$@PTY⊃EYB as photocatalyst upon irradiation for 4h.



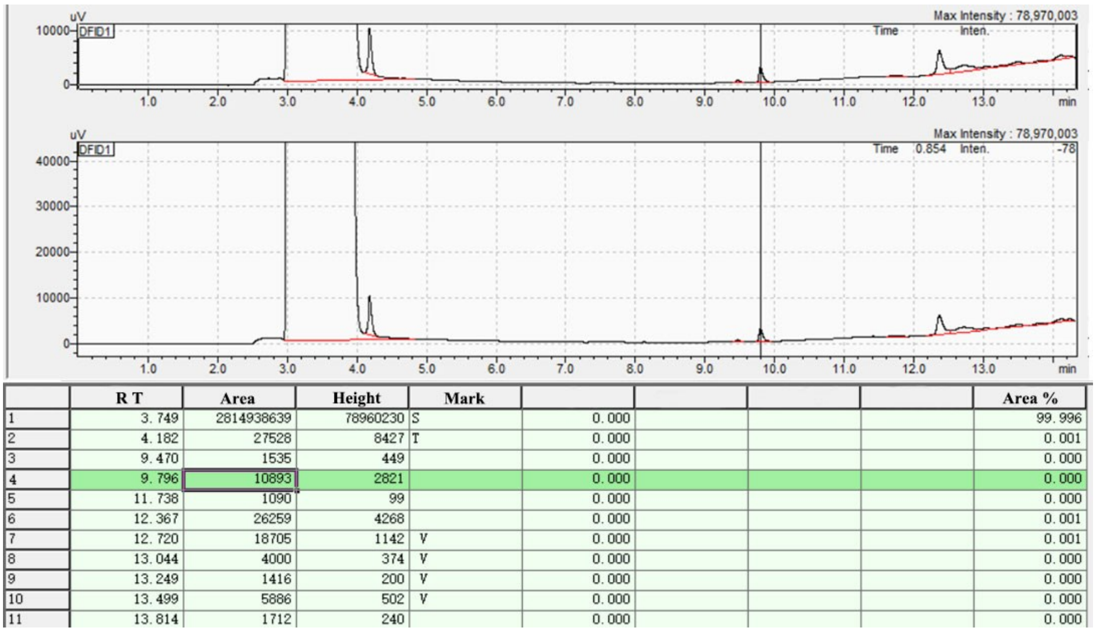
	R T	Area	Height	Mark					Area %
1	2. 698	23203	1159	V	0. 000				0. 001
2	3. 688	2423403598	73847918	SV	0. 000				99. 985
3	4. 107	22246	6710	T	0. 000				0. 001
4	9. 207	1637	483		0. 000				0. 000
5	9. 794	111873	29184	SV	0. 000				0. 005
6	10. 370	1318	193		0. 000				0. 000
7	10. 463	1365	290	V	0. 000				0. 000
8	10. 665	2860	463	V	0. 000				0. 000
9	10. 916	9713	656	V	0. 000				0. 000
10	11. 122	1736	340	V	0. 000				0. 000
11	11. 816	1867	174	V	0. 000				0. 000
12	11. 999	1455	172	V	0. 000				0. 000
13	12. 353	156280	30634		0. 000				0. 006
14	12. 728	5581	1138	V	0. 000				0. 000

Figure S28. GC spectra of the 6a using CsPbBr$_3$@PTY⊃EYB as photocatalyst upon irradiation for 8h.



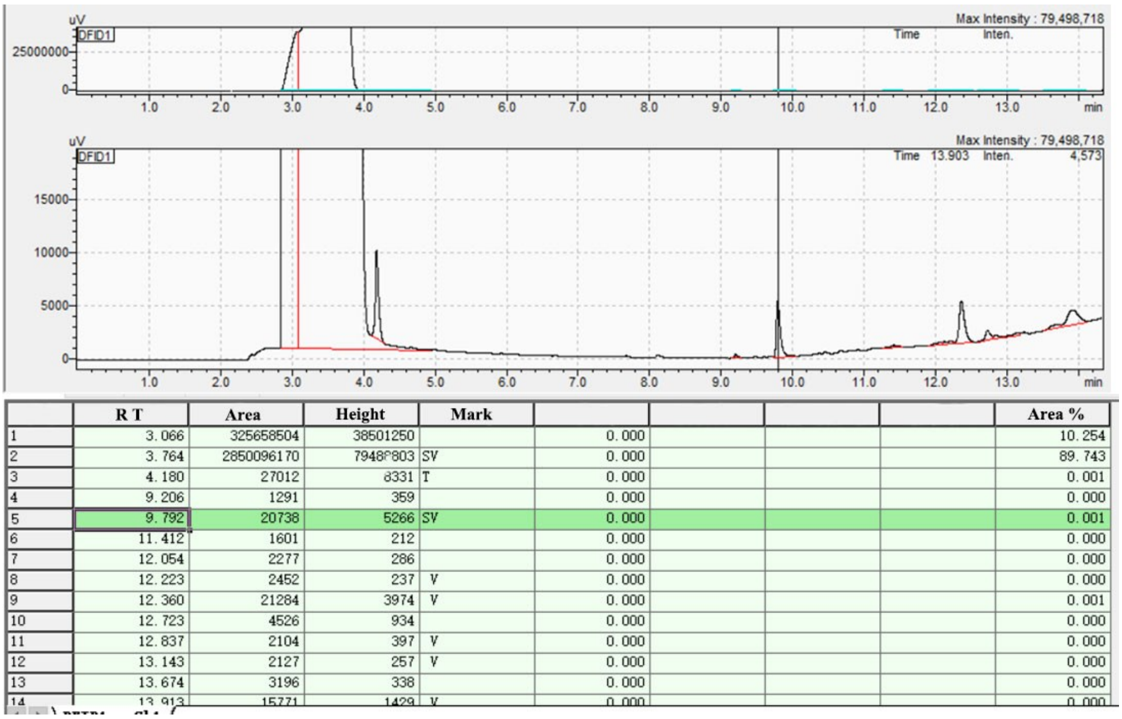
	R T	Area	Height	Mark					Area %		
11	7.940	1726	400	V	0.000				0.000	110175	7.714
12	8.075	12104	3399	V	0.000				0.000	127188	1.448
13	8.262	3535	1028		0.000				0.000	137977	2.082
14	8. 13	1746	348	V	0.000				0.000	66753	1.381
15	8.986	1519	291		0.000				0.000	78448	4.432
16	9.208	1025	261		0.000				0.000	123589	1.902
17	9.832	4018243	817387	SV	0.000				0.105	99276	5.437
18	10.581	63374	17575	V	0.000				0.002	215046	6.932
19	10.741	10157	2636	V	0.000				0.000	206248	1.719

Figure S29. GC spectra of the 6a using $CsPbBr_3$@PTY⊃EYB as photocatalyst upon irradiation for 12h.



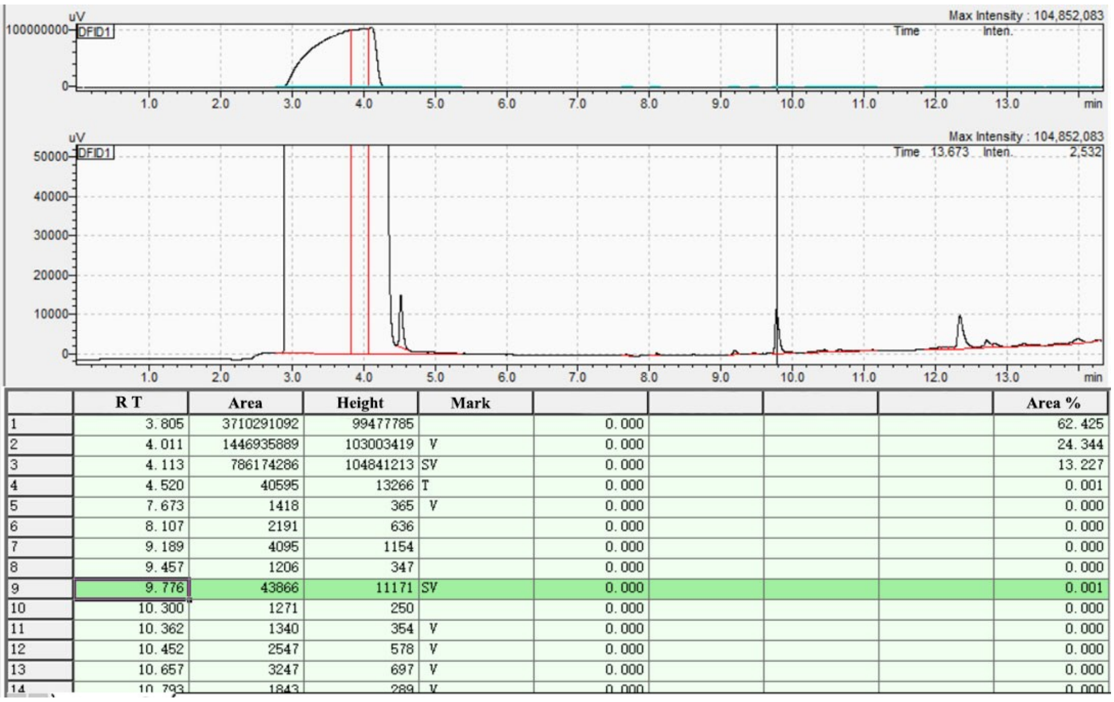
	R T	Area	Height	Mark					Area %
1	3.749	2814938639	78960230	S	0.000				99.996
2	4.182	27528	8427	T	0.000				0.001
3	9.470	1535	449		0.000				0.000
4	9.796	10893	2821		0.000				0.000
5	11.738	1090	99		0.000				0.000
6	12.367	26259	4268		0.000				0.001
7	12.720	18705	1142	V	0.000				0.001
8	13.044	4000	374	V	0.000				0.000
9	13.249	1416	200	V	0.000				0.000
10	13.499	5886	502	V	0.000				0.000
11	13.814	1712	240		0.000				0.000

Figure S30. GC spectra of the 6a using eosin Y as photocatalyst upon irradiation for 4h.



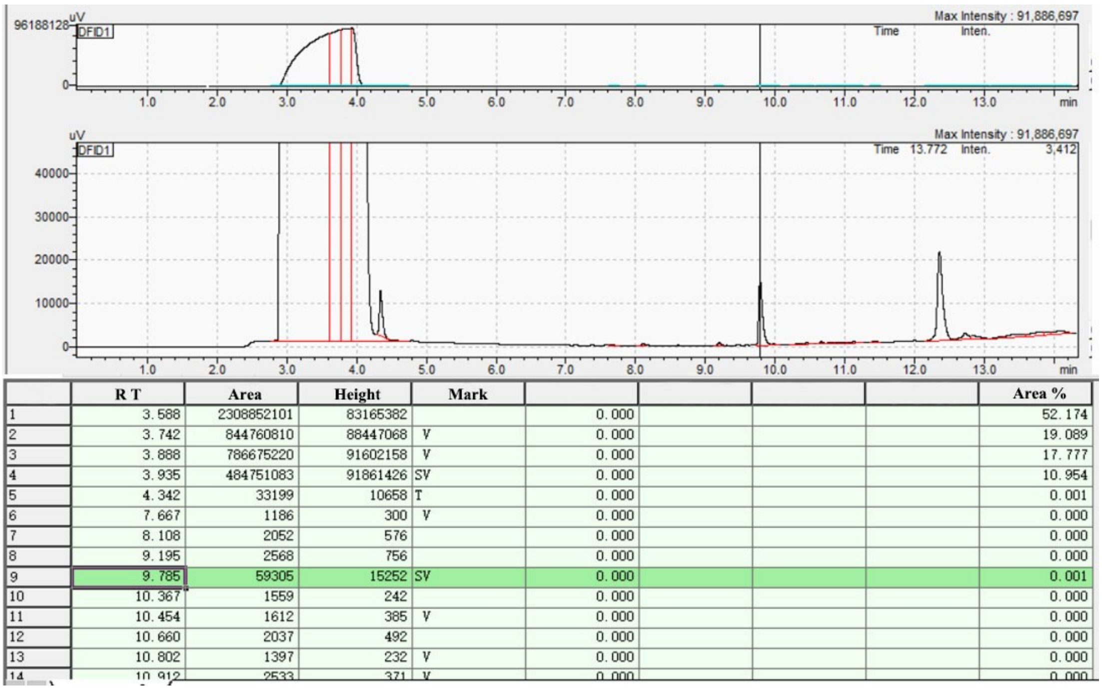
	R T	Area	Height	Mark					Area %
1	3.066	325658504	38501250		0.000				10.254
2	3.764	2850096170	79489803	SV	0.000				89.743
3	4.180	27012	8331	T	0.000				0.001
4	9.206	1291	359		0.000				0.000
5	9.792	20738	5266	SV	0.000				0.001
6	11.412	1601	212		0.000				0.000
7	12.054	2277	286		0.000				0.000
8	12.223	2452	237	V	0.000				0.000
9	12.360	21284	3974	V	0.000				0.001
10	12.723	4526	934		0.000				0.000
11	12.837	2104	397	V	0.000				0.000
12	13.143	2127	257	V	0.000				0.000
13	13.674	3196	338		0.000				0.000
14	13.913	15771	1429	V	0.000				0.000

Figure S31. GC spectra of the 6a using eosin Y as photocatalyst upon irradiation for 8h.



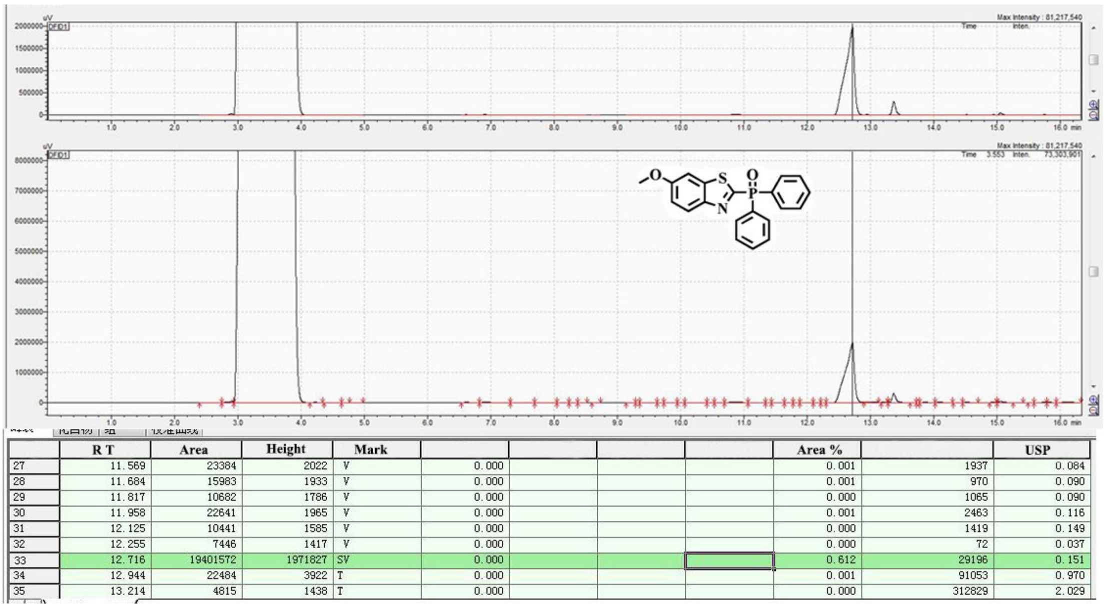
	R T	Area	Height	Mark					Area %
1	3.805	3710291092	99477785		0.000				62.425
2	4.011	1446935889	103003419	V	0.000				24.344
3	4.113	786174286	104841213	SV	0.000				13.227
4	4.520	40595	13266	T	0.000				0.001
5	7.673	1418	365	V	0.000				0.000
6	8.107	2191	636		0.000				0.000
7	9.189	4095	1154		0.000				0.000
8	9.457	1206	347		0.000				0.000
9	9.776	43866	11171	SV	0.000				0.001
10	10.300	1271	250		0.000				0.000
11	10.362	1340	354	V	0.000				0.000
12	10.452	2547	578	V	0.000				0.000
13	10.657	3247	697	V	0.000				0.000
14	10.793	1843	289	V	0.000				0.000

Figure S32. GC spectra of the 6a using eosin Y as photocatalyst upon irradiation for 12h.



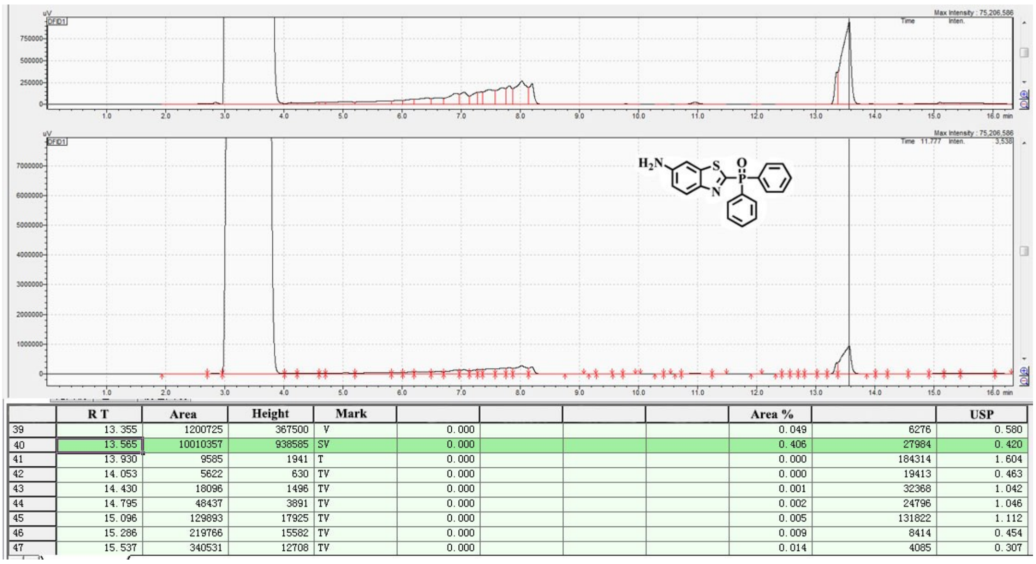
	R T	Area	Height	Mark					Area %
1	3.588	2308852101	83165382		0.000				52.174
2	3.742	844760810	88447068	V	0.000				19.089
3	3.888	786675220	91602158	V	0.000				17.777
4	3.935	484751083	91861426	SV	0.000				10.954
5	4.342	33199	10658	T	0.000				0.001
6	7.667	1186	300	V	0.000				0.000
7	8.108	2052	576		0.000				0.000
8	9.195	2568	756		0.000				0.000
9	9.785	59305	15252	SV	0.000				0.001
10	10.367	1559	242		0.000				0.000
11	10.454	1612	385	V	0.000				0.000
12	10.660	2037	492		0.000				0.000
13	10.802	1397	232	V	0.000				0.000
14	10.912	2533	371	V	0.000				0.000

Figure S33. GC spectra of the 6a using eosin Y as photocatalyst upon irradiation for 16h.



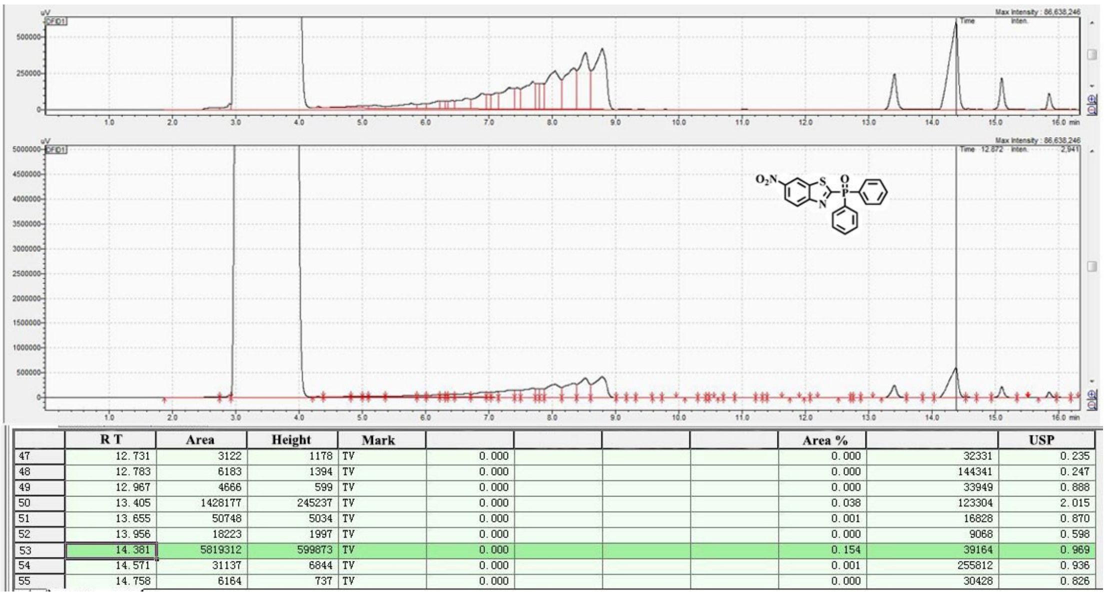
	R T	Area	Height	Mark					Area %		USP
27	11.569	23384	2022	V	0.000				0.001	1937	0.084
28	11.684	15983	1933	V	0.000				0.001	970	0.090
29	11.817	10682	1786	V	0.000				0.000	1065	0.090
30	11.958	22641	1965	V	0.000				0.001	2463	0.116
31	12.125	10441	1585	V	0.000				0.000	1419	0.149
32	12.255	7446	1417	V	0.000				0.000	72	0.037
33	12.716	19401572	1971827	SV	0.000				0.612	29196	0.151
34	12.944	22484	3922	T	0.000				0.001	91053	0.970
35	13.214	4815	1438	T	0.000				0.000	312829	2.029

Figure S34 GC spectra of the 6b using $CsPbBr_3$@PTY⊃EYB as photocatalyst upon irradiation for 12h.



	R T	Area	Height	Mark					Area %		USP
39	13. 355	1200725	367500	V	0. 000				0. 049	6276	0. 580
40	13. 565	10010357	938585	SV	0. 000				0. 406	27984	0. 420
41	13. 930	9585	1941	T	0. 000				0. 000	184314	1. 604
42	14. 053	5622	630	TV	0. 000				0. 000	19413	0. 463
43	14. 430	18096	1496	TV	0. 000				0. 001	32368	1. 042
44	14. 795	48437	3891	TV	0. 000				0. 002	24796	1. 046
45	15. 096	129893	17925	TV	0. 000				0. 005	131822	1. 112
46	15. 286	219766	15582	TV	0. 000				0. 009	8414	0. 454
47	15. 537	340531	12708	TV	0. 000				0. 014	4085	0. 307

Figure S35 GC spectra of the 6c using $CsPbBr_3$@PTY⊃EYB as photocatalyst upon irradiation for 12h.



	R T	Area	Height	Mark					Area %		USP
47	12. 731	3122	1178	TV	0. 000				0. 000	32331	0. 235
48	12. 783	6183	1394	TV	0. 000				0. 000	144341	0. 247
49	12. 967	4666	599	TV	0. 000				0. 000	33949	0. 888
50	13. 405	1428177	245237	TV	0. 000				0. 038	123304	2. 015
51	13. 655	50748	5034	TV	0. 000				0. 001	16828	0. 870
52	13. 956	18223	1997	TV	0. 000				0. 000	9068	0. 598
53	14. 381	5819312	599873	TV	0. 000				0. 154	39164	0. 969
54	14. 571	31137	6844	TV	0. 000				0. 001	255812	0. 936
55	14. 758	6164	737	TV	0. 000				0. 000	30428	0. 826

Figure S36 GC spectra of the 6d using $CsPbBr_3$@PTY⊃EYB as photocatalyst upon irradiation for 12h.

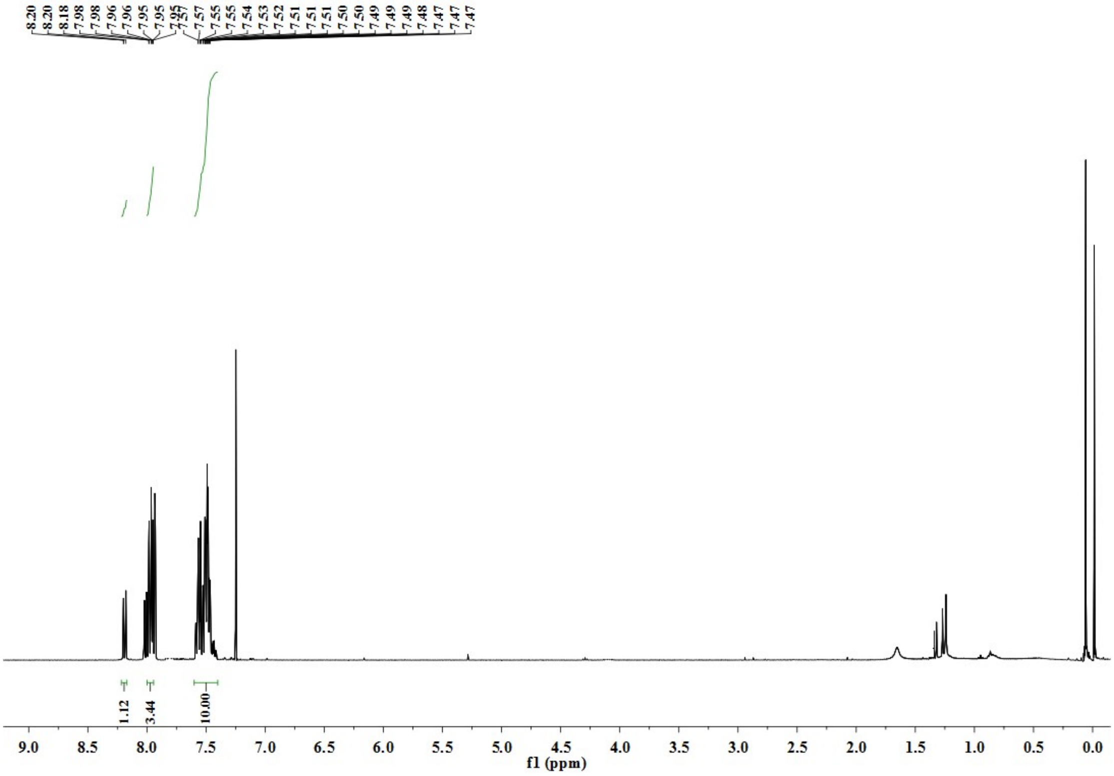


Figure S37 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6a.

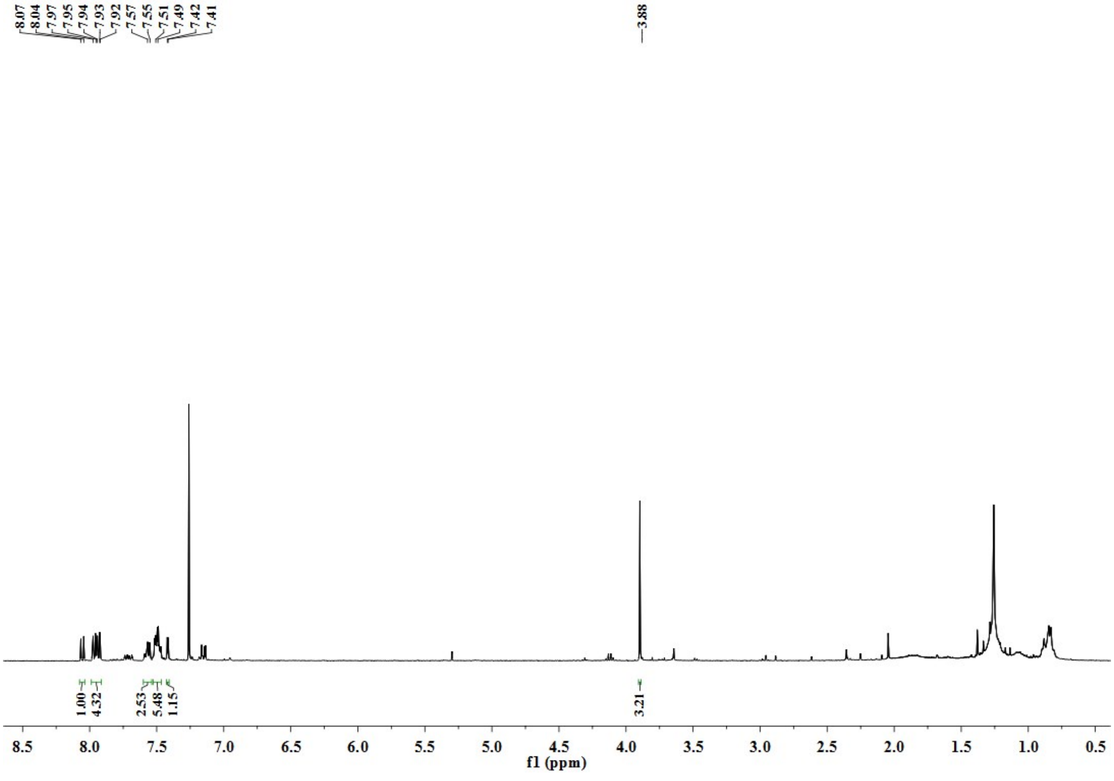


Figure S38 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6b.

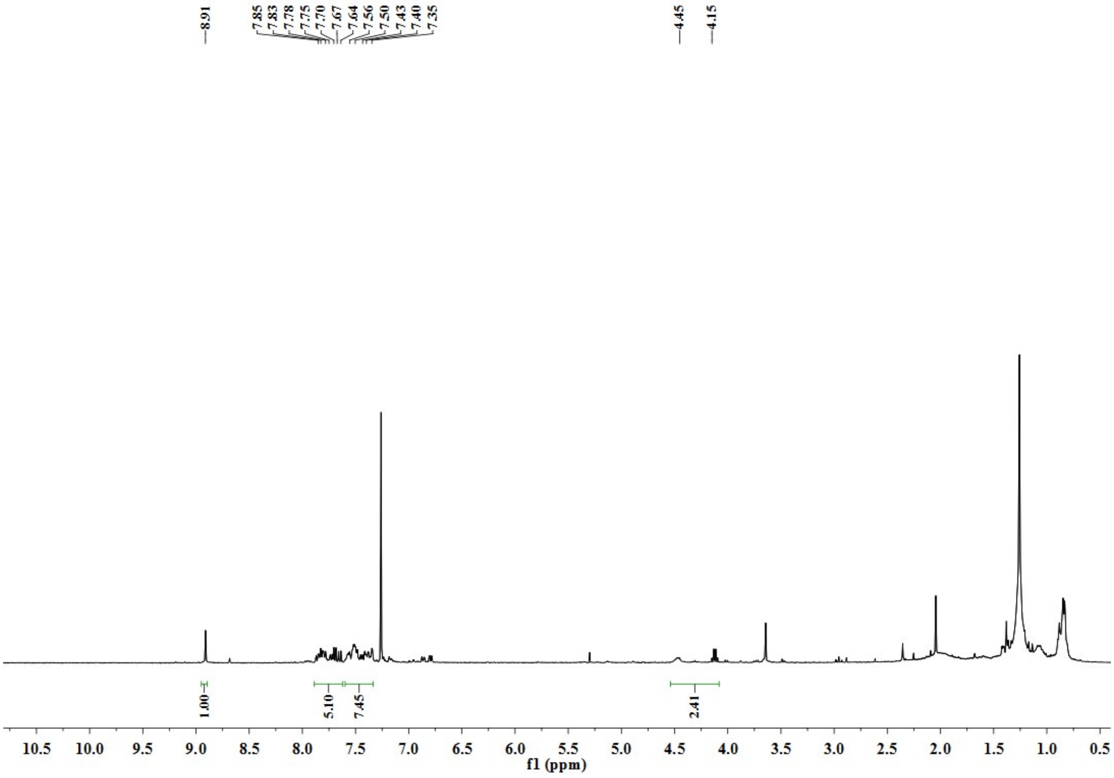


Figure S39 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6c.

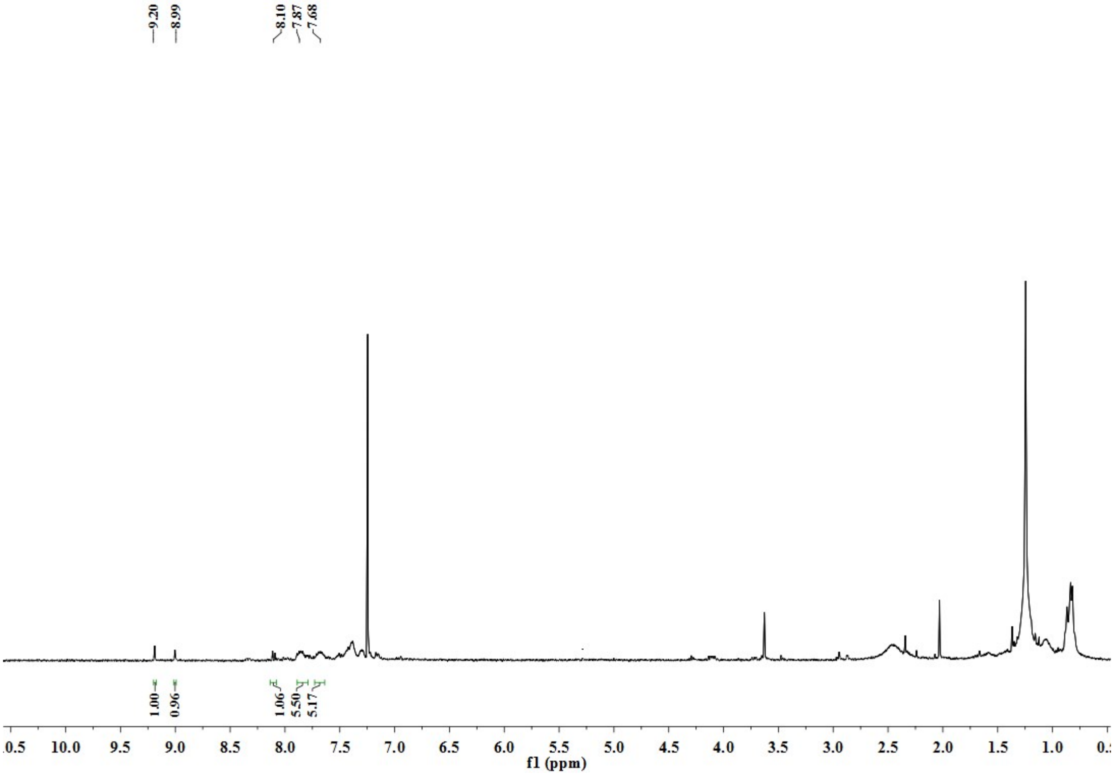


Figure S40 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6c.

References

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