Supporting Information for:

Deep Eutectic-Solvothermal Synthesis of Titanium-Oxo Clusters Protected by π-Conjugate Chromophores

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1 Materials and methods

All the reagents and solvents employed are commercially available and are used as received without further purification.

1.1 Analytical

Elemental analyses are performed using a Perkin-Elmer 240C elemental analyzer. X-ray powder diffraction (PXRD) analysis is performed on a Mini Flex-II diffractometer with Mo K_α radiation (λ = 1.54056 Å) in the 2θ range of 3–50 ° with a scanning rate of 1 ° min^{-1}. IR spectra (KBr pellets) were recorded on an ABB Bomem MB102 spectrometer over a range 400-4000 cm^{-1}. Thermal stability studies are carried out using a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 ℃ min^{-1} under a N_2 gas flow. Optical absorbance of solid state materials is measured by a solid state UV−Vis diffuse reflectance measurement method at room temperature with a Perkin-Elmer Lambda 950 UV/Vis spectrophotometer. The absorption data are calculated from the Kubelka-Munk function, (F(R) = (1-R)^2/2R),[1] where R representing the reflectance, K the absorption, and S the scattering. SEM images were recorded by a JEOL JSM6700F field-emission scanning electron microscope. Optical absorbance of liquid samples is measured by a UV-Vis diffuse reflectance measurement method at room temperature with a Perkin-Elmer Lambda 950 UV/VIS spectrophotometer. Particle size analysis is measured using Dynamic Light Scattering (DLS) technique with a NanoBrook Zetaplus Zeta Potential Analyzer and analyzed in ZetaPALS Particle Sizing Software version 5.32.

1.2 X-ray diffraction

Suitable single crystals are carefully selected under an optical microscope and glued to thin glass fibres. Crystals are found to be air stable at room temperature. Thereafter, single crystal X-ray diffraction analyses are performed on Super Nova diffractometer at room temperature. The structures are solved by direct methods and refined on F^2 by full matrix least-squares using new SHELXL program.[2,3] All of the nonhydrogen atoms are located from Fourier maps and are re-fined anisotropically. The crystallographic data is listed in *Table S1*. CCDC numbers 1542114-1542117 (**PTC-61** to **PTC-64)** contains the supplementary crystallographic data for this paper. Supplementary single crystal XRD data, including structure factors, is available free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

1.3 Photocatalytic hydrogen evolution experiments

The sample for photoinduced hydrogen production was located in a closed gas circulation system (Perfect Light Company Labsolar-III (AG). The 300W Xe lamp is used as the light source. The gas in

the system is analyzed by online-GC to determine the amount of hydrogen generated at each hour. Typically, 50mg of sample is dispersed in 50mL of H_2O with 10mL of triethanol amine (TEOA) as sacrificial agent, and then 33μL 1.0 wt% $H_2PtCl_6.xH_2O$ is added as co-catalyst. Hydrogen gas evolved after each hour is determined for a period of 6 hours. Cycling experiments for **PTC-62** and **PTC-64** are repeated with the same reaction conditions for three cycles for a period of four hours. After each cycle of four hours, 1 mL of TEOA is added to the reaction mixture prior to evacuation. Aging studies are also done for **PTC-62** and **PTC-64** with the same experimental conditions after storing the reaction solution undisturbed for more than one week.

1.4 Synthesis

1.4.1 Synthesis of DES. Deep eutectic solvent used for the synthesis of crystals in this system is prepared by mixing solids of choline chloride (13.9 g, 0.1 M) and phenol (18.8 g, 0.2 M) thoroughly for 30 minutes at room temperature to form colorless solvent and used without any further treatment.

1.4.2 Synthesis of PTC-61. A mixture of H_2O_3P-Phen (0.207 g, 2.0 mmol), and $Ti(O^iPr)_4$ (1mL) are dissolved in 2 mL of *DES* in a 20 mL scintillation vial, heated at 100 ℃ for 120 h, and then cooled to room temperature. Yellowish-red colored crystals of **PTC-61** are obtained, washed with excess amount of 2-propanol and dried in air (76% yield, based on H_2O_3P-Phen ligand). Elemental analysis for C_{78} H_{92} O_{26} P_4 Ti_6, Calcd (%): C, 50.42; H, 4.99; Found: C, 51.11; H, 4.12.

1.4.3 Synthesis of PTC-62. A mixture of H_2O_3P-Phen (0.107 g, 0.67 mmol), 1,10-phn (0.117 g, 0.64 mmol), and $Ti(O^iPr)_4$ (1mL) are dissolved in 2 mL of *DES* in a 20 mL scintillation vial, heated at 120 ℃ for 120 h, and then cooled to room temperature. Yellowish-red colored crystals of **PTC-62** are obtained, washed with excess amount of 2-propanol and dried in air (68% yield, based on H_2O_3P-Phen ligand). Elemental analysis for C_{150} H_{112} Cl_2 N_{12} O_{24} P_2 Ti_6, Calcd (%): C, 62.40; H, 3.91; N, 5.82. Found: C, 62.96; H, 4.21; N, 5.98.

1.4.4 Synthesis of PTC-63. A mixture of H_2O_3P-Phen (0.158 g, 1.0 mmol), 2,2'-bpy (0.631 g, 4.04 mmol), and $Ti(O^iPr)_4$ (1mL) are dissolved in 2 mL of *DES* in a 20 mL scintillation vial, heated at 100 ℃ for 120 h, and then cooled to room temperature. Yellowish-red colored crystals of **PTC-63** are obtained, washed with excess amount of 2-propanol and dried in air (65% yield, based on H_2O_3P-Phen ligand). Elemental analysis for $C_{132}H_{112}Cl_2$ $N_{12}O_{22}P_2Ti_6$, Calcd (%): C, 60.08; H, 4.28; N, 6.37. Found: C, 61.17; H, 4.12; N, 6.81.

1.4.5 Synthesis of PTC-64. A mixture of 1,10-phn (0.360 g, 2.0 mmol), and $Ti(OBut)_4$ (1mL) are dissolved in 2 mL of *DES* in a 20 mL scintillation vial, heated at 100 ℃ for 120 h, and then cooled to room temperature. Red colored crystals of **PTC-64** are obtained, washed with excess amount of 2-propanol and dried in air (78% yield, based on 1,10-phn ligand). Elemental analysis for $C_{323}H_{186}Cl_4N_{28}O_{74}Ti_{28}$, Calcd (%): C, 54.42; H, 2.63; N, 5.50. Found: C, 54.91; H, 2.12; N, 5.21.

2 Supporting data

2.1 Table S1. Crystal data and structure refinements summary for **PTC-61** to **PTC-64**.

Complex	**PTC-61**	**PTC-62**	**PTC-63**	**PTC-64**
CCDC No	1542114	1542115	1542116	1542117
formula	$C_{78}H_{92}O_{26}P_4Ti_6$	$C_{150}H_{112}Cl_2N_{12}O_{24}P_2Ti_6$	$C_{132}H_{112}Cl_2N_{12}O_{22}P_2Ti_6$	$C_{323}H_{186}Cl_4N_{28}O_{74}Ti_{28}$
formula weight	1856.17	2884.36	2636.37	7121.58
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	C2/c	P–1	P–1	C2/c
a [Å]	25.8073	14.8885	14.6424	43.438
b [Å]	15.8321	15.2403	15.0149	19.8705
c [Å]	21.8036	15.9842	15.2824	40.975
α [^{o}]	90	93.508	79.639	90
β [^{o}]	97.922	101.316	84.629	112.402
γ [^{o}]	90	103.043	79.585	90
V [Å^3]	8823.6	3443.46	3244.2	32968
Z	4	1	1	4
T [K]	293	293	293	293
ρ_c[gcm^{-3}]	1.390	1.393	1.350	1.447
μ [mm^{-1}]	5.707	4.024	4.203	6.443
reflns coll.	12441	23460	23497	47617
unique reflns	6984	12845	12873	25188

GOF	0.999	1.499	1.320	0.966
$R_1[I>2\sigma(I)]$[a]	0.1183	0.1029	0.1028	0.0797
$\omega R_2[I>2\sigma(I)]$[b]	0.3534	0.3403	0.3210	0.2829

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $\omega R_2 = \{\Sigma[\omega(F_o^2-F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$.

2.2 Powder X-ray Diffraction Studies

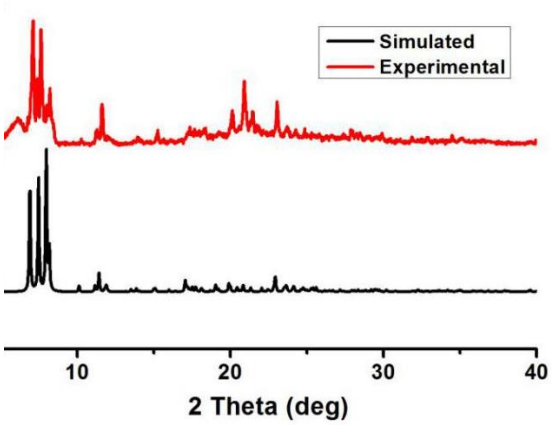


Figure S1. For **PTC-61**: Comparison of PXRD patterns of the simulated pattern from single crystal structure determination and as-synthesized product.

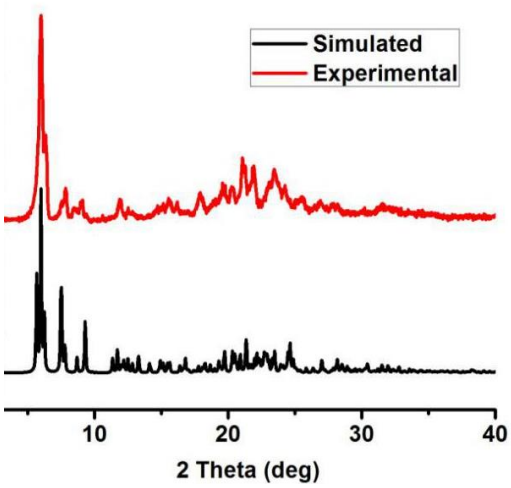


Figure S2. For **PTC-62**: Comparison of PXRD patterns of the simulated pattern from single crystal structure determination and as-synthesized product.

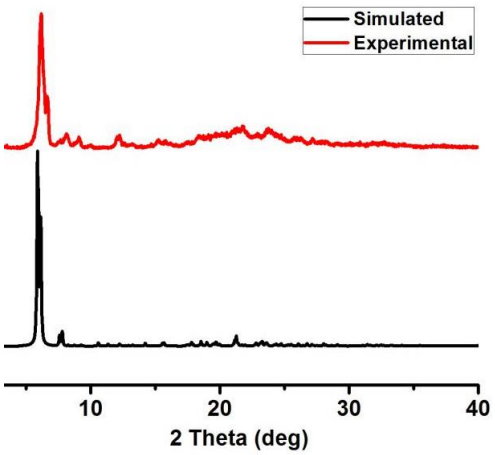


Figure S3. For **PTC-63**: Comparison of PXRD patterns of the simulated pattern from single crystal structure determination and as-synthesized product.

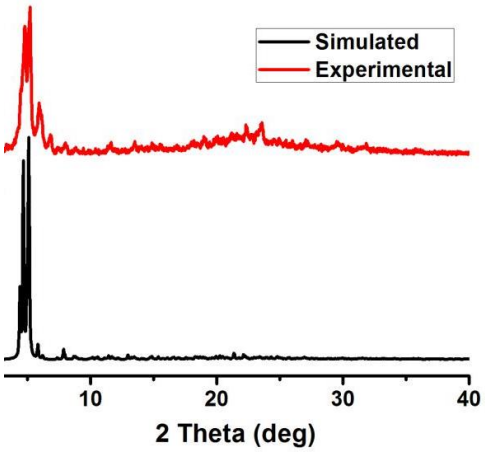


Figure S4. For **PTC-64**: Comparison of PXRD patterns of the simulated pattern from single crystal structure determination and as-synthesized product.

2.3 Fourier-Transform Infrared Spectroscopic studies

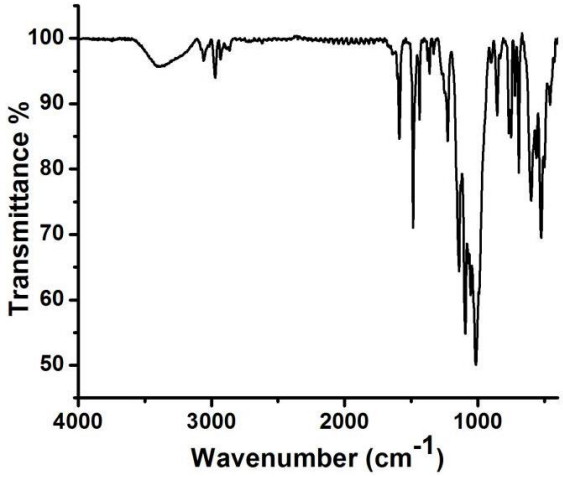


Figure S5. For **PTC-61**: Fourier-Transform Infrared (FT-IR) spectra of the sample.

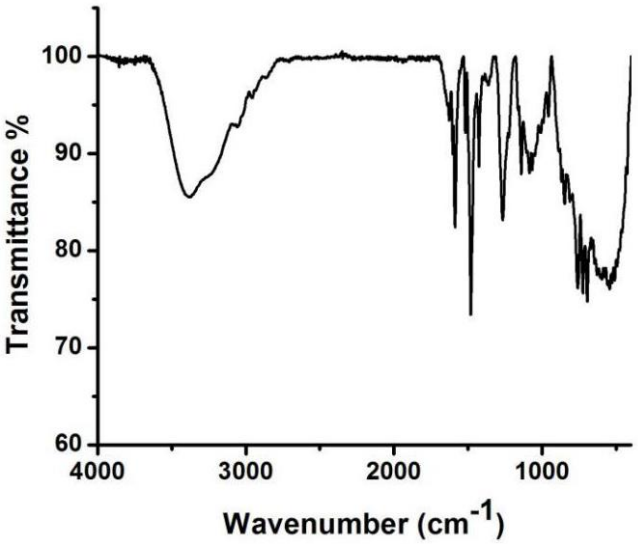


Figure S6. For **PTC-62**: Fourier-Transform Infrared (FT-IR) spectra of the sample.

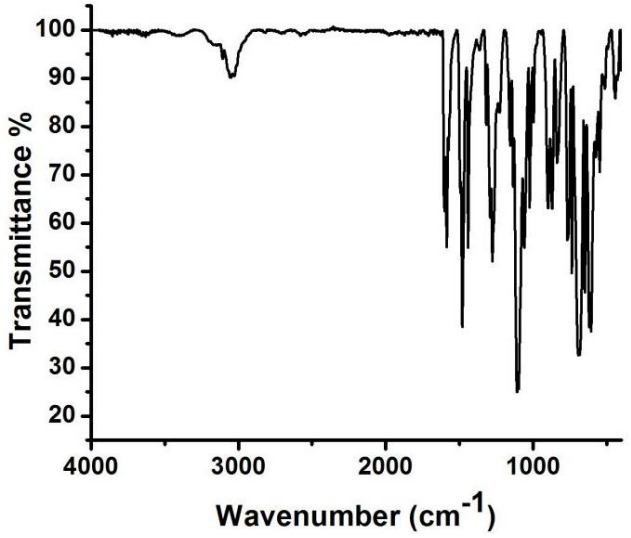


Figure S7. For **PTC-63**: Fourier-Transform Infrared (FT-IR) spectra of the sample.

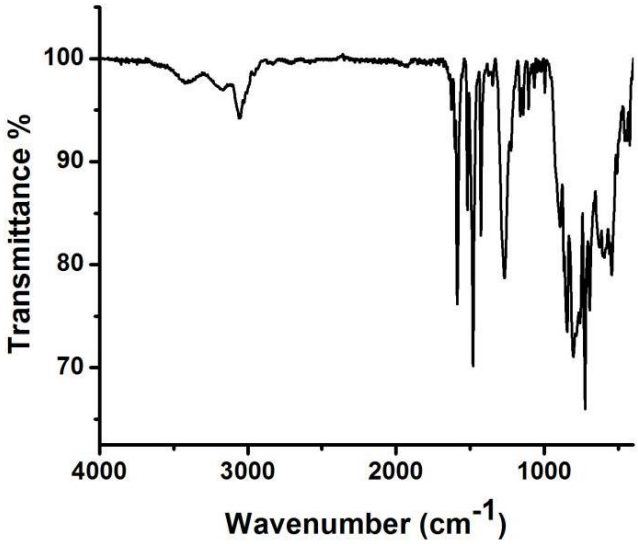


Figure S8. For **PTC-64**: Fourier-Transform Infrared (FT-IR) spectra of the sample.

2.4 Thermogravimetric Studies

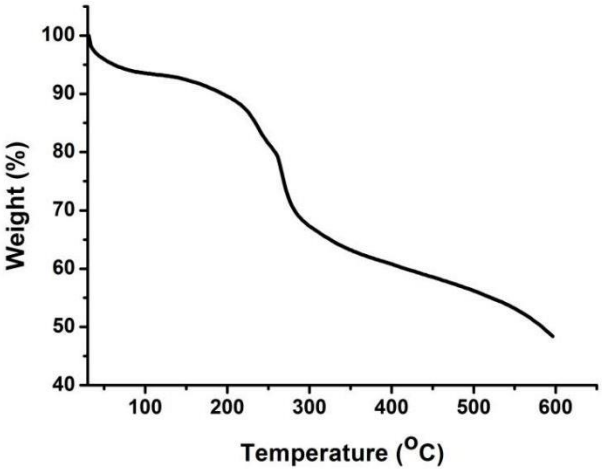


Figure S9. For **PTC-61**: Thermogravimetric Analysis (TGA) of the sample.

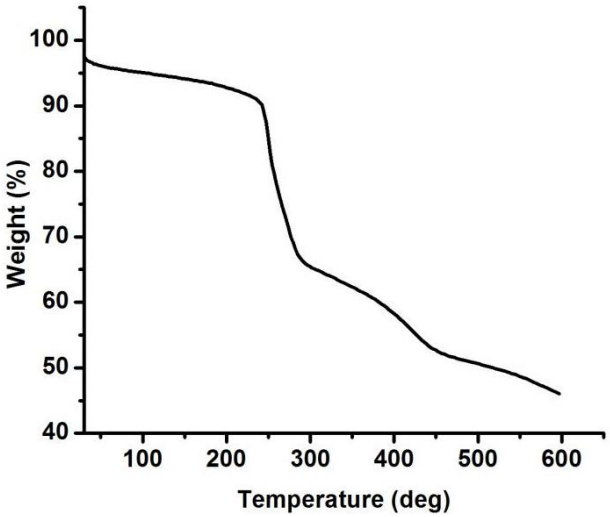


Figure S10. For **PTC-62**: Thermogravimetric Analysis (TGA) of the sample.

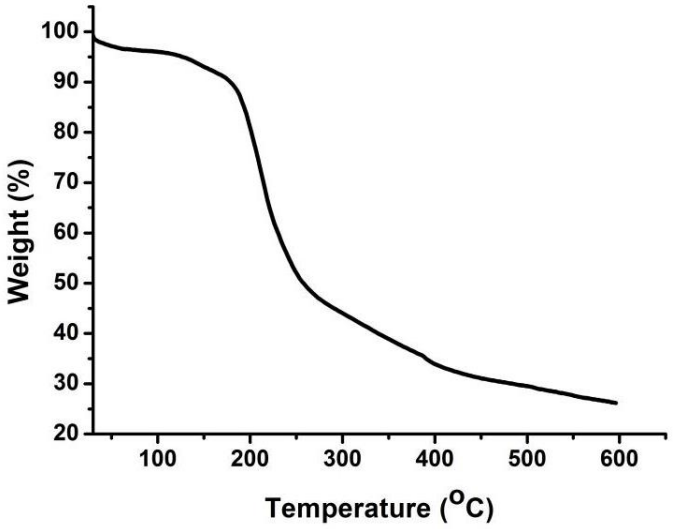


Figure S11. For **PTC-63**: Thermogravimetric Analysis (TGA) of the sample.

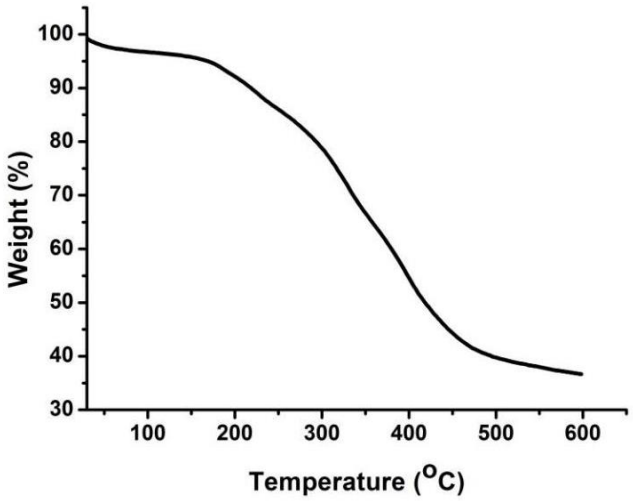


Figure S12. For **PTC-64**: Thermogravimetric Analysis (TGA) of the sample.

2.5 Solid state optical absorbance spectroscopic studies

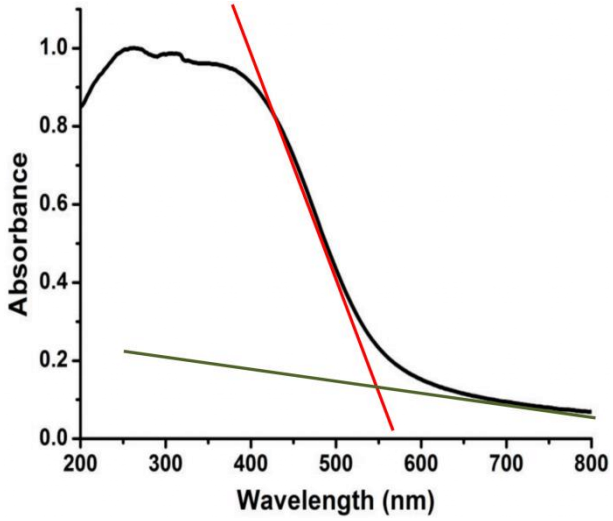


Figure S13. For **PTC-61**: Solid state optical absorbance spectra of the sample.

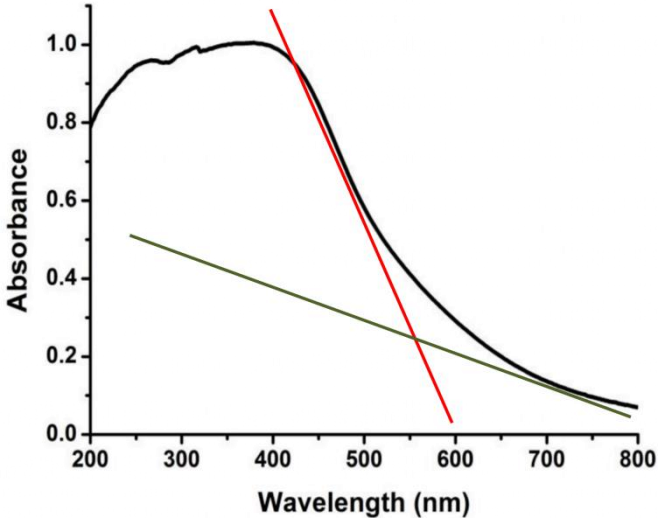


Figure S14. For **PTC-62**: Solid state optical absorbance spectra of the sample.

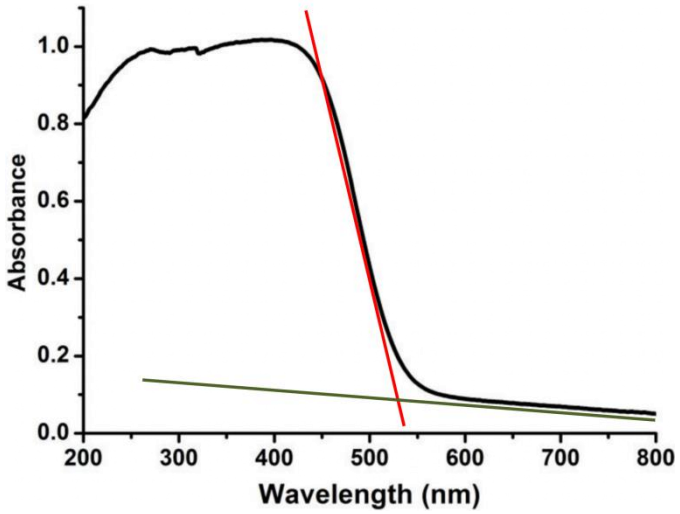


Figure S15. For **PTC-63**: Solid state optical absorbance spectra of the sample.

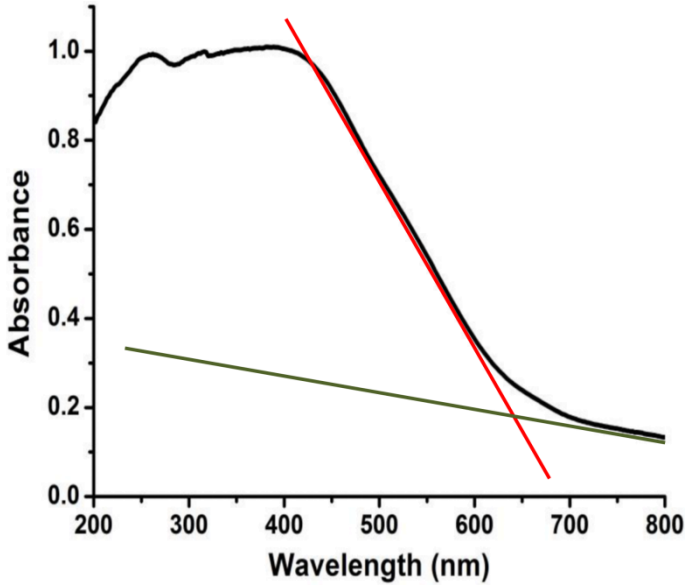


Figure S16. For **PTC-64**: Solid state optical absorbance spectra of the sample.

2.6 Comparative powder X-ray diffraction patterns-Immersed in water

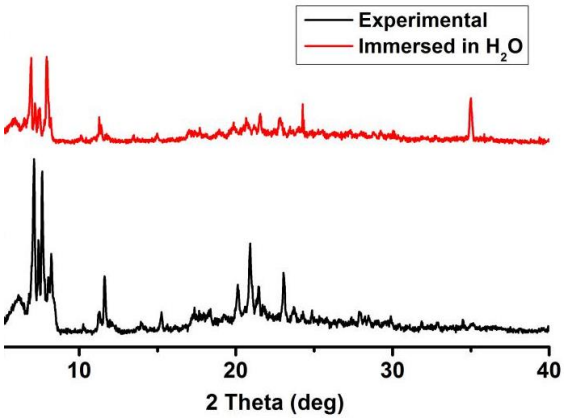


Figure S17. Comparative PXRD pattern for the water stability test of **PTC-61**, which was immersed in water for 24h.

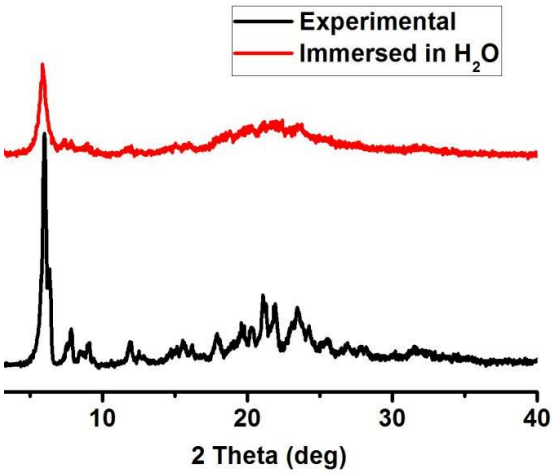


Figure S18. Comparative PXRD pattern for the water stability test of **PTC-62**, which was immersed in water for 24h.

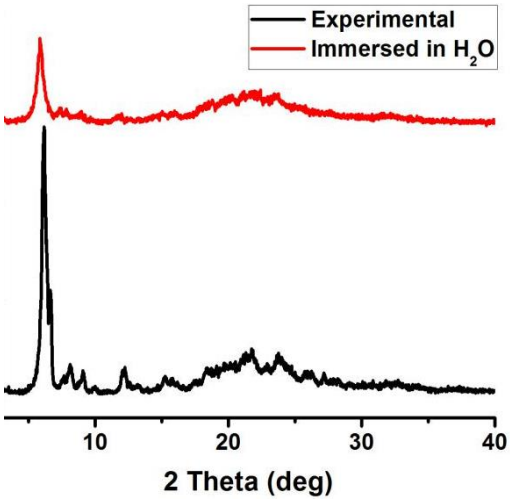


Figure S19. Comparative PXRD pattern for the water stability test of **PTC-63**, which was immersed in water for 24h.

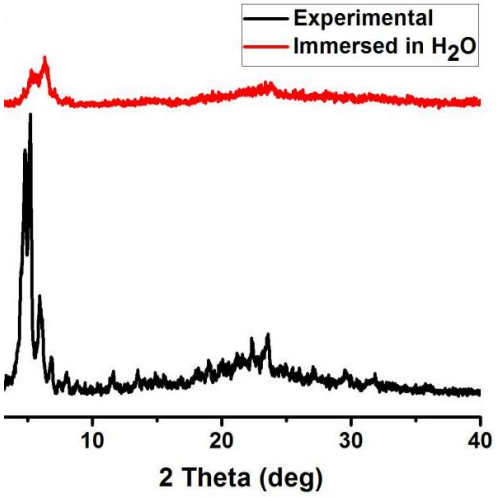


Figure S20. Comparative PXRD pattern for the water stability test of **PTC-64**, which was immersed in water for 24h.

2.7 Comparative liquid UV/Visible spectroscopic analysis of photocatalytic samples

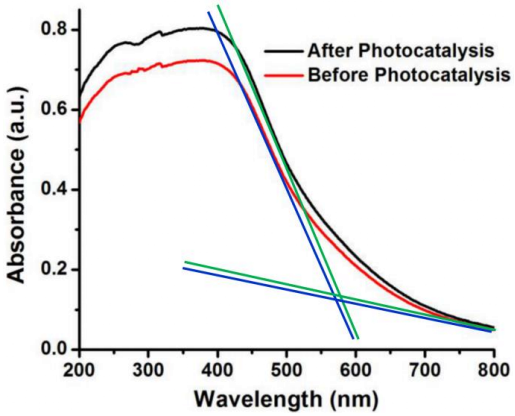


Figure S21. Comparative liquid UV/Vis spectra of **PTC-62**.

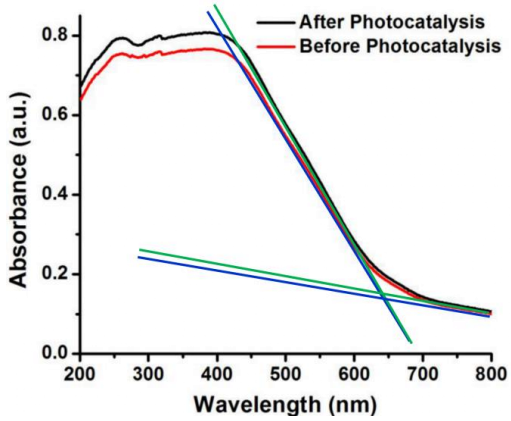
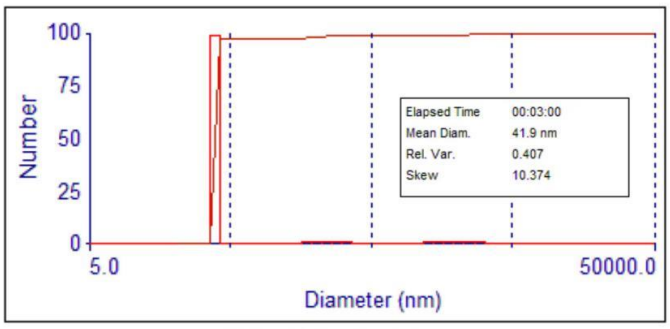


Figure S22. Comparative liquid UV/Vis spectra of **PTC-64**.

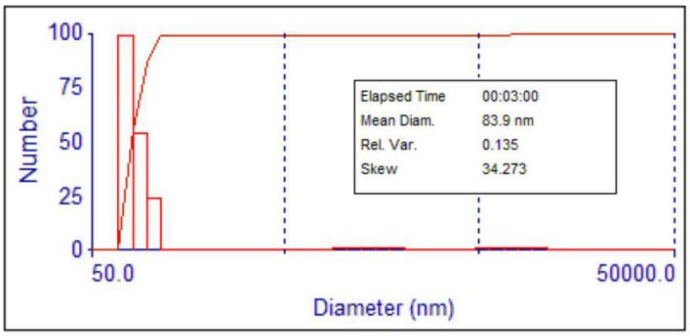
2.8 Dynamic light scattering (DLS) particle size analysis after photocatalysis



Multimodal Size Distribution

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
23.3	0	0	143.7	0	98	887.3	0	100
27.5	0	0	169.6	1	98	1047.0	0	100
32.4	0	0	200.1	1	99	1235.5	0	100
38.2	100	98	236.1	1	100	1457.9	0	100
45.1	0	98	278.6	0	100	1720.3	0	100
53.2	0	98	328.7	0	100	2029.9	0	100
62.8	0	98	387.9	0	100	2395.3	0	100
74.1	0	98	457.7	0	100	2826.4	0	100
87.5	0	98	540.1	0	100	3335.1	0	100
103.2	0	98	637.3	0	100	3935.4	0	100
121.8	0	98	752.0	0	100	4643.7	0	100

Figure S23. Dynamic Light Scattering (DLS) analysis of **PTC-62** solution after photocatalysis.



Multimodal Size Distribution

d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
45.2	0	0	289.1	0	100	1849.8	0	100
53.5	0	0	342.2	0	100	2189.9	0	100
63.3	0	0	405.1	0	100	2592.4	0	100
74.9	100	56	479.6	0	100	3069.0	0	100
88.7	54	87	567.7	0	100	3633.1	0	100
105.0	24	100	672.1	0	100	4301.0	0	100
124.3	0	100	795.6	0	100	5091.6	0	100
147.2	0	100	941.9	0	100	6027.5	0	100
174.2	0	100	1115.0	0	100	7135.5	0	100
206.3	0	100	1320.0	0	100	8447.2	0	100
244.2	0	100	1562.6	0	100	10000.0	0	100

Figure S24. Dynamic Light Scattering (DLS) analysis of **PTC-64** solution after photocatalysis.

2.9 SEM images of samples after photocatalysis

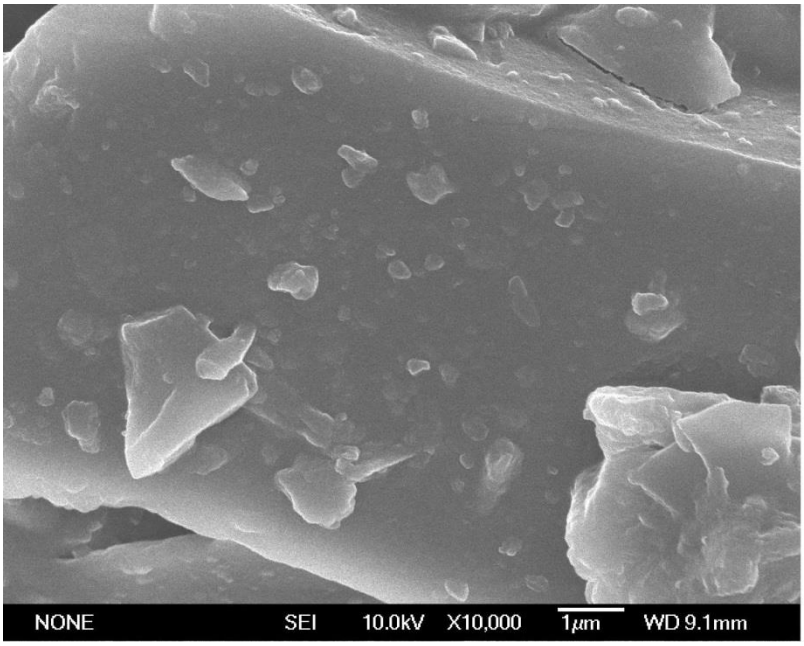


Figure S25. SEM image of **PTC-61** after photocatalysis studies.

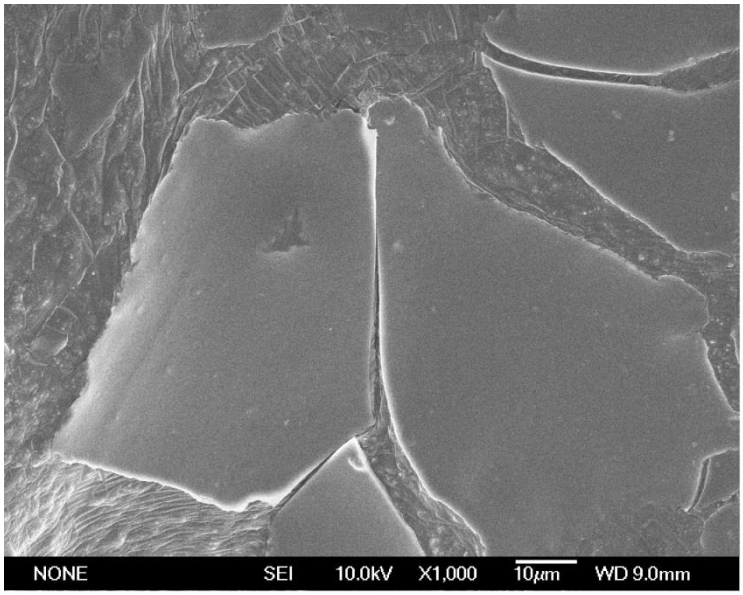


Figure S26. SEM image of **PTC-63** after photocatalysis studies.

2.10 Photocatalytic studies on PTC-62 and PTC-64

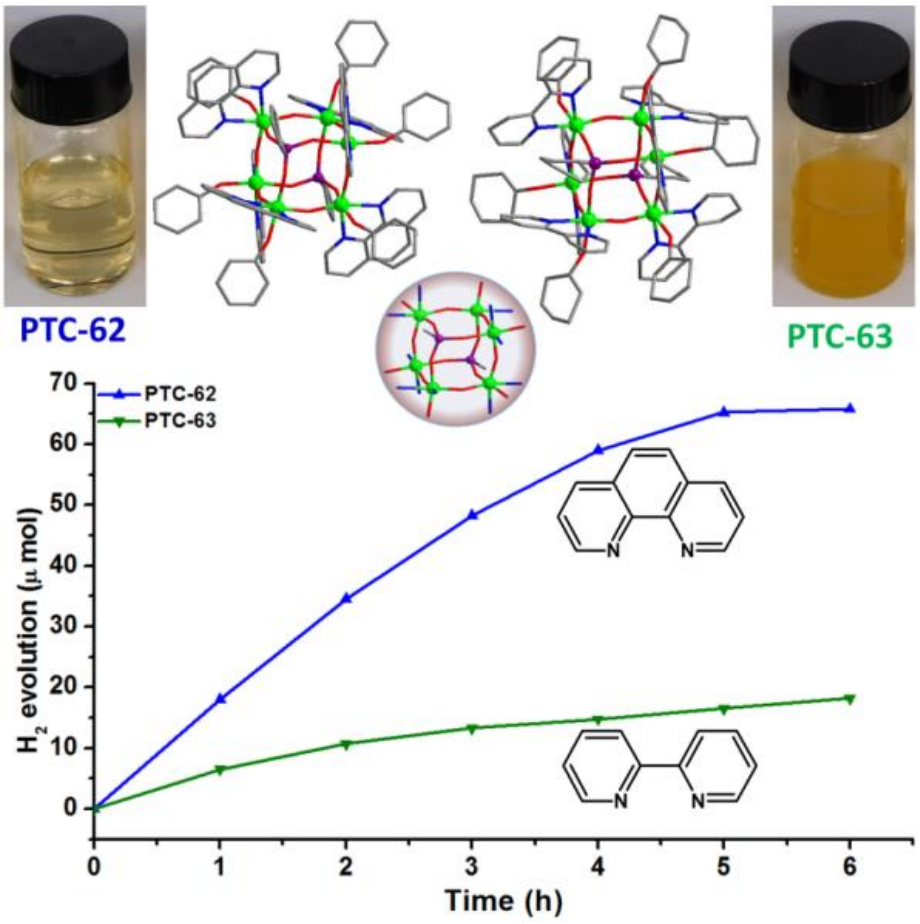


Figure S27. Contrastive hydrogen evolution investigation between **PTC-62** and **PTC-63**. The Ti_6 cluster core and the respective functionalizing π-conjugate ligands are highlighted.

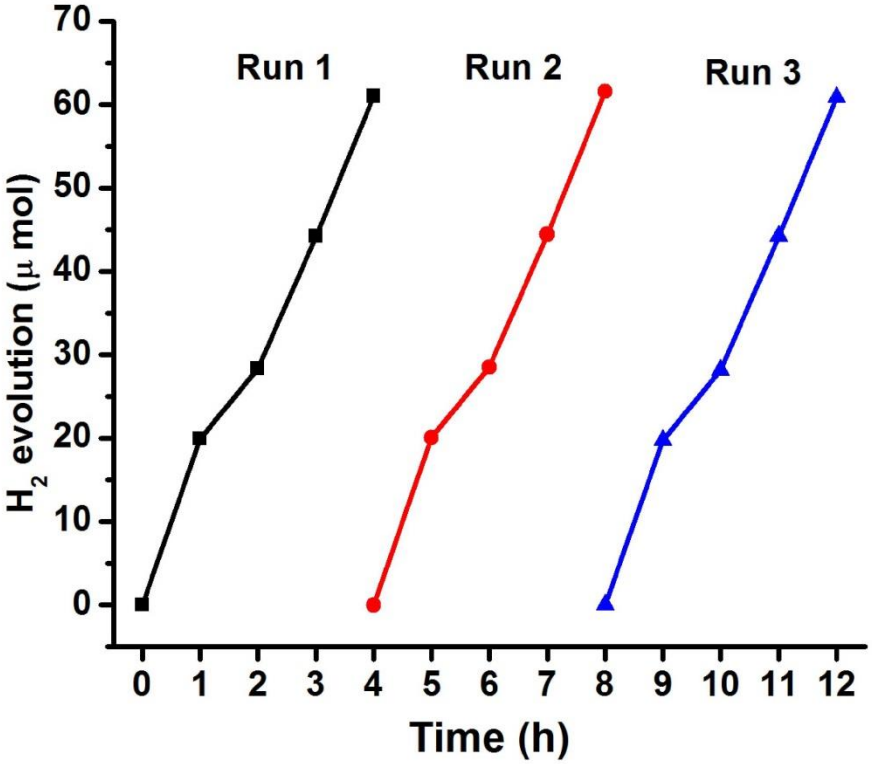


Figure S28. Cycling photocatalytic H_2 evolution curves of **PTC-62**.

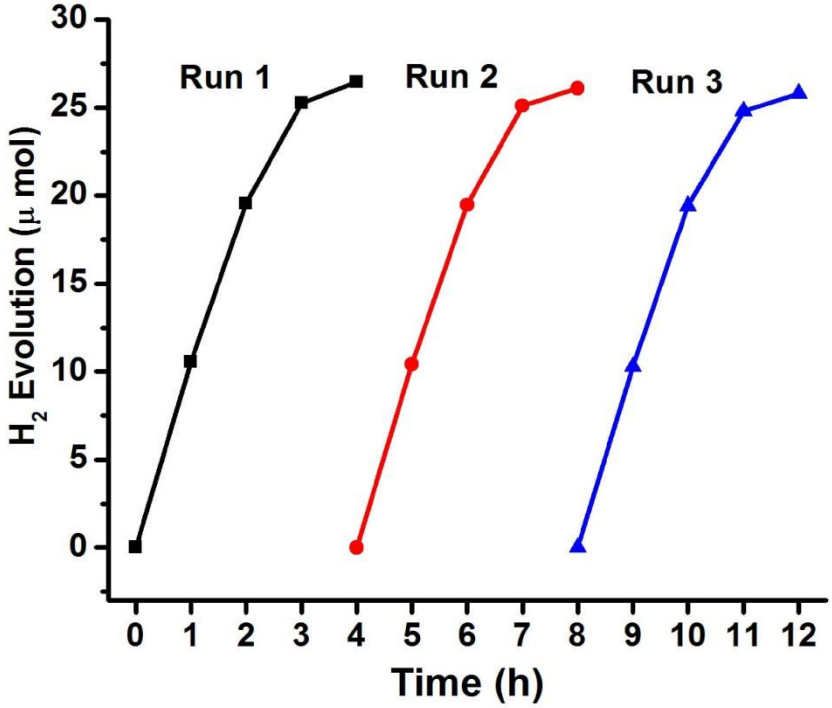


Figure S29. Cycling photocatalytic H_2 evolution curves of **PTC-64**.

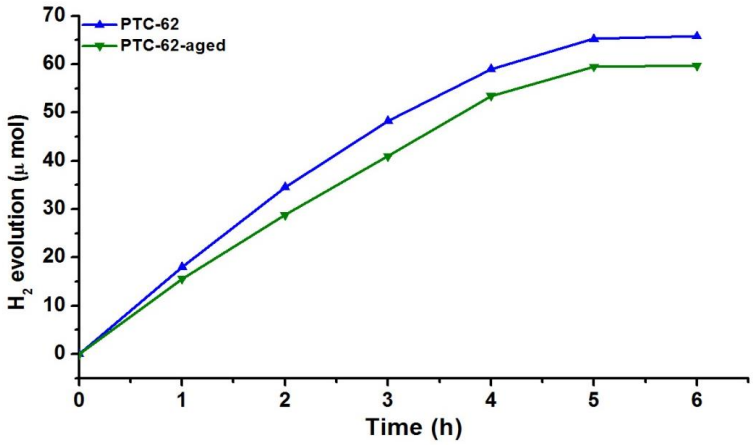


Figure S30. **P**hotocatalytic H_2 evolution curves of **PTC-62**: original and aged for 1 week.

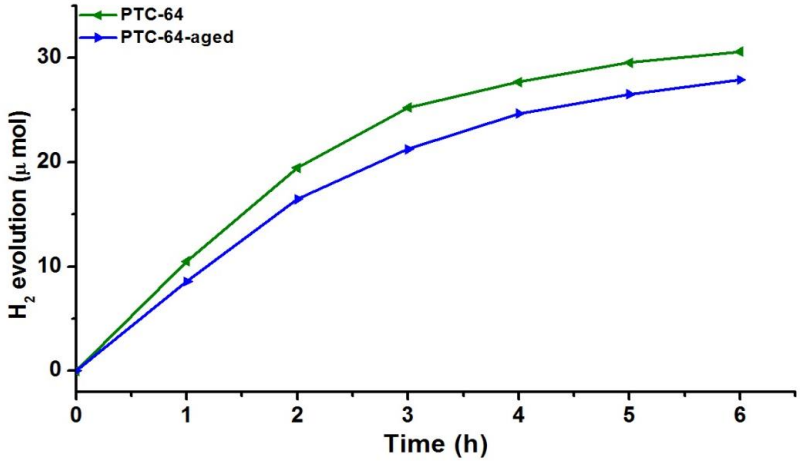


Figure S31. **P**hotocatalytic H_2 evolution curves of **PTC-64**: original and aged for 1 week.

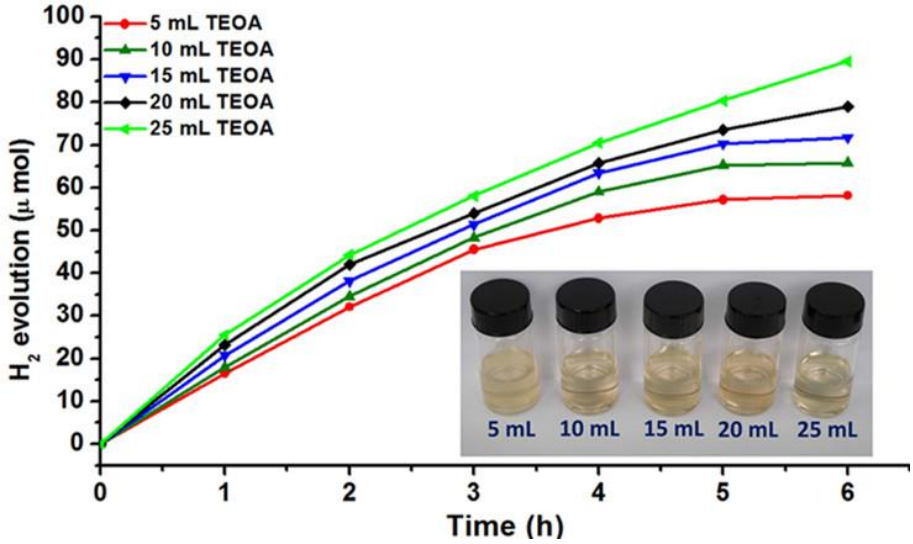


Figure S32. **P**hotocatalytic H_2 evolution curves of **PTC-62** when different amounts (5-25 mL) of sacrifacial agent used in the reaction solutions.

2.11 Photos of crystals in solid state at room temperature

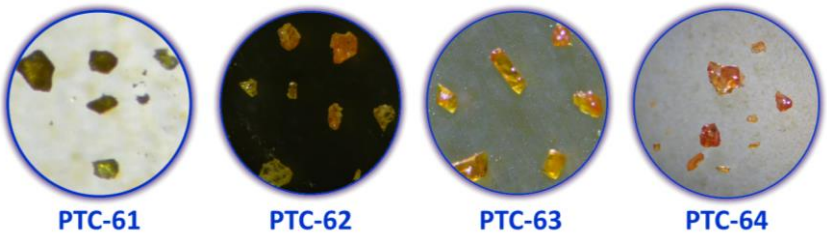


Figure S33. Photos of crystals of **PTC-61** to **PTC-64** in solid state at room temperature.

References

[1] W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience, New York, **1966**.

[2] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112.

[3] G. M. Sheldrick, SHELXL-2014, *University of Gottingen*, Germany, **2014**.