Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Triphenylamine and terpyridine–Zinc(II) complex based donor-acceptor soft hybrid as visible light-driven hydrogen evolution photocatalyst

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Materials. All commercially received reagents and solvents were used without further purification. Tris(4-aminophenyl)amine, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$ and cuprous iodide were acquired from Sigma-Aldrich Chemical Co. *n*-Bromobutane, iodine monochloride, hydroquinone, ethynyltrimethylsilane, tetrahydrofuran (THF), acetonitrile and triethylamine (NEt_3) were purchased from Spectrochem Pvt. Ltd., India. 1,4-dibutoxy-2,5-diiodobenzene (**1**),[1] 4-ethynylbenzaldehyde (**2**)[2] and 4'-ethynyl-2,2':6',2''-terpyridine (**4**)[3] were synthesized using literature reported procedure.

Physical Measurements

^{1}H NMR spectra were recorded either on a JEOL 400 MHz spectrometer or JEOL 500 MHz spectrometer operating, and mentioned in each synthesis procedure. The following notations have been used to describe splitting patterns of ^{1}H NMR signals: s = singlet, d = doublet, t = triplet, m = multiplate, dd = doublet of doublets and ddd = doublet of doublet of doublets. High Resolution Mass Spectra (HRMS) were recorded on a Agilent 6538 Ultra High Definition (UHD) Accurate-Mass Q-TOF-LC/MS system using electrospray ionization (ESI) mode. Elemental analyses were carried out using a Thermo Fischer Flash 2000 Elemental Analyzer. Thermogravimetric analyses (TGA) were performed using Metler Toledo instrument under N_2 atmosphere (flow rate = 50 mL min^{-1}, temperature range 30–800 °C and heating rate = 3 C min^{-1}). FT-IR spectra were measured utilizing a Bruker IFS 66v/S spectrophotometer (KBr pellets, 4000–400 cm^{-1}). UV-Vis spectrum was recorded on Perkin Elmer Lambda 900 UV-Vis Spectrometer. Fluorescence measurement of **TPA-Zn** was carried out using Perkin Elmer Ls 55 Luminescence spectrometer. The absolute fluorescence quantum yield of TPA-Zn as aqueous dispersion was measured by using an integrating sphere, developed by Horiba Jobin Yvon. Lifetime measurement was conducted on Edinburgh instrument utilizing EPL-405 ps pulsed diode laser as the excitation source (λ_{exc}= 405 nm). Powder X-ray diffraction (PXRD) patterns of the coordination polymer **TPA-Zn** was collected using a Bruker D8 Discover instrument using Cu−Kα radiation. Morphological studies have been carried out using Lica-S440I Field Emission Scanning Electron Microscope (FESEM) by placing samples on aluminium foil under high vacuum with an accelerating voltage of 100 kV. Gold coating on the sample was done prior FESEM analysis. Transmission Electron Microscopy (TEM) analysis has been performed using JEOL JEM-3010 with an accelerating voltage at 300 kV. Energy dispersive spectroscopy (EDS) analysis was performed with an EDAX genesis instrument attached to the FESEM column. Sample for the imaging studies was prepared by dispersing **TPA-Zn** in water.

Adsorption Measurements. N_2 adsorption study of **TPA-Zn** was carried out using QUNATACHROME QUADRASORD-SI analyzer at 77 K. In the sample tube, **TPA-Zn** (76 mg) was placed which had been degassed at 120 °C under a 1×10^{-1} Pa vacuum for about 12 h prior to

[1] K. Wariishi, S. I. Morishima and Y. Inagaki, *Org. Process Res. Dev.*, 2003, **7**, 98.
[2] W. Fu, L. Dong, J. Shi, B. Tong, Z. Cai, J. Zhi and Y. Dong, *Macromolecules*, 2018, **51**, 3254.
[3] V. Grosshenny, F. M. Romero and R. Ziessel, *J. Org. Chem.* 1997, 62, 5, 1491.

measurement of the isotherms. Helium gas (99.999% purity) at a certain pressure was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas adsorbed was calculated from the pressure difference (P_{cal} - P_e), where P_{cal} is the calculated pressure with no gas adsorption and P_e is the observed equilibrium pressure. All the operations were computer-controlled.

General Procedure for photocatalysis

1.5 mg of **TPA-Zn** was dispersed in 38 mL water and 2 mL triethylamine. The resulting dispersion was taken in a photocatalytic cell and degassed by pursing argon for 10 min. After degassing, the cell was placed in a photocatalytic chamber and irradiated with light (source: 290 MW xenon lamp, Oriel Instrument) to perform catalysis. Quantification of the produced dihydrogen was detected every hour by gas chromatography (Agilent Technologies, 7890B).

Quantum Efficiency Calculation

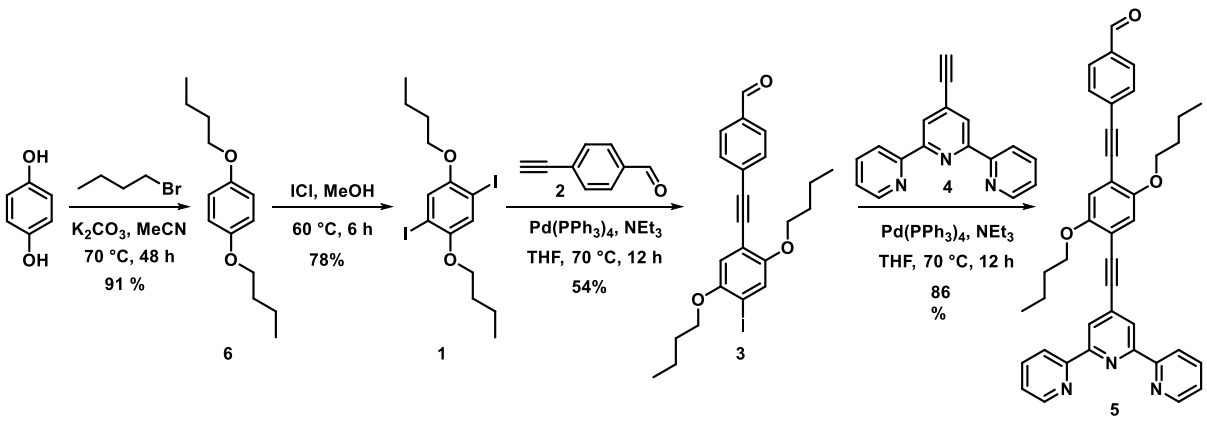
To determine quantum efficiency, a 400 nm filter having 0.8 mW cm^{-2} s^{-1} power was utilized for photoirradiation. A total of 1.77 μmol dihydrogen was produced after 1 h of light irradiation through a tubular shaped sample cell (*d* = 4 cm). Therefore, total energy flashed into the sample in 1 h = 0.8 mW cm^{-2} s^{-1} x 3600 s x 3.14 x 4 cm^{-2}= 3.62 x 10^4 mW.

Total number of photon flashed into the sample cell = 7.3 x 10^{19} [applying E= (nhc)/λ]

Total number of H_2 molecules produce in 1 h = 1.77 x 10^{-6} x 6.023 X 10^{23} = 1.1 x 10^{18}

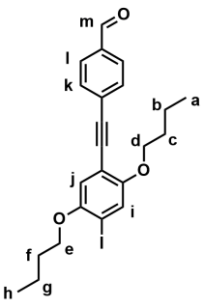
Quantum efficiency = {[No. of H_2 formed x 2]/ No. of photons } x 100 = 2.9%

Synthesis

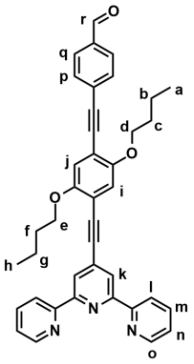


Scheme 1. Synthesis scheme of compound **5**.

Synthesis of 4-((2,5-dibutoxy-4-iodophenyl)ethynyl)benzaldehyde (3): 1,4-dibutoxy-2,5-diiodobenzene (**1**) (546 mg, 1.15 mmol), 4-ethynylbenzaldehyde (**2**) (100 mg, 768 µmol) and $Pd(PPh_3)_4$ (88.7 mg, 76.8 µmol) was taken in a double-neck round-bottomed (25 mL) under argon atmosphere. A mixture of tetrahydrofuran (5 mL) and triethylamine (5 mL) was thoroughly degassed using freeze-pump-thaw process and added to the reaction vessel. The reaction mixture was heated at 70 °C using oil bath for 12 hours for completion of the cross-coupling reaction. The resulting mixture was evaporated to dryness and the crude compound was treated for flash column chromatography (silica gel, *n*-hexane/ethylacetate = 90:10, R_f = 0.52) to obtain semi-pure compound **4** as pale yellow solid. The thus obtained solid was further purified by ultrasonication in methanol (50 mL) which selectively dissolves only **3** from the impure mixture. The methanolic solution of compound **3** was filtered through Whatman 40 filter paper and evaporated to dryness to afford compound **3** as white solid. mp = 78-80°C, yield: 54% (0.62 mmol, 296 mg). IR (KBr, $1/\upsilon_{max}$): 2957, 2928, 2871, 2730, 2209, 1702, 1600, 1560, 1506, 1485, 1464, 1380, 1301, 1269, 1165, 1100, 1066, 1025, 973, 844, 827, 771, 528 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.97-1.01 (m, 6H, a-, h-H), 1.61-1.45 (m, 4H, b-, g-H), 1.90-1.73 (m, 4H, c-, f-H), 3.89 - 4.12 (m, 4H, d-, e-H), 6.91 (s, 1H, i- or j-H), 7.32 (s, 1H, j- or i-H), 7.65 (d, ^3J = 8.2 Hz, 2H, k-H), 7.85 (d, ^3J =8.2 Hz, 2H, l-H), 10.01 (s, 1H, m-H) ppm; ^{13}C {^1H} NMR (100 MHz, $CDCl_3$) δ = 13.9 (2C), 19.2, 19.3, 31.3, 31.3, 69.5, 69.8, 88.8, 89.8, 93.2, 112.7, 115.9, 123.9, 129.6, 129.8, 131.9, 135.4, 151.9, 154.6, 191.4 ppm. Anal. Calcd for $C_{23}H_{25}IO_3$: C, 57.99; H, 5.29. Found: C, 56.82; H, 5.40.



Synthesis of 4-((4-([2,2':6',2''-terpyridin]-4'-ylethynyl)-2,5-dibutoxyphenyl)ethynyl)benzaldehyde (5). Compound **3** (100 mg, 209 µmol), **4** (54 mg, 209 µmol) and $Pd(PPh_3)_4$ (24.2 mg, 20.9 µmol) were taken into a two-neck round-bottomed flask. A mixture of tetrahydrofuran (5 mL) and triethylamine (5 mL) was thoroughly degassed using freeze-pump-thaw process and added to the reaction vessel. The resulting mixture was stirred at 75 °C for 12 h for completion of the cross-coupling reaction. The reaction mixture was then evaporated to dryness and the crude compound was ultrasonicated in methanol. The solid residue was then filtered through Whatman 40 filter paper to afford semi-pure desired compound. It was further purified through column chromatography (neutral Al_2O_3, CH_2Cl_2, R_f = 0.35) to produce compound **5** as yellow solid. mp = 140-142°C, yield: 86% (180 µmol, 109 mg). IR (KBr, $1/\upsilon_{max}$): 3055, 2957, 2928, 2870, 2731, 2210, 1699, 1599, 1583, 1566, 1510, 1495, 1466, 1445, 1419, 1390, 1301, 1278, 1207, 1165, 1119, 1095, 1068, 1026, 924, 889, 848, 828, 792, 775, 743, 690, 660, 619, 563, 520, 404 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 1.01-1.06 (m, 6H, a-, h-H), 1.57- 1.64 (m, 4H, b-, g-H), 1.84-1.91 (m, 4H, c-, f-H), 4.06-4.09 (m, 4H, d-, e-H), 7.04 (s, 1H, i- or j-H), 7.07 (s, 1H, j- or i-H), 7.35 (ddd, 2H, ^3J = 7.4 Hz, ^3J = 4.5 Hz, ^4J = 0.9 Hz, n-H), 7.68(d, ^3J = 8.5 Hz, 2H, p-H), 7.85-7.88 (m, 4H, 10-H, m-, q-H), 8.58 (s, 2H, k-



H), 8.62 (d, ^{3}J = 8.0 Hz, 2H, l-H), 8.72 (dd, ^{3}J = 4.5 Hz, ^{4}J = 1.0 Hz, 2H, o-H), 10.02 (s, 1H, r-H) ppm. ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ = 13.9, 13.9, 19.3, 19.4, 31.3, 31.4, 69.3, 69.6, 90.1, 90.3, 93.1, 94.2, 113.9, 117.1, 117.2, 121.2 (2C), 122.8, 124.0, 129.6, 129.8, 132.0, 133.4, 135.4, 136.9, 149.2, 153.9, 153.9, 155.6, 155.7, 191.4 ppm. Anal. Calcd for $C_{40}H_{35}N_3O_3$: C, 79.31; H, 5.82; N, 6.94. Found: C, 79.58; H, 5.66; N, 7.28.

Synthesis of the coordination polymer TPA-Zn. A solution of **5** (94.0 mg, 0.15 mmol) and tris(4-aminophenyl)amine (14.8 mg, 0.05 mmol) in acetonitrile (5 mL) was refluxed for 6 hours. The procedure resulted in an orange-red precipitate of **TPA-tpy** (Figure S1). Then $Zn(OTf)_2$ was added and the reaction mixture was further refluxed for 6 hours. The black colored precipitate of **TPA-Zn** was formed. The precipitate was filtered and washed with methanol, acetonitrile and dichloromethane, and dried under vacuum to afford 91% yield of **TPA-Zn**. Anal. Calcd. for $C_{94}H_{78}F_6N_{8.66}O_{10}S_2Zn$: C, 65.17; H, 4.54; N, 7.00; S, 3.70. Found: C, 65.41; H, 4.50; N, 7.23; S, 3.84. FT-IR (KBr, 1/υ_{max}): 3059, 2952, 2871, 2201, 1689, 1599, 1571, 1541, 1492, 1473, 1418, 1390, 1377, 1314, 1277, 1206, 1164, 1059, 1011, 973, 880, 831, 789, 726, 691, 658, 578 cm^{-1}.

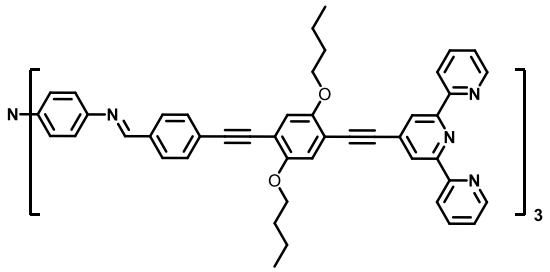


Figure S1. Chemical structure of **TPA-tpy** ligand.

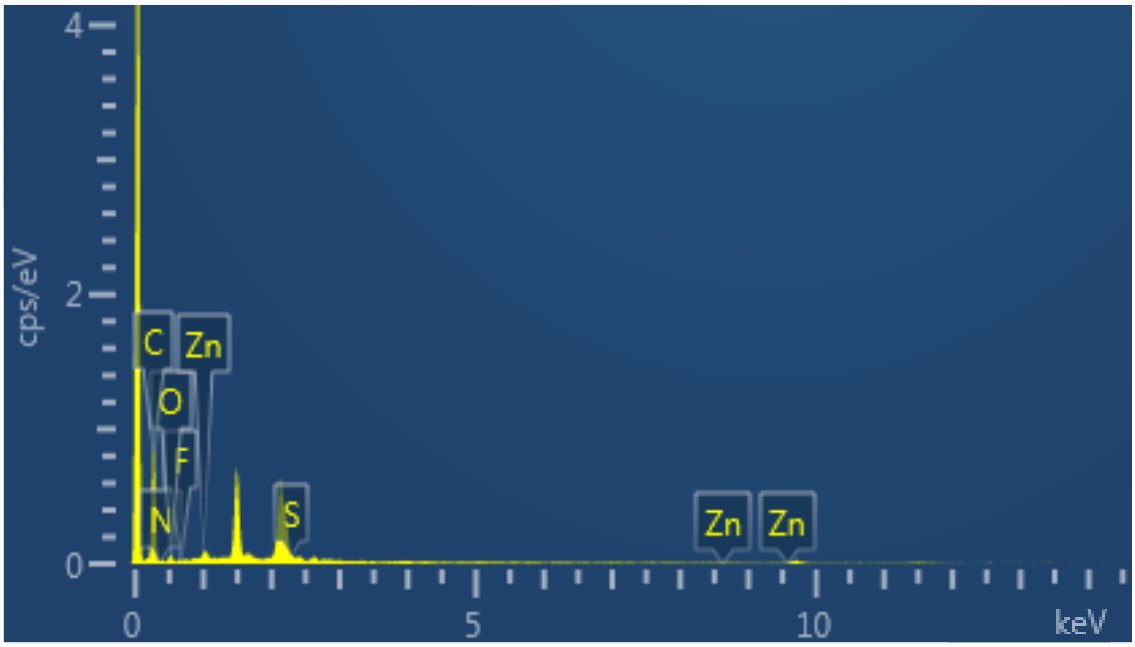


Figure S2. EDAX analysis of **TPA-Zn**.

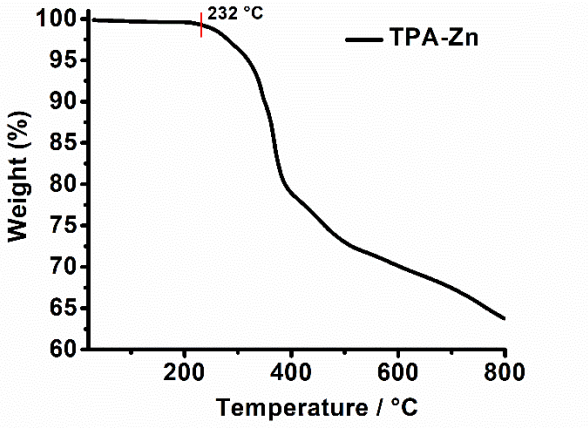


Figure S3. TGA profile of **TPA-Zn**.

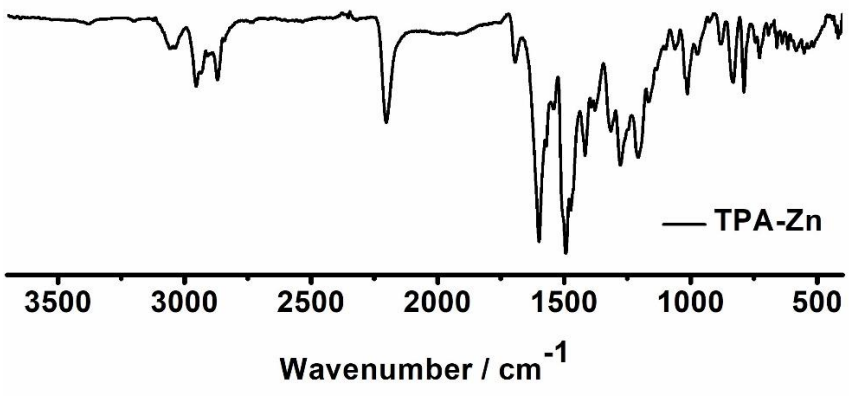


Figure S4. FT-IR spectrum of **TPA-Zn**.

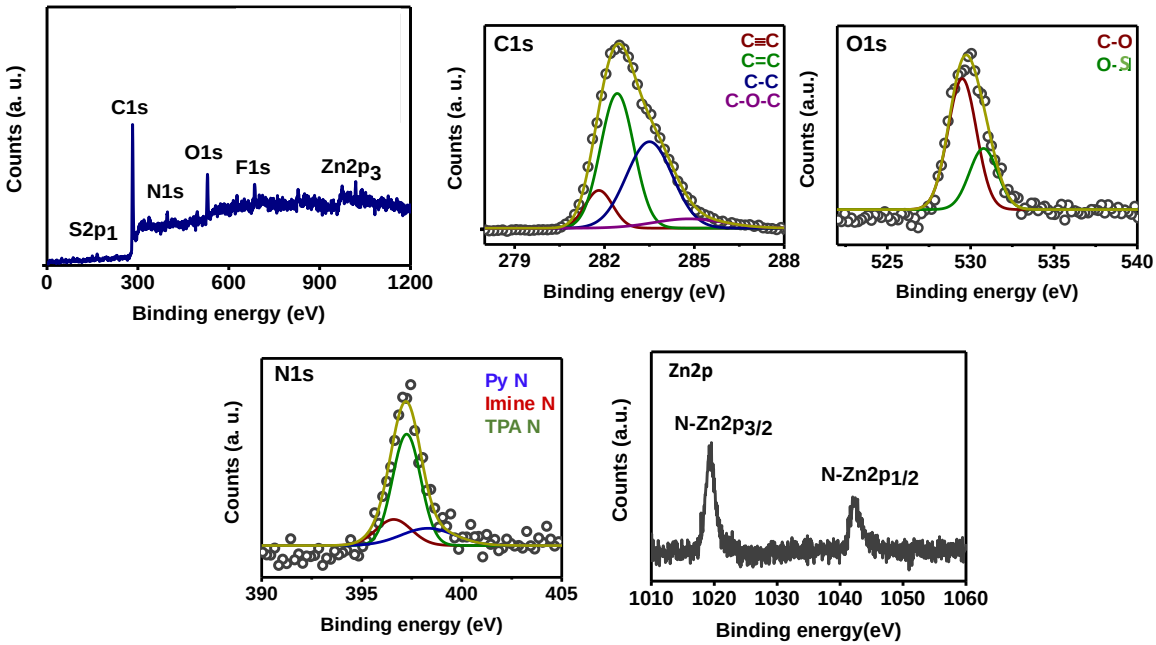


Figure S5. XPS analysis of **TPA-Zn.**

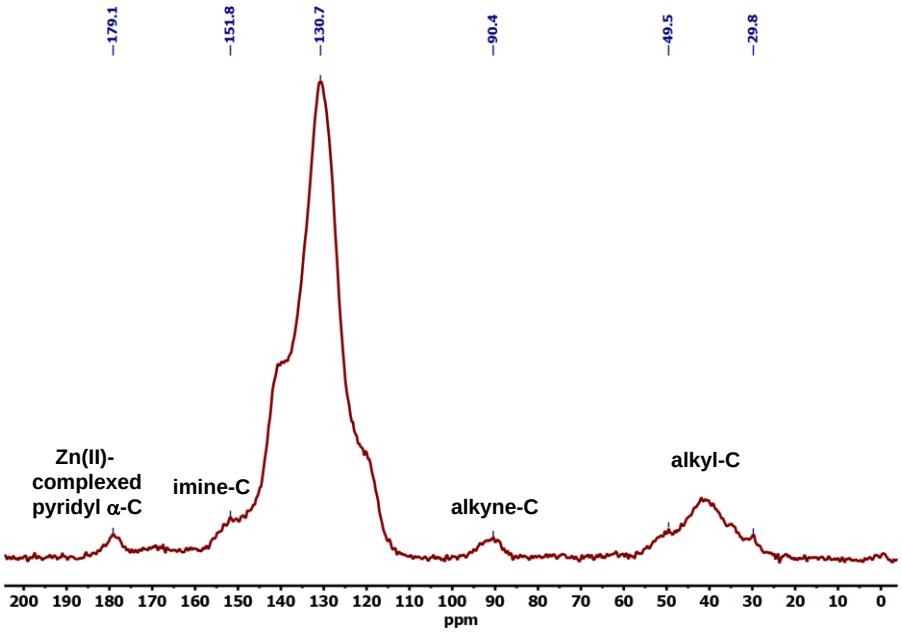


Figure S6. Solid state 13C NMR spectrum of **TPA-Zn**.

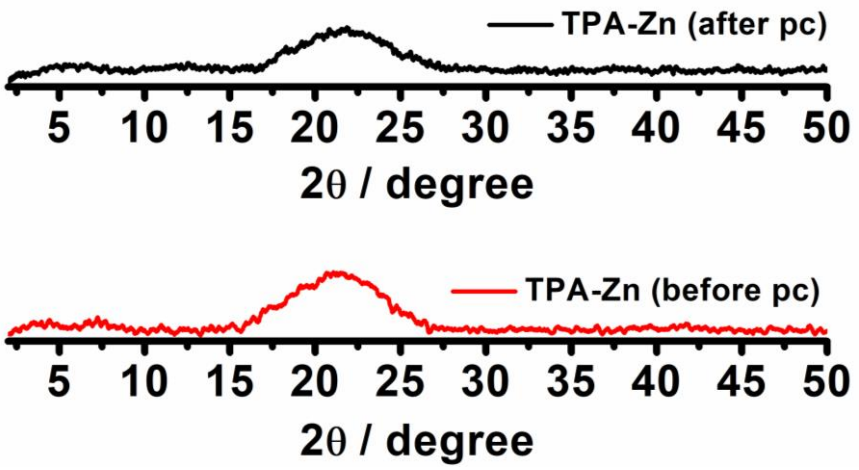


Figure S7. PXRD patterns of **TPA-Zn**, before (red) and after (black) photocatalysis.

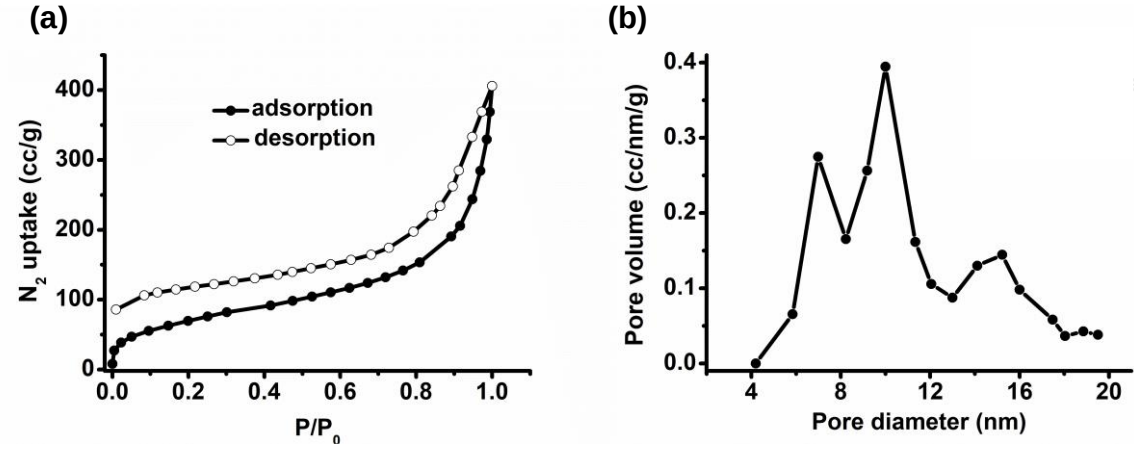


Figure S8. (a) N_2 adsorption isotherm of **TPA-Zn** at 77 K and (b) pore diameter distribution.

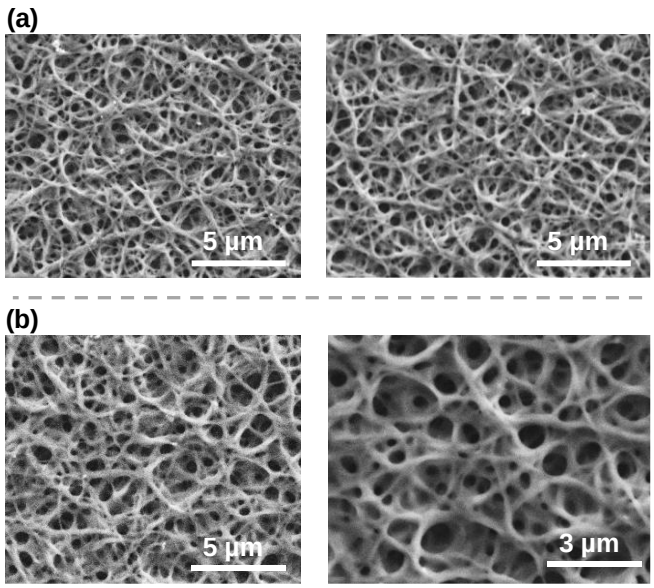


Figure S9. FESEM images of **TPA-Zn** (a) before and (b) after performing photocatalysis.

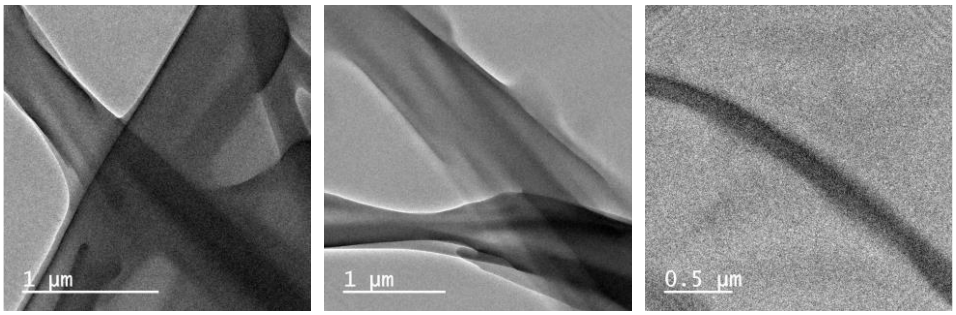


Figure S10. TEM images of **TPA-Zn**.

Table S1. Heterogenous photocatalytic water-splitting activity of several benchmark metal-organic hybrids.

No.	**Photocatalyst**	**H_2 production (µmol g^{-1} h^{-1})**	**Quantum yield**	**Reference**
1	Ti-MOF-NH_2	170	--	*Catal. Sci. Technol.* 2013, **3**, 2092
2	1.5 wt.% Pt/Ti-MOF-NH_2	500	1.3 at 420 nm	*Catal. Sci. Technol.* 2013, **3**, 2092
3	Small-sized Ni NPs anchored in MOF-	3022	7.8 at 520 nm	*Appl. Catal. B: Environ.* 2016, **190**, 12
4	UiO-66/CdS	1700	--	*Chem. Commun.* 2014, **50**, 8533
	UiO-66/CdS/1% RGO	2100	--	*Chem. Commun.* 2014, **50**, 8533
5	MoS_2/UiO-66/CdS	32500	23.6 at 420 nm	*Appl. Catal. B: Environ.* 2015, 166–167, 445
6	Ti-MOF-Ru(tpy)	200	0.2 at 500 nm	*Chem. Commun.* 2014, **50**, 6779
7	Pt complex immobilized MOF-253	58000	1.63 at 440 nm	*Energy Environ. Sci.* 2013, **6**, 3229
8	ErB dye-sensitized Pt/UiO-66 octahedrons		0.25 at 420 nm	*Appl. Catal. B: Environ.* 2015, 168–169, 572
9	Co_3O_4/TiO_2 p–n heterojunction	7000	--	*J. Mater. Chem. A* 2015, **3**, 20288

10	Hollow Fe_2O_3-TiO2-PtO_x	1100	--	*Phys. Chem. Chem. Phys.* 2014, **16**, 5937
11	Pt@UiO-66	3.9	--	*Mater. Sci. Semicond. Process.* 2014, **23**, 144
12	Pt@CdS@Cd(II)-MOF@TiO_2 in Cd-MOF	1416	2.05% at 420 nm	*Chem. Commun.*, 2015, **51**, 15906
13	NiS/CdS/h-TiO_2 in NH_2-MIL-125	2149.15	--	*Appl. Surf. Sci.*, 2019, **476**, 378
14	ZnO/ZnS-30 in MOF-5	435	--	*Adv. Sci.*, 2018, **5**, 1700590
15	30 wt% CdS/ZnxCo$_3$−xO$_4$ in ZnCo-ZIF	3978.6	--	*Nanoscale*, 2018, **10**, 4463
16	Cu(II) -rhodamine CP	7.88	--	*Angew. Chem. Int. Ed.* 2016, ***55***, 2073-2077

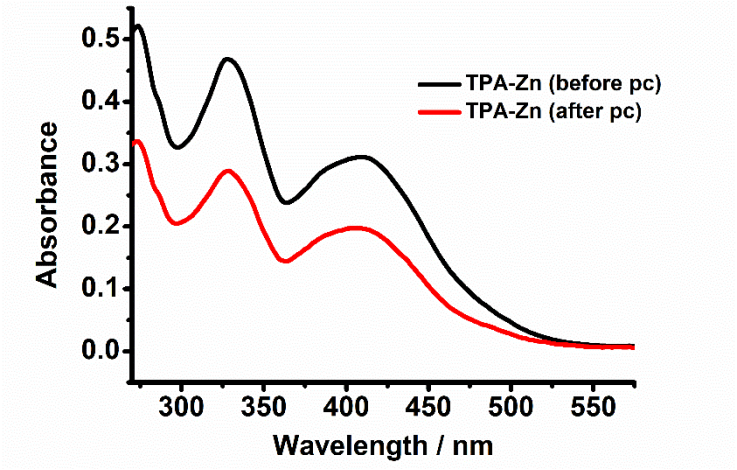


Figure S11. UV-Vis spectra of **TPA-Zn** as aqueous dispersion before (black) and after (red) photocatalysis.

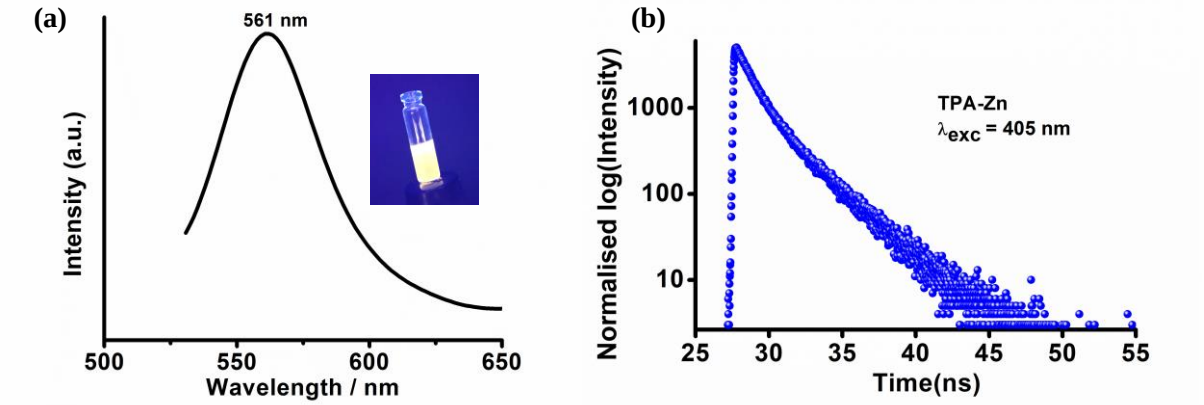


Figure S12. (a) PL spectrum of **TPA-Zn** as aqueous dispersion. Image of the dispersion under UV light is provided as inset. (b) Excited state fluorescence decay profile of **TPA-Zn**.

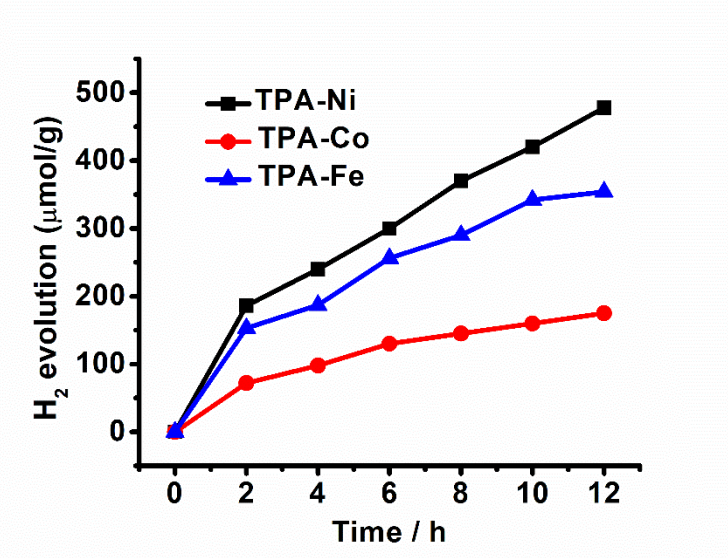


Figure S13. Photocatalytic dihydrogen production utilizing Ni^{II} (**TPA-Ni**), Co^{II} (**TPA-Co**) and Fe^{II} (**TPA-Fe**) catalyst.

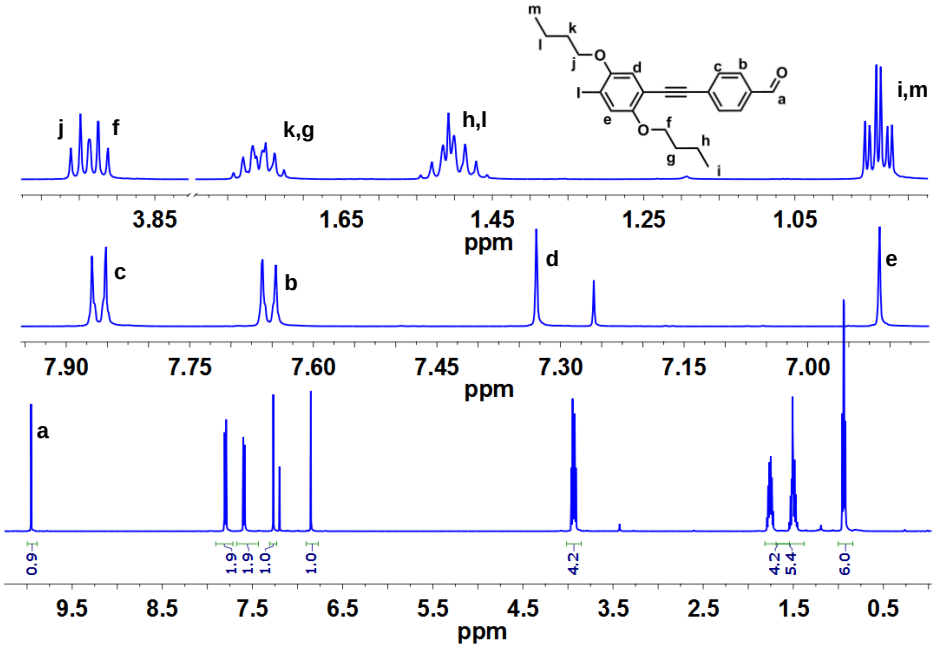


Figure S14. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **3**.

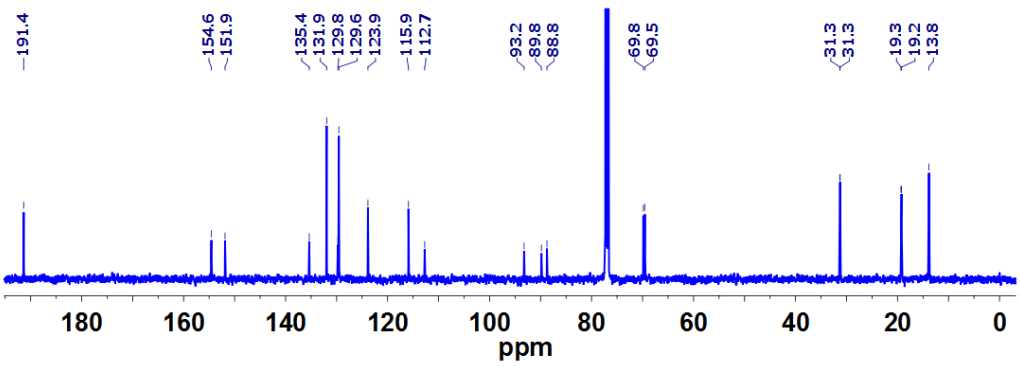


Figure S15. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **3**.

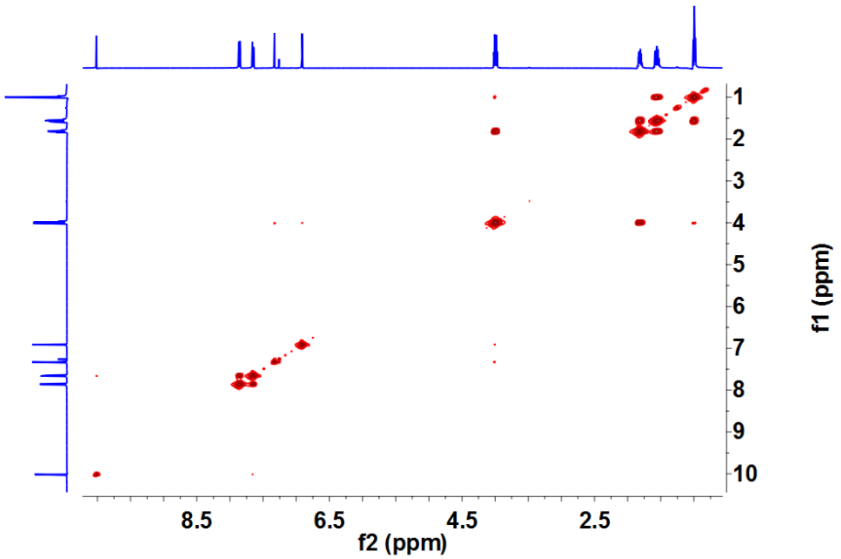


Figure S16. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **3**.

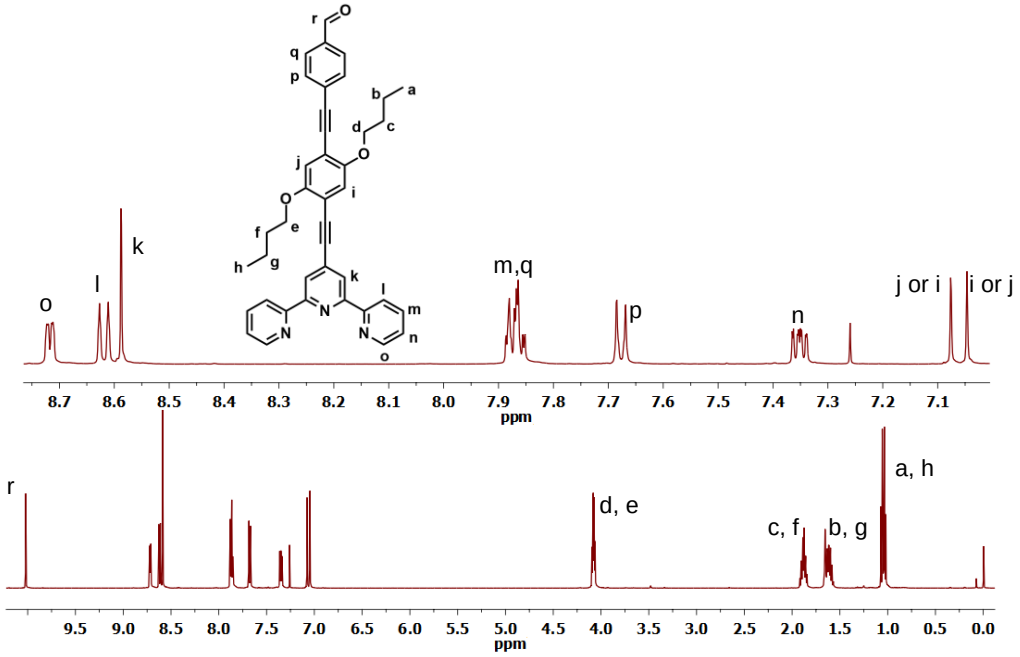


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of compound **5**.

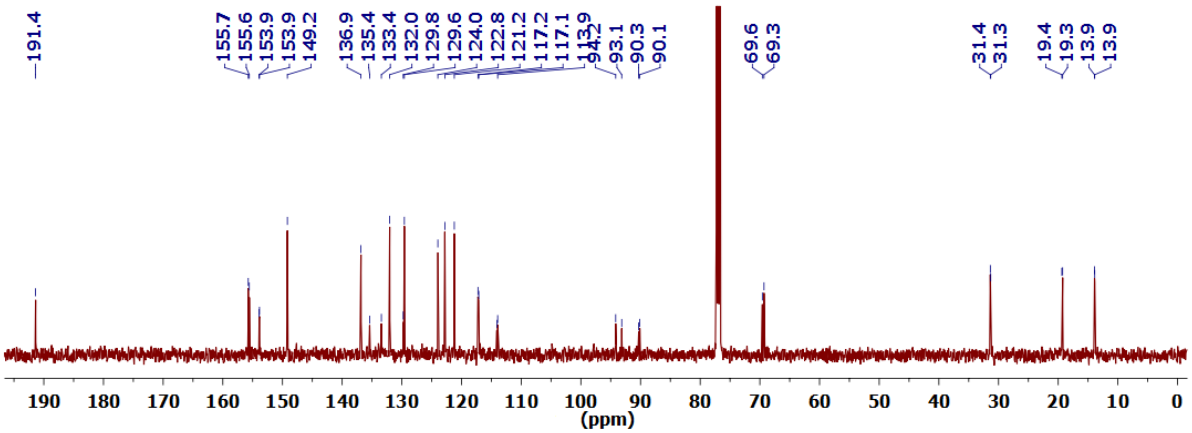


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **5**.

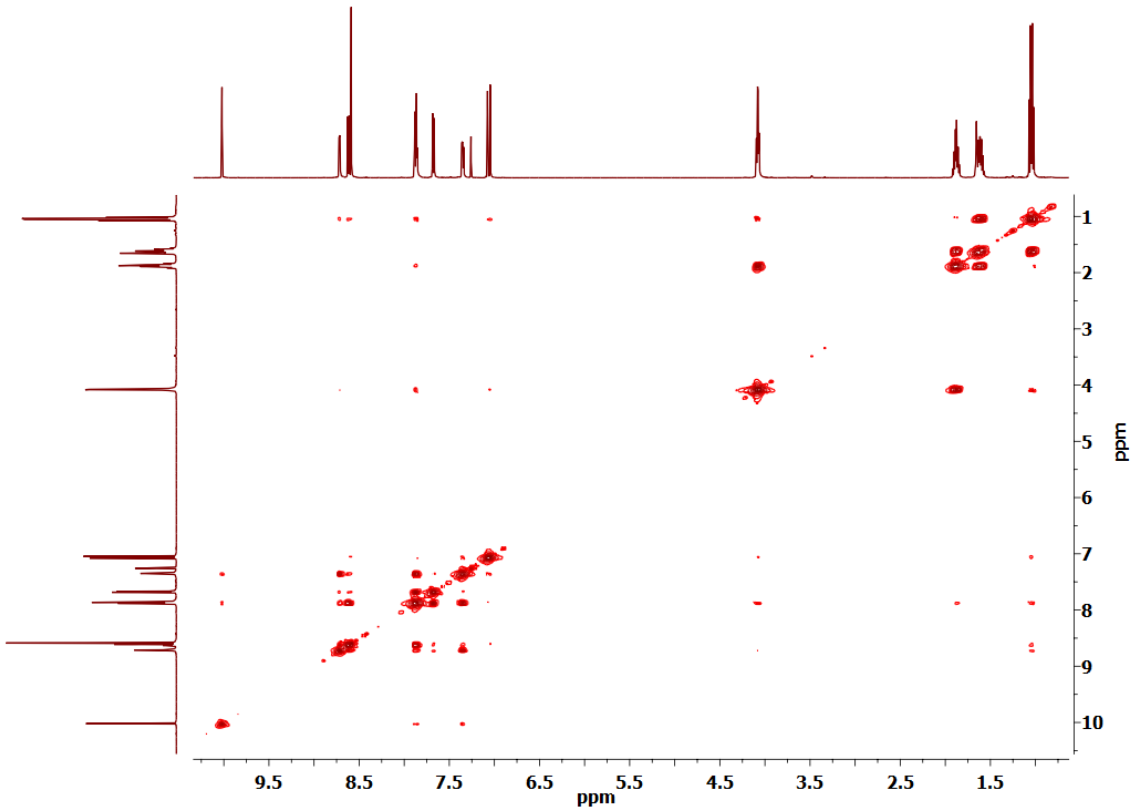


Figure S19. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **5** (full spectrum).

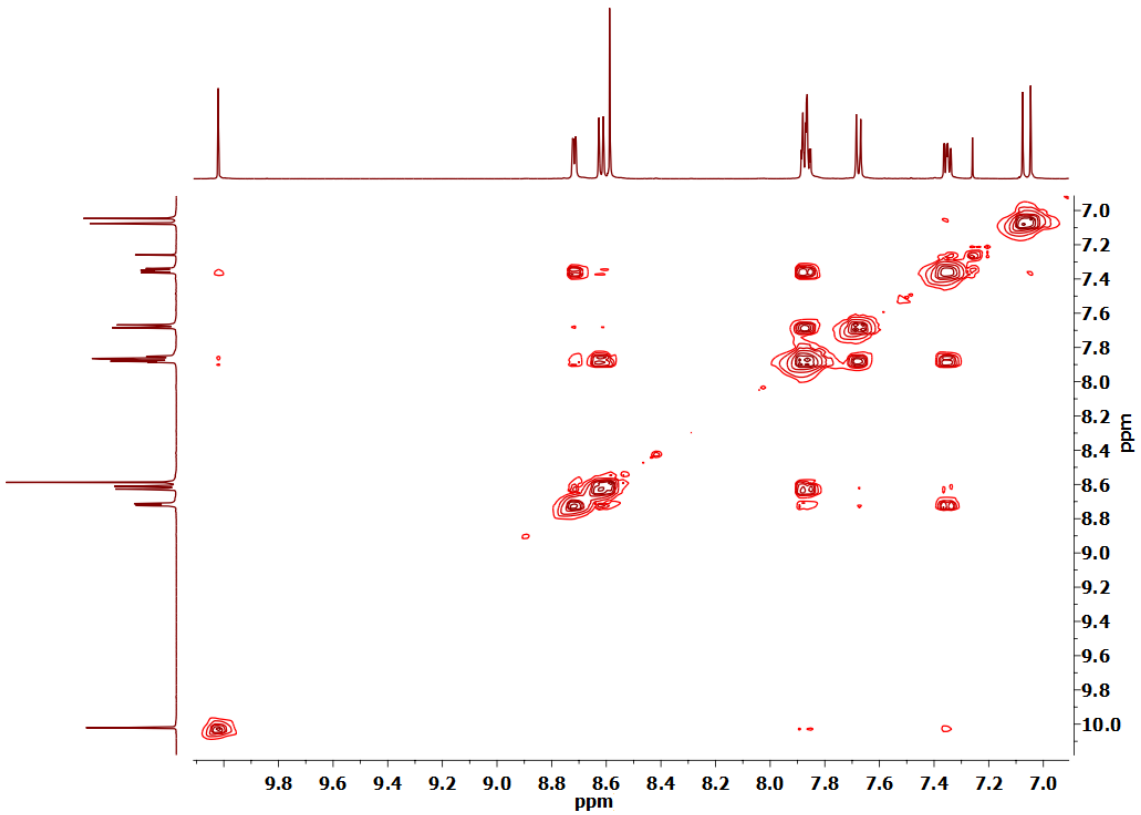


Figure S20. ^{1}H-^{1}H COSY NMR spectrum ($CDCl_3$, 500 MHz) of compound **5** (partial spectrum).

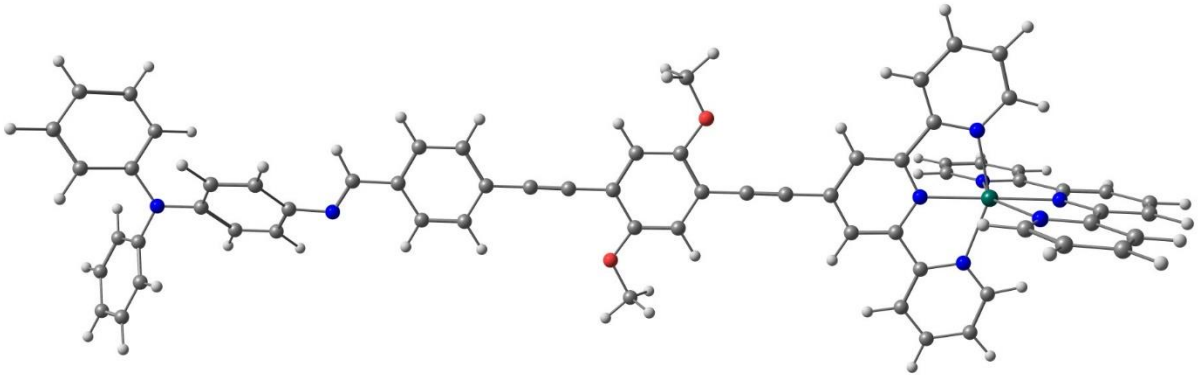


Figure S21. Structure of the model system considered for DFT computation at D3-B3LYP/6-31G(d) level (LANL2DZ: basis set and electron core potential of Zn; solvent = water)

XYZ coordinate of the model structure

Charge 2, multiplicity 1

C	5.518398000	1.167140000	0.174547000
C	6.904603000	1.181683000	0.173956000
C	6.992328000	-1.141639000	-0.163383000
C	5.609442000	-1.230832000	-0.170677000
C	4.822959000	-0.059420000	0.000253000
H	4.942377000	2.073715000	0.308119000
H	5.100133000	-2.176148000	-0.306612000
C	7.892666000	-2.315183000	-0.338328000
C	7.421511000	-3.622079000	-0.518293000
C	8.331429000	-4.663653000	-0.675359000
H	6.358323000	-3.828525000	-0.536148000
C	10.092237000	-3.062226000	-0.465904000
C	9.698704000	-4.383786000	-0.649937000
H	7.976927000	-5.680141000	-0.815625000
H	11.144625000	-2.792968000	-0.437670000
H	10.440837000	-5.165612000	-0.769040000
C	7.714038000	2.418981000	0.354768000
C	7.146528000	3.686691000	0.536494000
C	9.851243000	3.327102000	0.495389000
C	7.975584000	4.792525000	0.701906000
H	6.070931000	3.814286000	0.549635000
C	9.359880000	4.615087000	0.682632000
H	10.920823000	3.136917000	0.471914000
H	7.545712000	5.779244000	0.844001000
H	10.041333000	5.449305000	0.808669000
C	3.427675000	-0.119606000	-0.003579000
C	2.204960000	-0.204580000	-0.009867000
C	0.806830000	-0.280797000	-0.014111000
C	0.152981000	-1.540770000	-0.145581000
C	0.025523000	0.897693000	0.113698000
C	-1.236480000	-1.590393000	-0.144005000
C	-1.357614000	0.844800000	0.111570000
H	0.545697000	1.842038000	0.211764000
C	-2.013260000	-0.420055000	-0.018167000
H	-1.760335000	-2.532401000	-0.240487000
C	-3.417912000	-0.494230000	-0.020063000
C	-4.636347000	-0.573734000	-0.023031000
C	-6.047851000	-0.641661000	-0.023507000
C	-6.712665000	-1.884006000	-0.131104000
C	-6.821206000	0.541387000	0.085880000
C	-8.097767000	-1.936136000	-0.128765000
H	-6.127782000	-2.794537000	-0.214379000
C	-8.201996000	0.480271000	0.084373000
H	-6.311716000	1.496094000	0.169881000
C	-8.866874000	-0.760552000	-0.022145000
H	-8.600653000	-2.896563000	-0.211070000
H	-8.802034000	1.380094000	0.166459000
C	-10.323235000	-0.846018000	-0.023657000
H	-10.741206000	-1.859393000	-0.098001000
C	-12.450708000	0.143771000	0.025139000
C	-13.156483000	1.242514000	0.557635000
C	-13.204157000	-0.907338000	-0.546018000
C	-14.540177000	1.277307000	0.571943000
H	-12.581527000	2.055679000	0.989482000
C	-14.587278000	-0.870427000	-0.556093000
H	-12.700468000	-1.737666000	-1.032185000
C	-15.289009000	0.217374000	0.014789000
H	-15.055417000	2.121005000	1.016907000
H	-15.144029000	-1.671956000	-1.028915000
C	-17.447509000	-0.960488000	0.058829000
C	-17.120033000	-1.966491000	0.981640000
C	-18.540429000	-1.141275000	-0.802699000
C	-17.870117000	-3.140245000	1.028717000
H	-16.286454000	-1.818749000	1.660997000
C	-19.291454000	-2.313397000	-0.739343000
H	-18.792761000	-0.364098000	-1.516983000
C	-18.959068000	-3.319163000	0.171869000
H	-17.611280000	-3.910533000	1.749825000
H	-20.134239000	-2.444108000	-1.412163000
H	-19.545590000	-4.232012000	0.216513000
C	-17.392528000	1.490562000	-0.048761000
C	-17.025450000	2.472299000	-0.982319000
C	-18.468928000	1.728174000	0.819241000
C	-17.720823000	3.679052000	-1.034000000
H	-16.203282000	2.281382000	-1.664869000
C	-19.165604000	2.933327000	0.751497000

H	-18.750664000	0.969200000	1.542117000
C	-18.793842000	3.914856000	-0.170764000
H	-17.431658000	4.431116000	-1.762724000
H	-19.996087000	3.108648000	1.429429000
H	-19.337544000	4.853689000	-0.218629000
N	-16.690012000	0.248218000	0.007419000
N	-11.061735000	0.204962000	0.076352000
O	0.962055000	-2.621503000	-0.262999000
O	-2.178718000	1.915893000	0.224945000
C	0.360961000	-3.907779000	-0.391204000
H	-0.247872000	-4.151736000	0.487519000
H	-0.255940000	-3.970677000	-1.295541000
H	1.188497000	-4.614407000	-0.466735000
C	-1.598446000	3.206969000	0.352542000
H	-0.985700000	3.281492000	1.260345000
H	-0.988106000	3.458500000	-0.524571000
H	-2.435506000	3.902364000	0.422844000
Zn	9.734605000	0.123911000	0.007100000
C	12.582752000	0.055495000	1.159794000
C	12.561541000	0.429828000	-1.159048000
C	13.980534000	0.118207000	1.189938000
C	13.958835000	0.501723000	-1.193101000
C	14.666103000	0.343615000	-0.002516000
H	14.531025000	-0.002754000	2.114701000
H	14.492415000	0.676327000	-2.119180000
H	15.750307000	0.396297000	-0.003883000
C	11.691291000	0.583631000	-2.359396000
C	12.196417000	0.819486000	-3.642314000
C	11.310218000	0.947403000	-4.711045000
H	13.262507000	0.903328000	-3.816381000
C	9.514488000	0.603748000	-3.168818000
C	9.940990000	0.837212000	-4.475224000
H	11.687818000	1.130160000	-5.712271000
H	8.458394000	0.511364000	-2.931847000
H	9.217968000	0.929026000	-5.278377000
C	11.734422000	-0.179367000	2.362745000
C	12.264255000	-0.384510000	3.641000000
C	11.397375000	-0.593563000	4.712783000
H	13.334651000	-0.384161000	3.808705000
C	9.571118000	-0.385504000	3.182112000
C	10.022443000	-0.593848000	4.484384000
H	11.794095000	-0.753732000	5.710478000
H	8.509655000	-0.378671000	2.951213000
H	9.313735000	-0.751367000	5.290094000
N	10.361071000	0.480220000	-2.138577000
N	11.915070000	0.211301000	0.001285000
N	9.221662000	-2.052866000	-0.314171000
N	7.625403000	0.045667000	0.006679000
N	9.058960000	2.256436000	0.335585000
N	10.399036000	-0.184190000	2.148929000

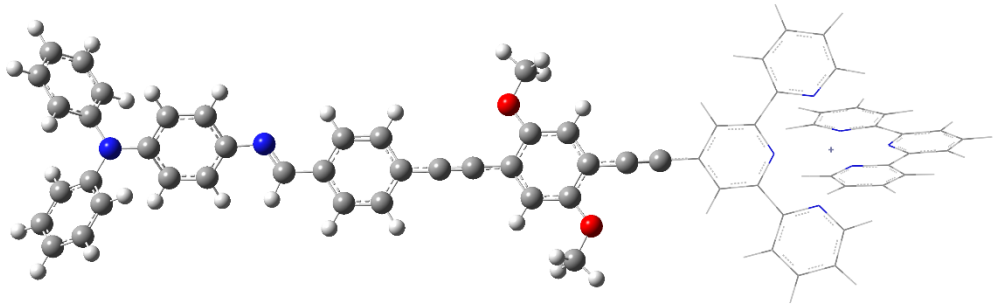


Figure S27. Structure of the charge-separated model system considered for DFT computation at D3-B3LYP/6-31G(d) level (LANL2DZ: basis set and electron core potential of Zn; solvent = water)

XYZ coordinate of the charge-separated model system model structure

Overall charge 2, multiplicity 1

C	-5.522223000	-1.096477000	-0.189664000	C	8.113788000	1.818437000	-0.090168000
C	-6.912999000	-1.133863000	-0.164390000	H	6.166187000	2.731385000	-0.160383000
C	-7.043771000	1.202768000	-0.030553000	C	8.153381000	-0.602892000	0.005983000
C	-5.657494000	1.323507000	-0.053273000	H	6.237707000	-1.575284000	0.010043000
C	-4.873438000	0.154071000	-0.131689000	C	8.849836000	0.621672000	-0.028750000
H	-4.930145000	-2.000373000	-0.247810000	H	8.639646000	2.769442000	-0.118963000
H	-5.169569000	2.288276000	-0.005594000	H	8.720590000	-1.526627000	0.052396000
C	-7.992599000	2.347253000	0.059655000	C	10.312611000	0.678136000	-0.001066000
C	-7.590799000	3.683616000	0.098333000	H	10.748828000	1.685485000	-0.049986000
C	-8.563433000	4.679259000	0.186208000	C	12.439450000	-0.284707000	0.055468000
H	-6.542039000	3.951527000	0.059859000	C	13.176263000	-1.247507000	0.768601000
C	-10.229104000	2.962806000	0.187102000	C	13.151306000	0.677380000	-0.688876000
C	-9.908648000	4.318162000	0.232276000	C	14.564384000	-1.218489000	0.792471000
H	-8.269317000	5.723301000	0.217482000	H	12.635669000	-2.001120000	1.333687000
H	-11.259449000	2.621735000	0.218588000	C	14.540187000	0.686097000	-0.697552000
H	-10.693979000	5.062310000	0.300651000	H	12.613380000	1.391351000	-1.305657000
C	-7.727042000	-2.379969000	-0.214555000	C	15.271132000	-0.251021000	0.055499000
C	-7.177743000	-3.657751000	-0.336071000	H	15.111656000	-1.952743000	1.374198000
C	-9.879031000	-3.253414000	-0.170621000	H	15.071449000	1.416877000	-1.298565000
C	-8.032031000	-4.759484000	-0.373579000	C	17.381927000	1.008456000	0.037904000
H	-6.106094000	-3.799631000	-0.403115000	C	16.953030000	2.077821000	0.840398000
C	-9.408699000	-4.559675000	-0.289135000	C	18.510967000	1.175568000	-0.779660000
H	-10.940737000	-3.037136000	-0.102221000	C	17.635705000	3.293143000	0.813181000
H	-7.622613000	-5.759896000	-0.468240000	H	16.084743000	1.949920000	1.478921000
H	-10.105318000	-5.389898000	-0.314495000	C	19.198957000	2.388198000	-0.786207000
C	-3.461153000	0.233064000	-0.145189000	H	18.843791000	0.352305000	-1.403749000
C	-2.245686000	0.301264000	-0.148375000	C	18.764266000	3.455670000	0.004586000
C	-0.832281000	0.358216000	-0.147129000	H	17.290775000	4.111495000	1.439418000
C	-0.165914000	1.610804000	-0.123412000	H	20.071336000	2.501782000	-1.424094000
C	-0.082064000	-0.836213000	-0.164351000	H	19.298294000	4.401332000	-0.008485000
C	1.227285000	1.638065000	-0.115914000	C	17.419760000	-1.448214000	0.064615000
C	1.308012000	-0.807422000	-0.155417000	C	17.025761000	-2.524620000	-0.745997000
H	-0.620774000	-1.774827000	-0.182580000	C	18.552169000	-1.585300000	0.882922000
C	1.976848000	0.446429000	-0.129941000	C	17.746064000	-3.718237000	-0.725906000
H	1.765307000	2.576982000	-0.096916000	H	16.154602000	-2.419554000	-1.384794000
C	3.393036000	0.495776000	-0.115677000	C	19.277765000	-2.775828000	0.882515000
C	4.609623000	0.542837000	-0.099753000	H	18.858011000	-0.756078000	1.512942000
C	6.029048000	0.575729000	-0.077535000	C	18.877781000	-3.850896000	0.083713000
C	6.724812000	1.802019000	-0.113751000	H	17.427873000	-4.542696000	-1.358246000
C	6.768854000	-0.628937000	-0.017352000	H	20.152291000	-2.866534000	1.521123000

H	19.440973000	-4.779545000	0.091486000
N	16.685083000	-0.230661000	0.055125000
N	11.040214000	-0.377603000	0.093315000
O	-0.961531000	2.709650000	-0.108898000
O	2.106755000	-1.906558000	-0.168803000
C	-0.343825000	3.998060000	-0.083211000
H	0.265446000	4.128226000	0.819065000
H	0.276749000	4.158454000	-0.972802000
H	-1.163922000	4.716735000	-0.076251000
C	1.488216000	-3.193304000	-0.192857000
H	0.866563000	-3.352701000	0.696587000
H	0.878459000	-3.324970000	-1.095001000
H	2.306921000	-3.913727000	-0.198628000
Zn	-9.727514000	-0.126861000	0.017909000
C	-12.397303000	-0.351195000	1.366235000
C	-12.553700000	-0.241943000	-0.972361000
C	-13.786799000	-0.440028000	1.491198000
C	-13.947997000	-0.326287000	-0.919884000
C	-14.558304000	-0.425803000	0.329828000
H	-14.262724000	-0.518568000	2.460524000
H	-14.548651000	-0.315427000	-1.820572000
H	-15.638924000	-0.492851000	0.398827000
C	-11.750912000	-0.134347000	-2.221429000
C	-12.311001000	-0.110331000	-3.500151000
C	-11.466574000	-0.008216000	-4.605602000
H	-13.383391000	-0.169992000	-3.639728000
C	-9.607435000	0.036828000	-3.101424000
C	-10.088933000	0.067163000	-4.408655000
H	-11.884374000	0.011744000	-5.606820000
H	-8.544660000	0.091496000	-2.885956000
H	-9.400049000	0.147230000	-5.241837000
C	-11.435456000	-0.351216000	2.502337000
C	-11.822422000	-0.435072000	3.841165000
C	-10.839251000	-0.426320000	4.830454000
H	-12.867800000	-0.505666000	4.115573000
C	-9.193512000	-0.254694000	3.103380000
C	-9.498739000	-0.334838000	4.460718000
H	-11.121647000	-0.490306000	5.876239000
H	-8.167590000	-0.181506000	2.755540000
H	-8.705551000	-0.325316000	5.199596000
N	-10.413923000	-0.060994000	-2.039319000
N	-11.828450000	-0.256225000	0.155617000
N	-9.299304000	2.005253000	0.103381000
N	-7.632740000	-0.002906000	-0.084769000
N	-9.063064000	-2.194395000	-0.134823000
N	-10.133213000	-0.262168000	2.152198000