

Electronic Supplementary Information (ESI)

s-Tetrazine Functionalized Hypercrosslinked Polymers for Efficient Photocatalytic Synthesis of Benzimidazoles

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1. Summary of Schemes and Figures

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2. General Information

Materials. 5-(4-methoxyphenyl)picolinonitrile (**1**)^[1] and 3,6-bis(5-(4-methoxyphenyl)pyridin-2-yl)-1,2,4,5-tetrazine (**2**)^[2] were prepared according to the literature procedures. Unless otherwise noted, the reagents (formaldehyde dimethyl acetal (FDA), benzene, 9H-fluorene and anhydrous FeCl₃, *etc.*) were purchased from Energy Chemical Reagent Co. Ltd and Adamas Reagent Co. Ltd could be used without further purification. 1,2-dichloroethane (DCE) was first dried by CaH₂ and further distilled before use. Suzuki coupling reaction mediated by Pd(PPh₃)₄ was carried out under N₂ by using Schlenk line techniques.

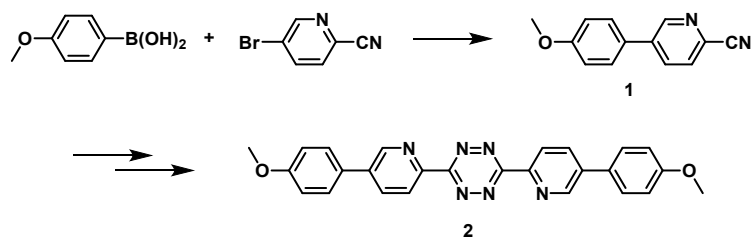
Methods. Flash column chromatography was carried out with silica gel (200-300 mesh). Liquid NMR spectra (¹H and ¹³C) were recorded on a Bruker Avance III 400 MHz NMR spectrometer (CDCl₃ or *d*₆-DMSO as solvent). The chemical shifts δ and coupling constants *J* are given in ppm and Hz, respectively. Solid-state NMR experiments were performed on a Bruker WB Avance II 400 MHz NMR spectrometer (4-mm double-resonance probe). The parameters were set as following: contact time was 3 ms (ramp 100), recycle delay was 2 s and the spinning rate was 10,000 \pm 1 Hz. FT-IR spectra were obtained with a Nicolet IS 20 instrument. The by-product 2-methyl benzimidazole was detected with a Shimadzu GCMS-QP2020 NX gas chromatography-mass spectrometer (GC-MS). Melting point (m.p.) was tested at a WRS-A1 apparatus under air atmosphere. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Quantachrome NovaWin 2200e system. The samples were outgassed at 120 °C for 8 h before analysis. Surface areas were calculated based on the adsorption data via the Brunauer-Emmett-Teller (BET) and Langmuir methods, respectively. The pore-size-distribution (PSD) curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. The pore volume was calculated from the amount of N₂ gas adsorbed at $p/p_0 = 0.99$ based on the t-plot analysis. Powder X-ray diffraction (PXRD) data were collected with a PANalytical X'Pert Pro diffractometer operated at 40 kV and 40 mA with Cu K α radiation at a scan rate of 15°/min.

Thermogravimetric analysis (TGA) measurements were used to study the thermal stability of the porous organic polymers. The tests were carried out on a SDT Q600 (V20.9 Build 20) instrument from 30 to 1000 °C under a N₂ atmosphere with a heating rate of 20 °C/min. Elemental analysis was performed on a Vario EL cube instrument. Scanning electron microscope (SEM) tests were applied to analysis the surface morphologies and microstructures of the obtained materials with Zeiss Merlin

compact SEM at a voltage of 10 kV. The samples used for SEM analysis were dispersed in ethanol, and then dipped and dried on a silicon wafer. Transmission electron microscopy (TEM) images were acquired by a FEI talos F200S transmission electron microscope (FEI, USA) operating at an acceleration voltage of 200 kV. The porous materials dispersed in ethanol were dipped and dried on copper meshes before TEM analysis. Part regions in TEM analytical samples were selected to collect the elemental Energy-dispersive X-ray spectroscopic (EDS) data at a voltage of 200 kV.

UV-Vis diffuse reflectance analysis for TZ-HCPs was recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. The bandgaps were estimated from the UV-Vis diffuse reflectance spectra through Kubelka-Munk function. Cyclic voltammetry (CV) experiments, photocurrent plots and electrochemical impedance spectra (EIS) were conducted on CHI660E Electrochemical Workstation (Shanghai Chen Hua Electrochemical Instrument) by using a three-electrode (a glassy-carbon or ITO working electrode, a saturated calomel reference electrode and a platinum wire counter electrode) electrochemical cell. For CV measurements, TZ-HCPs powder (6.0 mg) and Nafion were added into ethanol (0.5 mL) and ultrasound for 1 h. The working electrode could be obtained through drop-casting the slurry onto the glassy-carbon electrode, and then dried under air. All the tests were performed at a scan rate of 50 mV/s in degassed acetonitrile solution that contain Bu_4NPF_6 (0.1 M). EIS plots could be obtained by immersing the glassy-carbon electrode that covered with TZ-HCPs film in 0.1 M Na_2SO_4 aqueous solution. The experiments were performed with corresponding open-circuit voltage of TZ-HCP in the dark. The photocurrent measurements were performed in by illumination using 24 W LEDs at intervals of 10 seconds. The working electrodes were prepared by pasting slurry of TZ-HCPs (3.0 mg) in 5% Nafion (30 μL) onto the ITO conductive glass, dried under air, and then immersed in Na_2SO_4 aqueous solution (0.1 M).

3. Synthetic Procedures

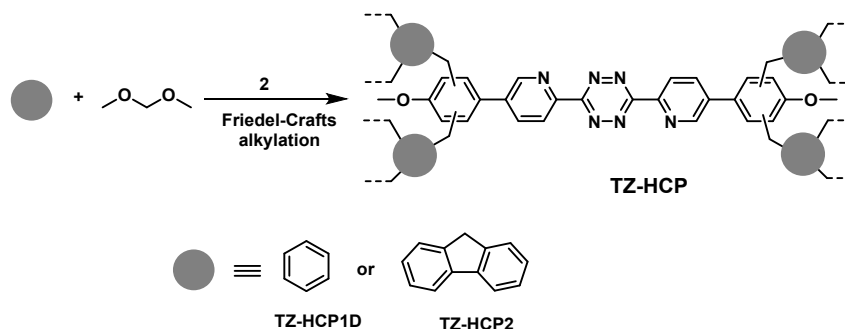


Scheme S1. Synthesis of functional building block 2.

Synthesis of compound 1.^[1] (4-methoxyphenyl)boronic acid (996 mg, 6.55 mmol), 5-bromopicolinonitrile (1.0 g, 5.46 mmol), potassium acetate (2.28 g, 16.38 mmol) and Pd(PPh₃)₄ (500 mg, 0.43 mmol) were added into a 100 mL two-neck flask. The system was degassed and back-filled with argon for three times, and then degassed THF/H₂O (2/1, 60 mL) was added under N₂ atmosphere. The reaction was stirred at 80 °C for 18 h. After removing the excess THF under reduced pressure, the system was extracted and dried with CH₂Cl₂ (50 mL × 3) and anhydrous Na₂SO₄, respectively. The obtained residual crude product after removal of the solvent was further purified by flash silica gel column chromatography (petroleum ether/ ethyl acetate = 4/1 as the eluent) to give product **1** as pale-yellow solid (1.12 g, 98% yield), m.p. 103.4-106.7 °C. ¹H NMR (400 MHz, CHCl₃): δ = 8.91 (dd, *J* = 0.8 Hz, 2.4 Hz, 1H), 7.95 (dd, *J* = 2.4 Hz, 8.0 Hz, 1H), 7.73 (dd, *J* = 0.8 Hz, 8.0 Hz, 1H), 7.57-7.54 (m, 2H), 7.06-7.03 (m, 2H), 3.88 (s, 3H) ppm; ¹³C NMR (100MHz, d₆-DMSO): δ = 160.8, 149.1, 139.4, 134.1, 131.4, 128.5, 128.4, 117.5, 114.9, 55.4 ppm.

Synthesis of monomer 2.^[2] Precursor **1** (371.4 mg, 1.76 mmol), sublimate sulphur (28 mg, 0.88 mmol) and ethanol (2 mL) were added into a dry two-neck flask. N₂H₄-H₂O (80%, 1.0 mL) was injected into the system under N₂ atmosphere and reflux. The mixtures were stirred for 18 h at 90 °C. After that, the reaction system was cooled to 0 °C, and then filtered, washed with ice ethanol (20 mL) to obtain brownish yellow powder. Without further purification, the intermediate was dispersed into 4 mL glacial acetic acid. Then, NaNO₂ (400 mg, 5.79 mmol) was added in batches at room temperature and stirred for 18 h at room temperature. The reaction mixtures were poured into saturated K₂CO₃ solution (100 mL) and left to stand for 20 min. Collected the precipitate through filtration and washed with water. The obtained solid was further dried in vacuum at 50 °C for 8 h and resulted in purplish red product **2** (34% yield for two steps), m.p. 272.5-274.2 °C. ¹H NMR (400

MHz, CF₃COOD): δ = 9.48 (d, J = 8.4 Hz, 2H), 9.44 (s, 2H), 9.184 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 4H), 7.34 (d, J = 8.0 Hz, 4H), 4.10 (s, 6H) ppm; ¹³C NMR (100 MHz, CF₃COOD): δ = 162.2, 159.0, 145.5, 144.2, 141.0, 137.8, 128.8, 128.6, 127.3, 124.5, 115.7, 54.9 ppm.



Scheme S2. Synthesis of TZ-HCPs.

Synthesis of TZ-HCP1D and TZ-HCP2. For TZ-HCP1D, photoactivate precursor **2** (165 mg, 0.37 mmol) and FeCl₃ (2.4 g, 14.8 mmol, 13.5 mol% relative to FDA and DCE) were added into a dry two-neck flask. Then, DCE (7.4 mL, 94.3 mmol) and benzene (0.66 mL, 7.43 mmol) were injected under argon atmosphere. The reaction was conducted for 0.5 h at room temperature before FDA (1.33 mL, 15.1 mmol) was added. The polymerization reaction was proceeded in stages at 45 °C first for 5 h and then 90 °C for 19 h. When the reaction was completed, MeOH (20 mL) was then added into the system and refluxed at 90 °C for 0.5 h. After cooling to ambient temperature, the precipitate was filtrated and washed in turn with water and MeOH. The collected solid was then stirred vigorously in con. HCl for 2 h to remove residual ferric salt and then filtrated, washed by saturated NaHCO₃ solution, water, DMF and MeOH. Afterward, the desired polymer was purified via a Soxhlet extraction for 24 h with MeOH/CH₂Cl₂ (1/1) and dried in vacuum oven for 12 h at 80 °C. Finally, TZ-HCP1D was obtained as brownish red powder (880 mg). Elemental analysis results (%) for TZ-HCP1D: C, 82.39; N, 2.70; H, 5.198. The same successive procedures were applied to prepare TZ-HCP2 except for the amounts and type of reagents: **2** (82.5 mg, 0.18 mmol), FeCl₃ (1.2 g, 7.38 mmol, 13.5 mol%), 9*H*-fluorene (612 mg, 3.68 mmol), DCE (3.7 mL, 47.2 mmol), FDA (0.67 mL, 7.57 mmol). TZ-HCP2 was obtained as brownish yellow powder (798 mg). Elemental analysis results (%) for TZ-HCP2: C, 83.61; N, 1.53; H, 4.806.

4. Characterization of TZ-HCP1D and TZ-HCP2

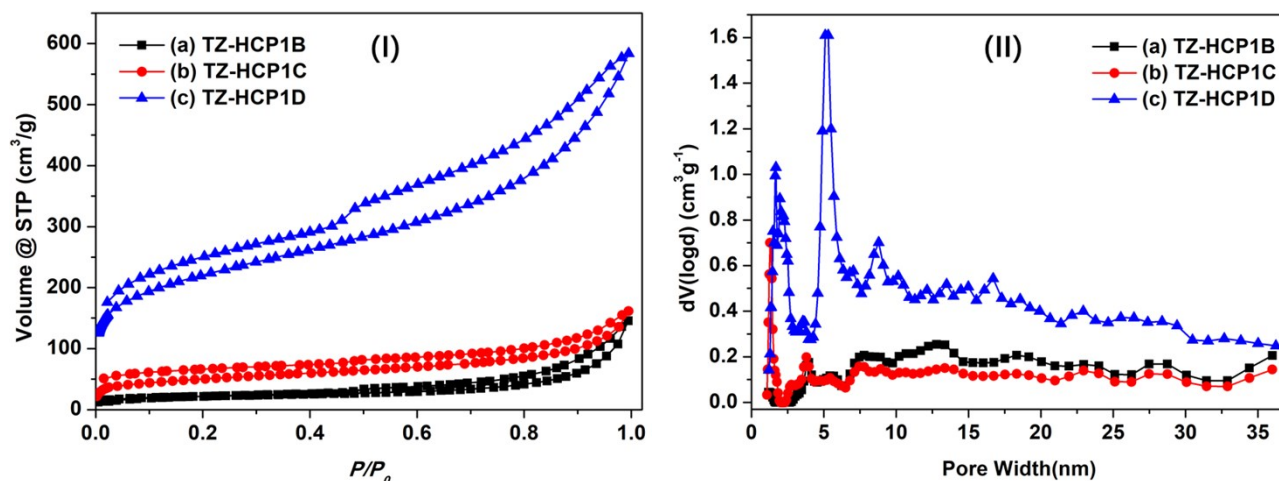


Figure S1. Nitrogen sorption isotherms (I) and pore size distribution (II) of TZ-HCP1B (a), TZ-HCP1C (b) and TZ-HCP1D (c).

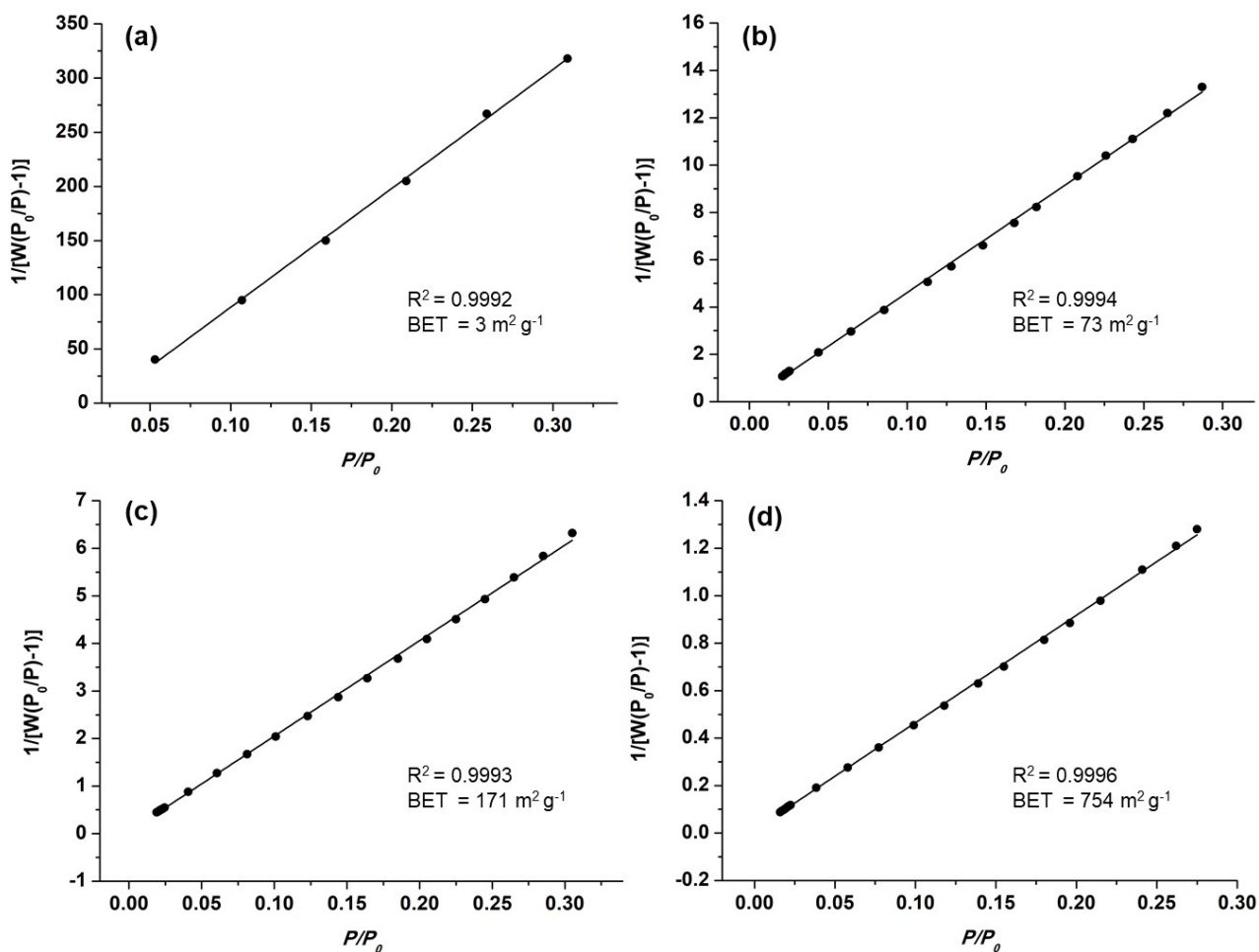


Figure S2. BET surface area plots of (a) TZ-HCP1A, (b) TZ-HCP1B, (c) TZ-HCP1C and (d) TZ-HCP1D.

In addition, we attempted to study the influence of FeCl_3 loading, and set it as a lower dosage, *e.g.*, 5.6 mol%. It should be noted that the same successive procedures and dosage of reagents except FeCl_3 (1.0 g, 6.17 mmol, 5.6 mol%) could only give 523 mg TZ-HCP1D as reddish black powder. In comparison with the TZ-HCP1D synthesized under standard conditions, the network obtained from 5.6% FeCl_3 has unsatisfactory BET surface areas ($231 \text{ m}^2\text{g}^{-1}$) and smaller pore volume ($0.32 \text{ cm}^3 \text{ g}^{-1}$) (Figure S3).

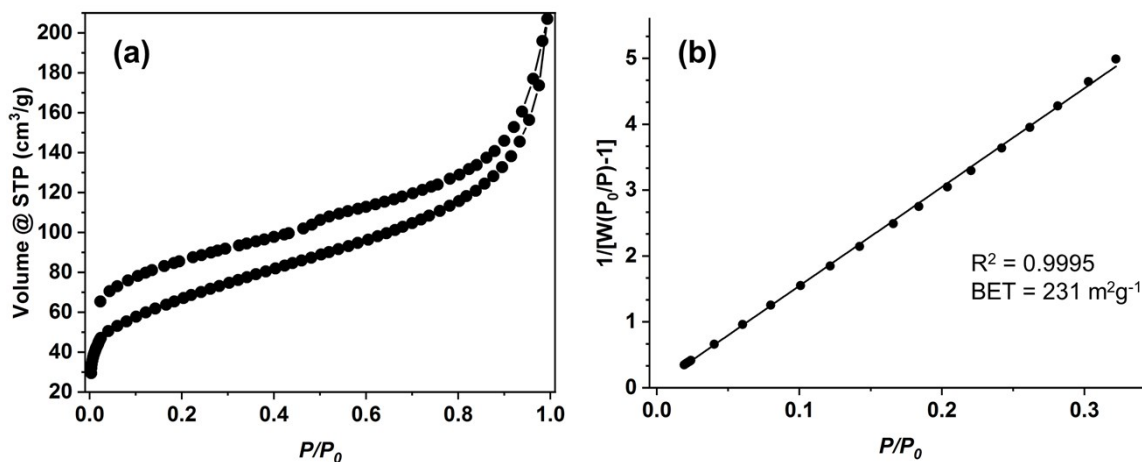


Figure S3. Nitrogen sorption isotherm (a) and BET surface area plot (b) of TZ-HCP1D synthesized under 5.6 mol% FeCl_3 .

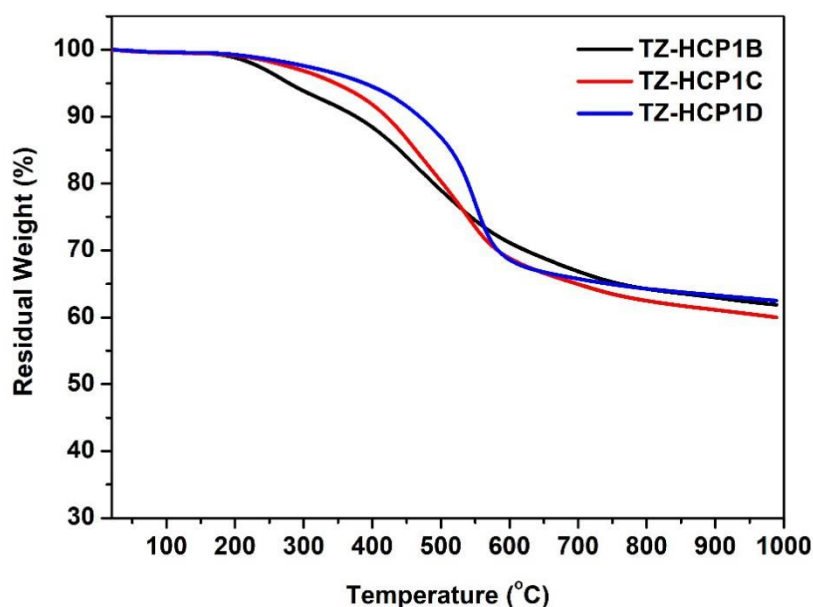


Figure S4. TGA curves of TZ-HCP1B (black), TZ-HCP1C (red) and TZ-HCP1D (blue).

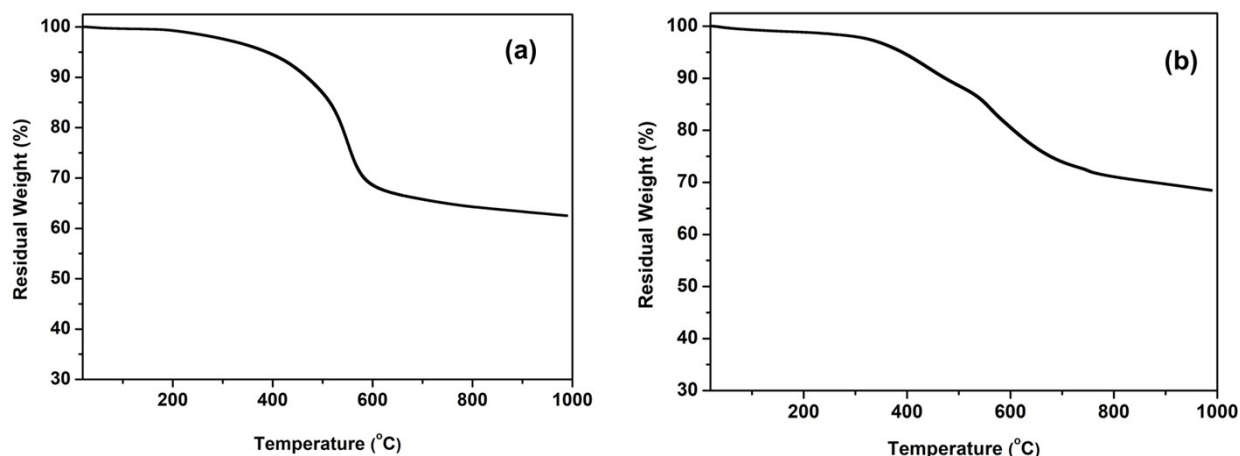


Figure S5. TGA curves of TZ-HCP1D (a) and TZ-HCP2 (b).

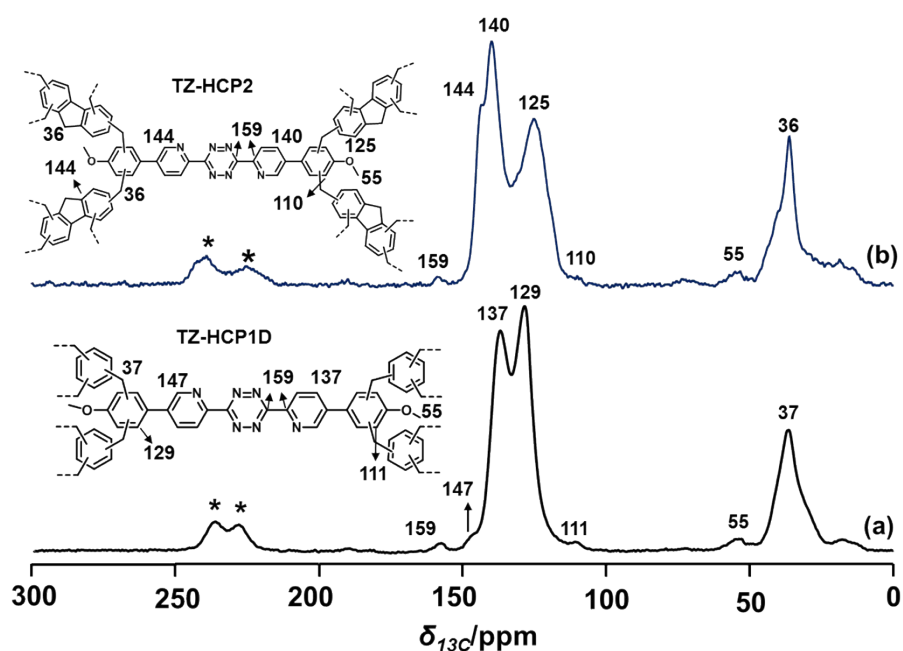


Figure S6. Solid-state ¹³C CP/MAS NMR spectra (100 MHz) of TZ-HCP1D (a) and TZ-HCP2 (b). The asterisks denote the spinning sidebands. As shown in Figure S5, the resonance peaks at $\delta = 110$ – 147 ppm are attributed to aromatic carbon in (non-)substituted benzene, pyridine and fluorene. Additional, NMR signals at ca. 36 ppm and 55 ppm indicated the existence of methylene carbon and methoxy group, while 159 ppm can be ascribed to the carbon atoms of C=N in pytz (pyridine and *s*-tetrazine rings).

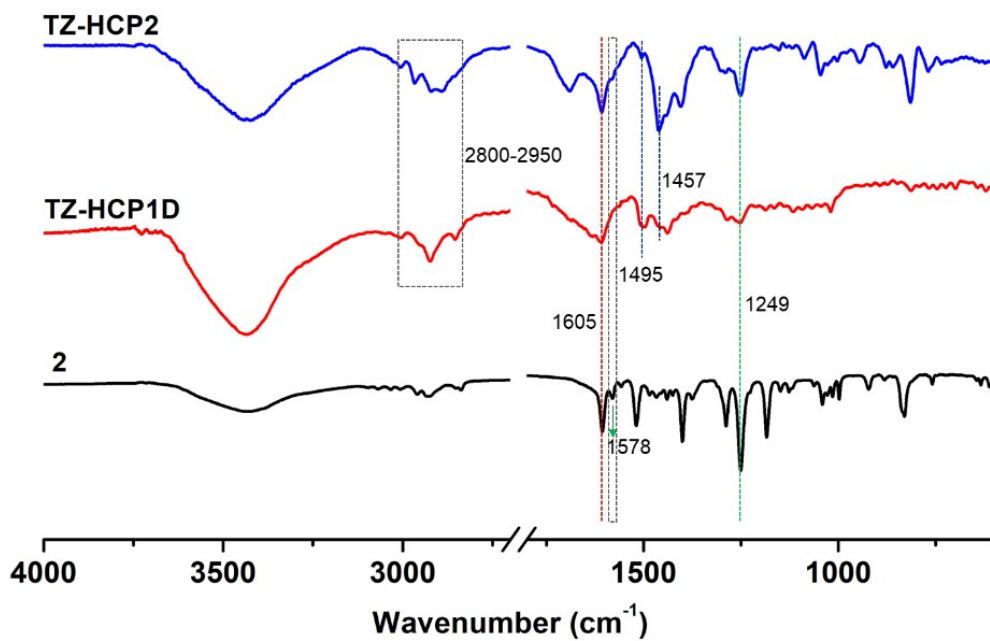


Figure S7. FT-IR spectra of monomer **2**, TZ-HCP1D (a) and TZ-HCP2. It should be noted that the weak signals at about 1578 cm^{-1} could be ascribed to the vibrations of C=N in pyridine rings.^[3]

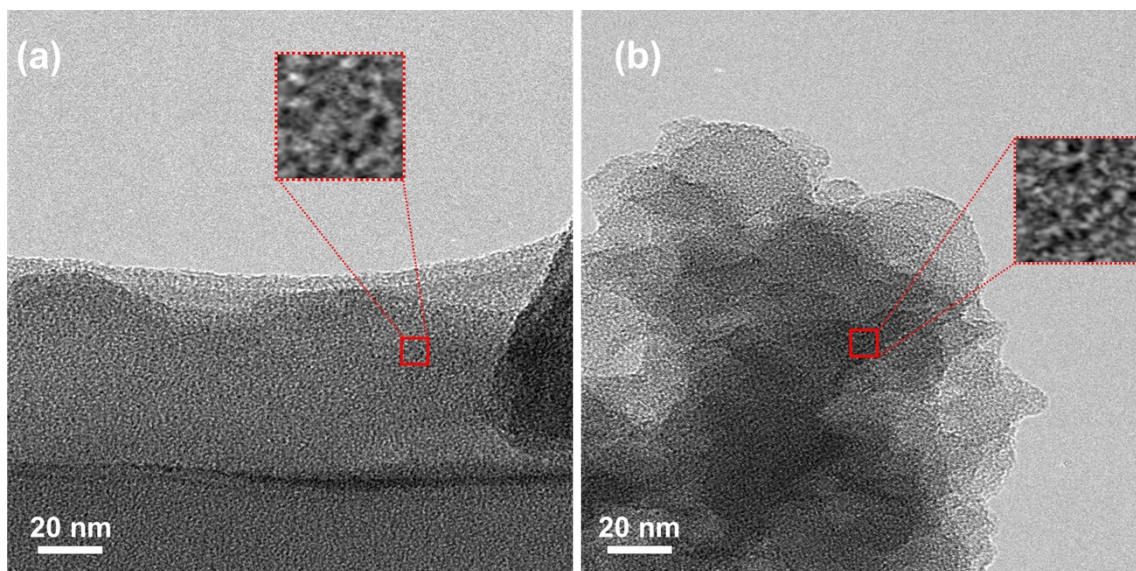


Figure S8. TEM images of TZ-HCP1D (a) and TZ-HCP2 (b).

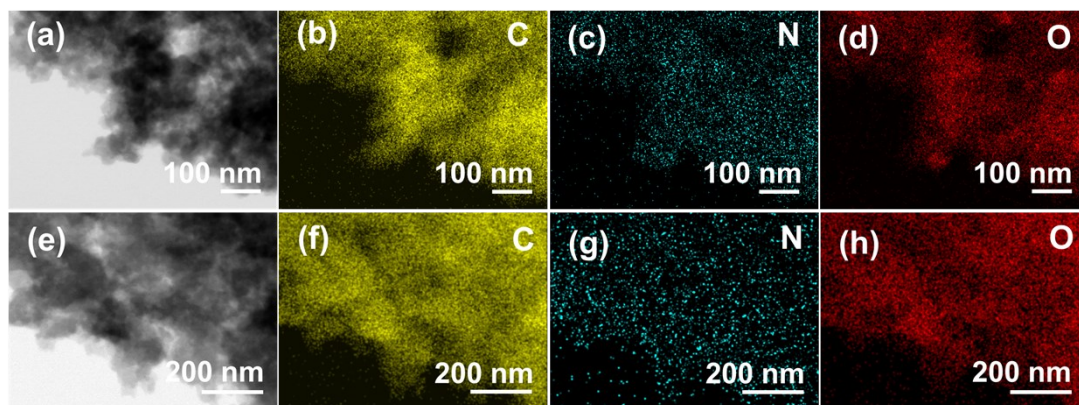


Figure S9. EDS mapping images of C, N and O for TZ-HCP1D (a-d) and TZ-HCP2 (e-h).

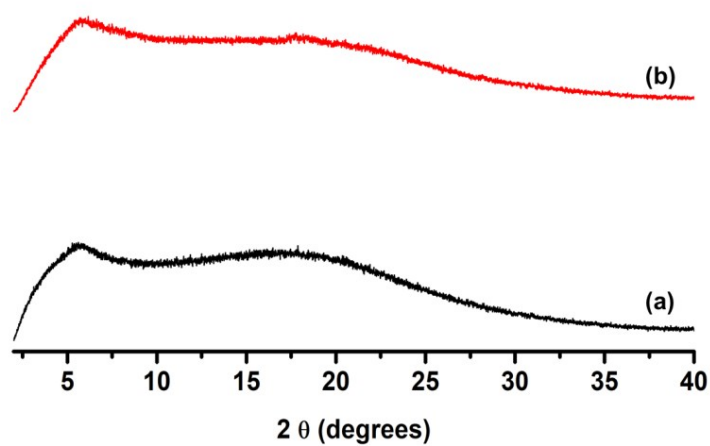


Figure S10. Powder X-ray diffraction of TZ-HCP1D (a) and TZ-HCP2 (b).

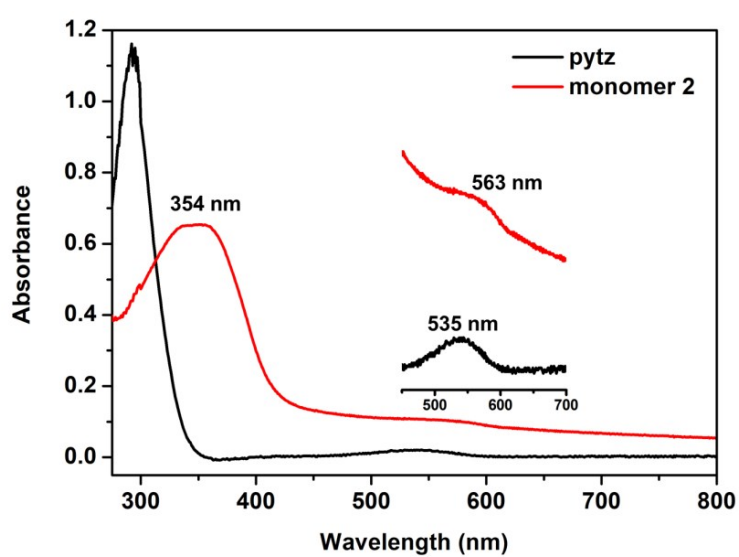


Figure S11. UV-vis absorption spectra of pytz and monomer 2 (in DMF).

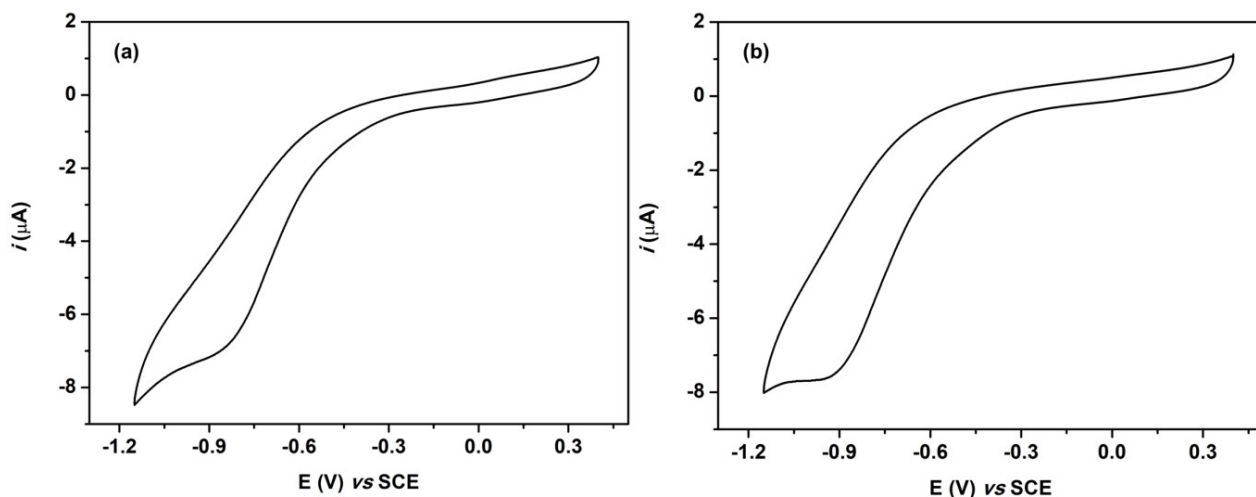


Figure S12. Cyclic voltammetry curves for TZ-HCP1D (a) and TZ-HCP2 (b). The experiments were performed in anhydrous MeCN solution of Bu_4NPF_6 (0.1 M) at a scan rate of 50 mV/s. According to Figure S12, the conduction band positions (vs. SCE) for TZ-HCP1D and TZ-HCP2D could be estimated as -0.48 V and -0.54 V, respectively.

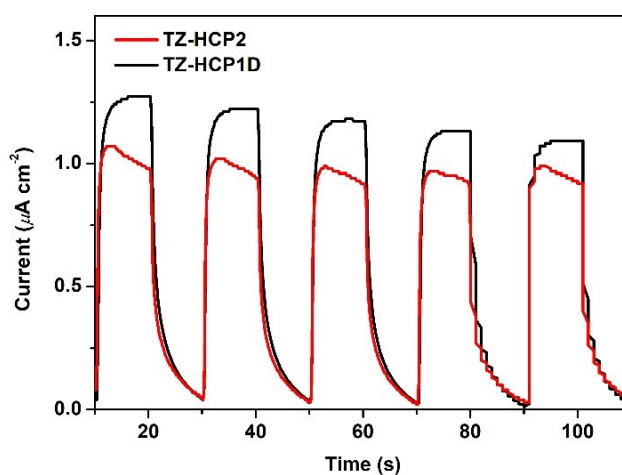


Figure S13. Transient photocurrent response of TZ-HCP1D and TZ-HCP2 with light on/off cycles under visible light irradiation (24 W white LEDs) in 0.1 M Na_2SO_4 electrolyte solution at 0.4 V vs. SCE.

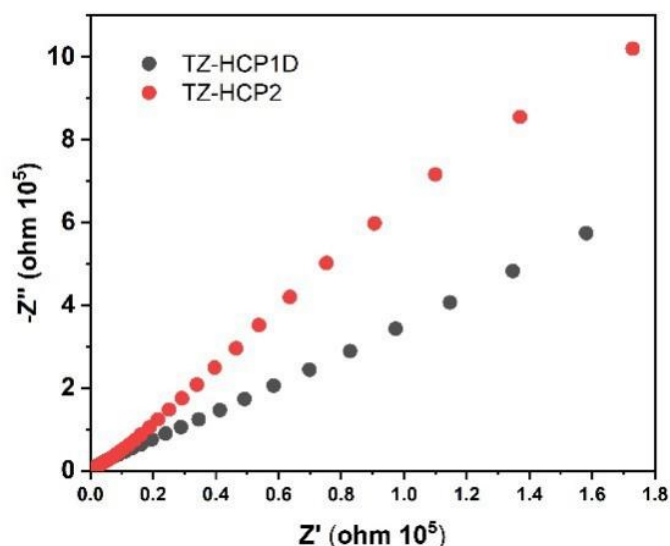
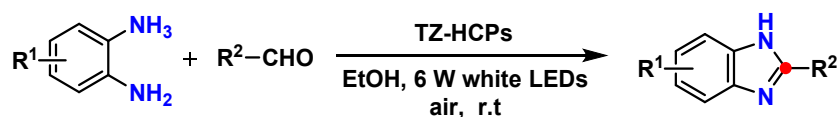
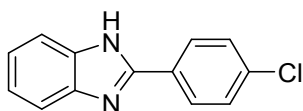


Figure S14. Electrochemical impedance spectroscopy of TZ-HCP1D and TZ-HCP2.

5. Typical Procedures to Synthesize Benzimidazoles under Visible Light

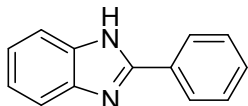


TZ-HCP1D (10 mg, 1.6 mol%) or TZ-HCP2 (17.8 mg, 1.6 mol%), *o*-aromatic diamine (0.2 mmol), aldehydes (0.2 mmol) and EtOH (4.0 mL) were added into a 10 mL pyrex glass tube. The reaction mixture was opened to air and stirred at room temperature under 6 W white LEDs (the distance between LEDs and reaction tube is about 10 cm, light intensity: 30 mW/cm²). Upon the completion of reaction as monitored by TLC, the heterogeneous catalyst could be isolated through centrifugation and thoroughly washed by acetone (4 mL × 3). After the organic solvent was removed by vacuum, the residue was further purified by flash column chromatography (with petroleum/acetone = 10/1~3/1 as eluent). Collected the effluent that contain product and removed the solvent, 2-substituted benzimidazoles could be obtained as solid powers. The dried pure solid above was then used to estimate the yield of product. The information (NMR data, melting point, isolated yield, *etc.*) of products catalyzed by TZ-HCP1D was summarized as bellow.

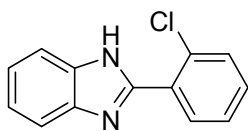


5a. Prepared according to the typical procedure with benzene-1,2-diamine and *p*-chlorobenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum

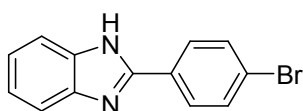
ether/acetone = 6/1 as eluent) to afford the product as a white solid (98% yield), m.p. = 290.2-292.8 °C.^[4] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.99 (br, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.64–7.22 (m, 4H), 7.23-7.21 (m, 2H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 150.6, 135.0, 131.6, 129.5, 129., 128.6, 122.6, 121.5 ppm.



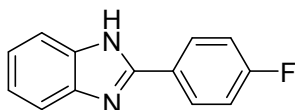
5b. Prepared according to the typical procedure with benzene-1,2-diamine and benzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 as eluent) to afford the product as a white solid (99% yield), m.p. = 291.5 -292.8°C.^[4] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.92 (br, 1H), 8.20 (d, *J* = 7.2 Hz, 2H), 7.62–7.50 (m, 5H), 7.23-7.21 (m, 2H) ppm; **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 151.7, 130.7, 130.3, 129.4, 126.9, 122.6 ppm.



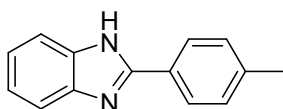
5c. Prepared according to the typical procedure with benzene-1,2-diamine and *o*-chlorobenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 4/1 as eluent) to afford the product as a white solid (99% yield), m.p. = 218.3-220.1 °C.^[4b, 5a] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.73 (br, 1H), 7.92-7.90 (m, 1H), 7.70-7.64 (m, 2H), 7.56-7.49 (m, 3H), 7.24 (d, 2H, *J* = 4.6 Hz); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 149.6, 143.7, 135.2, 132.6, 132.1, 131.7, 130.8, 130.5, 128.0, 123.2, 122.2, 119.6, 112.2 ppm.



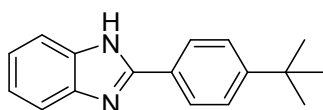
5d. Prepared according to the typical procedure with benzene-1,2-diamine and 4-bromobenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 as eluent) to afford the product as a white solid (96% yield), m.p. = 286.5-288.5 °C.^[4b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 13.00 (br, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.76 (d, 2H, *J* = 8.4 Hz), 7.67-7.54 (m, 2H), 7.22 (s, 2H) ppm; **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 150.2, 135.0, 132.1, 132.0, 129.4, 128.3, 123.2, 122.8, 121.8, 119.0, 111.4 ppm.



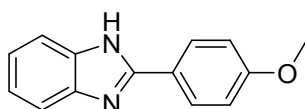
5e. Prepared according to the typical procedure with benzene-1,2-diamine and 4-fluorobenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 8/1 as eluent) to afford the product as a white solid (90% yield), m.p. = 252.6-253.4 °C.^[4b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.93 (br, 1H), 8.24-8.12 (m, 2H), 7.60 (s, 2H), 7.43-7.40 (m, 2H), 7.23-7.19 (m, 2H) ppm; **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 163.53 (d, *J* = 248.3 Hz), 150.8, 132.5, 129.2 (d, *J* = 8.7 Hz), 127.3 (d, *J* = 2.9 Hz), 122.6, 116.5 (d, *J* = 22.0 Hz) ppm.



5f. Prepared according to the typical procedure with benzene-1,2-diamine and 4-methylbenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 6/1 as eluent) to afford the product as a white solid (98% yield), m.p. = 273.5-275.2 °C.^[4b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.82 (br, 1H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.21-7.18 (m, 2H), 2.39 (s, 3H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 151.9, 144.3, 140.0, 135.4, 130.0, 127.9, 126.9, 122.8, 122.0, 119.2, 111.7, 21.4 ppm.

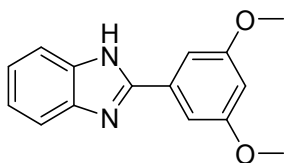


5g. Prepared according to the typical procedure with benzene-1,2-diamine and 4-(tert-butyl)benzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 as eluent) to afford the product as a white solid (97% yield), m.p. = 255.4-257.7 °C.^[5b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.83 (br, 1H), 8.12 (d, *J* = 8.2 Hz, 2H), 7.65-7.53 (m, 4H), 7.20 (s, 2H), 1.34 (s, 9H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 152.5, 151.3, 127.4, 126.2, 125.7, 121.9, 118.7, 111.3, 34.5, 30.9 ppm.

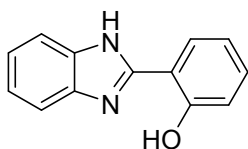


5h. Prepared according to the typical procedure with benzene-1,2-diamine and 4-methoxybenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 as eluent) to afford the product as a white solid (92% yield), m.p. = 227-228 °C.^[5b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.75 (br, 1H), 8.15-8.11 (m, 2H), 7.63-7.62 (m, 1H), 7.51-7.49 (m, 1H), 7.19-7.16 (m, 2H), 7.14-7.10 (m, 2H), 3.85 (s, 3H) ppm. **¹³C NMR** (101

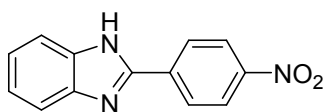
MHz, d_6 -DMSO): δ = 160.6, 151.3, 143.9, 135.0, 128.0, 122.7, 122.1, 121.4, 118.5, 114.4, 111.0, 55.3 ppm.



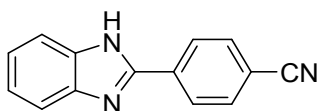
5i. Prepared according to the typical procedure with benzene-1,2-diamine and 3,5-dimethoxybenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (93% yield), m.p. = 215.3-216.7 °C. **$^1\text{H NMR}$** (400 MHz, d_6 -DMSO): δ = 12.89 (br, 1H), 7.65-7.56 (m, 2H), 7.38 (s, 2H), 7.38 (s, 2H), 6.62 (s, 1H), 3.85 (s, 6H); **$^{13}\text{C NMR}$** (101 MHz, d_6 -DMSO): δ = 161.3, 151.5, 144.1, 138.5, 135.4, 132.4, 123.1, 122.2, 119.4, 111.8, 104.7, 102.5, 55.9 ppm.



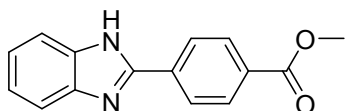
5j. Prepared according to the typical procedure with benzene-1,2-diamine and 2-hydroxybenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 as eluent) to afford the product as a pale yellow solid (87% yield), m.p. = 238.9-240.6 °C.^[4] **$^1\text{H NMR}$** (400 MHz, d_6 -DMSO): δ = 13.22 (br, 1H), 13.19 (br, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.73-7.61 (m, 2H), 7.40-7.36 (m, 1H), 7.28 (s, 2H), 7.06-7.00 (m, 2H); **$^{13}\text{C NMR}$** (101 MHz, d_6 -DMSO): δ = 158.0, 151.7, 140.9, 133.4, 133.2, 131.7, 126.2, 123.3, 122.4, 119.1, 118.0, 117.2, 112.3, 112.6, 111.5 ppm.



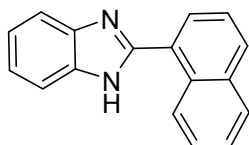
5k. Prepared according to the typical procedure with benzene-1,2-diamine and 4-nitrobenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a yellow solid (96% yield), m.p. 315.7-316.8.^[4b] **$^1\text{H NMR}$** (400 MHz, d_6 -DMSO): δ = 13.29 (br, 1H), 8.43-8.38 (m, 4H), 7.66 (s, 2H), 7.27 (s, 2H); **$^{13}\text{C NMR}$** (101 MHz, d_6 -DMSO): δ = 149.5, 148.3, 136.5, 127.8, 124.7, 123.3 ppm.



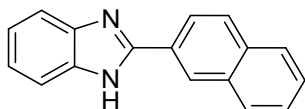
5l. Prepared according to the typical procedure with benzene-1,2-diamine and 4-formylbenzonitrile. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (99% yield), m.p. 265.9-268.2 °C.^[6a] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 13.19 (br, 1H), 8.35-8.33 (m, 2H), 8.04-8.02 (m, 2H), 7.67-7.64 (m, 2H), 7.27-7.26 (m, 2H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 149.8, 134.8, 133.5, 127.5, 123.8, 119.9, 119.1, 112.4 ppm.



5m. Prepared according to the typical procedure with benzene-1,2-diamine and methyl 4-formylbenzoate. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (95% yield), m.p. 233.4-235.2 °C.^[6a] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 13.12 (br, 1H), 8.32 (d, *J* = 8.0 Hz, 2H), 8.12 (d, *J* = 7.9 Hz, 2H), 7.70-7.57 (m, 2H), 7.24 (s, 2H), 3.89 (s, 3H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 165.8, 150.0, 143.8, 135.1, 134.3, 130.2, 129.8, 126.55, 123.1, 122.0, 119.2, 111.6, 52.3 ppm.

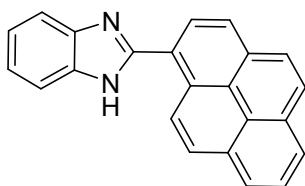


5n. Prepared according to the typical procedure with benzene-1,2-diamine and 1-naphthaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 10/1 as eluent) to afford the product as a white solid (99% yield), m.p. 268.3-270 °C.^[6b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.93 (br, 1H), 9.12 (d, *J* = 8.0 Hz, 1H), 8.12-8.10 (m, 1H), 8.07-8.01 (m, 2H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.72-7.58 (m, 4H), 7.31-7.24 (m, 2H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 151.8, 144.4, 134.9, 134.1, 131.0, 130.6, 128.9, 128.3, 128.0, 127.5, 126.8, 125.7, 123.1, 122.1, 119.5, 111.8 ppm.

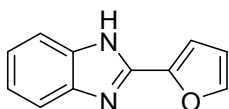


5o. Prepared according to the typical procedure with benzene-1,2-diamine and 2-naphthaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (96% yield), m.p. 212.2-214.1 °C.^[4b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 13.10 (br, 1H), 8.77 (s, 1H), 8.36-8.35 (m, 1H), 8.10-8.05

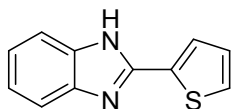
(m, 2H), 8.00-7.98 (m, 1H), 7.71-7.57 (m, 4H), 7.24-7.24 (m, 2H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 151.7, 144.4, 135.7, 134.0, 133.3, 126.7, 129.0, 128.9, 128.3, 128.1, 127.6, 127.4, 126.3, 124.4, 123.1, 122.3, 121.5, 119.4, 111.9$ ppm.



5p. Prepared according to the typical procedure with benzene-1,2-diamine and pyrene-1-carbaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 4/1 as eluent) to afford the product as a deep yellow solid (99% yield), m.p. 312.3-314.5 °C.^[7a] ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 13.12$ (br, 1H), 9.50 (d, $J = 8.8$ Hz, 1H), 8.55-8.48 (m, 2H), 8.36-8.30 (m, 5H), 8.16-8.15 (m, 2H), 7.85-7.65 (m, 2H), 7.30 (s, 1H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 151.7, 144.1, 134.7, 131.6, 130.9, 130.3, 129.6, 128.7, 128.5, 128.4, 127.3, 126.6, 125.9, 125.6, 124.8, 124.5, 124.3, 123.7, 122.7, 121.7, 119.1, 111.4$ ppm.

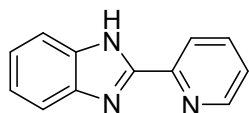


5q. Prepared according to the typical procedure with benzene-1,2-diamine and furan-2-carbaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 as eluent) to afford the product as a pale-yellow solid (92% yield), m.p. 283.1-285.3 °C.^[5b, 7b] ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 12.91$ (br, 1H), 7.94 (s, 1H), 7.62-7.49 (m, 2H), 7.20-7.19 (m, $J = 2.4$ Hz, 3 H), 6.727 (s, 1H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 145.6, 144.6, 143.6, 134.2, 131.4, 122.6, 121.8, 118.8, 112.3, 11.3, 110.5$ ppm.

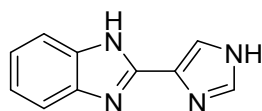


5r. Prepared according to the typical procedure with benzene-1,2-diamine and thiophene-2-carbaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 to 3/1 as eluent) to afford the product as a light brown solid (85% yield), m.p. > 320 °C.^[4b, 6b] ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 12.97$ (br, 1H), 7.84 (d, $J = 3.1$ Hz, 1H), 7.73 (d, $J = 4.8$ Hz, 1H), 7.62 (d, $J = 7.48$ Hz, 1H), 7.51 (d, $J = 7.48$ Hz, 1H), 7.25-7.16 (m, 3H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 147.0, 143.6, 134.7, 133.7, 128.7, 128.3, 126.7, 122.6,$

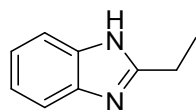
121.7, 118.5, 111.1 ppm.



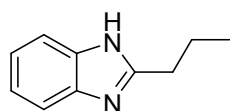
5s. Prepared according to the typical procedure with benzene-1,2-diamine and picolinaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 10/1 as eluent) to afford the product as a white solid (99% yield), m.p. 218.3-220 °C.^[3a, 7b] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 13.10 (br, 1H), 8.73 (d, *J* = 3.2 Hz, 1H), 8.33 (d, *J* = 7.6 Hz, 1H), 8.00 (t, *J* = 7.2 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.55-7.52 (m, 2H), 7.26-7.19 (m, 2H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 150.7, 149.3, 148.5, 143.9, 137.5, 134.9, 124.7, 123.1, 121.9, 121.4, 119.3, 112.0 ppm.



5t. Prepared according to the typical procedure with benzene-1,2-diamine and 1H-imidazole-4-carbaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 4/1 as eluent) to afford the product as a white solid (91% yield), m.p. 287.4-289.6 °C.^[7c] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.58 (br, 2H), 7.87-7.81 (m, 2H), 7.49 (s, 2H), 7.13-7.11 (m, 2H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 148.7, 137.0, 121.8, 117.7, 115.2 ppm.

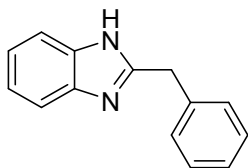


5u. Prepared according to the typical procedure with benzene-1,2-diamine and propionaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (98% yield), m.p. 164.4-166.1 °C.^[7d] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.17 (br, 1H), 7.47-7.45 (m, 2H), 7.12-7.10 (m, 2H), 2.86-2.80 (q, 2H), 1.32 (t, *J* = 7.52, 3H); **¹³C NMR** (101 MHz, *d*₆-DMSO): δ = 155.1, 120.0, 113.2, 21.0, 11.2 ppm.

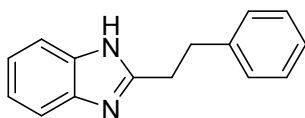


5v. Prepared according to the typical procedure with benzene-1,2-diamine and butyraldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (84% yield), m.p. 154.3-156.2 °C.^[8a] **¹H NMR** (400 MHz, *d*₆-DMSO): δ = 12.17 (br, 1H), 7.46 (s, 2H), 7.12-7.10 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H),

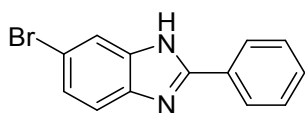
1.84-1.75 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H), 1.340-1.236 (m, 3H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 155.4, 121.5, 31.0, 21.4, 14.2$ ppm.



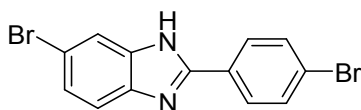
5w. Prepared according to the typical procedure with benzene-1,2-diamine and 2-phenylacetaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (82% yield), m.p. 182.6-184.8 °C.^[8b] ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 12.28$ (br, 1H), 7.48 (s, 2 H), 7.33-7.23 (m, 5H), 7.12 (s, 2H), 4.17 (s, 2H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 153.5, 137.6, 128.7, 128.4, 126.5, 121.2, 34.9$ ppm.



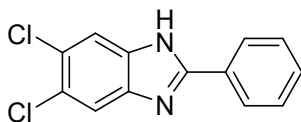
5x. Prepared according to the typical procedure with benzene-1,2-diamine and 3-phenylpropanal. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 3/1 as eluent) to afford the product as a white solid (86% yield), m.p. 187.3-189.1 °C.^[7c] ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 12.24$ (br, 1H), 7.48 (s, 2 H), 7.31-7.26 (m, 4H), 7.20-7.17 (m, 1H), 7.13-7.10 (m, 2H), 3.12 (s, 4H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 154.8, 141.5, 128.8, 128.7, 126.5, 121.6, 33.8, 30.8$ ppm.



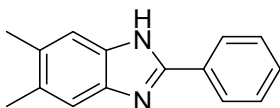
5y. Prepared according to the typical procedure with 4-bromobenzene-1,2-diamine and benzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 as eluent) to afford the product as a white solid (98% yield), m.p. 200.2-202 °C.^[7b] ^1H NMR (400 MHz, d_6 -DMSO): $\delta = 13.14$ -13.11 (d, br, 1H), 8.19-8.17 (m, 2H), 7.97-7.87 (m, 1H), 7.64-7.49 (m, 4H), 7.36-7.27 (m, 1H); ^{13}C NMR (101 MHz, d_6 -DMSO): $\delta = 131.2, 130.7, 130.1, 129.7, 129.5, 129.3, 129.0, 127.1, 121.7, 114.4, 113.6$ ppm.



5z. Prepared according to the typical procedure with 4-bromobenzene-1,2-diamine and 4-bromobenzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 10/1 to 6/1 as eluent) to afford the product as a white solid (95% yield), m.p. 210.9-212.8 °C. $^1\text{H NMR}$ (400 MHz, d_6 -DMSO): δ = 13.21-13.18 (br, 1H), 8.11 (d, J =8.5 Hz, 2H), 7.87-7.50 (m, 4H), 7.38-7.34 (m, 1H).



5aa. Prepared according to the typical procedure with 4,5-dichlorobenzene-1,2-diamine and benzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 4/1 as eluent) to afford the product as a white solid (98% yield), m.p. 216-217.3 °C.^[4a] $^1\text{H NMR}$ (400 MHz, d_6 -DMSO): δ = 13.126 (br, 1H), 8.19-8.17 (m, 2H), 7.97-7.80 (m, 2H), 7.65-7.49 (m, 3H); $^{13}\text{C NMR}$ (101 MHz, d_6 -DMSO): δ = 153.8, 132.9, 130.6, 129.29, 129.26, 129.1, 128.6, 126.7 ppm.



5ab. Prepared according to the typical procedure with 4,5-dimethylbenzene-1,2-diamine and benzaldehyde. The crude product was purified by flash column chromatography on silica gel (petroleum ether/acetone = 5/1 to 3/1 as eluent) to afford the product as a white solid (99% yield), m.p. 249.3-250.9 °C.^[4a] $^1\text{H NMR}$ (400 MHz, d_6 -DMSO): δ = 12.62 (br, 1H), 8.14-8.12 (m, 3H), 7.54-7.51 (m, 2H), 7.47-7.42 (m, 2H), 7.28 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, d_6 -DMSO): δ = 157.6, 150.8, 143.4, 143.0, 131.0, 130.9, 130.4, 129.9, 129.3, 126.7, 119.4, 111.8, 20.5 ppm.

6. Scale-up Experiment for the Synthesis of 5s

Benzene-1,2-diamine **3a** (1.08 g, 10 mmol), picolinaldehyde **4s** (1.07 g, 10 mmol), TZ-HCP1D (350 mg, 1.1 mol%) and EtOH (200 mL) were added into a one-neck flask. The reaction mixture was opened to air and stirred at room temperature under 12 W white LEDs (the distance between LEDs and reaction center is about 10 cm, 60 mW/cm²). After the reaction was completed (ca. 48 min, monitored by TLC), the heterogeneous catalyst could be isolated through filtration and thoroughly washed by acetone (10 mL \times 3). Collected the light brown mother liquid and removed the organic solvent under reduced pressure. The resulted crude product was further washed with a small amount

of cold petroleum/EtOH ether (v/v, 10/1), and then dried under vacuum for 10 h at 60 °C to give pure **5s** (1.87 g, 96% yield).

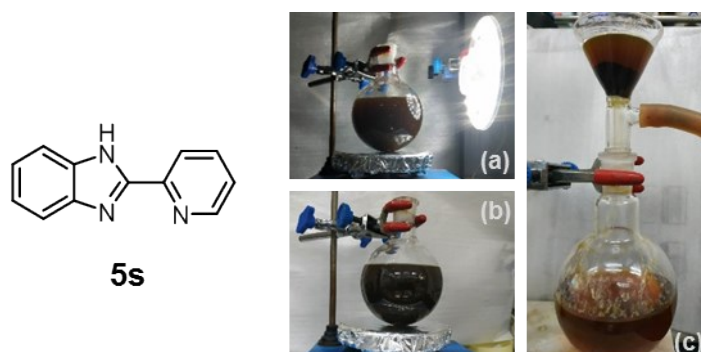
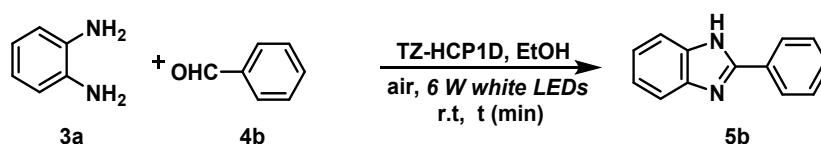


Figure S15. Scale-up experiment to synthesize **5s** with TZ-HCP1D as photocatalyst. (a) Photocatalytic reaction equipment (white LEDs, 12 W). (b) The completed reaction system that contain product **5s** and TZ-HCP1D; (c) Separation of **5s** and recovery of catalyst through filtration.

7. Recyclability Tests of TZ-HCP1D

The recycling experiments were carried out with *o*-phenylenediamine (**3a**) and benzaldehyde (**4b**) under the optimized reaction condition as in Table 2, entry 6. After the reaction, TZ-HCP1D was separated via filtration, then washed successively with EtOH or acetone to remove the guest molecules (*e.g.*, residual products) locked in the pore channels. The recycled TZ-HCP1D was dried and then subject to the next catalytic cycle. The polymer could be further purified to remove residual products via a Soxhlet extraction for 24 h with EtOH or acetone as solvent, and then dried in vacuum oven for 12 h at 80 °C. The catalytic results and porosity of TZ-HCP1D are summarized in Figure 3, S16 and S17 respectively.



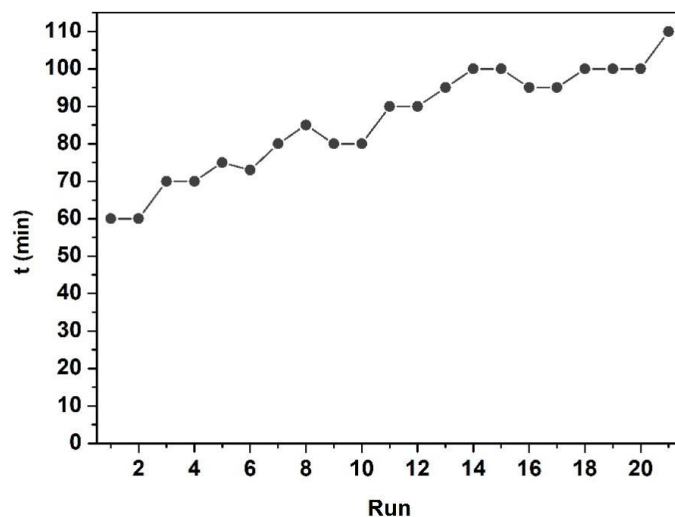


Figure S16. Reaction time variation for the recycling experiments of TZ-HCP1D. General Conditions: benzene-1,2-diamine (0.2 mmol), benzaldehyde (0.2 mmol), EtOH (4.0 mL).

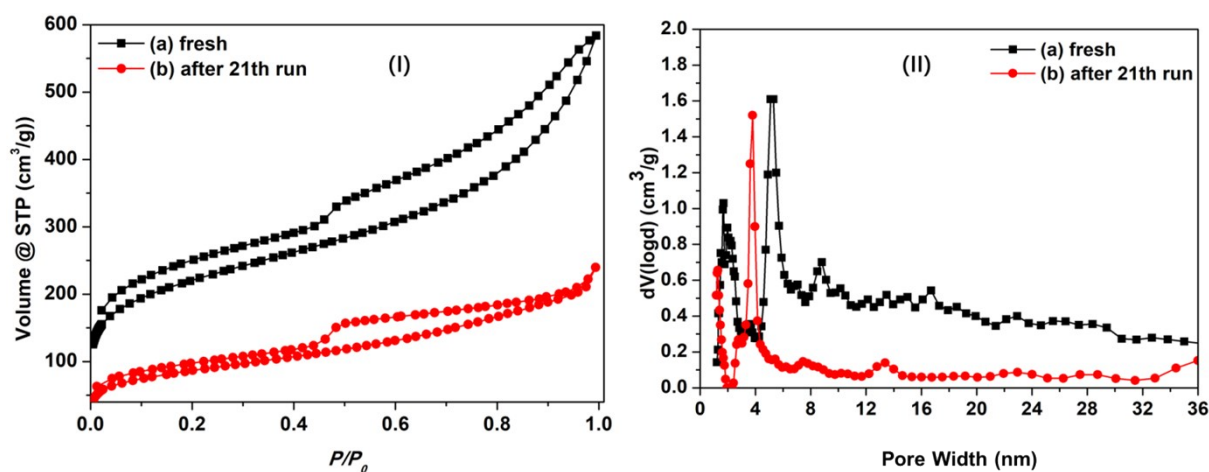


Figure S17. N₂ adsorption-desorption isotherms (I) and pore size distribution (II) of TZ-HCP1D: (a) fresh catalyst; (b) after 21th run. Herein, the porosity of TZ-HCP1D didn't decrease rapidly during reuse, but showed a gradual downward trend. The BET surface area of the recovered TZ-HCP1D after 21th run was 302 m² g⁻¹, which was lower than the fresh catalyst (754 m² g⁻¹). STP = standard temperature and pressure.

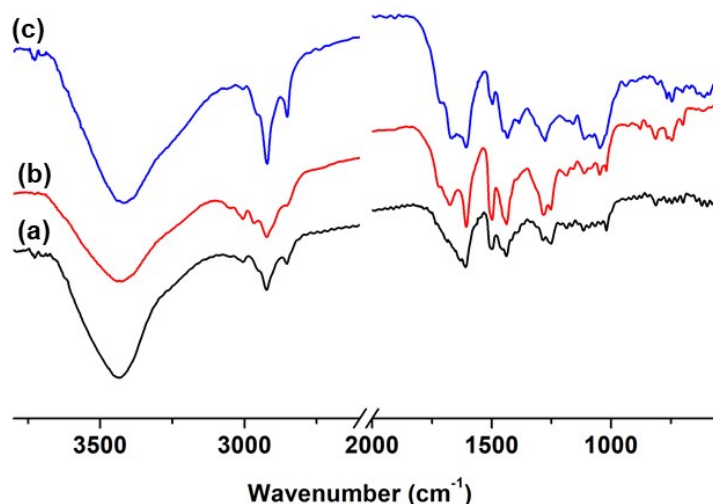
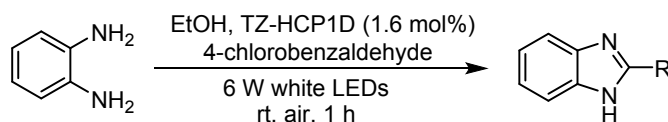


Figure S18. FT-IR spectra of TZ-HCP1D: (a) fresh catalyst, (b) after 1st run and (c) 21st run.

8. Study for the Reaction Mechanism



General conditions: EtOH (4 mL), TZ-HCP1D (10 mg, 1.6% mmol), *o*-phenylenediamine and 4-chlorobenzaldehyde (0.2 mmol), rt, 6W white LEDs, air.

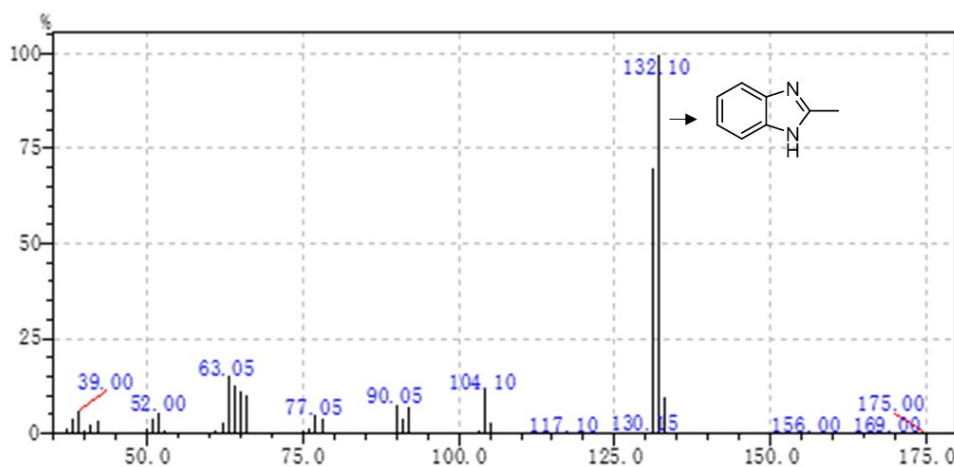


Figure S19. GC-MS spectrum for the detection of 2-methyl benzimidazole in the reaction system. The reaction was performed according to the conditions of entry 6 in Table 2: EtOH (4 mL), TZ-HCP1D (10 mg, 1.6% mmol), *o*-phenylenediamine and 4-chlorobenzaldehyde (0.2 mmol), rt, 6W white LEDs, air, 1 h.

The results indicated that EtOH could be oxidized to acetaldehyde by active species (h^+ or 1O_2). Then acetaldehyde would participate in the photocatalytic reaction with *o*-phenylenediamine.

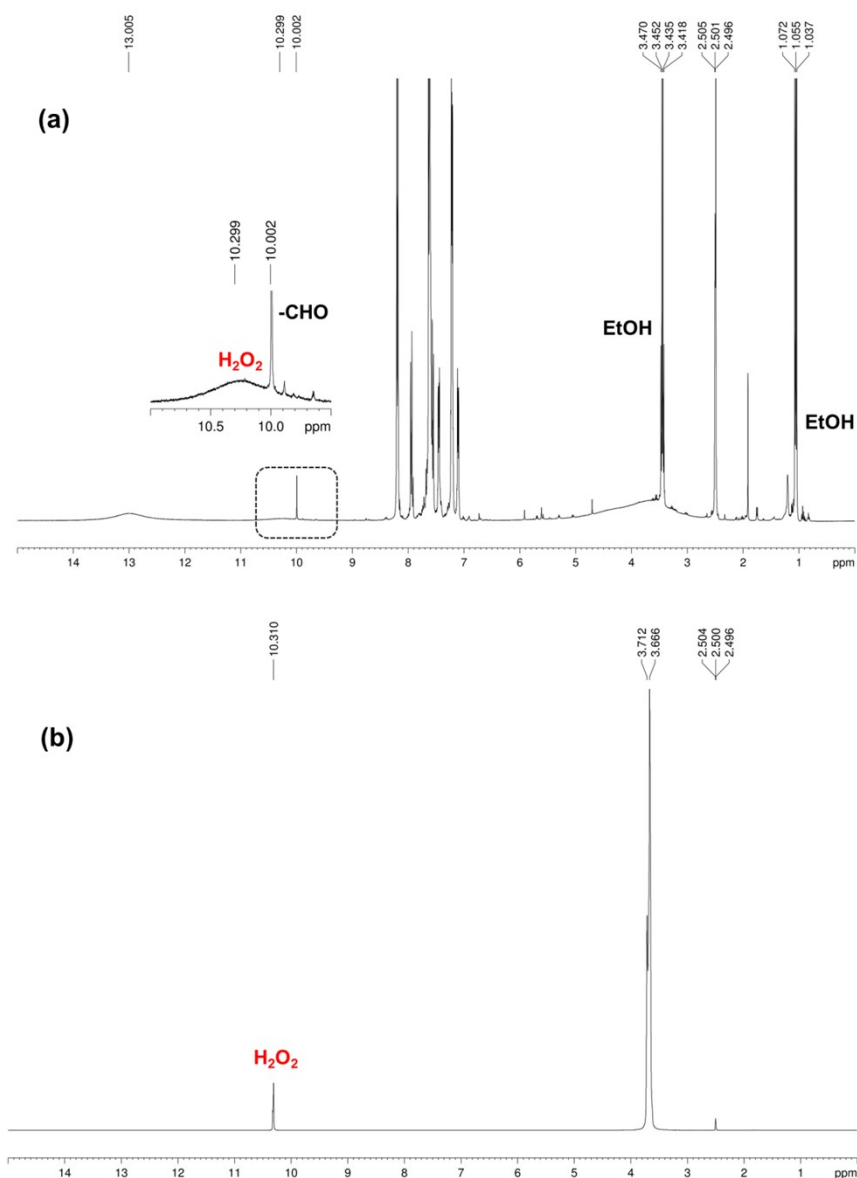


Figure S20. Detection of H_2O_2 via ^1H NMR (DMSO- d_6) spectra: (a) photocatalytic system ($3\text{a} + 4\text{a}$); (b) 30% H_2O_2 solution.

9. References

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10. Liquid NMR Spectra of Some Compounds

