

Supporting Information

Organic molecular sieve adorned with *s*-tetrazine: an efficient platform for gram-scale organic photoredox catalysis

Xin Xu,[#] Jingjing Ge,[#] Xin He, Tiantian Shang, Zhenliang Pan, Yunlai Ren, Lixia Xie and Wan-Kai An*

College of Science, Henan Agricultural University, Zhengzhou, Henan 450002 (China).

E-mail: anwk@henau.edu.cn.

List of Contents

I. Summary of Schemes, Figures and Tables	2
II. General Information.....	3
III. Synthetic Procedures	4
IV. Characterization of TZ-OMS.	7
V. Photocatalytic Performance of TZ-OMS.....	9
i) Typical Procedures to Synthesize Benzimidazoles under Visible Light	9
ii) Gram-scale synthesis of BIs in batch	15
iii) Gram-scale synthesis of BIs in continuous-flow.....	16
VI. Recyclability Tests of TZ-OMS.....	18
VII. The selected synthetic strategies for BIs.....	21
VIII. Catalytic comparison with some reported photocatalysts	22
IX. References	23
X. Liquid NMR spectra of some compounds.....	24

I. Summary of Schemes, Figures and Tables

Scheme S1. Synthesis of monomer ArPyTZ.....	4
Scheme S2. Synthesis of TZ-OMS.....	5
Scheme S3. Catalytic effects of TZ-OMS under solvent-free condition.....	15
Figure S1. N ₂ sorption isotherms and PSD of TZ-OMS tuned by different salts	7
Figure S2. N ₂ sorption isotherms and PSD of TZ-OMS tuned by NaCl.....	7
Figure S3. FT-IR spectra of TZ-OMS and ArPyTZ.....	8
Figure S4. The XPS high-resolution spectra of C1s and N 1s for TZ-OMS.....	8
Figure S5. Powder X-ray diffraction patterns of TZ-OMS.....	8
Figure S6. SEM images of TZ-OMS.....	9
Figure S7. The TGA curve of TZ-OMS.....	9
Figure S8. Scale-up experiments to synthesize BIs catalyzed by TZ-OMS in batch .	16
Figure S9. Continuous-flow photocatalytic reactor for gram-scale synthesis of BIs...	17
Figure S10. Pictures for the representative BIs obtained flow reaction.....	17
Figure S11. EPR spectra for TZ-OMS.....	18
Figure S12. Recycling performance of TZ-OMS at a scale of 0.2 mmol	19
Figure S13. Recycling performance of TZ-OMS at a scale of 5 mmol	19
Figure S14. FT-IR spectra of the fresh and the recovered TZ-OMS.....	20
Figure S15. Comparison of porosities for the fresh and recovered TZ-OMS.....	20
Table S1. Elemental analysis on the TZ-OMS.....	8
Table S2. Effects of temperature on the photoreaction yields.....	18
Table S3. Representative catalysts for the synthesis of BIs <i>via</i> Phillips-Ladenburg route.....	21
Table S4. Representative heterogeneous catalysts for the green synthesis of BIs.....	22

II. General Information

Materials. 5-(4-ethylphenyl) picolinonitrile,^[1, 2] 3,6-bis(5-(4-ethylphenyl)pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine and 3,6-bis(5-(4-ethylphenyl)pyridin-2-yl)-1,2,4,5-tetrazine^[2, 3] were prepared according to the literature procedures. Unless otherwise noted, the reagents (formaldehyde dimethyl acetal (FDA), benzene 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. FT-IR spectra were obtained with a Nicolet IS 20 instrument. 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.

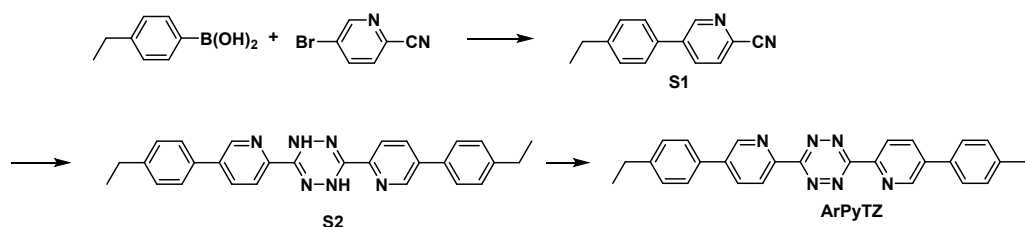
Thermogravimetric analysis (TGA) measurements were used to study the thermal stability of the TZ-OMS. The tests were carried out on a SDT Q600 (V20.9 Build 20) instrument from 30 to 1000 °C under a N₂ atmosphere with a heating rate of 10 °C/min. Scanning electron microscope (SEM) tests were applied to 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.

The elemental composition was determined through the classical method, i.e., by analysing the gas composition of the synthesized TZ-OMS after combustion. The determination was performed on an Elementar Analysensysteme UNICUBE elemental

analyzer under O₂ atmosphere. Three replicate measurements were performed using approximately 10 mg polymer samples to ensure precision and accuracy. The elemental analysis data were provided in the form of a data table.

UV-Vis diffuse reflectance analysis (DRS) for TZ-OMS 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 Tauc plots. Electrochemical experiments were conducted on CHI660E Electrochemical Workstation by using a three-electrode electrochemical cell (ITO working electrode, a saturated calomel electrode as reference electrode, platinum wire as counter electrode, 0.2 M Na₂SO₄ aq. as electrolyte). The photocurrent measurements were performed in by illumination using 40 W LEDs at intervals of 15 seconds. The working electrodes for photocurrent and electrochemical impedance spectroscopy (EIS) measurements were prepared by pasting slurry of TZ-OMS (5.0 mg) in 5% Nafion (50 μL) and EtOH (50 μL) onto the ITO conductive glass, dried under air, and then immersed in Na₂SO₄ aqueous solution (0.2 M). Electron paramagnetic resonance (EPR) spectra were conducted on Bruker A300.

III. Synthetic Procedures

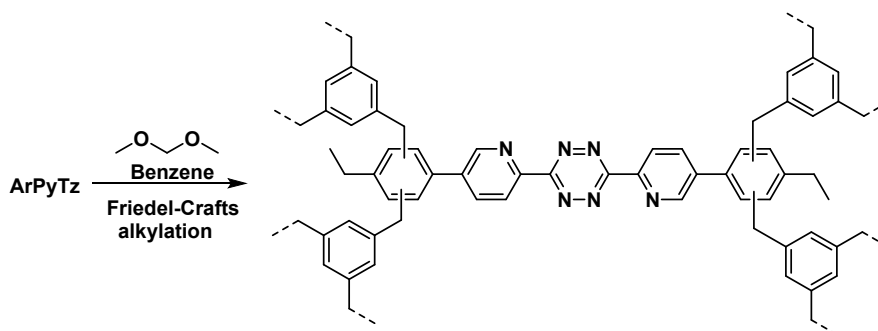


Scheme S1. Synthesis of monomer ArPyTZ.

Synthesis of compound S1.^[1, 2] (4-ethylphenyl) boronic acid (485 mg, 3.28 mmol), 5-bromopicolinonitrile (500 mg, 2.73 mmol), potassium acetate (1.14 g, 8.19 mmol) and Pd(PPh₃)₄ (250 mg, 0.22 mmol) were added into a 100 mL two-neck flask. The system was degassed and back-filled with N₂ for three times, and then THF/H₂O (2/1, 30 mL) was added. The system was stirred at 80 °C for 24 h. After the reaction, THF was removed under vacuum, the resulting mixture was extracted with CH₂Cl₂ and washed with water and brine, then dried over Na₂SO₄. After removing CH₂Cl₂ under vacuum, the obtained residual crude product was further purified by flash silica gel column chromatography (petroleum ether/ ethyl acetate = 16/1 as the eluent) to give product **S1**

as white solid (564.7 mg, 99% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 8.94(\text{d}, J=2.0$ Hz, 1H), 8.00-7.97 (m, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.53(d, $J = 8.0$ Hz, 2H), 7.36(d, $J = 8.0$ Hz, 2H), 2.73(q, $J = 7.6$ Hz, 2H), 1.29 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100MHz, CDCl_3): $\delta = 149.5, 146.0, 139.8, 134.5, 133.1, 131.8, 129.0, 128.9, 128.4, 127.2, 117.4, 115.1, 28.6, 15.4$ ppm.

Synthesis of monomer ArPyTZ.^[2, 3] Compound **S1** (366.1 mg, 1.76 mmol), sublimate sulphur (28 mg, 0.88 mmol) and ethanol (2 mL) were added into a dry 10 mL round-bottom flask. $\text{N}_2\text{H}_4\text{-H}_2\text{O}$ (80%, 0.4 mL) was injected into the system and the mixtures were stirred for 24 h at 90 °C. After the reaction, the system was cooled to 0 °C, and then filtered, washed with ice ethanol (20 mL) to obtain product **S2** as brownish yellow powder. Without further purification, the crude product **S2** was dispersed into 4 mL glacial acetic acid. Then, NaNO_2 (400 mg, 5.79 mmol) was added at room temperature and stirred at room temperature. The reaction mixture was poured into saturated K_2CO_3 solution (100 mL) after stirred for 24 h and left to stand for 20 min. Filtrated and washed with water to obtain solid, then dried in vacuum at 50 °C for 8 h and resulted in purple product **ArPyTZ** (34% yield for two steps). ^1H NMR (400 MHz, CF_3COOD): $\delta = 9.50$ (d, $J = 8.4$ Hz, 2H), 9.45 (d, $J = 1.6$ Hz, 2H), 9.22 (dd, $J = 8.4, 1.6$ Hz, 2H), 7.83 (d, $J = 8.0$ Hz, 4H), 7.59 (d, $J = 8.0$ Hz, 4H), 2.86 (dd, $J = 15.2, 7.6$ Hz, 4H), 1.38(t, $J = 7.6$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CF_3COOD): $\delta = 159.0, 150.3, 146.3, 144.8, 141.3, 138.0, 129.5, 128.3, 127.2, 126.8, 28.0, 13.2$ ppm.



Scheme S2. Synthesis of TZ-OMS.

General procedures for the preparation of TZ-OMS.^[2] A two-necked flask was charged with ArPyTZ (164.5 mg, 0.37 mmol) and FeCl_3 (2.4 g, 14.8 mmol, 13.5

mol% relative to FDA and DCE). Then, anhydrous DCE (7.4 mL, 94.3 mmol) and benzene (0.66 mL, 7.43 mmol) were injected under N₂. The mixture was stirred at 25 °C for 30 mins, followed by the addition of dimethoxymethane (1.33 mL, 15.1 mmol). The reaction temperature was then increased to 45 °C and maintained for 5 hours, and further raised to 90 °C to proceed for an additional 19 hours. After the reaction, 20 mL of methanol was added and stirred for 30 mins until the solid was evenly dispersed. The precipitate was filtered, washed with water and MeOH in sequence after cooling to room temperature. Then, *con.* HCl (20 mL) was added to the collected solid and stirred for 2 h. The precipitate was filtered and washed with saturated NaHCO₃ solution, water, DMF, MeOH, and DCM successively. Subsequently, the obtained polymer was purified by Soxhlet extraction with MeOH/DCM (1/1) for 24 h and dried in a vacuum oven at 80 °C for 12 h to yield TZ-OMS as brown-black powder (1.11 g). Elemental analysis results (wt%): C, 80.276; N, 2.014; H, 3.309. The result was also displayed in the characterization section for TZ-OMS.

Synthesis of TZ-OMS by adding inorganic salts. The same successive procedures were applied to prepare TZ-OMS except the following changes. The mixture of compound ArPyTZ (82.2 mg, 0.185 mmol), FeCl₃ (1.2 g, 7.4 mmol), and *inorganic salts* (250-750 mg NaCl, KCl, or Na₂SO₄) was added to a two-necked flask and degassed with N₂ three times. Anhydrous DCE (3.7 mL, 47.15 mmol) and benzene (0.33 mL, 3.72 mmol) were added to the mixture and stirred at 25 °C for 0.5 h. Then, dimethoxymethane (0.67 mL, 7.55 mmol) was introduced into the system and stirred at 45 °C for 5 h followed by stirring at 90 °C for 19 h.

IV. Characterization of TZ-OMS.

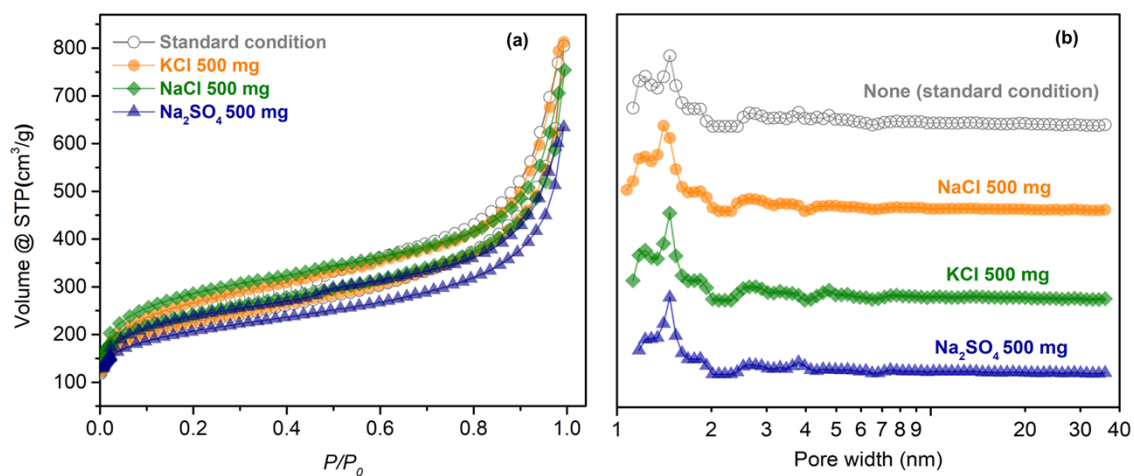


Figure S1. N_2 sorption isotherms (a) and pore size distribution (b) of TZ-OMS tuned by different salts

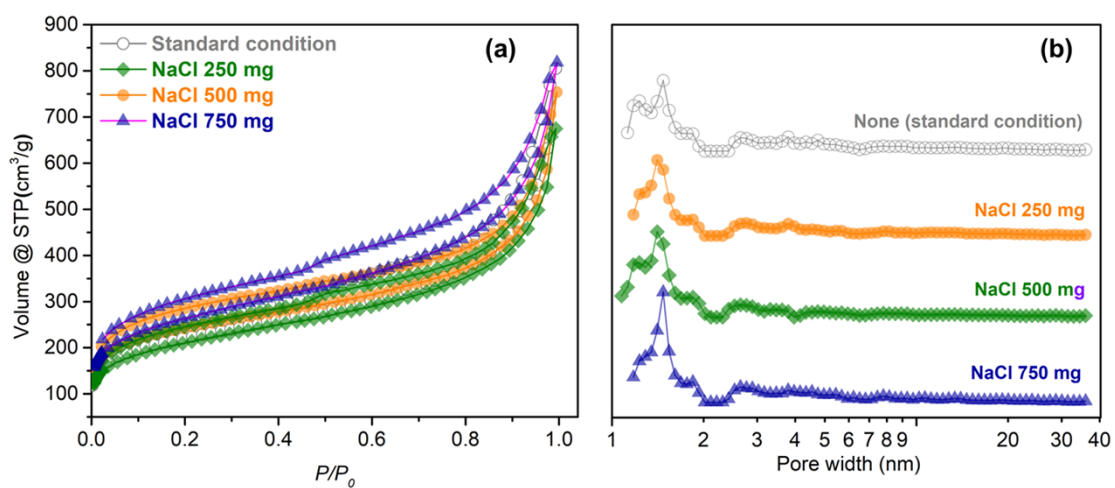


Figure S2. N_2 sorption isotherms (a) and pore size distribution (b) of TZ-OMS tuned by NaCl.

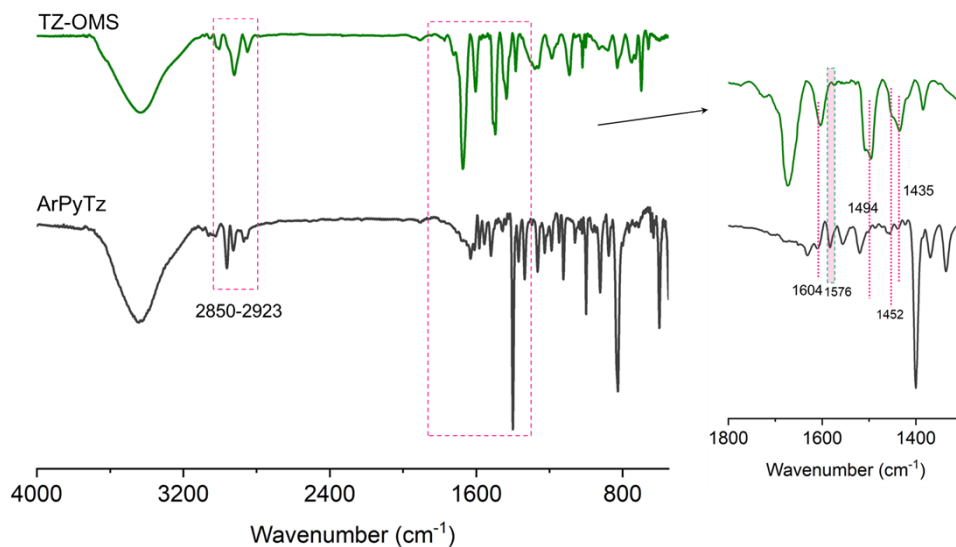


Figure S3. FT-IR spectra of TZ-OMS and ArPyTZ.

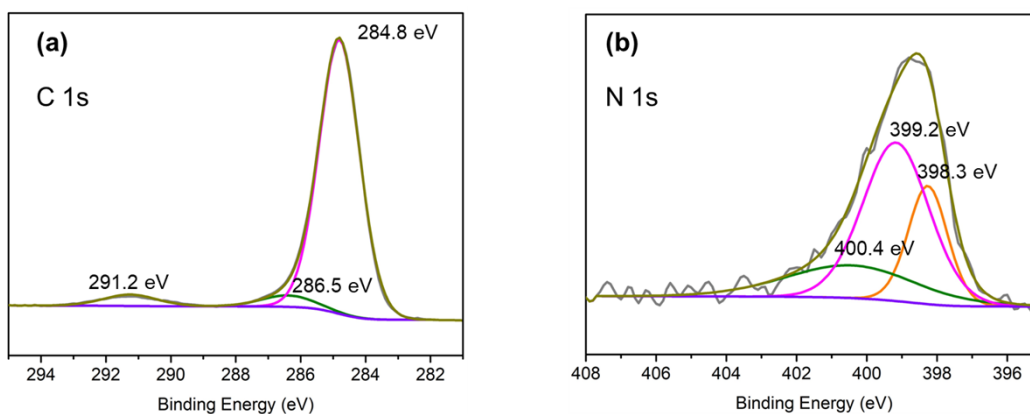


Figure S4. The XPS high-resolution spectra of C 1s (a), N 1s (b) for TZ-OMS.

Table S1. Elemental analysis on the TZ-OMS

Sample	C (wt%)	H (wt%)	N (wt%)
TZ-OMS	80.28	3.31	2.01

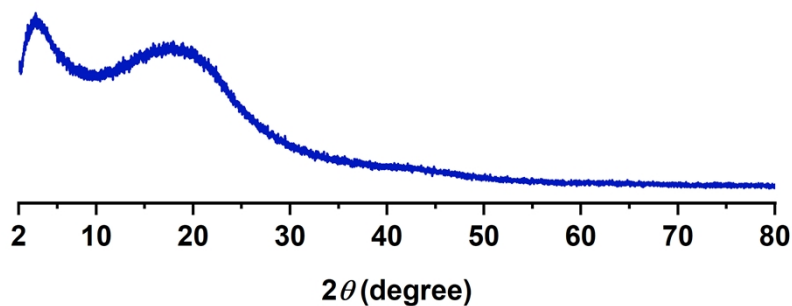


Figure S5. Powder X-ray diffraction (PXRD) patterns of TZ-OMS.

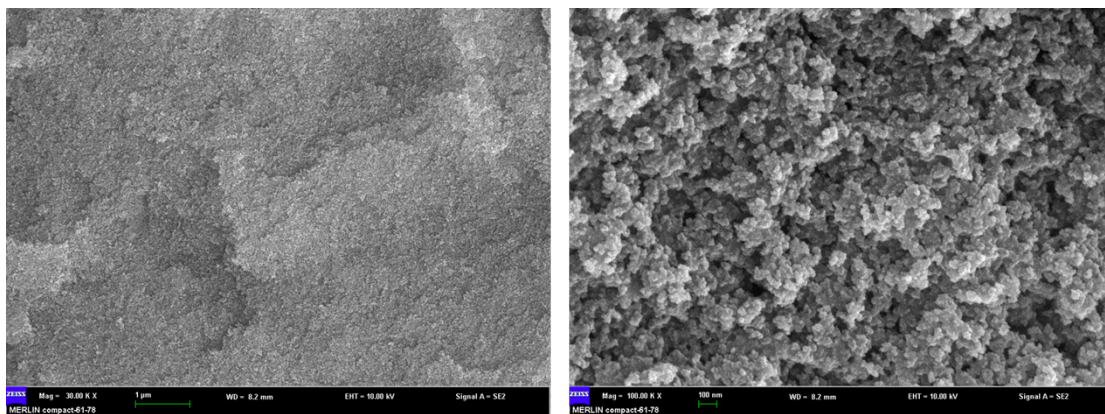


Figure S6. SEM images of TZ-OMS.

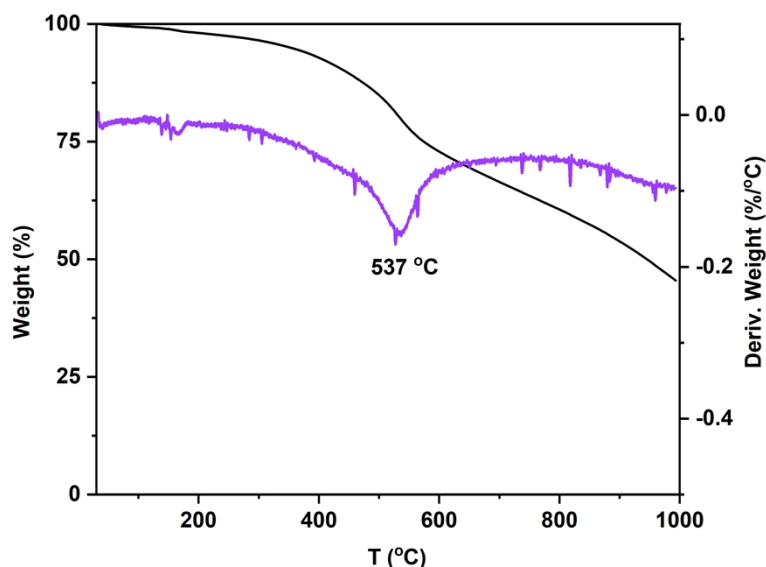
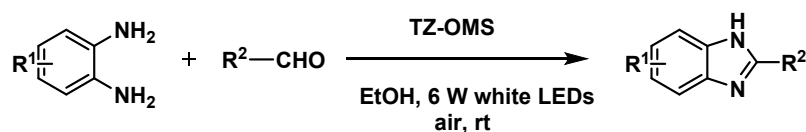


Figure S7. The TGA curve of TZ-OMS.

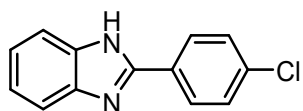
V. Photocatalytic Performance of TZ-OMS

i) Typical Procedures to Synthesize Benzimidazoles under Visible Light

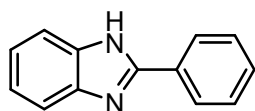


Benzene-1,2-diamine or its derivatives (0.2 mmol) and aromatic aldehyde (0.2 mmol) were added to a 10 mL Pyrex glass tube with TZ-OMS (10 mg, 1.2 mol%) and EtOH (4.0 mL). The reaction mixture was opened to air and stirred at room temperature under 6 W white LEDs (light intensity: 30 mW/cm²) until completion as monitored by TLC. After centrifugation and washing with acetone (3 × 4 mL), the heterogeneous catalyst was isolated, and the crude product was

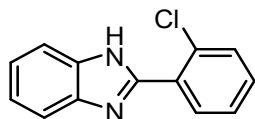
further purified by flash column chromatography (with petroleum/acetone = 10/1~3/1 as eluent) to obtain the product of 2-substituted benzimidazoles. Collected the effluent that contain product and removed the solvent, 2-substituted benzimidazoles could be obtained as solid powers. The dried pure solid above was then used to estimate the yield of product. All the NMR data (summarized as below) are consistent with reported references.^[2, 4-8]



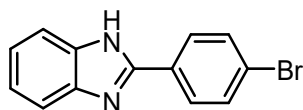
3a, White solid, 95% yield. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.99 (br, 1H), 8.18 (d, *J* = 8.8 Hz, 2H), 7.68–7.53 (m, 4H), 7.25–7.19 (m, 2H) ppm.



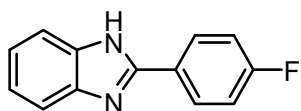
3b, White solid, 94% yield. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.91 (br, 1H), 8.19 (d, *J* = 7.2 Hz, 2H), 7.60–7.47 (m, 5H), 7.22–7.20 (m, 2H) ppm.



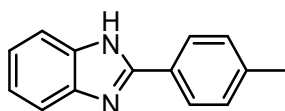
3c, White solid, 96% yield. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 12.72 (br, 1H), 7.91–7.89 (m, 1H), 7.69–7.63 (m, 2H), 7.57–7.50 (m, 3H), 7.24 (d, 2H, *J* = 2.8 Hz) ppm.



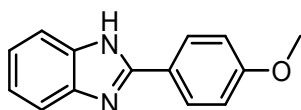
3d, White solid, 85% yield. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 13.00 (br, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.77 (d, 2H, *J* = 8.8 Hz), 7.68–7.53 (m, 2H), 7.25–7.18 (m, 2H) ppm.



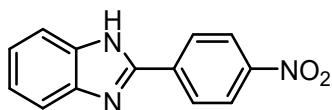
3e, White solid, 89% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.93$ (br, 1H), 8.24-8.20 (m, 2H), 7.66-7.52 (m, 2H), 7.42-7.38 (m, 2H), 7.24-7.20 (m, 2H) ppm. ^{19}F NMR (376 MHz, d_6 -DMSO): $\delta -111.14$ ppm.



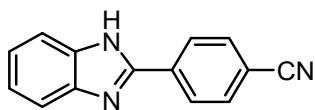
3f, White solid, 95% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.81$ (br, 1H), 8.06 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 7.2$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 6.0$ Hz, 2H), 2.38 (s, 3H) ppm.



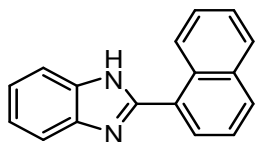
3g, White solid, 92% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.74$ (br, 1H), 8.12 (d, $J = 7.6$ Hz, 2H), 7.55 (s, 2H), 7.17-7.10 (m, 4H), 3.84 (s, 3H) ppm.



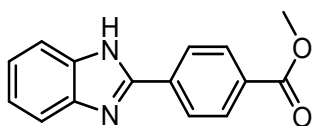
3h, Yellow solid, 90% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 13.31$ (br, 1H), 8.43 (s, 4H), 7.75-7.59 (m, 2H), 7.35-7.23 (m, 2H) ppm.



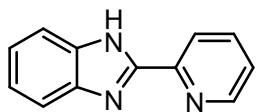
3i, Light yellow solid, 96% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 13.20$ (br, 1H), 8.35-8.33 (m, 2H), 8.04-8.02 (m, 2H), 7.72-7.57 (m, 2H), 7.28-7.24 (m, 2H) ppm.



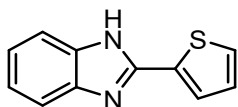
3j, White solid, 95 % yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 13.09 (br, 1H), 8.75(s, 1H), 8.33(d, J = 8.4 Hz, 1H), 8.09-8.04 (m, 2H), 8.00-7.98(m, 1H), 7.63-7.58 (m, 4H), 7.24-7.22 (m, 2H) ppm.



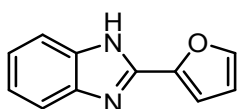
3k, Yellow solid, 83% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 13.15 (br, 1H), 8.32 (d, J = 8.0 Hz, 2H), 8.12 (d, J = 8.0 Hz, 2H), 7.70-7.56 (m, 2H), 7.24 (s, 2H), 3.89 (s, 3H) ppm.



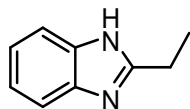
3l, White solid, 97% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 13.11 (br, 1H), 8.73 (d, J = 2.4 Hz, 1H), 8.33 (d, J = 7.2 Hz, 1H), 8.00 (t, J = 6.8 Hz, 1H), 7.71 (d, J = 6.8 Hz, 1H), 7.55-7.50 (m, 2H), 7.26-7.19 (m, 2H) ppm.



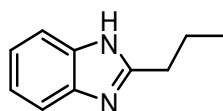
3m, Orange-yellow solid, 76% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 12.96 (br, 1H), 7.84 (d, J = 2.8 Hz, 1H), 7.72 (d, J = 4.8 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.24-7.17 (m, 3H) ppm.



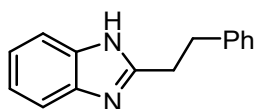
3n, Yellow solid, 68% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.93$ (br, 1H), 7.94 (d, $J = 0.8$ Hz, 1H), 7.63-7.48 (m, 2H), 7.23-7.16 (m, 3H), 6.73 (dd, $J = 3.6, 1.6$ Hz, 1H) ppm.



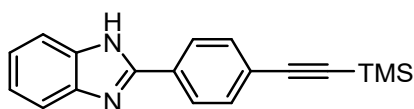
3o, White solid, 98% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.16$ (br, 1H), 7.46-7.44 (m, 2H), 7.11-7.09 (m, 2H), 2.85-2.79 (q, $J = 7.6$ Hz, 2H), 1.31 (t, $J = 7.6$ Hz, 3H) ppm.



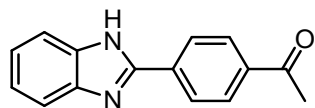
3p, White solid, 79% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.17$ (br, 1H), 7.46-7.44 (m, 2H), 7.13-7.08 (m, 2H), 2.83-2.75 (m, 2H), 1.79 (t, $J = 7.2$ Hz, 2H), 0.97-0.92 (m, 3H) ppm.



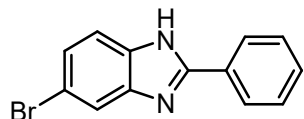
3q, Pale yellow solid, 78% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.27$ (br, 1H), 7.47 (s, 2H), 7.29-7.25 (m, 4H), 7.21-7.17 (m, 1H), 7.13-7.09 (m, 2H), 3.11 (s, 4H) ppm.



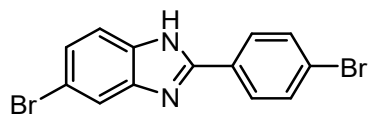
3r, White solid, 81% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 13.01$ (br, 1H), 8.18 (d, $J = 8.0$ Hz, 2H), 7.64-7.59 (m, 4H), 7.22 (dd, $J = 5.6, 2.8$ Hz, 2H), 0.25 (s, 9H) ppm.



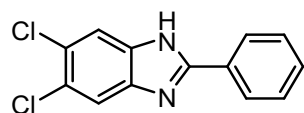
3s, Yellow solid, 76% yield. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): $\delta = 13.14$ (br, 1H), 8.32 (d, $J = 6.8$ Hz, 2H), 8.12 (d, $J = 6.8$ Hz, 2H), 7.71-7.56 (m, 2H), 7.24 (s, 2H), 2.64 (s, 3H) ppm.



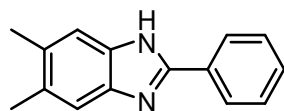
3t, White solid, 90% yield. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) $\delta = 13.13$ -13.09 (d, br, 1H), 8.18-8.16 (m, 2H), 7.86 (s, 1H), 7.64-7.50 (m, 4H), 7.36-7.32 (m, 1H) ppm.



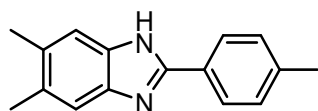
3u, White solid, 74% yield. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): $\delta = 13.21$ -13.17 (br, 1H), 8.10 (d, $J = 8.4$ Hz, 2H), 7.87-7.50 (m, 4H), 7.38-7.33 (m, 1H) ppm.



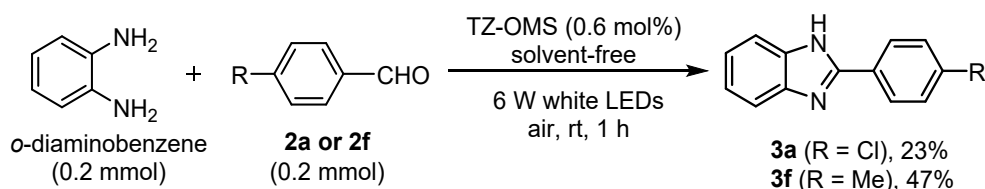
3v, White solid, 94% yield. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): $\delta = 13.26$ (br, 1H), 8.17 (d, $J = 7.6$ Hz, 2H), 7.94 (s, 1H), 7.76 (s, 1H), 7.59-7.52 (m, 3H) ppm.



3w, White solid, 84% yield. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.66$ (br, 1H), 8.14 (d, $J = 7.6$ Hz, 2H), 7.52 (t, $J = 7.2$ Hz, 2H), 7.45 (t, $J = 7.2$ Hz, 1H), 7.36 (s, 2H), 2.32 (s, 6H) ppm.



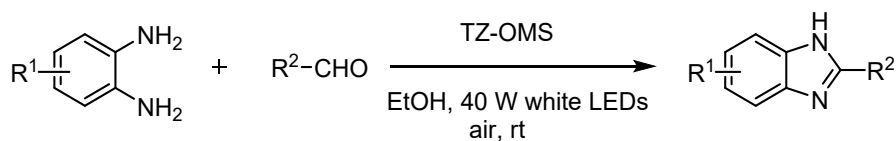
3x, White solid, 90% yield. $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): $\delta = 12.55$ (br, 1H), 8.02 (d, $J = 8.0$ Hz, 2H), 7.38-7.28 (m, 4H), 2.36 (s, 3H), 2.31 (s, 6H) ppm.



Scheme S3. Photocatalytic effects of TZ-OMS for BIs synthesis under solvent-free condition. (NMR yields were given here.)

Considering the green chemistry focus, solvent-free conditions were to be evaluated here. However, in the case where both the substrate (such as *o*-diaminobenzene and *p*-chlorobenzaldehyde **2a**) and TZ-OMS catalyst are solids, the catalytic effect (**3a**, 23% yield) mentioned above is limited due to insufficient molecular contact and inefficient light absorption. By replacing **2a** with a liquid aldehyde, *i.e.*, *p*-tolualdehyde (**2f**, 0.2 mmol, 25 μL), it can enhance the efficiency of molecular contact between the substrate and catalyst to some extent and thereby improve the catalytic effect (**3f**, 47% yield). Nevertheless, satisfactory outcomes have not yet been achieved.

ii) Gram-scale synthesis of BIs in batch



TZ-OMS (200 mg), *o*-aromatic diamine (5.0 mmol), aldehydes (5.0 mmol) and EtOH (100 mL) were added into a one-neck flask. The reaction mixture was opened to air and stirred at room temperature while irradiated with 40 W White LEDs. After the reaction was completed, the heterogeneous catalyst could be isolated through filtration and thoroughly washed by acetone (10 mL \times 3). The filtrate was collected and removed the organic solvent under reduced pressure. The resulting crude product was

subjected to additional purification steps, including washing with a solution of petroleum ether and ethyl acetate, followed by treatment with small amounts of ethanol and acetone. The solids were then dried under vacuum for 4 h at 60 °C to give pure **3a-3x**. Alternatively, purification (especially for the BIs with good solubleness in EtOH and acetone) was also achieved through flash column chromatography (with petroleum/acetone = 10/1~3/1 as eluent).

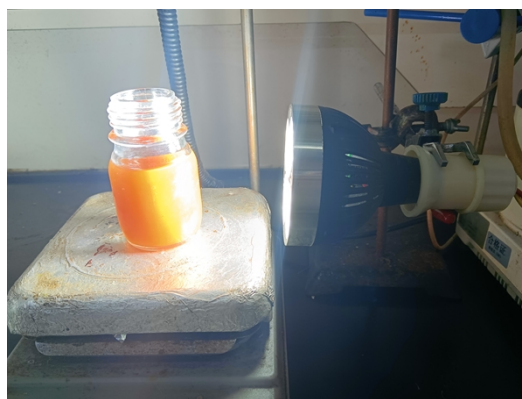


Figure S8. Scale-up experiments to synthesize BIs with TZ-OMS as photocatalyst in batch.

iii) Gram-scale synthesis of BIs in continuous-flow

The continuous flow chemical reactor was first established as the following procedures. Approximately 5 g of glass beads were packed as a subgrade at the bottom of a glass column ($\varphi = 1$ cm). Subsequently, the fixed glass column was filled with a mixture of glass beads (5.6 g, 30-50 mesh) and TZ-OMS (200 mg) to create the photocatalyst section ($l = 7$ cm). The top of the column was sealed with absorbent cotton, and white LED tape lights (40 W) were placed around the working section. Generally, the device was connected to a peristaltic pump and mixed with liquor containing 5 mmol of substrates ($T = 30$ °C) and 80 mL of dioxygen-saturated EtOH. The flow rate through the chemical reactor was approximately 1.2 mL/min (Figure S9).

After the reaction was completed, pure EtOH (100 mL) was used to wash the reactor and collect the product adequately. All reaction liquid was combined for recycling EtOH under reduced pressure. The crude product was purified by washing with a small amount of cold petroleum ether/ethyl acetate solution, followed by

treatment with minute amounts of ethanol and acetone. Finally, it was vacuum dried at 60 °C for 4 h to obtain the final products (**3a**, **3f**, **3h-3j**, **3l**, **3x**). Alternatively, purification (especially **3n** and **3o** that with good solubleness in EtOH and acetone) was also achieved through flash column chromatography (with petroleum/acetone = 10/1~3/1 as eluent).

Notes:

(1) For 0.5 mmol and 15 mmol (**3a**, **3n** and **3o**) scale substrates, 20 mL and 180 mL EtOH were used as solvent, respectively.

(2) For the synthesis of **3h** and **3i**, 100 mL of EtOH was used to dissolve the substrates, intermediates, or products and prevent blockage in the continuous-flow reactor. Specifically for **3h**, an additional 3 mL of acetone was introduced into the EtOH solution.

(3) After the completion of the reaction, if the product exhibits poor solubility, acetone can be employed for washing, except for ethanol. The washed reactor can then be used for the catalytic synthesis of another BIs.

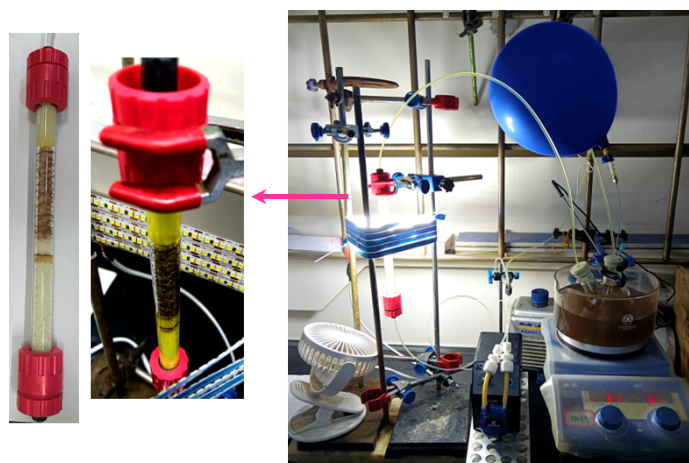
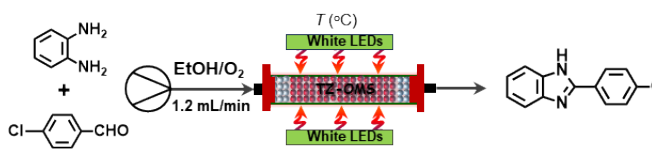


Figure S9. Continuous-flow photocatalytic reactor for gram-scale synthesis of BIs.



Figure S10. Pictures for the representative BIs obtained in TZ-OMS mediated flow reaction.

Table S2. Effects of temperature on the reaction yields in continuous-flow system.^a



Entry	T (°C)	t (h)	Yield ^b (%)
1	0	4.0	60
2	30	3.0	95
3	60	2.5	96

^aGeneral conditions: *o*-diaminobenzene (0.5 mmol), *p*-chlorobenzaldehyde (0.5 mmol), TZ-OMS (200 mg, 9.6 mol%), EtOH (20 mL), O₂ ball, 40 W white LED tape lights.

^bIsolated yields.

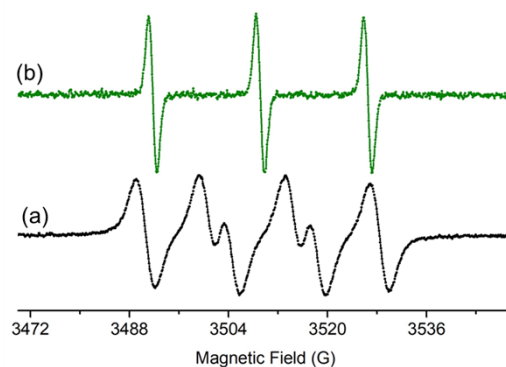


Figure S11. EPR spectra (under light for 8 min) for TZ-OMS (1.0 mg L⁻¹) in air-saturated solvent that contained (a) 0.1 M DMPO (MeCN) and (b) TEMP (MeOH).

VI. Recyclability Tests of TZ-OMS

i) Recyclability tests at a scale of 0.2 mmol substrate. The recycling experiments were carried out with benzene-1,2-diamine (**1a**, 0.2 mmol) and benzaldehyde (**2b**, 0.2 mmol) under the optimized reaction condition as in Table 1, entry 10. After the reaction was completed (monitored by TLC), the polymer was collected via filtration and then washed successively by EtOH (3 mL × 3) and acetone (3 mL × 3) to remove the residual products locked in the pore channels. ¹H NMR was used to analyze the yields with 1,4-dimethoxybenzene as internal standard compound. The recycled TZ-OMS was dried and then subject to the next catalytic cycle. Besides, the heterogeneous catalyst 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.

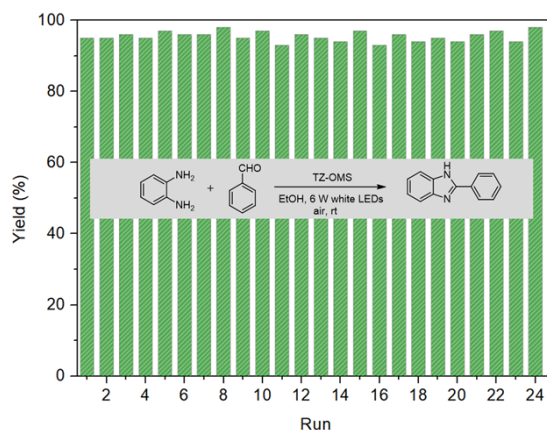


Figure S12. Photocatalytic recycling performance of TZ-OMS for the synthesis of **3b** at 0.2 mmol scale. General Conditions: **1a** and **2b** (0.2 mmol), 6W White LEDs, EtOH (4 mL), TZ-OMS as photocatalyst (10 mg), rt, air.

ii) Recyclability tests at a scale of 5.0 mmol substrate. Benzene-1,2-diamine (**1a**, 5.0 mmol) and benzaldehyde (**2b**, 5.0 mmol), TZ-OMS (200 mg, 1.2 mol%) and EtOH (100 mL) were added into a 150 mL flat-bottomed bottle. The reaction mixture was opened to air and stirred at room temperature under 40 W white LEDs (the distance between LEDs and reaction center is about 8-10 cm, 80 mW/cm²). After completion of the reaction (2-4 hours, monitored by TLC), TZ-OMS was isolated via filtration and thoroughly washed with EtOH (10 mL × 3) and acetone (10 mL × 3). The recovered catalyst was dried and subsequently utilized in the next catalytic cycle. The mother liquid was collected and the solvent was removed under reduced pressure. The resulting crude product was further purified by washing with a small amount of cold petroleum ether/ethyl acetate (v/v, 100/1) and then subjected to vacuum drying at 60 °C for 4 hours to obtain the final product.

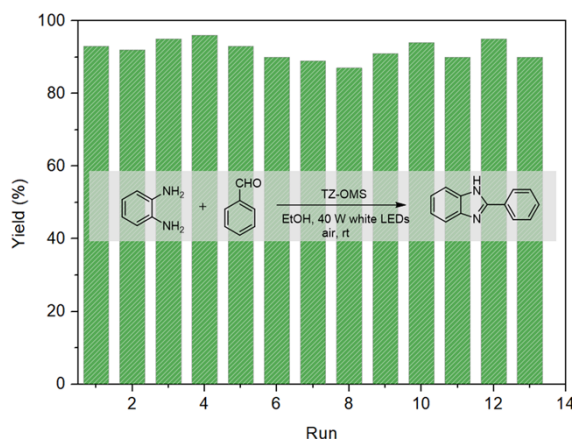


Figure S13. Photocatalytic recycling performance of TZ-OMS for the synthesis of **3b** at 5.0 mmol scale. General Conditions: **1a** and **2b** (5.0 mmol), 40 W White LEDs, EtOH (100 mL), TZ-OMS (200 mg), rt, air.

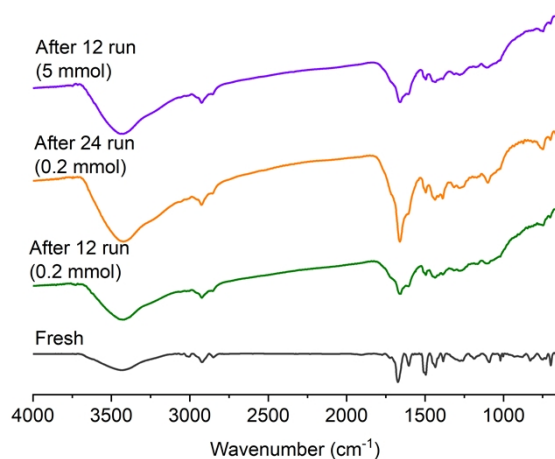


Figure S14. FT-IR spectra of the fresh and the recovered TZ-OMS.

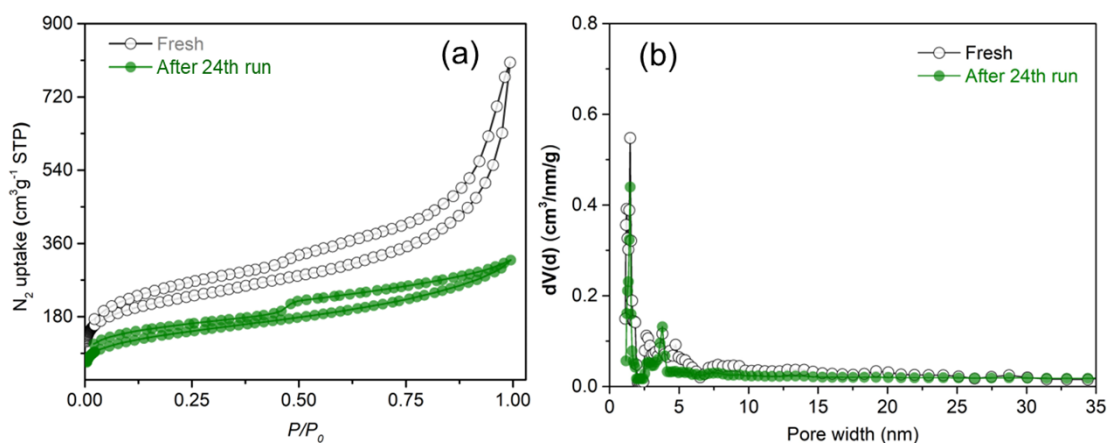
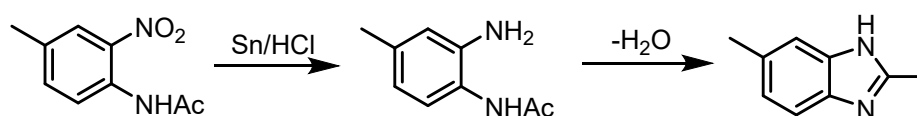


Figure S15. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of TZ-OMS: fresh (gray) and after the 24th run (olive). The porosity of TZ-OMS showed a gradual downward trend. The BET surface area of the recovered TZ-OMS after 24th run was 485 m² g⁻¹, which was lower than the fresh catalyst (750 m² g⁻¹). STP: standard temperature and pressure.

VII. The selected synthetic strategies for BIs

i). Reaction route proposed by Hoebrecker



Ref: F. Hoebrecker, *Ber. Dtsch. Chem. Ges.* **1872**, 5, 920-924.

ii) Reaction route proposed by Phillips-Ladenburg

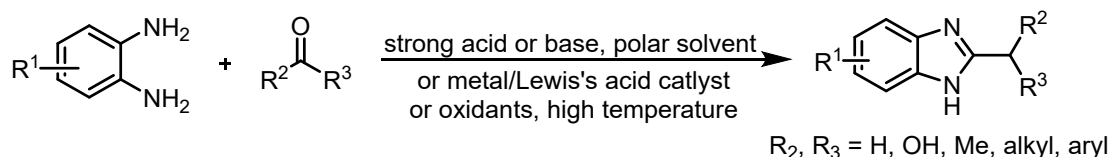
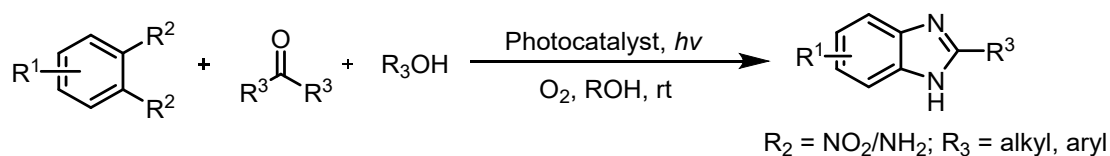


Table S3. Representative catalysts for the synthesis of BIs via Phillips-Ladenburg route

Catalyst	Ref.
[Dodeclm][HSO ₄], con. HCl, H ₃ PO ₄ , TsOH, TfOH, PPA, AcOH; Brønsted Acidic Reduced Graphene Oxide (G-SO ₃ H) Generally, high temperature is need (>200 °C)	<i>Tetrahedron</i> , 2019 , 75, 3543-3552; <i>Russian J. Org. Chem.</i> , 2020 , 56, 1628-1634; <i>Bioorg. Med. Chem.</i> 2002 , 10, 3997; <i>Macromolecules</i> , 1985 , 18, 2723; <i>ChemistrySelect</i> , 2021 , 6, 12628-12643; <i>New J. Chem.</i> , 2018 , 42, 17931-17938; <i>Chem. Eng. J.</i> 2021 , 410.
Merrifield Resin Supported Ionic Liquids/Iodide	<i>ChemistrySelect</i> , 2019 , 4, 2480-2483.
Metal nanoscopic cluster	<i>J. Heterocyclic Chem.</i> , 2019 , 56, 2702-2729.
Transition Metal Catalysts: TiCl ₃ OTf, FeCl ₃ , Fe(NO ₃) ₃ , AgNO ₃ , etc.	<i>J. Heterocyclic Chem.</i> , 2019 , 56, 2702-2729; <i>Tetrahedron Lett.</i> , 2016 , 57, 185-188
Oxidants: H ₂ O ₂ /CAN, tert-Butyl nitrite/O ₂ , Na ₂ S ₂ O ₅ (100 °C), DDQ, Pb(OAc) ₂ , Oxone	<i>J. Org. Chem.</i> , 2008 , 73, 6835-6837; <i>Tetrahedron Lett.</i> , 2020 , 61, 151735; <i>J. Med. Chem.</i> 2001 , 44, 2753; <i>ChemistrySelect</i> , 2021 , 6, 12628-12643.

iii). Photocatalytic Strategy



Ref.: *ChemistrySelect*, **2021**, 6, 12628-12643.

VIII. Catalytic comparison with some reported photocatalysts

Table S4. Representative heterogeneous catalysts for the green synthesis of BIs*

Photocatalyst	T (°C)	O ₂ (atm)	Light source	t (h)	Yield (%)	Ref.
BTT-CMP2	rt	1	30 W Blue LED lamp	2	91	<i>J. Mater. Chem. A</i> , 2021 , <i>9</i> , 3333-3340.
BTT-TPA-COF	rt	air	36 W Blue LED lamp	7	85	<i>J. Catal.</i> , 2021 , <i>402</i> , 52-60.
Fluorescein	rt	air	10 W Blue LED	2	90	<i>Green Chem.</i> , 2019 , <i>21</i> , 3602-3605.
BTP-CMP	rt	air	10 W Blue LEDs	3	93	<i>Catal. Sci. Technol.</i> , 2020 , <i>10</i> , 5171-5180.
TTA-CMP	rt	air	24 W Blue bulb	2	98	<i>Catal. Sci. Technol.</i> , 2021 , <i>11</i> , 3799-3809.
TZ-HCP1D	rt	air	6 W White LEDs	1	99	<i>Green Chem.</i> , 2021 , <i>23</i> , 1292-1299.
CbzCMP-12	rt	1	14 W Blue LED	2	99	<i>Catal. Sci. Technol.</i> , 2022 , <i>12</i> , 5942-5951.
TMU-34(-2H)	rt	air	400W mercury-vapor lamp	2	>99	<i>Inorg. Chem.</i> , 2022 , <i>61</i> , 19134-19143.
EDOT-COPs	rt	air	6 W Blue LEDs	1-2	92-95	<i>ACS Catal.</i> , 2023 , <i>13</i> , 9845-9856.
NQ-COF _{A1} -OPR	rt	1	18 W Blue LEDs	24	97	<i>Chem. Sci.</i> , 2023 , <i>14</i> , 1543-1550.
TPT-COF	rt	air	40 W Blue LED lamp	6	80	<i>J. Catal.</i> , 2024 , <i>433</i> , 115497.
Py-B-CMP	rt	air	40 W Blue LED lamp	5	99	<i>Appl. Catal. Gen.</i> , 2024 , <i>671</i> , 119576.
BO-COF _{F3}	rt	1	18 W Blue LED	24	95	<i>Angew. Chem.Int. Ed.</i> , 2024 , <i>63</i> , e202319909.
DCM-CMP2	rt	1	30 W Blue LED lamp	4	95	<i>Macromol. Rapid Commun.</i> , 2024 , 10.1002/marc.202400083.
TZ-OMS	rt	air	6 W White LEDs	2	94	This work

* With benzaldehyde and *o*-diaminobenzene as substrates.

IX. References

1. G. Zou, L. Zhao, L. Zeng, K. Luo, H. Ni, H. Wang, Q. Li, W. Yu and X. Li, *Inorg. Chem.* **2019**, *58*, 861-869.
2. W.-K. An, S.-J. Zheng, H.-X. Zhang, T.-T. Shang, H.-R. Wang, X.-J. Xu, Q. Jin, Y. Qin, Y. Ren, S. Jiang, C.-L. Xu, M.-S. Hou and Z. Pan, *Green Chem.* **2021**, *23*, 1292-1299.
3. P. Kissel, D. J. Murray, W. J. Wulftange, V. J. Catalano and B. T. King, *Nat. Chem.* **2014**, *6*, 774-778.
4. W.-K. An, S.-J. Zheng, Y.-N. Du, S.-Y. Ding, Z.-J. Li, S. Jiang, Y. Qin, X. Liu, P.-F. Wei, Z.-Q. Cao, M. Song and Z. Pan, *Catal. Sci. Technol.* **2020**, *10*, 5171-5180.
5. G. Brasche and S. L. Buchwald, *Angew. Chem. Int. Ed.* **2008**, *47*, 1932-1934.
6. Z. Geng, H.-y. Zhang, G. Yin, Y. Zhang and J. Zhao, *J. Chem. Res.* **2020**, *44*, 557-565.
7. D. Saha, A. Saha and B. C. Ranu, *Green Chem.* **2009**, *11*, 733-737.
8. Q. An, C. He, X. Fan, C. Hou, J. Zhao, Y. Liu, H. Liu, J. Ma, Z. Sun and W. Chu, *ChemElectroChem* **2020**, *7*, 3969-3974.

X. Liquid NMR spectra of some compounds

