

Supplementary Information

Reversible Tuning of Pore Size and CO₂ Adsorption in Azobenzene Functionalized Porous Organic Polymers

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1. Materials and measurements

All chemical reagents were commercially available and used without further purification unless otherwise indicated. 2, 5-Dibromoaniline^[1] and 1, 3, 5-triformylphloroglucinol^[2] were synthesized following the published procedures. 4-Methylnitrosobenzene and 4-tertbutylnitrosobenzene were also prepared according to the published procedures.^[3]

Flash column chromatography was performed by using a 100-150 times weight excess of flash silica gel 32-63 μm from Dynamic Absorbents Inc. Fractions were analyzed by TLC using TLC silica gel F254 250 μm precoated-plates from Dynamic Absorbents Inc.

NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer.

Powder X-Ray Diffraction (PXRD) was obtained from a Bruker D-8 Discover diffractometer, using monochromated Cu K_{α} ($\lambda = 1.542 \text{ \AA}$) radiation.

The FT-IR spectra of starting materials and as synthesized UCBZ series were obtained from Thermo Nicolet Avatar-370 spectrometer using KBr (IR grade) pellets.

Elemental analysis was taken at an Exeter Analytical-Model CE 440 CHN Analyzer, microanalysis laboratory, University of Illinois at Urbana-Champaign.

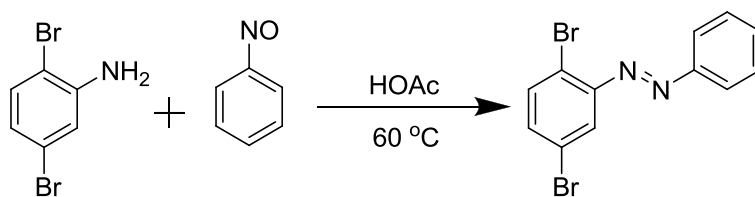
Thermogravimetric analyses (TGA) were performed on a thermogravimetric/differential thermal analyzer by heating the samples at $10 \text{ }^{\circ}\text{C min}^{-1}$ to $600 \text{ }^{\circ}\text{C}$ under the atmosphere of nitrogen.

The Quantachrome Autosorb ASiQ automated gas sorption analyzer was used to measure N_2 and CO_2 adsorption isotherms. The sample was heated at $100 \text{ }^{\circ}\text{C}$ and kept at this temperature for at least 22 hours for the activation. Ultra high purity grade (99.999 % purity) N_2 , CO_2 and He, oil-free valves and gas regulators were used for all free space corrections and measurements. For all of the gas adsorption measurements, the temperatures were controlled by using a refrigerated bath of liquid N_2 (77 K), ice water (273 K).

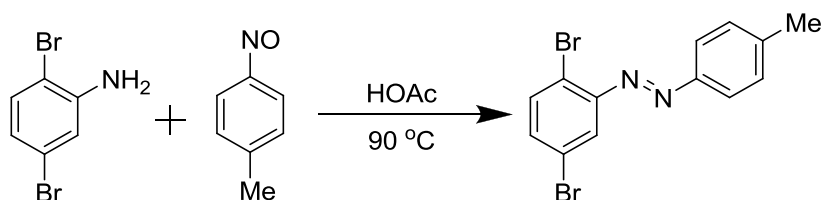
Scanning Electron Microscopy images (SEM) were recorded using a JSM-6480LV (LVSEM) at 5.0 kV. Samples were sputter coated with gold prior to analysis.

For the UV sources, a universal lamp supply-250 watts (model 1152/1144) was used for the diamines photoisomerization; a Hanovia mercury lamp (Model: 679A36, 450 watts) was used for the polymer photoisomerization; UV-Vis adsorption spectra of the diamines were collected in a 1 cm path length quartz cuvette by using an Agilent 8453 spectrophotometer equipped with tungsten and deuterium lamps.

2. General synthetic procedures

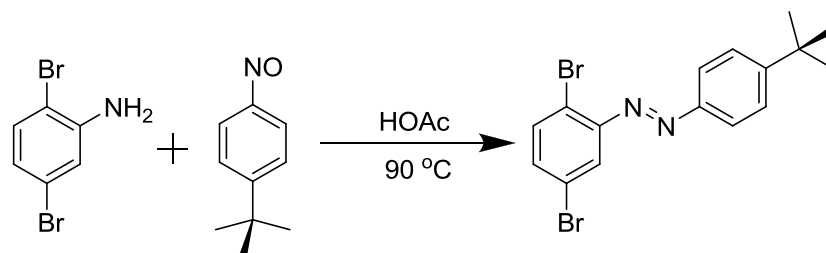


Synthesis of 1-(2,5-dibromophenyl)-2-phenyldiazene: A 100 mL Schlenk tube was charged with 2, 5-dibromoaniline (1.20 g, 4.8 mmol) and nitrosobenzene (0.90 g, 8.4 mmol). Acetic acid (15 mL) was added to this tube, and the resulting mixture was degassed and stirred at 90 °C for 36 hours. It was then cooled to room temperature, and acetic acid was neutralized by saturated sodium bicarbonate (Na_2CO_3) solution. The aqueous layer was extracted with dichloromethane (2 x 60 mL). The combined organic layer was dried over anhydrous sodium sulfate (Na_2SO_4), and the volatiles were removed under reduced pressure. The residue was purified by flash chromatography column (gradient elution, hexanes \rightarrow 20 % CH_2Cl_2 /hexane) to yield the pure product as an orange solid (0.82 g, 51 %): ^1H NMR (500 MHz, CDCl_3 , δ): 8.01-7.99 (m, 2H), 7.84 (d, 1H, $J = 2.5$ Hz), 7.64 (d, 1H, $J = 8.5$ Hz), 7.58-7.54 (m, 3H), 7.45 (q, 1H, $J_1 = 2.5$ Hz, $J_2 = 8.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3 , δ): 152.3, 150.0, 134.8, 134.4, 132.1, 129.2, 124.4, 123.6, 122.0, 121.0; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_8\text{N}_2\text{Br}_2$, 340.9112; found, 340.9107.

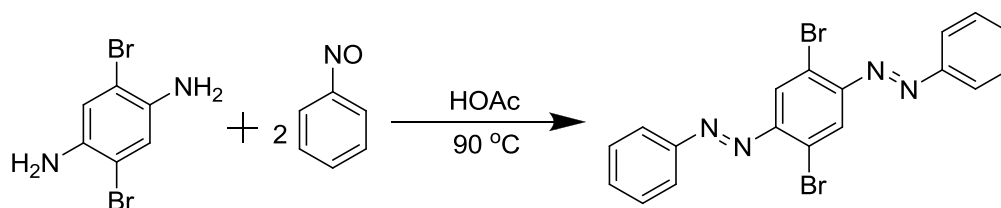


Synthesis of 1-(2, 5-dibromophenyl)-2-p-tolyldiazene: A 100 mL Schlenk tube was charged with 2, 5-dibromoaniline (0.82 g, 2.9 mmol) and 4-methylnitrosobenzene (0.82 g, 6.8 mmol). Acetic acid (10 mL) was added to this tube, and the resulting mixture was degassed and stirred at 90 °C for 36 hours. It was then cooled to room temperature, and acetic acid was neutralized by saturated sodium bicarbonate solution. The aqueous layer was extracted with dichloromethane (2 x 60 mL), and the combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography column (10% dichloromethane in hexanes as the eluent) to yield the pure product as an orange solid (0.24 g, 21 %): ^1H NMR (500 MHz, CDCl_3 , δ): 7.91 (d, 2H, $J = 8.0$ Hz), 7.83 (d, 1H, $J = 2.5$ Hz), 7.62 (d, 1H, $J = 8.5$ Hz), 7.43 (q, 1H, $J_1 = 2.5$ Hz, $J_2 = 8.5$ Hz), 7.35 (d, 2H, $J = 8.0$ Hz), 2.47 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 150.5, 150.2,

143.0, 134.8, 134.0, 129.9, 124.1, 123.6, 122.0, 121.0, 21.6; HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{13}H_{10}N_2Br_2$, 354.9269, found, 354.9274.

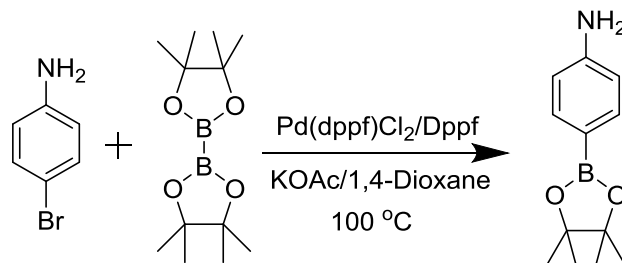


Synthesis of 4-tert-butylphenyl-1-(2,5-dibromophenyl)diazene: A 100 mL Schlenk tube was charged with 2, 5-dibromoaniline (0.73 g, 2.9 mmol) and 4-tert-butylnitrosobenzene (0.62 g, 3.8 mmol). Acetic acid (10 mL) and chloroform (10 mL) were added to this tube, and the resulting mixture was degassed and stirred at 90 °C for 36 hours. It was then cooled to room temperature, and acetic acid was neutralized by saturated sodium bicarbonate solution. The aqueous layer was extracted with dichloromethane (2 x 60 mL), and the combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography column (first hexanes then 10 % dichloromethane in hexanes as the eluent) to yield the pure product as an orange solid (0.37 g, 28 %): 1H NMR (500 MHz, $CDCl_3$, δ): 7.94 (d, 2H, $J = 9.0$ Hz), 7.82 (d, 1H, $J = 2.5$ Hz), 7.62 (d, 1H, $J = 8.5$ Hz), 7.57 (d, 2H, $J = 8.5$ Hz), 7.43 (q, 1H, $J_1 = 2.5$ Hz, $J_2 = 8.5$ Hz), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.9, 150.4, 150.2, 134.8, 134.0, 126.2, 124.1, 123.4, 122.0, 121.0, 35.1, 31.2; HRMS (ESI) m/z : $[M+H]^+$ calcd for $C_{16}H_{16}N_2Br_2$, 396.9739, found, 396.9738.

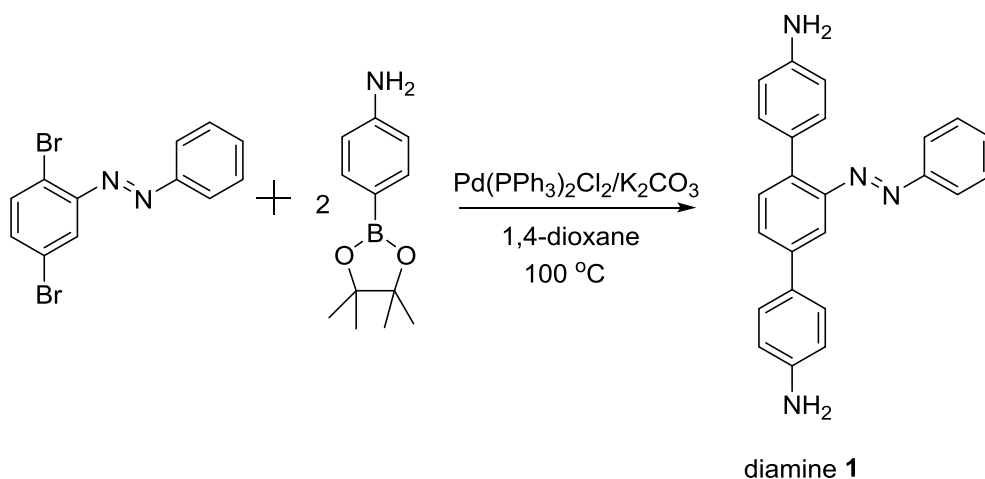


Synthesis of (1,1')-2,2'-(2,5-dibromo-1,4-phenylene)bis(1-phenyldiazene): A 100 mL Schlenk tube was charged with 2, 5-dibromo-4-aminoaniline (0.82 g, 3.1 mmol) and nitrosobenzene (1.32 g, 12.3 mmol). Acetic acid (10 mL) and chloroform (10 mL) was added to this tube, and the resulting mixture was degassed and stirred at 90 °C for 36 hours. It was then cooled to room temperature, and acetic acid was neutralized by saturated sodium bicarbonate solution. The aqueous layer was extracted with dichloromethane (2 x 60 mL), and the combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography column (gradient elution, hexanes→10 % dichloromethane in hexanes) to yield the pure

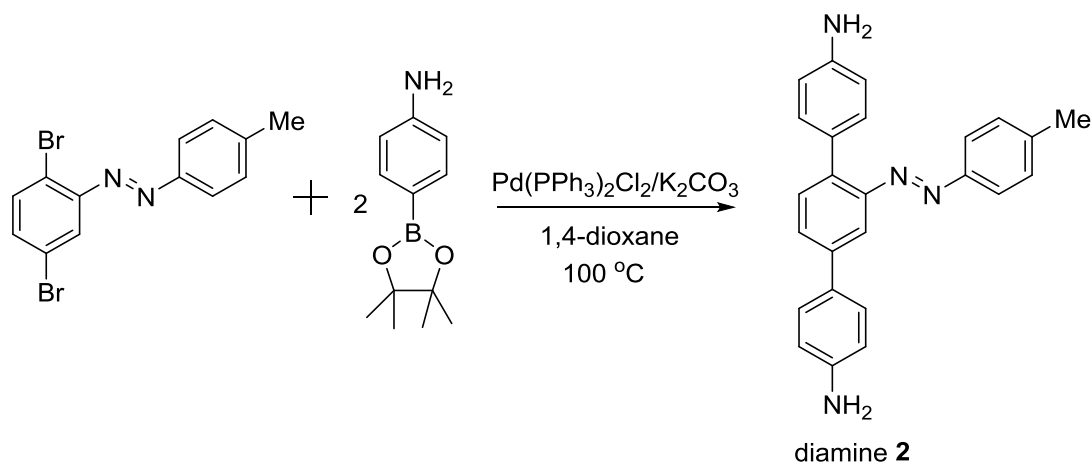
product as a dark orange solid (0.11 g, 9 %): ^1H NMR (500 MHz, CDCl_3 , δ): 8.11 (s, 2H), 8.04-8.06 (m, 4H), 7.57-7.59 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 152.5, 150.3, 132.4, 129.3, 125.1, 123.8, 122.4; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{12}\text{N}_4\text{Br}_2$, 444.9487, found, 444.9488.



Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline: A 100 mL Schlenk tube was charged with 4-bromoaniline (1.72 g, 10.0 mmol), bis(pinacolato)diboron (3.05 g, 12.0 mmol) and potassium acetate (3.00 g, 30.6 mmol). To this mixture, catalyst [1, 1'-Bis(diphenylphosphino)ferrocene]dichloropalladium (PdCl_2dppf) (210 mg, 0.29 mmol) and ligand 1,1'-Bis(diphenylphosphino)ferrocene (dppf) (160 mg, 0.30 mmol) were added, followed by anhydrous 1, 4-dioxane (50 mL). The resulting solution was degassed three times and stirred at 100 °C for 2 days. After cooled to room temperature, water (150 mL) was added. The aqueous layer was extracted with dichloromethane (2 x 150 mL), and the combined organic layer was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography column (gradient elution, dichloromethane \rightarrow 10 % ethyl acetate in dichloromethane). After removing a small amount of the bis(pinacolato)diboron contaminant by washing with a mixture of methanol/hexanes, the pure product was obtained as a white solid (1.44 g, 66 %): ^1H NMR (500 MHz, CDCl_3 , δ): 7.62 (d, 2H, $J = 8.5$ Hz), 6.66 (d, 2H, $J = 8.5$ Hz), 3.86 (s, 2H), 1.33 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 149.3, 136.4, 114.0, 83.3, 24.8. The NMR data are consistent with the literature report.^[4]

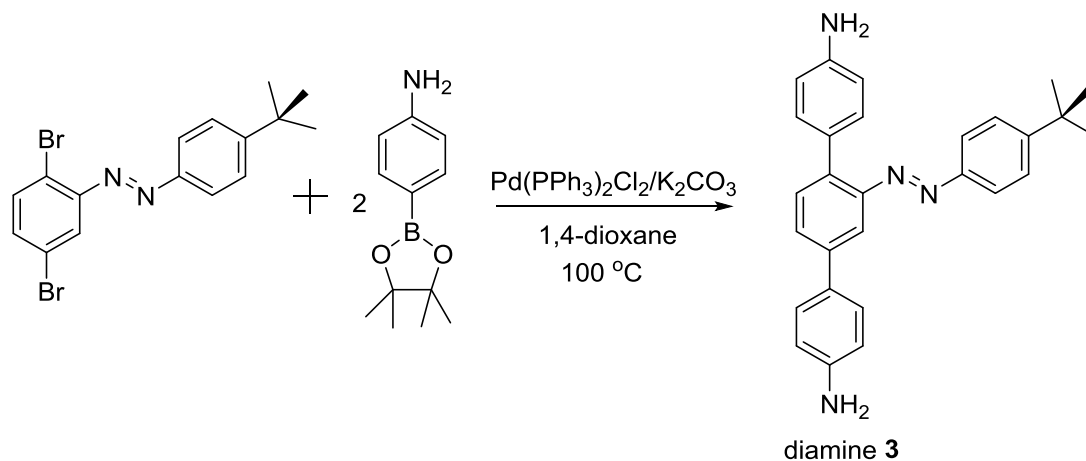


Synthesis of diamine 1: A 100 mL Schlenk tube was charged with 2,5-dibromophenyl-2-phenyldiazene (340 mg, 1.0 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (550 mg, 2.6 mmol). The catalyst Pd(PPh₃)₂Cl₂ (180 mg, 0.2 mmol) and K₂CO₃ (400 mg) were added followed by 1, 4-dioxane (20 mL) and water (4 mL). The resulting mixture was stirred at 100 °C for 36 hours. After cooled to room temperature, water (50 mL) was added. The product was extracted with dichloromethane (2 x 50 mL), and the combined organic layer was dried over anhydrous sodium sulfate (Na₂SO₄). The volatiles were removed under reduced pressure, and the residue was purified by flash column chromatography (gradient elution, dichloromethane→10% ethyl acetate in dichloromethane) to yield the pure product as a red orange solid (215 mg, 59%): ¹H NMR (500 MHz, CDCl₃, δ): 7.90 (d, 1H, *J* = 2.0 Hz), 7.88 (d, 2H, *J* = 7.0 Hz), 7.72 (q, 1H, *J*₁ = 2.0 Hz, *J*₂ = 8.0 Hz), 7.61 (d, 1H, *J* = 8.0 Hz), 7.55 (d, 2H, *J* = 8.0 Hz), 7.49 (m, 3H), 7.33 (d, 2H, *J* = 8.5 Hz), 6.80 (t, 4H, *J*₁ = 8.0 Hz, *J*₂ = 8.0 Hz), 3.80 (s, 2H), 3.78 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, δ): 152.9, 149.7, 146.0, 145.7, 140.0, 138.9, 132.0, 130.75, 130.69, 130.6, 129.0, 128.8, 128.6, 128.0, 123.3, 115.4, 114.4, 113.4; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₄H₂₀N₄, 365.1766, found, 365.1769.

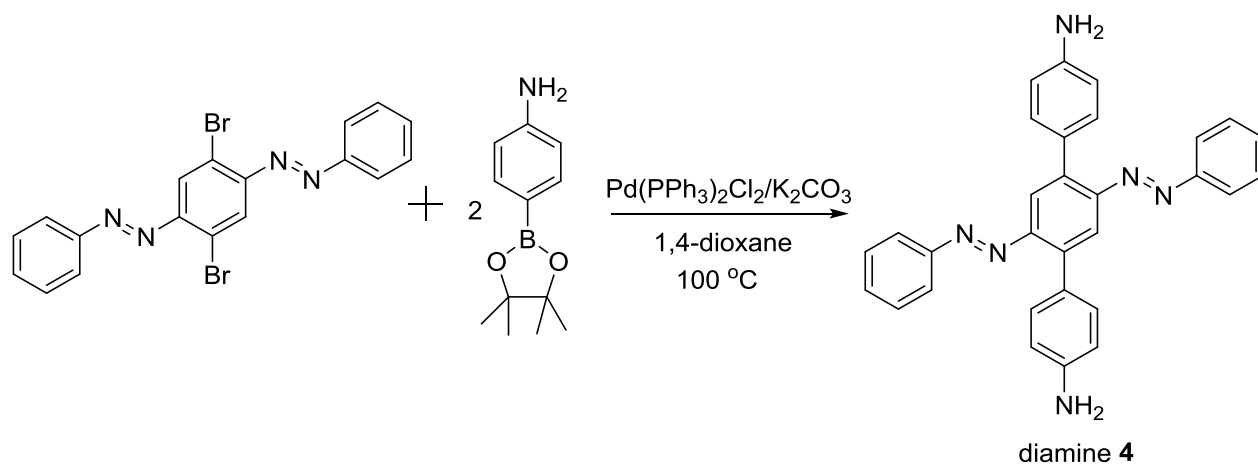


Synthesis of diamine 2: A 100 mL Schlenk tube was charged with 2,5-dibromophenyl-2-*p*-tolylidiazene (240 mg, 0.68 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (590 mg, 2.7 mmol). The catalyst Pd(PPh₃)₂Cl₂ (130 mg, 0.14 mmol) and K₂CO₃ (300 mg, 2.2 mmol) were added followed by 1, 4-dioxane (15 mL) and water (3 mL). The resulting mixture was stirred at 100 °C for 36 hours, and then cooled to room temperature. Water (50 mL) was added and the mixture was extracted with dichloromethane (2 x 50 mL). The combined organic layer was dried over anhydrous sodium sulfate (Na₂SO₄), and concentrated under reduced pressure. The residue was purified by flash column chromatography (gradient elution, dichloromethane→10 % ethyl acetate in dichloromethane) to yield the pure compound as a red orange solid (160 mg, 62 %): ¹H NMR (500 MHz, CDCl₃, δ): 7.86 (d, 1H, *J* = 1.5 Hz),

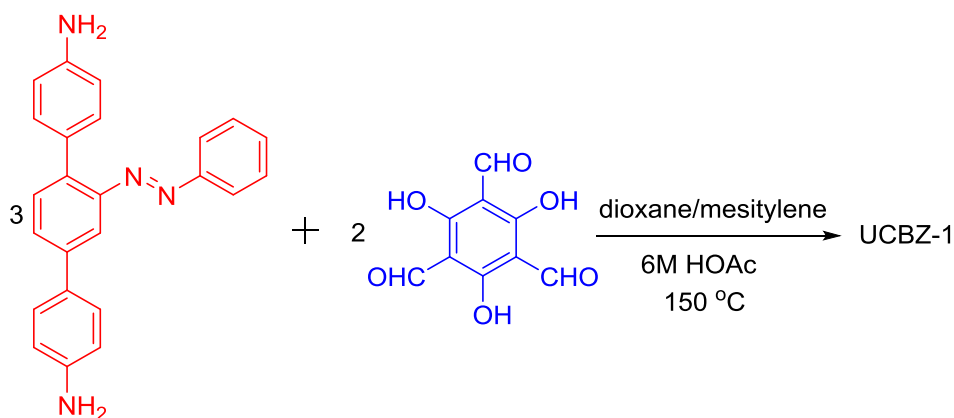
7.76 (d, 2H, $J = 8.5$ Hz), 7.69 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 8.0$ Hz), 7.59 (d, 1H, $J = 8.0$ Hz), 7.53 (d, 2H, $J = 8.5$ Hz), 7.31 (d, 2H, $J = 8.5$ Hz), 7.28 (d, 2H, $J = 8.0$ Hz), 6.78 (d, 2H, $J = 8.5$ Hz), 6.76 (d, 2H, $J = 8.5$ Hz), 3.76 (s, 4H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 151.0, 149.7, 145.9, 145.6, 141.1, 139.9, 138.5, 136.3, 131.9, 130.6, 129.6, 128.8, 128.2, 127.9, 123.2, 115.3, 114.3, 113.3, 21.4; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{22}\text{N}_4$, 379.1923, found, 379.1922.



Synthesis of diamine 3: A 100 mL Schlenk tube was charged with 4-tert-butylphenyl-2-(2,5-dibromophenyl)diazene (500 mg, 1.3 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (740 mg, 3.4 mmol). The catalyst $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (200 mg, 0.22 mmol) and K_2CO_3 (480 mg, 3.5 mmol) were added, followed by 1, 4-dioxane (24 mL) and water (5 mL). The resulting mixture was stirred at 100 °C for 36 hours, and cooled to room temperature. Water (50 mL) was added and the mixture was extracted with dichloromethane (2 x 50 mL). The combined organic layer was dried over anhydrous sodium sulfate, and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution, dichloromethane \rightarrow 10% ethyl acetate in dichloromethane) to yield the pure product as a red orange solid (160 mg, 30%): ^1H NMR (500 MHz, CDCl_3 , δ): 7.87 (d, 1H, $J = 2.0$ Hz), 7.82 (d, 2H, $J = 8.5$ Hz), 7.70 (q, 1H, $J_1 = 2.0$ Hz, $J_2 = 8.0$ Hz), 7.61 (d, 1H, $J = 8.0$ Hz), 7.55 (d, 2H, $J = 8.5$ Hz), 7.52 (d, 2H, $J = 8.5$ Hz), 7.33 (d, 2H, $J = 8.5$ Hz), 6.81 (d, 2H, $J = 8.5$ Hz), 6.78 (d, 2H, $J = 8.5$ Hz), 3.78 (d, 4H); ^{13}C NMR (100 MHz, CDCl_3 , δ): 154.2, 150.9, 149.9, 146.0, 145.6, 140.0, 138.6, 132.0, 130.7, 128.8, 128.3, 128.0, 125.9, 125.3, 123.0, 115.3, 114.4, 113.4, 35.0, 31.3; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{28}\text{N}_4$, 421.2392, found, 421.2381.

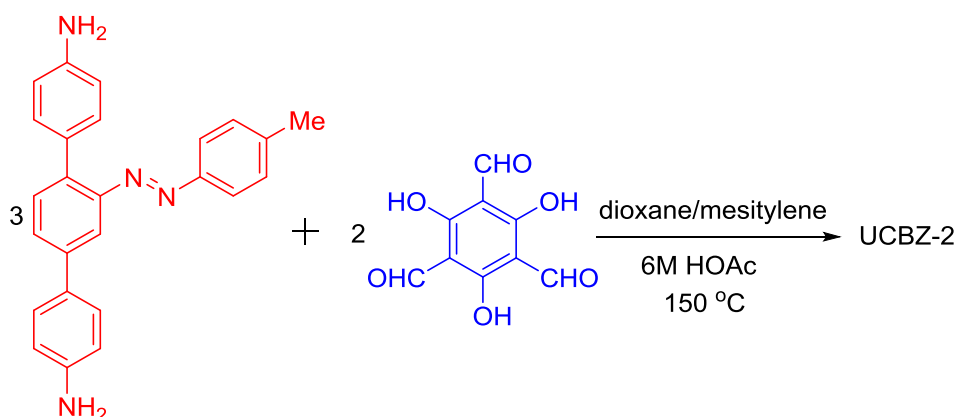


Synthesis of diamine 4: A 100 mL Schlenk tube was charged with 2,2'-(2,5-dibromo-1,4-phenylene)bis(1-phenyldiazene) (150 mg, 0.34 mmol) and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (280 mg, 1.3 mmol). The catalyst Pd(PPh₃)₂Cl₂ (70 mg, 0.08 mmol) and K₂CO₃ (150 mg, 1.1) were added followed by 1, 4-dioxane (8 mL) and water (1.5 mL). The resulting mixture was stirred at 100 °C for 36 hours, and cooled to room temperature. Water (50 mL) was added and the mixture was extracted with dichloromethane (2 x 50 mL). The combined organic layer was dried over anhydrous sodium sulfate and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (gradient elution, dichloromethane→10% ethyl acetate in dichloromethane) to yield the pure product as a red orange solid (63 mg, 40%): ¹H NMR (500 MHz, CDCl₃, δ): 7.92 (s, 2H), 7.89 (d, 4H, *J* = 8.5 Hz), 7.50 (m, 6H), 7.39 (d, 4H, *J* = 8.0 Hz), 6.80 (d, 4H, *J* = 8.0 Hz), 3.82 (s, 4H); ¹³C NMR (100 MHz, DMSO-*d*₆, δ): 152.9, 150.3, 149.1, 139.6, 132.0, 131.9, 130.0, 124.9, 123.3, 117.5, 113.8; HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₃₀H₂₄N₆, 469.2141, found, 469.2161.

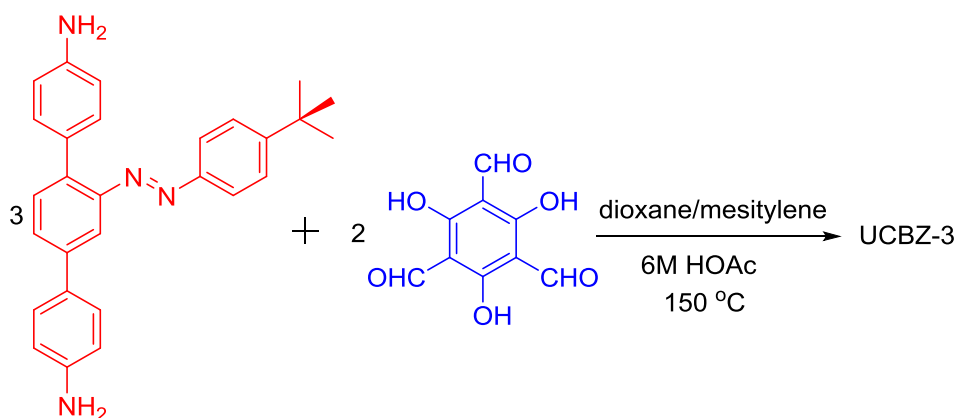


Synthesis of UCBZ-1: A customized glass tube (the outer diameter is 10 mm and the inner diameter is 8 mm) was charged with 1, 3, 5-triformylphloroglucinol (21 mg, 0.1 mmol),

diamine **1** (54 mg, 0.15 mmol), 1,4-dioxane (4 mL), mesitylene (2 mL) and 6 M acetic acid (0.2 mL). The tube was flash frozen at 77 K in liquid nitrogen bath and evacuated to the internal pressure about 100 mtorr, and then the tube was sealed under the frame. The mixture was warmed to room temperature, and the reaction temperature was slowly raised to 150 °C over 2 hours. The reaction was kept at this temperature for 3 days and cooled to room temperature over 12 hours. The orange precipitate was collected by vacuum filtration, washed with large amount of dichloromethane and acetone, and dried under vacuum to yield **UCBZ-1** (62 mg, 88 %): Elemental analysis calcd (%) for $(C_{28}H_{20}N_4O_4)_n$: C, 70.58; H, 4.23; N, 11.76. Found: C, 71.67; H, 4.02; N, 10.85.

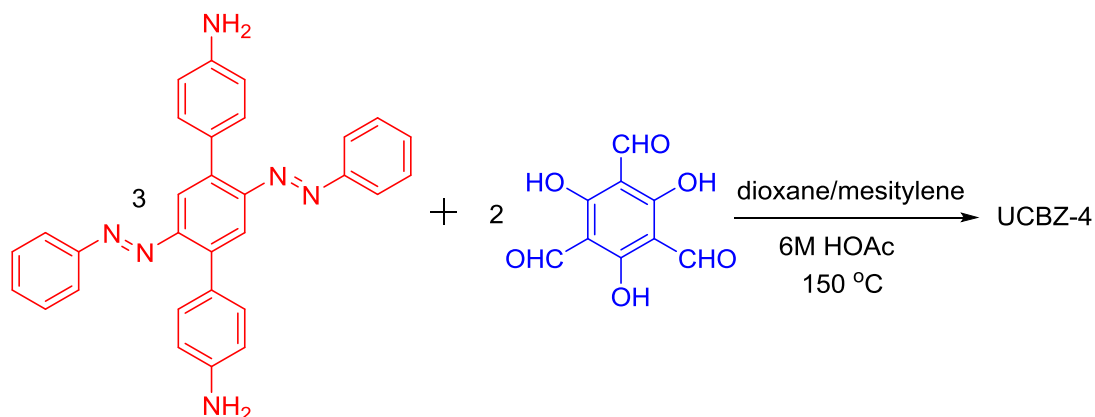


Synthesis of UCBZ-2: The above polymerization procedure for **UCBZ-1** was followed. Using 1, 3, 5-triformylphloroglucinol (21 mg, 0.1 mmol), diamine **2** (57 mg, 0.15 mmol), 1,4-dioxane (4 mL), mesitylene (2 mL), and 6 M acetic acid (0.2 mL), **UCBZ-2** was obtained as an orange precipitate (69 mg, 92 %): Elemental analysis calcd (%) for $(C_{29}H_{22}N_4O_4)_n$: C, 71.01; H, 4.52; N, 11.42. Found: C, 73.16; H, 4.03; N, 11.12.

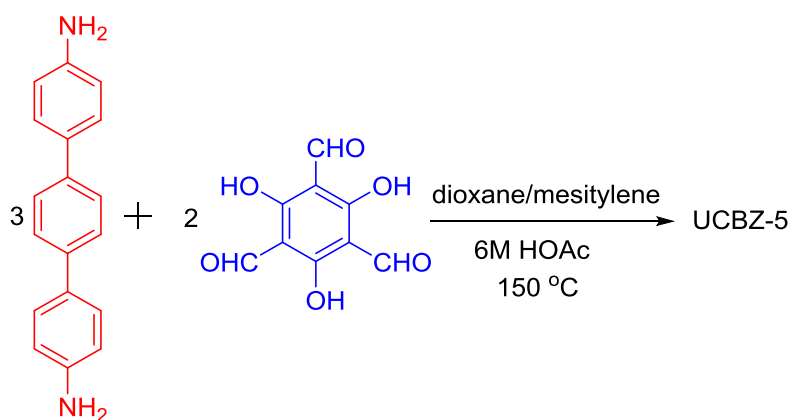


Synthesis of UCBZ-3: The above polymerization procedure for **UCBZ-1** was followed. Using 1, 3, 5-triformylphloroglucinol (21 mg, 0.1 mmol), diamine **3** (63 mg, 0.15 mmol), 1,4-dioxane (4 mL), mesitylene (2 mL), and 6 M acetic acid (0.2 mL), **UCBZ-3** was obtained as

an orange precipitate (66 mg, 79 %): Elemental analysis calcd (%) for $(C_{32}H_{28}N_4O_4)_n$: C, 72.16; H, 5.30; N, 10.52. Found: C, 74.76; H, 5.11; N, 9.92.



Synthesis of UCBZ-4: The above polymerization procedure for **UCBZ-1** was followed. Using 1, 3, 5-triformylphloroglucinol (18 mg, 0.086 mmol), diamine **4** (61 mg, 0.13 mmol), 1,4-dioxane (4 mL), mesitylene (2 mL), and 6 M acetic acid (0.2 mL), **UCBZ-4** was obtained as an orange precipitate (57 mg, 74%): Elemental analysis calcd (%) for $(C_{34}H_{24}N_6O_4)_n$: C, 70.29; H, 4.17; N, 14.48. Found: C, 68.91; H, 3.85; N, 11.30.



Synthesis of UCBZ-5: The above polymerization procedure for **UCBZ-1** was followed. Using 1, 3, 5-triformylphloroglucinol (21 mg, 0.1 mmol), 4, 4''-diamino-*p*-terphenyl (39 mg, 0.15 mmol), 1,4-dioxane (4 mL), mesitylene (2 mL), and 6 M acetic acid (0.2 mL), **UCBZ-5** was obtained as an orange precipitate (49 mg, 86%): Elemental analysis calcd (%) for $(C_{22}H_{16}N_2O_4)_n$: C, 70.96; H, 4.33; N, 7.52. Found: C, 75.75; H, 4.20; N, 7.48.

3. UV spectra of the azobenzene derivatives diamines

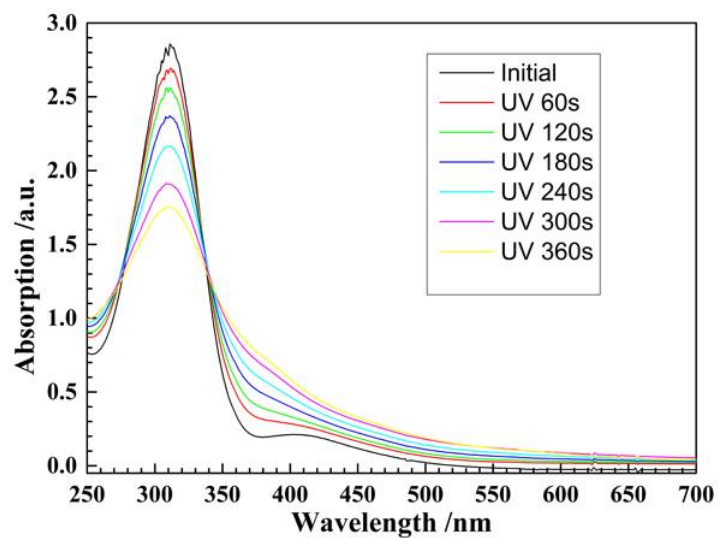


Figure S1. Changes in the adsorption spectra of diamine **1** in CH₂Cl₂ over the time during the irradiation with 320 nm light.

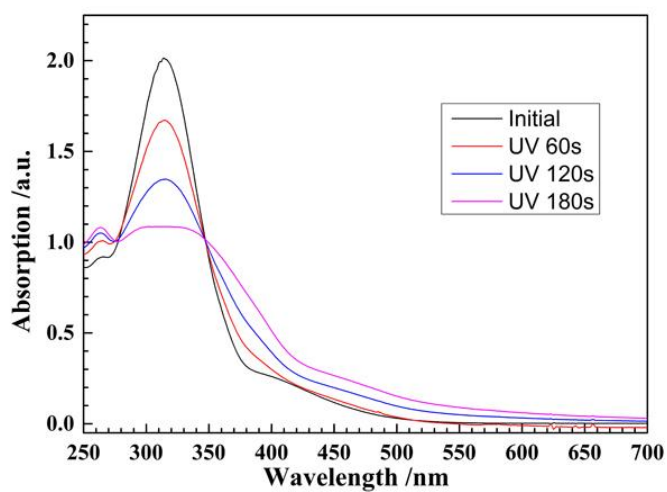


Figure S2. Changes in the adsorption spectrum of diamine **2** in dichloromethane over the time during the irradiation with 320 nm light.

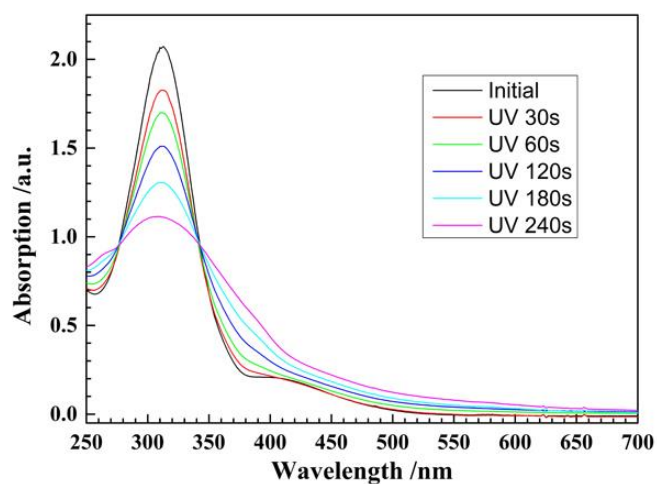


Figure S3. Changes in the adsorption spectrum of diamine **3** in dichloromethane over the time during the irradiation with 320 nm light.

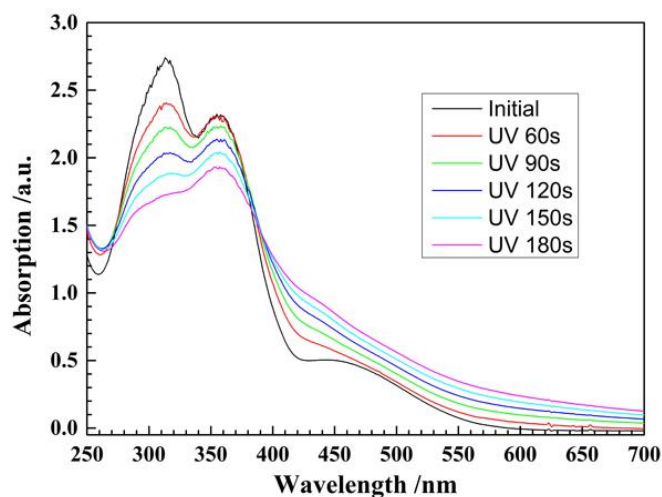


Figure S4. Changes in the adsorption spectrum of diamine **4** in dichloromethane over the time during the irradiation with 254 nm light.

4. NMR study of diamine **1**

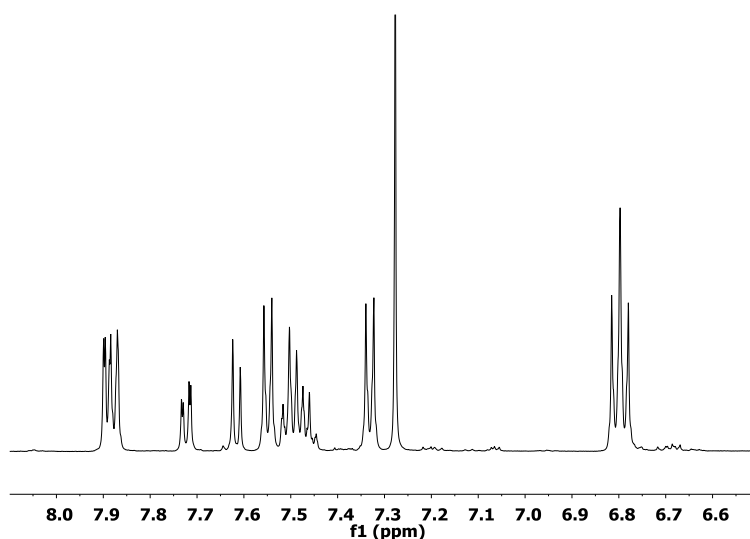


Figure S5. The ^1H NMR spectrum of as synthesized diamine **1**.

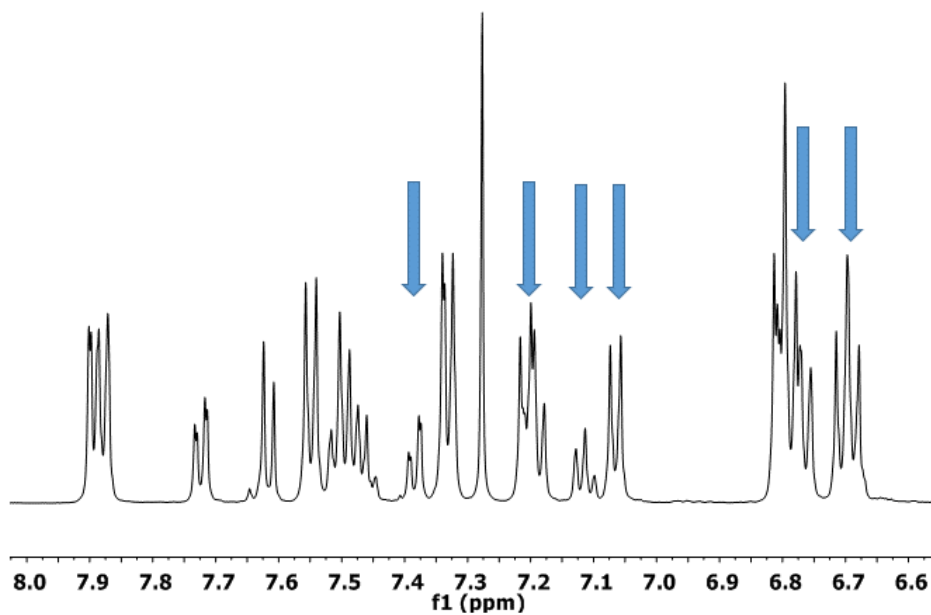


Figure S6. The ^1H NMR spectrum of diamine **1** after UV irradiation for 3 minutes.

5. TGA of UCBZ series

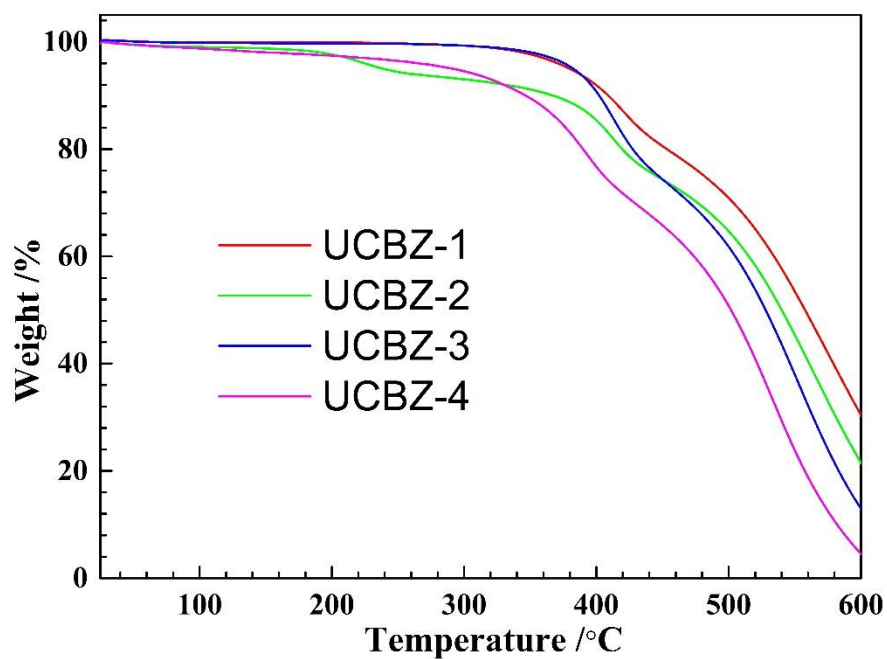


Figure S7. TGA curves of UCBZ series.

6. FT-IR of UCBZ series

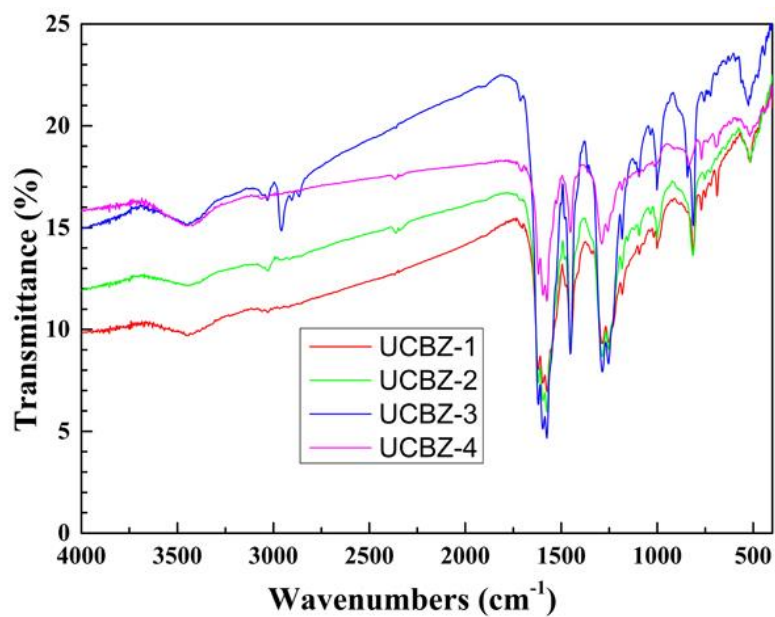


Figure S8. IR spectra of UCBZ series.

7. Powder X-Ray Diffraction of UCBZ series

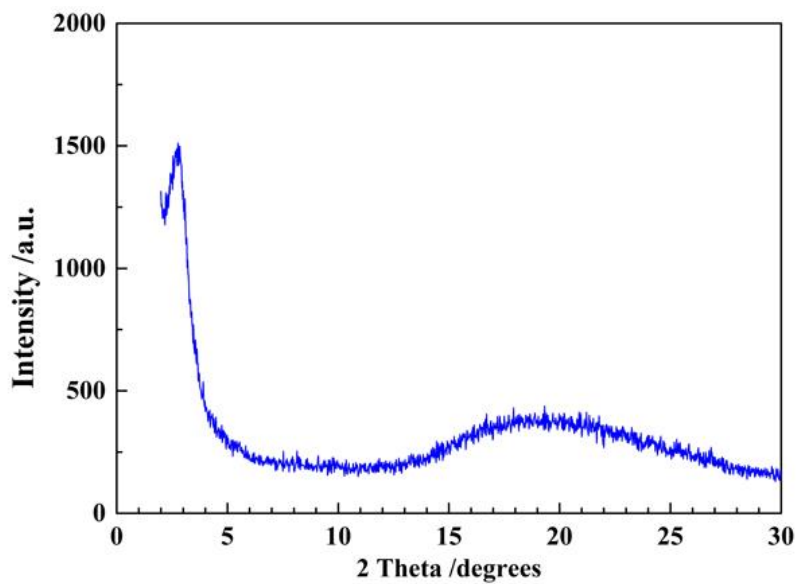


Figure S9. powder X-ray diffraction pattern of UCBZ-1.

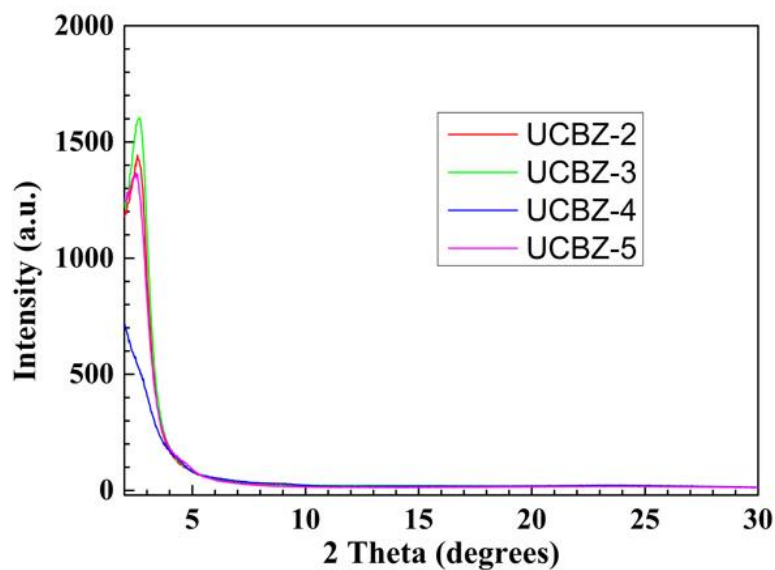


Figure S10. powder X-ray diffraction pattern of UCBZ-2, 3, 4, 5.

8. Additional gas adsorption data for UCBZ series

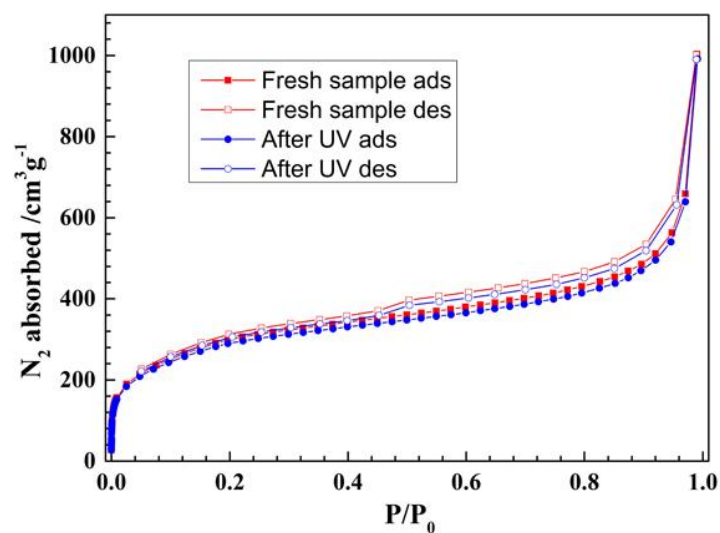


Figure S11. N₂ adsorption and desorption of UCBZ-5 before and after UV irradiation.

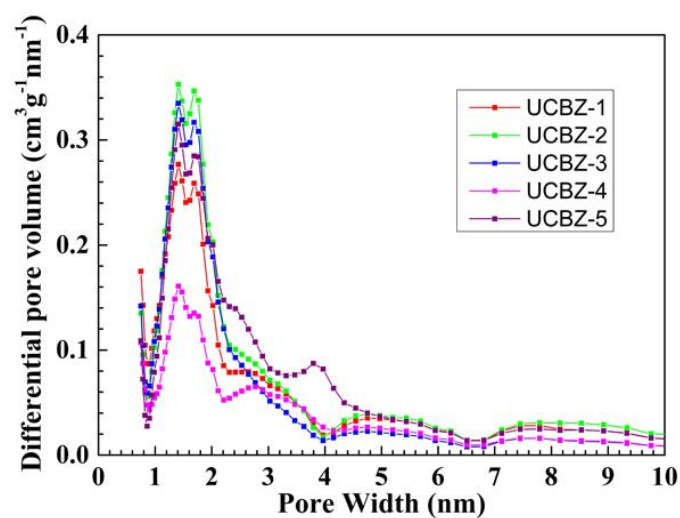


Figure S12. Pore size distribution of UCBZ series.

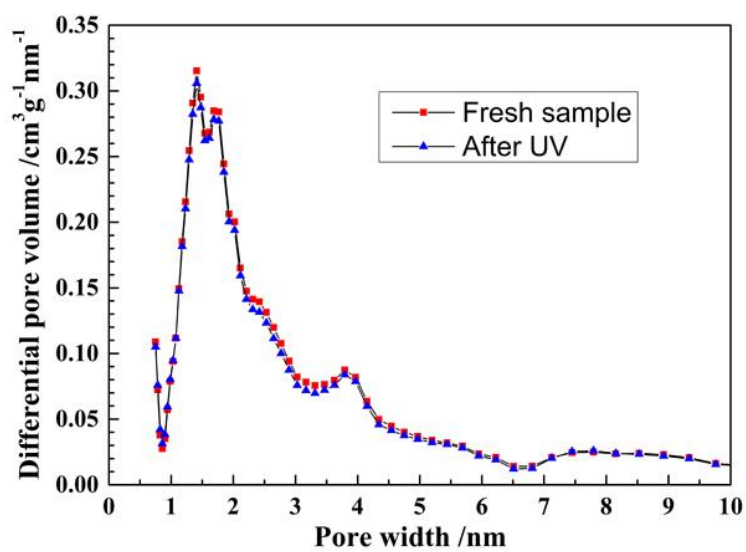


Figure S13. Pore size distribution of UCBZ-5 before and after UV irradiation.

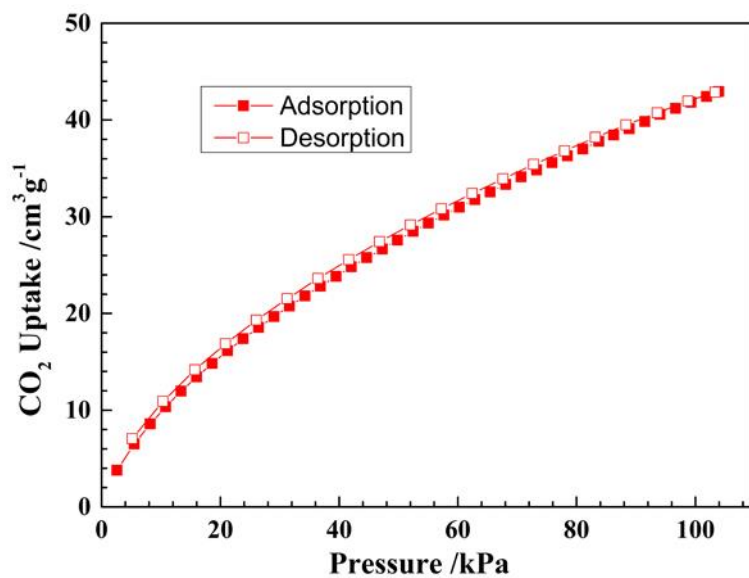


Figure S14. CO₂ adsorption isotherms for UCBZ-5 of the fresh activated sample.

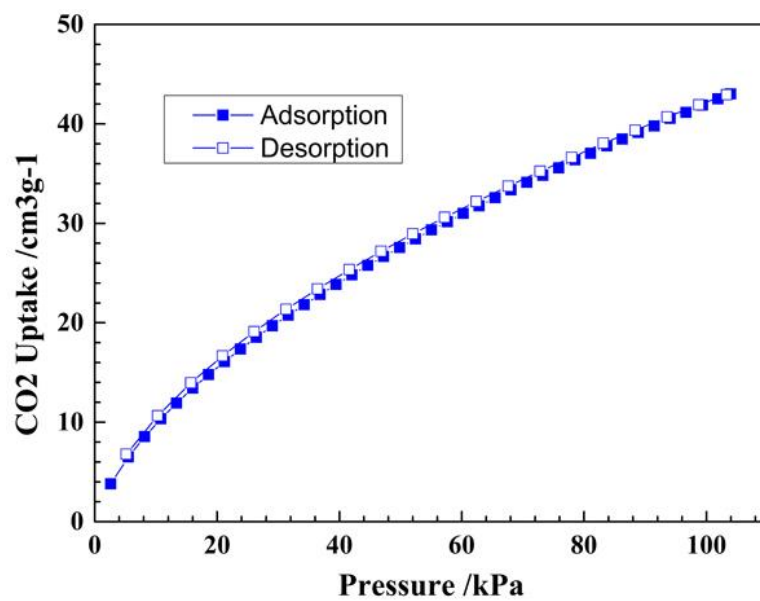
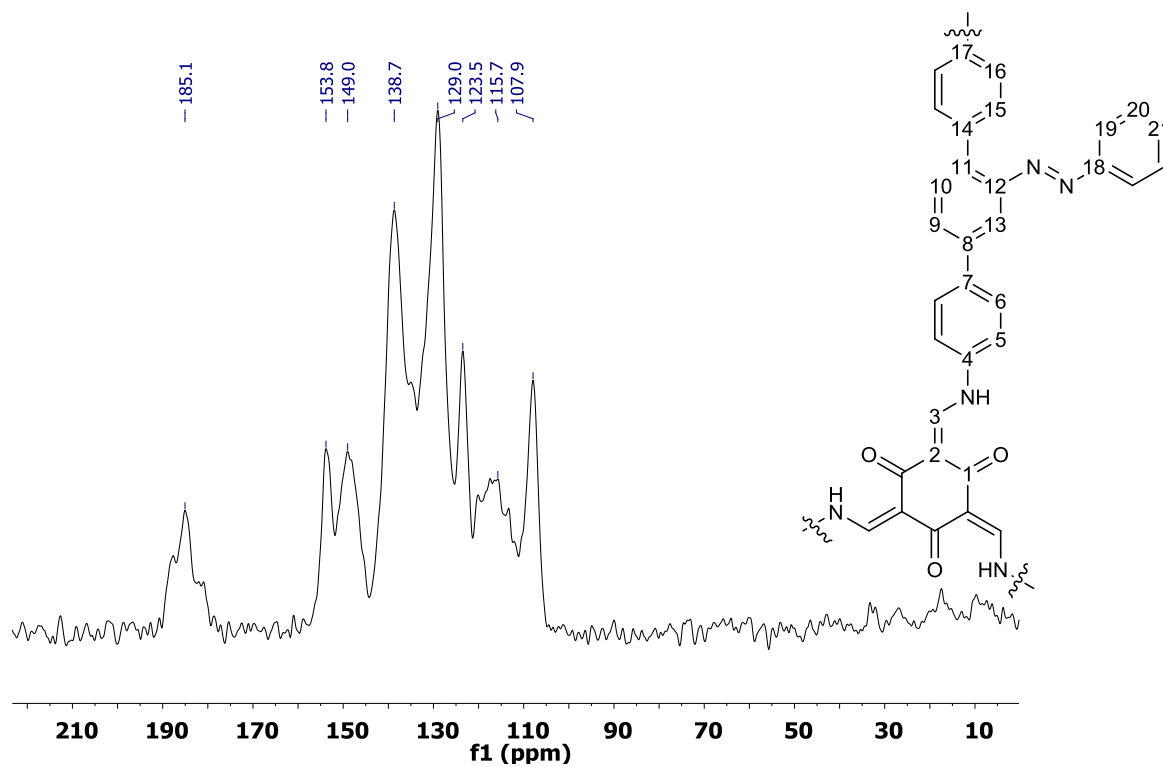


Figure S15. CO₂ adsorption isotherms for UCBZ-5 after UV irradiation.

9. Solid-State ^{13}C CP-MAS

(a)



(b)

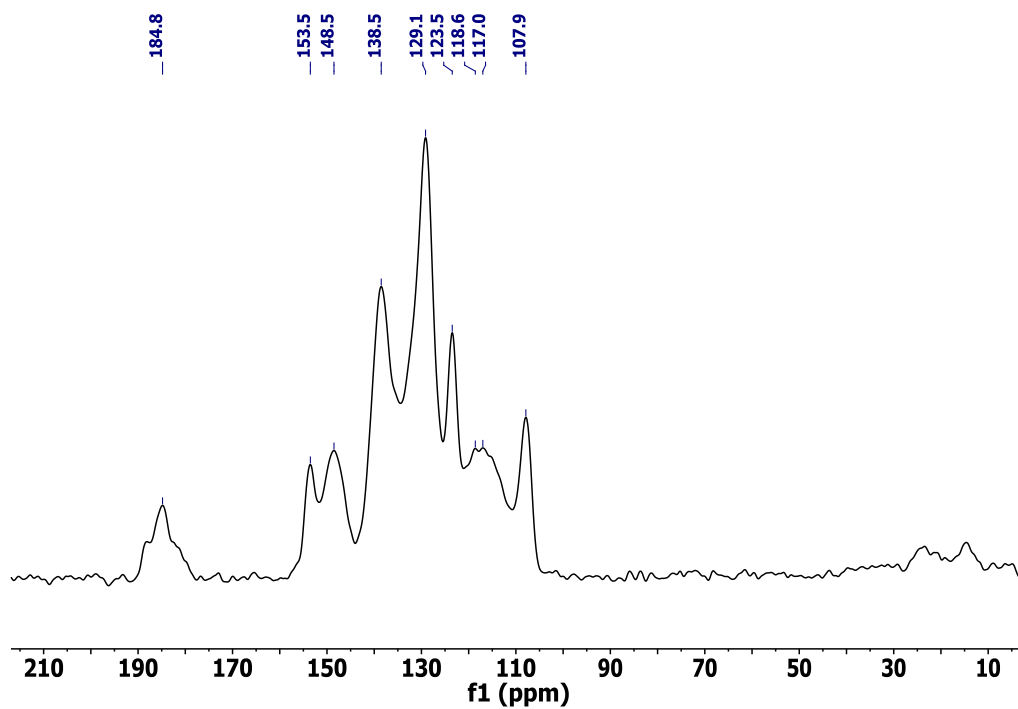


Figure S16. Solid State ^{13}C CP-MAS NMR spectrum of UCBZ-1: before UV irradiation (a); after UV irradiation (b).

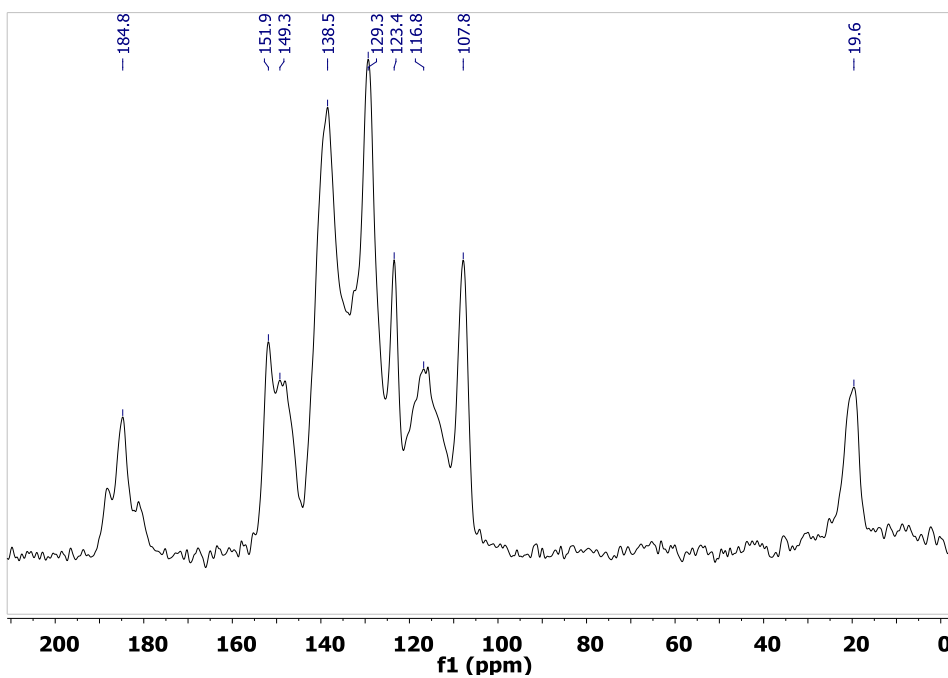
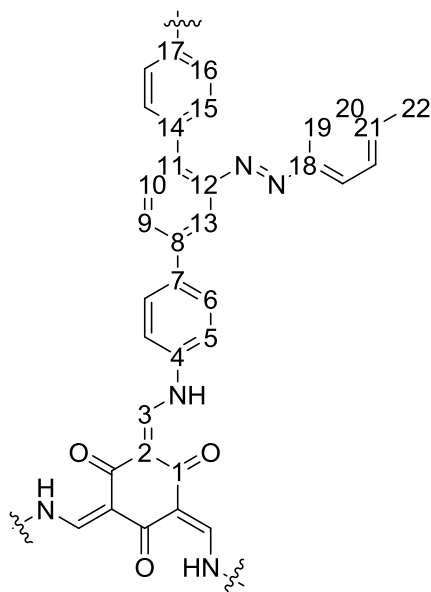


Figure S17. Solid State ^{13}C CP-MAS NMR spectrum of UCBZ-2.

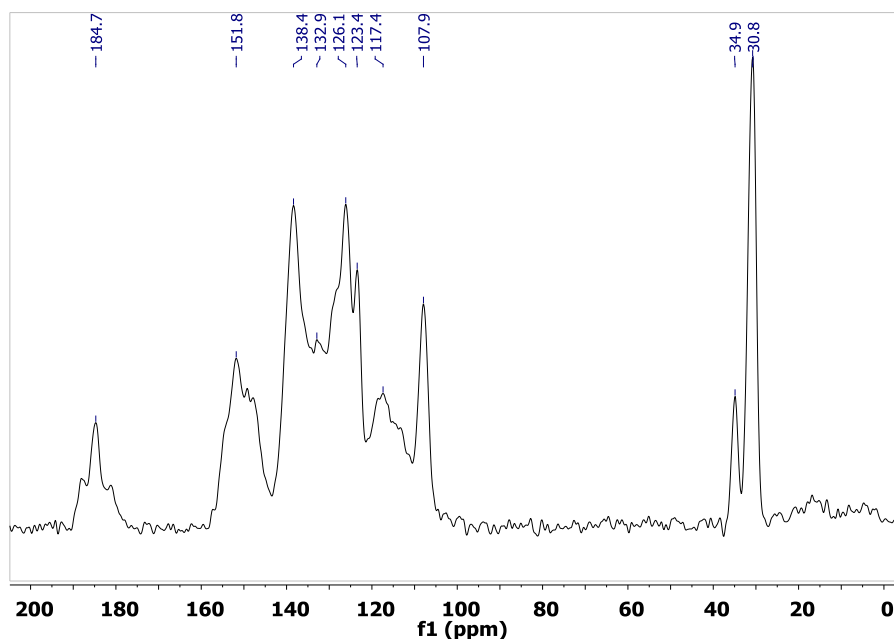
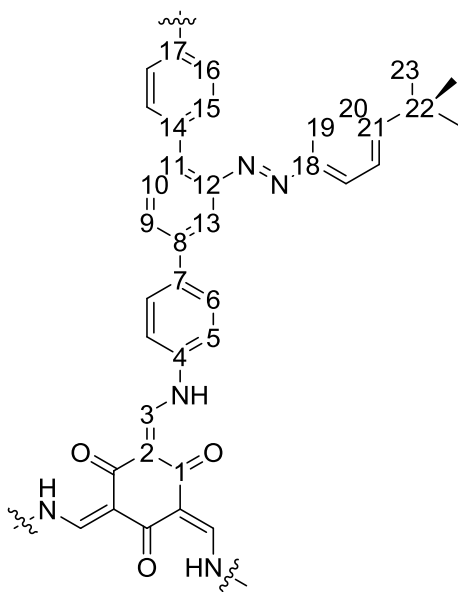


Figure S18. Solid State ^{13}C CP-MAS NMR spectrum of UCBZ-3.

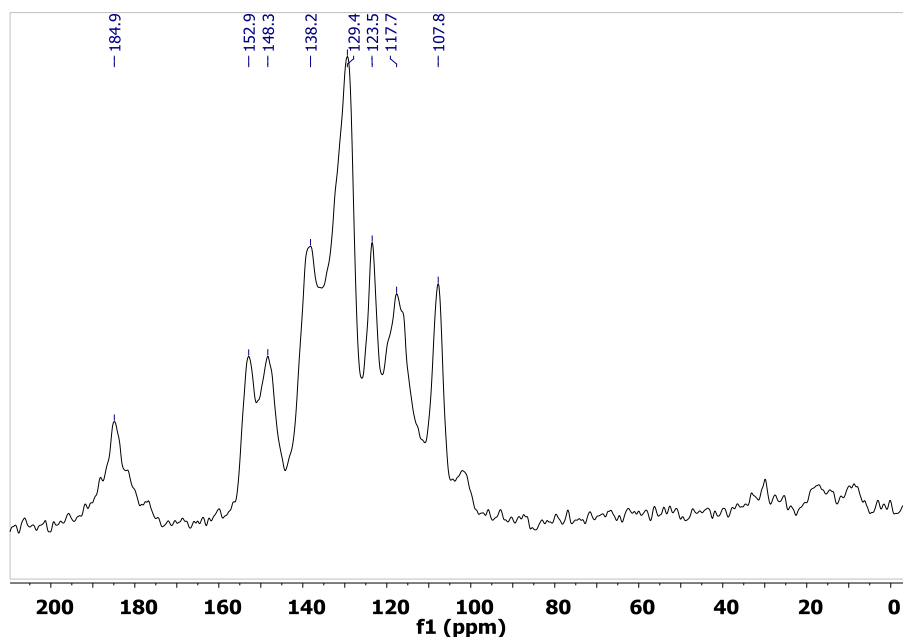
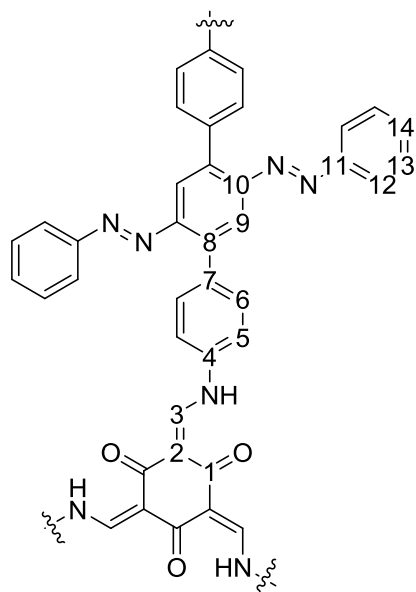


Figure S19. Solid State ^{13}C CP-MAS NMR spectrum of UCBZ-4.

10. SEM images of UCBZ series

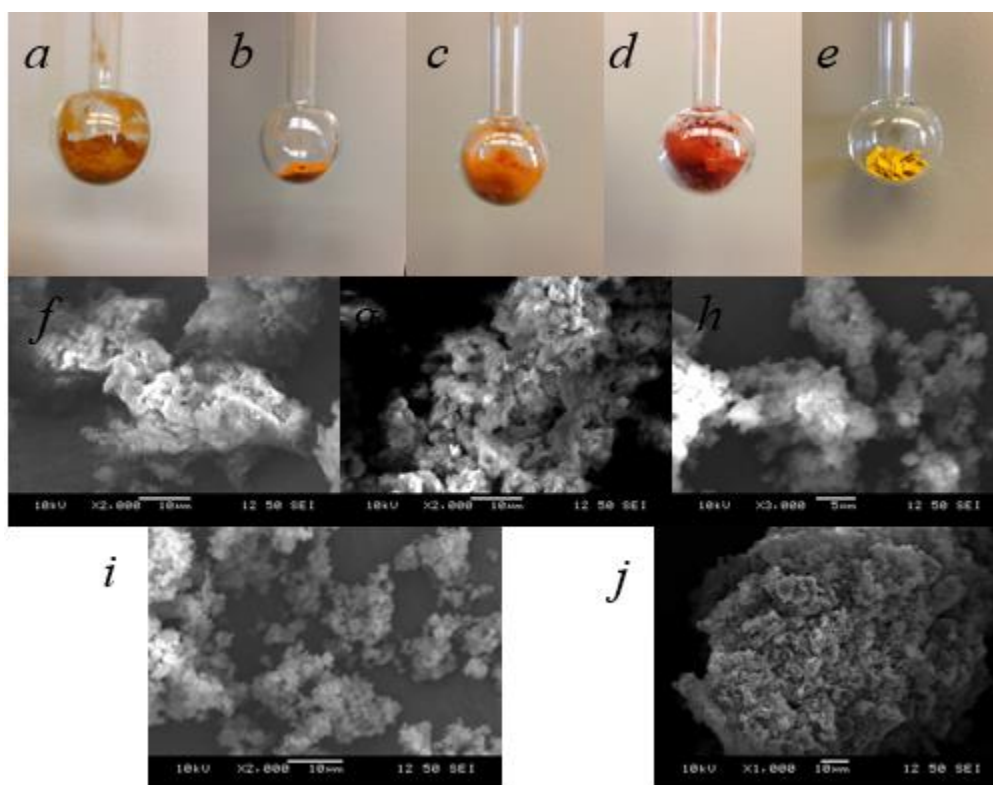


Figure S20. SEM images of UCBZ series.

11. References

- [1] a) F. Maya, and J. M. Tour, *Tetrahedron* 2004, **60**, 81; b) D. V. Kosynkin, and J. M. Tour, *Org. Lett.* 2001, **3**, 993.
- [2] C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao, and S. K. Prasad, *J. Org. Chem.* 2009, **74**, 3168.
- [3] D. B. Zhao, M. Johansson, and J. E. Backvall, *Eur. J. Org. Chem.* 2007, 4431.
- [4] A. Mallagaray, A. Canales, G. Dominguez, J. Jimenez-Barbero, and J. Perez-Castells, *Chem. Commun.* 2011, **47**, 7179.