# Supporting Information

# Unique structural micro-adjustment in a new benzothiadiazole-derived Zn(II) metal organic framework by simple photochemical decarboxylation

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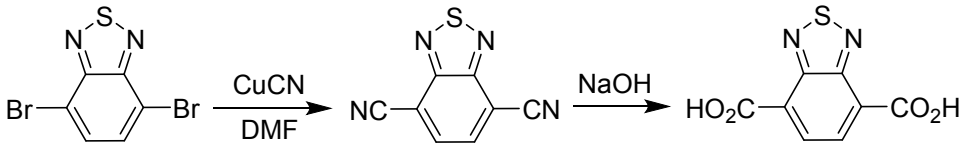
**Experimental section**

**General information and materials.**

The ligand $H_2$BTDC was synthesized according to the literature (Scheme S1). All reagents and solvents employed were of AR Grade from commercial sources and were used as received without further purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400-4000 $cm^{-1}$ region. Elemental analyses (C, H, N and S) were carried out on a FLASH EA 1112 elemental analyzer. PXRD patterns were recorded using Cu Kα radiation on a PANalytical X'Pert PRO diffractometer. Thermal analyses (TGA) were obtained on a Netzsch STA 449C thermal analyzer from room temperature at a heating rate of 10° C $min^{-1}$ in air. The electron paramagnetic resonance (EPR) spectra were recorded on a BRUKER EMX-10/12 EPR spectrometer. A Xenon lamp was employed as an irradiation light source by CEL-HXUV300. $^1H/^{13}C$ NMR spectra were recorded with a Bruker AVANCE III 400 spectrometer. X-ray photoelectron spectra (XPS) of samples were obtained by Thermo Scientific ESCALAB 250Xi with pass energy of 20.0 eV and the source gun type of Al K Alpha.

**Scheme S1.** Synthetic procedure for $H_2$BTDC**.**




**Photoluminescence Experiments.**

UV-vis absorption spectra in the solid state were measured from 200 to 900 nm by a JASCO V-750 spectrophotometer equipped with an integrating sphere. The measurements of steady-state emission spectra in the solid state were conducted on a JASCO FP-8300 fluorescence spectrophotometer at room temperature. The emission decay lifetime was measured on an Edinburgh instrument FLS980 fluorescence spectrometer.

**Gas Adsorption Experiments.**

Gas adsorption measurements were performed using a Micromeritics ASAP 2460M gas adsorption analyzer. Before the measurement, the samples of **Zn-BTDC-M1** were

soaked in methanol ($CH_3CH_2OH$) for 3 days to exchange solvent molecules in the channels, and then filtrated. Subsequently, supercritical $CO_2$ (SC-$CO_2$) activation was used to remove the solvent molecules in sample **Zn-BTDC-M1** by a custom-built system. At last, completely degassed samples **Zn-BTDC-M1** were obtained by using the "outgas" function of the surface area analyzer for 24 h at 140 °C. In addition, the adsorption properties of $NH_3$ at **Zn-BTDC-M1** before and after irradiation were investigated by temperature programmed desorption (TPD) using an Automated Gas Sorption Analyzer (Autosorb-iQ), respectively.

**Syntheses of Zn-BTDC-M1.**

A mixture of $Zn(Ac)_2 \cdot 2H_2O$ (21.9 mg, 0.1 mmol), $H_2BTDC$ (11.2 mg, 0.05 mmol), ethanol (2 mL) and DMF (3 mL) was sealed in a 15 mL Teflon-lined reactor. The pH of the solution was then adjusted with $HNO_3$ (3 drops). The reactor was heated at 80 °C for 72 h, and then cooled to room temperature at a rate of 5 °C·$h^{-1}$. Orange crystals of **1** were obtained in 47 % yield. Anal. Calcd (%) for $C_{20.5}H_{14.5}N_{5.5}O_{9.5}S_2Zn_2$ (M = 684.32 g $mol^{-1}$): C, 35.95; H, 2.12; N, 11.25. Found: C, 35.91; H, 2.52; N, 11.23. $^{13}C$ NMR (δ, 400 MHz): 174.3, 171.3, 168.5, 160.7, 152.9, 136.9, 132.5 and 125.2 ppm.

**Single-crystal structure determination.**

A suitable single crystal of MOFs **Zn-BTDC-M1** (as synthesized) was carefully selected. Crystal structure determination by X-ray diffraction was performed on a Rigaku XtaLAB Pro diffractometer with Cu-Kα radiation (λ = 1.54178 Å). The data of **Zn-BTDC-M1**, **Zn-BTDC-M1′** and **Zn-BTDC-M1″** were collected at temperature of 120 K. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques, based on $F^2$, using ShelXL. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. All the hydrogen atoms were included in the final refinement. The was applied to eliminate the free residues. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules

and, thereby, to produce a set of solvent-free diffraction intensities. The final formulas were determined by combing element analyses, TGA, $^{13}C$ SSNMR analysis and the electron count of the SQUEEZE results,[1-4] about 1.5 DMF molecules per asymmetric unit for **Zn-BTDC-M1**, **Zn-BTDC-M1′** and **Zn-BTDC-M1″**. Furthermore, crystallographic data for the same single crystal of **Zn-BTDC-M1** under UV light irradiation in 3 h (called **Zn-BTDC-M1′**) and 6 h (called **Zn-BTDC-M1″**) were also collected and analysed, respectively. Crystallographic parameters and structural refinement for the complexes are summarized in Table S1. For **Zn-BTDC-M1**, **Zn-BTDC-M1′**, **Zn-BTDC-M1″**, the Flack parameter is near 0.5, which may be twined or racemic compounds in chiral and achiral crystal space groups.[5] Selected bond lengths and bond angles of **Zn-BTDC-M1**, **Zn-BTDC-M1′** and **Zn-BTDC-M1″** are listed in Table S2-S3. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC numbers 1524729-1524731 for **Zn-BTDC-M1** (as synthesized), **Zn-BTDC-M1′** (under UV light irradiation in 3 h), **Zn-BTDC-M1″** (under UV light irradiation in 6 h).

**Molecular Modeling Analysis Method:**

The DFT calculations were performed using the Gaussian 09 program [6]. The geometries were fully optimized using B3LYP method [7, 8]. Basis set 6-31G(d, p) was employed for H, C, N, O, and S atoms, while LANL2DZ for Zn was used [9]. Then, frequency calculations at the same level of theory were carried out to identify all of the stationary points as minima (zero imaginary frequency) or transition state (only one frequency), and to provide corrections for free energies.

**Molecular modeling analysis**

With reaction species **R** (+5 charge, double) as the reactant, two possible pathways (pathways A and B) considered were for the dissociation of carbon dioxide. In pathway A depicted in Figure 4a, the transition state **TS** has been located, and the energy barrier via **TS** is only 5.3 kcal/mol, indicating that the dissociation of carbon dioxide can occur smoothly via pathway A. In addition, in dissociation pathway B of carbon dioxide, the transition state **TS′** could not be located, and the energy scan

results with the gradually lengthened C-C distance (depicted in Figure 4b) demonstrated the energy barrier would be higher than 40 kcal/mol. Hence, this pathway B can be excluded.

**Table S1.** Crystallographic data and structure refinement details for complexes **Zn-BTDC-M1**, **Zn-BTDC-M1′**, **Zn-BTDC-M1″**.

| Complex | **Zn-BTDC-M1** | **Zn-BTDC-M1′** (irradiation in 3 h) | **Zn-BTDC-M1″** (irradiation in 6 h) |
|---|---|---|---|
| formula | $C_{20.5}H1_4N_{5.5}O_{9.5}S_2Zn_2$ | $C_{20.5}H1_4N_{5.5}O_{9.5}S_2Zn_2$ | $C_{20.5}H1_4N_{5.5}O_{9.5}S_2Zn_2$ |
| fw | 684.23 | 684.23 | 684.23 |
| T/K | 120 | 120 | 120 |
| crystal system | tetragonal | tetragonal | tetragonal |
| space group | $P4_32_12$ | $P4_32_12$ | $P4_32_12$ |
| *a* (Å) | 19.3938(1) | 19.3596(14) | 19.3615(1) |
| *b* (Å) | 19.3938(1) | 19.3596(14) | 19.3615(1) |
| *c* (Å) | 14.1496(1) | 14.1336(15) | 14.1645(2) |
| *α* (deg) | 90 | 90 | 90 |
| *β* (deg) | 90 | 90 | 90 |
| *γ* (deg) | 90 | 90 | 90 |
| V (Å$^3$) | 5321.94(7) | 5297.19(10) | 5309.81(9) |
| Z | 8 | 8 | 8 |
| Dcalcd.(g·cm$^{-3}$) | 1.708 | 1.716 | 1.712 |
| abs coeff (mm$^{-1}$) | 4.241 | 4.261 | 4.250 |
| F (000) | 2748 | 2748 | 2748 |
| GOF | 1.081 | 1.065 | 1.036 |
| data/restraints/parameters | 5144 / 18 / 328 | 5093 / 30 / 331 | 5137 / 30 / 330 |
| Flack parameters | 0.43(3) | 0.44(4) | 0.40(5) |
| $R_1$(I>2sigma(I))[a] | 0.0285 | 0.0336 | 0.0418 |
| $wR_2$(I>2sigma(I))[b] | 0.0746 | 0.0900 | 0.1102 |

**Table S2** Selected Bond Lengths (Å) for **Zn-BTDC-M1**, **Zn-BTDC-M1, Zn-BTDC-M1′** (irradiation in 3 h) and **Zn-BTDC-M1″** (irradiation in 6 h).

| **Zn-BTDC-M1** | | **Zn-BTDC-M1′** | | **Zn-BTDC-M1″** | |
|---|---|---|---|---|---|
| Zn1-O1 | 1.973(3) | Zn1-O1 | 1.975(4) | Zn1-O1 | 1.975(5) |
| Zn1-O2[1] | 2.019(3) | Zn1-O2[1] | 2.018(4) | Zn1-O2[1] | 2.028(5) |
| Zn1-O7[2] | 2.399(3) | Zn1-O7[2] | 2.397(4) | Zn1-O7[2] | 2.386(6) |
| Zn1-O8[2] | 2.105(2) | Zn1-O8[2] | 2.100(3) | Zn1-O8[2] | 2.104(4) |
| Zn1-O8[3] | 2.041(2) | Zn1-O8[3] | 2.044(3) | Zn1-O8[3] | 2.043(4) |
| Zn1-N4[3] | 2.114(3) | Zn1-N4[3] | 2.106(4) | Zn1-N4[3] | 2.113(5) |
| Zn2-O4[4] | 2.134(3) | Zn2-O4[4] | 2.131(3) | Zn2-O4[4] | 2.127(4) |
| Zn2-O4[5] | 2.134(3) | Zn2-O4[5] | 2.131(3) | Zn2-O4[5] | 2.127(4) |
| Zn2-N2[5] | 2.100(3) | Zn2-N2[5] | 2.101(4) | Zn2-N2[5] | 2.109(5) |
| Zn2-N2[4] | 2.100(3) | Zn2-N2[4] | 2.101(4) | Zn2-N2[4] | 2.109(5) |
| Zn2-O5 | 1.963(5) | Zn2-O5[6] | 1.951(7) | Zn2-O5 | 1.963(9) |
| Zn2-O5[6] | 1.963(5) | Zn2-O5 | 1.951(7) | Zn2-O5[6] | 1.963(9) |
| Zn2-O5' | 2.073(5) | Zn2-O5' | 2.078(7) | Zn2-O5' | 2.048(9) |
| Zn2-O5'[6] | 2.073(5) | Zn2-O5'[6] | 2.078(7) | Zn2-O5'[6] | 2.048(9) |
| Zn3-O4 | 2.047(2) | Zn3-O4 | 2.041(3) | Zn3-O4 | 2.048(4) |
| Zn3-O4[4] | 2.047(2) | Zn3-O4[4] | 2.041(3) | Zn3-O4[4] | 2.048(4) |
| Zn3-O6 | 1.991(3) | Zn3-O6[4] | 1.987(3) | Zn3-O6[4] | 1.984(4) |
| Zn3-O6[4] | 1.991(3) | Zn3-O6 | 1.987(3) | Zn3-O6 | 1.984(4) |
| Zn3-O3[5] | 2.448(13) | Zn3-O3[4] | 2.450(16) | Zn3-O3 | 2.40(2) |
| Zn3-O3 | 2.448(13) | Zn3-O3 | 2.450(16) | Zn3-O3[4] | 2.40(2) |
| C1-C2 | 1.503(5) | C1-C2 | 1.490(7) | C1-C2 | 1.488(9) |
| C5-C8 | 1.491(6) | C5-C8 | 1.484(7) | C5-C8 | 1.467(9) |
| C9-C10 | 1.503(5) | C9-C10 | 1.504(7) | C9-C10 | 1.500(9) |
| C13-C16 | 1.487(5) | C13-C16 | 1.490(7) | C13-C16 | 1.503(9) |

Symmetry code:

**Zn-BTDC-M:** [1]3/2-Y,-1/2+X,-1/4+Z; [2]3/2-X,1/2+Y,3/4-Z; [3]1+Y,+X,1-Z; [4]+Y,+X,1-Z; [5]1-X,1-Y,-1/2+Z; [6]1-Y,1-X,1/2-Z; [7]1/2+Y,3/2-X,1/4+Z; [8]1-X,1-Y,1/2+Z; [9]3/2-X,-1/2+Y,3/4-Z; [10]+Y,-1+X,1-Z

**Zn-BTDC-M1′:** [1]3/2-Y,-1/2+X,-1/4+Z; [2]3/2-X,1/2+Y,3/4-Z; [3]1+Y,+X,1-Z; [4]+Y,+X,1-Z; [5]1-X,1-Y,-1/2+Z; [6]1-Y,1-X,1/2-Z; [7]1/2+Y,3/2-X,1/4+Z; [8]1-X,1-Y,1/2+Z; [9]3/2-X,-1/2+Y,3/4-Z; [10]+Y,-1+X,1-Z.

**Zn-BTDC-M1″:** [1]3/2-Y,-1/2+X,-1/4+Z; [2]3/2-X,1/2+Y,3/4-Z; [3]1+Y,+X,1-Z; [4]+Y,+X,1-Z; [5]1-X,1-Y,-1/2+Z; [6]1-Y,1-X,1/2-Z; [7]1/2+Y,3/2-X,1/4+Z; [8]1-X,1-Y,1/2+Z; [9]3/2-X,-1/2+Y,3/4-Z; [10]+Y,-1+X,1-Z.

**Table S3** Selected Angles (deg) for **Zn-BTDC-M1**, **Zn-BTDC-M1, Zn-BTDC-M1′** (irradiation in 3 h) and **Zn-BTDC-M1″** (irradiation in 6 h).

| **Zn-BTDC-M1** | | **Zn-BTDC-M1′** | | **Zn-BTDC-M1″** | |
|---|---|---|---|---|---|
| O1-Zn1-O2$^{1}$ | 94.7(2) | O1-Zn1-O2$^{1}$ | 94.5(2) | O1-Zn1-O2$^{1}$ | 95.5(3) |
| O1-Zn1-O7$^{2}$ | 90.51(19) | O1-Zn1-O7$^{2}$ | 90.4(2) | O1-Zn1-O7$^{2}$ | 90.0(3) |
| O1-Zn1-O8$^{2}$ | 96.73(13) | O1-Zn1-O8$^{2}$ | 96.35(16) | O1-Zn1-O8$^{2}$ | 95.9(2) |
| O1-Zn1-O8$^{3}$ | 90.13(11) | O1-Zn1-O8$^{3}$ | 90.00(13) | O1-Zn1-O8$^{3}$ | 89.94(18) |
| O1-Zn1-N4$^{3}$ | 172.34(17) | O1-Zn1-N4$^{3}$ | 172.3(2) | O1-Zn1-N4$^{3}$ | 172.4(3) |
| O2$^{1}$-Zn1-O7$^{2}$ | 156.96(11) | O2$^{1}$-Zn1-O7$^{2}$ | 156.86(13) | O2$^{1}$-Zn1-O7$^{2}$ | 156.30(18) |
| O2$^{1}$-Zn1-O8$^{3}$ | 108.39(11) | O2$^{1}$-Zn1-O8$^{3}$ | 108.78(13) | O2$^{1}$-Zn1-O8$^{3}$ | 109.80(17) |
| O2$^{1}$-Zn1-O8$^{2}$ | 99.68(11) | O2$^{1}$-Zn1-O8$^{2}$ | 99.78(12) | O2$^{1}$-Zn1-O8$^{2}$ | 99.27(17) |
| O2$^{1}$-Zn1-N4$^{3}$ | 91.67(19) | O2$^{1}$-Zn1-N4$^{3}$ | 92.0(2) | O2$^{1}$-Zn1-N4$^{3}$ | 90.9(3) |
| O8$^{2}$-Zn1-O7$^{2}$ | 57.38(9) | O8$^{2}$-Zn1-O7$^{2}$ | 57.15(11) | O8$^{2}$-Zn1-O7$^{2}$ | 57.15(15) |
| O8$^{3}$-Zn1-O7$^{2}$ | 93.99(10) | O8$^{3}$-Zn1-O7$^{2}$ | 93.81(12) | O8$^{3}$-Zn1-O7$^{2}$ | 93.19(16) |
| O8$^{3}$-Zn1-O8$^{2}$ | 150.44(9) | O8$^{3}$-Zn1-O8$^{2}$ | 150.16(11) | O8$^{3}$-Zn1-O8$^{2}$ | 149.65(14) |
| O8$^{3}$-Zn1-N4$^{3}$ | 83.85(12) | O8$^{3}$-Zn1-N4$^{3}$ | 83.98(14) | O8$^{3}$-Zn1-N4$^{3}$ | 84.07(19) |
| O8$^{2}$-Zn1-N4$^{3}$ | 86.31(12) | O8$^{2}$-Zn1-N4$^{3}$ | 86.62(15) | O8$^{2}$-Zn1-N4$^{3}$ | 87.0(2) |
| N4$^{3}$-Zn1-O7$^{2}$ | 85.19(18) | N4$^{3}$-Zn1-O7$^{2}$ | 85.3(2) | N4$^{3}$-Zn1-O7$^{2}$ | 85.6(3) |
| O4$^{4}$-Zn2-O4$^{5}$ | 168.91(13) | O4$^{4}$-Zn2-O4$^{5}$ | 169.24(17) | O4$^{4}$-Zn2-O4$^{5}$ | 168.7(2) |
| N2$^{4}$-Zn2-O4$^{5}$ | 89.45(12) | N2$^{4}$-Zn2-O4$^{5}$ | 89.75(14) | N2$^{4}$-Zn2-O4$^{5}$ | 89.45(19) |
| N2$^{5}$-Zn2-O4$^{4}$ | 89.45(12) | N2$^{5}$-Zn2-O4$^{4}$ | 89.75(14) | N2$^{5}$-Zn2-O4$^{4}$ | 89.45(19) |
| N2$^{4}$-Zn2-O4$^{4}$ | 82.80(12) | N2$^{4}$-Zn2-O4$^{4}$ | 82.85(14) | N2$^{4}$-Zn2-O4$^{4}$ | 82.78(18) |
| N2$^{5}$-Zn2-O4$^{5}$ | 82.80(12) | N2$^{5}$-Zn2-O4$^{5}$ | 82.85(14) | N2$^{5}$-Zn2-O4$^{5}$ | 82.78(18) |
| N2$^{5}$-Zn2-N2$^{4}$ | 91.4(3) | N2$^{5}$-Zn2-N2$^{4}$ | 93.3(4) | N2$^{5}$-Zn2-N2$^{4}$ | 93.1(5) |
| O5-Zn2-O4$^{4}$ | 91.09(17) | O5-Zn2-O4$^{5}$ | 90.5(2) | O5-Zn2-O4$^{5}$ | 90.4(3) |
| O5$^{6}$-Zn2-O4$^{4}$ | 98.39(18) | O5$^{6}$-Zn2-O4$^{5}$ | 98.7(2) | O5$^{6}$-Zn2-O4$^{5}$ | 99.4(3) |
| O5$^{6}$-Zn2-O4$^{5}$ | 91.09(17) | O5$^{6}$-Zn2-O4$^{4}$ | 90.5(2) | O5$^{6}$-Zn2-O4$^{4}$ | 90.4(3) |
| O5-Zn2-O4$^{4}$ | 98.39(18) | O5-Zn2-O4$^{4}$ | 98.7(2) | O5-Zn2-O4$^{4}$ | 99.4(3) |
| O5$^{6}$-Zn2-N2$^{4}$ | 103.4(3) | O5$^{6}$-Zn2-N2$^{5}$ | 102.7(4) | O5$^{6}$-Zn2-N2$^{5}$ | 103.8(6) |
| O5-Zn2-N2$^{4}$ | 164.0(3) | O5-Zn2-N2$^{5}$ | 162.6(4) | O5-Zn2-N2$^{5}$ | 161.7(6) |
| O5$^{6}$-Zn2-N2$^{5}$ | 164.0(3) | O5$^{6}$-Zn2-N2$^{4}$ | 162.6(4) | O5$^{6}$-Zn2-N2$^{4}$ | 161.8(6) |
| O5-Zn2-N2$^{5}$ | 103.4(3) | O5-Zn2-N2$^{4}$ | 102.7(4) | O5-Zn2-N2$^{4}$ | 103.8(6) |
| O5-Zn2-O5$^{6}$ | 62.8(6) | O5-Zn2-O5$^{6}$ | 62.4(8) | O5-Zn2-O5$^{6}$ | 60.5(11) |
| O5'$^{6}$-Zn2-O4$^{5}$ | 86.85(17) | O5'$^{6}$-Zn2-O4$^{4}$ | 86.5(2) | O5'$^{6}$-Zn2-O4$^{4}$ | 87.7(3) |
| O5'$^{6}$-Zn2-O4$^{4}$ | 98.93(16) | O5'$^{6}$-Zn2-O4$^{5}$ | 99.0(2) | O5'$^{6}$-Zn2-O4$^{5}$ | 98.5(3) |
| O5'-Zn2-O4$^{5}$ | 98.93(16) | O5'-Zn2-O4$^{4}$ | 99.0(2) | O5'-Zn2-O4$^{4}$ | 98.5(3) |
| O5'-Zn2-O4$^{4}$ | 86.85(17) | O5'-Zn2-O4$^{5}$ | 86.5(2) | O5'-Zn2-O4$^{5}$ | 87.7(3) |
| O5'-Zn2-N2$^{5}$ | 76.3(3) | O5'-Zn2-N2$^{4}$ | 74.9(4) | O5'-Zn2-N2$^{4}$ | 77.3(6) |
| O5'$^{6}$-Zn2-N2$^{5}$ | 164.0(3) | O5'$^{6}$-Zn2-N2$^{4}$ | 164.2(4) | O5'$^{6}$-Zn2-N2$^{4}$ | 166.5(6) |
| O5'$^{6}$-Zn2-N2$^{4}$ | 76.3(3) | O5'$^{6}$-Zn2-N2$^{5}$ | 75.0(4) | O5'$^{6}$-Zn2-N2$^{5}$ | 77.3(6) |
| O5'-Zn2-N2$^{4}$ | 164.0(3) | O5'-Zn2-N2$^{5}$ | 164.2(4) | O5'-Zn2-N2$^{5}$ | 166.5(6) |
| O5'$^{6}$-Zn2-O5' | 117.5(5) | O5'$^{6}$-Zn2-O5' | 118.4(7) | O5'$^{6}$-Zn2-O5' | 113.7(12) |
| O4$^{4}$-Zn3-O4 | 136.14(13) | O4$^{5}$-Zn3-O4 | 135.80(16) | O4$^{5}$-Zn3-O4 | 135.76(19) |
| O4-Zn3-O3$^{4}$ | 86.8(3) | O4-Zn3-O3$^{5}$ | 86.8(5) | O4-Zn3-O3$^{5}$ | 85.1(6) |

| | | | | | |
|---|---|---|---|---|---|
| O4[4]-Zn3-O3 | 86.8(3) | O4[5]-Zn3-O3 | 86.8(5) | O4[5]-Zn3-O3 | 85.1(6) |
| O4[4]-Zn3-O3[4] | 55.7(3) | O4[5]-Zn3-O3[5] | 55.4(4) | O4[5]-Zn3-O3[5] | 57.1(6) |
| O4-Zn3-O3 | 55.7(3) | O4-Zn3-O3 | 55.4(4) | O4-Zn3-O3 | 57.1(6) |
| O6[4]-Zn3-O4[4] | 105.89(12) | O6[5]-Zn3-O4[5] | 106.36(14) | O6[5]-Zn3-O4[5] | 106.47(18) |
| O6-Zn3-O4 | 105.89(12) | O6-Zn3-O4 | 106.36(14) | O6-Zn3-O4 | 106.47(18) |
| O6[4]-Zn3-O4 | 102.08(11) | O6[5]-Zn3-O4 | 101.81(12) | O6[5]-Zn3-O4 | 101.50(17) |
| O6-Zn3-O4[4] | 102.08(11) | O6-Zn3-O4[5] | 101.81(12) | O6-Zn3-O4[5] | 101.50(17) |
| O6-Zn3-O6[4] | 99.4(2) | O6-Zn3-O6[5] | 99.5(3) | O6-Zn3-O6[5] | 100.2(3) |
| O6-Zn3-O3 | 99.9(4) | O6-Zn3-O3 | 100.1(2) | O6-Zn3-O3 | 99.8(8) |
| O6-Zn3-O3[4] | 154.0(4) | O6-Zn3-O3[5] | 153.5(4) | O6-Zn3-O3[5] | 154.3(8) |
| O6[4]-Zn3-O3[4] | 99.9(4) | O6[5]-Zn3-O3[5] | 100.1(5) | O6[5]-Zn3-O3[5] | 99.8(8) |
| O6[4]-Zn3-O3 | 154.0(4) | O6[5]-Zn3-O3 | 153.5(4) | O6[5]-Zn3-O3 | 154.3(8) |
| O3-Zn3-O3[4] | 68.2(8) | O3-Zn3-O3[5] | 68.2(11) | O3-Zn3-O3[5] | 66.8(14) |

Symmetry code:

**Zn-BTDC-M1**: [1]3/2-Y,-1/2+X,-1/4+Z; [2]3/2-X,1/2+Y,3/4-Z; [3]1+Y,+X,1-Z; [4]+Y,+X,1-Z; [5]1-X,1-Y,-1/2+Z; [6]1-Y,1-X,1/2-Z; [7]1/2+Y,3/2-X,1/4+Z; [8]1-X,1-Y,1/2+Z; [9]3/2-X,-1/2+Y,3/4-Z; [10]+Y,-1+X,1-Z.

**Zn-BTDC-M1′**: [1]3/2-Y,-1/2+X,-1/4+Z; [2]3/2-X,1/2+Y,3/4-Z; [3]1+Y,+X,1-Z; [4]1-X,1-Y,-1/2+Z; [5]+Y,+X,1-Z; [6]1-Y,1-X,1/2-Z; [7]1/2+Y,3/2-X,1/4+Z; [8]1-X,1-Y,1/2+Z; [9]3/2-X,-1/2+Y,3/4-Z; [10]+Y,-1+X,1-Z.

**Zn-BTDC-M1″**: [1]3/2-Y,-1/2+X,-1/4+Z; [2]3/2-X,1/2+Y,3/4-Z; [3]1+Y,+X,1-Z; [4]1-X,1-Y,-1/2+Z; [5]+Y,+X,1-Z; [6]1-Y,1-X,1/2-Z; [7]1/2+Y,3/2-X,1/4+Z; [8]1-X,1-Y,1/2+Z; [9]3/2-X,-1/2+Y,3/4-Z; [10]+Y,-1+X,1-Z.

**Structure description of Zn-BTDC-M1.**

It crystallizes in the tetragonal $P4_32_12$ chiral space group with three different types of coordination environment around the Zn(II) centres (Figure S1). The $BTDC^{2-}$ ligand is haxadentate and coordinates to four Zn(II) ions via one nitrogen atoms and two carboxyl group (Figure S1). The Zn1 is hexa-coordinated by five carboxyl oxygen atoms and one nitrogen atoms to form distorted octahedron geometry. The equatorial plane is formed by the coordination of four O atoms. The axial positions are occupied by one O atoms and one N atom with the bond angle of 172.36(17) °. The Zn-O bond lengths fall in the range of 1.972(3)-2.399(3) Å, and the Zn-N bond lengths is 2.113(3) Å. The Zn2 is bonded by four carboxyl oxygen atoms and two nitrogen atoms to form a distorted *cis*-octahedral geometry. The equatorial plane is formed by the coordination of three O atoms and one N atom. The axial positions are occupied by one N atom and one O atom with the bond angle of 165.5(3) °. The Zn-O bond lengths fall in the range of 1.964(5)-2.134(3) Å, and the Zn-N bond lengths is 2.100(3) Å.The Zn3 adopts a six-coordinated distorted octahedron of six O donor set, four chelating carboxylate oxygen atoms and two monodentate carboxyl oxygen atoms from $BTDC^{2-}$ ligands. The equatorial plane is formed by the coordination of four O atoms. The axial positions are occupied by two O atoms with the bond angle of 155.4(3) °. The Zn-O bond lengths fall in the range of 1.991(3)-2.449(10) Å.

In Figure S1, the neighboring Zn(II) ions (Zn1···Zn1 and Zn2···Zn3) are further linked together through two carboxylate groups of $BTDC^{2-}$ ligands. One carboxylate group was a bridging tridentate coordination mode ($\mu_2$-$\eta^2$:$\eta^1$), and the other one was bidentate bridging coordination fashion ($\mu_2$-$\eta^1$:$\eta^1$) to form a dinuclear {Zn-Zn} unit. The distances of Zn··· Zn are 3.6756 and 3.6793 Å. The {Zn-Zn} units are connected by $BTDC^{2-}$ ligands along the special direction to construct a 3D metal-organic framework with 1D rectangular channel along the *c* axis, as displayed in Figure S1. There are two kinds of vertex in rectangular, one is {Zn1···Zn1} units, and another is {Zn2···Zn3} units. The $BTDC^{2-}$ ligands in crystal structure of **Zn-BTDC-M1** showed head-to-head chain structure with intermolecular S···N distances of 2.8260 and 2.9438 Å, and S···S distances of 3.5702 Å (Figure S2). They are shorter than those

reported for other literature values. The dihedral angle between the BTD-1 and BTD-2 moieties is 22.061 ° (Figure S2). Rectangular-shaped channels [9.0853 Å × 9.9191 Å] were generated inside the 3D extended structure and the walls of these channels were constructed from BTD moieties (Figure S1). In addition, application of the SQUEEZE routine in PLATON indicates a void volume of 40.8% in the total cell volume.

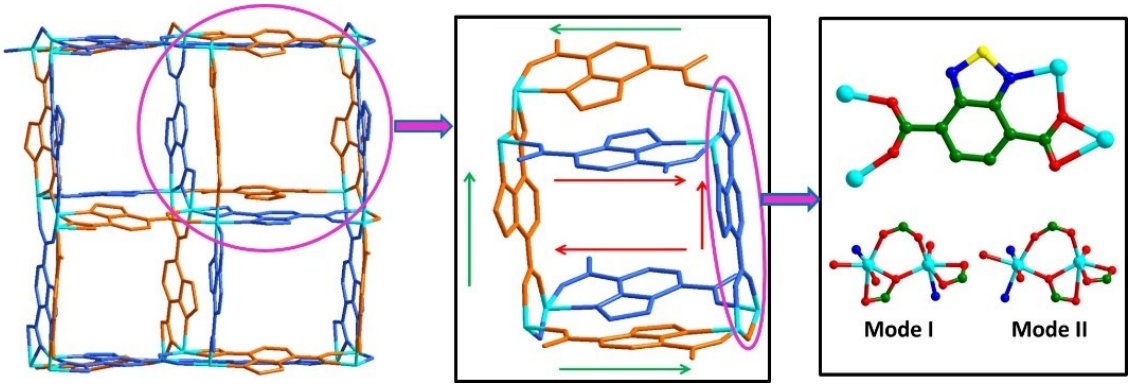



**Figure S1**. The 3D structure of **Zn-BTDC-M1**. Inset: arrangement of BTD subunit, coordination mode of $BTDC^{2-}$ and binuclear Zn-cluster substructure found in **Zn-BTDC-M1**.

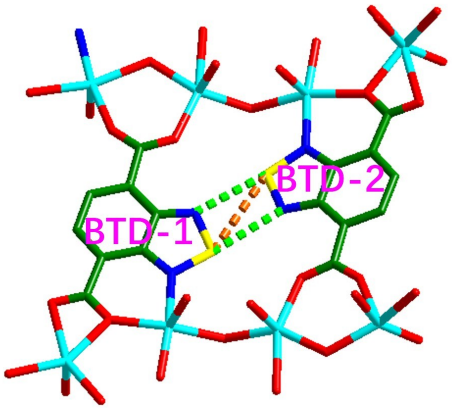



**Figure S2.** The ligands arranged in MOFs **Zn-BTDC-M1**, viewed along the *b* axis (green: S···N; organge: S···S).

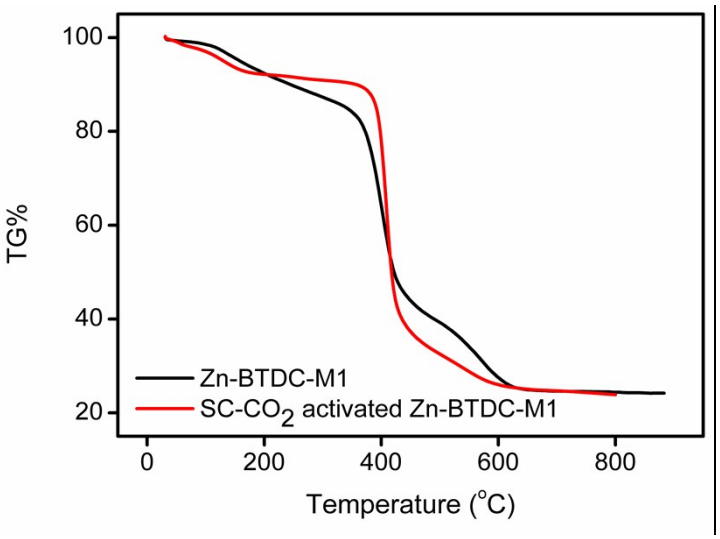



**Figure S3**. TGA curves of **Zn-BTDC-M1** and SC-$CO_2$ activated **Zn-BTDC-M1**.

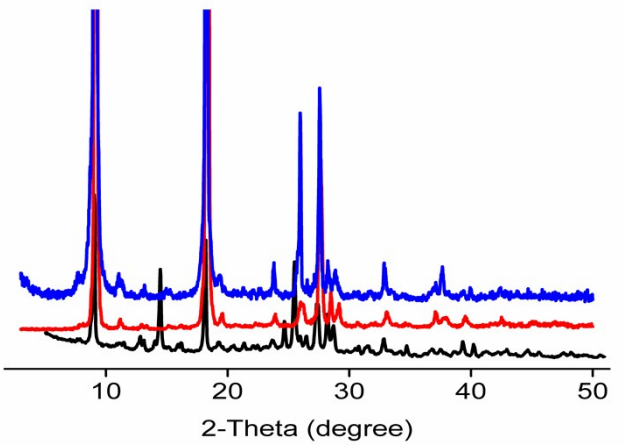



**Figure S4.** XRD of **Zn-BTDC-M1** (black), SC-$CO_2$ activated **Zn-BTDC-M1** (red) and using the "outgas" function for 24 h at 140 °C activated **Zn-BTDC-M1** (blue).

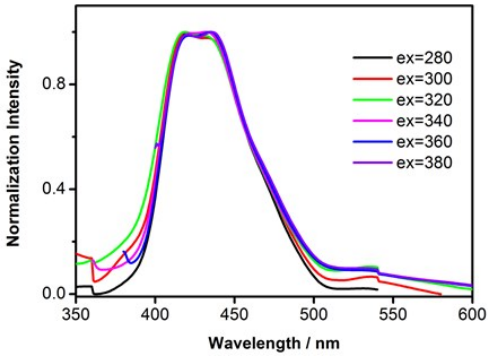



**Figure S5.** Emission spectra of **Zn-BTDC-M1** in the solid state at room temperature ($\lambda_{ex}$ = 280~380 nm).

**Table S4.** Absorption and steady-state fluorescence properties of crystals **Zn-BTDC-M1** at room temperature.

| Sample | $\lambda_{ab}$ / nm | $\lambda_{em}$ / nm | $\tau_F$ / ns |
|---|---|---|---|
| **Zn-BTDC-M1** | 250, 330, 478 | 430 | 0.99 |


**Figure S6.** The photographs of **Zn-BTDC-M1** before and after irradiation. ((a): before and after under irradiation in 5 min; (b): before and after under irradiation in 25 min).

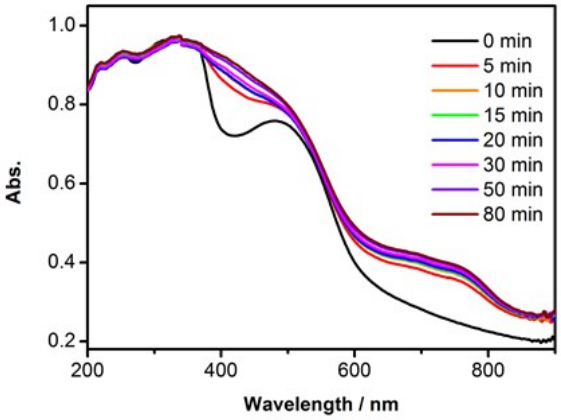



**Figure S7.** UV/Vis time-dependent absorbance spectra on UV irradiation of **Zn-BTDC-M1**.

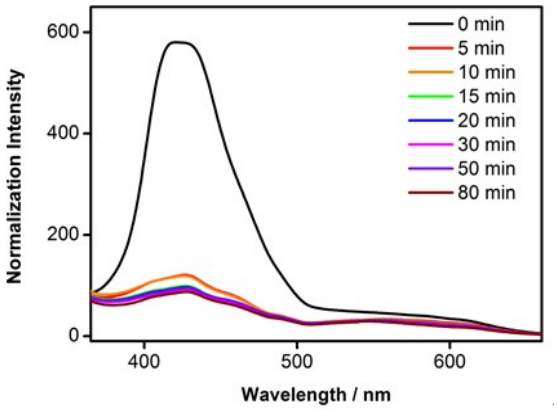



**Figure S8.** The time-dependent emission spectra on UV irradiation of **Zn-BTDC-M1** ($\lambda_{ex}$ = 340 nm).

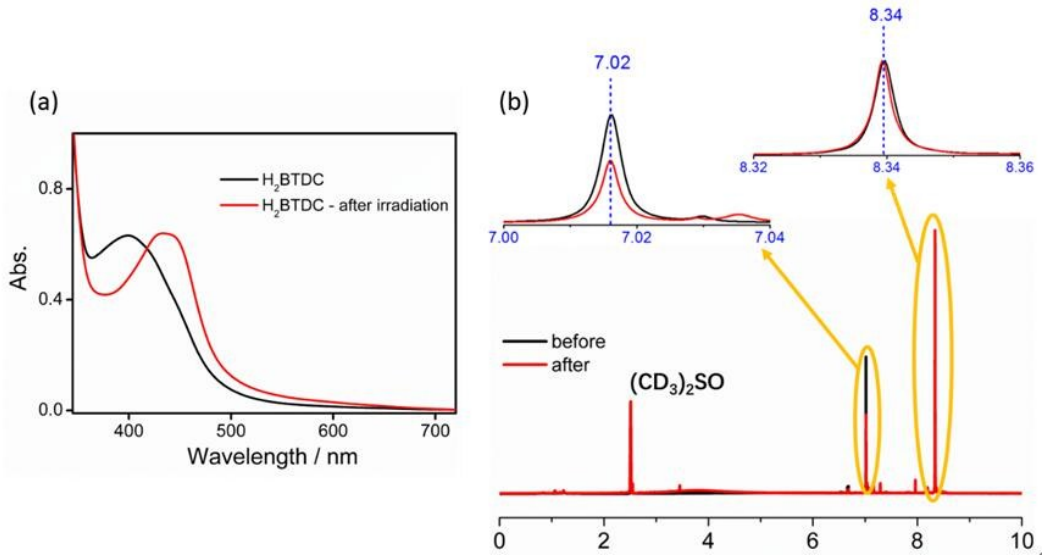



**Figure S9.** (a) UV-vis absorption spectra of $H_2$BTDC before and after irradiation in the pure EtOH ($4.5 \times 10^{-6}$ mol/L, black: 0 min, red:40 min). (b) $^1$H NMR of $H_2$BTDC before and after irradiation (DMSO-$d_6$, black: 0 min, red:120 min).

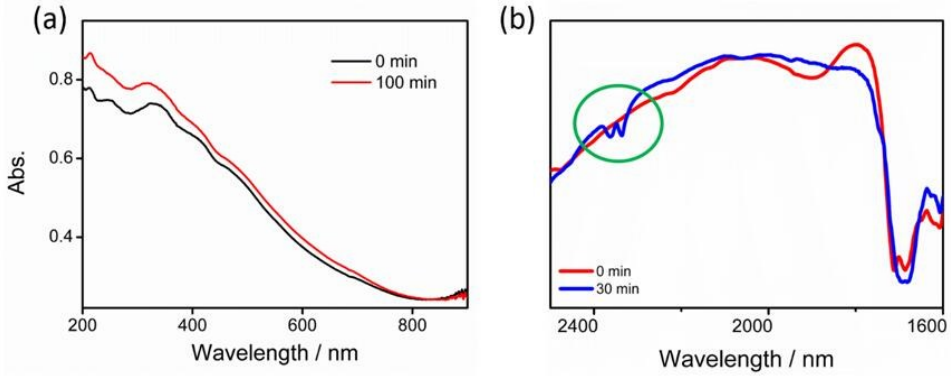



**Figure S10.** (a) UV-vis absorption spectra of $H_2$BTDC before and after irradiation. (b) IR spectra of $H_2$BTDC before and after irradiation.

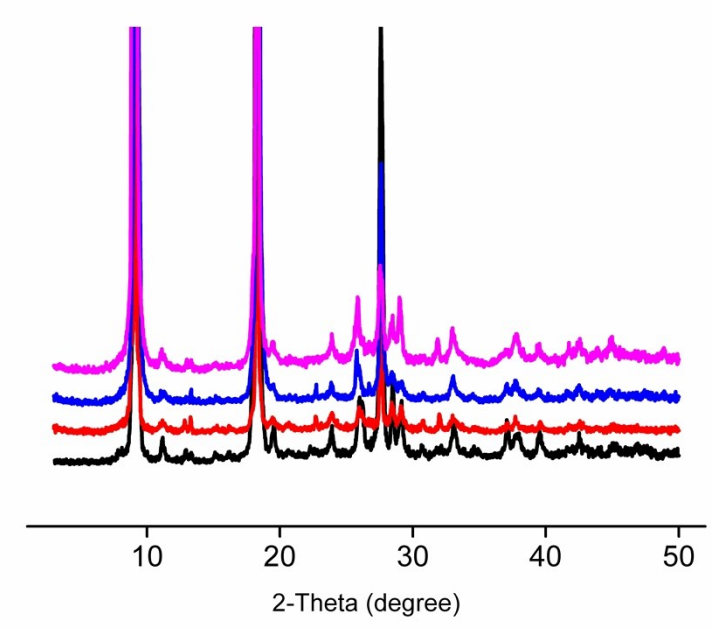
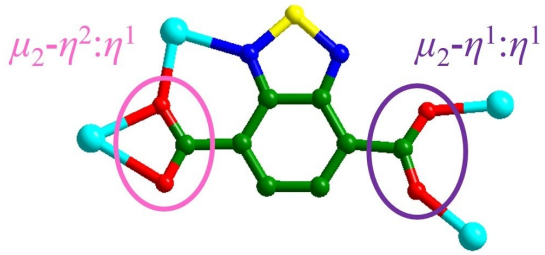



**Figure S11.** PXRD pattern of as-synthesized (black) and irradiated **Zn-BTDC-M1** (red), and irradiated **Zn-BTDC-M1** (blue) by SC-$CO_2$ activation and (rose) by using the "outgas" function for 24 h at 140 °C. Change in background noise has been observed for the case of radiated samples; however, the major peaks remained intact in all the cases.

**Table S5.** The dihedral angels between BTD rings and COO- groups in **Zn-BTDC-M1**, **Zn-BTDC-M1′** (irradiation in 3 h) and **Zn-BTDC-M1″** (irradiation in 6 h).

| |  | | | | | |
|---|---|---|---|---|---|---|
| | $\mu_2$-$\eta^2$:$\eta^1$ | | | $\mu_2$-$\eta^1$:$\eta^1$ | | |
| | O3-C8-O4 | O3′-C8-O4 | O7-C16-O8 | O1-C1-O2 | O5-C9-O6 | O5′-C9-O6 |
| **Zn-BTDC-M1** | 28.1(10) | 8.8(8) | 9.6(6) | 7.3(6) | 29.4(7) | 23.1(7) |
| **Zn-BTDC-M1′** | 27.0(14) | 9.3(11) | 9.7(7) | 6.6(8) | 28.0(9) | 26.0(9) |
| **Zn-BTDC-M1″** | 25.8(17) | 9.6(15) | 8.7(7) | 8.0(10) | 28.9(12) | 21.7(13) |

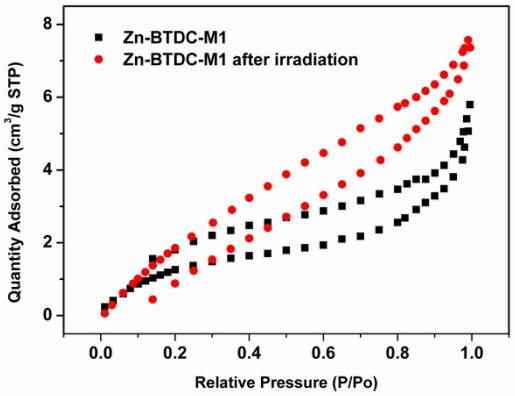



**Figure S12**. $N_2$ gas sorption isotherms of **Zn-BTDC-M1** (black) and irradiated **Zn-BTDC-M1** (red).

**Table S6.** $N_2$ adsorption for MOFs **Zn-BTDC-M1**.

| | BET Surface Area ($m^2/g$) | Langmuir Surface Area ($m^2/g$) |
|---|---|---|
| **Zn-BTDC-M1** | 5.5431 | 9.5826 |
| irradiated **Zn-BTDC-M1** | 12.6853 | 55.9775 |

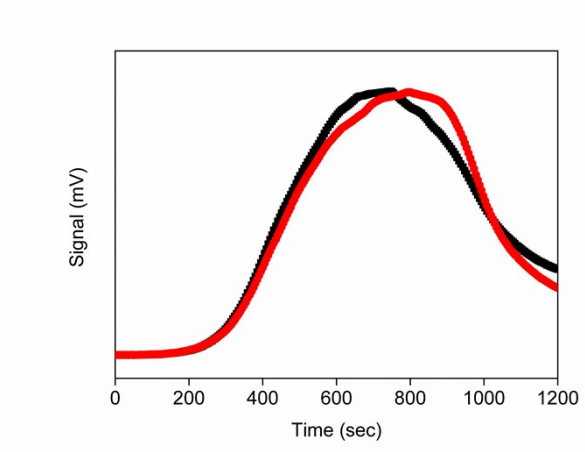



**Figure S13**. TPD curves of **Zn-BTDC-M1** (black) and irradiated **Zn-BTDC-M1** (red).

**Table S7.** Gas Sorption by TPD (Temperature Programmed Desorption).

| | $NH_3$-TPD |
|---|---|
| **Zn-BTDC-M1** | 85.43 mL/g |
| irradiated **Zn-BTDC-M1** | 82.28 mL/g |

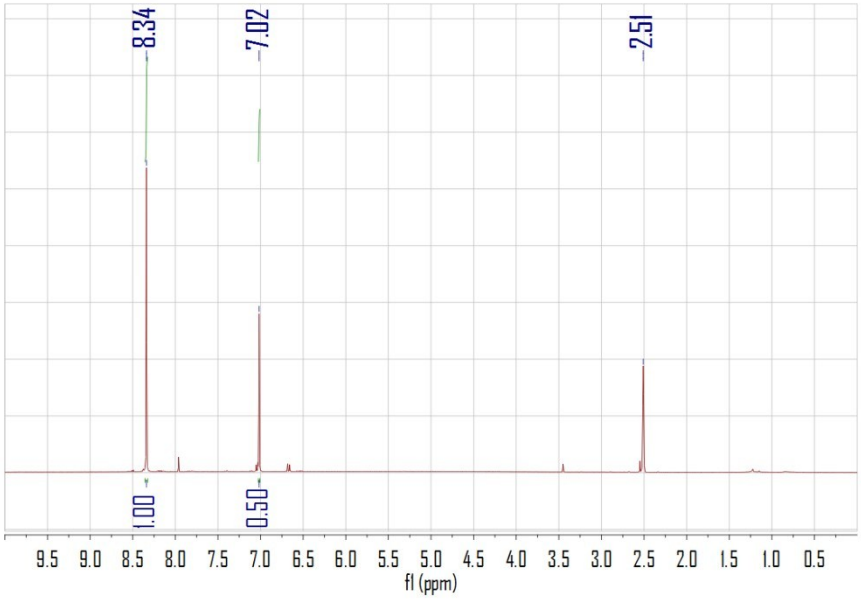



**Figure S14.** $^1$H NMR of $H_2$BTDC before irradiation (DMSO-$d_6$).

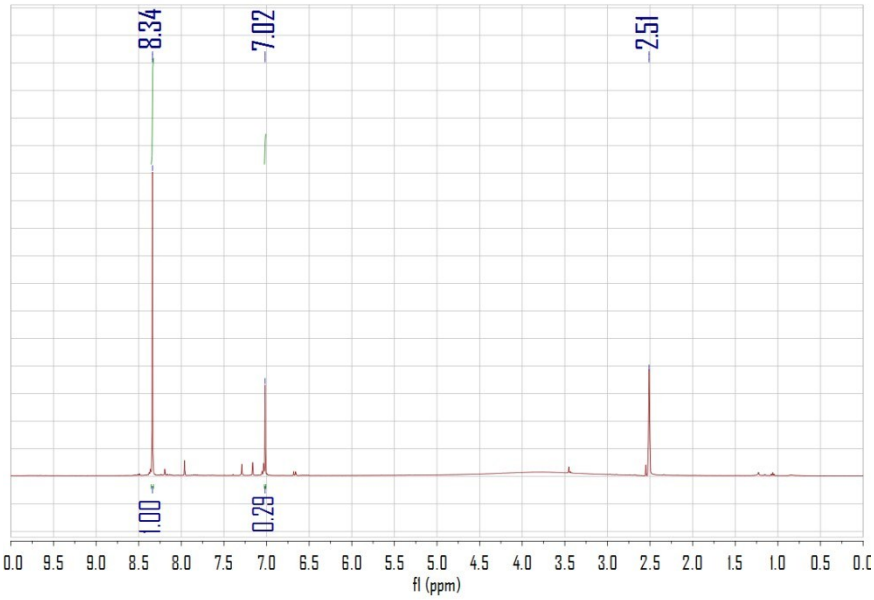



**Figure S15.** $^{1}H$ NMR of $H_2BTDC$ after irradiation (DMSO-$d_6$).

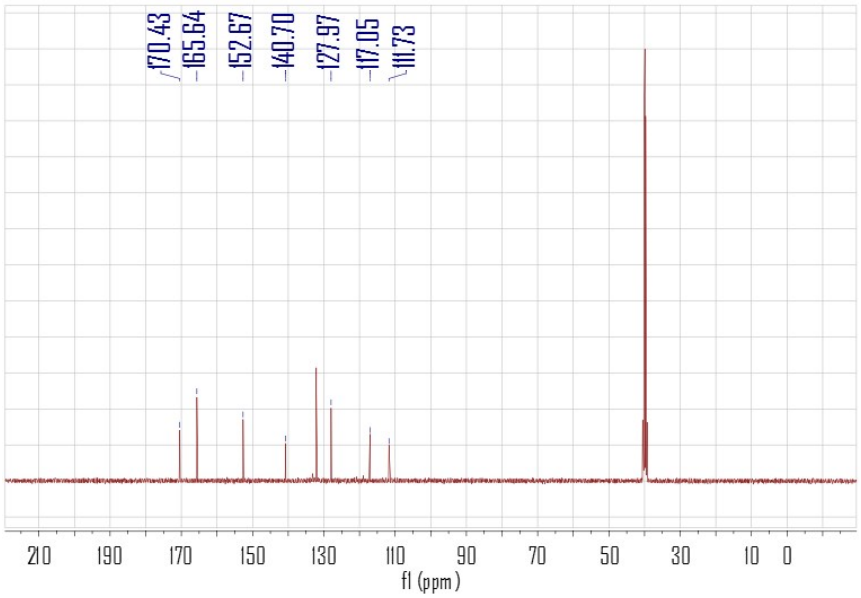



**Figure S16.** $^{13}C$ NMR of $H_2BTDC$ before irradiation (DMSO-$d_6$).

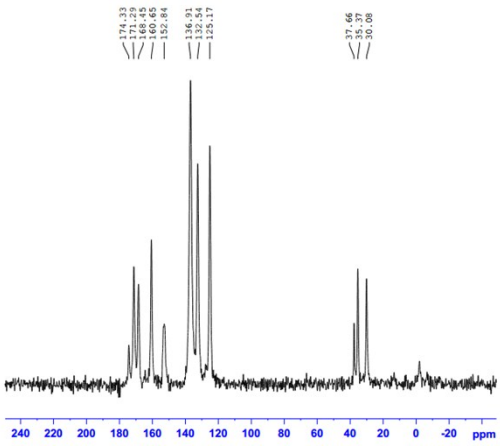



**Figure S17.** $^{13}C$ SSNMR of **Zn-BTDC-M1** before irradiation.

## Geometrical Coordinates of the Listed Complexes

Scan 1

| | | | |
|---|---|---|---|
| Zn | 5.42241000 | -2.33836900 | -0.64409000 |
| Zn | 3.43952200 | 2.26555700 | 0.58746300 |
| N | 1.45184500 | 2.03067700 | 0.50377300 |
| N | -1.00536600 | 2.02771000 | 0.46729300 |
| O | 3.93471000 | 0.44795000 | 0.11535400 |
| O | 3.65478500 | -1.68910000 | -0.43080200 |
| O | -3.36507700 | 0.63988500 | -0.57524800 |
| O | -3.35419600 | -1.45301700 | 0.29947800 |
| C | 3.16212400 | -0.53269800 | -0.13066700 |
| C | 1.66868700 | -0.42149500 | -0.09196200 |
| C | 0.88096000 | -1.54021500 | -0.34364200 |
| H | 1.36717300 | -2.48417400 | -0.56707300 |
| C | -0.54517200 | -1.52350600 | -0.32048200 |
| H | -1.06229000 | -2.45462200 | -0.52506600 |
| C | -1.26168000 | -0.36957900 | -0.07732100 |
| C | -0.49545800 | 0.82282900 | 0.18271900 |
| C | 0.95967400 | 0.80064500 | 0.19727300 |

| | | | |
|---|---|---|---|
| C | -2.79201900 | -0.39506300 | -0.11063500 |
| S | 0.15283100 | 3.09369500 | 0.74816200 |
| Zn | -4.93529500 | 1.55777800 | -1.29489700 |
| Zn | -4.66997000 | -2.73764100 | 1.05892900 |

Scan 15

| | | | |
|---|---|---|---|
| Zn | 5.97998400 | -2.28000600 | -0.46854800 |
| Zn | 3.25019300 | 2.35687300 | 0.44932200 |
| N | 1.27368000 | 2.07110900 | 0.36084100 |
| N | -1.18904400 | 2.03229100 | 0.31151400 |
| O | 4.21769500 | 0.69292600 | 0.13595300 |
| O | 4.17258900 | -1.52807700 | -0.28466100 |
| O | -3.55686300 | 0.54943000 | -0.34946500 |
| O | -3.42970400 | -1.65497000 | 0.15454800 |
| C | 3.66866000 | -0.40736600 | -0.06638800 |
| C | 1.47068600 | -0.39899000 | -0.04755000 |
| C | 0.79733100 | -1.56698400 | -0.22753400 |
| H | 1.31579900 | -2.50897800 | -0.38097400 |
| C | -0.64266100 | -1.57261400 | -0.21499200 |
| H | -1.13413800 | -2.52850200 | -0.35875000 |
| C | -1.39811400 | -0.42727600 | -0.05465200 |
| C | -0.67515400 | 0.81190300 | 0.12223900 |
| C | 0.78508900 | 0.81987700 | 0.14518800 |
| C | -2.91397400 | -0.51375400 | -0.08148400 |
| S | -0.04167100 | 3.13267400 | 0.51667500 |
| Zn | -5.07916500 | 1.61571300 | -0.92034400 |
| Zn | -4.74728800 | -2.98432500 | 0.70845300 |

**R**

| | | | |
|---|---|---|---|
| Zn | 5.50756600 | -2.46764000 | 0.34597400 |

| | | | |
|---|---|---|---|
| Zn | 3.56279400 | 2.31628000 | -0.30448200 |
| N | 1.57785900 | 2.06816400 | -0.24274100 |
| N | -0.87879100 | 2.06654300 | -0.21467700 |
| O | 4.04837700 | 0.44716000 | -0.05500300 |
| O | 3.76914700 | -1.74926400 | 0.21414200 |
| O | -3.27947300 | 0.60449200 | 0.52857700 |
| O | -3.20756500 | -1.50535300 | -0.43599500 |
| C | 3.28117000 | -0.55646700 | 0.05586100 |
| C | 1.78747700 | -0.44645500 | 0.02432900 |
| C | 0.99867700 | -1.59023300 | 0.11025500 |
| H | 1.48293800 | -2.56156800 | 0.19734200 |
| C | -0.42701000 | -1.57008400 | 0.08308100 |
| H | -0.95376100 | -2.51926700 | 0.14183500 |
| C | -1.13912400 | -0.38753400 | 0.00273400 |
| C | -0.37133100 | 0.83290000 | -0.08618300 |
| C | 1.07597500 | 0.80548400 | -0.10083000 |
| C | -2.66016500 | -0.42284300 | 0.02925000 |
| S | 0.27620500 | 3.15890900 | -0.34588500 |
| Zn | -5.17390800 | 0.99033200 | 0.86577400 |
| Zn | -5.08844700 | -2.06462400 | -0.71819400 |

**TS**

| | | | |
|---|---|---|---|
| Zn | -5.83528500 | -2.78684200 | 0.10081400 |
| Zn | -4.27310400 | 2.11908000 | 0.35420600 |
| N | -2.29204700 | 2.05957800 | 0.09959600 |
| N | 0.13810800 | 2.26732100 | -0.22652000 |
| O | -4.60806200 | 0.20200800 | 0.23555800 |
| O | -4.14954300 | -1.96431300 | 0.01074300 |
| O | 2.19650900 | 0.60844200 | -1.94870800 |
| O | 3.30919600 | -0.28275100 | -0.10146000 |

| | | | |
|---|---|---|---|
| C | -3.75698400 | -0.72800800 | 0.06961500 |
| C | -2.29325000 | -0.47941100 | -0.07158400 |
| C | -1.42178300 | -1.55283700 | -0.26431700 |
| H | -1.82370400 | -2.56110800 | -0.28655400 |
| C | -0.01155200 | -1.41332900 | -0.48246900 |
| H | 0.57177500 | -2.30682400 | -0.68924900 |
| C | 0.52094200 | -0.16287700 | -0.42845800 |
| C | -0.27533800 | 0.99778800 | -0.24619900 |
| C | -1.70998800 | 0.84153600 | -0.05503300 |
| C | 2.48416800 | 0.11424500 | -0.90627900 |
| S | -1.08881700 | 3.26221100 | -0.00118400 |
| Zn | 7.99452300 | -0.62237300 | 0.40112500 |
| Zn | 5.39881500 | -0.43738100 | 0.16460500 |

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