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

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The first example of micro-adjustment of MOF strucutre was observed in new Zn(II) metal organic framework (MOF) derived from benzothiadiazole-4,7-dicarboxylic acid (H₂BTDC) ligand (Zn-BTDC-M1), by light-driven decarboxylation process. Interestingly, such decarboxylation occurs at the non-chelated wing of ligand, which induces the changed capability of physical N₂ adsorption and chemical NH₃ gas adsorption.

During the this decade, optical-functional metal-organic frameworks (MOFs) system, have shown the very attractive application prospect in different areas,¹⁻⁴ including sensor, nonlinear optics, light-emitting technology, light-harvester and photocatalysis. Since that, constructing suitable MOFs to explore the excellent optical-functional material is always one interesting and noteworthy research. One important synthetic strategy is the modulation of centre metal ion in such system, typically in lanthanide-MOF (Ln-MOF) material.^{1C,5} However, the developments of relatively various transition metal ions in this area have been hindered by the photophysical nature of *d*-electron (major barrier, the nonradiative *d-d* transition)⁶ or full-filled *d*-orbital (like Zn(II), absent metal-to-ligand charge transfer state or ligand-to-metal charge transfer state). Hence, chromophore-derived MOF is one more convenient choice.⁷⁻¹²

In the recently several years, a new brilliant scaffold is to modulate the function of MOF material by light-driven force, such as photo-induced electron transfer or energy transfer.¹³⁻¹⁴ In 2016, Zhou group reported an interesting example that can control the generation of singlet Oxygen ($^{1}O_{2}$) in living cells by the tunable ratio of photochromic switch in MOF system.^{14b} Obviously, the cases reported in this rising research area are focused on the application of traditionally photochromic species.

In contrast, it is beyond unexplored that simple

photochemical reaction can be used as an attractive strategy for micro-adjustment of MOF structure to modulate its function. As we know, photochemical reaction based on electron transfer or energy transfer was usually fast and hardly controllable in solution, whereas in the suitable restricted media, the yield of selected product would be remarkably enhanced,¹⁵ such as photochemical decarboxylation.^{16,17} Recently, except for metal ion signaling in biology,¹⁸ photoinduced decarboxylation is also very useful for solid state actinometry.¹⁹ Hence, in chromophore-derived MOF scaffold, this new strategy might be praticed to adjust the microstructure of parent MOF.

As well-known, the ligand terephthalic acid is a super linker to construct many MOFs, including the famous pioneer MOF-5.²⁰ However, the structural character of terephthalic acid might hinder its direct application in optical-functional material. Herein, one analogue of terephthalic acid, benzothiadiazole-4,7-dicarboxylic acid (H2BTDC) as the linker was selected to construct chromophore-derived MOF. Commonly, benzothiadiazole (BTD) derivative is efficient chromophore with fine fluorescence capability,²¹ whilst highly polarized feature of BTD species is beneficial to afford the well-ordered crystal structure.^{21b} On the other hand, planar BTD unit is a typical electron acceptor, which is beneficial to trigger the photochemical decarboxylation in suitable condition. Attractively, if the photochemical decarboxylation only occurs in the one wing of ligand, the micro-adjustment of MOF structure can be observed, even that the cavity feature may be modulated. In this work, we reported the first exploration for micro-adjustment of MOF strucutre by unique



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Electronic Supplementary Information (ESI) available: Crystallographic information for MOFs **Zn-BTDC-M1**, **Zn-BTDC-M1**', **Zn-BTDC-M1**''in CIF format and additional figures and tables, photophysical properties of **Zn-BTDC-M1**. See DOI: 10.1039/x0xx00000x

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photochemical decarboxylation in new benzothiadiazolederived Zn(II) MOF, **Zn-BTDC-M1** (Scheme 1).

In Zn-BTDC-M1, there are three kinds of Zn(II) ions with different coordination environments, and the neighboring Zn(II) ions are further linked together through two kinds of carboxylate groups of BTDC²⁻ ligand (Figure S1-S2, Table S1-S3). In detail, one carboxylate group shows bridging tridentate coordination mode $(\mu_2 - \eta^2 : \eta^1)$, whilst the other one is a bidentate bridging coordination fashion $(\mu_2 - \eta^1 : \eta^1)$ to form a dinuclear {Zn-Zn} unit (Figure S1). The {Zn-Zn} units are connected by BTDC²⁻ ligands along the special direction to construct a 3D framework with 1D rectangular channel along the c axis. On the basis of crystallographic report, thermogravimetric (TG), ¹³C solid state NMR (SSNMR) and element analyses, there are non-volatile DMF (DMF = N,Ndimethylformamide) molecules in the cavity, which are diffecultly elimilated even after supercritical CO₂ (SC-CO₂) activation (Figure S3). Finally, MOF was outgassed to confirm removal of DMF molecules, and the phase structure of MOF was still maintained (Figure S4). Hence, according to the analyses described above, Zn-BTDC-M1 was defined as ([Zn₂(BTDC)₂]·1.5DMF. To consider BTD subunit arrangement in crystal and reported litertures, 22-23 Zn-BTDC-M1 obviously showed non-emissive J-dimmer absorption band at 478 nm (Table S4). Furthermore, only one emission was observed in **Zn-BTDC-M1** with lifetime of 0.99 ns (λ_{em} = 430 nm, Figure S5).

More interestingly, MOF Zn-BTDC-M1 displayed an irreversible photochromic phenomenon. When a visibly color change was observed under UV irradiation in Zn-BTDC-M1 at room temperature (Figure S6, movies), no color-recovery was observed kept in dark for several days. This phenomenon was totally different from that observed in typical photochromic system based on energy transfer, which was a possible signal of reaction triggered by photo-induced electron transfer. Moreover, new absorption band centered at ~715 nm was distinctly generated under irradiation in Zn-BTDC-M1 (Figure 1a, Figure S7). This band was probably anion radical signal of BTD species generated by a photo-induced electron transfer,²¹ which was supported by quenched emission behavior under irradiation (Figure S8). Besides, electron paramagnetic resonance (EPR) study (Figure 1b) displayed that no EPR signal was observed in the as-synthesized Zn-BTDC-M1. In contrast, a signal at g = 2.0045 appeared after irradiation, which was also supporting the existence of anion radical.



As we know, when photo-induced electron transfer is occured from carboxylate anion site to benzene ring, rapid loss of CO₂ from carboxy radical site will be subsequently induced to generate the decarboxylated product.¹⁶ Actually, fast photo-induced decarboxylation in H₂BTDC solution was traced by UV-vis absorption spectroscopy, and the decarboxylated product was further comfirmed by ¹H NMR instrument (Figure S9). In contrast, comparing to **Zn-BTDC-M1**, such photochemical process is extremly slow in powdered ligand (Figure S10a). Herein, FT-IR spectroscopy analysis is selected to reveal the group changes in decarboxylation reactions of **Zn-BTDC-M1** and powdered ligand, respectively (Figure 2a, Figure S10b). In **Zn-BTDC-M1** (Figure 2a), new peaks at 2335 and 2360 cm⁻¹ corresponding to asymmetrical stretching vibration of free CO₂ were remarkably visible under irradiation, which was the



Figure 2. (a) FT-IR spectra of **Zn-BTDC-M1** recorded before and after irradiation. (b) ¹³C solid state NMR (SSNMR) spectra of **Zn-BTDC-M1** (black) and irradiated **Zn-BTDC-M1** (red). Asterisks denote DMF molecules in the cavity; inset: the detail in the range of 180-140 ppm. (c) X-ray photoelectron spectra (XPS) of **Zn-BTDC-M1** (blue) and irradiated **Zn-BTDC-M1** (red) showing Zn2p and C 1s peaks.

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direct evidence of photo-induced decarboxylation. The initial $v_{\rm s}$ (C=O) double peaks at 1673/1663 cm⁻¹ were conversed to a single peak at 1666 cm⁻¹ in the irradiation process, while the u(C-O) band at 1216 cm⁻¹ belong to **Zn-BTDC-M1** was gradually weakened (Figure 2a). Especially, a relatively broadened single peak at 1094 cm⁻¹ was instead of v(C-O) bands of 1104 and 1089 cm⁻¹ in the photochemical process of **Zn-BTDC-M1** (Figure 2a). In fingerprint region (< 1000 cm^{-1} , Figure 2a), the signals of typical p-disubstituted benzene rings at 835/816 cm⁻¹ (C-H wagging) in as-synthesized Zn-BTDC-M1 were gradually weakened during the photochemical process, especially the peak of 835 cm⁻¹. In contrast, there was a new band at 823 cm⁻¹ generated under UV light irradiation in Zn-BTDC-M1. Oppositely, such decarboxylation evidences described above was obscure and difficult to identify in powdered ligand under irradiation (Figure S10b), which was consistent to the UV-vis absorption analysis.

Moreover, when photochemical decarboxylation reaction was occurred in Zn-BTDC-M1, ¹³C SSNMR spectra should be sensitively traced the weakened or completely disappeared peak of carboxyl group. As we expect, the ¹³C SSNMR analysis (Figure 2b) suggested that comparing to the initial intensity of the typical carboxyl group peak at 174.3 ppm in **Zn-BTDC-M1**, its intensity was less than one third in irradiated Zn-BTDC-M1, whilst no such changes were observed in the remaining peaks of BTDC²⁻ linker. Except for these, XPS spectra of Zn-BTDC-M1 before and after irradiation indicated that as shown in Figure 2c, the two peaks of Zn $2p_{1/2}$ and $2p_{3/2}$ in as-synthesized Zn-BTDC-M1 was appearing at 1045.5 and 1022.4 eV, respectively, while for the irradiated sample, such binding energies shifted towards a higher energy of 1045.6 and 1022.8 eV, respectively. In addition, the separation of the binding energy between $2p_{1/2}$ and $2p_{3/2}$ decreases from 23.1 to 22.8 eV. These results imply the relatively changed coordination environment of metallic zinc during the photochemical reaction.²⁴ At the same time, in C1s XPS spectrum of as-synthesized Zn-BTDC-M1, the typical C=C/C-C peak was at 284.8 eV, while their oxidative form peaks located at 286.0 eV (C-O) and 288.5 eV (C=O).²⁵ For irradiated Zn-BTDC-M1, the C=C/C-C peak was shifted to 285.2 eV, the intensity of which was visibly enhanced. Interestingly, the intensities of shifted oxidative form peaks were oppositely weakened in irradiated Zn-BTDC-M1 (Figure 2c). Obeviously, this evidence was further reveal the photochemical decarboxylation process in material designed. Accoring to these results, photochemical decarboxylation process should be occurred at one wing of BTDC²⁻. Because of the suitable restricted media we designed (Zn-BTDC-M1), it is much easier than pure ligand in solid state.

Significantly, PXRD data before and after irradiation (Figure S11) showed that main framework of **Zn-BTDC-M1** was maintained, indicating a crystalline-to-crystalline transformation feature. Based on this, control structure experiments of **Zn-BTDC-M1** before and after irridiation were analysed (**Zn-BTDC-M1**, **Zn-BTDC-M1**' and **Zn-BTDC-M1**'', collected by the same single crystal, as seen in movies). In **Zn-BTDC-M1**, C-C bond connected with BTD and carboxyl groups in chelated wings (C13-C16: 1.487(5)/C5-C8: 1.491(6) Å) is



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Figure 3. (a) The possible pathway A for the dissociation of carbon dioxide (distance: Å). (b) The possible pathway B for the dissociation of carbon dioxide (distance: Å). (c) Proposed scheme of decarboxylation by photo-induced electron transfer (PET) pathway. (d) Schematic illustration of the decarboxylation reaction.

visibly shorter than that in non-chelated wings (C9-C10: 1.503(5)/C1-C2: 1.503(5) Å). It supported that such C-C bond breaking in C1-C2/C9-C10 was easier than that in C5-C8/C13-C16. On the other hand, the dihedral angles between BTD rings and carboxylate planes were changed in the irradiation process (Table S5), which could relatively influence the electron cloud distribution of ligand. Herein, we speculate that it may delay the anionic radical ($^{\circ}OOC-BTD-COO^{\bullet}$) decay to enlarge the probability of subsequent decarboxylation.

Moreover, molecular modeling analysis shows that the decarboxylation energy barrier on non-chelated wings of BTDC²⁻ is only 5.3 kcal/mol, indicating a smoothly pathway (Figure 3a). In contrast, in chelated wings of BTDC²⁻, the decarboxylation can be excluded, because of the intermediate state hardly located with an energy barrier distinctly higher than 40 kcal/mol (Figure 3b). Hence, we speculated that the first step of photochemical decarboxylation was photo-induced electron transfer. When **Zn-BTDC-M1** was irradiated by UV light, electrons would tranfer from groud state (GS) to excited state (ES, Figure 3c). Subsequently, the photo-induced electron transfer from COO⁻ groups to BTD moieties was tending to occur at non-chelated wings of BTDC²⁻ because of small energy barrier. In the last step, free CO₂ were generated, and non-chelated wings of BTDC²⁻ were decarboxylated (Figure 3c-3d).

Furthermore, physical N₂ adsorption (Figure S12) and chemical NH₃ gas adsorption (Figure S13) studies were accomplished to explore the cavity feature before and after structural micro-adjustment by photochemical decarboxylation in Zn-BTDC-M1 case. Comparing to small surface area of **Zn-BTDC-M1** (Table S6),²¹ it was distinctly enlarged in irradiated one, especially the Langmuir surface area. On the other hand, NH₃ gas adsorption capability of material is very sensitive to its acidity. As we expect, NH₃ gas adsorption experiment (Table S7) demonstrated that the adsorption capability of irradiated material was weaker than that of as-synthesized material, which was resulted from the decreased acidity by photochemical decarboxylation.

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Conclusions

In summary, a new benzothiadiazole-derived Zn(II) MOF **Zn-BTDC-M1** showed the unique crystalline-to-crystalline microadjustment of structure by photochemical decarboxylation process. This first exploration in the BTD-derived MOF will extremely inspire more and more photochemical routes to modulate function MOFs materials in foreseeable future.

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