# **Supporting Information**

# Photochemically Crushable and Regenerative Metal–Organic Framework

Hiroshi Sato,<sup>\*,†</sup> Toshiya Matsui,<sup>†</sup> Zhiyi Chen,<sup>†</sup> Jenny Pirillo,<sup>§</sup> Yuh Hijikata,<sup>§</sup> and Takuzo Aida<sup>\*,†,‡</sup>

<sup>†</sup>Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

<sup>§</sup>Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Kita 21, Nishi 10, Kita-ku, Sapporo 001-0021, Japan

<sup>‡</sup>RIKEN Center for Emergent Matter Science, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

# Contents

1.	Materials and Methods	S2
2.	Synthesis	S3
3.	X-ray Crystallography	S3
4.	Le Bail Fitting	S3
5.	Computational Studies	S4
6.	Supporting Figures	S5
7.	Supporting Tables	S14
8.	References	S16

### 1. Materials and Methods

#### Materials

Unless otherwise noted, all of the commercially available chemicals were purchased from Wako Pure Chemical Industries Ltd, Tokyo Chemical Industry Co. Ltd. (TCI), and Sigma-Aldrich, and used without further purification.

### Methods

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL model JNM-ECA 500 spectrometer operating at 500.00 MHz and 125.65 MHz for <sup>1</sup>H and <sup>13</sup>C NMR, respectively, using partially or non-deuterated solvent residues as internal references. <sup>1</sup>H DOSY NMR spectral data were recorded on a Bruker Avance 500 MHz spectrometer equipped with a CP-TCI cryoprobe. Electronic absorption spectra were recorded on a JASCO type V-670 spectrophotometer. Powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku model SmartLab X-ray powder diffractometer equipped with a Cu sealed tube ( $\lambda$ = 1.54056 Å), which was operated at 40 kV and 40 mA. Powdery samples were put into a glass capillary (0.5 mm outside diameter) and their diffraction patterns were measured in a rotating capillary.

The PXRD data were collected in a range of  $3^{\circ}$  to  $45^{\circ}$  in  $2\theta$  by a step-scan mode with a step size of 0.05°. Thermogravimetric analysis (TGA) was conducted on a Mettler-Toledo model TGA/SDTA851° in a temperature range from 25 °C to 450 °C at a heating rate of 5 °C min<sup>-1</sup> under N<sub>2</sub> with a flow rate of 20 mL min<sup>-1</sup>. Single crystal X-ray diffraction (SCXRD) measurements were recorded on a Rigaku model VariMax Dual. Optical images were taken on a KEYENCE model VHX-S550E. UV or visible light irradiation was performed on ten fluorescent lamps with Toshiba GL8W or FL8W respectively. Pointwise dissolution of <sup>DTE</sup>MOF crystals was conducted on Asahi Spectra model MAX-301 300-W xenon light source with a 310 nm-bandpass filter.

#### 2. Synthesis

### Synthesis of <sup>DTE</sup>MOF ([Cd(nip)(<sup>Py</sup>DTE<sub>open</sub>)(DMF)<sub>2</sub>(H<sub>2</sub>O)]<sub>n</sub>)

To a glass vial (10 mL) containing 5-nitroisophthalic acid (nipH<sub>2</sub>, 3.4 mg, 16  $\mu$ mol), <sup>Py</sup>DTE<sub>open</sub> (8.4 mg, 16  $\mu$ mol), and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (4.9 mg, 16  $\mu$ mol) was added DMF (0.4 mL) and MeOH (0.4 mL). The mixture was stirred at 20 °C for 4 days and a white precipitate was obtained. The collected solid was washed with a mixture of DMF and MeOH (1/1,  $\nu/\nu$ ) for three times and dried in vacuo at 20 °C to give white powdery product of <sup>DTE</sup>MOF (yield: 60%, based on <sup>Py</sup>DTE<sub>open</sub>), which thermally decomposes at around 300 °C according to a thermogravimetric analysis (Figure S4). Colorless crystals of <sup>DTE</sup>MOF suitable for single crystal X-ray diffraction analysis were obtained in the similar procedure where the reaction mixture was left to stand at 20 °C for a week without stirring.

### 3. X-Ray Crystallography

A single crystal of <sup>DTE</sup>MOF was mounted using a MiTeGen MicroMount and subjected to single crystal X-ray diffractometry, where the diffraction data were collected at 93 K on a Rigaku model VariMax Dual diffractometer equipped with a fine-focus sealed-tube X-ray source ( $\lambda = 0.71075$  Å) and a confocal graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares cycles in SHELX97. All nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C were located at geometrically calculated positions and refined with isotropic thermal parameters. Because solvent molecules included in the MOF channels were disordered, the *SQUEEZE* command in *PLATON*<sup>S1</sup> was used in the structure refinement. The crystallographic data for <sup>DTE</sup>MOF were summarized in Table S1.

#### 4. Le Bail Fitting

The PXRD pattern was obtained for as-synthesized <sup>DTE</sup>MOF in air at 20 °C. The PXRD pattern was indexed using DIFFRACplus TOPAS® v4.2 software, followed by a Le Bail structureless profile fitting to extract diffraction intensities using RIETAN-FP program.<sup>S2</sup> The obtained cell parameters from the Le Bail fitting (Figure S3) were summarized in Table S2.

### 5. Computational Studies

## Model construction of <sup>DTE</sup>MOF

In order to investigate energetical destabilization that could be caused by the photoisomerization of <sup>Py</sup>DTE<sub>open</sub> to <sup>Py</sup>DTE<sub>closed</sub> in <sup>DTE</sup>MOF, we performed density functional (DFT) calculations using model structures referred to the crystal structure of <sup>DTE</sup>MOF. The optimized model structures are as shown in Figure S14. All calculations were carried with M06/cc-pVDZ level of theory<sup>S3</sup> using Gaussian 16 Rev. C01.<sup>S4</sup> The Stuttgart–Dresden–Bonn (SDD)<sup>S5,S6</sup> basis set was used for Cd, where the core electrons were replaced with the effective core potentials of the SDD. We fixed the positions of Cd and coordinating atoms to the Cd, except for nitrogen atoms in DTE, to consider the structural constrain in the MOF.

### 6. Supporting Figures



**Figure S1.** Coordination environment of Cd<sup>2+</sup> in <sup>DTE</sup>MOF. Atoms are colored as follows: Cd, light yellow; C, gray; N, blue; O, red; S, yellow; F, green.



**Figure S2.** (a) Crystal structure of <sup>DTE</sup>**MOF** adopting a tubular geometry with interlocked coordination networks. Hydrogen atoms are omitted for clarity. Nanotubes colored in blue and red are identical to each other crystallographically. (b) Perspective view of  $^{DTE}$ **MOF** along the *c* axis. Atoms are shown in a CPK model and colored as follows: Cd, light yellow; C, gray; H, white; N, blue; O, red; S, yellow; F, light blue.



**Figure S3.** Le Bail fitting of the PXRD pattern of as-prepared <sup>DTE</sup>MOF in air at 20 °C. Crystallographic data is summarized in Table S2.



**Figure S4.** TGA profiles of as-prepared (red) and guest-free (blue) <sup>DTE</sup>MOF. Guest-free <sup>DTE</sup>MOF was prepared by heating as-prepared <sup>DTE</sup>MOF at 110 °C under a reduced pressure for 14 h.



**Figure S5.** Pore size distribution of  ${}^{DTE}$ **MOF** evaluated from the CO<sub>2</sub> adsorption isotherm by Saito-Foley method.



**Figure S6.** NMR study of solid-state photochemical reaction of <sup>DTE</sup>MOF upon irradiation of UV and visible lights. <sup>1</sup>H NMR spectra of (a) as-prepared, (b) UV-exposed, and (c) UV-Vis-exposed <sup>DTE</sup>MOFs. As-prepared <sup>DTE</sup>MOF was exposed to UV light for 2 h in air at 20 °C. Successively, dark-blue UV-exposed <sup>DTE</sup>MOF was exposed to visible light for 24 h in air at 20 °C. The samples were digested in a mixture of DMSO- $d_6$ /DCl for the spectral measurements.



**Figure S7.** (a) PXRD patterns of as-prepared <sup>DTE</sup>MOF (black), the solid substances after irradiation of <sup>DTE</sup>MOF with UV (blue) and visible (green) lights in air at 20 °C, and a simulated pattern of as-prepared <sup>DTE</sup>MOF (broken, black). (b) PXRD patterns of as-prepared <sup>DTE</sup>MOF (black), the solid substances after irradiation of <sup>DTE</sup>MOF with UV (blue) and visible (purple) lights under saturated vapor of DMF at 20 °C, and a simulated pattern of as-prepared <sup>DTE</sup>MOF (broken, black).



**Figure S8.** Schematic representation of the experimental procedure to obtain the time course of the conversion of  $^{Py}DTE_{open}$  into  $^{Py}DTE_{closed}$ . A suspension of  $^{DTE}MOF$  in DMF/MeOH (1:1, v/v) was exposed to UV light (305–315 nm) at 20 °C. Aliquots of the suspension were taken occasionally, briefly centrifuged to remove insoluble fractions, and the supernatants were subjected to electronic absorption spectroscopy.



**Figure S9.** Electronic absorption spectra of  ${}^{Py}DTE_{closed}$  (black, 0.41 mM) and a dispersion containing  ${}^{Py}DTE_{closed}$ , nip<sup>2-</sup>, and Cd<sup>2+</sup> (blue, 0.41 mM for each component) in DMF/MeOH (1/1, *v/v*) at 20 °C. The dispersion was prepared by exposure of  ${}^{DTE}MOF$  to UV light for 30 min at 20 °C. The spectra were recorded using a 1 mm-thick cuvette.



**Figure S10.** <sup>1</sup>H NMR spectra of (a) <sup>Py</sup>**DTE**<sub>closed</sub>, (b) a mixture of <sup>Py</sup>**DTE**<sub>closed</sub> and nipH<sub>2</sub>, and (c) a photochemical reaction mixture containing <sup>Py</sup>**DTE**<sub>closed</sub>, nip<sup>2-</sup>, and Cd<sup>2+</sup> in DMF*d*<sub>7</sub>/MeOD-*d*<sub>4</sub> (1/1, *v*/*v*) at 20 °C. The photochemical reaction mixture was prepared by exposure of <sup>DTE</sup>**MOF** to UV light in DMF-*d*<sub>7</sub>/MeOD-*d*<sub>4</sub> (1/1, *v*/*v*) for 30 min at 20 °C.



(a) Mixture of <sup>Py</sup>DTE<sub>closed</sub> and nipH<sub>2</sub> (b) Photochemical Reaction Mixture of <sup>DTE</sup>MOF

**Figure S11.** <sup>1</sup>H DOSY NMR spectra (aromatic region) of (a) a mixture of <sup>Py</sup>DTE<sub>closed</sub> and nipH<sub>2</sub> and (b) a reaction mixture obtained by irradiation of <sup>DTE</sup>MOF with UV light for 30 min at 20 °C in DMF- $d_7$ /MeOD- $d_4$  (1/1, v/v).



**Figure S12.** <sup>1</sup>H NMR study of the processes for crushing and regenerating <sup>DTE</sup>MOF. A mixture of <sup>Py</sup>DTE<sub>open</sub> (10 mM) and nipH<sub>2</sub> (10 mM) was allowed to react with Cd(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O (10 mM) in DMF- $d_7$ /MeOD- $d_4$  (1/1, v/v). The mixture was stirred at 20 °C for three days in an NMR glass tube, then the obtained suspension of <sup>DTE</sup>MOF crystals were irradiated with UV light (305–315 nm) for 30 min upon stirring. Based on the <sup>1</sup>H NMR spectrum of the resulting dark-blue solution, a mole ratio of <sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>open</sub> was evaluated to be 96/4 (a). Successively, the solution was irradiated with visible light for 2 h, then the ratio of <sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>open</sub> turned to be 30/70 (b). Further irradiation of the reaction mixture with visible light at 20 °C for 2 h afforded the ratio of <sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>closed</sub>/<sup>Py</sup>DTE<sub>close</sub>



**Figure S13.** Optical images of reaction mixtures containing <sup>Py</sup>DTE, nip<sup>2–</sup>, and Cd<sup>2+</sup> (5 mM for each) in DMF/MeOH (1/1, v/v). Initial dispersion was prepared by exposure of as-prepared <sup>DTE</sup>MOF to UV light for 30 min at 20 °C. The resulting dispersion was irradiated with visible light for 6 h at 20 °C. Then, the reaction mixture was left in the dark for 3 days at 20 °C, affording colorless crystals of <sup>DTE</sup>MOF.



**Figure S14.** Optimized geometries of (a) open- (left, *P*-helical conformer) and closed (right, (*R*,*R*) enantiomer) isomers, and (b) open- (left, *M*-helical conformer) and closed (right, (*S*,*S*) enantiomer) isomers. Ocher, red, blue, green, yellow, and white colors indicate carbon, oxygen, nitrogen, fluorine, sulfur, and hydrogen atoms. Ball model of atoms mean the fixed atom during optimization. The estimated destabilization energies caused by photoisomerization of  $^{Py}DTE_{open}$  to  $^{Py}DTE_{closed}$  were 13.7 and 13.2 kcal/mol in the cases with *P*- and *M*-helical conformers as starting materials, respectively. Because the number of **DTE** ligands is eight in a unit cell, we can estimate the energetical destabilization of 105.6 kcal/mol per unit cell.



**Figure S15.** Schematic representation of the experimental setup for the pointwise dissolution of <sup>DTE</sup>MOF with UV light. <sup>DTE</sup>MOF crystals were attached on a photomask surface (a stainless-steel grid for transmission electron microscopy (TEM)) using double-sided tape. UV irradiation was conducted for <sup>DTE</sup>MOF crystals with the photomask in DMF/MeOH.

# 7. Supporting Tables

	DTEMOF
Empirical Formula	$C_{33}H_{19}Cd_1F_6N_3O_7S_2$
Formula Weight	860.05
Crystal System	Tetragonal
Space Group	$P4_2/n$
<i>a</i> (Å)	31.712(5)
<i>c</i> (Å)	10.0698(14)
$V(Å^3)$	10127(3)
Ζ	8
R <sub>int</sub>	0.1843
$\mu (\mathrm{cm}^{-1})$	5.718
$D_{ m calcd}/ m g$	1.128
<i>F</i> (000)	3424
Goodness of Fit	1.178
Temperature (K)	93
Reflections Collected	11553
Independent Reflections	11224
$R$ (I > 2.00 $\sigma$ (I), all data)	0.0691
$R_{\rm w}$ (I > 2.00 $\sigma$ (I), all data)	0.1840

 Table S1. Crystallographic data and structural refinement summary for <sup>DTE</sup>MOF

	DTEMOF
Crystal System	Tetragonal
Space Group	$P4_2/n$
<i>a</i> (Å)	32.5049(5)
<i>c</i> (Å)	10.1596(3)
$V(Å^3)$	10734.3(4)
Ζ	8
R <sub>wp</sub> (%)	2.349
Goodness of Fit	1.4319
Temperature (K)	298

 Table S2.
 The result of Le Bail fitting for <sup>DTE</sup>MOF in air at 20 °C

#### 8. References

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