

Trapping and Releasing of Oxygen in Liquid by Metal–Organic Framework with Light and Heat

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Nanoporous materials can adsorb small molecules into their nanospaces. However, the trapping of light gas molecules dissolved in solvents suffers from low concentration and poor adsorption affinity. Here, the reversible trapping and releasing of dissolved oxygen are shown through integrating photosensitization and chemical capturing abilities into a metal–organic framework (MOF), MOMF-1. 9,10-Di(4-pyridyl)anthracene (dpa) ligands in MOMF-1 generates singlet oxygen from triplet oxygen under photoirradiation without additional photosensitizers, and successively reacts with it to produce anthracene endoperoxide, forming MOMF-2, which is proved crystallographically. The reverse reaction also proceeds quantitatively by heating MOMF-2. Moreover, MOMF-1 exhibits excellent water resistance, and completely removes oxygen of ppm order concentrations in water. The new material shown in this report allows controlling of the amount of dissolved oxygen, which can be applicable in various fields relating to numerous oxidation phenomena.

1. Introduction

Trapping and releasing of molecules or ions dissolved in liquid phase are important in chemical industries, environmental remediation, and biological system; for instance, activated carbons and zeolites are widely used to purify water by removing dissolved organic/inorganic pollutants.^[1,2] In particular, those of dissolved gas molecules in liquid using

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nanoporous materials is quite challenging because: (1) the concentration of gas molecules, such as nitrogen, oxygen, and carbon dioxide, in liquid phase is generally quite low, and (2) the interactions between gas molecules and material surfaces are too weak to trap them at ambient temperatures without specific chemical interactions. On the other hand, biomolecules such as hemeprotein^[3] can recognize and trap oxygen dissolved in the blood at an alveolus, and release oxygen in peripheral tissue, which plays a vital role in vertebrate animals. Hemeprotein can be widely and homogeneously dispersed in the blood allowing efficient control of oxygen concentration. Although this is advantageous, the use of such biomolecules in industrial processes is nonetheless problematic because their separation from homoge-

neous solutions is very difficult after use, which means that such molecules may act as an eventual "pollutant" in the liquid. Therefore, it is highly desirable to develop insoluble heterogeneous adsorbents.

As a new class of porous material, metal-organic frameworks (MOFs)^[4,5] have been extensively studied as gas adsorbents due to their versatile structures and unique gas adsorption properties.^[6-15] In particular, structurally or chemically switchable MOFs under external stimulation are anticipated to act as dynamic sorption devices that can control its molecular trapping behavior as desired.^[16-22] MOFs except composite materials have not been able to trap oxygen in water at ambient temperatures due to the weak adsorption potential of their nanopores.^[23] Therefore, it is necessary to endow specific interaction ability to MOFs for oxygen^[24] although this is challenging because of the trade-off between an increase in interaction with oxygen and a loss of structural stability, in particular in water. With this background, we tried to integrate oxygen trapping and photosensitizing abilities in a single building block, with the objective of trapping oxygen in a MOF in liquid phase in ambient conditions and without any aid of additional photosensitizers (Figure 1).

We demonstrate the development of a single component MOF that can trap and release dissolved oxygen with the light and heat stimulation, and also show the mechanism of oxygen trapping crystallographically.





Figure 1. Schematic image to trap dissolved oxygen using a MOF constructed with dpa, which has photosensitizing and trapping abilities with oxygen.

2. Result and Discussion

2.1. Ligand Design

We selected 9,10-Di(4-pyridyl)anthracene (dpa) ligand as a building unit with considering three requirements. First, photosensitizing ability for oxygen must be given for the generation of singlet oxygen that cannot be obtained by direct photoexcitation.^[25–27] Second, the polycyclic aromatic surface of anthracene is a suitable receptor of oxygen because endoperoxide on its molecular π surface is formed with the singlet oxygen. In addition, heating of the resulting endoperoxide releases the singlet oxygen.^[28–30] Third, it is necessary to avoid destructive structural changes upon oxygen trapping. Accordingly, two 4-pyridyl modules are equipped at the 1 and 9 positions of the anthracene moiety for the ligand (dpa) to act as linear ligands at both oxygen free and endoperoxide forms.

The photosensitizing and oxygen trapping abilities for dpa molecule were confirmed experimentally. Dpa was converted to 9,10-di(4-pyridyl)anthracene endoperoxide (dpaep) under oxygen and UV-light (380 nm) in *N*,*N*-dimethylformamide (DMF) solution, which was observed in UV–vis absorption, nuclear magnetic resonance (NMR) and mass spectra (Figures S1–S3, Supporting Information). It is also confirmed that the heating of dpaep of DMF solution at 120 °C for 1 d gave rise to an original dpa molecule with releasing of an oxygen molecule.

2.2. Synthesis, Structure, and Oxygen Trapping Ability of MOMF-1

We prepared **MOMF-1** $([Zn_2(dpa)(2,6-NDC)_2] \cdot (DMF)_2),^{[31]}$ where 2,6-NDC is 2,6-naphthalenedicarboxylate, and its structure was determined by single-crystal X-ray diffraction (SXRD) analysis (**Figure 2**, **Table 1**). In **MOMF-1**, the Zn²⁺ and carboxylates of 2,6-NDC ligands form Zn²⁺ paddle-wheel units. The paddle wheel units are linked by 2,6-NDC to form a 2D sheet structure which is further linked by dpa ligands at the axial positions of the paddle wheel units (Figure 2a), forming a 3D network (Figure 2b). Each independent 3D network is mutually interpenetrated in a twofold fashion to form the nanospace in the framework filled by DMF molecules, and the total potential void volume was estimated to be 740.83 Å³ in the unit cell. A large 1D channel along the c axis (Channel C) and a small 1D channel along the *b* axis (Channel B) are interconnected by a further small one-dimensional channel along the a axis (Channel A) into 3D grid-like pore network (Figure S4, Supporting Information). One side of the π -surface of anthracene is exposed to Channel C with a pore window size of 7.6 $Å \times 4.4$ Å, which is sufficient to allow the diffusion of oxygen molecules (kinetic diameter of O2: 3.46 Å) into the pore and contact with anthracenes. The other side of the π -surface is parallel to a naphthalene π -plane forming π - π interaction (\approx 3.8 Å), and is adjacent to a C–H bond of pyridine with close contact (\approx 3.3 Å); therefore, no available voids exist around this side (Figure 2c). To evaluate the oxygen trapping ability of MOMF-1 in DMF, time course NMR spectra for the photoirradiated samples were measured (Figure 3a,b). The peaks assigned to dpa decreased with increasing photoirradiation time whereas those of dpaep increased. It is noteworthy that the conversion ratio after photoirradiation was estimated to be ≈100%, indicating that MOMF-1 can trap oxygen stoichiometrically with the formation of **MOMF-2** ([Zn₂(dpaep)(2,6-NDC)₂]·(DMF)₂). Furthermore, we successfully obtained the crystal structure of MOMF-2 (Figure 2d,f, Table 1). All anthracene moiety of dpa reacted with oxygen at the positions of the 9 and 10 carbons on its π -surface, thus forming endoperoxide (Figure 2d). Structural deformation of anthracene is observed due to the geometrical change of these carbons from triangular sp² to tetrahedral sp³. One of the benzene rings of the dpaep faces to naphthalene with an interplane distance of ≈4.1 Å (Figure 2f). Interestingly, the oxygen molecules in dpaep ligands were jammed into very narrow solvent-inaccessible channels. This suggests the rearrangement of Channel C upon the formation of endoperoxides, resulting in the shrinkage of Channel C and generation of Channel C'. The plausible mechanism can be described as follows: Upon addition of oxygen molecules to anthracenes, structural deformation causes steric repulsion from adjacent naphthalenes and pyridines, which leads to the change of relative position of each network forming a two-fold interpenetrated structure, i.e., one of the frameworks is detached from the other framework, glides in the pore, and reattaches on the other side (Figure 4).

To confirm the release of oxygen and the recovery of original **MOMF-1** from **MOMF-2**, we heated powder crystals of **MOMF-2** in DMF at 100 °C for 8 h. ¹H NMR spectrum for the resulting sample shows that all peaks of the dpaep disappeared whereas those of dpa were observed (Figure 3b). Release of O₂ molecules from **MOMF-2** was also observed in the thermogravimetric analyses (Figure S5, Supporting Information). Furthermore, the PXRD pattern of **MOMF-2** after heating recovered to that of the original **MOMF-1** (Figure 3c). The results proved the reversible conversion between **MOMF-1** and **MOMF-2** in DMF.

Previously, it was believed that the solvent molecules in the nanospaces of as-made compounds must be removed prior to the use of MOFs as gas adsorbents because these molecules prevent the access of gas molecules into the nanospace, i.e., the nanospace has to be cleaned up. However, our results herein indicate that even a light molecule, such as oxygen, could diffuse into the pore, passing through the remaining space among the DMF molecules or replacing them, although the mechanism is still not clear. This is a significant finding showing that





Figure 2. Crystal structures of **MOMF-1** and **MOMF-2**. DMF molecules are omitted from all of the structures for the clarity. Oxygen atoms on endoperoxides are highlighted to the ball model. a,d) Unit structures of **MOMF-1** and **MOMF-2** (Zn, steel blue; C, gray; N, blue; O, red; H, white). b,e) Twofold interpenetrated structure of **MOMF-1** and **MOMF-2**. Two independent networks are colored blue and yellow. c,f) Zoom-up image of (b) and (e), respectively. Atoms in short contacts are highlighted by CPK model. Carbon and hydrogen atoms derived from anthracene are colored green and others on pyridines/naphthalenes are colored by elements.

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Table 1. Crystallographic parameters for MOMF-1 and MOMF-2.

	MOMF-1	MOMF-2
Crystal system	triclinic	triclinic
Space group	ΡĪ	PĪ
a [Å]	12.9818(3)	12.9618(8)
b [Å]	13.1028(3)	13.1234(6)
<i>c</i> [Å]	17.1589(4)	17.8187(9)
α [°]	94.6111(17)	85.977(4)
β[°]	107.518(2)	69.271(5)
γ[°]	94.4214(18)	89.193(4)
V [Å ³]	2758.53(12)	2827.6(3)
μ [cm ⁻¹]	9.13	8.95
F [000]	908	940
Goodness of fit	1.013	1.029
Temperature [K]	93	93
Reflections collected	53 005	48 520
Independent reflections	12 339	12 741
$R_1 \left[l > 2\sigma[l] \right]$	0.0529	0.0819
$wR_2 [l > 2\sigma[l]]$	0.1483	0.2580

it is not always necessary to dry the MOF, even for gas adsorption. This will widen the application of MOFs, and contribute to saving time and energy in the activation process.

2.3. Theoretical Study for the Photosensitizing Ability of dpa and MOMF-1

The theoretical calculations were performed to estimate the photosensitizing ability of dpa (Figures 5 and 6). The vertical excitation energy from S_0 to S_1 assignable to π - π * excitation of the anthracene moiety was estimated to be 3.12 eV similarly to that of 9,10-di(phenyl)anthracene, 3.17 eV.^[32] The T₁ state locates at 1.72 eV higher than S₀ state, at which a part of excited dpa goes back to S₀ through T₁ via the intersystem crossing (ISC) from S_1 . The dpa at T_1 state can photosensitize ${}^{3}O_2$ to generate ${}^{1}O_{2}$, because the relative energy at the T₁ state to the S₀ is adequately higher than both the experimental (0.98 eV) and estimated (0.90 eV, calculated with the correction to eliminate the spin contamination^[33]) energy differences between ³O₂ and ¹O₂. In order to further evaluate the possibility of ISC from the S₁ to T₁ states, spin-orbit coupling (SOC) values, which are good indicator of ISC, were also calculated. At the optimized structure of isolated dpa molecule in the S₁ state, in which two pyridines were perpendicular to the anthracene moiety (Twist form, Figure 5), the estimated SOC value between the S_1 and T_1 states was zero (Table 2), indicating that the possibility of ISC is quite low. On the other hand, two pyridine moieties of dpa in the MOMF-1 (dpa@MOMF-1) slightly rotated in the S₁ state (Figure 6b) although that in the S_0 state was twist form (Figure 6a) similar to the isolated dpa in the S_0 state. The dihedral angle between pyridine and anthracene moieties was calculated to be 63°. In this case, the estimated SOC value between S_1 and T_1 states is 0.314 cm⁻¹ (Table 2), indicating that ISC can



Figure 3. a) Reaction scheme of conversion between dpa and dpaep. b) Time-course change of ¹H NMR spectra of **MOMF-1** digested in DCl/ DMSO- d_6 after photoirradiation. Black and white circles denote peak positions that are assignable to dpa and dpaep, respectively. ¹H NMR spectrum of **MOMF-2** heated at 100 °C for 8 h in DMF (turquoise) is also shown. c) PXRD patterns for **MOMF-1**, **MOMF-2** and heated **MOMF-2**.

be allowed. The effect of the rotation of the substituent on ISC in a polyaromatic compound has also been reported previously.^[34] For the further investigation of the importance of pyridine rotation, we performed a 2D scan for the rotation of the two pyridine moieties of dpa with an interval of 30°.

We found that some dpa molecules with rotated pyridine have similar energies to the optimized structure at the S₀ state (Figure S6, Supporting Information). We optimized two representative structures with different rotational orientations of pyridine (A form: 57°, -123°, and B form: 59°, -59°) at the S₁ state, and then evaluated the SOC values of them. The estimated SOC





Figure 4. Schematic representation of the plausible mechanism of the framework transformation from **MOMF-1** to **MOMF-2**.

value of A form was 0.000 whereas that of B form was 0.373. Thus, the rotation on the pyridine moieties requires little energy and the same directional rotation is important to increase the SOC value. In addition, it should be noted that the path of $S_1 - T_2 - T_1$ would be impossible because the calculated energy level of dpa for the T_2 state is much higher than that for the $S_1 (\approx 0.1 \text{ eV})$.^[35]



Figure 5. Schematic energy diagram for photosensitization of ${}^{3}O_{2}$ to form ${}^{1}O_{2}$. Isovalues to plot Kohn–Sham orbitals are 0.02.



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Figure 6. The optimized geometries of dpa@MOMF-1 at a) S_0 and b) S_1 states. c) The employed model structure, dpa@MOMF-1.

2.4. Trapping of Dissolved Oxygen in Water by MOMF-1

Little change of peak intensity in PXRD patterns was observed after the immersion of crystals of **MOMF-1** in water for 1 d (Figure S7, Supporting Information). It was also suggested that the crystallinity of **MOMF-1** was maintained within a wide range of temperatures (below 60 °C, Figure S8, Supporting Information) and pH (3–11, Figure S9, Supporting Information), while the structure of **MOMF-1** transformed to another structure above 60 °C. Taking advantage of the high stability of **MOMF-1** in water, we also demonstrated the removal of dissolved oxygen in water by **MOMF-1** with photoirradiation. The single-crystal sample of **MOMF-1** dispersed in water was kept under photoirradiation. The oxygen concentration which was monitored using a dissolved oxygen meter abruptly decreased with photoirradiation, and reach zero after 300 min, whereas it kept constant in the absence of **MOMF-1** as a control (**Figure 7**).

The formation of dpaep was confirmed by the NMR spectrum of the sample of **MOMF-1** after light irradiation (Figure S10, Supporting Information). When light irradiation was stopped, oxygen concentration did not change, which shows that the concentration of oxygen can be controlled as desired (Figure S11, Supporting Information). According to the stoichiometric conversion from dpa to dpaep, the capacity of oxygen adsorption for 1 g of **MOMF-1** is 35.9 mg, which is equivalent to the amount of oxygen dissolved in water of 4.35 L at 1 atm and 25 °C.

Table 2. Calculated dihedral angles and SOC values for dpa.

	isolated dpa	dpa@MOMF-1
Dihedral angle [°]	90.0	63.0
SOC [cm ⁻¹]	0.000	0.314







Figure 7. Time-course concentration of dissolved oxygen in water under photoirradiation a) with and b) without MOMF-1.

3. Conclusion

In this work, we synthesized a MOF with the ability to trap and release oxygen molecules dissolved in various solvents. It has not been expected that MOFs as a single component have been used as gas adsorbents in liquid phase because the concentration of light gas molecules in liquid phase is intrinsically too low to achieve their trapping, and the solvent molecules are usually occupied in the nanospaces which block adsorption. We believe that this provides a paradigm shift in the field of gas adsorption in nanospace science from "gas phase molecular adsorption."

4. Experimental Section

Synthesis of **MOMF-1**: Zn(NO₃)₂·6H₂O (59.5 mg, 0.200 mmol), dpa (33.2 mg, 0.100 mmol), and 2,6-H₂NDC (43.2 mg, 0.200 mmol) were dissolved in DMF (10 mL), which was placed in a Teflon-lined stainless-steel autoclave bomb and heated in an oven at 100 °C for 3 d. After cooling to the room temperature, block-shaped crystals suitable for single-crystal X-ray crystallographic analysis were obtained. Bulk powder sample of **MOMF-1** was synthesized by microwave heating of the solution at 120 °C for 2 h. The liquid was removed from the supernatant by decantation, and the solids were filtered and washed to give pale yellow powder crystals (91.0 mg, 87%). The number of crystal solvents was determined by ¹H NMR.

Synthesis of **MOMF-2** by Oxygen Trapping in **MOMF-1**: **MOMF-2** single crystals were obtained by UV-light irradiation ($\lambda = 380$ nm, HITACHI FL8BL black lights with the light power of 8 W × 18 = 128 W) to a suspension of single crystals of **MOMF-1** in DMF for 12 h at room temperature. The obtained solids were crystalline enough and were subjected to single-crystal X-ray structural analysis. The crystallographic parameters for **MOMF-2** are summarized in Table 1. The number of crystal solvents was determined by ¹H NMR.

Computational Details: Theoretical calculations were performed using a Gaussian 09^[36] software package. The geometries of isolated dpa and oxygen molecule at their ground states were optimized at the B3LYP/ cc-pVDZ^[37–39] level of theory. The geometry optimization at the excited singlet states and evaluation of the vertical excitation energies were performed at the time-dependent (TD)-B3LYP/cc-pVDZ level of theory. The geometry optimization of dpa@**MOMF-1** was performed starting from that of the crystal structure with fixing atoms which originally were coordinated to metals at their crystallographic positions with the same level of theory above. ONIOM model was employed,^[40] where dpa and other surrounding environments were assigned to a higher region with TD-B3LYP/cc-pVDZ level of theory and a lower region with UFF^[41] respectively, to confirm the consistency of the vertical excitation nature (π - π *) and energy (3.10 eV). The obtained dpa in dpa@MOMF-1 was used for the optimization of dpa at the S₁ state. To evaluate the SOC values, the spin orbit matrix elements were estimated by means of the quadratic-response TD-DFT approach^[42,43] as implemented in DALTON code.^[44,45] The TD-B3LYP/cc-pVDZ level of theory was used in the framework of the mean field approximation.^[46]

Monitoring of the Trapping of Dissolved Oxygen in Water: **MOMF-1** (10 mg) was washed several times with water and immersed in water (11 mL) in a screw vial. The suspension was irradiated by 380 nm UV-light, while dissolved oxygen concentration was recorded using an optical oxygen monitor (Ocean Optics, NeoFox-GT) (Figure S12, Supporting Information). As the control experiment, the same experiment was performed without **MOMF-1**.

[CCDC 1990809–1990811 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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