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Photochromism | Hot Paper

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Photochromic Metal–Organic Frameworks: Reversible Control of Singlet Oxygen Generation**

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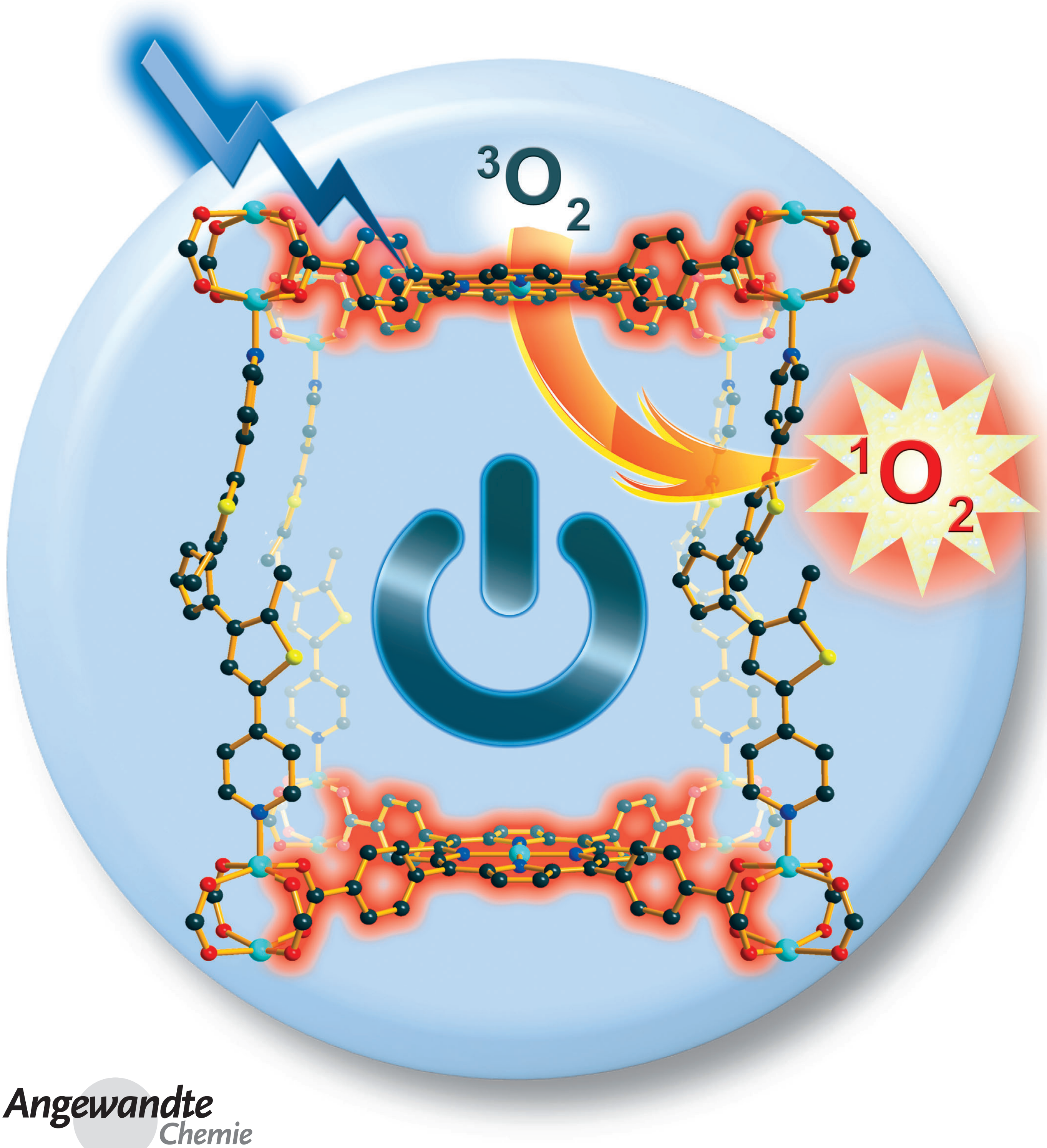

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Abstract: *The controlled generation of singlet oxygen is of great interest owing to its potential applications including industrial wastewater treatment, photochemistry, and photodynamic therapy. Two photochromic metal–organic frameworks, PC-PCN and SO-PCN, have been developed. A photochromic reaction has been successfully realized in PC-PCN while maintaining its single crystallinity. In particular, as a solid-state material which inherently integrates the photochromic switch and photosensitizer, SO-PCN has demonstrated reversible control of* $^1O_2$ *generation. Additionally, SO-PCN shows catalytic activity towards photooxidation of 1,5-dihydroxynaphthalene.*

Singlet oxygen ($^1O_2$) is a reactive oxygen species (ROS) which can be generated by cellular metabolism, redox chemistry, or photosensitization between a photosensitizer and molecular oxygen ($^3O_2$) upon irradiation.[1] The development of a photosensitizer for the generation of singlet oxygen is of great interest owing to potential applications including industrial wastewater, photochemical synthesis, and photodynamic therapy (PDT).[2] While progress has been made to advance photosensitizers, more recently the design of a system in which the production of singlet oxygen is can be controlled or activated, upon environmental changes or interaction with biomolecules or nanomaterials, has attracted growing attention.[2a,3] However, such methods often involve irreversible or passive interaction, which may lead to imprecise control over $^1O_2$ generation. In this sense, a system which inherently bears a photosensitizer and control functionality could be ideal to achieve controlled generation of singlet oxygen.

Photochromic molecules, which upon photoirradiation exhibit a reversible transformation between isomers having different properties, hold considerable promise for optical switches as a control unit in smart materials.[4] Of the many photochromic compounds, dithienylethene (DTE) derivatives are one of the most promising class of compounds because of their thermal stability, rapid response, and fatigue resistance.[4a,5] By employing the DTE photochromic switch and a porphyrinic photosensitizer in a homogeneous bicomponent system, Feringa et al. have recently demonstrated reversible control of singlet oxygen generation.[6]

Attachment of the catalyst onto solid support materials, such as silica or metal oxides, has shown the potential to integrate distinctive attributes of both homogeneous and heterogeneous catalysis.[7] For instance, a heterogeneous system of two or more incompatible components could be of great value because of the ability to accommodate various functionalities as well as efficient recovery and recyclability. Along these lines, researchers have strived to design a photosensitizer in a hybrid material form to incorporate these features into one system for photocatalysis.[8] However, most of the approaches suffer from synthetic difficulty, leaching, and improper spatial arrangement.[7a,9]

Metal–organic frameworks (MOFs) are an emerging class of porous materials and have captured widespread research interest because of their design flexibility and viability in potential applications such as gas storage/separation, sensing, and catalysis.[10,11] More recently, MOFs have been explored as light-harvesting platforms.[12] Because MOFs provide highly ordered structures in proximity to each other but not in direct contact, incorporation of chromophores as linkers to construct MOFs gives rise to an efficient platform for energy transfer. As a result of the structural diversity and tunability of MOFs, it is very convenient to introduce multiple functional moieties into the framework, thus making MOFs as ideal candidates for realizing cooperative functionalities based on periodic arrangement on a molecular scale.[13] Meanwhile, leaching of each component can be alleviated on account of the strong coordination bond. Moreover, the porous feature of MOFs allows all the functionalities within the framework to be accessible by incoming reactants regardless of their solubility.

Herein, we present two MOFs, namely PC-PCN (photochromic porous coordination network) and SO-PCN (singlet oxygen-generating porous coordination network) which contain 1,2-bis(2-methyl-5-(pyridin-4-yl)thiophen-3-yl)cyclopent-1-ene (BPDTE) as a photochromic switch. Notably, a molecular dyad system which contains a photochromic switch and photosensitizer was well established with SO-PCN. The reversible control over $^1O_2$ generation through a competition of energy transfer pathways upon irradiation at specific wavelengths in SO-PCN was studied. Also, SO-PCN was demonstrated as a heterogeneous catalyst for photooxidation of 1,5-dihydroxynaphthalene (DHN).

Porphyrin derivatives have been widely used for $^1O_2$ generation because of their well-known photochemistry and high efficiency in light harvesting.[2b,14] The dithienylethene derivative, BPDTE, serving as a photochromic switch can undergo a reversible 6π electrocyclic reaction upon photoirradiation at distinct wavelengths (e.g., ultraviolet or visible). The open and closed forms of BDPTE resulting from photoisomerization exhibit distinctive absorption properties, and can provide different energy transfer pathways for photosensitizers to control the $^1O_2$ generation (Figure 1 a,c). As one of the most frequently used linkers in porphyrinic MOFs, tetrakis(4-carboxyphenyl)-porphyrin (TCPP) has been extensively explored to construct different MOFs.[12c,d,15] Particularly, pillar-layer three-dimensional (3D) frameworks, which are constructed from TCPP mixed with linear dipyridyl linkers, have been widely studied because of the ease of design and synthesis. Simultaneously, BPDTE, having dipyridyl heads, is ideal for forming the pillar-layer structure with TCPP to provide a solid-state platform for the controlled generation of singlet oxygen.

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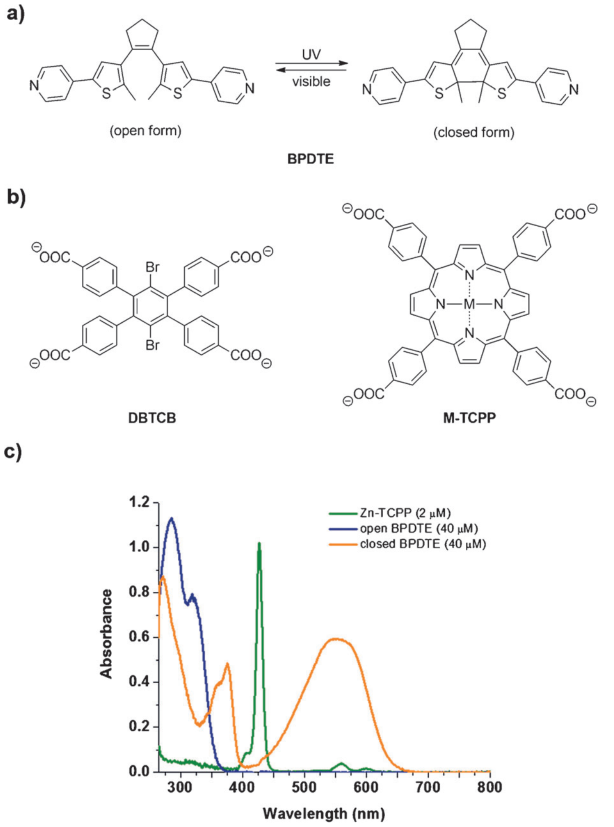

Figure 1. a) Photoisomerization of BPDTE under UV and visible light. b) Structures of ligands consist of two-dimensional layers in PC-PCN and SO-PCN, respectively. c) UV/Vis spectra of H_4Zn-TCPP and two different forms of BPDTE.

Such structures lead to a paddlewheel-type of inorganic building block and gives rise to a 1:1 ratio between the photosensitizer (TCPP) and the photochromic switch (BPDTE), and precisely matches the stoichiometry in an ideal energy transfer process. We selected Zn^{2+} as the inorganic species, because its d^{10} configuration is unlikely to disturb the energy transfer between TCPP and BPDTE. In general, photoisomerizations rarely occur in crystals because a large structural change is extremely unfavorable in the solid state. As an exceptional example, DTE derivatives undergo only a small structural change upon photoisomerization and therefore photochromism in the single crystalline phase can be achieved.[16] Thus BPDTE in the framework may still retain its photochromic property without significant alteration or breaking of the 3D structure.

The solvothermal reaction of BPDTE, TCPP (no metal), $Zn(NO_3)_2 \cdot 6H_2O$ in DMF and tetrafluoroboric acid at 85 °C for 15 hours resulted in platelike, dark-purple single crystals (SO-PCN). Although some of the single crystals are large enough in two of the three dimensions, because of the limited thickness of the crystals, diffractions from certain directions are too weak to determine the overall structure. Since the crystal growth behavior differs with the variation of the metal species within the TCPP center, as observed for a series of Zr-MOFs,[15e,i] we tried other metallo-TCPP (M-TCPP, where M is Cu, Co, Ni, Mn, and Fe) species and obtained much thicker crystals using Fe-TCPP. With better diffraction patterns, the space group of SO-PCN was determined to be *P4/mmm*, which has a unit cell parameter of $a \approx 16.63$ Å and $b \approx 22.28$ Å. From the solved structure, porphyrin layers are clearly observed while the pillars are missing because of the random orientation of the pillars resulting from the free rotation of the single bonds. However, the distance between Zn_2 paddlewheels in the adjacent layers precisely matches the length of BPDTE, which indicates the formation of our expected structure. The simulated structure showed good agreement with the experimental PXRD pattern of SO-PCN (see Figure S1 in the Supporting Information). ^{1}H NMR spectrum, upon digestion of SO-PCN, shows a 1:1 ratio between Zn-TCPP and BPDTE, and further confirms the structure.

Intuitively, direct evidence showing the presence of BPDTE in SO-PCN could be a color change of BPDTE upon photoirradiation. However, the dark-purple Zn-TCPP impedes the observation of the color change from the photochromic pillar. Hence, we chose a colorless tetratopic carboxylate linker DBTCB, which has been reported to form a similar structure with TCPP, to show the photochromism of the BPDTE pillar (Figure 1 b). Under similar solvothermal conditions, a colorless flake-shaped single crystal of PC-PCN, which has a light-yellow color in the bulk sample, was obtained (Figure 2). Single-crystal X-ray diffraction of PC-PCN shows dipyridine coordination but the BPDTE pillar was not clearly solved because of the significant disorder as discussed above. PC-PCN exhibits the same layer to layer distance (21.69 Å) as in SO-PCN and also exhibits a 1:1 ratio between BPDTE and DBTCB, thus further validating SO-PCN as our expected structure. When the open form of PC-PCN in the bulk was irradiated under ultraviolet (UV) light, deep-purple crystals of PC-PCN were clearly observed by the naked eyewithin 10 minutes, and suggests the pillar ligands were closed. Irradiation with visible light ($\lambda > 450$ nm) was performed on these purple crystals to re-open the closed pillars and the recovery of the light-yellow color was observed in 1 hour. We further examined the photochromic reaction in a single crystal to single crystal fashion in PC-PCN. As shown in Figure 2, single crystallinity of PC-PCN was almost completely maintained upon alternating irradiation, thus

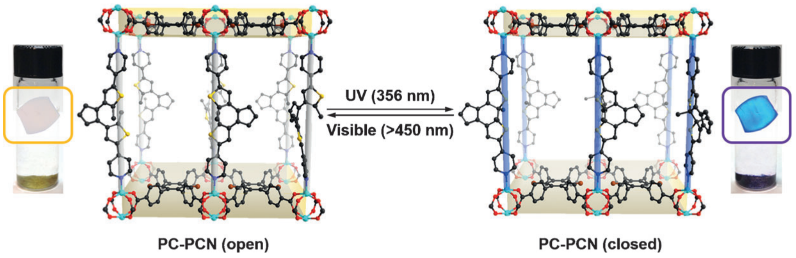

Figure 2. Illustration of reversible photochromic reaction in PC-PCN. Colorless single crystal (left, bulk in yellow) turns blue (right, bulk in purple) upon UV irradiation ($\lambda = 365$ nm) and it goes back to colorless form under visible light (with $\lambda = 450$ nm cut-on filter). Single crystals are highlighted in the insets.

demonstrating excellent structural reversibility of the BPDTE pillar within the framework.

Having demonstrated the photoisomerization of BPDTE in PC-PCN, we then examined SO-PCN for regulating $^1O_2$ generation. To evaluate the ability of SO-PCN in generating singlet oxygen, 1,3-diphenylisobenzofuran (DPBF), a well-known $^1O_2$ scavenger, was used to detect the $^1O_2$ produced in our system. Upon oxidative degradation of DPBF by $^1O_2$, the absorption of DPBF at $\lambda = 410$ nm decreased, thus serving as an indication of the singlet oxygen generated. First, the experiment was carried out using a visible light source ($\lambda > 450$ nm) at room temperature to examine the photosensitizing ability of SO-PCN. Prior to addition of the probe, SO-PCN was washed thoroughly with hot DMF followed by acetonitrile until no residual ligands in the supernatant were detected by UV/Vis spectroscopy. Acetonitrile was bubbled with oxygen for 20 minutes before the measurements. As a control experiment, DPBF (50 μM) in acetonitrile without SO-PCN was irradiated by visible light ($\lambda > 450$ nm). Only a negligible decrease in the absorbance of DPBF was observed during 150 seconds of irradiation, and indicates DPBF was stable under these conditions. Knowing this, we examined the photosensitization of the open form of SO-PCN (1.42 μmol) using DPBF (50 μM) in 2.8 mL of acetonitrile. Upon irradiation, the absorbance at $\lambda = 410$ nm showed a complete degradation within 150 seconds, thus suggesting excellent photosensitizing ability of SO-PCN (see Figure 4 a).

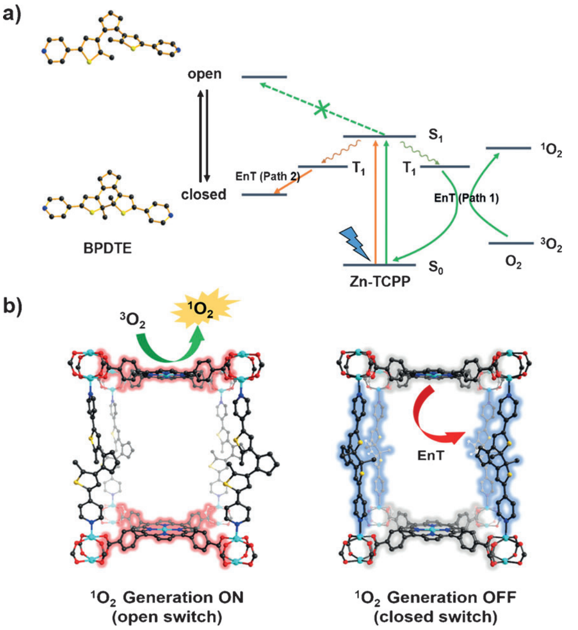

Figure 3. a) Proposed mechanism of energy transfer (EnT) in SO-PCN. b) Illustration of switching operation in SO-PCN.

Next, we investigated the control of the switch (BPDTE) embedded in SO-PCN for $^1O_2$ generation upon photoisomerization. Figure 3 a illustrates a proposed mechanism of control of $^1O_2$ generation in SO-PCN by an energy transfer (EnT) process. Energy transfer of excited Zn-TCPP is known to be dependent on triplet energy of BPDTE[6,17] because of different photophysical properties of its isomers. When Zn-TCPP in SO-PCN is excited, the triplet energy of ^{3}[Zn-TCPP]* can follow different pathways for energy transfer depending on the state of BPDTE. For example, $^1O_2$ can be generated when the EnT process occurs from ^{3}[Zn-TCPP]* in the open form of SO-PCN to $^3O_2$ (Path 1 in Figure 3 a). Another pathway is based on the energy state of closed form of BPDTE, which lies at a lower energy than that of ^{3}[Zn-TCPP]*, thus the energy transfer takes place to the closed BPDTE and results in quenching of $^1O_2$ generation. The feasibility of reversible energy transfer of the TCPP-BPDTE dyad in SO-PCN was evaluated by recording emission spectra. We chose a Soret band ($\lambda = 420$ nm) to excite the SO-PCN to circumvent potential interference of the switching operation. The emission spectrum of open SO-PCN shows emission maxima at $\lambda = 605$ nm and $\lambda = 655$ nm in CH_3CN ($\lambda_{ex} = 420$ nm). To close the BPDTE pillars in SO-PCN, UV light ($\lambda = 365$ nm) was used. The emission was gradually quenched by EnT to the closed BPDTE and no further quenching was observed after 30 minutes. Recovery of emission upon photoisomerization was subsequently carried out with visible light ($\lambda > 450$ nm), and a complete recovery was made in 120 minutes (Figure 4 b).

After validating reversibility in SO-PCN, the system was excited by a $\lambda = 405$ nm CW laser to examine the controlled $^1O_2$ generation by on/off switching (Figure 3 b). Evolution of

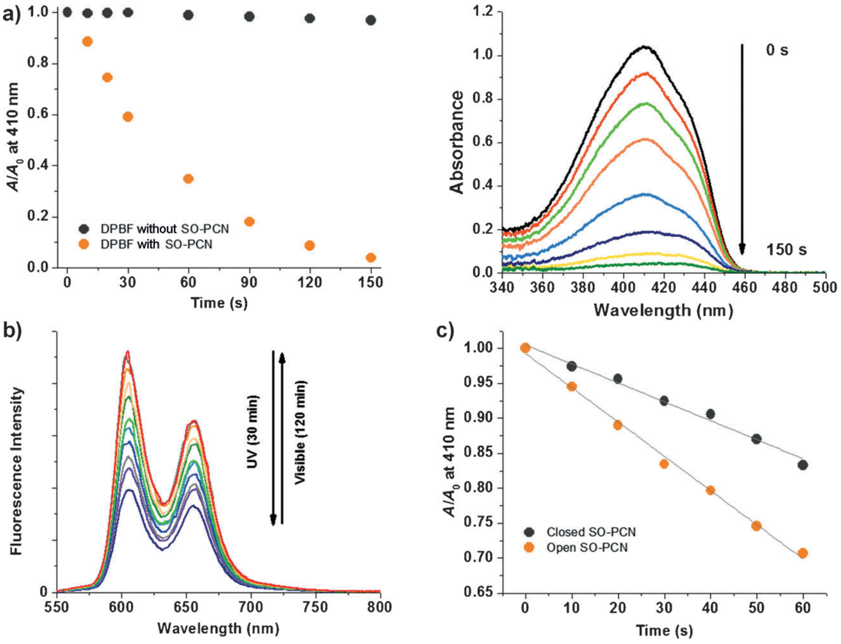

Figure 4. a) Absorbance decay of DPBF (left) and the corresponding spectra in the presence of SO-PCN (right). b) Emission spectra of SO-PCN showing reversibility. c) Comparison of decay rate of DPBF upon on/off switching.

$^1O_2$ with the open form of SO-PCN was monitored by UV/Vis spectra every 10 seconds. Over the course of 60 seconds with 6 mW cm^{-2} of laser power, 30 % of DPBF absorption decreased compared to its initial absorption, whereas the closed form of SO-PCN showed an approximately 15 % decrease in absorbance at $\lambda = 410$ nm. A steeper slope of the open form of SO-PCN suggests the energy of ^{3}[Zn-TCPP]* was transferred to $^3O_2$ to generate $^1O_2$, while that of the closed form was quenched by closed BPDTE, thus resulting in less efficient $^1O_2$ generation (Figure 4c). When we attempted to perform a control experiment, we found that the laser irradiation led to a complete degradation of DPBF in the absence of SO-PCN within 60 seconds (see Figure S11). Presumably because of the light sensitive nature of DPBF, the laser significantly affected DPBF solution in the absence of other chromophores. To obtain a practical blank of our system, we further examined the system with DPBF and the closed form of SO-PCN. An N_2 saturated solvent was employed to suppress the supply of oxygen so that we could examine the system solely with photodegradation of DPBF in the presence of closed SO-PCN (other chromophores). Interestingly in this control experiment, the rate and extent of decrease in absorption at $\lambda = 410$ nm of DPBF were very similar to previous experimental data of the closed SO-PCN with oxygen (Figure S11), and further confirms that a successful switching operation, using photoisomerization of BPDTE towards $^1O_2$ generation in SO-PCN, was demonstrated.

In addition to the ability to generate singlet oxygen, we further sought to study potential use of SO-PCN as a heterogeneous catalyst. Catalytic performance was demonstrated by photooxidation of DHN, which is mediated by $^1O_2$ and resulted in the corresponding oxidized product juglone (Figure 5a). The photooxidation was carried out with 0.036 mmol of DHN in acetonitrile with 10 % SO-PCN (open form) under visible light irradiation ($\lambda > 450$ nm). As the reaction occurred, the absorption peaks of the starting material at $\lambda = 298$ nm and 330 nm decreased, whereas a characteristic peak of juglone around $\lambda = 419$ nm increased. After 30 hours, a significant decrease in absorption of DHN was observed, while leaching was not seen (Figure 5b).

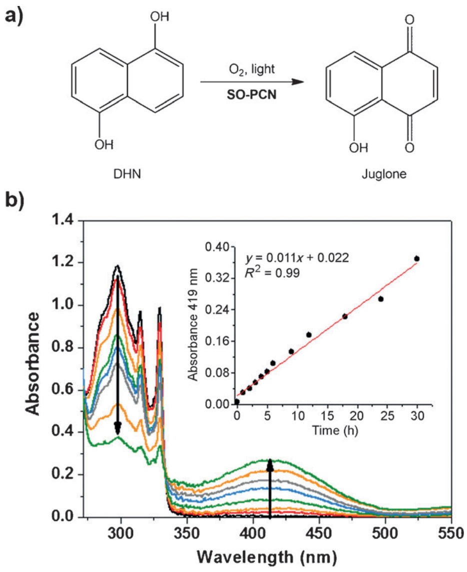

Figure 5. a) Photooxidation of DHN catalyzed by SO-PCN in the presence of oxygen and light irradiation. b) UV/Vis spectra of photooxidation of DHN in CH_3CN catalyzed by SO-PCN. Inset: Absorbance of juglone ($\lambda = 419$ nm) as a function of reaction time.

In summary, through a classical pillar-layer structure, we have developed two photochromic MOFs, PC-PCN and SO-PCN. Photochromism has been successfully realized in PC-PCN while maintaining its single crystallinity. In particular, as a solid-state material which inherently integrates a photochromic switch and photosensitizer, SO-PCN has demonstrated reversible control of $^1O_2$ generation. Meanwhile, SO-PCN shows catalytic activity towards photooxidation of DHN. Based on the photophysical properties of the chromophore dyads realized within the MOF regime, our findings can be extended to the design of materials for potential applications in photocatalysis, photoswitching, and sensing.

Experimental Section

Synthesis of SO-PCN: H_2-TCPP (10 mg), $Zn(NO_3)_2{\cdot}6H_2O$ (35 mg) in 2 mL of DMF/DEF were ultrasonically dissolved in a 4 mL Pyrex vial. The mixture was heated at 85 °C in a pre-heated oven for 2 h. After that, BPDTE (9 mg) and tetrafluoroboric acid (1 μL) were added and the mixture was heated for 12 h. After cooling to room temperature, purple crystals were harvested. Full experimental details can be found in the Supporting Information.

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