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The Combination of Charge and Energy Transfer Processes in MOFs for Efficient Photocatalytic Oxidative Coupling of Amines

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connects typical $Co_2(COO)_4$ paddle wheel clusters to form square lattices pillared by new PDI-type ligand L. FJI-Y10 as a heterogeneous and recyclable photocatalyst is applied for photooxidation of benzylamine and its derivatives with an excellent yield of 100%, which is much higher than that (59%) of the equivalent L ligand as a homogeneous photocatalyst under the same reaction



conditions. Such a high-efficiency photocatalytic activity attributes to the combination of charge and energy transfer processes in catalyst FJI-Y10 during the catalytic process.

INTRODUCTION

Imines are important nitrogen-containing active intermediate in pharmaceuticals and biosynthesis.^{1,2} Some reported synthetic methods for imines, including the condensation reaction of aldehydes or ketones with primary amines or the aerobic oxidation coupling of alcohols with amines, usually need unstable aldehydes and acid catalysts.^{3,4} Among these traditional synthesis methods, the catalytic coupling of amines requires external conditions such as heating, toxic oxidants (such as 2-iodobenzoic), and raw materials (aldehydes or ketones compound), which cause energy waste and environmental pollution. From the view of green chemistry, the direct photocatalytic oxidation of amines into imines based on molecular oxygen as an oxidant has received tremendous attention. Although some famous noble-metal photocatalysts, such as ruthenium-polypyridyl complexes and iridiumpolypyridyl complexes, have been shown to have great reactivity to the reaction by using oxygen as the oxidant, they are expensive and poorly recyclable, both issues which severely limit their extensive applications in catalytic synthesis.^{5,6} In past years, some synthetic methods for imines have been proposed to develop green catalytic processes to resolve the above problems. Some organic dyes, such as eosin Y,^{7–9} porphyrin,^{10,11} triphenylamine,^{12,13} naphthalimides,^{14,15} per-ylene diimide, and their derivatives^{16–18} have excellent holetransport properties and have been widely used as attractive photocatalysts to replace noble-metal catalysts for some photocatalytic reactions because they are usually relatively cheaper and less toxic.

Perylene diimide (PDI) as a class of dye molecules with a strong visible-light absorption ability and perfect chemical, thermal, and optical stability has outstanding application in the homogeneous process. $^{16,19-21}$ The consecutive photoinduced electron transfer (conPET) process of PDI radical anions overcomes the current energetic limitation of visible-light photoredox catalysis and allows the photocatalytic conversion of less reactive chemical bonds in organic synthesis. König's group reported that N,N-bis(2,6-diisopropylphenyl)perylene-3,4,9,10-bis(dicarboximide) as a homogeneous catalyst produced a stable radical anion under visible-light induction and that the subsequent excitation of the radical anion accumulated sufficient energy for the reduced aryl halide.¹⁷ The interesting result inspires chemists to use ligands containing PDI groups to construct metal-organic frameworks (MOFs) for heterogeneous photoconversion, since the well-defined structures constructed by metal nodes and organic linkers endow MOFs a semiconductor-like behavior for photocatalysis undergoing charge or energy transfer between the ligand-to-metal and $\pi - \pi^*$ transition of the delocalized linker, etc. Recently, Duan's groups reported a MOF, namely, Zn-PDI, which achieved photocatalysis for visible-light-driven oxidation of amines, due to the synergistic effects between Zn sites and PDI arrays with conPET, in which the generated ¹O₂ based on the energy

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Figure 1. (a) 2D regular prismatic square-grid motif of a $[Co_2(2,6-NDC)_2]_n$ layer. (b) View of the 2-fold interpenetrating **FJI-Y10** along the *c*-axis. (c) The conceivable interaction between the host framework and benzylamine molecules based on a molecular dynamics simulation. Note that all guest molecules and H atoms have been omitted for clarity.

transfer process in Zn-PDI featured as high electrophilicity to oxidize amines to imines directly.²² Except for 2-methoxybenzylamine, the yields of benzylamine and its derivatives catalyzed by Zn-PDI are lower than 74%, probably due to its narrow porous structure. In contrast, superoxide radicals $(O_2^{\bullet-})$ derived from photogenerated electrons transfer to O_2 can also oxidize benzylamine to PhCH₂NH₂^{$\bullet+}$ to further the coupling reaction. Therefore, the combination of $O_2^{\bullet-}$ generation via charge transfer and 1O_2 production via energy transfer contributes to the ultimate great activity of the MOFs. However, as we know, rare effort has been focused on this field.^{23,24} In the pursuit of a more efficient catalyst for oxidative coupling of amines, it is of great significance to develop new PDI-type ligands for synthesizing porous MOFs with the synergistic effect of charge and energy transfer processes.</sup>

Herein, we report the successful synthesis of new PDI-type ligand, bis(*N*-pyridyl) tetrachloroperylene peryleneimide (L), which was further used to assemble a porous MOF, namely, $Co_2(L)(2,6-NDC)_2$ -xguest (FJI-Y10), for enhancing the catalytic efficiency of L ligand. The photocatalytic activity of FJI-Y10 was assessed by using the amines oxide coupling reaction under mild conditions. The combination of charge and energy transfer processes in FJI-Y10 leads to its excellent catalytic activity.

EXPERIMENTAL SECTION

General Procedures. All chemical reagents and solvents were commercially available and used without any purification. Thermal gravimetric analyses (TGA) were executed at a heating rate of 10 °C/ min under nitrogen flow with a Netzsch STA 449C instrument. FT-IR spectra were collected as KBr pellets on the Vertex70 instrument. The powder X-ray diffraction (PXRD) patterns were obtained on a Rigaku Mini 600 X-ray diffractometer with Cu K α radiation (λ = 1.5406 Å); the collecting speed was 2 °/min, and the range of 2θ was 4° to 50°. Simulated PXRD patterns were calculated using the program Mercury via the single-crystal data. UV-vis absorption spectra were acquired on a PerkinElmer Lambda 950 UV-vis-NIR spectrophotometer with reference to the white standard of BaSO₄. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker-BioSpin E500 spectrometer with a 100 kHz magnetic field under room temperature. The N₂ adsorption measurements were performed on an ASAP 2020 system. The catalytic reaction products were detected by using gas chromatography (GC). The products were further determined and analyzed by using the GC and mass spectrometry (GC-MS) results. The light irradiation was obtained by a 300 W Xe lamp with a cutoff below 420 nm.

Synthesis of Bis(*N*-pyridyl) Tetrachloroperylene Peryleneimide (L) Ligand. 1,6,7,12-Tetrachloroperylene tetracarboxylic acid dianhydride (265 mg) and 4-aminopyridine (235 mg) were dissolved in 10 mL of propionic acid. The mixture was stirred in a 25 mL Teflon-lined autoclave for 2 h and then heated at 180 °C for 3 days. After they were washed with fresh acetonitrile (CH₃CN), red crystals were obtained in a yield of 76%.

Preparation of Co₂(L)(2,6-NDC)₂·xguest (FJI-Y10). A mixture of $Co(NO_3)_2$ ·6H₂O (15 mg), L (6.8 mg), 2,6-NDC (11.2 mg), 4 mL of *N*,*N*-dimethylformamide (DMF), and 1 mL of CH₃CN were added to an 8 mL vial. After ultrasonication for 2 h, the mixture was sealed and heated in a 120 °C oven for 2 days, and then it was allowed to cool to room temperature. After they were washed with DMF, black and purple crystals of FJI-Y10 were obtained (yield = 24 mg).

Crystal Data for FJI-Y10. $C_{70}H_{51}C_{14}Co_2N_8O_{16}$, M = 1519.85, triclinic, space group $P\overline{1}$, a = 13.0626(3) Å, b = 13.1226(3) Å, c = 26.3129(5) Å, $\alpha = 96.8686(17)^\circ$, $\beta = 94.9156(17)^\circ$, $\gamma = 97.9634(18)^\circ$, V = 4410.81(16) Å³, Z = 2, $D_c = 1.144$ g cm⁻³, $F_{000} = 2706$, Cu K α radiation, $\lambda = 1.54178$ Å, T = 115(2) K, $2\theta_{max} = 147.3^\circ$, 65311 reflections collected, 17147 unique ($R_{int} = 0.035$). Final GoF = 1.120, $R_1 = 0.0595$, $wR_2 = 0.1595$, R indices based on 14121 reflections with $I > 2\theta$ (refinement on F^2).

Typical Experimental Procedure for Oxidative Coupling of Amines. Benzylamine (1 mmol), catalyst FJI-Y10 (2 mmol % based on L ligand), and DMF (5 mL) were introduced into a 20 mL glass tube with a magneto. The tube was stirred at room temperature. Subsequently, the tube was vacuumed and filled with oxygen three times through connection with an oxygen balloon. The reaction mixture was exposed to a 300W Xe lamp. After completion of the reaction, 1,4-dioxane (1 mmol) as an internal standard was added into the tube, and next, the mixture was centrifuged to separate FJI-Y10. The yields were calculated by GC and further confirmed by GC-MS. A series of photocatalyst-free radical scavengers were used to control the photoactivity experiments, i.e., ammonium oxalate (AO) and $Mn(OAc)_2$ as the scavenger of photogenerated holes and electrons, tertbutyl-alcohol (TBA) as the scavenger of hydroxyl radicals (°OH), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as the scavenger of superoxide radical species (O2^{•-}), and 2,2,6,6-tetramethylpiperidine (TEMP) as the scavenger of singlet oxygen $({}^{1}O_{2})$, were carried out similarly to the photocatalytic experiments where the radical scavengers (1 mmol) were added to the reaction system.

Electrochemical Measurements. All the electrochemical measurements were completed on a ZM6ex electrochemical station (Zahner, Germany) in a standard three-electrode system with a fluoride-tin oxide (FTO) glassy electrode as the working electrode system, a Pt electrode as the counter electrode, and a Ag/AgCl electrode as the reference electrode. The catalyst (20 mg) was dispersed in 0.5 mL DMF to obtain a suspension, and 20 μ L of the suspension was scattered on the prepared FTO glass with an area of 0.25 cm². The coated FTO glass was then dried at room temperature in air. The Mott-Schottky and photocurrent plots were collected in 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) in CH_3CN solution and purged with $N_2\ prior$ to measurement. The Mott-Schottky plots of FJI-Y10 were measured at frequencies of 800, 1000, and 1500 Hz. The photocurrent signal was measured under chopped light, and the light source was the same as that used in the photoactivity tests described above.

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RESULTS AND DISCUSSION

A new ligand bis(N-pyridyl) tetrachloroperylene diimide (L) was first synthesized through the imidization of 1,6,7,12tetrachloroperylene tetracarboxylic acid dianhydride and 4aminopyridine, forming abundant red crystals that crystallized in the triclinic space group $P\overline{1}$. According to the single-crystal structure, L ligand has a noncoplanar structure with a twisty conjugate system (Figure S1a), which will increase its solubility for synthesizing MOFs. The solvothermal reaction of ligand L, 2,6-NDC, and Co(NO₃)₂·6H₂O in a mixed DMF/CH₃CN solvent generated compound FJI-Y10, namely, Co₂(L)(2,6-NDC)2.xguest. Single-crystal X-ray analysis indicated that FJI-**Y10** crystallized in the triclinic space group $P\overline{1}$. In the structure of FJI-Y10, each asymmetric unit is composed of one independent Co(II) atom, half of L, and one deprotonated 2,6-NDC ligand (Figure S1b). Each cobalt atom shows a square pyramidal geometry, coordinating to four O atoms from four 2,6-NDC ligands and one N atom from an L ligand. In Figure 1a, two adjacent equivalent Co(II) atoms are connected by four carboxylates from 2,6-NDC ligands to form a typical paddle wheel dimer $[Co_2(2,6-NDC)_2]$ with a Co(II)...Co(II) distance of 2.67 Å.^{25,26} These $[Co_2(COO)_4]$ dimers are bridged by naphthalene groups from 2,6-NDC ligands to form two-dimensional (2D) layers with a square grid, which are further pillared by L ligands to form a porous 3D framework with typical *pcu* topology (Figure S3).²⁷ In each *pcu* lattice, the Co…Co distance of 13.0769-23.6816 Å (Figure S2) provides enough clearance space to accommodate another equivalent network to form a 2-fold interpenetrating structure (Figure 1b).²⁸ There are face-to-face $\pi \cdots \pi$ stacking with the distance of 3.51 to 3.74 Å between the phenyl rings of L and 2,6-NDC ligands from different pcu lattices (Figure S4). For the host framework of FJI-Y10, the largest cavity diameter, the accessible surface area, and the accessible pore volume of the total crystal volume are 8.17 Å (Figure S5b), 1493.75 m²/g, and 51.4%, respectively, which are calculated by Zeo++ software.^{29,30}

On the basis of the crystal structure, FJI-Y10 possesses some necessary factors for efficient photocatalysis, including a photocatalytic activity center (PDI), high porosity, and open channels. However, N₂ sorption measurements are unsuccessful in giving the expected BET surface area by adopting various activated methods such as traditional solvent exchange, freezedrying, and even supercritical CO_2 exchange (Figure S5) because of the distortion of the framework upon solvent removal (Figure S6), a common phenomenon observed for porous MOFs. To further understand the interaction between the host framework and benzylamine molecules, a molecular dynamics simulation was performed to speculate the location of benzylamine in the pores after diffusion, and the simulation was further optimized using the VASP package. It is shown that benzylamine molecules occupy the central position of the pores and display face-to-face $\pi \cdots \pi$ stacking with the distance between phenyl rings of benzylamine and 2,6-NDC ligands measured at 3.55-3.75 Å (Figure 1c). In this case, the successive $\pi \cdots \pi$ stacking interaction among benzylamine, 2,6-NDC, and L ligands promotes charge transfer from the electron-rich benzylamines to the electron-poor L ligands for photocatalytic oxidative coupling of amines.

The phase purity of **FJI-Y10** is confirmed by powder X-ray diffraction (PXRD) (Figure S6). The thermal gravimetric analyses (TGA) curve of **FJI-Y10** indicates a weight loss of

~22.5% under 250 °C, corresponding to the release of guest molecules (Figure S8). The UV–vis spectrum of FJI-Y10 manifests a strong absorption band at 627.5 nm, maybe corresponding to the π – π * transition of L ligands (Figure S9a). The band gap energy of FJI-Y10 calculated by using the Kubelka–Munk function is 2.10 eV (Figure S9b). The electron paramagnetic resonance (EPR) spectrum of L shows a peak at g = 2.003, illustrating a free radicals signal (Figure S10) and exhibiting its ability to produce superoxide radicals (O₂^{•–}).

To explore the photocatalytic oxidative capacity of FJI-Y10 for amines, the benzylamine was chosen as a test model substrate. The control experiments indicated that photocatalyst FJI-Y10 and oxygen were all needed for the photooxidation of benzylamine (Table 1, entries 1-3). In order to illustrate that

Table 1. Aerobic Photooxidation Catalyzed of Benzylamine into an Imine by FJI-Y10 under Different Conditions⁴

	$\frac{2 \text{ mmol}\% \text{ cat.}}{\text{hv}, \text{O}_2, 40 \text{ °C}}$	
entry	conditions ^b	yield $(\%)^c$
1	no catalyst	1
2	no oxygen	4
3	no light	0
4	no light under 60 °C	2
5	FJI-Y10	100
6	L	59
7^d	FJI-Y10	100
8 ^e	FJI-Y10	97
9 ^f	FJI-Y10	96

^{*a*}Reaction conditions: benzylamine (1 mmol), catalyst (2 mmol %, basing on the L), DMF (5 mL), in O₂, 300 W Xe lamp with a cutoff below 420 nm. Reaction temperature: 40 °C. Reaction time: 6 h. ^{*b*}Additional reaction conditions. ^{*c*}Determined by GC areas with an internal standard of 1,4-dioxane (1 mmol). ^{*d*}Reused 1. ^{*e*}Reused 2. ^{*f*}Reused 3.

the coupling reaction of benzylamine is indeed a photocatalytic reaction rather than a thermocatalytic reaction, the reaction was heated at 60 °C under dark conditions for 6 h, and only trace product was formed (Table 1, entry 4). The yield of Nbenzylidenebenzylamine was up to 100% in the presence of FJI-Y10 and oxygen upon visible-light irradiation for 6 h in DMF (Table 1, entry 5), which is much higher than that (59%) of equivalent L ligands as a homogeneous photocatalyst under the same conditions. The same result can also be seen at the photocatalytic oxidation of heptylamine (Figure S12). The comparative experiments indicate that the careful modification of L fragments within metal-organic frameworks can greatly enhance the activity of the catalyst and transform a homogeneous catalysis into a heterogeneous catalysis to overcome these limitations of the homogeneous process. The photocatalytic activity of FJI-Y10 is much better than those of other MOFs, such as the typical NH₂-MIL-125(Ti) (86%),³¹ and Zn-PDI (74%),²² and is similar to those of PCN-222²⁴ and UNLPF-12.²³ To prove the heterogeneous mechanism of photocatalytic oxidation of amine, a leaching test of FJI-Y10 by removing the solid catalyst after 2 h (yield: 48%) and continuing reaction for another 4 h were performed, but no further conversion was observed, proving heterogeneity of FJI-Y10. The recyclability of the photocatalyst FJI-Y10 was also explored via using the same batch of FJI-Y10 for three

$R \qquad NH_2 \xrightarrow{2 \text{ mmol}\% \text{ Cat.}} R \qquad N \qquad R$				
Entry	Substrate	Product	Yield[%] ^b	
1	NH ₂		100	
2	F NH ₂		94	
3	F NH2	F N F	98	
4	F NH2		100	
5	NH ₂		50	
6	NH2		97	
7	NH ₂		98	
8			99	
9	NH ₂	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	55	

Table 2. Aerobic FJI-Y10 Catalyzed Oxidation of Different Amines to Imines under Visible-Light Irradiation^a

"Reaction conditions: substrate (1 mmol), catalyst (2 mmol %, basing on the L), O2 balloon, DMF (5 mL), Xe lamp (300 W, cutoff wavelengths below 420 nm). Reaction temperature: 40 °C. Reaction time: 6 h. ^bDetermined by GC areas with an internal standard of 1,4-dioxane (1 mmol).

consecutive catalytic cycles in the reaction. The results demonstrated that the catalytic activity of FJI-Y10 could be maintained well after three cycles (yields: \geq 96%) (Table 1, entries 7-9). PXRD measurements indicated that the recycled photocatalyst maintained its crystalline structure, confirming the stability of FJI-Y10 in the catalytic system (Figure S6). The IR spectra of free benzylamine showed an N-H stretching vibration doublet at 3363 and 3295 cm⁻¹. However, the N-H stretching vibration doublet of benzylamine trapped in FJI-Y10 shows an obvious red shift to 3331 and 3260 cm⁻¹, respectively, indicating the possible activation and strong adsorption of benzylamine in the pores of FJI-Y10 (Figure S13).

After the reaction conditions were optimized by using benzylamine as a model substrate, the heterogeneous conPET photocatalysis expands its scope with a series of substituted benzylamine (Table 2). FJI-Y10 can catalyze benzylamine derivates with both electron-withdrawing and electrondonating groups to give the corresponding imines with goodto-excellent yields of \geq 94%, (Table 2, entries 2–8), except for 2-methoxy-benzylamine, in which the -OMe group at the ortho position dramatically reduced the yield to 50% due to the

steric effects seriously hindering the photocatalytic process (Table 2, entries 5-7).

To further demonstrate the charge transfer process in FJI-Y10, Mott-Schottky plots were measured at different frequencies of 800, 1000, and 1500 Hz for FJI-Y10, and the positive slopes of $C^{-2}-V$ curves elucidate that the FJI-Y10 is a typical n-type semiconductor (Figure S14).³² Based on the UV-vis spectra and electrochemical characterizations for FJI-Y10, its energy diagrams of HOMO and LUMO are given in Figure S14. Catalyst FJI-Y10 exhibits a more negative potential of the LUMO level (-0.98 V vs NHE) than the reduction potential of $E(O_2/O_2^{\bullet-}) = -0.33$ V vs NHE.^{24,33} Therefore, catalyst FJI-Y10 is theoretically feasible for the photocatalytic conversion of O_2 to $O_2^{\bullet-}$. The PDI groups as a visible-light harvesting unit can contribute to the HOMO at +1.12 V vs NHE, calculated by the Tauc plot. The relatively lower occupied molecular orbital level guarantees a high oxidation ability for benzylamine $(E_{1/2}(M^+/M))$ of approximately +1.47 V vs NHE).^{23,24} The photocurrent response of FJI-Y10 was collected for several on-off cycles of visible light irradiation (Figure S15), and the typical on-off cycles of the photocurrent were renewable, illustrating the stability of photocatalyst FJI-

Y10. The strong photocurrent of FJI-Y10 indicates the high separation efficiency of photogenerated electrons. Therefore, the high separation efficiency of photogenerated carriers and large porosity in FJI-Y10 endow it with a superior photocatalytic performance.

It is indispensable to explore the photocatalytic oxidation of the amines reaction mechanism behind the above favorable photocatalytic performance of **FJI-Y10**. Here, benzylamine was used to investigate the mechanism of the photocatalytic oxidation coupling reaction. More evidence has been collected to capture the transfer pathway of photogenerated intermediates that happened in **FJI-Y10** and reactants. When $Mn(OAc)_2$ (quenching electrons) and TEMPO (quenching $O_2^{\bullet-}$) are added, the yields decrease to 27% and 78%, respectively (Figure 2). These results testify that the



Figure 2. Different radical scavengers were used to control photocatalytic benzylamine oxidation coupling over FJI-Y10 photocatalyst.

generation of electrons and $O_2^{\bullet-}$ play an important role in the selective oxidation of amines. Based on a typical electron transfer mechanism (Scheme 1), under light irradiation, the

Scheme 1. Speculated Mechanisms for the Visible Light-Driven Oxidation of Amines: Energy Transfer (ET) and Typical Charge Transfer (CT) Pathways



PDI groups in photocatalyst **FJI-Y10** are excited to form the excited state (PDI^{*}). Meanwhile, the electron-rich benzylamine transfers one electron to the electron-poor PDI groups and further is oxidized to a cationic amine radical (PhCH₂NH₂^{•+}). Then, the resulting PDI^{•-} anionic radical transfers one electron to O₂, forming reactive oxygen species $O_2^{\bullet-}$ and simultaneously oxidizing PDI^{•-} to its ground state.^{23,34,35} Then, PhCH₂NH₂^{•+} and O₂^{•-} are transformed into highly active phenylmethanimine (PhCH=NH) and H₂O₂. PhCH=NH and benzylamine undergo a nucleophilic addition reaction to generate the coupled imine product and ammonia gas.³⁶

In addition, an induction mechanism based on singlet oxygen $({}^{1}O_{2})$ oxidation of amine is also operable.³⁷ The photocatalytic oxidation yield was dramatically decreased to 48.3% in the presence of TEMP as ${}^{1}O_{2}$ scavenger, indicating that ¹O₂ is an indispensable driver for the photocatalytic reaction (Figure 2). In fact, the generation of ${}^{1}O_{2}$ is essentially a complex energy conversion process between long-lived excitons and ground state (³O₂) oxygen molecules.³⁸ Based on an energy transfer mechanism (Scheme 1), under light irradiation, the excited state PDI* transfers energy to O_{2} , forming reactive oxygen species 1O2 and simultaneously returning to its ground state. ¹O₂ captures two H atoms from benzylamine, forming H_2O_2 and a highly active phenylmethanimine (PhCH=NH) intermediate. The coupled imine product was generated by the nucleophilic addition reaction between PhCH=NH and benzylamine.³⁶ Therefore, the combination of $O_2^{\bullet-}$ (electrons transfer) and ${}^{1}O_2$ (energy transfer) contributes to the excellent activity of FJI-Y10.

CONCLUSIONS

In summary, we successfully synthesized FJI-Y10 with photoactive PDI groups and used it for aerobic coupling of amines reactions to form imines in the presence of molecular oxygen under visible light. Photocatalytic experiments illustrate that FJI-Y10 is a highly efficient heterogeneous photocatalyst for the reaction, exhibiting great yield and excellent recyclability of substrates to produce imines. Different quenching experiments were further carried out to indicate that the ${}^{1}O_{2}$ and $O_{2}^{\bullet-}$, resulting from photoinduced energy transfer and charge transfer processes of excited FJI-Y10, should be the main reactive oxygen species. The combination of charge and energy transfer processes in FJI-Y10 leads to the excellent catalytic activity under ambient conditions. This work provides an insightful understanding of charge and energy transfers in PDI-MOFs for promoting their further research on photocatalytic reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03743.

Additional figures, TGA results, powder X-ray diffraction patterns, IR spectra, and sorption isotherms (PDF)

Accession Codes

CCDC 1970996 and 1982251 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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