

Facile Control of the Charge Density and Photocatalytic Activity of an Anionic Indium Porphyrin Framework via in Situ Metalation

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S Supporting Information

ABSTRACT: An anionic indium porphyrin framework (UNLPF-10) consisting of rare Williams β -tetrakaidecahedral cages was constructed using an octatopic ligand linked with 4-connected $[\text{In}(\text{COO})_4]^-$ SBUs. Remarkably, the extent of indium metalation of porphyrin macrocycles in UNLPF-10 can be facily tuned in situ depending on the M/L ratio during synthesis, resulting in a controllable framework charge density and photocatalytic activity toward the selective oxygenation of sulfides.

Porphyrinic metal–organic frameworks (porph-MOFs) are a special class of porous coordination polymers that are composed of (metallo)porphyrin-based linkers interconnected by metal ions or metal carboxylate cluster secondary building units (SBUs).¹ In the past decade, porph-MOFs have received resurgent attention due to the persistent interests to assemble the tetrapyrrolic macrocycles that are quintessential in many fundamental biochemical, enzymatic, and photochemical functions.² Indeed, new porph-MOFs with excellent catalytic activity, light-harvesting capability, or ion conductivity have now emerged, demonstrating a promising potential for their future development and practical applications.³

In principle, metalation of porphyrin macrocycles provides a unique handle to control the chemical, optical, or catalytic properties of porph-MOFs. Both premetalation (i.e., free base porphyrin linkers are metalated before MOF synthesis)^{3a–c} and in situ metalation (i.e., free base porphyrin linkers are metalated during MOF synthesis)^{3d–f} are commonly used to tune the identity of the metalloporphyrin core. Recently, postsynthetic solvent-assisted linker exchange (SALE)⁴ and transmetalation⁵ were also employed to obtain porph-MOFs with specific metalloporphyrin cores that otherwise cannot be prepared by de novo synthesis. However, the extent of metalation, a parameter that also controls the properties of porph-MOFs, has not been well studied and utilized. To date, methods that can lead to the controllable metalation have not been reported.

Herein, we report the first example of controllable, in situ metalation of an anionic indium porph-MOF, UNLPF-10 (UNLPF: University of Nebraska–Lincoln porous framework). The extent of metalation of porphyrin macrocycles in UNLPF-10 is tunable by simply varying the In/L (indium to ligand) ratio during MOF synthesis. Since the indium-metalated porphyrin macrocycle (In-porph) exhibits a net +1 charge and outstanding photosensitizing capability, such in situ

metalation allows for the remarkably precise control of the charge density and photocatalytic activity of UNLPF-10.

UNLPF-10 was prepared using a solvothermal reaction of an octatopic ligand, $\text{H}_{10}\text{tbcppp}$ (tetrakis 3,5-bis[(4-carboxy)phenyl]phenylporphine⁶), and $\text{In}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ in *N,N*-dimethylformamide (DMF). Single crystal X-ray crystallographic studies revealed that each 8-connected tbcppp ligand links eight 4-connected $[\text{In}(\text{COO})_4]^-$ SBUs. Interestingly, six tbcppp ligands connect eight $[\text{In}(\text{COO})_4]^-$ SBUs and form a rare Williams β -tetrakaidecahedral cage, which consists of 14 faces, 24 vertices, and 36 edges (Figure 1a).⁷ Within each cage, two

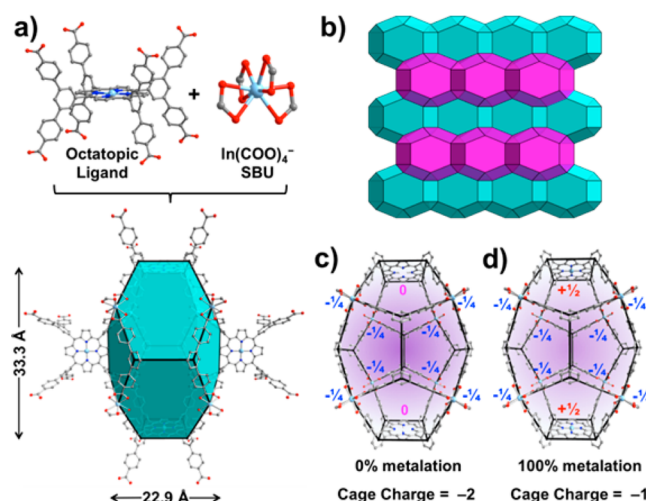


Figure 1. (a) Illustration of the octatopic ligand tbcppp and $[\text{In}(\text{COO})_4]^-$ SBU forming the Williams β -tetrakaidecahedral cage. (b) Close packing of tetrakaidecahedral cages. (c,d) Controlling the charge density of UNLPF-10 via indium metalation of porphyrins (charges are shown with respect to cage occupancy in the overall framework).

planar porphyrin macrocycles serve as the two square faces, and the pentagonal and hexagonal faces are formed with two tbcppp ligands linked by two $[\text{In}(\text{COO})_4]^-$ SBUs in orientations where two porphyrin macrocycles are perpendicular and parallel to each other, respectively (Figure S1, Supporting Information). The overall structure of UNLPF-10 can be viewed as the close packing of the tetrakaidecahedral cages

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(Figure 1b). UNLPF-10 is highly porous: the internal dimensions of the tetrakaidecahedral cage are $33 \times 23 \times 23$ Å, and the hexagonal and pentagonal window sizes are 19×16 Å and 17×13 Å, respectively. Notably, UNLPF-10 also exhibits channel-like pores along all three crystallographic axes (Figure S2, Supporting Information), an appealing feature for catalysis (vide infra). β -Tetrakaidecahedral cage-like topology is seldom observed in crystal structures.⁸ To the best of our knowledge, UNLPF-10 represents the first MOF that is composed of Williams β -tetrakaidecahedral cages.

Interestingly, highly crystalline samples of UNLPF-10 with comparable PXRD patterns can be obtained using a wide range of M/L ratios (5:1, 10:1, 20:1, 30:1, 40:1, and 50:1; Figure S3, Supporting Information). This is noteworthy since it is well-known that the high yield synthesis of a specific crystalline phase of MOFs typically requires a narrow range of M/L ratios.⁹ Thus, the assembly of UNLPF-10 is robust and not significantly affected by the M/L ratio. More importantly, single crystal X-ray structure analysis reveals partial occupancy of indium atoms at the porphyrin centers for two UNLPF-10 samples prepared at different M/L ratios: $U_{eq} = 1.045$ for M/L = 5:1 and $U_{eq} = 0.445$ for M/L = 30:1 (U_{eq} : equivalent isotropic displacement parameter). In crystallography, a significantly high U_{eq} value as compared to that of neighboring atoms usually indicates a low atomic occupancy. As a comparison, the occupancies of In atoms at the $[\text{In}(\text{COO})_4]^-$ SBUs in these two samples were found to be similar ($U_{eq} = 0.117$ and $U_{eq} = 0.121$, respectively). Therefore, a higher M/L ratio indeed results in a higher extent of metalation of porphyrins in UNLPF-10.

Next, we used nuclear magnetic resonance (NMR) spectroscopy to evaluate the extent of metalation at bulk level. ^1H NMR spectra of acid digested samples of UNLPF-10 showed two sets of signals in the aromatic region assigned to free base porphyrin (porph) and indium-metalated porphyrin (In-porph), respectively (Figure 2). Specifically, as the M/L ratio

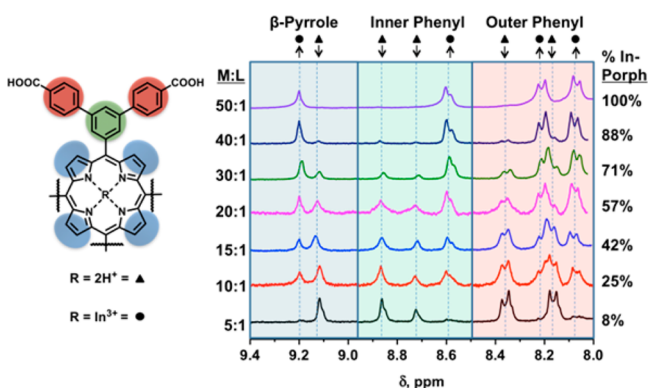


Figure 2. ^1H NMR spectra in the aromatic region of tbcppp linkers (circle, In-porph; triangle, porph) obtained via acid digestion of UNLPF-10 samples prepared at different M/L ratios.

increases, the peak intensities of porph at 8.25, 8.72, 8.85 (terphenyl), and 9.11 ppm (β -pyrrole) decrease, and the peak intensities of In-porph at 8.15, 8.60, and 9.21 ppm increase (Figure 2). Complete metalation with indium was only possible when the M/L ratio was 50:1, indicating slow reaction kinetics. This is in sharp contrast to the metalation of other metals such as zinc,^{3e} copper,^{3d} and cobalt,^{3f} for which a low M/L ratio can lead to a complete metalation. Interestingly, attempted

premetalation of tbcppp linkers with In^{3+} was unsuccessful (Figure S5, Supporting Information); thus, the observed in situ metalation is likely due to the tendency of minimizing the overall framework charge density (vide infra). Further, inductively coupled plasma mass spectrometry (ICP-MS) analysis shows a good correlation between the M/L ratio and the mass content of indium in UNLPF-10 (Figure S7, Supporting Information), suggesting that the M/L ratio indeed controls the extent of metalation in UNLPF-10.

Similar to many In-MOFs,¹⁰ UNLPF-10 forms as an anionic framework due to the presence of $[\text{In}(\text{COO})_4]^-$ SBUs. Me_2NH_2^+ is presumably the counter cation (Figure S8, Supporting Information) that is loosely bound within the framework. The anionic nature was also confirmed by ion exchange with organic dyes.¹¹ Specifically, cationic dyes such as methylene blue (MB^+), methylene green (MG^+), methyl violet (MV^+), and rhodamine B (RB^+) completely exchanged with Me_2NH_2^+ within 24 h (Figures 3a and S10, Supporting

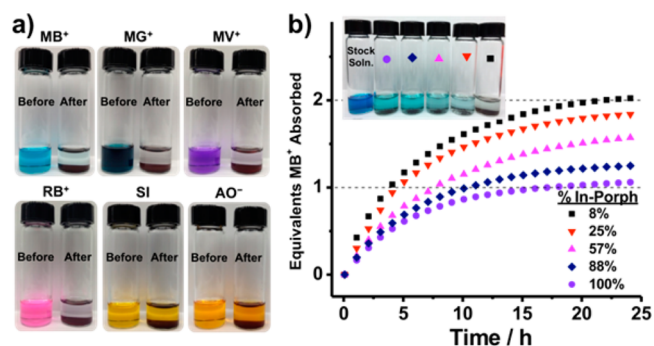


Figure 3. (a) Photographs of organic dye solutions before and after treating with UNLPF-10. (b) MB^+ exchange with UNLPF-10 with different percent of In-porph. The dye content was monitored by UV-vis in DMF ($\lambda_{max} = 665$ nm).

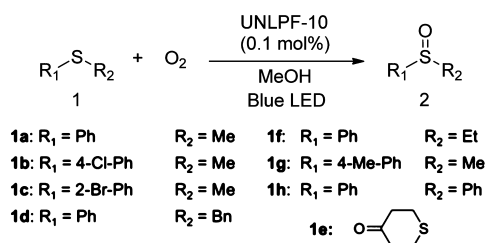
Information). However, UNLPF-10 shows weak adsorption of neutral Sudan I (Supporting Information) and no adsorption of anionic acid orange (AO^-) (Figure 3a). Clearly, the selective adsorption of cationic dyes is due to the Coulombic interaction of an anionic framework with cationic guests.

In-porph typically exhibits a +1 effective charge since the axially coordinated anion (NO_3^- in this case) has a strong tendency to dissociate in polar solution.¹² Therefore, we reasoned that the charge density of UNLPF-10 is dependent on the extent of porphyrin metalation. When the entire framework is composed of porph (0% metalation) or In-porph (100% metalation), the calculated charge density is -2 or -1 per cage, respectively (Figure 1c,d). We further quantified the charge density of UNLPF-10 by calculating the average amount of adsorbed MB^+ in one tetrakaidecahedral cage using UV-vis spectroscopy (see Supporting Information for detailed procedure). Remarkably, as the extent of metalation in UNLPF-10 increased, the equivalents of MB^+ absorbed per cage decreased from ~ 2 (8% metalation) to ~ 1 (100% metalation) (Figure 3b), corresponding to a charge density per cage of -2 and -1 , respectively. Further, ^1H NMR analysis of the $\text{MB}^+@$ UNLPF-10 samples using acid digestion treatment also confirmed the varying equivalents of extraframework MB^+ (Figure S11, Supporting Information).

Because of their rich photophysical and photochemical properties, porph-MOFs are of particular interest for artificial photosynthesis and photocatalysis.^{3c,g,13} In-porph and their

derivatives are excellent photosensitizers and have been used in photodynamic therapy;¹⁴ however, their use in light-promoted chemical reactions has not been documented. We evaluated the photocatalytic activity of UNLPPF-10 for the selective oxygenation of sulfides, which is an important industrial process, and the resulting sulfoxides are biologically active compounds commonly used in pharmaceuticals.¹⁵ The photocatalytic oxygenation of sulfides was investigated in the presence of O₂ (open to air) and UNLPPF-10 (0.1 mol % based on In-porph) under irradiation with blue LED (135 mW, λ_{max} = 465 nm; Figure S12, Supporting Information), and it generally proceeded in excellent yields (Table 1, entries 1–7). For

Table 1. Photo-Oxygenation of Sulfides



entry	substrate	conversion ^a	time (h)
1	1a	>99%	8
2	1b	96%	18
3	1c	73%	24
4	1d	98%	18
5	1e	>99%	18
6	1f	92%	24
7	1g	97%	24
8	1h	0%	48
9	1a	0% ^b	48
10	1a	0% ^c	48
11	1a	2% ^d	48
12	1a	97% ^e	8
13	1a	31% ^f	18
14	1a	73% ^g	18

^aDetermined by ¹NMR. ^bNo light. ^cNo catalyst. ^dUnder an Ar atmosphere. ^eAfter 5th recycle of UNLPPF-10. ^fTPP used as the catalyst. ^gIn-TPP used as the catalyst.

instance, thioanisole 1a was completely and selectively converted to the corresponding sulfoxide after 8 h (Table 1, entry 1). Electron-withdrawing groups such as -Cl and -Br were found to slightly decrease the reaction rate (Table 1, entries 2 and 3), consistent with previous reports.^{16a} UNLPPF-10 was not able to oxidize diphenyl sulfide 1h (Table 1, entry 8) due to the less accessible p_z orbital on the sulfur atom.^{16b} Control experiments revealed the essential role of light, photocatalyst, and O₂ in this reaction (Table 1, entries 9–11). UNLPPF-10 exhibits excellent stability indicated by its well-preserved crystalline nature after reactions (Figure S3–4, Supporting Information). Importantly, it can also be repeatedly used without decrease of activity (Table 1, entry 12). The possible overoxidized byproduct, sulfone, was not detected, suggesting that the reaction involves the singlet oxygen pathway,¹⁷ which was further supported by electron paramagnetic resonance (EPR) spectroscopy¹⁸ and a control reaction performed in the deuterated solvent (d₄-MeOD)¹⁹ (see Supporting Information for details).

We next demonstrated that the controllable in situ metalation of UNLPPF-10 leads to its tunable photocatalytic

activity: the rate of photo-oxygenation of thioanisole increased as the percent of In-porph sites increased (Figure 4). For

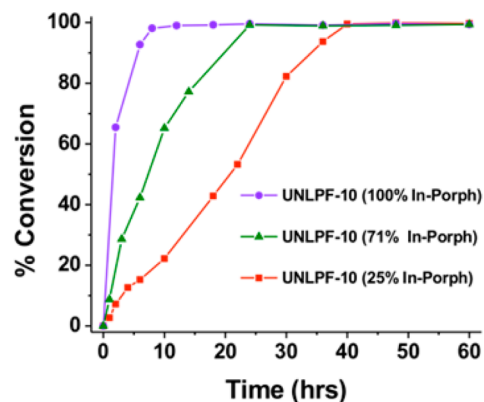


Figure 4. Photo-oxygenation of thioanisole-catalyzed UNLPPF-10 with 100% In-porph (purple), 71% In-porph (green), and 25% In-porph (red).

instance, UNLPPF-10 with ~25% In-porph sites required 40 h to achieve a complete conversion, whereas ~98% In-porph only requires 8 h (Figure 4). It is noted that free base porphyrin is also a common photosensitizer.²⁰ However, our result clearly shows that it is less photocatalytically active than In-porph for oxygenation of sulfides. Indeed, the photo-oxygenation using tetraphenylporphyrin (TPP) and its indium-metalated derivative (In-TPP) proceeded with conversions of 31% and 73%, respectively (Table 1, entries 13 and 14). This result also indicates the catalytic activity of heterogeneous UNLPPF-10 is superior to that of the homogeneous In-TPP.^{13a}

In summary, a new anionic indium porphyrin framework, UNLPPF-10, has been constructed as the first example of a MOF composed of close-packed Williams β-tetrakaidecahedral cages. The metalation of porphyrin macrocycles can be simply controlled by adjusting the M/L ratio during synthesis, resulting in fine-tuning of the charge density of the framework. UNLPPF-10 exhibits excellent photocatalytic activity toward the selective oxygenation of sulfides, which is also tunable by indium metalation. In light of its ionic feature, additional functions can be easily incorporated to UNLPPF-10 via ionic exchange with extra-framework guests with interesting chemical,²¹ catalytic,²² or optical²³ properties. Thus, this study paves a way for realizing new applications of porph-MOFs, and such investigations are currently underway in our laboratory.

■ ASSOCIATED CONTENT

📄 Supporting Information

Materials, general procedure, synthesis of UNLPPF-10, crystallographic data, dye uptake, and photocatalytic study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727.
- (2) (a) Diskin-Posner, Y.; Dahal, S.; Goldberg, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 1288. (b) Suslick, K. S.; Bhyrappa, P.; Chou, J. H.; Kosal, M. E.; Nakagaki, S.; Smithenry, D. W.; Wilson, S. R. *Acc. Chem. Res.* **2005**, *38*, 283. (c) Burnett, B. J.; Barron, P. M.; Choe, W. *CrystEngComm* **2012**, *14*, 3839. (d) Gao, W. Y.; Chrzanowski, M.; Ma, S. *Chem. Soc. Rev.* **2014**, *43*, 5841.
- (3) (a) Feng, D.; Gu, Z. Y.; Li, J. R.; Jiang, H. L.; Wei, Z.; Zhou, H. C. *Angew. Chem., Int. Ed.* **2012**, *51*, 10307. (b) Feng, D.; Chung, W. C.; Wei, Z.; Gu, Z. Y.; Jiang, H. L.; Chen, Y. P.; Darenbourg, D. J.; Zhou, H. C. *J. Am. Chem. Soc.* **2013**, *135*, 17105. (c) Jin, S.; Son, H. J.; Farha, O. K.; Wiederrecht, G. P.; Hupp, J. T. *J. Am. Chem. Soc.* **2013**, *135*, 955. (d) Wang, X.-S.; Meng, L.; Cheng, Q.; Kim, C.; Wojtas, L.; Chrzanowski, M.; Chen, Y.-S.; Zhang, X. P.; Ma, S. *J. Am. Chem. Soc.* **2011**, *133*, 16322. (e) Lee, C. Y.; Farha, O. K.; Hong, B. J.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 15858. (f) Meng, L.; Cheng, Q.; Kim, C.; Gao, W. Y.; Wojtas, L.; Chen, Y. S.; Zavorotko, M. J.; Zhang, X. P.; Ma, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 10082. (g) Son, H. J.; Jin, S.; Patwardhan, S.; Wezenberg, S. J.; Jeong, N. C.; So, M.; Wilmer, C. E.; Sarjeant, A. A.; Schatz, G. C.; Snurr, R. Q.; Farha, O. K.; Wiederrecht, G. P.; Hupp, J. T. *J. Am. Chem. Soc.* **2013**, *135*, 862. (h) Xu, G.; Otsubo, K.; Yamada, T.; Sakaida, S.; Kitagawa, H. *J. Am. Chem. Soc.* **2013**, *135*, 7438. (i) Zhao, M.; Ou, S.; Wu, C. D. *Acc. Chem. Res.* **2014**, *47*, 1199.
- (4) Takaishi, S.; DeMarco, E. J.; Pellin, M. J.; Farha, O. K.; Hupp, J. T. *Chem. Sci.* **2013**, *4*, 1509.
- (5) (a) Zhang, Z.; Zhang, L.; Wojtas, L.; Nugent, P.; Eddaoudi, M.; Zavorotko, M. J. *J. Am. Chem. Soc.* **2012**, *134*, 924. (b) Wang, X. S.; Chrzanowski, M.; Wojtas, L.; Chen, Y. S.; Ma, S. *Chem.—Eur. J.* **2013**, *19*, 3297.
- (6) (a) Johnson, J. A.; Lin, Q.; Wu, L. C.; Obaidi, N.; Olson, Z. L.; Reeson, T. C.; Chen, Y. S.; Zhang, J. *Chem. Commun.* **2013**, *49*, 2828. (b) Johnson, J. A.; Chen, S.; Reeson, T. C.; Chen, Y. S.; Zeng, X. C.; Zhang, J. *Chem.—Eur. J.* **2014**, *20*, 7632.
- (7) Williams, R. E. *Science* **1968**, *161*, 276.
- (8) Manakov, A. Y.; Voronin, V. I.; Kurnosov, A. V.; Teplykh, A. E.; Komarov, V. Y.; Dyadin, Y. A. *J. Inclusion Phenom.* **2004**, *48*, 11.
- (9) Stock, N.; Biswas, S. *Chem. Rev.* **2012**, *112*, 933.
- (10) (a) Sun, J.; Weng, L.; Zhou, Y.; Chen, J.; Chen, Z.; Liu, Z.; Zhao, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 4471. (b) Zhang, J.; Chen, S.; Bu, X. *Angew. Chem., Int. Ed.* **2008**, *47*, 5434. (c) Yang, S.; Lin, X.; Blake, A. J.; Walker, G. S.; Hubberstey, P.; Champness, N. R.; Schröder, M. *Nat. Chem.* **2009**, *1*, 487. (d) Xue, Y.-S.; He, Y.; Zhou, L.; Chen, F.-J.; Xu, Y.; Du, H.-B.; You, X.-Z.; Chen, B. *J. Mater. Chem. A* **2013**, *1*, 4525.
- (11) Zhao, X.; Bu, X.; Wu, T.; Zheng, S. T.; Wang, L.; Feng, P. *Nat. Commun.* **2013**, *4*, 2344.
- (12) Hoshino, M.; Katayama, S.; Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3360.
- (13) (a) Xie, M. H.; Yang, X. L.; Zou, C.; Wu, C. D. *Inorg. Chem.* **2011**, *50*, 5318. (b) Fateeva, A.; Chater, P. A.; Ireland, C. P.; Tahir, A. A.; Khimiyak, Y. Z.; Wiper, P. V.; Darwent, J. R.; Rosseinsky, M. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 7440.
- (14) (a) Dolmans, D. E.; Kadambi, A.; Hill, J. S.; Waters, C. A.; Robinson, B. C.; Walker, J. P.; Fukumura, D.; Jain, R. K. *Cancer Res.* **2002**, *62*, 2151. (b) Chen, Y.; Zheng, X.; Dobhal, M. P.; Gryshuk, A.; Morgan, J.; Dougherty, T. J.; Oseroff, A.; Pandey, R. K. *J. Med. Chem.* **2005**, *48*, 3692.
- (15) (a) Evans, D. A.; Faul, M. M.; Colombo, L.; Bisaha, J. J.; Clardy, J.; Cherry, D. *J. Am. Chem. Soc.* **1992**, *114*, 5977. (b) Legros, J.; Dehli, J. R.; Bolm, C. *Adv. Synth. Catal.* **2005**, *347*, 19. (c) Pellissier, H. *Tetrahedron* **2006**, *62*, 5559. (d) Fernández, I.; Khair, N. *Chem. Rev.* **2003**, *103*, 3651. (e) Carreño, M. C.; Hernández-Torres, G.; Ribagorda, M.; Urbano, A. *Chem. Commun.* **2009**, 6129.
- (16) (a) Dad'ová, J.; Svobodová, E.; Sikorski, M.; König, B.; Cibulka, R. *ChemCatChem* **2012**, *4*, 620. (b) Bonesi, S. M.; Fagnoni, M.; Monti, S.; Albini, A. *Photochem. Photobiol. Sci.* **2004**, *3*, 489.
- (17) (a) Tsuboi, T.; Takaguchi, Y.; Tsuboi, S. *Chem. Commun.* **2008**, 76. (b) Tanaka, H.; Nishikawa, H.; Uchida, T.; Katsuki, T. *J. Am. Chem. Soc.* **2010**, *132*, 12034.
- (18) Huang, L.; Cui, X.; Therrien, B.; Zhao, J. *Chem.—Eur. J.* **2013**, *19*, 17472.
- (19) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423.
- (20) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19.
- (21) (a) An, J.; Rosi, N. L. *J. Am. Chem. Soc.* **2010**, *132*, 5578. (b) Oisaki, K.; Li, Q.; Furukawa, H.; Czaja, A. U.; Yaghi, O. M. *J. Am. Chem. Soc.* **2010**, *132*, 9262. (c) Kong, G. Q.; Ou, S.; Zou, C.; Wu, C. D. *J. Am. Chem. Soc.* **2012**, *134*, 19851.
- (22) Genna, D. T.; Wong-Foy, A. G.; Matzger, A. J.; Sanford, M. S. *J. Am. Chem. Soc.* **2013**, *135*, 10586.
- (23) (a) Yu, J.; Cui, Y.; Xu, H.; Yang, Y.; Wang, Z.; Chen, B.; Qian, G. *Nat. Commun.* **2013**, *4*, 2719. (b) Sun, C. Y.; Wang, X. L.; Zhang, X.; Qin, C.; Li, P.; Su, Z. M.; Zhu, D. X.; Shan, G. G.; Shao, K. Z.; Wu, H.; Li, J. *Nat. Commun.* **2013**, *4*, 2717.