# Iron(III) Porphyrin-Based Porous Material as Photocatalyst for Highly Efficient and Selective Degradation of Congo Red

Zhenyu Xiao, Yan Zhou, Xuelian Xin, Qinhui Zhang, Liangliang Zhang, Rongming Wang, Daofeng Sun*

A highly efficient and selective photocatalyst, **UPC-CMP-1** has been successfully synthesized by a Sonogashira–Hagihara coupling reaction between iron(III) 5,10,15,20-tetrakis-(4′-bromophenyl) porphine and 1,4-diethynylbenzene. The scanning electron microscopy shows **UPC-CMP-1** possesses a dendrite-like nanostructure. Interestingly, within 120 s, **UPC-CMP-1** can decompose 88.3% of Congo red (CR) molecules under visible light irradiation. Furthermore, **UPC-CMP-1** exhibits high selectivity to CR over other dyes. These results reveal that conjugated microporous polymer should be an excellent candidate on the application of dye degradation.
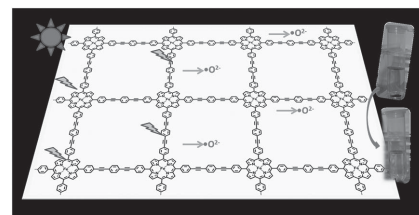
1. Introduction

Due to the generation of increasing amounts of wastewater by industrial plants, organic pollutants have been considered as one of the greatest environmental pollutant source in recent years. As one of the organic pollutants, organic dyes are normally toxic and difficult to be biologically degraded.[1,2] Thus, effective reduce of the concentration of organic dyes in wastewater is crucial to environmental protection and human health. Although some wastewater treatment technologies such as coagulation and adsorption are widely used in industries to separate organic dyes from wastewater, these technologies cannot completely destroy or degrade the organic dyes into less toxic organic debris or inorganic CO_2 and H_2O.[3]

Hence, the advanced oxidation processes (AOPs) such as photocatalysis, Fention reaction, ozonation, etc. have been considered as one of the most efficient technologies in the treatment of organic dyes, because these technologies can efficiently degrade the organic dyes into less toxic molecules.[4] In particular, the heterogeneous photocatalysis technology has been received much attention of chemists because of the low operating costs and high efficiency. Actually, some semiconductor catalysts including TiO_2, ZnO, CdS, etc. were widely used in highly efficient degradation of organic dyes in the past decade.[1a,1d,5] Unfortunately, one of the biggest drawbacks for these semiconductor catalysts is their weak photostability under operating conditions. Furthermore, easy agglomeration and difficulty in the post-separation of the catalysts have limited their practical application. Therefore, development of new photocatalysts with high photostability is needed for the highly efficient degradation of organic dyes.

Although a large number of metal-organic frameworks (MOFs) as photocatalysts have been synthesized and reported in recent years, the degradation efficiency and photostability are somewhat low and limit their application.[6] Covalent-organic frameworks (COFs) or conjugated micro- and mesoporous polymers (CMPs) are a new class of porous materials that can be synthesized by common organic reactions such as condensation reaction, Suzuki coupling, Sonogashira coupling, etc., through which organic units can be extended into periodic structures.[7,8]

Dr. Z. Xiao, Dr. Y. Zhou, Dr. X. Xin, Prof. Q. Zhang,
Dr. L. Zhang, Dr. R. Wang, Prof. D. Sun
State Key Laboratory of Heavy Oil Processing
College of Science
China University of Petroleum (East China)
Qingdao, Shandong 266580, P. R. China
E-mail: dfsun@upc.edu.cn

Early View Publication; these are NOT the final page numbers, use DOI for citation !!

Normally, COFs or CMPs exhibit much higher thermal and chemical stabilities than that of MOFs. Yaghi and co-workers pioneered the synthesis and application of covalent-organic frameworks based on condensation reaction.[9] Following that, numerous COFs or CMPs were synthesized and their application were also extended from gas adsorption/separation to catalysis. Recently, Jiang et al. reported CMPs based on metalloporphyrin polymers as a built-in heterogeneous catalyst.[10] The preparation of magnetically separable catalytic systems based on Fe-porphyrin CMP was also reported by Son and co-workers.[11] Several other CMPs based on porphyrin units and their properties were also reported in the past decade.[12] However, study of Fe-porphyrin CMP as photocatalyst in the application of dye degradation is unexplored to date. Herein, we describe a Fe-porphyrin-based CMP with highly efficient and selective degradation of organic dyes.

2. Results and Discussion

Sonogashira–Hagihara coupling reaction between iron(III) 5,10,15,20-tetrakis-(4¢-bromophenyl) porphine and 1,4-diethynylbenzene resulted in the formation of a large amount of precipitation. The crude product was washed

with H_2O, MeOH, THF, and CH_2Cl_2, then further purified by soxhlete extraction with H_2O, MeOH, THF, and CH_2Cl_2 as solvents for 4 d to give **UPC-CMP-1**. Due to the existence of Fe^{3+} ion with high-spin paramagnetic effect, characterization of **UPC-CMP-1** by the solid-state ^1H-^{13}C CP/MS failed. As the contrast, Fe-free porphyrin polymer (P-CMP) was further synthesized and characterized by the solid-state ^1H-^{13}C CP/MS. As shown in Figure S1 of the Supporting Information, four remarkable broad peaks emerge at 142, 132, 130, and 123 ppm which are assigned to the phenylene moiety and porphyrin macrocycle. The weak resonance peak at 90 ppm is attributed to the acetylene group.[13] Both **UPC-CMP-1** and P-CMP are insoluble in water and common organic solvents.

In order to obtain **UPC-CMP-1** material with larger surface area, the synthetic condition was optimized by changing the ratio of the starting materials, then the surface areas of the resultant materials were checked by nitrogen sorption isotherm measurements. The results indicate that the sample synthesized with the molecule ratio of 0.45 (Fe-porphyrin/1,4-diethynylbenzene) and activated in 150 °C possesses better Brunauer–Emmett–Teller (BET) and pore size distribution (Figure 5, Supporting Information). As shown in Figure 1, when the sample was activated at 150 °C for 6 h, it exhibits better
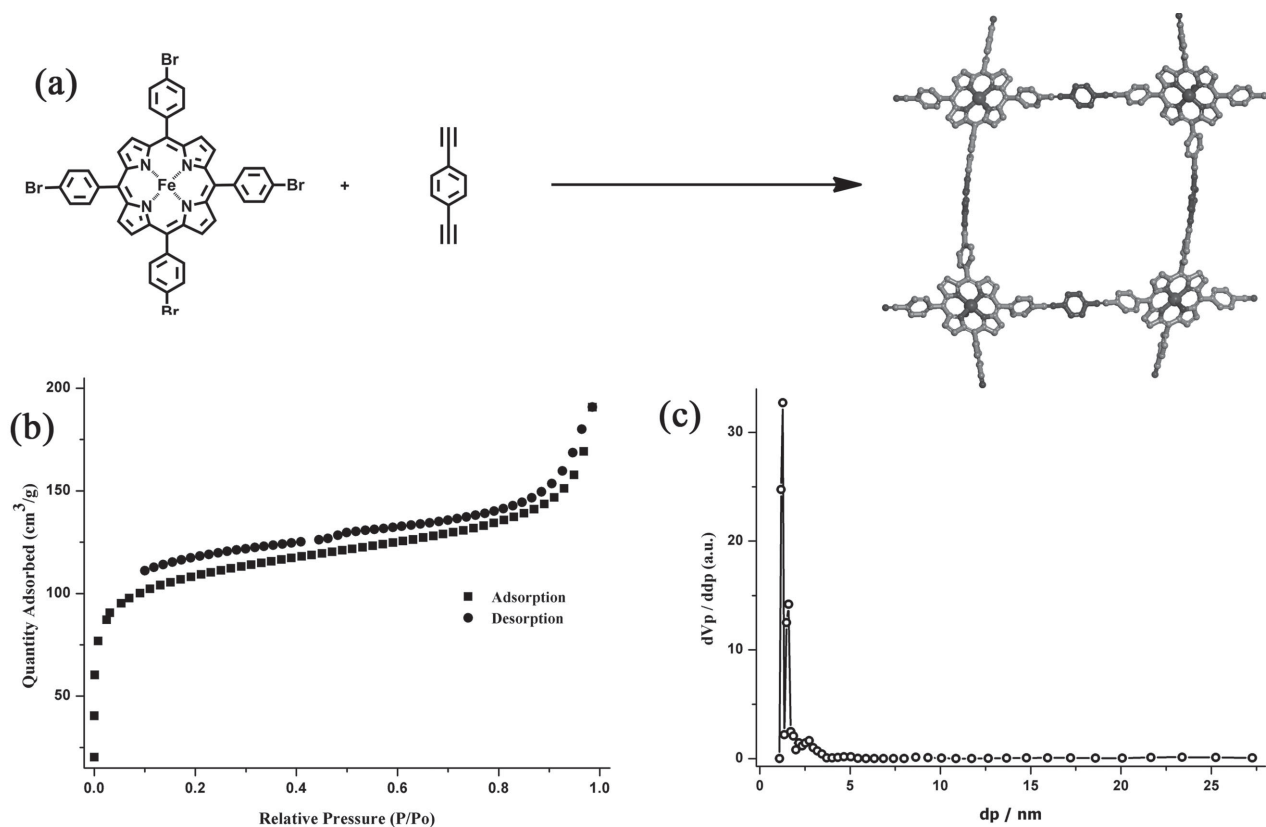

Figure 1. a) Synthetic route toward **UPC-CMP-1** using iron(III) 5,10,15, 20-tetrakis(4-bromophenyl)porphyrin and 1,4-diethynylbenzene as building units. b) N_2 sorption isotherm. c) Pore size distribution.

www.MaterialsViews.com

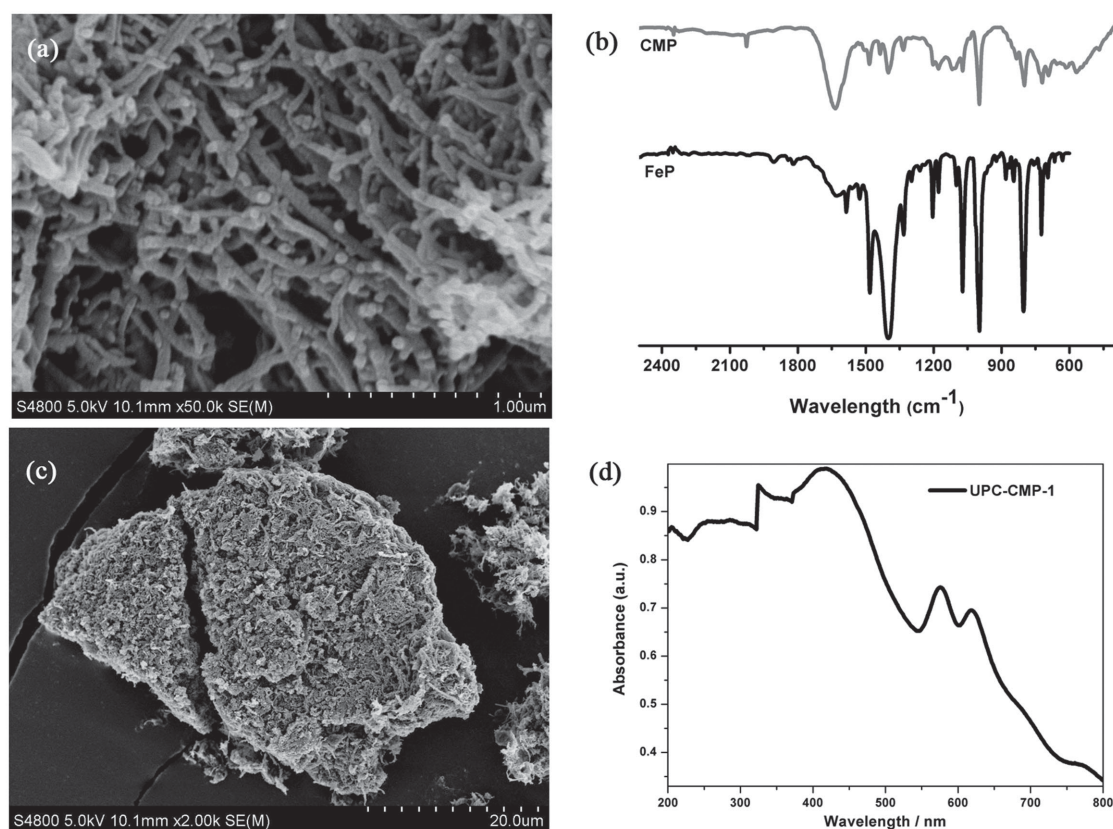Early View Publication; these are NOT the final page numbers, use DOI for citation !!

Figure 2. a,c) SEM images of the as-synthesized **UPC-CMP-1** with different magnifications. b) FT-IR spectra of FeP (red) and **UPC-CMP-1** (blue). d) UV–vis absorption spectra of **UPC-CMP-1**.

pore size distribution. **UPC-CMP-1** displays a typical Type-IV nitrogen sorption isotherm with the BET surface area of 416.4 m^2 g^{-1}, which is comparable to other FeP-CMP materials. The **UPC-CMP-1** has a centralized pore size distribution, with the pore widths centering between 1.3 and 1.7 nm, as calculated by the Nonlocalized density functional theory (NLDFT) method (Figure 1c). The total volume calculated with nitrogen gas adsorbed at P/P_0 = 0.99 was 0.174 cm^3 g^{-1}.

The morphology of **UPC-CMP-1** was investigated by the scanning electron microscopy (SEM). As shown in Figure 2a, **UPC-CMP-1** possesses a dendrite-like nanostructure with the diameter size about 30–80 nm of each branch, which is quite different from those reported structure. The tangle and chiasma of those dendrite-like nanostructures build the final organic particle (Figure 2c) with the size about 30 um. The optical absorption property of the as-synthesized product was determined by UV–vis absorption spectra (Figure 3d), which show strong response in the ultraviolet spectra region and weak absorption tail in the visible region with a characteristic excitation peak at Q-band and Soret band. Based on the band edge formula of $ahv = A(hv - E_g)^{1/2}$, we can get the band gap of UPC-CMP-1 being about 1.76 eV. The

characteristic N–Fe in-plane bending at 964 cm^{-1} appears in the FT-IR spectrum (Fourier Transform infrared spectroscopy) of **UPC-CMP-1**, indicating the coordination of iron. Moreover, the presence of alkyne's characteristic bands at 2026 cm^{-1} can be indicative of a successful coupling reaction (Figure 2b).

Considering that **UPC-CMP-1** exhibits better pore size distribution with larger pore widths, as well as its color character that can extend the photoresponse to the visible region, the photocatalytic degradation of organic dyes by **UPC-CMP-1** were carried out for the first time. Before the experiments, the stability of the coordinated Fe^{3+} on the porphyrin core was checked by the cyclic voltammogram (CV). As shown in Figure S2 of the Supporting Information, the CV shows a reductive peak at +0.35 V versus SCE and the corresponding oxidation peak appears at +0.5 V versus SCE. This redox couple indicates the Fe^{3+}/Fe^{2+} redox process. The consecutive scans overlap each other, even with the first scan, represent excellent stability on the electrode, as well as the coordination of Fe^{3+} in the **UPC-CMP-1** structure. Furthermore, the same experiment was carried out at 0.1 V s^{-1} scan rate with 50 cycles (Figure S4, Supporting Information), still, no sign of decreasing in peak current or shift in peak potential,
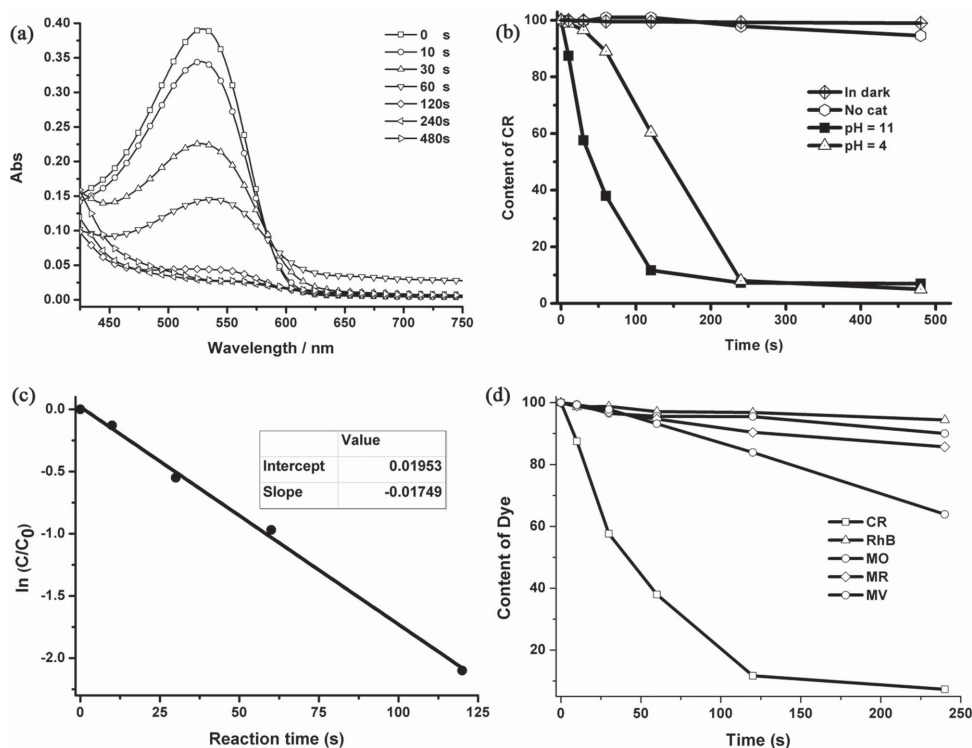
Early View Publication; these are NOT the final page numbers, use DOI for citation !!

Figure 3. a) The change of UV–vis spectra for CR with the reaction time in the presence of **UPC-CMP-1**. b) The degradation curves of CR solution in dark, without photocatalyst and over different pH values under visible light irradiation. c) The normalized concentration of CR as a function of reaction time in both logarithmic scale. d) Selective degradation of **UPC-CMP-1** on different organic dyes.

indicates that no Fe ions were diffused in or out of the **UPC-CMP-1** structure during the redox process. The shift of redox peak position compare with 0.02 V s^{-1} scan rate is reasonable due to the relatively slow electrode kinetics, which may be due to the Nafion film or the less conductive **UPC-CMP-1** structure. These results conclude that the **UPC-CMP-1** structure is stable during the redox process, which indicates the long term durability of the material in the redox catalytic reactions.

Because of the poor dispersibility of **UPC-CMP-1** in water solution, DMF was used as the solvent to test the photocatalytic performance. As shown in Figure 3d, five dye molecules including methyl orange (MO), Congo red (CR), methyl red (MR), methyl violet (MV), rhodamine B (RhB) were selected, in which MO and CR belong to anionic dyes, MR are neutral dyes, whereas MV and RhB are cationic dyes. The photocatalytic degradation experiments were carried out under visible light irradiation. Unexpectedly, **UPC-CMP-1** material exhibits highly selectivity in the degradation of dye molecules.

As shown in Figure 3, **UPC-CMP-1** shows highly photocatalytic activity to CR molecule. As is known, the adsorption capacity for dye molecules is one of the key factors for the enhancement of their catalytic degradation. As shown in Figure S7 of the Supporting Information, **UPC-CMP-1** exhibits obvious adsorption of CR, which is beneficial to the enhancement of photocatalytic activity.

Figure 3a shows the evolution of the absorption spectra of CR with reaction time, which indicates that 88.3% of CR molecules can be rapidly degraded within 120 s under visible light irradiation in the presence of **UPC-CMP-1**. The function of ln(C/C$_0$) versus reaction time (t) within 120 s displays a linear relationship (Figure 3c), indicating that the reaction follows first-order kinetics with the rate constant determined to be 17.5 × 10^{-3} s^{-1}. In contrast, experiments without photocatalyst were also conducted under the same conditions (Figure 3b) and the results indicate that CR is quite stable toward incident light. For other dye molecules such as RhB, MO, MR, and MV, only 3.2%, 4.5%, 9.6%, and 16.1%, respectively, were degraded within 120 s under visible light irradiation in the presence of **UPC-CMP-1**, indicating the high selectivity of **UPC-CMP-1** on the degradation of dye molecules. Meanwhile, zinc and cobalt porphyrin-based polymers have been synthesized in similar condition, and the photocatalytic degradation experiments for CR molecule were also investigated. The degradation efficiency of metal porphyrin-based polymers follows Fe > Zn > Co (Figure 9, Supporting Information).

It is reasonable that the charge of dye molecule will significantly affect the photocatalyst degradation ratio. Hence, the influence of pH value on the degradation of CR molecule was studied. In the fresh solution (pH = 11.3), CR molecule exists in the form of negative bivalent anions.
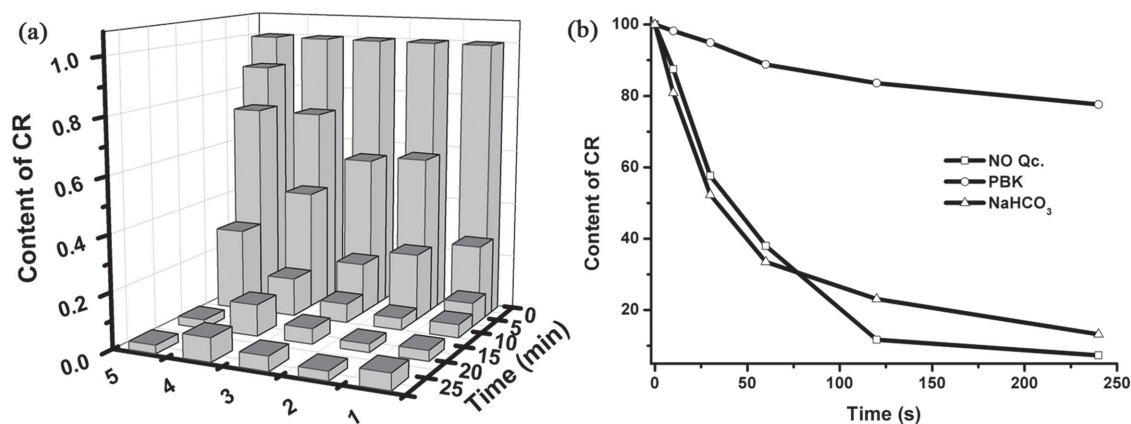
www.MaterialsViews.com

Figure 4. a) The degradation bar graph of CR solution for five successive reactions catalyzed with the same batch of **UPC-CMP-1**. b) Photo-degradation kinetics of CR in **UPC-CMP-1** DMF dispersion under visible light irradiation with different scavengers (10 × 10^{-3} M NaHCO$_3$ and 5 × 10^{-3} M p-benzoquinone).

Thus, the $\ln(C/C_0)$ versus reaction time (t) within 120 s can keep a linear relationship. When the pH value of CR solution was changed to 4, the initial degradation rate was obviously decreased. In the first 60 s, 62% of CR molecule could be degraded in pH = 11.3 solution, but only 11.2% of CR molecule were degraded in pH = 4.0 solution (Figure 3b). Interestingly, with the increase of degradation time, the degradation rate also increases in pH = 4.0 solution. To explain this phenomenon, the final pH value of reaction system was measured, indicating that the alkalinity of reaction solution was gradually up to pH = 10. As the basicity increased, the negative charge of CR molecule may be enhanced, which may be the key point that degradation rate was improved.

Besides the degradation efficiency, the durability or stability of a photocatalyst is also very important for practical application. Hence, we try to measure the cyclic degradation experiments in DMF solution. However, we find that it was difficult to collect the catalyst for catalysing a new run. Hence, we chose EtOH with low density as the solvent, in which the photocatalyst activity of **UPC-CMP-1** is a little lower than that in DMF solution (Figure S8, Supporting Information), to test the stability and durability of the catalyst. After one reaction was completed, the catalyst was collected (by centrifuging the solution) to catalyze a new one. Figure 4a shows the degradation kinetics of CR for 5 runs of reactions using the same batch of photocatalyst. The results indicate that the photocatalytic efficiency of **UPC-CMP-1** slightly decreased, which may due to the inevitable loss of catalyst during the recovery process.

As is known, in the process of oxidative degradation of dye molecule, •OH, h$^+$, and •O^{2-} are supposed to be possible reactive species. In order to further elucidate the involved active species in the degradation reaction, p-benzoquinone (PBQ 5 × 10^{-3} M, scavenger for •O^{2-}) and NaHCO$_3$ (10 × 10^{-3} M, scavenger for h$^+$ and adsorbed •OH) were selectively introduced to the reaction system. As shown in Figure 4b, the degradation of CR is significantly depressed by the p-benzoquinone of the •O^{2-} scavenger, leading to only 20% degradation of CR after 240 s. However, the introduction of HCO^{3-} almost has no effect on the degradation process. Hence, we can get that the reactive species in the degradation process is most likely to be •O^{2-}.[14]

3. Conclusions

In summary, through Sonogashira–Hagihara coupling reaction between iron(III) 5,10,15,20-tetrakis-(4′-bromophenyl) porphine and 1,4-diethynylbenzene, an iron(III) porphyrin-based conjugated microporous polymer, **UPC-CMP-1**, was synthesized and characterized. **UPC-CMP-1** exhibits highly efficient and selective degradation of CR in DMF solution. This is the first report on the conjugated microporous polymer as photocatalysts in the application of dye degradation. Although the organic solvent used in the degradation reaction may limit the practical application of **UPC-CMP-1**, this work reveals that conjugated microporous polymer should be an excellent candidate on the application of dye degradation. Further study will focus on improving the dispersibility of **UPC-CMP-1** in water phase to achieve the efficient degradation of dye molecules in water solution.

Supporting Information

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

Early View Publication; these are NOT the final page numbers, use DOI for citation !!

[1] a) M. Saquib, M. Muneer, *Dyes Pigm.* **2002**, *53*, 237; b) C. H. Zhang, L. H. Ai, J. Jiang, *Ind. Eng. Chem. Res.* **2015**, *54*, 153; c) J. Z. Wang, C. H. An, J. X. Liu, G. Z. Xi, W. Jiang, S. T. Wang, Q.-H. Zhang, *J. Mater. Chem. A* **2013**, *1*, 2827; d) H. Zhang, X. J. Lv, Y. M. Li, Y. Wang, J. H. Li, *ACS Nano* **2010**, *4*, 380.

[2] a) A. A. Adeyemo, I. O. Adeoye, O. S. Bello, *Toxicol. Environ. Chem.* **2012**, *94*, 1846; b) J. Levec, A. Pintar, *Catal. Today* **2007**, *124*, 172; c) V. K. Gupta, Suhas, *J. Environ. Manage.* **2009** *90*, 2313; d) H. S. Rai, M. S. Bhattacharyya, J. Singh, T. K. Bansal, P. Vats, U. C. Banerjee, *Crit. Rev. Environ. Sci. Technol.* **2005**, *35*, 219.

[3] a) D. Parasuraman, M. J. Serpe, *ACS Appl. Mater. Interfaces* **2011**, *3*, 4714; b) M. Chhabra, S. Mishra, T. R. Sreekrishnan, *Biochem. Eng. J.* **2015**, *93*, 17; c) P. Cañizares, F. Martínez, C. Jiménez, J. Lobato, M. A. Rodrigo, *Environ. Sci. Technol.* **2006**, *40*, 6418; d) T. Wang, K. Kailasam, P. Xiao, G. Chen, L. Q. Chen, L. H. Wang, J. L. Li, J. J. Zhu, *Microporous. Mesoporous. Mater.* **2014**, *187*, 63; e) U. I. Gaya, A. H. Abdullah, *J. Photochem. Photobiol.C* **2008**, *9*, 1; f) P. Padmanabhan, K. Sreekumar, T. Thiyagarajan, R. Satpute, K. Bhanumurthy, P. Sengupta, G. Dey, K. Warrier, *Vacuum* **2006**, *80*, 1252.

[4] a) J.-R. Li, C.-C. Wang, G. S. Guo B, *Energy Environ. Sci.* **2014**, *7*, 2831; b) J. Lü, J.-X. Lin, X.-L. Zhao, R. Cao, *Chem. Commun.* **2012**, *48*, 669.

[5] a) C. H. Li, C. Koenigsmann, W. D. Ding, B. Rudshteyn, K. R. Yang, K. P. Regan, S. J. Konezny, V. S. Batista, G. W. Brudvig, C. A. Schmuttenmaer, J.-H. Kim, *J. Am. Chem. Soc.* **2015**, *137*, 1520; b) J. Feng, J. X. Liu, G. J. Wei, J. Zhang, S. T. Wang, Z. J. Wang, C. H. An, *RSC Adv.* **2014**, *4*, 36665; c) W. Jiang, C. H. An, J. X. Liu, S. T. Wang, L. M. Zhao, W. Y. Guo, J. X. Liu, *Dalton Trans.* **2013**, *43*, 300; d) M. C. Das, H. Xu, Z. Wang, G. Srinivas, W. Zhou, Y. F. Yue, V. N. Nesterov, G. Qian, B. Chen, *Chem. Commun.* **2011**, *47*, 11715.

[6] a) C. H. Zhang, L. H. Ai, J. Jiang, *Ind. Eng. Chem. Res.* **2015**, *54*, 153; b) F. X. Llabresi Xamena, A. Corma, H. Garcia, *J. Phys. Chem. C* **2007**, *111*, 80; c) M. Alvaro, E. Carbonell, B. Ferrer, F. X. Llabrés, I. Xamena, H. Garcia, *Chem. — Eur. J.* **2007**, *13*, 5106; d) F. X. Llabrés, I Xamena, P. Calza, C. Lamberti,

C. Prestipino, A. Damin, S. Bordiga, E. Pelizzetti, A. Zecchina, *J. Am. Chem. Soc.* **2003**, *125*, 2264.

[7] a) F. Xu, X. Chen, Z. Tang, D. Wu, R. Fu, D. Jiang, *Chem. Commun.* **2014**, *50*, 4788; b) S. D. Silab, H. Bildirir, R. Dawson, A. Thomas, Y. Yagci, *Macromolecules* **2014**, *47*, 4607; c) J-X Jiang, F. B. Su, A. Trewin, C. D. Wood, H. Niu, J. T. A. Jones, Y. Z. Khimyak, A. I. Cooper, *J. Am. Chem. Soc.* **2008**, *130*, 7710; d) R. S. Sprick, J.-X. Jiang, B. Bonillo, S. J. Ren, T. Ratvijitvech, P. Guiglion, M. A. Zwijnenburg, D. J. Adams, A. I. Cooper, *J. Am. Chem. Soc.* **2015**, *137*, 3265; e) S.-Y. Ding, W. Wang, *Chem. Soc. Rev.* **2013**, *42*, 548; f) X. Feng, X. Ding, D. L. Jiang, *Chem. Soc. Rev.* **2012**, *41*, 6010.

[8] a) K. V. Rao, S. Mohapatra, C. Kulkarni, T. K. Maji, S. J. George, *J. Mater. Chem.* **2011**, *21*, 12958; b) Q. Chen, D.-P. Liu, J.-H. Zhu, B.-H. Han, *Macromolecules* **2014**, *47*, 5926; c) X. M. Liu, Y. H. Xu, D. L. Jiang, *J. Am. Chem. Soc.* **2012**, *134*, 8738; d) R. K. Totten, L. L. Olenick, Y.-S. Kim, S. Chakraborty, M. H. Weston, O. K. Farha, J. T. Hupp, S. T. Nguyen, *Chem. Sci.* **2013**, *5*, 782; e) U. H. F. Bunz, K. Seehafer, F. L. Geyer, M. Bender, I. Braun, E. Smarsly, J. Freudenberg, *Macromol. Rapid Commun.* **2014**, *35*, 1466; f) Y. Xu, S. Jin, H. Xu, A. Nagai, D. L. Jiang, *Chem. Soc. Rev.* **2013**, *42*, 8012.

[9] a) A. P. Cote, *Science* **2005**, *310*, 1166; b) Y. F. Zeng, R. Y. Zou, Z. Luo, H. C. Zhang, X. Yao, X. Ma, R. Q. Zou, Y. L. Zhao, *J. Am. Chem. Soc.* **2015**, *137*, 1020; c) X. Feng, L. Chen, Y. P. Dong, D. L. Jiang, *Chem. Commun.* **2011**, *47*, 1979.

[10] a) L. Chen, Y. Yang, D. L. Jiang, *J. Am. Chem. Soc.* **2010**, *132*, 9138; b) X. M. Liu, Y. H. Xu, Z. Q. Guo, A. Nagai, D. L. Jiang, *Chem. Commun.* **2013**, *49*, 3233; c) X. Chen, M. Addicoat, E. Jin, L. P. Zhai, H. Xu, N. Huang, Z. Q. Guo, L. L. Liu, St. Irle, D. L. Jiang, *J. Am. Chem. Soc.* **2015**, *137*, 3241.

[11] J. Yoo, N. Park, J. H. Park, S. Kang, S. M. Lee, H. J. Kim, H. Jo, J. Park, S. U. Son, *ACS Catal.* **2015**, *5*, 350.

[12] a) A Sigen, Y. W. Zhang, Z. P. Li, H. Xia, M. Xue, X. M. Liu, Y. Mu, *Chem. Commun.* **2014**, *50*, 8495; b) A. Modak, M. Nandi, J. Mondal, A. Bhaumik, *Chem. Commun.* **2011**, *48*, 248; c) L. Zhang, K. Wang, X. M. Qian, H. B. Liu, Z. Q. Shi, *ACS Appl. Mater. Interfaces* **2013**, *5*, 2761; d) K. Y. Wu, J. Guo, C. C. Wang, *Chem. Commun.* **2014**, *50*, 695; e) Q. P. Lin, J. Z. Lu, Z. D. Yang, X. C. Zeng, J. Zhang, *J. Mater. Chem. A* **2014**, *2*, 14876.

[13] J.-X. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, *Angew. Chem. Int. Ed.* **2007**, *46*, 8574.

[14] a) C. Hu, T. W. Peng, X. X. Hu, Y. L. Nie, X. F. Zhou, J. H. Qu, H. He, *J. Am. Chem. Soc.* **2010**, *132*, 857; b) C. H. An, J. X. Liu, S. T. Wang, J. Zhang, Z. J. Wang, R. Long, Y. G. Sun, *Nano Energy* **2014**, *9*, 204; c) C. H. An, J. Z. Wang, C. Qin, W. Jiang, S. T. Wang, Y. Li, Q. H. Zhang, *J. Mater. Chem.* **2012**, *22*, 13153.

www.MaterialsViews.com

Early View Publication; these are NOT the final page numbers, use DOI for citation !!