

Cite this: *Chem. Sci.*, 2021, 12, 16092

All publication charges for this article have been paid for by the Royal Society of Chemistry

Porphyrin-based donor–acceptor COFs as efficient and reusable photocatalysts for PET-RAFT polymerization under broad spectrum excitation†

Yifan Zhu,^{†a} Dongyang Zhu,^{†b} Yu Chen,^{†b} Qianqian Yan,^a Chun-Yen Liu,^{†b} Kexin Ling,^c Yifeng Liu,^a Dongjoo Lee,^b Xiaowei Wu,^{†de} Thomas P. Senftle^{†b} and Rafael Verduzco^{†*ab}

Covalent organic frameworks (COFs) are crystalline and porous organic materials attractive for photocatalysis applications due to their structural versatility and tunable optical and electronic properties. The use of photocatalysts (PCs) for polymerizations enables the preparation of well-defined polymeric materials under mild reaction conditions. Herein, we report two porphyrin-based donor–acceptor COFs that are effective heterogeneous PCs for photoinduced electron transfer-reversible addition–fragmentation chain transfer (PET-RAFT). Using density functional theory (DFT) calculations, we designed porphyrin COFs with strong donor–acceptor characteristics and delocalized conduction bands. The COFs were effective PCs for PET-RAFT, successfully polymerizing a variety of monomers in both organic and aqueous media using visible light (λ_{max} from 460 to 635 nm) to produce polymers with tunable molecular weights (MWs), low molecular weight dispersity, and good chain-end fidelity. The heterogeneous COF PCs could also be reused for PET-RAFT polymerization at least 5 times without losing photocatalytic performance. This work demonstrates porphyrin-based COFs that are effective catalysts for photo-RDRP and establishes design principles for the development of highly active COF PCs for a variety of applications.

Received 30th September 2021
Accepted 24th November 2021

DOI: 10.1039/d1sc05379e

rsc.li/chemical-science

Introduction

Covalent organic frameworks (COFs) are an emerging class of porous crystalline organic materials featuring high surface areas and excellent thermal and chemical stabilities.^{1–3} Their use as photocatalysts (PCs) is particularly intriguing because they have a high surface area for adsorption, tunable pore and surface functionalities, and variable optical and electronic properties determined by the properties of the COF building blocks.^{4–6} Prior work has taken advantage of this tunability to

increase interactions with a specific molecule or substrate, and their optical and electronic properties can also be tailored for a specific photocatalytic application.^{4,7} For example, the use of donor–acceptor building blocks increases the lifetime of excitonic carriers in a charge-transfer state,^{8–10} and the bandgap can be tuned to increase visible light adsorption.¹¹ Furthermore, the highly crystalline and conjugated structure can accelerate charge transport,⁵ and the conjugated structure in both the in-plane and stacking directions facilitates high charge carrier mobility.¹¹ In light of these attractive features, COFs have been explored as PCs for a variety of reactions and applications, including hydrogen evolution,^{12,13} carbon dioxide reduction,¹⁴ degradation of organic pollutants,¹⁵ and other organic transformations.^{16–18}

Recently, there has been significant interest in the development of PCs for reversible deactivation radical polymerization (RDRP) methodologies,^{19–21} such as atom transfer radical polymerization (ATRP)²² and reversible addition–fragmentation chain-transfer (RAFT) polymerization.²³ The use of PCs for polymerizations offers access to well-defined polymeric materials with complex architectures under mild reaction conditions,²⁰ and heterogeneous PCs offer added advantages such as easy separation, recycling, and excellent purity of the final product free of catalysts contaminants.²⁴ Examples include small molecular PCs immobilized on heterogeneous supports,²⁵

^aDepartment of Materials Science and NanoEngineering, Rice University, Houston, Texas, 77005, USA

^bDepartment of Chemical and Biomolecular Engineering, Rice University, Houston, Texas, 77005, USA. E-mail: tsenftle@rice.edu; rafaelv@rice.edu

^cDepartment of Chemistry, Rice University, Houston, Texas, 77005, USA

^dCAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of Research on the Structure of Matter (FJIRSM), Chinese Academy of Sciences, Fuzhou, 350002, China. E-mail: xmwuxiaowei@fjirsm.ac.cn

^eXiamen Key Laboratory of Rare Earth Photoelectric Functional Materials, Xiamen Institute of Rare Earth Materials (XMIREM), Haixi Institutes, Chinese Academy of Sciences, Xiamen, 361021, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1sc05379e

‡ Y. Z., D. Z., and Y. C. contributed equally to the work.



Table 1 Results from PET-RAFT polymerizations using RICE COFs^a

Monomer	Monomer	Solvent	Light sources	CTA	Time (h)	Conv. ^b (%)	$M_{n, \text{GPC}}^c$ (kDa)	$M_{n, \text{th}}^d$ (kDa)	\bar{D}^d
1 ^e	MA	DMF	Blue	BTPA	17	85.0	13.9	14.2	1.06
2	MA	DMF	Blue	BTPA	17	79.6	13.4	13.3	1.05
3	MA	DMF	Green	BTPA	24	61.8	10.9	10.4	1.10
4	MA	DMF	Red	BTPA	36	50.1	8.6	8.4	1.10
5	MA	DMAC	Blue	BTPA	17	91.3	15.7	15.2	1.07
6	MA	MeCN	Blue	BTPA	17	82.1	14.9	14.4	1.09
7	MA	Toluene	Blue	BTPA	17	61.5	10.9	10.3	1.13
8	DMA	H ₂ O	Blue	BTPA	12	92.1	19.5	17.6	1.14
9	BA	DMF	Blue	BTPA	14	74.0	16.1	18.2	1.07
10	TFEA	DMF	Blue	BTPA	14	88.9	27.0	26.3	1.06
11	MMA	DMF	Blue	CPADB	17	44.9	11.1	8.8	1.11
12	St	DMF	Blue	CPADB	29	32.9	9.3	6.8	1.09

^a General conditions: target DP = 190. COF loading = 1 mg ml⁻¹. Light intensity = 15 mW cm⁻². RICE-2 was used as PC except for entry 1.

^b Conversion was measured by ¹H NMR. ^c M_n measured by GPC in tetrahydrofuran, based on linear polystyrene as the calibration standard.

^d $M_{n, \text{th}} = \text{DP} \times \text{conversion} \times \text{MW} (\text{monomer}) + \text{MW} (\text{initiator})$. ^e RICE-1 was used as PC.

61.5% for the same reaction time while still maintaining a low \bar{D} of 1.13 (Table 1, entry 7). Moreover, RICE-2 COF successfully photocatalyzed PET-RAFT polymerization in water. Aqueous phase polymerization is always of general interest as it provides both environmentally friendly reaction conditions and access to functional hydrophilic polymers, which could be useful for specific bio-applications.^{43–45} The polymerization of water-soluble monomer *N,N*-dimethylacrylamide (DMA) was rapid, giving rise to 92.1% monomer conversion in 12 hours (Table 1, entry 8). An increased k_p^{app} of the polymerization of DMA was also observed with the increased dielectric constant of the solvents (Fig. S16 and S17[†]). More importantly, we observed a high level of functional group tolerance for the PET-RAFT polymerization catalyzed by COF. The polymerization of butyl acrylate (BA) and 2,2,2-trifluoroethyl acrylate (TFEA) were successful, and we achieved considerable monomer conversions of 74.0% and 88.9%, respectively (Table 1, entries 9–10), after 14 hours of irradiation without sacrificing control over the polymerization reaction. Furthermore, we achieved 44.8% monomer conversion for the polymerization of methyl methacrylate (MMA) with a slightly higher \bar{D} of 1.11 compared to acrylates (Table 1, entry 11). We found that the polymerization of styrene (St) was relatively slow and had only 32.9% conversion after 29 hours of reaction time (Table 1, entry 12). We attribute this to the lower reactivity of styrene compared to acrylates.⁴⁶

Strong evidence for a living polymerization mechanism was obtained through chain extension studies and kinetic analysis of chain growth. As shown in Fig. 3c, we successfully chain extended poly(methyl acrylate) (PMA) using a macroinitiator with M_n of 7.2 kDa to produce a final polymer with M_n of 23.9 kDa and a low \bar{D} of 1.11, indicative of living characteristics. Furthermore, as shown in Fig. 3d and e the polymerization followed first-order kinetics as evidenced by the linear relationship of $\ln([M]_0/[M])$ versus the irradiation time, the linear increase in M_n with monomer conversion, and decreased \bar{D} with increased monomer conversion. A high degree of temporal control of the polymerization was illustrated by light “on” and “off” experiments (Fig. 3f), with no polymerization even for

a dark period as long as 1100 minutes. Based on these results, we propose a PET-RAFT polymerization mechanism *via* the oxidation quenching cycle (Scheme 2). Briefly, after irradiation, photoexcited COF electrons reduce dormant RAFT chain transfer agents (CTAs), giving rise to radical species which can initiate or propagate chain growth, participate in the chain transfer process, or deactivate through reaction with the oxidized COF radical cations to form dominant state polymers and the ground-state COFs.

An important advantage of heterogeneous catalysts such as COFs over small molecular catalysts is that they can be easily recycled and reused. In our studies, RICE-2 was easily separated from the reaction mixture by centrifugation. The UV-vis of the reaction mixture after removing COFs showed negligible absorption or scattering peaks attributed to COF (Fig. S18[†]). Furthermore, PXRD and FT-IR showed that recycled COF maintained its crystallinity and structural integrity after reaction (Fig. S19 and S20[†]). The COF could be reused for PET-RAFT polymerization of MA at least 5 times, reaching stable monomer conversions (around 80%) and small $\bar{D} < 1.15$ (Fig. S21 and Table S2[†]). The recyclability is also comparable to previously reported efficient PC, MOF-525 (Zn) (Table S3[†]).³⁰

Conclusions

In conclusion, we developed two porphyrin-based donor-acceptor COFs as PCs with a broad spectrum absorption. These COFs had exceptional photocatalytic performance in the PET-RAFT polymerization of various monomers under different solvents and irradiation conditions, resulting in high monomer conversions, excellent control over MW, and narrow molecular weight dispersities. The COF photocatalyzed RAFT polymerization exhibited features of a living polymerization reaction, including excellent temporal control over the polymerization, high chain-end fidelity of products, and a linear growth in polymer molecular weight with monomer conversion. This study demonstrates how COF photocatalysts can be rationally designed through proper choice of building blocks and



provides opportunities for leveraging COFs as photocatalysts for a wide range of applications.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

Author contributions

Y. Z., D. Z. and R. V. designed and conceptualized the research; Y. Z., D. Z., Q. Y., K. L., Y. L. and D. L. performed research; Y. C., C. Y. L. and T. P. S. performed the DFT analysis; all authors analyzed the data and discussed the results; Y. Z., D. Z., Y. C., C. Y. L., X. W., T. P. S. and R. V. wrote and revised the paper. R. V supervised the whole project.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

R. V. acknowledges financial support from the Army Research Laboratory (W911NF-18-2-0062), the Welch Foundation for Chemical Research (C-1888), and NSF Nanosystems Engineering Research Center for Nanotechnology-Enabled Water Treatment (ERC1449500). T. P. S. acknowledge financial support from Rice startup funds. X. W thanks the National Natural Science Foundation of China (22105202) and Natural Science Foundation of Jiangsu Province (BK20200476).

References

- K. Geng, T. He, R. Liu, S. Dalapati, K. T. Tan, Z. Li, S. Tao, Y. Gong, Q. Jiang and D. Jiang, *Chem. Rev.*, 2020, **120**, 8814–8933.
- S. Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548–568.
- R. P. Bisbey and W. R. Dichtel, *ACS Cent. Sci.*, 2017, **3**, 533–543.
- J. Guo and D. Jiang, *ACS Cent. Sci.*, 2020, **6**, 869–879.
- D. D. Medina, T. Sick and T. Bein, *Adv. Energy Mater.*, 2017, **7**, 1700387.
- H. Wang, H. Wang, Z. Wang, L. Tang, G. Zeng, P. Xu, M. Chen, T. Xiong, C. Zhou, X. Li, D. Huang, Y. Zhu, Z. Wang and J. Tang, *Chem. Soc. Rev.*, 2020, **49**, 4135–4165.
- K. D. Q Wang, *Chem. Rev.*, 2020, **120**, 919–985.
- T. Banerjee, F. Podjaski, J. Kröger, B. P. Biswal and B. V. Lotsch, *Nat. Rev. Mater.*, 2020, **6**, 168–190.
- P. Pachfule, A. Acharjya, J. Roeser, R. P. Sivasankaran, M. Y. Ye, A. Brückner, J. Schmidt and A. Thomas, *Chem. Sci.*, 2019, **10**, 8316–8322.
- J. Zhao, J. Ren, G. Zhang, Z. Zhao, S. Liu, W. Zhang and L. Chen, *Chem. –Eur. J.*, 2021, **27**, 10781–10797.
- J. Byun and K. A. I. Zhang, *Mater. Horizons*, 2020, **7**, 15–31.
- E. Jin, Z. Lan, Q. Jiang, K. Geng, G. Li, X. Wang and D. Jiang, *Chem.*, 2019, **5**, 1632–1647.
- X. Wang, L. Chen, S. Y. Chong, M. A. Little, Y. Wu, W. H. Zhu, R. Clowes, Y. Yan, M. A. Zwijnenburg, R. S. Sprick and A. I. Cooper, *Nat. Chem.*, 2018, **10**, 1180–1189.
- Z. Fu, X. Wang, A. M. Gardner, X. Wang, S. Y. Chong, G. Neri, A. J. Cowan, L. Liu, X. Li, A. Vogel, R. Clowes, M. Bilton, L. Chen, R. S. Sprick and A. I. Cooper, *Chem. Sci.*, 2020, **11**, 543–550.
- S.-Y. Hu, Y.-N. Sun, Z.-W. Feng, F.-O. Wang and Y. Lv, *Chemosphere*, 2022, **286**, 131646.
- S. Li, L. Li, Y. Li, L. Dai, C. Liu, Y. Liu, J. Li, J. Lv, P. Li and B. Wang, *ACS Catal.*, 2020, **10**, 8717–8726.
- R. Chen, J.-L. Shi, Y. Ma, G. Lin, X. Lang and C. Wang, *Angew. Chem., Int. Ed.*, 2019, **58**, 6430–6434.
- X. Kang, X. Han, C. Yuan, C. Cheng, Y. Liu and Y. Cui, *J. Am. Chem. Soc.*, 2020, **142**, 16346–16356.
- N. Corrigan, S. Shanmugam, J. Xu and C. Boyer, *Chem. Soc. Rev.*, 2016, **45**, 6165–6212.
- M. Chen, M. Zhong and J. A. Johnson, *Chem. Rev.*, 2016, **116**, 10167–10211.
- A. M. Doerr, J. M. Burroughs, S. R. Gitter, X. Yang, A. J. Boydston and B. K. Long, *ACS Catal.*, 2020, **10**, 14457–14515.
- J. C. Theriot, C.-H. Lim, H. Yang, M. D. Ryan, C. B. Musgrave and G. M. Miyake, *Science*, 2016, **352**, 1082–1086.
- J. Xu, K. Jung, A. Atme, S. Shanmugam and C. Boyer, *J. Am. Chem. Soc.*, 2014, **136**, 5508–5519.
- Y. Zhu and E. Egap, *ACS Polym. Au*, 2021, **1**, 76–99.
- S. Shanmugam, S. Xu, N. N. M. Adnan and C. Boyer, *Macromolecules*, 2018, **51**, 779–790.
- Y. Zhu, Y. Liu, K. A. Miller, H. Zhu and E. Egap, *ACS Macro Lett.*, 2020, **9**, 725–730.
- Y. Zhu and E. Egap, *Polym. Chem.*, 2020, **11**, 1018–1024.
- Y. Zhu, T. Jin, T. Lian and E. Egap, *J. Chem. Phys.*, 2021, **154**, 204903.
- K. Hakobyan, T. Gegenhuber, C. S. P. McErlean and M. Müllner, *Angew. Chem., Int. Ed.*, 2019, **58**, 1828–1832.
- L. Zhang, X. Shi, Z. Zhang, R. P. Kuchel, R. Namivandi-Zangeneh, N. Corrigan, K. Jung, K. Liang and C. Boyer, *Angew. Chem.*, 2021, **133**, 5549–5556.
- L. Zhang, G. Ng, N. Kapoor-Kaushik, X. Shi, N. Corrigan, R. Webster, K. Jung and C. Boyer, *Angew. Chem., Int. Ed.*, 2021, **60**, 22664–22671.
- Y. Huang, X. Li, Y. C. Zhang, Z. Shi, L. Zeng, J. Xie, Y. Du, D. Lu, Z. Hu, T. Cai and Z. Luo, *ACS Appl. Mater. Interfaces*, 2021, **13**, 44488–44496.
- J. Jiang, G. Ye, F. Lorandi, Z. Liu, Y. Liu, T. Hu, J. Chen, Y. Lu and K. Matyjaszewski, *Angew. Chem., Int. Ed.*, 2019, **58**, 12096–12101.
- Z. Lu, X. Fu, H. Yang, Y. Zhao, L. Xiao and L. Hou, *Polym. Chem.*, 2021, **12**, 183–188.
- Z. Lu, H. Yang, X. Fu, R. Zhao, Y. Zhao, J. Cai, L. Xiao and L. Hou, *Eur. Polym. J.*, 2021, **157**, 110670.
- Z. Lu, H. Yang, X. Fu, Y. Zhao, L. Xiao, Z. Zhang and L. Hou, *Macromol. Rapid Commun.*, 2021, 2100384.
- K. Wang, X. Kang, C. Yuan, X. Han, Y. Liu and Y. Cui, *Angew. Chem., Int. Ed.*, 2021, **60**, 19466–19476.



- 38 S. Shanmugam, J. Xu and C. Boyer, *J. Am. Chem. Soc.*, 2015, **137**, 9174–9185.
- 39 Y. Zhu, D. Zhu, Q. Yan, G. Gao, J. Xu, Y. Liu, S. B. Alahakoon, M. M. Rahman, P. M. Ajayan, E. Egap and R. Verduzco, *Chem. Mater.*, 2021, **33**, 6158–6165.
- 40 M. O'Keeffe, M. A. Peskov, S. J. Ramsden and O. M. Yaghi, *Acc. Chem. Res.*, 2008, **41**, 1782–1789.
- 41 F. Ambrosio, J. Wiktor, F. De Angelis and A. Pasquarello, *Energy Environ. Sci.*, 2018, **11**, 101–105.
- 42 S. Shanmugam, J. Xu and C. Boyer, *Angew. Chem., Int. Ed.*, 2016, **55**, 1036–1040.
- 43 T. Zhang, J. Yeow and C. Boyer, *Polym. Chem.*, 2019, **10**, 4643–4654.
- 44 J. Xu, K. Jung, N. A. Corrigan and C. Boyer, *Chem. Sci.*, 2014, **5**, 3568.
- 45 Y. Zhu, E. Ramadani and E. Egap, *Polym. Chem.*, 2021, **12**, 5106–5116.
- 46 Y. Huang, Y. Zhu and E. Egap, *ACS Macro Lett.*, 2018, **7**, 184–189.

