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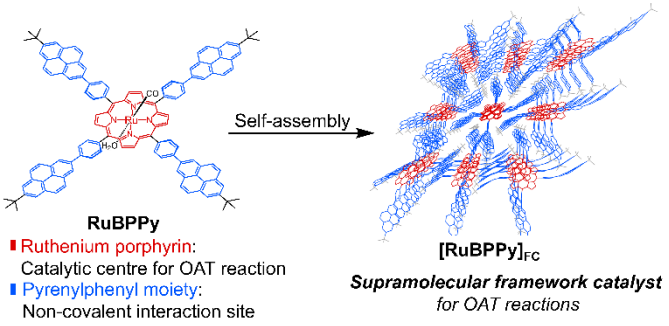
A new microporous supramolecular-framework Ru(II)–porphyrin catalyst containing non-covalent interactions between pyrenylphenyl moieties at the *meso*-position of the porphyrin ring is synthesised and structurally characterised. This recyclable catalyst expedites styrene epoxidation more efficiently than homogeneous Ru–porphyrin catalytic systems.

Catalysts for oxygen atom transfer (OAT) reactions have recently gained significant attention in both synthetic and biological systems.[1–3] Theses reactions, with metal-oxo species comprising the key active species, facilitate the conversion of hydrocarbons into alcohols and epoxides, which are valuable raw materials for chemical products.[1] In nature, Fe–porphyrins in cytochrome P450 enzymes are capable of catalysing a variety of OAT reactions under mild conditions *via* Fe-oxo intermediates.[2] Inspired by this natural system, metalloporphyrins have been studied and applied as catalysts for OAT reactions over the past half century.[4] Among them, Ru–porphyrins have received considerable attention because of the rich coordination and redox chemistry of Ru as well as its close periodic relationship with the biologically significant metal iron.[5]

In the catalytic oxidation reaction of Ru–porphyrins, Ru–oxo–porphyrin complexes show three different oxidation states with $[Ru^{VI}(por)(O)_2]$,[6] $[Ru^{V}(por)(O)(L)]$,[7] and $[Ru^{IV}(por)(O)(L)]$[8] (por = porphyrin in general, L = monodentate ligand) as active species that can oxidize a wide variety of organic substrates, particularly various alkenes, benzylic hydrocarbons, and arenes.[9] Notably, Ru–porphyrins can be activated by mild oxidants such as heteroaromatic *N*-oxides.[6d] Due to these unique properties, Ru–porphyrins exhibit high potential as catalysts for OAT reactions; the literature contains several examples of Ru–porphyrins that function as catalysts for OAT reactions.[9]

Scheme 1 Schematics of the structure and features of the new Ru–porphyrin complex (**RuBPPy**) developed in this work and the supramolecular framework ($[\mathbf{RuBPPy}]_{FC}$) construction strategy



The heterogenization of Ru–porphyrins could improve their catalytic performance. To date, there are many reports on the synthesis of molecule-based heterogeneous-framework catalysts by the self-assembly of metal complexes through coordination bonds (forming metal–organic frameworks (MOFs))[10–12] or non-covalent interactions.[13,14] These framework catalysts generally show unique features derived from the catalytic centres immobilized in their structures and a heterogeneous porous nature. Thus, catalytic materials enabling the accumulation of substrates, a high reaction selectivity and recyclable properties can be synthesized. However, the literature contains very few reports on molecule-based heterogeneous framework catalysts containing Ru–porphyrins.[15] Furthermore, to the best of our knowledge, no Ru–porphyrin-based heterogenous framework catalysts for OAT reactions are reported to date.

Herein, we report the development of a new Ru–porphyrin-based supramolecular-framework catalyst containing non-covalent interactions for styrene epoxidation. A Ru(II)–

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porphyrin complex with pyrenylphenyl moieties at the *meso* position, aquacarbonyl{5,10,15,20-tetrakis(4-(7-tert-butyl)pyrene-2-yl)phenyl)porphyrinato}ruthenium(II) (**RuBPPy**), was used as the building unit of the catalyst. **RuBPPy** contains two key features: a Ru-based catalytic centre for the OAT reaction and pyrene moieties as non-covalent interaction sites (Scheme 1). The self-assembly of **RuBPPy** *via* non-covalent interactions results in the supramolecular framework catalyst, [**RuBPPy**]$_{FC}$, which shows excellent OAT catalysis.

For the synthesis of **RuBPPy**, the free base porphyrin 5,10,15,20-tetrakis(4-(7-tert-butyl)pyrene-2-yl)phenyl) porphyrin (**HBPPy**), which was synthesised according to a previously reported procedure,[13d] was reacted with $Ru_3(CO)_{12}$ for 3 h in 1,2,4-trichlorobenzene at 165 °C under argon (Scheme S1, ESI†).[7d] The formation of **RuBPPy** was confirmed by NMR spectroscopy, UV–vis spectroscopy, and elemental analysis (Figs. S1-3, ESI†).

The UV–vis absorption spectrum of **RuBPPy** exhibited bands attributed to pyrene moieties at 313, 326, and 342 nm, a Soret band at 418 nm, and Q-bands at 532 and 566 nm (Fig. S3, ESI†). Compared with the spectrum of **HBPPy**, a blue shift of the Soret band and reduction in the number of Q-bands were observed in the spectrum of **RuBPPy**, confirming Ru-ion insertion into the porphyrin ring of **RuBPPy**. The cyclic voltammogram of **RuBPPy** in a tetra-*n*-butyl ammonium perchlorate (TBAP) / 1,2-dichlorobenzene solution (0.1 M) indicated one reversible oxidation and one reversible reduction wave at 0.30 and –2.15 V (*vs*. Fc/Fc$^+$), respectively (Fig. S6, ESI†), corresponding to porphyrin-centred redox, as reported in the literature.[16]

Subsequently, the formation of a framework catalyst *via* the self-assembly of **RuBPPy** was investigated. To produce single crystals of as-synthesised **RuBPPy** (i.e., [**RuBPPy**]$_{as\text{-}syn}$, Figs. S7 and 8 and Table S2, ESI†, the description of the crystal structure), an **RuBPPy** solution in a mixed solvent comprising chloroform and acetonitrile (2:1) was gradually evaporated. The removal of residual solution from the crystals of [**RuBPPy**]$_{as\text{-}syn}$ and drying at 25 °C *in vacuo* afforded dried crystals ([**RuBPPy**]$_{FC}$). The single-crystal X-ray diffraction (SC–XRD) analysis of [**RuBPPy**]$_{FC}$ indicated that self-assembled **RuBPPy** comprised the supramolecular framework of [**RuBPPy**]$_{FC}$ in the triclinic system with the *P*-1 space group. Figure 1a and Table S3 (ESI†) contain an Oak Ridge Thermal Ellipsoid Program (ORTEP) drawing and summary of the crystallographic data of [**RuBPPy**]$_{FC}$,

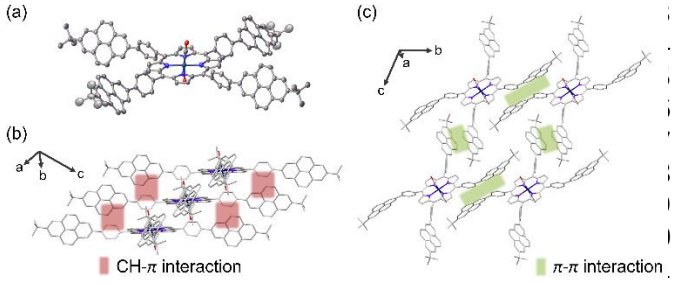

Fig. 1 a) An ORTEP drawing of **RuBPPy** (50% probability ellipsoids). Hydrogen atoms and disordered atoms are omitted for clarity. C = gray, N = blue, O = red, and Ru = dark blue. b) 1D columnar structure of [**RuBPPy**]$_{FC}$. c) Intercolumnar interactions observed in [**RuBPPy**]$_{FC}$.

respectively. The Ru–N distance (2.046(3)–2.057(3) Å) in the synthesized crystals lies within the normal range of Ru–N distances in similar porphyrin-based Ru(II) compounds (Table S4, ESI†).[6f,6g,17] Moreover, the coordination of carbon monoxide and water molecules at the axial positions indicates the presence of an Ru(II) centre in the system.[6f,6g] Notably, the packing structure of the crystal comprises a 1D columnar structure stabilised by CH–π interactions between the pyrenylphenyl rings along the *a* axis (Fig. 1b), which is further stabilised by π–π interactions between the pyrenyl and phenyl moieties (Fig. 1c), resulting in the formation of a porous framework structure (Fig. S9, ESI†). Considering the van der Waals radii of the constituent atoms, the size of the pore entrance is estimated to be 4.8×2.8 Å^2. Therefore, pyrenylphenyl moieties contribute towards the formation and maintenance of the supramolecular framework structure of [**RuBPPy**]$_{FC}$, even after the removal of guest solvent molecules.

The diffuse reflectance spectrum of [**RuBPPy**]$_{FC}$ contained characteristic absorption bands at 328 and 343 nm corresponding to pyrene moieties, a Soret band at 421 nm, and Q-bands at 537 and 572 nm attributed to the Ru–porphyrin moiety (Fig. S4a, ESI†), similar to the absorption bands of **RuBPPy** in the solution state (*vide supra*). The FT–IR spectrum of [**RuBPPy**]$_{FC}$ contained the characteristic carbonyl stretching band of the coordinated axial ligand at 1949 cm^{-1} and a sharp band corresponding to the rocking vibration of the pyrrole units of the porphyrin ring at 1006 cm^{-1} (Fig. S5, ESI†), indicating the formation of the Ru(II) state.[18]

The experimental powder X-ray diffraction (PXRD) pattern and simulated spectrum constructed using single-crystal diffraction data were consistent, confirming the phase purity of [**RuBPPy**]$_{FC}$ (Fig. S4b, ESI†). This framework is stable in cyclohexane, hexane, acetonitrile and mixed solvents (Fig. S9, ESI†). The CO_2 adsorption isotherm was measured at 195 K to investigate the porosity of [**RuBPPy**]$_{FC}$ (Fig. S4c, ESI†). The maximum uptake was 71 cm^3 g^{-1}, which is comparable to some previously reported porphyrin-based supramolecular frameworks.[13d,19] The Brunauer–Emmett-Teller (BET) surface area was estimated to be 206 m^2 g^{-1}. The thermogravimetric analysis (TGA) of the sample (dried at 80 °C for 30 min *in vacuo*) within 25–600 °C under N_2 flow with a heating rate of 2 °C min^{-1} was used to investigate the thermal stability of [**RuBPPy**]$_{FC}$ (Fig. S4d, ESI†). [**RuBPPy**]$_{FC}$ showed a weight loss of 2.0% within 60–135 °C corresponding to the release of H_2O molecules. Subsequently, the TGA curve showed a relatively stable plateau up to 260 °C, followed by the decomposition of the framework. Therefore, [**RuBPPy**]$_{FC}$ comprises a porous molecule-based supramolecular framework that shows thermal stability up to 260 °C, retaining the characteristics of the mononuclear complex **RuBPPy**.

Next, the activity of the crystalline solid, [**RuBPPy**]$_{FC}$ in the catalytic epoxidation of styrene was examined (see the ESI† for the experimental details (P.S19). Styrene epoxidation under heterogeneous conditions by [**RuBPPy**]$_{FC}$ was carried out in a mixed solvent comprising benzene (5.0%) in cyclohexane with the mild oxidant 2,6-dichloropyridine *N*-oxide at 20 °C for 18 h in an argon atmosphere under Xe-lamp photoirradiation (400

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nm ≤ λ, 300 W). Photoirradiation was used for the decarbonylation of the Ru-centre.[20] GC-FID analysis after the reaction showed that the [**RuBPPy**]$_{FC}$-catalysed epoxidation of styrene generated styrene oxide with a turnover number (TON) of 19 without overoxidation (Table 1, Entry 1). The porphyrin skeleton is maintained in the post catalyst (Fig. S16, ESI†) and no increase of TON was observed in the filtrate from which the catalyst was removed (Fig. S12, ESI†). Control experiments conducted in the absence of [**RuBPPy**]$_{FC}$, the oxidant, or photoirradiation resulted in no epoxide production, confirming the necessity of all these elements in the target reaction (Table 1, Entry 2-4). No oxidized products were obtained under conditions in which O_2 or H_2O_2 was used instead of 2,6-dichloropyridine *N*-oxide. The catalytic activity with p-substituted styrene was investigated and the TON with non-substituted styrene was the highest in this system (Table S5, ESI†). This trend is distinct from that of previously reported systems[6h,7d,21], in which styrene derivatives with electron-donating groups exhibited higher activities. This difference in reactivity can be attributed to the effects of the pore structure of the catalyst. There was no light wavelength dependence on the catalytic activity, indicating that the excitation of the porphyrin unit is essential for the catalysis (see the ESI† (P.S22) for details). These catalytic epoxidation results indicate that styrene is oxidised by Ru-oxo species generated *via* the reaction of the photochemically decarbonylated Ru(II) centre with 2,6-dichloropyridine *N*-oxide.[22]

Subsequently, the effect of the framework structure of the catalyst on its activity was investigated by comparing the activity of **RuBPPy** (homogeneous state) with that of heterogeneous [**RuBPPy**]$_{FC}$. The time course of the reaction in Fig. 2a indicates that the TON increases linearly for a significant duration; moreover, the TON in the heterogeneous system is approximately four times higher than that in the homogenous system. In addition, the TON reached 134 for 96 h in the optimized conditions (Table S8, ESI†). Recycling tests were used to investigate the recyclability of the catalytic system. After catalysing styrene epoxidation for 18 h, [**RuBPPy**]$_{FC}$ was filtered, washed several times with acetonitrile, and dried at 70 °C for 30 min *in vacuo*. This powder was used to catalyse epoxidation in the subsequent reaction cycle. Fig. 2b shows that the catalytic activity was maintained for three cycles. Therefore, [**RuBPPy**]$_{FC}$ shows efficient catalysis, durability, and recyclability, confirming the high performance of heterogeneous Ru–porphyrin catalytic systems. The reaction mechanism for the epoxidation mediated by [**RuBPPy**]$_{FC}$ is proposed as shown in Scheme S2 (For details, see the ESI† (P.S27)). Further attempts to clarify the mechanism is underway, and the results will be reported in the future.

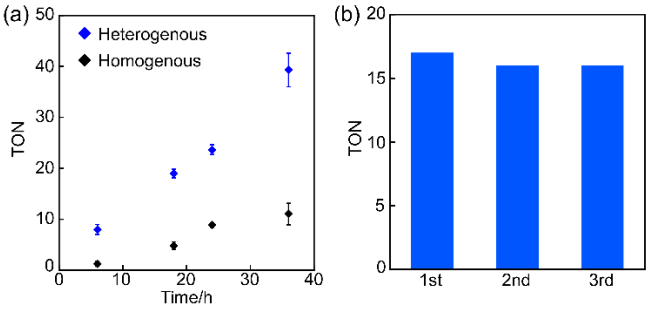
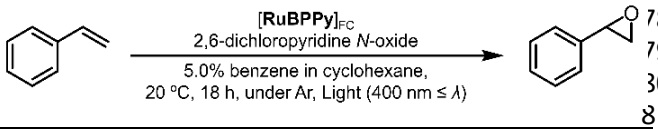


Fig. 2 (a) Time course of the TON for styrene epoxidation by [**RuBPPy**]$_{FC}$ in a heterogeneous system containing a mixed solvent (cyclohexane/benzene) (blue) and by **RuBPPy** in a homogenous system containing benzene (black). All the other reaction conditions are the same as those listed in Table 1. (b) Recyclability tests of [**RuBPPy**]$_{FC}$ for 18 h over three cycles.

Table 1 Epoxidation of styrene with 2,6-dichloropyridine *N*-oxide and [**RuBPPy**]$_{FC}$[a]



Entry	Deviation from standard conditions	TON[b]
1	None	19 ± 0.8[c]
2	No catalyst	0
3	No oxidant	0
4	No light	0

[a]Standard reaction conditions: [**RuBPPy**]$_{FC}$ = 0.14 μmol, [2,6-dichloropyridine *N*-oxide] = 7.0 mM (100 equiv.), [styrene] = 43 mM (620 equiv.) in 5.0% benzene in cyclohexane (2.0 mL) at 20 °C for 18 h under argon under visible light irradiation from a Xe lamp (400 nm ≤ λ, 300 W). [b]Determined by GC–FID based on the [**RuBPPy**]$_{FC}$. [c]Average value over 3 runs with standard deviation.

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Data Availability Statement

The data supporting this article are included as part of the ESI.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 (a) R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401–1449. (d) K. A. Joergensen, *Chem. Rev.*, 1989, **89**, 431–458. (b) Z. Chen and C. Yin, *Chem. Soc. Rev.*, 2015, **44**, 1083–1100. (c) M. Guo, F. Corona, K. Ray and W. Nam, *ACS Cent. Sci.*, 2019, **5**, 13–28. (d) G. M. Tomboc, Y. Park, K. Lee and K. Jin, *Chem. Sci.*, 2021, **12**, 8967–8995. (e) T. Ishizuka, H. Sugimoto, S. Itoh and T. Kojima, *Coord. Chem. Rev.*, 2022, **466**, 214536.

2 (a) K. D. Dubey and S. Shaik, *Acc. Chem. Res.*, 2019, **52**, 3889–399. (b) P. C. E. Moody and E. L. Raven, *Acc. Chem. Res.*, 2018, **51**, 427–435. (c) T. L. Poulos, *Chem. Rev.*, 2014, **114**, 3919–3962.

3 C. W. Koo and A. C. Rosenzweig, *Chem. Soc. Rev.*, 2021, **50**, 3424–3436.

4 (a) J. J. D. Sacramento and D. P. Goldberg, *Acc. Chem. Res.*, 2018, **51**, 2641–2652. (b) X. Huang and J. T. Groves, *Chem. Rev.*, 2018, **118**, 2491–2553. (c) M. M. Pereira, L. D. Dias and M. J. F. Calvete, *ACS Catal.*, 2018, **8**, 10784–10808. (d) Y. Yan, J. Wu, G. Hu, C. Gao, L. Guo, X. Chen, L. Liu and W. Song, *Synth. Syst. Biotechnol.*, 2022, **7**, 887–899. (e) E. Y. Tyulyaeva, *Russ. J. Inorg. Chem.*, 2023, **68**, 1537–1561.

5 (a) J. T. Groves, K. Shalyaev and J. Lee, in *The Porphyrin Handbook*, ed. K. M. S. Kadish and R. Guilard, 2000, vol. 4, pp. 17–40. (b) R. A. Sheldon, *Metalloporphyrins in Catalytic Oxidations*, Marcel Dekker, New York, 1994.

6 (a) J. T. Groves and R. Quinn, *Inorg. Chem.*, 1984, **23**, 3844–3846. (b) J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790–5792. (c) W. H. Leung and C. -M. Che, *J. Am. Chem. Soc.*, 1989, **111**, 8812–8818. (d) H. Ohtake, T. Higuchi and M. Hirobe, *heterocycles*, 1995, **40**, 867–903. (e) R. Zhang, W. Yu and C.-M. Che, *Tetrahedron Asymmetry*, 2005, **16**, 3510–3526. (f) E. Gallo, A. Caselli, F. Ragaini, S. Fantauzzi, N. Masciocchi, A. Sironi and S. Cenini, *Inorg. Chem.*, 2005, **44**, 2039–2049. (g) C.-M. Che, J.-L. Zhang, R. Zhang, J.-S. Huang, T.-S. Lai, W.-M. Tsui, X.-G. Zhou, Z.-Y. Zhou, N. Zhu and C.-K. Chang, *Chem. Eur. J.*, 2005, **11**, 7040–7053. (h) C. Wang, K. Shalyaev, M. Bonchio, T. Carofiglio and J. T. Groves, *Inorg. Chem.*, 2006, **45**, 4769–4782. (i) J. Malone, S. Klaine, E. Alcantar, F. Bratcher and R. Zhang, *New J. Chem.*, 2021, **45**, 4977–4985. (j) Q. Cao, M. Diefenbach, C. Maguire, V. Krewald, M. J. Muldoon, U. Hintermair, *Chem. Sci.*, 2024, **15**, 3104-3113.

7 (a) C.-M. Che, C. Ho and T.-C. Lau, *J. Chem. Soc., Dalton Trans.*, 1991, 1259–1263. (b) E. Vanover, Y. Huang, L. Xu, M. Newcomb and R. Zhang, *Org. Lett.*, 2010, **12**, 2246–2249. (c) R. Zhang, E. Vanover, W. Luo and M. Newcomb, *Dalton Trans.*, 2014, **43**, 8749–8756. (d) K.-P. Shing, B. Cao, Y. Liu, H. K. Lee, M.-D. Li, D. L. Phillips, X.-Y. Chang and C.-M. Che, *J. Am. Chem. Soc.*, 2018, **140**, 7032–7042.

8 (a) J. T. Groves and K. H. Ahn, *Inorg. Chem.*, 1987, **26**, 3831–3833. (b) T.-H. Chen, Z. Yuan, A. Carver and R. Zhang, *Appl. Catal. A*, 2014, **478**, 275–282.

9 (a) T. Higuchi and M. Hirobe, *J. Mol. Catal. A*, 1996, **113**, 403–422. (b) C.-M. Che and J.-S. Huang, *Chem. Commun.*, 2009, **27**, 3996–4015.

10 (a) H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444. (b) H.-C. J. Zhou and S. Kitagawa, *Chem. Soc. Rev.*, 2014, **43**, 5415–5418. (c) Z. Chen, K. O. Kirlikovali, P. Li and O. K. Farha, *Acc. Chem. Res.*, 2022, **55**, 579–591.

11 (a) J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450–1459. (b) C. F. Pereira, M. M. Q. Simões, J. P. C. Tomé and F. A. A. Paz, *Molecules*, 2016, **21**, 1348. (c) Z. Wu, Y. Li, C. Zhang, X. Huang, B. Peng and G. Wang, *Chem. Catal.*, 2022, **2**, 1009–1045. (d) K.-Y. Wang, J. Zhang, Y.-C. Hsu, H. Lin, Z. Han, J. Pang, Z. Yang, R.-R. Liang, W. Shi and H.-C. Zhou, *Chem. Rev.*, 2023, **123**, 5347–5420.

12 (a) O. K. Farha, A. M. Shultz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, *J. Am. Chem. Soc.*, 2011, **133**, 5652–5655. (b) X.-L. Yang, M.-H. Xie, C. Zou, Y. He, B. Chen, M. O'Keeffe and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 10638–10645. (c) Z. Wang, P. Yeary, X. Feng and W. Lin, *J. Am. Chem. Soc.*, 2023, **145**, 8647–8655. (d) K. Hou, J. Börgel, H. Z. H. Jiang, D. J. SantaLucia, H. Kwon, H. Zhuang, K. Chakarawet, R. C. Rohde, J. W. Taylor, C. Dun, M. V. Paley, A. B. Turkiewicz, J. G. Park, H. Mao, Z. Zhu, E. E. Alp, J. Zhao, M. Y. Hu, B. Lavina, S. Peredkov, X. Lv, J. Oktawiec, K. R. Meihaus, D. A. Pantazis, M. Vandone, V. Colombo, E. Bill, J. J. Urban, R. D. Britt, F. Grandjean, G. J. Long, S. DeBeer, F. Neese, J. A. Reimer and J. R. Long, *Science*, 2023, **382**, 547–553.

13 (a) T. Itoh, M. Kondo, M. Kanaike and S. Masaoka, *CrystEngComm.*, 2013, **15**, 6122–6126. (b) T. Itoh, M. Kondo, H. Sakamoto, K. Wakabayashi, M. Kanaike, K. Itami and S. Masaoka, *Dalton Trans.*, 2015, **44**, 15334–15342. (c) P. Chinapang, M. Okamura, T. Itoh, M. Kondo and S. Masaoka, *Chem. Commun.*, 2018, **54**, 1174–1177. (d) M. Tasaki, Y. Okabe, H. Iwami, C. Akatsuka, K. Kosugi, K. Negita, S. Kusaka, R. Matsuda, M. Kondo and S. Masaoka, *Small*, 2021, **17**, e2006150. (e) K. Kosugi, C. Akatsuka, H. Iwami, M. Kondo and S. Masaoka, *J. Am. Chem. Soc.*, 2023, **145**, 10451–10457.

14 (a) Zhang Z, Li J, Yao Y, Sun S, *Cryst. Growth Des.*, 2015, **15**, 5028–5033. (b) B. Han, H. Wang, C. Wang, H. Wu, W. Zhou, B. Chen and J. Jiang, *J. Am. Chem. Soc.*, 2019, **141**, 8737–8740. (c) Q. Yin, E. V. Alexandrov, D.-H. Si, Q.-Q. Huang, Z.-B. Fang, Y. Zhang, A.-A. Zhang, W.-K. Qin, Y.-L. Li, T.-F. Liu and D. M. Proserpio, *Angew. Chem. Int. Ed.*, 2022, **134**, e202115854. (d) A.-A. Zhang, D. Si, H. Huang, L. Xie, Z.-B. Fang, T.-F. Liu and R. Cao, *Angew. Chem. Int. Ed.*, 2022, **61**, e202203955.

15 (a) L. Chen, H. Cui, Y. Wang, X. Liang, L. Zhang and C.-Y. Su, *Dalton Trans.*, 2018, **47**, 3940–3946. (b) G. M. Eder, D. A. Pyles, E. R. Wolfson and P. L. McGrier, *Chem. Commun.*, 2019, **55**, 7195–7198.

16 D. P. Rillema, J. K. Nagle, L. F. Barringer Jr. and T. J. Meyer, *J. Am. Chem. Soc.*, 1981, **103**, 56–62.

17 (a) J. J. Bonnet, S. S. Eaton, G. R. Eaton, R. H. Holm and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 2141–2149. (b) G. Jiang, J. Chen, H.-Y. Thu, J.-S. Huang, N. Zhu and C.-M. Che, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 6638–6642.

18 C.-M. Che and W.-Y. Yu, *Pure & Appl. Chem.*, 1999, **71**, 281–288.

19 (a) W. Yang, B. Li, H. Wang, O. Alduhaish, K. Alfooty, M. A. Zayed, P. Li, H. D. Arman and B. Chen, *Cryst. Growth Des.*, 2015, **15**, 2000–2004. (b) Q. Yin, J. Lü, H.-F. Li, T.-F. Liu and R. Cao, *Cryst. Growth Des.*, 2019, **19**, 4157–4161.

20 K. Ishii, S. Hoshino and N. Kobayashi, *Inorg. Chem.*, 2004, **43**, 7969–7971.

21 J.-L. Zhang and C.-M. Che, *Chem. Eur. J.*, 2005, **11**, 3899–3914.

22 J. T. Groves, M. Bonchio, T. Carofiglio and K. Shalyaev, *J. Am. Chem. Soc.*, 1996, **118**, 8961–8962.

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Data availability statements

The data supporting this article have been included as part of the Supplementary Information.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 2368114 for [**RuBPPy**]$_{\text{as-syn}}$ and 2368115 for [**RuBPPy**]$_{\text{FC}}$. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.