## **Supplementary Information**

# Structural Isomers of Imine-Linked Covalent Organic Cages with Divergent Photocatalytic Properties

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#### Section S1. General Materials and Methods

#### 1.1 Materials

All reagents were commercially available and used as received without further purification. Tris(4aminophenyl)amine (97%), tris(4-formylphenyl)amine (95%), and scandium(III) triflate (Sc(OTf)<sub>3</sub>, 99%) were purchased from Bide Pharmatech Co., Ltd. (China). 1,8-Dichloroanthraquinone ( $\geq$ 98%), 1,8-dinitroanthraquinone (96%), sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O, 99%), zinc powder (99.99%), copper(I) cyanide (CuCN, 99%), tetrabutylammonium tetrafluoroborate (TBA·BF<sub>4</sub>, 98%), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, 99.0%), nafion d-520 dispersion (5%), diisobutylaluminium hydride (DIBAL-H, 1.0 M solution in hexane), methylene blue trihydrate (MBT,  $\geq$ 82.0%), rhodamine B (RhB), sodium borohydride (NaBH<sub>4</sub>, 98.0%), ammonium hydroxide (NH<sub>4</sub>OH, 25-28%), molecular sieve (3Å, 99.9%), N-methyl-2-pyrrolidinone (NMP, 99.5%), acetonitrile (99.9%) and pyridine (99.5%) were purchased from Shanghai Titan Scientific Co., Ltd. (China). N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), dichloromethane (DCM), 1,2-dichloroethane (DCE), chloroform (CHCl<sub>3</sub>), ethanol (EtOH), methanol (MeOH), isopropanol, petroleum ether (PE), and HCl (37%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water (DW) with a resistivity of 18.25 MΩ was used to prepare aqueous solutions.

#### 1.2 Characterization

Nuclear Magnetic Resonance (NMR): NMR spectra were measured using a Bruker Avance 500 (500 MHz) instrument at room temperature. The chemical structures of the synthesized compounds were recorded in CDCl<sub>3</sub> or DMSO- $d_6$  with an internal deuterium lock to ensure the stability of the residual protons. The solid-state <sup>13</sup>C CP/MAS NMR spectra of COC isomers were measured using a Bruker AVANCE NEO 500 (500 MHz) instrument at room temperature.

**Mass Spectrometry (MS):** Mass spectra of the synthesized compounds were taken on a Quadrupole Time-of-Flight Mass Spectrometer (LC-MS) equipped with an ESI/APCI ion source (Bruker impact II, Germany).

**Fourier Transform Infrared (FT-IR) Spectroscopy:** FT-IR spectra were acquired with a Perkin-Elmer Paragon 100 spectrometer from 4000 to 450 cm<sup>-1</sup> at 25 °C. The sample powder was mixed with KBr and formed into pellets.

**Single Crystal X-ray Diffraction (SC-XRD):** Single crystals of COC isomers were successfully grown by slow solvent diffusion. Initially, TNCA was dissolved in DCE, and the gradual diffusion of acetonitrile into this solution resulted in the formation of needle-shaped single crystals. For TCNA, a solvent system of acetonitrile and pyridine was used. SC-XRD data were gathered with a Bruker D8 Venture diffractometer, maintaining the crystal at 100-173 K. Using Olex<sup>21</sup>, the structure was solved with the SHELXT<sup>2</sup> structure solution program using Intrinsic Phasing and refined with the SHELXL<sup>3</sup> refinement package using Least Squares minimisation..

**Ultraviolet–Visible Diffuse Reflectance Spectroscopy (DRS):** DRS of the COC isomers powder, both in the dark and under irradiation, were recorded using a Perkin-Elmer Lambda 750S UV–Vis Spectrophotometer with BaSO<sub>4</sub> as a reference. The band gaps (Eg) of the as-synthesized samples were calculated according to Eq. S1<sup>4</sup>:

$$ahv = A(hv - Eg)^{\frac{1}{n}}$$
 (Equation S1)

Here, a, v, h, Eg, and A represent the absorption coefficient, light frequency, Planck constant, band gap, and a constant, respectively. The value of n depends on the type of optical transition in the semiconductor: n = 1/2 indicates a direct band-gap transition, while n = 2 suggests an indirect transition. For COC isomers, n was set to 1/2,

reflecting its direct transition nature.

Electron Paramagnetic Resonance (EPR) Spectroscopy: EPR analysis of local lattice defects in COC isomers powder was carried out at 293 K using a Bruker EMXplus-9.5/12 spectrometer operating in the X-band ( $\approx$  9.83 GHz). The samples were exposed to a 300 W Xe lamp (LOT Oriel) with a 420 nm cutoff filter. Measurements were consistently conducted under the same parameters: microwave power of 10.02 mW, receiver gain of 30 dB, modulation amplitude of 2 G, and scan time of 60.3 s. For the detection of superoxide anion (O<sub>2</sub>··), a solution of COC isomers (10 g/L) and DMPO ( $2.0 \times 10^{-2}$  mol/L) was prepared in 5 mL of air-saturated methanol, and the EPR spectra were recorded for 5 minutes under both dark and light conditions. The hydroxyl radical (•OH) was detected in deionized water under the same conditions.

Ultraviolet–Visible (UV–Vis) and Photoluminescence (PL) Spectroscopy: UV–Vis absorption spectra were recorded with a Shimadzu UV-2600i spectrometer in the range of 800 to 200 nm. PL emission spectra and transient fluorescence lifetime of TNCA and TCNA were detected on an Fluorolog-QM visual steady state & time-resolved fluorescence spectrometry system (Horiba, Japan). PL emission spectra were measured from 700 to 415 nm. Measurements were performed using dilute solutions in degassed spectral grade dichloromethane within a 1 cm square quartz cell. A standard curve was created by measuring the absorbance of several COC isomer solutions with known concentrations. A linear calibration curve for COC isomers concentration was developed by diluting a 4.7 mg/ml COC isomers stock solution to achieve concentrations ranging from  $2.5 \times 10^{-6}$  to  $4.0 \times 10^{-5}$  mol/L. The molar extinction coefficient ( $\varepsilon$ ) of the COC isomers were calculated according to Beer-Lambert Law (Eq. S2):

$$A = \varepsilon c l \qquad (Equation S2)$$

Here, A represents absorbance,  $\varepsilon$  is the molar absorptivity of the substance, typically measured in L/(mol·cm), c represents the concentration of the substance in the solution, usually in mol/L, and l is the path length of the light through the sample, typically in cm. In this case, l=1. The linear relationship between COC isomers concentration and absorbance is shown in Figures S17-18.

**Computational Study:** Time-dependent DFT (TD-DFT) calculations for the optimized structures of COC isomers were performed using Gaussian 16w with the B3LYP/6-31G(d,p) level of theory. The results, including the energy levels of frontier molecular orbitals and the atomic charge distribution, were visualized using GaussView 6.0.

**Electrochemical Measurements:** 5 mg of COC isomers powder was mixed with 200 µl of ethanol and sonicated until the mixture became homogeneous, forming a slurry. Then, 50 µl of 5% Nafion was added to the slurry and sonicated again. The slurry was uniformly coated onto pre-treated FTO glass. After air-drying, the electrode had an effective area of 0.5 cm<sup>2</sup>. All tests were conducted on a CHI760e workstation using a standard three-electrode setup, with a platinum sheet (1 cm<sup>2</sup>) as the counter electrode and an Ag/AgCl electrode (saturated KCl) as the reference electrode. The photocurrent (i-T) measurements were conducted using a 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH 7) as the electrolyte. Visible light was directed onto the working electrode from the front, generated by a 300W xenon lamp (PLS-SXE300+/UV, Beijing Perfect Light Technology Co., Ltd.) with a 420 nm cutoff filter and manually chopped. Electrochemical impedance spectra (EIS) were measured in the dark at open-circuit voltage with a 5 mV AC amplitude across a frequency range of 0.1 Hz to 10<sup>6</sup> Hz. For Mott–Schottky (M–S) measurements, a 5 mV perturbation signal was applied with a frequency range of 2000-4000 Hz. The redox capability of COC isomers was assessed using cyclic voltametry (CV) in acetonitrile at a scan rate of 100 mV·s<sup>-1</sup>, with 0.1 M tetra-n-butylammonium tetrafluoroborate (TBA·BF4) as the supporting electrolyte.

The applied potentials vs. Ag/AgCl were converted to NHE potentials using the following equation<sup>5,6</sup>:

$$E_{RHE} = E_{(Ag/AgCl)} + 0.0591pH + E_{(Ag/AgCl)}^{\theta}$$
(Equation S3)

$$E_{\text{NHE}} = E_{(\text{Ag/AgCl})} + E_{(\text{Ag/AgCl})}^{\theta} (E_{(\text{Ag/AgCl})}^{\theta} = 0.199)$$
(Equation S4)

**Photocatalytic Dye Degradation:** In the photocatalytic process, 0.1 mg of COC isomers powder was dissolved in 50 ml of DMSO containing MBT or RhB ( $C_0 = 10 \text{ mg/L}$ ), resulting in a clear solution. This solution was stirred in the dark for 30 min to achieve adsorption-desorption equilibrium. Dye degradation was then tested under light irradiation with a 300-watt xenon lamp and a UV cutoff filter ( $\lambda > 420 \text{ nm}$ ). Samples were collected at various time intervals, and the absorbance of the supernatant at 670 nm for MBT and 564 nm for RhB was measured using a UV–Vis spectrophotometer. The reusability for MBT or RhB degradation of COC isomers was then tested by adding dye.

**Thermal gravimetric analysis (TGA):** TGA was performed on a Discovery TGA550 instrument with a heating ramp from 50 to 800 °C ( $10 \circ C \cdot min^{-1}$ ) under nitrogen atmosphere.

#### Section S2. Synthesis Procedures of COC Isomers

Anthracene-based reactants and COC isomers were synthesized following the procedures outlined in relevant literature.<sup>7,8</sup>

#### 2.1 Synthesis of anthracene-based blocks



Scheme S1. The synthetic route of An-2NH<sub>2</sub> and An-2CHO.

**Synthesis of Aq-2NH<sub>2</sub>:** (yield 99%).1,8-Dinitroanthraquinone (10.00 g, 33.53 mmol) and  $Na_2S \cdot 9H_2O$  (30.60 g, 127.40 mmol) were refluxed overnight in a solution of EtOH (161.30 ml) and DW (645.20 ml) under nitrogen atmosphere. After cooling to room temperature, the mixture was poured into ice water to stop the reaction. The red precipitate was filtered, washed with excess water, and vacuum-dried to yield 8.00 g of red powder.

Synthesis of An-2NH<sub>2</sub>: (yield 57%). Nitrogen gas was introduced into a solution of Aq-NH<sub>2</sub> (6.00 g, 25.18 mmol) in isopropanol (250 ml) for 15 minutes using a double-neck flask. NaBH<sub>4</sub> (12.00 g, 317.21 mmol) was subsequently added to the reaction mixture. The reaction was then refluxed under nitrogen atmosphere and in the dark for 60 hours. After cooling to room temperature, the excess NaBH<sub>4</sub> was quenched by transferring the reaction mixture to an ice-water bath (750 mL). The resulting suspension was filtered, and the residue was washed with water and PE. The product was purified by column chromatography on silica gel, with a 0-5% methanol solution in DCM as the eluent. The final product was obtained as a dark red solid with a total amount of 3.00 g. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d, *J* = 13.7 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.31 (s, 1H), 7.29 (s, 1H), 6.76 (d, *J* = 7.3 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  142.06, 132.48, 127.16, 126.03, 123.10, 119.31, 113.03, 107.94. MS (ESI): Calculated for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>, [M+H]<sup>+</sup> 209.1073, found 209.1078.

Synthesis of An-2Cl: (yield 47%). 1,8-Dichloroanthraquinone (10.00 g, 36.00 mmol) and NH<sub>4</sub>OH (400 ml) were added to a 1000 ml reaction flask equipped with a reflux condenser. When the reaction mixture was cooled to 10 °C, activated Zn powder (50.00 g) was added in batches over 15 minutes and stirred vigorously. The reddishbrown mixture was then gradually heated to 100 °C and refluxed for 4 hours. After cooling down to room temperature, the reaction mixture was filtered. The filtrate was extracted with DCM and concentrated under reduced pressure. The remaining solids were redissolved in isopropanol (200 ml) and recrystallized at 80 °C, resulting in 4.20 g of light yellow needle-like crystals. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.30 (s, 1H), 8.51 (s, 1H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 8.1 Hz, 2H).

Synthesis of An-2CN: (yield 67%). A 100 ml two-neck round-bottom flask equipped with a reflux condenser was

charged with An-2Cl (4.67 g, 19.00 mmol), CuCN (7.40 g, 83.00 mmol), and dry NMP (50 ml). The mixture was refluxed under a nitrogen atmosphere. After 17 hours, additional CuCN was added, and the reaction continued for another 50 hours. The mixture was then cooled in an ice bath and poured into 100 ml of water with vigorous stirring. Aqueous NH<sub>4</sub>OH (100 ml) was added, and the mixture was stirred for 2 days. The resulting brown precipitate was filtered, washed with water, and retreated with aqueous NH<sub>4</sub>OH (20 ml). After further filtration and washing with water. The solid was then filtered, washed, dried, and recrystallized from DMF (300 mL) to yield 2.9 g of pure An-2CN. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.15 (s, 1H), 8.65 (s, 1H), 8.30 (d, *J* = 8.6 Hz, 2H), 8.07 (d, *J* = 7.0 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H).

**Synthesis of An-2CHO:** (yield 79.0%). An-2CN (2.25 g, 9.86 mmol) was dissolved in dry DCM (100 ml) under argon for 10 minutes. The solution was cooled to 0 °C and treated with DIBAL-H (20 mL of 1 M hexane solution, 20 mmol) via syringe, followed by an additional 10 ml after 15 minutes. The mixture was stirred at 0 °C for 15 minutes, then at room temperature for 30 minutes. It was poured into aqueous sulfuric acid (50%, 80 ml) at 0 °C, generating aluminum salts. The mixture was diluted with water (100 ml), and the aqueous layer was extracted with DCM. The organic extracts were washed with water, dried over MgSO<sub>4</sub>, filtered, and purified by column chromatography on silica gel with DCM/PE (5:1 v/v) as the eluent. The final product was obtained as a bright yellow solid with a total yield of 1.80 g. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  11.19 (s, 1H), 10.61 (s, 2H), 8.60 (s, 1H), 8.30 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 6.8 Hz, 2H), 7.70 (d, *J* = 8.5, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  192.87, 137.77, 135.59, 132.13, 131.75, 129.53, 128.09, 125.16, 121.71. MS (ESI): Calculated for C<sub>16</sub>H<sub>10</sub>O<sub>2</sub>, [M+Na]<sup>+</sup> 257.0573, found 257.0572.

#### 2.2 Synthesis of COC Isomers



Scheme S2. The synthetic route of TNCA.

**Synthesis of TNCA:** (yield 74%). Under nitrogen, a CH<sub>3</sub>CN (5 mL) solution of Sc(OTf)<sub>3</sub> (20 mg, 0.04 mmol) was dropped in a mixture of 4,4',4"-triaminotriphenylamine (90.00 mg, 0.31 mmol), An-2CHO (108.80 mg, 0.47 mmol), and 3 Å molecular sieves in DMF (100 ml). The brown-red solution was stirred at room temperature for 1 day, then filtered through a short silica gel column to remove insoluble polymer and sieves. DMF was evaporated by vacuum distillation, and the residue was dissolved in a small amount of DCM. Adding 400 ml of PE caused the precipitation of the cage-shaped TNCA (0.14 g) as brown-red powder. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  11.60 (s, 1H), 9.42 (s, 2H), 8.83 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 2H), 8.22 (d, *J* = 7.7 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 4H), 7.17 (d, *J* = 8.6 Hz, 4H). MS (APCI): Calculated for C<sub>84</sub>H<sub>54</sub>N<sub>8</sub>, [M] 1175.4544, found 1175.4592.



Scheme S3. The synthetic route of TCNA.

Synthesis of TCNA: (yield 45%). The imine cage TCNA was obtained as an orange powder from a DCM solution containing 3 equivalents of An-NH<sub>2</sub> and 2 equivalents of 4,4',4"-nitrilotribenzaldehyde, using the same synthesis procedure. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) 1H NMR (500 MHz, DMSO-d6)  $\delta$  9.28 (s, 1H), 8.65 (s, 2H), 8.58 (s, 1H), 8.14 (d, J = 8.6 Hz, 4H), 7.96 (d, J = 8.5 Hz, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.34 (d, J = 8.5 Hz, 4H), 7.16 (d, J = 7.0 Hz, 2H). MS (APCI): Calculated for C<sub>84</sub>H<sub>54</sub>N<sub>8</sub>, [M] 1175.4544, found 1175.4822.

# Section S3. Supplemental Data

Entry	Туре	Isomer types	Reference
1	COC	Structural isomer from linkage orientation	This work
2	COC	Structural isomer from block orientation	J. Am. Chem. Soc. 2022, 144, 9212–9216.
			J. Am. Chem. Soc. 2024, 146, 6638–6651.
3	COC	Chiral isomer from chiral block	J. Org. Chem. 2022, 87, 3491–3497.
			Angew. Chem. Int. Ed. 2023, 62, e202312733.
			J. Chromatogr. A. 2025, 1740, 465561.
4	COF	Structural isomer from linkage orientation	Mol. Syst. Des. Eng. 2019, 4, 325-331.
			Nat. Commun. 2020, 13, 6317.
			Chem. Mater. 2022, 34, 529–536.
			Angew. Chem. Int. Ed. 2023, 62, e202216073.
			Chem. Commun. 2024, 60, 4423.
			J. Mater. Chem. A, 2024, 12, 227–232.
5	COF	Structural isomer from block orientation	J. Am. Chem. Soc. 2018, 140, 12922–12929.
			J. Am. Chem. Soc. 2020, 142, 33, 14350–14356
			Chem. – Asian J. 2021, 16, 3781–3789.
6	COF	Chiral isomer from chiral block	Angew. Chem. Int. Ed. 2023, 62, e202216310.
6			Angew. Chem. Int. Ed. 2024, 63, e202413171.
7	COF	Structural isomer caused by isomeric block	Angew. Chem. Int. Ed. 2023, 62, e202216795.
			J. Am. Chem. Soc. 2023, 145, 26871–26882.
			Angew. Chem. Int. Ed. 2024, 63, e202320037.

Table S1. Summary of work on COF isomers and COC isomers





Figure S2. The <sup>13</sup>C-NMR spectra of An-2NH<sub>2</sub> in CDCl<sub>3</sub>.



Figure S3. The ESI mass spectrum of An-2NH<sub>2</sub>.



Figure S4. The <sup>1</sup>H-NMR of An-2Cl in CDCl<sub>3</sub>.



Figure S5. The <sup>1</sup>H-NMR spectra of An-2CN in CDCl<sub>3</sub>.



Figure S6. The <sup>1</sup>H-NMR spectra of An-2CHO in CDCl<sub>3</sub>.



Figure S7. The <sup>13</sup>C-NMR spectra of An-2CHO in CDCl<sub>3</sub>.



Figure S8. The ESI mass spectrum of An-2CHO.



Figure S9. The <sup>1</sup>H-NMR spectra of TNCA in DMSO-*d*<sub>6</sub>.



Figure S10. The APCI mass spectrum of TNCA.



Figure S11. The <sup>1</sup>H-NMR spectra of TCNA in DMSO-*d*<sub>6</sub>.



Figure S12. The APCI mass spectra of TCNA.



Figure S13. Solid state <sup>13</sup>C CP/MAS NMR spectra of COC isomers.



Figure S14. The FT-IR spectra of COC isomers.



**Figure S15.** Normalized UV–Vis and PL spectra of a) TNCA and b) TCNA in dichloromethane. (insert: Optical photos of TNCA and TCNA powder, respectively).



Figure S16. Transient fluorescence lifetime of TNCA and TCNA in dichloromethane.



Figure S17. UV–Vis spectra and standard curves of TNCA in dichloromethane.



Figure S18. UV–Vis spectra and standard curves of TCNA in dichloromethane.



Figure S19. Optical microscope photos of a-b) TNCA and c-d) TCNA crystals.



Figure S20. The packing modes in single crystals of a) TNCA and b) TCNA.

CCDC	2375697	2375696
Name	TNCA	TCNA
Identification code	cu_lijiaji_20240515_0m	t
Empirical formula	C84H54N8	C84H54N8, 8(C5H5N)
Formula weight	1175.35	1175.35
Temperature/K	100(2) K	173(2) K
Crystal system	monoclinic	Triclinic
Space group	$P2_1/n$	P-1
a/Å	23.0146(5)	10.8437(4)
b/Å	9.9226(2)	25.2054(9)
c/Å	36.4335(8)	37.5571(14)
$\alpha/^{\circ}$	90	73.902(2)
β/°	95.3290(10)	83.492(2)
γ/°	90	77.695(2)
Volume/Å <sup>3</sup>	8284.2(3)	9619.9(6)
Ζ	4	4
Data completeness	0.997	0.973
GOF on F <sup>2</sup>	1.028	0.974
R(reflections)	0.0694(7917)	0.0776(14695)
wR2(reflections)	0.2502(15218)	0.2589(33070)
F000	2456.0	2456.0

# Table S2. Crystal data and structure refinement.



Figure S21. UV–Vis DRS of COC isomers in the solid state under both dark and light irradiation conditions.



Figure S22. CV curves of TNCA and TCNA.



Figure S23. Mott–Schottky plots of a) TNCA and b) TCNA.



Figure S24. Energy diagrams and pictorial representations of the frontier MOs of a) TNCA and b) TCNA calculated at the B3LYP/6-31G(d,p) level of theory.



Figure S25. UV–Vis spectra of the dye photodegradation of a-c) MBT and d-f) RhB under light irradiation with or without COC isomers as photocatalyst.



Figure S26. Investigation on reusability of COC isomers for photocatalytic degradation of dye a) MBT and b) RhB.



Figure S27. The FT-IR spectra of COC after reusability test.



Figure S28. TGA curves of COC isomers under N<sub>2</sub> flow.



Figure S29. Normalized UV–Vis spectra for photochemical stability of a) TNCA and b) TCNA.



**Figure S30.** EPR detection of a)  $O_2$  and b)  $\cdot OH$  trapped by DMPO.



Figure S31. The Mechanism of photocatalytic activity of MBT and RhB dye degradation under visible light irradiation ( $\lambda > 420$  nm).

#### References

- 1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, J. Appl. Cryst., 2009, 42, 339–341.
- 2 S. George M., Acta Cryst., 2015, A71, 3-8.
- 3 S. George M., Acta Cryst., 2015, C71, 3-8.
- 4 C. Hilsum, Phys. Bull., 1979, 30, 528-528.
- 5 W. Dong, Z. Qin, K. Wang, Y. Xiao, X. Liu, S. Ren and L. Li, Angew. Chem. Int. Ed., 2023, 62, e202216073.
- 6 X. Ren, M. Wen, X. Hou, J. Sun, F. Bai and Y. Li, Chem. Commun., 2024, 60, 4423-4426.
- 7 G.-H. Ning, P. Cui, I. V. Sazanovich, J. T. Pegg, Q. Zhu, Z. Pang, R.-J. Wei, M. Towrie, K. E. Jelfs, M. A. Little and A. I. Cooper, *Chem*, 2021, 7, 3157–3170.
- 8 R. Guilard, M. A. Lopez, A. Tabard, P. Richard, C. Lecomte, S. Brandes, J. E. Hutchison and J. P. Collman, J. *Am. Chem. Soc.*, 1992, **114**, 9877–9889.