

**Determining the Coordination Environment and Electronic Structure of Polymer-Encapsulated Cobalt Phthalocyanine under Electrocatalytic CO<sub>2</sub> Reduction Conditions using *In Situ* X-Ray Absorption Spectroscopy**

**Supporting Information**

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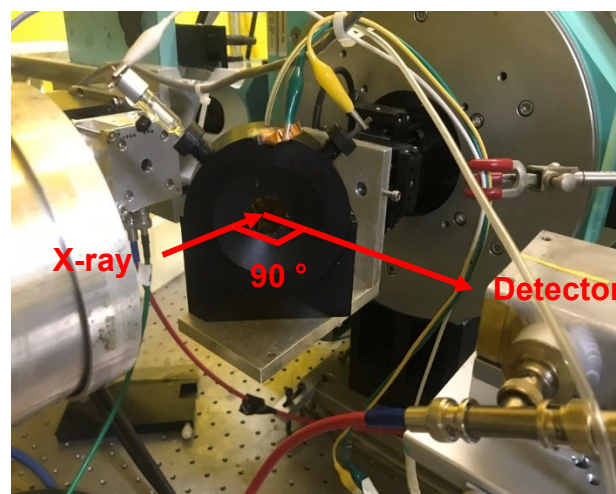
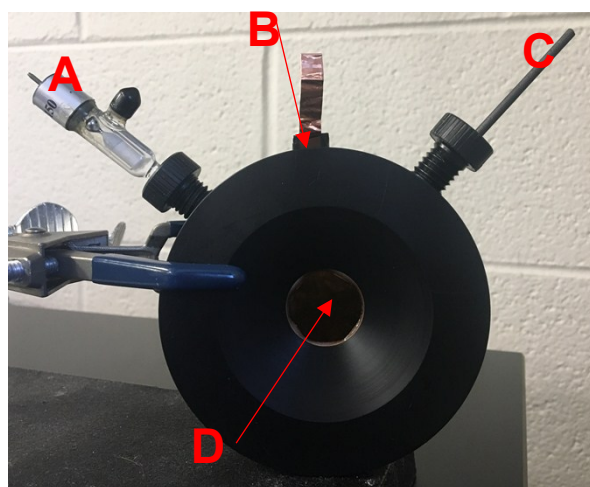
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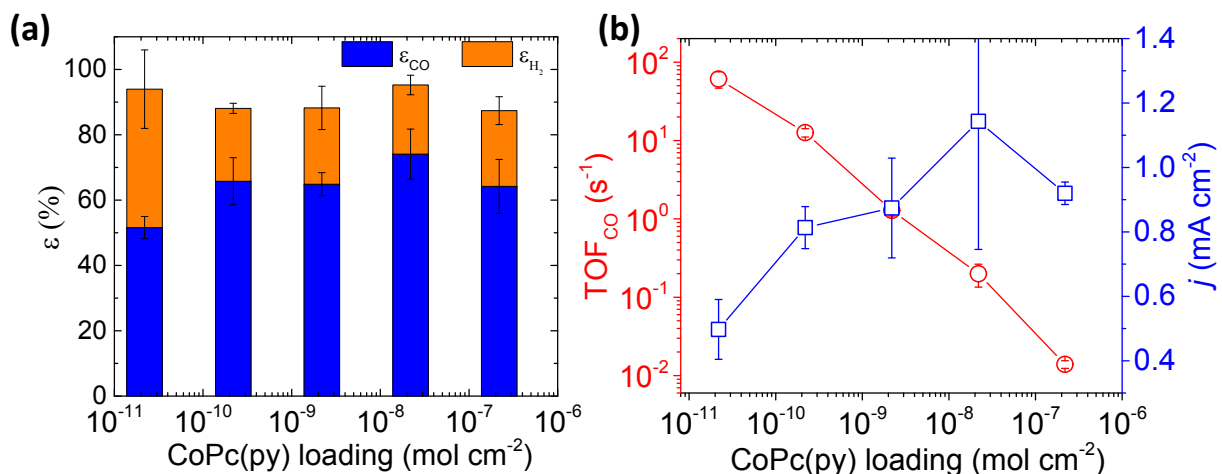
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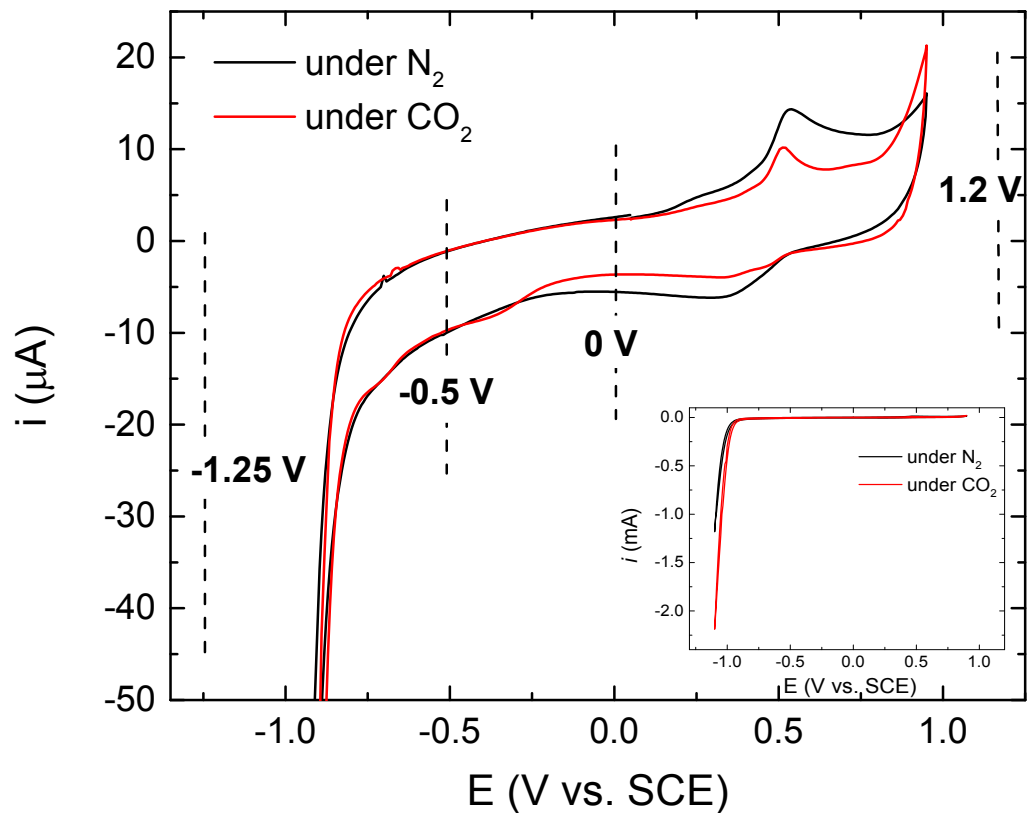
<sup>#</sup>These authors contributed equally to this work.



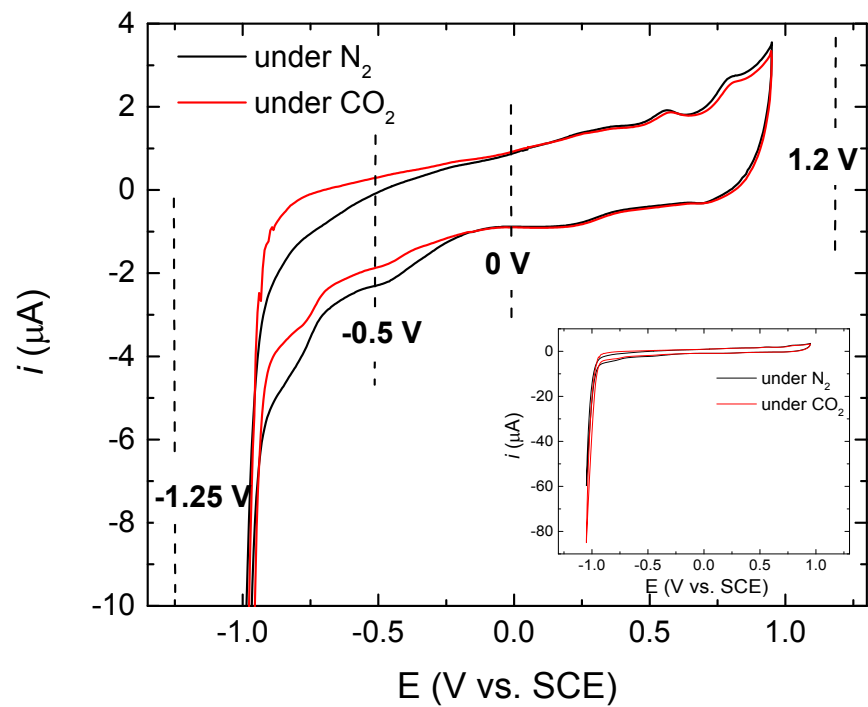
**Figure S1.** Photograph of custom spectro-electrochemical reaction XAS cell: (A) SCE reference electrode, (B) catalyst modified carbon paper working electrode, (C) Carbon rod auxiliary electrode, (D) Kapton film.



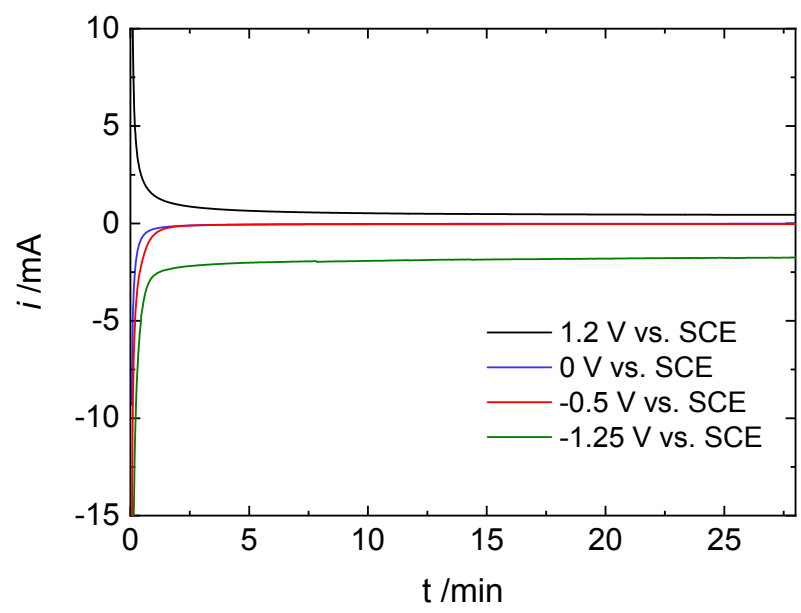
**Figure S2.** CO<sub>2</sub>RR results of 2-h CPE at different CoPc(py) loadings (a) Faradaic efficiencies for CO and H<sub>2</sub>, (b) TOF<sub>CO</sub> and overall current densities (*j*) obtained from 2-h CPE at -1.25 V vs. SCE at different CoPc(py) loadings in CO<sub>2</sub> saturated pH 5 phosphate electrolyte under CO<sub>2</sub> atmosphere. Errors are given as standard deviations. CoPc(py) was independently synthesized following the previously-reported procedures.<sup>1</sup> The decrease in TOF for CO<sub>2</sub>RR with increasing CoPc(py) loading suggests the aggregation of CoPc(py), which shows relatively the same aggregation as CoPc and CoPc-P4VP.<sup>2</sup> We propose that even though all CoPc immobilized are redox active, only those CoPc sites on the surface of the aggregates are electrocatalytically active for CO<sub>2</sub>RR.



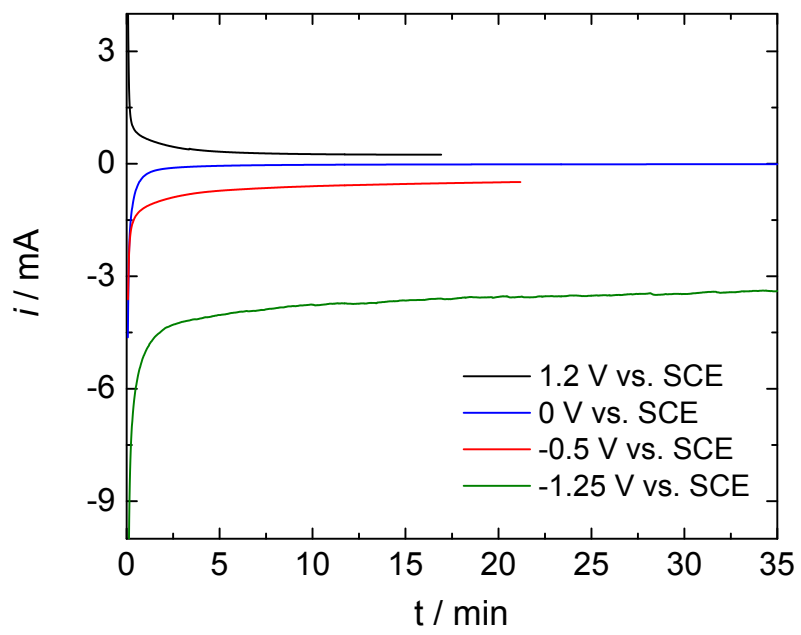
**Figure S3.** Cyclic voltammogram (CV) of CoPc-P4VP modified edge plane graphite (EPG) electrode in pH 5 phosphate electrolyte solution under  $\text{N}_2$  and  $\text{CO}_2$  atmosphere. The main figure shows the main electrochemical features preceding catalysis, and the inset shows the catalytic features as well.



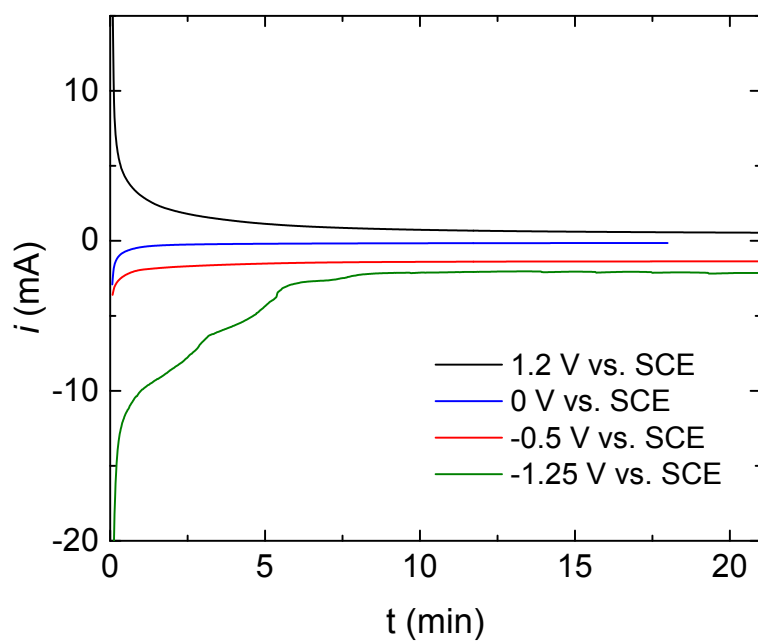
**Figure S4.** Cyclic voltammogram (CV) of CoPc(py) modified edge plane graphite (EPG) electrode in pH 5 phosphate electrolyte solution under  $\text{N}_2$  and  $\text{CO}_2$  atmosphere. The main figure shows the main electrochemical features preceding catalysis, and the inset shows the catalytic features as well.



**Figure S5.** Representative chronoamperometric (CA) measurements of CoPc modified carbon paper electrode in pH 5 phosphate electrolyte solution conducted at different potentials under  $N_2$  atmosphere.

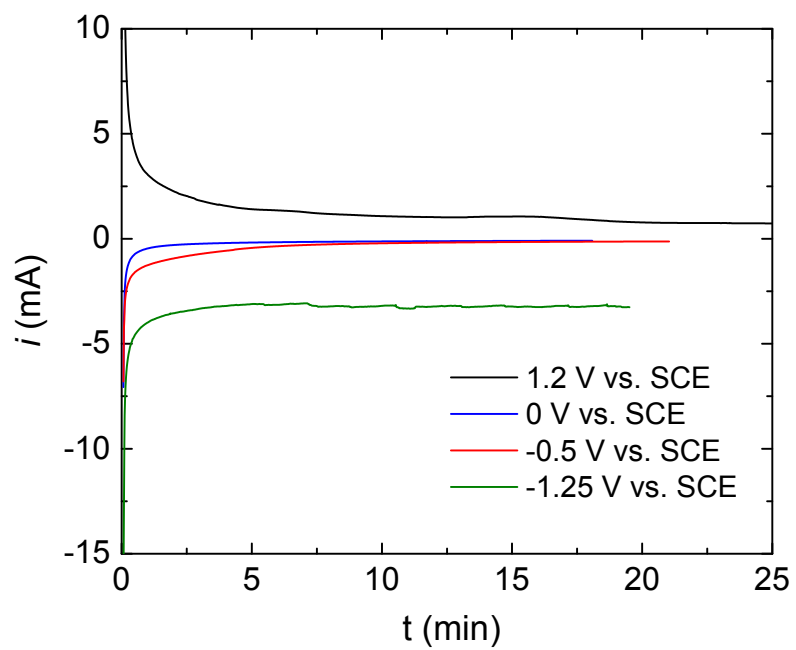


**Figure S6.** Representative chronoamperometric (CA) measurements of CoPc modified carbon paper electrode in pH 5 phosphate electrolyte solution conducted at different potentials under CO<sub>2</sub> atmosphere.

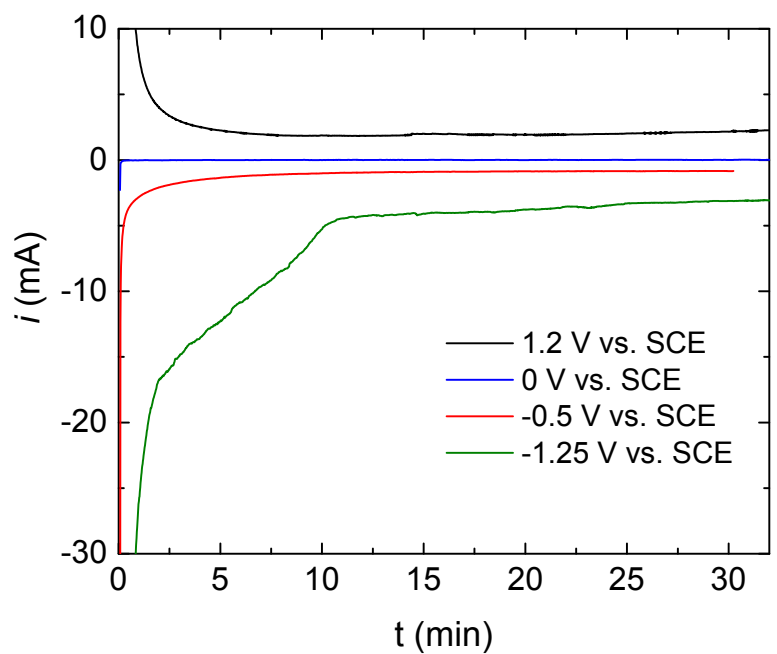


**Figure S7.** Representative chronoamperometric (CA) measurements of CoPc(py) modified carbon paper electrode in pH 5 phosphate electrolyte solution conducted at different potentials under  $N_2$  atmosphere. The dissimilarity of CA curve shape at  $-1.25$  V in 0-7 min time range compared to the one under  $CO_2$  (Figure S8) might be attributed to the higher electrochemical activity for HER compared to  $CO_2RR$ .

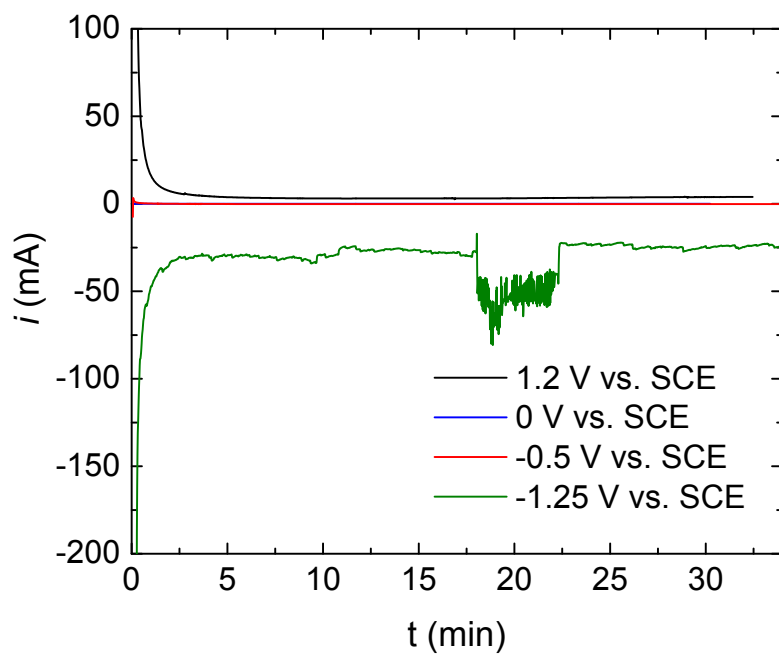




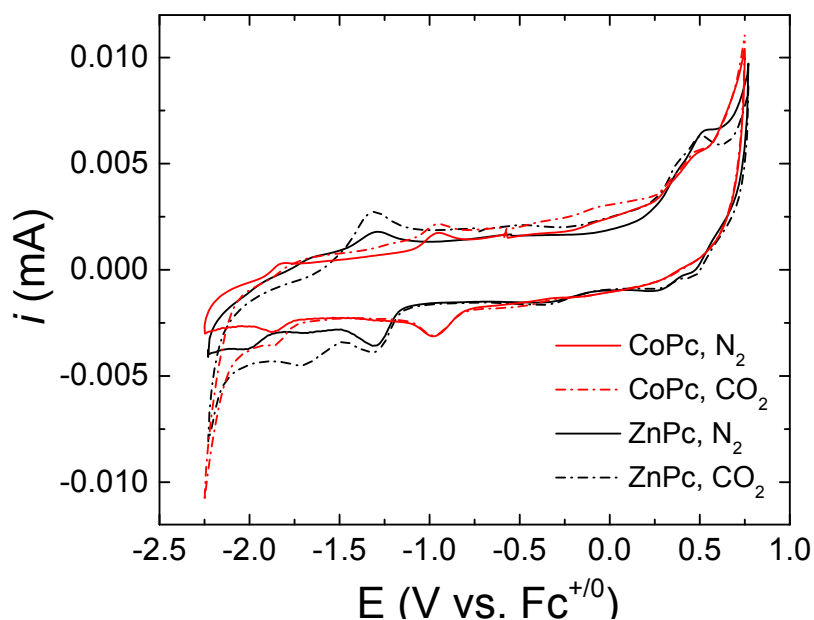
**Figure S8.** Representative chronoamperometric (CA) measurements of CoPc(py) modified carbon paper electrode in pH 5 phosphate electrolyte solution conducted at different potentials under CO<sub>2</sub> atmosphere.



**Figure S9.** Representative chronoamperometric (CA) measurements of CoPc-P4VP modified carbon paper electrode in pH 5 sodium phosphate solution conducted at different potentials under  $N_2$  atmosphere. The dissimilarity of CA curve shape at  $-1.25$  V in 0-10 min time range compared to the one under  $CO_2$  (Figure S10) might be attributed to the higher electrochemical activity for HER compared to  $CO_2RR$ .



**Figure S10.** Representative chronoamperometric measurements of CoPc-P4VP modified carbon paper electrode in pH 5 sodium phosphate solution conducted at different potentials under  $\text{CO}_2$  atmosphere. Note that the noise at -1.25 V is due to gas product generation.



**Figure S11.** Cyclic voltammogram (CV) of 0.1 mM CoPc and 0.1 mM ZnPc in DMSO with 0.1 M  $n\text{Bu}_4\text{NPF}_6$  under  $\text{N}_2$  and  $\text{CO}_2$ . Conditions: scan rate: 100 mV/s; working electrode: glassy carbon working electrode; reference electrode:  $\text{Ag}/\text{AgNO}_3$  (1 mM); auxiliary electrode: Pt wire. All CVs have been  $iR$  compensated. CoPc and ZnPc have similar redox features which suggests that the metal center may be redox inactive in both complexes. However, the peak potentials for CoPc are shifted more positive compared to ZnPc which suggests that although the Co center may be redox inactive, it still influences the energy of the frontier molecular orbitals of the complex.

## References

1. F. Cariati, D. Galizzioli, F. Morazzoni and C. Busetto, *J. Chem. Soc., Dalton Trans.*, 1975, DOI: 10.1039/DT9750000556, 556-561.
2. Y. Liu and C. C. L. McCrory, *Nat. Commun.*, 2019, **10**, 1683.