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Improving co-electrocatalytic carbon dioxide reduction by optimizing the relative potentials of the redox mediator and catalyst†

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The effects of fixing the redox mediator (RM) reduction potential relative to a series of Cr-centered complexes capable of the reduction of CO₂ to CO are disclosed. The greatest co-electrocatalytic activity enhancement is observed when the reduction potentials of the catalyst and RM are identical, implying that controlling the speciation of the Cr complex relative to RM activation is essential for improving catalytic performance. In all cases, the potential where co-catalytic activity is observed matches the reduction potential of the RM, regardless of the relative reduction potential of the Cr complex.

As the global energy demand continues to grow, so have anthropogenic emissions of carbon dioxide (CO₂), with a corresponding increasing severity of associated climate change effects.^{1,2} One possibility for mitigating these negative effects is through the development of electrocatalytic systems capable of the carbon dioxide reduction reaction (CO₂RR), which can use renewable electricity to produce useful carbon-containing products.^{3,4} The study of molecular catalysts for the CO₂RR provides fundamental understanding of how the catalytic active sites can be tuned through mechanistic study. While molecular catalysts for CO₂ reduction have been studied for decades,^{5–16} the incorporation of redox mediators (RMs) to assist in the transfer of electrons (often with protons) to catalyst active sites is a growing area of interest in the field.¹⁷ While examples of RMs used with catalysts for the reduction of CO₂ are currently limited,^{18–23} a few additional examples exist for the electrocatalytic conversion of a variety of small molecules.^{23–35}

Previously, the co-electrocatalytic reduction of CO₂ with Cr-centered catalysts derived from dianionic N₂O₂ ligand frameworks and sulfone-based RMs has been studied.^{19–21} Initial studies used Cr(^tbu₂dhbpy)Cl(H₂O) as the catalyst and dibenzothiophene-5,

5-dioxide (DBTD; Fig. 1) as the RM, where CO₂ was reduced to carbon monoxide (CO) under both aprotic and protic conditions.¹⁹ Under protic conditions it was proposed that the DBTD RM operates *via* an inner-sphere electron transfer mechanism, where the reduced RM, [RM][–], binds to the intermediate resting state of the intrinsic catalytic cycle, [Cr–CO₂H][–]. This binding occurs *via* an equilibrium displacement of an axial solvent molecule, the favorability of which is due to three forces: Cr–O bond formation, dispersion interactions, and through-space electronic conjugation (specifically pancake bonding (PB) under protic conditions). A PB interaction is defined by two highly delocalized π -based radicals with short vertical distance and high atom–atom overlap, differentiating it from weaker π – π stacking interactions.^{36–39} The resulting [RM–Cr–CO₂H]^{2–} adduct has a lower barrier for the rate-determining step of the reaction (C–OH bond cleavage), so the

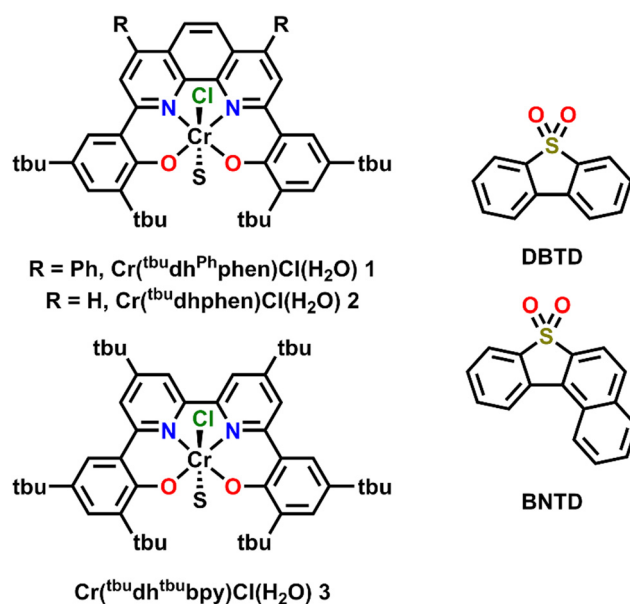


Fig. 1 Structures of Cr catalysts and RMs discussed here.

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favorability of this pre-equilibrium step controls the observed activity. After this initial report, additional studies interrogated the role of the ligand and RM aromaticity on favoring the co-catalytic mechanism of the CO₂RR by comparing the experimentally observed activity of the catalysts Cr(^{tbu}dhphen)Cl(H₂O) (**2**) and Cr(^{tbu}dh^{tbu}bpy)Cl(H₂O) (**3**) (Fig. 1) with a series of DBTD-derived RMs.^{20,21} From these results, it was proposed that the PB interaction of the key intermediate of the co-catalytic cycle could be strengthened when the reduction potential of the RM is closer to that of the catalyst and when there is less steric clash between the RM and catalyst, since these changes should favor vertical atom–atom overlap.

Here, the relative position of the Cr catalytic potential is varied with respect to RM potential, demonstrating that co-electrocatalytic activity is pinned to the RM potential under all conditions, even when the catalyst is formally reduced at more negative potentials. A new Cr-centered catalyst with phenyl groups substituted to the ligand phenanthroline backbone, Cr(^{tbu}dh^{Ph}phen)Cl(H₂O) (**1**) is reported, as well as a new RM, benzonaphthothiophene-7,7-dioxide (BNTD), which is tested with complexes **1**, **2**, and **3** (Fig. 1). Interestingly, these studies suggest that the optimal co-electrocatalytic response occurs when the RM and Cr catalyst are potential matched, implying that tuning the relative concentrations in the reaction–diffusion layer offers additional reaction control.

A di-phenyl substituted phenanthroline ligand framework, 6,6'-di(3,5-di-*tert*-butyl-2-hydroxybenzene)-4,7-di-phenyl-1,10-phenanthroline (^{tbu}dh^{Ph}phen(H)₂), was synthesized from 2,9-dichloro-4,7-diphenyl-1,10-phenanthroline using Pd-catalyzed cross-coupling methods (see ESI† and Fig. S1 and S2). Subsequent metalation to make Cr(^{tbu}dh^{Ph}phen)Cl(H₂O) (**1**) used a modified literature procedure (see ESI†) and was characterized by UV-vis (Fig. S3, ESI†), NMR (Table S2, ESI†), electrospray ionization-mass spectrometry (ESI), and microanalysis (ESI).

Cyclic voltammetry (CV) experiments were performed on **1** in *N,N*-dimethylformamide (DMF) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Under argon (Ar) saturation conditions, **1** exhibits three redox features ($E_{1/2} = -1.55$ and -1.93 V and $E_p = -1.70$ V *versus* ferrocenium/ferrocene (Fc^{+/Fc})); minimal changes are observed under CO₂ saturation conditions (Fig. S6A, ESI†). This redox response is similar to what was previously observed for Cr-centered catalysts with structurally related N₂O₂ ligand frameworks.^{20,21,40} the first two redox features relate to a chloride-loss equilibrium through solvent displacement and the molecule is reduced by two electrons overall by -1.93 V *vs.* Fc^{+/Fc}.

Upon the addition of phenol (PhOH) under Ar saturation, only minor changes are observed (Fig. S6A, ESI†). However, under CO₂ saturation with PhOH present, there is an increase in current density with complete loss of reversibility at the third reduction feature, indicating electrocatalytic reduction of CO₂. When comparing the catalytic CV current density of **1** with that of **2** and **3**, the relative current increase is consistent with a normal scaling relationship: as the $E_{cat/2}$ of the catalyst becomes more negative the catalytic current density increases

Table 1 Results of CPE experiments with PhOH under CO₂ saturation conditions in DMF

Conditions	Potential (V <i>vs.</i> Fc/Fc ⁺)	FE _{CO} (%)	FE _{H₂} (%)	TOF _{CPE} (s ⁻¹)	η (V)
1 + PhOH ^a	-2.10	91 ± 3	6 ± 2	0.24	0.09
1 + DBTD + PhOH ^b	-2.30	77 ± 2	18 ± 1	27.4	0.41
1 + BNTD + PhOH ^b	-2.20	97 ± 2	NQ	34.0	0.12
2 + PhOH ^{21 c}	-2.30	101 ± 3	—	4.90	0.12
2 + DBTD + PhOH ^{21 b}	-2.30	94 ± 7	—	56.3	0.41
2 + BNTD + PhOH ^b	-2.20	103 ± 5	—	328	0.12
3 + PhOH ^{20 d}	-2.30	95 ± 8	—	9.29	0.16
3 + DBTD + PhOH ^{20 e}	-2.30	109 ± 9	—	163	0.41
3 + BNTD + PhOH ^e	-2.20	100 ± 2	—	63.4	0.12

^a 0.5 mM catalyst and 0.8 M PhOH. ^b 0.1 mM catalyst, 0.5 mM RM, and 1.0 M PhOH. ^c 0.5 mM catalyst and 1.0 M PhOH. ^d 0.1 mM catalyst and 0.12 M PhOH. ^e 0.1 mM catalyst, 0.5 mM RM, and 0.12 M PhOH; NQ = non-quantifiable.

(Fig. S6B, ESI†). The catalytic activity of **2** and **3** was previously found to be first-order with respect to the catalyst, PhOH, and CO₂.^{20,21} When comparable variable concentration CV experiments were performed for **1**, the system was found to be first-order with respect to **1** (Fig. S9, ESI†), but mixed-order kinetics were observed for both PhOH (Fig. S10, ESI†) and CO₂ (Fig. S11, ESI†) concentrations. This is attributed both to the decreased intrinsic activity of **1**, with a corresponding saturation of the current response at relatively low substrate concentrations, as well as pre-equilibrium interactions between phenol and the aromatic backbone.

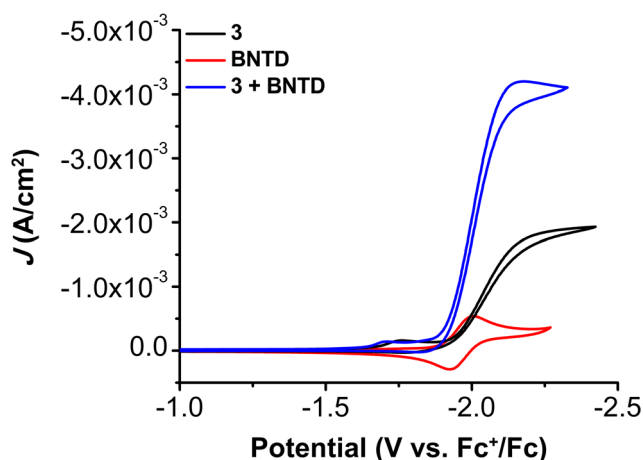
Controlled potential electrolysis (CPE) was performed with **1** and 0.8 M PhOH under CO₂ saturation at an applied potential of -2.1 V *vs.* Fc^{+/Fc} in order to determine the selectivity and turnover frequency (TOF_{CPE}) of the catalyst (Fig. S12, ESI†). A 91 ± 3% Faradaic efficiency for CO (FE_{CO}) at an overpotential of 90 mV (6 ± 2% H₂ detected, Table S3, ESI†) and a TOF_{CPE} of 0.24 s⁻¹ were observed (Table 1). The measured TOF_{CPE} for **1** is much lower than that of **2** and **3**, in agreement with the observed CV current density trends and a normal Tafel scaling relationship based on the $E_{cat/2}$ of the catalysts.⁵ It is important to note that the CPE experiments with **1** were performed at more positive potentials than the other catalysts due to the increase in competitive hydrogen evolution reaction (HER) by the electrode at more negative potentials, which is attributed to its low intrinsic activity.

To examine how the relative position of the RM reduction potential with respect to the reduction potentials of **1**, **2**, and **3** impacts co-electrocatalysis, it was necessary to prepare a new RM, benzonaphthothiophene-7,7-dioxide (BNTD; see ESI† Fig. 2 and Fig. S4, S5). Under Ar saturation, BNTD displays a single reversible redox feature with an $E_{1/2} = -1.96$ V *vs.* Fc^{+/Fc}, corresponding to a single-electron reduction that remains unchanged upon the addition of PhOH and CO₂ (Fig. S15, ESI†). The $E_{1/2}$ of BNTD is more negative than the $E_{cat/2}$ of complex **1**, equal to that of complex **2**, and more positive than that of complex **3**, enabling a systematic study of the relationship between $E_{cat/2}$ and the RM $E_{1/2}$. Additionally, since BNTD is a similar size and shape to other tested derivatives,^{20,21} changes





CPE experiments were performed to determine the product selectivity and activity for CO₂ reduction with PhOH present for



The results presented here suggest that once the equilibrium binding interaction is favorable enough, the relative composition of the reaction–diffusion layer also becomes important. That is, if the RM is generated at positive enough potentials, the co-catalytic cycle must compete less with the intrinsic catalytic cycle of the Cr complexes. Indeed, co-catalytic activity peaks with the combination of **2** and BNTD, where both active species are generated at an identical reduction potential. However, it is also clear from the results with complex **3** that even minor concentrations of the reduced catalyst are sufficient for co-catalysis to occur, given the general favorability of RM association and the corresponding rate enhancement. Using the Nernst equation, at 40 mV positive of the standard reduction potential it can be estimated that approximately 17.4% of **3** in the reaction–diffusion layer has been reduced to its active form (see ESI[†]), consistent with the reduced co-catalytic enhancement observed. Smith *et al.* made a similar

observation in their original report, proposing that a minimal potential difference offered the best enhancement for co-electrocatalysis.¹⁸ In that previous study, the requirement for the RM to transfer $2e^-/2H^+$ for co-catalysis introduced a kinetic penalty, which was compounded by the high intrinsic activity of the catalyst, leading to greater competition between the intrinsic and co-catalytic pathways.¹⁷

It is striking that the $E_{1/2}$ of BNTD becomes the $E_{\text{co-cat}/2}$ potential in all cases, regardless of the relative position of the Cr-based redox potential. This clearly demonstrates that the co-catalytic benefit can be thought of as increasing the inventory of available electrons for catalytic CO_2 conversion: the Cr complex becomes effectively over-reduced once the RM is activated, enhancing the TOFs and, in the event that equilibrium binding is sufficiently favorable, forming as the only catalytic species in solution with minimal concentrations of activated catalyst. Going forward, these results suggest that effective co-catalyst design strategies must begin to incorporate an understanding of relative speciation to achieve the highest activities, in addition to leveraging components of molecular design.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Notes and references

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