Through-Space Electronic Conjugation Enhances Co-Electrocatalytic Reduction of CO_2 to CO by a Molecular Cr Complex

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ABSTRACT:

The electrocatalytic reduction of CO_2 represents an appealing method for converting renewable energy sources into value-added chemical feedstocks. Here, we report a co-electrocatalytic system for the reduction of CO_2 to CO comprised of a molecular Cr complex, $Cr(^{tbu}dhbpy)Cl(H_2O)$ **1**, where 6,6′-di(3,5-di-tert-butyl-2-phenolate)-2,2′-bipyridine = $[^{tbu}dhbpy]^{2-}$ and dibenzothiophene-5,5-dioxide (DBTD) as a redox mediator which achieves high activity ($1.51\text{-}2.84 \times 10^5$ s^{-1}) and quantitative selectivity. Under aprotic or protic conditions, DBTD produces a co-electrocatalytic response with **1** by coordinating *trans* to the site of CO_2 binding and mediating electron transfer from the electrode with quantitative efficiency for CO. This assembly is in part reliant on through-space electronic conjugation between the π frameworks of DBTD and the bpy fragment of the catalyst ligand, with important contributions from dispersion interactions and weak sulfone coordination to Cr. Experimental and computational results suggest that this interaction stabilizes a key intermediate in a new aprotic catalytic pathway and lowers the rate-determining transition state under protic conditions. To the best of our knowledge through-space electronic conjugation has not been explored in molecular electrocatalytic systems.

MAIN TEXT:

Concerns over increasing energy demands and climate change have led to continued interest in molecular electrocatalysis.[1-4] The conversion of CO_2 to value-added products, as part of a carbon neutral (or negative) cycle, is an attractive strategy for addressing the challenges associated with the rising atmospheric CO_2 concentration.[5-9] The electrocatalytic reduction of CO_2 to CO could significantly alter the emissions impact of industrial processes related to Fischer-Tropsch chemistry and syngas, if hydrogen from renewable sources is used.[10-13]

The reduction of CO_2 to CO by molecular electrocatalysts requires the sequential transfer of two electrons and an oxo acceptor (e.g. $2H^+$ or CO_2).[14-15] The general paradigm is for a catalyst to accept electrons from the electrode prior to substrate binding. During energy conversion in living cells, chemical bonds are modified by synergistic systems, like the electron transport chain, which achieve high energy efficiency and selectivity by pairing redox-active moieties with metal centers to direct the flow of reducing equivalents. Analogous reactivity has been translated to only one example of homogenous co-electrocatalytic CO_2 reduction,[16] while similar reactivity is known for other electrocatalytic reactions.[17-20] An alternative mechanism for directing electron transfer is through-space electronic conjugation (TSEC), a mechanism of electronic communication between stacked π systems which enables efficient energy and charge transport which has found application in optoelectronic materials and for studying conductance in molecular junctions (**Figure 1**).[21-24]

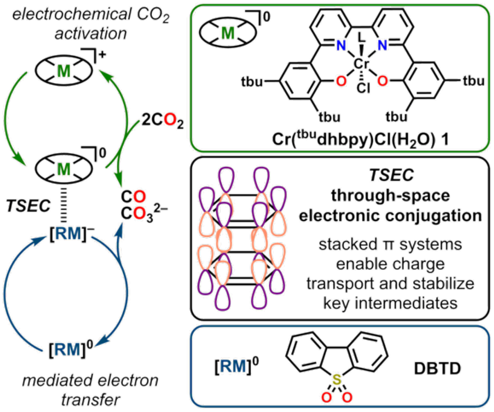

Figure 1. Overview of co-electrocatalytic system based on TSEC between DBTD and $Cr(^{tbu}dhbpy)Cl(H_2O)$ **1**.

Intrigued by the notion that TSEC could enhance catalytic activity by generating co-catalyst assemblies, we sought to identify a suitable RM and transition metal complex. We selected dibenzothiophene-5,5-dioxide (DBTD) as the RM (**Figure 1**), which is derived from a petroleum contaminant[25] and has well-defined electrochemical properties at reducing potentials,[26] to pair with a Cr-based catalyst developed in our lab, $Cr(^{tbu}dhbpy)Cl(H_2O)$ (**Figure 1**).[27-28] Herein, we report to our knowledge the only example where TSEC has been used to develop a homogeneous co-electrocatalytic system.

Cyclic voltammetry (CV) experiments were carried out in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) with *N,N*-dimethylformamide (*N,N*-DMF) as the solvent. Under argon (Ar) saturation conditions, DBTD displays a reversible redox feature with an $E_{1/2} = -2.25$ V versus the ferrocenium/ferrocene (Fc^+/Fc) internal standard (**Figure S1**). Control CVs show minimal reactivity with CO_2 or phenol (PhOH) on the CV timescale**.** Coulometry under aprotic conditions established that this redox feature is a one-electron process, in contrast to a prior report (**Figure S2**).[26] A control electrolysis experiment was performed with DBTD under CO_2 saturation conditions (**Figure S3**) and again with added PhOH (**Figure S4**): CO and H_2 were detected with low Faradaic efficiencies (FEs) and less than one turnover was achieved based on [DBTD] in both cases (**Table 1** and **Table S1**). Under aprotic CO_2 saturation conditions, **1** does not achieve a single turnover of CO production in electrolysis experiments (**Figures S5-S6**); no co-products were detected (**Table 1** and **Table S2**).

The addition of DBTD (2.5 mM) to a solution of **1** (1.0 mM) under Ar saturation conditions suggests minimal interaction occurs at the $DBTD^{0/-}$ reduction (**Figure S5**). Conversely, under CO_2 saturation conditions this mixture generates a large irreversible increase in current at the$DBTD^{0/-}$ couple, suggestive of a multielectron process (**Figure 2**, blue and **Figure S5**, blue).[29] *This reactivity is not intrinsic to either component in control reactions*: **1** and DBTD do not individually possess electrocatalytic activity for aprotic CO_2 reduction. Further, this confirms that DBTD does not act simply as an outer-sphere RM, but rather that the one-electron reduction of DBTD results in the formation of a new adduct that modifies the electronic structure of **1**, enabling co-electrocatalytic CO_2 reduction. It is also worth noting that sulfones are poor ligands with few reports on their coordination chemistry, suggesting that the molecular interaction cannot be ascribed to a metal-donor atom interaction alone.[30-31] No co-electrocatalytic activity is observed in control experiments with decamethylcobaltocene and **1**, reinforcing the limited role of outer-sphere electron transfer (**Figure S7**).

Bulk electrolysis experiments at –2.3 V vs Fc^+/Fc show 91±10% efficiency for CO, with carbonate confirmed as the co-product by NMR, indicating that the reductive disproportionation of CO_2 is occurring (**Table 1** and **S3**; **Figure S8**).[32] Variable concentration studies were carried out via CV (**Figures S9-S11**), indicating that catalytic current has a dependence on DBTD and **1**. Comparable experiments with CO_2 showed a first-order concentration dependence (**Figure S11**). Varying the concentration of a fixed ratio of DBTD to **1** showed consistent increases in current with sustained irreversibility at the DBTD reduction potential (**Figure S12**). We note that the complexity of the proposed reaction pathway and overlapping current responses precludes the accuracy of more detailed analyses.

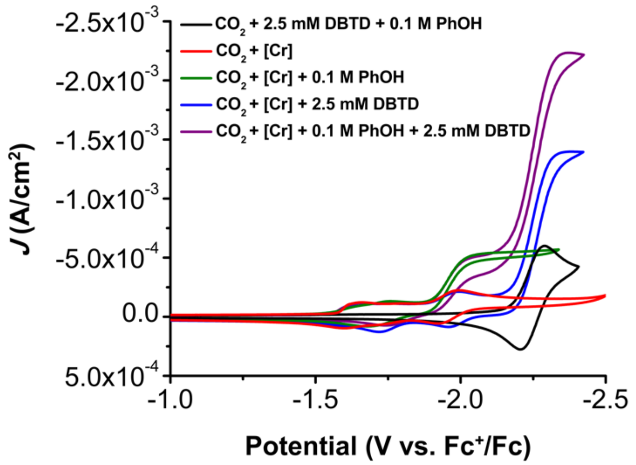

Figure 2. CVs comparing the reactivity of Cr(^{tbu}dhbpy)Cl(H_2O) **1** (1.0 mM) and DBTD under aprotic and protic conditions; 100 mV/s, 0.1 M $TBAPF_6$/DMF.

When 0.1 M PhOH is added to **1** and DBTD under CO_2 saturation conditions, minimal difference compared to identical conditions in the absence of DBTD is observed[27] until the DBTD$^{0/-}$ couple (**Figure 2**). A comparison of all catalytic conditions indicates that the increase in current density does not correspond to a simple overlay of the independent catalytic responses: PhOH and **1** produce 0.542 mA/cm^2 catalytic current density under CO_2 saturation, **1** and DBTD generate 1.39 mA/cm^2, and the combination of PhOH, DBTD and **1** yield 2.23 mA/cm^2. Bulk electrolysis experiments at –2.3 V vs Fc$^+$/Fc with **1**, DBTD, and PhOH present 102±14% efficiency for CO (**Figure S4**, **Table 1** and **Table S4**). Variable concentration studies were subsequently analyzed to establish kinetic relationships between **1**, DBTD, PhOH, and CO_2 (**Figures S13-S16**). These data again show current proportional to **1** (**Figure S14**), DBTD (**Figure S15**), and the combination of the two (**Figure 17**), as well as the PhOH (**Figure 13**) and CO_2 (**Figure 16**).

Table 1. Results from CPE experiments under CO_2 saturation conditions.

Conditions	Potential (V vs Fc$^+$/Fc)	FE$_{CO}$ (%)	TOF$_{CPE}$ s^{-1}	η (V)	TON$_{CO}$ (w.r.t [1])	TON$_{CO}$ (w.r.t [DBTD])
[Cr]	-2.7	57±3	-	-	0.81	-
DBTD	-2.3	32±1	-	-	-	0.90
[Cr] + DBTD	-2.3	91±10	1.51 x 10^5	0.75	16	3.1
DBTD + PhOH	-2.3	28±1	-	-	-	0.52
[Cr] + PhOH[a]	-2.1	96±8	1.79 x 10^4	0.11	15[a]	-
[Cr] + PhOH + DBTD	-2.3	102±14	2.84 x 10^5	0.41	29	5.8

* –[Cr] = Cr(^{tbu}dhbpy)Cl(H_2O) **1**. PhOH = 0.6 M [PhOH]. Turnovers correspond to moles of electrons passed in coulometry studies divided by two to account for CO formation. [a] – previously reported results.[27]

Given our previous success in modeling the intrinsic catalytic cycle of **1** computationally,[28] we conducted DFT studies to locate probable reaction pathways under aprotic and protic conditions with DBTD present (**See SI**). The calculated redox potential for DBTD shows good agreement with experiment and suggests charge localization in the aromatic fragment (**Figure S17**). We propose the following co-catalytic mechanism under aprotic conditions (**Figure 3**). Beginning from the four-coordinate monoanionic species [Cr(^{tbu}dhbpy)]$^{-}$, CO_2 binding is kinetically accessible in an overall endergonic reaction pathway (**Figures S18-S19**).[27-28] Subsequently, the most likely pathway is the binding of a second equivalent of CO_2 (**Figure S20).**

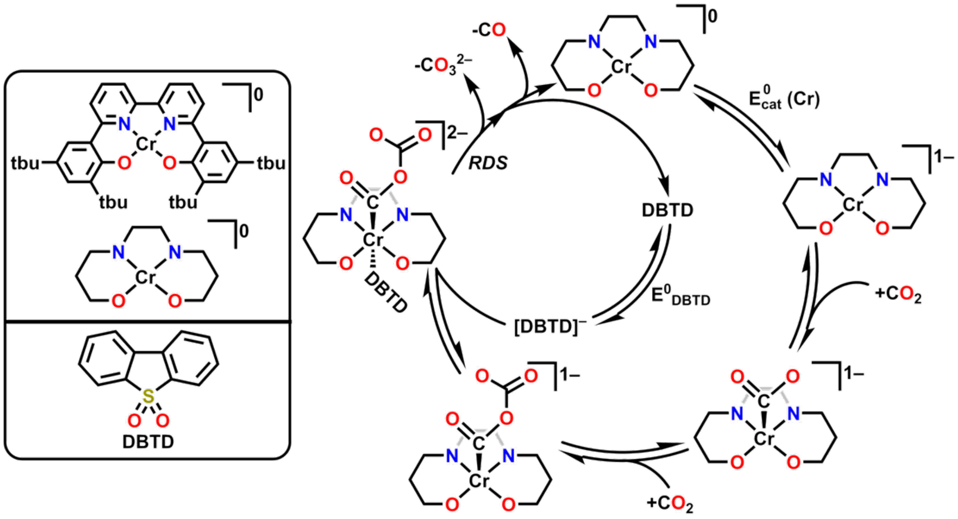

Figure 3. Proposed mechanism for co-electrocatalytic CO_2 reduction by **1** and DBTD under aprotic conditions.

Notably, despite the anticipated Coulombic repulsion, binding of [DBTD]$^{-}$ in the axial position to produce [Cr(^{tbu}dhbpy)(CO_2CO_2)(DBTD)]$^{2-}$ (S = 1) is favorable (–5.5 kcal/mol), relative to DMF coordination (**Figure S21**). We hypothesize that carbonate dissociation then produces a neutral Cr-CO, from which facile and irreversible CO loss occurs.[28] Examination of the electronic structure of [Cr(^{tbu}dhbpy)(CO_2CO_2)(DBTD)]$^{2-}$ through Kohn-Sham orbital projections, spin density plots, and Atoms in Molecules (AIM)[33] analysis suggests that the stability of this species originates in part from TSEC between [DBTD]$^{-}$ and the bpy fragment of the catalyst (**Figures 4** and **S20**).[34-36] Including dispersion corrections at the optimization stage is crucial to obtain reliable molecular geometries[37]: no true minimum for the bimolecular assembly can be located in the S = 1 manifold without dispersion corrections and that located for the higher energy S = 2 alternative suggests the stabilizing effect is of ca 20 kcal/mol (**Figure S22**). Thus, while TSEC alters key aspects of the electronic structure relevant to the observed co-catalytic response, dispersion effects are a primary force in driving association.

The mechanistic possibilities are more complex when PhOH is present, since the DBTD$^{0/–}$ couple is more negative than the intrinsic response of **1**. We cannot exclude DBTD functioning as an outer-sphere reductant, however, DFT calculations suggest that a viable pathway for increased rate through DBTD$^{–}$ coordination exists. From the six-coordinate monoanionic [Cr-CO$_2$H]$^{–}$ species identified previously,[28] replacement of an axial DMF ligand by DBTD$^{–}$ to create a dianionic species is thermodynamically favorable. Examination of the Kohn-Sham orbitals of the DBTD and [DBTD]$^{–}$ adducts with [Cr-CO$_2$H]$^{–}$ supports the proposal that a favorable interaction between the singly-occupied bpy and DBTD π* orbitals is a key component of the electronic structure (**Figure S23**). The transition state for C−OH bond cleavage from [Cr(^{tbu}dhbpy)(CO$_2$H)(DBTD)]$^{2–}$ is lower than in the absence of the mediator (**Figure S24**). Thus, although TSEC cannot be assigned as the exclusive source of the enhanced rates observed experimentally, a viable mechanistic pathway exists. Kohn-Sham projections and spin density plots are consistent with TSEC (**Figure S23**); AIM analysis again indicates bond critical points between [DBTD]$^{–}$ and the bpy fragment of the [Cr-CO$_2$H]$^{–}$ complex (**Figure S25**).[34-36]

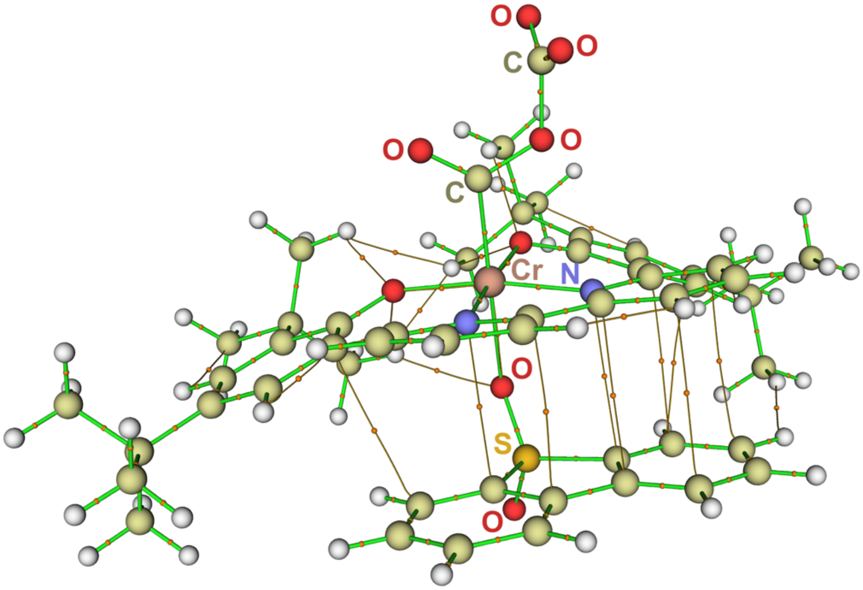

Figure 4. Results of AIM analysis[33] showing (3,-1) bond critical points (bronze lines) between [DBTD]$^{–}$ and the [Cr(^{tbu}dhbpy)(CO$_2$CO$_2$)]$^{–}$ fragment.[34-36]

In conclusion, we report what is, to the best of our knowledge, the only example of the TSEC-driven assembly of a RM and a transition metal complex to co-electrocatalytically reduce CO$_2$. The addition of DBTD demonstrates nascent electrocatalytic CO$_2$ reduction activity under aprotic conditions, conditions where **1** has no intrinsic catalytic response in its absence. Substitution of DBTD with decamethylcobaltocene does not result in any co-electrocatalytic activity (**Figure S7**). DFT studies indicate that dispersive interactions, TSEC, and weak sulfone coordination are all required to achieve co-electrocatalytic activity enhancement by directing the association of DBTD and **1** (**Figure 4**)**.** With a proton donor present, substitution of axial DMF ligands with the reduced RM are thermodynamically favorable, resulting in a lower overall rate-determining transition state (**Figure S24**). TSEC interactions have been described in studies of electrical conduction in molecular systems[38] and we propose that the viability of an electron transfer pathway between DBTD and **1** also contributes to the observed kinetic enhancement. These results suggest that RMs which interact with redox-active ligand frameworks can be a powerful way to alter electrocatalytic mechanisms and improve kinetic rates. Computational and experimental studies to optimize this system are ongoing.

ASSOCIATED CONTENT

Supporting Information. Additional CV, UV-vis, NMR, and electrochemical data is included in the SI. This material is available on request.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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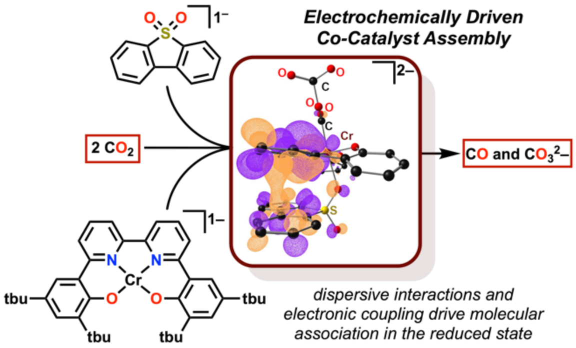
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dispersive interactions and electronic coupling drive molecular association in the reduced state