An Elusive Intermediate Uncovered in the Pathway for Electrochemical Carbon Dioxide Reduction by Ruthenium Polypyridyl Catalysts – A Combined Spectroscopic and Computational Investigation

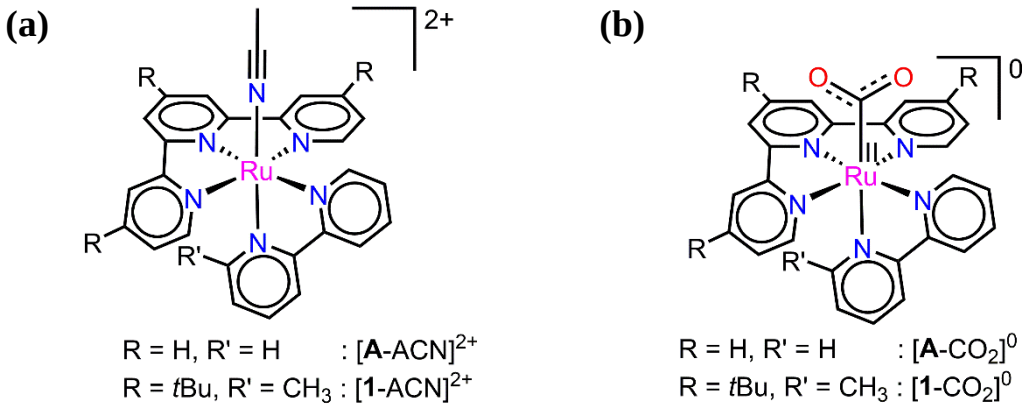
ABSTRACT: A scrutinous study of the catalytic cycle for electrochemical CO_2 reduction by the ruthenium 2,2′:6′,2′′-terpyridine (tpy) 2,2′-bipyridine (bpy) class of catalysts is presented. An unprecedented η^2-(*C*,*O*′)-carboxycarboxylatoruthenium(II) metalacyclic intermediate, critical for C-O bond dissociation at low overpotentials, so **far** precluded from mechanistic considerations of polypyridyl transition metal complex catalysts, is unearthed by infra-red spectroscopy coupled to controlled potential electrolysis in corroboration with density functional theory (DFT) investigations. Thermodynamic and kinetic analyses of the intermediate reveal the important role of the structural flexibility of polypyridyl ligands and fine electronic tunability of the metal center, along with kinetic *trans effect*, in propelling catalysis at lower overpotentials. The choice of metal center, Ru in the present case, points to the fact that the requirement of an additional Lewis acid to enhance C-O bond dissociation, hence increase the catalytic rate or turnover, can be circumvented.

Electrochemical reduction of CO_2 to CO (eCRR) is an attractive reaction as it can assist in mitigating atmospheric CO_2, it is a step for storage of renewable energy in energy dense materials, and CO itself has wide use as a synthetic reagent in the chemical industry. While the reaction has a thermodynamic potential of -1.28 V vs Fc^+/Fc under standard conditions, it typically suffers from too high overpotentials for efficient implementations. The overpotentials can largely be tracked to a few kinetically slow steps, that require excessive reduction of the catalytic center. On molecular catalysts there are three key steps that have been identified and modification of the catalyst structure has been focused on enhancing the rates of these steps: 1)

CO_2 binding to the catalyst 2) the C-O cleavage 3) CO dissociation. Another concern for molecular catalysts is the stability, which is typically addressed by using multidentade ligands, such as polypyridyl ligands or porphyrins. Of the three steps listed we focus on the C-O cleavage step herein. Normally, additional reduction on the metal or ligand can facilitate the C-O cleavage but will typically occur at very negative potentials, thus leading to high overpotentials. In nature the carbon monoxide dehydrogenase enzymes (CODH) can efficiently and reversibly convert CO to CO_2. In the active site of CODH there is a Ni/Fe/S cluster where the Ni is the redox and chemically active center. In close proximity is a redox inactive Fe(III) Lewis acidic center that facilitates the C-O cleavage by stabilizing a dissociating OH^- group. This function has been mimicked in artificial systems, *e.g.* by Buss et al. who found that introduction of fluorinated triaryl boranes led to enhancement of proton assisted C-O cleavage (JACS 2018, 10121–10125). Hong et al. reported a Ni(II) complex where a Lewis acid was incorporated in the coordination structure of the complex through binding of metal ions to non-coordinated pyridyl groups. Divalent ions led to ten times higher CO yields compared to the complex without ions. There are also several examples of metal complexes with Brønsted acidic groups positioned close to the reactive center that have been proposed to facilitate the C-O cleavage. (*Science* 2012, 338, 90-94, *Chem. – Eur*. J., 2017, 23(20), 4782–4793, *ACS Cent. Sci.*, 2018, 4(3), 397–404, *J. Am. Chem. Soc.*, 2017, 139(7), 2604–2618, *Inorg. Chem.*, 2015, 54(11), 5285–5294, *Dalton Trans.*, 2019, 48, 12730-12737).

In the current report we have identified a way to facilitate the C-O bond cleavage step that does not require additional reduction of the catalyst, no external Lewis acid, and can proceed in absence of protic solvent of ligands. The catalyst is the recently reported $[Ru(tBu_3tpy)(m\text{-}CH_3bpy)MeCN]^{2+}$ complex, which we recently showed to be an active CO_2 to CO reduction catalyst already at the first reduction peak. We have identified a key intermediate using a

combination of spectroscopic and computational methods. A key feature of the catalyst is the hemilabile bonding of the ligands that create enough stability, without hampering two-site reactivity.



Scheme 1. Pictorial representation of (a) complexes [**A**-ACN]$^{2+}$ and [**1**-ACN]$^{2+}$, (b) the metala-η^1-*C*-carboxylate intermediate [Ru^{II}-CO$_2^{2-}$]^0.

Meyer *et al*. proposed that the that the tpy-bpy analogue complex forms a [**A**-CO$_2$]^0 intermediate after two reductions and exchange of a solvent ligand for CO$_2$ (Scheme 1). It was proposed to then undergo the addition of a third electron onto the tpy in the next step of the catalytic cycle.[6] We computed the potential for the addition of a third electron onto the similar [**1**-CO$_2$]^0 to -2.52 V (*vs.* Fc$^{+/0}$), indicating that this reduction is unlikely at an applied potential of -1.82 V[19], which is the cathodic peak potential at 0.2 V s^{-1} under CO$_2$. An alternative reaction involves another CO$_2$ molecule that form a bond to the electron-rich oxygen of the Ru-bound CO$_2$ in [**1**-CO$_2$]^0 in a "head-to-tail"[41] fashion. The activation energy ($\Delta G^{\ddagger}$) for this step is calculated to be 15.4 kcal mol^{-1}, the reaction free energy 8.0 kcal mol^{-1} (Scheme S1). The activation free energy indicates a rapid reaction; however, the reaction free energy indicates that the product complex could be part of the mechanism but should not be detectable.

The IR spectrum in our previous report of a bulk electrolyzed 1.0 mM solution of [**1**-ACN]$(PF_6)_2$ in anhydrous CH_3CN under CO_2 (0.28 M) (Figure S6),[19] displays the evolution of three major peaks centered at 1684 cm^{-1}, 1645 cm^{-1} and 1304 cm^{-1}. The peaks were assigned to the CO_3^{2-}/HCO_3^{2-} in CH_3CN.[19,42] A weak shoulder at 1740 cm^{-1} along with some unresolvable structured transitions near 1250 cm^{-1} evolves as the reaction proceeded (Figure S6). The calculated spectra of [**1**-CO_2]^0 has a peak at 1701 cm^{-1}, while [**1**-CO_2CO_2]^0 has a peak 1784 cm^{-1}. The observed shoulder at 1740 cm^{-1} falls in between the calculated structures and likely belong to a different species. We therefore studied the potential steps after the formation of [**1**-CO_2CO_2]^0.

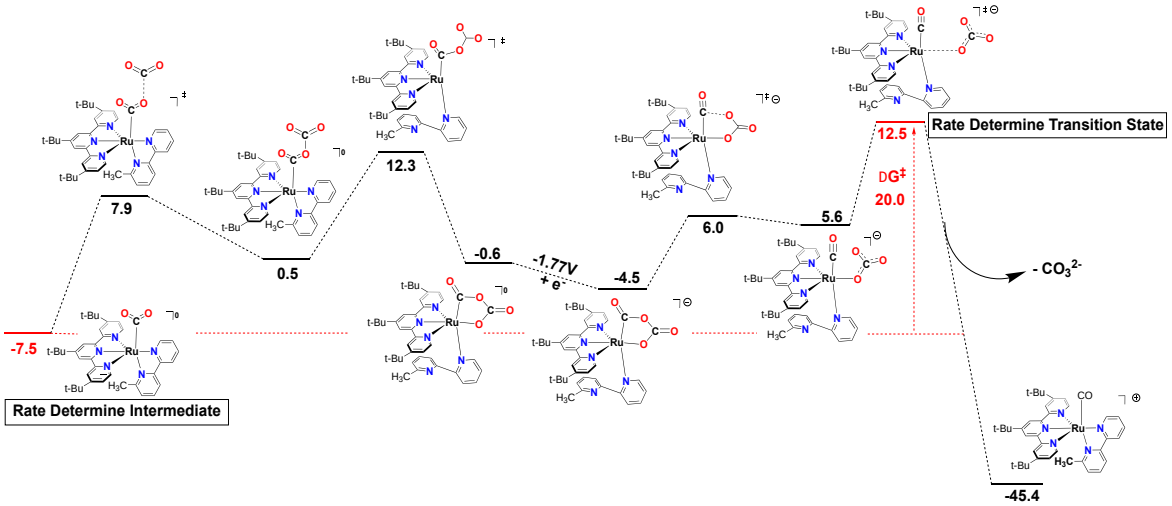
A possible route from [**1**-CO_2CO_2]^0 is direct C-O bond dissociation, producing CO_3^{2-} and the carbonyl complex (Scheme S2(a)). However, the calculated $\Delta G^{\ddagger}$ for this reaction is extremely high (60.5 kcal mol^{-1}). After a second CO_2 has bonded [**1**-CO_2CO_2]^0 can be expected to be more electrophilic than [**1**-CO_2]^0 and could be reduced at a less negative potential. However, our calculated potential -2.13 V (*vs.* $Fc^{+/0}$) is higher than the applied potential indicating that some other process is operating. The negatively charged terminal oxygen in [**1**-CO_2CO_2]^0 could attack the Ru center in another vicinal 5-coordinate intermediate [**1**]$^+$, the latter obtained by dissociation of CH_3CN on [**1**-ACN]$^{2+}$,[19] forming a bimetallic intermediate with -C(O)O-C(O)O- bridge (Scheme S2(b)), similar to one proposed for $Re^I(bpy)(CO)_3X$ catalysts.[7,12,43] However, this scenario is unlikely given that the catalytic current shows a first order dependence on the concentration of the catalyst in the range 0.05 mM to 1.0 mM.[19] Therefore the last alternative left is structural re-organization of the complex, either to facilitate C-O bond cleavage or to drive the subsequent reduction at a more positive potential. In [**1**-$COOCO_2$]^0 both the -CO_2CO_2 ligand and the 6-Mebpy are potential bidentate ligands. We explored the ligand exchange of the equatorial nitrogen of 6-Mebpy for the terminal oxygen of -CO_2CO_2.

The reaction was found to have a $\Delta G^{\ddagger}$ of 11.8 kcal mol^{-1} relative to [**1**-CO_2CO_2]^0 giving an overall activation energy of 19.8 kcal mol^{-1} relative to [**1**-CO_2]^0. The optimized structure of [**1**-CO_2CO_2]^{0,c} (Figure S9(a)) displays non-coplanarity of the *py* and *py*^{Me} rings with respect to each other, the interplanar angle (N4-C*b*-C*b′*-N5 dihedral; Table S3) being 22.7º, due to the steric repulsion between *py*^{Me} and *t*Bu$_3$tpy. [**1**-CO_2CO_2]^{0,c} is more stable than [**1**-CO_2CO_2]^0 by 1.1 kcal mol^{-1} (Scheme 3). A similar partial de-coordination and rotation around the C-C′ bond of 2,2′-bipyridine (bpy) fragment of a hexadentate ligand in a Co complex was proposed by Lucarini *et a.*.[44] The structural flexibility of 6-Mebpy, in combination with the steric clash between the -CH_3 (on 6-Mebpy) and *t*Bu$_3$tpy in makes the rearrangement facile in our case. There are a few examples 5-membered metallacycles from two CO_2 molecules as in [**1**-CO_2CO_2]^{0,c},[45-51] albeit with phosphorous containing ligands only and manifesting *stoichiometric* activation of CO_2.

Despite being 1.4 kcal more stable than [**1**-CO_2CO_2]^{0,c,t} (*i.e.* when a Ru-tpy bond breaks), the calculated spectra of [**1**-CO_2CO_2]^{0,c,b} (*i.e.* when a Ru-bpy bond breaks) does not have the peak in the 1740 cm^{-1} region that shows on the experimental IR. The DFT calculated IR spectrum of [**1**-CO_2CO_2]^{0,c} (Figure S8(b)) displays a strong peak at 1747 cm^{-1}, which corresponds to the symmetric C=O stretch (Figure S8(c)), along with less intense peaks at 1642 and 1258 cm^{-1}, corresponding to the asymmetric C=O stretch and a C-O stretch, respectively. The first peak agrees well with experimentally observed shoulder at 1740 cm^{-1} and the peak at 1258 cm^{-1} corresponds well to the smaller peak at 1250 cm^{-1}.

Still the calculated Gibbs free energy of [**1**-CO_2CO_2]^{0,c} is relatively high indicating that it is not observable. We also considered the possible reduction of [**1**-CO_2CO_2]^{0,c} to [**1**-CO_2CO_2]$^{-1,c}$. The potential was calculated to merely -1.77 V which makes it more likely to observed at the applied potential, with a calculated free energy of 3.5 kcal mol^{-1} relative to [**1**-CO_2]^0. The structure of

the reduced complex [**1**-CO_2CO_2]$^{-1,c}$ is similar to [**1**-CO_2CO_2]^{0,c} but with a broken bond to the bipyridine which is just weakly interacting with the catalyst. The IR spectra of [**1**-CO_2CO_2]$^{-1,c}$ has very similar features as that of [**1**-CO_2CO_2]^{0,c} with peaks at 1744cm^{-1}, 1688cm^{-1}, and 1287 cm^{-1}, corresponding well to the experimental spectrum.

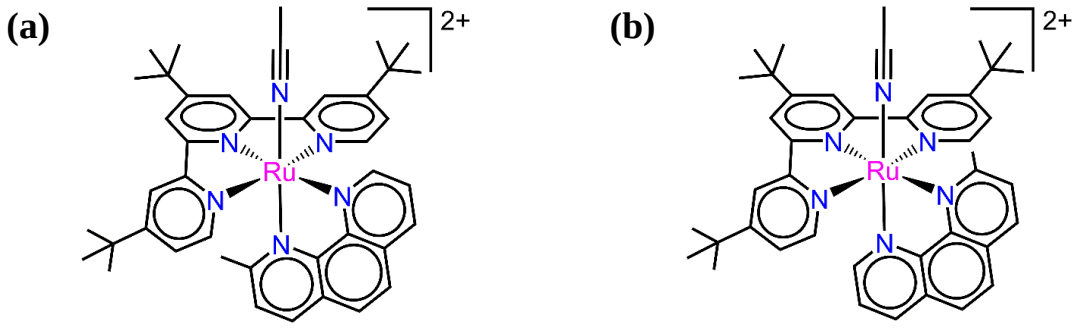


Scheme 3. Pathway to CO_3^{2-} *via* the cyclic two-electron reduced intermediate [**1**-$COOCO_2$]^{0,c}.

The structure of [**1**-CO_2CO_2]$^{-1,c}$ has some interesting features that could have implications for the C-O cleavage. Compared to the non-cyclic [**1**-CO_2CO_2]^0, where C-O cleavage has an activation energy of 60.5 kcal mol^{-1}, the C-O bond that will be cleaved is elongated from 1.36Å to 1.42Å indicating more single bond character. We located a transition state for the C-O cleavage just 10.5 kcal mol^{-1} above [**1**-CO_2CO_2]$^{-1,c}$ resulting in [**1**(CO)(OCO_2)]$^{-1}$, where the Ru-N distance is very long at 2.7Å but some interaction can be seen, at 13.1 kcal mol^{-1} relative to [**1**-CO_2]^0. Dissociation of carbonate then proceeds with an activation energy at 20.0 kcal mol^{-1}, which is accompanied with reformation of the Ru-bpy interaction. It appears that not only does the [**1**-CO_2CO_2]$^{-1,c}$ form, it leads to very facilitated C-O cleavage by weakening of the C-O single bond. The weakening is induced by the Lewis acidic nature of the site of oxygen

coordination at Ru, and hence, Ru acts as both a Lewis base in the formation of the Ru-C bond and a Lewis acid in the formation of the Ru-O-bond. It is likely that the formation of the metallacycle also induces some strain, that further weakens the C-O bond, as evidenced by the small O-Ru-C angle of 78.8° in [**1**-CO_2CO_2]$^{-1,c}$. In scheme 3 the reaction from [**1**-CO_2CO_2]^{0} to [**1**-CO]$^{-1}$ is outlined. The highest point is the formation of [**1**-CO_2CO_2]^{0,c} at 19.1 kcal mol^{-1} but with the dissociation of carbonate transition state at a similar free energy of X.X kcal mol^{-1}. The experimental TOF of 1.14 s^{-1} corresponds to an activation free energy of 17.5 kcal mol^{-1}, in good agreement with our calculated number.

A key to the potential involvement of [**1**-CO_2CO_2]$^{-1,c}$ in the mechanism is the hemi-labile coordination of the 6-Mebpy ligand. To test its involvement we synthesized a complex where the 6-Mebpy was replaced by 2-Mephen. It is well known that 1,10-phenanthroline (phen) forms more stable metal complexes compared to bpy.



Scheme 4. Pictorial representation of [**2**-ACN]$^{2+}$: (a) *distal* isomer, (b) *proximal* isomer.

Complex [**2**-ACN]$(PF_6)_2$ was synthesized following the same protocol as for [**1**-ACN]$(PF_6)_2$ (see Experimental Section for details). The NMR spectrum (Figure S4) of the complex indicates its diamagnetic nature, as well as the presence of both *proximal* and *distal* isomers. The cyclic voltammogram (CV) of [**2**-ACN]$(PF_6)_2$ displayed four one-electron redox waves, ox1, red1, red2 and red3, under Ar (Figure S10, Table S4). The red2 and red3 waves become reversible at scan rates above 0.75 Vs^{-1} (Figure S10(b), Table S4(b)). The reversibility of the wave at first

reduction, red1 ($E_{p,c}$ = -1.82 V (*vs*. $Fc^{+/0}$)), under Ar was lost under CO_2 (0.28 M)[55], with concomitant enhancement in cathodic current; $\frac{i_{p,c}\,(CO_2)}{i_{p,c}\,(Ar)} \approx 2$, where $i_{p,c}\,(CO_2)$and $i_{p,c}\,(Ar)$ represent the cathodic peak currents under CO_2 and Ar respectively (Figure 3). The current increase under CO_2 at the first reduction was however less than it was for [**1**-ACN]$(PF_6)_2$, the latter exhibiting $\frac{i_{p,c}\,(CO_2)}{i_{p,c}\,(Ar)} \approx 4$.[19] The cathodic currents under CO_2 increased further at more negative potentials (Figure S11).

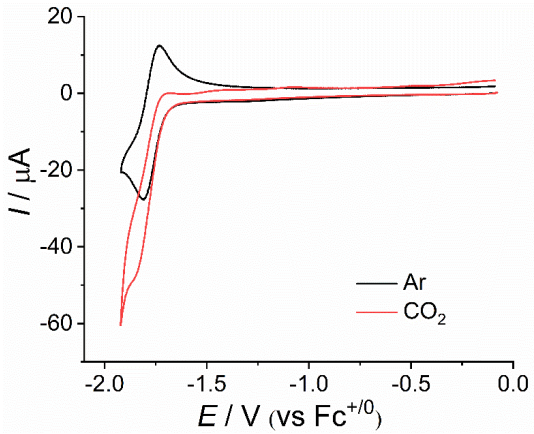


Figure 3. Cyclic voltammograms displaying the redox waves at first reduction for a 1.0 mM solution of [**2**-ACN]$(PF_6)_2$ under Ar (black) and CO_2 (red) at 0.2 V s^{-1}.

Initially, we were surprised by the current enhancement of [**2**-ACN]$(PF_6)_2$ under CO2. We therefore recorded the time evolved IR spectra during the CPE of [**2**-ACN]$(PF_6)_2$ at -1.82 V (*vs*. $Fc^{+/0}$) under CO_2 (0.28 M), which displayed the evolution of bands at 1735, 1612 and 1272 cm^{-1} along with 1686, 1645, and 1302 cm^{-1} (Figure 4), the latter three being present in case of [**1**-ACN]$(PF_6)_2$ as well.[19] The bands are thus very similar to the bands of [**1**-CO_2CO_2]^{0,c} and [**1**-CO_2CO_2]$^{-1,c}$, despite the blocking of the potential decoordination of the equatorial nitrogen. It is however possible that the terpyridine ring has similar hemi-lability. We optimized the structure of [**2**-$COOCO_2$]^{0,c} (Figure S9(c)). Its calculated IR spectrum in CH_3CN displays peaks at 1746 (symmetric C=O stretches), 1690 (asymmetric C=O stretches), and 1257 (C-O stretches) cm^{-1} (Figures S12 and S8(c)), which correspond well to the experimentally obtained bands at

1735, 1686, and 1272 cm^{-1} (Figure 4) respectively. Further support for the assignment of these IR bands to the metalacyclic intermediate comes from the complex $Ir(PMe_3)_3(Cl)(COOCOO)$, reported by Herskovitz *et. al.*,[45] incorporating a (η^2-C,O′)Ir cycle similar to the one proposed in the present work. It was the first complex reported to possess two CO_2 molecules in a "head-to-tail" arrangement, made by stoichiometric and reversible CO_2 activation. It exhibited IR bands at 1725, 1680, 1648 (sh), 1605, and 1290 cm^{-1} which were ascribed to the -C(O)OC(O)O- moiety of the metallacycle.

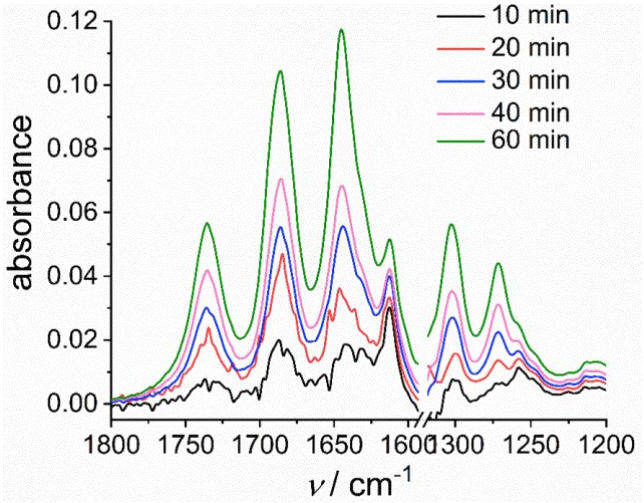


Figure 4. Fourier transformed infra-red (FT-IR) absorbance spectra of aliquots of 1 mM solution of [**2**-ACN]$(PF_6)_2$ in CH_3CN/0.1 M $TBAPF_6$ saturated with CO_2 (0.28 M), taken during its controlled potential electrolysis at an applied potential of -1.82 V (*vs*. $Fc^{+/0}$) at 298 K.

The rate of C-O bond dissociation is presumably lower in [**2**-CO_2CO_2]^{0,c} than [**1**-CO_2CO_2]^{0,c} or [**1**-$COOCO_2$]$^{-1,c}$, since unlike the latter two intermediates, we were able to observe the former unambiguously in the IR spectrum during CPE. Further detailed thermodynamic and kinetic investigations of the catalytic activity of [**2**-ACN]$(PF_6)_2$ towards electrochemical CO_2 reduction are underway.

The current work presents for the first time, the involvement of an unprecedented 5-membered *ruthenacyclic* intermediate in the catalytic cycle of electrochemical CO_2 reduction by Ru-polypyridyl complexes. The fine tuning of the electronic and steric properties by utilizing the *flexibility* feature of the polypyridyl ligands with respect to rotation around C-C′ bonds renders the spectroscopic observation of such an intermediate possible, without destroying the structural integrity of the catalyst. This particular class of catalysts also showcases a unique example of a sole metal center performing the roles of both a Lewis base (for attachment of CO_2 *via* C atom) and a Lewis acid (for attachment of CO_2 *via* O atom), hence portraying the impressive tunability of the electronic nature of the metal center in the course of catalysis.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publications Website at DOI:

Experimental details, Figures, Tables

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Notes

The authors declare no competing financial interest.

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