Contents lists available at ScienceDirect



Journal of Photochemistry & Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

# Photochemistry and Photobiology A: Chemistry

# Electron transfer from photoexcited naphthalene-1,4:5,8-bis(dicarboximide) radical anion to $Mn(bpy)(CO)_3X$ and $Re(bpy)(CO)_3X CO_2$ reduction catalysts linked via a saturated methylene bridge



Jose F. Martinez, Nathan T. La Porte, Michael R. Wasielewski\*

Department of Chemistry and Institute for Sustainability and Energy at Northwestern, Northwestern University, Evanston, IL 60208-3113, United States

ARTICLE INFO	A B S T R A C T
Keywords: Femtosecond spectroscopy Electrochemistry Electron transfer Radical anions CO <sub>2</sub> reduction Solar energy	Supramolecular systems that connect a naphthalene-1,4:5,8-bis(dicarboximide) (NDI) radical anion donor to Mn (bpy)(CO) <sub>3</sub> Br or Re(bpy)(CO) <sub>3</sub> Cl CO <sub>2</sub> reduction catalysts via a methylene bridge have been synthesized and studied by femtosecond transient visible, near-infrared and mid-infrared spectroscopy. The use of the methylene bridge to link NDI to the complexes does not affect the reduction potentials of the metal complexes. Selective photoexcitation of NDI <sup>-</sup> to <sup>2*</sup> NDI <sup>-</sup> results in ultrafast reduction of the bipyridine (bpy) ligands on both the Mn and Re complexes to form Mn(I)(bpy <sup>-</sup> )(CO) <sub>3</sub> X and Re(I)(bpy <sup>-</sup> )(CO) <sub>3</sub> X in near unity quantum yield, respectively. The initial formation of Mn(I)(bpy <sup>-</sup> )(CO) <sub>3</sub> X is unexpected based on previous electrochemical data that indicates the Mn(I) center is reduced at a more positive potential than the bpy ligand. Moreover, the rate of forward electron transfer in the Mn complex was faster than in the Mn complex.

# 1. Introduction

In the past several decades, many research groups have focused a great deal of eff ;ort on harnessing solar photons to power chemical reactions for artificial photosynthesis that produce fuels [1–7]. One way to do so is by transforming solar energy into chemical bonds, as plants do during photosynthesis through the transformation of carbon dioxide into glucose [8,9]. In green plant photosynthesis, this is accomplished by the absorption of a photon by chlorophyll that initiates a series of electron transfer events that reduce nicotinamide adenine dinucleotide phosphate (NADP), so that it can effectively bind a proton to give NADPH, which serves as the reducing agent in the biochemical reactions that convert CO<sub>2</sub> into glucose [9]. In artificial photosynthesis, this can be done by utilizing solar energy to transfer electrons to catalysts that can bind and convert carbon dioxide into liquid fuel. Natural photosynthesis ultimately provides the design principles and demonstrates how to eff ;ectively balance light absorption, charge separation, and catalysis, giving chemists a blueprint for developing effective artificial supramolecular systems.

A proven strategy to replicate these processes is to use supramolecular donor-acceptor assemblies [10]. The simplest supramolecular systems for  $CO_2$  reduction consist of an electron donor (D) that is appended to an acceptor (A) through a linking bridge unit (B). In the case of supramolecular systems for CO<sub>2</sub> reduction, the acceptor is the catalyst and the electron donor is a photosensitizer that can be selectively excited to ultimately transfer an electron to the catalyst. For example, Ishitani and co-workers covalently linked a Ru<sup>II</sup>(bpy)<sub>3</sub><sup>2+</sup> photosensitizer to Re(bpy)(CO)<sub>3</sub>X via a series of saturated alkyl (C<sub>x</sub>H<sub>y</sub>) bridges [10-12]. They demonstrated that the nature of the linking bridge can play a major role in the efficiency and turnover number (TON) for CO<sub>2</sub> reduction of these supramolecular systems. In contrast, they saw a dramatic decrease in TON by using a phenanthroline-imidazolyl (<sup>im</sup>phen) motif to link  $Ru^{II}(bpy)_2(^{im}phen)^{2+}$  and Re(dmb) (CO)<sub>3</sub>Cl or an ethylene bridge to link  $Ru^{II}(bpy)_3^{2+}$  and  $Re(dmb)(CO)_3Cl$ [10]. Perutz and Whitwood utilized an amide bridge to link zinc porphyrins to Re analogues, and saw a decrease in TON when compared to a saturated alkyl linkage [13]. Ishitani showed further that the decrease in photocatalytic performance is due to the use of bridges that extend the bpy conjugation in either the photosensitizer/donor or the catalyst. Linkers that extend the bpy  $\pi$ -conjugation shift its reduction potential to more positive potentials. As the bpy reduction potential of the catalyst shifts more positive, the one-electron reduced complex that is formed upon electron transfer from the photosensitizer has a decreased ability to bind CO<sub>2</sub>; thus the reductive catalytic activity of the Re(bpy) (CO)<sub>3</sub>X unit is diminished. Additionally, if the bpy reduction potential of the photosensitizer shifts more positive, electron transfer from the

\* Corresponding author.

E-mail address: m-wasielewski@northwestern.edu (M.R. Wasielewski).

https://doi.org/10.1016/j.jphotochem.2018.11.047

Received 15 October 2018; Received in revised form 26 November 2018; Accepted 30 November 2018 Available online 30 November 2018 1010-6030/ © 2018 Published by Elsevier B.V.



**Fig. 1.** Previously studied donor acceptor complexes incorporating NDI<sup>-</sup> to Re (bpy)(CO)<sub>3</sub>Cl or Mn(bpy)(CO)<sub>3</sub>Br via a phenyl bridge.

photosensitizer MLCT state to the catalyst will no longer be spontaneous and will decrease the yield of the active catalyst. For these reasons, the supramolecular systems with the highest TON for photocatalytic  $CO_2$  reduction currently utilize saturated alkyl bridges to link the donor/photosensitizer to the acceptor/catalyst.

Our previous work examined supramolecular systems that had either a naphthalene-1,4:5,8-bis(dicarboximide) (NDI) or perylene-3,4:9,10-bis(dicarboximide) (PDI) radical anion donor linked to Re (bpy)(CO)<sub>3</sub>Cl via a phenyl bridge to form Re(bpy-Ph-NDI or PDI) (CO)<sub>3</sub>Cl [14-17]. These supramolecular structures were also extended to form Mn analogues Mn(bpy-Ph-NDI)(CO)<sub>3</sub>Br, see Fig. 1 [18]. The NDI subunit within the supramolecular system can be selectively reduced, either chemically or electrochemically to form Re(bpy-Ph-NDI<sup>•-</sup>)(CO)<sub>3</sub>Cl or Mn(bpy-Ph-NDI<sup>•-</sup>)(CO)<sub>3</sub>Br. The NDI radical anion (NDI<sup>-</sup>) has an excited state oxidation potential of -2.1 V vs. SCE upon excitation with visible or near-infrared light [19]. This oxidation potential is more negative that of  $Ru^{II}(bpy)_3^{2+}$  or other metalorganic chromophores such as Ir(ppy)<sub>3</sub> and Ir(ppy)<sub>2</sub>(bpy)<sup>+</sup> [20,21]. Upon selective excitation of the NDI<sup>-</sup> to form <sup>2\*</sup>NDI<sup>-</sup>, we observed rapid electron transfer to Re(bpy)(CO)<sub>3</sub>Cl with a quantum yield of near unity to form Re(bpy<sup>·-</sup>-Ph-NDI<sup>°</sup>)(CO)<sub>3</sub>Cl or Mn(bpy<sup>·-</sup>-Ph-NDI<sup>°</sup>)(CO)<sub>3</sub>Br, the first step in the photocatalytic reduction of CO<sub>2</sub> [18,22]. However, in these complexes, because the NDI<sup>•-</sup> chromophore was linked to the bpy ligand with a phenyl substituent, the reduction potential of bpy was shifted positive due to the extension of the conjugation onto the bridging phenyl. For this reason, we have now investigated complexes in which NDI<sup>•-</sup> is linked to bpy via a methylene bridge to maintain the reducing power of the one-electron reduced catalyst.

Re(bpy)(CO)<sub>3</sub>Cl and its derivatives have been shown repeatedly to reduce CO<sub>2</sub> within donor-acceptor systems, while Mn(bpy)(CO)<sub>3</sub>Br has received little attention despite having similar electro- and photocatalytic properties as the Re analogues [10,23-27]. Only recently has photoinduced electron transfer to a Mn(bpy)(CO)<sub>3</sub>Br complex been investigated [18]. For these reasons, we sought to link NDI<sup>-</sup> to both Re (bpy)(CO)<sub>3</sub>Cl and Mn(bpy)(CO)<sub>3</sub>Br via a CH<sub>2</sub> bridge. In this report, we show that the incorporation of the NDI $^{-}$  to a CH<sub>2</sub> bridge does not affect the bpy reduction potential. Excitation of NDI<sup>•-</sup> to form <sup>2\*</sup>NDI<sup>•-</sup> leads to the rapid formation of Re(bpy' - CH<sub>2</sub>-NDI°)(CO)<sub>3</sub>Cl, the first step in the photocatalytic reduction of CO<sub>2</sub>, and the quantum yield of forward electron transfer is near unity. We also extended this study to the analogous Mn complex to photochemically reduce Mn(bpy)(CO)<sub>3</sub>Br to Mn(bpy<sup>•</sup>)(CO)<sub>3</sub>Br. The initial formation of Mn(I)(bpy<sup>•</sup>)(CO)<sub>3</sub>X is unexpected based on previous electrochemical data that indicate the Mn(I) center is reduced at a more positive potential than is the bpy ligand. [28] The time constant of electron transfer was found to be faster in Mn(4-NDI<sup>•–</sup> – CH<sub>2</sub>-bpy)(CO)<sub>3</sub>Br,  $\tau_{A \rightarrow B(Mn)} = 0.3 \pm 0.1 ps$  vs.

 $\tau_{A \rightarrow B(Re)} = 0.5 \pm 0.1 \, ps$ , while the time constant for back electron transfer was faster for Re(4-NDI<sup>-</sup> – CH<sub>2</sub>-bpy)(CO)<sub>3</sub>Cl,  $\tau_{B \rightarrow C(Re)} = 0.7 \pm 0.1 \, ps$  vs.  $\tau_{B \rightarrow C(Mn)} = 1.5 \pm 0.1 \, ps$ . Additionally, while the NDI reduction potentials of the two complexes are very similar to that of NDI itself, the double reduction of the Mn complex occurred at ~ 200 mV more positive than the double reduction of the Re complex, as expected [27,28].

# 2. Materials and methods

# 2.1. Materials

Dichloromethane (DCM), acetonitrile (MeCN), and N,N-dimethylformamide (DMF) used for synthesis and spectroscopic experiments were dried using a commercial system (Pure Process Technology, Nashua, NH). For spectroscopy, DMF and MeCN were transferred under argon into a N<sub>2</sub>-filled glovebox (MBraun Unilab) for use and storage. Carbon dioxide (Research Grade) was obtained from Airgas and used without further purification. Commercially available reagents were purchased from Sigma-Aldrich or Oakwood Chemicals and used as received. Compounds were reduced in the glovebox using tetrakis(dimethylamino)ethylene (TDAE) from Tokyo Chemical Industries. Detailed synthetic procedures and compound characterization are shown in the Supplementary Material.

#### 2.2. Steady-state spectroscopy

UV–vis spectra were acquired on a Shimadzu UV-1800 spectrophotometer at room temperature. The samples were normalized to the greatest peak. FTIR spectra were measured on a Shimadzu IRAffinity spectrophotometer in absorbance mode at  $2 \text{ cm}^{-1}$  resolution. Samples were prepared in DMF under an argon atmosphere, contained in a liquid demountable cell (Harrick Scientific) with 2.0 mm thick CaF<sub>2</sub> windows and 500 µm Teflon spacers.

# 2.3. Electrochemistry

Electrochemical measurements were performed using a CH Instruments Model 660 A electrochemical workstation. A single-compartment cell was used for all cyclic voltammetry experiments with a 1.0 mm diameter glassy carbon disk working electrode, a platinum counter electrode, a silver wire pseudoreference electrode, and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte in DMF or MeCN. The ferrocene/ferrocenium redox couple (0.45 V vs SCE in DMF or 0.40 V vs SCE in MeCN) [29] was used as an internal standard. TBAPF<sub>6</sub> was recrystallized twice from ethanol prior to use. Electrochemical cells were shielded from light and all solutions were continuously purged with argon before and during the cyclic voltammetry measurements.

# 2.4. Femtosecond transient visible absorption spectroscopy

Femtosecond transient absorption experiments were performed employing a regeneratively amplified Ti:sapphire laser system operating at 828 nm and a 1 kHz repetition rate as previously described [30,31]. The output of the amplifier was frequency-doubled to 414 nm using a BBO crystal and the 414 nm pulses were used to pump a laboratory-built collinear optical parametric (OPA) amplifier for visiblelight excitation [32] or a commercial non-collinear optical parametric amplifier (TOPAS-White, Light-Conversion, LLC.) for NIR excitation. Approximately 1–3 mW of the fundamental was focused into a continuously rastered CaF<sub>2</sub> disk to generate the UV–vis white light probe spanning 340–800 nm, or into a proprietary medium (Ultrafast Systems, LLC) to generate the NIR white-light probe spanning 850–1620 nm. The total instrument response function was 300 fs. Experiments were performed at a randomized pump polarization to suppress contributions from orientational dynamics. Spectral and kinetic data were collected with a CMOS or InGaAs array detector for visible and NIR detection, respectively, and a 8 ns pump-probe delay track (customized Helios, Ultrafast Systems, LLC). Transient spectra were averaged for at least 3 s. Gaps shown in the spectra are due to either scattering of the pump or idler beam, or regions not covered by the detectors. Samples prepared in DMF had an absorbance of 0.2-0.7 at the excitation wavelength and were irradiated in 2 mm quartz cuvettes with 0.4-0.8 µJ/pulse focused to  $\sim 0.2 \text{ mm}$  diameter spot. Samples were stirred to avoid effects of local heating or sample degradation. The samples were prepared in the glovebox. The fsTA data were corrected for group delay dispersion, or chirp, and scattered light prior to the kinetic analysis using Surface Xplorer (Ultrafast Systems, LLC). The kinetic analysis was performed using home-written programs in MATLAB [33] and was based on a global fit to selected single-wavelength kinetics. The time resolution is given as w = 300 fs (full width at half-maximum); the assumption of a uniform instrument response across the frequency domain and a fixed time zero are implicit to global analysis. The data were globally fit either to specified kinetic models or a sum of exponentials. The data set was then deconvoluted with the resultant populations or amplitudes to reconstruct the species-associated or decay-associated spectra. The procedures and kinetic models used to fit the data have been previously described in detail [14].

#### 2.5. Femtosecond time-resolved Mid-IR spectroscopy

Femtosecond transient mid-IR absorption (fsIR) spectroscopy was performed using a commercial Ti:sapphire oscillator/amplifier (Solstice 3.5 W, Spectra-Physics) to pump two optical parametric amplifiers (TOPAS-C, Light Conversion), one which provided a 100 fs, 605 nm excitation pulse and the other provided 100 fs pulses at 2150–1800 cm<sup>-1</sup>. The overall instrument response was 300 fs. The spectra were acquired with a liquid N<sub>2</sub>-cooled dual channel ( $2 \times 64$ ) MCT array detector that is coupled to a Horiba HR320 monochromator as part of a Helios-IR spectrometer (Ultrafast Systems, LLC). Samples with a maximum optical density of 1.5 at the excitation wavelength were prepared in DMF contained in a liquid demountable cell (Harrick Scientific) with 2.0 mm thick CaF<sub>2</sub> windows and a 500 µm Teflon spacer. During data acquisition, the cell was mounted and rastered on a motorized stage to prevent sample degradation.

#### 3. Results

#### 3.1. Synthesis

Complexes **1** Re(4-NDI-CH<sub>2</sub>-bpy)(CO)<sub>3</sub>Cl and **2** Mn(4-NDI-CH<sub>2</sub>-bpy) (CO)<sub>3</sub>Br were synthesized as illustrated in Scheme 1 and detailed in the Supplementary Material. 4-Methyl-4'-aminomethyl-2,2'-bpy was prepared as previously reported [34]. Condensation of this amine with N-(2,5-di-t-butyl)naphthalene-(1,4)-dicarboximide-(5,8)-

dicarboxyanhydride [14] led to the final ligand. The ligand was then refluxed in dry dichloromethane under argon with rhenium(I)pentacarbonylchloride or bromopentacarbonylmanganese(I) to form complexes **1** and **2**, respectively.

#### 3.2. Electrochemistry

The cyclic voltammograms of complexes 1 and 2 are shown in Fig. 2 with their reduction potentials summarized in Table 1. Complex 1 displays four reduction waves with NDI having reversible first and second reduction potentials at -0.48 and -0.98 V, respectively. The third and fourth reductions are well separated from those of NDI as well as from each other. The reversible reduction at -1.45 V is assigned to bpy, while the irreversible reduction at -1.94 V is assigned to Re(I) in the complex. Complex 2 also displays four reduction waves with the first two reversible waves at -0.48 and -0.99 V, once again resulting from NDI. The third and fourth reductions at -1.38 and -1.73 V are well separated from one another but irreversible, and in contrast to the Re complex are assigned to Mn(I) and bpy reduction, respectively [35]. These assignments are in good agreement with previous work that integrates NDI with Re(bpy)(CO)<sub>3</sub>X and other electrochemical studies of Re and Mn(N^N)(CO)<sub>3</sub>X complexes [16,18,35].

# 3.3. Electron transfer energetics

Based on the redox potentials discussed above, the Gibbs free energy for the excited state electron transfer reactions of complexes 1 and 2 can be estimated using the following equation:

$$\Delta G_{ET} = E(NDI^{-}/NDI) - E(A^{-}/A) - E_{D1}(^{2*}NDI^{-}).$$
(1)

where  $E(\text{NDI}^-/\text{NDI})$  is the reduction potential of NDI and  $E(\text{A}^-/\text{A})$  is the reduction potential of the complex of interest, and  $E_{\text{D1}}$  is the energy of the <sup>2\*</sup>NDI<sup>-</sup> excited state, assuming electron transfer occurs from the D<sub>1</sub> state. The D<sub>1</sub>  $\leftarrow$  D<sub>0</sub> transition of NDI<sup>-</sup> absorbs at 785 nm, making  $E_{\text{D1}} = 1.58 \text{ eV}$ . There is no electrostatic work term for this reaction because the reaction is a charge shift, not a charge separation. In addition, there is no solvation correction term because the fsTA and electrochemical experiments are performed in the same high polarity solvent. The Gibbs free energy for the thermal back electron transfer reactions can be estimated using the following equation:

$$\Delta G_{ET} = E(A^{\bullet -}/A) - E(NDI^{\bullet -}/NDI)$$
<sup>(2)</sup>

From the equations above, the Gibbs free energies for each electron transfer step are shown in Table 2 below.

# 3.4. Steady-state spectroscopy

#### 3.4.1. Steady-State FTIR

The FTIR spectra of complexes **1** and **2** were collected in solution (Fig. 3) and the  $\nu$ (CO) are tabulated in Table 3. Complexes **1** and **2** show



Scheme 1. Synthesis of complexes 1 and 2.



Fig. 2. Cyclic voltammograms of 1.0 mM solutions of (A) 1 and (B) 2 in DMF, recorded at 100 mV s<sup>-1</sup> at room temperature with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte under argon.

# Table 1

Redox potentials of complexes 1 and 2 vs SCE in DMF.

Compound	NDI <sup>0/-</sup>	NDI <sup>-/2-</sup>	3rd	4th
Re (1)	-0.48	- 0.98	-1.45	-1.94
Mn (2)	-0.48	- 0.99	-1.38	-1.73

Table 2							
Free energy	changes	for electro	on transfer	reactions	in complex	1 <sup>•–</sup>	and 2

Compound process $\Delta G$	
- <u>D*</u> -	(eV)
1 <sup></sup> 2 <sup>-</sup> NDI <sup>-</sup> $\rightarrow$ Re(bpy)(CO) <sub>3</sub> Cl       -(         2 <sup>-</sup> 2 <sup>*</sup> NDI <sup>-</sup> $\rightarrow$ Mn(bpy)(CO) <sub>3</sub> Br       -(         2 <sup></sup> 2 <sup>*</sup> NDI <sup>-</sup> $\rightarrow$ Mn(bpy)(CO) <sub>3</sub> Br       -(         1 <sup></sup> Re(bpy <sup>-</sup> )(CO) <sub>3</sub> Cl $\rightarrow$ NDI <sup>*</sup> -(         2 <sup></sup> Mn(bpy <sup>-</sup> )(CO) <sub>3</sub> Cl $\rightarrow$ NDI <sup>*</sup> -(         2 <sup></sup> Mn(bpy <sup>-</sup> )(CO) <sub>3</sub> Cl $\rightarrow$ NDI <sup>*</sup> -(	).61 ).33 ).68 ).97 1.25
$2^{-}$ Mn <sup>·−</sup> (bpy)(CO) <sub>3</sub> Cl → NDI° – 0	).90

three characteristic  $\nu$ (CO) stretches for facially coordinated tricarbonyl complexes. It is known that the energies of and separation between the two lower-energy bands depend on the axial ligand X [36]. Typically, two well-developed bands are observed in complexes with halide ligands [36]. The spectra of complexes **1** and **2** are in agreement with this observation because the two low energy bands are separated by 18–23 cm<sup>-1</sup>.

# 3.4.2. Steady state UV-vis absorption

The normalized steady-state electronic absorption spectra of 1 and 2 are shown in Fig. 4. In complexes 1 and 2, the NDI absorptions dominate the spectrum of the unreduced compounds. In complex 1, the Re (bpy)(CO)<sub>3</sub>X MLCT absorption band tails out from underneath the NDI absorptions. This is similar for complex 2 where the Mn(bpy)(CO)<sub>3</sub>X LMCT absorption band is broad and tails out to ~500 nm. [24] When TDAE is added to complex 1 and 2, to form 1<sup>--</sup> and 2<sup>--</sup>, the NDI

Table 3 CO stretching frequencies of complexes  ${\bf 1}$  and  ${\bf 2}$  in DMF.

Compound	A′(1)	A′(2)	Α″
Re (1)	2019	1914	1891
Mn (2)	2024	1932	1914

absorptions disappear while the NDI<sup>-</sup> absorptions appear at 471, 605, 700, and 785 nm. [19] In the chemically reduced complexes 1<sup>-</sup> and 2<sup>-</sup>, the Re(bpy)(CO)<sub>3</sub>X MLCT and Mn(bpy)(CO)<sub>3</sub>X LMCT bands underly the strong absorptions of NDI<sup>-</sup>.

# 3.5. Electron transfer dynamics

#### 3.5.1. Transient absorption spectroscopy

The intramolecular electron transfer behavior of complexes 1<sup>•–</sup> and  $\mathbf{2}^{\cdot-}$  was investigated using pump-probe femtosecond transient absorption (fsTA) spectroscopy. Figs. 5 and 6 display the fsTA spectra at selected time delays following selective photoexcitation of NDI<sup>--</sup> with a pump pulse centered at  $\lambda_{ex} = 605$  nm for each complex. Excitation of complexes  $1^{-}$  and  $2^{-}$  at 605 nm results in instrument-limited bleaching of the ground-state absorption of NDI<sup>--</sup> at 473 nm, and the appearance of a broad absorption spanning 410–450 nm, corresponding to the induced absorptions of <sup>2\*</sup>NDI<sup>-</sup>. The <sup>2\*</sup>NDI<sup>-</sup> absorptions decay in < 1 ps, and are accompanied by the appearance of absorptions at 362 and 382 nm, which result from the absorption of NDI°, indicating that electron transfer to the metal complex has occurred. For complexes 1<sup>•</sup> and 2<sup>•</sup>, the data are best fit to an  $A \rightarrow B \rightarrow C \rightarrow GS$  kinetic model. The species-associated spectra corresponding to species A, B, and C and the transient kinetics at selected wavelengths are shown in Figs. 5 and 6. The population dynamics are shown in Figs. S3-S4 and the corresponding rate constants are given in Table 4.



Fig. 3. FTIR spectra of complexes (A) 1 and (B) 2 in DMF.



Fig. 4. Electronic absorption spectra of complexes (A) 1 and (B) 2 in DMF with and without the TDAE reductant added.

# 3.5.2. Time-resolved mid-IR spectroscopy

To certify that the metal complexes in 1 and 2 were indeed reduced, the CO-stretching region of their IR spectra  $(1850-2100 \text{ cm}^{-1})$  was monitored using femtosecond time-resolved mid-IR transient absorption (TRIR) experiments. TRIR spectra and kinetic traces at selected energies are shown below in Figs. 7 and 8. Complexes 1<sup>-</sup> and 2<sup>-</sup> exhibited similar spectral features but with different kinetics. For example, induced absorptions appear at 1869 cm<sup>-1</sup> and 2001 cm<sup>-1</sup> in complex 1<sup>•-</sup> following excitation at 605 nm. These induced absorptions decay with the same kinetics that the ground state bleaches at 1911 cm<sup>-</sup> <sup>1</sup> and 2019 cm<sup>-1</sup> decay. As is the case for  $1^{-1}$ , the kinetics of the induced absorption decay for complex  $2^{-}$  at 1935 cm<sup>-1</sup> and 2024 cm<sup>-1</sup> following 605 nm excitation are essentially the same as the bleach recovery kinetics at 1895 cm<sup>-1</sup> and 2003 cm<sup>-1</sup>. The magnitudes of these frequency shifts have been previously reported by us and by other groups in photo- and electrochemical experiments in which Re(bpy) (CO)<sub>3</sub>X or Mn(bpy)(CO)<sub>3</sub>X are reduced by one electron to form Re (bpy<sup>•-</sup>)(CO)<sub>3</sub>X or Mn(bpy<sup>•-</sup>)(CO)<sub>3</sub>X, respectively.

The fsIR spectra were fit to the same  $A \rightarrow B \rightarrow C \rightarrow GS$  model as the fsTA data, with a modification to account for the A species (associated with excitation of the NDI<sup>-</sup> fragment) exhibiting no change in the mid-IR relative to the ground state and with the  $\tau_{A \rightarrow B}$  fixed at the value obtained from the fsTA fit. This fitting gave  $\tau_{B \rightarrow C} = 0.4 \pm 0.3$  ps and  $\tau_{C \rightarrow GS} = 18 \pm 10$  ps for 1<sup>-</sup>, and  $\tau_{B \rightarrow C} = 1 \pm 0.5$  ps and  $\tau_{C \rightarrow GS} = 50 \pm 40$  ps for 2<sup>-</sup>. The large error bars for  $\tau_{C \rightarrow GS}$  result from the low signal-to-noise of the TRIR data, but in general the values are similar to those obtained from the fitting the fsTA data.

# 4. Discussion

#### 4.1. Electrochemistry

In complexes 1 and 2, there are four well-separated reduction processes in their cyclic voltammograms. The first two reduction processes of complexes 1 and 2 are NDI localized and are similar to that of the free NDI chromophore. [19] The electrochemical data shown in Table 1 show that the attachment of NDI to bpy via a CH<sub>2</sub> bridge has a negligible effect on the reduction potentials of NDI. The third reduction in complex 1 is reversible, while the third reduction in complex 2 is not. In complex 1, the third reduction is attributed to bpy reduction to form Re  $(bpy^{-})(CO)_{3}Cl$ , while in complex 2, the third reduction is attributed to the reduction of the metal center to form  $Mn^{\circ}(bpy)(CO)_3$  [28]. In complex 2, the third reduction leads to the simultaneous loss of the halide ligand to form a five-coordinate Mn° complex. On the electrochemical time scale (100 mV/s), rapid dimerization occurs upon the first metal-based reduction in complex 2. This is evident in the reverse sweep by the oxidative cleavage of the dimer complex Mn°-Mn° at -0.18 V. In contrast, the first metal-based reduction in complex 1 is bpy localized and the loss of the halide ligand does not occur. Upon the fourth reduction in complex 1, the rhenium center is formally reduced, and the halide ligand simultaneously dissociates to form Re°(bpy'-)  $(CO)_3$ . Upon the fourth reduction in complex 2, the bpy is reduced, and the dimer complex is cleaved to form Mn°(bpy<sup>•-</sup>)(CO)<sub>3</sub>. Complexes 1 and 2 are freely diffusing in solution according to the Randles-Sevcik equation (Figs. S1-S2). These assignments and observations are in complete agreement with the literature. [25,27,28,35,37,38]

#### 4.2. Femtosecond transient absorption spectroscopy

The intramolecular electron transfer behavior of complex 1<sup>•-</sup> and 2<sup>•-</sup> was probed using transient absorption spectroscopy in the visible region. The fsTA spectrum, the species associated spectra for each decay component, and the multiple wavelength kinetics and fits are shown in Figs. 5 and 6. For complex 1<sup>•-</sup>, following excitation at  $\lambda_{ex} = 605$  nm, the photoinduced charge shift dynamics were fit to an A $\rightarrow$ B $\rightarrow$ C $\rightarrow$ GS model, where A represents the promotion of NDI<sup>•-</sup> to its excited state Re(4-<sup>2\*</sup>NDI<sup>•-</sup>-bpy)(CO)<sub>3</sub>Cl, B represents the photoinduced charge shifted species Re(4-NDI<sup>°</sup>-bpy<sup>•-</sup>)(CO)<sub>3</sub>Cl, C potentially represents a



Fig. 5. (A) fsTA spectra of complex  $1^{-}$  (B) species-associated spectra (C), transient kinetics at selected wavelengths.  $\lambda_{ex} = 605 \text{ nm}$ , solvent = DMF.



Fig. 6. (A) fsTA spectra of complex  $2^{-}$  (B) species-associated spectra (C), transient kinetics at selected wavelengths.  $\lambda_{ex} = 605$  nm, solvent = DMF.

Table 4 Observed time constants and rates of electron transfer for complexes  $1^{\cdot-}$  and  $2^{\cdot-}$ .

	$\tau_{A \rightarrow B}$ (ps)	$\tau_{B \to C}$ (ps)	$\tau_{C \rightarrow GS}$ (ps)	$k_{A \rightarrow B}$ (s <sup>-1</sup> )	$k_{B \rightarrow C} (s^{-1})$	$k_{C \rightarrow GS} $ (s <sup>-1</sup> )	$\Phi_{FET}$
1'-	$0.5 \pm$	$0.7 \pm 0.1 \text{ ps}$	$8.1 \pm 0.2$	$2.0\times10^{12}$	$1.4\times10^{12}$	$1.2\times10^{11}$	0.99
2'-	0.3 ± 0.1 ps	1.5 ± 0.1 ps	84.7 ± 2.0 ps	$3.3\times10^{12}$	$\textbf{6.6}\times 10^{11}$	$1.2\times10^{10}$	0.99

structural change or vibrational cooling, GS represents the original ground state Re(4-NDI<sup>\*-</sup>-bpy)(CO)<sub>3</sub>Cl. For complex **2**<sup>\*-</sup>, following excitation at  $\lambda_{ex} = 605$  nm, the photoinduced charge shift dynamics were fit to an A→B→C→GS model, where A represents the promotion of NDI<sup>\*-</sup> to its excited state Mn(4-<sup>2\*</sup>NDI<sup>\*-</sup>-bpy)(CO)<sub>3</sub>Br, B represents the photoinduced charge-shifted species Mn(4-NDI<sup>\*</sup>-bpy<sup>\*-</sup>)(CO)<sub>3</sub>Br, C potentially represents a structural change or vibrational cooling, GS represents the original ground state Mn(4-NDI<sup>\*-</sup>-bpy)(CO)<sub>3</sub>Br.

The quantum yield of forward electron transfer was estimated by comparing the intrinsic <sup>2\*</sup>NDI<sup>-</sup> excited state lifetime ( $\tau = 141 \text{ ps}$ ) with its lifetime in each complex [19]. In comparison to the previously studied complexes that utilized a conjugated phenyl bridge instead of a saturated CH<sub>2</sub> bridge, complexes **1** and **2** also demonstrate a quantum yield of forward electron transfer close to unity, indicating that the use of a saturated CH<sub>2</sub> bridge is as effective as the phenyl bridge in facilitating a charge shift from <sup>2\*</sup>NDI<sup>-</sup> to the corresponding metal complex. One key difference between the two types of bridges is that the back electron transfer from the CH<sub>2</sub> bridged complexes is faster than the conjugated phenyl bridge. For example, in the previously studied Re complex, the time constant for back electron transfer rate for Re(bpy<sup>--</sup>Ph-NDI<sup>\*</sup>)(CO)<sub>3</sub>Cl is 9.5 ± 0.7 ps. This is approximately 14 times slower in the CH<sub>2</sub>-linked complex. This is likely a manifestation of two

different effects, the distance between the NDI and Re components and the Gibbs free energy for back electron transfer. For example, in complexes 1 and 2 that are separated by a  $CH_2$  bridge, the NDI and metal complex are separated by one carbon whereas the complexes that are separated by a phenyl bridge are separated by four carbons. Additionally, the Gibbs free energies for back electron transfer with the  $CH_2$  bridges (-0.97 V and -1.25 V) are more negative than those of the conjugated phenyl substituents (-0.78 V and -1.05 V). With respect to electrochemical reduction, the bpy is easier to reduce in the complexes with a phenyl bridge. This is expected as the extension of the conjugation from the bpy into the phenyl substituent decreases the bpy  $\pi^*$  orbital energy, making the bpy<sup>0/-</sup> reduction more facile and shifting its reduction potential more positive. In the case of the CH<sub>2</sub> bridges, the bpy reduction potentials in complexes 1 and 2 are more negative due to the electron donating ability of the methyl and methylene groups at the 4 positions of bpy that increase the bpy  $\pi^*$  orbital energy. [26,27,38]

#### 4.3. Time-resolved Mid-IR spectroscopy

Time-resolved mid-IR (TRIR) spectroscopy has been used to observe facile differentiation among the various oxidation and ligand-field states of Re(bpy)(CO)<sub>3</sub>X and more recently has been employed for Mn (bpy)(CO)<sub>3</sub>X complexes. Using TRIR spectroscopy following excitation of NDI<sup>-</sup> at 605 nm, we can determine the nature of the charge-shifted product states. Excitation of complexes 1<sup>•</sup> and 2<sup>•</sup> leads to a 25–45 cm shift of  $\nu$ (CO) to lower frequencies. These induced absorptions are assigned to the formation of Re(4-NDI°-bpy<sup>•</sup>)(CO)<sub>3</sub>Cl and Mn(4-NDI°-bpy<sup>•</sup>)(CO)<sub>3</sub>Br, respectively. [39] For complex 1<sup>•</sup>, this is expected as the first reduction of the metal complex is bpy localized. In contrast, for complex 2<sup>•</sup>, while the electrochemical data shows that first reduction of the metal complex is the function of the TRIR data shows that the electron is transferred initially to bpy. The induced absorption changes that would correspond to a 5-coordinate Mn species



Fig. 7. (A) TRIR spectra of complex 1<sup>•-</sup> (B) transient kinetics and kinetic fits at selected  $\nu$ (CO) of 1<sup>•-</sup>.  $\lambda_{ex} = 605$  nm, solvent = DMF.



Fig. 8. (A) TRIR spectra of complex 2<sup>•-</sup> (B) transient kinetics and kinetic fits at selected  $\nu$ (CO) of 2<sup>•-</sup>.  $\lambda_{ex} = 605$  nm, solvent = DMF.

are not observed. [40] The charge shift from bpy<sup>•-</sup> to the Mn center is not observed because the back-electron transfer step from bpy<sup>•-</sup> to NDI°  $(k_{B \to C})$  is faster. More extensive studies are currently being pursued in our laboratory to elucidate the nature of the singly reduced 6-coordinate Mn species and the required energetics/kinetics for the formation of a 5-coordinate Mn species.

#### 5. Conclusions

This work has several important implications for designing supramolecular donor-acceptor systems with Re(bpy)(CO)<sub>3</sub>Cl and Mn(bpy) (CO)<sub>3</sub>Br CO<sub>2</sub> reduction catalysts. First, incorporating NDI<sup>•-</sup> to bpy via a CH<sub>2</sub> bridge does not affect the quantum yield of forward electron transfer. In photocatalytic systems based on longer saturated linker, this ensures that each photon absorbed by NDI  $\bar{}$  results in formation of Re (bpy<sup>•–</sup>)(CO)<sub>3</sub>X or Mn(bpy<sup>•–</sup>)(CO), the first intermediate in the catalytic cvcle. Second, the attachment of the NDI $^-$ -CH<sub>2</sub> to bpy does not shift the reduction of the bpy positive, indicating that the potential needed for CO<sub>2</sub> reduction by the singly reduced complex Re(bpy<sup>•-</sup>)(CO)<sub>3</sub>X and Mn(bpy')(CO)<sub>3</sub>X is maintained. This is important as extended conjugation leads to more positive reduction potentials, which, in turn, leads to a weaker one-electron reduced species and a decrease in the potential required for CO2 reduction, a fault seen in previous conjugated chromophores. Third, surprisingly, as observed via the aforementioned transient experiments, the initial reduction of the Mn complex occurs at bpy, counter to what is observed in the much slower electrochemical experiments (femtoseconds vs seconds). Moreover, the subsequent charge shift from bpy<sup>-</sup> to Mn(I) is not observed in 2 because the back charge shift repopulating  $\mathrm{NDI}^{\text{--}}$  is faster. Fourth, NDI can easily be modified to attach the complex to an electrode surface, allowing for quick regeneration of NDI<sup>-</sup> to inhibit back electron transfer, thereby rendering the lifetime of the charge-separated state sufficiently long to allow a second electron transfer from  $2^*$ NDI<sup>•–</sup> to the Re or Mn complex that can result in CO<sub>2</sub> binding to start the catalytic cycle. These and other modifications are currently being pursued.

# **Competing interests**

The authors declare no competing interests.

# Acknowledgements

We thank Dr. Saman Shafaie for collecting high-resolution mass spectrometric data. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-FG02-99ER14999 (M.R.W.). This publication was made possible by NPRP Grant No. 9-174-2-092 from the Qatar National Research Fund (a member of Qatar Foundation). The findings achieved herein are solely the responsibility of the authors. NMR and MS measurements in this work were performed at the IMSERC at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF NNCI-1542205); the State of Illinois and International Institute for Nanotechnology (IIN).

#### References

- M.R. Wasielewski, Photoinduced electron transfer in supramolecular systems for artificial photosynthesis, Chem. Rev. 92 (1992) 435–461.
- [2] S. Berardi, S. Drouet, L. Francàs, C. Gimbert-Suriñach, M. Guttentag, C. Richmond, T. Stoll, A. Llobet, Molecular artificial photosynthesis, Chem. Soc. Rev. 43 (2014) 7501–7519.
- [3] J. Su, L. Vayssieres, A place in the sun for artificial photosynthesis? ACS Energy Lett. 1 (2016) 121–135.
- [4] M. Natali, F. Scandola, Supramolecular artificial photosynthesis, in: G. Bergamini, S. Silvi (Eds.), Applied Photochemistry: When Light Meets Molecules, Springer International Publishing, Cham, 2016, pp. 1–66.
- [5] J.H. Alstrum-Acevedo, M.K. Brennaman, T.J. Meyer, Chemical approaches to artificial photosynthesis. 2, Inorg. Chem. 44 (2005) 6802–6827.
- [6] L. Hammarström, Accumulative charge separation for solar fuels production: coupling light-induced single electron transfer to multielectron catalysis, Acc. Chem. Res. 48 (2015) 840–850.
- [7] A. Nicola, B. Vincenzo, Solar electricity and solar fuels: status and perspectives in the context of the energy transition, Chem. A Eur. J. 22 (2016) 32–57.
- [8] I. McConnell, G. Li, G.W. Brudvig, Energy conversion in natural and artificial photosynthesis, Chem. Biol. 17 (2010) 434–447.
- [9] J. Barber, P.D. Tran, From natural to artificial photosynthesis, J. R. Soc. Interface 10 (2013).
- [10] Y. Tamaki, O. Ishitani, Supramolecular photocatalysts for the reduction of CO<sub>2</sub>, ACS Catal. 7 (2017) 3394–3409.
- [11] Y. Tamaki, K. Watanabe, K. Koike, H. Inoue, T. Morimoto, O. Ishitani, Development of highly efficient supramolecular CO<sub>2</sub> reduction photocatalysts with high turnover frequency and durability, Faraday Discuss. 155 (2012) 115–127.
- [12] K. Koike, S. Naito, S. Sato, Y. Tamaki, O. Ishitani, Architecture of supramolecular metal complexes for photocatalytic CO<sub>2</sub> reduction: iii: effects of length of alkyl chain connecting photosensitizer to catalyst, J. Photochem. Photobiol. A: Chem. 207 (2009) 109–114.
- [13] C.D. Windle, M.W. George, R.N. Perutz, P.A. Summers, X.Z. Sun, A.C. Whitwood, Comparison of rhenium-porphyrin dyads for CO<sub>2</sub>photoreduction: photocatalytic studies and charge separation dynamics studied by time-resolved IR spectroscopy, Chem. Sci. 6 (2015) 6847–6864.
- [14] N.T. La Porte, J. Martinez, S. Hedstrom, B. Rudshteyn, B.T. Phelan, C.M. Mauck, R.M. Young, V.S. Batista, M.R. Wasielewski, Photoinduced electron transfer from rylenediimide radical anions and dianions to Re(bpy)(CO)<sub>3</sub> using red and near-infrared light, Chem. Sci. (2017).
- [15] S. Hedstrom, S. Chaudhuri, N.T. La Porte, B. Rudshteyn, J.F. Martinez, M.R. Wasielewski, V.S. Batista, Thousandfold enhancement of photoreduction lifetime in Re(bpy)(CO)<sub>3</sub> via spin-dependent electron transfer from a perylenediimide radical anion donor, J. Am. Chem. Soc. 139 (2017) 16466–16469.
- [16] N.T. La Porte, J.F. Martinez, S. Chaudhuri, S. Hedstrom, V.S. Batista, M.R. Wasielewski, Photoexcited radical anion super-reductants for solar fuels catalysis. Coord. Chem. Rev. 361 (2018) 98–119.
- [17] J.F. Martinez, N.T. La Porte, C.M. Mauck, M.R. Wasielewski, Photo-driven electron transfer from the highly reducing excited state of naphthalene diimide radical anion to a CO<sub>2</sub> reduction catalyst within a molecular triad, Faraday Discuss. 198 (2017) 235–249.
- [18] A. Sinopoli, N.T. La Porte, J.F. Martinez, M.R. Wasielewski, M. Sohail, Manganese carbonyl complexes for CO<sub>2</sub> reduction, Coord. Chem. Rev. 365 (2018) 60–74.
- [19] D. Gosztola, M.P. Niemczyk, W. Svec, A.S. Lukas, M.R. Wasielewski, Excited doublet states of electrochemically generated aromatic imide and diimide radical anions, J. Phys. Chem. A 104 (2000) 6545–6551.
- [20] Y. Kuramochi, O. Ishitani, Iridium(III) 1-phenylisoquinoline complexes as a

photosensitizer for photocatalytic CO<sub>2</sub> reduction: a mixed system with a Re(I) catalyst and a supramolecular photocatalyst, Inorg. Chem. 55 (2016) 5702–5709.
[21] D.M. Arias-Rotondo, J.K. McCusker, The photophysics of photoredox catalysis: a

- roadmap for catalyst design, Chem. Soc. Rev. 45 (2016) 5803–5820.
   J.F. Martinez, N.T. La Porte, M.R. Wasielewski, Electron transfer from photoexcited naphthalene diimide radical anion to electrocatalytically active Re(bpy)(CO)<sub>3</sub>Cl in a molecular triad, J. Phys. Chem. C 122 (2018) 2608–2617.
- [23] J. Hawecker, J.-M. Lehn, R. Ziessel, Efficient photochemical reduction of CO2 to CO by visible light irradiation of systems containing Re(bipy)(CO)<sub>3</sub>X or Ru(bipy)<sub>3</sub><sup>2+</sup>-CO<sub>2</sub> combinations as homogeneous catalysts, J. Chem. Soc. Chem. Commun. (1983) 536–538.
- [24] H. Takeda, H. Koizumi, K. Okamoto, O. Ishitani, Photocatalytic CO<sub>2</sub> reduction using a mn complex as a catalyst, Chem. Commun. (Cambridge, U.K.) 50 (2014) 1491–1493.
- [25] M. Bourrez, F. Molton, S. Chardon-Noblat, A. Deronzier, [Mn(bipyridyl)(CO)<sub>3</sub>Br]: an abundant metal carbonyl complex as efficient electrocatalyst for CO<sub>2</sub> reduction, Angew. Chem. Int. Ed. 50 (2011) 9903–9906.
- [26] J.M. Smieja, C.P. Kubiak, Re(bipy-tBu)(CO)<sub>3</sub>Cl-improved catalytic activity for reduction of carbon dioxide: IR-spectroelectrochemical and mechanistic studies, Inorg. Chem. 49 (2010) 9283–9289.
- [27] J.M. Smieja, M.D. Sampson, K.A. Grice, E.E. Benson, J.D. Froehlich, C.P. Kubiak, Manganese as a substitute for rhenium in CO<sub>2</sub> reduction catalysts: the importance of acids, Inorg. Chem. 52 (2013) 2484–2491.
- [28] C. Riplinger, M.D. Sampson, A.M. Ritzmann, C.P. Kubiak, E.A. Carter, Mechanistic contrasts between manganese and rhenium bipyridine electrocatalysts for the reduction of carbon dioxide, J. Am. Chem. Soc. 136 (2014) 16285–16298.
- [29] N.G. Connelly, W.E. Geiger, Chemical redox agents for organometallic chemistry, Chem. Rev. 96 (1996) 877–910.
- [30] R.M. Young, S.M. Dyar, J.C. Barnes, M. Juricek, J.F. Stoddart, D.T. Co, M.R. Wasielewski, Ultrafast conformational dynamics of electron transfer in exbox4 + ⊂ perylene, J. Phys. Chem. A 117 (2013) 12438–12448.
- [31] N.E. Horwitz, B.T. Phelan, J.N. Nelson, M.D. Krzyaniak, M.R. Wasielewski, Picosecond control of photogenerated radical pair lifetimes using a stable third

radical, J. Phys. Chem. A 120 (2016) 2841-2853.

- [32] S.R. Greenfield, M.R. Wasielewski, Near-transform-limited visible and near-IR fs pulses from OPA using type II β-barium borate, Opt. Lett. 20 (1995) 1394–1396.
- [33] I. The Mathworks, Matlab Release 2016a, The Mathworks, Inc., Natick, Massachusetts, United States, 2016.
- [34] Z. Fang, A. Ito, S. Keinan, Z. Chen, Z. Watson, J. Rochette, Y. Kanai, D. Taylor, K.S. Schanze, T.J. Meyer, Atom transfer radical polymerization preparation and photophysical properties of polypyridylruthenium derivatized polystyrenes, Inorg. Chem. 52 (2013) 8511–8520.
- [35] M.D. Sampson, A.D. Nguyen, K.A. Grice, C.E. Moore, A.L. Rheingold, C.P. Kubiak, Manganese catalysts with bulky bipyridine ligands for the electrocatalytic reduction of carbon dioxide: eliminating dimerization and altering catalysis, J. Am. Chem. Soc. 136 (2014) 5460–5471.
- [36] A. Vlček, Ultrafast excited-state processes in Re(I) carbonyl-diimine complexes: from excitation to photochemistry, in: A.J. Lees (Ed.), Photophysics of Organometallics, Springer, Berlin Heidelberg, Berlin, Heidelberg, 2010, pp. 115–158.
- [37] S.K. Hayashi, B.S. Brunschwig, E. Fujita, Involvement of a binuclear species with the Re-C(O)O-Re moiety in CO<sub>2</sub>reduction catalyzed by tricarbonyl rhenium(I) complexes with diimine ligands: Strikingly slow formation of the Re-Re and Re-C(O)O-Re species from Re(dmb)(CO)<sub>3</sub>S (dmb = 4,4'-dimethyl-2,2'-bipyridine, S = solvent), J. Am. Chem. Soc. 125 (2003) 11976–11987.
- [38] M.L. Clark, P.L. Cheung, M. Lessio, E.A. Carter, C.P. Kubiak, Kinetic and mechanistic effects of bipyridine (bpy) substituent, labile ligand, and bronsted acid on electrocatalytic CO<sub>2</sub> reduction by Re(bpy) complexes, ACS Catal. (2018) 2021–2029.
- [39] C.W. Machan, M.D. Sampson, S.A. Chabolla, T. Dang, C.P. Kubiak, Developing a mechanistic understanding of molecular electrocatalysts for CO<sub>2</sub> reduction using infrared spectroelectrochemistry, Organometallics 33 (2014) 4550–4559.
- [40] D.C. Grills, J.A. Farrington, B.H. Layne, S.V. Lymar, B.A. Mello, J.M. Preses, J.F. Wishart, Mechanism of the formation of a Mn-based CO<sub>2</sub> reduction catalyst revealed by pulse radiolysis with time-resolved infrared detection, J. Am. Chem. Soc. 136 (2014) 5563–5566.