Journal Name

COMMUNICATION

Cationic Dirhodium(II,II) Complexes for the Electrocatalytic Reduction of CO_2 to HCOOH

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Suzanne Witt,[a] Travis A. White,[a] Zhanyong Li,[b] Kim R. Dunbar,*[,b] Claudia Turro*[,a]

Two formamidinate bridged dirhodium(II,II) complexes with chelating diimine ligands L, $[Rh_2(\mu\text{-DTolF})_2(L)_2]^{2+}$, were shown to electrocatalytically reduce CO_2 in the presence of H_2O. Analysis of the reaction mixture and headspace following bulk electrolysis revealed H_2 and HCOOH as the major products. The variation in relative product formation is discussed.

Carbon dioxide represents an abundant source for the production of fuels and chemicals useful in industrial processes. Therefore, facile and efficient means to convert of CO_2 into useful chemical feedstocks and fuels is highly desirable.[1,2] Within recent years, research focused on homogeneous electrocatalytic CO_2 reduction has garnered substantial interest owing to their highly tunable and controllable nature.[2-4] The distribution of products formed from electrocatalytic CO_2 reduction is dependent on multiple factors, including the catalyst used, acid concentration, and electron availability,[1-4] such that judicious choice of reaction components are required to attain the formation of desired products. The $2e^-/2H^+$ transformation of CO_2 to HCOOH is an attractive process that can provide a source of formic acid for the textile, cleaning, and preservatives industries. In addition, this transformation can also to provide a method for the storage of hydrogen fuel in a condensed form.[5]

It has been proposed that the formation of HCOOH from the reduction of CO_2 proceeds *via* the insertion of CO_2 into a metal-hydride bond, as the direct coordination of CO_2 to the metal center followed by reduction typically results in the formation of CO.[6] Transition metal complexes of Fe, Co, Ni, Ru, Os, and Ir are known to catalyze HCOOH production from CO_2,[6-18] but molecular Rh-based catalysts for CO_2 reduction are less common.[11,19-24] Rhodium hydride compounds react with CO_2 and water to form dihydrido bicarbonato Rh(III) complexes, which then react further with CO_2 to form Rh(I) carbonyl compounds.[19] In contrast, mononuclear rhodium complexes that contain diphosphine or polypyridyl ligands were shown to reduce CO_2 to formate anions.[11,20-24]

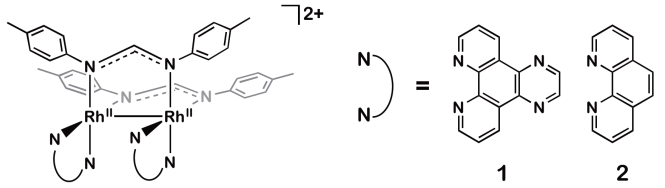

Figure 1. Schematic representation of the molecular structures of **1** and **2**.

Herein we present a bimetallic dirhodium(II,II) architecture bridged by formamidinate ligands for the electrocatalytic reduction of CO_2. Each metal in these cationic complexes is chelated by a diimine ligand, with overall formula $[Rh_2(\mu\text{-DTolF})_2(dpq)_2]^{2+}$ (**1**; DTolF = *p*-ditolylformamidinate, dpq = dipyrido[3,2-*f*:2',3'-*h*]quinoxaline) and $[Rh_2(\mu\text{-DTolF})_2(phen)_2]^{2+}$ (**2**; phen = 1,10-phenanthroline), whose structures are shown in Figure 1. The excited state properties of the series $[Rh_2(\mu\text{-DTolF})_2(L)_2]^{2+}$, L = dqp, dppz (dipyrido[3,2-*a*:2',3'-*c*]phenazine), and dppn (benzo[*i*]dipyrido[3,2-*a*:2',3'-*h*]quinoxaline) were previously reported by us, showing that these and related complexes are powerful reducing agents in the excited state,[25-27] and that they function as efficient and robust electrocatalysts for H^+ reduction.[28] A proposed intermediate within the electrocatalytic H^+ reduction cycle of these complexes involves formation of a $Rh_2^{II,III}$–H hydride species that may be exploited to afford CO_2 reduction to HCOOH *via* CO_2 insertion into the Rh-H bond. In the present work, **1** and **2** are explored for the electrocatalytic reduction of CO_2 and the resulting products are reported.

Cyclic voltammograms of **1** and **2** were collected under a N_2 atmosphere in CH_3CN and are compared to those recorded in saturated CO_2 solutions (Figure 2). Under N_2, **1** exhibits a $Rh_2^{III,II/II,II}$ reduction at $E_{½} = -0.38$ V *vs* Ag/AgCl; this couple is slightly shifted to a more negative potential $E_{½} = -0.45$ V *vs* Ag/AgCl in **2**. Similar shifts of this metal-centered wave were observed in the $[Rh_2(DTolF)_2(L)_2]^{2+}$ (L = dpq, dppz, dppn)

---

[a] Department of Chemistry and Biochemistry, The Ohio State University
[b] Department of Chemistry, Texas A&M University

† Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

series.[25,28] The ligand-based $dpq^{0/-}$ reduction in **1** is observed at $E_{½}$ = −1.07 V *vs* Ag/AgCl, whereas the $phen^{0/-}$ couple appears at $E_{½}$ = −1.21 V *vs* Ag/AgCl in **2**, such that phen reduction is more negative than that of dpq with a shift, ΔE, of 0.14 V. This shift is consistent with the presence of the pyrazine moiety in the dpq ligand, which serves to extend the π-system and make it easier to reduce than phen. Similar shifts have been previously reported extensively for Ru(II) complexes with these and related ligands,[29-31] with the first ligand-based reduction appearing at 0.18 V more negative potential in $[Ru(bpy)_2(phen)_2]^{2+}$ as compared to $[Ru(bpy)_2(dpq)]^{2+}$.[29,30] The metal-centered $Rh_2^{II,II/II,I}$ couples are observed at $E_{½}$ = −1.55 V and at $E_{½}$ = −1.77 V *vs* Ag/AgCl in **1** and **2**, respectively (Figure 2). The $Rh_2^{II,II/II,I}$ reduction occurs at a potential more negative than that of the first diimine ligand reduction in each complex; this couple observed at a 0.22 V a more positive potential in **1** as compared to **2**. This shift is believed to arise because the reduced pyrazine moiety of dpq ligand in **1** is further away from the metal, such that it contributes less electron density to the Rh_2 core than a reduced phen ligand in **2**. The reduction of the second dpq ligand in **1** is evident at $E_{½}$ = −1.72 V *vs* Ag/AgCl, but the reduction of the second phen ligand is not observed in the cyclic voltammogram of **2**, likely because it lies outside of the scanned solvent window. These assignments in CH_3CN agree with those previously made by our group in DMF as the solvent.[28]

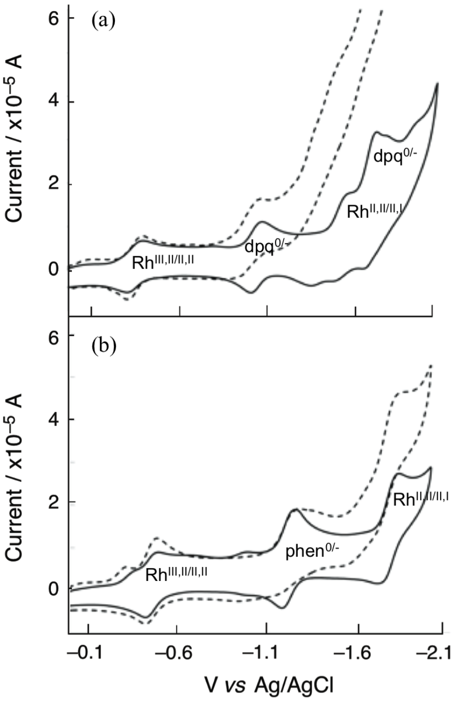

Figure 2: Cyclic voltammograms of 0.5 mM (a) **1** and (b) **2** in 0.1 M $TBAPF_6/CH_3CN$ under N_2 (solid lines) and CO_2 (dashed lines).

Cyclic voltammograms collected in CO_2-saturated CH_3CN, $[CO_2]$ ~0.28 M,[32] display current enhancement with an onset at approximately −0.90 V for **1** and at −1.55 V for **2** *vs* Ag/AgCl, consistent with CO_2 reduction (Figure 2, dashed lines). For **1**, a small, non-catalytic current increase and a loss of reversibility occurs at the first dpq ligand reduction in the presence of CO_2 (Figure 2a), which can be attributed to protonation of the nitrogen atom on the pyrazine portion of the reduced dpq ligand, as previously reported in the presence of acid.[28] As the potential is scanned to further negative values, significantly greater catalytic current enhancement is observed. The possibility that catalysis occurs at the dpq ligand must be considered, since the pyrazine moiety possesses a lone pair of electrons on each nitrogen atom that may interact with a proton or the δ+ carbon atom within CO_2. However, CV scans of $[Ru(bpy)_2(dpq)]^{2+}$, which possesses a dpq ligand and lacks an open coordination site on the metal center, show no catalytic behavior and only a small current increase attributed to ligand protonation (Figure S1). Therefore, it may be concluded that the catalysis observed in **1** is occurring at one of the Rh centers, and not on the dpq ligand. In addition, this result provides further evidence that the current increase observed at the first dpq ligand reduction is associated with protonation of the ligand, [28] since the addition of CO_2 to CH_3CN is known to increase the acidity of the solution.[24]

For **2**, the first $phen^{0/-}$ couple becomes irreversible in the presence of CO_2, while the current remains unchanged (Figure 2b, dashed line). Given that the phen ligand does not possess accessible nitrogen atoms, the phen ligand is not expected to undergo protonation or to interact with CO_2. As such, no current increase or shift in the peak potential is observed for this couple. The loss of reversibility may be indicative of protonation or CO_2 binding at the Rh metal center, and the continued increase in current following the first phen ligand reduction is evidence of catalytic behavior. For **1** and **2**, significantly greater catalytic current enhancement was observed when 3 M H_2O was added to the reaction mixture as a proton source (Figure 3).

Bulk electrolysis experiments were conducted at −1.40 V and −1.60 V *vs* Ag/AgCl for 3 hours to determine the products of CO_2 reduction (Table 1). Gas phase products from the head space of each sample were analyzed using gas chromatography following electrolysis. No CO production was detected, however, H_2 evolution was observed in each case (Figure S2). To determine the products present in solution after each bulk electrolysis experiment, the solvent was evaporated and the sample was reconstituted in D_2O for ^1H NMR analysis. In this manner, the presence of HCOOH was confirmed as a singlet at ~8.23 ppm, which agrees with the ^1H NMR spectrum of the formic acid standard and differs from that of the formate anion standard, which has a chemical shift of ~8.44 ppm (Figure S3). The faradaic efficiencies, FEs, for **1** remained relatively constant for H_2 production at –1.4 V and –1.6 V, 56-63%, whereas those for HCOOH production decreased from 12% to 3.5%, respectively (Table 1). In contrast, the results show that no HCOOH is generated by complex **2** at –1.4 V, but 7.0% FE for formic acid formation is observed at –1.6 V vs Ag/AgCl. In addition, the relative TON (turnover number) for the generation of HCOOH vs H_2, R_{TON} = $TON(H_2)/TON(HCOOH)$, decreases for **1** from –1.4 V to –1.6 V, but the trend is reversed for **2**. In the latter, no HCOOH is formed at –1.4 V, but TON of 10.8 ± 0.4 was measured at –1.6

Please do not adjust margins

Table 1. Turnover Number (TON) and Percent Faradaic Efficiency (%FE) Following Bulk Electrolysis of **1** and **2** in the Presence of CO_2 and H_2O at Various Potentials.[a]

		H_2		HCOOH		
Complex	Potential / V	TON	%FE	TON	%FE	R_{TON}[b]
1	−1.40	48.7 ± 8.1	56 ± 4	4.3 ± 1.1	12 ± 4	0.09
	−1.60	187 ± 15	63 ± 6	4.9 ± 1.1	3.5 ± 2	0.03
2	−1.40	17.8 ± 1.8	49 ± 6	0	0	0
	−1.60	118 ± 8.0	77 ± 4	10.8 ± 0.4	7.0 ± 0.4	0.09

[a] [Complex] = 0.5 mM, 0.1 M $TBAPF_6/CH_3CN$ with ~0.28 M CO_2 and 3 M H_2O; held at each potential for 3 hours conducted in triplicate. [b] Relative TON, R_{TON}, $TON(HCOOH)/TON(H_2)$.

V vs Ag/AgCl. Bulk electrolyses under identical conditions in the absence of catalyst were conducted as control experiments at both –1.4 V and –1.6 V, which generated small amounts of H_2 and HCOOH (see Supporting Information). The quantities from these experiments were subtracted from those obtained from bulk electrolysis in the presence of catalyst in order to calculate TON values and %FE.

In addition, bulk electrolysis at –1.6 V under N_2 in the presence of catalyst was performed to confirm CO_2 as the source of carbon for HCOOH formation and the details of the results appear in the Supporting Information. For both **1** and **2** a small amount of HCOOH was detected which can be attributed to the graphite electrode interacting with H_2O in solution. The electrochemical exfoliation of graphite has been documented throughout the literature.[33-35] When water is reduced at the electrode, hydroxyl anions may oxidize bulk graphite, corroding the electrode surface.[33-35] However, yield of HCOOH produced in the absence of CO_2 is very low, clearly showing that complexes **1** and **2** act as catalysts for this reaction.

To confirm that the carbon in HCOOH originates from the electrocatalytic reduction of CO_2, experiments were conducted with $^{13}CO_2$. Bulk electrolysis of **2** was performed at –1.6 V in the presence of $^{13}CO_2$ and the products were analyzed by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectra, a singlet corresponding to $H^{12}COOH$ was observed, as well as a doublet corresponding to $H^{13}COOH$ (Figure S5). The coupling constant for the latter, J ~ 185 Hz, agrees well with the literature value for $H^{13}COOH$.[36] The amount of $H^{12}COOH$ formed is consistent with that measured for graphite exfoliation (2.2 μmol), and the amount of $H^{13}COOH$ formed is similar to the values measured for electrocatalytic CO_2 reduction with **2** (12.4 μmol, 8.25 TON, 5.5 %FE; Table 1). Two singlets are observed in the ^{13}C NMR spectra, which are consistent with reported values for carbonate and HCOOH (Figure S6).[37] These peaks are not observed prior to electrolysis. The formation of carbonate during electrolysis may account for the remaining 15-35% of charge. Absorption spectra collected before and after electrolysis are inconsistent with catalyst decomposition (Figure S7). Slight spectral changes and a small increase in the baseline can be attributed to the formation of a black precipitate known to arise from graphite exfoliation.

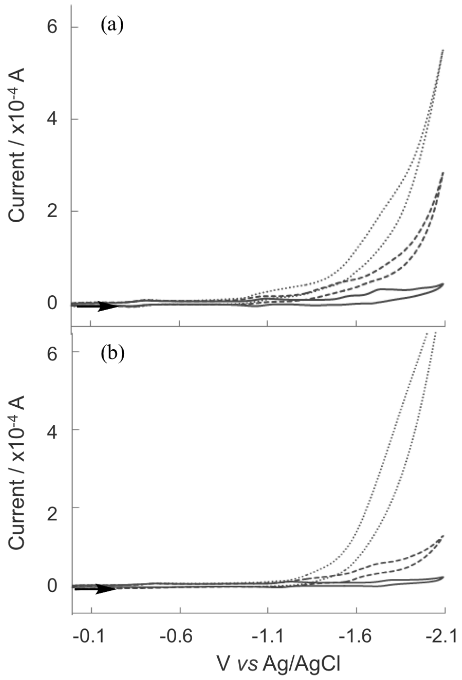

Figure 3: Cyclic voltammograms of 0.5 mM (a) **1** and (b) **2** in 0.1 M $TBAPF_6/CH_3CN$ purged with N_2 (solid lines), CO_2 (dashed lines), and with CO_2 and 3 M H_2O (dotted lines).

The clear trend of the increase in TON for H_2 production for **1** and **2** as the applied bias is increased to more negative potential. A turn-on of the HCOOH production is observed when the potential is increased from −1.40 V to −1.60 V for **2**. In this complex, at −1.40 V, the first phen ligand has been reduced, which is not proposed as the active catalytic species. It is only when the applied potential begins to encroach on the $Rh_2^{II,II/II,I}$ reduction that HCOOH is detected. This explanation is supported by the low TON measured for H_2 production for **2** at –1.4 V compared to –1.6 V and by the values for complex **1**. The $Rh_2^{II,II/II,I}$ couple occurs at ~220 mV more positive potential in **1** than in **2**, so catalysis is possible at both –1.4 V and –1.6 V as the active catalytic species has been generated. Therefore, the activities should be compared using –1.4 V for **1** and –1.6 V for **2**, since these values are ~200 mV beyond the potential at which the active species is formed in each catalyst. Comparing these values, it is clear that **2** is a more active catalyst than **1**, however the selectivity for CO_2 is very similar. The lower activity observed in **1** is consistent with our previous work, in

Please do not adjust margins

which we showed that the protonation of the nitrogen atoms on the reduced dpq ligand consume substrate, but that species is not catalytic.[28]

As mentioned previously, the bulk electrolysis data shows that both complexes produce significantly more H_2 than HCOOH, indicating selectivity for the reduction of protons over CO_2. If HCOOH formation proceeds through CO_2 insertion into a Rh–H hydride bond, that process must occur before the metal center is protonated a second time to evolve H_2. Therefore, the relative concentrations of protons and CO_2 in solution are expected to play a significant role on the outcome of electrolysis. Current work is underway on methods to improve the selectivity for CO_2 reduction, such as increasing the pH of the reaction mixture. Additionally, since the identity of the diimine ligand appears to have little effect on the selectivity, ongoing work will focus on manipulating the bridging ligand and blocking one or both axial positions.[38]

In conclusion, $[Rh_2(\mu\text{-DTolF})_2(L)_2]^{2+}$ (L = dpq, phen) complexes were shown to exhibit electrocatalytic activity under a CO_2 atmosphere. HCOOH and H_2 were formed upon bulk electrolysis of the complexes in acetonitrile in the presence of CO_2 and water. Further analysis indicated that catalysis is occurring at the metal center, and not on the diimine ligand. Complex **1** is a less active catalyst than **2**, likely because the pyrazine moiety of the dpq ligands in **1** may be protonated to consume substrate. However, the active catalytic species, $Rh_2^{II,I}$, is formed at a more positive potential in **1**, so catalysis may occur at a lower overpotential than in **2**. Both complexes are selective for proton reduction to H_2 under the current conditions.

The authors are grateful for the generous support of the U.S. Department of Energy, Office of Science, Office of Basic Research (CT: DE-SC0010542; KRD: DE-SC0010721).

Notes and references

1 M. Aresta and A. Dibenedetto, *Dalton Trans.,* 2007, **28**, 2975-2992.
2 J. Qiao, Y. Liu, F. Hong, and J. Zhang, *Chem.Soc.Rev.,* 2014, **43**, 631-675.
3 C. Costentin, M. Robert, and J. –M. Saveant, *Chem. Soc. Rev.*, 2013, **42**, 2423-2436.
4 E. E. Benson, C. P. Kubiak, A. J. Sathrum, and J. M. Smieja, *Chem. Soc. Rev.*, 2009, **38**, 89.
5 S. Moret, P.J. Dyson, and G. Laurenczy, *Nat.Commun.,* 2014, **5**, 1-7.
6 J. R. Pugh, M. R. M. Bruce, B. P. Sullivan, and T. J. Meyer, *Inorg.Chem.,* 1991, **30**, 86-91.
7 L. Chen, Z. Guo, X. Wei, C. Gallenkamp, J. Bonin, E. Anxolabehere-Mallart, K. Lau, T. Lau, and M. Robert, *J.Am.Chem.Soc.,* 2015, **137**, 10918-10921.
8 M. R. M. Bruce, E. Megehee, B. P. Sullivan, H. H. Thorp, T. R. O'Toole, A. Downard, J. R. Pugh, and T. J. Meyer, *Inorg.Chem.,* 1992, **31**, 4864-4873.
9 H. Ishida, K. Tanaka, and T. Tanaka, *Organometallics,* 1987, **6**, 181-186.
10 P. Kang, T. J. Meyer, and M. Brookhart, *Chem.Sci.,* 2013, **4**, 3497-3502.
11 S. C. Rasmussen, M. M. Richter, E. Yi, H. Place, and K. J. Brewer, *Inorg.Chem.,* 1990, **29**, 3926-3932.
12 H. Ishida, H. Tanaka, K. Tanaka, and T. Tanaka, *J.Chem.Soc., Chem.Commun.,* 1987, 131-132.
13 J. P. Collin, A. Jouaiti, and J. P. Sauvage, *Inorg.Chem.,* 1988, **27**, 1986-1990.
14 C. Arana, S. Yan, M. Keshavarz-K, K. T. Potts, and H. D. Abruña, *Inorg.Chem.,* 1992, **31**, 3680-3682.
15 S. Pun, W. Chung, K. Lam, P. Guo, P. Chan, K. Wong, C. Che, T. Chen, and S. Peng, *J.Chem.Soc., Dalton Trans.,* 2002, 575-583.
16 M. D. Rail, and L. A. Berben, *J.Am.Chem.Soc.,* 2011, **133**, 18577-18579.
17 P. Kang, C. Cheng, Z. Chen, C. K. Schauer, T. J. Meyer, and M. Brookhart, *J.Am.Chem.Soc.,* 2012, **134**, 5500-5503.
18 S. T. Ahn, E. A. Bielinski, E. M. Lane, Y. Chen, W. H. Bernskoetter, N. Hazari, and G. T. Palmore, *Chem.Commun.(Cambridge, U.K.),* 2015, **51**, 5947-5950.
19 T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers, and S. Otsuka, *J.Am.Chem.Soc.,* 1979, **101**, 4212-4221.
20 S. Slater, and J. H. Wagenknecht, *J.Am.Chem.Soc.,* 1984, **106**, 5367-5370.
21 C. M. Bolinger, B. P. Sullivan, D. Conrad, J. A. Gilbert, N. Story, and T. J. Meyer, *J.Chem.Soc., Chem.Commun.,* 1985, 796-797.
22 C. M. Bolinger, N. Story, B. P. Sullivan, and T. J. Meyer, *Inorg.Chem.,* 1988, **27**, 4582-4587.
23 P. Paul, B. Tyagi, A. K. Bilakhiya, M. M. Bhadbhade, E. Suresh, and G. Ramachandraiah, *Inorg.Chem.,* 1998, **37**, 5733-5742.
24 C. Caix, S. Chardon-Noblat, and A. Deronzier, *J. Electroanal. Chem.,* 1997, **434**, 163-170.
25 Z. Li, N. A. Leed, N. Dickson-Karn, K. R. Dunbar, and C. Turro, *Chem.Sci.,* 2014, **5**, 727-737.
26 (a) P. M. Bradley, B. E. Bursten, and C. Turro, *Inorg. Chem.,* 2001, **40**, 1376-1379. (b) P. K. L. Fu, P. M. Bradley, and C. Turro, *Inorg. Chem.,* 2001, **40**, 2476-2477.
27 D. A. Lutterman, N. N. Degtyareva, D. H. Johnston, J. C. Gallucci, J. L. Eglin, and C. Turro, *Inorg. Chem*., 2005, **44**, 5388-5396.
28 T. A. White, S. E. Witt, Z. Li, K. R. Dunbar, and C. Turro, *Inorg.Chem.,* 2015, **54**, 10042-10048.
29 J. V. Caspar and T. J. Meyer, *Inorg. Chem.*, 1983, **22**, 2444-2453.
30 A. Delgadillo, P. Romo, A. M. Leiva, and B. Loeb, *Helv. Chim. Acta.*, 2003, **86**, 2110-2120.
31 A. A.Vlcek, E. S. Dodsworth, W. J. Pietro, and A. B. P. Lever, *Inorg. Chem.*, 1995, **34**, 1906-1913.
32 Y. Tomita, S. Teruya, O. Koga, and Y. Hori, *J. Electrochem. Soc.*, 2000, **147**, 4164-4167.
33 C. T. J. Low, F.C. Walsh, M. H. Chakrabarti, M. A. Hashim, and M. A. Hussain, *CARBON,* 2013, **54**, 1–21.
34 A. M. Abdelkader, A. J. Cooper, R. A. W. Dryfe, and I. A. Kinloch, *Nanoscale*, 2015, **7**, 6944–6956.
35 Z. Y. Xia, G. Giambastiani, C. Christodoulou, M. V. Nardi, N. Koch, E. Treossi, V. Bellani, S. Pezzani, F. Corticelli, V. Morandi, A. Zanelli, and V. Palermo, *ChemPlusChem*, 2014, **79**, 439-446.
36 S. M. Ng, C. Yin, C. H. Yeung, T. C. Chan, and C. P. Lau, *Eur. J. Inorg. Chem.*, 2004, 1788-1793.
37 Z. Chen, C. Chen, D. R. Weinberg, P. Kang, J. J. Concepcion, D. P. Harrison, M. S. Brookhart, and T. J. Meyer, *Chem. Commun.*, 2011, **47**, 12607-12609.
38 J. D. Aguirre, D. A. Lutterman, A. M. Angeles-Boza, K. R. Dunbar, and C. Turro, *Inorg. Chem.,* 2007, **46**, 7494-7502.

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins