



## Electrocatalytic reduction of carbon dioxide by a polymeric film of rhenium tricarbonyl dipyridylamine

Kwong-Chak Cheung<sup>a</sup>, Peng Guo<sup>a</sup>, Ming-Him So<sup>a</sup>, Lawrence Yoon Suk Lee<sup>a</sup>, Kam-Piu Ho<sup>a</sup>, Wing-Leung Wong<sup>a</sup>, Kam-Han Lee<sup>a</sup>, Wing-Tak Wong<sup>b</sup>, Zhong-Yuan Zhou<sup>a</sup>, Kwok-Yin Wong<sup>a,\*</sup>

<sup>a</sup> Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Yuk Choi Road, Hung Hom, Kowloon, Hong Kong SAR, China

<sup>b</sup> Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China

### ARTICLE INFO

#### Article history:

Received 9 February 2009

Received in revised form 25 April 2009

Accepted 27 April 2009

Available online 5 May 2009

#### Keywords:

Carbon dioxide

Electrocatalysis

Rhenium complex

Polypyrrole films

### ABSTRACT

A dipyridylamine ligand with a pendant pyrrole (*N*-(3-*N,N'*-bis(2-pyridyl)propylamino)pyrrole, PPP) and its corresponding rhenium(I) complex,  $\text{Re}(\text{CO})_3(\kappa^2\text{-}N,N\text{-PPP})\text{Cl}$ , were synthesized. The structure of  $\text{Re}(\text{CO})_3(\kappa^2\text{-}N,N\text{-PPP})\text{Cl}$  was determined by X-ray crystallography. Electrochemical polymerization of the pyrrole moiety resulted in the immobilization of poly[ $\text{Re}(\text{CO})_3(\kappa^2\text{-}N,N\text{-PPP})\text{Cl}$ ] film onto a glassy carbon electrode, which exhibited electrocatalytic activity for the reduction of  $\text{CO}_2$  to CO.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Electrochemical reduction of carbon dioxide ( $\text{CO}_2$ ) has drawn much attention from both researchers and industries for the past three decades [1]. The growing concerns about energy crisis due to depletion of fossil fuels as well as the global warming caused by ever-increasing atmospheric  $\text{CO}_2$  level have stimulated the search for an economical process to produce useful energy-bearing chemicals from  $\text{CO}_2$ . Such processes as the reduction of  $\text{CO}_2$  would be beneficial to balancing the carbon cycle and also of interest as a potential component in a carbon-based energy cycle, i.e.,  $\text{CO}_2 + \text{energy} \rightarrow \text{fuel} \rightarrow \text{CO}_2 + \text{energy}$ . Synthesis of hydrocarbons from  $\text{CO}_2$  involves a multi-step reaction where carbon monoxide (CO) is one of the important intermediates [2]. Carbon monoxide, which bears significant fuel value as it is, also plays useful role as a precursor to myriad chemicals, and yet obtaining it from the reduction of highly stable  $\text{CO}_2$  requires an efficient catalytic system.

A number of transition metal complexes have been studied for photo- and electrocatalytic reduction of  $\text{CO}_2$  [3], for they require relatively mild conditions and lower over-potentials than the direct reduction of  $\text{CO}_2$  at bulk metal electrodes. In particular, rhenium complexes of the type *fac*- $[\text{Re}(\text{CO})_3(\text{L})\text{X}]$ , (where L is a bidentate ligand such as 2,2'-bipyridine and X is an anion) gained great interests [3c,4], since Lehn and coworkers [5] first demonstrated promising electrocatalytic property of  $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$

(bpy = 2,2'-bipyridine) for the reduction of  $\text{CO}_2$  to CO. The electrochemical reduction of  $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$  proceeds with an initial one-electron reversible reduction of the bipyridine ligand to form  $[\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}]^-$  followed by the second one-electron reduction of Re(I) to Re(0). The reduced complex then undergoes ligand dissociation with loss of chloride to yield an unsaturated radical anion  $[\text{Re}(\text{CO})_3(\text{bpy})]^-$  [4d,6], which readily coordinates  $\text{CO}_2$  into the Re center and reduces it to CO in another one-electron step.

Deronzier and coworkers [7] further developed this electrocatalyst to a mediated electrocatalytic system by polymerizing a pyrrole-substituted 2,2'-bipyridine of Re(I) complex onto the electrode surface. Such chemically modified electrodes for electrocatalysis have potential advantages over homogeneous systems, such as the stabilization of catalyst, easier recovery of products and catalyst, and the use of lower quantities of catalyst. However, the difficulty in modification of 2,2'-bipyridine with the pyrrole substituent has limited the wide application of this electrocatalytic system.

We report, herein, a novel 2,2'-dipyridylamine ligand with a pendant pyrrole moiety. The amine nitrogen bridge between two pyridines in 2,2'-dipyridylamine allows the easy attachment of pyrrole tag. The electrochemical reduction of  $\text{CO}_2$  on an electrode modified with a Re(I)-electrocatalyst via electropolymerization of this pyrrole-attached ligand will be presented.

## 2. Results and discussion

A pyrrole-tagged ligand *N*-(3-*N,N'*-bis(2-pyridyl)propylamino)pyrrole (PPP) was prepared from the reaction of 2-bromopyridine

\* Corresponding author. Tel.: +852 3400 8686; fax: +852 2364 9932.  
E-mail address: [bckywong@polyu.edu.hk](mailto:bckywong@polyu.edu.hk) (K.-Y. Wong).

and *N*-(3-aminopropyl)pyrrole. Fig. 1 shows the X-ray crystal structure of the Re(I)-complex, *fac*-[Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl], synthesized from the reaction of PPP and Re(CO)<sub>5</sub>Cl in an acetonitrile–heptane solution under refluxing conditions. The rhenium ion is coordinated with two pyridyl nitrogen atoms of the κ<sup>2</sup>-*N,N*-PPP ligand, one chloride, and three carbonyl ligands in facial orientation to adopt a slightly distorted octahedral geometry. The Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl complex itself is not chiral. There is a mirror plane bisecting the Re–Cl bond, one of the CO ligand and the κ<sup>2</sup>-*N,N*-PPP ligand, and the complex crystallizes in a polar space group *P*4<sub>1</sub>2<sub>1</sub>2 (#92). The pendant pyrrole groups are arranged in a clockwise direction, which results in asymmetry in the crystal structure. There are short intramolecular C–H...O interaction between the C–H hydrogen on the alkyl chain (C(15)–H(15B)) with the carbonyl oxygen O(3), and intermolecular C–H...O interaction between the C–H hydrogen on the pyridine ring (C(10)–H(10A)) with the carbonyl oxygen O(1A) in the lattice (see Fig. S2 and Table S3 in the Supplementary materials). In acetonitrile solution, the FTIR spectrum of the rhenium complex exhibits three strong CO absorption bands at 2020, 1912 and 1893 cm<sup>-1</sup>, respectively. The rhenium–carbonyl bond distances Re–C(11) (1.899(3) Å), Re–C(13) (1.894(3) Å) and Re–C(12) (1.907(3) Å) are similar to those observed in other rhenium bipyridine (bpy) and dipyrpyridylamine (dpa) complexes such as [Re<sub>2</sub>(bpy)<sub>2</sub>(CO)<sub>6</sub>(μ-H)Cl] [8], Re(CO)<sub>3</sub>(bpy)(PO<sub>2</sub>F<sub>2</sub>) [9], and [Re(CO)<sub>3</sub>(L)(H<sub>2</sub>O)](CF<sub>3</sub>SO<sub>3</sub>) (where L is 1-methyl-1-(3-*N,N'*-bis(2-pyridyl)propyl)pyrrolidinium) [10]. The bond angle and bond distances of N(1)–Re–N(2) in Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl (79.33(9)° and 2.188(2), 2.189(2) Å) are similar to those in [Re(CO)<sub>3</sub>(L)(H<sub>2</sub>O)](CF<sub>3</sub>SO<sub>3</sub>) (79.2° and 2.18(3) Å) [10]. These similarities strongly suggest that the coordinations around the rhenium metal center remain unchanged after the attachment of pyrrole pendant to the dipyrpyridylamine ligand.

The monomer Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl can be easily electropolymerized onto a glassy carbon electrode in CH<sub>3</sub>CN with 0.1 M tetrabutylammonium perchlorate (TBAP) supporting electrolyte. Repeated voltammetric scans from –0.4 to 0.9 V (vs. ferrocene/ferrocene, Cp<sub>2</sub>Fe<sup>+0</sup>) resulted in a gradual increase of a peak current at ca. 0.3 V which is indicative of the formation of poly[Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl] film on the electrode surface (Fig. 2a). This pseudo-reversible couple corresponds to the formation of polypyrrole and shifts to anodic direction with the film growth, as in the

case for polypyrroles with a large pendant group [7a]. The immobilization of poly[Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl] was also visually confirmed by yellow coloration of the electrode surface. The scanning electron microscopy (SEM) image revealed that the resulting polymer has relatively compact and continuous morphology with irregular protrusions (Fig. 2b).

Fig. 3 shows the cyclic voltammograms (CVs) measured on a poly[Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl]-modified glassy carbon electrode in CH<sub>3</sub>CN + 1.0 M TBAP under 1 atm of Ar and CO<sub>2</sub>. In the absence of CO<sub>2</sub> (dotted line), an irreversible reductive peak was observed at *E*<sub>1/2</sub> = –2.4 V vs. Cp<sub>2</sub>Fe<sup>+0</sup>. This peak, which was also observable from a solution of Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl at a bare electrode, was assigned to the reduction of Re<sup>I</sup> to Re<sup>0</sup>. Electrochemical reduction of the κ<sup>2</sup>-*N,N*-PPP ligand only occurs at potential beyond –2.6 V. An enhancement of the cathodic current was observed when Ar was replaced with CO<sub>2</sub> (solid line). It clearly shows that Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl catalysts are active for electrochemical reduction of CO<sub>2</sub> after the polymerization onto the electrode surface. The lower catalytic reduction current of the polymer film compared with the free complex (see the voltammograms in Fig. S1 of Supplementary materials) can be attributed to the diffusion barrier in the polymer film for the dissociated chloride anions and the incoming carbon dioxide molecules.

A series of *in situ* FTIR spectroelectrochemical measurements were taken to identify the reduction products (Fig. 4). With a constant potential of –2.5 V applied to a poly[Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl]-modified electrode in the presence of CO<sub>2</sub>, a gradually increasing signal at 2138 cm<sup>-1</sup> was detected. This signal is consistent with typical ν<sub>CO</sub> value assigned to CO absorption [11] and no other signals for alternative reduction products such as formate were detected, confirming the selective electroreduction of CO<sub>2</sub> to CO.

### 3. Experimental

#### 3.1. Materials

2,2'-Dipyridylamine (99%), lithium aluminum hydride (LiAlH<sub>4</sub>, 95%), lithium perchlorate (LiClO<sub>4</sub>, 99%), tetrabutylammonium perchlorate (TBAP, 98%) and *t*-BuONa (97%) were purchased from Aldrich Co. 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP,

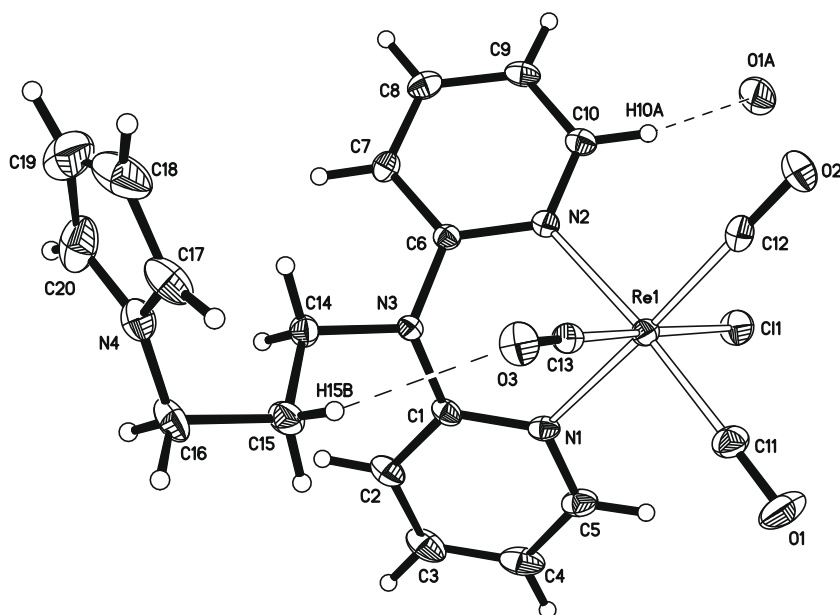
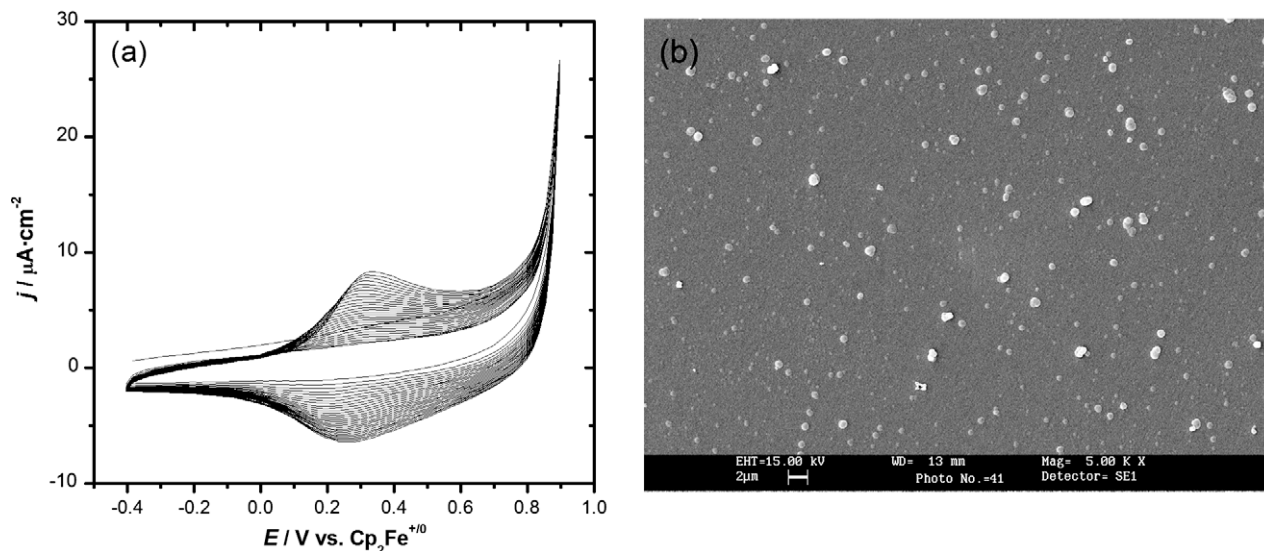
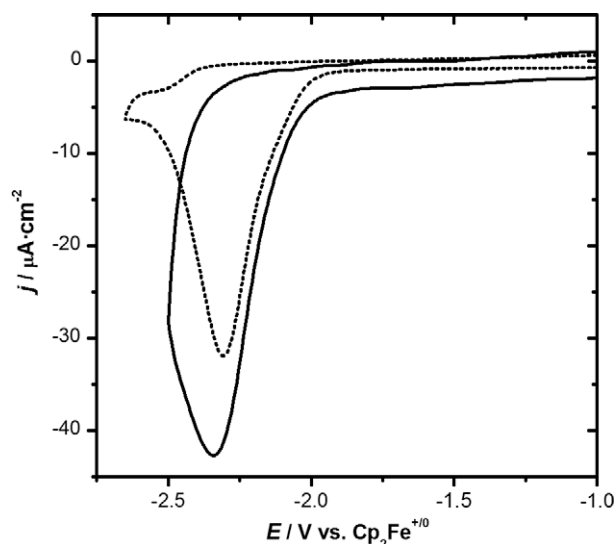


Fig. 1. ORTEP plot of Re(CO)<sub>3</sub>(κ<sup>2</sup>-*N,N*-PPP)Cl (κ<sup>2</sup>-*N,N*-PPP = *N*-(3-*N,N'*-bis(2-pyridyl)propylamino)pyrrole) with 50% thermal ellipsoids.



**Fig. 2.** (a) Cyclic voltammograms for the electropolymerization of 0.5 mM  $\text{Re}(\text{CO})_3(\kappa^2\text{-N,N-PPP})\text{Cl}$  in  $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$  solution under argon atmosphere. Working electrode: glassy carbon; scan rate:  $50 \text{ mV s}^{-1}$ . (b) Scanning electron microscopy (SEM) image of poly $[\text{Re}(\text{CO})_3(\kappa^2\text{-N,N-PPP})\text{Cl}]$  film prepared from 1.0 mM  $\text{Re}(\text{CO})_3(\kappa^2\text{-N,N-PPP})\text{Cl}$  in  $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$  solution onto a glassy carbon electrode.

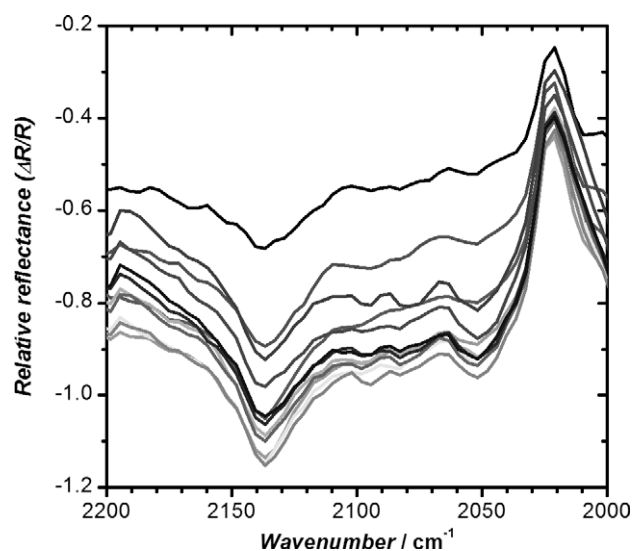


**Fig. 3.** Cyclic voltammograms of a poly $[\text{Re}(\text{CO})_3(\kappa^2\text{-N,N-PPP})\text{Cl}]$ -modified glassy carbon electrode measured in  $\text{CH}_3\text{CN} + 0.1 \text{ M TBAP}$  solution under Ar (dotted line) and under  $\text{CO}_2$  (solid line). Working electrode: glassy carbon; scan rate:  $50 \text{ mV s}^{-1}$ .

98%, racemic) and rhenium pentacarbonyl chloride ( $\text{Re}(\text{CO})_5\text{Cl}$ , 99%) were purchased from Strem Co. *N*-(3-aminopropyl)pyrrole [12] and  $\text{Pd}_2(\text{dba})_3$  (dba = dibenzylideneacetone) [13] were synthesized according to the literature procedures. Elemental analyses were performed on a VarioEL elemental analyzer at the Test and Analysis Center of Wuhan University, Hubei, China.

### 3.2. *N*-(3-*N,N'*-bis(2-pyridyl)propylamino)pyrrole (PPP)

A mixture of 2-bromopyridine (5 mmol, 0.5 mL), *N*-(3-aminopropyl)pyrrole (6 mmol, 0.75 g),  $\text{Pd}_2(\text{dba})_3$  (0.2 mmol, 8 mmol% Pd, 90 mg), BINAP (0.2 mmol, 0.125 g) and *t*-BuONa (10 mmol, 0.67 g) was stirred at room temperature under argon for 5 min. A solution of 2-bromopyridine in toluene (0.5 mL of 2-bromopyridine in 45 mL toluene, 0.11 M) was added to the above mixture at room temperature. The resulting mixture was heated to  $70^\circ\text{C}$  under argon for 16 h, and stirred at room temperature for another



**Fig. 4.** A series of normalized time resolved FTIR spectra in the region of 2200–2000  $\text{cm}^{-1}$  ( $8 \text{ cm}^{-1}$  resolution, 100 scans) collected from a poly $[\text{Re}(\text{CO})_3(\kappa^2\text{-N,N-PPP})\text{Cl}]$ -modified glassy carbon electrode. The electrode was immersed in a  $\text{CO}_2$ -saturated  $\text{CH}_3\text{CN}$  solution of 0.1 M TBAP at an applied potential of  $-2.5 \text{ V vs. Cp}_2\text{Fe}^{+/0}$ . The time interval between each collected spectrum is about 1.5 min and the temperature of the electrolyte was maintained at  $-0.5^\circ\text{C}$ .

4 h. After this period, 50 mL of saturated brine was added, and the mixture was extracted with diethyl ether ( $3 \times 50 \text{ mL}$ ). The organic layers were combined and dried over anhydrous sodium sulfate, and the solvent was removed under vacuum to yield a dark brown oil. The crude product was purified on a silica column using ethyl acetate/*n*-hexane (1:2) containing 0.5–1% triethylamine as eluent to give a yellow–brown oil. Yield: 45%.  $^1\text{H NMR}$  (400 MHz  $\text{D}_2\text{O}$ ):  $\delta$  2.16–2.23 (m, 2H), 4.00 (t, 2H,  $J = 7 \text{ Hz}$ ), 4.24 (t, 2H,  $J = 7 \text{ Hz}$ ), 6.10 (d, 2H,  $J = 2 \text{ Hz}$ ), 6.63 (d, 2H,  $J = 2 \text{ Hz}$ ), 6.88 (t, 2H,  $J = 6 \text{ Hz}$ ), 7.02 (d, 2H,  $J = 8 \text{ Hz}$ ), 7.52 (t, 2H,  $J = 8 \text{ Hz}$ ), 8.35 (d, 2H,  $J = 6 \text{ Hz}$ ). IR: 3369 (s), 3298 (m), 3121 (s), 3097 (s), 2931 (s), 2867 (s), 1599 (s), 1552 (s), 1501 (s), 1499 (m), 1280 (s), 1090 (s), 727 (s), 618 (s). ESI-MS:  $m/z$  279 ( $\text{M}+\text{H}^+$ ), UV-Vis( $\text{CH}_2\text{Cl}_2/\lambda_{\text{max}}$ , nm/ $\epsilon$ ,  $\text{M}^{-1} \text{ cm}^{-1}$ ): 292 (18 300). Elemental Anal. Calc. for  $\text{C}_{17}\text{H}_{18}\text{N}_4$ : C, 73.4; H, 6.5; N, 20.1. Found: C, 72.1; H, 6.4; N, 18.8%.

### 3.3. [Re(CO)<sub>3</sub>(κ<sup>2</sup>-N,N-PPP)Cl]

A mixture of Re(CO)<sub>5</sub>Cl (0.361 g, 1 mmol), PPP (0.278 g, 1 mmol), 10 mL of acetonitrile, and 3 mL of heptane was refluxed for about 2 h. The resulting mixture was allowed to cool to room temperature, followed by rinse with 20 mL of diethyl ether. The pale yellow precipitate was collected and dried to yield the rhenium complex. Yield: 0.45 g (77.1%). ESI-MS: *m/z* 583. IR (CH<sub>3</sub>CN, cm<sup>-1</sup>): ν(C=O) 2020, 1912, 1893. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>/λ<sub>max</sub>, nm/ε, M<sup>-1</sup> cm<sup>-1</sup>): 292 (17 011). <sup>1</sup>H NMR (400 MHz D<sub>2</sub>O): δ 2.20–2.40 (m, 2H), 3.87 (t, 2H, *J* = 8 Hz), 4.05 (t, 2H, *J* = 6 Hz), 6.24 (t, 2H, *J* = 2 Hz), 6.69 (t, 2H, *J* = 2 Hz), 6.97 (d, 2H, *J* = 8 Hz), 7.17 (t, 2H, *J* = 7 Hz), 7.81 (t, 2H, *J* = 7 Hz), 8.87 (d, 2H, *J* = 7 Hz). Elemental Anal. Calc. for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>ClO<sub>3</sub>Re: C, 41.1; H, 3.1; N, 9.6. Found: C, 41.2; H, 3.1; N, 9.6%.

### 3.4. X-ray structure analysis

X-ray diffraction data of Re(CO)<sub>3</sub>(κ<sup>2</sup>-N,N-PPP)Cl were collected on a Bruker CCD detector diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data were collected in the range of θ = 1.71–27.47° and corrected for Lorentz polarization effect. The crystal structure was solved using Patterson function methods and expanded by difference Fourier synthesis, and refined by full-matrix least-squares on *F*<sup>2</sup> using Bruker Smart and Bruker SHELXTL program packages.

### 3.5. Electrochemistry and scanning electron microscopy (SEM)

Electrochemical polymerization of Re(CO)<sub>3</sub>(κ<sup>2</sup>-N,N-PPP)Cl was performed using a potentiostat BAS 100 W (Bioanalytical Systems). A conventional three electrode system was employed. A glassy carbon electrode (surface area = 0.2 cm<sup>2</sup>) was used as the working electrode, a Pt wire as the auxiliary electrode, and an Ag/AgNO<sub>3</sub> (0.1 M) electrode was used as reference electrode. The electrolyte solution, 0.1 M TBAP/CH<sub>3</sub>CN, was saturated with CO<sub>2</sub> by purging with CO<sub>2</sub> (purity ≥ 99.8%, Hong Kong Oxygen and Acetylene Co., Ltd.) for 15 min prior to each experiment. In the control experiments, Ar was purged for 15 min prior to the measurements. *In situ* FTIR spectroelectrochemistry was performed with a thin layer spectroelectrochemical cell similar to the one reported in literature [11b]. The infrared spectra were recorded on a Nicolet Magna IR 550 spectrometer in the reflectance mode and the collected spectra are reported in the form of difference spectra. Details of the *in situ* FTIR spectroelectrochemical measurements are given in the Supplementary materials.

SEM spectra were obtained on a Leica Stereoscan 440 scanning electron microscope. The samples for SEM were prepared by polymerizing rhenium complex onto a demountable glassy carbon disk electrode (surface area = 0.2 cm<sup>2</sup>). The resulting polymer films were dried under an air blower and sputter-coated with gold.

## 4. Conclusion

A novel dipyrildylamine ligand (PPP) with a pendant pyrrole linked to a bridging nitrogen between two pyridines was synthesized and coordinated into a rhenium(I)-complex, Re(CO)<sub>3</sub>(κ<sup>2</sup>-N,N-

PPP)Cl. The film of poly[Re(CO)<sub>3</sub>(κ<sup>2</sup>-N,N-PPP)Cl] deposited on the electrode surface via electropolymerization of pyrrole exhibited electrocatalytic activity for the reduction of CO<sub>2</sub> to CO.

## Acknowledgements

This work was supported by The Hong Kong Polytechnic University and the Research Grants Council (PolyU 5015/05P). L.Y.S.L. acknowledges the award of a postdoctoral fellowship administered by the Research Committee of The Hong Kong Polytechnic University. We also thank Prof. Richard Adams for helpful comments on this manuscript.

## Appendix A. Supplementary material

CCDC 718658 contains the supplementary crystallographic data for Re(CO)<sub>3</sub>(κ<sup>2</sup>-N,N-PPP)Cl. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.04.034](https://doi.org/10.1016/j.jorganchem.2009.04.034).

## References

- [1] (a) F.R. Keene, B.P. Sullivan, in: B.P. Sullivan, K. Krist, H.E. Guard (Eds.), *Electrochemical and Electrocatalytic Reactions of Carbon Dioxide*, Elsevier, Amsterdam, 1993, p. 118; (b) E.E. Benson, C.P. Kubiak, A.J. Sathrum, J.M. Smieja, *Chem. Soc. Rev.* 38 (2009) 89; (c) C.M. Sanchez-Sanchez, V. Montiel, D.A. Tryk, A. Aldaz, A. Fujishima, *Pure Appl. Chem.* 73 (2001) 1917.
- [2] (a) Y. Hori, A. Murata, R. Takahashi, S. Suzuki, *J. Am. Chem. Soc.* 109 (1987) 5022; (b) J.J. Kim, D.P. Summers, K.W. Frese, *J. Electroanal. Chem.* 245 (1988) 223; (c) D.W. DeWulf, T. Jin, A.J. Bard, *J. Electrochem. Soc.* 136 (1989) 1686; (d) S. Cosnier, A. Deronzier, J.C. Moutet, *New J. Chem.* 14 (1990) 831.
- [3] (a) C.M. Lieber, N.S. Lewis, *J. Am. Chem. Soc.* 106 (1984) 5033; (b) C.R. Cabrera, H.D. Abruna, *J. Electroanal. Chem.* 209 (1986) 101; (c) T.R. O'Toole, L.D. Margerum, T.D. Westmoreland, W.J. Vining, R.W. Murray, T.J. Meyer, *J. Chem. Soc., Chem. Commun.* (1985) 1416; (d) A. Begum, P.G. Pickup, *Electrochem. Commun.* 9 (2007) 2525.
- [4] (a) A.I. Breikss, H.D. Abruna, *J. Electroanal. Chem.* 201 (1986) 347; (b) S. Van Wallendael, R.J. Shaver, D.P. Rillema, B.J. Yoblinski, M. Stathis, T.F. Guarr, *Inorg. Chem.* 29 (1990) 1761; (c) B.D. Rossenaar, Cornelis J. Kleverlaan, D.J. Stufkens, A. Oskam, *J. Chem. Soc., Chem. Commun.* (1994) 63; (d) T. Scheiring, A. Klein, W. Kaim, *J. Chem. Soc., Perkin Trans. 2* (1997) 2569; (e) D.H. Gibson, X. Yin, H. He, M.S. Mashuta, *Organometallics* 22 (2003) 337.
- [5] J. Hawecker, J.M. Lehn, R. Ziessel, *J. Chem. Soc., Chem. Commun.* (1984) 328.
- [6] F.P.A. Johnson, M.W. George, F. Hartl, J.J. Turner, *Organometallics* 15 (1996) 3374.
- [7] (a) G. Bidan, A. Deronzier, J.C. Moutet, *J. Chem. Soc., Chem. Commun.* (1984) 1185; (b) S. Cosnier, A. Deronzier, J.C. Moutet, *J. Mol. Catal.* 45 (1988) 381.
- [8] J. Guilhem, C. Pascard, J.M. Lehn, R. Ziessel, *J. Chem. Soc., Dalton Trans.* (1989) 1449.
- [9] E. Horn, M.R. Snow, *Aust. J. Chem.* 33 (1980) 2369.
- [10] W.-L. Wong, K.-C. Cheung, P.-H. Chan, Z.-Y. Zhou, K.-H. Lee, K.-Y. Wong, *Chem. Commun.* (2007) 2175.
- [11] (a) P.A. Christensen, A. Hamnett, A.V.G. Muir, N.A. Freeman, *J. Electroanal. Chem.* 288 (1990) 197; (b) P.A. Christensen, A. Hamnett, A.V.G. Muir, J.A. Timney, *J. Chem. Soc., Dalton Trans.* (1992) 1455.
- [12] N.C. Foulds, C.R. Lowe, *Anal. Chem.* 60 (1988) 2473.
- [13] T. Ukai, H. Kawazura, Y. Ishii, J.J. Bonnet, J.A. Ibers, *J. Organometal. Chem.* 65 (1974) 253.