Supplementary Information for

**Electrocatalytic Reduction of CO2 by Thiophene-substituted Rhenium(I) Complexes and by their Polymerized Films**

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**Materials and Methods:**

All reactions were performed under inert atmosphere. All microwave (MW) reactions were performed in single-mode Biotage Initiator 2.5. Column chromatography was performed on a Biotage Isolera flash purification system. $^1$H NMR spectra were recorded on a Bruker Avance 200 NMR and JEOL EX 400 NMR.

**Synthesis**

**Compound ETT** was synthesized following a pathway similar to the previously described strategy, by connecting a terpyridine to the 3'-ethynyl-2,2':5',2''-tertiophene.$^{1,2}$ The compounds 4, 5 and 6 were prepared according to these references.$^{1,2}$ Compound TT was synthesized by transforming the 3'-bromo-2,2':5',2''-terthiophene$^{1,2}$ (4) into [2,2':5',2''-terthiophen]-3'-ylboronic acid (7) as previously described$^{3-5}$ and using the resulting boronic acid for the final coupling with 4-bromo-2,2'-bipyridine. The compound T was prepared by Suzuki reaction between 3-thiopheneboronic acid and 4-Bromo-2,2'-bipyridine at 80°C.$^6$

The 4-bromo-2,2'-bipyridine was synthesized according to a literature procedure.$^7$

**4-(thiophen-3-yl)-2,2'-bipyridine (T).** $^1$H NMR (200 MHz, CDCl$_3$) δ 8.77 – 8.64 (m, 1H), 8.46 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.58 (dd, $J = 5.1$, 1.4 Hz, 1H), 7.52 (dd, $J = 5.1$, 1.9 Hz, 1H), 7.45 (dd, $J = 5.1$, 2.9 Hz, 1H), 7.34 (ddd, $J = 7.5$, 4.8, 1.2 Hz, 1H).

**4-((2,2':5',2''-terthiophen)-3'-ylethylnyl)-2,2'-bipyridine (ETT).** $^1$H NMR (200 MHz, CDCl$_3$) δ 8.66 (t, $J = 5.1$ Hz, 2H), 8.54 (s, 1H), 8.43 (d, $J = 7.9$ Hz, 1H), 7.83 (t, $J = 7.1$ Hz, 1H), 7.44 (t, $J = 4.4$ Hz, 2H), 7.32 (t, $J = 5.7$ Hz, 2H), 7.26 – 7.10 (m, 3H), 7.10 – 6.90 (m, 2H).


Scheme 1. Synthesis of the proposed ligands. Reactions conditions: (i) Pd(PPh$_3$)$_4$, DME, Na$_2$CO$_3$ 1.5 M, 80°C, 24 h; (ii) 2-methyl-3-buten-2-ol, Pd(PPh$_3$)$_4$, Cul, DIPA, Argon, reflux, 20 h; (iii) KOH, Toluene:MeOH 1:1, reflux; (iv) 4-bromo-2,2'-bispyridine, Pd(PPh$_3$)$_4$, Cul, DIPA, Argon, reflux, 24 h; (v) LDA, THF, trimethylborate, -60°C; (vi) (PPh$_3$)$_4$, DME, Na$_2$CO$_3$ 1.5 M, MW, 120°C, 30 min.
Fig. S1: CV of MeCN homogeneous solution of complexes 1 (left), 2 (middle) and 3 (right).

Fig. S2. Plot of the current peak of the first reduction vs. square root of scan rate for 1-3.

Fig. S3. HOMO (left) and LUMO (right) of (bpy)Re(CO)$_3$Cl
Fig. S4. HOMO (down), HOMO-1 (middle) and LUMO (up) for complexes 1, 2 and 3.

Electro-polymerization of complex 3: the behavior is similarly to the electrode modified with 2 (Fig. 3). The coverage Γ was estimated to be $42.65 \times 10^{-10}$ mol·cm$^{-2}$.

Fig. S5 left: CVs of the electrode modified by 3 (the sharp peak vanish when the steady state is obtained); center: CV at 2.0 V/s of the steady state electrode; right: plot of the current vs scan rate of the steady state electrode.
Fig. S6 CV under CO₂ of the steady state electrode modified with 3. Γ = 85.3×10⁻¹⁰ mol·cm⁻². The current ratio \(i_c/i_p=89\) at -2.16 V is almost 500 times than its counterpart in homogeneous solution.