

Supplementary Information for

## Electrocatalytic Reduction of CO<sub>2</sub> 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. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 200 NMR and JEOL EX 400 NMR.

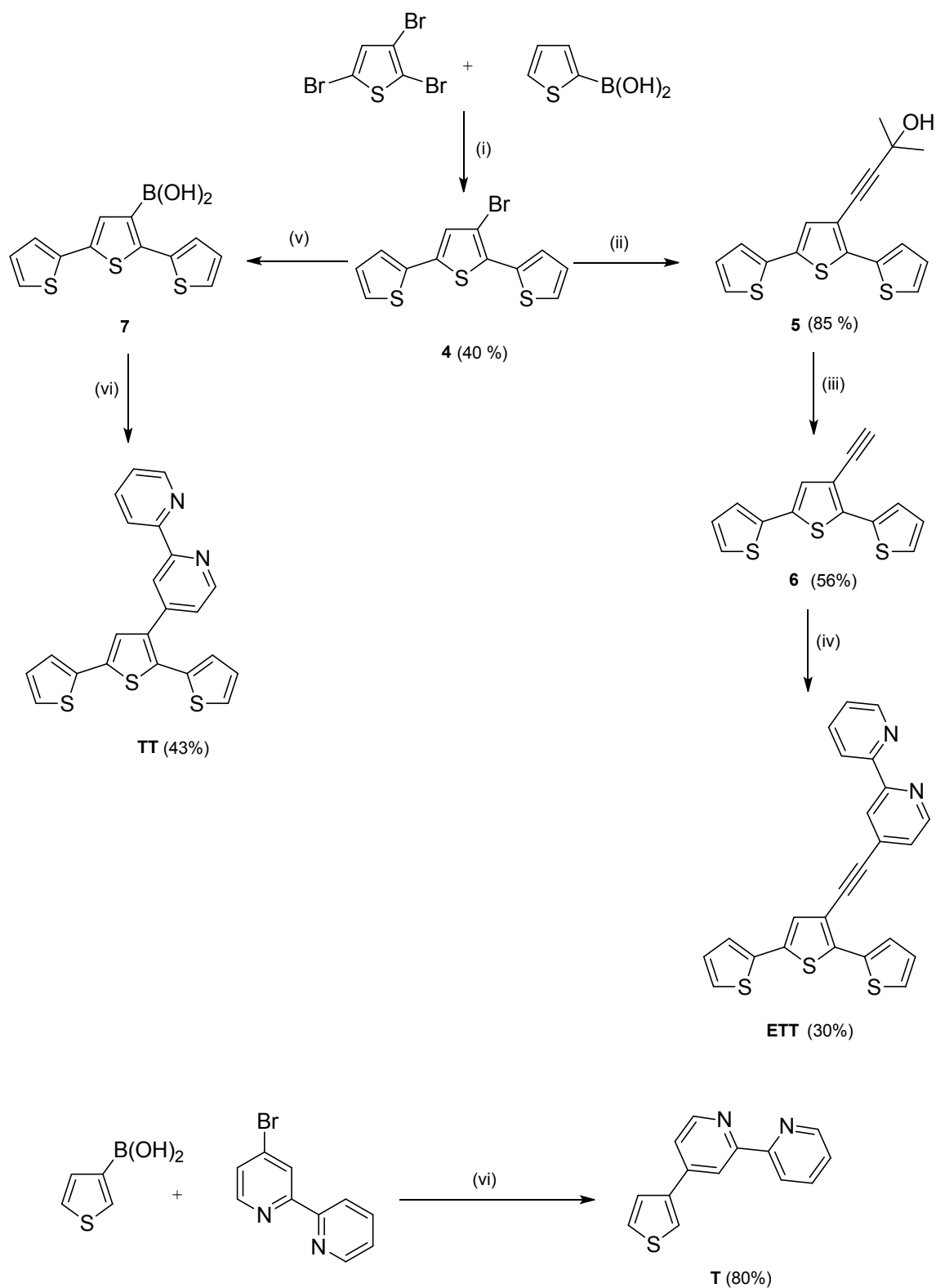
### Synthesis

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''-terthiophene.<sup>1,2</sup> The compounds **4**, **5** and **6** were prepared according to these references<sup>1,2</sup>. Compound **TT** was synthesized by transforming the 3'-bromo-2,2':5',2''-terthiophene<sup>1,2</sup> (**4**) into [2,2':5',2''-terthiophen]-3'-ylboronic acid (**7**) as previously described<sup>3-5</sup> 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.<sup>6</sup> The 4-bromo-2,2'-bipyridine was synthesized according to a literature procedure.<sup>7</sup>

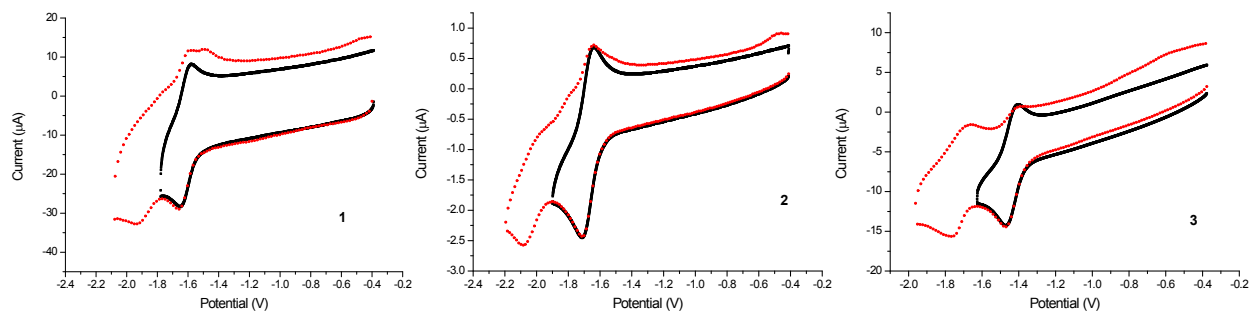
**4-(thiophen-3-yl)-2,2'-bipyridine (T)**. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 8.77 – 8.64 (m, 1H), 8.46 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.87 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.83 – 7.78 (m, 1H), 7.58 (dd, *J* = 5.1, 1.4 Hz, 1H), 7.52 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.45 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.34 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H).

**4-([2,2':5',2''-terthiophen]-3'-ylethynyl)-2,2'-bipyridine (ETT)**. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) 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).

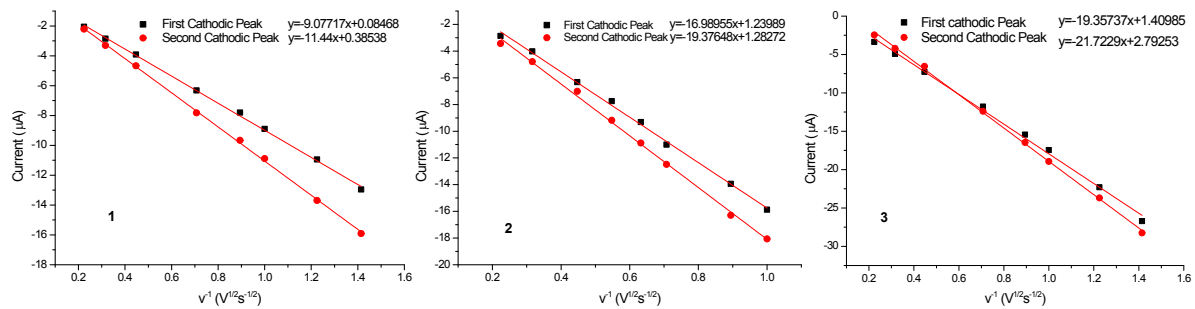
- 1) P. Manca, M.I Pilo, G. Casu, S. Gladiali, G. Sanna, R. Scanu, N. Spano, A. Zucca, C. Zanardi, D. Bagnis, L. Valentini *Journal of Polymer Sci. A: Polymer Chemistry*, **2011**, 3513-3523.
- 2) T.-Y. Lee, Y.-B. Shim, S.C. Shin *Synth. Met.* **2002**, *126*, 105-110.
- 3) A. de Bettencourt-Dias, S. Viswanathan, A. Rollett *J. Am. Chem. Soc.* **2007**, *129*, 15436-15437.
- 4) G. E. Collins, A.K. Burrell, S.M. Scott, D.L. Officer *J. Org. Chem.* 2003, *68*, (23), 8974-8983;
- 5) G. Noronha, J. Cao, C.P. Chow, J. Renick PCT Int. Appl., 2009026345, WO 2009/026345.
- 6) S. Gronowitz, K. Lavitz *Chem. Scr.*, **1984**, *24*, 5-6.
- 7) D.A. Mbi Egbe, A.M. Amer, E. Klemm *Designed Monomers Polym.*, **2011**, *4*, 169–175.



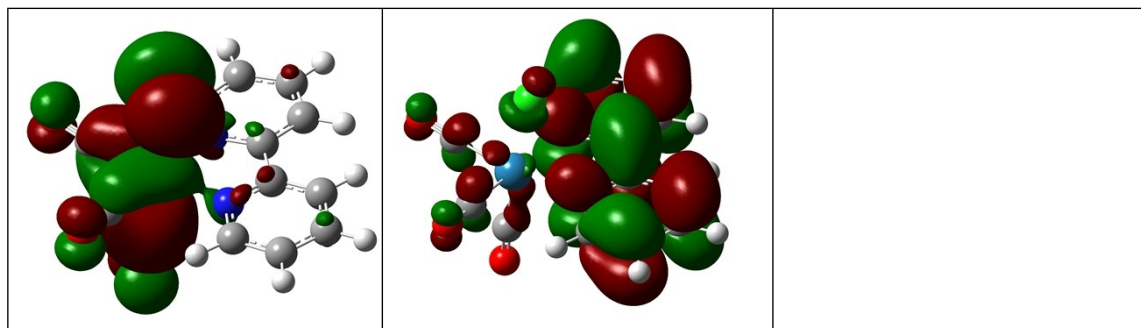
Scheme 1. Synthesis of the proposed ligands. Reactions conditions: (i)  $\text{Pd(PPh}_3)_4$ , DME,  $\text{Na}_2\text{CO}_3$  1.5 M,  $80^\circ\text{C}$ , 24h.; (ii) 2-methyl-3-butyn-2-ol,  $\text{Pd(PPh}_3)_4$ , CuI, DIPA, Argon, reflux, 20 h; (iii) KOH, Toluene:MeOH 1:1, reflux; (iv) 4-bromo-2,2'-bipyridine,  $\text{Pd(PPh}_3)_4$ , CuI, DIPA, Argon, reflux, 24 h; (v) LDA, THF, trimethylborate,  $-60^\circ\text{C}$ ; (vi)  $(\text{PPh}_3)_4$ , DME,  $\text{Na}_2\text{CO}_3$  1.5 M, MW,  $120^\circ\text{C}$ , 30 min.



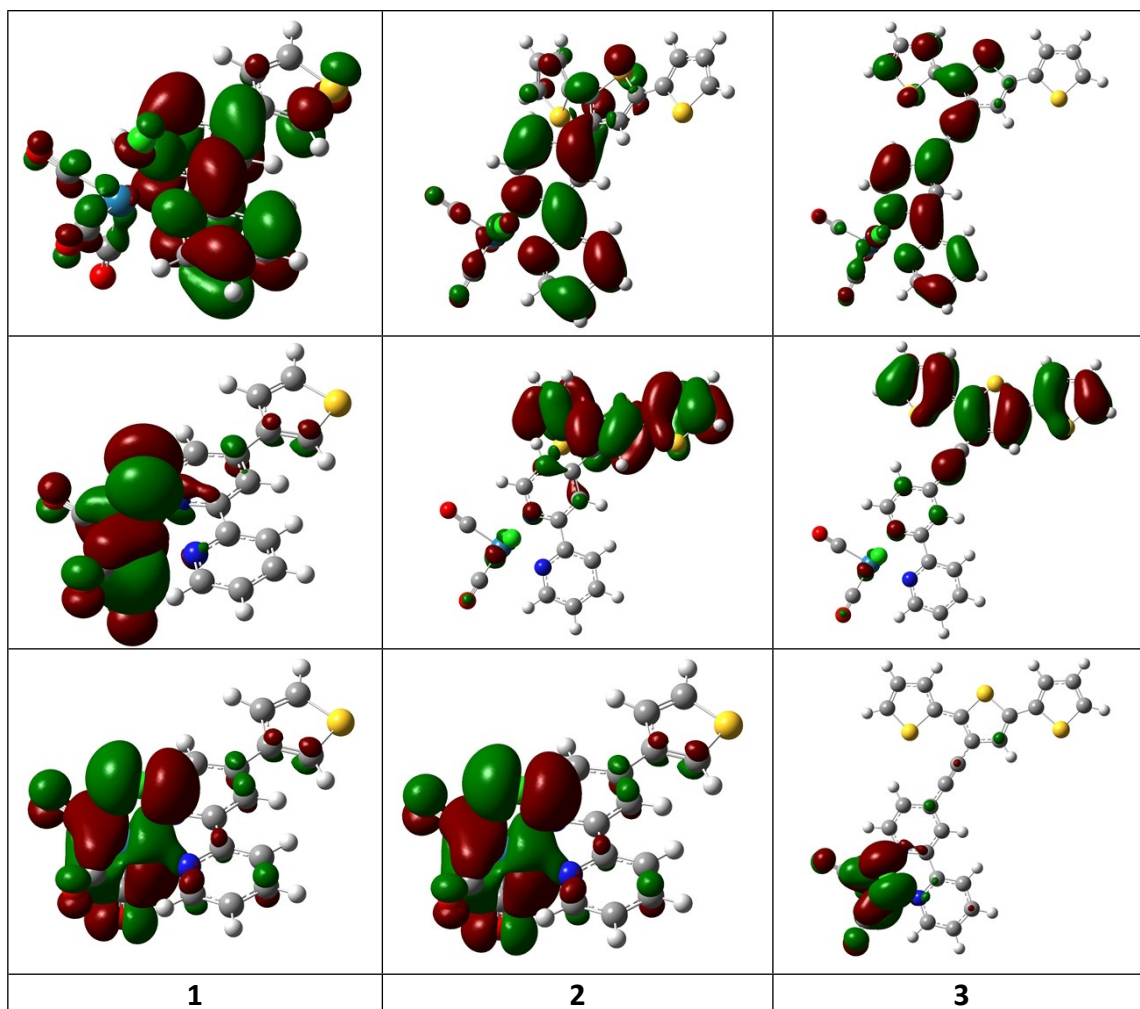
**Fig. S1:** CV of MeCN homogeneous solution of complexes **1** (left), **2** (middle) and **3** (right).



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

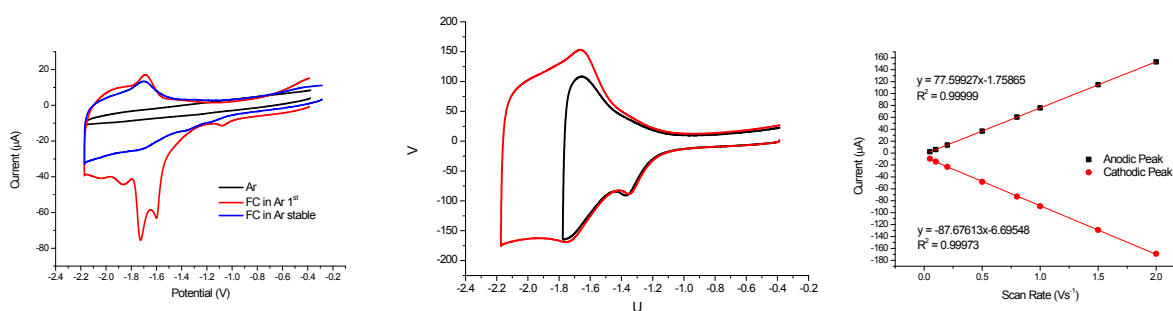


**Fig. S3.** HOMO (left) and LUMO (right) of (bpy)Re(CO)<sub>3</sub>Cl

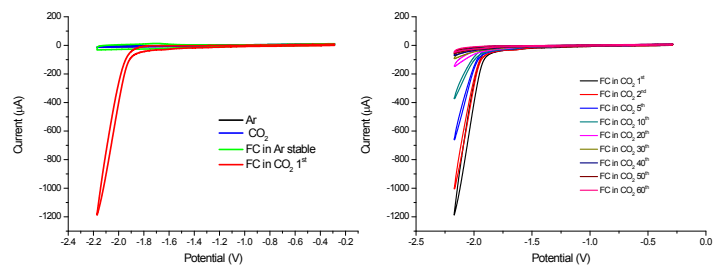


**Fig. S4.** HOMO (down), HOMO-1 (middle) and LUMO (up) for complexes **1**, **2** and **3**.

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



**Fig. S5** left: CVs of the electrode modified by **3** (the sharp peak vanishes 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 CO<sub>2</sub> of the steady state electrode modified with **3**.  $\Gamma = 85.3 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ . The current ratio  $i_c/i_p=89$  at -2.16 V is almost 500 times than its counterpart in homogeneous solution.