Supplementary information

Electroactive chain-like compounds constructed from trimetallic clusters and 4,4'-bipyridine spacers: one-pot synthesis, characterization and surface binding

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^{1}H NMR data of **1a**–**4a** and **1b**–**4b** in CD_3CN *including coupling constants.*
Assignments of the resonances are provided in Table 1 of the text.

1a: δ 2.01 (s, 12H), 1.88 (s, 6H).

2a: δ 9.35 (d, 4H, J = 6.3 Hz), 8.69 (d, 4H, J = 6.3 Hz), 2.08 (s, 12H), 2.03 (s, 12H), 1.90 (s, 12H).

3a: δ 9.41 (d, 4H, J = 6.3 Hz), 9.37 (d, 4H, J = 6.6 Hz), 8.75 (d, 4H, J = 6.6 Hz), 8.71 (d, 4H, J = 6.6 Hz), 2.093 (s, 12H), 2.090 (s, 12H), 2.04 (s, 12H), 1.90 (s, 12H + 6H).

4a: δ 9.42 (d, 4H, J = 6.6 Hz), 9.41 (d, 4H, J = 6.3 Hz), 9.36 (d, 4H, J = 6.6 Hz), 8.78 (d, 4H, J = 6.3 Hz), 8.76 (d, 4H, J = 6.6 Hz), 8.72 (d, 4H, J = 6.3 Hz), 2.102 (s, 12H), 2.096 (s, 12H), 2.089 (s, 12H), 2.04 (s, 12H), 1.92 (s, 12H), 1.90 (s, 12H).

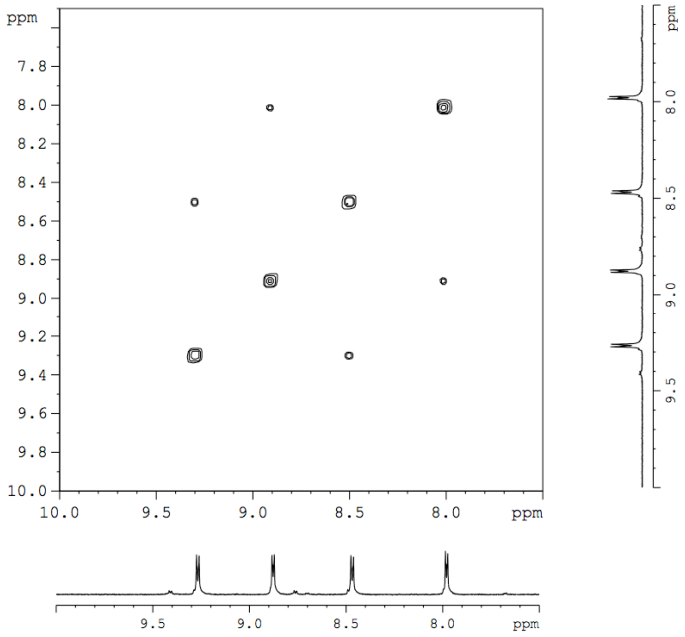
1b: δ 9.27 (d, 4H, J = 6.6 Hz), 8.88 (d, 4H, J = 6.0 Hz), 8.47 (d, 4H, J = 6.6 Hz), 7.98 (d, 4H, J = 6.0 Hz), 2.13 (s, 12H), 1.81 (s, 6H).

2b: δ 9.41 (d, 4H, J = 6.6 Hz), 9.28 (d, 4H, J = 6.6 Hz), 8.88 (d, 4H, J = 6.0 Hz), 8.76 (d, 4H, J = 6.6 Hz), 8.49 (d, 4H, J = 6.6 Hz), 7.99 (d, 4H, J = 6.0 Hz), 2.08 (s, 12H), 2.04 (s, 12H), 1.86 (s, 12H).

3b: δ 9.42 (overlapping signals: d + d, 4H + 4H), 9.28 (d, 4H, J = 6.3 Hz), 8.89 (d, 4H, J = 5.7 Hz), 8.78 (overlapping signals: d + d, 4H + 4H), 8.49 (d, 4H, J = 6.6 Hz), 7.99 (d, 4H, J = 6.0 Hz), 2.10 (s, 12H), 2.08 (s, 12H), 2.05 (s, 12H), 1.869 (s, 12H), 1.865 (s, 6H).

4b: 9.42 (overlapping signals: d + d + d, 4H + 4H + 4H), 9.28 (d, 4H, J = 6.6 Hz), 8.89 (d, 4H, J = 5.7 Hz), 8.78 (overlapping signals: d + d + d, 4H + 4H + 4H), 8.49 (d, 4H, J = 6.6 Hz), 7.99 (d, 4H, J = 5.7 Hz), 2.11 (s, 12H), 2.10 (s, 12H), 2.08 (s, 12H), 2.05 (s, 12H), 1.87 (overlapping signals: s + s, 12H + 12H)

(a)



(b)

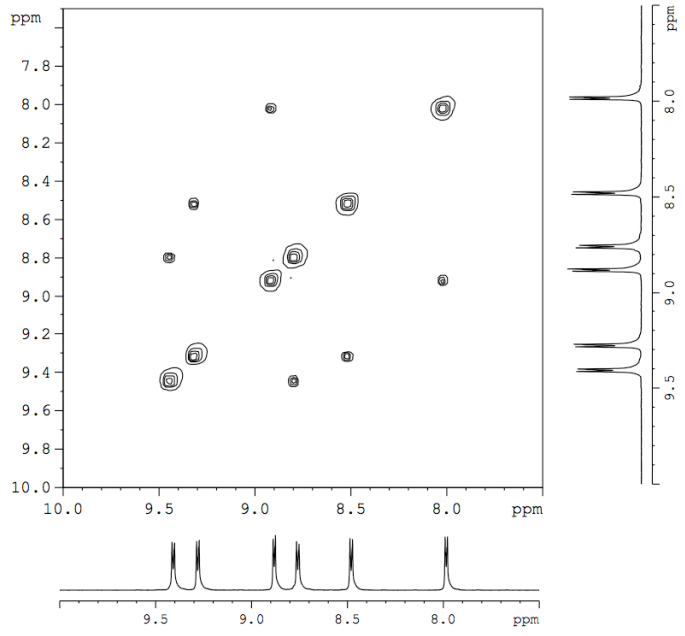


Fig. S1 ^{1}H–^{1}H COSY spectra of (a) **1b** and (b) **2b** in CD_3CN.

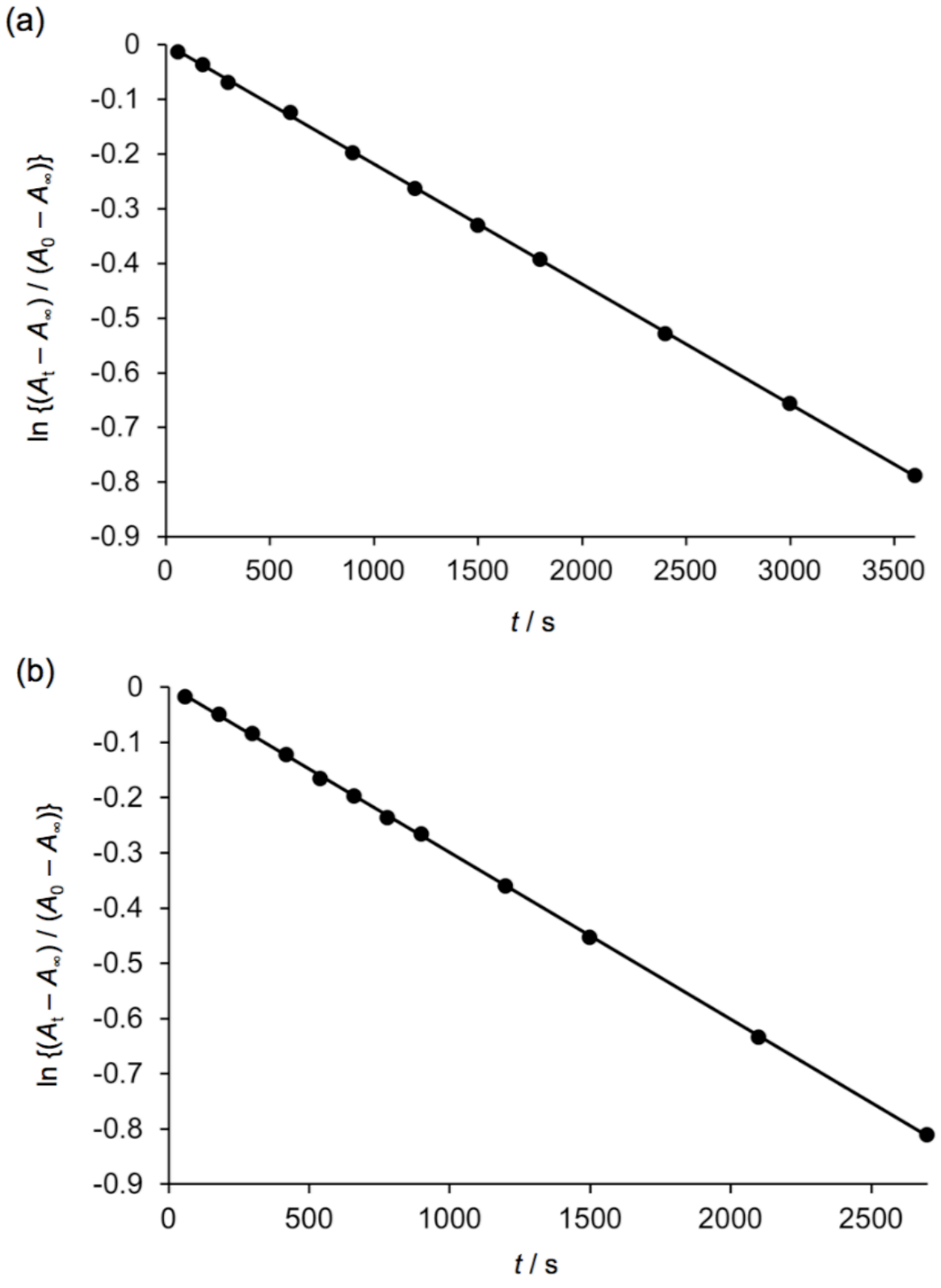


Fig. S2 The first-order plots for photodissociation of CO from (a) **2a** and (b) **3a** in CH_3CN.

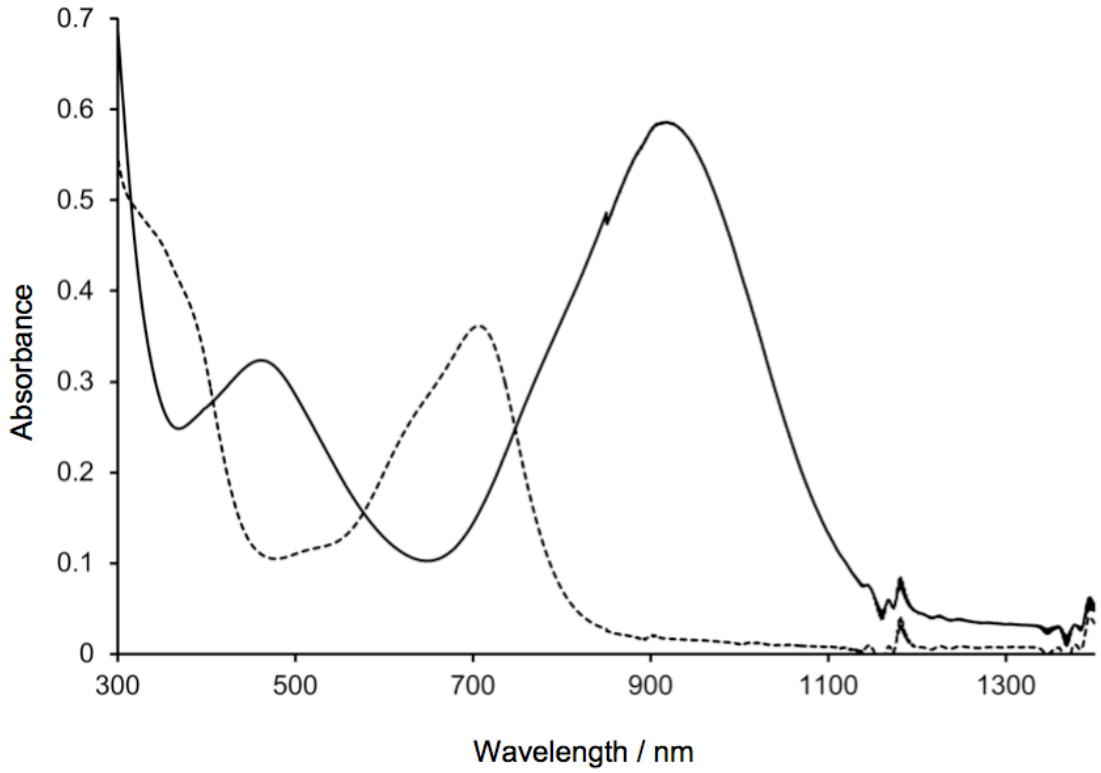


Fig. S3 UV/vis and near IR spectra of **2a'** (solid line) and [**2a'**]$^{2+}$ (broken line). The latter was *in situ* prepared by addition of NH_4PF_6 to the solution of **2a'** in an optical cell (1-mm path length) in air.

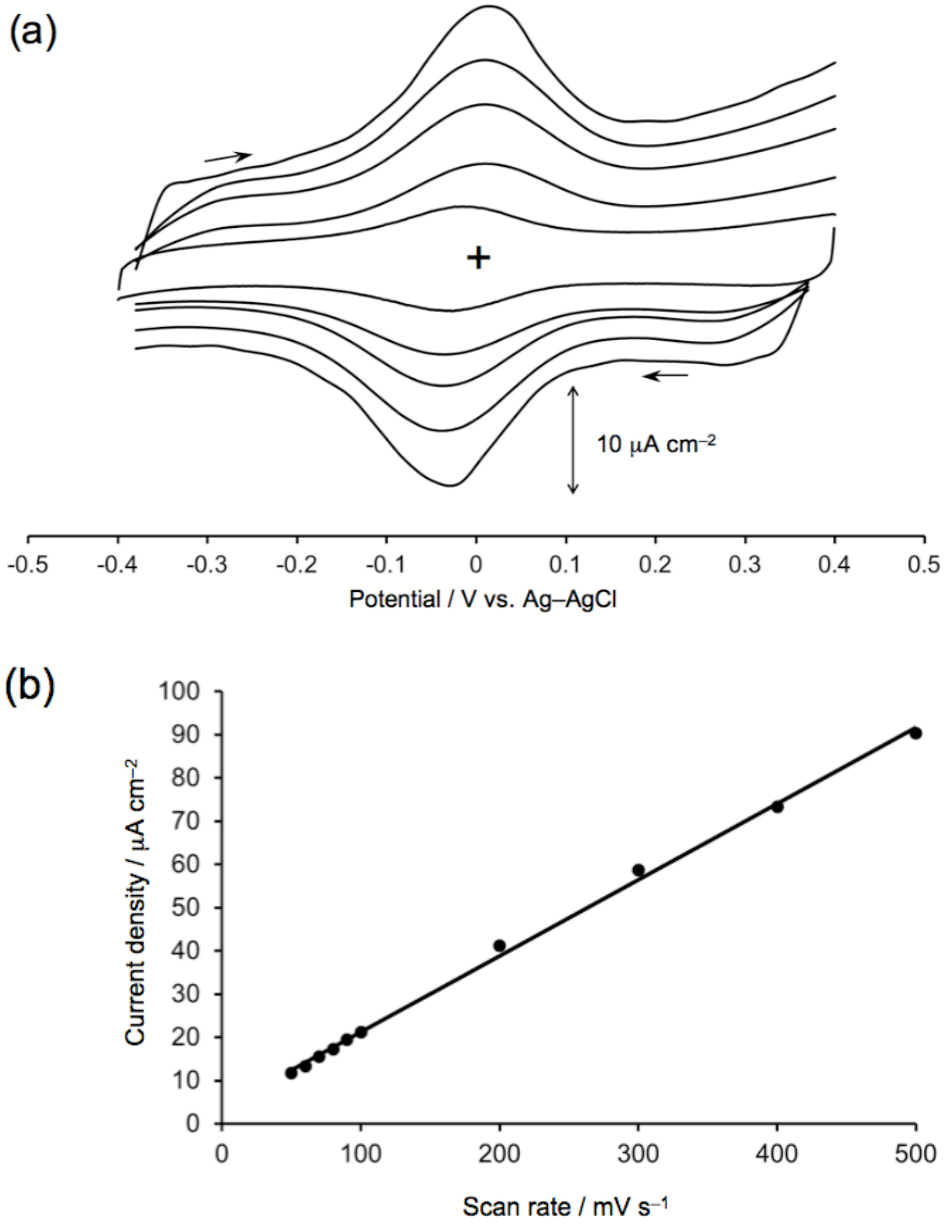


Fig. S4 (a) Scan rate dependence of CVs of an Au(111) working electrode covered with **2a**/pmla SAMs after the treatment of electrochemical multiple potential cycles. Counter electrode: a Pt coil. Reference electrode: Ag–AgCl. Electrolyte solution: an aqueous solution of $HClO_4$ (0.1 M). Scan rate: 0.1, 0.2, 0.3, 0.4 and 0.5 V s^{-1}. (b) A linear relationship of current peak intensity with the scan rate.