Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPORTING INFORMATION (ESI) FOR:

Metal-mediated transport of electrons across molecular films

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Figure S1 ^{1}H NMR spectrum of disulphide **1** in CD_3OD (top) and its progressive conversion to dithiolate **1** by reduction with $NaBH_4$ (middle and bottom).

Figure S2 ^{13}C NMR spectrum of disulphide **1** in CD_3OD before (top) and after reduction with $NaBH_4$ (bottom; * indicates starting disulphide **1**).

Figure S3 ESI-MS (+ ion) spectrum of disulphide **1** (top) and of mixtures containing equimolar amounts of disulphide **1** and $ZnCl_2$ (middle) and $CuCl_2$ (bottom) in methanol/acetonitrile solutions**.**

Figure S4 CV of an acetonitrile solution (0.1 M $TBABF_4$ as supporting electrolyte, Pt disk working electrode) obtained by reacting equimolar amounts of $CuCl_2$ and **1**. Scan rate 0.1 V s^{-1}, T = 293K.

Figure S5 CV of the bare and monolayer modified gold electrodes in 0.1 M $HClO_4$. Scan rate 0.1 V s^{-1}, T = 293K.

Figure S6 Carbon 1s, oxygen 1s, nitrogen 1s and sulphur 2p X-ray photoelectron spectra of the film of **1** on Au.

Figure S7 Carbon 1s, oxygen 1s, nitrogen 1s, sulphur 2p, chlorine 2p and zinc 2p X-ray photoelectron spectra of the film of Zn-**1** on Au.

Figure S8 Carbon 1s, oxygen 1s, nitrogen 1s, sulphur 2p, chlorine 2p and copper 2p X-ray photoelectron spectra of the film of Cu-**1** on Au.

Materials.

Reagents were obtained from commercial sources and used as received unless otherwise noted. Solvents were dried and purified under N_2 by using standard methods and were distilled immediately before use. All the reactions were carried out under N_2.

*Synthesis of disulphide **1**.* Mono(6-amino-2-pyridylmethyl)bis(2-pyridylmethyl)amine[1] (0.28 g, 0.92 mmol) was dissolved in 7 mL of dichloromethane. Thioctic acid (0.19 g, 0.92 mmol) and 1,3- dicyclohexylcarbodiimide (0.57 g, 2.76 mmol) were added to this solution. The mixture was allowed to stir for about 72 hours at 45° C under N_2 atmosphere. The solution was allowed to cool down to room temperature. The precipitate was removed by filtration and the filtrate was extracted with 2 M HCl (10 mL) and DCM (10 mL). The water layer was neutralized with 2 M NaOH and extracted with DCM (20 mL). Finally, the organic phase was evaporated under vacuum to obtain the pure product as an oily brown solid (0.136 g, 30%).

^{1}H NMR (CD_3OD, 360.1 MHz): δ_H/ppm 8.54 (d, 2H, J = 5.0 Hz), 7.93 (d, 1H, J = 7.9 Hz), 7.87 (t, 2H, J = 7.6 Hz), 7.73 (t, 1H, J = 7.6 Hz), 7.68 (m, 2H), 7.37 (m, 2H), 7.22 (d, 1H, J = 7.2 Hz) 4.08 (s, 4H), 3.92 (s, 2H), 3.61-3.42 (m, 1H), 3.20-3.10 (m, 2H), 2.51-2.46 (m, 3H), 1.95-1.46 (m, 8H).
^{13}C (90 MHz, CD_3OD): δ_C/ppm 172.8, 156.7, 155.0, 150.8, 147.5, 138.1, 137.3, 123,2, 122.4, 118.5, 112.1, 58.4, 58.4, 55.6, 39.4, 37.4, 35.8, 33.9, 27.9, and 24.4.
MS (+ ion) calcd for $[\mathbf{1}\text{-H}]^+$, m/e 494.20, found 493.98 (100%).

*Synthesis of dithiolate **1**.* In a typical reaction, *disulphide* **1** (10 mg, 0.02 mmol) was dissolved in 1 mL of oxygen-free methanol solution. Then, $NaBH_4$ (approx. 2 equiv.) was added, leading to immediate bubbling of H_2. The reaction was monitored by NMR (CD_3OD), showing clean conversion to the dithiolate in less than 30 min. (see

^{1}H NMR spectra in Fig. S1). Over longer time (e.g. overnight), a small amount of disulphide **1** is re-formed (see ^{13}C NMR spectra in Fig. S2).

^{1}H NMR (CD_3OD, 360.1 MHz): δ_H/ppm 8.49 (d, 2H, J = 5.8 Hz), 7.86 (d, 1H, J = 8.0 Hz), 7.80 (t, 2H, J = 7.6 Hz), 7.72 (t, 1H, J = 7.6 Hz), 7.68 (m, 2H), 7.33 (m, 2H), 7.22 (d, 1H, J = 7.2 Hz) 3.90 (s, 4H), 3.80 (s, 2H), 2.96-2.92 (m, 1H), 2.80-2.60 (m, 2H), 2.51-2.47 (m, 3H), 1.97-1.50 (m, 8H).

^{13}C (90 MHz, CD_3OD): δ_C/ppm 172.8, 158.2, 156.5, 150.8, 147.8, 137.8, 136.8, 123,0, 122.0, 118.3, 111.8, 59.0, 58.7, 42.4, 38.1, 37.9, 35.9, 25.7, 24.4, and 20.8.

Metal complexes for monolayer preparation. Copper and zinc complexes of **1** were prepared by mixing equimolar amounts of the ligand **1** and the corresponding metal dichlorides. In a typical reaction, the ligand **1** (10 mg, 0.02 mmol) and corresponding metal chlorides $CuCl_2$ (3.02 mg, 0.02 mmol) or $ZnCl_2$ (2.72 mg, 0.02 mmol) were dissolved in 10 mL of acetonitrile. The resulting mixture was stirred for about 1 hour under N_2 atmosphere. During the reaction we have observed a color change from yellow to green in the case of Cu-**1** and no color change in the case of Zn-**1**. Then, the solvent was removed under vacuum to prepare the methanol solutions (10 mM) for monolayer preparation. ESI-MS analysis of the products show peaks due to M-**1** and MCl-**1** species (M = Zn, Cu; Fig. S3).

Monolayer preparation. Gold slides for XPS studies were chemically cleaned by immersing in a piranha solution for 5-10 minutes. *Caution: piranha solution reacts violently with organic materials and therefore must be handled with extreme care.*

Then, the slides were rinsed with water and methanol, dried under N_2 and used immediately. Before SAM formation, the gold disk electrodes (Metrohm, d = 0.2 cm) were electrochemically cleaned by potential cycling in an aqueous solution of 0.1 M $HClO_4$ to obtain the characteristic Au oxide formation and stripping peaks corresponding to bare Au surface using cyclic voltammetry. After electrochemical cleaning, the electrodes were rinsed with water and methanol, and dried under a stream of N_2.

Monolayers of **1**, Cu-**1** and Zn-**1** were prepared by immersing the cleaned gold disk electrode (electrochemistry) or gold slide (XPS) into 10 mM methanol solutions of these compounds in the presence of $NaBH_4$ for about 15-16 hours under N_2. After this, the SAM modified gold surfaces were rinsed with methanol and water and used immediately for the analysis.

Physical Measurements.

Electrochemistry. All electrochemical studies were performed with an Autolab PGSTAT 20 instrument. The electrochemical blocking ability of the monolayers towards electron transfer was studied by cyclic voltammetry and electrochemical impedance spectroscopy using $[Fe(CN)_6]^{3-|4-}$ redox couple as a probe. The electrolyte solutions used for electrochemical measurements were prepared with millipore water having a resistivity of 17 MΩ. Cyclic voltammetry and impedance measurements were conducted in a three-electrode glass cell at 20 ºC. A platinum rod, a saturated calomel electrode (SCE) and a monolayer-modified gold disk electrode were used as a counter, reference and working electrode respectively. Cyclic voltammetry was performed in 1mM potassium ferrocyanide aqueous solution containing 0.1M NaCl as a supporting electrolyte. Impedance measurements were carried out at the formal redox potential (as determined from cyclic voltammetry) in an aqueous solution containing equal concentrations of oxidized and reduced forms of $[Fe(CN)_6]^{3-|4-}$ with NaCl as a supporting electrolyte. The frequency range used was from 10 KHz to 0.1 Hz with an ac amplitude of 10mV. Impedance spectroscopy data were analysed to determine the charge transfer (R_{CT}), and for **1,** also the surface coverage ($\theta = 1 - (R_{ct} / R'_{ct})$, where R_{ct} is the charge transfer resistance of the bare Au and R'_{ct} is the charge transfer resistance of the **1**-modified electrode).[2] The surface coverage (θ) values were also determined from gold oxide formation/stripping studies ($\theta = 1 - (Q_{SAM} / Q_{Bare\ Au})$, where Q_{SAM} is the charge calculated from the area under the gold oxide formation peak of the SAM modified electrodes and $Q_{Bare\ Au}$ is the charge corresponding to the unmodified Au electrode).[2] The following values were found (Figure S5): $Q_{Bare\ Au} = 4.2 \times 10^{-4}$ C $Q_{SAM\text{-}\mathbf{1}} = 1.102 \times 10^{-6}$ C, $Q_{SAM\text{-}\mathbf{Cu\text{-}1}} = 2.56 \times 10^{-5}$ C and $Q_{SAM\text{-}\mathbf{Zn\text{-}1}} = 1.35 \times 10^{-5}$ C.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectra were obtained with a VG Scientific Sigma Probe (UK) XPS system. The Al Kα anode X-ray source ($h\upsilon = 1486.6$ eV) was operated at 200W and the take-off angle for photoelectrons was 37º. Samples were mounted with a spring clip. In a typical experiment, a few survey scans in the 100 to 1200 eV kinetic energy range were collected at a resolution of 1 eV. Then, detailed scans of 20-60 eV over a single feature (Figs S6-S8) were collected at a resolution of 0.2 eV. During the measurements the pressure was 10^{-9}-10^{-10} Torr.

References

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2 (a) H.O. Finklea, S. Avery, M. Lynch and T. Furtsch, *Langmuir*, 1987, **3**, 409; (b) E. Sabatani and I. Rubinstein, *J. Phys. Chem.*, 1987, **91**, 6663; (c) H.O. Finklea, D.A. Snider, J. Fedyk, E. Sabatani, Y. Gafni and I. Rubinstein, *Langmuir*, 1993, **9**, 3660; (d) R.P. Janek, W. Ronald Fawcett and A. Ulman, *Langmuir*, 1998, **14**, 3011; (e) V. Ganesh and V. Lakshminarayanan, *Langmuir*, 2006, **22**, 1561; (f) V. Ganesh and V. Lakshminarayanan, *J. Phys. Chem. B*, 2005, **109**, 16372.

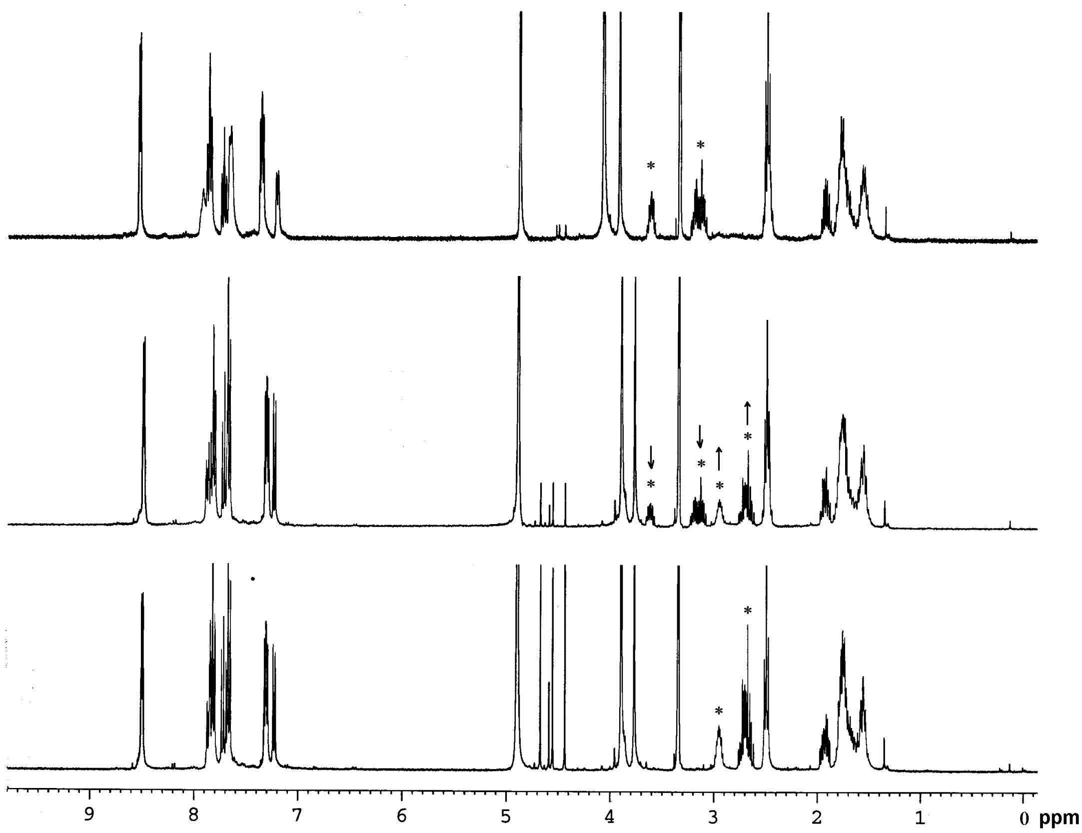


Figure S1.

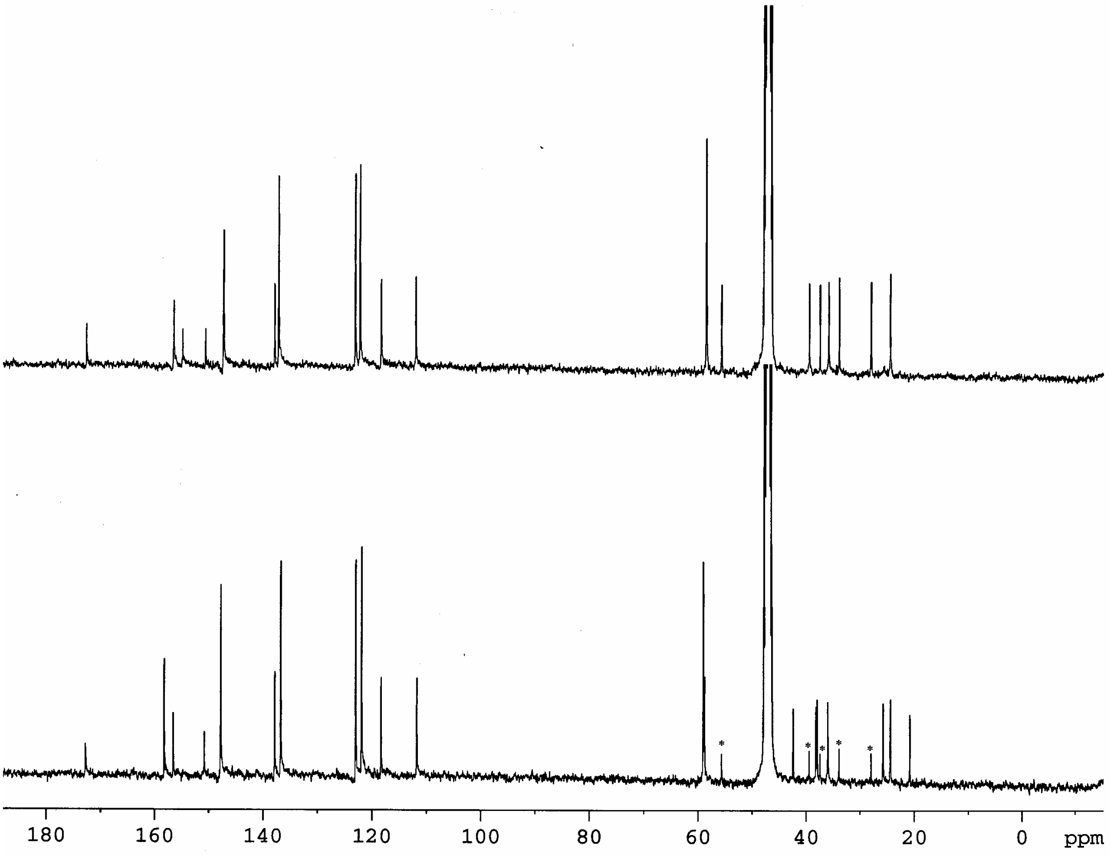
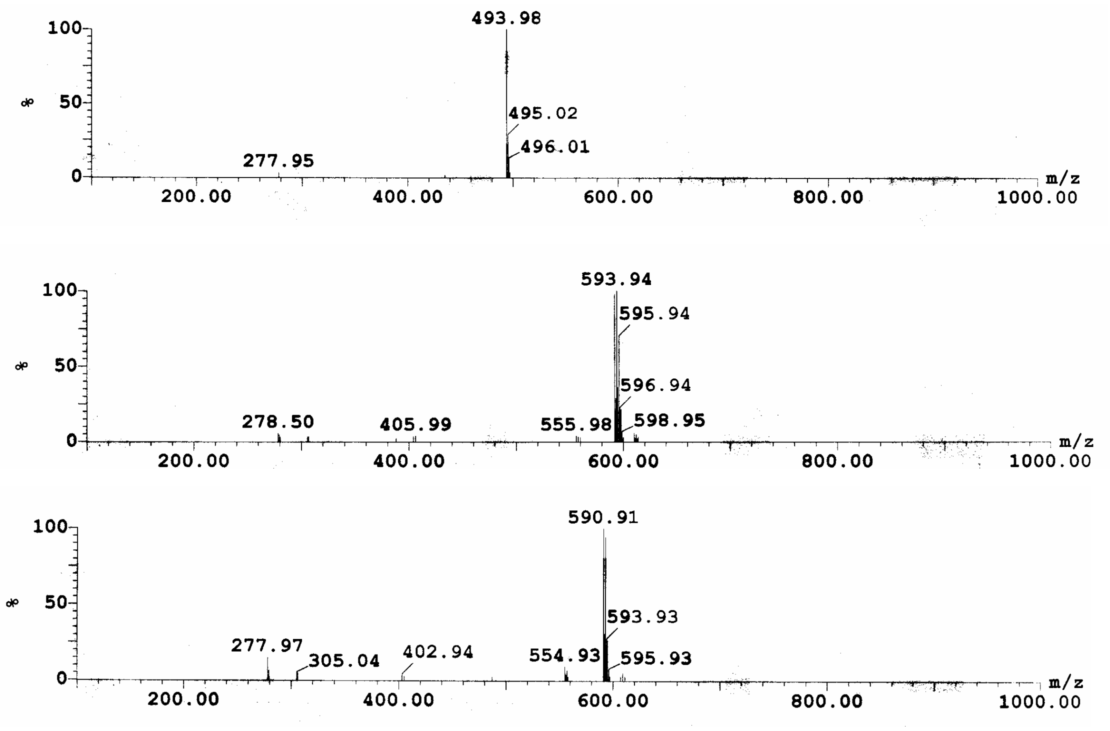


Figure S2.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277.97
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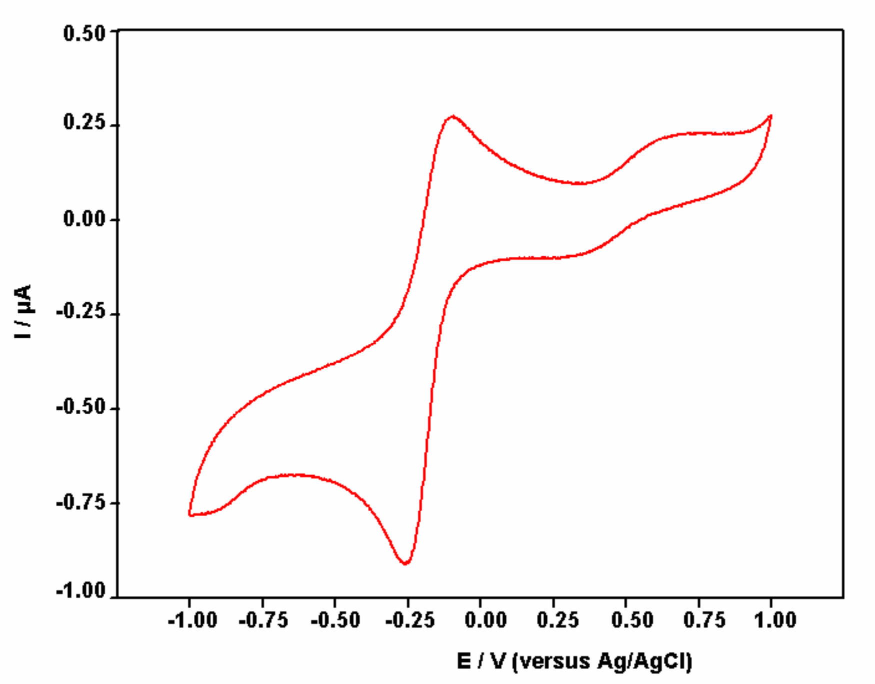
m/z

Figure S3.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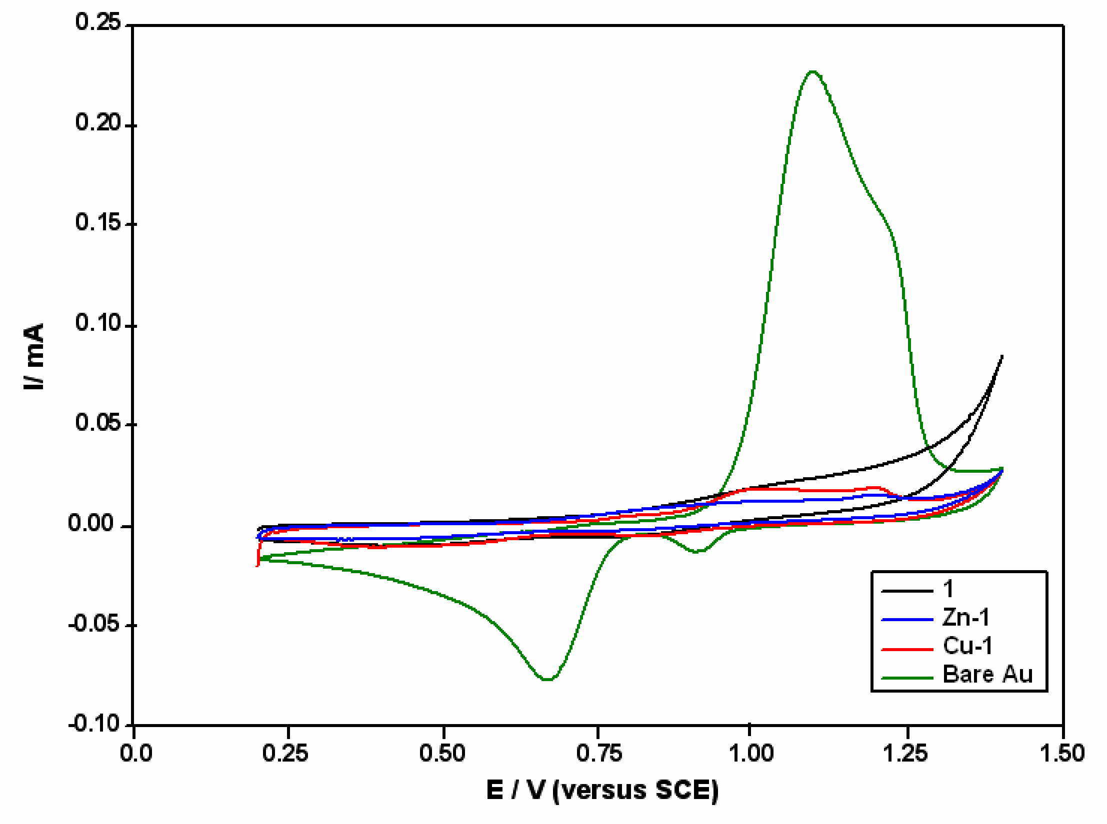
0.75
1.00
E / V (versus Ag/AgCl)

Figure S4.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0.50
0.75
1.00
1.25
1.50
E / V (versus SCE)
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Zn-1
Cu-1
Bare Au

Figure S5.

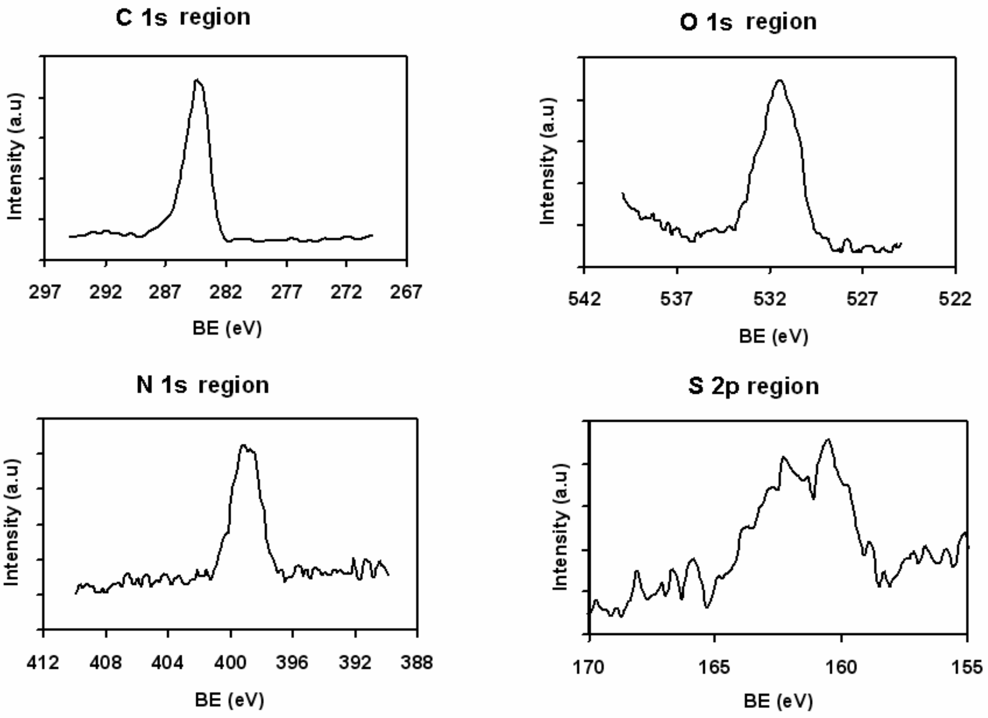
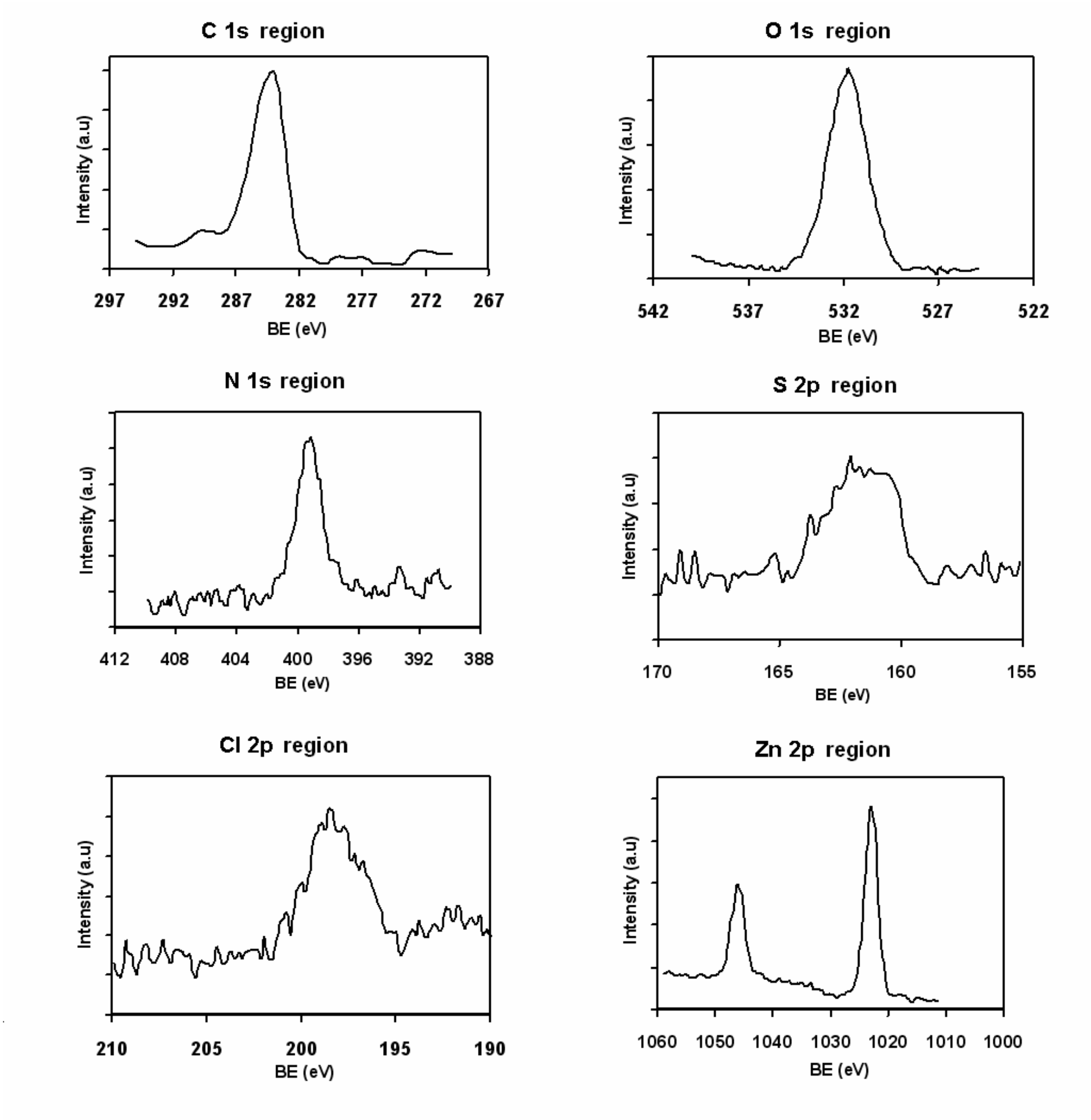

C 1s region
Intensity (a.u)
297
292
287
282
277
272
267
BE (eV)
O 1s region
Intensity (a.u)
542
537
532
527
522
BE (eV)
N 1s region
Intensity (a.u)
412
408
404
400
396
392
388
BE (eV)
S 2p region
Intensity (a.u)
170
165
160
155
BE (eV)

Figure S6.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BE (eV)
O 1s region
Intensity (a.u)
542 537 532 527 522
BE (eV)
N 1s region
Intensity (a.u)
412 408 404 400 396 392 388
BE (eV)
S 2p region
Intensity (a.u)
170 165 160 155
BE (eV)
Cl 2p region
Intensity (a.u)
210 205 200 195 190
BE (eV)
Zn 2p region
Intensity (a.u)
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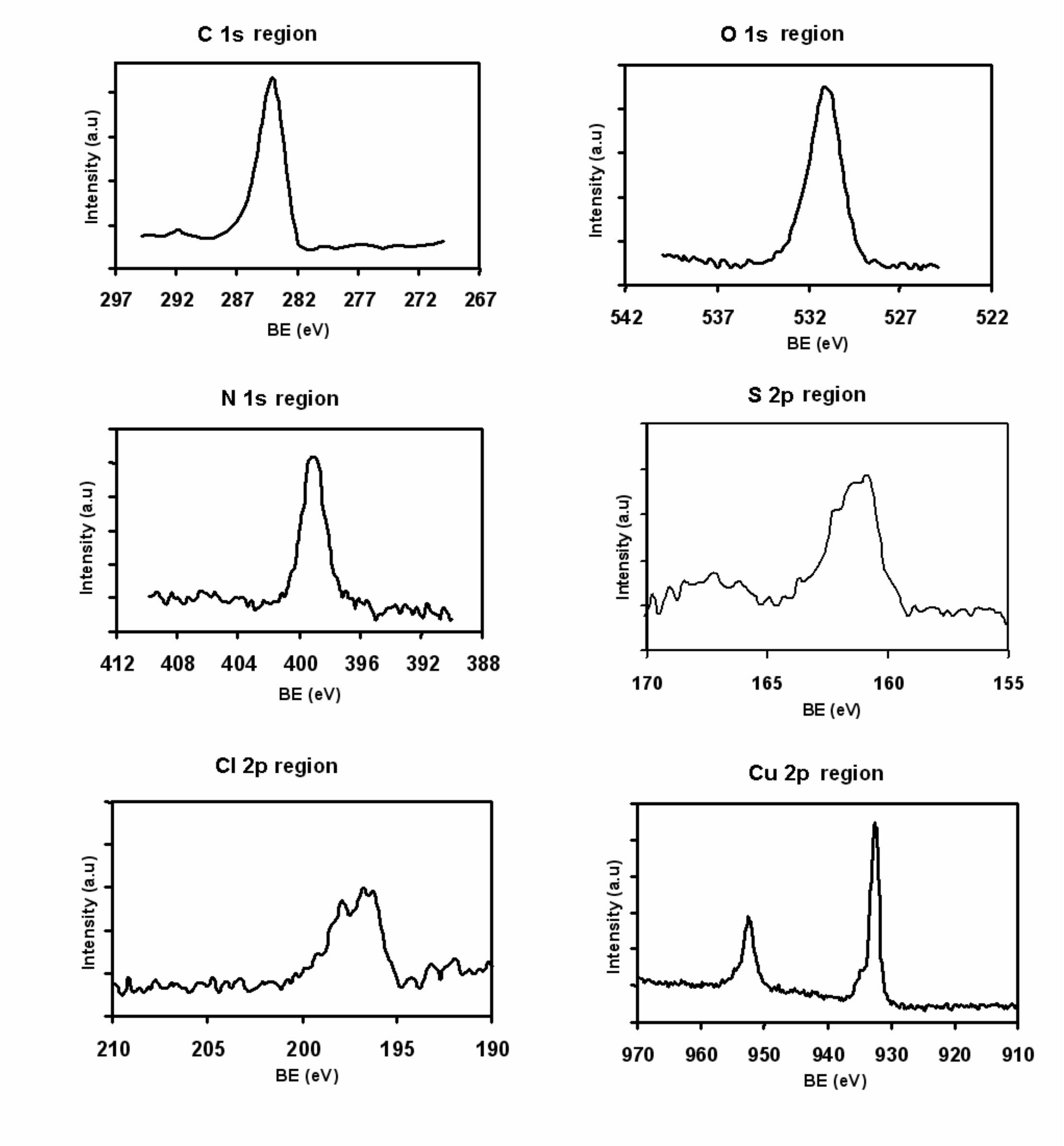
BE (eV)

Figure S7.


C 1s region
Intensity (a.u)
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BE (eV)
O 1s region
Intensity (a.u)
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BE (eV)
N 1s region
Intensity (a.u)
412 408 404 400 396 392 388
BE (eV)
S 2p region
Intensity (a.u)
170 165 160 155
BE (eV)
Cl 2p region
Intensity (a.u)
210 205 200 195 190
BE (eV)
Cu 2p region
Intensity (a.u)
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BE (eV)

Figure S8.