

Electronic supplementary information (ESI)

An insight into ion-conduction phenomenon of gold nanocluster ligand based metallo-supramolecular polymers

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Synthesis of ligand 4'-[4-(Mercapto)phenyl]-2,2':6',2''-terpyridine (L)

Synthesis of 4'-[4-(Mercapto)phenyl]-2,2':6',2''-terpyridine (**L1**) was done by our previously reported method.¹ 4'-(4-Chlorophenyl)-2,2':6',2''-terpyridine (1.375 g, 4 mmol) was added with sodium ethanethiolate (1.68 g, 20 mmol) in presence of 12 mL of anhydrous DMF under N₂. The mixture was stirred in reflux condition for 16 h and the reaction progress was monitored by TLC. The DMF was distilled off and the reaction mixture was poured into a 0.1 N HCl (60 mL). The mixture was extracted with diethyl ether and the organic layer was washed with water (50 mL × 3). The solution was dried over sodium sulfate and evaporated to dryness. Column chromatography in silica gel using chloroform eluent was done with the crude product to get L3 as white solid. (1.25 g, 92%)

¹H NMR (300 MHz, CDCl₃, r.t) δ ppm: 8.73 (m, 2H), 8.69 (s, 2H), 8.67 (d, 2H, J = 8 Hz), 7.88 (td, 2H, J = 7.7 Hz, 1.8 Hz), 7.80 (dd, 2H), 7.40 (m, 2H), 7.35 (m, 2H), 3.57 (1H, s, SH) ppm. ¹³C NMR (75 MHz, CDCl₃, r.t.) δ ppm: 156.32, 156.12, 149.49, 149.26, 137.02, 135.86, 132.61, 129.49, 128.01, 123.92, 121.48, 118.54. MALDI-TOF: [M⁺] calcd. for C₂₁H₁₅N₃S: 341.098, [(M + H)⁺] found 342.46. HRMS: found *m/z* 342.106 [(M + H)⁺]; C₂₁H₁₅N₃S requires 342.107.

Synthesis of terpyridine containing Au-nanoparticle (AuL)

HAuCl₄·4H₂O (100 mg, 0.243 mmol) in 10 mL deionized water was added to a vigorously stirred solution of tetrabutylammonium bromide (344.7 mg, 1.06 mmol) in 13 mL of toluene. A solution of a thiol ligand (L) (77.64 mg, 0.227 mmol) in 8 mL of toluene was added, and the resulting solution was stirred for 20 min at room temperature. NaBH₄ (101.8 mg, 2.69 mmol) in 6 mL of deionized water was then added. The mixture was stirred for 3 h at room temperature. After stirring the organic phase was evaporated to 5-6 mL in vacuo and mixed with EtOH (150 mL) and given time to settle down. The EtOH was decant off and resulting precipitate was washed several times with EtOH. The nanoparticles were redissolved in CHCl₃ to purify and again poured into EtOH, and then centrifuged (5000 rpm). These processes were repeated until no free thiol or phase transfer catalyst remained, as detected by TLC and ¹H NMR spectroscopy. The overall process gives 120 mg of **AuL** nanoparticles as a deep purple solid (96%).

Synthesis of polyFe

PolyFe was prepared according to literature.² An equimolar amount of 4',4''''-(1,4-phenylene)bis(2,2':6',2''-terpyridine) and Fe(II)-acetate was refluxed in acetic acid for 24 h. The reaction solution was cooled to room temperature and then filtered to remove a very small amount of insoluble residues. The filtrate was placed in a Petri dish and the solvent evaporated slowly to dryness. The film was collected and dried further under vacuum overnight to give the corresponding **polyFe** as a purple solid (>95%).

From the standard atomic weight of the Au we can calculate 100 mg of HAuCl₄·4H₂O contains 47.6 mg of Au. Again, we used 77.64 mg of thiol ligand for nanoparticle preparation and if 100% conversion takes place then from its molecular weight we can calculate 77.41 mg

terpyridine containing thiol ligand would be there in nanoparticle. So, theoretical weight of **AuL** nanoparticle should be $(77.41+47.6) \text{ mg} = 125.01 \text{ mg}$. We have taken terpyridine derivative in whole **AuL** is 0.227 mmol . So, we have calculated the terpyridine derivative in per mg of **AuL** nanoparticle is to be 0.00182 mmol . This calculation is used for further polymerization of **AuL** in the present manuscript.

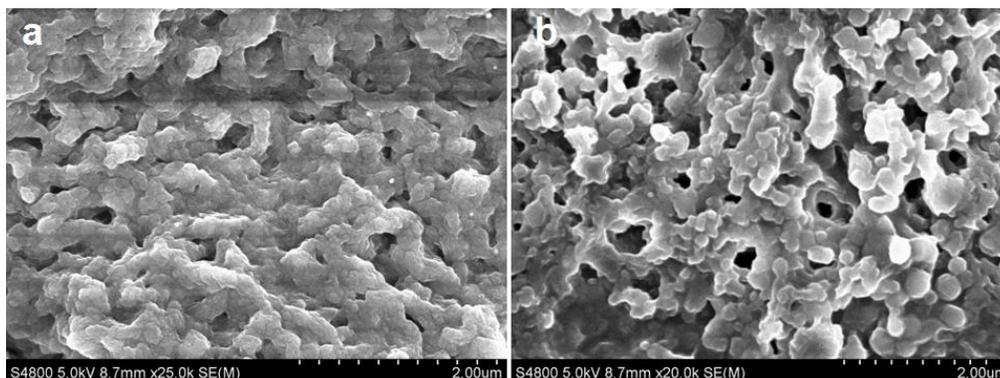


Fig. S1. SEM images of (a) **polyAuFe1** and (b) **polyAuFe2**. Porous morphology can be seen in the images, especially in **polyAuFe2**.

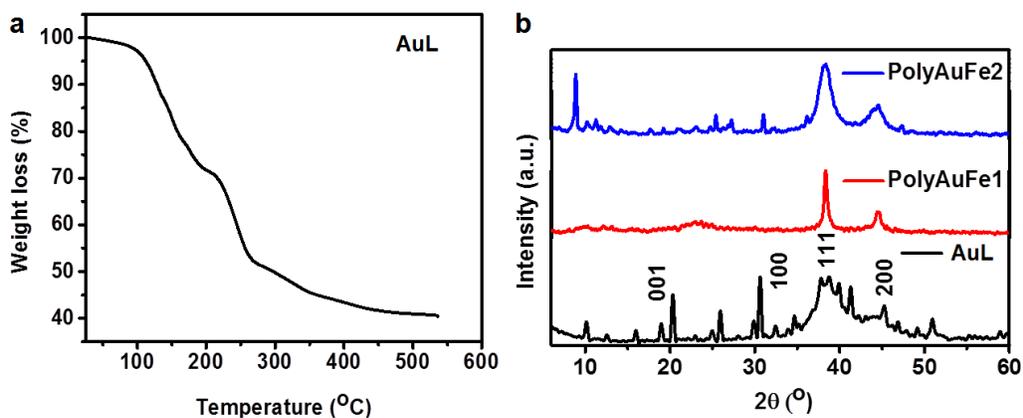


Fig. S2. (a) TGA analysis of **AuL** and (b) WXR D of **polyAuFe2**, **polyAuFe1** and **AuL**.

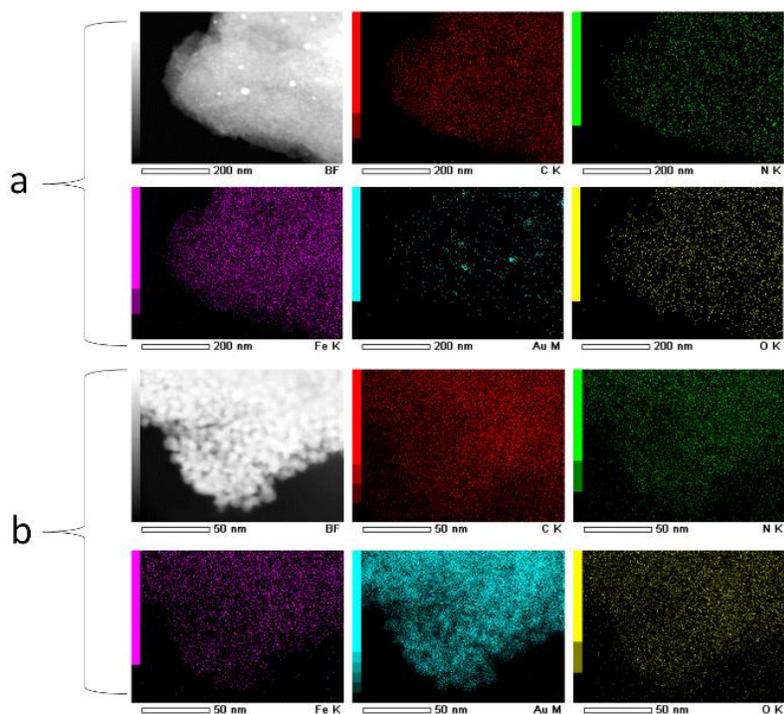


Fig. S3. STEM images of (a) complexation of **AuL** and bisterpyridine (bistpy) ligands with Fe(II) salt (**polyAuFe1**) and (b) complexation of **AuL** ligand with Fe(II) salt (**polyAuFe2**).

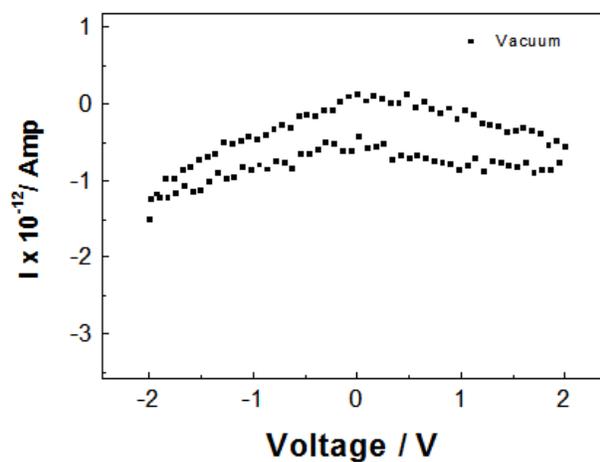


Fig. S4. I - V characteristics of **polyAuFe2** under vacuum showing negligible current.

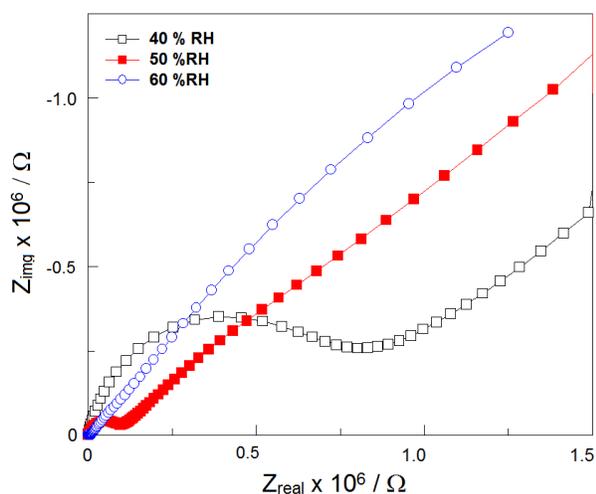


Fig. S5. Nyquist plots at lower % RH for **polyAuFe2**.

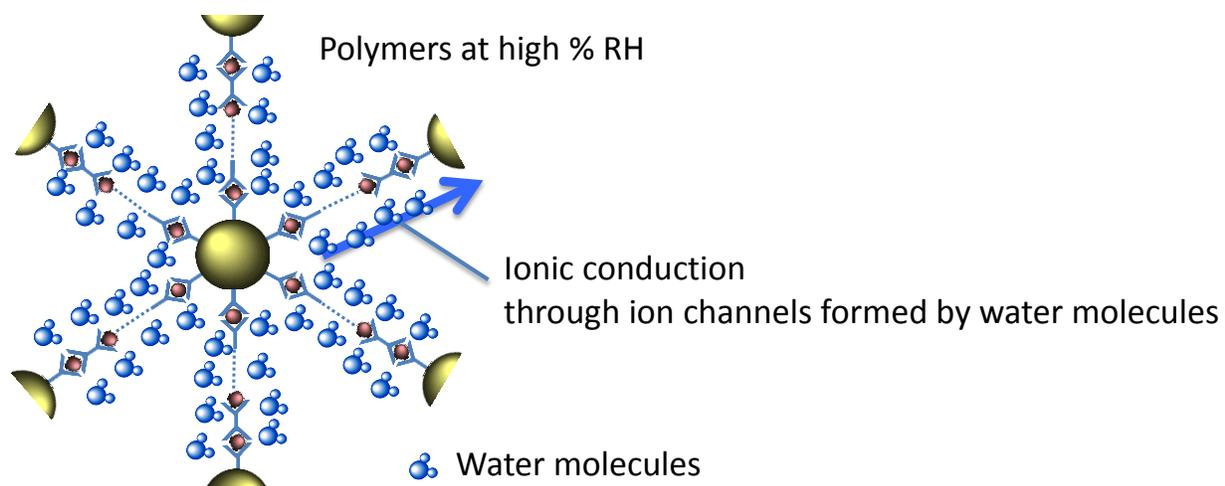


Fig. S6. A simplistic schematic representation of the ion conduction process in the polymers. The arrow direction is just to indicate the mobility of ions.

Reference:

1. C. Chakraborty *et al.* *ACS Appl. Mater. Interfaces* 2015, **7**, 19034–19042.
2. M. Higuchi *et al.* *Chem. Rec.* 2007, **7**, 203-209.