Supporting Information

Coordination-driven opto-electroactive molecular thin films in electronic

circuits

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Synthesis of 4'-amino phenyl terpyridine and bis terpyridine Preparation of 3-(4-nitrophenyl)-1-(pyridine-2-yl) prop-2-en-1-one (1)

Both the compounds were prepared according to literature methods.^{1,2} In brief, 1.25 mL of an aqueous solution of 10% NaOH was added to a suspension of 3.12 g (20.7 mmol) of 4-nitrobenzaldehyde in 25 mL of ethanol. The resulting mixture was cooled at 0°C. Then 2.5 g (20.6 mmol) of 2-acetylpyridine was added dropwise added to the mixture. The solution was stirred at 0°C for 3 h. The principate formed was collected by filtration and washed with ethanol (Yield 72%). ¹H NMR (500 MHz, CDCl₃) δ 8.73 (d, *J* = 4.7 Hz, 1H), 8.41 (d, *J* = 16.1 Hz, 1H), 8.24 (d, *J* = 11.1 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.90 (m, 1H), 7.90 – 7.86 (m, 1H), 7.86 – 7.82 (m, 2H), 7.53 – 7.49 (m, 1H).

Preparation of pyridyl pyridinium (PPI, 2)

2-acetyl pyridine (3.025 g, 25 mmol) was added dropwise to the stirring solution of iodine (6.34 g, 25 mmol) in 60 mL of dry pyridine, and refluxed for 1 h followed by cooling in an ice-bath. The black ppt was collected by filtration and washed with a mixture of ether:ethanol (9 : 1 v/v 25 mL). Subsequently, the black solid was dissolved in 25 mL of hot methanol, and a small amount (50 mg) of activated charcoal was added. After refluxing for 30 min, the solution was filtered through a celite pad while hot to yield a clear yellow solution. On cooling at room temperature, golden yellow crystals were obtained and washed with cold methanol and dried under vacuum (Yield 94%). ¹H NMR (400 MHz, DMSO-D6) δ 8.97 (d, *J* = 5.8 Hz, 2H), 8.83 (d, *J* = 4.5 Hz, 2H), 8.69 (t, *J* = 7.8 Hz, 2H), 8.23 (t, *J* = 7.0 Hz, 1H), 8.09 (t, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 7.7 Hz, 1H), 7.86 – 7.69 (m, 1H), 6.47 (s, 1H).

Preparation of 4'-nitrophenyl terpyridine

To a solution of 10% dry ammonium acetate in 20 mL of ethanol, 1 g (3 mmol) of PPI and 0.78 g (3 mmol) of compound **1** were added. The mixture was refluxed for 2 days. The solvent was removed, and the product was used without further purification (Yield 90%). (1H NMR (500 MHz CDCl₃): δ 8.75 (s, 2H), 8.73 (d, J= 4.7 Hz, 2H), 8.68 (d, J= 7.9 Hz, 2H), 8.73 (d, J= 8.8 Hz, 2H), 8.05 (d, J= 8.8 Hz, 2H), 7.90 (td, J=7.7, 1.8 Hz, 2H), 7.38 (ddd, J=7.4, 4.8, 1.1 Hz, 2H).

Preparation of 4'-aminophenyl terpyridine (3):

To the stirring solution of hot EtOH/THF (50 ml, 1:1), add solid 4'-nitrophenyl terpyridine (375 mg, 1.06 mmol) and stir until it dissolves entirely, then add 5% Pd/C (320 mg) in catalytic amount followed by dropwise addition of 1.3 ml (excess) hydrazine hydrate over 30 min. After refluxing 8hrs, the hot solution was filtered through celite pad to remove the Pd/C from the solution and cooled at room temperature. Yellow needle crystals were obtained after three days. The crystals were washed through cold ethanol and dried under vacuum (Yield 60%). ¹H-NMR (500 MHz, DMSO-D6): δ 8.71 (dd, J= 4.3, 1.4 Hz, 2H), 8.60

(d, J= 7.9 Hz, 2H), 8.59 (s, 2H), 7.79 (td, J= 7.7, 1.8 Hz, 2H), 7.63 (d, J=8.6 Hz, 2H), 7.46 (ddd, J= 7.4, 4.7. 1.0 Hz, 2H), 6.71 (d, J=8.6 Hz, 2H), 5,56 (s, 2H).

Preparation of bis-terpyridine:

Bis-terpyridine has been synthesis by using a known procedure.³ 2-acetylpyridine was added to the ethanolic solution after terepthaldehyde. Then add an aqueous solution of sodium hydroxide followed by a 40 mL aqueous ammonia (35%) solution. The reaction mixture was then stirred at 25°C for 10 h. A yellow solid was formed, collected by filtration, washed with ethanol several times, and dried in air. The dried product was obtained as a greenish solid (Yield 72%). ¹H NMR (400 MHz, CDCl₃) δ 8.78 (s, 4H), 8.73 (d, J = 4.4 Hz, 4H), 8.66 (d, J = 7.9 Hz, 4H), 8.05 (s, 4H), 7.88 (t, J = 7.0 Hz, 4H), 7.39 – 7.32 (m, 4H).



Figure S1: ¹H NMR of 4'-aminophenyl terpyridine ligand (500 MHz, DMSO-d₆).



Figure S2: HRMS (ESI-MS positive mode) of 4'-aminophenyl terpyridine ligand.



Figure S3: ¹H NMR of bis-terpyridine ligand (recorded in CDCl₃).



Figure S4: HR-MS (ESI-MS positive mode) of bis-terpyridine ligand.

XPS spectra:



Figure S5: XPS survey spectra of a) ITO/tpy-[Fe(bis-tpy)]₅, b) ITO/tpy-[Co(bis-tpy)]₅, c) C 1s, and d) N 1s of ITO/tpy (template layer).



Figure S6: UV-vis spectrum recorded on ITO/tpy-[Fe(bis-tpy)]₅/gel electrolyte/ITO/tpy-[Co(bis-tpy)]₅.



Figure S7: a) CVs recorded on bare ITO (black), ITO/tpy (red), ITO/tpy-[Fe(bis-tpy)]₅ (blue), b) CV of ITO/tpy-[Fe(bis-tpy)]₅ recorded in presence of ferrocene.



Figure S8: a) Cyclic voltammetry of ITO/tpy-[Co(bis-tpy)₅] with an increasing number of metal/bis-tpy deposition steps. b) Surface coverage of the layer with an increasing number of the depositions (R^2 =0.94), c) Cyclic voltammograms of at different scan rates, d) Relationship between anodic (I_{pa}) and cathodic (I_{pc}) peak current at different scan rate, (R^2 = 0.98 (anodic) and 0.99 (cathodic)).

CV of ITO/tpy-[Fe]₅-tpy, ITO/tpy-[Fe]₅-tpy and ITO/tpy-[Fe]₅-[Co]₅-tpy:



Figure S9: CVs of a) ITO/tpy-[Fe(bis-tpy)]₅, b) ITO/tpy-[Co(bis-tpy)]₅, c) ITO/tpy-[Co(bis-tpy)]₅/[Fe/(bis-tpy)]₅ recorded at 50 mV/s scan rate.

Rate of Kinetic electron transfer of ITO/tpy-[Fe(bis-tpy)]₁₀:

Considering the cyclic voltammograms data recorded at varying scan rates, an electron transfer rate constant, K_{ET} was estimated using an well-established Laviron method.⁴ To deduce K_{ET} , redox peak

potential vs. logarithm of scan rate are plotted and obtained a linear fitting which produces anodic slope (S_a) and cathodic slope (S_c). By using equation, (i), charge transfer coefficient, α were calculated which were then used for deducing the K_{ET} following the equation (ii). For instances, Fe²⁺ containing molecular assembly, the calculated rate of electron transfer for oxidation and reduction is 16.1 and 13.6 s⁻¹, respectively.

$$\kappa = \frac{Sa}{Sa - Sc}$$
(i)

$$\kappa = \frac{\alpha nF\vartheta c}{RT} = \frac{(1 - \alpha)nF\vartheta a}{RT}$$



Figure S10: The plot of anodic and cathodic peak potential as a function of log(scan rate) for Fe-containing thin film.

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