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Electronic Supplementary Information (ESI)

# Transmissive to blackish-green NIR electrochromism in a Co(II)-

# based interfacial co-ordination thin-film

Susmita Roy, and Chanchal Chakraborty\*

Department of Chemistry, BITS Pilani Hyderabad Campus, Jawahar Nagar, Telangana,

500078, India

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### **Materials and Methods**

All the reagents were reagent grade and used as received. The extra-pure dichloromethane and Millipore Milli-Q water (18 MU cm) were used as the reaction solvent. LiClO<sub>4</sub> from Sigma-Aldrich (>95%) whereas, propylene carbonate (PC) (>98%) was purchased from TCI Chemicals (India) Pvt. Ltd. 2-(hydroxymethyl)-2-methylpropane-1,3-diol (>98%) and powdered KOH (extrapure) were obtained from Sisco Research Laboratories Pvt. Ltd. (SRL)-India. Indium Tin Oxide (ITO) coated glass slide with resistivity  $\approx 20\Omega$  and transmittance  $\geq$  90% were purchase from Shilpa Enterprise, India. was used where required.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a BRUKER ASEND 400 instrument at 400 and 100 MHz, respectively, at room temperature using CDCl<sub>3</sub> as the solvent and tetramethyl-silane (TMS) as reference. The Fourier-transform infrared spectroscopy (FTIR) of tpy-L and Co-CONASH were carried out using a JASCO/FTIR-4200 instrument by preparing KBr pellets of the compounds. The thermo-gravimetric analysis (TGA) was performed using a Shimadzu DTG-60 at 30-700°C temperature with a heating rate of 10°C min<sup>-1</sup> under N<sub>2</sub> atmosphere. Morphological analysis of Co-CONASH on ITO were done by field emission scanning electron microscope (FESEM) study using FEI, Apreo SEM instrument with an operating voltage of 30 kV. Prior to the analysis, the nanosheet surface was gold-coated by 30 sec sputtering to reduce surface potential. The elemental analysis of the nanosheet on ITO was done by X-ray photoelectron spectra (XPS), recorded on Thermo Scientific K-ALPHA surface analysis spectrometer using Al Kα radiation (1486.6 eV).

# Synthesis of Ligand (4',4''''-((2-(((2,2':6',2''-terpyridin]-4'-yloxy) methyl)-2methylpropane-1,3-diyl) bis(oxy)) di-2,2':6',2''-terpyridine) (tpy-L)

The synthetic scheme is shown below. In short, 25 mg (0.206 mmol) of 2-(hydroxymethyl)-2methylpropane-1,3-diol and 172 mg of (3.12 mmol) of KOH powder were heated in 10 mL anhydrous dimethyl sulfoxide (DMSO) for 2 h at 60 °C under N<sub>2</sub> atmosphere. Afterwards, 206 mg (0.76 mmol) of 4'-chloro-2,2':6',2''-terpyridine was added to the suspension and stirred continuously for another 50 h at 60 °C. After cooling to room temperature, the crude product was precipitated out in ice-cold water precipitate and further collected by filtration followed by with cold water and diethyl ether. The product was dried in a hot air oven at 70°C and collected as a fluffy white powder with melting point ~220°C. Yield: 100 mg, 59%.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ ppm: 8.68 (ddd, 6 H), 8.58 (d, 6 H), 8.07 (s, 6 H), 7.82 (dt, 6 H), 7.30 (ddd, 6 H), 4.47 (s, 6 H), 1.48 (s, 3 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ ppm: 166.90, 157.14, 155.99, 149.02, 136.74, 123.77, 121.32, 107.42, 69.76, 40.55, 17.35. ESI-MS found m/z: 814 [M + H]<sup>+</sup> (calcd m/z 814.32), 836 [M + Na]<sup>+</sup> (calcd m/z 836.91).



Scheme 1 Synthesis of ligand (tpy-L).



Fig. S1 <sup>1</sup>H NMR spectra of tpy-L in CDCl<sub>3</sub>.



Fig. S2 <sup>13</sup>C NMR spectra of tpy-L in CDCl<sub>3</sub>.



Fig. S3 ESI- Mass spectra of tpy-L.

## Synthesis of Co-tpy-L

The *in-situ* thin-film of Co-tpy-L was synthesized on a bi-layer interface as shown in the following scheme S2. First, a 0.1 mM solution of tpy-L was prepared by dissolving 0.813 mg of tpy-L in 10 mL of DCM and the solution was transferred into a beaker of 60 mm diameter, 75 mm height, and 40 mL volume quantity. On the other hand, a 10 mL of 100 mM aqueous solution of Co(II)-salt was prepared by dissolving 256 mg of CoCl<sub>2</sub>.6H<sub>2</sub>O. Both the inorganic and organic solutions were filtered prior to use. Then the aqueous solution was slowly added to the organic layer through the wall by slow pipetting. The whole setup was covered properly and was kept aside without any disturbance. A film was grown gradually at DCM/water interface collected after 2 days and air dried under vacuum.



Scheme 2 Schematic representation of interfacial synthesis of Co-tpy-L.

### Collection of the Co-tpy-L thin-film

The formed Co-tpy-L thin-film in the interface was collected by replacing the aqueous solution with pure water, followed by the removal of both the solvents. Subsequently, a 1:1 solution mixture of dichloromethane and ethanol was added to the film, which resulted in a redispersion and washing of Co-tpy-L film. The film was deposited on the desired small substrates such as ITO and coverslip by dropping the suspension on the substrate. The film was then dried in vacuum and used for further characterization.

Similarly, the thin-film suspension was dropped on the active area of glassy carbon electrode (GCE) and dried adequately to get a Co-tpy-L modified GCE for electrochemical study.

To transfer a big size nanosheet on transparent ITO coted glass for electrochemical or electrochromism, one ITO glass (2.5 cm x 1 cm) was first positioned at the bottom of the organic layer before layering of Co(II) solution during the interface complexation. After the

construction of the thin-film, both the organic and water phases were removed to allow the thin-film to cover the substrate surface. The thin-film on the ITO glass was then washed with a 1:1 mixture of ethanol and dichloromethane and finally by water to remove excess ligand, metal ions, and entanglement in the film, followed by the removal of the solvent through vacuum drying. After drying, one side of the film was itched for clamping and finally provided 2 cm x 1 cm active film area.

### **Preparation of tpy-L film on ITO**

The film of tpy-L ligand on ITO was prepared by dissolving 5 mg of ligand in 1 mL of DCM and subsequently drop-casting of 200  $\mu$ L ligand solution on a 2.5 cm x 1 cm ITO substrate. The film on ITO was first air dried and then dried in vacuum and used for further studies. Finally, the one side of the film was itched for clamping and we found the active film area of 2 cm x 1 cm.



**Fig S4.** (a) UV-Vis titration of a methanolic solution of tpy-L with  $CoCl_2.6H_2O$  at room temperature, (b) The absorption changes at 453 nm as a function of the  $[Co^{2+}] / [tpy-L]$  ratio.



**Fig. S5** (a) Survey spectra and (b) core level XP spectra of tpy-L (black) and Co-tpy-L thinfilm (red) focusing on Cl 2p. (c) TGA thermograph of Co-tpy-L thin-film.



**Fig. S6** (a) Scan rate dependent redox cycles of Co-tpy-L thin-film deposited on an GC in 0.1 M KCl/water, The linear correlations between the peak current and the (b) square root of scan rate and (c) scan rate during the redox cycle.



Fig. S7 Schematic representation of Solution state electrochromic device.



**Fig. S8** CV study of tpy-L ligand and nanosheet films on ITO using Ag/AgCl reference electrode and Pt as counter electrode. The active area of the films on ITO is 2 cm x 1 cm.



**Fig. S9** The transmittance changes of Co-tpy-L deposited on ITO at the interim voltages during EC colour change in 0.1 M KCl/water electrolyte.



Fig. S10 The EC switching stability monitored in different wavelength in 0.1 M KCl/water electrolyte.



**Fig. S11** Chronoamperometry study of Co-tpy-L film deposited on ITO at pulse voltage between -1.4 V and 0.0 V at a pulse width of 10 s in each step in 0.1 M KCl/water.



**Fig. S12** The EC switching stability monitored in different wavelength in 0.1 M LiClO<sub>4</sub>/PC electrolyte.



Fig. S13 Chronoamperometry study of the film during EC mechanism in different electrolytes.