Electronic Supplementary Information (ESI)

A fast-switching electrochromic device with a surface-confined 3D metalloorganic coordination assembly

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Methods and materials

¹H and ¹³C {¹H} NMR spectra were recorded in Bruker AVANCE III 400 MHz spectrometer at room temperture. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard (DMSO: 2.50 ppm for ¹H spectra, 39.5 ppm for ¹³C{¹H} spectra). The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. UV-vis spectra were recorded on Agilent Technology Cary 100 UV-Vis spectrophotometer. Electrochemical measurements were done using CHI 620E Electrochemical Analyzer. Field emission scanning electron microscopy (FESEM) was performed using a Carl Zeiss (Ultra Plus) instrument. XPS analysis was conducted in PHI 5000 Versa Probe II instrument from FEI Inc. at IIT Kanpur, India. The film thickness was measured on silicon substrates using a J. A. Woollam (Lincoln, USA) model M-2000V variable angle spectroscopic ellipsometer with the Complete EASE software. Iron(II) perchlorate Fe(ClO₄)₂, tetra-n-butyl ammonium hexafluorophosphate ($^{n}Bu_{4}NPF_{6}$), tris(4-bromophenyl) amine, imidazole and other reagents were purchased from Sigma Aldrich and used without further purification. 4-([2,2':6',2''-terpyridin]-4'-yl)aniline (P1) and 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine (P2) were synthesized following literature procedure.^{\$1,\$2} 2,6-di(pyridin-2-yl)pyridin-4-yl-4-phosphonic acid (terpyPO₃H₂) was synthesized as per the procedures available in literature.^{S3,S4,S5,S6}

Synthesis of tris(4-(1H-imidazol-1-yl)phenyl)amine (P3)



Scheme S1 Synthesis of P3

Tris(4-bromophenyl) amine (480 mg, 0.99 mmol), imidazole (820 mg, 12.04 mmol), potassium carbonate (728 mg, 5.26 mmol) and copper sulphate (10 mg, 0.04 mmol) were heated at 150 °C for 48 h in a pressure tube. The off-white solid formed, was washed with water and kept in vacuo for 8 h to afford the desired product (yield = 77%). ¹H NMR (400 MHz, DMSO-d₆) δ 8.21 (s, 3H), 7.71 (s, 3H), 7.60 (d, 6H), 7.18 (d, 6H), 7.11 (s, 3H).

Synthesis of the imidazolium-containing tris-terpyridine ligand, L1



Scheme S2 Synthesis of L1

The compound tris(4-(1H-imidazol-1-yl)phenyl)amine (**P3**) (271 mg, 0.06 mmol) and 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine (**P2**) (1.47 g, 3.65 mmol) were dissolved in 15 mL DMF and stirred at 100 °C for 72 h. After this period, the reaction mixture was cooled to room temperature and then added to acetone (70 mL) in a dropwise manner with vigorous stirring. A large amount of precipitate was formed. It was then filtered and washed with diethylether to furnish the product as an off-white powder which was further dried in vacuo for 4 h (yield = 71%). ¹H NMR (400 MHz, DMSO-d₆) δ 9.95 (s, 3H), 8.74 – 8.65 (m, 18H), 8.32 (s, 3H), 8.09 (s, 3H), 8.09 – 8.02 (m, 12H), 7.81 (d, 6H), 7.73 (d, 6H), 7.52 (s, 6H), 7.34 (d, 6H), 5.62 (s, 6H). ¹³C{¹H} NMR (126 MHz, DMSO-d₆) δ 155.67, 154.74, 149.26, 148.77, 147.18, 137.96, 137.45, 135.50, 135.39, 130.29, 129.51, 127.54, 125.06, 124.53, 123.65, 123.26, 121.70, 120.92, 117.95, 52.03. HRMS (ESI) m/z = 469.8626 (calculated for [C₉₃H₆₉N₁₆]³⁺ = 469.8625), m/z = 745.2539 (calculated for [[C₉₃H₆₉N₁₆](Br)]²⁺ = 745.2525). In addition to the above two peaks corresponding to the parent species, two more fragments were detected due to dissociation of the parent compound under ESI-MS conditions. These two peaks are: m/z = 322.1353 (calculated for [C₂₂H₁₆N₃]¹⁺ = 322.1339), m/z = 543.7281 (calculated for [C₇₁H₅₃N₁₃]²⁺ = 543.7268).

Activation of the ITO glass substrates

ITO-coated glass slides (Corning low alkaline earth boro-aluminosilicate glass, 7 mm × 50 mm × 0.7 mm, ITO-coated one surface, Rs = 5-15 Ω) were purchased from Delta Technologies Ltd. (Loveland, USA). The substrates were cleaned by ultra-sonication, 10 min each in n-hexane, dichloromethane, acetone, and ethanol followed by drying with flow of nitrogen and kept overnight in an oven at 100 $^{\circ}$ C. The activated ITO-coated glass substrates were used for further experiments.

Activation of the silicon substrates

Doped P-type silicon (100) wafers having resistivity 10.0-20.0 Ω were purchased from Wafernet, Inc. USA. The wafers were cut in to 0.8 cm × 3 cm pieces for further use. The substrates were washed ultrasonically in acetone and isopropanol for 15 min each followed by drying with flow of N₂ gas prior to use.

Synthesis of [tpy|ITO/glass] template



Scheme S3 Procedure for *in situ* electrografting of tpy ligand on ITO-coated glass surface



Fig. S1 Cyclic voltammogram obtained using ITO-coated glass substrate as working, Pt as counter and Ag/AgCl as a reference electrode in an acetonitrile solution containing in situ-generated diazonium salt. ⁿBu₄PF₆ (0.1 M) is used as a supporting electrolyte. Scan rate = 30 mV/s.

The diazonium salt solution was generated in situ by mixing 2,2':6',2"-terpyridine (**tpy**) (136.79 mg, 105.55 mM), NaNO₂ (29.5 mg, 105.5 mM) and HClO₄ (211 mM) in 4 mL dry and degassed (with argon for 30 min) acetonitrile. The resulting solution was stirred in dark at room temperature for 1 h under the flow of argon. A dark red solution was obtained, which was further used for electrografting as shown in **Scheme S3**. A three-electrode system having activated ITO substrate as working, Pt as counter and Ag/AgCl as a reference electrode were used for the cyclic voltammetry experiment. "Bu₄NPF₆ (0.1 M) was used as the supporting electrolyte. The electrografting was carried out for a minimum of 10 cycles with a single ITO substrate in the potential range of 0 to -1 V at a scan rate 30 mV/s. A reduction peak was observed at -0.68 V for the first cycle, and this reduction peak was diminished in the consecutive cycles indicating the saturation of the vacant sites on the ITO surface with the ligand (**Fig. S1**). After the electrografting, the template ITO substrates ([**tpy**|ITO/glass]) were washed ultrasonically in acetonitrile and ethanol respectively (for 10 min each) to remove the unreacted species from the surface. It was further dried under the flow of argon and used for stepwise assembly formation.

Chemical attachment of terpyPO₃H₂ on silicon substrate

The silicon substrates were dipped into a 0.34 mM solution of **terpyPO3H2** in water/DMF (1:1, v/v) for 36 h to form the terpy-templated surface. Then the templated substrates were washed ultrasonically with water and ethanol followed by drying with the flow of argon. These templates were further used for the stepwise assembly formation, followed by ellipsometry experiments.

Preparation of stepwise assembly formation on [tpy|ITO/glass] template

A 2 mM solution of **L1** in 5 mL of DCM:MeOH (4.5:0.5, v/v) and a 10 mM solution of $Fe(CIO_4)_2$ in 15 mL acetonitrile were prepared separately. The [**tpy**|ITO/glass] template was dipped into the $Fe(CIO_4)_2$ solution (10 min) and after this step the substrate was washed ultrasonically with acetonitrile and ethanol (5 min each). After washing step, the substrate was dipped into the **L1** solution (10 min) followed by ultrasonic washing with dichloromethane and ethanol (5 min each). These dipping and washing steps were performed alternatively and consecutively. One deposition cycle consists of dipping the substrate once in $Fe(CIO_4)_2$ solution and once in **L1** solution. After each cycle, the substrates were dried with flow of argon gas. The procedure was repeated several times to obtain coordination assembly on the surface ([{**Fe₃(L1)**}_n-**tpy**|ITO/glass]).

For the measurement of XPS and SEM of the coordination assembled substrates and the template substrates, $7 \text{ mm} \times 5 \text{ mm}$ slides were used.

Electrochemical measurements

The electrochemical measurements were carried out using CHI 620 electrochemical analyzer. The $[{Fe_3(L1)}_n-tpy|ITO/glass]$ substrates were used as the working electrode. The areas of the electrodes were the area that had been electrografted. Ag/AgCl was used as the reference electrode and Pt wire was used as a counter electrode. The experiments were carried out in a homemade glass cell as the electrochemical cell. 0.1 M TBAPF₆ in CH₃CN was used as supporting electrolyte. Dry solvents were degassed for 30 min with N₂ gas prior to use.

The current density measurements were recorded with different $[{Fe_3(L1)}_n-tpy|ITO/glass]$ substrates. The surface coverage was calculated by the integration of the voltammogram peaks. The area of $[{Fe_3(L1)}_n-tpy|ITO/glass]$ substrates were 1.89 cm².

Experiments for validation of film-porosity

A 2 mM solution of redox-active probe (ferrocene and hydroquinone) in CH₃CN was taken for the cyclic voltammogram experiments. Ag/AgCl and Pt wire were used as the reference electrode and counter electrode respectively. To the same solution, different working electrodes, such as (i) bare ITO/glass, (ii) [tpy|ITO/glass] template, and (iii) [{Fe₃(L1)}_n-tpy|ITO/glass] substrate, were used separately to record the electrochemical responses of the redox-active probe via cyclic voltammetry. The CVs were recorded at 50 mV/s scan rate (Figs. S2). The resulting reversible CV responses pertinent to the redox-active probes obtained with the [{Fe₃(L1)}_n-tpy|ITO/glass] electrode, similar to the bare ITO/glass electrode, suggested that the probe molecules diffused through the film and were thereby addressed electrochemically at the ITO electrode surface.





Explanation on the observed nature of the electrochemical response: The template layer on ITOcoated glass substrate ([**tpy**|ITO/glass]) is covered with terpyridine units formed via electrochemical diazonium ion reduction, corresponding to the cleavage of the diazo (N2) groups concomitant with the formation of aryl radicals. During this process also, after the saturation of the terpyridine layer deposition on the ITO surface, no further redox-activity of the solution-phase diazonium species was observed as evident from the inhibition of the electrochemical signal of the diazonium reduction process (Fig. S1, peak at –0.68 V vs Ag/AgCl). This suggests that this terpyridine template layer acts as an insulating film leading to the blockage of the current through the ITO electrode. This kind of insulating effect of substituted phenyl layer is well-known and was demonstrated earlier.^{S7} The similar effect was observed when the hydroquinone and ferrocene redox-probes were used in solution with the [**tpy**|ITO/glass] working electrode.

On the other hand, after the first coordination with Fe(II) to the **tpy** layer on [**tpy**|ITO/glass], it becomes a redox-active layer due to the formation of redox-active Fe^{II}(tpy)-coordination complex and no more an insulating aryl layer. Therefore, in case of [**{Fe3(L1)}n-tpy**|ITO/glass] electrode, strong electrochemical response was observed for the redox-probes which could diffuse through the film and were addressed electrochemically at the now-redox-active electrode interface.

Fabrication of the solid-state device

The gel electrolyte was synthesized with a reported procedure with some modification.⁵⁸ LiClO₄ was dried in an oven at 100 °C for 12 h before use. Poly(methyl methacrylate) (PMMA) (210 mg), LiClO₄ (90 mg), propylene carbonate (PC) (0.6 mL) and acetonitrile (1 mL) were mixed and stirred at 25 °C under nitrogen atmosphere until the gelation occurred. The transparent gel electrolyte was then spread over the [{Fe₃(L1)}_n-tpy|ITO/glass] using a syringe. A bare ITO was placed on it to make a sandwich. It was then kept in the oven at 100 °C for 1 h. With a two-electrode system having [{Fe₃(L1)}_n-tpy|ITO/glass] as working and bare ITO substrate as counter electrode, the chronoabsorptometry experiments were performed. A copper tape was attached on the conducting side of the ITO substrate. A copper wire was soldered with the tape, and the wires were connected with the respective clamps of the potentiostat. For the CV measurements of the device, the reference electrode clamp was connected with the bare ITO substrate. A representative image of the color switching of the device is provided below (Figs. S3). The corresponding movie file can be accessed separately in the ESI.



Fig. S3 Images of the solid-state device in oxidized/bleached (lower) and reduced/colored state (upper). A video file was also available as ESI.

Fabrication of "OSML"-printed solid-state device

The conductive side of the ITO-coated glass substrate was covered with a one-sided adhesive tape. The word "**OSML**" was written by cutting the thin adhesive film using a sharp thin film cutter. The "**OSML**"-printed ITO-coated glass substrate was further used for electrografting and thus only the "**OSML**"-printed portion was electrografted. Next, the stepwise growth of the coordination assembly was performed to establish a purple-coloured "**OSML**"-printed assembly on the surface. The device was fabricated in a similar method as described earlier. A representative image of the color switching of the device is provided below (**Figs. S4**).



Fig. S4 Images of "OSML" printed device in oxidized/bleached (lower) and reduced/colored state (upper).

Fabrication of "OSML"-patterned solid-state device

The word **"OSML"** was written by cutting a one-sided adhesive tape using sharp thin film cutter. It was then placed upon an already prepared [$\{Fe_3(L1)\}_n$ -tpy|ITO/glass] substrate so that only **"OSML"**-patterned portion was open to contact with the gel electrolyte which was covered on it and dried. Next, a bare ITO slide (as counter electrode) was placed on top of the gel-electrolyte it to make the sandwich. The device was fabricated in a similar method as described earlier. A representative image of the color switching of the device is provided below (Figs. S5). The corresponding movie file can be accessed separately in the ESI.



Fig. S5 Images of "OSML"-patterned device in oxidized/bleached (lower) and reduced/colored state (upper). A video file was also available as ESI.

Additional figures



Fig. S6 CVs of [**Fe₃(L1)**}_n-**tpy**|ITO/glass] recorded after two deposition cycle interval by immersing the modified ITO substrate in to 0.1 M TBAPF₆ in CH₃CN solutions. Ag/AgCl and Pt electrode were taken as reference and counter electrode, respectively. The CV was run at 50 mV scan rate.



Fig. S7 Linear correlation of surface coverage with an increase in deposition cycle (R²= 0.99).



Fig. S8 Representative XPS data for [tpy|ITO/glass] focusing on N1s region.



Fig. S9 Dependency of peak current on scan rate.

Table S1 Electrochromic device performance parameters of some reported solid-state ECDs

 fabricated with Fe(II)-terpy systems (in addition to refs. 6 and 7 in the main article)

EC properties of solid-state devices						Reference
ΔOD	Q _d (mC/cm ²)	η (cm²/C)	Voltage sweep (V)	t (s) (c/b)	Stability (cycle)	
NA	0.5	585	+3 to -1	0.48/0.83	400	ACS Appl. Mater. Interfaces, 2018, 10 , 35334-35343
0.44	2.96	148.6	+3 to -1	NA	1488	ACS Appl. Mater. Interfaces, 2017, 9 , 40438-40445
1.01	2.46/2.26	414.1	+3 to -2	0.45/0.93	300	J. Mater. Chem. C, 2019, 7 , 2871-2879
NA	NA	NA	+2.5 to -2.5	0.73/1.44	300	ACS Appl. Mater. Interfaces, 2019, 11 , 11893-11903
0.278	1.01/1.27	275	+3.2 to -2	0.49/0.90	4500	This work
Δ OD = Change in optical density; Q _d = Injected/ejected charge per unit area; η = Coloration efficiency; t = Switching/response time; t (c/b) = switching/response time for coloring/bleaching						

¹H NMR, ¹³C{¹H} NMR, and ESI-HR mass spectra



¹H NMR of compound **P3** (400 MHz, DMSO-d₆)







 $^{13}C\{^{1}H\}$ NMR of ligand L1 (126 MHz, DMSO-d₆)





HRMS (ESI positive mode) of ligand L1

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