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Supporting Information

Optical and Electrochemical Properties of Covalent Assembled bis(4’-carboxylic phenyl terpyridyl) Ru(II) monolayer

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Synthesis of 4’-carboxyphenyl-terpyridyl:

(i) *4’-Methylphenyl*-2,2’:6’,2”-*terpyridyl (4’-Mephpytpy)*: 2-acetylpyridine (2.3 mL, 20 mmol) was added to a stirred solution of ^{t}BuOK (3.37 g, 30 mmol) in 70 mL anhydrous THF. A solution of p-tolualdehyde (1.20 g, 10 mmol) in 40 mL anhydrous THF was added drop wise under Ar. Consequently, the reaction mixture was stirred overnight at room temperature under Ar atmosphere. During this time, the color of the solution changed to dark red. Subsequently, excess solid NH_4OAc (0.36 g, 466 mmol) and 140 mL methanol was added into the reaction mixture followed by refluxed for 4h. A thick residue was obtained after removal of the solvent by rotary evaporation. The solid was recrystallized from hot methanol to obtain yellow needle shape crystals.

^{1}H NMR (400 MHz, $CDCl_3$); δ/ppm: 8.73 (s, 2H, $H^{3'}$), 8.73 (d, 2H, *J* = 6 Hz, H^6), 8.66 (d, 2H, *J* = 8 Hz, H^3), 7.87 (dt, 2H, *J* = 8.1 & 1.8Hz, H^4), 7.81 (d, 2H, *J* = 7.99 Hz, H^o), 7.35 (dt, 2H, *J* = 8.5,4.8 & 1.6 Hz, H^5), 7.31 (d, 2H, *J* = 9.02 Hz, H^m), 2.43 (s, 3H, $-CH_3$). UV-vis (DMSO) λ_{max}: 257, 282 and 324 nm. FTIR (KBr): 2364 (w), 1586 (m), 1388 (m), 790 (vs) cm^{-1}.

(ii) *4’-carboxyphenyl*-2,2’:6’,2”-*terpyridyl*: Conc. nitric acid (0.5 mL) in water (8 mL) was added to 200 mg (0.6 mmol) of 4’-methyl-phenyl-terpyridine in a 25 mL of teflon-lined autoclave, which was placed in a programmable oven for 36h at 180°C. Upon slow cooling to room temperature, pale yellow crystalline product was obtained after washing with cold water.

^{1}H NMR (400 MHz, DMSO-d_6); δ/ppm: 13.18 (br s, 1H, $-CO_2H$), 8.77 (d, 2H, *J* = 5.7 Hz, H^6), 8.75 (s, 2H, $H^{3'}$), 8.69 (d, 2H, *J* = 8.16 Hz, H^3), 8.14 (d, 2H, *J* = 8.4 Hz, H^m), 8.15 (d, 2H, *J* = 8.5 Hz, H^o), 8.05 (dt, 2H, *J* = 7.8 & 1.8 Hz, H^4), 7.54 (dt, 2H, *J* = 7.8, 5.8 & 1.5 Hz, H^5). UV-vis (DMSO), λ_{max}: 257, 282 and 324 nm. FTIR (KBr): 3402 (m), 1600 (s), 1702 (s), 1384 (vs), 772 (s) cm^{-1}.

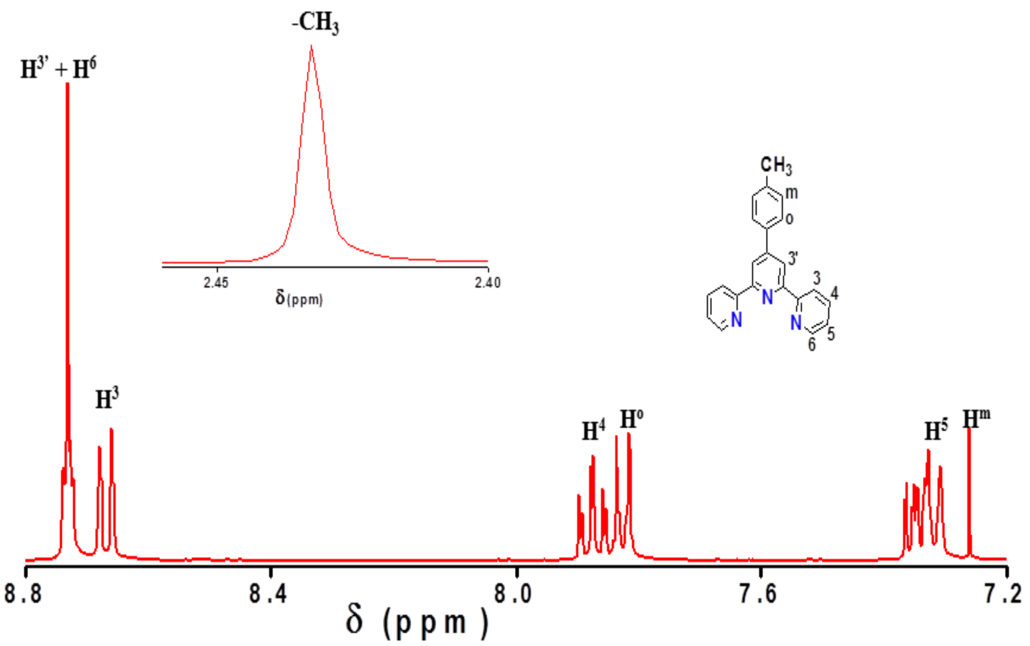

Fig. S1: ^{1}H NMR spectrum of 4'-Methylphenyl-2,2':6',2"-terpyridyl in $CDCl_3$.

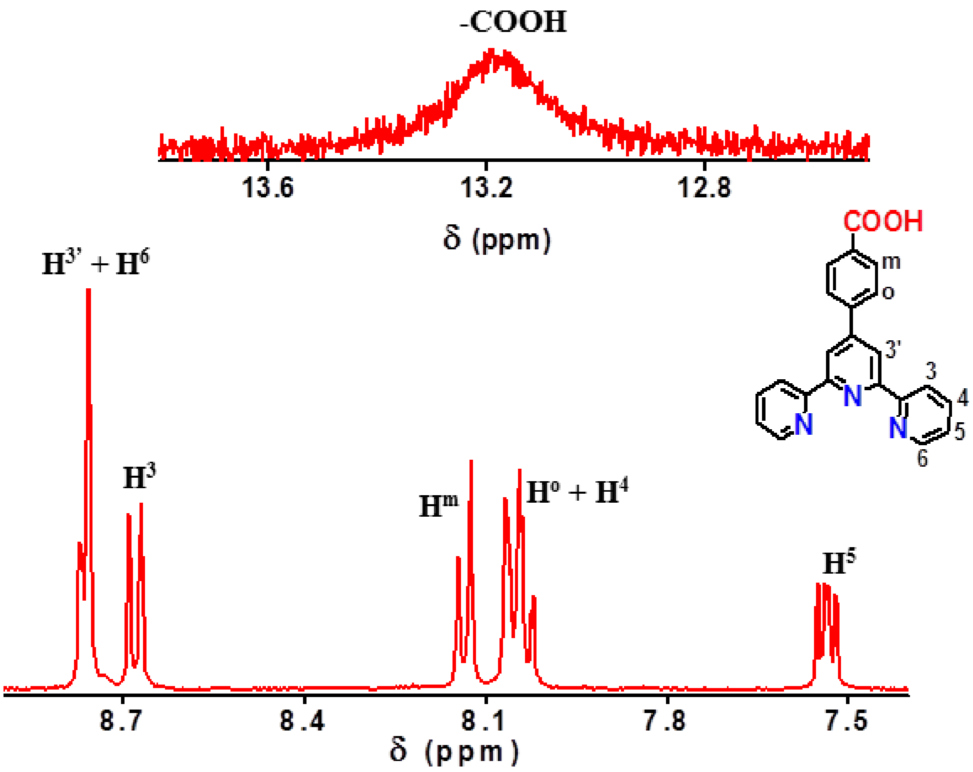

Fig. S2: ^{1}H NMR spectrum of 4'-carboxy-phenyl-2,2':6',2"-terpyridyl in DMSO-d_6.

Preparation of **1**: In brief, $RuCl_3·3H_2O$ (31.7 mg, 0.12 mmol) and 4'-carboxyphenyl-terpyridine (85.5 g, 0.24 mmol) were suspended in 20 mL ethane-1,2-diol and then 2 drops of

N-ethyl morpholine (NEM) was added to the reaction mixture was refluxed at 150^{o}C under argon with constant stirring for 24h under dark (see Scheme 1). The resulting red solution was cooled to room temperature and treated with a solution of NH_4PF_6 in ethanol and allowed to settle the precipitate. The product was collected over celite, washed with plenty of water followed by diethyl ether. Subsequently the product was dried under vacuum and it was dissolved in acetonitrile. The solution was kept at room temperature for slow evaporation under dark condition which yields red microcrystalline product. ^{1}H NMR (400 MHz, CD_3CN); δ/ppm: 9.04 (s, 4H, H$^{3'}$), 8.66 (d, 4H, J = 7.5 Hz, H3), 8.4 (d, 4H, J = 9.0 Hz, H^{o}), 8.30 (d, 4H, J = 8.5 Hz, H^{m}), 7.95 (dt, 4H, J = 7.6 & 4.8 Hz, H^{4}), 7.43 (dd, 4H, J = 5.6 & 3.6 Hz, H^{6}), 7.19 (dt, 4H, J = 7.6 & 5.2 Hz, H^{5}). UV-vis (CH_3CN) λ_{max}/nm: (ε/10^3 dm^3 mol^{-1} cm^{-1}): 491 (29.00). FTIR (KBr): 3422 (w), 1702 (m), 1282 (s) 839 (vs), 558 (m) cm^{-1}.

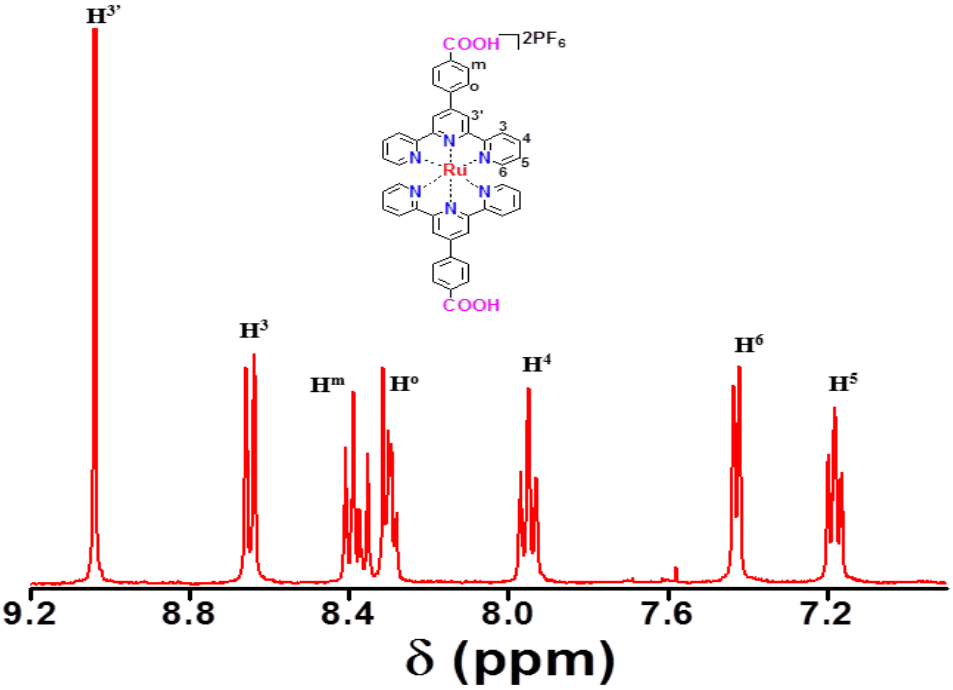

Fig. S3: ^{1}H NMR spectrum of **1** in CD_3CN.

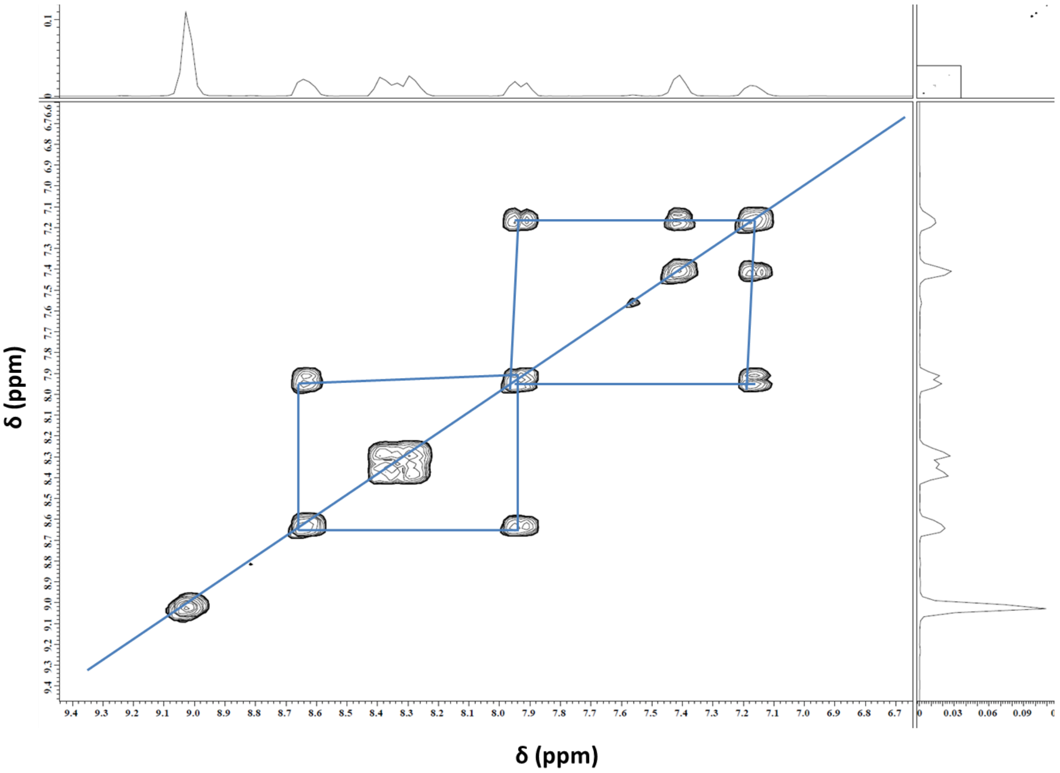

Fig. S4: ^1H-^1H (2D) NMR spectra of **1** in CD_3CN.

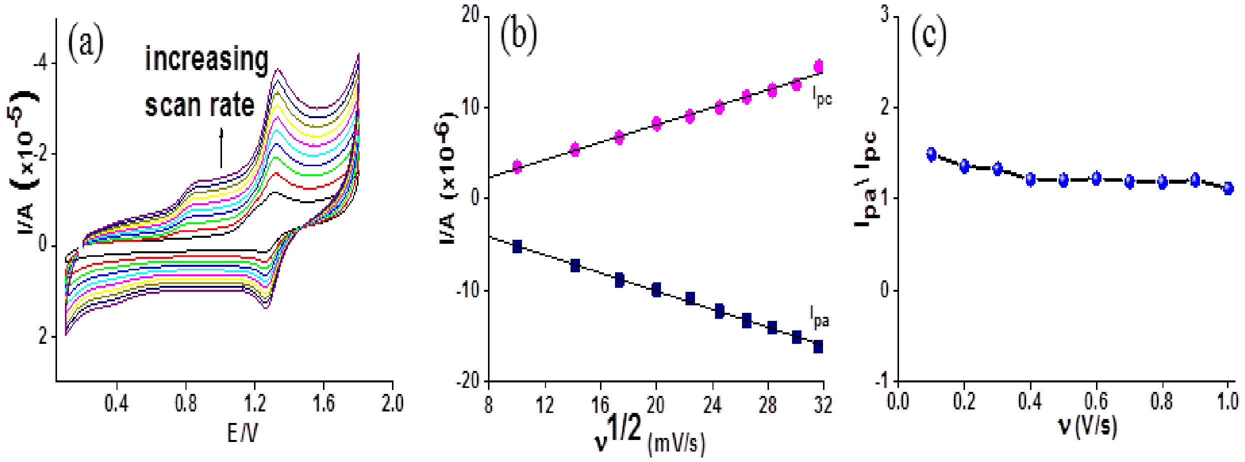

Fig. S5: (a) Cyclic Voltammogram of **1** in dry acetonitrile (1 mM solution in 100 mM of $TBAP_6$), (b) peak current densities (I_{pa} and I_{pc}) as a function of square root of scan rates (ν, mV/s) and (c) plot of ratio of anodic current density to cathodic current (I_{pa}/I_{pc}) as a function of scan rates (ν, V/s).

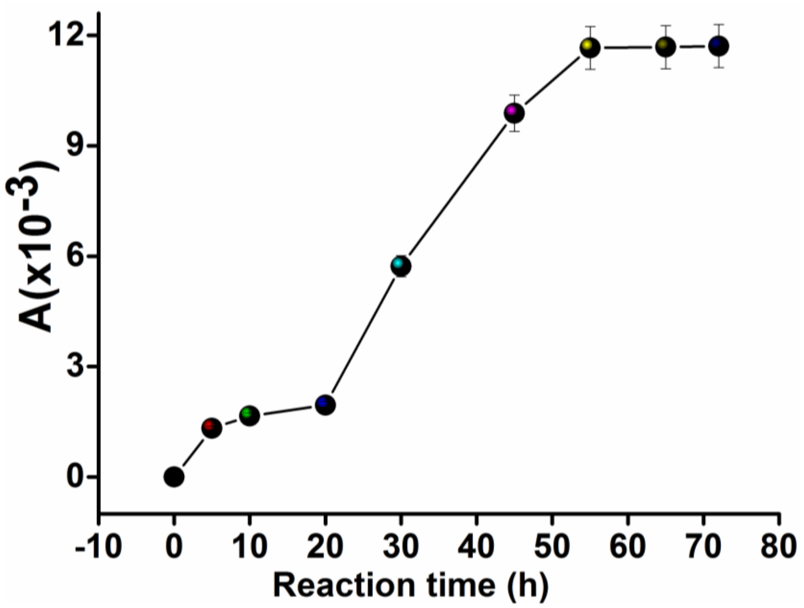

Fig. S6: Ex-situ UV-vis monitoring of growth process of **1** on glass substrates.

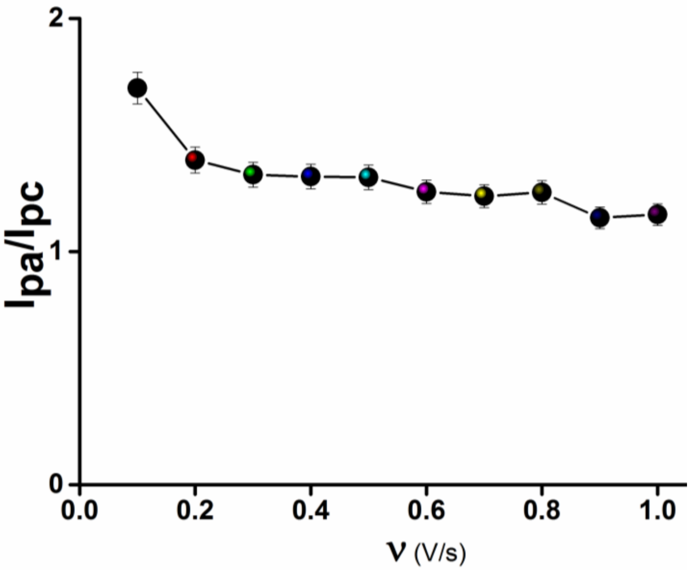

Fig. S7: Plot of ratio of anodic current to cathodic current as a function of scan rates (ν, V/s) for 1-based monolayer on ITO-coated glass.

Table S1: CV characteristics of 1-based monolayer on ITO-coated glass

ν (V/s)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$E_{1/2}$ (V)	0.89	0.89	0.90	0.90	0.90	0.91	0.91	0.91	0.91	0.91
ΔE_p (mV)	30	30	31	33	34	34	36	37	39	40

Thermal and temporal stability of 1-based covalent assembled monolayers:

The thermal and temporal stabilities **1**-based covalent assembled monolayers on glass substrates were monitored by UV-vis spectrophotometry. The glass substrates modified with **1** were subjected to thermal stress. The substrates were placed inside a sealed glass pressure tube under air and sequentially kept at different increased temperatures such as 30, 60, 90, 120, 150, 180, 190, 210 and 220°C for ~1h in a temperature controlled oven. The UV-vis measurements of the substrates were performed between the individual heating steps (see Fig. 3). Each time the samples were allowed to attain room temperature, followed by a proper rinsing with acetonitrile and gentle wiping with kimwipes. In another experiment, the CAMs were kept at 100°C for >2h and it was found that negligible loss of molecules from the substrates (~ 6%) as displayed in Figure S8.

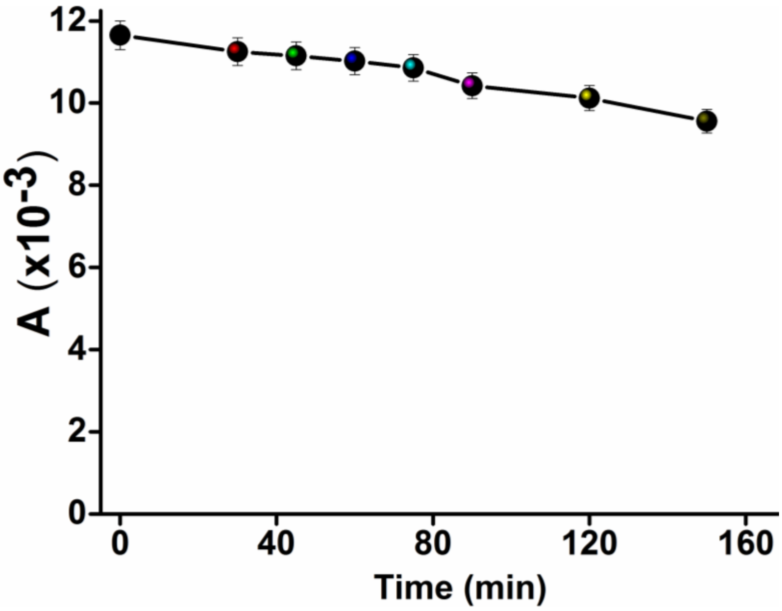

Fig. S8: Ex-situ UV-vis monitoring of temporal stability of template layers on glass. The substrates were kept at 100°C.