

Supporting Information.

Electrochemical probing of hydrogelation induced by the self-assembly of a donor-acceptor complex comprising pyranine and viologen

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(a) Physical Measurements and Instrumentation. Milli-Q grade water was used for all physical measurements.

Gelation Studies. In a typical two component gelation test, a stock aqueous solution of desired concentration of Py^{3+} was prepared. Different aliquots of this stock solution were diluted with Milli-Q water to get Py^{3+} solution of required concentration into each of which was added a weighed amount of acceptor (P^+ -16, $\text{CH}_3\text{-V}^{2+}$ -12 and $\text{CH}_3\text{-V}^{2+}$ - CH_3). Then, the suspension was bath sonicated in Transsonic T460/H at 60-70 °C for 15 min to get a practically homogeneous solution. The clear suspension was incubated at room temperature for 15 min to check the stability of the gel using inverse flow method. Each experiment was performed in duplicate. If a gel was formed, it was evaluated quantitatively by determining the minimum gelator concentration (MGC) which has been defined as the minimum amount of hydrogelator required to immobilize 1 mL water.

Scanning Electron Microscopy (SEM). 20 μL of each representative sample was carefully transferred onto brass stub. The sample was freeze-dried, then coated with 10-nm thick gold films using a BAL-TEC SSD-500 sputter coater instrument. Finally, the morphology of the sample was imaged on a FEI-Quanta 200 SEM operated at 25 kV.

Atomic Force Microscopy (AFM). AFM image the hydrogel was obtained by using Bruker Dimension ICON with ScanAsyst instrument. The hydrogel was heated to form sol and 50 μL of each representative sol was drop casted on freshly cleaved mica and air dried at room temperature. Each of the samples was analyzed using Veeco Innova instrument (made in Germany).

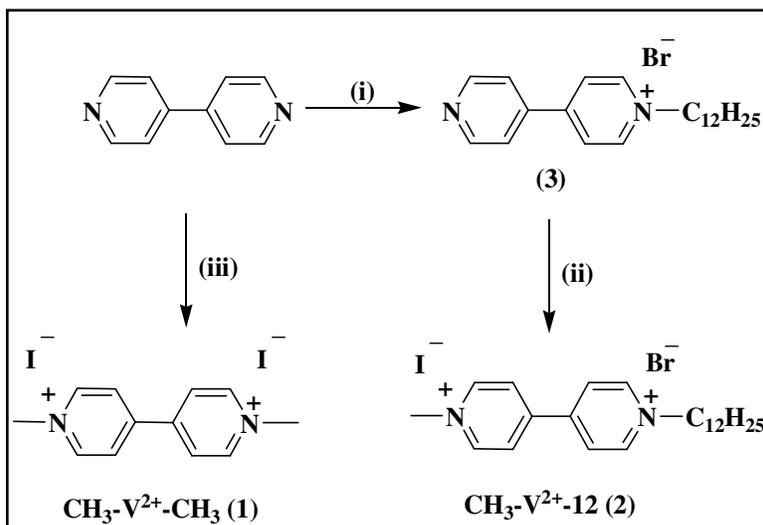
UV-Vis, Fluorescence and Raman Spectroscopy. The UV-Vis and fluorescence spectra of aqueous solutions were recorded on a Shimadzu model 2100 spectrophotometer and Hitachi F-4500 spectrofluorimeter respectively. The Raman spectra were recorded on a Raman spectrometer (Renishaw inVia model). The 785 nm laser diode of 300 mW was used as an excitation source.

Electrochemical Measurement. The cyclic voltammetry experiments were carried out in CH608C, CH instrument with a conventional three-electrode cell (solution volume of 5 mL). Teflon stopper (provided with holes for insertion of the electrodes) was used as cover to exclude atmospheric oxygen. The working electrode was a glassy carbon electrode with a geometrical area of 0.09 cm² and mounted in Teflon. The electrode was polished before each experiment with 3 and 0.3 μm alumina pastes followed by extensive rinsing with ultrapure Milli-Q water. Platinum wire was used as the counter electrode and saturated calomel electrode, SCE, as reference electrode. 0.1 M LiCl solution in Milli-Q water was used as supporting electrolyte and was routinely deoxygenated by argon bubbling. All potential values are given versus the calomel saturated electrode SCE. Cyclic voltammetry experiments were conducted within the potential range of -0.2 to -1.2 V at a scan rate of 0.1 V s⁻¹.

Rheological Studies. For rheological measurement of the samples, an Anton Paar 100 rheometer using a cone and plate geometry (CP 25-2) with an adjustable peltier temperature controlling system was used. All the measurements were done fixing the gap distance between the cone and the plate at 0.05 mm. The gels were scooped on the plate of the rheometer. An oscillatory stress amplitude sweep experiment was performed at a constant oscillation frequency of 1 Hz for the applied stress range 0.01-150 Pa at 20 °C. The software US-200 converted the torque measurements into either G' (the storage modulus) and G'' (the loss modulus) and represent G' and G'' with either strain or shear stress.

(b) Materials and Reagents. 4,4'-Bipyridine, 1-bromododecane, methyl iodide and cetyl pyridinium bromide were bought from Aldrich. 8-Hydroxy-1,3,6-pyrene-trisulphonic acid trisodium salt was procured from Eastman Kodak company, USA. All other chemicals, solvents and silica gel for TLC and column chromatography were obtained from the well-known commercial sources and were used without further purification, as appropriate. Solvents were distilled and dried by standard procedure before use. ¹H-NMR and ¹³C-NMR spectra were recorded in Bruker-400 Avance NMR spectrometer at 400 and 100 MHz respectively.

(c) Scheme S1.



(i) $n\text{-C}_{12}\text{H}_{25}\text{Br}$, CH_3CN , reflux, 18 h, yield = 62%; (ii) CH_3I , CH_3CN , reflux, 24 h, yield = 78%; (iii) CH_3I , CH_3CN , reflux, 24 h, yield = 68%.

(d) **Synthesis.** Compounds **1**, **2** and **3** were synthesized according to scheme S1 as reported previously.¹⁻⁴

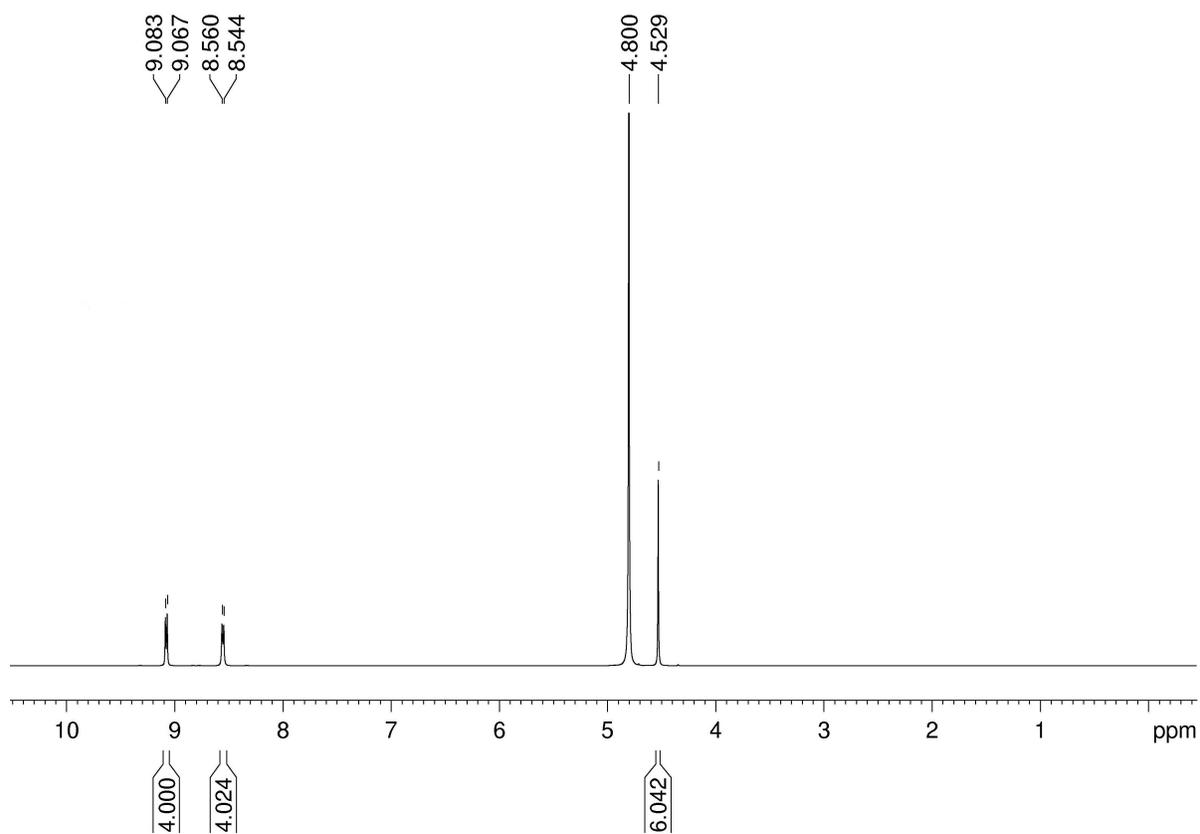


Figure S1. $^1\text{H-NMR}$ spectrum of compound **1** in D_2O .

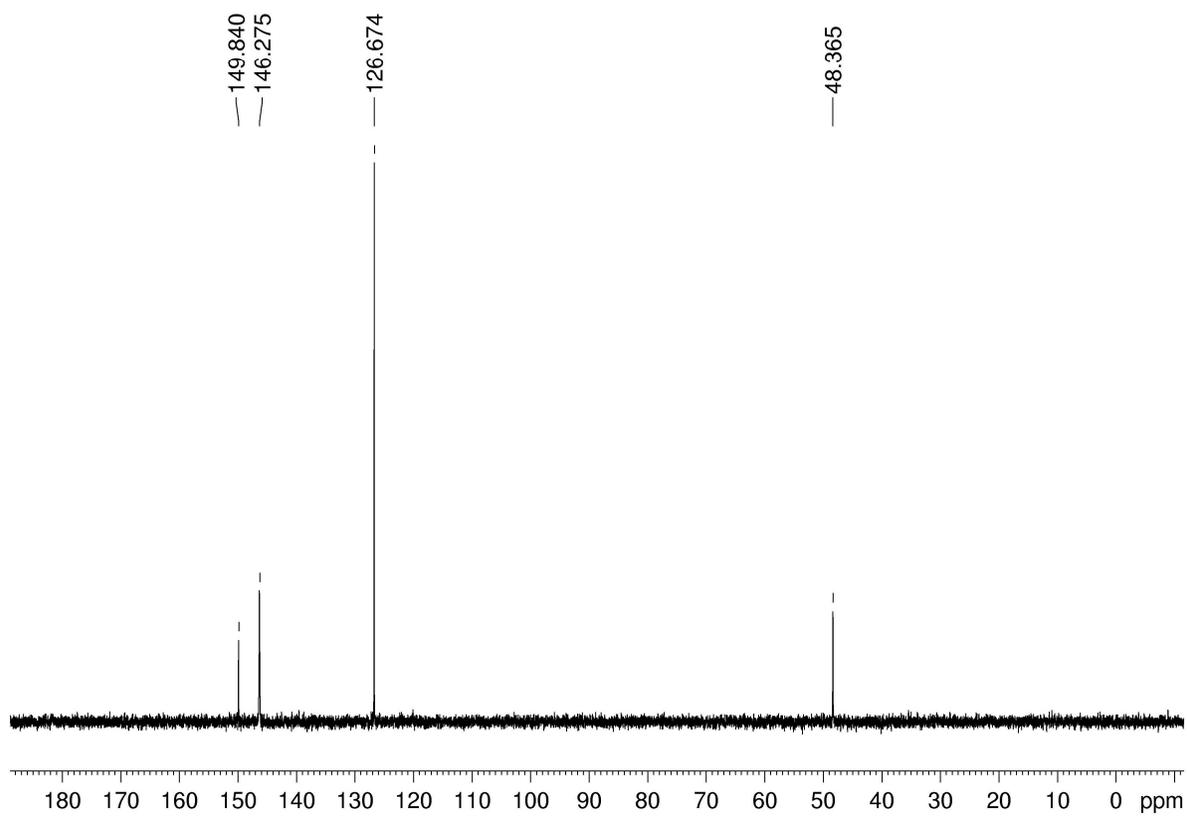


Figure S2. ^{13}C -NMR spectrum of compound **1** in D_2O .

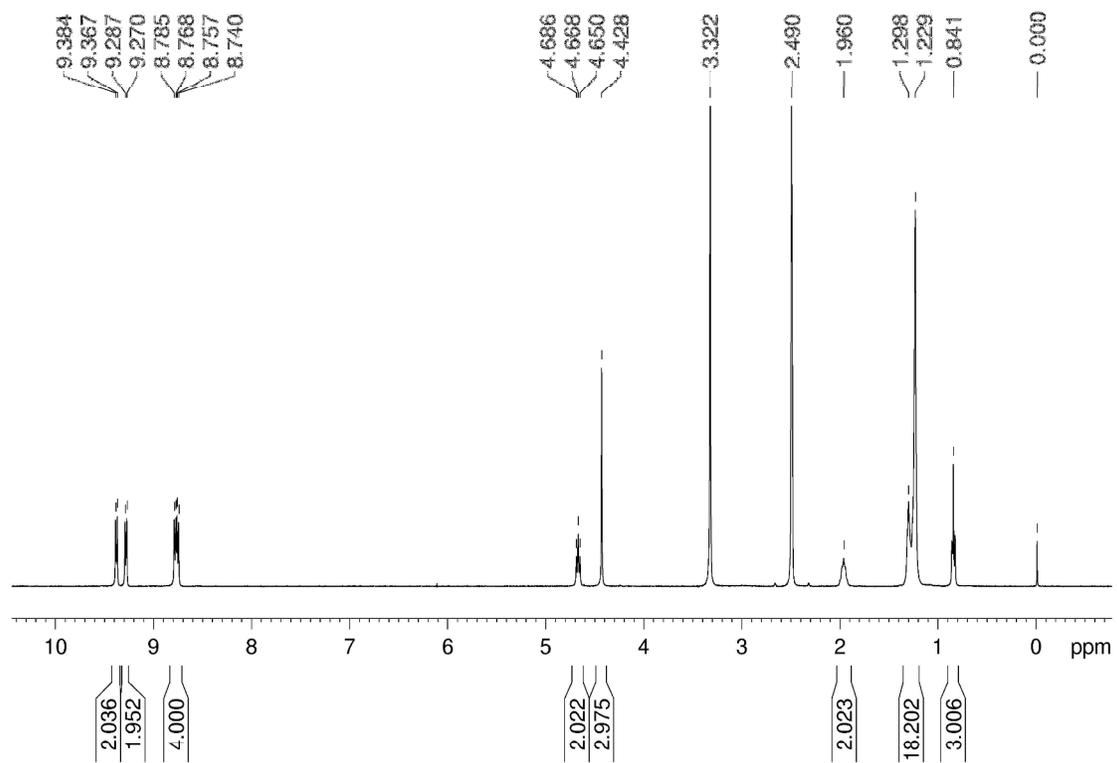


Figure S3. ¹H-NMR spectrum of compound **2** in (CD₃)₂SO.

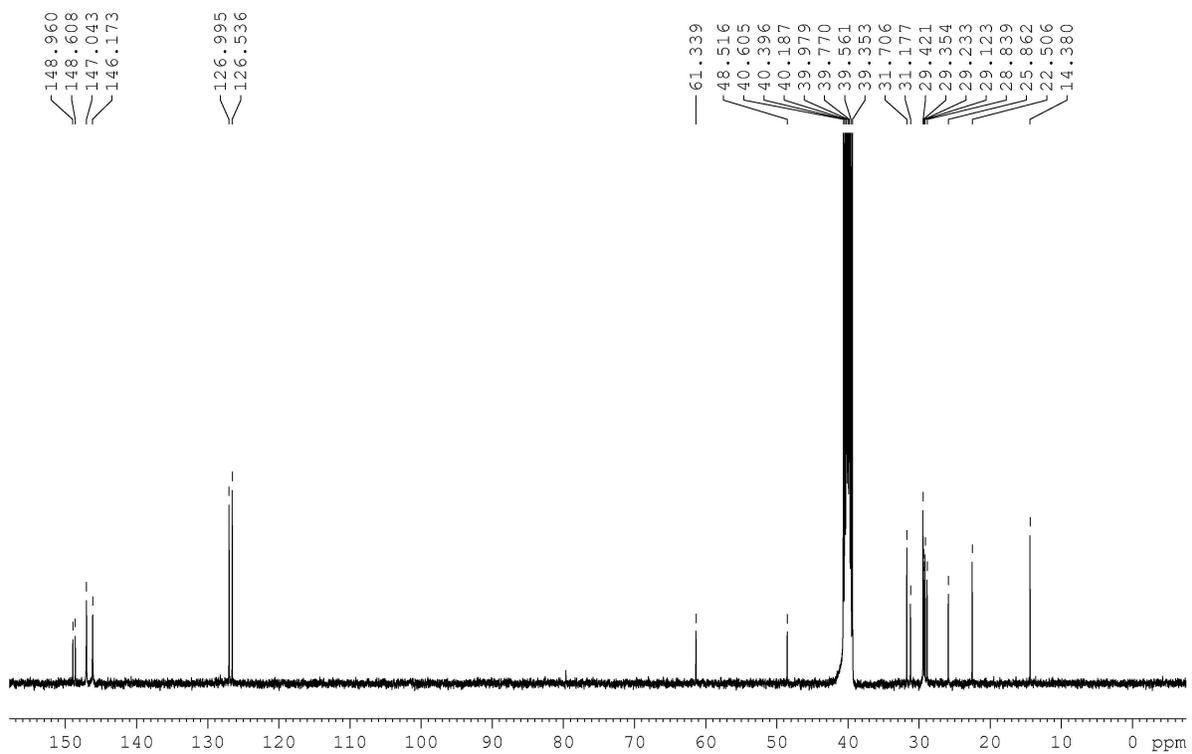


Figure S4. ^{13}C -NMR spectrum of compound 2 in $(\text{CD}_3)_2\text{SO}$.

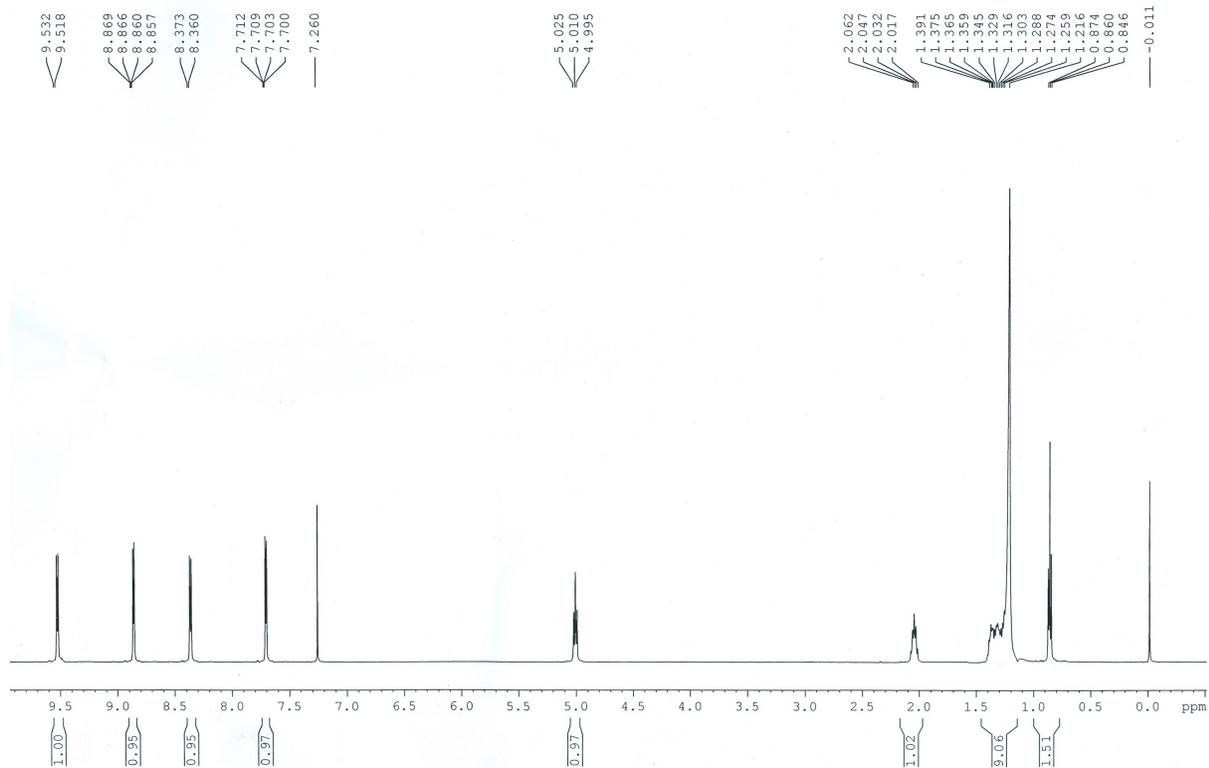


Figure S5. ¹H-NMR spectrum of compound **3** in CDCl₃.

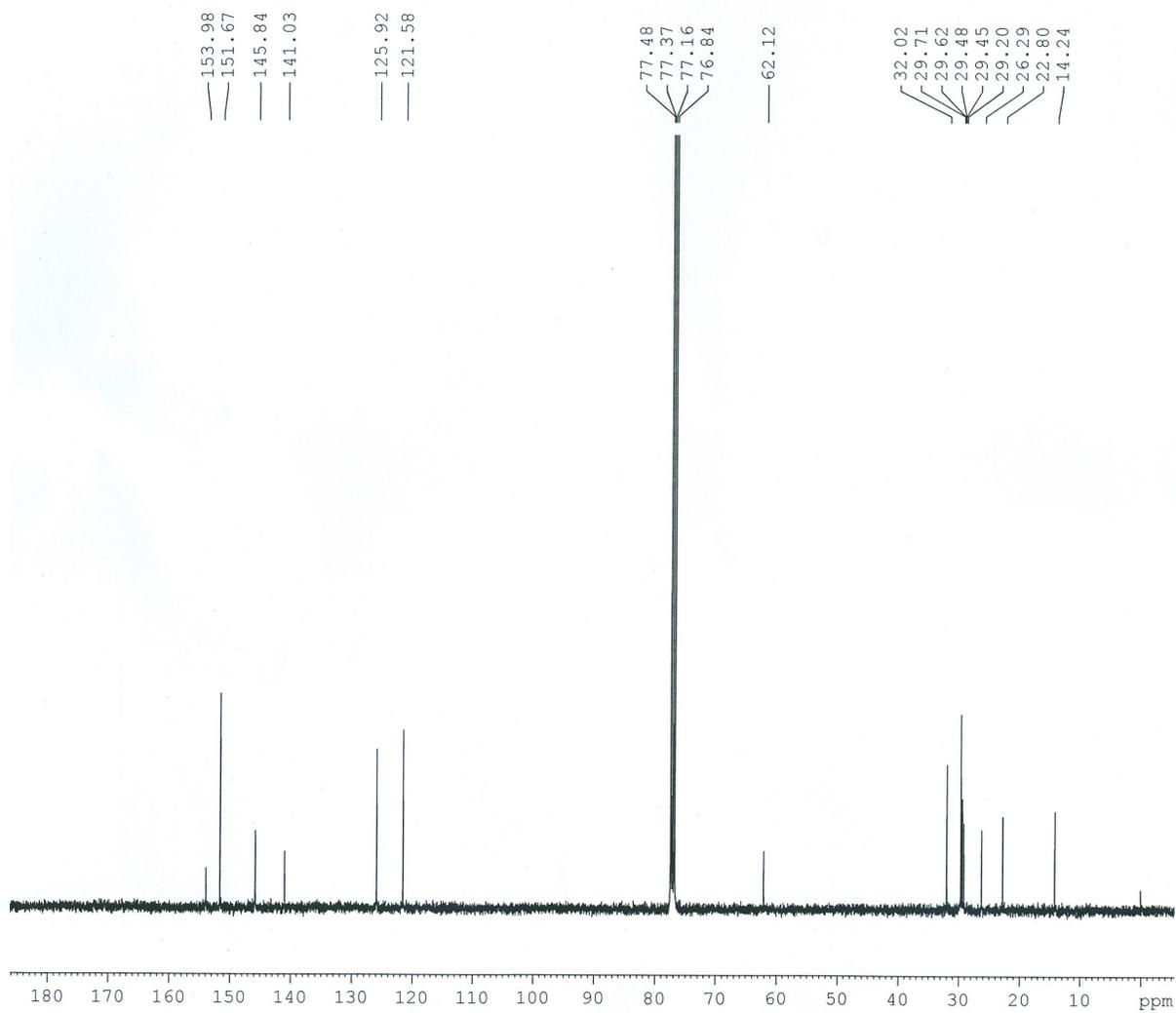


Figure S6. ¹³C-NMR spectrum of compound **3** in CDCl₃.

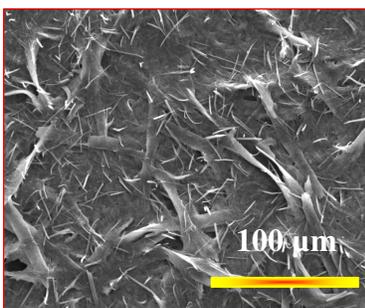


Figure S7. SEM image of $\text{P}^+-16-(\text{Py}^{3-})$ at the concentration of 9 mM in each case.

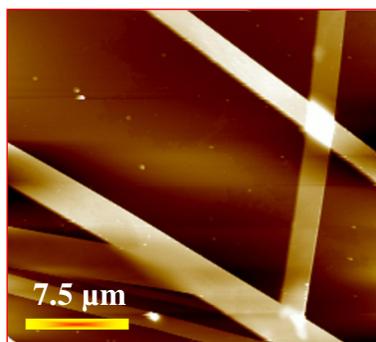


Figure S8. AFM image of $\text{P}^+-16-(\text{Py}^{3-})$ at the concentration of 9 mM.

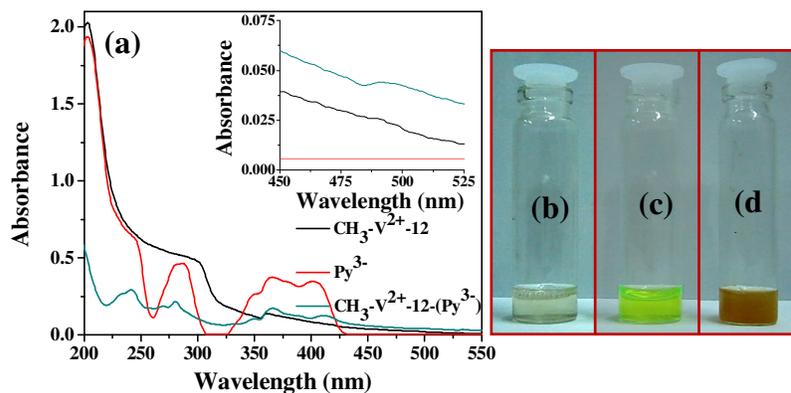


Figure S9. (a) UV-Vis spectra of aq. solutions of $\text{CH}_3\text{-V}^{2+}\text{-12}$, Py^{3-} and $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})$ at the concentration of 0.05 mM in each case; Inset shows magnification for clarity. Photographs of aq. solution of (b) $\text{CH}_3\text{-V}^{2+}\text{-12}$, (c) Py^{3-} and (d) $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})$ are shown in the right.

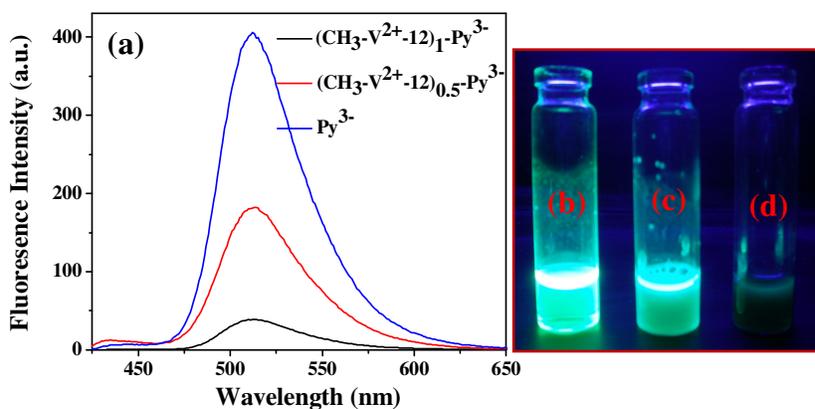


Figure S10. (a) Stoichiometry-dependent changes in the emission spectra of aq. solutions of $(\text{CH}_3\text{-V}^{2+}\text{-12})_n\text{-Py}^{3-}$ [$n = 0, 0.5$ and 1]; Concentration of Py^{3-} is 0.05 mM in each case; Photographs of aq. solution of (b) Py^{3-} and $(\text{CH}_3\text{-V}^{2+}\text{-12})_n\text{-Py}^{3-}$ [$n =$ (c) 0.5 and (d) 1] under long UV-light (365 nm) are shown in the right.

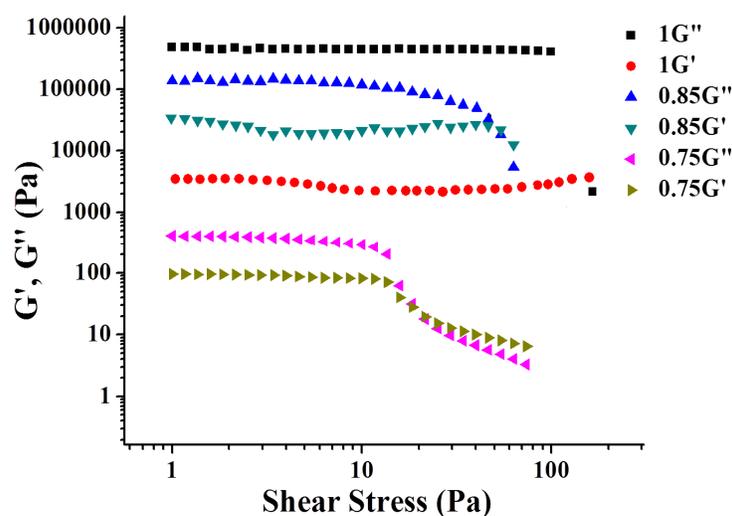


Figure S11. Rheological measurements show oscillatory amplitude sweep experiments of two-component systems comprising $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})_n$ in water, where $n = 0.75, 0.85$ and 1 ; Concentration of $\text{CH}_3\text{-V}^{2+}\text{-12}$ is 9 mM in each case.

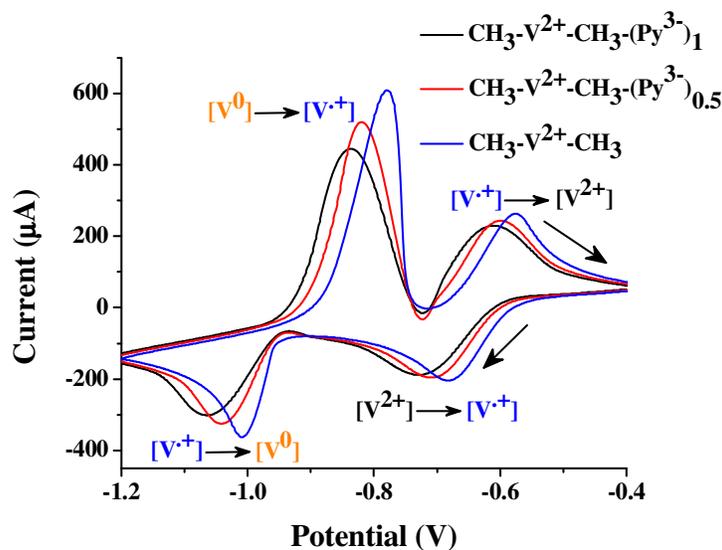


Figure S12. Cyclic voltammograms of $\text{CH}_3\text{-V}^{2+}\text{-CH}_3\text{-(Py}^{3-})_n$ ($n = 0, 0.5$ and 1) on glassy carbon electrode in water in the presence of 0.1 M LiCl as a supporting electrolyte at a scan rate of 100 mV/sec at the concentration of 9 mM in each case.

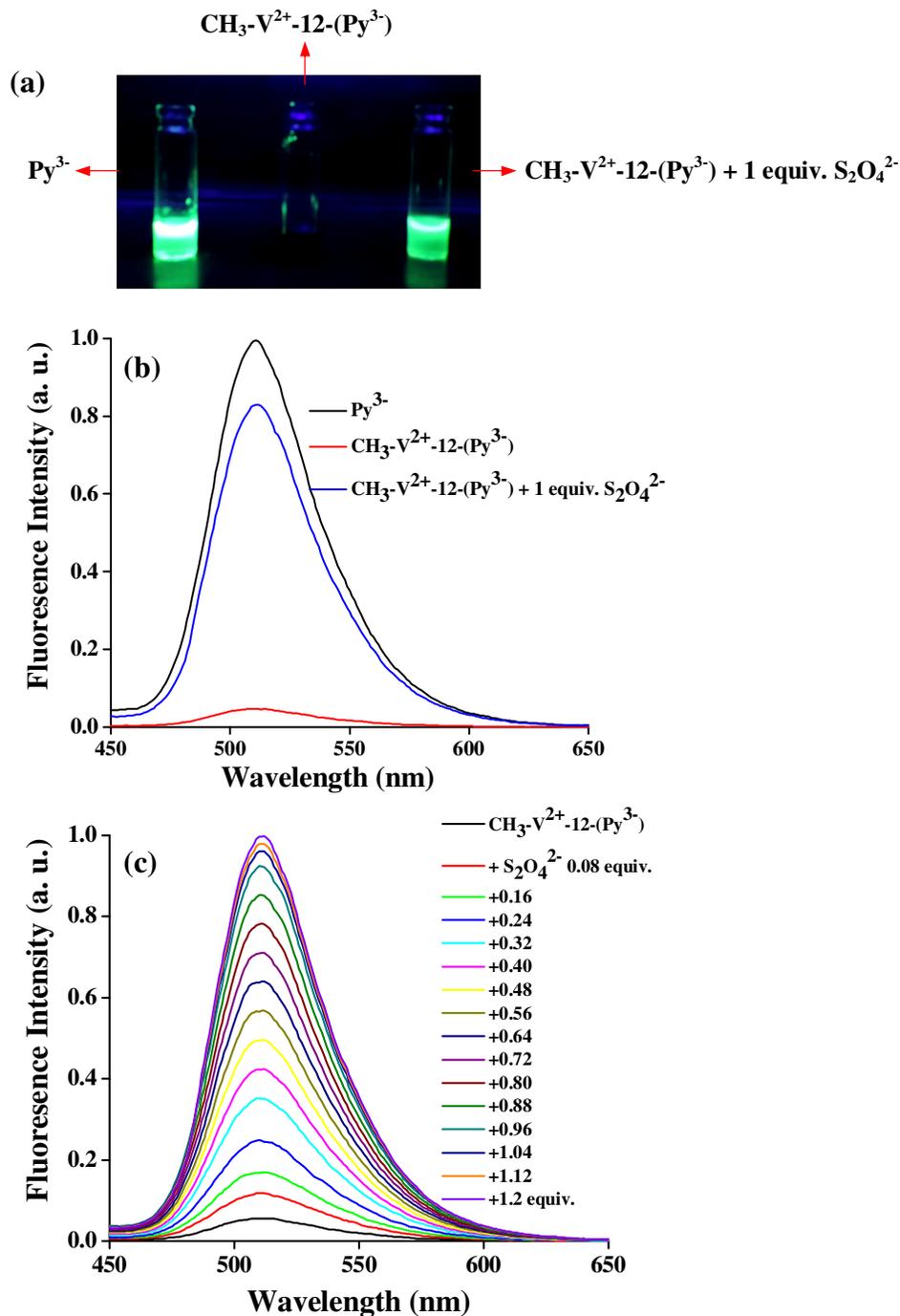


Figure S13. (a) Photographs and (b) emission spectra of Py^{3-} , $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})$ and $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-}) + 1 \text{ equiv. S}_2\text{O}_4^{2-}$; (c) Changes in the emission spectra of $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})$ upon gradual addition of $\text{S}_2\text{O}_4^{2-}$; concentration is 9 mM in each case.

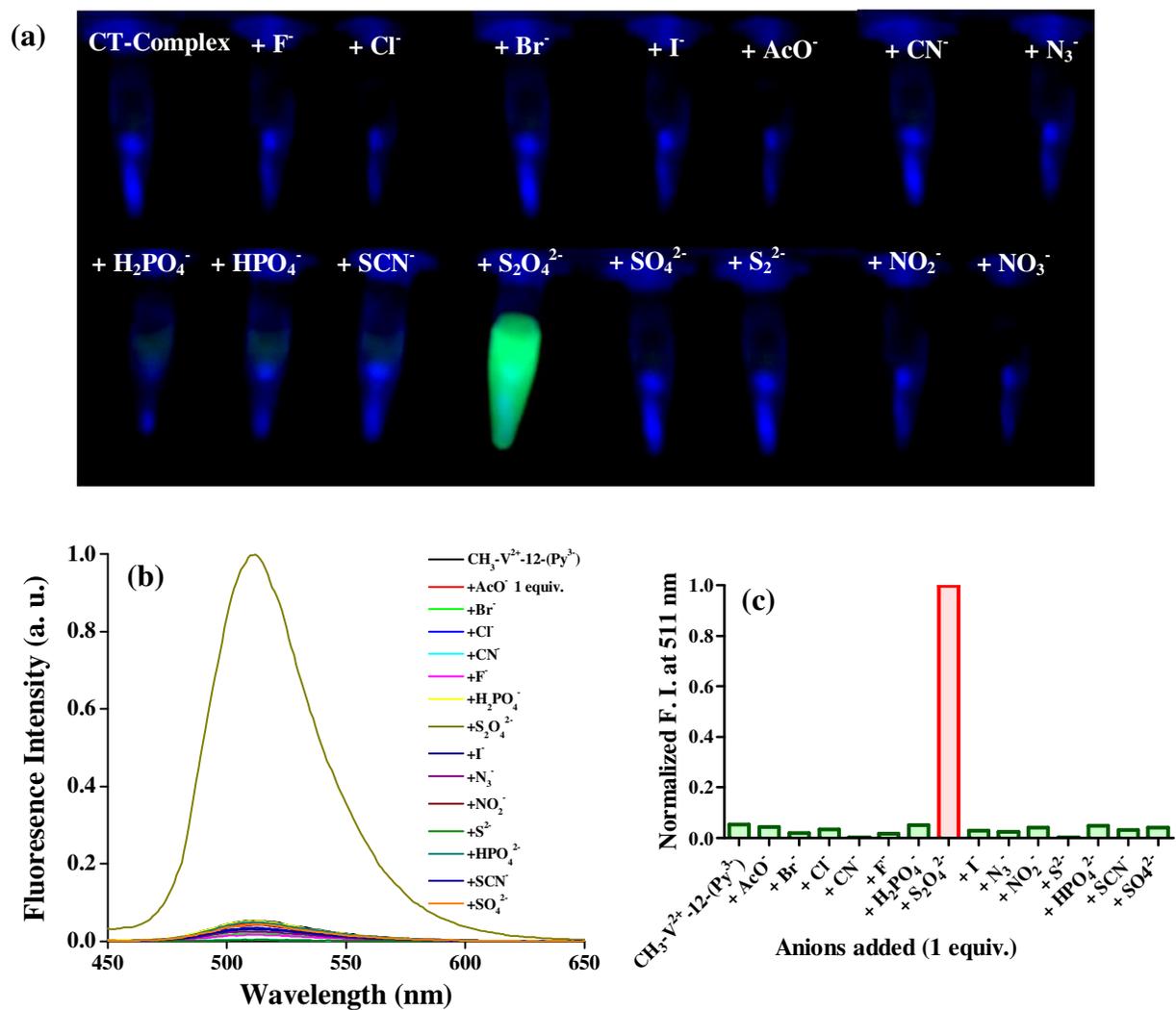


Figure S14. (a) Images showing the changes in the fluorescence emission of $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^3\text{)}$ under 365 nm UV lamp upon addition of different anions (1 equiv.); (b) fluorescence spectra and (c) changes in the emission intensity at 511 nm of $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^3\text{)}$ upon addition of 1 equiv. of different anions; concentration is 9 mM in each case.

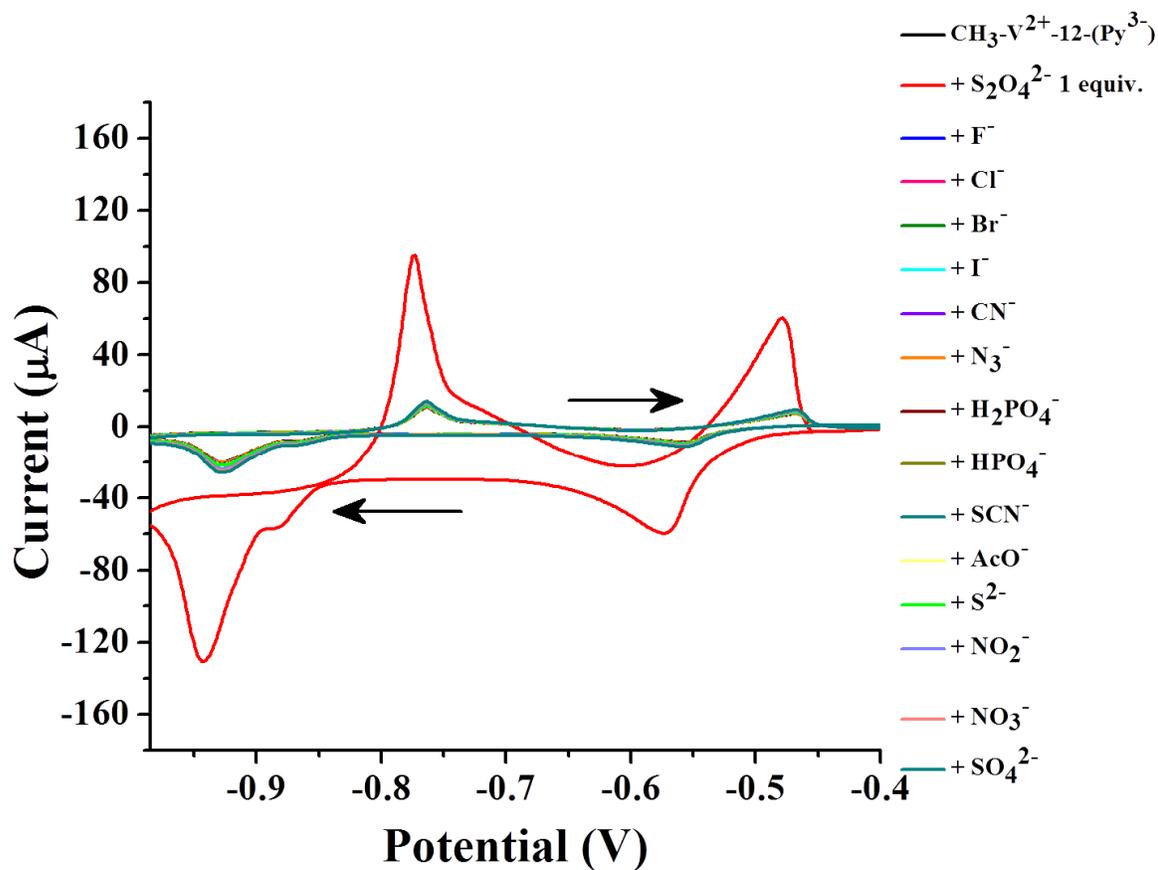


Figure S15. Changes in the cyclic voltammograms of $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^3\text{-)}$ on glassy carbon electrode in water upon addition of 1 equiv. of different anions in the presence of 0.1 M LiCl as a supporting electrolyte at a scan rate of 100 mV/sec at the concentration of 9 mM in each case.

Table S1. Half-wave reduction potential ($E_{1/2}^1$ in mV vs. SCE) and cathodic peak current (i_{pc}^1 in μA) associated with the first reduction step of $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})_n$ at various Py^{3-} stoichiometry ($n = 0, 0.5$ and 1) in presence of 0.1 (M) LiCl as supporting electrolyte.^[a]

Complex	$E_{1/2}^1$ (mV)	i_{pc}^1 (μA)
$\text{CH}_3\text{-V}^{2+}\text{-12}$	-500	-72.6
$\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})_{0.5}$	-527	-26.4
$\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})_1$	-558	-8.46

^[a] The number of electrons appearing in half-reaction for the redox couple (n) is 1; the electrode area (A) is 0.09 cm^2 ; scan rate (v) is $100 \times 10^{-3}\text{ V/s}$; concentration of $\text{CH}_3\text{-V}^{2+}\text{-12}$ (C) is $0.009 \times 10^{-3}\text{ mol/cm}^3$ in each case.

Table S2. Calculated diffusion coefficients (D) using Randles-Sevcik equation associated with the first reduction step of $\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})_n$ at various Py^{3-} stoichiometry ($n = 0, 0.5$ and 1) in presence of 0.1 (M) LiCl as supporting electrolyte.^[a]

Complex	i_{pc}^1 (μA)	D (cm^2/sec)
$\text{CH}_3\text{-V}^{2+}\text{-12}$	-72.6	10×10^{-6}
$\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})_{0.5}$	-26.4	1.32×10^{-6}
$\text{CH}_3\text{-V}^{2+}\text{-12-(Py}^{3-})_1$	-8.46	1.36×10^{-7}

^[a] The number of electrons appearing in half-reaction for the redox couple (n) is 1; the electrode area (A) is 0.09 cm^2 ; scan rate (v) is $100 \times 10^{-3}\text{ V/s}$; concentration of $\text{CH}_3\text{-V}^{2+}\text{-12}$ (C) is $0.009 \times 10^{-3}\text{ mol/cm}^3$ in each case.

References.

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2. C. Wang, Y. Guo, Z. Wang and X. Zhang, *Langmuir*, 2010, **26**, 14509.
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