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Electronic Supplementary Information

Evaluation of negolyte properties of supramolecular binary complexes based on viologen-cucurbit[7]urils

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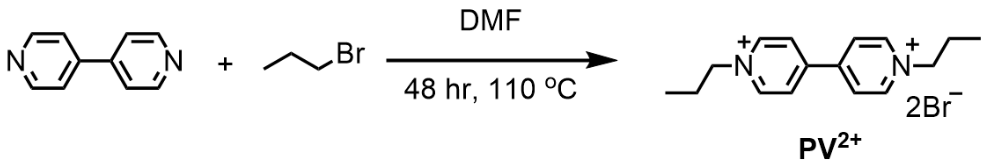
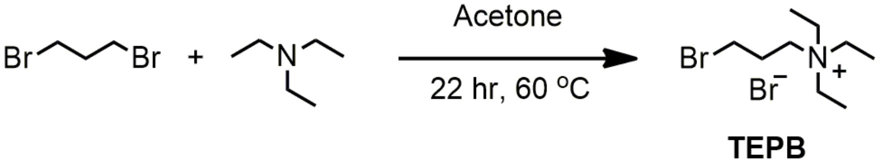
Preparation of PV^{2+}



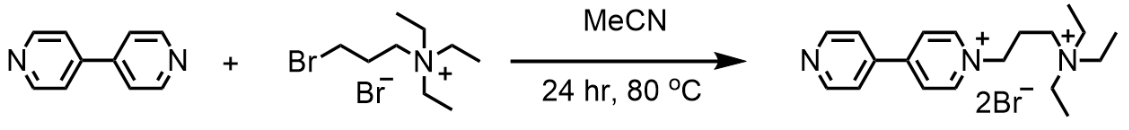
4,4′-Bipyridine (1.0 g, 6.4 mmol) and 1-bromopropane (4.72 g, 38.3 mmol) was dissolved in 20 ml DMF and stirred at 110 °C. The progress of the reaction was monitored by TLC (MeOH: HOAc: H_2O –10:4:1). The reaction mixture was stirred for 24 h in total, and then cooled to room temperature, after which the precipitate was filtered, washed three times with CH_3CN (10 ml) and dried under reduced pressure to yield yellow solid (2.20 g, 85%). ^1H NMR (500 MHz, D_2O) δ 9.04 (d, J = 10.3 Hz, 4H), 8.47 (, J = 5.9 Hz, 4H), 4.62 (t, J = 6.9 Hz, 4H), 2.02 (m, J = 6.7, 6.2 Hz, 4H), 0.91 (t, J = 5.7 Hz, 6H). ^{13}C NMR (126 MHz, D_2O) δ 150.1, 145.4, 127.0, 63.6, 24.2, 9.7. Anal. Calcd for $C_{16}H_{22}Br_2N_2$: C, 47.78; H, 5.51; N, 6.97. Found: C, 48.01; H, 5.29; N, 7.23.

Preparation of 3-bromo-N,N,N-triethylpropan-1-aminium bromide (TEPB)



1,3-Dibromopropane (20.19 g, 100 mmol) in anhydrous acetone (35 mL) was stirred at 60 °C. To this solution freshly distilled triethylamine (7.0 mL, 50.0 mmol) in 20 mL of anhydrous acetone was added dropwise for 8 hour. The reaction mixture was stirred for 22 hour at the same temperature, after which the mixture was cooled to room temperature. The resulting precipitate was washed with acetone (20 mL, thrice) and dried under vacuum. The yield of the white solid is 61.9% (9.39 g). ^1H NMR (500 MHz, DMSO-d_6) δ 3.48 (t, J = 7.4 Hz, 2H), 3.17 (m, 2H), 3.12 (q, J = 2.5 Hz 6H), 2.09 – 1.99 (m, 2H), 1.05 (t, J = 7.3 Hz, 9H).^{13}C NMR (126 MHz, DMSO-d_6) δ 52.9, 52.7, 31.1, 24.9, 7.6.

Preparation of MPV^{2+}



MPV^{2+}

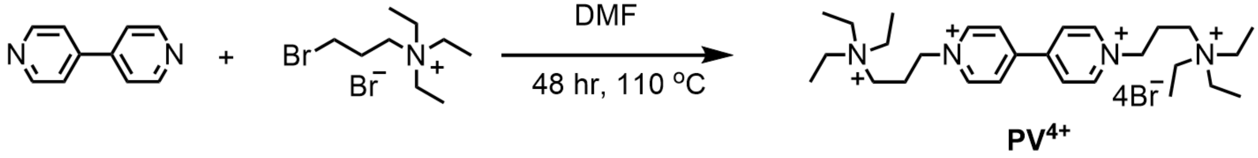
4,4′-Bipyridine (1.0 g, 6.4 mmol) was dissolved in 15 ml CH_3CN and stirred at 80 °C. To this solution, TEPB (0.38 g, 1.28 mmol) dissolved in (10 ml) CH_3CN was added slowly over 8 h. The progress of the reaction was monitored by TLC (MeOH: HOAc: H_2O –10:4:1). The reaction mixture was stirred for 24 h in total, and then cooled to room temperature, after which the precipitate was filtered, washed three times with CH_3CN (10 ml) and dried under reduced pressure to yield pale yellow solid (0.46 g, 79.8%). ^{1}H NMR (500 MHz, D_2O) δ 9.02 (d, *J* = 7.1 Hz, 2H), 8.79 (d, *J* =6.9 Hz, 2H), 8.45 (d, *J* = 6.9 Hz, 2H), 8.00 (d, *J* = 7.1 Hz, 2H), 3.36 (t, *J* = 7.9 Hz, 2H), 3.30 (q, *J* = 7.8 Hz, 6H), 2.55 – 2.45 (m, 2H), 1.23 (t, *J* = 7.3 Hz 9H). ^{13}C NMR (126 MHz, D_2O) δ 154.0, 148.6, 145.0, 144.1, 126.6, 123.3, 57.8, 53.1, 52.7, 23.4, 6.7.

Preparation of PV^{3+}

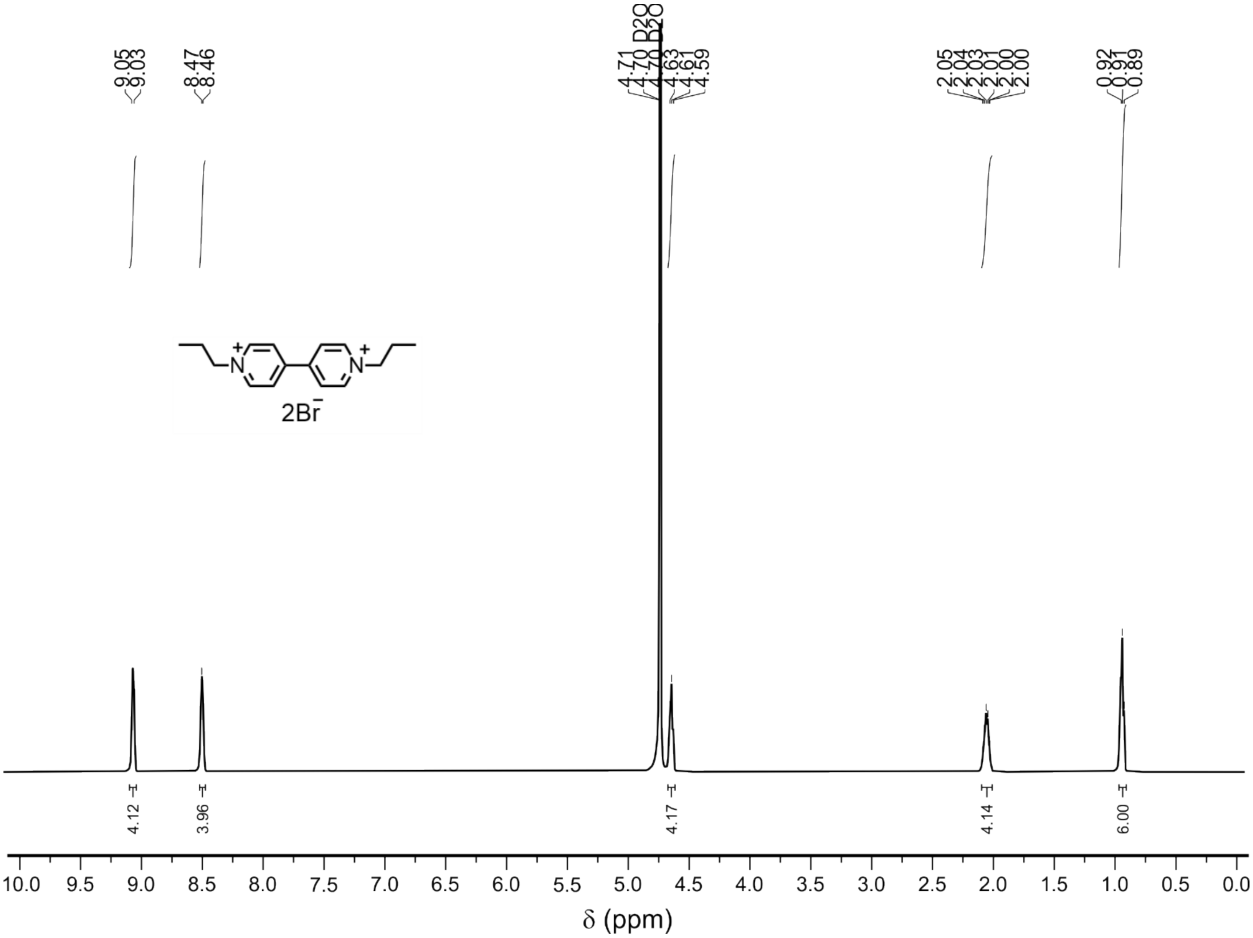
PV^{3+}

MPV^{2+} (0.2g, 0.44 mmol) and 1-bromopropane (0.27g, 2.2mmol) were dissolved in 7 ml DMF and stirred at 110 °C. The progress of the reaction was monitored by TLC (MeOH: HOAc: H_2O – 10:4:1). The reaction mixture was stirred for 48 h in total, and then cooled to room temperature. Reaction mixture was diluted with acetone (50 mL), the resulting precipitate was filtered, washed three times with acetone (10 ml) and dried under reduced pressure to yield brown solid (0.21 g, 84.6%). ^{1}H NMR (500 MHz, D_2O) δ 9.26 (d, 2H), 9.17 (d, *J* = 6.9 Hz, 2H), 8.66 (d, 2H), 8.62 (d, *J* = 6.2 Hz, 2H), 4.92 (t, *J* = 7.9 Hz, 2H), 4.74 (t, *J* = 7.3 Hz, 3H), 3.49 (t, *J* = 7.3 Hz, 2H), 3.41 (q, *J* = 7.3 Hz, 6H), 2.69 – 2.58 (m, 2H), 2.20 – 2.12 (m, 2H), 1.35 (t, *J* = 7.3 Hz, 9H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, D_2O) δ 150.8, 149.7, 145.6, 145.5, 127.4, 127.0, 63.6, 58.2, 53.2, 52.7, 24.2, 23.4, 9.7, 6.8. Anal. Calcd for $C_{22}H_{36}Br_3N_3$: C, 45.38; H, 6.23; N, 7.22. Found: C, 44.99; H, 6.49; N, 6.98.

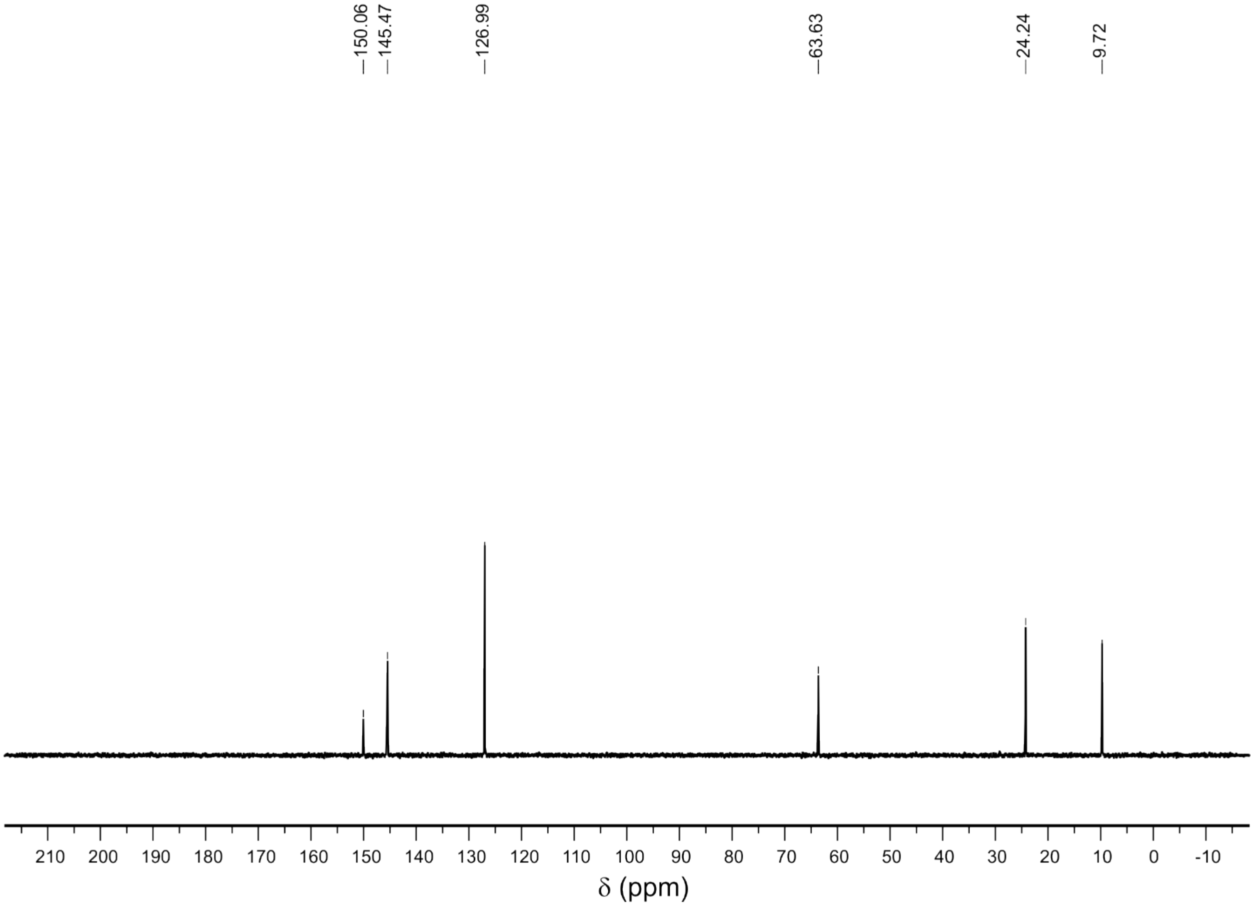
Preparation of PV^{4+}



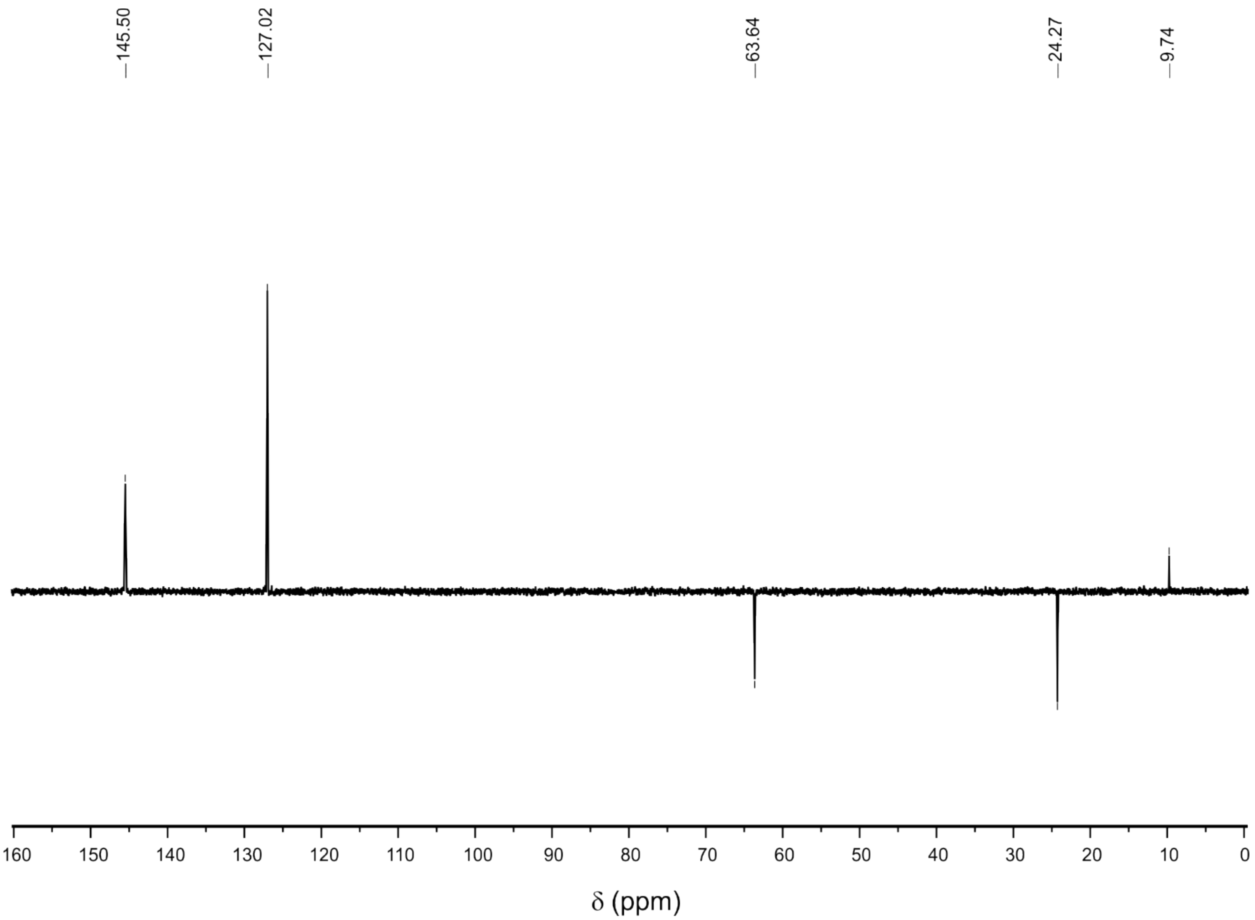
4,4′-Bipyridine (0.1 g, 0.64 mmol) and TEPB (1.8 g, 6.0 mmol) was dissolved in 7 ml DMF and stirred at 110 °C. The progress of the reaction was monitored by TLC (MeOH: HOAc: H_2O – 10:4:1). The reaction mixture was stirred for 72 h in total, and then cooled to room temperature, after which the precipitate was filtered, washed three times with CH_3CN (10 ml) and dried under reduced pressure to pale brown solid (0.43 g, 76.7%).^{1}H NMR (400 MHz, D_2O) δ 9.12 (d, J = 6.9 Hz, 4H), 8.53 (d, J = 6.9 Hz, 4H), 4.79 – 4.74 (m, 4H), 3.37 – 3.30 (m, 4H), 3.26 (q, J = 7.3 Hz, 12H), 2.54 – 2.42 (m, 4H), 1.20 (t, J = 7.2 Hz, 18H). ^{13}C NMR (101 MHz, D_2O) δ 150.5, 145.7, 127.5, 58.2, 53.1, 52.6, 23.4, 6.7. Anal. Calcd for $C_{28}H_{50}Br_4N_4$: C, 44.11; H, 6.61; N, 7.35. Found: C, 44.46; H, 6.29; N, 7.63.



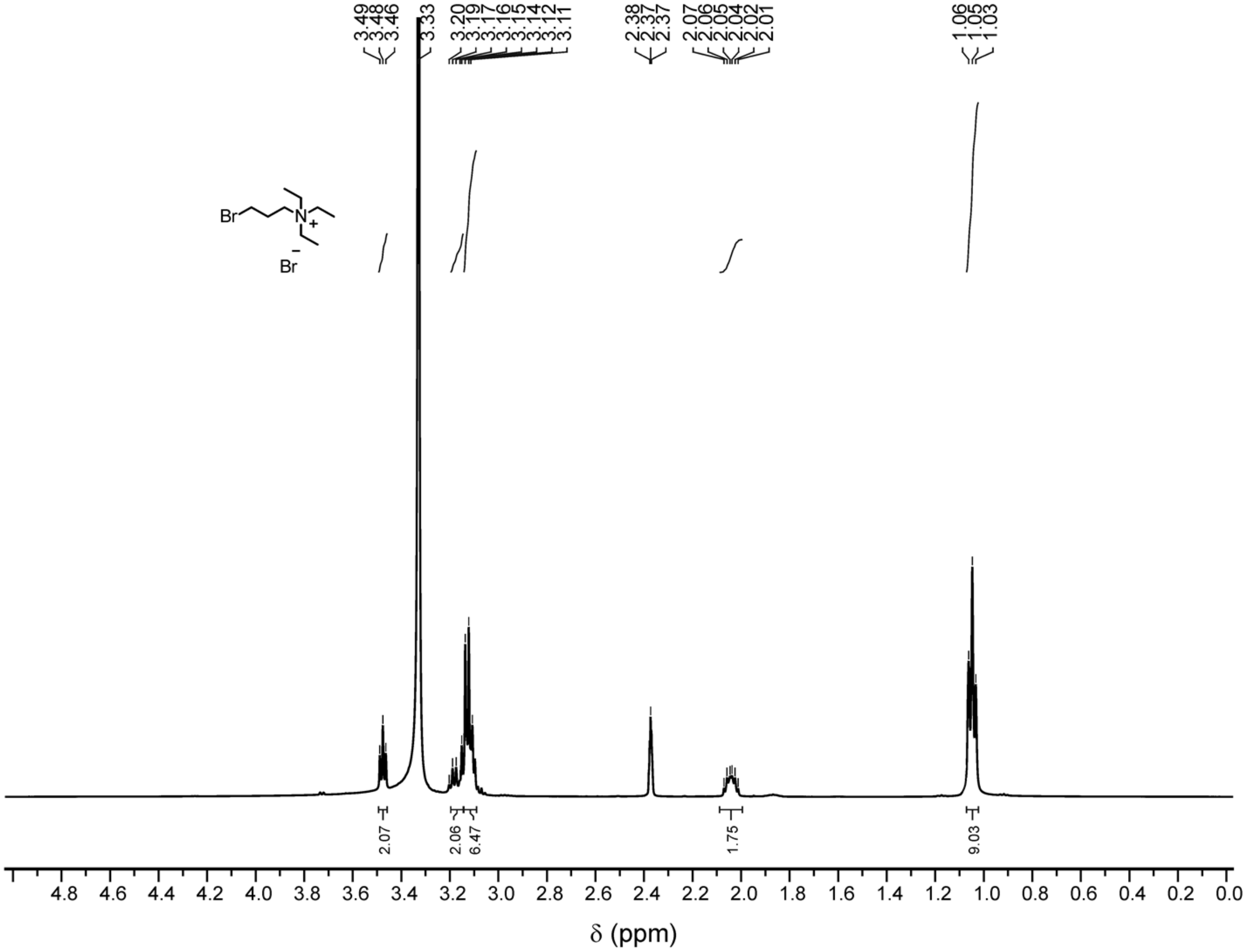
^{1}H NMR spectrum of PV^{2+}



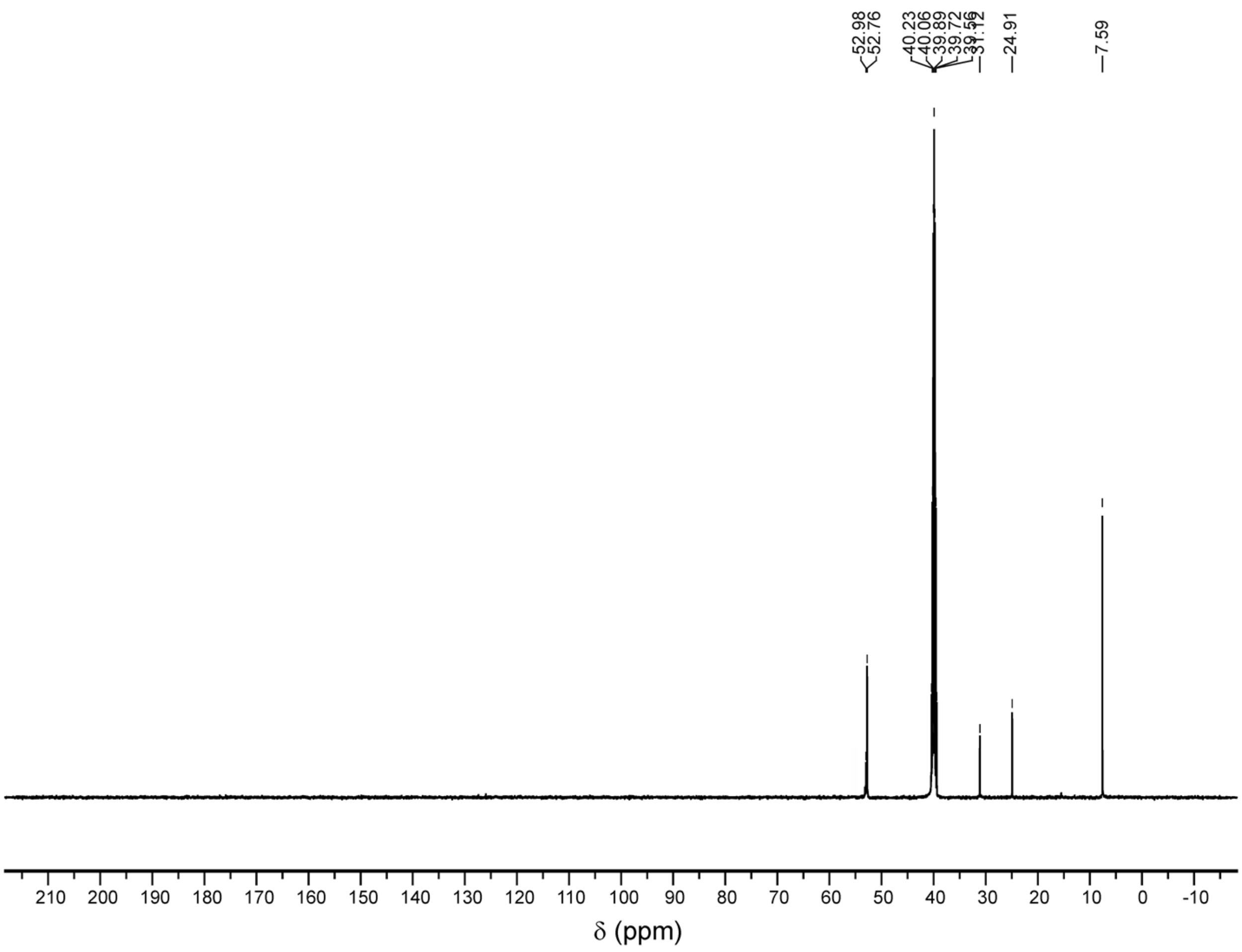
^{13}C NMR spectrum of PV^{2+}



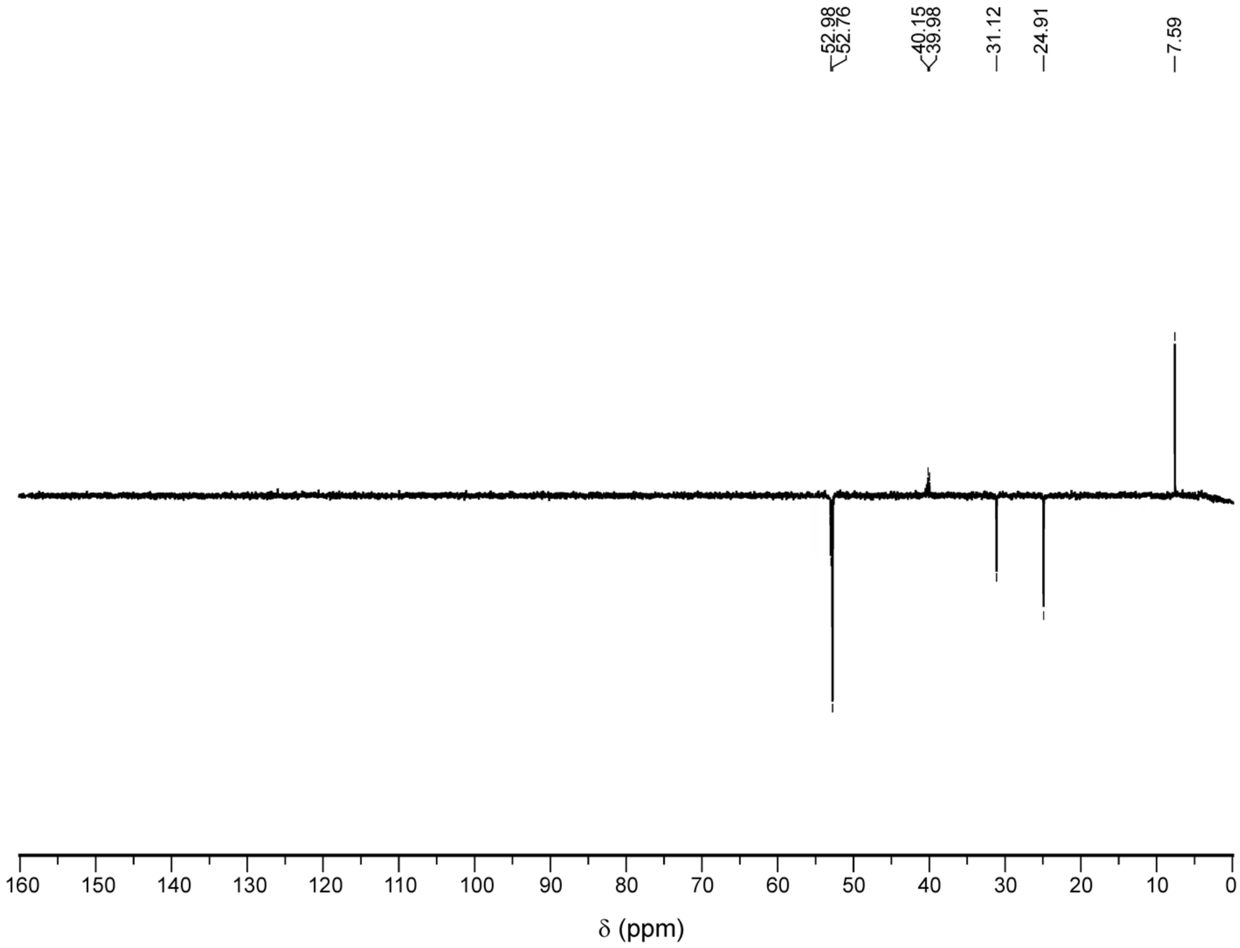
DEPT spectrum of PV^{2+}



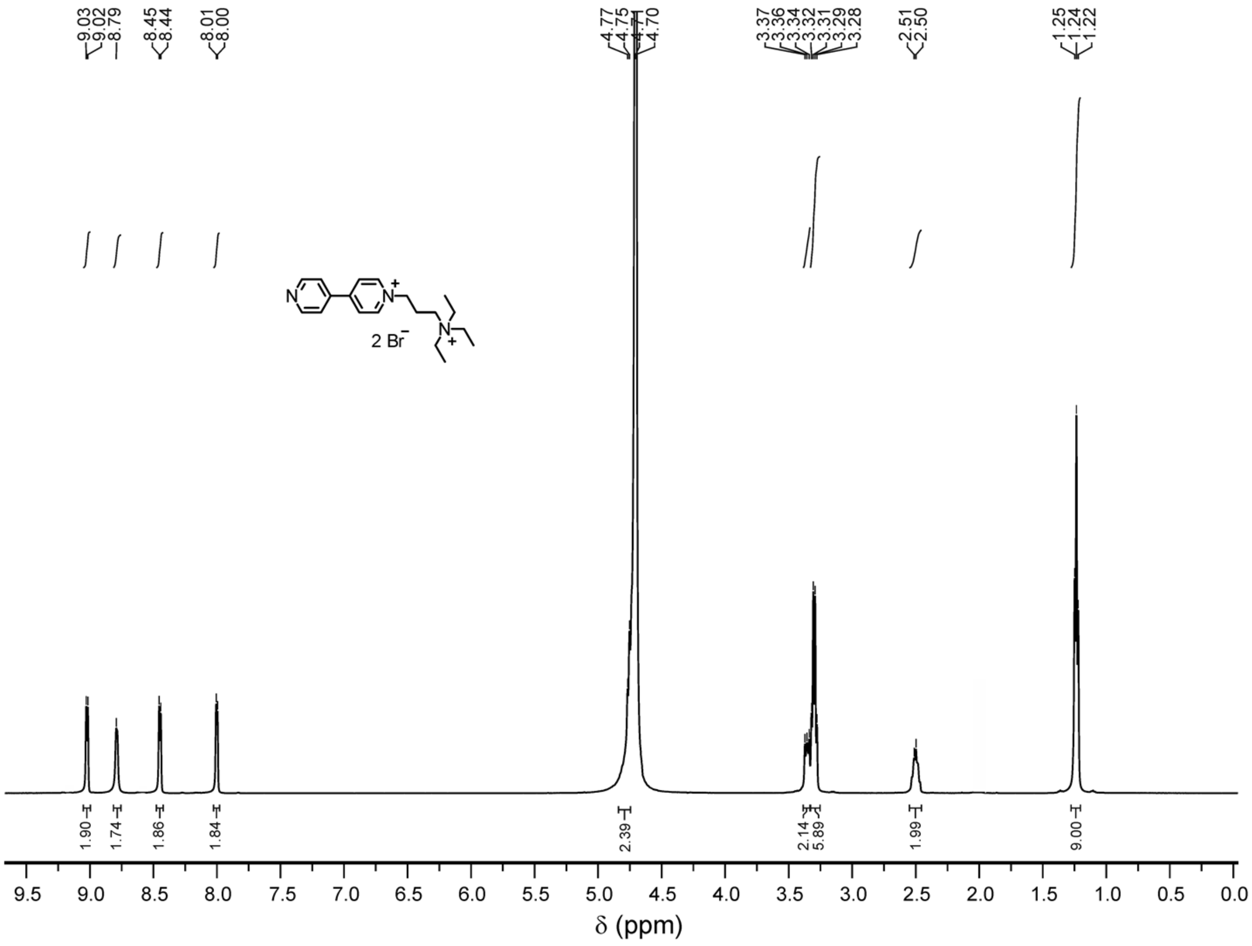
^{1}H NMR spectrum of TEPB



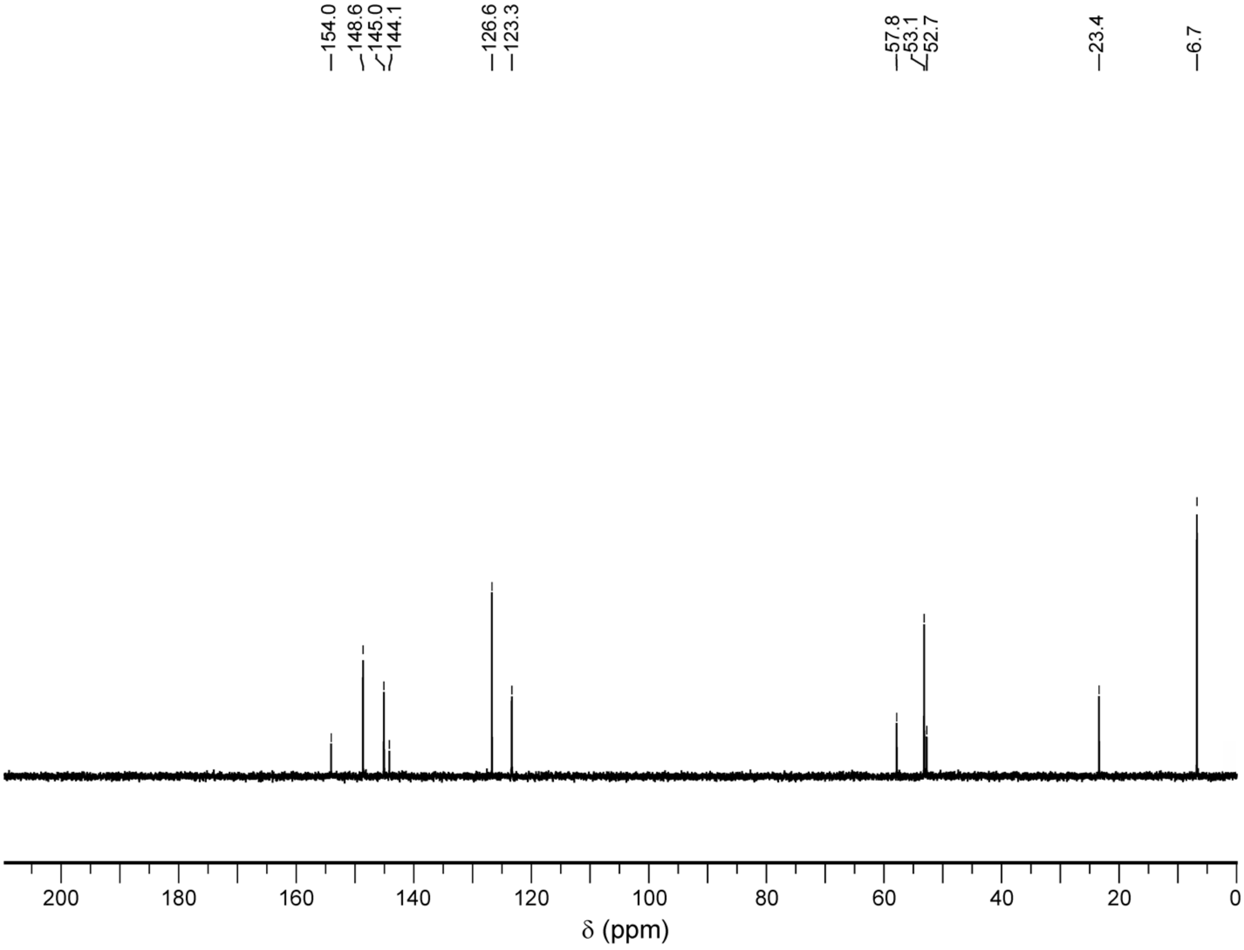
^{13}C NMR spectrum of TEPB



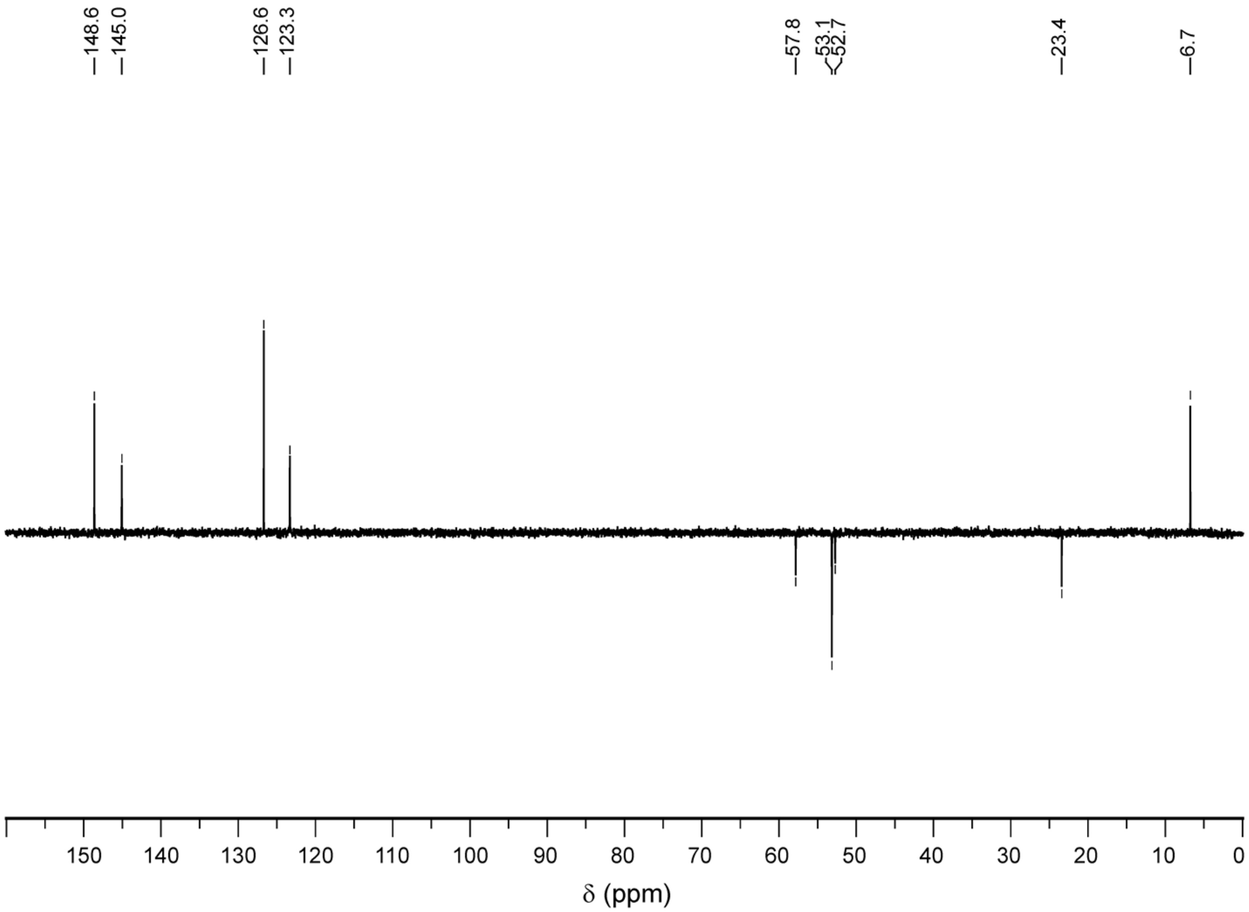
DEPT spectrum of TEPB



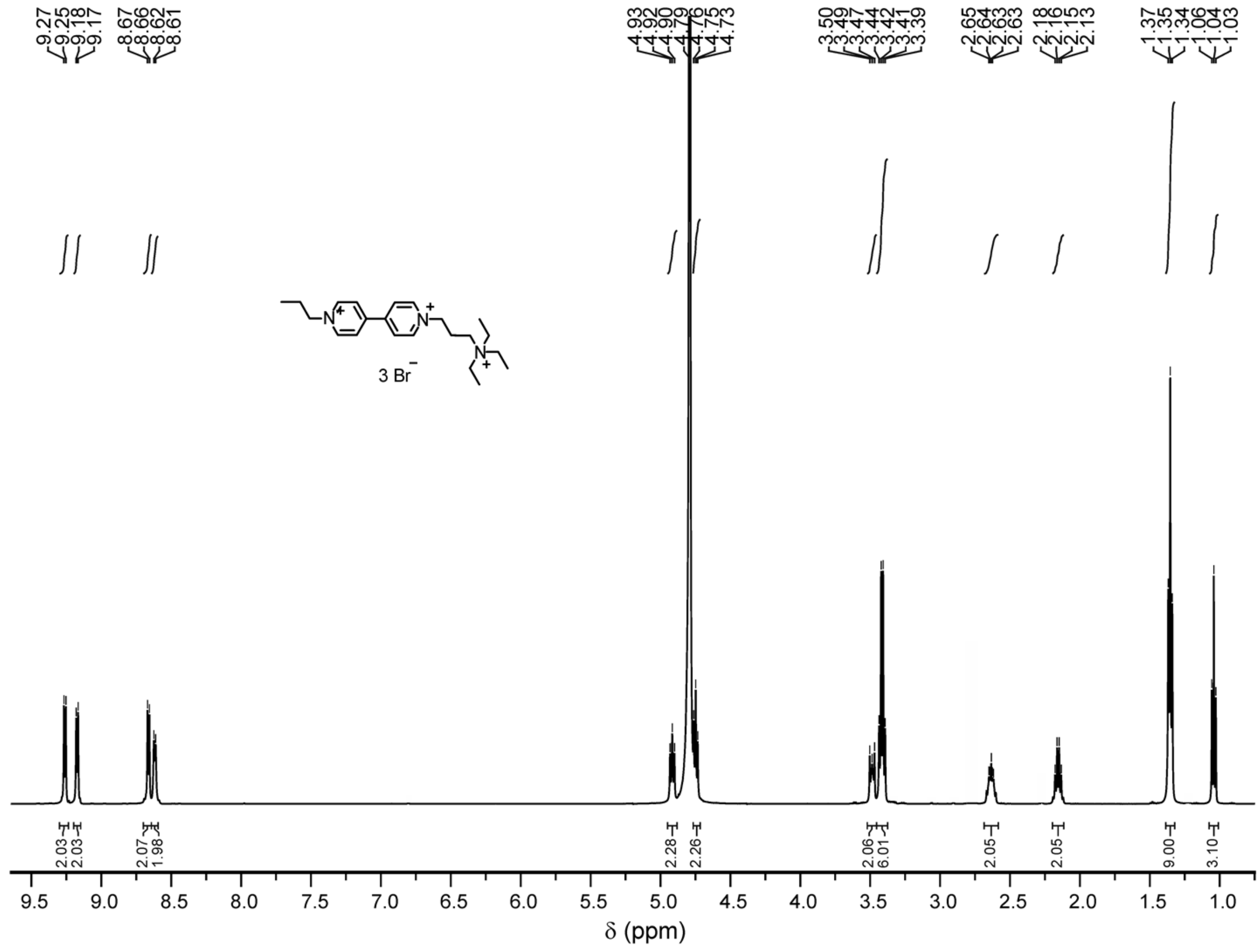
^{1}H NMR spectrum of MPV^{2+}



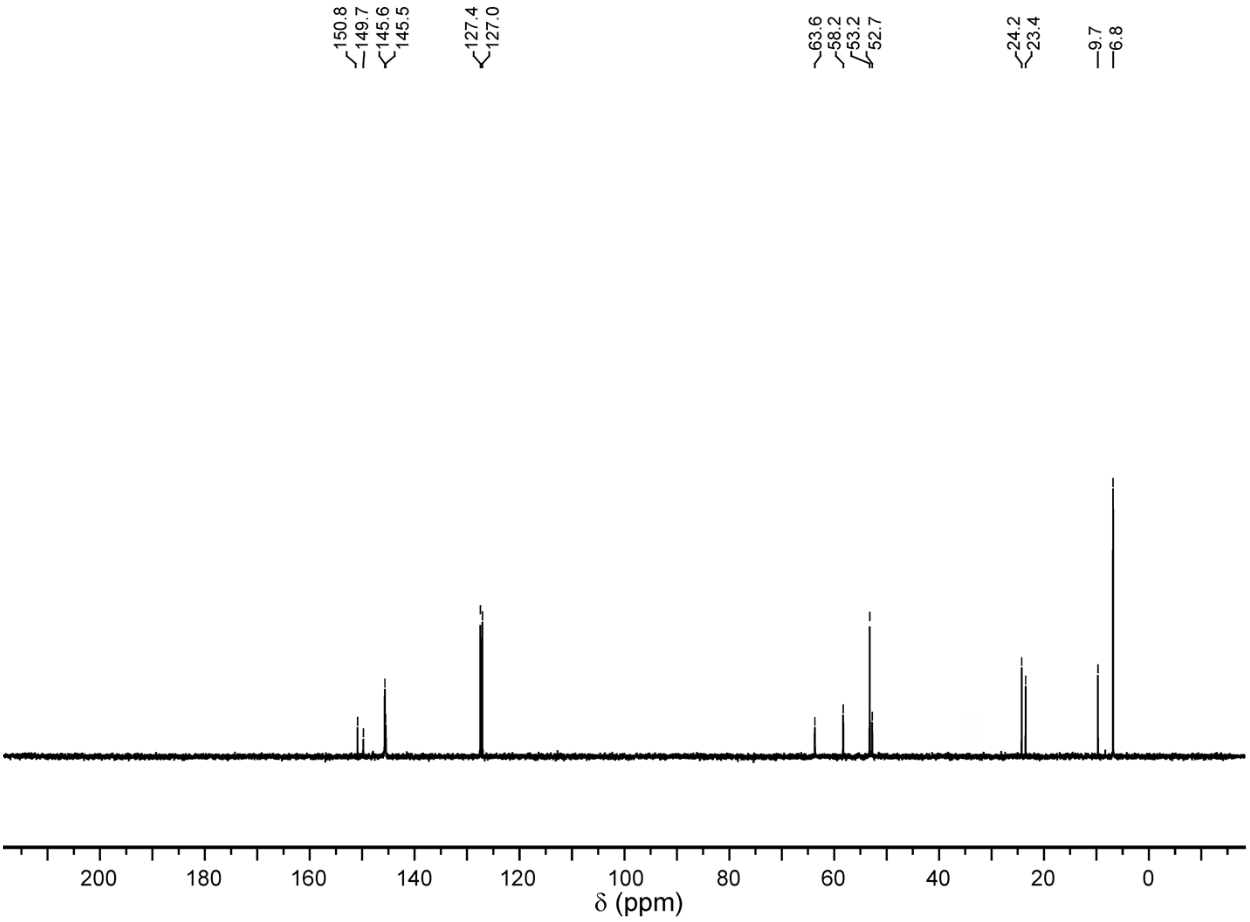
^{13}C NMR spectrum of MPV^{2+}



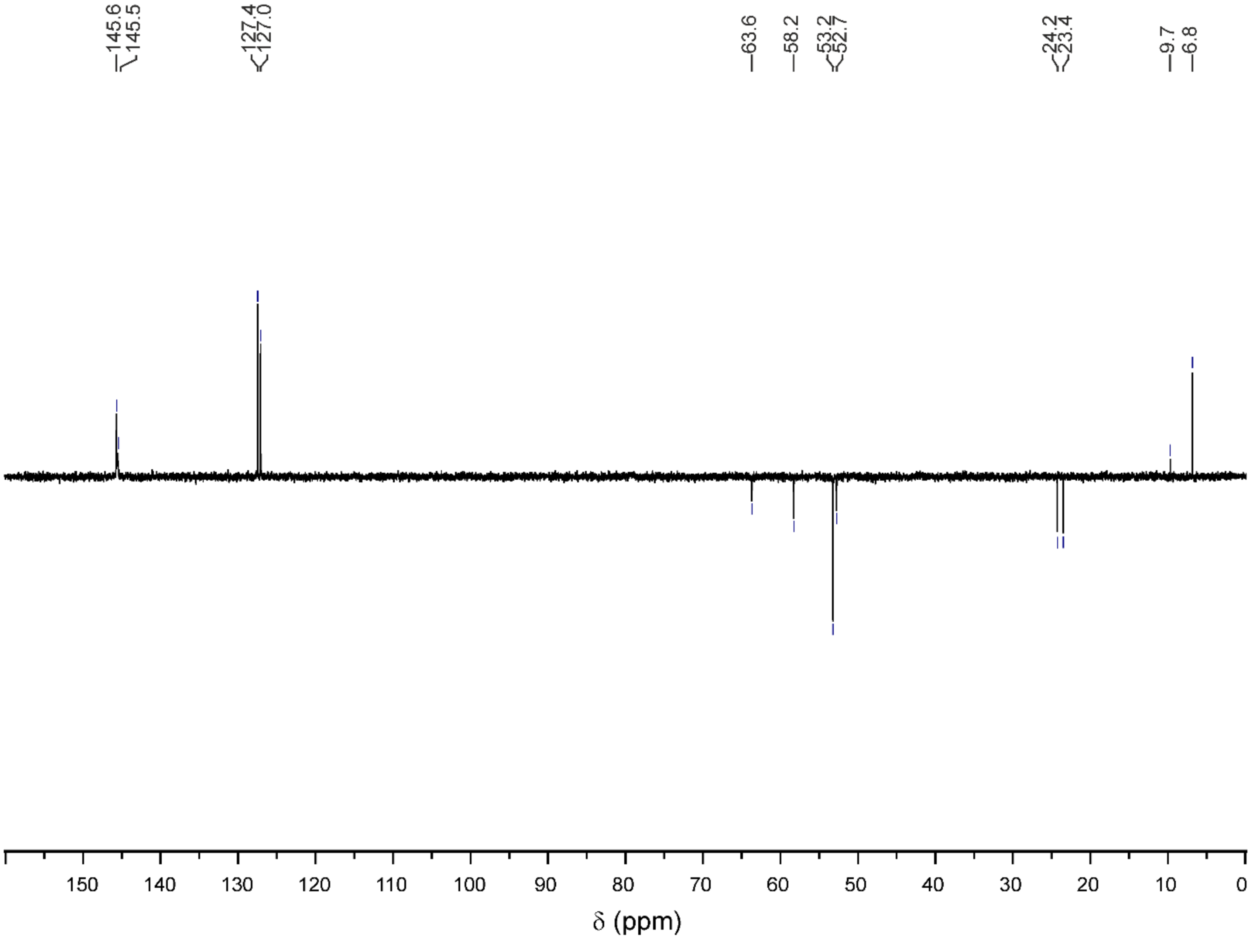
DEPT Spectrum of MPV^{2+}



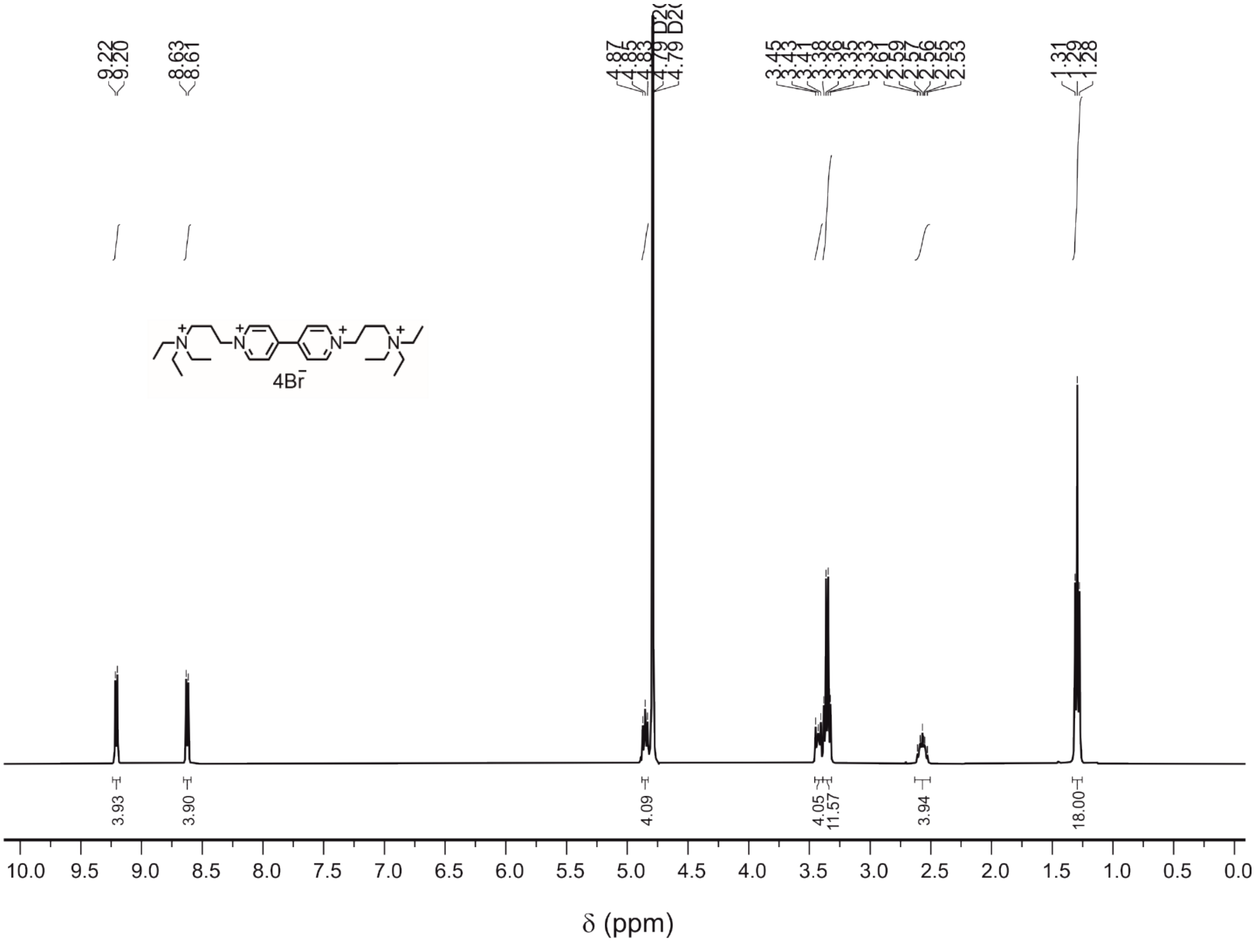
^{1}H NMR Spectrum of PV^{3+}



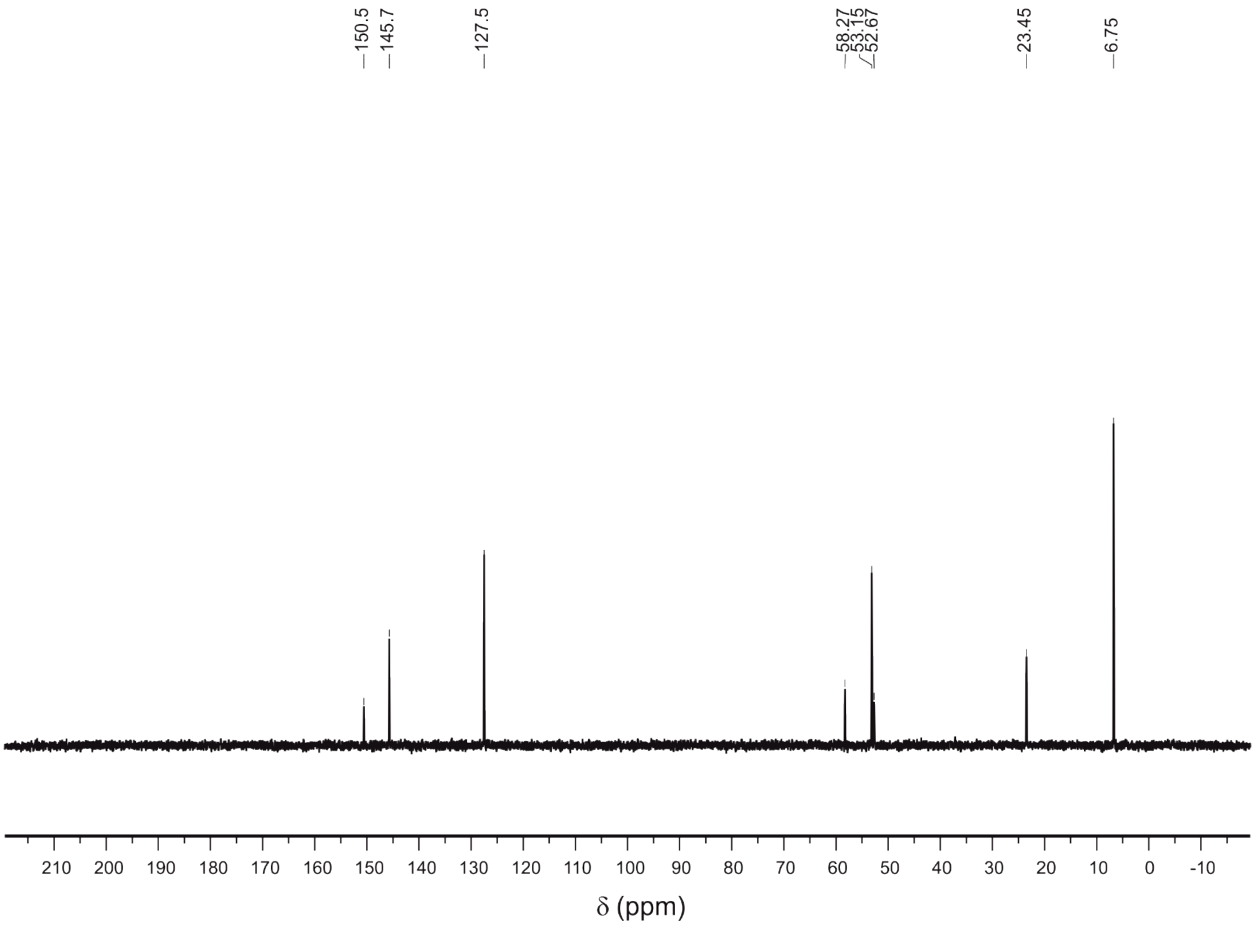
^{13}C NMR Spectrum of PV^{3+}



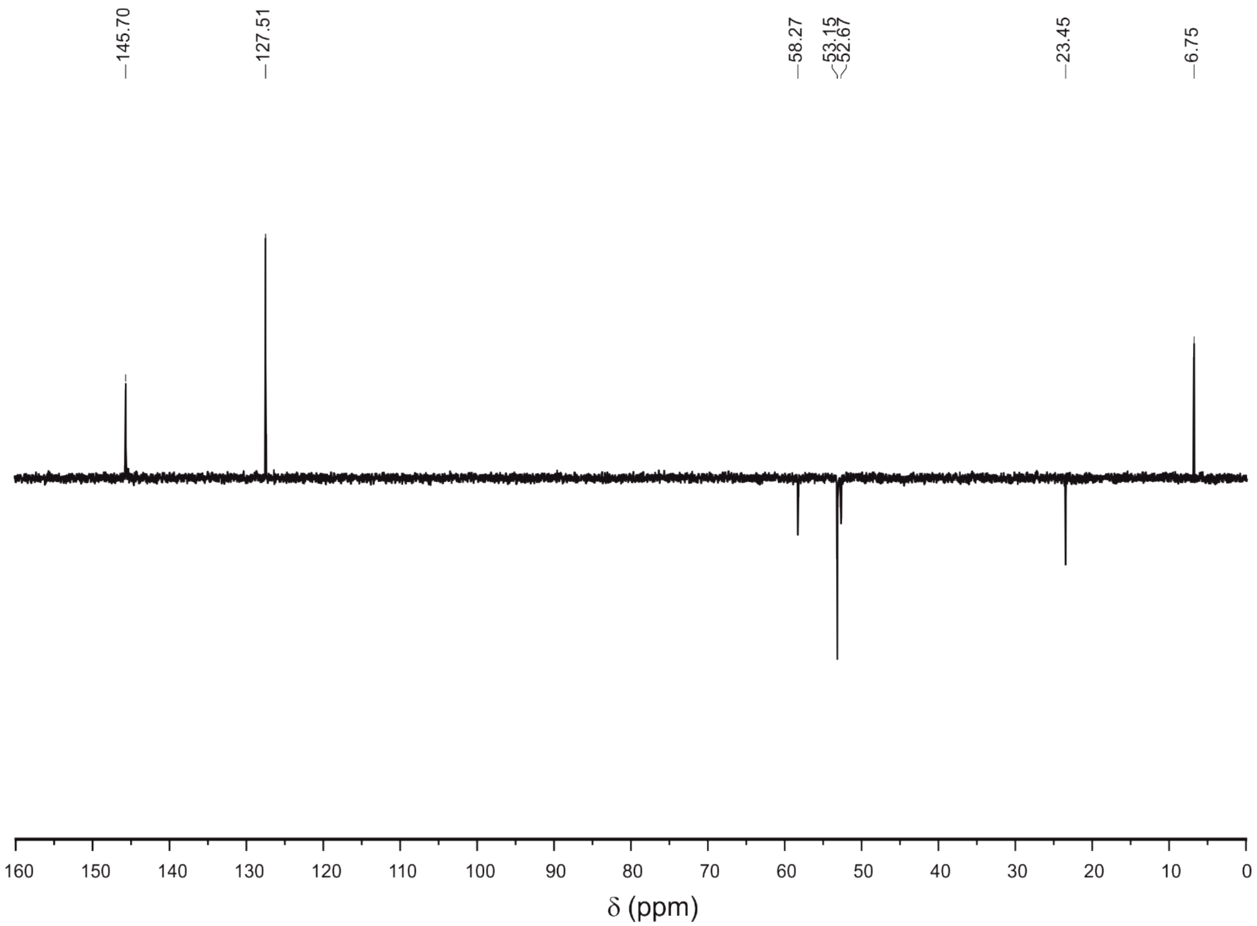
DEPT Spectrum of PV^{3+}



^{1}H NMR Spectrum of PV^{4+}



^{13}C NMR Spectrum of PV^{4+}



DEPT Spectrum of PV^{4+}

Cyclic voltammogram

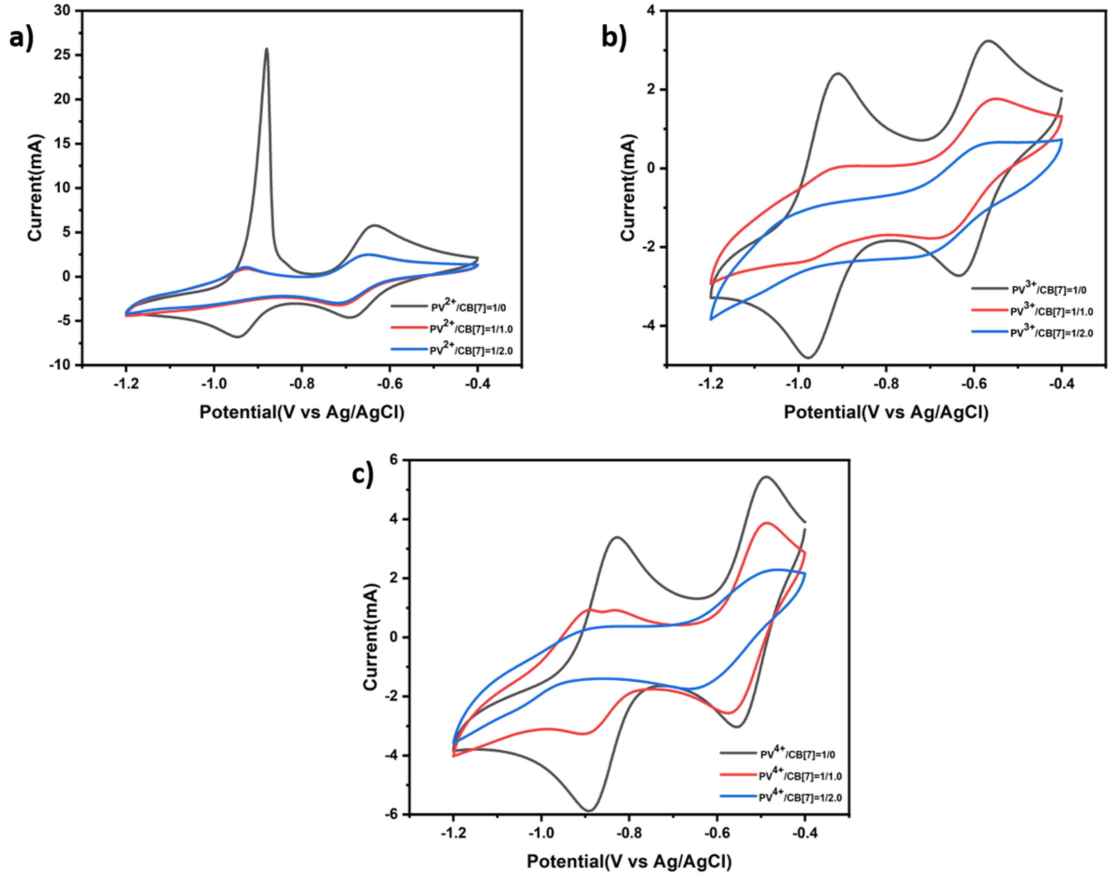


Fig. S1 Cyclic voltammetry profile of 0.5 mM of (a) PV^{2+}, (b) PV^{3+} and (c) PV^{4+} recorded in 50 mM NaCl solution with one and two equivalent of CB[7] host at a scan rate of 50 mV s^{-1}.

Fig. S1 shows CV profile of all the three compounds PV^{2+}, PV^{3+} and PV^{4+}. The redox behavior of viologen is evident from the figure. In the case of a) dipropyl viologen (PV^{2+}), the intensity as well as the peak of first oxidation from neutral viologen to cation radical was different from that of the others (a spike was observed). This is attributed to the oxidation of adsorbed neutral viologen on the surface to monocation radical. Upon two-electron reduction, viologen is converted to a neutral molecule (quinoid type planar structure) which is least soluble in aqueous solutions. Hence it preferentially gets adsorbed on to the electrode surface. Upon oxidation, this is observed as a spike and the monocation radical formed on the electrode surface is then soluble and it gets into the solution, indicating normal second oxidation behavior.

Cyclic voltammetry at different scan rate

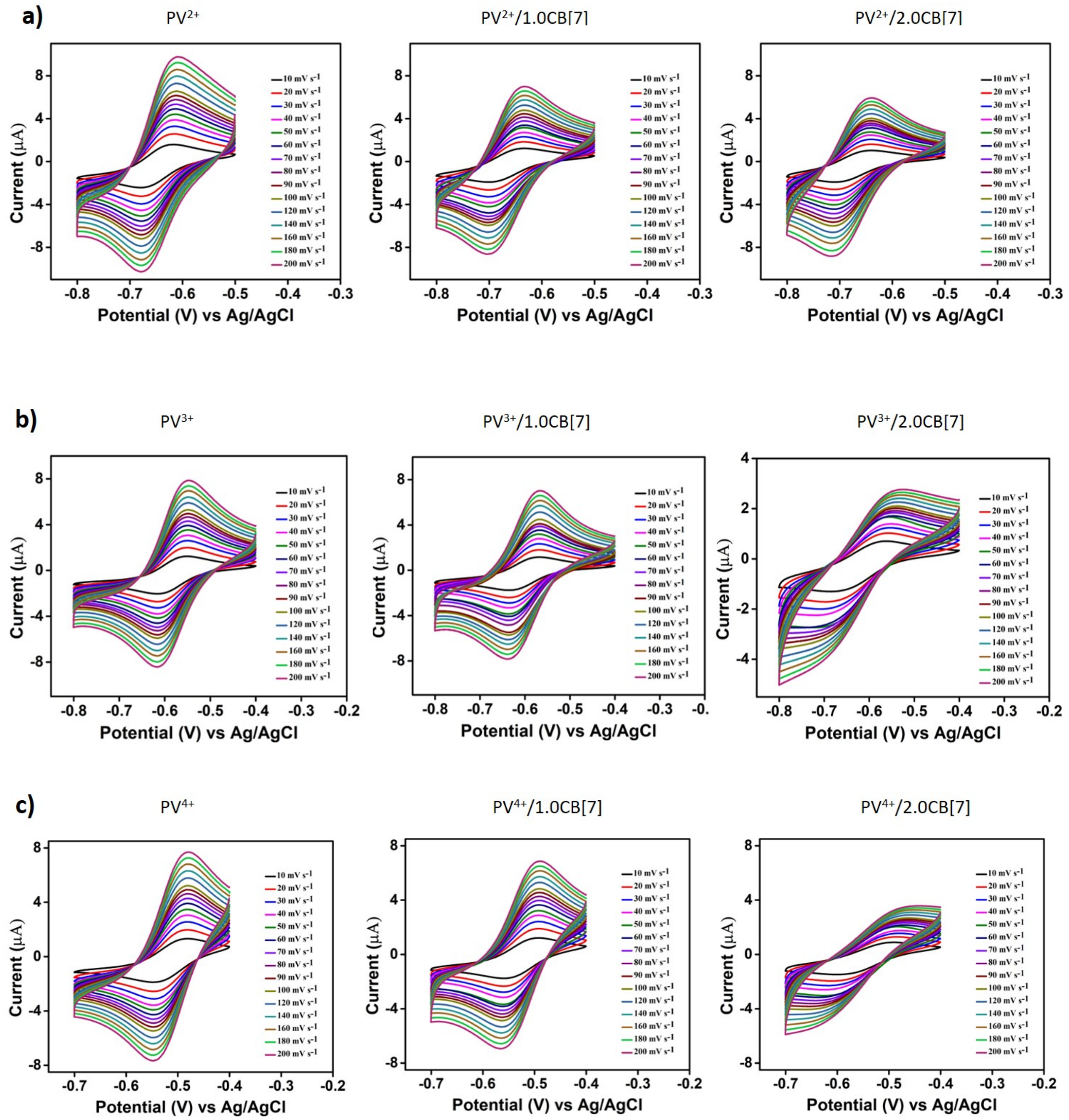


Fig. S2 Cyclic voltammograms of PV^{2+}, PV^{3+} as well as PV^{4+} and their complexes at different scan rates.

Current Vs Scan rate Plot

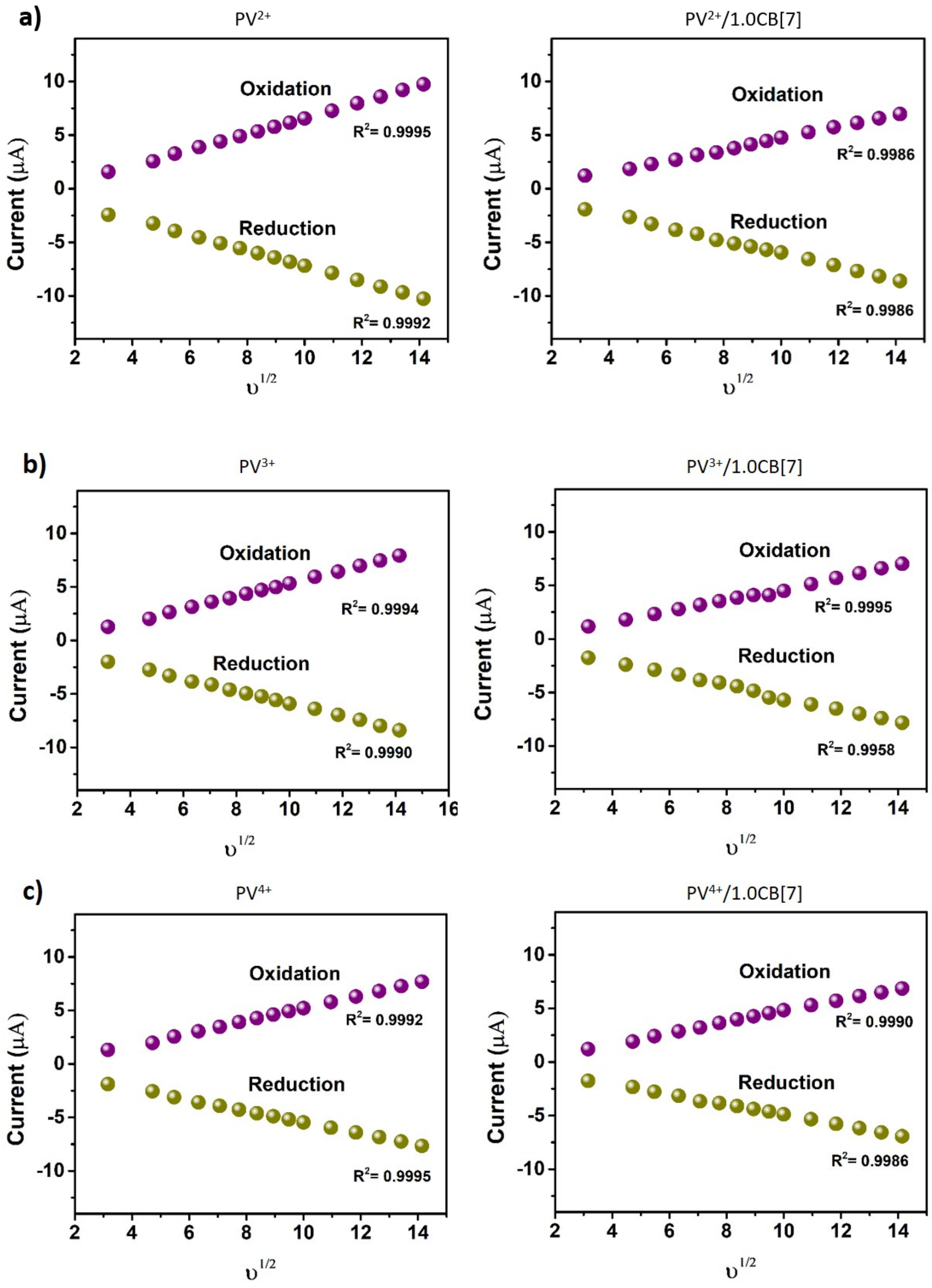


Fig. S3 Current vs. scan rate plot of PV^{2+}, PV^{3+} as well as PV^{4+} and their 1:1 complex.

Binding constant

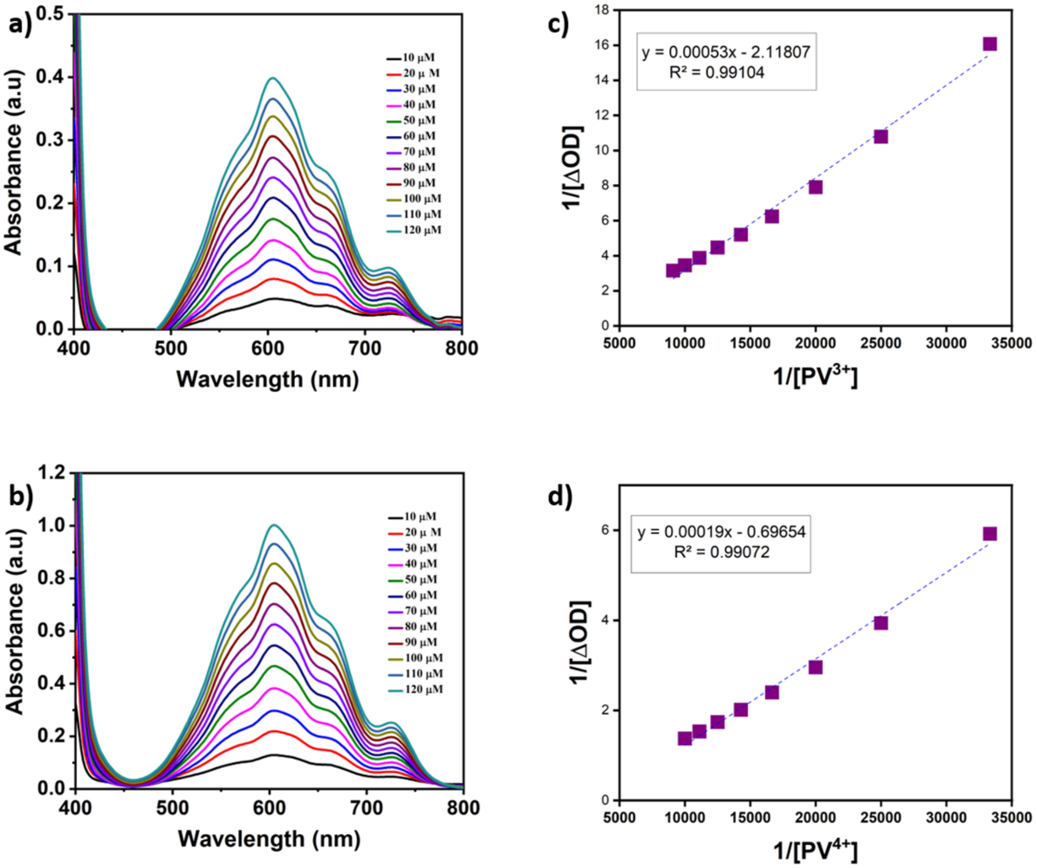


Fig. S4. Absorption spectrum of a) PV^{3+} radical cation- CB[7] b) PV^{4+} radical cation - CB[7]. Benesi-Hildebrand plot of c) PV^{3+} radical cation- CB[7] b) PV^{4+} radical cation - CB[7]. Binding constant (K$_a$)values for PV^{3+} and PV4^{+} radical complexes are 3.99 x 10^{3} M^{-1} and 3.67 x 10^{3} M^{-1} respectively (0.1 M PBS buffer, RT).

UV-Vis absorbance trend

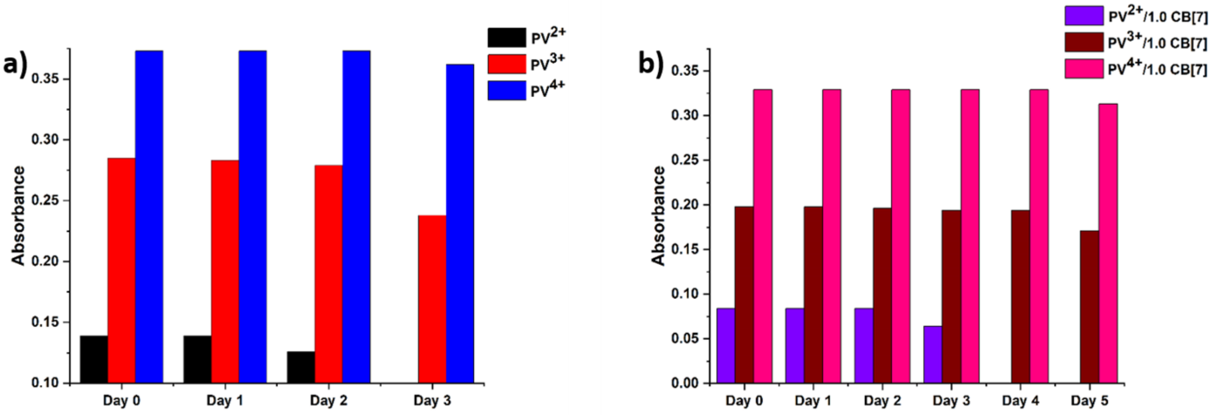


Fig. S5. UV-vis absorbance trend of (a) PV^{2+}, PV^{3+} and PV^{4+} monocation radicals (b) PV^{2+}, PV^{3+}, and PV^{4+} 1:1 radical cation complexes

Diffusion Coefficient

Material	Oxidation D (cm^2/s)	Reduction D (cm^2/s)
PV^{2+}	$6.3x10^{-6}$	$5.8x10^{-6}$
PV^{2+}/1.0 CB[7]	$3.2x10^{-6}$	$4.2x10^{-6}$
PV^{3+}	$4.2x10^{-6}$	$3.8x10^{-6}$
PV^{3+}/1.0 CB[7]	$3.1x10^{-6}$	$3.6x10^{-6}$
PV^{4+}	$3.9x10^{-6}$	$3.1x10^{-6}$
PV^{4+}/1.0 CB[7]	$3.0x10^{-6}$	$2.4x10^{-6}$

Diffusion coefficient was calculated using Randles-Sevick equation from the I vs $\nu^{1/2}$ plot