Supporting Information

Synergistic Effect of Hydrophobic and Hydrogen Bonding Interactions-Driven Viologen-Pyranine Charge-Transfer Aggregates: Adenosine Monophosphate Recognition

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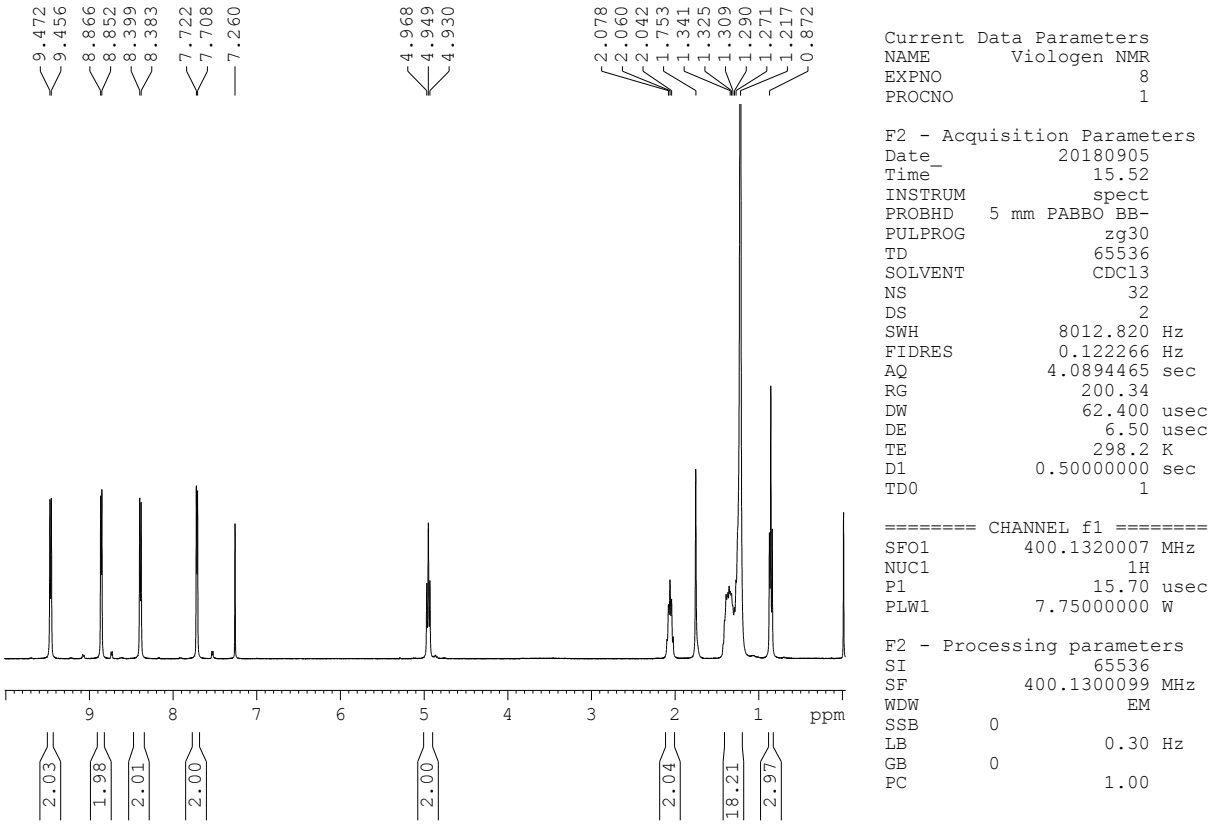

Figure S1: ^{1}H NMR spectrum of compound 1

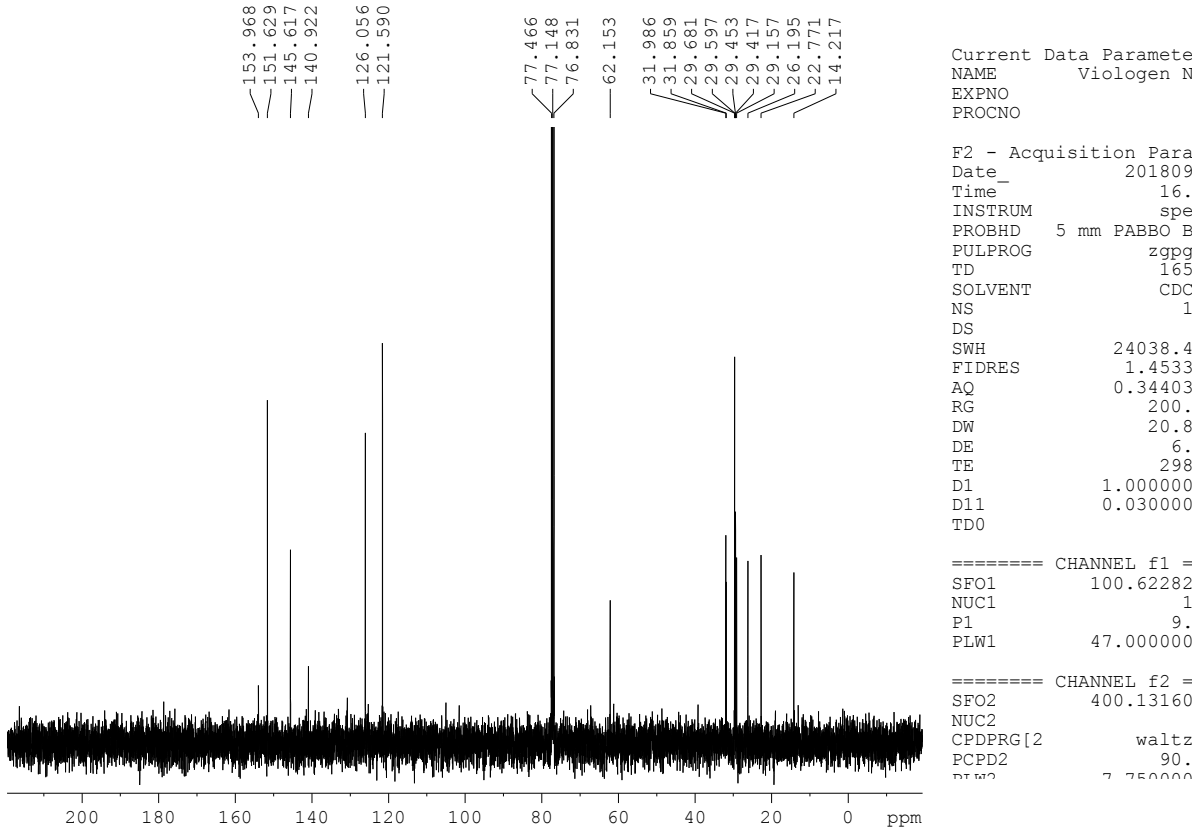

Figure S2: ^{13}C NMR spectrum of compound 1

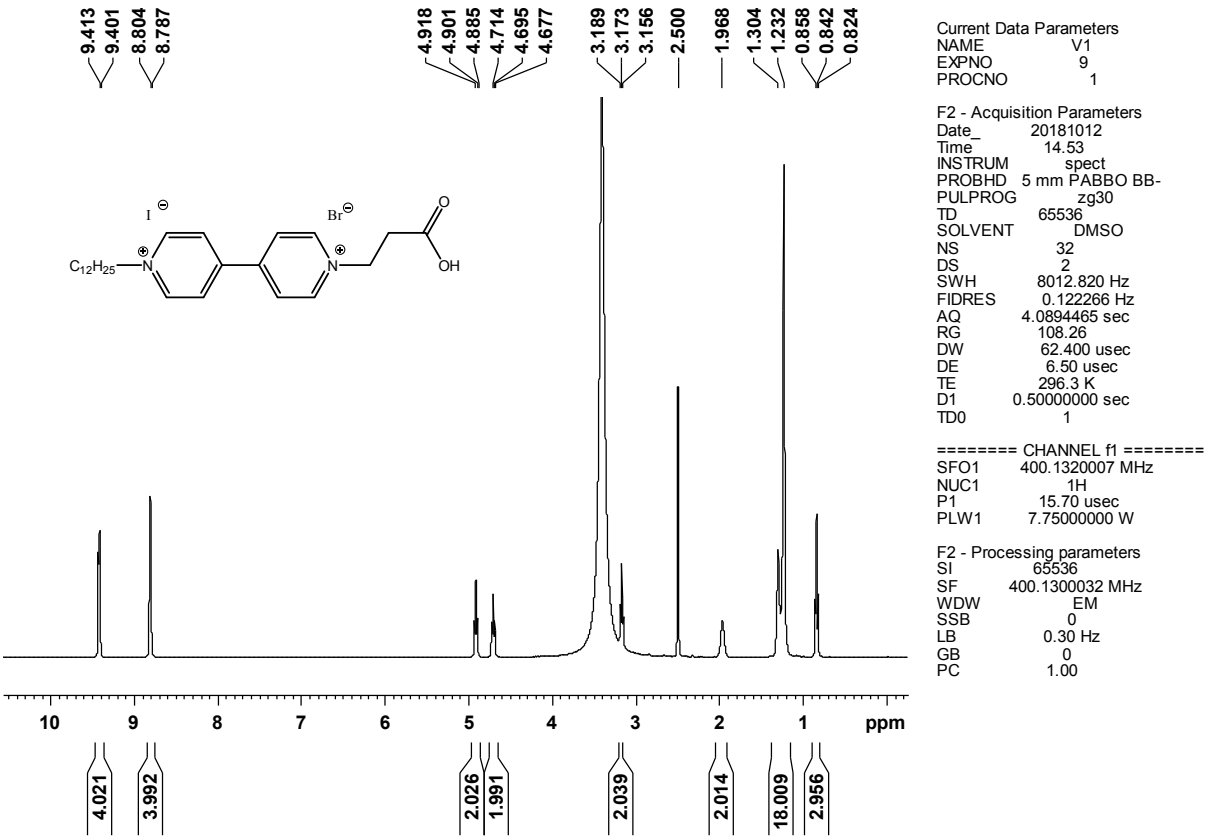

Figure S3: ^{1}H NMR spectrum of V1

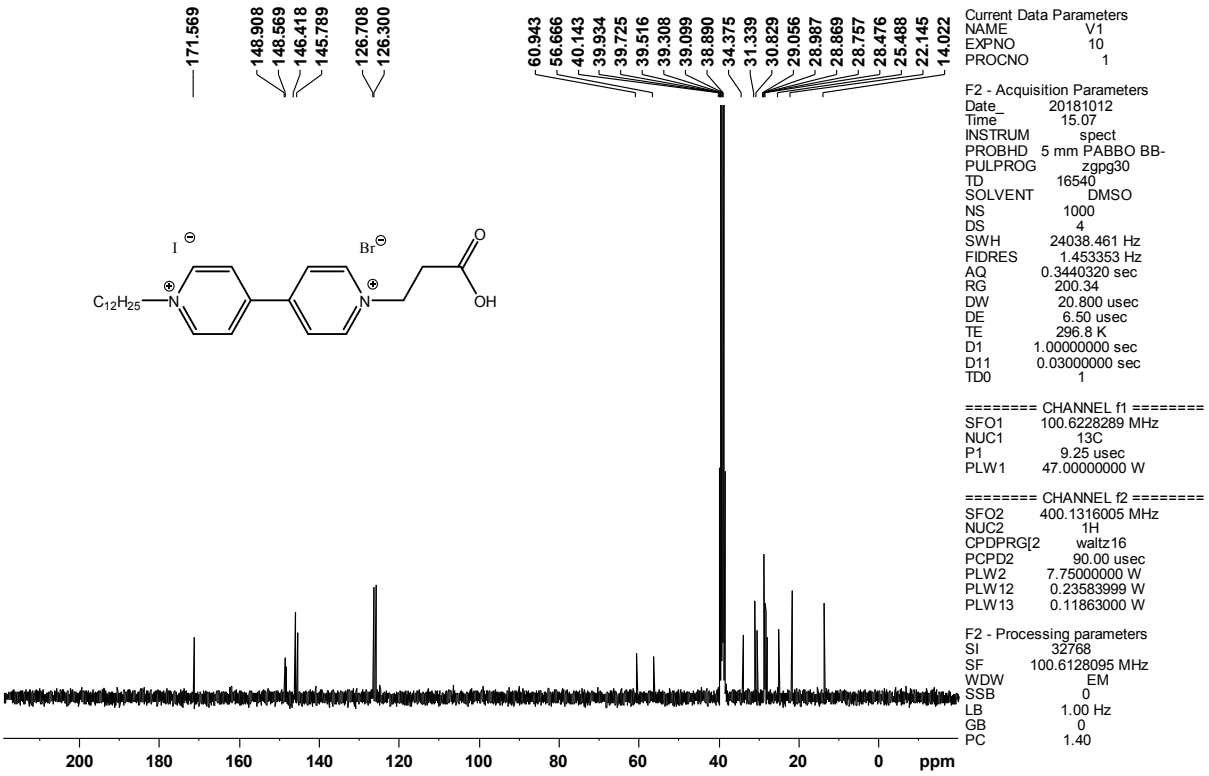

Figure S4: ^{13}C NMR spectrum of V1

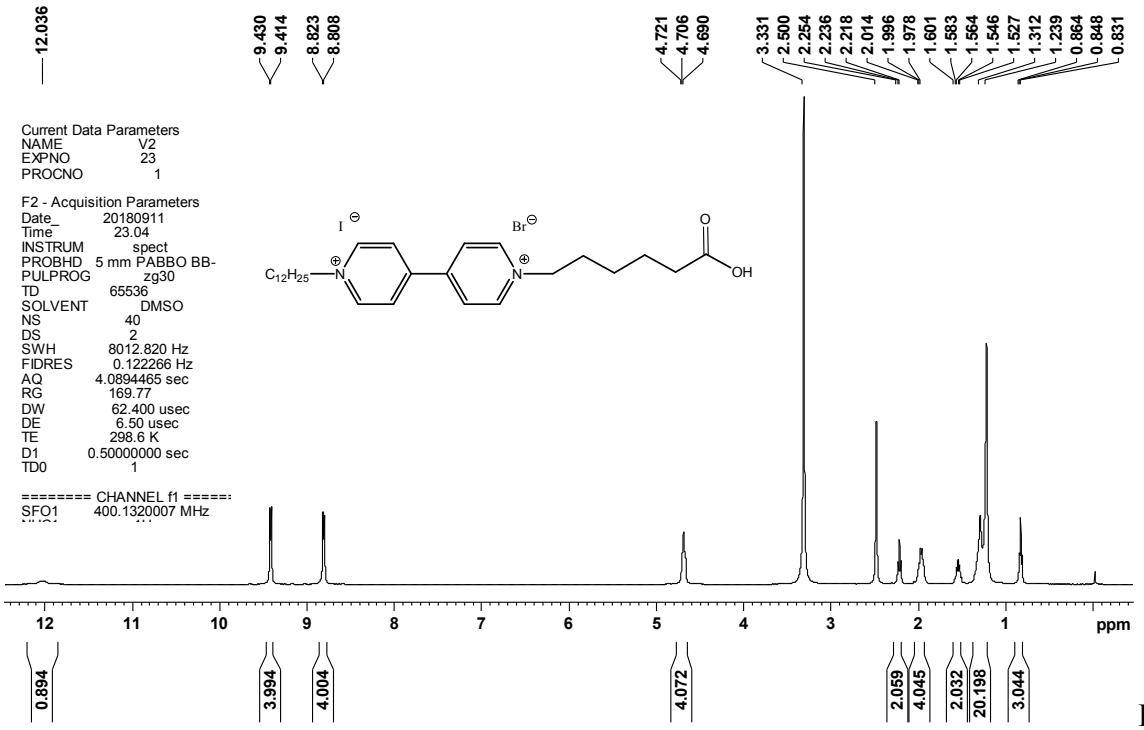

Figure S5: ^{1}H NMR spectrum of V2

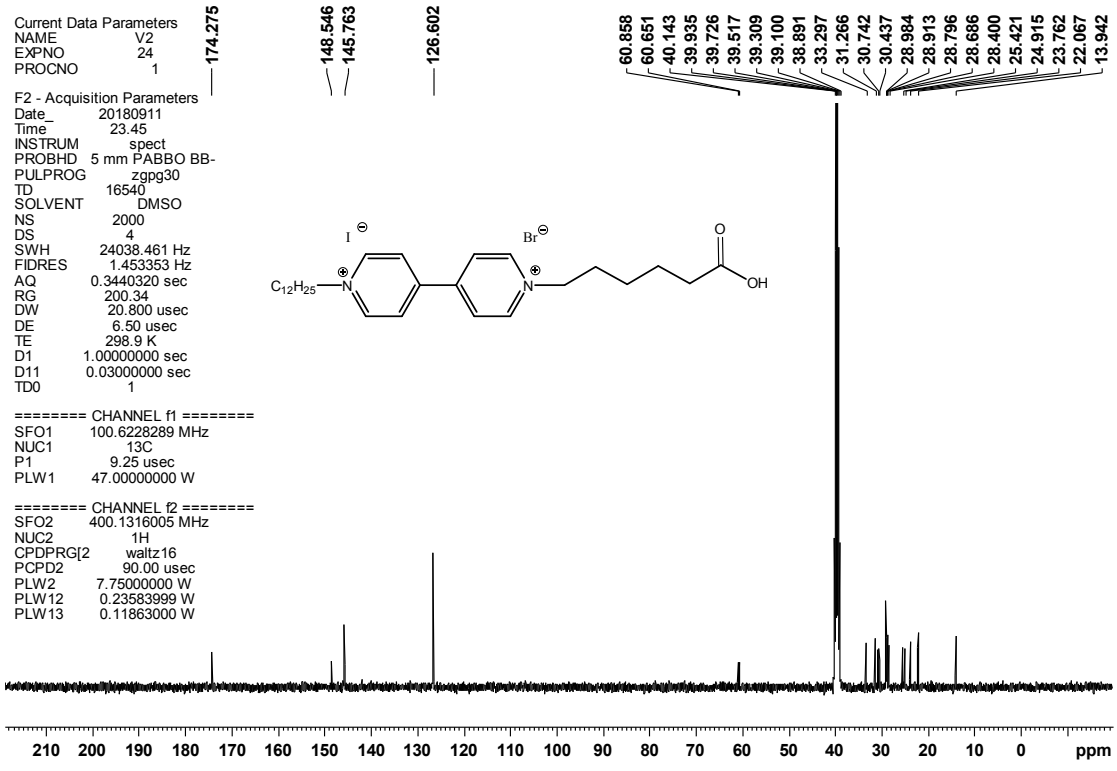

Figure S6: ^{13}C NMR spectrum of V2

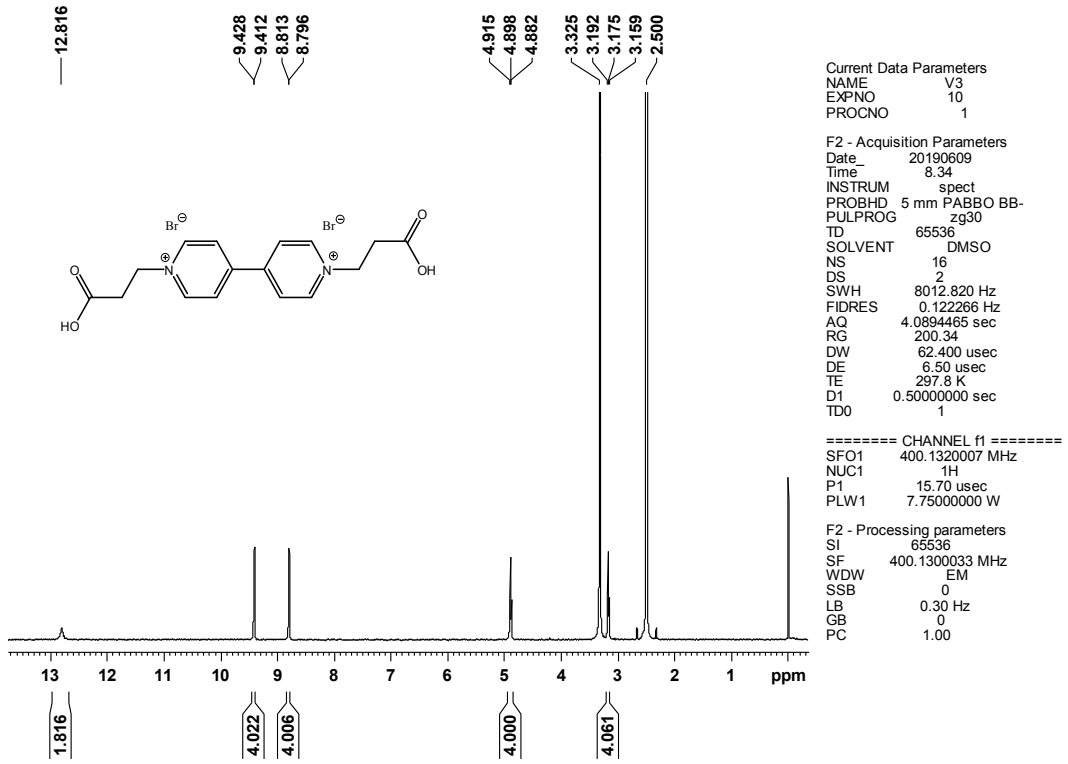

Figure S7: ^{1}H NMR spectrum of V3

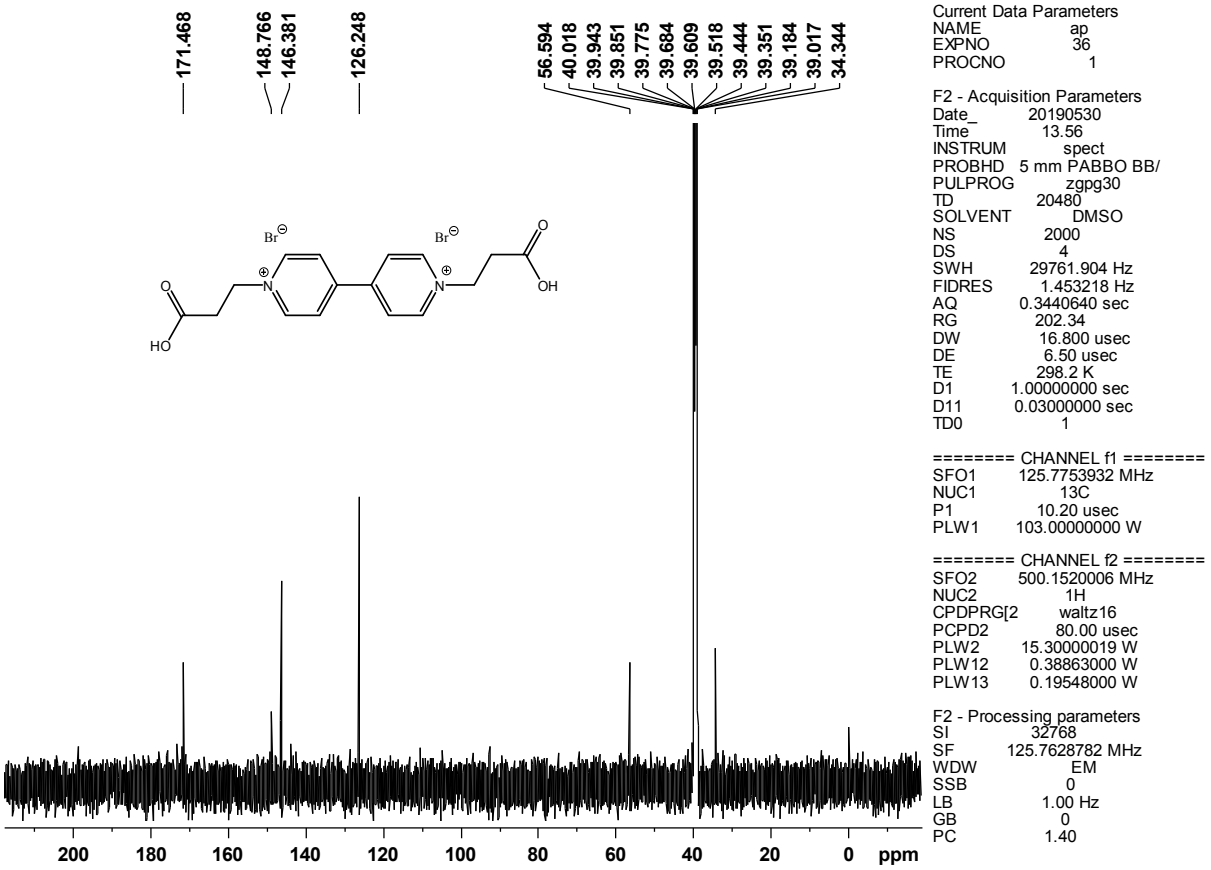

Figure S8: ^{13}C NMR spectrum of V3

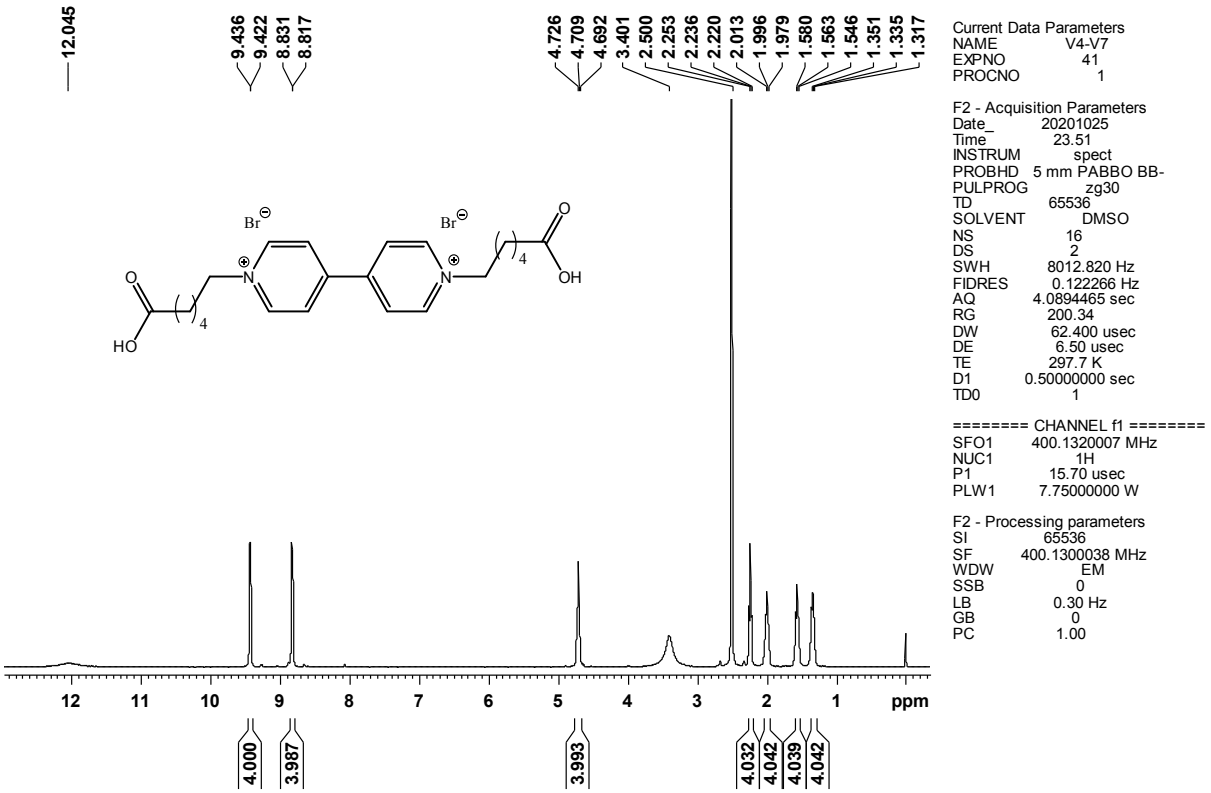

Figure S9: ^{1}H NMR spectrum of V4

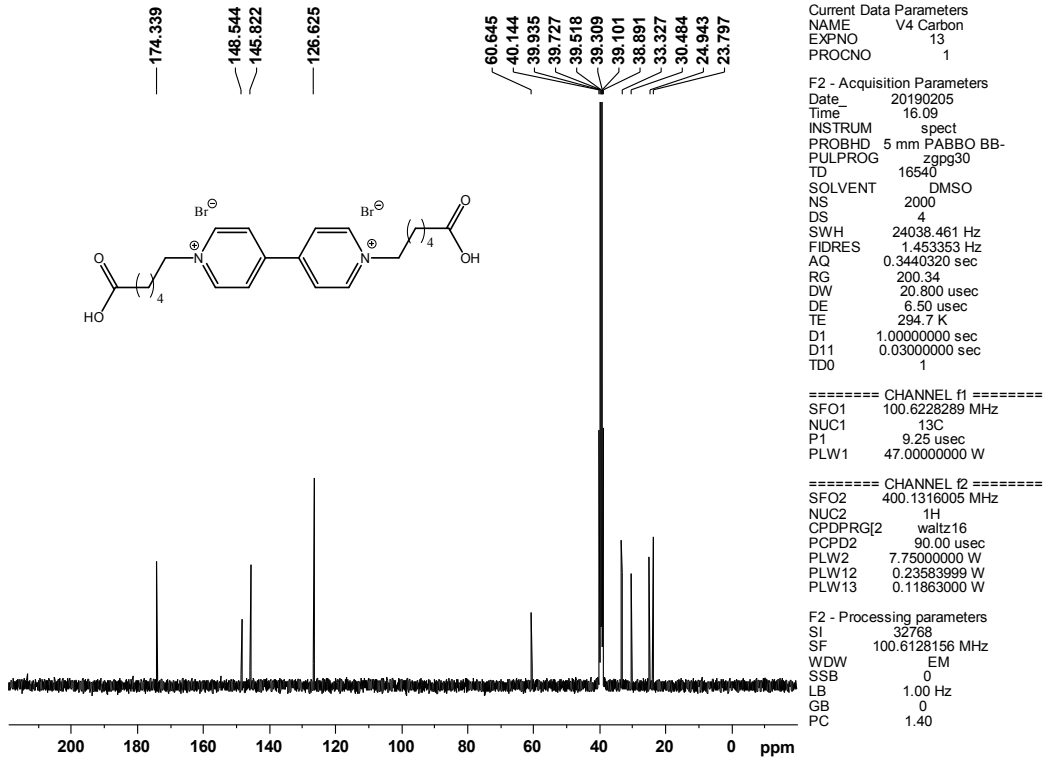

Figure S10: ^{13}C NMR spectrum of V4

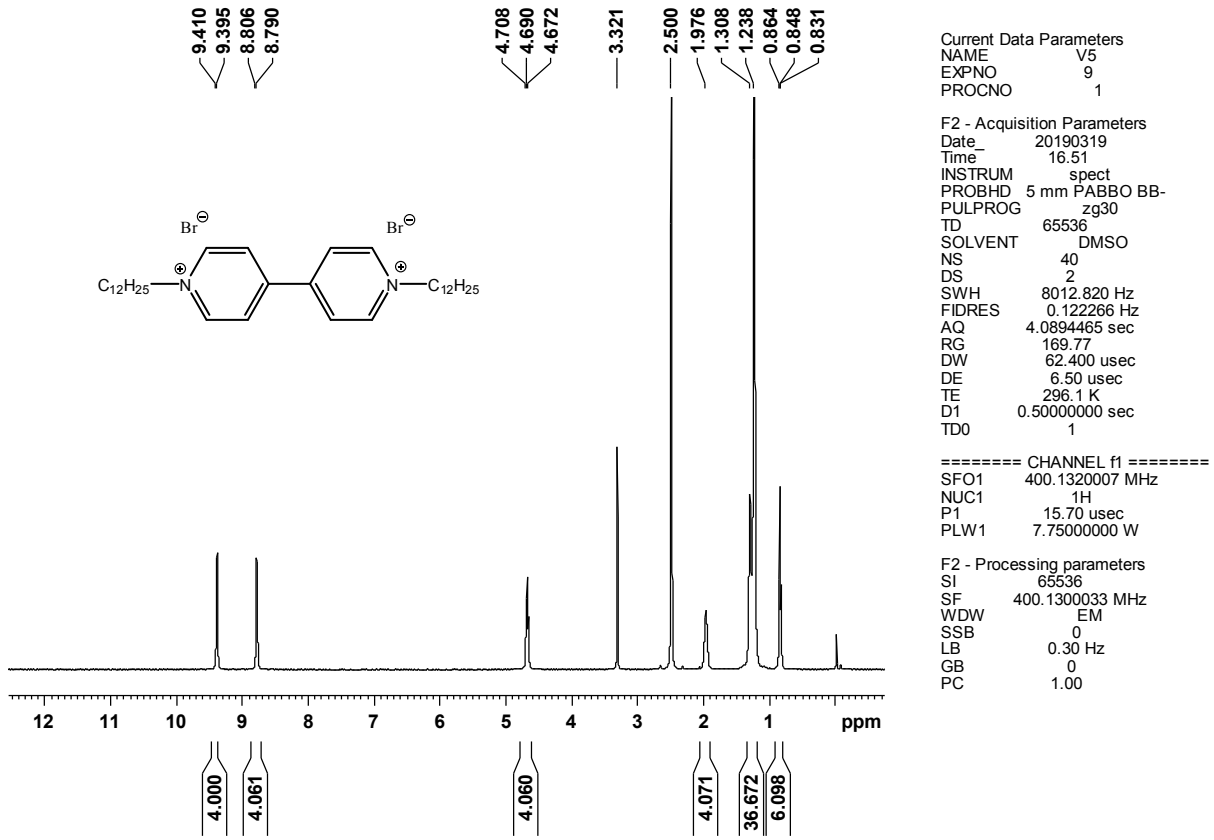

Figure S11: ^{1}H NMR spectrum of V5

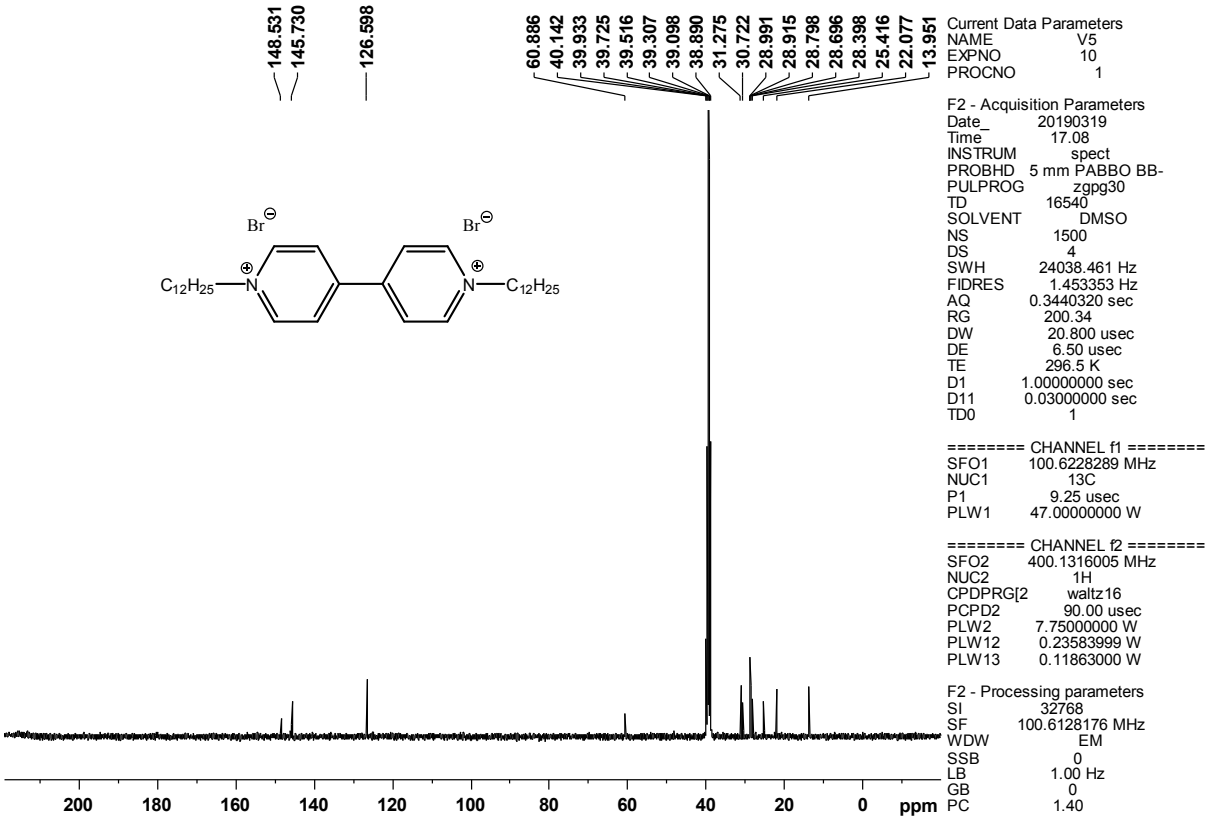

Figure S12: ^{13}C NMR spectrum of V5

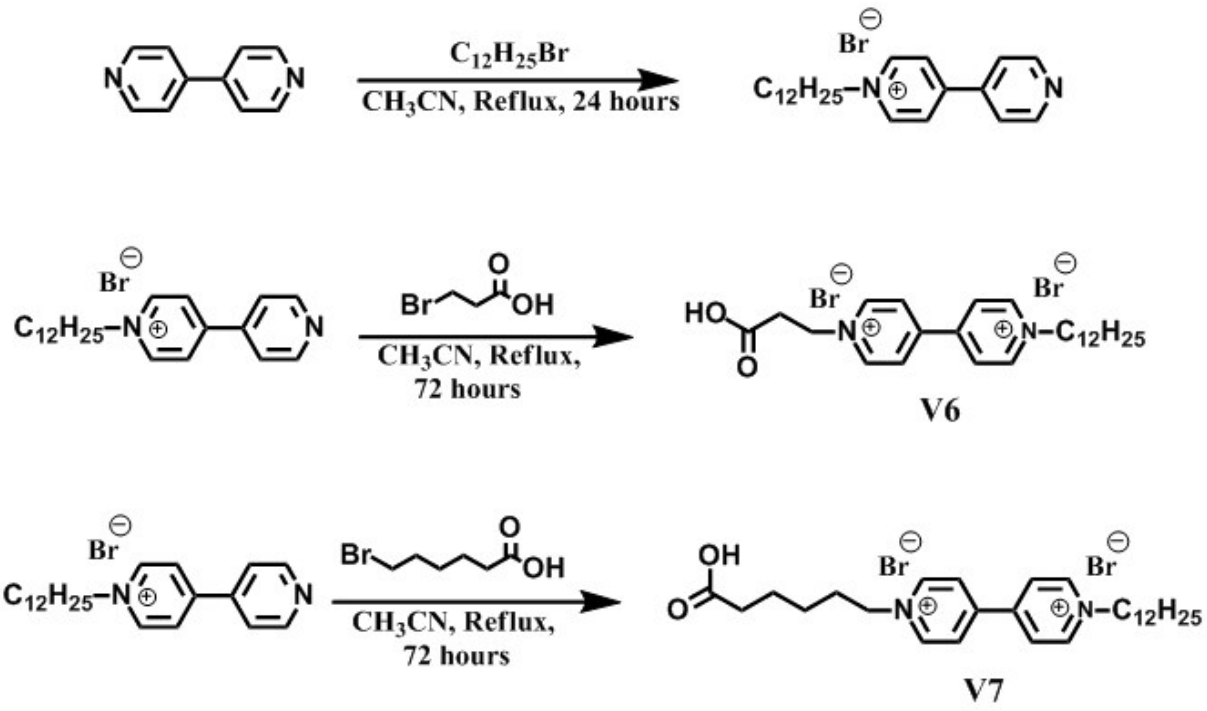

Figure S13 Synthetic scheme for viologen derivatives V6 and V7

V6 and V7 are synthesized by reacting 1-dodecyl-4-(4-pyridyl)pyridiniumbromide with 3-bromopropionic acid and 6-bromohexanoic acid (Figure S13) according to the procedure adopted for synthesizing V1 and V2.

V6 NMR: ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): δ =12.76 (broad singlet), 9.42-9.34 (t, 4H), 8.81-8.79 (d, 4H), 4.92-4.89 (t, 2H), 4.71-4.68 (t, 2H), 3.19-3.16 (t, 2H), 1.99-1.96 (t, 2H), 1.31-1.24 (m, 18H), 0.87-0.84 (t, 3H) ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ = 171.5, 148.8, 148.5, 146.4, 145.8, 126.6, 126.2, 60.9, 56.6, 34.3, 31.3, 30.8, 29.0, 28.9, 28.8, 28.7, 28.4, 25.4, 22.1, 13.9. ESI-HRMS: calculated for $C_{25}H_{38}Br2N_2O_2$ 556.1290; found m/z 559.1264 $(M+H)^+$, 581.1189 $(M+Na)^+$.

V7 NMR: ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ =12.05 (broad singlet), 9.41-9.40 (d, 4H), 8.81-8.79 (d, 4H), 4.71-4.67 (m, 4H), 2.25-2.22 (t, 2H), 2.02-1.96 (q, 4H), 1.59-1.53 (q, 4H), 1.36-1.23 (m, 20H), 0.86-0.84 (t, 3H) ^{13}C NMR (125 MHz, DMSO-d_6, 25°C): δ = 174.3, 148.6, 145.8, 126.6, 60.9, 607, 33.3, 31.3, 30.8, 30.5, 29.0, 28.9, 28.8, 28.7, 28.4, 25.4, 24.9, 23.8, 22.1, 14.0. ESI-HRMS: calculated for $C_{28}H_{44}B2rN_2O_2$ 598.1761; found m/z 621.1663 $(M+Na)^+$.

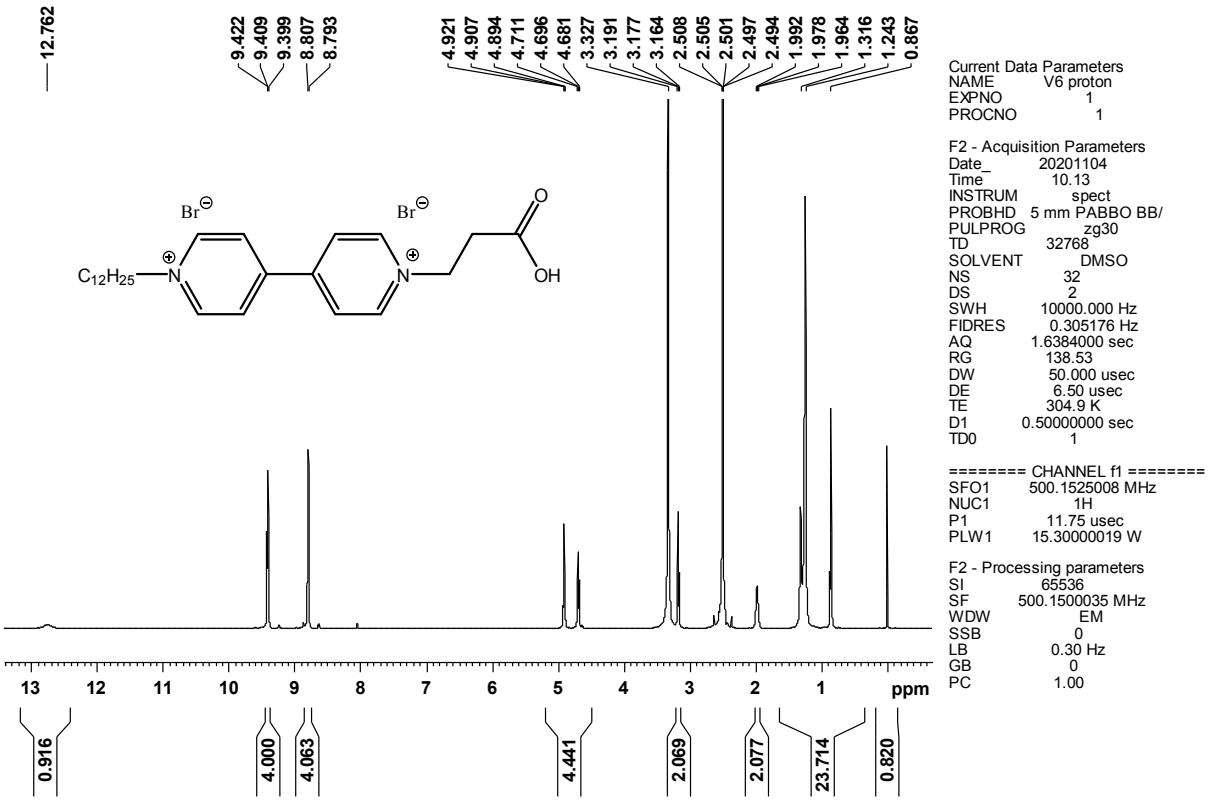

Figure S14: ^{1}H NMR Spectrum of V6

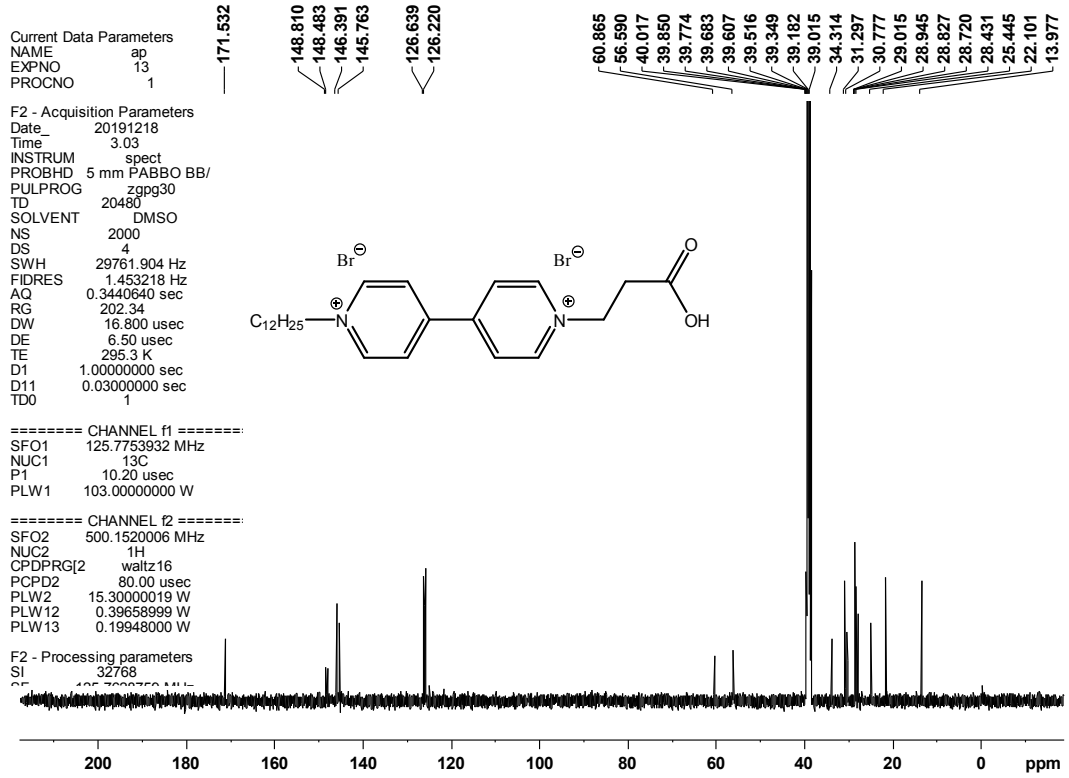

Figure S15: ^{13}C NMR Spectrum of V6

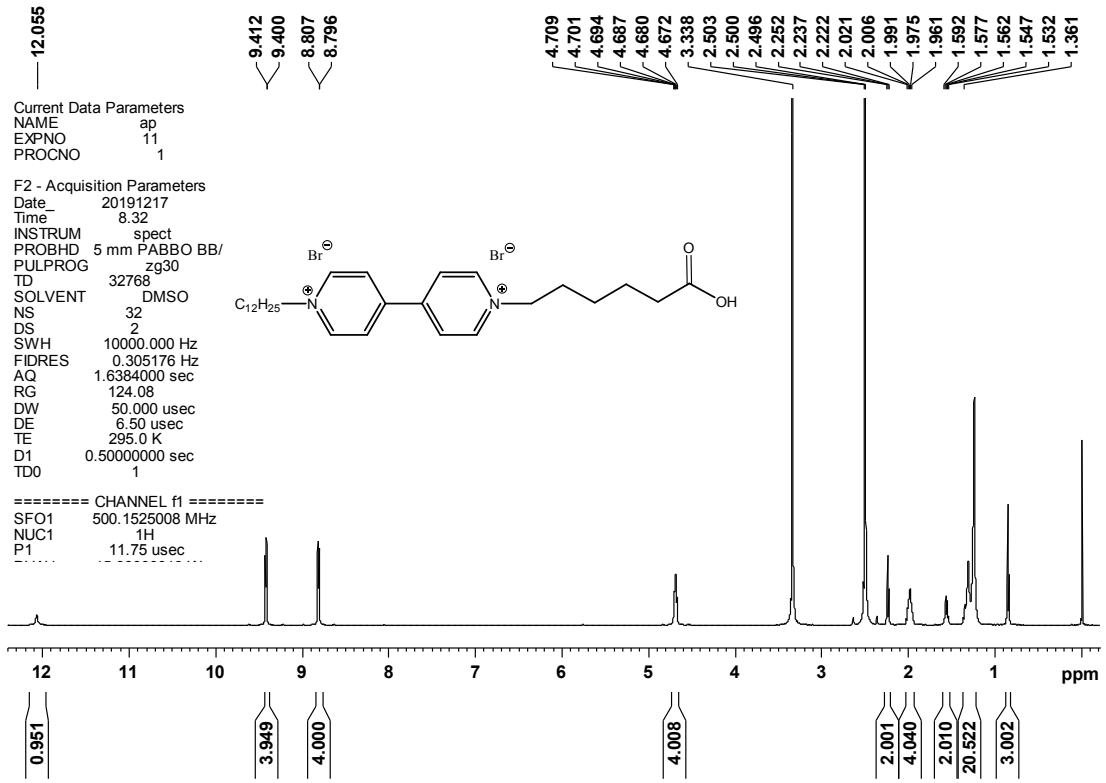

Figure S16: ^{1}H NMR Spectrum of V7

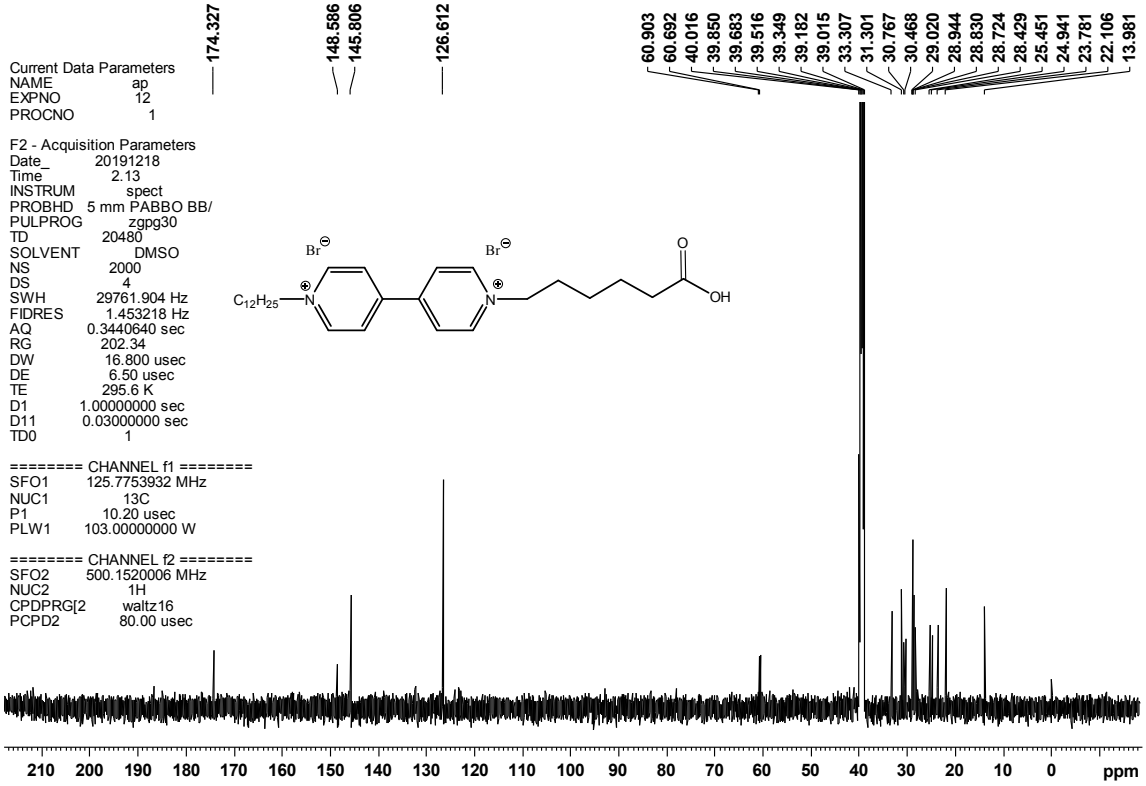

Figure S17: ^{13}C NMR Spectrum of V7

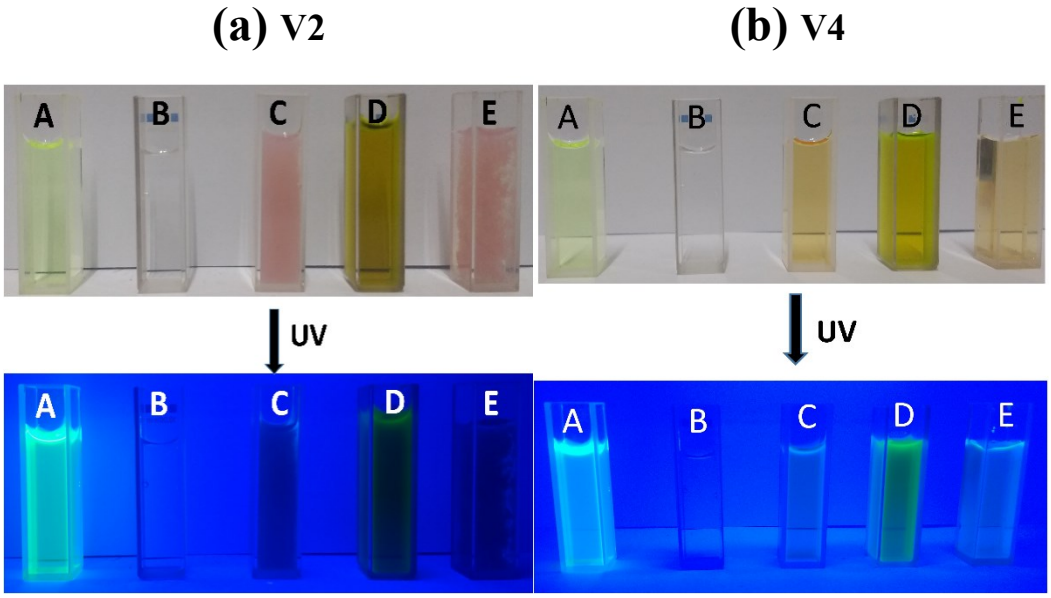

Figure S18 (a) Photographs of [V2-Pyr] and [V4-Pyr] CT aggregates in aqueous medium. **A**: Pyranine; **B**: V2; **C**: V2-Pyranine complex; **D:** V2-Pyranine complex + 20µL of 1M NaOH; **E**: D + 20 µL of 1M HCl; **(b)A**: Pyranine; **B**: V4; **C**: V4-Pyranine complex; **D**: V4-Pyranine complex + 20µL of 1M NaOH; **E**: D + 20 µL of 1M HCl; (*Top* – Photographs of aqueous solutions and suspensions taken under room light; *Bottom* – Photographs of aqueous solutions and suspensions taken under UV irradiation at 365 nm)

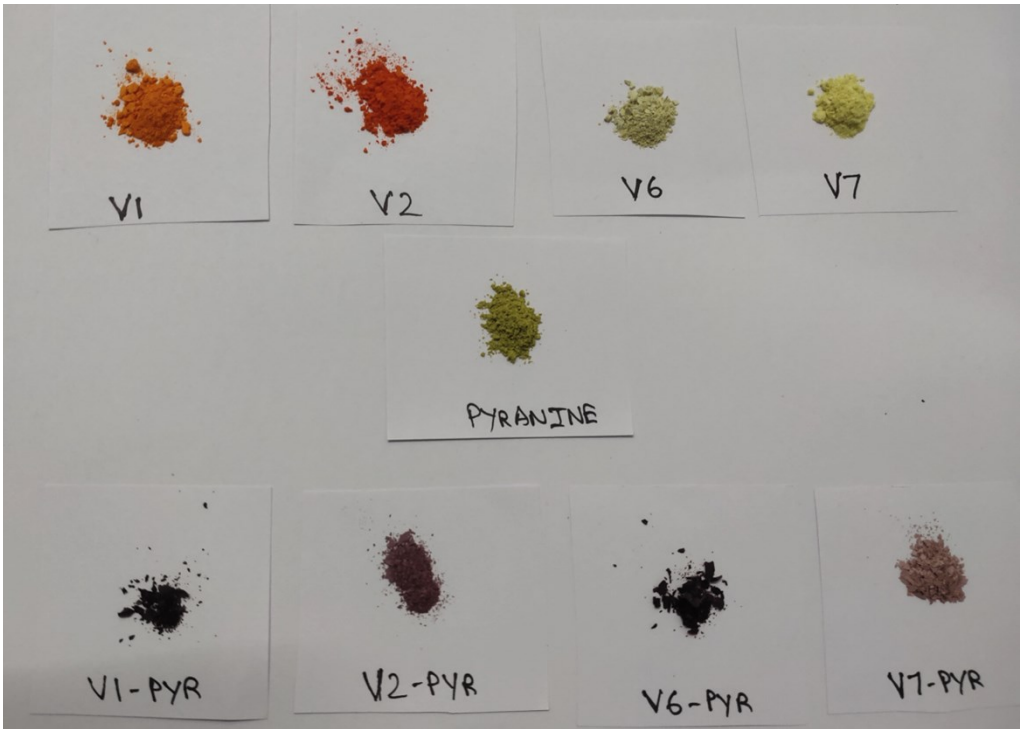

Figure S19: Visual appearance of the viologen derivatives, pyranine and the corresponding CT aggregates after vacuum drying.

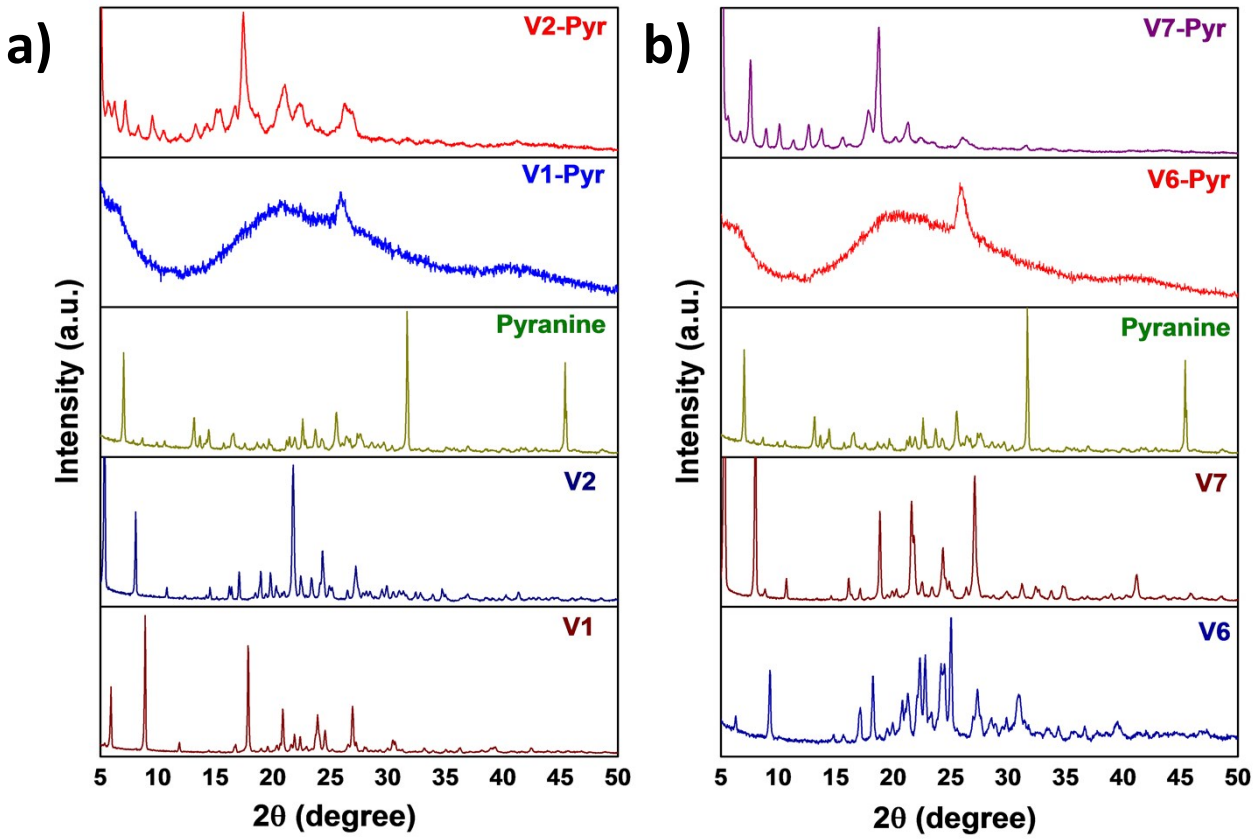

Figure S20 (a) PXRD spectral patterns of V1, V2, Pyranine, [V1-Pyr] and [V2-Pyr] complexes. **(b)** PXRD patterns of V6, V7, Pyranine and [V6-Pyr] and [V7-Pyr] complexes.

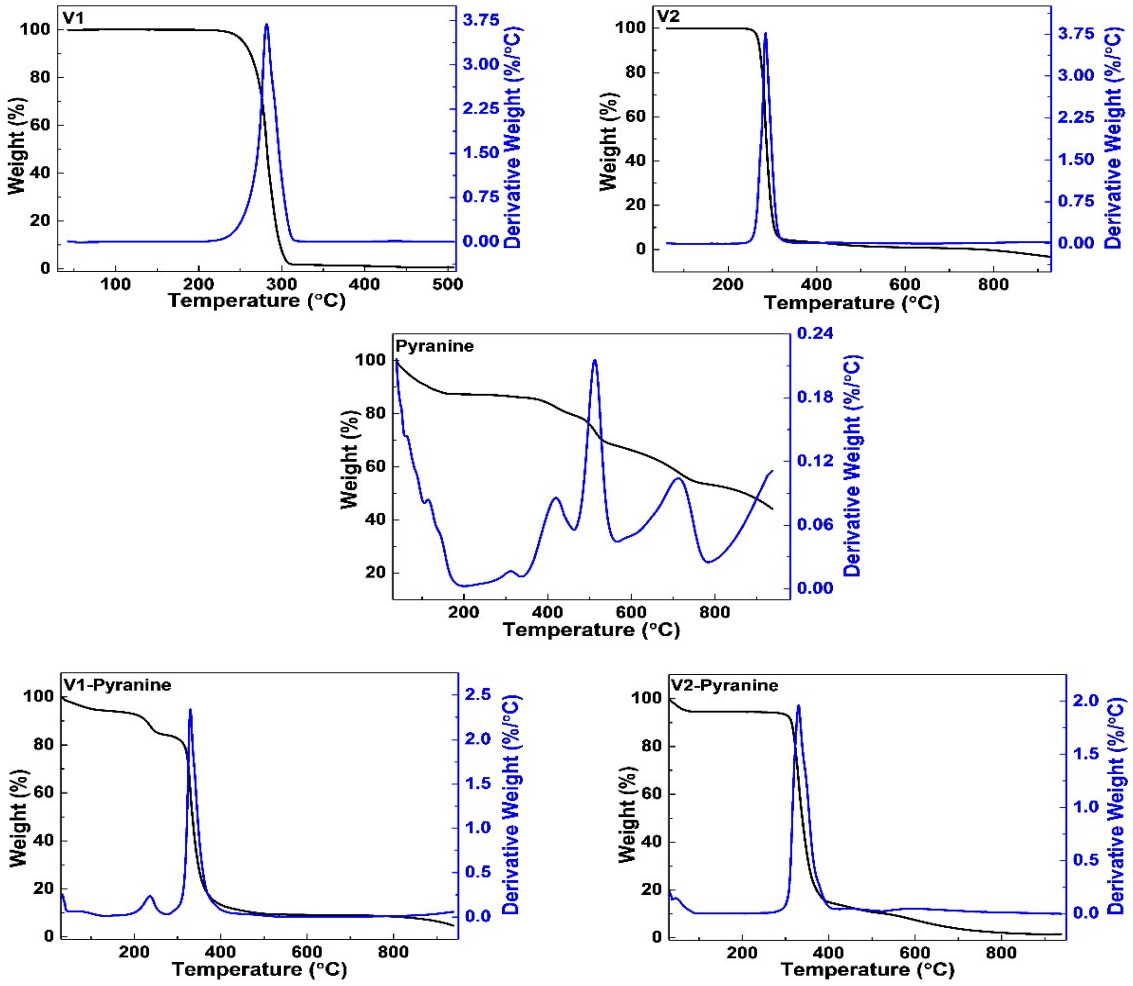

Figure S21. TG-DTA analysis of of V1, V2, Pyranine, and their charge transfer complexes [V1-Pyr] and [V2-Pyr].

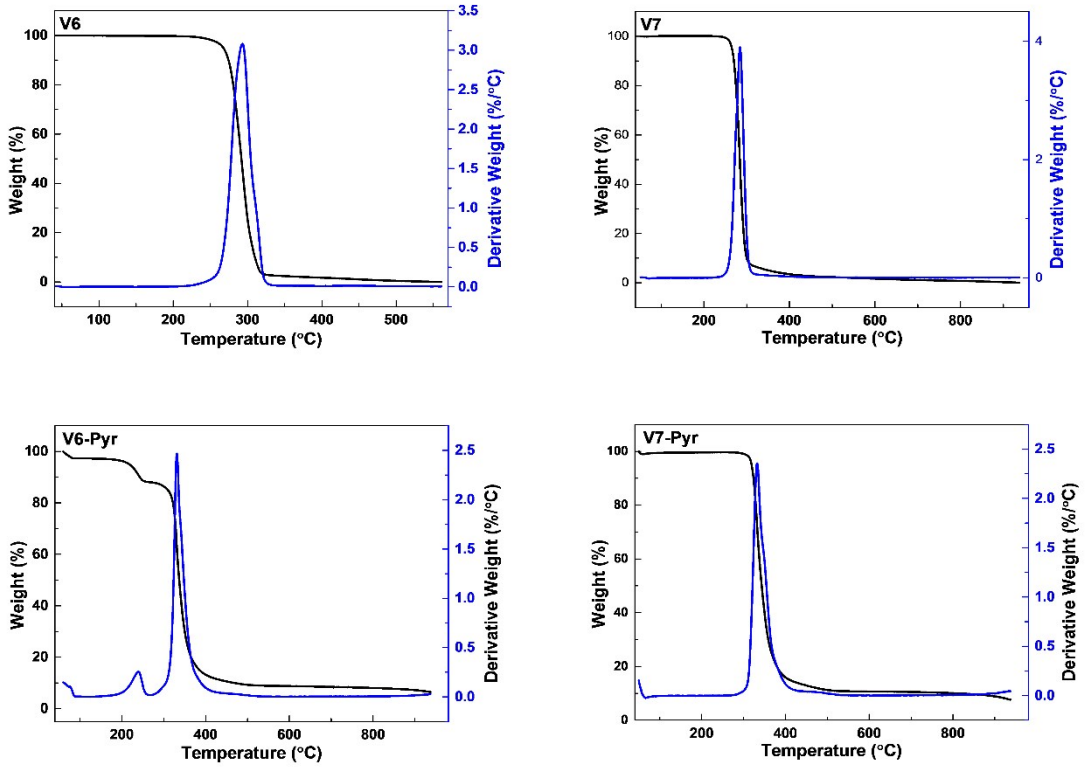

Figure S22. TG-DTA analysis of V6, V7, Pyranine, and their charge transfer complexes [V6-Pyr] and [V7-Pyr].

Both V1 and V2 exhibited single stage decomposition within temperature ranges of 235°C to 313°C and 253°C to 339.69°C (Figure S17). Within 340°C, V1 decomposed upto 98% of its weight and V2 decomposed upto 95% of its initial weight. Pyranine exhibited incomplete decomposition upto 44% of its initial weight upto 937°C. In stark contrast to the precursors, [V1-Pyr] CT aggregate exhibited four stages of decomposition; 6% weight loss from 93 to 99°C (loss of adsorbed moisture), 10% weight loss from 189 to 286° C, a major step of decomposition amounting to 72% weight loss around 298°C to 431°C. Ultimately, a 6% weight loss from 431°C to 921°C was seen leaving behind a residue of less than 6% of its initial weight. On the other hand, [V2-Pyr] exhibited three stages of decomposition, the first one amounting to the loss of adsorbed moisture (6%) upto 183°C and a major step of decomposition amounting to 79% from 295.81°C to 405°C. The remaining 15% of residual material decomposed from 405°C to 921°C leaving behind a residue of less than 1.5%. TG-DTA data of viologens V6, V7 and their corresponding CT aggregates [V6-Pyr] and [V7-Pyr] too exhibited decomposition pathways identical to [V1-Pyr] and [V2-Pyr] without a marked deviation (Figure S21, SI).

[V1-Pyr]	Experimental (%)	Theoretically calculated (%)	
		(1:1)	(3:2)
Carbon	57.33	56.15	61
Hydrogen	5.21	5.17	6.12
Nitrogen	3.75	3.19	3.98
Oxygen	-	21.89	19.74
Sulphur	-	10.96	9.13

Table S1 CHN analysis data of [V1-Pyr] CT aggregates, calculated for 1:1 and 3:2 aggregates of V1 and pyranine.

[V2-Pyr]	Experimental (%)	Theoretically calculated (%)	
		(1:1)	(3:2)
Carbon	58.82	57.50	62.39
Hydrogen	5.14	5.59	5.95
Nitrogen	3.53	3.04	3.76
Oxygen	-	20.89	18.63
Sulphur	-	10.46	9.13

Table S2 CHN analysis data of [V2-Pyr] CT aggregates, calculated for 1:1 and 3:2 aggregates of V2 and pyranine.

[V6-Pyr]	Experimental (%)	Theoretically calculated (%)	
		(1:1)	(3:2)
Carbon	60.41	56.15	61
Hydrogen	5.47	5.17	6.12
Nitrogen	3.82	3.19	3.98
Oxygen	-	21.89	19.74
Sulphur	-	10.97	9.13

Table S3 CHN analysis data of [V6-Pyr] CT aggregates, calculated for 1:1 and 3:2 aggregates of V6 and pyranine.

[V7-Pyr]	Experimental (%)	Theoretically calculated (%)	
		(1:1)	(3:2)
Carbon	60.27	57.50	62.39
Hydrogen	5.62	5.59	5.95
Nitrogen	3.63	3.04	3.76
Oxygen	-	20.89	18.63
Sulphur	-	10.46	9.13

Table S4 CHN analysis data of [V7-Pyr] CT aggregates, calculated for 1:1 and 3:2 aggregates of V7 and pyranine.

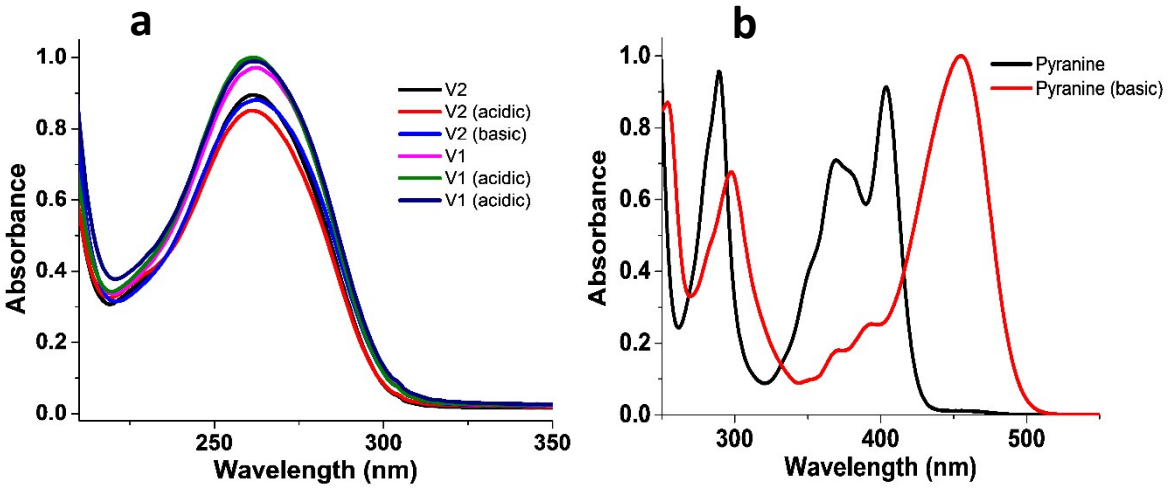

Figure S23 pH dependent optical properties of (a) Viologen derivatives (V1, V2) at different pH conditions (acidic, pH = 1and basic, pH = 13) and (b) Pyranine.

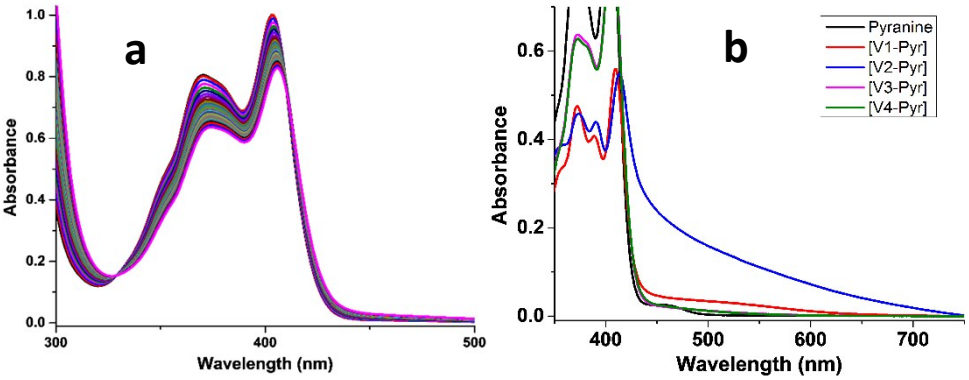

Figure S24. (a) Absorption spectra of 50 µM pyranine upon stepwise addition of V3 (from 0 µM to 120 µM). **(b)** Depiction of predominant Mie scattered absorbance for V2-Pyr and V1-Pyr.

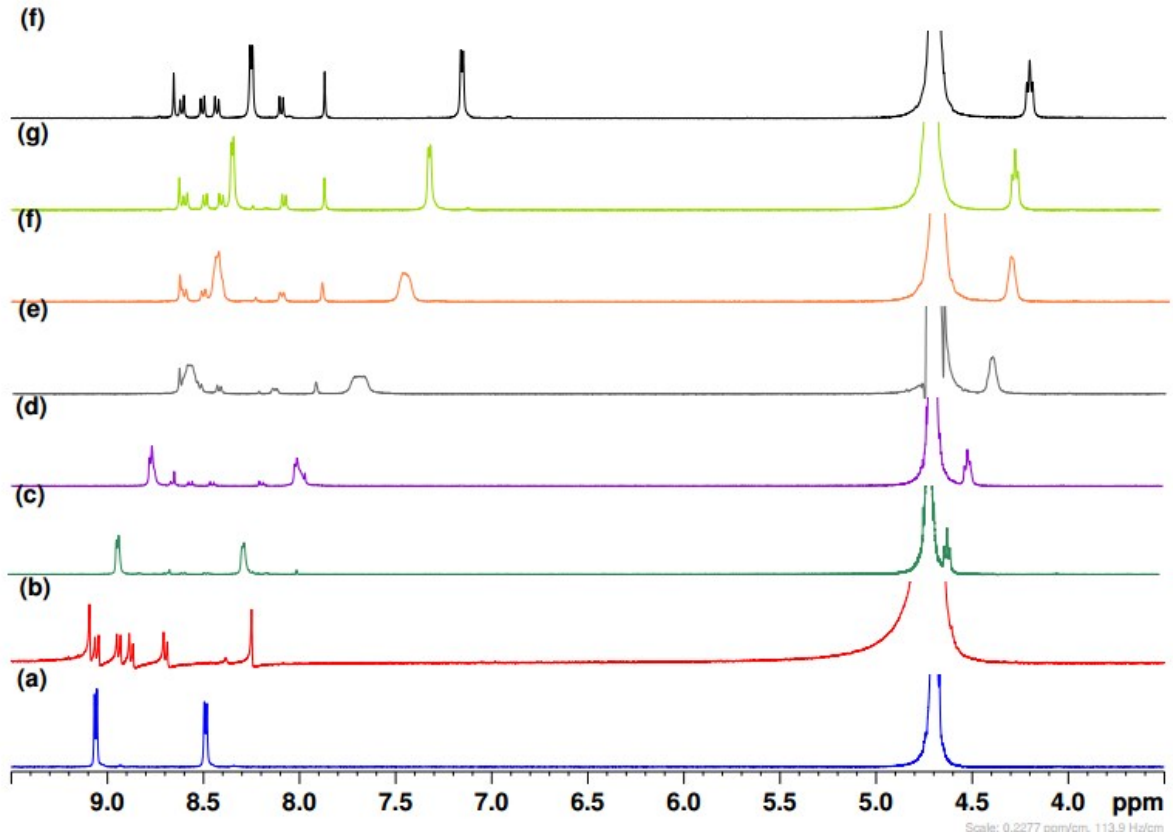

Figure S25 NMR titration of V4 with pyranine in D_2O: (a) V4, (b) Pyranine (pyr), (c) V4 + 0.25 eq. pyr, (d) V4 + 0.5 eq. pyr, (e) V4 + 0.75 eq. pyr, (f) V4 + 1 eq. pyr, (g) V4 + 1.25 eq. pyr, (h) V4 + 1.5 eq. pyr

Figure S26: Redox reactions of viologens

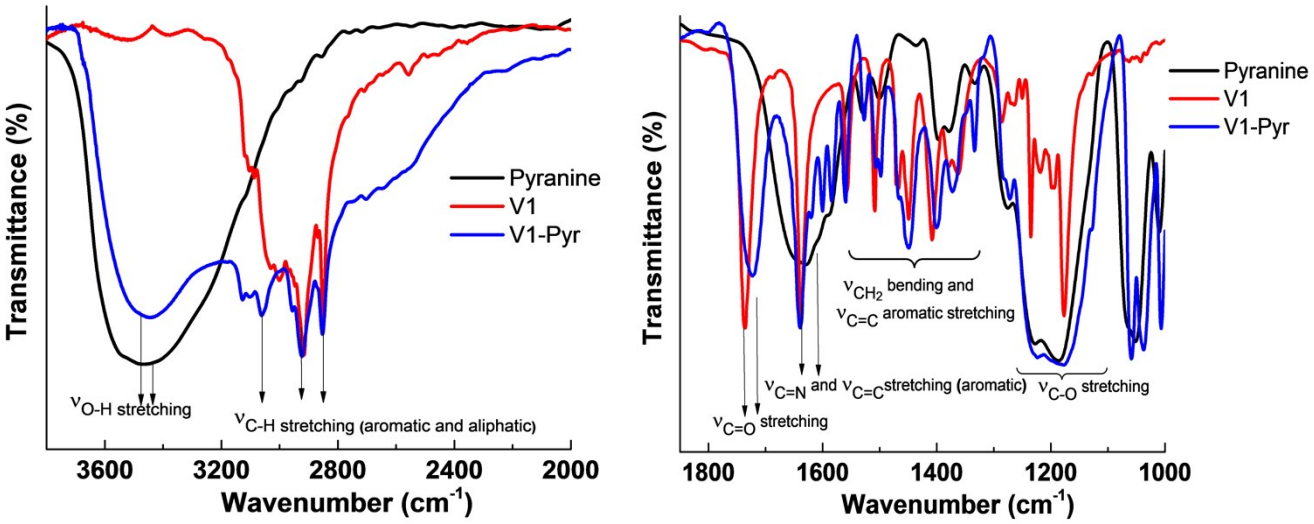

Figure S27: IR Spectra of V1, Pyranine and [V1-Pyr] aggregates.

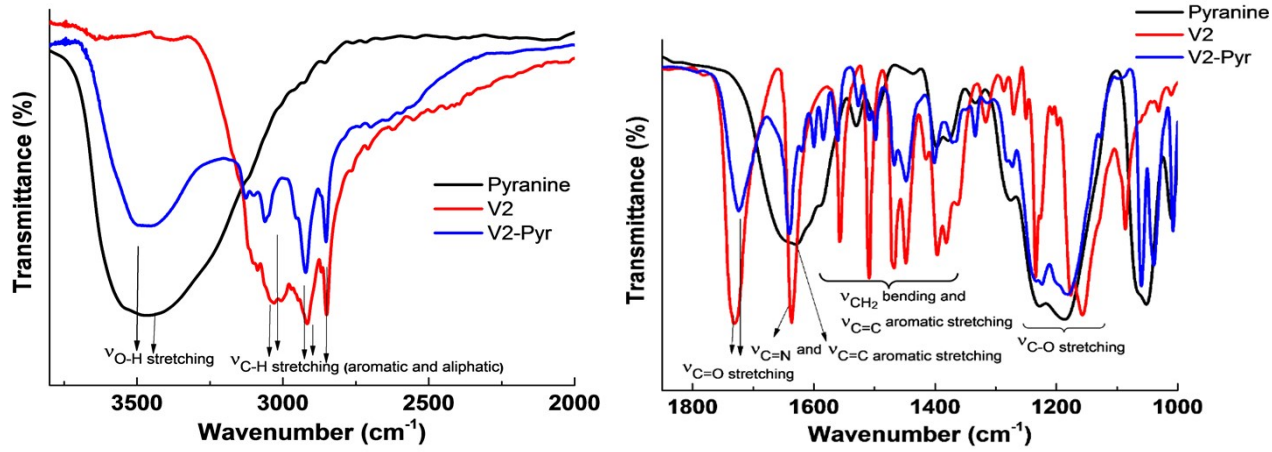

Figure S28: IR Spectra of V2, Pyranine and [V2-Pyr] aggregates.

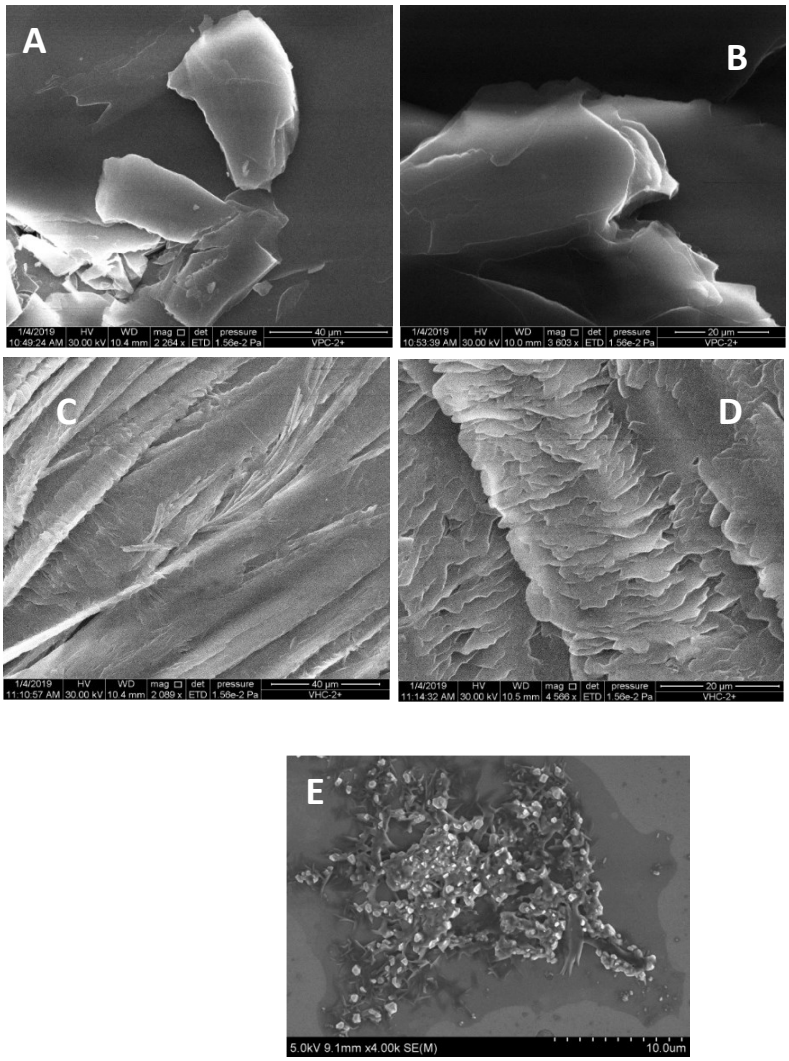

Figure S29: SEM Images of (A) and (B) - V1, (C) and (D) - V2, (E) – [V4-Pyr] CT complex

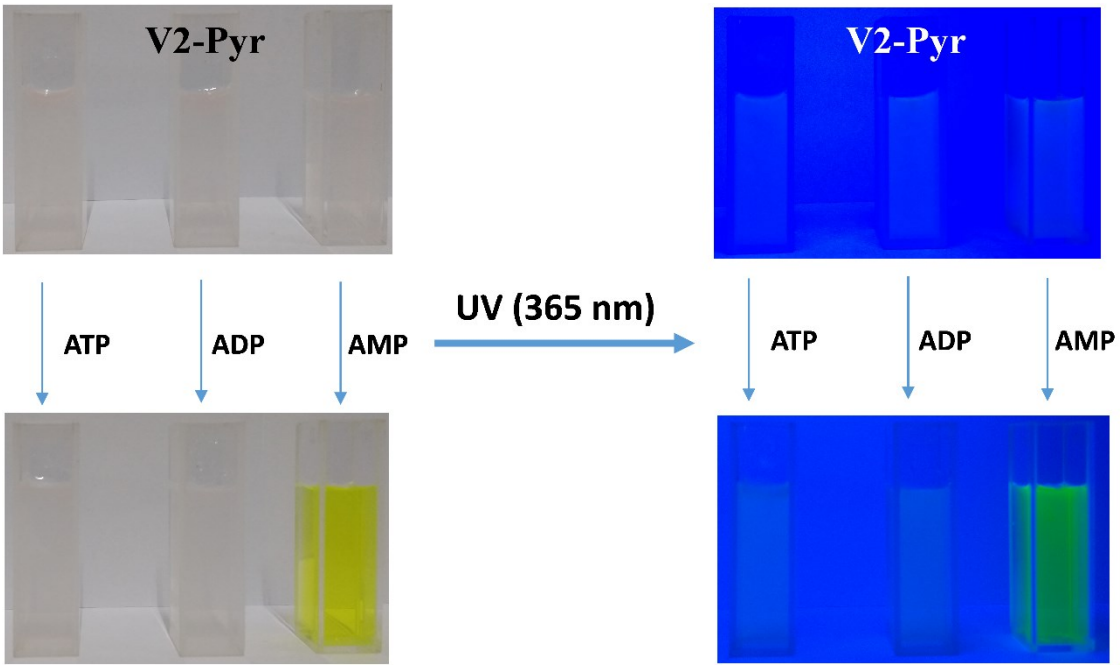

Figure S30 Visual appearance of disaggregation induced recognition of AMP by [V2-Pyr] CT aggregates in water.

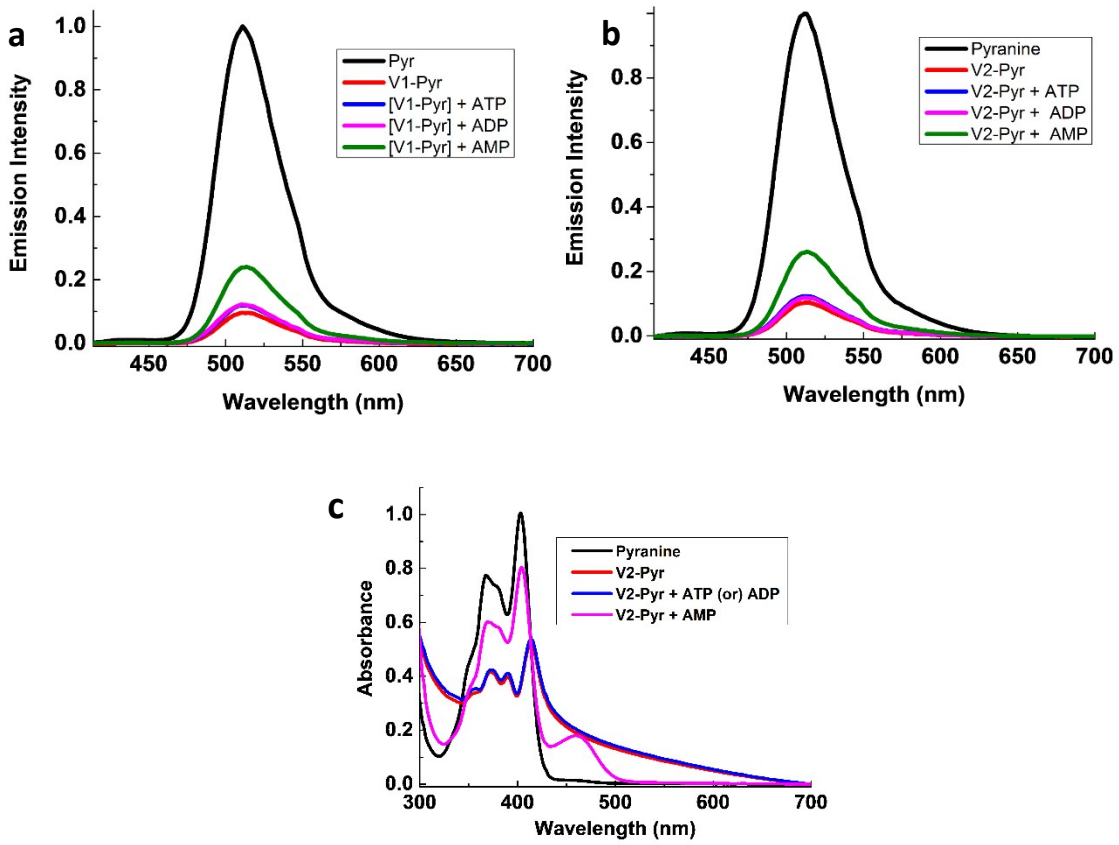

Figure S31 Emission spectral response of (a) [V1-Pyr] and (b) [V2-Pyr] CT complex towards adenosine nucleotides in aqueous HEPES buffer (pH = 7.4). (In HEPES buffer, the aggregates dissolved giving rise to a clear solution). (c) Absorption spectra of [V2-Pyr] aggregates in presence of adenosine nucleotides.