

Electronic supplementary information for

A three-dimensional cross-linking supramolecular polymer stabilized by the cooperative dimerization of viologen radical cation

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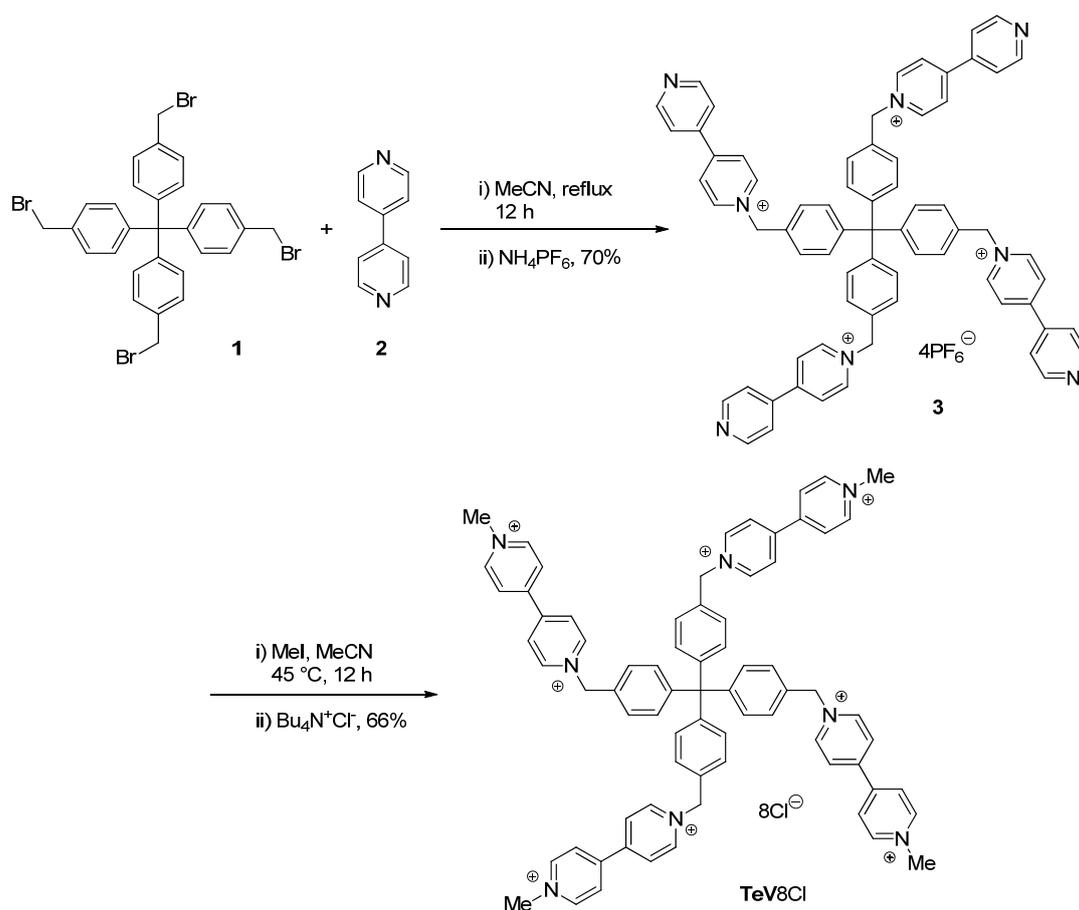
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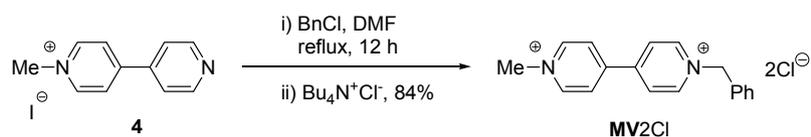
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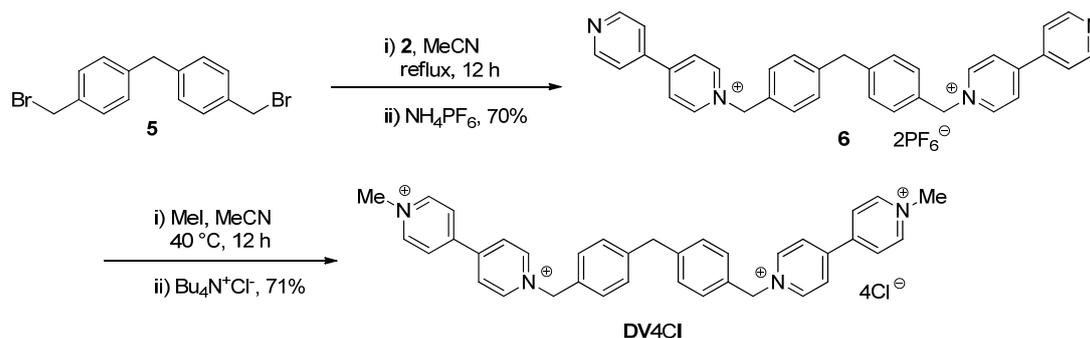


Compound 3. To a refluxed solution of 4,4'-bipyridyl **2** (2.00 g, 12.8 mmol) in acetonitrile (10 mL) was added a solution of compound **1** (1.00 g, 1.44 mmol) in acetonitrile (10 mL) in 1 h. The mixture was heated under reflux for 12 h and then cooled to room temperature. The formed precipitate was filtrated and washed with acetonitrile (50 mL) and then subjected to column chromatography (methanol/water/saturated ammonium chloride solution 6:3:1) to give rise to the corresponding tetrabromide salt. The salt was then dissolved in water and to the solution was added dropwise saturated ammonium hexafluorophosphate solution until no precipitate was formed. The solid was then filtrated and washed with water and then dried in vacuo to give compound **3** as a white solid (1.71 g, 70 %). mp > 300 °C. ^1H NMR (400 MHz, CD_3CN): δ 9.31 (d, $J = 6.3$ Hz, 8H), 8.88 (d, $J = 5.4$ Hz, 8H), 8.64 (d, $J = 6.3$ Hz, 8H), 8.00 (d, $J = 5.4$ Hz, 8H), 7.43 (d, $J = 8.1$ Hz, 8H), 7.22 (d, $J = 8.1$ Hz, 8H), 5.80 (s, 8H). ^{13}C NMR (100 MHz, CD_3CN): δ 154.2, 150.7, 147.3, 144.6, 141.0, 131.2, 130.8, 128.6, 126.0, 121.7, 64.2, 63.2. MS (ESI) m/z : 643.2 $[\text{M}-2\text{PF}_6]^{2+}$, 380.5 $[\text{M}-3\text{PF}_6]^{3+}$. HRMS (ESI-FT): calcd for $\text{C}_{69}\text{H}_{56}\text{F}_{12}\text{N}_8\text{P}_2$ $[\text{M}-2\text{PF}_6]^{2+}$: 643.19357. found: 643.19503; calcd. for $\text{C}_{69}\text{H}_{56}\text{F}_6\text{N}_8\text{P}$ $[\text{M}-3\text{PF}_6]^{3+}$: 380.47511, found: 380.47383.

Compound TeV8Cl. A solution of compound **3** (0.20 g, 0.12 mmol) and methyl iodide (0.36 g, 2.50 mmol) in acetonitrile was stirred at 45 °C for 12 h and then was added tetrabutylammonium chloride (2.78 g, 10.0 mmol). The solution was cooled to room temperature and the formed solid was filtrated and washed with acetonitrile (100 mL). The crude product was further recrystallized from water and acetonitrile to give compound **TeV8Cl** as a yellow solid (0.11 g, 66 %). mp > 300 °C. ^1H NMR (400 MHz, D_2O): δ 9.15 (d, $J = 6.0$ Hz, 8H), 9.06 (d, $J = 6.4$ Hz, 8H), 8.56 (d, $J = 6.4$ Hz, 8H), 8.52 (d, $J = 6.0$ Hz, 8H), 7.52 (d, $J = 8.4$ Hz, 8H), 7.47 (d, $J = 8.4$ Hz, 8H), 5.91 (s, 8H), 4.51 (s, 12H). ^{13}C NMR (100 MHz, D_2O): δ 150.3, 149.6, 147.8, 146.3, 145.5, 131.8, 130.4, 129.2, 127.4, 126.8, 64.5, 64.2, 48.5. HRMS (ESI): calcd for $\text{C}_{73}\text{H}_{68}\text{Cl}_4\text{N}_8$ $[\text{M}-4\text{Cl}]^{4+}$: 299.1072, found: 299.1055.

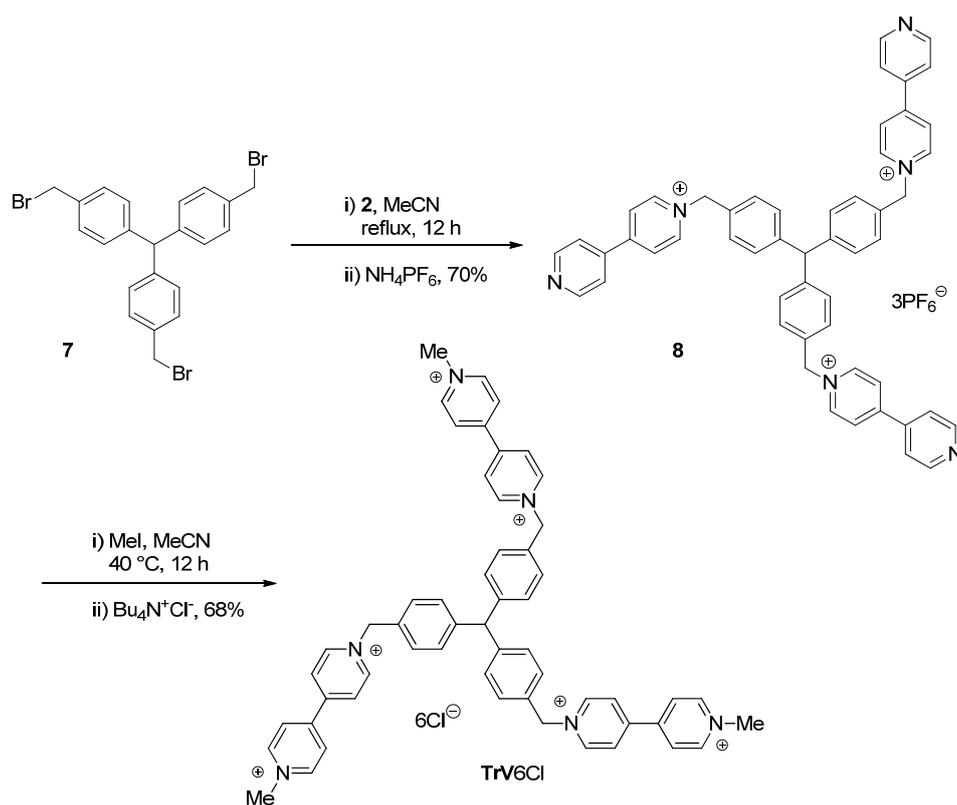


Compound MV2Cl. A solution of compound **4** (0.30 g, 1.00 mmol) and benzyl chloride (0.38 g, 3.00 mmol) in DMF was stirred under reflux for 12 h and then tetrabutylammonium chloride (2.78 g, 10.0 mmol) was added. The solution was cooled to room temperature and the formed solid was filtrated off. The solid was washed with acetonitrile (50 mL) and dried in vacuo to give compound **MV2Cl** as a yellow solid (0.28 g, 84%). mp 273.2–275.2 °C. ^1H NMR (300 MHz, D_2O): δ 9.06 (d, $J=7.2$ Hz, 2H), 8.94 (d, $J=6.9$ Hz, 2H), 8.45–8.38 (m, 4H), 7.42 (s, 5H), 5.83 (s, 2H), 4.38 (s, 3H). MS (ESI) m/z : 261.1 [$\text{M}-2\text{Cl}$] $^+$.



Compound 6. To a refluxed solution of compound **5** (1.56 g, 10.0 mmol) in acetonitrile (10 mL) was added a solution of compound **2** (0.50 g, 1.41 mmol) in acetonitrile in 1 h. The refluxing was continued for 12 h and then cooled to room temperature. The formed precipitate was filtrated and washed with acetonitrile (50 mL) and then dissolved in a minimum amount of water. Saturated ammonium hexafluorophosphate solution was added dropwise until no precipitate was formed. The precipitate was filtrated off and washed with cold water and dried in vacuo to give compound **6** as a white solid (0.79 g, 70%). mp 185.4–186.3.2 °C. ^1H NMR (400 MHz, CD_3CN): δ 9.34 (d, $J=6.4$ Hz, 4H), 8.85 (d, $J=6.0$ Hz, 4H), 8.66 (d, $J=6.4$ Hz, 4H), 7.96 (d, $J=6.0$ Hz, 4H), 7.61 (d, $J=8.0$ Hz, 4H), 7.41 (d, $J=8.0$ Hz, 4H), 6.07 (s, 4H), 4.08 (s, 2H). ^{13}C NMR (100 MHz, CD_3CN): δ 155.4, 152.0, 145.9, 144.1, 142.4, 132.0, 130.9, 130.5, 127.3, 123.0, 64.9, 41.6. MS (ESI): m/z 651.2 [$\text{M}-\text{PF}_6$] $^+$. HRMS (ESI): calcd for $\text{C}_{35}\text{H}_{30}\text{F}_6\text{N}_4\text{P}$ [$\text{M}-\text{PF}_6$] $^+$: 651.21068, found: 651.2125.

Compound DV4Cl. A solution of compound **6** (80 mg, 0.10 mmol) and methyl iodide (0.36 g, 2.50 mmol) in acetonitrile (10 mL) was stirred at 40 °C for 12 h and then tetrabutylammonium chloride (2.78 g, 10 mmol) was added. The solution was cooled to room temperature and the formed precipitate was filtrated and washed with acetonitrile and dried in vacuo to give compound **DV4Cl** as a yellow solid (48 mg, 71 %). mp > 300 °C. ^1H NMR (400 MHz, D_2O): δ 9.21–8.98 (m, 8H), 8.51 (br, 8H), 7.57–7.25 (m, 8H), 5.88 (s, 4H), 4.50 (s, 6H), 4.06 (s, 2H). ^{13}C NMR (100 MHz, D_2O): δ 150.4, 149.7, 146.4, 145.4, 143.3, 130.3, 130.0, 129.8, 127.1, 126.7, 64.5, 48.3, 40.5. MS (ESI): m/z 536.3 [$\text{M}-4\text{Cl}$] $^+$. HRMS (ESI): calcd for $\text{C}_{37}\text{H}_{36}\text{N}_4$ [$\text{M}-4\text{Cl}$] $^+$: 536.2935, found: 536.2946.



Compound 8. To a refluxed solution of compound 2 (2.00 g, 12.8 mmol) in acetonitrile (20 mL) was added dropwise a solution of compound 7 (0.92 g, 1.76 mmol) in acetonitrile (10 mL) in 2 h. The mixture was stirred under reflux for 12 h and then cooled to room temperature. The formed precipitate was filtrated and washed with acetonitrile (50 mL) and then subjected to column chromatography (methanol/water/saturated ammonium chloride solution 6:3:1) to give the trichloride salt. The salt was dissolved in a minimum amount of water. Saturated ammonium hexafluorophosphate solution was added dropwise until no more precipitate was formed. The precipitate was filtrated and washed with cold water and dried in vacuo to afford compound 8 (1.46 g, 70 %) as a white solid. mp > 300 °C. ¹H NMR (300 MHz, CD₃CN): δ 9.31 (d, *J* = 6.6 Hz, 6H), 8.85 (d, *J* = 5.4 Hz, 6H), 8.63 (d, *J* = 6.6 Hz, 6H), 7.96 (d, *J* = 5.4 Hz, 6H), 7.63 (d, *J* = 8.1 Hz, 6H), 7.31 (d, *J* = 8.1 Hz, 6H), 6.07 (s, 6H), 5.82 (s, 1H). ¹³C NMR (100 MHz, CD₃CN): δ 155.5, 152.0, 145.9, 142.3, 132.5, 131.2, 130.5, 127.3, 122.9, 64.7, 56.3. MS (ESI) *m/z*: 1041.3 [M-PF₆]⁺, 448.2 [M-2PF₆]²⁺. HRMS (ESI-FT): calcd for C₅₂H₄₃F₁₂N₆P₂ [M-PF₆]⁺: 1041.28273, found: 1041.28181; calcd. for C₅₂H₄₃F₆N₆P [M-2PF₆]²⁺: 448.15900, found: 448.15789.

Compound TrV6Cl. A solution of compound 8 (0.17 g, 0.14 mmol) and methyl iodide (0.36 g, 2.50 mmol) in acetonitrile was stirred at 40 °C for 12 h and then Bu₄NCl (2.78 g, 10.0 mmol) was added. The mixture was stirred for 1 h and then cooled to room temperature. The precipitate was filtrated and washed with acetonitrile (100 mL) and recrystallized from water and acetonitrile to afford compound TrV6Cl as a yellow solid (98 mg, 68%, it should be noted that there is still a very small amount of impurity after recrystallization). mp > 300 °C. ¹H NMR (400 MHz, D₂O): δ 9.14 (d, *J* = 6.0 Hz, 6H), 9.05 (d, *J* = 6.0 Hz, 6H), 8.54-8.51 (m, 12H), 7.51 (d, *J* = 8.0 Hz, 6H), 7.35 (d, *J* = 8.0 Hz, 6H), 5.92 (s, 6H), 5.84 (s, 1H), 4.51 (s, 9H). ¹³C NMR (100 MHz, CD₃CN): δ 150.4, 149.7, 146.3, 145.4, 145.1, 130.8, 130.5, 129.7, 127.2, 126.7, 64.4, 55.1, 48.4. MS (ESI): *m/z*: 625.3 [M-6Cl-C₁₁H₁₁N₂]⁺. HRMS (ESI): calcd for C₄₄H₄₁N₄ [M-6Cl-C₁₁H₁₁N₂]⁺: 625.3326, found: 625.3324.

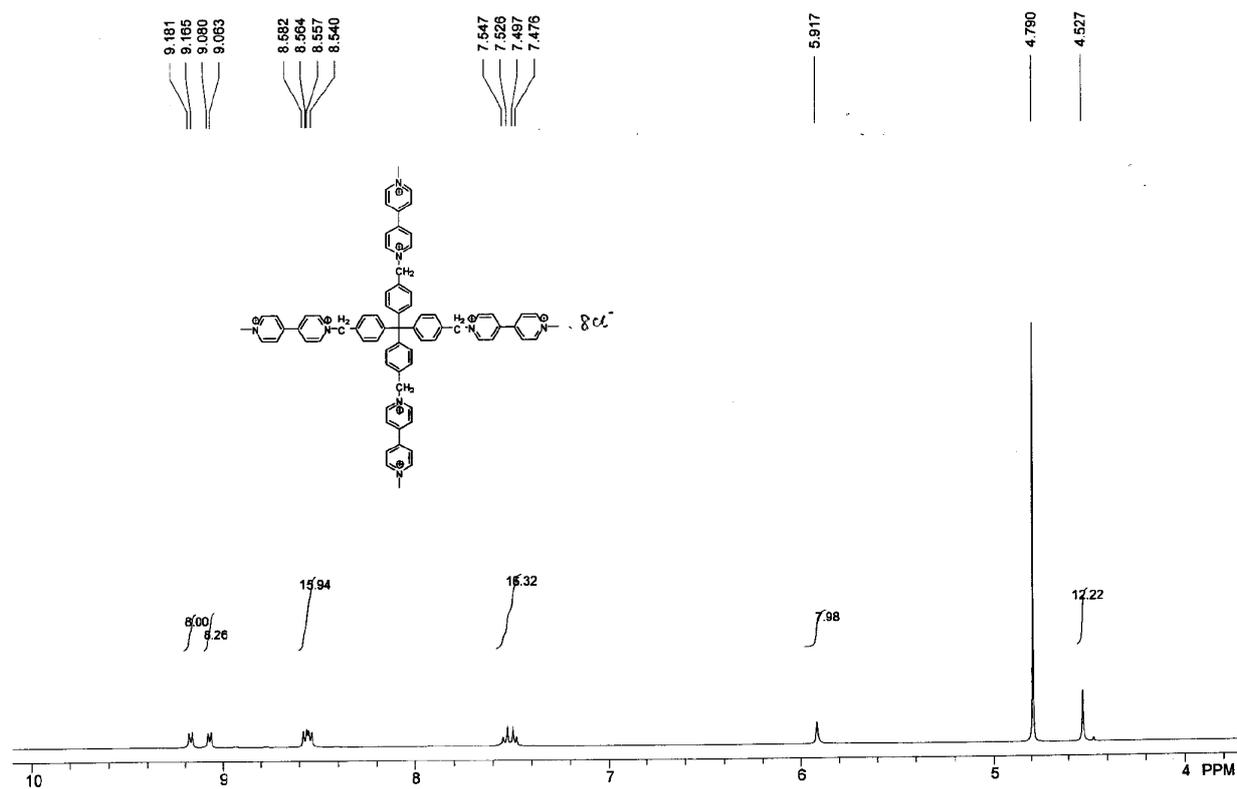


Figure 1S. ¹H NMR spectrum (400 MHz) of TeV8Cl in D₂O (0.5 mM).

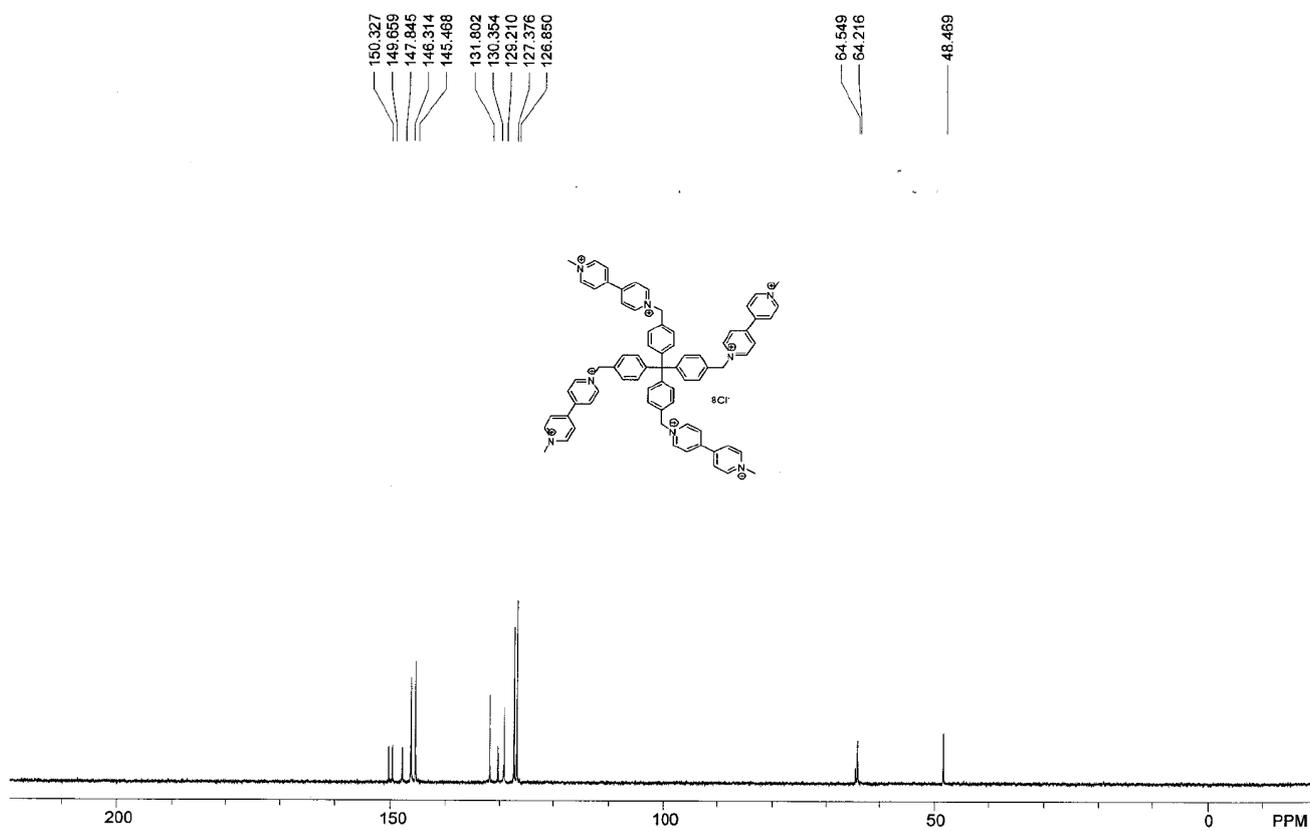


Figure 2S. ¹³C NMR spectrum (100 MHz) of TeV8Cl in D₂O (10 mM).

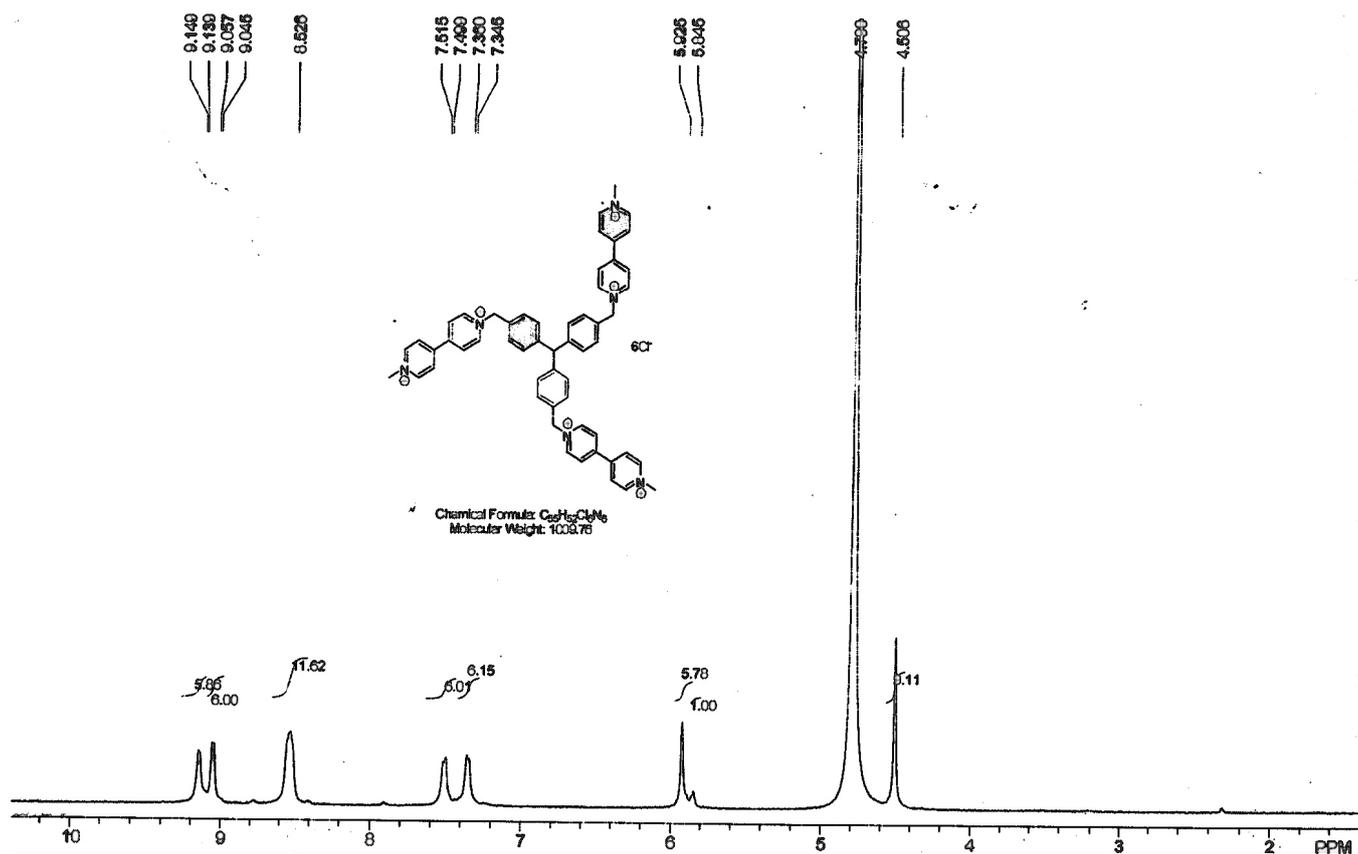


Figure 3S. 1H NMR spectrum (400 MHz) of TrV6Cl in D_2O (1 mM).

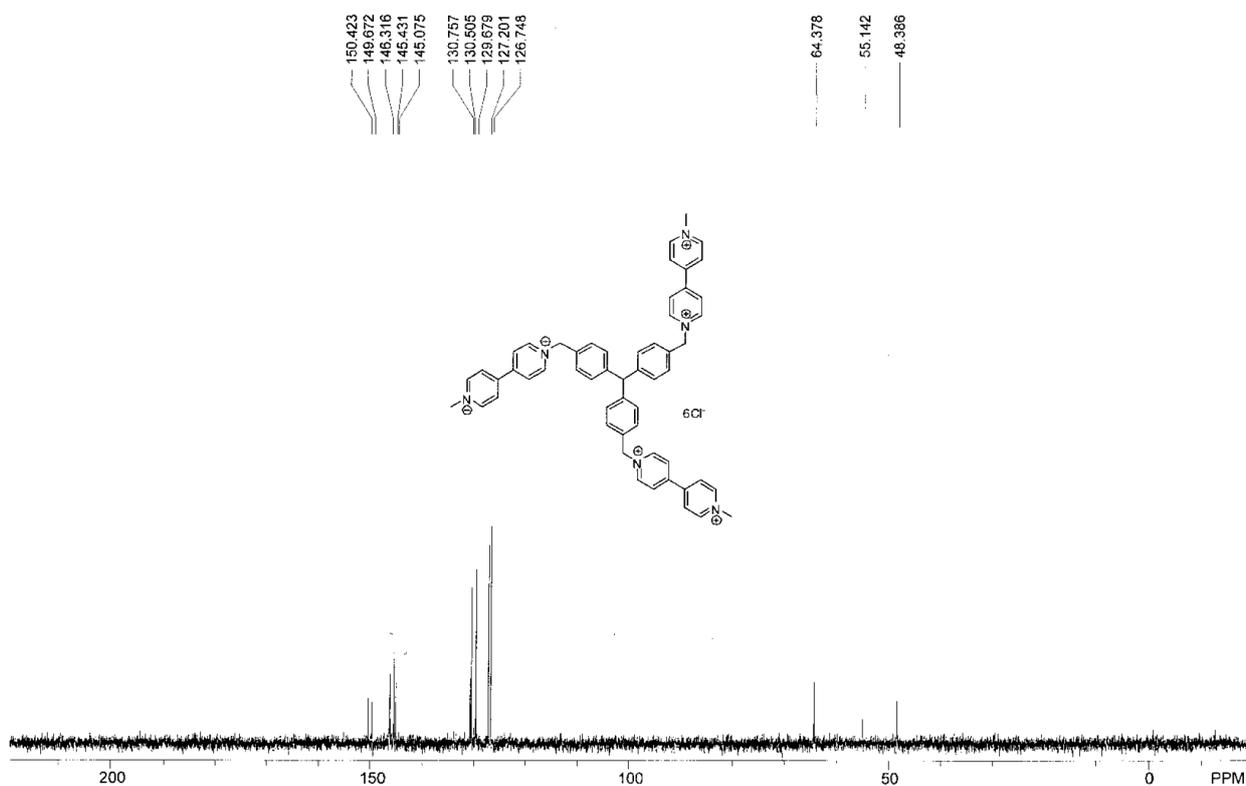
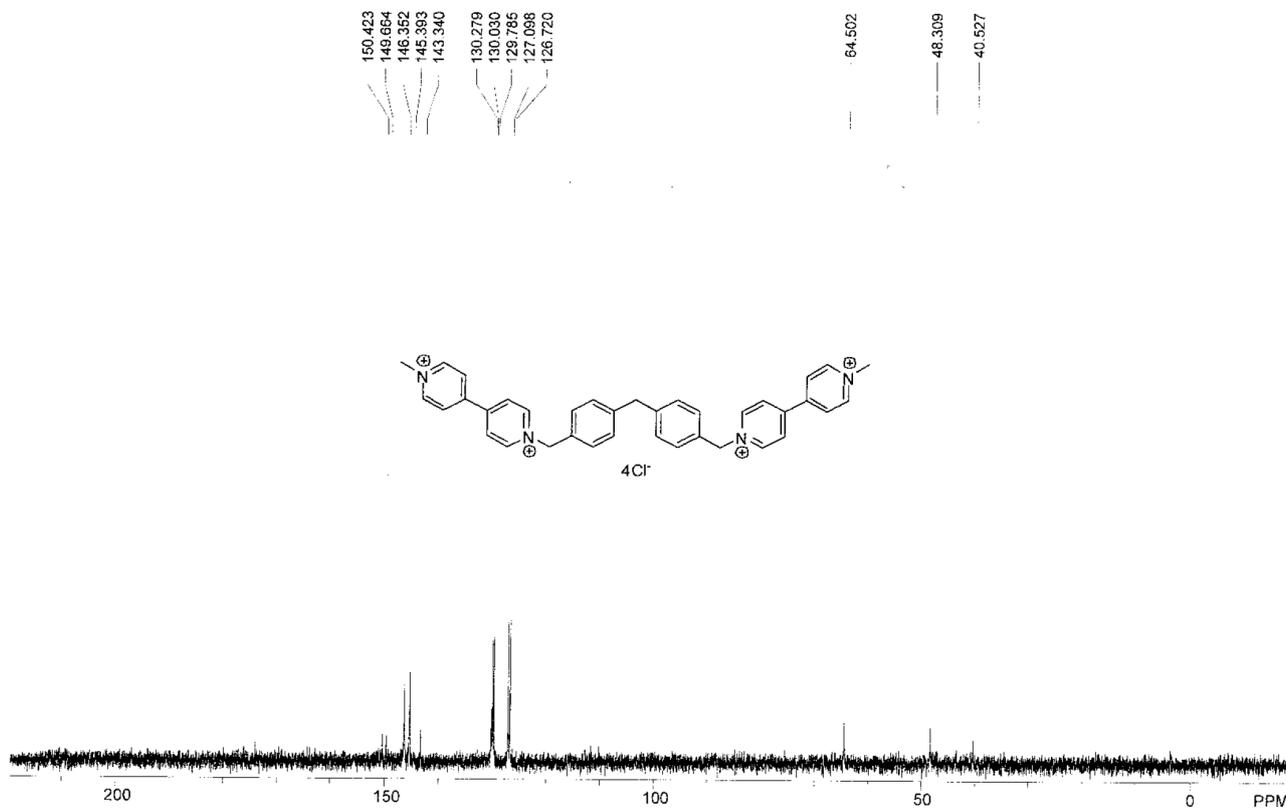
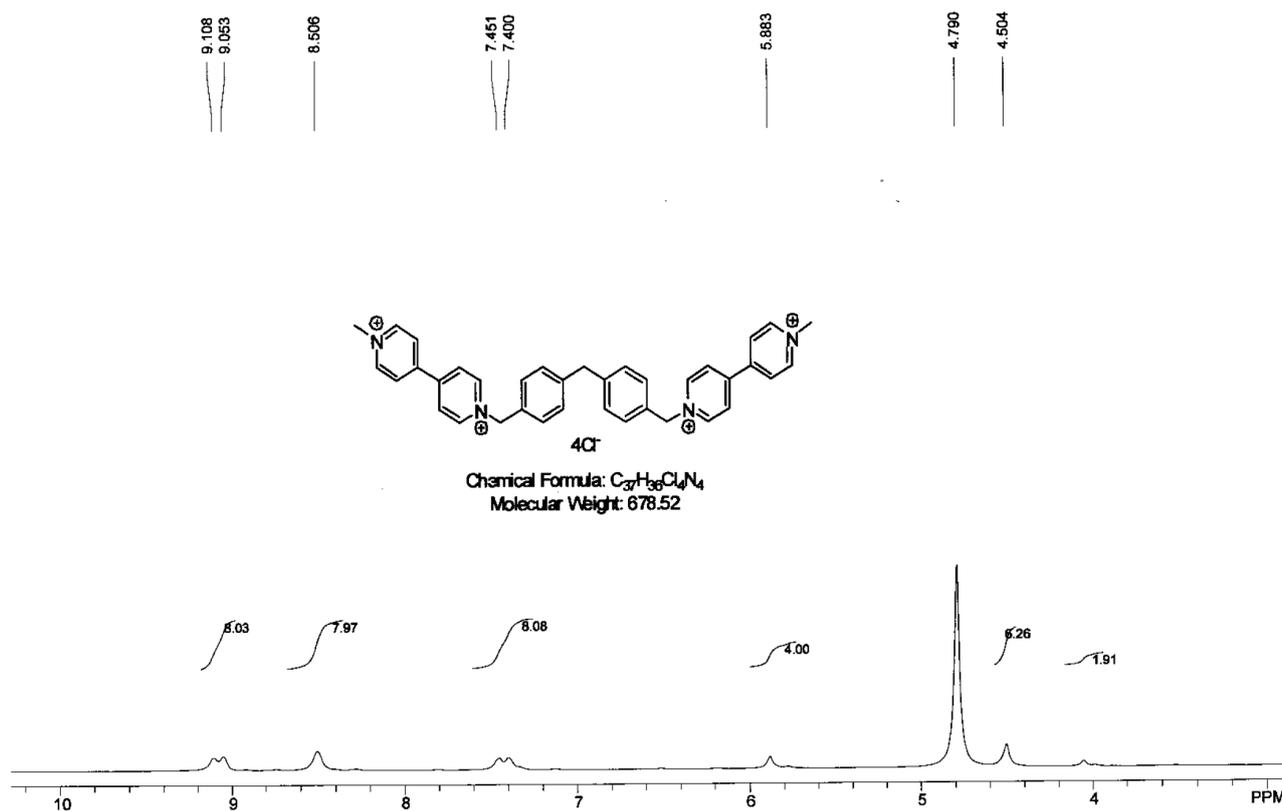


Figure 4S. ^{13}C NMR spectrum (100 MHz) of TrV6Cl in D_2O (10 mM).



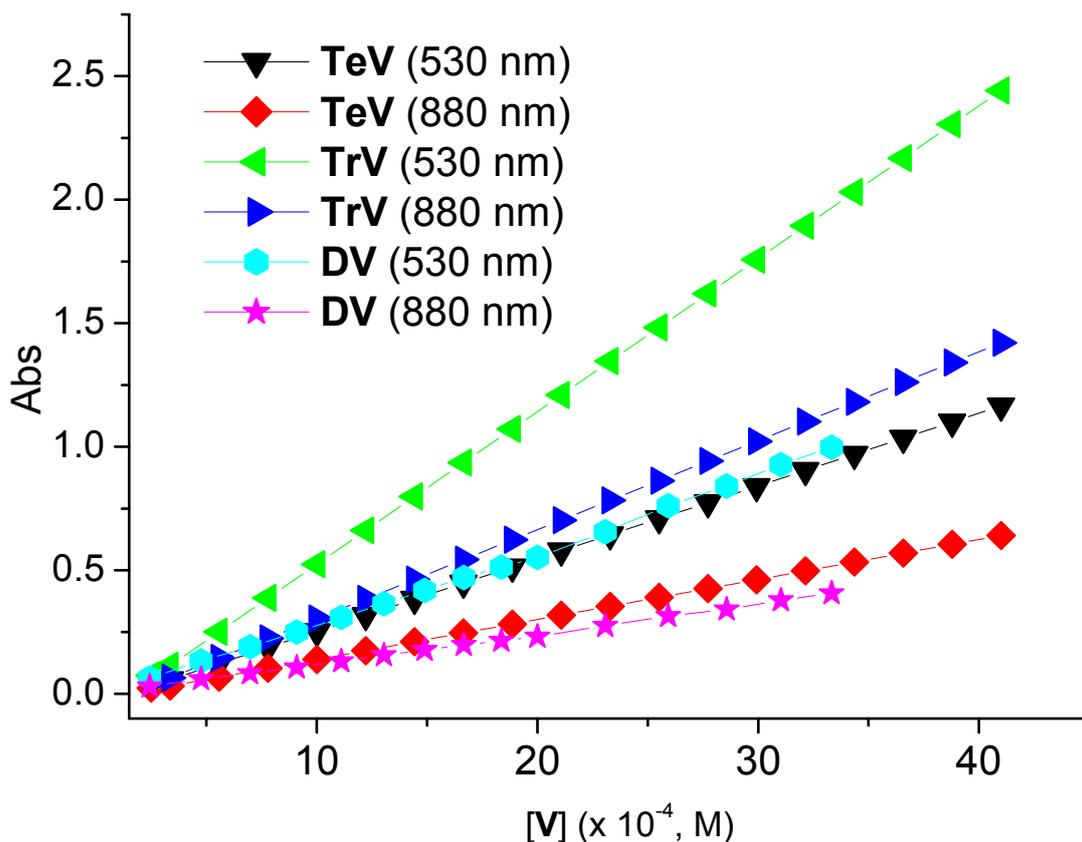


Figure 7S. Plots of absorbance at 530 and 880 nm for $\text{TeV}^{4(+)}$, $\text{TrV}^{3(+)}$, and $\text{DV}^{2(+)}$ versus the concentration of their $[V]$ units, showing that in all cases absorption obeys the Lambert–Beer law.

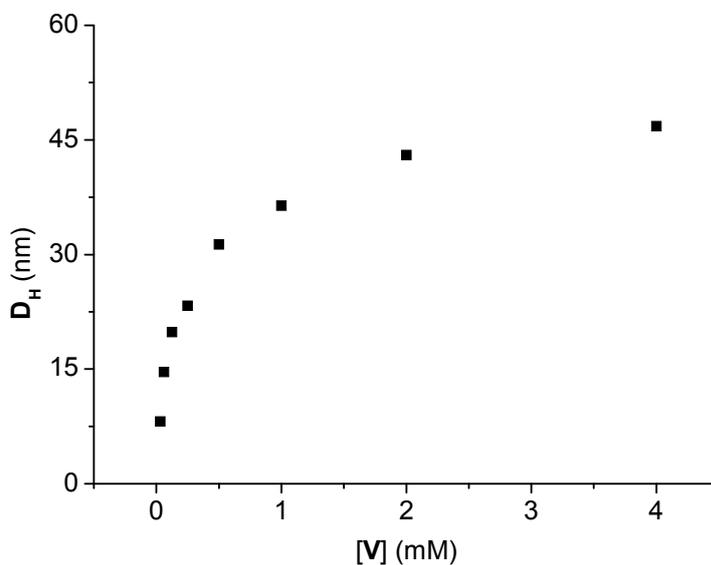


Figure 8S. The concentration dependence of D_H of $\text{TeV}^{4(+)}$ in aqueous solution in the presence of sodium dithionite (50 mM) at 25 °C.