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Efficient access to conjugated 4,4'-bipyridinium oligomers using the Zincke reaction: synthesis, spectroscopic and electrochemical properties

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Supporting Information

Efficient access to conjugated 4,4'-bipyridinium
oligomers using the Zincke reaction: Synthesis,
spectroscopic and electrochemical properties.

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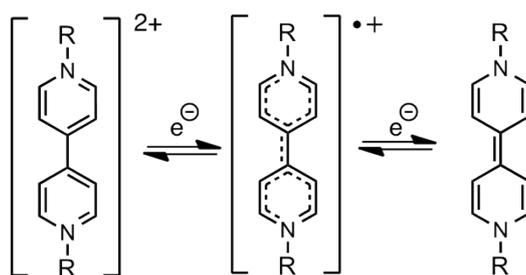
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Scheme S1 Electrochemical interconversion of 4,4'-bipyridinium units between dicationic, radical cationic and neutral, quinoidal forms

Chemical reduction and reoxidation of 1 and 2

We observed that oligomers **1** and **2** can readily be reduced both chemically with triethylamine, TEA, to yield corresponding radical cations. This causes the formation of paramagnetic species and consequent loss of signals in the ^1H NMR spectrum. These signals re-appear after the addition of trifluoroacetic acid, TFA.¹

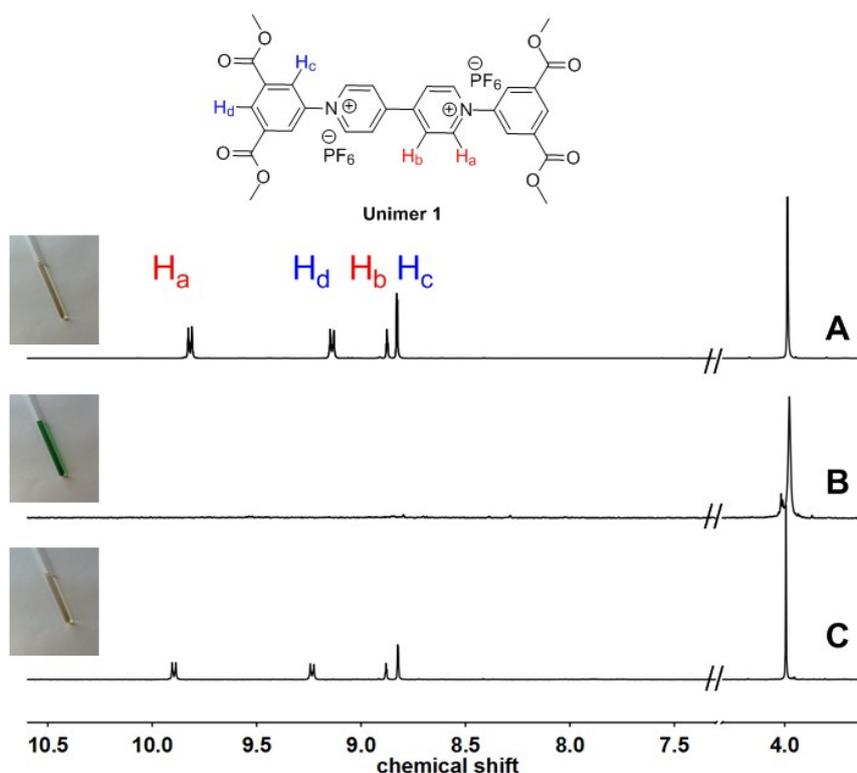


Figure S1. Partial ^1H NMR (400 MHz) spectra of compound **1** alone in $\text{acetone-}d_6$ (spectrum A), after addition of 10 equivs triethylamine (spectrum B), and after subsequent addition of an excess of TFA (spectrum C).

Note: In Figure S1, the spectra show that upon the addition of excess triethylamine (spectrum B), the signals corresponding to both protons on the 4,4'-bipyridinium (H) moiety and the adjacent aromatic rings (H) disappear. However, the signals corresponding to the unconjugated methoxy groups remain. Addition of TFA, not only regenerates the original colour of the solution but also restores the missing signals in the ^1H NMR spectrum.

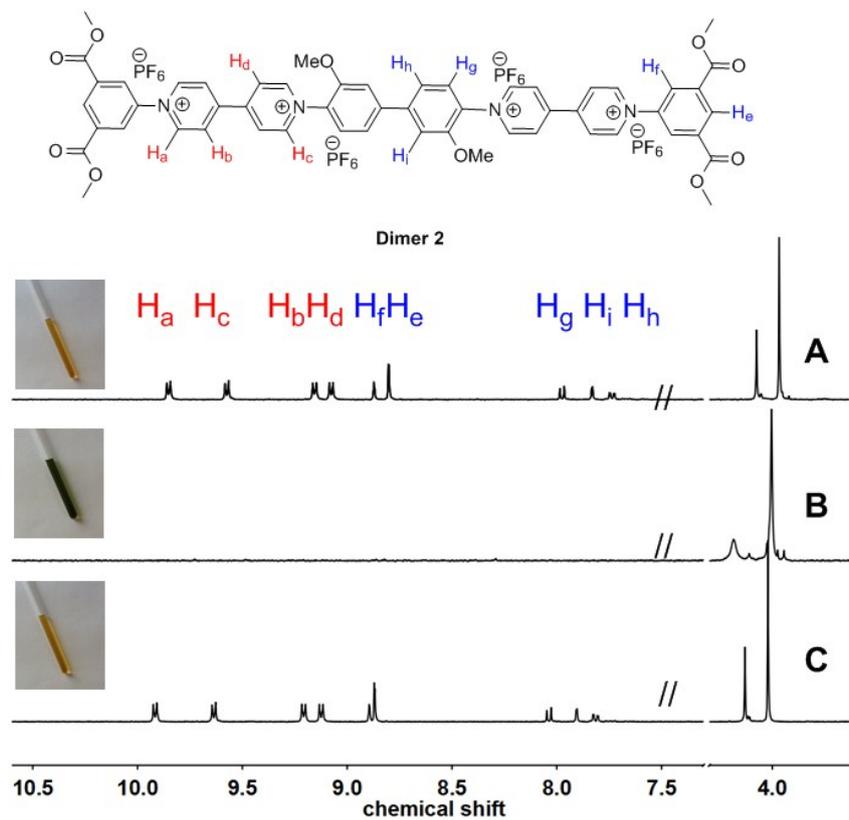


Figure S2. Partial ^1H NMR (400 MHz) spectra of compound **2** alone in acetone- d_6 (spectrum A), after addition of 20 equivs triethylamine (spectrum B), and after subsequent addition of an excess of TFA (spectrum C).

^1H and ^{13}C NMR spectra

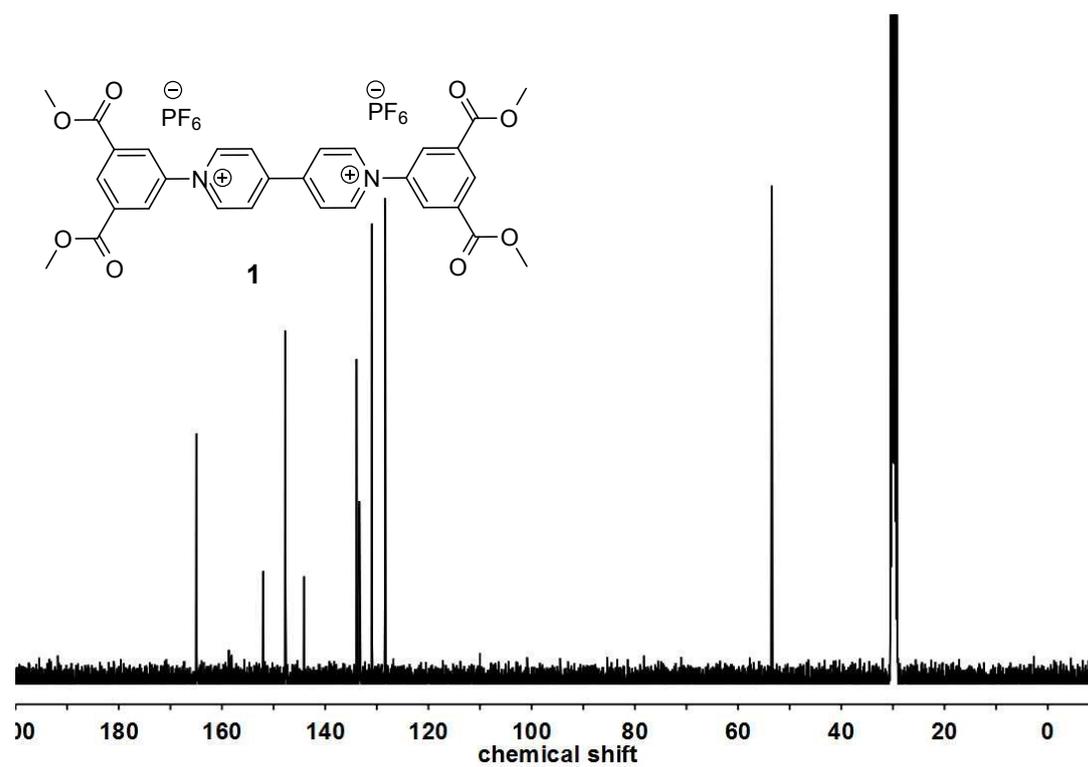
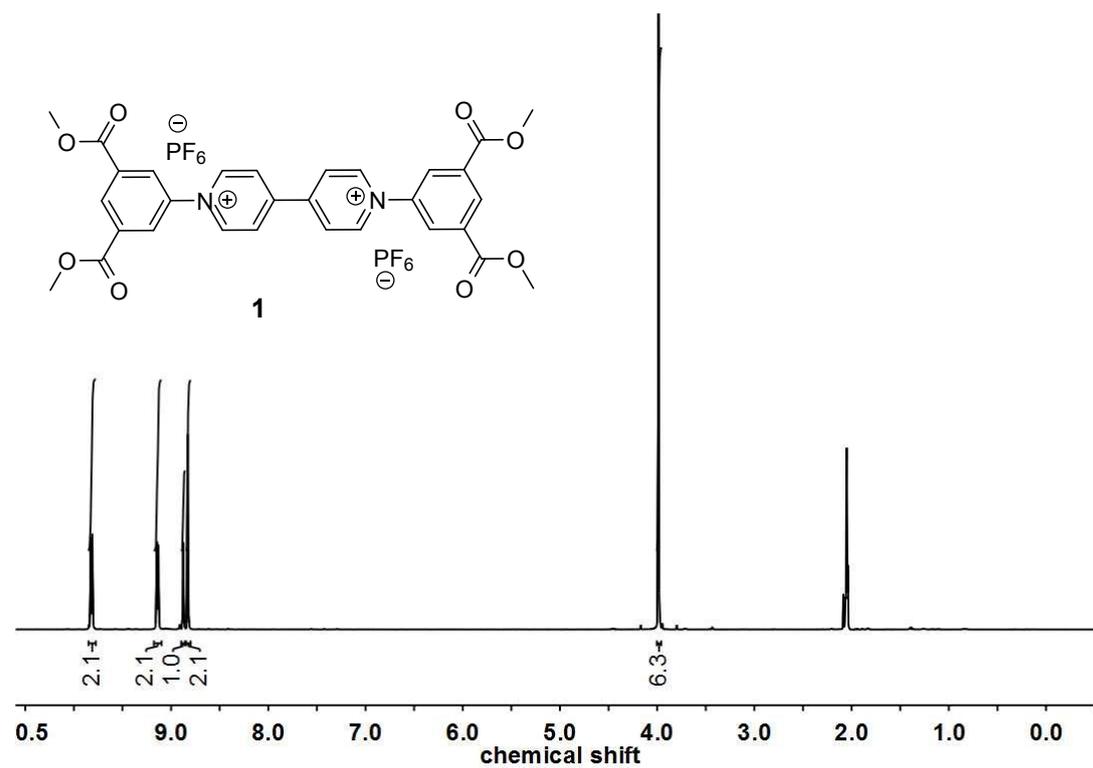


Figure S15. ^1H and ^{13}C NMR spectra of compound **1** (in acetone- d_6 containing 1% of TFA)

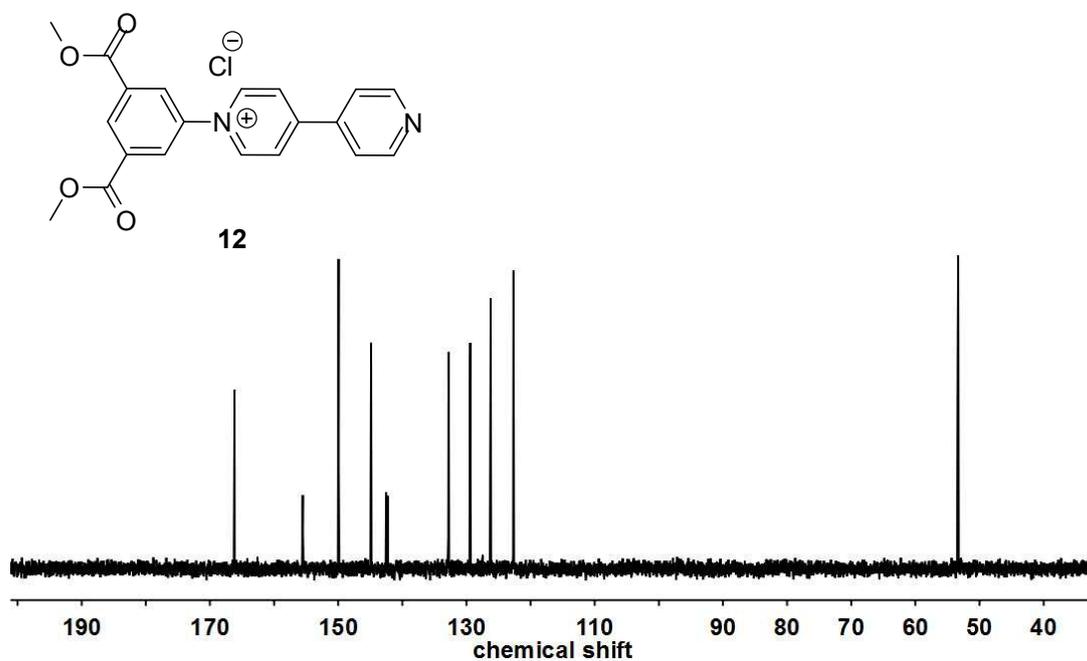
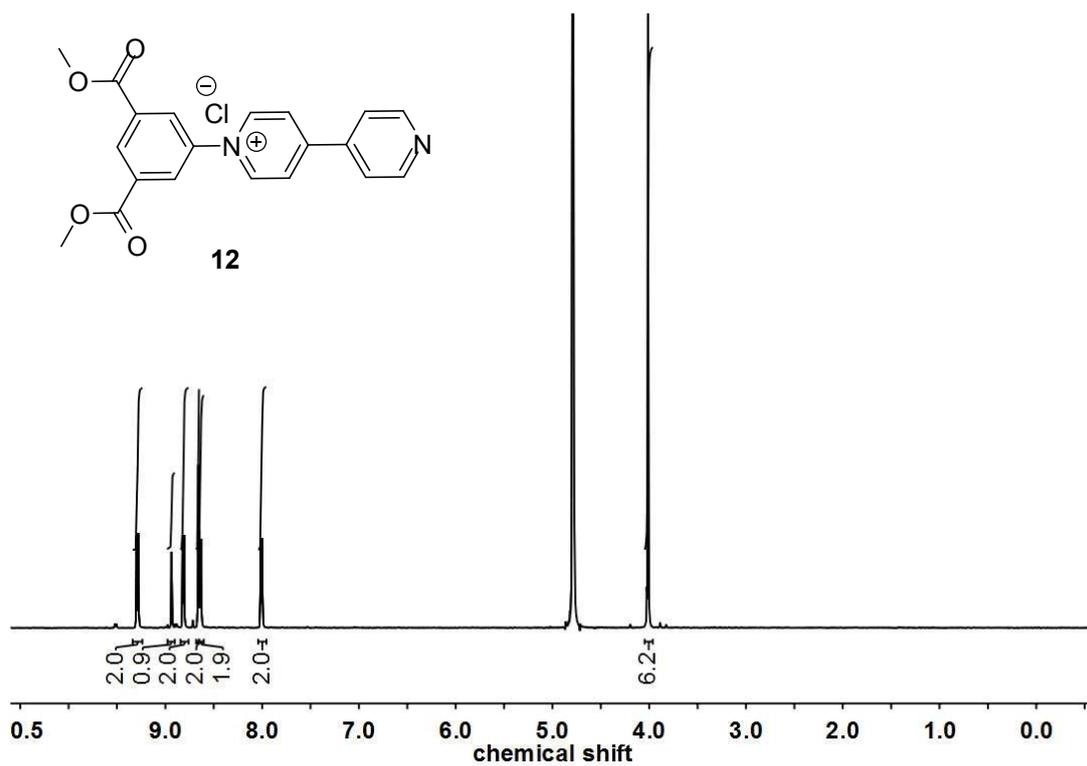


Figure S16. ^1H and ^{13}C NMR spectra (D_2O) of 1-(3,5-bis(methoxycarbonyl)phenyl)-[4,4'-bipyridin]-1-ium chloride, **12**

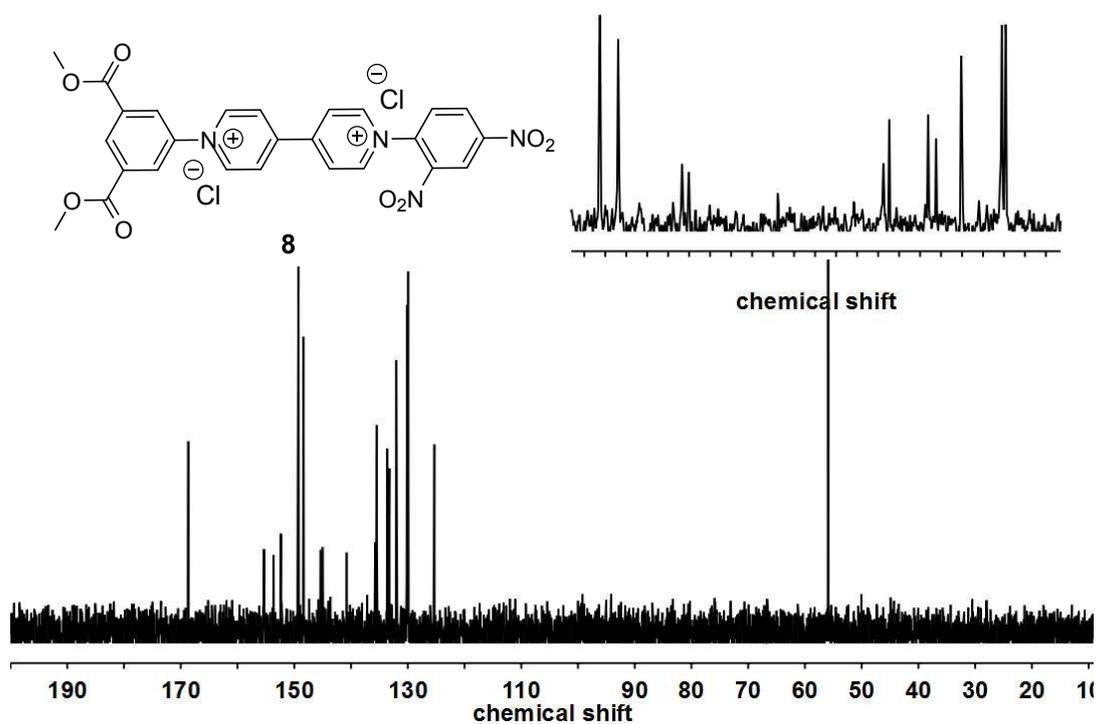
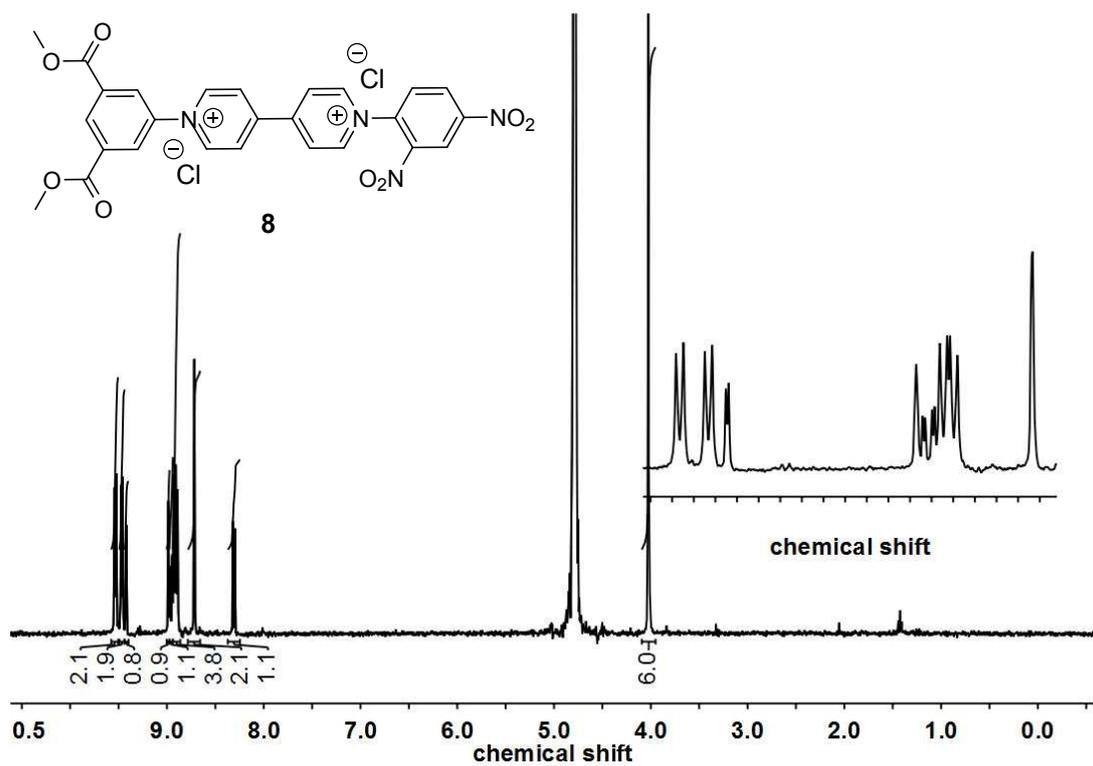


Figure S17. ¹H and ¹³C NMR spectra (D₂O) of 1-(3,5-bis(methoxycarbonyl)phenyl)-1'-(2,4-dinitrophenyl)-[4,4'-bipyridin]-1,1'-dium chloride, **8**

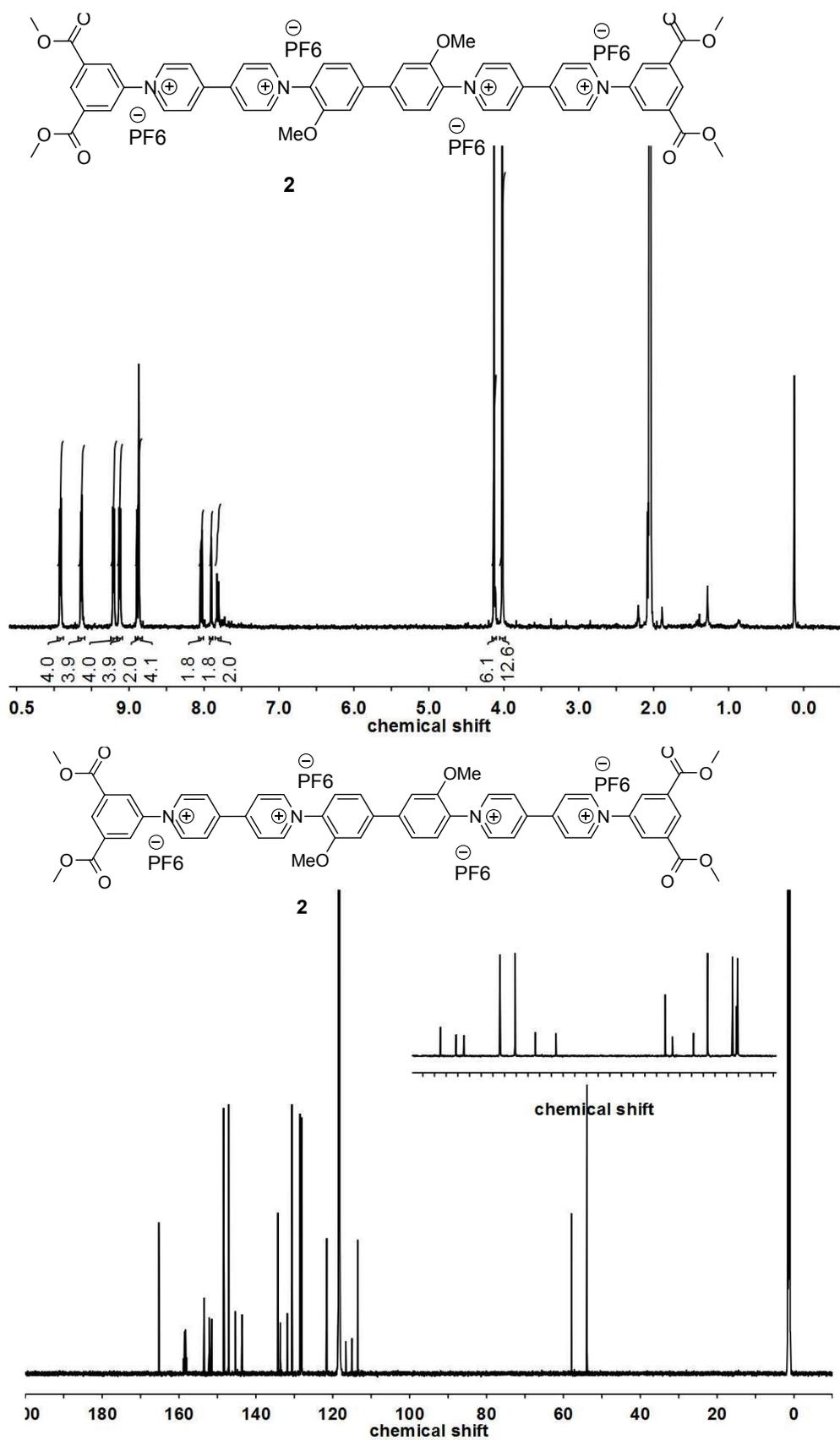


Figure S18. ¹H NMR spectra (acetone-d₆ containing 1% of TFA) and ¹³C NMR (CD₃CN containing 1% of TFA) of compound **2**

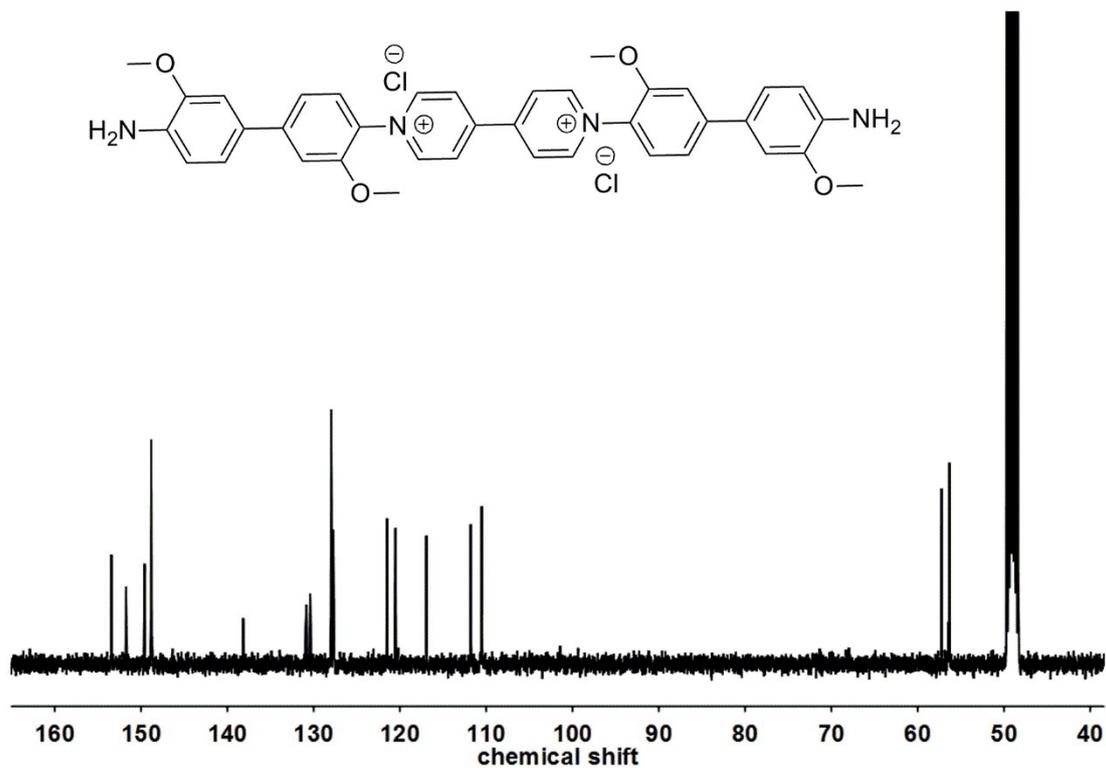
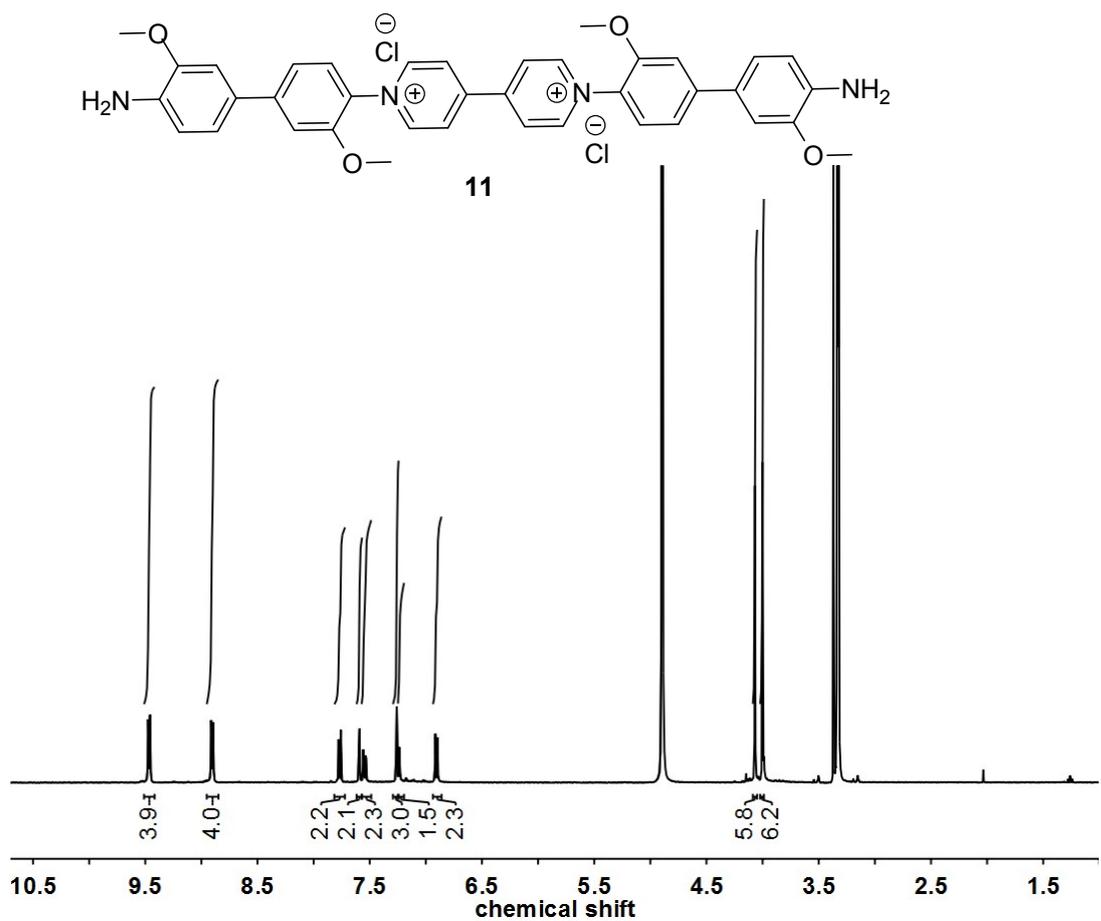


Figure S19. ^1H and ^{13}C NMR spectra (both in CD_3OD) of compound **11**

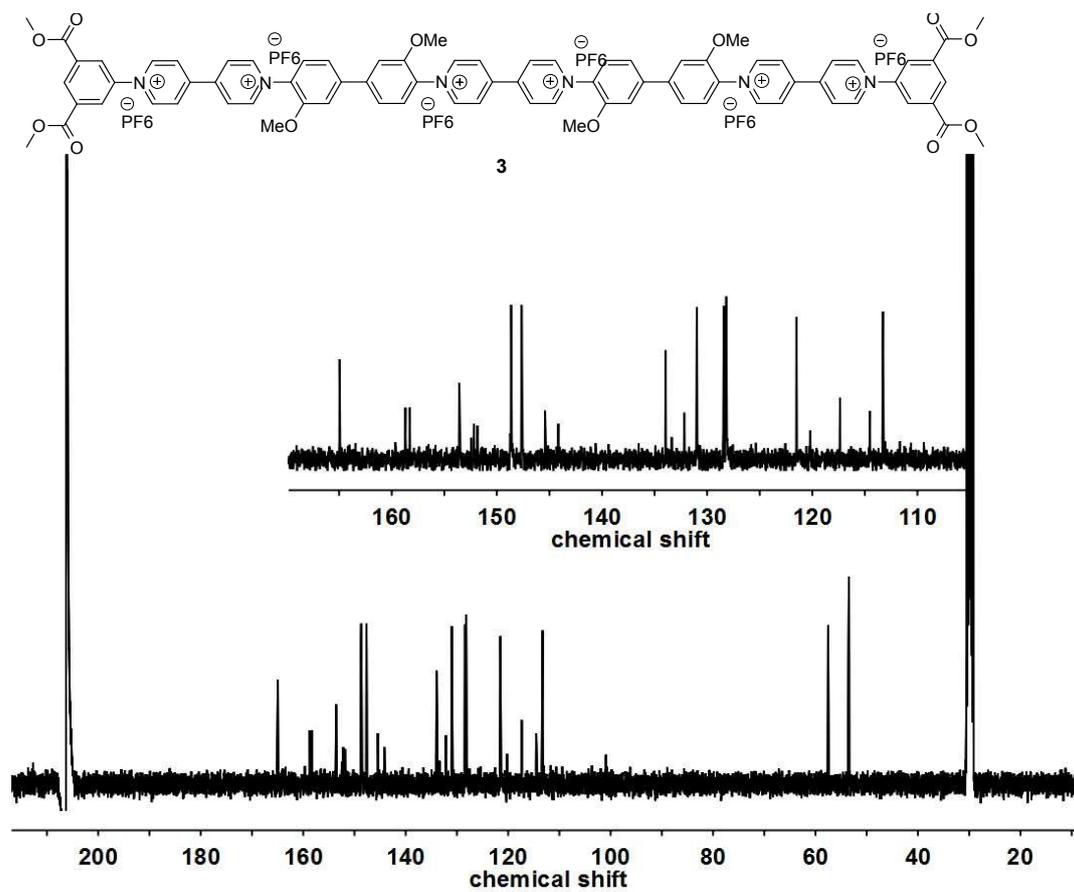
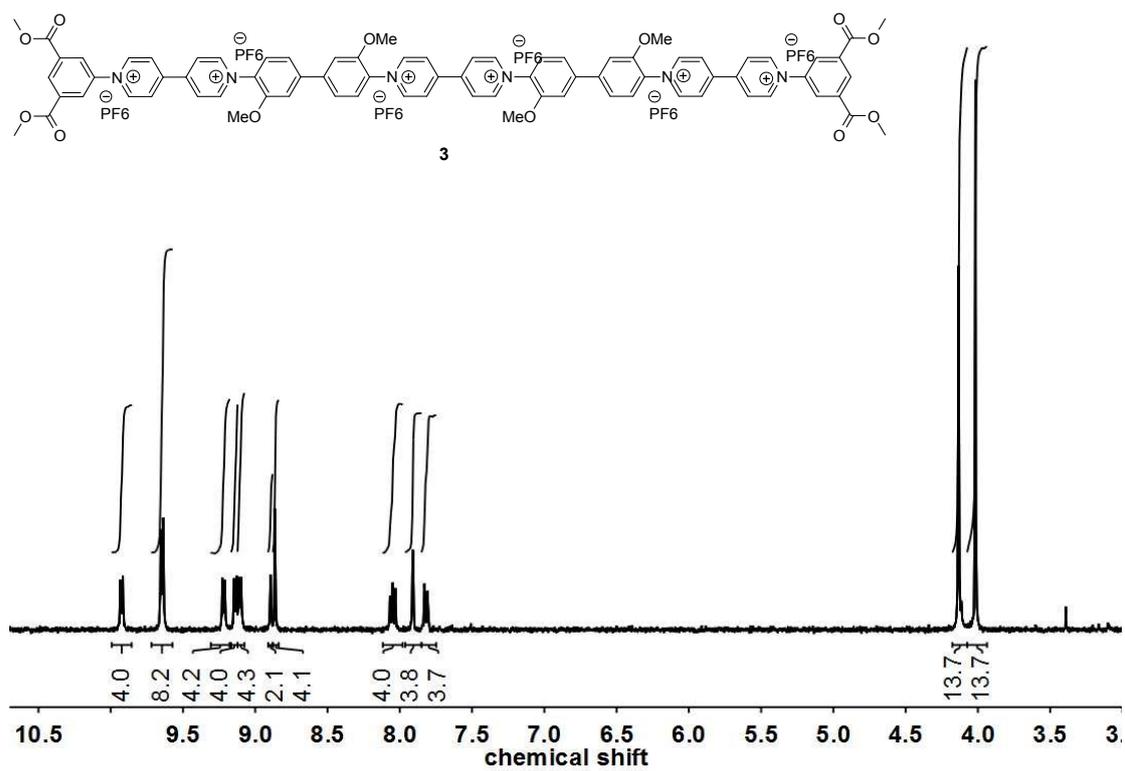


Figure S20. ^1H and ^{13}C NMR spectra (in acetone- d_6 containing 1% of TFA) of compound **3**

Electrochemistry

CV and SWV of compound 1

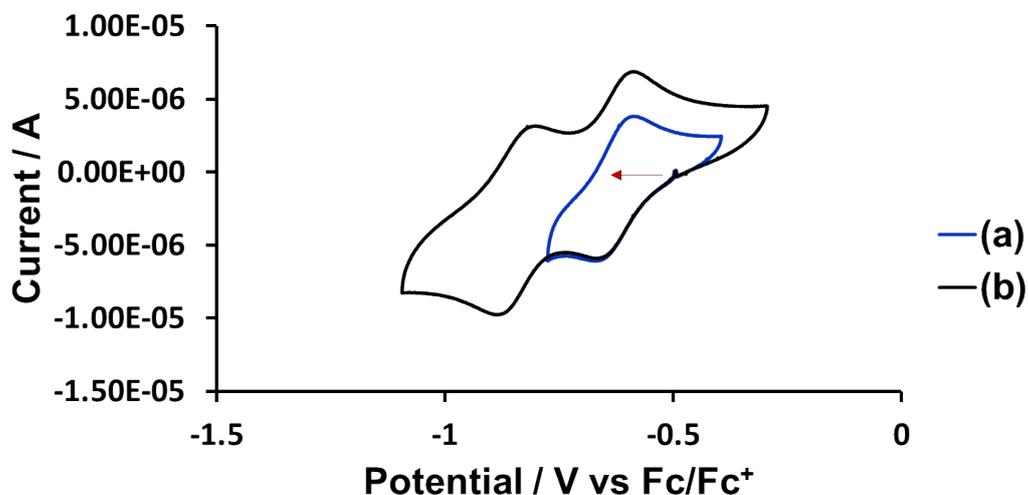


Figure S3. Cyclic voltammogram obtained for compound **1** (0.2 mM) at a glassy carbon disc electrode in anhydrous DMF: (a) 1st reversible reaction (blue line) and (b) 2nd reversible reaction (black line) at $v = 500 \text{ mV s}^{-1}$.

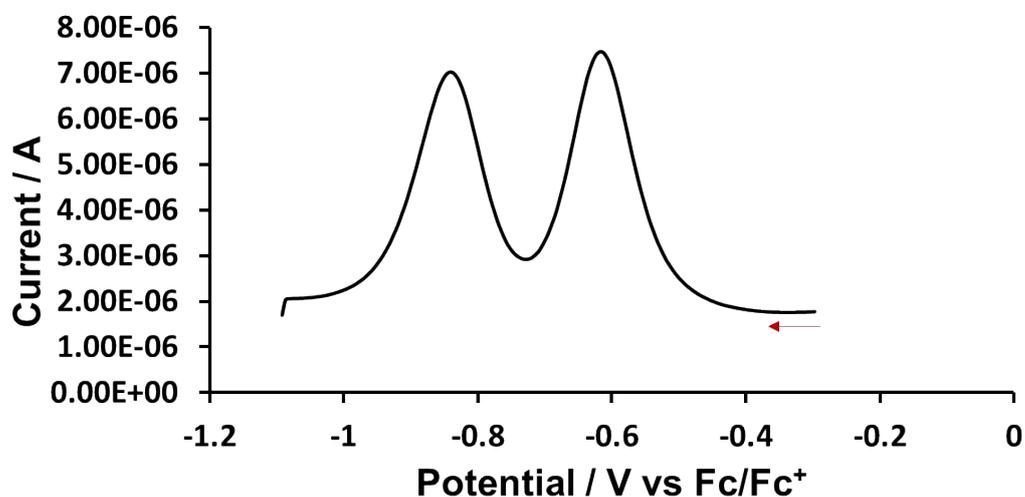


Figure S4. Square wave voltammogram of unimer **1** (0.2 mM) at a glassy carbon disc electrode in anhydrous DMF and TBAPF₆ (0.1 M).

CV and SWV of compound 2

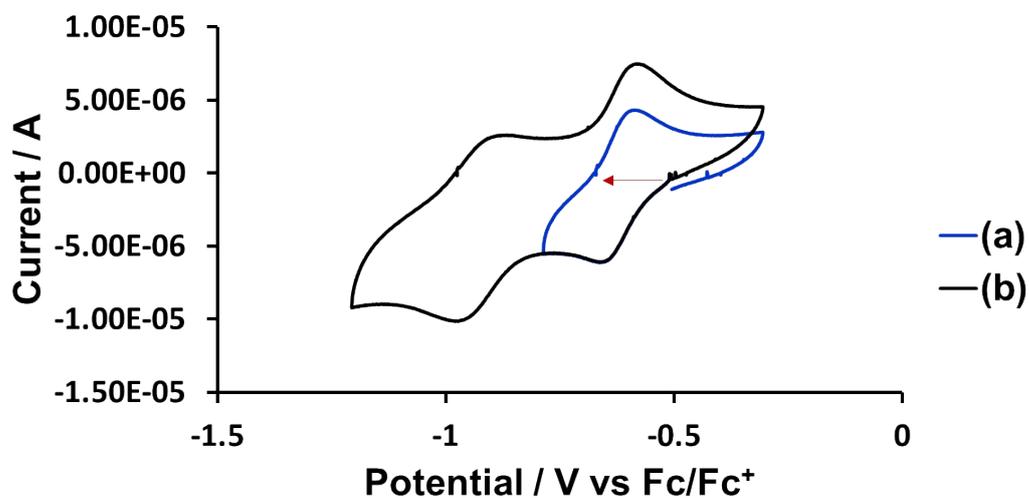


Figure S5. Cyclic voltammogram obtained for compound **2** (0.2 mM) at a glassy carbon disc electrode in anhydrous DMF at $\nu = 500 \text{ mVs}^{-1}$.

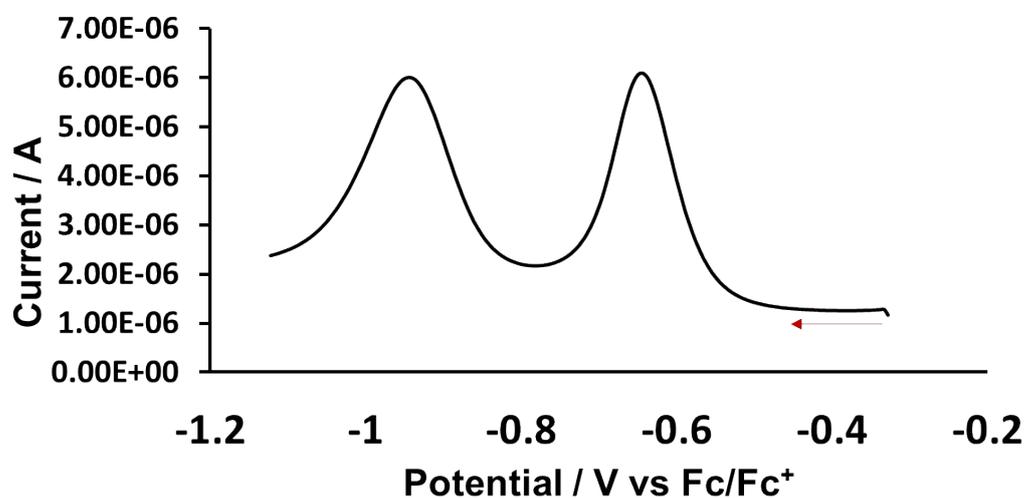


Figure S6. Square wave voltammogram of compound **2** (0.2 mM) at a glassy carbon electrode in anhydrous DMF and TBAPF₆ (0.1 M).

CV and SWV of compound 3

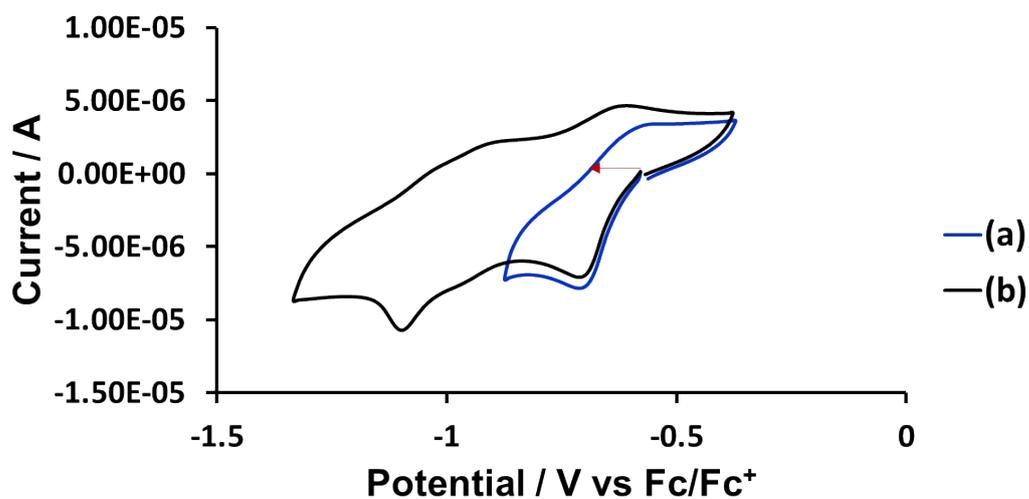


Figure S7. Cyclic voltammogram obtained for compound **3** (0.2 mM) at a glassy carbon disc electrode in anhydrous DMF at $v = 500 \text{ mVs}^{-1}$.

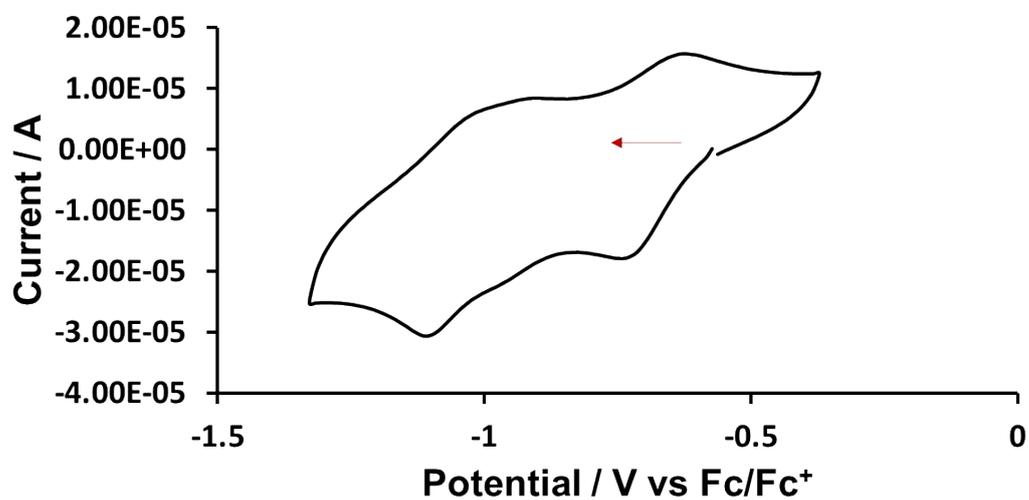


Figure S8. Cyclic voltammogram of compound **3** (0.2 mM) at a glassy carbon disc ($d = 2 \text{ mm}$) electrode in anhydrous DMF at $v = 3 \text{ V s}^{-1}$.

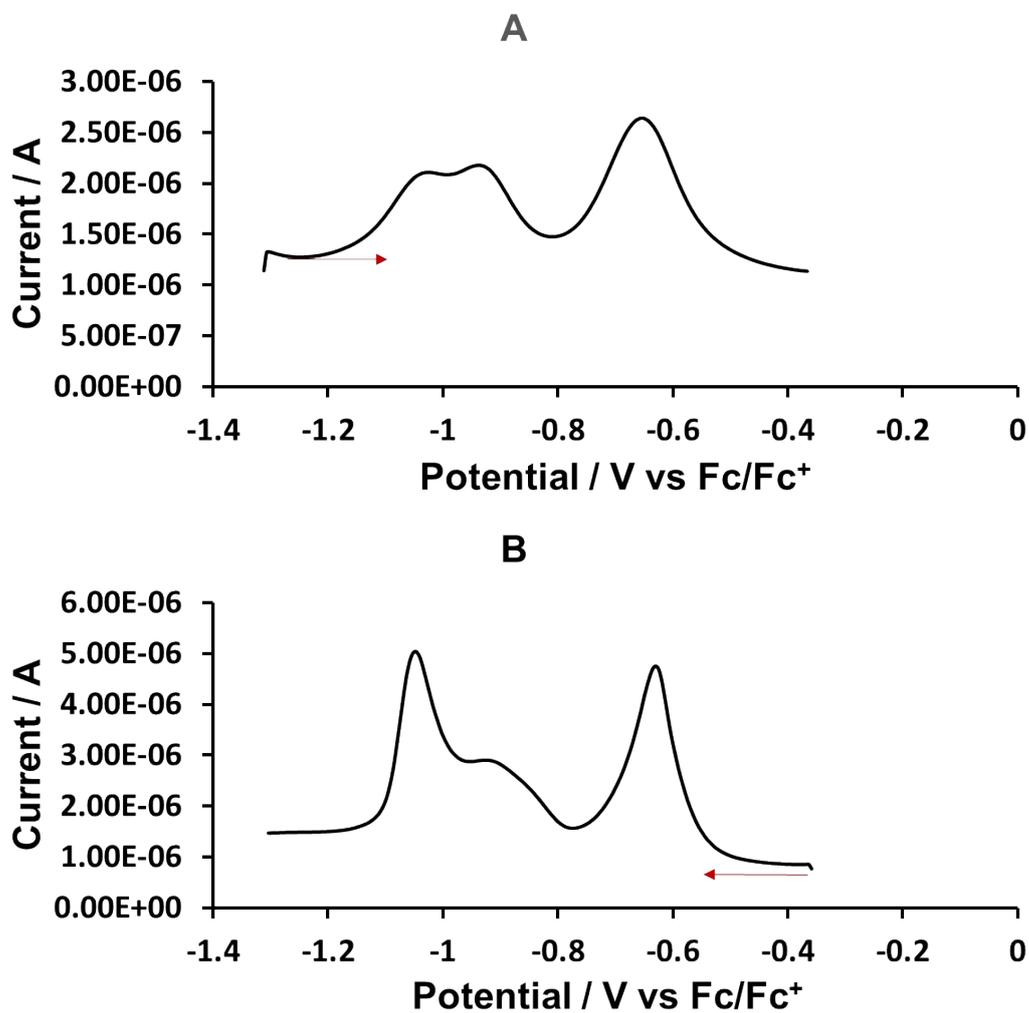


Figure S9. Square wave voltammograms of compound **3** (0.2 mM) at a glassy carbon disc ($d = 2$ mm) electrode in anhydrous DMF and TBAPF₆ (0.1M): (A) Scan from negative potential to positive potential, and (B) scan from positive potential to negative potential, at a frequency of 10 Hz.

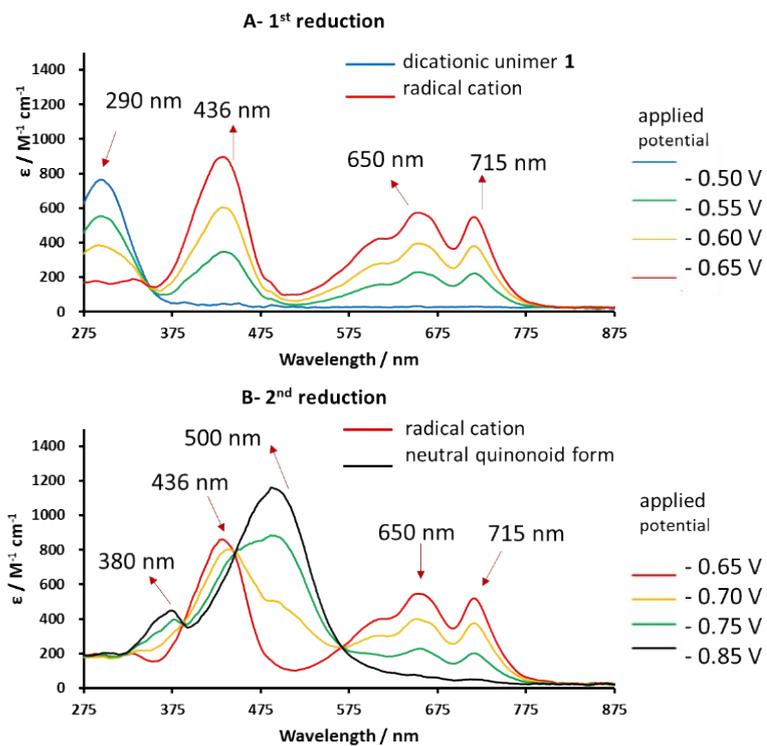


Fig. S11 Reversible UV-vis spectral changes accompanying the stepwise 1e reduction of dicationic unimer **1** to the corresponding radical cation (spectrum A) and the neutral quinoid form (spectrum B). Spectra recorded in anhydrous DMF/0.1M TABPF₆, using an OTTLE cell.

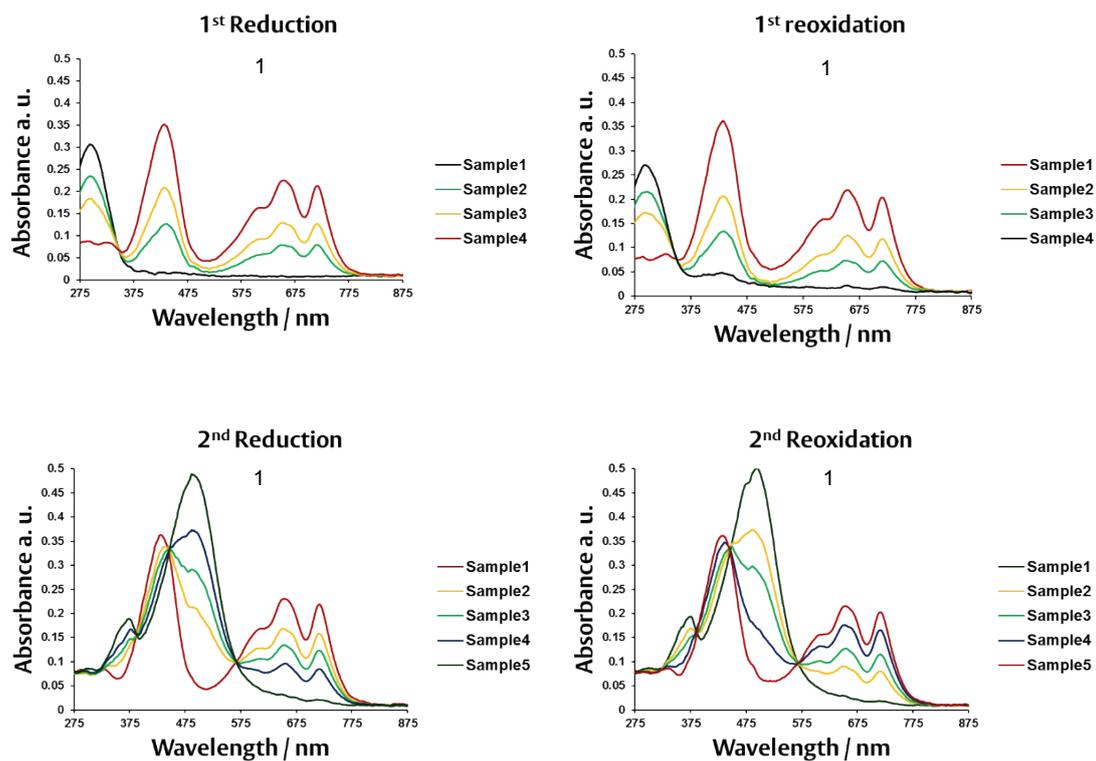


Figure S12. Reversible UV-vis spectral changes accompanying the stepwise one-electron reductions of dicationic unimer **1** (0.2 mM) to the corresponding radical cation (1st reduction) and the neutral form (2nd reduction) in anhydrous DMF/0.1 M TABPF₆ within an OTTLE cell.

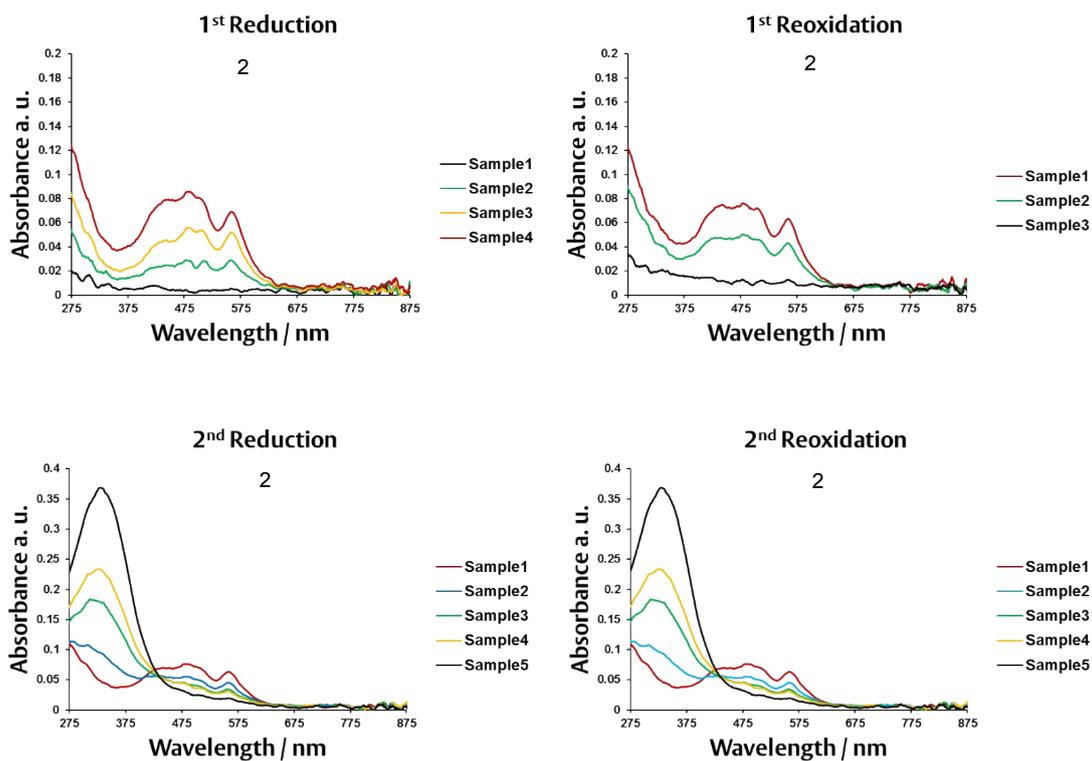


Figure S13. Reversible UV-vis spectral changes accompanying the stepwise two-electron reductions of tetracationic dimer **2** (0.2 mM) to the corresponding radical cation (1st reduction) and the neutral form (2nd reduction) in anhydrous DMF/0.1 M TABPF₆ within an OTTLE cell.

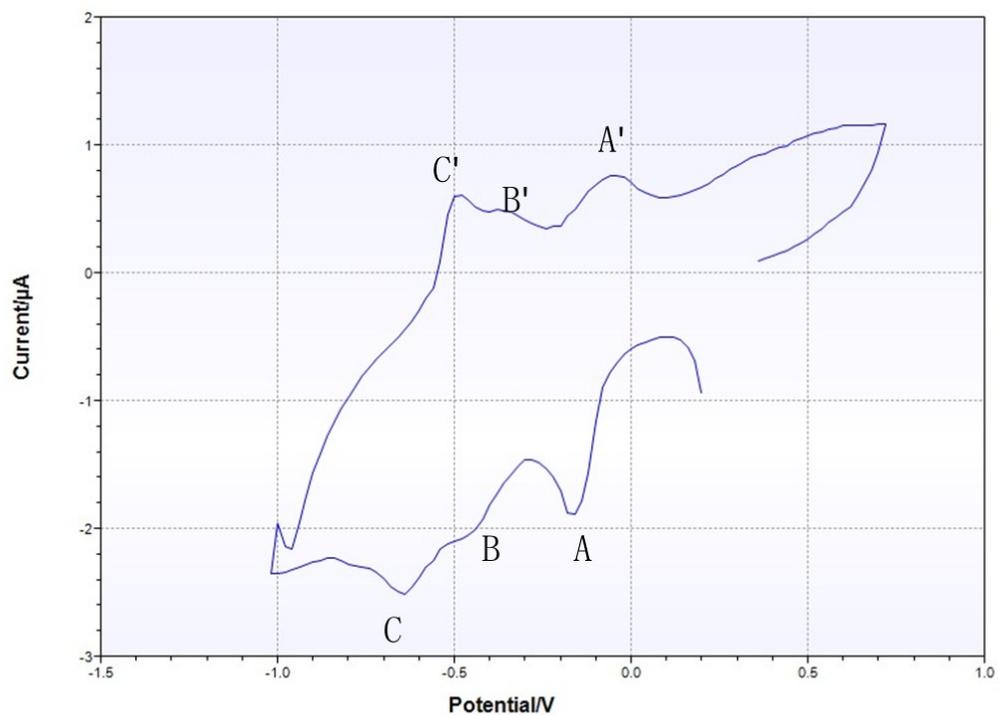


Figure S14. Cathodic thin-layer cyclic voltammogram recorded in the course of the UV-Vis spectral monitoring of the three reductions (Table 1) of hexacationic trimer **3** (0.2 mM) in anhydrous DMF within an OTTLE cell at $\nu = 2 \text{ mV s}^{-1}$ at room temperature. The potential scale is arbitrary (Ag wire pseudoreference electrode was used).

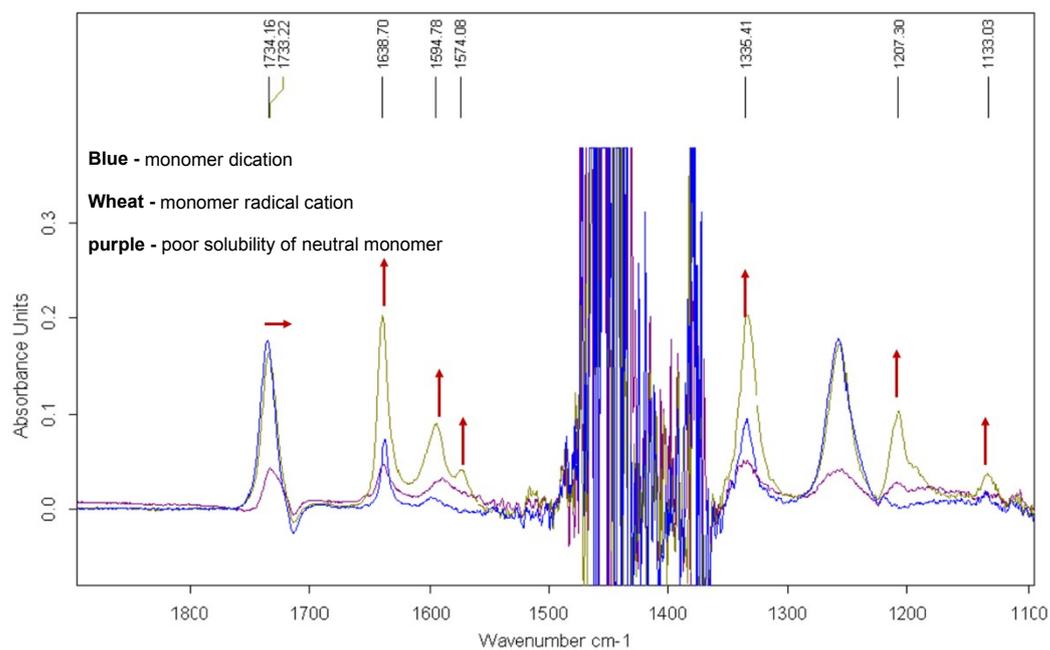


Figure S10. IR spectral changes accompanying the stepwise one-electron reduction of dicationic unimer **1** (blue, 1 mM) to the corresponding radical cation (khaki) and then to the ultimate neutral form (purple) in anhydrous *n*-butyronitrile /0.1 M TABPF₆ within an OTTLE cell. Solvent absorptions overload the instrument between 1350 and 1500 cm⁻¹.

References

- (1) Colquhoun, H. M.; Greenland, B. W.; Zhu, Z.; Shaw, J. S.; Cardin, C. J.; Burattini, S.; Elliott, J. M.; Basu, S.; Gasa, T. B.; Stoddart, J. F. *Org. Lett.* **2009**, *11*, 5238-5241.
- (2) Krejčík, M.; Daněk, M.; Hartl, F. *J Electroanal. Chem. Interfacial Electrochem.* **1991**, *317*, 179-187.