Probing the Role of Glycol Chain Lengths in π-Donor-Acceptor [2]Pseudorotaxanes Based on Monopyrrolo-Tetrathiafulvalene and Cyclobis(paraquat-*p*-phenylene)

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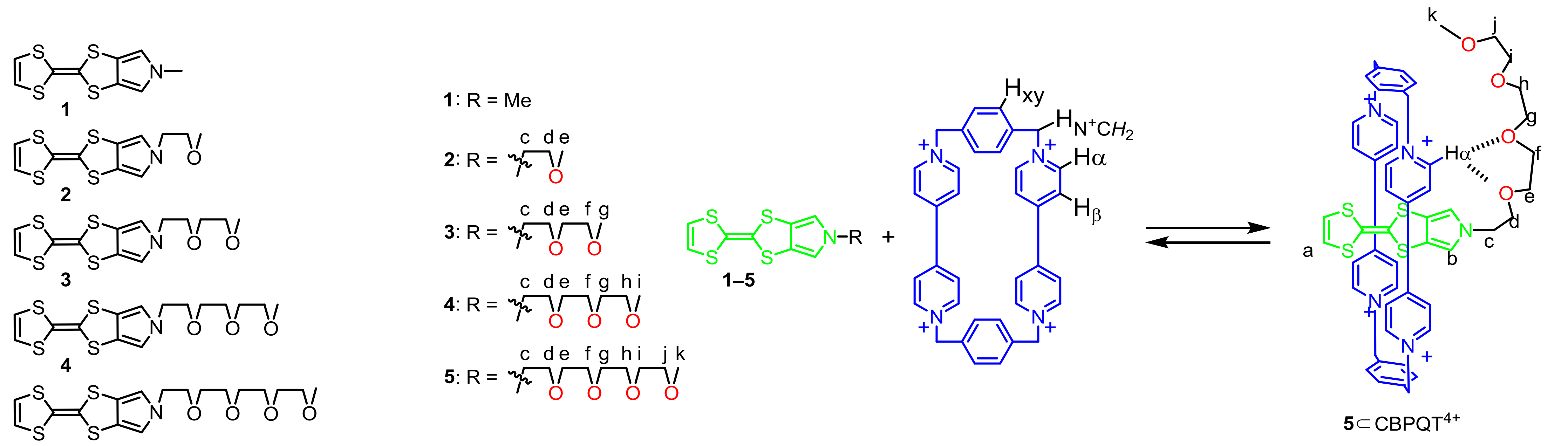
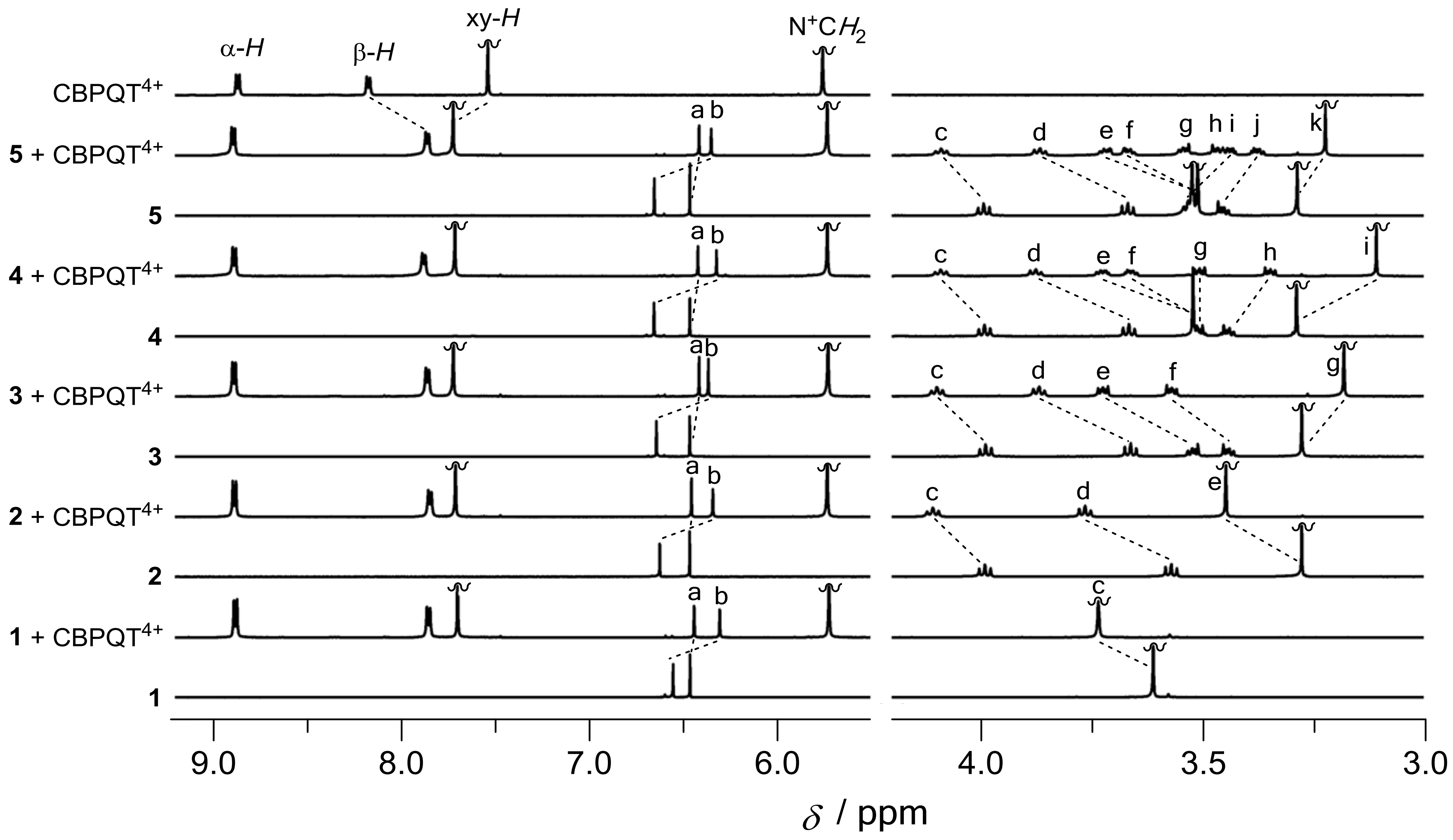
Aim of the Project

A homologous series of *N*-substituted monopyrrolo-tetrathiafulvalenes (MPTTF), only differing in the number of ethyleneoxy units were synthesized. These formed [2]pseudorotaxanes upon mixing with cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}). The resulting [2]pseudo-rotaxanes were investigated in order to probe the role of the glycol chain lengths on the complexation between **1**–**5** and CBPQT^{4+}. [1]

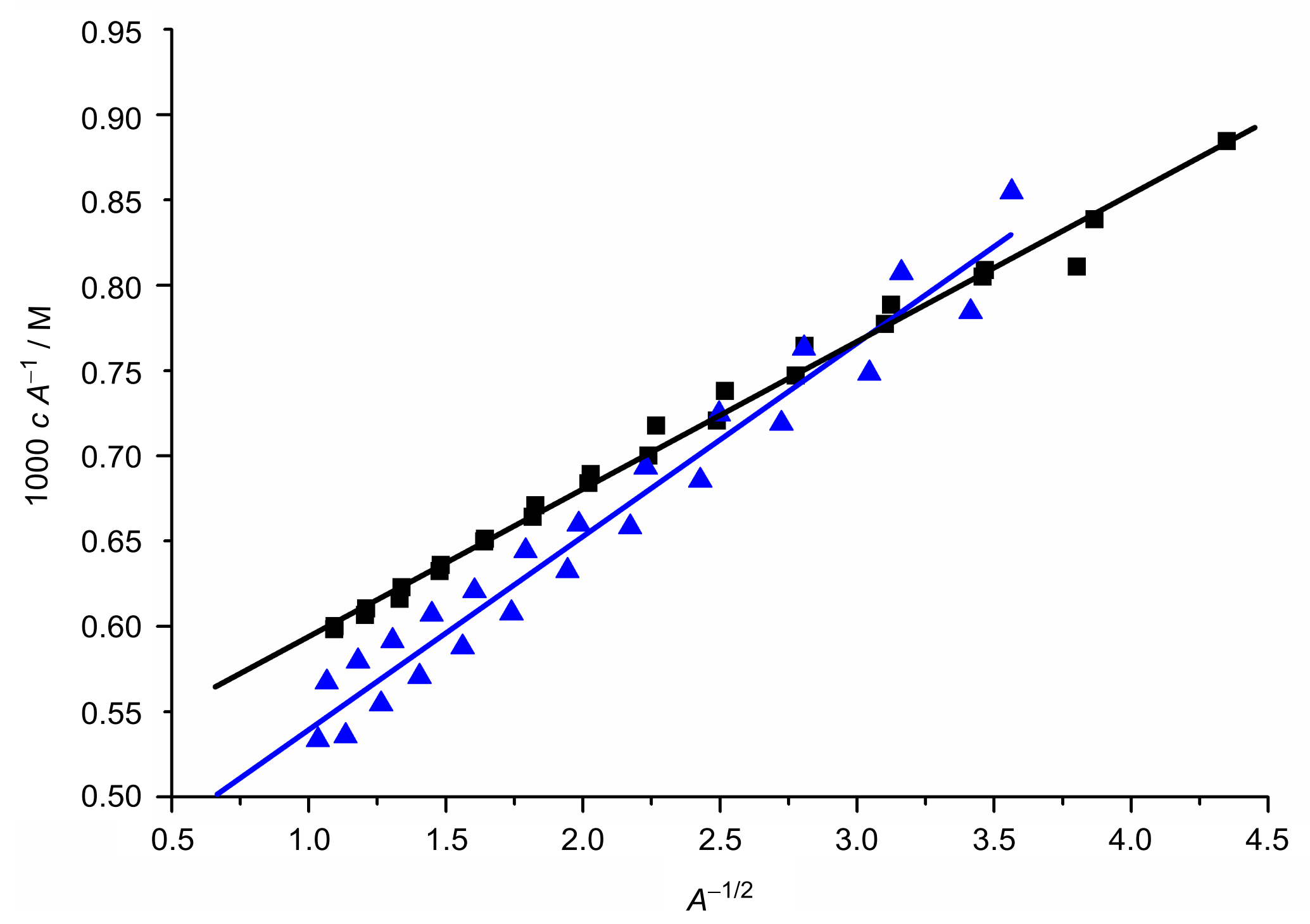


^{1}H NMR Spectroscopic Studies



Partial ^{1}H NMR spectra (400 MHz) recorded in CD_3CN (c = 1.5 mM) at 298 K of CBPQT^{4+}, the MPTTF derivatives **1**–**5**, and equilibrated solutions containing **1**–**5** mixed with equimolar amounts of CBPQT^{4+}.

UV-Vis-NIR Studies

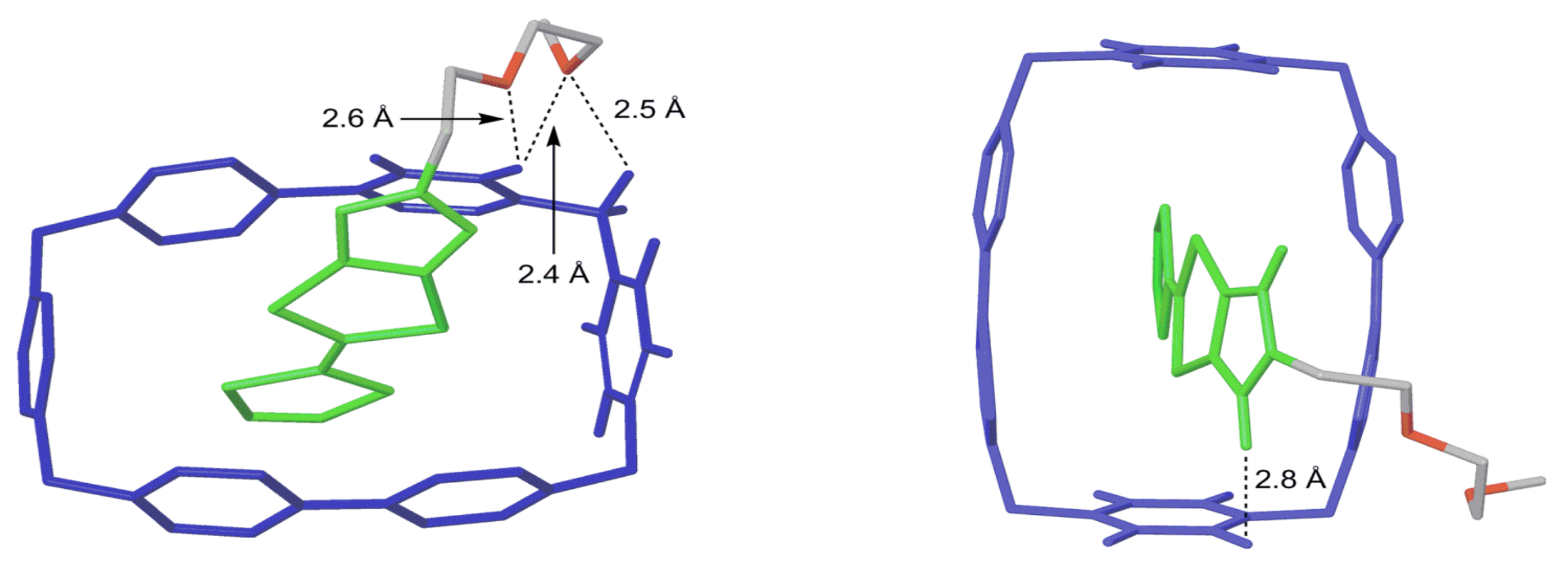


Linear plots of 1000 $c\ A^{-1}$ against $A^{-1/2}$ for a 1:1 mixture of CBPQT^{4+} and MPTTF derivative **1** (blue line) and **3** (black line).

Binding Constants (K_a Values) and Derived Free Energies of Complexation ($\Delta G°$) between the MPTTF Derivatives **1**–**5** and CBPQT^{4+} Determined by UV-Vis-NIR Absorption Spectroscopy at 298 K in MeCN.

compound	λ_{max} (nm)	data points	correlation coefficient	K_a (M^{-1})	$\Delta G°$ (kcal mol^{-1})
1	877	24	0.960	33000 ± 4000	–6.2 ± 0.1
2	854	28	0.987	41000 ± 4000	–6.3 ± 0.1
3	854	27	0.991	68000 ± 8000	–6.6 ± 0.1
4	856	28	0.986	64000 ± 8000	–6.6 ± 0.1
5	854	29	0.999	63000 ± 7000	–6.6 ± 0.1

Molecular Modelling and Cyclic Voltammetry



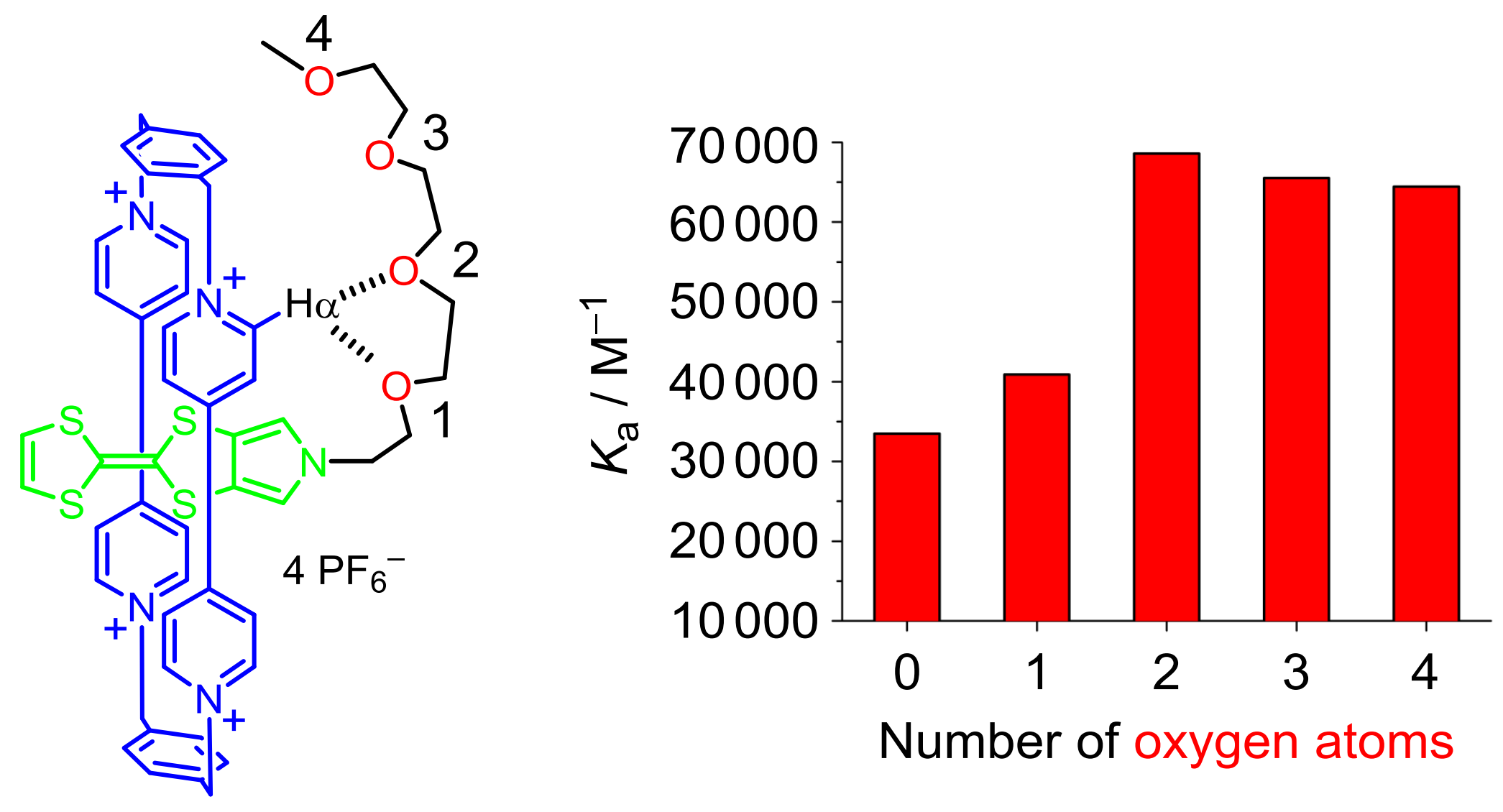
M06-L/6-31G** geometry optimized superstructure of the [2]pseudorotaxane **3**⊂CBPQT^{4+} (solvent corrected, MeCN) shown at two different angles. The MPTTF unit is colored green and the CBPQT^{4+} ring is blue, whereas carbon and oxygen atoms in the glycol chain are colored gray and red, respectively.

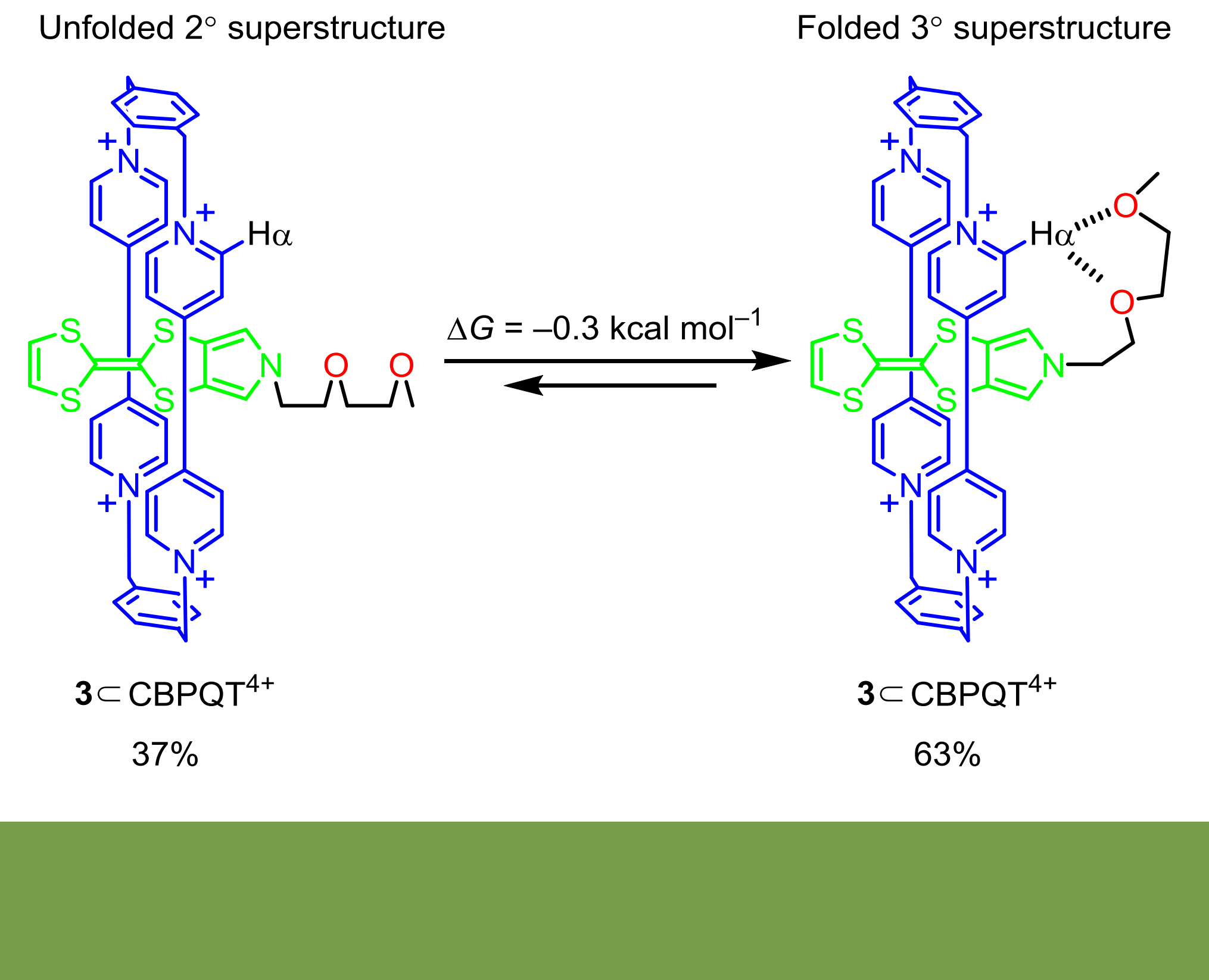
The first ($E_{1/2}^1$) and second ($E_{1/2}^2$) redox potentials for the MPTTF derivatives **1**–**5** obtained by cyclic voltammetry (CV) at 298 K in MeCN.

Compound	$E_{1/2}^1$ (V)	$E_{1/2}^2$ (V)
1	+0.030	+0.400
2	+0.025	+0.415
3	+0.020	+0.415
4	+0.020	+0.415
5	+0.020	+0.415

Conclusions

- The MPTTF-derivatives **1**–**5** show similar redox potentials, so the change in binding constants is not ascribed to come from a change in electron donor properties
- The [2]pseudorotaxanes **1**–**5**⊂CBPQT^{4+} show a trend towards higher binding energy, the longer the glycol chain. The biggest change in binding energy is seen for compounds **2** and **3**
- Investigations suggest that hydrogen bonds can form between the first and second oxygen atoms and CBPQT^{4+} in the [2]pseudorotaxanes, providing an extra stabilization of $\Delta G°$ = –0.3 kcal mol^{-1} to the [2]pseudorotaxanes





3⊂CBPQT^{4+}
37%

3⊂CBPQT^{4+}
63%

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[1] Kristensen, R.; Andersen, S. S.; Olsen, G.; Jeppesen, J. O., *J. Org. Chem.*, **2017,** *82*, 1371-1379.