

Anions Effect on the Complexation between Electron Donors and Cyclobis(paraquat-*p*-phenylene)

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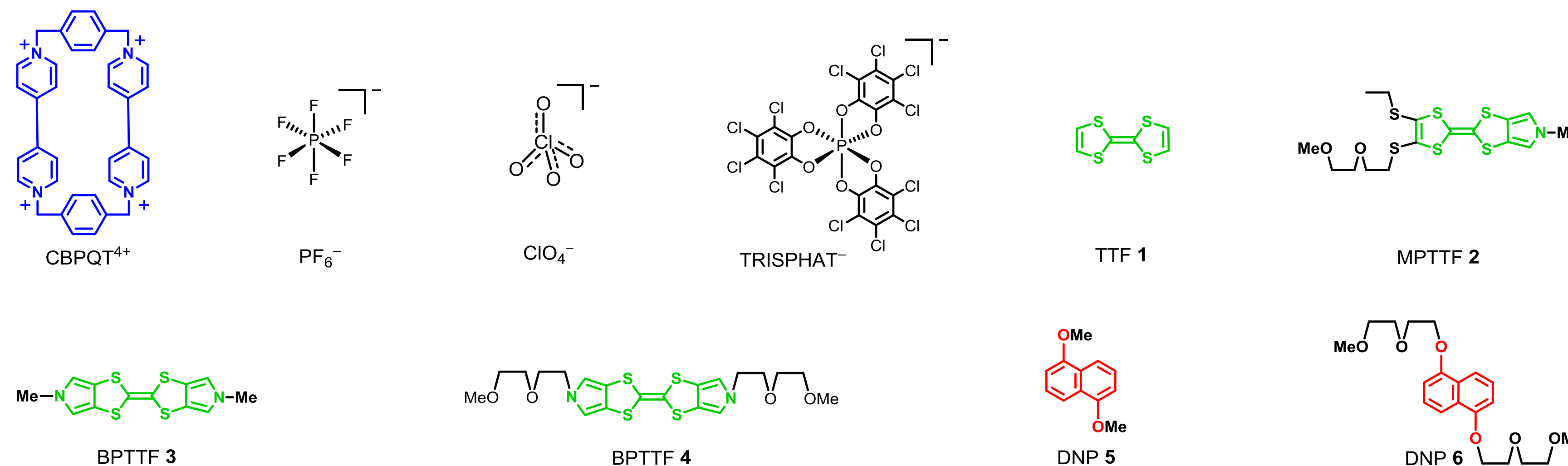
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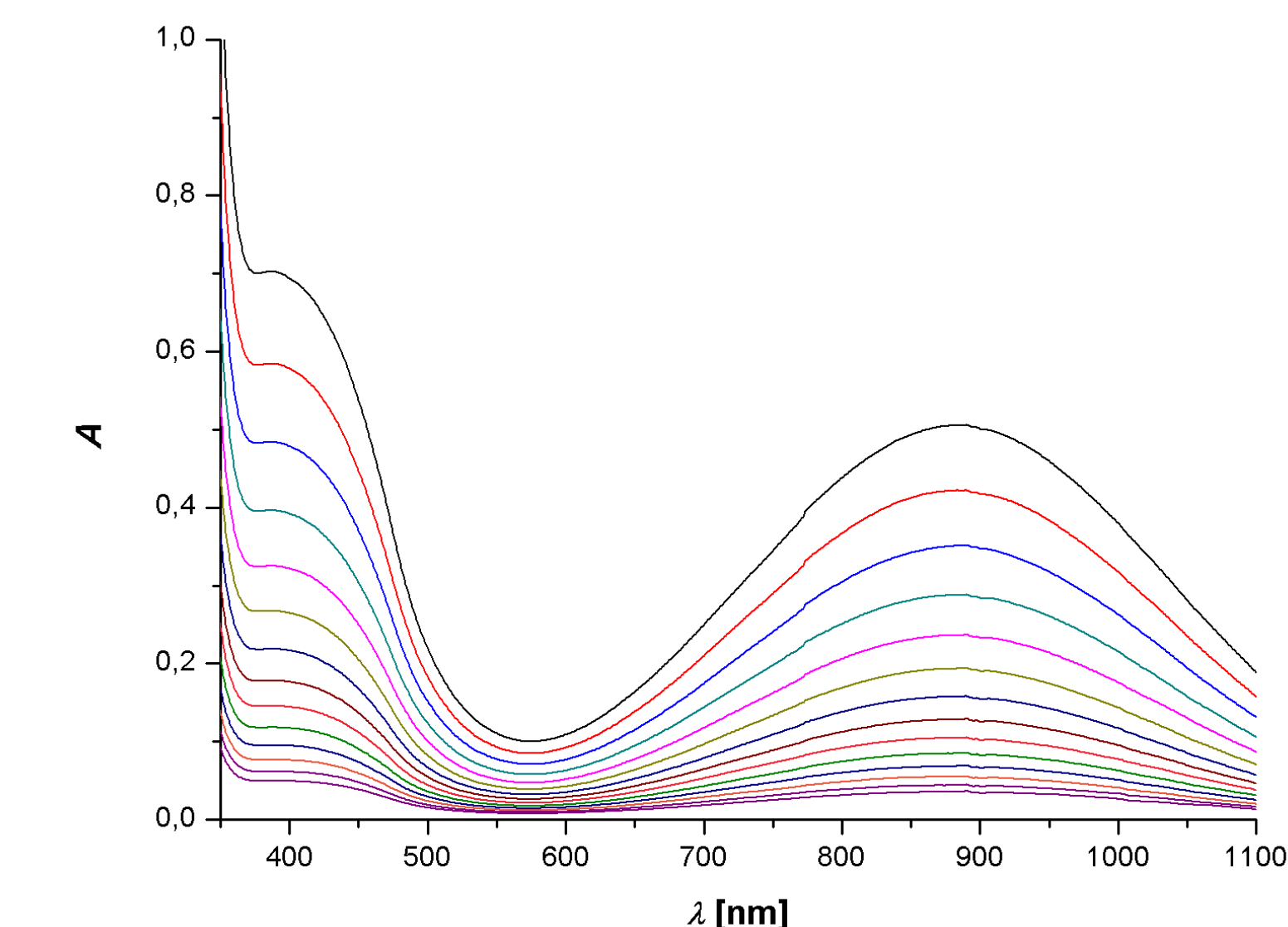
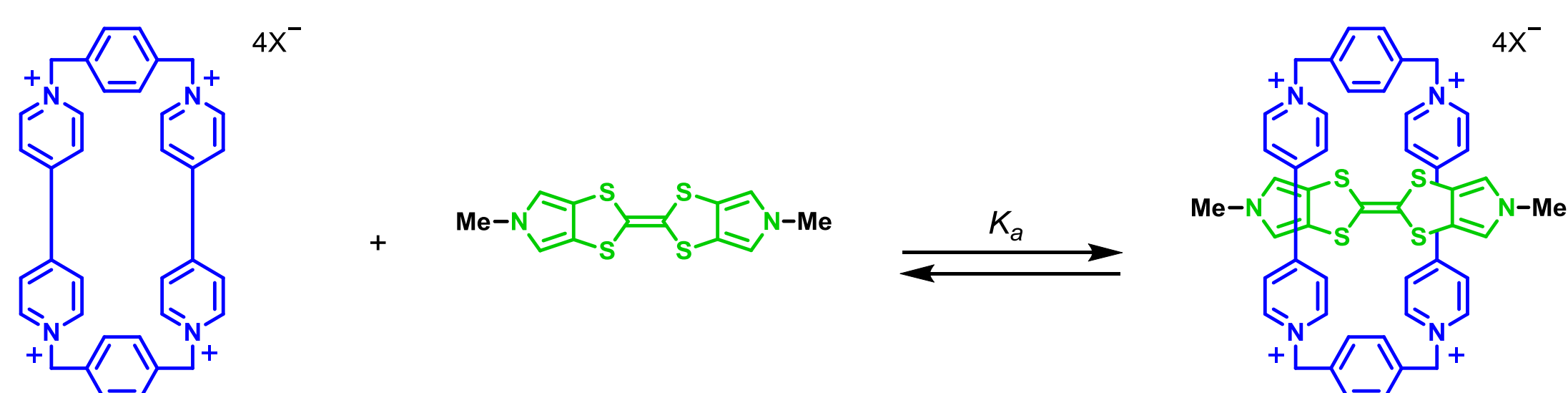
INTRODUCTION

The electron accepting macrocyclic tetracationic host cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) has been used intensively as the ring component for the construction of switchable donor-acceptor bistable [2]catenanes^{1,2} and [2]rotaxanes.³ In these constructions, derivatives of the electron donating tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) have been widely used as guests.



It will be shown that the complexation between an electron donor and CBPQT⁴⁺ is not only influenced by the nature of the donor, but also by the nature of the counteranions.⁴ Binding studies between CBPQT⁴⁺ and derivatives of TTF and DNP in the presence of differently sized counteranions (X⁻ = TRISPHAT⁻, PF₆⁻, and ClO₄⁻) reveal that both the nature and the concentration of the anion have a large impact on the association strength of the resulting host-guest complex.

COMPLEXATION STUDIES



UV/Vis-NIR spectra of a 1:1 mixture of **3** and CBPQT•4TRISPHAT recorded in MeCN at 298 K. The concentration has been reduced with 1/6 between each spectrum.

The complexation between the electron donors **1–6** and CBPQT⁴⁺ was investigated using UV/Vis-NIR spectroscopy. The absorbance was measured at λ_{\max} for the CT absorption band at various concentration, and was used to calculate the binding constant K_a of the donor-acceptor complex.

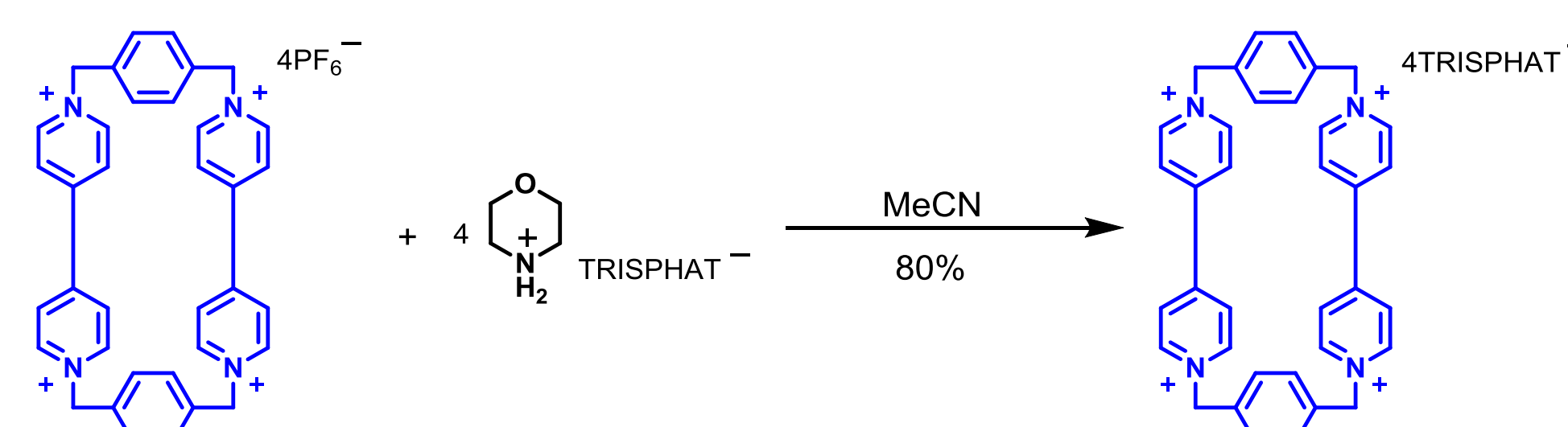
RESULTS

Comparison of binding constants (K_a) and derived free energies (ΔG°) between A) the electron donors **1–6** and CBPQT•4PF₆ and CBPQT•4TRISPHAT and B) 2•CBPQT•4PF₆ + 0.1 M *n*-Bu₄N•PF₆ and 2•CBPQT•4PF₆ + 0.1 M *n*-Bu₄N•ClO₄ determined by absorption spectroscopy at 298 K in MeCN using the TTF/ CBPQT⁴⁺ (**1–4**) or the DNP/ CBPQT⁴⁺ (**5–6**) CT bands as probes.

A	CBPQT•4PF ₆		CBPQT•4TRISPHAT	
	K_a (M ⁻¹)	ΔG° (kcal mol ⁻¹)	K_a (M ⁻¹)	ΔG° (kcal mol ⁻¹)
1	15 000 ± 2300	-5.70 ± 0.09	37 000 ± 6200	-6.23 ± 0.10
2	13 000 ± 900	-5.61 ± 0.04	20 000 ± 900	-5.87 ± 0.03
3	84 000 ± 3000	-6.72 ± 0.03	176 000 ± 12 000	-7.16 ± 0.05
4	231 000 ± 12 200	-7.32 ± 0.04	286 300 ± 30 000	-7.45 ± 0.07
5	2000 ± 100	-4.50 ± 0.04	< 10	< 1.4
6	35 100 ± 1500	-6.21 ± 0.03	64 700 ± 7200	-6.57 ± 0.07

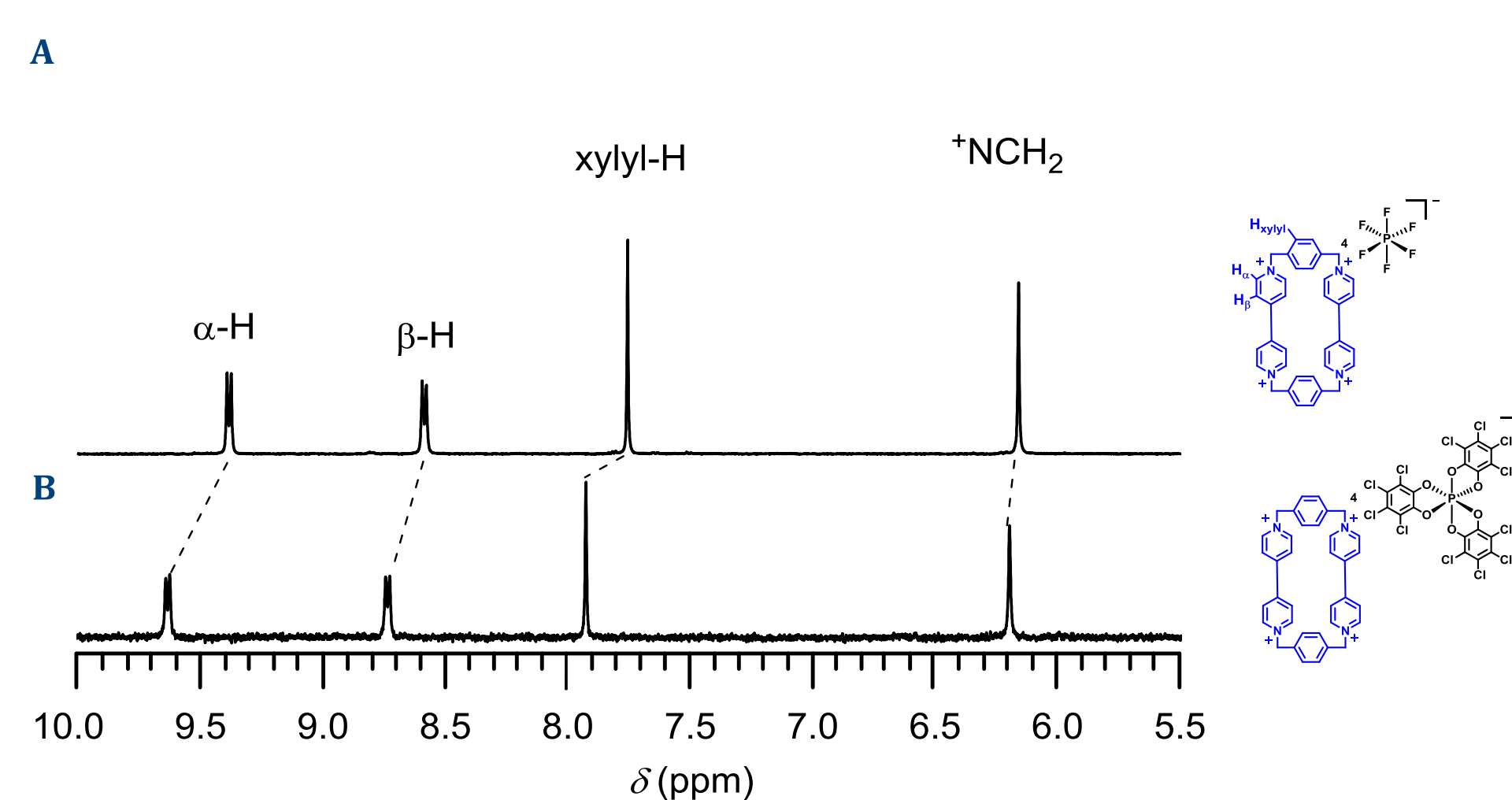
B	K_a (M ⁻¹)	ΔG° (kcal mol ⁻¹)
	2•CBPQT•4PF ₆ + 0.1 M <i>n</i> -Bu ₄ N•PF ₆	5600 ± 100
2•CBPQT•4PF ₆ + 0.1 M <i>n</i> -Bu ₄ N•ClO ₄	3700 ± 100	-4.87 ± 0.02

SYNTHESIS OF CBPQT•4TRISPHAT

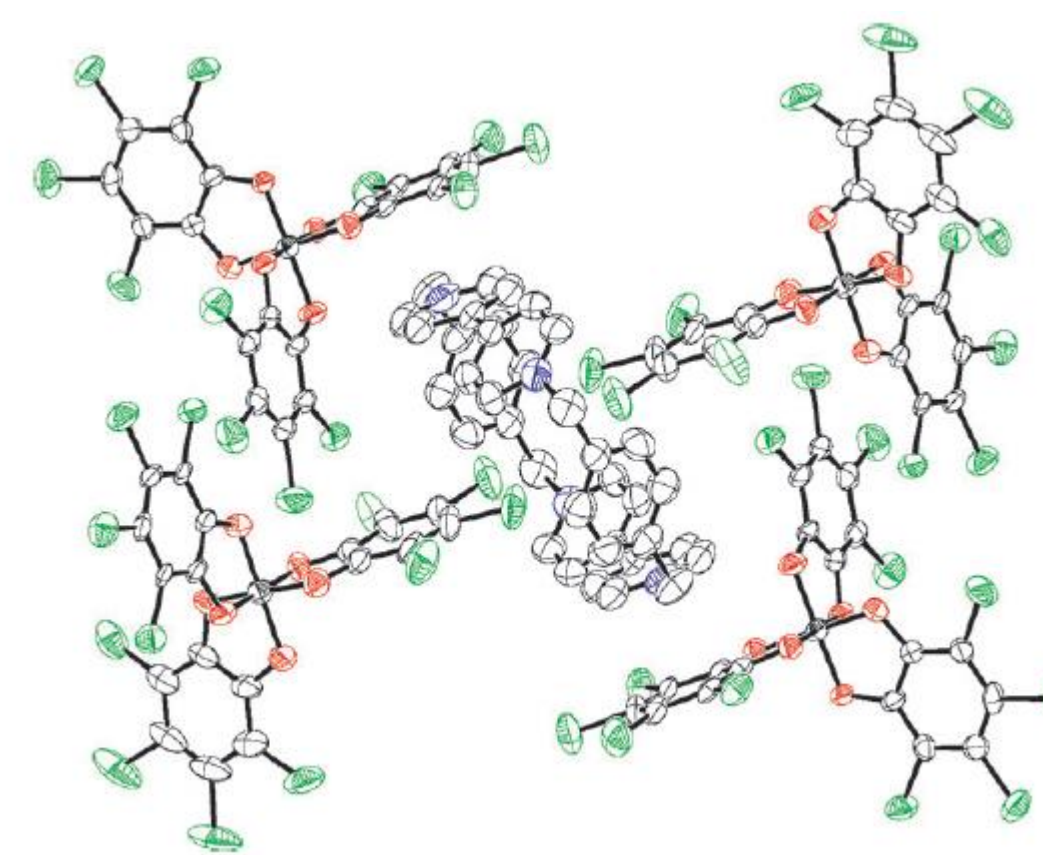


CHARACTERIZATION

The protons in CBPQT⁴⁺ are less shielded when TRISPHAT⁻ is the counterion as compared to the situation where PF₆⁻ is the counterion. Consequently, all resonances of the protons in CBPQT⁴⁺ are shifted downfield in the ¹H NMR spectrum. This observation can be explained by the different size of the two ions. The bigger TRISPHAT⁻ increases the distance between itself and CBPQT⁴⁺. Therefore, the interaction between TRISPHAT⁻ and CBPQT⁴⁺ is weaker than the interaction between PF₆⁻ and CBPQT⁴⁺.



¹H NMR spectra (400 MHz, 298 K) recorded in CD₃COCD₃ of A) CBPQT•4PF₆ and B) CBPQT•4TRISPHAT.



The X-ray crystal structure of CBPQT•4TRISPHAT shows that the cavity of CBPQT⁴⁺ is occupied by four chlorine atoms from TRISPHAT⁻, which have to be expelled from the cavity before any electron donor can bind.

CONCLUSION

CBPQT•4TRISPHAT has been synthesized and characterized and it has been shown that it is a better host for the electron donating TTF derivatives **1–4** as compared to CBPQT•4PF₆. Regarding the DNP derivatives (**5–6**), the results support the hypothesis that binding between DNP derivatives and CBPQT⁴⁺ is not primarily governed by electron donation but by C–H... π interactions. C–H...O hydrogen bonds could be the reason that the binding constant generally is larger for **6** than for **5**. Since there is more room for the glycol chains when TRISPHAT⁻ is the counterion, the entropy is bigger and the binding constant will increase compared to the case where PF₆⁻ is the counterion. Furthermore, in the presence of *n*-Bu₄N•PF₆ and *n*-Bu₄N•ClO₄, the formation of tighter ion-pairs significantly reduces the hosting ability of CBPQT⁴⁺ toward the MPPTF derivative **2**. From all this, it can be concluded that larger counteranions give rise to stronger host-guest donor-acceptor complexes. This knowledge is important regarding future design of mechanically interlocked systems based on CBPQT⁴⁺.