Extending the Family of Heteroditopic Calix[4]diquinone Receptors for Cooperative AND Ion-Pair Recognition

Anna J. McConnell, Christopher J. Serpell, and Paul D. Beer

Supplementary Information

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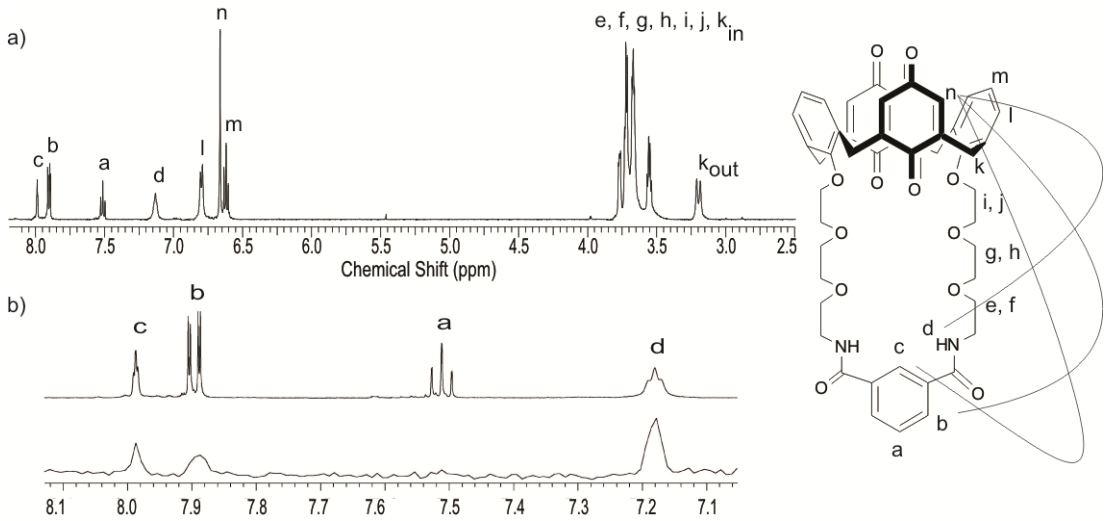

Figure S1 a) ^{1}H NMR spectrum of receptor **5** in CD_3CN at 298 K and b) ROESY analysis showing correlations between proton *n* of the calix[4]diquinone unit and protons *b*-*d* of the anion binding unit.

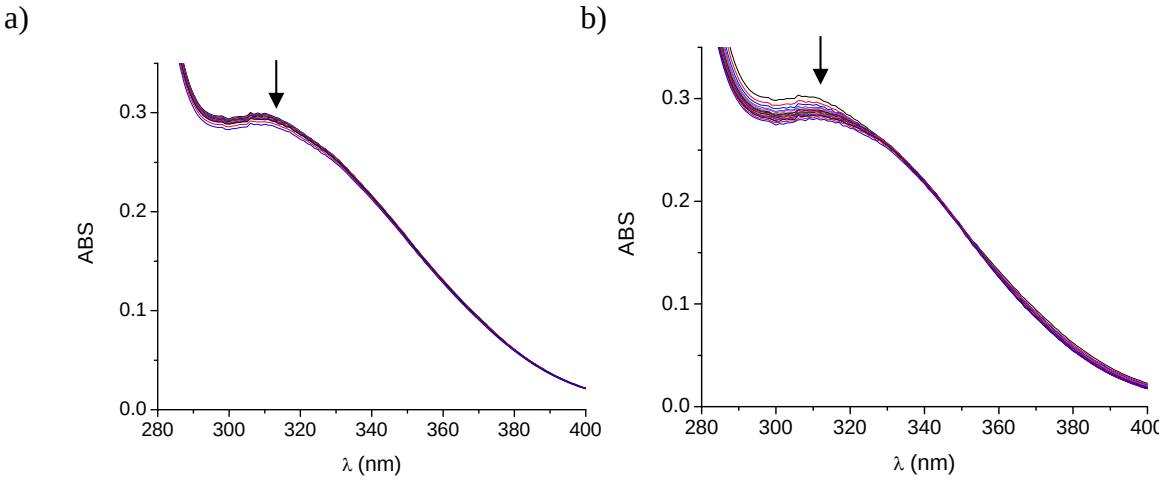

Figure S2 Changes in the absorbance of receptor **4** upon addition of NH_4^+ cations in the a) absence and b) presence of one equivalent of chloride ions in CH_3CN at 298 K.

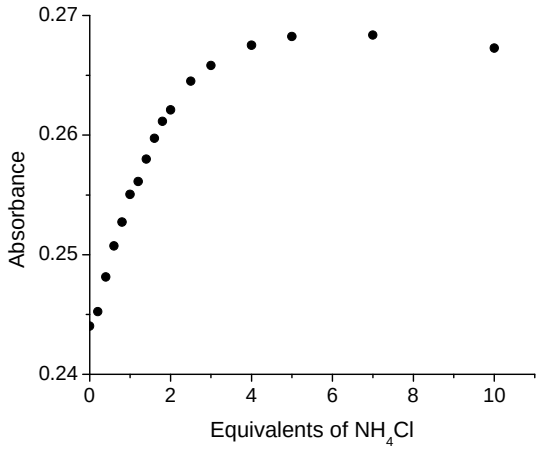

Figure S3 Variation in the absorbance upon addition of aqueous NH_4Cl to receptor **1** in 0.5% H_2O/CH_3CN at 298 K.

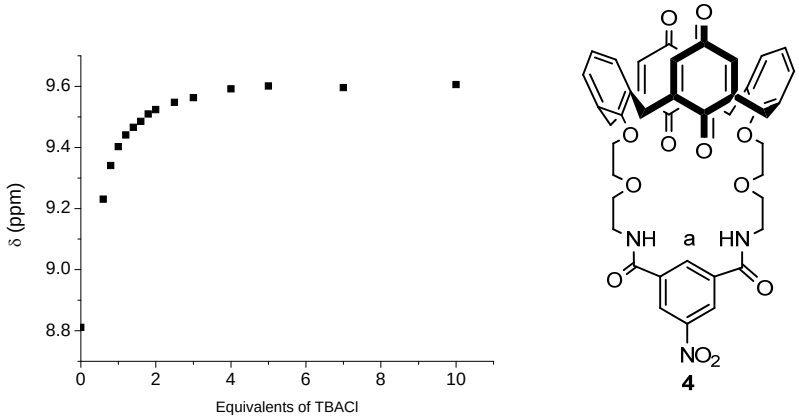

Figure S4 Chemical shift changes of the isophthaloyl proton *a* of receptor **4** upon addition of TBACl in the presence of one equivalent of NH_4PF_6 in 98:2 CD_3CN/D_2O at 298 K.

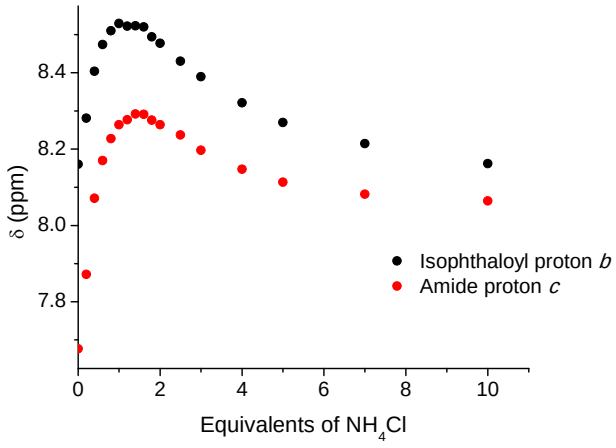

Figure S5 Variation in the chemical shift of isophthaloyl proton *b* and amide proton *c* upon addition of aqueous NH_4Cl to receptor **1** in 0.5% H_2O/CD_3CN at 298 K.

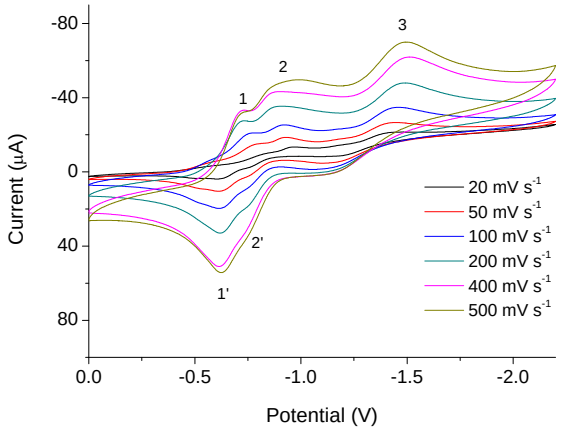

Figure S6 CVs of receptor **5** at different scan rates in CH_3CN at 298 K. Conditions: 4 mM solution of receptor **5**, 0.1 M $TBAPF_6$ supporting electrolyte, glassy carbon working electrode, platinum auxiliary electrode, Ag/AgCl reference electrode.

a) b)

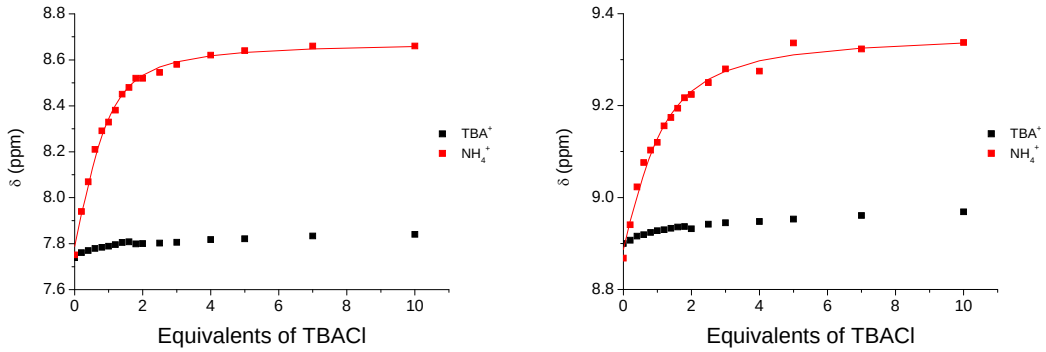

Figure S7 Chemical shift change of the amide proton upon addition of TBACl in the presence and absence of coordinating ammonium cations to a solution of a) receptor **1** and b) receptor **2** at 298 K in 98:2 CD_3CN/D_2O. Square symbols represent the experimental data points and the lines represent the calculated curves

Part II: Crystallographic Data

X-Ray Crystal Structure of Receptor 1

Single crystals of receptor **1** were grown by slow evaporation of a CH_2Cl_2 solution.

Table S1 Crystallographic data for receptor **1**

Crystal identification	5503
Chemical formula	$C_{56}H_{64}N_2O_{10}$
Formula weight	925.09
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	13.4651(3)
b (Å)	13.4770(3)
c (Å)	13.6637(4)
α (°)	98.499(1)
β (°)	93.210(1)
γ (°)	98.034(1)
Cell volume (Å^3)	2420.79(10)
Z	2
Calculated density (Mg/m^3)	1.269
Absorption coefficient (mm^{-1})	0.087
F_{000}	988
Crystal size (mm)	0.12 x 0.10 x 0.09
Description of crystal	Clear intense yellow block
Absorption correction	Semi-empirical from equivalents
Transmission coefficients (min, max)	0.992, 0.923
θ range for data collection (°)	$5.10 \leq \theta \leq 27.42$
Index ranges	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-17 \leq l \leq 17$
Reflections measured	17257
Unique reflections	10797
R_{int}	0.0669
Observed reflections ($I > 2\sigma(I)$)	5572
Refinement method	Full-matrix least-squares on F^2

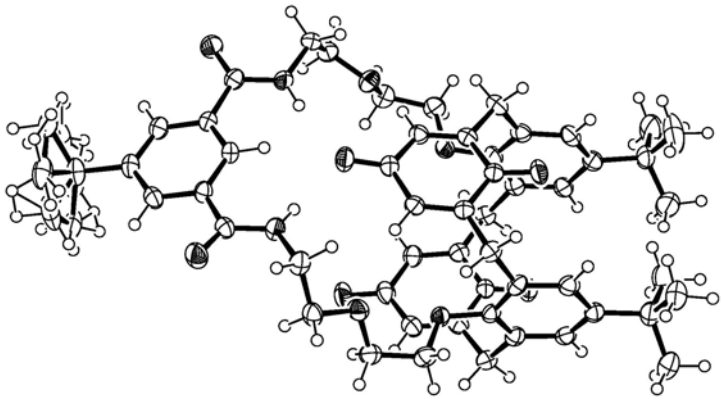

Figure S8 ORTEP thermal ellipsoid plot of the single crystal structure of receptor **1** at 50% probability. Solvent has been omitted for clarity.

X-Ray Crystal Structure of Receptor 3

Single crystals of receptor **3** were grown by slow evaporation of a $CHCl_3/CH_3CN$ solvent mixture.

Table S2 Crystallographic data for receptor **3**

Crystal identification	014CJS09
Chemical formula	$C_{44}H_{40}N_2O_{10}\cdot 0.96(CHCl_3)\cdot 0.54(C_2H_3N)$
Formula weight	893.34
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	11.5030 (3)
b (Å)	13.4039 (4)
c (Å)	14.5562 (5)
α (°)	76.3517 (14)
β (°)	82.0783 (15)
γ (°)	81.4218 (14)
Cell volume ($Å^3$)	2144.24 (11)
Z	2
Calculated density (Mg/m^3)	1.384
Absorption coefficient (mm^{-1})	0.27
F_{000}	930.900
Crystal size (mm)	0.24 × 0.12 × 0.10
Description of crystal	Yellow block
Absorption correction	Multi-scan DENZO/SCALEPACK[1]
Transmission coefficients (min, max)	0.85, 0.97
θ range for data collection (°)	$5.2 \leq \theta \leq 27.5$
Index ranges	$-13 \leq h \leq 14$, $-17 \leq k \leq 17$, $-18 \leq l \leq 16$
Reflections measured	30051
Unique reflections	9701
R_{int}	0.075
Observed reflections ($I > 2\sigma(I)$)	6290
Refinement method	Full-matrix least-squares on F^2
Parameters refined	604
Weighting scheme	Modified Sheldrick
Goodness of fit	1.0
R	0.066
wR	0.175
Residual electron density (min, max) ($eÅ^{-3}$)	-0.6, 0.6

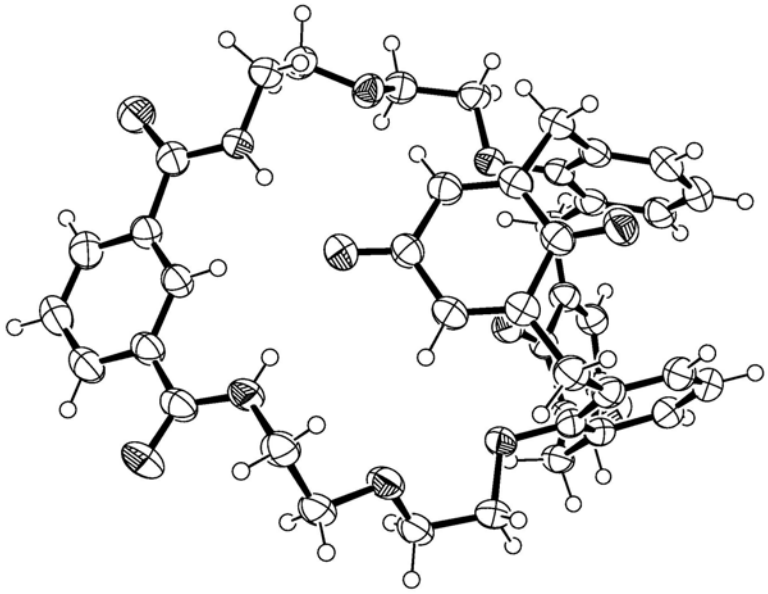

Figure S9 ORTEP thermal ellipsoid plot of the single crystal structure of receptor **3** at 50% probability. Solvent has been omitted for clarity.

X-Ray Crystal Structure of Precursor 12

Single crystals of precursor **12** were grown by slow evaporation of an EtOAc/hexane mixture.

Table S3 Crystallographic data for precursor **12**

Crystal identification	5378
Chemical formula	$C_{52}H_{46}N_2O_{10}$
Formula weight	858.94
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P\ 2_1/c$
a (Å)	12.5858(2)
b (Å)	20.2654(2)
c (Å)	17.1345(2)
α (°)	90
β (°)	99.8495(5)
γ (°)	90
Cell volume (Å^3)	4305.85(10)
Z	4
Calculated density (Mg/m^3)	1.325
Absorption coefficient (mm^{-1})	0.092
F_{000}	1808
Crystal size (mm)	0.28 x 0.34 x 0.42
Description of crystal	Colourless block
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min, max)	0.96, 0.97
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-16 \leq h \leq 16$, $0 \leq k \leq 26$, $0 \leq l \leq 22$
Reflections measured	49220

Unique reflections	10052
R_{int}	0.045
Observed reflections (I > 3σ(I))	5775
Refinement method	Full-matrix least-squares on *F*
Parameters refined	585
Weighting scheme	Chebychev 3-term polynomial
Goodness of fit	1.1083
R	0.0350
wR	0.0393
Residual electron density (min, max) ($eÅ^{-3}$)	-0.17, 0.20

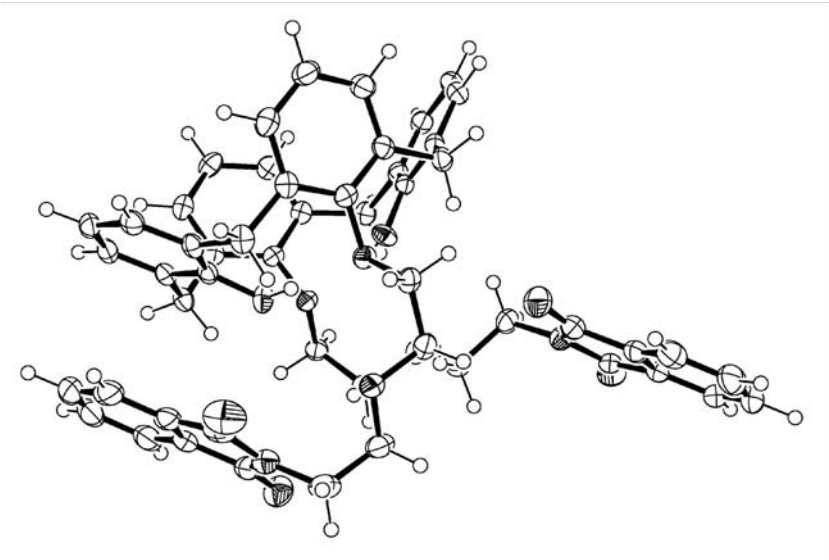

Figure S10 ORTEP thermal ellipsoid plot of the single crystal structure of precursor **12** at 50% probability. Solvent has been omitted for clarity.

X-Ray Crystal Structure of Macrocycle 17

Single crystals of macrocycle **17** were grown by slow evaporation of an EtOAc/acetone mixture.

Table S4 Crystallographic data for macrocycle **17**

Crystal identification	5386
Chemical formula	$C_{44}H_{43}N_3O_{10}\cdot H_20\cdot 0.5(C_5H_{10}O_2)$
Formula weight	842.92
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/a
a (Å)	13.3790 (1)
b (Å)	15.0967 (2)
c (Å)	20.7767 (3)
α (°)	90
β (°)	103.7671 (5)
γ (°)	90
Cell volume ($Å^3$)	4075.89 (9)
Z	4
Calculated density (Mg/m^3)	1.374

Absorption coefficient (mm^{-1})	0.10
F_{000}	1784
Crystal size (mm)	0.44 × 0.32 × 0.20
Description of crystal	Colourless plate
Absorption correction	Multi-scan DENZO/SCALEPACK[1]
Transmission coefficients (min, max)	0.82, 0.98
θ range for data collection (°)	$5.0 \leq \theta \leq 29$
Index ranges	$-18 \leq h \leq 18$, $-20 \leq k \leq 20$, $-28 \leq l \leq 28$
Reflections measured	87793
Unique reflections	10734
R_{int}	0.069
Observed reflections ($I > 2\sigma(I)$)	6235
Refinement method	Full-matrix least-squares on F
Parameters refined	559
Weighting scheme	Modified Sheldrick
Goodness of fit	1.08
R	0.052
wR	0.06
Residual electron density (min, max) ($eÅ^{-3}$)	-0.58, 0.39

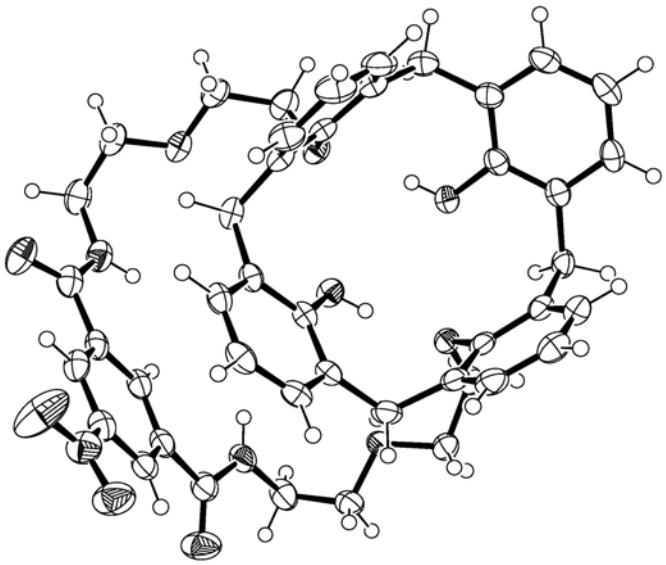

Figure S11 ORTEP thermal ellipsoid plot of the single crystal structure of macrocycle **17** at 50% probability. Solvent has been omitted for clarity.

Part III: Titration Protocols

^{1}H NMR Spectroscopy Titrations

^{1}H NMR spectra were recorded on a Varian Unity Plus 500 spectrometer at 298 K. Anion binding titration studies were carried out by titrating a solution of the guest anion as its tetrabutylammonium salt (TBAX) into a solution of the host species. The initial sample volume was 500 μL, the starting concentration of the host species was 1.5 mM and the concentration of the anion solution was 0.075 M. Seventeen aliquots of the anion solution were added until a total of 10 equivalents of anion had been added. The following volumes of anion were added: 10 x 2 μL, 2 x 5 μL, 2 x 10 μL, 1 x 20 μL, 1 x 30 μL. After each addition

the solution was thoroughly shaken and the ^{1}H NMR spectrum was recorded monitoring the changes in the chemical shift of the ortho pyridinium proton of the host.

The resulting titration data were analysed using the winEQNMR2[2] computer program. The observed chemical shift data, host and guest concentrations at each titration point and estimates for the binding constant, limiting chemical shifts and complex stoichiometry were added to the input file. The parameters were refined by non-linear least-squares analysis to achieve the best fit between the observed and calculated chemical shifts. The parameters were varied until values for the association constant converged. There was good agreement between the experimental and calculated binding curves which demonstrated that the model was appropriate.

UV/visible Spectroscopy Titrations

UV/visible spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer or a Shimadzu UV-2401PC spectrometer at 298 K. Cation binding titration studies were carried out by titrating a solution of the guest cation as its hexafluorophosphate or perchlorate salt into a solution of the host species. Where necessary, a 1:1 mixture of the host and TBACl was also prepared. The initial sample volume was 3 mL, the starting concentration of the host species was 0.1 mM and the concentration of the cation solution was 0.03 M. Seventeen aliquots of the cation solution were added until a total of 10 equivalents of cation had been added. The following volumes of cation were added: 10 x 2 μL, 2 x 5 μL, 2 x 10 μL, 1 x 20 μL, 1 x 30 μL. After each addition, the UV/visible spectrum was recorded monitoring changes of the calix[4]diquinone n-π* absorption band.

The resulting titration data were analysed using the SPECFIT[3] computer program. The spectra, host and guest concentrations at each titration point, complex stoichiometry and whether the component species were coloured were included in the input file. The parameters were refined by global analysis using singular value decomposition and non-linear modelling by the Levenberg-Marquardt method. The parameters were varied until values for the association constant converged. There was good agreement between the experimental and calculated binding curves, calculated concentration profiles and calculated spectra of the complexes, demonstrating that the model was appropriate.

Electrochemistry Titrations

Electrochemical studies on selected calix[4]diquinone receptors were carried out using square wave and cyclic voltammetric techniques. Voltammograms were recorded under a N_2 atmosphere at 298 K using a glassy carbon working electrode, platinum auxiliary electrode and Ag/AgCl reference electrode connected to a Potentiostat (Autolab PGSTAT12 using GPES software). Square wave voltammograms were recorded at 30 MHz and cyclic voltammograms were recorded at 100 mV s^{-1}, unless specified otherwise. The starting concentration of the host species was 4 mM in dry degassed CH_3CN, with 0.1 M $TBAPF_6$ as the supporting electrolyte, and the initial sample volume was 2.5 mL. Titrations were carried out by titrating a 0.25 M solution of the guest species ($NaClO_4$, KPF_6 or TBACl) into a solution of the host species. Four aliquots of the guest species were added until a total of 5 equivalents of guest had been added. The following volumes of guest were added: 2 x 5 μL, 2 x 10 μL, 1 x 20 μL. In some cases, four aliquots of another guest species were added to investigate ion-pair recognition. After each addition, the square wave and cyclic voltammograms were recorded monitoring potential changes of the calix[4]diquinone redox waves.

Part IV: References

1. Z. Otwinowski and W. Minor, *Methods in Enzymology*, Eds. C. W. Carter Jr. and R. M. Sweet, Academic Press, New York, 1997.

2. M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311-312.

3. SPECFIT v. 2.02, Spectrum Software Associates, Chapel Hill, NC.