Supplementary Information for

Triazole- and triazolium-containing porphyrin cages for optical anion sensing

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Characterisation of Target Triazole- and Triazolium-Containing Porphyrin Cages

Compound 5

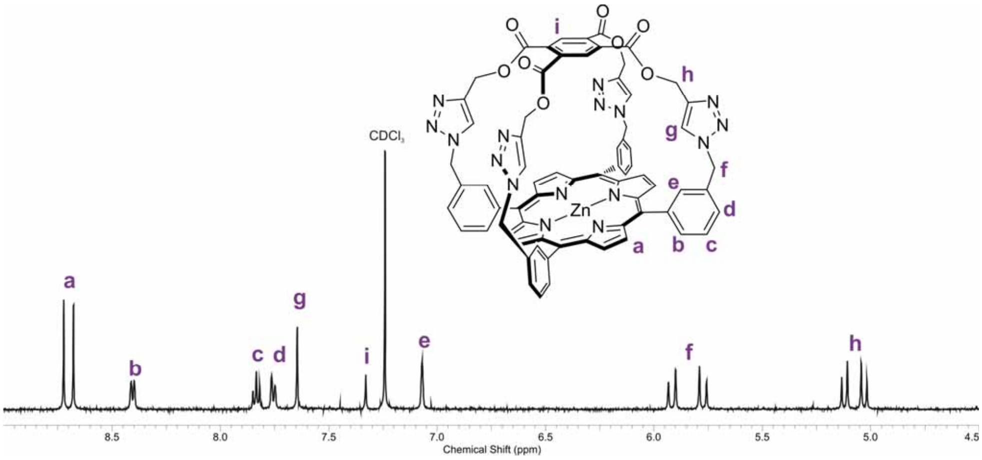

Figure S1: ^{1}H NMR spectrum of **5** in $CDCl_3$ at 293 K.

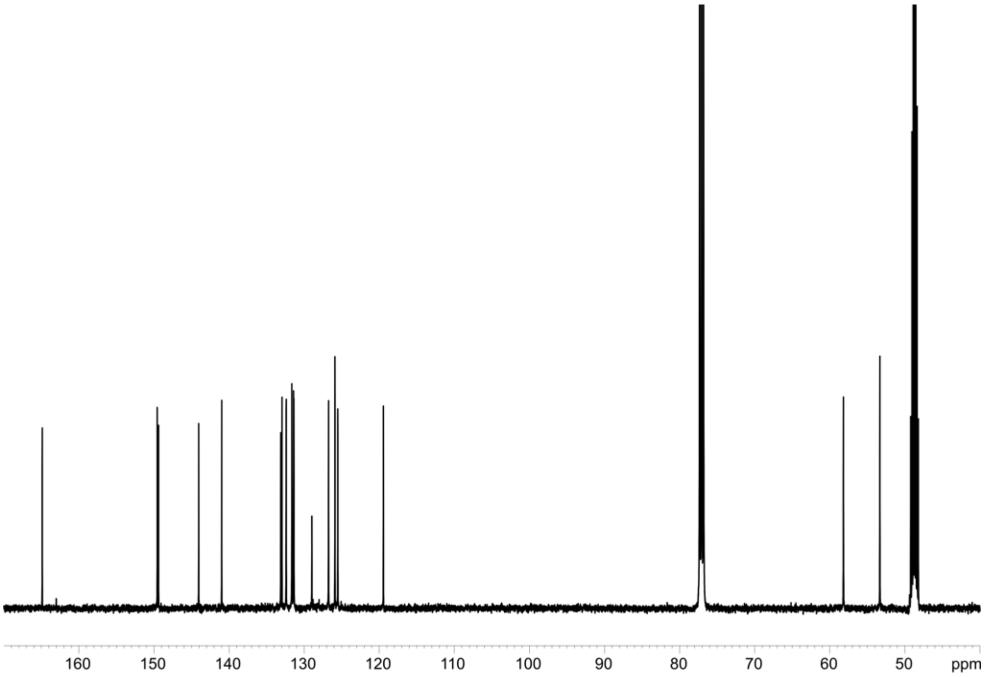

Figure S2: ^{13}C NMR spectrum of **5** in 9:1 $CDCl_3$:CD_3OD

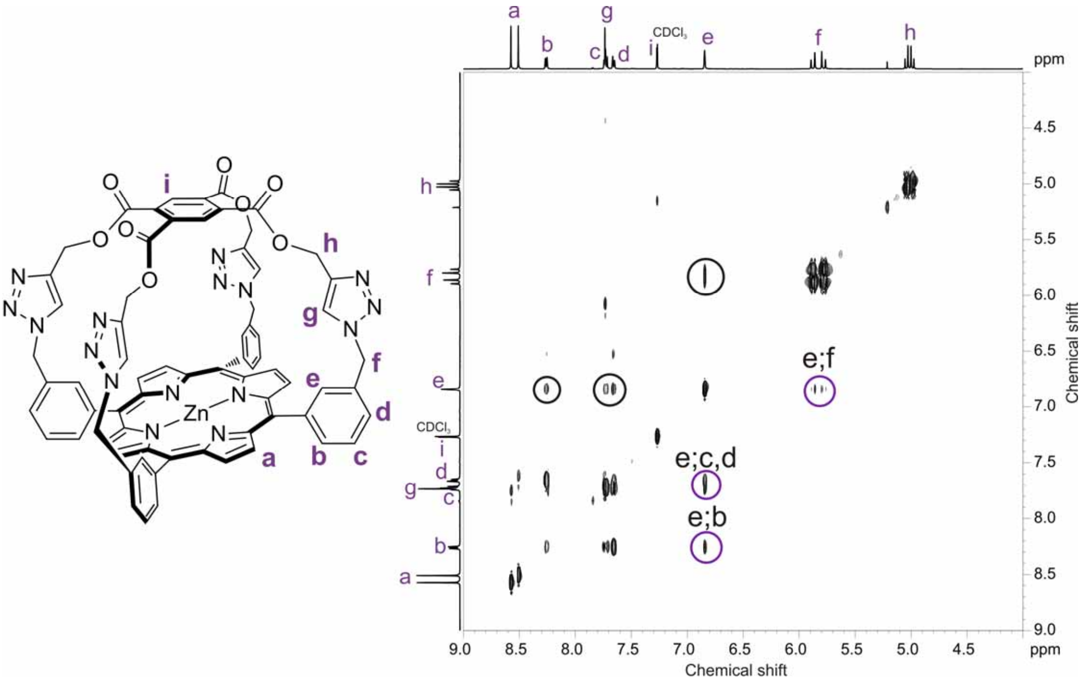

Figure S3: Partial ^{1}H-^{1}H TOCSY spectrum of **5** in 9:1 $CDCl_3$:CD_3OD

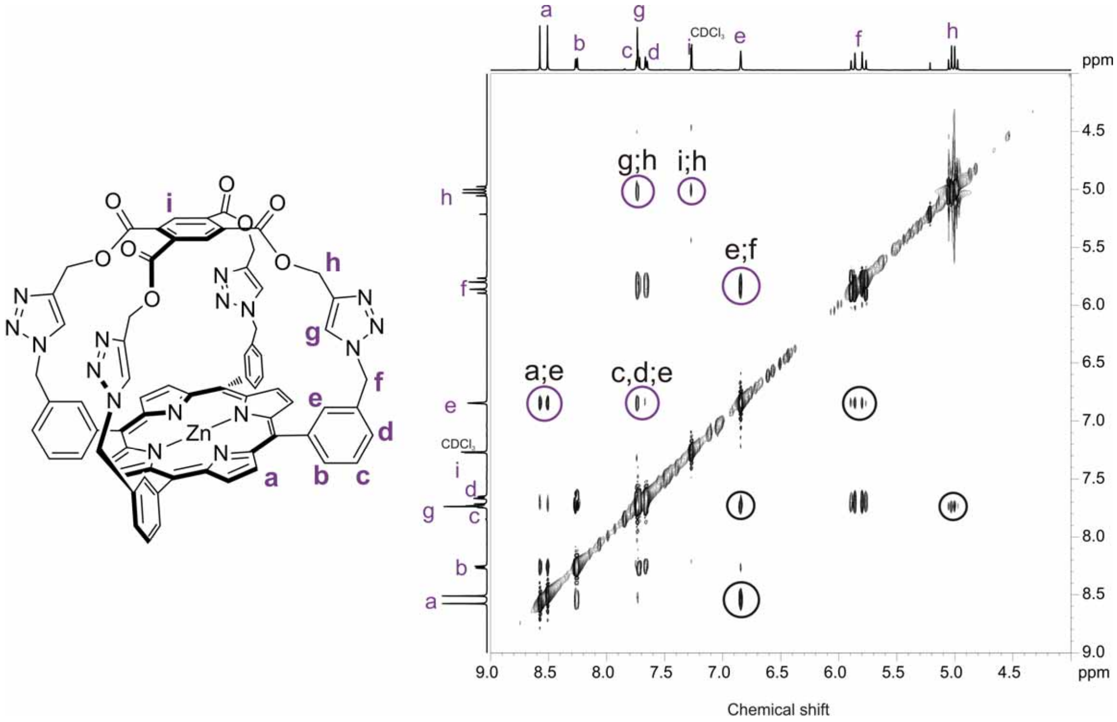

Figure S4: Partial ^{1}H-^{1}H ROESY spectrum of **5** in 9:1 $CDCl_3$:CD_3OD

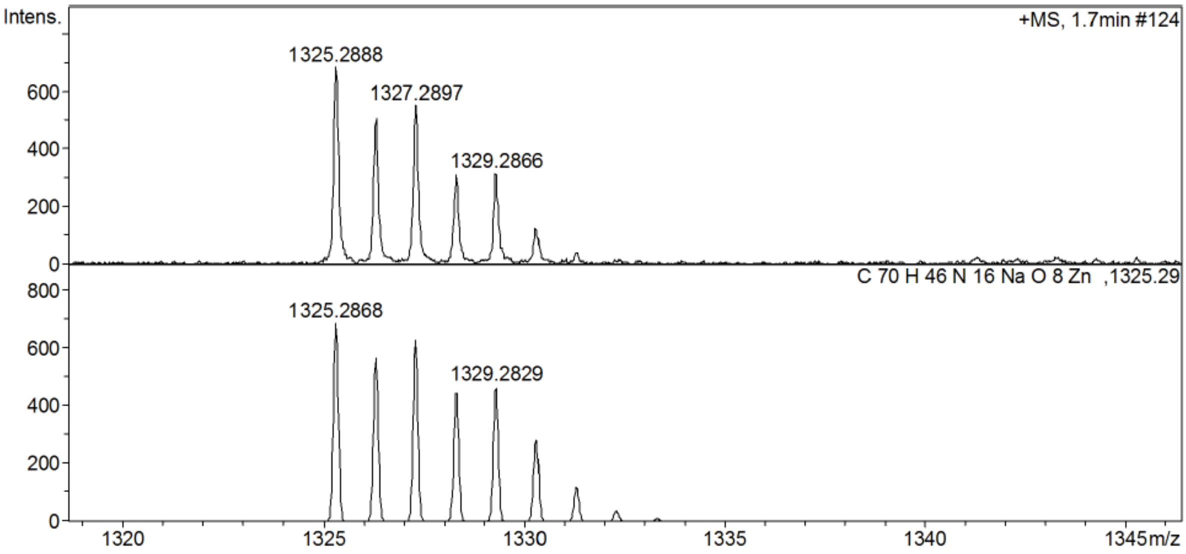

Figure S5: ESI mass spectrum of **5**.

Compound 6·$(PF_6)_4$

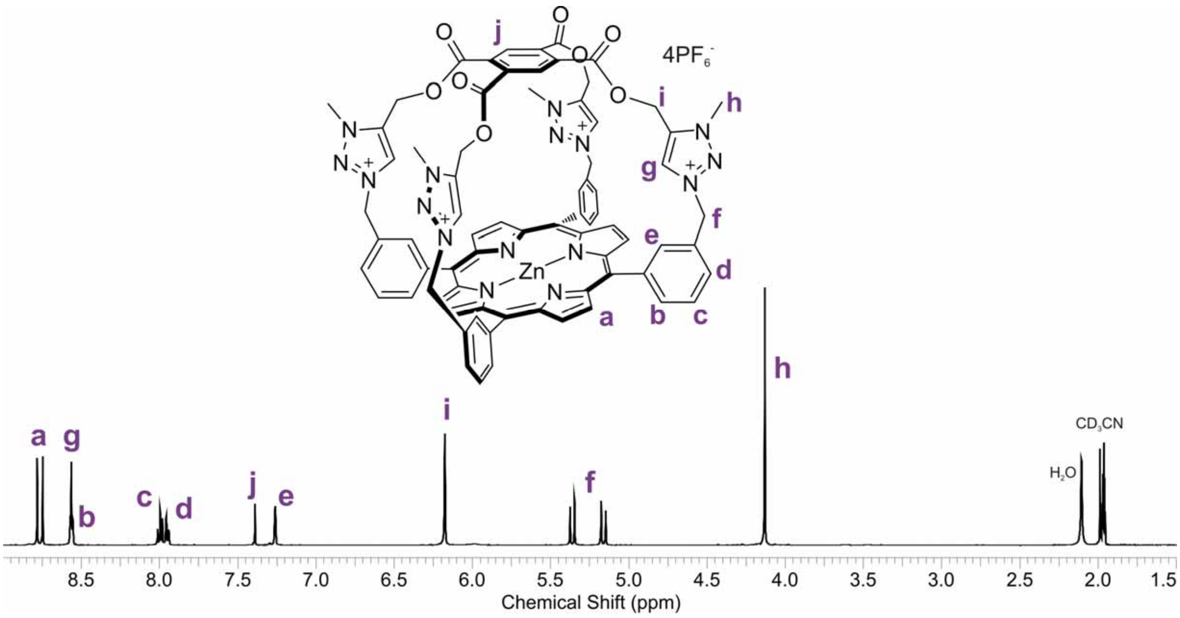

Figure S6: ^{1}H NMR spectrum of **6·$(PF_6)_4$** in CD_3CN at 293K.

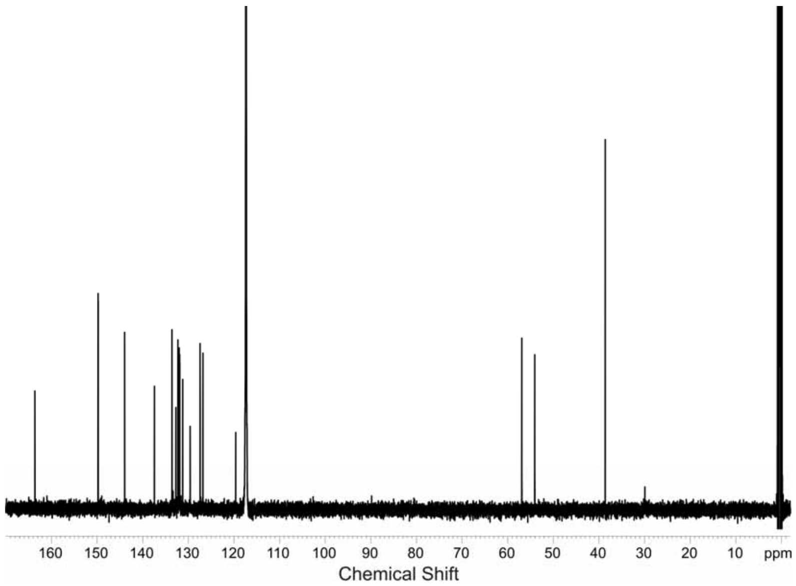

Figure S7: ^{13}C NMR of **6·(PF$_6$)$_4$** in CD$_3$CN at 293 K.

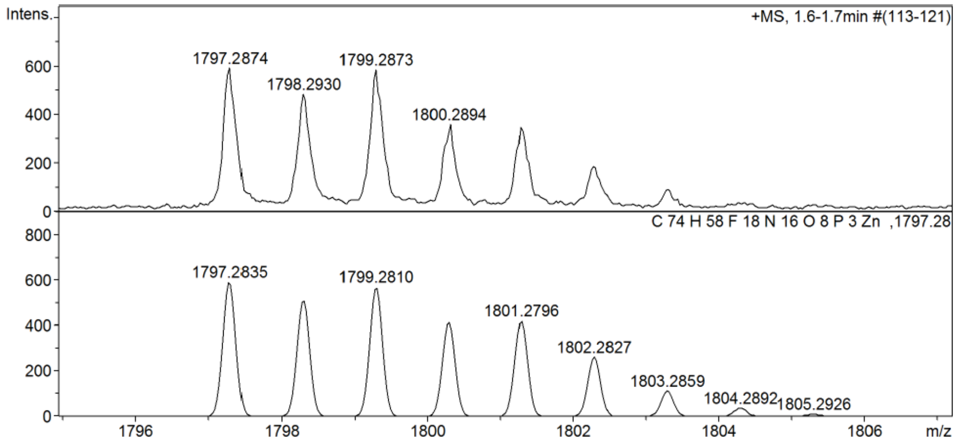

Figure S8: ESI mass spectrum of **6·(PF$_6$)$_4$**

^{1}H NMR Spectroscopic Titrations

Procedure:

^{1}H NMR Titration spectra were recorded on a Varian Unity Plus 500 spectrometer. A solution of anion was added to a solution of host (0.5 ml) at 298 K. The chemical shift(s) of specific host proton(s) were monitored for seventeen titration points (for 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, and 10.0 equivalents of added guest). The resulting data were analysed using the WinEQNMR2 computer program in experiments where association of guest and host was fast on the NMR timescale. Anion binding experiments were carried out using salts of the non-complexing tetrabutylammonium (TBA) cation as the guest species titrated into the porphyrin **5** host. A 0.0956 mol dm^{-3} solution of anion was added to a 0.00191 mol dm^{-3} solution of host. The volumes of salt solution added were 10 x 2 μL, 2 x 5 μL, 2 x 10 μL, 1 x 20 μL and 1 x 30 μL.

When using the WinEQNMR2 computer program, the values of the observed chemical shift and the guest concentration were entered for every titration point and estimates of the association constant, limiting chemical shift and binding stoichiometry were made. The parameters were refined using non-linear least squares analysis to obtain the best fit between the observed and calculated chemical shifts; the program plots observed shift versus the guest concentration, revealing the accuracy of the experiment and suitability of the model used. The input values were varied until the best-fit values of the stability constants, and their errors, converged.

UV/Visible Spectroscopic Titrations

Procedure:

UV/visible experiments were carried out on a PG instruments T60U spectrometer at 293 K. Aliquots of guest were added to a 2.5 mL solution of host in a cuvette. Spectra were recorded after each addition and the sample was mixed thoroughly before each measurement. The concentration of host species was chosen to give an absorbance between 0.5 and 1.0. The concentration of the guest species was varied according to the strength of binding in order to obtain suitable experimental data for association constant determination.

Stability constants were obtained by analysis of the resulting titration data using the SPECFIT computer program. 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 the values for the stability constants converged. Comparison of the theoretical binding isotherms, calculated concentration profiles and calculated spectra of the complexes with the experimental data confirmed that the models used were correct.

Job Plots:

Solutions of host and guest (2 mM in acetone or acetone/water mixture) were mixed in varying ratios in such a way to maintain an overall constant total concentration. The absorbance was measured (A). This was then subtracted from the absorbance of the host A_{obs} and multiplied by the host concentration (A_{obs}-A)[H]. Plotting (A_{obs}-A)[H] v. χ_H gave the corresponding Job plots. Maxima at $\chi_H = 0.5$ indicate a 1:1 binding stoichiometry.

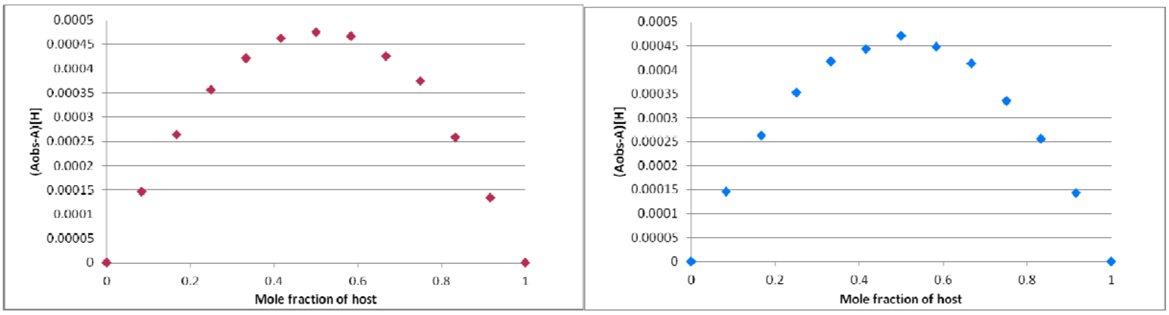

Figure S9: Job plots of **5** with F^- (left) and SO_4^{2-} (right) in acetone

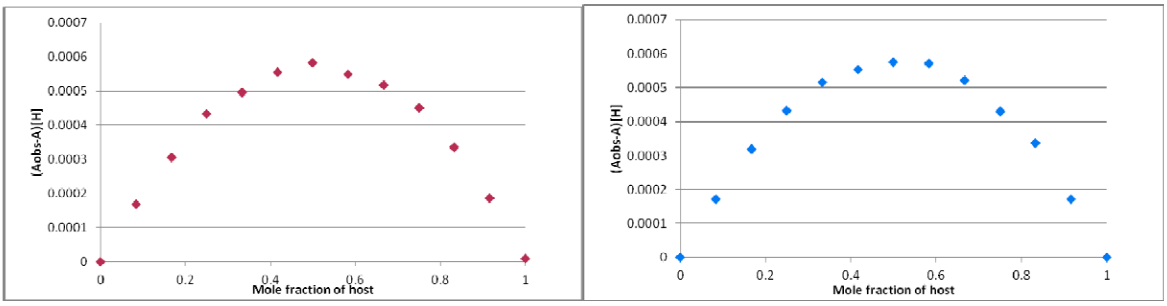

Figure S10: Job plots of ZnTPP with F^- and SO_4^{2-} in acetone

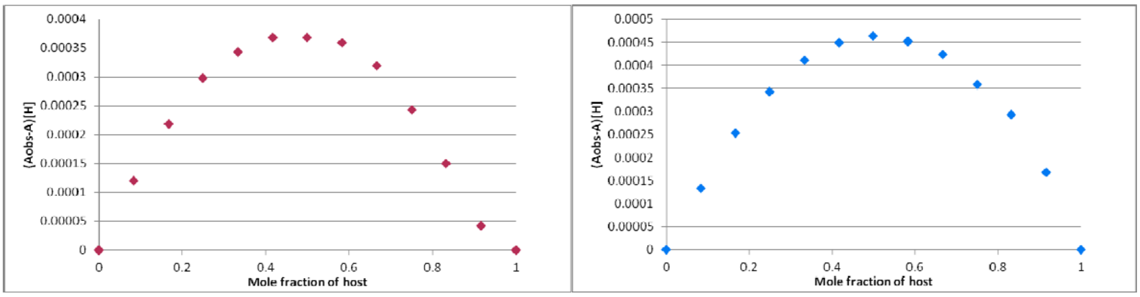

Figure S11: Job plots of **6·(PF$_6$)$_4$** with F^- and SO_4^{2-} in 5% H_2O/acetone

Binding Curves:

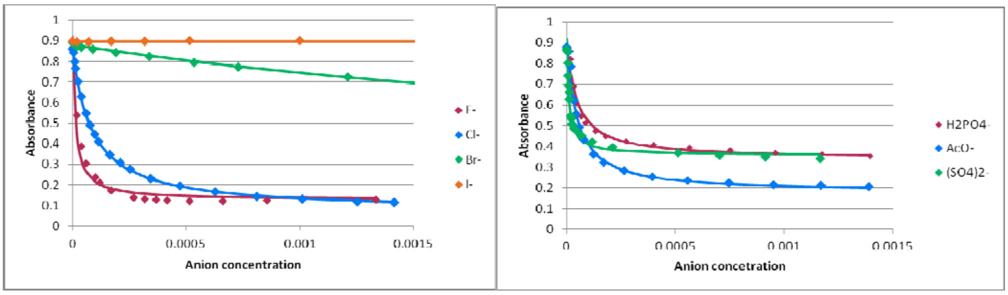

Figure S12: Changes in the absorbance of the Soret band (421 nm) on addition of anions as their TBA salts to 2 μM solutions of **5** in acetone at 293 K. Square data points represent experimental data; continuous lines represent theoretical binding isotherms

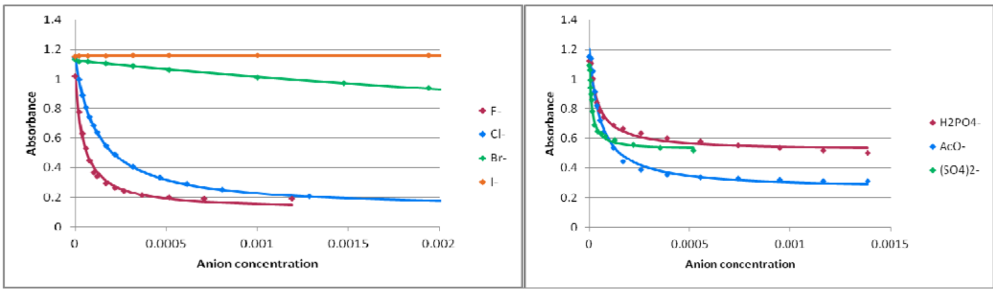

Figure S13: Changes in the absorbance of the Soret band (420 nm) on addition of anions as their TBA salts to 2 μM solutions of ZnTPP in acetone at 293 K. Square data points represent experimental data; continuous lines represent theoretical binding isotherms

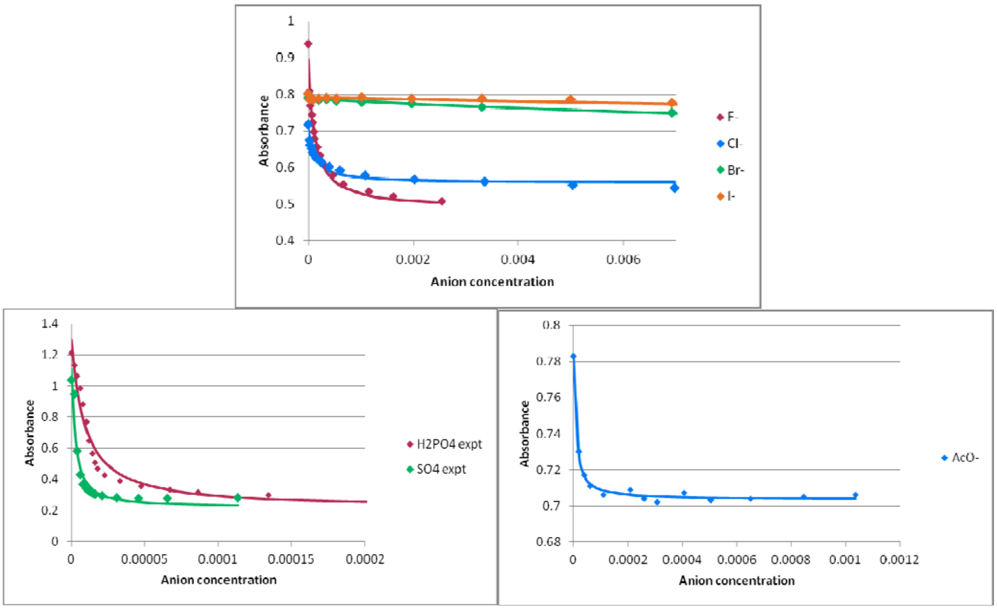

Figure S14: Changes in the absorbance of the Soret band (425 nm) on addition of anions as their TBA salts to 2 μM solutions of $\mathbf{6{\cdot}(PF_6)_4}$ in 5% H_2O/acetone at 293 K. Square data points represent experimental data; continuous lines represent theoretical binding isotherms.

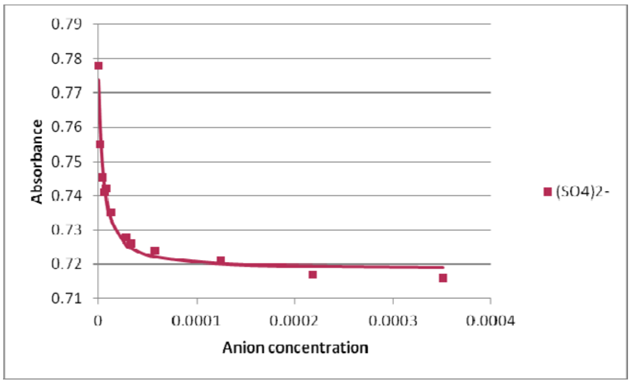

Figure S15: Changes in the absorbance of the Soret band (423 nm) on addition of TBA_2SO_4 to 2 μM solutions of **6·$(PF_6)_4$** in 15% H_2O/acetone at 293 K. Square data points represent experimental data; continuous lines represent theoretical binding isotherms.

Crystallographic Data:

Table S1: Crystal structure data for **5**·5(C_3H_6O)

Compound reference	**5**
Chemical formula	$C_{73}H_{52}N_{16}O_9Zn{\bullet}4(C_3H_6O)$
Formula Mass	1595.02
Crystal system	Monoclinic
a/Å	14.7594(2)
b/Å	19.6725(2)
c/Å	26.8029(3)
α/°	90
β/°	99.6681(11)
γ/°	90
Unit cell volume/Å^3	7671.81(16)
Temperature/K	150
Space group	$P2_1/c$
No. of formula units per unit cell, Z	4
Absorption coefficient, μ/mm^{-1}	1.079
No. of reflections measured	56994
No. of independent reflections	16008
R_{int}	0.0427
Final R_1 values ($I > 2\sigma(I)$)	0.0560
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1563
Final R_1 values (all data)	0.0639
Final $wR(F^2)$ values (all data)	0.1612
Goodness of fit on F^2	1.0464
CCDC Number	863074

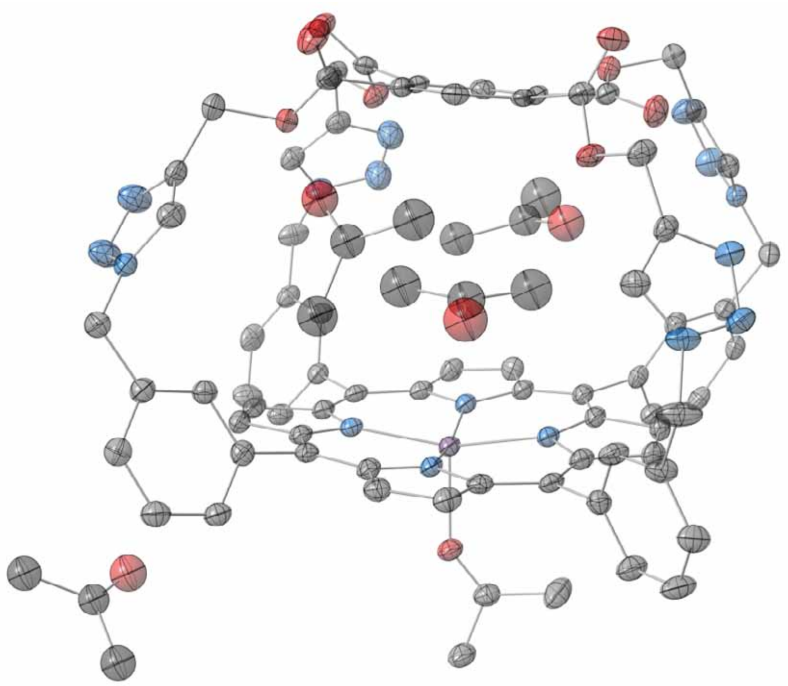

Figure S16: Thermal ellipsoid plot of asymmetric unit of **5**·5(C_3H_6O). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are omitted for clarity.