Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supporting Information

Synthesis and Characterization of Indolocarbazole-Quinoxalines with Flat Rigid Structure for Sensing Fluoride and Acetate Anions

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Complete Reference

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UV-Vis Anion Recognition Study

Stock solutions of the host molecule being studied were made up in dichloromethane with the final concentrations being between 1.5×10^{-5} M. Stock solutions of the guest in question were prepared by dissolving 100 - 300 equivalents of the tetrabutylammonium salts of the selected anions in 5 mL of a stock solution of the host. Making up the anion source solutions in this way allowed the binding studies to be carried out without having to make mathematical corrections to account for changes in host concentration as the result of dilution effects. The general procedure for the UV-Vis binding studies involved making sequential additions of titrant (anionic guest) using Hamilton pipettes to a 2 mL aliquot of the host stock solution in the spectrometric cell. The data was then collated and combined to produce plots that showed the changes in host spectral features as a function of changes in the concentration of the guest. Equilibrium constants were calculated using equation 4.5 of Connors. The change in absorbance, ΔA, was calculated at a λ value where the spectral change was maximal.

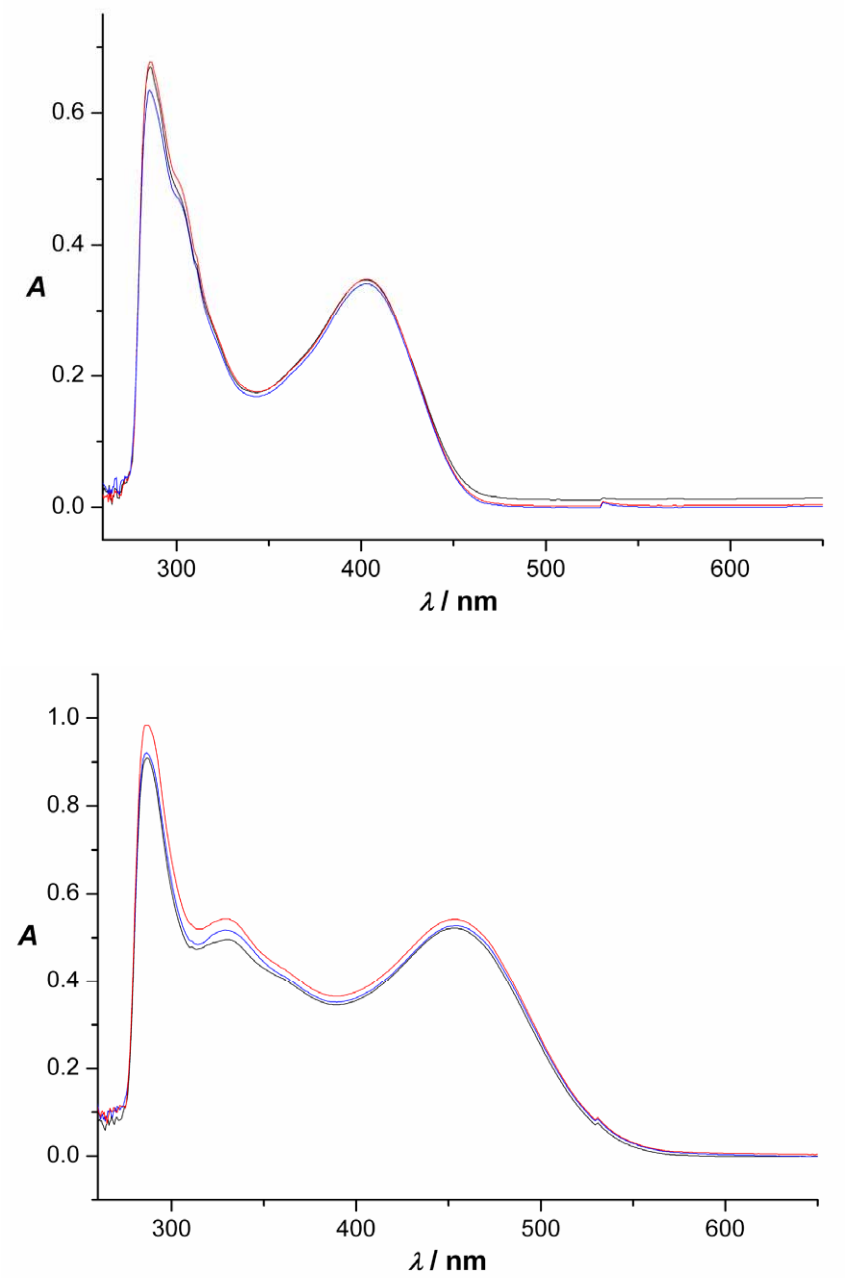

Figure S1. UV-vis spectral changes of receptors **4** (top) and **5** (bottom) (3.5×10^{-5} M) observed upon addition of fluoride and acetate anions (10 equiv) in DMSO. Black line: receptor; Red line: receptor + F^-; Blue line: receptor + CH_3COO^-.

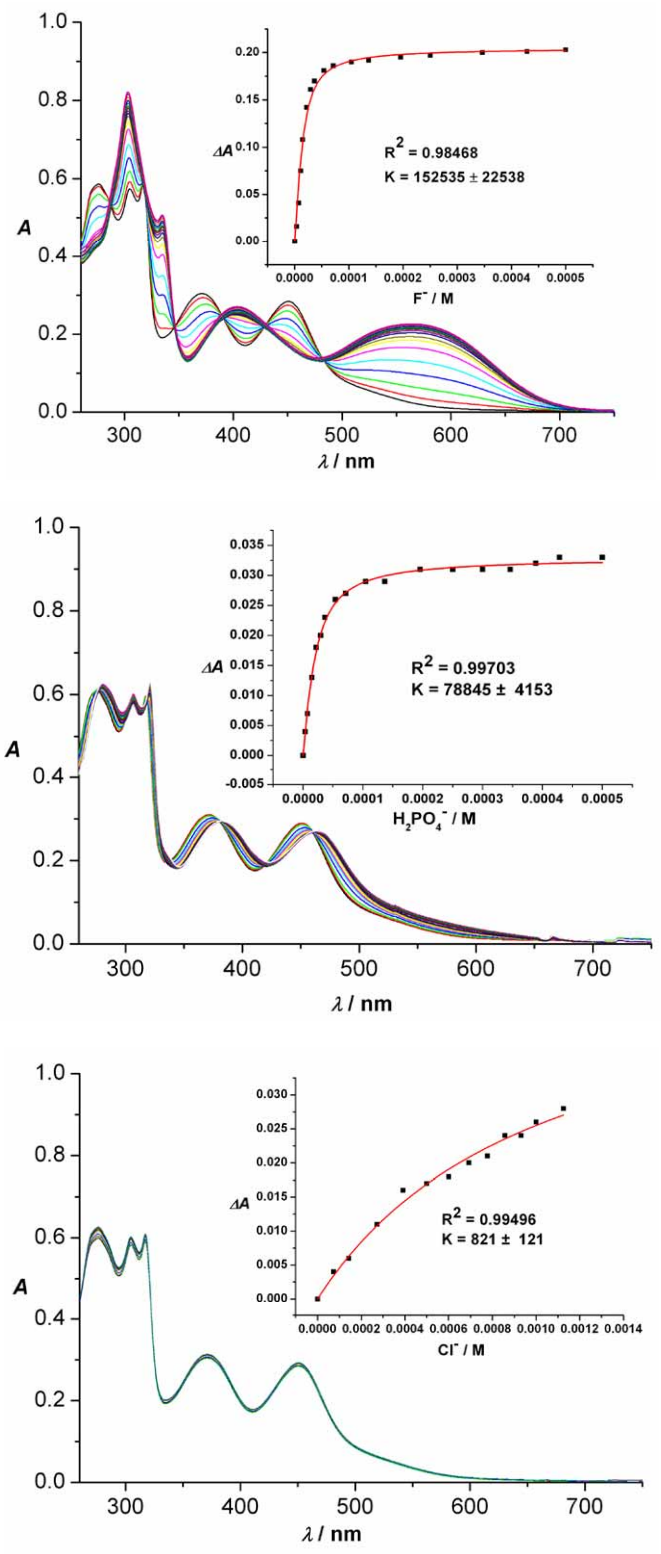

Figure S2. UV-vis spectral changes of receptor **7** (1.5×10^{-5} M) observed during titration with F^- (top), $H_2PO_4^-$ (middle) and Cl^- (bottom) in DMSO. (Inset) Binding isotherms

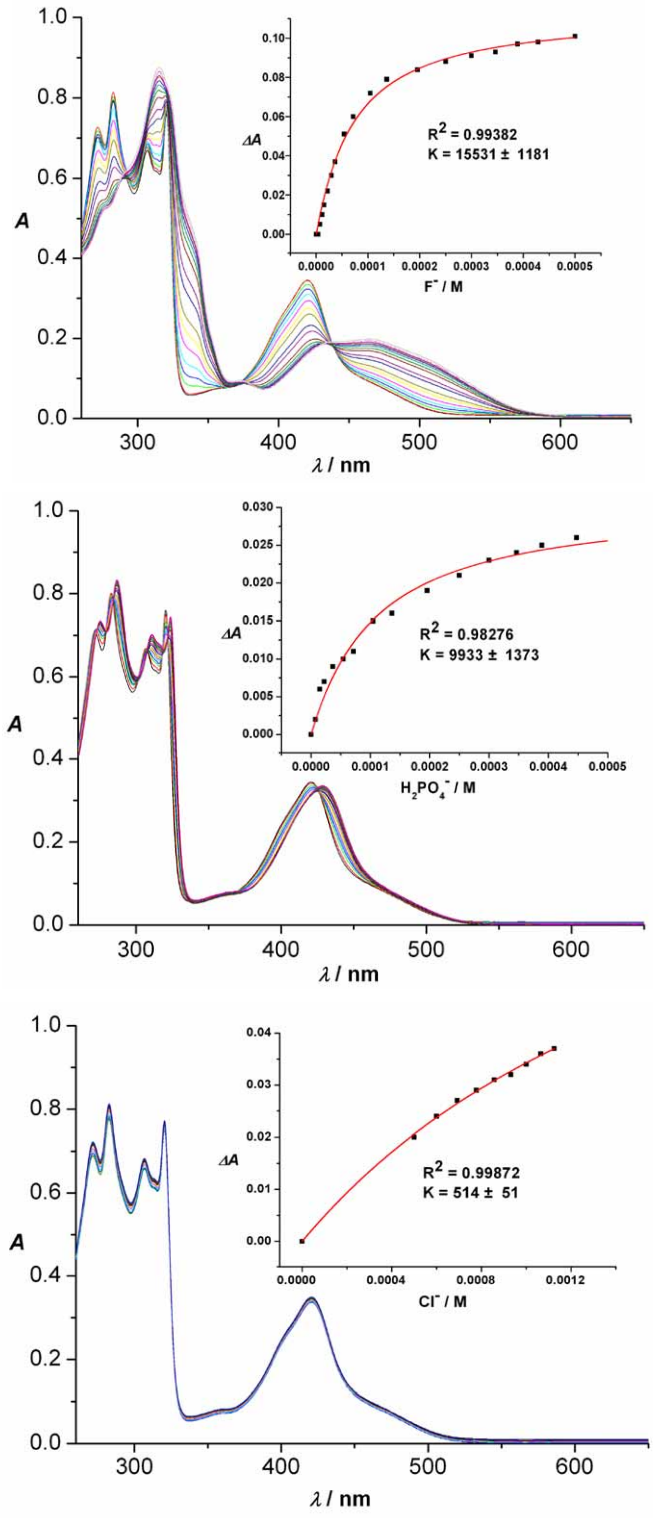

Figure S3. UV-vis spectral changes of receptor **6** (1.5×10^{-5} M) observed during titration with F^- (top), $H_2PO_4^-$ (middle) and Cl^- (bottom) in DMSO. (Inset) Binding isotherms

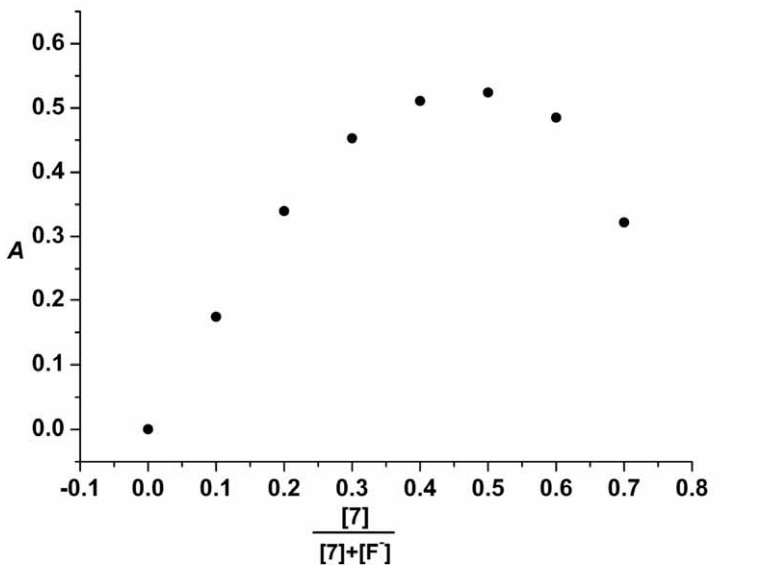

Figure S4. Job's plot for receptor **7** with fluoride anion, indicating 1:1 binding stoichimetry. [**7**] + [TBAF] = 1.2×10^{-4} M.

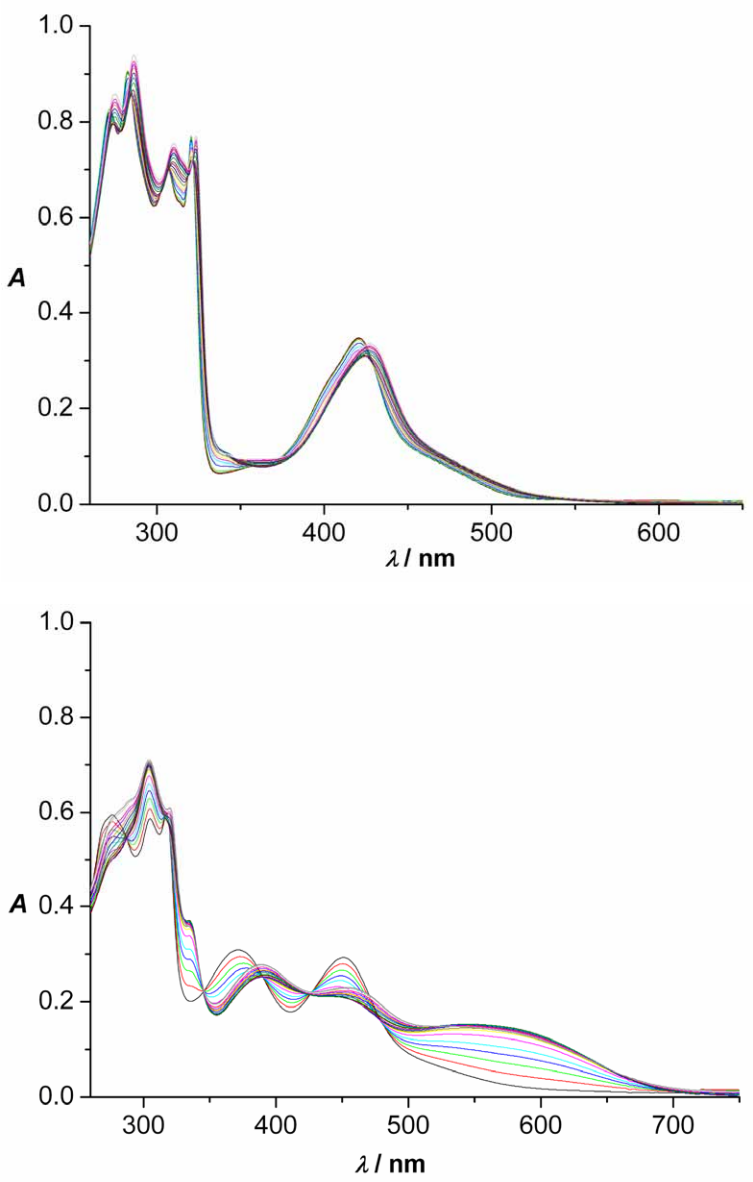

Figure S5. UV-vis spectral changes of receptors **6** (top) and **7** (bottom) upon the addition of acetate anion. Note the unclear isosbestic points. It may be caused by the biphasic behavior or the completion of water in the system. It is difficult to determine the binding constant through the UV-vis absorption titration.

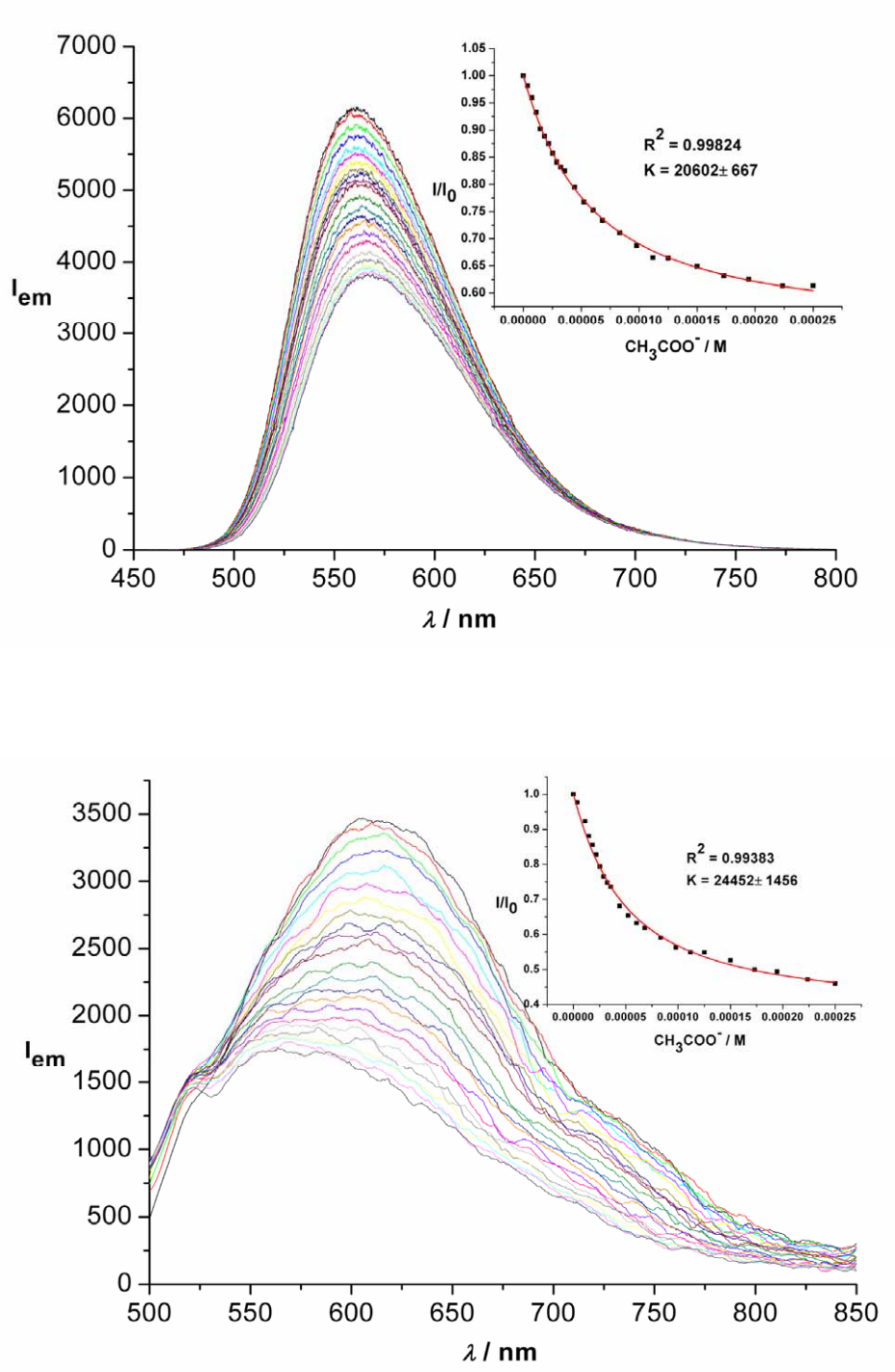

Figure S6. Fluorescence quenching of receptors **6** (top) and **7** (bottom) (1.5×10^{-5} M) upon titration with CH_3COO^- in DMSO. (Inset) Titration plot.

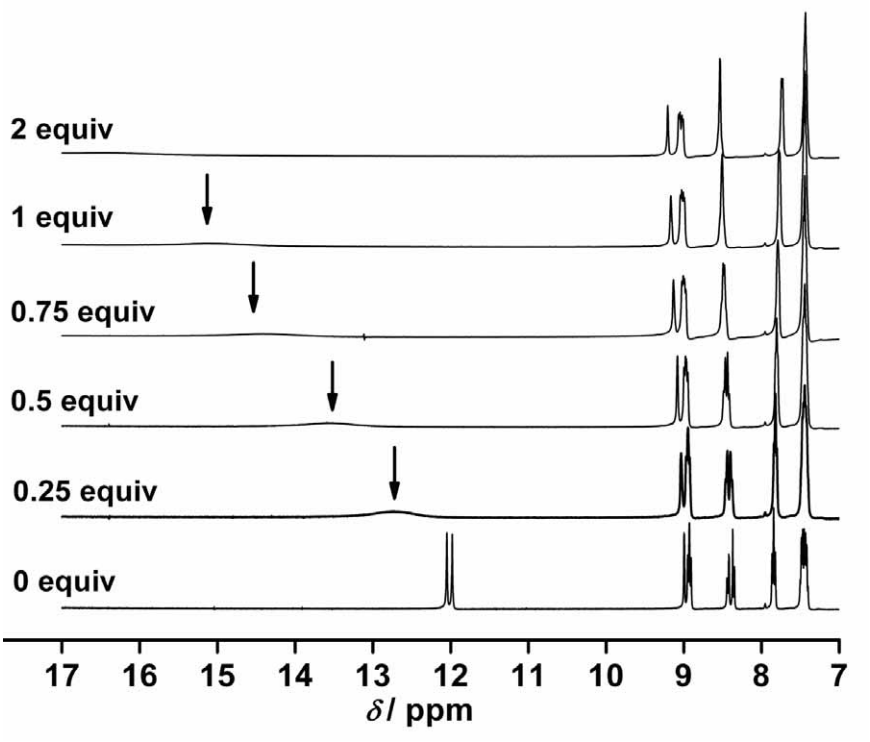

Figure S7. ^{1}H NMR spectra of receptor **7** upon addition of CH_3COO^- in DMSO-d_6

Table S1. Crystal data and structure refinement for **7**·TBACl

Empirical formula	C40 H49 Cl N6 O2	
Formula weight	681.30	
Temperature	113(2) K	
Wavelength	0.71070 Å	
Crystal system	Triclinic,	
space group	P -1	
Unit cell dimensions	a = 10.0553(19) Å	α = 64.024(7)°.
	b = 13.715(2) Å	β = 80.245(12)°.
	c = 15.384(3) Å	γ = 70.714(10)°.
Volume	1799.5(6) $Å^3$	
Z	2	
Calculated density	1.257 Mg/m^3	
Absorption coefficient	0.150 mm^{-1}	
F(000)	728	
Crystal size	0.32 x 0.20 x 0.16 mm	
Theta range for data collection	1.73 to 25.00°.	
Limiting indices	-11 <=h<=11, -16<=k<=16, -17<=l<=18	
Reflections collected / unique	18561 / 6329 [R(int) = 0.0403]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9764 and 0.9535	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6329 / 2 / 455	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0609, wR2 = 0.1600	
R indices (all data)	R1 = 0.0756, wR2 = 0.1702	

Largest diff. peak and hole	1.079 and -0.467 e.Å^{-3}

Table S2. Crystal data and structure refinement for **7**·TBACH_3COO·$CHCl_3$·1/2H_2O. Water molecule, a chloride atom of $CHCl_3$ and the nitro group of receptor **7** were disordered and refined in two positions with equal occupancies

Empirical formula	C43 H54 Cl3 N6 O4.50	
Formula weight	833.27	
Temperature	113(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
space group	P -1	
Unit cell dimensions	a = 12.077(2) Å	α= 108.73(3)°.
	b = 13.878(3) Å	β= 107.18(3)°.
	c = 14.279(3) Å	γ= 95.52(3)°.
Volume	2116.4(7) Å^3	
Z	2	
Calculated density	1.308 Mg/ m^3	
Absorption coefficient	0.267 mm^{-1}	
F(000)	882	
Crystal size	0.14 x 0.12 x 0.08 mm	
Theta range for data collection	1.59 to 25.02°.	
Limiting indices	-14<=h<=14, -16<=k<=16, -16<=l<=13	
Reflections collected / unique	13051 / 7406 [R(int) = 0.0260]	
Completeness to theta = 25.02°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9687 and 0.9485	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7406 / 92 / 643	
Goodness-of-fit on F^2	1.144	
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1127	
R indices (all data)	R1 = 0.0658, wR2 = 0.1181	
Largest diff. peak and hole	0.203 and -0.299 e. Å^{-3}	