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Supporting Information

Fluorescent and Colorimetric Molecular Recognition Probe for Hydrogen Bond Acceptors

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General Experimental Section

All compounds were purchased from Sigma-Aldrich unless otherwise stated. Chloroform was purchased from Acros as 99+% for spectroscopic grade. Tributylphosphine oxide, TBACl, TBASCN, $TBAN_3$, and trioctylphosphine oxide were purchased from Aldrich. TBAOBz and triethyl phosphate were purchased from Fluka. Trimethylphosphine oxide and tricyclohexylphosphine oxide were purchased from Alfa Aesar. All compounds were used as received. The measurements of solids were carried out on a Precisa 125A balance. The following abbreviations are employed: Bu = Butyl, Cy = cyclohexyl, Et = ethyl, Hex = hexyl, Me = methyl, Oct = octyl, TBA = tetrabutylammonium.

Standard Method for UV/vis Absorption Titrations[1]

Titrations were carried out using a Cary 3 Bio UV/vis spectrophotometer, using standard titration protocols. A 10 mL sample of the host, 1-naphthol (**1**) was prepared at a known concentration (typically between 0.16 mM and 0.20 mM in $CHCl_3$, between 0.14 mM and 0.21 mM in CH_2Cl_2 and between 0.10 mM and 0.14 mM in CCl_4). 2 mL of this solution was removed and added to a quartz cuvette and the UV-vis spectrum was recorded. The guest (**2-12**) was then dissolved in 1 mL or 2 mL of the host solution to avoid dilution of the host during the titration and aliquots of this solution were successively added to the cuvette and the UV/vis absorption spectrum was recorded after each addition. The changes in the UV/vis absorption spectra were analysed using a Microsoft Excel spreadsheet to fit the changes in the absorption at fixed wavelengths to a 1:1 binding isotherm or a 1:1 binding isotherm accounting for a non-specific interaction optimising the association constant and absorption of the free and bound host using purpose written VBA macros.

All H-bond donors **1** display bathchromatic shifting of their characteristic UV/vis absorption bands upon complexation with hydrogen bond acceptors **2-12** in the studied solvents.[2-5]

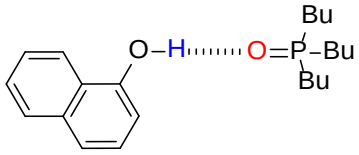
Standard Method for Fluorescence Titrations

Titrations were carried out using a Cary Eclipse fluorescence spectrophotometer (Agilent). A 10 mL sample of the host, 1-naphthol (**1**) was prepared at a known concentration (typically between 0.04 mM and 0.09 mM in $CHCl_3$ and between 0.05 mM and 0.06 mM in CH_2Cl_2). 2 mL of this solution was removed and added to a quartz cuvette and the fluorescence spectrum was recorded. The guest (**2-12**) was then dissolved in 1 mL or 2 mL of the host solution to avoid dilution of the host during the titration and aliquots of this solution were successively added to the cuvette and fluorescence emission spectrum was recorded after each addition. The changes in the fluorescence emission spectra were analysed using a Microsoft Excel spreadsheet to fit the changes in the absorption at fixed wavelengths to a 1:1 binding isotherm or a 1:1 binding isotherm accounting for a non-specific interaction optimising the association constant and absorption of the free and bound host using purpose written VBA macros.

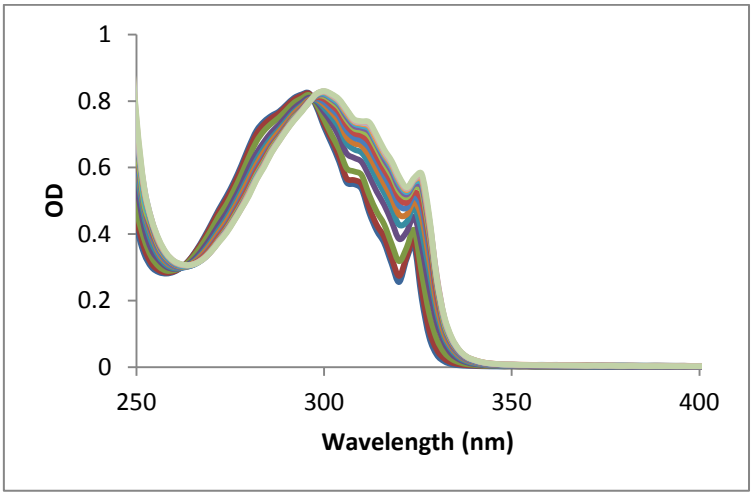
Association constants (K / M^{-1}) were determined for neutral H-bonded complexes **1**·**2-12** by fitting the titration data to either a 1:1 binding isotherm allowing for a second weaker non-specific binding event or by fitting to a 1:1 binding isotherm.[4] In all cases, the [guest] was chosen to obtain a binding isotherm of ≥ 50% saturation. The specific [guest] used in each experiment can be seen in the binding isotherm for each titration.

2. Titration Curves for 1-naphthol (1) in Chloroform

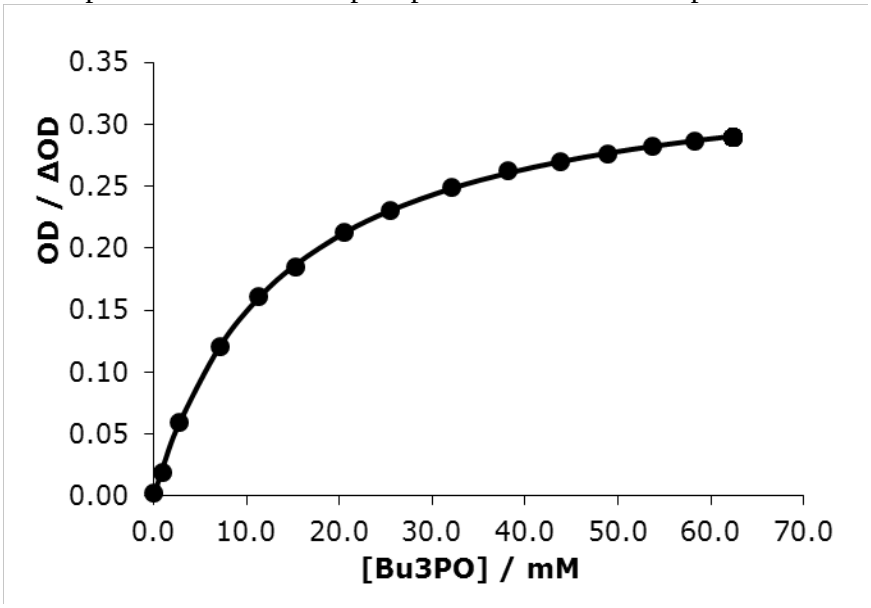
a) Titration of 1-naphthol with phosphine oxide in chloroform



Host: 1-naphthol = 0.16 mM
Guest: phosphine oxide = 184 mM



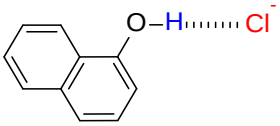
Graph S1. UV/vis spectra of titration of phosphine oxide with 1-naphthol in chloroform.



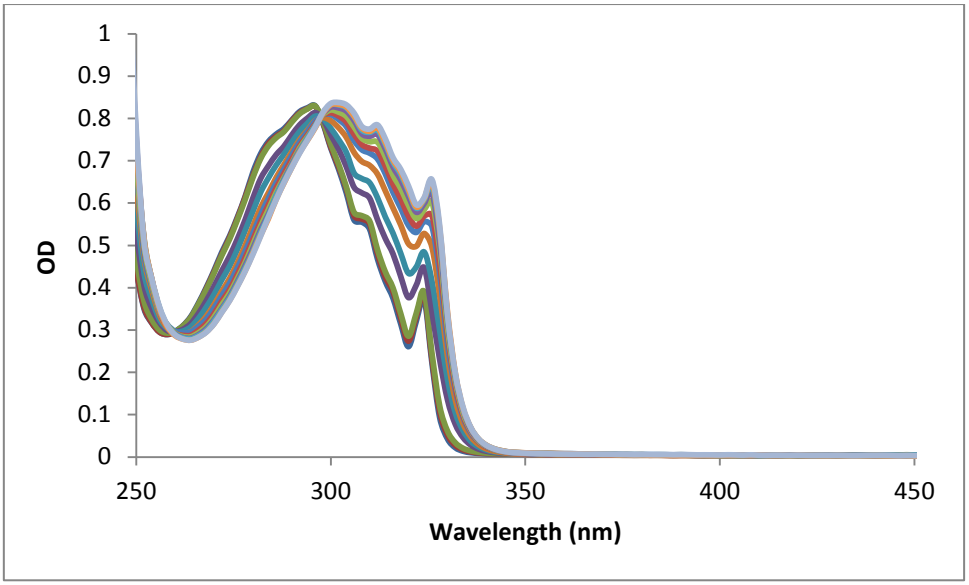
Graph S2. Binding isotherm for titration using 1:1 fitting program for titration of phosphine oxide against 1-naphthol in chloroform. [1-naphthol] = 0.16 mM and [phosphine oxide] = 184 mM, $\Delta\lambda$= 14 nm, ΔOD = 0.354.

$$K_a = 77 \pm 8\ M^{-1} \qquad 82\%\ \text{bound}$$

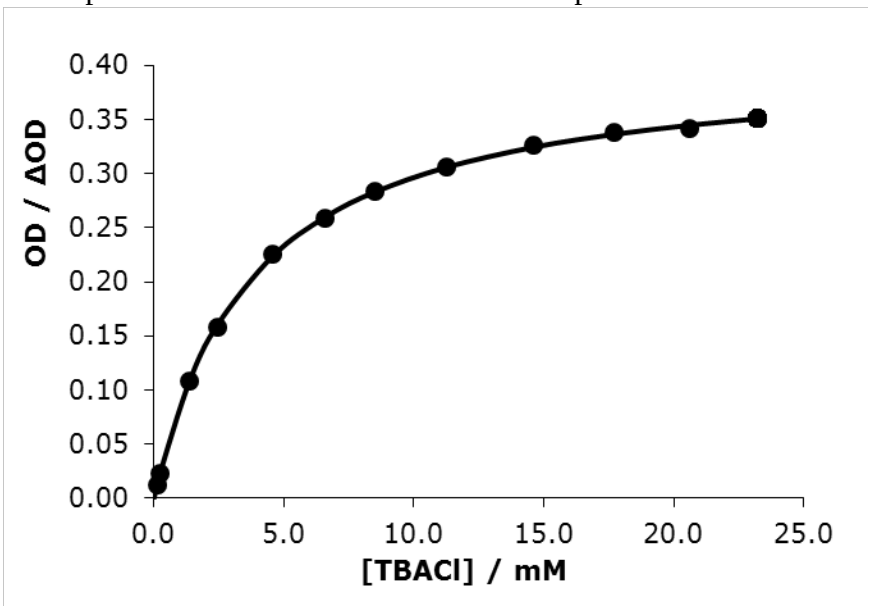
b) Titration of 1-naphthol with TBACl in chloroform



Host: 1-naphthol = 0.16 mM
Guest: TBACl = 92 mM



Graph S3. UV/vis spectra of titration of TBACl with 1-naphthol in chloroform.

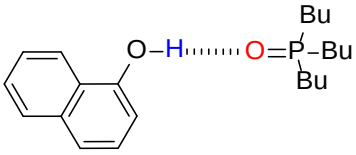


Graph S4. Binding isotherm for titration using 1:1 fitting program for titration of TBACl against 1-naphthol in chloroform. [1-naphthol] = 0.16 mM and [TBACl] = 92 mM, $\Delta\lambda$= 22 nm, ΔOD = 0.351.

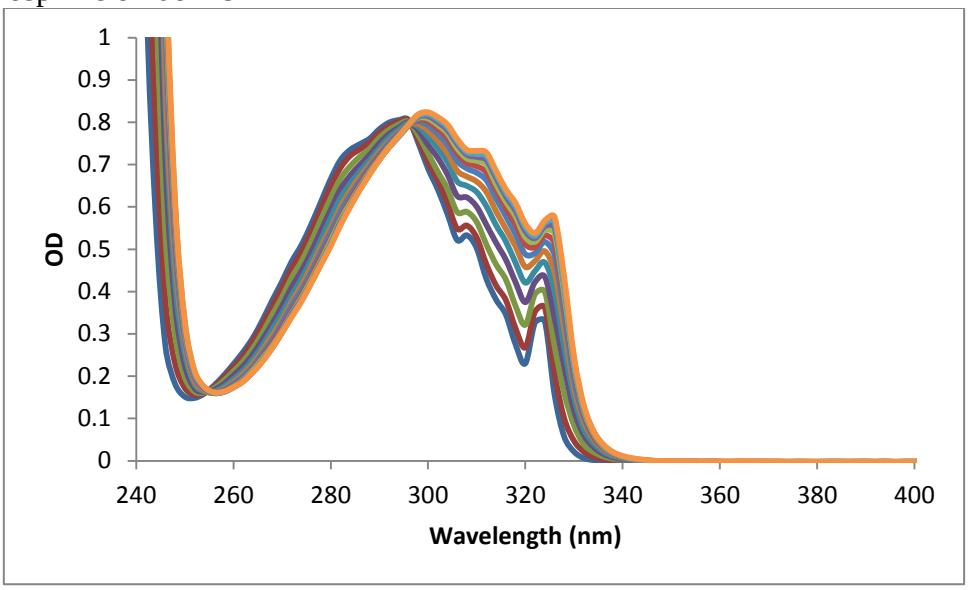
$$K_a = \quad 260 \pm 40\ M^{-1} \qquad\qquad 86\%\ \text{bound}$$

2. Titration Curves for 1-naphthol (1) in Dichloromethane

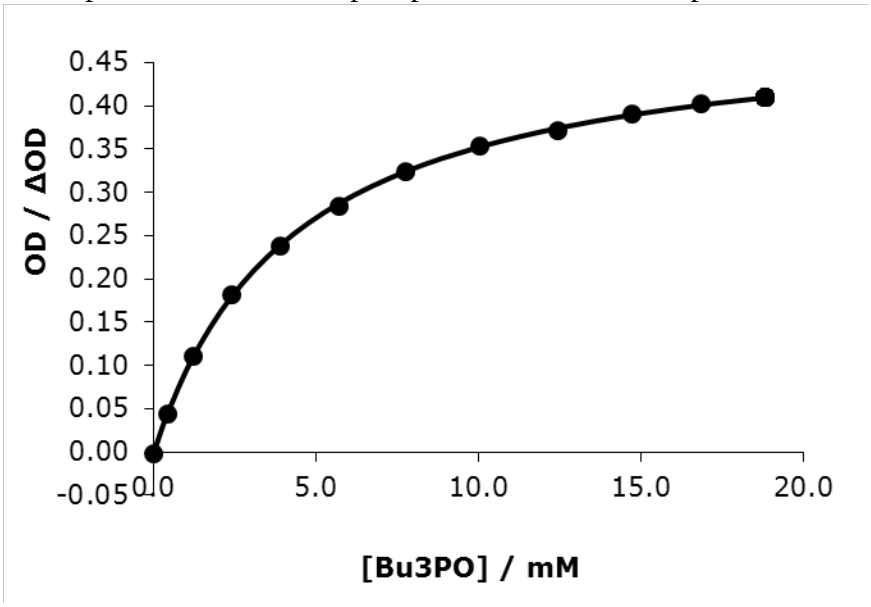
a) Titration of 1-naphthol with phosphine oxide in dichloromethane



Host: 1-naphthol = 0.16 mM
Guest: phosphine oxide = 82 mM



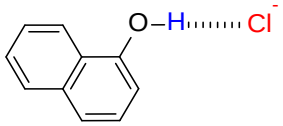
Graph S5. UV/vis spectra of titration of phosphine oxide with 1-naphthol in dichloromethane.



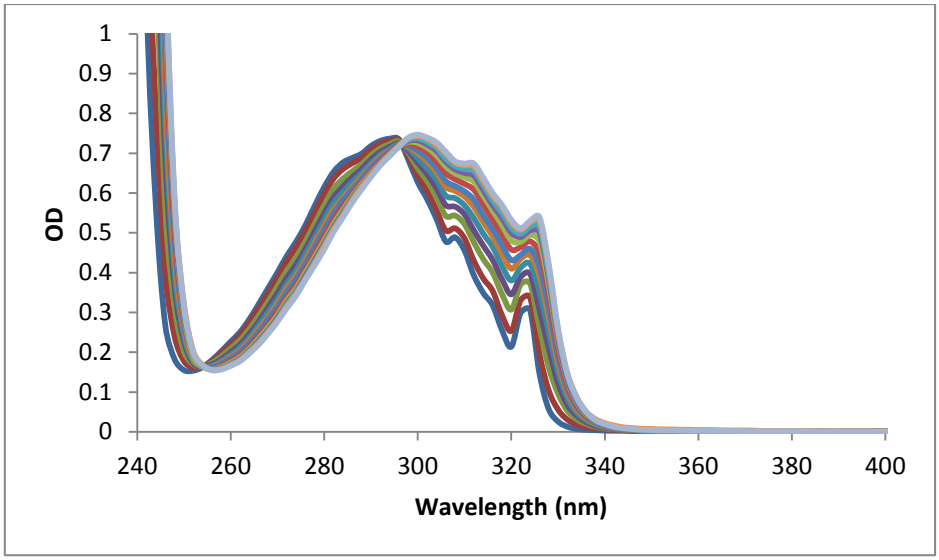
Graph S6. Binding isotherm for titration using 1:1 fitting program and accounting for a nonspecific interaction for titration of phosphine oxide against 1-naphthol in dichloromethane. [1-naphthol] = 0.16 mM and [phosphine oxide] = 82 mM, $\Delta\lambda$= 28 nm, ΔOD = 0.501.

$$K_a = 260 \pm 59\ M^{-1} \qquad 82\%\ \text{bound}$$

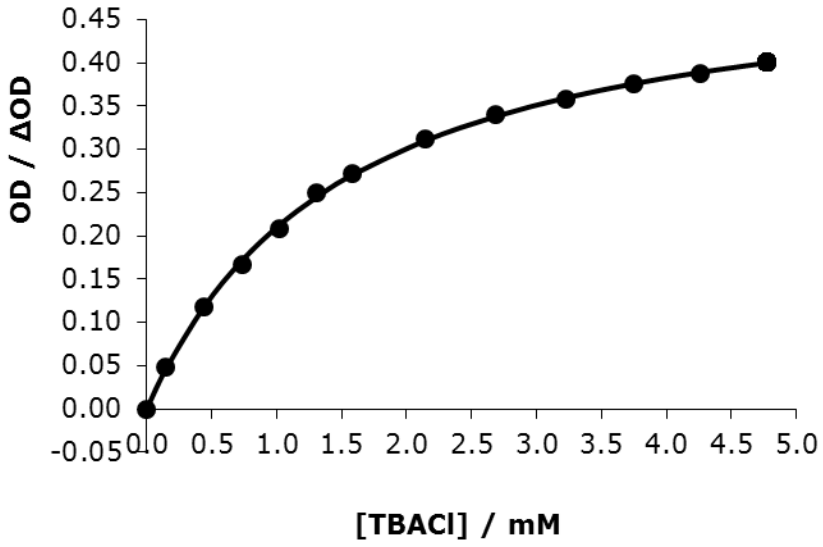
b) Titration of 1-naphthol with TBACl in dichloromethane



Host: 1-naphthol = 0.15 mM
Guest: TBACl = 59 mM



Graph S7. UV/vis spectra of titration of TBACl with 1-naphthol in dichloromethane.

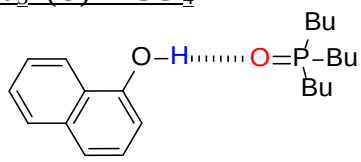


Graph S8. Binding isotherm for titration using 1:1 fitting program for titration of TBACl against 1-naphthol in dichloromethane. [1-naphthol] = 0.15 mM and [TBACl] = 59 mM, Δλ= 28 nm, ΔOD = 0.518.

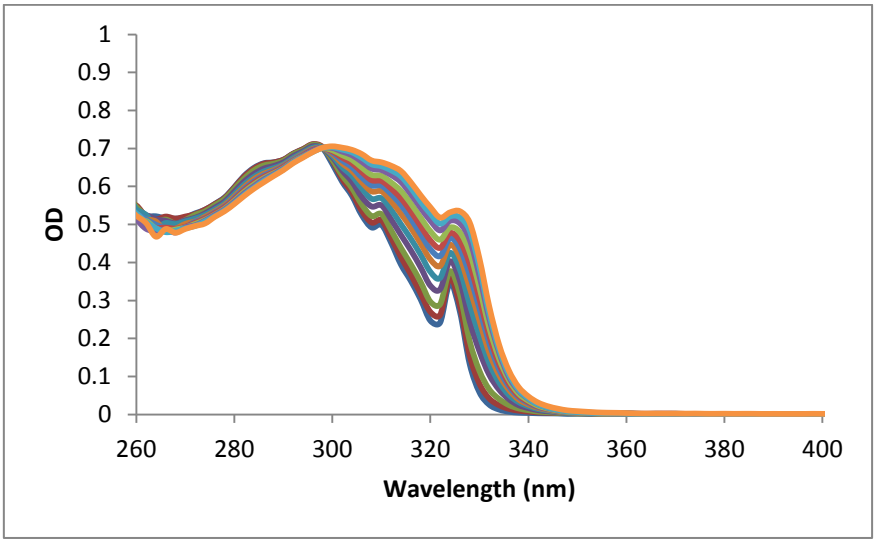
K_a = 810 ± 240 M^{-1} 77% bound

3. Titration Curves for 1-naphthol (1) in CCl_4

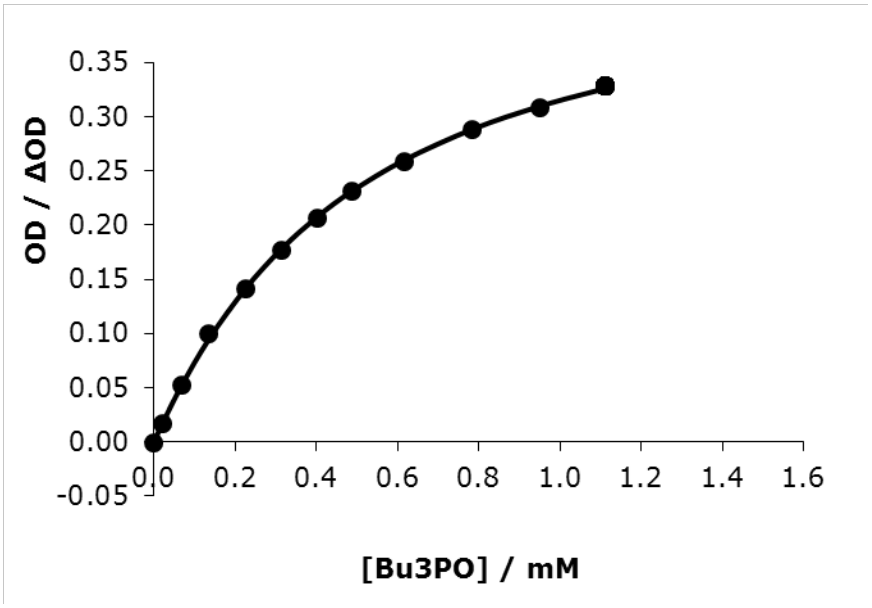
a) Titration of 1-naphthol with $Bu_3P(O)$ in CCl_4



Host: 1-naphthol = 0.14 mM
Guest: $Bu_3P(O)$ = 18 mM



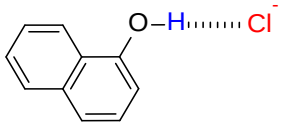
Graph S9. UV/vis spectra of titration of $Bu_3P(O)$ with 1-naphthol in CCl_4.



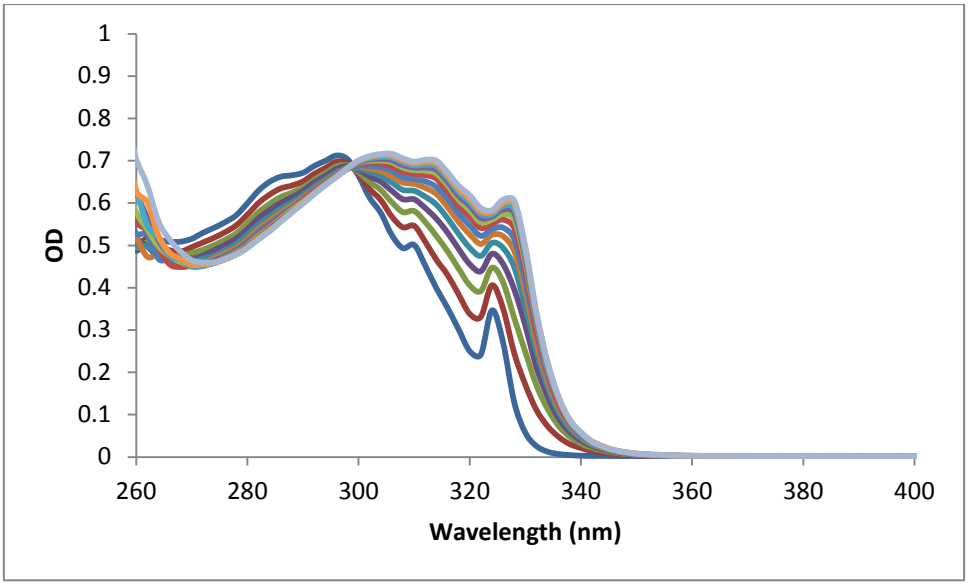
Graph S10. Binding isotherm for titration using 1:1 fitting program interaction for titration of $Bu_3P(O)$ against 1-naphthol in CCl_4. [1-naphthol] = 0.14 mM and [$Bu_3P(O)$] = 18 mM, $\Delta\lambda$ = 34 nm, ΔOD = 0.458.

$$K_a = 2500 \pm 200\ M^{-1} \qquad 71\%\ \text{bound}$$

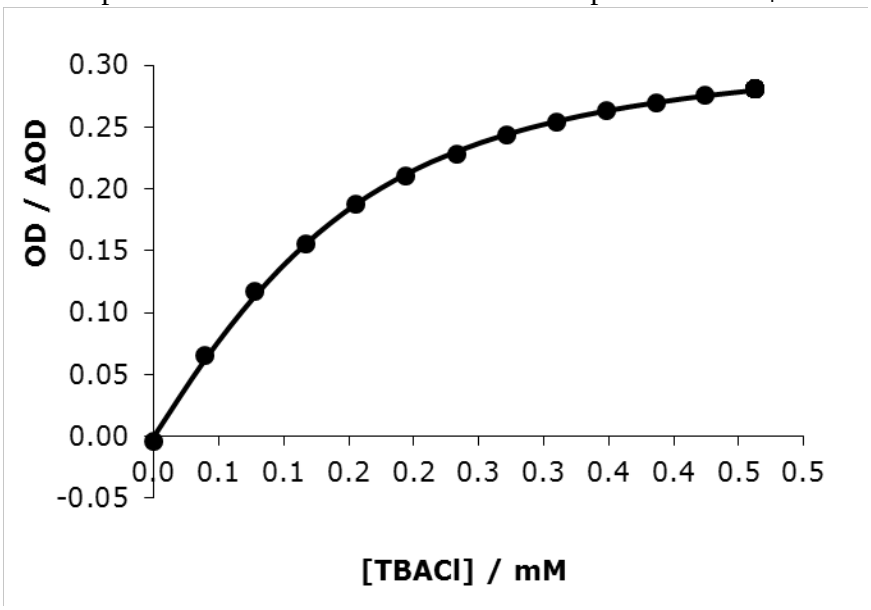
b) Titration of 1-naphthol with TBACl in CCl_4



Host: 1-naphthol = 0.14 mM
Guest: TBACl = 39 mM



Graph S11. UV/vis spectra of titration of TBACl with 1-naphthol in CCl_4

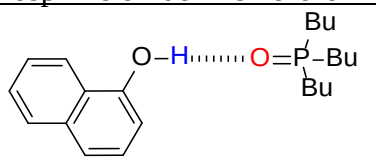


Graph S12. Binding isotherm for titration using 1:1 fitting program for titration of TBACl against 1-naphthol in CCl_4. [1-naphthol] = 0.14 mM and [TBACl] = 39 mM, $\Delta\lambda$= 22 nm, ΔOD = 0.325.

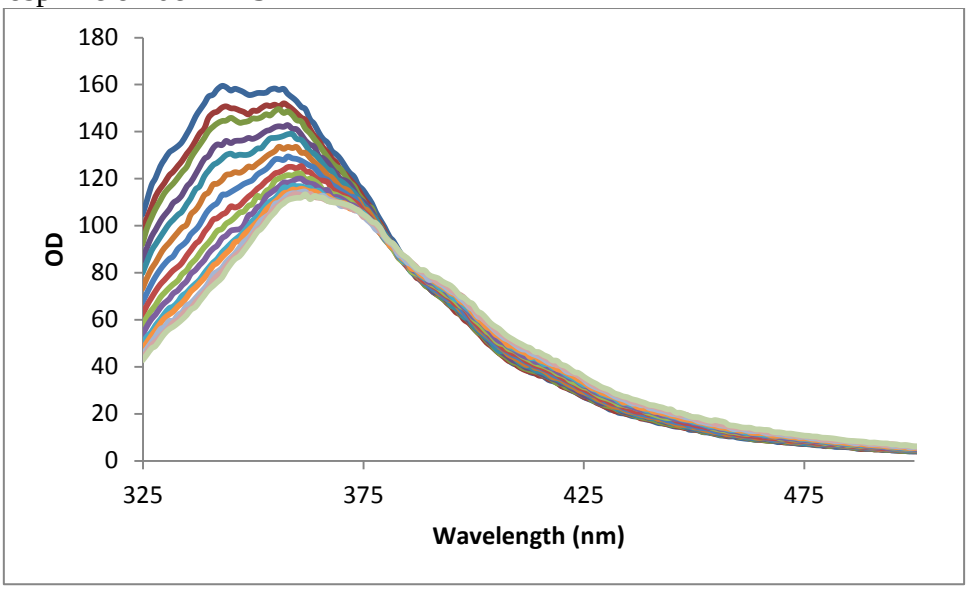
$$K_a = 16000 \pm 5000\ M^{-1} \qquad 86\%\ \text{bound}$$

4. Fluorescence Titration Curves for 1-naphthol (1) in Chloroform

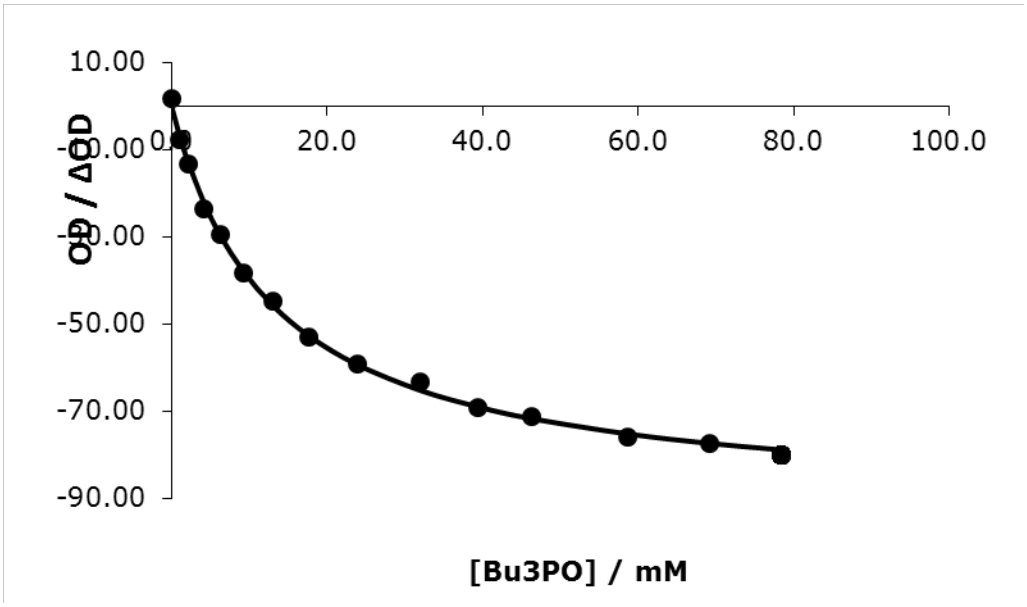
a) Titration of 1-naphthol with phosphine oxide in chloroform



Host: 1-naphthol = 0.041 mM
Guest: phosphine oxide = 215 mM



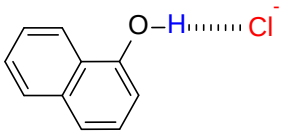
Graph S13. Fluorescence spectra of titration of phosphine oxide with 1-naphthol in chloroform.



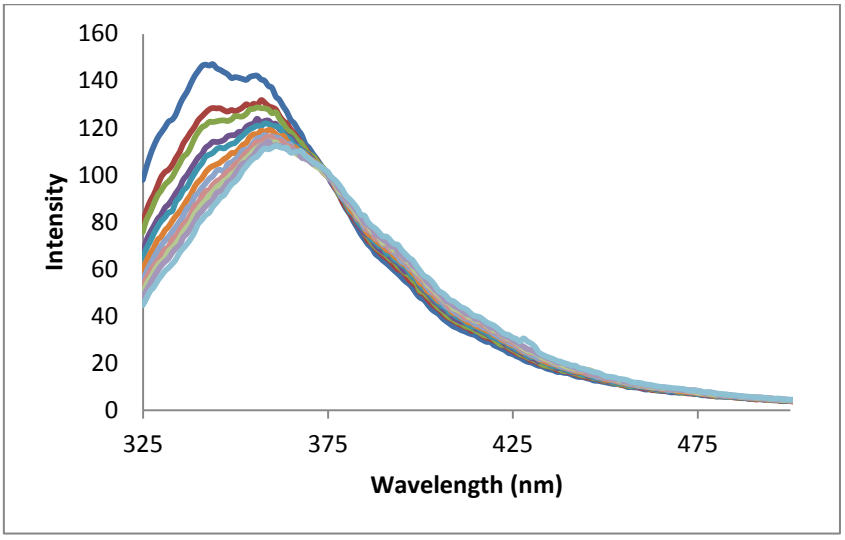
Graph S14. Binding isotherm for titration using 1:1 fitting program for titration of phosphine oxide against 1-naphthol in chloroform. [1-naphthol] = 0.041 mM and [phosphine oxide] = 215 mM.

$$K_a = 74 \pm 7\ M^{-1} \qquad 86\%\ \text{bound}$$

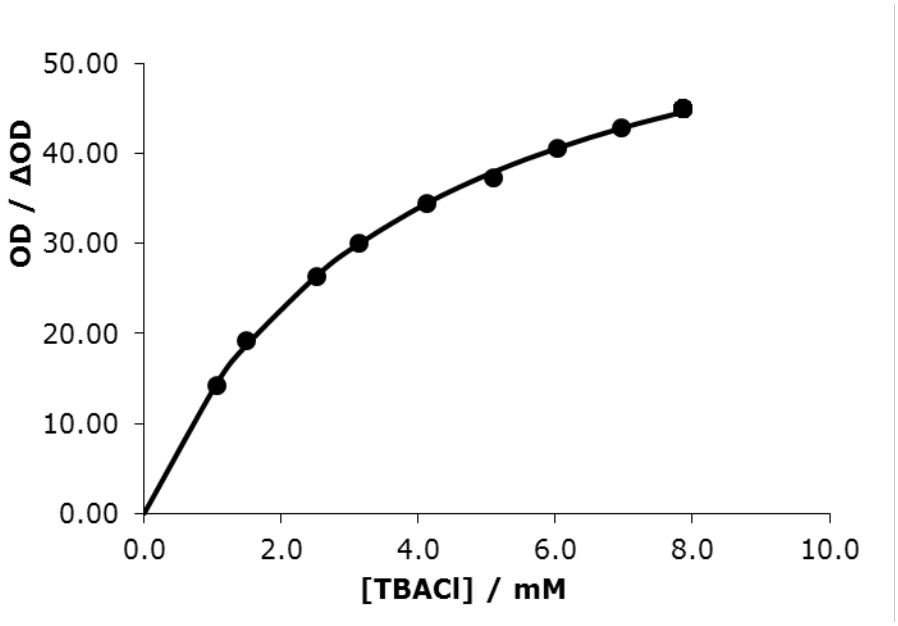
b) Titration of 1-naphthol with TBACl in chloroform



Host: 1-naphthol = 0.039 mM
Guest: TBACl = 87 mM



Graph S15. Fluorescence spectra of titration of TBACl with 1-naphthol in chloroform.

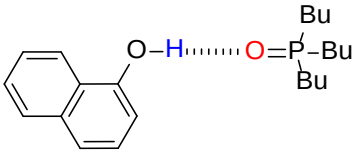


Graph S16. Binding isotherm for titration using 1:1 fitting program for titration of TBACl against 1-naphthol in chloroform. [1-naphthol] = 0.039 mM and [TBACl] = 87 mM.

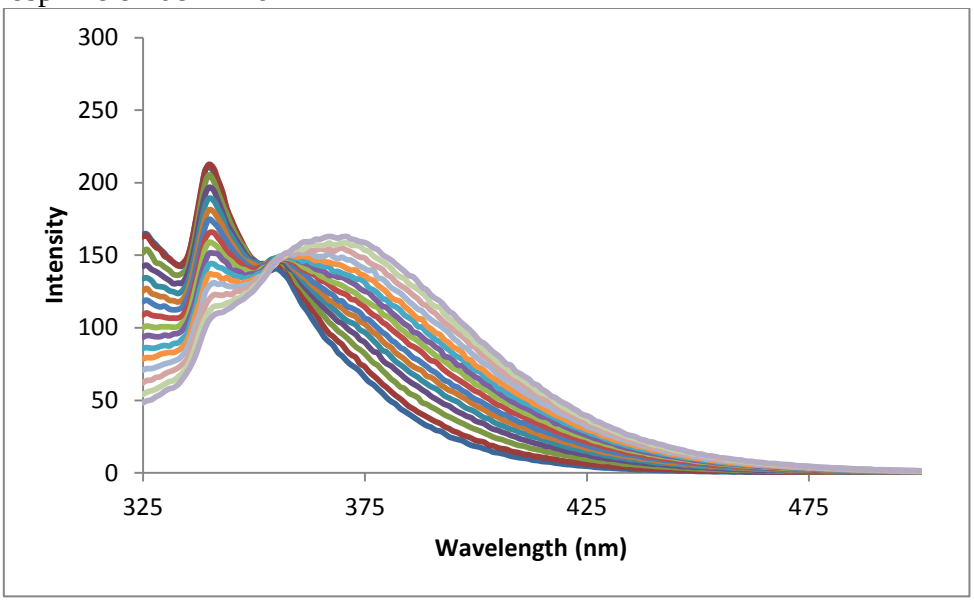
K_a = 270 ± 21 M^{-1} 76% bound

5. Fluorescence Titration Curves for 1-naphthol (1) in Dichloromethane

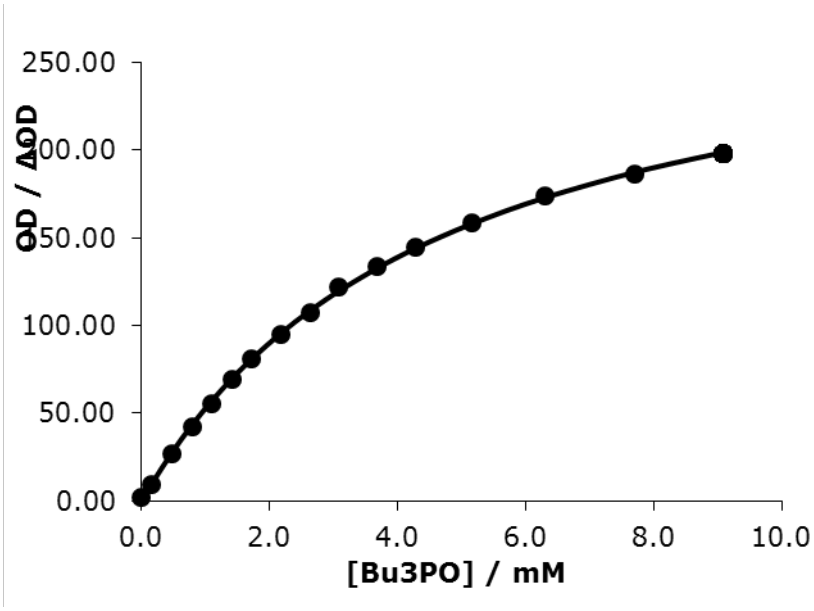
a) Titration of 1-naphthol with phosphine oxide in dichloromethane



Host: 1-naphthol = 0.055 mM
Guest: phosphine oxide = 126 mM



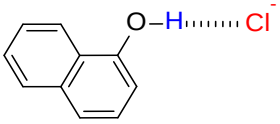
Graph S17. Fluorescence spectra of titration of phosphine oxide with 1-naphthol in dichloromethane.



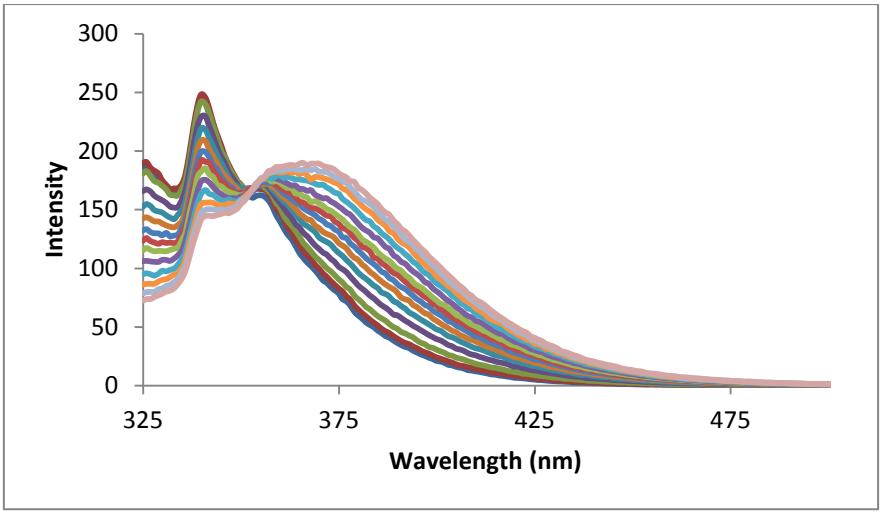
Graph S18. Binding isotherm for titration using 1:1 fitting program for titration of phosphine oxide against 1-naphthol in dichloromethane. [1-naphthol] = 0.055 mM and [phosphine oxide] = 126 mM.

$$K_a = \quad 200 \pm 40\ M^{-1} \qquad\qquad 66\%\ \text{bound}$$

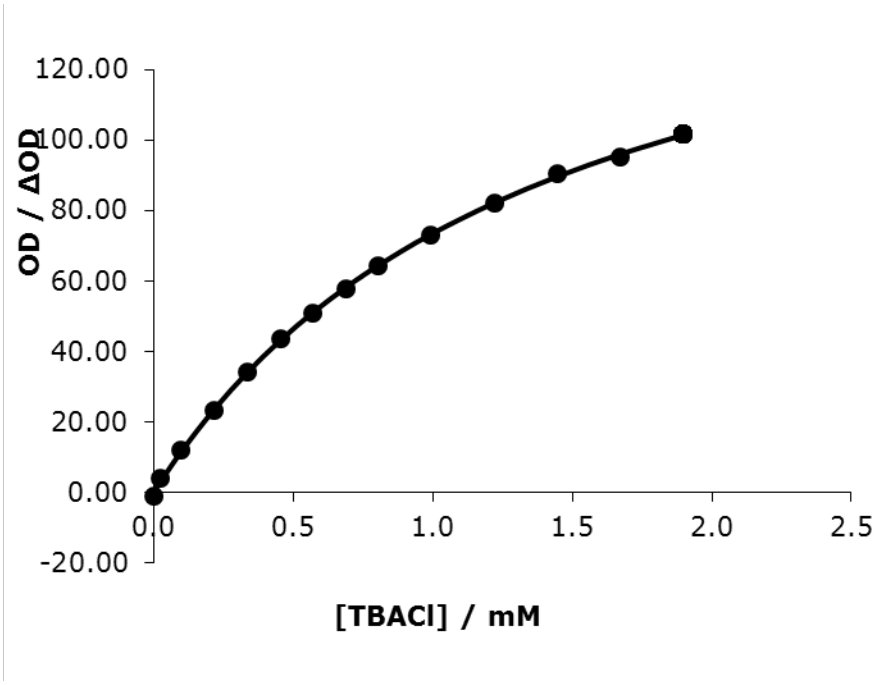
h) Titration of 1-naphthol with TBACl in dichloromethane



Host: 1-naphthol = 0.062 mM
Guest: TBACl = 48 mM



Graph S19. Fluorescence spectra of titration of TBACl with 1-naphthol in dichloromethane.



Graph S20. Binding isotherm for titration using 1:1 fitting program for titration of TBACl against 1-naphthol in dichloromethane. [1-naphthol] = 0.062 mM and [TBACl] = 48 mM.

K_a = 700 ± 140 M^{-1} 59% bound

6. Summary of Association Constants (K / M^{-1}) for all Studied H-bonded Complexes in Carbon Tetrachloride, Dichloromethane and Chloroform

Hydrogen Bond Donor	Hydrogen Bond Acceptor	Spectroscopic Technique	Solvent	K (M^{-1})[a]
1-naphthol	Bu_3PO	Fluorescence	Chloroform	74 ± 7
1-naphthol	Bu_3PO	UV/Vis	Chloroform	77 ± 8
1-naphthol	Oct_3PO	Fluorescence	Chloroform	91 ± 15
1-naphthol	Oct_3PO	UV/Vis	Chloroform	81 ± 16
1-naphthol	Me_3PO	Fluorescence	Chloroform	52 ± 9
1-naphthol	Me_3PO	UV/Vis	Chloroform	58 ± 3
1-naphthol	Cy_3PO	Fluorescence	Chloroform	150 ± 60
1-naphthol	Cy_3PO	UV/Vis	Chloroform	136 ± 6
1-naphthol	EtO_3PO	Fluorescence	Chloroform	21 ± 5
1-naphthol	EtO_3PO	UV/Vis	Chloroform	29 ± 10
1-naphthol	TBACl	Fluorescence	Chloroform	270 ± 21
1-naphthol	TBACl	UV/Vis	Chloroform	260 ± 40
1-naphthol	TBASCN	Fluorescence	Chloroform	120 ± 42
1-naphthol	TBASCN	UV/Vis	Chloroform	110 ± 8
1-naphthol	$TBAN_3$	Fluorescence	Chloroform	440 ± 100
1-naphthol	TBAOBz	Fluorescence	Chloroform	2700 ± 700
1-naphthol	Bu_3PO	Fluorescence	Dichloromethane	200 ± 40
1-naphthol	Bu_3PO	UV/Vis	Dichloromethane	260 ± 59
1-naphthol	Oct_3PO	Fluorescence	Dichloromethane	280 ± 42
1-naphthol	Oct_3PO	UV/Vis	Dichloromethane	340 ± 40
1-naphthol	Me_3PO	Fluorescence	Dichloromethane	140 ± 24
1-naphthol	Me_3PO	UV/Vis	Dichloromethane	180 ± 13
1-naphthol	Cy_3PO	Fluorescence	Dichloromethane	320 ± 48
1-naphthol	Cy_3PO	UV/Vis	Dichloromethane	370 ± 14
1-naphthol	EtO_3PO	Fluorescence	Dichloromethane	52 ± 9
1-naphthol	EtO_3PO	UV/Vis	Dichloromethane	47 ± 8
1-naphthol	Bu_2SO	Fluorescence	Dichloromethane	55 ± 14
1-naphthol	$Hex_2NC(O)Me$	Fluorescence	Dichloromethane	43 ± 9
1-naphthol	TBACl	Fluorescence	Dichloromethane	700 ± 140
1-naphthol	TBACl	UV/Vis	Dichloromethane	810 ± 240
1-naphthol	TBASCN	Fluorescence	Dichloromethane	210 ± 18
1-naphthol	TBASCN	UV/Vis	Dichloromethane	200 ± 60
1-naphthol	$TBAN_3$	UV/Vis	Dichloromethane	1300 ± 400
1-naphthol	TBAOBz	UV/Vis	Dichloromethane	12200 ± 4400
1-naphthol	Bu_3PO	UV/Vis	Carbon tetrachloride	2500 ± 200
1-naphthol	Oct_3PO	UV/Vis	Carbon tetrachloride	3000 ± 110
1-naphthol	Me_3PO	UV/Vis	Carbon tetrachloride	1900 ± 550
1-naphthol	Cy_3PO	UV/Vis	Carbon tetrachloride	5400 ± 200
1-naphthol	EtO_3PO	UV/Vis	Carbon tetrachloride	340 ± 96
1-naphthol	Bu_2SO	UV/Vis	Carbon tetrachloride	290 ± 51

1-naphthol	$Hex_2NC(O)Me$	UV/Vis	Carbon tetrachloride	220 ± 76
1-naphthol	TBACl	UV/Vis	Carbon tetrachloride	16000 ± 5000

Table S1. Association constants for the H-bonded complexes formed between **1** and **2**-**12** in the different solvents at 298 K. [a]Experimental results are the average of at least two titrations and errors are quoted at the 95% confidence limit.

7. Summary of α, α_s and β_s values of solvents and solutes

Solute or solvent	α	α_s	β_s
1-naphthol	3.9	-	-
CCl_4	-	1.4[3]	0.6[3]
CH_2Cl_2	-	1.8	1.4
$CHCl_3$	-	2.1	1.3[4]

Table S2. Summary of α, α_s and β_s values of solvents and solutes employed in the study.

Dichloromethane has previously been identified to have a $\alpha_s = 1.7$ and $\beta_s = 1.5$ in ref 5 although it was noted that the experimental data employed to obtain the hydrogen bond parameters of dichloromethane led to a large range of possible values; $1.3 < \alpha_s < 2.0$ and $0.5 < \beta_s < 2.5$. In ref 6, a $\beta_s = 1.1$ is employed for dichloromethane. A α_s value of 2.2 is given for $CHCl_3$ in ref 4.

Calculation of β value for hydrogen bond acceptors:

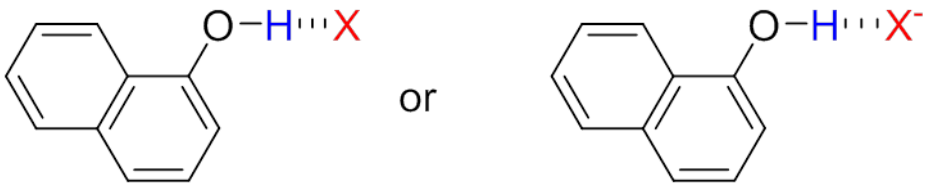
$$\Delta G° \text{ (kJ mol}^{-1}) = -RT \ln K = -(\alpha - \alpha_s)(\beta - \beta_s) + 6 \qquad (1)$$

The free energy of the system ($\Delta G°$), K is the equilibrium constant for the formation of the hydrogen bonding interaction (Table 1), α is the hydrogen bond donor ability of the solute, α_s and βs is the hydrogen bond donor and acceptor parameters of the solvent respectively (Table *S2*).

Given a α value of the donor, the α_s and β_s parameters of the solvent, and experimentally determined association constants (K) (Table *S1*), the β value of a hydrogen bond acceptor can be readily calculated through rearrangement of eq 1 to give eq 2.

$$\beta = \beta_s + (RT \ln K + 6) / (\alpha - \alpha_s) \qquad (2)$$

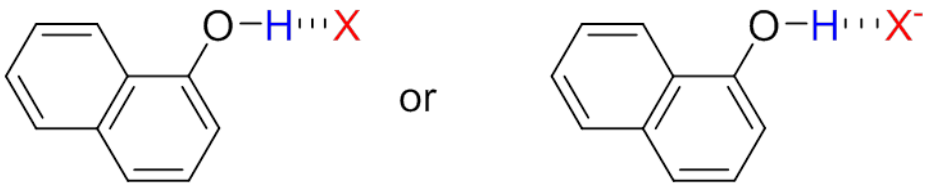
8. Summary of $\Delta G°_{exp}$ and β values for UV/Vis titrations of 1-naphthol with the studied anions in the chloroform



Hydrogen bond acceptor	Chloroform		Carbon Tetrachloride		Dichloromethane	
	$\Delta G°_{exp}$ / kJ mol^{-1}	β value	$\Delta G°_{exp}$ / kJ mol^{-1}	β value	$\Delta G°_{exp}$ / kJ mol^{-1}	β value
Bu_3PO	10.6 ± 0.3	10.6 ± 0.2	19.4 ± 0.2	10.7 ± 0.1	13.8 ± 0.6	10.8 ± 0.3
Cy_3PO	12.2 ± 0.1	11.3 ± 0.1	21.3 ± 0.4	11.5 ± 0.1	14.7 ± 0.1	11.3 ± 0.3
Oct_3PO	10.9 ± 0.5	10.7 ± 0.3	20.2 ± 0.5	11.0 ± 0.2	14.4 ± 0.3	11.0 ± 0.1
Me_3PO	10.1 ± 0.1	10.2 ± 0.1	18.9 ± 0.7	10.4 ± 0.3	12.9 ± 0.2	10.3 ± 0.1
EtO_3PO	8.3 ± 1.1	9.2 ± 0.6	14.4 ± 0.5	8.7 ± 0.2	9.5 ± 0.4	8.8 ± 0.2
Bu_2SO	-	-	14.0 ± 0.5	8.6 ± 0.2	-	-
$Hex_2NC(O)Me$	-	-	13.4 ± 0.9	8.3 ± 0.3	-	-
TBACl	13.8 ± 0.4	12.2 ± 0.2	24.0 ± 0.8	12.5 ± 0.3	16.6 ± 0.7	12.1 ± 0.3
TBASCN	11.6 ± 0.2	11.1 ± 0.1	-	-	13.1 ± 0.8	10.4 ± 0.4
$TBAN_3$	-	-	-	-	17.8 ± 1.0	12.6 ± 0.5
TBAOBz	-	-	-	-	23.3 ± 0.8	15.3 ± 0.4

Table S3. Summary of $\Delta G°_{exp}$ and β values for the H-bonded complexes involving **1** for UV/Vis titrations performed in chloroform, dichloromethane and carbon tetrachloride. Where X = neutral acceptor and X^- = charged acceptor

9. Summary of $\Delta G°_{exp}$ and β values for Fluorescence titrations of 1-naphthol with the studied anions in the chloroform



Hydrogen bond acceptor	Chloroform		Dichloromethane	
	$\Delta G°_{exp}$ / kJ mol^{-1}	β value	$\Delta G°_{exp}$ / kJ mol^{-1}	β value
Bu_3PO	10.6 ± 0.2	10.6 ± 0.1	13.2 ± 0.5	10.5 ± 0.2
Cy_3PO	12.4 ± 1.0	11.5 ± 0.5	14.2 ± 0.4	11.0 ± 0.2
Oct_3PO	11.2 ± 0.4	11.1 ± 0.2	13.8 ± 0.1	10.8 ± 0.1
Me_3PO	9.7 ± 0.5	10.0 ± 0.3	12.3 ± 0.4	10.1 ± 0.3
$(OEt)_3PO$	7.6 ± 0.5	8.8 ± 0.3	9.9 ± 0.4	9.0 ± 0.2
$Hex_2NC(O)Me$	-	-	9.3 ± 0.5	8.6 ± 0.3
Bu_2SO	-	-	9.9 ± 0.8	8.9 ± 0.4
TBACl	13.9 ± 0.2	12.3 ± 0.1	16.2 ± 0.5	11.9 ± 0.2
TBASCN	11.9 ± 1.0	11.2 ± 0.5	13.2 ± 0.2	10.5 ± 0.1
$TBAN_3$	15.0 ± 0.6	12.9 ± 0.3	-	-
TBAOBz	19.5 ± 0.7	15.4 ± 0.4	-	-

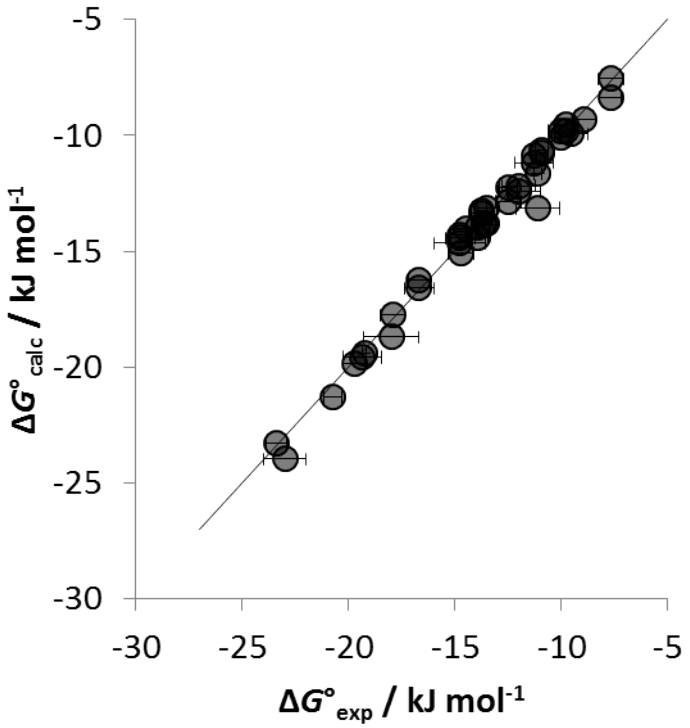
Table S4. Summary of $\Delta G°_{exp}$ and β values for the H-bonded complexes involving **1** for fluorescence emission spectroscopy titrations performed in chloroform and dichloromethane. Where X = neutral acceptor and X^- = charged acceptor

10. Summary of average β values for the studied anions and neutral solutes

Hydrogen bond acceptor	Average β value
TBAOBz	15.4 ± 0.1
$TBAN_3$	12.8 ± 0.4
TBACl	12.2 ± 0.4
TBASCN	10.8 ± 0.8
Cy_3PO	11.3 ± 0.4
Oct_3PO	10.9 ± 0.3
Bu_3PO	10.6 ± 0.3
Me_3PO	10.2 ± 0.2
$(OEt)_3PO$	8.9 ± 0.4
Bu_2SO	8.8 ± 0.4
$Hex_2NC(O)Me$	8.5 ± 0.4

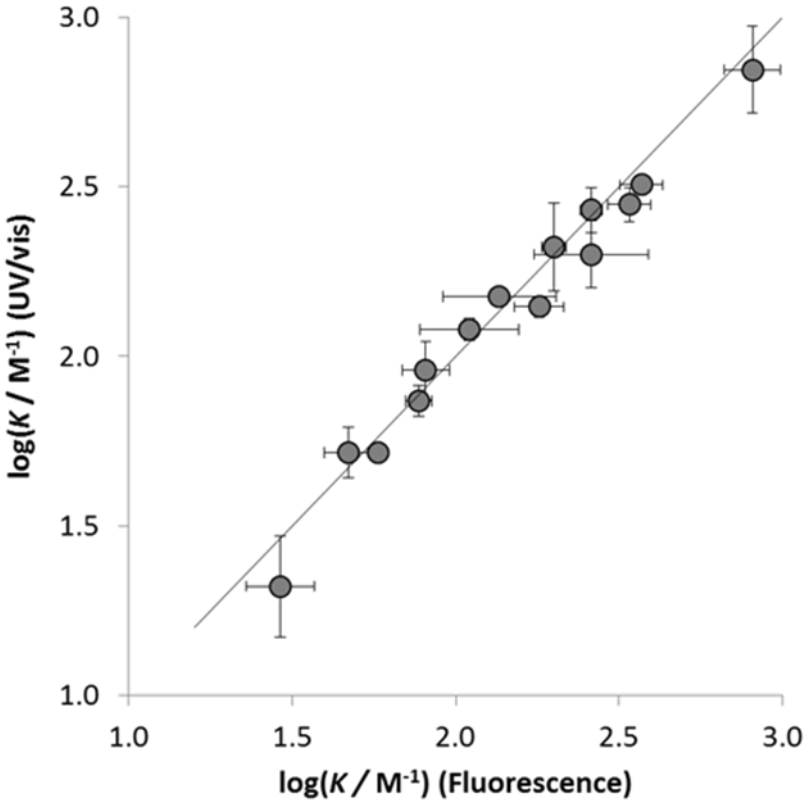
Table S5. Summary of average β values for the studied anions and neutral solutes.

11. Summary of $\Delta G°_{exp}$ and β values for titrations of 1 with the studied anions and neutral solutes in chloroform, dichloromethane and carbon tetrachloride



Graph S21. Graph showing comparison of experimental free energy on complexation ($\Delta G°_{exp}$) with the values calculated using eq 2 ($\Delta G°_{calc}$) for the H-bonded complexes (**1·X**, **2·X** and **3·X**) in the different solvents. The line represents $\Delta G°_{calc} = \Delta G°_{exp}$.

12. Comparison of log (K / M^{-1}) values obtained using UV/vis absorption spectroscopy and fluorescence emission spectroscopy



Graph S22. Comparison of the log(K /M^{-1}) obtained for the H-bonded complexes **1**·**X** when calculated from the experimental data obtained using fluorescence emission spectroscopy and UV/vis absorption spectroscopy. The line represents log(K / M^{-1}) (fluorescence emission spectroscopy) = log(K / M^{-1}) (UV/vis absorption spectroscopy).

13. Histogram of β values for hydrogen bond acceptors

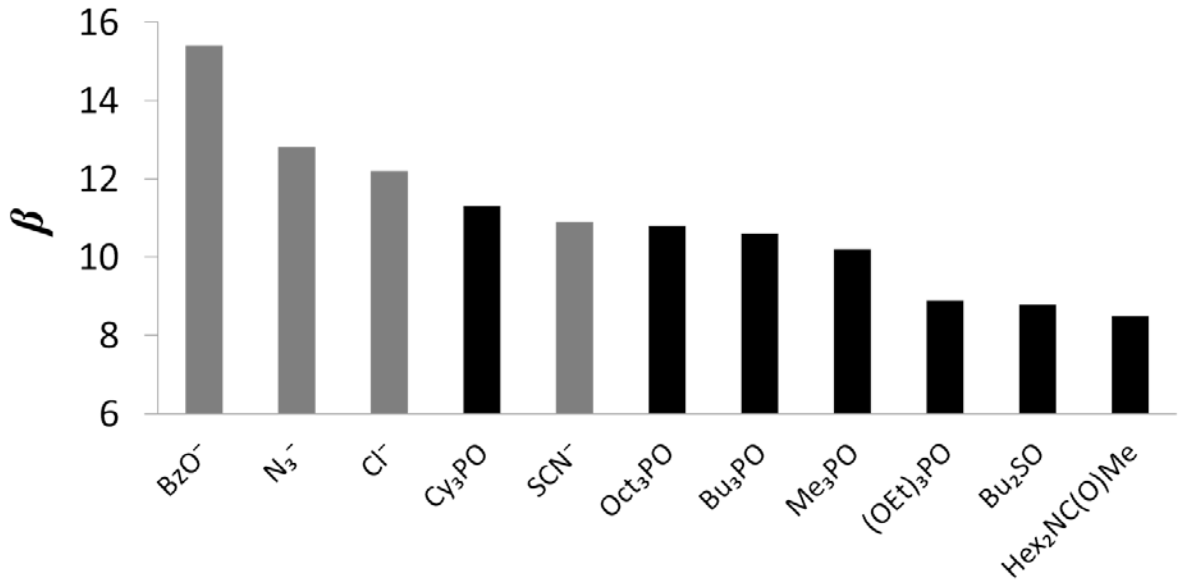


Figure S1. β values for anions and neutral solutes (the charged acceptors are shown in grey and the neutral acceptors are shown in black).

14. References

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