Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

N-Alkyl ammonium resorcinarene salts: Multivalent halogen bonded deep cavity cavitands

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Supporting Information

Table of Contents

I General Information………….………………………………..……………………………2

II X-Ray Crystallographic Analyses …………………………………………………………...2

III NMR Spectroscopic Analyses…….….…………………....…………………………………..5

IV Fluorescence Analyses…………………………………..…………………………………13

V References………………………………………………...……………….…………..….13

I General Information

The *N-cyclo*hexyl ammonium resorcinarene halides **1-3** were synthesized according to reported procedures.[1] The iodoperfluorinated halogen bond donors **4-5** and the fluorophores guests **6-8** were commercially available. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer (500 MHz for ^{1}H NMR and 470 MHz for ^{19}F NMR). Fluorescence spectra were obtained on a Varian Cary Eclipse Fluorescence spectrophotometer.

II X-Ray Crystallographic Analyses

Single crystal X-ray diffraction data for EtOH_$C_2H_4Cl_2$@**3** (Figure S1a) and $CHCl_3$@[**1**•(**5**)$_4$] (Figure S1b) were collected on an Agilent SuperNova dual wavelength diffractometer with a micro-focus X-ray source and multilayer optics monochromatized Cu-Kα (λ = 1.54184 Å) radiation. All the data collection and reduction were performed using the program *CrysAlisPro*.[2] The intensities were corrected for absorption using gaussian face index absorption correction method.[3] The structures were solved by direct methods with *SHELXS-2013*[4] (EtOH_$C_2H_4Cl_2$@**3**) or with *SIR2011*[5] ($CHCl_3$@[**1**•(**5**)$_4$]) and refined by full-matrix least-squares methods using *OLEX2*[6], which utilizes the *SHELXL-2013* module[4].

In EtOH_$C_2H_4Cl_2$@**3** one of the propyl side chains of resorcinarene host is disordered and the chain end carbon is divided over two sites (77:23) in the refinement. Also, the 1,2-dichloroethane guest molecule shows disorder, in which the first Cl end shows different electron density distribution over two sites (71:29) than the other Cl end (52:48). Furthermore, some weak electron densities were observed in the cavity, which may indicate more complex disorder of the guest molecules. However, they were too weak to be assigned or refined reasonably. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were treated with the riding model. Geometrical restraints were used to rationalize the bond distances in disordered side chain and 1,2-dichloroethane molecule. Restraints on anisotropic displacement parameters were also applied for disordered side chain and 1,2-dichloroethane to make the atoms more isotropic (spherical).

In $CHCl_3$@[**1**•(**5**)$_4$] only ¼ of the structure was shown in asymmetric unit. Bromide anion shows disorder over two sites (60:40). Chloroform guest is located on the four-fold axis (carbon and one chlorine atoms in special position), which leads to unrealistic four positions for two chlorine atoms (not sitting on symmetry axis) of the molecule with irrational bond angles. The chloroform location is only half populated and additional electron densities in the cavity were also found, but it was impossible to reasonably refine them. All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms bonded to carbon and nitrogen were treated with the riding model. Hydrogen atoms bonded to oxygen were found from the electron density map and restrained to the ideal distances (O−H 0.84 Å) from the parent atoms with isotropic thermal parameters [U_{eq}(H)] of 1.5U_{eq}(O). Restraints were also applied for chloroform and 1,4-diiodotetrafluorobenzene molecules to make the anisotropic displacement parameters of atoms around the bonds more similar.

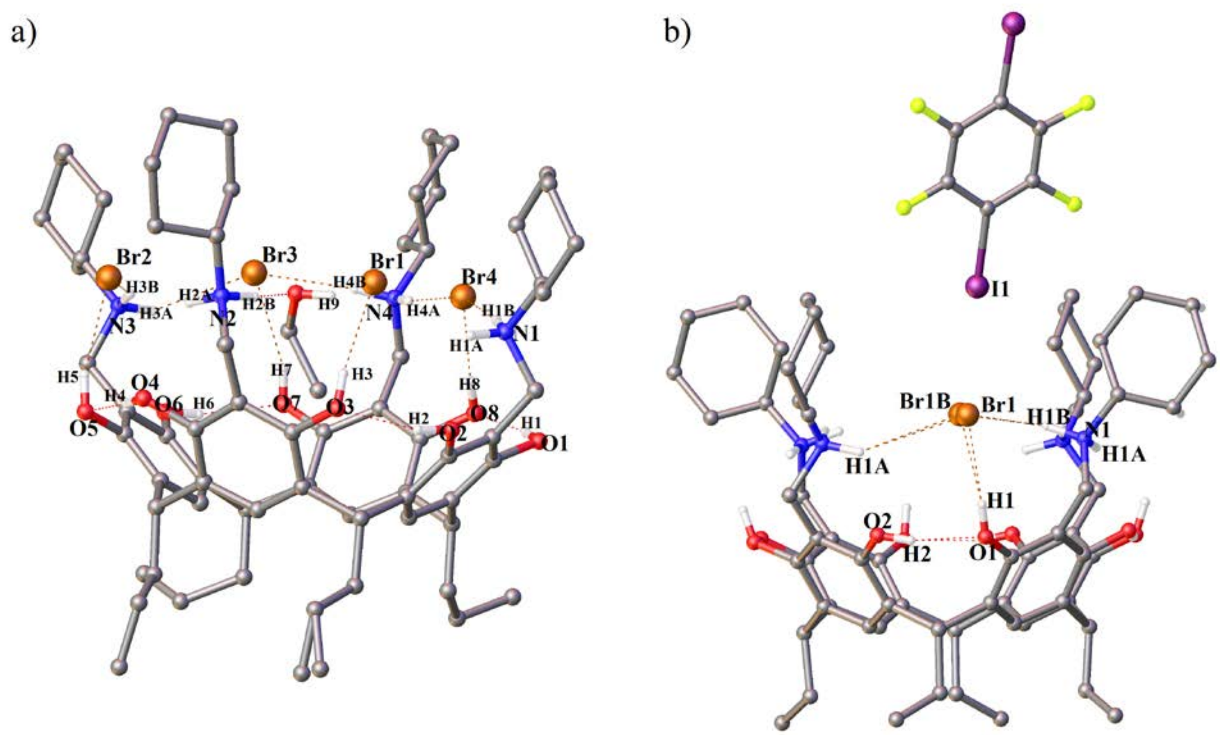

Figure S1. Crystal structures of EtOH_$C_2H_4Cl_2$@**3** and $CHCl_3$@[**1**•(**5**)$_4$].

Crystal data, information concerning data collection and reduction, and convergence results are documented in Table XRD S1. The classical hydrogen bonds in all the structures are listed in Table XRD S2.

Table S1. Crystallographic data and parameters of EtOH_$C_2H_4Cl_2$@**3** and $CHCl_3$@[**1**•(**5**)$_4$].

Identification code	EtOH_$C_2H_4Cl_2$@**3** (CCDC-1038851)	$CHCl_3$@[**1**•(**5**)$_4$] (CCDC-1038850)
Empirical formula	$C_{72}H_{114}Br_4Cl_2N_4O_9$	$C_{153}H_{176}Br_8Cl_3F_{16}I_8N_8O_{16}$
Fw. / $gmol^{-1}$	1570.21	4447.84
T / K	123.0(2)	123.0(2)
Wavelength / Å	1.54184	1.54184
Crystal system	Orthorhombic	Tetragonal
Space group	*Pbca*	*P*4/*ncc*
Unit cell dimensions		
a / Å	23.3371(3)	18.4165(3)
b / Å	23.5232(2)	18.4165(3)
c / Å	27.0473(3)	27.9044(7)
α / °	90	90
β / °	90	90
γ / °	90	90
V / $Å^3$	14848.0(3)	9464.3(4)
Z	8	2
ρ_{calc} / Mgm^{-3}	1.405	1.561
μ / mm^{-1}	3.753	13.246
F(000)	6560	4354
Crystal size / mm^3	0.18 × 0.12 × 0.11	0.28 × 0.13 × 0.03
θ range / °	3.13 – 76.75	3.17 – 62.45
Index ranges	$-17 \leq h \leq 22$ $-29 \leq k \leq 27$ $-33 \leq l \leq 33$	$-20 \leq h \leq 21$ $-20 \leq k \leq 15$ $-18 \leq l \leq 30$
Reflections collected	55172	12766
R_{int}	0.0619	0.0236
Completeness to θ / %	99.9	86.5
Absorption correction	Gaussian	Gaussian
Max. / min. transmission	0.831 / 0.741	0.663 / 0.293
Data^a / restraints / parameters	12047 / 61 / 684	3715 / 38 / 265
Reflections [$I>2\sigma(I)$]	9727	2424
Goodness-of-fit on F^2	1.051	1.204
Final R indices [$I>2\sigma(I)$]	R1 = 0.0778 wR2 = 0.2208	R1 = 0.0911 wR2 = 0.2971
R indices (all data)	R1 = 0.0905 wR2 = 0.2411	R1 = 0.1085 wR2 = 0.3281
Largest diff. peak & hole / e.$Å^{-3}$	2.038 / -1.152	1.303 / -1.131

Table S2. Hydrogen bond geometry in the structures of EtOH_$C_2H_4Cl_2$@**3** and $CHCl_3$@[**1**•(**5**)$_4$].

Donor−H···Acceptor				
EtOH_$C_2H_4Cl_2$@**3**	D-H (Å)	H…A (Å)	D…A (Å)	D-H…A (°)
O(1)-H(1)...O(8)	0.84	1.93	2.746(6)	164.4
O(2)-H(2)...O(3)	0.84	1.92	2.711(5)	156.5
O(3)-H(3)...Br(1)	0.84	2.27	3.102(5)	171.4
O(4)-H(4)...O(5)	0.84	1.92	2.755(6)	176.2
O(5)-H(5)...Br(2)	0.84	2.33	3.121(4)	157.8
O(6)-H(6)...O(7)	0.84	1.96	2.753(4)	157.2
O(7)-H(7)...Br(3)	0.84	2.35	3.164(3)	161.9
O(8)-H(8)...Br(4)	0.84	2.33	3.168(4)	174.4
N(1)-H(1A)...Br(1)	0.99	2.63	3.493(4)	146.3
N(1)-H(1A)...O(2)	0.99	2.46	3.034(7)	116.3
N(1)-H(1B)...Br(4)	0.99	2.38	3.368(5)	173.6
N(2)-H(2A)...Br(2)	0.99	2.68	3.606(5)	155.8
N(2)-H(2A)...O(4)	0.99	2.39	2.975(6)	116.7
N(2)-H(2B)...Br(1)	0.99	2.89	3.526(5)	122.7
N(2)-H(2B)...O(9)	0.99	1.93	2.854(7)	153.3
N(3)-H(3A)...Br(3)	0.99	2.55	3.440(4)	149.9
N(3)-H(3A)...O(6)	0.99	2.54	3.074(6)	113.9
N(3)-H(3B)...Br(2)	0.99	2.36	3.260(5)	150.8
N(4)-H(4A)...Br(4)	0.99	2.33	3.306(5)	167.5
N(4)-H(4B)...Br(3)	0.99	2.27	3.253(4)	172.9
O(9)-H(9)...Br(1)	0.84	2.68	3.280(6)	129.9
$CHCl_3$@[**1**•(**5**)$_4$]				
O(1)-H(1)...Br(1)[a]	0.84(2)	2.29(5)	3.112(9)	166(19)
O(1)-H(1)...Br(1B)[a]	0.84(2)	2.43(4)	3.252(10)	168(17)
O(2)-H(2)...O(1)[b]	0.84	2.08(16)	2.684(12)	129(17)
O(2)-H(2)...O(1)[b]	0.84	2.08(16)	2.684(12)	129(17)
N(1)-H(1A)...Br(1)	0.99	2.99	3.889(9)	151.0
N(1)-H(1A)...Br(1B)	0.99	2.68	3.549(9)	146.9
N(1)-H(1A)...O(2)	0.99	2.35	2.943(13)	117.7
N(1)-H(1B)...Br(1)[a]	0.99	2.60	3.384(9)	135.7
N(1)-H(1B)...Br(1B)[a]	0.99	2.35	3.250(9)	151.3
N(1)-H(1B)...Cl(2)[a]	0.99	2.89	3.726(11)	142.6

[a] -y+1/2, x, z; [b] y, -x+1/2, z

III NMR Spectroscopic Analyses

Spectra Changes

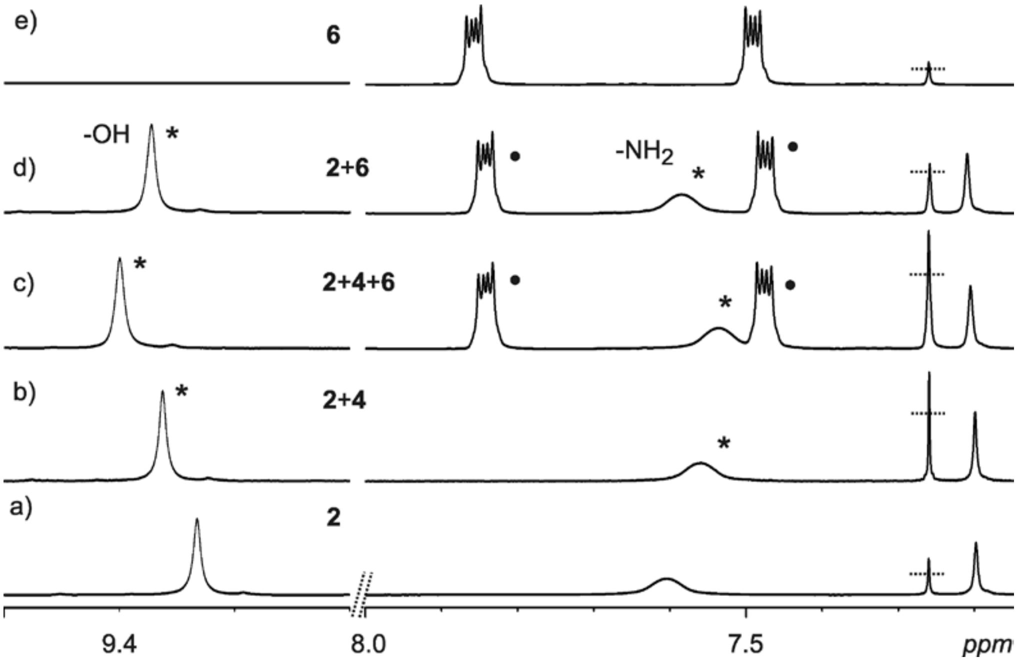

Figure S2. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **2** (30 mM), b) 1:4 mixture of **2** and **4**, c) 1:4:2 mixture of **2**, **4** and **6**, d) 1:2 mixture of **2** and **6**, e) **6** (30 mM).

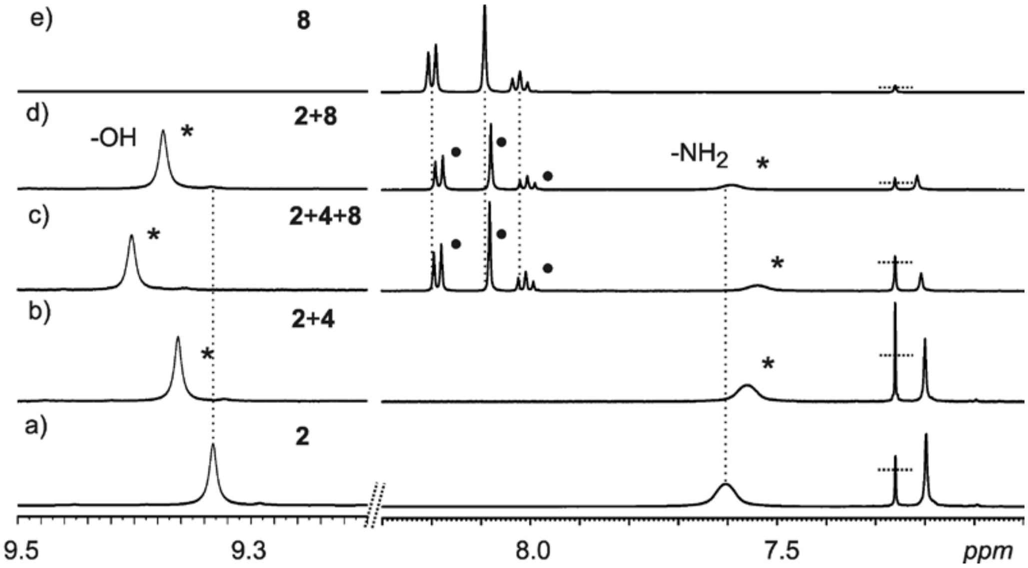

Figure S3. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **2** (30 mM), b) 1:4 mixture of **2** and **4**, c) 1:4:2 mixture of **2**, **4** and **8**, d) 1:2 mixture of **2** and **8**, e) **8** (30 mM).

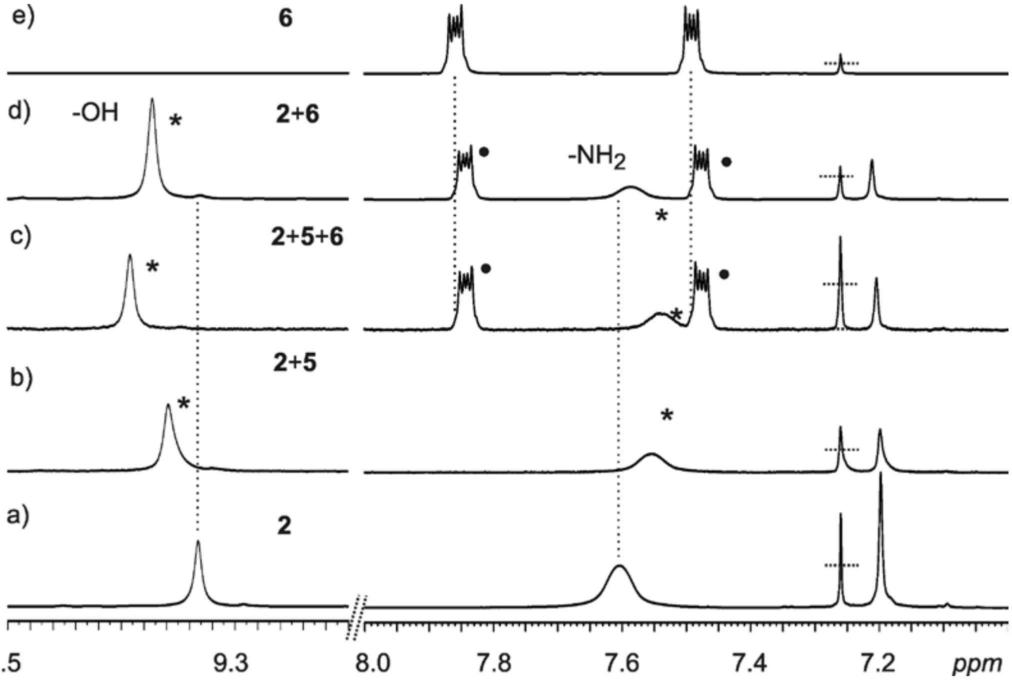

Figure S4. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **2** (30 mM), b) 1:4 mixture of **2** and **5**, c) 1:4:2 mixture of **2**, **5** and **6**, d) 1:2 mixture of **2** and **6**, e) **6** (30 mM).

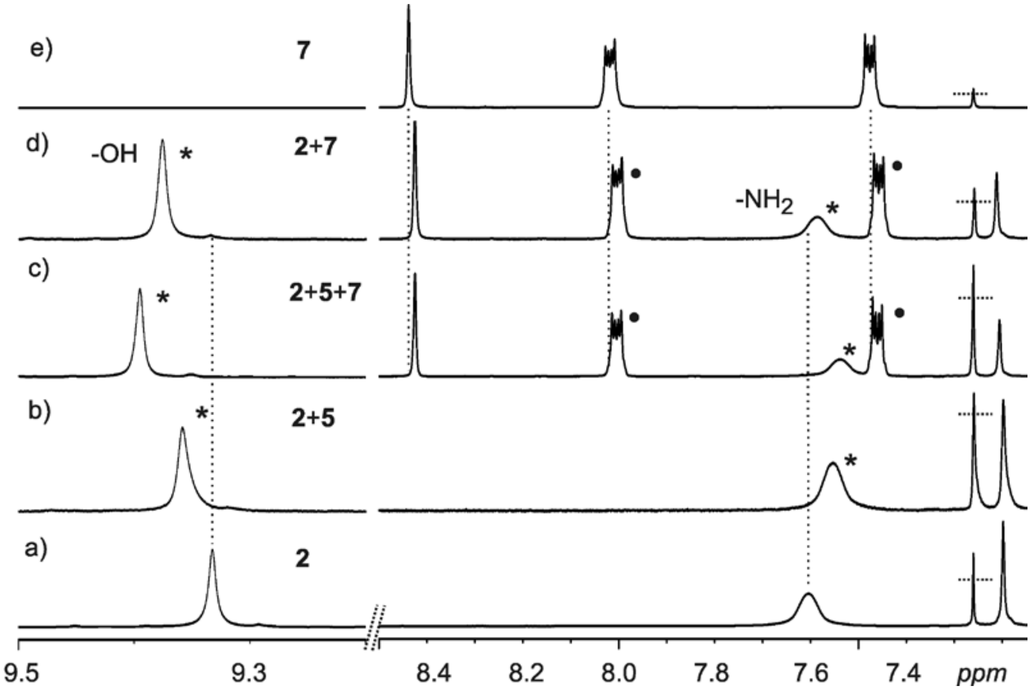

Figure S5. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **2** (30 mM), b) 1:4 mixture of **2** and **5**, c) 1:4:2 mixture of **2**, **5** and **7**, d) 1:2 mixture of **2** and **7**, e) **7** (30 mM).

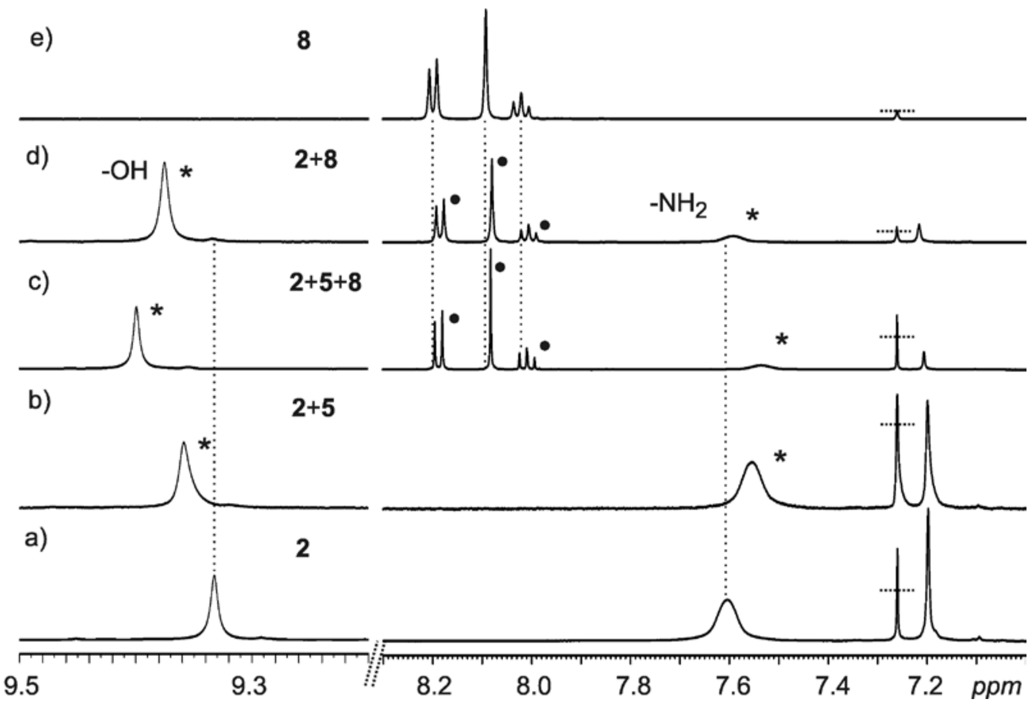

Figure S6. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **2** (30 mM), b) 1:4 mixture of **2** and **5**, c) 1:4:2 mixture of **2**, **5** and **8**, d) 1:2 mixture of **2** and **8**, e) **8** (30 mM).

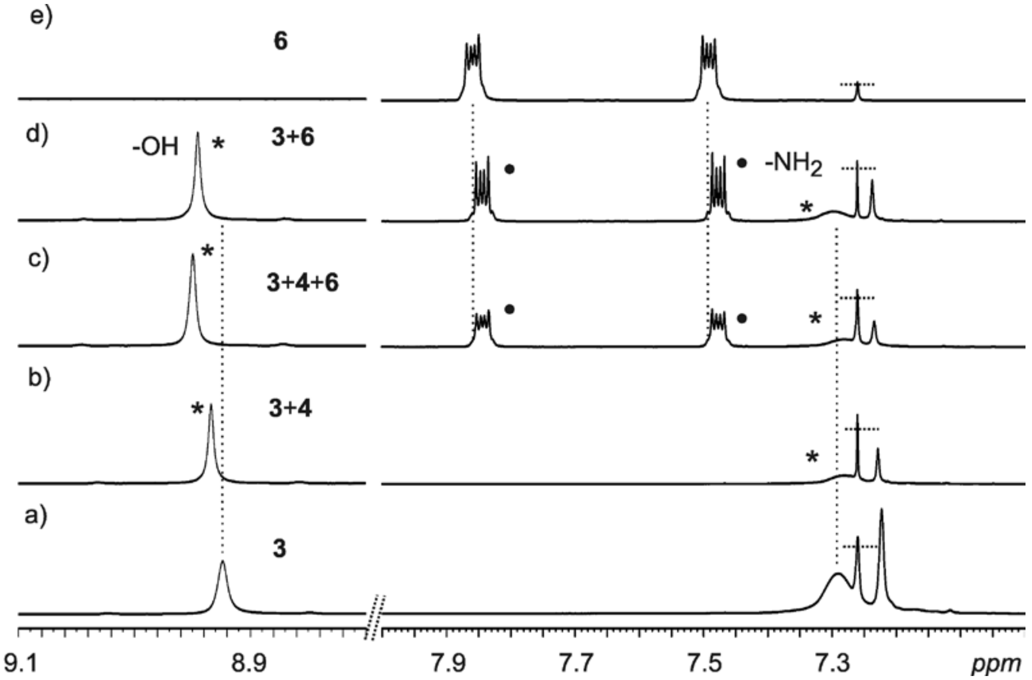

Figure S7. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **3** (30 mM), b) 1:4 mixture of **3** and **4**, c) 1:4:2 mixture of **3**, **4** and **6**, d) 1:2 mixture of **3** and **6**, e) **6** (30 mM).

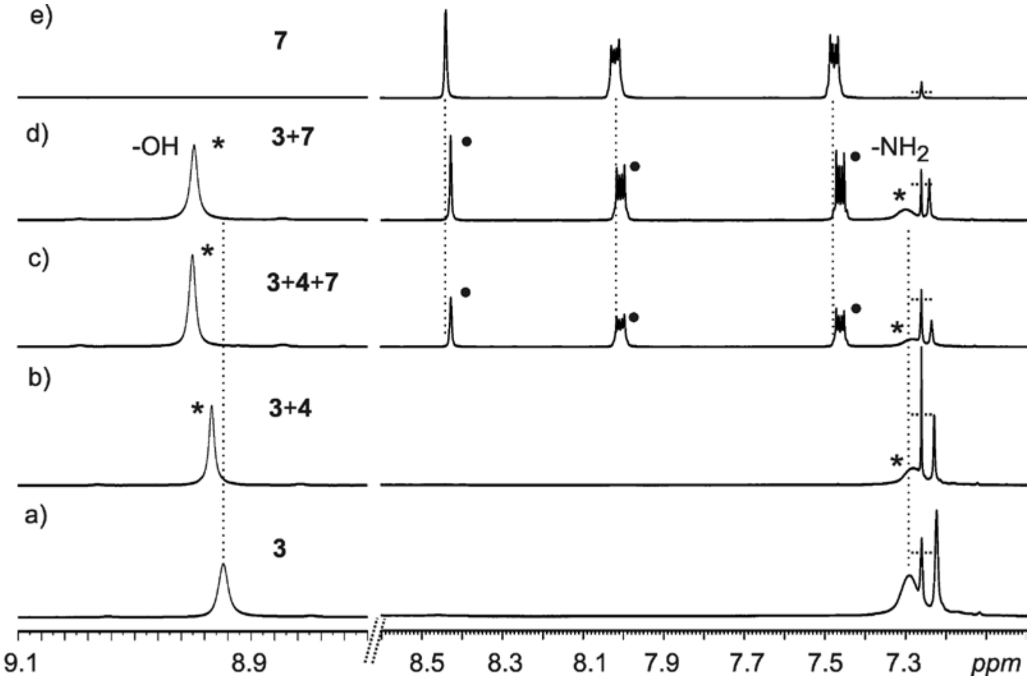

Figure S8. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **3** (30 mM), b) 1:4 mixture of **3** and **4**, c) 1:4:2 mixture of **3**, **4** and **7**, d) 1:2 mixture of **3** and **7**, e) **7** (30 mM).

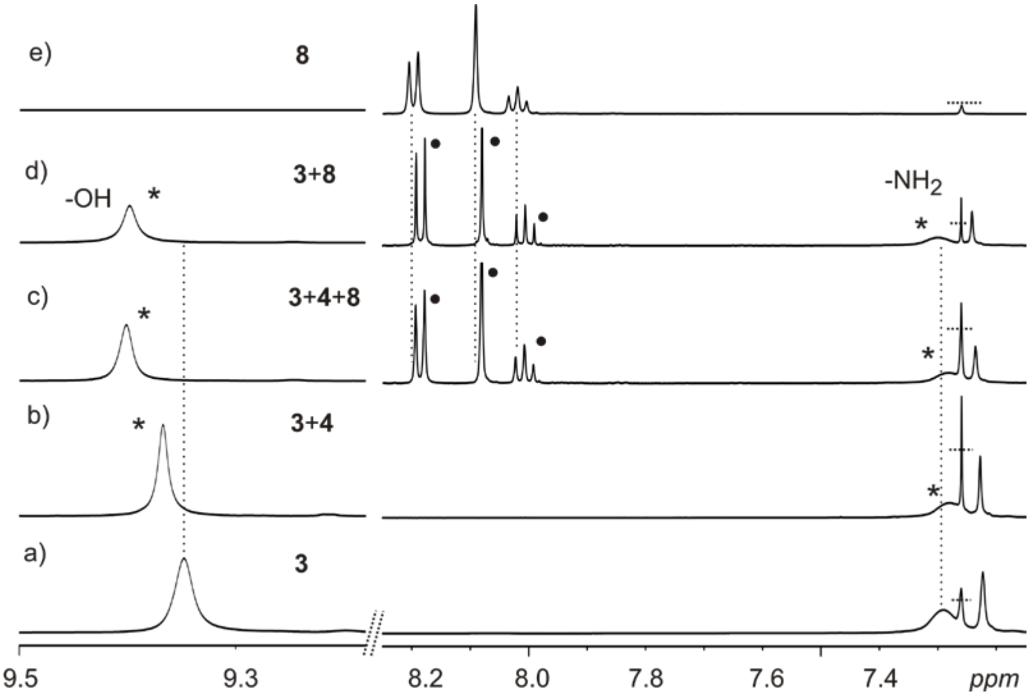

Figure S9. ^{1}H NMR (in $CDCl_3$ at 303 K) of: a) **3** (30 mM), b) 1:4 mixture of **3** and **4**, c) 1:4:2 mixture of **3**, **4** and **8**, d) 1:2 mixture of **3** and **8**, e) **8** (30 mM).

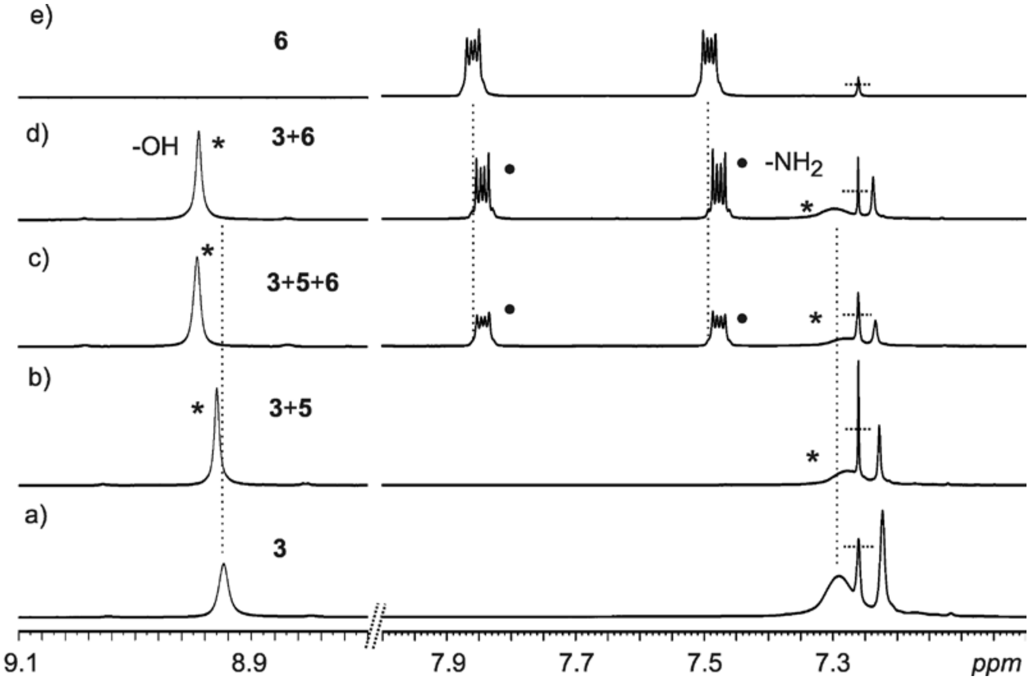

Figure S10. ^{1}H NMR (in CDCl$_3$ at 303 K) of: a) **3** (30 mM), b) 1:4 mixture of **3** and **5**, c) 1:4:2 mixture of **3**, **5** and **6**, d) 1:2 mixture of **3** and **6**, e) **6** (30 mM).

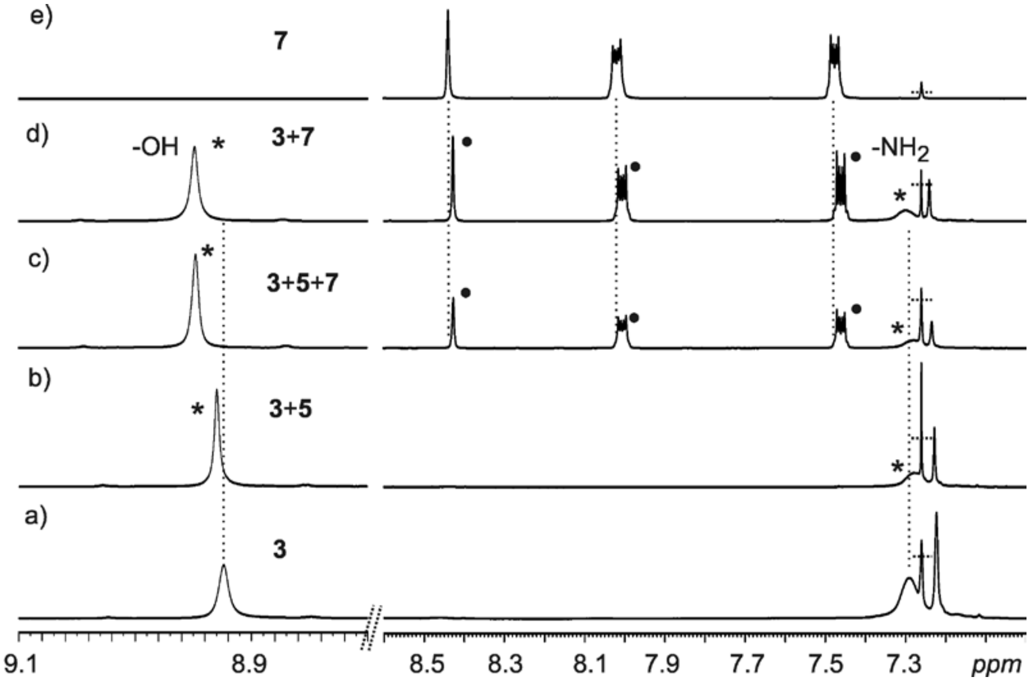

Figure S11. ^{1}H NMR (in CDCl$_3$ at 303 K) of: a) **3** (30 mM), b) 1:4 mixture of **3** and **5**, c) 1:4:2 mixture of **3**, **5** and **7**, d) 1:2 mixture of **3** and **7**, e) **7** (30 mM).

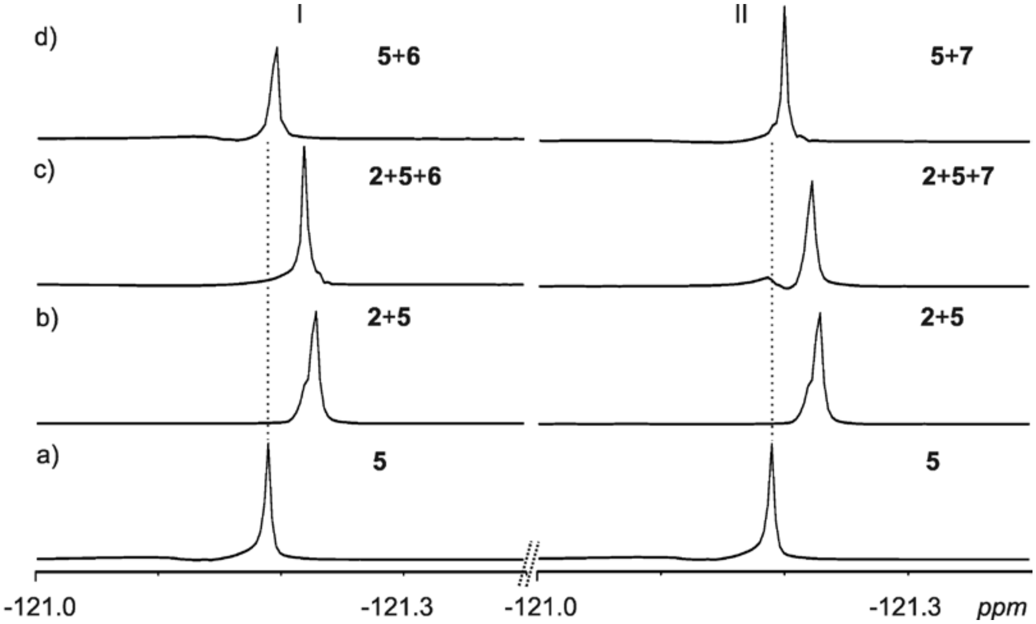

Figure S12. ^{19}F NMR (in $CDCl_3$ at 303 K) of: I: a) **5** (30 mM), b) 1:4 mixture of **2** and **5**, c) 1:4:2 mixture of **2**, **5** and **6**, d) 1:1 mixture of **5** and **6**; II: a) **5** (30 mM), b) 1:4 mixture of **2** and **5**, c) 1:4:2 mixture of **2**, **5** and **7**, d) 1:1 mixture of **5** and **7**.

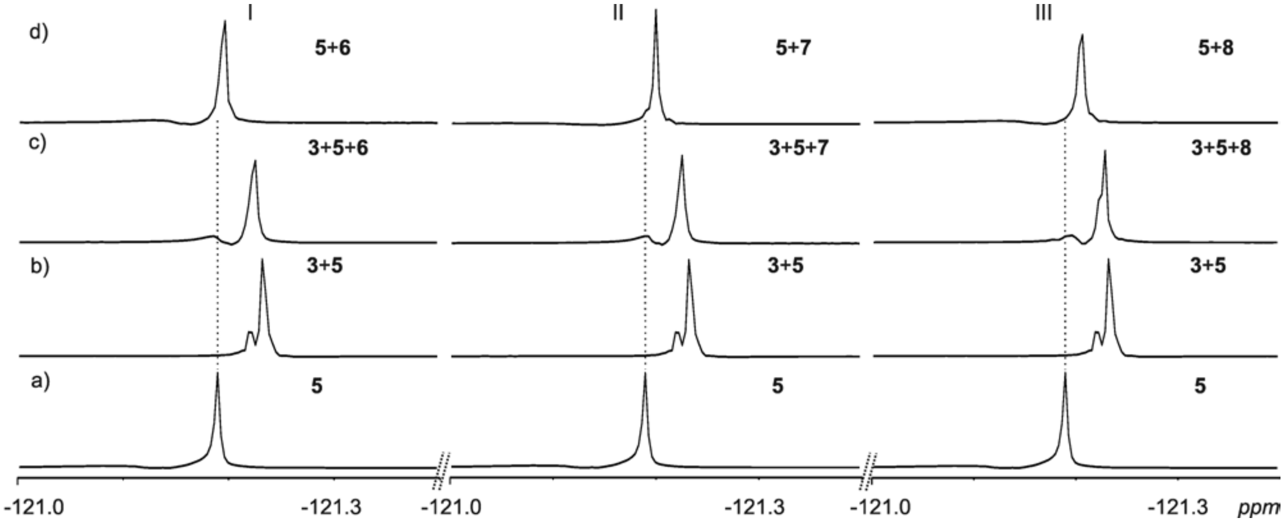

Figure S13. ^{19}F NMR (in $CDCl_3$ at 303 K) of: I: a) **5** (30 mM), b) 1:4 mixture of **3** and **5**, c) 1:4:2 mixture of **3**, **5** and **6**, d) 1:1 mixture of **5** and **6**; II: a) **5** (30 mM), b) 1:4 mixture of **3** and **5**, c) 1:4:2 mixture of **3**, **5** and **7**, d) 1:1 mixture of **5** and **7**; III: a) **5** (30 mM), b) 1:4 mixture of **3** and **5**, c) 1:4:2 mixture of **3**, **5** and **8**, d) 1:1 mixture of **5** and **8**.

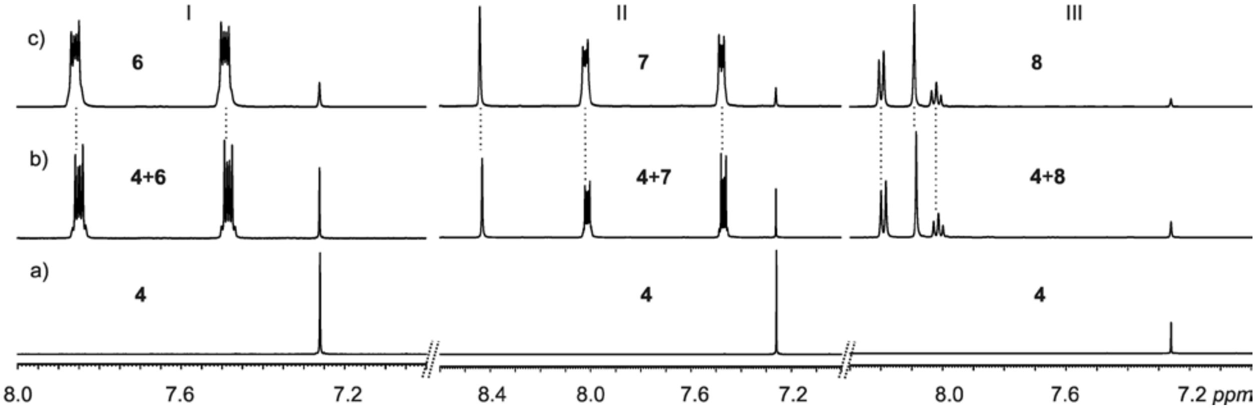

Figure S14. ^{1}H NMR (in $CDCl_3$ at 303 K) of: I: a) **4** (30 mM), b) 1:1 mixture of **4** and **6**, c) **6** (30mM); II: a) **4** (30 mM), b) 1:1 mixture of **4** and **7**, c) **7** (30 mM); III: a) **4** (30mM), b) 1:1 mixture of **4** and **8**, c) **8** (30 mM).

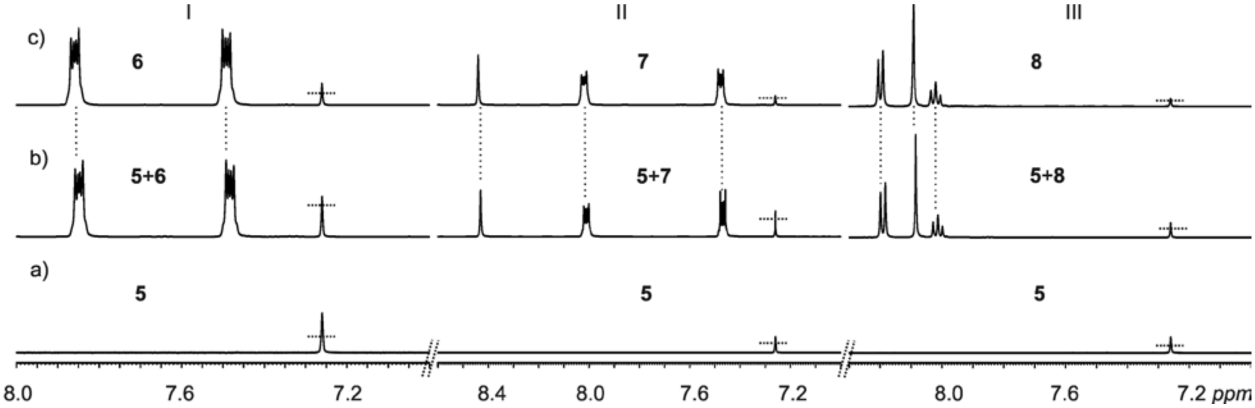

Figure S15. ^{1}H NMR (in $CDCl_3$ at 303 K) of: I: a) **5** (30 mM), b) 1:1 mixture of **5** and **6**, c) **6** (30 mM); II: a) **5** (30 mM), b) 1:1 mixture of **5** and **7**, c) **7** (30 mM); III: a) **5** (30mM), b) 1:1 mixture of **5** and **8**, c) **8** (30 mM).

IV Fluorescence Analyses

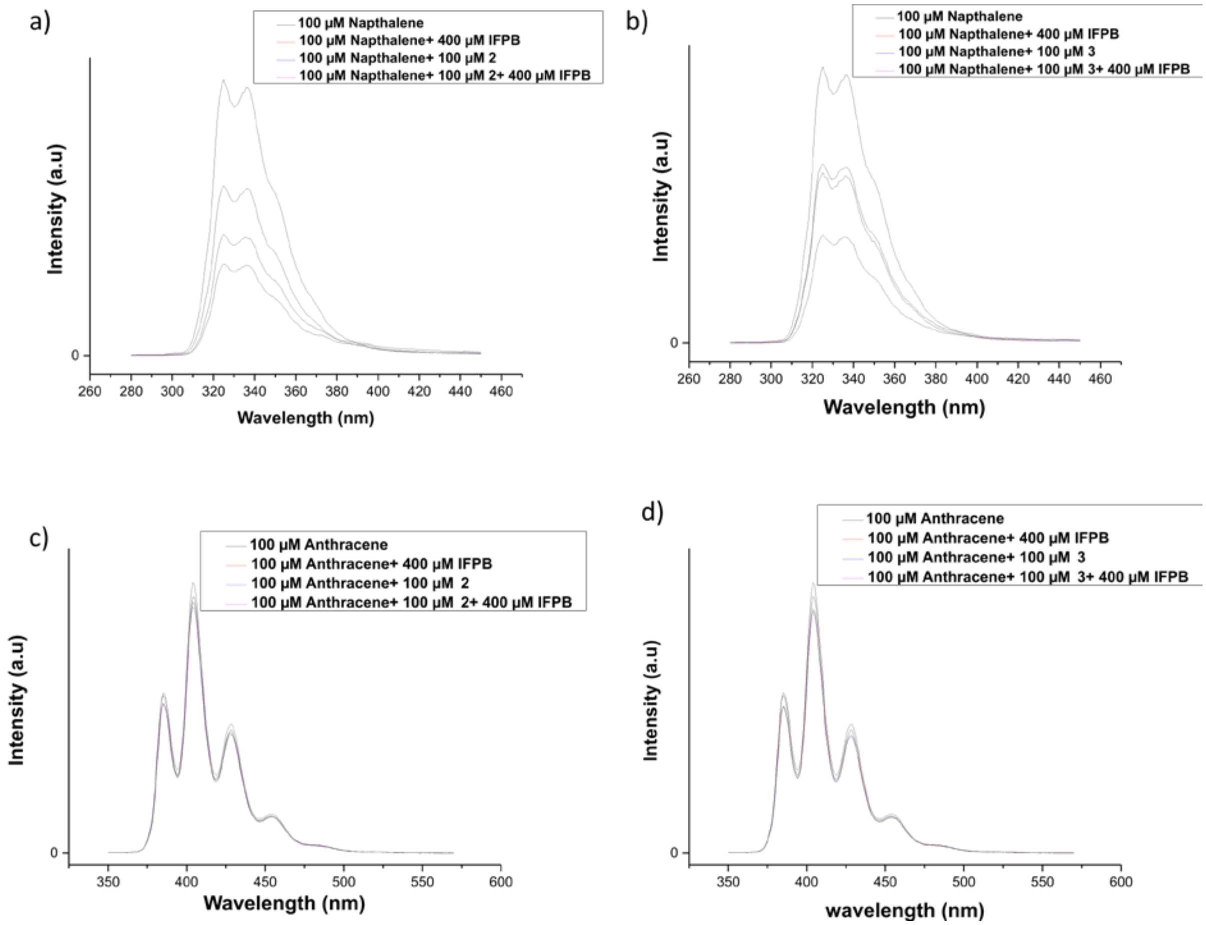

Figure S16. Emission spectra of **6** (100 μM) in presence of **4** (400 μM) and a) **2**(100 μM) & b) **3**(100 μM) in $CHCl_3$. λ_{ext} = 265 nm; Emission spectra of **7** (100 μM) in presence of **4** (400 μM) and a) **2**(100 μM) & b) **3**(100 μM) in $CHCl_3$. λ_{ext} = 330 nm.

Significant quenching is observed in case of naphthalene in presence of **4** even in the absence of **2** or **3.** The quenching could be attributed to donor-acceptor (electron rich naphthalene and electron deficient **4**) interactions but no form of host-guest interaction could be verified based on these results.

IV References

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