Supplementary Information

Crystallographic Observation of 'Induced Fit' in a Cryptophane Host-Guest Model System

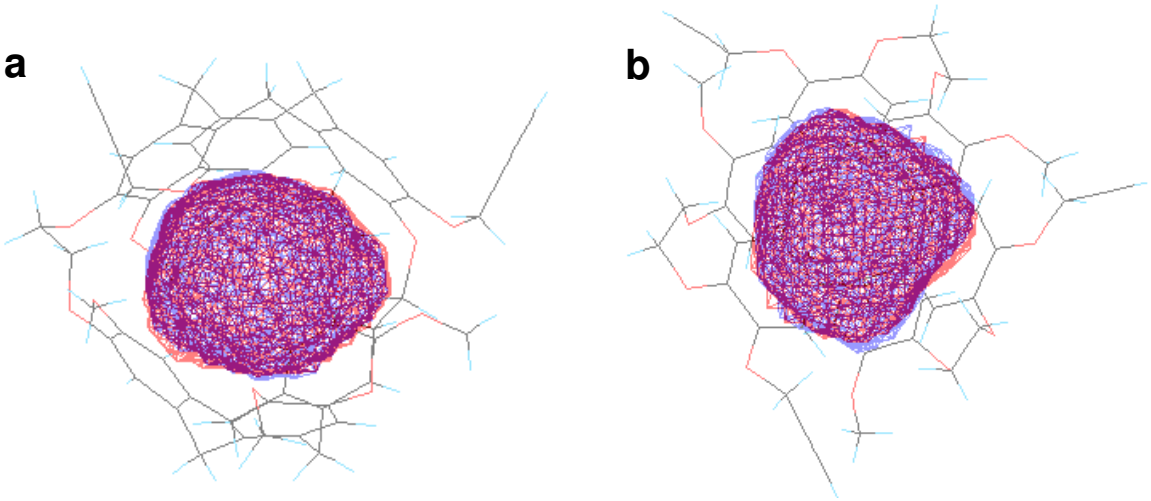
Olena Taratula, P. Aru Hill, Najat S. Khan, Patrick J. Carroll, and Ivan J. Dmochowski[*]

Department of Chemistry, University of Pennsylvania, 231 South 34th St., Philadelphia, PA 19104

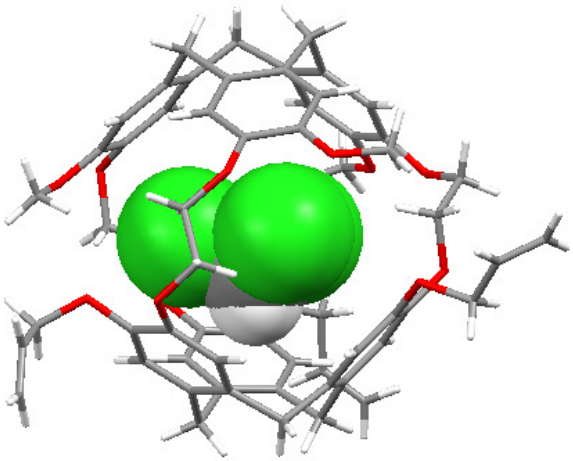
[*]Corresponding author: Dmochowski, Ivan J.

Email: ivandmo@sas.upenn.edu

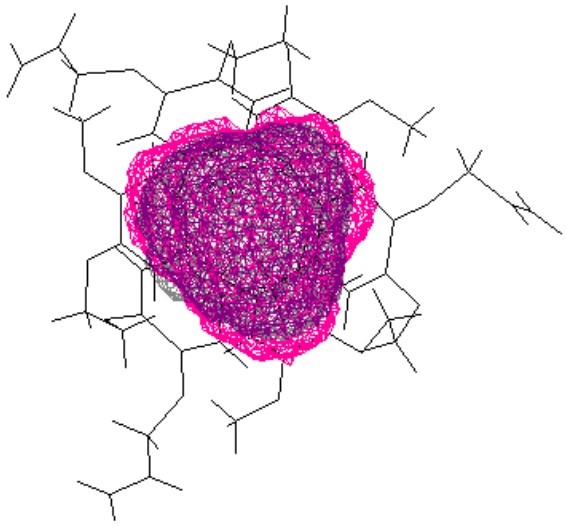
Fax: 215-573-6329



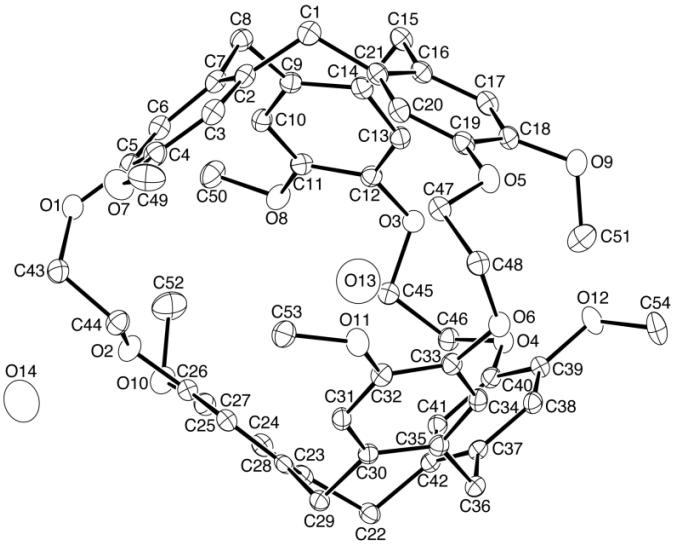
Supplementary Figure S1 | Side (a) and top (b) views of tri-propargyl cryptophane 1. Internal cavities were calculated by Swiss Pdb Viewer for **1** only partially occupied (structure CC-**1**, blue) and with Xe as guest (structure **1**-Xe, red). The two overlaid cavities are virtually indistinguishable.



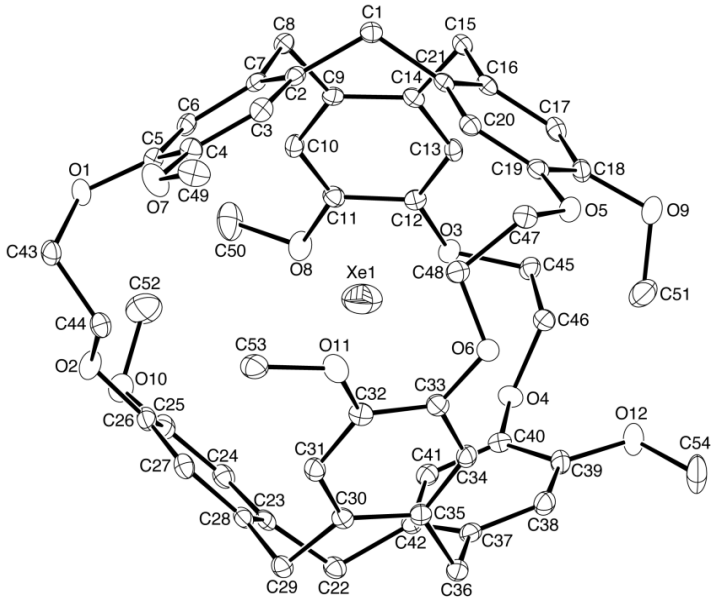
Supplementary Figure S2 | X-ray crystal structure of $CDCl_3$-2 complex in side view.



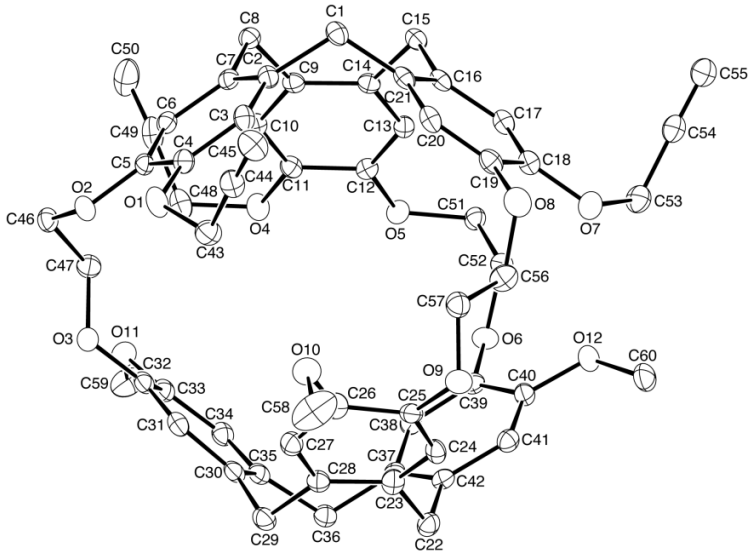
Supplementary Figure S3 | Top view of X-ray crystal structure for tri-allyl cryptophane 2. Internal cavities were calculated by Swiss Pdb Viewer and overlaid for **2** complexed with MeOH (grey) and $CDCl_3$ (pink). The cavity is more compact with MeOH guest.



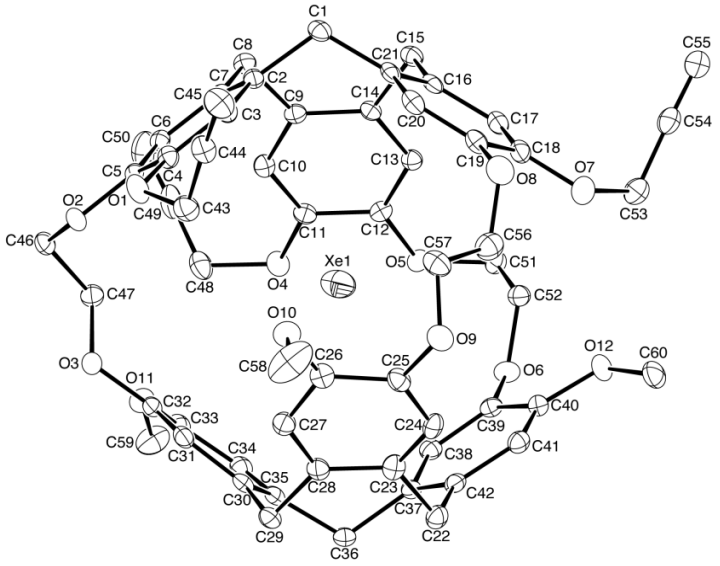
Supplementary Figure S4a | ORTEP representations of cryptophane-A-H_2O complex (CCDC-778896, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity. A model was devised that included what amounts to ¼ of a water molecule outside the cage and seven partially occupied oxygen positions inside the cage.



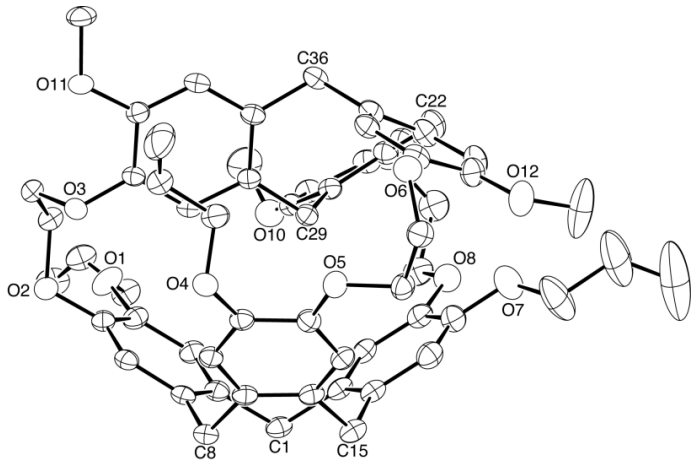
Supplementary Figure S4b | ORTEP representations of cryptophane-A-Xe complex (CCDC-778897, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity.



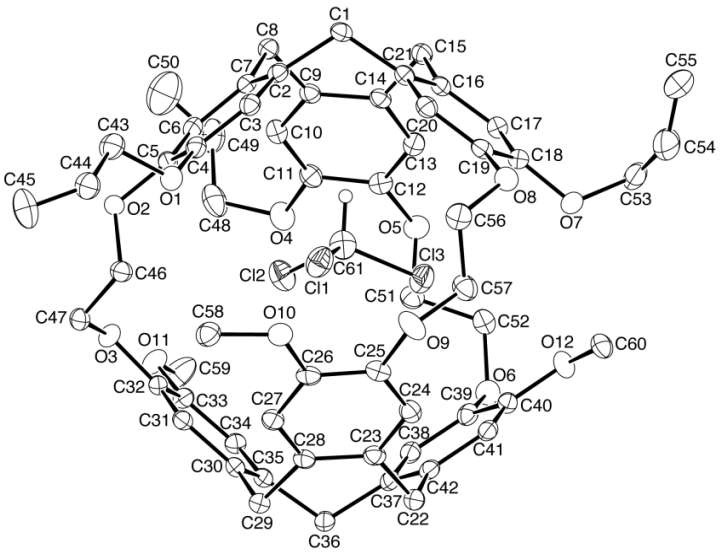
Supplementary Figure S4c | ORTEP representations of only partially occupied tri-propargyl cryptophane 1 (CCDC-778902, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity.



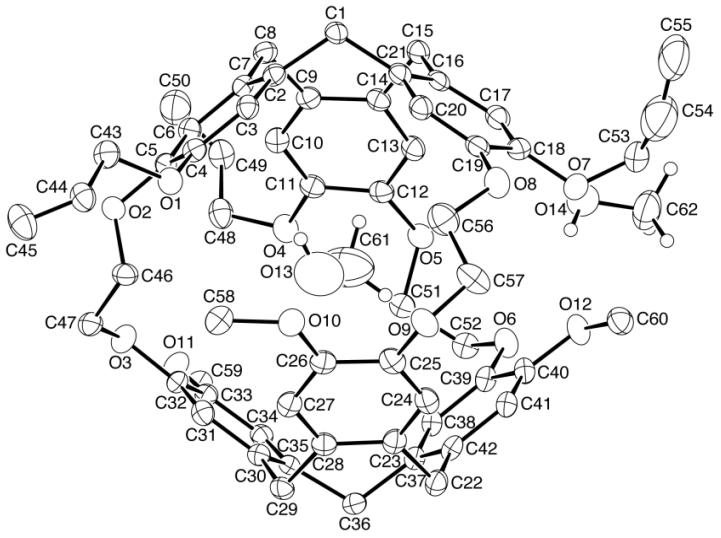
Supplementary Figure S4d | ORTEP representations of tri-propargyl cryptophane 1-Xe complex (CCDC-778903, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity.



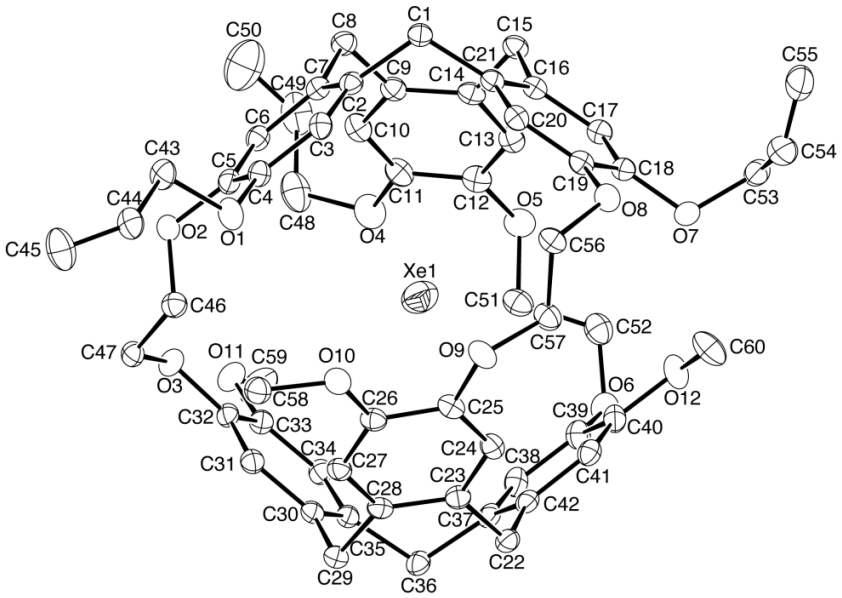
Supplementary Figure S4e | ORTEP representations of collapsed tri-allyl cryptophane 2 (CCDC-778898, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity.



Supplementary Figure S4f | ORTEP representations of tri-allyl cryptophane 2-$CDCl_3$ complex (CCDC-778899, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity. Here only conformer 1 is shown; the other has the same numbering scheme, but with "primes" on the numbers.



Supplementary Figure S4g | ORTEP representations of tri-allyl cryptophane 2-MeOH complex (CCDC-778900, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity.



Supplementary Figure S4h | ORTEP representations of tri-allyl cryptophane 2-Xe complex (CCDC-778901, shown at the 30% probability level). Hydrogen atoms have been omitted for clarity. Here only conformer 1 is shown; the other has the same numbering scheme, but with "primes" on the numbers.

Xe-atom	C-atom	*D*, Å	Xe-atom	C-atom	*D*, Å
Xe1	C24	4.042(2)	Xe1	C34	4.365(2)
Xe1	C23	4.076(2)	Xe1	C10	4.366(2)
Xe1	C5	4.106(2)	Xe1	C40	4.371(2)
Xe1	C41	4.106(2)	Xe1	C37	4.372(2)
Xe1	C42	4.121(2)	Xe1	C17	4.378(2)
Xe1	C14	4.126(2)	Xe1	C21	4.410(2)
Xe1	C7	4.130(2)	Xe1	C11	4.457(3)
Xe1	C32	4.146(2)	Xe1	C26	4.484(2)
Xe1	C31	4.168(2)	Xe1	C27	4.492(2)
Xe1	C13	4.179(2)	Xe1	C38	4.621(2)
Xe1	C9	4.188(2)	Xe1	C39	4.645(2)
Xe1	C25	4.229(2)	Xe1	C18	4.609(2)
Xe1	C2	4.263(2)	Xe1	C19	4.727(2)
Xe1	C30	4.273(2)	Xe1	C20	4.627(2)
Xe1	C16	4.276(2)	Xe1	C46	4.535(2)
Xe1	C33	4.281(2)	Xe1	C47	5.209(2)
Xe1	C28	4.290(2)	Xe1	C51	4.565(3)
Xe1	C4	4.297(2)	Xe1	C52	5.282(3)
Xe1	C3	4.335(2)	Xe1	C56	5.411(2)
Xe1	C12	4.345(2)	Xe1	C57	4.684(3)
Xe1	C35	4.346(2)			

Supplementary Table S1 | Distances (*D*) calculated with ORTEP between Xe atom and nearest carbon atoms for tri-allyl cryptophane 2-Xe complex. See Supplementary Figure S4h for atom labeling. Closest carbon atoms come from the phenyl rings of the CTGs. Calculated Xe-carbon atom distances for the ethylene linkers are reported under dotted line.

2-$CDCl_3$	-**2**-MeOH	*D*, Å	**2**-$CDCl_3$	-**2**-MeOH	*D*, Å
O9	- O9	0.522	C27	- C27	0.166
O8	- O8	0.559	C26	- C26	0.161
O6	- O6	0.89	C25	- C25	0.270
O5	- O5	0.288	C24	- C24	0.251
O3	- O3	0.141	C23	- C23	0.145
O2	- O2	0.136	C22	- C22	0.101
C57	- C57	0.618	C21	- C21	0.202
C56	- C56	0.647	C20	- C20	0.313
C52	- C52	1.056	C19	- C19	0.339
C51	- C51	0.583	C18	- C18	0.232
C47	- C47	0.141	C17	- C17	0.167
C46	- C46	0.117	C16	- C16	0.158
C42	- C42	0.22	C15	- C15	0.130
C41	- C41	0.289	C14	- C14	0.106
C40	- C40	0.426	C13	- C13	0.189
C39	- C39	0.544	C12	- C12	0.240
C38	- C38	0.454	C11	- C11	0.204
C37	- C37	0.293	C10	- C10	0.125
C36	- C36	0.263	C9	- C9	0.075
C35	- C35	0.236	C8	- C8	0.031
C34	- C34	0.220	C7	- C7	0.040
C33	- C33	0.197	C6	- C6	0.092
C32	- C32	0.182	C5	- C5	0.082
C31	- C31	0.193	C4	- C4	0.056
C30	- C30	0.219	C3	- C3	0.105
C29	- C29	0.197	C2	- C2	0.089
C28	- C28	0.141	C1	- C1	0.156

Supplementary Table S2 | Distances (*D*) between matched atoms generated with CrystMol 2.1 for 2-$CDCl_3$ complex superimposed with 2-MeOH complex. See Supplementary Figures S4f and S4g for atom labeling.

Compound	CCDC-778896 (Crypt.-A + H_2O),	CCDC-778897 (Crypt.-A + Xe),
Empirical formula	$C_{54}H_{54}O_{13.25}$	$C_{54}H_{54}O_{12}Xe$
Formula weight	914.97	1026.27
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Cell constants:		
a	22.2761(15) Å	22.0490(9)Å
b	11.2688(6) Å	11.4109(5)Å
c	20.5348(14) Å	20.7802(9)Å
α	90.000	90.000
β	113.8120(10)°	117.599(2)°
γ	90.000	90.000
Volume	4715.9(5) $Å^3$	4633.4(3)$Å^3$
Z	4	4
Density (calculated)	1.292 g/cm^3	1.471 g/cm^3
Absorption coefficient	0.92 cm^{-1}	8.10 cm^{-1}
F(000)	1946	2112
Crystal size	0.42 x 0.22 x 0.08 mm^3	0.28 x 0.20 x 0.05 mm^3
Theta range for data collection	2.51 to 25.03°	5.12 to 50.1°
Index ranges	$-26 \le h \le 24$, $-13 \le k \le 13$, $-24 \le l \le 24$	$-26 \le h \le 26$; $-13 \le k \le 13$; $-24 \le l \le 24$
Reflections collected	35655	36314
Independent reflections	8293 [R(int) = 0.0252]	8203 [R(int)=0.0306]
Completeness to maximum theta	99.5%	99.8%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8747	1.0000 and 0.9181
Data / restraints / parameters	8293 / 0 / 640	8203 / 0 / 611
Goodness-of-fit on F2	1.067	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1218	R_1=0.0410, wR_2=0.0804
R indices (all data)	R1 = 0.0571, wR2 = 0.1302	R_1=0.0581, wR_2=0.0888
Extinction coefficient	0.0028(4)	not refined
Largest diff. peak and hole	0.403 and -0.269 e/$Å^3$	0.805 and -1.183 e/$Å^3$

Supplementary Table S3 | Summary of structure determination data for CCDC-778896 and 778897.

Compound	CCDC-778902 (**1** partial fill)	CCDC-778903 (**1** + Xe)	CCDC-778898 (**2** collapsed)
Empirical formula	$C_{60}H_{54}O_{12}$	$C_{60}H_{54}O_{12}Xe$	$C_{60}H_{60}O_{12}$
Formula weight	967.03	1098.33	973.08
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Cell constants:			
a	11.8090(13) Å	11.8046(10) Å	15.917(2)Å
b	12.9971(15) Å	12.9936(11) Å	12.4013(11)Å
c	17.8807(19) Å	17.8574(15) Å	28.262(3)Å
α	89.531(4)°	89.704(3)°	90.000
β	89.764(4)°	89.716(3)°	105.389(3)°
γ	88.396(3)°	88.259(3)°	90.000
Volume	2743.2(5) $Å^3$	2737.7(4) $Å^3$	5378.8(9)$Å^3$
Z	2	2	4
Density (calculated)	1.171 g/cm^3	1.332 g/cm^3	1.202 g/cm^3
Absorption coefficient	0.81 cm^{-1}	6.91 cm^{-1}	0.83 cm^{-1}
F(000)	1020	1128	2064
Crystal size	0.28 x 0.18 x 0.15 mm^3	0.46 x 0.10 x 0.08 mm^3	0.38 x 0.20 x 0.15 mm^3
Theta range for data collection	2.56 to 25.02°	2.56 to 25.01°.	5.3 to 50.02°
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-19 \le l \le 21$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-21 \le l \le 20$	$-18 \le h \le 15$; $-12 \le k \le 14$; $-33 \le l \le 32$
Reflections collected	42110	40228	21843
Independent reflections	9641 [R(int) = 0.0248]	9620 [R(int) = 0.0264]	9274 [R(int)=0.0272]
Completeness to maximum theta	99.5%	99.7%	99.3%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	none
Max. and min. transmission	1.0000 and 0.9235	1.0000 and 0.8559	
Data / restraints / parameters	9641 / 14 / 698	9620 / 14 / 707	9274 / 0 / 690
Goodness-of-fit on F2	1.063	1.064	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0527, wR2 = 0.1531	R1 = 0.0462, wR2 = 0.1273	R_1=0.0698, wR_2=0.1991
R indices (all data)	R1 = 0.0597, wR2 = 0.1604	R1 = 0.0546, wR2 = 0.1350	R_1=0.0841, wR_2=0.2171
Extinction coefficient	not refined	not refined	not refined
Largest diff. peak and hole	0.265 and -0.253 e/$Å^3$	0.587 and -0.933 e/$Å^3$	463 and -0.372 e/$Å^3$

Supplementary Table S4 | Summary of structure determination data for CCDC-778898, -778902, -778903.

Compound	CCDC-778899 (**2** + $CDCl_3$)	CCDC-778900 (**2** + MeOH)	CCDC-778901 (**2** + Xe)
Empirical formula	$C_{61}H_{61}O_{12}Cl_3$	$C_{61.5}H_{66}O_{13.5}$	$C_{60}H_{60}O_{12}Xe$
Formula weight	1092.45	1021.14	1104.38
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Cell constants:			
a	21.822(2)Å	21.374(4)Å	21.594(2)Å
b	12.3143(11)Å	11.973(2)Å	12.2085(11)Å
c	39.621(4)Å	22.305(4)Å	39.916(4)Å
α	90.000	90.000	90.000
β	97.3610(10)°	111.010(4)°	97.674(2)°
γ	90.000	90.000	90.000
Volume	10560(2)$Å^3$	5329(2)$Å^3$	10429(2)$Å^3$
Z	8	2	8
Density (calculated)	1.374 g/cm^3	1.273 g/cm^3	1.407 g/cm^3
Absorption coefficient	2.40 cm^{-1}	0.89 cm^{-1}	7.25 cm^{-1}
F(000)	4592	2172	4560
Crystal size	0.32 x 0.25 x 0.25 mm^3	0.32 x 0.12 x 0.10 mm^3	0.38 x 0.35 x 0.30 mm^3
Theta range for data collection	5.02 to 50.04°	5.02 to 50.04°	5.06 to 54.92°
Index ranges	$-25 \le h \le 25$; $-14 \le k \le 10$; $-47 \le l \le 40$	$-24 \le h \le 25$; $-14 \le k \le 9$; $-21 \le l \le 26$	$-28 \le h \le 28$; $-14 \le k \le 15$; $-31 \le l \le 51$
Reflections collected	58766	27444	67636
Independent reflections	18536 [R(int)=0.0353]	9345 [R(int)=0.0455]	23575 [R(int)=0.0423]
Completeness to maximum theta	99.4%	99.4%	98.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7802	1.0000 and 0.7115	1.0000 and 0.7304
No. parameters	1385	688	1394
Goodness-of-fit on F2	1.061	1.048	1.036
Final R indices [I>2sigma(I)]	R_1=0.0634, wR_2=0.1661	R_1=0.0871, wR_2=0.2323	R_1=0.0574, wR_2=0.1583
R indices (all data)	R_1=0.0820, wR_2=0.1835	R_1=0.1308, wR_2=0.2902	R_1=0.0725, wR_2=0.1715
Extinction coefficient	not refined	not refined	not refined
Largest diff. peak and hole	+1.268 and -0.554 e/$Å^3$	+0.688 and -0.428 e/$Å^3$	+0.610 and -1.500 e/$Å^3$

Supplementary Table S5 | Summary of structure determination data for CCDC-778899-778901.