Structural diversity of anthraquinone substituted *p-tert*-butylthiacalix[4]arene in the *partial cone* conformation upon external stimuli

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Supplementary Data

Table S1 Dihedral angles between the plane passing through four S atoms and the phenyl rings forming the macrocycle.

Crystal Structure	C5 (°)	C31 (°)	C57 (°)	C83 (°)
PC1a	33	89	85	90
PC1b	31	86	84	88
PC1c	60	83	87	83
PC1d	62	88	85	89

Table S2 Intramolecular interactions present in **PC1a** and **PC1b**.

PC1a				PC1b			
D-H···A	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**	**D-H···A**	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**
N1-H1···O3	2.00	2.649(3)	130	N1-H1···O3	2.02	2.650(3)	132
N2-H2···O7	1.98	2.635(2)	137	N2-H2···O7	1.94	2.631(2)	140
N3-H3···O11	1.91	2.610(3)	141	N3-H3···O11	1.92	2.611(2)	140
N4-H4···O15	1.87	2.618(2)	139	N4-H4···O15	1.94	2.620(2)	139
C40-H40···O6	2.22	2.820(3)	120	C40-H40···O6	2.24	2.835(3)	120
C92-H92···O14	2.20	2.821(3)	122	C92-H92···O14	2.20	2.832(3)	123
C66-H66···O10	2.25	2.859(3)	122	C66-H66···O10	2.24	2.856(3)	122
C11-H11A···O7	2.49	3.053(3)	116	C11-H11A···O7	2.41	3.030(3)	120
C79-H79C···O10	2.39	3.256(9)	148	C79-H79B···O10	2.43	3.271(3)	144
N1-H1···O14	2.80	3.260(3)	114	N1-H1···O14	2.80	3.277(3)	119
C11-H11A···O5	2.70	3.279(3)	118	C11-H11A···O5	2.66	3.264(2)	120
C58-H58···O14	2.61	3.292(3)	129	C58-H58···O14	2.58	3.262(3)	129
C11-H11A···S1	2.69	3.342(2)	124	C11-H11A···S1	2.68	3.330(2)	124
C55-H55A···O14	2.52	3.355(3)	144	C55-H55B....O3	2.77	3.566(3)	139
C53-H53C···O3	2.55	3.362(3)	140	C53-H53B···O3	2.58	3.438(3)	147
C89-H89B···S4	2.81	3.395(2)	118	C89-H89B···S4	2.79	3.382(2)	119
C37-H37B···S2	2.90	3.398(2)	112	C37-H37B···S2	2.89	3.405(2)	113
C29-H29C···O10	2.94	3.431(6)	112	C29-H29B···O10	2.86	3.409(4)	116
C84-H84···O10	2.75	3.447(3)	131	C84-H84···O10	2.80	3.497(3)	131
C63-H63A···S3	3.00	3.505(2)	113	C63-H63A···S3	3.02	3.516(2)	112
C55-H55A···O3	2.73	3.522(3)	138	C55-H55B···O14	2.57	3.399(3)	143
C63-H63B···S2	3.01	3.522(3)	113	C63-H63B···S2	3.01	3.519(2)	113
C52-H52···O2	2.90	3.772(3)	153	C52-H52···O2	2.81	3.643(3)	146
C79A-H79E···O10	2.42	3.39(2)	173	C14-H14···O2	2.35	2.829(3)	110

Table S3 Selected π···π interactions present in **PC1a** and **PC1b**.

PC1a		PC1b	
D-H···A	**H-A (Å)**	**D-H···A**	**H-A (Å)**
Cg11···Cg14^{i}	3.4301(13)	Cg11···Cg14^{i}	3.4579(1)
Cg3···Cg8	3.4577(14)	Cg3···Cg8	3.4364(1)
Cg3···Cg14	3.5418(13)	Cg3···Cg14	3.6410(1)
Cg12···Cg15^{i}	3.5496(14)	Cg12···Cg15^{i}	3.5749(1)

Cg is the centroid of the aromatic rings: Cg11 (C69-C74), Cg3 (C17-C22), Cg14 (C91-C96), Cg12 (C72-C78), Cg8 (C46-C52), Cg15 (C95-C100); symmetry code: (i) 1-x,1-y,1-z.

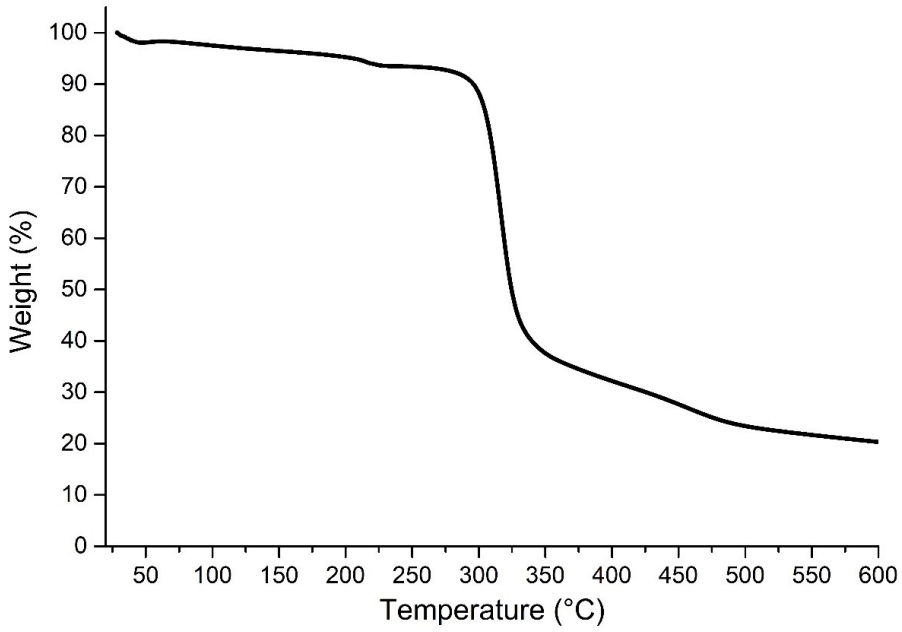

Figure S1 Thermogram of **PC1a**.

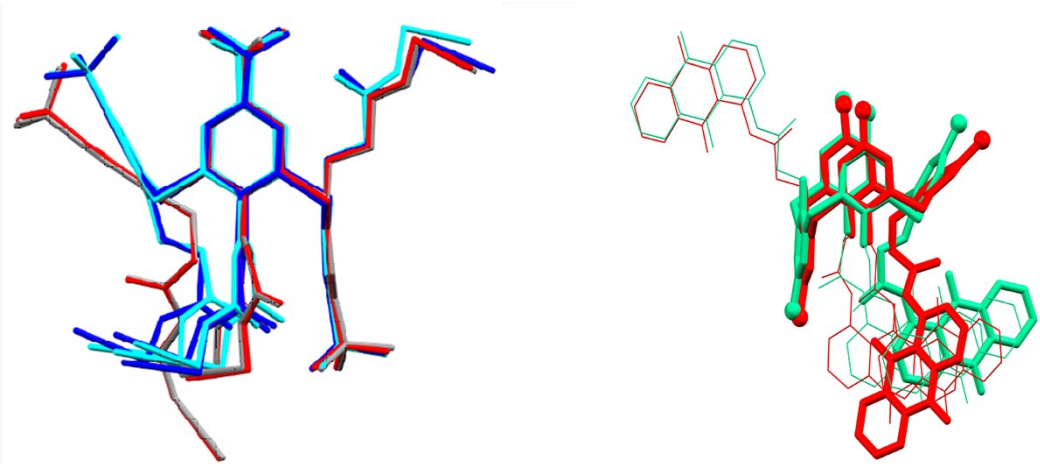

Figure S2 On the left: overlay of calixarene molecules (**PC1a** – red, **PC1b** – grey, **PC1c** – blue, **PC1d** – cyan), indicating the differences in dihedral angles between the plane passing through four S atoms and the phenyl rings, as well as in the orientation of the bulky anthraquinone substituents. Hydrogen atoms and disorder have been omitted, and the anthraquinone moiety has been simplified, for clarity. On the right: overlay of **PC1a** with **PC1c**, indicating more clearly the changes in the molecular structures of the host molecules.

Table S4 Intramolecular interactions present in **PC1c** and **PC1d**.

PC1c				PC1d			
D-H···A	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**	**D-H···A**	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**
N1-H1···O3	1.85	2.58(1)	139	N1-H1···O3	1.95	2.652(4)	136
N2-H2···O7	1.97	2.63(1)	130	N2-H2···O7	1.89	2.608(4)	138
N3-H3···O11	2.06	2.73(1)	133	N3-H3···O11	1.92	2.639(4)	138
N4-H4···O15	1.95	2.64(1)	133	N4-H4···O15	1.96	2.650(4)	135
C14-H14···O2	2.25	2.89(1)	124	C14-H14···O2	2.13	2.784(4)	125
C92-H92···O14	2.15	2.77(1)	122	C92-H92···O14	2.22	2.847(4)	123
C40-H40···O6	2.25	2.84(1)	119	C66-H66···O10	2.19	2.827(4)	124
C66-H66···O10	2.31	2.98(1)	128	C62-H62···O6	2.83	3.529(4)	131
C11-H11B···O13	2.18	3.13(1)	161	C11-H11B···O13	2.23	3.186(4)	163
C11-H11A···O5	2.32	3.17(1)	143	C11-H11A···O5	2.41	3.170(4)	133
C53-H53C···O2	2.4	3.29(1)	150	C53-H53A···O6	2.52	3.234(4)	129
C81-H81C···O10	2.41	3.30(1)	149	C36-H36···O10	2.44	3.208(5)	138
C11-H11B···S4	2.71	3.367(8)	124	C11-H11B···S4	2.75	3.384(4)	123
C63-H63A···S3	2.97	3.485(9)	113	C63-H63A···S3	2.91	3.463(3)	116
C55-H55A···O2	2.76	3.54(1)	136	C40-H40···O6	2.26	2.876(4)	122
C55-H55A···O14	2.85	3.55(1)	129	C54-H54A···O2	2.38	3.221(4)	143
C53-H53A···O6	2.91	3.56(1)	125	C53-H53A···O2	2.74	3.478(5)	132
C29-H29C···O10	2.86	3.59(1)	132	C37-H37A···S1	2.81	3.398(4)	119
C62-H62···O6	2.85	3.71(1)	150	C40-H40···O6	2.26	2.876(4)	122
C79-H79A···O10	2.95	3.74(1)	138	C79-H79C···O10	2.85	3.439(7)	119
C84-H84···O10	3.15	3.79(1)	126	C89-H89A···S3	2.79	3.375(3)	118

Table S5 Intermolecular interactions present in **PC1c** and **PC1d**.

PC1c				PC1d			
D-H···A	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**	**D-H···A**	**H-A (Å)**	**D-A (Å)**	**D-H···A (°)**
C3-H3B···O12	2.48	3.412(9)	158	C42-H42···O8^{i}	2.65	3.163(4)	115

C54-H54A···O14^{i}	2.57	3.48(1)	154	C94-H94···O16^{ii}	2.73	3.199(5)	111
C15-H15···O8^{ii}	2.63	3.49(1)	151	C68-H68···O4^{iii}	2.6	3.280(4)	129
C75-H75···O10^{iii}	2.96	3.50(1)	118	C51-H51···O3^{iv}	2.77	3.351(6)	120
C80-H80A···O16^{iv}	2.58	3.51(1)	159	C89-H89B···O11^{v}	2.73	3.356(4)	122
C55-H55C···O14^{i}	2.6	3.52(1)	156	C50-H50B···Cg1^{iv}	2.53	3.3548(1)	145
C29-H29A···O6^{v}	2.62	3.54(1)	158	C16-H16···O12	2.62	3.384(4)	137
C89-H89B···O15^{iv}	2.61	3.57(1)	164	C28-H28A···O6^{vi}	2.6	3.405(6)	140
C77-H77···O16^{i}	2.93	3.63(1)	131	C41-H41···O12	2.78	3.465(4)	130
C103-H103···O4^{vi}	2.89	3.70(1)	145	C1-H1B···O12	2.82	3.668(4)	145
C79-H79C···O16^{iv}	2.96	3.81(1)	145	C24-H24···S1^{iv}	2.98	3.734(4)	138
C24-H24···O16^{vi}	2.95	3.82(1)	154	C79-H79B···O14^{v}	2.87	3.802(7)	159
C27-H27C···S1^{vii}	2.94	3.87(1)	160	C37-H37B···S2^{vi}	2.99	3.828(3)	142
C37-H37B···S2^{v}	2.94	3.915(9)	168	C80-H80B···O14	3.00	3.866(6)	148
				C89-H89A···S3^{v}	2.96	3.918(4)	163
				C125-H125···O4	2.56	3.18(2)	123
				C111-H111···O11^{vii}	2.67	3.266(6)	122
				C63-H63B···Cg2	2.66	3.4274(1)	135
				C110-H110···O7^{vi}	2.74	3.461(6)	133
				C107-H107···Cg3	2.94	3.4650(1)	118
				C114-H114···O4^{iii}	2.67	3.54(1)	152
				C80-H80···Cg4	2.94	3.9131(1)	171

Cg is the centroid of the aromatic ring: Cg1 (C5-C10) C48, Cg2 (C106-C111), Cg3 (C57-C62), Cg4 (C113-C118); symmetry codes: **(PC1c)** (i) 1-x,1-y,-z, (ii) 1-x,1-y,-1-z, (iii) 1-x,-y,1-z, (iv) -x,1-y,-z, (v) 1-x,-y,-z, (vi) -x,1-y,-1-z, (vii) -x,-y,-z; **(PC1d)** (i) -x,1-y,-z, (ii) -x,-y,-z, (iii) -1+x,y,-1+z, (iv) 1-x,1-y,-z, (v) 1-x,-y,1-z, (vi) 1-x,1-y,1-z, (vii) 1+x,y,1+z.

Table S6 Selected π···π interactions present in **PC1c** and **PC1d**.

PC1c		**PC1d**	
Cg···Cg	**Cg···Cg (Å)**	**Cg···Cg**	**Cg···Cg (Å)**
Cg6···Cg12^{i}	3.4916(4)	Cg8···Cg11^{i}	3.4727(1)
Cg2···Cg15	3.4942(4)	Cg4···Cg7	3.5398(1)
Cg2···Cg7	3.5244(4)	Cg3···Cg6	3.5640(1)
Cg3···Cg16	3.5515(4)	Cg12···Cg15^{ii}	3.5892(1)
Cg11···Cg11^{ii}	3.6390(4)	Cg7···Cg10^{i}	3.6160(1)
Cg12···Cg10^{ii}	3.6411(4)	Cg2···Cg15	3.6519(1)
Cg2···Cg6	3.6427(4)	Cg11···Cg14^{ii}	3.6644(1)
Cg7···Cg11^{i}	3.6482(4)		
Cg10···Cg11^{ii}	3.6664(4)		
Cg7···Cg3	3.6915(4)		

Cg is the centroid of the aromatic ring: (**PC1c**) Cg2 (C13-C18), Cg3 (C17-C22), Cg6 (C39-C44), Cg7 (C43-C48), Cg10 (C65-C70), Cg11 (C69-C74), Cg12 (C72-C78), Cg15 (C95-C100), Cg16 (C98-C101); (**PC1d**) Cg2 (C13-C18), Cg3 (C17-C22), Cg4 (C20-C26), Cg6 (C39-C44), Cg7 (C43-C48), Cg8 (C46-C52), Cg10 (C65-C70), Cg11 (C69-C74), Cg12 (C72-C78), Cg14 (C91-C96), Cg15 (C95-C100); symmetry codes: (**PC1c**) (i) x,y,1+z, (ii) 1-x,2-y,-1-z; (**PC1d**) (i) 1-x,1-y,1-z, (ii) 1-x,-y,1-z.

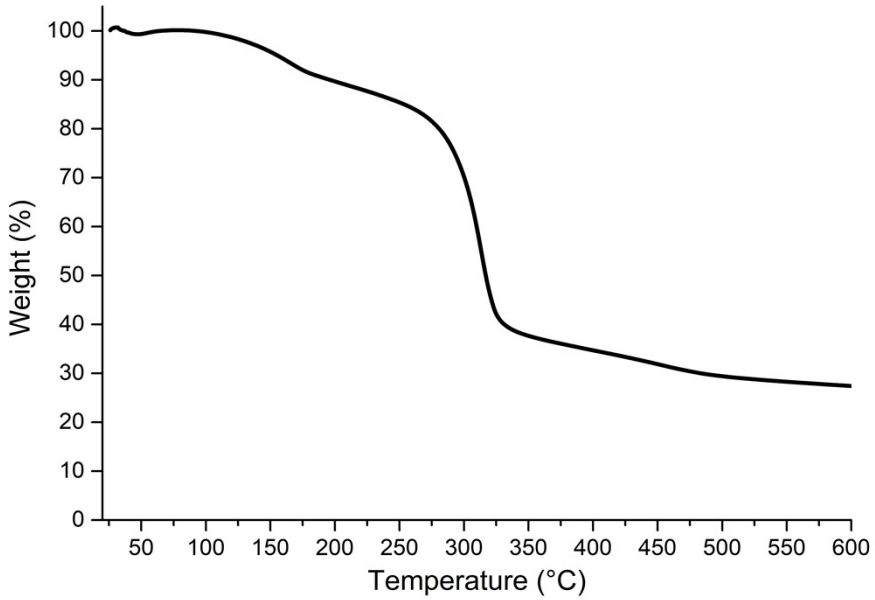

Figure S3 Thermogram of **PC1d**.