Supplementary Information

Solvatomorphs of 25,26,27,28- tetrahydroxycalix[4]arene and 5,11,17,23-tetramino-25,26,27,28-tetrabutoxycalix[4]arene: quenching photoluminescence through switching the guest

Felipe Terra Martins,[a,b,] Lauro June Queiroz Maia,[c] Leonardo da Silva Neto,[b] Cleiton Moreira da Silva,[b] Ariel M. Sarotti,[d] and Ângelo de Fátima[b,]**

[a]*Instituto de Química, Universidade Federal de Goiás, Campus Samambaia, Goiânia, GO, PO Box 131, 74690-900, Brazil*

[b]*Grupo de Estudos em Química Orgânica e Biológica (GEQOB), Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Pres. Antônio Carlos, 6627, Belo Horizonte, MG, 31270-901, Brazil.*

[c]*Instituto de Física, Universidade Federal de Goiás, Campus Samambaia, Goiânia, GO, PO Box 131, 74690-900, Brazil*

[d]*Instituto de Química Rosario (IQUIR), Universidad Nacional de Rosario– CONICET, Suipacha 531, S2002LRK Rosario, Argentina.*

* To whom correspondence should be addressed.

FTM (E-mail: felipe@ufg.br; Phone: +55 62 3521 1097; Fax: +55 62 3521 1167)

AF (E-mail: adefatima@qui.ufmg.br; Phone: +55 31 3409 6373; Fax: +55 31 3409 5700)

Table S1. Crystal data and refinement statistics of the calixarene solvatomorphs disclosed here.

		1a	**1b**	**2a**[i]	**2b**
structural formula		$(C_{44}H_{60}N_4O_4)(H_2O)_2$	$(C_{44}H_{60}N_4O_4)\ (C_2H_6OS)\ (H_2O)_2$	$(C_{28}H_{24}O_4)_3(CH_4O)_4\ (H_2O)$	$(C_{28}H_{24}O_4)(C_2H_6OS)_2$
fw		744.99	823.12	1419.60	580.73
cryst syst		triclinic	monoclinic	monoclinic	triclinic
space group		*P*-1	*Cc*	*C*2/*m*	*P*-1
Z		2	8	4	6
T (K)		296(2)	296(2)	296(2)	296(2)
unit cell dimensions	*a* (Å)	10.0009(5)	47.845(9)	18.5360(13)	17.286(3)
	b (Å)	10.7218(5)	10.2532(12)	33.680(3)	18.154(3)
	c (Å)	21.5824(11)	19.755(4)	16.0933(11)	18.412(3)
	α (°)	81.629(3)	90	90	114.488(9)
	β (°)	81.306(3)	102.025(11)	113.747(4)	93.801(9)
	γ (°)	73.137(3)	90	90	116.859(9)
V (Å^3)		2176.58(19)	9479(3)	9196.3(12)	4456.4(14)
calculated density (Mg/m^3)		1.137	1.154	1.025	1.298
absorption coefficient (mm^{-1})		0.075	0.119	0.070	0.222
Absorption correction		Multi-scan	Multi-scan	Multi-scan	Multi-scan
		T_{min} / T_{max} = 0.941	T_{min} / T_{max} = 0.912	T_{min} / T_{max} = 0.988	T_{min} / T_{max} = 0.915
θ range for data collection (°)		1.920 – 25.376	1.741 – 25.444	1.543 – 25.416	1.390 – 25.037
index ranges		-11 to 11	-56 to 57	-22 to 22	-20 to 20
		-12 to 12	-12 to 12	-40 to 40	-21 to 20
		-25 to 25	-20 to 23	-16 to 19	-21 to 20
data collected		23,426	34,920	49,580	39,564
unique reflections		7,729	15,095	8,509	15,426
unique reflections with $I > 2\sigma(I)$		4,259	6,709	3,701	4,904
symmetry factor (R_{int})		0.0380	0.0560	0.0388	0.0988
completeness to $\theta_{max.}$		97.1	97.4	98.4	97.8
F (000)		808	3568	3016	1848
parameters refined		533	1,033	488	1081
goodness-of-fit on F^2		1.037	0.971	1.485	1.114
final R_1 factor for $I > 2\sigma(I)$		0.0704	0.0795	0.1648	0.1415
wR2 factor for all data		0.2377	0.2472	0.4633	0.4586
largest diff. peak / hole (*e*/Å^3)		0.323/-0.235	0.230/-0.270	1.273/-0.318	0.800/-0.745
CCDC deposit number		1511506	1511507	1511509	1511508

[i] Even though the data have been squeezed with PLATON (A. L. Spek, *J. Appl. Crystallogr.,* 2003, **36**, 7), the electron count removed from structure factors was not assigned to solvent molecules (most probably methanol and water) because of uncertainty in their proportion and missing strong reflections even at low resolution shell.

Table S2. Metrics for the main intermolecular contacts found in crystal forms of compound **1**.

Crystal Form	D-H…A	D-H[i]/ Å	H...A/ Å	D...A/ Å	D-H…A/°
1a	O1W-H1W...O2W	0.99	1.80	2.697(11)	148
	O2W-H3W...O2W	0.85	2.45	2.778(8)	104
	N4-H4B...N3	0.86	2.33	3.181(5)	170
	O2W-H4W...N2	0.85	2.40	3.192(7)	156
	N1-H1D...N4	0.86	2.83	3.611(4)	152
	N1-H1C...O1W'	0.86	2.19	2.955(13)	148
	O1W-H2W...Cg(B)	0.99	2.47	3.424(8)	160
	O1W'-H1W'...Cg(C)	0.99	2.27	3.255(11)	170
	O1W'-H2W'...Cg(A)	0.99	2.45	3.348(13)	151
	N2-H2d...Cg(D)	0.86	2.98	3.679(4)	140
1b	N2A-H2A1...O4W	0.86	1.65	2.41(4)	147
	O1W-H1W...N3B	0.99	2.16	3.11(4)	163
	N2A-H2A2...O1W	0.86	2.50	3.17(4)	136
	N2A-H2A2...O2W	0.86	2.33	3.17(2)	165
	O1W-H2W...O2W	0.98	1.77	2.23(4)	104
	O1W-H2W...N4B	0.98	2.33	3.17(4)	143
	O2W-H3W…N4B	1.02	2.48	3.16(2)	124
	O2W-H4W...O1SA	0.99	2.08	2.93(2)	141
	N3B-H3B1...O1SA	0.86	2.23	3.057(15)	161
	O3W-H5W...O1SB	1.00	2.04	2.94(2)	148
	N3B-H3B2...N2A	0.86	2.41	3.255(13)	170
	O3W-H6W...O4W	0.99	1.80	2.46(6)	121
	O4W-H7W...N1A	0.99	2.05	2.96(6)	151
	O4W-H8W…O3W	1.00	1.91	2.46(6)	112
	O4W-H8W...N4A	1.00	2.52	3.36(5)	142
	N2B -H2B1...O3W	0.86	2.32	3.15(2)	162
	N2B-H2B1...O4W	0.86	2.48	3.11(4)	131
	N2B-H2B2...O1W	0.86	1.73	2.44(4)	139
	N1B-H1B1...O1SA	0.86	2.22	3.079(14)	176
	N3A-H3A1...O1SB	0.86	2.25	3.11(2)	178
	N1A-H1A1...O1SB	0.86	2.23	3.063(15)	162
	N1A-H1A2...N2B	0.86	2.41	3.26(2)	170
	N1A-H1A2...O4W	0.86	2.58	2.96(2)	108
	C1SA-H1S1...Cg(A)A[ii]	0.96	2.76	3.617(13)	150
	C1SA-H1S3...Cg(B)A	0.96	2.93	3.506(12)	120
	C1SA-H1S2...Cg(C)A	0.96	2.74	3.628(14)	154
	C2SA-H2S4...Cg(D)A	0.96	2.87	3.527(15)	127
	C1SB-H1S6...Cg(A)B	0.96	2.75	3.635(13)	154
	C1SB-H1S5...Cg(B)B	0.96	2.96	3.552(16)	121
	C1SB-H1S4...Cg(C)B	0.96	2.73	3.603(15)	151
	C2SB-H2S1...Cg(D)B	0.96	2.87	3.536(18)	127
	S1A...Cg(N1A-C5A)	3.380(6)			
	S1A'...Cg(N3A-C19A)	3.193(9)			
	S1B...Cg(N3B-C19B)	3.407(6)			
	S1B'...Cg(N1B-C5B)	3.198(9)			

[i] It can be also refer to S…Cg measurement, wherein Cg denotes centroid calculated through certain atoms shown in parentheses. [ii] All carbons of a phenyl ring whose label is shown in parentheses were used in the centroid calculation. After parentheses, the capital letter A or B means the crystallographically independent molecule.

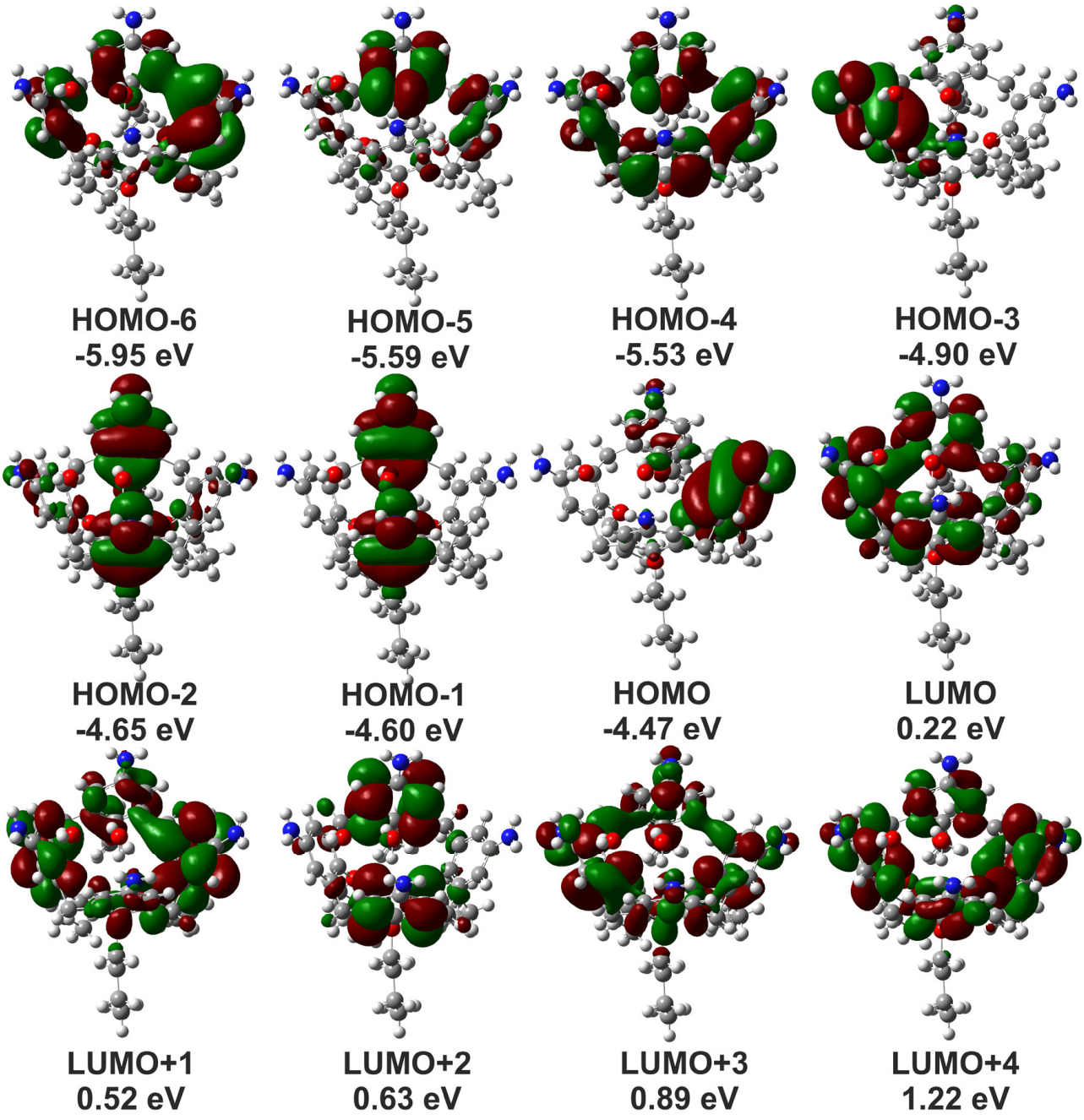

Figure S1. Molecular orbitals calculated at the B3LYP/6-31G* level of theory on the crystal geometry of **1a**, together with water molecule bearing O2W and that fraction bearing O1W'.

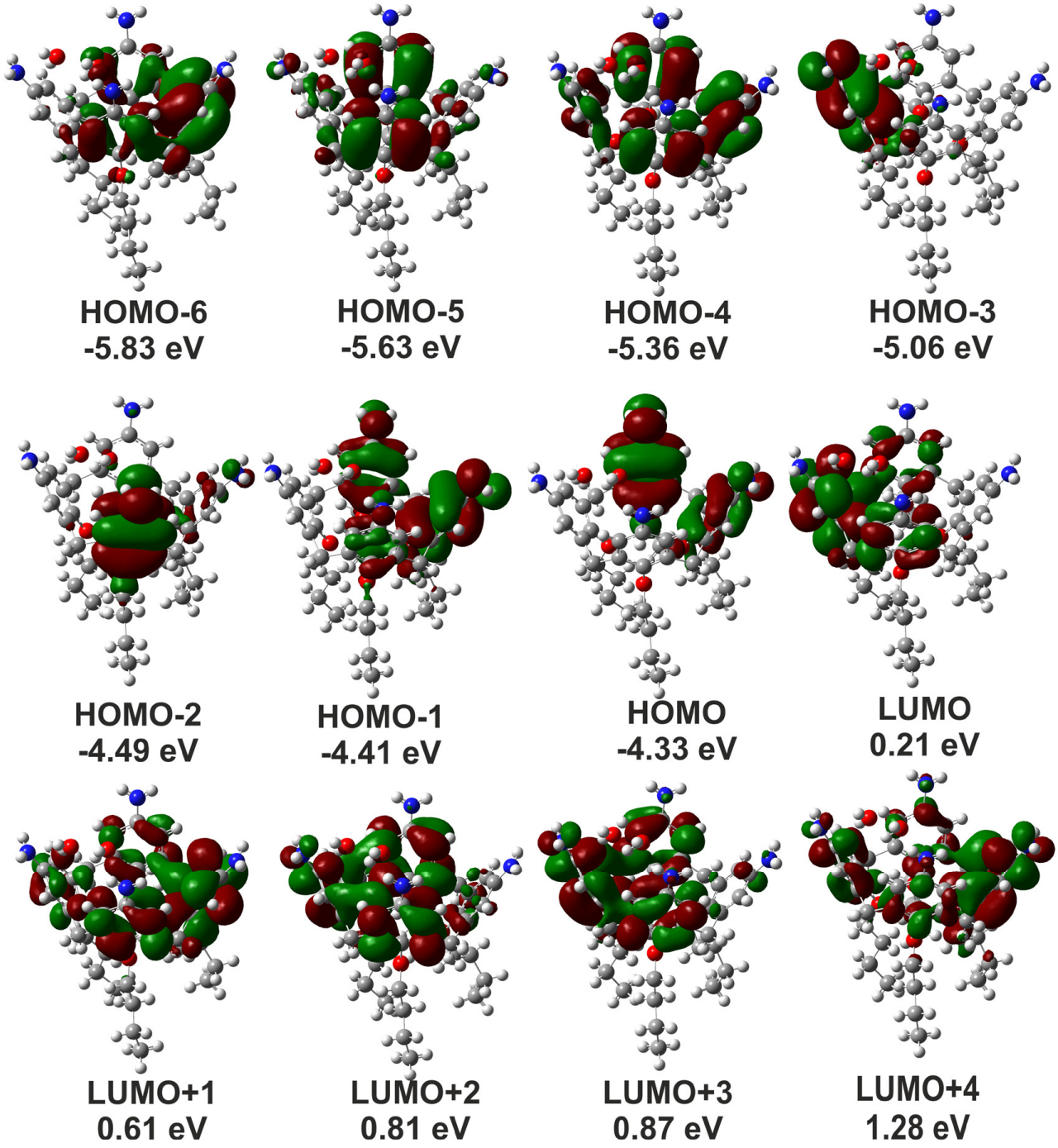

Figure S2. Molecular orbitals calculated at the B3LYP/6-31G* level of theory on the crystal geometry of **1a**, together with water molecule bearing O2W and that fraction bearing O1W.

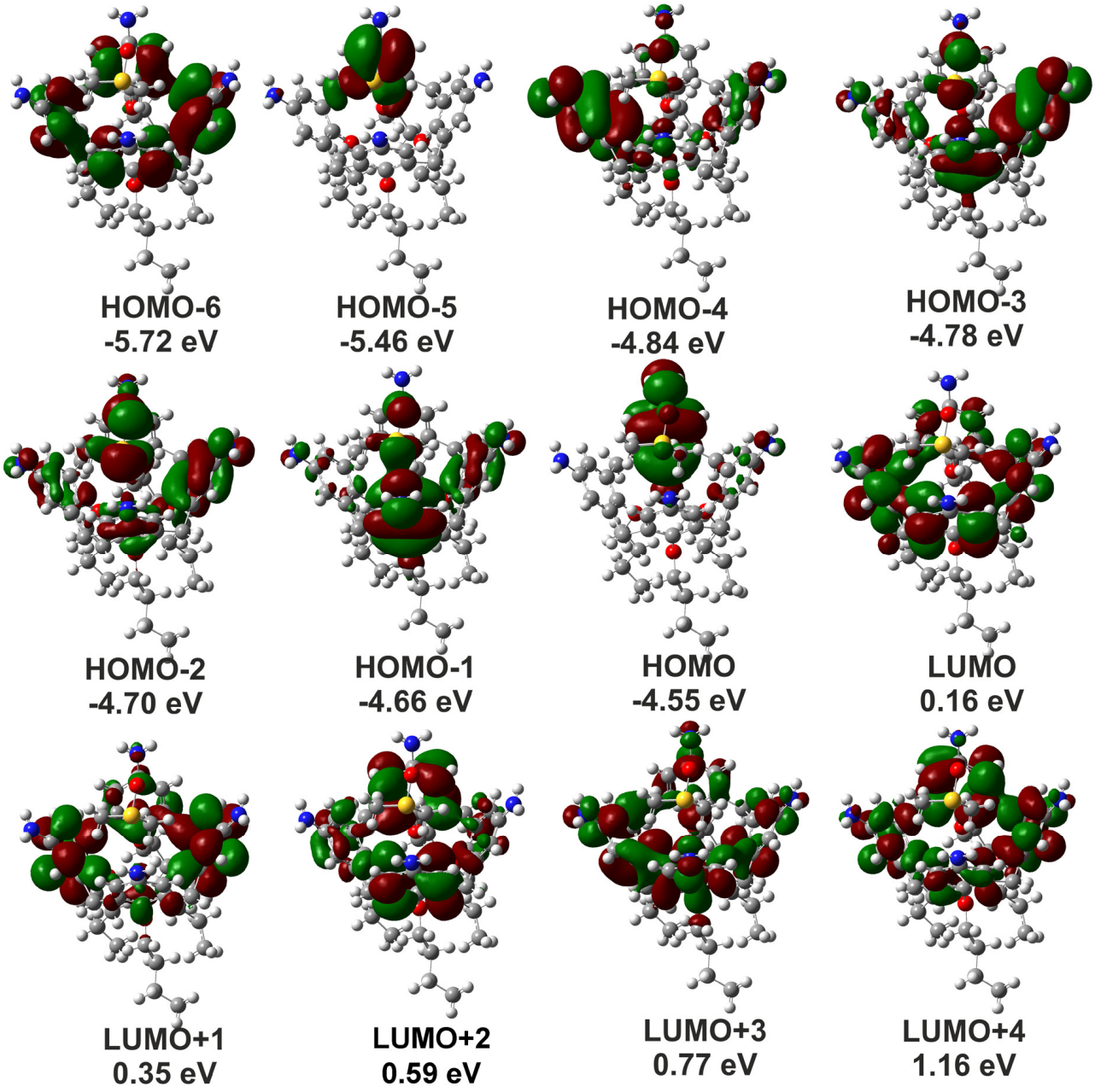

Figure S3. Molecular orbitals calculated at the B3LYP/6-31G* level of theory on the crystal geometry of **1b** (calixarene labeled as A and its entrapped DMSO molecule bearing S1A).