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Halogen-Bonded Solvates of Tetrahaloethynyl Cavitands

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Supporting Information

I GENERAL INFORMATION

The cavitands **1**, **2** and **3** were synthesized according to reported procedures.[1,2]. All the solvents used for syntheses and crystal growth are reagent grade, and were used as received.

II SOLID STATE ANALYSES

Crystals of the assembly **1**•acetone, **1**•$CHCl_3$, **2**•MeCN, **3**•acetone, **2**•DMF and **3**•DMF were obtained by slow evaporation of corresponding solution containing the corresponding cavitands. Crystals of **3**•DMSO were crystallized from the chloroform solution in the presence of few drops of DMSO. Data for **1**•acetone and **1**•$CHCl_3$, were collected at 170 K on an Agilent SuperNova diffractometer with Atlas detector using mirror-monochromated Mo-*K*α radiation ($\lambda = 0.71073$ Å). Data for **2**•MeCN, **2**•DMF, **3**•DMF and **3**•acetone were collected at 123 K (120 K for **3**•DMSO) on an Agilent SuperNova Dual diffractometer with Atlas detector using mirror-monochromatized Cu-Kα radiation ($\lambda = 1.54184$ Å). *CrysAlisPro*[3] was used for both data collection and processing. The intensities were corrected for absorption using analytical face index absorption correction method[4] for **1**•acetone, **1**•$CHCl_3$, **2**•MeCN and **3**•DMSO. While for **2**•DMF and **3**•acetone, empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm[5] was used.

The structures were solved by Direct method with *SHELXS*[6] and refined by full-matrix least-squares methods using the *OLEX2*,[7] which utilizes the *SHELXL-2013* module.[6] All non-hydrogen atoms in the four structures were refined with anisotropic thermal parameters, except for some carbon atoms in the hexyl groups and part of the guest molecules in structure **3**•DMF and **3**•acetone.

In **1**•acetone, all the hexyl groups and the acetone molecule were involved in disorder, however, only one was treated with split (terminal C57 and C58). All the other disordered atoms or groups restrained with "ISOR 0.01 0.02" and "SADI 0.01" commands for their ADP and geometry, respectively.

In **1**•$CHCl_3$, three of the four hexyl groups were disordered, which were treated by split for the related carbon atoms. Among them, C46B was also restrained by "ISOR 0.02 0.04" command for its ADP.

The structure of **2**•DMF is in bad disorder, particularly in the hexyl groups and the lattice solvent molecules. The positional disorder of the hexyl group and the DMF molecule is correlated. The motifs belong to one disordered part were kept with the same occupancy. The heavy disorder made it impossible to freely refine the geometry and the ADPs. Thus, some of the atoms were refined with fixed isotropic thermal parameters, and the geometry was also strongly restrained with "DFIX", "SADI" and "DANG" commands according chemical reasonability.

In **3**•DMF, two cavitand molecules are present in the asymmetric unit. In each of them, two of the four hexyl groups were disordered, the thermal parameters of which were kept isotropic and fixed at 0.16 and 0.18, respectively, for the secondary and terminal carbons. In addition, geometry and

ADP restraints were applied to the necessary groups due to the disorder. Strong electron densities were found around I4, which was also assigned as iodine atom with a refined occupancy of 0.065. “EADP” command was used to constrain the two parts of the iodine atom with the same ADP.

Two of the four DMSO molecules in **3**•DMSO were in disorder. The sulphur atoms were found disordered over two positions, for which the occupancies of each disordered part was refined. Some of the hexyl carbon atoms were also clearly disordered, reflected by their relatively large ADPs. However, no split was applied for them, but the anisotropic displacement parameters were restrained by “ISOR 0.02 0.04”. One of the iodine atoms was also treated by split because a large residual density was observed close to it. The refined occupancy for the smaller part was 0.083. The ADP of this iodine atom was strongly restrained by “ISOR 0.001 0.002”. Relatively large peak and hole in the difference Fourier map were also present around I1 (3.18 eÅ^{-3}) and I2 (-2.51 eÅ^{-3}), respectively. They might be the result of unsuitable absorption correction for the heavy iodine atoms.

In **3**•acetone, the quality of the crystal as well as the diffraction were not good due to the large amount of heavily disordered groups, reflected by the high final R1 and wR2 values. For the groups involved in disorder, strong ADP restraints (ISOR 0.01 0.02 and ISOR 0.005 0.01) were applied to 85 atoms out of the in total 100 non-hydrogen atoms. In addition geometry restraints were also used to model the hexyl groups (SADI/DFIX) and one of the acetone molecules (FLAT) in the structure. Five carbon atoms in the four hexyl groups were refined with isotropic model, since they were disordered over more than two positions, but only the main part was assigned with full occupancy. Thus the anisotropic refinement would result in very large thermal parameters.

In all the cases, all the hydrogen atoms were refined using riding models with Ueq(H) of 1.5Ueq(parent) for hydroxyl and terminal methyl groups, and 1.2 Ueq(parent) for other groups. The information concerning crystal data, data collection and refinement results have been documented in table S1.

Table S1. Crystallographic information concerning crystal data, data collection and refinement results.

	1•acetone	**1**•$CHCl_3$	**2**•MeCN	**2**•DMF
Crystal data				
Chemical formula	$C_{64}H_{68}Br_4O_8 \cdot C_3H_6O$	$C_{64}H_{68}Br_4O_8 \cdot CHCl_3$	$C_{64}H_{68}I_4O_8 \cdot C_2H_3N$	$C_{64}H_{68}I_4O_8 \cdot 2.5(C_3H_7NO) \cdot C_{1.5}H_{5.5}N_{0.5}O_{0.5}$
M_r	1342.90	1404.19	1513.83	1694.08
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $C2/m$
Temperature (K)	170	170	123	123
a, *b*, *c* (Å)	14.1022 (10), 24.4684 (11), 18.3507 (13)	14.4249 (2), 25.2475 (3), 17.8123 (3)	14.2220 (2), 24.9361 (3), 18.1166 (3)	22.1144 (11), 22.3258 (17), 17.2116 (6)
β (°)	98.970 (7)	100.8364 (16)	98.6494 (16)	101.036 (4)
V ($Å^3$)	6254.6 (7)	6371.46 (18)	6351.82 (17)	8340.6 (8)
Z	4	4	4	4
Radiation type	Mo *K*α	Mo *K*α	Cu *K*α	Cu *K*α
μ (mm^{-1})	2.63	2.71	15.83	12.15
Crystal size (mm)	0.20 × 0.12 × 0.10	0.31 × 0.11 × 0.09	0.21 × 0.17 × 0.11	0.14 × 0.07 × 0.06
Data collection				
T_{min}, T_{max}	0.667, 0.750	0.585, 0.812	0.590, 0.721	0.621, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	21217, 11207, 6181	40713, 11503, 8282	25434, 11246, 8938	11003, 6292, 4268
R_{int}	0.043	0.038	0.045	0.026
$(\sin \theta/\lambda)_{max}$ ($Å^{-1}$)	0.600	0.600	0.596	0.562
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.089, 0.272, 1.02	0.051, 0.150, 1.03	0.052, 0.146, 1.02	0.101, 0.332, 1.06
No. of reflections	11207	11503	11246	6292
No. of parameters	747	778	717	504
No. of restraints	57	6	12	179
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$)	1.91, -1.81	0.74, -0.75	1.97, -1.53	1.74, -1.84

	3•DMF	**3**•DMSO	**3**•acetone
Crystal data			
Chemical formula	$C_{68}H_{73}I_4O_8)\cdot 3.5(C_3H_7NO)$	$C_{68}H_{76}I_4O_8\cdot 4(C_2H_6OS)$	$C_{68}H_{76}I_4O_8\cdot 3.5(C_3H_6O)$
M_r	1784.72	1841.39	1732.16
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Triclinic, *P*-1
Temperature (K)	123	120	123
a, *b*, *c* (Å)	16.7987 (4), 20.0128 (4), 24.3284 (7)	12.8712 (5), 16.8782 (7), 20.3485 (12)	16.4002 (10), 17.5718 (8), 19.1603 (10)
α, β, γ (°)	90.053 (2), 92.142 (2), 97.4128 (19)	111.180 (5), 95.315 (4), 99.321 (3)	114.995 (5), 91.376 (6), 116.803 (6)
V (Å^3)	8104.7 (4)	4012.3 (3)	4306.9 (5)
Z	4	2	2
μ (mm^{-1})	12.54	13.62	11.77
Crystal size (mm)	0.10 × 0.07 × 0.04	0.21 × 0.02 × 0.02	0.35 × 0.29 × 0.25
Data collection			
T_{min}, T_{max}	0.807, 0.903	0.284, 0.781	0.291, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	62988, 28379, 18131	25862, 16087, 8816	30875, 16680, 10948
R_{int}	0.088	0.082	0.060
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.596	0.631	0.622
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.094, 0.306, 1.04	0.092, 0.289, 1.03	0.220, 0.526, 1.04
No. of reflections	28379	16087	16680
No. of parameters	1740	904	904
No. of restraints	105	24	565
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	3.57, -2.83	2.28, -2.62	5.44, -2.27

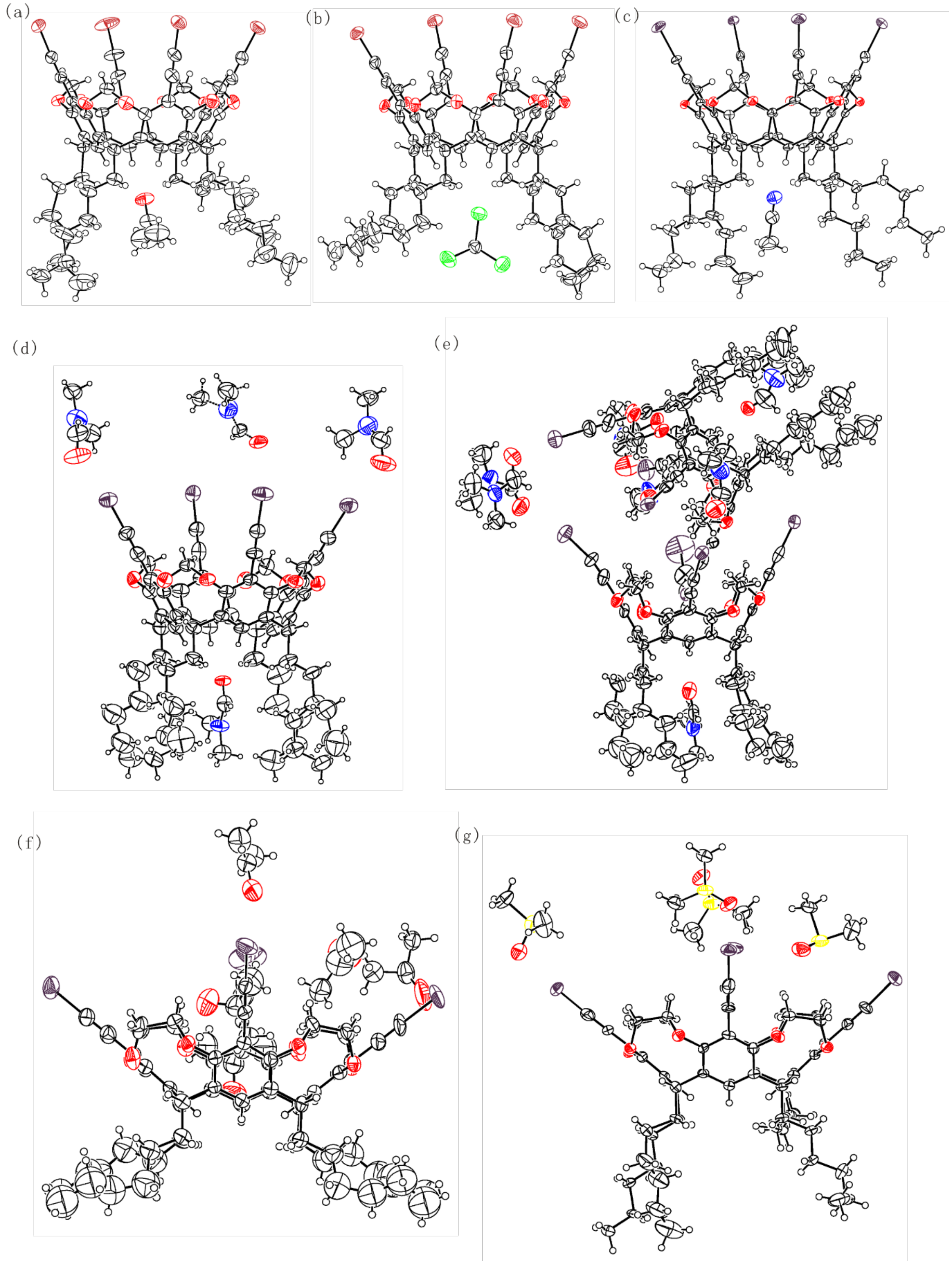


Figure S1. The ORTEP type molecular structures drawn at 50% probability level for (a) **1**·acetone, (b) **1**·$CHCl_3$, (c) **2**·MeCN, (d) **2**·DMF, (e) **3**·DMF (f) **3**·acetone and (g) **3**·DMSO.

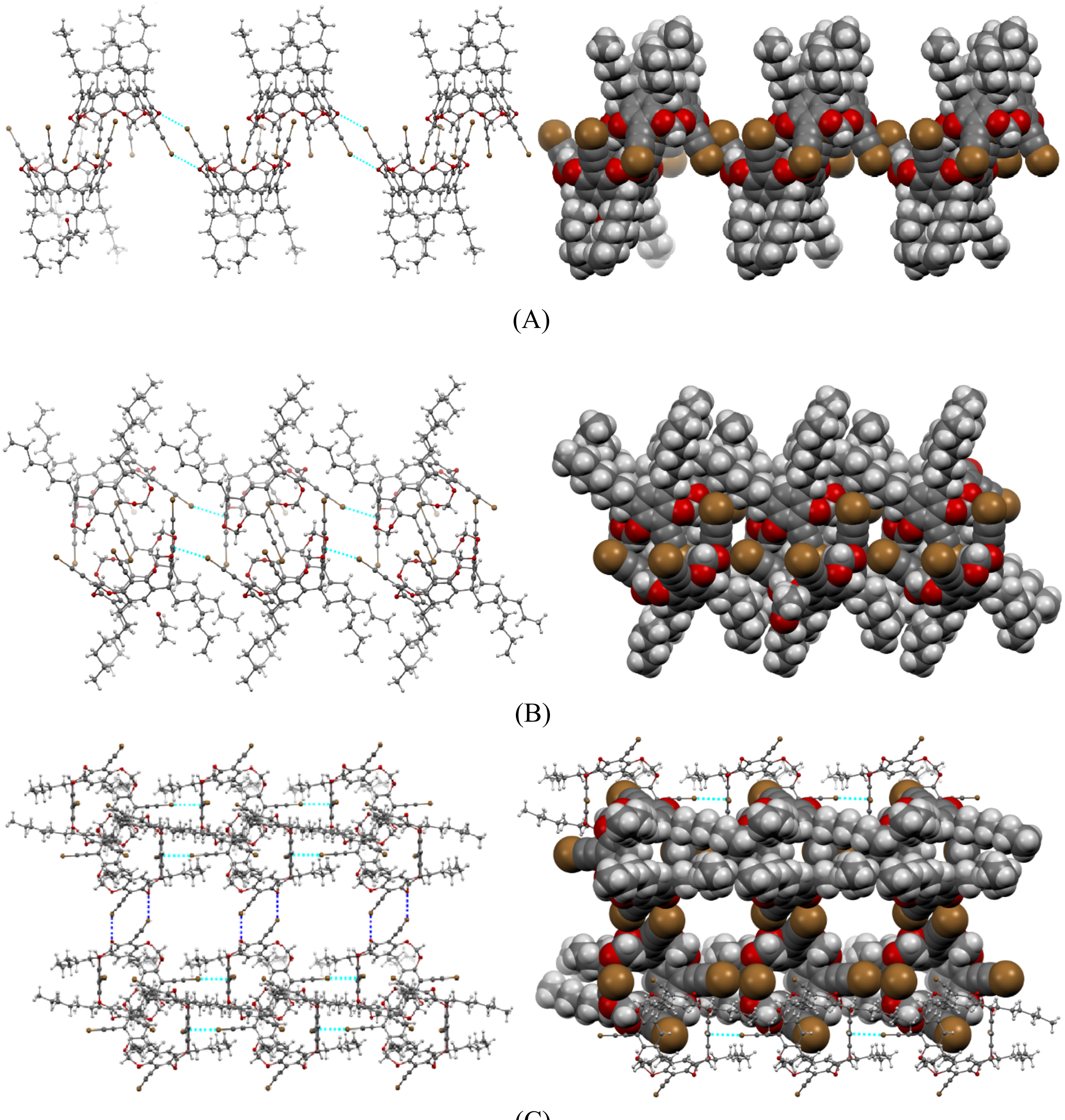
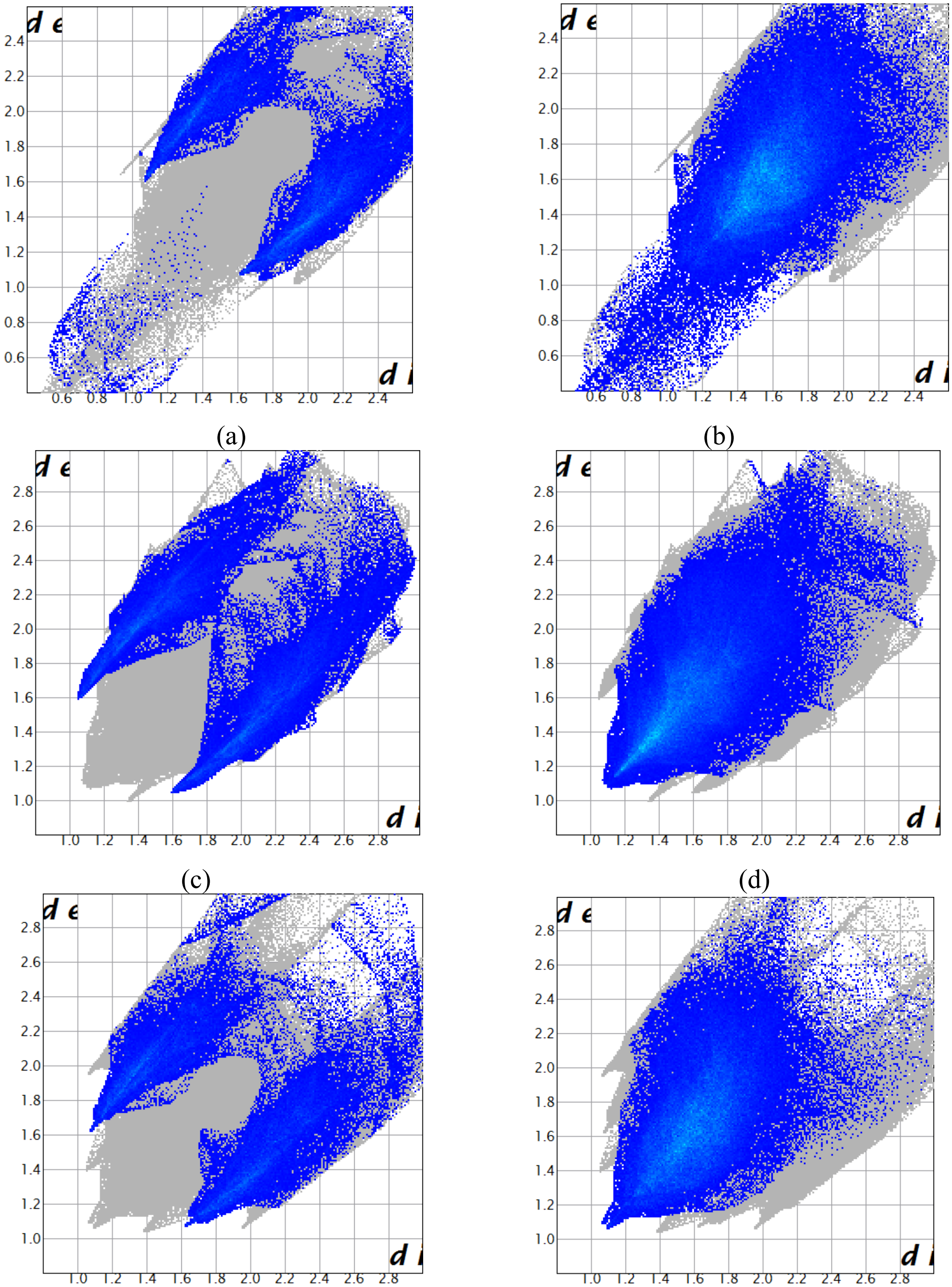


Figure S2. The Br•••O (A), Br•••π (B) interactions leading the structures into 2D assemblies (C) in **1**•acetone. The supramolecular connections in **2**•MeCN and **1**•$CHCl_3$ are the same.



(a) (b) (c) (d) (e) (f)

Figure S3. The statistic analysis of the close contacts from C···H contacts (a 16.4%, c 17.7%, e 17.1%) and H···H (b 44.9%, d 35.4 %, f 38.8%) in (a, b) **1**•aceone, (c, d) **1**•CHCl$_3$ and (e, f) and **2**•MeCN.

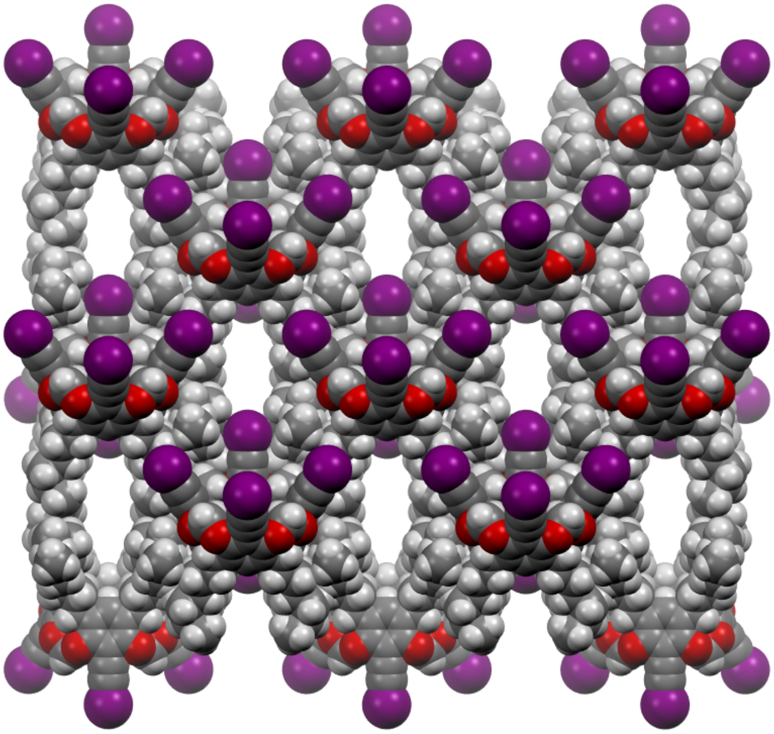
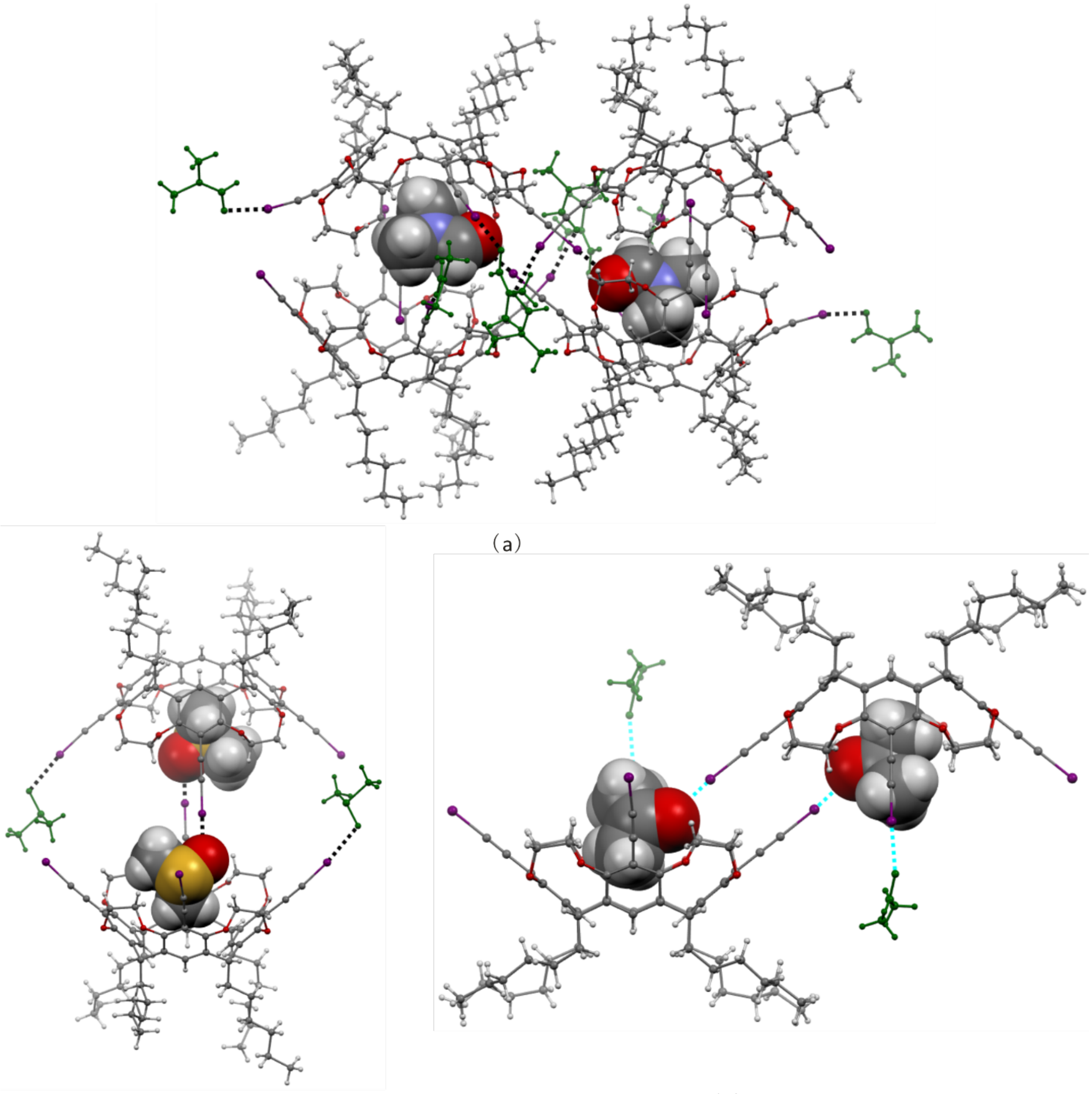


Figure S4. Packing of the cavitands in the structure of **2**•DMF in CPK mode by manually removing the guests.



(a)

(b)

(c)

Figure S5. The XB interactions between the cavitand **3** and solvent molecules in (a) **3**•DMF, (b) **3**•DMSO, (c) **3**•acetone, forming the 4:10 (a), 2:4 (b) and 2:4 (c) assemblies, respectively.

III ELECTROSTATIC POTENTIAL CALCULATIONS

The electrostatic potentials for all the three cavitands (the hexyl groups at lower rim were simplified by methyl groups) and solvents used in this study were calculated with DFT-B3LYP method with the basis set of 6-311+G** in a vacuum. The calculations were carried out using Spartan 14 software.[8] The electrostatic charge (ESP) was mapped onto the electron density surface at isovalue of 0.002 electron/bohr^3. The wave functions for the solvates were calculated with DFT method at B3-LYP/6-311G* level in a vacuum from the 3-21 geometry with the starting point from the X-ray crystal structures.

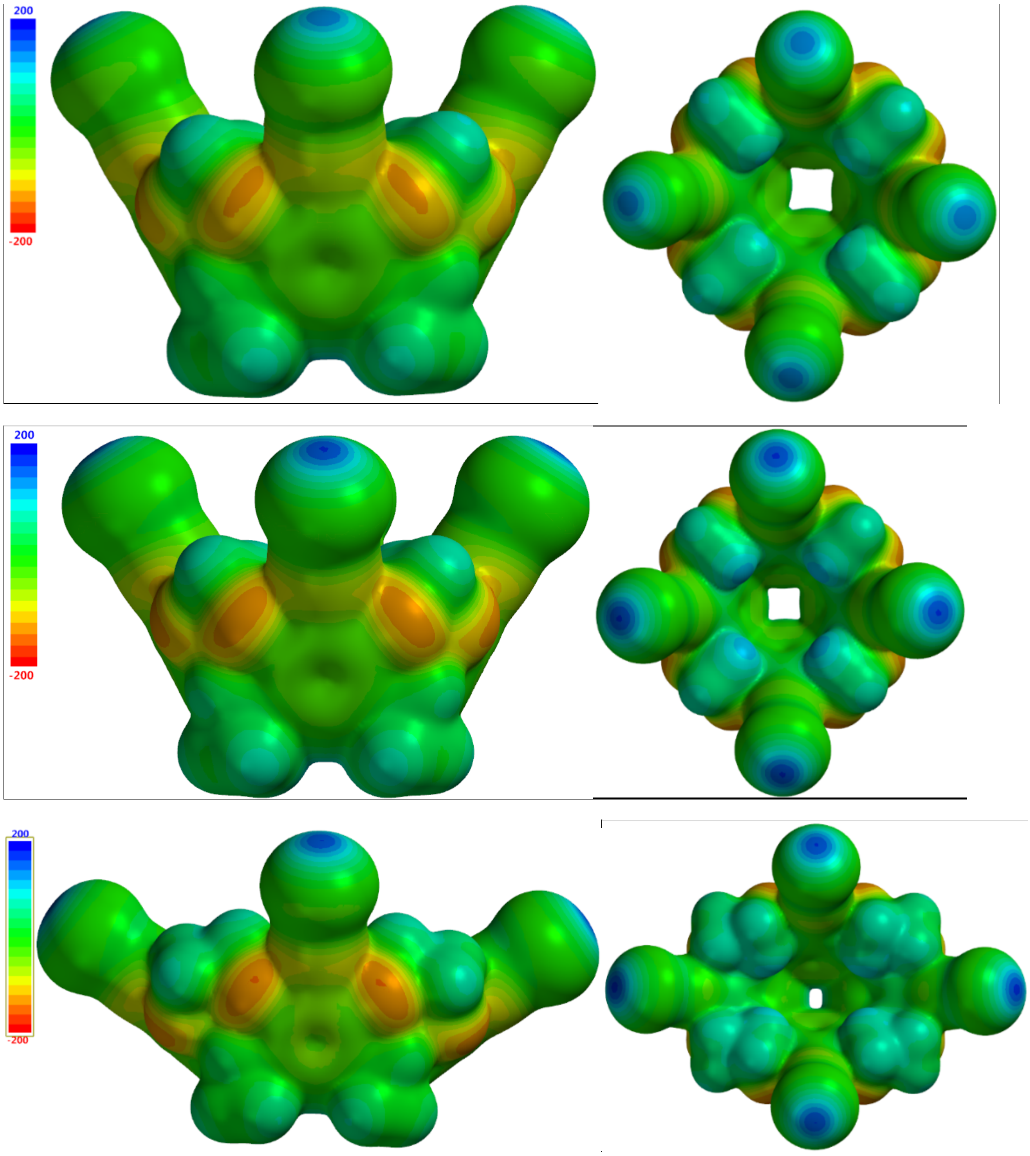


Figure S6. The ESP figures mapped on the electron density surface at isovalue of 0.002 e bohr^{-3} of the cavitands (top) **1**, (middle) **2** and (down) **3**. Side view on the left and top view on the right. The legends in the figures show the ESP from -200 to 200 KJ/mol.

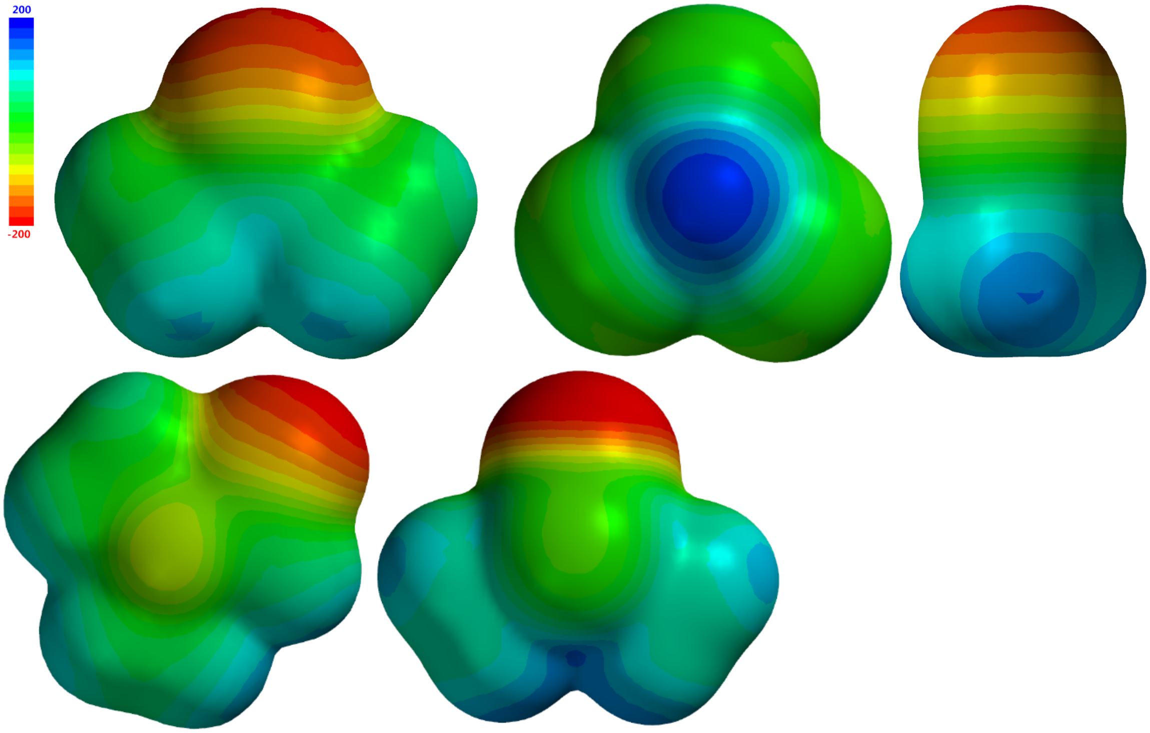


Figure S7. The ESP mapped on the electron density surface at isovalue of 0.002 e bohr^{-3} for acetone, chloroform, acetonitrile, DMF and DMSO in the order from left to right & up to down. The legends in the figures show the ESP from -200 to 200 KJ/mol.

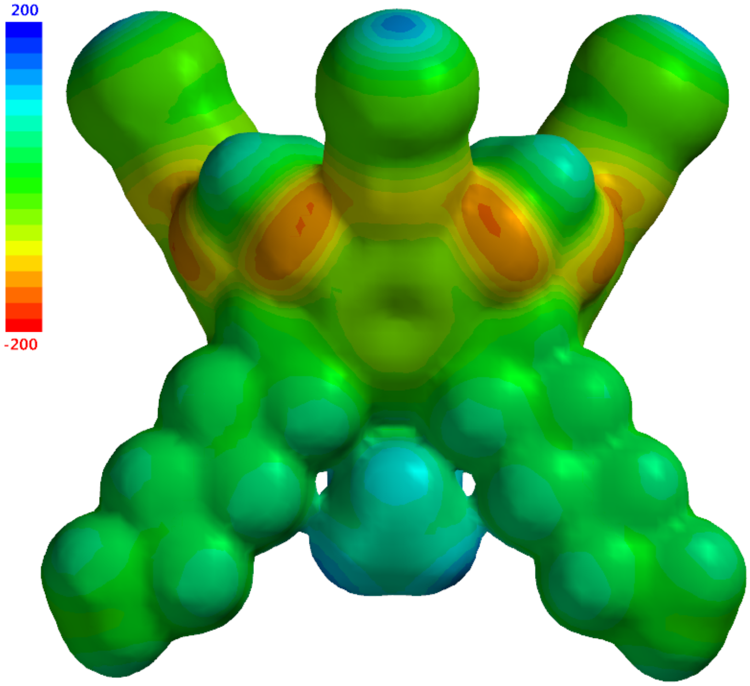
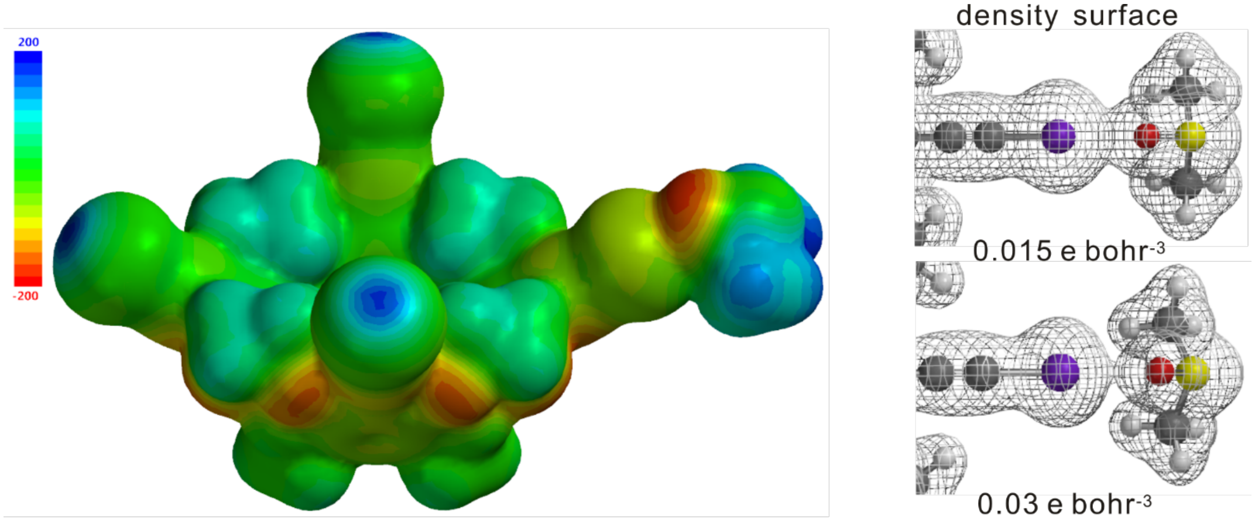
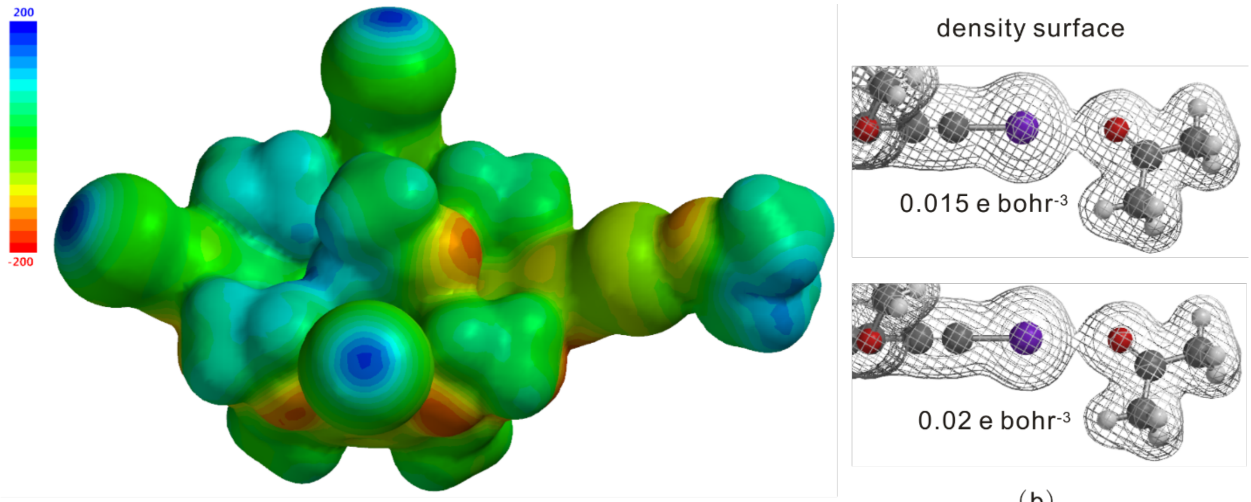


Figure S8. The ESP figures mapped on the electron density surface at isovalue of 0.002 e bohr^{-3} in the solvates **1**•acetone. The legends in the figures show the ESP from -200 to 200 KJ/mol.



(a) (b)

Figure S9. The ESP mapped on the isosurface of 0.002 e bohr^{-3} (a); and the electron density surfaces (b) in **3**•DMSO. The hexyl groups of the cavitand were removed for the calculations.



(a) (b)

Figure S10. The ESP mapped on the isosurface of 0.002 e bohr^{-3} (a); and the electron density surfaces (b) in **3**•acetone. The hexyl groups of the cavitand were removed for the calculations.

IV REFERENCES

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