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ROY Confined in Hydrogen-Bonded Frameworks: Coercing Conformation of a Chromophore

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Materials 5-Methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile (a.k.a. ROY) was purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan).

The various organosulfonic acids or their sodium salts were purchased or synthesized using standard procedures.[1,2] Sodium salts of the sulfonic acids were converted to the acid form by passing them through an Amberlyst 36 ion-exchange column. Guanidinium organosulfonate apohosts were prepared by combining acetone solutions of approximately 1.10 molar equivalents of guanidinium tetrafluoroborate and 1.0 molar equivalents of a selected organosulfonic acid to produce a precipitate of the corresponding guest-free apohost of the GS compound[3]. The mixture was dried in a rotary evaporator and the resulting solid was washed with acetone several times and dried *in vacuo*, affording the apohost of the GS compound. GS-ROY inclusion compounds were prepared according to the specifications below. Single crystals of the inclusion compounds were sometimes accompanied by crystals of ROY, but the inclusion compound crystals were distinguished readily by their morphology and color.

Single crystal X-ray diffraction. Single crystal X-ray diffraction data **1** through **5** was obtained using a Bruker SMART APEX II diffractometer equipped with a CCD detector. The X-ray beam generated from a sealed Mo tube was monochromated by a graphite crystal and collimated by a MonoCap collimator. The wavelength from the Mo Kα radiation is 0.71073 Å. Crystal temperature (100 K) was controlled by an Oxford Cryosystems 700+ Cooler. Crystals were mounted on a 0.2 mm MicroMount (MiTeGen) with Type B immersion oil (Cargille Labs). Crystal **6** was measured at 100 K at the ChemMatCARS beamline of the Advanced Photon Source at Argonne National Laboratory, using a Bruker APEX II CCD detector and an Oxford Cryojet Cooler. A double monochromatic incident X-ray beam of 0.2 mm × 0.2 mm in size was used, conditioned using Si(111) and Si(311) monochromators to have an energy of 30 keV (λ = 0.41328 Å). The detector was mounted orthogonally to the beam path with a sample-to-detector distance of 80 mm. Two ϕ scans were performed with an exposure time of 0.2 seconds per frame. The structures were solved by SHELXT[4] and refined with full-matrix least squares by SHELXL (Sheldrick 2014).[5] The refinement details are described below. Crystallographic data of these structures, including cif, fcf, and hkl files, have been deposited with the Cambridge Crystallographic Data Centre with Numbers 1992984-1992989. Copies of these data can be requested, free of charge, from the CCDC website at https://www.ccdc.cam.ac.uk/structures/.

Compound 1. Non-hydrogen atoms of compound **1** were refined with anisotropic displacement parameters (ADPs), and hydrogen atoms were placed in idealized positions and refined with riding models except the hydrogen on amino group of the ROY molecule, in which the position of the N-H hydrogen was refined with the restrained distance of 0.86 Å using the DFIX command. This refinement routine was applied to all six structures unless there was any difference, which is described where relevant. In compound **1** one of the biphenyl groups of the sulfonate anions is disordered over the inversion center; so both of its phenyl rings were refined using the rigid ideal model (a regular hexagon with a C-C distance of 1.39 Å with the AFIX 66 command) and ADPs of each six carbons were constrained to be equal to prevent from becoming non positive definite (NPD, i.e. one of three principal mean square atomic displacements turns negative) using the EADP command.

Compound 2. There are two independent molecules of Compound **2** per an asymmetric unit. No disorder was observed. The only restraints were applied to the N-H distance of each ROY molecule (DFIX).

Compound 3. There are two independent molecules of Compound **3** per an asymmetric unit. One of two phenyl rings of each azobenzenedisulfonate anion is disordered. Similar to compound **1**, the rigid model was applied to these phenyl rings with AFIX and EADP commands. One ROY and one methanol molecules with 50% occupancy are disordered over inversion center. In addition, another ROY molecule is also disordered in two conformations and two conformers have a refined occupancy ratio of almost 50%:50%. Some ADP constraints (EADP) were applied to these disordered molecules whenever necessary and only one distance restraint (DFIX) was used for one of the S-C bond.

Compound 4. No disorder was observed in Compound **4**. The only restraint was applied to the N-H distance of a ROY molecule (DFIX).

Compound 5. No disorder was observed in Compound **5**. No restraint was applied.

Compound 6. The CN group of the ROY molecule in compound **6** is disordered in three positions with a refined occupancy ratio of 53.6%:26.6%:19.8%. The constraints on their ADPs (EADP) and restraints on the C-N bond distances (SADI) were applied to these disordered units.

Preparation of compound 1. Slow evaporation under ambient conditions of 0.5 mL of methanol and 1 mL of acetonitrile containing 3 mg guanidinium 4,4'-biphenyldisulfonate and 1 mg ROY (2.85:1 molar ratio) for 48 hours afforded orange red plates of G_2BPDS⊃$(ROY)_{2/3}$ (**1**) mixed with single crystals of ROY.

Preparation of compound 2. Slow evaporation under ambient conditions of 1 mL of methanol and 0.5 mL of acetonitrile containing 3 mg guanidinium 1,2-bis(4-sulfonatophenyl)ethane (G_2BSPE) and 1 mg ROY (2.59:1 molar ratio) for 48 hours afforded red plates of G_2BSPE⊃ROY (**2**) mixed with single crystals of ROY.

Preparation of compound 3. Slow evaporation under ambient condition of 0.50 mL of ethyl acetate and 0.5 mL methanol containing 10 mg guanidinium azobenzenedisulfonate (G_2ABDS) and 3 mg ROY (3.47:1 molar ratio) for 72 hours afforded red slabs of G_2ABDS⊃$(ROY)_{3/4}$(methanol)$_{1/4}$ (**3**) mixed with single crystals of ROY.

Preparation of compound 4. Slow evaporation under ambient conditions of 0.75 mL of methanol and 0.5 mL of acetonitrile containing 4 mg guanidinium 4,4'-silbenedisulfonate (G_2SDS) and 1.5 mg ROY (2.32:1 molar ratio) for 48 hours afforded red needles of G_2SDS⊃ROY (**4**) mixed with single crystals of ROY.

Preparation of compound 5. Slow evaporation under ambient conditions of 0.75 mL of methanol and 0.5 mL of acetonitrile containing 5 mg guanidinium 1,2-bis(4-sulfonatophenoxy)ethane (G_2BSPOE) and 1.5 mg ROY (2.60:1 molar ratio) for 48 hours afforded red needles of G_2BSPOE⊃ROY (**5**) mixed with single crystals of ROY.

Preparation of compound 6. Slow evaporation under ambient conditions of 0.5 mL of methanol and 1 mL of acetonitrile containing 2 mg guanidinium 2,6-anthracenedisulfonate (G_2ADS) and 1 mg ROY(1.75:1 molar ratio) for 48 hours afforded yellow plates of G_2ADS⊃$(ROY)_2$ (**6**) mixed with single crystals of ROY.

Table S1. Crystallographic data of inclusion compounds **1 - 6**.

Compound name	G_2BPDS⊃ $(ROY)_{2/3}$	G_2BSPE⊃ ROY	G_2ABDS⊃ $(ROY)_{3/4}(methanol)_{1/4}$	G_2SDS⊃ROY	G_2BSPOE⊃ ROY	G_2ADS⊃ $(ROY)_2$
Compound no.	**1**	**2**	**3**	**4**	**5**	**6**
Lab code	19mdw13h	18mdw9l	19mdw15h	19mdw12h	19mdw9h	18mdw1r-APS
CCDC no.	1992984	1992985	1992986	1992987	1992988	1992989
Formula by X-ray	$C_{33}H_{39}N_{12}O_{11}S_4$	$C_{28}H_{33}N_9O_8S_3$	$C_{93}H_{111}N_{41}O_{31}S_{11}$	$C_{28}H_{31}N_9O_8S_3$	$C_{28}H_{33}N_9O_{10}S_3$	$C_{40}H_{38}N_{12}O_{10}S_4$
Formula weight	908.00	719.81	2651.88	717.80	751.81	975.09
Crystal habit	red plate	red plate	red slab	red needle	red needle	yellow plate
Crystal size (mm)	0.56×0.24×0.02	0.23×0.16×0.09	0.02×0.10×0.36	0.06×0.06×0.44	0.29×0.04×0.03	0.35×0.20×0.02
Crystal system	triclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic	orthorhombic
Space group (no.)	$P\bar{1}$ (2)	*P*c(7)	C2/c (15)	*P*bca (61)	$P2_12_12_1$ (19)	*P*bca (61)
***a* (Å)**	7.5436(11)	17.657(3)	35.6995(9)	14.4038(11)	7.3192(4)	12.1138(6)
***b* (Å)**	14.768(2)	14.581(2)	7.3345(2)	13.1032(10)	17.1147(9)	12.6936(6)
***c* (Å)**	18.565(3)	13.1035(19)	48.5783(12)	34.569(3)	27.6428(14)	28.9704(14)
α (°)	91.078(3)	90	90	90	90	90
β (°)	96.757(2)	104.786(2)	109.3873(7)	90	90	90
γ (°)	94.637(3)	90	90	90	90	90
***V* (Å^3)**	2046.2(5)	3261.9(8)	11998.4(5)	6524.5(8)	3462.7(3)	4454.7(4)
Z	2	4	4	8	4	4
***D*$_c$ (g cm^{-3})**	1.474	1.466	1.468	1.461	1.442	1.454
***F*(000)**	946	1504	5520	2992	1568	2024
μ (mm^{-1})	0.305	0.291	0.293	0.291	0.282	0.078
Total reflections	31243	40997	102340	74912	49006	167081
Unique reflections	7541	12366	10939	6675	6121	8673
***R*$_{int}$**	0.0693	0.0784	0.0894	0.0547	0.0996	0.0688
***R*$_1$[a] [*I* > 2σ(*I*)]**	0.0558	0.0541	0.0556	0.0792	0.0462	0.0500
***wR*$_2$[b] (all data)**	0.1582	0.1191	0.1407	0.1421	0.1085	0.1528
GOF (all data)	1.020	1.000	1.017	1.075	1.022	1.046
Flack parameter	n.a.*	0.01(4)	n.a.	n.a.	-0.04(7)	n.a.

* n.a. = not applicable

Table S2. Structural features of inclusion compounds **1** through **6**.

No.	Formula	Architecture	V_{pillar} (Å^3)[a]	V_g (Å^3)[b]	V_{inc} (Å^3)[b]	Overall packing fraction[c]	% V_{inc} occupied
1	G_2BPDS⊃(ROY)$_{2/3}$	Bilayer	166	207	479	70.8%	43.3%
2	G_2BSPE⊃ROY	Bilayer	200	207	433	70.4%	47.8%
3	G_2ABDS⊃(ROY)$_{3/4}$(methanol)$_{1/4}$	Bilayer	188	214	432	72.2%	49.4%
4	G_2SDS⊃ROY	Bilayer	196	208	436	70.1%	47.7%
5	G_2BSPOE⊃ROY	Double brick	198	207	471	68.0%	43.9%
6	G_2ADS⊃(ROY)$_2$	Zigzag brick	185	208	381	68.9%	54.6%

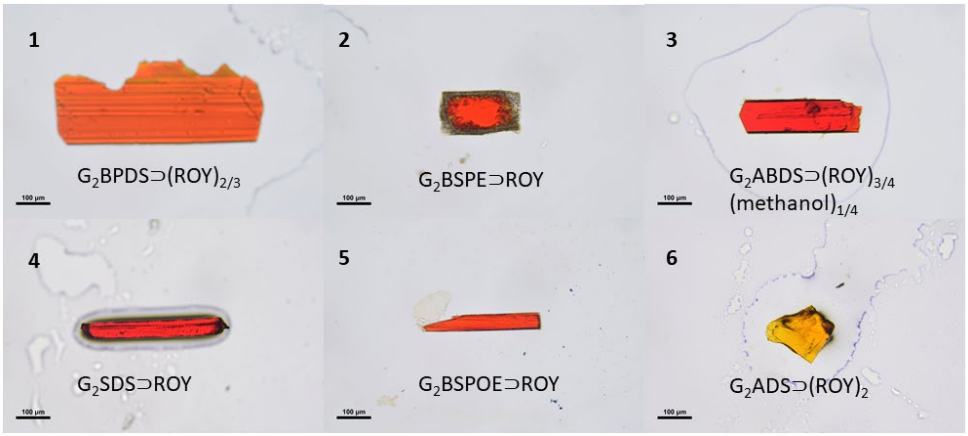
[a] V_{pillar} values are available in our previous publication[6]. [b]Molecular volume (V_g, V_{inc}) calculations were performed using BIOVIA Materials Studio 2018. Guest molecule (V_g) and organosulfonate pillar (V_{pillar}) volumes were determined from Connolly surfaces using a probe radius of zero. Inclusion cavity volumes (V_{inc}) were determined from Connolly surfaces using a 0.5 Å probe. All volumes are normalized to one formula unit. V_{pillar} corresponds to the organic component only. [c]Overall packing fraction was calculated as the sum of volume of organosulfonate pillars (including sulfonate groups), guest molecules and guanidinium cations (55 Å^3 per cation) in each unit cell divided by the volume of the unit cell.

Table S3. Physical properties of ROY polymorphs[7, 8, 9]

	R	**R05**	**ORP**	**OP**	**ON**	**YN**	**Y**	**YT04**	**PO13**
Color	Red	Red	Orange-red	Orange	Orange	Yellow	Yellow	Yellow	Pumpkin-orange
θ_{thio} (°)	21.7	34/44.9	39.4	46.1	52.6	104.1	104.7	112.8	122.1
υ_{CN} (cm^{-1})	2212	2205	2217	2226	2224	2222	2231	2224	2228.2

Table S4. Interplanar angles and distances between ROY and organosulfonate pillars.

		Interplanar angles (degrees)		Interplanar distances (Angstroms)	
Inclusion Compound	ROY (θ_{thio} degrees)	(Pillar)phenyl: (thiophene)ROY	(Pillar)phenyl: (pehnyl)ROY	(Pillar)phenyl: (thiophene)ROY	(Pillar)phenyl: (pehnyl)ROY
1	10.53	7.81	4.68	3.52	3.22
2	14.74	4.55	4.19	3.30	3.33
	14.32	5.06	4.30	3.29	3.34
3	16.15	25.18	1.70	2.95	3.37
	17.33	3.91	0.57	3.53	3.62
4	25.08	6.43	1.88	3.25	3.33
5	32.56	20.15	8.83	3.29	3.45
6	56.38	N/A	6.81	N/A	3.51



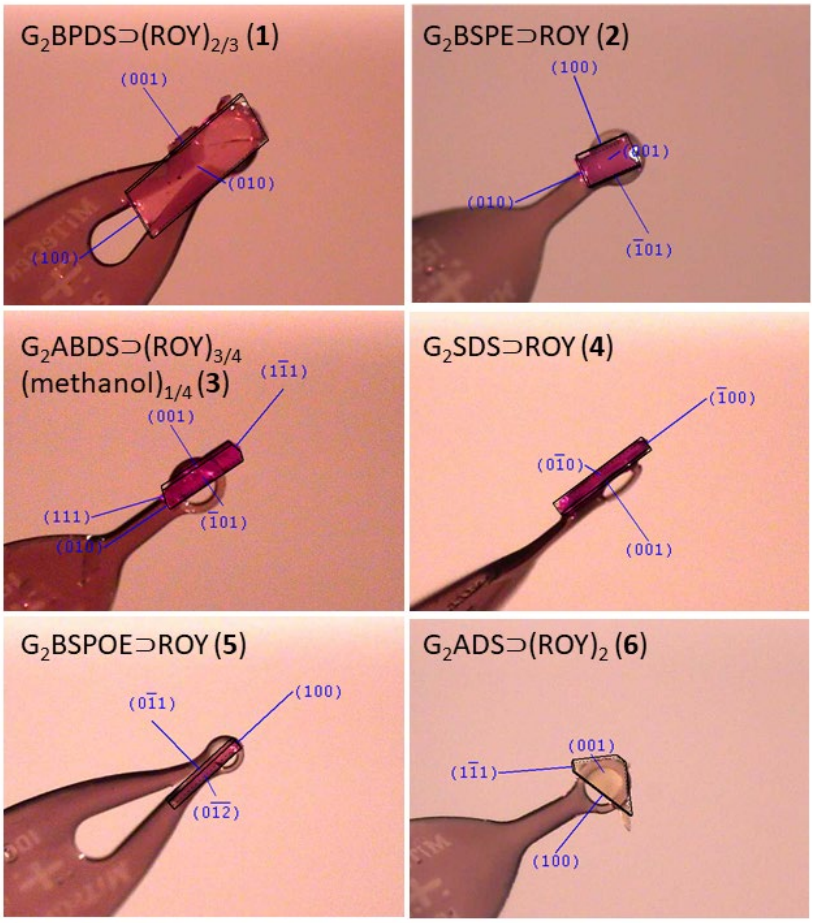


Fig. S1. (top) Images of single crystals of inclusion compounds **1** - **6**. (bottom) Crystals mounted on diffraction loops with Miller indices assigned.

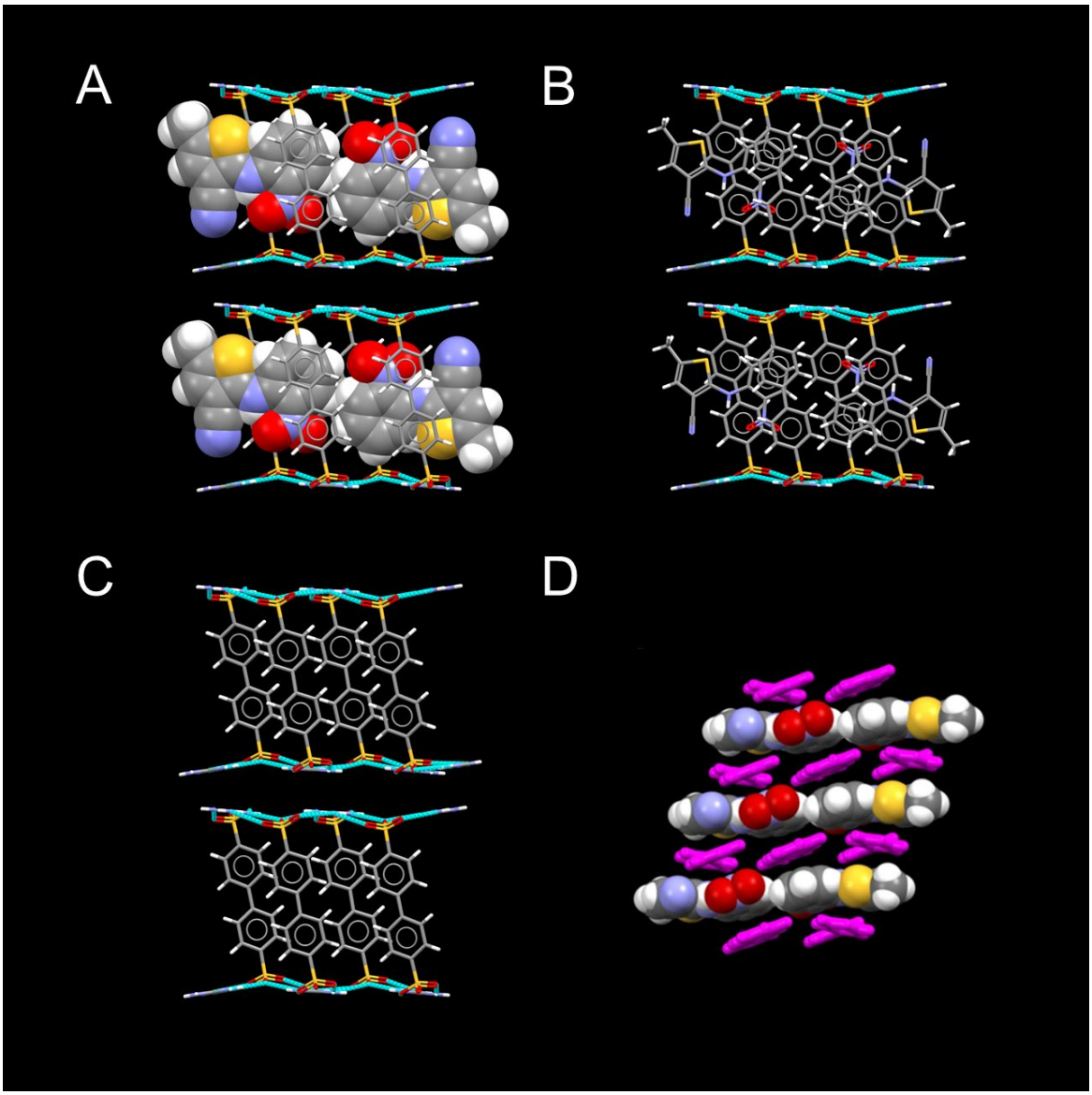


Fig. S2. Crystal structure of **1** viewed down the *a*-axis. (A) Guest molecules are rendered as space-filled and the host framework as stick. (B) Guests and host framework both rendered as stick. (C) View of the host framework *ac* plane without guests, illustrating the bilayer framework. (D) View of the *ac* plane with guanidinium and sulfonate ions removed to reveal the packing of the organic residues (magenta) of the organosulfonate pillars and the guests.

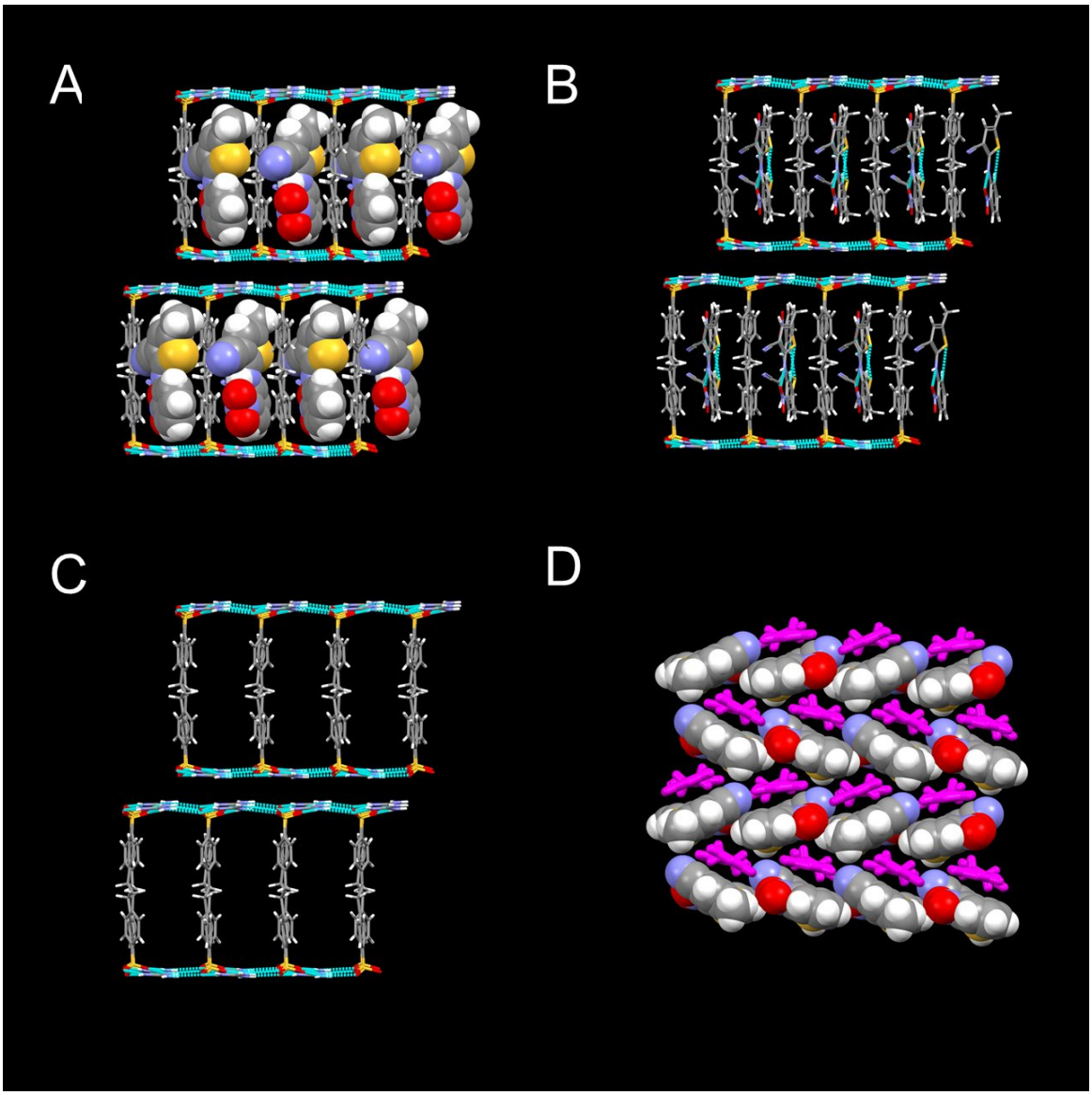


Fig. S3. Crystal structure of **2** viewed down the *b*-axis. (A) Guest molecules are rendered as space-filled and the host framework as stick. (B) Guests and host framework both rendered as stick. (C) View of the host framework *ac* plane without guests, illustrating the bilayer framework. (D) View of the *bc* plane with guanidinium and sulfonate ions removed to reveal the packing of the organic residues (magenta) of the organosulfonate pillars and the guests.

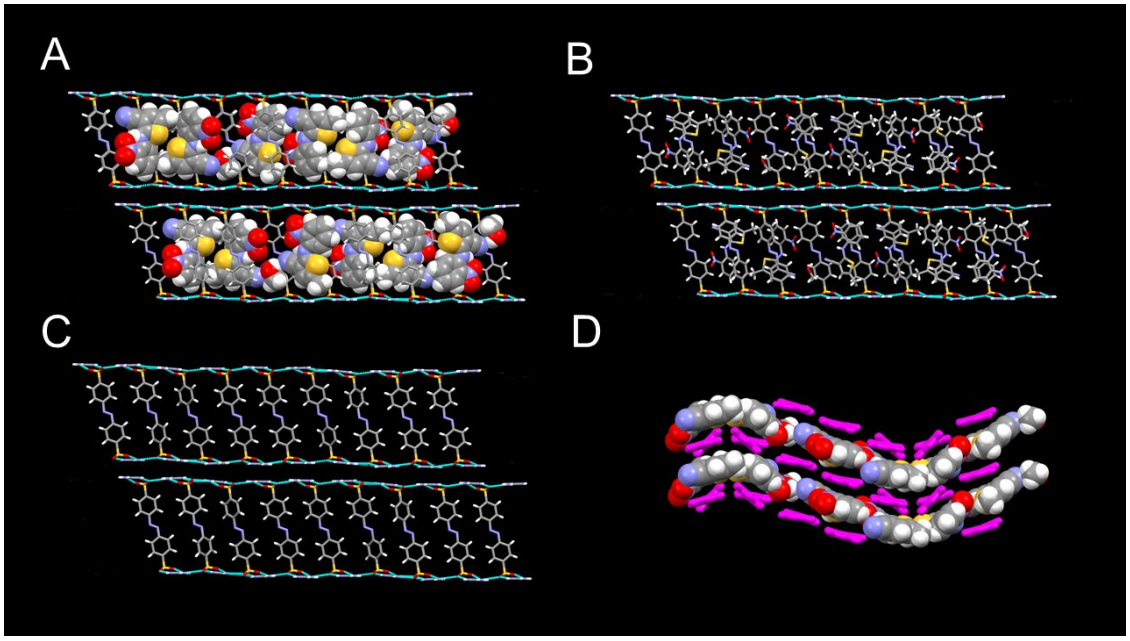


Fig. S4 Crystal structure of **3** viewed down the *b*-axis. (A) Guest molecules are rendered as space-filled and the host framework as stick. (B) Guests and host framework both rendered as stick. (C) View of the host framework *ac* plane without guests, illustrating the bilayer framework. (D) View of the *bc* plane with guanidinium and sulfonate ions removed to reveal the packing of the organic residues (magenta) of the organosulfonate pillars and the guests.

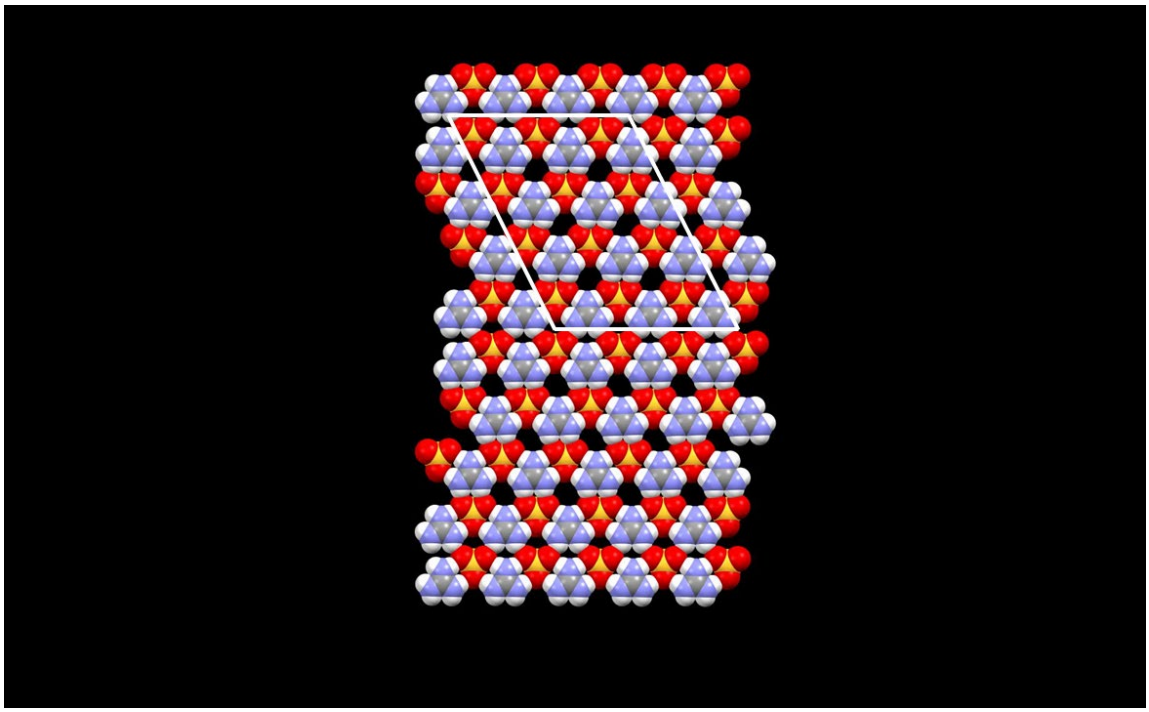


Fig. S5 View of the hydrogen-bonded sheet of compound **3**, rendered as space-filled. The parallelogram (from top to bottom) captures the four GS ribbons, preceded and followed by a ribbon that is shifted.

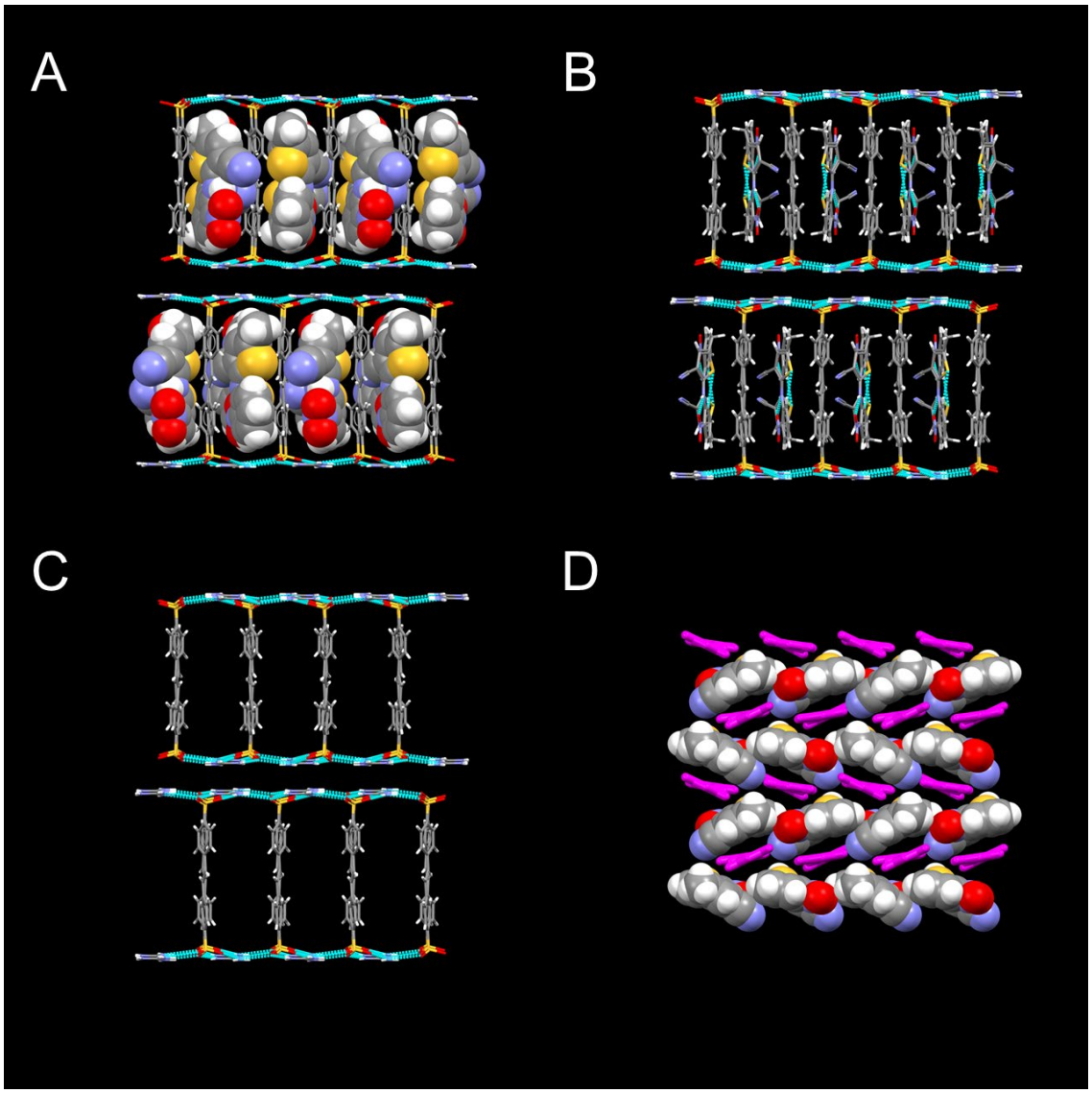


Fig. S6. Crystal structure of **4** viewed down the *a*-axis. (A) Guest molecules are rendered as space-filled and the host framework as stick. (B) Guests and host framework both rendered as stick. (C) View of the host framework *ac* plane without guests, illustrating the bilayer framework. (D) View of the *ab* plane with guanidinium and sulfonate ions removed to reveal the packing of the organic residues (magenta) of the organosulfonate pillars and the guests.

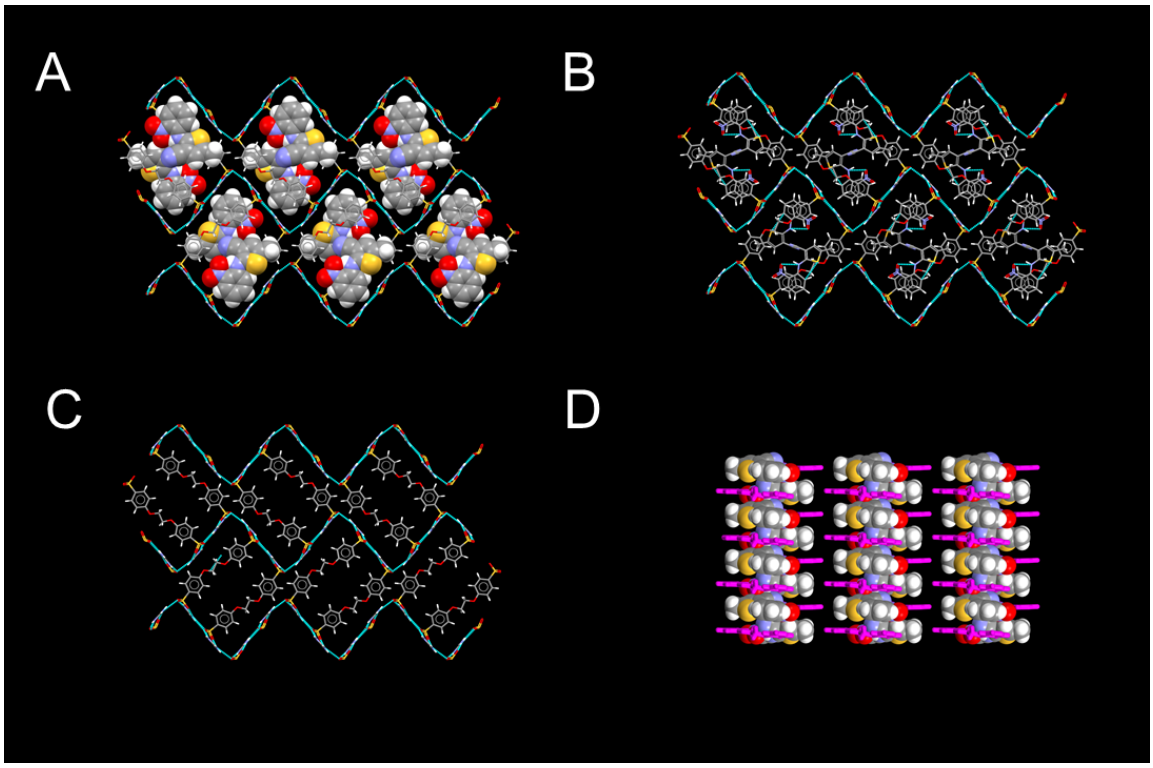


Fig. S7. Crystal structure of **5** viewed down the *a*-axis. (A) Guest molecules are rendered as space-filled and the host framework as stick. (B) Guests and host framework both rendered as stick. (C) View of the host framework *ac* plane without guests, illustrating the double brick framework. (D) View of the *ab* plane with guanidinium and sulfonate ions removed to reveal the packing of the organic residues (magenta) of the organosulfonate pillars and the guests.

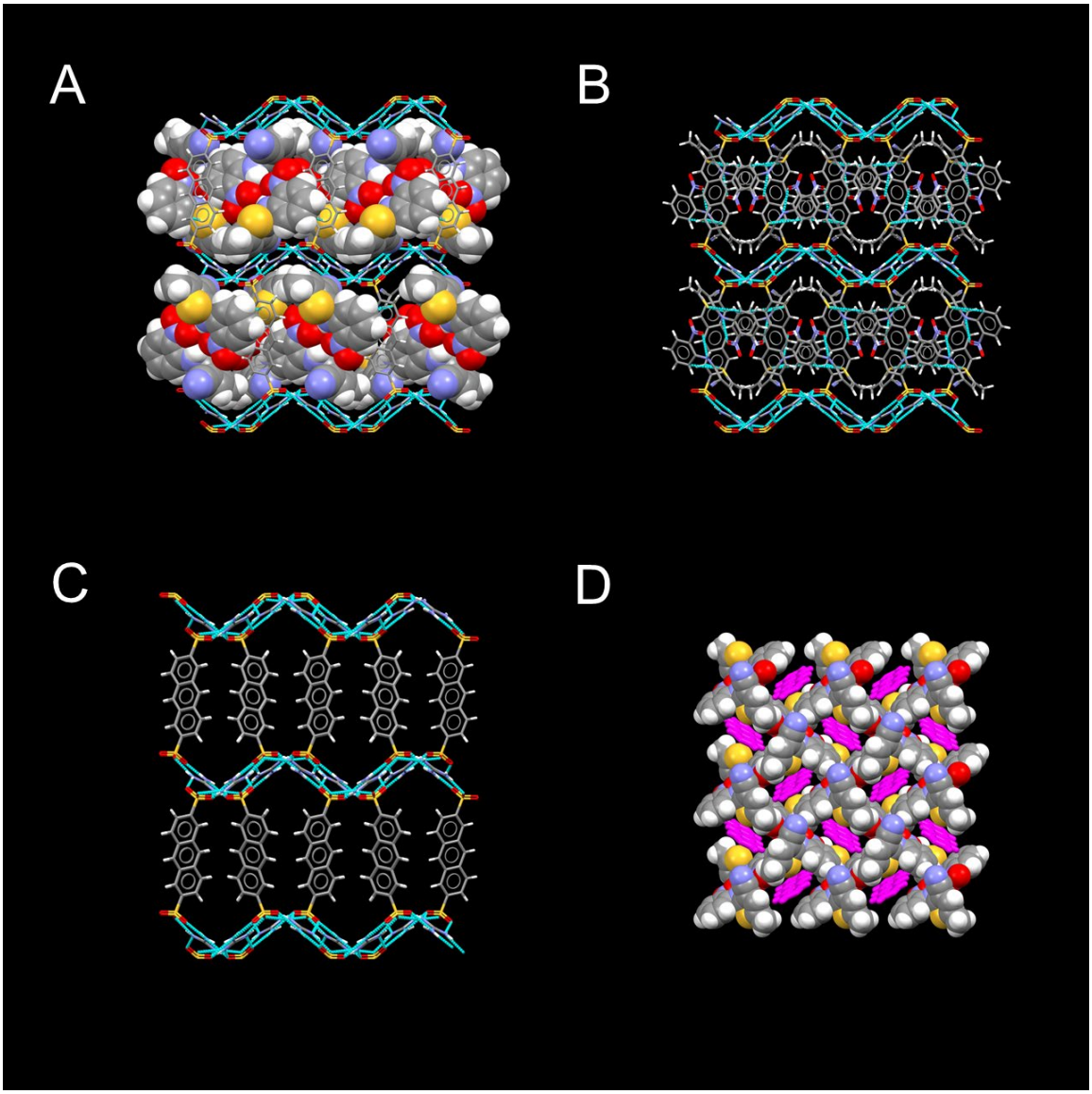


Fig. S8. Crystal structure of **6** viewed down the *b*-axis. (A) Guest molecules are rendered as space-filled and the host framework as stick. (B) Guests and host framework both rendered as stick. (C) View of the host framework *ac* plane without guests, illustrating the zigzag brick framework. (D) View of the *ab* plane with guanidinium and sulfonate ions removed to reveal the packing of the organic residues (magenta) of the organosulfonate pillars and the guests.

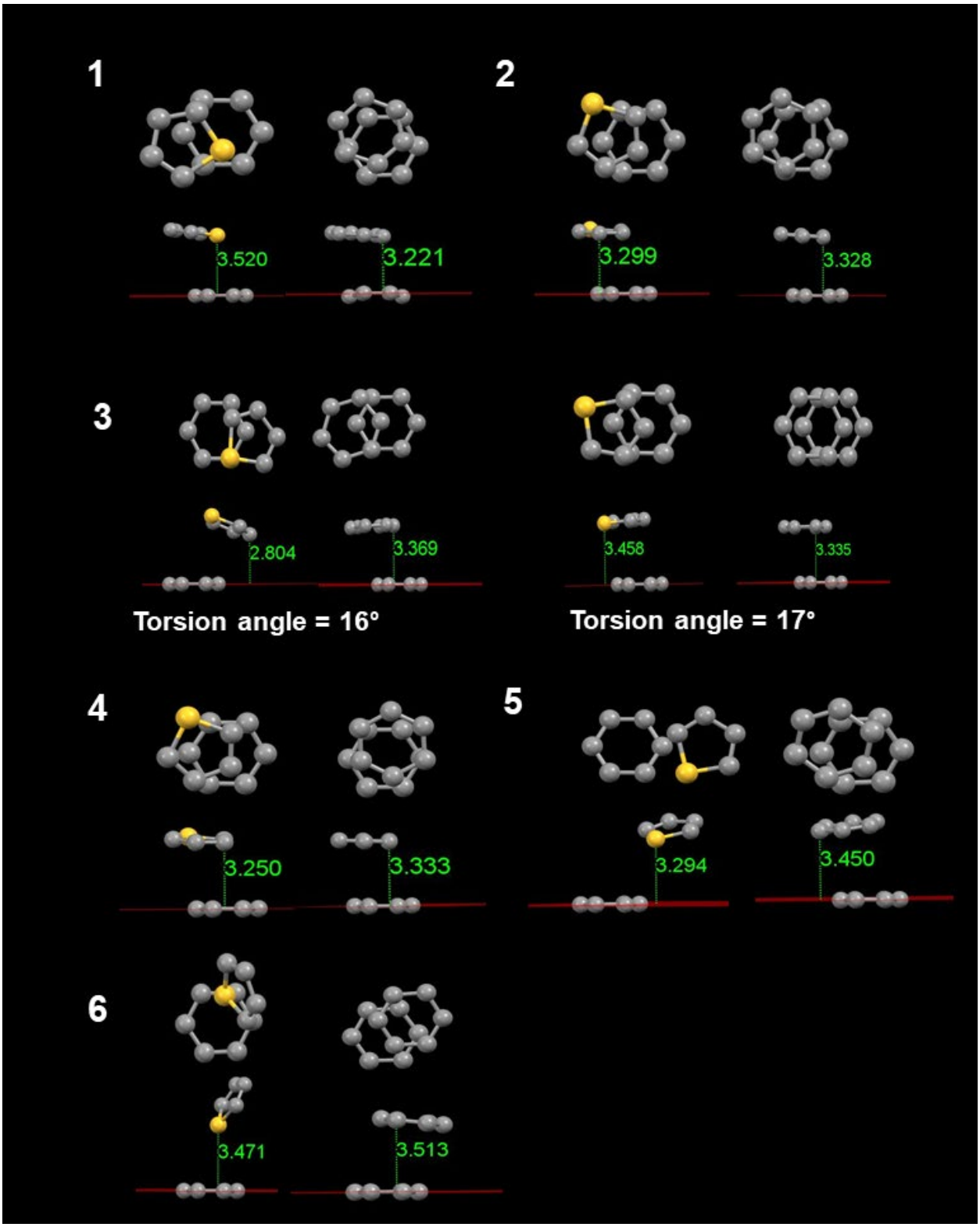


Fig. S9. Offset and distances between the ROY thiophene and phenyl ring planes and nearest pillar phenyl rings for inclusion compounds **1** - **6**.

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