Electronic Supporting Information

Supramolecular assemblies with water-soluble *p*-sulfonatothiacalix[6]arene lanthanide complexes: one-dimensional 'ladder-type' coordination polymers and hydrogen-bonded polymers

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Supporting Information Comprises:

Supplementary Table S1 S-π interactions as type I in crystals of **I-II** and type II in crystals of **III-VII**.

Supplementary Table S2 Hydrogen bonding among thiacalixarene, aquated Ln cations, and free water molecules within the pseudo 'up-down' cavities in crystals of **III-VII**.

Supplementary Figure S1 The molecular structures of complex **I** a) and complex **II** b) showing intramolecular hydrogen bonding and S···O interactions between a base half of unit of three sulfonated phenols and a reversed half unit of three other ones (light blue and pink dotted lines).

Supplementary Figure S2 The overall crystal structures of complexes a) **I** and b) **II** showing alternately stacking of two different directional layers when viewed along the [101] plane.

Supplementary Figure S3 The overall crystal structures of complexes a) **I** and b) **II** when viewed along the [011] plane

Supplementary Figure S4 The enlarged view of the same directional arrayed polymers of a) **I** and b) **II** showing the geometry of S-π interactions.

Supplementary Figure S5 Extended structures of complexes **I** and **II** showing S-π interactions and hydrogen bonding between the same directional arrayed polymers (green and light blue dotted lines).

Supplementary Figure S6 Extended structures of complexes **I** and **II** showing S···S interactions and hydrogen bonding between the different directional arrayed polymers (pink and blue dotted lines).

Supplementary Figure S7 The typical molecular structure of complexes **III-VII** showing intramolecular hydrogen bonding at a base half of unit of three phenols and a reversed half unit of three other ones (light blue dotted lines).

Supplementary Figure S8 Hydrogen bonding of thiacalixarene molecule and two aquated lanthanide metal cations in the 'up-down' double partial cone cavities of complex **III**; each aquo-metal cation experiences two hydrogen bond interactions between sulfonate groups of the thiacalixarene molecule (light blue dotted lines). Non-coordinated water molecules omitted for clarity.

Supplementary Figure S9 The enlarged projection showing hydrogen bonding among sulfonate groups of the thiacalixarene molecule, water molecules, and aquo-metal cation in complex **III** (light blue dotted lines). Hydrogen atoms of two disordered water molecules are not considered. Disordered positions of water molecules have been omitted for clarity.

Supplementary Figure S10 Projection of the thiacalixarene showing intramolecular OH···aromatic π and ArOH···O hydrogen bonding of the water molecules with the thiacalixarene molecule in the pseudo 'thiacalix[3]arene-like' cavities of complex **III** (light blue dotted lines).

Supplementary Figure S11 The overall crystal structures of complex **III** showing alternately stacking of two different directional layers when viewed along the [011] plane.

Supplementary Figure S12 The bilayer structure of complex **III** when viewed along the [101] plane.

Supplementary Figure S13 The enlarged view of the same directional arrayed polymers of complex **III** showing the geometry of S-π interactions.

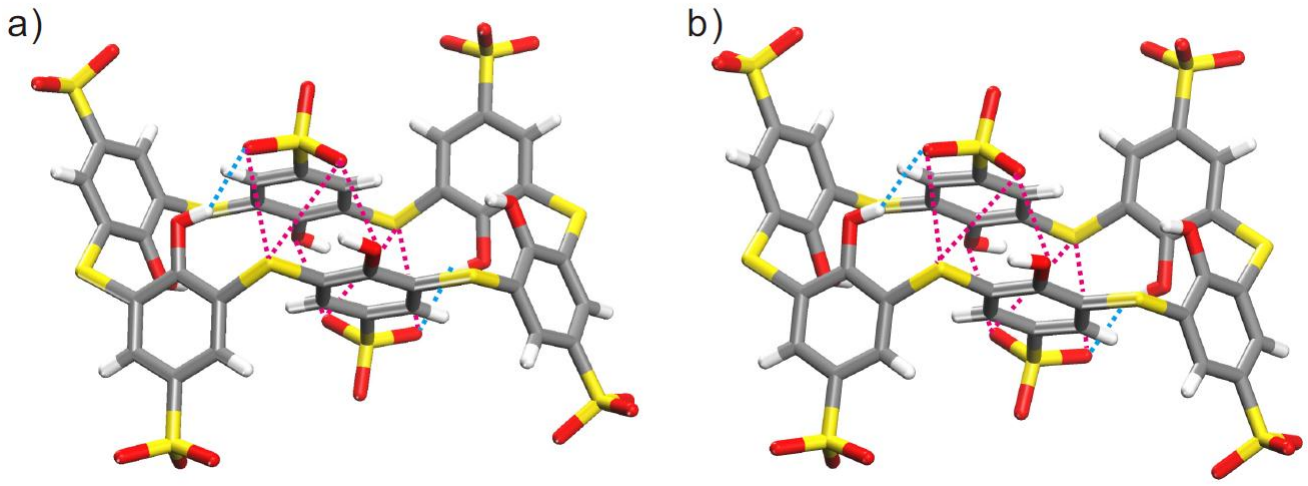
Supplementary Table S1 S-π interactions as type I in crystals of **I-II** and type II in crystals of **III-VII**.

	r (Å)	*d* (Å)	φ (º)	α (º)	α' (º)
I	3.429	3.681	88.94	92.39	127.62
II	3.394	3.560	87.81	93.65	127.54
III	3.450	3.212	68.55	92.10	166.19
IV	3.444	3.210	68.72	92.16	166.11
V	3.441	3.206	68.65	92.14	166.42
VI	3.442	3.205	68.60	92.20	166.53
VII	3.684	3.401	67.08	91.29	164.67

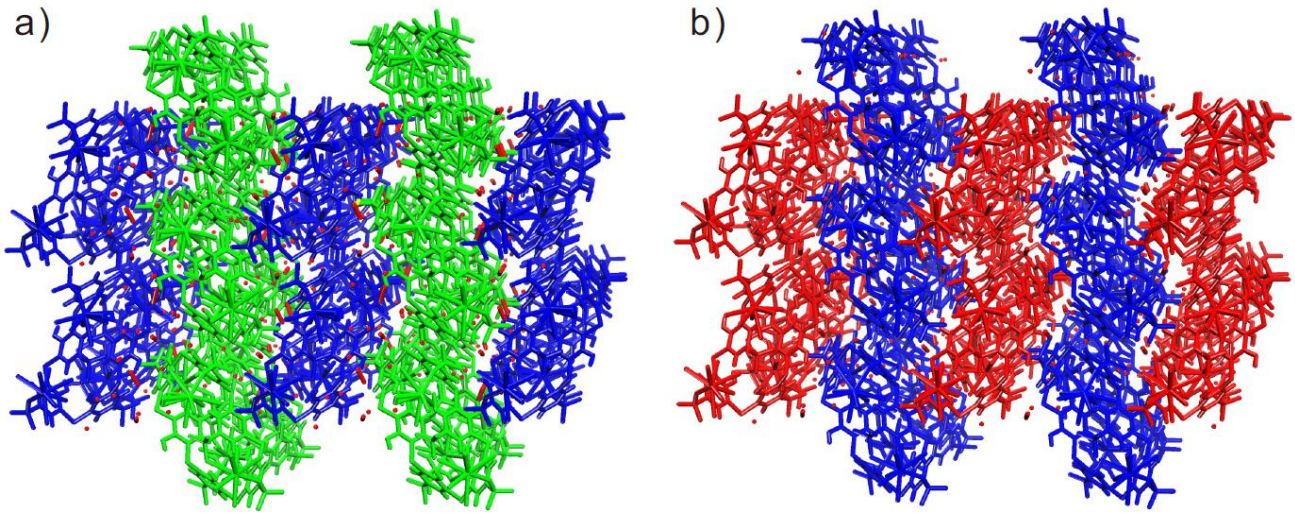
Supplementary Table S2 Hydrogen bonding among thiacalixarene, aquated Ln cations, and free water molecules within the pseudo 'up-down' cavities in crystals of **III-VII**.

	Ln-OH···O-SO_2 [1)] (Ln-O···O-SO_2) (Å)	O_2S-O···O[2)] (Å)	HOH···OH_2 [3)] (O···O) (Å)	HOH···π [4)] (O···π) (Å)	Ar-OH···O[5)] (Å)
III	1.997, 2.236 (2.795, 2.983)	2.806	1.883- 1.965 (2.681-2.702)	2.532 (3.263)	1.923
IV	2.079, 2.207 (2.792, 2.985)	2.797	1.812-1.971 (2.598-2.736)	2.559 (3.267)	1.926
V	1.957, 2.158 (2.794, 2.987)	2.816	1.836-1.950 (2.600-2.741)	2.555 (3.251)	1.875
VI	- (2.780, 2.984)	2.827	- (2.600-2.757)	- (3.273)	1.919
VII	- (2.706, 2.739)	2.852	- (2.638-3.025)	- (3.344)	2.079

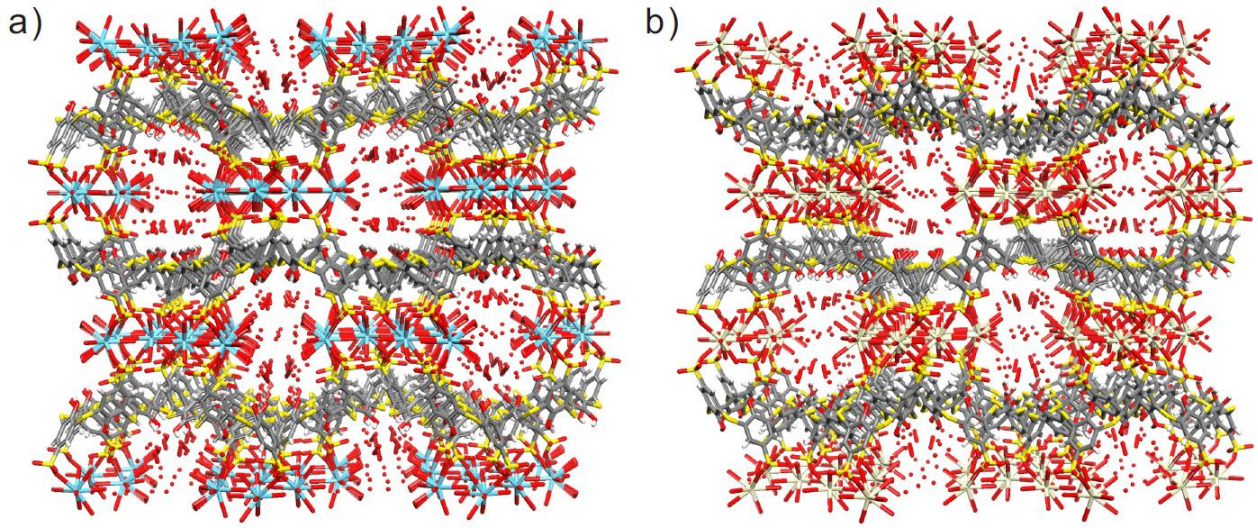
1) Hydrogen bonding between aquo-metal cations and sulfonate groups of the thiacalixarene. In **VI-VII**, hydrogen atoms of coordinated water molecules and free water molecules were not considered.
2) Hydrogen bonding between sulfonate group of the thiacalixarene and imbedded disordered water molecule (hydrogen atoms of the disordered water molecules are not considered).
3) Hydrogen bonding between imbedded disordered water molecules and coordinated water molecules of aquated lanthanide metal cations. In **VI-VII**, hydrogen atoms of coordinated water molecules and free water molecules were not considered.
4) OH-aromatic π hydrogen bonding between imbedded water molecules and aromatic moieties in the thiacalixarene molecule. In **VI-VII**, hydrogen atoms of coordinated water molecules and free water molecules were not considered.
5) Hydrogen bonding between the pendent phenolic hydroxyl group and embedded water molecule in each cavity.



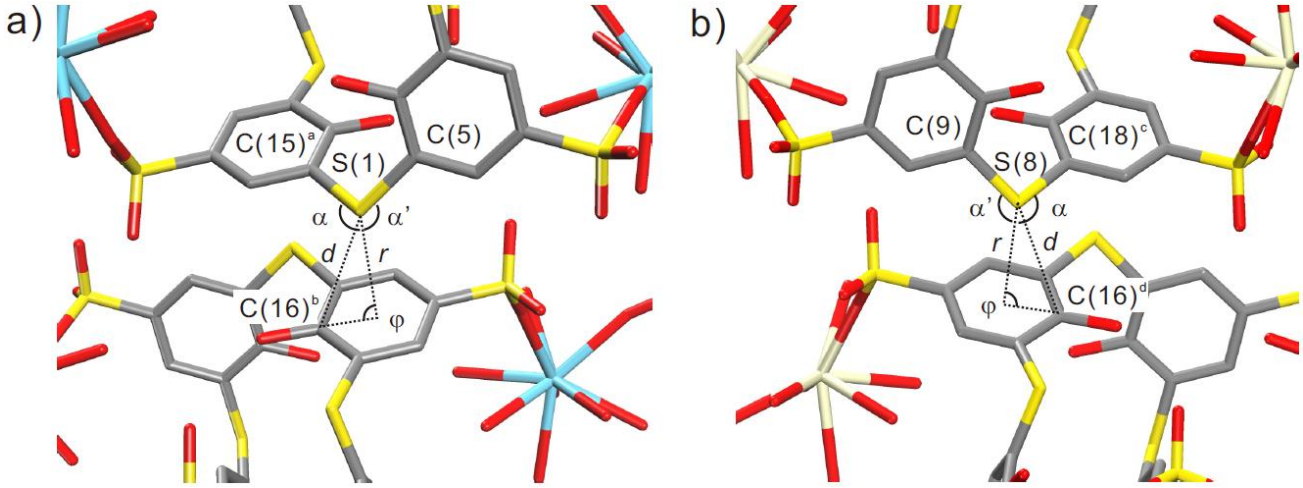
Supplementary Figure S1 The molecular structures of complex **I** a) and complex **II** b) showing intramolecular hydrogen bonding and S···O interactions between a base half of unit of three sulfonated phenols and a reversed half unit of three other ones (light blue and pink dotted lines). Selected distances of complex **I**: SO···O-Ar 3.232 Å, SO···HO-Ar 2.051 Å, SO···S 3.384 and 3.468 Å. Selected distances of complex **II**: SO···O-Ar 3.138 Å, SO···HO-Ar 2.103 Å, SO···S 3.367 and 3.429 Å.



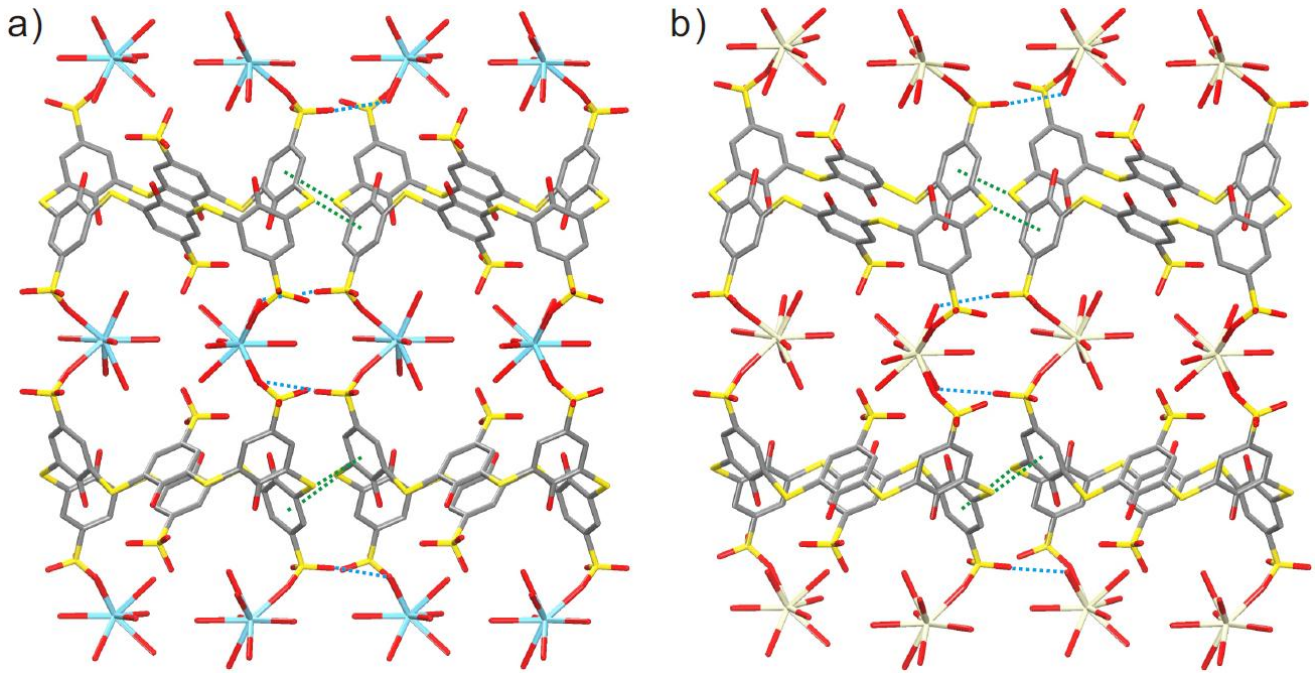
Supplementary Figure S2 The overall crystal structures of complexes a) **I** and b) **II** showing alternately stacking of two different directional layers when viewed along the [101] plane.



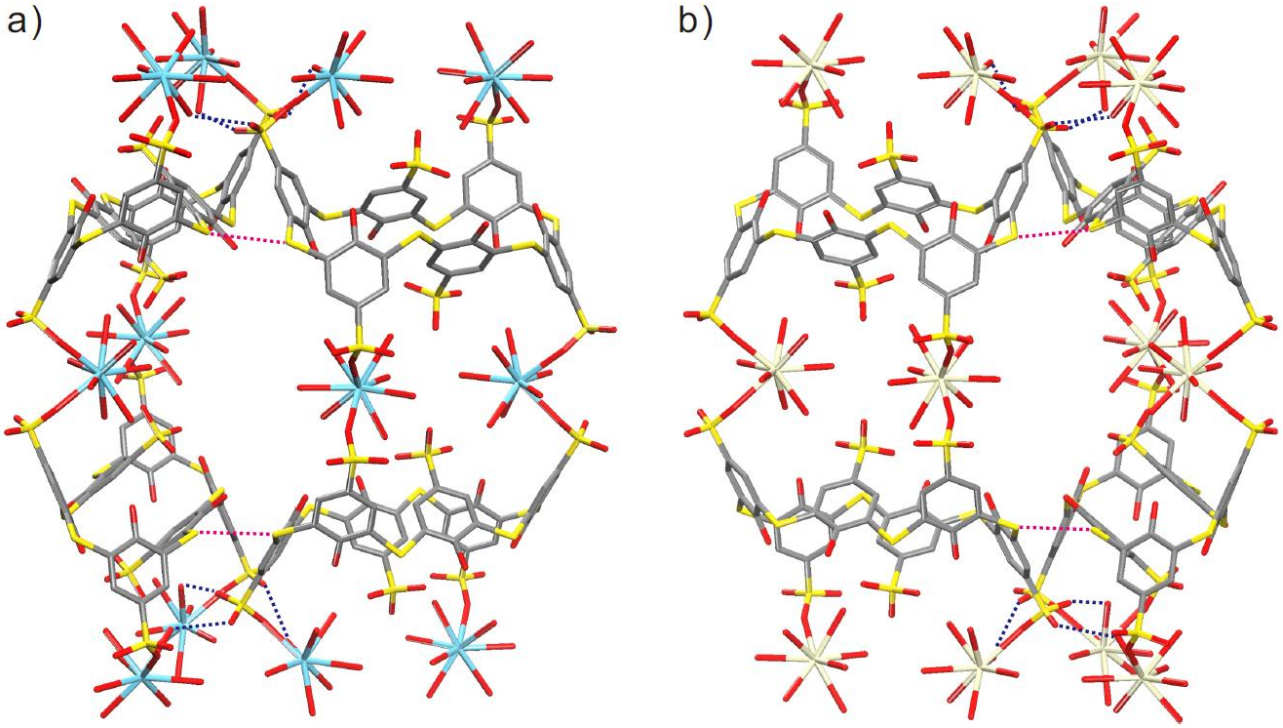
Supplementary Figure S3 The overall crystal structures of complexes a) **I** and b) **II** when viewed along the [011] plane.



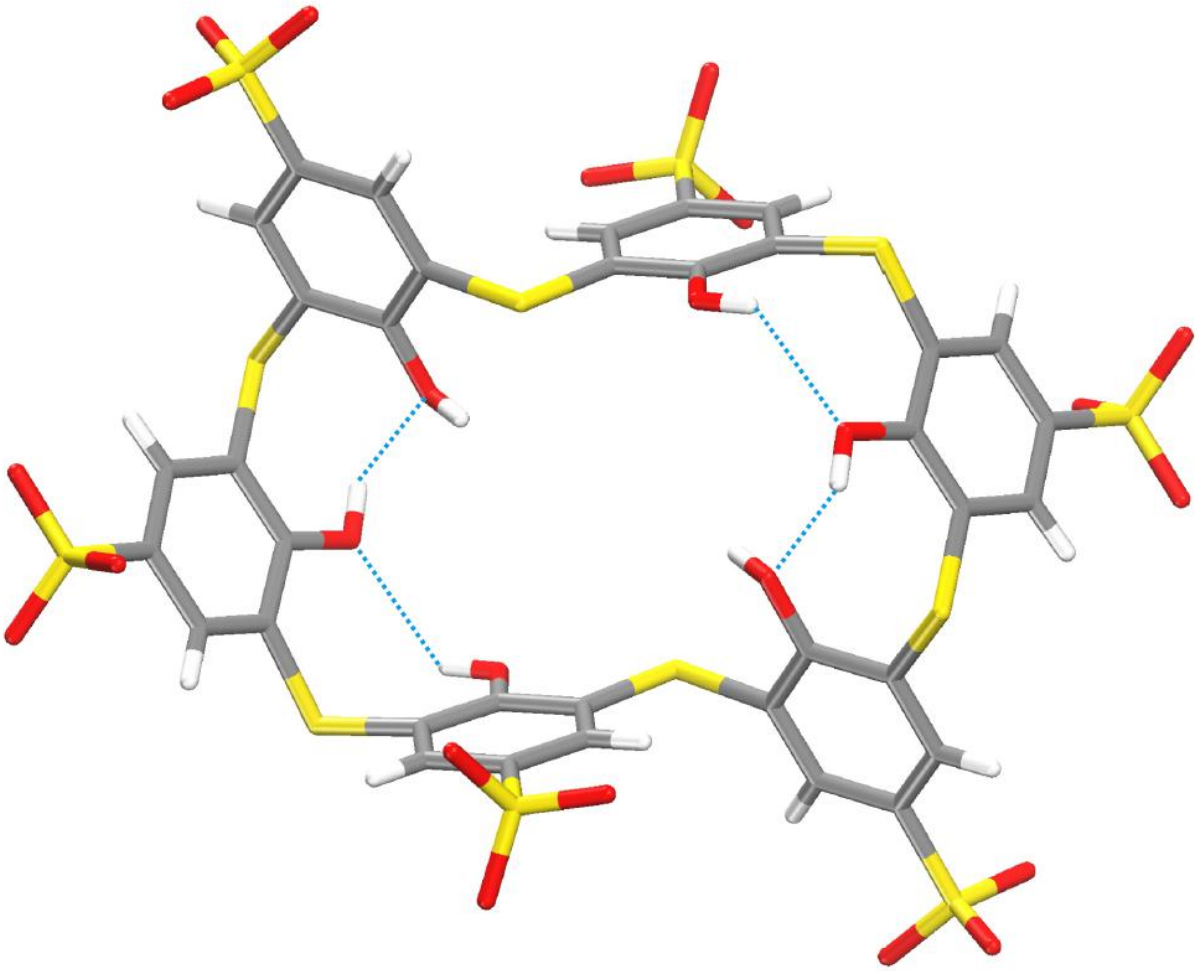
Supplementary Figure S4 The enlarged view of the same directional arrayed polymers of a) **I** and b) **II** showing the geometry of S-π interactions. Selected distances and angles of complex **I**: S(1)···centroid (*r*) 3.429 Å, S(1)···C(16)^{e} (*d*) 3.681 Å, C(15)^{a} -S(1)-centroid (α) 92.39º and C(5)-S(1)-centroid (α') 127.62º, and S(1)-centroid-C(16)^{b} (*φ*) 88.94º. Selected distances and angles of complex **II**: S(8)···centroid (*r*) 3.394 Å, S(8)···C(16)^{d} (*d*) 3.600 Å, C(18)^{c} -S(8)-centroid (α) 93.65º and C(9)-S(8)-centroid (α') 127.54º, and S(8)-centroid-C(16)^{d} (*φ*) 87.81º . Symmetry codes: ^{a}, 1–*x*, 1–*y*, 2–*z*; ^{b}, –1+*x*, *y*, *z*; ^{c}, 1–*x*, 1–*y*, 1–*z*; ^{d}, 1+*x*, *y*, *z*.



Supplementary Figure S5 Extended structures of complexes **I** and **II** showing S-π interactions and hydrogen bonding between the same directional arrayed polymers (green and light blue dotted lines).



Supplementary Figure S6 Extended structures of complexes **I** and **II** showing S···S interactions and hydrogen bonding between the different directional arrayed polymers (pink and blue dotted lines).



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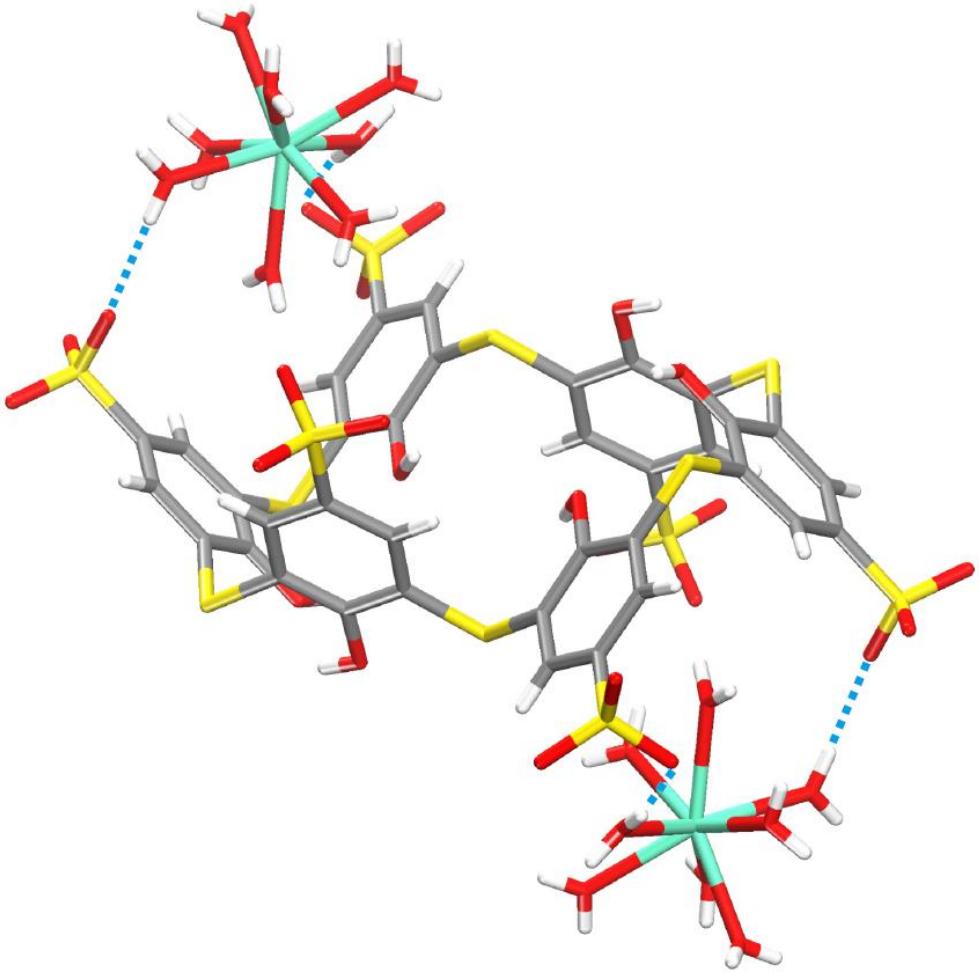

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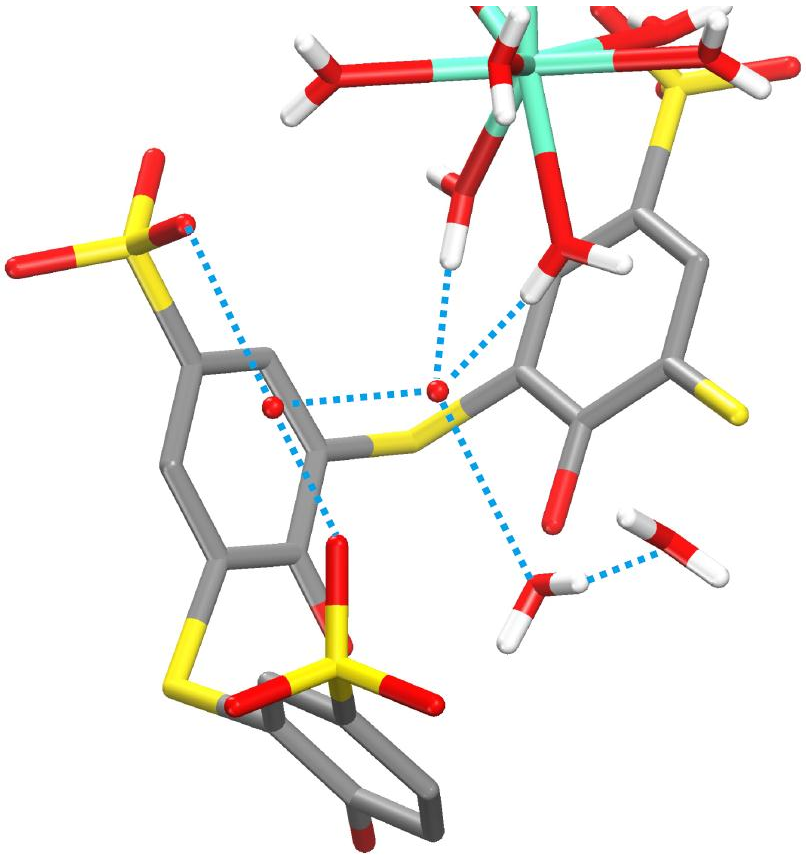

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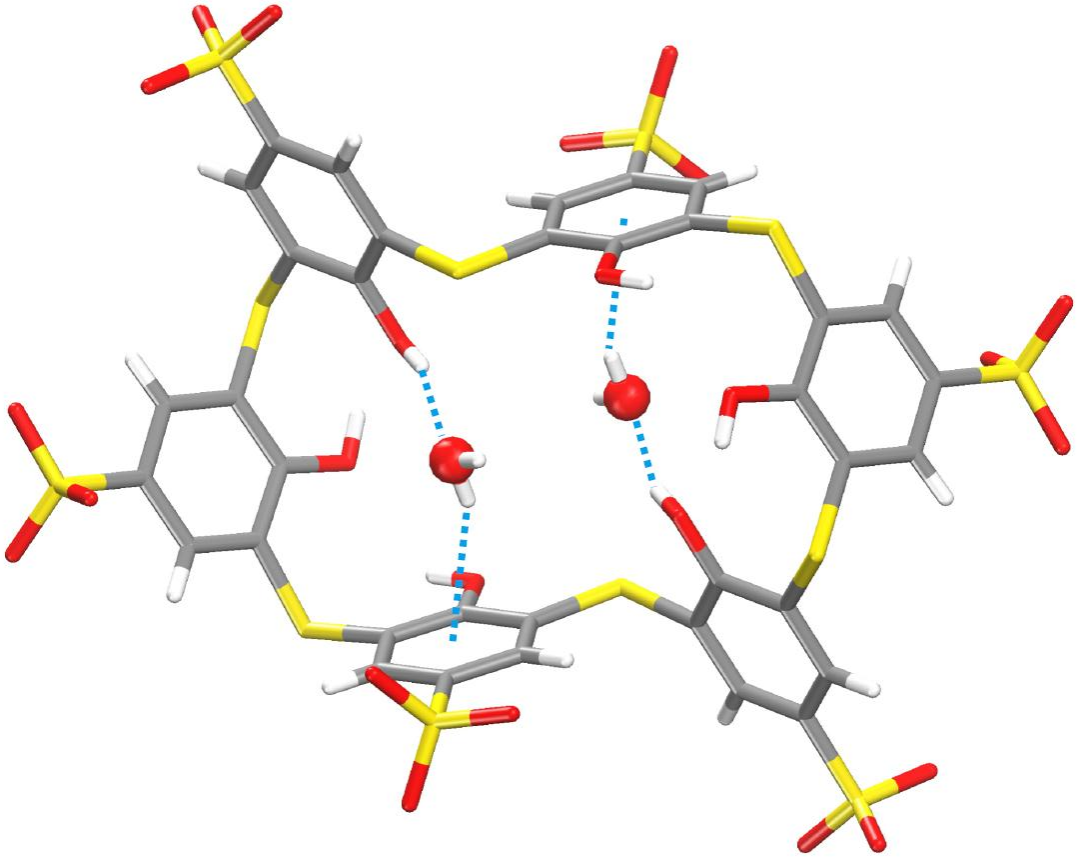

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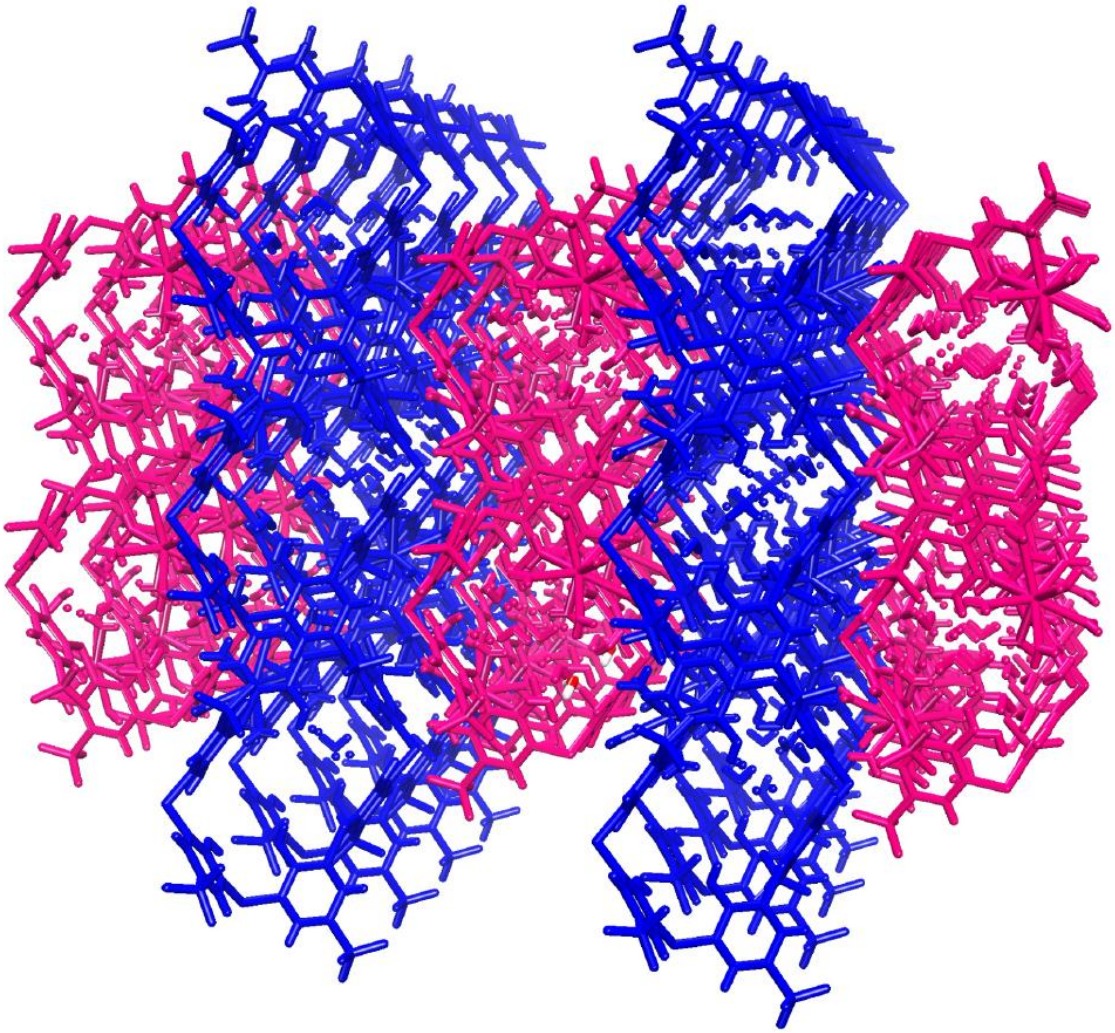

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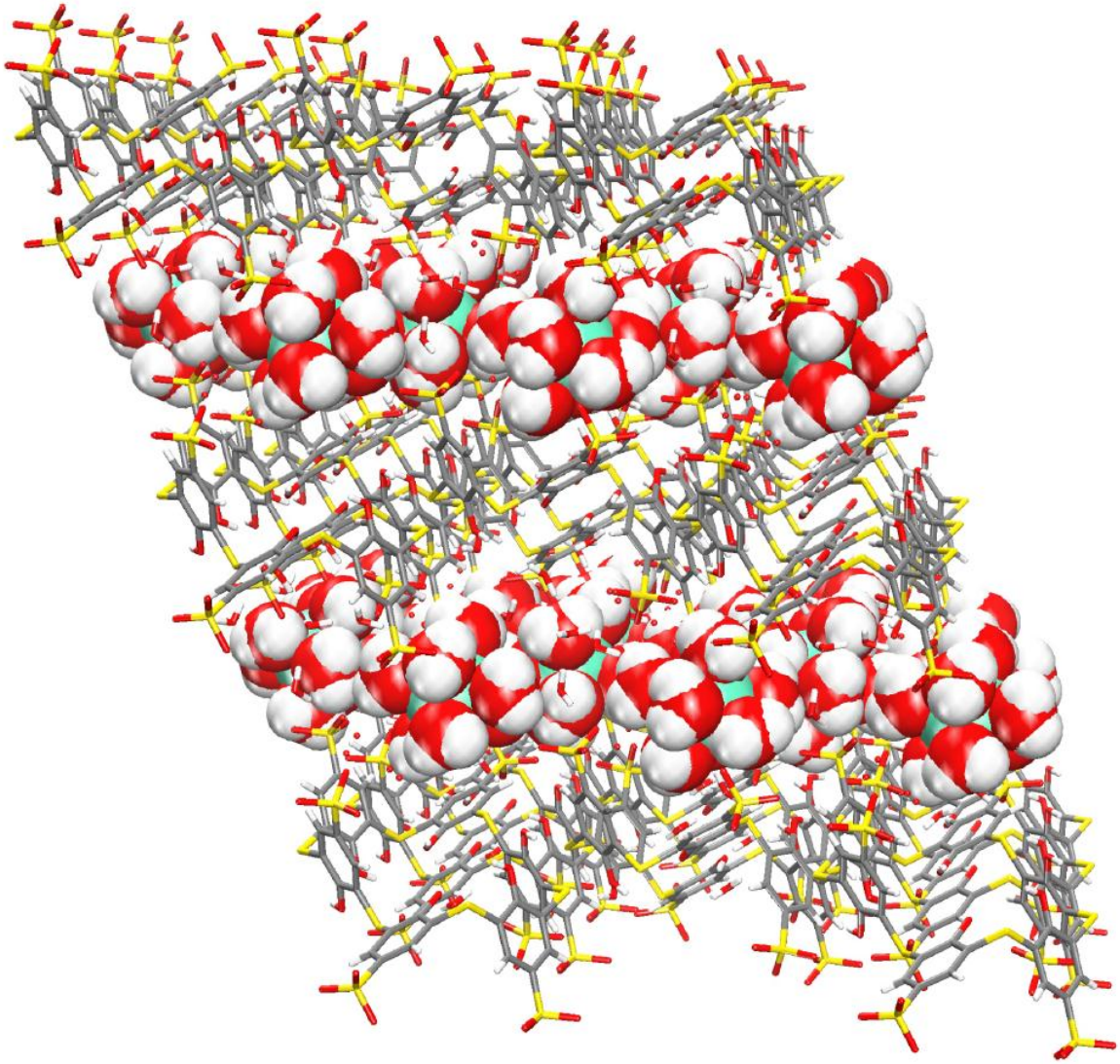

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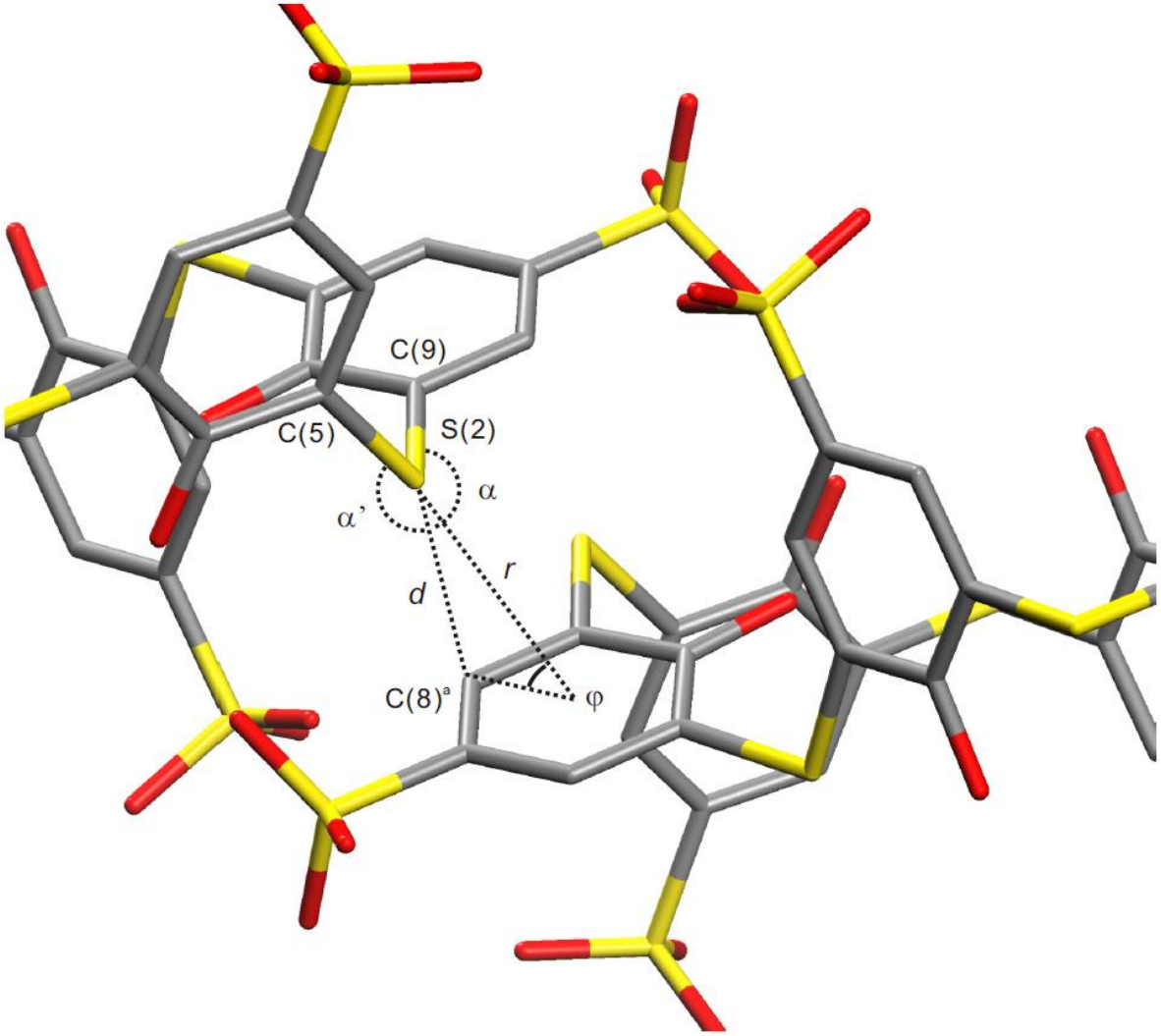

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