Supporting Information

Halogen–halogen interactions and halogen bonding in thiacalixarene systems

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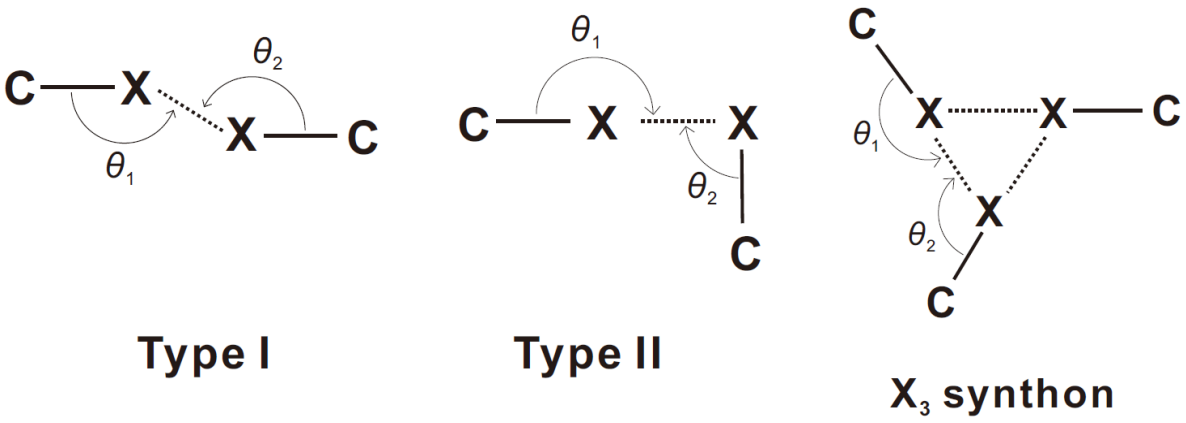
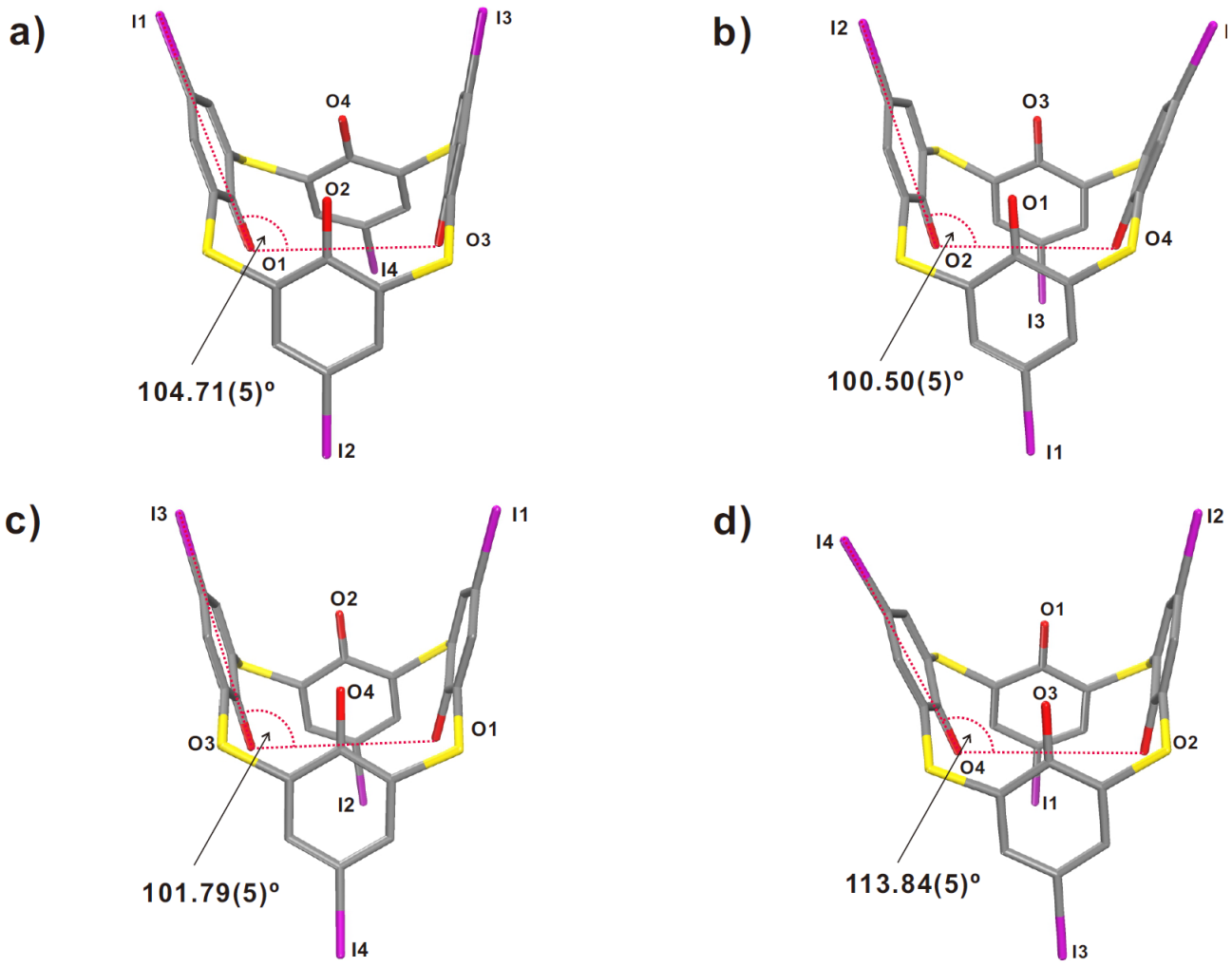
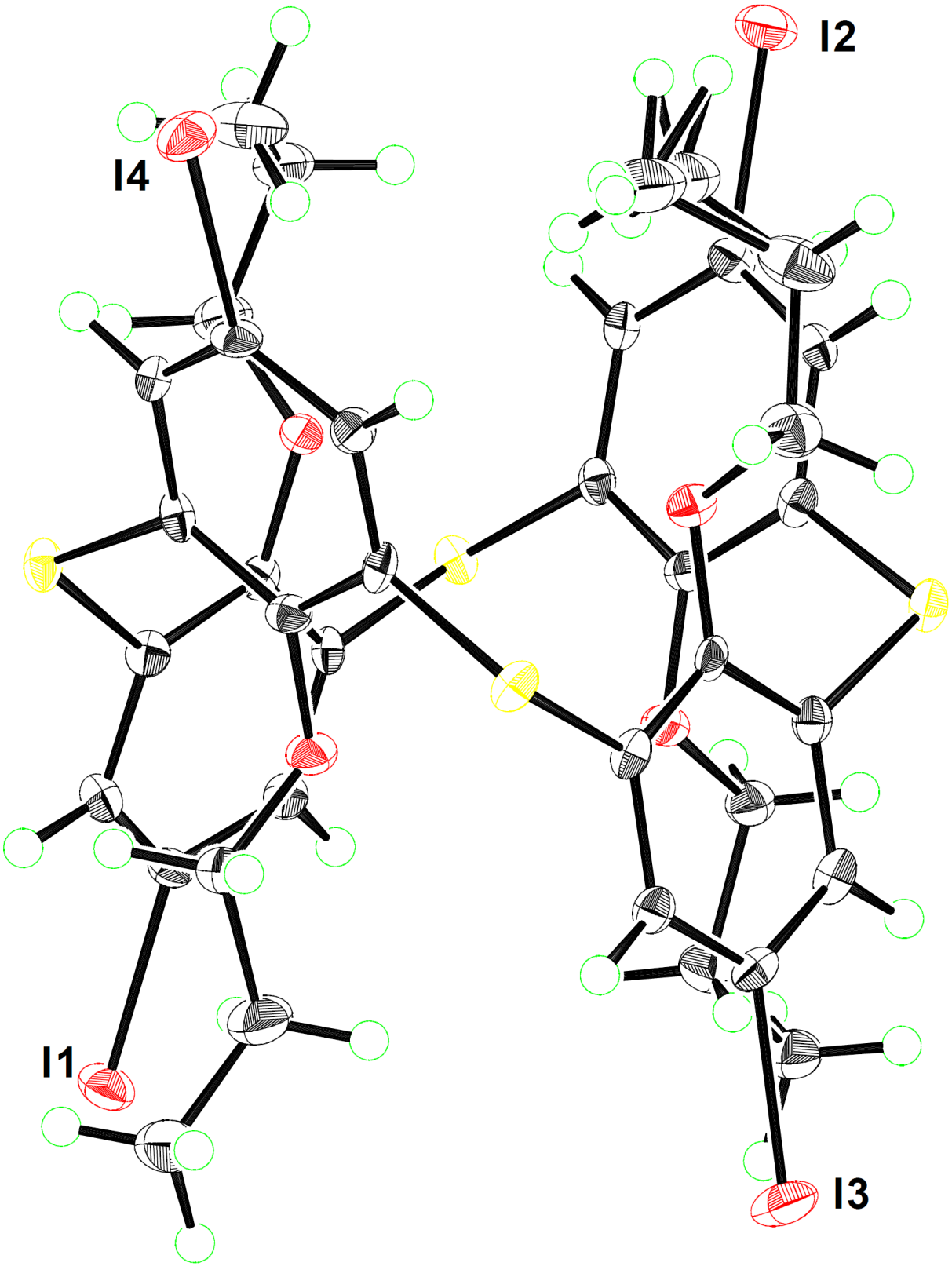


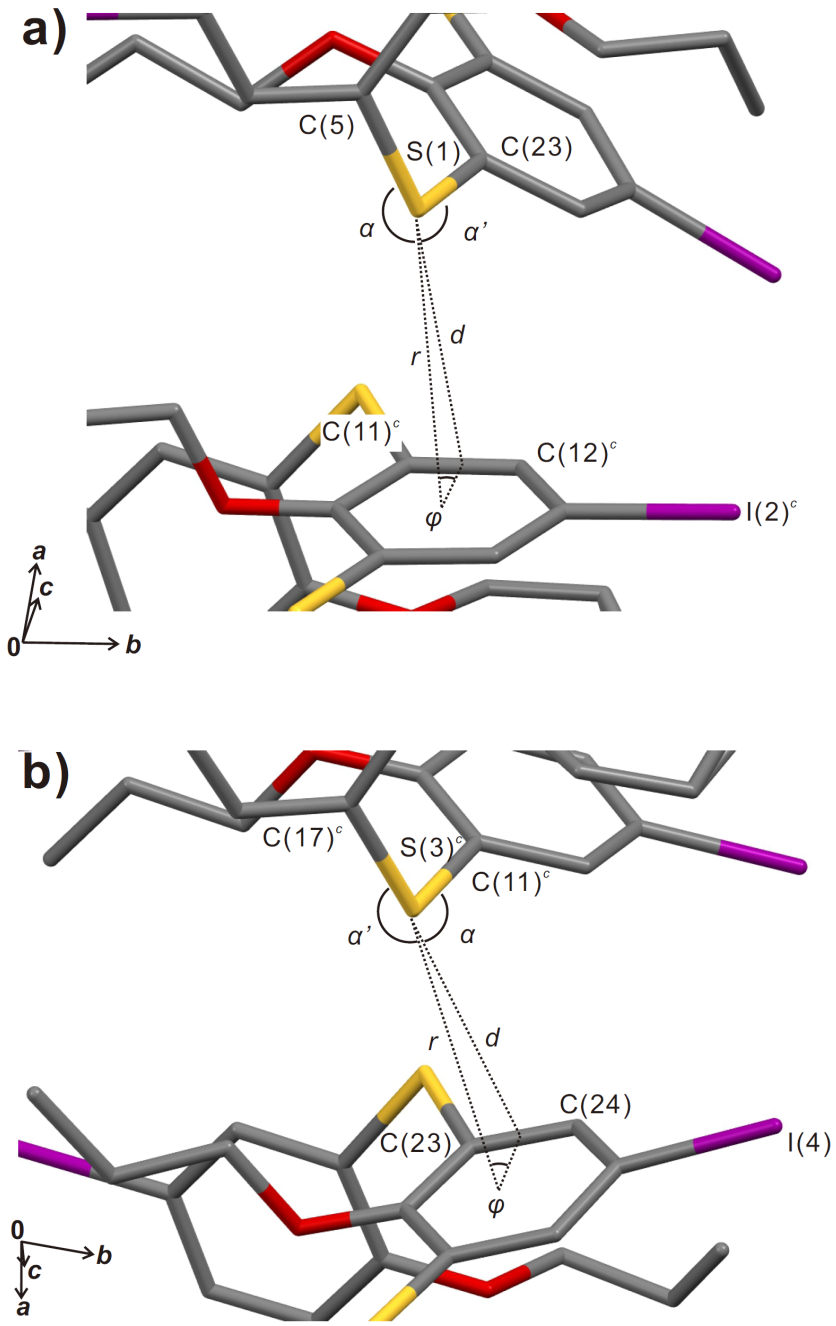
Supplementary Figure S1 Schematic representations of Type I, Type II, and X_3 synthon halogen-halogen contacts. The angles: Type I (θ_1=θ_2=140–180º) and Type II (θ_1=150–180º, θ_2=90–120º). The X_3 synthon is a trigonal array of halogen atoms with attractive electrophile-nucleophile Type II contacts.



Supplementary Figure S2 A comparison of each angle in the molecular structure of **2**. In a)–d) hydrogen atoms and the propyl groups have been removed for clarity. I = purple, S = yellow, O = red, C = gray. Selected bond angles: a) I(1)–O(1)–O(3) 104.71(5)º, b) I(2)–O(2)–O(4) 100.50(5)º, c) I(3)–O(3)–O(1) 101.79(5)º, d) I(4)–O(4)–O(2) 113.84(5)º.



Supplementary Figure S3 The ORTEP diagram of the asymmetric unit of crystal **2** with thermal ellipsoids at 50% probability.



Supplementary Figure S4 The intermolecular S–π interaction between the linking sulfur atom of thiacalixarene molecule and aromatic moiety of thiacalixarene molecule in crystals of **2**. I = purple, S = yellow, O = red, C = gray. All hydrogen atoms have been removed for clarity.

Symmetry operation: ^{c}, –1+*x*, *y*, *z*.

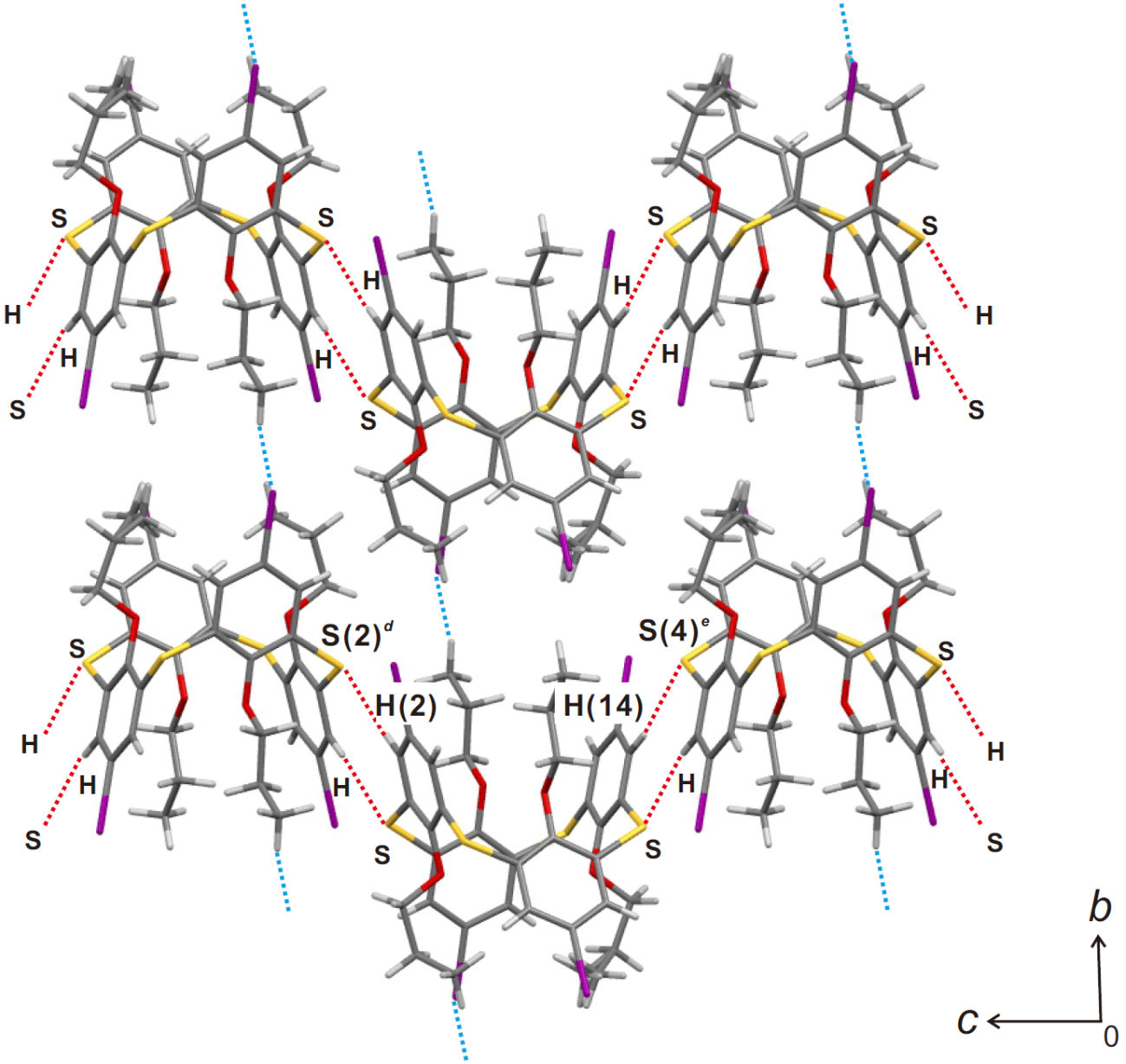
a) r = 3.746 Å, d = 3.613 Å, α = 98.22º, α' = 155.24º, and φ = 74.36º.

b) r = 3.782 Å, d = 3.636 Å, α = 96.77º, α' = 159.60º, and φ = 73.85º.

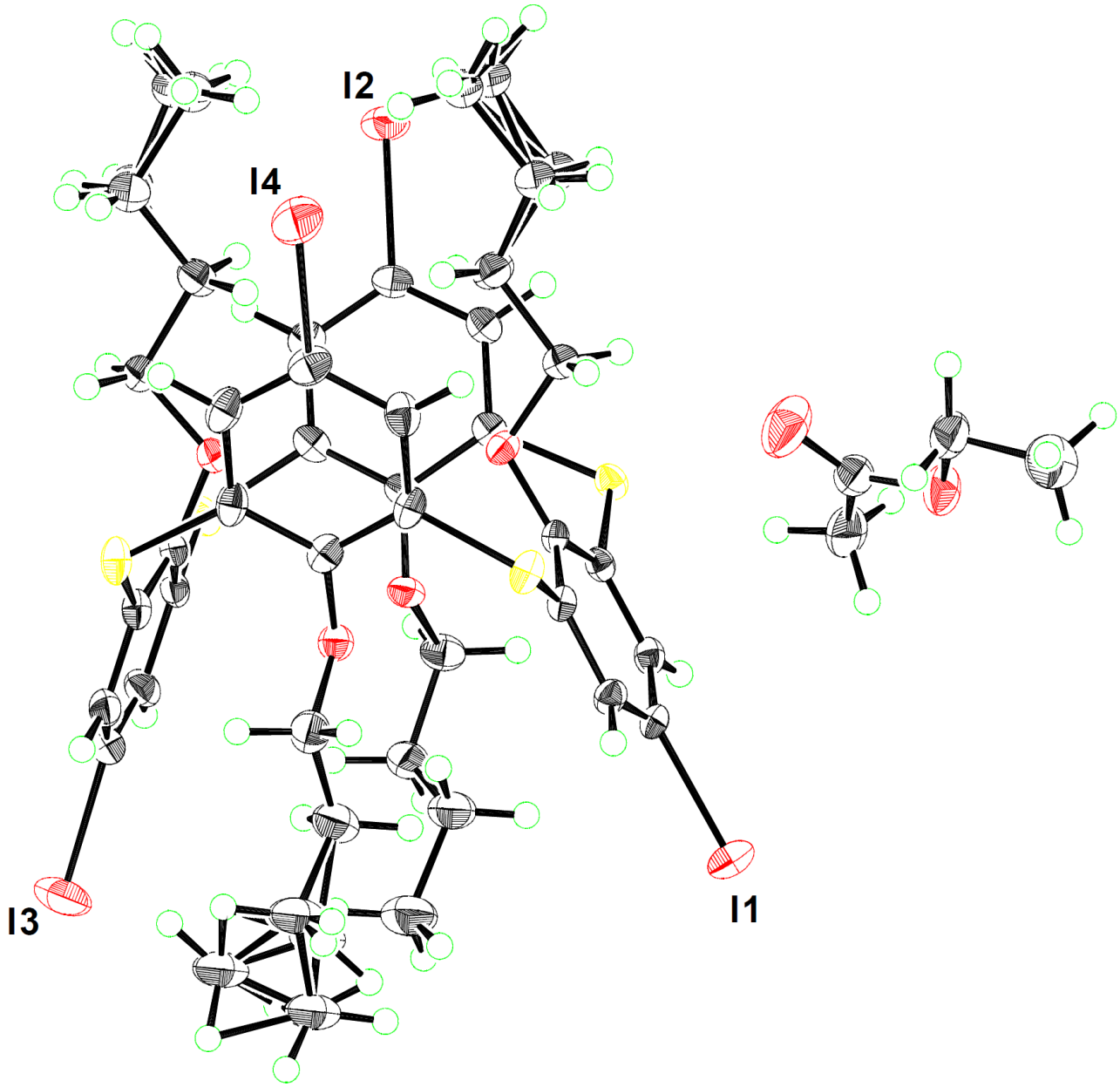
The parameter values of r, d, α, α', and φ lie in the allowable range of S–π interactions.[S1]

Reference

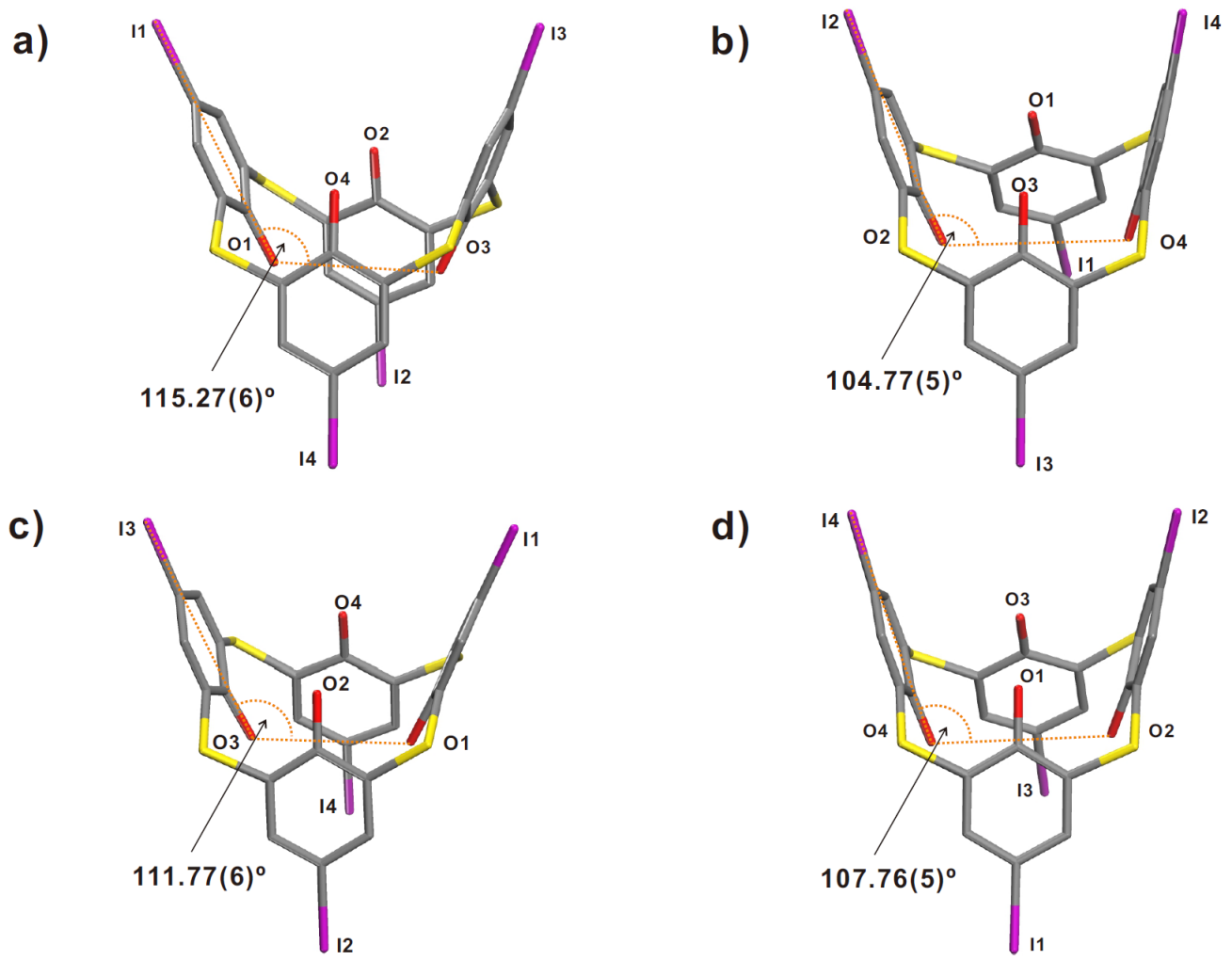
S1 C. –Q. Wan, J. Han and C. W. M. Thomas, *New J. Chem.*, 2009, **33**, 707–712



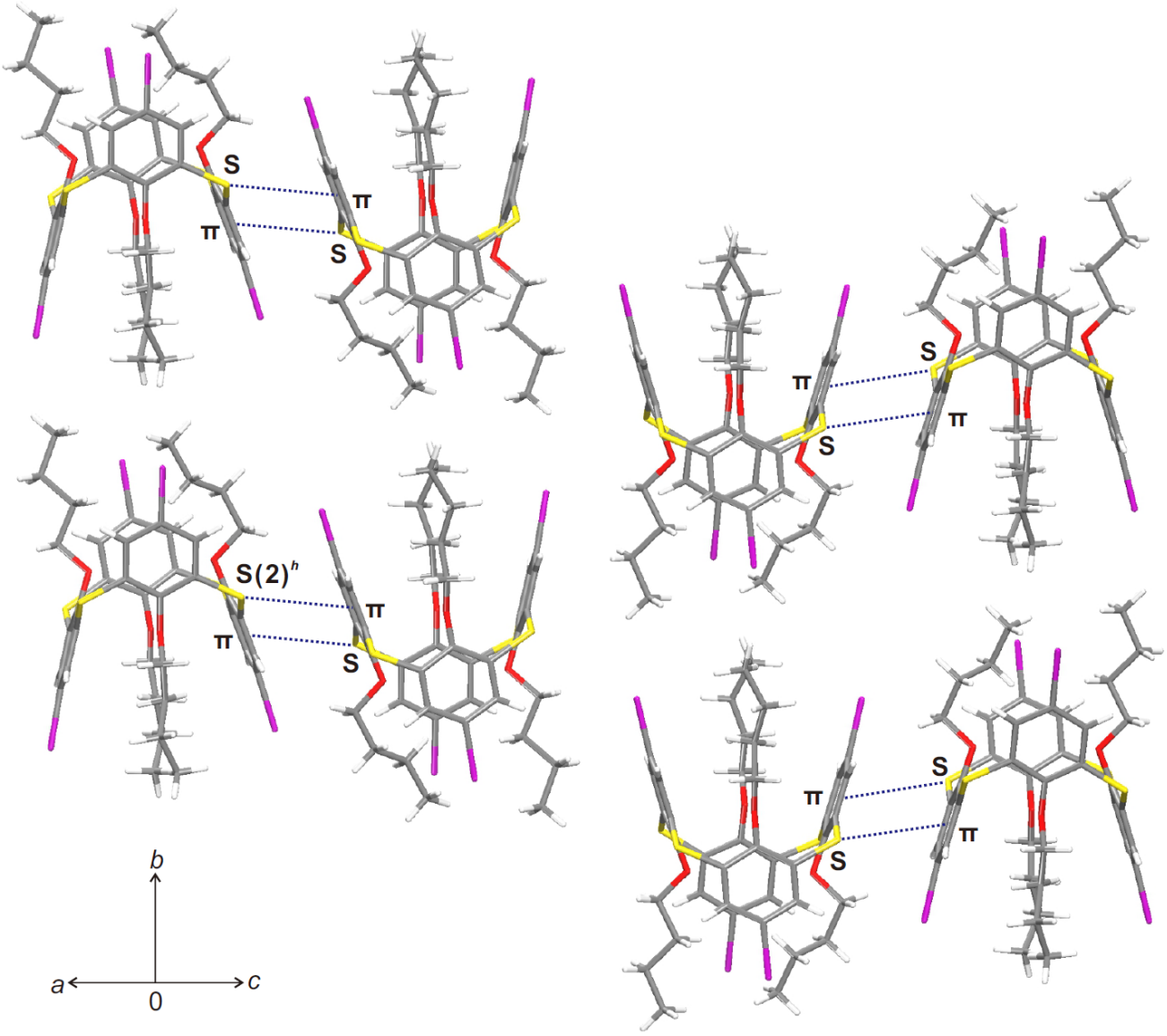
Supplementary Figure S5 Stick diagram showing hydrogen bonding (red dotted lines) and CH···I interactions (light-blue dotted lines) in crystal structure of **2**, viewed along the [011] plane. Symmetry operations: [d], 2–*x*, –*y*, 1–*z*; [e], 1–*x*, –*y*, 2–*z*.



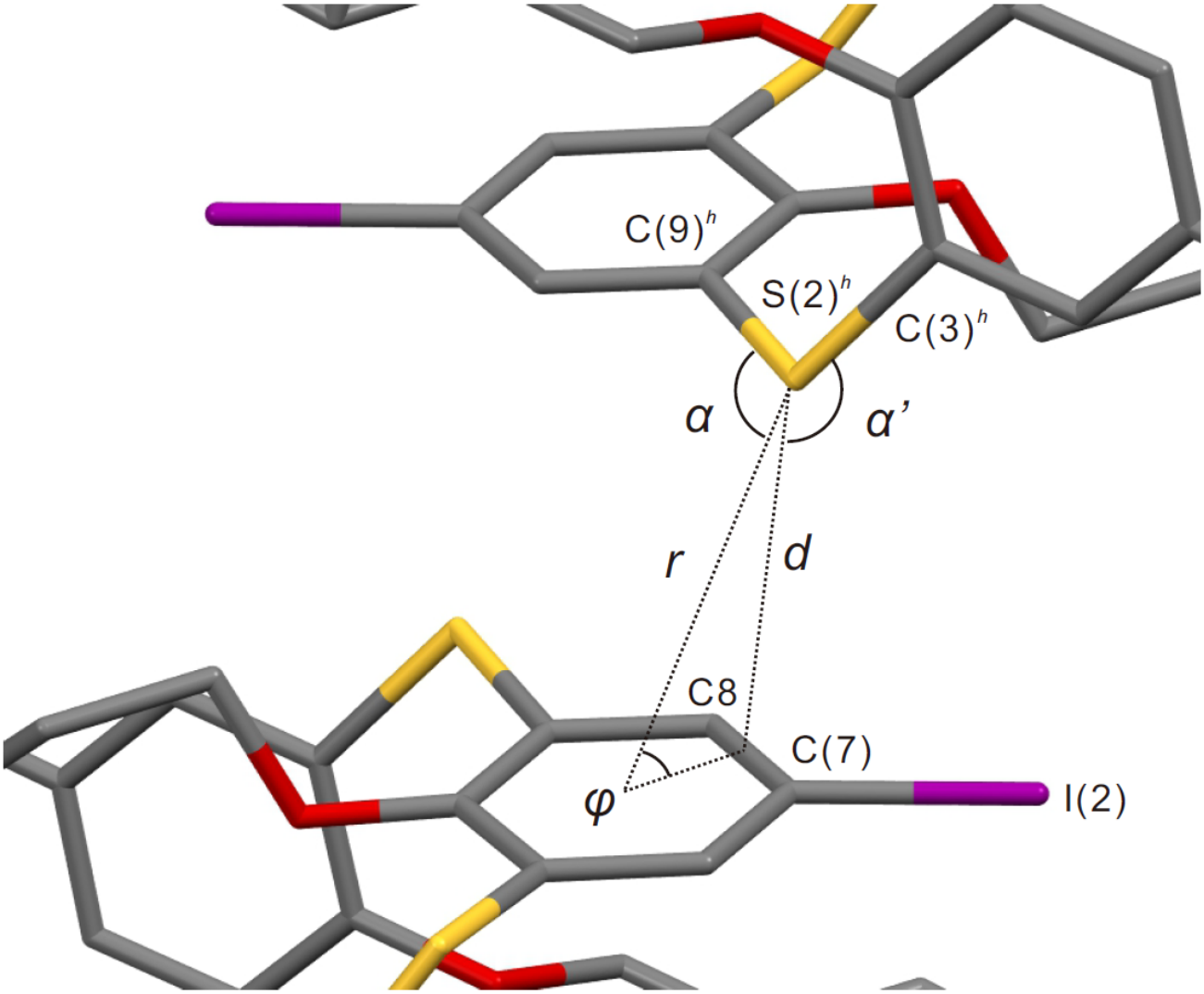
Supplementary Figure S6 The ORTEP diagram of the asymmetric unit of crystal **3** with thermal ellipsoids at 50% probability.



Supplementary Figure S7 A comparison of each angle in the molecular structure of **3**. In a)–d) hydrogen atoms and the propyl groups have been removed for clarity. I = purple, S = yellow, O = red, C = gray. Selected bond angles: a) I(1)–O(1)–O(3) 115.27(6)º, b) I(2)–O(2)–O(4) 104.77(5)º, c) I(3)–O(3)–O(1) 111.77(6)º, d) I(4)–O(4)–O(2) 107.76(5)º.



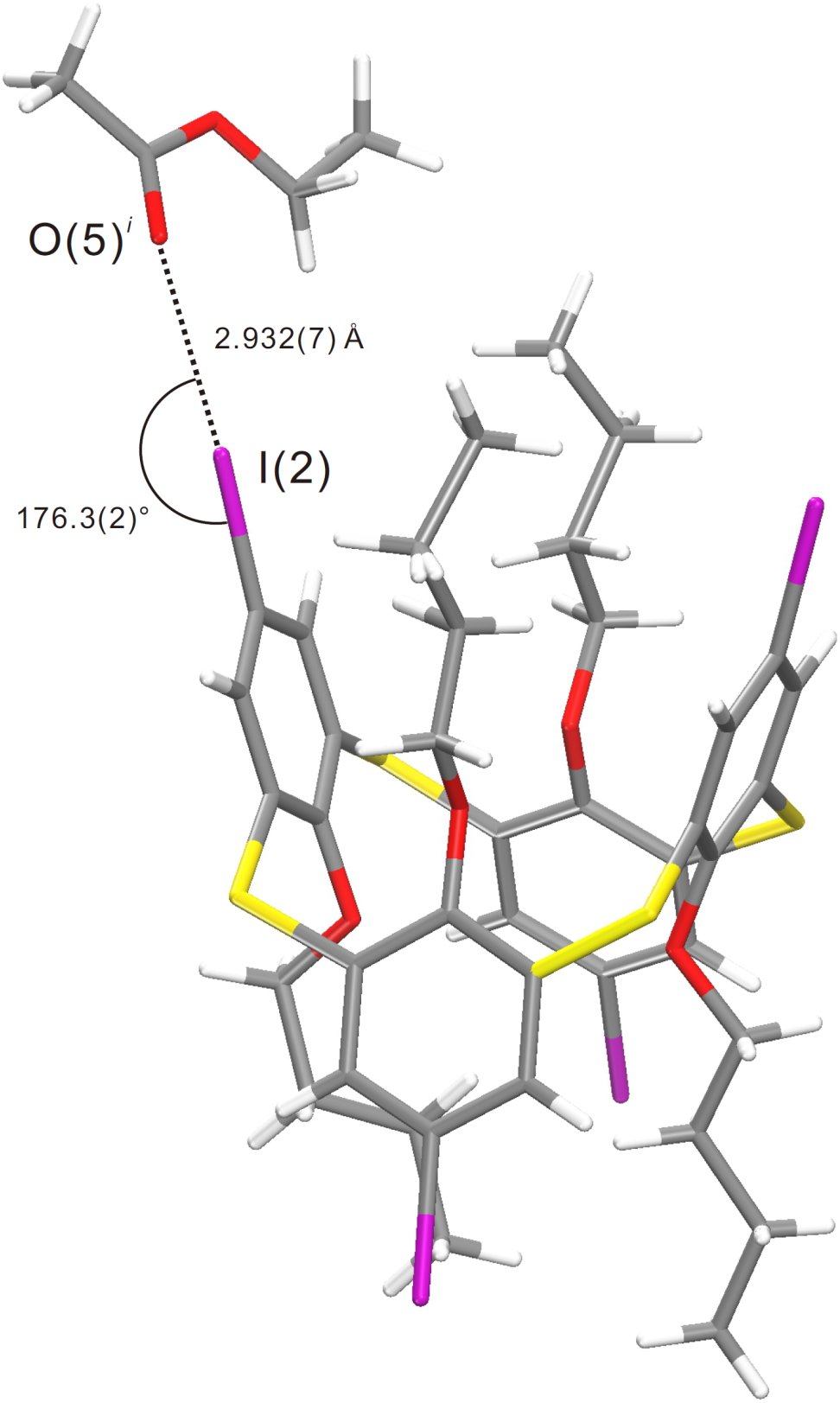
Supplementary Figure S8 Stick diagram showing S–π interactions (blue dotted lines) in the crystal structure of **3**. Disordered moieties have been removed for clarity. Symmetry operations: ^{h}, 2–*x*, 2–*y*, 1–*z*.



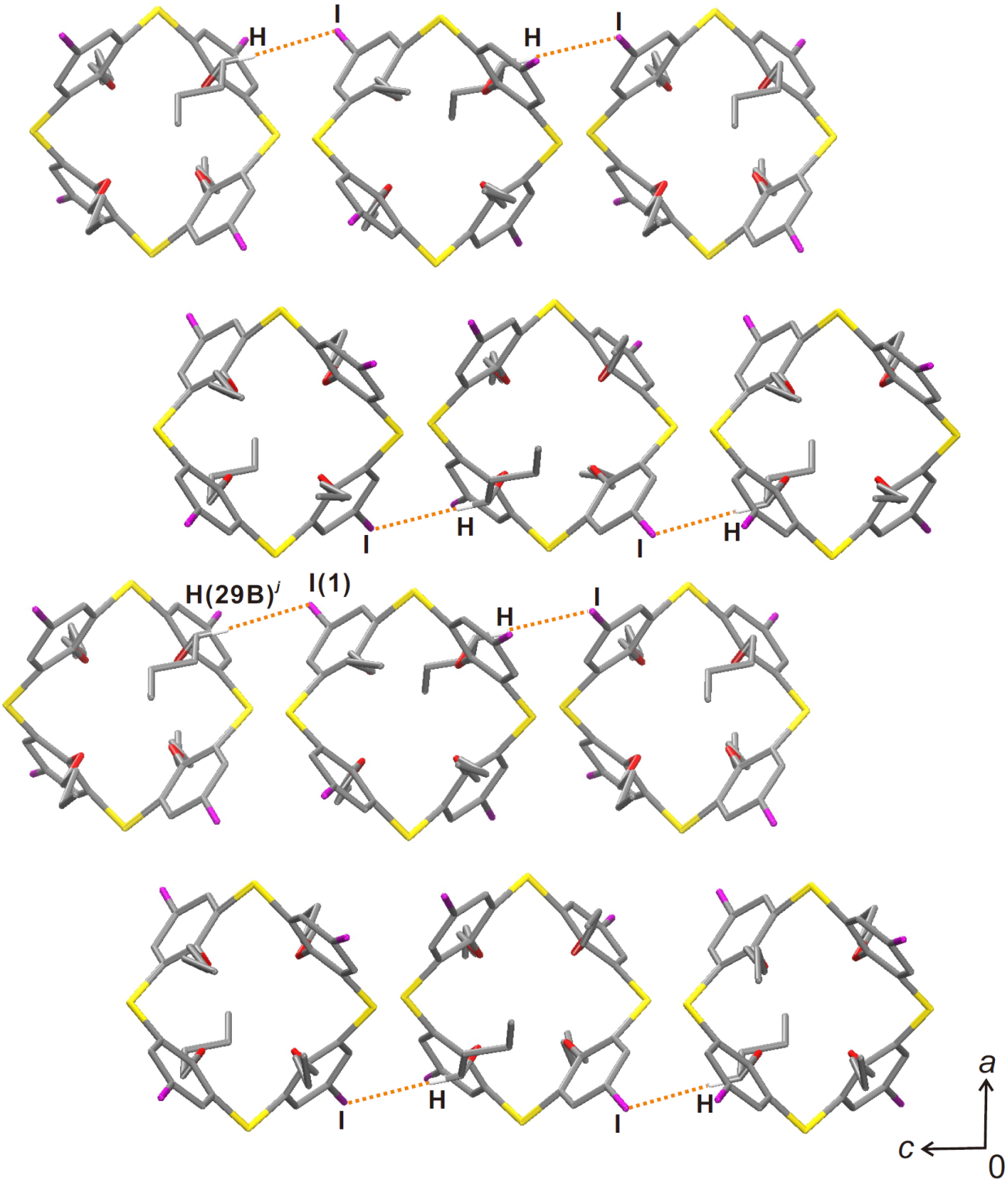
Supplementary Figure S9 The intermolecular S–π interaction between the linking sulfur atom of thiacalixarene molecule and aromatic moiety of thiacalixarene molecule in crystals of **3**. I = purple, S = yellow, O = red, C = gray. All hydrogen atoms have been removed for clarity.
Symmetry operation: ^{h}, 2–*x*, 2–*y*, 1–*z*.
r = 3. 928 Å, *d* = 3.514 Å, α = 96.27º, α' = 154.49º, and φ = 61.36º.
The parameter values of *r*, *d*, α, α', and φ lie in the allowable range of S–π interactions.[S1]

Reference

S1 C. –Q. Wan, J. Han and C. W. M. Thomas, *New J. Chem*., 2009, **33**, 707–712



Supplementary Figure S10 Stick diagram showing O···I halogen bonding (black dotted lines) in crystal structure of **3**. The disordered moieties have been removed for clarity. The O···I distance is 2.932(7) Å. The angle is 176.3(2)º. Symmetry operation: ^{i}, *x*, 5/2–*y*, –1/2+*z*.



Supplementary Figure S11 Stick diagram showing C–H···I halogen bonding (orange dotted lines) in crystal structure of **3**, viewed along the [101] plane. Almost hydrogen atoms and the disordered moieties have been removed for clarity. The C–H···I distance is 3.1568(3) Å. Symmetry operation: ^{j}, 2 –*x*, –1/2+*y*, 3/2–*z*.