Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Deciphering the helicity switching mechanism: A case study of the rigid three-tiered stacked architecture

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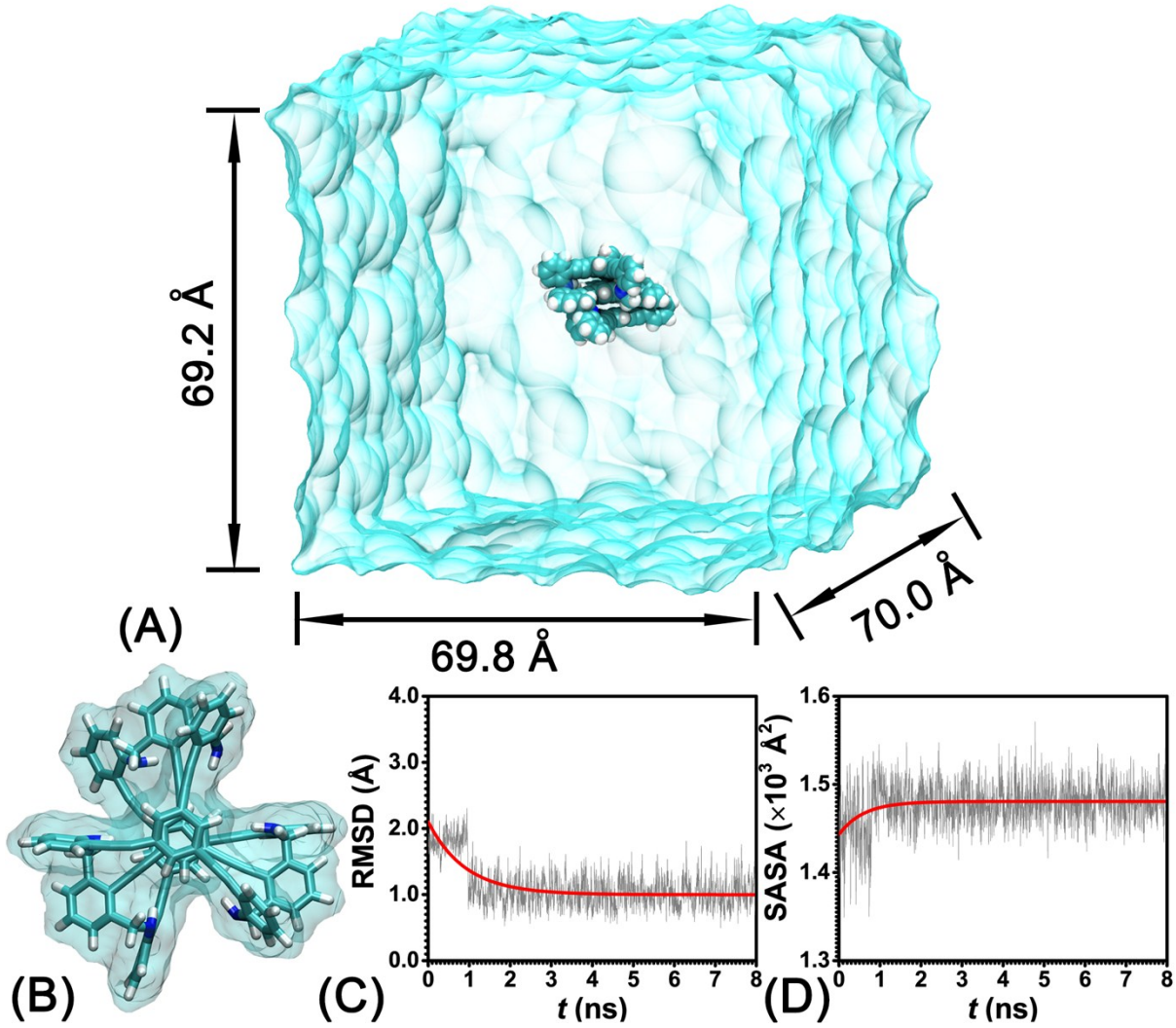

Figure S1. (A) Initial structure of the molecular system for the three-tiered stacked architecture (**3T**) within a toluene box. (B) Connolly surface of **3T**. The evolution of (C) the root-mean-square deviation and (D) the area of Connolly surface of **3T** in the 8 ns equilibrium simulation.

Evaluation of correlations for the rotation of rings within 3T.

Three benzene rings attached to the middle tier rotate simultaneously in a synchronous manner (clockwise-clockwise-clockwise or anticlockwise-anticlockwise-anticlockwise, see Figure S2D). In order to identify the correlated movement of rings, the percentages of the conformations of **3T** with three, two, and zero simultaneously rotating ring(s) were monitored in the course of the helicity switching as shown in Figure S2E. In the whole switching process, the ones involving three, two, and none simultaneously rotating ring(s) occupy ca. 70 %, 20 %, and 10 %, respectively. These ratios fluctuate around initial values. In can be concluded that rotations of three peripheral rings attached to the middle tier are coupled. In the metastable state, the conformations with three simultaneously rotating rings occupy a major share, not a dominating share.

Three benzene rings within the same chain rotate simultaneously in an alternative manner (clockwise-anticlockwise-clockwise or anticlockwise-clockwise-anticlockwise, see Figure S2F). In order to identify the correlated movement of benzene rings, the percentages of the conformations of **3T** with three, two, and zero simultaneously rotating ring(s) were monitored in the course of the helicity switching as shown in Figure S2G, S2H, and S2I. In the region near 0º and 180º, corresponding to the stable states, there are ca. 15 % conformations with none correlated rings. In all the conformations, the ones involving three simultaneously rotating rings occupy ca. 70 %. In the metastable region, there are at least two simultaneously rotating rings in every conformation. Conformations with three simultaneously rotating rings occupy 90 %. The same trend can be observed in Figure S2H and S2I. In can be concluded that three peripheral rings in each chain tend to rotate simultaneously, especially in the metastable region.

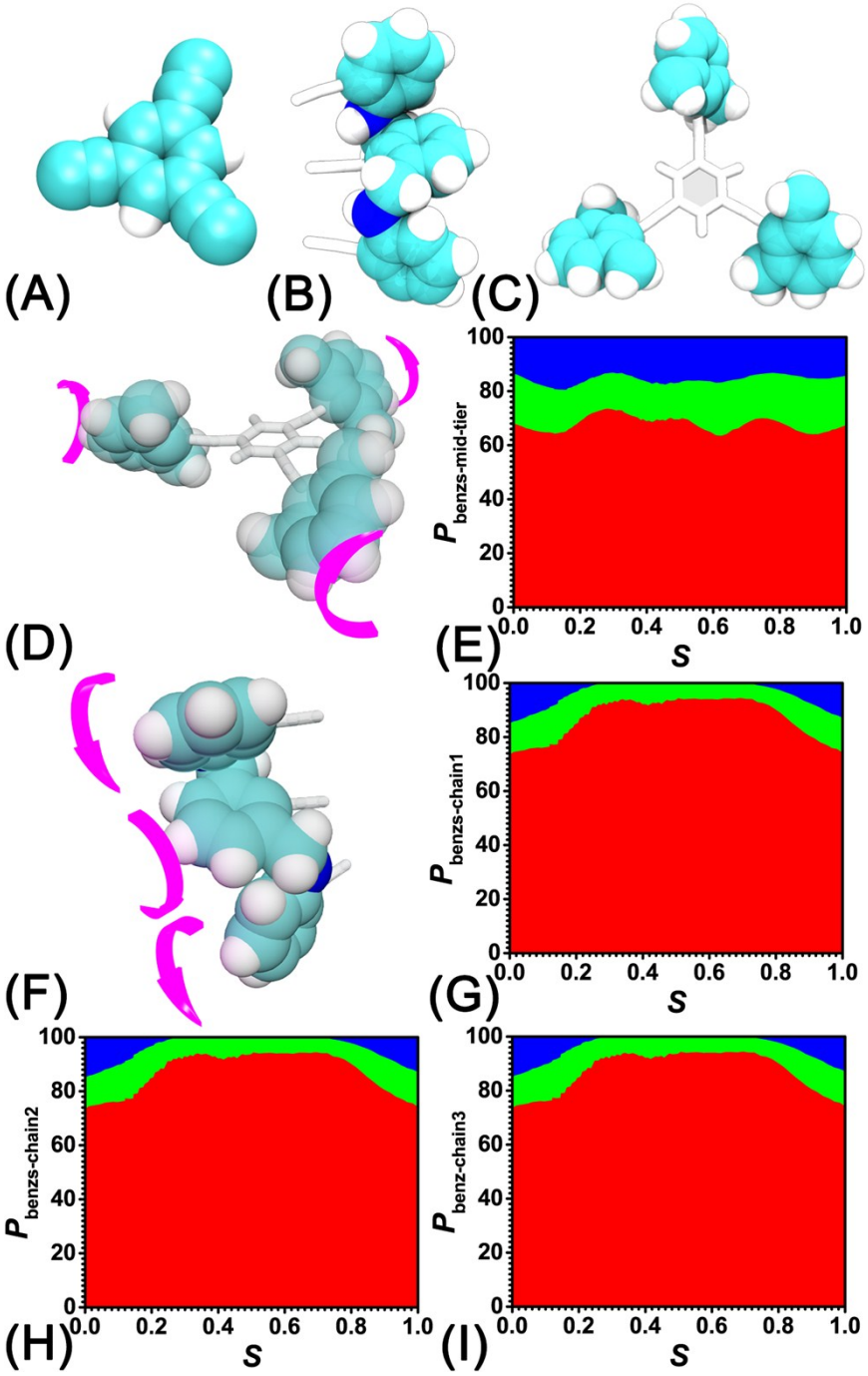

Figure S2. The three-dimensional structure of (A) one core, (B) one chain, and (C) the middle tier with three aromatic rings attached on a benzene ring. (D) The simultaneous rotation in a synchronous manner adopted by three peripheral rings within the middle tier. (E) Evolution of the percentage of conformations with 3-(red), 2-(green), and 0-(blue) simultaneously rotating peripheral ring(s). (F) The simultaneous rotation in an alternative manner adopted by three peripheral rings within one chain. The evolution of the percentage of conformations with 3-(red), 2-(green), and 0-(blue) simultaneously rotating peripheral ring(s) in (G) the chain1, (H) the chain2, and (I) the chain3.

Cartesian coordinates (pdb format)

The coordinates of one representative configuration for the metastable state of the main molecule, **3T**.

(For clarity, the coordinates of solvent molecules have been omitted.)

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