Supplementary Information for

Adsorption conformation induced kondo switch of fluorenyl radicals on metal surface

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Supplementary Methods

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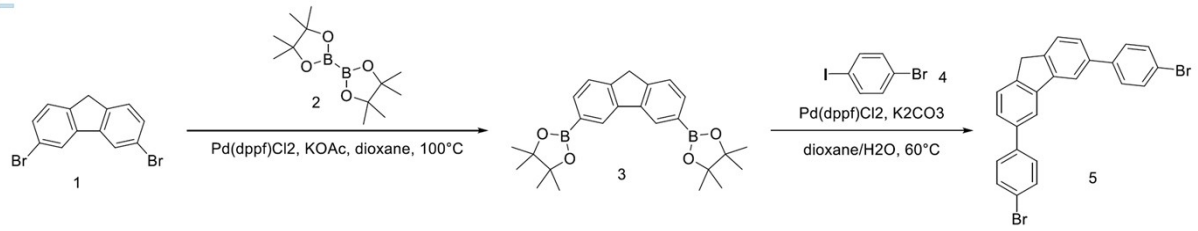
Supplementary Methods

The synthesis of 3,6-bis(4-bromophenyl)-9*H*-fluorene **5** is achieved by the following two-step reaction.

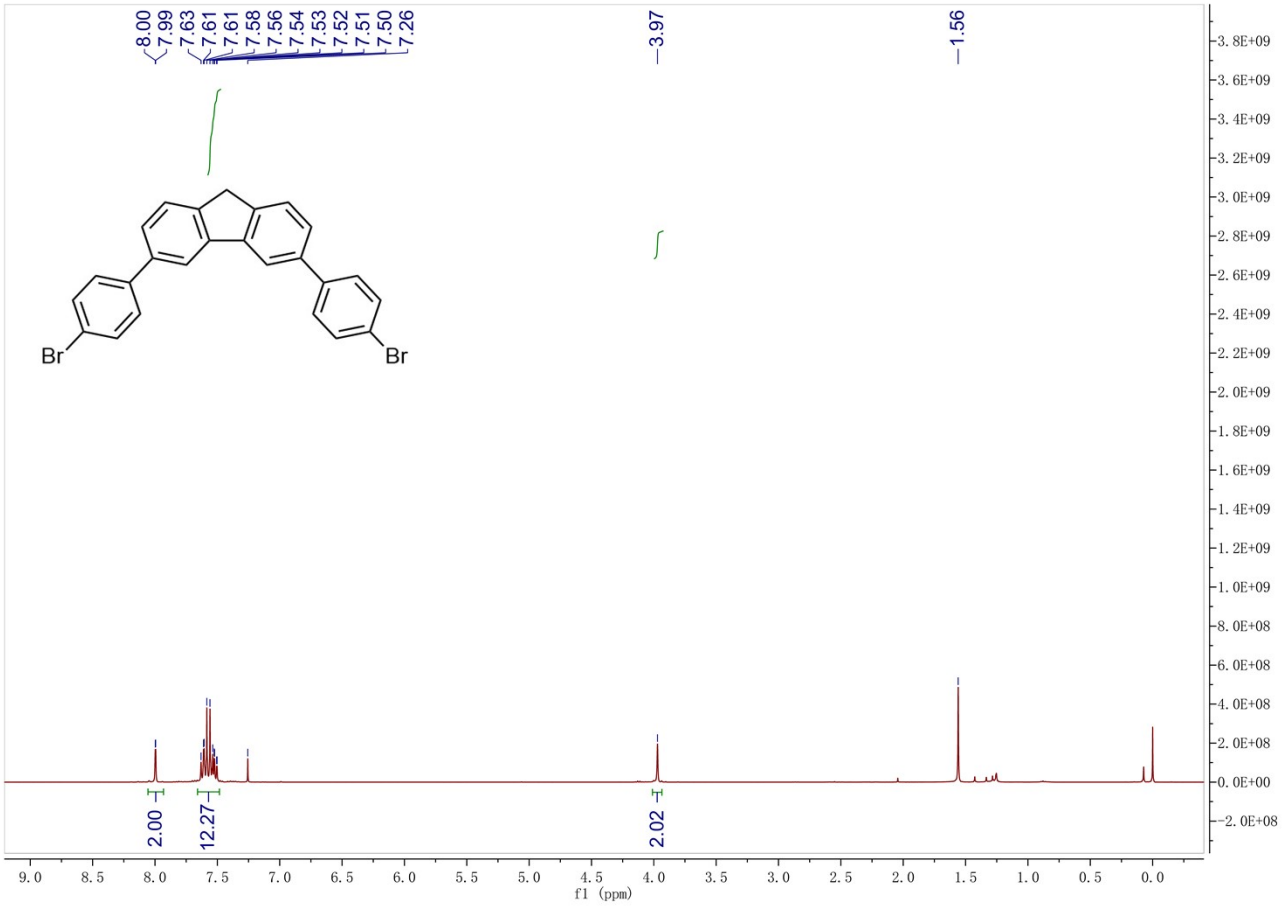


Synthesis of Compound 3

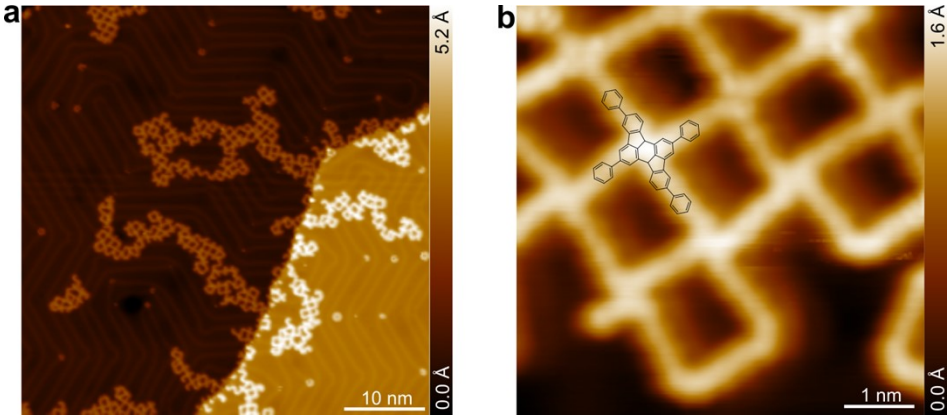
Compound **1** (161 mg) and compound 2 (254 mg) were placed in a 50 mL three-necked round-bottom flask, followed by the addition of 1,4-dioxane as solvent. Bis(1,1′-diphenylphosphino)ferrocene palladium(II) dichloride (Pd(dppf)Cl_2, 73.2 mg) and potassium acetate (196 mg) were then added to the reaction mixture. The resulting suspension was refluxed at 100 °C for 16 h under stirring. After completion of the reaction, the mixture was cooled to room temperature. The crude product was adsorbed onto silica gel and purified by column chromatography to afford compound 3 as a white solid (160 mg, 77% yield).

Synthesis of Compound 5

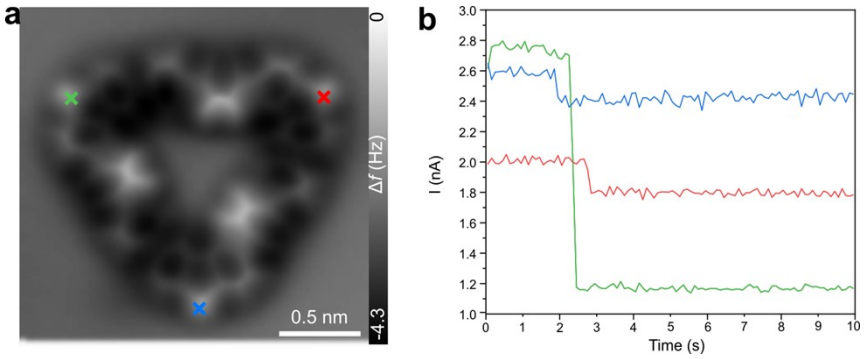
Compound **3** (160 mg) was added to a 50 mL three-necked round-bottom flask, followed by the addition of 1,4-dioxane and water. Subsequently, *p*-bromoiodobenzene (215 mg), bis(1,1′-diphenylphosphino)ferrocene palladium(II) dichloride (Pd(dppf)Cl_2, 56 mg), and potassium carbonate (262.6 mg) were added. The reaction mixture was stirred at 100 °C for 2 h. After cooling to room temperature, the crude product was adsorbed onto silica gel and purified by column chromatography to give compound 5 as a white solid (90 mg, 50% yield). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.00–7.99 (m, 2H), 7.63–7.50 (m, 10H), 7.26 (s, 1H), 3.97 (s, 2H), 1.56 (s, 2H) was measured, as shown in Supplementary Fig. 1.



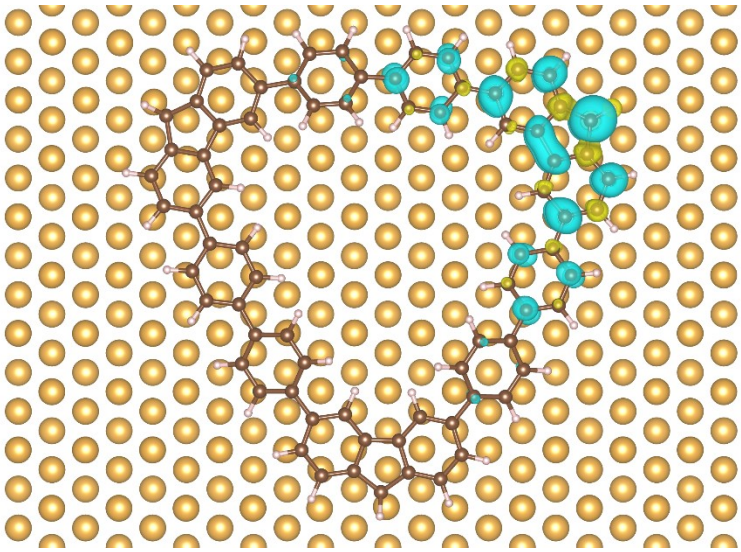
Supplementary Figure 1. ^{1}H-NMR spectrum. Liquid-state ^{1}H-NMR spectrum of compound 3,6-bis(4-bromophenyl)-9*H*-fluorene **5**.



Supplementary Figure 2. (a) Large-scale STM image of the covalent product after annealing the sample in Fig. 1e to 623 K. (b) Magnified STM image of a section of grid-like structural motif. Scanning parameters: (a,b) U = -1 V, I = 20 pA.



Supplementary Figure 3. Tip-induced dehydrogenation of the covalent trimer macrocycle. (**a**) Constant-height nc-AFM image of the covalent trimer macrocycle shown in Fig. 1g. Crosses indicate the tip positions used for site-selective hydrogen removal from the CH_2 groups. (**b**) Tunneling current recorded as a function of time during the application of a 2.8 V voltage pulse at a CH_2 site. The abrupt downward jump in the current indicates the removal of a single hydrogen atom.



Supplementary Figure 4. DFT Calculated spin density of the trimer macrocycle consisting of two chemisorbed and one physisorbed fluorenyl radicals.