

Supporting Information

On-surface reaction of aryl chloride and porphyrin macrocycle via merging two reactive sites into a single precursor

Chen-Hui Shu,^a Yu-Li Xie,^a An Wang,^a Ke-Ji Shi,^a Wei-Feng Zhang,^{b,*} Deng-Yuan Li^{a,*} and
Pei-Nian Liu^{a,*}

^aShanghai Key Laboratory of Functional Materials Chemistry, State Key Laboratory of Chemical Engineering and School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, China.

E-mail: liupn@ecust.edu.cn; dengyuanli@ecust.edu.cn

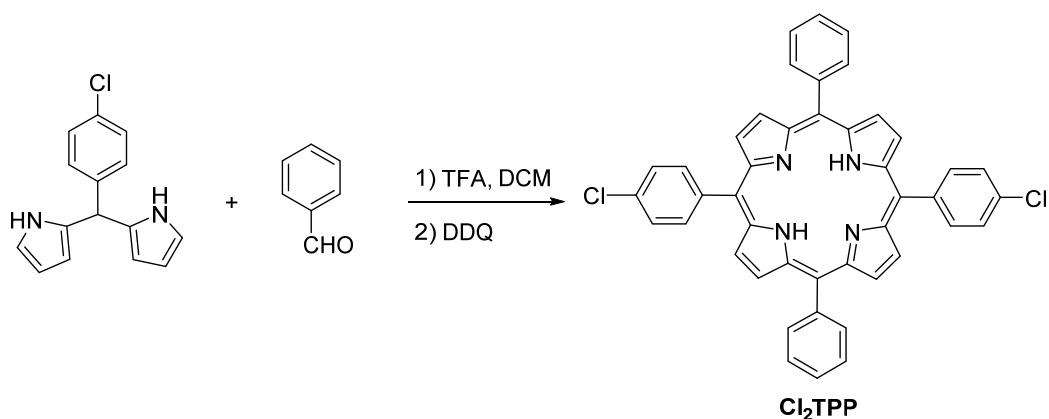
^bKey Laboratory of Photovoltaic Materials of Henan Province, Henan University, Kaifeng 475004, China.

E-mail: wfzhang6@163.com

Content

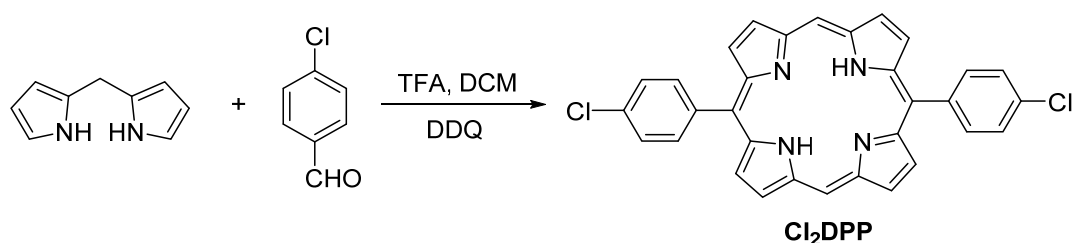
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1. Synthesis of organic molecules



Synthesis of 5,15-di(4-chlorophenyl)-10,20-diphenylporphyrin (Cl₂TPP).¹

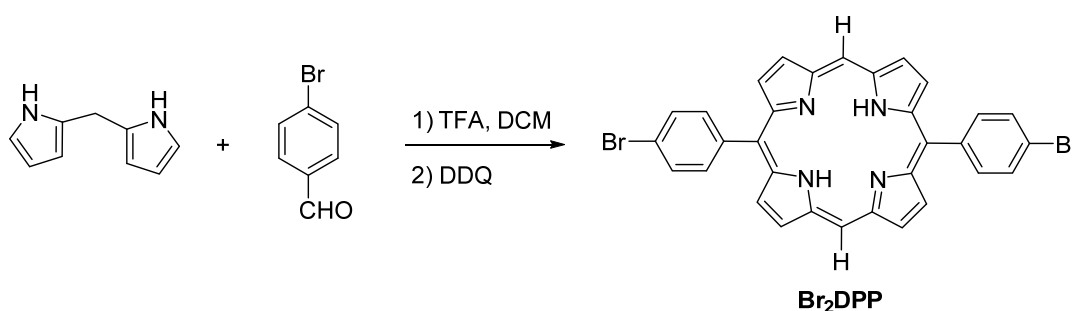
5-(4-Chlorophenyl)dipyrromethane (300 mg, 1.18 mmol), benzaldehyde (0.14 mL, 1.18 mmol), trifluoroacetic acid (60 μ L) and dichloromethane (30 mL) were combined and stirred under N₂ at room temperature for 1 h. 2,3-Dicyano-5,6-dichlorobenzoquinone (0.6 g, 2.45 mmol) was added and then stirred for 2 more hours. Triethylamine (0.5 mL) was added to quench the reaction and the solvent of the reaction mixture was removed by reduced pressure distillation. Column chromatography on silica gel (eluent: petroleum ether:CH₂Cl₂ = 3:1) gives the crude product, which was recrystallized from chloroform/acetone to afford the product as purple crystals (41 mg, 12% yield). Mp >300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 8.86 (d, J = 4.4 Hz, 4H), 8.21 (d, J = 7.6 Hz, 4H), 8.14 (d, J = 8.0 Hz, 4H), 7.76-7.71 (m, 10H), -2.81 (s, 2H); HRMS calcd for C₄₄H₂₉N₄Cl₂⁺ (M+H): 683.1764, found 683.1768.



Synthesis of 5,15-bis(4-chlorophenyl)porphyrin (Cl₂DPP).²

Di(1*H*-pyrrol-2-yl)methane (730 mg, 5 mmol), 4-chlorobenzaldehyde (700 mg, 5 mmol), trifluoroacetic acid (250 μ L) and dichloromethane (200 mL) were combined and stirred under N₂ at room temperature for 3 h.

2,3-Dicyano-5,6-dichlorobenzoquinone (1.38 g, 6.35 mmol) was added and then stirred for 1 h. Triethylamine (2 mL) was added to quench the reaction and the solvent of the reaction mixture was removed by reduced pressure distillation. Column chromatography on silica gel gave the crude product, which was recrystallized from chloroform/acetone to afford the product as purple crystals (45 mg, 3.4% yield). Mp >300 °C; $^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 10.35 (s, 2H), 9.43 (d, $J = 4.64$ Hz, 4H), 9.07 (d, $J = 4.64$ Hz, 4H), 8.21 (d, $J = 8.24$ Hz, 4H), 7.80 (d, $J = 8.28$ Hz, 4H), -3.16 (s, 2H); **HRMS (ESI, TOF)** calcd for $\text{C}_{32}\text{H}_{20}\text{Cl}_2\text{N}_4^+$ $[\text{M} + \text{H}]^+$: 530.1060, found: 531.1106.



Synthesis of 5,15-bis(4-bromophenyl)porphyrin (**Br₂DPP**).³

Di(1*H*-pyrrol-2-yl)methane (250 mg, 1.71 mmol), 4-bromobenzaldehyde (317 mg, 1.71 mmol), trifluoroacetic acid (90 μL) and dichloromethane (30 mL) were combined and stirred under N_2 at room temperature for 1 h. 2,3-Dicyano-5,6-dichlorobenzoquinone (0.5 g, 2.2 mmol) was added and then stirred for 2 h. Triethylamine (0.5 mL) was added to quench the reaction and the solvent of the reaction mixture was removed by reduced pressure distillation. Column chromatography on silica gel gave the crude product, which was recrystallized from chloroform/acetone to afford the product as purple crystals (42 mg, 16% yield). Mp >300 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3 , 25 °C) δ 10.35 (s, 2H), 9.43 (d, $J = 4.84$ Hz, 4H), 9.07 (d, $J = 4.40$ Hz, 4H), 8.16 (d, $J = 8.00$ Hz, 4H), 7.97 (d, $J = 8.00$ Hz, 4H), -3.17 (s, 2H); **HRMS** calcd for $\text{C}_{32}\text{H}_{21}\text{N}_4\text{Br}_2^+$ $[\text{M} + \text{H}]^+$: 619.0128, found 619.0129.

2. General procedure for STM experiments

STM imaging was performed using a commercial ultrahigh vacuum system (base pressure, 2×10^{-10} mbar) equipped with a variable temperature scanning tunneling microscope (SPECS, Aarhus 150), a molecular evaporator, and standard facilities for sample preparation. Single-crystalline Cu(111) surfaces were cleaned through cycles of argon ion sputtering and annealing. After thorough degassing, samples of **Cl₂TPP**, **Cl₂DPP** and **Br₂DPP** were deposited onto the substrate by thermal sublimation and annealed to the indicated temperature. STM measurements were taken at ~ 120 K.

3. General procedure for the calculations

The calculations were carried out in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP).^{4,5} The projector augmented wave method was used to describe the interaction between ions and electrons.^{6,7} We used the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof(PBE) formalism to treat exchange–correlation interaction,⁸ and van der Waals (vdW) interactions were considered by using the DFT-D3 developed by Grimme.⁹ The structures were relaxed until the forces on all unconstrained atoms were ≤ -0.1 eV/Å. Surface were modeled by two layered slabs separated by at least 15 Å of vacuum, the bottom layer was fully fixed. Calculated lattice constant of Cu is 3.59 Å (experimental lattice constants is 3.61 Å for Cu).¹⁰ All calculations were done with a $1 \times 1 \times 1$ k-point sampling and a 400 eV kinetic energy cutoff.

4. Supplementary STM Figures

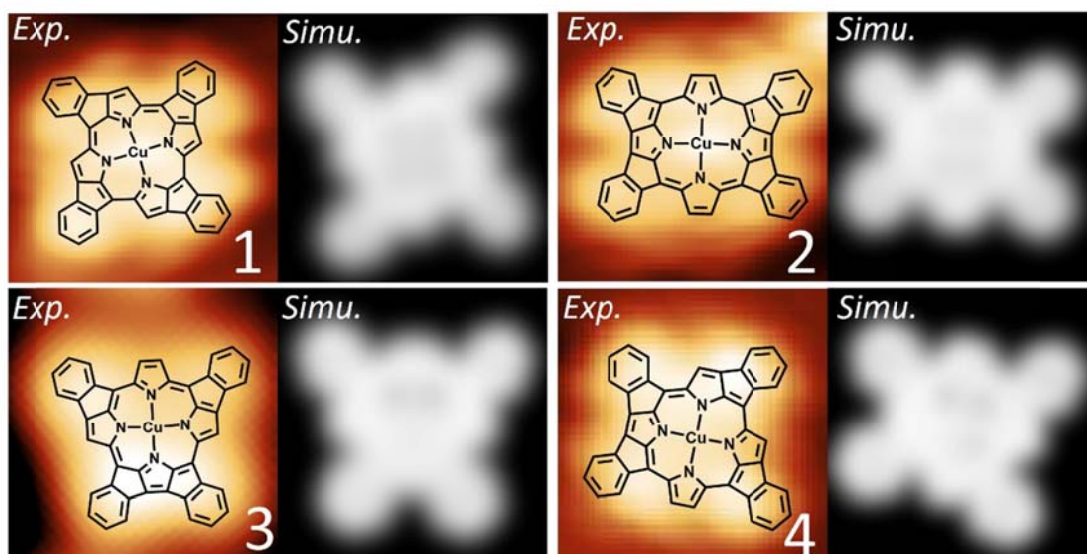


Figure S1. STM images and the corresponding simulations for the intramolecular cyclodehydrogenation products of Cl_2TPP .

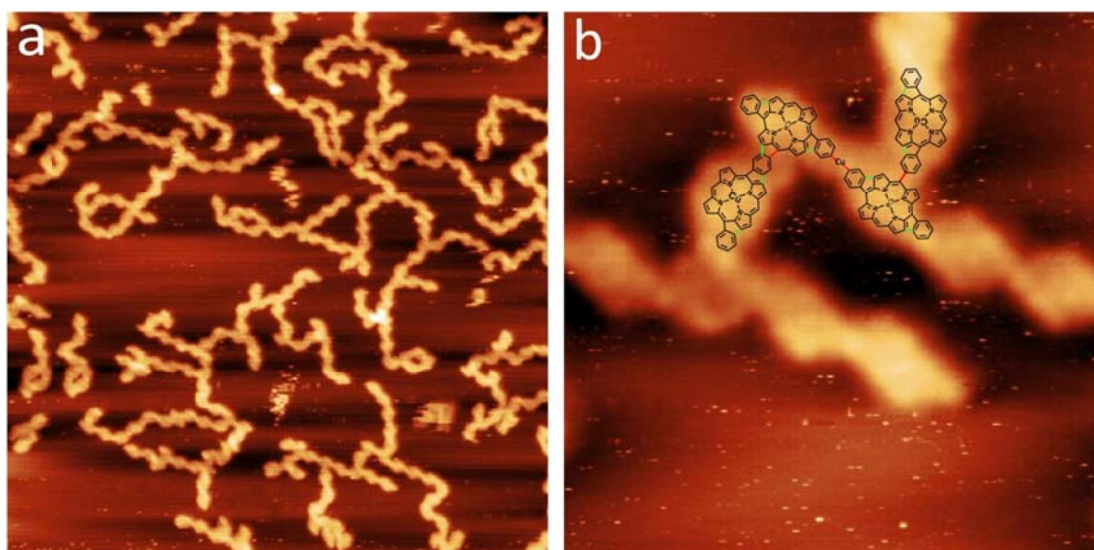


Figure S2. (a, b) STM image of Cl_2DPP annealed to 453 K on Cu(111). Scanning parameters: (a) $I = 0.11 \text{ nA}$, $U = -1.73 \text{ V}$; (b) $I = 0.10 \text{ nA}$, $U = -1.73 \text{ V}$.

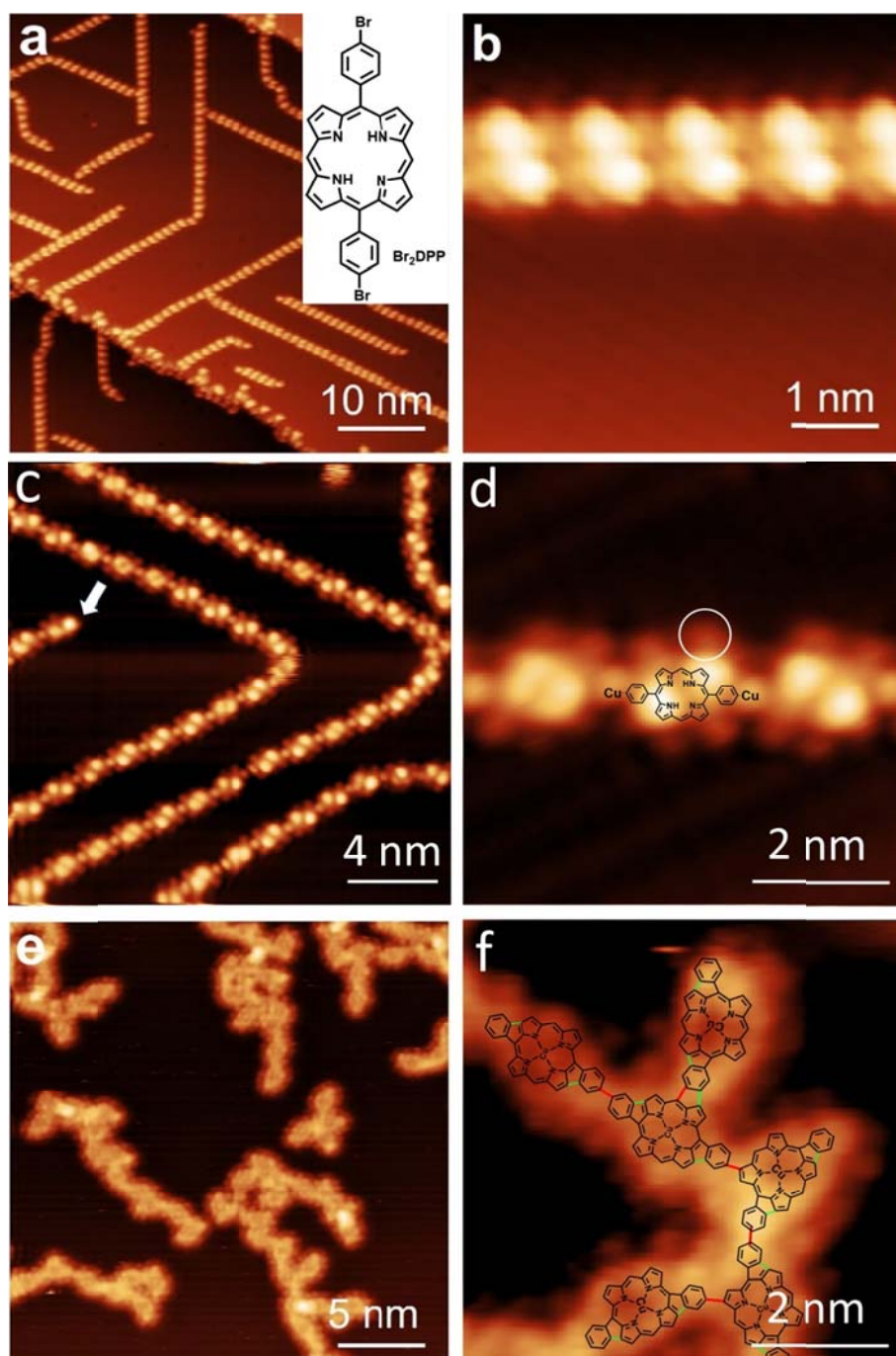


Figure S3. STM images of Br_2DPP on Cu(111). (a) Self-assembly after deposition at ~ 200 K. (b) The close-up STM image at ~ 200 K. (c) Annealing to 393 K, a white arrow indicates an end of organometallic chain without Br atom attached. (d) The zoom-in STM image of organometallic chain, white circles indicate Br atoms near the porphyrin macrocycle. (e) Annealing to 500 K. (f) The zoom-in STM image of oligomer structure. Scanning conditions: (a, b) $I = 0.11$ nA, $U = -1.68$ V; (c, d) $I = 0.09$ nA, $U = -1.85$ V; (e, f) $I = 1.31$ nA, $U = -1.53$ V.

Reference:

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5. ¹H NMR data of the molecules

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