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Supplementary Information

Interaction strength in molecular junctions consisting of π-stacked antiaromatic molecules

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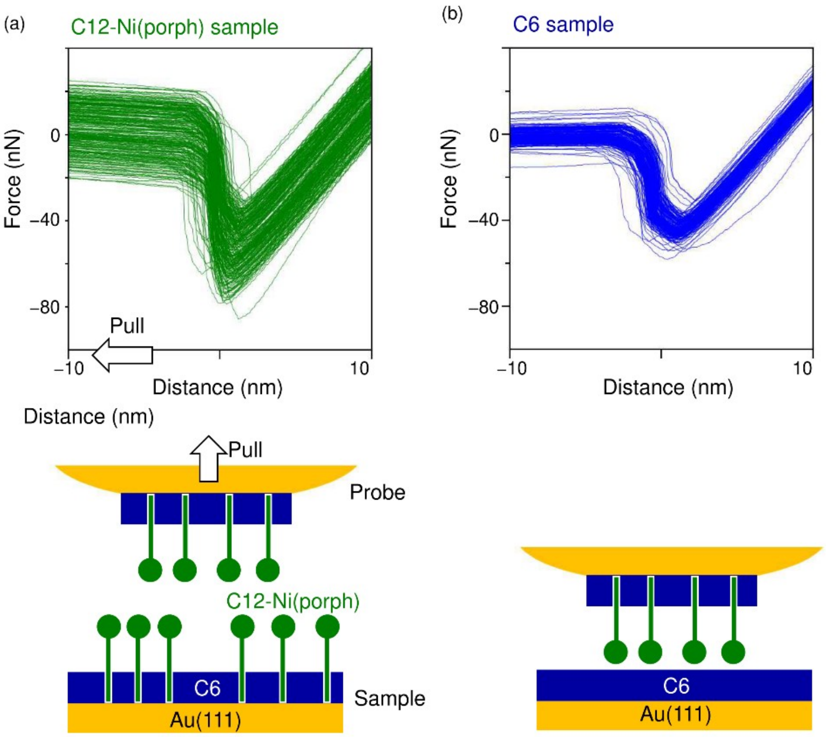

Fig. S1 (a,b) Force curves measured on C6 matrix with and without C12-Ni(porph). Schematics of the experimental systems are shown at the bottom.

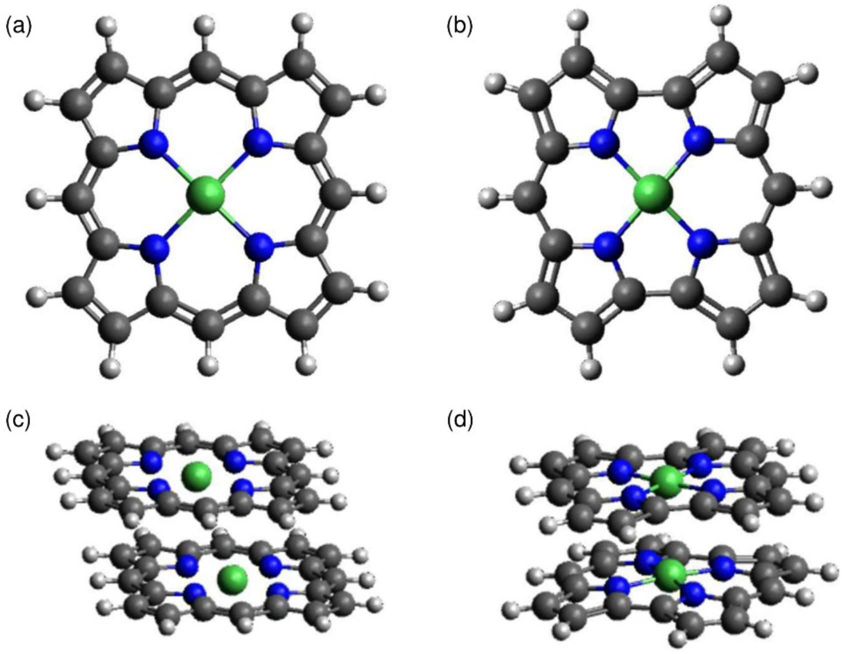

Fig. S2 (a,b) Optimized geometry of (a) aromatic and (b) antiaromatic moieties. (c,d) Optimized geometry of dimers of pairs of the (c) aromatic and (d) antiaromatic moieties.

1. Theoretical calculations

Calculations were performed with B3LYP 6-31+G(d)/SDD basis set and GD3BJ empirical dispersion corrections[1] using the Gaussian 16/A03 software package.[2] Figure S2a,b shows optimized geometry of isolated single aromatic and antiaromatic moieties, respectively. Compared with the isolated states, stabilization energies due to the formation of π-π stacking (Fig. S2c,d) are calculated to be 1.34 and 1.58 eV for the aromatic and antiaromatic moieties, respectively.

2. Synthesis

C12-Ni(nor)

A mixture of Ni(II) diphenylnorcorrole[3] (9.9 mg, 20 µmol), triethylamine (2.8 µL, 20 µmol), 1,12-dodecandithiol monoacetate[4] (5.2 µL, 20 µmol), and DMF (2.0 mL) was stirred at –10 °C for 72 h. Water and EtOAc were then added. The organic layer was separated, washed with brine, and evaporated under reduced pressure to leave a solid residue. The residue was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 4/1 as an eluent) to afford C12-Ni(nor) in 4% yield (0.6 mg, 0.8 µmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.88–6.84 (m, 4H, Ph), 6.73 (t, J = 7.7 Hz, 2H, Ph), 6.24 (d, J = 8.0 Hz, 2H, Ph), 6.12 (d, J = 8.0 Hz, 2H, Ph), 2.87 (t, J = 7.3 Hz, 2H, S-CH_2), 2.63 (d, J = 4.4 Hz, 1H, β-H), 2.35 (d, J = 4.0 Hz, 1H, β-H), 2.33 (s, 3H, AcS-Me), 2.22 (d, J = 4.4 Hz, 1H, β-H), 2.15 (d, J = 4.0 Hz, 1H, β-H), 2.10 (d, J = 4.0 Hz, 1H, β-H), 2.07 (d, J = 4.0 Hz, 1H, β-H), 2.01 (s, 1H, β-H), 1.48 (quint, J = 7.3 Hz, 2H, alkyl), 1.50 (t, J = 6.9 Hz, 2H, alkyl), 1.40–0.79 (m, 18H, alkyl) ppm.

C12-Ni(porph)

A Schlenk tube charged with Pd_2dba_3•$CHCl_3$ (2.5 mol %), JohnPhos (20 mol %), Ni(II) 10-bromo-5,15-diphenylporphyrin[5] (15 mg, 0.025 mmol), and Cs_2CO_3 (32.6 mg, 0.1 mmol) was degassed and purged with nitrogen. Then 1,12-dodecandithiol (46.9 mg, 0.2 mmol) and toluene (2.5 mL) were added. The reaction mixture was heated in an oil bath with stirring for 24 h. The reaction mixture was diluted with dichloromethane, washed with water, and concentrated in vacuo. The solid residue was dissolved with dichloromethane (5.0 mL) and pyridine (2.0 mL) and acetic anhydride (40 µL) were added. After stirring for 6 h, the mixture was extracted with water and dichloromethane. The organic layer was concentrated in vacuo. The residue was purified with silica gel column chromatography. Further purification by recycling GPC-HPLC afforded C12-

Ni(porph) in 8% yield (1.6 mg, 2.0 µmol). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.88 (d, *J* = 5.0 Hz, 2H, *β*-H), 9.79 (s, 1H, *meso*), 9.11 (d, *J* = 4.8 Hz, 2H, *β*-H), 8.84 (dd, *J* = 4.8, 2.2 Hz, 4H, *β*-H), 8.02 (m, 4H, Ph), 7.72 (m, 6H, Ph), 3.11 (t, *J* = 7.3 Hz, 2H, alkyl), 2.80 (t, *J* = 7.4 Hz, 2H, alkyl), 2.29 (s, 3H, AcS-Me), 1.48 (quint, *J* = 7.4 Hz, 2H, alkyl), 1.03–1.17 (m, 18H, alkyl) ppm.

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