

Supplementary Materials for
Highly efficient charge transport across carbon nanobelts

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1. Synthetic Details

1.1 General Information

(6,6)CNB and [6]CPP were purchased from Tokyo Chemical Industry (TCI), and directly used without further purification. [6]CNB_M6 and [6]CNB_N3 were synthesized using reported methods. All reagents including dry solvents and starting reactants for syntheses were purchased from commercial suppliers (Aldrich or Acros) and used directly. All glassware used in experiments was oven-dried and cooled under an inert atmosphere of argon. All air-sensitive reactions were performed under argon atmosphere by standard Schlenk techniques. Flash column chromatography was carried out on silica gel (200 ~ 300 mesh). Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker BioSpin (^1H 400 MHz, ^1H 600 MHz, ^{19}F 400 MHz, ^{13}C 100 MHz) spectrometer. Chemical shifts are quoted in ppm relative to CHCl_3 (δ 7.26 ppm), CH_3OH (δ 3.31 ppm) or tetramethylsilane (δ 0.00 ppm) for ^1H NMR and relative to CDCl_3 (δ 77.0 ppm) for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, m=multiplet), coupling constant (Hz), and integration. High-resolution mass spectrum (HR-MS) was acquired using MALDITOF-MS techniques.

1.2 Synthesis of [6]CNB_M6

[6]CNB_M6 was prepared according to the sequence shown in Scheme S1. Individual steps are following a modified literature procedure (14).

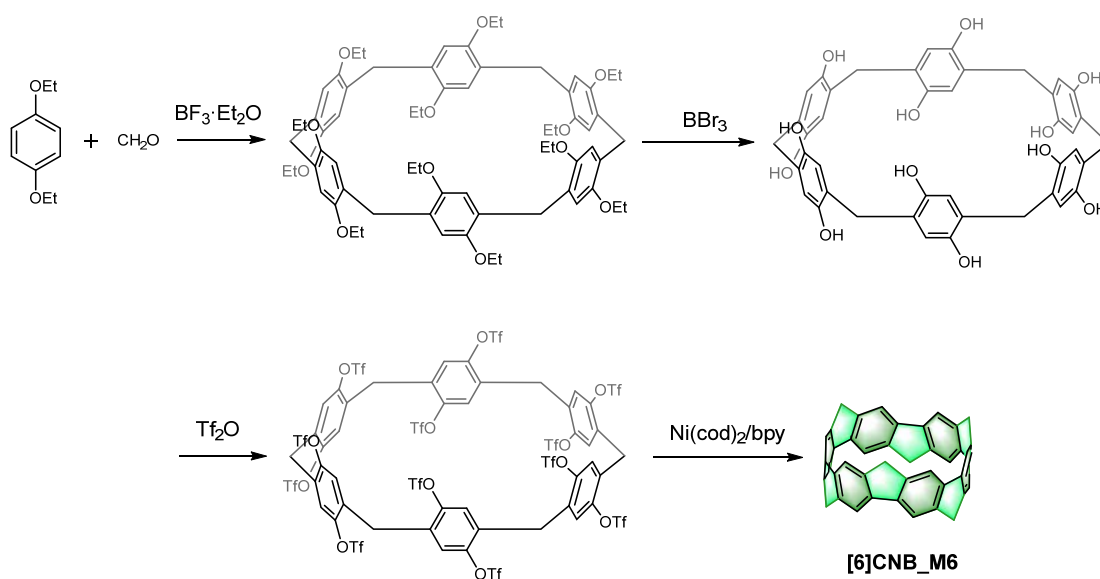


Figure S1. The synthetic route leading to [6]CNB_M6.

Synthesis of triflate-functionalized pillar[6]arene: The solution of hydroxylated pillar[6]arene (491 mg, 0.670 mmol) was added to anhydrous dichloromethane (100 mL) under argon atmosphere. Pyridine (1.0 mL, 12 mmol) and trifluoromethanesulfonyl anhydride (Tf_2O , 1.8 mL, 10.7 mmol) were then added to the mixture at 0 °C. The mixture was then warmed to room temperature and stirred for 36 h. The reaction was quenched slowly with 20 mL H_2O at 0 °C. The reaction mixture was concentrated until large amount of precipitation remained and the precipitate was collected by filtration and washed with copious amounts of water. The residue was purified by column chromatography (*n*-hexane/acetone = 5:1) to afford triflate-functionalized pillar[6]arene (350 mg, 0.151 mmol, 23%) as a white solid. ^1H and ^{19}F NMR spectra are consistent with the previous report (14). ^1H NMR (400MHz, CDCl_3): δ 7.23 (s, 12H), 4.15 (s, 12H). ^{19}F NMR (400MHz, CDCl_3): δ -73.62.

Synthesis of [6]CNB_M6: Bis(cyclooctadiene)nickel(0) (74 mg, 0.27 mmol), 2,2'-bipyridine (42 mg, 0.27 mmol) were dissolved in *N*-methyl-2-pyrrolidone (NMP) (3.0 mL) and stirred for 10 mins at 80 °C under argon atmosphere in the absence of light for activation of nickel catalyst, and a dark purple solution of the complex was obtained. A solution of triflate-functionalized pillar[6]arene (52 mg, 0.023 mmol) in NMP (4.5 mL) under argon atmosphere was quickly added to the reaction mixture and stirred for 4

hours at same temperature. After cooling to ambient temperature, the reaction was quenched by saturated aqueous solution of NH₄Cl. After extraction of organic layer with dichloromethane washing with brine, the organic layer was separated and dried over MgSO₄. After removing solvent in vacuo, the crude product was purified by column chromatography (CH₂Cl₂/*n*-hexane/CS₂ = 25:50:2, *v/v/v*) to afford the target compound [6]CNB_M6 (1.4 mg, 12%) as a red solid. ¹H NMR and mass spectrum spectra are consistent with the previous report (14). ¹H NMR (600 MHz, CDCl₃) δ 7.87 (s, 12H), 4.30 (d, *J* = 17.0 Hz, 6H), 4.10 (d, *J* = 17.0 Hz, 6H). HR-MS (MALDI-TOF) *m/z* calcd. for: C₄₂H₂₄[M]⁺: 528.1878, found: 528.1896.

2. Additional Experimental Data and Analysis

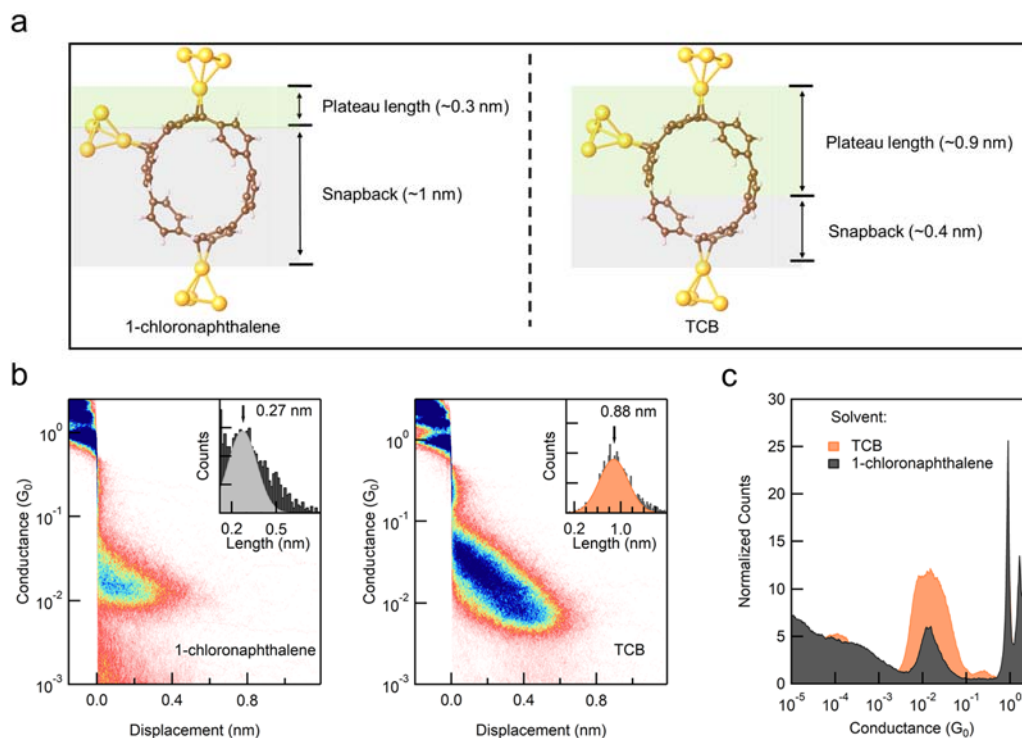


Figure S2. Solvent effects. (a) Schematics of snapback effect on the formation of single [6]CPP junction in 1-chloronaphthalene and TCB solvent. (b) 2D histograms of [6]CPP measured in 1-chloronaphthalene and TCB solvent. Inset: the relative length distributions. (c) 1D histograms of [6]CPP measured in 1-chloronaphthalene and TCB solvent. In 1-chloronaphthalene solvent, the Au snapback (~1 nm) is much larger, which leads to decreased Au-CPP binding sites and causes less varied conductance distributions when compared with that in TCB solvent.

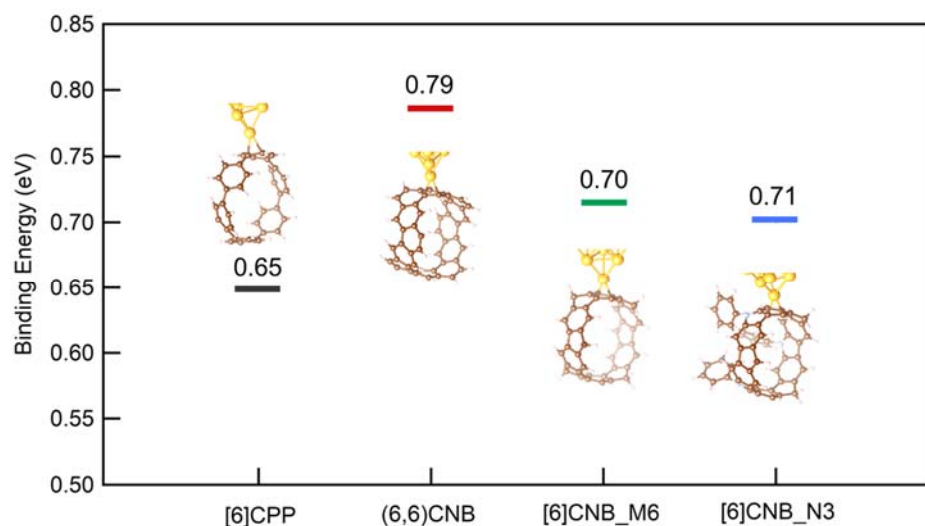


Figure S3. Calculated binding energies for the optimal binding site of [6]CPP, (6,6)CNB, [6]CNB_M6 and [6]CNB_N3.

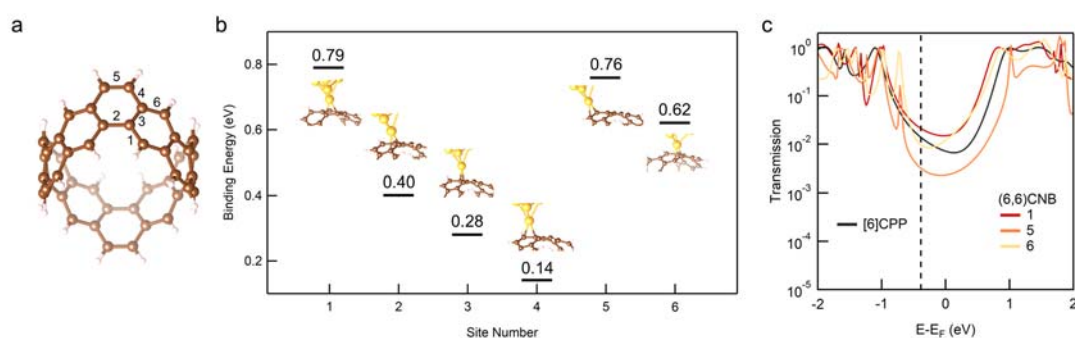


Figure S4. Binding energy and transmission calculations for (6,6)CNB. (a) Schematics for possible binding sites in (6,6)CNB. (b) Calculated binding energies for different binding configurations for (6,6)CNB. (c) Calculated transmission functions for (6,6)CNB junctions formed with different Au-molecule binding sites.

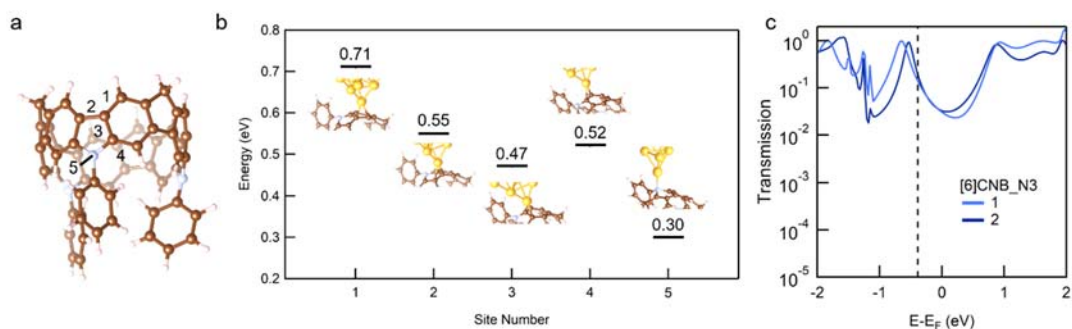


Figure S5. Binding energy and transmission calculations for [6]CNB_N3. (a) Schematics for possible binding sites in [6]CNB_N3. (b) Calculated binding energies for different binding configurations for [6]CNB_N3. (c) Calculated transmission functions for [6]CNB_N3 junctions formed with different Au-molecule binding sites.

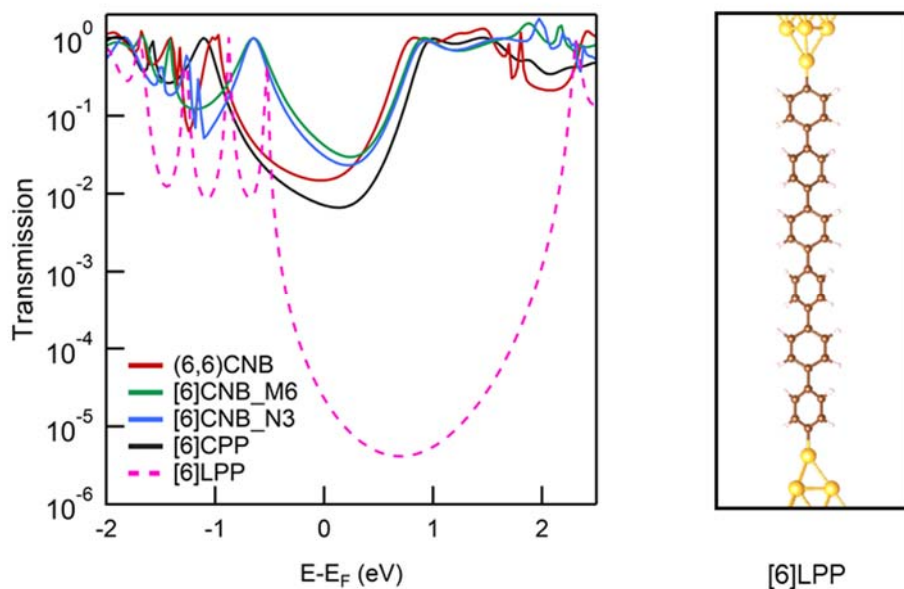


Figure S6. DFT-based transmission calculations for [6]LPP and CNBs. [6]LPP shows a much smaller coupling and a lower transmission near the Fermi energy.

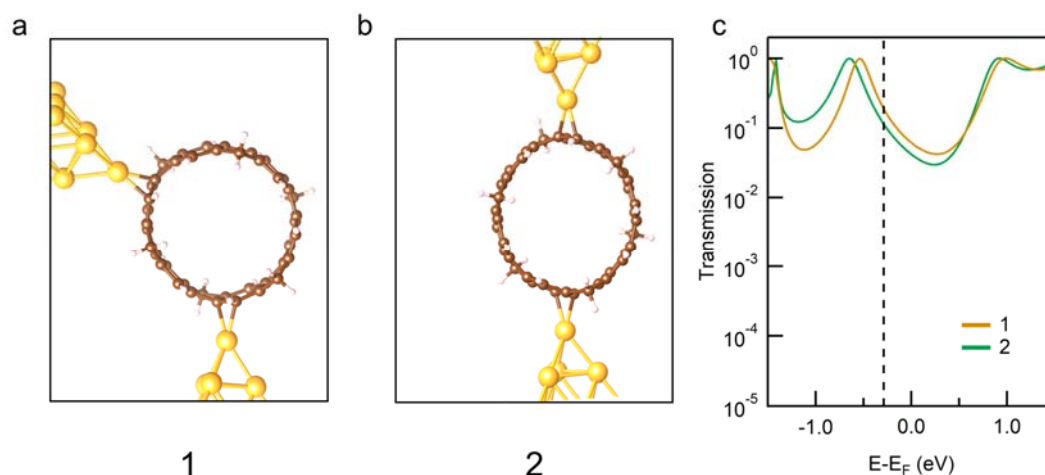


Figure S7. Transmission calculations for CNB_M6. (a-b) Two sample single [6]CNB_M6 junctions formed through electrode-molecule binding at different phenylene pairs. (c) Calculated transmission functions for the two sample single [6]CNB_M6 junctions.

Table S1. Comparison of [6]CPP, (6,6)CNB, [6]CNB_M6 and [6]CNB_N3^a

Molecule	[6]CPP	(6,6)CNB	[6]CNB_M6	[6]CNB_N3
Diameter (Å) ^b	8.09	8.05	7.76	7.72
HOMO (eV) ^b	-4.90	-4.92	-4.40	-4.36
LUMO (eV) ^b	-1.78	-1.97	-1.74	-1.69
Energy gap (eV) ^b	3.22	2.95	2.66	2.67

^aOptimized at B3LYP/6-31G* level. ^bData of [6]CPP (49), (6,6)CNB (9), [6]CNB_M6 (14) and [6]CNB_N3 (15) were taken from references.