

Supporting Information for:

Directing and Sensing Changes in Molecular Conformation on Individual Carbon Nanotube Field Effect Transistors

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Experimental details for SWCNT device fabrication

Individual SWCNTs were grown by a chemical vapor deposition (CVD) process from CoMo-doped mesoporous SiO₂ catalyst particles process using ethanol as the carbon source. The process is the same as has been described in the literature [see: (a) Huang, L.; Cui, X.; White, B.; O'Brien, S. P. *J. Phys. Chem. B* **2004**, *108*, 16451-16456; (b) Huang, L.; Wind, S. J.; O'Brien, S. P. *Nano Letters* **2003**, *3*, 299-303]. The catalyst particles were patterned on doped silicon wafers that have 300 nm of thermally grown SiO₂ on the surface. Source and drain electrodes (5 nm of Cr followed by 50 nm of Au) separated by $\sim 20\ \mu\text{m}$ were deposited through a metal shadow mask onto the carbon nanotube samples using the thermal evaporator.

1. Supporting Current-Voltage curves:

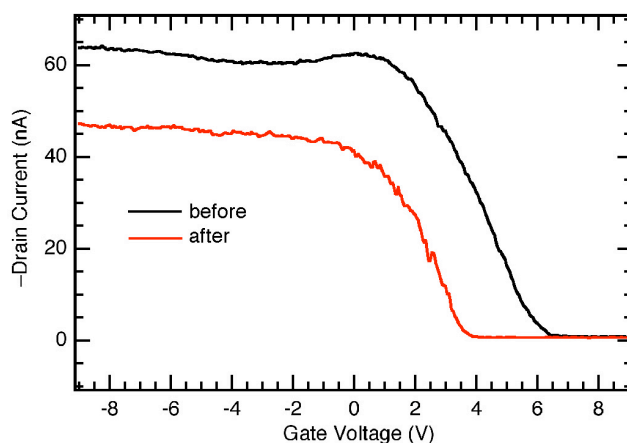


Figure S1. SWCNT before and after **2a** is assembled on a SWCNT transistor from THF solution.

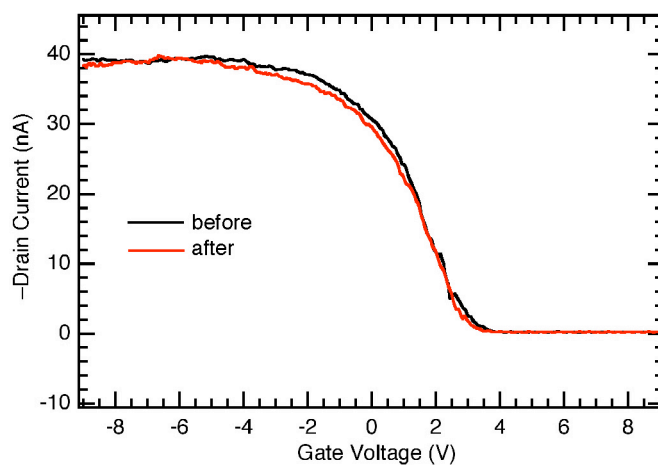


Figure S2. Control experiment before and after immersion in THF solution.

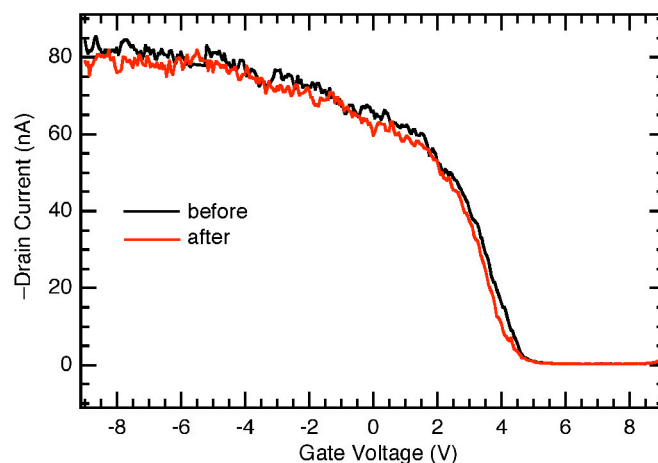


Figure S3. Control experiment showing before and after immersion in a 1.0 mM solution of the parent spiropyran that lacks a surface tether.

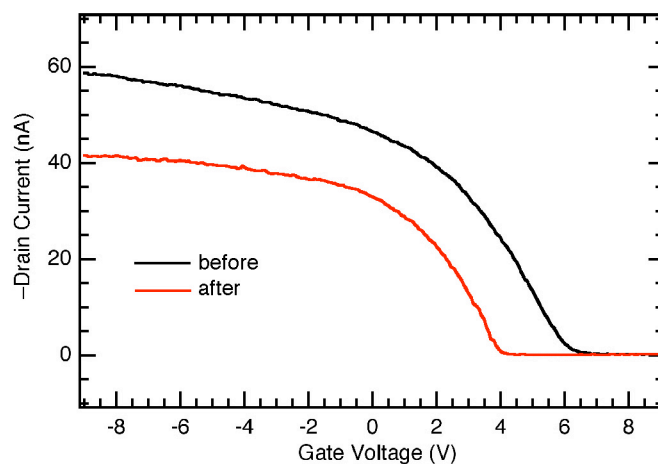


Figure S4. Before and after pyrene is assembled on the surface of the CNT showing similar threshold shifts to those from **2a** (shown in Figure S1).

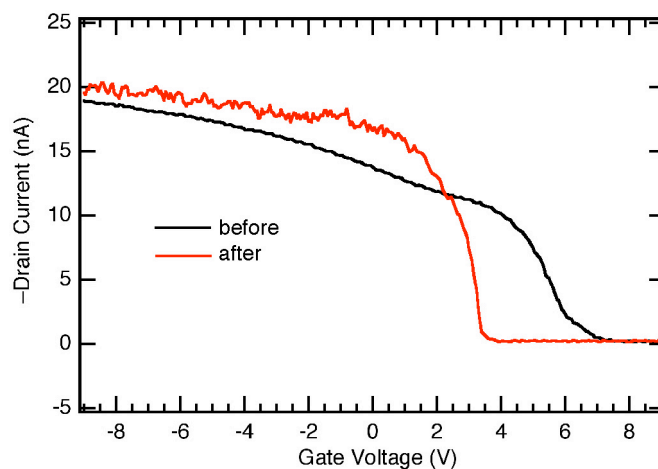


Figure S5. Before and after dodecane is assembled on the surface of the CNT showing similar threshold shifts to those from **1a** (shown in Figure 2c).

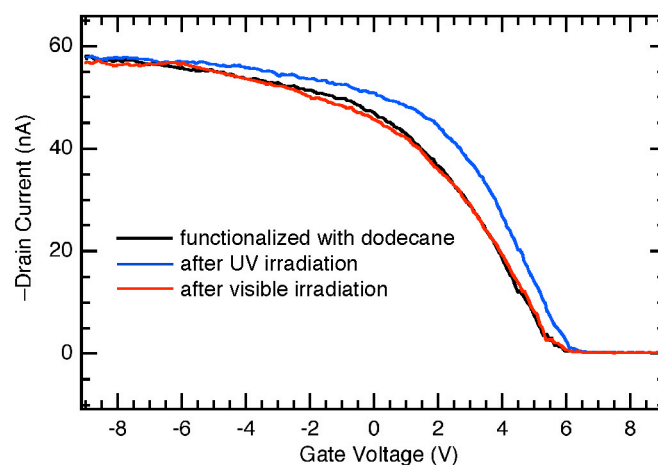


Figure S6. SWCNT functionalized noncovalently with dodecane (black curve). Blue curve is after UV (365 nm) and the red curve is after visible light irradiation (633 nm) irradiation.

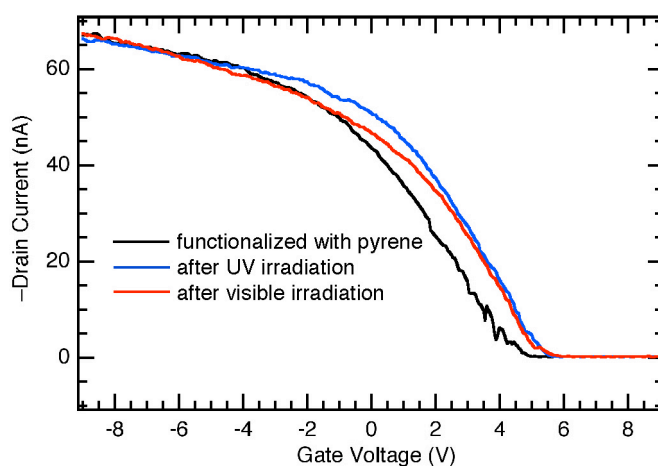


Figure S7. SWCNT functionalized noncovalently with pyrene (black curve). Blue curve is after UV (365 nm) and the red curve is after visible light irradiation (633 nm) irradiation.

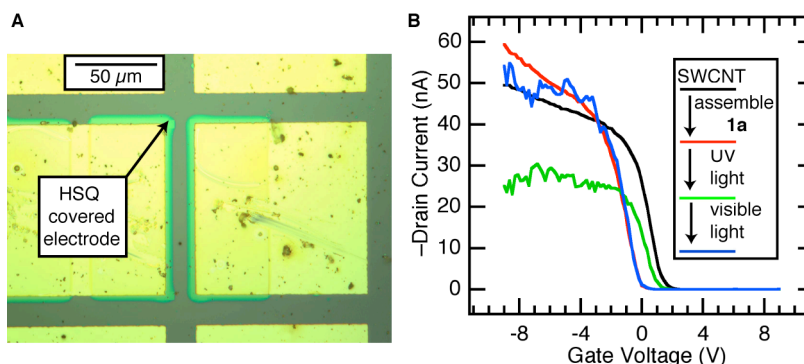


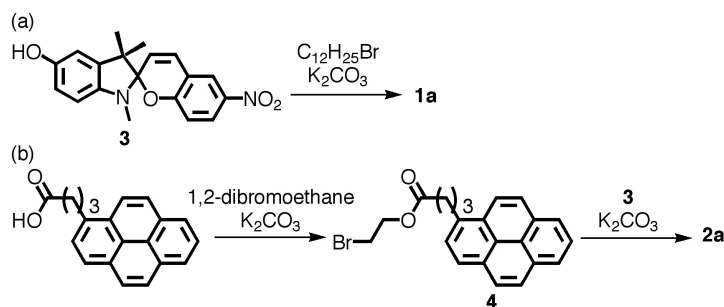
Figure S8. (A) Optical micrograph showing devices with HSQ resin coating the gold electrodes. (B) Change in drain current of an individual SWCNT device with HSQ covered junctions as a function of V_g . The source drain bias voltage is held at 50 mV. Black curve is device before assembly; red curve is device after assembly of **1a**; green curve after irradiation with UV light for ~ 10 minutes; blue curve after irradiation with visible light.

2. Synthesis

General. Reagents employed were either commercially available or prepared according to a known procedure as noted below. Anhydrous and oxygen-free THF and DMF were obtained from a Schlenk manifold with purification columns packed with activated alumina and supported copper catalyst (Glass Contour, Irvine, CA). Unless otherwise noted, all reactions were run in oven-dried glassware, and monitored by TLC using silica gel 60 F254 precoated plates (EM Science) when necessary. Column chromatography was performed on a CombiFlash® Sg100c system using RediSep™ normal phase silica columns (ISCO, Inc., Lincoln, NE). ^1H NMR (300MHz) and ^{13}C NMR (75MHz) spectra were recorded on Bruker DRX-300 spectrometers at room temperature unless otherwise noted. HRMS were recorded on JEOL JMS-HX110A/110A Tandem mass spectrometer.

Starting Materials. 1',3'-Dihydro-5'-hydroxyl-1',3',3'-trimethyl-6-nitrospiro-[2H-1-benzopyran-2,2'-(2H)-indole] (**3**) was synthesized according to the reported

procedure.¹ 1-pyrenebutyric acid was purchased from Aldrich Chemical Company and used without purification.



Scheme S1. Synthesis of **1a** and **2a**.

Synthesis of 1a. To the solution of **3** (0.30g, 0.89mmol) in 20 mL of degassed anhydrous DMF was added anhydrous K_2CO_3 (2.45g, 17.7mmol) and 1-bromododecane (2.21g, 8.87mmol). The mixture was stirred at room temperature for 2 days before 150 mL of H_2O was added. The aqueous solution was extracted with dichloromethane (3 x 70 mL), and the combined organic extracts were washed with H_2O (2 x 40 mL), saturated aqueous NaCl (20 mL), and then dried over $MgSO_4$. After filtering and concentrating under reduced pressure **1a** was obtained as yellow powder (0.14 g, 28%) after chromatography on silica gel with CH_2Cl_2 /hexane (1:3, v/v) eluant. 1H -NMR ($CDCl_3$) δ (ppm): 0.92 (t, J = 6.5 Hz, 3H), 1.21 (s, 3H), 1.29-1.57 (m, 21H), 1.93 (m, 2H), 2.71 (s, 3H), 3.94 (t, J = 6.5 Hz, 2H), 5.85 (d, J = 10.3 Hz, 1H), 6.45 (d, J = 10.3 Hz, 1H), 6.76 (m, 3H), 6.93 (d, J = 9.8 Hz, 1H), 8.04 (m, 2H). ^{13}C -NMR ($CDCl_3$) δ (ppm): 14.5, 20.3, 23.1, 26.2, 26.5, 29.8-30.0 (8), 32.3, 52.8, 69.2, 107.2, 107.6, 110.6, 113.3, 115.9, 119.1, 122.1, 123.1, 126.3, 128.6, 138.0, 141.2, 142.2, 154.1, 160.3. HRMS (FAB+): cald. for $C_{31}H_{42}O_4N_2$: 506.3145 M/Z ; found: 506.3129 M/Z .

Synthesis of 4. To the solution of 1-pyrenebutyric acid (0.50g, 1.73mmol) in 20 mL of degassed anhydrous DMF was added anhydrous K_2CO_3 (2.45g, 17.7mmol) and 1,2-dibromoethane (3.26g, 17.3mmol). Then the mixture was stirred at room temperature for 1 day before 100 mL of H_2O was added. The aqueous solution was extracted with dichloromethane (3 x 50 mL), and the combined organic extracts were washed with H_2O (2 x 40 mL) saturated aqueous NaCl (20 mL), and then dried over $MgSO_4$. After filtering and concentrating under reduced pressure, **4** was obtained as white powder (0.63 g, 91%) after chromatography on silica gel with CH_2Cl_2 /hexane (1:1, v/v) eluant. 1H -NMR ($CDCl_3$) – (ppm): 2.20 (m, 2H), 2.49 (t, J = 7.2 Hz, 2H), 3.39 (t, J = 7.8 Hz, 2H), 3.48 (t, J = 6.1 Hz, 2H), 4.38 (t, J = 6.1 Hz, 2H), 7.85 (d, J = 7.8 Hz, 1H), 7.94-8.00 (m, 3H), 8.09-8.14 (m, 4H), 8.28 (d, J = 9.3 Hz, 1H). ^{13}C -NMR ($CDCl_3$) – (ppm): 27.1, 29.2, 33.1, 34.0, 64.2, 123.7, 125.2, 125.4, 126.3, 127.2, 127.8, 129.2, 130.4, 131.3, 131.8, 135.9, 173.4. HRMS (FAB+): calcd. for $C_{22}H_{19}O_2Br$: 394.0568, 396.0551 M/Z ; found: 394.0568, 396.0545 M/Z .

Synthesis of 2a. To the solution of **4** (0.21 g, 0.53 mmol) in 20 mL of degassed anhydrous DMF was added anhydrous K_2CO_3 (0.74 g, 5.31 mmol) and **3** (0.27 g, 8.08 mmol). Then the mixture was stirred at room temperature for 3 days before 200 mL of H_2O was added. The aqueous solution was extracted with dichloromethane (3 x 80 mL), and the combined organic extracts were washed with H_2O (2 x 40 mL), saturated aqueous K_2CO_3 (20 mL), saturated aqueous NaCl (20 mL), and then dried over anhydrous $MgSO_4$. After filtering and concentrating under reduced pressure, **2a** was obtained as a dark red powder (69 mg, 19%) after recrystallization with CH_2Cl_2 /hexane (1:1, v/v). The compound exists as a mixture of **2a** and **2b** that aggregate strongly, similar to what has

been observed for other dyes that form H-aggregates.²⁻⁴ ¹H-NMR (CDCl₃) δ (ppm): 1.22 (s, 3H), 1.31 (s, 3H), 2.32 (m, 2H), 2.62 (m, 2H), 2.76 (s, 3H), 3.51 (m, 2H), 4.24 (m, 2H), 4.53 (m, 2H), 5.91 (d, J = 10.1 Hz, 1H), 6.51 (d, J = 10.1 Hz, 1H), 6.81 (m, 3H), 6.85 (d, J = 10.3 Hz, 1H), 7.96 (d, J = 7.9 Hz, 1H), 8.09-8.22 (m, 9H), 8.37 (d, J = 9.5 Hz, 1H). ¹³C-NMR (CDCl₃) δ (ppm): 20.0, 26.1, 27.2, 30.1, 33.5, 34.2, 52.8, 63.5, 67.4, 107.2, 107.6, 110.9, 113.2, 115.9, 119.1, 122.0, 123.1, 123.7, 124.7, 125.2, 125.5, 126.3, 127.1, 127.9, 128.9, 129.1, 130.4, 131.3, 131.8, 136.1, 139.0, 141.3, 143.4, 153.0, 160.3, 174.0. HRMS (FAB+): calcd. for C₄₁H₃₆O₆N₂ ([M+H]⁺): 653.2652 *M/Z*; found: 653.2643 *M/Z*.

3. UV and visible light irradiation of CNT samples

UV light and visible light irradiations were performed with 8 W handheld FisherBiotech Ultraviolet lamps (λ = 365 nm) and 0.95 mW uniphase Helium-neon laser equipment (λ = 633 nm), separately. For each UV light irradiation, the lamp was straightly fixed above the samples by 20 cm, while for each IR illumination, the laser was fixed away from samples by 0.5 m.

References:

- 1 Guo, X.; Zhang, D.; Zhou, Y.; Zhu, D. *J. Org. Chem.* **2003**, *68*, 5681-5687.
- 2 Guo, X.; Zhou, Y.; Zhang, D.; Yin, B.; Liu, Z.; Liu, C.; Lu, Z.; Huang, Y.; Zhu, D. *J. Org. Chem.* **2004**, *69*, 8924-8931.
- 3 Seki, T.; Ichimura, K. *J. Phys. Chem.* **1990**, *94*, 3769-3775.
- 4 Nueesch, F.; Gratzel, M. *Chem. Phys.* **1995**, *193*, 1-17.