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A Photodegradable Hexaaza-Pentacene Molecule for Selective Dispersion of Large-Diameter Semiconducting Carbon Nanotubes

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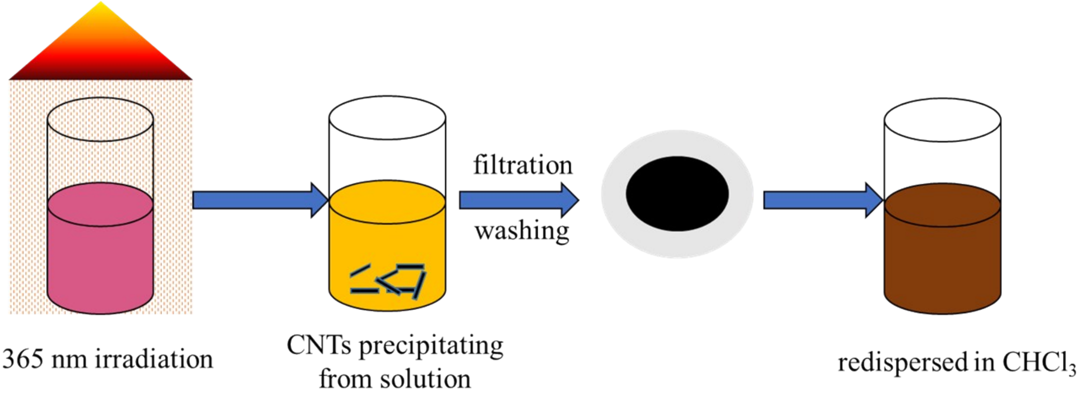
Experimental section

Materials: HiPco and Arc-discharged SWCNTs were purchased from Nanointegris Technologies Inc. PFO, P3DDT and F8T2 were purchased from Derthon Optoelectronics Materials.

Dispersion of SWCNTs: For all the organic dispersions, 2 mg dispersants (4HP, PFO, P3DDT, F8T2, PFPXX and 4HP) and 1 mg SWCNTs were added to 4 ml of toluene. The solutions were ultrasonicated with a top-tip dispergator (Misonix XL2000) for 2 h at 3 W, and then were centrifuged at 20000 g for 2 h (Allegra X-22R centrifuge) to remove the bundles and insoluble materials. The supernatants were collected for characterization and fabrication of TFTs.

Optical absorption spectroscopy: All the dispersions were measured by UV-Vis-NIR spectrophotometer (Lambda 750). 2 mm and 1 cm path length quartz cells were used for all the samples and reference solution.

Fabrication of s-SWCNTs with clean surface: The scheme S1 shows the process of obtaining clean-surface s-SWCNT dispersion. After irradiation under a laser beam at 365 nm or blue light with 10 watt power, the 4HP solution was faded into light yellow solution in 15 minutes. Then most the photodegradable products could be removed with 0.1 μm filtration membrane, and the "sediments" left on the membrane. Finally, the collected s-SWCNT powders could be redispersed the in chloroform.



Scheme S1. The process of obtaining less-dispersant s-SWCNT dispersion.

Fabrication of samples for XPS and Raman characterization: The samples were fabricated with drop-coating method. 200 μl s-SWCNT solution in chloroform was dropped on a 1cm*1cm Si substrate. When the residual chloroform were dried, the samples were washed with toluene. Finally, the samples were baked at 120 centidegree for 30 min.

Fabrication of s-SWCTN thin film for TFT: The fabrication of s-SWCNT thin film is based on the traditional dip-coating method. The 300 nm SiO_2 substrate was immersed in the above mentioned s-SWCNT dispersion in chloroform for 10 h. Then take the substrate out the 4HP-SWCNT solution and blowing it with 99.999 % N_2. Wash the sample with amount of tetrahydrofuran and acetone at 80 °C. Finally, bake the substrate at 120 °C for 0.5 h. This process not only provided us a method to fabricate high-density film in a short time, but also confirmed the deposited s-SWCNTs contained less dispersants.

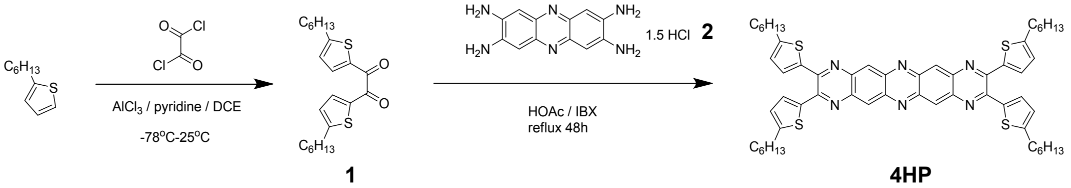
TFT fabrication: The TFTs were back-gated. Heavily doped p-type Si wafers were used as the substrate. A thermally grown 300-nm thick SiO_2 layer was used as the gate insulator. The source and drain electrodes were fabricated by electron-beam evaporation containing two layers: 3 nm Ti and 50 nm Au followed by lift-off. The patterned wafer was immersed in the 4HP-SWCNTs inks under 365 UV or red light for 6 h to high-dense and uniform network films. The patterned wafer was then carefully pulled out from the solution and blew off the solvent and the free polymers. Then the wafer was baked at 130 centidegree.

Calculation of the mobility of TFTs: the mobility was calculated by the following equation:

$$\mu = \frac{\partial I_{ds}}{\partial V_{gs}} \cdot \frac{L}{W} \cdot \frac{1}{V_{ds} C_{ox}}.$$

Here, $\frac{\partial I_{ds}}{\partial V_{gs}}$ could be calculated from the transfer curve. L and W represent the channel length and width, respectively. V_{ds} is the voltage applied between the source and drain electrodes. C_{ox} is the capacitance per unit area.

Synthesis route of 4HP:



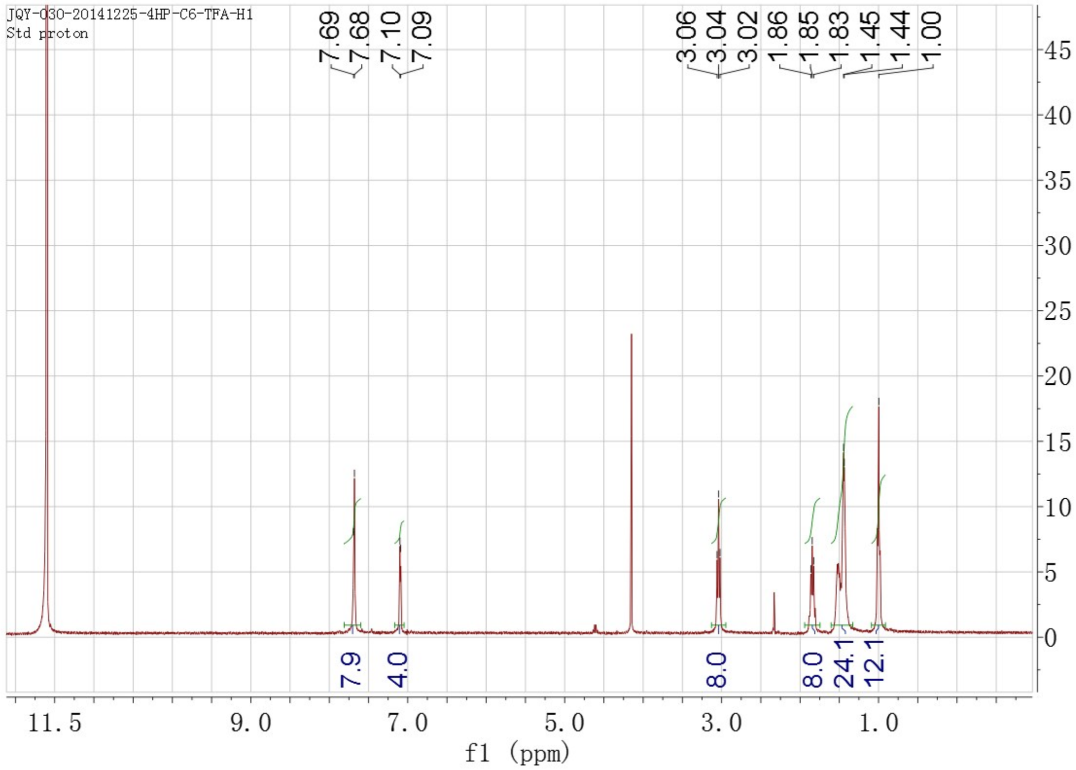
Scheme S2. Synthetic procedures of compound **4HP**.

(1) Synthesis of 1,2-Bis(5-hexylthiophene-2-yl)ethane-1,2-dione(1)

To a solution of $AlCl_3$ (4.46 g, 33.31 mmol) in anhydrous 1,2-dichloroethane (20 mL) cooled down to -78 ^{o}C was added dropwise, in succession, a solution of oxalyl chloride (0.95 g, 7.5 mmol) in anhydrous 1,2-dichloroethane (5 mL). A solution of 2-hexylthiophene (2.74 g, 16.25 mmol) and pyridine (1.16 g, 14.71 mmol) in anhydrous 1,2-dichloroethane (5 ml). After keeping the mixture for 1h between -20 ^{o}C and -15 ^{o}C, the temperature was raised to 0 ^{o}C and the mixture was poured over ice and extracted with methylene chloride. The extract was washed to neutral with water and dried over magnesium sulfate. Removing the solvent under reduced pressure, the residue was purified by column chromatography (eluent, hexane/DCM, 1:2) to give **1** as a yellow solid (2.06g, yield, 70%). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.86-7.85 (d, 2H), 6.88-6.87 (d, 2H), 2.90-2.85 (t, 4H), 1.76-1.66 (m, 4H), 1.39-1.25 (m, 12H), 0.91-0.86 (t, 6H). MS-TOF: found 391.9 (M^+ + H), calcd 391.1 (M^+ + H).

(2) Synthesis of 1,2,5,6-Tetra(5-hexylthiophene-2-yl)-Hexaazapentacene (4HP)

250 mL schlenk tube was added compound **1** (1.09 g, 2.79 mmol), 2,3,6,7-tetraaminophenazine hydrochloride (**2**) (0.369 g, 1.26 mmol), IBX (24 mg, concentration, 45%) and acetic acid (40 mL). the vessel was degassed with argon, then heated to refluxed for 48 hours. Cooled to room temperature, the reaction mixture was poured into water, filtered and the solids were rinsed with water and ethanol. Further purification was carried out with column chromatography (eluent, hexane/THF, 3/1). The resultant dark purple solids were crystallized from $CHCl_3$/hexane to yield target product **4HP** (0.48 g), yield 40 %. ^{1}H NMR (400 MHz, *TFA,* δ ppm) 7.69 (d, 4H), 7.64 (s, 4H), 7.10 (d, 4H), 3.04 (t, 8H), 1.91 – 1.80 (m, 8H), 1.58 – 1.36 (m, 31H), 1.00 (t, 12H). MS-TOF: found 948.4 (M^+ + H), calcd 948.4 (M^+ + H).



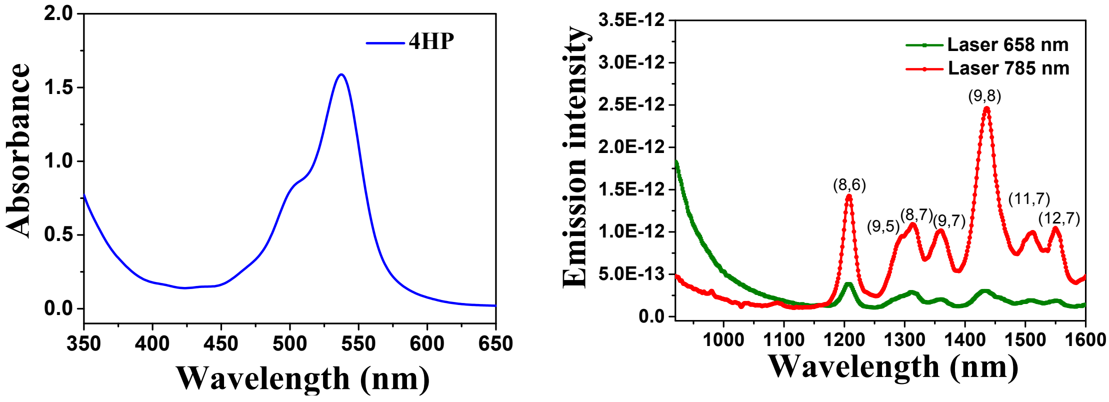


Fig. S1 (a) Absorption spectra of 4HP; (b) The Fluorescence spectra of 4HP-HiPco-SWCNTs .

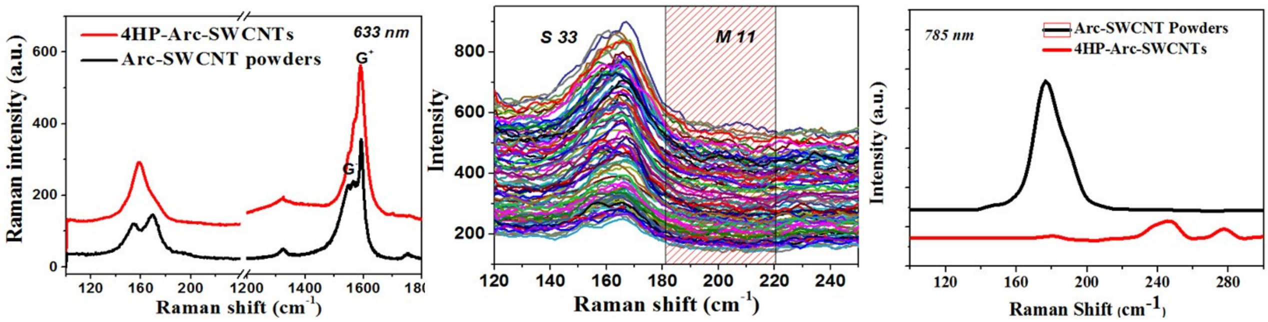


Fig. S2 (a) Raman spectra of 4HP dispersed Arc-discharged SWCNTs (red line) and as-prepared Arc-discharged SWCNTs powders (black line) at 633 nm; (b) Raman mapping of 4HP-dispersed Arc-SWCNTs at 633 nm; (c) Raman spectra of 4HP-dispersed Arc-SWCNTs at 785 nm.

As is shown in the fig. S2a, Raman scanning characterization over the whole area of the as-deposited s-SWCNT film under 633 nm demonstrated the high purity of the s-SWCNTs. The peak at 158.4 cm^{-1} represents the s-SWCNT with diameter of 1.58 nm estimated by $\omega_{\mathrm{RBM}} = 234/D_t + 10$, which is correspond to the absorption spectra of 4HP-Arc-SWCNTs, which the diameter of the selective SWCNTs mainly focus on 1.5 nm. For the Arc-SWCNTs, the G- is corresponded to the Breit-Wigne-Fano profile because of phonon-plasmon coupling only in metallic nanotubes. The G+ and G- features which represent the tangential modes of SWCNTs were frequently used to verify the purity. Compared to Arc-SWCNTs powders, the G- mode of 4HP-SWCNTs nearly disappeared, which further indicated the 4HP-dispersed s-SWCNTs were pure. Furthermore, Raman mappings with 633 nm laser were conducted on the thin-film transistor and no metallic peaks were found, which further demonstrated the high purity of 4HP-dispersed Arc-s-SWCNTs (fig. S2b). 785 nm Raman spectra could detect some metallic peaks more sensitively. Fig. S2c indicate the sorted s-SWCNTs by 4HP have a high purity.

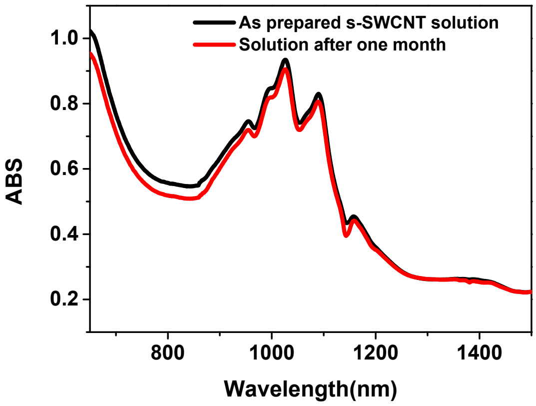
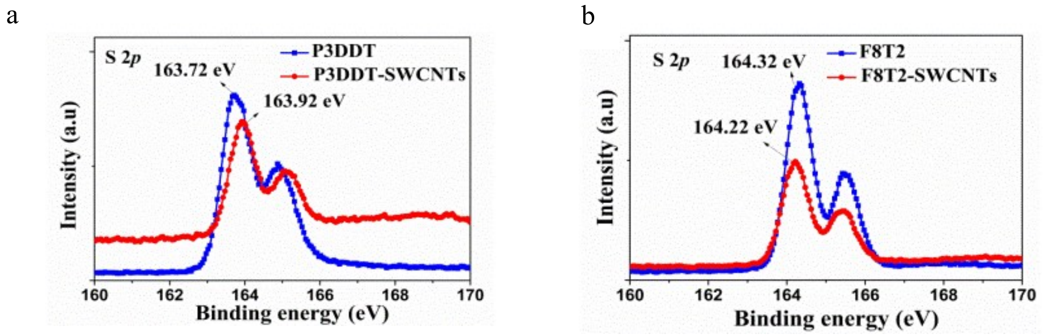


Fig. S3 The verification of stability of s-SWCNT dispersions by UV-Vis-NIR spectra.

As the 4HP molecules are photodegradable, the stability of the sorted s-SWCNT dispersions should be considered. Therefore, the verification of stability of s-SWCNT dispersions has been conducted in the past months. We found little changes have happened in the 4HP-SWCNT dispersions by UV-Vis-NIR spectra after one month (figure S3). In addition, only in high-power UV or blue light, 4HP molecules are photodegradable. In generally, the glass could deplete the most UV light. So the dispersions of 4HP-SWCNT could exhibit good stability in atmosphere.



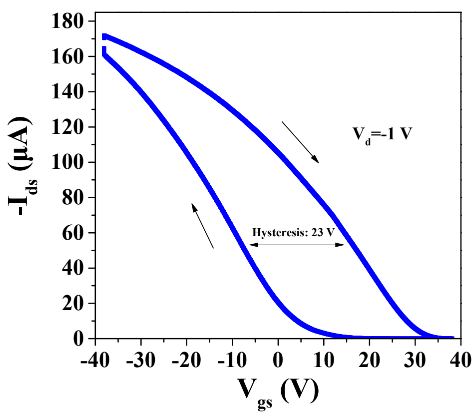
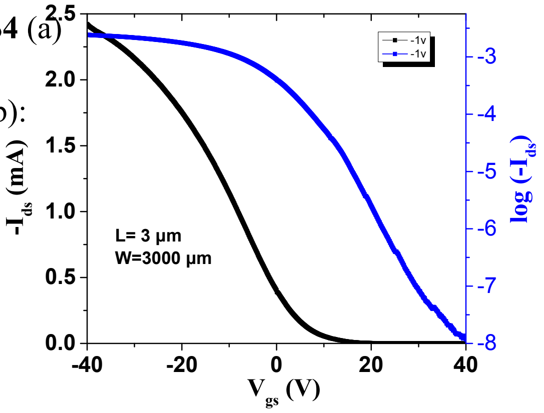


Fig. S4 (a) and (b):



Comparative analysis of S 2p peak of P3DDT and F8T2 containing thiophene groups in backbone structures before and after interaction with s-SWCNTs, respectively.

Fig. S5 (a) The transfer curve of the transistor with a channel length of 20 μm and width of 200 μm; (b) The transfer curve of the transistor with channel width of 3000 μm.

The hysteresis is an important parameter for the FFTs, especially for the frequency devices. Fig. S5 shows the forward and reverse curves in the transfer curves. The hysteresis is about 23 V, which be caused by the doping of O_2 and H_2O in air.

In order to estimate the purity of s-SWCNTs sorted by 4HP, we also fabricate the TFTs with channel length of 3 μm and width 3000 μm by drop coating, which also showed an on-off ratio ＞10^4.