Electronic Supporting Information (ESI) for

A Flavin-Cu²⁺ Supramolecular Complex for Highly Selective Sorting of Semiconducting Single-walled Carbon Nanotubes with Specific Chiralities

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Materials and characterization

HiPco-SWNTs (0.7~1.2 nm diameter) are purchased from Unydim and used as received. Toluene (spectra analysis grade) was purchased from Tokyo Chemical Industry Co., LTD. Japan. Synthesis of a new SWNT solubilizer is described below.

Synthesis Scheme



Synthesis of 4,5-bis (dodecylthio)benzene-1,2-diamine

Synthetic scheme



In a 300-mL three-necked flask, xantphos (600 mg, 1 mmol), 4,5-dibromo-1,2-phenylenediamine(2.66 g, 10 mmol), $Pd_2(dba)_3(456$ mg, 0.5 mmol), 1,4-dioxane (100 mL) were placed, then removed oxygen under vacuo, to which triethylamine (6 mL, 30 mmol), 1-dodecanethiol (7.5 mL, 50 mmol) were added,

then removed oxygen again under vacuo. The obtained solution was heated at 110 °C for 3.5 h. After evaporating the solvent, the obtained crude sample dissolved in hexane and store in a refrigerator for one night to obtain a white solid, which was dried under vacuo for 3 h. The obtained product (yield, 4.2g) was used for the next step.

Synthesis of a precursor of ddtC12 (4,5-bis (dodecylthio)benzene-1-N-dodecyl,2-amine)

The synthesis of a precursor of **ddtC12** was carried out by the reaction of 4,5-bis (dodecylthio)benzene-1,2diamine (1.52 g, 3 mmol) and n-dodecyl chloride (0.36 mL, 1.5 mmol) in THF (5 mL) containing triethylamine (10 mL) at reflux temperature for 64 h under N₂ flow. Then, THF and triethylamine were removed by evaporation, followed by gel chromatographic technique (eluent: hexane/ethyl acetate = 4/1v/v). By the removal of the solvent from the obtained solution, a crude product (1.5 g) was provided, which was used for the next step.

Synthesis of ddtC12 Synthetic scheme



The precursor (1.51 g) and alloxane monohydrate (0.284 g, 2 mmol) were reacted in acetic acid (60 mL) containing B_2O_3 (0.42 g, 6.0 mmol) at 60 °C for 17.5 h. After adding sodium carbonate to neutralize the solution, then extracted using water and chloroform. After the separation of the organic phase, MgSO₄ was added and stored for overnight. By the solvent removal, a crude product was obtained, which was purified by chromatography (silica gel; eluent= hexane/ethyl acetate= 1/1 v/v, then 1/2 v/v). Evaporation of the solvents provided a red-colored solid (64 mg), which was characterized by ¹H NMR and MS analyses.



Fig. S1. ¹H NMR (300MHz) spectrum of **ddtC12** in CDCl₃. δ 8.38(1H, s), 8.02(1H, s), 7.19(1H, s), 4.67(2H, broad t), 3.11(2H, t, *J*=7Hz), 3.05(2H, t, *J*=8Hz), 1.86(6H, m, *J*=8Hz), 1.75(2H, q, *J*=8Hz), 1.52(2H, m, *J*=8Hz), 1.26(48H, m), 0.88(3H, t, *J*=6Hz).



Fig. S2. MS spectrum of ddtC12.

SWNT solubilization and characterization

Typical SWNT solubilization procedure is as follows. The SWNTs and **ddtC12** were placed in a glass vessel, then sonicated in toluene for 1 h using a bath-type sonicator (Branson, 5510) followed by centrifugation at 10,000 g (25 °C) for 1 h using a centrifuge (Hitachi-Koki, Himac CF-15R). The supernatant (top 80%) was collected for use in UV-vis-NIR absorption (JASCO, V670) and Raman (Nanophoton Corporation, RAMANtouch, excitation at 633-nm) spectral measurements. Molecular orbital (HOMO and LUMO) calculations were carried out using a Gaussian 09 software (exchange-correlation function: B3LYP/6-311G). The molecular-mechanics simulations were carried out by using the MacroModel program (Schrodinger, version 10.2) with the OPLS-2005 force field. The dielectric constant of toluene (2.3) was used in the calculations. Minimization of the calculations was carried out by using the Polak-Ribiere conjugate gradient

(PRCG) with a convergence threshold on the gradient of 0.05 kJ/mol. Default values have been used for all the other parameters.



Fig. S3. Photos of ddtC12 before



Fig. S4. Visible absorption spectra of **ddtC12** before (black) and after (red) the addition of $Cu(ClO_4)_2$ in toluene.



Fig. S5. Procedure of the solubilization of SWNTs using **ddtC12** and the photos of the obtained solutions.



Fig. S6. Vis-NIR spectra of a solubilized SWCNT solution using **ddtC12** in absence (**left**) and the presence (**right**) of $Cu(ClO_4)_2$ in toluene. Optical path length, 1.0 mm.



Fig. S7. Procedure of the solubilization of SWNTs using **ddtC12** in the presence of Cu ion and the photos of the obtained solutions.



Fig. S8. Side view of SWCNT sem-(8,6) with the adsorbed flavin-Cu2+ supramolecular complex.