Supporting Information

Synthesis, Characterization and Photophysical Properties of a SWNT-Phthalocyanine Hybrid

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Experimental section

Techniques. UV-Vis-NIR spectra were recorded in 1 cm quartz cuvettes on a Varian Cary 5000 spectrophotometer or a Hewlett-Packard 8453 spectrophotometer. The thermogravimetric analyses were performed with a TGA Q500 TA Instruments at 10°C/min under N_2. IR spectra were recorded on a Bruker Vector 22, or in a Bruker IFS60v spectrophotometer. Elemental analyses were perfomed in a Perkin Elmer 2400 CHN analyzer. ^{1}H NMR spectra were recorded with a BRUKER AC-300 (300 MHz) instrument with solvent used as internal reference. MALDI-TOF MS spectra were obtained from an Applied Biosystem 4700 instrument equipped with a Nd:YAG laser operating at 335 nm. Melting points (m.p.) were determined in a Büchi 504392-S equipment and are uncorrected. For the TEM analyses: a small amount of the functionalized SWNTs was suspended in DMF and a drop of the suspension was placed on a copper grid (3.00 mm, 200 mesh, coated with carbon film). After air-drying the sample was investigated by TEM Philips EM 208, accelerating voltage of 100 kV. For the AFM analyses: the samples were prepared by spin coating on silicon wafers from a solution of SWNTs in DMF and then investigated with a Veeco Multimode Scanning Probe Microscope equipped with a Nanoscope IIIa controller.

Photophysical Measurements. Femtosecond transient absorption studies were performed with 387 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:Sapphire laser system (Model CPA 2101, Clark-MXR Inc.). Nanosecond Laser Flash Photolysis experiments were performed with 532-nm laser pulses from a Quanta-Ray CDR Nd:YAG system (6 ns pulse width) in a front face excitation geometry. For all photophysical experiments an error of 10% must be considered. Fluorescence lifetimes were measured with a Laser Strobe Fluorescence Lifetime Spectrometer (Photon Technology International) with 337 nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the Laser Strobe systems are described on the manufactures web site, http://www.pti-nj.com. Emission spectra were recorded with a SLM 8100 Spectrofluorometer.

Materials. Solvents were purchased from SDS and Fluka. All dry solvents were freshly distilled under argon over an appropriate drying agent before use. Chemicals were purchased from Sigma-Aldrich or Acros Organics and used as received without further purification. 4,5-tert-butylphenoxyphthalonitrile[1] and amino acid **3**[2] were prepared using described procedures. HiPCO SWNTs were purchased from Carbon Nanotechnologies Inc. (www.cnanotech.com) and purified following literatures procedures.[3]

Synthesis.

2,3,9,10,16,17-hexa-tert-butylphenoxy-23-(hydroxymethyl)phenylphthalocyanine (6) A mixture of 4-(hydroxymethyl)phenylphthalonitrile (0.11g, 0.47 mmol), 4,5-tert-butylphenoxyphthalonitrile (0.60 g, 1.41 mmol) and lithium (0.012 g, 1.69 mmol) was refluxed in 1-pentanol (6 ml) for 18 h under argon atmosphere. The solution was then reduced to dryness. Glacial acetic acid (30 ml) was added and the suspension stirred for 30 minutes. The product was then extracted with CH_2Cl_2 and washed with H_2O (3 x 30 ml). The organic layer was separated, dried over Mg_2SO_4 and reduced in volume to obtain a green product that was subjected to column chromatography on silica gel (toluene/methanol 10:1) to yield H_2Pc **6** as a green product (0.11 g, 16 %). mp > 300ºC. ^{1}H-NMR (300 MHz, $CDCl_3$, 25ºC): δ= 8.95 (s, 1H, arom H), 8.69 (d, 1H, arom H), 8.62 (d, 1H, arom H), 8.56 (s, 1H, arom H), 8.44 (s, 1H, arom H), 8.35 (s, 1H, arom H), 8.05 (d, 1H, arom H), 7.96 (d, 2H, AA'BB'), 7.60 (d, 2H, AA'BB'), 7.53 (d, 2H, arom H), 7.49-7.37 (m, 16H, phenyl H), 7.29-7.19 (m, 8H, phenyl H), 4.91 (s, 2H, CH_2O), 1.55-1.33 (m, 54H, $C(CH_3)_3$) ppm; IR (KBr): υ= 2961, 2902, 2867 (CH), 1601 (C=N), 1505, 1488, 1441, 1267, 1217, 1176, 1086, 1012, 880, 828, 747 cm^{-1}; UV/vis ($CHCl_3$): λ_{max}(logε/dm^3 mol^{-1} cm^{-1})= 348(4.8), 611(4.4), 647(4.6), 672(5.1), 706(5.1) nm; MALDI-TOF MS: m/z = 1509 $[M+H]^+$, 1508 $[M^+]$; elemental analysis for $C_{99}H_{98}O_7N_8 \cdot H_2O$: Calcd: C 77.72, H 6.58, N 7.32. Found: C 77.55, H 6.49, N 7.38.

2,3,9,10,16,17-hexa-tert-butylphenoxy-23-formylphenylphthalocyanine (7)

Manganese oxide (II) (0.0041g, 0.047 mmol) was added to a solution of phthalocyanine 1 (0.065g, 0.043 mmol) in chloroforme (30 ml). The mixture was stirred for 5h at 60ºC. The resulting reaction crude was filtered through celite to remove unreacted MnO_2. The filtrate was evaporated and washed with methanol to give **7** (0.06g, 94%). mp>300ºC; ^{1}H-NMR (300 MHz, $CDCl_3$, 25ºC): δ= 10.23 (s, 1H, CHO), 9.15 (s, 1H, arom H), 8.77(d, 1H, arom H), 8.69 (s, 2H, arom H), 8.51 (s, 1H, arom H), 8.31 (d, 1H, arom H), 8.15 (m, 4H, AA'BB'), 8.06 (d, 1H, arom H), 7.54 (d, 2H, arom H), 7.49-7.30 (m, 16H, phenyl H), 7.24-7.12 (m, 8H, phenyl H), 1.5-1.3 (m, 54H, $C(CH_3)_3$) ppm. IR (KBr): υ= 2960, 2903, 2866 (CH), 1704 (CHO), 1603 (C=N), 1505, 1470, 1450, 1402, 1267, 1217, 1176, 1088, 1014, 882, 747 cm^{-1}. UV/vis ($CHCl_3$): λ_{max}(logε/dm^3 mol^{-1} cm^{-1}): 347(4.6), 611(4.2), 646(4.4), 672(4.8), 706(4.9); MALDI-TOF MS: m/z= 1507 $[M+H]^+$, 1506 $[M^+]$; elemental analysis for $C_{99}H_{96}N_8O_7 \cdot H_2O$: Calcd. C 77.93, H 6.34, N 7.34. Found: C 77.95, H 6.43, N 7.36.

2,3,9,10,16,17-hexa-tert-butylphenoxy-23-carboxyphenylphthalocyanine (4)

Sulfamic acid (0.0064 g, 0.066 mmol) and sodium chlorite (0.006 g, 0.066 mmol) were added to a solution of phthalocyanine 2 (0.050 g, 0.033 mmol) in THF/H_2O (6:1). The mixture was stirred for 3h at room temperature. The resulting reaction crude was washed with water and the organics dried to give **4** as a green powder (0.050 g, 87%). mp> 300ºC; ^{1}H-NMR (300MHz, THF-d_8, 25ºC): δ= 9.26 (s, 1H, arom H), 8.81 (s, 1H, arom H), 8.6 (bs, 2H, arom H), 8.49 (s, 1H, arom H), 8.41 (d, 2H, AA'BB'), 8.25 (d, 1H, arom H), 8.18 (d, 2H, AA'BB'), 8.12 (d, 1H, arom H), 7.66 (d, 2H, arom H), 7.53-7.40 (m, 16H, phenyl H), 7.29-7.22 (m, 8H, phenyl H), 1.5-1.2 (m, 54H, $C(CH_3)_3$) ppm. IR (KBr): υ= 2961, 2904, 2867 (CH), 1733 (C=O), 1606 (C=N), 1507, 1461, 1442, 1270, 1217, 1172, 1087, 1012, 880, 829, 749 cm^{-1}; UV/vis (THF): λ_{max}(logε/dm^3 mol^{-1} cm^{-1})= 347(4.9), 609(4.6), 641(4.8), 669(5.2), 703(5.3) nm; MALDI-TOF MS: m/z = 1523 $[M+H]^+$, 1522 $[M^+]$; elemental analysis for $C_{99}H_{98}O_7N_8{\cdot}H_2O$: Calcd: C 77.01, H 6.39, N 7.26. Found: C 76.80, H 6.37, N 7.21.

4-(Hydroxymethyl)phenylphthalonitrile (5) $Pd(PPh_3)_4$ (0.0076 g, 0.0066 mmol) was added to a solution of 4-iodophthalonitrile (0.167 mg, 0.66 mmol) in dry THF (6 ml). After stirring the reaction mixture under argon for 20 min, K_2CO_3 (0.091 g, 0.66 mmol), 4-(hydroxymethyl)phenylboronic acid (0.1 g, 0.66 mmol) and water (1.7 ml) were added. The mixture was refluxed for 24 h, then cooled to room temperature and THF evaporated. The solid suspended in water was filtered through a glass frit and washed with more water. The residue was dissolved in THF and dried over anhydrous Na_2SO_4. After removing the solvent under reduced pressure, the crude product was purified by column chromatography in silica gel (hexane/THF, 2:1) to give compound **5** (0.327 g, 71%) as a white solid. mp= 129 – 130 ºC; ^{1}H-NMR (300 MHz, MeOH-d_4, 25ºC): δ = 8.25 (dd, J = 1.9, 0.4 Hz, 1H; H-3), 8.11 (dd, J = 8.2, 1.9 Hz, 1H; H-5), 8.00 (dd, J = 8.2, 0.4 Hz, 1H; H-6), 7.72 (d, J = 8.6 Hz, 2H; H-2',H-6'), 7.51 (d, J = 8.6, 2H; H-3', H-5') ppm; ^{13}C-NMR (75 MHz, MeOH-d_4, 25ºC, TMS): δ = 147.5 (C-4), 144.7 (C-4'), 137.2 (C-1'), 135.4 (C-6), 133.0 (C-5), 132.7 (C-3), 128.8 (C-3', C-5'), 128.4 (C-2', C-6'), 117.4 (C-2), 116.8 (CN), 116.7 (CN), 114.8 (C-1), 64.6 (CH_2OH) ppm. IR (KBr): υ= 3354 (OH), 3105, 3072, 3047, 2231 (C≡N), 1567, 1382, 1163, 1099, 852, 747 cm^{-1};

elemental analysis for $C_{15}H_{10}N_2O$: Calcd. C 76.91, H 4.30, N 13.66. Found: C 76.74, H 4.37, N 13.59.

Functionalised SWNT (2) A suspension of microwave purified SWNT (30 mg) in dry DMF (100 ml) was first sonicated for 30 min and then amino acid **3** (400 mg) and paraformaldehyde (400 mg) were added portionwise (100 mg every 24h.) and the reaction mixture was heated at 120°C for 5 days. After cooling to room temperature, the suspension was sonicated and centrifugated. The black supernatant was filtered on a Millipore membrane (PTFE 0.22μm) and the black solid was washed several times with fresh DMF (sonicated, centrifugated and filtered) until the supernatant solution remained colorless (see Fig. S3). The solid on the filter was washed with CH_2Cl_2 and diethyl ether affording functionalized SWNTs **2** (13 mg).

SWNT-H_2Pc (1) In a suspension of f-SWNT **2** (10 mg) in dry DMF was bubbled gaseous HCl, the nanotubes immediately initiated to precipitate. The reaction mixture was stirred at room temperature for 1h. then filtered on a Millipore membrane (PTFE 0.22μm) and washed with CH_2Cl_2 and diethyl ether. The deprotected SWNTs were immediately re-suspended in fresh dry DMF (50 ml) and then *N*-ethyldiisopropylamine (2 ml), H_2Pc **4** (10 mg), of *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide (EDC) (50 mg) and 1-hydroxybenzotriazole (HOBt) (50 mg) were added. The reaction mixture was stirred at room temperature for 4 days, then filtered on a Millipore membrane (PTFE 0.22μm) and the black solid was extensively washed with THF and CH_2Cl_2 to remove the excess of phthalocyanine.

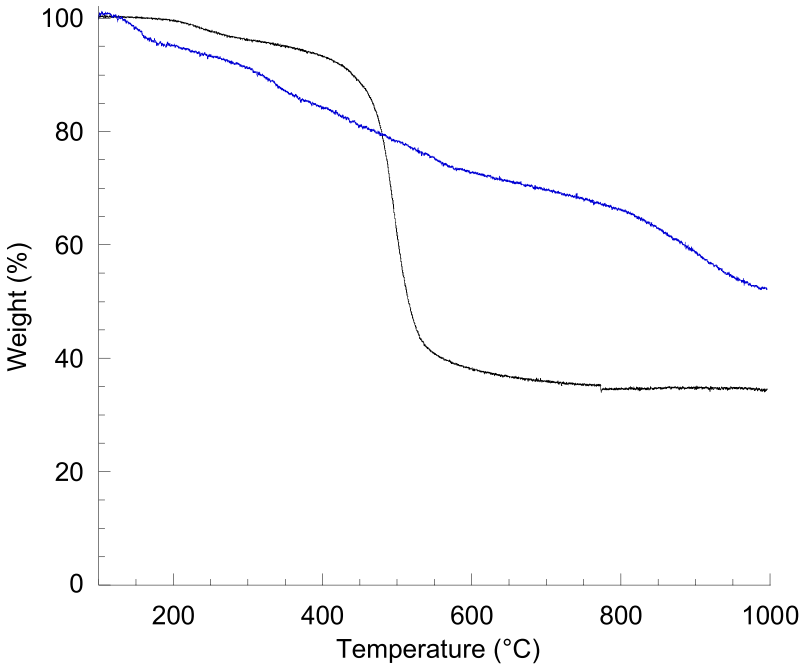

Fig. S1 Thermogravimetric analysis of the SWNT-H_2Pc nanoconjugate **1** (blue) and of the phthalocyanine **4** (black).

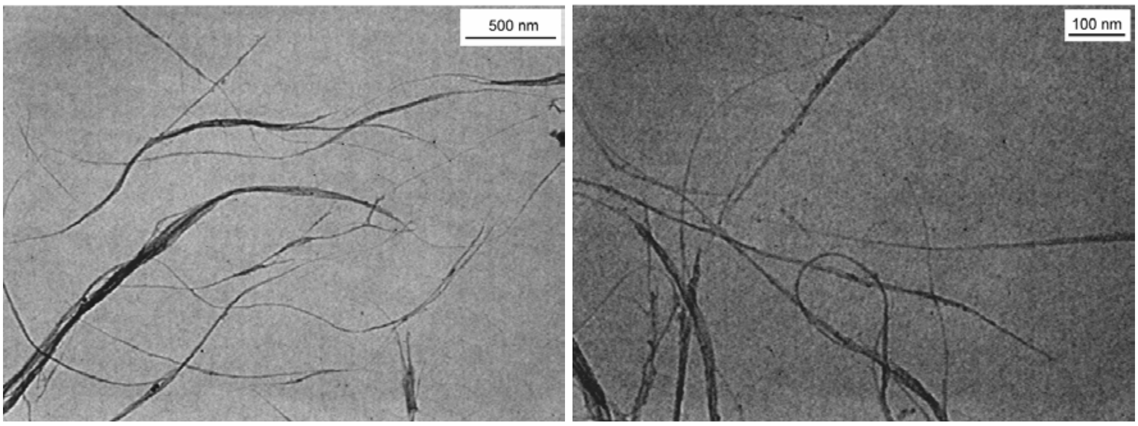

Fig. S2 TEM pictures of SWNT-H_2Pc nanoconjugate **1**. Left image: general view showing large aspect ratio material. Right image: higher magnification picture showing the quasi-absence of metal catalyst nanoparticles on the nanotubes.

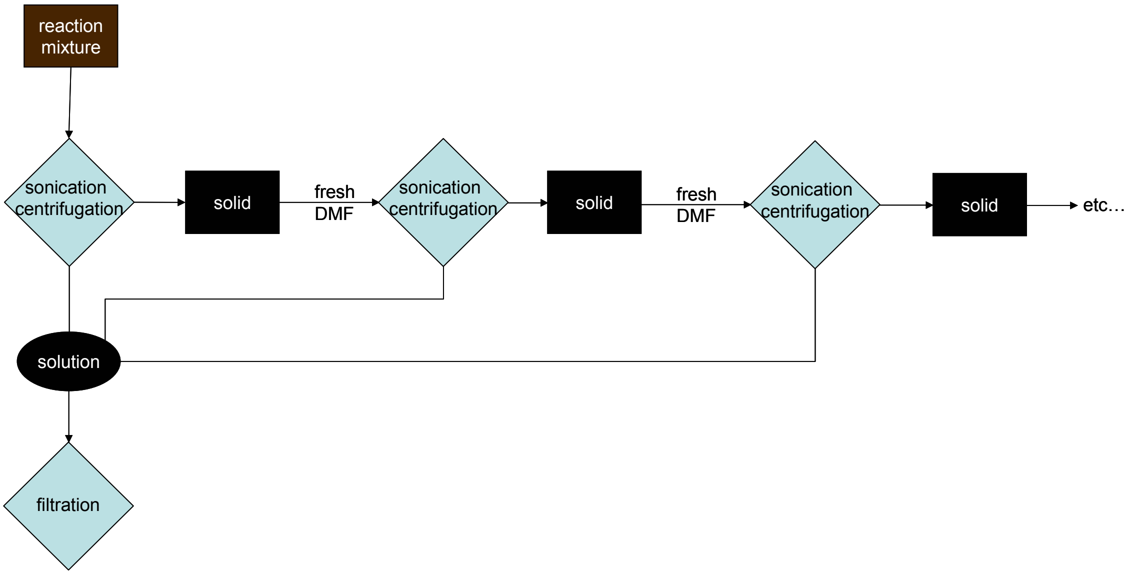

Fig. S3 Schematic representation of the work up procedure for the synthesis of f-SWNT **1**.

References.

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