

Supporting Information

Peripheral versus Axial Substituted Phthalocyanine-Double- Walled Carbon Nanotube Hybrids as Light Harvesting Systems

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Experimental section: Materials and instruments

Synthesis and characterization of new compounds

All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. The crude compound was purified by a Combiflash Rf chromatography system (Teledyne Technologies, Inc., Thousand Oaks, CA). SiO₂ (40–63 μm) TLC plates coated with SiO₂ 60F254 were visualized by UV light. NMR spectra were measured with a Bruker AC 300. UV-vis spectra were recorded with a Helios Gamma, Jasco V-670 and Shimadzu UV 3600 spectrophotometers. Mass spectra were obtained from a Bruker Microflex matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) and from an Agilent Technologies 5973N electronic impact spectrometer. The thermogravimetric analysis was performed using a TGA/DSC Linea Excellent instrument by Mettler-Toledo, collected under inert atmosphere of nitrogen, with a rate of 10°C min⁻¹, and the weight changes were recorded as a function of temperature.

Raman spectroscopy

Raman measurements were carried out with a Renishaw inVia Reflex Confocal Raman Microscope at room temperature using laser excitation of 785 nm. Measurements were taken with 10 s of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 100x objective. Raman spectra were collected on numerous spots on the sample and recorded with a Peltier cooled CCD camera. The sample was measured on glass without any sample preparation. The intensity ratio ID/IG was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software.

XPS analysis

Photoelectron spectra (XPS) were recorded with a VG Escalab 200R spectrometer provided with a hemispherical electron analyser and a MgKα (hν = 1253.6 eV) X-ray source, powered at 100 W. The background pressure in the ultra-high vacuum chamber was maintained below 8x10⁻⁹ mbar during data acquisition. The XPS data signals were taken in increments of 0.1 eV with dwell times of 50 ms. For each sample, survey and high resolution spectra were recorded at pass energies of 200 and 50 eV, respectively, by scanning a number of times in order to get good signal-to-noise ratios. Charge effects on the samples were corrected by taking the binding energy (BE) of the C 1s peak at 284.8 eV. High resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software "XPS peak". The raw data were used with no preliminary smoothing. Symmetric Gaussian-Lorentzian lines (90% G-10% L) were used to approximate the line shape of the fitting components.

AFM and HR-TEM microscopies

AFM images were obtained with a Multimode V8.10 (Veeco Instruments Inc., Santa Barbara, USA) with a NanoScope V controller (Digital Instruments, Santa Barbara, USA). The sample was prepared by drop casting as dispersion on a silicon wafer. TEM observations were carried out using TOPCON002B (Topcon CO.) at an acceleration voltage of 120 kV.

Electrochemical characterization

Osteryoung Square Wave Voltammetry (OSWV) was performed in benzonitrile and tetrahydrofuran. tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M as supporting electrolyte) was purchased from Aldrich-Sigma and used without purification. Solutions were deoxygenated by argon bubbling prior to each experiment, which was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a carbon working electrode (diameter = 2 mm) and a platinum wire counter electrode. A scan rate of 0.1 V.s⁻¹ was used. An Ag/AgNO₃ electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc⁺) before and after each experiment.

Photophysical studies

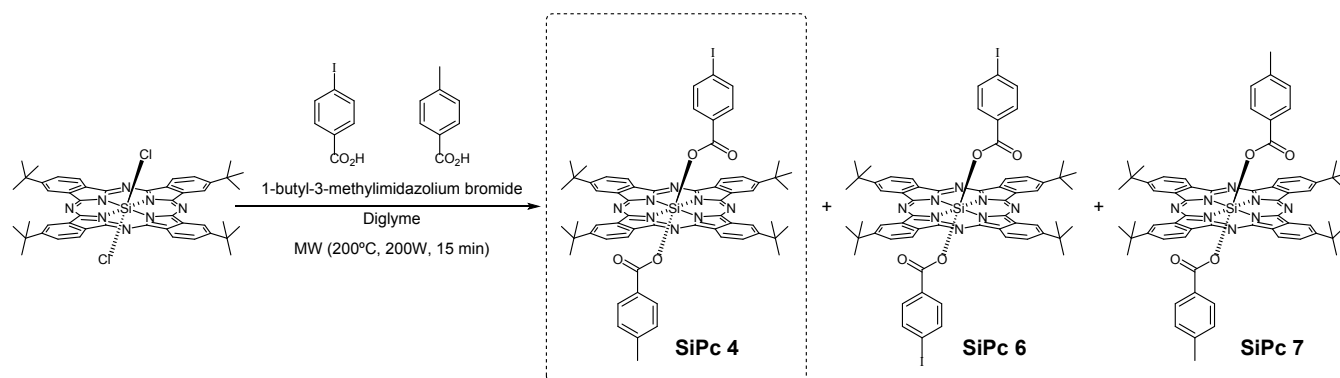
The steady-state fluorescence was recorded by using a Horiba Jobin Yvon Nanolog spectrofluorimeter equipped with PMT (for UV-visible) and InGaAs (for near-IR) detectors. The fluorescence lifetimes were measured with the Time Correlated Single Photon Counting (TCSPC) option with nano-LED excitation source (λ_{ex} = 494 nm) on the Nanolog. All the solutions were purged prior to spectral measurements using argon gas.

Femtosecond transient absorption spectroscopy experiments were performed using an Ultrafast Femtosecond Laser Source (Libra) by Coherent incorporating diode-pumped, mode locked Ti:Sapphire laser (Vitesse) and diode-pumped intra cavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.45 W. For optical detection, a Helios transient absorption spectrometer coupled with femtosecond harmonics generator both provided by Ultrafast Systems LLC was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.45 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into harmonic generator, which produces second and third harmonics of 400 and 267 nm besides the fundamental 800 nm for excitation, while the rest of the output was used for generation of white light continuum. In the present study, the second harmonic 400 nm excitation pump

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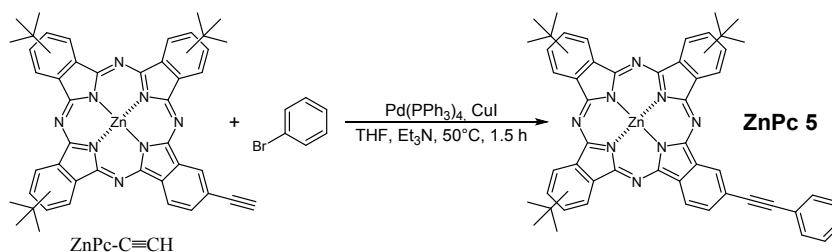
was used in all the experiments. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Data analysis was performed using Surface Xplorer software supplied by Ultrafast Systems. All measurements were conducted in degassed solutions at 298 K.

Synthesis of SiPc 4



(*t*-Bu)₄SiPcCl₂ (100 mg, 0.12 mmol), 4-iodobenzoic acid (160 mg, 0.65 mmol), 4-methylbenzoic acid (89 mg, 0.65 mmol), and 1-butyl-3-methylimidazolium bromide (33 mg, 0.15 mmol) were mixed in diglyme (1.5 ml) in a 10 ml capped microwave reaction tube. The contents were stirred and microwave-irradiated to a set temperature of 200°C for 15 min. The crude reaction mixture was added over 200 ml of aqueous NaOH 1M and vacuum-filtered, and the resulting-green-blue powder was dissolved in hot CHCl₃ (100 mL). Filtration and removal of solvent in vacuo provided the corresponding crude product, which was purified by Combiflash chromatography (0–100% of toluene in hexane) and yielded the desired product. First compound eluted: **SiPc 6** (26 mg, 17% yield) ¹H NMR (300 MHz, CDCl₃): δ 9.77–9.55 (8H, m, 8xH-SiPc), 8.48–8.42(4H, m, 4xH.SiPc), 6.58 (4H, d, *J* = 8.6 Hz, 4xH-Ar-I), 4.84 (4H, d, *J* = 8.6 Hz, 4xH-Ar-I), 1.85–1.78 (36H, m, 4x(CH₃)₃). UV-vis (CHCl₃) λ_{max}/nm (log ε): 360 (4.91), 625 (4.58), 665 (4.52), 695 (5.39). FTIR (KBr): ν/cm⁻¹ 2960.7, 2892.6, 2855.9, 1685.8, 1613.6, 1576.8, 1531.9, 1474.7, 1417.5, 1327.7, 1286.2, 1079.7, 1001.4, 935.3, 759.0. HR-MS (MALDI-TOF). *m/z*: calcd for C₆₂H₅₆I₂N₈O₄Si: 1258.229 [M]⁺, found: 1258.384. Second compound eluted: **SiPc 4** (23 mg, 17% yield): ¹H NMR (300 MHz, CDCl₃): δ 9.76–9.55 (8H, m, 8xH-SiPc), 8.46–8.41(4H, m, 4xH.SiPc), 6.58 (2H, d, *J* = 8.6 Hz, 2xH-Ar-I), 6.03 (2H, d, *J* = 8.4 Hz, 2xH-Ar-CH₃), 5.03 (2H, d, *J* = 8.4 Hz, 2xH-Ar-CH₃), 4.84 (2H, d, *J* = 8.6 Hz, 2xH-Ar-I), 1.84–1.78 (36H, m, 4x(CH₃)₃), 1.68 (3H, s, CH₃). UV-vis (CHCl₃) λ_{max}/nm (log ε): 360 (4.91), 624 (4.57), 663 (4.51), 694 (5.38). FTIR (KBr): ν/cm⁻¹ 2961.2, 2900.8, 2867.5, 1684.1, 1614.2, 1583.5, 1529.2, 1481.7, 1412.2, 1327.2, 1285.4, 1079.8, 942.3, 759.1. HR-MS (MALDI-TOF). *m/z*: calcd for C₆₃H₅₉I₂N₈O₄Si: 1146.348 [M]⁺, found: 1146.423. Third compound eluted: **SiPc 7**¹ (6 mg, 5% yield): ¹H-NMR (500 MHz, CDCl₃): δ 9.75–9.56 (8H, m, Pc-Ar-H), 8.46–8.41 (4H, m, Pc-Ar-H), 6.02 (4H, d, *J* = 8.3 Hz, Ph-Ar-H), 5.03 (4H, d, *J* = 8.3 Hz, Ph-Ar-H), 1.81–1.80 (36H, m, 4x(CH₃)₃), 1.68 (6H, s, 2xCH₃). UV/Vis (CHCl₃), λ_{max}/nm (log ε): 361 (4.89), 624 (4.54), 662 (4.48), 693 (5.33). FT-IR (KBr) ν/cm⁻¹ 2961, 2867, 1681, 1612, 1529, 1484, 1411, 1293, 1174, 1080, 942, 759 cm⁻¹. HR-MS (MALDI-TOF): *m/z*: calcd for C₆₄H₆₂N₈O₄Si: 1034.4658 [M]⁺, found: 1034.4711.

Synthesis of ZnPc 5



A solution of bromobenzene (12 mg, 8 μl, 0.08 mmol) in 1 mL of THF and 4.5 mL of trimethylamine was injected by syringe into a two neck round bottom flask containing tetrakis(triphenylphosphine)palladium(0) (1.2 mg, 10⁻³ mmol) and CuI (0.3 mg, 1·10⁻³ mmol) under argon. Then another THF solution of (tri-*tert*-butyl-ethynylphthalocyaninato)zinc(II)² (15 mg, 0.02 mmol) was injected by syringe. Subsequently, the temperature was raised to 50 °C and held for 1.5 hours. The crude was washed with 1M HCl solution and water, and extracted with dichloromethane. After the solvent was evaporated the product was chromatographed (silica gel, hexane/dioxane 5:1) yielding a blue-green solid (50%).³

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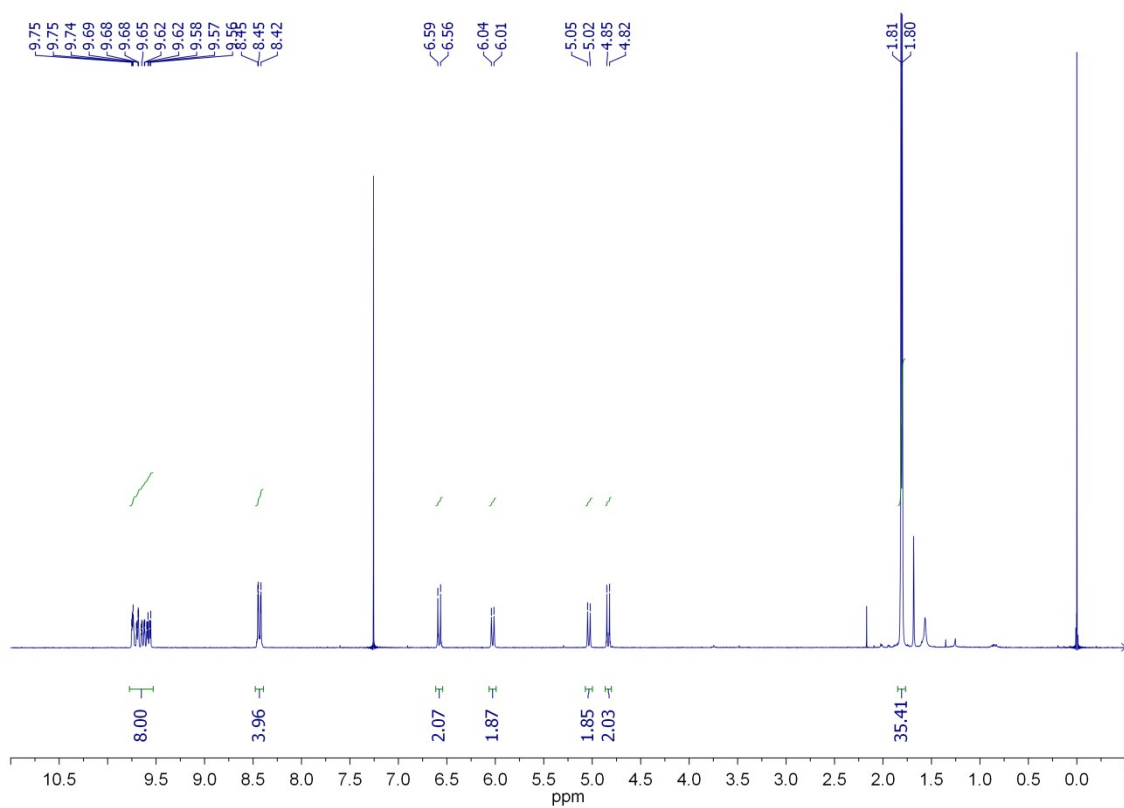
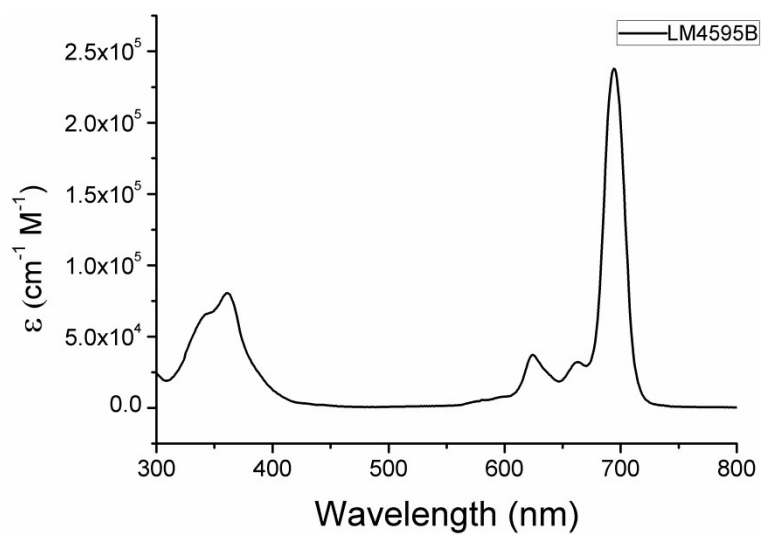
Figure S 1: $^1\text{H-NMR}$ spectrum of SiPc 4

Figure S 2: UV-vis spectrum of SiPc 4

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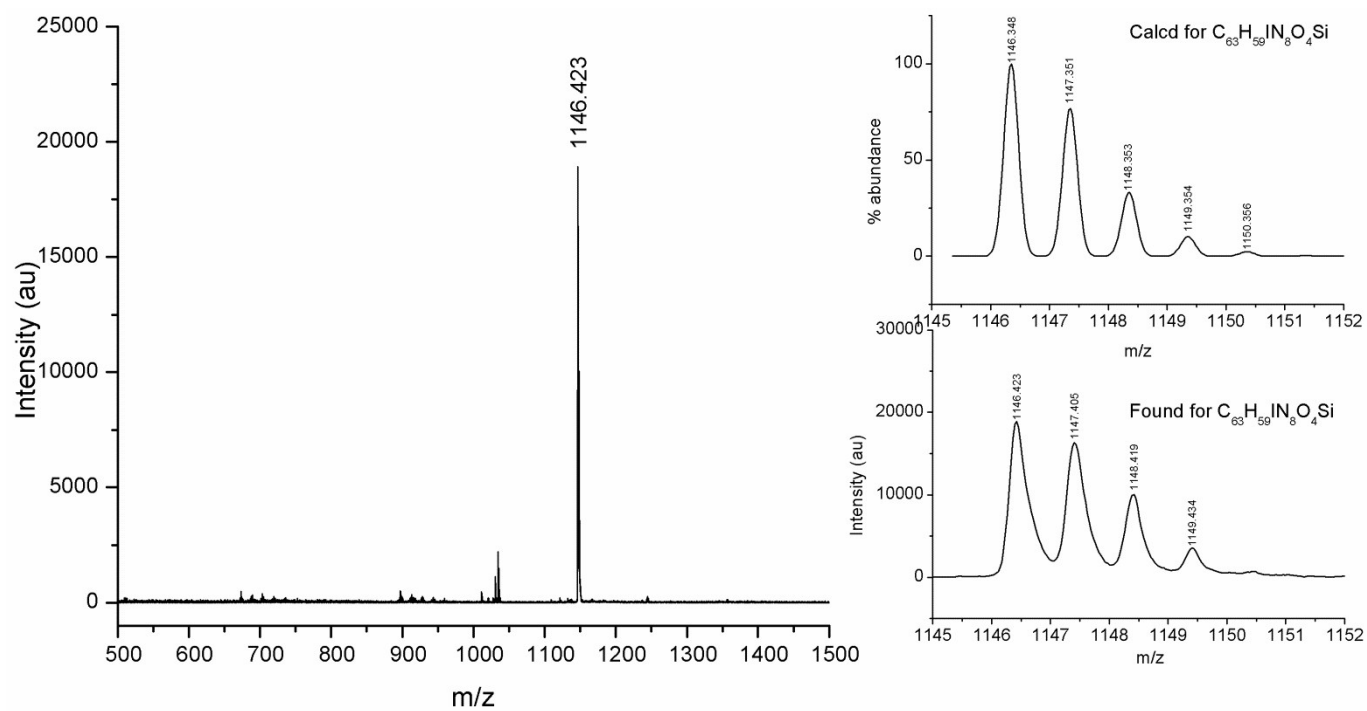
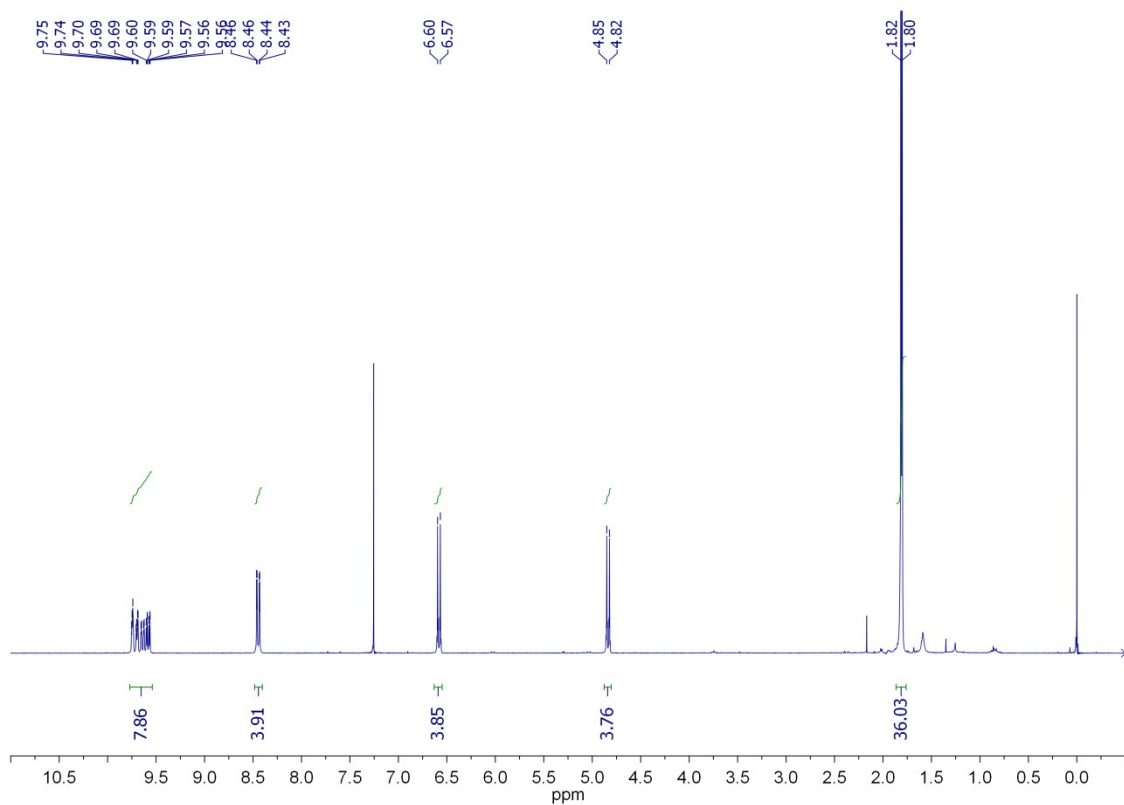


Figure S 3: HR-MS (MALDI-TOF) spectrum of SiPc 4

Figure S 4: 1H -NMR spectrum of SiPc 6

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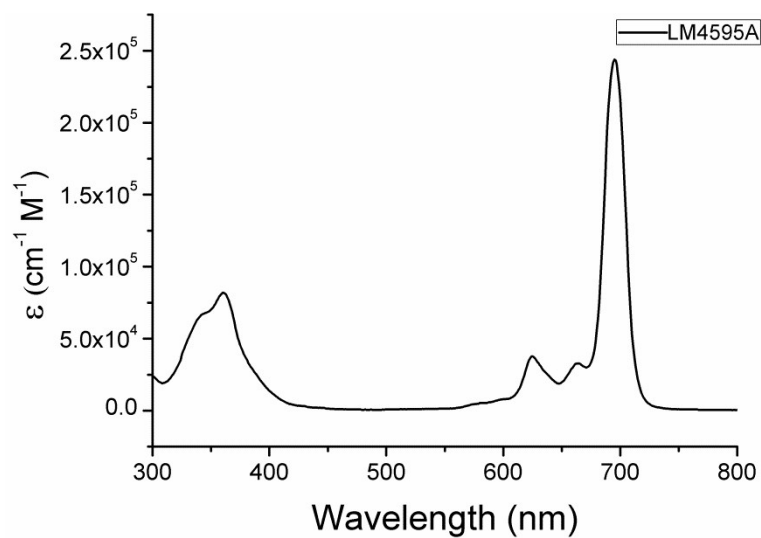


Figure S 5: UV-vis spectrum of SiPc 6

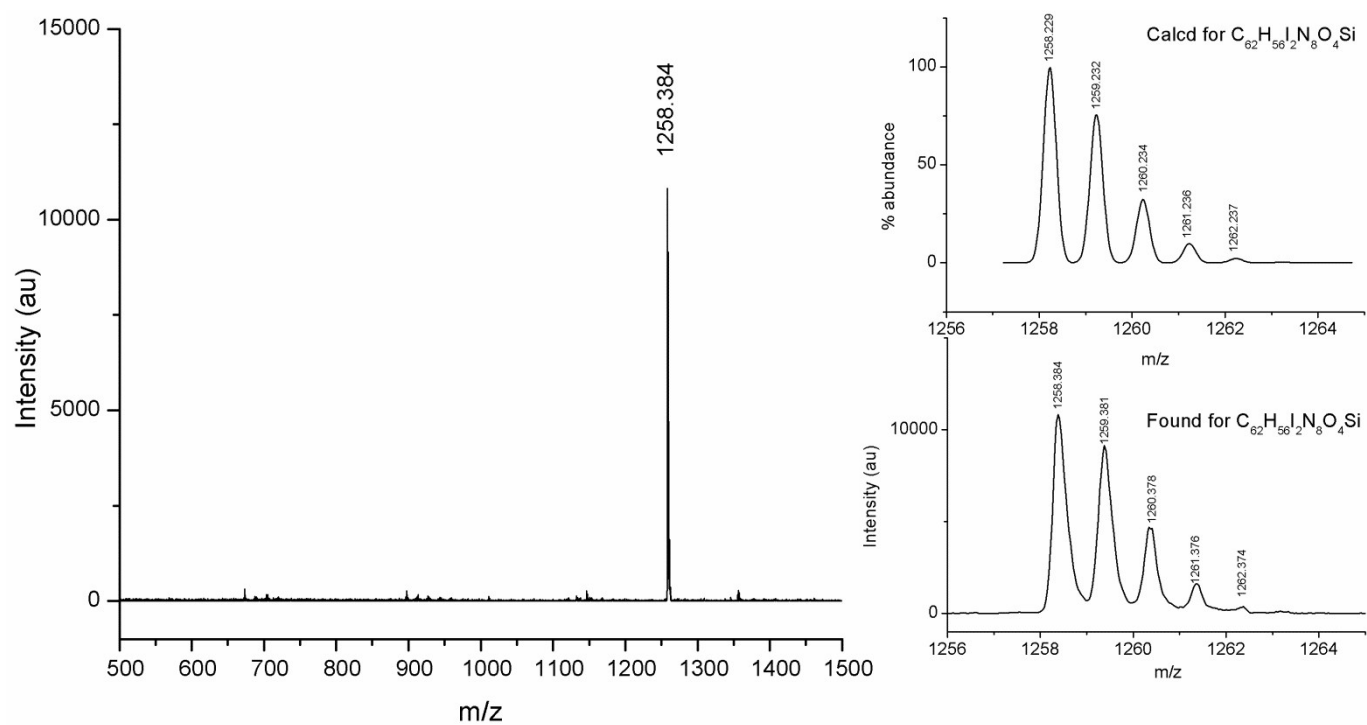


Figure S 6: HR-MS (MALDI-TOF) spectrum of SiPc 6

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Sample	C1s BE (eV)						O1s BE (eV)		N1s BE (eV)		Si2p BE (eV)	Zn2p _{3/2} BE (eV)	I3d _{5/2} BE (eV)
	sp ² C	sp ³ C	C-O	C=O	COO	π-π*	O=C	O-C	=N-	-NH-			
<i>pristine-DWCNT</i>	284.8 (69)		286.2 (16)	287.7 (6)	289.2 (4)	291.4 (5)	531.8 (49)	533.3 (51)					
DWCNT-TMS	284.8 (66)	285.3 (3)	286.3 (26)	287.7 (5)			532.0 (38)	533.4 (62)			101.3		
ZnPc 3	284.8 (65) 286.3 (10)	285.3 (25)							398.6 (74)	399.0 (75)		1022.3	621.4
SiPc 4	284.8 (60) 286.3 (3)	285.3 (33)			289.3 (4)				399.9 (76)	400.2 (25)	101.3		621.3
DWCNT-ZnPc 1	284.8 (72)	285.3 (2)	286.3 (20)	287.7 (6)			531.8 (40)	533.2 (60)	398.7 (75)	400.3 (25)		1022.3	
DWCNT-SiPc 2	284.8 (70)	285.3 (2)	286.3 (20)	287.7 (8)			531.8 (38)	533.1 (62)	398.8 (76)	400.3 (24)	103.8		

Table S 1: Binding energy (eV) of the core-level atoms of DWCNT samples and its precursors. The peak percentages are indicated in brackets.

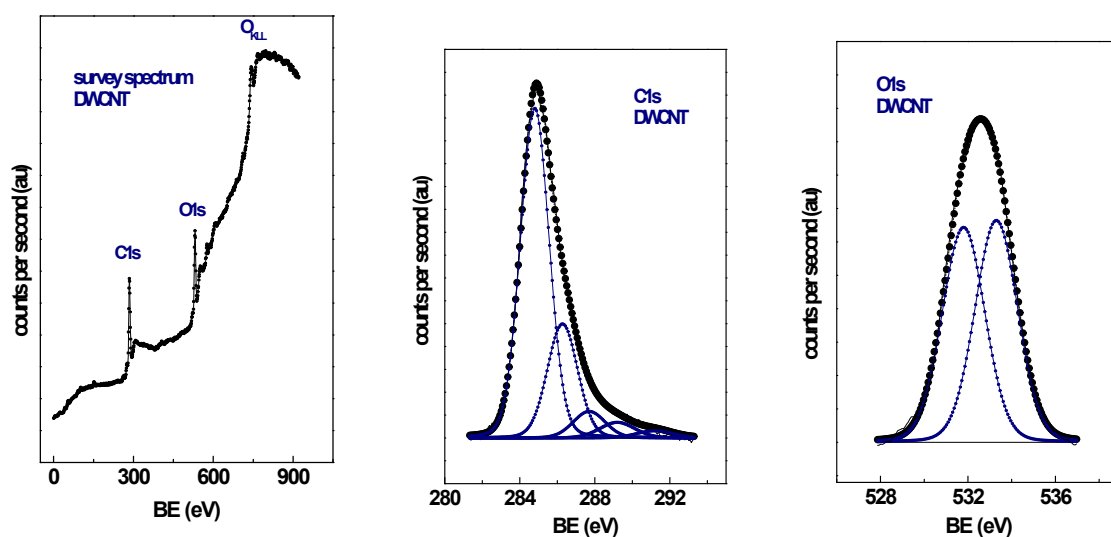


Figure S 7: Survey, C1s and O1s core-level spectra of pristine DWCNT

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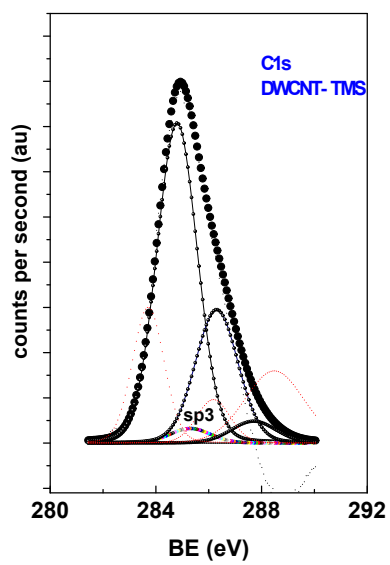
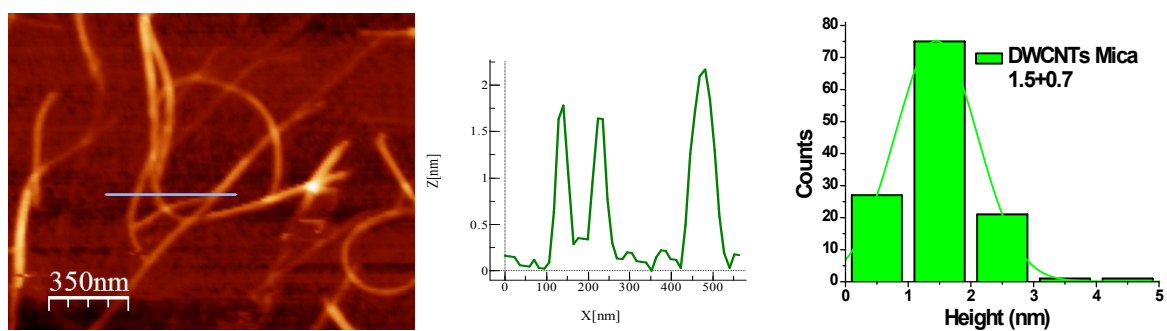


Figure S 8: C1s core-level spectra of DWCNT-TMS

Figure S 9. AFM image and height profile along the region indicated for *pristine* DWCNT together with its height distribution histogram showing the diameter distribution of the sample.

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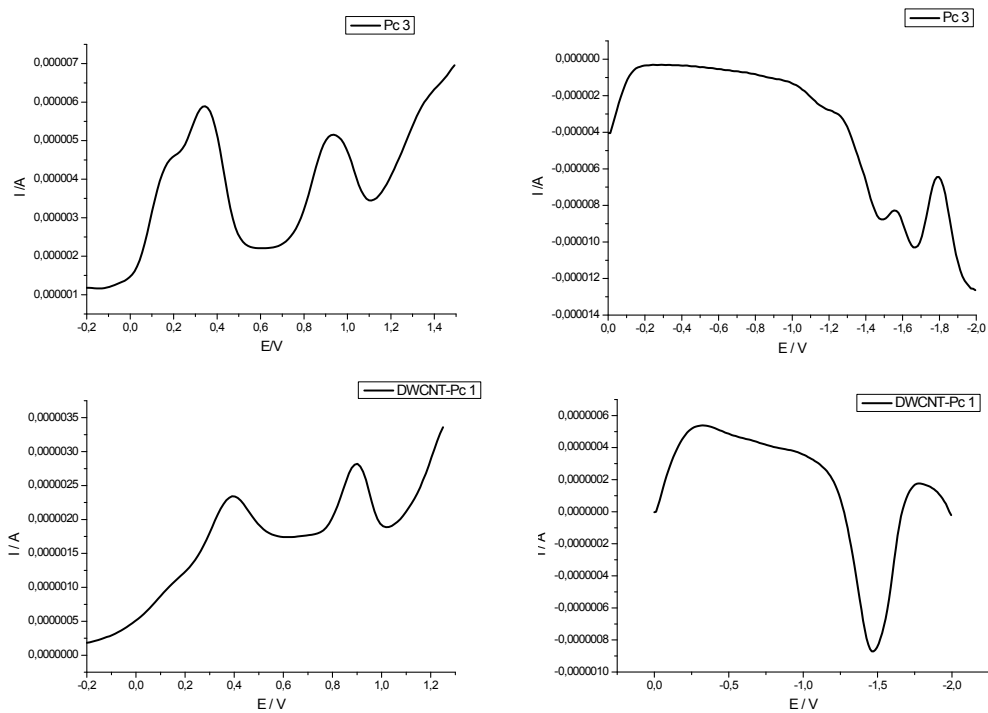


Figure S 10: Osteryoung Square Wave Voltammetry (scan rate = $0.1 \text{ V}\cdot\text{s}^{-1}$) of **DWCNT-ZnPc 1** and **ZnPc 3** in THF solution containing $0.1 \text{ M NBu}_4\text{PF}_6$ at room temperature.

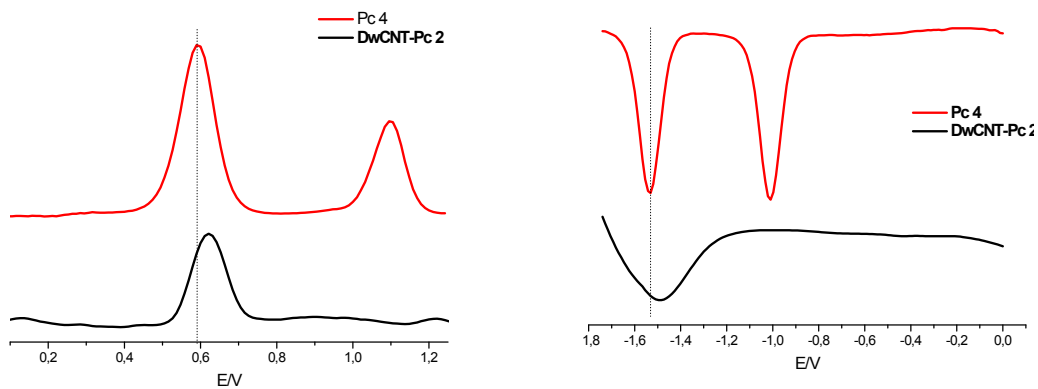


Figure S 11: Osteryoung Square Wave Voltammetry (scan rate = $0.1 \text{ V}\cdot\text{s}^{-1}$) of **DWCNT-SiPc 2** and **SiPc 4** in benzonitrile solution containing $0.1 \text{ M NBu}_4\text{PF}_6$ at room temperature.

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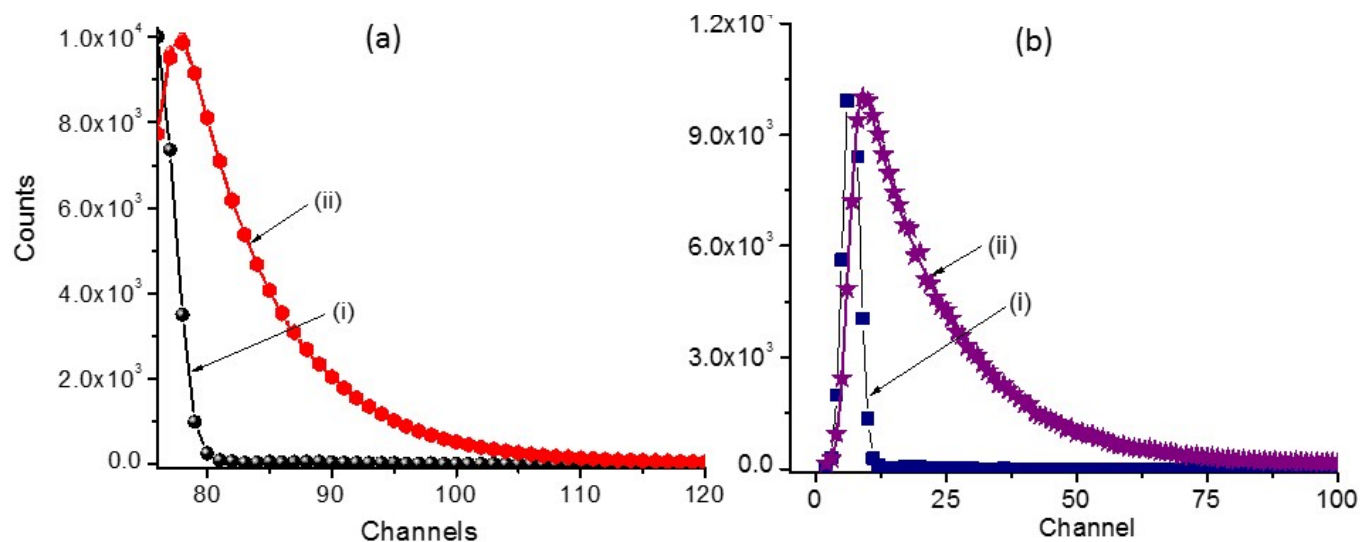


Figure S 12: Time resolved fluorescence emission of (a) ZnPc and (b) SiPc in DMF as the excitation wavelength of 494 nm (nanoLED). Curve (i) represent response of the prompt and curve (ii) represents the decay curve of the donor.

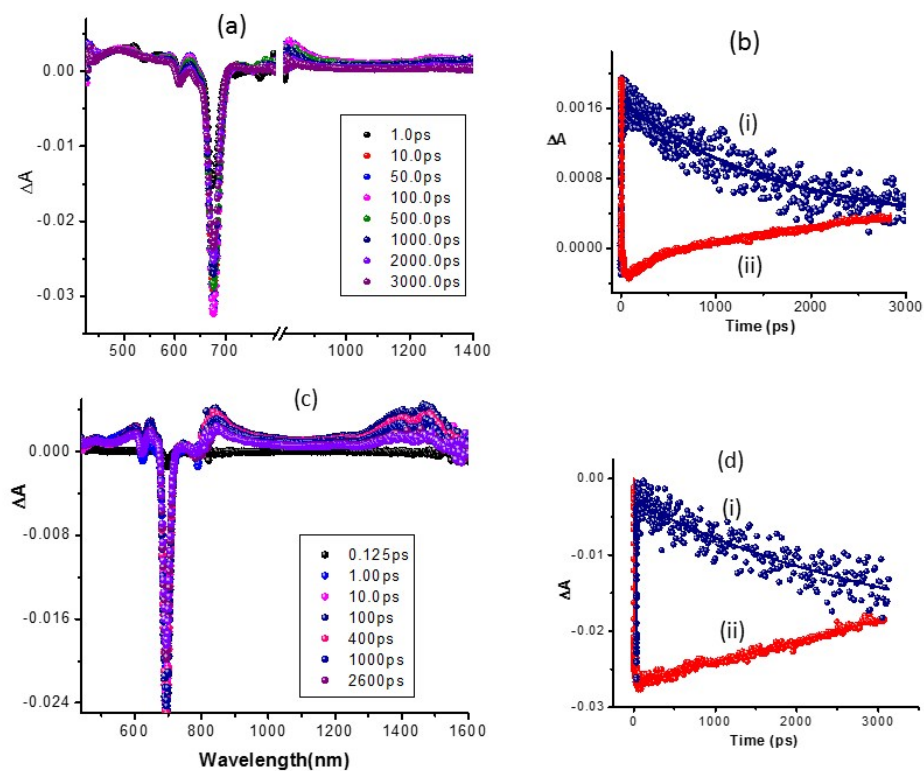


Figure S 13: (a) Femtosecond transient spectra of (a) ZnPc and (c) SiPc in DMF at the indicated delay times. The time profiles of the 678 (curve ii) and 1300 nm (curve i) peak of ZnPc, and 695 (curve ii) and 1476 nm (curve i) peaks of SiPc are shown in panel b and d, respectively.

Supporting Information

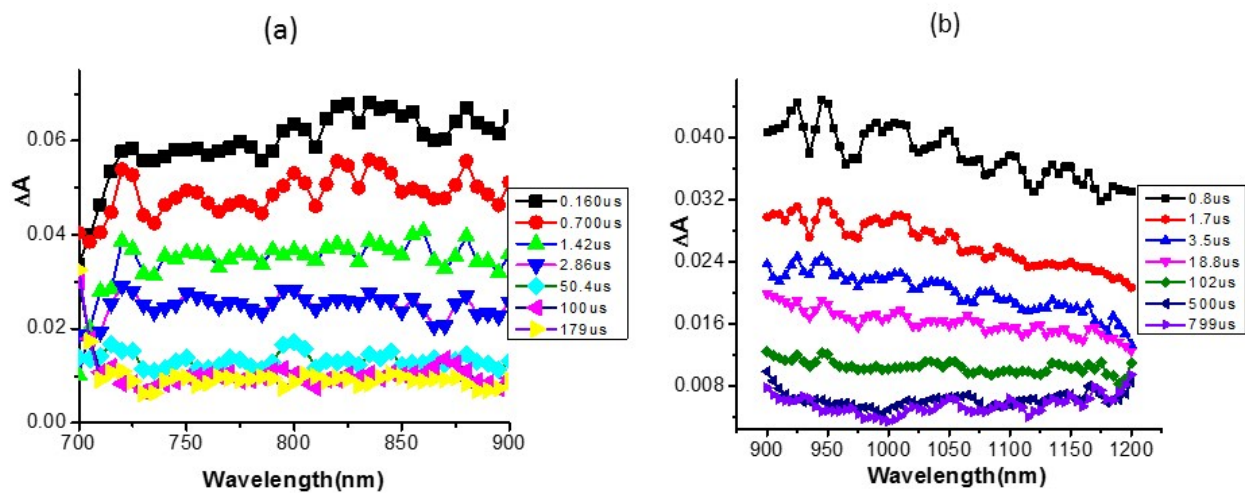


Figure S 14: Nanosecond transient absorption spectra of DWCNT-SiPc hybrid in DMF at the excitation wavelength of 355 nm (8 ns pulses) covering (a) visible and (b) near-infrared spectral regions.

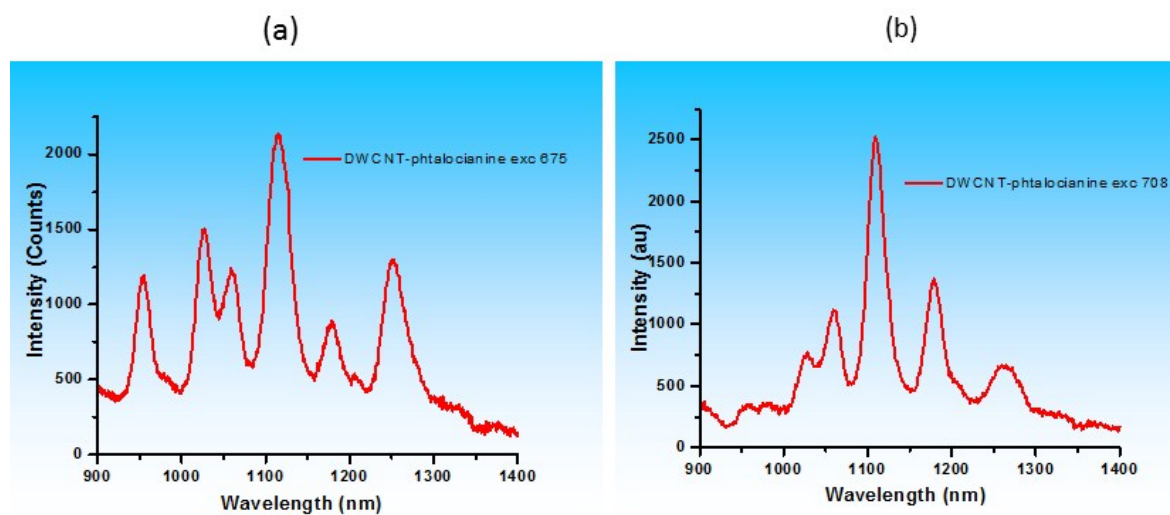


Figure S 15: Photoluminescence spectrum of DWCNT-ZnPc 1 at the excitation wavelength of (a) 675 and (b) 708 nm in SDBS micellar media.