

Electronic Supporting Information

Triplet Photosensitizer-Nanotube Conjugates: Synthesis, Characterization and Photochemistry of Charge Stabilizing, Palladium Porphyrin/Single-Walled Carbon Nanotube Conjugates

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Materials and Instrumentation

Materials:

All reactions were carried out under argon using oven-dried glassware. All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. (6,5) and (7,6) enriched nanotubes were produced for CoMoCAT,[®] SouthWest Nano Technologies Inc. (www.swentnano.com) and purchased from Sigma Aldrich Co. The denoted as (6,5)- SWNTs (0.7-0.9 nm in diameter, average length: 1 micron, mostly semiconducting, 95% purity) and the denoted as (7,6)- SWNTs (0.7-1.1 nm in diameter, average length: 1 micron, mostly semiconducting, 95% purity).

Dry triethylamine (NEt₃) was prepared according to the literature procedure.¹ The palladium (II) 5 ethynyltrimethylsilane-[10,15,20-tri-(N,N-diphenylaniline)-] porphinato **4** was prepared according to literature procedures.^{2,3}

TLC was performed on Merck silica gel 60 F254; chromatograms were visualized with UV light (254 and 360 nm). Flash column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh).

Sonication:

Sample sonication was carried out using an Elmasonic P 300 H sonicator bath (37 kHz).

Microwave:

Microwaves reactions were performed in a CEM Discover reactor, equipped with optical fiber temperature detector and pressure control.

Nuclear magnetic resonance (NMR):

NMR spectra were recorded on a Bruker Avance 400 (¹H: 400 MHz; ¹³C: 100 MHz) spectrometer at 298 K, unless otherwise stated, using partially deuterated solvents as

¹ D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, vol 1, 2nd ed. Pergamon, 1980.

² A. Aljarilla, J. N. Clifford, L. Pellejà, A. Moncho, S. Arrechea, P. de la Cruz, F. Langa and E. Palomares, *J. Mater. Chem. A*, **2013**, *1*, 13640-13647.

³ S. Fu Xunjin Zhu, G. Zhou, W.-Y. Wong, C. Ye, W.-K. Wong and Z. Li, *Eur. J. Inorg. Chem.* **2007**, 2004–2013.

internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm.

Mass spectrometry:

Mass spectra (MALDI-TOF) were recorded on a VOYAGER DETM STR mass spectrometer using dithranol as matrix.

FT-IR spectroscopy:

FTIR spectra were carried out using pellets in dried KBr. The instrument used was a Fourier Transform IR spectrophotometer (Avatar 370) in a spectral range from 400 cm^{-1} to 4000 cm^{-1} .

Thermogravimetric analysis (TGA):

Thermogravimetric analysis was performed using a TGA/DSC Linea Excellent instrument by Mettler-Toledo, collected under a flow of nitrogen (90 mL min^{-1}). About 0.5 mg initial sample mass was used and introduced inside a platinum crucible and equilibrated at 40 °C followed by a 10 °C/min ramp in the range of 40 and 1000 °C. The weight changes were recorded as a function of temperature.

UV-vis-NIR spectroscopy:

UV-vis-NIR spectra were recorded on a Jasco V-670 spectrophotometer in quartz cuvettes with a path length of 1 cm.

Fluorescence spectroscopy:

Steady-state emission spectra (1D and 3D) and fluorescence lifetimes were evaluated by using a Horiba Yvon Nanolog coupled with time-correlated single photon counting with nanoLED excitation sources. A right angle detection method was used.

Fluorescence excitation-emission maps were recorded on a HORIBA Jobin Yvon Nanolog 4 Spectrofluorometer equipped with a multichannel InGaAs detector. The pristine and the functionalized SWCNTs were prepared with 2% wt. sodium dodecyl benzene sulfate

(SDBS) in distilled water. The concentration of the prepared solutions was adjusted to be the same.

X-ray Photoelectron spectroscopy (XPS):

All XPS examinations were completed using a VG Escalab 200 R electron spectrometer employing non-monochromatic Mg K α (15 mA, 10 kV) X-rays. The base pressure of the analytical chamber during sample analysis was below 2×10^{-8} mbar. The survey spectra were obtained at pass energy of 200 eV, a 1.0 eV energy step, over a binding energy (BE) range of 1240 eV–500 eV. Analyses of the Pd3d, N1s, O 1s and C 1s envelopes were carried out at a pass energy of 50 eV and energy step size of 0.05 eV. All XPS spectra were analysed using XPS peak software. The backgrounds from both the survey and high-resolution scans were removed using a Shirley baseline.⁴ All elemental concentrations were calculated using the relative sensitivity factors specific to the spectrometer. The elemental concentrations in atomic percent (at %) for C, O, N and Pd species were calculated using the recorded high-resolution spectra. Fixed combinations of the 90% Gaussian–10% Lorentzian lines were used to model the characteristic shapes of specific chemical species. All surfaces contained varying amounts of adventitious carbon. Fitting of the C 1s spectra showed the presence of a strong C-C line, which was charge corrected to a BE of 284.8 ± 0.1 eV, and this value was used to calibrate all high-resolution spectra.⁵

Raman spectroscopy:

Measurements were acquired with a Renishaw inVia Reflex Confocal Raman Microscope equipped with a 785 nm laser. Raman spectra were collected on numerous spots on the sample and recorded with a Peltier cooled CCD camera. Each sample was deposited onto SiO₂ wafers and was measured in multiple regions. The intensity ratio I_D/I_G was obtained by taking the peak intensities following any baseline corrections. The data were collected and analysed with Renishaw Wire and Origin software.

⁴ D. A. Shirley, *Phys. Rev. B: Cond. Mater.*, **1972**, 5, 4709–4714.

⁵ G. Beamson, D. Briggs, *High-Resolution XPS of Organic Polymers – The Scienta ESCA300 Database*, Wiley Interscience, **1992**.

Atomic Force Microscopy (AFM):

AFM images were recorded in tapping mode using a Multimode 8 system (Veeco Instruments Inc., Santa Barbara, USA) with a NanoScope V controller (Digital Instruments, Santa Barbara, USA) operating at room temperature in ambient air conditions. RTESP-300 Bruker silicon cantilevers with a resonance frequency of 300 kHz and a nominal force constant of 40 Nm^{-1} were used for AFM measurements. The images were processed using WSxM⁶ (freely downloadable scanning probe microscopy software from <http://www.wsxmsolutions.com>).

Sample preparation: Preparation of Aqueous Dispersed SWCNT: *pristine* SWCNT and functionalized samples (0.5 mg/mL) were dispersed by ultrasonication (37 kHz, 380 W) in Milli-Q aqueous solution containing 2 wt% sodium dodecylbenzene sulphonate (SDBS) during 120 minutes. To remove the aggregates, the resulting suspensions were centrifuged at 13000 rpm until they had no solid.

Deposition of samples on surface: The samples investigated by AFM were prepared by drop-cast (15 μL) the diluted surfactant solutions onto SiO_2 wafers and left the drop for 20 minutes. This is followed by surfactant removal by washing the substrates generously with Milli-Q water and dried under an argon flow. Prior to deposition, the surfaces were functionalize with (3-aminopropyl) triethoxysilane Milli-Q aqueous solution (0.5% v/v), subsequently washed with 2-propanol and Milli-Q water, and then dried with a stream of argon.

Electrochemical measurements:

Osteryoung Square Wave Voltammetry (OSWV) was performed in benzonitrile solution. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M), used 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

⁶ I. Horcas, R. Fernandez, J.M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, **2007**, 78, 013705.

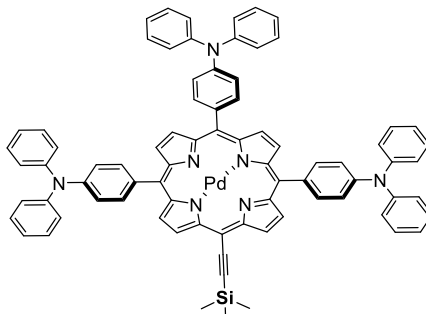
carbon working electrode (diameter = 2 mm) and a platinum wire counter electrode. A scan rate of 0.1 V.s^{-1} was used. An Ag/AgNO₃ electrode was used as reference and checked against the ferrocene/ferrocenium couple (Fc/Fc⁺) before and after each experiment.

Femtosecond transient absorption spectroscopy

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 intracavity doubled Nd:YLF laser (Evolution) to generate a compressed laser output of 1.5 W. For optical detection, a Helios transient absorption spectrometer provided by Ultrafast Systems LLC coupled with an optical parametric amplifier (OPA) provided by Light Conversion was used. The source for the pump and probe pulses were derived from the fundamental output of Libra (Compressed output 1.5 W, pulse width 100 fs) at a repetition rate of 1 kHz. 95% of the fundamental output of the laser was introduced into the OPA, while the rest of the output was used for generation of the white light continuum. In the present study, the maximum absorption wavelength for each compound 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 Explorer software supplied by Ultrafast Systems for initial analysis. All measurements were conducted in degassed solutions at 298 K.

Experimental details and spectroscopic data

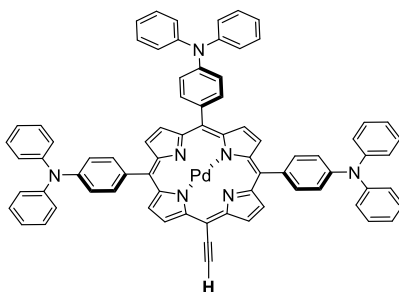
Synthesis of (TPA)₃PdP-TMS (4)



A 100 mL Schlenk flask was charged with 30 mL of dry chloroform (CHCl₃) and free base of (TPA)₃P-TMS² (50 mg, 0.04 mmol). Subsequently, tris(dibenzylideneacetone) palladium (0) (Pd(OAc)₂) (55 mg, 0.24 mmol) dissolved in 8 mL of MeOH were added. The mixture was refluxed overnight under inert atmosphere. After the completion of the reaction (followed by TLC), the solvent was removed under reduced pressure. The crude was purified by chromatography (silica gel, hexane/ DCM 1:1) giving compound **4** as a brown-purple solid (25 mg, 45%).

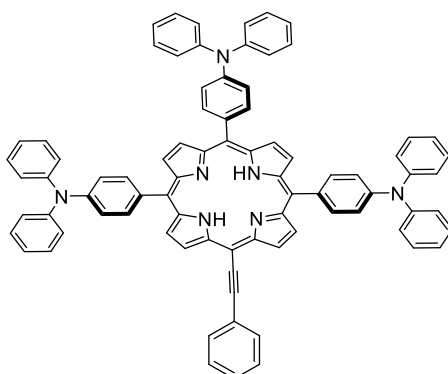
¹H-NMR (CDCl₃, 400 MHz), δ/ppm, J (Hz): 9.67 (d, 2H, ³J = 4.8 Hz), 9.02 (d, 2H, ³J = 4.7 Hz), 8.93 (m, 4H), 8.10 – 7.96 (m, 6H), 7.53 – 7.35 (m, 30H), 7.16 (m, 6H), 0.62 (s, 9H). ¹³C NMR (CDCl₃, 100 MHz,) δ/ppm: 147.8, 147.7, 147.6, 143.9, 142.2, 141.5, 135.1 (2), 135.0, 134.9, 131.9, 131.2, 130.8, 130.2, 129.5, 124.9, 123.3, 122.3, 121.3, 121.2, 106.2, 101.7, 101.0. UV-vis (NMP) λ_{max}/nm (log ε): 582 (4.1), 541 (4.3), 434 (5.0), 302 (4.8). Melting point: over 300°C. MS (MALDI-TOF): (*m/z*) calculated for C₇₉H₅₉N₇PdSi: 1239.36, found (M⁺): 1239.77.

Synthesis of (TPA)₃PdP-CCH (**3**)



To a solution of **4** (82 mg, 0.07 mmol) in DCM (14 mL) was added tetra-*n* butylammonium fluoride (TBAF, 1M in THF) (1.25 mmol). The mixture was maintained under an argon atmosphere and stirred at room temperature for 2.5 hours. The reaction was quenched with H₂O and extracted with DCM (3 x 50 mL). The combined organic layers were dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure to obtain the unprotected porphyrin **3** quantitatively.

Synthesis of free base (TPA)₃P-Ph (**5**)

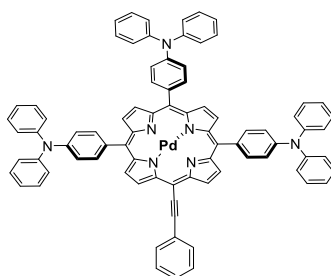


Into a dried 100 mL 2-neck round bottom flask equipped with a condenser, Pd₂(dba)₃ (21.2 mg, 0.02 mmol) and AsPh₃ (47.2 mg, 0.15 mmol) were added. The flask was degassed and backfilled with argon for 1 hour. Subsequently, dry tetrahydrofuran (THF) (230 mL/mmol),

free base (TPA)₃P-TMS² (82 mg, 0.08 mmol), 4-iodobenzene (0.10 mL, 0.88 mmol) and dry Et₃N (45 mL/mmol) were charged to the flask. The mixture was heated under reflux overnight. On cooling to room temperature, the crude reaction was filtered over celite and the solvent was removed under reduced pressure. The crude was purified by chromatography (silica gel, hexane/THF 7:3) affording a green solid **5** (62.5 mg, 71 %).

¹H-NMR (CDCl₃, 400 MHz), δ/ppm, J (Hz): 9.77 (d, 2H, ³J = 4.8 Hz), 9.06 (d, 2H, ³J = 4.9 Hz), 8.98 – 8.89 (m, 4H), 8.13 – 8.01 (m, 8H), 7.67 – 7.32 (m, 31H), 7.16 (m, 8H), -2.22 (s, 2H).
Melting point: over 300°C. MS (MALDI-TOF): (m/z) calculated for C₈₂H₅₇N₇: 1139.47; found (M⁺): 1140.95.

Synthesis of reference compound (TPA)₃PdP-Ph (**6**)



To a solution of free base porphyrin **5** (50 mg, 0.04 mmol) in DCM (30 mL) under argon atmosphere was added a solution of Pd(OAc)₂ (54 mg, 0.24 mmol) in MeOH (8 mL). The mixture was stirred and refluxed for 3 hours under argon atmosphere. After the completion of the reaction, the solvent was removed under reduced pressure. The crude metallated product was purified by column chromatography (silica gel, hexane/ CHCl₃, 1:1) giving compound **6** as a purple solid (24.5 mg, 45 %).

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz), δ/ppm , J (Hz): 9.77 (d, 2H, $^3J = 4.9$ Hz), 9.05 (d, 2H, $^3J = 4.9$ Hz), 8.94 (d, 4H), 8.11 – 7.96 (m, 8H), 7.65 – 7.36 (m, 31H), 7.23 – 7.13 (m, 8H). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz), δ/ppm : 147.8, 147.6, 143.6, 142.2, 141.6, 141.5, 135.2, 135.0, 135.0, 131.9, 131.7, 131.2, 130.9, 130.0, 129.5, 128.7, 128.6, 124.9, 124.0, 123.3, 123.1, 122.4, 121.3, 101.4, 96.4, 91.2. UV-vis (NMP) $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$): 587 (4.4), 545 (4.5), 439 (5.3), 302 (5.0). Melting point: over 300°C. MS (MALDI-TOF): (m/z) calculated for $\text{C}_{82}\text{H}_{55}\text{N}_7\text{Pd}$: 1243.36; found (M^+): 1243.91.

Synthesis of iodophenyl enriched SWCNTs (SWCNTs-I (6,5) and (7,6)): *Pristine* (6,5) or (7,6) enriched SWCNT (40 mg, 3.33 mmol) was dispersed in NMP (80 mL) by ultrasonication for 10 min. Nitrogen was bubbled through the suspension for 2 min and 4-iodoaniline (1.46 g, 6.66 mmol) and isoamyl nitrite (1.07 mL, 8 mmol) were added. The reaction mixture was stirred for 12 h at 70 °C under an argon atmosphere. The reaction mixture was cooled to room temperature and filtered through a 0.1 μm pore size OMNIPORE membrane and the black solid was collected and washed with different solvents (NMP, methanol and DCM) several times until the filtrate was colorless. Finally, the black solid material was dried overnight in a vacuum oven at 55 °C to obtain the carbon-based materials **SWCNT-I (6,5)** and **SWCNT-I (7,6)** as black solids.

Synthesis of hybrids 1-2: To a solution of **4** (40 mg, 0.03 mmol) in DCM (8 mL) was added TBAF, (1M in THF) (1.25 mmol). The mixture was maintained under an argon atmosphere and stirred at room temperature for 5 h. The reaction was quenched with water and extracted with DCM (3 \times 25 mL). The combined organic layers were dried over anhydrous NaSO_4 and the solvent was removed under reduced pressure to afford the unprotected porphyrin **3** quantitatively. *Functionalized* iodophenyl

SWCNTs-I (6,5) or (7,6) (30 mg) and NMP (45 mL) were placed in a microwave glass vessel, sonicated for 15 min at room temperature and degassed; then **3** (40 mg, 0.03 mmol), tris(dibenzylideneacetone) dipalladium(0) ($\text{Pd}_2(\text{dba})_3$) (3 mg, 3.27×10^{-3} mmol), triphenylarsine (AsPh_3) (21 mg, 0.07 mmol) and degassed NEt_3 (15 mL) were added and the glass vessel was stoppered with a septum and placed in the microwave reactor. Microwave irradiation (50 W) was applied for 1 h at 150 °C. The resulting paste was filtered through a 0.1 μm pore size OMNIPORE membrane to remove the solvent and the unreacted reagents. The product was washed thoroughly with NMP, methanol, acetone and DCM until a persistently colorless filtrate was obtained. The black material was dried under vacuum at 55 °C to afford *functionalized* SWCNTs **1** and **2**.

^1H , ^{13}C -NMR and MALDI-TOF spectra

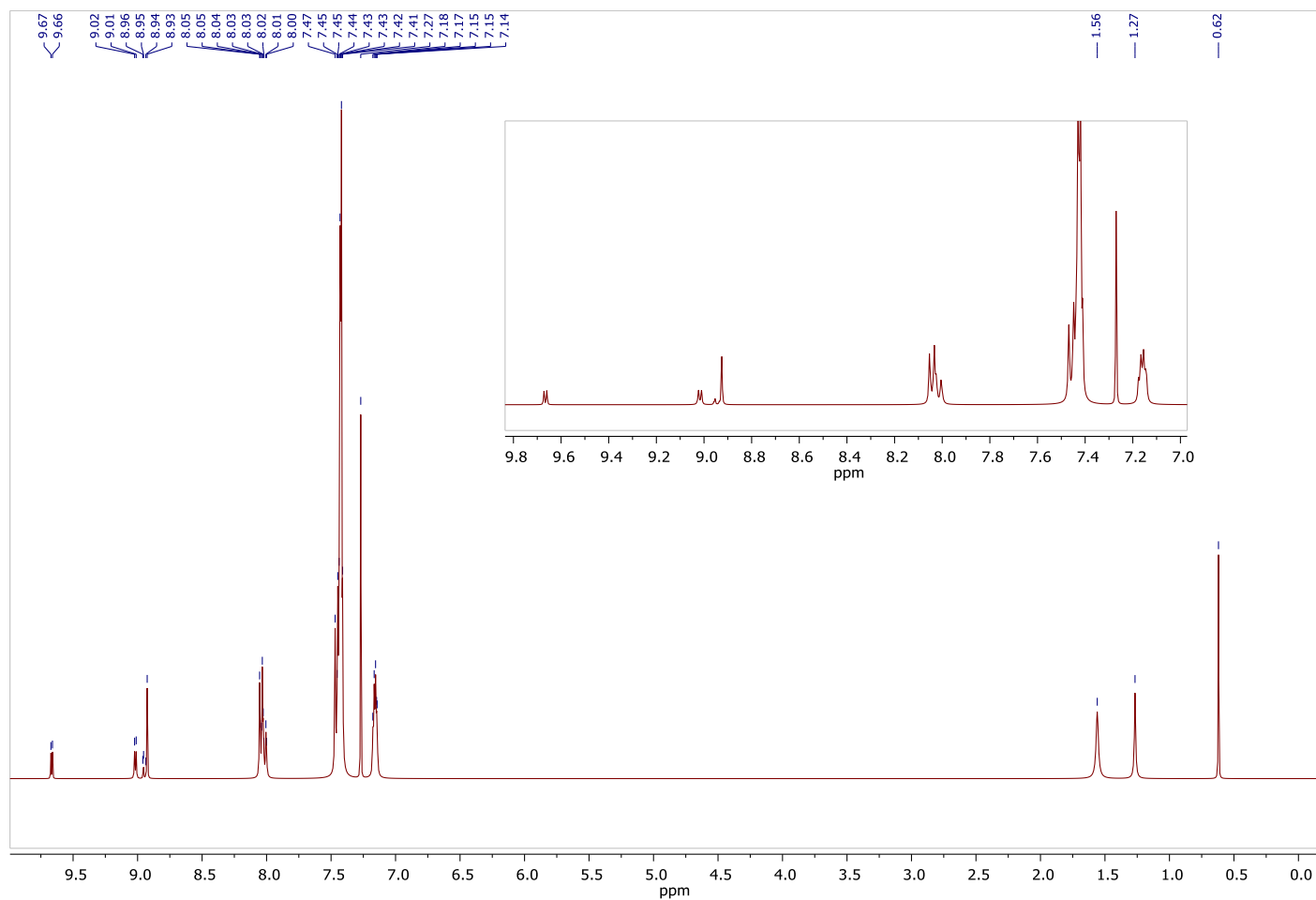


Figure S1. ^1H -NMR spectrum (400 MHz, CDCl_3) of $(\text{TPA})_3\text{PdP-TMS 4}$.

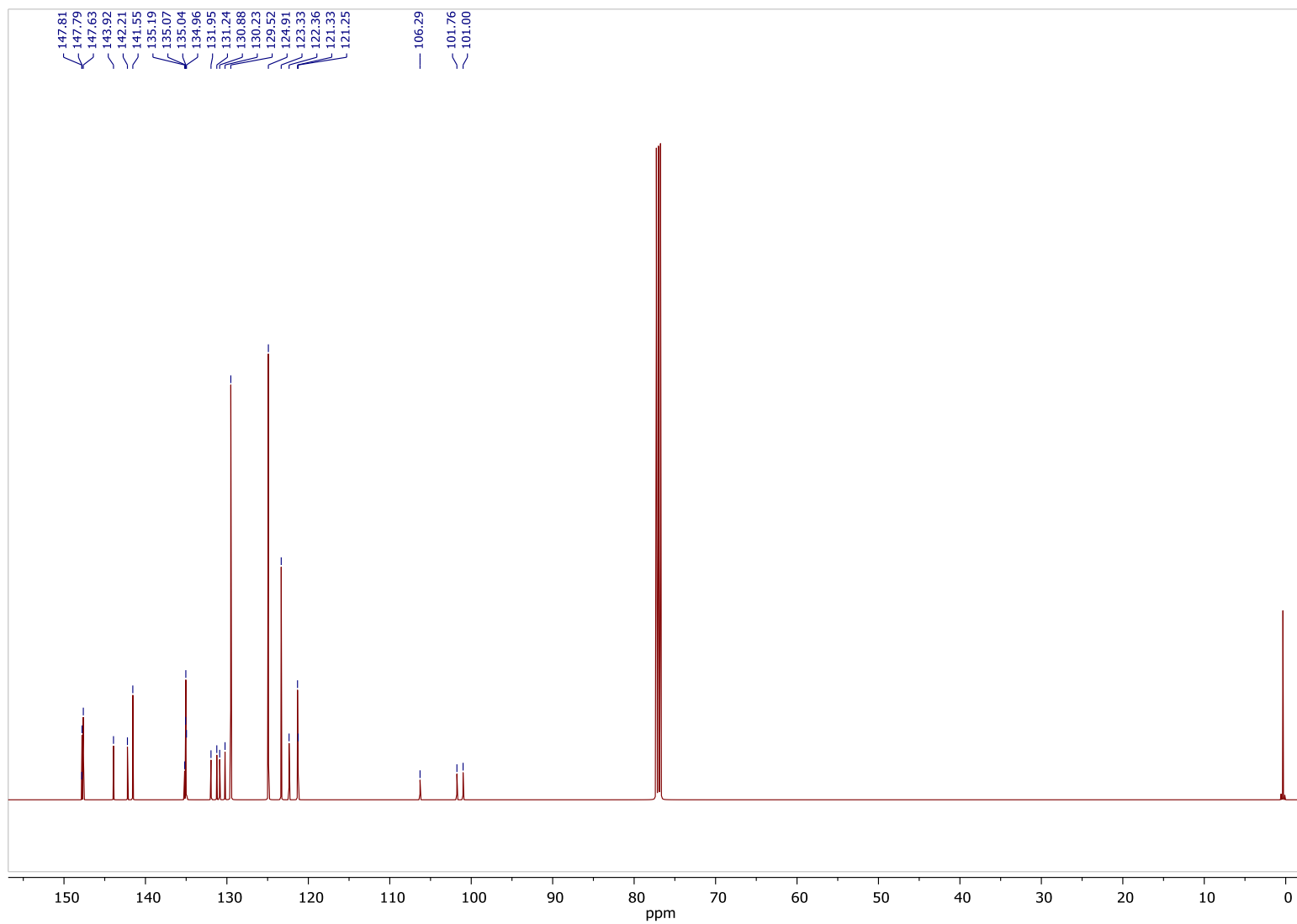


Figure S2. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of $(\text{TPA})_3\text{PdP-TMS 4}$.

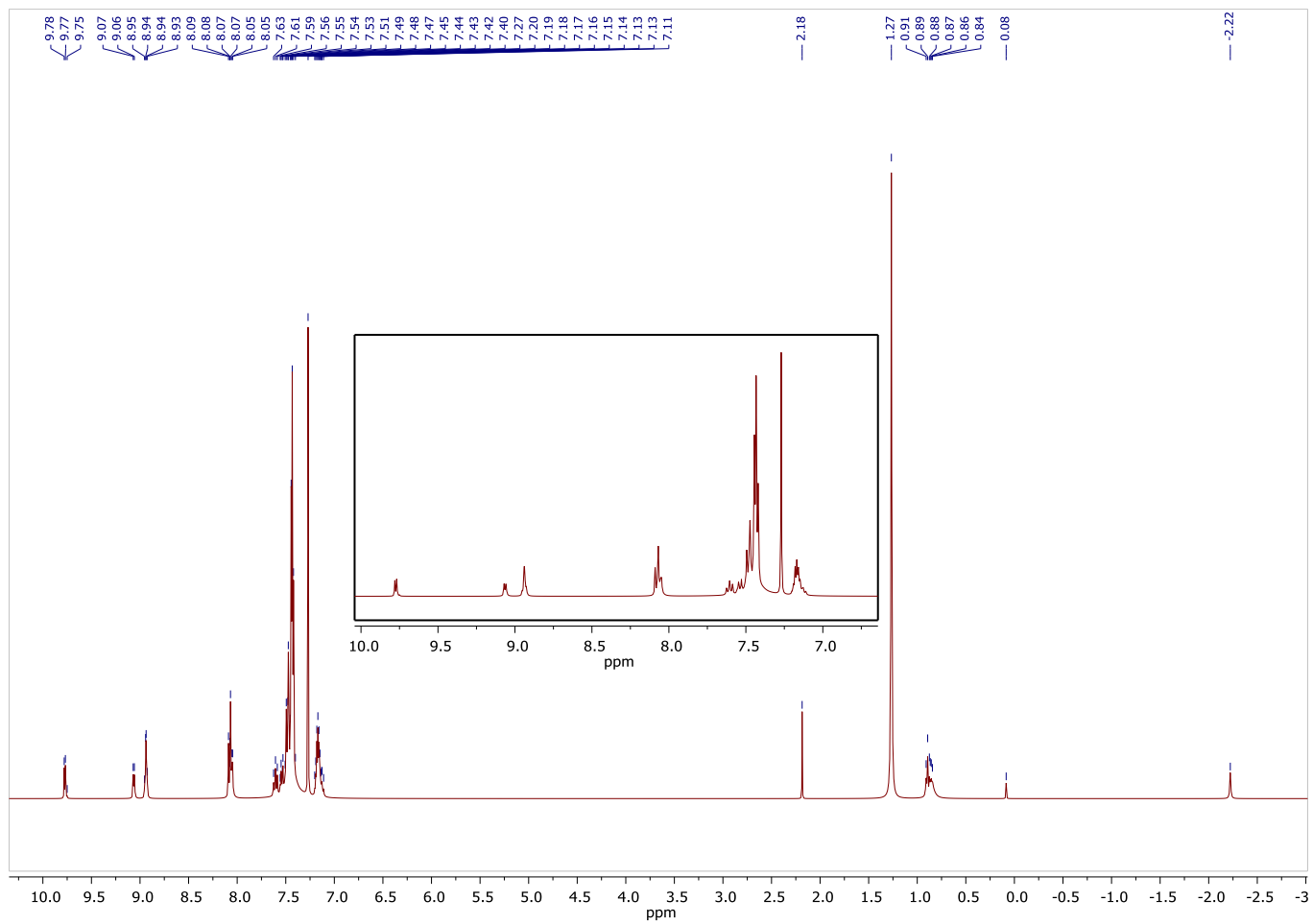


Figure S3. ¹H NMR spectrum (400 MHz, CDCl₃) of free base (TPA)₃P-Ph 5.

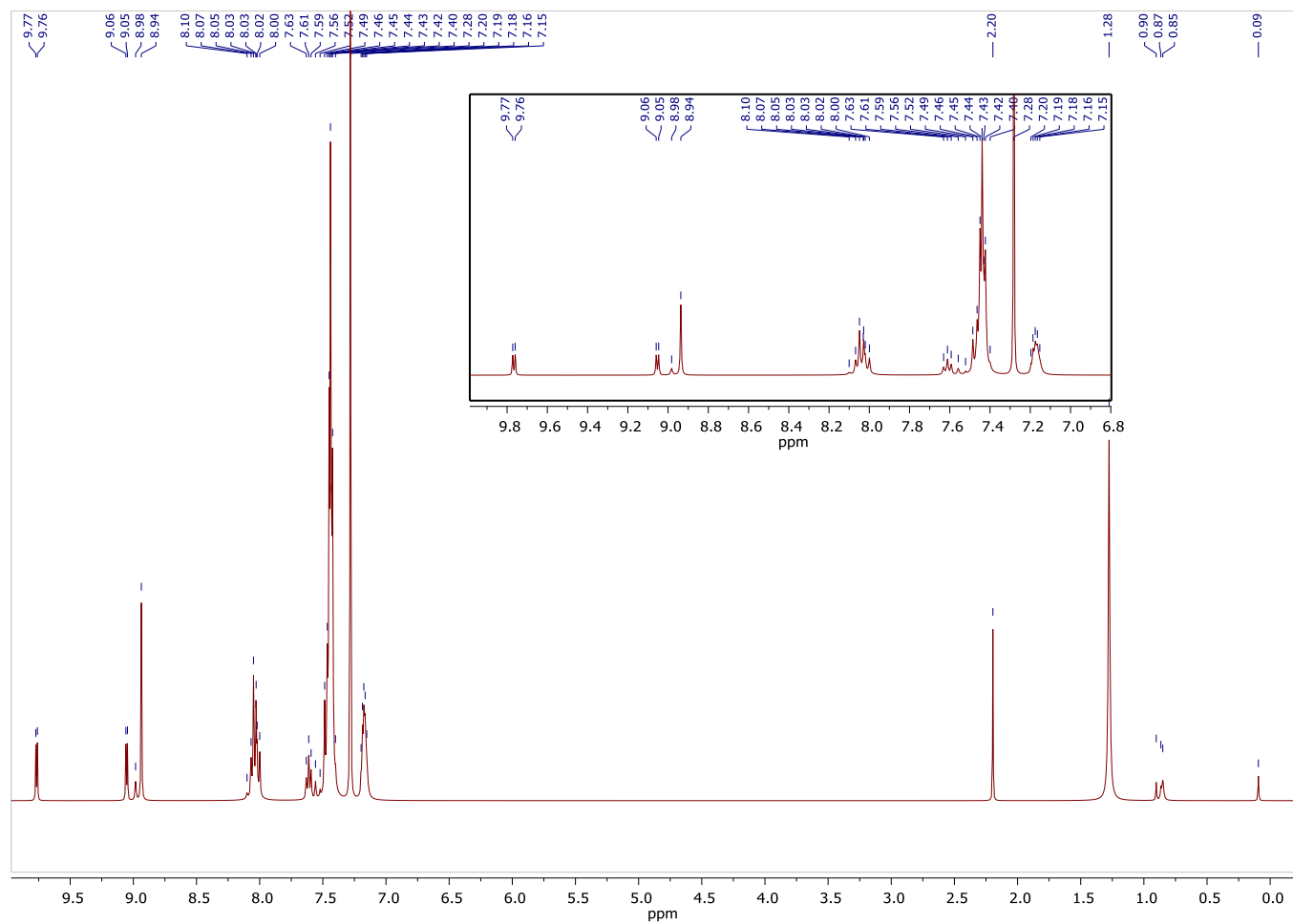


Figure S4. ¹H-NMR spectrum (400 MHz, CDCl₃) of reference compound (TPA)₃PdP-Ph 6.

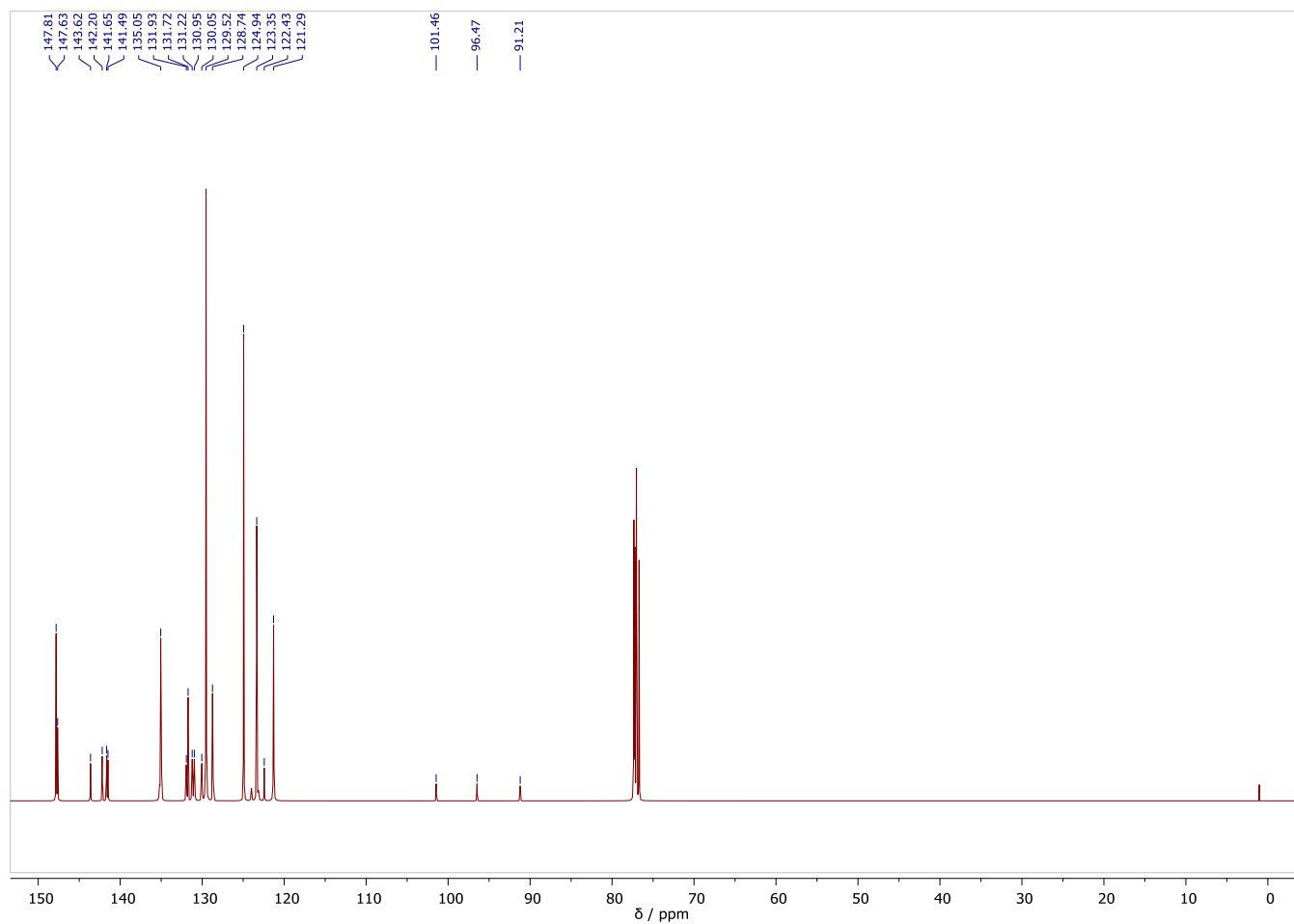


Figure S5. ^{13}C -NMR spectrum (100 MHz, CDCl_3) of reference compound $\text{Pd}(\text{TPA})_3\text{-Ph 6}$.

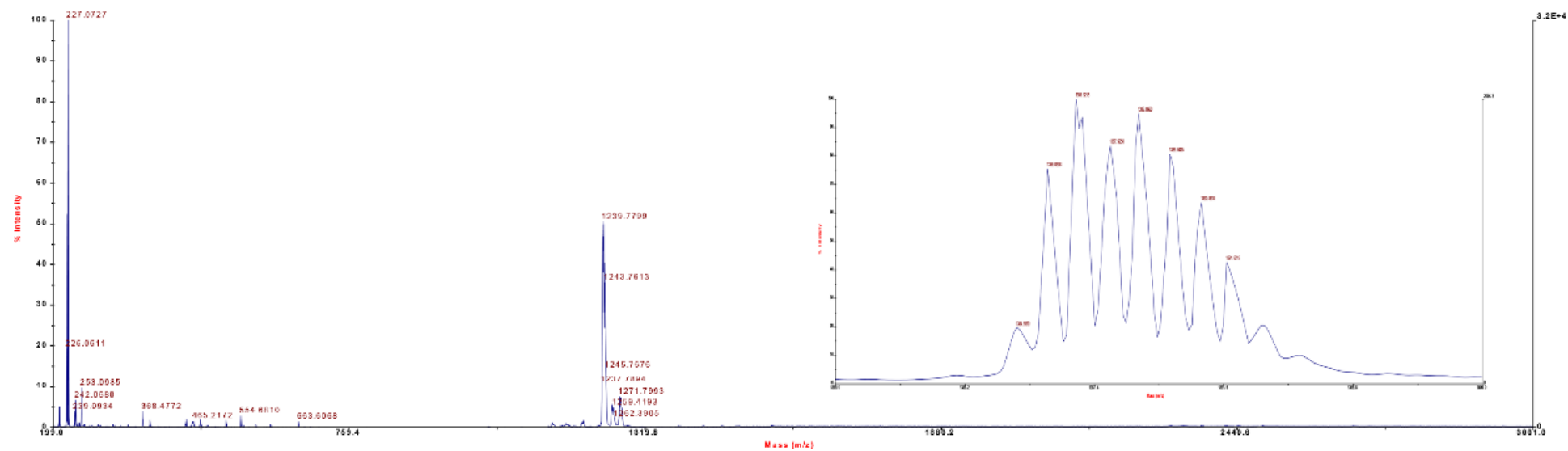


Figure S6. MALDI-TOF analysis spectrum for (TPA)₃PdP-TMS 4.

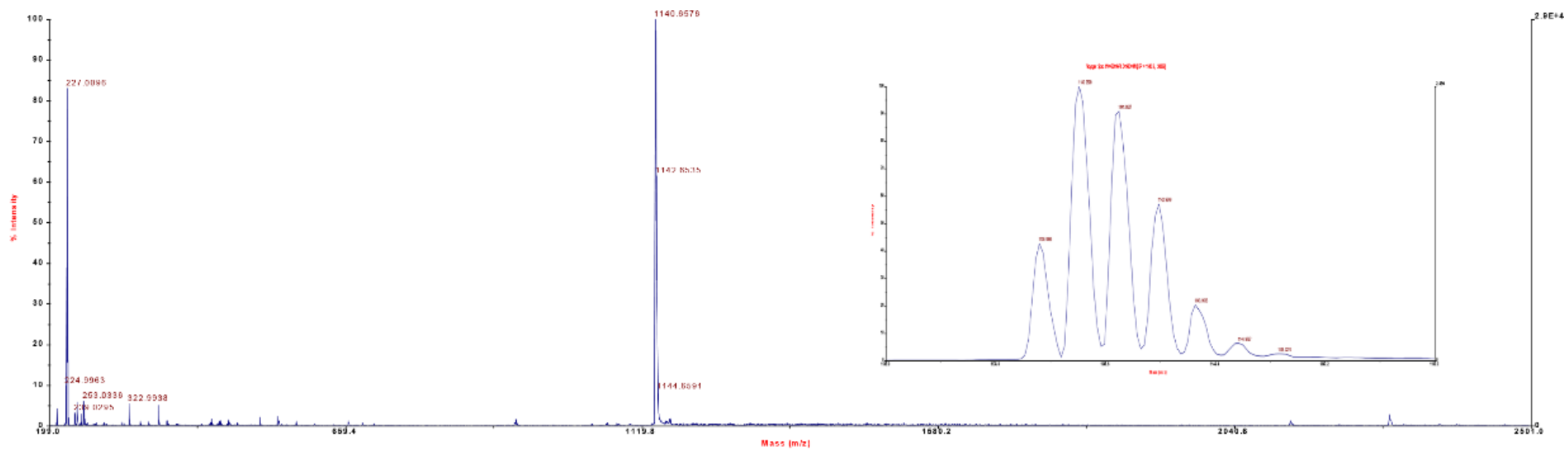


Figure S7. MALDI-TOF analysis spectrum for (TPA)₃P-Ph 5

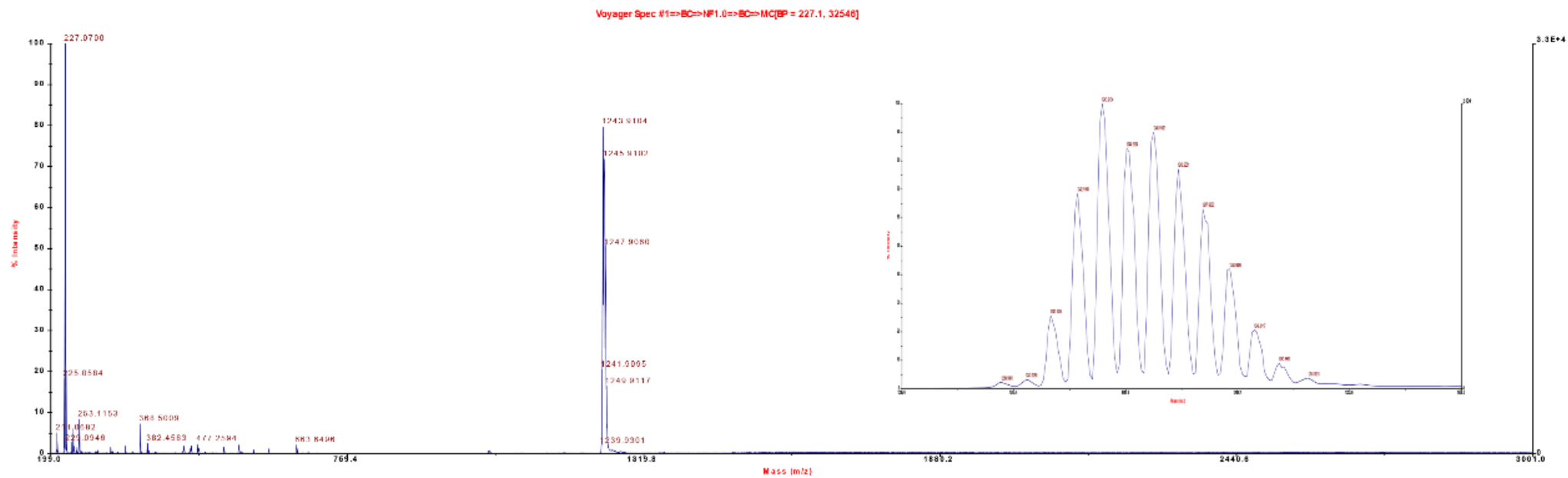


Figure S8. MALDI-MS spectrum of $(\text{TPA})_3\text{PdP-Ph 6}$ (Matrix: Ditrinol)

As shown in Figure S9 (right) at 700 °C, the thermograms revealed a loss of weight of about 10.1% for *pristine* SWCNT (7,6), 22.6% for SWCNTs-I (7,6) and 30.8% for **2**. The corrected weight losses due to the functional groups on carbon nanotubes were then estimated to be 12.5.% and 20.7% SWCNTs-I (7,6) and hybrid **2**, respectively (weight loss difference of SWCNTs-I (7,6) – *pristine* SWCNT (7,6) and **2** – *pristine* SWCNT (7,6)). The number of iodophenyl functional groups in SWCNTs-I (7,6) was then estimated as 1 per 131 carbon atoms. With the same calculation, we estimated the amount of functional groups as 1 per 457 carbon atoms for hybrid Pd(TPA)₃P-SWCNT(7,6). On the other hand, at 700 °C porphyrin **6** shows a weight loss of 48%. Since the weight loss corresponding to the coupled porphyrin is about 8.2% in hybrid **2** (**2** – SWCNTs-I (7,6)), the amount of grafting porphyrin in Pd(TPA)₃P-SWCNT(7,6) may correspond to a real ratio of *ca.* 17% (8.2%/48%). Then, the number of functional groups in this case can be estimated to one porphyrin per 78 carbon atoms. The differences observed in these calculations are corroborated by XPS data (see Tables S1-S2), confirming that the extent of the Sonogashira coupling reaction was limited.

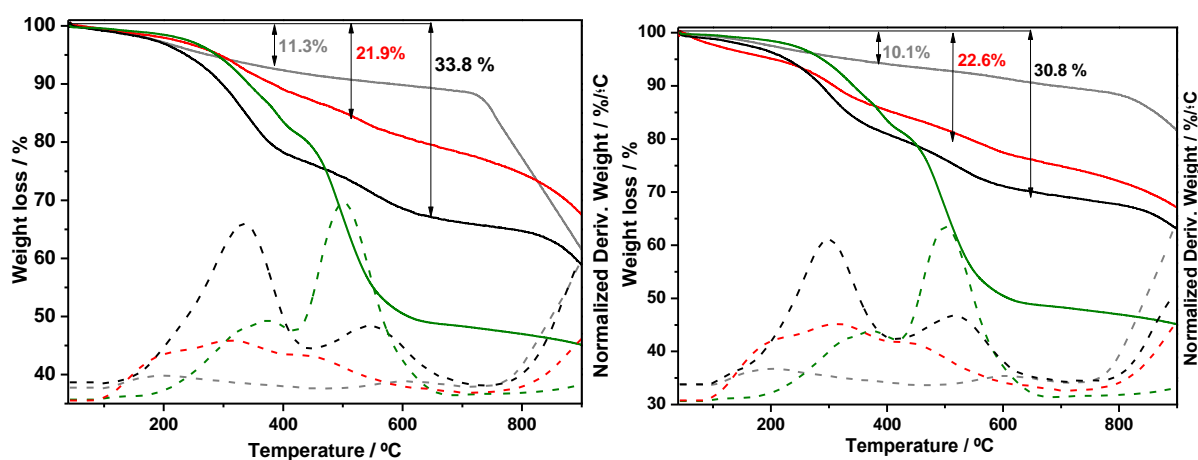


Figure S9. TGA weight loss and first derivative curves of (left) *pristine* SWCNT (6,5) (—),SWCNT-I (6,5) (—) and nanoconjugate **1** (—) compared with reference **6** (—) and (right) *pristine* SWCNT (7,6) (—),SWCNT-I (7,6) (—) and nanoconjugate **2** (—) compared with reference **6** (—). Heating rate 10°C under a nitrogen atmosphere.

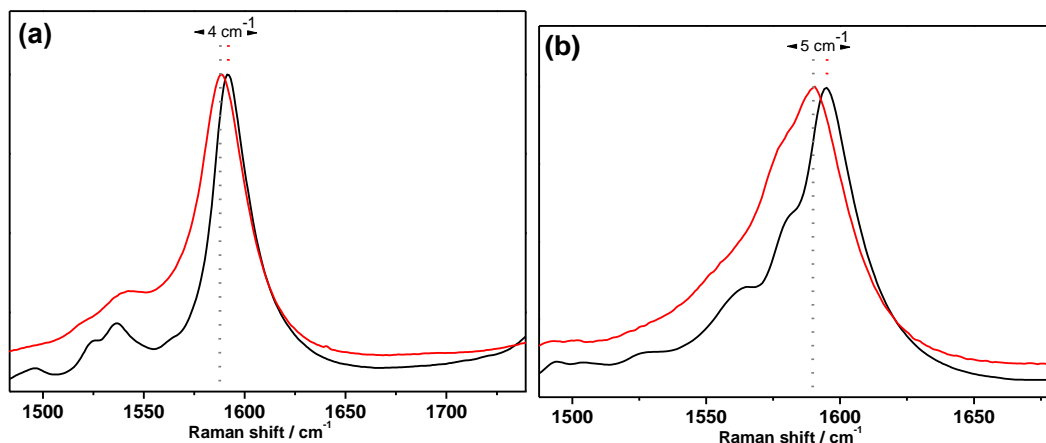


Figure S10. Comparison of G-band of (a) *pristine* SWCNT (6,5) (—) and **1** (—); (b) *pristine* SWCNT (7,6) (—) and **2** (—). Excitation: 785 nm.

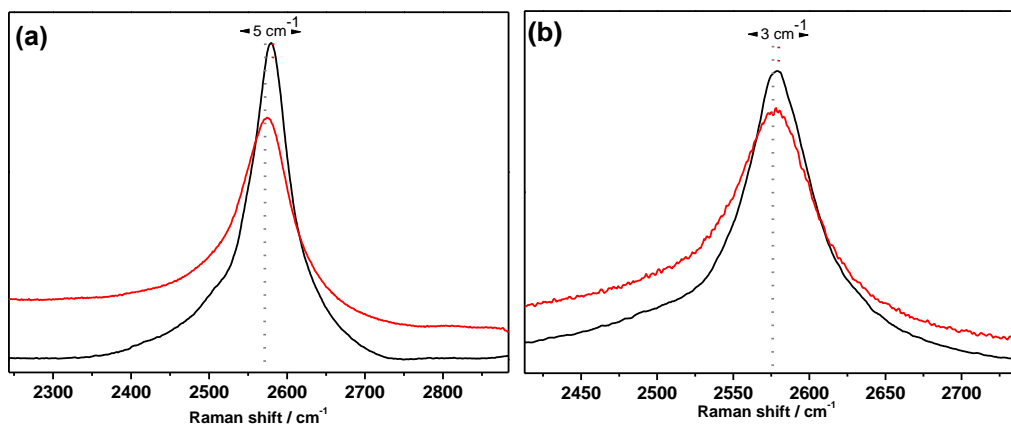


Figure S11. Comparison of 2D band of (a) *pristine* SWCNT (6,5) (—) and **1** (—); (b) *pristine* SWCNT (7,6) (—) and **2** (—). Excitation: 785 nm.

Table S1. XPS binding energies (eV) of starting enriched SWCNTs, reference Pd-porphyrin **6** and *functionalized* samples **1** and **2**.

	C1s	N1s	Pd3d	I3d	O1s
SWCNT (6,5)	284.8 (69) 286.3 (17) 287.8 (11) 291.3 (3)	-	-	-	531.3 (6) 532.6 (38) 533.8 (56)
SWCNT (7,6)	284.8 (67) 286.3 (23) 287.8 (7) 291.3 (3)	-	-	-	531.3 (21) 532.6 (43) 533.8 (36)
SWCNT-I (6,5)	284.8 (80) 286.2 (16) 287.8 (4)	-	-	621.0	531.4 (26) 532.6 (54) 533.8 (20)
SWCNT-I (7,6)	284.8 (81) 286.2 (15) 287.9 (4)	-	-	621.1	531.4 (28) 532.6 (52) 533.8 (20)
6	284.8 (85) 286.2 (15)	398.9 (43) 400.2 (57)	338.5	-	-
1	284.8 (79) 286.3 (17) 288.0 (4)	398.9 (43) 400.2 (57)	336.1 (44) 338.4 (56)	621.1	531.4 (26) 532.6 (45) 533.8 (29)
2	284.8 (81) 286.3 (15) 288.0 (4)	398.9 (44) 400.2 (56)	336.0 (45) 338.2 (55)	621.1	531.4 (15) 532.6 (30) 533.8 (55)

Table S2. Surface atomic ratios of starting SWCNTs, reference Pd-porphyrin **6** and *functionalized* samples **1** and **2**.

	C1s(%)	O1s(%)	N1s(%)	I3d(%)	Pd3d(%)
SWCNT(6,5)	97.1	2.9	-	-	-
SWCNT (7,6)	97.5	2.5	-	-	-
SWCNT-I (6,5)	94.1	1.6	-	4.3	-
SWCNT-I (7,6)	94.2	1.4	-	4.4	-
6	96.2	-	3.3	-	0.5
1	95.9	1.5	1.3	1.1	0.2
2	95.1	1.4	1.9	1.3	0.3

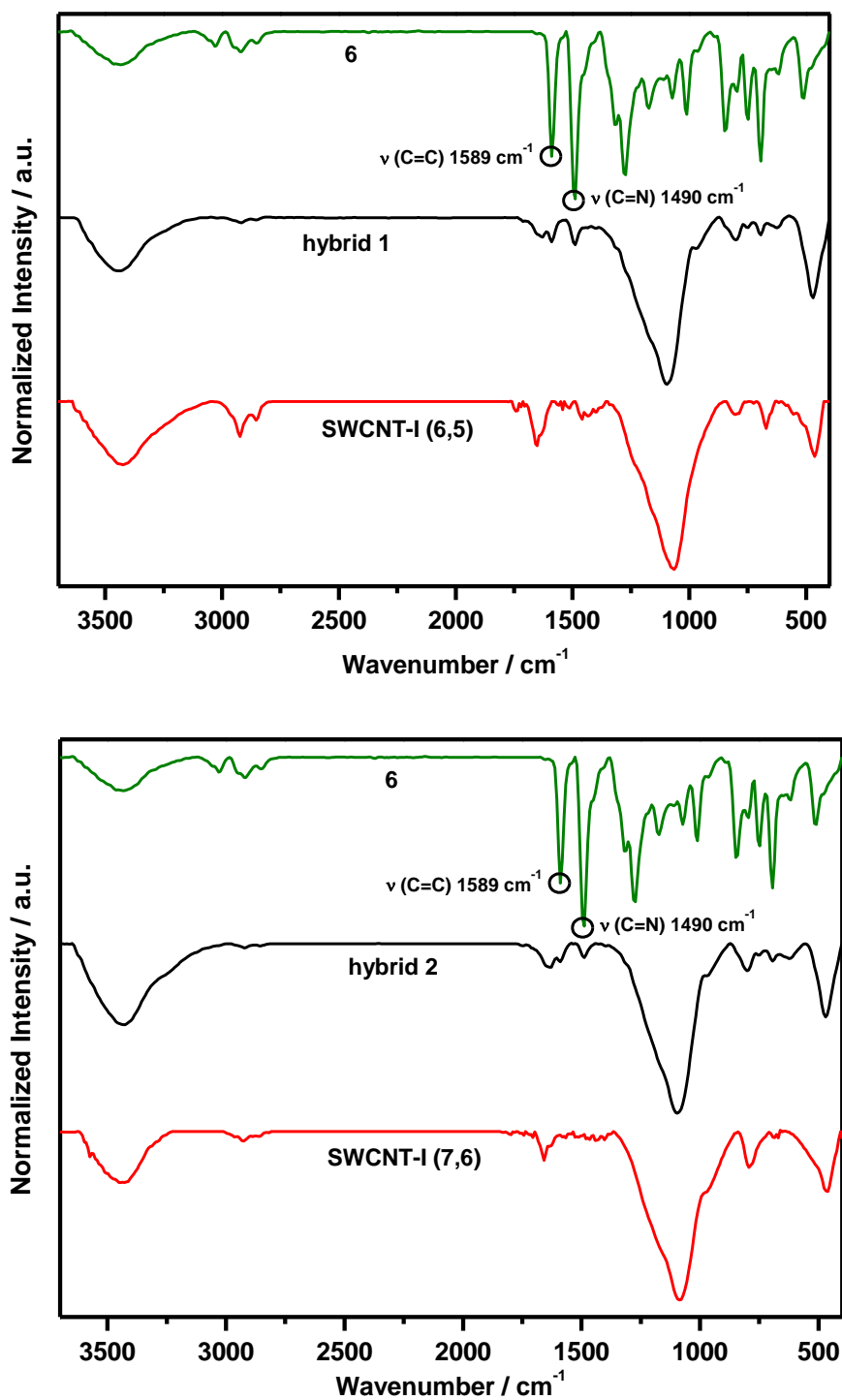


Figure S12. FTIR spectra of (upper panel) *functionalized* enriched SWCNTs **1** (—), SWCNT-I (6,5) (—) and reference Pd-porphyrin **6** (—) and (bottom panel) *functionalized* enriched SWCNTs **2** (—), SWCNT-I (7,6) (—) and the reference Pd-porphyrin **6** (—).

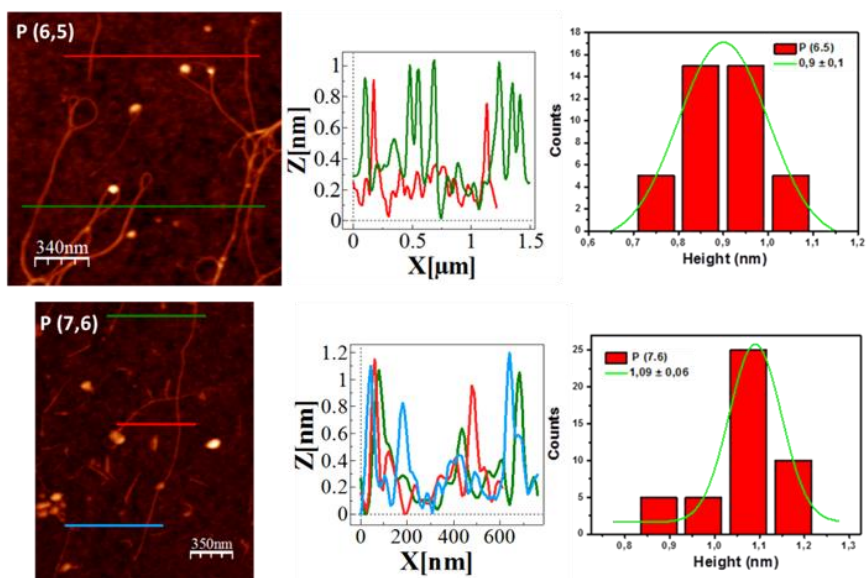


Figure S13. AFM images and height profiles along the regions indicated for *pristine* enriched SWCNT (6,5) and enriched (7,6) together with their height distribution histogram showing the diameter distribution of the sample.

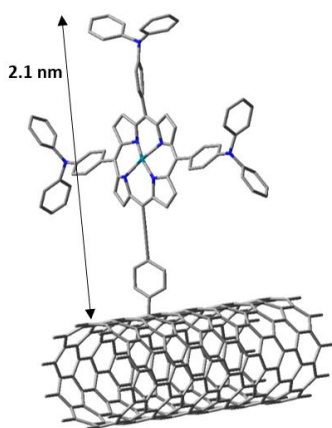


Figure S14. Modelling structure optimized using semiempirical PM3 method for hybrid **1** and **2**.

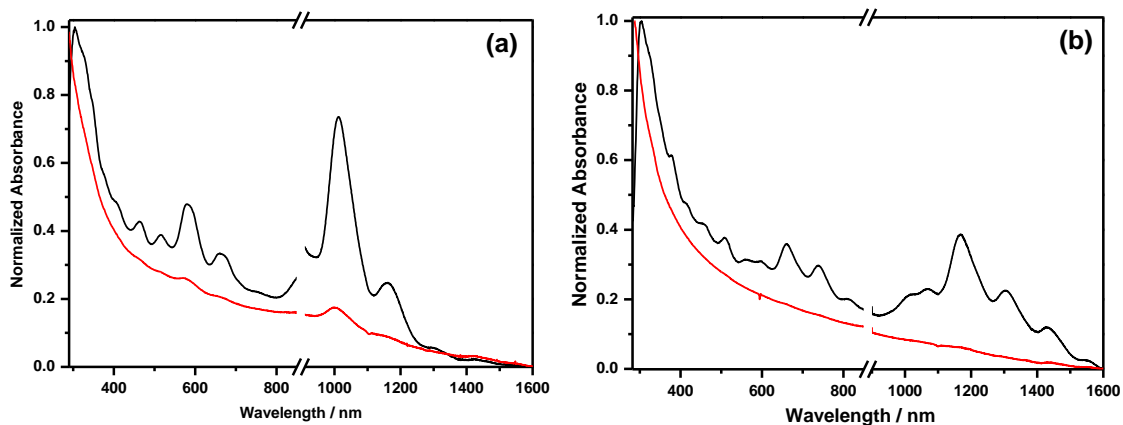


Figure S15. Steady-state absorption spectra of: (a) *pristine* SWCNT (6,5) (—) and SWCNTs-I (6,5) (—) and (b) *pristine* SWCNT (7,6) (—) and SWCNTs-I (7,6) (—), registered in NMP.

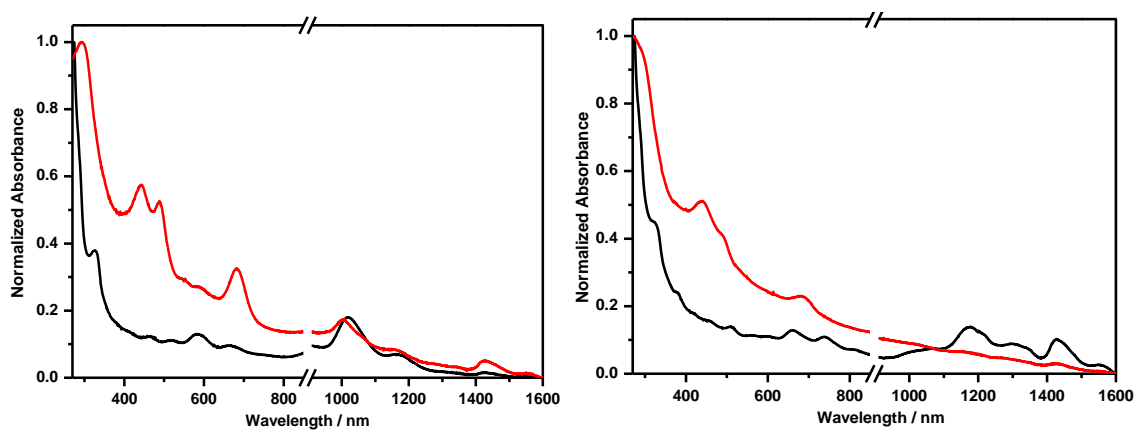


Figure S16. Absorption spectra of (left) *pristine* enriched SWCNT (6,5) compared to *functionalized* enriched SWCNT **1** and (right) SWCNT (7,6) (—) compared to **2** (—) in DMF.

Table S3. PL peak positions of pristine enriched (6,5) SWNT, *iodophenyl* derivative and hybrid **1**.

SWCNT material	PL (E_{11}) (nm) peak position	PL (E_{11}^*) (nm) peak position
Pristine SWCNT (6,5)	981	---
SWCNT-I (6,5)	981	1128
1	988	1129

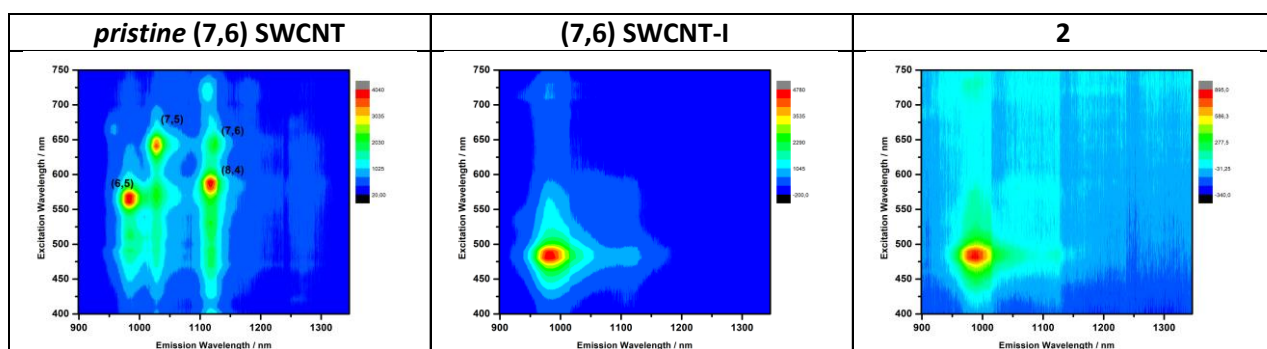


Figure S17. Excitation–emission PL maps of (a) *pristine* enriched SWCNT (7,6), (b) SWCNT-I (7,6) and (c) hybrid **2**. All spectra recorded in D₂O with 2% SDBS as surfactant and acquired at room temperature.

Table S4. Electrochemical data for the prepared nanohybrids **1** and **2** and porphyrins **5** and **6**, as determined by OSWV.^a

Compound	E _{ox} ¹ (V)	E _{ox} ² (V)	E _{ox} ³ (V)
5	+0.49	+0.71	+0.88
6	+0.61	+0.87	-
1	+0.65	-	-
2	+0.64	-	-

^a Obtained in PhCN solution containing 0.1 M TBAPF₆ and using Ag/AgNO₃ as a reference electrode, glassy carbon as working electrode and a Pt wire counter electrode. Scan rate: 100 mV/s. Potential are referenced to Fc /Fc⁺.

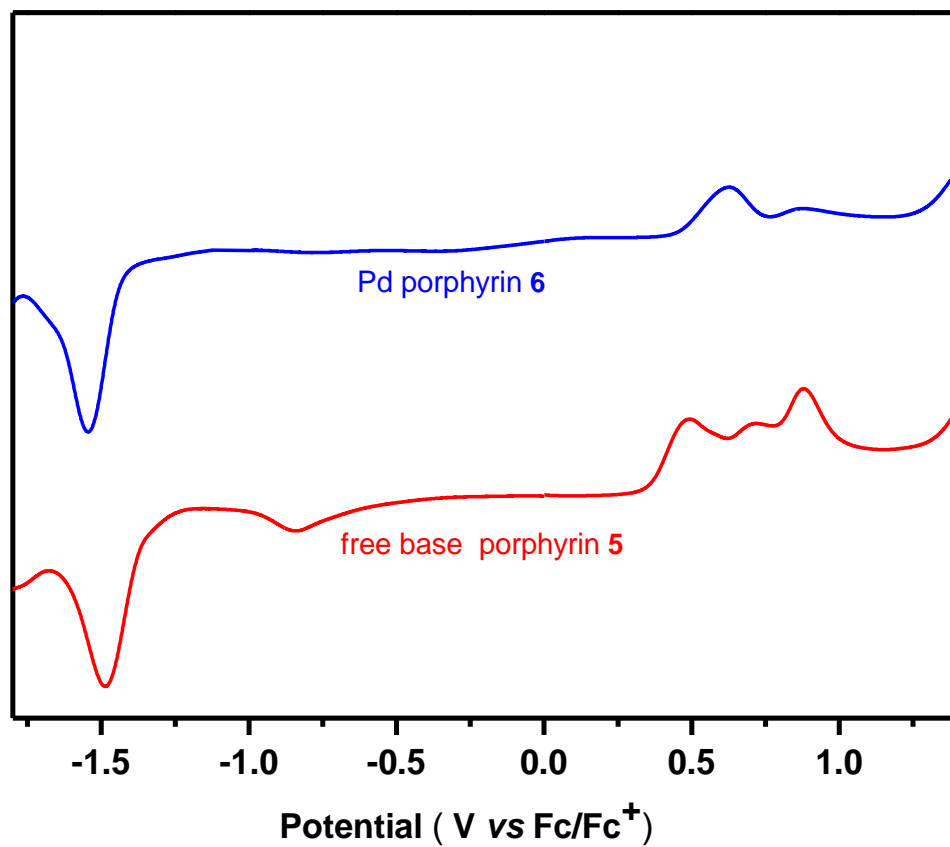


Figure S18. OSWV of free base porphyrin 5 and Pd-Porphyrin 6 in benzonitrile.