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Organic & Biomolecular Chemistry

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Grafting of Porphyrin Oligomers on Single-Walled Carbon Nanotubes by *Hay* Coupling

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The fabrication of nanotube-based functional materials is still limited by the difficulty of incorporating highly engineered molecules onto the nanotube surface. To overcome this difficulty, the development of procedures involving two subsequent reaction steps on the nanotubes appeared particularly promising. It was previously demonstrated that "click chemistry" (CuAAC) permits to functionalise efficiently nanotubes with a wide variety of materials (from inorganic to biological). In this work, we present an original strategy based on *Hay* coupling (*i.e.* the oxidative coupling between triple bonds) to fabricate nanotube-porphyrin conjugates. Porphyrins containing ethynyl functional groups were attached on single-wall carbon nanotubes (SWNT) bearing phenylacetylene groups and the resulting materials were fully characterised.

Introduction

Among the different classes of nanomaterials, carbon nanotubes (CNTs) are extremely promising materials for applications in electronics,[1-3] energy storage and conversion,[4-7] catalysis[8-12] and composites.[13] The interest for the fabrication of carbon nanotube functional materials led us and others to investigate the covalent and non-covalent methodologies to incorporate new organic or inorganic moieties on their surfaces with the final goal to combine in a proper way the properties of the nanotubes with those of the addends.[14-19]

The fabrication of nanotube-based functional materials is also limited because of the difficulty to incorporate highly engineered molecules onto the nanotube surface. This issue can be due to the incompatibility between the functionality of the molecules to be added and the reaction conditions required for nanotube functionalisation. Moreover, reactions on CNTs require a large excess of reagent which is difficult or impossible to recycle. To overcome these difficulties, the development of procedures involving two subsequent steps appeared particularly promising.[15,20,21] In these approaches, the nanotubes were first functionalised with small addends and then the molecules of interest were incorporated. In order to achieve an efficient functionalisation, the second step requires the use of clean and efficient reactions. We demonstrated that the Cu-catalyzed alkyne azide cycloaddition reaction (CuAAC) offered the possibility to easily incorporate organic chromophores on the nanotube sidewalls.[22-25]

Therefore CuAAC was proved very efficient to functionalise carbon nanotubes but our search for the fabrication of new photoactive nanotube conjugates encouraged us to explore also other strategies. Starting with nanotubes containing
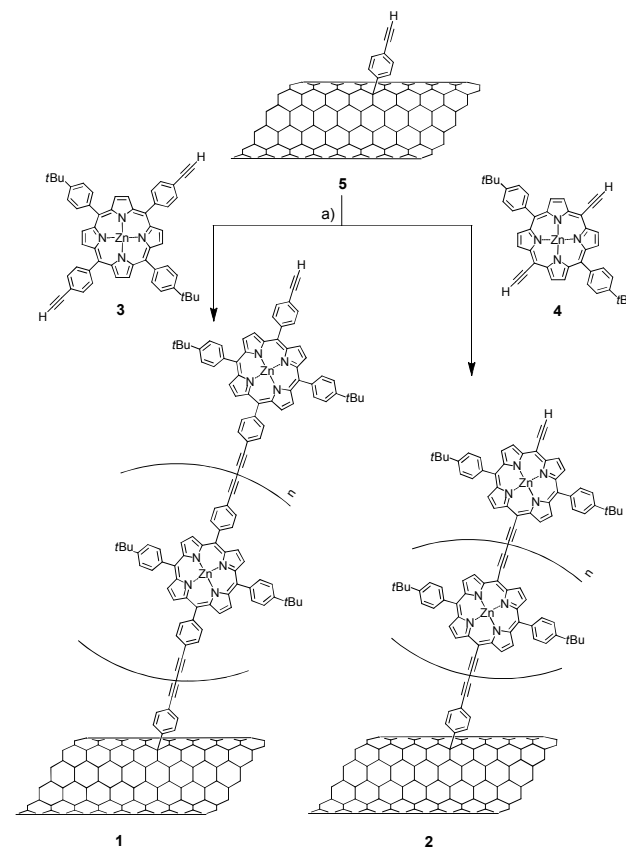
Scheme 1. a) *N,N,N',N'*-tetramethylethylenediamine (TMEDA), CuCl, O₂, *N*-methylpyrolidone (NMP), rt, 24h.

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phenylacetylene moieties, one can envision the grafting of molecules *via* Hay coupling[26,27] – that is the oxidative coupling between two triple bonds in the presence of Cu(I). Here we report on the synthesis and characterisation of two SWNT-ZnP conjugates **1** and **2** fabricated by polymerisation of zinc(II) 5,15-(4-ethynylphenyl)-10,20-(4-*ter*-butylphenyl)porphyrin (**3**) or zinc(II) 5,15-ethynyl-10,20-(4-*ter*-butylphenyl)porphyrin (**4**), respectively (Scheme 1). **SWNT-ZnP 2** was specially designed to allow the conjugation between the π-system of the porphyrin monomers. This allows decreasing the HOMO-LUMO gap improving the overall absorption of the chromophores in the visible and near infrared.[28-30]

Results and discussion

The synthesis of SWNT-ZnP **1** and **2** is depicted in Scheme 1; porphyrins **3** and **4** were reacted with *f*-SWNT **5** in the presence of CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) under oxygen in *N*-methylpyrrolidone to give **SWNT-ZnP 1** and **SWNT-ZnP 2**, respectively. After the reaction, the mixture was filtered and extensively washed with NH4Cl solution to remove the catalyst and with NMP, THF and dichloromethane to remove the reagents and the oligomers not covalently attached to the nanotubes. It is worth mentioning that Hay coupling can occur not only between the phenylacetylene groups of the nanotubes and the porphyrins but also between the nanotubes themselves to form highly insoluble aggregates. To decrease this possibility, the reactions are performed with diluted solutions of well dispersed nanotubes (less than 0.1 mg/mL) and relatively large amounts of porphyrin are added. Finally, after functionalization with porphyrins, the nanotube derivatives are more soluble than the starting materials. This observation supports the fact that the cross-linking between the nanotubes is limited; however we do not have any proofs that it does not happen and it can constitute a limitation of the method compared to CuAAC, for example.

The synthesis of the Zn-porphyrin derivatives **3** and **4** is depicted in Scheme 2. 5-(4-terbutylphenyl)dipyrromethane[31] reacted with 4-[(trimethylsilyl)ethynyl]benzaldehyde or 3-(trimethylsilyl)-2-propynal in the presence of trifluoroacetic acid in CH2Cl2; the porphyrinogens were oxidised with chloranil to give porphyrin **6** and **7**, respectively. The porphyrins were metallated with Zn^{2+} to give **8** and **9** which were treated with tetrabutylamonium fluoride to deprotect the acetylenic functions. Porphyrins **3** and **4** were polymerised in the presence of CuCl and TMEDA but in the absence of nanotubes to produce the reference porphyrin oligomers **10** and **11**, respectively. The nanotube/porphyrin conjugates **SWNT-ZnP 1** and **SWNT-ZnP 2** were characterised by UV-Vis absorption and emission spectroscopy, Raman and X-ray photoelectron (XPS) spectroscopy and scanning electron microscopy (SEM). It is worth mentioning that NMP which is one the most efficient solvent for the dispersion of nanomaterials leads to decomposition products upon sonication.[32-34] In our experiments, we try to limit the sonochemical reaction of the

solvent by dispersing SWNT with anhydrous NMP using bath sonication.
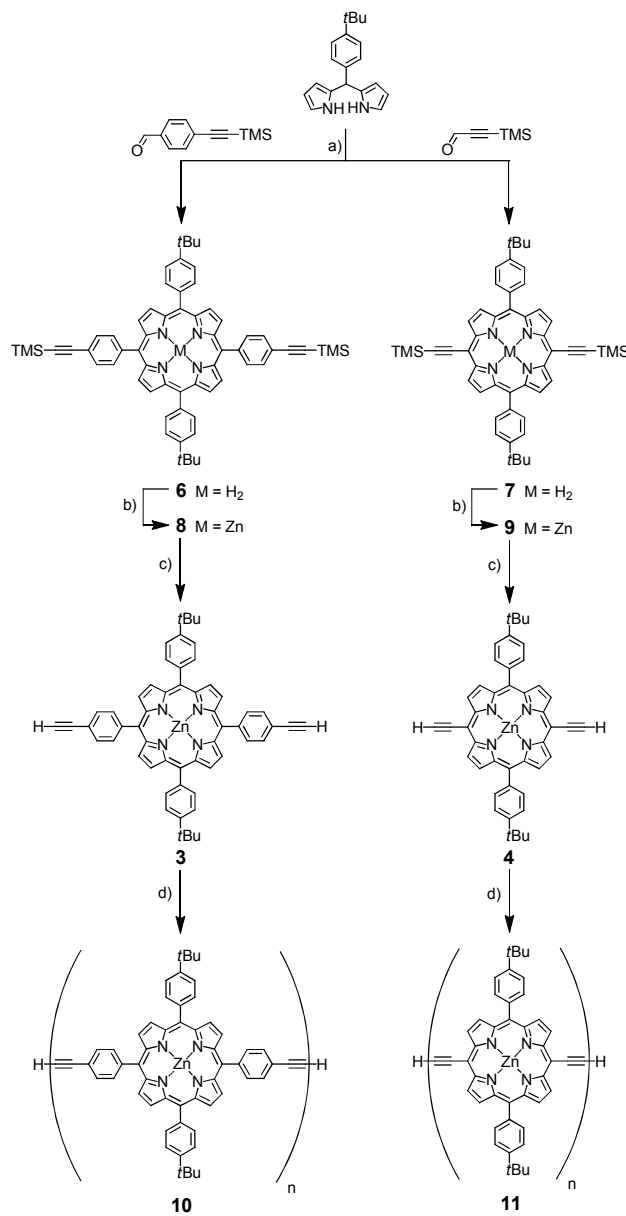
Scheme 2. a) CH2Cl2, TFA, Ar, rt, 3h then chloranil, rt, 1h, **6** 31%, **7**, 23%; b) Zn(OAc)2, 2 H2O, CH2Cl2/MeOH, rt, **8** 95%, **9**, 96%; c) NBu4F (1M THF), THF, Ar, rt, 1h, **3** 95%, **4**, 94%; d) TMEDA, CuCl, O2, CH2Cl2/NMP, rt, 24h.

Steady state absorption and emission spectroscopy of **SWNT-ZnP 1** and **SWNT-ZnP 2** and of the reference porphyrin oligomers **10** and **11** are shown in Fig. 1a and 1b. One can observe that **SWNT-ZnP 1** and oligomer **10** exhibit the typical absorption of the Soret band of the porphyrins at *ca.* 420 nm. The signal of the porphyrin in the absorption spectra of the oligomer and of the nanotube conjugate is identical to the one of the porphyrin monomer. Indeed, in **SWNT-ZnP 1** and oligomer **10**, the porphyrin cores are linked through phenylacetylene moieties, the phenyl rings are tilted of *ca.* 90° with respect to the plane of the porphyrin causing the rupture

of the π-conjugation. On the contrary, in **SWNT-ZnP 2** and oligomer **11**, the porphyrins are linked directly in meso position through 1,3-butadiyne spacers which allow the system to be coplanar increasing the delocalisation. This effect is well-known[30,35] and is clearly visible in the spectra of Fig. 1b with the presence of two large bands between 400-500 nm and 700-900 nm for **SWNT-ZnP 2** and oligomer **11**. In comparison, the absorption spectrum of the porphyrin monomer **4** exhibits two low intensity Q-bands characteristic of a Zn-metallated porphyrin. Emission spectra of **SWNT-ZnP 1** and **SWNT-ZnP 2** are shown in the insets of Fig. 1a and 1b. In both cases, a quenching of the fluorescence of the porphyrins by the SWNTs units is observed indicating energy and/or charge transfers between the chromophores and the nanotubes. The maximum of the emissions of the porphyrin oligomers in **SWNT-ZnP 2** and in **11** are centered at *ca.* 820 and 810 nm, respectively. According to the analysis of the emission wavelength as a function of size performed by Anderson and coworkers[35] for the same kind of porphyrin oligomers, these emission wavelengths corresponds to the emission of trimers/tetramers.

Quantitative analysis of the nanotube-porphyrin conjugates were performed by means of XPS. The survey and core energy level spectra of **SWNT-ZnP 1** and **SWNT-ZnP 2** are shown in Fig. 1c and 1d. The spectra show the presence of zinc and nitrogen (in addition to carbon and oxygen) coming from the grafting of porphyrin onto the nanotube sidewalls. The analysis of the Zn 2p core level shows the presence of two sharp peaks at 1021.6 eV and 1044.7 eV corresponding to Zn $2p_{3/2}$ and Zn $2p_{1/2}$. The deconvolution of the C 1s core-level signal was performed with four Gaussian-Lorentzian curves centred at *ca.* 284.5, 285.3, 286.3 and 287.1 eV. Considering that the first

peak obtained at 284.5 eV corresponds mainly to the electrons collected from the sp^2 carbons, we estimated the nanotube/porphyrin ratio by calculating the ratio of the peak areas C 1s/Zn $2p_{3/2}$. We found a ratio of 1 porphyrin for 110 carbon atoms for **SWNT-ZnP 1** and 1 porphyrin for 65 carbon atoms for **SWNT-ZnP 2**. This result shows a significantly higher amount of porphyrin on the nanotube sidewalls for nanotube/porphyrin conjugates synthesised by *Hay* coupling compared to what we reported earlier for the conjugation by "click chemistry".[23,25]

Raman spectra of **SWNT-ZnP 1** and **SWNT-ZnP 2** as well as those of the reference compounds (purified SWNT, functionalised SWNT **5**, porphyrin oligomers **10** and **11**) are given in Fig 1e-f. The spectrum of the purified nanotubes (in black) exhibits the typical features of SWNTs (*i.e.* RBM, G- and 2D-bands). The spectrum of f-SWNT **5** presents in addition two new bands at *ca.* 1300 cm^{-1} and 2900 cm^{-1}, the first is attributed to the sp^3 carbons caused by the covalent grafting of phenylacetylene moieties on the nanotube sidewalls (D-band) and the second is a combination of the G and D modes. The D/G intensity ratio for purified SWNT is 0.024, it increases to 0.325 for *f*-SWNT **5**. After the functionalisation of the nanotubes *via* Hay coupling, the spectra of **SWNT-ZnP 1** and **SWNT-ZnP 2** (Fig. 1g) show many additional bands which are attributed to the presence of the porphyrin oligomers in the 200 – 1600 cm^{-1} region and bands at 2210 (**SWNT-ZnP 1** and porphyrin oligomer **10**) and 2175 cm^{-1} (**SWNT-ZnP 2** and porphyrin oligomer **11**) arising from the 1,3-butadiyne spacer.[36] Unfortunately the D/G ratio cannot be calculated for the SWNT-ZnP hybrids **1** and **2** because the D-bands are hidden by strong peaks arising from the porphyrin oligomers (Fig. S13).
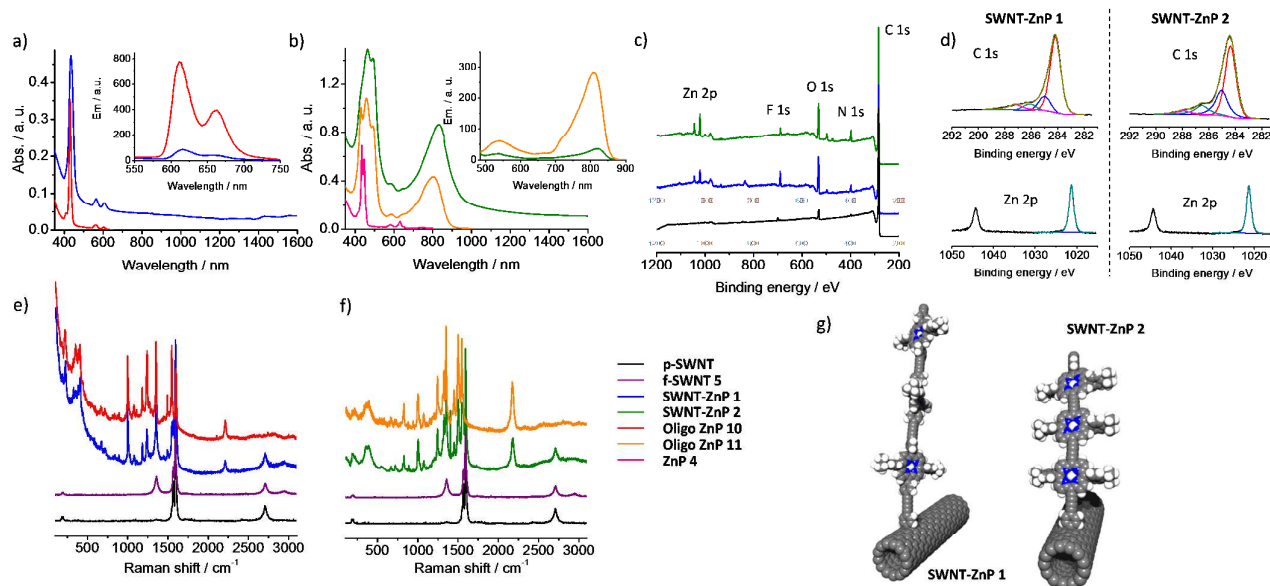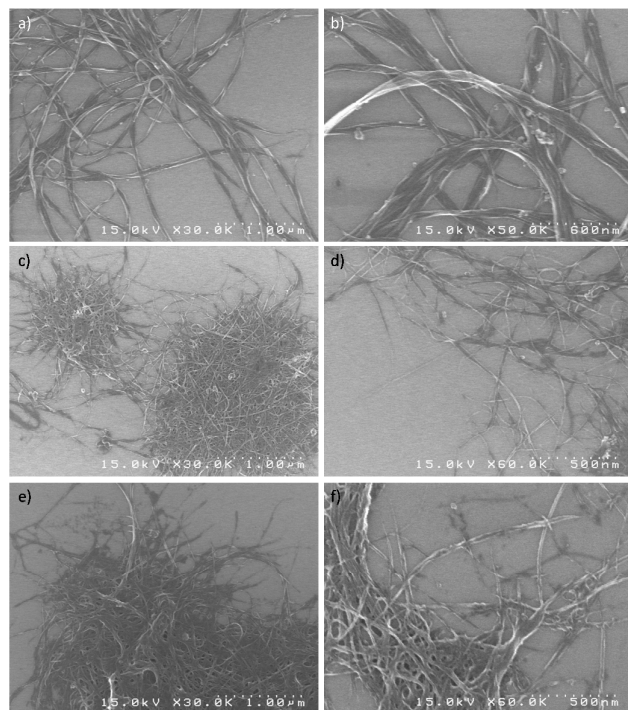

Fig. 1 a) Absorption and emission in inset (λ$_{exc}$ = 430 nm) spectra of the porphyrin oligomer **10** (red) and of of **SWNT-ZnP 1** (blue); b) Absorption and emission in inset (λ$_{exc}$ = 465 nm) spectra of the porphyrin monomer **4** (pink), porphyrin oligomer **11** (orange) and of **SWNT-ZnP 1** (green); c) XPS spectra of purified SWNT (black), **SWNT-ZnP 1** (blue) and **SWNT-ZnP 2** (green) – the presence of fluorine in the spectra is due to the PTFE membrane on which the nanotubes are filtered; d) High resolution XPS spectra of carbon C 1s and Zn 2p of **SWNT-ZnP 1** and **SWNT-ZnP 2**; e)-f) Raman spectra recorded after excitation at 457.9nm of purified SWNT (black), phenylactetylene-functionalised f-SWNT **5** (purple), **SWNT-ZnP 1** (blue), porphyrin oligomer **10** (red), **SWNT-ZnP 2** (green) and porphyrin oligomer **11** (orange); g) representation of the grafted porphyrin oligomers on the nanotubes **SWNT-ZnP 1** and **SWNT-ZnP 2**.

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Fig. 2 SEM images taken at different magnification of a)-b) purified SWNT; c)-d) SWNT-ZnP 1; e)-f) SWNT-ZnP 2 deposited on Si/SiO2 surface.

Purified SWNT and the nanotube/porphyrin conjugates were investigated by scanning electron microscopy. The SEM micrographs of purified SWNT (Fig. 2a-b) show the presence of large bundles of nanotubes of several tenths of nanometers in diameter. On the contrary, **SWNT-ZnP 1** and **SWNT-ZnP 2** formed thinner aggregates and at the periphery individual nanotubes can be observed (Fig. 2c-f). Indeed, the functionalisation helps the individualisation and dispersion of the nanotubes.

Conclusions

Here, we described the synthesis of two single walled carbon nanotube/porphyrin conjugates **SWNT-ZnP 1** and **SWNT-ZnP 2** containing porphyrin connected either *via* 1,4-phenyl-1,3-butadiyne or 1,3-butadiyne spacers. The nanoconjugates were obtained by polymerisation of acetylene-containing porphyrins in the presence of functionalised SWNT containing phenylacetylene moieties *via* Hay coupling. **SWNT-ZnP 2** was specially designed to allow the conjugation between the π-system of the porphyrin monomers what permits to decrease the HOMO-LUMO gap improving the overall absorption of the chromophores in the visible and near infrared. XPS analyses

showed that we were able to introduce *ca.* 1 porphyrin for 110 carbon atoms for **SWNT-ZnP 1** and 1 porphyrin for 65 carbons for **SWNT-ZnP2**. This study provides an easy and efficient method to functionalise carbon nanotubes that could be used for the fabrication of materials for optoelectronic or electrocatalytic applications.

Experimental

Materials and methods.

UV-Vis-NIR spectra were recorded in 1 cm quartz cuvettes on a Perkin Elmer Lambda 900 UV-Vis-NIR spectrophotometer. FT-IR spectra were recorded on a Bruker Alpha FT-IR spectrometer. ^{1}H NMR spectra were recorded with a BRUKER AC-300 (300 MHz) for ^{1}H NMR or on a BRUKER AVANCE II (500 MHz) for ^{13}C NMR with solvent used as internal reference. MALDI-TOF MS spectra were obtained from a Perseptive Biosystems Voyager DE-STR instrument. Raman spectra were collected by a T64000 Jobin-Yvon spectrometer (in triple or single configuration) through an optical microscope (Olympus BX41, objective 100X), choosing the excitation source among the lines of an Ar-Kr laser; the spot size was about 1μm. For X-ray photoelectron spectroscopy (XPS) a Kratos Analytical Axis Ultra DLD, using an Al Kα source monochromatised at 1486.6 eV was used. We used a hemispherical analyzer working at pass energy of 50 eV for the global spectrum, and 20 eV when focusing on the sole core levels. The samples were supported on PTFE membranes or on gold-coated glass. For SEM, the samples were prepared by drop casting from NMP solutions on silicon substrates and the images were performed on a SEM Hitachi S4500 operating at 15 kV.

Chemicals were purchased from Aldrich and were used as received. Solvents were purchased form Aldrich or SDS Carlo Erba and were used as received. For synthesis, CH_2Cl_2 (CaH_2, N$_2$), THF (K/benzophenone, N$_2$) were distilled before use. Laser ablation SWNTs were obtained from Dr. Oliver Jost (Dresden University); they were purified and functionalised with phenylacetylene groups (f-SWNT **5**) as described previously.[23] 5-(4-terbutylphenyl)dipyrromethane[31] and the A2B2 porphyrin derivatives[37] were synthesised according literature procedures.

Synthetic procedures.

Compound 6. 5-(4-*ter*butylphenyl)dipyrromethane (750 mg, 2.7 mmol) and 4-[(trimethylsilyl)ethynyl]benzaldehyde (550 mg, 2.7 mmol) were dissolved in dry CH_2Cl_2 (300 mL). After the solution was purged with argon for 20 min, TFA (263 μL) was added, and the resulting solution was stirred under argon for 3 h. After 3 h, chloranil (1.00 g, 4.05 mmol) was added. The

solution was stirred for an additional 1 h, at which time the solvent was evaporated and **6** was purified with a column chromatography (toluene/heptane 6:4) (0.390 g, 31%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.88 (m, 4H), 8.79 (m, 4H), 8.14 (m, 8H), 7.87 (d, *J* = 8.1 Hz, 4H), 7.75 (d, *J* = 8.1 Hz, 4H), 1.61 (s, 18H), 0.38 (s, 18H), -2.79 (s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.52, 134.51, 134.45, 134.39, 130.37, 130.34, 1330.32, 123.66, 123.63, 123.59, 34.91, 31.69, 0.07. FT-IR (KBr) υ (cm^{-1}) 3272, 2960, 2941, 2918, 2871, 2156, 1690, 1674, 1561, 1550, 1495, 1475, 1478,1396, 1391, 1339, 1249, 1223, 1225, 1110, 1071, 997, 967, 859, 842, 798, 725, 719, 657. UV-Vis. (NMP) λ$_{max}$ (nm) 425, 459, 550, 612, 675. MALDI-TOF MS *m/z* calcd. for C$_{62}$H$_{62}$N$_4$Si$_2$: 918.45; found: 918.35 (M$^+$).

Compound 7. 5-(4-*ter*butylphenyl)dipyrromethane (750 mg, 2.7 mmol) and 3-(trimethylsilyl)-2-propynal (340 mg, 2.7 mmol) were dissolved in dry CH$_2$Cl$_2$ (300 mL). After the solution was purged with argon for 10 min, TFA (263 µL) was added, and the resulting solution was stirred under argon for 3 h. After 3 h, chloranil (1.50 g, 6.10 mmol) was added. The solution was stirred for an additional 1 h, at which time the solvent was evaporated and **7** was purified with a column chromatography (toluene/heptane 1:1) (0.240 g, 23%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.55 (d, 4H), 8.83 (d, 4H), 8.07 (d, 4H), 7.75 (d, 4H), 1.59 (s, 18H), 0.56 (s, 18H), -2.20 (s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.79, 138.22, 134.39, 123.81, 121.94, 120.50, 79.61, 34.93, 31.68, 0.27. FT-IR (KBr) υ (cm^{-1}) 3319, 2961, 2915, 2882, 2140, 1560, 1505, 1474, 1399, 1348, 1246, 1235, 1200, 1134, 1110, 1061, 1043, 974, 841, 798, 759, 730, 694. UV-Vis. (NMP) λ$_{max}$ (nm) 433, 449, 586, 625, 685. MALDI-TOF MS *m/z* calcd. for C$_{50}$H$_{54}$N$_4$Si$_2$: 766.39; found: 766.41 (M$^+$).

Compound 8. A solution of Zn(OAc)$_2$, 2H$_2$O (0.02 g, 0.1 mmol) in MeOH (5 mL) was added to a solution of porphyrin **6** (0.05 g, 0.054 mmol) in CH$_2$Cl$_2$ (50 mL) in a 100-mL Schlenk flask equipped with a magnetic stir bar. The reaction mixture was refluxed for 3 h. After extraction and evaporation, the crude product was purified by silica column chromatography (toluene/heptane 1:1 v/v) to give pure **8** (0.043 g, 95%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.84 (m, 8H), 8.16 (m, 8H), 7.90 (d, 4H), 7.76 (d, 4H), 1.62 (s, 18H), 0.36 (s, 18H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.43, 150.34, 150.26, 149.75, 143.22, 13967, 139.54, 134.30, 134.25, 132.40, 131.56, 130.21, 123.47, 120.16, 105.13, 95.33, 34.89, 31.71, 29.70, 0.08. FT-IR (KBr) υ (cm^{-1}) 3250, 2952, 2940, 2902, 2882, 2163, 1688, 1681, 1554, 1495, 1480, 1478,1395, 1392, 1345, 1250, 1233, 1225, 1113, 1068, 992, 959, 858, 841, 778, 722, 710, 642. UV-Vis. (NMP) λ$_{max}$ (nm) 425, 460, 550, 610, 672. MALDI-TOF MS *m/z* calcd. for C$_{62}$H$_{60}$N$_4$Si$_2$Zn: 980.36; found: 980.41 (M$^+$).

Compound 9. A solution of Zn(OAc)$_2$, 2H$_2$O (0.02 g, 0.1 mmol) in MeOH (5 mL) was added to a solution of porphyrin **7** (0.06 g, 0.078 mmol) in CH$_2$Cl$_2$ (50 mL) in a 100-mL Schlenk flask equipped with a magnetic stir bar. After extraction and evaporation, the reaction mixture was refluxed for 3 h. The crude product was purified by silica column chromatography (toluene/heptane 1:1 v/v) to give pure **9** (0.051 g, 96%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 9.43 (d, 4H), 8.52 (d, 4H), 8.10 (d, 4H), 7.75 (d, 4H), 1.48 (s, 18H), 0.53 (s, 18H). ^{13}C NMR (125

MHz, CDCl$_3$): δ 152.08, 150.49, 150.40, 139.00, 134.25, 132.93, 131.11, 123.60, 122.84, 107.44, 101.81, 101,20, 34.91, 31.71, 29.71, 0.33. FT-IR (KBr) υ (cm^{-1}) 3265, 2955, 2928, 2869, 2904, 2076, 1738, 1525, 1497, 1462, 1398, 1362, 1345, 1335, 1268, 1212, 1110, 1074, 1066, 1000, 935, 852, 829, 806, 795, 736, 712, 677, 611. UV-Vis. (NMP) λ$_{max}$ (nm) 436, 579, 626. MALDI-TOF MS *m/z* calcd. for C$_{50}$H$_{52}$N$_4$Si$_2$Zn: 828.30; found: 828.35 (M$^+$).

Porphyrin 3. To a solution of porphyrin **8** (20 mg, 0.021 mmol) in THF (10 mL) at 0°C under Ar was added a solution of TBAF (117 µL of a 1M solution in THF). After stirring for 1h at room temperature and under Ar, 40 mL of water was added. The solution was concentrated under reduced pressure, filtered, and washed with water. After drying, porphyrin **3** was obtained with 95 % yield (0.016 g). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.90 (m, 8H), 8.15 (m, 8H), 7.87 (d, 4H), 7.74 (d, 4H), 1.61 (s, 18H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.61, 150.51, 143.02, 142.83, 142.71, 139.23, 139.07, 138.96, 129.02, 128;21, 123.62, 121.55, 121.43, 120.85, 120.38, 118.55, 83.77, 34.90, 31.68, 29.70. FT-IR (KBr) υ (cm^{-1}) 3271, 2955, 2944, 2915, 2868, 1746, 1604, 1527, 1492, 1464, 1396, 1365, 1338, 1319, 1268, 1235, 1206, 1189, 1110, 1068, 997, 856, 809, 799, 720, 761. UV-Vis. (NMP) λ$_{max}$ (nm) 430, 561, 603. MALDI-TOF MS *m/z* calcd. for C$_{56}$H$_{44}$N$_4$Zn: 836.29; found: 836.28 (M$^+$).

Porphyrin 4. To a solution of porphyrin **9** (25 mg, 0.030 mmol) in THF (10 mL) at 0°C under Ar was added of TBAF (120 µL of a 1M solution in THF). After stirring for 1h at room temperature and under Ar, 40 mL of water was added. The solution was concentrated under reduced pressure, filtered, and washed with water. After drying, porphyrin **4** was obtained with 94% yield (0.019 g); unfortunately the low solubility of **4** did not permitted to obtain ^{13}C NMR spectrum. ^{1}H NMR (pyridine-*d$_5$*): δ 9.63 (d, 4H), 8.85 (d, 4H), 8.11 (d, 4H), 7.83 (d, 4H), 1.72 (s, 18H). FT-IR (KBr) υ (cm^{-1}) 3265, 2955, 2928, 2869, 2904, 2076, 1738, 1525, 1497, 1462, 1398, 1362, 1345, 1335, 1268, 1212, 1110, 1074, 1066, 1000, 935, 852, 829, 806, 795, 736, 712, 677, 611. UV-Vis. (NMP) λ$_{max}$ (nm) 435, 448, 591, 635. MALDI-TOF MS *m/z* calcd. for C$_{44}$H$_{36}$N$_4$Zn: 684.22; found: 684.24 (M$^+$).

General procedure for the synthesis of SWNT-ZnP 1 and SWNT-ZnP 2. To a suspension of phenylacetylene-functionalised **SWNT 5**[23] (2 mg) in NMP (24 mL) was added either porphyrin **3** or porphyrin **4** (0.015 mmol, 12 mg for **3** or 10 mg for **4**). Then a solution of TMEDA (75 µL, 0.5 mmol) and copper (I) chloride (25 mg, 0.25 mmol) was added before the oxygen was bubbled into the solution. The reaction mixture was stirred for 24 h at room temperature under O$_2$. The suspension was filtered on a PTFE membrane (0.2 µm), and the black solid was washed with NMP, deionised water, saturated NH$_4$Cl solution to remove the copper salts, and then water and NMP. In order to remove the eventual products absorbed on the nanotubes, the buckypaper was redispersed in NMP, then refiltered and washed with NMP, THF, and CH$_2$Cl$_2$. The nanotubes derivatives were characterised by absorption, emission, Raman and XPS spectroscopy.

General procedure for the synthesis of the reference porphyrin oligomers 10 and 11. To a suspension of either porphyrin **3** or porphyrin **4** (6 µmol, 5 mg for 3 or 4 mg for 4) in

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a mixture of CH_2Cl_2 and NMP (7/3 mL) was added a mixture of TMEDA (20 µL, 0.13 mmol) and copper (I) chloride (7 mg, 0.07 mmol) in NMP. The reaction mixture was bubbled with oxygen and stirred for 24h at room temperature. The reaction was diluted in CH_2Cl_2, washed with NH_4Cl then water, dried over $NaSO_4$ and evaporated. The oligomers were dispersed in a minimum amount of CH_2Cl_2 and precipitated in MeOH.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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