Supplementary Material (ESI) for Chemical Communications


Electronic Supplementary Information

# Zn-Porphyrin/Zn-Phthalocyanine Dendron for SWNT Functionalisation†

Khanh Hy Le Ho,[a] Lucie Rivier,[a] Bruno Jousselme,[b] Pascale Jégou,[b] Arianna Filoramo,[a] and Stéphane Campidelli*[a]

[a]CEA, IRAMIS, SPEC, Laboratoire d'Electronique Moléculaire, 91191 Gif sur Yvette, France. Fax: +33 (0)1 69 08 66 40; Tel: +33 (0)1 69 08 88 77; e-mail: stephane.campidelli@cea.fr

[b]CEA, IRAMIS, SPCSI, Laboratoire de Chimie des Surfaces et Interfaces, 91191 Gif sur Yvette, France.

† This article is part of the 'Carbon Nanostructures' web-theme issue for ChemComm

## Experimental section

**Techniques.** UV-Vis spectra were recorded in 1 cm quartz cuvettes on a Perkin Elmer Lambda 900 UV-Vis-NIR spectrophotometer. Emission spectra were recorded with a Cary Eclipse spectrofluorimeter. 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) instrument 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 triple spectrometer (subtractive 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 monochromatized at 1486.6 eV was used. We used a hemispheric analyzer working at pass energy of 50 eV for the global spectrum, and 20 eV when focusing on the sole core levels. All samples were supported on PTFE Membrane. The electrochemical experiments were carried out using EG&G potentiostat, model 273A in a three-electrode electrochemical cell. The experiments, in a glovebox, were conducted in anhydrous THF or methylene chloride with tetrabutylammonium hexafluorophosphate $[Bu_4N]PF_6$ as the supporting electrolyte. The auxiliary electrode was a platinum wire. The reference electrode was based on the $Ag/AgNO_3$ $10^{-2}$ M couple. The working electrodes (S = 0.32 cm$^2$) were either a bare platinum electrode for the references ZnPc **4**, ZnP **5,** dend-ZnPc **9** or dend-ZnP/ZnPc **12** and a platinum electrode with a coated film of SWNT-ZnPc **1**, SWNT-ZnPc **2** or SWNT-ZnP/ZnPc **3**. Functionalised SWNTs were dispersed under ultrasounds in SDS/water, filtered on cellulose nitrate filter (Sartorius, 0.2 μm), then the membrane was deposited on a Pt electrode and dissolved through washings with acetone. For AFM and SEM characterisation: the samples were deposited on polylysine-coated silicon wafers from a NMP solution and were incubated overnight. After washing with methanol and soft $N_2$ drying, the samples were investigated with a Veeco Multimode Scanning Probe Microscope equipped with a Nanoscope IIIa controller for AFM and with a Hitachi S-4500 Scanning Electron Microscope for SEM.

**Materials.** Laser ablation SWNTs were obtained from Dr. Oliver Jost (Dresden University). Chemicals were purchased form Aldrich and were used as received. Solvents were purchased form Aldrich or VWR and were used as received. For synthesis, $CH_2Cl_2$ ($CaH_2$, $N_2$), THF (K / benzophenone, $N_2$) were distilled before use. Functionalised SWNTs **8**,[1] zinc tri-(*ter*-butyl)-aminophthalocyanine **6**,[2] zinc porphyrin **5**,[1;3] 3,5-(dipropargyloxy)benzyl chloride[4] and tris-

(hydroxypropyltriazolylmethyl)amine[5] (THPTA) were synthesized according to the literature procedure.

**Synthesis. zinc tri-(*ter*-butyl)-azidophthalocyanine 7.** To a solution of zinc tri-(*ter*-butyl)-aminophthalocyanine **6** (110 mg, 0.14 mmol) in a mixture of THF (20 ml) and TFA (500 µl) at 0°C were added sodium nitrite (30 mg, 0.43 mmol) in water (500 µl) and sodium azide (94 mg, 1.45 mmol) in water (500 µl). The reaction mixture was stirred at 0°C for 2h, then saturated $NaHCO_3$ solution was added and the mixture was extracted with $CH_2Cl_2$. The organic phase was dried on $Na_2SO_4$, filtered and evaporated to dryness. Purification of the residue by column chromatography (eluent $CH_2Cl_2/EtO_2$ 95/5 to 90/10) gave pure **7** (80 mg, 71% yield) as a blue powder. $^1$H NMR (300 MHz, $CDCl_3$) δ 8.80-6.10 (series of m, 12H, Arom. H), 1.75-1.35 (series of s, 27H, $C(CH_3)_3$). FT-IR (KBr) υ ($cm^{-1}$) 2951, 2852, 2102 ($N_3$), 1609, 1484, 1389, 1329, 1254, 1146, 1084, 1044, 920, 825, 743, 671, 525. UV-Vis (toluene) $\lambda_{max}$ (nm) 679, 612, 347. MALDI-TOF MS $C_{44}H_{39}N_{11}Zn$ (785,27) *m/z* = 785.33 [$M^+$].

**Compound 4.** To a solution of zinc tri-(*ter*-butyl)-azidophthalocyanine **7** (20 mg, 0.025 mmol) in THF (10 ml) were added phenylacetylene (13 mg, 0.127 mmol), $Cu(MeCN)_4PF_6$ (9,5 mg, 0.025 mmol), 2,6-lutidine (200 µl), water (1 ml) and a spatula tip of THPTA. The reaction mixture was frozen and the oxygen was removed by several cycle of vacuum/argon. Finally, the solution was stirred at room temperature for 48h, then water was added and the mixture was extracted with $CH_2Cl_2$, the organic phase was dried on $Na_2SO_4$, filtered and evaporated to dryness. Purification of the residue by column chromatography (eluent $CH_2Cl_2/Et_2O$ 95/5) gave pure **4** (15 mg, 66% yield) as a blue powder. $^1$H NMR (300 MHz, $CDCl_3$+2 drops THF-$d_8$) δ 9.60-6.60 (series of m, 18H, Arom. H), 2.10-1.60 (m, 27H, $C(CH_3)_3$). FT-IR (KBr) υ ($cm^{-1}$) 2953, 2857, 1712, 1612, 1483, 1391, 1326, 1255, 1083, 1045, 1021, 918, 828, 746, 689, 582. UV-Vis (toluene) $\lambda_{max}$ (nm) 684, 613, 347. MALDI-TOF MS $C_{52}H_{45}N_{11}Zn$ (887.32) *m/z* = 887.31 [$M^+$].

**Compound 9.** To a solution of zinc tri-(*ter*-butyl)-azidophthalocyanine **7** (50 mg, 0.064 mmol) in THF (20 ml) were added 3,5-(dipropargyloxy)benzyl chloride (7.5 mg, 0.032 mmol), $Cu(MeCN)_4PF_6$ (12 mg, 0.032 mmol), 2,6-lutidine (200 µl), water (1 ml) and a spatula tip of THPTA. The reaction mixture was frozen and the oxygen was removed by several cycle of vacuum/argon. Finally, the solution was stirred at 40°C overnight, then water was added and the mixture was extracted with $CH_2Cl_2$, the organic phase was dried on $Na_2SO_4$, filtered and evaporated to dryness. Purification of the residue by column chromatography (eluent toluene/THF 95/5) gave pure **9** (44 mg, 76% yield) as a blue powder. Note that about 8 mg of mono-adduct **11** (compound containing only 1 phthalocyanine) were

recovered from column chromatography; the mono-adduct was verified by MALDI-TOF MS ($C_{57}H_{50}ClN_{11}O_2Zn$ (1019.31) *m/z* = 1019.18 [$M^+$]) and used directly for the synthesis of **12**. $^1$H NMR (300 MHz, $CDCl_3$+2 drops mixt1/1 THF-$d_8$ pyridine-$d_5$) δ 9.50-6.50 (series of m, 29H, Arom. H), 5.70-5.55 (broad s, 4H, $CH_2O$) 4.62-4.53 (broad s, 2H, $CH_2Cl$) 2.00-1.60 (m, 54H, $C(CH_3)_3$). FT-IR (KBr) υ ($cm^{-1}$) 2953, 2856, 1717, 1612, 1488, 1441, 1389, 1314, 1255, 1148, 1085, 1046, 918, 827, 746, 670, 526. UV-Vis (toluene) $\lambda_{max}$ (nm) 685 with shoulder 675, 612, 348. MALDI-TOF MS $C_{101}H_{89}ClN_{22}O_2Zn_2$ (1804.58) *m/z* = 1804,61 [$M^+$].

**Compound 10.** To a solution of dendron **9** (30 mg, 0.017 mmol) in THF (5 ml) were added sodium azide (54 mg, 0.829 mmol) in water (1 ml). The reaction mixture was stirred at 60°C overnight, then water was added and the mixture was extracted with $CH_2Cl_2$, the organic phase was dried on $Na_2SO_4$, filtered and evaporated to dryness. Purification of the residue by column chromatography (eluent toluene/THF 95/5) gave pure **10** (22 mg, 73% yield) as a blue powder. $^1$H NMR (300 MHz, $CDCl_3$+2 drops mixt1/1 THF-$d_8$ pyridine-$d_5$) δ 9.55-6.45 (series of m, 29H, Arom. H), 5.70-5.55 (broad s, 4H, $CH_2O$) 4.35-4.25 (broad s, 2H, $CH_2N_3$) 2.00-1.60 (m, 54H, $C(CH_3)_3$). FT-IR (KBr) υ ($cm^{-1}$) 2953, 2864, 2098, 1613, 1488, 1459, 1392, 1366, 1329, 1255, 1147, 1086, 1043, 918, 828, 746, 671, 526. UV-Vis (toluene) $\lambda_{max}$ (nm) 675, 644, 342. MALDI-TOF MS $C_{101}H_{89}N_{25}O_2Zn_2$ (1811.62) *m/z* = 1811.72 [$M^+$].

**Compound 12.** To a solution of **11** (20 mg, 0.020 mmol) in THF (10 ml) were added 5,10,15-tris-(4-*tert*-butylphenyl)-20-(4-azidophenyl)porphyrinato zinc (17.5 mg, 0.020 mmol), $Cu(MeCN)_4PF_6$ (7.3 mg, 0.020 mmol), 2,6-lutidine (200 µl), water (1 ml) and a spatula tip of THPTA. The reaction mixture was frozen and the oxygen was removed by several cycle of vacuum/argon. Finally, the solution was stirred at 40°C overnight, then water was added and the mixture was extracted with $CH_2Cl_2$, the organic phase was dried on $Na_2SO_4$, filtered and evaporated to dryness. Purification of the residue by column chromatography (eluent toluene/AcOEt 90/10) gave pure **12** (22 mg, 59% yield) as a green-brown powder. $^1$H NMR (300 MHz, $CDCl_3$+2 drops mixt1/1 THF-$d_8$ pyridine-$d_5$) δ 9.90-6.50 (series of m, 41H, Arom. H), 5.60-5.45 (m, 4H, $CH_2O$) 4.60-4.46 (m, 2H, $CH_2Cl$) 1.90-1.20 (m, 54H, $C(CH_3)_3$). FT-IR (KBr) υ ($cm^{-1}$) 2953, 2854, 1718, 1612, 1489, 1456, 1390, 1313, 1255, 1147, 1085, 1044, 918, 830, 762, 746, 676, 526. UV-Vis (toluene) $\lambda_{max}$ (nm) 698, 550, 424, 346. MALDI-TOF MS $C_{113}H_{101}ClN_{18}O_2Zn$ (1904.66) *m/z* = 1904.69[$M^+$].

**Compound 13.** To a solution of dendron **12** (16 mg, 0.008 mmol) in THF (10 ml) were added sodium azide (6 mg, 0.092 mmol) in water (1 ml). The reaction mixture was stirred at 60°C overnight, then water was added and the mixture was extracted with $CH_2Cl_2$, the organic phase was dried on $Na_2SO_4$, filtered and evaporated to dryness. Purification of the residue by

column chromatography (eluent toluene/AcOEt 80/20) gave pure **13** (12 mg, 75% yield) as a green-brown powder. $^1$H NMR (300 MHz, $CDCl_3$+2 drops mixt1/1 THF-$d_8$ pyridine-$d_5$) δ 9.80-6.50 (series of m, 41H, Arom. H), 5.60-5.40 (m, 4H, $CH_2O$) 4.33-4.20 (m, 2H, $CH_2N_3$) 1.90-1.20 (m, 54H, $C(CH_3)_3$). FT-IR (KBr) υ ($cm^{-1}$) 2956, 2864, 2097, 1611, 1490, 1441, 1392, 1363, 1335, 1258, 1153, 1088, 1043, 996, 921, 859, 808, 794, 748, 691, 576, 525. UV-Vis (toluene) $\lambda_{max}$ (nm) 702, 549, 424, 345. MALDI-TOF MS $C_{113}H_{101}N_{21}O_2Zn_2$ (1911.70) *m/z* = 1911.88 [$M^+$].

**SWNT-ZnPc 1.** To a suspension of *f*-SWNTs (2 mg) in NMP (40 ml) at 0°C was added a solution of tetrabutylammonium fluoride (1 M in THF) (100 µl). The reaction mixture was stirred at room temperature for 1 h then filtered on a PTFE membrane (0.2µm), washed with NMP THF and $CH_2Cl_2$ then redispersed in NMP (40 ml). Azidophthalocyanine **6** (10 mg, 12.7 µmol), $Cu(MeCN)_4PF_6$ (5 mg, 13,0 µmol), 2,6-lutidine (500 µl) and THPTA (a spatula tip) were added and then oxygen in the mixture was removed by several cycle vacuum/argon. The reaction mixture was stirred at room temperature for 48 h and then filtered on a PTFE membrane (0.2µm), washed with NMP, deionized water, saturated $NH_4Cl$ solution then water and NMP. In order to remove the eventual products absorbed on the nanotubes, the bucky paper was redispersed in NMP, then refiltered and washed with NMP, THF and $CH_2Cl_2$. These operations were repeated until the filtrate contains no phthalocyanine (checked by UV-Vis absorption).

**SWNT-ZnPc 2.** To a suspension of *f*-SWNTs (0,5 mg) in NMP (40 ml) at 0°C was added a solution of tetrabutylammonium fluoride (1 M in THF) (50 µl). The reaction mixture was stirred at room temperature for 1 h then filtered on a PTFE membrane (0.2µm), washed with NMP THF and $CH_2Cl_2$ then redispersed in NMP (40 ml). Phthalocyanine dendron **10** (5 mg, 2.7 µmol), $Cu(MeCN)_4PF_6$ (5 mg, 13,0 µmol), 2,6-lutidine (200 µl) and THPTA (a spatula tip) were added and then oxygen in the mixture was removed by several cycle vacuum/argon. The reaction mixture was stirred at room temperature for 48 h and then filtered on a PTFE membrane (0.2µm), washed with NMP, deionized water, saturated $NH_4Cl$ solution then water and NMP. In order to remove the eventual products absorbed on the nanotubes, the bucky paper was redispersed in NMP, then refiltered and washed with NMP, THF and $CH_2Cl_2$. These operations were repeated until the filtrate contains no phthalocyanine (checked by UV-Vis absorption).

**SWNT-ZnP/ZnPc 3.** To a suspension of *f*-SWNTs (0,5 mg) in NMP (40 ml) at 0°C was added a solution of tetrabutylammonium fluoride (1 M in THF) (50 µl). The reaction mixture was stirred at room temperature for 1 h then filtered on a PTFE membrane (0.2µm), washed

with NMP THF and $CH_2Cl_2$ then redispersed in NMP (40 ml). Dendron **13** (5 mg, 2.6 μmol), $Cu(MeCN)_4PF_6$ (5 mg, 13,0 μmol), 2,6-lutidine (200 μl) and THPTA (a spatula tip) were added and then oxygen in the mixture was removed by several cycle vacuum/argon. The reaction mixture was stirred at room temperature for 48 h and then filtered on a PTFE membrane (0.2μm), washed with NMP, deionized water, saturated $NH_4Cl$ solution then water and NMP. In order to remove the eventual products absorbed on the nanotubes, the bucky paper was redispersed in NMP, then refiltered and washed with NMP, THF and $CH_2Cl_2$. These operations were repeated until the filtrate contains no porphyrin and phthalocyanine (checked by UV-Vis absorption).

**XPS analyses.**

XPS analysis of functionalised SWNTs **8**, SWNT-ZnPc **1**, SWNT-ZnPc **2** and SWNT-ZnPc/ZnP **3** derivatives clearly shows peaks due to carbon and oxygen for all the samples (Fig. S4) and in some cases to nitrogen and zinc. The oxygen presents in the all samples comes from defects (alcohol or carboxylic acid functions) formed during the purification process of the SWNTs. The nitrogen presents in the functionalised SWNTs **8** sample with a peak centered at 400.3 eV can be attributed to the presence of NMP and is due to the ability of SWNTs to be spontaneously filled with fluids that have surface tensions below 100-200 mN/m[6] (note that NMP possesses a surface tension of 40.7 mN/m). The expanded N1s regions of SWNT-ZnPc **1**, SWNT-dend-ZnPc/ZnPc **2** and SWNT-dend-ZnPc/ZnP **3** (Fig. S5) show three peaks: a single N1s peak at binding energy of 398.3 eV is observed for ZnPc and ZnP as expected for the metalloporphyrin;[7] a N1s peak located at 401.8 eV is attributed to one nitrogen of the triazole formation ring;[8] the two other nitrogen are located around 400.3 eV. We can note the absence of unreacted physisorbed azide species which normally exhibit a peak at 405 eV.[9] These observation allowed us to unambiguously prove the covalent linkage between the porphyrins and the nanotubes. Analysis of the Zn2p region of SWNT-ZnPc **1**, SWNT-ZnPc **2** and SWNT-ZnPc/ZnP **3** samples (Fig. S5) shows two sharp peaks with a bonding energy at 1021.9 eV and 1044.9 eV corresponding to $2p_{3/2}$ and $2p_{1/2}$ with a ratio of 2:1. Those two peaks are assigned to Zn(II) ion of phthalocyanines and porphyrins. A deconvolution of C1s energy level signal was performed for SWNT-ZnPc **1**, SWNT-ZnPc **2** and SWNT-ZnPc/ZnP **3** samples (Fig. S5) with three Gaussian-Lorentzien curves at 284.4, 285.4 and 286.6 eV. Considering that the peak obtained at 284.4 eV corresponds mainly to the electrons collected from the $sp^2$ carbons of CNTs, the calculation of the intensity ratio of [Zn $2p_{3/2}$ / C 1s] allows us to estimate the number of functional groups for each nanotube

derivative. We found that SWNT-ZnPc **1,** SWNT-ZnPc **2** and SWNT-ZnPc/ZnP **3** contain respectively about 1 functional group for 320, 380 and 440 carbons.

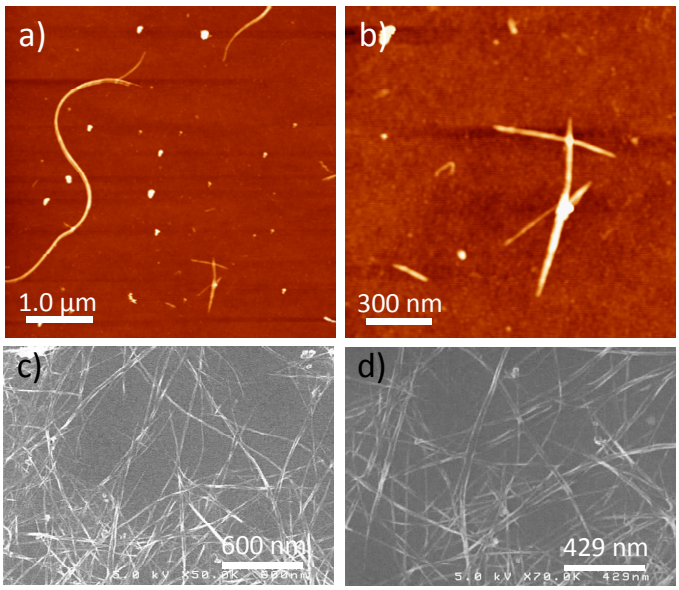


**Fig. S1** a) and b) AFM images of SWNT-ZnP/ZnPc **3**; The topographic images reveal the presence of thin bundle and individual SWNTs with the typical lengths that range from 500 nm to few micrometers. c) and d) SEM micrographs of SWNT-ZnPc **2** which reveal the presence of thin bundles of nanotubes as spaghetti-like aggregates. For investigation by microscopy, the SWNT derivatives were deposited on silicon surface.

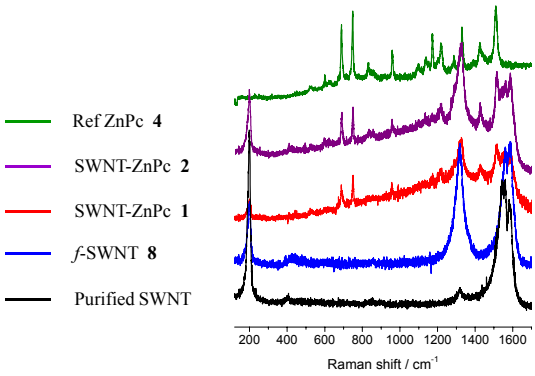


**Fig. S2** Raman spectra of the SWNT-ZnPc series ($\lambda_{exc}$ 647.1 nm).

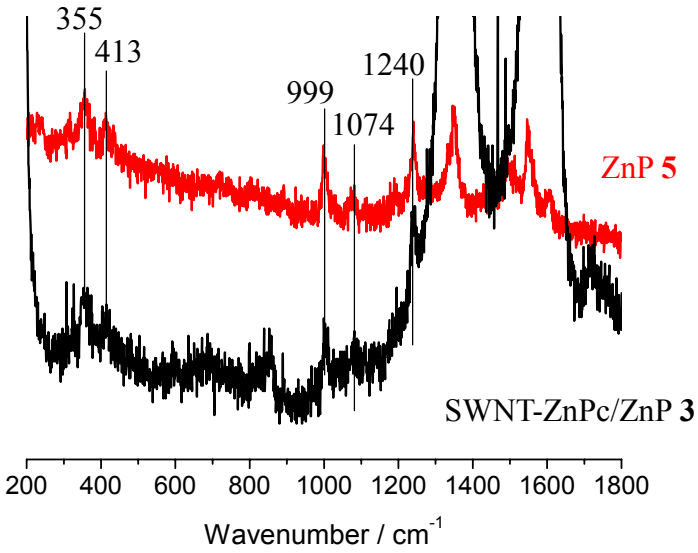


**Fig. S3** zoom of the Raman spectra (the excitation set to 457.1 nm) of SWNT-ZnP/ZnPc **3** (black) and of ZnP **5** (red). Careful examination of the spectrum of **3** shows the presence of bands at 355, 413, 999, 1074 and 1240 $cm^{-1}$ which is attributed to the presence of the tetraphenyl porphyrin moiety on the SWNT conjugate.

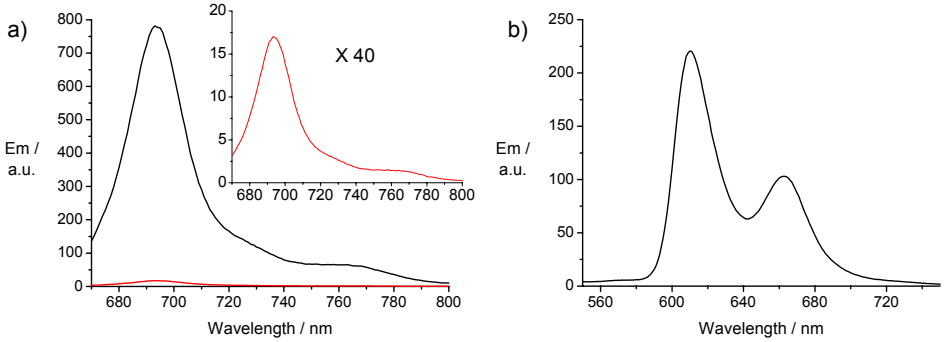


**Fig. S4** a) emission spectra of ZnPc **4** in NMP with the excitation set to 665nm or 430 nm (black or red spectra respectively). Note that when excited at 430 nm the fluorescence of the phthalocyanine is significantly lower than the same solution excited at 665 nm. b) emission spectra of ZnP **5** in NMP with the excitation set to 430 nm.

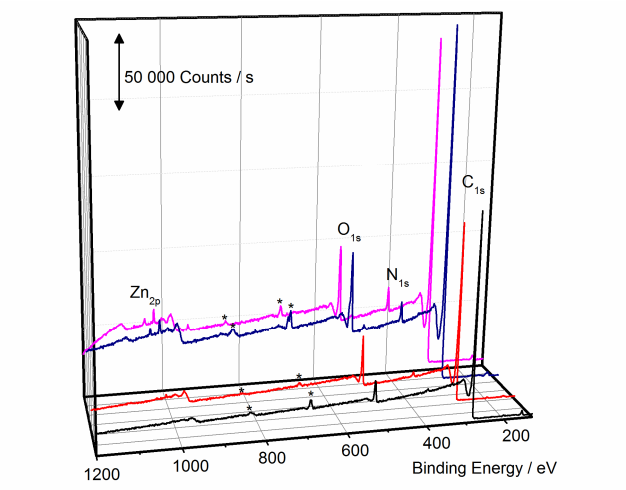


**Fig. S5** XPS spectra of functionalised SWNTs **8** (black), SWNT-ZnPc **1** (red), SWNT-dend-ZnPc **2** (blue) and SWNT-dend-ZnPc/ZnP **3** (pink) supported on PTFE membrane (the stars in the spectra show the fluorine from the membrane).

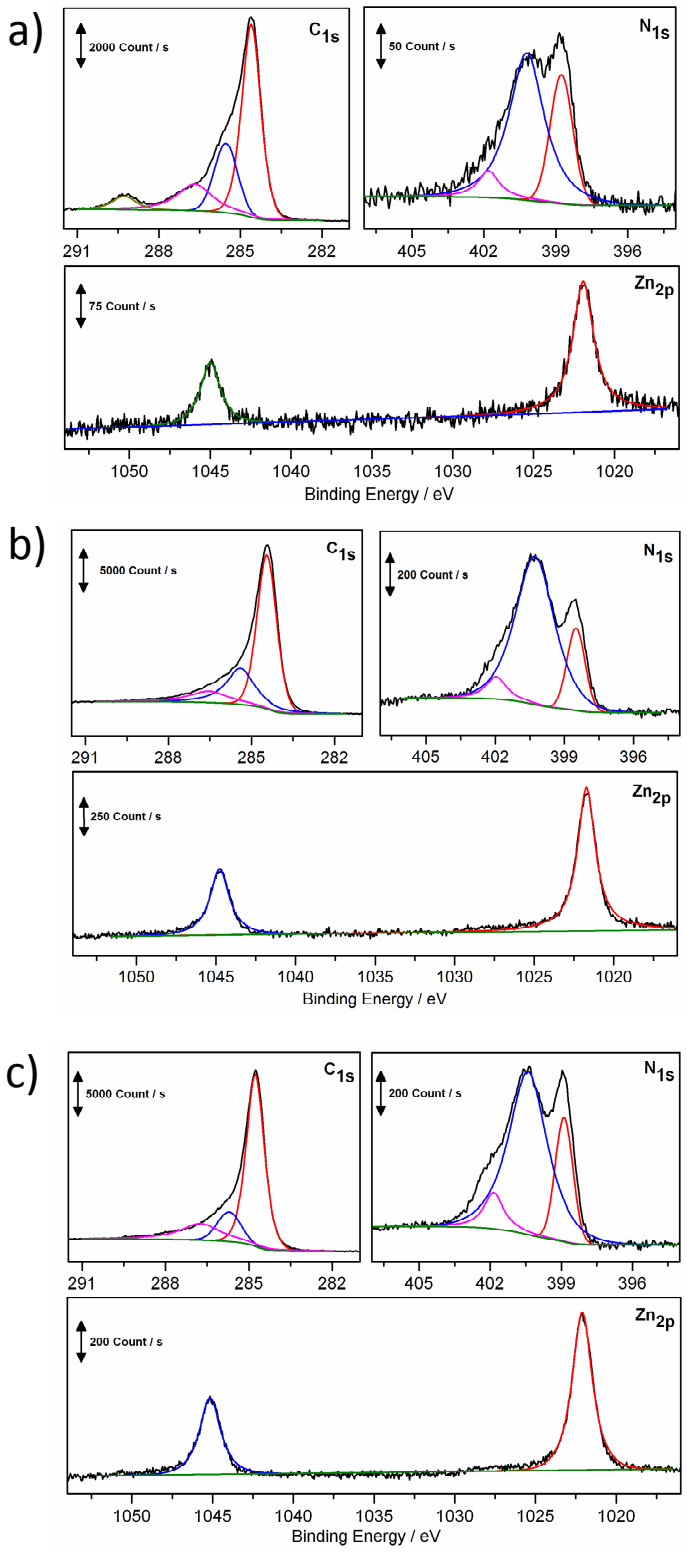


**Fig. S6** XPS analysis of SWNT-ZnPc **1** (a), SWNT-ZnPc **2** (b) and SWNT-ZnP/ZnPc **3**. In each case core level spectra: C 1s (top left), N 1s (top right) and Zn 2p (bottom).

**Table S1** electrochemical Data of **4**, **5**, **9** and **12** in 0.1 M $Bu_4NPF_6$ / THF and **1**, **2** and **3** coated on platinum working electrode in 0.1 M $Bu_4NPF_6$ / $CH_2Cl_2$; potentials *vs* $Ag/Ag^+$ (10 mM).

| Compound | $E^{ox}$/mV | | |
|---|---|---|---|
| ZnPc **4** | | 290 | 470 |
| ZnP **5** | | | 450 |
| Dend-ZnPc **9** | 90 | 260 | 440 |
| Dend-ZnP/ZnPc **12** | 40 | 290 | 550 |
| SWNT-ZnPc **1** | | 210 | |
| SWNT-ZnPc **2** | 100 | 350 | |
| SWNT-ZnP/ZnPc **3** | | 260 | |

# Reference List

1. T. Palacin, H. Le Khanh, B. Jousselme, P. Jégou, A. Filoramo, C. Ehli, D. M. Guldi and S. Campidelli, *J. Am. Chem. Soc.* 2009, **131**, 15394.

2. S. V. Kudrevich, H. Ali and J. E. van Lier, *J. Chem. Soc., Perkin Trans.1* 1994, 2767.

3. M. Séverac, L. Le Pleux, A. Scarpaci, E. Blart and F. Odobel, *Tetrahedron Lett.* 2007, **48**, 6518.

4. P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless and V. V. Fokin, *Angew. Chem., Int. Ed.* 2004, **43**, 3928.

5. X.-M. Liu, A. Thakur and D. Wang, *Biomacromolecules* 2007, **8**, 2653.

6. T. W. Ebbesen, *J. Phys. Chem. Solids* 1996, **57**, 951.

7. G. Polzonetti, C. Battocchio, A. Goldoni, R. Larciprete, V. Carravetta, R. Paolesse and M. V. Russo, *Chem. Phys.* 2004, **297**, 307.

8. S. Ciampi, T. Böcking, K. A. Kilian, M. James, J. B. Harper and J. J. Gooding, *Langmuir* 2007, **23**, 9320.

9. J. P. Collman, N. K. Devaraj, T. P. A. Eberspacher and C. E. D. Chidsey, *Langmuir* 2006, **22**, 2457.