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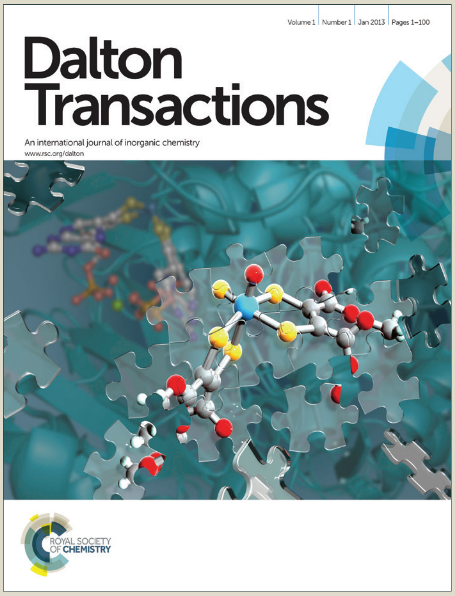

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ARTICLE TYPE

Linking Pd(II) and Ru(II) Phthalocyanines to Single-Walled Carbon Nanotubes

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The preparation of new Pc-SWCNT hybrid materials is described. The synthesis of both Pd(II)Pc-SWCNT **7** and Ru(II)bis(pyridine)Pc -SWCNT **9** was carried out by esterification reaction between modified SWCNTs and the corresponding unsymmetric Pcs **1** and **2**, both endowed with three solubilizing *tert*-butyl groups and a hydroxymethyl function. Compound **1** was prepared following the straightforward, statistical condensation of the corresponding phthalonitriles. However the preparation of Ru(II)bis(pyridine)Pc **2** required a multistep procedure relying on consecutive cyclotetramerization, protection, metallation and deprotection reactions. Modified SWCNT **6** was prepared, as previously described, by Prato reaction between HiPCo nanotubes, *N*-methylglycine and 4-formylbenzoic acid. The COOH-containing material **6** was successfully reacted with Pd(II)Pc **1** to give Pd(II)Pc-SWCNT **7**, which was fully characterized by different techniques. However, the incorporation of Ru(II)bis(pyridine)Pc **1** did not take place when applying the above mentioned conditions. The preparation of SWCNT **8** endowed with 4-carboxyphenyl moieties was found to be essential to covalently link Ru(bis(pyridine))Pc **1** to the nanotube material by ester bond formation. Although spectroscopic characterization supports the covalent binding of Pc molecules to the modified SWCNT sidewalls, direct evidence of the presence of Ru(II) in the hybrid material could not be obtained.

Introduction

The outstanding properties of single-walled carbon nanotubes (SWCNTs) have aroused tremendous interest to implement these novel carbon allotropes into practical applications. In particular, SWCNTs are one-dimensional nanowires that readily accept charges, which can then be transported along their tubular axis. The electrical conductivity, morphology, and good chemical stability of SWCNTs are promising features that stimulate their integration into electronic devices.[1,2] In this regard, the covalent attachment of electron donors to the nanotube surface is at the forefront of investigations. Dyes such porphyrins and phthalocyanines (Pcs), which have been used as light-harvesting units and electron-donor components in organic planar heterojunction solar cells and dye-sensitized solar cells (DSSCs),[3-12] have been also implemented to the SWCNT surface aiming at preparing donor-acceptor nanoconjugate systems[13] for the ultimate conversion of solar energy into electricity.[14,15] In particular, Zn(II)Pc and H_2Pc-SWCNT ensembles have been prepared by covalent[16,17] and non-covalent approaches.[18-20]

In most cases, Zn(II) metallomacrocycles (i.e. phthalocyaninates and porphyrinates) are used as dyes/electron donor components due to their long-lived (>1 ns) singlet excited states. Though, Ru(II)Pcs have been seriously considered as alternatives to Zn(II)Pcs, for instance as dyes in DSSCs, due to both the appropriate HOMO-LUMO levels these compounds present, and to their axial coordination capabilities which avoid macrocycle aggregation.[21,22] Also, Pd(II)Pcs have shown to behave as efficient donor materials, for instance, in planar heterojunction Pd(II)Pc/C_{60} solar cells.[23]

In the current work, we report on the preparation of new Pd(II)Pc-SWCNT and Ru(II)bis(pyridine)Pc-SWCNT donor-acceptor hybrids through a covalent, stepwise approach involving a previous modification of HiPco SWCNTs to anchor COOH groups to the sidewalls, followed by an esterification reaction with new Pd(II) and Ru(II) Pcs, both endowed with three solubilizing *tert*-butyl groups and a hydroxymethyl function.

Results and discussion

Synthesis and characterization of phthalocyanines

The stepwise approach for the functionalization of SWCNTs with Pcs is advantageous, since chemical modification of SWCNTs usually requires a large excess of the reactants. Therefore, we planned to functionalize the SWCNTs in a first step *via* the well-known Prato cycloaddition reaction using the inexpensive 4-formylbenzoic acid and *N*-methylglycine. In this way, subsequent esterification reactions of the resulting pyrrolidine-SWCNT material bearing pendant COOH moieties

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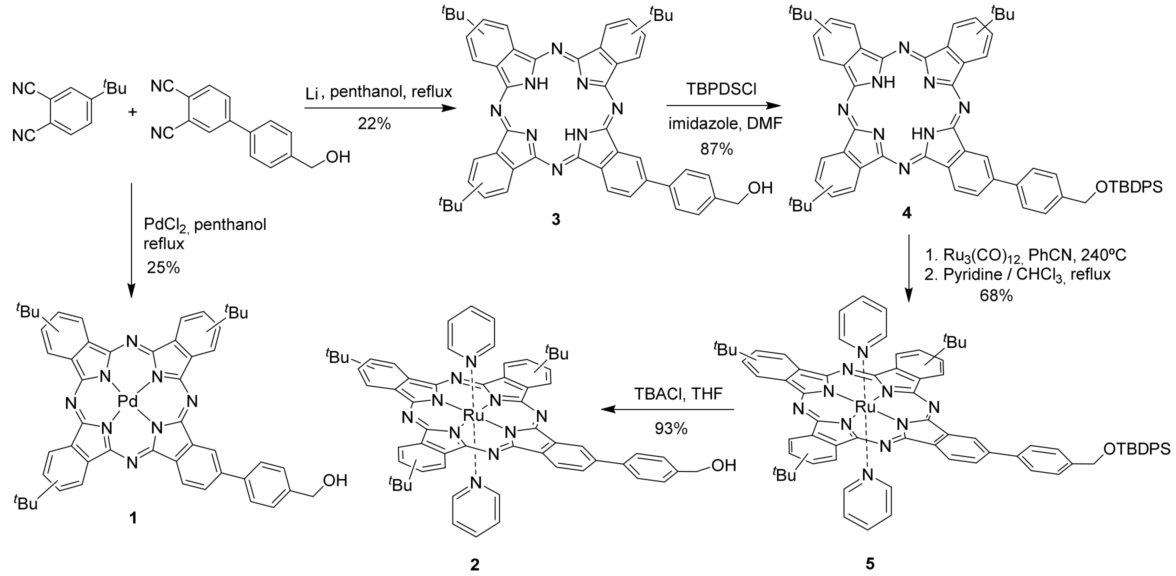

Scheme 1. Synthesis of unsymmetrically substituted Pcs **1** and **2**.

with Pcs endowed with three solubilizing *tert*-butyl groups and a hydroxymethyl function, namely Pd(II)Pc **1** and Ru(II)(bis(pyridine))Pc **2**, would proceed at nearly stoichiometric conditions.

The synthesis of Pcs **1** and **2** is depicted in Scheme 1. In particular, Pd(II)Pc **1** was prepared by statistical condensation in a 3:1 ratio of 4-*tert*-butyl-phthalonitrile and 4-(hydroxymethyl) phthalonitrile[24] in the presence of $PdCl_2$, followed by chromatographic separation from the statistical mixture of Pd(II)Pcs of the target compound **1**, which was obtained in 25% yield (Scheme 1). However, the synthesis of Ru(II)(bis(pyridine))Pc **2** requires a multistep procedure that involves the former synthesis of the metal-free derivative **3** by statistical condensation of 4-*tert*-butyl-phthalonitrile and 4-(hydroxymethyl)phthalonitrile,[24] followed by the incorporation of Ru(II) in the central cavity of the macrocycle. For such a Ru(II)-metallation, it was necessary to previously protect the hydroxymethyl moiety as a silyl ether (i.e., compound **4**), by treatment of **3** with *tert*-butyldiphenylsilyl chloride (TBDPSCl). Following previously reported conditions,[25] protected derivative **4** was then treated with $Ru_3(CO)_{12}$ and benzonitrile at 240ºC to obtain the Ru(II)(dibenzonitrile)Pc intermediate complex, that was further treated with pyridine in chloroform to obtain the more stable, Ru(II)(bis(pyridine))Pc **5**. Last, deprotection of the terminal hydroxyl group with tetrabutylammonium chloride (TBACl) afforded target compound **2** in overall 12% yield.

All the compounds were characterized by standard spectroscopic techniques, as detailed in the Experimental Section. In particular, ^{1}H NMR spectra are consistent with the proposed structures. Exceptionally well-resolved signals are obtained for the two Ru-containing Pcs **2** and **5** (Figure 1), because the two axial pyridyl ligands prevent aggregation. Even though, the presence of several regioisomers in all the compounds brings about multiplets for all the protons. Resonances corresponding to the Pc core split into two groups of signals, one at 9.0-9.4 ppm and the other at 7.3-8.1 ppm. The latter includes the ABAB system of the pending phenyl ring. Noteworthy, the signals corresponding to the protons of the pyridyl ligands are high-field shifted with regard to the typical pyridine resonances (i.e. 6.03, 5.23 and 2.50 ppm), as a consequence of the shielding exerted by the aromatic current of the Pc macrocycle. UV-vis spectra of all the Pc derivatives show the typical Soret and Q bands. As previously reported, the Q band of Ru(II)(bis(pyridine))Pc **2** is rather broadened, probably as a consequence of the splitting of the electronic levels of the Pc due to the bis(pyridine)-coordination (see below in Figure 4).

Synthesis of phthalocyanine-SWCNT hybrids

Then, we performed the modification of HiPco SWCNT sidewalls (Scheme 2) using – as previously described – 1.3 equivalents of *N*-methylglycine and 4-formylbenzoic acid per carbon atom of the nanotube structure in refluxing *o*-dichlorobenzene. The amount of pyrrolidine-COOH moieties in **6** was estimated to be 1 per 90 C atoms by TGA (18% weight loss, excluding initial weight losses due to adsorbants, Figure 2a). This functionalized SWCNT material dispersed in DMF was reacted with an excess (*ca.* 2.2 eq. per COOH groups) of either Pd(II)Pc **1** or Ru(bis(pyridine))Pc **2** in the presence of EDC/HOBt condensation mixture (Scheme 2). After 4 day reaction, the resulting SWCNT-based hybrid materials were respectively

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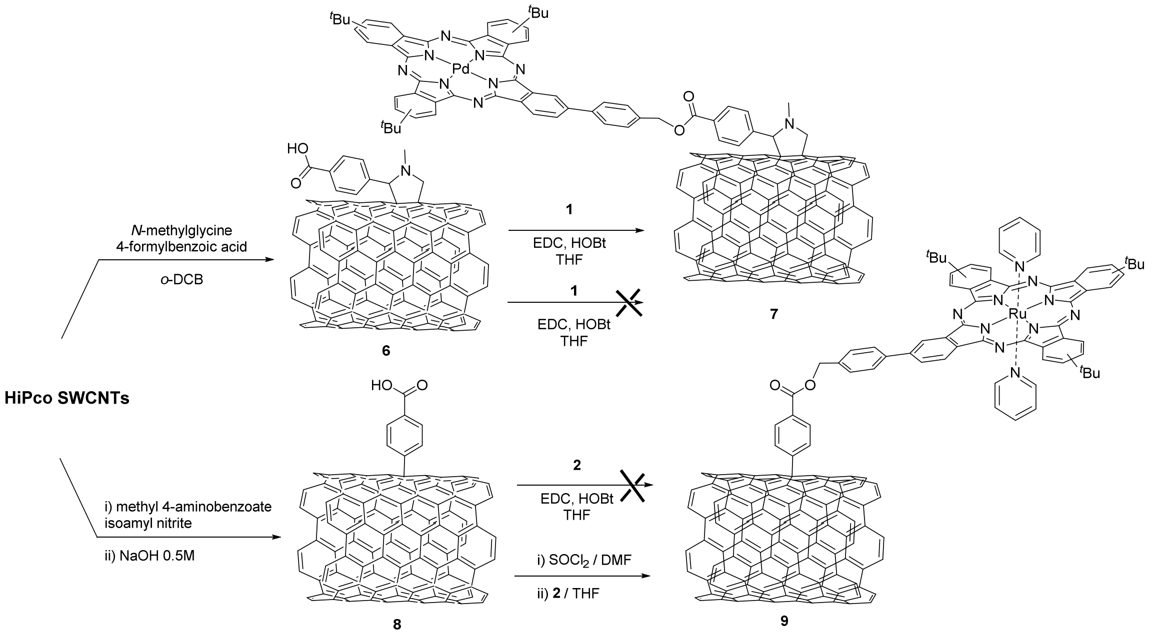

Scheme 2. Synthesis of hybrids Pd(II)Pc-SWCNT **7** and Ru(II)bis(pyridine)Pc-SWCNT **9**.

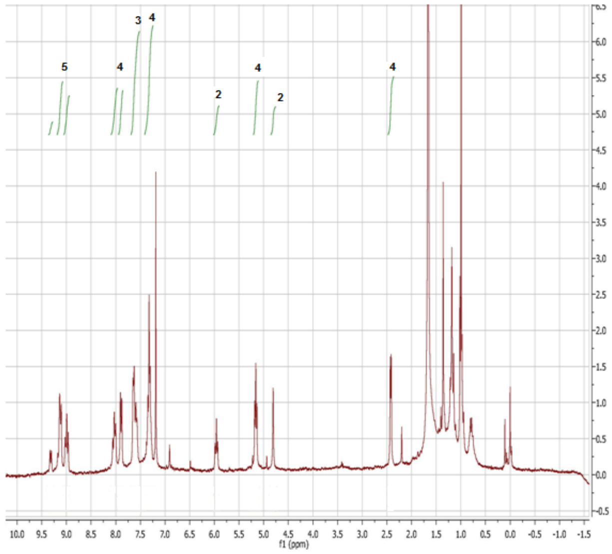

Figure 1. ^{1}H NMR of Ru(bis(pyridine))Pc **2**.

filtered through a PTFE membrane and washed with several solvents. Pd(II)Pc-SWCNT hybrid **7** was successfully obtained and characterized by different techniques (TGA, IR, XPS, UV-vis, see below), but the material obtained by reaction of **6** with Ru(II)(bis(pyridine))Pc **2** did not show traces of the presence of Pc molecules, neither by spectroscopic nor by thermogravimetric studies. In particular, the UV-vis of the as-prepared material did not show the typical Q band of the Ru(II)(bis(pyridine))Pc molecules, and the weight loss observed in the TGA analysis was rather similar to that observed in the precursor SWCNT-COOH **6**. Similar results were obtained when the esterification reaction with Ru(bis(pyridine))Pc **2** followed the activation of the COOH groups in **6** as acid chlorides by reaction with $SOCl_2$.

A plausible explanation for the different reactivity of the two Pcs with **6** is that the reaction with **2** is sterically hindered with regard to **1**. Considering that the COOH moieties in the pyrrolidine-SWCNT material are very close to the surface of the nanotube, the approach of Pc **2** to these COOH groups in **6** is probably hindered by the presence of the two axially-ligated pyridyl moieties. To support this hypothesis, and aiming at preparing a SWCNT functionalized with Ru(II)(bis(pyridine))Pc molecules, we prepared a modified-SWCNT by Tour reaction[26] between HiPco SWCNTs and methyl 4-aminobenzoate in isoamyl nitrite (Scheme 2). Hydrolysis of the methyl ester moiety led to SWCNT material **8**, endowed with COOH groups pointing out orthogonally to the nanotube surface. TGA analysis of **8** indicates a functionalization degree of *ca.* 1 organic addenda per 60 C atoms (15% weight loss, excluding initial weight losses due to adsorbants). Condensation reaction conditions using

EDC/HOBt were applied for the reaction between SWCNT-COOH **8** and Pc **2**, but they proved fruitless. Then, SWCNT-COOH **8** was transformed into the acid chloride derivative by reaction with $SOCl_2$ and, afterwards, it was reacted with 1.5 equivalents (with regard to the calculated carboxyphenyl-functionalization) of Ru(II)(bis(pyridine))Pc **2**. The material (i.e. **9**) obtained was characterized by TGA, IR, XPS and UV-vis.

Characterization of phthalocyanine-SWCNT hybrids

The content of Pc molecules in Pd(II)Pc-SWCNT **7** was determined by TGA analysis. An additional 8% weight loss at 700 ºC is observed in TGA when compared with that measured for SWCNT-COOH precursor **6** (see Supporting Information, Figures S1 and S2), which is directly related to the decomposition of the Pd(II)Pc molecules in Pd(II)Pc-SWCNT **7**. Considering that the thermogram of Pd(II)Pc **1** gives rise to an overall decomposition of *ca.* 80% at this temperature, a functionalization degree of *ca.* 1 Pd(II)Pc every 600 C atoms was estimated. Similarly, Ru(II)bis(pyridine)Pc-SWCNT **9** shows in TGA an additional weight loss of 4% at 600 ºC with regard to that of SWCNT-COOH **8** (see Supporting Information, Figures S3 and S4). Considering that the precursor Ru(II)(bis(pyridine))Pc **2** shows a weight loss of *ca* 70% at the same temperature, an incorporation of around 1 Ru(II)Pc every 1200 carbon atoms was calculated. Covalent functionalization of SWCNT-COOH **6** and **8** with Pcs **1** and **2**, respectively, was supported by FTIR spectroscopy. Even though the low degree of functionalization leads to rather weak signatures, a small band at 1753 cm^{-1} (in the case of **7**) and 1744 cm^{-1} (in the case of **9**) are discernible in the spectra (Figure 2), which can be assigned to C=O stretch vibrations of the ester groups. Vibrations of the unreacted COOH moieties (i.e. carboxyl groups which did not form ester bond with the corresponding hydroxyPc) appear at lower frequencies. Signatures of the Pc molecules can be discerned in the IR of **7** and **9**, but the typical vibration of C=N bonds of Pcs at 1605 cm^{-1} coincides with the C=C stretching of the nanotubes.

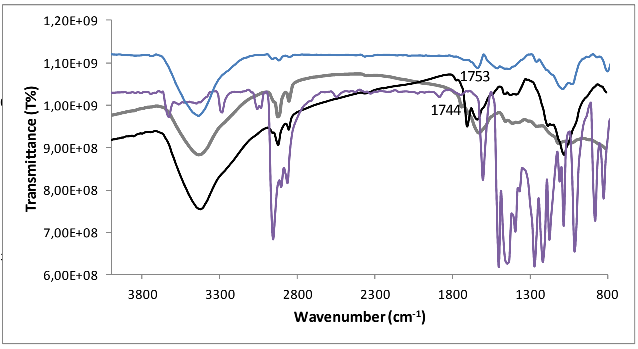

Figure 2. IR spectra of HiPCo nanotubes (blue line), Pc **1** purple line), Pd(II)Pc-SWCNT **7** (black line) and Ru(II)bis(pyridine)Pc-SWCNT **9** (grey line).

UV-vis spectrum of **7** shows the typical Q band absorption of Pd(II)Pcs, namely, a maximum at 667 nm (Figure 3a). However, Ru(II)bis(pyridine)Pc-SWCNT **9** exhibits a broadened absorption in the visible range between 610-660 nm, and a well-defined maximum at 685 nm, whereas Ru(II)(bis(pyridine))Pc **2** presents a broad Q band with a maximum at 625 nm (Figure 3b). As mentioned above, Ru(II)Pc derivatives have different absorption in the visible depending on the axial coordination. For instance, Ru(pyridyl)COPc derivatives reported in the literature[25] present narrow absorptions in the visible centered at around 680 nm. Probably, the coordination of the Ru(II)Pc molecules in **9** is somehow changed with respect to the precursor **1**, or even some degree of demetallation could happen during the reaction, but, still, it can be concluded that incorporation of Pc molecules to the surface of the SWCNT has occurred in **9**.

Evidence in support of the successful covalent functionalization between modified SWCNT-COOH materials and Pcs **1** and **2** was obtained from control experiments, in which SWCNT-COOH **6** and **8** were reacted with Pd(II)Pc **1** and Ru(bis(pyridine))Pc **2**, respectively, without adding condensation agents. In this case, the resulting SWCNT materials obtained after filtration and deep washing with several organic solvents of the crude did not show traces of the typical Q band absorptions of Pcs **6** and **8** in their UV-vis spectra. Therefore, the presence of adsorbed Pc molecules on the SWCNT surface of **7** and **9** could be ruled out.

X-ray photoelectron spectroscopy (XPS) provides a means to probe the anchorage of Pcs to the nanotube surface. XPS spectrum of nanohybrid **7** (Figure 4) shows, in addition to the signature of C 1s (284 eV), peaks at 401 eV, corresponding to N 1s, at 532 eV, corresponding to O 1s, and a small peak at 338 eV, which corresponds to the binding energy of Pd $3d_{5/2}$. Analysis of the data indicates that the ratio of the atomic concentrations of O 1s vs N 1s is higher than expected for the atomic composition of the organic addenda anchored to the SWCNTs. This can be ascribed to a partial oxidation of the SWCNT during the purification and functionalization behavior. On the other hand, XPS spectrum of Ru(II)bis(pyridine)Pc-SWCNT **9** exhibits peaks at the binding energies of N 1s and O1s, but the presence of ruthenium could not be confirmed, which can be a consequence of the low Ru(II)bis(pyridine)Pc-to-carbon content in **9**, and also to a partial overlapping of the Ru $3d_{5/2}$ peak with the C 1s signal. Even, a partial demetallation of the Ru(II)(bis(pyridine))Pc molecules during the esterification reaction with **8** could not be ruled out, which would also justify the optical behavior of **9** (see discussion above and Figure 3b).

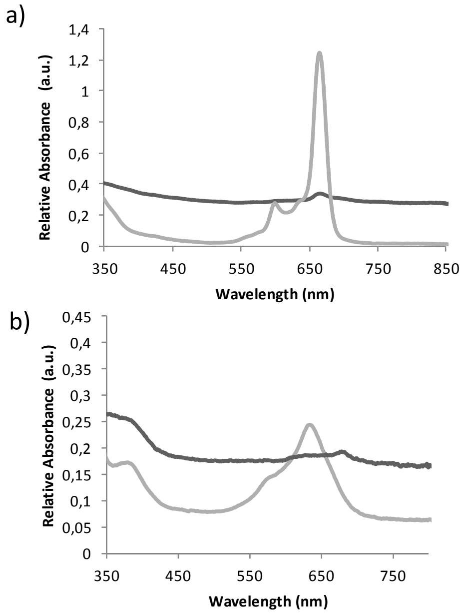

Figure 3. UV-vis spectra of a) Pd(II)Pc **1** in $CHCl_3$ (light grey line) and Pd(II)Pc-SWCNT **7** in DMF dispersion (dark grey line); and b) Ru(II)(bis(pyridine))Pc **2** in $CHCl_3$ (light grey line**)** and Ru(II)(bis(pyridine))Pc -SWCNT **9** in DMF dispersion (dark grey line).

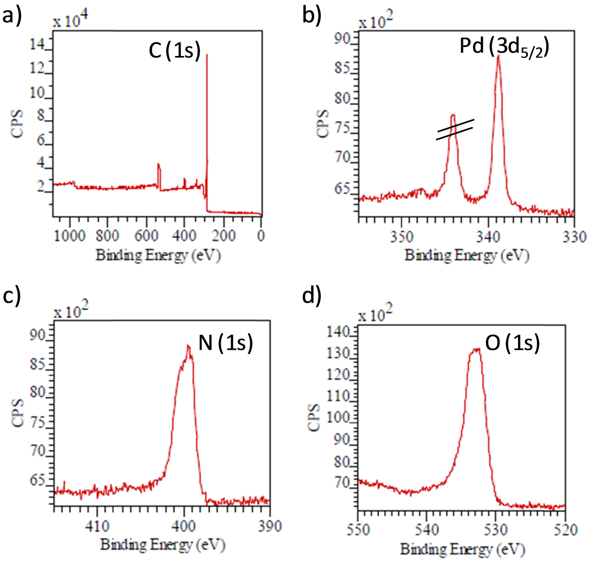

Figure 4. a) XPS spectrum (survey) of Pd(II)Pc-SWCNT **7**. Zoom into: b) 335-330 eV region (the crossed out peak corresponds to Ca impurities); c) 415-390 eV region; d) 550-220 eV region

Experimental

General:

^{1}H NMR spectra were recorded at 300 MHz at 25 °C with a BRUKER AC-300 instrument. NMR data: chemical shifts are given in parts per million, coupling constants are given in hertz. UV–Vis spectra were recorded with a JASCO V-660 spectrophotometer. Thermogravimetric analyses were performed with a thermobalance TGA Q500 TA Instrument equipped with an EGA oven at 10°C/min under N_2 (90ml/min flux). XPS measurements were carried out with a SPECS GmbH instrument, with UHV system and PHOIBOS 150 9MCD energy analyzer. Pass energy for survey acquirement = 75 eV; step energy = 1 eV. Pass energy for specific regions = 25 eV; step energy = 0.1 eV.

Materials:

HiPco SWCNTs were purchased from Carbon Nanotechnologies Inc. The rest of chemicals were purchased from Aldrich.

Synthetic procedures:

2(3),9(10),16(17)-tris-*tert*-butyl-23-(4-hydroxymethyl)phenylphthalocyaninato palladium(II) (1)

A two necked flask, equipped with refrigerant and magnetic stir bar, was charged with 4-*tert*-butylphthalonitrile (0.474 g, $2.38\cdot10^{-3}$ mol), 4-(hydroxymethyl)phthalonitrile[24] (0.200 g, $8.6\cdot10^{-4}$ mol) and 10 mL of *n*-penthanol. The mixture was heated at 100°C and, after complete dissolution of both phthalonitriles, $PdCl_2$ (0.287g, $1.62\cdot10^{-3}$ mol) and DBU (0.493 g, $3.24\cdot10^{-3}$ mol) were added and the mixture was refluxed overnight under Ar atmosphere. The solvent was evaporated under vacuum, the crude dissolved in $CHCl_3$, washed several times with water and dried with Na_2SO_4. The crude was purified on silica gel using hexane/THF (2:1) as eluent, to obtain **1** (0.20 g, 25 %). ^{1}H-NMR (300 MHz, THF-d_6), δ (ppm) = 9.7 (bs, 16 H, H-arom), 8.2-7.5 (m, 4H, H-phenyl), 4.57 (d, 2H, CH_2O), 1.74 (m, 27 H, $C(CH_3)_3$). UV-Vis ($CHCl_3$), λ_{max} (log ε): 2.84 (4.99), 331 (4.77), 599 (4.56), 636 (4.54), 665 (5.17). MS (MALDI), m/z: 892, 893, 894, 895 $[M+H]^+$.

2(3),9(10),16(17)-tri-*tert*-butyl-23-(hydroxymethyl)phenylphthalocyanine (3)

A two necked flask, equipped with a magnetic stir bar and reflux condenser, was charged with *tert*-butylphthalonitrile (0.237g, $1.29\cdot10^{-4}$ mo), 4-(hydroxymethyl)phthalonitrile[24] (0.1 g, $4.30\cdot10^{-4}$ mol,) and 10 mL of *n*-penthanol. The mixture was heated to 100°C, and, after complete dissolution of the reagents, lithium (0.011g, $1.58\cdot10^{-4}$ mol) was added and then the temperature was brought to reflux. The reaction was left refluxing overnight under Ar atmosphere. After cooling, the solvent was evaporated and the crude was dissolved in 100 mL of $CHCl_3$ and washed several times with H_2O. The crude was purified on silica gel using as eluent a mixture of hexane/THF (2:1). The second band contained the desired Pc **3** (0.075 g, 22%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.5-9.2 (broad signal, 16 H, H-arom), 4.94 (d, 2H, CH_2O), 1.85 (m, 27 H, $C(CH_3)_3$). UV/Vis ($CHCl_3$), λ_{max} (log ε): 706 (5.1), 672 (5.1), 647 (4.6), 611 (4.4), 348 (4.8). MS (MALDI), m/z: 789 $[M+H^+]$.

2(3),9(10),16(17)-tri-*tert*-butyl-23-(4-*tert*-butyldiphenylsilyloxymethyl)phenylphthalocyanine (4)

3 (0.050 g, $6.34\cdot10^{-5}$ mol) was dissolved in 10 mL of dry DMF, then imidazole ($9.4\cdot10^{-3}$ g, $1.39\cdot10^{-4}$ mol) was added followed by *tert*-butyldiphenylsilyl chloride (0.038g, $1.39\cdot10^{-4}$ mol). The reaction was stirred until completion (followed by TLC). Solvent was removed under vacuum, the crude was diluted with CH_2Cl_2 and washed several times with water followed by brine. The organic layer was dried (Mg_2SO_4) and concentrated under vacuum. The resulting residue was purified by flash chromatography (SiO_2) using CH_2Cl_2 as eluent, to give **4** (0.057 g, 87%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm) = 7.5-9.2 (broad signal, 26 H, H-arom), 5.11 (d, 2H, CH_2O), 1.85 (m, 27 H, $C(CH_3)_3$), 1.34 (m, 9 H, $C(CH_3)_3$-Si). UV/Vis ($CHCl_3$), λ_{max} (log ε): 704 (5.1), 669 (5.1), 645 (4.6), 609 (4.4), 349 (4.8). MS (MALDI), m/z: 1027 [M + H^+].

Bis(pyridine)-2(3),9(10),16(17)-tri-*tert*-butyl-23-(4-*tert*-butyldiphenylsilyloxymethyl)phenylphthalocyaninato]ruthenium(II) (5).

A 10 mL flask, equipped with magnetic stir bar and reflux condenser, was charged with **4** (0.037 g, $3.60\cdot10^{-5}$ mol), $Ru_3(CO)_{12}$ (0.046 g, $7.20\cdot10^{-5}$ mol) and 5 mL of benzonitrile. The mixture was heated to 240°C under Ar atmosphere and refluxed overnight. After removing the solvent, the crude was purified by flash chromatography, eluting firstly with toluene to remove the last tracks of benzonitrile, and then using hexane/THF (2:1), to obtain 0.033 g of product. ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm) = 9.42 (m, 1H), 9.32 (m, 2H), 9.13 (m, 2H), 8.11 (m, 1H), 8.08 (m, 1H), 8.02 (m, 2H), 7.82 (m, 3H), 7.65 (m, 2H), 7.45 (m, 6H), 7.15 (m, 6H), 6.85 (m, 2H), 6.51 (m, 4H), 5.65 (m, 4H), 4.97 (m, 2H, CH_2O), 1.75 (m, 27 H, $C(CH_3)_3$), 1.18 (m, 9 H, $C(CH_3)_3$). To this product dissolved in 8 mL of CH_2Cl_2, pyridine (0.0063 mL) was added and the mixture was refluxed for 4 h. The solvent was evaporated and the residue obtained was washed with methanol and filtered to obtain **5** (0.03 g, 68%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm) = 9.42 (m, 1H), 9.22 (m, 2H), 9.06 (m, 2H), 8.15 (m, 1H), 8.06 (m, 1H), 7.97 (m, 2H), 7.82 (m, 3H), 7.64 (m, 2H), 7.48 (m, 6H), 7.15 (m, 6H), 6.03 (m, 2H), 5.23 (m, 4H), 4.97 (s, 2H, CH_2O), 2.50 (m, 4H), 1.75 (m, 27 H, $C(CH_3)_3$), 1.20 (m, 9 H, $C(CH_3)_3$). UV/Vis ($CHCl_3$), λ_{max} (log ε): 318 (5.00), 383 (4.32), 575 (4.32), 625 (4.80). MS (MALDI), m/z: 1127, 1128, 1129, 1130 $[M-(2Py)+H]^+$.

Bis(pyridine)-2(3),9(10),16(17)-tri-*tert*-butyl-23-(4-hydroxymethyl)phenylphthalocyaninato ruthenium(II) (2)

5 (0.053 g, $4.12\cdot10^{-5}$ mol) was dissolved in THF (~2 M), then the solution was cooled to 0°C and deoxygenated. A solution of tetrabutylamonium chloride (6.18 µL, 1 M in THF) was added dropwise. The mixture was left to warm to room temperature and stirred for 3 h. The solvent was removed under vacuum and the crude was purified by flash chromatography using hexane/THF (1:1) as eluent, to obtain **2** (0.04 g, 93%). ^{1}H-NMR: (300 MHz, $CDCl_3$), δ (ppm) = 9.37 (m, 1H), 9.15 (m, 2H), 9.04 (m, 2H), 8.08 (m, 2H), 7.95 (m, 2H), 7.67 (m, 3H), 7.31 (m, 4H), 6.04 (m, 2H), 5.24 (m, 4H), 4.90 (s, 2H, CH_2O), 2.52 (m, 4H), 1.75 (m, 27 H, $C(CH_3)_3$). UV/Vis ($CHCl_3$), λmax (log ε): 319 (5.10), 379 (4.68), 577 (4.61), 625 (4.87). MS (MALDI), m/z: m/z: 889, 890, 891, 892 $[M-(2Py)+H]^+$.

SWCNT-COOH (6) (through Prato reaction)

HiPco nanotubes (0.040 g) were sonicated for 15 min in 40 mL of *o*-DCB. 4-Formylbenzoic acid (0.64 g, 1.3 eq) was added to the suspension, and the mixture was heated to 180 °C. Then, *N*-methylglycine (0.36 g, 1.3 eq) was added in portions (4 x 0.090 g every 24 h), and the reaction was stopped after 5 days. The crude was filtered over a PTFE (0.45 µm) membrane to separate the carbon-based material, which was subsequently sonicated in DMF and centrifugated. The supernatant was separated, and the solid residue was re-suspended in DMF, filtered again and washed consecutively with $CHCl_3$, ethyl acetate, acetone, acetonitrile, methanol, and diethyl ether and then dried overnight in a vacuum oven at 55 °C to obtain 0.045 g of **6**.

Pd(II)Pc-SWCNT (7)

Pd(II)Pc **1** (0.015 g, $8.5\cdot10^{-6}$ mol, 2.2 eq) and EDC (0.00135 g, $8.5\cdot10^{-6}$ mol, 2.2 eq) were dissolved in 5 mL of dry THF. To this solution was added HOBt (0.0015 g, $8.5\cdot10^{-6}$ mol, 2.2 eq). Subsequently, a suspension of COOH-SWCNTs **6** (0.005 g) in dry DMF (4 mL) was added, and the resulting mixture was stirred for 4 days. Then, the paste was sonicated and filtered through a PTFE (0.45 µm) membrane. The solid was washed with DMF until the filtrate became colorless, then with water, methanol, acetone and ether. The product was dried overnight in a vacuum oven at 55°C to obtain 0.015 g of **6**.

SWNT-COOH (8) (through Tour reaction)

HiPco nanotubes (0.006 g, $5.0\cdot10^{-4}$ mol of carbon) and methyl 4-aminobenzoate (0.302g, $2.0\cdot10^{-3}$ mol, 4 eq) were added to flask equipped with a reflux condenser and a magnetic stir bar. After slow addition of isoamyl nitrite (0.32 mL, 0.0024 mol, 4.8 eq) through a syringe, the paste was heated to 60 °C under Ar atmosphere and vigorous stirring. After 3 h, the paste was diluted with DMF, sonicated and filtered through a PTFE (0.45 µm) membrane. The solid was washed with DMF until the filtrate became colorless, then with water, acetone and ether. The obtained SWNT-COOMe (0.007 g) was sonicated in 30 mL of $NaOH_{(aq)}$ 0.5 M for 1h, and then the suspension was refluxed for 24 h. After cooling, the pH of the mixture was brought to pH 2 using a solution of $HCl_{(aq)}$ 1 M. The acidic mixture was sonicated for 10 m and filtered on PTFE (0.45 µm). The solid was washed several times with DMF, THF, EtOAc, $CHCl_3$, H_2O, acetone and Et_2O, and dried overnight in a vacuum oven at 55°C to obtain 0.007 g of **8**.

Ru(bis(pyridine)Pc-SWCNT (9)

A 10 mL flask, equipped with magnetic stir bar, was charged with SWCNT-COOH **8** (0.005 g) and 0.5 mL of DMF. The suspension was sonicated for 30 min, cooled to 0°C and then $SOCl_2$ (1,5 mL) was added dropwise. The reaction mixture was heated to 70°C and stirred for 24 h. After cooling down, the suspension was centrifuged and the yellow supernatant was eliminated. The solid was re-dispersed in dry THF, sonicated, centrifuged and the supernatant was decanted, this operation being repeated until a colorless supernatant was obtained. The solid was filtered and dried to obtain 0.005 g of SWCNT-COCl, which was then re-dispersed in 6 mL of dry THF after sonication for 10 m. This suspension was added to 3 mL of RuPcOH solution (0.009 g, $9\cdot10^{-6}$ mol, 1,5 eq) in dry THF. The mixture was refluxed under Ar atmosphere for four days, then the paste was sonicated and filtered through a PTFE (0.45 µm) membrane. The solid was washed with DMF until the filtrate became colorless, then with THF, water, methanol, acetone and ether. The solid was dried overnight in a vacuum oven at 55°C to obtain 0.005 g of solid.

Conclusions

We have succeeded on the preparation of new Pc-SWCNT hybrid materials. The synthesis of Pd(II)Pc-SWCNT **7** proceeded smoothly by esterification reaction between modified SWCNT **6** and the hydroxymethyl-containing Pd(II)Pc **1**, using classical condensation conditions. The hybrid material has been fully characterized. However, the incorporation of Ru(II)(bis(pyridine))Pc **2** did not take place when applying the above mentioned approach. The preparation of SWCNT **8** endowed with 4-carboxyphenyl moieties was found to be essential to succeed in the covalent linkage of Ru(bis(pyridine))Pc **2** by ester-bond formation. Spectroscopic characterization supports the covalent binding of Pc molecules to the modified SWCNT sidewalls, but direct evidence of the presence of Ru in the hybrid material could not be obtained.

Notes and references

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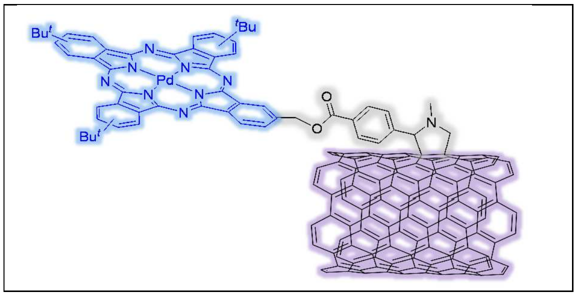

The preparation of novel, covalent Pd(II)-SWCNT and Ru(II)(bipyridyl)Pc-SWCNT hybrid materials by means of two-step synthetic procedures is described.