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Efficient Cycloaddition of Arynes to Carbon Nanotubes under Microwave Irradiation

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Abstract:

We report herein the functionalization of single-wall carbon nanotubes (SWCNT) by cycloaddition reactions with arynes under microwave irradiation. The efficiency of the functionalization was monitored by XPS, FTIR and Raman spectroscopies and also TGA analysis. All experimental results point to the formation of SWCNT with a high degree of functionalization, with mass increases ranging from 6.4% to 15.1% depending on the aryne substitution.

Keywords: arynes; single-wall carbon nanotubes; cycloaddition; microwave irradiation

1. Introduction

Carbon nanotubes (CNT) are amongst the most studied nano-materials for their application in numerous fields [1,2] as a result of their unique mechanical [3], thermal [4], and electronic [5,6] and optical [7,8] properties. However, the lack of solubility of CNT in many common solvents limits the exploration of their potential applications. For this reason, it is important to investigate new procedures to functionalize these materials [9-13] in order to improve their solubility and their processability. Furthermore, functionalization can modify the physical properties of CNT and thus expand their potential applications.

In general, functionalization reactions on CNT are very slow and take several days to proceed. However, when carbon nanotubes are exposed to microwave irradiation, strong absorptions are observed, and these produce intense heating and light emission[14]. This strong absorption can be used to assist in the functionalization of CNT [15-17]. Our research group has significant experience in the functionalization of these materials through different kinds of reactions, including Diels–Alder reaction [18] and 1,3-dipolar cycloaddition involving nitrile oxides [19]. It is known in organic chemistry that certain reactions can be microwave-assisted to improve selectivity and reduce reaction times, in comparison to similar syntheses based on conventional heating. In general, the reactions conditions applied to CNT under microwave irradiation are similar to those used under classical heating, but higher levels of

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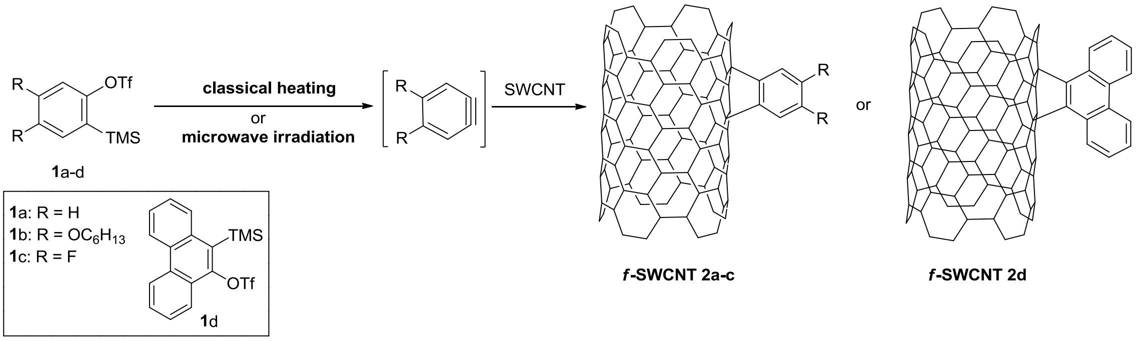
functionalization and shorter reaction times are achieved in comparison to classical heating [20, 21].

Arynes are very reactive intermediates that can react with unsaturated species such as alkenes, dienes and aromatic compounds by [2+2] or [4+2] cycloadditions [22-24]. It therefore seemed reasonable to expect that aryne cycloadditions could be used to functionalize CNT. In fact, it was proposed that these reactions could be used to modify the electronic properties of CNT [25] and to prepare molecular gears [26-28], but these proposals were not tested experimentally. Dyke and Tour attempted the reaction of CNT with benzyne, generated under solvent-free conditions either from benzenediazonium 2-carboxylate or *o*-(trimethylsilyl)phenyl trifluoromethanesulfonate, but met with limited success [29]. We recently reported appropriate conditions for these functionalization reactions [30] and the aim of this paper is to present a complete study of this reaction, in which the microwave methodology was used as a source of energy and to extend the scope of this type of functionalization to other benzynes. A comparative study was carried out into the cycloaddition reactions between arynes and carbon nanotubes using classical heating and microwave activation. This novel functionalization of SWCNT allows a variety of substituents to be introduced into the structure of the benzene ring and leads to increased solubility of functionalized SWCNT (*f*-SWCNT). The reaction products were characterized by several spectroscopic, analytical and microscopic techniques.

2. Results and Discussion

Pristine SWCNT were functionalized by cycloaddition using different arynes under microwave irradiation and classical heating (Scheme 1). The corresponding arynes were generated by fluoride induced elimination of TMS and triflate from 2-(trimethylsilyl)aryl triflate **1**(**a**–**d**). Under classical heating, a solution of **1a**–**d** in acetonitrile (CH_3CN) was added to a suspension of SWCNT in *o*-dichlorobenzene (ODCB) under Ar. 18-Crown-6 ether and dry CsF were then added and the mixture was heated under reflux for 12 hours. The resulting suspension was filtered through a PTFE filter (0.2 μm pore size) and washed with H_2O and hexane. The solid was purified by washing several times with Et_2O, DMF, H_2O and MeOH to afford *f*-SWCNT **2a**–**d**.



Scheme 1. Chemical cycloaddition of arynes to SWCNT. *Classical heating*: CsF, 16-crown-8, ODCB/CH_3CN 70 ºC, 12h; *Microwave irradiation*: CsF, 18-crown-6, ODCB/CH_3CN, 120 ºC, 15 min, 5W.

The reaction time was reduced from 12 hours to only 15 minutes in all cases by following the same procedure but with microwave irradiation as the energy source (see Scheme 1). The reactions were carried out in a CEM focused microwave reactor, model Discover, in a closed quartz tube with control of pressure.

X-ray photoelectron spectroscopy (XPS) was used to provide evidence for the formation of *f*-SWCNT by identifying and quantifying the functional groups anchored to the surface [33,34]. As the XP survey scan is an effective way to determine the identity of elements present on the surface of a material, wide energy scans were recorded for the *pristine* SWCNT and *f*-SWCNT samples prepared under both methodologies, classical heating and microwave irradiation to give approximate relative ratios of the elements detected (Table 1 and 2).

Tables 1 and **2.** C1s, O1s and F1s core-level spectra of *pristine* SWCNT and *f*-SWCNT **2a-d**, (upper panel) under microwave irradiation and (bottom panel) under classical conditions. In parentheses are peak percentages.

Sample	**BE (eV) C1s (%)**						**BE (eV) O1s (%)**		**BE (eV) F1s (%)**
	sp^2 C	**sp^3 C**	**C-O**	**C=O**	**COO/C-F**	**π-π***	**O=C**	**O-C**	
***pristine* SWCNT**	284.8 (64)	-	286.3 (23)	287.7 (3)	289.2 (6)	291.3 (4)	532.3 (77)	533.6 (23)	
***f*-SWCNT 2a**	284.8 (67)	-	286.2 (17)	287.7 (5)	289.2 (5)	291.2 (6)	532.3 (79)	533.6 (21)	
***f*-SWCNT 2b**	284.8 (58)	285.5 (11)	286.3 (21)	287.7 (4)	289.2 (4)	291.2 (2)	532.1 (82)	533.3 (18)	
***f*-SWCNT 2c**	284.8 (59)	-	286.3 (23)	287.7 (9)	289.2 (4)	291.3 (5)	532.1 (74)	533.8 (26)	688.3
***f*-SWCNT 2d**	284.8 (81)	-	286.2 (11)	287.7 (1)	289.2 (2)	291.4 (5)	532.2 (69)	533.8 (31)	

Sample	**BE (eV) C1s (%)**						**BE (eV) O1s (%)**		**BE (eV) F1s (%)**
	sp^2 C	**sp^3 C**	**C-O**	**C=O**	**COO/C-F**	**π-π***	**O=C**	**O-C**	
***pristine* SWCNT**	284.8 (64)	-	286.3 (23)	287.7 (3)	289.2 (6)	291.3 (4)	532.3 (77)	533.6 (23)	
***f*-SWCNT 2a**	284.8 (78)	-	286.3 (14)	287.9 (3)	-	291.3 (5)	531.3 (29)	533.3 (71)	
***f*-SWCNT 2b**	284.8 (55)	285.5 (4)	286.6 (23)	288.1 (18)	-	-	531.3 (44)	532.9 (56)	
***f*-SWCNT 2c**	284.8 (50)	-	286.1 (30)	287.5 (16)	289.7 (4)	-	531.4 (30)	533.4 (70)	689.6
***f*-SWCNT 2d**	284.8 (71)	-	286.3 (18)	287.8 (7)	-	291.3 (4)	531.6 (27)	533.3 (73)	

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For all the samples, high-resolution C 1s, O 1s and F 1s core-level spectra were recorded and the corresponding binding energies are collected in Table 1 and 2. The C 1s, O 1s and F 1s spectra of a representative *f*-SWCNT sample **2c,** prepared under microwave irradiation, are displayed in Fig. 1(a–c), respectively. The C 1s peak was satisfactorily curve-resolved with six components (Figure 1a) according to the peak assignment used by Stankovich et al. [35] The most intense peak, at 284.8 eV, is assigned to sp^2 C-atoms of the graphene structure. This peak, together with the weak $\pi \rightarrow \pi^*$ plasmon component at 291.3 eV, is indicative of the nanotube structure. The component at 286.3 eV is often assigned to C–OH, and the components at 287.7 and 289.2 eV to C=O and –COO– species, respectively [36]. Moreover, the C 1s line profile of the *f*-SWCNT **2b** sample exhibited an additional weak component at 285.5 eV associated with sp^3 C–C bonds from the alkyl substituent.

Similarly, the O 1s spectrum was curve-resolved with two components (Fig. 1b). The main component at 532.1 eV corresponds to O=C surface groups and the minor one at 533.8 eV is often associated with the O–C bond [36] thus demonstrating the existence of oxygen functional groups. The high-resolution F 1s spectrum (Fig. 1c) displays a single component at a binding energy of 688.3 eV and this belongs to F–C bonds in the benzene ring and not to $–CF_2$ and/or CF_3 moieties [37].

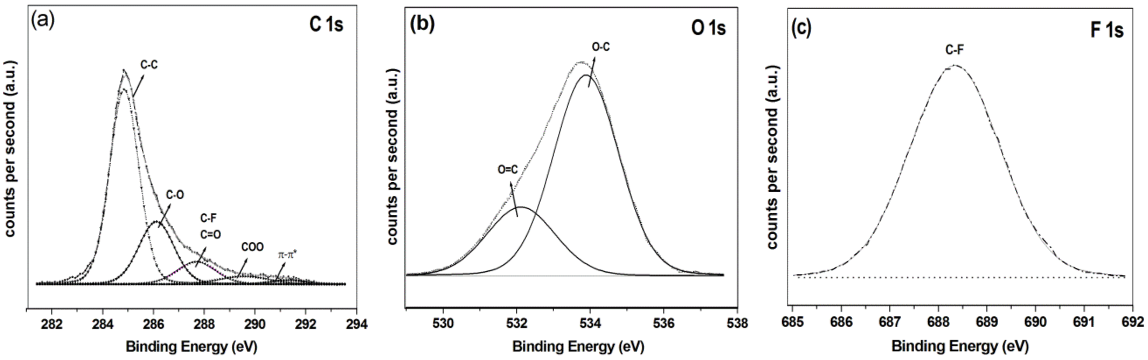

Fig. 1. XPS high-resolution C 1s (a), O 1s (b) and F 1s (c) spectra of *f*-SWCNT **2c,** prepared under microwave irradiation.

Surface atomic percentages of elements were also been calculated from XPS spectra. The atomic percentage of C, O and F atoms for *pristine* SWCNT and *f*-SWCNT samples **2a**–**d** are summarized in Table 3. It can be seen that the *pristine* SWCNT sample has the highest O-content. This is due to the silica impurities present in the original sample. In the survey spectrum of *pristine* SWCNT, the Si 2p and Si 2s core level spectra are a little more intense than in the functionalized samples. As Si 2s level is less intense than the Si 2p, the former practically is not detected in functionalized samples. It can be also taken into account that the photoelectron cross section of silicon atom is about 2.5 times lower than that of oxygen and that there are two O-atoms per Si-atom in silica, a small Si 2p (or Si 2s) signal adds significantly to O 1s signal. In other hand, the slight drop in O-content observed in SWCNT sample after microwave irradiation can be explained in terms of: (i), loss of some COOH functional groups under microwave heating and/or (ii), by discounting the contribution of O-atoms coming from the SiO_2 impurity detected. While type (i) contribution is operative, type (ii) contribution cannot be discarded because the high resolution Si 2p spectrum displayed measurable intensity and obviously twice O atoms per Si atom contribute to the O 1s envelop. Although are cases in which the binding energy of O1s peak of an oxide impurity is substantially lower than that coming from C-O/C=O bonds and therefore peak fitting procedures allows separate components, it is not the case in the present work because the BE of O1s in SiO_2 falls somewhere around 532.7 eV which is just the same than recorded from covalent C-O/CO bond from SWCNT. Due to the similarity of the BE values of the two O1s contributions our realistic approach was to subtract twice the Si atoms (O coming from SiO_2, O/Si = 2) from the total O atoms. Interestingly, comparison of the results for *f*-SWCNT **2b** and the other functionalized counterparts shows that the O-content is higher (6.6% at under classical conditions and 5.9% at under microwave irradiation) in the former. This result represents indirect evidence for the efficient SWCNT sidewall anchorage of OR moieties.

Table 3. Comparative study of surface atomic composition of *pristine* SWCNT and *f*-SWCNT **2a–d,** prepared under classical heating and microwave irradiation.

Sample	C (%at)		O (%at)		F (%at)	
	classical heating	microwave irradiation	classical heating	microwave irradiation	classical heating	microwave irradiation
pristine SWCNT[a]	90.3	93.8	7.0	4.5	-	-
f-SWCNT **2a**	96.7	96.4	3.3	3.6	-	-
f-SWCNT **2b**	93.4	94.1	6.6	5.9	-	-
f-SWCNT **2c**	91.3	90.8	4.9	4.2	3.8	5.0
f-SWCNT **2d**	95.9	97.7	4.1	2.3	-	-

[a] *pristine* SWCNT shows besides the C and O emissions, those of Si due to impurities (2.7% before microwave irradiation and 1.7% after microwave irradiation).

Raman spectroscopy provided important information concerning the covalent modification of the CNT [38-40]. In the Raman scattering spectra, important data related to the characteristics of nanotubes could be obtained from the disorder mode (*D-band*) at ~1340 cm^{-1} and the tangential mode (*G-band*) at ~1570 cm^{-1}. Generally, the intensity of the D-band relative to that of the G-band (I_D/I_G) can be used as an indicator to estimate the extent of functionalization onto the nanotube surface. In this case, this technique allowed us to confirm the functionalization of the sidewall of the SWCNT through the cycloaddition of *o*-benzynes. The spectra of the functionalized materials (*f*-SWCNT **2a–d**) exhibited an increased intensity of the D-band, indicating functionalization of SWCNT since functional groups introduce sp^3 defects in the sp^2 network of the nanotube (Fig. 2, excitation at 785 nm). It can also be observed in Fig. 2 that the I_D/I_G ratio is enhanced as the extent of SWCNT functionalization is increased. Indeed, for samples **2c** (Fig. 2) and **2d** (see Table 4) a high degree of functionalization was obtained on applying microwave energy.

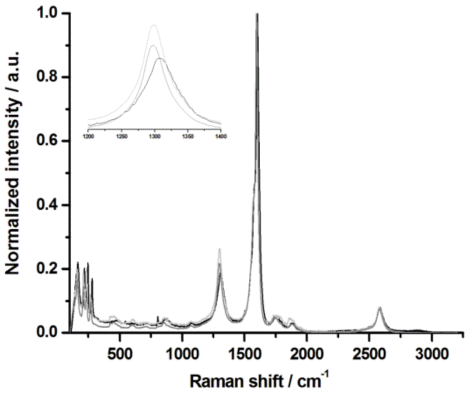

Fig. 2. Normalized Raman spectra (785 nm) of *pristine* SWCNT (black line) and *f*-SWCNT sample **2c** under classical heating (gray line) and microwave irradiation (light gray line). In the inset, the magnified D-band region.

Additionally, radial breathing modes (RBMs) have frequencies that are inversely proportional to the tube diameter and these provide an indication of the diameter distribution in a given sample [41]. It is important to note the changes observed in the RBM zone of *functionalized* samples **2a**–**d**. Recently, Lefrant et al.[42] demonstrated that functionalization of SWCNT not only causes changes in the D/G intensity ratio but, notably, modifications are observed in RBM intensities; these authors found a down shift of RBM frequencies after functionalization as a result of charge transfer, as may occur in doped systems. In our case, a down shift of ~ 6–18 cm^{-1} in the RBM frequencies was observed after functionalization for each sample **2a**–**d**, regardless of the source of energy used. As a representative example, the RBM zone of *f*-SWCNT **2d**, prepared by both methods (classical heating and microwave irradiation), is shown in Fig. 3 along with that of the *pristine* SWCNT, with a downshift observed at all frequencies. In addition, the decrease in peak intensity is more marked for carbon nanotubes functionalized using microwave activation (light gray line), a finding consistent with the TGA results (see Table 4).

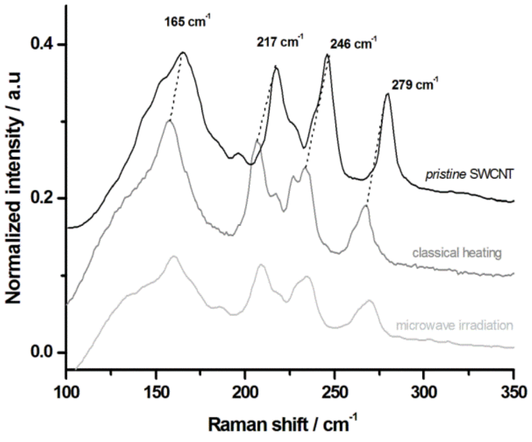

Fig. 3. Detailed normalized RBM region of the Raman spectra (785 nm) of *pristine* SWCNT (black line) and *f*-SWCNT **2d** [gray line (under classical heating) and light gray line (using microwave irradiation)].

The degree of functionalization and therefore the number of organic groups in the *f*-SWCNT, was calculated from the results of thermogravimetric analysis (TGA) under flowing N$_2$ (ΔT=10 ºC.min^{-1}) (see Table 4). For *f*-SWCNT **2a**–**d** the weight losses between 200 and 650 ºC are the steepest and these are due to the expected organic decomposition. Under classical conditions, weight losses of around 12.3% for *pristine* SWCNT, 21.3% for **2a**, 27.4% for **2b**, 18.7% for **2c** and 23.2% for **2d** were observed at 650ºC. The weight loss observed for *pristine* SWCNT between 100 and 650 °C may be due to the destruction of residual amorphous carbon still present in the carbon nanotubes and to decarboxylation of the oxidized species (supported by XPS data). The corrected weight losses due to the functional groups on nanotubes (weight losses difference of **2a** – *pristine* SWCNT, **2b** - pristine SWCNT, **2c** – *pristine* SWCNT and **2d** – *pristine* SWCNT) were then estimated to be 9% for *f*-SWCNT **2a**, 15.1% for *f*-SWCNT **2b**, 6.4% for *f*-SWCNT **2c** and 10.9% for *f*-SWCNT **2d**. From these results, the degrees of functionalization can be estimated as one functional group for every ~ 64 (**2a**), 130 (**2b**), 136 (**2c**) and 120 (**2d**) carbon atoms, respectively.

When the reaction takes place under microwave irradiation, some changes are observed. In the case of *f*-SWCNT **2c** and **2d** (see Table 4), higher degrees of functionalization are observed in the materials produced with microwave activation in comparison with the same *f*-SWCNT obtained under classical heating. This finding is in good agreement with the results observed in the Raman spectra. A comparative study of the functionalization of samples **2a**–**d**, prepared by both classical heating and microwave irradiation, can be made from the results in Table 4. It should be considered that aryne precursors can lead to complex mixtures of byproducts, although we have no evidences of the formation of aryne-based polymers. These mixtures are soluble in solvents such as DCM (used to wash functionalized CNTs). So, it is plausibly that some byproducts from aryne precursor **1d** aggregate with CNTs by π-stacking due to the extended aromatic core of this polycyclic aryne compare to monocyclic arynes. This fact could lead to a less efficient purification step in this particular case and it could explain in some extension the discrepancy found between TGA and the Raman data for **2d**.

Table 4. Comparative study of the degree of functionalization of samples **2a**–**d.**

Sample	[a]**TGA weight loss (%)**		[b]**Functional group coverage**		[c, d] **Raman D/G ratio**	
	classical heating	microwave irradiation	classical heating	microwave irradiation	classical heating	microwave irradiation
f-SWCNT **2a**	9	5.3	64	114	0.30	0.27
f-SWCNT **2b**	15.1	15.3	130	127	0.30	0.31

f-SWCNT **2c**	6.4	12.5	136	65	0.21	0.26
f-SWCNT **2d**	10.9	19.3	120	61	0.19	0.27

[a] TGA results show relative weight loss. [b] Number of carbon atoms per functional group [c] Calculated D/G ratios from Raman spectra. [d] Raman D/G ratio for *pristine* SWCNT = 0.16

In order to fully characterize the functionalized SWCNT, we also measured the Fourier-Transform Infrared Spectra (FTIR) of *f*-SWCNT samples **2a**–**d**, and the most characteristic features were observed in each case. All samples present a common signal for the C=C stretching vibration at 1620 cm^{-1}, due to the incorporation of the benzene ring onto the sidewall of SWCNT. In the case of *f*-SWCNT **2b**, intense peaks at ~ 2850 and 2910 cm^{-1} (C–H stretch vibrations) were also observed due to the alkyl chains. In the case of fluorinated *f*-SWCNT **2c** an intense peak at 1208 cm^{-1} is correlated to the characteristic C–F stretching vibrations. Finally, for functionalized sample **2d**, a band at ~ 1400 cm^{-1} was observed and this can be attributed to C–H bending vibrations. These results suggest the presence of the benzyne moiety onto the sidewall of the SWCNT.

3. Conclusion

SWCNT can be efficiently functionalized by cycloaddition reactions with arynes under microwave irradiation, as proven by XPS, FTIR and Raman spectroscopies and TGA analysis. All experimental results point to the formation of SWCNT with a high degree of functionalization, with mass increases ranging from 5.3 to 19.3% depending on the aryne substitution.

4. Experimental

4.1. Chemicals

All reactions were carried out under argon using oven-dried glassware. Aryne precursors 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1a) [31], 4,5-bis(hexyloxy)-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1b) [30], 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1c) [31] and 10-(trimethylsilyl)phenanthren-9-yl trifluoromethanesulfonate (1d) [31] were prepared by previously reported synthetic procedures and showed identical spectroscopic properties to those reported therein. Single-wall carbon nanotubes (SWCNT), prepared by a CCVD process, were purchased from Nanocyl (www.nanocyl.com). Commercial reagents and anhydrous solvents were purchased from ABCR GmbH, Aldrich Chemical Co., or Strem Chemicals Inc., and were used without further purification.

4.2. Sample characterization

Microwave irradiations were carried out in a CEM Discover reactor, with fiber optic temperature and pressure control, stirring, and air-cooling option. IR spectrum was taken using a FT-IR AVATAR 370 Thermo Nicolet spectrometer in the 4000-400 cm^{-1} frequency range, using powdered samples diluted in KBr pellets. Raman spectra were recorded at room temperature using a Renishaw in Via Raman microscope equipped with a CCD camera and a Leica microscope. As an excitation source HPNIR 785 laser were used. Measurements were taken with 10 seconds of exposure times at varying number of accumulations. The laser spot was focused on the sample surface using a long working distance 50x and 100x objectives. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. All spectra were recorded on solid samples over several regions and were referenced to the silicon line at 520 cm^{-1}. The data was collected and analysed with Renishaw Wire and Origin software. X-ray photoelectron spectroscopy measurements were performed using a VG Escalab 200R electron spectrometer equipped with a Mg Kα x-rays ($h.\nu$ = 1253.6 eV) source and a spherical section analyzer. The instrument has five element multichannel detectors. The X-ray beam used was a 120 W, 240 µm diameter beam. The X-ray beam was incident normal to the sample and the photoelectron detector was at 45° off-normal. Wide scan data were collected using pass energy of 100 eV whereas high energy resolution spectra were recorded using pass energy of 20 eV. As the samples experienced variable degrees of charging the binding energy scale was referenced using the C1s line at 284.8 eV. The samples were analyzed after a base pressure of 2×10^{-9} mbar was reached within the analysis camber. Data processing was performed with the "*XPS peak*" program. The spectra were decomposed with the least squares fitting routine provided with the software, with Gauss/Lorentz lines (90G/10L) and after subtracting a Shirley background. Atomic ratios were calculated from the peak areas using sensitivity factors provided with the data system and background subtraction. The thermogravimetric analyses was performed using a TGA Q500 instrument by TA Instrument and in a TGA/DSC Linea Excellent instrument by Mettler-Toledo, an inert atmosphere of nitrogen, with a rate of 10ºC min^{-1}, and the weight changes were recorded as a function of temperature.

4.3. General procedures for functionalization of SWCNT with arynes

Procedure (A) (classical conditions): To a suspension under argon of SWCNT in ODCB (20 mL) was added a solution of 2-(trimethylsilyl)aryl trifluoromethanesulfonate **1a**–**d** in CH_3CN (10 mL). 18-Crown-6 ether and dry CsF were added and the mixture was heated under reflux overnight. The resulting suspension was filtered (filter from Omnipore Membrane, PTFE, filter type 0.2 µm, diameter: 47 mm) and the solid was washed with H_2O and hexane. The solid was purified by washing several times with Et_2O, DMF, and MeOH to afford *f*-SWCNT **2a**–**d**.

f-SWCNT **2a** and **2b** were prepared as previously described [30].

f-SWCNT **2c:** From *pristine* **SWCNT** (10 mg), **1c** (1.113 g, 3,33 mmol), 18-crown-6 ether (791 mg, 2.99 mmol) and dry CsF (1.514 mg, 9.96 mmol) to afford compound *f*-SWCNT **2c** (22 mg).

f-SWCNT **2d:** From *pristine* **SWCNT** (10 mg), **1d** (1.321 g, 3.32 mmol), 18-crown-6 ether (791 mg, 2.99 mmol) and dry CsF (1.514 mg, 9.96 mmol) to afford compound *f*-SWCNT **2d** (76 mg).

Procedure (B) (microwave irradiation): To a suspension of SWCNT in ODCB in a microwave glass vessel under argon was added a solution of 2-(trimethylsilyl)aryl trifluoromethanesulfonate **1a**–**d** in CH_3CN was added. 18-Crown-6 ether and dry CsF were added and the vessel was placed in the microwave reactor. The initial power was 5 W, the preselected temperature was set at 120 ºC and the reaction time at 15 minutes (ramp time: 5 minutes + hold time: 10 minutes). The resulting suspension was filtered (filter from Omnipore Membrane, PTFE, filter type 0.2 µm, diameter: 47 mm) and the solid was washed with H_2O and hexane. The solid was purified by washing several times with Et_2O, DMF and MeOH to afford *f*-SWCNT **2a**–**d**.

f-SWCNT **2a**: According to the procedure B, from *pristine* **SWCNT** (10 mg), ODCB (20 mL), **1a** (1.00 g, 3.36 mmol), CH_3CN (10 mL), 18-crown-6 ether (798 mg, 3.02 mmol) and dry CsF (1.5 mg, 10.08 mmol) to afford *f*-SWCNT **2a** (23 mg).

f-SWCNT **2b:** According to the procedure B, from *pristine* **SWCNT** (5.75 mg), ODCB (11.5 mL), **1b** (450 mg, 0.56 mmol), CH_3CN (5.75 mL), 18-crown-6 ether (460 mg, 1.70 mmol) and CsF (414 mg, 2.72 mmol) to afford *f*-SWCNT **2b** (7.4 mg).

f-SWCNT **2c:** According to the procedure B, from *pristine* **SWCNT** (10 mg), ODCB (20 mL), **1c** (1.12 g, 3.35 mmol), CH_3CN (10 mL), 18-crown-6 ether (798 mg, 3.02 mmol) and CsF (1.5 mg, 10.08 mmol) to afford *f*-SWCNT **2c** (17 mg).

f-SWCNT **2d:** According to the procedure B, from *pristine* **SWCNT** (7.5 mg), ODCB (15 mL), **1d** (1 g, 2.51 mmol), CH_3CN (7.5 mL), 18-crown-6 ether (600 mg, 2.27 mmol) and CsF (1.149 g, 756 mmol) to afford *f*-SWCNT **2d** (15 mg).

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