

Epoxidation of Multi-Walled Carbon Nanotubes by Organocatalytic Oxidation

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Dedicated to the memory of Professor Ruggero Curci^[‡]

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Even though many functionalization methodologies for covalent modification of carbon nanotubes (CNTs) have been proposed, mild but effective approaches are still needed. Here we describe the epoxidation of multi-walled carbon nanotubes (MWCNTs) with dioxirane for an environmentally friendly oxidation process with an organocatalyst. Thank to the choice of dioxiranes (accessible and easy to handle and

to store), multiple oxidation cycles could be performed on the same sample, thus allowing for a final improvement in the degree of oxidation at the CNT sidewall. The obtained derivatives were then used as electrophilic platforms for successive modification with an amine, with a high degree of functionalization (about 750 $\mu\text{mol g}^{-1}$ from TGA analysis) being obtained.

Introduction

Since their accidental discovery and subsequent fabrication in 1991, carbon nanotubes (CNTs) have received considerable attention from scientific, industrial, and public bodies because of their unique physical, chemical, electrical, and mechanical properties. CNTs are classified into two main categories: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), according to the number of rolled-up graphene layers.

They all have enormous potential for applications in nanotechnology, such as in photovoltaic devices,^[1,2] superconductors,^[3] gas storage media,^[4] high-performance polymer composites,^[5–8] biomaterials, drug delivery platforms,^[9] and imaging and sensing devices,^[10] owing to their excellent intrinsic properties such as high elastic modulus, high thermal stability, excellent conductivity, and large surface areas.

The development of new methodologies for the covalent functionalization of CNTs, with the goal of integrating these nanomaterials into more complex functional structures, is still an area of great interest.^[11–13]

Chemical functionalization by attaching different functional groups directly to the CNTs' sidewalls is a well-established approach for facilitating solubility and has broad applicability in prominent fields such as biomedicine and catalysis.^[13–16]

Recent studies have shown that surface modification on the exterior surfaces of CNTs can not only endow CNTs with water solubility, but can also produce functional moieties that enable linking organic molecules, the functional groups of which can effectively change the electronic structures and properties of the nanotubes.^[17]

Therefore, surface functionalization of CNTs has been extensively studied, with the goal of tailoring their physical properties and, hence, improving the interactions between CNTs and polymer matrices, solvents, or biomolecules and thus expanding their application into more advanced fields. The general idea of these methods is that chemical functionalization enables the introduction of functional groups at the nanotube surface, and that these may react with the functional groups of organic molecules, forming permanent bonds.^[18]

In this regard, the oxidation of carbon nanotubes can provide access to functional groups at the surfaces of the CNTs that could react with other chemicals, introducing new moieties.

Chemical oxidation with acids damages the graphite-like structure and generates chemically active defects, but does

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allow the attachment of various chemical groups.^[13] However, nondestructive methods are preferred, in order to permit the introduction of functional groups without heavily altering the CNT surface.

For this reason, a more benign approach to oxidizing CNTs that involves the development of milder oxidation methods, capable of generating oxygen functional groups at the CNT sidewalls while preserving (almost unchanged) their original morphological characteristics, represents a very challenging issue for the production of flexible and chemically versatile CNT platforms.

Organic peroxy acids, such as the classical 3-chloroperbenzoic acid (*m*-CPBA),^[19,20] ozone,^[21] and oxidizing mixtures based on methyltrioxorhenium (ReMeO₃)/hydrogen peroxide,^[22] have allowed relatively mild and effective epoxidation of CNT sidewalls. Similarly, dioxiranes (typically prepared in situ) are expected, on the basis of both theoretical^[23] and experimental studies,^[24] to be suitable oxidizing agents for the preparation of ox-CNTs.

Moreover, Limnios and Kokotos have recently reported an environmentally friendly method for the epoxidation of alkenes with 2,2,2-trifluoroacetophenone as an organocatalyst in combination with a green oxidant – aqueous H₂O₂ in acetonitrile and *tert*-butyl alcohol.^[25,26]

As part of a continuing effort to devise selective methods for oxidation of key organic compounds, we decided to apply both dioxiranes^[28] and the efficient Limnios procedure,^[26] which is an effective and more convenient way to induce the attachment of oxygen groups to the surface of a MWCNT. As mentioned, these methods function under milder conditions, which should minimize potential damage to nanotubes and produce high levels of oxidation.

We have shown recently that the facile epoxidation of SWCNTs can be carried out by treatment with isolated methyl(trifluoromethyl)dioxirane (TFDO, **1b**, Figure 1).^[27] Indeed, the efficient epoxidation of simple and/or structurally complex alkenes under mild and neutral conditions is the highlight of the chemistry of these oxidants, and can be successfully applied as an easily tunable approach to the sidewall decoration of SWCNTs with epoxides and their subsequent derivatization (ring opening) upon treatment with reactive nucleophiles.

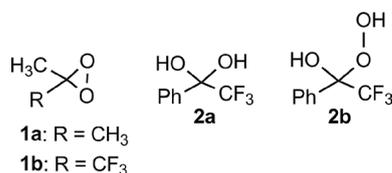


Figure 1. Activated forms of ketones: dioxiranes **1a** and **1b**, hydrate **2a**, and perhydrate **2b**.

Both the dioxirane-based approach and the Limnios procedure are based ultimately on ketones in combination with a source of oxygen, are environmentally friendly, and do not give rise to waste products.

The catalytic cycle for oxidations with a perfluoroaryl ketone/H₂O₂ involves, in an aqueous environment, the activated ketone (hydrate form **2a**, Figure 1) that, in conjunction with hydrogen peroxide, could lead to a perhydrate – **2b** – as the active species.^[25,26]

In this work the modification and functionalization of CNTs with some organic groups such as epoxides and amines was investigated. The modification of MWCNTs was assessed by TGA analysis, FTIR spectroscopy, Raman and X-ray photoelectron spectroscopy (XPS). In addition, transmission electron microscopy (TEM) was used to characterize the morphological properties of the as-oxidized MWCNT samples.

As discussed above, the most promising organic oxidants for efficient epoxidation of alkenes include perhydrates^[26] and dioxiranes.^[27,28] These reagents are derived from ketones in conjunction with an oxygen source. Because of their better environmental acceptance and their ability to act without requiring special reaction conditions, nonmetal organic oxidants have been developed and employed in oxidation reactions. Furthermore, the use of a perfluoro ketone (e.g., 2,2,2-trifluoroacetophenone) in conjunction with environmentally benign H₂O₂ as an oxidant (instead of caroate) is cheap, clean, and safe and gives water as the only byproduct.^[25]

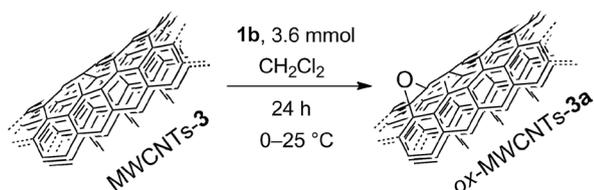
Results and Discussion

As part of a continuing effort to devise methods for oxidation of CNTs, we decided to apply both oxidants – dioxiranes **1** and perhydrate **2b** – to probe the direct introduction of epoxide groups onto the MWCNT surface.

The yields of the reactions, the simple workup, the easy availability of reagents, and the low cost are strong practical points of the method presented here. Moreover, it represents a green approach for the preparation of these materials.

Synthesis of ox-MWCNTs with Methyl(trifluoromethyl)-dioxirane (TFDO, **1b**)

Methyl(trifluoromethyl)dioxirane (TFDO, **1b**) is an efficient, selective, and environmentally friendly oxygen-transfer reagent capable of operating at temperatures as low as at 0 °C in the epoxidation of C=C double bonds. A stock solution (0.5–0.6 M) of **1b** can be prepared by literature procedures^[28] from 1,1,1-trifluoropropanone (TFP) and conveniently stored at –20 °C for months without any apparent alteration. In a general oxidation procedure, an aliquot (3.6 mmol) of the standardized cold solution of dioxirane **1b** is added to a well sonicated and cold (0 °C) CH₂Cl₂ (20 mL) suspension of pristine MWCNTs. The reaction mixture is then stirred at room temp. for a further 24 hours (Scheme 1).

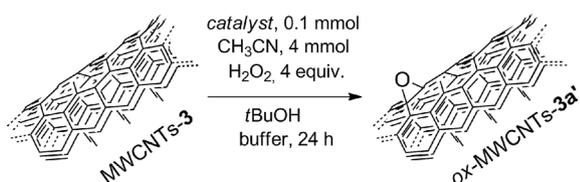


Scheme 1. MWCNT epoxidation by **1b**. Samples **3a** prepared upon treatment of pristine MWCNTs with 3.6 mmol of **1b**.

Afterwards, *ox*-MWCNTs **3a** are recovered from the reaction mixture by a simple filtration/washing workup procedure, dried, and characterized.

Synthesis of *ox*-MWCNTs with 2,2,2-Trifluoroacetophenone as Catalyst and H₂O₂

An alternative method developed by Limnios et al.^[26] involves the use of an organocatalytic oxidation, in the presence of a perfluoro ketone employed as catalyst in this reaction, with hydrogen peroxide (H₂O₂, Scheme 2).



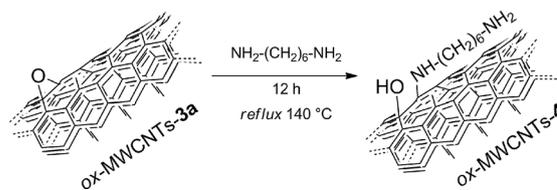
Scheme 2. MWCNT epoxidation by the Limnios procedure. Samples **3a'** prepared with the aid of 0.1 mmol of catalyst.

In a typical procedure similar to that used for the TFDO epoxidation, a suspension of pristine MWCNTs was treated with 2,2,2-trifluoroacetophenone, *tert*-butyl alcohol (3 mL), aqueous buffer solution, acetonitrile, and 30% aqueous H₂O₂, added consecutively. The reaction mixture was allowed to stir for 24 h at room temperature. The oxidized nanotubes (**3a'**) were washed and characterized.

As control, the reaction was performed in the absence of catalyst, and no appreciable oxidation was observed (see Figure S1 in the Supporting Information).

Post-Functionalization of *ox*-MWCNTs **3a** with 1,6-Hexamethylenediamine

The *ox*-MWCNT samples are reactive platforms for successive functionalization/derivatization, and a model reaction protocol has been set up.^[27] In view of the ability of epoxides to undergo nucleophilic attack with subsequent ring opening, the reaction between *ox*-MWCNT and an aliphatic diamine was investigated. A diamine reagent was chosen in order to impart multimodality to the final samples (Scheme 3).



Scheme 3. MWCNT epoxide functionalization with 1,6-hexamethylenediamine.

Indeed, the simultaneous generation of hydroxy and amine functional groups at the nanomaterial sidewalls and tips constitutes a step forward to highly functionalized and versatile nanostructured CNTs.

In a typical procedure, **3a** is dispersed in 1,6-hexamethylenediamine and heated at reflux for 12 h under inert atmosphere (N₂). Afterwards, the resulting suspension is subjected to successive sonication/washing cycles before being filtered through a 0.2 μm PTFE membrane filter. As a control *p*-MWCNTs were treated under the same conditions, without their structures being affected.

Evidence of the CNT functionalization is provided by thermogravimetric analyses (TGA) of the samples (Figure 2).

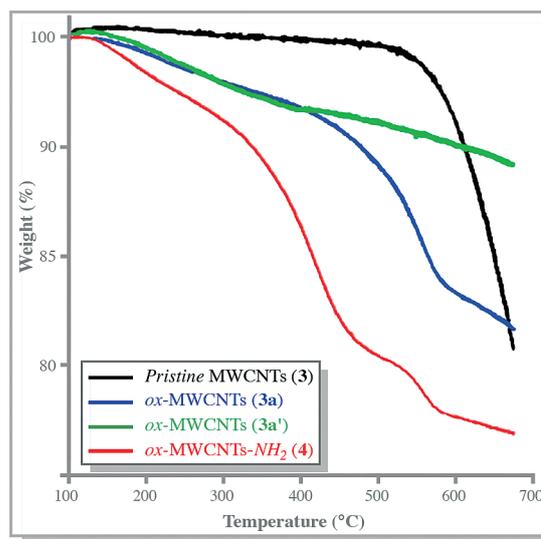


Figure 2. TGA plots of pristine MWCNTs, oxidized MWCNTs **3a** and **3a'**, and amino-functionalized MWCNTs **4**.

Under the applied analysis conditions, the pristine MWCNTs were stable up to 550 °C, whereas all the other studied samples presented weight loss that could be attributed to easy degradation of the introduced organic functionalization. In the cases of **3a** and **3a'** the calculated weight losses at 450 °C are in the same range (4 and 3.3%, respectively) whereas derivative **4** presented a significant loss (8.7%, without allowance for the weight loss related to the precursor **3a**), which corresponded to a functionalization of 750 μmol g⁻¹ with hexamethylenediamine, presumably introduced by opening of the epoxide rings. The oxidized derivatives **3a** and **3a'** present an interesting difference in stability at higher temperatures: whereas **3a** presents a

weight loss of 10.9% at 580 °C, with behavior similar to that of the analogue obtained with SWCNTs^[27] and also evident in the case of derivative **4**, compound **3a'** proves to be more stable. The latter compound shows a weight loss of 4.6% (at 580 °C, absolute value), suggesting that the treatment with 2,2,2-trifluoroacetophenone and H₂O₂ might introduce functionalization without excessively affecting the carbon skeletons of the tubes, the thermal stability of which is higher.

A morphological study of the compounds was carried out by transmission electron microscopy (TEM) analysis. TEM micrographs do not show any significant changes, in morphological terms, before and after oxidative treatment either with TFDO (Figure 3, b) or with catalyst/H₂O₂ (Figure 3, c). Also, the degree of tube aggregation does not change dramatically despite the functionalization, but this is quite understandable in view of the fact that the introduced epoxide units partially enhance dispersibility in polar solvents with respect to the starting material but not to any great extent.

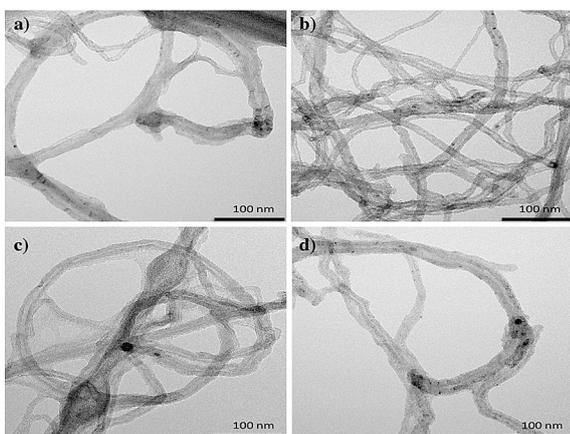


Figure 3. TEM micrographs recorded on (a) the pristine MWCNTs, (b) *ox*-MWCNTs produced with **1b** (**3a**), (c) *ox*-MWCNTs produced with **2b** (**3a'**), and (d) *ox*-MWCNT-NH₂ (**4**).

Raman spectroscopy is a very valuable tool for the characterization of carbon-based nanostructures. The Raman spectra of pristine and functionalized MWCNTs (**3a**, **3a'**, and **4**) excited with the 633 nm laser line are shown in Figure 4.

All the sample exhibited the characteristic bands: the disorder-induced D band at 1322 cm⁻¹, indicating the presence of defects on the nanotube surface, the G band corresponding to the crystalline graphitic structures at ca. 1580 cm⁻¹, and the overtones at about 2650 and 2910 cm⁻¹.

Whereas for SWCNTs the intensity variation of the D and the G bands is highly significant and the I_D/I_G ratio is a very important tool to specify the functionalization of the CNT walls, for MWCNTs the variations might not be so informative. In fact, in the pristine compounds the D band is already very intense and the modified surface of *ox*-MWCNTs does not display any significant variation in the I_D/I_G ratio with respect to unmodified MWCNTs, the crystalline graphitic structure being already altered by the

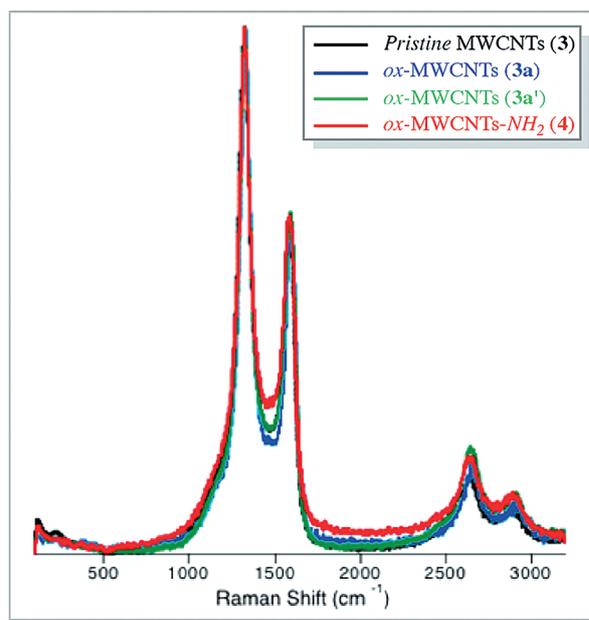


Figure 4. Raman spectra of pristine MWCNTs, *ox*-MWCNT samples obtained through treatment by different oxidation methods (**3a** and **3a'**), and of *ox*-MWCNT-NH₂ (**4**) derivatives.

presence of defects. In some cases a decrease in this ratio after functionalization of MWCNTs has also been reported, in cases in which the chemical treatment removes amorphous carbon present in the sample (this material also contributes to the D band intensity).^[29]

The FTIR spectra of pristine MWCNTs, *ox*-MWCNTs (**3a**), and *ox*-MWCNTs-NH₂ (**4**) (see Figure S2 in the Supporting Information) showed similar characteristic peaks, indicating similarity in the structures of the MWCNTs.

Further, there are peaks at ca. 1159 and 1620 cm⁻¹ in the IR spectra of oxidized MWCNTs corresponding to stretching of carbon-oxygen bond of epoxide, alcohol sp³ and carbonyl sp², respectively. Moreover, the FTIR spectrum of the *ox*-MWCNT-NH₂ (**4**) shows characteristic absorbance peaks around 1310 and 1390 cm⁻¹ (Figure S2 in the Supporting Information) that can be assigned to the C-N stretching mode and at 1150 cm⁻¹ (C-O stretching).^[27] In the pristine MWCNTs, these peaks are not present. These results indicate that after the oxidation step, oxygen-based functional groups such as epoxides are formed on the surface of MWCNTs.

Additionally, X-ray photoemission spectroscopy (XPS) unambiguously reveals a significant increase in nitrogen-containing groups in sample **4**, with respect to the pristine materials. Whereas the survey spectra recorded for both samples show the presence of characteristic C 1s and O 1s core level photoemission peaks, only in the case of **4** was the presence of N 1s significant (see Table 1).

From the dispersion of the values registered in the case of **4**, as evident from the standard deviation reported in Table 1, it is possible to assume that the functionalization is not equally distributed on the samples, even though the registration of four XPS spectra per sample does not give any statistically meaningful result.

Table 1. XPS analysis of *p*-MWCNTs and **4**.

Sample	Amount of element (atom-% values)			N	F
	C	O			
<i>p</i> -MWCNTS (3)	90.7 ± 1.6	8.7 ± 1.3	0.7 ± 0.3	–	–
4	77.1 ± 8.6	6.3 ± 2.5	4.5 ± 1.9	12.1 ± 8.6	–

The surface fluorine contamination in the wide-scan survey spectrum of sample **4** probably originates from the use of TFDO in the epoxidation of **3** (Scheme 1), mostly from the TFP cosolvent of the reaction. We considered it unnecessary to purify product **3a** because the presence of fluorine does not affect the reaction.

Conclusions

The results reported here constitute a useful reference for gaining additional insights of practical value into the organic functionalization of complex carbon nanostructures. Here we have described an original approach to the convenient and facile heterodecoration of multiwalled carbon nanotubes. Our methodology relies on flexible, versatile, and easy access to epoxy-decorated MWCNTs by use of TFDO under mild conditions close to neutrality, achievable by using an isolated dioxirane. Moreover, we have also applied to MWCNTs, a better, green, efficient, and fast oxidative protocol employed for the epoxidation of alkenes by utilizing 2,2,2-trifluoroacetophenone as the catalyst in combination with the green oxidant H₂O₂.

Likewise, product isolation is quite simple. A successive transformation of the epoxide functionalities at the CNT sidewall is straightforwardly achieved by treatment (epoxide ring-opening) with a model primary diamine.

Such an approach highlights the versatility of the *ox*-MWCNTs as valuable platforms for their successive functionalization/derivatization with selected reactive nucleophiles, providing multimodality to the final derivatives.

Experimental Section

General: Thermogravimetric analyses were recorded with a TGA Q500 instrument (TA Instruments) under flowing nitrogen. The samples (about 1 mg per sample) were equilibrated at 100 °C for 20 min and then heated at a rate of 10 °C min⁻¹ up to 800 °C.

Transmission electron microscopy analyses were performed with a TEM Philips EM208 instrument and use of an accelerating voltage of 100 kV. The samples were prepared by dropping aliquots of the DMF dispersions onto TEM grids (200 mesh, Nichel, carbon only).

Raman spectra were recorded with an Invia Renishaw microspectrometer equipped with a He–Ne laser at 633 nm and use of a 50 × objective. The exposure time and the accumulations were selected to provide sufficiently informative spectra.

Infrared analyses were performed in the 400–4000 cm⁻¹ range (36 scans) with a Fourier-transform infrared (FTIR) spectrometer (PerkinElmer 2000) equipped with ATR.

The surface chemical analysis of the MWCNTs was carried out by X-ray Photoelectron Spectroscopy (XPS) with a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK). Spectra were collected by use of monochromatized Al-K_α radiation (1486.6 eV). The surface-normal emitted photoelectrons were analyzed with a double-focusing hemispherical analyzer and recorded with a multi-channel detector. All the spectra were acquired in the constant analyzer energy mode. The Thermo Scientific Avantage software (Thermo Fisher Scientific) was used for digital acquisition and data processing. XPS analyses were repeated on four different spots of each sample.

Materials: Common commercial solvents and reagents of high purity were employed. Commercial Carcoat® triple salt (2 KHSO₅·KHSO₄·K₂SO₄), a gift from United Initiators GmbH, Germany, was the source of potassium monoperoxysulfate. Commercial MWCNTs (purity > 90 wt.-%, diameter between 0.7 and 1.4 nm) are commercially available from Aldrich in powder form.

Preparation of *ox*-MWCNTs (3a**) with TFDO (**1b**):** The following procedure is representative. MWCNTs (66 mg) were placed in CH₂Cl₂ (20 mL), and the mixture was sonicated for 30 min. An aliquot (3.6 mmol) of the standardized cold solution of methyl(trifluoromethyl)dioxirane (**1b**, TFDO, 7.5 mL, 0.5 M) in 1,1,1-trifluoropropanone (TFP) was then added in one portion to the mixture, which was stirred and kept at 0 °C. After 24 h the reaction was complete, the mixture was filtered, and CNTs **3a** were washed several times with CH₂Cl₂ followed by MeOH, with recovery of 77 mg.

Preparation of *ox*-MWCNTs (3a'**) with Catalyst/H₂O₂:** In a general procedure, MWCNTs (100 mg) were placed in a round-bottomed flask, and 2,2,2-trifluoroacetophenone (18 mg, 0.1 mmol) *tert*-butyl alcohol (3 mL), aqueous buffer solution [3 mL, K₂CO₃ (0.6 M), EDTA tetrasodium salt (4 × 10⁻⁵)], acetonitrile (0.22 mL, 4.00 mmol), and aqueous H₂O₂ (30%, 0.5 mL, 4.00 mmol) were added consecutively. The reaction mixture was allowed to stir for 24 h at room temperature. The mixture was then filtered, and CNTs **3a'** were washed several times with CH₂Cl₂ followed by MeOH, with recovery of 105 mg.

Functionalization of *ox*-MWCNT (3a**) with 1,6-Hexamethylenediamine:** Oxidized nanotubes **3a** (11 mg) were dispersed in 1,6-hexamethylenediamine (3.7 g), and the mixture was heated under N₂ at reflux at 140 °C for 12 h. After this, the reaction mixture was diluted with methanol (20 mL) and filtered through a PTFE membrane filter paper (0.2 μm) and the filtrate was washed extensively several times with CH₂Cl₂ followed by MeOH to remove any excess 1,6-hexamethylenediamine, leading to *ox*-MWCNT-NH₂ (**4**, 13 mg).^[27]

Acknowledgments

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