Supporting information for

Noncovalent functionalization of multiwall carbon nanotubes by methylated-β-cyclodextrins modified by a triazole group

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Materials

The MWNT Graphistrenght U100 used in this paper was purchased from Arkema. Typical Graphistrength carbon nanotubes diameter is 10 to 15 nm and typical length is between 1 to 10 μm. Agglomerated bundles of multi wall carbon nanotubes have average dimensions of about 400 microns. Prior to use, the MWNT solid was washed with acid according to the following procedure: 1 g of MWNT were dispersed into 500 mL of HNO_3 (10 mM). The mixture was refluxed during 24h at 100 °C under stirring. After cooling to ambient temperature, the MWNT particles were filtered and thoroughly washed with deionized water until the pH value of the washing water was the same as that of deionized water. The MWNT particles were dried in an oven at 100°C for 2 days and finally ground to powder in an agate mortar.

The randomly methylated β-cyclodextrin with an average substitution degree of 1.8 (Me-β-CD (1.8)) was kindly provided by Roquette. CDSBE and CDTOH were synthesized according to procedures described in the literature (See : P. Blach, D. Landy, S. Fourmentin, G. Surpateanu, H. Bricout, A. Ponchel, F. Hapiot and E. Monflier, *Adv. Synth. Catal.*, **2005**, *347*, 1301 and M. Mourer, F. Hapiot, S. Tilloy, E. Monflier and S. Menuel, *Eur. J. Org. Chem.*, **2008**, *34*, 5723). CDTpolyOH and $CDTSO_3Na$ were synthesized according to the experimental procedures described below. All other chemicals were purchased from Acros and Aldrich Chemicals in their highest purity. All solvents were used as supplied without further purification. Distilled water was used in all experiments. NMR spectra were recorded with a Bruker DRX300 spectrometer operating at 300 MHz for ^1H nuclei and at 75 MHz for ^{13}C nuclei. $CDCl_3$ (99.50% isotopic purity), [D6]DMSO (99.80% isotopic purity) and D_2O (99.92% isotopic purity) were purchased from Euriso-Top. Mass spectra were recorded with a MALDI-TOF/TOF Bruker Daltonics Ultraflex II spectrometer in positive reflectron mode with 2,5-DHB as the matrix.

Synthesis and analytical data of CDTpolyOH and $CDTSO_3Na$

N-((1-(randomly methylated 6^A-deoxy-β-D-cyclodextrin)yl-1H-1,2,3-triazol-4-yl)methyl)-D-gluconoamide [CDTpolyOH]

Randomly methylated mono-6-azido-6^A-deoxy-*β*-D-cyclodextrin (See : M. Mourer, F. Hapiot, S. Tilloy, E. Monflier and S. Menuel, *Eur. J. Org. Chem.*, **2008**, *34*, 5723) (1.5 mmol) and hydrated copper sulfate (3 mmol) were added to a solution of the *N*-propargyl-D-gluconoamide (See : E.-H. Ryu and Y. Zhao, *Org. Lett.*, **2005**, *7(6)*, 1035) (1.8 mmol) in DMF (40 mL). After the subsequent dropwise addition of a freshly prepared solution of sodium ascorbate (6 mmol) dissolved in water (5 mL), the solution was stirred for 18h at room temperature. After evaporation of the solvent, the crude product was dissolved in an ammonia solution (8%) and stirred for 2h before being purified by column chromatography on silica gel with water as eluent to give the product as a white powder. After evaporation of the solvent, the product was dissolved in 50 mL of water and extracted by 500 mL of

chloroform (2×250 mL). The organic phases were collected, dried with anhydrous Na_2SO_4, filtered and concentrated to give a yellowish powder (1.85 g, 77%).

^{1}H NMR (300 MHz, D_2O, δ = ppm): 7.97 (s, 1 H), 5.33 (m, 6.5 H), 4.98 (m, 5.4H), 4.56 (m, 4.0 H), 3.18 (m, 3.2 H), 3.99–3.86 (m, 17.5 H), 3.71–3.53 (m, 69.9 H), 3.37–3.14 (m, 29.4 H).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20°C, δ = ppm): 173.0 ; 144.0 ; 124.8 ; 102.6-100.7 ; 92.9-81.4 ; 79.0 ; 73.8 ; 72.7 ; 71.3 ; 70.3 ; 63.3 ; 60.8 ; 59.7-58.7 ; 50.0 ; 31.1.

MS: *m*/*z* (%) = 1570.06 (4.1) (calcd. 1569.63 for $[C_{62}H_{106}N_4O_{40} + Na]^+$), 1584.09 (25.5) (calcd. 1583.64 for $[C_{63}H_{108}N_4O_{40} + Na]^+$), 1593.11 (62.0) (calcd. 1597.66 for $[C_{64}H_{110}N_4O_{40} + Na]^+$), 1612.12 (8.3) (calcd. 1611.68 for $[C_{65}H_{112}N_4O_{40} + Na]^+$).

Sodium (1-(randomly methylated 6^A-deoxy-β-D-cyclodextrin)yl-1H-1,2,3-triazol-4-yl)methanesulfonate [CDTSO$_3$Na]

Randomly methylated mono-6-azido-6^A-deoxy-*β*-D-cyclodextrin (See : M. Mourer, F. Hapiot, S. Tilloy, E. Monflier and S. Menuel, *Eur. J. Org. Chem.*, **2008**, *34*, 5723) (1.5 mmol) and hydrated copper sulfate (3 mmol) were added to a solution of sodium propargyl sulfonate (See : E.-H. Ryu and Y. Zhao, *Org. Lett.*, **2005**, *7(6)*, 1035) (1.8 mmol) in DMF (40 mL). After the subsequent dropwise addition of a freshly prepared solution of sodium ascorbate (6 mmol) dissolved in water (5 mL), the solution was stirred for 18h at room temperature. After evaporation of the solvent, the crude product was dissolved in an ammonia solution (8%) and stirred 2h before being purified by column chromatography on silica gel with water as eluent to give the product as a white powder. After evaporation of the solvent, the product was dissolved in 25 mL of water and extracted by 500 mL of chloroform (2×250 mL). The organic phases were collected, dried with anhydrous Na_2SO_4, filtered and concentrated. The product was dissolved in 50 mL of water and 25 g of Amberlyst 15 resin (Na form) was then added. The resin was filtered off on a glass filter and washed with 15 mL of water. The solution was lyophilized to give a yellowish powder (1.25 g, 55%).

^{1}H NMR (300 MHz, D_2O, δ = ppm): 8.12 (s, 1 H), 5.34 (m, 5.1 H), 5.02 (m, 4.1H), 4.60 (m, 4.6 H), 4.06–3.92 (m, 13.2 H), 3.83–3.39 (m, 57.8 H), 3.21–3.12 (m, 5.7 H), 2.43–2.28 (m, 2.4 H).

^{13}C NMR (75.5 MHz, $CDCl_3$, 20°C, δ = ppm): 140.1 ; 126.8 ; 103.2-101.3 ; 84.2-79.3 ; 74.3 ; 73.4-70.9 ; 61.6-59.1 ; 52.0 ; 47.9 ; 29.9.

MS: *m*/*z* (%) = 1478.51 (2.2) (calcd. 1478.51 for $[C_{56}H_{94}N_3NaO_{37}S + Na]^+$), 1492.93 (27.2) (calcd. 1492.52 for $[C_{57}H_{96}N_3NaO_{37}S + Na]^+$), 1506.96 (60.1) (calcd. 1506.54 for $[C_{58}H_{98}N_3NaO_{37}S + Na]^+$),

1520.97 (9.5) (calcd. 1520.56 for $[C_{59}H_{100}N_3NaO_{37}S + Na]^+$), 1534.98 (0.9) (calcd. 1534.57 for $[C_{60}H_{102}N_3NaO_{37}S + Na]^+$).

Preparation of the MWNT suspensions

1 mg of MWNT was ground using a mortar and pestle for 5 minutes in 1 mL of deionized water (pH 5.2). MWNT were introduced into a bottle containing 9 mL of deionized water. Then a controlled amount of dispersing agent was added to the mixture in order to have a concentration of 0.87 mM. This mixture was finally sonicated in a NEY ULTRASONIK bath (Power, 160 W) for 30 min.

Characterization of the MWNT-based materials

The solid materials (MWNT, $CDTSO_3Na$-MWNT and CDTOH-MWNT) were characterized by different techniques. Concerning the case of the $CDTSO_3Na$-MWNT and CDTOH-MWNT hybrid materials, these materials were recovered from the corresponding aqueous suspension by filtration and thoroughly washed with distilled water (2×30 mL) in order to eliminate the excess of modified cyclodextrin. Then, these materials were dried for 24h under vacuum at 70°C and the resulting material was finally ground to powder in an agate mortar.

Specific area measurement

Porosity measurements were obtained from nitrogen adsorption/desorption isotherms at T = -196°C using a Nova 2200 apparatus from Quantachrom Corporation, carried out on powders previously outgassed overnight at 100°C. Specific areas were calculated from the BET equation using P/Po values in the 2.5 10^{-3} and 1.7 10^{-2} range.

ATR-FTIR spectroscopy

ATR-FTIR spectra were recorded on a Shimadzu IR Prestige-21 spectrometer from 4000 to 700 cm^{-1} using germanium ATR (Attenuated Total Reflectance)-FTIR spectroscopy which is adapted to black samples. Samples are directly introduced into the ATR cell and compressed on germanium crystal surface.

Thermogravimetric analysis under N_2

Taking into account that MWNT could be oxidized at high temperature and under air, we checked the thermal stability of the material by TGA analysis under nitrogen atmosphere. Measurements were performed using a SDT 2960 analyzer from TA instrument under nitrogen flow (80 $mL.min^{-1}$) with an increase rate of temperature of 2°$C.min^{-1}$.

The amount of cyclodextrin adsorbed onto the surface of the MWNT has been calculated considering $M(CDTSO_3Na) = 1474\ g.mol^{-1}$ and $M(CDTOH) = 1404\ g.mol^{-1}$.

Fluorescence spectroscopy

Experiments were carried out with a Perkin Elmer LS-50B fluorimeter (right angle measurements) and a quartz cell with optical path length of 1.00 cm, at 298°K. The control of temperature was realised by the use of a thermostated bath linked to the cell holder (accuracy: ± 0.1°K). The spectra of $CDTSO_3Na$ were collected from 345 nm to 545 nm with a scan rate equal to 60 $nm.min^{-1}$, for a fixed cyclodextrin concentrations equal to 15 μM and concentrations of MWNT varying from 0 to 10 $mg.L^{-1}$. The excitation wavelength of the fluorescence spectra was 327 nm (excitation and emission slits: 8 nm). Each solution was sonicated for 30 min before acquisition of fluorescence spectra.

T-ROESY (300 MHz, D_2O, 36 mmol.L^{-1}) of 1-(randomly methylated 6^A-deoxy-β-D-cyclodextrin)yl-1*H*-1,2,3-triazol-4-yl)ethan-2-ol *[CDTOH]*

The 2D T-ROESY experiments were run using the software supplied by Bruker on a Bruker DRX300 spectrometer operating at 300 MHz for ^1H nuclei. T-ROESY experiments were preferred to classical ROESY experiments as this sequence provides reliable dipolar cross-peaks with a minimal contribution of scalar transfer. Mixing times for T-ROESY experiments were set at 300 ms. The data matrix for the T-ROESY was made of 512 free induction decays, 1 K points each, resulting from the coaddition of 32 scans. The real resolution was 1.5–6.0 Hz/point in F2 and F1 dimensions. They were transformed in the non phase-sensitive mode after QSINE window processing.

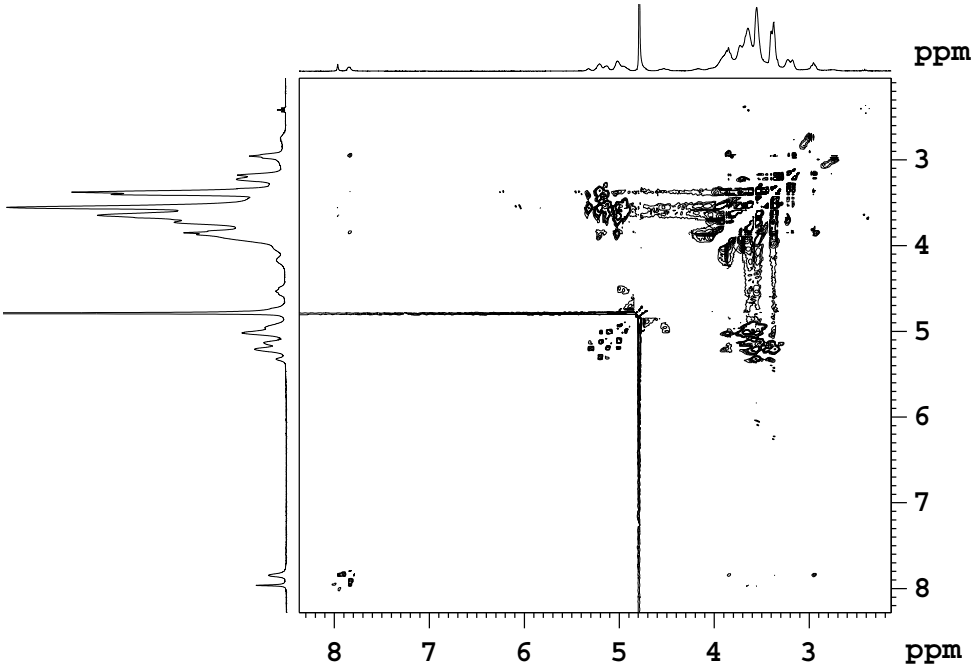

Fig. S1. T-ROESY ^1H NMR spectrum (300 MHz) of a 36 mM solution of CDTOH in D_2O at 298°K.

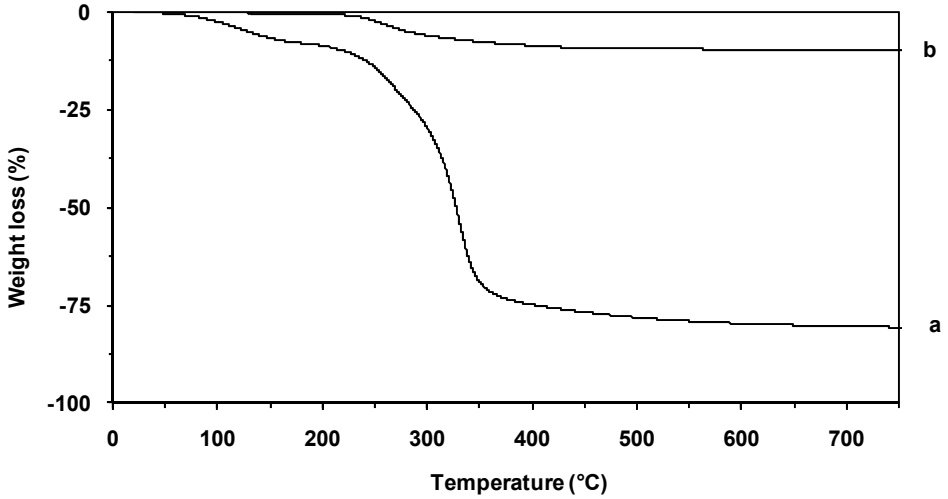

Fig. S2 Thermogravimetric profiles under N_2 atmosphere (heating rate of 2°C.min^{-1}) of (a) $CDTSO_3Na$ and (b) $CDTSO_3Na$-MWNT hybrid material.

TGA analysis of pure $CDTSO_3Na$ has been realized. The thermal decomposition of the $CDTSO_3Na$ moieties is observed in the 160-360°C temperature range (Fig. S2, curve a) where a rapid weight loss is obtained which coincides with the thermal decomposition obtained with $CDTSO_3Na$-MWNT hybrid material (Fig. S2, curve b). Consequently, this analysis clearly shows the adsorption of $CDTSO_3Na$ onto the MWNT.

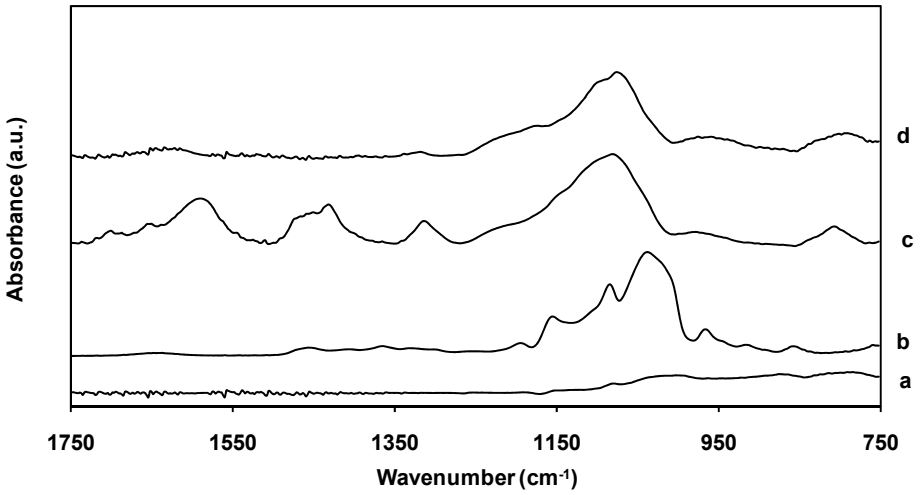

Fig. S3. ATR-FTIR spectra of (a) MWNT, (b) RAME-β-CD, (c) $CDTSO_3Na$ and (d) $CDTSO_3Na$-MWNT hybrid material.

The $CDTSO_3Na$-MWNT material has been characterized by ATR-FTIR spectroscopy (Fig. S3). By contrast with the spectrum of MWNT that exhibits no marked peaks in the 1750-750 cm^{-1} region (Fig. S3, spectrum a), the spectrum of the bulk $CDTSO_3Na$ displays intense peaks in the same spectral region (Fig. S3, spectrum c). Thus, the FTIR spectrum can be divided into two main parts, i.e. *i)* the 1250-750 cm^{-1} region characterizing the vibrational modes of the oligosaccharide part of $CDTSO_3Na$ and *ii)* the 1700-1250 cm^{-1} region characterizing the vibrational modes of the triazole group in $CDTSO_3Na$ [C=C (1580 cm^{-1}; 1450 cm^{-1}), N=N (1425 cm^{-1}) and C-N (1300 cm^{-1})]. Concerning the $CDTSO_3Na$-MWNT hybrid material (Fig. S3, spectrum d), the fact that the bands of the glucose units are clearly observed confirms the presence of the $CDTSO_3Na$ moieties onto the MWNT surface. It is worth noting that there is a strong decrease in the intensity of the specific vibrational modes of the triazole cycle, proving that the anchorage of the $CDTSO_3Na$ onto MWNT effectively occurs *via* the triazole part of the CD.