Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Contents:

1. Materials and Methods:

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance (300 MHz or 700 MHz for ^{1}H-NMR and 75 MHz or 175 MHz for ^{13}C-NMR, respectively). Unless otherwise indicated, chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) as internal standard at room temperature using deuterated solvents. Abbreviations used for splitting patterns are s = singlet, br s = broad singlet, d = doublet, t = triplet and m = multiplet. UV-Vis spectra were recorded in a UV-3600 Shimadzu Spectrophotometer. Circular Dichroism spectra were performed in a Jasco *J*-815 CD spectrometer at room temperature. Fluorescence spectroscopy was performed in a Fluoromax-4 spectrofluorometer (HORIBA). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a MAT 95 thermo spectrometer using dithranol matrix. Column chromatography was carried out on Merck silica gel 60 (70-230 mesh). Reagents were purchased from Sigma-Aldrich and were used without further purification.

Transmission electron microscopy (TEM): TEM images were performed using a JEOL 2000-FX electron microscope, operating at 200 kV accelerating voltage. The samples were prepared by drop-casting of the respective nanohybrids on carbon film 200 square mesh copper grids (CF200-Cu). TEM images were obtained after drying the sample by air for 24 hours and performing then a negative staining of the samples with a 2 % uranile acetate solution.

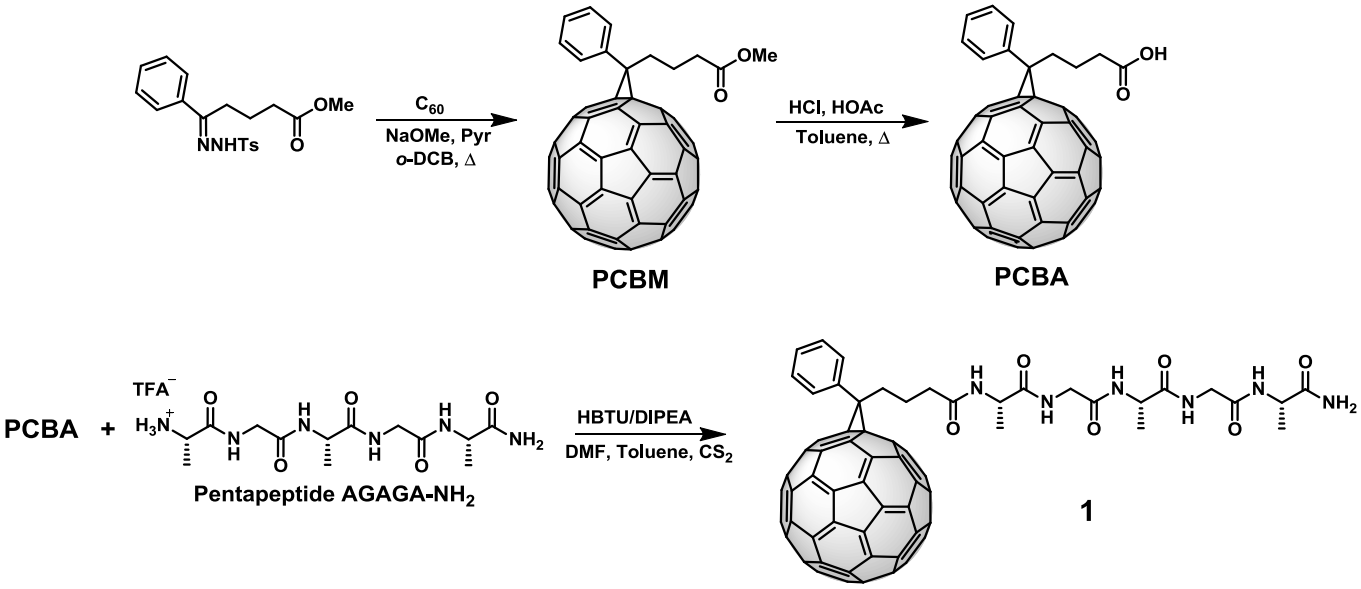
Atomic Force Microscopy (AFM): AFM images of the different nanohybrids were acquired under ambient conditions using SPM Nanoscope IIIa multimode working on tapping mode with a RTESPA tip (Veeco) at a working frequency of ~235 kHz. The samples were prepared by drop-casting on a freshly cleaved mica surface and were dried under ambient conditions for 24 hours.

Scanning Electron Microspope (SEM): SEM images were acquired by using a JEOL JSM 6335F microscope working at 10 kV. The nanohybrids were deposited by drop-casting on silicon substrate, dried under ambient conditions and metallized with Au before observation.

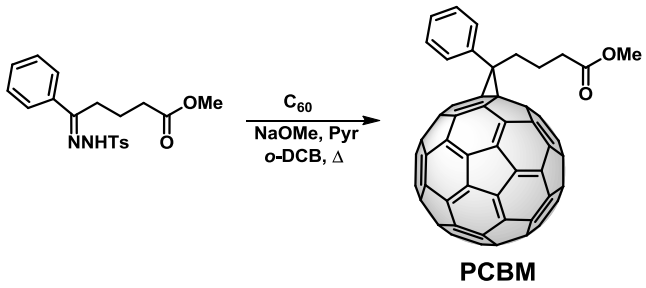
General method for nanofibers preparation:

The fullerene derivative (**1**-**3**) is dissolved in DMSO (1 mg/0.15 mL). This mixture is heated at 60ºC and 1,1,2,2-tetrachloroethane was added dropwise (1.35 mL). Then the mixture is left to room temperature and aged for 1 day before exploration by microscopic techniques.

1.1- Synthesis of compound 1



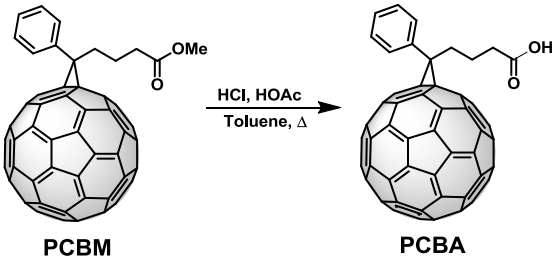
1.1.1 Synthesis of PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester)[1]:



To a solution of the tosylhydrazone (169 mg, 0.451 mmol) in 10 mL of anhydrous pyridine, sodium methoxide (28 mg, 0.521 mmol) was added and this mixture was stirred at room temperature for 15 minutes under argon atmosphere. Then, a solution of C_{60} (250 mg, 0.347 mmol) in 40 mL of *o*-DCB was added and the mixture is heated at reflux for 48 hours. Then the solvent was evaporated until dryness and a silica gel column chromatography was performed, using first CS_2 to recover the unreacted C_{60}, and then using toluene. The product was obtained as a brownish solid with a yield of 42%. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$): δ 2.14-2.27 (m, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.87-2.99 (m, 2H), 3.69 (s, 3H), 7.46-7.52 (m, 1H, Ar-H), 7.52-7.60 (m, 2H, Ar-H), 7.94 (d, *J* = 7.5 Hz, 2H, Ar-H) ppm.

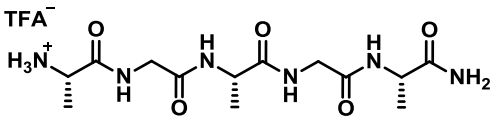
[1] J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, *J. Org. Chem*. **1995**, 60, 532-538

1.1.2 Synthesis of PCBA ([6,6]-phenyl-C_{61}-butyric acid)[1]:



To a solution of PCBM (200 mg) in 120 mL of toluene, 20 mL of HCl conc. and 50 mL of glacial acetic acid were added. This mixture was refluxed for 48 hours. Then the solvent was evaporated until dryness. The crude was dissolved in the minimum volume of toluene and then cold diethyl ether was added to precipitate the product. The solid was washed with diethyl ether giving rise to the desired product as a brownish solid with a yield of 90%. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$): δ 2.17-2.28 (m, 2H), 2.50-2.62 (m, 2H), 2.88-3.01 (m, 2H), 7.45-7.59 (m, 3H, Ar-H), 7.93 (d, *J* = 6.9 Hz, 2H, Ar-H) ppm.

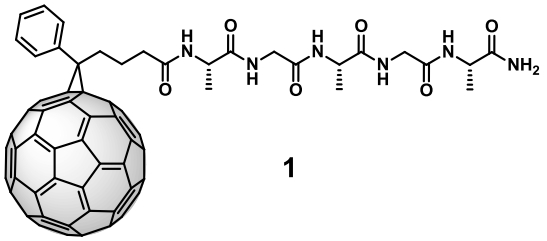
1.1.3-Synthesis of the chiral pentapeptide (AGAGA-NH_2):



Standard solid phase 9-fluorenylmethoxycarbonyl (Fmoc) chemistry on a 4-methyl-benzydrylamine (MBHA) resin was used to synthesize the AGAGA pentapeptide. Fmoc deprotection was performed by mixing the N-terminal Fmoc-peptide-resine with a solution of piperidine (20%) in DMF for five minutes at room temperature. This process was repeated at least five times. After this, the resin was washed several times with DMF and DCM. Before the first amino acid coupling to the resin, the latter was swelled and rinsed with DMF and DCM. The amino acid couplings were performed, in general, by adding to the resin a DMF solution with the Fmoc-protected amino acid (3eq., relative to the resin load) activated with 3 eq. of *O*-Benzotriazole-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HBTU) and 7 eq. of diisopropylethylamine (DIPEA). Mixtures were shaken at room temperature for one hour. Then the resin was washed with DMF and DCM. Every step (amino acid couplings and Fmoc cleavage) was checked by the Kaiser test taking few beads from the chamber. The cleavage of the pentapeptide from the resin was performed with a solution of trifluroacetic acid (TFA) and H_2O (95:5) giving rise to the desired

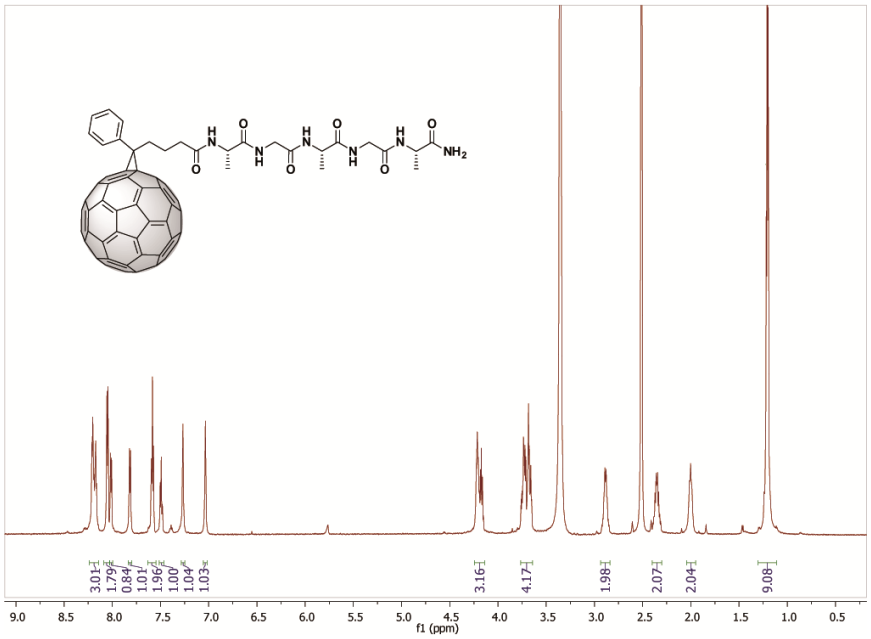
product with an amine and an amide groups at the N-terminus and C-terminus positions, respectively. The resin was removed by filtration and washed with DCM. The filtrate was concentrated under reduce pressure and the peptide was precipitated by adding cold diethyl ether. The precipitate was filtered and washed with cold diethyl ether to obtain the peptide as a white solid. ^{1}H-NMR (300 MHz, D_2O): δ 1.38 (d, *J* =7.22 *Hz*, 3H, CH_3), 1.40 (d, *J* =7.16 *Hz*, 3H, CH_3), 1.54 (d, *J* =7.11 *Hz*, 3H, CH_3), 3.93 (s, 2H, CH_2-Gly), 4.01 (s, 2H, CH_2-Gly), 4.13 (q, *J* =7.11 *Hz*, 1H, CH-Ala), 4.26-4.38 (m, 2H, CH) ppm. ^{13}C-NMR (75 MHz, D_2O): δ 16.4, 16.5, 16.7, 42.2, 42.4, 49.1, 49.4, 49.9, 170.9, 171.1, 171.4, 175.7, 177.8 ppm. HRMS (ESI) [M^+] Calc. for $C_{13}H_{25}N_6O_5$: 345.1881; found [M^+]: 345.1886.

1.1.4-Synthesis of compound 1.

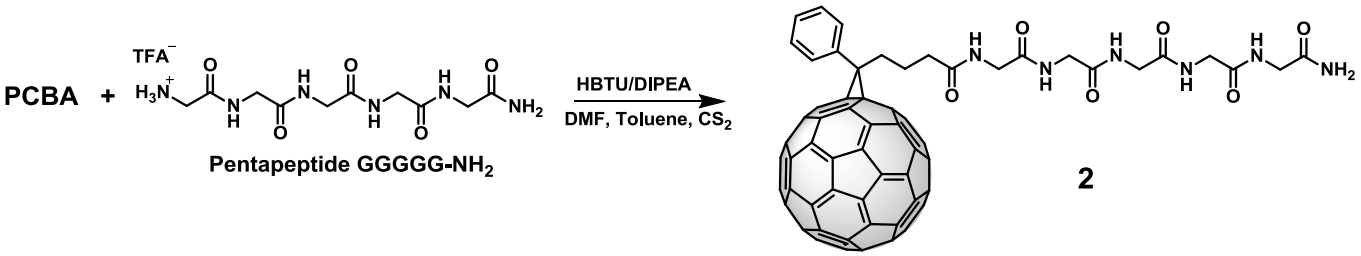


1

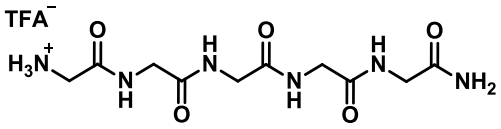
The coupling between the PCBA and the pentapeptide (AGAGA-NH_2) was performed in liquid phase. In a round bottom-flask, 30 mg (0.0334 mmol) of PCBA in a mixture of anhydrous DMF (4 mL), dry toluene (4 mL) and CS_2 (2 mL) were activated by adding HBTU (0.0668 mmol) and DIPEA (0.234 mmol). After 5 minutes of activation, a solution of the pentapeptide (0.0334 mmol) in anhydrous DMF (2 mL) was added. The reaction was performed under argon atmosphere at room temperature. After 10 minutes of reaction the precipitation of a solid was observed and more amount of this solid was observed with time. After 2 hours of stirring the mixture was filtered and the solid was washed thoroughly with toluene, CS_2, diethyl ether and MeOH. The product was obtained as a brownish solid with a yield of 62%. ^{1}H-NMR (700 MHz, DMSO-d_6) δ 1.23-1.29 (m, 9H, CH_3-Ala), 1.98-2.03 (m, 2H), 2.32-2.38 (m, 2H), 2.85-2.92 (m, 2H), 3.64-3.77 (m, 4H, CH_2-Gly), 4.15-4.23 (m, 3H, CH-Ala), 7.03 (s, 1H, NH_2), 7.27 (s, 1H, NH_2), 7.49 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.56-7.60 (m, 2H, Ar-H), 7.82 (d, *J* = 7.4 Hz, 1H, NH-Ala), 8.01 (d, *J* = 6.6 Hz, 1H, NH-Ala), 8.05 (d, *J* = 7.4 Hz, 2H, Ar-H), 8.16-8.23 (m, 3H, NH-Ala+2NH-Gly) ppm. ^{13}C-NMR (175 MHz, DMSO-d_6) δ 18.3, 18.4, 18.6, 23.2, 33.6, 35.2, 42.4, 42.6, 48.4, 49.0, 80.7, 128.7, 128.8, 132.6, 136.9, 137.1, 138.2, 140.5, 140.7, 142.0, 142.1, 142.3, 142.89, 142.92, 143.7, 143.8, 143.9, 144.2, 144.4, 144.6, 144.7, 145.0, 145.10, 145.12, 145.7, 146.4, 148.7, 149.9, 168.7, 169.3, 172.3, 173.1, 173.3, 174.6 ppm. HRMS ESI: [M + Na]$^+$ Calc. for $C_{84}H_{34}N_6O_6Na$: 1245.2432; found [M + Na]$^+$: 1245.2455 Mp: > 350 ºC.



1.2- Synthesis of compound 2



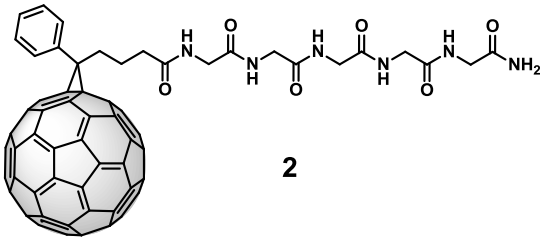
1.2.1-Synthesis of the achiral pentapeptide (GGGGG-NH_2):



Standard solid phase 9-flourenylmethoxycarbonyl (Fmoc) chemistry on a 4-methyl-benzydrylamine (MBHA) resin was used to synthesize the GGGGG-NH_2 pentapeptide. Fmoc deprotection was performed by mixing the N-terminal Fmoc-peptide-resine with a solution of piperidine (20%) in DMF for five minutes at room temperature. This process was repeated at least five times. After this, the resin was washed several times with DMF and DCM. Before the first amino acid coupling to the resin, the latter was swelled and rinsed with DMF and DCM. The amino acid couplings were performed, in general, by adding to the resin a DMF solution with the Fmoc-protected amino acid (3eq., relative to the resin load) activated with 3 eq. of *O*-Benzotriazole-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HBTU) and 7 eq. of diisopropylethylamine (DIPEA). Mixtures were shaken at room temperature for one hour. Then the resin was washed with DMF and DCM. Every step (amino acid couplings and Fmoc cleavage) was

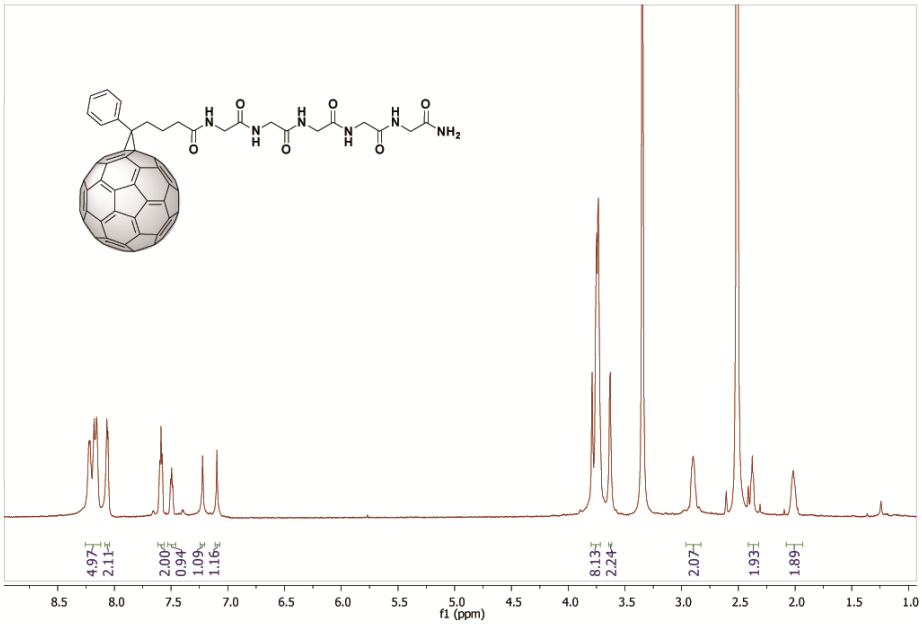
checked by the Kaiser test taking few beads from the chamber. The cleavage of the pentapeptide from the resin was performed with a solution of TFA:H_2O (95:5) giving rise to the desired product with an amine and an amide groups at the N-terminus and C-terminus positions, respectively. The resin was removed by filtration and washed with DCM. The filtrate volume was concentrated under reduce pressure and the peptide was precipitated by adding cold diethyl ether. The precipitate was filtered and washed with cold diethyl ether to obtain the peptide as a white solid. ^{1}H-NMR (300 MHz, D_2O): δ 3.75 (s, 2H, CH_2-Gly), 3.78 (s, 2H, CH_2-Gly), 3.84 (s, 2H, CH_2-Gly), 3.86 (s, 2H, CH_2-Gly), 3.91 (s, 2H, CH_2-Gly) ppm. ^{13}C-NMR (75 MHz, D_2O): δ 40.4, 41.9, 42.3, 42.41, 42.46, 167.9, 171.9, 172.0, 172.2, 174.2 ppm. ESI-MS: calc for $C_{10}H_{19}N_6O_5^+$: 303.14, found: [M^+]: 303.10.

1.2.2-Synthesis of compound 2.

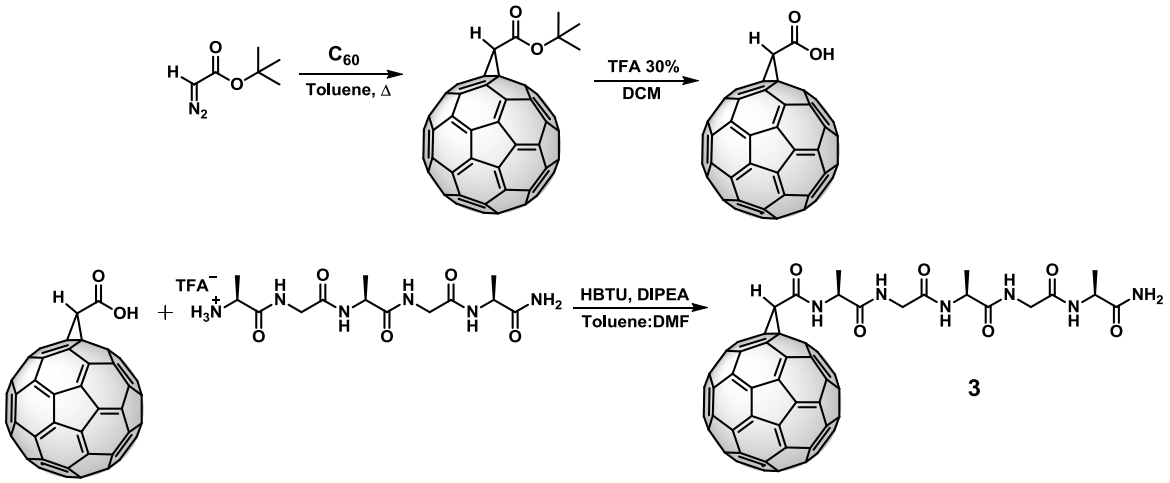


2

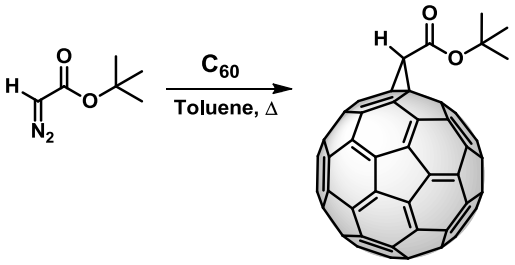
The coupling between the PCBA and the pentapeptide (GGGGG-NH_2) was performed in liquid phase. In a round bottom-flask, HBTU (0.0668 mmol) and DIPEA (0.234 mmol) were added to a solution of PCBA (30 mg, 0.0334 mmol) in a mixture of anhydrous DMF (4 mL), dry toluene (4 mL) and CS_2 (2 mL). After 5 minutes of activation, a solution of the pentapeptide (0.0334 mmol) in anhydrous DMF (2 mL) was added. The reaction was performed under argon atmosphere at room temperature. After 10 minutes of reaction the precipitation was observed. After 2 hours of stirring the mixture was filtered and the solid was washed thoroughly with toluene, CS_2, diethyl ether and MeOH. The product was obtained as a brownish solid with a yield of 59%. ^{1}H-NMR (700 MHz, DMSO-d_6) δ 1.98-2.04 (m, 2H), 2.35-2.39 (m, 2H), 2.87-2.91 (m, 2H), 3.63 (d, J = 5.3 Hz, 2H, CH_2-Gly), 3.70-3.80 (m, 8H, CH_2-Gly), 7.10 (s, 1H, NH_2), 7.22 (s, 1H, NH_2), 7.50 (t, J = 7.3 Hz, 1H, Ar-H), 7.56-7.61 (m, 2H, Ar-H), 8.06 (d, J = 6.9 Hz, 2H, Ar-H), 8.14-8.24 (m, 5H, NH-Gly) ppm. ^{13}C-NMR (175 MHz, DMSO-d_6) δ 23.3, 33.7, 35.3, 42.3, 42.4, 42.5, 42.6, 42.6, 80.7, 128.7, 128.9, 132.6, 136.9, 137.1, 138.2, 140.4, 140.6, 142.1, 142.2, 142.89, 142.92, 143.7, 143.8, 143.9, 144.2, 144.4, 144.6, 144.7, 145.1, 145.8, 146.4, 148.7, 149.9, 169.4, 169.8, 169.8, 169.9, 171.3, 172.6 ppm. HRMS ESI: [M + Na]$^+$ Calc. for $C_{81}H_{28}N_6O_6Na$: 1203.1963; found [M + Na]$^+$: 1203.1933. Mp: > 350 ºC.



1.3- Synthesis of compound 3:



1.3.1 Synthesis of [6,6]-methanofullerene-C_{61}-tert-butyl ester[2]:

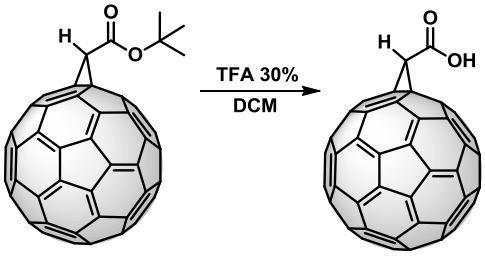


To a solution of C_{60} (100 mg, 0.139 mmol) in dry toluene (100 mL), tert-butyldiazoacetate (0.139 mmol) was added. The mixture was refluxed for 4 hours and then the solvent was evaporated until dryness. Under these conditions the formation of three isomers was achieved (two [5,6]-opened isomers and the [6,6]-closed one) and their isolation was performed by a silica gel column chromatography using CS_2 as

[2] Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta*, **1993**, 76, 1231-1250.

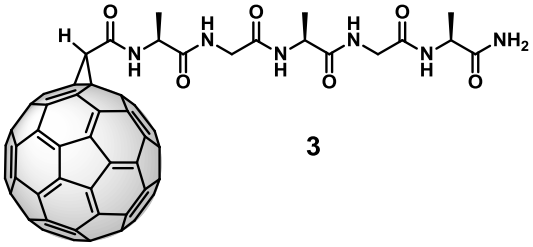
eluent recovering in first place the unreacted C_{60} and then the isomers (with identical Rf values). The desired product ([6,6]-closed) was obtained by a thermal treatment refluxing the mixture of isomers in toluene for 24 hours. The mixture was cooled to room temperature and then the solvent was removed giving rise to a brownish solid with a yield of 38%. ^{1}H-NMR (300 MHz, $CDCl_3/CS_2$): δ 1.73 (s, 9H), 4.72 (s, 1H) ppm.

1.3.2 Synthesis of [6,6]-methanofullerene-C_{61}-carboxylic acid[3]:



The fullerene tert-butyl ester derivative (40 mg) is dissolved in 4 mL of a mixture of DCM:CS_2 (3:1). Then, TFA (1.7 mL) was added and the mixture was stirred for 3 hours at room temperature. The formation of a precipitate was observed and it was filtered and washed with diethyl eter and CS_2 several times. The product was obtained as a brownish solid with a yield of 87%. ^{1}H-NMR (300 MHz, DMF-d_7 /CS_2): δ 5.28 (s, 1H) ppm.

1.3.3 Synthesis of compound 3:

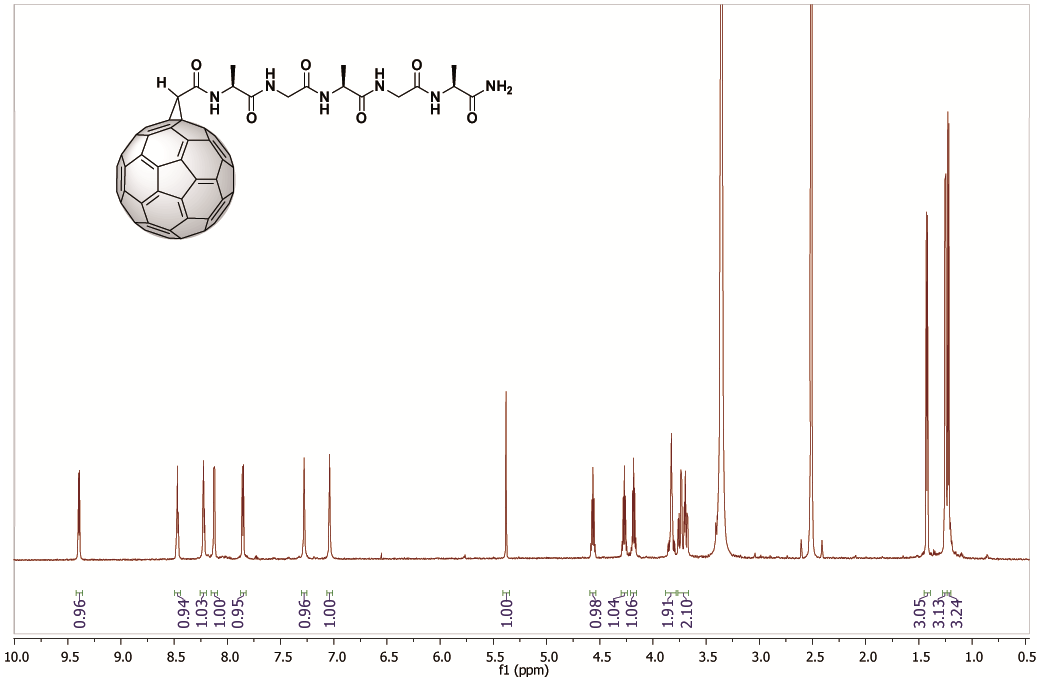


3

The coupling between the [6,6]-methanofullerene-C_{61}-carboxylic acid and the pentapeptide (AGAGA-NH_2) was performed in liquid phase. In a round bottom-flask, 30 mg (0.0334 mmol) of [6,6]-methanofullerene-C_{61}-carboxylic acid in a mixture of anhydrous DMF (4 mL) and dry toluene (4 mL) were activated by adding HBTU (0.0668 mmol) and DIPEA (0.234 mmol). After 5 minutes of activation, a solution of the pentapeptide (0.0334 mmol) in anhydrous DMF (2 mL) was added. The reaction was performed under argon atmosphere at room temperature. After 10 minutes of reaction, a precipitation was observed. After 2 hours of stirring the mixture was filtered and the solid was washed thoroughly with toluene, CS_2, diethyl ether and MeOH. The product was obtained as a brownish solid with a yield of 71%. ^{1}H-NMR (700 MHz, DMSO-d_6) δ 1.22 (d, J = 7.1 Hz, 3H, CH_3-Ala), 1.25 (d, J = 7.1 Hz, 3H, CH_3-Ala), 1.42 (d, J = 7.1 Hz, 3H, CH_3-Ala), 3.67-3.76 (m, 2H, CH_2-Gly), 3.79-3.87 (m, 2H, CH_2-Gly), 4.16-4.21

[3] Isaacs, L.; Diederich, F. *Helv. Chim. Acta*, **1993**, 76, 2554-2464.

(m, 1H, CH-Ala), 4.24-4.30 (m, 1H, CH-Ala), 4.54-4.59 (m, 1H, CH-Ala), 5.38 (s, 1H), 7.04 (s, 1H, NH_2), 7.28 (s, 1H, NH_2), 7.85 (d, *J* = 7.5 Hz, 1H, NH-Ala), 8.12 (d, *J* = 6.8 Hz, 1H, NH-Ala), 8.22 (t, *J* = 5.8 Hz, 1H, NH-Gly), 8.47 (t, *J* = 5.7 Hz, 1H, NH-Gly), 9.39 (d, *J* = 7.0 Hz, 1H, NH-Ala) ppm. ^{13}C-NMR (175 MHz, DMSO-d_6) δ 18.5, 18.7, 18.9, 40.5, 42.4, 42.5, 48.5, 49.0, 49.5, 73.2, 73.4, 136.2, 140.0, 140.1, 140.6, 140.9, 142.0, 142.1, 142.2, 142.58, 142.59, 142.72, 142.74, 142.82, 142.83, 142.88, 142.90, 143.0, 143.2, 143.7, 143.86, 143.88, 143.97, 144.01, 144.17, 144.20, 144.3, 144.5, 144.8, 144.89, 144.94, 145.0, 145.1, 145.6, 145.7, 146.07, 146.14, 147.9, 148.2, 149.97, 150.04, 164.4, 168.7, 169.2, 172.8, 173.0, 174.6. HRMS ESI: $[M + Na]^+$ Calc. for $C_{75}H_{24}N_6O_6Na$: 1127.1650; found $[M + Na]^+$: 1127.1633. Mp: > 350 ºC.



2. Supplementary Figures

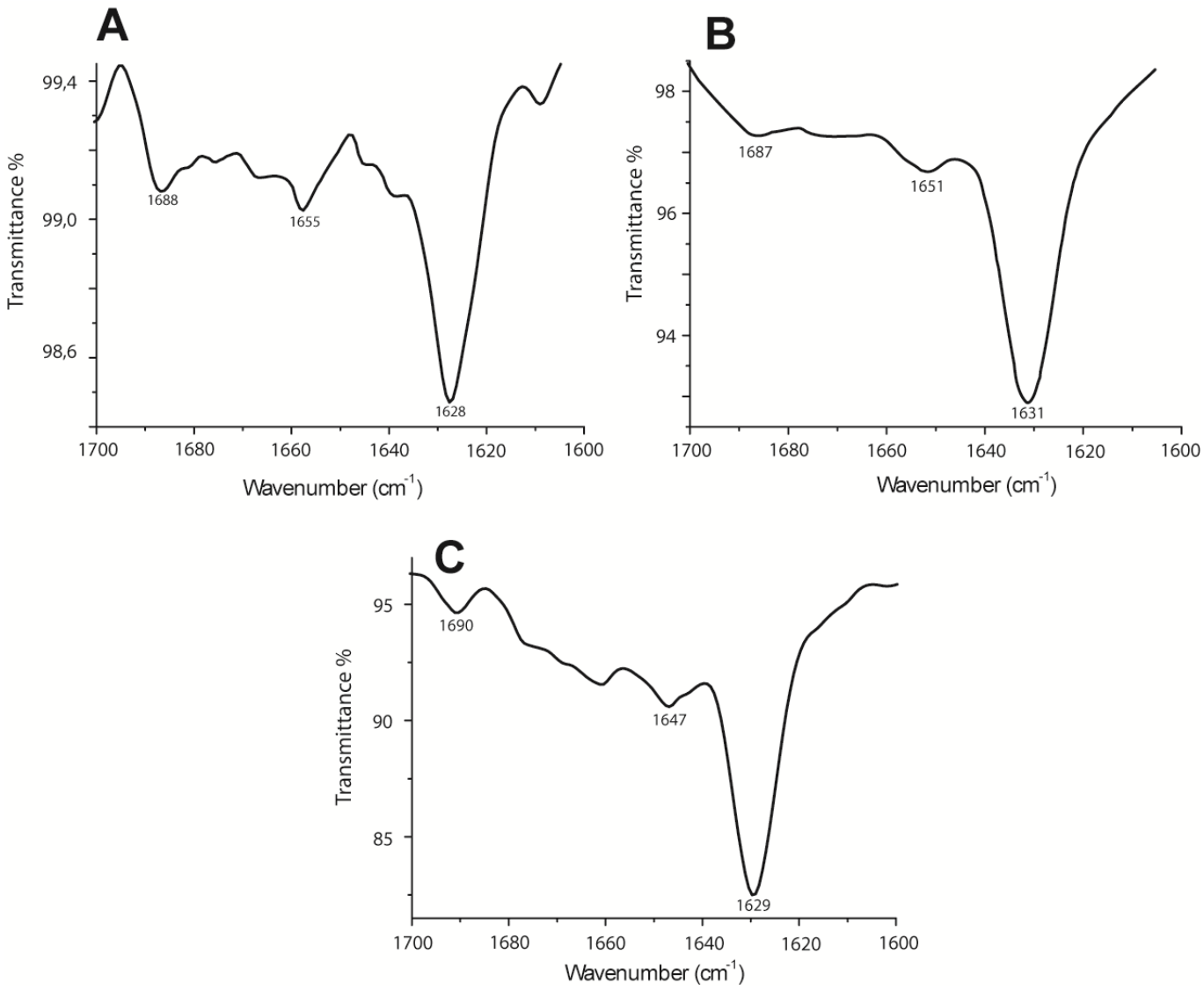


Figure S1. ATR-FTIR of compounds **1** (A), **2** (B) and **3** (C) in the mixture TCE:DMSO (10%). All the compounds show the amide I band around 1630 cm^{-1} and a weak shoulder around 1690 cm^{-1} which is in agreement with the existence of a β-sheet in an antiparallel fashion. The band at 1650 cm^{-1} suggests the existence of random coil aggregates.

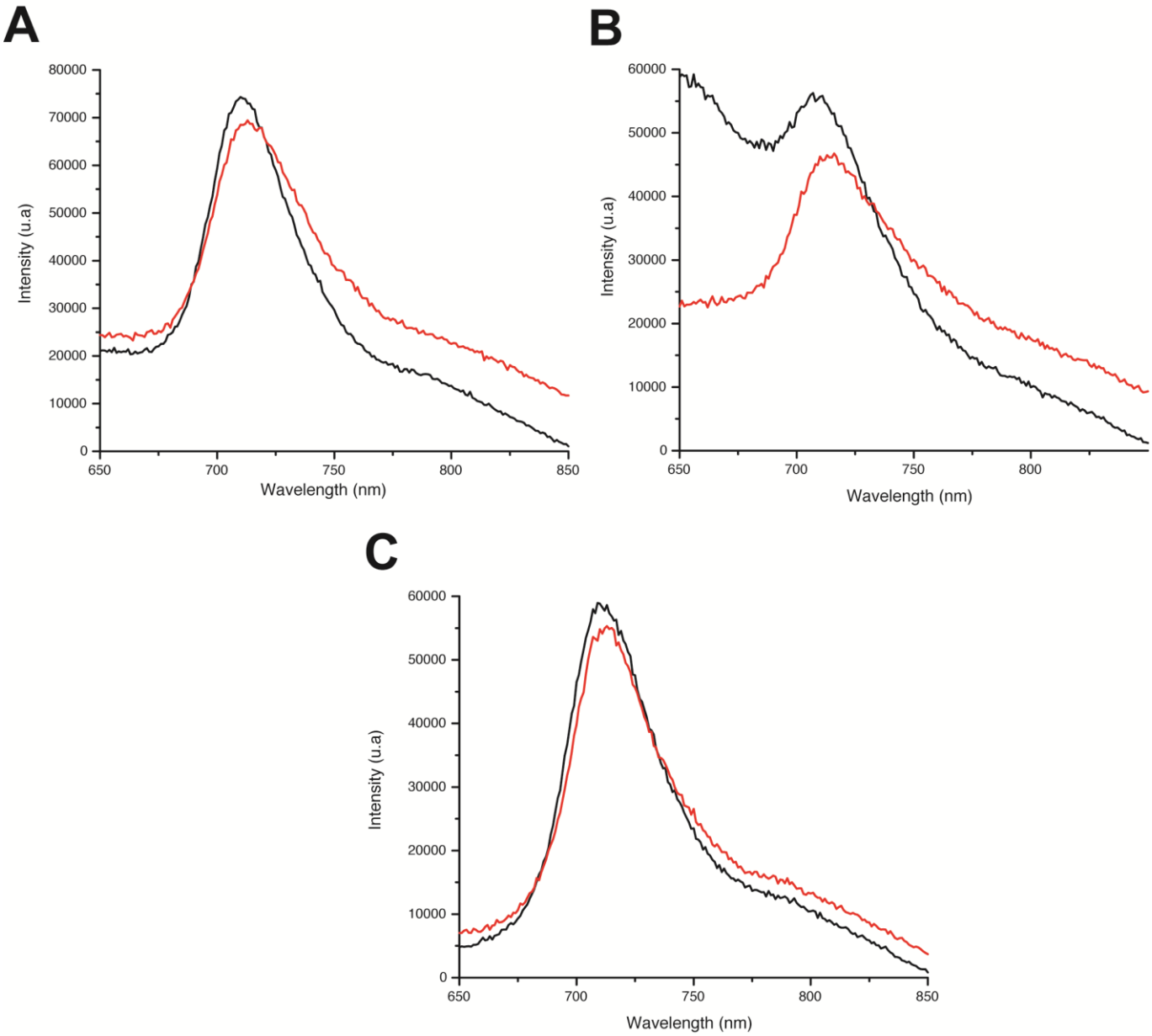


Figure S2. Fluorescence spectra of compounds **1** (A), **2** (B) and **3** (C) in DMSO (black lines) and the mixture TCE:DMSO (10%) (red lines) (λ_{exc}= 463 nm). The intensity of the [60]fullerene fluorescence with maxima at ~709 nm decreased and shifted slightly in the mixture TCE:DMSO compared to that obtained in DMSO.

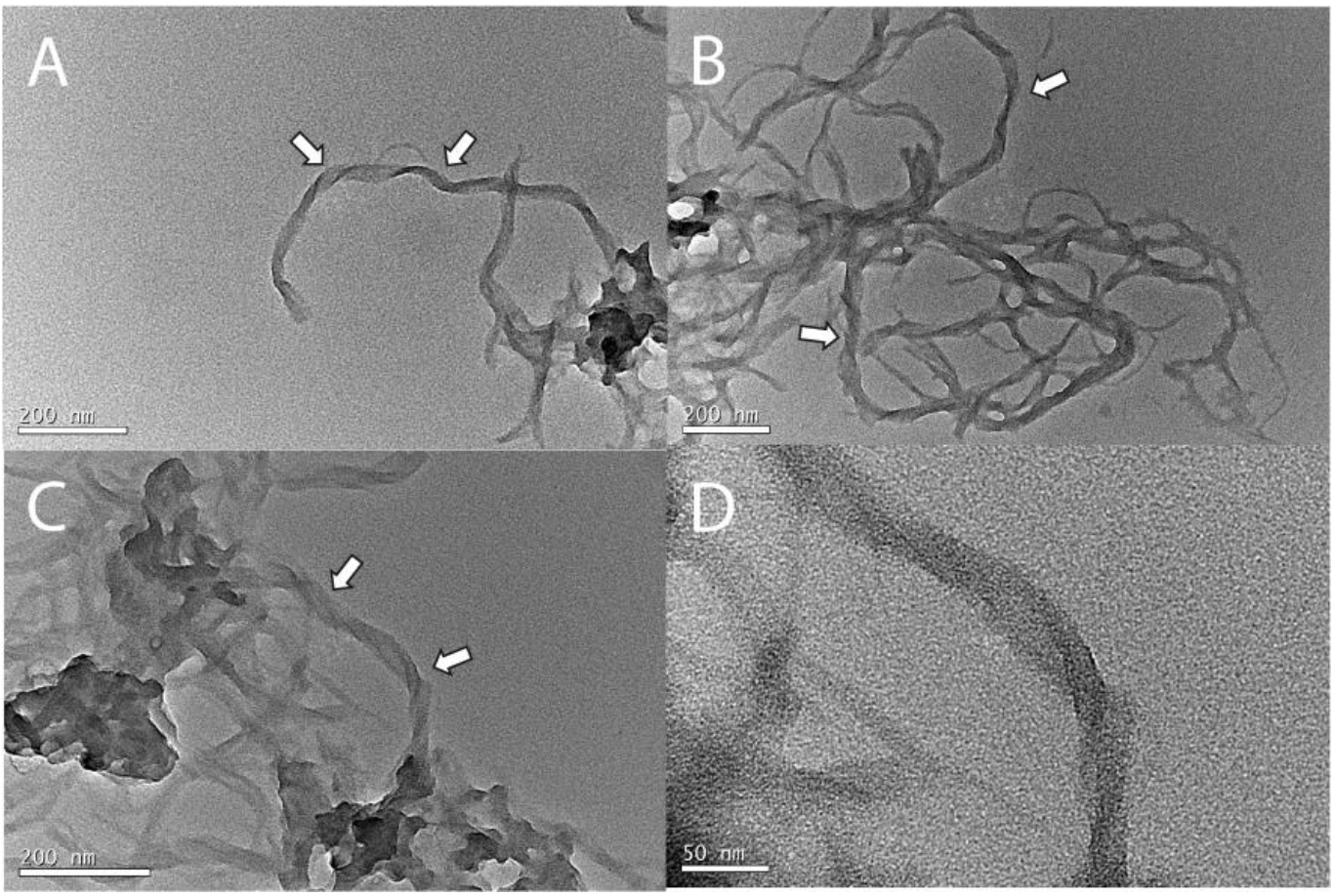


Figure S3. TEM images of compound **1** in a mixture of TCE:DMSO (10%). White arrows indicate how fibers are twisted in some points.

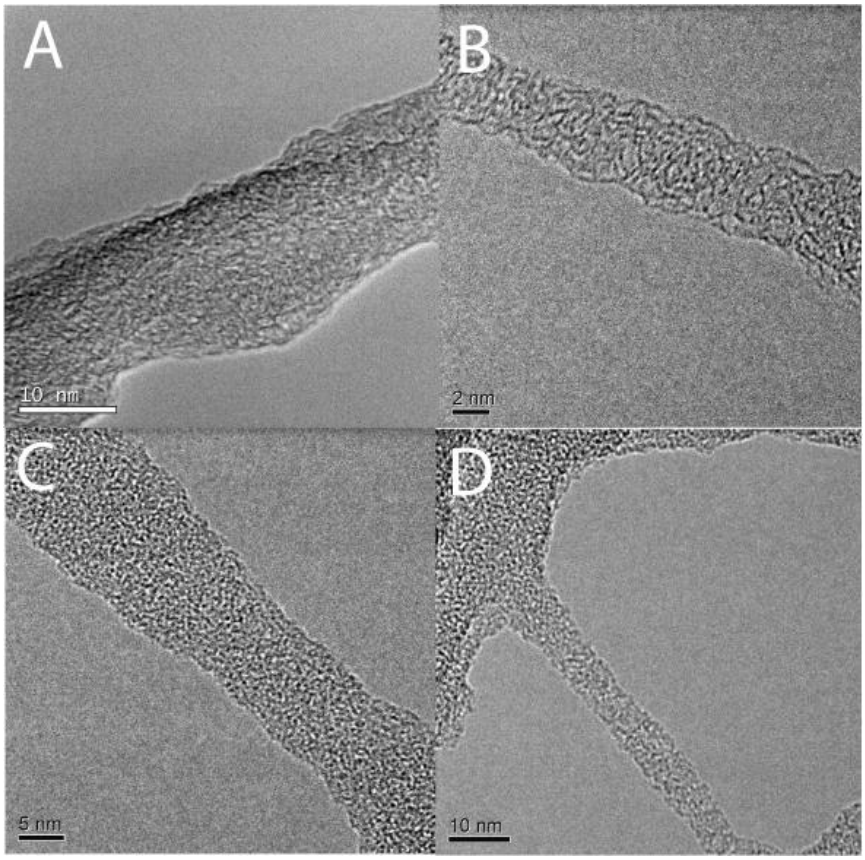


Figure S4. HRTEM images of compounds **2** (A-B) and **3** (C-D) in a mixture of TCE:DMSO (10%).