Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supporting Information

Ultrafast Electron Transfer in All-Carbon-Based SWCNT-C_{60} Donor-Acceptor Nanoensembles connected by Poly(phenylene-ethynylene) Spacers

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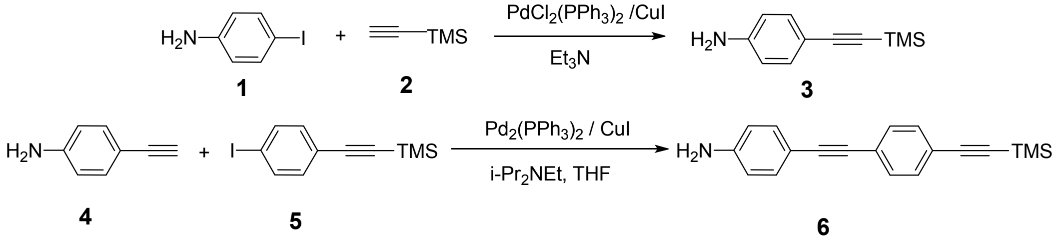
Contents

1. Synthesis of oligo(phenylene ethynylene)



Scheme S1. Structures of the desired molecules **3** and **6**.

Synthesis of 4-[(Trimethylsilyl)ethynyl]aniline (3)[1]

To a stirring solution of 4-iodoaniline (5 gr, 22.8 mmol) in triethylamine (40 mL) was added at room temperature bis(triphenylphosphine)palladium(II) dichloride (80 mg, 0.114 mmol), copper(I) iodide (43.4 mg, 0.2 mmol) and TMSA (3.5 mL, 1.1 equiv.). The mixture was stirred overnight. Then, the mixture was filtered and the filtrate was washed with ether (100 mL). The combined organic phase was then washed with NH_4Cl (2 M) (2x 100 mL), brine and dried over Na_2SO_4 to give the desired product as a white solid (4.2 gr, 97%). ^{1}H-RMN (400 MHz, $CDCl_3$, δ/ppm): 7.30 (d, 2H, J=8.8 Hz), 6.40 (d, 2H, J=8.4 Hz), 3.65 (s, 2H), 0.15 (s, 9H).

Synthesis of (4-Iodo-phenylethynyl)trimethylsilane (5)[1]

To a round-bottom flask fitted with an addition funnel and nitrogen inlet was added $BF_3(O(C_2H_5)_2)$ (2.6 mL, 21.1 mmol, 4 equiv.) which was then chilled in a dry ice-acetone bath (-20 ºC). To the reaction flask was added dropwise over 5 minutes a solution of the aniline derivative **3** (1 gr, 5.28 mmol, 1 equiv.) in dry ether, followed by a solution of *tert*-butylnitrite (2.2 mL, 18.48 mmol, 3.5 equiv.) also in dry ether. The mixture was then stirred an additional 10 minutes, and the cold bath was allowed to warm to 5 ºC over 15 minutes. To the mixture was added diethyl ether, and the mixture was chilled in an ice-bath for 15 minutes. The solid was collected by filtration, washed with diethyl ether, and dried to give the diazonium salt. After briefly air-drying, the diazonium salt was dissolved in acetonitrile (CH_3CN) and then added dropwise *via* cannula to a solution of NaI (870 mg, 5.8 mmol, 1.1 equiv.) and I_2 (134.5 mg, 0.5 mmol, 0.1 equiv.) in CH_3CN. The mixture was stirred at room temperature for 1 hour, then $Na_2S_2O_3$ (aq) (2 M) was added to the mixture. The mixture was extracted with CH_2Cl_2 (3x80mL), and the organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography (silica gel), first with hexane and then mixtures of hexane/EtOAc to give the desired product (600 mg, 38%). ^{1}H-RMN (400 MHz, $CDCl_3$, δ/ppm): 7.64 (d, 2H, *J*=8.5 Hz), 7.19 (d, 2H, *J*=8.5 Hz), 0.25 (s, 9H).

Synthesis of 4-Ethynylaniline (4)

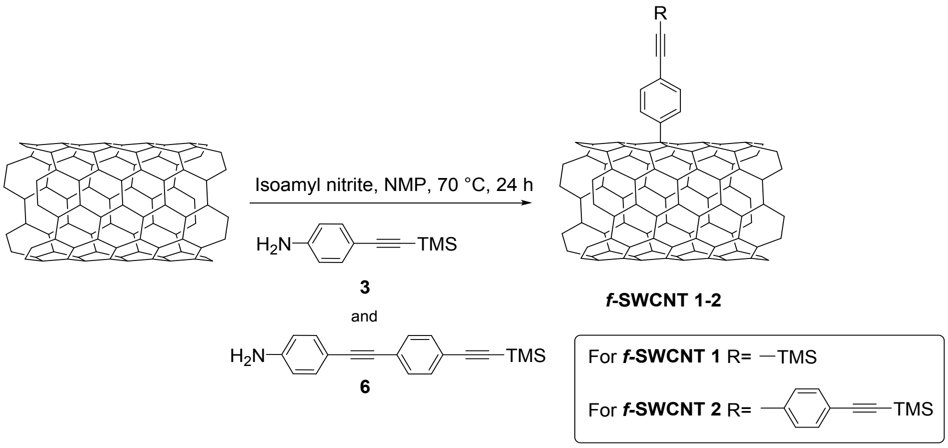
The silylated alkyne (1gr, 5.28 mmol, 1 equiv.) was dissolved in a mixture of CH_2Cl_2/MeOH (50:50). Potassium carbonate (1,45 gr, 10.6 mmol, 2 equiv.) was added, and the reaction was stirred overnight. Water was added and the reaction mixture was extracted with CH_2Cl_2, dried with $MgSO_4$, filtered, and then the solvent was removed under reduced pressure. The resulting product was used without further purification (700 mg, 5.06 mmol, 96%).^{1}H-RMN (400 MHz, $CDCl_3$, δ/ppm): 7.31 (d, 2H, *J*=8.6 Hz), 6.61 (d, 2H, *J*=8.6 Hz), 2.97 (s, 1H).

Synthesis of 1-trimethylsilylethynyl-4-((4-aminophenyl)-ethynyl)benzene (6)[2]

A slight excess of 4-ethynylaniline (1.2 equiv, 500 mg, 4.27 mmol) was added to a solution of the iododerivative (1.05 gr, 3.56 mmol, 1 equiv), *N,N*-Diisopropylethylamine (4 equiv,2.5 mL, 14.2 mmol), 2 mol% of $PdCl_2(PPh_3)_2$ and 4 mol % of CuI in THF (50 mL). After stirring 24 hours under argon at room temperature, the solvent was evaporated, water was added and the crude was extracted with CH_2Cl_2.

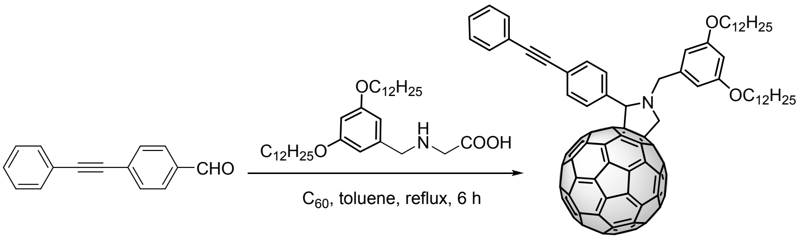
The organic layer was dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel) using hexane/EtOAc mixtures (8:2) as eluent to yield the desired product as a yellow solid (520 mg, 1.79 mmol, 50%). ^{1}H-RMN (400 MHz, $CDCl_3$) δ/ppm: 7.42 (s, 4H), 7.35 (d, 2H, *J*=8.4 Hz), 6.67 (d, 2H, *J*= 8.1 Hz), 4.13 (br s, 2H, NH_2).

2. Scheme S2. Synthesis of hybrids 1-2



Scheme S2. Preparation of *f*-SWCNTs **1** and **2** by the Tour reaction.

3. Scheme S3. Synthesis of control fulleropyrrolidine sample 8



control 8

Scheme S3. Synthetic route for the preparation of the control sample.

Synthesis of control fulleropyrrolidine 8

A solution of C_{60} (785 mg, 1.09 mmol), (3,5-bis(dodecyloxy)benzyl)glycine[3] (194.12 mg, 0.36 mmol) and diphenylacetylene-4-carboxaldehyde[4] (75 mg, 0.36 mmol) in toluene was heated under reflux for 6 h. The mixture was cooled, filtered and the solvent was evaporated under reduced pressure. Column chromatography (SiO_2, CH_2Cl_2/hexane 2:8) yielded the desired product (40 mg, 8%) as a brown solid.

7. Figure S1. TGA

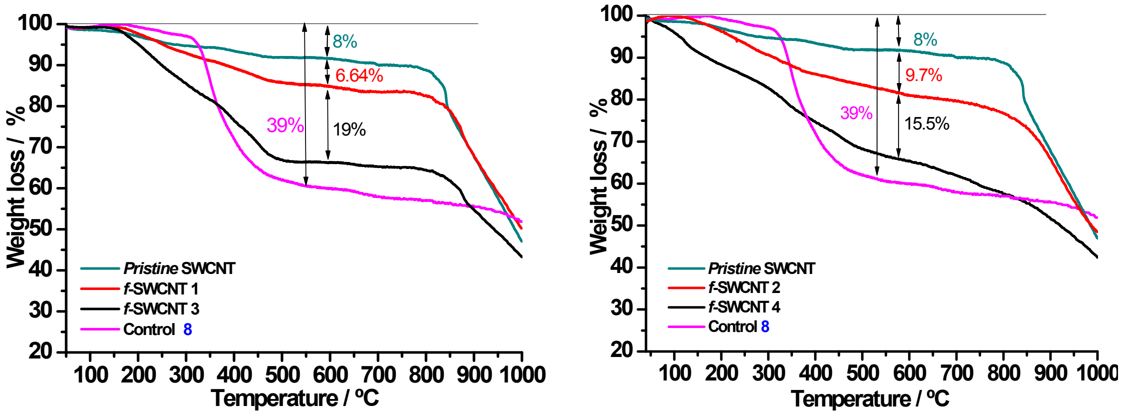


Figure S1. TGA graphs for *pristine* SWCNT, functionalized samples *f*-SWCNT **3** (left) and *f*-SWCNT **4** (right) and the control fullerene derivative **8**.

8. Figure S2 Raman

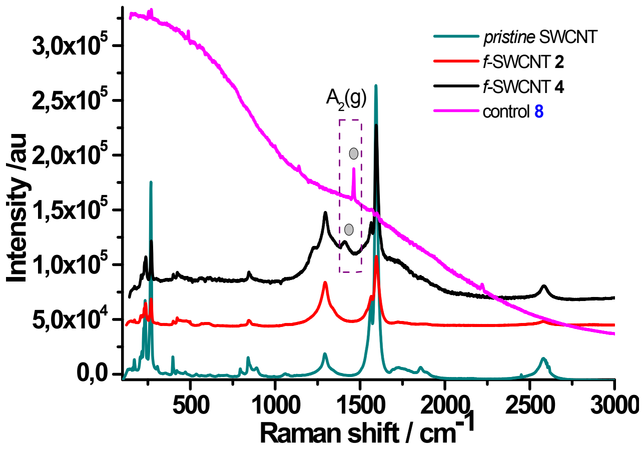


Figure S2. Raman spectra of *pristine* SWCNT, the functionalized samples *f*-SWCNT **2** and *f*-SWCNT **4** and the control sample **8**, λ_{exc} = 785 nm.

9. Figures S3-S6. XPS data

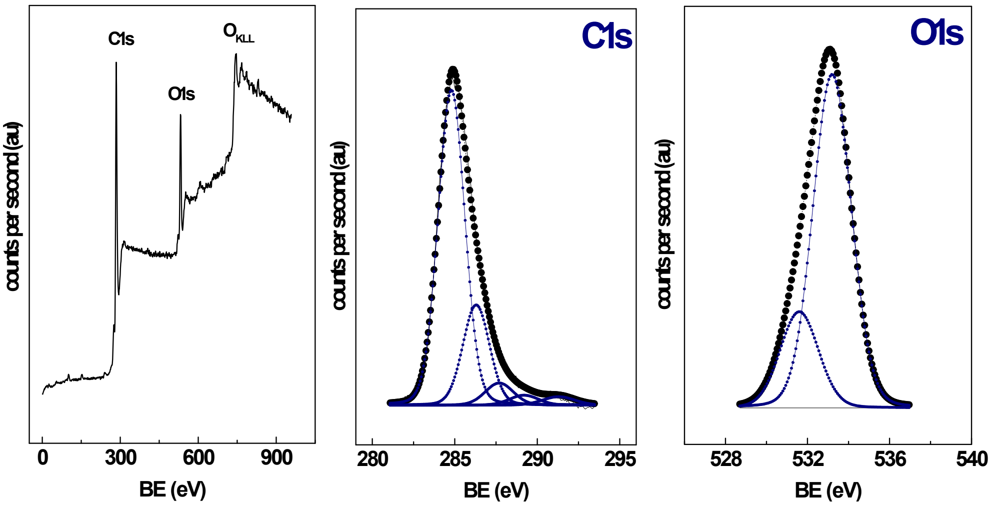


Figure S3. Survey, C1s and O1s core-level spectra of *pristine* SWCNT.

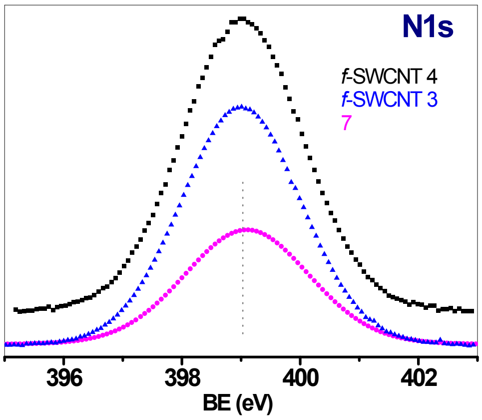


Figure S4. XPS high-resolution spectra the N 1s regions for nanohybrids **3** and **4** and also its precursor **7**.

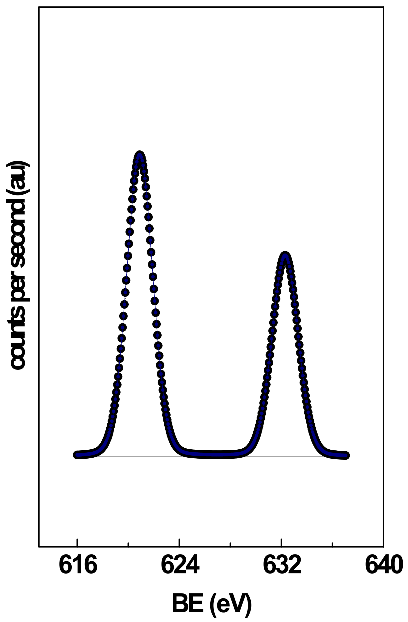


Figure S5. I 3d core-level spectra of pyrrolidine fullerene **7**.

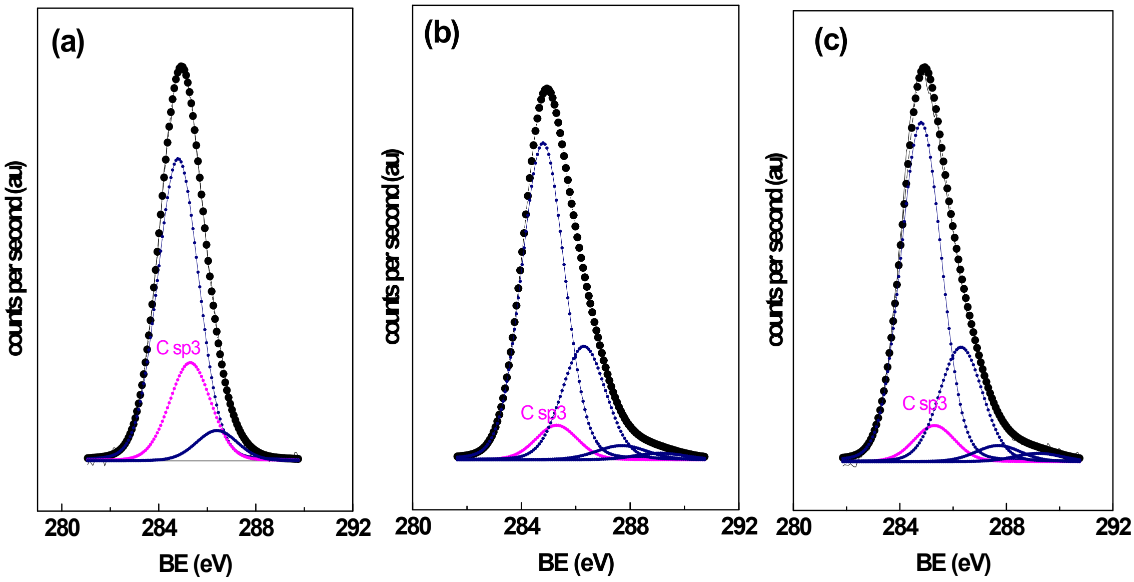


Figure S6. C1s core-level spectra of (a) pyrrolidino derivative **7**, (b) *f*- SWCNT **3** and (c) *f*- SWCNT **4**.

7. Figure S7 FTIR spectra

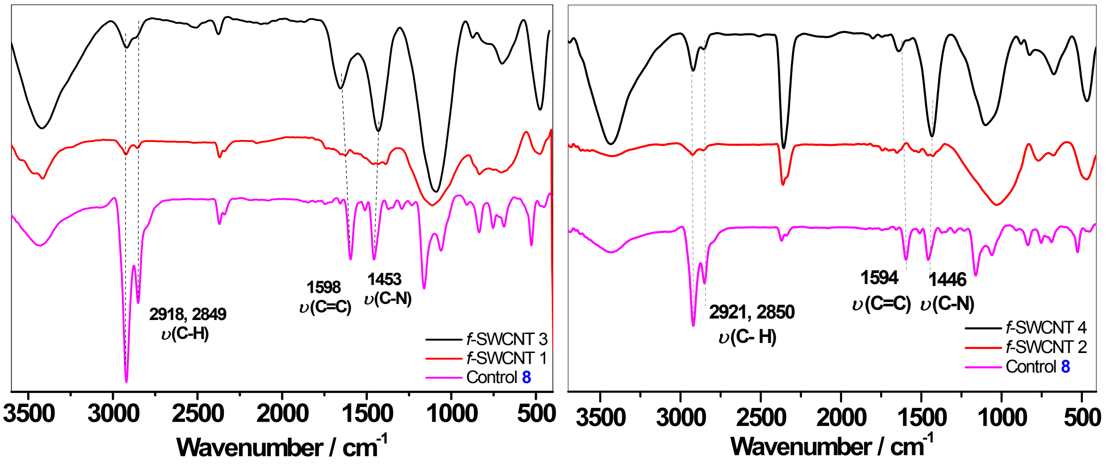


Figure S7. FTIR spectra of the functionalized samples *f*-SWCNT **3** and *f*-SWCNT **4** compared to the **control** sample **8**.

8. Figure S8 AFM images

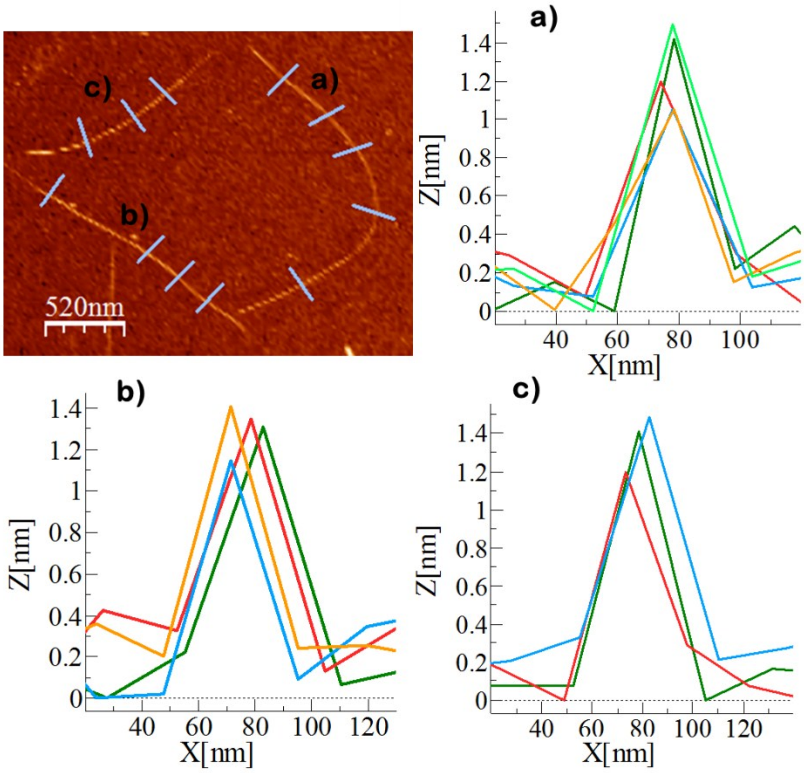


Figure S8. AFM Images of HiPco SWCNTs on a SiO_2 surface. The Z-profiles show an average diameter of ~1.2 nm.

9. Figure S9. Molecular mechanic calculations

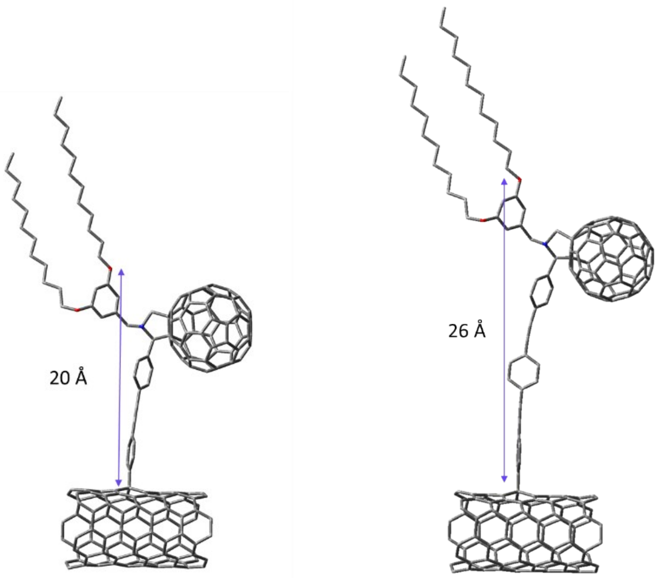


Figure S9. Modelling structures optimized using semiempirical PM3 method implemented on HyperChem 8.0 program package.

10. Figure S10. HR-TEM images

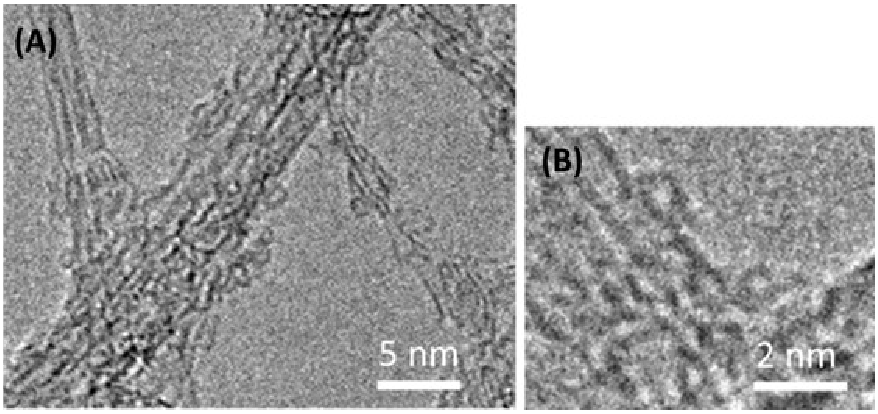


Figure S10. TEM images of *f*-SWCNT **3**.

11. Figure S11. Molecular mechanic calculations

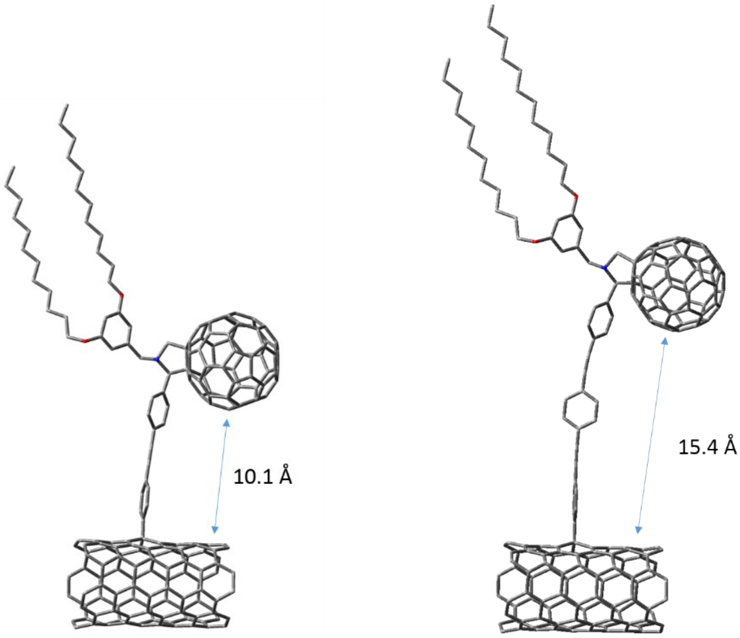


Figure S11. Modelling structures optimized using semiempirical PM3 method implemented on HyperChem 8.0 program package.

12. Figure S12 UV-vis spectra

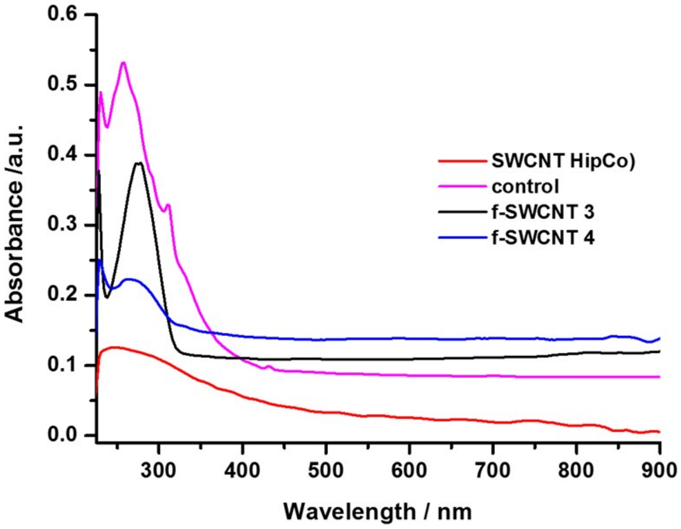


Figure S12. Absorption spectra of suspensions of nanoensembles **3** and **4**, the fullerene control compound **8** and *pristine* SWCNT in DMF.

13. Figure S13 Chemical oxidation of SWCNT

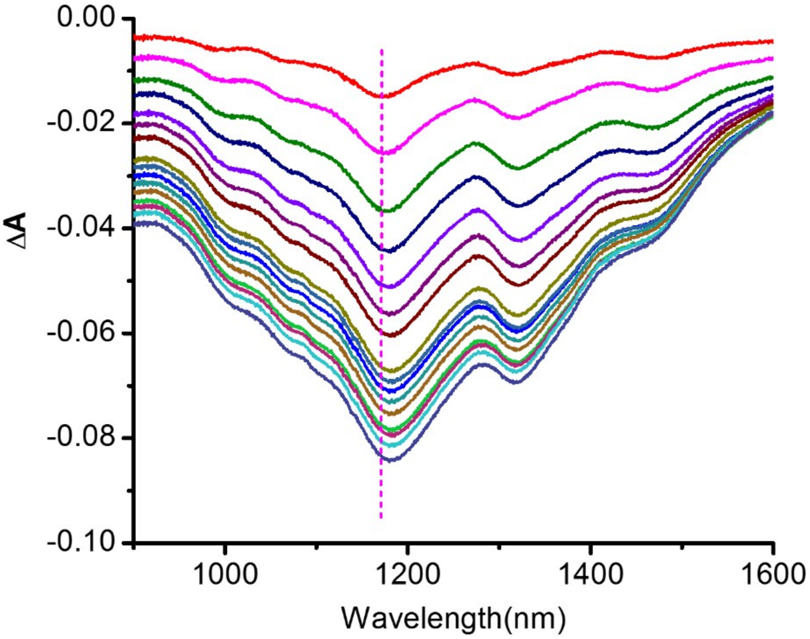


Figure S13. Differential absorption spectra of SWCNT upon increasing addition of nitrosonium hexafluoroborate in *o*-dichlorobenzene.

14. Figure S14 Transient spectra

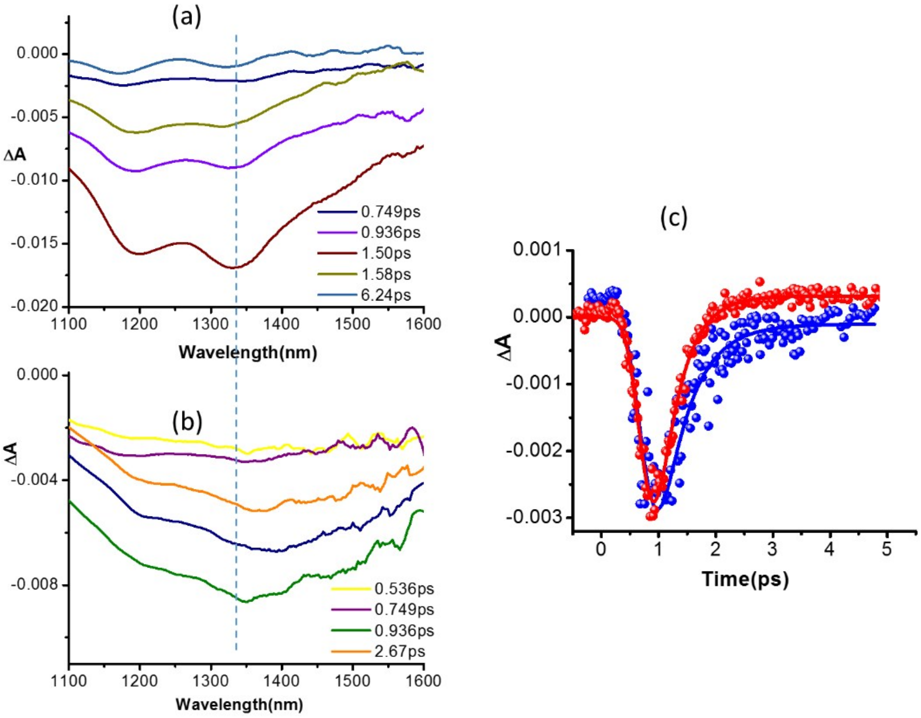


Figure S14. Femtosecond transient absorption spectra of (a) pristine SWCNT (HIPCo) and (b) *f*-SWCNT **3** in NMP at the excitation wavelength of 400 nm at the indicated delay times. (c) Time profile of the 1330 nm peak of pristine SWCNT (blue) and 1352 nm peak of *f*-SWCNT **3** (red).

15. Figure S15 Transient spectra

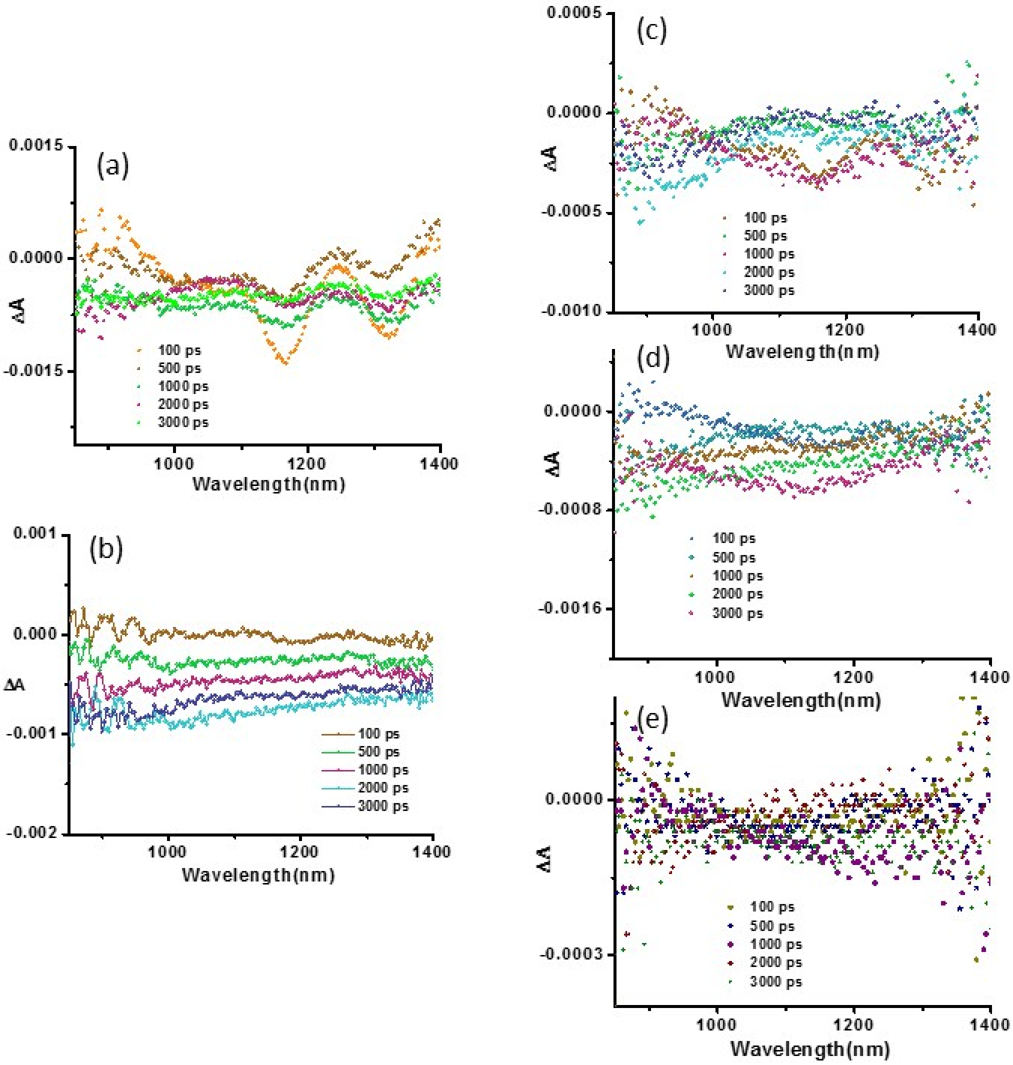


Fig S15. Femtosecond transient spectra at the indicated delay times of (a) SWCNT-HIPCO and (b) *f*-SWCNT **3** in DMF at the excitation wavelength of 400 nm. Femtosecond transient spectra at the indicated delay times of (c) SWCNT-HIPCO, (d) *f*-SWCNT **3** and (e) *f*-SWCNT **4** in DMF at the excitation wavelength of 800 nm.

16. Table S1 Binding energies

Table S1. Binding energy (eV) of the core-level atoms of SWCNTs samples and its precursors. The peak percentages are indicated in brackets.

Sample	C1s	O1s	N1s	Si2p	I3d
pristine SWCNT	284.8 (69) 286.3 (22) 287.7 (5) 289.2 (2) 291.3 (2)	531.6 (27) 533.2 (73)	-	-	-
7	284.8 (66) 285.3 (22) 286.3 (7) 287.7 (5)	532.4	399.0	-	620.9
f-SWCNT **1**	284.8 (65) 286.3 (24) 288.1 (11)	531.7 (24) 533.3 (76)	-	102.0	-
f-SWCNT **2**	284.8 (64) 286.3 (24) 287.7 (12)	531.6 (23) 533.2 (77)	-	102.1	-
f-SWCNT **3**	284.8 (74) 286.3 (23) 287.7 (2) 289.2 (1)	531.6 (36) 533.1 (64)	399.1	-	-
f-SWCNT **4**	284.8 (76) 286.3 (21) 287.7 (2) 289.2 (1)	531.6 (34) 533.2 (66)	399.0	-	-

17. Table S2 Electrochemistry

Table S2. Electrochemical data [V *vs.* Ag/AgNO$_3$] for the reduction processes of *f*-SWCNTs **3** and **4**, and their reference compounds (control sample **8** and C$_{60}$) determined by OSWV.[a]

Sample	E^{1}red(V)	E^{2}red(V)	E^{3}red(V)
C$_{60}$	–1.02	–1.42	–1.90
control 8	–1.13	–1.53	–2.07
f-SWCNT **3**	–1.19	–1.54	–2.09
f-SWCNT **4**	–1.15	–1.51	–2.04

[a] In *o*-DCB/acetonitrile (4 : 1 v/v) solution (0.1 M TBAPF$_6$) at room temperature. Values referenced to Fc/Fc$^+$ internal standard.

18. References

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1 J. J. Hwang and J. M. Tour, *Tetrahedron*, 2002, **58**, 10387.

2 G. Pera, S. Martín, L. M. Ballesteros, A. J. Hope, P. J. Low, R. J. Nichols and P. Cea, *Chem. Eur. J.*, 2010, **16**, 13398.

3 F. Ajamaa, T. M. Figueira Duarte, C. Bourgogne, M. Holler, P. W. Fowler and J.-F. Nierengarten, *Eur. J. Org. Chem.*, **2005**, 3766–3774.

4 K. Worm-Leonhard and M. Melda, *Eur. J. Org. Chem.*, 2008, **31**, 5244.