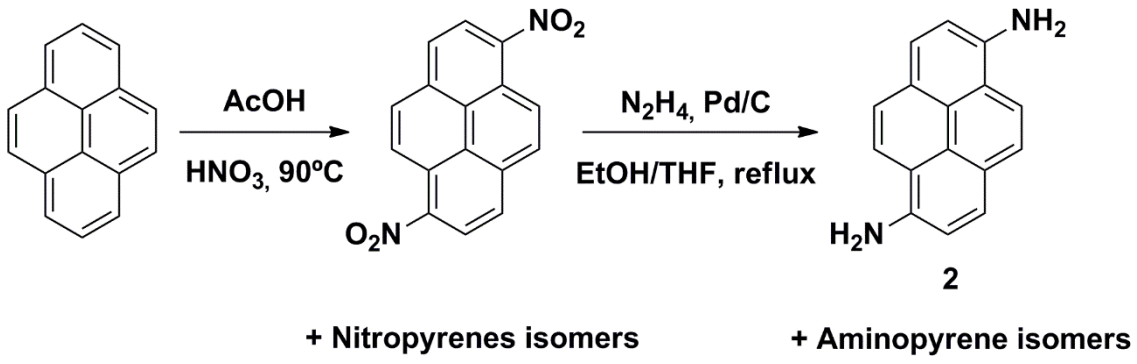
Supplementary Information

Synthesis and characterization

General. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh, or Scharlau 60, 230-240 mesh). Analytical thin layer chromatographies (TLC) were performed using aluminium-coated Merck Kieselgel 60 F254 plates. The NMR experiments were performed on a Bruker Avance 400 spectrometer (Magnet Ascend 400), operating at a frequency of 400 MHz and Bruker Avance 300 spectrometer (Magnet Ascend 400), operating at a frequency of 300 MHz at 298 K, unless otherwise stated, using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Fast atom bombardment (FAB) ionization experiments were recorded on a Waters VG AutoSpec spectrometer and Matrix-assisted Laser desorption ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a HP1100MSD spectrometer and a Bruker REFLEX spectrometer, respectively. Thermogravimetric analyses (TGA) were performed using a TA Instruments TGAQ500 with a ramp of 50 °C/min under nitrogen from 100 to 1000 °C.

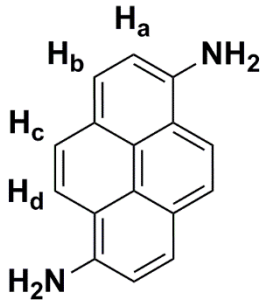
Synthesis of compound **2**



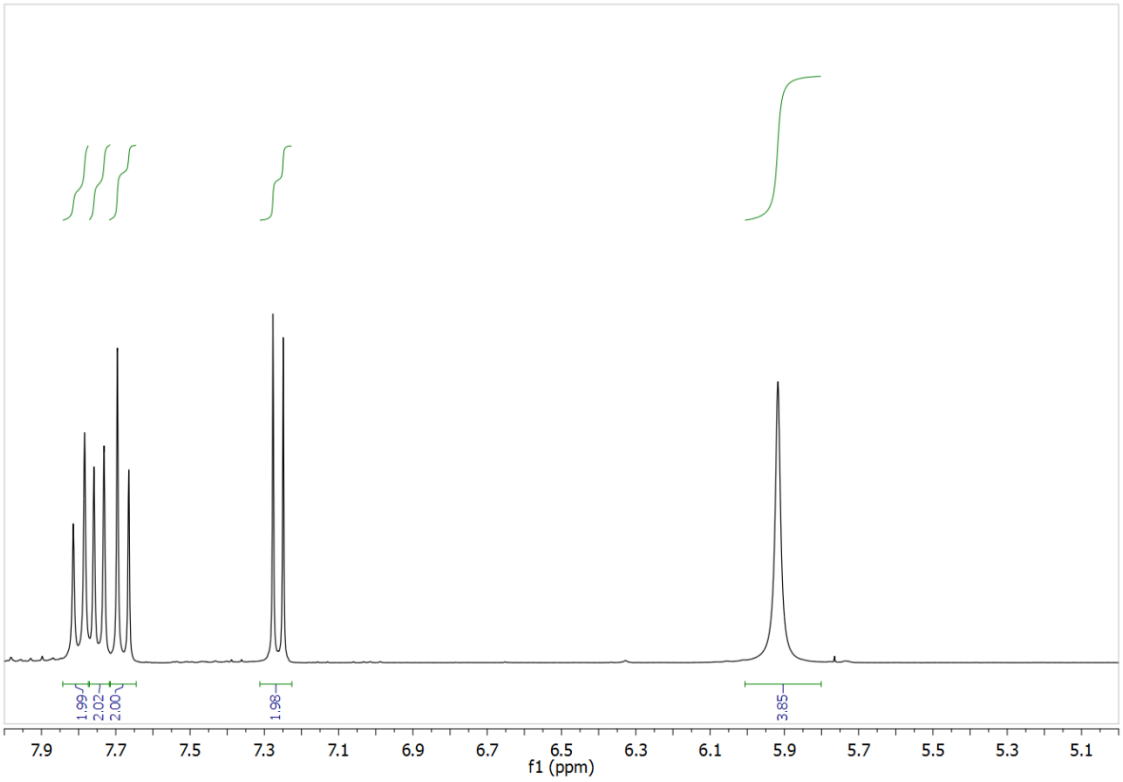
Nitropyrenes were synthetized as described in *Chem. Pharm. Bull.*, **1984**, *32*, 1992-1997.

Nitropyrenes (1.45 g) were dissolved in a mixture of ethanol and tetrahydrofuran (2:1, 12 mL) and palladium on activated charcoal (27 mg) was added over the solution. The mixture was refluxed, hydrazine (1.8 mL, 37 mmol) was added and then refluxed for 12 h. The mixture was filtered and the solvent was removed under vacuum. The aminopyrenes were purified by column chromatography (silica gel, 10% Ethyl acetate in dichloromethane).

Rf (10% Ethyl acetate in dichloromethane) values were 0.9 for 1-aminopyrene (Compound **8c**, 20%), 0.6 for 1,6-diaminopyrene (Compound **2**, 25%), 0.4 for 1,3-diaminopyrene and 0.3 for 1,8-diaminopyrene.



Compound **2**. ^{1}H NMR (300 MHz, DMSO-d6) δ 7.80 (d, J = 9.2 Hz, 2H, H_c), 7.75 (d, J = 8.2 Hz, 2H, H_b), 7.68 (d, J = 9.2 Hz, 2H, H_d), 7.26 (d, J = 8.2 Hz, 2H, H_a), 5.92 (s, 4H, NH_2). ^{13}C NMR (75 MHz, DMSO-d6) δ 142.8, 127.1, 125.5, 124.3, 123.1, 117.3, 116.6, 113.4. MS *m/z* calculated for $C_{16}H_{12}N_2$ [M^+] 232.1 found MALDI-TOF 232.1.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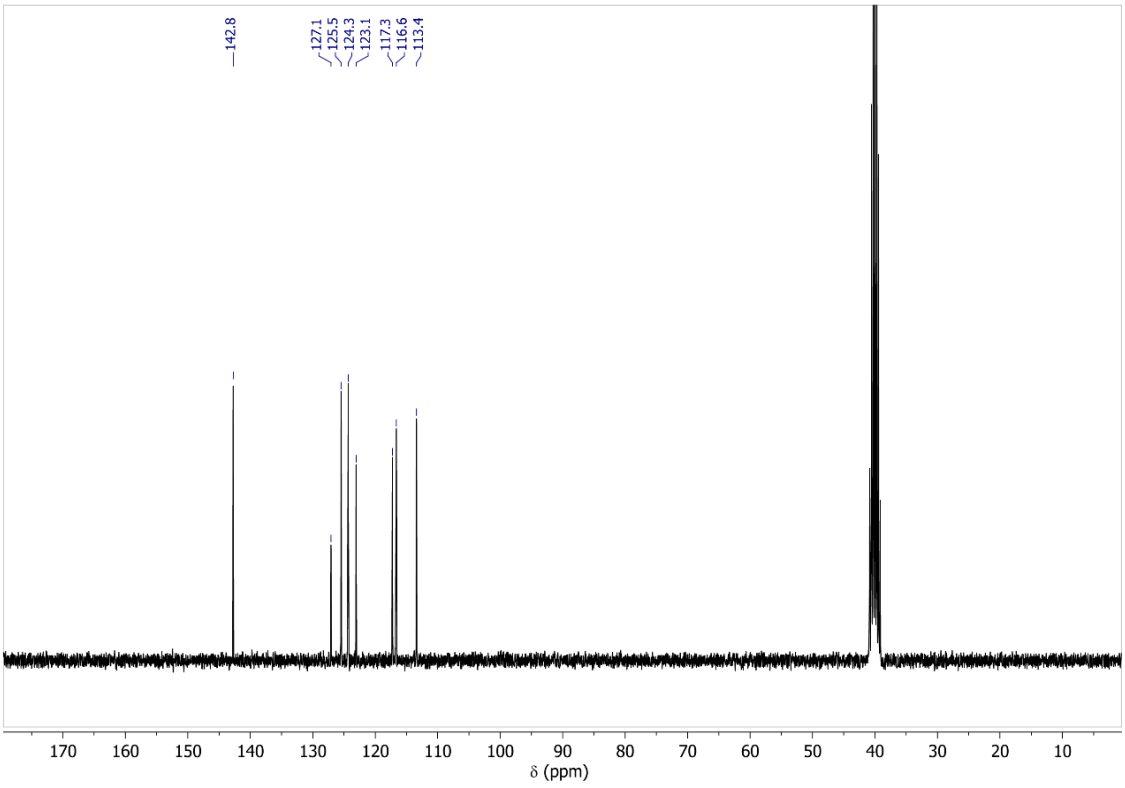
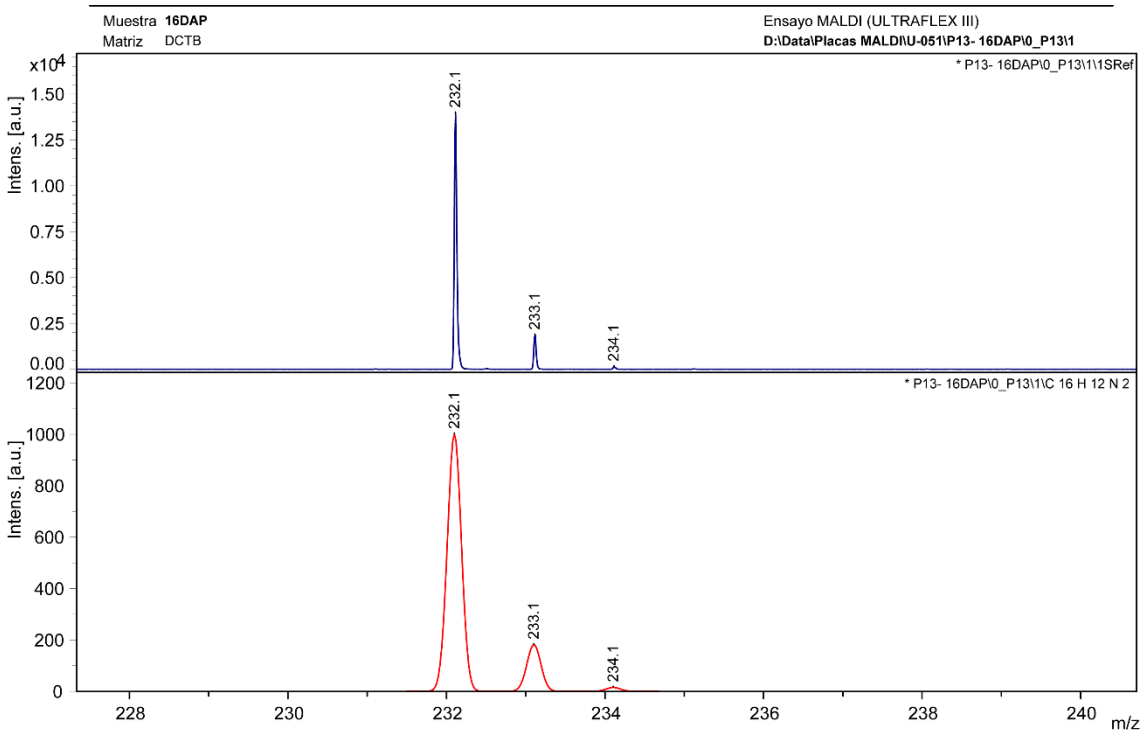
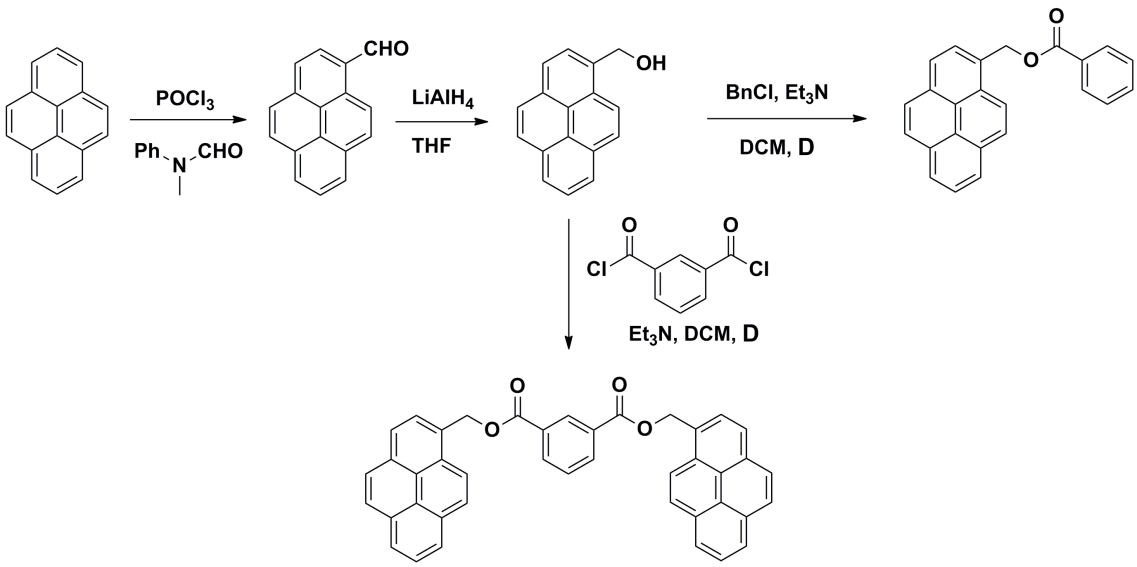
2.00
1.98
3.85
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
6.3
6.1
5.9
5.7
5.5
5.3
5.1
f1 (ppm)


142.8
127.1
125.5
124.3
123.1
117.3
116.6
113.4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
δ (ppm)



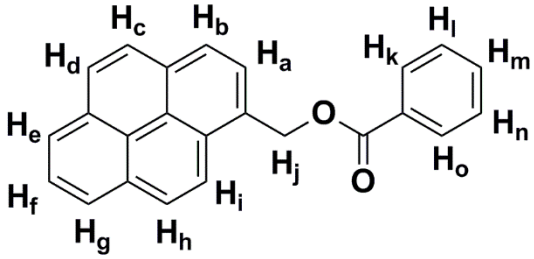
Synthesis of compound**s 3** and **4**



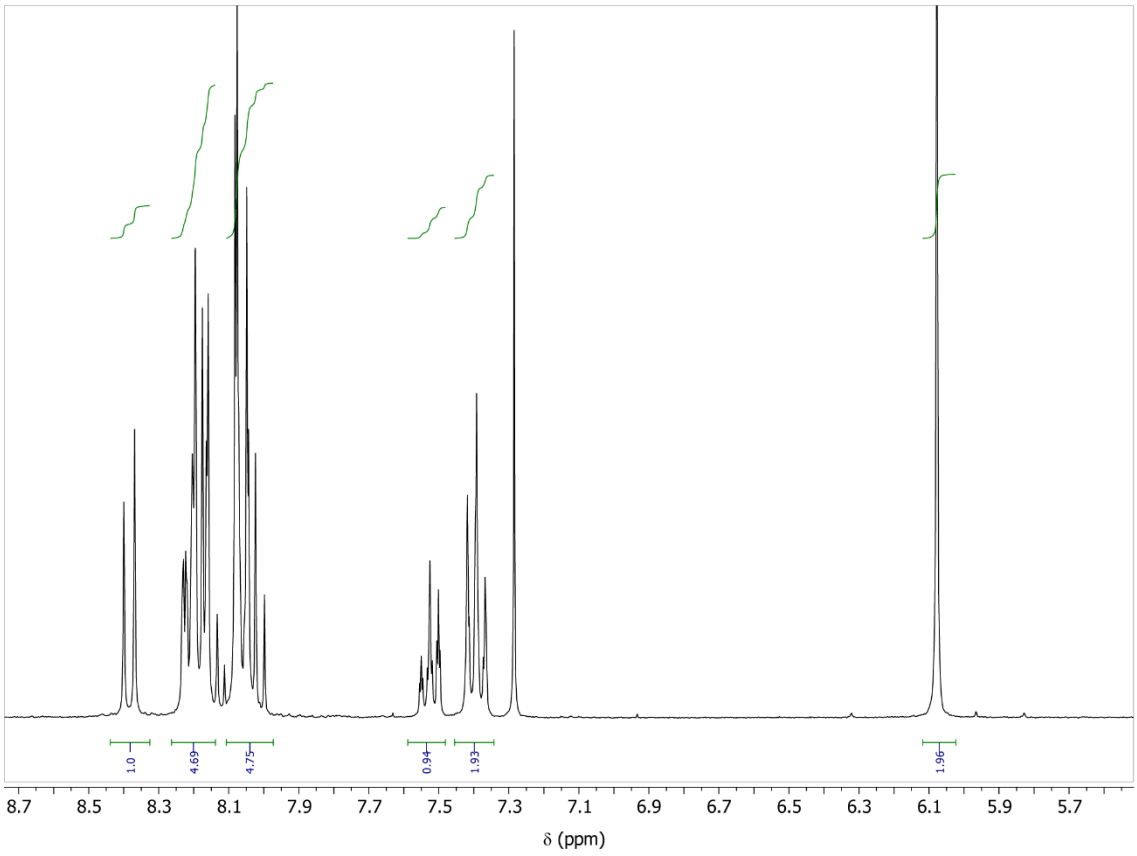
1-pyrenemethanol was synthetized as described in *Chem. Eur. J.* **2010**, *16*, 9154.

Compound **3.** 1-pyrenemethanol (1.05 g, 4.48 mmol) was dissolved in chloroform (40 mL) and triethylamine (0.93 mL, 6.72 mmol) was added. Then benzoyl chloride (0.94 g, 6.72 mmol) was added and the mixture was refluxed for 3 h. After this time the solvent

was removed under vacuum and hexane was added. The product was recovered by filtration and washed several times with hexane to obtain compound **3** in quantitative yield.



Compound **3.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, J = 9.2 Hz, 1H, H_e), 8.24 – 8.15 (m, 5H, $H_{b+g+f+k+o}$), 8.10 – 7.99 (m, 5H, $H_{a+c+i+h+d}$), 7.59 – 7.47 (m, 1H, H_m), 7.43 – 7.35 (m, 2H, H_{l+n}) 6.08 (s, 2H, H_j).^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 133.1, 131.8, 131.3, 130.8, 130.2, 129.8, 129.7, 129.0, 128.4, 128.4, 127.9, 127.8, 127.4, 126.2, 125.6, 125.5, 125.0, 124.7, 123.0, 65.4. MS *m/z* calculated for $C_{24}H_{16}O_2$ [M^+] 336.1 found MALDI-TOF 336.2.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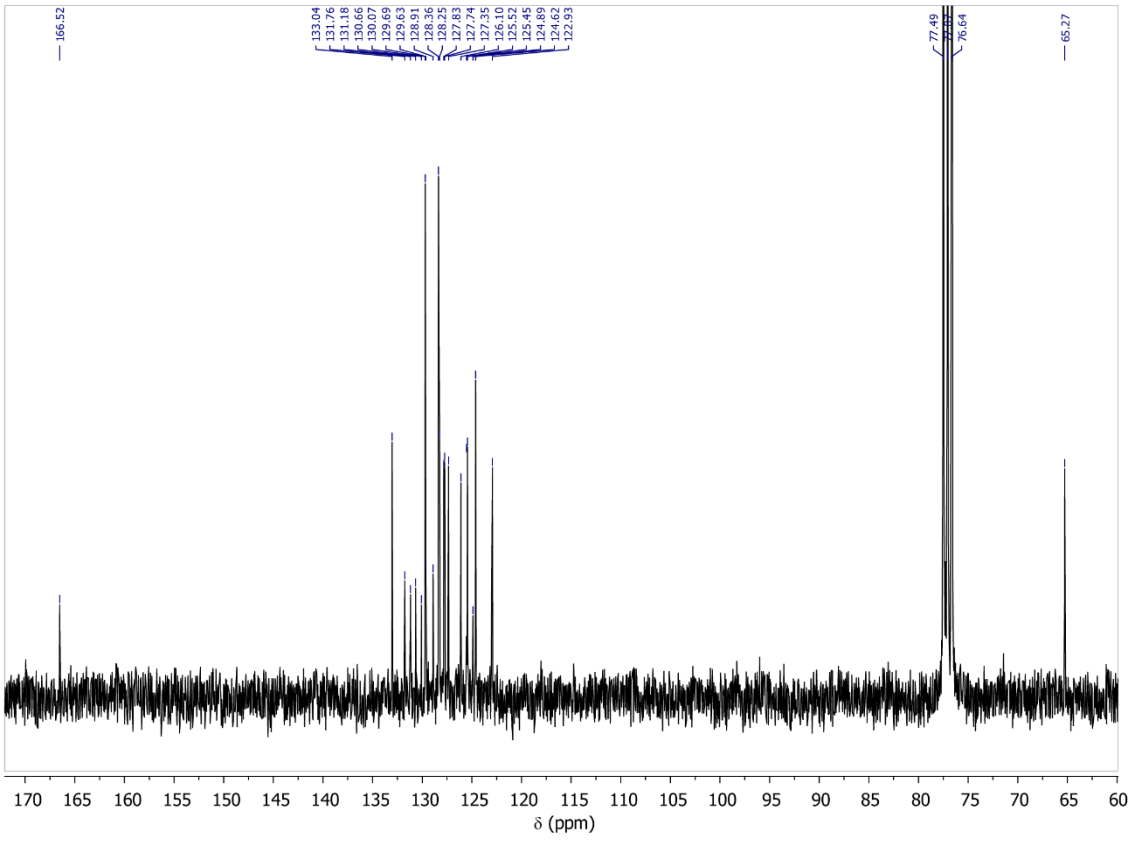
4.69
4.75
0.94
1.93
1.96
8.7 8.5 8.3 8.1 7.9 7.7 7.5 7.3 7.1 6.9 6.7 6.5 6.3 6.1 5.9 5.7
δ (ppm)


166.52
133.04
131.76
131.18
130.66
130.07
129.69
129.63
128.91
128.36
128.25
127.83
127.74
127.35
126.10
125.52
125.45
124.89
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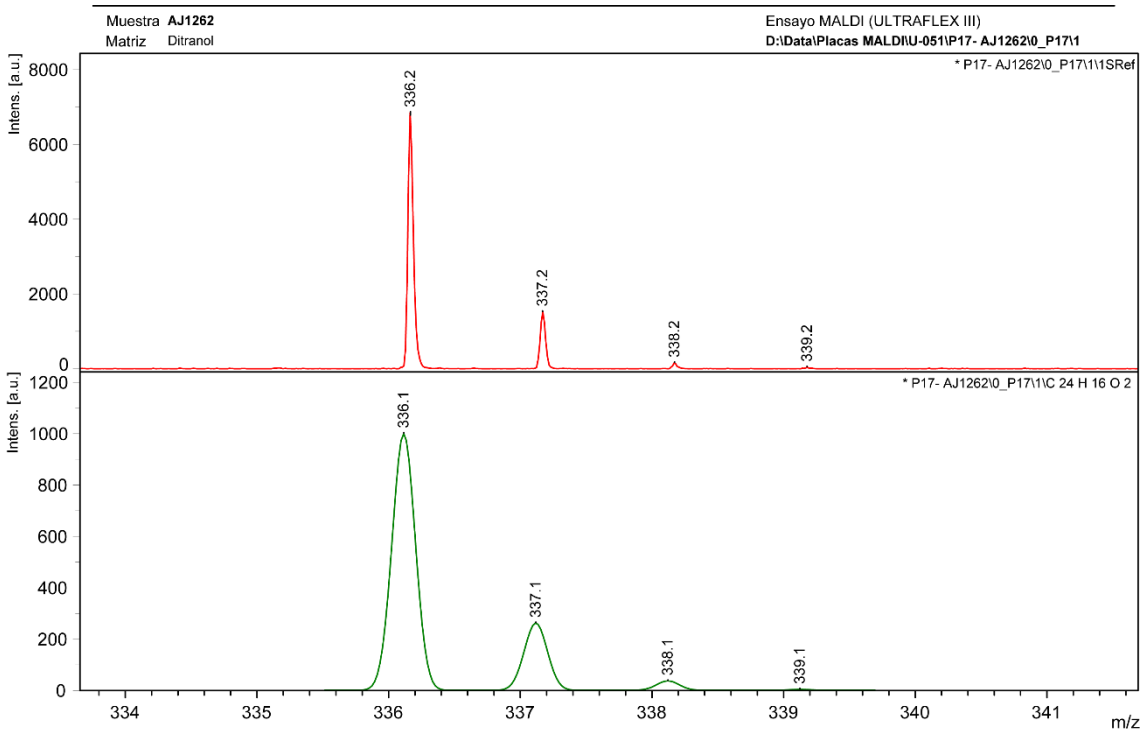
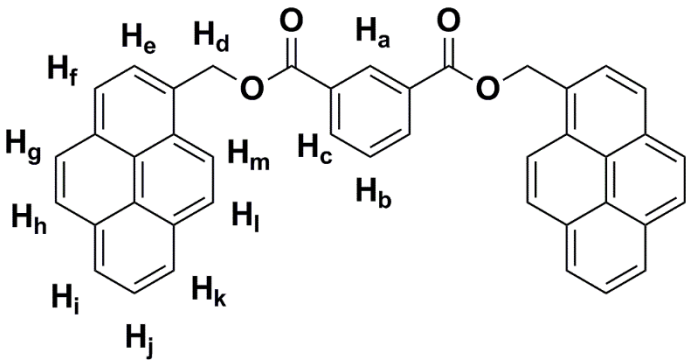
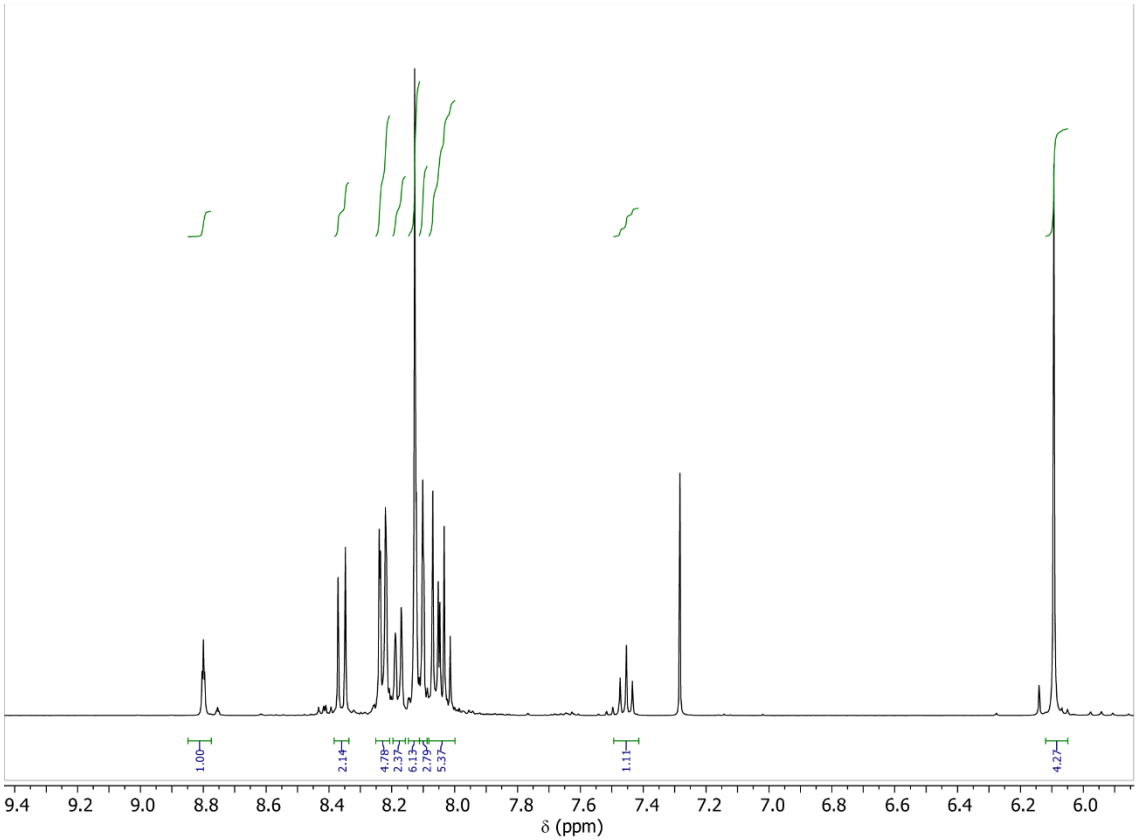
65.27
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60
δ (ppm)

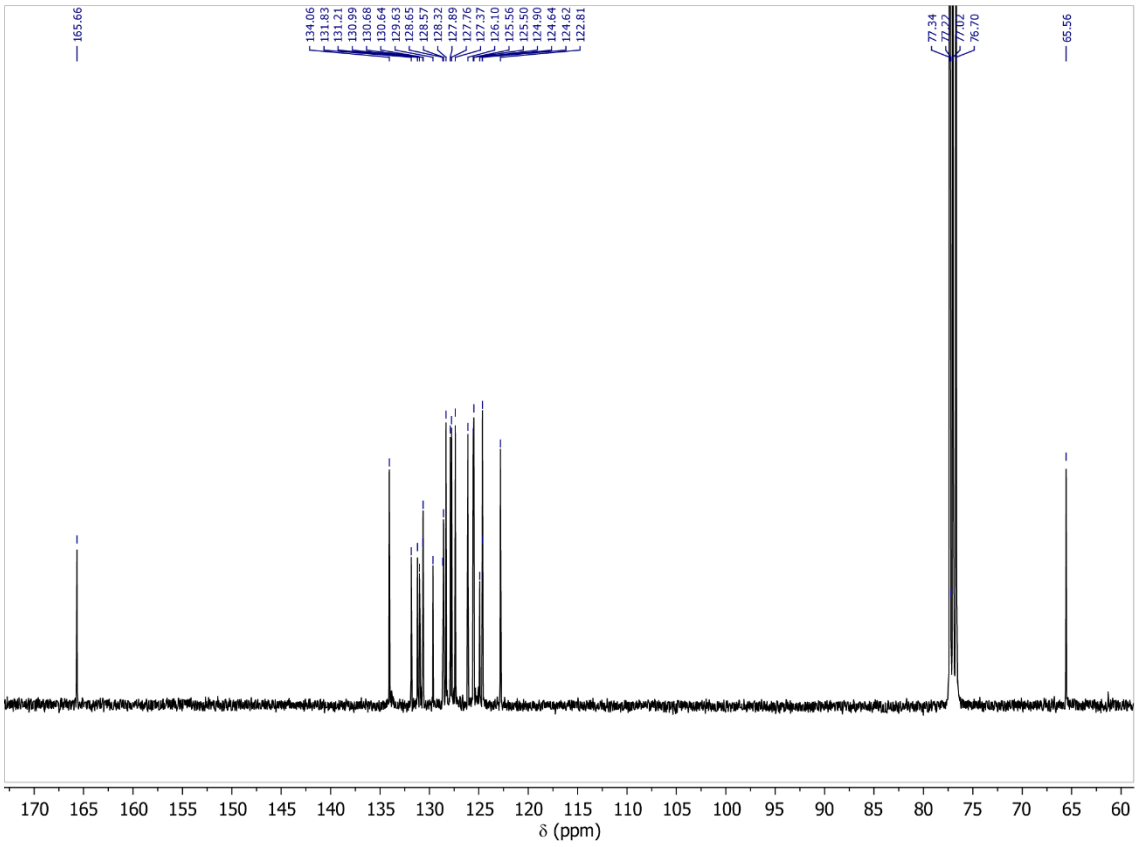


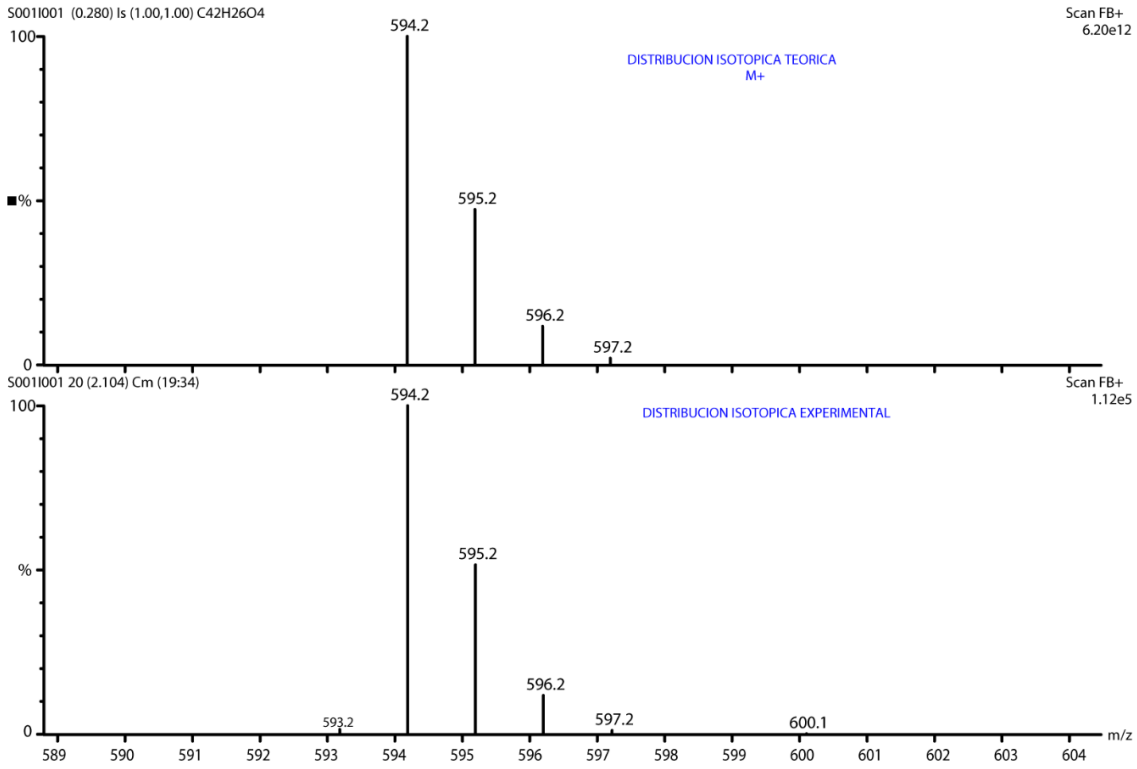
Compound **4.** 1-pyrenemethanol (1 g, 4.27 mmol) was dissolved in chloroform (20 mL) and triethylamine (0.6 mL, 4.27 mmol) was added. Isophtaloyl dichloride (0.21 g, 1.07 mmol) was added and the mixture was refluxed for 4h. After this time an additional 30 mL of chloroform were added, and the solution washed sequentially with 50 mL of hydrochloric acid 2N, 50 mL of 5% $NaHCO_3$ aqueous solution and water. The organic layer was separated, dried over Na_2SO_4 and the solvent removed under vacuum to obtain a solid. Compound **4** (65%) was purified by column chromatography (silica gel, dichloromethane).



Compound **4**.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (t, J = 1.2 Hz, 1H, H_a), 8.37-8.34 (m, 2H, H_i), 8.24 – 8.16 (m, 4H, H_{f+c}), 8.18 (d, J = 7.6 Hz, 2H, H_k), 8.15 – 8.11 (m, 6H, H_{j+h+g}), 8.11 – 8.09 (m, 2H, H_m), 8.08 – 8.00 (m, 4H, H_{e+l}), 7.45 (t, J = 7.8 Hz, 1H, H_b), 6.09 (s, 4H, H_d). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 134.1, 131.8, 131.2, 131.0, 130.7, 130.6, 129.6, 128.6, 128.6, 128.3, 127.9, 127.8, 127.4, 126.1, 125.6, 125.5, 124.9, 124.6, 124.6, 122.8, 77.3, 65.6. MS *m/z* calculated for $C_{42}H_{26}O_4$ [M^+] 594.2 found FAB 594.2.




165.66
134.06
131.83
131.21
130.99
130.68
130.64
129.63
128.65
128.57
128.32
127.89
127.76
127.37
126.10
125.56
125.50
124.90
124.64
124.62
122.81
77.34
77.22
77.02
76.70
65.56
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60
δ (ppm)


S001I001 (0.280) Is (1.00,1.00) C42H26O4
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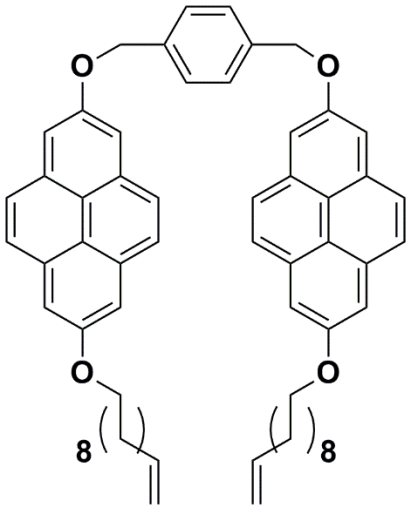
6.20e12
100
%
0
594.2
595.2
596.2
597.2
DISTRIBUCION ISOTOPICA TEORICA
M+
S001I001 20 (2.104) Cm (19:34)
Scan FB+
1.12e5
DISTRIBUCION ISOTOPICA EXPERIMENTAL
593.2
600.1
589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604
m/z

Synthesis of compound **5**



5

Compound **5** was synthetized as described in *Chem. Commun.* **2015**, *51*, 5421.

General procedure for titration

The titration curve for each host is formed using the TGA results of independent incubation experiments performed with different host concentration.

Each experiment proceeds as follows: the host molecule was dissolved in the corresponding solvent. Carbon nanotubes were added (1 mg/mL) and the suspension was stirred for 2 h at room temperature. Then, the mixture was filtered through a 0.2 μm-pore size polytetrafluorethylene membrane. The solid obtained was dried under vacuum and characterized by thermogravimetric analysis (N_2, ramp of 50 ºC/min, weight loss was measured from 100 ºC to 600 ºC).

Each independent experiment for each host concentration was repeated 3 times and the different results were averaged. A blank to determine the solvent adsorbed on or encapsulated in the carbon nanotube was carried out, and subtracted in the data analysis.

Table S1. Summary of results obtained from titrations at 298 K.

	Solvent	K_a (M^{-1})	Error (M^{-1})	Saturation (%)	r^2
1·pp-SWNTs	THF[a]	16.4	0.8	56	0.999
1·pp-SWNTs	THF	24	6	26	0.979
1·pp-SWNTs	THF[b]	21	4	28	0.985
1·pp-SWNTs	DMF	9	3	47	0.978
1·pp-SWNTs	TCE	4.5	0.9	59	0.987
1·pp-SWNTs	MeOH	2.6×10^3	0.2×10^3	15	0.998
1·(6,5)-SWNTs	THF	41	8	19	0.987
1·(6,5)-SWNTs	DMF	1.6	0.4	73	0.985
1·(6,5)-SWNTs	TCE	1.6	0.1	67	0.998
1·(6,5)-SWNTs	MeOH	1.0×10^3	0.1×10^3	12	0.994
2·pp-SWNTs	DMF	2.2×10^2	0.5×10^2	18	0.986
2·(6,5)-SWNTs	DMF	29	3	27	0.995
3·pp-SWNTs	THF	9×10	3×10	26	0.937
3·pp-SWNTs	TCE	20	5	24	0.965
4·pp-SWNTs	THF	6.5×10^3	0.6×10^3	13	0.998
4·pp-SWNTs	TCE	4×10^3	1×10^3	9	0.986
5·pp-SWNTs	THF	7×10^3	2×10^3	21	0.951

[a] 0.1 mg/mL of pp-SWNTs

[b] 10 mg/mL of pp-SWNTs

Thermogravimetric analysis

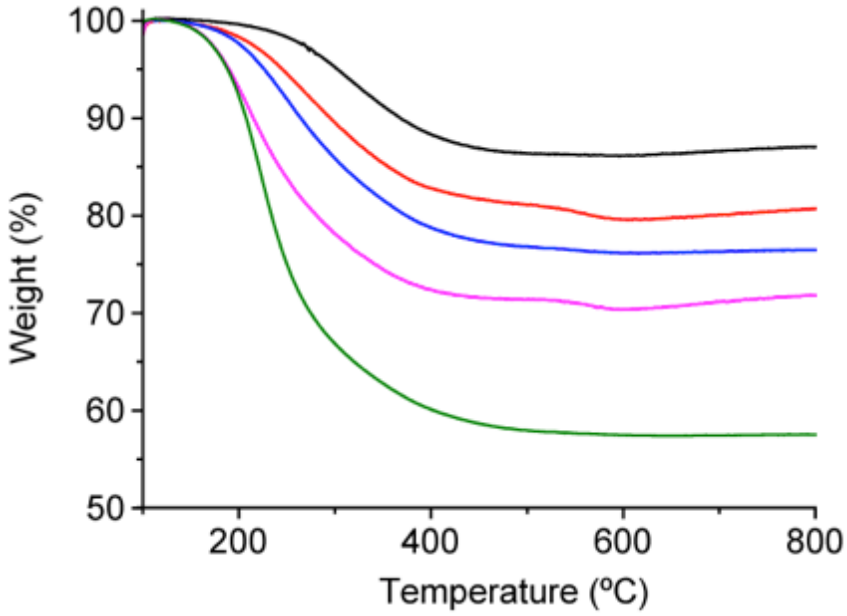


Figure S1. TG analysis of titration of **1** *vs* pp-SWNTs in THF at 0.1 mg/mL of SWNTs.

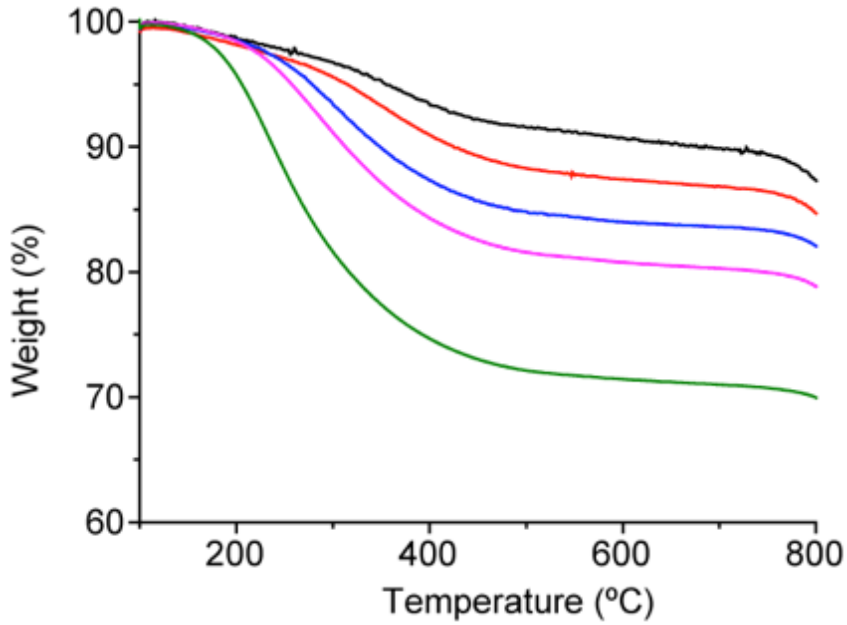


Figure S2. TG analysis of titration of **1** *vs* pp-SWNTs in THF at 1 mg/mL of SWNTs.

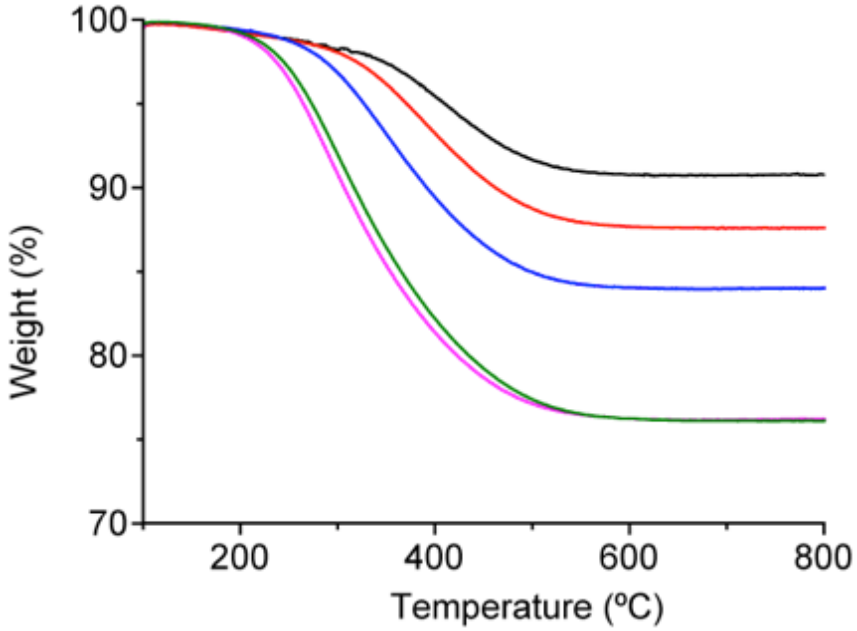


Figure S3. TG analysis of titration of **1** *vs* pp-SWNTs in THF at 10 mg/mL of SWNTs.

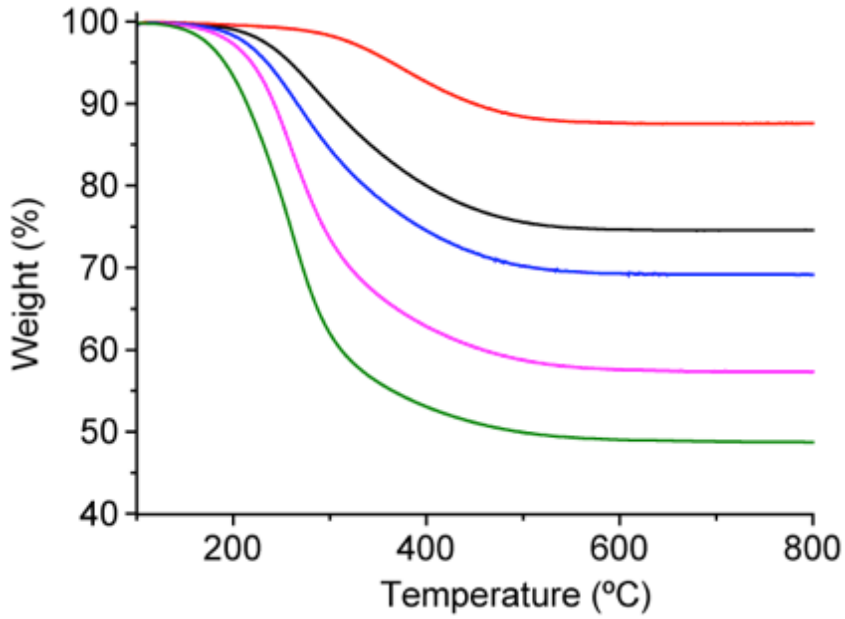


Figure S4. TG analysis of titration of **1** *vs* pp-SWNTs in DMF at 1 mg/mL of SWNTs.

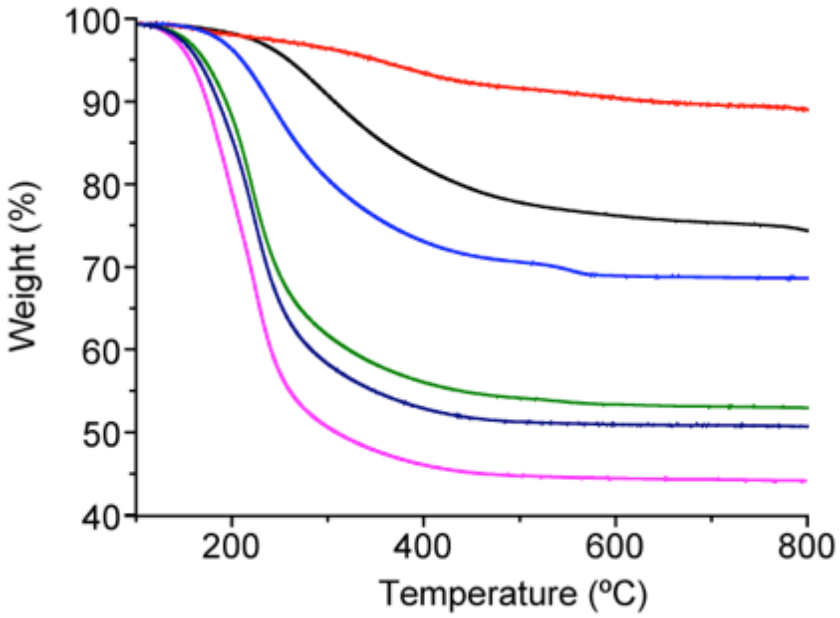


Figure S5. TG analysis of titration of **1** *vs* pp-SWNTs in TCE at 1 mg/mL of SWNTs.

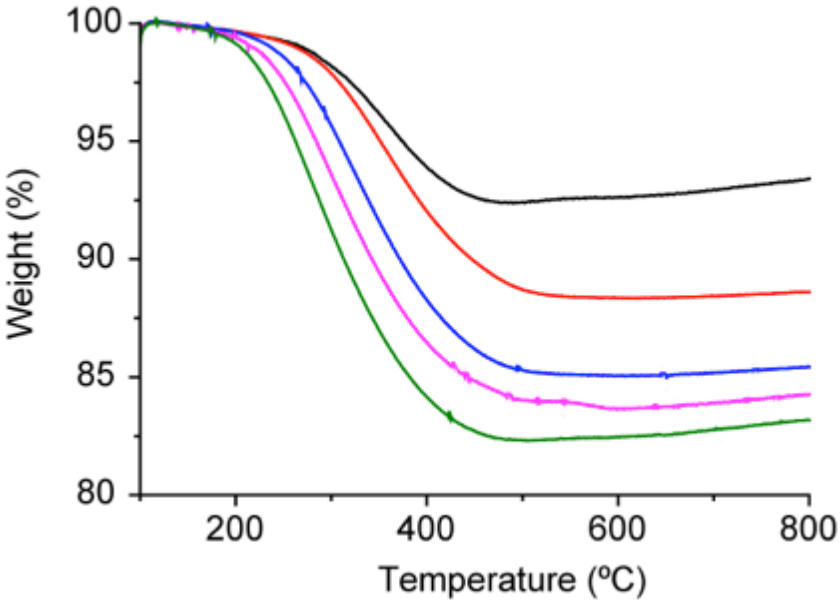


Figure S6. TG analysis of titration of **1** *vs* pp-SWNTs in MeOH at 1 mg/mL of SWNTs.

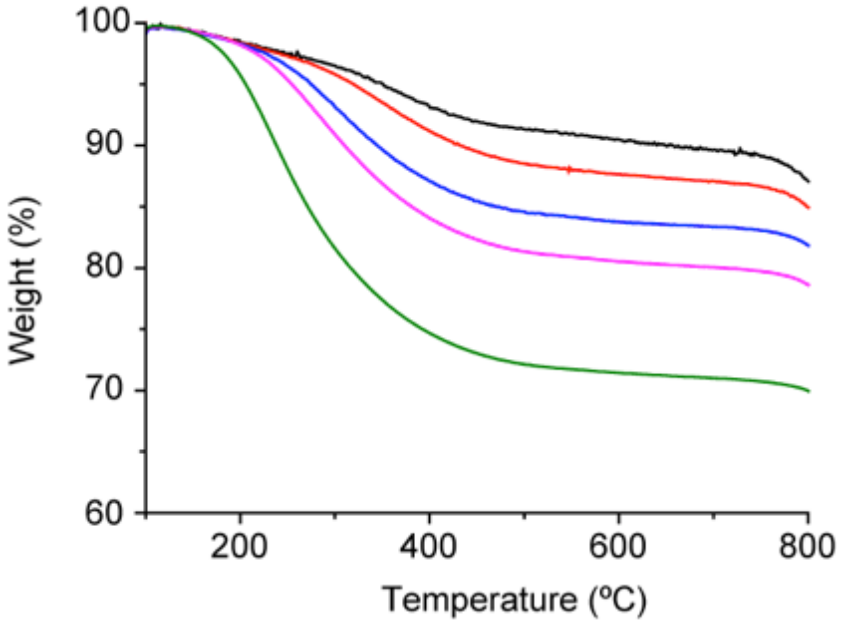


Figure S7. TG analysis of titration of **1** *vs* (6,5)-SWNTs in THF at 1 mg/mL of SWNTs.

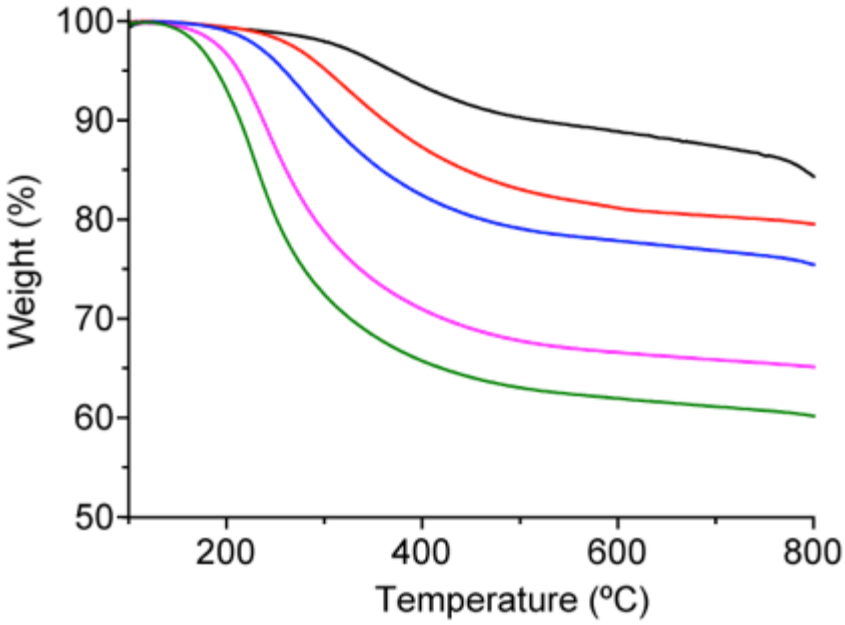


Figure S8. TG analysis of titration of **1** *vs* (6,5)-SWNTs in DMF at 1 mg/mL of SWNTs.

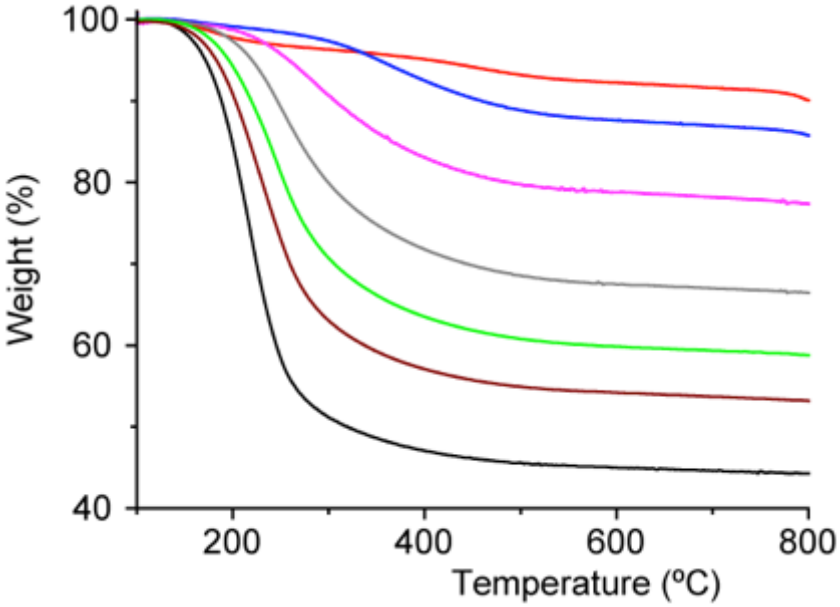


Figure S9. TG analysis of titration of **1** *vs* (6,5)-SWNTs in TCE at 1 mg/mL of SWNTs.

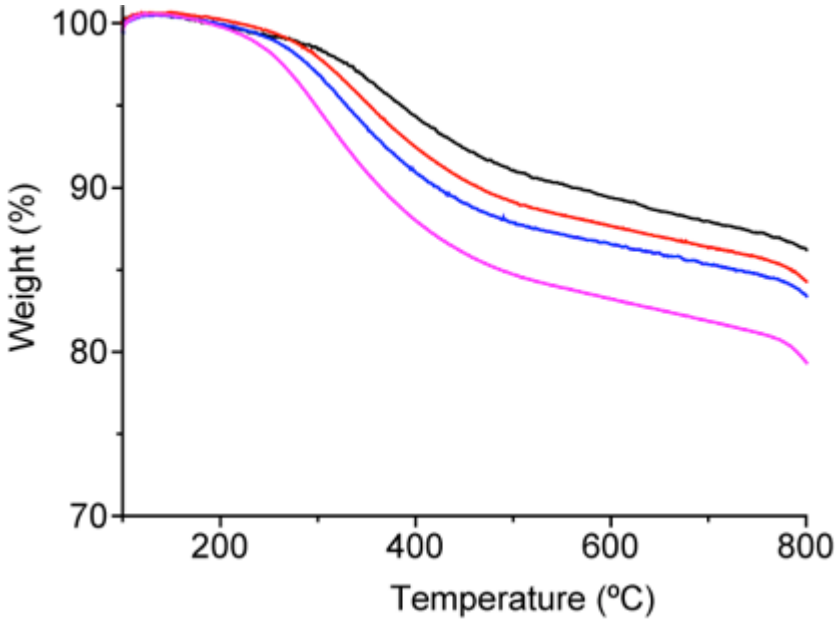


Figure S10. TG analysis of titration of **1** *vs* (6,5)-SWNTs in MeOH at 1 mg/mL of SWNTs.

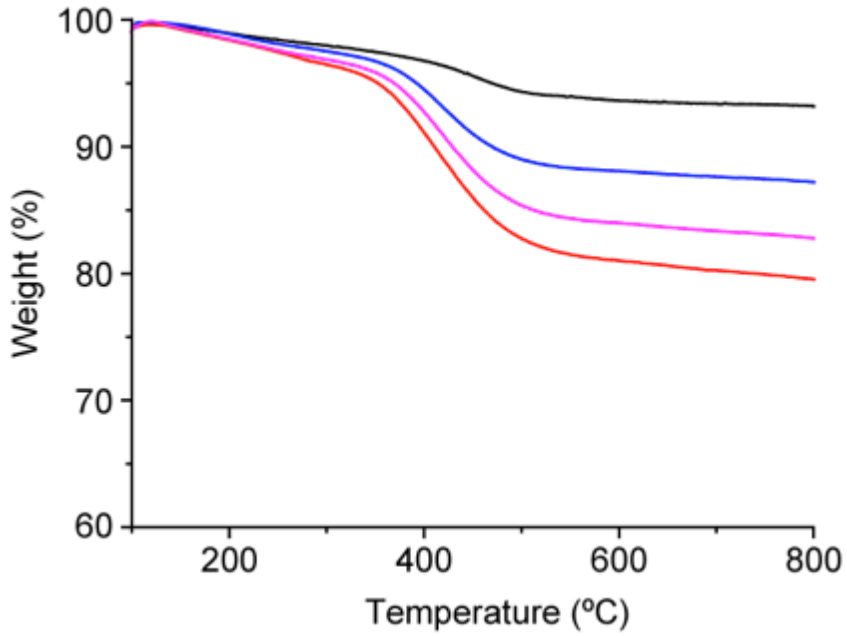


Figure S11. TG analysis of titration of **2** *vs* pp-SWNTs in DMF at 1 mg/mL of SWNTs.

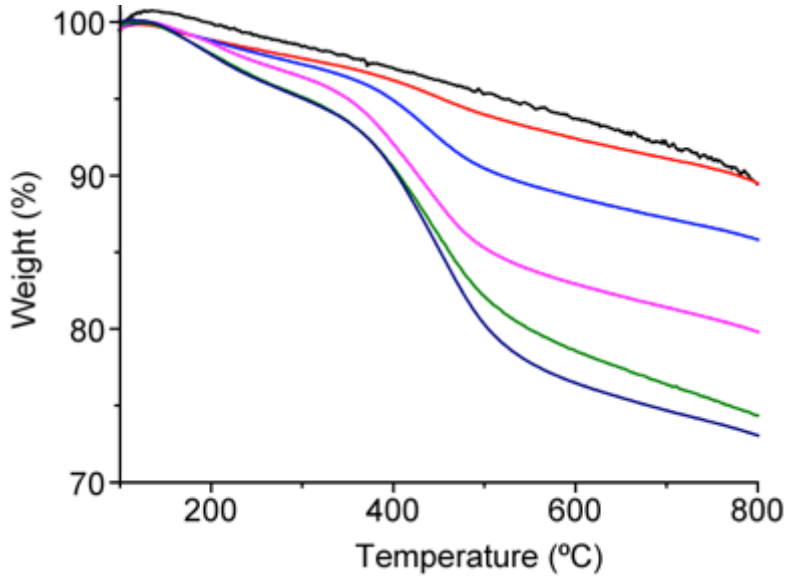


Figure S12. TG analysis of titration of **2** *vs* (6,5)-SWNTs in DMF at 1 mg/mL of SWNTs.

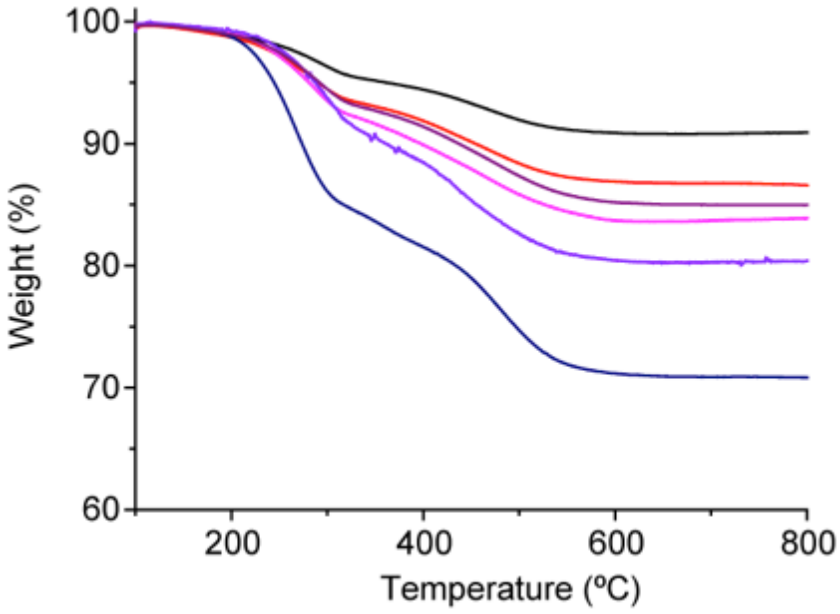


Figure S13. TG analysis of titration of **3** *vs* pp-SWNTs in THF at 1 mg/mL of SWNTs.

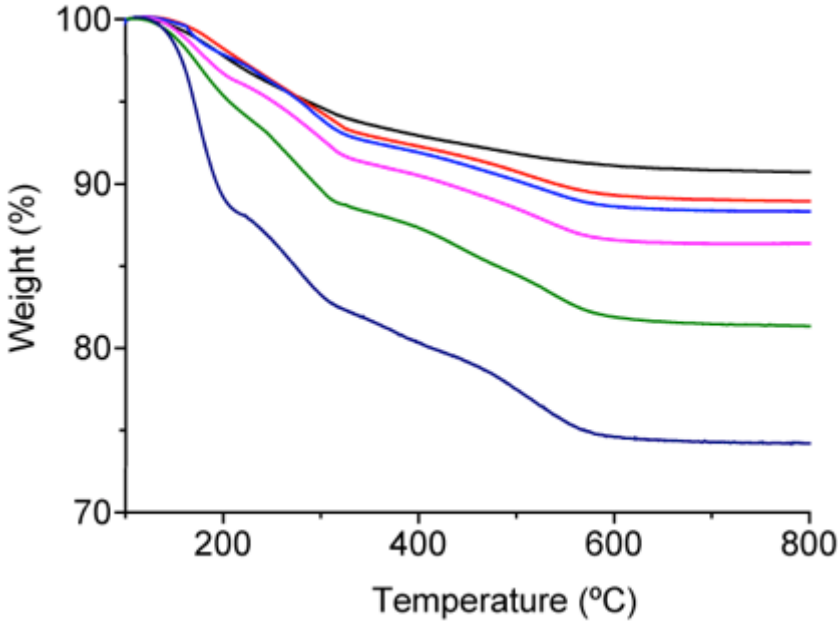


Figure S14. TG analysis of titration of **3** *vs* pp-SWNTs in TCE at 1 mg/mL of SWNTs.

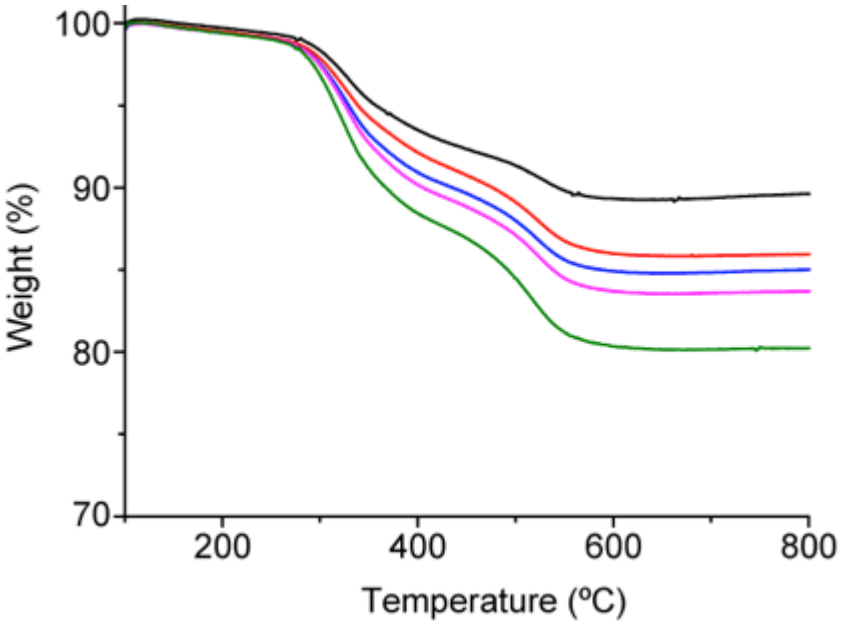


Figure S15. TG analysis of titration of **4** *vs* pp-SWNTs in THF at 1 mg/mL of SWNTs.

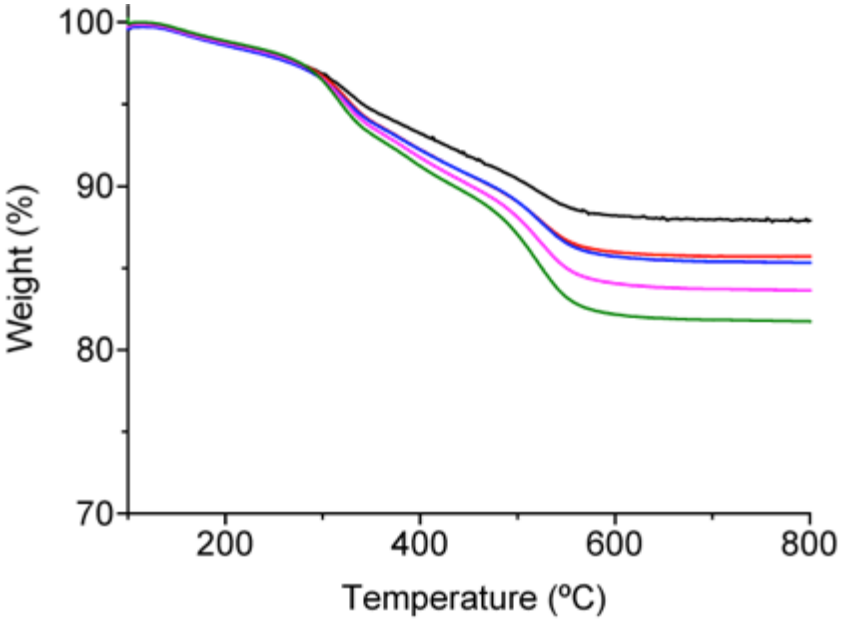


Figure S16. TG analysis of titration of **4** *vs* pp-SWNTs in TCE at 1 mg/mL of SWNTs.

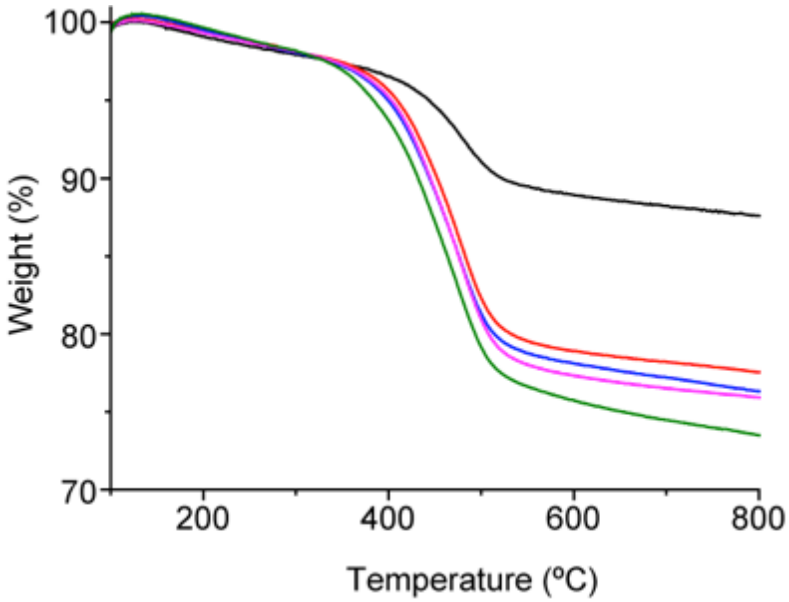


Figure S17. TG analysis of titration of **5** *vs* pp-SWNTs in THF at 1 mg/mL of SWNTs.

Adsorption isotherms not shown in the main text

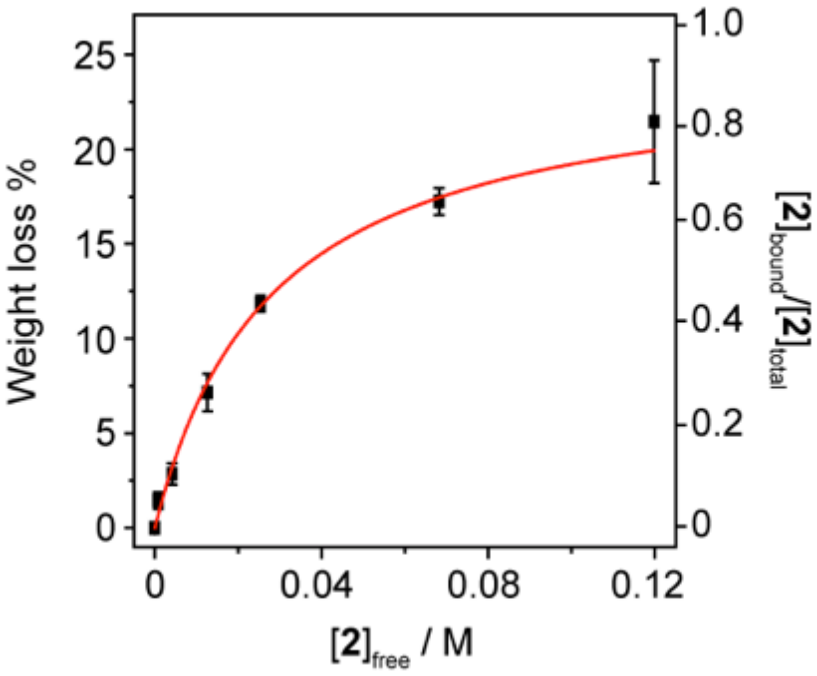


Figure S18. Titration of **2** *vs* (6,5) SWNTs in DMF at 298 K (K_a = 29 ± 3 M^{-1}, r^2 = 0.995)

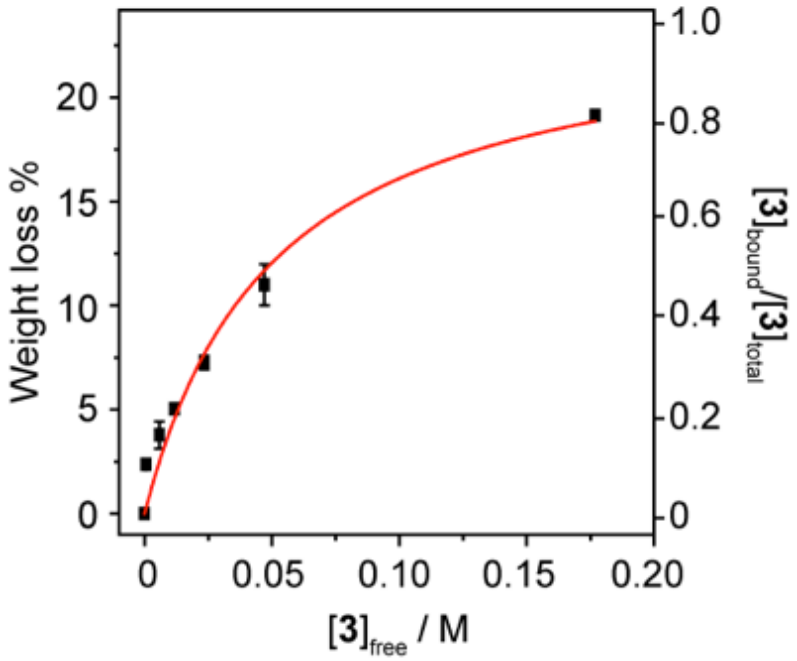


Figure S19. Titration of **3** *vs* pp-SWNTs in TCE at 298 K (K_a = 20 ± 5 M^{-1}, r^2 = 0.965)

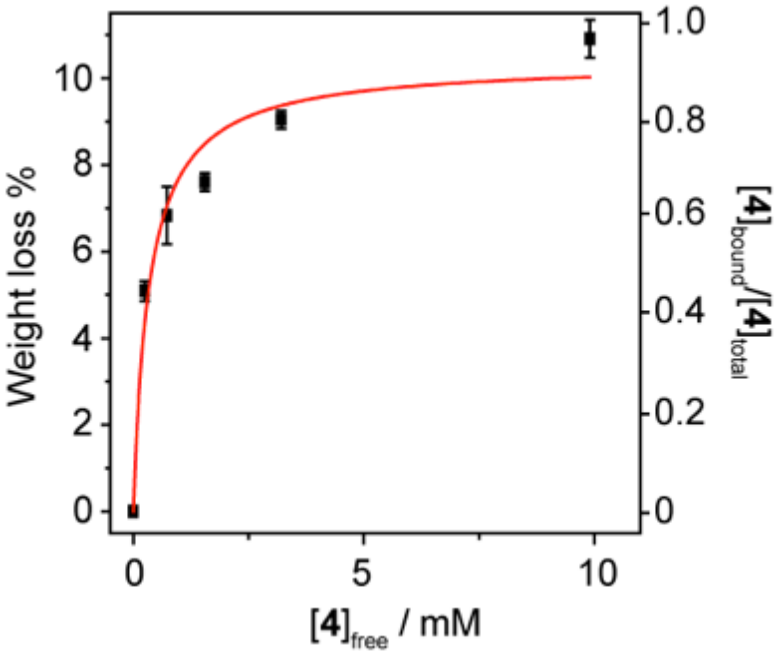


Figure S20. Titration of **4** *vs* pp-SWNTs in TCE at 298 K (K_a = 2.9± 0.8 × 10^3 M^{-1}, r^2 = 0.960).

Theoretical calculations

Table S2. Binding energy (kcal/mol) depending on the nanotube length for the parallel and perpendicular dispositions of the supramolecular **1**·pp-SWNT complex calculated at the PBE0-D3/6-31G** level of theory.

		Binding energy (kcal/mol)	
		Semi-rigid	Fully relaxed
parallel	**1**·$C_{40}H_{20}$	-11.05	-11.25
	1·$C_{80}H_{20}$	-17.80	-18.11
	1·$C_{120}H_{20}$	-21.79	-21.76
	1·$C_{200}H_{20}$	-21.18	-21.42
perpendicular	**1**·$C_{40}H_{20}$	-10.88	-11.12
	1·$C_{80}H_{20}$	-16.40	-17.11
	1·$C_{120}H_{20}$	-19.46	-19.60
	1·$C_{200}H_{20}$	-18.85	-17.97

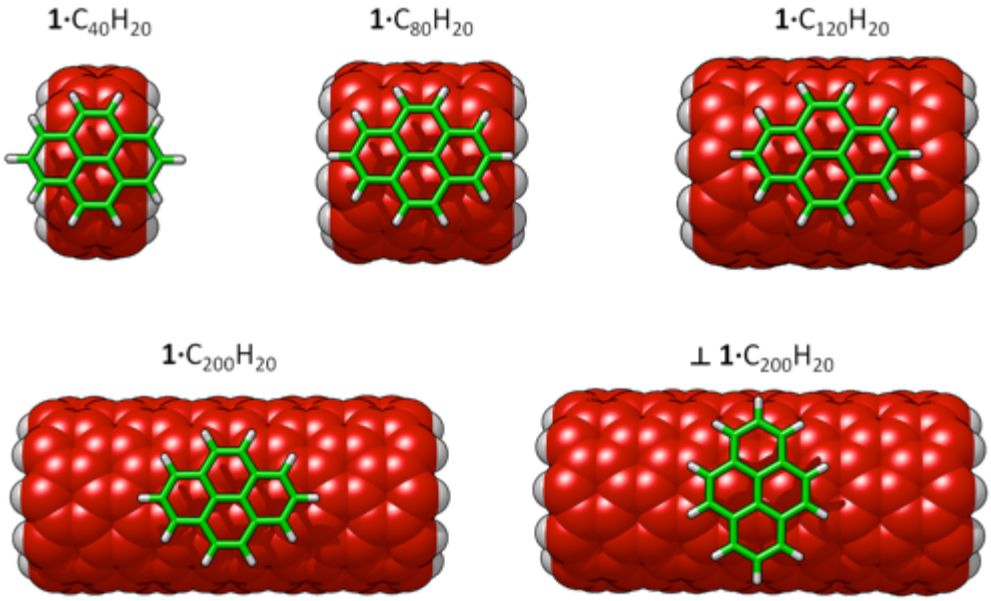


Figure S21. Minimum-energy geometries of parallel **1**·pp-SWNT assemblies and the perpendicular ↖ **1**·$C_{200}H_{20}$ calculated at the PBE0-D3/6-31G** level from a semi-rigid optimization with fixed intramolecular parameters.

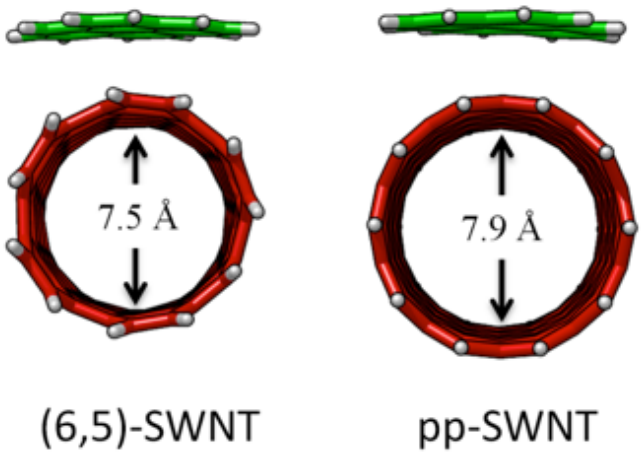


Figure S22. Side view of the supramolecular complex formed by pyrene and two types of SWNTs.

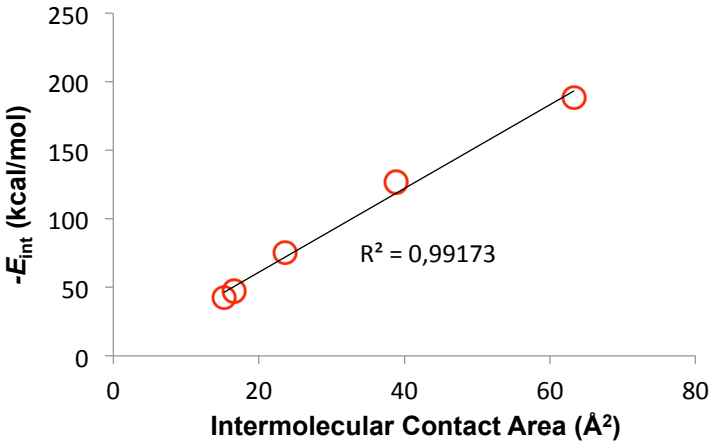


Figure S23. Relationship between the intermolecular contact area and the interaction energy for the **host**·pp-SWNTs assemblies.