

Electronic Supplementary Information (ESI)

Influence of molecular weight on selective oligomer-assisted dispersion of single-walled carbon nanotubes and subsequent polymer exchange.

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1. Synthetic procedures

General. All chemicals were used without purification unless otherwise indicated. 2,7-Dibromo-9,9-didodecylfluorene **3** was purchased from Aldrich. Poly(9,9-didodecylfluorene-2,7-diyl) (PDDF)¹, poly(9,9-didodecylfluorene-2,7-*alt*-benzo-2,1,3-thiadiazole-4,7-diyl) (PDDF-BT),² 2-bromo-9,9-didodecylfluorene **1**, diboronic ester **7** and bisfluorene **F2**³ were synthesized as previously reported. Toluene was dried by distillation over sodium before use. All reactions were performed under nitrogen atmosphere. Column chromatography was carried out using *Merck* silica gel 60 (0.040-0.063 mm). ¹H NMR and ¹³C NMR spectra were recorded with a *Bruker* Ultra Shield Plus 500 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm). Mass spectra were recorded using electron spray ionization (ESI) technique with a *Bruker* micrOTOF-Q II. Analytical size exclusion chromatography (SEC) characterization was performed in chloroform on an *Agilent* 1200 series station equipped with a 300 mm \times 7.5 mm 3 μ m Mesopore column and a 300 mm \times 7.5 mm 5 μ m Polypore column (*Polymer Laboratories*) in series and a UV-vis. diode-array detector. The calibration curve was obtained using ten monodisperse polystyrene narrow standards (pss-pskitr1 kit from *PSS*). Elemental analyses were performed using an Elementar Analysensysteme vario Micro cube. Absorption spectra were recorded using a *Varian Cary 500* spectrophotometer.

9,9-Didodecyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)fluorene (2). 9,9-didodecyl-2-bromofluorene (**1**) (2.18 g, 3.75 mmol), bis(pinacolato)diboron (1.10 g, 4.32 mmol), dry KOAc (1.11 g, 11.26 mmol) and Pd(dppf)Cl₂ (0.18 g, 0.23 mmol) were dissolved in dry dioxane (45 mL) under nitrogen atmosphere. The solution was stirred at 80°C overnight, cooled down, filtered, evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (9:1) to afford boronic ester **2** as a colorless oil (2.27 g, 96%): ¹H NMR (CDCl₃, 500 MHz) δ 0.59 (4H), 0.86 (t, J = 7.0 Hz, 6H), 0.99–1.08 (m, 12H), 1.10–1.30 (m, 24H), 1.39 (s, 12H), 1.97 (m, 4H), 7.29–7.35 (m, 3H), 7.69 (d, J = 7.5 Hz, 1H), 7.71 (m, 1H), 7.74 (s, 1H), 7.80 (d, J = 7.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 14.1, 22.7, 23.7, 25.0, 29.2, 29.3, 29.5, 29.6, 29.6, 30.0, 31.9, 40.2, 55.1, 83.7, 118.9, 120.1, 122.9, 126.6, 127.5, 128.8, 133.7, 140.9, 144.1, 149.9, 151.3; MS (ESI) m/z (rel. intensity) 651.6 (100) [M + Na]⁺; Anal. Calcd. for C₄₃H₆₉BO₂: C 82.13, H 11.06 Found: C 82.05, H 10.74.

7-Bromo-9,9,9',9'-tetrakis(dodecyl-2,2'-bifluorene (4). 2,7-Dibromo-9,9-didodecylfluorene (**3**) (0.99 g, 1.50 mmol), 9,9-didodecyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)fluorene (**2**) (0.94 g, 1.50 mmol) and Pd(PPh₃)₄ (0.14 g, 0.12 mmol) were dissolved in toluene (30 mL). A 1 M aqueous Na₂CO₃ (13.0 mL, 13.0 mmol) was added. The solution was stirred under nitrogen at 95°C for 3 days, cooled down. The suspension was extracted with Et₂O (50 mL), washed with water (2 \times 50 mL), filtered,

evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane to afford bromide **4** as a white powder (0.54 g, 33%): ^1H NMR (CDCl_3 , 500 MHz) δ 0.70 (m, 8H), 0.86 (t, $J = 6.9$ Hz, 12H), 1.02–1.30 (m, 72H), 2.01 (m, 8H), 7.30–7.38 (m, 3H), 7.47 (m, 2H), 7.57–7.66 (m, 5H), 7.73 (d, $J = 7.7$ Hz, 2H), 7.77 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.1, 22.7, 23.85, 23.89, 29.25, 29.3, 29.5, 29.6, 29.6, 29.97, 30.05, 31.9, 40.26, 40.36, 55.24, 55.59, 119.7, 119.8, 120.0, 120.9, 121.0, 121.5, 121.6, 123.0, 126.1, 126.3, 126.8, 127.0, 130.0, 139.2, 139.9, 140.4, 140.5, 140.8, 141.2, 151.1, 151.2, 151.6, 153.4; MS (ESI) m/z (rel. intensity) 1103.9 (93), 1104.9 (90), 1105.9 (100), 1106.9 (74), 1107.9 (60) $[\text{M} + \text{Na}]^+$; Anal. Calcd. for $\text{C}_{74}\text{H}_{113}\text{Br}$: C 82.10, H 10.52 Found: C 82.40, H 10.56.

9,9,9',9'-Tetrakisdodecyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-2,2'-bifluorene (5). 7-Bromo-9,9,9',9'-tetrakisdodecyl-2,2'-bifluorene (**4**) (0.61 g, 0.56 mmol), bis(pinacolato)diboron (0.20 g, 0.79 mmol), dry KOAc (0.33 g, 3.39 mmol) and $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.028 g, 0.03 mmol) were dissolved in dry dioxane (20 mL) under nitrogen atmosphere. The solution was stirred at 80°C overnight, filtered, evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (15:1) to afford boronic ester **5** as a colorless oil (0.37 g, 58%): ^1H NMR (CDCl_3 , 500 MHz) δ 0.69 (8H), 0.86 (m, 12H), 0.99–1.32 (m, 72H), 1.40 (s, 12H), 2.03 (m, 8H), 7.28–7.38 (m, 4H), 7.59–7.66 (m, 3H), 7.73 (d, $J = 7.2$ Hz, 2H), 7.75–7.81 (m, 3H), 7.83 (dd, $J = 0.6, 7.5$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.12, 22.69, 23.81, 23.84, 24.96, 29.27, 29.34, 29.59, 29.61, 29.63, 30.05, 31.92, 40.24, 40.36, 55.16, 55.24, 83.72, 119.02, 119.71, 119.86, 120.31, 121.47, 121.52, 122.93, 126.03, 126.77, 126.98, 127.20, 128.76, 128.91, 133.8, 140.11, 140.35, 140.45, 140.79, 141.00, 143.82, 150.21, 151.03, 151.46, 152.09; MS (ESI) m/z (rel. intensity) 1152.0 $[\text{M} + \text{Na}]^+$; Anal. Calcd. for $\text{C}_{80}\text{H}_{125}\text{BO}_2$: C 85.06, H 11.15 Found: C 85.31, H 11.21.

7-Bromo-9,9,9',9',9'',9'''-hexakisdodecyl-2,2'-7',2''-terfluorene (6) and 9,9,9',9',9'',9''',9''''-Decakisdodecyl-2,2'-7',2''-7''',2''''-7''''-2'''''-pentafluorene (F5). 2,7-Dibromo-9,9-didodecylfluorene (**3**) (0.25 g, 0.31 mmol), 9,9,9',9'-tetrakisdodecyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-2,2'-bifluorene (**5**) (0.35 g, 0.31 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.028 g, 0.024 mmol) were dissolved in toluene (10 mL). A 1 M aqueous Na_2CO_3 (2.7 mL, 2.7 mmol) was added. The solution was stirred under nitrogen at 95°C for 3 days, extracted with Et_2O , washed with water, filtered, evaporated, the residue was purified by column chromatography on silica gel eluting with hexane/ CH_2Cl_2 (60:1) to afford **6** as a colorless oil (0.14 g, 29%) and pentafluorene **F5** was also isolated as a colorless oil (30 mg, 4%).

7-Bromo-9,9,9',9',9'',9'''-hexakisdodecyl-2,2'-7',2''-terfluorene (6): ^1H NMR (CDCl_3 , 500 MHz) δ 0.72 (bs, 8H), 0.81 (m, 4H), 0.84–0.90 (m, 18H), 1.02–1.33 (m, 108H), 2.03 (m, 12H), 7.30–7.39 (m, 3H), 7.47 (m, 2H), 7.58–7.69 (m, 9H), 7.72–7.83 (m, 5H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.12,

22.69, 23.79, 23.85, 23.93, 29.28, 29.35, 29.59, 29.63, 29.98, 30.04, 30.06, 31.92, 40.28, 40.34, 40.38, 55.17, 55.32, 55.53, 119.71, 119.88, 119.96, 120.96, 121.06, 121.42, 121.48, 122.94, 126.02, 126.14, 126.22, 126.78, 126.99, 129.99, 139.20, 139.85, 139.89, 140.16, 140.23, 140.34, 140.44, 140.57, 140.79, 141.00, 151.01, 151.12, 151.49, 151.78, 151.84, 153.27; MS (ESI) m/z (rel. intensity) 1604.4 (61), 1605.4 (69), 1606.4 (100), 1607.4 (85), 1608.4 (51), 1609.4 (22) $[M + Na]^+$; Anal. Calcd. for $C_{111}H_{169}Br$: C 84.20, H 10.76 Found: C 84.56, H 10.68. **9,9,9',9'',9''',9''''-Decakis(dodecyl-2,2'-7',2''-7''',2''''-7''''-pentafluorene (F5):** 1H NMR ($CDCl_3$, 500 MHz) δ 0.74 (bs, 8H), 0.86 (m, 42H), 1.04–1.31 (m, 180H), 2.05 (m, 8H), 2.12 (m, 12H), 7.30–7.40 (m, 6H), 7.63–7.71 (m, 16H), 7.75 (d, $J = 7.3$ Hz, 2H), 7.79 (d, $J = 7.8$ Hz, 2H), 7.81–7.85 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.13, 22.70, 23.86, 23.96, 29.31, 29.36, 29.61, 29.64, 29.68, 30.08, 31.93, 40.39, 55.18, 55.33, 119.72, 119.89, 119.97, 121.42, 121.51, 121.74, 122.94, 126.03, 126.15, 126.38, 126.79, 126.99, 139.98, 140.02, 140.26, 140.33, 140.48, 140.71, 140.80, 151.02, 151.49, 151.80, 151.82; MS (ESI) m/z (rel. intensity) 2529.5 (100) $[M + Na]^+$; Anal. Calcd. for $C_{185}H_{282}$: C 88.66, H 11.34 Found: C 88.35, H 11.33.

9,9,9',9'',9''',9''''-Hexakis(dodecyl-2,2'-7',2''-terfluorene (F3). 9,9-didodecyl-2,7-dibromofluorene (**3**) (46 mg, 70 μ mol), 9,9-didodecyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)fluorene (**2**) (0.17 g, 0.27 mmol) and $Pd(PPh_3)_4$ (20 mg, 17 μ mol) were dissolved in toluene (10 mL). A 1 M aqueous Na_2CO_3 (2.0 mL, 2.0 mmol) was added. The solution was stirred under nitrogen at 90°C for 2 days, extracted with Et_2O , washed with water, dried over $MgSO_4$, filtered, evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane/ CH_2Cl_2 (40:1) to afford terfluorene **F3** as a colorless oil (72 mg, 69%): 1H NMR ($CDCl_3$, 500 MHz) δ 0.76 (m, 8H), 0.87 (m, 22H), 1.05–1.36 (m, 108H), 2.06 (m, 8H), 2.13 (m, 4H), 7.30–7.41 (m, 6H), 7.63–7.71 (m, 8H), 7.76 (m, 2H), 7.80 (d, $J = 7.8$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 14.1, 22.7, 23.8, 23.9, 29.3, 29.4, 29.6, 29.6, 29.7, 30.1, 31.9, 40.4, 55.2, 55.3, 119.7, 119.9, 120.0, 121.4, 121.5, 122.9, 126.0, 126.1, 126.8, 127.0, 140.0, 140.3, 140.5, 140.5, 140.8, 151.0, 151.5, 151.8; MS (ESI) m/z (rel. intensity) 1527.5 $[M + Na]^+$; Anal. Calcd. for $C_{111}H_{170}$: C 88.61, H 11.39 Found: C 88.94, H 11.42.

9,9,9',9'',9''',9''''-Octakis(dodecyl-2,2'-7',2''-7''',2''''-tetrafluorene (F4). 7,7'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-9,9,9',9'-tetrakis(dodecyl)-2,2'-bifluorene (**7**) (75.4 mg, 0.06 mmol), 9,9-didodecyl-2-bromofluorene (**1**) (70 mg, 0.12 mmol) and $Pd(PPh_3)_4$ (15 mg, 13 μ mol) were dissolved in toluene (6 mL). A 1 M aqueous Na_2CO_3 (0.5 mL, 0.51 mmol) was added. The solution was stirred under nitrogen at 95°C for 2 days, extracted with Et_2O (150 mL), washed with water (2×150 mL), dried over $MgSO_4$, filtered, evaporated, and the residue was purified by column chromatography on silica gel eluting with hexane/ CH_2Cl_2 (9:1) to afford tetrafluorene **F4** as a colorless oil (16 mg, 13%): 1H NMR ($CDCl_3$, 500 MHz) δ 0.73 (m, 8H), 0.86 (m, 32H), 1.08–1.28 (m, 144H),

151.82; SEC (Da eq. PS) $M_n = 5997$, $M_w = 6058$, $PDI = 1.01$; Anal. Calcd. for $C_{296}H_{450}$: C 88.69, H 11.31 Found: C 88.19, H 11.41.

Poly(9,9-didodecylfluorene-2,7-diyl) (PDDF).¹ SEC (Da eq. PS) $M_n = 12880$, $M_w = 53510$, $PDI = 4.2$.

Poly(9,9-didodecylfluorene-2,7-*alt*-benzo-2,1,3-thiadiazole-4,7-diyl) (PDDF-BT).² SEC (Da eq. PS) $M_n = 29000$, $M_w = 58000$, $PDI = 2.0$.

2. Preparation and characterization of SWNTs dispersions

Preparation of SWNTs dispersions. Typically, 1 mg of HiPco SWNTs (Unidym) was dispersed for 1 h in 15 mL of toluene with 50 mg of the oligo- or polymer, using a ϕ 0.5 in. titanium sonotrode driven by a 200 W, 20 kHz sonicator (Bandelin) at 20% power.

Polymer exchange. 5 mL of a HiPco SWNTs/**F8** dispersion in toluene were collected immediately after sonication and were added to a solution of poly(9,9-didodecylfluorene-2,7-*alt*-benzo-2,1,3-thiadiazole-4,7-diyl) (PDDF-BT) (15 mg) in toluene (3mL). The resulting solution was stirred for a few minutes at room temperature before centrifugation.

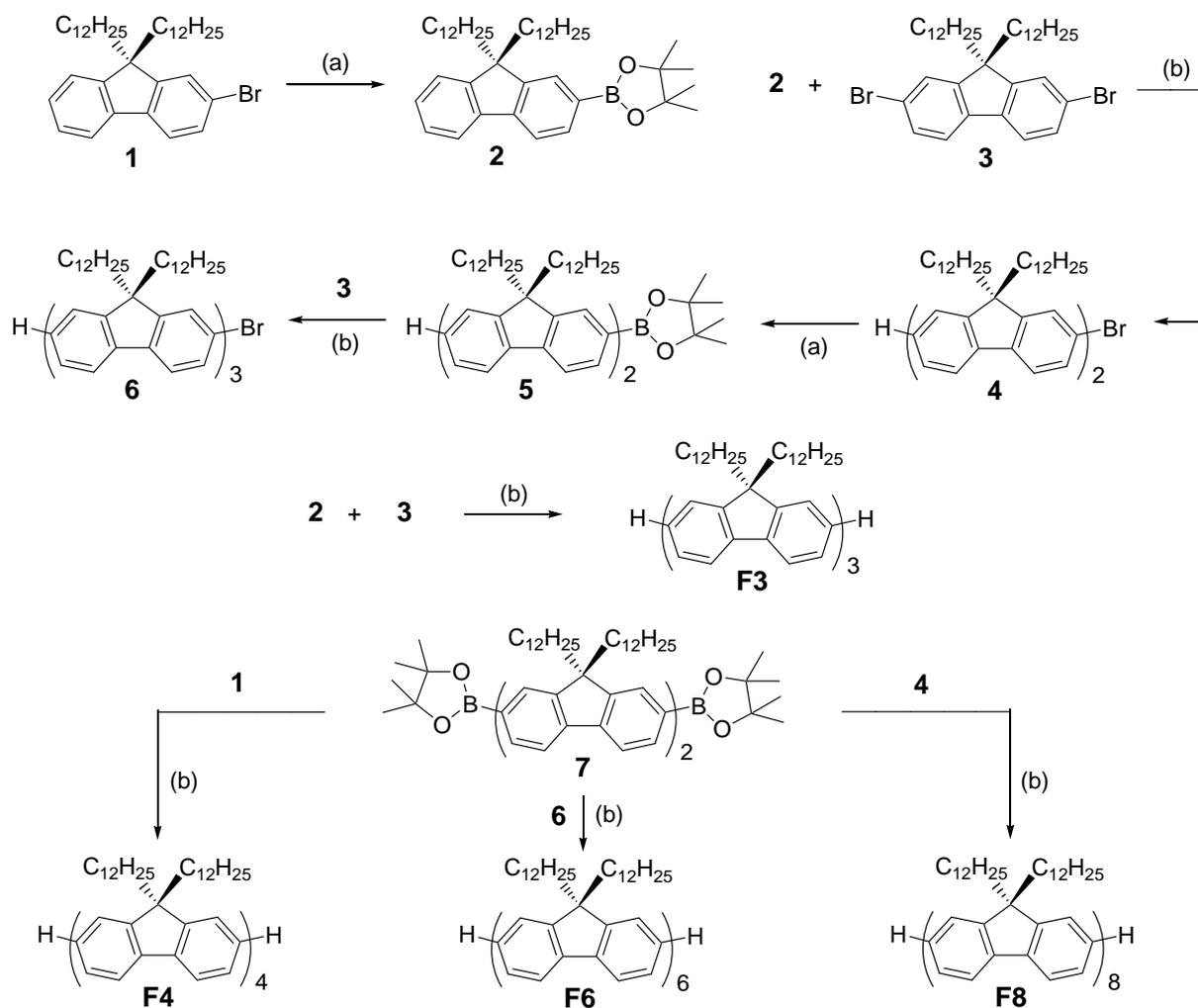
Centrifugation. When centrifugation was applied, dispersions were sealed into 8 mL Quick-Seal polyallomer centrifuge tubes and rotated for 10 min at 15 °C and 10 000 rpm, corresponding to a centripetal acceleration of ~ 5000 g at the middle of the centrifuge tube, in an Optima Max-E centrifuge (*Beckman-Coulter*) equipped with a ML-80 fixed angle rotor.

Filtration and redispersion. The HiPco SWNTs/**F8**/PDDF-BT dispersion (~ 3 mL) was filtered through a 0.2 μ m nylon membrane filter (*Whatman*). The SWNTs were washed with toluene until the filtrate was colorless and exhibited no fluorescence. The nylon membrane was then sonicated in toluene (1 mL) for 1 minute using an ultrasonic bath to redisperse the SWNTs.

Spectroscopic characterizations. Photoluminescence-excitation (PLE) maps were measured in the emission range of 934–1700 nm and excitation range of 500–950 nm (scanned in 3 nm steps) using a modified FTIR spectrometer (*Bruker IFS66*) equipped with a liquid-nitrogen-cooled Ge-photodiode and a monochromatized excitation light source as described elsewhere.⁴ Absorption spectra were

recorded using a *Varian* Cary 500 spectrophotometer. For PL and absorbance measurements of dispersions before centrifugation, the upper 1 mL was collected 2 min after sonication.

3. Additional schemes and figures



Scheme S1 Synthesis of oligofluorenes. Reagents and conditions: (a) bis(pinacolato)diboron, Pd(dppf)Cl₂, KOAc, dioxane, 80°C; (b) Pd(PPh₃)₄, 1 M aq. Na₂CO₃, toluene, 95°C.

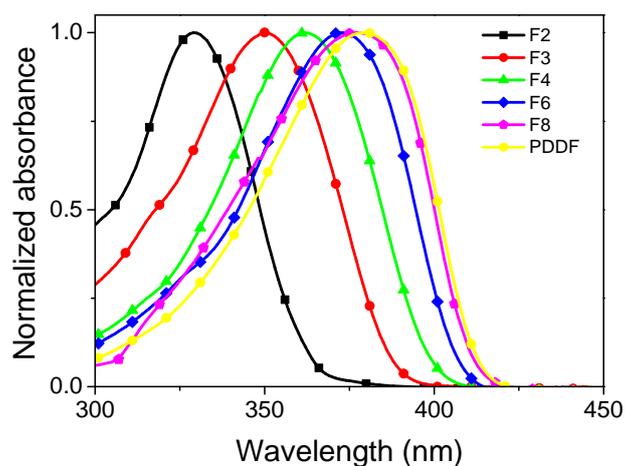


Fig S1 Absorbance spectra of oligofluorenes **F2** to **F8** and PDDF in toluene.

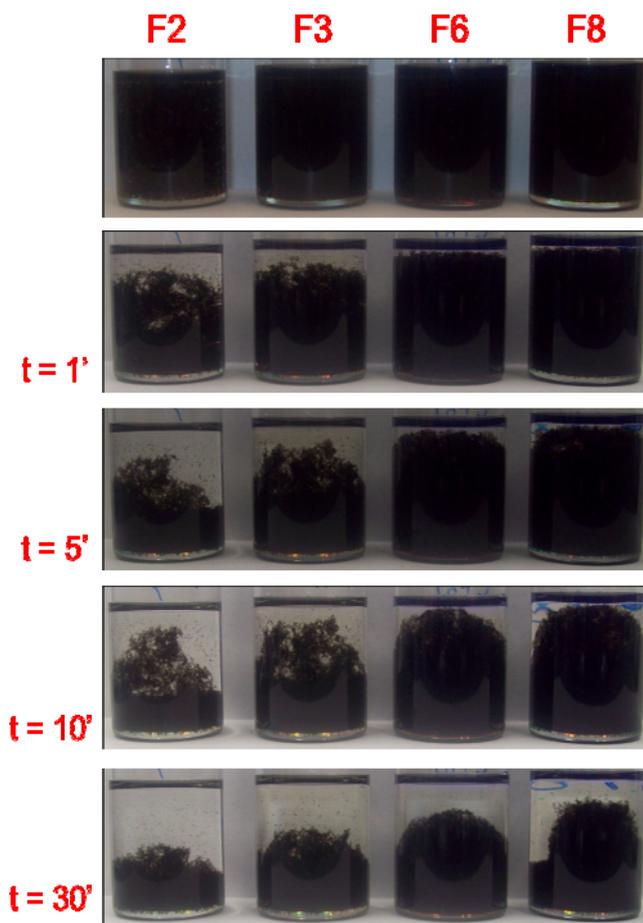


Fig S2 Pictures of dispersions of HiPco SWNTs obtained in toluene using oligomers **F2**, **F3**, **F6**, **F8** immediately after sonication, and after resting for 1, 5, 10 and 30 minutes (from top to bottom).

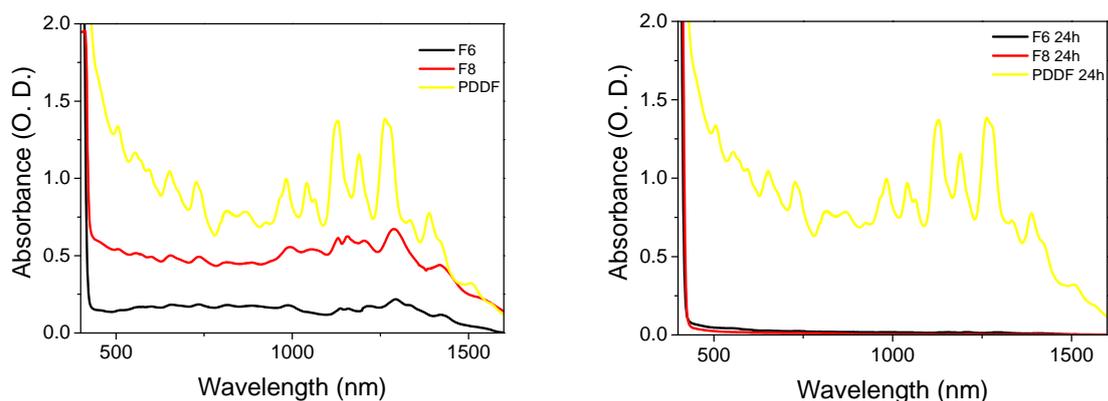


Fig S3 Absorbance spectra of HiPco SWNTs dispersed in toluene using oligomers **F6** and **F8** (measurement performed on the as prepared dispersion), and polymer PDDF (concentration/3) in toluene immediately after sonication (left) and after 24 h (right). The SWNTs/PDDF dispersion is stable over a period of 24 h while absorption characteristics of SWNTs in the wavelength range 500–1600 nm have completely disappeared in **F6** and **F8** solutions.

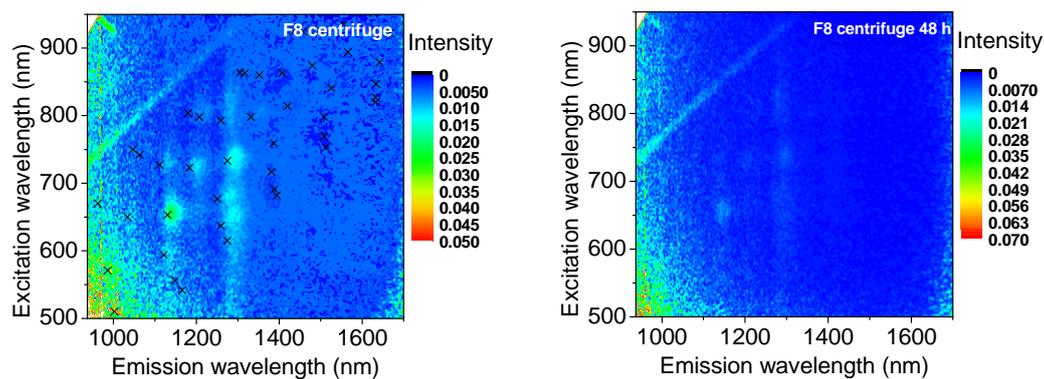


Fig S4 PLE map of HiPco SWNTs dispersed in toluene using **F8** after centrifugation (left) and after 48 h (right).

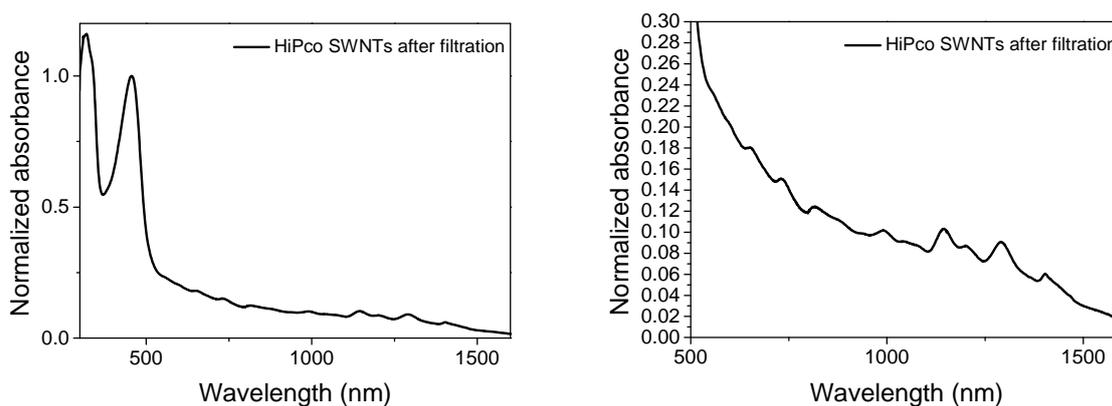


Fig S5 Absorbance spectrum of HiPco SWNTs after dispersion using oligomer **F8** in toluene followed by exchange with PDDF-BT, centrifugation, then filtration and redispersion in toluene: full spectrum (left) and zoom in the absorption range of SWNTs (right).

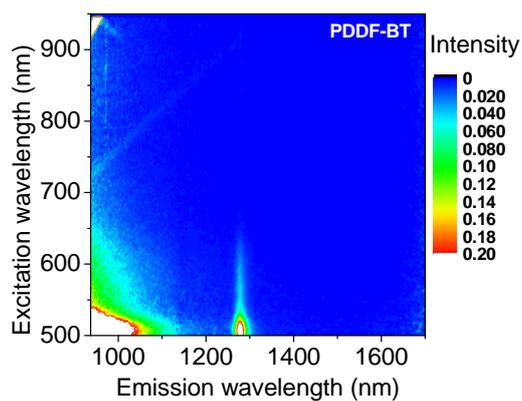


Fig S6 PLE map of PDDF-BT in toluene (2 mg/mL). Upon irradiation at around 509 nm (*i.e.* the onset of absorption band of PDDF-BT in toluene), the strong characteristic emission centered at 1277 nm corresponds to the excitation energy of oxygen from triplet $^3\text{O}_2$ to singlet $^1\text{O}_2$ (~ 0.97 eV) and can be attributed to emission from dissolved oxygen photosensitized via a polymer excited state.^{5,6}

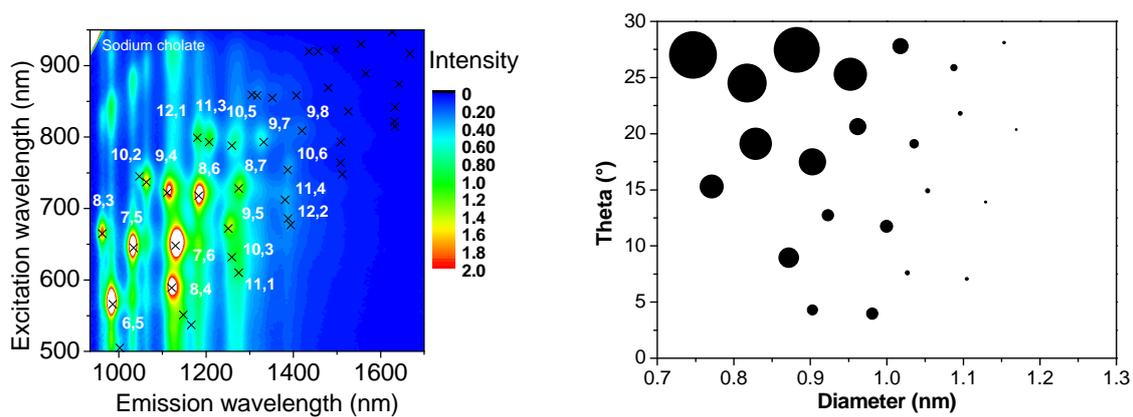


Fig S7 Absorption spectrum (left) and corresponding PLE map (right) of HiPco SWNTs dispersed in D₂O using sodium cholate as dispersant.

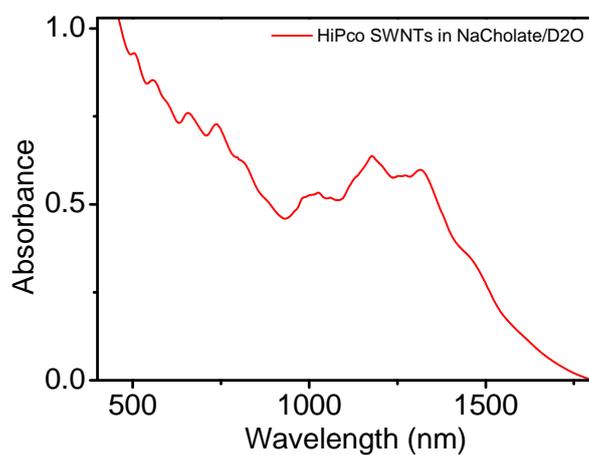


Fig S8 Absorption spectrum of HiPco SWNTs dispersed in D₂O using sodium cholate as dispersant.

Table S1 Initial distribution of HiPco SWNTs and distribution of HiPco SWNTs after dispersion in toluene using oligomer **F8**, as estimated from the PLE peak intensities.*

(n,m) SWNT	Diameter (nm)	Theta (°)	Initial distribution (%)	F8 /SWNTs dispersion (%)
(6,5)	0.747	27.0	12.19	13.22
(8,3)	0.771	15.3	6.11	-
(7,5)	0.817	24.5	9.92	7.78
(8,4)	0.829	19.1	8.21	5.58
(7,6)	0.882	27.5	11.70	18.80
(10,2)	0.872	8.9	5.19	4.41
(9,4)	0.903	17.5	6.94	5.46
(8,6)	0.952	25.3	8.47	8.46
(11,1)	0.903	4.3	2.85	-
(10,3)	0.923	12.7	3.13	2.94
(9,5)	0.962	20.6	4.42	7.64
(8,7)	1.018	27.8	4.15	12.36
(12,1)	0.981	4.0	3.16	-
(11,3)	1.000	11.7	3.35	2.06
(10,5)	1.036	19.1	2.31	5.87
(9,7)	1.088	25.9	1.73	5.43
(13,2)	1.104	7.1	0.84	-
(12,4)	1.129	13.9	0.64	-
(11,6)	1.169	20.4	0.46	-
(10,8)	1.223	26.3	0.23	-
(12,2)	1.027	7.6	1.08	-
(11,4)	1.053	14.9	1.17	-
(10,6)	1.096	21.8	1.04	-
(9,8)	1.153	28.1	0.71	3.85

*The proportion of near-armchair SWNTs (*i.e.* the (6,5), (7,5), (7,6), (8,6), (8,7), (9,7) and (9,8) species) estimated from PLE maps rises from 49% in the initial distribution to 70% when dispersed with oligomer **F8**.

¹ F. Lemasson, J. Tittmann, F. Hennrich, N. Stürzl, S. Malik, M. M. Kappes and M. Mayor, *Chem. Commun.*, 2011, **47**, 7428.

² F. Lemasson, N. Berton, J. Tittmann, F. Hennrich, M. M. Kappes and M. Mayor, *Macromolecules*, DOI: 10.1021/ma201890g.

³ N. Berton, F. Lemasson, J. Tittmann, N. Stürzl, F. Hennrich, M. M. Kappes and M. Mayor, *Chem. Mater.*, 2011, **23**, 2237.

⁴ S. Lebedkin, F. Hennrich, O. Kiowski and M. M. Kappes, *Phys. Rev. B*, 2008, **77**, 165429.

⁵ S. Lebedkin, I. Kareev, F. Hennrich and M. M. Kappes, *J. Phys. Chem. C*, 2008, **112**, 16236.

⁶ As 509 nm coincides with the onset of absorption band of PDDF-BT, the excitation at 509 nm seems to indicate that formation of the β -phase (planar backbone) occurs in concentrated solutions. Oxygen sensitization might occur through the formation of PDDF-BT excimers. See also: M. Tange, T. Okazaki and S. Iijima, *J. Am. Chem. Soc.*, 2011, **133**, 11908.