Supplementary Material (ESI) for Chemical Communications

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Efficient Dispersions of Singlewalled Carbon Nanotubes by Novel Amphiphilic Dendrimer in water and Efficient Substitution of the Pre-adsorbed Dendrimers with Conventional Surfactants and Lipids

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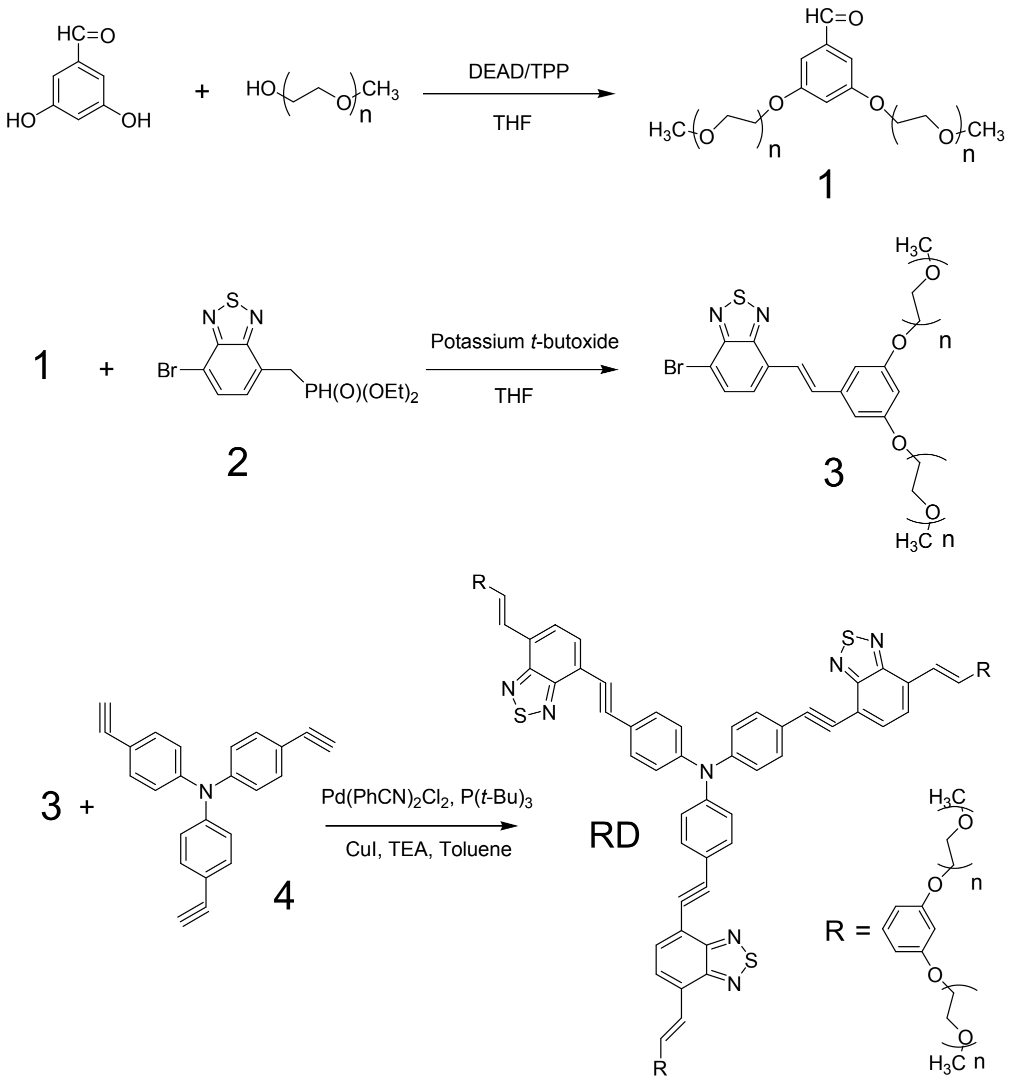
1. Syntheses and experimental details



Scheme S1. Procedure for the synthesis of the amphiphilic dendrimer with triphenylamine cores, benzothiadiazole branches and poly(ethylene oxide) **(PEO)** shells.

Materials and characterizations. 3,5-dihydroxy benzaldehyde and poly(ethylene oxide) monomethyl ether (Mn 550) were used as received from Alfa Aesar and Polymer Scientific Co, respectively. Tetrahydrofuran (THF) and toluene (DMF) from Aldrich were purified with standard method. Triethylamine, copper iodide, sodium bicarbonate, bis(benzonitrile) palladium(Π) chloride, were purchased from Aldrich. Triphenylphosphine, diethyl azodicarboxylate (DEAD), potassium *tert*-butoxide, sodium dodecylbenzene sulfonate (SDBS) and tri-*tert*-butylphosphine were obtained from Aldrich. HiPCO SWNTs was obtained from Carbon Nanotechnoligies Inc. Lysophospholipid (LPC 18:0) was purchased from Avanti. 4-Bromo-7-(diethylphosphonomethyl)benzo-2,1,3-thiadiazole (**2**)[1] and tris(4-ethynylphenyl) amine (**4**)[2] were synthesized according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz. UV/VIS/NIR spectra were recorded on a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer, while photoluminescence emissions (PL) were measured on a Perkin-Elmer LS 55 spectrometer. X-ray photoelectron spectroscopy measurements were recorded on a VG Microtech ESCA 2000 using monochromatic Mg Kα radiation at a power of 300W. Thermogravimetric analysis (TGA) was carried out using TA instruments TGA Q500 under nitrogen. Transmission electron microscope (TEM) measurements were carried out using a JOEL JEM-2100F.

3,5-di(polyethylene oxide monomethyl ether)benzaldehyde (1). Diethyl azodicarboxylate (DEAD) (1.39 g, 7.96 mmol) in 10ml dry THF was added dropwise to the mixture of 3,5-dihydroxybenzaldehyde (0.55 g, 3.98 mmol), poly(ethylene oxide) monomethyl ether, *Mn* = 550, (4.35 g, 7.96 mmol) and triphenyl phosphine (2.09 g, 7.96 mmol) in 50 ml dry THF. The solution was stirred in the dark at room temperature for 24 hrs. After evaporation of solvent, the reaction mixture was purified by silica gel column chromatography using ethyl acetate/methanol (6/1) to yield **1** as yellowish oil (2.06 g, 43 %). ^{1}H NMR (300MHz, $CDCl_3$, ppm) δ: 3.38 (s), 3.54 -3.75 (m), 3.87 (t, *J* = 4.7 Hz), 4.16 (t, *J* = 4.7 Hz), 6,76 (t, *J* = 2.3 Hz, 1H), 7.02 (d, *J* = 2.3 Hz, 2H), 9.88 (s, 1H). ^{13}C NMR (300MHz, $CDCl_3$) δ: 191.7, 160.2, 138.1, 108.4, 107.7, 71.7, 70.4, 70.3, 70.1, 69.3, 67.7, 58.8. MALDI-TOF MS 1245.4 m/z $[M^+Na]^+$ (calcd for average Mn of polyethyleme oxide shell is 550: 1234.1 m/z $[M]^+$).

4-(3,5-di(polyethyleneoxide monomethyl ether)styryl)-7-bromobenzo[c][1,2,3]benzothiadiazole (3). 3,5-Di(polyethylene oxide monomethyl ether)benzaldehyde (**1,** 1.50 g, 1.25 mmol) and 4-bromo-7-(diethylphosphonomethyl)benzo-2,1,3-thiadiazole (**2**, 0.46 g, 1.25 mmol) were dissolved in 20 ml of dry THF under nitrogen at room temperature. Two equivalents of potassium *t*-butoxide (0.28 g, 2.50 mmol) in 5 ml of dry THF were added dropwise. The reaction mixture was stirred for 2 hrs and then quenched with water. The THF was evaporated under reduced pressure and the residue was dissolved in $CHCl_3$. The organic layer was then washed with brine, speparated and dried over $MgSO_4$. After solvent evaporation, the residue was subjected to column chromatography using chloroform/methanol (5/1) to produce **3** as yellowish viscous oil (0.65 g, 37 %). ^{1}H NMR (300MHz, $CDCl_3$, ppm) δ: 3.38 (s), 3.53 -3.75 (m,), 3.88 (t, *J* = 4.8 Hz), 4.17 (t, *J* = 4.8 Hz), 6.48 (t, *J* = 2.0 Hz), 6.81 (d, *J* = 2.0 Hz, 4H), 7.52 (d, *J* = 16.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 16.4 Hz, 1H) ^{13}C NMR (300MHz, $CDCl_3$, ppm) δ : 160.0, 153.6, 152.7, 138.8, 132.2, 129.9, 127.0, 124.0, 112.39, 105.8, 101.8, 71.9, 70.8, 70.6,

70.5, 69.7, 67.4, 59.0. MALDI-TOF MS 1455.4 m/z $[M^{+}Na]^{+}$ (calcd for average Mn of polyethyleme oxide shell is 550: 1445.2 m/z $[M]^{+}$).

Tris(4-(2-(4-(3,5-bis(polyethylene oxide monomethyl ether)styryl)benzo[c][1,2,5]thiadiazol-7-yl)ethynyl)phenyl)amine. ,5-Di(polyethylene oxide monomethyl ether)benzaldehyde (**1,** 0.41g, 0.29 mmol), bis(benzonitrile) palladium(Π) chloride (4.40 mg, 0.011 mmol) and copper iodide (1.90 mg, 0.01mmol) were dissolved in 5 ml of anhydrous toluene under nitrogen. Tris(4-ethynylphenyl) amine (**4**, 23 mg, 0.073 mmol), tri-*tert*-butylphosphine (5.14 mg, 0.025 mmol) and 1 ml of triethylamine were successively added. The reaction flask was wrapped in aluminum foil to keep the reaction mixture in dark. The reaction mixture was stirred for 24 h at room temperature. After reaction the mixture was partitioned with methylene chloride and aqueous sodium bicarbonate solution. The organic phase was separated and dried over $MgSO_4$. After solvent evaporation, the residue was subjected to column chromatography using chloroform/methanol (4/1) to produce target amphiphilic dendrimer as reddish viscous oil (95 mg, 30 %). ^{1}H NMR (300MHz, $CDCl_3$, ppm) δ: 3.38 (s), 3.53 -3.76 (m), 3.87 (t, *J* = 4.6 Hz), 4.18 (t, *J* = 4.6 Hz), 6.49 (t, *J* = 1.8 Hz, 3H), 6.82 (d, *J* = 1.8 Hz, 6H), 7.15 (d, *J* = 9.0 Hz, 6H), 7.55 – 7.67 (m, 12H), 7.80 (d, *J* = 7.2 Hz, 3H), 7.96 (d, *J* = 16.4 Hz, 3H) ^{13}C NMR (300MHz, $CDCl_3$, ppm) δ : 160.1, 155.2, 153.0, 147.0, 139.1, 134.3, 133.3, 132.8, 130.6, 126.8, 124.7, 124, 106.0, 71.9, 70.8, 70.6, 70.5, 69.7, 67.6, 59.0. MALDI-TOF MS 4443.3 m/z $[M^{+}Na]^{+}$ (calcd for average Mn of polyethyleme oxide shell is 550: 4410.3 m/z $[M]^{+}$).

Solubilization of SWNTs and replacement of pre-absorbed dendrimer with surfactant and lipids. Firstly for the solubilization of SWNTs, 1.2 mg of SWNTs and 7.6 mg amphiphilic dendrimers were mixed with 30 ml of deionized water. The mixture was sonificated for 30 min. The dark brown solution was analyzed with UV-Vis NIR and PL spectroscopy. For the replacement of pre-adsorbed dendrimers, the removal of free dendrimers is critical. To eliminate free dendrimers, the solution was filter through a 0.45 μm nylon filter membrane and washed with water several times. The collected filtrates were re-dispersed in water using sonication and filtered again. Then the product was dried in reduced pressure (0.5 mmHg) at 50 ºC overnight. For PL measurements, 2 ml of aqueous solution of re-dispersed SWNTs-dendrimer complexe was placed in UV couvette with magnetic stirrer bar and PL spectra were consecutively measured each time after small portions of surfactants or lipids from stock solution were added with vigorous stirring for 3 minutes. For the preparation of SWNTs-SDBS complex, the SWNTs-dendrimer complex was re-dispersed in water and sonificated for 15 min with 1 wt% SDBS solution. Then the above purification process with filtering and washing was applied for two times and the final products were dried in reduced pressure (0.5 mmHg) at 50 ºC overnight.

2. Results and discussions

- TGA data

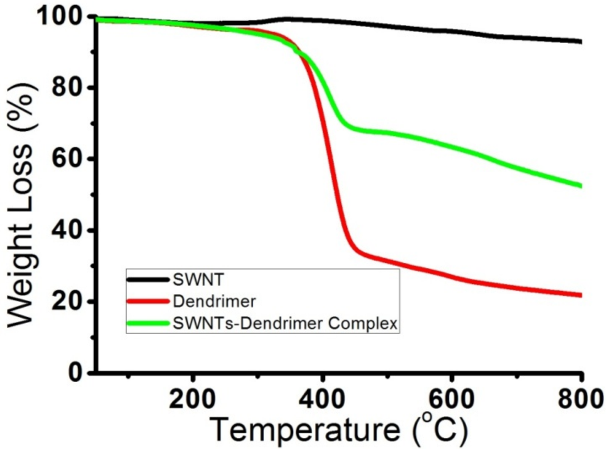


***Fig. S1**. Thermogravimetric curves for SWNTs, dendrimers and SWNTs-dendrimer complex under nitrogen atmosphere.*

- PL data

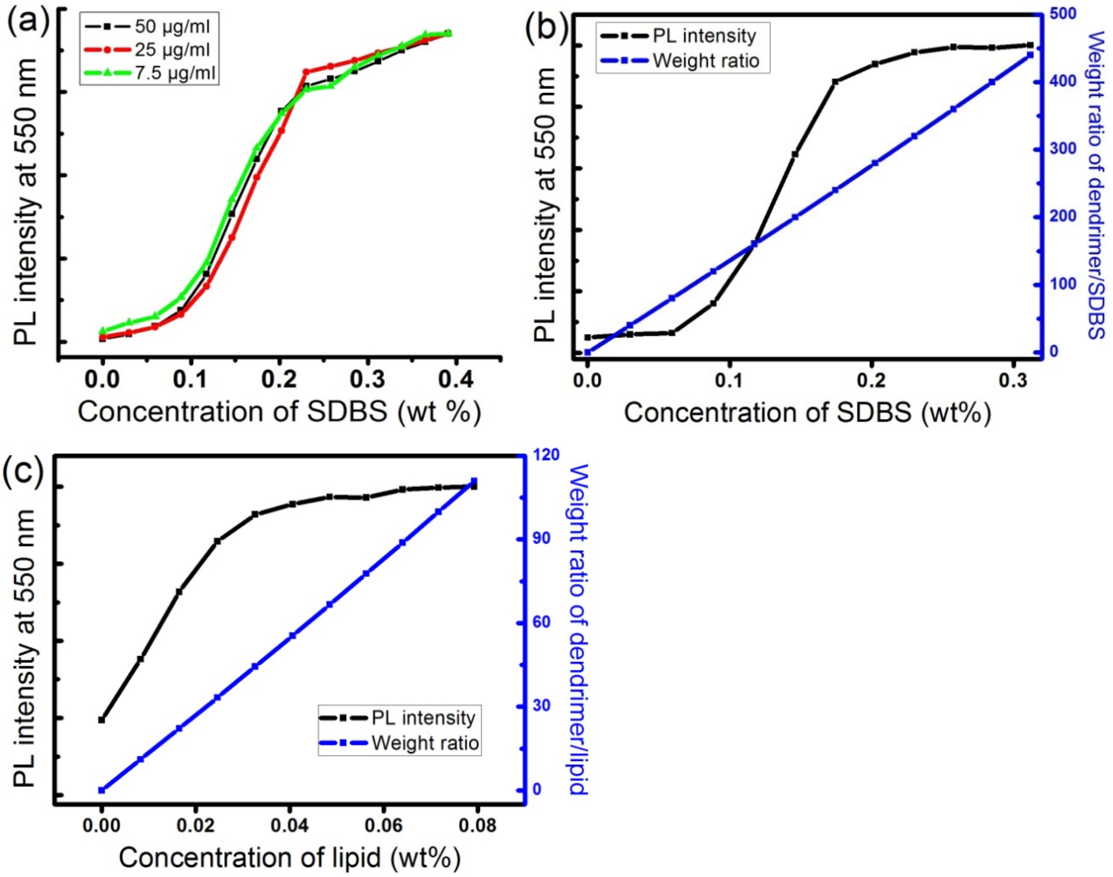


***Fig. S2**. (a) The normalized PL intensity at 550 nm as a function of SDBS concentrations with different SWNTs-dendrimer complex concentrations, (b) the normalized PL intensity and weight ratio of dendrimer/SDBS and (c) the normalized PL intensity and weight ratio of dendrimer/lysophospholipid 18:0. The concentration SWNTs-dendrimer complex was 25μl/ml in (b) and (c).*

- TEM data

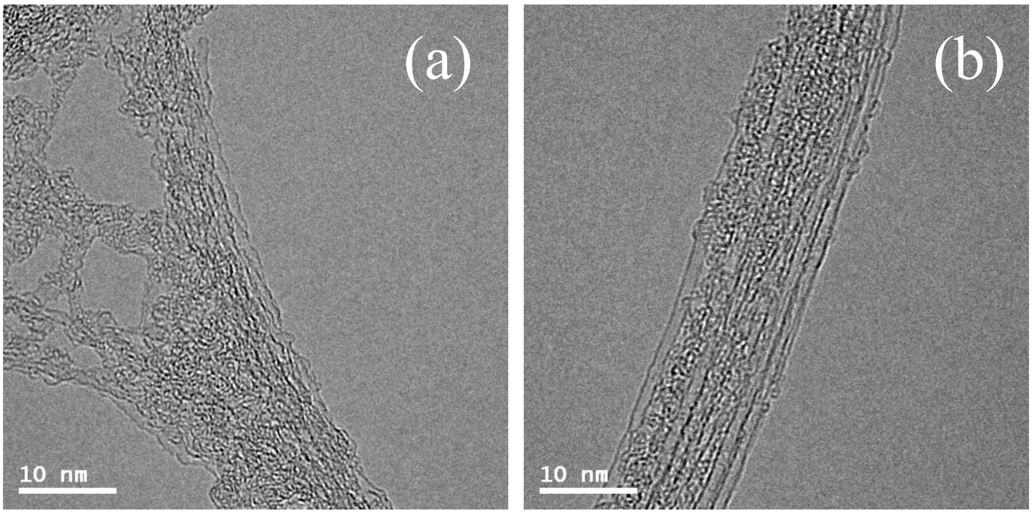


Fig. S3. *TEM images of (a) SWNTs-dendrimer complex and (b) SWNTs-SDBS complex after replacement of dendrimers with SDBS.*

3. References

1. M. Jorgensen and F. C. Krebs, *J. Org. Chem.,* 2005, **70**, 6004.
2. S. P. Mcilroy, E. Clo, L. Nikolajsen, P. K. Frederiksen, C. B. Nielsen, K. V. Mikkelsen, K. V. Gothelf and P. R. Ogilby, *J. Org. Chem.,* 2005, **70**, 1134.