Effect of Organic Modification on Multiwalled Carbon Nanotube Dispersions in Highly Concentrated Emulsions

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1. Sedimentation behaviour of unmodified and modified MWCNTs

The unmodified and modified MWCNTs were dispersed in THF and studied the sedimentation behaviour. Around 1 mg of MWCNTs was ultrasonicated in 20 ml of THF with a bath-type ultrasonicator (PCI Analytics, 20 Hz) for 30 min. In order to make sure equal amount of MWCNTs in all the dispersions, 2 mg and 3 mg of modified MWCNTs were used for 1:1 and 1:2 (w/w) modifications, respectively. Figure S1 demonstrates the photographs of the dispersions of unmodified and modified MWCNTs in THF. The images were captured after 24 hours of the ultrasonication. The dispersion of the unmodified
MWCNTs was highly unstable, and sedimentation was observed after a few minutes of ultrasonication. On the other hand, both 1:1 and 1:2 modified MWCNTs were stable for a few days in THF.

Figure S1. Sedimentation observation study of dispersions of the modified and the unmodified MWCNTs in THF: (a) unmodified MWCNTs (b) 1:1 TOPy-Modified MWCNTs; (c)1:2 TOPy-Modified MWCNTs; (d) 1:1 TDPy-Modified MWCNTs; (e) 1:2 TDPy-Modified MWCNTs. (MWCNTs concentration is 0.05 g/L; all the images are captured after 24 hours of ultra-sonication)

2. Dispersion studies: Dispersion state of MWCNTs in the oil blend

The dispersion studies of MWCNTs were carried out in the oil blend, where the oil blend composition was the same as that of the continuous phase of the emulsion. Figure S2 shows the optical micrographs of the oil blend–MWCNTs dispersion for unmodified and modified MWCNTs, where the concentration of MWCNTs was 3 mg in 10 g of oil blend. The micrographs depict the remaining MWCNT agglomerates for unmodified MWCNTs [Figure S2 (a, b)], TOPy-modified MWCNTs [Figure S2 (c, d)] and TDPy-modified MWCNTs [Figure S2 (e, f)] in the oil blend. Both, 1:1 and 1:2 (w/w) modified MWCNTs were used. The optical micrographs were data processed using ImageJ software in order to quantitatively investigate the effect of the non-covalent modification on the average size of the remaining
MWCNT agglomerates. A minimum of 1200 MWCNT agglomerates was considered by processing around 20-30 micrographs for each type of MWCNTs, in order to assure the accuracy of the analysis. The dispersion with unmodified MWCNTs exhibited a higher average agglomerate size when compared to all the modified MWCNTs. For the modified MWCNTs, the average size of the MWCNT agglomerates was reduced with increasing weight ratio of TOPy and TDPy. The average agglomerate sizes of the MWCNTs in the oil blend dispersion and the agglomerate-size distribution of modified and unmodified MWCNTs are provided in Figure S3.

**Figure S2.** Effect of the noncovalent modification on the average agglomerate size of MWCNTs in the MWCNT/oil blend dispersions: (a, b) dispersion of unmodified MWCNTs; (c) dispersion of 1:1 (w/w) TOPy-modified MWCNTs; (d) dispersion of 1:2 (w/w) TOPy-modified MWCNTs in oil blend; (e) dispersion of 1:1 (w/w) TDPy-modified MWCNTs; (f) dispersion of 1:2 (w/w) TDPy-modified MWCNTs. (MWCNTs concentration was 3 mg in 10 g of oil blend).
| Type of modification | Weight ratio (wt/wt) | Agglomerate size distribution | Average agglomerate size (μm²) |
|----------------------|----------------------|-------------------------------|-----------------------------|
| Unmodified MWCNTs    | -                    | ![Unmodified MWCNTs](image)    | 218.2                       |
| TOPy-modified MWCNTs | 1:1                  | ![TOPy-modified MWCNTs](image) | 109.9                       |
|                      | 1:2                  | ![TOPy-modified MWCNTs](image) | 75.6                        |
| TDPy-modified MWCNTs | 1:1                  | ![TDPy-modified MWCNTs](image) | 93.4                        |
|                      | 1:2                  | ![TDPy-modified MWCNTs](image) | 73.2                        |

**Figure S3.** Average size of the MWCNT agglomerates in MWCNT/oil blend dispersions for the unmodified, TOPy- and TDPy- modified MWCNTs.
3. FTIR spectroscopic measurements

FTIR spectra for unmodified, 1:1 \( \text{TOPy} \) and 1:1 \( \text{TDPy} \)-modified MWCNTs in the full wavelength range is shown in Figure S10.

![FTIR spectra](image)

**Figure S4.** FTIR spectra of for unmodified, 1:1 (w/w) \( \text{TOPy} \) and 1:1(w/w) \( \text{TDPy} \)-modified MWCNTs.

4. Fluorescence Spectroscopy measurements

A set of fluorescence spectroscopy experiments was run at different concentrations of MWCNTs in the modifier solution in THF. As observed from Figure S5, upon excitation, the fluorescence spectra of the MWCNTs again exhibit superimposable profiles with respect to the free \( \text{TOPy} \) and \( \text{TDPy} \) molecules in THF. However, there is a significant quenching in the fluorescence emission intensity in the presence of MWCNTs when compared to the emission intensity of the modifier molecules alone in THF (Figure S5).

The strong fluorescence emission intensity decreased in a non-linear, exponential fashion upon addition of MWCNTs. The intensity of the fluorescence was quenched by 56% and 77% upon addition of the MWCNTs to \( \text{TOPy} \) at 1:0.4 and 1:1 (w/w) ratios, respectively. It implies that the adsorption of the \( \text{TOPy} \) and \( \text{TDPy} \) on the surface of MWCNTs possibly
affects the decay of singlet-excited pyrene moieties. Moreover, the fluorescence quenching implies the interaction that occurs between the MWCNTs and the modifier molecules. There is no significant spectral shifting in the presence of MWCNTs. However, the slight shift of the lowest wavelength peak (437 nm) is dependent on the concentration and is due to reabsorption of the fluorescence emission.\textsuperscript{1} The pyrene moiety is planar and a locked conformer with a rigid structure. Therefore, natural structure of both the modifiers is ideal for mapping to MWCNTs. Hence, the mapping does not lead to a red shift of the peak maximum.

**Figure S5.** Fluorescence quenching curves for TOPy and TDPy with increase in the concentrations of MWCNTs: (a) TOPy solution in THF ([TOPy] = 31.5 µM) with MWCNTs (0–20 mg/l); (b) TOPy solution in THF ([TOPy] = 36.3 µM) with MWCNTs (0–28 mg/l); ($\lambda_{ex}$ = 426 nm, excitation and emission slit width is 2.5 nm).

5. Characterisation of modifier molecules: TOPy and TDPy

Both the alkylated pyrene derivatives were characterised using NMR, FTIR, UV–visible spectroscopy and fluorescent spectroscopy and the corresponding spectra are given below: Figure S6 ($^1\text{H}$-NMR spectrum of TOPy in CDCl$_3$); Figure S7 ($^{13}\text{C}$-NMR spectrum of TOPy in CDCl$_3$), Figure S8 ($^1\text{H}$-NMR spectrum of TDPy in CDCl$_3$); Figure S9 ($^{13}\text{C}$-NMR spectrum of TDPy in CDCl$_3$); Figure S10 (FTIR spectra of TOPy and TDPy) and Figure S11 (UV-Vis absorbance spectra and fluorescence emission spectra).
Figure S6. $^1$H-NMR spectrum of TOPy in CDCl$_3$.

Figure S7. $^{13}$C-NMR spectrum of TOPy in CDCl$_3$. 
Figure S8. $^1$H-NMR of TDPy in CDCl$_3$.

Figure S9. $^{13}$C-NMR of TDPy in CDCl$_3$. 
Figure S10. FTIR spectra of TOPy and TDPy.

Figure S11. (a) UV-Vis absorbance and (b) Fluorescence emission spectra for TOPy and TDPy in THF. (excitation at 426 nm and excitation and emission slit width is 2.5 nm).