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COMMUNICATION

Salting-in effect in organic dispersions of poly(3-hexyl thiophene)- carbon-nanotubes

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Accepted oothC. Bounioux,^a A. Bar-Hen^a and R. Yerushalmi - Rozen^{a, b*}

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Addition of small concentrations of different inorganic salts to THF solutions of poly(3-hexyl thiophene) that contain non-dispersed powder of Multi-Walled Carbon Nanotubes (MWNT) was found to "salt-in" the precipitated tubes leading to the formation of a stable dispersion of the MWNT. The effect seems to result from a salt-induced conformational change of polymer chains adsorbed onto the CNT, resulting in the onset of (entropic) steric repulsion among polymer-decorated chains.

Solution processing of carbon-nanotubes (CNTs) in organic solvents is a prerequisite for their application as structural and functional elements in a variety of nano-composite materials and devices¹⁻³ including polymer-based organic solar cells⁴. Yet, CNTs are hard to disperse due to the large cohesion energy between the tubes¹. Among the efficient dispersing agents are derivatives of polythiophenes, and in particular poly(3-hexylthiophene) P3HT^{5,6}. P3HT disperses CNT in chlorinated solvents such as chloroform or dichlorobenzene at low polymer concentration in the range of 30-60 µg/ml enabling Multi walled Carbon Nanotubes (MWNT) loadings of above one mg/ml. P3HT as well as other Poly(3-alkyl thiophenes), P3ATs, are comb-like polymers where the main chain is composed of covalently linked thiophene rings and the derivatives differ by the length of the alkyl side-chains. It is now well accepted that sonication -assisted dispersion of CNT in solutions of P3ATs proceeds by adsorption of the polymers from solution onto the CNT⁶. The adsorbed polymers form helical (or double helical) wrapping around the CNT driven by π - π interactions between the thiophene rings and the CNT surface. The alkyl side chains of the adsorbed polymers^{7,8} protrude into the solution and induce steric repulsion among polymer-wrapped tubes that prevents re-aggregation of the coated tubes. While high dispersing efficiency is measured in chlorinated solvents, some applications such as printing of polymer-based organic solar cells and industrial scale fabrication of functional CNT-based nanocomposites^{9,10} may benefit from using chlorine-free solvents such as Tetrahydrofuran (THF) and Toluene. Yet, the dispersing efficiency of P3ATs is very low in these solvents. Here we report a surprising observation: we find that small concentrations of inorganic salts in a concentration range of 0.08 to 10 mM enable the dispersion of MWNT in THF solution of P3HT. More specifically, when salt is added to a polymer solution that

contains a non-dispersed powder of MWNT and sonicated (1h, 80Watt) a stable dispersion is formed. Similar sonication does not lead to formation of a stable dispersion in the absence of salt. In Fig. 1 (A, D) we present images of vials containing P3HT solutions in THF at two concentrations: (0.1 and 0.25 mg/ml). Following sonication (1h, 80 Watt) a dark dispersion is obtained. Within few minutes after the sonication the dispersion separates into a clear solution (figure 1 (B, E)) and a precipitate of aggregated MWNT coated by the adsorbed polymer. The polymer concentration in the upper phase is significantly lower than the initial concentration of the solvated P3HT, as indicated by the colour change of the solution (Fig. 1: B is almost colourless, as compared to A and the colour of E is brighter as compared to D). Following the addition of KBr to a final concentration of 0.1 mM (Fig. 1C) or AlCl₃ (Fig. 1F) and sonication (1h 80W) a stable dispersion of MWNT is formed.

The effect is not salt-specific, and observed in different types of salts, as presented in Table 1, where the minimal concentration of P3HT required for formation of stable dispersion of MWNT-MER in the presence of salts is presented.

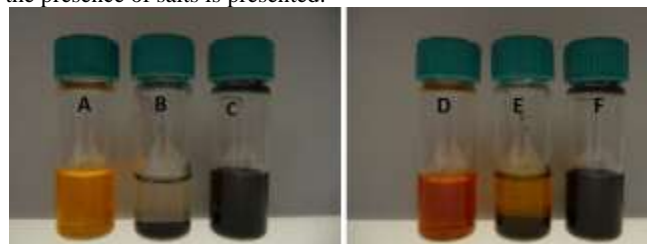


Fig.1 Images of vials containing THF solution of (A) 0.1 mg/ml P3HT (B) after addition of 2 mg/ml of MWNT-MER and sonication for 3h (C) After addition of KBr to a final concentration of 0.5 mM and re-sonication for 1h (D) 0.25 mg/ml P3HT (E) after addition of 2 mg/ml of MWNT-MER and sonication for 3h (F) After addition of AlCl₃ to a final concentration of 1.2 mM and re-sonication for 1h.

The microstructure of the dispersions as investigated via transmission electron microscopy (TEM) is presented in Fig.2. In Fig.2 (A) we present an overview of the dispersion, showing the random orientation of the dispersed tubes. Fig.2 (B) and (C) present

a higher magnification of the MWNT surface where the adsorbed polymer can be seen.

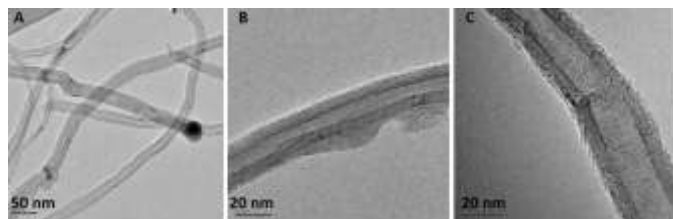


Fig. 2 Specimens prepared from a dried dispersion of MWNT-MER in (A) THF solution of 0.25 mg/ml of P3HT and 0.8 mM KI (B) THF solution of 0.25 mg/ml of P3HT and 1.2 mM AlCl₃ (C) THF solution of 0.1 mg/ml of P3HT and 0.5 mM KBr

Table 1: Dispersions of 2mg/ml MWNT-MER in P3HT-solvent + salt solutions

THF	Monomer concentration in mg/ml & molarity	Molar concentration of the salt mM	Ratio: salt to monomer
KBr	0.1 (0.7 mM)	0.5mM	0.7
TBAB	0.1 (0.7 mM)	10 mM	14
AlCl ₃	0.25 (1.5 mM)	1.2 mM	0.8
KI	0.25 (1.5 mM)	0.8mM	0.5
Toluene			
TBAB	0.5 (3 mM)	10mM	3

We also found that addition of Tetra-*n*-butylammonium bromide (TBAB 10 mM) to toluene solutions of P3HT at polymer concentration of 0.5 mg/ml or P3OT concentration of 0.25 mg/ml followed by sonication (1h 80W) results in the formation of stable dispersions of MWNT-MER. We note that the salts used in this study are sparingly soluble in THF, at concentrations indicated in Table 1SI.

Previous studies reported that mM concentrations of KI decrease the thermodynamic stability of CNT dispersions in *n*-methylpyrrolidone, NMP, leading to bundle formation and precipitation of pre-dispersed CNT¹¹. The "salting out" of the CNT from NMP was attributed to the depletion of the ions from the CNT surface and a resulting increase in the CNT solvophobicity of the CNT upon salt addition. Here we observe a "salting in" effect. To elucidate the molecular origins of the phenomenon we investigated the UV-Vis absorption spectra of thin films prepared from P3HT solutions in the presence of the different salts (Fig.3 and Table 2).

Table 2: Spectral features appearing Fig.3 (Thin films).

	Salt free	KI 0.8mM	KBr 0.5mM	TBAB 10mM	AlCl ₃ 1.2mM
S1(nm)	523	517	520	509	516
S2(nm)	556	561	559	551	553
S3(nm)	607	602	603	604	602

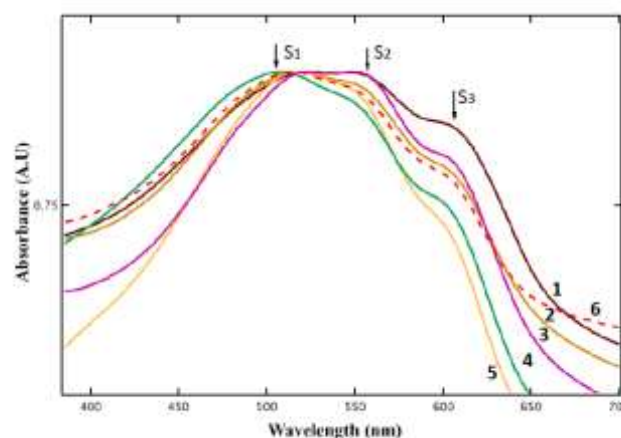


Fig.3 Absorption spectra of P3HT thin films (about 50 nm thick), prepared from THF solutions of P3HT (0.25 mg/ml) and different salts by drop-casting onto a glass substrate (1) P3HT (no salt) (2) P3HT +0.8 mM KI (3) P3HT + 0.5mM KBr (4) P3HT + 1 mM TBAB (5) P3HT +0.1 mM AlCl₃ (6) MWNT in P3HT+10 mM TBAB.

The solid-state absorption spectra of the native P3HT is characterized a peak at 523 nm (S1), 556 nm (S2), and a shoulder at 607 nm (S3). These three bands can be attributed to the π - π^* transition and in a thin solid film reflect the interaction among neighboring chains. The blue-shift in λ_{max} (S1) in Table 2, as compared to that measured in thin films of salt-free P3HT suggests that the inter-chain packing is disturbed by the addition of salt. We also observe that the relative intensity of the shoulder observed at around 600 nm (S3) is decreased as compared to the S1 peak, providing an additional indication for the disruption of the inter-chain packing¹²⁻¹⁴. Though the absolute concentration of the salts in the solution is small, the relative number of salt molecules per polymer chains is quite significant (Table 1) and ranges from 1 salt molecule for every 2 monomers (KI in THF) to 14 salt molecules per every monomer (TBAB in THF).

The dispersion mechanism of CNT by P3ATs relies on adsorption of the solvated polymer chains onto the CNT during the sonication period via π - π interactions between the thiophene rings and the CNT surface, and the onset of excluded-volume repulsion among the alkyl side-chains of the adsorbed polymers^{15,16}. It is well known that adsorption of polythiophene derivatives onto CNT is determined by the conjugation length of the polymer, the solvent, and the curvature of the CNT¹⁷. For a given type of CNT and a solvent, a lower conjugation length is expected to reduce the driving force for polymer adsorption onto the CNT. Yet, we observe that the addition of salt both causes a blue-shift in the absorbance (indicating a shorter conjugation length) and leads to "salting in" of the CNT. The seemingly inconsistency is resolved by the realization that in the experimental sequence described here, polymer adsorption onto the MWNT takes place in salt-free solutions (Fig. 1). When salt is added to the solution that contains non-dispersed polymer-wrapped CNT it modifies the conformation of the (adsorbed) polymer chains leading to a higher effective excluded volume among the alkyl side chains and triggers a high enough steric repulsion among polymer-coated CNT so as to induce "salting-in" of the CNT. The change in the colour of the solution (Fig.1A vs. B, and D vs. E) supports the mechanism described above: it indicates that the concentration of P3HT in the upper (liquid) phase of CNT dispersions is reduced as compared to the native solutions probably due to adsorption onto the (non-dispersed) CNT powder. To further

investigate this point we carried an additional experiment: MWNT-MER were sonicated in THF solution of P3HT 0.6 mg/ml and 0.25 mg/ml for 1h. Following the sonication the CNT powder aggregated and precipitated (Fig.4B (left vial)).

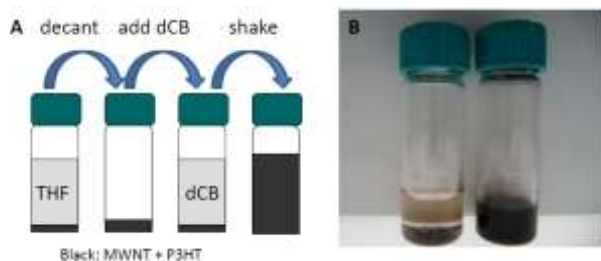


Fig.4 (A) Solvent exchange process results in dispersion of P3HT-coated MWNT-MER as described in the text. (B) Left: THF solution of 0.6 mg/ml P3HT after addition of 2 mg/ml of MWNT-MER and sonication for 3h. Right: Following the removal of the upper phase and addition of a similar volume of 1,2dCB (as illustrated in (A)) a stable dispersion is spontaneously formed.

Then the solution was decanted from above the precipitate, and 1,2 dCB was added to the precipitate, leading to spontaneous formation of a stable dispersion (Fig.4A). The results of this experiment suggest that P3HT chains adsorb onto MWNT-MER from THF yet a dispersion is not formed. THF is a moderate to good solvent for P3HT at room temperature¹⁷ and when replaced by a better solvent (1,2 dCB) the increase in excluded volume results, as in the case of salt addition, in the onset of a larger steric barrier among the polymer-coated MWNT leading to the dispersion of the MWNT.

Conclusions

Low concentrations of inorganic salts may be used to induce the formation of stable dispersions of MWNT in organic solutions of P3HT. The "salting in" of polymer-coated CNT seems to result from a conformational change of the adsorbed polymer chains due to the solvated salt. The dispersions can be used for preparation of functional fibers for photovoltaic applications via electrospinning, where the presence of the salt improves the conductivity of the solution and thus assists in the spinning process¹⁸.

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Notes and references

^a Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

^b The Ilse Katz Institute for Nanoscale Science and Technology Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel.

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