

# Controlled Aggregation of Biopolymer-Wrapped Carbon Nanotubes in Aqueous Suspension, Induced by Cationic Porphyrin

E. S. Zarudnev, V. A. Karachevtsev\*

**Summary:** Unusual aggregation of biopolymer-wrapped single-walled carbon nanotubes (SWCNTs) induced by cationic porphyrin meso-tetrakis(4-N-methylpyridyl)porphine (TMPyP4) in aqueous suspension has been studied by absorption spectroscopy and molecular dynamics simulation. After the addition of a small dose of TMPyP4 ( $10^{-6}$  M) into poly(rC):SWCNTs aqueous suspension, nanotubes begin to aggregate, but the aggregates are stable without precipitation during a few days. Spectral observations indicate that the porphyrin core stacked with  $\pi$ -systems of the biopolymer:SWCNT hybrid and all nanotube species take part in this aggregate formation without any selection. Molecular dynamic simulation demonstrates that the stable complex consisting of two nanotubes can be formed when TMPyP4 molecules bound nanotubes both owing to  $\pi$ - $\pi$  stacking of the porphyrin core with the surface of one nanotube and with the oligonucleotide adsorbed onto another nanotube. TMPyP4 molecules not only couple the biopolymer:nanotube hybrids, but also they stitch polymer's strands wrapping around each nanotube resulting in continuous floatation of aggregates in water. It was shown that the aggregate is stable even at 373 K. At this temperature additional contacts between two neighbor's polymers appear which strengthen this aggregate too. The controlled aggregation of biopolymer-wrapped carbon nanotubes can be employed at the fabrication of multifunctional supramolecular assemblies, photovoltaic cells and in biosensing.

**Keywords:** biopolymers; carbon nanotube aggregation; cationic porphyrin; molecular dynamics; van der Waals interaction

## Introduction

Owing to their unique quasi-one-dimensional structure SWCNTs have great potential in electronics, optics, mechanics, and biosensing. To integrate the carbon nanotube into multicomponent structures or devices, an approach based on self-assemblies from individual carbon nanotubes can be very efficient.<sup>[1]</sup> For this purpose DNA which wraps tightly around the nanotube in water<sup>[2]</sup> can be applied as a very useful interface polymer which has an excellent

molecular recognition capability and which exploits widely to develop different nanostructures.<sup>[3]</sup> The controlled aggregation of individual nanotubes with a possibility of the formation of high density of DNA-wrapped individual nanotubes in aqueous suspension is the first stage in the route of the integration of these quasi one-dimensional materials into technology.

Controlled aggregation of individual nanotubes can be realized by the hybridization of a free long ssDNA chain simultaneously with two complementary polymers adsorbed to different nanotubes.<sup>[4,5]</sup> Proteins or enzymes which bind effectively to DNA in water can also cause an aggregation of nanotubes covered with DNA.<sup>[6]</sup>

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