

Carbon nanotube-porphyrin/naphthalocyanine hybrids for photo-induced electron transfer studies

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Abstract: Nanoscience and technology is an emerging field for scientists and engineers due to remarkable mechanical and electronic properties of carbon nanotubes (CNTs), and their application in designing optoelectronic and photovoltaic devices. In this report, single wall carbon nanotubes (SWCNTs) are solubilized via non-covalent, π - π stacking with pyrene-functionalized with phenyl imidazole co-ordinating ligand and self-assembled donor-acceptor nanohybrids were formed with electron donors, Zinc porphyrin (ZnP) or Zinc naphthalocyanine (ZnNC). The nanohybrids are fully characterized by TEM, UV-Vis, NIR, and electrochemical studies. Efficient electron transfer from the donor ZnP and ZnNC entities to the acceptor SWCNTs and generation of the photo-excited state is revealed by steady-state and time resolved emission studies respectively

1. Introduction

Carbon nanostructures, due to their unique electronic properties, are among the most promising candidates for the development of optical and photovoltaic devices. Single wall carbon nanotubes (SWCNTs) are of particular interest because of their excellent mechanical and electronic properties. Due to the insolubility of SWCNTs in various polar and non-polar solvents, preparation of model systems in solution poses a problem. Solubilization and utilization of SWCNTs in building donor-acceptor nanohybrids is of considerable interest in the field of photovoltaics.

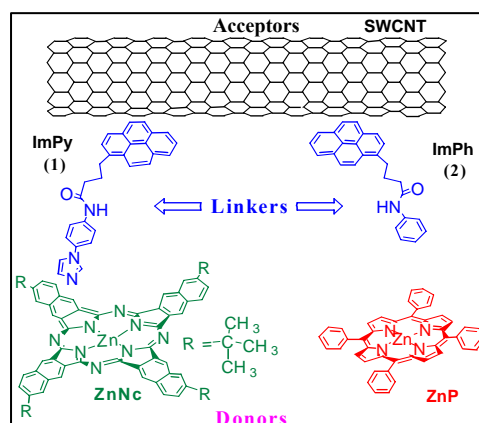
In the present system, SWCNTs are solubilized via non-covalent, π - π stacking with pyrene-functionalized phenyl imidazole coordinating ligand. Using the pyrene-appended phenylimidazole ligand (PyIm) of the SWCNT-PyIm, Zinc porphyrin(ZnP) or Zinc naphthalocyanine (ZnNC) electron donors are axially coordinated to yield SWCNT-PyIm-ZnP and SWCNT-PyIm-ZnNC nanohybrids, respectively. The nanohybrids are fully characterized by transmission electron microscopy (TEM), UV-Vis, NIR, and electrochemical studies. Efficient electron transfer from the donor ZnP and ZnNC entities to the acceptor SWCNTs was revealed by steady-state emission studies. The generation of the photo-excited species was further confirmed by time-resolved studies. The results presented confirm the assembling of these nanohybrids and the generation the long-lived charge separated state.

2. Experimental, Results, and Discussion

Synthesis of imidazole and phenyl functionalized pyrene derivatives

N-[4-(1-H-Imidazolyl)phenyl-4-pyreneyl butanamide (ImPy) (**1**): This compound was prepared by condensation of 1-Pyrene butyric acid and 4-(1-H-Imidazolyl)-aniline in presence of 1, 3-dicyclohexycarbodiimide and 4-(dimethylamino) pyridine in 50 ml dry CH_2Cl_2 . The reaction mixture was stirred for 24 hrs and the solvent was evaporated under reduced pressure. The crude compound was purified on silica gel column using CHCl_3 : ethylacetate (20:80 v/v) as eluent. Yield: 144 mg (20%).

N-Phenyl-4-pyreneyl butanamide (PhPy) (**2**): This compound was



prepared according to the above described procedure by using aniline. The crude compound was purified on a silica gel column using hexane: CHCl_3 (60:40 v/v) as eluent. Yield: 125 mg (25%).

Preparation of ImPy-SWNTm or PhPy-SWNT conjugates

A 1.5 mg aliquot of purified HiPCO SWCNTs was added to 3.2 mg of ImPy or PhPy dissolved in 15 ml of dry dimethylformamide (DMF), tetrahydrofuran (THF) or *o*-dichlorobenzene (DCB) and the reaction mixture was stirred for 48 hrs at room temperature. The resulting mixture was sonicated (Fisher Scientific, 60 Hz, 40 W) for 6 hrs at 20 °C followed by centrifugation (Fisher scientific, 50/60 CY) for 2 hrs. The excess of ImPy or PhPy was removed by repeated centrifugation at 20°C. At the end, 10 ml of fresh solvent was added to the resulting deposit and sonicated for 15 min. at 20 °C. This homogenous black dispersion was stable at room temperature for weeks and was used in the aforementioned studies.

Transmission electron microscopy studies

The ImPy or PhPy treated SWCNTs yielded soluble samples in THF, DCB or DMF solvents. Analysis of these solubilized samples using TEM revealed an appreciable decrease in branches of several SWNT stacked together compared with untreated commercial high purity SWCNT sample. Additionally, the adopted solubilization procedure removed most of the amorphous carbon and the Fe nanoparticles present in the untreated SWCNT.

Ground state and excited state electron transfer studies

Evidence for the presence of SWCNTs in solubilized samples of ImPy-SWNT or PhPy-SWNT was obtained by UV-visible-NIR spectroscopic studies. The fine structures of the bands corresponding to solubilized SWCNT, ranging from 400-1100 nm, indicated the preserved electronic structure of the SWNT after immobilization using ImPy or PhPy. The broadened peaks of pyrene moiety, due to π stacking with SWCNTs, were also observed in the UV region. The formation of supramolecular donor-acceptor conjugates featuring ZnNC or ZnP with ImPy-SWNT was observed by the decreased intensity of 772 nm and 424 nm peaks (followed by red shift) of ZnNC and ZnP respectively. The evidence for the facile electron transfer and free-energy changes for charge separation and charge recombination within this nanohybrid were obtained from electrochemical studies.

Steady state and time-resolved emission studies revealed efficient fluorescence quenching of the donor ZnP and ZnNc entities in the nanohybrids. Nanosecond transient absorption spectra revealed that the photoexcitation of the ZnNc or ZnP moiety resulted in the one-electron oxidation of the donor unit with a simultaneous one-electron reduction of SWNT.

3. Conclusion

Supramolecular non-covalent donor-acceptor nanohybrids comprised of zinc naphthalocyanine or zinc porphyrin as electron donor and non-covalently functionalized SWNT as electron acceptor were constructed and characterized by various physico-chemical techniques including TEM, UV-visible-NIR, and electrochemical methods. Using imidazole ligand of the functionalized pyrene, zinc naphthalocyanine or zinc porphyrin was axially coordinated to yield ZnNc-ImPy-SWNT or ZnP-ImPy-SWNT nanohybrids. Photoinduced electron transfer from the singlet excited donor entity to the SWNT acceptor entity was probed by the steady-state and time-resolved emission studies which revealed efficient quenching of the donor entity in these nanohybrids. Free energy changes pertaining to these electron transfer reactions were deduced from electrochemical data.

4. Acknowledgements

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[1] R. Chitta, A. S. D. Sandanayaka, A. L. Schumacher, L. D'Souza, Y. Araki, O. Ito, F. D'Souza *J. Phys. Chem C* **2007**, submitted.