

A theoretical and experimental exploration of the mechanism of microwave assisted 1,3-dipolar cycloaddition of pyridinium ylides to single walled carbon nanotubes



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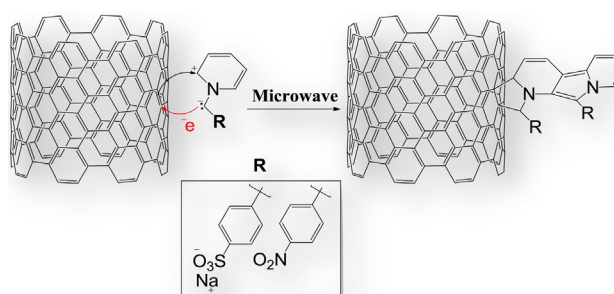
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HIGHLIGHTS

- PM3 (RHF) type calculations suggest that charges are probably transferred from HOMO of pyridinium ylides to LUMO of SWNTs.
- Theoretical predictions indicate a $\text{HOMO}_{\text{ylide}}-\text{LUMO}_{(8,8)\text{ SWNT}}$ controlled 1,3-DC reaction (Type I).
- Pyridinium ylides with smaller HOMO–LUMO energy gap is experimentally found to be more selective to large diameter SWNTs.
- Reactivity of pyridinium ylide might be manipulated using strong electron withdrawing groups.
- Graphene surface modification may be anticipated using the same approach.

GRAPHICAL ABSTRACT



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ABSTRACT

Cycloaddition reactions have widely been used for surface functionalization of single walled carbon nanotubes (SWNTs). Here, 1,3-dipolar cycloaddition (1,3-DC) of two new pyridinium ylides, generated *in-situ* via the addition of triethylamine (NEt_3) to the Kröhnke salts *N*-(4-methyl sodium benzene sulfonate)-pyridinium bromide and *N*-(4-nitrobenzyl)-pyridinium bromide, to SWNTs under microwave conditions are assessed both theoretically using PM3 (RHF) type calculations and experimentally. Evidence of covalent surface modification is provided by FTIR, UV–vis–NIR and resonance Raman spectroscopy. Solubility of the modified SWNTs increases when compared to as-received SWNTs. Quantification of surface groups is performed via TGA–MS and XPS. 1,3-DC of pyridinium ylides with smaller HOMO–LUMO energy gap is found to be more selective to large diameter SWNTs. Theoretically predicted smaller energy gaps between $\text{HOMO}_{\text{ylides}}$ and $\text{LUMO}_{(8,8)\text{ SWNT}}$ suggest that the charges are probably transferred from pyridinium ylides to SWNTs indicating $\text{HOMO}_{\text{ylide}}-\text{LUMO}_{(8,8)\text{ SWNT}}$ controlled 1,3-DC. Regioselectivity of second ylide addition as addendum to ylide–SWNT adduct is also discussed.

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1. Introduction

Carbon nanotubes (CNTs) have gained increasingly more scientific attention in nanoscience due to their exceptional electrical,

thermal and mechanical properties and might find application in areas diverse as composite materials, energy storage, sensors, field emission devices and nanoscale electronic components [1,2]. However, the poor solubility of raw material both in aqueous and organic medium is an issue while being processed. Covalent surface modification of CNTs enhances the solubility and processability of them together with offering possible reactive functional side groups for further applications and separation [3–8]. Covalent functionalization strategies including 1,3-dipolar cycloadditions (1,3-DCs) to sort CNTs in terms of their helicity and diameter has recently been reviewed [9,10]. The use of 1,3-DCs has also been extended to the covalent surface modification of graphene [11,12]. Practicality of 1,3-DCs of a series of 1,3-dipoles to armchair SWNTs (5,5) was theoretically examined and, versatility of using azomethine ylides, ozone, nitrile ylides and nitrile imines were also predicted theoretically [13]. In agreement with the solid-state physics description of band structures [14], electronic structure and chemical reactivity of carbon nanotubes were also described using real-space orbital representations and traditional concepts of aromaticity, orbital symmetry and frontier orbital [15]. Experimentally, azomethine ylides, typically generated *in-situ* by the thermal condensation of aldehydes and α -amino acids, have successfully introduced to produce pyrrolidine rings with solubilizing triethylene glycol chains or octyl groups [6,7]. Functionalized SWNTs showed one pyrrolidine ring correspond to about 95 carbon atoms of the SWNT and solubility values closer to 50 mg mL⁻¹ in chloroform. 1,3-DC of nitrile imines and nitrile oxides has been carried out to attach 2,5-diarylpyrazoline or pyridyl-isoxazoline rings, respectively on nanotube surface [16,17]. Microwave induced functionalization of carbon nanotubes has also been described showing that 1,3-DC of nitrile imines to SWNT sidewall under microwave conditions was faster than conventional heating [18]. Brunetti et al. reported the microwave-assisted rapid cycloaddition to pristine nanotubes in solvent free conditions using octyl substituted aziridines [19]. Modified SWNTs displayed ~1 functional group for every 51 SWNT carbon atom and they were slightly soluble in DMF (0.13 mg mL⁻¹) and dichloromethane (0.11 mg mL⁻¹). It was shown that the microwave assisted cycloaddition of aziridines were much more efficient than the classical thermal conditions for azomethine ylides [6].

In our research group, it has been demonstrated that SWNTs can undergo 1,3-DC with azomethine imines, 3-phenyl-phthalazinium-1-olate, to yield a bridged phenyl phthalazine groups with coordination sites for various metals including Cu, Co, and Pt [4]. We have also shown that pyridinium ylides generated from simple Kröhnke salts undergo a 1,3-DC to SWNTs to afford indolizine functionalized fluorescent SWNTs [5]. Reaction was believed to occur with the pyridinium ylide first adding to the nanotube surface to form a pyrrolidine ring, closely followed by the addition of a second ylide to the addendum on the nanotube surface to afford an indolizine. The mechanism of pyridinium ylide cycloaddition was attributed to electron transfer from the SWNT to the 1,3-dipole assuming similar selective addition of diazonium salt to SWNTs, which is in agreement with metallic SWNTs, which have a finite DOS at the Fermi level, being more reactive than semiconducting SWNTs [20]. However, it is believed that reactivity/mechanism/regioselectivity of pyridinium ylide cycloaddition to SWNTs might be different from diazonium salt addition to SWNTs since it is well studied that HOMO–LUMO energy levels of both dipole (pyridinium ylide) and dipolarophile (C=C bond on CNT surface) participate a significant role during cycloaddition reactions [21].

In this paper, the reactivity/mechanism of pyridinium ylide addition to SWNTs is therefore assessed theoretically using semi-empirical PM3 (RHT) calculations. The regioselectivity of the second ylide addition (as addendum) to pyridine ring to afford an

indolizine is also discussed theoretically. 1,3-DC of two new pyridinium ylides, readily prepared from simple Kröhnke salts *N*-(4-methyl sodium benzenesulfonate)-pyridinium bromide and *N*-(4-nitrobenzyl)-pyridinium bromide, is presented. Structural assignment of Kröhnke salts is carried out by NMR and FTIR. Covalent addition to SWNT surface is probed via UV–vis–NIR, FTIR, TGA–MS, XPS and resonance Raman spectroscopy.

2. Material and methods

2.1. Computational method

All computational work to have the optimized, well-defined structures of SWNTs and ylides and exploration of their reactivity were held by using HyperChem 7.0 package program using semi-empirical PM3 (RHT) calculations [22]. As a minimization algorithm throughout the calculations, a conjugate gradient, Polak–Ribiere (convergence limit of 0.0001 kcal mol⁻¹) and the RMS gradient condition of 0.0001 kcal (Å mol)⁻¹ were chosen.

2.2. Preparation of purified SWNTs

Purified SWNTs produced by the HiPco method and supplied by Unidym, USA, were further purified by heating in air at 400 °C, then soaking in 6 M HCl overnight, followed by filtration over a polycarbonate membrane (0.2 µm), and washing with de-ionized water until neutral pH was reached [23]. The purified SWNTs were annealed under vacuum (10⁻² mbar) at 900 °C to remove residual carboxylic acid functional groups and any adsorbed gases or solvents.

2.3. SWNT–indolizine (SWNT2)

SWNTs (10 mg) were dispersed in *N,N*-dimethylformamide (DMF) (15 mL) using mild sonication in an ultrasonic bath (Ultra-wave U50, 30–40 kHz) for 5 min. The pyridinium salt (1) (1.468 g, 4.17 mmol) and triethylamine (0.58 mL, 4.177 mmol) was then added to the dispersion. The reaction mixture was then heated to 150 °C at 2 bar pressure, in a heat and pressure resistant vessel, with microwaves for 1 h (150 W for 5 min followed by 20 W for 50 min at 2.54 GHz) using a Biotage Initiator Sixty which resulted in the formation of SWNT2 following the pyrrolidine attached SWNT intermediate (SWNT1) formation. The functionalized SWNTs were collected via filtration through a PTFE membrane (0.2 µm). The solid SWNTs were then transferred to a cellulose thimble, and impurities and unreacted reagents were removed by Soxhlet extraction using acetonitrile for 18 h. The SWNTs were then dispersed in de-ionized water (50 mL) and filtered through a PTFE membrane (0.2 µm), dispersed in acetone (50 mL) and filtered through a PTFE membrane (0.2 µm), and finally dispersed in ethanol (50 mL) and filtered through a PTFE membrane (0.2 µm) and dried overnight at 120 °C to afford SWNT–indolizine (SWNT2).

2.4. SWNT–indolizine (SWNT4)

SWNT4 was synthesized as described above following the formation of SWNT3 intermediate using 10 mg of SWNTs, pyridinium salt (2) (1.230 g, 4.17 mmol) and triethylamine (0.58 mL, 4.177 mmol).

2.5. Characterization

¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance-400 spectrometer operating at (¹H) 400.13 MHz and (¹³C) 100.62 MHz. Chemical shifts are reported in ppm. Infrared spectra

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