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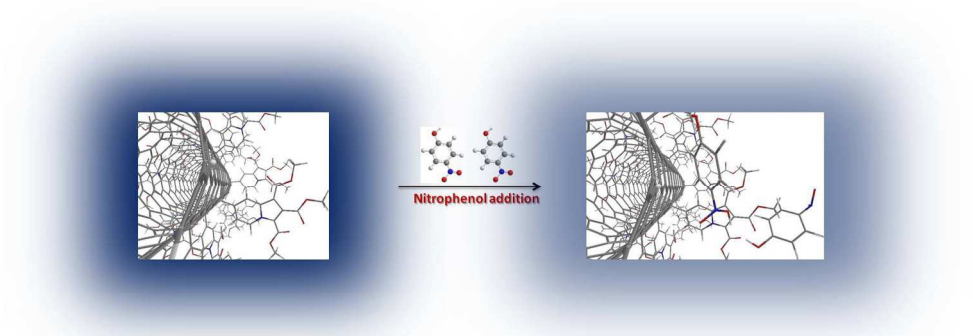
Fluorescent single walled carbon nanotube-mediated sensors with detection limit of ~10^{-8} M for nitrophenol based chemical warfare agents and environmental pollutants.



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Sensing Properties of Light-Emitting Single Walled Carbon Nanotubes Prepared via Click Chemistry of Ylides Bound to Nanotube Surface

M.K. Bayazit, *[a,b] L.O. Pålsson[a] and K.S. Coleman[a]

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Pyridinium ylide functionalized single-walled carbon nanotubes (SWCNTs) generated from simple quaternary pyridinium salts covalently bound to SWCNT surface undergo a 1,3 dipolar cycloaddition with dimethyl acetylenedicarboxylate in a '*click*' chemistry type fashion to yield indolizine modified light-emitting SWCNTs. Conversion of quaternary pyridinium salts into indolizines on SWCNT surface was confirmed by XPS, fluorescence spectroscopy and optical microscopy. The resulting modified SWCNTs were found to emit blue light when excited at 330 nm. Fluorescent quenching experiments performed via nitroaromatic compounds displayed that the fluorescence of modified SWCNTs quenched by nitrophenol derivatives in both solution-state and solid-state, probably due to strong H-bonding interaction between host and guest molecule. Functionalized SWCNTs were further characterized using TGA-MS, FTIR and UV-vis-NIR spectroscopy.

Introduction

Chemical sensing has gained much attention due to increasing demand for monitoring environmental pollution, detecting warfare and security threats, developing diagnostics for medical care and providing efficient and sensitive tools for quality control in industrial applications[1]. Due to their interesting chemical and physical properties carbon nanotubes (CNTs) have been used for chemical sensor applications, each based on alterations in a particular feature of functional material including conductivity for chemiresistors[2, 3] and back gate field effect transistors[3-6] and intensity of scattered light resulted by the adsorption of chemical species for photo chemical or optical sensors[7-11]. Substantial effort, therefore, has been devoted in fabricating SWCNT based sensors and the surface functionalization of CNTs in order for utilizing them for sensing. Following the discovery of bright fluorescence in the 800- to 1600 nm wavelength range of the near infrared from one-dimensional direct band gap semiconducting tubes,[12] a SWCNT based near-infrared optical sensor for glucose detection was fabricated by assembling a monolayer of the enzyme on nanotube surface followed by ferricyanide functionalisation.[13] Pyrene-modified *β*-cyclodextrin-decorated SWCNT field-effect transistor device as a photosensor was used to probe a fluorescent adamantyl-modified Ru complex through a charge-transfer mechanism from pyrenecyclodextrin-SWCNT hybrids to adamantyl-modified Ru complex.[14] A chemiresistive sensor based on SWCNT and hexafluoroisopropanol functionalised polythiophene for the detection of chemical warfare agents including sarin gas and dimethyl methylphosphonate has been shown by a simple spin-casting technique,[3] where the sensory response was investigated measuring the conductance of the SWCNT deposition. Fabrication of fluorescent chemosensors were achieved by covalently quinoline modified CNTs for Cu^{2+} and Zn^{2+} ions[15, 16] and CNTs bearing adsorbed DNA with 6-carboxyfluorescein groups for Hg^{2+}.[17]

Introducing surface groups also enhanced the processability of CNTs, particularly SWCNTs, in both aqueous and non-aqueous solvents by interrupting the strong van der Waals forces causing aggregation or bundling of the material. Covalent strategies to functionalize SWCNTs have included carbene,[18] radical,[19, 20] cycloaddition,[21-24] organolithium addition[25, 26] and oxidation[27, 28] reactions and been recently reviewed.[29] Among radical reactions aryl diazonium salts addition[19, 30-34] has widely been studied using diazonium salts directly[30] or generating them in-situ by oxidation of the corresponding aniline with inorganic[31] or organic[32] oxidants. In our research group, it was shown that pyridine diazonium salts underwent a radical addition reaction to SWCNTs to yield pyridine-functionalized SWCNTs which were able to act as cross-linkers and hydrogen bond to poly(acrylic acid) to form SWCNT hydrogels.[35] '*Click*' chemistry, defined as a modular reaction bringing together two simple units to generate a more complex substance, is gaining momentum in materials science.[21, 36] For CNTs 'click' chemistry is predominately based around the Huisgen cycloaddition of azides to alkynes and has been used to attach polystyrene,[37] β-cyclodextrin[38] and phthalocyanines[39] to the surface of nanotubes. Although other simple 1,3-dipolar cycloaddition reactions also fit the criteria of 'click' chemistry such as the reaction described here.

Herein diazonium salt addition and 1,3-dipolar cycloaddition reactions were utilized in a modular type fashion to introduce light emitting groups to the surface of SWCNTs in a 'click' chemistry type fashion at low temperatures. Fluorescent SWCNTs were tested as sensor to probe nitroaromatic compounds in both solution-state and solid-state.

Experimental

Material Preparation. 1. SWCNTs. Purified SWCNTs, produced by the HiPco method, were purchased from Unidym, USA, and further purified by heating in air at 400 ºC and soaking in 6M HCl overnight. The purified SWCNTs were isolated by filtration over a polycarbonate membrane (0.2 μm, Whatman), and washed with copious amounts of high-purity water until pH neutral. The purified SWCNTs were annealed under vacuum (10^{-2} mbar) at 900ºC to remove residual oxygen containing functional groups and any adsorbed gases or solvents.

2. SWCNT-Pyridine (SWCNT-Py). SWCNT-Py was prepared following the literature procedure.[35] In brief, pyridine diazonium salt generated was reacted with SWCNTs at 0 °C in *N*,*N*-dimethylformamide (DMF). The modified SWCNTs were filtered

through a nylon membrane (0.2 µm, Whatman), re-dispersed in 2 M HCl (100 mL), filtered and washed with copious amount of water until pH neutral. The resulting solid material was dispersed in 2 M NaOH (100 mL) and stirred overnight to ensure deprotonation of the pyridinium salt to pyridine. The functionalized SWCNTs were then isolated by filtration through a nylon membrane (0.2 µm, Whatman) and washed with water until pH neutral and re-dispersed and filtered using THF (2 × 30 mL), acetone (2 × 30 mL) and ethanol (2 × 30 mL), respectively and dried overnight at 80 °C to afford **SWCNT-Py**.

3. SWCNT-Pyridinium Ester Salt (1a). To a dispersion of **SWCNT-Py** (5 mg) in dry DMF (10 mL), dispersed using an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 5 mins, was added ethyl-2-bromoacetate (5 mL, 7.53 g, 45.09 mmol) and the reaction mixture stirred at room temperature for 12 hours. The SWCNTs were then filtered through a nylon membrane (0.2 µm, Whatman), re-dispersed in acetone (30 mL), filtered and washed with acetone (2 × 30 mL) and dried overnight at 80 °C to afford SWCNT-pyridinium ester (**1a**).

Results and discussion

Herein, an elegant synthetic protocol to introduce light-emitting groups to the surface of SWCNTs via diazonium salt addition followed by '*click*' chemistry is demonstrated using the reactivity of pyridine lone pair. The pyridinium ylide, rather than reacting with the CNT surface directly, is covalently bonded to the nanotube which then undergoes 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate (DMAD) to yield fluorescent indolizines, **Scheme 1**. In contrast to previously reported method,[21, 23] combined diazonium salt-click chemistry approach described here offers high yielding indolizine formations at low temperatures, more control on reaction conditions, possible choice of dipoles/dipolarophiles with desired side groups (*e.g.* cyclodextrins,[40] activated alkynes or alkenes at low temperatures[41]) and the characterization of reaction intermediates. It may further provide a route to generate various quaternary pyridinium salts bearing alkyl, aryl or polymers (*e.g.* poly(ethylene glycol)) that is likely to enhance the solubility and processability of SWCNT material. However, multistep surface functionalization of SWCNTs resulted in low yields of isolated products that had noteworthy effect on the characterization of modified SWCNTs by concentration/thickness dependent techniques including FTIR and XPS.

In agreement with the previous literature findings,[35] electronic spectrum of SWCNT-Py in DMF showed suppressed van Hove singularities, indicative of covalent surface modification. (***see ESI Figure S1***) A stable dispersion of SWCNT-Py had a concentration of ~160 µg mL^{-1}, calculated using the Beer's law and an extinction coefficient of 30 mL mg^{-1} cm^{-1} and absorption values at λ = 700 nm,[42] which decreased dramatically to 0.2 µg mL^{-1} upon the addition of ethyl-2-bromoacetate to form the Kröhnke salt (**1a**) which increased to 40 µg mL^{-1} following '*click*' reaction to form the indolizine functionalized SWCNTs (**1b**). Table 1 shows the solubility of the stable dispersion of Kröhnke salt modified SWCNTs (**1a, 2a** and **3a**), indolizine functionalized SWCNTs (**1b, 2b and 3b**) and pyridine functionalized SWCNTs (**SWCNT-Py**) in both DMF and ethanol (EtOH). Solubility of SWCNT-Py in both DMF and EtOH decreased after the formation of **1a, 2a** and **3a**. However, solubility in DMF increased after the cycloaddition reaction to yield indolizines while the solubility of in EtOH decreased, probably due to solute/solvent interactions.

Table 1. Solubility data (µg/mL) of 1a-3a, 1b-3b and SWCNT-Py in both DMF and EtOH.

	SWCNT-Py	1a	2a	3a	1b	2b	3b
DMF	160	0.2	8.4	3.9	40.0	47.4	10.1
EtOH	72.4	34.0	28.5	3.1	16.4	19.3	1.26

The ATR-FTIR spectra of **1b- 3b**, **Figure 1**, displayed the presence of the ester groups attached to the indolizine ring as a broad band (ν_{CO}) centred around 1730 cm^{-1} (along with multiple bands between 1600-1300 cm^{-1}, presumably from the formation of the indolizine).[43] The bands *ca.* 2850-2990 cm^{-1} in the spectrum of **3b** that are up-shifted compared with **1b** were attributed to the aromatic **C-H** stretching, and the band at 1270 cm^{-1} indicated the -**NO_2** symmetric stretching (ν_{NO} 1270 cm^{-1}), confirming the presence of nitro groups.[44, 45] The FTIR spectrum of **2b** was noisy compared to others, probably due to the thickness of the film prepared.

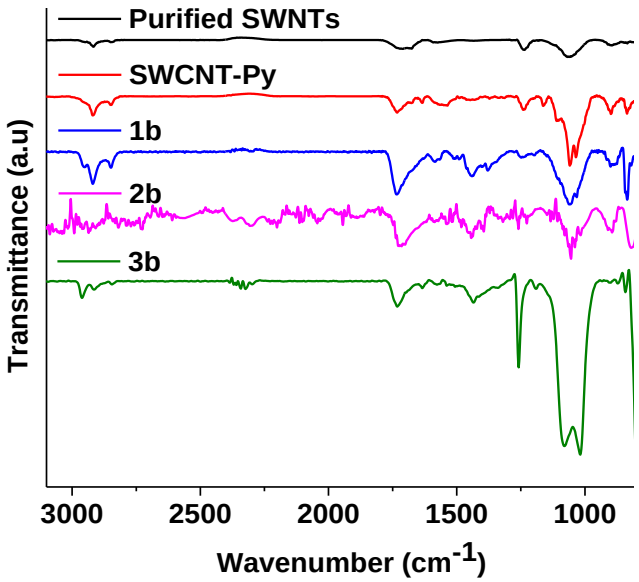
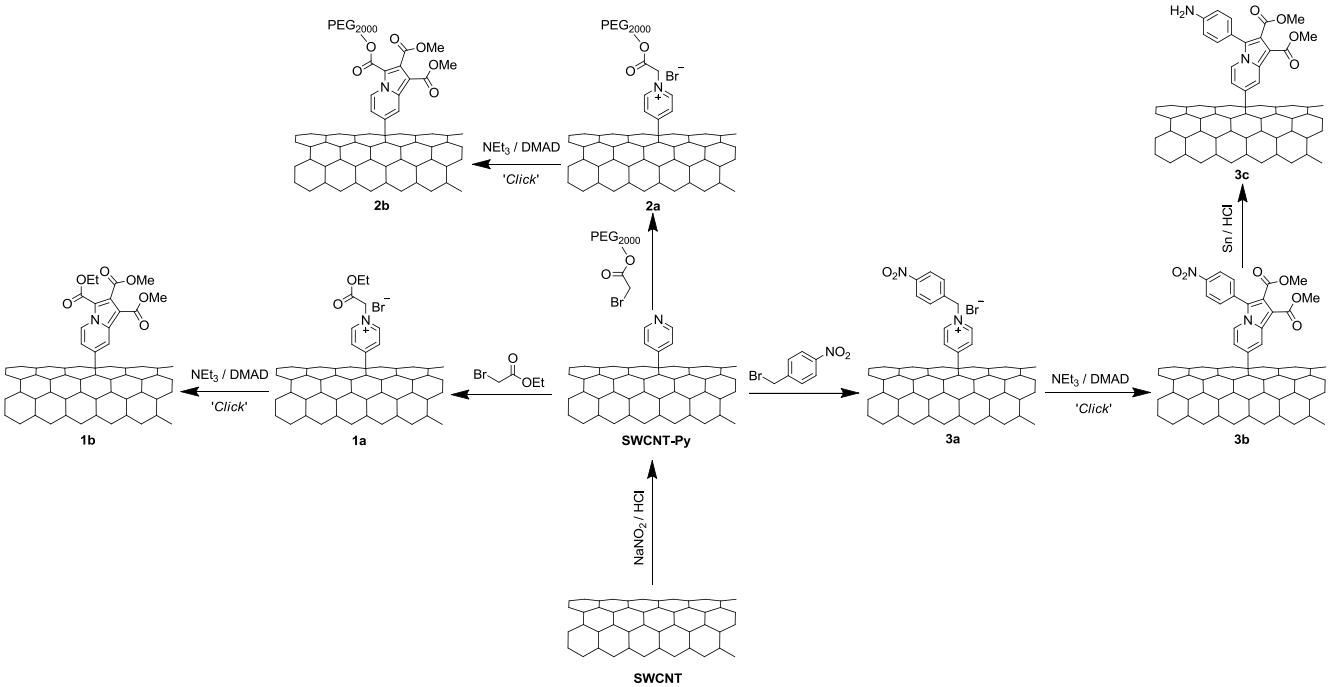


Figure 1. Normalized and offset ATR-FTIR spectra of purified SWCNTs (black line), SWCNT-Py (red line), **1b** (blue line), **2b** (magenta line) and **3b** (olive line). All spectra were recorded using SWCNT films. Curves in are in top-down, respectively.

TGA of **1b, 2b** and **3b** showed a weight loss of ~38, 35 and 64% respectively, at 600 °C compared to *ca.* 7% for purified SWCNTs (**Figure 2**). Weight losses of **1b, 2b** and **3b** correspond to the presence of approximately 1 indolizine group for every 56 (*1.77 N%*), 76 (*1.32 N%*) and 142 (*0.70 N%*) nanotube carbon atoms, respectively, assuming the whole weight loss is due to removal of surface indolizines. Mass spectrometry results revealed that the indolizine groups were covalently attached to nanotube surface, showing common fragments at high temperatures for the indolizine modified SWCNTs (**Figure 3**). The mass fragments detected by mass spectrometry demonstrated that **1b** fragmented into methyl ester group (*OMe, 31 amu*), ethyl ester group (*OEt, 45 a*mu) and *N*-methylpyridinium (C_6H_8N, *94 amu*) *ca.* 300-500 °C, although the parent ion of the indolizine was not observed.

Scheme 1. Multistep synthesis of quaternary pyridinium salt and indolizine modified SWCNTs (**1a-3a**, **1b-3b** and **3c**).



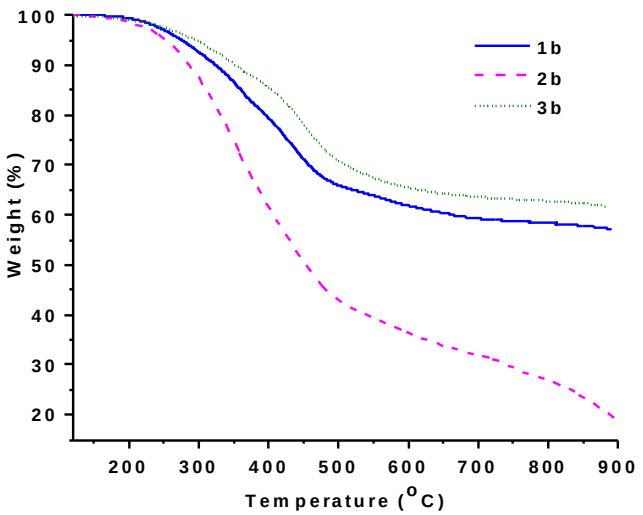


Figure 2. TGA data of **1b** (blue line), **2b** (magenta dashed line) and **3b** (green dotted line). Data were recorded in flowing He (20 mL min^{-1}) at a ramp rate of 10 °C min^{-1} to 900 °C after being held at 120 °C for 30 mins to remove any residual solvent.

Mass spectrometry data recorded for the poly(ethylene glycol) containing indolizine modified SWCNTs (**2b**) displayed the presence of methyl ester (*OMe, 31amu*), *N*-methylpyridinium (C_6H_8N, *94 amu*) and ethyl formyl group ($OCOCH_2CH_3$, *73 amu*) as an indicative of the poly(ethylene glycol) grafted indolizine modified SWCNTs. Fragmented methyl ester group (*OMe, 31 amu*), *N*-methylpyridinium (C_6H_8N, *94 amu*), phenyl group (C_6H_4, *76 amu*), nitroso group (*NO, 30 amu*) and phenoxy group (C_6H_4O, *93 amu*) confirmed the presence of a nitro phenyl group attached on **3b**.

In order to confirm the pyridinium salt formation and their conversion into indolizine via '*click*' reaction, quaternary pyridinium salt modified (**1a** and **3a**) and indolizine modified (**1b** and **3b**) SWCNTs were further analyzed by X-ray photoelectron spectroscopy (XPS). **Figure 4** shows deconvoluted N 1s XPS spectra of (**1a, 1b, 3a and 3b**). The deconvoluted N 1s XPS spectrum of **1a** showed three peaks that can be probably attributed to the quaternary nitrogen (N^+) at *ca.* 402.3 eV,[23, 46] pyridinic nitrogen at 398.9 eV[21, 23, 35] and pyridine radical cation ($N^{+\bullet}$) at 400.2 eV.[47, 48] After the '*click*' reaction of **1a** with DMAD, the deconvoluted N 1s XPS spectrum of **1b** displayed two unchanged peaks positioned at *ca.* 399.9 and 398.9 eV and a new peak generated at 401.4 eV that probably correspond to indolizine ring nitrogen (-N<).[49] The deconvoluted N 1s XPS spectrum of **3a** showed signature of nitro group ($-NO_2$),[23] pyridine diazo (-N=N),[50] quaternary nitrogen (N^+)[23] and pyridine radical cation ($N^{+\bullet}$)[47, 48] at *ca.* 406.2, 403.8, 402.4 and 400.1, respectively. Similar to **1b**, after the '*click*' reaction, the deconvoluted N 1s XPS spectrum of **3b** displayed a new peak formation positioned at *ca.* 401.5 eV as an indication of indolizine formation. N 1s XPS spectra of both **1b** and **3b** showed no peak related to quaternary pyridinium nitrogen (N^+), confirming that pyridinium salts were successfully converted into pyridinium ylides, which subsequently reacted with DMAD to yield indolizines. Compared to the atomic per cent (at.%) nitrogen (2.90 %) found in SWCNT-Py, XPS elemental analysis results of **1b**, **2b** and **3b** verified the presence of 2.22±0.33, 1.60±0.22 and 2.16±0.56 atomic per cent (at.%) nitrogen, respectively, suggesting nitrogen free new group addition (*e.g.* DMAD, PEG, benzene ring etc.) to SWCNT surface.

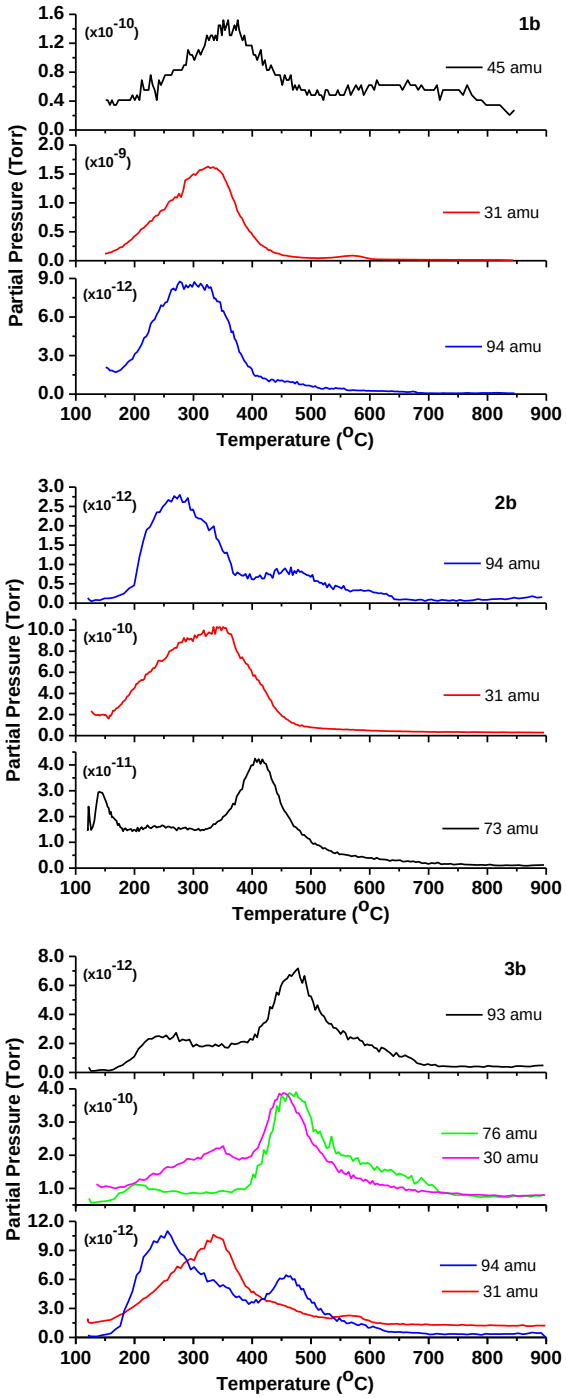


Figure 3. Mass trace of ethoxy (45 amu), methoxy (31 amu) and methylpyridinium (94 amu) fragment given off during the heating of **1b**; Mass trace of methylpyridinium (94 amu), methoxy (31 amu) and ethyl formyl (73 amu) fragment given off during the heating of **2b**; Mass trace of phenoxy (93 amu), (green) phenyl (76 amu), (magenta) nitroso (30 amu), (red) methoxy (31 amu) and (blue) methylpyridinium (94 amu) fragment given off during the heating of **3b**. Data were recorded in flowing He (20 mL min^{-1}) at a ramp rate of 10 °C min^{-1} to 900 °C after being held at 120 °C for 30 mins to remove any residual solvent.

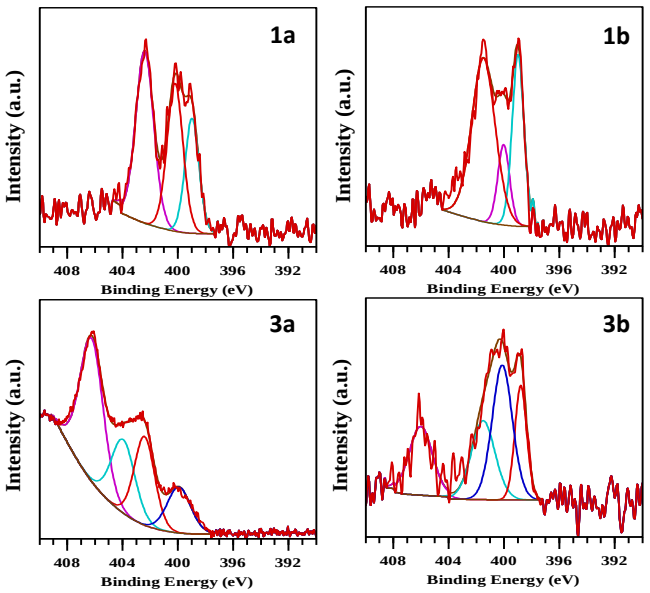


Figure 4. Deconvoluted N 1s XPS spectra of the pyridinium salt modified SWCNTs (**1a** and **3a**) and indolizine modified SWCNTs (**1b** and **3b**). The data were fitted using a Tougaard background. Peak positions were constrained to ±0.2 eV and were fitted using a GL(30) lineshape. Peak FWHM was also constrained in the region 1-3.

Fluorescence properties of indolizine modified light-emitting SWCNTs. The presence of fluorescent groups, so-called indolizine heterocycles, on nanotube surface was also confirmed by fluorescence spectroscopy where the studies showed that the indolizine functionalized SWCNTs (**1b** and **2b**) emitted light upon excitation (**Figure 5**). Excitation of **1b** and **2b** at 330 nm resulted in a blue emission at *ca.* 404 nm. To compare, free indolizine (**FI**), 3-ethyl 1,2-dimethyl indolizine-1,2,3-tricarboxylate was synthesised following the literature[45] via the addition of ethyl-2-bromoacetate to pyridine to afford *N*-(ethoxycarbonylmethyl)-pyridinium bromide which undergoes the 1,3-dipolar cycloaddition reaction with DMAD in the presence of a base (NEt_3). (***see experimental section and ESI Scheme S1***) Compared to **1b** and **2b**, excitation of **FI** at 330 nm resulted in a blue shifted emission at *ca.* 382 nm, suggesting an electron transfer between electron rich indolizine and SWCNT upon the covalent attachment of indolizines to SWCNT surface. Control experiments mechanically mixing the FI with purified SWCNTs followed by washing with THF, acetone and ethanol showed no sign of fluorescence indicating that the fluorescence is not due to the physically adsorbed fluorescent indolizines (**Figure 5**). In contrast to **1b** and **2b**, excitation of **3b** at 330 nm showed no sign of fluorescence (**Figure 5**). It was no surprise since the structures like **3b** bearing strong electron withdrawing groups (*e.g.*–NO_2 groups) are likely to be quenched.[51] Nitro groups of **3b** were reduced to amine (-NH_2) moieties using Sn/HCl[52] to synthesize amino group modified SWCNTs (**3c**) (**Scheme 1**). As expected, excitation of **3c** at 330 nm emitted at 430 nm following the conversion (**Figure 5**). XPS was used to confirm the reduction of nitro (NO_2) groups into amines (NH_2). N 1s XPS spectrum of **3c** showed three components positioned at 406.4, 401.0 and 399.2 eV, corresponding to nitro groups (-NO_2),[23] the indolizine ring nitrogen (-N<)[49] and pyridinic nitrogen,[35] respectively (***see ESI Figure S2***). Decrease in the ratio of the relative peak intensity between the peak positioned at *ca.* 406.4 eV (nitro group nitrogen) and ~400 eV (pyridinic nitrogen) (I_{406}/I_{400}= 0.57) in N 1s XPS spectrum of **3b** (***see Figure 4***)

suggested that nitro groups were almost reduced when compared to the N 1s XPS spectrum of **3c** with I_{406}/I_{400} ratio of 0.08 (**see *ESI Figure S2***) .

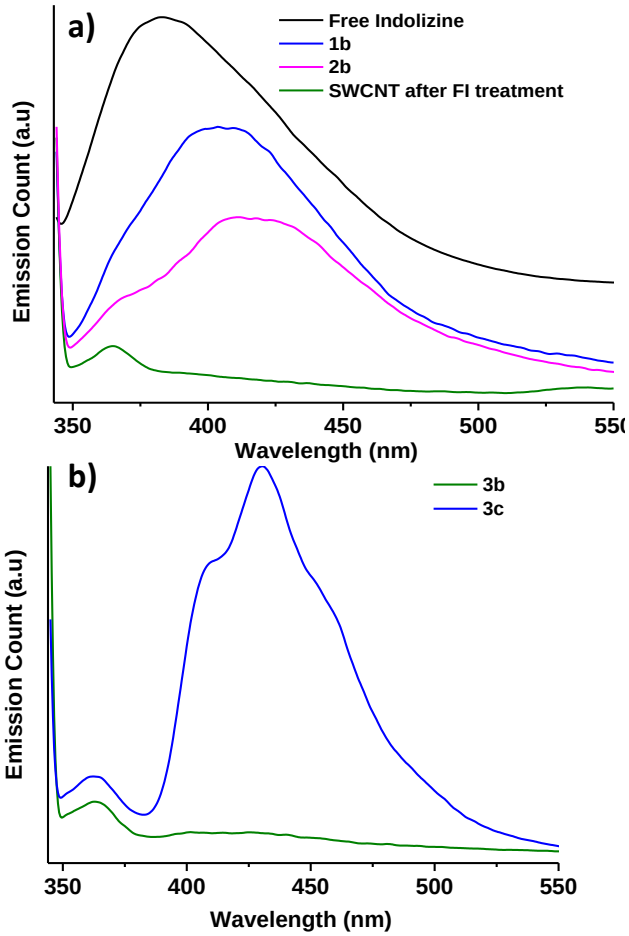


Figure 5. Normalized and offset fluorescence spectra of a) synthesized free indolizine (**FI**) structure (black line), **1b** (blue line), **2b** (magenta line), the control experiment of mechanically mixing purified SWCNTs with FI (olive line) recorded in CH_3CN; b) **3b** (olive line) and **3c** (blue line) recorded in CH_3CN. Curves in Figure 6a and 6b are in top-down and down-top order, respectively.

Furthermore, the presence of a significant tail in the green region (~500 nm) of the emission spectra allowed us to optically image modified SWCNT materials (**1b**, **2b** and **3c**). **Figure 6** shows the white light optical image (left) and the epi-fluoresence image (right) of indolizine modified SWCNTs (**1b**, **2b** and **3c**). Fluorescence images were recorded using excitation light transmitted through a 420 to 480 nm excitation filter and fluorescence observed after passage through a 500 nm emission filter (Olympus CX-DMB-2 cube). The green spots can be clearly seen on the epi-fluoresence image (right) of modified SWCNTs (**1b**, **2b** and **3c**) as an indication of covalently attached light emiting indolizine groups on SWCNT surface, suggesting that the quantum efficiency of the emitted light is probably sufficient for practical applications (*e.g.* fluorescent imaging) (**Figure 6**). However, we were unable to calculate the absolute quantum efficiencies of the indolizine modified SWCNTs (**1b**, **2b** and **3c**) due to the strong scattering and absorption of the SWCNTs. As comparison it was possible to determine the quantum yield of the **FI** heterocycle. The fluorescence quantum yield (Φ_f) of **FI** was determined from the corrected fluorescence spectra as 0.055, using anthracene dissolved in ethanol as a standard (Φ^{st}_f = 0.27 at 25 °C).[51]

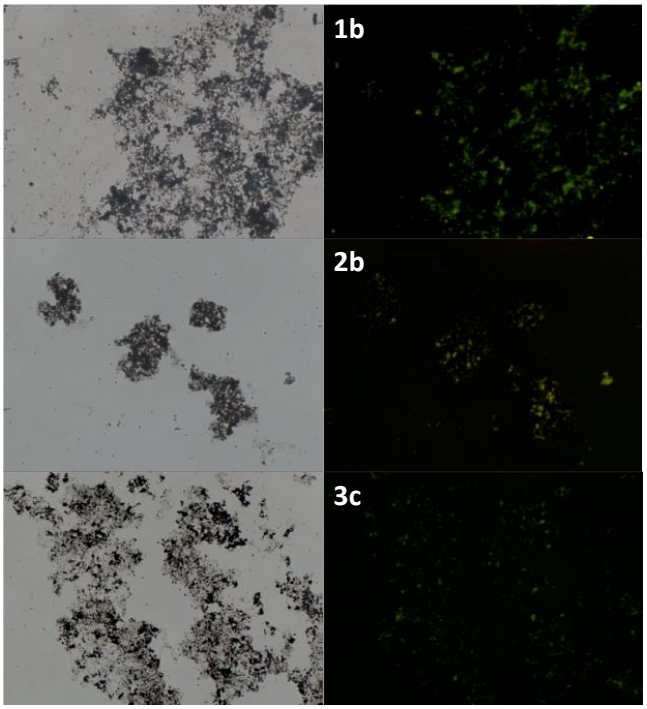


Figure 6. Unmodified white light transmission image (left) and fluorescence image (right) of indolizine functionalized SWCNTs (**1b**, **2b** and **3c**) taken using an Olympus CX41 optical microscope, field of view 718 x 533 µm.

Solution state photochemical sensing properties of indolizine modified light-emitting SWCNTs. With the given fluorescent properties it is expected that indolizine modified SWCNTs may be used as molecular sensing probes. Indolizine modified light-emitting SWCNTs (**1b**) was used as a *host molecule* to probe potentially dangerous nitroaromatics photochemically in solution-state. Phenol (**P**), 2-nitrophenol (**2NP**), 3-nitrophenol (**3NP**), 4-nitrophenol (**4NP**), 4-nitrotoluene (**4NT**) and 2,4-dinitrotoluene (**2_4NT**) were selected as guest molecules. A literature method has been followed to evaluate the solution phase photochemical sensing properties of **1b**.[53] Shortly, a stock solution of **1b** (~1.50 µg/mL, ~1.25×10^{-4} mol/L) and the guest molecules (1×10^{-4} mol/L) were prepared in acetonitrile (CH_3CN) for fluorescence spectral analysis. Each time a 3 mL solution of **1b** was filled in a quartz cell of 1cm optical path length, and stock solutions of guest molecules were added into quartz cell portion wise (2, 2, 2, 2, 2, 5, 5, 5, 25, 25, 25, 100 µL) and mixed for 10 seconds. Measurements were performed immediately after mixing. An excitation wavelength of 330 nm and a temperature of 25 °C were employed in all experiments. Emission spectra of the guest molecules in CH_3CN showed no emission upon excitation at 330 nm (***see ESI Figure S3***). Fluorescence response of **1b** (3 mL, ~1.25×10^{-4} mol/L) to the guest molecules was initially tested by adding known amount of aromatic compound (**P**, **2NP**, **3NP**, **4NP**, **4NT** and **2_4NT**) (200 µL, 1×10^{-4} mol/L). Aromatic nitrophenol derivatives (**2NP**, **3NP** and **4NP**) caused a significant decrease in the fluorescence intensity of **1b** compared to **P** and nitrotoluene derivatives (**4NT** and **2_4NT**). (***see ESI Figure S4***) Fluorescence spectra of **1b** after the guest molecule addition suggested that fluorescent quenching efficiency (FQE) of **4NP** was the highest

among the guest molecules although it was not the least electron deficient one. FQE was observed in the order of 4NP>2NP>3NP>P>4NT>2,4NT. (***see ESI Figure S4***). As expected, portion wise addition of **4NP** (2, 2, 2, 2, 2, 5, 5, 5, 25, 25, 25, 100 µL) showed a significant, regular decrease trend in fluorescence intensity of **1b**, suggesting an intermolecular interaction between **1b** and **4NP** (**Figure 7**).

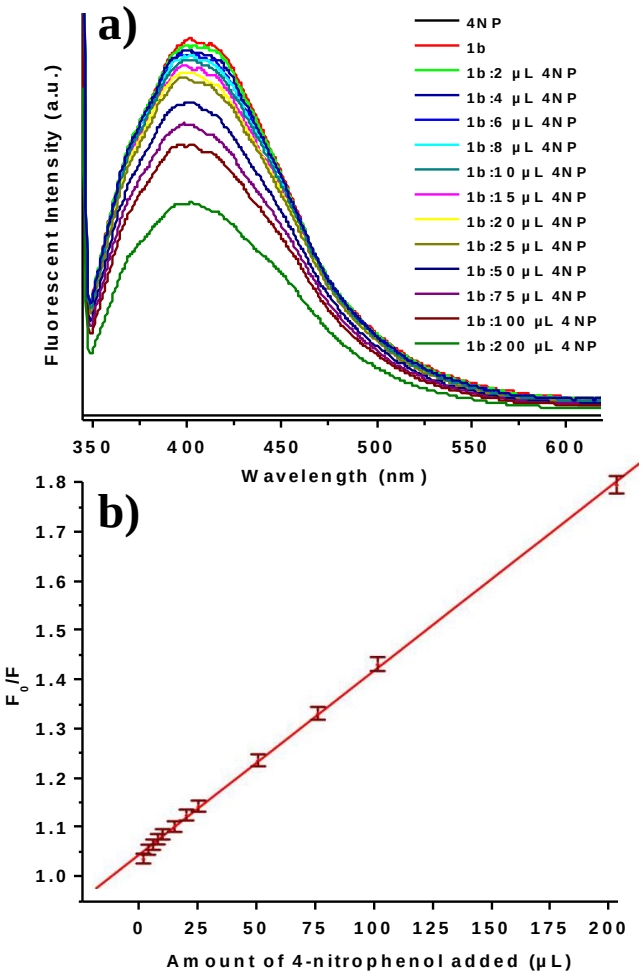


Figure 7. a) Change in the fluorescence spectra of **1b** (1.25×10^{-4} M) excited at 330 nm after the addition of of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 µL equivalent of 4NP (1×10^{-4} M) dissolved in CH_3CN; b)Stern-Volmer plot of the emission data provided by the change in fluorescence intensity after each 4NP addition.

Detection limit of photochemical sensing was estimated as 6.66×10^{-8} mol/L, considering the final concentration of **4NP** after 2 µL addition. However, the detection limit may be lower than the estimated value since some of **4NP** molecules are likely to be physically adsorbed by SWCNT surface and reduce the concentration of free **4NP** in analysed solution. Adsorption of **4NPs** was previously shown where a SWCNT based device was developed assembling nanotubes to electrodes using AC dielectrophoresis technique which allows the real-time detection of adsorbed nitrophenols in aqueous solution.[54] The Stern-Volmer relationship allows us to investigate the kinetics of a photophysical intermolecular deactivation process and, luminescence in solution obeys the linear Stern-Volmer relationship,[55] $F_0 / F = 1 + k_q\tau_0 . [Q]$, where F_0 denotes the initial intensity of the fluorescent species without quencher, F represents the final intensity of the fluorescent species with quencher, k_q is the quencher rate coefficient, τ_0 is the fluorescence lifetime of the fluorescent species without a quencher and [Q] is the concentration of the quencher. The Stern-Volmer plot constructed by the emission data obtained from the addition of **4NP** to **1b** displayed a linear profile, probably indicating a single set of fluorophores, all equally accessible to the quencher (**Figure 8**).[56] Similarly, fluorescent quenching of **1b** using other guest molecules (**P**, **2NP**, **3NP**, **4NT** and **2,4NT**) was also studied. Addition of **2NP** and **3NP** displayed similar decreasing trend in fluorescent intensity of **1b** while the change in the fluorescent intensity upon the addition of **P, 4NT** and **2,4NT** is not significant. (***see ESI Figure S5-S9***).

In order to further explore the intermolecular interactions between **1b** and **4NP,** photochemical sensing properties of free indolizine (**FI**) structure, as a model, were also studied by fluorescence spectroscopy, FTIR and NMR. In agreement with **1b**, fluorescence spectral analysis of **FI** (3 mL, 2.09×10^{-7} M**)** in the presence of **P**, **2NP**, **3NP**, **4NP**, **4NT** and **2,4NT** (200 µL, 1×10^{-4} mol/L) showed similar decreasing trend in the fluorescent intensity of **FI,** displaying a FQE order of 4NP>2NP>3NP>P>4NT>2,4NT. (***see ESI Figure S4***) Given the highest ability of **4NP** to quench the fluorescence of **FI** this process was further investigated performing binding experiments. Similar to **1b**, **FI** was titrated with **4NP**. As expected, similar trend in the fluorescence intensity of **FI** was observed after the addition of **4NP**, confirming that the change in intensity is purely due to the intermolecular interactions between host and guest molecules. (***see ESI Figure S10***) It further confirmed that SWCNTs were functionalized by light-emitting indolizine groups that are able to sense particularly nitrophenol derivatives.

To investigate the nature of intermolecular interactions between **FI** and **4NP**, spectroscopic analysis of the **FI**, **4NP** and possible **FI:4NP** complex were carried out by NMR and FTIR. Equimolar amounts of vacuum-dried **FI** (10.64 mg, 3.28×10^{-2} mmol) and **4NP** (4.5 mg, 3.28×10^{-2} mmol) were dissolved in 1 mL of anhydrous freeze-dried $CDCl_3$ for NMR spectroscopy analysis. Dry experimental conditions ensured that there was no possible proton exchange with water. **Figure S11** shows the ^{1}H NMR spectra of **FI**, **4NP** and the mixture (**FI:4NP**). The ^{1}H NMR spectrum of **FI:4NP** showed that the hydroxyl proton of **4NP** ($\mathbf{H_a}$) at 5.74 ppm disappeared upon mixing with **FI**, suggesting a strong intermolecular interaction that can probably be attributed to H-bonding interaction/proton transfer between hydroxyl proton of **4NP** and **FI**.[43, 57, 58] However, no significant signal shift was observed for the aromatic protons $\mathbf{H_c}$, $\mathbf{H_e}$, $\mathbf{H_j}$ and $\mathbf{H_k}$, probably indicating weak or no π-π interactions between **FI** and **4NP**. Complementary FTIR spectroscopy further confirmed the possible H-bonding interaction between **FI** and **4NP**. FTIR spectra of compounds were recorded by dropping the stock solutions of the compounds (**FI** and **4NP**) and the mixture (**FI:4NP**) on vacuum dried KBr disk. (***see ESI Figure S12***) FTIR spectrum of **FI** displayed three $\nu_{C=O}$ stretching vibrations at 1740, 1710 and 1695 cm^{-1} due to the presence of ethoxy and methoxy ester carbonyl groups. In contrast, FTIR spectrum of the mixture (**FI:4NP**) showed a strong broad $\nu_{C=O}$ stretching at 1700 cm^{-1}. Significant change in shape and position of the $\nu_{C=O}$ stretching bands of **FI** after the addition of **4NP** revealed a strong intermolecular interaction, probably H-bonding between ester carbonyl of **FI** and hydroxyl proton of **4NP**.[43, 53, 59]

Solid state photochemical sensing properties of indolizine modified light-emitting SWCNTs. Due to their exceptional physical and chemical properties, SWCNTs can be used as solid

support materials for various applications including sensors.[60, 61] Previously, it was shown that calculated photoluminescence quantum yield (**PLQY**) of fluorescent systems could be used as a tool to probe the sensing properties of fluorescent materials.[62] Similar to previous work, solid state photophysical properties of **1b** and **3c** were studied by exposing them to saturated **4NP** vapour using a commercial spectrometer coupled with an integrating sphere.[62] The vapour pressure of **4NP** at room temperature was previously reported as 1.9×10^{-5}mm Hg that corresponds to a vapour concentration of 19 ppb.[63] Fluorimetry experiments were performed on a quartz substrate coated with light-emitting SWCNTs. An excitation wavelength of 340 nm was selected for all measurements. PLQY of **1b** and **3c** was determined using the formalism outlined by de Mello where Φ_{PL} is PLQY, E_i (λ) and E_0 (λ) are, respectively, the integrated luminescence as a result of direct excitation of SWCNTs and secondary excitation, L_i (λ) and L_0 (λ) are the integrated excitation when SWCNTs are directly excited and the excitation light first hits the sphere wall, respectively and, L_e (λ) is the integrated excitation profile for an empty sphere.[64]

$$\phi_{PL} = \frac{E_i(\lambda) - (1-A)E_0(\lambda)}{L_e(\lambda)A} \qquad A = \frac{L_0(\lambda) - L_i(\lambda)}{L_0(\lambda)}$$

Using the equation, PLQY of **1b** and **3c** was calculated as 0.9 and 0.3 %, respectively (**Figure 8**). As expected the PLQY of the modified SWCNTs was less than the free indolizines (**FI** and $\mathbf{FI_{NH2}}$[43]) with calculated PLQY of 5.5 and 3.5 %, respectively, probably due to the charge transfer from the electron rich indolizine system to the electron poor SWCNTs. These findings were in agreement with the blue-shift in emission spectra of **1b** and **3c** compared to pure spectra of **FI** and $\mathbf{FI_{NH2}}$.[43] Similar decreasing trend in PLQY due to interaction between surface groups and SWCNT walls was previously reported in which the emission quantum yield of 2,4,6-triphenylpyrylium functionalized SWCNTs (Φ = 1%) was lower than 2,4,6-triphenylpyrylium alone (Φ = 33%).[65]

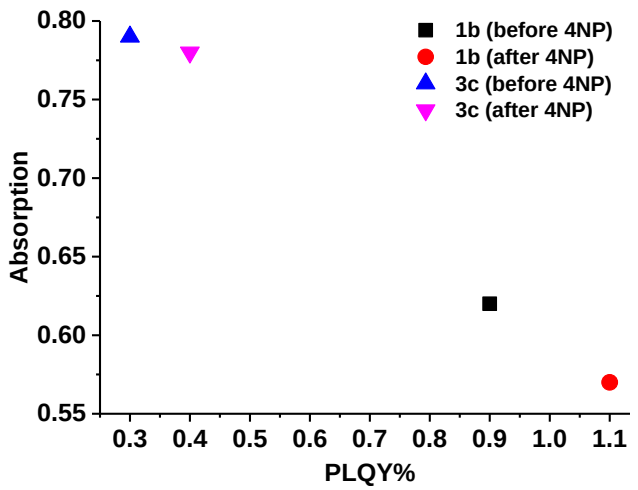


Figure 8. Calculated photoluminescence quantum yield of **1b** and **3c** versus absorption of **1b** and **3c** before/after exposing them to **4NP** vapour at room temperature.

The change in absorption (A in the equation) of the corresponding indolizine modified SWCNTs (**1b** and **3c**) can be used as a measure of the photochemical response to **4NP** vapour since the absorption of fluorescent material is expected to change upon the adsorption of **4NP** to modified SWCNT surface.[62] Before exposing to **4NP** vapour, the absorption values of **1b** and **3c** were determined as 0.62 and 0.79, respectively. The values decreased to 0.57 and 0.78 after exposing fluorescent SWCNTs to **4NP** vapour for 10 seconds (**Figure 8**). Furthermore, the calculated PLQY of **1b** and **3c** slightly increased to 1.1 and 0.4 %, respectively following **4NP** exposure (**Figure 8**). The change in absorption (A in the equation) of the corresponding indolizine modified SWCNTs (**1b** and **3c**) together with the change in the calculated PLQYs revealed that nitrophenol derivatives can be photo chemically probed by indolizine modified light-emitting SWCNTs in solid-state at room temperature on a solid substrate.

Conclusions. A low temperature, highly controllable and efficient synthetic protocol to prepare indolizine modified light-emitting SWCNTs from pyridinium ylides generated on SWCNT surface was presented. Reactivity of the pyridine nitrogen lone pairs allowed the preparation of several quaternary pyridinium salt modified SWCNTs, which were subsequently used to synthesize pyridinium ylide functionalized SWCNTs and indolizine functionalized SWCNTs via '*click*' chemistry. Shortly, the current study proposed a new perspective for the synthesis of carbon nanotube supported fluorescent molecules and their use in sensing of potentially dangerous nitrophenol derivatives. The indolizine modified light-emitting SWCNTs (**1b, 2b** and **3c**) were shown to emit blue light (400-450 nm) upon excitation at *ca*. 330 nm. Fluorescent quenching of **1b** demonstrated that trace analysis of nitrophenol derivatives could be performed by indolizine modified light-emitting SWCNTs in both solution-state and solid-state. The florescent quenching was discussed work equally as well with **3c**. ^{1}H NMR and FTIR analysis of free indolizine (FI) structure suggested that the fluorescence of the modified materials quenched via probably an electron transfer from electron-rich indolizine to electron- deficient nitrophenolics through H-bonding interaction between ester carbonyls of indolizine and hydroxyls of nitrophenol. Optical microscopy images together with solid-state photophysical data revealed that indolizine modified fluorescent SWCNTs may potentially be used for imaging in cell transfection and drug delivery due to their high enough quantum efficiencies. Described methodology can be further expanded to introduce various molecules including cyclodextrins and cucurbituril with fluorescent indolizine tags on SWCNT surface that may be used for protein sensing and crystallisation. Furthermore the preparation of fluorescent hierarchical networks of carbon nanomaterials (*e.g.* carbon nanotubes and graphene) are anticipated via the reaction of bisdipolarophiles (*e.g.* bisacetylenes) with pyridinium ylides generated on carbon materials. The principles outlined here are expected to be applicable to other low dimensional materials including graphene and related inorganic layered materials.

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Notes and references

[a]Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK.
[b]Current Address: Department of Chemical Engineering, University College London, London WC1E 7JE, UK

Electronic Supplementary Information (ESI) available: Normalized (at 330 nm) UV/vis-NIR spectra, recorded in *N*,*N*-dimethylformamide, of

purified SWCNTs and SWCNT-Py (Figure S1). Schematic representation of the synthesis of 3-ethyl 1,2-dimethyl indolizine-1,2,3-tricarboxylate (Free Indolizine) (Scheme S1). Devonvoluted N 1s XPS spectrum of **3c** (Figure S3)**.** Fluorescent spectra of 1b, P, 2NP, 3NP, 4NP, 4NT and 2_4NT in CH_3CN (Figure S4). Percentage decrease in fluorescence intensity of 1b and FI upon the addition of P, 2NP, 3NP, 4NP, 4NT and 2_4NT (Figure S5). Fluorescence spectra of 1b in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 μL equivalent of P, 2NP, 3NP, 4NT and 2_4NT (Figure S6-S10). Fluorescence spectra of FI in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 μL equivalent of 4NP (Figure S11). ^{1}H NMR spectra of 4NP, FI and possible FI:4NP complex formed Figure S12). FTIR spectra of FI, 4NP and possible FI:4NP complex formed (Figure S13). See DOI: 10.1039/b000000x/

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