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

Mustafa K. Bayazit[a,b,*], Lars Olof Palsson[a] and Karl S. Coleman[a]

[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

Email: m.bayazit@ucl.ac.uk

Supporting Information

Experimental Details

1. SWCNT-Indolizine (1b). To a dispersion of **1a** (5 mg) in dry DMF (10 mL), dispersed using an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 5 mins, was added dimethyl acetylenedicarboxylate (DMAD) (5 mL, 5.78 g, 40.67 mmol). The reaction mixture was stirred at room temperature for 1 h and then triethylamine (1 mL, 0.73 g, 7.17 mmol) added and the reaction stirred for a further 5 h at room temperature and then 15 h at 60 °C. The reaction was quenched by the addition of high purity water (50 mL) and the mixture filtered through a PTFE membrane (0.2 μm, Whatman). The SWCNTs were re-dispersed and filtered through a PTFE membrane using THF (2 × 30 mL), acetone (2 × 30 mL) and ethanol (2 × 30 mL), respectively to remove any residual organic material and dried overnight at 80 °C to afford SWCNT-indolizine (**1b**).

2. PEG_{2000}-yl 2-bromoacetate. PEG_{2000}-yl 2-bromoacetate was prepared following the literature procedure[1] and characterized using FTIR, ^{1}H and ^{13}C NMR. IR (ATR) ($\nu_{C=O}$ 1745 cm^{-1}), (ν_{C-H} 2885 cm^{-1}), ($\nu_{H2C-O-CH2}$ 1096 cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$,): 4.3-4.4 (t, $COOCH_2$), 3.8-3.9 (s, CH_2Br), 3.6-3.7 (m, PEG chain protons), 3.4-3.5 (m, CH_2OH), 3.3-3.4 (s, OH; ^{13}C NMR (100MHz, $CDCl_3$): 167.9 (COOR), 71.4 (OCH_2CH_2O), 26.2 (CH_2Br).

3. SWNT-Pyridinium PEG-Ester Salt (2a). To a dispersion of **SWNT-Py** (5 mg) in dryDMF (10 mL), dispersed using an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 5 mins, was added PEG_{2000}-yl 2-bromoacetate (11.1 g, 5 mmol) and the reaction mixture stirred at room temperature for 12 hours. The modified SWCNTs were washed and isolated using the method described above for **1a** and dried overnight at 80 °C to afford SWCNT-pyridinium ester salt (**2a**).

4. SWCNT-Indolizine (2b). SWNT-Pyridinium PEG-Ester Salt (**2a**) (5 mg) in dry DMF (10 mL) was dispersed using an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 10 mins and heated to 80 ^{o}C in an oil bath. Dimethylacetylenedicarboxylate (5 mL, 40.67 mmol) and triethylamine (1 mL, 7.17 mmol) were then added to nanotube dispersion, respectively. The reaction mixture was stirred for 15 h at 80 °C. The modified SWCNTs were washed and isolated using the method described above for 1b and dried overnight at 80 °C to afford SWCNT-Indolizine (**2b**).

5. SWCNT-Pyridinium Nitrobenzyl Salt (3a). To a dispersion of **SWNT-Py** (5 mg) in dry DMF (10 mL), dispersed using an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 5 mins, was added p-nitrobenzyl bromide (5.4 g, 25 mmol) and the reaction mixture stirred at room temperature for 12 hours. The modified SWCNTs were washed the method described above for 1a and dried overnight at 80 °C to afford SWCNT-Pyridinium nitrobenzyl salt (**3a**).

6. SWCNT-Indolizine (3b). *SWCNT-Pyridinium Nitrobenzyl Salt* (**3a**) (5 mg) in dry *DMF* (10 mL) was dispersed using an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 10 mins and heated to 80 ^{o}C in an oil bath. Dimethylacetylenedicarboxylate (5 mL, 40.67 mmol) and triethylamine (1 mL, 7.17 mmol) were then added to nanotube dispersion, respectively. The reaction mixture was stirred for 15 h at 80 °C. The modified SWCNTs were washed and isolated using the method described above for **1b** and dried overnight at 80 °C to afford SWCNT-Indolizine (**3b**).

7. SWCNT-Indolizine (3c). SWNT-indolizine (**3b**) was reduced using the literature procedure.[2] The modified SWCNTs were re-dispersed and filtered through a nylon membrane using THF (2 × 30 mL), acetone (2 × 30 mL) and ethanol (2 × 30 mL), respectively to remove any residual organic material and dried overnight at 80 °C to afford SWNT-indolizine (**3c**).

8. 3-ethyl 1,2-dimethyl indolizine-1,2,3-tricarboxylate (FI). Pyridine (7.91g, 100 mmol) was added to ethyl bromoacetate (18.37g, 110 mmol) and the mixture stirred for 12 h at room temperature. The resulting off-white solid was washed with diethyl ether (3 x 20 mL) to afford the pyridinium bromide salt *N*-(ethoxycarbonylmethyl)-pyridinium bromide (22.64 g, 92%). At room temperature with vigorous stirring, $N(CH_2CH_3)_3$ (0.283g, 2.8 mmol) was added to the pyridinium bromide salt (0.689g, 2.8 mmol) in 10 mL $CHCl_3$ followed by drop wise addition of dimethylacetylenedicarboxylate (DMAD) (0.308g, 2.8 mmol). After solvent removal, the product was eluted with chloroform and crystallized from diethylether. Yield 75% (0.596 g); mp 115.5-116.5 °C; R_f 0.47 ($CHCl_3$); IR (neat) (υ_{CO} 1740 cm^{-1}), (υ_{CO} 1708 cm^{-1}); ^1H NMR (400MHz, $CDCl_3$): 9.47 (d, *J*=7.15 Hz, 1H), 8.26 (d, *J*=9.05 Hz, 1H), 7.31 (m, *J*=8.04 Hz, 1H), 6.97 (m, *J*=7.01 Hz, 1H), 4.30 (q, *J*=7.20 Hz, 2H), 3.92 (s, 3H), 3.82 (s, 3H), 1.32 (t, *J*=7.12 Hz, 3H). ^{13}C NMR (100MHz, $CDCl_3$): 165.2, 162.3, 159.1, 151.3, 136.8, 129.5, 126.9, 125.6, 118.9, 114.3, 101.9, 59.9, 51.7, 50.6, 13.1; *m/z (ES$^+$)*: 305 (M^+, 100 %).

Characterization. XPS. XPS studies were performed at NCESS, Daresbury laboratory using a Scienta ESCA 300 hemispherical analyser with a base pressure under 3×10^{-9} mbar. The analysis chamber was equipped with a monochromated Al K_α X-ray source (*hv*= 1486.6 eV). Charge compensation was achieved (if required) by supplying low energy (<3 eV) electrons to the samples. XPS data were referenced with respect to the corresponding C 1s binding energy of 284.5 eV which is typical for carbon nanotubes.[17] Photoelectrons were collected at

a 45 degree take-off angle, and the analyzer pass energy was set to 150 eV giving an overall energy resolution of 0.4 eV.

UV-vis-NIR spectroscopy. The UV-vis-NIR absorption spectra were recorded on a Perkin Elmer Lambda 900 spectrometer. The samples were prepared by dispersing the nanotube material in either DMF or ethanol (EtOH) by sonication in an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 15 mins. Dispersions of modified SWCNTs were left for settling overnight before recording the UV-vis-NIR spectra. Stable supernatant solutions of the corresponding materials were used to calculate the solubility of each of the modified SWCNTs.

TGA-MS. Thermogravimetric analysis – mass spectrometry (TGA-MS) data were recorded on 1–3 mg of sample using a Perkin Elmer Pyris I coupled to a Hiden HPR20 mass spectrometer. As a standard procedure, prior to the thermal analysis solid materials were finely ground in an agate mortar to prepare homogeneous samples. 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.

FTIR Spectroscopy. Infrared spectra were recorded on thick films using a Perkin Elmer Spectrum 100 equipped with a Pike ATR fitted with a Ge crystal.

Fluorescence Spectroscopy. Fluorescence spectra were recorded on a Perkin Elmer LS55 luminescence spectrometer using an excitation wavelength of 335 nm. Samples were prepared by dispersing SWCNTs in either DMF (10 μg mL^{-1}) or CH_3CN (10 μg mL^{-1}) by sonication in an ultrasonic bath (Ultrawave U50, 30 – 40 kHz) for 15 mins, and allowing them to settle for 8h followed by filtration through a plug of cotton wool.

Fluorimeter. Luminesence spectra of the indolizine modified SWCNTs (solid sample) were recorded using a Jobin Yvon Horiba Fluoromax-3 coupled wth a PTFE-coated integrating sphere (Glen Spectra). The sample material was drop-dried onto a 10 mm

diameter quartz substrate and mounted about 20 mm into the sphere from a holder in the entry port facing the excitation light beam. The measured spectra were background corrected by subtracting the spectrum obtained using a blank substrate and subsequently corrected for the wavelength sensitivity of the fluorimeter and spectral response of the sphere. The spectral response of the sphere was determined using a calibrated tungsten lamp (Ocean Optic) and the fluorimeter as detector.[3]

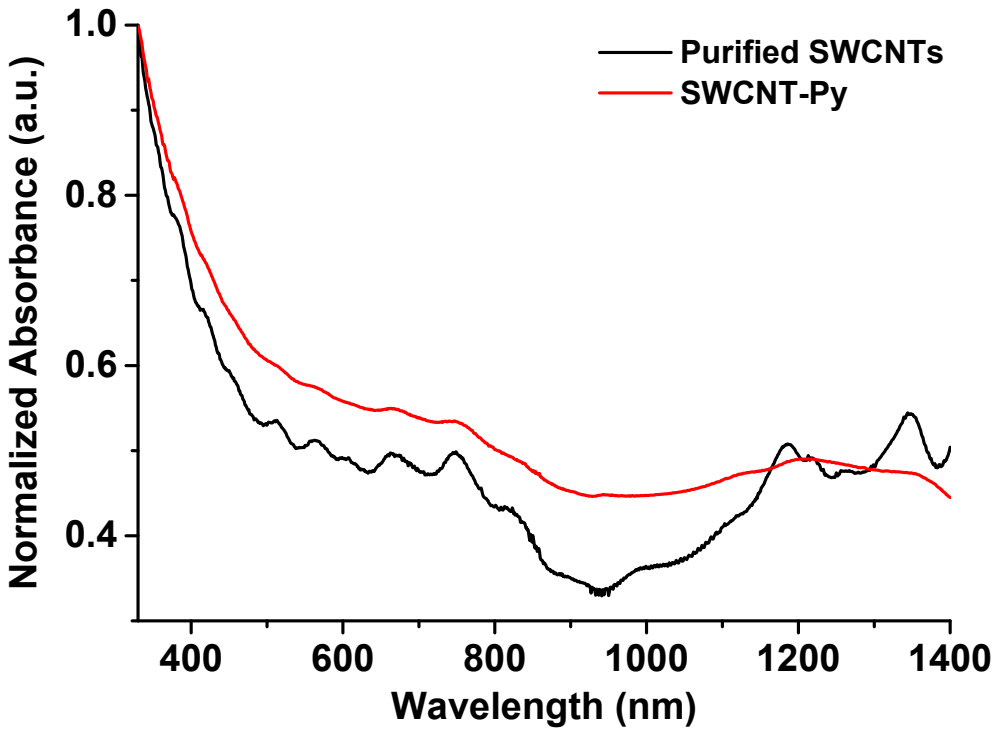
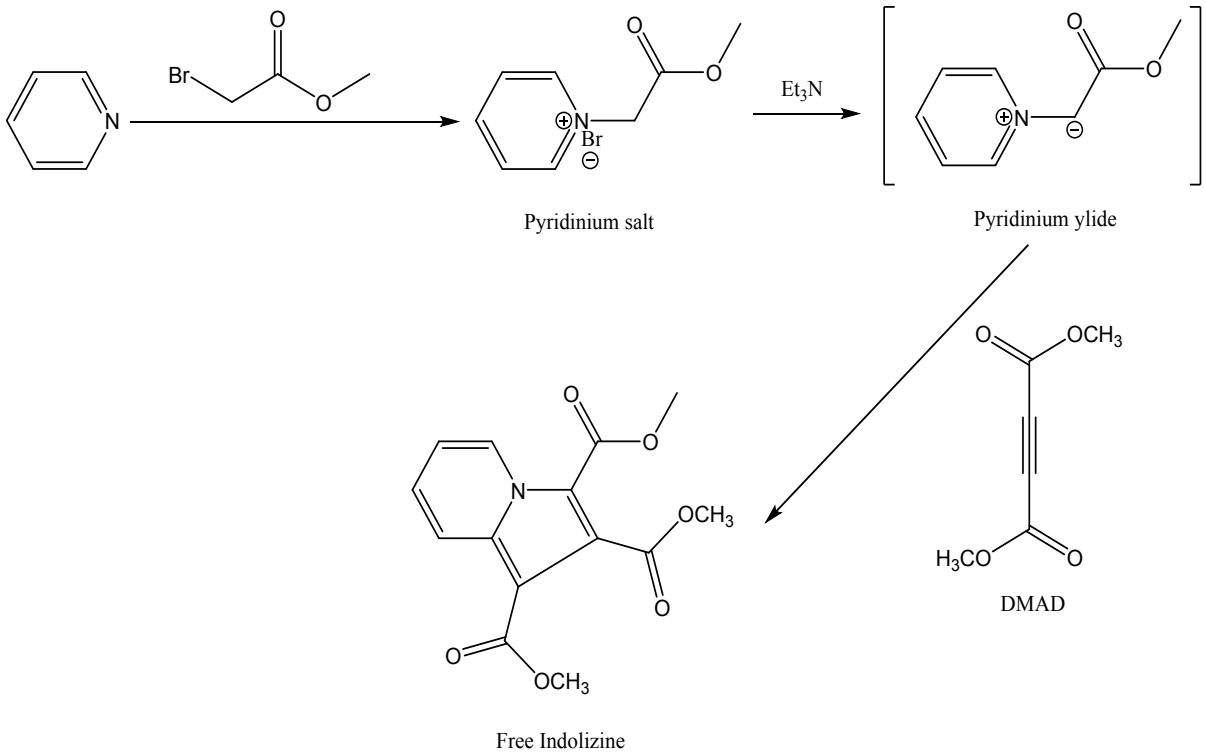


Figure S1 Normalized (at 330 nm) UV/vis-NIR spectra, recorded in *N*,*N*-dimethylformamide, of purified SWCNTs (black) and pyridine-functionalized SWNTs (red). SWCNT-Py shows suppressed electronic transition bands compared to unmodified purified SWCNTs.



Scheme S1 Schematic representation of the synthesis of 3-ethyl 1,2-dimethyl indolizine-1,2,3-tricarboxylate (Free Indolizine).

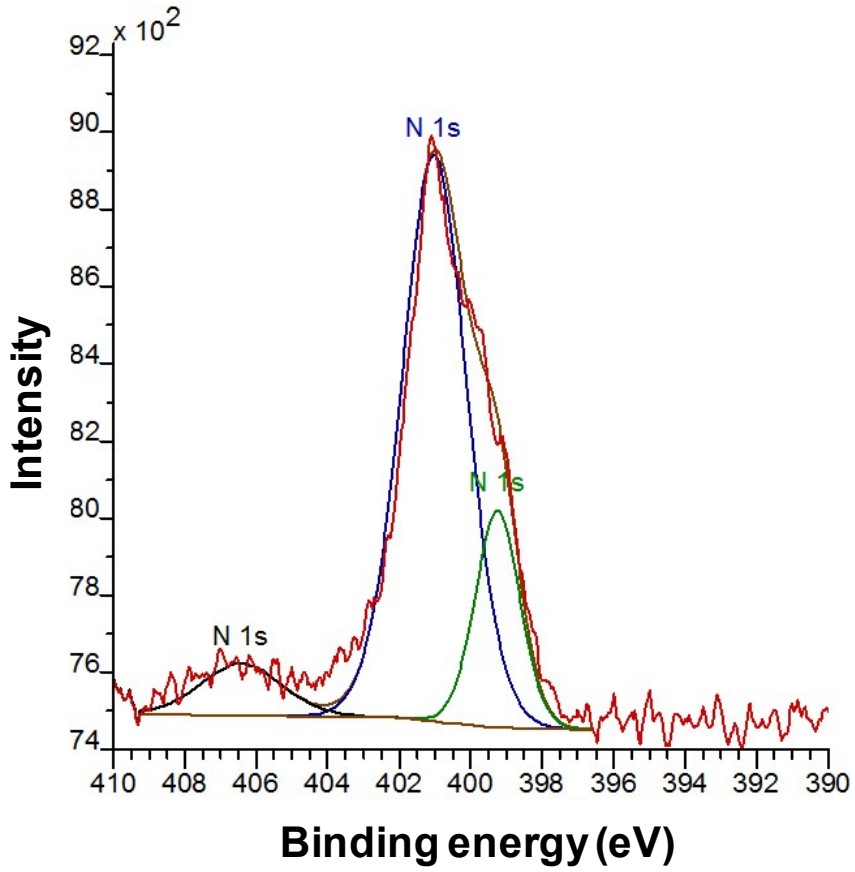


Figure S2 Devonvoluted N 1s XPS spectrum of the indolizine modified SWCNTs (**3c**). Curves were fitted after auto Shirley background using the CASAXPS software provided with XPS system. Figure shows suppressed NO_2 group based N 1s XPS spectrum at *ca.* 406 eV compared to 3b. From the spectrum it is clear that whole NO_2 groups were not converted into NH_2 groups.

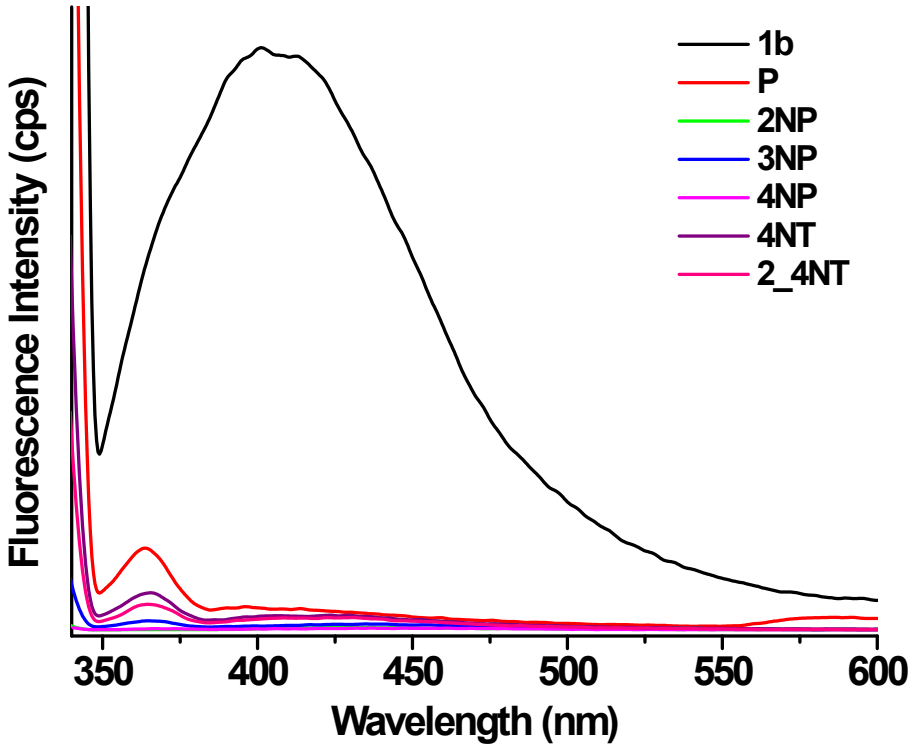


Figure S3 Fluorescent spectra of indolizine modified SWCNTs (1b), phenol (P), 2-nitrophenol (2NP), 3-nitrophenol (3NP), 4-nitrophenol (4NP), 4-nitrotoluene (4NT) and 2,4-dinitrotoluene (2_4NT) in CH_3CN. Figure shows that analysed aromatic compounds has no significant contribution to the fluorescent intensity of 1b.

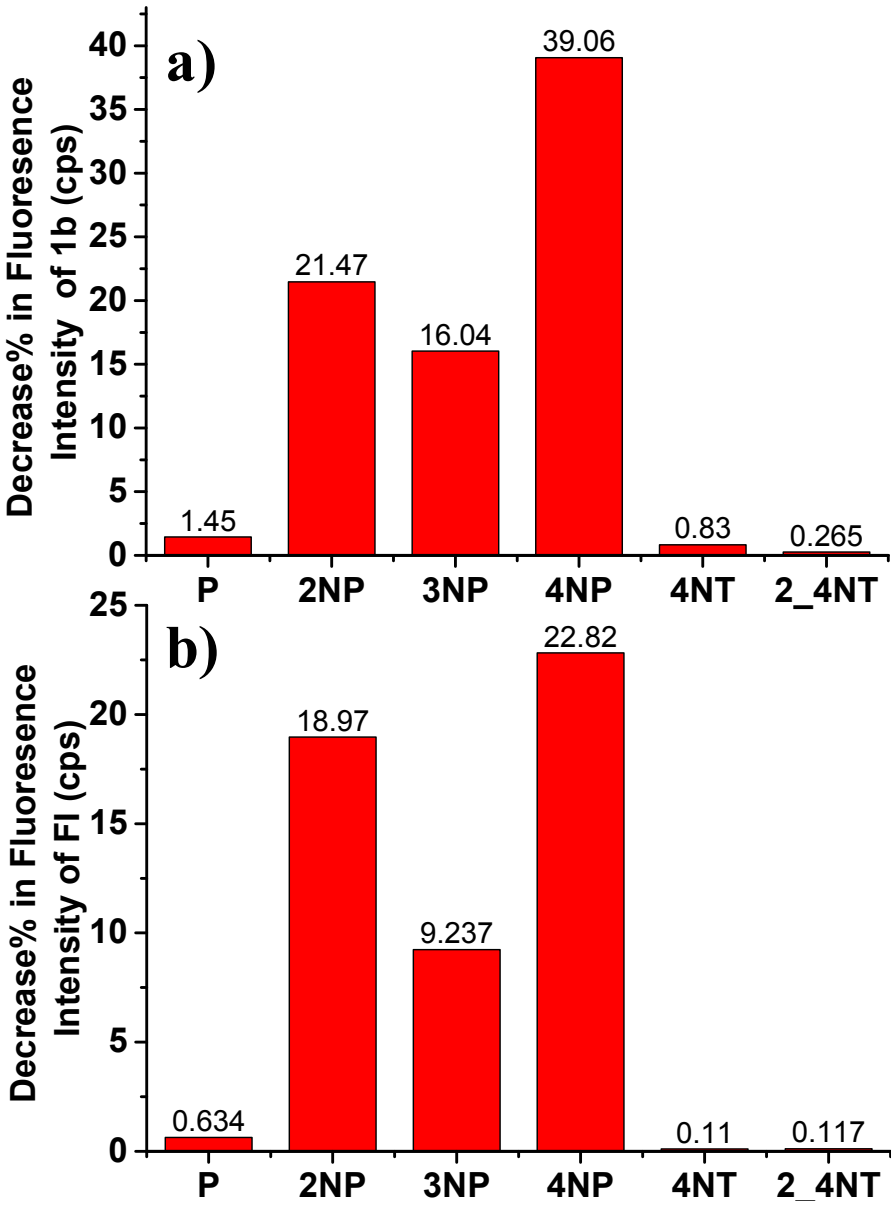


Figure S4 (**a**) Percentage decrease in fluorescence intensity of indolizine functionalized SWCNTs (1b) (3 mL, 1.25 × 10^{-4} M); (**b**) free indolizine (FI) (3 mL, 2.09 × 10^{-7} M) upon the addition of (200 μL, 1 ×10^{-4} M) phenol (P), 2-nitrophenol (2NP), 3-nitrophenol (3NP), 4-nitrophenol (4NP), 4-nitrotoluene (4NT) and 2,4-dinitrotoluene (2,4NT).

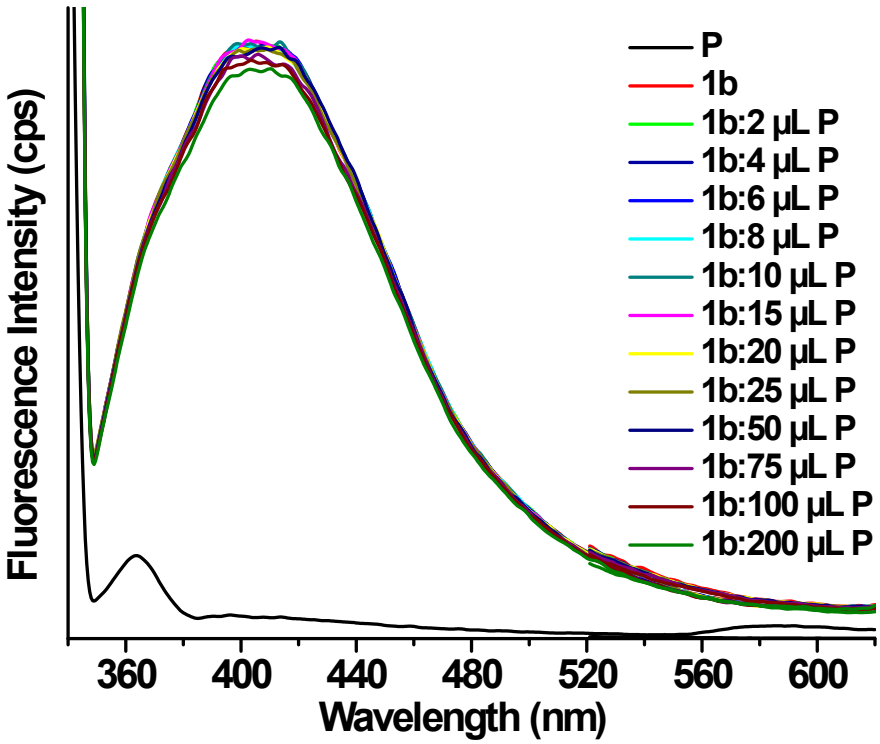


Figure S5 Fluorescence spectra of 1b (3 mL, 1.25×10^{-4} M) excited at 330 nm in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 µL equivalent of P (1×10^{-4} M) dissolved in CH_3CN.

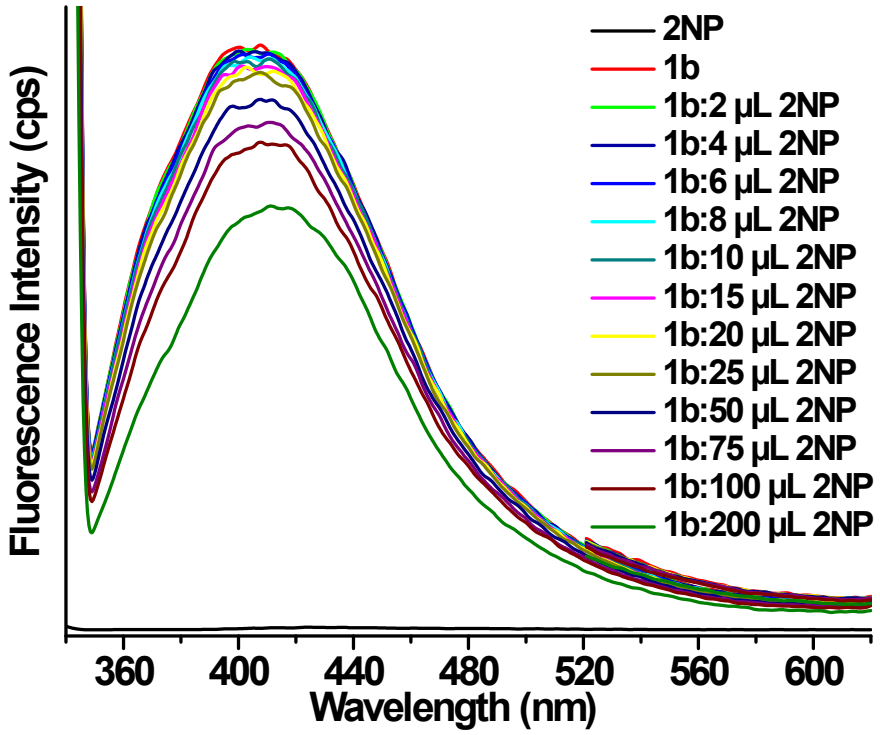


Figure S6 Fluorescence spectra of 1b (3 mL, 1.25×10^{-4} M) excited at 330 nm in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 µL equivalent of 2NP (1×10^{-4} M) dissolved in CH_3CN.

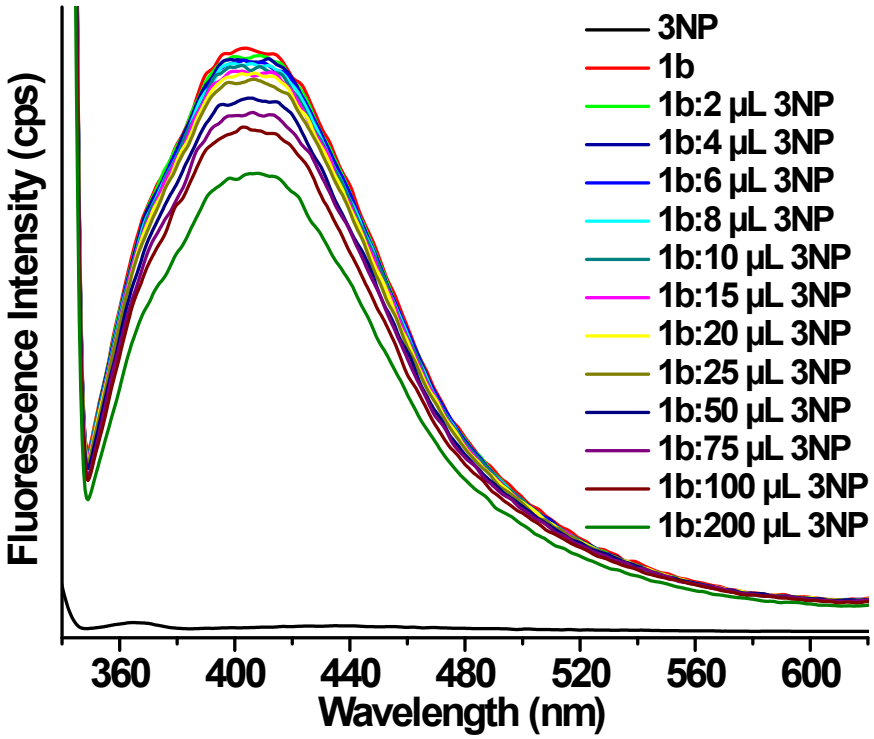


Figure S7 Fluorescence spectra of 1b (3 mL, 1.25×10^{-4} M) excited at 330 nm in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 µL equivalent of 3NP (1×10^{-4} M) dissolved in CH_3CN.

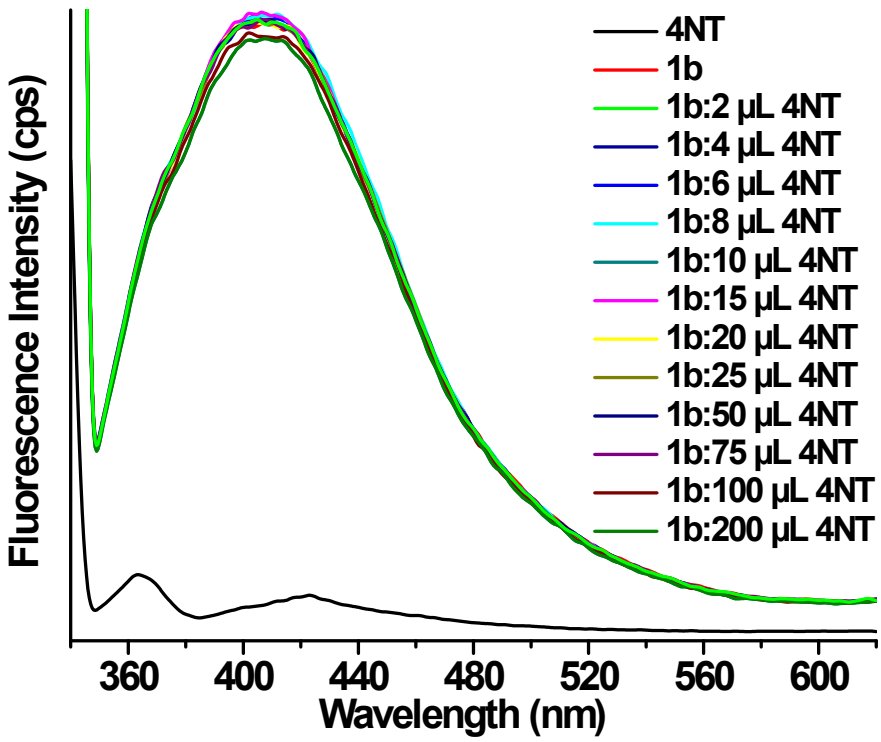


Figure S8 Fluorescence spectra of 1b (3 mL, 1.25×10^{-4} M) excited at 330 nm in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 µL equivalent of 2NT (1×10^{-4} M) dissolved in CH_3CN.

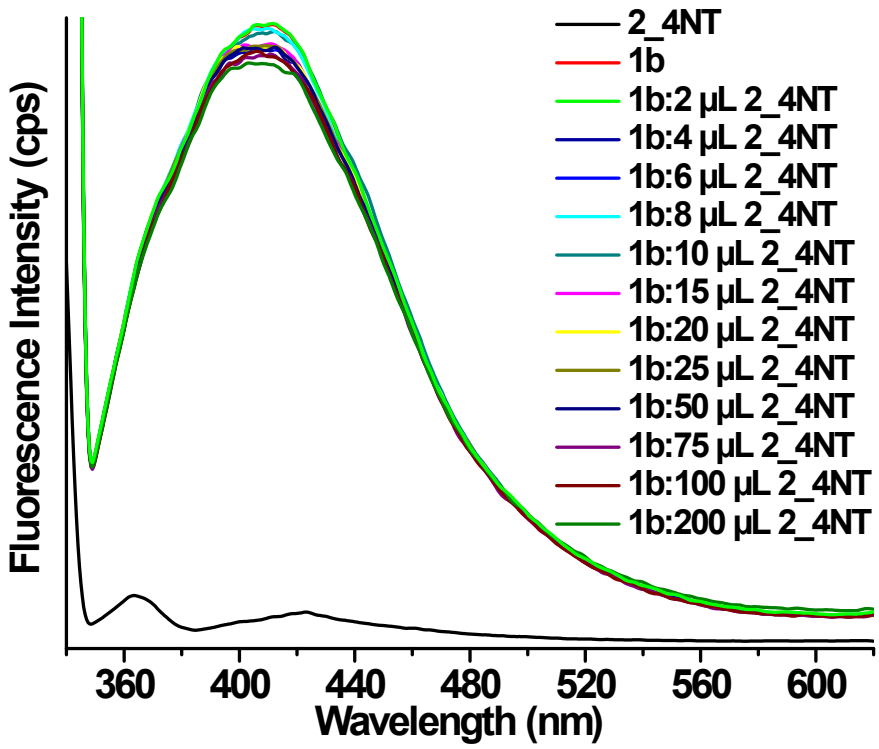


Figure S9 Fluorescence spectra of 1b (3 mL, 1.25×10^{-4} M) excited at 330 nm in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 µL equivalent of 2_4NT (1×10^{-4} M) dissolved in CH_3CN.

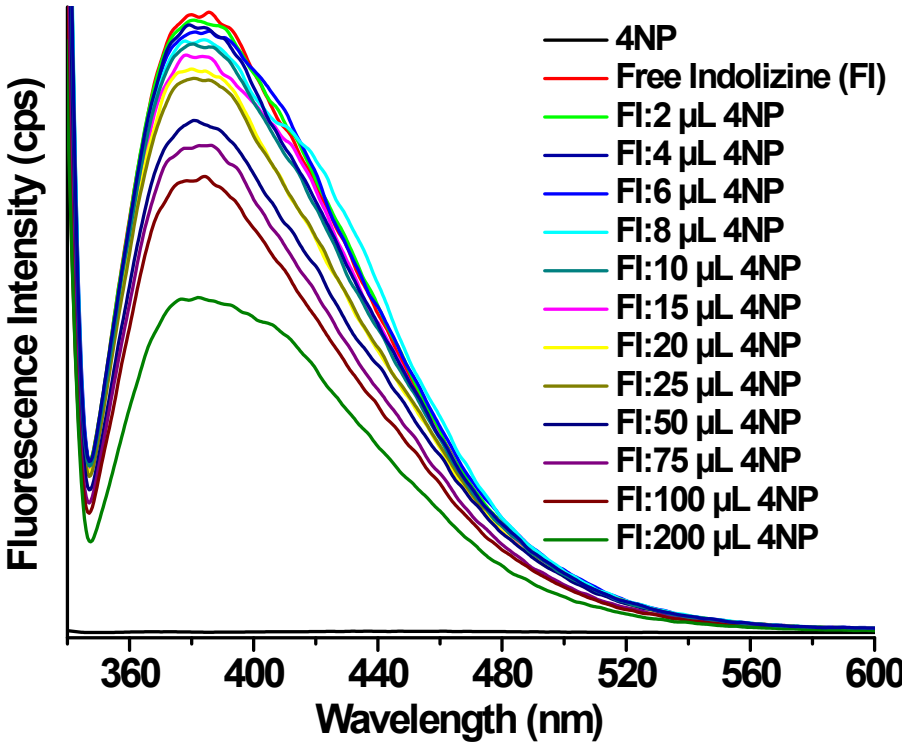


Figure S10 Fluorescence spectra of FI (3 mL, 2.09×10^{-7} M) excited at 330 nm in the presence of 2, 4, 6, 8, 10, 15, 20, 25, 50, 75, 100, 200 µL equivalent of 4NP (1×10^{-4} M) dissolved in CH_3CN.

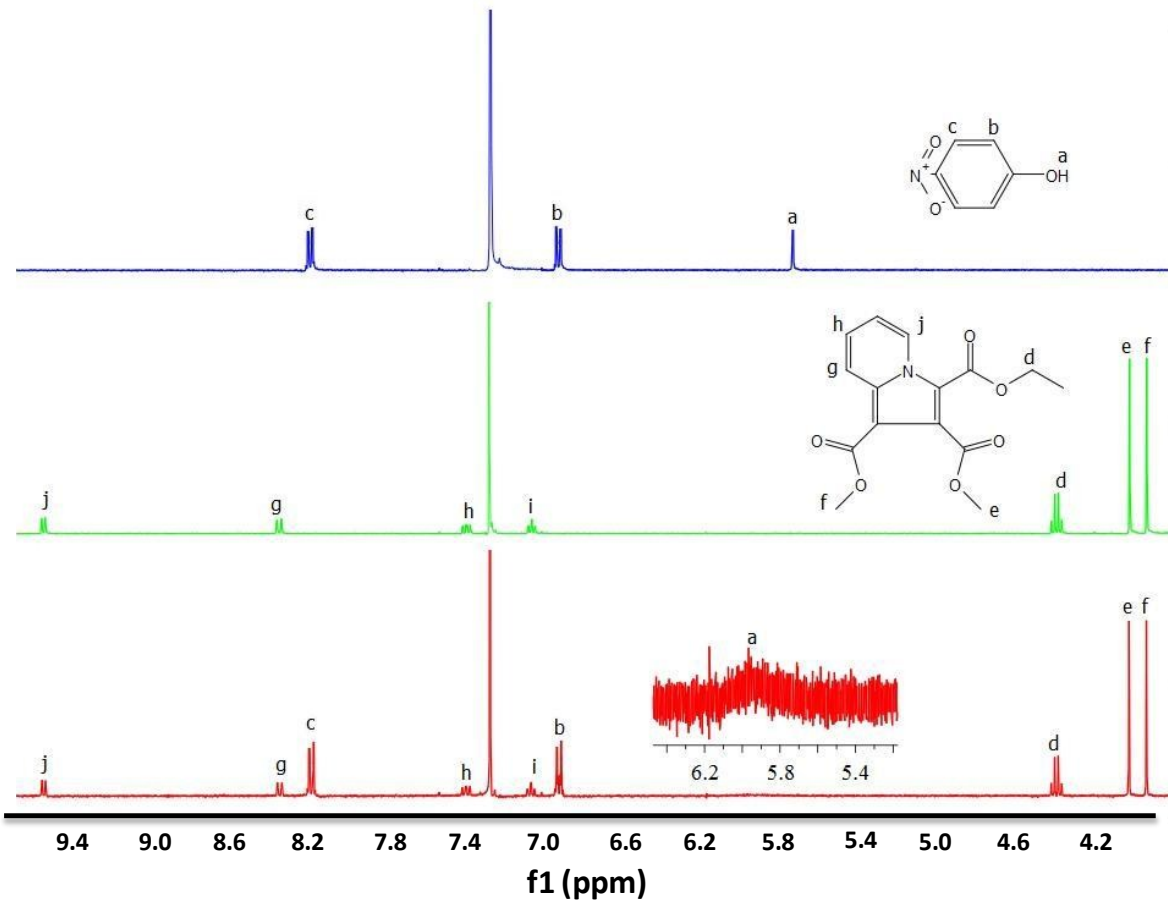


Figure S11 ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of 4NP, FI and possible FI:4NP complex formed.

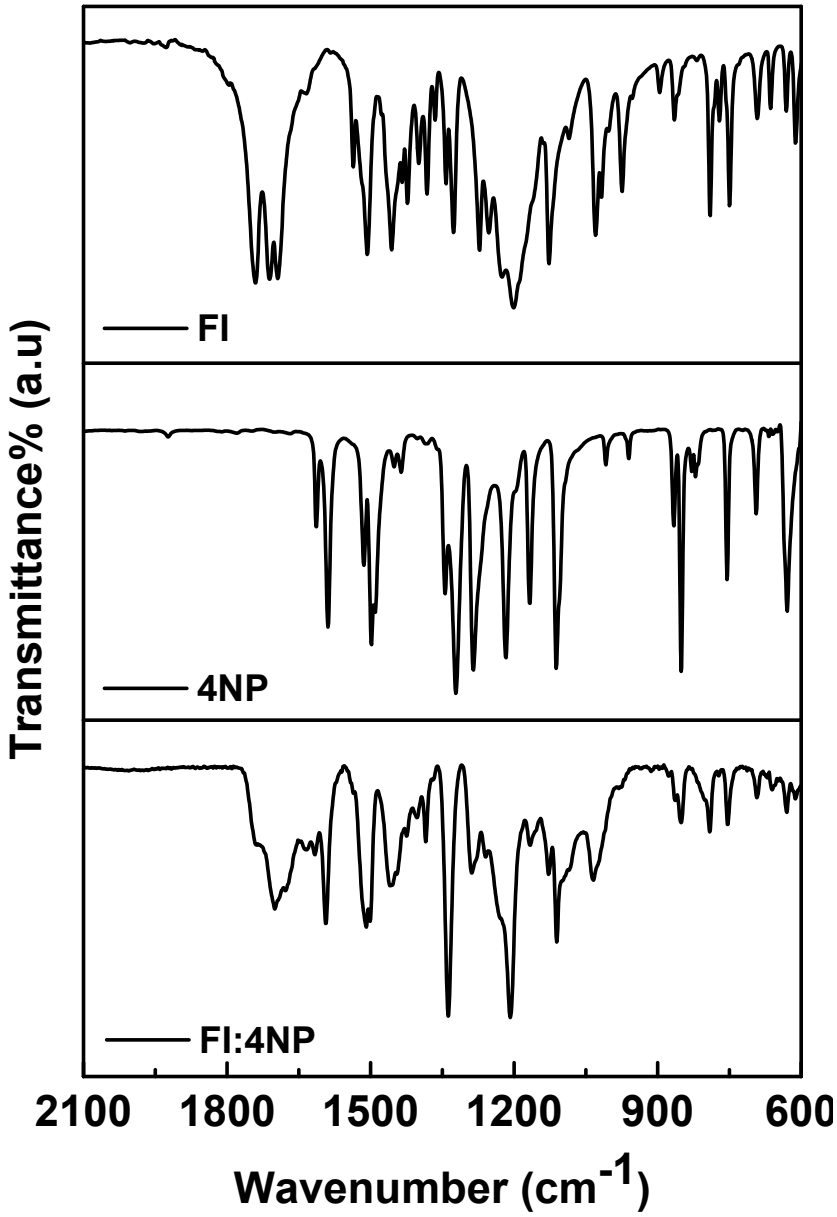


Figure S12 FTIR spectra of FI, 4NP and possible FI:4NP complex formed.

1. G. H. Yue, Y. D. Wan, S. J. Song, G. C. Yang and Z. X. Chen, *Bioorganic & Medicinal Chemistry Letters*, 2005, **15**, 453-458.
2. F. D. Bellamy and K. Ou, *Tetrahedron Letters*, 1984, **25**, 839-842.
3. L. O. Palsson and A. P. Monkman, *Adv. Mater.*, 2002, **14**, 757-758.