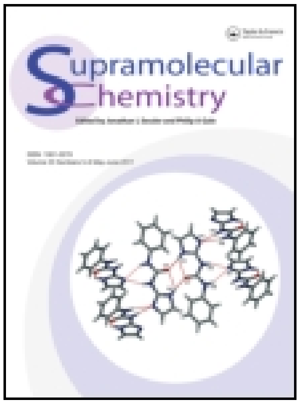

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Kevin Flavin [a] , Ilona Kopf [a] , Julie Murtagh [b] , Marco Grossi [b] , Donal F. O'Shea [b] & Silvia Giordani [a]

[a] Trinity College Dublin, School of Chemistry/CRANN, College Green, Dublin 2, Ireland
[b] Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland

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Kevin Flavin[a], Ilona Kopf[a], Julie Murtagh[b], Marco Grossi[b], Donal F. O'Shea[b]* and Silvia Giordani[a]*

[a]*Trinity College Dublin, School of Chemistry/CRANN, College Green, Dublin 2, Ireland;* [b]*Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland*

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The synthesis and characterisation of an on/off fluorescence switchable boron difluoride azadipyrromethene single-wall carbon nanotube conjugate are presented and the ability to reversibly switch on and off the excited state by modulation of pH is illustrated.

Keywords: boron azadipyrromethene; pH switch; carbon nanotubes; functionalisation; fluorescence

1. Introduction

As the electronics industry moves towards the limits of traditional top-down semiconductor processing techniques, the search is ongoing for paradigm shifting technologies or concepts that will allow the continued progress in size reduction of electronic components (*1*). Molecular electronics is a bottom-up approach in which single molecules or macromolecules may be used in such electronics applications as interconnects, transistors, switches and logic gates, and it has been envisaged as a potential pathway for surpassing the limits of traditional techniques (*2*).

Carbon-based nanomaterials, such as fullerenes, single-wall carbon nanotubes (SWNTs) and graphene, are anticipated to be important building blocks if molecular electronics are to become a successor to the current top-down approach. In recent years, interest in the study of carbon nanomaterials as acceptor materials in electron donor–acceptor systems has grown significantly as a result of their potential in switching, sensing and photovoltaic applications and ultimately in the assembly of molecular electronic devices (*3*). A variety of donor molecules have been investigated including porphyrins (*4–6*) and related phthalocyanines (*7*); however, we have also demonstrated recently the successful use of near infrared active boron difluoride azadipyrromethenes (*8*). These donor molecules were covalently conjugated to SWNTs, and using transient absorption spectroscopy it was observed that following excitation electron transfer to the SWNT acceptor takes place.

In this article, we demonstrate the conjugation of a switchable boron azadipyrromethene molecule to SWNTs and illustrate their ability to switch the donor excited state *on* and *off* using chemical signalling, i.e. pH. The rationale behind this is taken from nature, where in living organisms signalling, information transport and storage are performed by molecular or ionic substrates (*9*). Although information processing in traditional electronics differs from that found in nature, the move towards the use of molecular electronics introduces the possibility of using switching or signalling mechanisms akin to those found in living organisms.

2. Experimental

2.1 Materials

Raw HiPco SWNTs were purchased from Unidym®, Inc. Sunnyvale, CA 94089, (Lot No. R0513). Reagents and solvents were purchased as reagent/spectroscopic grade from Fisher Scientific Ireland Ltd, or Sigma–Aldrich Ireland and used without further purification.

2.2 Synthesis

2.2.1 Deprotection of 1

A quantity of 9.7 mg of Boc-protected fluorophore **1** was dissolved in dichloromethane (2 ml). An aliquot of trifluoroacetic acid (0.2 ml) was slowly added and the reaction mixture was stirred at room temperature for 2 h. Saturated aqueous $NaHCO_3$ was added and the resulting suspension was extracted with dichloromethane (2×15 ml). The combined organic phases were washed with water, dried over Na_2SO_4, evaporated to dryness and directly used for conjugation to f-SWNTs **3**.

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*Corresponding authors. Email: donal.f.oshea@ucd.ie; giordans@tcd.ie

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2.2.2 *Synthesis of p-SWNTs*

A quantity of 300 mg of raw SWNTs (r-SWNTs) was dispersed in 7.9 M HNO_3 (1000 ml) by sonication at maximum power for 5 min and subsequently at minimum power for 10 min. The mixture was then stirred under reflux at 100°C for 4 h, quenched with ice. The dispersion was then filtered through a Millipore system, Billerica, MA 01821 (0.2 μm Isopore™ filter) and washed with distilled water until the filtrate ran neutral. The wet solid was transferred to a Teflon® tub dispersed in 2 M NaOH (400 ml) by sonication at maximum power for 5 min and subsequently stirred overnight at 100°C under a nitrogen atmosphere. The mixture was cooled to room temperature, filtered through over an Isopore™ filter and washed with more 2 M NaOH (400 ml). The solid was washed with distilled water until the filtrate pH became neutral and the sample was subjected to the NaOH treatment again. Following filtration, the wet solid was dispersed in 10% H_2O_2 (600 ml) by sonication at maximum power for 5 min and subsequently stirred for 1 h at 100°C. The dispersion was quenched with ice, filtered over an Isopore™ filter and washed with copious amounts of distilled water. The solid was subsequently subjected to a final NaOH treatment, then it was filtered and washed with 2 M NaOH (400 ml), distilled water until neutral pH, 1 M HCl (400 ml), and distilled water until neutral pH, respectively. The wet solid was redispersed in distilled water and was freeze dried to afford 80 mg black solid (yield: 27%).

2.2.3 *Synthesis of f-SWNTs **3***

A quantity of 45 mg of p-SWNTs was dispersed in *N*-methyl-2-pyrrolidone (200 ml) by sonication for 20 min at full power. Following addition of 4-aminobenzoic acid (1.10 g, 8 mmol, 2 equiv. C), the reaction mixture was kept in a nitrogen atmosphere. The reaction mixture was stirred overnight at 70°C, following addition of isoamyl nitrite (1.6 ml, 12 mmol, 3 equiv. C) *via* syringe. After cooling to room temperature, the mixture was briefly sonicated to redisperse the sample and was then filtered through a 0.2 μm fluoropore FG filter, washing with 1-Methyl-2-pyrrolidone (NMP) until the filtrate ran clear. The sample was redispersed in NMP (200 ml), and the entire procedure was repeated twice. Finally, the solid was washed with methanol and dried under vacuum to afford 49 mg of black solid.

2.2.4 *Synthesis of f-SWNTs **4***

A quantity of 10.4 mg of f-SWNTs **3** was dispersed in thionyl chloride (25 ml) by sonication at maximum power for 10 min. The mixture was subsequently refluxed at 70°C under a nitrogen atmosphere for 48 h. The dispersion was filtered through a 0.2 μm fluoropore FG filter, washed with dry Tetrahydrofuran (THF) and directly redispersed in dry THF (50 ml) by brief sonication under a nitrogen atmosphere. An aliquot of dry triethylamine (60 μl), followed by compound **2** dissolved in dry THF (25 ml) was syringed into the reaction mixture, respectively. The mixture was subsequently stirred for 15 h at 80°C under a nitrogen atmosphere. The mixture was allowed to cool down to room temperature and was subsequently dispersed in DMSO (200 ml) by brief sonication. The dispersion was filtered through a 0.2-μm fluoropore FG filter and washed with 1% acetic acid in ethanol (150 ml), ethanol, methanol, THF and methanol, respectively, with sonication following each solvent washing step. Finally the sample, prior to absorption and emission experiments, was dispersed in 2% aqueous sodium dodecyl benzene sulphonate (SDBS), the concentration was adjusted to 0.05 M with a concentrated solution of NaOH and was stirred overnight at room temperature. The solution was filtered, washed with 0.05 M HCl and washed with copious amounts of water. This was carried out in order to hydrolyse any phenolic ester linkages formed with the SWNTs during the amidation reaction.

2.3 *Characterisation techniques*

Micro-Raman scattering measurements were performed at room temperature on the solid SWNT sample in the backscattering geometry using Renishaw 1000 micro-Raman system (Renishaw, Gloucestershire, UK) equipped with a CCD camera and a Leica microscope. A grating of 1800 lines mm^{-1} was used for all measurements, providing a spectral resolution of $\pm 1\,cm^{-1}$. As an excitation source the Helium Neon laser (633 nm) was used. Measurements were taken with 10 s of exposure time and four accumulations. The laser spot was focused on the sample surface using a 50 × objective with short-focus working distance. Raman spectra were collected on numerous spots on the sample and recorded with Peltier cooled CCD camera. The data were collected and analysed with Renishaw Wire and GRAMS software.

All FTIR spectra were measured in the solid state on a Perkin-Elmer FTIR Spectrometer Spectrum 100 (Perkin Elmer, Waltham, MA 02451) with a universal ATR sampling accessory (diamond/ZnSe crystal). The spectra for organic compounds and functionalised SWNTs were recorded at 36 and 256 scans, respectively, with a $4\,cm^{-1}$ resolution.

Atomic force microscopy (AFM) topographic images were collected in semi-contact mode with an NTEGRA Spectra inverted configuration system (NT-MDT, Moscow, Russia). Silicon tips with reflectance gold coated on the back, tip apex radius 10 nm, force constant 2 N/m and frequency 170 kHz were used. The data were collected and analysed with NT-MDT Nova software. Samples were prepared by dispersing the nanotubes in high purity DMF by sonication, spray coated onto freshly cleaved mica substrates and dried overnight in oven at 90°C.

UV–vis absorption spectra were recorded on a Perkin-Elmer UV–vis Spectrometer Lambda 35 (Perkin Elmer, Waltham, MA 02451) after one cycle, with an interval of 1 nm, slit width of 2 nm and scan speed of 240 nm min^{-1}.

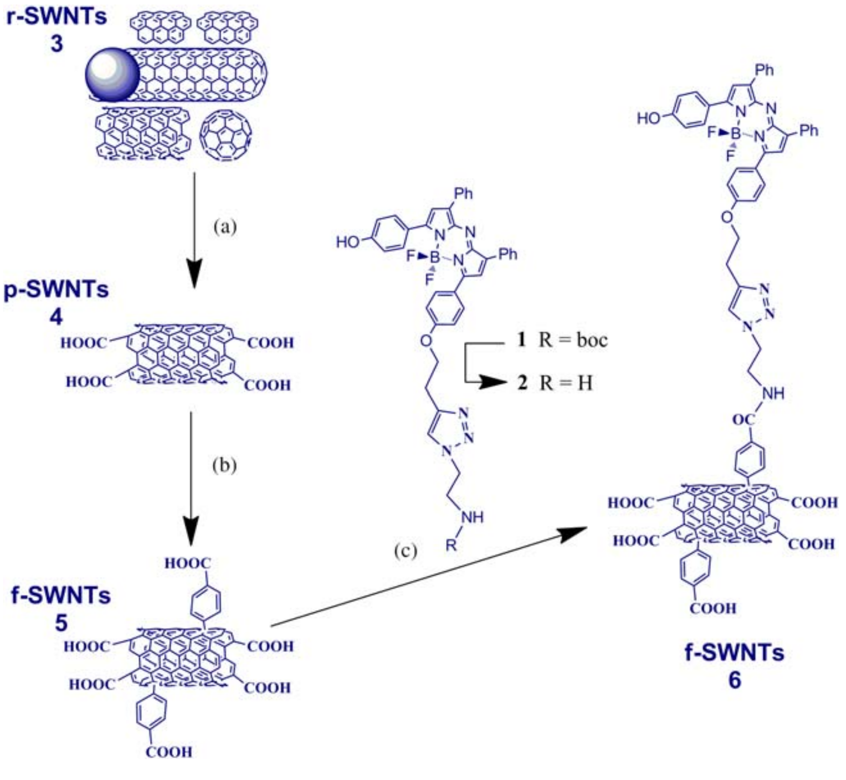
Emission spectra were taken in a HORIBA Jobin Yvon Fluorolog-3 Spectrofluorometer equipped with a 450 Xenon CV lamp after one cycle with slit width of 10 nm and integration time 0.1 s.

3. Results and discussion

The synthetic procedure used to prepare the switchable boron azadipyrromethene SWNT conjugate (f-SWNTs **4**) is illustrated in Scheme 1. As previously reported, the r-SWNTs were purified by consecutive treatments with nitric acid, sodium hydroxide and hydrogen peroxide in order to remove unwanted catalyst and carbonaceous material from the sample (*8*). This purified material (p-SWNTs) was covalently functionalised using the Tour reaction to produce benzoic acid functionalised and easily dispersible f-SWNTs **3** (*10*). NHBoc-protected boron azadipyrromethene **1** was synthesised exploiting a versatile azide cycloaddition reaction strategy as previously described (*11*). Deprotection using trifluoroacetic acid formed **2** which could be coupled to f-SWNTs **3** following the conversion of the benzoic acid groups to the corresponding electrophilic acid chloride moieties.

Raman spectroscopy was used to monitor the functionalisation procedure and the full spectra following each synthetic step are shown in Figure S1 of the Supplementary Information, available online. It is evident that only slight changes in the RBM, G and 2D bands are observed. The D band in contrast, activated by defects present on the nanotube surface (*12*), is clearly affected, as illustrated in Figure 1(a), where the *D*/*G* ratio does not change following purification, however, is substantially enhanced following the Tour reaction indicating covalent functionalisation. Background emission is evident from the spectrum when excited at 633 nm following attachment of **2** (Figure S1 of the Supplementary Information, available online), and a peak characteristic of the C=C and C=N in plane vibration of the pyrrole rings in the azadipyrromethene can be seen at approximately 1420 cm^{-1} (Figure 1(a)).

FTIR spectroscopy was used to assess functional group introduction, where the spectra are illustrated in Figure 1(b). Following the purification procedure very little change is evident; however, after the diazonium treatment new absorption bands can be observed in the fingerprint region of the spectrum, notably the carbonyl stretching band near 1700 cm^{-1}. Following conjugation of **2** to SWNTs, a series of sharp characteristic vibrational bands that correspond to the attached molecule are evident (Figure S2 of the Supplementary Information, available



Scheme 1. (a) 7.9 M HNO_3, 4 h; 2 M NaOH, 12 h; 10% H_2O_2, 1 h; 2 M NaOH, 12 h. (b) 4-Aminobenzoic acid, isoamyl nitrite, NMP, 70°C, 14 h, N_2. (c) $SOCl_2$, 70°C, 48 h, N_2; **2**, TEA, THF, 80°C, 15 h, N_2.

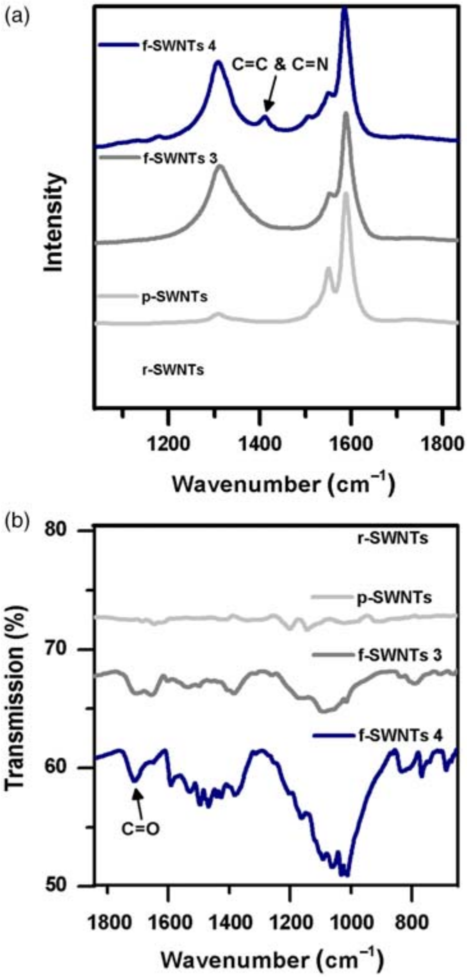


Figure 1. (a) Raman spectra ($\lambda_{exc} = 633\,\text{nm}$) and (b) ATR–FTIR spectra of raw, purified and functionalised SWNTs.

online). As previously seen, there is a change in both frequency and intensity of the carbonyl band indicating conversion of the acid to an amide suggesting covalent attachment to SWNTs.

AFM was used to investigate the effect of purification and functionalisation on the integrity of the SWNTs (Figure 2). Comparing r-SWNTs and p-SWNTs, it is clear that the purification procedure was successful in removing catalyst and carbonaceous material from the sample leaving behind mainly small SWNTs bundles (*13*). Following the functionalisation procedures, it is evident that the f-SWNTs **3** and **4** have retained their integrity and that the samples are relatively clean as a result of the stringent washing procedures utilised. Dispersibility of the samples was also much improved following the functionalisation as previously observed (*8*).

The presence of the attached fluorophore is clearly evident from the absorption spectrum of f-SWNTs **4** (Figure S3 of the Supplementary Information, available online), where as previously seen, the fluorophore assigned bands appear broadened, suggesting electronic communication between the components indicating covalent conjugation of **2** as opposed to physisorption. Upon comparison of the emission spectra, at equal values of optical absorption, it is evident that the emission from the fluorophore is quenched by over an order of magnitude (Figure S4 of the Supplementary Information, available online), which we previously demonstrated to be a consequence of electron transfer to the SWNT acceptor (*8*).

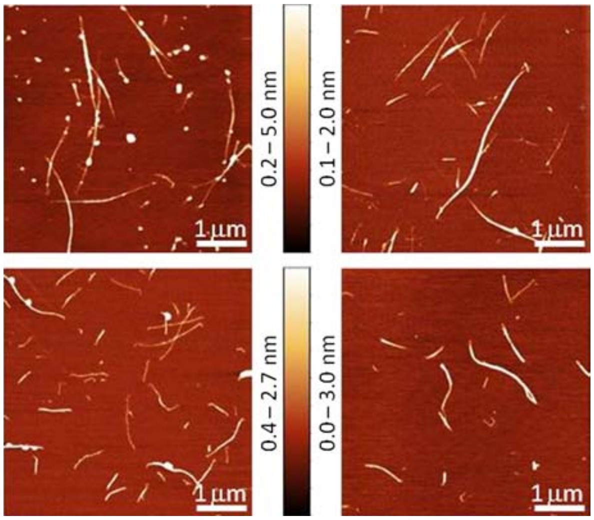


Figure 2. AFM of raw, purified and functionalised SWNTs.

The *on*/*off* switching mechanism of f-SWNTs **4** was designed to be controlled by the phenol/phenolate interconversion on the fluorophore (Figure 3(a)) (*14*). When protonated, the irradiation of f-SWNTs **4** at 690 nm excites the fluorophore to the singlet excited state (S1) and subsequently either emission or intersystem crossing to the triplet state (T1) and electron transfer can occur (*8*, *15*). It has been shown for **1** that upon deprotonation to the phenolate the singlet excited state becomes non-emissive, which when applied to our current construct could be viewed as illustrated in Figure 3(a) (*11*). The switching ability of f-SWNTs **4** was investigated by dispersing in water using SDBS and monitoring changes in the adsorption and emission behaviour upon alteration of the pH between a value of 5 (protonated) and 9 (deprotonated). The absorption spectra clearly demonstrate the switching (Figure 3(b)), where the absorption band at 700 nm disappears and is replaced by a band at 775 nm assignable to the deprotonated form as was previously recorded for compound **1** (*11*). This is confirmed by the emission results (Figure 3(c)), where the characteristic fluorophore emission band (although quenched with respect to compound **1**) is evident at pH 5 and disappears immediately upon addition of base, indicating complete quenching of the excited state. The *on*/*off* switching of the

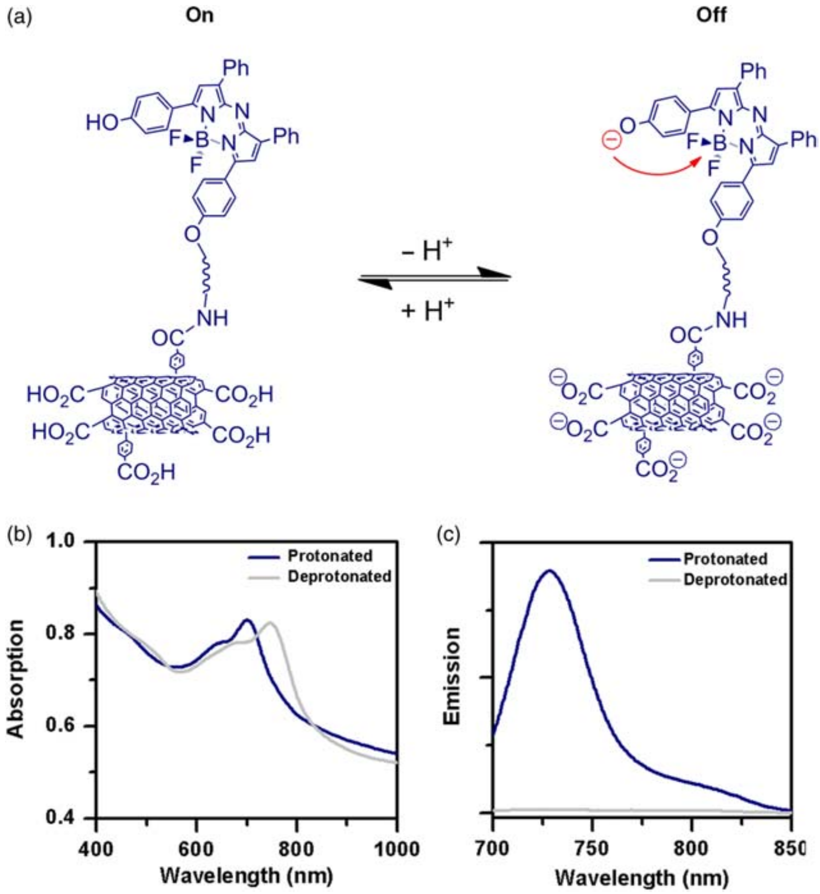


Figure 3. (a) Schematic representation of on/off switching of f-SWNTs **4** with corresponding (b) absorption and (c) emission ($\lambda_{exc} = 690\,nm$) spectra.

excited state of f-SWNTs **4** is seen to be completely reversible, where modulation or cycling of the emission band at 725 nm, following repeat additions of aqueous acid and base, is displayed in Figure 4(a). A sigmoidal plot of pH versus fluorescence intensity interestingly predicted an apparent pK_a of 6.7 (Figure 4(b)), which is only slightly lower than the pK_a of 6.9 found for compound **1** when measured in a neutral surfactant (*11*). This is most likely due to confinement of the fluorophore in close proximity to unreacted carboxylic acid groups on the surface of the SWNT. This effect is also seen in enzymes where the pK_a of acidic or basic residues may altered considerably

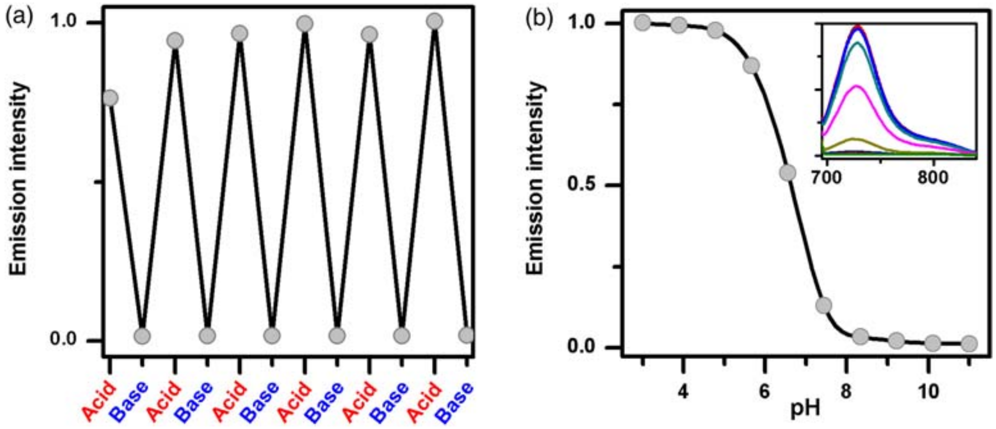


Figure 4. (a) Modulation of f-SWNTs **4** emission at 725 nm and (b) sigmoidal plot predicting a pK_a value of 6.7.

depending on the nature or type of neighbouring residues (*16*). This also clearly illustrates that the supramolecular photonic switching properties of molecule **1** are maintained once covalently bonded to SWNT framework.

4. Conclusions

In summary, a pH switchable boron difluoride azadipyrromethene SWNT conjugate has been synthesised and characterised. The ability to reversibly switch *on* and *off* the fluorophore excited state by modulation of pH has been demonstrated. As we have previously shown that electron transfer to the SWNT occurs following excitation of the boron azadipyrromethene component, it could be anticipated that the ability to switch *on/off* its excited state may consequently result in an *on/off* switching of the electron transfer to the SWNT acceptor. This is currently under investigation and time-resolved photophysical characterisation of this switchable SWNT conjugate will be reported in due course.

Electronic Supplementary Information (ESI) available: Supplementary Raman, FTIR, absorption and emission spectroscopy figures are available.

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