



Effects of number of ring substituents on the physicochemical properties of zinc aminophenoxy phthalocyanine-single walled carbon nanotube conjugate



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ABSTRACT

This work reports on the linking of zinc monoaminophenoxy (ZnMAPPc) or zinc tetraaminophenoxy phthalocyanine (ZnTAPPc) complexes to single walled carbon nanotubes (SWCNTs) through either covalent or non-covalent (adsorption) bonding. The functionalized complexes showed better thermal stability when compared to the SWCNT-COOH, ZnMAPPc and ZnTAPPc alone as confirmed by thermogravimetric analyses. The covalently linked ZnMAPPc-SWCNT showed higher electron transfer rate constant and photoinduced electron efficiency when compared to adsorbed complexes. ZnMAPPc-SWCNT complexes (linked and adsorbed) showed better photophysical and photochemical properties when compared to ZnTAPPc-SWCNT complexes. The triplet, singlet oxygen and fluorescence quantum yields of ZnMAPPc (or ZnTAPPc) decrease upon linking or adsorption onto SWCNTs.

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1. Introduction

Metallophthalocyanines (MPcs) have found applications in various fields including as photosensitizers in photodynamic therapy (PDT) [1–3], in nonlinear optics [4] and as electrochemical sensors [5]. The physical, electronic and optical properties of MPc complexes can be further modified by introducing substituents to the peripheral (β) or non-peripheral (α) position of the phthalocyanine ring [6–9]. Although, MPcs have been reported to be excellent PDT agents [3], the problem of transportation to the cancerous cells has remained a huge challenge to researchers. We report herein, the functionalization of zinc monoaminophenoxy phthalocyanine (ZnMAPPc) (or zinc tetra aminophenoxy phthalocyanine (ZnTAPPc)) with single walled carbon nanotubes (SWCNTs) as drug carriers. The physicochemical properties of these bi-functional agents are presented. ZnMAPPc presents only one point of coordination with SWCNTs, whereas ZnTAPPc presents four points of coordination. For both complexes, it is possible that more than one Pc complex coordinates to one SWCNT. For ZnTAPPc, the possibility of more than one SWCNTs coordinating to the Pc is unfavourable due to size considerations. The effects of one versus four amino

groups on the physicochemical properties of the Pc-SWCNT conjugates will be examined.

SWCNTs are one-dimensional nano materials that readily accept charge when interfaced with excited-state electron donors via functionalization [10]. SWCNTs have emerged as a potential delivery system for therapeutic molecules [11–13]. Carbonaceous tubules absorb light in the near-infrared region and they may induce cell death by a localized photothermal (PTT) therapeutic effect [14]. The properties of SWCNTs can be tuned via functionalization which could be achieved by either covalent or non-covalent interaction. Covalent functionalization involves the introduction of functional groups to either the ends or the side wall of the SWCNTs by creating defect sites through oxidation. This process affects the extended π -system of the SWCNTs backbone, thus influencing its electronic properties [15–19]. Non-covalent functionalization (adsorption), on the other hand, involves π - π interactions between aromatic groups and the sidewalls of the SWCNTs [20–22], and this has the major advantage of preserving the properties of SWCNTs since the carbon backbone is not affected. Functionalized SWCNTs have the additional advantage of moving across cellular membranes with less cytotoxic effects compared to the unfunctionalized SWCNTs [11]. Hence, the SWCNTs used in this study were functionalized with carboxylic acid and further functionalized with ZnMAPPc (or ZnTAPPc). We therefore, employ the SWCNTs in this study, as a potential drug carrier and a photothermal agent.

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The photophysical and photochemical properties of ZnMAPPc (or ZnTAPPc) when alone and upon functionalization with SWCNTs (by covalent linking and adsorption) were studied. The triplet state parameters for ZnMAPPc on its own are known [23], but in a different solvent system to that employed in this work, hence will be reported here (together with singlet oxygen quantum yields) in DMSO in the absence and presence of SWCNT. The physicochemical properties of ZnTAPPc (when alone or in the presence of SWCNT) are reported here for the first time.

2. Experimental

2.1. Materials

Dimethylsulfoxide (DMSO), dicyclohexylcarbodiimide (DCC), ethanol and dimethyl formamide (DMF) were obtained from SAARCHM. Diphenylisobenzofuran (DPBF) and zinc phthalocyanine were obtained from Sigma–Aldrich. Single-walled carbon nanotubes (SWCNT, 1–5 nm in diameter and 1–5 μm in length) were obtained from Nanolab. Zinc monoaminophenoxy phthalocyanine (ZnMAPPc, **1**) [24] and zinc tetraaminophenoxy phthalocyanine (ZnTAPPc, **2**) [25] were synthesized according to literature methods.

2.2. Equipment

Absorption spectra were recorded on a Shimadzu UV-Vis 2550 spectrophotometer and fluorescence emission and excitation spectra on a Varian Eclipse spectrofluorimeter using a 360–1100 nm filter. Infrared spectra were recorded on a Perkin–Elmer Universal ATR Sampling accessory spectrum 100 FT-IR spectrometer.

Laser flash photolysis experiments were performed to determine the triplet decay kinetics. The excitation pulses were produced by a tunable laser system consisting of an Nd:YAG laser (355 nm, 135 mJ/4–6 ns) pumping an optical parametric oscillator (OPO, 30 mJ/3–5 ns) with a wavelength range of 420–2300 nm (NT-342B, Ekspla). The details have been reported [26]. Solutions for triplet state studies were de-aerated with argon for 15 min before measurement. The absorbance of the solution at the Q band was 1.5 for these studies. Triplet lifetimes were determined by exponential fitting of the kinetic curves using OriginPro 8 software.

Photo-irradiation for singlet oxygen determinations was done using a general electric quartz line lamp (300 W) as described [27,28]. Light intensities were measured with a POWER MAX5100 (mole electron detector incorporated) power metre and were found to 2.97×10^{16} photons $\text{s}^{-1} \text{cm}^{-2}$.

Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH). The excitation source was a diode laser (LDH-P-670 driven by PDL 800-B, 670 nm, 20 MHz repetition rate, 44 ps pulse width, Picoquant GmbH). Fluorescence was detected under the magic angle with a peltier cooled photomultiplier tube (PMT) (PMAC-C 192-N-M, Picoquant) and integrated electronic (PicoHarp 300E, Picoquant GmbH) as described in detail elsewhere [26]. Transmission electron microscopy (TEM) images were obtained using a Zeiss Libra TEM 120 model operated at 90 kV.

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Discover XRD equipped with a Lynx Eye Detector, using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter). Details have been previously reported [23,26].

Raman spectra were obtained with a Bruker Vertex 70 – Ram II spectrometer (equipped with a 1064 nm Nd:YAG laser and liquid nitrogen cooled germanium detector). Solid samples diluted with KBr were used. Thermal gravimetric analysis (TGA) were recorded on a Shimadzu DTG-TG 60H with a gas flow of 120 ml/min and operated under a nitrogen atmosphere at $10^\circ\text{C}/\text{min}$.

2.3. Synthesis

2.3.1. Functionalization of single-walled carbon nanotubes (SWCNT-COOH)

SWCNTs were functionalized with carboxylic acid (represented as SWCNT-COOH), using established methods [29]. Briefly, the SWCNTs (60 mg) were suspended in a 3:1 mixture of concentrated H_2SO_4 and concentrated HNO_3 . The solution was then stirred for 2 h at 70°C . The resulting mixture was centrifuged and washed with Millipore water several times until a pH of 5 was attained. The SWCNT-COOH were subsequently dried in an oven at 110°C for 12 h. SWCNT-COOH: IR [(ATR) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3296–3200 (O–H), 1751 (C=O). [Raman $\nu_{\text{max}}/\text{cm}^{-1}$]: 2551(G*), 1592 (G), 1276 (D).

2.3.2. Synthesis of the linked SWCNT-COOH and ZnMAPPc (ZnMAPPc-SWCNT linked **3**) or ZnTAPPc (ZnTAPPc-SWCNT linked **4**) conjugates, Scheme 1A

SWCNT-COOHs were chemically modified with ZnMAPPc (or ZnTAPPc) via diimide-activated amidation according to literature [30]. Briefly, 20 mg of SWCNT-COOH was stirred with 10 mg (0.048 mmol) of DCC for 24 h in DMF. After this time 20 mg (0.029 mmol) of ZnMAPPc (or 20 mg (0.02 mmol) of ZnTAPPc) was added and the solution stirred at room temperature for 48 h. The solids were precipitated out using a solvent mixture of ethanol and hexane (1:1) and the solid products were obtained by centrifugation. Unreacted ZnMAPPc (or ZnTAPPc) and DCC were removed by repeated washing in ethanol. ZnMAPPc-SWCNT linked **3**: IR [(ATR) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3205–3047 (N–H str.), 1656 (C=O amide), 1605 (N–H bend). [Raman $\nu_{\text{max}}/\text{cm}^{-1}$]: 2549 (G*), 1590 (G), 1283 (D). ZnTAPPc-SWCNT linked **4**: IR [(ATR) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3316–3154 (N–H str.), 1650 (C=O amide), 1650 (N–H bend). [Raman $\nu_{\text{max}}/\text{cm}^{-1}$]: 2548(G*), 1589 (G), 1283 (D).

2.3.3. Synthesis of the non-covalent (adsorbed) SWCNTs and ZnMAPPc (ZnMAPPc-SWCNT adsorbed **5**) or ZnTAPPc (ZnTAPPc-SWCNT adsorbed **6**) conjugates, Scheme 1B

ZnMAPPc (or ZnTAPPc) were immobilized onto SWCNT-COOH according to literature methods for immobilization of other Pc [31] with slight modification as follows: 20 mg of SWCNT-COOH were ultrasonicated for 20 min in 5 ml of dry DMF to give a brown coloured suspension. ZnMAPPc **1**, (20 mg, 0.029 mmol) (or ZnTAPPc **2**, (20 mg, 0.02 mmol)) was then added to the solution to give a green suspension and the resulting mixture was stirred for 18 days to give a dark green suspension indicating the adsorption of complex **1** (or **2**) onto SWCNT-COOH. The reaction mixture was precipitated out of solution using the solvent mixture of ethanol and hexane (1:1) and the solid products were obtained by centrifugation. Unadsorbed **1** (or **2**) was removed by repeated centrifugation and dispersion in ethanol. ZnMAPPc-SWCNT adsorbed **5**: IR [(ATR) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3356–3194 (N–H str.), 1704 (C=O), 1570 (N–H bend). [Raman $\nu_{\text{max}}/\text{cm}^{-1}$]: 2548 (G*), 1589 (G), 1285 (D). ZnTAPPc-SWCNT adsorbed **6**: IR [(ATR) $\nu_{\text{max}}/\text{cm}^{-1}$]: 3357–3200 (N–H str.), 1709 (C=O), 1653 and 1605 (N–H bend). [Raman $\nu_{\text{max}}/\text{cm}^{-1}$]: 2548(G*), 1591 (G), 1281 (D).

2.4. Photophysical and photochemical parameters

2.4.1. Triplet quantum yields and lifetimes

Triplet quantum yields (Φ_T) were determined using a comparative method based on triplet decay [32] using ZnPc as the standard, Eq. (1)

$$\Phi_T = \Phi_{T(\text{std})} \frac{\Delta A_T \cdot \varepsilon T^{\text{std}}}{\Delta A_T^{\text{std}} \cdot \varepsilon T} \quad (1)$$

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