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Novel BODIPY-Cyclotriphosphazene- Fullerene triads: Synthesis, characterization and singlet oxygen generation efficiency

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ABSTRACT

Novel heavy atom free triad type triplet photosensitizers composed of unsubstituted and distyryl BF_2-chelated dipyrromethene (BODIPY), cyclotriphosphazene and fullerene- C_{60}, were newly synthesized using multistep synthetic procedure. Rigid cyclotriphosphazene core enabled fixed non-geminal-*cis-tris* arrangement of chromophores (BODIPY) and fullerene- C_{60} as spin converter. All newly synthesized compounds were characterized by MALDI-MS, ^{1}H, ^{13}C and ^{31}P NMR. Optical absorption and emission studies were systematically performed in solution by comparing with the reference compounds to establish the photophysical properties of the triads. The new heavy atom free triplet photosensitizers contain three light harvesting antennas as well as combined with different absorption wavelengths resulting in high molar extinction coefficients. Singlet oxygen generation capacities of novel triads are measured using the trap molecule 1,3-diphenylisobenzofuran. Also, both triads demonstrate chemical and photo stability under the environment of singlet oxygen measurement.

1. Introduction

Rationally designed molecules have important implications for the development of materials with useful chemical and physical properties [1]. In particular, cores with well-defined structure and size are beneficial building blocks for construction of giant architectures through covalent bonds. The construction of assemblies by covalent bonding is intriguing where the constituent molecules can be directed easily giving rise to development of new building blocks that is highly desirable. Cyclic phosphazenes can be distinguished by six or more reactive sites in the molecules, where a variety of organic groups can be introduced into the phosphazenes ring [2–4]. Furthermore, in some organocyclotriphosphazenes the organic groups are located almost perpendicularly above and below a nearly planer phosphazenes ring [5,6]. The combination of these two sets of properties allows the use of cyclotriphosphazenes for the construction of new architectures.

Boron dipyrromethenes (BODIPYs) are extensively used as functional constituents with high stability and favorable photophysical and photochemical properties, that can be easily tuned readily through chemical modification of the BODIPY core [7–9]. They have attracted increasing attention because of their high extinction coefficients, high fluorescence quantum yields, and relatively long singlet excited state lifetimes [10]. As a result, they are frequently used as energy-absorbing and -transferring antenna molecules [11,12]. Multimodular systems assembled using different photo-active species have been extensively studied to explore the photophysical and photochemical properties under various conditions [13]. Such assembled multimodular systems were found to be useful in predetermined applications. The covalent functionalization of fullerenes, especially fullerene- $C_{60,}$ to synthesize versatile systems has improved rapidly [14]. The popularity of fullerenes in science is due to years of intense research activity that shown fullerene- C_{60} is a powerful building block for use in materials science [15]. Fullerenes can have several interesting properties as a result of linking which provide various photophysical properties [16,17] such as multicomponent systems that could be used in light-harvesting systems [18,19].

Toward the goal of constructing new multicomponent systems that provide the ability to convert light into chemical energy, we devised visible light-harvesting BODIPY- cyclotriphosphazene-fullerene triads. Unsubstituted and distyryl- BODIPYs act as the light harvesting antennas, fullerene- C_{60} unit as the spin convertor and cyclotriphosphazene ring used as carrier-router to locate active groups precisely.

First, we synthesized non-geminal *cis-tris*- azidoethanoxy substituted cyclotriphosphazene (**2**). The following reaction between compound **2** and 4-hydroxybenzaldehyde gave cyclotriphosphazene core (**3**). As light harvesting antennae, unsubstituted- BODIPY (**5**) and distyryl- BODIPY (**7**) were synthesized according to standard procedure. BODIPYs **5** and **7** were reacted with compound **3** via click reaction to give BODIPY- cyclotriphosphazene dyads **8** and **9**, respectively. Prato reactions between compounds **8** and **9** with fullerene- C_{60} gave

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BODIPY- cyclotriphosphazene- fullerene triads (**10**– **11**). The identities of newly synthesized cyclotriphosphazene derivatives (**2**, **3**), BODIPYs (**5**, **7**), BODIPY- cyclotriphosphazene dyads (**8**, **9**) and BODIPY- cyclotriphosphazene- fullerene triads (**10**, **11**) were confirmed by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and matrix-assisted laser desorption/ionization time-of- flight mass spectrometry (MALDI).

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, (trimer) which was obtained from Aldrich was purified by fractional crystallization from n-hexane. Thin layer chromatography (TLC) and column chromatography were carried out on Merck silica gel plates (Kieselgel 60, F_{254} indicator, 0.25 mm) and silica gel (Kieselgel 60, 230–400 mesh), respectively. The deuterated solvent ($CDCl_3$) for NMR spectroscopy and the following chemicals were obtained from Merck; sodium azide, trifluoroacetic acid, *p*-chloranil, triethylamine (≥99%), piperidine (≥99%), glacial acetic acid, acetonitrile, dichloromethane, acetone, ethanol. 2-bromoethanol (97%), propargyl bromide (80% in toluene, stab. with MgO), boron trifluoride diethyl etherate (98 + %) and 1-bromohexan (99%), sodium ascorbate, Copper(II)sulfate pentahydrate were obtained from Alfa Aesar. 4-hydroxybenzaldehyde (99%) and 2,4- dimethylpyrrole (97%) were purchased from Acros Organics. Potassium carbonate (≥99%), fullerene- C_{60} (98%), sodium hydride, tetrahydrofuran, benzene, n- hexan and toluene were obtained from Sigma-Aldrich. Methanol was obtained from VWR and sarcosine (> 98%) was purchased from TCI. Unless otherwise stated, all other chemicals were of analytical reagent quality and used as received.

2.2. Equipment

Electronic absorption spectra were recorded with a Shimadzu 2101 UV spectrophotometer in the UV–visible region. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. The fluorescence lifetimes were obtained using Horiba- Jobin-Yvon-SPEX Fluorolog 3-2iHR instrument with Fluoro Hub-B Single Photon Counting Controller at an excitation wavelength of 500 nm and 570 nm. Signal acquisition was performed using a TCSPC module. Mass spectra were acquired in linear modes with average of 50 shots on a Bruker Daltonics Microflex mass spectrometer (Bremen, Germany) equipped with a nitrogen UV- Laser operating at 337 nm. ^{31}P, ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on a Varian 500 MHz spectrometer. The synthetic routes employed for the preperation of the BODIPY-cyclotriphosphazene-fullerene triads are shown in Scheme 1.

2.3. The parameters for fluorescence quantum yields

The fluorescence quantum yields (Φ_F) of compounds **8**– **11** were determined by the comparative method (Eq. (1)) [20].

$$\varnothing\ F = \varnothing F_{Std} \frac{F.A_{Std}.\ n^2}{F_{Std}.\ A.\ n^2_{Std}} \tag{1}$$

where F and F_{Std} are the areas under the fluorescence emission curves of the compounds (**8**– **11**) and the standard, respectively. A and A_{Std} are the respective absorbances of compounds (**8**–**11**) and the standard at the excitation wavelengths, respectively. The refractive indices (n) of the solvents were employed in calculating the fluorescence quantum yields in different solvents. Fluorescein ($\Phi_F = 0.95/0.1$ N NaOH) and zinc (II) phthalocyanine ($\Phi_F = 0.2$/DMSO) were employed as the standard [21].

2.4. The parameters for singlet oxygen quantum yields

Singlet oxygen generating capability of compounds **8**–**11** were done using singlet oxygen trap molecule 1,3- diphenylisobenzofuran (DPBF) and methylene blue (MB) as reference. Singlet oxygen can be monitored using photobleaching and subsequent decrease in absorbance of DPBF. 516 (2.1 mW/cm^2) and 630 (4.0 mW/cm^2) nm led bulb was used as light source. Light was exposed from 5 cm cell distance and absorbances were taken intervals for each solution (Eq. (2)).

$$\varphi(traid) = \varphi\Delta(ref)\left[\frac{k(triad)}{k(ref)}\right]\left[\frac{F(ref)}{F(triad)}\right]\left[\frac{PF(ref)}{PF(triad)}\right] \tag{2}$$

where triad and ref designate the “BODIPY- cyclotriphosphazene- fullerene photosensitizer” and “MB” respectively. k is the slope of difference in change in absorbance of DPBF (414 nm) with the irradiation time. F is the absorption correction factor, which is given by $F = 1–10^{-OD}$ (OD at the irradiation wavelength), and PF is light intensity (energy flux, mW/cm^2).

3. Synthesis

2-azidoethanol (**1**) [22], compound **4** [23], compound **5** [24] and compound **6** [25] were prepared according to their respective literature reports.

3.1. Synthesis of compound 2

Hexachlorocyclotriphosphazene (2.06 g; 5.90 mmol) and compound **1** (1.50 g, 17.00 mmol) were dissolved in 30 mL dry THF and cooled down in liquid N_2/acetone bath. Sodium hydride (0.71 g (60%), 17.80 mmol) was then added to the solution and stirred for 4 h at −78 °C. Reaction mixture was filtered from G4 sintered filter and the solvent was removed under reduced pressure. Compound **2** was isolated from column chromatography with silica gel using n-hexan/THF (4:1, v/v) as the mobile phase (0.71 g, 1.42 mmol, 20%).

Spectral data of **2**: ^{31}P NMR (202 MHz, $CDCl_3$, δ ppm): 21.65 (s, 3P), spin system: A_3. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ ppm): 3.57 (t, $J = 4.98$ Hz, 6H, N_3CH_2—), 4.31 (t, $J = 4.17$ Hz, 6H, —OCH_2—). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K, δ ppm): 50.09, 66.75 MS (MALDI-TOF) (DHB) *m/z* Calc.: 499.52; found: 499.74 $[M]^+$.

3.2. Synthesis of compound 3

The solution of compound **2** (0.25 g; 0.50 mmol) in dry THF (10 mL) was cooled down to 0 °C. 4-hydroxybenzaldehyde (0.06 g; 0.50 mmol) and sodium hydride (0.01 g; 0.50 mmol) were dissolved in dry THF (10 mL) and this solution was dropwise added to a magnetically stirred solution of compound **2** under argon atmosphere. Afterward the reaction mixture was stirred at room temperature for 6 h and the reaction followed by TLC. Sodium chloride (NaCl) was removed by filtration, the solvent removed under reduced pressure, and the resulting colorless oil was subjected to column chromatography using dichloromethane as eluent.

Spectral data of compound **3**: ^{31}P NMR (202 MHz, $CDCl_3$, δ ppm): 7.80 (t, 1P, $J_{AX} = 81.88$ Hz, P(OBODIPY)(OBA)), 23.77 (d, 2P, PCl (OBODIPY)). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, δ ppm): 3.48 (bs, 6H, N_3CH_2—), 4.19 (t, $J = 4.05$ Hz, 6H, —OCH_2—), 7.39 (d, $J = 8.31$ Hz, 2H, Ar—CH), 7.91 (d, $J = 7.92$ Hz, 2H, Ar—CH), 9.99 (s, 1H, ArCHO). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K, δ ppm): 50.10, 66.58, 121.61, 131.49, 133.81, 154.77, 190.68. MS (MALDI-TOF) (DIT) *m/z* Calc.: 585.18; found: 586.11 $[M]^+$.

3.3. Synthesis of compound 7

A mixture of the compound **5** (0.10 g, 0.26 mmol), compound **6**