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Naphthalimide-cyclophosphazene combination: Synthesis, crystal structure, photophysics and solid-state fluorescence

Şule Şahin Ün*, Sevinc Zehra Topal, Yunus Zorlu

Gebze Technical University, Faculty of Science, Department of Chemistry, 41400 Gebze, Kocaeli, Turkey

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ABSTRACT

New fluorophore molecules based on combination of naphthalimide and phosphazene groups (**4** and **5**) were obtained in high yields via one-step nucleophilic substitution reactions and characterized by spectroscopic methods. Also, crystal structures of 2-[2-(4-hydroxy-phenyl)-ethyl]-benzo[de]isoquinoline-1,3-dione (**1**) and the novel molecule (**5**) were determined by single-crystal X-ray diffraction technique. Electronic absorption, steady-state and time resolved fluorescence measurements were performed to determine photophysical properties of the compounds. In addition, their solid-state fluorescence spectra were recorded by using fiber optic system. Their fluorescence properties evidence the excimer emission in the visible region (~460 nm) in solution and solid-state. This excimer emission is attributed to the π-π stacking interactions which is further supported from crystal structures of the molecules. Moreover, both compounds exhibited high molar extinction coefficients in solution and moderate fluorescence emission especially in solid–state.

1. Introduction

In the field of materials science, organic molecules such as naphthalimide [1,2], pyrene [3], perylene [4] and anthracene [5] have the advantages of ease of synthesis and purification, and also attractive photophysical properties (high molar extinction coefficient and high fluorescence intensities, etc.). Naphthalimide derivatives which are highly luminescent organic compounds have been widely used in different applications such as chemosensors [6–8], solar cells [9–11], electroluminescent devices [12], organic semiconductors [13] and self-assembly [1], etc. It is well known that molecular systems can undergo inter- or intra-molecular π-π stacking or molecular aggregation state. These interactions can be result in excimer emission which improve photophysical properties [14] and also can be advantage for designing self–assembled nanostructures for use as potential molecular materials [1]. For example, intra-molecular excimer emission was observed for pyrenyloxy substituted cyclotriphosphazenes [15] and cystine-derived bis-naphthalimides [2]. Since fluorescence properties of the compounds in solution and solid-state can be different, understanding of the emission behavior in both forms is of great importance to use in different application such as organic light-emitting devices (OLEDs) [14]. A wide variety of photophysical properties of the naphthalimide fluorophores can be improved with combination of other convenient groups to achieve targeted properties. Naphthalimide-phthalocyanine pentads can be given as an example of these combinations which were reported in our previous work [16]. Phosphazene compounds, which have characteristic P=N double bonds and consist of a significant class of inorganic compounds [17], can be also candidate for this purpose. The most interesting and effective property of phosphazenes is achieving to design different molecules via substitution of P atoms [18,19]. In cyclophosphazenes, functional substituted groups constructed above and below the planar cyclophosphazene ring enable these molecules to constitute different types of molecules such as dendimeric structures [20,21] and hyperstructured molecules [22]. Recently, interesting and attractive works including phosphazene derivatives have been reported to design systems for different applications such as phosphorescent organic light-emitting diodes (PHOLEDs) [23,24], liquid crystals [25,26], catalysts [27] and drug delivery [28], etc. Therefore, our attention turn to cyclophosphazenes in order to increase naphthalimide units in the target molecule to improve the fluorescence properties. To address this issue, we propose to design molecules which constitute combination of 1,8-naphthalimide and cyclophosphazenes.

In this context, we have prepared two cyclophosphazene compounds **4** and **5** which have different numbers of naphthalimide unit. The compounds have been characterized by spectroscopic techniques including single-crystal X-ray diffraction. The electronic absorption and steady-state emission spectra of the compounds were recorded in solution and solid-state. Their photophysical properties such as fluorescence quantum yields and lifetimes were also determined. In both solution and solid-state, aggregation of the compounds resulted in excimer emission in the visible region (~460 nm). To the best of our knowledge, the naphthalimide-cyclophosphazene combination and

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* Corresponding author.

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their photophysical properties have been reported for the first time in this study.

2. Experimental

2.1. Materials and equipment

All reaction solvents were dried and purified as described by Perrin and Armarego [29]. All other reagents were purchased from commercial suppliers and used without any purification. The mass spectra were recorded on a LCQ-ion trap equipped with an ES (Electrospray) source and MALDI (matrix assisted laser desorption ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid as matrix. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions using TMS as an internal reference and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions using 85% H_3PO_4 as an external reference on a Varian 500 MHz spectrometer. Thermal properties of compounds were investigated on a Mettler Toledo TGA/SDTA 851. Thermogravimetric analysis (TGA) was carried out at temperature range from room temperature to 700 °C at a heating rate of 10 °C/min under a nitrogen gas atmosphere. Absorption spectra were recorded with a Shimadzu 2001 UV spectrophotometer using a 1 cm path length cuvette at room temperature. Steady-state fluorescence emission spectra were recorded by using Varian Cary Eclipse fluorescence spectrophotometer.

2.2. X-ray crystallography

2.2.1. X-ray data collection and structure refinement

Data were obtained with Bruker APEX II QUAZAR three-circle diffractometer. Indexing was performed using APEX2 [30]. Data integration and reduction were carried out with SAINT [31]. Absorption correction was performed by multi-scan method implemented in SADABS [32]. The structures were solved and refined using the Bruker SHELXTL software package [33]. Aromatic and aliphatic C-bound H atoms were positioned geometrically and refined using a riding mode. In **1**, the positions of the O-bound H atoms were placed at calculated positions. In **5**, the unit cell consists of a large region of disordered solvent which could not be modelled as discrete atomic sites. Herein, the contributions of seriously disordered solvent molecules were eliminated from the structure using SQUEEZE subroutine [34] in the PLATON software [35] program suite. MERCURY software [36] was used for visualization of the cif files.

2.3. Photophysical measurements

2.3.1. Fluorescence quantum yield (ϕ_F) determination

William's method was used to calculate fluorescence quantum yields of the molecules **4** and **5**. For this purpose, 2-aminopyridine in 0.1 M H_2SO_4 ($\Phi_F = 0.60$, $\lambda_{max}^{eml} = 365$ nm) [37] was used as reference molecule whose emission maxima was at similar wavelength region of the molecules **4** and **5**. The absorbance and fluorescence emission spectra of 2-aminopyridine and the molecules **4** and **5** were recorded in $CHCl_3$ at three different concentrations. The integrated fluorescence intensities were plotted vs absorbance for 2-aminopyridine and corresponding dyes. To calculate Φ_F values, following Eq. (1) was used where Std designates standard, and Grad is the gradient of the plot and *n* is the refractive index of the solvent, respectively [38]. In this method, the ratio of the gradients of the plots was proportional to the quantum yields.

$$\Phi_F = \Phi_F^{Std}\left(\frac{Grad}{Grad_{Std}}\right)\left(\frac{n^2}{n_{Std}^2}\right) \tag{1}$$

2.3.2. Solid-state fluorescence emission measurements

Fluorescence spectra of the molecules in solid-state were recorded by Varian Cary Eclipse fluorescence spectrometer with the fiber optic accessory (λ = 330 nm, excitation slit: 5.0; emission slit 10.0).

2.3.3. Fluorescence lifetime (τ_F) measurements

Fluorescence lifetimes were recorded using Horiba FL3-2IHR with a Time Correlated Single Photon Counting (TCSPC) system. The instrument was equipped with a nanoLED-310 and nanoLED-390 nm as the excitation sources. During the measurements, the Instrument Response Function (IRF) was obtained from a non-fluorescence suspension of a colloidal silica (LUDOX 30%, Sigma Aldrich) in water, held in 10 mm path length quartz cell and was considered to be wavelength independent.

2.4. Synthesis

2-[2-(4-hydroxy-phenyl)-ethyl]-benzo[de]isoquinoline-1,3-dione (**1**) was synthesized according to the literature procedure [39].

2.4.1. Reaction of 2-[2-(4-hydroxy-phenyl)-ethyl]-benzo[de]isoquinoline-1,3-dione with $N_3P_3Cl_6$ to obtain compound

Trimer ($N_3P_3Cl_6$) (0.2 g, 0.576 mmol) was dissolved in 20 ml dry THF in a 100 ml three-necked round-bottomed flask at room temperature under an argon atmosphere. Then 2-[2-(4-hydroxy-phenyl)-ethyl]-benzo[de]isoquinoline-1,3-dione (1.46 g, 4.6 mmol) in 30 ml dry THF and NaH (0.18 g, 4.6 mmol) were added to this reaction mixture. The reaction mixture was stirred two days at room temperature under an argon atmosphere and followed by TLC, which indicated products. The reaction mixture was filtered to remove the sodium chloride formed and the solvent removed under reduced pressure. The resulting oil was subjected to column chromatography using DCM:THF (20:1) as mobile phase. The compound **4** was isolated as a white solid (0.78 g, 67%). Anal. Calc. for: $C_{120}H_{84}N_9O_{18}P_3$: C, 70.90; H, 4.16; N, 6.20%; (M, 2032.92). Found: C, 70.80; H, 4.15; N, 6.18%; ([M + H]$^+$, 2033.767*m/z*). ^{1}H NMR data for **4**; (298 K, $CDCl_3$): δ (ppm) = 8.35 (d, 2H, ArH), 8.06 (d, 2H, ArH), 7.54 (t, 2H, ArH), 7.18 (d, 2H, ArH), 6.90 (d, 2H, ArH), 4.36 (m, 2H, benzyl), 3.01 (t, 2H, N-CH_2). ^{13}C NMR data for **4**; (298 K, CDCl3): δ (ppm) = 166.45, 151.82, 137.98, 136.13, 134.06, 133.55, 132.52, 130.68, 129.38, 125.35, 123.68, 44.46 (benzyl), 36.15 (N-CH2).

2.4.2. Reaction of 2-[2-(4-hydroxy-phenyl)-ethyl]-benzo[de]isoquinoline-1,3-dione with $N_4P_4Cl_8$ to obtain compound

Tetramer ($N_4P_4Cl_8$) (50 mg, 0.11 mmol) was dissolved in 10 ml dry THF in a 50 ml three-necked round-bottomed flask at room temperature under an argon atmosphere. Then 2-[2-(4-hydroxy-phenyl)-ethyl]-benzo[de]isoquinoline-1,3-dione (0.34 g, 1.1 mmol) in 20 ml dry THF and NaH (44 mg, 1.1 mmol) were added to this reaction mixture. The reaction mixture was stirred two days at room temperature under an argon atmosphere and followed by TLC, which indicated products. The reaction mixture was filtered to remove the sodium chloride formed and the solvent removed under reduced pressure. The resulting oil was subjected to column chromatography using DCM: Ethyl acetate (8:1) as mobile phase. The compound was **5** isolated as a white solid (0.18 g, 60%). Anal. Calc. for: $C_{160}H_{112}N_{12}O_{24}P_4$: C, 70.90; H, 4.16; N, 6.20%; (M, 2710.56). Found: C, 70.82; H, 4.17; N, 6.22%; ([M]$^+$, 2710.743*m/z*). ^{1}H NMR data for **5**; (298 K, $CDCl_3$): δ (ppm) = 8.32 (d, 2H, ArH), 8.00 (d, 2H, ArH), 7.49 (t, 2H, ArH), 7.16 (d, 2H, ArH), 6.92 (d, 2H, ArH), 4.34 (m, 2H, benzyl), 2.99 (t, 2H, N-CH_2). ^{13}C NMR data for **5**; (298 K, CDCl3): δ (ppm) = 166.55, 152.49, 137.85, 136.49, 134.16, 133.48, 132.13, 130.85, 129.80, 125.51, 123.48, 44.45 (benzyl), 36.15 (N-CH2).