

Synthesis and spectral properties of a hexameric pyrene-fluorene chromophore based on cyclotriphosphazene



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ARTICLE INFO

Article history:

Received 1 May 2014

Accepted 18 June 2014

Available online 2 July 2014

Keywords:

Cyclotriphosphazene

Pyrene

Fluorene

Thermally stable

Fluorescence

ABSTRACT

A new fluorene substituted methoxybenzene-pyrene chromophore (**3**), [1-(9,9-dimethylfluorene)-8-(4-methoxyphenyl)]pyrene, was synthesized by the Suzuki cross-coupling reactions of 1,8-dibromopyrene with 4-methoxyphenylboronic acid and 9,9-dimethylfluorene-2-boronic acid pinacol ester, respectively. The hexameric compound (**5**), hexakis[1-oxyphenyl-8-(9,9-dimethylfluorene)pyrene] cyclotriphosphazene, was prepared by a nucleophilic displacement reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with (**4**), [1-(9,9-dimethylfluorene)-8-(4-hydroxyphenyl)]pyrene, which was obtained from the deprotection of compound (**3**). The newly synthesized compounds were fully characterized by standard spectroscopic techniques. The spectral properties of compound (**5**) were investigated by thermogravimetric analysis, differential scanning calorimetry, UV-Vis and fluorescence spectroscopy, and cyclic voltammetry. In addition, fluorescence quantum yields, fluorescence lifetimes and fluorescence quenching behavior by 1,4-benzoquinone were investigated in dichloromethane. It was found that the hexameric compound (**5**) emitted in the blue-light spectral region with a maxima of 455 nm, with a quantum yield of 0.63 in dichloromethane. Compound (**5**) was amorphous in nature and exhibited excellent thermal stability, with a decomposition temperature of 498 °C and a high glass-transition temperature of 58 °C.

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1. Introduction

Cyclic phosphazenes, composed of alternating nitrogen and phosphorus atoms, are a commonly used building block with an inorganic $(P=N)_n$ ($n = 3$ or 4) core, and are extensively used as an interior core or a pendent group to develop dendrimers or polymers, respectively. Cyclic and polymeric phosphazenes are an important class of inorganic heterocyclic ring systems [1,2]. They readily undergo nucleophilic substitution reactions with alkoxides, aryloxides or amines on halocyclophosphazenes or high polymers [3–5] and their physical and chemical properties can be tailored via appropriate substituted groups on the phosphorus atoms [6]. This allows for the preparation of various types of dendrimers and polymers for varied applications, including thermal stability, catalytic properties, electrical conductivity, liquid crystals, biomedical activity and luminescent materials [5–7].

The field of luminescent materials is attracting interest because of their many applications, including emitting materials for organic

light emitting diodes (OLEDs), light harvesting materials for photocatalysis and fluorescent sensors for organic or inorganic analyzers [8]. In the area of active OLED materials, both small molecules and polymers are the current preferred candidates [9,10]. Cyclic phosphazene based materials are a suitable platform as luminescent materials because they provide high thermal stability and the functional groups are projecting in three dimensions, thus producing a rigid spherical core for attaching the dendrons of interest. Moreover, when attaching organic chromophores onto cyclic phosphazene cores, their optical and electronic properties are not noticeably affected compared to the molecular analogue [11–13]. These rigid spheres have been shown to have amorphous properties that are known to be important for electroluminescent devices. Hence, there has been considerable interest in fluorescent compounds based on cyclic phosphazene cores for use in OLEDs [14–18].

Pyrene and its electron-rich aromatic derivatives have been widely used in many applications, such as materials science and organic electronic devices [19]. For example, fluorene-pyrene functional materials have been extensively well-documented as active ingredients for electroluminescence devices [20–26]. Pyrenyl-functionalized fluorene chromophores have demonstrated great potential and advantages for OLEDs [20–23], and organic semi-conductors [24–26]. Recently cyclophosphazene derivatives

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decorated with fluorene and pyrene [11,14,15,27] groups were reported for the development of electroluminescent devices. To the best of our knowledge, there is no report on the synthesis of both chromophores being linked to cyclotriphosphazene together. Hence, we thought that it would be interesting to prepare a hexameric fluorene-pyrene chromophore based on a cyclic phosphazene core, which may allow favorable thermal and optical properties as desired for electroluminescent devices.

Herein, we reported the design and synthesis of a new fluorene substituted methoxybenzene-pyrene chromophore using Suzuki cross-coupling reactions. After that, a hexameric structure was prepared by a nucleophilic displacement reaction of hexachlorocyclotriphosphazene, $N_3P_3Cl_6$, with the newly synthesized pyrene-fluorene chromophore (Fig. 1). The chemical structures of the newly synthesized compounds were characterized by standard spectroscopic techniques. Selected properties of the hexameric structure were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), UV-Vis, fluorescence spectroscopy and cyclic voltammetry (CV).

2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (trimer) (Otsuka Chemical Co. Ltd) was purified by fractional crystallization from n-hexane. The deuterated solvent ($CDCl_3$) for NMR spectroscopy and the following chemicals were obtained from Merck: tetrahydrofuran (THF), toluene, 1,4-dioxane, potassium carbonate (K_2CO_3), sodium sulfate (Na_2SO_4), sodium carbonate (Na_2CO_3), hydrochloric acid (37%); Aldrich: pyrene, 9,9-dimethylfluorene-2-boronic acid pinacol ester, palladium tetrakis(triphenylphosphine) ($Pd(PPh_3)_4$), bromine, Aliquat; Alfa Aesar: 4-methoxybenzeneboronic acid, cesium carbonate (Cs_2CO_3), tetrabutylammonium bromide (TBAB); Fluka: hydromic acid (HBr). All other reagents and solvents were reagent grade quality and obtained from commercial suppliers.

2.2. Equipment

Elemental analyses were carried out using a Thermo Finnigan Flash 1112 Instrument. UV-Vis spectra were recorded with a Shimadzu 2001 UV spectrophotometer. Infrared spectra were

recorded on a Perkin Elmer Spectrum 100 Optica FT-IR spectrometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorometer using 1 cm pathlength cuvettes at room temperature. Mass spectra were acquired in the linear mode with an average of 50 shots on a Bruker Daltonics Microflex mass spectrometer equipped with a nitrogen UV-Laser operating at 337 nm. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230–400 mesh; for 3 g crude mixture, 100 g silica gel was used in a column of 3 cm in diameter and 60 cm in length) and preparative thin layer chromatography was performed on silica gel 60 P F_{254} . 1H , ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ solution on a Varian 500 MHz spectrometer. The thermal properties of the compounds were investigated on a Mettler Toledo TGA/SDTA 851 thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) DSC 821^e equipped with Mettler Toledo Star^e software at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a nitrogen flow (50 mL min^{-1}). Electrochemical behaviors were investigated using a CHIModel840B electrochemical analyzer.

2.3. Fluorescence quantum yields and lifetimes

The fluorescence quantum yield (Φ_F) was determined by the comparative method (Eq. (1)) [28].

$$\Phi_F = \Phi_F(\text{Std}) \frac{F A_{\text{Std}} n^2}{F_{\text{Std}} A n_{\text{Std}}^2} \quad (1)$$

where F and F_{Std} are the areas under the fluorescence emission curves of the sample (5) and the standard, respectively. A and A_{Std} are the respective absorbances of the samples and standard at the excitation wavelengths, respectively. The refractive indices (n) of the solvents were employed in calculating the fluorescence quantum yields in different solvents. Quinine sulfate (in 0.1 M H_2SO_4) ($\Phi_F = 0.54$) [29] was employed as the standard. Both the sample and standard were excited at the same wavelength. The concentration of the solutions at the excitation wavelength was fixed at $2 \times 10^{-7}\text{ mol dm}^{-3}$. Natural radiative (T_0) lifetimes were determined using the Photochem CAD program, which uses the Strickler-Berg equation [30]. The fluorescence lifetimes (T_F) were evaluated using Eq. (2).

$$\Phi_F = \frac{\tau_F}{\tau_0} \quad (2)$$

The rate constant for the fluorescence (k_F) values were calculated using Eq. (3).

$$k_F = \Phi_F / \tau_F \quad (3)$$

2.4. Fluorescence quenching by 1,4-benzoquinone (BQ)

Fluorescence quenching experiments on the hexameric derivative (5) were carried out by the addition of different concentrations of BQ to a fixed concentration of the compound, and the concentrations of BQ in the resulting mixtures were 0, 0.008, 0.016, 0.024 and 0.032 M. The fluorescence spectrum of compound (5) at each BQ concentration was recorded, and the changes in fluorescence intensity related to BQ concentration by the Stern-Volmer (S-V) equation [31] (Eq. (4)):

$$\frac{I_0}{I} = 1 + K_{SV}[BQ] \quad (4)$$

where I_0 and I are the fluorescence intensities of the fluorophore in the absence and presence of quencher, respectively. $[BQ]$ is the concentration of the quencher and K_{SV} is the Stern-Volmer constant, which is the product of the bimolecular quenching constant (k_q) and T_F , as is expressed in Eq. (5).

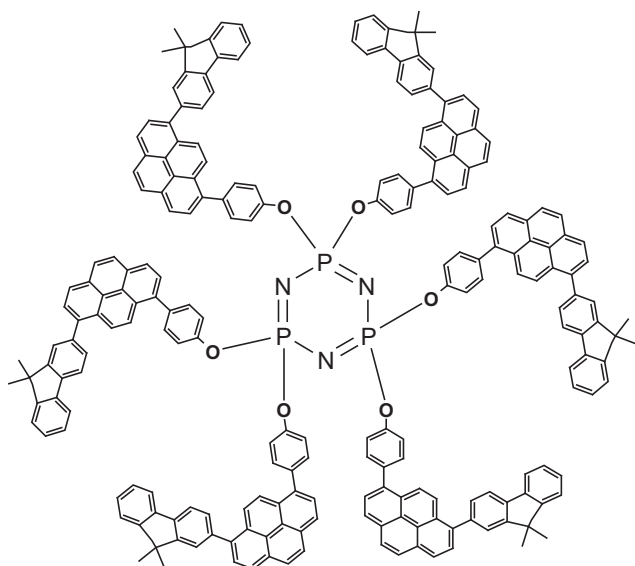


Fig. 1. Molecular structure of the hexameric compound (5).

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