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Highly efficient energy transfer in BODIPY–pyrene decorated cyclotriphosphazene

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ABSTRACT

In this study, two different cyclophosphazene compounds bearing five pyrene units and one borondipyrromethene unit were designed and synthesized. All compounds were fully characterized by elemental analysis, matrix-assisted laser desorption/ionization time-of-flight mass spectrometry, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The photophysical properties of the new compounds were investigated by means of absorption and fluorescence spectroscopies in dilute dichloromethane solutions. Both systems exhibit a highly efficient energy transfer process, from the excited pyrene units to the borondipyrromethene units. The photophysical studies indicated that the compounds exhibit large Stokes' shifts unlike reference simple BODIPY dyes.

1. Introduction

Supramolecular systems containing two or more chromophores have attracted the interest of the scientific community due to their potential for important applications ranging from light harvesting and storage to sensors and optoelectronic devices [1,2]. Such considerations have led to the preparation and characterization of a large number of dendritic constructs decorated with different chromophores selected for their specific photophysical properties. The study of the photophysical properties of these compounds is particularly interesting and highly dependent on the functional dye systems [3,4] Although many photoactive dendritic constructs have been documentated to date, only a few articles about 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene cores (borondipyrromethene, BODIPY)–pyrene systems have been published [5]. Pyrenes are also part of a very important family of fluorophores, which have been widely studied in macromolecular and materials science. The unique photophysical properties of pyrene and its ability to form an excimer led to a widespread use as a fluorescent label in various macromolecules [6–8]. Several photoactive units have been incorporated into pyrenes in order to tune their electronic and photophysical properties [9,10]. The BODIPY dyes are especially suitable for this purpose due to their bright high absorption coefficients, high fluorescence yields, long excited state lifetimes, and good solubility in organic solvents [11]. However, most BODIPY dyes have the fatal disadvantage because of their small Stokes' shift. A small Stokes' shift can cause self-quenching and errors in the measurement of excitation light and scattered light. Both of these can decrease the detection using advanced fluorescence techniques. Therefore, BODIPY dyes with larger Stokes shifts would be potentially useful for fluorescence bioassays [12,13].

The phosphazenes are an important class of inorganic heterocyclic ring systems in fundamental and applied science [14]. They are usually prepared by nucleophilic substitution reactions of alkoxides, aryloxides or amines on halocyclophosphazenes or higher polymers [15] and their physical and chemical properties can be tailored via appropriate substituted groups on phosphorus atoms. Additionally phosphazenes are relatively inert and stable to a variety of reaction conditions. There has been recently considerable interest in fluorescent compounds based on cyclic phosphazene cores [16,17] or cyclolinear polymers with the cyclotriphosphazene units [18,19] for development of electroluminescent devices.

Hexachlorocyclotriphosphazene might be an excellent scaffold to anchor two or more chromophores. To our best knowledge, there is no report of synthesis of pyrene and BODIPY being linked to cyclotriphosphazene together. Therefore, to combine BODIPY and pyrene chromophores we desired the use of cyclotriphosphazene as a platform. In this work, we describe the

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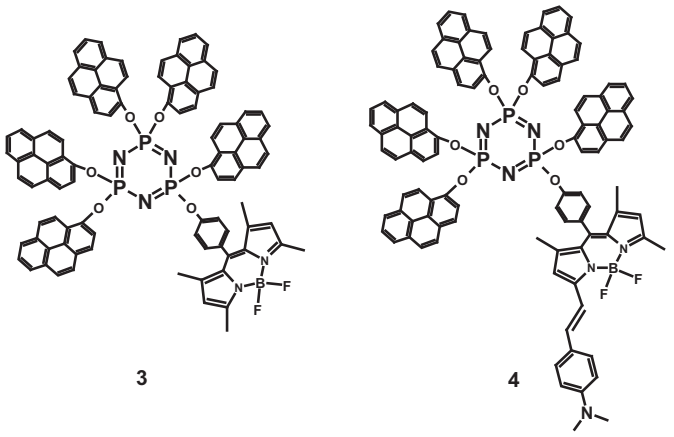


Fig. 1. Structure of pyrene–BODIPY substituted (**3** and **4**) cyclic phosphazenes.

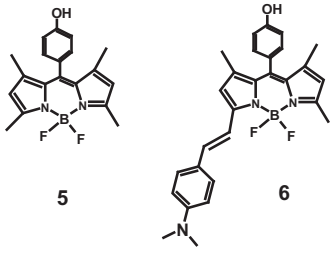


Fig. 2. The reference compounds **5** and **6**.

synthesis and characterization of compounds **3** and **4** (Fig. 1). Compounds **3** and **4** were studied by absorption and emission spectroscopy to investigate from pyrene to BODIPY energy transfer. Cyclophosphazene compounds exhibit excellent optical performance with a high energy transfer efficiency (up to 99%) and large Stokes' shift (up to 75 nm).

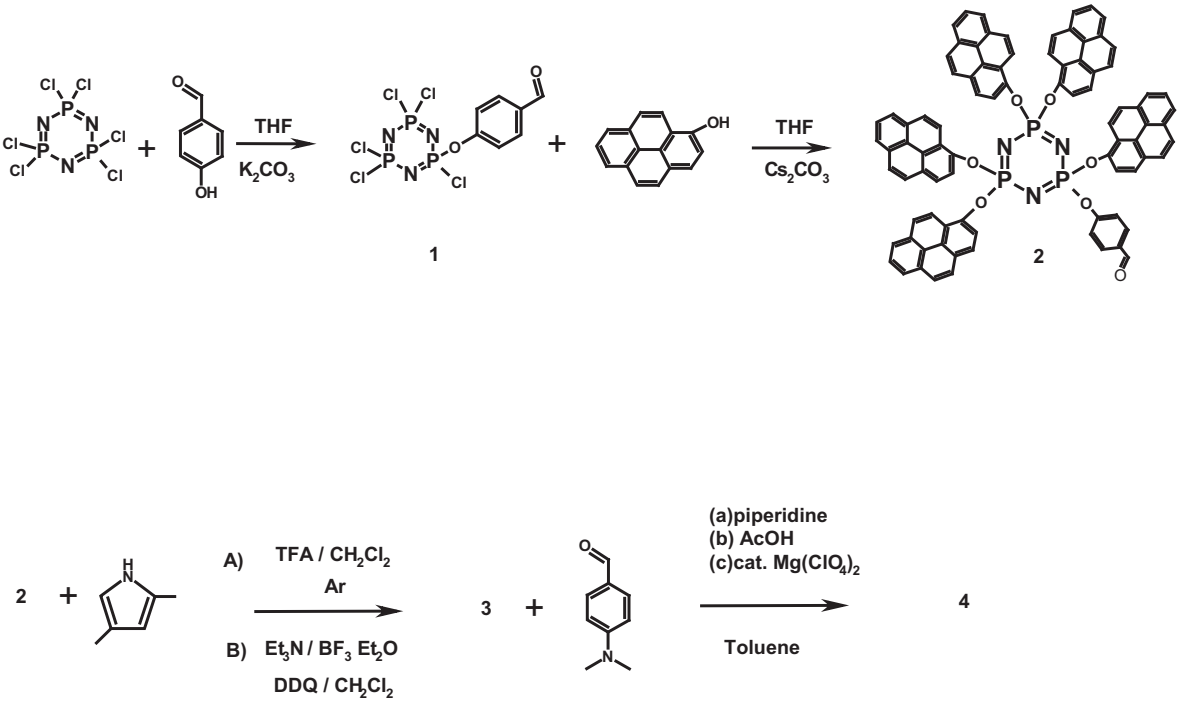
2. Experimental

2.1. Materials

Hexachlorocyclotriphosphazene (Otsuka Chemical Co. Ltd) was purified by fractional crystallization from *n*-hexane. $CDCl_3$ was employed for NMR spectroscopy and the following chemicals were obtained from Merck; $BF_3.OEt_2$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), magnesiumperchlorate [$Mg(ClO_4)_2$], 2,4-dimethyl pyrrole, 4-hydroxybenzaldehyde, 1-hydroxypyrene, K_2CO_3, Cs_2CO_3, TFA, triethylamine, silica gel 60, tetrahydrofuran, dichloromethane, 1,8,9-Anthracenetriol for MALDI matrix were obtained from Fluka. 4-Dimethylaminobenzaldehyde was obtained from Alfa-Aesar. All other reagents and solvents were reagent grade quality and obtained from commercial suppliers.

3. Equipment

Absorption spectra in the UV–visible region were recorded with a Shimadzu 2101 UV Pc spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter using 1 cm path length cuvettes at room temperature. 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. 1,8,9-Anthracenetriol MALDI matrix yielded the best MALDI-MS spectra. 1,8,9-anthracenetriol (20 mg/mL in tetrahydrofuran) matrix for compounds **3** and **4** were prepared. MALDI samples were prepared by mixing compounds **3** and **4** (2 mg/mL in tetrahydrofuran) with the matrix solution (1:10 v/v) in a 0.5 mL eppendorf micro tube. Finally 1 μL of this mixture was deposited on the sample plate, dried at room temperature and then analyzed. ^{13}P, ^{1}H



Scheme 1. Chemical structure and synthetic pathway of **1**–**4.**