Accepted Manuscript

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PII:	S0040-4039(18)30459-3
DOI:	https://doi.org/10.1016/j.tetlet.2018.04.016
Reference:	TETL 49879
To appear in:	Tetrahedron Letters
Received Date:	15 February 2018
Revised Date:	27 March 2018
Accepted Date:	10 April 2018



Please cite this article as: Kursunlu, A.N., Baslak, C., A BODIPY-bearing pillar[5]arene for mimicking photosynthesis: multi-fluorophoric light harvesting system, *Tetrahedron Letters* (2018), doi: https://doi.org/10.1016/j.tetlet.2018.04.016

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A BODIPY-bearing pillar[5]arene for mimicking photosynthesis: multi-fluorophoric light harvesting system

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ABSTRACT

Herein, we submitted to the original synthesis, characterization, energy transfer mechanism of the Bodipy-bearing pillar[5]arene Bodipy and its reactants by employing of infrared, ¹H, ¹¹B, ¹³C, ¹⁹F-NMRs, UV-vis, fluorescence spectroscopy, melting point apparatus, CHN elemental analysis and mass spectroscopy. Preliminary UV-vis, fluorescence and excitation measurements were carried out in CH₂Cl₂ and the results revealed an effective fluorescence resonance energy transfer (FRET) system based on the interaction of pillar[5]arene and Bodipy derivative. ε_{max} of target molecule reached to a maximum value and it was found as 955 000 M⁻¹cm⁻¹. This fluorescent macromolecule worked well for mimicking a light harvesting system with an energy transfer efficiency up to 92%.

Keywords: Pillar[5]arene, Bodipy, light harvesting, energy transfer, fluorescence

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Light harvesting-capable systems have attracted much interest owing to their widespread fields in technology and scientific application such as solar energy units, energy suppliers, nanodevices, memory storages, smart molecules and sensor materials¹⁻ ⁵. Fluorescence resonance energy transfer (FRET) is most famous among energy transfers carried out in light harvesting systems that the interaction of the donor and acceptor via a non-radiative transfer of energy from an excited donor fluorophore to a ground state acceptor ^{6,7}. The sunlight is vital for the living cells capable of photosynthesis, similarly, an efficient energy transfer is very important for the mimicking photosynthetic light-harvesting devices such as organic light-emitting diodes, fluorescent dye-sensitized solar cells and other optoelectronic supramolecules. Chemist and biochemists focused on light-harvesting devices obtained by the combination of donor and acceptor organic groups. Both fluorescent dyes and macromolecules contributed together towards the improving of the mimicking photosynthetic light-harvesting systems⁸⁻¹⁰. Calixarenes, crown ethers, pillararenes etc. as a macromolecule and Bodipy, phthalocyanine, porphyrin, dansyl chloride etc. as a fluorescent dye were used in these systems¹¹⁻¹⁸. Among macromolecules, pillararene compounds linked with methylene bridges at para-positions have multi-terminals and they can be possessed for various applications such as smart polymer, drug delivery, chemosensor, transmembrane¹⁹⁻²². However, pillararenes have been just reported in a few literatures for FRET-based lightharvesting systems^{23,24}. Ogoshi and co-workers synthesized a pillar[5]arene derivative including pyrene/perylene for an effective light-harvesting application that a FRET process carried out from pyrene to pervlene depending on the smart interlocked structure²⁵.

To make a more efficient process of the electron-transfer, various donor and acceptor linked dyads were developed. Among most dyes, Bodipy's have been extensively used as antenna molecule in artificial photosynthetic systems due to their excellent properties such as high molar absorption coefficient, high fluorescence yield, long lifetimes good photostability²⁶⁻²⁸.

Herein, we summarize a multifluorophoric combination for artificial photosynthesis device. For this aim, pillar[5]arene bearing ten Bodipy units has been designed as a light harvesting antennae (Scheme 1). The spectroscopic measurement of compounds show that it can possibly provide a strategy for the enhancement of light harvesting ability of pillar[5]arene linked Bodipy moieties making them attractive for various applications. To the best of our knowledge, this paper is a pioneer study used both pillar[5]arene and Bodipy for the lightharvesting materials.

Decameric Bodipy-bearing pillar[5]arene (8) (see Scheme 1) was prepared by a Schiff base condensation between AA/BB-type Bodipy (with amino terminal) and pillar[5]arene containing ten aldehyde fragments.

FRET property of **8** was investigated by the spectroscopic techniques as UV–Vis and fluorescence and excitation for mimicking a photosynthetic light-harvesting system. In order to achieve the synthesis of **8**, it was prepared in the several synthetic steps. A boron-dipyrromethene (**5**) derivative containing benzylchloro moiety was firstly synthesized. This compound was converted to benzylazido (**6**) by sodium azide and then reduced to amino group (**7**) for Schiff base reaction. The main framework of **4** was obtained in several steps from a reaction of **3** and 4-hydroxybenzaldehyde in presence of potassium carbonate. The details of syntheses of all compounds can be found in the Suppl. Info. Target multifluorophoric compound (**8**) was obtained from a reaction between Bodipy (**7**) and pillar[5]arene in chloroform. To this aim, Bodipy was used in ten equivalent due to decameric terminals of pillar[5]arene. The chemical structures of the compounds were optionally illuminated by ¹H-NMR, ¹¹B-NMR, ¹³C-NMR, ¹⁹F-NMR, elemental analysis, melting point and MS.



Scheme 1 Chemical structures of reactants and target supramolecule

The ground-state absorption spectra of Compounds 3, 4, 5, 6, 7 and target compound (8) initially recorded in dichloromethane $(3x10^{-7} \text{ M})$ in order to examine the assemblies to the natural photosynthesis system (Fig.1). Fig. 1 shows that free-Bodipy derivatives 5, 6 and 7 exhibited to three main transition around 275, 390 and 530 nm. These transitions assign to

 $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $S_0 \rightarrow S_1$ band of classical Bodipy compounds, respectively. Their bandwidth at 530 nm and gradually broadened in order 6, 5 and 7. Thus, the molar absorption coefficients (ε_{max}) also significantly changed depending on behaviors of different auxochrome moieties involving the lone pair of electrons while no shift in the absorption maximum. ε_{max} values are calculated as 450 000 $M^{-1}cm^{-1}$, 224 000 $M^{-1}cm^{-1}$ and 151 000 $M^{-1}cm^{-1}$ for 6, 5 and 7, respectively. Otherwise, the pillar[5]arene derivatives (3 and 4) exhibited a more different bands. The most important difference between the absorption spectra of 3 and 4 is the broadening of absorption band around 275 nm ($\epsilon = 63\ 000\ M^{-1}\ cm^{-1}$, 416 300 $M^{-1}\ cm^{-1}$, respectively). This change can be explained by the binding of 4-hydroxybenzaldehyde moieties to the skeleton of pillar[5] arene and thus, the increasing number of π -electrons. The main absorption band of 8 broadened and slightly red-shifted due to intramolecular like other reactants interactions of pillar[5]arene skeleton with the bonded Bodipy subunits, when compared to those typically observed for a Bodipy derivative. $\boldsymbol{\epsilon}_{max}$ of $\boldsymbol{8}$ reached to a higher value and calculated as 955 000 M⁻¹cm⁻¹. In addition to, more specific mounds were observed at 280, 330 and 370 nm owing to multi-electronic transitions in macromolecule as unlike other reactants.

CCE



Fig. 1 Absorption spectra of compounds 3, 4, 5, 6, 7 and 8 recorded in CH₂Cl₂ at 25°C

The emission and excitation spectra recorded in same solvent (CH₂Cl₂) and concentration (3. 10^{-7} M) for reactants and target compound are depicted in Fig. 2 and Fig. 3. While the emission maximum of fluorescent compounds, **5**, **6**, **7** and **8**, almost centered around 540 nm, their fluorescence intensities are very different values. Moreover, the fluorescent enhancement in compound **8** can attributed due to the rotation restriction of Bodipy groups and linked other aromatic fragments. However, it was thought that Bodipy moities are more effective in this process owing to their excellent π -conjugation.



Fig. 2 a) Emission spectra of compounds 3, 4, 5, 6, 7 and 8 recorded in CH₂Cl₂ in 3. 10⁻⁷ M (25°C, λ_{exc} = 475 nm, slit: 3). b) Normalized UV-vis absorption spectra of 4, 7 and fluorescence emission spectra of 4, 7 and 8 (5°C, λ_{exc} = 475 nm, slit: 3).

Fig. 2b shows the normalized UV-vis absorption spectra of compounds 4, 7 and the fluorescence emission spectra of 4, 7 and 8. The titration experiments for the 4+7 compounds have now been studied and gave in FigS28. The maximum emission wavelength shifted slightly to red with the continuously extended π -system.

These results were further photographed under longwave light (365 nm) and daylight (Fig. 3). The solutions of compounds **3** and **4** are transparent, however, other solutions are bright green and sparkling yellow due to their excellent fluorescent character. Meanwhile, the

corresponding fluorescent color of fluorescent reactant, 7, converted from green to yellow following to the reaction with other reactants, 4, under longwave. All observations are consistent with the emission data and the outcome can be explained by an energy transfer mechanism.



Fig. 3 Corresponding color changes of compound solutions (3, 4, 5, 6, 7 and 8) under longwave (365 nm) and daylight

The FRET efficiency E can be defined as the fraction of the donor de-excited via energy transfer to the acceptor. In our system, the efficiency E was calculated according to the following equation:

$E=1-I/I_0$

where I and I_0 are the fluorescence intensities of the donor in the presence and absence of the acceptor, respectively²³. The I and I_0 values were measured as 72 and 1093, respectively and the efficiency were calculated to be 92% for **8**.

This energy transfer mechanism was also supported by the excitation spectra measured for the fluorescent compounds (5, 6, 7 and 8) (Fig. 4) at the fixed I_{em} in the 560 nm. Two

main band were observed in the excitation spectra and these curves are similar to the absorption spectrum of compounds. As observed, the excitation curve of reactant **7** broadened in target compound **8** and this difference was ascribed to the change in the increasing fluorescent moieties and intramolecular folded-interactions. As a result of these interaction, an efficient energy transfer carried out between chromophore groups and pillar[5]arene aromatic subunit. Moreover, the broadness can be explained by the J-aggregated formation enhanced among ten fluorophoric Bodipy cores¹⁵. So, the aggregation cause to a perturbation in the electronic structure of molecule by the alternation of the ground and excited state electronic structures.



Fig. 4 Excitation spectrum recorded for compounds 5, 6, 7 and 8 recorded in CH_2Cl_2 at 25°C (3.10⁻⁷ M, λ_{em} =570 nm, slit:3).

In conclusion, we have successfully synthesized an efficient FRET system by the combination of the pillar[5]arene and Bodipy moieties. To the best of our knowledge, this compound is one of few examples on pillar[5] arenes consisting of Bodipy with alkyl-amino terminal. We plan to prepare another pillararenes having higher wavelength with different Bodipy to increase the a more effective FRET system and to illuminate overall shuttling process of the ANUS pillararene macromolecules within Bodipy's.

Acknowledgements

The authors express their appreciation to Prof. J.-F. Nierengarten and Dr. I. Nierengarten for helpful discussions. Financial support for this work is provided by the Research Foundation of Selcuk University (BAP) and is gratefully acknowledged.

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Acceleration



Highlights

- Results revealed an effective energy transfer based on pillar[5]arene and Bodipy.
- ϵ_{max} of target molecule reached to a maximum value, calculated as 955 000 M⁻¹cm⁻¹.
- Macromolecule worked for a light harvesting system with energy transfer up to 92%. •