Journal of Photochemistry and Photobiology B: Biology 130 (2014) 199–204

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

journal homepage: www.elsevier.com/locate/jphotobiol

Construction of energy transfer pathways self-assembled from DNA-templated stacks of anthracene

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ARTICLE INFO

Article history:
Received 7 August 2013
Received in revised form 13 November 2013
Accepted 13 November 2013
Available online 26 November 2013

Keywords:
Acene
DNA
Energy transfer
Excimer
Nanostructures
Self-assembly

ABSTRACT

We describe optical properties of anthracene stacks formed from single-component self-assembly of thymidylic acid-appended anthracene 2,6-bis[5-(3′-thymidylic acid)pentyloxy] anthracene (TACT) and the binary self-assembly of TACT and complementary 20-meric oligoadenylic acid (TACT/dA_{20}) in an aqueous buffer. UV–Vis and emission spectra for the single-component self-assembly of TACT and the binary self-assembly of TACT/dA_{20} were very consistent with stacked acene moieties in both self-assemblies. Interestingly, time-resolved fluorescence spectra from anthracene stacks exhibited very different features of the single-component and binary self-assemblies. In the single-component self-assembly of TACT, a dynamic Stokes shift (DSS) and relatively short fluorescence lifetime (τ = 0.35 ns) observed at around 450 nm suggested that the anthracene moieties were flexible. Moreover, a broad emission at 530 nm suggested the formation of an excited dimer (excimer). In the binary self-assembly of TACT/dA_{20}, we detected a broad, red-shifted emission component at 534 nm with a lifetime (τ = 0.4 ns) shorter than that observed in the TACT single-component self-assembly. Combining these results with the emission spectrum of the binary self-assembly of TACT/5′-HEX dA_{20}, we concluded that the energy transfer pathway was constructed by columnar anthracene stacks formed from the DNA-templated self-assembly of TACT.

1. Introduction

Acene molecules, which comprise linearly fused benzene rings, are expected to become a new source of organic electronic materials [1]. For example, one-dimensional stacks of acene molecules provide efficient electronic transport channels because they are characterized by efficient overlap of π-orbitals along the stacking direction; hence they are promising materials for organic semiconductors [2,3]. One-dimensional fibers formed from stacked acene molecules have extensive light-harvesting properties [4,5]. In such assemblies, manipulation of the orientation of the acene molecules has been shown to greatly affect the electronic properties. However, the strong intermolecular interactions between acene molecules cause them to tend to aggregate. In addition, a herringbone morphology, in which the overlap of the π-orbitals is relatively small, is often observed in their crystals [6,7]. Therefore, assembling acene molecules in well-defined, one-dimensional architectures is a key technology to control and to develop organic nanodevices made of acene molecules [8,9].

Meanwhile, DNA has attracted the attention of many researchers as a template to accumulate molecules along its structure. For example, a DNA template that includes some chemically modified nucleobases can produce one-dimensional clusters of metal ions or dye molecules by the formation of double strands [10,11]. We have achieved the DNA-templated self-assembly of bola-shaped molecular building blocks that possess nucleotide moieties with complementary base pairs at both ends of a long oligomethylene chain [12,13]. More than several thousand molecular building blocks accumulate, and the complementary base pairs are aligned helically at both ends of the building block molecules in an arrangement similar to the DNA double helix. The DNA-templating method can also be extended to accumulate π-conjugated molecules that have excellent optical and electronic properties [14–20]. Interestingly, π-conjugated molecules are not characterized by a herringbone morphology but instead, guided by the template DNA, form columnar stacks. This method of assembly is therefore a promising strategy to control the orientation and distance between acene molecules so as to achieve an efficient overlap of π-orbitals. In such an aggregate, we can expect efficient energy transfer along the π-stacks by Förster's mechanism. Following up on these ideas, we used DNA as a template to construct a one-dimensional anthracene dye assembly with lengths ranging from several hundred nanometer to several micrometer, and succeeded in forming an anthracene J-aggregate [12]. In this work, to examine the optical properties of uniform aggregates in size, we have improved the procedure for the self-assembly, and report on the ability of the

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http://dx.doi.org/10.1016/j.jphotobiol.2013.11.013

DNA-templated self-assembly to efficiently transfer energy along the columnar anthracene stacks. The template DNA plays important roles not only by arranging the anthracene stacks but also by providing protection from non-radiative energy transfer caused by attack from the solvent molecules or molecular motions.

2. Experimental section

2.1. Materials

2,6-Bis[5-(3′-thymidylic acid) pentyloxy] anthracene (TACT, MW = 990) was prepared according to previously described procedures [12]. The 20-meric oligoadenylic acid (dA_{20}, MW = 6202) and oligoadenylic acid (5-HEX dA_{20}, HPLC purification grade) modified at the 5-end with hexachloro fluorescein (HEX) dye were purchased from Tsukuba Oligo Service Co. Ltd. (Ibaraki, Japan). Tris(hydroxymethyl) aminomethane and 35% hydrochloric acid were purchased from Merck (Darmstadt, Germany) and Kanto Chemical Co. Inc. (Tokyo, Japan), respectively.

2.2. Preparation of self-assemblies

We newly prepared single-component and binary self-assemblies by methods different from those described in the previous literature [12] to produce more homogeneous and stable self-assemblies. For the single-component self-assembly, TACT was dissolved in 1 × TE buffer solution (10 mM Tris–HCl, 1 mM ethylenediaminetetraacetic acid, pH 8.0) by heating at 90 °C and sonication for 1 h. The binary self-assembly of TACT and dA_{20} (hereafter abbreviated TACT/dA_{20}) was obtained by adding dA_{20} to the TACT aqueous solution just after heating at 90 °C. The concentration of TACT and dA_{20} were adjusted to 1×10^{-2} M and 1×10^{-3} M, respectively. The resultant solution of the self-assembly was slowly cooled from 80 °C to 20 °C (cooling rate = 0.1 °C/min), and kept at 4 °C for at least 1 month.

2.3. UV/Vis and fluorescence spectroscopy

UV/Vis spectra were measured in a quartz cell (path length: 0.01 cm) with a UV-1800 spectrometer (Shimazu, Kyoto, Japan). The fluorescence spectra were recorded on an RF-5300 (Shimadzu, Kyoto, Japan). For both measurements, the samples were equilibrated at room temperature (25 °C) for 30 min. before the measurements.

2.4. Time-resolved fluorescence measurements

The sample solutions were excited by a UV-pulsed beam from a Nd:YAG laser (EKSPLA 2143A; third harmonic, 355 nm; pulse duration, 30 ps; repetition rate, 10 Hz; beam power, 1.0 mJ/pulse, not focused on the sample). The time-resolved fluorescence spectra of the solutions were measured with a spectrometer (Hamamatsu Photonics C5094) equipped with a streak camera (Hamamatsu Photonics C4334). Signals from 512 pulses were accumulated for each measurement. All experiments were performed at room temperature (298 K) and repeated three times.

2.5. Gel filtration chromatography

Gel filtration chromatography was carried out with an LC-9204 (Japan Analytical Industry Co., Ltd., Japan) with a JAIGEL-GS310 column (21.5 mm ID × 500 mm L, exclusion limit MW = 40,000) and UV (Japan Analytical Industry Co., Ltd., Japan, UV-3740, detected at a wavelength of 250 nm) and RI (ERC INC., Reflactomax 520) detectors. Tris–HCl buffer solution containing self-assembly of TACT (1×10^{-2} M) (100 μl) was filtered through a Millex-LG filter (pore size 200 nm, MILLIPORE) before injection. The gel filtration column was equilibrated with 10 mM Tris–HCl buffer solution (pH 8.0) and run at 25 °C and flow rate of 5 mL/min. For the estimation of the molecular weight of the self-assembly, we used polyethylene glycol/polyethylene oxide as a standard (232 < Mp < 44,700, Sigma–Aldrich, Switzerland).

3. Results and discussion

3.1. Confirmation of assembly formation by gel filtration chromatography

To estimate the molecular weights of the self-assembly, we carried out gel filtration chromatography (GFC) by using 10 mM Tris–HCl buffer (pH 8) as the eluent. The sample of thymidylic acid-appended anthracene 2,6-bis[5-(3′-thymidylic acid)pentyloxy] anthracene (TACT) (Fig. 1a, MW = 990) in 10 mM Tris–HCl buffer (pH 8) just after sonication provided two clearly separated peaks with retention times (RT) of 14.9 and 17.3 min (not shown). These peaks corresponded to peak molecular weights (Mp) of 9700 and 2700, respectively, in polyethylene glycol/polyethylene oxide (PEG/PEO) equivalent. This result suggests that TACT molecules aggregate in an aqueous solution. Interestingly, one month after the preparation of the self-assembly, a new peak appeared in the

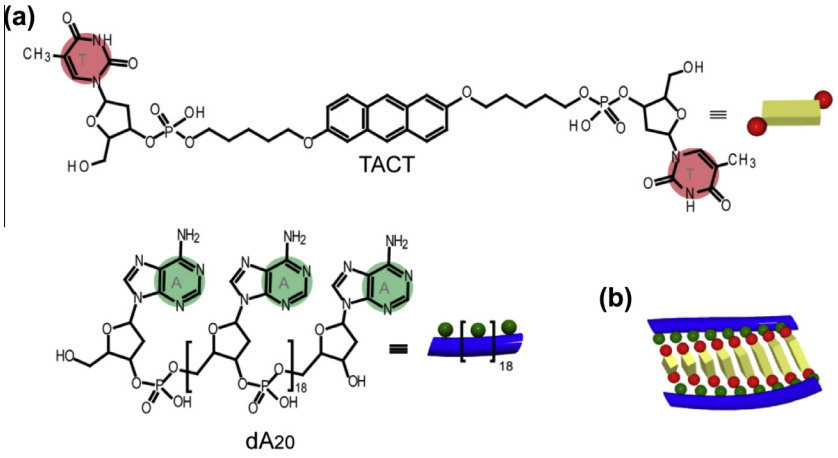

Fig. 1. (a) Molecular formulae for the thymidylic acid-appended anthracene TACT and 20-meric oligoadenylic acid dA_{20}, and (b) schematic illustration of the binary self-assembly formed from TACT/dA_{20}.