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Short communication

Synthesis and near-infrared absorption properties of linearly π-extended squarylium oligomers

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ABSTRACT

Linear squarylium oligomers bearing extended π-conjugation systems were newly synthesized, and their near-infrared (NIR) light-absorbing properties were investigated. Replacement of the iodo substituent in a 5-iodinated indolino-squarylium dye to the 2-hydroxy-3,4-dioxocyclobut-1-en-1-yl functional group *via* the Pd-catalyzed cross-coupling with a tributylstannylsquarate followed by condensation with a quaternary indolium salt afforded the semi-squarylium-attached squarylium derivative, *i.e.*, the squarylium dimer. The introduction of the semi-squarylium unit gave rise to a significant bathochromic shift towards the NIR region ($\lambda_{abs} = 763$ nm in $CHCl_3$ at 298 K). Starting from a 5,5′-diiodinated indolino-squarylium, the iterative extension of semi-squarylium units successfully yielded the linearly π-extended trimer and pentamer, that showed absorption maxima at 862 and 940 nm in $CHCl_3$ at 298 K, respectively. Especially, the pentamer exhibited a considerably low optical band gap of 1.1 eV.

1. Introduction

Squaryliums, often called squaraines, are well-known functional dyes because their unique optical properties such as intense light absorption and moderately efficient fluorescence emission in visible-to-NIR regions are useful for various applications; chemosensors and chemodosimeters for various chemicals [1–7], noncovalent fluorescent probes for bioanalyses [8–12], organic light-emitting diodes [13,14], supramolecular architectures [15–18], and so on. In the last decade, squaryliums have also received increasing attention as photosensitizers in dye-sensitized solar cells [19–23] because their excellent electron donating properties along with large light absorptivity are suitable for the sensitization of a TiO_2 nanocrystalline electrode *via* the photoinduced electron transfer mechanism [24].

Another valuable property of squaryliums is the photoconductivity in the solid states [25]. Various types of symmetrical and unsymmetrical squaryliums have been prepared by Law and coworkers [26–29], and their photoconductive properties were enthusiastically investigated towards application as photoreceptors in xerographic devices [30–32]. Such a unique optoelectronic property has also made them applicable to thin-film organic photovoltaic devices. Indeed, p-n heterojunction solar cells [33,34] as well as bulk-heterojunction solar cells [35–37] have been developed using squarylium-based organic semiconductors. The semiconductive behaviour of squaryliums is believed to be based on well-organized stacking of the intramolecular donor–acceptor–donor structure consisting of a cyclobutene core with aromatic/heterocyclic components at both ends. Varying the aromatic/heterocyclic components allows us to tune the optical and electronic properties of squaryliums.

Nowadays, squarylium-derived molecules bearing low optical band gaps receive considerable attention because they are expected to work well in the field of organic photovoltaics to harvest sunlight in the NIR regions. Although several types of squarylium-based low optical band gap polymers have so far been reported [38–40], further investigation on new synthetic strategies is eagerly required to obtain various types of squarylium-based π-extended chromophores [41,42]. We have so far reported the syntheses of various types of NIR-absorbing squaryliums and related chromophores, as shown in Fig. 1a; unsymmetrical squaryliums [43], methine-bridged bis-squaryliums [44–46], and bis-squarylium dyes with π-spacers [47,48]. These synthetic protocols have opened the door to novel squarylium-based π-extended chromophores with low optical band gaps. In the present study, we show a new approach to construct squarylium-based π-conjugation systems,

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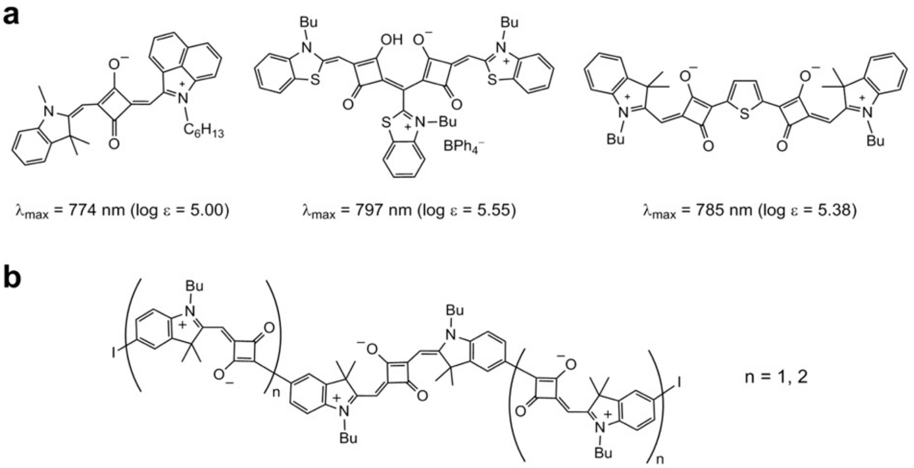


Fig. 1. Structures of π-extended squarylium derivatives; (a) unsymmetrical squarylium and symmetrically π-extended bis-squaryliums, and (b) linearly π-extended bis-squaryliums targeted in the present study.

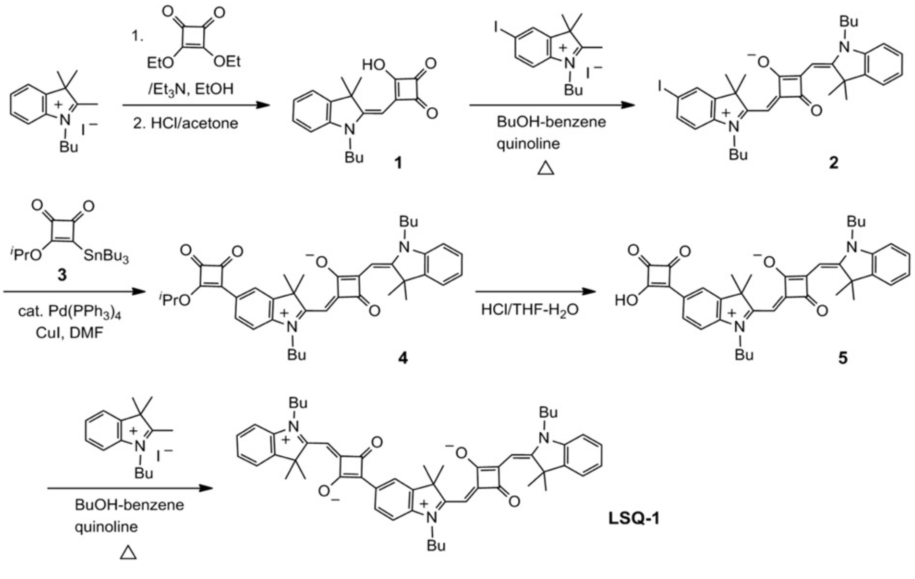
that is, the synthesis of novel linearly π-extended squarylium oligomers (Fig. 1b).

2. Results and discussion

2.1. Synthesis and light-absorbing properties of lineary π-extended squarylium dimers

First, we attempted to develop the linear dimeric squarylium **LSQ-1**, bearing two cyclobutene cores and three dimethylindoline components (Scheme 1), because this is the minimum extension of the squarylium array in the present system. The key reaction is the introduction of a squaric acid moiety on the iodinated site of the indole ring in the squarylium precursor **2**. We obtained **2** by the stepwise unsymmetrical squarylium synthesis employing a semi-squarylium precursor **1** [43,49]. Then, according to the Liebeskind's method [50], **2** was successfully reacted with the tributylstannylsquarate **3** under Pd-catalyzed conditions to afford the squarate-attached squarylium **4** in 65% yield, which was hydrolyzed to the corresponding squaric acid derivative **5** under acidic conditions (67%). The subsequent condensation with a heterocyclic quaternary salt under typical conditions for squarylium synthesis was expected to afford **LSQ-1**. Indeed, the reaction of **5** with 1-butyl-2,3,3-trimethylindolium iodide under azeotropic conditions (1-butanol–benzene, reflux) in the presence of a small amount of quinoline afforded the desired linear dimer **LSQ-1** in 50% yield, the structure of which was characterized by ^{1}H NMR, IR, and HRMS spectra.

In Fig. 2 are shown the Vis-NIR absorption spectra of **2**, **4**, and **LSQ-1** in $CHCl_3$ at 298 K, and the detailed data are summarized in Table 1. The squarylium **2** exhibits intense absorption at 642 nm with a molar absorption coefficient (ε_{abs}) of 2.34×10^5 M^{-1} cm^{-1}. This spectral profile is similar to that of the unsubstituted symmetrical indolino-squarylium dye, except for a 12 nm bathochromic shift of the absorption maximum (λ_{abs}) [51]. Thus, the iodo substituent in **2** has little influence on the light absorption property of the indolino-squarylium dye. On the other hand, when a squarate moiety is introduced in place of the iodo group,



Scheme 1.