



Synthesis and peripheral substituent effects of bay-annulated indigo derivatives

Taniyuki Furuyama*, Daichi Tamura, Hajime Maeda, Masahito Segi

Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan



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ABSTRACT

In this study, indolo-naphthyridine-6,13-diones (**5a–d**) with four different peripheral substituents were prepared via bay-annulation reactions of indigo. The resulting compounds (**5a–d**) exhibited fluorescence in the red to near-IR region, while the parent indigo molecule showed no fluorescence. Although the peripheral substituents were oriented to the exterior of the π -conjugated system, the electronic structure affected the absorption and fluorescence spectra. Moreover, calculated molecular orbitals and absorption spectra successfully reproduced the experimental absorption spectra and cyclic voltammograms.

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There are numerous organic dyes found in nature and their bright colors have attracted a great deal of interest for a long time. However, the development of artificial dyes with bright colors has been a challenging topic in synthetic organic chemistry in the past century [1]. The bright visible color originates from a small HOMO-LUMO gap, which is derived from the delocalized π -electrons on the chromophore. Since delocalized π -electrons show unique optical/electronic properties, natural/artificial organic dyes are part of many organic materials, such as dye-sensitized solar cells (DSSCs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs), and chemical sensors [2].

Indigo is one of the most famous natural pigments and is derived from *Indigofera tinctoria* and *Indigofera suffruticosa* (representative). Its attractive blue color is widely used in the textile industry on a large worldwide scale [3]. The structure of the indigo dye is a dimeric 3-indolinone (Fig. 1), which is firmly fixed by strong hydrogen bonds and a C–C double bond at 2 position. The π -electrons on the indigo skeleton are highly delocalized and cause an intense visible-light absorption (~ 600 nm). Recently, several groups proposed novel artificial dyes based on the indigo skeleton that have improved solubility, synthetic procedure, and light absorption properties in the near-IR region [4–7]. For instance, bay-annulation of indigo yields novel structures (indolo-naphthyridine-6,13-diones, bay-annulated indigo, BAI) that could be employed as new electron-acceptor monomer units of D-A

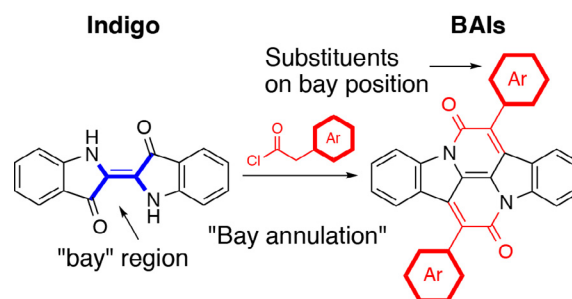


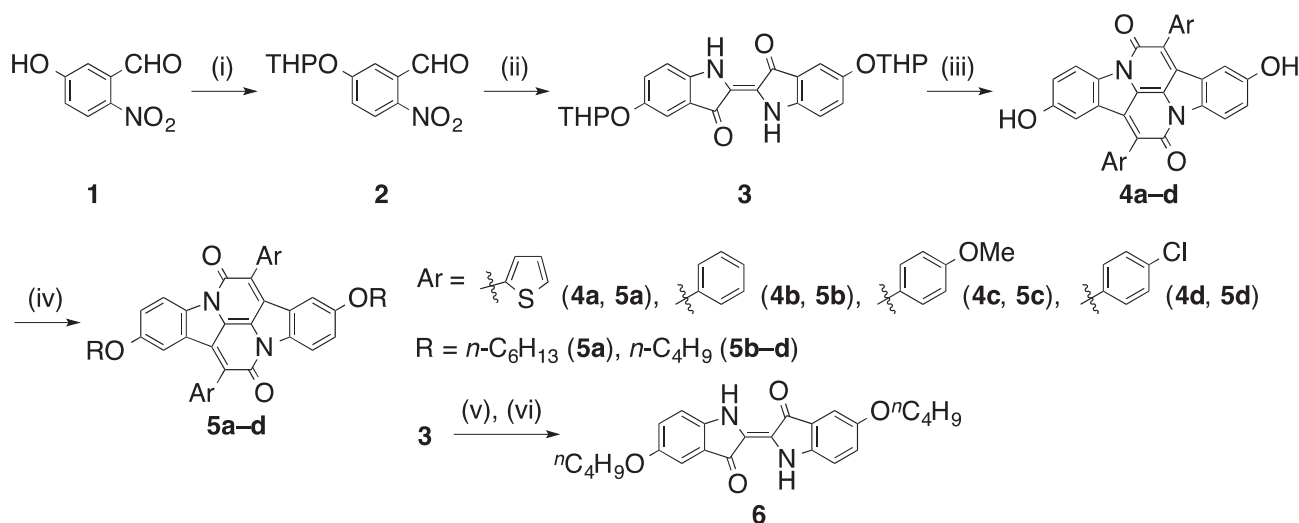
Fig. 1. Representative procedure of bay-annulation reaction.

(Donor-Acceptor) type polymers for near-IR light absorbing OPVs [8–10]. A key step of the BAI monomer unit formation is the direct double annulation of the indigo core by arylacetyl chloride derivatives. The reaction may introduce various aryl derivatives into the bay position of the annulated indigo. However, the synthesis of various BAI derivatives as discrete molecules has been limited [11].

In this communication, we focused on the peripheral substitution effect of BAIs. The wide π -deficient structure of the BAI core is a potent electron acceptor. Although the aryl groups at the bay position lie at the exterior of the π conjugation system, the peripheral substitution effect was expected to control the optical properties, as suggested by our previous work on aryl-substituted tetraazaporphyrin phosphorus(V) complexes [12]. Moreover, we performed a quantitative analysis combining electrochemical properties and theoretical calculations.

* Corresponding author.

E-mail address: tfuruyama@se.kanazawa-u.ac.jp (T. Furuyama).



Scheme 1. Synthesis of bay-annulated indigo derivatives **5a–d**. Reagents and conditions: (i) 3,4-Dihydro-2H-pyran (1.5 eq), PPTS (cat.), CH₂Cl₂, rt, 12 h, 84%; (ii) KOH aq (0.2 M), acetone, –10 °C, 15 min, then KOH aq (0.4 M), acetone, rt, 24 h, 58%; (iii) arylacetyl chloride derivatives (6 eq), xylene, reflux, 24 h, then NaOH (5 eq) in MeOH, rt, 12 h, up to 58%; (iv) ⁿC₄H₉I or ⁿC₆H₁₃I (20 eq), K₂CO₃ (30 eq), DMF, 60 °C, 24 h, up to 21%; (v) H₂SO₄ (5 eq), MeOH, rt, 12 h, 88%; (vi) ⁿC₄H₉I (3 eq), K₂CO₃ (9 eq), DMF, 60 °C, 12 h, 10%. THP = Tetrahydropyranyl.

The synthetic procedure of BAIs **5a–d** is shown in Scheme 1. Indigo derivative **3** was synthesized in a good yield according to a literature procedure [9]. Subsequent heating of a mixture of **3** and arylacetyl chloride derivatives in xylene under reflux yielded the BAI skeleton. The arylacetyl chloride generated by arylcarboxylic acid and thionyl chloride reacted with **3** in a one-pot procedure. Since the solubility of hydroxy-substituted BAIs **4a–d** was extremely low in various organic solvents, they were *O*-alkylated in order to improve their solubility. Similar to previous reports [9], low *O*-alkylation yields were observed, which may be due to the low solubility of **4a–d**. The resulting *O*-alkylated derivatives **5a–d** exhibited enough solubility to characterize their structures by ¹H NMR and HR-FAB-MS spectroscopies. Moreover, *O*-alkylated indigo **6** was synthesized according to the procedure used for the synthesis of **5a–d**. Unfortunately, single crystals of **5a–d** and **6** suitable for X-ray diffraction analysis could not be obtained.

Fig. 2 shows the absorption and emission spectra of **5a–d** and **6** in dichloromethane. The optical properties were summarized in Table S1, Supporting Information. Sharp and intense absorption bands in the visible region appeared in the spectra of the BAI derivatives. The positions of these peaks depended on the substituent group at the bay position. The peaks of thienyl derivative **5a** appeared redshifted in comparison to those of the other derivatives. In contrast, the peak positions of **5b–d** were close, indicating that the substituent effect at the phenyl group was relatively small. Moreover, a small solvent effect was observed in the absorption spectra of **5a** in various solvents (Fig. S1, Supporting Information). In contrast, the spectrum of **6** was an absorption envelope of typical indigos, with broader peaks than those of the BAI derivatives, implying that **6** had a smaller absorption coefficient than the other examined compounds. In addition, **5a–d** exhibited an emission in the visible-to-near-IR regions [13,14] in moderate fluorescence quantum yields ($\Phi_F = 0.04–0.13$ in dichloromethane), while indigo **6** showed no emission [15].

The first oxidation and reduction potentials of chemicals are essential to their application to electronic materials such as OPVs. Fig. 3 displays the cyclic voltammograms of **5a–d** and **6**. Since the exact oxidation potentials could not be estimated, their anodic

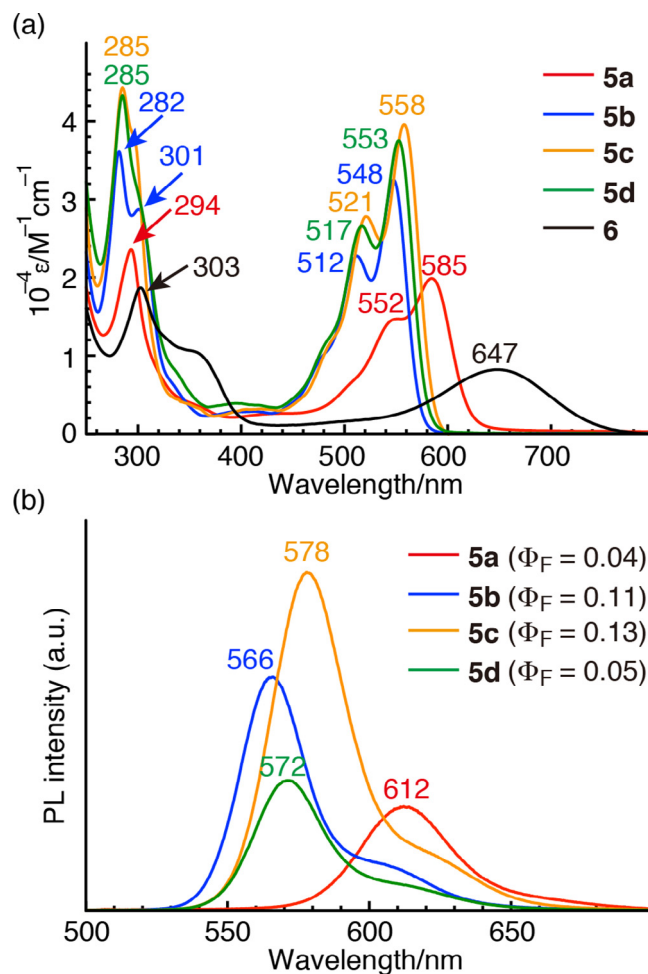


Fig. 2. (a) UV–vis absorption and (b) fluorescence spectra of **5a–d** and **6** in CH₂Cl₂. Excited wavelength (λ_{ex}) is 490 nm. No fluorescence peak of **6** was observed in this condition.

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