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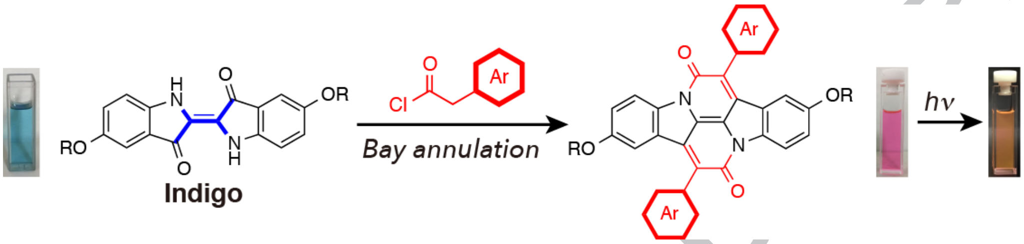

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Synthesis and peripheral substituent effects of bay-annulated indigo derivatives

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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.

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 (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]

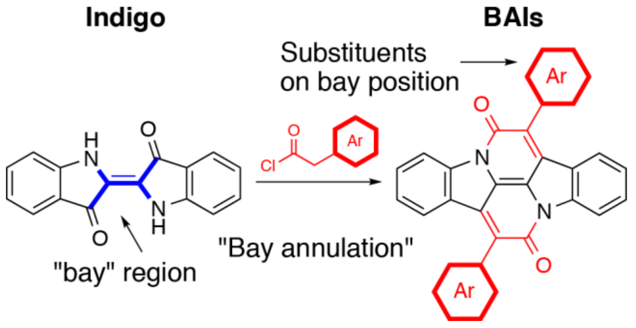

Figure 1. Representative procedure of bay-annulation reaction.

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.

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

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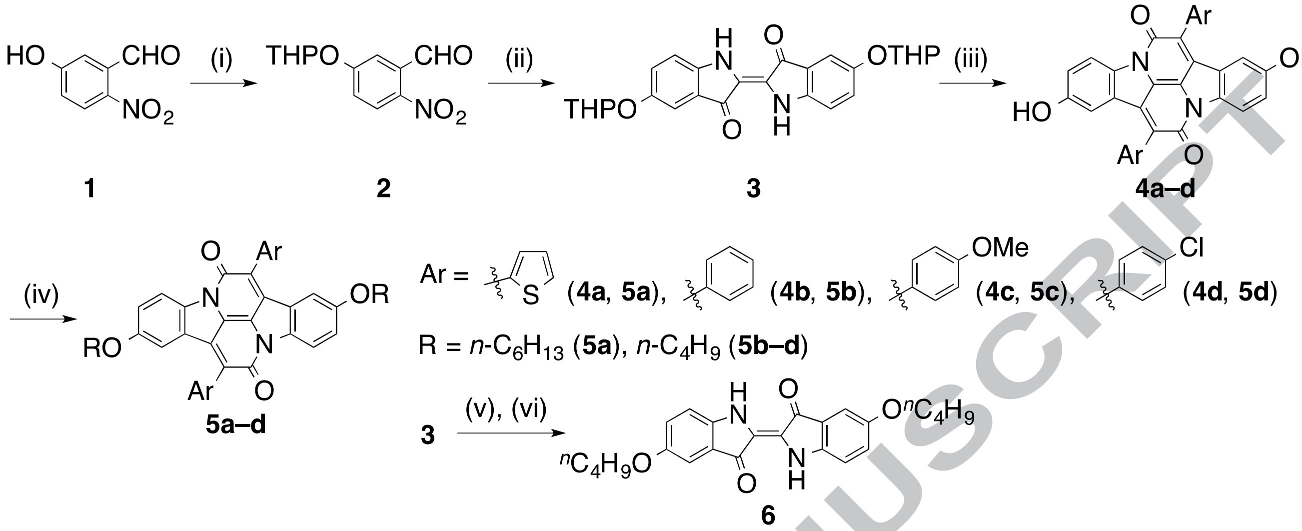
4a–d was extremely low in various organic solvents, they were *O*-alkylated in order to improve their solubility. Similar to previous reports,[9] low *O*-alkylation yields were observed, which may be due to the low solubility of **4a–d**. The resulting *O*-alkylated derivatives **5a–d** exhibited enough solubility to characterize their structures by ^{1}H 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.



Scheme 1. Synthesis of bay-annulated indigo derivatives **5a–d**. Reagents and conditions: (i) 3,4-Dihydro-2*H*-pyran (1.5 eq), PPTS (cat.), CH_2Cl_2/hexane, rt, 12 h, 84%; (ii) KOHaq (0.2 M), acetone, –10°C, 15 min, then KOHaq (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) ^{n}C$_4$H$_9$I or ^{n}C$_6$H$_{13}$I (20 eq), K_2CO_3 (30 eq), DMF, 60°C, 24 h, up to 21%; (v) H_2SO_4 (5 eq), MeOH, rt, 12 h, 88%; (vi) ^{n}C$_4$H$_9$I (3 eq), K_2CO_3 (9 eq), DMF, 60°C, 12 h, 10%. THP = Tetrahydropyranyl.

Fig. 2 shows the absorption and emission spectra of **5a–d** and **6** in dichloromethane. The optical properties were summarlized in Table S1, Supporting Infromation. 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 (Φ_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 peak potentials (E_{pa}) were used as indexes of the first oxidation potential values. The E_{pa} values of **5a–d** shifted anodically and the close first reduction potentials (E_{red1}) showed that the HOMOs of **5a–d** were stabilized after the bay-annulation. In fact, the substituent groups at the bay position affected both the oxidation and reduction potentials. The E_{pa} of **5a** shifted cathodically compared to that of the other BAIs (**5b–d**), indicating that the thienyl group destabilized the HOMO energy. The position of the absorption bands (548–647 nm) was also in accord with the order of the (E_{pa}–E_{red1}) values.

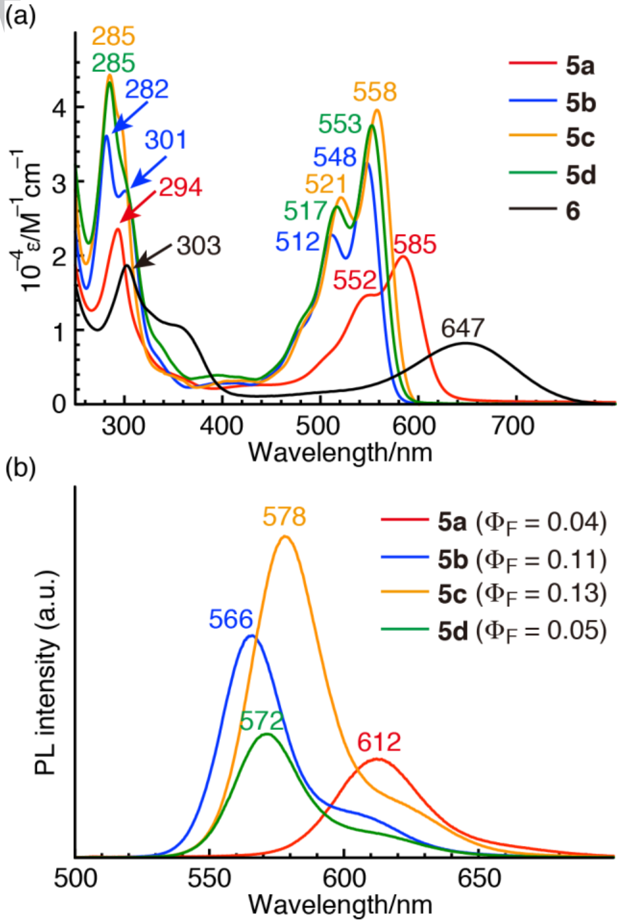


Figure 2. (a) UV-vis absorption and (b) fluoresence spectra of **5a–d** and **6** in CH_2Cl_2. Excited wavelength (λ_{ex}) is 490 nm. No fluorescence peak of **6** was observed in this condition.

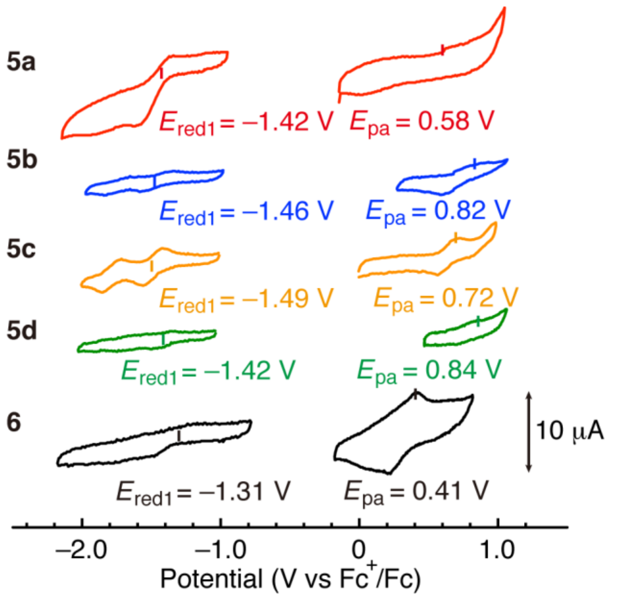


Figure 3. Cyclic voltammetry data for **5a–d** and **6**. Cyclic voltammograms were acquired from 0.5 mM solutions of analyte in 0.1 M ^{n}Bu$_4$NClO$_4$/*o*-DCB. Ferrocene was used as an internal standard and set to 0 V.

In order to enhance the interpretation of the electronic structures and substituent effects on the BAIs, MO calculations of the model structures **5a–d’** and **6’** were preformed. Model structures whose substituents on the *O*-alkyl groups were replaced by a methyl group were used because these groups affected the absorption spectra only marginally (Fig. S2, Supporting Information). Partial MOs related to the intense band in the visible region are shown in Fig. 4, the respective calculated transition energies, oscillator strengths (*f*), and configurations are summarized in Table 1, and calculated absorption spectra are shown in Fig. S3, Supporting Information. The calculated intense absorption band in the visible region (545–650 nm) could be assigned to the π–π* transition, which was composed of both HOMOs and LUMOs. The fact that the calculated HOMO–LUMO gaps of **5a–d’** were larger than that of **6’** indicated that the absorption spectra of **5a–d** were blueshifted. Interestingly, the HOMO of **6’** was delocalized over the entire indigo skeleton, while those of **5a–d’** were localized on the central part of the BAI skeleton. In contrast, the LUMOs of **5a–d’** were delocalized over the entire BAI skeleton. This difference was reflected in the large changes in the HOMO energies compared to that of **6’**, causing the resulting BAIs to have large HOMO–LUMO gaps. Although **5a–d’** have similar HOMO–LUMO gaps, the energy levels depend on the substituent groups at the bay position. The fact that both the HOMO and LUMO are partially localized on the substituent groups at this position suggested that the electronic structure at the bay position can change the absorption and redox properties. Moreover, the calculated absorption spectra, position of the intense absorption band, and energies of the frontier orbitals were reproduced and correlated well to the experimental spectra. The exemplary relationship between the experimental and calculated spectra can be useful in fashioning new functional dyes based on BAIs, designed to access appropriate properties in various fields.

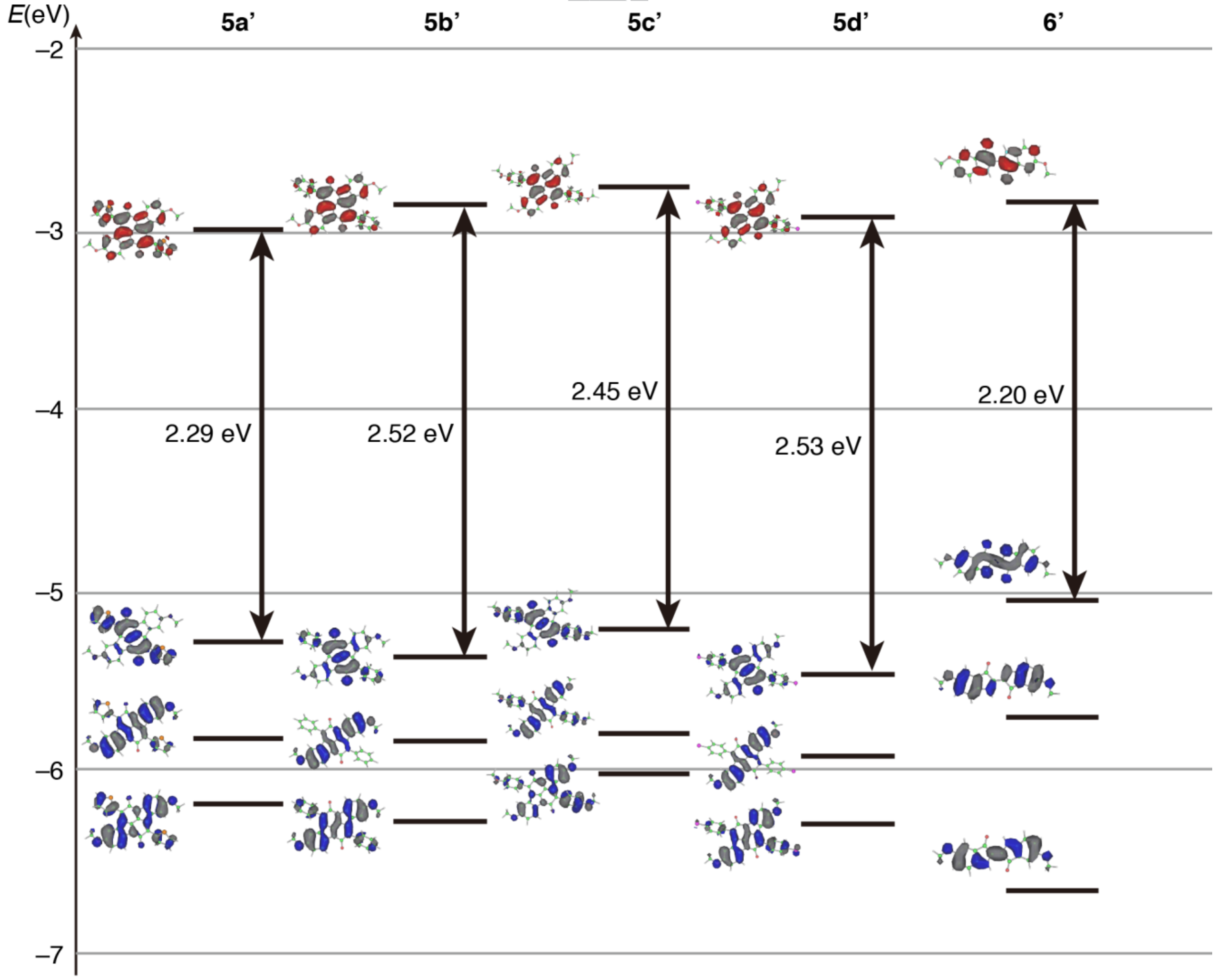


Figure 4. Energy levels of frontier MOs and their contour plots obtained from calculations. Blue and red plots indicate occupied and unoccupied MOs, respectively. Calculations were preformed at the B3LYP/6-31G* level, using the polarizable continuum model (PCM) that mimicked the solvation effect of CH_2Cl_2.

Table 1. Calculated excited wavelength (λ) and oscillator strengths (*f*) for components of selected transition energies.

Compound	λ_{calcd} (nm)	λ_{exp} (nm)[a]	*f*	Composition (%)
5a’	588.4	585	0.72	HOMO–>LUMO (100%)
5b’	541.2	548	0.57	HOMO–>LUMO (99%)
5c’	558.8	558	0.75	HOMO–>LUMO (99%)
5d’	544.8	553	0.62	HOMO–>LUMO (99%)
6’	649.6	647	0.27	HOMO–>LUMO (100%)

[a] The data were taken from Fig. 2.

In summary, the first systematic synthesis of indigo-based BAIs was shown herein. Various substituent groups such as electron-donating and withdrawing groups, and heterocycles were introduced into the bay position via a bay-annulation reaction. Although the π–skeletons of the BAIs were larger than that of the indigo dye, blueshifted absorption spectra were obtained. BAIs have an emission, while the indigo has no fluorescence. Additionally, it was found that the position of the absorption peaks and redox potentials depended on the substituent groups, with them being oriented to the exterior of the π-conjugated system. Moreover, the calculated absorption spectra and energies of the frontier orbitals successfully reproduced the experimental properties. All in all, it was concluded that the optical and electronic properties of a series of BAIs can be changed via a simple synthetic procedure, which could lead to the development of new methods to designing fine-tuned optic materials in the visible to near-IR regions. Further work is currently underway to expand the scope of the substituent groups and prepare BAI-based stimuli-responsive materials.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.XXXX.XX.XXX.

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Highlights:

Bay-annulated indigos (BAIs) with four different peripheral substituents have been synthesized.
These materials exhibited fluorescence in the red to near-IR region.
The calculated absorption spectra and energies of the frontier orbitals reproduced the experimental properties.