

Highly Electron-Donating 3,3'-Diaryl-1,1'-bi(isobenzofuran)s Synthesized by Photochemical Exocyclic [2 + 2 + 2] Cycloaddition

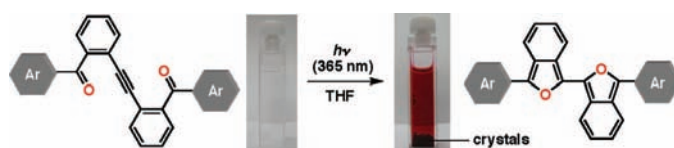
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ABSTRACT



Facile photochemical exocyclic [2 + 2 + 2] cycloaddition produced a series of electron-donating 1,1'-bi(isobenzofuran)s having various aryl groups at the 3,3' positions. The 1,1'-bi(isobenzofuran) skeleton with a highly coplanar structure is a useful building unit to construct the narrow bandgap π -conjugated systems with low oxidation potentials.

Isobenzoheteroles (benzo[*c*]heteroles), such as isobenzothiophene, -pyrrole, and -furan, are 10π electron systems with a quinoid nature, which makes them attractive as a unique building unit for oligomeric and polymeric π -conjugated compounds.¹ For instance, poly(isobenzothiophene)² is the most representative example of narrow bandgap polymers, which have been the subject of extensive research in the area of conducting polymers for the past two decades.³ The chemistry of isobenzofuran, however, is still in its infancy in view of a building unit for π systems, mainly due to the difficult synthesis of the π -extended derivatives as well as their instability.⁴ Whereas isobenzofurans are long

recognized as useful dienes in the Diels–Alder reaction⁵ and can provide access to a variety of acenes,⁶ no example of π -conjugated molecule consisting of more than two isobenzofuran units has been synthesized.⁷ We now disclose the synthesis of a series of 1,1'-bi(isobenzofuran)-containing π -conjugated systems based on a simple photochemical reaction. These compounds have highly coplanar structures with excellent π - π stacking in the crystals and exhibit unique electronic properties with low oxidation potentials and

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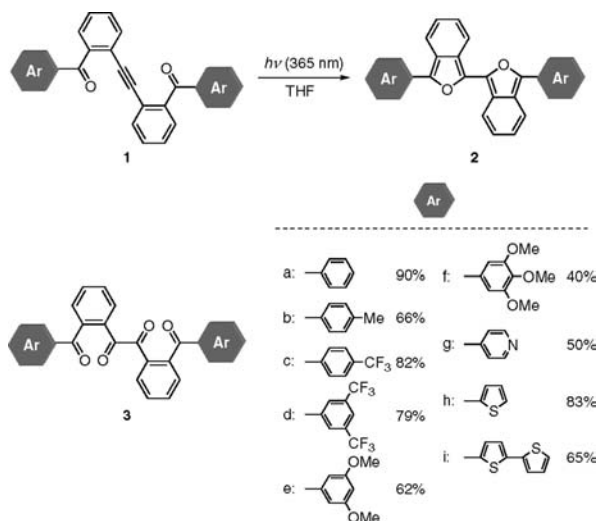
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(7) Calculations of oligo(isobenzofuran)s, see refs 2e and 2f.

narrow bandgaps. Their facile and general synthesis, structures, and fundamental properties are presented.

A series of π -extended 1,1'-bi(isobenzofuran)s **2** having various aryl groups at the 3,3' positions were synthesized in one pot from bis[*o*-(arylcarbonyl)phenyl]acetylenes **1**, as shown in Scheme 1. The precursors **1a–i** were synthesized

Scheme 1. Synthesis of **2** by Photochemical Exocyclic [2 + 2 + 2] Cycloaddition



via the dilithiation of bis(*o*-bromophenyl)acetylene followed by the reaction with aryl aldehydes and then oxidation with MnO_2 . Upon the irradiation of light (365 nm) on the dilute THF solutions for 4 h, the dicarbonylalkynes **1a–i** undergo an exocyclic [2 + 2 + 2] cycloaddition to produce the doubly cyclized **2a–i** in moderate to good yields (40–90%).⁸

A similar reaction was reported in the literature⁹ and also used for the preparation of 3,3'-dimethyl-1,1'-bi(isobenzofuran),¹⁰ which, however, was unstable and only isolated by trapping with an electron-deficient alkyne. Our successful isolation of the 3,3'-diaryl derivatives **2** in this form is mainly due to their high crystallinity. The irradiation of light quickly turned the color of the reaction mixture from colorless to red with a reddish orange emission at room temperature. The cyclized products then spontaneously precipitated as bright deep red crystals within 1 h. Notably, the products **2a–i** were isolated in an analytically pure form simply by filtration without further purification. While the isolated compounds exhibit poor solubility in common organic solvents and some of them could not be characterized by NMR spectroscopy, their structures were verified by means of high-resolution mass spectrometry, elemental analysis, and/or X-ray crystal-

(8) The moderate yields for some derivatives were mainly due to the incomplete conversion of the reaction.

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lography (**2c**, **2f**, and **2i**).¹¹ Whereas compounds **2a–i** are readily oxidized in solution by atmospheric oxygen to generate the corresponding ring-opened tetraketones **3**,¹² they are quite stable in the solid state.¹³

Among these compounds, the crystal structure of bis-(bithienyl) derivative **2i** is shown in Figure 1. This compound

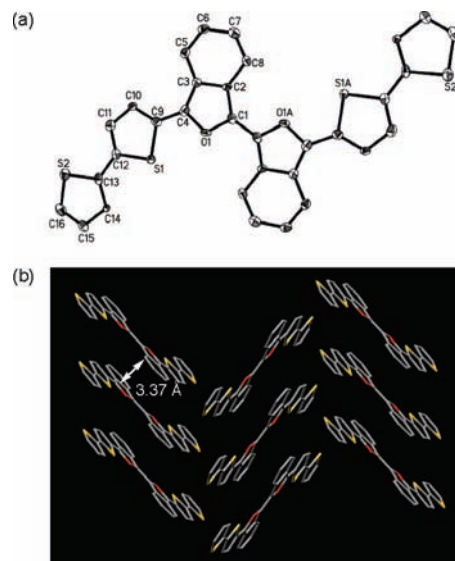


Figure 1. Crystal structures of **2i**: (a) ORTEP drawing with 50% probability for thermal ellipsoids and (b) herringbone packing structure (red, oxygen; yellow, sulfur).

has a center of symmetry between the two isobenzofuran units with a completely coplanar conformation. This compound also maintains a highly coplanar π -conjugated framework with dihedral angles of 4.3° between the isobenzofuran unit and the neighboring thiophene ring and of 2.0° between the two thiophene rings. This fact suggests that the π -conjugation is effectively extended over the entire molecule. Similar planar structures were also observed for **2c** and **2f**, indicating that this is the general structural feature for the 3,3'-diaryl-1,1'-bi(isobenzofuran)s. In addition, we noted that compound **2i** forms an interesting packing structure, as shown in Figure 1b. Each isobenzofuran moiety π -stacks with an adjacent molecule with the interfacial distance of ca. 3.37 Å. The resulting one-dimensional columns are further packed into a herringbone structure, where a half-part of molecules has close proximity with the molecules in the neighboring column. This structure might be of interest with regard to the carrier transport.

(11) Crystal data for **2c**, **2f**, and **2i**: see the Supporting Information. CCDC-683557 (**2c**), CCDC-683558 (**2f**), and CCDC-683559 (**2i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(12) For example, **2a** was oxidized by atmospheric oxygen to produce the corresponding tetraketone **3a** in 87% yield. See the Supporting Information.

(13) Compounds **2a–i** are also thermally stable. Upon heating the compounds in a sealed capillary in vacuum, no decomposition was observed until melting or sublimation. See the Supporting Information.

The absorption and fluorescence spectra of **2a–i** in CH₂Cl₂ are shown in Figure 2. Their data are summarized in Table

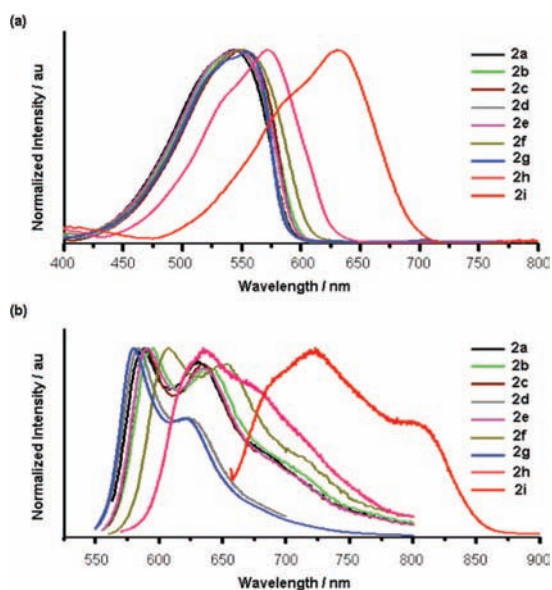


Figure 2. Photophysical properties of 3,3'-diaryl-1,1'-bi(isobenzofuran)s **2a–i**: (a) UV/vis absorption and (b) fluorescence spectra in CH₂Cl₂.

S1 (Supporting Information), together with those of 1,3-diphenylisobenzofuran (IBF) for comparison.^{14,15} 3,3'-Di-phenyl-1,1'-bi(isobenzofuran) **2a** has its absorption maximum at 543 nm and emission maximum at 587 nm, which are 128 and 101 nm red-shifted compared to IBF ($\lambda_{\text{abs}} = 415$ nm, $\lambda_{\text{em}} = 486$ nm), respectively. This comparison clearly shows the significant effect of the insertion of one isobenzofuran unit.

All of the substituted phenyl derivatives **2b–f** show their absorption maxima around 540–550 nm and reddish orange emission around 590–610 nm with moderate fluorescence quantum yields of 0.20–0.25. These data indicate that the electron-withdrawing (**2c** and **2d**) or electron-donating (**2e** and **2f**) substituents only subtly affect their photophysical properties. In contrast, the introduction of the electron-rich thiophene substituents significantly affects the photophysical properties. The absorption and emission of the thiophene derivative **2h** peak at 574 and 637 nm, respectively, which are red-shifted about 31 and 50 nm in comparison with **2a**. Moreover, the bis(bithienyl) derivative **2i** exhibits an absorption at 631 nm and broad emission in the near-infrared (NIR) region with the maximum at 723 nm, which are red-shifted about 88 and 136 nm when compared to **2a**, demonstrating its quite narrow bandgap electronic structure.

Another notable feature of the present π systems **2a–i** is their low oxidation potentials. The electrochemical properties

were studied by cyclic voltammetry, and their data are summarized in Table 1. The cyclic voltammogram of **2a**

Table 1. Electrochemical Properties of **2a–i** in CH₂Cl₂^a

compd	$E_{\text{ox}}^{\text{p1}}$ (V) ^b	$E_{\text{ox}}^{1/2}$ (V)	$E_{\text{ox}}^{\text{p2}}$ (V) ^b	$E_{\text{red}}^{\text{p1}}$ (V) ^b	$E_{\text{red}}^{\text{p2}}$ (V) ^b
2a	−0.11	−0.20	+0.67	−2.19	−2.41
2b	−0.18	−0.23	+0.56	−2.24	<i>c</i>
2c	+0.09		+0.66	−2.11	−2.25
2d	+0.31		<i>c</i>	−1.85	−2.03
2e	−0.09	−0.19	+0.72	−2.16	−2.36
2f	−0.15	−0.21	+0.40	−2.23	−2.42
2g	+0.20		+0.85	−1.86	−2.03
2h	−0.18	−0.24	+0.46	−2.15	−2.35
2i	−0.17	−0.18	+0.21	−1.98	−2.17
IBF	+0.41	+0.35	<i>c</i>	<i>c</i>	<i>c</i>

^a Potentials are given against ferrocene/ferrocenium ion couple (Fc/Fc⁺).
^b Peak potentials. ^c Not observed.

shows a reversible first oxidation at $E_{\text{ox}}^{1/2} = -0.20$ V and an irreversible second oxidation peak at $E_{\text{ox}}^{\text{p2}} = +0.67$ V (vs Fc/Fc⁺) in CH₂Cl₂, while it shows two irreversible reduction peaks at $E_{\text{red}}^{\text{p1}} = -2.17$ V and $E_{\text{red}}^{\text{p2}} = -2.39$ V (see the Supporting Information). Notably, the $E_{\text{ox}}^{1/2}$ of **2a** is negatively shifted by 0.55 V compared to **IBF** ($E_{\text{ox}}^{1/2} = +0.35$ V) and even more negative than that of ferrocene, demonstrating its highly electron-donating character as well as the significant effect of the bi(isobenzofuran) skeleton.

The substituent effect on the redox properties is investigated. While the introduction of the electron-withdrawing aryl groups (**2c** and **2d**) or electron-poor pyridyl group (**2g**) to the bi(isobenzofuran) skeleton results in the increase in the oxidation potential ($E_{\text{ox}}^{\text{p1}} = +0.09$ V, +0.31 V, and +0.20 V for **2c**, **2d**, and **2g**, respectively), the introduction of the electron-donating groups, including even thienyl or bithienyl groups, does not further lower the oxidation potential compared to **2a**. All of the compounds **2b**, **2e**, **2f**, **2h**, and **2i** have their first oxidation potentials around $E_{\text{ox}}^{1/2} = -0.18$ to -0.24 V, suggesting that their low oxidation potentials mainly reflect the character of the bi(isobenzofuran) skeleton. However, it is worth noting that all of these compounds show reversible first oxidation peaks. This is in contrast to the cases of compounds **2c**, **2d**, and **2g** having electron-withdrawing (hetero)aryl groups, which only show irreversible oxidation processes. The stability toward the one-electron oxidation is dependent on the aryl groups at the 3,3' positions.

To obtain a deeper insight into the electronic structures of these π systems, we carried out the density functional theory (DFT) calculations of **2a–i** at the B3LYP/6-31G(d) level. All of the compounds have the high-lying HOMO (−5.01 to −4.20 eV) and narrow HOMO–LUMO gaps (1.79 to 2.32 eV), as shown in Figure 3a. Both of their HOMOs and LUMOs are delocalized over the entire skeleton (Figure 3b). Notable features are summarized as follows. First, the electron-withdrawing substitutes have significant effects on the orbital energies. Compared with **2a**, compounds **2c**, **2d**,

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(15) We also measured the absorption spectra of **2a–i** in the solid state using the KBr pellet containing their crystals. Compared to those in solution, the absorption bands significantly broaden and new bands appear at the longer wavelengths presumably due to the formation of aggregates. See the Supporting Information.

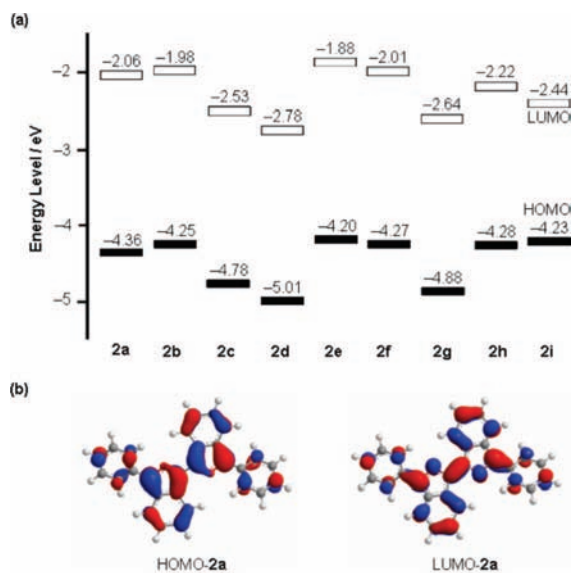


Figure 3. DFT calculations of **2a–i** (B3LYP/6-31G(d)): (a) a plot of the Kohn–Sham HOMO and LUMO energy levels and (b) pictorial presentation of the HOMO and LUMO of **2a**.

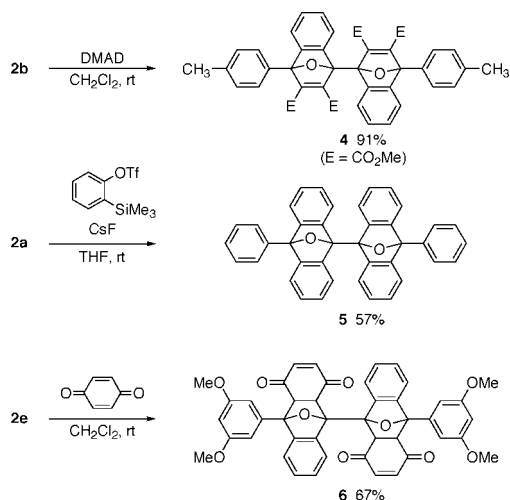
and **2g** having electron-withdrawing (hetero)aryl groups significantly decrease both the HOMO and LUMO levels. In contrast, second, compounds **2b**, **2e**, **2f**, **2h**, and **2i**, having electron-donating (hetero)aryl groups, only slightly increase the HOMO levels compared to **2a**. This is consistent with the observations in the cyclic voltammetry. Third, the introduction of the thienyl or bithienyl groups primarily affects not the HOMO levels but the LUMO levels. The LUMO levels of **2h** and **2i** are lower by 0.16 and 0.38 eV, respectively, compared to **2a**. This is the origin of the narrow bandgap electronic structures observed in the absorption spectra for **2h** and **2i**.

We also carried out the NICS(0) calculations to evaluate the aromaticity of the isobenzofuran skeleton. The calculated NICS(0) value of the six-membered ring of the isobenzofuran moiety in **2a** is -4.2 ppm, which is much higher than that of benzene (-9.7 ppm),¹⁶ suggesting that the six-membered ring indeed lacks the aromaticity and has a significant quinoid character. The increase in the quinoid character of the π -conjugated backbone with the detriment of the aromaticity has been the main strategy for synthesizing narrow bandgap π -conjugated systems.¹⁷

Notably, the produced bi(isobenzofuran)s are useful precursors for further transformations. Preliminary experiments revealed that the bi(isobenzofuran)s could smoothly undergo the Diels–Alder reactions with certain dienophiles and be

transformed into the corresponding adducts. When a reaction of **2b** with DMAD was conducted at room temperature in an argon atmosphere, **4** was obtained in 91% yield. Similar cycloadducts **5** and **6** were also obtained when **2a** or **2e**, respectively, were treated with in situ generated benzyne or *p*-benzoquinone (Scheme 2). We believe this reactivity paves

Scheme 2. Diels–Alder Reactions of 3,3'-Diaryl-1,1'-bi(isobenzofuran)s



the way to the synthesis of bi(acene)s, such as bi(naphthalene) and bi(anthrathene).

In summary, we have demonstrated that the 1,1'-bi(isobenzofuran) skeleton is a powerful building unit to construct narrow bandgap π systems with low oxidation potentials. It is particularly worth noting that a series of 3,3'-diaryl derivatives are synthesized by a very facile photochemical exocyclic [2 + 2 + 2] cycloaddition reaction. The simple filtration of the spontaneously produced crystals allows us to obtain these inherently unstable π -conjugated systems. Further studies on the applications of these materials to electronic devices, as well as the synthesis of substituted bi(acene)s, are currently in progress in our laboratory.

Acknowledgment. This work was partly supported by Grants-in-Aid (Nos. 19675001 and 17069011) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

Supporting Information Available: Experimental procedures, spectral data for all new compounds, photophysical and electrochemical data, theoretical calculation, and crystallographic data in CIF format and ORTEP drawings of **2c** and **2f**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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