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Synthesis and Properties of Butterfly-Shaped Expanded Naphthofuran Derivatives

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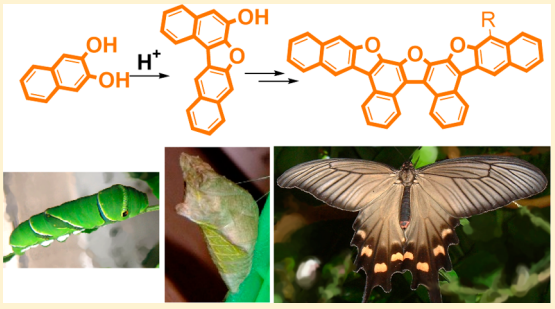
Supporting Information

ABSTRACT: The construction of dinaphtho[2,1-*b*;2′,3′-*d*]furan-6-ol was developed via a dehydration reaction involving two molecules of 2,3-dihydroxynaphthalene in the presence of a strong acid. Starting from the dinaphthofuran, a variety of butterfly shaped derivatives were synthesized. The optical properties of these compounds were investigated with special attention to the dihedral angle formed by adjacent dinaphthofuran rings and/or the sizes of the fused aromatic rings.



INTRODUCTION

Oxygen-containing polycyclic aromatic compounds, especially furan-containing polycyclic aromatics,[1] are expected to provide relatively high HOMO levels and offer utility in electronic devices, such as organic light-emitting diodes (OLEDs)[2] and organic field-effect transistors (OFETs).[3] Many furan ring-containing compounds, for example hexafuranylbenzenes[4] and oxahelicenes,[5] have been synthesized, and their properties have been examined. Recently, dinaphtho[2,1-*b*:1′,2′-*d*]furan[6a] and dinaphtho[1,2-*b*:2′,1′-*d*]furan[6b] systems were developed and used in, respectively, single-crystal OFETs and p-type semiconductors. This manuscript reports the synthesis and properties of a dinaphtho[2,1-*b*;2′,3′-*d*]furan system[7] and its butterfly shaped derivatives, the functions of which have not been reported previously.

RESULTS AND DISCUSSION

During an attempted acid-catalyzed coupling reaction between 2,3-dihydroxynaphthalene (**1**) and 2-naphthalenethiol, we noticed the generation of a blue fluorescent byproduct. Although the structure of the byproduct was difficult to ascertain using NMR, MS, and IR measurements, an X-ray analysis of the acetate unambiguously revealed the structure. To our surprise, the structure of the byproduct was a dinaphtho-[2,1-*b*;2′,3′-*d*]furan-6-ol (**2**) derived from the homocoupling of **1**, which was introduced through successive dehydration reactions from two hydroxy groups at the 2-positions, and the dehydration reaction between a hydroxy group at the 3-position of one 2,3-dihydroxynaphthalene (**1**) and a proton at the 1-position of another molecule of **1** (Figure 1). Although the skeleton of **2** was fascinating, dinaphtho[2,1-*b*;2′,3′-*d*]furan frameworks have been reported only in a few papers as the

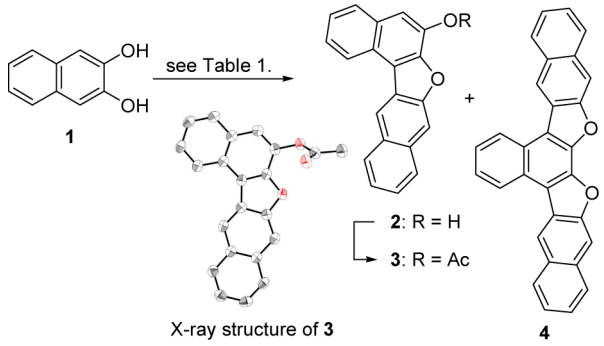


Figure 1. The unexpected formation of the naphthofuran derivatives **2** and **4** and the X-ray structure of **3**.

thermolysis products of naphthols.[7] Intuiting that **2** may potentially be useful as a π-conjugated material, we examined **2** and its related materials more closely.

Optimization of the Reaction Conditions for the Synthesis of Compound 2. First, we modified the dehydration reaction conditions (Table 1). Treatment of **1** in the presence of 5 equiv of *p*-toluenesulfonic acid under toluene reflux conditions for 12 days generated trace amounts of **2**, as detected by TLC (entry 1). Changing the solvent to *o*-xylene and heating at 130 °C for 3 days yielded the desired **2** in a yield of 12% (entry 2). As a protic acid, methanesulfonic acid was found to be suitable for this condensation, affording **2** in a 33% yield under 23 h of refluxing. Furthermore, the heretofore unknown trimeric fused ring system **4** was isolated in a 1% yield

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Table 1. Optimization of the Reaction Conditions

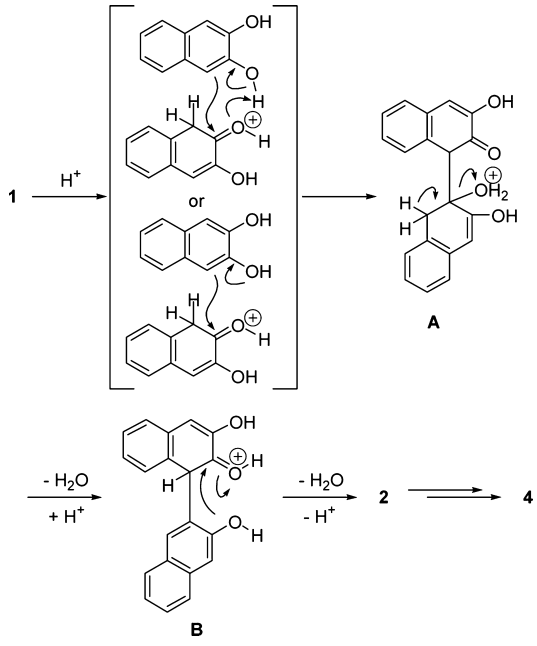
entry	acid (equiv)	solvent	temp (°C)	time	isolated yield (%) 2	4
1	*p*-TsOH·H_2O (5)	toluene	110	12 d	trace	–[a]
2	*p*-TsOH·H_2O (5)	*o*-xylene	130	3 d	12	–[a]
3	CH_3SO_3H (5)	*o*-xylene	130	23 h	33	1
4	CH_3SO_3H (25)	–[b]	130	1.5 h	17	–[a]

[a]Not detected. [b]No solvent was used.

as a yellow fluorescence emitter (entry 3). The use of methanesulfonic acid as the solvent, with no other solvents, led mainly to a tar-like material. After a troublesome purification procedure, the desired **2** was afforded in a 17% yield (entry 4). The above results suggested that entry 3 provided optimal reaction conditions. It is worth noting that compound **4** was synthesized via **2**, because **4** was obtained in a 13% yield by reacting the dimer **2** with the monomer **1** (5 equiv) under the reaction conditions.

Scheme 1 shows a plausible mechanism for the condensation reaction. Initially, protonation takes place on the 1-position of **1**

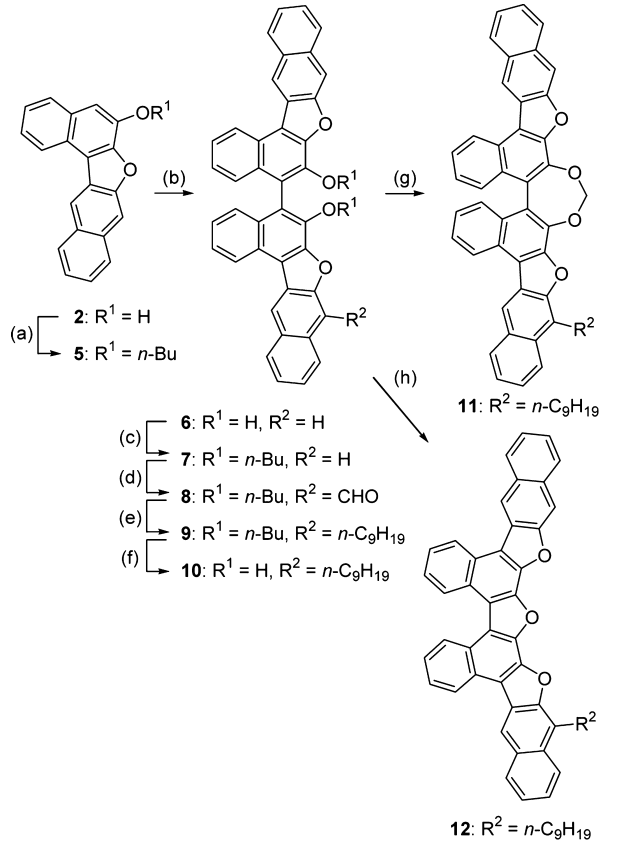
Scheme 1. Proposed Mechanism for the Generation of the Dimeric 2 and Trimeric 4



to generate an activated carbonyl compound. An ene-type reaction between the activated compound and another molecule of **1**, or a stepwise nucleophilic attack from the 1-position of **1** to the activated carbonyl carbon of another molecule of **1**, affords the intermediate **A**.[7a] The intermediate **B** is obtained through aromatization. The hydroxy oxygen on the lower naphthalene subsequently reacts with the activated carbonyl carbon to generate the corresponding dinaphthofuran **2**. Repeating the process on a dinaphthofuran **2** in combination with **1** provides the trimeric **4**.

Synthesis of Compounds 5–12. Next, we synthesized the more extended π-conjugated compounds **5**–**12** using **2** as a key synthon (Scheme 2). The solubility of the reactants in common organic solvents and the stability of the reactants in air were

Scheme 2. Syntheses of the Butterfly-Shaped Naphthofuran Derivatives[a]



[a]Conditions: (a) *n*-BuBr, K_2CO_3, 94%; (b) $Cu(NO_3)_2·3H_2O$, phenylethylamine, 98%; (c) *n*-BuBr, K_2CO_3, 99%; (d) *n*-BuLi, DMF, 50%; (e) $Ph_3P{=}CHC_7H_{15}$, then H_2, Pd/C, 84%; (f) BBr_3, 87%; (g) CH_2Br_2, K_2CO_3, 44%; (h) CH_3SO_3H, 32%.

enhanced by protecting the phenolic hydroxy group of **2** with a butyl group in the presence of K_2CO_3 and *n*-butyl bromide to give compound **5** in a 94% yield. On the other hand, compound **2** was treated with $Cu(NO_3)_2·3H_2O$ and phenylethylamine to induce the oxidative homocoupling to afford the butterfly-shaped **6** in a 98% yield.[8,9] Two butyl groups were introduced to the hydroxy groups of **6** to give **7** in a 99% yield. Compound **7** was monolithiated by *n*-BuLi and allowed to react with DMF to convert the formyl derivative **8** and recover **7** with respective yields of 50% and 39%. The formyl group of **8** was converted to a nonyl group through a Wittig reaction and a successive hydrogenation reaction to afford the monoalkylated **9** in an 84% yield in two steps. The butyl groups of **9** were then removed using BBr_3 to give the key compound **10** in an 87% yield.

The dihedral angle between the two dinaphthofuran systems was found to be related to the system's optical properties.[10] The dihedral angle of each system was fixed by ensuring that the dihedral axis was part of the seven-or five-membered ring system. Compound **11**, which was prepared with a 1,3-dioxepin system, was obtained through a double Williamson ether synthesis using dibromomethane in a 44% yield.[11] Compound **12**, prepared with a furan system, was afforded by an acid-catalyzed dehydration reaction between the central hydroxy groups of **10** in a 32% yield.[5c,e,12]

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Optical Properties of Compounds 5, 4, 7, 11, and 12. With the compounds in hand, the optical properties of the various derivatives were investigated. The functional differences between the structurally similar compounds, especially compound **4** and the reported indenofluorenes **13a–b** indicating the biradical characters, were intriguing (Figure 2).[13]

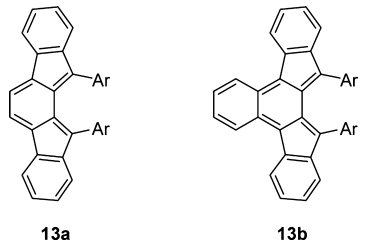

Figure 2. Indenofluorenes **13a–b**.[13]

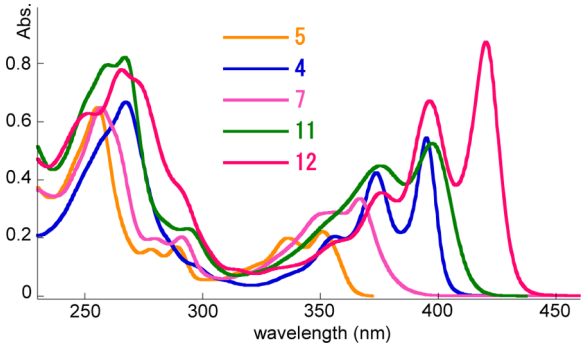

Figure 3. UV–vis spectra of compounds **5**, **4**, **7**, **11**, and **12**. Conditions: THF, 1.0×10^{-5} M, light path length = 1.0 cm, temp = 25 °C.

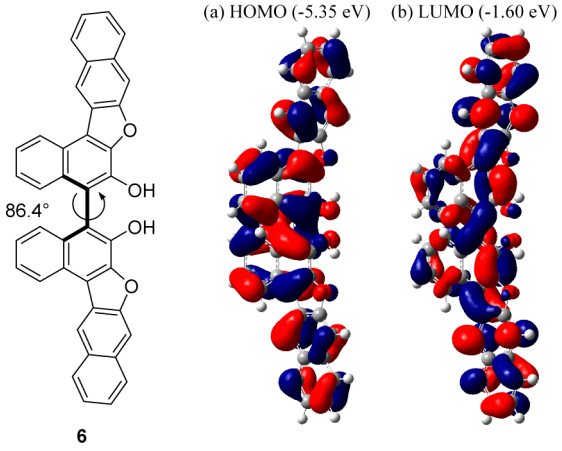

Figure 4. HOMO and LUMO of **6** by the DFT (B3LYP/6-31G(d)) calculations.

We first focused on the UV–vis spectra of these compounds (Figure 3). Based on previous studies of the 1,4-connected oligonaphthalene system,[14] the intensity of the UV–vis spectrum of compound **5** was initially expected to be half that of the dimeric **7**. Additionally, the spectra were not expected to shift significantly toward the red due to the orthogonality of the two dinaphthofuran rings in **7**. Surprisingly, the absorption intensity of **7** was high and the spectrum displayed a large red shift (about 20 nm). Density functional theory (DFT) calculations, at the B3LYP/6-31G(d) level of theory,[15] of the optimized structure of **6** (which lacks of the alkyl chain of **7**) indicated that (1) the dihedral angle between adjacent dinaphthofuran systems was 86.4° and (2) the HOMO and LUMO levels were distributed over the molecule, despite the nearly orthogonal orientations of the ring systems (Figure 4).[16]

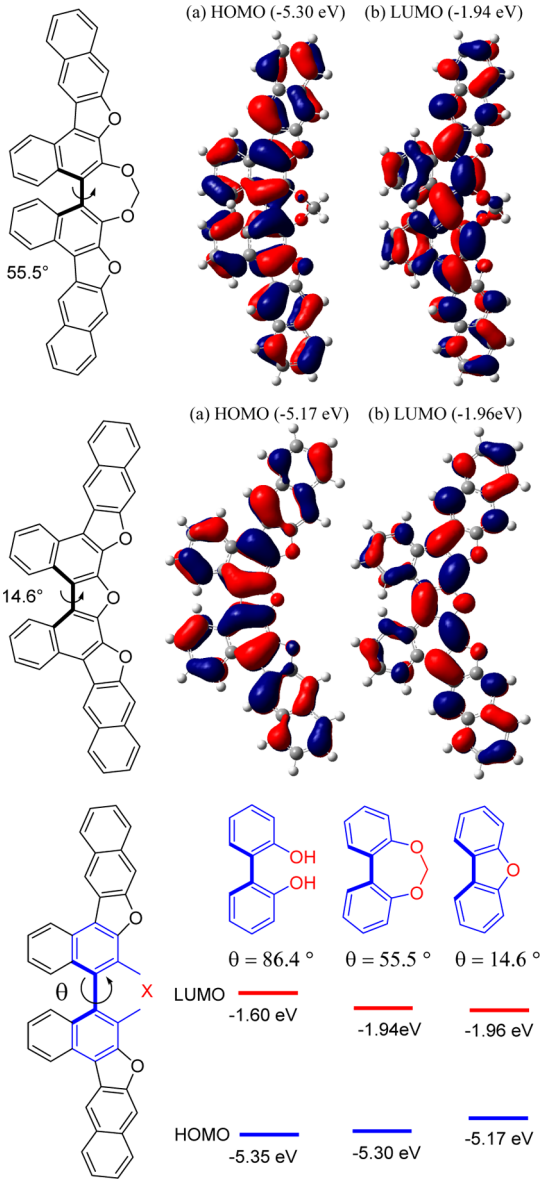

Figure 5. HOMO, LUMO and their energy levels of dealkylated **7** (= **6**), dealkylated **11**, and dealkylated **12** calculated at the B3LYP/6-31G(d) level.

The butterfly shaped compounds **7**, **11** and **12**, which displayed distinct dihedral angles around the central bonds, displayed λ_{max} values, molar absorbance coefficients (ε), and calculated dihedral angles (calculated from the dealkyl derivatives using DFT methods at the B3LYP/6-31G(d) level) as follows: **7** (λ_{max} = 366 nm, ε = 33 400, θ = 86.4°), **11** (λ_{max} = 397 nm, ε = 52 400, θ = 55.5°), and **12** (λ_{max} = 420 nm, ε = 87 300, θ = 14.6°). Thus, as the dihedral angle became more acute, the λ_{max} of the corresponding absorption bands, which were ascribed to HOMO–LUMO transitions, increased in intensity and were clearly red-shifted. The DFT calculations indicated that the HOMO–LUMO energy gaps were narrowed

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due to an increase in the corresponding HOMO levels and a decrease in the LUMO levels (Figure 5). The calculated values were consistent with the experimentally measured data.[16,17]

In addition, as the number of aromatic rings increased among the highly planar compounds, red and hyperchromic shifts were observed (dimeric **5** (λ_{max} = 351 nm, ε = 22 200), trimeric **4** (λ_{max} = 395 nm, ε = 54 400), and tetrameric **12** (λ_{max} = 420 nm, ε = 87 300)). These results also indicated that the π-conjugated systems were most effectively delocalized over large molecules.

We next examined the fluorescence properties of these compounds. The compounds synthesized displayed bright fluorescence in the solid state. As shown in Figure 6a,

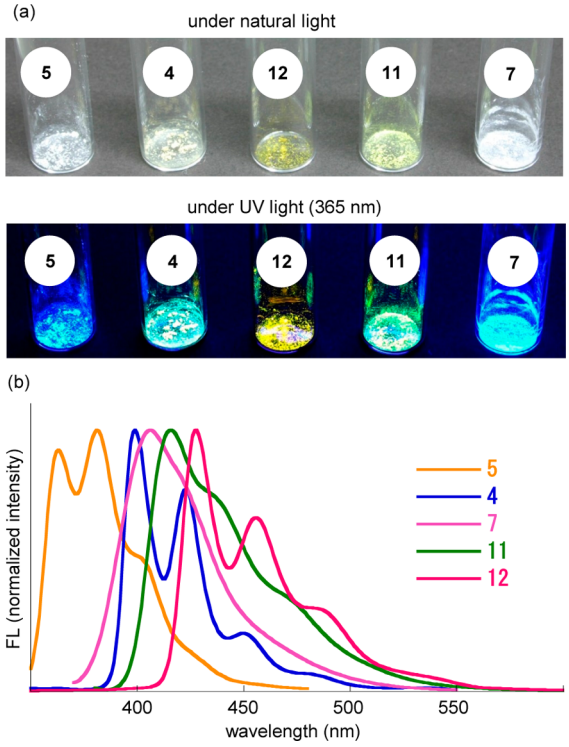

Figure 6. (a) Pictures of solid-state fluorescence under 365 nm light. (b) Normalized fluorescent spectra of compounds **5**, **4**, **7**, **11**, and **12**. Conditions: THF, 1.0×10^{-6} M, light path length = 1.0 cm, temp = 25 °C, **5** (λ_{ext} = 340 nm), **4**, **7**, and **11** (λ_{ext} = 360 nm), **12** (λ_{ext} = 370 nm).

compounds **5** and **7** fluoresced in the blue, compounds **4** and **11** emitted in the yellow-green, and compound **12** fluoresced yellow under UV (365 nm) excitation. In a THF solution state, these compounds displayed high quantum yields (0.63–0.79) and a small Stokes shift (4–39 nm) (Figure 6b and Table 2). As with the UV–vis absorption spectra, the fluorescence spectra became increasingly red-shifted as the planarity of the molecule and the number of aromatic rings increased. Compound **4**, which was the most rigid and planar molecule in the group, exhibited the highest quantum yield (0.79) and the smallest Stokes shift (4 nm).

CONCLUSIONS

We discovered a peculiar dimerization reaction involving 2,3-dihydroxynaphthalene to yield a dinaphthofuran framework. Although the reaction yield remains moderate, this reaction has utility in synthetic chemistry, especially in the field of heterocyclic chemistry, because the one-step procedure is simple. This method was used to synthesize a variety of butterfly-shaped naphthofurans derived from the above-mentioned dinaphthofuran key intermediate. The λ_{max} of the absorbance and emission spectra varied with the dihedral angle formed between adjacent aryl groups (**7**, **11**, and **12**) and/or with electron delocalization across the aromatic ring systems (**5**, **4**, and **12**). Future efforts will focus on the naphthofuran skeletons. A synthetic study of higher-order oligonaphthofurans and their functions is currently underway in our laboratories.

Table 2. Optical Data of Compounds 5, 4, 7, 11, and 12

					Stokes shift	
compd	$\lambda_{Abs.\ max}$ (nm)	ε ($\lambda_{Abs.\ max}$)	λ_{em} (nm)	Φ^a	(nm)	(cm^{-1})
5	351	22 200	381	0.63	30	2243
4	395	54 400	399	0.79	4	253
7	366	33 400	406	0.75	39	2691
11	397	52 400	416	0.70	19	1151
12	420	87 300	428	0.75	8	446

[a]Conditions: THF, 1.0×10^{-6} M, light path length = 1.0 cm, temp = 25 °C, **5** (λ_{ext} = 340 nm), **4**, **7**, **11** (λ_{ext} = 360 nm), **12** (λ_{ext} = 370 nm). The fluorescence quantum yields were determined using a solution of quinine sulfate in 2 N H_2SO_4 as a reference standard (Φ = 0.546).

EXPERIMENTAL SECTION

Synthesis of Compound 2. A solution of 2,3-dihydroxynaphthalene (**1**) (80.0 mg, 0.5 mmol) and methanesulfonic acid (162 μL, 2.5 mmol) in *o*-xylene (3.0 mL) was stirred at 130 °C under a N_2 atmosphere for 23 h. The reaction mixture was poured into an aqueous $NaHCO_3$ solution and extracted by chloroform. The organic layer was separated, washed with brine, and dried over sodium sulfate, and the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, chloroform) to afford compound **2** as a white powder (23.7 mg, 33%).

Mp 216–217 °C; IR (KBr) 3375, 3051, 1591, 1533, 1458, 1284, 1223, 1113, 858, 737, 471 cm^{-1}; ^{1}H NMR (270 MHz, DMSOd-6) δ7.39 (s, 1H), 7.42–7.58 (m, 4H), 7.88 (d, J = 8.1 Hz, 1H), 8.02–8.05 (m, 1H), 8.18–8.23 (m, 1H), 8.23 (s, 1H), 8.73 (d, J = 8.4 Hz, 1H), 9.11 (s, 1H), 10.74 (s, 1H); ^{13}C NMR (68 MHz, DMSOd-6) δ 107.2, 111.0, 117.6, 120.7, 123.1, 124.4, 124.5, 124.9, 125.2, 125.7, 127.3, 127.5, 128.4, 130.3, 131.4, 131.6, 143.0, 147.0, 153.7; HRMS (EI$^+$, double-focusing magnetic sector) calcd for $C_{20}H_{12}O_2$, 284.0837; found, 284.0834.

Synthesis of Compound 3. Acetyl chloride (5 μL, 0.07 mmol) was added to a solution of **2** (16.8 mg, 0.06 mmol) and triethylamine (27.6 μL, 0.198 mmol) in CH_2Cl_2 (2 mL) under ice-bath cooling. The solution was stirred for 1 h at the same temperature. The reaction mixture was poured into the mixed solvent of ethyl acetate and 1 M hydrochloric acid solution. The organic layer was separated and washed successively with water and brine. After the organic fraction was dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2, hexane/chloroform = 1/1) to afford to compound **3** as a pale yellow powder (16.3 mg, 83%).

Mp 196–197 °C; IR (KBr) 3051, 1766, 1529, 1371, 1194, 864, 746, 472 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.52 (s, 3H), 7.49–7.56 (m, 3H), 7.71 (s, 1H), 7.72 (dt, J = 7.8 Hz, 1.4 Hz, 1H), 7.92–7.98 (m, 2H), 8.00 (s, 1H), 8.06–8.10 (m, 1H), 8.67 (d, J = 8.4 Hz, 1H), 8.75 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.0, 107.5, 119.1, 120.4, 120.6, 123.2, 124.5, 125.0, 125.6, 125.7, 127.1, 127.3, 127.6, 128.4, 128.9, 130.3, 130.4, 132.0, 135.5, 148.1, 154.4, 168.6; HRMS (EI$^+$, double-focusing magnetic sector) calcd for $C_{22}H_{14}O_3$, 326.0943; found, 326.0944.

Synthesis of Compound 4. A solution of 2,3-dihydroxynaphthalene (**1**) (123 mg, 0.77 mmol), compound **2** (43.5 mg, 0.153 mmol), and methanesulfonic acid (50 μL, 0.77 mmol) in *o*-xylene (3.0 mL) was stirred at 130 °C under a N_2 atmosphere for 5 d. The

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reaction mixture was poured into water and extracted by chloroform. The organic layer was separated, washed with brine, and dried over sodium sulfate, and the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, chloroform) and preparative gel filtration chromatography (chloroform) to afford compound **4** as a yellow powder (8.0 mg, 13%).

Mp > 300 °C; IR (KBr) 3051, 2920, 2850, 1620, 1504, 1460, 1288, 1215, 854, 739, 472 cm $^{-1}$; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57−7.62 (m, 4H), 7.91 (dd, J = 6.6 Hz, 3.0 Hz, 2H), 8.08 (d, J = 7.8 Hz, 2H), 8.20 (d, J = 7.8 Hz, 2H), 8.22 (s, 2H), 8.99 (s, 2H), 9.02 (dd, J = 6.6 Hz, 3.3 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 108.0, 119.2, 120.8, 124.7, 124.9, 125.9, 126.05, 126.09, 126.6, 127.8, 128.6, 130.9, 132.3, 142.8, 155.2; HRMS (EI$^+$, double-focusing magnetic sector) calcd for $C_{30}H_{16}O_2$, 408.1150; found, 408.1148.

Synthesis of Compound 5. *n*-Butyl bromide (63 μL, 0.588 mmol) was added to a suspension of **2** (55.6 mg, 0.196 mmol) and K_2CO_3 (81.3 mg, 0.588 mmol) in DMF (2 mL). The suspension was stirred for 16.5 h at 50 °C. The reaction mixture was poured into the mixed solvent of ethyl acetate and 1 M hydrochloric acid solution. The organic layer was separated and washed successively with water and brine. After the organic fraction was dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2, chloroform) to afford compound **5** as a white powder (63.0 mg, 94%).

Mp 151−152 °C; IR (KBr) 3059, 2956, 2870, 1595, 1464, 1298, 852, 739, 472 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.06 (t, J = 7.3 Hz, 3H), 1.56−1.70 (m, 2H), 1.94−2.05 (m, 2H), 4.28 (t, J = 6.5 Hz, 2H), 7.24 (s, 1H), 7.47−7.54 (m, 3H), 7.61 (t, J = 7.0 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.96−7.99 (m, 1H), 8.06 (s, 1H), 8.06−8.09 (d, J = 7.0 Hz, 1H), 8.61 (d, J = 8.1 Hz, 1H), 8.73 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.0, 19.4, 31.2, 68.7, 107.6, 107.9, 118.2, 120.4, 123.1, 124.3, 124.4, 124.8, 124.9, 125.5, 125.9, 127.7, 127.8, 128.3, 130.4, 131.4, 131.9, 145.0, 147.5, 154.5; HRMS (EI$^+$, double-focusing magnetic sector) calcd for $C_{24}H_{20}O_2$, 340.1463; found, 340.1464.

Synthesis of Compound 6. To a mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (918 mg, 3.8 mmol) in methanol (10 mL), phenylethylamine (1.2 mL, 9.18 mmol) was added under a N_2 atmosphere with ice-bath cooling. After 1.5 h, a solution of **2** (435 mg, 1.53 mmol) in THF (40 mL) was added and the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was poured into the mixed solvent of 1 M hydrochloric acid solution and ethyl acetate. The organic layer was separated, washed successively with water and brine, and dried over sodium sulfate, and the solvent was evaporated to give a residue. The residue was rinsed with THF to afford compound **6** as a white powder (423 mg, 98%). Mp > 300 °C; IR (KBr) 3521, 3059, 1525, 1460, 1215, 1113, 962, 858, 742, 476 cm^{-1}; ^{1}H NMR (270 MHz, DMSOd-6) δ 7.22 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 8.4 Hz, 2H), 7.60−7.68 (m, 6H), 8.16−8.19 (m, 2H), 8.33−8.37 (m, 2H), 8.37 (s, 2H), 8.96 (d, J = 8.4 Hz, 2H), 9.32 (s, 2H), 10.06 (s, 2H); ^{13}C NMR (68 MHz, DMSOd-6) δ 106.9, 117.22, 117.24, 120.5, 123.3, 123.5, 124.28, 124.31, 124.7, 125.3, 125.46, 125.51, 127.3, 128.2, 130.3, 131.1, 131.5, 141.4, 147.4, 153.6; HRMS (FAB$^+$, double-focusing magnetic sector) calcd for $C_{40}H_{22}O_4$, 566.1518; found, 566.1519.

Synthesis of Compound 7. *n*-Butyl bromide (171 μL, 1.59 mmol) was added to a suspension of **6** (300 mg, 0.53 mmol) and K_2CO_3 (220 mg, 1.59 mmol) in DMF (4 mL). The suspension was stirred for 16.5 h at 50 °C. The reaction mixture was poured into the mixed solvent of chloroform and 1 M hydrochloric acid solution. The organic layer was separated and washed successively with water and brine. After the organic fraction was dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2, chloroform) to afford compound **7** as a white powder (355 mg, 99%).

Mp 239−240 °C; IR (KBr) 3055, 2956, 2870, 1522, 1456, 1323, 1117, 858, 742 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.51 (t, J = 7.3 Hz, 6H), 0.82−1.05 (m, 4H), 1.36−1.48 (m, 4H), 4.14−4.22 (m, 2H), 4.37−4.43 (m, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.56−7.59 (m, 4H), 7.69 (t, J = 7.2 Hz, 2H), 8.04−8.07 (m, 2H), 8.16 (s, 2H), 8.18−8.22 (m, 2H), 8.86 (d, J = 8.4 Hz, 2H), 8.96 (s, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 18.6, 32.1, 73.3, 107.5, 118.9, 120.5, 123.3, 124.5, 124.9, 125.4, 125.7, 125.8, 126.01, 126.05, 127.2, 127.7, 128.4, 130.6, 131.2, 143.0, 149.9, 154.6; HRMS (FAB$^+$, double-focusing magnetic sector) calcd for $C_{48}H_{38}O_4$, 678.2770; found, 678.2780.

Synthesis of Compound 8. To a solution of compound **7** (300 mg, 0.44 mmol) in dry THF (5 mL), *n*-BuLi (1.62 M, hexane solution, 326 μL, 0.53 mmol) was added dropwise and stirrred for 15 min at 0 °C under a N_2 atmosphare. DMF (68 μL, 0.88 mmol) was added with subsequent stirring for 8 h at 0 °C. The reaction mixture was poured into the mixed solvent of chloroform and 1 M hydrochloric acid solution. The organic layer was separated and washed with brine. After the organic fraction was dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was roughly purified by column chromatography (SiO_2, chloroform) and repurified by column chromatography (SiO_2, chloroform/*n*-hexane = 1/1) to afford to compound **8** as a yellow powder (155 mg, 50%).

Mp 150−151 °C; IR (KBr) 3057, 2956, 2870, 1684, 1522, 1456, 1363, 1217, 1117, 746 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.53−0.61 (m, 6H), 0.90−1.10 (m, 4H), 1.41−1.49 (m, 4H), 4.19−4.29 (m, 2H), 4.38−4.50 (m, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.44−7.60 (m, 5H), 7.65−7.74 (m, 3H), 7.98−8.02 (m, 1H), 8.08−8.15 (m, 2H), 8.10 (s, 1H), 8.72 (d, J = 8.1 Hz, 1H), 8.83 (d, J = 8.4 Hz, 1H), 8.88 (s, 1H), 9.02 (s, 1H), 9.47 (d, J = 8.4 Hz, 1H), 11.27 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 18.68, 18.74, 32.1, 73.3, 73.5, 107.5, 112.7, 117.8, 119.1, 120.5, 123.1, 123.4, 124.5, 124.8, 125.0, 125.3, 125.4, 125.5, 125.7, 125.82, 125.85, 125.9, 126.0, 126.2, 126.4, 126.9, 127.4, 127.6, 128.3, 128.4, 128.8, 128.9, 129.2, 130.50, 130.52, 131.1, 131.6, 132.0, 142.7, 142.9, 149.66, 149.70, 154.5, 160.0, 188.6; HRMS (FAB$^+$, double-focusing magnetic sector) calcd for $C_{49}H_{38}O_5$, 706.2719; found, 706.2725.

Synthesis of Compound 9. To a solution of *n*-octyltriphenylphosphonium bromide (387 mg, 0.85 mmol) in dry THF (100 mL), *n*-BuLi (1.62 M, *n*-hexane solution, 326 μL, 0.53 mmol) was added dropwise at −78 °C under a N_2 atmosphare. The dry ice/aceton bath was temporarily removed, and the solution was stirrerd for 10 min at room temperature. After the solution was again cooled down at −78 °C, a solution of compound **8** in dry THF (12 mL) was added dropwise with subsequent stirring for 3.5 h at room temperature. The reaction mixture was poured into the mixed solvent of chloroform and 1 M hydrochloric acid solution. The organic layer was separated and washed with brine. After the organic fraction dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was roughly purified by column chromatography (SiO_2, *n*-hexane/chloroform = 2/1) to afford a residue (*E*/*Z* mixture of the Wittig adducts). A suspension of the residue and 10% Pd/C (20 mg) in THF (3 mL) was stirred at room temperature for 12 h under a H_2 atmosphere. After Pd/C was removed by filtration, the filtrate was evaporated in vacuo to give desired **9** as a white powder (189 mg, 84%).

Mp 152−153 °C; IR (KBr) 3059, 2927, 2854, 1522, 1454, 1325, 1217, 1117, 860, 741 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.51 (t, J = 7.3 Hz, 3H), 0.60 (t, J = 7.3 Hz, 3H), 0.84 (t, J = 6.8 Hz, 3H), 0.90−1.13 (m, 4H), 1.24−1.60 (m, 16H), 1.86−1.98 (m, 2H), 3.53 (t, J = 7.8 Hz, 2H), 4.13−4.29 (m, 2H), 4.34−4.48 (m, 2H), 7.29−7.36 (m, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.53−7.72 (m, 6H), 8.03−8.07 (m, 1H), 8.15 (s, 1H), 8.18−8.26 (m, 3H), 8.82 (s, 1H), 8.86 (d, J = 8.4 Hz, 2H), 8.95 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.5, 13.6, 14.2, 18.6, 18.8, 22.7, 26.1, 29.4, 29.7, 30.2, 30.4, 31.9, 32.1, 32.2, 73.2, 73.3, 107.5, 118.6, 118.8, 119.3, 120.1, 120.5, 123.3, 123.5, 123.9, 124.5, 124.8, 124.9, 125.0, 125.2, 125.3, 125.6, 125.7, 125.8, 126.04, 126.09, 126.11, 127.1, 127.2, 127.7, 128.4, 129.2, 130.5, 130.6, 131.12, 131.14, 131.3, 132.1, 143.0, 143.1, 149.5, 150.0, 152.7, 154.6; HRMS (FAB$^+$, double-focusing magnetic sector) calcd for $C_{57}H_{56}O_4$, 804.4179; found, 804.4184.

Synthesis of Compound 10. Compound **9** (189 mg, 0.24 mmol) was dissolved in CH_2Cl_2 (3 mL), and BBr_3 (1.0 M CH_2Cl_2 solution, 0.59 mL, 0.59 mmol) was added at room temperature with subsequent stirring for 1 h. The reaction mixture was poured into the mixed solvent of chloroform and water. The organic layer was separated and washed with brine. After the organic fraction dried over sodium sulfate,

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the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2, chloroform) and preparative gel filtration chromatography (chloroform) to afford compound **10** as a yellow powder (140.7 mg, 87%).

Mp 153−155 °C; IR (KBr) 3516, 3059, 2924, 2852, 1525, 1460, 1219, 1115, 964, 862, 744, 478 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.82 (t, J = 6.8 Hz, 3H), 1.22−1.37 (m, 10H), 1.44−1.54 (m, 2H), 1.76−1.87 (m, 2H), 3.33 (t, J = 7.8 Hz, 2H), 5.88 (s, 1H), 5.94 (s, 1H), 7.32−7.45 (m, 4H), 7.51−7.65 (m, 6H), 7.86 (s, 1H), 7.92−7.96 (m, 1H), 8.13−8.19 (m, 3H), 8.53 (d, J = 8.1 Hz, 1H), 8.61 (s, 1H), 8.63 (d, J = 8.1 Hz, 1H) 8.70 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.2, 22.7, 25.7, 29.4, 29.57, 29.64, 30.0, 30.3, 31.9, 107.5, 113.4, 114.0, 118.7, 119.3, 119.9, 120.5, 123.47, 123.58, 123.60, 123.9, 124.4, 124.7, 124.9, 125.08, 125.17, 125.22, 125.24, 125.3, 125.5, 125.6, 125.7, 125.8, 127.8, 128.3, 129.2, 130.28, 130.36, 130.38, 130.62, 131.0, 132.1, 140.3, 140.6, 145.8, 145.9, 152.4, 154.1; HRMS (FAB^+, double-focusing magnetic sector) calcd for $C_{49}H_{40}O_4$, 692.2927; found, 692.2917.

Synthesis of Compound 11. Dibromomethane (13.6 μL, 0.195 mmol) was added to a suspension of **10** (45.0 mg, 0.065 mmol) and K_2CO_3 (27.7 mg, 0.195 mmol) in DMF (3 mL). The suspension was stirred for 3 d at 60 °C. The reaction mixture was poured into the mixed solvent of ethyl acetate and 1 M hydrochloric acid solution. The organic layer was separated and washed with brine. After the organic fraction dried over sodium sulfate, the solvent was evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2, chloroform) and preparative gel filtration chromatography (chloroform) to afford compound **11** as a yellow powder (20.2 mg, 44%).

Mp 295 − 296 °C; IR (KBr) 3059, 2924, 2854, 1616, 1577, 1522, 1458, 1327, 1217, 1105, 1084, 735 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.84 (t, J = 6.8 Hz, 3H), 1.25−1.61 (m, 12H), 1.88−1.99 (m, 2H), 3.56 (t, J = 7.6 Hz, 2H), 6.12 (s, 2H), 7.34−7.41 (m, 2H), 7.52−7.63 (m, 2H), 7.73−7.78 (m, 4H), 8.02−8.05 (m, 1H), 8.14−8.25 (m, 4H), 8.79 (s, 1H), 8.87−8.93 (m, 3H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 29.4, 29.7, 29.9, 30.4, 32.0, 103.6, 107.8, 118.8, 119.8, 120.4, 120.6, 120.8, 123.7, 123.8, 124.1, 124.5, 124.65, 124.70, 125.1, 125.6, 126.0, 126.6, 126.7, 127.5, 127.6, 127.8, 127.9, 128.5, 128.7, 129.2, 129.4, 130.8, 131.0, 131.3, 132.5, 138.5, 138.7, 148.9, 149.1, 153.2, 155.0; HRMS (FAB^+, double-focusing magnetic sector) calcd for $C_{50}H_{40}O_4$, 704.2927; found, 704.2928.

Synthesis of Compound 12. A solution of compound **10** (17.0 mg, 0.0234 mmol) and methanesulfonic acid (16 μL, 0.245 mmol) in *o*-xylene (3 mL) in a sealed tube was stirred at 165 °C for 4.5 d. The reaction mixture was poured into water and extracted by chloroform. The organic layer was separated, washed with brine, and dried over sodium sulfate, and the solvent was evaporated to give a residue. The residue was purified by column chromatography (SiO_2, chloroform) and preparative gel filtration chromatography (chloroform) to afford compound **12** as a yellow powder (5.2 mg, 32%).

Mp 280−281 °C; IR (KBr) 3045, 2920, 2850, 1566, 1458, 1321, 1281, 1217, 1120, 966, 858, 737 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3H), 1.26−1.53 (m, 10H), 1.60−1.70 (m, 2H), 1.85−1.97 (m, 2H), 3.42 (t, J = 7.8 Hz, 2H), 7.30−7.45 (m, 4H), 7.50−7.59 (m, 4H), 7.74−7.88 (m, 3H), 7.84 (s, 1H), 8.19 (s, 1H), 8.26 (s, 1H), 8.35−8.41 (m, 2H), 8.87−8.92 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.2, 22.8, 26.0, 29.5, 29.8, 29.9, 30.3, 30.6, 32.1, 107.3, 117.5, 118.2, 120.0, 120.3, 121.4, 121.7, 123.4, 123.8, 123.9, 124.0, 124.1, 124.3, 124.5, 125.0, 125.1, 125.2, 125.4, 125.5, 125.6, 126.38, 126.44, 127.0, 127.1, 127.5, 128.2, 129.1, 130.5, 130.6, 131.2, 131.9, 140.9, 142.1, 142.2, 153.0, 154.8; HRMS (FAB^+, double-focusing magnetic sector) calcd for $C_{49}H_{38}O_3$, 674.2821; found, 674.2828.

Absorption and Emission Measurement. UV−vis and fluorescence spectra were measured at 25 °C in THF for spectroscopy without degassing (concentration: 10^{-5}−10^{-6} M).

■ ASSOCIATED CONTENT

Supporting Information

The coordinates of naphthofuran derivatives (dihedral angle fixed compound **6**, optimized structures of compound **6**, dealkylated compound **11**, and dealkylated compound **12** in the absence or presence of THF) by DFT calculation, ^1H and ^{13}C NMR spectra for all new compounds, and CIF of compound **3** (CCDC 986435). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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