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Cyclization of Tetraaryl-Substituted Benzoquinones and Hydroquinones through the Scholl Reaction

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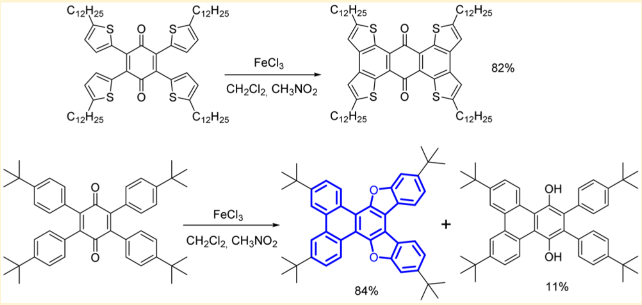
S *Supporting Information*

ABSTRACT: 2,3,5,6-Tetrakis(5′-dodecylthiophen-2-yl)-benzoquinones and 2,3,5,6-tetrakis(5′-dodecylthiophen-2′-yl)-hydroquinones were prepared via the Stille or Suzuki cross-coupling reactions, followed by oxidation by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in the case that aryl groups are dodecylthiophenyl. 2,3,5,6-Tetrakis(5′-dodecylthiophen-2′-yl)benzoquinone and 2,3,5,6-tetrakis(5′-dodecylthiophen-2′-yl)-1,4-bis(dodecyloxy)benzene underwent the Scholl reaction to give their corresponding predictable cyclization products anthra[2,1-*b*:3,4-*b*′:6,5-*b*″:7,8-*b*‴]tetrathiophene-7,14-dione (**3**) and anthra[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7-*b*‴]tetrathiophene (**5**), respectively. Cyclization of 2,3,4,5-tetra(*p*-*tert*-butyl-phenyl) benzoquinones through the Scholl reaction, however, gave rise to a mixture of two cyclization products including an unusual major product, benzo[4′,5′]furo[3′,2′:3,4]triphenyleno[1,2-*b*]benzofuran (**9**), with 84% yield and a minor product, 2,3-diphenyltriphenylene-1,4-diol (**10**), with 11% yield. In contrast, cyclization of 2,3,4,5-tetrakis(*p*-dodecyloxyphenyl)benzoquinone only afforded 2,3-diphenyltriphenylene-1,4-diol (**8**) with 34% yield. The optical and electrochemistry properties of these fused aromatics were studied. Light emitting diode devices using compound **9** as the fluorescent dopant were fabricated. A maximum external quantum efficiency of 3.23% was achieved for a 4,4′-bis(carbazole)biphenyl/**9** based device, revealing the potential for such fused aromatics as dopant to be a blue LED component, subject to the functionalization on these novel π-structures as well as further device optimization.



■ INTRODUCTION

Scholl reaction, or oxidative dehydrogenative cyclization reaction, used for the construction of new carbon−carbon bonds by fusion of π-systems, has been witnessed as a useful chemical strategy for the synthesis of novel π-frameworks for organic electronics materials[1] and functional dyes.[2] Wide studies on the mechanistic aspects of this reaction have been carried out both experimentally and theoretically to better understand the unique characteristics of this intriguing reaction.[3] The cyclization of various substrates has been successfully demonstrated for vicinal diaryls (phenyls, thiophenes, etc.),[4] multiple aryls (oligomeric and polymeric),[5] and more sophisticated functional dyes such as porphyrins[6] and boron-dipyrromethenes.[7] Due to the characteristics of the Scholl reactions, unexpected cyclization routes are frequently observed for substrates with special reactivities.[8]

In our current study, we are particularly interested in substrates that have a tetraaryl-substituted benzoquinone backbone (Figure 1). In these substrates, the reactive center is just next to carbonyl groups, and the Scholl reactivity would be influenced by the neighboring carbonyl groups. Such vision is based on recent publications of a series of azaoxa[8]circulenes[9] and previous work on tetraoxa[8]circulenes[10] originating from the special reactivity of carbonyl or hydroxy groups in the presence of Lewis acid. We have successfully prepared a series of tetraaryl-substituted benzoquinones, and their reactivity under the Scholl reaction conditions (Scheme 1) was examined. Interestingly, as the identity of the substituting groups varied, the substrates exhibited several different reaction pathways, and a variety of different oxidation products were isolated and characterized. A novel unprecedented π-framework, namely, benzo[4′,5′]furo[3′,2′:3,4]triphenyleno[1,2-*b*]benzofuran, was prepared for the first time owing to the special reactivity of tetraaryl-substituted benzoquinones. This novel π-structure was evaluated using light emitting diode devices to seek its potential as functional organic electronics materials.

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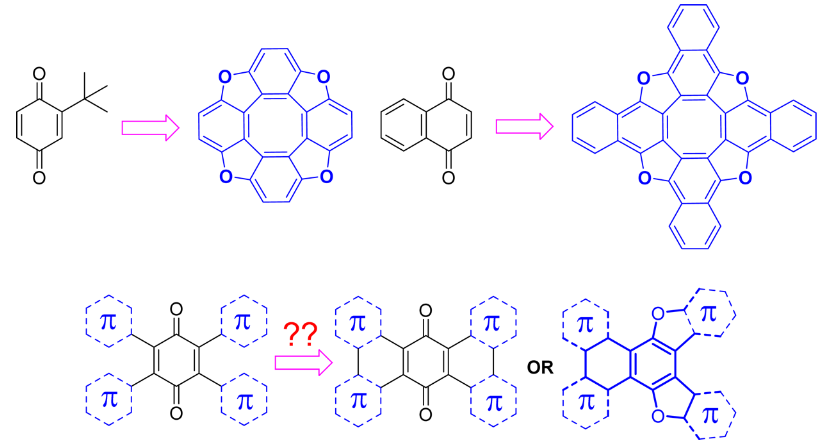
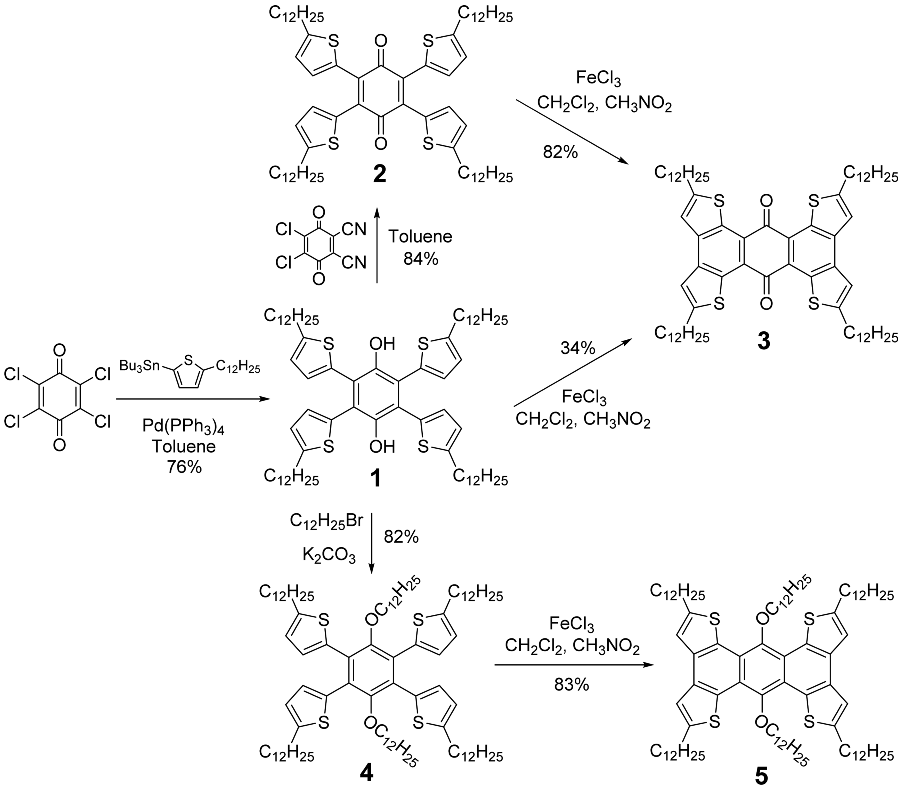


Figure 1. Synthesis of tetraoxa[8]circulene and tetranaphthotetraoxa[8]circulene. Proposed reaction pathways for tetra-aryl substituted benzoquinones.

Scheme 1. Synthetic Procedures of Fused Aromatic Compounds 3 and 5

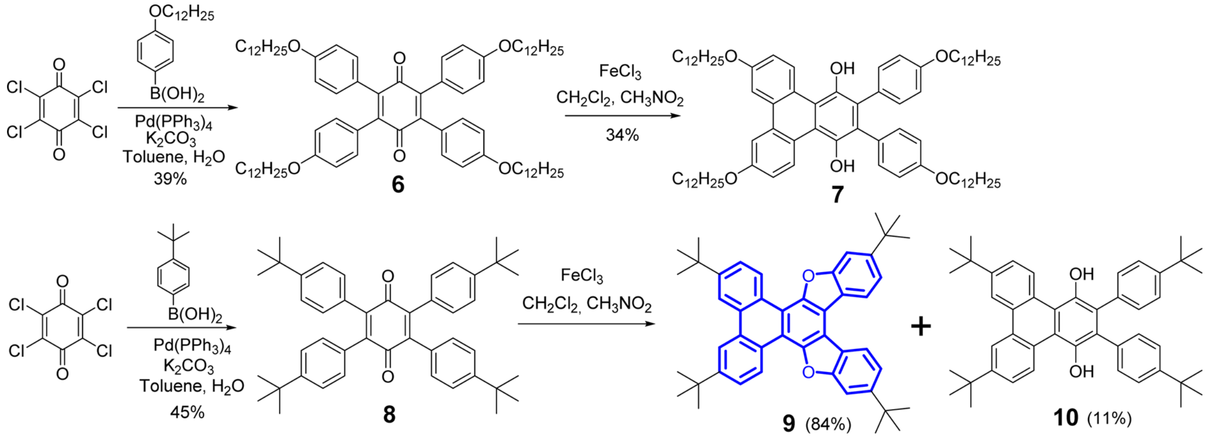


■ RESULTS AND DISCUSSION

To probe the Scholl-type reactivity of tetraaryl-substituted benzoquinone substrates, the thiophene substituted analogues were prepared and studied. Stille reaction between *p*-chloranil and tributyl(5-dodecylthiophen-2-yl)stannane was adopted to introduce four thiophene substituents onto the benzoquinone unit in 76% yield. Interestingly, instead of the substituted benzoquinone, the reduced dihydroxy form, **1**, was obtained as the major product, which could be ascribed to a concurrent reduction reaction assisted by organo-tin reagents.[11] The reduced form **1** could be conveniently converted to the benzoquinone analogue **2** in the presence of equimolar oxidant 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Ferric chloride ($FeCl_3$) has been routinely used as the oxidant and Lewis acid for Scholl-type oxidative dehydrogenative cyclization reactions. In our current study, both **1** and **2** were subject to Scholl-type cyclization reactions in the presence of $FeCl_3$. For substrate **1**, the Scholl-type reaction generated a series of products, and the cyclized product **3** was obtained after careful column chromatography separation in 34% yield. The active hydrogen atoms on the hydroxy groups would possibly be involved in the radical reaction and generate diverse pathways, hence hampering the reaction yield. In contrast, as substrate **2** was subjected to Scholl-type reaction, the product **3** was obtained more effectively with 82% yield. We also blocked the hydroxy groups on **1** by attachment of long alkyl chain dodecyl groups. The alkylated species **4** was obtained in 82% yield from **1**. As substrate **4** was subjected to Scholl-type reaction, the expected product **5** was obtained in satisfactory 83% yield.

The tetraphenyl-substituted benzoquinones were also prepared to further explore the reactivity of tetraaryl-substituted

Scheme 2. Synthesis of Cyclized Aromatic Compounds 7, 9, and 10



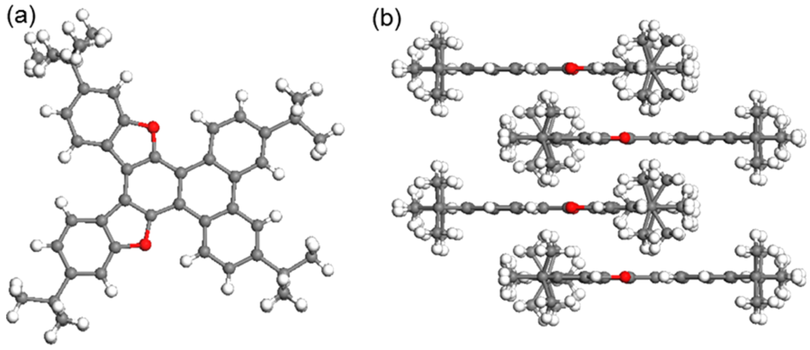


Figure 2. Single crystal structure of compound **9** and its solid state packing. Solvent molecules are omitted for clarity.

benzoquinones in the Scholl reaction. Two such substrates, the 4-dodecyloxyphenyl-substituted and 4-*tert*-butylphenyl-substituted benzoquinones **6** and **8**, were prepared via Suzuki cross coupling reactions. No reduced dihydroxy forms of **6** and **8** were isolated. As substrate **6** was subjected to Scholl reaction, only the partially cyclized product **7** was obtained in a reduced form in 34% yield. Attempts to further cyclize compound **7** failed with only an intact mixture of products obtained together with ca. 50% of unreacted starting material. Cyclization of substrate **8** happened smoothly, however, to generate an unexpected cyclized product **9** in 84% yield, together with the partially cyclized dihydro-compound **10** in 11% yield. The strikingly different behaviors of substrates **6** and **8** would be due to different electronic densities of the reactive sites induced by the different electron donating ability of the substituents. This is the first time that the π-structure benzo[4′,5′]furo[3′,2′:3,4]triphenyleno-[1,2-*b*]benzofuran (highlighted in blue in Scheme 2) has been prepared in the literature. Because Lewis acid and oxidant assisted in fusion of hydroxy or carbonyl to phenyl groups to generate benzofuran and related structures have been known,[9,10,12] it is rational to envisage that the mechanism of formation of compound **9** would involve a cascade reaction that includes Scholl-type cyclization of two phenyl rings and Lewis acid-assisted fusion of the carbonyl or hydroxy groups to the neighboring phenyl groups. The chemical structure of **9** was further confirmed by single-crystal X-ray crystallography as shown in Figure 2. Suitable single crystals of **9** for diffraction studies were obtained by slow vapor diffusion of methanol into the chloroform solution of **9**. The π-structure of **9** was essentially planar with minimal distortion. It packed in a slipped face-to-face manner with an interface spacing of 3.49 Å.

Photophysical Properties. The photophysical properties of the cyclized products **3**, **5**, and **9** were characterized in both solution and thin film states, and the spectra are shown in Figure 3. Compound **5** showed strong absorption peaks at 342 nm and weak absorption peaks at 372 and 394 nm, which is analogous to its isoelectronic structure phenanthro[9,10-*b*]triphenylene.[13] In thin film state, compound **5** exhibited minor aggregation behavior, and vibronic structures of the absorption bands remained essentially the same. This could be ascribed to the staggered dodecyloxy groups, which would hamper the effective $\pi-\pi$ stacking of central aromatic backbones. The oxidized quinoidal form, compound **3**, exhibited totally different absorption behavior, and a broad absorption band from 400 to 530 nm was observed. Compound **3** demonstrated much stronger solid state aggregation behavior as evidenced from broadened low-energy absorption band and red-shift of the absorption edge of about 28 nm. The much stronger aggregation behavior of **3** compared with **5** could be explained by the planar π-structure and absence of substitutions at the central ring. Compound **9** exhibited absorption with vibronic structures from 300 to 400 nm. Compound **5** exhibited moderate emission with λ_{max} = 457 nm, whereas compound **3** exhibited almost no emission, possibly originating from the donor−acceptor conjugated system. The new π-structure **9** exhibited strong blue emission in chloroform solution with λ_{max} = 392 nm with fluorescence quantum efficiency of Φ_f = 0.62 relative to 9,10-diphenylanthracene (Φ_f = 0.86 in cyclohexane).[14] A small Stokes shift of 329 cm^{-1} with $\Delta\lambda$ = 5 nm reflected the structural rigidity of **9**. Time-dependent density functional theory (TDDFT) calculation was adopted to elaborate the electronic properties of compound **9** at B3LYP/6-31+G(d) theory level. The calculated

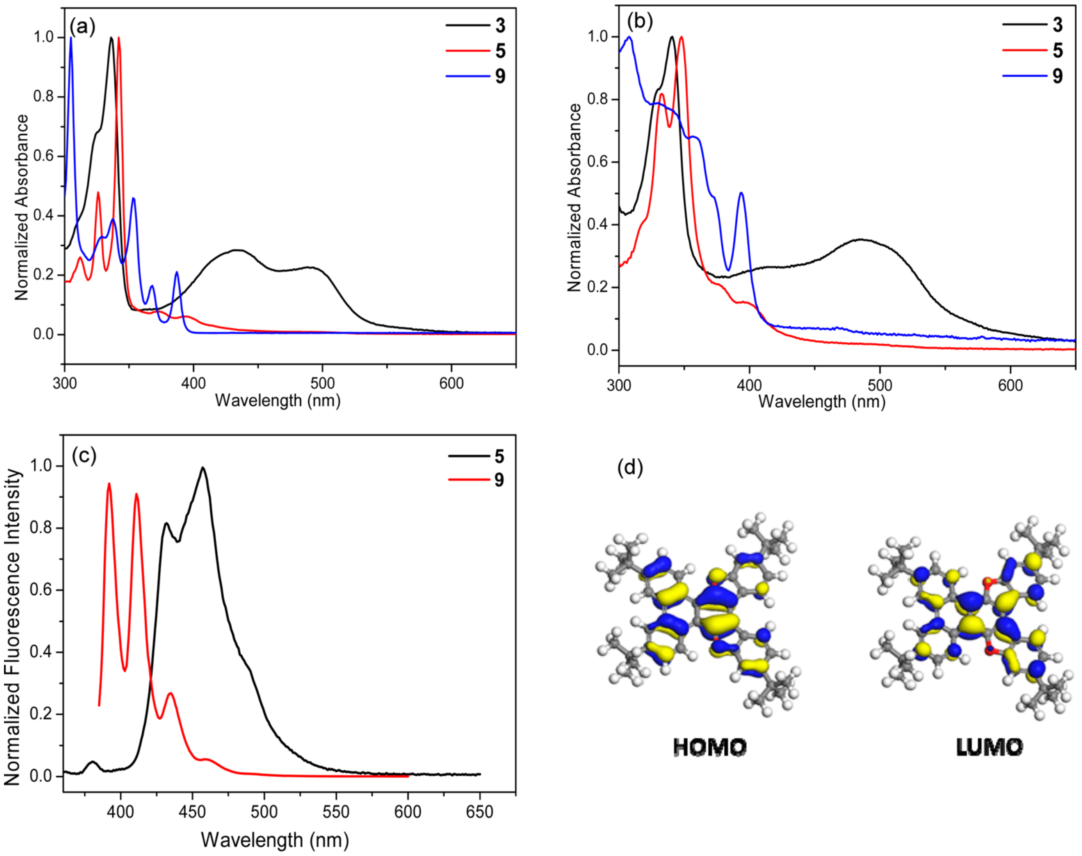


Figure 3. Normalized UV−vis absorption spectra of compounds **3**, **5**, and **9** (a) in chloroform solution and (b) in thin films, (c) photoluminescence spectra of compounds **5** and **9** in chloroform solution, and (d) calculated frontier molecular orbitals (HOMO and LUMO) for compound **9**.

frontier orbitals (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) were found well distributed over the whole π-system (Figure 3d), which is believed to be beneficial for better frontier orbital overlapping and efficient intermolecular charge transport. The UV−vis absorption spectrum of compound **9** is simulated by TDDFT calculations, and the detailed assignment of the transition peaks is shown in Table S7. In general, the predicted spectrum agrees well with the observation, and the absorption transition with the longest wavelength is assigned to HOMO − 1 → LUMO (63%) and HOMO → LUMO + 1 (29%). Compound **9** is envisioned to be a promising candidate for charge transport materials as well as blue light emitting materials.

Electrochemical Properties. The electrochemical properties of the cyclized products **3**, **5**, and **9** were characterized by cyclic voltammetry (CV) in dichloromethane, and the voltammograms are shown in Figure 4. Both compounds **3** and **5** exhibited irreversible oxidation and reduction curves, reflecting the instability of both radical cation and radical anion on both frameworks. The frontier orbital energy levels, that is, HOMO and LUMO, were calculated to be −5.72 and −3.67 eV and −5.91 and −3.54 eV for compounds **3** and **5**, respectively. In contrast, compound **9** exhibited a reversible oxidation curve and an irreversible reduction curve. The HOMO and LUMO energy levels of **9** were calculated to be −5.49 and −3.44 eV, respectively.

Light-Emitting Diode Device Characterizations. Compound **9** with a novel cyclized π-structure is believed to be a blue-emitting diode material, and devices with **9** acting as the fluorescent dopant were fabricated to the following the general configuration of MoO_3 (6 nm)|NPB (70 nm)|CBP or (TCTA/CBP)/**9** (20 nm, 10%)|TPBi (30 nm)|LiF (1 nm)|Al.[15] 4,4′-Bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) or tris(4-carbazoyl-9-ylphenyl)amine (TCTA)/CBP were used as the host material, and compound **9** was used as the dopant, and the output data are given in Figure 5. The turn-on voltages for CBP/**9** and (TCTA/CBP)/**9** based devices are 4.5 and 3.8 V, respectively. The emitted light output of both devices increased sharply with the applied voltage. The maximum brightness of these two devices reached 1217 and 1866 cd m^{-2}, respectively. The current efficiency of the CBP/**9** based device is over 1 cd A^{-1} for brightness ranging from 10 to 500 cd m^{-2}. Maximum external quantum efficiency up to 3.23% was achieved for the CBP/**9** based device, while the device made with (TCTA/CBP)/**9** showed the maximum external quantum efficiency of 2.6%. Furthermore, both deep-blue devices revealed high color purity with favorable CIE coordinates of (0.16, 0.04) and (0.16, 0.02), respectively, which perfectly matched with the standards of National Television System Committee (NTSC, USA) and European Broadcasting Union (EBU) on CIE coordinates of (x = 0.15, y = 0.08) and (x = 0.15, y = 0.06) for deep-blue light sources. Such preliminary results are promising and favorable among the best results for deep-blue fluorescent OLEDs (Table S8). It is believed that further optimization of both the functionalization on the novel π-structure and device engineering would generate even better performance.

■ CONCLUSION

In conclusion, the Scholl reactions of tetraaryl-substituted benzoquinones in the presence of $FeCl_3$ were studied. The

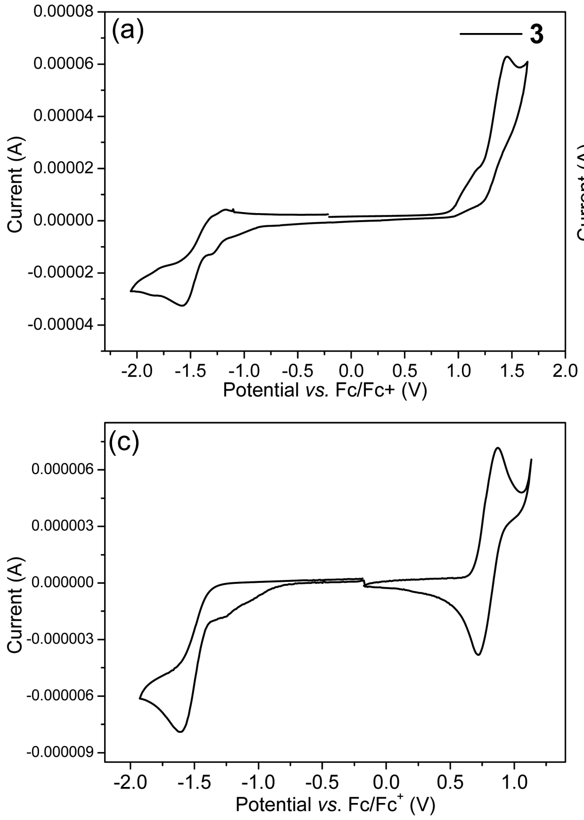


Figure 4. Cyclic voltammograms of (a) compound **3**, (b) compound **5**, and (c) compound **9**. Ferrocene/ferrocenium couple was used as external standard. The energy levels of the frontier orbitals were calculated based on the following formula: HOMO = $-(4.8 + E_{\mathrm{ox}}^{\mathrm{onset}})$ (eV) and LUMO = $-(4.8 + E_{\mathrm{red}}^{\mathrm{onset}})$ (eV).

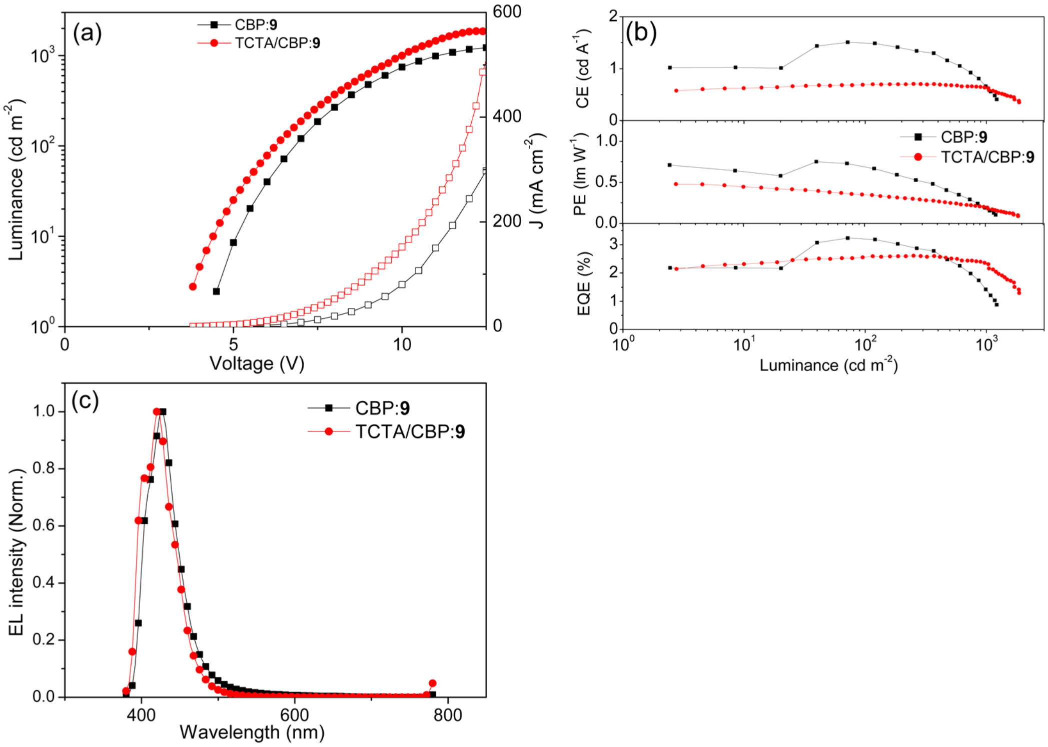


Figure 5. (a) Luminance− and current density (*J*)−voltage curves of the devices. (b) Efficiency curves of the devices. (c) Emission spectra of the active layers in the device.

tetraaryl-substituted benzoquinone system had been witnessed as an interesting system for Scholl reaction as evidenced by the formation of various types of cyclization products. Upon treatment with $FeCl_3$ in a mixture of dichloromethane and

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nitromethane at room temperature, tetrathienyl-substituted benzoquinones led to the formation of an expected cyclization product. In contrast, tetra(*p*-alkoxyphenyl)-substituted benzoquinone only gave a typical cyclization product 2,3-diphenyltriphenylene-1,4-diol derivative. However, apart from the formation of 2,3-diphenyltriphenylene-1,4-diol derivative, tetra(*tert*-butyl-phenyl)-substituted benzoquinones afforded a unique cyclization structure, benzo[4′,5′]furo[3′,2′:3,4]triphenyleno-[1,2-*b*]benzofuran, as a major product under the same conditions. This novel structure was confirmed by the single-crystal X-ray crystallography. Moreover, the light emitting properties of this new π-structure were evaluated by fabrication of light emitting devices, and overall external quantum efficiency up to 3.23% was achieved. It would be envisaged that this novel π-system would be a promising candidate as well for hole-transporting materials for field-effect transistors[16] or perovskite solar cells[17] given further functionalization engineering at the periphery of the π-framework. Such approaches are currently under investigation in our lab.

■ EXPERIMENTAL SECTION

Characterization of Materials. NMR spectra were recorded in $CDCl_3$ on a 400 MHz NMR spectrometer. All absorption spectra were recorded using a UV−vis−NIR spectrophotometer. Mass spectra were acquired from a mass spectrometer using atmospheric pressure chemical ionization (APCI) or electron impact (EI) as an ionization method. The mass analyzer type used for the HRMS measurements is quadrupole time-of-flight (Q-TOF). A potentiostat/galvanostat was used for cyclic voltammetry experiments. Cyclic voltammetry was performed in a glovebox under inert atmosphere with a glass carbon electrode, Pt wire, and Ag wire as the working, counter, and pseudo-reference electrode, respectively, at a scan rate of 50 mV s^{-1}. A 0.1 M lithium perchlorate/dichloromethane electrolyte/solvent couple was used. The pseudo-reference electrode was calibrated with respect to the ferrocene/ferrocenium redox couple, and the energy level was taken to occur at −4.8 V below vacuum.

Device Fabrication and Testing. Before loading into a deposition chamber, the ITO substrate was cleaned with detergents and deionized water, dried in an oven at 120 °C for 4 h, and treated with oxygen plasma for 3 min. Devices were fabricated by evaporating organic layers at a rate of 0.1−0.2 nm s^{-1} onto the ITO substrate sequentially at a pressure below 4×10^{-4} Pa. Onto the electron-transporting layer, a layer of LiF with 1 nm thickness was deposited at a rate of 0.1 nm s^{-1} to improve electron injection. Finally, a 100 nm-thick layer of Al was deposited at a rate of 0.6 nm s^{-1} as the cathode. The emission area of the devices was 0.09 cm^2 as determined by the overlap area of the anode and the cathode. After fabrication, the devices were immediately transferred to a glovebox for encapsulation with glass coverslips using epoxy glue. The EL spectra and CIE coordinates were measured using a spectra colorimeter. The current-density−voltage and brightness−voltage curves of the devices were measured using a source meter and a calibrated silicon photodiode. All the measurements were carried out at room temperature under ambient conditions.

All chemical reagents were obtained from commercial vendors and were used without further purification.

Synthesis of 2,3,5,6-Tetrakis(5-dodecylthiophen-2-yl)-benzene-1,4-diol, 1. To a dry round-bottom flask were added chloranil (3.0 g, 12.2 mmol), tributyl(5-dodecylthiophen-2-yl)stannane (33 g, 61 mmol), $Pd(PPh_3)_4$ (1.1 g, 0.976 mmol), and toluene (200 mL). The mixture was degassed for 30 min before heating at 110 °C for 2 days. After cooling to room temperature, the solvent was removed by rotary evaporation, and the residue was subject to silica gel column chromatography (Hex/$CHCl_3$ = 3:1) to afford the target molecule as brown powder (10.3 g, yield = 76%). ^1H NMR (400 MHz, $CDCl_3$): δ ppm = 6.81, 6.80 (d, *J* = 3.6 Hz, 4H), 6.65, 6.64 (d, *J* = 3.6 Hz, 4H), 5.54 (br, 2H), 2.75, 2.73, 2.71 (t, *J* = 7.6 Hz, 8H), 1.60−1.58 (m, 8H), 1.26 (m, 72H), 0.90, 0.88, 0.87 (t, *J* = 6.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 148.6, 145.7, 133.8, 129.3, 124.1, 122.5, 32.3, 32.0, 30.5, 29.8, 29.4, 23.1, 14.5. HRMS (APCI) *m*/*z*: $[M + H]^+$ Calcd for $C_{70}H_{111}O_2S_4$ 1111.7461; Found 1111.7480. Mp: 68−71 °C.

Synthesis of 2,3,5,6-Tetrakis(5-dodecylthiophen-2-yl)-cyclohexa-2,5-diene-1,4-dione, 2. To a dry round-bottom flask were added 2,3,5,6-tetrakis(5-dodecylthiophen-2-yl)benzene-1,4-diol (**1**, 1.0 g, 0.9 mmol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (205 mg, 0.9 mmol), and dry toluene (10 mL). The mixture was stirred at room temperature overnight. The solvent was then removed by rotary evaporation, and the residue was subject to silica gel column chromatography (Hex/$CHCl_3$ = 3:1) to afford the target compound as brown powder (0.84 g, yield = 84%). ^1H NMR (400 MHz, $CDCl_3$): δ ppm = 6.96, 6,95 (d, *J* = 3.6 Hz, 4H), 6.68, 6.67 (d, *J* = 3.6 Hz, 4H), 2.80, 2.78, 2.76 (t, *J* = 7.2 Hz, 8H), 1.65−1.63 (m, 8H), 1.32−1.26 (m, 72H), 0.89, 0.88, 0.86 (t, *J* = 6.4 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 186.0, 152.3, 135.2, 132.9, 131.5, 124.8, 32.3, 32.0, 31.9, 30.6, 30.1, 30.0, 29.8, 29.5, 23.1, 14.5. HRMS (APCI) *m*/*z*: $[M + H]^+$ Calcd for $C_{70}H_{109}O_2S_4$ 1109.7305; Found 1109.7314. Mp: 71−73 °C.

Synthesis of 2,5,9,12-Tetradodecylanthra[1,2-b:4,3-b′:5,6-b″:8,7-b‴]tetrathiophene-7,14-dione, 3. ***Compound 3 Prepared Starting from Compound 1.*** To a dry round-bottom flask were added 2,3,5,6-tetrakis(5-dodecylthiophen-2-yl)benzene-1,4-diol (**1**, 0.50 g, 0.45 mmol) and dry dichloromethane (20 mL). Anhydrous ferric chloride (292 mg, 1.8 mmol) was dissolved in nitromethane (1 mL) and added into the solution dropwise. The solution was purged with nitrogen and stirred at room temperature for 30 min. Methanol (20 mL) was injected into the solution, and the mixture was stirred for another 30 min. The precipitate was collected by suction filtration and subjected to silica gel column chromatography (Hex/$CHCl_3$ = 3:1) to afford the target molecule as a red solid (168 mg, yield = 34%).

Compound 3 Prepared Starting from Compound 2. To a dry round-bottom flask were added 2,3,5,6-tetrakis(5-dodecylthiophen-2-yl)cyclohexa-2,5-diene-1,4-dione (**2**, 0.50 g, 0.45 mmol) and dry dichloromethane (20 mL). Anhydrous ferric chloride (4 equiv, 1.8 mmol, 292 mg) was dissolved in nitromethane (1 mL) and added into the solution dropwise. The solution was purged with nitrogen and stirred at room temperature for 30 min. Methanol (20 mL) was injected into the solution, and the mixture was stirred for another 30 min. The precipitate was collected by suction filtration and subjected to silica gel column chromatography (Hex/$CHCl_3$ = 3:1) to afford the target molecule as a red solid (410 mg, yield = 82%).^1H NMR (400 MHz, $CDCl_3$): δ ppm = 7.37 (s, 4H), 3.04 (m, 8H), 1.86 (m, 8H), 1.43−1.26 (m, 72H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 183.9, 157.7, 140.0, 134.5, 124.3, 118.0, 32.3, 31.6, 31.4, 30.0, 29.9, 29.8, 29.7, 23.0, 14.4. HRMS (APCI) *m*/*z*: $[M + H]^+$ Calcd for $C_{70}H_{105}O_2S_4$ 1105.6992; Found 1105.7021. Mp: 172−174 °C.

Synthesis of 5,5′,5″,5‴-(3,6-Bis(dodecyloxy)benzene-1,2,4,5-tetrayl)tetrakis(2-dodecylthiophene), 4. To a dry round-bottom flask were added 2,3,5,6-tetrakis(5-dodecylthiophen-2-yl)benzene-1,4-diol (**1**, 500 mg, 0.45 mmol), dodecyl bromide (280 mg,1.13 mmol), potassium carbonate (250 mg, 1.8 mmol), and acetone (10 mL). The mixture was stirred at 60 °C overnight. After it was cooled to room temperature, the solvent was removed by rotary evaporation, and the residue was directly subjected to silica gel column chromatography (Hex/$CHCl_3$ = 1:1) to afford the target molecule as yellow powder (535 mg, yield = 82%). ^1H NMR (400 MHz, $CDCl_3$): δ ppm = 6.67, 6.66 (d, *J* = 3.6 Hz, 4H), 6.55, 6.54 (d, *J* = 3.6 Hz, 4H), 3.24, 3.22, 3.21 (t, *J* = 6.8 Hz, 4H), 2.75, 2.73, 2.71 (t, *J* = 7.2 Hz, 8H), 1.76−1.68 (m, 4H), 1.25 (m, 116H), 0.89−0.86 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm = 152.5, 147.1, 134.9, 130.7, 129.0, 123.5, 73. 6, 32.4, 32.2, 30.4, 30.3, 30.1, 29.8, 29.4, 26.1, 23.1, 14.5. HRMS (APCI) *m*/*z*: $[M + H]^+$ Calcd for $C_{94}H_{159}O_2S_4$ 1448.1207; Found 1448.1209. Mp: 75−77 °C.

Synthesis of 2,5,9,12-Tetradodecyl-7,14-bis(dodecyloxy)-anthra[1,2-*b*:4,3-*b*′:5,6-*b*″:8,7 *b*‴]tetrathiophene, 5. To a dry round-bottom flask were added 5,5′,5″,5‴-(3,6-bis(dodecyloxy)-benzene-1,2,4,5-tetrayl)tetrakis(2-dodecylthiophene) (**4**, 300 mg, 0.207 mmol) and dry dichloromethane (10 mL). Into the solution was added ferric chloride (134 mg, 0.83 mmol) in nitromethane (1 mL). The mixture was purged with argon and stirred at room temperature for 40 min. Methanol (5 mL) was then added to quench the reaction. The solvent was removed by rotary evaporation, and the residue was subjected to silica gel column chromatography (Hex/CHCl$_3$ = 1:1 as eluent) to afford the target molecule as a red solid (250 mg, yield 83%). ^{1}H NMR (400 MHz, CDCl$_3$): δ ppm = 7.45 (s, 4H), 4.05−3.96 (m, 4H), 3.08, 3.06, 3.05 (t, J = 7.2 Hz, 8H), 2.54 (m, 4H), 1.89−1.84 (m, 8H), 1.56−1.27 (m, 108H), 0.88−0.86 (m 18H). ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm = 148.3, 145.8, 134.3, 129.0, 128.8, 120.3, 119.2, 76.3, 32.3, 32.1, 31.0, 30.6, 30.4, 30.1, 29.9, 29.84, 29.77, 29.6, 26.2, 23.1, 14.5. HRMS (APCI) m/z: [M + H]$^+$ Calcd for $C_{94}H_{155}O_2S_4$ 1445.0904; Found 1445.0888. Mp: 85−88 °C.

Synthesis of 4,4″-Bis(dodecyloxy)-4′,5′-bis(4-(dodecyloxy)-phenol)-[1,1′:2′,1″-terphenyl]-3′,6′-dione, 6. To a dry round-bottom flask were added *p*-chloranil (1.00 g, 4.07 mmol), 4-dodecyloxyphenylboronic acid (7.5 g, 24.40 mmol), Pd(PPh$_3$)$_4$ (375 mg,0.326 mmol), potassium carbonate (4.50 g, 32.56 mmol), toluene (30 mL), and water (3 mL). The mixture was degassed for 20 min and then heated to 100 °C for 2 days. After cooling to room temperature, the solvent was removed by rotary evaporation, and the residue was dissolved in chloroform and extracted by water. The collected organic portion was dried over anhydrous magnesium sulfate, and the organic solvent was dried by rotary evaporation. The residue was subjected to silica gel column chromatography (Hex/CHCl$_3$ = 1:1 as eluent) to afford the target molecule as orange powder (1.8 g, yield = 39%) ^{1}H NMR (400 MHz, CDCl$_3$): δ ppm = 7.03, 7.01 (d, J = 8.8 Hz, 8H), 6.75, 6.72 (d, J = 8.8 Hz, 8H), 3.92, 3.90, 3.89 (t, J = 6.4 Hz, 8H), 1.76−1.72 (m, 8H), 1.57−1.26 (m, 72H), 0.90, 0.88, 0.86 (t, J = 6.4 Hz, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm = 187.9, 159.4, 142.4, 132.9, 125.7, 114.1, 68.3, 32.3, 30.0, 29.8, 29.7, 29.6, 26.4, 23.1, 14.5. HRMS (APCI) m/z: [M + H]$^+$ Calcd for $C_{78}H_{117}O_6$ 1149.8845; Found 1149.8809. Mp: 57−59 °C.

Synthesis of 7,10-Bis(dodecyloxy)-2,3-bis(4-(dodecyloxy)-phenyl)triphenylene-1,4-diol, 7. To a dry round-bottom flask were added 4,4″-bis(dodecyloxy)-4′,5′-bis(4-(dodecyloxy)phenol)-[1,1′:2′,1″-terphenyl]-3′,6′-dione (**6**, 500 mg, 0.435 mmol) and dichloromethane (20 mL). Ferric chloride (280 mg, 1.74 mmol) in nitromethane (1 mL) was added dropwise into the solution. The mixture was purged with argon and stirred at room temperature for 40 min. Methanol (10 mL) was added to quench the reaction, and the mixture was stirred for another 10 min. The solvent was dried by rotary evaporation, and the residue was extracted over CHCl$_3$/H$_2$O. The collected organic portion was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. The concentrated residue was then subject to silica gel column chromatography (Hex/CHCl$_3$ = 1:1 as the eluent) to afford the product as the only identifiable compound, pale yellow powder (170 mg, yield = 34%). ^{1}H NMR (400 MHz, CDCl$_3$): δ ppm = 7.72, 7.70 (d, J = 8.4 Hz, 4H), 7.38, 7.35 (d, J = 8.8 Hz, 2H), 7.16, 7.14 (d, J = 8.8 Hz, 4H), 7.03, 7.02 (d, J = 2 Hz, 2H), 6.72−6.69 (m, 2H), 4.13, 4.11, 4.10 (t, J = 6.4 Hz, 4H), 4.00, 3.98, 3.96 (t, J = 6.8 Hz, 4H), 1.91−1.87 (m, 4H), 1.81−1.77 (m, 4H), 1.43−1.26 (m, 72H), 0.89−0.86 (m, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm = 159.6, 159.5, 159.0, 151.1, 131.7, 126.6, 122.8, 121.2, 118.0, 115.1, 111.4, 97.4, 68.9, 68.6, 32.3, 30.0, 29.9, 29.8, 29.6, 26.6, 26.4, 23.1, 14.5. Anal. Calcd for $C_{78}H_{116}O_6$: C, 81.48; H, 10.17. Found: C, 81.19; H, 10.40. APCI-MS: m/z [M]$^+$ = 1147.9. Mp: 61−63 °C.

Synthesis of 4,4″-Di-*tert*-butyl-4′,5′-bis(4-(*tert*-butyl)phenyl)-[1,1′:2′,1″-terphenyl]-3′,6′-dione, 8. To a dry round-bottom flask were added *p*-chloranil (1.00 g, 4.07 mmol), 4-*tert*-butylphenyl boronic acid (4.34 g, 24.40 mmol), Pd(PPh$_3$)$_4$ (375 mg, 0.326 mmol), potassium carbonate (4.5 g,32.56 mmol), toluene (30 mL), and water (3 mL). The mixture was degassed for 20 min and then heated to 100 °C for 2 days. After cooling to room temperature, the solvent was removed by rotary evaporation, and the residue was dissolved in chloroform and extracted by water. The collected organic portion was dried over anhydrous magnesium sulfate, and the organic solvent was dried by rotary evaporation. The residue was subject to silica gel column chromatography (Hex/CHCl$_3$ = 1:1 as eluent) to afford the target molecule as orange crystalline powder (1.2 g, yield = 45%). ^{1}H NMR (400 MHz, CDCl$_3$): δ ppm = 7.21, 7.19 (d, J = 8.4 Hz, 8H), 7.02, 7.00 (d, J = 8.4 Hz, 8H), 1.25 (s, 36H). ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm = 187.7, 151.5, 143.2, 131.1, 130.5, 124.8, 35.0, 31.6. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{46}H_{52}O_2$ 636.3962; Found 636.3964. Mp: >250 °C.

Synthesis of 3,6,11,16-Tetra-*tert*-butylbenzo[4′,5′]furo-[3′,2′:3,4]triphenyleno[1,2-*b*]benzofuran, 9. To a dry round-bottom flask were added 4,4″-di-*tert*-butyl-4′,5′-bis(4-(*tert*-butyl)-phenyl)-[1,1′:2′,1″-terphenyl]-3′,6′-dione (**8**, 500 mg, 0.786 mmol) and dry dichloromethane (10 mL). Ferric chloride (500 mg, 3.14 mmol) in nitromethane (2 mL) was added dropwise into the solution. The mixture was purged with argon and stirred at room temperature for 40 min. Methanol (10 mL) was injected into the solution to quench the reaction, and the mixture was stirred for another 10 min. The solvent was removed by rotary evaporation, and the residue was extracted by CHCl$_3$/H$_2$O. The organic portion was dried over anhydrous magnesium sulfate and concentrated by rotary evaporation. The residue was subject to silica gel column chromatography (Hex/CHCl$_3$ = 2:1) to afford the target molecule as white crystalline powder (420 mg, yield = 84%). ^{1}H NMR (400 MHz, CDCl$_3$): δ ppm = 10.00, 9.98 (d, J = 8.8 Hz, 2H), 8.83, 8.82 (d, J = 1.6 Hz, 2H), 8.52, 8.50 (d, J = 8.4 Hz, 2H), 7.95−7.93 (m, 4H), 7.64−7.62 (m, 2H), 1.57 (s, 18H), 1.54 (s, 18H). ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm = 157.1, 151.4, 151.1, 150.1, 130.7, 128.8, 126.8, 125.8, 122.5, 121.6, 121.2, 119.1, 116.9, 116.6, 109.2, 35.8, 35.5, 32.1, 31.9, 30.1. HRMS (EI) m/z: [M]$^+$ Calcd for $C_{46}H_{48}O_2$ 636.3654; Found 636.3953. Mp: >250 °C.

At the same time, 7,10-di-*tert*-butyl-2,3-bis(4-(*tert*-butyl)phenyl)-triphenylene-1,4-diol (**10**; 55 mg, yield = 11%) was isolated as pale yellow powder. ^{1}H NMR (400 MHz, CDCl$_3$): δ ppm = 7.77, 7.75 (d, 4H, J = 8 Hz), 7.66, 7.64 (d, 4H, J = 8 Hz), 7.57 (s, 2H), 7.44, 7.42 (d, 2H, J = 8.4 Hz), 7.21, 7.19 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ ppm = 158.1, 151.6, 151.5, 151.0, 131.6, 130.3, 126.0, 122.3, 122.1, 121.9, 120.1, 119.1, 109.0, 35.6, 35.3, 31.9. Anal. Calcd for $C_{46}H_{52}O_2$: C, 86.75; H, 8.23. Found: C, 86.41; H, 8.51. EI-MS: m/z [M-2H]$^+$ = 634.7. Mp: >250 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01785.

^{1}H and ^{13}C NMR spectra of all new compounds, MS spectra, crystal information on compound **9**, and computational details (PDF)

Crystallographic information for compound **9** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, *107*, 718. (b) Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem., Int. Ed.* **2013**, *52*, 9900. (c) Cao, Y.; Wang, X.-Y.; Wang, J.-Y.; Pei, J. *Synlett* **2014**, *25*, 313.

(2) Jiao, C.; Wu, J. *Synlett* **2012**, *2012*, 171.

(3) (a) Rempala, P.; Kroulík, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002. (b) Rempala, P.; Kroulík, J.; King, B. T. *J. Org. Chem.* **2006**, *71*, 5067. (c) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279. (d) Zhai, L.; Shukla, R.; Wadumethrige, S. H.; Rathore, R. *J. Org. Chem.* **2010**, *75*, 4748.

(4) (a) Niu, Q.; Zhou, Y.; Wang, L.; Peng, J.; Wang, J.; Pei, J.; Cao, Y. *Adv. Mater.* **2008**, *20*, 964. (b) Liu, N.; Zhou, Y.; Wang, L.; Peng, J.; Wang, J.; Pei, J.; Cao, Y. *Langmuir* **2009**, *25*, 665. (c) Yin, J.; Zhou, Y.; Lei, T.; Pei, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 6320. (d) Ye, Q.; Chang, J.; Huang, K. − W.; Chi, C. *Org. Lett.* **2011**, *13*, 5960. (e) Ye, Q.; Chang, J.; Shao, J.; Chi, C. *J. Mater. Chem.* **2012**, *22*, 13180. (f) Ye, Q.; Chang, J.; Huang, K. − W.; Dai, G.; Zhang, J.; Chen, Z. − K.; Wu, J.; Chi, C. *Org. Lett.* **2012**, *14*, 2786. (g) Wöhrle, T.; Kirres, J.; Kaller, M.; Mansueto, M.; Tussetschläger, S.; Laschat, S. *J. Org. Chem.* **2014**, *79*, 10143. (h) Laschat, S.; Baro, A.; Wöhrle, T.; Kirres, J. *Liq. Cryst. Today* **2016**, *25*, 48.

(5) (a) Ong, B. S.; Wu, Y.; Liu, P.; Gardner, S. *J. Am. Chem. Soc.* **2004**, *126*, 3378. (b) Narita, A.; Wang, X. − Y.; Feng, X.; Müllen, K. *Chem. Soc. Rev.* **2015**, *44*, 6616. (c) Li, X. − G.; Liao, Y.; Huang, M. − R.; Kaner, R. B. *Chem. Sci.* **2015**, *6*, 2087.

(6) See representative examples and review: (a) Kamo, M.; Tsuda, A.; Nakamura, Y.; Aratani, N.; Furukawa, K.; Kato, T.; Osuka, A. *Org. Lett.* **2003**, *5*, 2079. (b) Kurotobi, K.; Kim, K. S.; Noh, S. B.; Kim, D.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 3944. (c) Ikeda, T.; Aratani, N.; Osuka, A. *Chem. - Asian J.* **2009**, *4*, 1248. (d) Jiao, C.; Huang, K. − W.; Guan, Z.; Xu, Q. − H.; Wu, J. *Org. Lett.* **2010**, *12*, 4046. (e) Tanaka, T.; Osuka, A. *Chem. Soc. Rev.* **2015**, *44*, 943.

(7) (a) Ni, Y.; Wu, J. *Org. Biomol. Chem.* **2014**, *12*, 3774. (b) Heyer, E.; Retailleau, P.; Ziessel, R. *Org. Lett.* **2014**, *16*, 2330.

(8) (a) Dou, X.; Yang, X.; Bodwell, G. J.; Wagner, M.; Enkelmann, V.; Müllen, K. *Org. Lett.* **2007**, *9*, 2485. (b) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279. (c) Wadumethrige, S. H.; Rathore, R. *Org. Lett.* **2008**, *10*, 5139. (d) Ormsby, J. L.; Black, T. D.; Hilton, C. L.; King, B. T.; Bharat. *Tetrahedron* **2008**, *64*, 11370. (e) Pradhan, A.; Dechambenoit, P.; Bock, H.; Durola, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 12582. (f) Danz, M.; Tonner, R.; Hilt, G. *Chem. Commun.* **2012**, *48*, 377. (g) Waghray, D.; de Vet, C.; Karypidou, K.; Dehaen, W. *J. Org. Chem.* **2013**, *78*, 11147. (h) Pradhan, A.; Dechambenoit, P.; Bock, H.; Durola, F. *J. Org. Chem.* **2013**, *78*, 2266. (i) Chua, M. H.; Huang, K. − W.; Xu, J.; Wu, J. *Org. Lett.* **2015**, *17*, 4168. (j) He, J.; Mathew, S.; Kinney, Z. J.; Warrell, R. M.; Molina, J. S.; Hartley, C. S. *Chem. Commun.* **2015**, *51*, 7245. (k) He, J.; Mathew, S.; Kinney, Z. J.; Warrell, R. M.; Molina, J. S.; Hartley, C. S. *Chem. Commun.* **2015**, *51*, 7245. (l) Liu, J.; Narita, A.; Osella, S.; Zhang, W.; Schollmeyer, D.; Beljonne, D.; Feng, X.; Müllen, K. *J. Am. Chem. Soc.* **2016**, *138*, 2602.

(9) (a) Nielsen, C. B.; Brock-Nannestad, T.; Hammershøj, P.; Reenberg, T. K.; Schau-Magnussen, M.; Trpcevski, D.; Hensel, T.; Salcedo, R.; Baryshnikov, G. V.; Minaev, B. F.; Pittelkow, M. *Chem. - Eur. J.* **2013**, *19*, 3898. (b) Hensel, T.; Trpcevski, D.; Lind, C.; Grosjean, R.; Hammershøj, P.; Nielsen, C. B.; Brock-Nannestad, T.; Nielsen, B. E.; Schau-Magnussen, M.; Minaev, B.; Baryshnikov, G. V.; Pittelkow, M. *Chem. - Eur. J.* **2013**, *19*, 17097. (c) Plesner, M.; Hensel, T.; Nielsen, B. E.; Kamounah, F. S.; Brock-Nannestad, T.; Nielsen, C. B.; Tortzen, C. G.; Hammerich, O.; Pittelkow, M. *Org. Biomol. Chem.* **2015**, *13*, 5937.

(10) (a) Erdtman, H.; Högberg, H. − E. *Chem. Commun.* **1968**, *0*, 773. (b) Erdtman, H.; Hogberg, H. − E. *Tetrahedron Lett.* **1970**, *11*, 3389. (c) Berg, J. − E.; Erdtman, H.; Högberg, H. E.; Karlsson, B.; Pilotti, A. − M.; Søderholm, A. − C. *Tetrahedron Lett.* **1977**, *18*, 1831. (d) Erdtman, H.; Högberg, H.-E. *Tetrahedron* **1979**, *35*, 535−540. (e) Brock-Nannestad, T.; Nielsen, C. B.; Schau-Magnussen, M.; Hammershøj, P.; Reenberg, T. K.; Petersen, A. B.; Trpcevski, D.; Pittelkow, M. *Eur. J. Org. Chem.* **2011**, *2011*, 6320.

(11) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

(12) (a) Ogata, T.; Okamoto, I.; Doi, H.; Kotani, E.; Takeya, T. *Tetrahedron Lett.* **2003**, *44*, 2041. (b) Takeya, T.; Doi, H.; Ogata, T.; Otsuka, T.; Okamoto, I.; Kotani, E. *Tetrahedron* **2004**, *60*, 6295. (c) Rathore, R.; Abdelwahed, S. H. *Tetrahedron Lett.* **2004**, *45*, 5267. (d) Nielsen, C. B.; Brock-Nannestad, T.; Reenberg, T. K.; Hammershøj, P.; Christensen, J. B.; Stouwdam, J. W.; Pittelkow, M. *Chem. - Eur. J.* **2010**, *16*, 13030. (e) VanVeller, B.; Schipper, D. J.; Swager, T. M. *J. Am. Chem. Soc.* **2012**, *134*, 7282.

(13) Zander, M. *Chem. Ber.* **1959**, *92*, 2744−2749.

(14) Morris, J. V.; Mahaney, M. A.; Huber, J. R. *J. Phys. Chem.* **1976**, *80*, 969.

(15) (a) Han, C.; Zhang, Z.; Xu, H.; Yue, S.; Li, J.; Yan, P.; Deng, Z.; Zhao, Y.; Yan, P.; Liu, S. *J. Am. Chem. Soc.* **2012**, *134*, 19179. (b) Han, C.; Zhu, L.; Li, J.; Zhao, F.; Zhang, Z.; Xu, H.; Deng, Z.; Ma, D.; Yan, P. *Adv. Mater.* **2014**, *26*, 7070.

(16) (a) Jiang, W.; Li, Y.; Wang, Z. *Chem. Soc. Rev.* **2013**, *42*, 6113. (b) Zhang, W.; Liu, Y.; Yu, G. *Adv. Mater.* **2014**, *26*, 6898.

(17) (a) Swetha, T.; Singh, S. P. *J. Mater. Chem. A* **2015**, *3*, 18329. (b) Chueh, C. − C.; Li, C. − Z.; Jen, A. K. − Y. *Energy Environ. Sci.* **2015**, *8*, 1160.