

Synthesis and Photovoltaic Properties of Efficient Organic Dyes Containing the Benzo[b]furan Moiety for Solar Cells

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New organic dyes composed of the benzo[b]furan donor, thiophene-conjugated bridge, and cyano acrylic acid acceptor have been newly synthesized through the one-pot coupling cyclization key step. Nanocrystalline TiO₂ dye-sensitized solar cell was fabricated using this dye. A solar-to-electric conversion efficiency of 6.65% and 4.70% is achieved with 1 and 2, respectively.

Introduction

Dye-sensitized solar cells (DSSCs) are currently attracting widespread interest as low-cost alternatives to conventional solid-state photovoltaic devices.¹ Until now only three polypy-ridyl ruthenium(II) complexes have achieved power conversion efficiencies over 10% in standard air mass 1.5 sunlight.² Although the metal-complexed dyes exibited high efficiency and stability, they are quite expensive and hard to purify compared to the metal-free organic dyes. Recently, impressive photovoltaic performance has been obtained with some organic

coumarin,³ indoline,⁴ oligoene,⁵ merocyanine,⁶ and hemicyanine dyes⁷ having efficiencies in the range of 5–9%. Nevertheless,

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 ^{(1) (}a) O'Regan, B.; Grätzel, M. Nature 1991, 353, 737. (b) Grätzel,
 M.; Nature 2001, 414, 338. (c) Yanagida, M.; Yamaguchi, T.; Kurashige,
 M.; Hara, K.; Katoh, R.; Sugihara, H.; Arakawa, H. Inorg. Chem. 2003,
 42, 7921. (d) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin,
 S. M.; Grätzel, M. J. Am. Chem. Soc. 2005, 127, 808. (e) Jang, S.-R.; Lee,
 C.; Ko, J.; Lee, J.; Vittal, R.; Kim, K.-J. Chem. Mater. 2006, 18, 5604.

^{(2) (}a) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru.B.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835. (b) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613.

^{(3) (}a) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. J. Phys. Chem. B 2003, 107, 597. (b) Hara, K.; Kurashige, M.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. New J. Chem. 2003, 27, 783. (c) Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. Chem. Commun. 2001, 569.

^{(4) (}a) Horiuchi, T.; Miura, H.; Uchida, S. Chem. Commun. 2003, 3036.
(b) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. J. Am. Chem. Soc. 2004, 126, 12218. (c) Schmidt-Mende, L.; Bach, U.; Humphry-Baker, R.; Horiuchi, T.; Miura, H.; Ito, S.; Uchida, S.; Grätzel, M. Adv. Mater. 2005, 17, 813. (d) Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Péchy, P.; Takada, M.; Miura, H.; Uchida, S.; Grätzel, M. Adv. Mater. 2006, 18, 1202.

many organic dyes have often presented low conversion efficiency and low operation stability compared to metalcomplexed dyes. The major factor for the low conversion efficiency of many organic dyes in the DSSCs is due to the formation of dye aggregates on the semiconductor surface. The low stability of organic dyes is due to the formation of unstable radical species during redox reaction cycles.

Thus, we became interested in the development of efficient new organic dyes, which are not aggregated and stable. The highly efficient organic dyes have an almost push—pull structure such as nonlinear optical molecules, which are composed of a donor, conjugated bridge, and acceptor, and many researchers have attempted to create organic dyes through the structural modification of each donor,^{3a,4a,5a} conjugated bridge,^{3c,4a,5b,8} or acceptor unit.^{3a} Among these approaches, we are especially interested in the structural modification of the organic dye's donor unit and concerned about their structures and related efficiencies for DSSC.

Very recently, we reported highly efficient and stable organic dyes that have a bis-dimethylfluorenyl amino phenyl donor unit.⁹ The bis-dimethylfluorenyl moiety was introduced to prevent aggregation *via* molecular stacking by the bulky nonplanar structure and to ensure greater resistance to degradation when exposed to light and high-temperature.¹⁰

In this article, as part of our efforts to develop more efficient organic dyes, we report new organic dyes containing [bis(9,9-dimethylfluoren-2-yl)amino]benzofuran as the electron donor and cyanoacrylic acid as the electron acceptor bridged by a thiophene unit. Although many structural frameworks such as coumarin, aniline, and indoline have been employed as good electron donor units, an organic dye containing the benzo[*b*]-furan structural motif has never been explored for DSSCs.

Results and Discussion

Scheme 1 illustrates the synthetic procedures of organic dyes 1 and 2 starting from 2-iodo-5-nitrophenol acetate 3 and 4-[bis-(9,9-dimethylfluoren-2-yl)amino]-2- hydroxybenzaldehyde 8¹¹ The key step in the synthesis of 1 and 2 relies on the cyclization of 3 and 9. Organic dye 1 was prepared by one-pot coupling cyclization of 3 and 2-trimethylsilylacetyl-5-thiophene-carboxyaldehyde 2,2-dimethylpropane-1,3-diyl acetal¹² followed by reduction of the nitro group in **4** using Raney Ni¹³ and N-arylation under Ullmann conditions.¹⁴ Subsequent cleavage of the 1,3-dioxalane protecting group in aqueous acid produced the free aldehyde **7**. The aldehyde, upon reaction with cyanoacetic acid in the presence of a catalytic amount of piperidine in CH₃CN, produced the **1** dye. Organic dye **2** was prepared by alkylation of **8** with bromoacetaldehyde diethyl acetal followed by ring closure reaction of **9**¹⁵ and coupling reaction of aldehyde **10** with phosphonate under Horner–Emmons–Wittig coupling conditions using potassium *tert*-butoxide in THF.¹⁶ The thiophene derivative **11** was converted into thiophene-aldehyde **12** which produced the organic dye **2** upon treatment with cyanoacetic acid.

Figure 1 shows the UV/vis spectrum of the 1 sensitizer measured in ethanol solution, and the data is collected in Table 1. The absorption spectrum of the 1 sensitizer shows two absorption maxima of 463 nm ($\epsilon = 25\ 300\ \text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$) and 358 nm ($\epsilon = 36700 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) which are due to the $\pi - \pi^*$ transitions of the conjugated molecule. Under similar conditions, the 2 sensitizer exhibits absorption bands at 479 nm $(\epsilon = 33\ 300\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}})$ and 367 nm ($\epsilon = 40\ 600\ \mathrm{dm^3}$ $mol^{-1} cm^{-1}$) that are red-shifted compared to the 1 sensitizer. When the 1 sensitizer was absorbed to TiO_2 electrode, a slight red shift from 463 to 468 nm was found due to the interaction of the anchoring group with the surface titanium anions. The absorption spectrum of the 1 on the TiO₂ electrode is broadened. Similar broadening and red shift have been reported in several organic dyes on TiO₂ electrodes.^{6,16} When the **1** sensitizer is excited within its $\pi - \pi^*$ bands in an air-equilibrated solution at 298 K, it exhibits strong luminescence maximum at 627 nm.

To thermodynamically evaluate the possibility of electron transfer from the excited-state of the dye to the conduction band of the TiO₂ electrode, a cyclic voltammogram was carried out to determine the redox potentials (Table 1). The redox potentials of two organic dyes on TiO₂ films were measured in MeCN with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBA- PF_6). The reference electrode was a silver wire calibrated with Fc/Fc⁺ as an internal reference. The two organic dyes absorbed on TiO₂ films showed quasireversible behaviors. The oxidation potential of 1 dye was measured to be 0.60 V vs Fc/Fc^+ , an oxidation potential energetically favorable for iodide oxidation. The reduction potential of **1** dye calculated from the oxidation potential and the E_0-0 determined from the intersection of absorption and emission spectra is listed in Table 1. The excitedstate oxidation potential (E_{OX}^*) of the dyes (1: -1.70 V vs Fc/Fc⁺, -1.07 V vs NHE; 2: -1.67 V vs Fc/Fc⁺, -1.04 V vs NHE) are much more negative than the conduction band level of TiO_2 at approximately -0.5 V vs NHE.

In order to obtain the geometrical configuration and characteristic features of the electronic structure, molecular orbital

^{(5) (}a) Hara, K.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H.; *Chem. Commun.* **2003**, 252. (b) Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S.; *Chem. Mater.* **2004**, *16*, 1806. (c) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Yoshihara, T.; Murai, M.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Arakawa, H. *Adv. Funct. Mater.* **2005**, *15*, 246.

^{(6) (}a) Sayama, K.; Tsukagoshi, S.; Hara, K.; Ohga, Y.; Shinpou, A.; Abe, Y.; Suga, S.; Arakawa, H. *J. Phys. Chem. B.* **2002**, *106*, 1363. (b) Sayama, K.; Hara, K.; Mori, N.; Satsuki, M.; Suga, S.; Tsukagoshi, S.; Abe, Y.; Sugihara, H.; Arakawa, H. *Chem. Commun.* **2000**, 1173.

^{(7) (}a) Yao, Q.-H.; Shan, L.; Li, F.-Y.; Yin, D.-D.; Huang, C.-H. New J. Chem. 2003, 27, 1277. (b) Wang, Z.-S.; Li, F.-Y.; Huang, C.-H. Chem. Commun. 2000, 2063

^{(8) (}a) Li, S. L.; Jiang, K. J.; Shao, K. F.; Yang, L. M. *Chem. Commun.* **2006**, 2792. (b) Koumura, N.; Wang, Z. X. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256. (c) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *Chem. Commun.* **2006**, 2245.

⁽⁹⁾ Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J.-H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, Md. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701.

^{(10) (}a) Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto, K.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11021. (b) Kim, S.; Song, K.-H.; Kang, S. O.; Ko, J. *Chem. Commun.* **2004**, 68.

⁽¹¹⁾ Dai, W.-M.; Lai, K. W. Tetrahedron Lett. 2002, 43, 9377.

^{(12) (}a) Osuka, A.; Fujikane, D.; Shinmori, H.; Kobatake, S.; Irie, M. *J. Org. Chem.* **2001**, *66*, 3913. (b) Shultz, D. A.; Gwaltney, K. P.; Lee, H. *J. Org. Chem.* **1998**, *63*, 4034.

⁽¹³⁾ Plé, P. A.; Green, T. P.; Hennequin, L. F.; Curwen, J.; Fennell, M.; Allen, J.; Lambert van der Brempt, C.; Costello, G. J. Med. Chem. 2004, 47, 871.

⁽¹⁴⁾ Bushby, R. J.; McGill, D. R.; Ng, K. M.; Taylor, N. J. Mater. Chem. 1997, 7, 2343.

⁽¹⁵⁾ Yoshimura, H.; Yoshimura, H.; Kikuchi, K.; Hibi, S.; Tagami, K.; Satoh, T.; Yamauchi, T.; Ishibahi, A.; Tai, K.; Hida, T.; Tokuhara, N.; Nagai, M. J. Med. Chem. **2000**, *43*, 2929.

⁽¹⁶⁾ Zhang, C.; Harper, A. W.; Dalton, L. R. Synth. Commun. 2001, 31, 1361.



calculation of **1** was performed with B3LYP/3-21G*. The HOMO is delocalized over the π -conjugated system via the amino unit through benzo[*b*]furan moiety. Examination of the HOMO and LUMO of **1** indicates that HOMO–LUMO excitation moved the electron distribution from the bisdimeth-ylfluorenyl amino framework to the cyanoacrylic acid group (Figure 2). Therefore, the change in electron distribution induced by photoexcitation results in an efficient charge separation. The **2** dye showed similar configuration geometry to **1**.

For the preparation of DSSC, the washed FTO (8 Ω sq⁻¹, 2.3 mm thickness) glass plate was immersed in 40 mM TiCl₄ of aqueous solution at 60 °C for 30 min and washed with water and ethanol as reported by the Grätzel group.¹⁸ A transparent nanocrystalline layer on the FTO glass plate was prepared by

screen printing TiO₂ paste (13 nm anatase) and was sintered at 450 °C for 30 min. Then, a paste for the transparent layer was coated with a scattering layer (HWP-400) and was again sintered at 450 °C for 30 min. The resulting layer was composed of a 13 μ m thick transparent layer and 10 μ m thick scattering layer. The TiO₂ electrodes were treated again by NbCl₅ followed by oxidation at 500 °C for 30 min. The TiO₂ electrode was immersed into the 1 solution (0.3 mM dye in ethanol containing 10 mM 3a,7a-dihydroxy-5b-cholic acid (Cheno)) and kept at room temperature for 18 h. The chenodeoxycholic acid was added to the dye solution to enhance the cell efficiency of dye on the TiO₂ electrode.¹⁹ A counter electrode was coated with a drop of H₂PtCl₆ solution (2 mg Pt in 1 mL ethanol) on a FTO plate and heated at 400 °C for 15 min. The dye-adsorbed TiO₂ electrode and Pt counter electrode were assembled into a sealed sandwich type cell by heating with a Surlyn film (25 μ m thickness) as a spacer between the electrode. The electrolyte was then introduced into the cell, which was composed of 0.6

^{(17) (}a) Nüesch, F.; Moser, J. E.; Shklover, V.; Grätzel, M. J. Am. Chem. Soc. **1996**, 118, 5420. (b) Li, S.-L.; Jiang, K.-J.; Shao, K.-F.; Yang, L.-M. Chem. Commun. **2006**, 2792.

⁽¹⁸⁾ Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. J. Am. Chem. Soc. **1993**, 115, 6382.

⁽¹⁹⁾ Kay, A. Grätzel, M. J. Phys. Chem. 1993, 97, 6272.



FIGURE 1. Absorption and emission spectra of the 1 (blue line) dye and 2 (red line) in EtOH compared with the absorption spectrum of the dye anchored to TiO_2 (dashed line). The emission spectra (dotted line) were obtained by exciting the same solution at 450 nm at 298 K. The concentration for the solution was 10^{-5} M.

TABLE 1. Optical, Redox, and DSSC Performance Parameters of Dyes

dye	λ_{abs} , ^{<i>a</i>} nm (ϵ /dm ³ M ⁻¹ cm ⁻¹)	$E_{\mathrm{ox}},^{b}(\Delta E_{\mathrm{p}})/\mathrm{V}$	E_{0-0} , ^c eV	$E_{\text{LUMO}},^d \text{V}$	$J_{\rm sc}({\rm mA~cm^{-2}})$	$V_{\rm oc}({ m V})$	FF	η^{e} (%)
1 2	463 (25300) 479 (33300)	0.60 (0.36) 0.52 (0.28)	2.30 2.19	-1.70 -1.67	$\begin{array}{c} 14.39 \pm 0.25 \\ 11.43 \pm 0.22 \end{array}$	$\begin{array}{c} 0.70 \pm 0.01 \\ 0.67 \pm 0.01 \end{array}$	$\begin{array}{c} 0.66 \pm 0.01 \\ 0.62 \pm 0.02 \end{array}$	$\begin{array}{c} 6.65 \pm 0.20 \\ 4.70 \pm 0.15 \end{array}$

^{*a*} Absorption spectra were measured in ethanol solution. ^{*b*} Oxidation potential of dyes on TiO₂ was measured in CH₃CN with 0.1 M (n-C₄H₉)₄NPF₆ with a scan rate of 50 mVs⁻¹ (vs Fc/Fc⁺). ^{*c*} E_{0-0} was determined from the intersection of absorption and emission spectra in ethanol. ^{*d*} E_{LUMO} was calculated by $E_{ox} - E_{0-0}$. ^{*e*} Performances of DSSCs were measured with 0.18 cm² working area. ϵ : absorption coefficient; E_{ox} : oxidation potential; ΔE_p : $E_{pa} - E_{pc}$; E_{0-0} : voltage of intersection point between absorption and emission spectra; J_{sc} : short-circuit photocurrent density; V_{oc} : open-circuit photovoltage; FF: fill factor; η : total power conversion.



FIGURE 2. Isodensity surface plots of the HOMO and LUMO of 1 (a) and 2 (b).

M 3-hexyl-1,2-dimethylimidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidium thiocyanate, and 0.28 M *tert*butylpyridine in acetonitrile. The photovoltaic measurements were recorded under the simulated AM 1.5 irradiation (1000 W xenon light).

The *J-V* curve and incident mono-chromatic photon-to-current conversion efficiency (IPCE) for the DSSCs based on the **1** and

2 dyes are presented and compared with N719 dye in Figure 3. Under standard global AM 1.5 solar conditions, the **1** and **2** sensitized cell gave the short circuit photocurrent density (J_{sc}) of 14.39 ± 0.25 and 11.43 ± 0.22 mA cm⁻², open circuit voltage (V_{oc}) of 0.70 ± 0.01 and 0.67 ± 0.01 V and a fill factor of 0.66 ± 0.01 and 0.62 ± 0.02, corresponding to an overall conversion efficiency η , derived from the equation: $\eta = J_{sc}V_{oc}$ -



FIGURE 3. J-V curves of DSSCs prepared with film of N719 (--), 1 (----), and 2 (---). The inset shows IPCE spectra of DSSCs containing 1 and 2. Light intensity was 100 mW/cm².

FF/light intensity, of 6.65 \pm 0.20 and 4.70 \pm 0.15%, respectively. In the same condition, the N719 sensitized cell gave a $J_{\rm sc}$ of 18.44 \pm 0.40 mA cm⁻², $V_{\rm oc}$ of 0.75 \pm 0.01 V and a fill factor of 0.67 \pm 0.01, corresponding to η of 9.16 \pm 0.25%. The IPCE data of **1** and **2** sensitizer plotted as a function of excitation wavelength exhibits a high plateau at 77% and 66%, respectively.

From these results, we have observed that the $V_{\rm oc}$ and $J_{\rm sc}$ of dye 1 were higher than that of dye 2 even though dye 2 exhibited a similar LUMO level and greater absorption strength. The 2 had a more enhanced optical data than the 1 dye. To explain these results clearly, we investigated the amounts of 1 and 2 adsorbed on TiO2 film. However, we cannot explain the differences of their adsorbed amounts because they were very similar. On the other hand, we believed that because the more conjugated organic dyes with a vinyl bridge unit are more flexible on TiO₂ surface than that of short conjugated dye or rigid conjugated dyes, the flexible conjugated organic dyes can lie on the neighboring TiO₂ surface and can affect the electronic state of the band potential of the TiO₂ conduction band, and these effects can reduce the electron injection efficiency from dye to TiO₂. Thus, the J_{sc} and V_{oc} of dye **2** may be lower than that of dye 1 due to these reasons. Now, we are working on finding evidence to support these explanations.

Conclusion

This work has demonstrated that the two organic dyes, 1 and 2 containing bis-dimethylfluorenyl amino benzo[*b*]furan moiety are very efficient dyes for dye-sensitized solar cells. And that dye 1 was newly synthesized through the one-pot coupling cyclization key step. We believe that the development of alternative highly efficient organic dyes to ruthenium complexes is possible through more sophisticated structural modifications, and these works are now in progress.

Experimental Section

Cyclovoltagram. A three-electrode system was used and consisted of a gold disk, working electrode, and a platinum wire electrode. Redox potential of dyes on TiO_2 were measured in CH₃-CN with 0.1M (n-C₄H₉)₄N-PF₆ a scan rate between 50 mVs⁻¹ (vs Fc/Fc⁺).

2-Trimethylsilylethynyl-5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophene. A mixture of 2-bromo-5-thiophenecarboxyaldehyde 2,2dimethylpropane-1,3-diyl acetal (1.40 g, 5.1 mmol), trimethylsilylacetylene (0.78 mL, 5.6 mmol), Pd(PPh₃)₄ (5 mol %), and CuI (5 mol %) were dissolved in degassed triethylamine (30 mL). The solution was refluxed for 8 h. After the solution was cooled, H₂O (30 mL) and dichloromethane (50 mL) were added to the solution. The organic layer was separated and dried with MgSO₄. The organic layer was removed in vacuo. The pure product was obtained brown oil by silica gel chromatography (eluent MC:Hx = 1:1, $R_{\rm f} = 0.4$) to afford acetal (1.38 g) in 92% yield. ¹H NMR (CDCl₃): δ 7.09 (d, J = 3.90 Hz, 1H), 6.95 (d, J = 3.90 Hz, 1H), 5.56 (s, 1H), 3.73 (d, J = 11.10 Hz, 2H), 3.60 (d, J = 11.10 Hz, 2H), 1.25 (s, 3H),0.79 (s, 3H), 0.24 (s, 9H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (CDCl₃): δ 143.1, 132.2, 124.8, 123.6, 99.1, 97.9, 97.7, 77.6, 30.3, 23.0, 21.9, 0.0. MS: m/z 294 [M⁺]. Anal. Calcd. for C₁₅H₂₂SSiO₂: C, 61.18; H, 7.53. Found: C, 61.02; H, 7.44.

2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophene-2-yl)-6-nitrobenzofuran (4). A mixture of 3 (1.00 g, 3.8 mmol), 2-trimethylsilylethynyl-(5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophene (1.11 g, 3.8 mmol), K₂CO₃ (1.05 g, 7.6 mmol), Pd(PPh₃)₄ (5 mol %), and CuI (5 mol %) were dissolved in degassed diethylamine (10 mL) and acetonitrile (50 mL). The solution was refluxed for 8 h. After the solution was cooled, H₂O (30 mL) and dichloromethane (50 mL) were added to the solution. The organic layer was separated and dried with MgSO₄. The organic layer was removed in vacuo. The pure product 4 was obtained by silica gel chromatography (eluent MC:Hx = 1:1, $R_f = 0.4$) to afford **4** (0.12 g) in 44% yield. Mp: 142 °C. ¹H NMR (CDCl₃)): δ 8.37 (s, 1H), 8.17 (d, J = 8.70 Hz, 1H), 7.60 (d, J = 8.70 Hz, 1H), 7.48 (d, J = 3.90 Hz, 1H), 7.16 (d, J = 3.90 Hz, 1H), 6.92 (s, 1H), 5.67 (s, 1H) 3.79 (d, J = 11.40Hz, 2H), 3.67 (d, J = 11.40 Hz, 2H), 1.30 (s, 3H), 0.82 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 156.6, 144.3, 143.5, 135.4, 134.3, 131.9, 126.2, 120.4, 119.3, 116.2, 107.6, 101.2, 97.9, 77.7, 30.4, 23.1, 21.9. MS: *m*/*z* 359 [M⁺]. Anal. Calcd. for C₁₈H₁₇NO₅S: C, 60.15; H, 4.77. Found: C, 59.87; H, 4.68.

2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophene-2-yl)-6-aminobenzofuran (5). Methanol (30 mL), Raney nickel (0.020 g), and hydrazine hydrate (0.097 mL, 2 mmol) were warmed to 55-60 °C, and 4 (0.18 g, 0.5 mmol) was added portionwise. The reaction mixture was then heated to reflux for 5 h. The catalyst was removed by filtration, the solvent evaporated, and the residue dissolved in water and extracted with dichloromethane. The organic phase was dried over magnesium sulfate and the solvent evaporated. The pure product 5 was obtained by silica gel chromatography (eluent MC, $R_f = 0.5$) to afford 5 (0.064 g) in 39% yield. Mp: 160 °C. ¹H NMR (CDCl₃)): δ 7.28 (d, J = 8.10 Hz, 1H), 7.25 (d, J = 3.60 Hz, 1H), 7.08 (d, J = 3.60 Hz, 1H), 6.79 (s, 1H), 6.72 (s, 1H), 6.59 (d, J = 8.10 Hz, 1H), 5.64 (s, 1H), 3.77 (d, J = 11.40Hz, 2H), 3.65 (d, J = 11.40 Hz, 2H), 1.30 (s, 3H), 0.80 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 156.2, 149.3, 144.7, 140.6, 134.1, 125.8, 122.8, 121.2, 121.0, 112.5, 101.5, 98.2, 97.3, 77.6, 30.3, 23.0, 21.9. MS: *m/z* 329 [M⁺]. Anal. Calcd. for C₁₈H₁₉NO₃S: C, 65.63; H, 5.81. Found: C, 65.39; H, 5.68.

2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophene-2-yl)-6-*N*,*N*-bis-(**9,9-dimethylfluoren-2-yl)aminobenzofuran** (**6**). A stirred mixture of **5** (0.2 g, 0.6 mmol), 2-iodo-9,9-dimethylfluorene (0.42 g, 1.3 mmol), powdered anhydrous potassium carbonate (0.36 g, 2.7 mmol), copper bronze (0.13 g, 0.2 mmol), 18-crown-6 (0.02 g, 0.07 mmol), and 1,2-dichlorobenzene (40 mL) was refluxed for 48 h. After cooling, the insoluble inorganic material was filtered off under suction and the dark brown filtrate collected. The insoluble material was washed with dichloromethane (3 × 30 mL). The combined filtrate and organic phase was washed with dilute aqueous ammonia and water and dried with magnesium sulfate. The solvent was removed under reduced pressure. The pure product **6** was obtained by silica gel chromatography (eluent MC:Hx = 1:1, $R_f = 0.5$) to afford **6** (0.22 g) in 51% yield. Mp: 193 °C. ¹H NMR (CDCl₃)): δ 7.70 (s, 1H), 7.65 (d, J = 6.90 Hz, 2H), 7.59 (d, J = 7.80 Hz, 2H), 7.42 (d, J = 8.10 Hz, 1H), 7.39 (d, J = 6.90 Hz, 2H), 7.35 (d, J = 7.80 Hz, 2H), 7.35 (t, J = 7.80 Hz, 2H), 7.32 (t, J = 7.80 Hz, 2H), 7.31 (d, J = 7.80 Hz, 2H), 7.28 (s, 2H), 7.15–7.05 (m, 3H), 6.82 (s, 1H), 5.64 (s, 1H) 3.77 (d, J = 11.10 Hz, 2H), 3.65 (d, J = 11.10 Hz, 2H), 1.42 (s, 12H), 1.39 (s, 3H), 0.81 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 166.8, 156.4, 155.2, 153.7, 139.3, 134.4, 132.2, 127.1, 126.5, 126.0, 125.1, 122.6, 120.8, 119.6, 118.4, 117.4, 112.5, 111.6, 107.3, 105.8, 101.5, 101.0, 98.2, 95.7, 93.0, 72.0, 47.0, 30.3, 27.2, 23.1, 21.9 MS: m/z 713 [M⁺]. Anal. Calcd. for C₄₈H₄₃NO₃S: C, 80.75; H, 6.07. Found: C, 80.42; H, 5.97.

2-(5-Formylthiophene-2-yl)-6-bis(9,9-dimethylfluoren-2-yl)aminobenzofuran (7): THF (30 mL) and water (10 mL) were added to a flask containing 6 (0.1 g, 0.14 mmol). Then, TFA (2 mL) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried MgSO₄. The organic layer was removed in vacuo. The pure product 7 was obtained by silica gel chromatography (eluent EA:Hx = 1:2, $R_f = 0.5$) to afford 7 (0.06 g) in 70% yield. Mp: 188 °C. ¹H NMR (CDCl₃): δ 9.90 (s, 1H), 7.71 (d, J = 3.60 Hz, 1H), 7.63 (d, J = 6.90 Hz, 2H), 7.59 (d, J =7.80 Hz, 2H), 7.46 (s, 1H), 7.45 (d, J = 3.60 Hz, 1H), 7.40 (d, J = 6.90 Hz, 2H), 7.33 (t, J = 7.80 Hz, 2H), 7.32 (t, J = 7.80 Hz, 2H), 7.28 (d, J = 8.10 Hz, 1H), 7.24 (s, 2H), 7.16 (d, J = 8.10 Hz, 1H), 7.12 (d, J = 7.80 Hz, 2H), 7.06 (s, 1H), 1.42 (s, 12H). ¹³C-{¹H} NMR (CDCl₃): δ 182.6, 156.8, 155.4, 153.7, 149.7, 147.5, 147.1, 142.5, 139.1, 137.1, 134.6, 127.2, 126.8, 124.3, 124.0, 123.5, 122.7, 121.6, 121.2, 120.8, 119.6, 118.9, 112.3, 106.7, 105.1, 47.0, 27.2. MS: m/z 627 [M⁺]. Anal. Calcd. for C₄₃H₃₃NO₂S: C, 82.27; H, 5.30. Found: C, 82.09; H, 5.22.

(E)-3-(5-(6-(Bis(9,9-dimethylfluoren-2-yl)amino)benzofuran-2-yl)thiophene-2-yl)-2-cyanoacrylic Acid (1): A mixture of 7 (0.03 g, 0.05 mmol) and cyanoacetic acid (0.01 g, 0.1 mmol) were vacuum-dried and added MeCN (60 mL) and piperidine (0.003 mL). The solution was refluxed for 6 h. After the solution was cooled, the organic layer was removed *in vacuo*. The pure product **1** was obtained by silica gel chromatography (eluent EA:MeOH = 10:1, $R_{\rm f} = 0.1$) to afford 1 (0.016 g) in 47% yield. Mp: 229 °C. ¹H NMR (DMSO): δ 8.03 (s, 1H), 7.75 (d, J = 8.10 Hz, 2H), 7.74 (d, J = 7.50 Hz, 2H), 7.69 (d, J = 3.60 Hz, 1H), 7.63 (d, J = 3.60 Hz)Hz, 1H), 7.60 (d, J = 8.40 Hz, 1H), 7.50 (d, J = 7.50 Hz, 2H), 7.40 (s, 1H), 7.32 (t, J = 8.10 Hz, 2H), 7.30–7.26 (m, 4H), 7.10 (s. 1H), 7.05 (d, J = 8.40 Hz, 1H), 7.04 (d, J = 8.10 Hz, 2H), 1.37 (s, 12H). ¹³C{¹H} NMR (DMSO): δ 158.2, 155.2, 154.8, 153.2, 146.9, 145.7, 138.3, 137.4, 136.6, 133.8, 127.9, 127.5, 127.1, 125.0, 124.3, 123.1, 122.8, 121.2, 119.6, 118.1, 117.6, 116.9, 114.2, 109.0, 107.2, 104.6, 104.0, 99.6, 46.5, 26.7. MS: m/z 694 [M⁺]. Anal. Calcd. for C₄₆H₃₄N₂O₃S: C, 79.51; H, 4.93. Found: C, 79.48; H, 4.90.

3-(N,N-Bis(9,9-dimethylfluoren-2-yl)aminoanisole. A stirred mixture of m-aminoanisole (1.04 mL, 9.23 mmol), 2-iodo-9,9dimethylfluorene (6.5 g, 20.3 mmol), powdered anhydrous potassium carbonate (5.62 g, 40.6 mmol), copper bronze (1.93 g, 30.5 mmol), 18-crown-6 (0.29 g, 1.11 mmol), and 1,2-dichlorobenzene (70 mL) was refluxed for 48 h. After cooling, the insoluble inorganic material was filtered off and the dark brown filtrate was collected. The insoluble material was washed with dichloromethane $(3 \times 50 \text{ mL})$. The combined filtrate and organic phase was washed with dilute aqueous ammonia and water and dried with magnesium sulfate. The solvent was removed under reduced pressure. The pure product was obtained by silica gel chromatography (eluent MC: Hx = 1:2, $R_f = 0.4$) in 41% yield (1.92 g). Mp: 243 °C. ¹H NMR (CDCl₃): δ 7.66 (d, J = 7.50, 2H), 7.60 (d, J = 8.40 Hz, 2H), 7.40 (d, J = 7.50 Hz, 2H), 7.32 (t, J = 8.40 Hz, 2H), 7.30 (t, J =8.40 Hz, 2H), 7.25 (s, 2H), 7.18 (t, J = 8.10 Hz, 1H), 7.10 (d, J = 8.40 Hz, 2H), 6.78 (d, J = 8.10 Hz, 2H), 6.76 (s, 1H), 6.61 (d, J = 8.10 Hz, 1H), 3.72 (s, 3H), 1.42 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ 160.6, 155.1, 153.7, 149.4, 147.5, 139.1, 134.3, 129.9, 127.1, 126.6, 123.4, 122.6, 120.7, 119.5, 118.8, 116.5, 109.6, 108.5, 55.3, 46.9, 27.2. MS: m/z 507 [M⁺]. Anal. Calcd. for C₃₇H₃₃NO: C, 87.54; H, 6.55. Found: C, 87.30; H, 6.43.

3-(N,N-Bis(9,9-dimethylfluoren-2-yl)aminophenol. 3-(N,N-Bis-(9.9-dimethylfluoren-2-yl)aminoanisole (0.13 g, 0.26 mmol) was dissolved in CH₂Cl₂ (50 mL). BBr₃ (0.05 mL, 0.52 mol) was added dropwise into the solution at-78 °C. The mixture was further stirred for 8 h at room temperature. Saturated aqueous Na₂CO₃ (30 mL) was added to quench the reaction. The organic layer was separated. The aqueous layer was extracted with dichloromethane (2×50) mL). The combined extracts were washed with water and dried with MgSO₄. The organic layer was removed in vacuo. The pure product phenol was obtained by silica gel chromatography (eluent MC:Hx = 1:1, $R_f = 0.1$), 66% yield (0.085 g). Mp: 221 °C. ¹H NMR (CDCl₃): δ 7.65 (d, J = 7.80, 2H), 7.60 (d, J = 8.10 Hz, 2H), 7.40 (d, J = 7.80 Hz, 2H), 7.32 (t, J = 8.10 Hz, 2H), 7.29 (t, J = 8.10 Hz, 2H), 7.23 (s, 2H), 7.13 (t, J = 7.80 Hz, 1H), 7.10 (d, J = 8.10 Hz, 2H), 6.77 (d, J = 7.80 Hz, 1H), 6.66 (s, 1H), 6.51 (d, J = 7.80 Hz, 1H), 1.41 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ 156.5, 155.2, 153.7, 149.6, 147.4, 139.1, 134.4, 130.2, 127.1, 126.6, 123.5, 122.6, 120.7, 119.6, 119.0, 116.5, 110.8, 119.6, 47.0, 27.2. MS: m/z 493 [M⁺]. Anal. Calcd. for C₃₆H₃₁NO: C, 87.59; H, 6.33. Found: C, 87.36; H, 6.19.

4-(Bis(9,9-dimethylfluoren-2-yl)amino)-2-hydroxybenzaldehyde (8). A mixture of POCl₃ (1.05 g, 10.9 mmol) in DMF (10 mL) was cooled at 0 °C. 3-(N,N-Bis(9,9-dimethylfluoren-2-yl)aminophenol (2.7 g, 5.47 mmol) was dissolved in DMF (20 mL). The POCl₃ solution was then added dropwise into 3-(N,N-bis(9,9dimethylfluoren-2-yl)aminophenol at 0 °C. The reaction mixture was reacted for 2 h and then hydrolyzed with water (40 mL) for 6 h. The crude product was extracted with CH_2Cl_2 (3 \times 50 mL). The combined extracts were washed with water and dried with MgSO₄. The organic layer was removed in vacuo. The pure product 8 was obtained by silica gel chromatography (eluent MC:Hx = 1:1, $R_{\rm f} = 0.1$) to afford **8** (1.97 g) in 69% yield. Mp: 196 °C. ¹H NMR (CDCl₃): δ 11.43 (s, 1H), 9.63 (s, 1H), 7.69 (d, J = 8.10Hz, 4H), 7.42 (d, J = 8.10 Hz, 2H), 7.35 (t, J = 8.10 Hz, 2H), 7.33 (t, J = 11.10 Hz, 2H), 7.31 (d, J = 8.40 Hz, 1H), 7.25 (s, 2H), 7.2 (d, J = 8.10 Hz, 2H), 6.62 (d, J = 8.40 Hz, 1H), 6.50 (s, 1H), 1.43 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ 192.5, 163.8, 155.8, 155.6, 153.9, 145.1, 138.6, 136.9, 134.8, 127.4, 127,3, 125.7, 122.8, 121.1, 120.3, 114.7, 113.0, 111.6, 105.5, 47.1, 27.2. MS: m/z 521 [M⁺]. Anal. Calcd. for C₃₇H₃₁NO₂: C, 85.19; H, 5.99. Found: C, 84.92; H, 5.78.

4-(Bis(9,9-dimethylfluoren-2-yl)amino)-2-(2,2-diethoxyethoxy)benzaldehyde (9). A solution of 8 (0.47 g, 0.92 mmol), K₂CO₃ (0.25 g, 1.84 mmol), and bromoacetaldhyde diethylacetal (0.14 mL, 0.92 mmol) in DMF (50 mL) was refluxed for 6 h. DMF was removed under reduced pressure. The crude mixture was redissolved in ethyl acetate (100 mL). The organic layer was washed with water (100 mL) and collected. The aqueous layer was extracted with ethyl acetate (2 \times 50 mL). The combined extracts were dried with MgSO₄. The organic layer was removed in vacuo. The pure product 9 was obtained by silica gel chromatography (eluent EA:Hx = 1:5, $R_{\rm f} = 0.5$) to afford 9 (1.08 g) in 72% yield. Mp: 131 °C. ¹H NMR (CDCl₃): δ 10.41 (s, 1H), 7.80 (d, J = 8.40 Hz, 1H), 7.71 (d, J =7.80 Hz, 4H), 7.44 (d, J = 7.80 Hz, 2H), 7.38 (s, 2H), 7.31 (t, J = 7.80 Hz, 4H), 7.23 (d, J = 7.80 Hz, 2H), 6.77 (d, J = 8.40 Hz, 1H), 6.74 (s, 1H), 4.85 (t, J = 5.10 Hz, 1H), 3.92 (d, J = 5.10 Hz, 2H), 3.75 (m, 2H), 3.61 (m, 2H), 1.48 (s, 12H), 1.22 (t, J = 6.60Hz, 6H),. ¹³C{¹H} NMR (CDCl₃): δ 187.4, 162.2, 155.2, 154.8, 153.5, 145.4, 138.4, 136.2, 129.4, 127.1, 124.9, 122.5, 120.9, 120.4, 119.7, 118.5, 113.2, 103.2, 100.2, 68.9, 62.9, 62.3, 46.8, 26.9, 15.2. MS: m/z 637 [M⁺]. Anal. Calcd. for C₄₃H₄₃NO₄: C, 80.97; H, 6.80. Found: C, 80.68; H, 6.66.

6-(Bis(9,9-dimethylfluoren-2-yl)amino)-2-formylbenzofuran (10). A solution of 9 (0.13 g, 0.20 mmol) in acetic acid (50 mL) was refluxed for 6 h. Saturated aqueous NaHCO₃ (50 mL) and dichloromethane were added to quench the reaction. The organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 50 mL). The combined extracts were dried with MgSO₄. The organic layer was removed *in vacuo*. The pure product **10** was obtained by silica gel chromatography (eluent MC: Hx = 1:1, $R_f = 0.3$) to afford **10** (0.033 g) in 30% yield. Mp: 184 °C. ¹H NMR (CDCl₃): δ 9.75 (s, 1H), 7.68 (d, J = 7.50 Hz, 2H), 7.65 (d, J = 8.10 Hz, 2H), 7.57 (d, J = 8.40 Hz, 1H), 7.49 (s, 1H), 7.42 (d, J = 7.50 Hz, 2H), 7.35 (t, J = 8.10 Hz, 2H), 7.32 (s, 1H), 7.16 (d, J = 8.10 Hz, 2H), 1.43 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ 178.8, 158.1, 155.5, 153.7, 152.8, 150.3, 146.7, 138.8, 135.5, 127.2, 127.0, 124.2, 123.8, 122.7, 121.2, 121.0, 120.7, 120.0, 119.7, 118.7, 105.0, 47.0, 27.2. MS: *m/z* 545 [M⁺]. Anal. Calcd. for C₃₉H₃₁NO₂: C, 85.84; H, 5.73. Found: C, 85.68; H, 5.58.

Diethyl (5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophene-2-yl)methylphosphonate. A mixture of 2-methylphosphonate-5-formylthiophene (10.5 g, 40.0 mmol), neopentylglycol (5.0 g, 48.0 mmol), and *p*-toluenesulfonic acid (0.76 g) were dissolved in benzene (80 mL). The reaction mixture was refluxed for 3 h and then cooled and washed with aqueous sodium bicarbonate (100 mL). The combined benzene layers were then dried with MgSO₄, filtered, and evaporated *in vacuo* to yield acetal as a yellow oil (13.2 g, 95%). ¹H NMR (CDCl₃): δ 6.98 (d, *J* = 3.60 Hz, 1H), 6.87 (d, *J* = 3.60 Hz, 1H),5.57 (s, 1H), 4.07 (m, 4H), 3.74 (d, *J* = 11.10 Hz, 2H), 3.62 (d, *J* = 11.10 Hz, 2H), 3.32 (d, *J* = 21.60 Hz, 2H), 1.29 (t, *J* = 7.20 Hz, 6H), 1.26 (s, 3H), 0.79 (s, 3H). ¹³C{¹H} NMR (CDCl₃): δ 140.4, 132.7, 128.0, 126.4, 124.7, 97.9, 76.5, 62.1, 29.9, 22.7, 21.5, 16.1. MS: *m/z* 348 [M⁺]. Anal. Calcd. for C₁₅H₂₅-SO₂P: C, 51.71; H, 7.23. Found: C, 51.46; H, 7.16.

(E)-2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)thiophene-2-yl)vinyl-6-N,N-bis(9,9-dimethylfluoren-2-yl)aminobenzofuran (11). A mixture of 10 (0.15 g, 0.28 mmol), diethyl (5-(5,5-dimethyl-1,3dioxan-2-yl)thiophene-2-yl)methylphosphonate (0.12 g, 0.33 mmol), and potassium tert-butoxide (0.04 g, 0.33 mmol) was vacuum-dried and THF (30 mL) was added. The solution was refluxed for 6 h. THF was removed under reduced pressure. The crude mixture was redissolved in dichloromethane, washed with water, and dried with MgSO₄. The organic layer was removed in vacuo. The pure product 11 was obtained by silica gel chromatography (eluent MC:Hx =1:1, $R_{\rm f} = 0.4$) to afford **11** (0.12 g) in 58% yield. Mp: 201 °C. ¹H NMR (CDCl₃): δ 7.66 (d, J = 7.20 Hz, 2H), 7.60 (d, J = 8.10Hz, 2H), 7.39 (d, J = 7.20 Hz, 2H), 7.38 (s, 1H), 7.33 (t, J = 8.10Hz, 2H), 7.31 (d, J = 16.50 Hz, 1H), 7.30 (t, J = 8.10 Hz, 2H), 7.25 (s, 2H), 7.25 (d, J = 8.40 Hz, 1H), 7.11 (d, J = 8.10 Hz, 2H), 7.10 (d, J = 8.40 Hz, 1H), 7.02 (d, J = 3.30 Hz, 1H), 6.97 (d, J = 3.30 Hz, 1H), 6.77 (d, J = 16.50 Hz, 1H), 6.60 (s, 1H), 5.61 (s, 1H), 3.77 (d, J = 11.10 Hz, 2H), 3.64 (d, J = 11.10 Hz, 2H), 1.42 (s, 12H), 1.29 (s, 3H), 0.81 (s, 3H). $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (CDCl₃): δ 156.1, 155.2, 154.7, 153.7, 147.8, 147.1, 145.9, 144.1, 142.7, 140.7, 139.2, 134.2, 128.9, 127.1, 126.5, 124.9, 123.1, 122.6, 121.1, 120.7, 119.5, 118.5, 117.1, 116.1, 110.3, 105.8, 98.3, 77.4, 47.0, 30.4, 27.2, 23.1, 22.0. MS: *m*/*z* 739 [M⁺]. Anal. Calcd. for C₅₀H₄₅SO₃: C, 81.16; H, 6.13. Found: C, 81.09; H, 6.10.

(E)-2-(5-Formylthiopheneyl)vinyl-6-N,N-bis(9,9-dimethylfluoren-2-yl)aminobenzofuran (12). THF (30 mL) and water (10 mL) were added to a flask containing 11 (0.1 g, 0.13 mmol). Then, TFA (2 mL) was added to the solution. The resulting reaction mixture was stirred for 2 h at room temperature, quenched with saturated aqueous sodium bicarbonate, and extracted with dichloromethane. The combined dichloromethane phases were then washed with aqueous sodium bicarbonate and dried with MgSO₄. The organic layer was removed in vacuo. The pure product 12 was obtained by silica gel chromatography (eluent EA:Hx = 1:2, $R_f = 0.4$) to afford 12 (0.06 g) in 72% yield. Mp: 180 °C. ¹H NMR (CDCl₃): δ 9.85 (s, 1H), 7.66 (d, J = 6.90 Hz, 2H), 7.65 (d, J = 3.90 Hz, 1H), 7.61 (d, J = 8.10 Hz, 2H), 7.42 (d, J = 8.10 Hz, 1H), 7.39 (d, J = 6.90Hz, 2H), 7.32 (t, J = 8.10 Hz, 2H), 7.32–7.26 (m, 4H), 7.25 (s, 2H), 7.14 (d, J = 3.90 Hz, 1H), 7.11 (d, J = 8.10 Hz, 2H), 7.10 (d, J = 8.10 Hz, 1H), 6.99 (d, J = 15.90 Hz, 1H), 6.75 (s, 1H),1.42 (s, 12H). ¹³C{¹H} NMR (CDCl₃): δ 174.7, 165.5, 165.1, 163.1, 158.4, 156.5, 155.2, 154.5, 153.7, 153.1, 151.0, 150.0, 147.6, 141.7, 139.1, 134.4, 129.2, 128.5, 128.2, 127.3, 124.0, 122.6, 121.0, 119.6, 118.8, 117.5, 96.3, 47.0, 25.8. MS: m/z 653 [M⁺]. Anal. Calcd. for C₄₅H₃₅NO₂S: C, 82.66; H, 5.40. Found: C, 82.35; H, 5.27.

(Z)-3-(5-((E)-2-(6-(Bis(9,9-dimethylfluoren-2-yl)amino)benzofuran-2-yl)vinyl)thiophene-2-yl)-2-cyanoacrylic Acid (2). A mixture of 12 (0.11 g, 0.17 mmol) and cyanoacetic acid (0.03 g, 0.34 mmol) were vacuum-dried, and MeCN (60 mL) and piperidine (0.005 mL) were added. The solution was refluxed for 6 h. After the solution was cooled, the organic layer was removed in vacuo. The pure product 2 was obtained by silica gel chromatography (eluent EA:MeOH = 10:1, $R_f = 0.1$) to afford 2 (0.061 g) in 51% yield. Mp: 239 °C. ¹H NMR (DMSO): δ 8.12 (s, 1H), 7.70 (d, J = 8.10 Hz, 4H), 7.62 (d, J = 3.30 Hz, 1H), 7.50 (d, J = 8.40Hz, 1H), 7.46 (d, J = 8.10 Hz, 2H), 7.32 (t, J = 8.10 Hz, 2H), 7.31 (d, J = 15.60 Hz, 1H), 7.29 (d, J = 3.30 Hz, 1H), 7.28 (s, 2H), 7.27 (t, J = 8.10 Hz, 2H), 7.22 (d, J = 8.40 Hz, 1H), 7.17 (s, 1H), 7.09 (d, J = 15.60 Hz, 1H), 7.02 (s, 1H), 7.01 (d, J = 8.10Hz, 2H), 1.32 (s, 12H). ¹³C{¹H} NMR (DMSO): δ 163.7, 159.7, 155.4, 154.8, 153.9, 153.1, 151.8, 146.9, 146.5, 145.6, 143.3, 142.6, 138.3, 136.4, 136.2, 133.8, 128.1, 127.1, 126.7, 124.4, 122.7, 121.8, 121.1, 120.5, 119.5, 119.1, 118.1, 117.8, 109.2, 107.5, 46.4, 26.7. MS: m/z 720 [M⁺]. Anal. Calcd. for C₄₈H₃₆N₂O₃S: C, 79.97; H, 5.03. Found: C, 79.72; H, 4.91.

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Supporting Information Available: General experimental, cyclovoltamogram, geometrical configuration, and ¹H and ¹³C NMR spectra for the new compounds described in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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