Benzodipyrrole-2,6-dione-3,7-diylidenedimalononitrile Derivatives for Air-Stable n-Type Organic Field-Effect Transistors: Critical Role of **N-Alkyl Substituent on Device Performance**

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Supporting Information

ABSTRACT: Benzodipyrrole-2,6-dione-3,7-diylidenedimalononitriles (BDPMs) were synthesized as active materials for the use in air-stable *n*-type organic field-effect transistors (OFETs), whose optical and electrochemical properties were examined. BDPM-based small molecules exhibit deep lowest unoccupied molecular orbital levels, which are required in airstable n-type OFETs. An OFET device that was based on BDPM-But and fabricated by vapor deposition provided a maximum electron mobility of 0.131 cm² V⁻¹ s⁻¹ under ambient conditions.

INTRODUCTION

Air-stable p- and n-type organic field-effect transistors (OFETs) have received substantial attention during the past decade in both academia and industry because of their potential applications in large-area, flexible, and low-cost complementary circuits.¹ The development of *n*-type organic semiconductors (OSCs) lags that of their *p*-type counterparts, especially regarding performance and ambient stability. Therefore, the design of novel high-performance and air-stable *n*-type OSC materials has become an important challenge. To obtain high-performance air-stable *n*-type OFET, the material must have a low-lying lowest unoccupied molecular orbital (LUMO) close to the work function of the source/drain electrode and strong intermolecular $\pi - \pi$ interaction in the solid state to facilitate high electron mobility.³ Air-stable *n*-type OFET materials must generally have high electron affinity (EA), preventing common redox reactions of water and oxygen that can occur during device operation, causing degradation. Incorporating strong electron-withdrawing substituents such as dicarboxylic imides onto rylenes and cyanos onto quinoidal oligothiophenes and diketopyrrolopyrrole derivatives 4-6 has been proved to be an effective strategy for lowering LUMO energy levels and strengthening intermolecular $\pi - \pi$ interaction, supporting the realization of air-stable *n*-type OFETs.

Rylene diimides, such as pyromelliticdiimide (PyDI), naphthalene diimides (NDIs), and perylenediimides (PDIs), have served as some of the most important building blocks in the construction of OSCs for *n*-type OFETs because of their chemical accessibility, high stability, high electron affinity, and high electron mobility. PyDI is the smallest rylene core with



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sufficient electron affinity for electron injection and transport. Previous studies have demonstrated that *n*-type OFETs that are based on this core have promising electron mobilities under ambient conditions.^{4d} Recently, dicyanomethylenesubstituted compounds have attracted much interest as *n*-type OSCs because of the superior electron-withdrawing characteristics of their cyanovinyl groups, which stabilize their LUMO levels.⁵ Certain dicyanomethylene-substituted quinoidal OSCs have shown very promising performance in OFET devices. To date, the highest electron mobility of furanthiophene-based quinoidal OSC (TFT-CN) is 7.7 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, based on microsized ribbon transistors.^{5a} For use in solutionprocessed transistors, dicyanomethylene-substituted quinoidal terthiophenes (2DQTT-o-B) have reached an electron mobility as high as 5.2 cm² V⁻¹ s⁻¹ under ambient conditions.^{5b} We recently reported on angular naphthalene bis(1,5-diamide-2,6-divlidene)malononitriles (NBAMs) with low-lying LUMO levels and a maximum electron mobility of $0.63 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ under ambient conditions.^{5e}

Based on the above considerations, dicyanomethylenesubstituted compounds are good candidates for high-performance air-stable *n*-type OSCs. Herein, we present the design and synthesis of benzodipyrrole-2,6-dione-3,7-diylidenedimalononitrile (BDPM) derivatives for air-stable high-performance ntype OFETs (Scheme 1). The maximum electron mobility of an OFET that is based on BDPM-But exhibits a moderate electron mobility of 0.131 cm² V⁻¹ s⁻¹ and an on/off ratio of

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 4.2×10^3 under ambient conditions. To the best of the authors' knowledge, this is the first report of BDPM-based small molecules in air-stable *n*-type OFETs.

RESULTS AND DISCUSSION

Synthesis. Scheme 1 describes the synthesis of BDPM derivatives. 1,4-Dibromo-2,5-diiodo-benzene (1) was prepared from readily accessible 1,4-dibromobenzene in a good yield.⁷ Compound 1 was subjected to a Buchwald-Hartwig amination coupling reaction in the presence of a palladium catalyst to give the diamine products 2/3. The Sonogashira coupling reaction of trimethylsilylacetylene with dibromo compounds 2/3 in the presence of a palladium(0) catalyst and a copper(I) cocatalyst yielded alkynylanilines 4/5. The TMS group was removed from this intermediate using tetrabutylammonium fluoride, and subsequent treatment of 6/7 with CuI and Et₃N in DMF at 90 °C for 2 h led to smooth cyclization to furnish pyrroloindole derivatives 8/9. The oxidation of pyrroloindoles 8/9 with I_2O_5 gave the corresponding bisisatins 10/11. Finally, the bisisatins 10/11were treated with malononitrile via the Knoevenagel condensation reaction to obtain the target compounds BDPM-Oct and BDPM-But in 67-70% yield. Both BDPM-Oct and BDPM-But exhibited good solubility in common organic solvents such as chloroform, THF, and dichloromethane (DCM). Both BDPM-Oct and BDPM-But are highly thermally stable with decomposition temperatures of 326 and 325 °C for 5% weight loss (Figure S1), respectively, as determined by thermal gravimetric analysis (TGA).

Theoretical Calculations and Optical and Electrochemical Properties. To elucidate the electronic structures and optimized geometries of BDPM derivatives, density functional theory (DFT) calculations were performed at the B3LYP/6-31G** level using the GAUSSIAN 09 program. As presented in Figure 1, the optimized molecular geometries of BDPM derivatives are completely planar. The electron density distributions at the HOMO levels are concentrated on the benzene core, while those at the LUMO levels are widely delocalized over the entire BDPM core. The calculated LUMO levels for BDPM-Oct and BDPM-But are -4.42 and -4.44 eV, respectively. The optical and electrochemical properties of BDPM-Oct and BDPM-But were investigated using UV-vis absorption spectroscopy and cyclic voltammetry (CV). The absorption spectra of BDPM-Oct and BDPM-But in DCM solution were almost identical, as depicted in Figure 2a. The



Figure 1. DFT-optimized geometries and frontier molecular orbitals of (a) BDPM-Oct and (b) BDPM-But.



Figure 2. (a) UV–vis absorption spectra of BDPM derivatives in DCM (10^{-5} M) and thin films and (b) cyclic voltammograms of BDPM derivatives in DCM containing 0.1 M *n*-Bu₄NPF₆.

Table	e 1.	Photopl	iysical	and	Electroc	hemical	Properties	of I	BDPM	Oct	and	BDP	M-B	ut
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compound	$\lambda_{\mathrm{abs,max}}$ solution (nm)	$\lambda_{ m abs,max}$ thin film (nm)	$E_{\rm g}~({\rm eV})^a$	$E_{1/2\text{red1}}$ (V) ^b	$E_{\rm fc}$ (V)	LUMO (eV) ^c	HOMO $(eV)^d$
BDPM-Oct	294, 389, 751	299, 420, 751	1.30	0.06	0.43	-4.43	-5.73
BDPM-But	295, 388, 748	299, 414, 746	1.30	0.07	0.44	-4.42	-5.72
^{<i>a</i>} Calculated from	λ_{onset} of absorption spect	tra in DCM solution. ^b In	DCM $(10^{-3} N)$	1), <i>n-</i> Bu ₄ NPF ₆ (0	.1 M), 295 I	K, scan rate = 100	mV/s, versus Fc ⁺ /
Fc. ^c Determined	from $E_{\text{LUMO}} = -[E_{\text{red}1/2}]$	$-E_{(Fc+/Fc)} + 4.8$] eV. ^d C	Calculated from	m $E_{\text{HOMO}} = E_{\text{LUN}}$	$AO - E_{g}$		

absorption spectra show dual absorption bands, and the highenergy absorption band, located at 280-430 nm, corresponds to $\pi - \pi^*$ transitions; the low-energy band, spanning from 550 to 950 nm, can be attributed to intramolecular charge-transfer (ICT) transitions. The absorption spectra of the thin films of BDPM-Oct and BDPM-But were significantly redshifted relative to those of the solution states, revealing strong $\pi - \pi$ intermolecular interaction and close packing of the conjugated backbone in the solid state. The energy band gaps (E_{σ}) , estimated from the onsets of the absorption spectra in DCM solution, were 1.30 eV for both BDPM-Oct and BDPM-But. The electrochemical behavior of BDPM derivatives was investigated by cyclic voltammetry (CV) in DCM solution containing 0.1 M n-tetrabultylammonium hexafluorophosphate $(n-Bu_4NPF_6)$ as a supporting electrolyte. The ferrocene/ ferrocenium (Fc⁺/Fc) redox couple was used as an internal standard for the calibration of the potentials. The CV spectra of all compounds revealed well-defined reversible reduction waves, as shown in Figure 2b. The LUMO levels of BDPM-Oct and BDPM-But estimated using the equation $E_{\text{LUMO}} =$ $-[E_{red}^{1/2} - E_{(Fc+/Fc)} + 4.8]$ eV, were approximately -4.43 and -4.42 eV, respectively, consistent with the calculated values that are summarized in Table 1. The deep LUMO levels of BDPM-Oct and BDPM-But are attributed to the strong electron-withdrawing character of the dicyanovinylene group, favoring the injection of electrons from the electrode into the active layer and improving the stability of *n*-type OFETs in air.

Single-Crystal Structures and Electron-Transfer Integrals. Sheet-like single crystals of BDPM derivatives were obtained using the solvent vapor diffusion method (chloroform/isopropanol). The high planarity of the BDPM core was consistent with the optimized structure. Both BDPM-Oct and BDPM-But exhibited one-dimensional columnar π -stacking structures parallel to the crystallographic *a* axis with very short $\pi-\pi$ distances of 3.28 and 2.92 Å (Figure 3), respectively, favoring charge transfer between molecules. The electrontransfer integrals (t^-) for BDPM derivatives in different directions are calculated at the PW91/TZ2P level using the



Figure 3. Molecular packing viewed along the crystallographic *b* axis and schematic illustration of BDPM orientation on the substrate of (a, b) **BDPM-Oct** and (c, d) **BDPM-But**.

Amsterdam density functional (ADF) theory program (Figure 3a,c).⁸ The maximum t^- values of **BDPM-Oct** and **BDPM-But** are 32 and 100 meV, respectively, indicating that the electron transfer in the devices of **BDPM-Oct** and **BDPM-But** is along the crystallographic *b* axis (D2) of **BDPM-Oct** and *a* axis (D1) of **BDPM-But**, respectively. Notably, the t^- values of **BDPM-Oct** and **BDPM-But** in the π -column stacking direction (D1) are 19 and 100 meV, respectively. Figure 4a shows the merger



Figure 4. (a) Merger between D1s of BDPM-Oct and BDPM-But, (b) electron density distributions for the LUMO of BDPM-But, and (c) electron density distributions for the LUMOs of D1 dimers of BDPM derivatives. Side chains in (a, b) were omitted for simplicity.

between D1s of BDPM-Oct and BDPM-But. For clarification, the backbones of one molecule of BDPM-Oct and BDPM-But were overlapped as shown in red. Molecular pairs in red and blue/green represent the D1s of BDPM-Oct/BDPM-But. The center-to-center distances along D1 directions of BDPM-Oct and BDPM-But are 8.68 and 9.37 Å, respectively. In BDPM-Oct, the nitrogen atom of the cyano group of one molecule is superimposed over the center of the pyrrole ring of the other molecule where the electron density in the LUMO level is absent (Figure 4b); likewise, the carbon atom of the carbonyl group of one molecule is superimposed over the carbon atom of the cyano group of the other molecule that is a node in the LUMO level, explaining its small t^- value along the D1 direction. The higher t^- value of **BDPM-But** along D1 than that of BDPM-Oct is probably a result of the different slipped distances along the molecular long axis and the shorter $\pi - \pi$ distance in BDPM-But (2.92 Å), which is consistent with stronger bonding character for the LUMO of the D1 dimer of BDPM-But than that of BDPM-Oct (Figure 4c). Overall, BDPM-But may have higher electron mobility than BDPM-Oct, according to the Marcus electron-transfer theory and the Einstein relation.⁹ This result indicates that variation of the Nalkyl chain length may influence the molecular packings and charge mobilities of BDPM derivatives.

Molecular Packing, Morphology, and Charge Transport Properties. The charge carrier transport properties of BDPM derivatives were tested using a thin-film transistor with top-contact bottom-gate architecture. The thin films of BDPM-Oct and BDPM-But were fabricated by vacuum

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deposition on Si/SiO₂ substrates that were modified with a cyclic olefin copolymer (COC) at various substrate temperatures (t) to optimize the device performance. Subsequently, Au drain/source electrodes were vacuum-deposited to yield OFET devices. The thin films were characterized by atomic force microscopy (AFM) and X-ray diffraction (XRD) to elucidate the relationships between molecular structure, film morphology/crystallinity, and device performance. The X-ray diffraction (XRD) spectra of BDPM-based films revealed layered structures with sharp (00l) reflections, as depicted in Figure 5. The corresponding d-spacings of the thin films of



Figure 5. XRD patterns of BDPM derivatives films at different substrate temperatures: (a) BDPM-Oct and (b) BDPM-But.

BDPM-Oct and BDPM-But were 15.43 and 11.45 Å, respectively, which are consistent with half length of the crystallographic c axis of BDPM-Oct (15.53 Å) and length of the crystallographic *c* axis of **BDPM-But** (11.32 Å), indicating that BDPM derivatives have the edge-on molecular orientation on the substrate, as presented in Figure 3b,d. Notably, this orientation is advantageous for charge transport in the OFET geometry. All compounds exhibited typical *n*-type responses, as expected from the low-lying LUMO energy levels. Figure 6 and Figures S5 and S6 display their transfer characteristics. The mobility of the OFETs was calculated in the saturation current regimes. Table 2 presents the device characteristics of BDPM derivatives, including the electron carrier mobility (μ_e) , threshold voltage $(V_{\rm T})$, and current on/off ratios $(I_{\rm on}/I_{\rm off})$. At t = 40 °C, **BDPM-Oct**-based OFETs showed a maximum electron mobility of 0.046 cm² V⁻¹ s⁻¹, and when *t* was further increased to 60 °C, the maximum electron mobility slightly drops to 0.036 cm² V⁻¹ s⁻¹. The atomic force microscopy (AFM) images of **BDPM-Oct** films that were deposited at 40 and 60 °C reveal similar polycrystalline morphology with flat terraces (Figure 7a,b); however, the crystallinity decreases at t

= 60 $^{\circ}$ C (Figure 5a), which agrees with device performance. The maximum electron mobilities of BDPM-But-based OFETs decrease from 0.131 to 0.055 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as the substrate temperature increases from 40 to 60 °C because of the low coverage and discontinuous morphology of the **BDPM-But** film (Figure 7d). At t = 60 °C, only a few channels of BDPM-But-based OFET work owing to its discontinuous morphology. Overall, BDPM-But-based OFETs showed a highest electron mobility of 0.131 cm² V⁻¹ s^{-1} , slightly exceeding that of BDPM-Oct devices (0.046 cm² V^{-1} s⁻¹). A comparison of **BDPM-Oct** and **BDPM-But** with the same π -conjugated backbone demonstrates that the *N*-alkyl chain significantly affects the electron-transporting characteristics, which are consistent with molecular packing and electron-transfer integrals. It is noted that the large difference in the transfer integral and small difference in the electron mobility between BDPM-Oct and BDPM-But devices may indicate that the fabrication conditions of BDPM-But are not optimized yet. The crystallinity of BDPM-But films increases as substrate temperature raises from 40 to 60 °C (Figure 5b); however, the maximum electron mobility of BDPM-But-based OFET decreases at a substrate temperature of 60 °C because of the low coverage and discontinuous morphology (Figure 7d). Zhu et al. showed that the two-step deposition is an effective method to improve thin-film uniformity and continuity.^{6a} The electron mobility of OFET fabricated by two-step deposition was increased by more than seven times than that of OFET deposited in one step. Therefore, we believe that the performance of BDPM-But can be further improved by two-step deposition.

Molecular Structure-Property Relationship of Isatylidene Malononitrile Analogues. Since angular-shaped naphthalene bis(1,5-diamide-2,6-diylidene)malononitrile (NBAM) derivatives have recently been synthesized as *n*-type OSCs for the use in air-stable OFETs, 5^{6} the isatylidene malononitrile analogues provide a series of n-type OSCs to investigate the molecular structure-property relationship. Both NBAM and BDPM derivatives exhibited low-lying LUMO levels (lower than -4.0 eV) and excellent air stability of *n*-type characteristics due to strong electron-accepting ability of ketone and dicyanomethylene groups.^{5e} The reorganization energy (λ^{-}) values for electron transfer of NBAM-EH and BDPM-But calculated at the B3LYP/6-31G** level are 229 and 256 meV, respectively. The result demonstrates that the extension of molecular conjugation length of similar compounds reduces the λ^- values, consistent with the trend of the oligoacenes, naphthalene to hexacene.¹⁰ Both of NBAM-EH and BDPM-But display one-dimensional face-to-face stacking with a short $\pi - \pi$ distance of ~3 Å. The electron-transfer integral (t^{-}) of linear-shaped **BDPM-But** (100 meV) along the π -column stacking direction (D1) is slightly larger than that of angular-shaped NBAM-EH (80 meV), indicating the linearshaped structures may be a benefit to charge transfer. According to the Marcus electron-transfer theory, reaching a high charge-transfer rate requires minimizing λ and maximizing t values. Therefore, linear-shaped NBAM derivatives with a longer conjugation length compared to BDPM derivatives may have promising potential for the use in high-performance airstable *n*-type OFET. The synthesis of linear-shaped NBAM derivatives is in progress.

(a) 1.4

1.2 1.0

(**Y**¹) 0.8

_____0.6

0.4

0.2

0.0

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40





Figure 6. Output and transfer curves characteristics of OFET devices based on (a, b) BDPM-Oct ($t = 40 \degree C$) and (c, d) BDPM-But ($t = 40 \degree C$).

Table 2. Summary of Electrical Characteristics of OFETs Based on BDPM Derivatives

device	t (°C)	max $\mu_{\rm e} ~({\rm cm}^2 ~{\rm V}^{-1} ~{\rm s}^{-1})$	$V_{\rm T}$ (V)	on/off
BDPM-Oct	40	$0.046 \ (0.040 \pm 0.006)^a$	25-33	$10^2 - 10^3$
	60	$0.036 \ (0.031 \pm 0.005)^a$	28-35	$10^2 - 10^3$
BDPM-But	40	$0.131 (0.111 \pm 0.02)^a$	18-22	$10^{3} - 10^{4}$
	60	~0.055	~22	$\sim 10^{3}$

^{*a*}Electron (μ_{e}) mobilities were obtained from 10 channels.



Figure 7. AFM images $(3 \ \mu m \times 3 \ \mu m)$ of vacuum-deposited films of BDPM derivatives on COC-modified Si/SiO₂ substrates at different substrate temperatures of (a, b) **BDPM-Oct** and (c, d) **BDPM-But**. White circles in (d) indicate the substrate.

CONCLUSIONS

In summary, a new series of BDPM derivatives of *n*-type OSCs were designed and synthesized. BDPM derivatives have low-

lying LUMO levels (-4.4 eV below the vacuum level) that are suitable for the use in air-stable *n*-type OFETs. The OFET that was based on **BDPM-But** with *N*-butyl side chains had greater electron mobility than that was based on **BDPM-Oct** with *N*octyl side chains under ambient conditions, implying that the nature of the *N*-alkyl substituent strongly affected the performance of OFETs in which BDPM derivatives are used. Further modifications of the electron-accepting π -units are underway.

Experimental Section. General Preparation. All reagents were purchased from commercial suppliers and used as received without further purification. All oxygen and moisture-sensitive reactions were performed under a nitrogen atmosphere. Toluene, THF, and ethanol were distilled over sodium and dimethylformamide (DMF) was distilled over CaH₂. Crude product solutions were dried on MgSO₄ and concentrated with a rotary evaporator below 40 °C at 30 Torr. Silica gel column chromatography was performed employing 230-400 mesh silica gels. ¹H and ¹³C NMR spectra were recorded using a Bruker Avance II (300 MHz) NMR spectrometer with TMS as an internal reference; chemical shifts (δ) are reported in parts per million. ¹H NMR data are presented as follows: chemical shift, multiplicity (s = singlet, br = broad singlet, d = doublet, t = triplet, m = multiplet and/ormultiple resonances), coupling constant in Hz (Hertz), integration. High-resolution mass spectra (HRMS) were determined on a JEOL JMS-700 spectrometer for the EI mode. Thermogravimetric analyses (TGA) were collected from 30 to 800 °C at 10 °C min⁻¹ under a dry nitrogen atmosphere by using a Thermo Cahn Versa TGA. Sample masses of approximately 5 mg were used. Melting points (Mp) were recorded with a Fargo (MP-1D) apparatus. The UV-vis absorption spectra of BDPM derivatives were obtained using a

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Scinco S-3100 UV-vis spectrophotometer in dichloromethane (10^{-5} M) . High-resolution mass spectra were determined on a JEOL JMS-700 MStation mass spectrometer. The molecular order of BDPM films was determined by X-ray diffraction (XRD, Rigaku 18 kW rotating anode X-ray generator) using Cu K α radiation ($\lambda_{K\alpha 1} = 1.54$ Å). Atomic force microscopy (AFM) images were obtained using a Veeco Dimension 5000 scanning probe microscope. Cyclic voltammograms (CV) were recorded on a CHI1040B electrochemical work station with a three-electrode configuration, using a Pt plate as the counter electrode, a glassy carbon as the working electrode, and an Ag/ AgCl electrode as the reference electrode. Samples were dissolved in CH_2Cl_2 (10⁻³ M) with *n*-tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆, 0.1 M) as the supporting electrolyte. The scan speed was 0.1 V s⁻¹. An energy level of -4.8 eV below the vacuum level was used for reference Fc/Fc⁺. The LUMO levels estimated from $E_{\text{LUMO}} = -[E_{\text{red}}^{1/2} E_{(Fc+/Fc)}$ + 4.8] eV. Compound 1 was synthesized according to the literature.⁷ Single crystals of BDPM derivatives were successfully obtained using the solvent vapor diffusion method (chloroform/isopropanol). Single-crystal X-ray diffraction was performed on a Bruker APEX DUO at 100(2) K. Data were collected and processed by using an APEX II 4K CCD detector. Geometry optimization and frontier molecular orbitals were obtained from the GAUSSIAN 09 program at the B3LYP/6-31G** level.

Device Fabrication and Evaluation. Cyclic olefin copolymer (COC, purchased from Polyscience) was used as received. OFET devices were made using heavily n-doped Si substrates with 300 nm of thermally oxidized SiO₂. The substrates were successively cleaned with deionized (DI) water, piranha solution $(H_2SO_4:H_2O_2 = 7:3)$, DI water and finally blown dry with N2 gas. Then, 2.0 wt % solution of COC in dry toluene were spin-coated at 5000 rpm for 30 s by the onthe-fly-dispensing spin-coating method.¹¹ Finally, the COCmodified substrates (capacitance $C_i = 4.05 \text{ nF cm}^{-2}$) were baked at 120 °C in an oven for 1 h to remove the residual toluene. Thin films (40 nm) of BDPM derivatives were thermally evaporated onto the COC-modified substrates at a rate of 0.1–0.2 Å s⁻¹ under a pressure of 5×10^{-6} Torr. The substrates were maintained at constant temperatures of 40 and 60 °C. Finally, top-contact Au source-drain electrodes (40 nm) were thermally evaporated onto the active layers with a channel length (L) and width (W) of 100 and 1000 μ m, respectively. All of the transistors were characterized under ambient conditions using an Agilent Technologies B1500A semiconductor device analyzer. The charge mobility (μ) was calculated from the saturation regime using the formula, I_d = $(WC_{\rm i}/2L)\mu(V_{\rm g}-V_{\rm th}).^2$

2,5-Dibromo- N', N^4 -dioctylbenzene-1,4-diamine (2). A two-necked flask was charged under argon with the corresponding 1,4-dibromo-2,5-diiodobenzene 1 (1.0 g, 2.06 mmol), Pd₂(dba)₃ (10 mol %), and BINAP (20 mol %), anhydrous toluene (10 mL), and t-BuONa (0.59 g, 6.1 mmol) that were added, and the mixture was purged with nitrogen for 20 min. Amine (0.79 g, 6.1 mmol) was added via a syringe and the mixture is stirred under nitrogen at 110 °C in an oil bath for 2 h. The reaction mixture was cooled to room temperature, and 20 mL of water was added slowly, extracted with ethyl acetate, and washed with brine. The organic phase was dried over MgSO₄, filtered, and evaporated to afford the crude product. The residue was purified by column chromatography (eluent: hexane/dichloromethane = 9/1) to obtain 2 (0.5 g,

50%) as a pale yellow solid. Mp: 83–84 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.79 (s, 2H), 3.71 (s, 2H), 3.04 (t, *J* = 7.2 Hz, 4H), 1.58–1.65 (m, 4H), 1.29–1.39 (m, 20H), 0.87–0.90 (m, 6H) ppm.¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 137.7, 115.9, 110.0, 44.8, 31.8, 29.3, 29.2, 27.1, 22.6, 14.1 ppm. LRMS (EI) *m*/*z* [M]⁺ 490. HRMS (EI) *m*/*z* [M]⁺ calcd for C₂₂H₃₈Br₂N₂, 490.1381; found, 490.1380.

2,5-Dibromo- N^1 , N^4 -**dibutylbenzene-1,4-diamine (3).** Compound 3 was synthesized as for compound 2 and obtained as a pale yellow solid in 45% yield. Mp: 80–83 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.80 (s, 2H), 3.71 (s, 2H), 3.05 (t, *J* = 7.2 Hz, 4H), 1.57–1.64 (m, 4H), 1.40–1.47 (m, 4H), 0.94–0.99 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 137.6, 115.7, 109.9, 44.3, 31.2, 20.1, 13.7 ppm. LRMS (EI) *m*/*z* [M]⁺ 378. HRMS (EI) *m*/*z* [M]⁺ calcd for C₁₄H₂₂Br₂N₂, 378.0129; found, 378.0122.

N¹, N⁴-Dioctyl-2, 5-bis((trimethylsilyl)ethynyl)benzene-1,4-diamine (4). To a flame-dried two-necked flask with a reflux condenser were added compound 2 (1 g, 2.0 mmol) in toluene (10 mL), PdCl₂(PPh₃)₂ (20 mol %), CuI (20 mol %), and dry Et₃N (10 mL) under a nitrogen atmosphere, and the reaction vessel was evacuated and backfilled with nitrogen. Finally, trimethylsilylacetylene (0.60 g, 6.1 mmol) was added to the flask via a syringe and the flask was evacuated and filled with nitrogen once more. The resulting solution was allowed to stir at 90 °C in an oil bath for 2 h. The reaction mixture was cooled to room temperature, and 40 mL of water was added slowly, extracted with ethyl acetate, and washed with brine. The organic phase was dried over MgSO₄, filtered, and evaporated to afford the crude product. The residue was purified by column chromatography (eluent: hexane/dichloromethane = 9/1) to obtain 4 (0.69 g, 65%) as a yellow solid. Mp: 91-92 °C. ¹H NMR (300 MHz, $CDCl_3$: $\delta = 6.60$ (s, 2H), 4.01 (bs, 2H), 3.07 (t, J = 6.9 Hz, 4H), 1.60-1.63 (m, 4H), 1.28 (m, 20H), 0.88 (m, 6H), 0.26 (s, 18 H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 141.4, 113.6, 109.8, 102.3, 101.1, 44.4, 31.8, 29.4, 29.2, 27.1, 22.6, 14.0, 0.0 ppm. LRMS (EI) m/z [M]⁺ 524. HRMS (EI) m/z $[M]^+$ calcd for C₃₂H₅₆N₂Si₂, 524.3982; found, 524.3981.

 N^{1} , N^{4} -Dibutyl-2, 5-bis((trimethylsilyl)ethynyl)benzene-1,4-diamine (5). Compound 5 was synthesized as for compound 4 and obtained as a pale yellow solid in 63% yield. Mp: 146−147 °C. ¹H NMR (300 MHz, CDCl₃): δ = 6.60 (s, 2H), 4.04 (bs, 2H), 3.07 (m, 4H), 1.58−1.63 (m, 4H), 1.40−1.47 (m, 4H), 0.95 (m, 6H), 0.25 (s, 18 H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 141.2, 113.4, 109.6, 102.2, 100.9, 43.9, 31.3, 20.0, 13.6, −0.1 ppm. LRMS (EI) m/z[M]⁺ 412. HRMS (EI) m/z [M]⁺ calcd for C₂₄H₄₀N₂Si₂, 412.2730; found, 412.2733.

2,5-Diethynyl-*N*¹*,N*⁴**-dioctylbenzene-1,4-diamine (6).** The compound 4 (0.8 g, 1.52 mmol) was suspended in dry THF (10 mL) and cooled in an ice bath. TBAF (1 M in THF, 1 g, 3.81 mmol) was added and the reaction mixture was stirred at 0 °C in an ice bath for 30 min. The mixture was concentrated in vacuo, diluted with EtOAc, and washed with sat aq NH₄Cl. The organic layer was concentrated to provide the crude product 6, which was used directly in the next step (0.46 g, 80%). ¹H NMR (300 MHz, CDCl₃): δ = 6.66 (s, 2H), 4.05 (bs, 2H), 3.43 (s, 2H), 3.07 (t, *J* = 7.2 Hz, 4H), 1.42–1.64 (m, 4H), 1.27–1.42 (m, 20H), 0.86–0.90 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 141.3, 114.3, 108.9, 83.3, 80.9, 44.44, 31.7, 29.3, 29.3, 29.1, 27.0, 22.6, 14.0 ppm.

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LRMS (EI) m/z [M]⁺ 380. HRMS (EI) m/z [M]⁺ calcd for C₂₆H₄₀N₂, 380.3191; found, 380.3190.

*N*¹,*N*⁴-Dibutyl-2,5-diethynylbenzene-1,4-diamine (7). Compound 7 was synthesized as for compound 6 and obtained as a yellow solid in 80% yield, which was used directly in the next step. ¹H NMR (300 MHz, CDCl₃): $\delta = 6.66$ (s, 2H), 4.04 (bs, 2H), 3.43 (s, 2 H), 3.08 (m, 4H), 1.56–1.65 (m, 4H), 1.36–1.48 (m, 4H), 0.92–0.97 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): $\delta = 141.4$, 114.3, 108.8, 83.4, 81.0, 44.1, 31.5, 20.2, 13.8 ppm. LRMS (EI) *m*/*z* [M]⁺ 268. HRMS (EI) *m*/*z* [M]⁺ calcd for C₁₈H₂₄N₂, 268.1939; found, 268.1920.

1,5-Dioctyl-1,5-dihydropyrrolo[2,3-f]indole (8). To a flame-dried two-necked flask with a reflux condenser were added crude compound 6 (0.6 g, 1.5 mmol) in DMF (5 mL), CuI (0.06 g, 0.3 mmol), and Et₃N (0.47 g, 4.7 mmol) under a nitrogen atmosphere, and the mixture was heated to 100 °C in an oil bath for 2 h. The reaction mixture was cooled to room temperature, and 40 mL of water was added slowly, extracted with ethyl acetate, and washed with brine. The organic phase was dried over MgSO₄, filtered, and evaporated to afford the crude product. The residue was purified by column chromatography (eluent: hexane/dichloromethane = 9/1) to obtain 8 (0.45 g, 75%) as a white solid. Mp: 67–68 $^{\circ}$ C. ¹H NMR (300 MHz, CDCl₃): δ = 7.53 (s, 2H), 7.14 (d, J = 3.3 Hz, 2 H), 6.54 (d, J = 3 Hz, 2 H), 4.16 (t, J = 7.2 Hz, 4H), 1.88-1.93 (m, 4H), 1.31-1.37 (m, 20H), 0.90-0.94 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 133.1, 128.5, 126.3, 99.1, 98.5, 46.5, 31.7, 29.8, 29.2, 29.1, 27.0, 22.6, 14.0 ppm. LRMS (EI) m/z [M]⁺ 380. HRMS (EI) m/z [M]⁺ calcd for C₂₆H₄₀N₂, 380.3191; found, 380.3195.

1,5-Dibutyl-1,5-dihydropyrrolo[**2,3-f**]**indole** (**9**). Compound **9** was synthesized as for compound **8** and obtained as a white solid in 72% yield. Mp: 64–65 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.48 (s, 2H), 7.11 (d, *J* = 3.3 Hz, 2 H), 6.49 (d, *J* = 3 Hz, 2 H), 4.14 (t, *J* = 7.2 Hz, 4H), 1.80–1.90 (m, 4H), 1.30–1.42 (m, 4H), 0.91–0.96 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 133.1, 128.5, 126.3, 99.1, 98.6, 46.2, 31.9, 20.2, 13.7 ppm. LRMS (EI) *m*/*z* [M]⁺ 268. HRMS (EI) *m*/*z* [M]⁺ calcd for C₁₈H₂₄N₂, 268.1939; found, 268.1938.

1,5-Dioctylpyrrolo[2,3-f]indole-2,3,6,7(1H,5H)-tetraone (10). Pyrroloindole 8 (0.5 g, 1.3 mmol), DMSO (5 mL), and I_2O_5 (1.7 g, 5.2 mmol) were added into a flask and vigorously stirred at 90 °C in an oil bath under air. The reaction was stopped until pyrroloindole was completely consumed as monitored by TLC analysis. After the completion of reaction and cooling to room temperature, 40 mL of water was added slowly, extracted with ethyl acetate, and washed with brine. The organic phase was dried over MgSO₄, filtered, and evaporated to afford the crude product. The residue was purified by column chromatography (eluent: hexane/dichloromethane = 9/1) to obtain 10 (0.28 g, 50%) as a blue solid. Mp: 183–185 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.16 (s, 2H), 3.72 (t, J = 7.5 Hz, 4H), 1.65–1.70 (m, 4H), 1.25–1.33 (m, 20H), 0.88-0.84 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, $CDCl_3$): $\delta = 183.3$, 156.6, 147.3, 123.1, 106.7, 40.8, 31.6, 29.0, 27.0, 26.8, 22.5, 14.0 ppm. LRMS (EI) *m*/*z* [M]⁺ 440. HRMS (EI) m/z [M]⁺ calcd for C₂₆H₃₆N₂O₄, 440.2675; found, 440.2678.

1,5-Dibutylpyrrolo[**2,3-f**]**indole-2,3,6,7(1H,5H)-tetraone (11).** Compound **11** was synthesized as for compound **10** and obtained as a blue solid in 48% yield. Mp: 216–218 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.16 (s, 2H), 3.74 (t, *J* = 7.2 Hz, 4H), 1.64–1.67 (m, 4H), 1.38–1.41 (m, 4H), 0.94–0.99 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 183.3, 156.6, 147.3, 123.1, 106.7, 40.5, 29.0, 20.1, 13.5 ppm. LRMS (EI) m/z [M]⁺ 328. HRMS (EI) m/z [M]⁺ calcd for C₁₈H₂₀N₂O₄, 328.1423; found, 328.1420.

2,2'-(1,5-Dioctyl-2,6-dioxo-1,2,5,6-tetrahydropyrrolo-[2,3-f]indole-3,7-divlidene)dimalononitrile (BDPM-Oct). In a 50 mL flame-dried two-necked flask with a reflux condenser was added compound 10 (0.2 g, 0.45 mmol) in anhydrous EtOH (5 mL) and malononitrile (90 mg, 1.36 mmol) under a nitrogen atmosphere. After that, the mixture was refluxed in an oil bath for 2 h. Then, the solvent was evaporated under vacuum and the residue was purified by column chromatography (eluent: hexane/dichloromethane = 1/1) to afford the corresponding product **BDPM-Oct** (0.17 g, 70%) as a blue solid. Mp: 295-297 °C. ¹H NMR (300 MHz, $CDCl_3$: δ = 7.64 (s, 2H), 3.75 (t, J = 7.2 Hz, 4H), 1.66–1.71 (m, 4H), 1.26-1.32 (m, 20H), 0.85-0.89 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 161.1, 147.6, 142.7, 124.2, 109.8, 106.7, 86.3, 40.9, 31.5, 28.9, 27.0, 26.8, 22.5, 13.9 ppm. LRMS (EI) m/z [M]⁺ 536. HRMS (EI) m/z [M]⁺ calcd for C₃₂H₃₆N₆O₂, 536.2900; found, 536.2906.

2, **2**' - (**1**, **5** - **D** i **b** u t y l - **2**, **6** - d i o x o - **1**, **2**, **5**, **6**-tetrahydropyrrolo[**2**, **3**-*f*]indole-**3**, **7**-diylidene)-dimalononitrile (BDPM-But). Compound BDPM-But was synthesized as for compound BDPM-Oct and obtained as a blue solid in 67% yield. Mp: 319–320 °C. ¹H NMR (300 MHz, CDCl₃): δ = 7.65 (s, 2H), 3.76 (t, *J* = 6.9 Hz, 4H), 1.63–1.70 (m, 4H), 1.35–1.43 (m, 4H), 0.94–0.99 (m, 6H) ppm. ¹³C{¹H} NMR (75 MHz, CDCl₃): δ = 161.1, 147.5, 142.7, 124.2, 111.9, 109.8, 106.7, 86.4, 40.6, 29.0, 20.0, 13.4 ppm. LRMS (EI) *m*/*z* [M]⁺ 424. HRMS (EI) *m*/*z* [M]⁺ calcd for C₂₄H₂₀N₆O₂, 424.1648; found, 424.1647.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.9b02207.

Thermogravimetric analyses, computation coordinates, X-ray crystallographic data (CIF), OFET characteristics, and ${}^{1}\text{H}/{}^{13}\text{C}$ NMR spectra (PDF)

X-ray crystallographic data for **BDPM-But** (CIF) X-ray crystallographic data for **BDPM-Oct** (CIF)

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Notes

The authors declare no competing financial interest.

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