

[1]Benzothieno[3,2-*b*]benzothiophene-Based Organic Dyes for Dye-Sensitized Solar Cells

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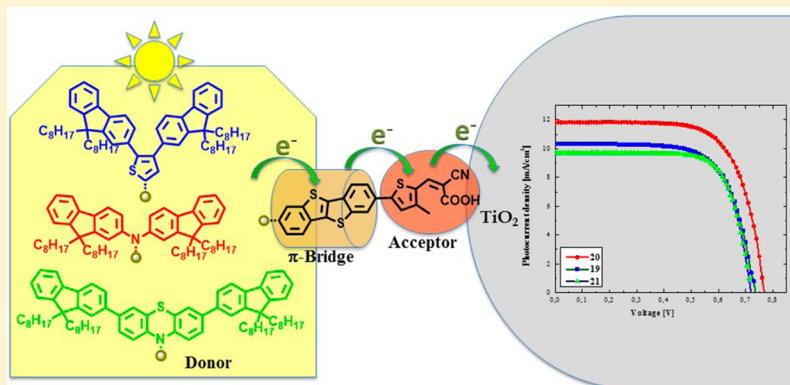
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S Supporting Information



ABSTRACT: Three new metal-free organic dyes with the [1]benzothieno[3,2-*b*]benzothiophene (BTBT) π -bridge, having the structure donor- π -acceptor (D- π -A) and labeled as **19**, **20** and **21**, have been designed and synthesized for application in dye-sensitized solar cells (DSSC). Once the design of the π -acceptor block was fixed, containing the BTBT as the π -bridge and the cyanoacrylic group as the electron acceptor and anchoring unit, we selected three donor units with different electron-donor capacity, in order to assemble new chromophores with high molar extinction coefficients (ϵ), whose absorption features well reflect the good performance of the final DSSC devices. Starting with the **19** dye, which shows a molar extinction coefficient ϵ of over $14,000 \text{ M}^{-1} \text{ cm}^{-1}$ and takes into account the absorption maximum at the longer wavelength, the substitution of the BFT donor unit with the BFA yields a great enhancement of absorptivity (molar extinction coefficient $\epsilon > 42,000 \text{ M}^{-1} \text{ cm}^{-1}$), until reaching the higher value ($\epsilon > 69,000 \text{ M}^{-1} \text{ cm}^{-1}$) with the BFPhz donor unit. The good general photovoltaic performances obtained with the three dyes highlight the suitable properties of electron-transport of the BTBT as the π -bridge in organic chromophore for DSSC, making this very cheap and easy to synthesize molecule particularly attractive for efficient and low-cost photovoltaic devices.

INTRODUCTION

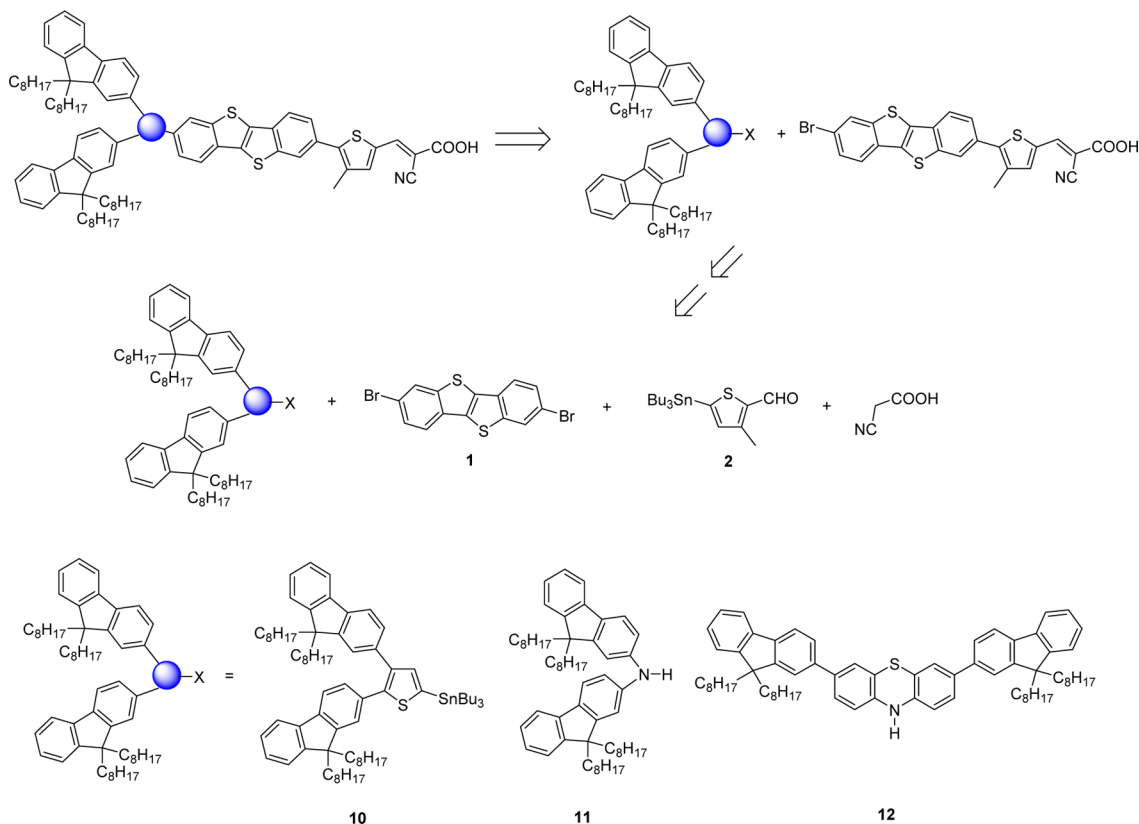
Since the pioneering work of O'Regan and Grätzel in 1991,¹ dye-sensitized solar cells (DSSC) have been attracting widespread attention both in the academic world and the industrial area, as the most promising inexpensive and environmentally friendly alternative to the inorganic photovoltaic.^{2–6} The efficiencies of DSSCs are strictly dependent on the nature of organic dye, photoanode, counter electrode, electrolyte, and the intricate interactions between all these components. The

organic sensitizer plays a key role in the performance and device stability, and it is one of the most important components to investigate, in order to gain further advances in cell efficiency. The great research efforts allowed devices based on zinc, ruthenium complex, and metal-free organic dyes to reach power conversion efficiencies (PCE) of over 13%,⁷ 10%,⁸ and 12%,⁹

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Scheme 1. Synthetic Pathway to Organic Dyes 19–21 by the Retrosynthetic Approach



respectively. Compared to metal–organic sensitizers, pure organic dyes have unique advantages such as low cost, nontoxicity, high extinction coefficients, flexible molecular designing, and easy tunability of molecular structure and then of absorption and electrochemical properties to increase cell performance.^{10–13} Despite these attractive features, some drawbacks such as high recombination losses and lower open circuit voltages (V_{oc} s) limit the PCE in the final device.^{14–16} However, very recently several reports have been published with efficiencies over 10% for metal-free dyes using I^-/I_3^- ^{17,18} and Co(II/III) redox shuttle,^{17,19–24} until gaining the PCE record of 12.5% with a single sensitizer device configuration.⁹ The most common and researched structural architecture of the best performing organic dyes is donor- π -bridge-acceptor, D- π -A, where A is mainly the cyanoacrylic moiety,^{25–33} while D and π are the units on which the research has been primarily focused, the chemico-structural design in order to gain improvements of photovoltaic performances. Besides high device efficiency, the ideal sensitizer should possess other important requisites prior to gaining commercial appeal, such as chemical and thermal stability and ease and low-cost of the entire synthetic methodology developed for its preparation. Since the very cheap cyanoacetic acid has been chosen as the reagent to build the acceptor unit, the design of the other two fundamental units, donor and π -bridge, becomes very crucial for the global synthetic strategy. As for the donor system, the aryl amines,^{9,18,22,23,27} undoubtedly, resulted in the best performing, and the research efforts have been focused mainly on the strengthening of the electron-donating power and on the introduction of bulky chains to prevent aggregation and recombination processes on the TiO₂. Regarding the π -bridge, it links the donor D and the acceptor A and plays an important

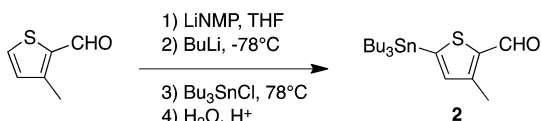
role by adjusting the HOMO–LUMO levels and extending the absorption range.¹⁰ Moreover, the π -bridge has to facilitate the electron migration from the donor to the acceptor, so its geometry should be preferably planar (fused rings) rather than distorted. In fact, reports in the literature show that dyes containing fused-ring planar structures as the π -bridge ensure, in general, high performance.^{18,22,34–40} In the present work, we report the synthetic routes, electro-optical properties, and photovoltaic performances of three new dyes for DSSC solar cells, based on the molecular architecture D- π -A and focused on the [1]benzothieno[3,2-*b*]benzothiophene (BTBT) block as the π -bridge, with the cyanoacrylic group as the electron-acceptor unit A and three different electron-donor groups as the unit D. The BTBT fused-ring planar system has been largely investigated for its excellent charge mobility in field-effect transistors.^{41–43} To the best of our knowledge, studies on the potentialities of this molecule for photovoltaic applications are lacking. We thought the charge-transport properties of the fused-ring planar structure of BTBT, associated with a very easy and cheap synthetic access, could be very suitable for photovoltaic purpose, especially in DSSC devices. With this aim, we selected three donor groups with different electron-donating capabilities to link the BTBT through the cell performances, in order to verify that the BTBT behaves as a general, good π -core in DSSC devices. The results demonstrate the suitable ability of the BTBT structure to act as a good electron-transporting bridge in dyes for DSSC, disclosing a new interesting family of organic molecules for photovoltaic applications.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic general strategy followed to prepare the organic dyes is outlined in Scheme 1.

The intermediate 2,7-dibromobenzothieno[3,2-*b*]benzothiophene **1** was synthesized following the literature procedure.⁴⁴ The stannil derivative **2** was synthesized starting from 3-methyl-2-thiophenecarbaldehyde and adapting a literature procedure⁴⁵ (Scheme 2).

Scheme 2. Synthesis of 3-Methyl-5-tributyltin-2-thiophenecarbaldehyde **2**

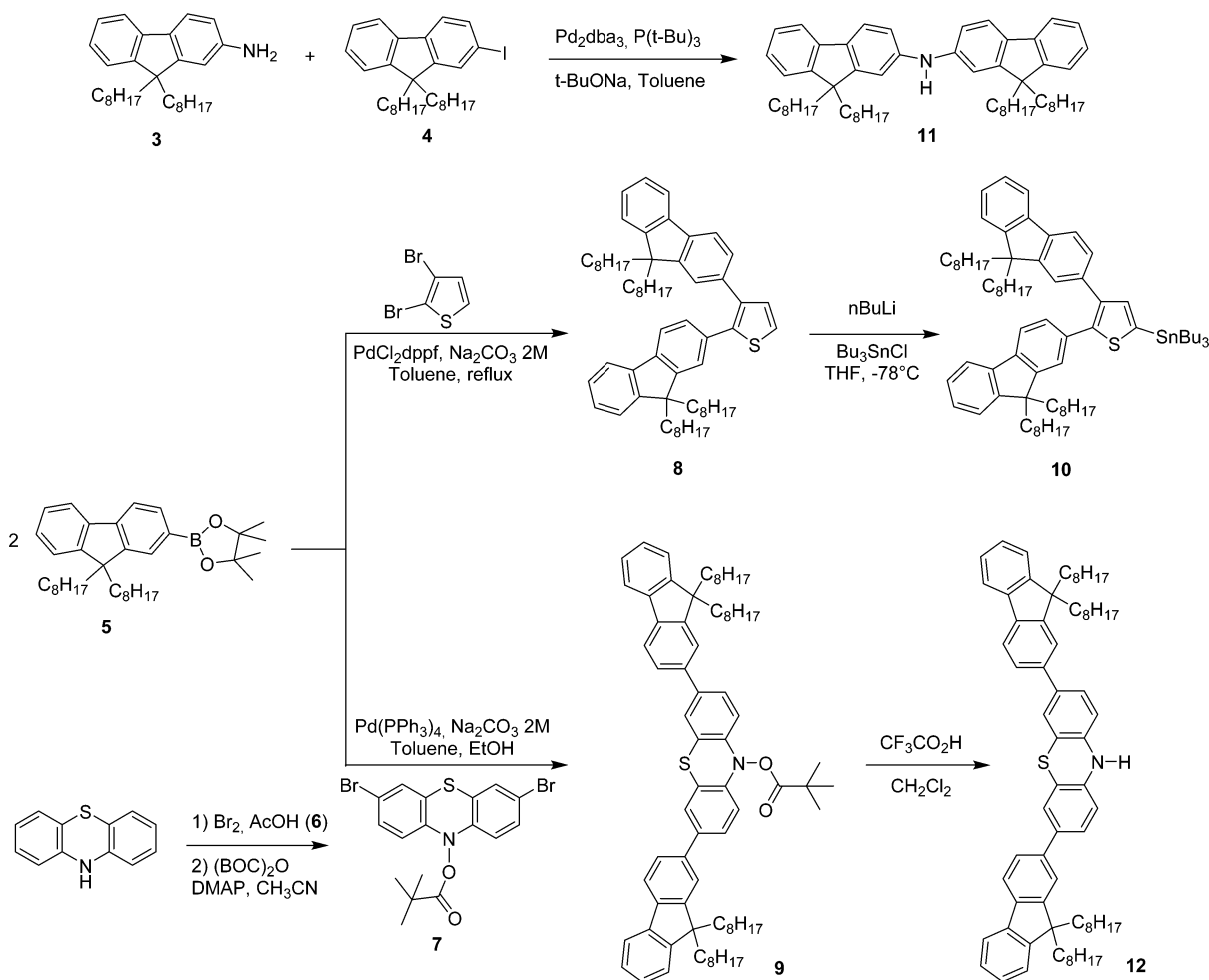


The reagent 3-methyl-2-thiophenecarbaldehyde was metalated by lithium *N*-methylpiperazide, in situ prepared by adding butyl lithium to *N*-methylpiperazide. The resulting metalated derivative was treated before with tributyltin chloride and then with acidic aqueous solution to yield the organotin derivative **2**.

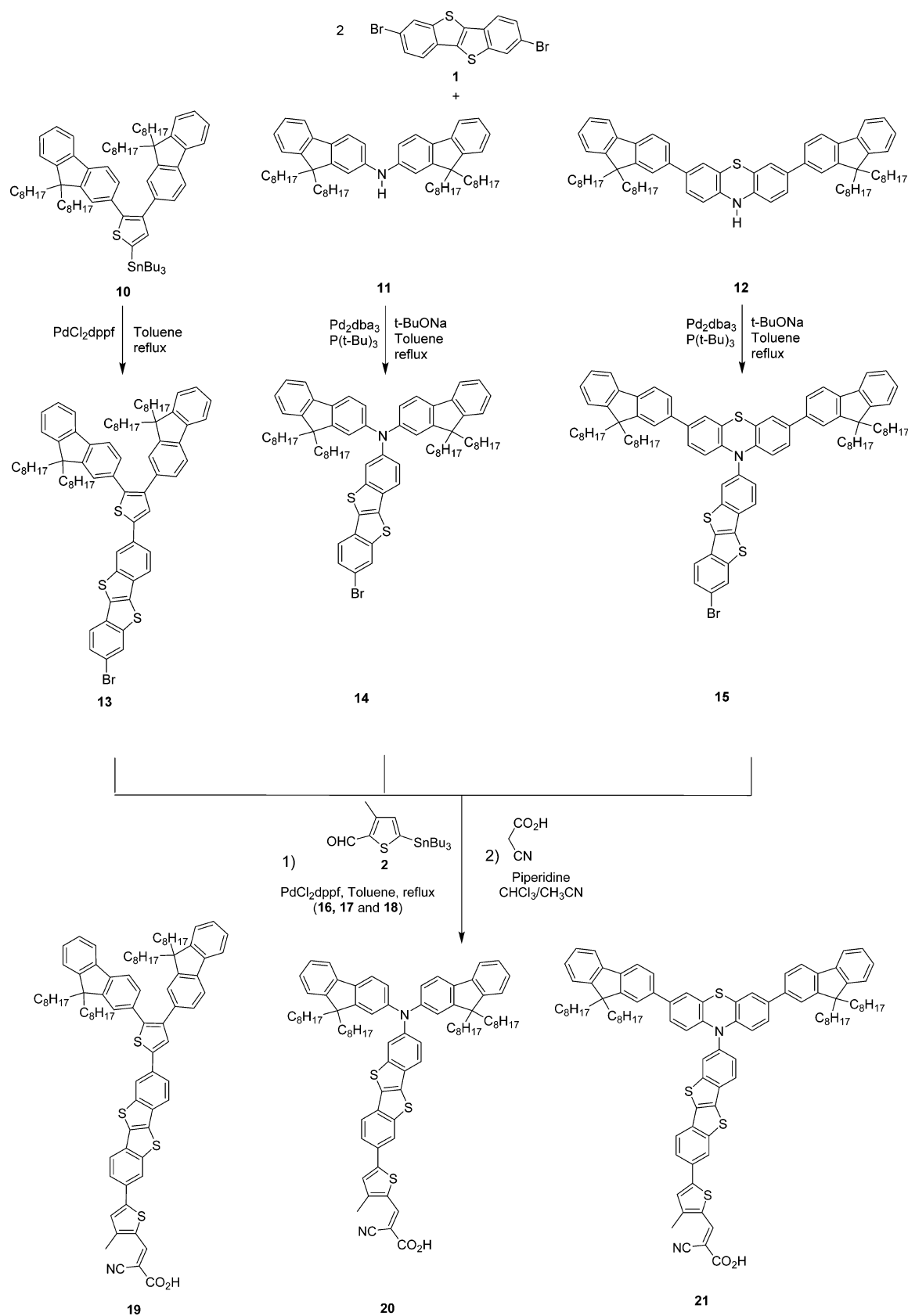
The three intermediate reagents **10**, **11**, and **12** were synthesized as reported in Scheme 3.

The donor building block **11** was synthesized by reacting the 2-amino 9,9-dioctylfluorene⁴⁶ **3** with the 9,9-dioctyl-2-iodo-fluorene⁴⁷ **4** in the presence of Pd(0) and P(*t*-Bu)₃ as the catalytic system, *t*-BuONa as a base, and toluene as the solvent. The reaction mixture was refluxed overnight, and the resulting crude product was purified by column chromatography to yield the pure product **11** as a dense brown liquid. The building blocks **10** and **12** were synthesized starting from the same organoborane reagent **5**, coupled with two different dibromoaryl reagents, the 2,3-dibromothiophene and the dibromophenothiazine derivative **7**. In the first pathway, the organoborane **5** was coupled with the 2,3-dibromothiophene in the Suzuki reaction conditions, using PdCl₂dppf as the catalyst, to yield the intermediate **8**, recovered as a dense light-green liquid. Compound **8** was purified by column chromatography and submitted to a stannilation reaction by BuLi and Bu₃SnCl to yield the final compound **10**, recovered as a dense green liquid. In the second pathway, the organoborane **5** was coupled with the dibromophenothiazine **7** in the Suzuki reaction conditions, using Pd(PPh₃)₄ as the catalyst, to yield the intermediate **9**. Compound **9** was purified by column chromatography and obtained as a light-yellow dense liquid. Subsequently, compound **9** was submitted to hydrolysis of the BOC protecting group by CF₃CO₂H in dichloromethane to yield, after purification by column chromatography, the pure product **12** as a light brown dense liquid.

Scheme 3. Synthetic Pathway to Intermediate Compounds 10–12



Scheme 4. Synthetic Pathway to Dyes 19–21



The intermediate **7** was synthesized as reported in the literature⁴⁸ in two steps by brominating the commercial phenothiazine with bromine in acetic acid and then reacting

the resulting 3,7-dibromophenothiazine **6** with di-*tert*-butyl dicarbonate $(\text{Boc})_2\text{O}$, in the presence of dimethylaminopyridine DMAP and CH_3CN as the solvent. Compound **7** was

collected as a colorless powder in an almost quantitative yield from the reaction mixture, after adding water and filtering the resulting precipitate. The three dyes 19–21 were synthesized as reported in Scheme 4.

The intermediates 10–12 containing the electron-donor units were then reacted with the 2,7-dibromobenzothieno[3,2-*b*]benzothiophene 1. The intermediate 1 was used in molar excess (2 equiv) with respect to the donor reagents, in order to prevent the double cross-coupling reaction. The organotin reagent 10 was reacted with the dibromo BTBT 1 in the Stille cross-coupling reaction to yield the intermediate 13, which was purified by column chromatography and obtained as a light-green solid. Subsequently, 13 was coupled in the Stille reaction conditions with the organotin derivative 2, and then the resulting intermediate 16 was finally reacted with the cyanoacetic acid. The dye 19 was recovered as a red-orange solid. The reagent 11 was reacted with the dibromo BTBT 1 in a palladium-catalyzed amination process to yield the intermediate 14, which was purified by column chromatography and obtained as a light-green powder. Subsequently, 14 was coupled in the Stille reaction conditions with the organotin 2, and the resulting intermediate 17 was finally reacted with the cyanoacetic acid. The dye 20 was recovered as a red solid. The reagent 12 was reacted with the dibromo-BTBT 1 in the Stille cross-coupling reaction to yield the intermediate 15, which was purified by column chromatography and obtained as a yellow grassy solid. Subsequently, 15 was coupled in the Stille reaction conditions with the organotin derivative 2, and then the resulting intermediate 18 was finally reacted with the cyanoacetic acid. The dye 21 was recovered as a light-red solid.

Optical and Electrochemical Properties. Molar absorption spectra in solution of the three dyes are shown in Figure 1.

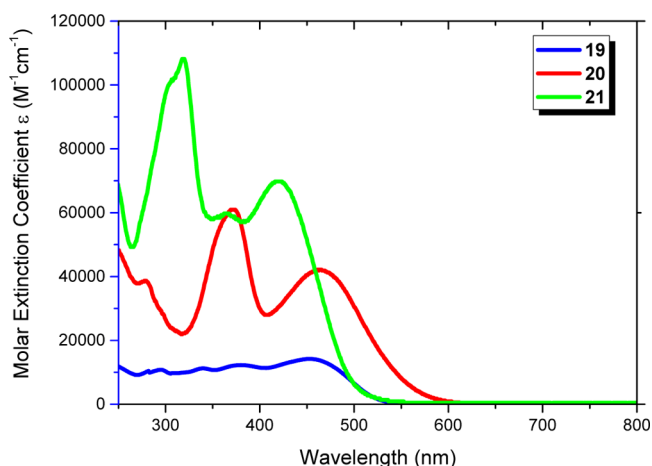


Figure 1. Molar absorptivity of 19–21 in chloroform solution.

The dye 19 show a broaden absorption in the range 250–500 nm with an extinction coefficient over 10,000 with a maximum value of 14,190 at 453 nm. The substitution of the donor unit BFT with the stronger electron-donating arylamine unit BFA in 20 outlined a variation of the absorption profile such as a strong enhancement of the absorption capacity. In fact, two absorption bands can be observed in the range 300–550 nm, picked at 372 and 464 nm, with extinction coefficient of over 60,000 and 42,000, respectively. This improvement of the absorption properties led to an enhancement of the photovoltaic performance, as reported below. Introducing a more complex

arylamine donor system, based on the phenothiazine molecular structure bearing two fluorene molecules, in 21 determined a further increase of the absorption capacity as well as a blue shift of the absorption spectrum. Two main absorption bands can be observed in the range 250–500 nm, picked at 320 and 420 nm, with extinction coefficients of over 100,000 and 69,000, respectively. Despite the enormous increasing of the extinction coefficient in 21, its photovoltaic performances did not show significant improvement, due to the blue shift of the absorption spectra.

Electrochemical Properties. To evaluate the possibility of electron injection from the excited state of the organic dyes to the conduction band (CB) of TiO₂ and the regeneration of the dyes, the redox behavior was studied by cyclic voltammetry (Figure 2, Table 1).

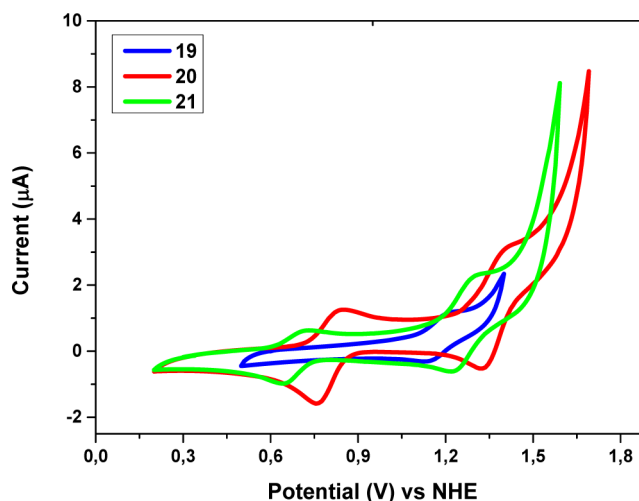


Figure 2. Cyclic voltammograms of dyes in CH₂Cl₂.

Table 1. Electrochemical Data, Absorption Maxima, and Molar Extinction Coefficients

dye	λ_{\max}^a (nm)/ ϵ (M ⁻¹ cm ⁻¹)	HOMO (V) (vs NHE)	E_{0-0} (eV)	LUMO (V) (vs NHE)
19	453/14190	1.22	2.38	-1.16
20	464/42130 372/60890	0.85	2.21	-1.36
21	420/69800 320/108120	0.75	2.50	-1.75

^aAbsorption maximum of the dyes measured in chloroform with a concentration ca. 2 μ M. ϵ molar extinction coefficient at λ_{\max} . HOMO of the dyes by cyclic voltammetry in CH₂Cl₂, using tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte, Ag/AgCl as the reference electrode, and Pt as the counter electrode. Scanning rate: 100 mV s⁻¹. LUMO was calculated as the difference HOMO - E_{0-0} . E_{0-0} was estimated from the absorption spectral onsets of the dyes.

The first oxidation versus normal hydrogen electrode (vs NHE), corresponding to the highest occupied molecular orbital (HOMO) level of the dye, was calibrated by Fc/Fc⁺ (0.63 V vs NHE). As shown in Table 1, the HOMO levels of 19, 20, and 21 were found to be 1.22, 0.85, and 0.75 V, respectively. They are more positive than the redox potential of I⁻/I₃⁻ (0.4 V vs NHE),⁴⁹ indicating that the oxidized dye molecules formed after electron injection into the conduction band of TiO₂ could be regenerated by the reducing species in the electrolyte solution. The energy gaps (E_{0-0}) between HOMO and LUMO levels

calculated from onset of the absorption spectra for **19–21** were found to be 2.38, 2.21, and 2.50 eV, respectively. The lowest unoccupied molecular orbitals (LUMOs) were estimated to be -1.16 , -1.36 , and -1.75 V, calculated from $E_{0-0} = E_{\text{HOMO}} - E_{\text{LUMO}}$.⁵⁰ The LUMO levels of the dyes are sufficiently more negative than the conduction band edge of TiO_2 (-0.5 V vs NHE), suggesting a sufficient driving force for electron injection from the excited dyes to the conduction band of TiO_2 .⁵¹ Therefore, the electrochemical parameters suggest these organic dyes could be efficiently used as good sensitizers in DSSCs.

Theoretical Study. The electronic and optical properties of the dyes were studied using density functional theory (DFT) and time-dependent (TD) DFT calculations.^{52–56} The TD-DFT results are reported in Table S1 (SI) and agree well with the experimental spectra. The calculations showed that in all three dyes, the lowest optically active singlet excited state has a significant charge-transfer character and is characterized by single-particle transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

A similar indication was also obtained from the isodensity plots of the frontier orbitals, reported in Figure 3. The two

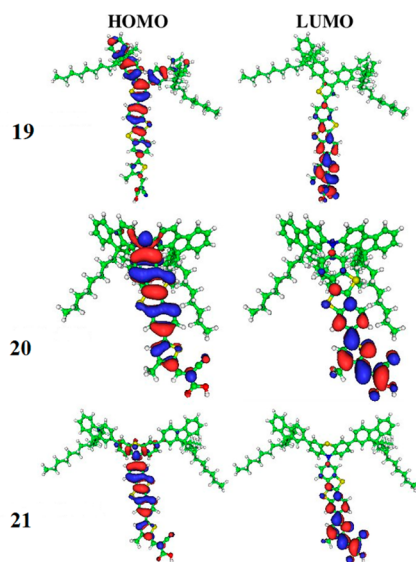


Figure 3. Isodensity plots of the most relevant frontier orbitals of **19–21**.

indicators Λ and Δr ^{57,58} (Table S1, SI) revealed that the charge separation upon excitation is the largest in **19**, while it was slightly smaller for the other two dyes. This finding can be possibly traced back to the absence of an additional thiophene unit in **20** and **21**, which is not disturbing the electron-withdrawing effect of the carboxylic acid, placed on the opposite side of the molecule. This same effect appears to have also a notable influence on the energy of the LUMO orbitals, which results are more stabilized in the **20** and **21** dyes with respect to **19** (LUMO energies are -2.06 , -2.01 , and -1.97 eV in **19–21**, respectively). As a consequence, because the HOMO energy is instead almost the same for the three molecules, a similar trend as for the LUMO was observed also for the single-particle gap. Nevertheless, this is not reflecting directly in an analogous trend for the lowest-lying excitation energies since all excited states, but the lowest singlet of **20**, are not fully characterized by a

unique single-particle transition, but display important many-body effects.

Photovoltaic Performance. Favorable characteristics emerge, in terms of potential photovoltaic properties, from the characterization of **19–21** dyes concerning their light-harvesting capability. Therefore, the properties of the three dyes were tested in photoelectrochemical solar cells. Due to the high planarity of the sensitizers, favored by the presence of the BTBT spacer, a fast intramolecular charge transfer should be expected as well as an unfavorable π - π stacking during the uptake process, which may lead to intermolecular quenching or back transfer of the injected electrons from the TiO_2 conduction band. In these cases, the addition of chenodeoxycholic acid (CDCA) to the dyeing solutions could be useful; by competing with the dye for the binding at the titania surface, the CDCA can in fact insert itself between the sensitizers minimizing detrimental dye aggregation effects.^{59–61} Moreover, the use of a coadsorbent such as CDCA ensures a uniform coverage of the inorganic semiconductor, thereby lowering the probability of recombination between injected electrons with I_3^- and other acceptor species. On the other hand, CDCA could unfavorably contend with the dyes for attachment to the TiO_2 surface, lowering the amount of sensitizers loaded on the working electrode. On this basis, the use of CDCA as co-adsorbent has been evaluated: we prepared 0.2 mM solutions of **19–21** dyes in THF with or without 10 mM CDCA and studied the influence of the amount of additive on photovoltaic parameters and on the dye loading, which are shown in Table 2. Notwithstanding the

Table 2. Photovoltaic Parameters for DSSCs Based on **19–21** Dyes

dye	CDCA (mM)	PCE (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	dye loading (mol/cm ²)
19	0	4.20	0.704	9.18	0.65	2.9×10^{-7}
	10	5.16	0.735	10.33	0.68	2.4×10^{-7}
20	0	5.76	0.736	11.50	0.68	3.0×10^{-7}
	10	6.25	0.765	11.85	0.69	2.4×10^{-7}
21	0	4.54	0.689	9.56	0.69	2.8×10^{-7}
	10	5.00	0.719	9.67	0.72	2.2×10^{-7}

decrease in dye loading with the addition of 10 mM CDCA the performances of the **19**-, **20**- and **21**-sensitized device were significantly improved. In particular, the open-circuit voltage (V_{oc}) increased from 0.704 up to 0.735, from 0.736 to 0.765, and from 0.689 to 0.719 V for **19–21**, respectively, suggesting that the detrimental recombination processes at the TiO_2 /dye/electrolyte interface were partially suppressed with the use of CDCA additive.

Moreover, the short-circuit photocurrent density (J_{sc}) augmented from 9.18 to 10.33, from 11.50 to 11.85, and from 9.56 to 9.67 mA/cm² for **19–21**, respectively. On the whole, PCE of 5.16, 6.25, and 5.0% has been achieved with **19**-, **20**- and **21**-sensitized devices, respectively. The I - V curves of DSSCs based on the three sensitizers in the presence of 10 mM CDCA are shown in Figure 4.

Comparing the photovoltaic parameters of the three dyes in their better testing condition, we can observe that the higher photocurrent density is related to the presence of the bisfluorenylamine derivative (BFA) as the electron-donor group, suggesting its better capability to generate electrons and/or to be adequately regenerated by the iodine/iodide electrolyte. Further information from the analysis of the

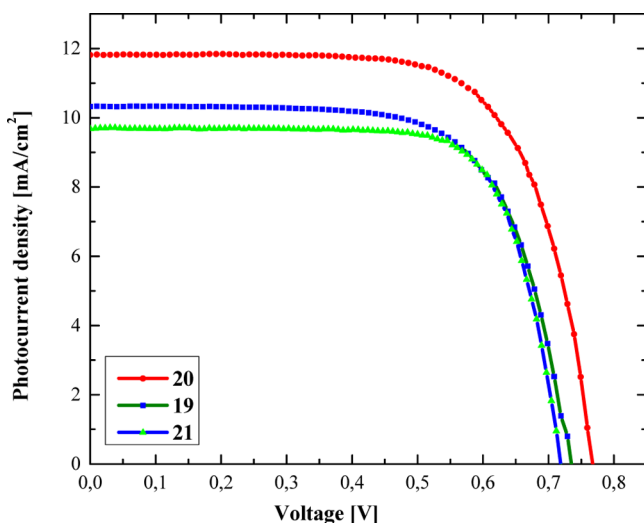


Figure 4. *I*–*V* curves of DSSCs fabricated with the three dyes in the presence of 10 mM CDCA.

monochromatic incident photon-to-current conversion efficiencies (IPCEs) recorded for the DSSCs (Figure 5). Notwithstand-

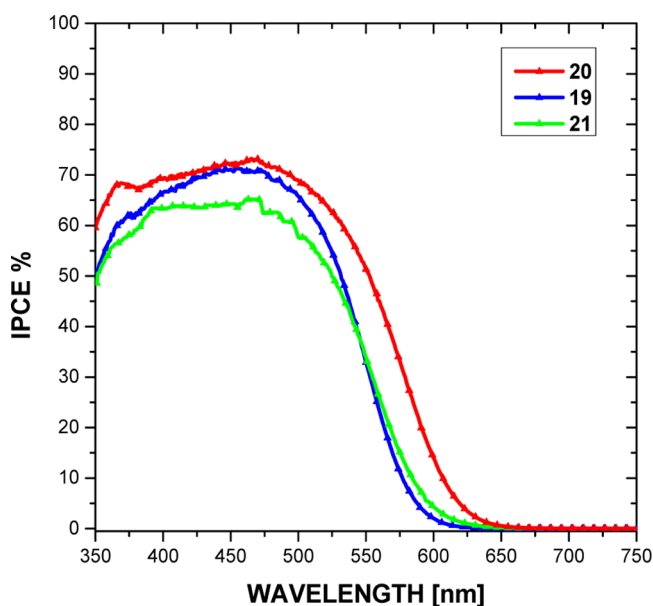


Figure 5. IPCEs spectra recorded for DSSCs devices fabricated with the three dyes.

ing the competitive absorption of FTO-glass, TiO₂, and electrolyte, the IPCE spectra seem to be in agreement with the light-harvesting range of sensitizers, although the presence of large TiO₂ scattering nanoparticles in the photoanode broadens their shape. The IPCE spectra of **20** dye showed a maximum of ~60% at 500 nm, slightly higher with respect to the ~55% obtained for the **19**-based device at 450 nm and to the plateau at 50%, ranging from 400 to 470 nm, observed for **21**; this confirms the superior photovoltaic properties of the **20** dye.

The dyes of the present work show, on balance, good photovoltaic parameters, with efficiencies in the range 4–6. Comparing these values with those reported in literature for dyes based on fused-ring systems, although they are not as high as some optimized structures,^{18,22,23,35,39} they are comparable^{38,62–65} and sometimes competitive^{31,37,66–69} with other

reported dyes. These achievements support the rationale behind the choice of the BTBT system as a π -core of dyes for DSSC.

CONCLUSIONS

In summary, we have synthesized three new D- π -A dyes based on the BTBT unit as the π -bridge, disclosing a new interesting class of organic dyes for DSSC. Varying the donor unit D in the general selected structure, all dyes exhibited remarkable solar-to-energy conversion efficiencies thanks to favorable light-harvesting capacity and high absorptivity, highlighting the good transporting properties of the planar BTBT unit, suitable for photovoltaic applications. With a right choice of donor units D the optical properties can be tuned in order to adjust the absorption range and increase the absorption capability to optimize the photovoltaic performances. Due to the high planarity of the BTBT, the addition of CDCA additive helps the efficiency of the final device by minimizing detrimental dye aggregation effects. In fact, all dyes show a better PCE value in the presence of CDCA co-adsorbent. Overall, the BTBT intermediate is very easy to synthesize and can be prepared in very large amounts, making the family of dyes based on this structure very promising for cheap applications. Even though the performances gained with the three dyes are not as high as the best performing dyes, they are however very good, and this clearly reveals an intrinsically good potentiality of the BTBT molecular structure for DSSCs. New structures can be engineered by selecting different donor units D and anchoring groups A, as partners of the π -bridge BTBT, in order to deeper recognize the potentialities of this new class of organic dyes. Experiments are in progress in this direction.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, all reagents and solvents of ACS purity were purchased from commercial sources and used without further purification. All reactions sensitive to air were carried out under a nitrogen atmosphere with anhydrous solvents, distilled immediately prior to use. Toluene and THF were distilled from sodium/benzophenone; DMF and CH₃CN were distilled from 4 Å molecular sieves; CHCl₃ was distilled from P₂O₅. Column chromatography was performed using silica gel 60, 40–63 μ m. Silica gel 60 F254 aluminum sheets were used for analytical TLC. FT-IR spectra were measured on a spectrophotometer using dry KBr pellets. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or (CD₃)₂CO or CDCl₃/DMSO-*d*₆ on a 500 MHz spectrometer at 500 and 125.7 MHz, respectively. The residual signals at $\delta = 7.24$ (CDCl₃) or $\delta = 2.05$ ((CD₃)₂CO) or $\delta = 2.5$ (CDCl₃/DMSO-*d*₆) ppm were used as the standard for ¹H NMR spectra. The signals at $\delta = 77.0$ (CDCl₃) or $\delta = 30.83$ ((CD₃)₂CO) ppm were used as the standard for ¹³C NMR spectra. MS spectra were recorded on a mass spectrometer. Elemental analyses were done by an elemental analyzer. Melting points were determined on a Gallenkamp capillary melting point apparatus. UV–vis spectra of the organic compounds were recorded on a UV–vis spectrophotometer.

Synthesis of 3-Methyl-5-(tributylstannyl)thiophene-2-carbaldehyde 2. In a 250 mL three-necked round-bottom flask *N*-methylpiperazine (3.4 mL, 30 mmol) and anhydrous THF (60 mL) were added under a nitrogen atmosphere. The solution was cooled to –78 °C, and *n*BuLi (2.5 M, 12 mL, 30 mmol) was added dropwise. The resulting mixture was stirred at –78 °C for 30 min, then a solution of 3-methylthiophene-2-carbaldehyde (3.4 g, 27 mmol) in anhydrous THF (15 mL) was added dropwise. The mixture was stirred at –78 °C for 30 min, then *n*BuLi (2.5 M, 12 mL) was added dropwise, and the resulting mixture was stirred at –20 °C for 5 h. A solution of *n*Bu₃SnCl (8.3 mL, 30 mmol) in anhydrous THF (20 mL) was added dropwise at –78 °C, and the mixture was allowed to warm at rt and stirred overnight. To the mixture, 1 N HCl (150 mL) was added at 0 °C for 20 min and then

neutralized with aq Na₂CO₃ solution. The mixture was extracted with hexane, and the organic layer washed with aq 40% KF solution and dried over Na₂SO₄. After evaporation of the solvent under a reduced pressure, the crude residue was purified by distillation with a kugelrohr apparatus (9×10^{-6} Torr, $T = 70^\circ\text{C}$) to yield the pure product **2** (9.2 g, 82% yield) as a light-yellow liquid. ¹H NMR (500 MHz, CDCl₃): δ 9.98 (s, 1H), 7.00 (s, 1H), 2.56 (s, 3H), 1.59–1.52 (m, 6H), 1.33 (sext, $J = 7.3$, 6H), 1.13 (t, $J = 7.3$, 6H), 0.89 (t, $J = 7.3$, 9H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 181.5, 150.4, 147.4, 142.5, 139.8, 28.8, 27.2, 13.9, 13.6, 10.9 ppm. FT-IR (KBr): ν 2955 (s), 2917 (s), 2870 (s), 2848 (s), 1662 (s), 1458 (m), 1415 (s), 1377 (s), 1216 (s), 1075 (m), 902 (s), 671 (s) cm⁻¹. MS (70 eV) m/e (%): 359 ([M – Bu]⁺, 94), 303 (100), 247 (65). Anal. calcd for C₁₈H₃₂OSSn: C, 52.07; H, 7.77; O, 3.85; S, 7.72; Sn, 28.59. Found: C, 52.15; H, 7.81; S, 7.70.

Synthesis of 2,3-Bis(9,9-dioctyl-9H-fluoren-2-yl)thiophene 8. In a 250 mL three-necked round-bottom flask, under a nitrogen atmosphere, were added 2,3-dibromothiophene (0.6 g, 2.5 mmol), 2-(9,9-dioctyl-9H-fluoren-2-yl)4,4,5,5-tetramethyl-1,3,2-dioxaborolane **5** (2.84 g, 5.5 mmol), PdCl₂dppf (0.04 g, 0.055 mmol) and toluene (30 mL). The mixture was degassed with a nitrogen flow for 30 min, then 2 M Na₂CO₃ aq (25 mL, 50 mmol) previously degassed was added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with water, and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane as the eluent to yield the pure product **8** (1.65 g, 77% yield) as a light-green dense liquid. ¹H NMR (500 MHz, CDCl₃): δ 7.71–7.66 (m, 2H), 7.61 (d, $J = 7.8$, 1H), 7.60 (d, $J = 8.3$, 1H), 7.41 (d, $J = 5.2$, 1H), 7.38–7.32 (m, 10H), 7.31 (d, $J = 5.2$, 1H), 2.00–1.78 (m, 8H), 1.32–0.98 (m, 40H), 0.90 (t, $J = 7.3$, 12H), 0.77–0.56 (m, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 150.8, 150.78, 150.77, 150.76, 140.9, 140.7, 140.4, 139.8, 139.3, 138.8, 135.5, 133.2, 130.5, 128.3, 128.0, 127.1, 126.9, 126.7, 126.7, 124.0, 123.9, 123.7, 122.71, 122.69, 119.7, 119.6, 119.6, 119.5, 55.0, 54.96, 40.44, 40.38, 31.8, 30.1, 30.0, 29.4, 29.34, 29.32, 29.31, 23.78, 23.76, 22.6, 14.1 ppm. FT-IR (KBr): ν 2953 (s), 2925 (s), 2853 (s), 1466 (m), 1456 (m), 831 (w), 740 (s) cm⁻¹. Anal. calcd for C₆₂H₈₄S: C, 86.45; H, 9.83; S, 3.72. Found: C, 86.40; H, 9.88; S, 3.75.

Synthesis of tert-Butyl 3,7-Bis(9,9-dioctyl-9H-fluoren-2-yl)-10H-phenothiazine-10-carboxylate 9. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, were added tert-butyl 3,7-dibromo-10H-phenothiazine-10-carboxylate **7** (0.3 g, 0.66 mmol), 2-(9,9-dioctyl-9H-fluoren-2-yl)4,4,5,5-tetramethyl-1,3,2-dioxaborolane **5** (0.77 g, 1.5 mmol), Pd(PPh₃)₄ (0.05 g, 0.04 mmol), toluene (20 mL) and EtOH (5 mL). The mixture was degassed with a nitrogen flow for 30 min, then 2 M Na₂CO₃ aq (7.5 mL, 15 mmol) previously degassed was added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NH₄Cl, and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH₂Cl₂ (6/4) as the eluent to yield the pure product **9** (0.6 g, 85% yield) as a light-yellow dense liquid. ¹H NMR (500 MHz, CDCl₃): δ 7.79 (d, $J = 7.8$, 2H), 7.75 (d, $J = 7.2$, 2H), 7.71 (s, 2H), 7.70 (d, $J = 7.2$, 2H), 7.64–7.55 (m, 6H), 7.41–7.31 (m, 6H), 2.00–1.98 (m, 8H), 1.61 (s, 9H), 1.28–1.03 (m, 40H), 0.85 (t, $J = 0.9$, 12H), 0.76–0.65 (bs, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 152.47, 151.45, 151.0, 140.7, 140.6, 139.9, 138.6, 137.7, 132.3, 127.2, 127.1, 126.9, 125.9, 125.8, 125.5, 122.6, 121.4, 120.0, 119.8, 82.3, 55.1, 40.1, 40.3, 31.8, 30.0, 29.18, 29.16, 28.2, 23.8, 22.6, 14.1 ppm. FT-IR (KBr): ν 2952 (s), 2924 (s), 2851 (s), 1717 (s), 1475 (s), 1465 (s), 1449 (s), 1392 (w), 1367 (m), 1324 (s), 1298 (m), 1251 (m), 1235 (m), 1162 (s), 1095 (w), 1048 (w), 1023 (s), 878 (w), 823 (m), 739 (s) cm⁻¹. Anal. calcd for C₇₃H₉₇NO₂S: C, 83.67; H, 9.08; N, 1.30; O, 2.97; S, 2.98. Found: C, 83.75; H, 9.20; N, 1.28; S, 3.02.

Synthesis of [4,5-Bis(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl]tributylstannane 10. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 2,3-bis(9,9-dioctyl-9H-fluoren-2-yl)thiophene **8** (0.8 g, 0.9 mmol) was dissolved in anhydrous THF (30 mL). The solution was cooled at -78°C , and *n*BuLi (2.5 M, 0.45 mL,

1.1 mmol) was added dropwise. The resulting mixture was stirred at -78°C for 30 min and -30°C for another 30 min. Then the reaction mixture was cooled at -78°C , and a solution of Bu₃SnCl (0.36 mL, 1.1 mmol) in anhydrous THF (10 mL) was added dropwise. The resulting mixture was allowed to warm to rt and stirred overnight. The reaction mixture was quenched with water and extracted with ethyl acetate. The organic layer was washed with 40% aq KF (2 \times 20 mL), dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by flash chromatography using hexane as the eluent to yield the pure product **10** (0.9 g, 87% yield) as a dense green liquid. ¹H NMR (500 MHz, CDCl₃): δ 7.71–7.65 (m, 2H), 7.62 (dd, $J = 7.6$, 0.8, 1H), 7.57 (dd, $J = 7.8$, 0.6, 1H), 7.40–7.29 (m, 11H), 1.99–1.80 (m, 8H), 1.79–1.64 (m, 6H), 1.48 (sext, $J = 7.3$, 6H), 1.38–0.96 (m, 55H), 0.90 (t, $J = 7.3$, 6H), 0.89 (t, $J = 7.3$, 6H), 0.80–0.50 (bs, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 150.80, 150.78, 150.72, 150.70, 145.3, 141.0, 140.8, 140.1, 141.1, 139.6, 138.8, 135.84, 135.77, 133.5, 128.1, 128.0, 126.9, 126.8, 126.67, 126.65, 123.78, 123.77, 122.68, 122.67, 119.7, 119.6, 119.5, 119.4, 55.0, 54.9, 40.5, 40.4, 31.9, 31.8, 30.09, 30.05, 29.37, 29.36, 29.35, 29.32, 29.0, 27.4, 23.80, 23.75, 22.7, 14.10, 14.09, 13.7, 11.0 ppm. FT-IR (KBr): ν 2955 (s), 2925 (s), 2852 (s), 1464 (m), 1456 (m), 1376 (w), 1074 (w), 1025 (w), 830 (w), 739 (s) cm⁻¹. Anal. calcd for C₇₄H₁₁₀SSn: C, 77.26; H, 9.64; S, 2.79; Sn, 10.32. Found: C, 77.20; H, 9.54; S, 2.84.

Synthesis of Bis(9,9-dioctyl-9H-fluoren-2-yl)amine 11. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, were added 9,9-dioctyl-9H-fluoren-2-amine **3** (0.7 g, 1.7 mmol), 2-iodo-9,9-dioctyl-9H-fluorene **4** (0.89 g, 1.7 mmol), Pd₂dba₃ (0.016 g, 0.017 mmol), P(*t*Bu)₃ (7 mg, 0.034 mmol), *t*-BuONa (0.18 g, 1.9 mmol), and anhydrous toluene (20 mL). The mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NH₄Cl, and extracted with CH₂Cl₂. The organic layer was dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH₂Cl₂ (8.5/1.5) as the eluent to yield the pure product **11** (1.1 g, 81% yield) as a light-yellow-green waxy solid. ¹H NMR (500 MHz, (CD₃)₂CO): δ 7.43–7.33 (bs, 1H), 7.28–7.14 (m, 4H), 6.98–6.88 (m, 4H), 6.84 (t, $J = 7.4$, 2H), 6.77 (t, $J = 7.4$, 2H), 6.62 (d, $J = 8.0$, 2H), 1.67–1.48 (m, 8H), 0.84–0.58 (m, 40H), 0.38 (t, $J = 7.0$, 12H), 0.35–0.15 (m, 8H) ppm. ¹³C NMR (125 MHz, (CD₃)₂CO): δ 153.5, 151.6, 145.2, 143.5, 135.6, 128.6, 127.5, 124.4, 122.5, 120.4, 118.9, 112.5, 56.7, 42.4, 33.5, 31.9, 31.1, 31.0, 25.7, 24.3, 15.4 ppm. FT-IR (KBr): ν 3373 (s), 2955 (s), 2924 (s), 2853 (s), 1608 (s), 1586 (s), 1491 (s), 1452 (s), 1408 (s), 1313 (m), 1272 (m), 820 (w), 738 (m) cm⁻¹. Anal. calcd for C₅₈H₈₃N: C, 87.70; H, 10.53; N, 1.76. Found: C, 87.75; H, 10.59; N, 1.69.

Synthesis of 3,7-Bis(9,9-dioctyl-9H-fluoren-2-yl)-10H-phenothiazine 12. In a 100 mL three-necked round-bottom flask, a solution of tert-butyl 3,7-bis(9,9-dioctyl-9H-fluoren-2-yl)-10H-phenothiazine-10-carboxylate **9** (0.56 g, 0.5 mmol), CF₃CO₂H (5 mL), and CH₂Cl₂ was stirred overnight at rt. The reaction mixture was quenched at 0°C in a 5% NaOH aq solution and then extracted with CHCl₃. The organic layer was dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH₂Cl₂ (7/3) as the eluent to yield the pure product **12** (0.45 g, 92% yield) as a light-brown dense liquid. ¹H NMR (500 MHz, (CD₃)₂CO): δ 8.09 (s, 1H), 7.81 (d, $J = 8.0$, 2H), 7.80–7.76 (m, 2H), 7.69 (d, $J = 1.1$, 2H), 7.57 (dd, $J = 7.9$, 1.5, 2H), 7.46–7.41 (m, 2H), 7.41–7.37 (m, 2H), 7.36–7.34 (m, 2H), 7.34–7.29 (m, 4H), 6.83 (d, $J = 8.0$, 2H), 2.20–2.00 (m, 8H), 1.23–0.97 (m, 40H), 0.79 (t, $J = 7.2$, 12H), 0.72–0.57 (m, 8H) ppm. ¹³C NMR (125 MHz, (CD₃)₂CO): δ 153.2, 152.7, 143.1, 142.8, 142.0, 140.9, 137.3, 128.9, 128.7, 128.0, 126.8, 126.5, 124.7, 122.3, 121.9, 121.5, 119.8, 116.8, 57.0, 41.9, 33.5, 31.6, 30.90, 30.86, 25.5, 24.3, 15.3 ppm. FT-IR (KBr): ν 3420 (s), 2924 (s), 2853 (s), 1465 (s), 1449 (s), 1297 (m), 814 (w), 740 (m) cm⁻¹. Anal. calcd for C₇₀H₈₉NS: C, 86.10; H, 9.19; N, 1.43; S, 3.28. Found: C, 86.21; H, 9.18; N, 1.45; S, 3.25.

Synthesis of 2-(4,5-Bis(9,9-dioctyl-9H-fluoren-2-yl)thiophene-2-yl)-7-bromobenzo[*b*]benzo[4,5]thieno[2,3-*d*]thiophene 13. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, [4,5-bis(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl]tributylstannane **10** (0.56 g, 0.49 mmol), 2,7-dibromobenzo[*b*]benzo[4,5]thieno[2,3-*d*]-

thiophene **1** (0.4 g, 1.0 mmol), PdCl₂dppf (7 mg, 9.6 μmol), and anhydrous toluene (20 mL) were added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NH₄Cl, and extracted with ethyl acetate. The organic layer was washed with 40% aq KF solution (2 × 20 mL), dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH₂Cl₂ (9/1) as the eluent to yield the pure product **13** (0.38 g, 65% yield) as a light-green solid. Mp 43–44 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.63–7.57 (m, 2H), 7.54–7.49 (m, 3H), 7.42 (s, 1H), 7.39 (d, *J* = 8.4, 1H), 7.34 (d, *J* = 1.8, 1H), 7.30–7.20 (m, 10H), 7.17 (dd, *J* = 8.0, 1.8, 1H), 7.04 (d, *J* = 8.0, 1H), 1.92–1.68 (m, 8H), 1.34–0.90 (m, 40H), 0.8 (t, *J* = 7.3, 12H), 0.68–0.40 (bs, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 150.99, 150.98, 150.86, 150.8, 145.5, 143.1, 141.0, 140.7, 140.4, 140.3, 139.7, 139.2, 139.1, 138.3, 137.6, 134.5, 132.2, 131.8, 130.4, 128.3, 128.2, 128.0, 127.7, 127.6, 127.3, 127.1, 126.8, 126.7, 125.6, 124.9, 123.7, 123.5, 122.76, 122.75, 122.2, 121.3, 119.8, 119.71, 119.69, 119.60, 55.1, 55.0, 49.7, 42.7, 40.4, 40.3, 31.83, 31.82, 31.6, 30.04, 29.99, 29.34, 29.33, 29.31, 29.28, 23.8, 23.7, 22.7, 22.64, 22.63, 14.12, 14.08 ppm. FT-IR (KBr): ν 2952 (s), 2923 (s), 2853 (s), 1606 (s), 1463 (s), 1442 (s), 1378 (m), 1306 (s), 1251 (m), 805 (s), 740 (s) cm⁻¹. Anal. calcd for C₇₆H₈₉BrS₃: C, 77.45; H, 7.61; Br, 6.78; S, 8.16. Found: C, 77.29; H, 7.67; S, 8.23.

Synthesis of 7-Bromo-N,N-bis(9,9-dioctyl-9H-fluoren-2-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophene-2-amine 14. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, bis(9,9-dioctyl-9H-fluoren-2-yl)amine **11** (0.34 g, 0.43 mmol), 2,7-dibromobenzo[b]benzo[4,5]thieno[2,3-d]thiophene **1** (0.3 g, 0.86 mmol), Pd₂dba₃ (8 mg, 9.0 μmol), P(*t*Bu)₃ (4 mg, 20 μmol), *t*BuONa (41 mg, 0.43 mmol), and anhydrous toluene (20 mL) were added. The resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NH₄Cl, and extracted with ethyl acetate. The organic layer was washed with 40% aq KF solution (2 × 20 mL), dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH₂Cl₂ (9/1) as the eluent to yield the pure product **14** (0.38 g, 65% yield) as a light-green solid. Mp 56–57 °C. ¹H NMR (500 MHz, CDCl₃): δ 8.04 (dd, *J* = 1.7, 0.4, 1H), 7.73 (d, *J* = 8.6, 1H), 7.69–7.60 (m, 6H), 7.54 (dd, *J* = 8.4, 1.7, 1H), 7.38–7.24 (m, 9H), 7.13 (dd, *J* = 8.4, 1.7, 2H), 2.06–1.78 (m, 8H), 1.34–1.02 (m, 40H), 0.87 (t, *J* = 7.1, 12H), 0.82–0.62 (m, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 152.2, 150.6, 146.8, 146.5, 143.9, 143.3, 140.77, 136.76, 133.8, 132.1, 131.5, 128.2, 127.6, 126.8, 126.5, 126.4, 123.5, 122.7, 122.0, 121.8, 121.5, 120.5, 119.2, 119.17, 118.0, 117.5, 55.1, 40.3, 31.9, 30.1, 29.4, 29.3, 24.0, 22.7, 14.1 ppm. FT-IR (KBr): ν 2953 (s), 2914 (s), 2851 (s), 1660 (s), 1592 (s), 1488 (s), 1451 (s), 1277 (s), 1024 (s), 805 (s), 741 (s) cm⁻¹. Anal. calcd for C₇₂H₈₈BrNS₂: C, 77.80; H, 7.98; Br, 7.19; N, 1.26; S, 5.77. Found: C, 77.92; H, 7.85; N, 1.22; S, 5.66.

Synthesis of 10-(7-Bromobenzo[b]benzo[4,5]thieno[2,3-d]thiophene-2-yl)-3,7-bis(9,9-dioctyl-9H-fluoren-2-yl)-10-phenothiazine 15. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 3,7-bis(9,9-dioctyl-9H-fluoren-2-yl)-10H-phenothiazine **12** (0.3 g, 0.3 mmol), 2,7-dibromobenzo[b]benzo[4,5]thieno[2,3-d]thiophene **1** (0.25 g, 0.6 mmol), Pd₂dba₃ (8 mg, 9.0 μmol), P(*t*Bu)₃ (4 mg, 20 μmol), *t*BuONa (32 mg, 0.33 mmol), and anhydrous toluene (20 mL) were added. The resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NH₄Cl, and extracted with ethyl acetate. The organic layer was washed with 40% aq KF solution (2 × 20 mL), dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH₂Cl₂ (8.5/1.5) as the eluent to yield the pure product **15** (0.27 g, 68% yield) as a yellow grassy solid. ¹H NMR (500 MHz, CDCl₃/DMSO-*d*₆): δ 8.19 (d, *J* = 1.6, 1H), 8.16 (d, *J* = 8.3, 1H), 8.07 (d, *J* = 1.6, 1H), 7.83 (d, *J* = 8.4, 1H), 7.66 (d, *J* = 8.4, 2H), 7.64 (dd, *J* = 6.3, 1.6, 2H), 7.56 (dd, *J* = 8.4, 1.8, 1H), 7.51 (dd, *J* = 8.4, 1.8, 1H), 7.45–7.37 (bs, 4H), 7.32 (d, *J* = 2.0, 2H), 7.30–7.18 (m, 6H), 7.14 (dd, *J* = 8.6, 2.0, 2H), 6.32 (d, *J* = 8.6, 2H), 2.04–1.79 (bs, 8H), 1.17–0.83 (m, 40H), 0.71 (t, *J* = 7.1, 12H), 0.63–0.42 (bs, 8) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 151.4,

150.9, 144.3, 143.9, 140.7, 140.3, 138.4, 134.4, 133.4, 132.6, 131.7, 128.6, 127.7, 126.74, 126.65, 125.6, 125.1, 123.6, 122.8, 122.73, 120.70, 119.9, 119.7, 119.1, 116.5, 55.1, 40.4, 31.8, 30.0, 29.21, 29.18, 23.8, 22.6, 14.1 ppm. FT-IR (KBr): ν 2950 (s), 2922 (s), 2850 (s), 1465 (s), 1447 (s), 1309 (s), 807 (s), 739 (s), cm⁻¹. Anal. calcd for C₈₄H₉₄BrNS₃: C, 77.98; H, 7.32; Br, 6.18; N, 1.08; S, 7.44. Found: C, 78.04; H, 7.45; N, 1.18; S, 7.56.

Synthesis of 5-(7-(4,5-Bis(9,9-dioctyl-9H-fluoren-2-yl)thiophene-2-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophene-2-yl)-3-methylthiophene-2-carbaldehyde 16. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 2-(4,5-Bis(9,9-dioctyl-9H-fluoren-2-yl)thiophene-2-yl)-7-bromobenzo[b]benzo[4,5]thieno[2,3-d]thiophene **13** (0.2 g, 0.17 mmol), 3-methyl-5-(tributylstannyl)thiophene-2-carbaldehyde **2** (0.085 g, 0.2 mmol), PdCl₂dppf (3 mg, 4 μmol), and anhydrous toluene (20 mL) were added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NH₄Cl, and extracted with ethyl acetate. The organic layer was washed with 40% aq KF solution (2 × 10 mL), dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/ethyl acetate (9/1) as the eluent to yield the pure product **16** (0.17 g, 85% yield) as a yellow-orange solid. Mp 64–65 °C. Due to molecular aggregations, ¹³C NMR spectrum cannot be recovered. ¹H NMR (500 MHz, CDCl₃): δ 9.91 (s, 1H), 8.24 (s, 1H), 8.21 (s, 1H), 7.91 (d, *J* = 7.8, 2H), 7.82 (dd, *J* = 7.8, 1.6, 1H), 7.79–7.72 (m, 2H), 7.66–7.56 (m, 4H), 7.53 (d, *J* = 7.8, 1H), 7.49 (d, *J* = 4.1, 1H), 7.35–7.26 (m, 9H), 1.96–1.73 (m, 8H), 1.36–0.92 (m, 40H), 0.83 (t, *J* = 7.1, 6H), 0.82 (t, *J* = 7.1, 6H), 0.72–0.48 (m, 8H) ppm. FT-IR (KBr): ν 2953 (s), 2925 (s), 2853 (s), 1662 (s), 1437 (s), 1262 (s), 1096 (s), 1060 (s), 1025 (s), 804 (s), 740 (m) cm⁻¹. Anal. calcd for C₈₂H₉₄OS₄: C, 80.47; H, 7.74; O, 1.31; S, 10.48. Found: C, 80.32; H, 7.62; S, 10.53.

Synthesis of 5-(7-Bis(9,9-dioctyl-9H-fluoren-2-yl)amino)benzo[b]benzo[4,5]thieno[2,3-d]thiophene-2-amine 14. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 7-bromo-N,N-bis(9,9-dioctyl-9H-fluoren-2-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophene-2-amine **14** (0.2 g, 0.18 mmol), 3-methyl-5-(tributylstannyl)thiophene-2-carbaldehyde **2** (0.09 g, 0.2 mmol), PdCl₂dppf (3 mg, 4 μmol), and anhydrous toluene (20 mL) were added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NH₄Cl, and extracted with ethyl acetate. The organic layer was washed with 40% aq KF solution (2 × 10 mL), dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/ethyl acetate (8.5/1.5) as the eluent to yield the pure product **17** (0.18 g, 86% yield) as an orange solid. Mp 101–102 °C. ¹H NMR (500 MHz, CDCl₃): δ 10.04 (s, 1H), 8.17 (dd, *J* = 1.6, 0.4, 1H), 7.80 (d, *J* = 8.3, 1H), 7.74 (d, *J* = 8.7, 1H), 7.71 (dd, *J* = 8.3, 1.6, 1H), 8.67–8.59 (m, 5H), 7.37–7.23 (m, 10H), 7.12 (d, *J* = 7.4, 2H), 2.61 (s, 3H), 1.98–1.82 (m, 8H), 1.32–1.00 (m, 40H), 0.86 (t, *J* = 7.1, 12H), 0.80–0.64 (m, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 181.7, 152.6, 152.3, 150.6, 148.3, 142.7, 136.5, 135.1, 133.9, 129.4, 127.5, 126.8, 126.5, 123.3, 122.7, 122.0, 121.5, 121.4, 120.5, 119.3, 119.2, 55.1, 40.3, 31.8, 30.1, 29.4, 29.3, 24.0, 22.7, 14.3, 14.1 ppm. FT-IR (KBr): ν 2916 (s), 2848 (s), 1731 (s), 1661 (s), 1593 (s), 1451 (s), 1263 (s), 1097 (s), 1025 (s), 803 (s), 739 (s) cm⁻¹. Anal. calcd for C₇₈H₉₃NOS₃: C, 80.99; H, 8.10; N, 1.21; O, 1.38; S, 8.32. Found: C, 81.13; H, 8.22; N, 1.30; S, 8.42.

Synthesis of 5-(7-(3,7-Bis(9,9-dioctyl-9H-fluoren-2-yl)-10H-phenothiazin-10-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophene-2-yl)-3-methylthiophene-2-carbaldehyde 18. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 10-(7-bromobenzo[b]benzo[4,5]thieno[2,3-d]thiophene-2-yl)-3,7-bis(9,9-dioctyl-9H-fluoren-2-yl)-10-phenothiazine **15** (0.21 g, 0.16 mmol), 3-methyl-5-(tributylstannyl)thiophene-2-carbaldehyde **2** (0.08 g, 0.19 mmol), PdCl₂dppf (3 mg, 4 μmol), and anhydrous toluene (20 mL) were added. The resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with saturated aq NaHCO₃, and extracted with chloroform. The organic layer was washed with 40% aq KF solution (2 × 10 mL), dried over Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was purified by column

chromatography using hexane/CH₂Cl₂ (1/1) as the eluent to yield the pure product **18** (0.19 g, 88% yield) as an orange solid. Mp 111–112 °C. Due to molecular aggregations, ¹³C NMR spectrum cannot be recovered. ¹H NMR (500 MHz, CDCl₃): δ 10.06 (s, 1H), 8.26 (d, *J* = 1.2, 2H), 7.96 (d, *J* = 8.4, 2H), 7.85–7.50 (bs, 6H), 7.79 (dd, *J* = 8.4, 1.2, 2H), 7.50–7.00 (bs, 15H), 2.64 (s, 3H), 2.05–1.87 (m, 8H), 1.25–0.95 (m, 40H), 0.80 (t, *J* = 7.2, 12H), 0.70–0.58 (bs, 8H) ppm. FT-IR (KBr): ν 2921 (s), 2849 (s), 1652 (s), 1465 (s), 1457 (s), 1447 (s), 1310 (m), 811 (s), 740 (s) cm⁻¹. Anal. calcd for C₉₀H₉₉NOS₄: C, 80.73; H, 7.45; N, 1.05; O, 1.19; S, 9.58. Found: C, 80.81; H, 7.49; N, 1.10; S, 9.53.

Synthesis of 3-(5-(7-(4,5-Bis(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophen-2-yl)-3-methylthiophen-2-yl)-2-cyanoacrylic Acid 19. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 5-(7-(4,5-bis(9,9-dioctyl-9H-fluoren-2-yl)thiophen-2-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophen-2-yl)-3-methylthiophene-2-carbaldehyde **16** (0.15 g, 0.12 mmol), cyanoacetic acid (17 mg, 0.2 mmol), piperidine (0.1 g, 1.2 mmol), anhydrous CHCl₃ (10 mL) and CH₃CN (10 mL) were added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with water, and extracted with chloroform. The organic layer was dried over anhydrous Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was washed with hexane, then dissolved in chloroform, and washed with 1 N aq HCl. The organic layer was dried over anhydrous Na₂SO₄, and the solvent removed at a reduced pressure to yield the pure product **19** (0.15 g, 94% yield) as an orange solid. Mp 45–46 °C. Due to molecular aggregations, ¹³C NMR spectrum cannot be recovered. ¹H NMR (500 MHz, [CD₃]₂CO): δ 8.46 (d, *J* = 1.0, 1H), 8.40 (s, 1H), 8.37 (d, *J* = 1.0, 1H), 8.03–7.98 (m, 2H), 7.96 (d, *J* = 4.0, 1H), 7.92–7.85 (m, 2H), 7.77 (d, *J* = 4.0, 1H), 7.71–7.65 (m, 2H), 7.64 (d, *J* = 7.7, 1H), 7.60 (d, *J* = 7.7, 1H), 7.43–7.35 (m, 4H), 7.34 (d, *J* = 7.7, 1H), 7.32–7.26 (m, 4H), 1.98–1.81 (m, 8H), 1.23–0.95 (bs, 40H), 0.86 (t, *J* = 6.6, 12H), 0.71–0.47 (bs, 8H) ppm. FT-IR (KBr): ν 3434 (s), 2955 (s), 2918 (s), 2846 (s), 1715 (m), 1582 (m), 1427 (m), 1260 (s), 1093 (s), 1021 (s), 802 (s), 738 (m) cm⁻¹. Anal. calcd for C₈₈H₉₅N₂O₂S₄: C, 79.08; H, 7.42; N, 1.09, O, 2.48; S, 9.94. Found: C, 79.21; H, 7.56; N, 1.03; S, 9.83.

Synthesis of 3-(5-(7-(Bis(9,9-dioctyl-9H-fluoren-2-yl)amino)-benzo[b]benzo[4,5]thieno[2,3-d]thiophen-2-yl)-3-methylthiophen-2-yl)-2-cyanoacrylic acid 20. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 5-(7-bis(9,9-dioctyl-9H-fluoren-2-yl)-10-phenothiazin-10-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophen-2-yl)-3-methylthiophene-2-carbaldehyde **17** (0.15 g, 0.13 mmol), cyanoacetic acid (17 mg, 0.2 mmol), piperidine (0.13 mL, 1.3 mmol), and anhydrous CHCl₃ (10 mL) and CH₃CN (10 mL) were added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with water, and extracted with chloroform. The organic layer was dried over anhydrous Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was washed with hexane, then dissolved in chloroform, and washed with 1 N aq HCl. The organic layer was dried over anhydrous Na₂SO₄, and the solvent removed at a reduced pressure to yield the pure product **20** (0.155 g, 94% yield) as a red solid. Mp 238–239 °C. ¹H NMR (500 MHz, (CDCl₃/DMSO-*d*₆): δ 8.48 (s, 1H), 8.24 (s, 1H), 7.89 (d, *J* = 8.3, 1H), 7.83 (d, *J* = 8.7, 1H), 7.80 (dd, *J* = 8.3, 1.5, 1H), 7.74–7.62 (m, 5H), 7.59 (d, *J* = 2.1, 1H), 7.33 (d, *J* = 7.4, 2H), 7.31–7.19 (m, 5H), 7.17 (d, *J* = 1.9, 2H), 7.06 (dd, *J* = 8.2, 1.9, 1H), 2.44 (s, 3H), 1.92–1.75 (b, 8H), 1.30–0.90 (bs, 40H), 0.77 (t, *J* = 7.0, 12H), 0.69–0.48 (bs, 8H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 152.2, 150.6, 146.7, 144.1, 140.8, 136.7, 126.8, 126.4, 123.5, 122.7, 120.5, 119.2, 55.0, 53.4, 40.3, 31.8, 30.9, 30.1, 29.7, 29.4, 29.3, 24.0, 22.6, 14.1 ppm. FT-IR (KBr): ν 3434 (s), 2952 (s), 2923 (s), 2851 (s), 1598 (s), 1450 (s), 1388 (s), 1322 (s), 1275 (m), 740 (s) cm⁻¹. Anal. calcd for C₈₁H₉₄N₂O₂S₃: C, 79.49; H, 7.74; N, 2.29, O, 2.61; S, 7.86. Found: C, 79.40; H, 7.78; N, 2.33; S, 7.95.

Synthesis of 3-(5-(7-(3,7-Bis(9,9-dioctyl-9H-fluoren-2-yl)-10H-phenothiazin-10-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophen-2-yl)-3-methylthiophen-2-yl)-2-cyanoacrylic acid 21. In a 100 mL three-necked round-bottom flask, under a nitrogen atmosphere, 5-(7-(3,7-bis(9,9-dioctyl-9H-fluoren-2-yl)-10H-phenothiazin-10-yl)benzo[b]

benzo[4,5]thieno[2,3-d]thiophen-2-yl)-3-methylthiophene-2-carbaldehyde **18** (0.17 g, 0.13 mmol), cyanoacetic acid (17 mg, 0.2 mmol), piperidine (0.13 mL, 1.3 mmol), and anhydrous CHCl₃ (10 mL) and CH₃CN (10 mL) were added, and the resulting mixture was refluxed overnight. The reaction mixture was cooled at rt, quenched with water, and extracted with chloroform. The organic layer was dried over anhydrous Na₂SO₄, and the solvent removed under a reduced pressure. The crude residue was washed with hexane, then dissolved in chloroform, and washed with 1 N aq HCl. The organic layer was dried over anhydrous Na₂SO₄, and the solvent removed at a reduced pressure to yield the pure product **21** (0.17 g, 95% yield) as a light-red solid. Mp 245–246 °C. Due to molecular aggregations, ¹³C NMR spectrum cannot be recovered. ¹H NMR (500 MHz, CDCl₃/DMSO-*d*₆): δ 8.49–8.35 (m, 2H), 8.33 (s, 1H), 8.28–8.19 (m, 2H), 8.06–7.93 (m, 1H), 7.85–7.75 (m, 3H), 7.71 (d, *J* = 8.1, 1H), 7.70–7.63 (m, 3H), 7.61 (d, *J* = 7.9, 1H), 7.37–7.30 (m, 3H), 7.30–7.22 (m, 4H), 7.20 (dd, *J* = 8.6, 1.6, 1H), 6.89 (d, *J* = 8.9, 1H), 6.35 (d, *J* = 8.6, 1H), 2.44 (s, 3H), 2.07–1.86 (bs, 8H), 1.17–0.87 (bs, 40H), 0.80–0.65 (m, 12H), 0.63–0.45 (bs, 8H) ppm. FT-IR (KBr): ν 3430 (s), 2922 (s), 2849 (s), 1603 (s), 1464 (s), 1448 (s), 1383 (s), 1318 (s), 1242 (s), 811 (m), 740 (s) cm⁻¹. Anal. calcd for C₉₃H₁₀₀N₂O₂S₄: C, 79.44; H, 7.17; N, 1.99, O, 2.28; S, 9.12. Found: C, 79.56; H, 7.34; N, 2.13; S, 9.01.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00192.

Computational details, atom coordinates, energy fabrication of DSSC, and photovoltaic measurement NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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