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

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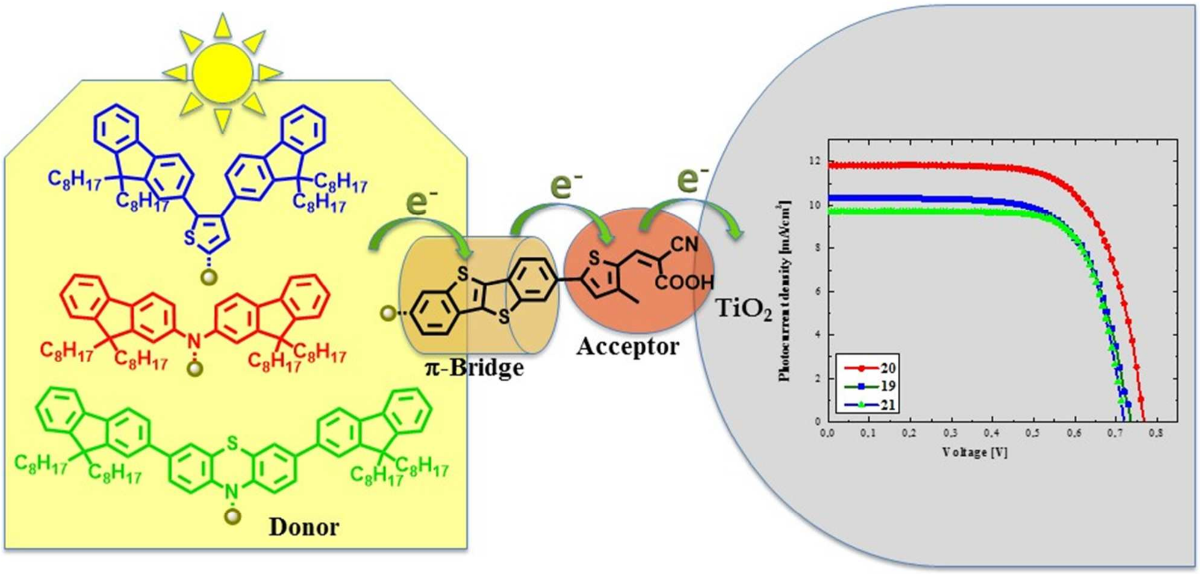
Graphical Abstract



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 labelled as **19**, **20** and **21**, have been designed and synthesized for application in dye sensitized solar cells (DSSC). Once fixed the design of the π-acceptor block, containing the BTBT as the π-bridge and the cyanoacrylic group as the electron acceptor and anchoring unit, we have 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 from the **19** dye, which show a molar extinction coefficient ε of over 14000 $M^{-1}cm^{-1}$, take in account the absorption maximun at the longer wavelength, the substitution of the BFT donor unit with the BFA, yield a great enhancement of absorptivity (molar extinction coefficient ε > 42000 $M^{-1}cm^{-1}$), until to reach the higher value (ε > 69000 $M^{-1}cm^{-1}$) 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

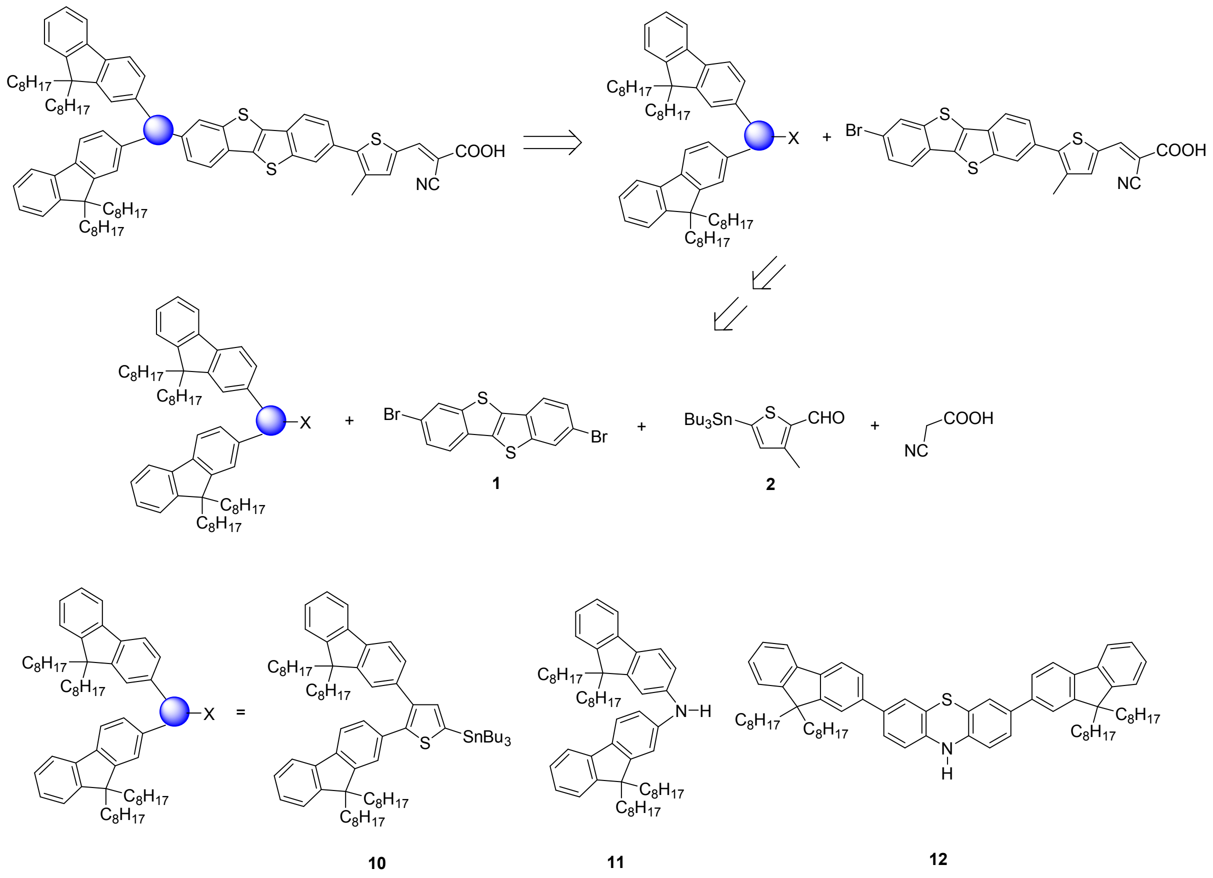
Since the pioneeristic work of O'Regan and Grätzel in 1991,[1] dye-sensitized solar cells (DSSC) have been attracting a widespread attention both in academic world and industrial area, as the most promising inexpensive and environmentally friendly alternative to the inorganic photovoltaic.[2-6] The efficiencies 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 on the performance and device stability, and it is one of the most important components to investigate, in order to gain further advance in cell efficiency. The great research efforts allowed to reach in devices based on zinc, ruthenium complex and metal-free organic dyes, power conversion efficiencies (PCE) of over 13%,[7] 10%,[8] and 12%,[9] respectively. Compared to metal-organic sensitizers, pure organic dyes have unique advantages such as: a) low cost, b) non-toxicity, c) high extinction coefficients, d) flexible molecular designing, e) easy tunability of molecular structure and then of absorption and electrochemical properties to increase cell performance.[10-13] Despite these attracting features, some drawbacks such as high recombination losses and lower open circuit voltages (Vocs) 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 to gain 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, with A being mainly the cyanoacrylic moiety,[25-33] while D and π being the units on which the research has been primarily focused the chemico-structural design in order to gain improvements of photovoltaic performances. Beside high device efficiency, the ideal sensitizer should possess other important requisites prior to consolidate your commercial appealing, such as chemical and thermal stability, ease and low-cost of the entire synthetic methodology developed for its preparation. Since the very cheap cyanacetic 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. About the donor system, the aryl amines,[9,18,22,23,27] undoubtedly, resulted 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 TiO_2. 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 as dyes containing fused-rings planar structures as 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] Are lacking, to the best of our knowledge, studies on the potentialities of this molecule for photovoltaic applications. 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. For this aim, we selected three donor groups with different electron-donating capabilities to link the BTBT, in order to verify, through the cell performances, if 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

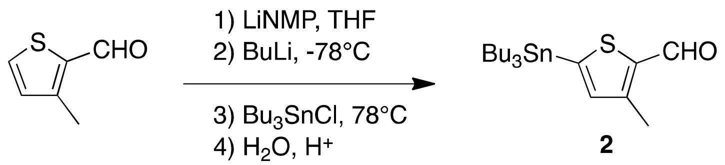
The synthetic general strategy followed to prepare the organic dyes is outlined in Scheme 1.

Scheme 1. Synthetic pathway to organic dyes 19, 20 and 21 by the retrosynthetic approach.



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-thiophencarbaldehyde adapting a literature procedure[45] (Scheme 2).

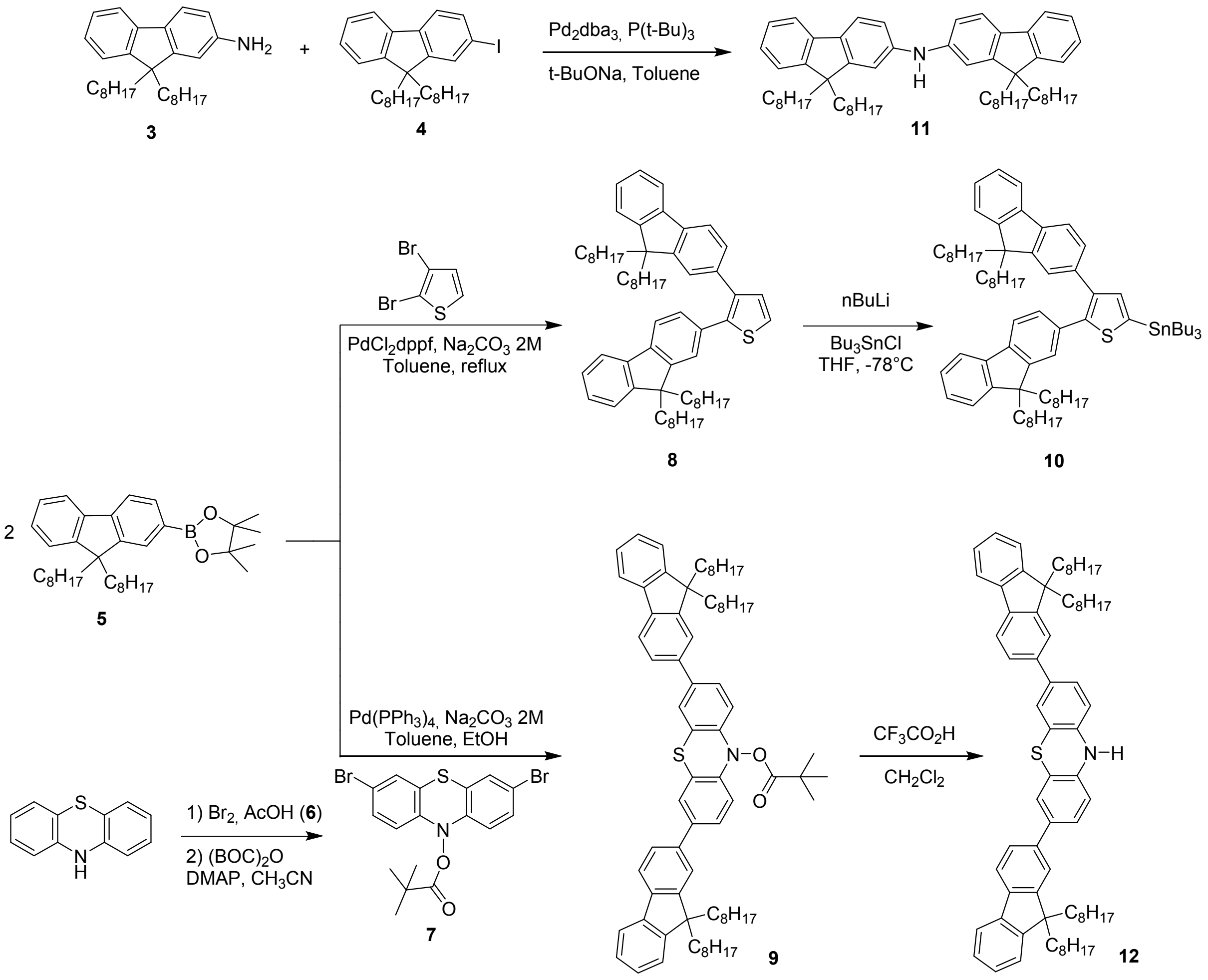
Scheme 2. Synthesis of 3-methyl-5-tributyltin-2-thiophencarbaldehyde 2.



The reagent 3-methyl-2-thiophenecarbaldehyde was metallated by lithium N-methylpiperazide, *in situ* prepared by adding butyl lithium to N-methylpiperazide. The resulting metallated derivatives 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.

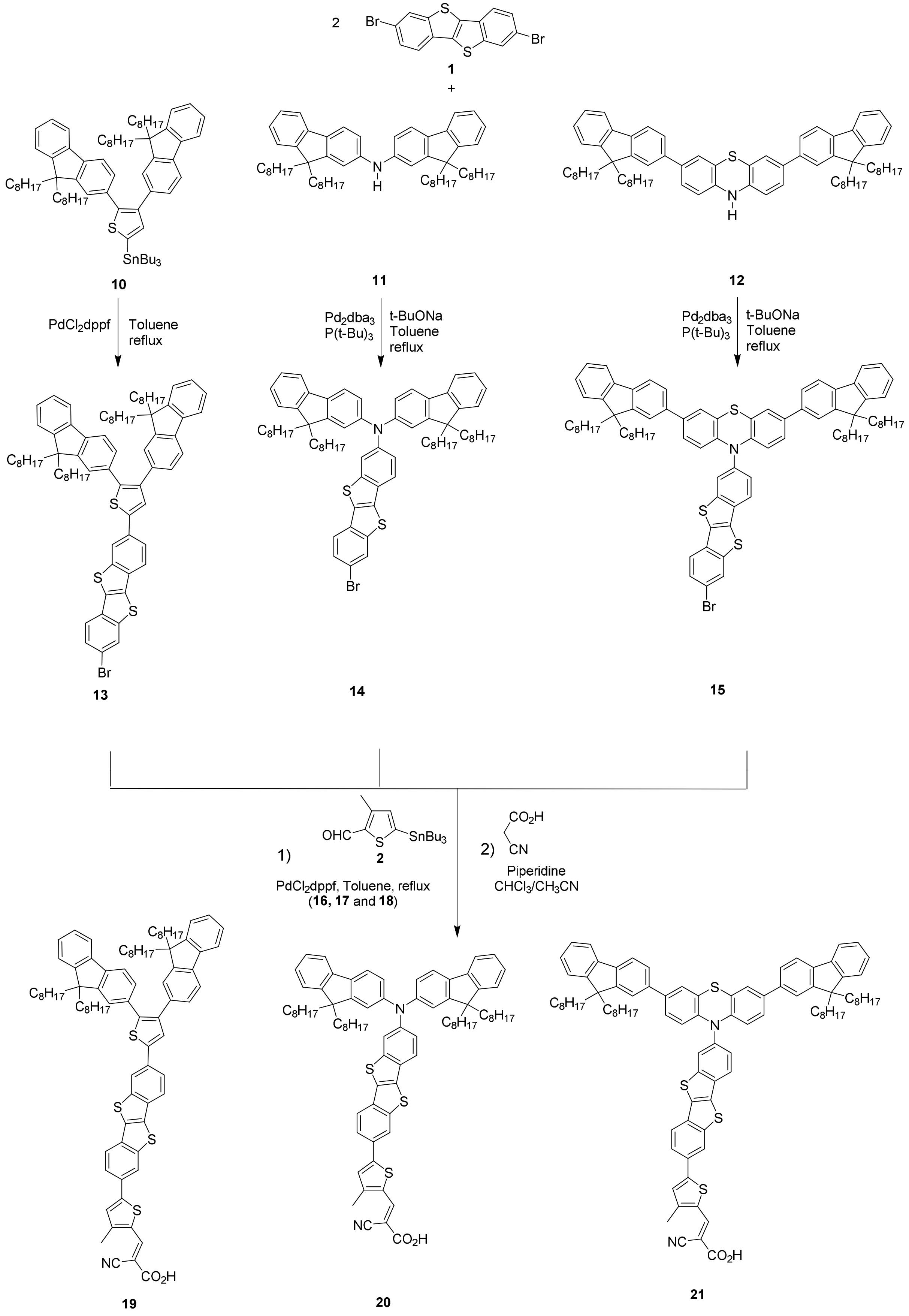
Scheme 3. Synthetic pathway to intermediate compounds 10, 11 and 12.



The donor building block **11** was synthesized by reacting the 2-amino 9,9-dioctylfluorene[46] **3** with the 9,9-dioctyl-2-iodo-fluorene[47] **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 PdCl$_2$dppf 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 Bu$_3$SnCl, 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 $Pd(PPh_3)_4$ as the catalyst, to yield the intermediate **9**. Compound **9** was purified by column chromatography and obtained as a light brown solid. Subsequently, compound **9** was submitted to hydrolysis of the BOC protecting group by CF_3CO_2H in dichloromethane, to yield, after purification by column chromatography, the pure product **12** as a brown solid.

The intermediate **7** was synthesized as reported in the literature[48] in two steps, by brominating the commercial phenothiazine with bromine in acetic acid, then reacting the resulting 3,7-dibromphenothiazine **6** with di-*tert*-butyl dicarbonate $(Boc)_2O$, in the presence of dimethyalmminopyridine DMAP and CH_3CN as the solvent. Compound **7** was collected as a colourless powder in an almost quantitative yield from the reaction mixture, after adding water and filtering the resulting precipitate. The three dyes **19**, **20** and **21** were synthesized as reported in Scheme 4.

Scheme 4. Synthetic pathway to dyes 19, 20 and 21.


2
Br
S
S
Br
1
+
C_8H_{17}
SnBu$_3$
10
PdCl$_2$dppf
Toluene
reflux
N
H
11
Pd$_2$dba$_3$
P(t-Bu)$_3$
t-BuONa
Toluene
reflux
12
13
14
15
OHC
SnBu$_3$
2
1)
PdCl$_2$dppf, Toluene, reflux
(**16, 17** and **18**)
2)
CO$_2$H
CN
Piperidine
CHCl$_3$/CH$_3$CN
NC
CO$_2$H
19
20
21

The intermediates **10**, **11** and **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 eq.) 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 light green 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.

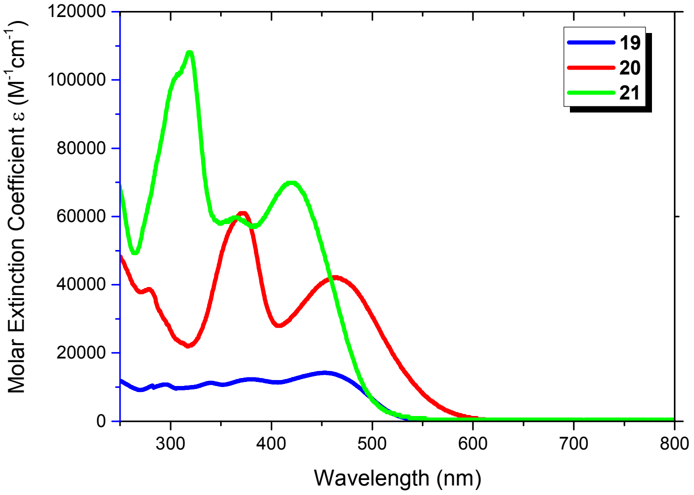


Figure 1. Molar absorptivity of **19, 20** and **21** in chloroform solution.

The dye **19** show a broaden absorption in the range 250-500 nm with an extinction coefficient over 10000 with a maximum value of 14190 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 60000 and 42000, 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 the **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 100000 and 69000, respectively. Despite the enormous increasing of the extinction coefficient in **21**, its photovoltaic performances didn't 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 TiO_2 and the regeneration of the dyes, the redox behaviour was studied by cyclic voltammetry (Fig. 2, Table 1).

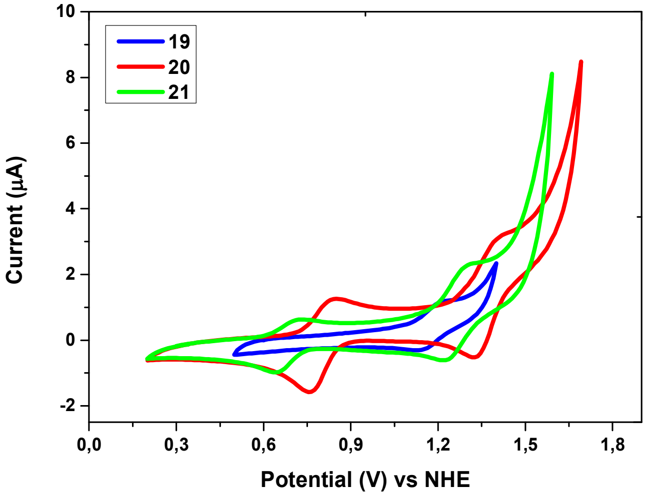


Figure 2. Cyclic voltammograms of dyes in CH_2Cl_2

The first oxidation versus normal hydrogen electrode (*vs*. NHE), corresponding to the highest occupied molecular orbital (HOMO) level of the dye, has been 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^-/I_3^- (0.4 V *vs*. NHE),[49] indicating that the oxidized dye molecules formed after electron injection into the conduction band of TiO_2 could be regenerated by the reducing species in the electrolyte solution. The energy gaps ($E_{0\text{-}0}$) between HOMO and LUMO levels calculated from onset of the absorption spectra for **19**, **20** and **21** were found to be 2.38, 2.21 and 2.50 eV, respectively. The lowest unoccupied molecular orbitals (LUMOs), has been estimated to be -1.16, -1.36 and -1.75 V, calculated from $E_{0\text{-}0} = E_{HOMO}\text{-}E_{LUMO}$.[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.

Table 1. Electrochemical data, absorption maxima and molar extinction coefficients.

Dye	$^a\lambda_{max}$(nm)/ ε(M-1cm-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

[a] Absorption maximum of the dyes measured in chloroform with a concentration ca 2 μM. ε molar extinction coefficient at λ_{max}. HOMO of the dyes by cyclic voltammetry in CH_2Cl_2, 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 mVs^{-1}. LUMO was calculated as the difference HOMO-E_{0-0}. E_{0-0} was estimated from the absorption spectral onsets of the dyes.

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 (ESI) 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 lowest occupied orbitals to the higher unoccupied molecular orbital (LUMO).

A similar indication was also obtained from the isodensity plots of the frontier orbitals, reported in Figure 3. The two indicators Λ and Δr[57,58] (Table S1, ESI) 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 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**, **20,** and **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.

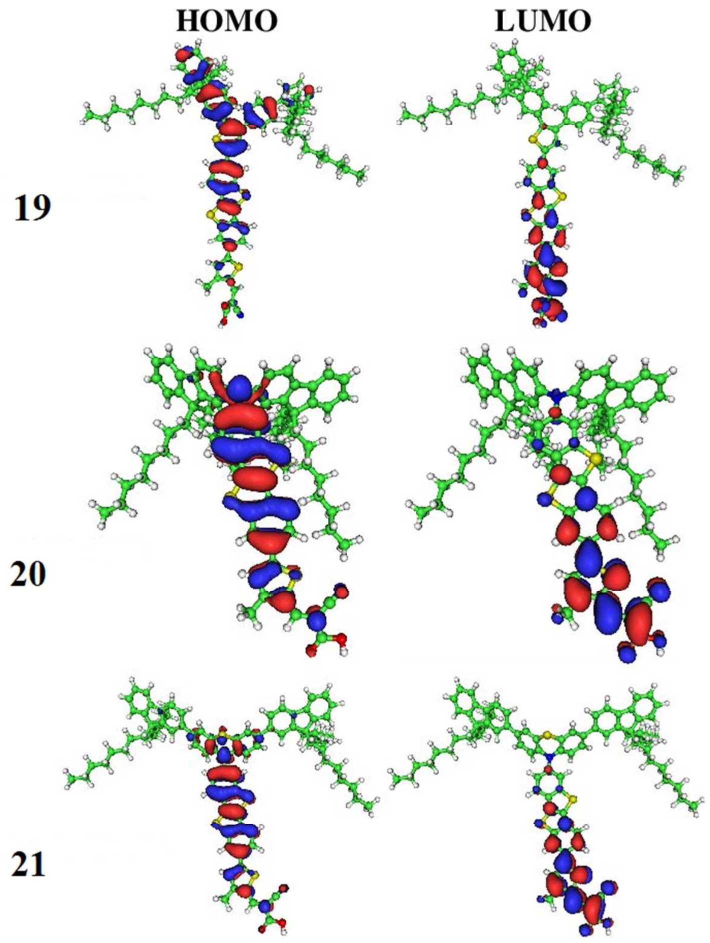


Figure 3. Isodensity plots of the most relevant frontier orbitals of 19, 20 and 21.

Photovoltaic performance

Favourable characteristics emerge, in terms of potential photovoltaic properties, from the characterization of **19**, **20** and **21** dyes concerning in particular their light harvesting capability. Therefore, the properties of the three dyes were tested in photo-electrochemical solar cells. Due to the high planarity of the sensitizers, favoured by the presence of the [1]benzothieno[3,2-b]benzothiophene (BTBT) spacer, a fast intramolecular charge transfer should be expected as well as an unfavourable 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 co-adsorbent 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 the attachment to the TiO_2 surface lowering the amount of sensitizers loaded on the working electrode. On these basis, the use of chenodeoxycholic acid (CDCA) as coadsorbent has been evaluated: we prepared 0.2 mM solutions of **19**, **20** and **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 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 V, from 0.736 to 0.765 and from 0.689 to 0.719 for **19**, **20** and **21**, respectively, suggesting that the detrimental recombination processes at the TiO_2/dye/electrolyte interface were partially suppressed with the use of CDCA additive.

Table 2. Photovoltaic parameters for DSSCs based on 19, 20 and **21 dyes**.

Dye	*CDCA (mM)*	*PCE (%)*	*Voc (V)*	*Jsc (mA/cm^2)*	*FF*	*Dye loading (mol/cm^2)*
19	0	4.20	0.704	9.18	0.65	$2.9x10^{-7}$
	10	5.16	0.735	10.33	0.68	$2.4x10^{-7}$
20	0	5.76	0.736	11.50	0.68	$3.0x10^{-7}$
	10	6.25	0.765	11.85	0.69	$2.4x10^{-7}$
21	0	4.54	0.689	9.56	0.69	$2.8x10^{-7}$
	10	5.00	0.719	9.67	0.72	$2.2x10^{-7}$

Moreover, the short-circuit photocurrent density (J_{SC}) augmented from 9.18 to 10.33 mA/cm^2, from 11.50 to 11.85 and from 9.56 to 9.67 for **19**, **20** and **21**, respectively. On the whole, power conversion efficiencies (PCE) of 5.16, 6.25 and 5.0% has been achieved with **19-**, **20-** and **21-** sensitized device, respectively. The I-V curves of DSSCs based on the three sensitizers in the presence of 10 mM CDCA, are shown in Figure 4.

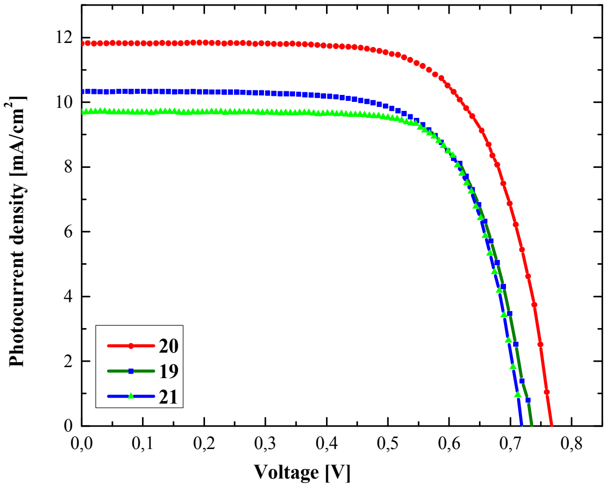


Figure 4. I-V curves of DSSCs fabricated with the three dyes in the presence of 10 mM CDCA.

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 emerge from the analysis of the monochromatic incident photon-to-current conversion efficiencies (IPCEs) recorded for the DSSCs (Figure 5). Notwithstanding the competitive absorption of FTO-glass, TiO_2 and electrolyte, the IPCE spectra seem to be in agreement with the light-harvesting range of sensitizers, although the presence of large TiO_2 scattering nanoparticles in the photoanode broaden their shape. The IPCE spectra of **20** dye showed a maximun 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.

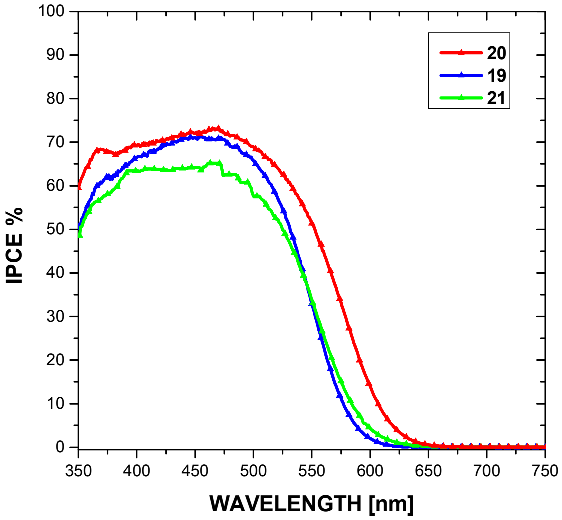


Figure 5. IPCEs spectra recorded for DSSCs devices fabricated with the three dyes.

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 others reported dyes. These achievements support the rationale behind the choice of the [1]benzothieno[3,2-b]benzothiophene 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 favourable 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 help the efficiency of the final device by minimizing detrimental dye aggregation effects. In fact, all dyes show better PCE value in the presence of CDCA coadsorbent. Overall, the BTBT intermediate is very easy to synthesize and can be prepared in very large amount, 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 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 CH_3CN were distilled from 4Å molecular sieves; $CHCl_3$ was distilled from P_2O_5. Column chromatography was performed using silica gel 60, 40-63 μm. Silica gel 60 F254 aluminium sheets were used for analytical TLC. FT-IR spectra were measured on a spectrophotometer using dry KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2CO$ or $CDCl_3$/DMSO-d_6 on a 500 MHz spectrometer at 500 MHz and 125.7 MHz, respectively. The residual signals at $\delta = 7.24$ ($CDCl_3$) or $\delta = 2.05$ ($(CD_3)_2CO$) or $\delta = 2.5$ ($CDCl_3$/DMSO-d_6) ppm were used as the standard for ^{1}H NMR spectra. The signals at $\delta = 77.0$ ($CDCl_3$) or $\delta = 30.83$ ($(CD_3)_2CO$) ppm were used as the standard for ^{13}CNMR 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-(tributylstannil)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 nBuLi (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 nBuLi (2.5 M, 12 mL) was added dropwise, and the resulting mixture was stirred at -20°C for 5h. A solution of nBu_3SnCl (8.3 mL, 30 mmol) in anhydrous THF (20 mL) was added dropwise at -78°C and the mixture was allowed to warm at r. t. and stirred overnight. To the mixture 1N HCl (150 mL) was added at 0°C for 20 min, then neutralized with aq. Na_2CO_3 solution. The mixture was extracted with hexane and the organic layer washed with aq 40% KF solution and dried over Na_2SO_4. After evaporation of the solvent under a reduced pressure, the crude residue was purified by distillation with a kugelrohr apparatus ($9x10^{-6}$ torr, T = 70°C) to yield the pure product **2** (9.2 g, 82% yield) as a light yellow liquid. ^1H NMR (500 MHz, $CDCl_3$): 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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 ($[M\text{-}Bu]^+$, 94), 303 (100). 247 (65). Anal. Calcd for $C_{18}H_{32}OSSn$: 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), Pd_2dba_3 (0.05 g, 0.055 mmol), $AsPh_3$ (0.135 g, 0.44 mmol), toluene (30 mL) and EtOH (6 mL). The mixture was degassed with a nitrogen flow for 30 min, then 2M Na_2CO_3 aq. (25 mL, 50 mmol) previously degased was added and the resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 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, $CDCl_3$): 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. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 150.8, 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, 29.311, 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 $C_{62}H_{84}S$: 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), $Pd(PPh_3)_4$ (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 2M Na_2CO_3 aq. (7.5 mL, 15 mmol) previously degased was added and the resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with saturated aq. NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH_2Cl_2 (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, $CDCl_3$): 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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{75}H_{97}NO_2S$: 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 nBuLi (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 Bu_3SnCl (0.36 mL, 1.1 mmol) in anhydrous THF (10 mL) was added dropwise. The resulting mixture was allowed to warm to r.t. and stirred overnight. The reaction mixture was quenched with water and extracted with ethyl acetate. The organic layer was washed with 40% aq. KF (2x20 mL), dried over Na_2SO_4 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 light yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): 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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{74}H_{110}SSn$: 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), Pd_2dba_3 (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 r.t., quenched with saturated aq. NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH_2Cl_2 (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. ^{1}H NMR (500 MHz, $(CD_3)_2CO$: 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. ^{13}C NMR (125 MHz, $(CD_3)_2CO$: 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 $C_{58}H_{83}N$: 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), CF_3CO_2H (5 mL) and CH_2Cl_2 was stirred overnight at r.t. The reaction mixture was quenched at 0°C in a 5% NaOH aq. solution, then extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH_2Cl_2 (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, $(CD_3)_2CO$): 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. ^{13}C NMR (125 MHz, $(CD_3)_2CO$): 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 $C_{70}H_{89}NS$: 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), $PdCl_2$dppf (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 r.t., quenched with saturated aq NH_4Cl and extracted with ethyl acetate. The organic layer was washed with 40% aq KF solution (2x20 mL), dried over Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH_2Cl_2 (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. ^{1}H NMR (500 MHz, $CDCl_3$): 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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{76}H_{89}BrS_3$: 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), Pd_2dba_3 (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 r.t., quenched with saturated aq NH_4Cl and extracted with ethyl acetate. The organic layer was washed with 40% aq KF solution (2x20 mL), dried over Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH_2Cl_2 (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. ^{1}H NMR (500 MHz, $CDCl_3$): 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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{72}H_{88}BrNS_2$: 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), Pd_2dba_3 (8 mg, 9.0 μmol) $P(tBu)_3$ (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 r.t., quenched with saturated aq. NH_4Cl and extracted with ethyl acetate. The organic layer was washed with 40% aq. KF solution (2x20 mL), dried over Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH_2Cl_2 (8.5/1.5) as the eluent, to yield the pure product **15** (0.27 g, 68% yield) as a yellow grassy solid. ^{1}H NMR (500 MHz, $CDCl_3$/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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{84}H_{94}BrNS_3$: 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-(tributylstannil)thiophene-2-carbaldehyde **2** (0.085 g, 0.2 mmol), $PdCl_2dppf$ (3 mg, 4 μmol) and anhydrous toluene (20 mL) were added and the resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with saturated aq. NH_4Cl and extracted with ethyl acetate. The organic layer was washed with 40% aq. KF solution (2x10 mL), dried over Na_2SO_4 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, ^{13}C NMR spectrum cannot be recovered. ^1H NMR (500 MHz, $CDCl_3$): 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 $C_{82}H_{94}OS_4$: 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]thiophen-2-yl)-3-methylthiophene-2-carbaldehyde 17. 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-(tributylstannil)thiophene-2-carbaldehyde 2 (0.09 g, 0.2 mmol), $PdCl_2dppf$ (3 mg, 4 μmol) and anhydrous toluene (20 mL) were added and the resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with saturated aq. NH_4Cl and extracted with ethyl acetate. The organic layer was washed with 40% aq. KF solution (2x10 mL), dried over Na_2SO_4 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. ^{1}H NMR (500 MHz, $CDCl_3$): 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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{78}H_{93}NOS_3$: 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]thiophen-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-(tributylstannil)thiophene-2-carbaldehyde **2** (0.08 g, 0.19 mmol), $PdCl_2$dppf (3 mg, 4 μmol) and anhydrous toluene (20 mL) were added. The resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with saturated aq. $NaHCO_3$ and extracted with chloroform. The organic layer was washed with 40% aq. KF solution (2x10 mL), dried over Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/CH_2Cl_2 (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, ^{13}C NMR spectrum cannot be recovered. ^{1}H NMR (500 MHz, $CDCl_3$): 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 $C_{90}H_{99}NOS_4$: 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)thiophene-2-yl)benzo[b]benzo[4,5]thieno[2,3-d]thiophene-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) and anhydrous $CHCl_3$ (10 mL) and CH_3CN (10 mL) were added and the resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with water and extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was washed with hexane, then dissolved in chloroform and washed with 1N aq. HCl. The organic layer was dried over anhydrous Na_2SO_4 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, ^{13}C NMR spectrum cannot be recovered. ^{1}H NMR (500 MHz, $[CD_3]_2CO$): 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 $C_{85}H_{95}NO_2S_4$: 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 $CHCl_3$ (10 mL) and CH_3CN (10 mL) were added and the resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with water and extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was washed with hexane, then dissolved in chloroform and washed with 1N aq. HCl. The organic layer was dried over anhydrous Na_2SO_4 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. ^{1}H NMR (500 MHz, ($CDCl_3$/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. ^{13}C NMR (125 MHz, $CDCl_3$): 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 $C_{81}H_{94}N_2O_2S_3$: 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 $CHCl_3$ (10 mL) and CH_3CN (10 mL) were added and the resulting mixture was refluxed overnight. The reaction mixture was cooled at r.t., quenched with water and extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was washed with hexane, then dissolved in chloroform and washed with 1N aq. HCl. The organic layer was dried over anhydrous

Na_2SO_4 and the solvent removed at a reduced pressure, to yield the pure product **21** (0.17 g, 95% yield) as a red solid. Mp 245-246 °C. Due to molecular aggregations, ^{13}C NMR spectrum cannot be recovered. ^1H NMR (500 MHz, $CDCl_3$/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 $C_{93}H_{100}N_2O_2S_4$: 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.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: …...

Computational details, atom coordinates, energies

Fabrication of DSSC and photovoltaic measurement

NMR spectra

References for Supporting Information

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