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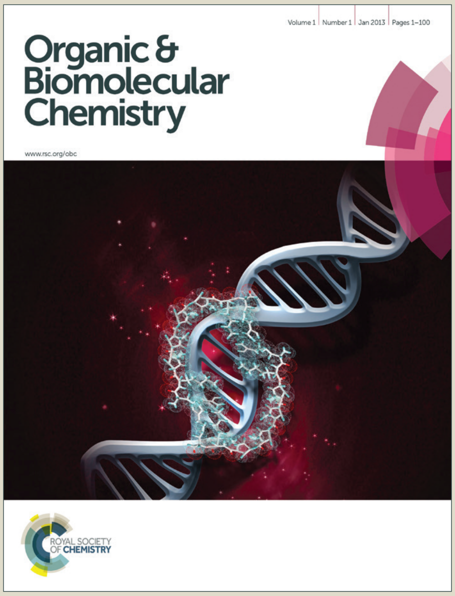

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TOC entry

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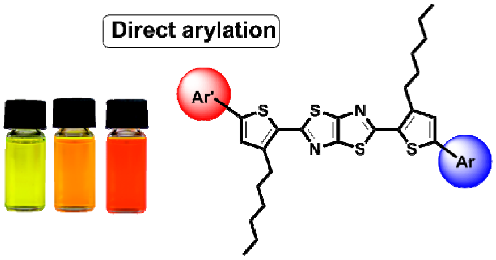

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PAPER

Direct arylation as a versatile tool towards thiazolo[5,4-*d*]thiazole-based semiconducting materials

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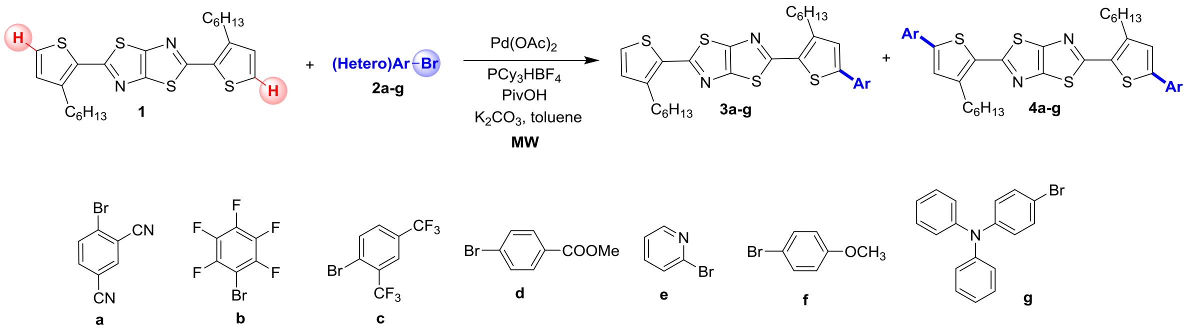
A series of thiazolo[5,4-*d*]thiazole-based small molecule organic optoelectronic materials is synthesized via a straighforward microwave-activated Pd-catalyzed C-H arylation protocol. The procedure allows to obtain extended 2,5-dithienylthiazolo[5,4-*d*]thiazole chromophores with tailor-made energy levels and absorption patterns, depending on the introduced (het)aryl moieties and the molecular (a)symmetry, by shortened sequences without organometallic intermediates. The synthesized materials can be applied as either electron donor or electron acceptor light-harvesting materials in molecular bulk heterojunction organic solar cells.

Introduction

Optoelectronic devices based on organic semiconductors – organic solar cells, transistors, light-emitting diodes and related applications – are steadily entering the market as the organic components allow to develop very thin and flexible large area devices with tunable color and transparency at a low cost using solution-based deposition techniques such as roll-to-roll printing. The optoelectronic properties of the active materials can readily be optimized through versatile organic synthesis protocols. In the design of potent organic semiconductors, careful consideration of molecular properties such as oxidation potentials, electron affinities, light-harvesting/emitting and/or charge transport features, solubility and intermolecular π-π interactions is of crucial importance. Oligothiophene structures have been shown to possess excellent semiconductor characteristics and a wide range of heterocycles has been introduced in thiophene-based π-conjugated small molecule materials to optimize particular properties.[1] The thiazolo[5,4-*d*]thiazole (TzTz) fused biheterocyclic system possesses a number of features – a rigid planar structure, strong electron deficient character, high oxidative stability, and high charge mobility – that render TzTz derivatives particularly attractive for organic electronics.[2-5] Nevertheless, their application has been quite limited, until recently, when the high potential of these molecules was more widely recognized, notably in the field of solution-processed organic photovoltaics (OPV).[6-8] Despite the strong rise in interest in these molecules, the synthetic chemistry behind TzTz-based materials has only been developed to a minor extent, and there is certainly room for improvement and broadening of the material scope.[2]

In previous work, we have synthesized a number of 5'-aryl-substituted 2,5-bis(3'-hexylthiophen-2'-yl)thiazolo[5,4-*d*]thiazole derivatives via Suzuki and Stille cross-coupling reactions and these expanded semiconductors were investigated as active materials for solution-processable organic field-effect transistors (OFET's).[9] On the other hand, it was shown that charge transfer (in the weak driving force limit) occurs in blends of dithienyl-TzTz's and MDMO-PPV (poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene]) towards fullerene-free OPV devices with high open-circuit voltages (V_{oc}).[10] Fullerenes till now turn out to be the superior electron acceptors in organic solar cells. The promises of more generic and versatile low-cost non-fullerene small molecules as acceptors in solution-processed bulk heterojunction (BHJ) organic solar cells have not been fulfilled so far, with maximum efficiencies around 4% (and routinely below 2%).[11] It has recently been calculated though that the cumulative energy demand (CED) required to produce BHJ OPV's, although on average 50% less than for conventional inorganic photovoltaics, is strongly affected by the presence of fullerenes, comprising 18–30% of the CED, despite being present in small quantities.[12] On the other hand, recent progress in the field of solution-processed molecular OPV, based on small molecule electron donor materials and fullerene acceptors, has afforded power conversion efficiencies in the same range as the best polymer BHJ OPV systems.[1b,13] In this line of thought, we now report on a series of TzTz-based small molecules, synthesized via microwave-activated direct arylation reactions, allowing to tune the energy levels and light absorption towards applications in OPV, either as small molecule electron donor materials or alternative electron acceptors.



Scheme 1 Synthesis of 5'-mono- (**3a–g**) and diarylated (**4a–g**) 2,5-bis(3'-hexylthiophen-2'-yl)thiazolo[5,4-*d*]thiazole derivatives via C-H arylation.

Results and discussion

Direct arylation reactions, in which the Pd-catalyzed coupling occurs directly between an (hetero)aryl bromide and an (hetero)aryl compound with activated C-H groups, have a number of advantages over traditional cross-coupling techniques, i.e. fewer synthetic operations and potentially higher yields, lower catalyst loadings, and, most importantly, no need for (high purity) organometallic intermediates (resulting in toxic byproducts, *e.g.* trialkyltin compounds), rendering it an ideal strategy for the synthesis of advanced materials for organic electronics.[14] C-H arylation procedures are often conducted in combination with microwave activation to speed up the reactions. Direct arylation protocols have recently been employed for the synthesis of low bandgap small molecules[15] and polymer materials[16] for organic solar cells, but they haven't been applied on TzTz materials so far. In this work, we have used a C-H arylation strategy to synthesize a series of TzTz-based semiconductors with varying electron affinities to be applied in organic solar cells, with a particular emphasis on monosubstitution, enabling to obtain asymmetrical push-pull derivatives to broaden the absorption window.

As the activated C-H part we have chosen 2,5-bis(3'-hexylthiophen-2'-yl)thiazolo[5,4-*d*]thiazole (**1**) (Scheme 1), which was prepared in a straightforward way (in 60% yield) via a condensation reaction at elevated temperature (130 °C) between dithiooxamide and 3-hexylthiophene-2-carbaldehyde in nitrobenzene, according to a modified literature procedure.[17] It's worth to mention that in this method only a stoichiometric amount of aldehyde (vs the 6 equiv used before[9,17]) has to be used. Dithienyl-TzTz **1** was then combined with different (hetero)aryl bromides **2a–g** (Scheme 1), chosen as such to generate a family of compounds with varying electron affinities. The reaction conditions (PdOAc$_2$, PCy$_3$HBF$_4$, pivalic acid, K$_2$CO$_3$, toluene, microwave heating)[14b] were first optimized for the combination of TzTz **1** and methyl 4-bromobenzoate (**2d**) (Table 1), in particular aiming at selective monoarylation as this provides an entry into unprecedented asymmetrically substituted TzTz materials. For that purpose, 1.1 equivalents **2d** were used and the reaction time was varied between 4 and 7 hours, whereas the reaction temperature was gradually increased from 100 to 180 °C. The highest yield was achieved at 180 °C (64% **3d**, 34% **4d**), although the selectivity was still modest. It should be mentioned here that the yield for the disubstituted product **4d** is based on the amount of TzTz **1** (a minority of 0.55 equiv with respect to **2d**) and might therefore look somewhat overestimated. In this respect, the isolated product amounts (as mentioned in the experimental section) might be more illustrative for the reaction selectivity (mono- vs disubstitution). At lower temperatures, quite some starting material (TzTz **1**) remained. Running the reaction at 100 °C for a longer time (7 h) did not significantly change the reaction outcome. Addition of an extra portion of fresh catalyst (2 mol%)[18] after 4 hours of reaction at 100 °C (and stirring for another 3 h at the same temperature) did not give any significant increase in the yield of **3d** and **4d** (49 and 7%, respectively) either.

Table 1 Optimization (of reaction time and temperature) for the direct arylation of TzTz **1** and methyl 4-bromobenzoate (**2d**) (1.1 equiv)

T (°C)	Time	**3d**	**4d**[a]
100	4h	43	8[b]
120	4h	41	30[b]
140	4h	57	33[b]
160	4h	60	33
180	4h	64	34
100	7h	46	4[b]

[a] Reaction yields for the disubstituted product **4d** might be somewhat misleading as they are based on the reaction partner in minority (TzTz **1**). [b] The remaining of the crude reaction mixture is mainly starting material (TzTz **1**).

The direct arylation of TzTz **1** was then extended to different types of aryl bromides **2a–g** using the same protocol (180 °C, 4 h) (Scheme 1, Table 2). The amount of (hetero)aryl bromide was adjusted for either mono- (1.1 equiv) or diarylation (2.1 equiv). Whenever separation and purification of the mono- and disubstituted compounds proved difficult, preparative size exclusion chromatography (SEC) was applied (see exp. section). In general, good overall yields were achieved, but selectivities remained rather modest (with some notable exceptions, see Table 2). From the results obtained, it is hard to detect clear trends in either yields or selectivities considering electronic substituent effects.

Table 2 Overview of the (isolated) yields and selectivities for the reactions between TzTz **1** and (hetero)aryl bromides **2a–g**

(Hetero)Ar-Br **2a–g**	Yields			
	1.1 equiv		2.1 equiv	
	3	**4**[b]	**3**	**4**[b]
a	49	44	34	52
b	35 49[a]	27 36[a]	30[a]	69[a]
c	33 58[a]	20 42[a]	27[a]	58[a]
d	64	34	6	92
e	69	27	34	50
f	28	70[b]	32	64[b]
g	50	38[b]	46	38[b]

[a] These reactions were run for 7 h (instead of the standard 4 h). [b] Reaction yields for the disubstituted products might be somewhat misleading as they are based on the reaction partner in minority (TzTz **1**).

All TzTz derivatives were completely characterized by ^{1}H and ^{13}C NMR and HRMS. UV-Vis absorption spectra of the functionalized TzTz molecules were collected to evaluate their light-harvesting properties, and the corresponding data (λ_{max} and ε) are gathered in Table 3. The (normalized) absorption spectra of all mono- and disubstituted TzTz's in chloroform solution are depicted in Fig. 1. All UV-Vis spectra display two distinct absorption bands in the UV (λ_{max} 250–320 nm) and visible region (λ_{max} 400–470 nm), attributed to the π–π* electronic transition and intramolecular charge transfer, respectively.[19] As expected, the difunctionalized TzTz's show a more red-shifted (10–28 nm) absorption. In addition, they have broader absorption spectra and higher molar absorptivities. Optical HOMO-LUMO gaps were determined from the onset (λ_{onset}) of the absorption spectra in solution. The optical HOMO-LUMO gaps are between 2.32 and 2.72 eV (Table 3), hence still rather high for OPV applications. The electron donating character of the triphenylamine substituent (**3g**/**4g**), together with the extended conjugation length, results in a broad and red-shifted absorption with the smallest HOMO-LUMO gap. Basic electrochemical properties were investigated by cyclic voltammetry (CV) and the derived frontier orbital energy levels are depicted in Table 3. The presence of electron withdrawing substituents such as cyano, fluoro and trifluoromethyl groups endows the molecules with deeper LUMO levels (as derived from the reduction onset by CV or calculated from the HOMO level, as derived from the oxidation onset, and the optical HOMO-LUMO gap), rendering them possible candidates for n-type acceptor materials for organic solar cells. As known from our former work,[10] dithienyl-TzTz semiconducting molecules with electron accepting substituents can be combined with a donor polymer (in this case MDMO-PPV) to afford photoinduced charge transfer (CT) in the resulting blends. The CT efficiencies were shown to be strongly correlated with increasing acceptor strength. Some of the new compounds (notably **3a**/**4a**) have lower LUMO values as compared to the published TzTz materials, which could possibly improve the CT efficiency and the final solar cell performance (considering also other potential loss mechanisms and sufficient electron mobility), increasing the very low efficiency of 0.1% previously observed.[10] Fig. 2 gives an overview of the energy levels obtained for all materials, together with prototype electron donor polymers (MDMO-PPV and P3HT or poly(3-hexylthiophene)) and the most used acceptor PCBM ([6,6]-phenyl-C_{61}-butyric acid methyl ester). Whereas previously only MDMO-PPV could be applied as donor material for the bis(4-cyanophenyl)-substituted dithienyl-TzTz acceptor (HOMO -5.76 eV, LUMO -3.25 eV),[10a] the LUMO levels of some of the novel materials (notably **4a**) are sufficiently low to enable combination with more effective low bandgap polymers such as PCPDT-DTTzTz[7f] (poly{[4-(2'-ethylhexyl)-4-octyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6-diyl]-*alt*-[2,5-di(3'-hexylthiophen-2'-yl)thiazolo[5,4-*d*]thiazole-5',5''-diyl]}), also containing TzTz as the electron deficient part.

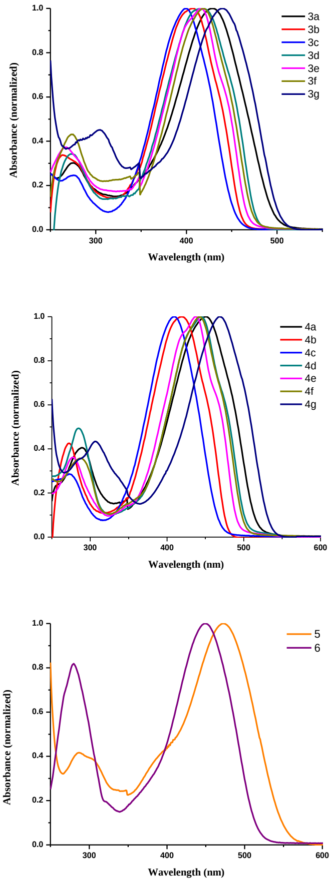


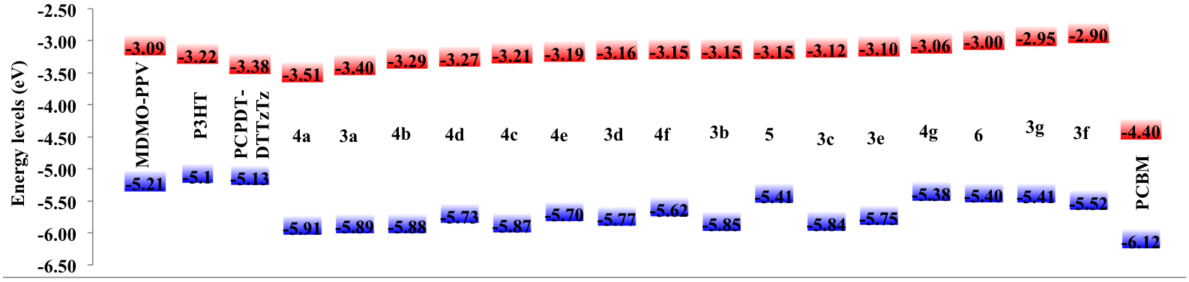
Fig. 1 Normalized UV-Vis absorption spectra of the synthesized TzTz's in $CHCl_3$ solution.

Table 3 Optical and electrochemical properties of the synthesized TzTz's (and some reference materials).

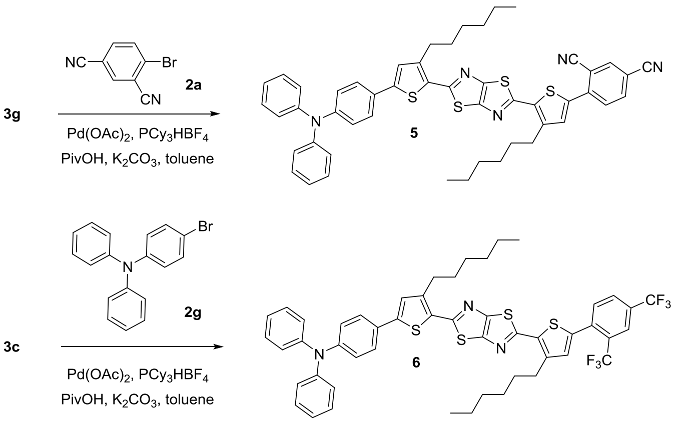
TzTz	λ_{max} (nm)[b] (log ε)[c]	ΔE_{opt}[d]	E^{ox}_{onset} (V)	HOMO (eV)[g]	E^{red}_{onset} (V)	LUMO (eV)[i]	ΔE_{ec}[j]	LUMO$_{calc}$ (eV)[k]
3a	427 (4.54)	2.49	1.04[e]	-5.89	-1.46[e]	-3.38	2.50	-3.40
4a	451 (4.70)	2.40	1.06[e]	-5.91	-1.41[e]	-3.43	2.47	-3.51
3b	406 (4.55)	2.70	1.00[f]	-5.85	-1.79[f]	-3.05	2.80	-3.15
4b	421 (4.58)	2.59	1.04[f]	-5.88	-1.72[f]	-3.12	2.76	-3.29
3c	400 (4.60)	2.72	1.00[f]	-5.84	-1.75[h]	-3.10	2.75	-3.12
4c	410 (4.69)	2.66	1.03[e]	-5.87	-1.75[f]	-3.10	2.78	-3.21
3d	417 (4.40)	2.61	0.92[f]	-5.77	-1.78[e]	-3.06	2.71	-3.16
4d	445 (4.45)	2.46	0.88[e]	-5.73	-1.79[h]	-3.06	2.67	-3.27
3e	416 (4.58)	2.65	0.91[f]	-5.75	-1.76[f]	-3.09	2.66	-3.10
4e	440 (4.65)	2.51	0.85[e]	-5.70	-1.73[e]	-3.12	2.58	-3.19
3f	418 (4.65)	2.62	0.67[e]	-5.52	-1.91[e]	-2.94	2.58	-2.90
4f	442 (4.80)	2.47	0.77[e]	-5.62	-1.89[e]	-2.96	2.66	-3.15
3g	440 (4.70)	2.46	0.57[e]	-5.41	-1.89[e]	-2.96	2.45	-2.95
4g	469 (4.88)	2.32	0.53[e]	-5.38	-1.81[e]	-3.04	2.34	-3.06
5	473 (4.66)	2.26	0.56[e]	-5.41	-1.51[e]	-3.34	2.07	-3.15
6	449 (4.73)	2.40	0.56[e]	-5.40	-1.80[e]	-3.05	2.35	-3.00
PCBM	\	1.72	1.26	-6.12	-0.83	-4.03	2.09	-4.40
P3HT[a]	\	1.88	0.13	-5.10	-2.09	-2.87	2.22	-3.22
MDMO-PPV[a]	\	2.12	0.24	-5.21	-2.03	-2.93	2.28	-3.09

[a] CV data in film. [b] Measured in $CHCl_3$ solution. [c] Molar extinction coefficient ε, determined at λ_{max} in $CHCl_3$ solution. [d] Optical HOMO-LUMO gap, $\Delta E_{opt} = 1240/(\lambda_{onset})$. [e] Reversible. [f] Quasi-reversible. [g] Determined from the oxidation onset. [h] Irreversible. [i] Determined from the reduction onset. [j] Electrochemical HOMO-LUMO gap. [k] LUMO$_{calc}$ = ΔE_{opt} + HOMO.

Fig. 2 HOMO-LUMO energy level diagram for the functionalized TzTz's (data from Table 3; LUMO$_{calc}$).



A second particular goal was to prepare asymmetrical donor-TzTz-acceptor molecules with broadened absorption profiles by sequential direct coupling reactions, as these compounds are of high appeal as photoactive (electron donor) materials for OPV. The few literature examples of asymmetrically extended TzTz derivatives were prepared via traditional Suzuki cross-coupling reactions in moderate overall yields.[8e,20] Push-pull TzTz compounds **5** and **6** were synthesized from monoarylated derivatives **3g** and **3c** in 85 and 88% yield, respectively (Scheme 2). The UV-Vis absorption spectra of these materials (Fig. 1) indeed show extended absorption (up to λ_{max} 473 nm for **5**).



Scheme 2 Synthesis of asymmetrically substituted TzTz derivatives **5** and **6** via stepwise C-H arylation.

Conclusions

A facile and versatile microwave-assisted procedure was developed for the direct arylation of 2,5-dithienylthiazolo[5,4-*d*]thiazoles with various electron rich and poor (hetero)aryl bromides towards a variety of molecular chromophores with an extended conjugated backbone. Unsymmetrical derivatives were readily obtained by a sequential direct arylation approach. These materials are designed to be applied as solution-processable solar photon-harvesting materials for bulk heterojunction organic photovoltaics, either as small molecule electron donor or acceptor constituents. Efforts in this direction are currently ongoing within our group. In a more general sense, the synthetic chemistry developed in this work can stimulate further progress on the development of controllable direct arylation protocols as powerful ‘atom-economic’ reactions towards advanced organic materials for printable electronics.

Acknowledgements

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Experimental section

General experimental methods

Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. Toluene was dried using an MBraun solvent purification system (model MB-SPS 800) equipped with alumina drying columns. Microwave reactions were carried out in a CEM Discovery microwave at the given temperature by varying the irradiation power. A thick-walled pyrex reaction vessel (10 mL) with teflon septum was used for the microwave reactions. NMR chemical shifts (δ) were determined relative to the residual $CHCl_3$ absorption (7.26 ppm) or the ^{13}C resonance shift of $CDCl_3$ (77.16 ppm) or C_6D_5Cl (134.19 ppm). ^{13}C signals split up by *J*-coupling with ^{19}F are indicated by their chemical shifts. High resolution electrospray ionization mass spectrometry (ESI-MS) analysis of the samples was performed using an LTQ Orbitrap Velos Pro mass spectrometer (Thermo-Fischer Scientific) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m/z* range 220–2000 using a standard solution containing caffeine, MRFA and Ultramark 1621. UV-Vis absorption spectra were recorded with an Agilent Cary 500 Scan UV-Vis-NIR spectrometer in a continuous run from 200 to 800 nm at a scan rate of 600 nm min^{-1}. Infrared spectra were collected with a resolution of 4 cm^{-1} (16 scans) using films drop-casted on a NaCl disk from $CHCl_3$ solution. Preparative size exclusion chromatography (SEC) was performed on JAIGEL 1H and 2H columns attached to an LC system equipped with a UV detector (path 0.5 mm) and a switch for recycling and collecting the eluent ($CHCl_3$: flow rate 3.5 mL min^{-1}, injection volume 2.5 mL). Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 30 potentiostat/galvanostat using a three-electrode microcell equipped with a Pt wire working electrode, a Pt wire counter electrode and a $Ag/AgNO_3$ reference electrode (Ag wire dipped in a solution of 0.01 M $AgNO_3$ and 0.1 M NBu_4PF_6 in anhydrous MeCN). Samples were prepared in anhydrous CH_2Cl_2 containing 0.1 M NBu_4PF_6, and ferrocene was used as an internal standard. The respective TzTz products were dissolved in the electrolyte solution, which was degassed with Ar prior to each measurement. To prevent air from entering the system, the experiments were carried out under a curtain of Ar. Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1}. The HOMO-LUMO energy levels of the products were determined using CV data and spectroscopic absorption data. For the conversion of V to eV, the onset potentials of the first oxidation/reduction peaks were used and referenced to ferrocene/ferrocenium, which has an ionization potential of -4.98 eV *vs.* vacuum. This correction factor is based on a value of 0.31 eV for Fc/Fc^+ *vs.* SCE[21a] and a value of 4.68 eV for SCE *vs.* vacuum[21b]: $E_{HOMO/LUMO}$ (eV) = -4.98 - $E_{onset\ ox/red}^{Ag/AgNO3}$ (V) + $E_{onset\ Fc/Fc+}^{Ag/AgNO3}$ (V). The HOMO energy levels of the TzTz products were determined from the CV data. The LUMO energy levels were either determined from the CV data or calculated as the difference between the HOMO values and the optical HOMO-LUMO gaps. To estimate the optical HOMO-LUMO gap, the wavelength at the intersection of the tangent line drawn at the low energy side of the (solution) absorption spectrum with the x-axis was used (E_g (eV) = 1240/(wavelength in nm)).

2,5-Bis(3'-hexylthiophen-2'-yl)thiazolo[5,4-*d*]thiazole (1). TzTz **1** was prepared by adding 3-hexylthiophene-2-carbaldehyde (1.96 g, 0.02 mol, 2 equiv) and dithiooxamide (2.39 g, 0.01 mol, 1 equiv) to nitrobenzene (20 mL) and heating the reaction mixture for 24 h at 130 °C under a nitrogen atmosphere. Nitrobenzene was removed by vacuum distillation. The black solid residue was evaporated on silicagel and consequently purified via column chromatography (eluent hexanes/EtOAc 95/5). The tubes containing yellow/brown TLC spots (R_f 0.5) were evaporated. The product was then crystallized from a MeOH/EtOAc mixture (2/1) to afford TzTz **1** (1.40 g, 60%) as a yellow crystalline powder. Material identity and purity were checked via ^{1}H NMR and HRMS and were found to be identical to literature data.[9,17]

General procedure for the direct arylation reactions. 2,5-Bis(3'-hexylthiophen-2'-yl)thiazolo[5,4-*d*]thiazole (**1**) (119 mg, 0.25 mmol, 1 equiv), K_2CO_3 (52 mg, 0.375 mmol 1.5 equiv), $Pd(OAc)_2$ (1.1 mg, 5 μmol, 2 mol%), PCy_3HBF_4 (3.7 mg, 10.0 μmol, 4 mol%) and pivalic acid (7.7 mg, 0.075 mmol, 30 mol%) were weighed in air and placed in a microwave vial (10 mL) equipped with a magnetic stirring bar. The solid aryl bromides (**2a,d,f,g**) were added at this point (1.1 or 2.1 equiv). The vial was purged with Ar and dry toluene (1 mL; 0.25 M final concentration of TzTz **1**) was added. The liquid aryl bromides (**2b,c,e**) were added at this point (1.1 or 2.1 equiv). The reaction mixture was vigorously stirred under microwave irradiation at 180 °C for 4 h. The solution was then cooled down to room temperature and diluted with CH_2Cl_2 and H_2O. The aqueous phase was extracted with CH_2Cl_2. The organic fractions were combined and dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The obtained product mixture was separated by column chromatography or preparative SEC to afford the pure mono- (**3a–g**) and disubstituted (**4a–g**) TzTz's.

4-{4-Hexyl-5-[5-(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazol-2-yl]thiophen-2-yl}isophthalonitrile (3a). 4-Bromoisophthalonitrile (**2a**) (57 mg, 0.275 mmol, 1.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 4/1–1/1) to afford **3a** (74 mg, 49%) and **4a** (41 mg, 44%); Red solid; Mp 110–111 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 1.1 Hz, 1H), 7.86 (dd, J = 8.3, 1.1 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.73 (s, 1H), 7.37 (d, J = 5.1 Hz, 1H), 7.00 (d, J = 5.1 Hz, 1H), 3.09–2.89 (m, 4H), 1.87–1.64 (m, 4H), 1.55–1.41 (m, 4H), 1.40–1.26 (m, 8H), 0.99–0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 159.7, 151.0, 150.4, 144.2, 143.8, 140.4, 138.1, 138.0, 136.0, 135.9, 132.7, 131.8, 131.1, 130.0, 128.0, 117.1, 116.7, 112.0, 110.7, 31.8, 31.7, 30.5, 30.4, 30.1, 30.0, 29.47, 29.45, 22.8 14.3; IR (NaCl) ν_{max} 2953/2928/2857 (saturated C-H), 2223 cm^{-1} (CN); HRMS (ESI) *m/z* calcd for $C_{32}H_{33}N_4S_4$ [M + H]$^+$ 601.1510; found 601.1564; UV-Vis ($CHCl_3$) λ_{max} (log ε) 427 nm (4.54).

4,4'-[Thiazolo[5,4-*d*]thiazole-2,5-diyl-bis(4-hexylthiophene-5,2-diyl)]diisophthalonitrile (4a). 4-Bromoisophthalonitrile (**2a**) (109 mg, 0.525 mmol, 2.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 4/1–1/1) to afford **3a** and **4a** in 34 and 52% yield (96 and 52 mg), respectively; Red solid; Mp 285–286 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 1.7 Hz, 2H), 7.88 (dd, J = 8.2, 1.7 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.74 (s, 2H), 3.06–2.98 (m, 4H), 1.85–1.72 (m, 4H), 1.55–1.44 (m, 4H), 1.42–1.31 (m, 8H), 0.91 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 151.3, 144.7, 140.4, 138.5, 138.1, 136.1, 135.7, 132.8, 130.1, 117.0, 116.7, 112.2, 110.9, 31.8, 30.6, 30.0, 29.4, 22.8, 14.2; IR (NaCl) ν_{max} 2950/2927/2856 (saturated C-H), 2220 cm^{-1} (CN); HRMS (ESI) *m/z* calcd for $C_{40}H_{35}N_6S_4$ [M + H]$^+$ 727.1728; found 727.1773; UV-Vis ($CHCl_3$) λ_{max} (log ε) 451 nm (4.70).

2-[3-Hexyl-5-(perfluorophenyl)thiophen-2-yl]-5-(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole (3b). 1-Bromo-2,3,4,5,6-pentafluorobenzene (**2b**) (33 μL, 0.275 mmol, 1.1 equiv); The reaction was run for 7 h; The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 9/1–3/2). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3b** and **4b** in 49 and 36% yield (78 and 36 mg), respectively; Yellow solid; Mp 84–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.36 (d, J = 5.2 Hz, 1H), 6.98 (d, J = 5.2 Hz, 1H), 3.05–2.87 (m, 4H), 1.84–1.64 (m, 4H), 1.57–1.41 (m, 4H), 1.41–1.30 (m, 8H), 0.96–0.86 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 160.2, 150.7, 150.4, 144.3 (d, ^1J = 250 Hz), 143.6, 142.7, 140.3 (d, ^1J = 250 Hz), 138.2 (d, ^1J = 250 Hz), 134.4 (t, ^3J = 4.1 Hz), 133.7 (d, ^2J = 5.8 Hz), 131.8, 131.0, 127.8 (m), 127.7, 109.5 (dt, ^2J = 14.9 Hz; ^3J = 4.3 Hz), 31.8, 30.3, 30.0, 29.5, 22.8, 14.2; HRMS (ESI) *m/z* calcd for $C_{30}H_{30}F_5N_2S_4$ [M + H]$^+$ 641.1212; found 641.1212; UV-Vis ($CHCl_3$) λ_{max} (log ε) 406 nm (4.55).

2,5-Bis[3-hexyl-5-(perfluorophenyl)thiophen-2-yl]thiazolo[5,4-*d*]thiazole (4b). 1-Bromo-2,3,4,5,6-pentafluorobenzene (**2b**) (65 μL, 0.525 mmol, 2.1 equiv); The reaction was run for 7 h; The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 9/1–3/2). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3b** and **4b** in 30 and 69% yield (49 and 140 mg), respectively; Yellow solid; Mp 158–159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 2H), 3.05–2.96 (m, 4H), 1.83–1.69 (m, 4H), 1.52–1.43 (m, 4H), 1.40–1.30 (m, 8H), 0.91 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, C_6D_5Cl) δ 160.8, 151.1, 145.9, 144.2 (d, ^1J = 250 Hz), 143.1, 140.1 (d, ^1J = 250 Hz), 138.0 (d, ^1J = 250 Hz), 134.6, 133.7, 109.6 (m), 31.8, 30.3, 30.0, 29.5, 22.8, 14.1 (Due to the poor compound solubility in $CDCl_3$, C_6D_5Cl was used for the ^{13}C NMR measurement. The solvent peaks obscure 4 signals between 133 and 124 ppm.); HRMS (ESI) *m/z* calcd for $C_{36}H_{29}F_{10}N_2S_4$ [M + H]$^+$ 807.1025; found 807.1054; UV-Vis ($CHCl_3$) λ_{max} (log ε) 421 nm (4.58).

2-{5-[2,4-Bis(trifluoromethyl)phenyl]-3-hexylthiophen-2-yl}-5-(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole (3c). 1-Bromo-2,4-bis(trifluoromethyl)benzene (**2c**) (46 μL, 0.275 mmol, 1.1 equiv); The reaction was run for 7 h; The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 9/1–6/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3c** and **4c** in 58 and 42% yield (99 and 47 mg), respectively; Yellow solid; Mp 77–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.36 (d, J = 5.1 Hz, 1H), 7.07 (s, 1H), 6.99 (d, J = 5.1 Hz, 1H), 3.07–2.88 (m, 4H), 1.84–1.62 (m, 4H), 1.56–1.41 (m, 4H), 1.39–1.28 (m, 8H), 0.98–0.82 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 160.6, 150.5, 150.2, 143.5, 143.1, 139.3, 136.8, 133.9, 133.6, 132.3 (q, ^3J= 3 Hz), 131.9, 131.0 (q, ^2J = 34 Hz) 129.8 (q, ^2J = 32 Hz) 128.5 (q, ^3J = 3 Hz), 127.7, 125.2, 124.1, 123.4 (q, ^1J = 273 Hz), 123.3 (q, ^1J = 273 Hz), 31.8 (2C's), 30.4, 30.3, 30.1, 29.9, 29.5, 29.3, 22.8, 14.2; HRMS (ESI) *m/z* calcd for $C_{32}H_{33}F_6N_2S_4$ [M + H]$^+$ 686.3530; found 686.1429; UV-Vis ($CHCl_3$) λ_{max} (log ε) 400 nm (4.60).

2,5-Bis{5-[2,4-bis(trifluoromethyl)phenyl]-3-hexylthiophen-2-yl}thiazolo[5,4-*d*]thiazole (4c). 1-Bromo-2,4-bis(trifluoromethyl)benzene (**2c**) (89 µL, 0.525 mmol, 2.1 equiv); The reaction was run for 7 h; The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 9/1–6/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3c** and **4c** in 27 and 58% yield (23 and 131 mg), respectively; Yellow solid; Mp 152–153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.08 (s, 2H), 3.04–2.93 (m, 4H), 1.82–1.70 (m, 4H), 1.53–1.42 (m, 4H), 1.38–1.31 (m, 8H), 0.91 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 150.6, 143.3, 139.5, 136.8, 133.8, 133.6, 132.4 (q, ^3J = 3Hz), 130.9 (q, ^2J = 33 Hz), 129.9 (q, ^2J = 34 Hz), 128.6 (q, ^3J = 3 Hz), 124.1, 123.4 (q, ^1J = 273 Hz), 123.3 (q, ^1J = 273 Hz), 31.8, 30.4, 30.0, 29.3, 22.8, 14.2; HRMS (ESI) *m/z* calcd for $C_{40}H_{35}F_{12}N_2S_4$ [M + H]$^+$ 899.1413; found 899.1486; UV-Vis ($CHCl_3$) λ_{max} (log ε) 410 nm (4.69).

Methyl 4-{4-hexyl-5-[5-(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazol-2-yl]thiophen-2-yl}benzoate (3d). Methyl 4-bromobenzoate (**2d**) (59 mg, 0.275 mmol, 1.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 12/1–10/1) to afford **3d** and **4d** in 64 and 34% yield (98 and 32 mg), respectively; Red solid; Mp 95–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 5.1 Hz, 1H), 7.31 (s, 1H), 6.99 (d, J = 5.1 Hz, 1H), 3.92 (s, 3H), 3.04–2.90 (m, 4H), 1.84–1.65 (m, 4H), 1.54–1.41 (m, 4H), 1.40–1.23 (m, 8H), 0.98–0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 162.0, 161.0, 150.4, 150.3, 144.3, 144.0, 143.4, 137.8, 132.6, 131.9, 131.0, 130.5, 129.6, 128.1, 127.6, 125.6, 52.4, 31.8 (2 C's), 30.6, 30.3, 30.1, 29.5, 22.8 14.3; IR (NaCl) ν_{max} 2956/2929/2857 (saturated C-H), 1719 cm^{-1} (COOMe); HRMS (ESI) *m/z* calcd for $C_{32}H_{37}N_2O_2S_4$ [M + H]$^+$ 609.1738; found 609.1730; UV-Vis ($CHCl_3$) λ_{max} (log ε) 417 nm (4.40).

Dimethyl 4,4'-[(thiazolo[5,4-*d*]thiazole-2,5-diyl)-bis(4-hexylthiophene-5,2-diyl)]dibenzoate (4d). Methyl 4-bromobenzoate (**2d**) (113 mg, 0.525 mmol, 2.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 12/1–10/1) to afford **3d** and **4d** in 6 and 92% yield (9 and 178 mg), respectively; Red solid; Mp 211–213 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 4H), 7.70 (d, J = 8.2 Hz, 4H), 7.24 (s, 2H), 3.92 (s, 3H), 2.96–2.89 (m, 4H), 1.80–1.68 (m, 4H), 1.53–1.44 (m, 4H), 1.40–1.32 (m, 8H), 0.92 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 161.1, 150.5, 144.3, 144.0, 137.7, 132.6, 130.5, 129.5, 128.0, 125.5, 52.4, 31.8, 30.6, 30.0, 29.6, 22.8, 14.3; IR (NaCl) ν_{max} 2950/2925/2853 (saturated C-H), 1718 cm^{-1} (COOMe); HRMS (ESI) *m/z* calcd for $C_{32}H_{37}N_2O_2S_4$ [M + H]$^+$ 743.2106; found 743.2067; UV-Vis ($CHCl_3$) λ_{max} (log ε) 445 nm (4.45).

2-[3-Hexyl-5-(pyridin-2-yl)thiophen-2-yl]-5-(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole (3e). 2-Bromopyridine (**2e**) (26 µL, 0.275 mmol, 1.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–7/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3e** and **4e** in 69 and 27% yield (96 and 22 mg), respectively; Red solid; Mp 98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (dd, J = 4.7, 0.8 Hz, 1H), 7.75–7.63 (m, 2H), 7.54 (s, 1H), 7.34 (d, J = 5.1 Hz, 1H), 7.23–7.15 (m, 1H), 6.98 (d, J = 5.1 Hz, 1H). 3.05–2.90 (m, 4H), 1.83–1.65 (m, 4H), 1.56–1.39 (m, 4H), 1.37–1.29 (m, 8H), 0.98–0.79 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9, 161.4, 151.6, 150.5, 150.3, 149.6, 144.8, 144.4, 143.3, 137.2, 133.5, 132.0, 130.9, 128.5, 127.5, 122.6, 119.3, 31.8 (2C's), 30.5, 30.3, 30.1, 30.0, 29.8, 29.5, 22.8, 14.3; HRMS (ESI) *m/z* calcd for $C_{34}H_{34}N_3S_4$ [M + H]$^+$ 552.1636; found 552.1635; UV-Vis ($CHCl_3$) λ_{max} (log ε) 416 nm (4.58).

2,5-Bis[3-hexyl-5-(pyridin-2-yl)thiophen-2-yl]thiazolo[5,4-*d*]thiazole (4e). 2-Bromopyridine (**2e**) (50 µL, 0.525 mmol, 2.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–7/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3e** and **4e** in 34 and 50% yield (47 and 78 mg), respectively; Red solid; Mp 168–169 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, J = 4.7 Hz, 2H), 7.80–7.60 (m, 4H), 7.50 (s, 2H), 7.21–7.15 (m, 2H), 3.08–2.87 (m, 4H), 1.85–1.61 (m, 4H), 1.57–1.40 (m, 4H), 1.40–1.29 (m, 8H), 0.98–0.85 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 151.8, 150.6, 149.9, 145.4, 144.4, 136.8, 133.3, 128.2, 122.6, 119.2, 31.8, 30.5, 30.0, 29.4, 22.8, 14.3; HRMS (ESI) *m/z* calcd for $C_{34}H_{37}N_4S_4$ [M + H]$^+$ 629.1901; found 629.1881; UV-Vis ($CHCl_3$) λ_{max} (log ε) 440 nm (4.65).

2-[3-Hexyl-5-(4-methoxyphenyl)thiophen-2-yl]-5-(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazole (3f). 1-Bromo-4-methoxybenzene (**2f**) (51 mg, 0.275 mmol, 1.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–7/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3f** and **4f** in 28 and 70% yield (41 and 60 mg), respectively; Orange solid; Mp 83–84 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 5.1 Hz, 1H), 7.08 (s, 1H), 6.97 (d, J = 5.1 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H), 3.01–2.86 (m, 4H), 1.81–1.61 (m, 4H), 1.53–1.25 (m, 8H), 0.96–0.81 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 161.4, 159.9, 150.2, 149.9, 145.7, 144.3, 143.1, 132.0, 130.9, 130.1, 127.4, 127.2, 126.4, 125.7, 114.5, 55.5, 31.8, 30.6, 30.3, 30.1, 30.0, 29.5, 22.8, 14.3; HRMS (ESI) *m/z* calcd for $C_{31}H_{37}N_2OS_4$ $[M + H]^+$ 581.1789; found 581.1765; UV-Vis ($CHCl_3$) λ_{max} (log ε) 418 nm (4.65).

2,5-Bis[3-hexyl-5-(4-methoxyphenyl)thiophen-2-yl]thiazolo[5,4-*d*]thiazole (4f). 1-Bromo-4-methoxybenzene (**2f**) (98 mg, 0.525 mmol, 2.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–7/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3f** and **4f** in 32 and 64% yield (55 and 93 mg), respectively; Red solid; Mp 166–167 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, J = 8.8 Hz, 4H), 7.08 (s, 2H), 6.92 (d, J = 8.8 Hz, 4H), 3.84 (s, 6H), 3.00–2.87 (m, 4H), 1.83–1.65 (m, 4H), 1.53–1.40 (m, 4H), 1.40–1.29 (m, 8H), 0.90 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 159.9, 150.0, 145.6, 144.2, 130.2, 127.2, 126.4, 125.7, 114.5, 55.5, 31.8, 30.7, 30.0, 29.6, 22.8, 14.3; HRMS (ESI) *m/z* calcd for $C_{38}H_{43}N_2O_2S_4$ $[M + H]^+$ 687.2207; found 687.2187; UV-Vis ($CHCl_3$) λ_{max} (log ε) 442 nm (4.80).

4-{4-Hexyl-5-[5-(3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazol-2-yl]thiophen-2-yl}-*N*,*N*-diphenylaniline (3g). 4-Bromo-*N*,*N*-diphenylaniline (**2f**) (89 mg, 0.275 mmol, 1.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–7/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3g** and **4g** in 50 and 38% yield (90 and 46 mg), respectively; Yellow viscous oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 5.1 Hz, 1H), 7.32–7.26 (m, 4H), 7.17–7.04 (m, 9H), 6.98 (d, J = 5.1 Hz, 1H), 3.02–2.87 (m, 4H), 1.81–1.67 (m, 4H), 1.54–1.40 (m, 4H), 1.40–1.31 (m, 8H), 0.97–0.82 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.6, 161.4, 150.2, 149.9, 148.2, 147.4, 145.7, 144.4, 143.2, 132.0, 130.9, 130.2, 129.5, 127.4, 127.2, 126.7, 125.8, 124.9, 123.6, 123.2, 31.8, 30.6, 30.3, 30.2, 30.0, 29.5 (2C's), 22.8, 14.3; HRMS (ESI) *m/z* calcd for $C_{42}H_{44}N_3S_4$ $[M + H]^+$ 718.2340; found 718.2375; UV-Vis ($CHCl_3$) λ_{max} (log ε) 440 nm (4.70).

4,4'-{5,5'-[Thiazolo[5,4-*d*]thiazole-2,5-diyl]-bis(4-hexylthiophene-5,2-diyl)}-bis(*N*,*N*-diphenylaniline) (4g). 4-Bromo-*N*,*N*-diphenylaniline (**2f**) (170 mg, 0.525 mmol, 2.1 equiv); The mixture was purified by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–7/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **3g** and **4g** in 46 and 38% yield (83 and 91 mg), respectively; Red solid. Mp: 89–91 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.6 Hz, 4H), 7.35–7.26 (m, 7H), 7.18–7.01 (m, 19H), 3.05–2.84 (m, 4H), 1.85–1.66 (m, 4H), 1.54–1.43 (m, 4H), 1.43–1.29 (m, 8H), 0.96–0.88 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3, 150.1, 148.2, 147.4, 145.6, 144.3, 130.3, 129.5, 127.3, 126.7, 125.8, 125.0, 123.6, 123.3, 31.8, 30.6, 30.0, 29.5, 22.8, 14.3; HRMS (ESI) *m/z* calcd for $C_{50}H_{57}N_4S_4$ $[M + H]^+$ 961.3466; found 961.3423; UV-Vis ($CHCl_3$) λ_{max} (log ε) 469 nm (4.88).

4-{5-[5-(5-(4-(*N*,*N*-diphenylamino)phenyl)-3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazol-2-yl]-4-hexylthiophen-2-yl}isophthalonitrile (5). Triphenylamine-monosubstituted TzTz **3g** (65 mg, 0.091 mmol, 1.0 equiv), 4-bromoisophthalonitrile (**2a**) (20.6 mg, 0.10 mmol, 1.1 equiv), K_2CO_3 (18.7 mg, 0.135 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.4 mg, 2.7 μmol, 2 mol%), PCy_3HBF_4 (1.3 mg, 3.6 μmol, 4 mol%), pivalic acid (2.7 mg, 0.027 mmol, 30 mol%), toluene (0.4 mL); 180 °C for 4 h; Purification by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–6/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford TzTz **5** in 85% yield (64 mg); Red solid; Mp 172–173 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 1.7 Hz, 1H), 7.86 (dd, J = 8.3, 1.7 Hz, 1H), 7.79 (d, J = 8.3 Hz, 1H), 7.74 (s, 1H), 7.53–7.45 (m, 2H), 7.33–7.26 (m, 4H), 7.17–7.03 (m, 9H), 3.06–2.88 (m, 4H), 1.85–1.65 (m, 4H), 1.56–1.42 (m, 4H), 1.42–1.28 (m, 8H), 1.00–0.81 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 159.3, 151.2, 150.2, 148.3, 147.4 (2C's), 146.3, 145.0, 144.1, 140.5, 138.1, 137.9, 136.1 (2C's), 132.8, 130.0, 129.9, 129.6 (4C's), 127.0, 126.7, 125.9, 125.0 (4C's), 123.7 (2C's), 123.1 (2C's), 117.1, 116.7, 112.0, 110.7, 31.8, 31.75, 30.7, 30.5, 30.0, 29.5 (2C's), 22.8, 14.3; IR (NaCl) ν_{max} 2955/2925/2855 (saturated C-H), 2232 cm^{-1} (CN); HRMS (ESI) *m/z* calcd for $C_{50}H_{46}N_5S_4$ $[M + H]^+$ 844.2558; found 844.2576; UV-Vis ($CHCl_3$) λ_{max} (log ε) 473 nm (4.66).

4-{5-[5-(5-(2,4-Bis(trifluoromethyl)phenyl)-3-hexylthiophen-2-yl)thiazolo[5,4-*d*]thiazol-2-yl]-4-hexylthiophen-2-yl}-*N*,*N*-diphenylaniline (6). Bis(trifluoromethyl)phenyl-monosubstituted TzTz **3c** (100 mg, 0.146 mmol, 1.0 equiv), 4-bromo-*N*,*N*-diphenylaniline (**2g**) (51.9 mg, 0.160 mmol, 1.1 equiv), K_2CO_3 (30.2 mg, 0.218 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.6 mg, 2.9 μmol, 2 mol%), PCy_3HBF_4 (1.3 mg, 3.6 μmol, 4 mol%), pivalic acid (4.5 mg, 0.044 mmol, 30 mol%), toluene (0.6 mL); 180 °C for 4 h; Purification by column chromatography (eluent gradient petroleum ether/$CHCl_3$ 10/1–6/1). Since fine separation was not possible by column chromatography, the compounds were additionally purified by preparative SEC to afford **6** in 88% yield (119 mg); Red solid; Mp 94–95 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.50 (d, J = 8.7 Hz, 2H), 7.34–7.26 (m, 4H), 7.18–7.02 (m, 10H), 3.09–2.88 (m, 4H), 1.87–1.66 (m, 4H), 1.59–1.42 (m, 4H), 1.41–1.30 (m, 8H), 1.01–0.81 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 160.3, 150.6, 150.0, 148.3, 147.4, 146.0, 144.6, 143.0, 139.2, 136.9, 134.0, 133.6, 132.3 (m), 130.9 (q, ^2J = 33 Hz), 130.1, 129.8 (q, ^2J = 33 Hz), 129.5, 128.5 (m), 127.1, 126.7, 125.8, 125.0, 124.1, 123.6, 123.4 (q, ^1J = 273 Hz), 123.3 (q, ^1J = 273 Hz), 123.2, 31.8, 30.7, 30.4, 30.0 (2C's), 29.5, 29.3, 22.8, 14.2; HRMS (ESI) *m/z* calcd for $C_{50}H_{46}F_6N_3S_4$ $[M + H]^+$ 930.2479; found 930.2432; UV-Vis ($CHCl_3$) λ_{max} (log ε) 449 nm (4.73).

Notes and references

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