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A one-pot dilithiation–lithium–zinc exchange–Negishi coupling approach to 2,6-di(hetero)aryl substituted dithienothiazines – a novel class of electronically fine-tunable redox systems†‡

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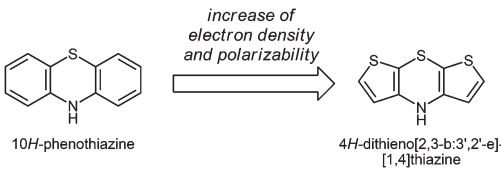
2,6-Di(hetero)aryl and 2-(hetero)aryl substituted dithienothiazines are prepared from *N*-aryl dithienothiazines by a lithiation–lithium–zinc exchange–Negishi cross-coupling sequence with (hetero)aryl iodides in a one-pot fashion in good to excellent yields. These novel extended π-electron systems can be reversibly oxidized and fine-tuned in their electronic properties as supported by cyclo voltammetric, and absorption and emission spectroscopic studies.

Introduction

Over the past few years, interest in electroactive organic molecules as functional π-systems[1] has enormously increased due to important potential technological applications ranging from organic light-emitting diodes[2] over organic photovoltaic devices[3] to organic field-effect transistors.[4] The main advantages of using organic materials are their low production costs, favorable properties such as flexibility, transparency and light weight, tunability of their properties, and their good processability.[5] As a consequence, the exploration of novel semiconducting molecular materials has become an ongoing challenge to synthetic organic chemistry. Moreover, small redox-active molecules can be considered as molecular wires[6] and, therefore, open new alleys to unimolecular electronics.[7] Recently we presented 4*H*-dithieno[2,3-*b*:3′,2′-*e*][1,4]thiazines, congeners to the well-established class of phenothiazines, as novel electron-rich organic π-systems (Scheme 1).[8] As a consequence of their unique electronic properties showing two reversible oxidations with Nernstian behavior at low oxidation potentials, dithienothiazines qualify, in principle, well for use as conducting materials or as a donor component in donor–acceptor conjugates.



Scheme 1 4*H*-Dithieno[2,3-*b*:3′,2′-*e*][1,4]thiazine – a congener of 10*H*-phenothiazine with increased electron density.

For potential applications, functionalization of the heterocyclic core represents a key step and major challenge. Most interestingly, the thiophene anellation offers an easy entry to thiophene characteristic transformations, such as lithiation at the α-positions with respect to the sulfur atom,[9] which is also suitable for sequential one-pot processes.[10] This concept was very successfully transposed to the 2,6-difunctionalization of *N*-substituted dithienothiazines *via* a dilithiation–electrophilic trapping sequence.[11] Therefore, a one-pot dilithiation–cross-coupling strategy to 2,6-di(hetero)aryl substituted dithienothiazines lies at hand. Here, we report a consecutive one-pot dilithiation–transmetallation–Negishi coupling sequence to 2,6-di(hetero)aryl substituted dithienothiazines and 2-(hetero)-aryl substituted dithienothiazines and the elucidation of their electronic properties by cyclic voltammetry, absorption and emission spectroscopy, and DFT calculations.

Results and discussion

Synthesis and structure

Interestingly, the electrophile addition to 2,6-dilithio dithienothiazine[11] opens up rapid access to highly reactive organo-

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† Dedicated to Professor Ei-ichi Negishi on the occasion of his 80th birthday.

‡ Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra, UV/Vis and fluorescence spectra of compounds **5**, **6**, **7**, and **8**; computed *xyz*-coordinates of the S_0 state of the pyrazoles **5c**, **6d**, and **8b**, computed UV/Vis spectra of TD-DFT calculated structures of **5c**, **6d**, and **8b**, and computed *xyz*-coordinates of the S_1 state of pyrazole **6d**. See DOI: 10.1039/c5qo00046g

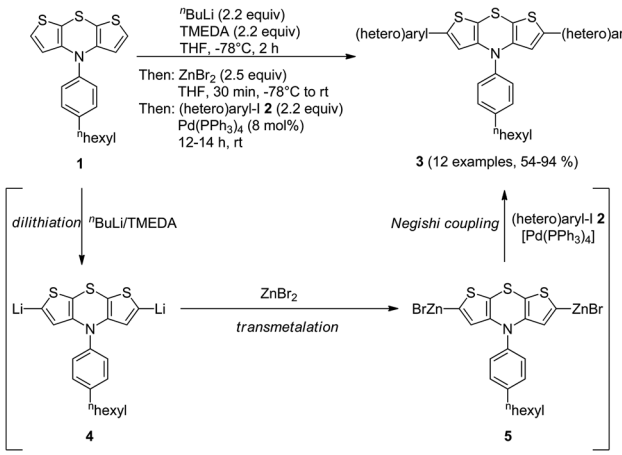
metallic species setting the stage for a subsequent cross-coupling reaction in a consecutive one-pot fashion.[10] Therefore, we set out to introduce zinc bromide as an electrophile for generating symmetrical bis(organozinc halides), suitable nucleophiles for envisioned Negishi coupling.[12]

The twofold lithiation of *N*-[4-(*n*-hexyl)phenyl] 4*H*-dithieno-[2,3-*b*:3′,2′-*e*][1,4]thiazine (**1**) with a slight excess of *n*-BuLi–TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) at −78 °C was ensured by reverse addition[13] of dithienothiazine **1** to a pre-cooled solution of *n*-BuLi–TMEDA (Scheme 2). Addition of freshly dried zinc bromide to the 2,6-dilithio dithienothiazine **4** furnished the organozinc bromide species **5**. The subsequent addition of (hetero)aryl iodides **2** and a catalytic amount of $Pd(PPh_3)_4$ gave rise to the twofold Negishi cross-coupling as a terminating step of this one-pot process, furnishing, after workup and flash chromatography on silica gel, 2,6-di(hetero)-aryl substituted dithienothiazines **3** in moderate to excellent yields (Table 1). The structures of all compounds **3** have been unambiguously assigned by spectroscopy (NMR, IR, and MS) and elemental analysis or HRMS. In the NMR spectra, expectedly, characteristic single sets of signals are found for the methine proton singlets around δ 6.2–6.6 and methine carbon nuclei at δ 115–120 of the central dithienothiazine cores.

The synthesis proceeds smoothly with a variety of aromatic (**2a–j**) and heteroaromatic iodides (**2k** and **2l**), and the substituents can be electron donating (**2a**, **2b**), electro-neutral (**2c**), and electron withdrawing substituents (**2d–g**). Moreover, it is remarkable that the sequence can be conducted with nearly equistoichiometric amounts of reagents to give the targeted structures with excellent efficiency.

Likewise we probed the synthesis of 2-(hetero)aryl substituted dithienothiazines **6** in three representative examples by employing equimolar amounts of reagents. With this adapted stoichiometry under dropwise addition of *n*-BuLi to a THF solution of **1** and TMEDA, the intermediacy of a monolithiated specimen furnished after workup and chromatography 2-(hetero)aryl substituted dithienothiazines **6** in moderate to good yields (Scheme 3) and the structures of these monosubstituted derivatives **6** have been unambiguously assigned by spectroscopy (NMR, IR, MS) and elemental analysis or HRMS. The lower symmetry of the structures **6** in comparison with the disubstituted derivatives **3** manifests in the appearance of three distinct methine signals, two as doublets at δ 6.1 and 7.15 with coupling constants J = 5.5 Hz and one as singlets between δ 6.2 and 6.6 in the proton NMR spectra, and three resonances for the methine carbon nuclei of the central dithienothiazine cores between δ 116 and 125 in the ^{13}C NMR spectra.

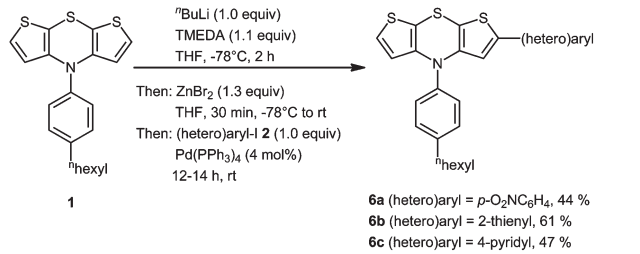
The structure of the symmetrically disubstituted dithienothiazines **3** was additionally corroborated by studying the DFT-optimized geometries[14] (B3LYP functional[15] and 6-311G*[16] basis set) for the parent compound **1** and selected derivatives of **3**, where the *n*-hexyl substituent has been truncated to an ethyl group for reducing the computational time (Table 2). The *para*-ethylphenyl substituent on the thiazine core was always oriented in a quasi-axial configuration to ensure global energy minima of the computed structures. The influence of the substituents at positions 2 and 6 on the central 1,4-thiazine folding angle and the thienyl-aryl torsional dihedral angle was studied for electron-releasing (structure



Scheme 2 One-pot synthesis of 2,6-di(hetero)aryl substituted dithienothiazines **3** by dilithiation–transmetalation–Negishi coupling sequence.

Table 1 One-pot synthesis of 2,6-di(hetero)aryl substituted dithienothiazines **3**

Entry	(Hetero)aryl iodide **2**	2,6-Di(hetero)aryl dithienothiazines **3** (yield)
1	(Hetero)aryl = 4-$MeOC_6H_4$ (**2a**)	**3a** (65%)
2	(Hetero)aryl = 4-MeC_6H_4 (**2b**)	**3b** (82%)
3	(Hetero)aryl = Ph (**2c**)	**3c** (87%)
4	(Hetero)aryl = 4-ClC_6H_4 (**2d**)	**3d** (78%)
5	(Hetero)aryl = 4-$MeO_2CC_6H_4$ (**2e**)	**3e** (80%)
6	(Hetero)aryl = 4-$F_3CC_6H_4$ (**2f**)	**3f** (95%)
7	(Hetero)aryl = 4-NCC_6H_4 (**2g**)	**3g** (69%)
8	(Hetero)aryl = 4-$O_2NC_6H_4$ (**2h**)	**3h** (78%)
9	(Hetero)aryl = 3-$O_2NC_6H_4$ (**2i**)	**3i** (77%)
10	(Hetero)aryl = 2-$O_2NC_6H_4$ (**2j**)	**3j** (54%)
11	(Hetero)aryl = 3-pyridyl (**2k**)	**3k** (63%)
12	(Hetero)aryl = 10-*n*-hexyl-10*H*-phenothiazin-3-yl (**2l**)	**3l** (94%)



Scheme 3 One-pot synthesis of 2-(hetero)aryl substituted dithienothiazines **6** by monolithiation–transmetalation–Negishi coupling sequence.

Table 2 Selected DFT-calculated dihedral angles of structures **1**, **3a**, **3c**, and **3g–j**

Structure[a]	Central 1,4-thiazine folding angle	Thienyl-aryl torsional dihedral angle
1	140.2°	—
3a	140.3°	30.8°
3c	140.7°	33.4°
3g	141.1°	28.2°
3h	141.1°	28.0°
3i	140.6°	28.1°
3j	141.1°	59.8°

[a] In contrast to the synthesized structures **1** and **3** the *n*-hexyl substituent has been truncated to an ethyl group.

3a), electroneutral (structure **3c**), electron-withdrawing (structure **3g**), and electron-withdrawing *para*- (structure **3h**), *meta*- (structure **3i**), and *ortho*-substituents (structure **3j**).

While the central 1,4-thiazine folding angle lies in a narrow margin between 140.2 and 141.1° the thienyl-aryl torsional dihedral angle is diminished to 28° for remote electron-withdrawing substituents (structures **3g–i**) in contrast to 30° (structure **3a**) and 33° (structure **3c**) for electron-releasing and electroneutral substituents. For the former a more efficient overlap of the π-systems can be expected in the electronic ground state. Expectedly, an *ortho*-nitrophenyl substituent (structure **3j**) results in a torsion of 60° from coplanarity.

Electronic properties

The electronic properties of 2,6-di(hetero)aryl substituted dithienothiazines **3** and 2-(hetero)aryl substituted dithienothiazines **6** were experimentally investigated by cyclic voltammetry and by absorption and emission spectroscopy (Table 3), and for elucidating the electronic structure, DFT and TDDFT calculations were performed for selected molecular structures.

The first oxidation $E_{1/2}^{0/+1}$ of 2,6-di(hetero)aryl substituted dithienothiazines **3** and 2-(hetero)aryl substituted dithienothiazines **6** are found between 270 and 500 mV, while the second oxidations $E_{1/2}^{+1/+2}$ from the radical cations to the dications occur between 1000 and 1250 mV. With the exception of compounds **3k** and **6c** all other 2,6-di(hetero)aryl substituted dithienothiazines **3** and 2-(hetero)aryl substituted dithienothiazines **6** show two clearly separated reversible oxidation waves with Nernstian behavior (Fig. 1).

Interestingly, the oxidation potentials in the series of the 2,6-diaryl substituted dithienothiazines **3a–3i** vary with the electronic nature of the substituent. This strong dependence of the reversible first and second oxidation potentials on the electronic substituent effect is shown in a good linear correlation with the Hammett σ_p or σ_m substitution parameters[17] ($E_0^{0/+1}$, $R^2 = 0.9889$; $E_0^{+1/+2}$, $R^2 = 0.9406$) (Fig. 2). Upon oxidation, radical cations $\mathbf{3}^{+\bullet}$ and dications $\mathbf{3}^{2+}$ are successively formed and their stabilities are achieved by both inductive and resonance effects. The three nitrosubstituted regioisomers **3h–j** nicely illustrate the influence of remote conjugative and inductive substituent effects on the first oxidation potentials as shown by the *para*-substituted derivative **3h** ($E_{1/2}^{0/+1}$ = 500 mV) and the *meta*-substituted compound **3i** ($E_{1/2}^{0/+1}$ = 480 mV) whereas for compound **3j** ($E_{1/2}^{0/+1}$ = 440 mV) the lack of overlap by torsion out of coplanarity underlines the stereoelectronic effect of the *ortho*-substitution.

Table 3 Selected electronic properties (absorption and emission data, Stokes shift $\Delta\tilde{\nu}$, oxidation potentials, and semiquinone formation constant K_{SEM}) of dithienothiazine **1**, 2,6-di(hetero)aryl and 2-(hetero)aryl substituted dithienothiazines **3** and **6**

Compound	Absorption maxima $\lambda_{max,abs}$ (ε)[a] [nm] (L cm^{-1} mol^{-1})	Emission $\lambda_{max,em}$[b] [nm]	Stokes-shift $\Delta\tilde{\nu}$[c] [cm^{-1}]	$E_{1/2}^{0/+1}$[d] [mV]	$E_{1/2}^{+1/+2}$[d] [mV]	K_{SEM}[e]
1	240 (22 000), 318 (6000)	—	—	360	1230	55.7×10^{13}
3a	295 (46 100), 367sh (6000)	—	—	270	1000	0.21×10^{13}
3b	294 (48 200), 385 (5700)	—	—	320	1080	1.04×10^{13}
3c	290 (49 500), 400 (5300)	—	—	340	1120	1.26×10^{13}
3d	296 (49 550), 409 (6000)	—	—	380	1130	0.44×10^{13}
3e	309 (49 600), 455 (8800)	—	—	420	1160	0.38×10^{13}
3f	298 (62 900), 431 (8500)	—	—	440	1180	0.44×10^{13}
3g	310 (43 600), 457 (7200)	—	—	480	1210	0.26×10^{13}
3h	254 (31 300), 332 (46 000), 524 (17 900)	—	—	500	1240	0.32×10^{13}
3i	286 (40 100), 440 (4800)	—	—	480	1230	0.68×10^{13}
3j	264 (30 250), 452 (2900)	—	—	440	1250	4.76×10^{13}
3k	292 (32 450), 414 (3900)	434sh, 560[f]	6300	410	—[g]	—
3l	239sh (27 900), 267sh (30 300), 291 (36 250), 349 (14 300), 422sh (8500)	497[h]	3800	290	840,[i] 1090[j]	0.07×10^{13}
6a	250 (25 550), 328 (22 850), 511 (7300)	—	—	430	1210	1.94×10^{13}
6b	237sh (12 400), 300 (12 700), 355sh (3000), 420sh (1900)	569[k]	6200	360	1130	1.37×10^{13}
6c	238sh (9800), 292 (13 300), 367 (1900), 449 (2200)	606[l]	5800	440	—[h]	—

[a] Recorded in CH_2Cl_2 UVASOL at rt. [b] Recorded in CH_2Cl_2 UVASOL at rt with λ_{exc} = 310.0 nm. [c] $\Delta\tilde{\nu} = 1/\lambda_{max,abs} - 1/\lambda_{max,em}$[cm^{-1}]. [d] Recorded in CH_2Cl_2, T = 293 K, 0.1 M electrolyte [^{n}Bu$_4$N][PF$_6$], Pt working, Ag/AgCl reference, and Pt counter electrodes; potentials are corrected against decamethylferrocene as an external standard with $E_0^{0/+1} = -95$ mV. [e] $K_{SEM} = 10^{\frac{\left|E_0^{0/+1} - E_0^{+1/+2}\right|}{0.059}}$ (potentials are inserted in [V] and potential differences are dimensionless). [f] $\lambda_{max,exc}$ = 380 nm. [g] The oxidation is irreversible. [h] $\lambda_{max,exc}$ = 420 nm. [i] $E_{1/2}^{+1/+3}$. [j] $E_{1/2}^{+3/+4}$. [k] $\lambda_{max,exc}$ = 425 nm. [l] $\lambda_{max,exc}$ = 450 nm.

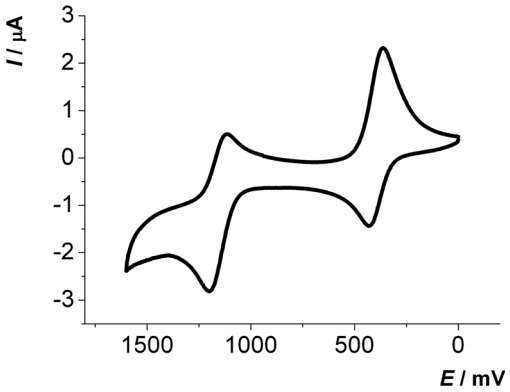


Fig. 1 Cyclic voltammogram of compound **3c** (recorded in CH_2Cl_2, T = 293 K, 0.1 M electrolyte [$^nBu_4N$][PF_6], scan rate ν = 100 mV s^{-1}, Pt working, Ag/AgCl reference and Pt counter electrodes).

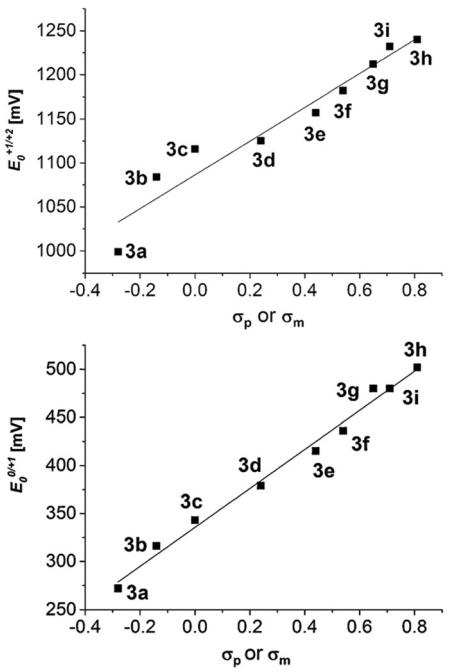


Fig. 2 Linear correlation plots of the first oxidation potentials $E_0^{0/+1}$ [mV] (bottom) and second oxidation potentials $E_0^{+1/+2}$ [mV] (top) of 2,6-diaryl-substituted dithienothiazines **3a–i** against Hammett σ_p or σ_m parameters ($E_0^{0/+1}$ = 201 $\sigma_{p/m}$ + 336 [mV], r^2 = 0.9889; $E_0^{+1/2}$ = 192 $\sigma_{p/m}$ + 1086 [mV], r^2 = 0.9406).

The electrochemistry of the 2,6-di(phenothiazine-3-yl) substituted dithienothiazine **3l** is more complicated because phenothiazinyl substituents are additionally redox-active. In this case three distinctly separated, reversible oxidations appear in the cyclic voltammogram. The first and third oxidations at $E_0^{0/+1}$ = 290 mV and $E_0^{+3/+4}$ = 1090 mV clearly show Nernstian behavior, but the second oxidation at $E_0^{+1/+3}$ = 840 mV reveals a large difference $\Delta E_{1/2}$ = 112 mV for anodic and cathodic peak potentials with an overall increased intensity of the current

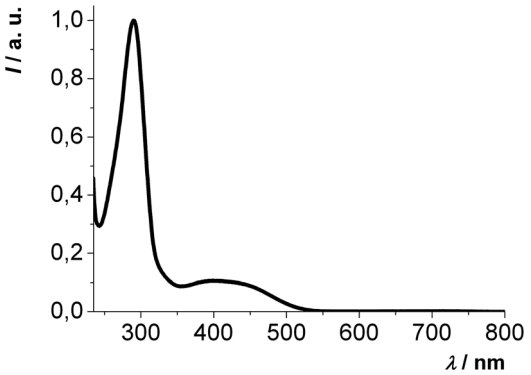


Fig. 3 Absorption spectrum of compound **3c** (recorded in CH_2Cl_2, T = 293 K).

density. Therefore, the first and third one-electron oxidations can be assigned as dithienothiazinyl centered oxidation events, whereas the second oxidation rather represents two simultaneously occurring phenothiazinyl centered oxidations as quasi-reversible events.

In addition, the differences between the first and second oxidations are relatively large and indicate considerable stability of the electrochemically generated radical cations $\mathbf{3}^{+\bullet}$. By calculation of the semiquinone formation constants K_{SEM}[18] for the comproportionation of **3** and $\mathbf{3}^{2+}$ furnishing two moles of $\mathbf{3}^{+\bullet}$ the stability can be quantified to lie between 0.07×10^{13} and 4.76×10^{13}. In comparison with the 2,6-unsubstituted mother compound **1** the K_{SEM} are approximately 1–2 orders of magnitude lower. Likewise, the K_{SEM} of the 2-substituted derivatives **6** are one order of magnitude lower.

The absorption spectra of all 2,6-di(hetero)aryl substituted dithienothiazines **3** reveal similar absorption characteristics. An intense absorption band appears around 300 nm and the less intensive longest wavelength absorption is found in a range from 367 to 525 nm (Fig. 3). In comparison with the 2,6-unsubstituted mother compound **1** ($\lambda_{max,abs}$ = 318 nm) the red shift of the longest wavelength absorption bands of the 2,6-di(hetero)aryl substituted derivatives **3** accounts for extended π-electron systems.

The absorption behavior can be plausibly rationalized by a TD-DFT calculation[14–16] of compound **3f**, where the *n*-hexyl substituent has been truncated to an ethyl group for reducing the computational time. The experimental UV/vis spectrum of **3f** is nicely reproduced by the computation (Fig. 4). While the longest wavelength absorption maximum at 455 nm consists of a 48% contribution of the HOMO–LUMO transition, the strongest absorption band at around 315 nm consists of a 43% contribution from a HOMO–LUMO+2 transition and the shoulder at 350 nm arises from 40% contribution from the HOMO−1–LUMO transition. In addition, the Kohn–Sham frontier molecular orbitals of **3f**, *i.e.* HOMO and LUMO (Fig. 5), which are predominantly involved in constituting the longest wavelength absorption band, display considerable coefficient densities in the central *N*-aryl dithienothiazine core in the

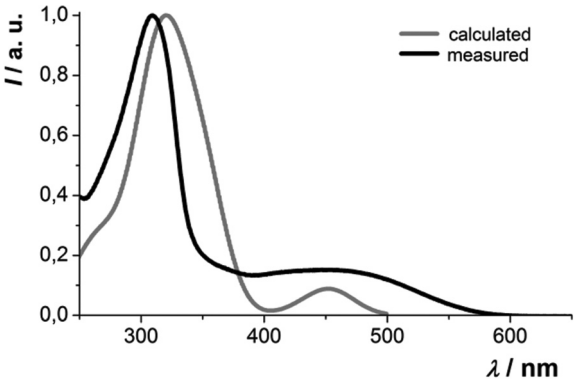


Fig. 4 Experimental (black) and calculated (grey) absorption spectra of compound **3f**.

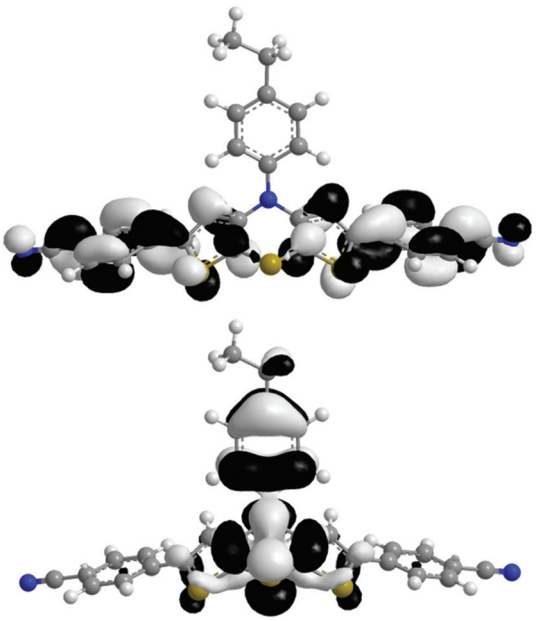


Fig. 5 Frontier molecular orbitals (HOMO, bottom, and LUMO, top) of compound **3f** (DFT computations with B3LYP functional and 6-311G* basis set).

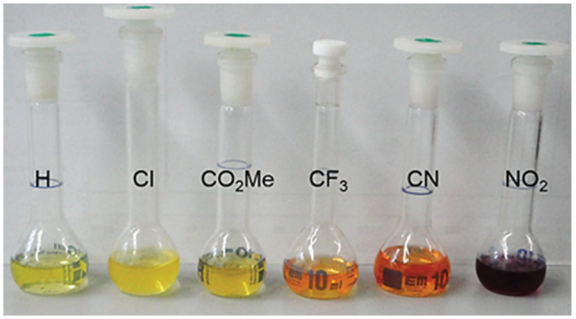


Fig. 6 Bathochromic shift of equimolar dichloromethane solutions of compounds **3c–h** with increasing acceptor strength under daylight.

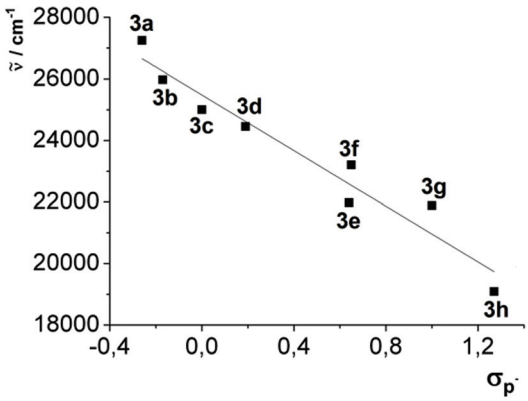


Fig. 7 Linear correlation plot of the longest wavelength absorption maxima $\tilde{\nu}_{max,abs}$ [cm^{-1}] of 2,6-diaryl-substituted dithienothiazines **3a–h** against the Hammett parameter σ_p^- ($\tilde{\nu}$ = −4522 × σ_p^- + 25 480 [cm^{-1}], r^2 = 0.9421).

HOMO and in the 2- and 6-aryl substituents in the LUMO. Thereby this transition is accompanied by a considerable charge transfer character from the central donor moiety to the outer acceptor units.

Furthermore the considerable charge transfer character of the longest wavelength absorption band becomes qualitatively apparent for naked eyes by comparing the bathochromic shift of the color of equimolar dichloromethane solutions of compounds **3c–h** with increasing acceptor strength under daylight (Fig. 6).

This observation can be additionally quantified by a good linear correlation of the longest wavelength absorption maxima of compounds **3a–h** with the Hammett substitution parameter[17] σ_p^- (R^2 = 0.942) (Fig. 7), whereby σ_p^- indicates the immediate influence of the resonance stabilization of negative charges by mesomeric and inductive substituents.

While the absorption characteristics of 2-(hetero)aryl substituted dithienothiazines **6** indicate three distinct absorption bands, the UV/vis spectrum of 2,6-di(phenothiazine-3-yl) substituted dithienothiazine **3l** shows multiple absorption bands and shoulders, indicating the behavior of an extended π-electron system rather than a simple additive behavior of the underlying subchromophores.

Finally, among the 2,6-di(hetero)aryl substituted and 2-(hetero)aryl substituted dithienothiazines **3** and **6** the most peculiar electronic feature is reflected that in contrast to many dithienothiazines, which are essentially nonluminescent (see also Table 3),[8,11] the four derivatives show intense luminescence at 560 nm (**3k**), 497 nm (**3l**), 569 nm (**6b**), and 606 nm (**6c**) with broad unstructured emission bands and large Stokes shifts (Fig. 8).

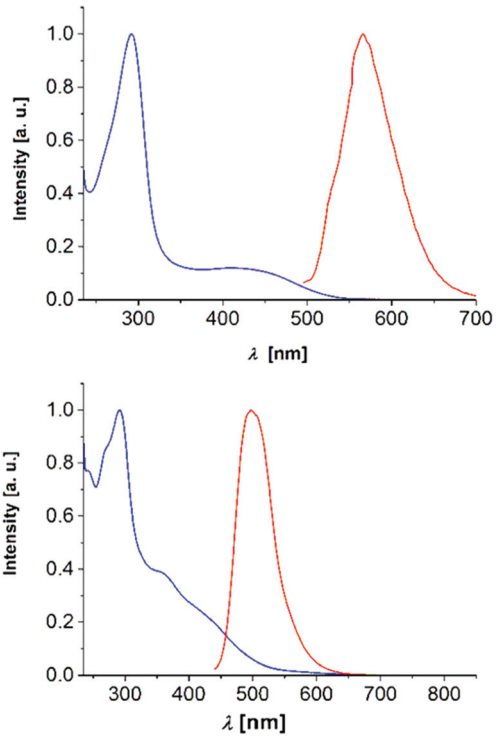


Fig. 8 Normalized absorption (blue) and emission (red) spectra of compounds **3k** (top, $\lambda_{max,exc}$ = 380 nm) and **3l** (bottom, $\lambda_{max,exc}$ = 420 nm) (recorded in CH_2Cl_2, T = 293 K).

Conclusions

The hitherto unknown classes of 2,6-di(hetero)aryl and 2-(hetero)aryl substituted dithienothiazines are readily accessible from *N*-aryl dithienothiazines by lithiation, lithium–zinc exchange, and subsequent Negishi cross-coupling with (hetero)aryl iodides in good to excellent yields and in a one-pot fashion. The title compounds possess an extended π-electron conjugation and display characteristic electronic features. While the electronic ground state properties, investigated by cyclic voltammetry and UV/vis spectroscopy, indicate a strong influence of the remote substituents that can be semiquantitatively treated by excellent Hammett's linear free enthalpy correlations with σ_p (oxidation potentials) and σ_p^- ($\lambda_{max,abs}$), luminescence as an excited state characteristic is only found for four derivatives with characteristic heterocyclic substitution. In principle this emission behavior is unusual for *N*-aryl dithienothiazines, but it establishes a novel class of redox active lumophores. The rapid access of 2,6-di(hetero)aryl dithienothiazines with remote substitution furnishing tunable electronic properties renders this class of electron rich reversible multistep redox systems highly intriguing as potential hole conductor materials. Further studies exploiting this expedient synthetic strategy to functional dithienothiazines are currently underway.

Experimental

Synthetic procedures

General procedure for the dilithiation–Negishi coupling synthesis of 2,6-di(hetero)aryl dithienothiazines 3 (GP1). Dry THF (3 mL) and dry TMEDA (0.17 mL, 1.2 mmol) were placed in a 50 mL Schlenk flask under nitrogen. Then, the solution was cooled to −78 °C (dry ice/acetone) and 1.6 M *n*-BuLi in hexane (0.72 mL, 1.2 mmol) was added dropwise to the solution. 4-(4-*n*-Hexylphenyl)-4*H*-dithieno[2,3-*b*:3′,2′-*e*][1,4]-thiazine (**1**) (186 mg, 0.50 mmol) was added to this solution and the reaction mixture was stirred at −78 °C for 2 h. In the meantime a solution of freshly dried zinc bromide (300 mg, 1.33 mmol) in dry THF (1.5 mL) was prepared which was added dropwise using a syringe to the reaction mixture at −78 °C. After stirring at −78 °C for 30 min, palladium tetrakis(triphenylphosphane) (47 mg, 8 mol%) and 2.2 equiv. of the (hetero)aryl iodide **2** (1.1 mmol) were successively added to the reaction mixture (for experimental details see Table 4). The reaction mixture was allowed to come to room temperature upon stirring for 12–14 h. Then, a mixture of deionized water (20 mL) and dichloromethane (20 mL) was added, the organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried with anhydrous magnesium sulfate and the solvents were removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluent containing 2% of triethylamine) under nitrogen to give the pure products **3**. Further purification could be achieved by fractional crystallization.

*4-(4-n-Hexylphenyl)-2,6-bis(4-methoxyphenyl)-4H-dithieno[2,3-b:3′,2′-e][1,4]thiazine (**3a**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane–ethyl acetate 20 : 1 with 2% of triethylamine) and after crystallization from ethanol–ethyl acetate (1 : 1), compound **3a** (189 mg, 65%) was obtained as yellow needles.

Table 4 Experimental details of the dilithiation–Negishi coupling synthesis of 2,6-di(hetero)aryl dithienothiazines **3**

Entry	(Hetero)aryl iodide **2** [mg] (mmol)	2,6-Di(hetero)aryl dithienothiazines **3** [mg] (%)
1	257 (1.10) of 1-iodo-4-methoxybenzene (**2a**)	189 (65) of **3a**
2	240 (1.10) of 1-iodo-4-methylbenzene (**2b**)	226 (82) of **3b**
3	224 (1.10) of iodobenzene (**2c**)	227 (87) of **3c**
4	262 (1.10) of 1-chloro-4-iodobenzene (**2d**)	231 (78) of **3d**
5	288 (1.10) of methyl 4-iodobenzoate (**2e**)	257 (80) of **3e**
6	299 (1.10) of 4-iodobenzotrifluoride (**2f**)	313 (95) of **3f**
7	252 (1.10) of 4-iodobenzonitrile (**2g**)	198 (69) of **3g**
8	274 (1.10) of 1-iodo-4-nitrobenzene (**2h**)	241 (78) of **3h**
9	274 (1.10) of 1-iodo-3-nitrobenzene (**2i**)	236 (77) of **3i**
10	274 (1.10) of 1-iodo-2-nitrobenzene (**2j**)	165 (54) of **3j**
11	226 (1.10) of 3-iodopyridine (**2k**)	164 (63) of **3k**
12	450 (1.10) of 3-iodo-10-*n*-hexyl-10*H*-phenothiazine (**2l**)	441 (94) of **3l**

R_f (*n*-hexane–ethyl acetate 20 : 1): 0.19, Mp 170 °C. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 0.96 (t, ^3J = 7.1 Hz, 3 H), 1.37–1.48 (m, 6 H), 1.75 (p, ^3J = 7.4 Hz, 2 H), 2.71–2.77 (m, 2 H), 3.79 (s, 6 H), 6.24 (s, 2 H), 6.80–6.85 (m, 4 H), 7.21–7.29 (m, 4 H), 7.33–7.41 (m, 4 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 14.9 (CH_3), 23.8 (CH_2), 29.9 (CH_2), 32.3 (CH_2), 32.8 (CH_2), 36.6 (CH_2), 55.7 (CH_3), 102.3 (C_{quat}), 115.2 (CH), 115.5 (CH), 127.1 (CH), 127.2 (C_{quat}), 129.2 (CH), 131.1 (CH), 142.1 (C_{quat}), 142.4 (C_{quat}), 143.3 (C_{quat}), 144.7 (C_{quat}), 160.4 (C_{quat}). MALDI-TOF MS: m/z 583.2 $[M]^+$. IR (ATR): $\tilde{\nu}$ 602 cm^{-1} (m), 615 (s), 627 (m), 633 (m), 644 (s), 698 (s), 723 (s), 760 (m), 795 (s), 802 (s), 812 (s), 829 (m), 947 (m), 999 (w), 1018 (w), 1032 (s), 1057 (w), 1076 (w), 1111 (m), 1153 (w), 1177 (s), 1250 (s), 1296 (m), 1375 (m), 1439 (m), 1463 (m), 1501 (s), 1564 (w), 1568 (w), 1607 (w), 2833 (w), 2853 (w), 2922 (w), 2947 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 295 nm (46 100), 367 (6000, sh). Anal. calcd for $C_{34}H_{33}NO_2S_3$ (583.8): C 69.95, H 5.70, N 2.40, S 16.48; found: C 69.67, H 5.63, N 2.29, S 16.59.

*4-(4-Hexylphenyl)-2,6-di-p-tolyl-4H-dithieno[2,3-b:3′,2′-e][1,4]-thiazine (**3b**).* According to the GP1 and after flash chromatography on silica gel (*n*-pentane with 0.5% of triethylamine), compound **3b** (134 mg, 78%) was obtained as an orange oil.

R_f (*n*-hexane): 0.14. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 1 : 1): δ 0.93 (t, ^3J = 7.0 Hz, 3 H), 1.35–1.44 (m, 6 H), 1.70–1.76 (m, 2 H), 2.31 (s, 6 H), 2.72–2.76 (m, 2 H), 6.37 (s, 2 H), 7.11–7.14 (m, 4 H), 7.24–7.27 (m, 4 H), 7.38–7.43 (m, 4 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 1): δ 14.7 (CH_3), 21.4 (CH_3), 23.6 (CH_2), 30.0 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 36.5 (CH_2), 102.6 (C_{quat}), 115.9 (CH), 125.6 (CH), 129.3 (CH), 130.5 (CH), 131.3 (CH), 138.5 (C_{quat}), 142.0 (C_{quat}), 142.6 (C_{quat}), 143.5 (C_{quat}), 145.0 (C_{quat}). MALDI-TOF MS: m/z 551.2 $[M]^+$. IR (ATR): $\tilde{\nu}$ 617 cm^{-1} (w), 638 (w), 667 (w), 710 (w), 760 (m), 804 (s), 945 (w), 999 (w), 1018 (w), 1038 (w), 1057 (w), 1111 (w), 1121 (w), 1182 (w), 1217 (w), 1280 (m), 1310 (w), 1357 (m), 1435 (m), 1504 (s), 1537 (w), 1574 (w), 1611 (w), 2853 (w), 2924 (m), 2953 (w), 3022 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 294 nm (48 200), 385 (5700). HRMS (ESI) calcd for $C_{34}H_{33}NS_3$: 551.17751; found: 551.17757.

*4-(4-Hexylphenyl)-2,6-diphenyl-4H-dithieno[2,3-b:3′,2′-e][1,4]-thiazine (**3c**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane with 2% of triethylamine) and after crystallization from ethanol–ethyl acetate (20 : 1), compound **3c** (227 mg, 87%) was obtained as an orange powder.

R_f (*n*-hexane): 0.09, Mp 114 °C. ^{1}H NMR (300 MHz, acetone-d_6–CS_2 1 : 1): δ 0.96 (t, ^3J = 7.0 Hz, 3 H), 1.33–1.50 (m, 6 H), 1.76 (p, ^3J = 7.6 Hz, 2 H), 2.70–2.82 (m, 2 H), 6.36 (s, 2 H), 7.18–7.47 (m, 14 H). ^{13}C NMR (75 MHz, acetone-d_6–CS_2 1 : 4): δ 15.1 (CH_3), 23.8 (CH_2), 29.9 (CH_2), 32.3 (CH_2), 32.8 (CH_2), 36.6 (CH_2), 103.1 (C_{quat}), 115.9 (CH), 125.5 (CH), 128.2 (CH), 129.3 (CH), 129.5 (CH), 131.0 (CH), 134.1 (C_{quat}), 141.5 (C_{quat}), 141.9 (C_{quat}), 143.2 (C_{quat}), 144.4 (C_{quat}). MALDI-TOF MS: m/z 523.2 $[M]^+$. IR (ATR): $\tilde{\nu}$ 673 cm^{-1} (w), 685 (s), 712 (w), 748 (s), 810 (w), 822 (m), 889 (w), 945 (w), 1003 (w), 1072 (w), 1098 (w), 1192 (w), 1273 (w), 1368 (w), 1418 (w), 1425 (w), 1451 (m), 1489 (m), 1508 (w), 1528 (w), 1566 (w), 1597 (w), 2359 (w), 2851 (w), 2920 (w), 2053 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 290 nm (49 500), 400 (5250). Anal. calcd for $C_{32}H_{29}NS_3$ (522.8): C 73.38, H 5.58, N 2.67; found: C 73.19, H 5.55, N 2.74.

*2,6-Bis(4-chlorphenyl)-4-(4-hexylphenyl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazine (**3d**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane with 2% of triethylamine) and after crystallization from *n*-hexane, compound **3d** (231 mg, 78%) was obtained as light red crystals.

R_f (*n*-hexane): 0.18, Mp 131 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.91 (t, ^3J = 7.0 Hz, 3 H), 1.30–1.41 (m, 6 H), 1.69 (p, ^3J = 7.5 Hz, 2 H), 2.67–2.72 (m, 2 H), 6.31 (s, 2 H), 7.24–7.37 (m, 12 H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 14.4 (CH_3), 23.2 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.2 (CH_2), 36.2 (CH_2), 103.0 (C_{quat}), 116.2 (CH), 126.6 (CH), 129.0 (CH), 129.5 (CH), 130.9 (CH), 132.7 (C_{quat}), 133.7 (C_{quat}), 140.4 (C_{quat}), 141.2 (C_{quat}), 143.7 (C_{quat}), 144.8 (C_{quat}). MALDI-TOF MS: m/z 591.1 $[M]^+$. IR (ATR): $\tilde{\nu}$ 615 cm^{-1} (w), 627 (w), 644 (w), 669 (w), 694 (w), 714 (w), 731 (w), 766 (w), 806 (s), 814 (s), 820 (m), 943 (w), 1003 (w), 1059 (w), 1094 (m), 1117 (w), 1179 (w), 1192 (w), 1273 (w), 1371 (m), 1398 (w), 1431 (m), 1485 (m), 1508 (w), 1568 (m), 1888 (w), 2853 (w), 2924 (w), 2053 (w), 3030 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 296 nm (49 550), 409 (6000). Anal. calcd for $C_{32}H_{27}Cl_2NS_3$ (591.7): C 64.85, H 4.59, N 2.36; found: C 64.80, H 4.81, N 2.26.

*Dimethyl 4,4′-(4-(4-hexylphenyl)-4H-dithieno[2,3-b:3′,2′-e][1,4]-thiazin-2,6-diyl)dibenzoate (**3e**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane–ethyl acetate 10 : 1 with 2% of triethylamine) and after crystallization from dichloromethane–*n*-hexane, compound **3e** (257 mg, 80%) was obtained as a red solid.

R_f (*n*-hexane–ethyl acetate 10 : 1): 0.28, Mp 199 °C. ^{1}H NMR (300 MHz, acetone-d_6–CS_2 1 : 1, T = 293 K): δ 0.96 (t, ^3J = 7.0 Hz, 3 H), 1.36–1.50 (m, 6 H), 1.69 (p, ^3J = 7.6 Hz, 2 H), 2.74–2.81 (m, 2 H), 3.86 (s, 6 H), 6.51 (s, 2 H), 7.39–7.54 (m, 8 H), 7.89–7.96 (m, 4 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 14.9 (CH_3), 23.8 (CH_2), 30.2 (CH_2), 32.3 (CH_2), 32.8 (CH_2), 36.6 (CH_2), 52.3 (CH_3), 98.9 (C_{quat}), 117.4 (CH), 125.3 (C_{quat}), 126.0 (CH), 128.1 (CH), 130.0 (C_{quat}), 131.03 (CH), 131.4 (CH), 138.3 (C_{quat}), 143.9 (C_{quat}), 144.9 (C_{quat}), 146.2 (C_{quat}), 166.2 (C_{quat}). MALDI-TOF MS: m/z 639.1 $[M]^+$. IR (ATR): $\tilde{\nu}$ 665 cm^{-1} (w), 694 (m), 725 (w), 766 (s), 818 (m), 851 (w), 947 (w), 962 (w), 1001 (w), 1016 (w), 1063 (w), 1109 (s), 1186 (m), 1192 (w), 1244 (w), 1273 (s), 1317 (w), 1377 (w), 1406 (w), 1420 (w), 1431 (m), 1500 (w), 1539 (w), 1560 (w), 1572 (w), 1603 (m), 1722 (s), 2332 (w), 2361 (w), 2853 (w), 2924 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 309 nm (49 600), 455 (8750). Anal. calcd for $C_{36}H_{33}NO_4S_3$ (639.9): C 67.58, H 5.20, N 2.19; found: C 67.51, H 5.01, N 2.16.

*4-(4-Hexylphenyl)-2,6-bis(4-(trifluormethyl)phenyl)-4H-dithieno-[2,3-b:3′,2′-e][1,4]thiazine (**3f**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane with 2% of triethylamine) and after crystallization from *n*-hexane–ethyl acetate, compound **3f** (313 mg, 95%) was obtained as fine coral red crystals.

R_f (*n*-hexane): 0.19, Mp 215 °C. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 0.95 (t, ^3J = 7.0 Hz, 3 H), 1.37–1.49 (m, 6 H), 1.75 (p, ^3J = 7.6 Hz, 2 H), 2.74–2.79 (m, 2 H), 6.54 (s, 2 H), 7.44 (q, ^3J = 8.4 Hz, 4 H), 7.59 (dd, J = 8.3 Hz, 29.7 Hz,

8 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 14.7 (CH_3), 23.7 (CH_2), 30.1 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 36.6 (CH_2), 105.4 (C_{quat}), 117.8 (CH), 125.1 (C_{quat}, $^1J_{CF}$ = 271.6 Hz), 126.0 (CH), 126.9 (CH, $^3J_{CF}$ = 3.8 Hz), 129.5 (CH), 129.9 (C_{quat}, $^2J_{CF}$ = 32.5 Hz), 131.5 (CH), 137.9 (C_{quat}), 140.5 (C_{quat}), 141.6 (C_{quat}), 144.0 (C_{quat}), 145.3 (C_{quat}). MALDI-TOF MS: m/z 659.1 $[M]^+$. IR (ATR): $\tilde{\nu}$ 610 cm^{-1} (w), 638 (w), 652 (w), 691 (w), 714 (w), 735 (w), 773 (w), 822 (s), 837 (m), 949 (w), 1003 (w), 1013 (m), 1069 (s), 1109 (s), 1121 (m), 1163 (m), 1194 (w), 1246 (w), 1275 (w), 1290 (w), 1325 (s), 1379 (w), 1406 (w), 1435 (m), 1508 (m), 1566 (w), 1611 (w), 2855 (w), 2901 (w), 2926 (w), 2959 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 298 nm (62 850), 431 (8500). Anal. calcd for $C_{34}H_{27}F_6NS_3$ (659.8): C 61.89, H 4.12, N 2.12; found: C 61.70, H 4.21, N 2.06.

*4,4′-(4-(4-Hexylphenyl)-4H-dithieno[2,3-b:3′,2′-e][1,4]thiazin-2,6-diyl)dibenzonitrile (**3g**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane–ethyl acetate 10 : 1), compound **3g** (198 mg, 69%) was obtained as dark red crystals.

R_f (*n*-hexane–ethyl acetate 10 : 1): 0.11, Mp 175 °C. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 0.96 (t, ^3J = 7.1 Hz, 3 H), 1.39–1.48 (m, 6 H), 1.75 (p, ^3J = 7.5 Hz, 2 H), 2.75–2.78 (m, 2 H), 6.53 (s, 2 H), 7.39–7.46 (m, 4 H), 7.53 (d, J = 8.3 Hz, 4 H), 7.54–7.58 (d, J = 8.4 Hz, 4 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 14.8 (CH_3), 23.7 (CH_2), 30.1 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 36.6 (CH_2), 111.8 (C_{quat}), 116.7 (CH), 118.0 (C_{quat}), 118.8 (C_{quat}), 126.0 (CH), 127.6 (CH), 131.5 (CH), 133.6 (CH), 138.1 (C_{quat}), 140.2 (C_{quat}), 141.8 (C_{quat}), 144.1 (C_{quat}), 146.4 (C_{quat}). MALDI-TOF MS: m/z 573.1 $[M]^+$. IR (ATR): $\tilde{\nu}$ 617 cm^{-1} (w), 632 (w), 719 (w), 760 (w), 773 (w), 814 (s), 835 (m), 950 (w), 1001 (w), 1065 (w), 1109 (w), 1179 (m), 1248 (w), 1277 (m), 1312 (w), 1381 (m), 1404 (s), 1427 (s), 1497 (s), 1507 (m), 1574 (m), 1599 (s), 2220 (m), 2853 (w), 2924 (w), 2953 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 310 nm (43 600), 457 (7200). Anal. calcd for $C_{34}H_{27}N_3S_3$ (573.8): C 71.17, H 4.74, N 7.32; found: C 70.94, H 4.73, N 7.06.

*4-(4-Hexylphenyl)-2,6-bis(4-nitrophenyl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazine (**3h**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane–dichloromethane 10 : 3 with 2% of triethylamine) and after crystallization from dichloromethane–*n*-hexane, compound **3h** (241 mg, 78%) was obtained as a dark violet powder.

R_f (*n*-hexane–dichloromethane 10 : 3): 0.21, Mp 192 °C. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.92 (t, ^3J = 7.1 Hz, 3 H), 1.32–1.43 (m, 6 H), 1.71 (p, ^3J = 7.5 Hz, 2 H), 2.68–2.76 (m, 2 H), 6.43 (s, 2 H), 7.34 (d, ^3J = 8.3 Hz, 2 H), 7.40 (d, ^3J = 8.4 Hz, 2 H), 7.45–7.48 (m, 4 H), 8.10–8.13 (m, 4 H). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 14.4 (CH_3), 23.2 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 32.2 (CH_2), 36.2 (CH_2), 106.0 (C_{quat}), 117.6 (CH), 124.8 (CH), 125.4 (CH), 129.1 (CH), 131.2 (CH), 139.0 (C_{quat}), 139.9 (C_{quat}), 140.7 (C_{quat}), 144.3 (C_{quat}), 145.1 (C_{quat}), 147.0 (C_{quat}). MALDI-TOF MS: m/z 613.1 $[M]^+$. IR (ATR): $\tilde{\nu}$ 687 cm^{-1} (w), 746 (m), 822 (w), 833 (w), 849 (m), 1069 (w), 1107 (m), 1188 (w), 1215 (w), 1248 (w), 1273 (w), 1329 (s), 1385 (w), 1404 (w), 1427 (m), 1489 (m), 1514 (m), 1572 (w), 1589 (m), 2855 (w), 2926 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 254 nm (31 300), 332 (46 000), 524 (17 900). Anal. calcd for $C_{32}H_{27}N_3O_4S_3$ (613.8): C 62.62, H 4.43, N 6.85; found: C 62.43, H 4.44, N 6.57.

*4-(4-Hexylphenyl)-2,6-bis(3-nitrophenyl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazine (**3i**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane–dichloromethane 10 : 3 with 2% of triethylamine), compound **3i** (236 mg, 77%) was obtained as a chestnut brown solid.

R_f (*n*-hexane–dichloromethane 10 : 3): 0.22, Mp 199 °C. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 0.93 (t, ^3J = 7.1 Hz, 3 H), 1.37–1.48 (m, 6 H), 1.75 (p, ^3J = 7.6 Hz, 2 H), 2.74–2.78 (m, 2 H), 6.63 (s, 2 H), 7.45 (s, 4 H), 7.62 (t, J = 8.0 Hz, 2 H), 7.80 (ddd, J = 0.9 Hz, 1.8 Hz, 7.8 Hz, 2 H), 8.08 (ddd, J = 0.9 Hz, 1.8 Hz, 8.2 Hz, 2 H), 8.17 (t, J = 2.0 Hz, 2 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 1, T = 313 K): δ 14.7 (CH_3), 23.6 (CH_2), 30.1 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 36.5 (CH_2), 105.7 (C_{quat}), 118.2 (CH), 120.0 (CH), 122.9 (CH), 129.4 (CH), 131.3 (CH), 131.45 (CH), 131.53 (CH), 136.0 (C_{quat}), 139.7 (C_{quat}), 141.6 (C_{quat}), 144.1 (C_{quat}), 145.4 (C_{quat}), 149.8 (C_{quat}). MALDI-TOF MS: m/z 613.1 $[M]^+$. IR (ATR): $\tilde{\nu}$ 671 cm^{-1} (m), 694 (w), 712 (w), 727 (m), 732 (m), 762 (w), 797 (m), 835 (w), 860 (w), 897 (w), 997 (w), 1067 (w), 1073 (w), 1101 (w), 1202 (w), 1281 (m), 1306 (w), 1352 (s), 1385 (w), 1427 (m), 1477 (m), 1510 (m), 1524 (s), 1578 (w), 1614 (w), 2335 (w), 2851 (w), 2922 (w), 2951 (w), 3084 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 286 nm (40 100), 440 (4800). Anal. calcd for $C_{32}H_{27}N_3O_4S_3$ (613.8): C 62.62, H 4.43, N 6.85, S 15.67; found: C 62.40, H 4.51, N 6.72, S 15.44.

*4-(4-Hexylphenyl)-2,6-bis(2-nitrophenyl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazine (**3j**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane–dichloromethane 10 : 3 with 2% of triethylamine), compound **3j** (165 mg, 54%) was obtained as a chestnut brown oil.

R_f (*n*-hexane–dichloromethane 10 : 3): 0.35. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 1 : 1): δ 0.91 (t, ^3J = 7.1 Hz, 3 H), 1.31–1.42 (m, 6 H), 1.69 (p, ^3J = 7.5 Hz, 2 H), 2.68–2.72 (m, 2 H), 6.17 (s, 2 H), 7.29–7.32 (m, 2 H), 7.35–7.38 (m, 2 H), 7.52 (dd, J = 1.3 Hz, 7.8 Hz, 2 H), 7.57 (td, J = 1.4 Hz, 7.6 Hz, 2 H), 7.66 (td, J = 1.3 Hz, 7.6 Hz, 2 H), 7.77 (dd, J = 1.2 Hz, 8.0 Hz, 2 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 1): δ 14.8 (CH_3), 23.6 (CH_2), 30.0 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 36.4 (CH_2), 106.0 (C_{quat}), 120.4 (CH), 124.8 (CH), 127.6 (C_{quat}), 128.7 (CH), 130.2 (CH), 131.2 (CH), 132.3 (CH), 133.1 (CH), 135.6 (C_{quat}), 141.3 (C_{quat}), 143.6 (C_{quat}), 144.8 (C_{quat}), 149.8 (C_{quat}). MALDI-TOF MS: m/z 613.2 $[M]^+$. IR (ATR): $\tilde{\nu}$ 608 cm^{-1} (w), 652 (m), 681 (w), 696 (w), 710 (s), 721 (m), 748 (s), 775 (s), 824 (m), 831 (w), 837 (w), 853 (m), 949 (w), 988 (w), 999 (w), 1019 (w), 1063 (w), 1113 (w), 1142 (w), 1163 (w), 1188 (w), 1279 (m), 1302 (w), 1358 (s), 1379 (m), 1425 (m), 1481 (m), 1508 (m), 1526 (s), 1566 (w), 1576 (w), 1605 (w), 2855 (w), 2928 (w), 2955 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 264 nm (30 250), 452 (2850). Anal. calcd for $C_{32}H_{27}N_3O_4S_3$ (613.8): C 62.62, H 4.43, N 6.85, S 15.67; found: C 62.24, H 4.61, N 6.57, S 15.27.

*4-(4-Hexylphenyl)-2,6-di(pyridin-3-yl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazine (**3k**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane–ethyl acetate 4 : 1 with 2% of triethylamine), compound **3k** (164 mg, 63%) was obtained as an intense orange oil.

R_f (*n*-hexane–ethyl acetate 4 : 1): 0.15. ^{1}H NMR (300 MHz, acetone-d_6–CS_2 1 : 1): δ 0.95 (t, ^3J = 7.0 Hz, 3 H), 1.33–1.50 (m, 6 H), 1.74 (p, ^3J = 7.5 Hz, 2 H), 2.71–2.79 (m, 2 H), 6.45 (s, 2 H), 7.27 (ddd, J = 0.8 Hz, 4.8 Hz, 8.0 Hz, 2 H), 7.41 (s, 4 H), 7.67 (ddd, J = 1.6 Hz, 2.4 Hz, 8.0 Hz, 2 H), 8.41 (dd, J = 1.5 Hz, 4.7 Hz, 2 H), 8.59 (dd, J = 0.7 Hz, 2.4 Hz, 2 H). ^{13}C NMR (75 MHz, acetone-d_6–CS_2 1 : 1): δ 14.9 (CH_3), 23.7 (CH_2), 30.2 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 36.6 (CH_2), 104.5 (C_{quat}), 117.2 (CH), 124.3 (CH), 129.3 (CH), 130.0 (C_{quat}), 131.3 (CH), 132.2 (CH), 138.6 (C_{quat}), 141.4 (C_{quat}), 143.7 (C_{quat}), 145.1 (C_{quat}), 146.6 (CH), 149.4 (CH). MALDI-TOF MS: m/z 525.2 $[M]^+$. IR (ATR): $\tilde{\nu}$ 619 cm^{-1} (w), 660 (w), 679 (w), 704 (s), 725 (w), 760 (w), 799 (s), 827 (w), 837 (w), 941 (m), 995 (w), 1022 (w), 1063 (w), 1101 (w), 1180 (w), 1234 (w), 1281 (m), 1339 (w), 1379 (m), 1418 (m), 1429 (s), 1477 (s), 1508 (m), 1539 (w), 1574 (m), 1585 (w), 2853 (w), 2924 (m), 2953 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 292 nm (32 450), 414 (3900). Anal. calcd for $C_{30}H_{27}N_3S_3$ (525.7): C 68.53, H 5.18, N 7.99, S 18.30; found: C 68.13, H 5.26, N 7.75, S 18.51.

*3,3′-(4-(4-Hexylphenyl)-4H-dithieno[2,3-b:3′,2′-e][1,4]thiazin-2,6-diyl)bis(10-hexyl-10H-phenothiazine) (**3l**).* According to the GP1 and after flash chromatography on silica gel (*n*-hexane with 2% of triethylamine) and trituration with *n*-hexane under ultrasound, compound **3l** (441 mg, 94%) was obtained as an orange solid.

R_f (*n*-hexane): 0.32, Mp 95 °C. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 1 : 2): δ 0.90 (t, ^3J = 7.1 Hz, 6 H), 0.97 (t, ^3J = 7.1 Hz, 3 H), 1.30–1.44 (m, 18 H), 1.75–1.82 (m, 6 H), 2.73-2.79 (m, 2 H), 3.85–3.89 (m, 4 H), 6.25 (s, 2 H), 6.83 (d, J = 8.6 Hz, 2 H), 6.87–6.91 (m, 4 H), 7.04 (dd, J = 1.5 Hz, 6.7 Hz, 2 H), 7.06 (d, J = 2.2 Hz, 2 H), 7.10–7.15 (m, 4 H), 7.34–7.38 (m, 2 H), 7.39–7.43 (m. 2 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 1 : 2): δ 14.8 (CH_3), 14.9 (CH_3), 23.7 (CH_2), 23.8 (CH_2), 27.5 (CH_2), 27.7 (CH_2), 30.2 (CH_2), 32.4 (CH_2), 32.5 (CH_2), 32.8 (CH_2), 36.6 (CH_2), 48.1 (CH_2), 102.2 (C_{quat}), 115.5 (CH), 116.4 (2 × CH), 123.4 (CH), 124.1 (CH), 124.78 (C_{quat}), 124.81 (C_{quat}), 126.3 (C_{quat}), 128.0 (CH), 128.2 (CH), 128.8 (CH), 129.3 (CH), 131.2 (CH), 141.4 (C_{quat}), 141.7 (C_{quat}), 143.4 (C_{quat}), 144.8 (C_{quat}), 145.36 (C_{quat}), 145.38 (C_{quat}). MALDI-TOF MS: m/z 933.3 $[M]^+$. IR (ATR): $\tilde{\nu}$ 613 cm^{-1} (w), 677 (w), 680 (w), 710 (w), 723 (w), 743 (s), 752 (m), 783 (w), 804 (s), 822 (w), 864 (w), 879 (w), 930 (w), 997 (w), 1042 (w), 1059 (w), 1109 (w), 1142 (w), 1167 (w), 1188 (w), 1246 (m), 1285 (w), 1333 (w), 1362 (m), 1373 (m), 1404 (w), 1439 (m), 1466 (s), 1493 (m), 1539 (w), 1572 (w), 1599 (w), 2853 (w), 2868 (w), 2926 (w), 2951 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 239 nm (sh, 27 900), 267 (sh, 30 250), 291 (36 250), 349 (14 300), 422 (sh, 8500). Anal. calcd for $C_{56}H_{59}N_3S_5$ (933.4): C 71.98, H 6.36, N 4.50, S 17.16; found: C 71.83, H 6.22, N 4.42, S 17.31.

General procedure for the lithiation–Negishi coupling synthesis of 2-(hetero)aryl dithienothiazines 6 (GP2). Dry THF (3 mL), dry TMEDA (0.08 mL, 0.6 mmol) and 4-(4-*n*-hexylphenyl)-4*H*-dithieno[2,3-*b*:3′,2′-*e*][1,4]thiazine (**1**) (186 mg, 0.50 mmol) were placed in a 50 mL Schlenk flask under nitrogen. Then, the solution was cooled to −78 °C (dry ice/acetone), and 1.6 M *n*-BuLi in hexane (0.32 mL, 0.5 mmol) and *n*-hexane Acrosil® (0.66 mL) were added successively and dropwise to the solution and the reaction mixture was stirred at −78 °C for 2 h. In the meantime a solution of freshly dried zinc bromide (150 mg, 0.67 mmol) in dry THF (1.0 mL) was prepared which was added dropwise using a syringe to the reaction mixture at −78 °C. After stirring at −78 °C for 30 min, palladium tetrakis (triphenylphosphane) (23 mg, 4 mol%) and 1.0 equiv. of the (hetero)aryl iodide **2** (0.5 mmol) were successively added to the reaction mixture (for experimental details see Table 5). The reaction mixture was allowed to come to room temperature upon stirring for 12–14 h. Then, a mixture of deionized water (20 mL) and dichloromethane (20 mL) was added, the organic layer was separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried with anhydrous magnesium sulfate and the solvents were removed *in vacuo*. The crude product was purified by flash chromatography on silica gel (eluent containing 2% of triethylamine) to give the pure products **6**. Further purification could be achieved by fractional crystallization.

Table 5 Experimental details of the lithiation–Negishi coupling synthesis of 2-(hetero)aryl dithienothiazines **6**

Entry	(Hetero)aryl iodide **2** [mg] (mmol)	2-(Hetero)aryl dithienothiazines **6** [mg] (%)
1	125 (0.50) of 1-iodo-4-nitrobenzene (**2h**)	108 (44) of **6a**
2	105 (0.50) of 2-iodothiophene (**2m**)	138 (61) of **6b**
3	103 (0.50) of 4-iodopyridine (**2n**)	105 (47) of **6c**

*4-(4-Hexylphenyl)-2-(4-nitrophenyl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazine (**6a**).* According to the GP2 and after twofold flash chromatography on silica gel (*n*-hexane–dichloromethane with 2% of triethylamine and *n*-hexane–toluene 10 : 1 with 1% of triethylamine), compound **6a** (108 mg, 44%) was obtained as a dark violet oil.

R_f (*n*-hexane–dichloromethane 10 : 1): 0.09. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 2 : 1): δ 0.94 (t, ^3J = 7.1 Hz, 3 H), 1.36–1.46 (m, 6 H), 1.72 (p, ^3J = 7.5 Hz, 2 H), 2.72–2.76 (m, 2 H), 6.11 (d, J = 5.5 Hz, 1 H), 6.64 (s, 1 H), 7.19 (d, J = 5.5 Hz, 1 H), 7.36–7.39 (m, 2 H), 7.41–7.44 (m, 2 H), 7.61–7.65 (m, 2 H), 8.15–8.19 (m, 2 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 2 : 1): δ 14.7 (CH_3), 23.6 (CH_2), 30.1 (CH_2), 32.4 (CH_2), 32.7 (CH_2), 36.5 (CH_2), 102.7 (C_{quat}), 107.9 (C_{quat}), 118.5 (CH), 120.7 (CH), 125.0 (CH), 125.2 (CH), 125.9 (CH), 129.3 (CH), 131.4 (CH), 139.2 (C_{quat}), 140.3 (C_{quat}), 141.7 (C_{quat}), 143.8 (C_{quat}), 144.4 (C_{quat}), 146.1 (C_{quat}), 147.4 (C_{quat}). MALDI-TOF MS: m/z 492.1 $[M]^+$. IR (ATR): $\tilde{\nu}$ 611 cm^{-1} (m), 629 (m), 687 (s), 696 (s), 714 (m), 748 (s), 799 (s), 818 (s), 847 (s), 948 (w), 999 (m), 1017 (s), 1061 (m), 1096 (s), 1107 (s), 1175 (w), 1203 (w), 1260 (s), 1329 (s), 1380 (m), 1329 (s), 1380 (m), 1402 (m), 1427 (m), 1491 (m), 1506 (s), 1562 (w), 1589 (m), 2853 (w), 2922 (w), 2957 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 250 nm (25 550), 328 (22 850), 511 (7300). HRMS (ESI) calcd for $C_{26}H_{24}N_2O_2S_3$: 492.09999, found: 492.09937.

*4-(4-Hexylphenyl)-2-(thiophen-2-yl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazine (**6b**).* According to the GP2 and after flash chromatography on silica gel (*n*-hexane with 2% of triethylamine), compound **6b** (138 mg, 61%) was obtained as a pale orange oil.

R_f (*n*-hexane): 0.19. ^{1}H NMR (600 MHz, acetone-d_6–CS_2 5 : 1): δ 0.93 (t, ^3J = 7.0 Hz, 3 H), 1.36–1.44 (m, 6 H), 1.72 (p, ^3J = 7.6 Hz, 2 H), 2.71–2.75 (m, 2 H), 6.10 (d, J = 5.5 Hz, 1 H), 6.20 (s, 1 H), 6.98 (dd, J = 3.6 Hz, 5.1 Hz, 1 H), 7.04 (dd, J = 1.1 Hz, 3.6 Hz, 1 H), 7.15 (d, J = 5.5 Hz, 1 H), 7.29 (dd, J = 1.1 Hz, 5.1 Hz, 1 H), 7.32–7.35 (m, 2 H). 7.39–7.41 (m, 2 H). ^{13}C NMR (150 MHz, acetone-d_6–CS_2 2 : 1): δ 14.7 (CH_3), 23.6 (CH_2), 29.9 (CH_2), 32.4 (CH_2), 32.7 (CH_2), 36.5 (CH_2), 102.7 (C_{quat}), 103.2 (C_{quat}), 116.6 (CH), 120.6 (CH), 124.4 (CH), 124.6 (CH), 125.7 (CH), 128.8 (CH), 129.3 (CH), 131.2 (CH), 135.6 (C_{quat}), 137.2 (C_{quat}), 141.8 (C_{quat}), 143.6 (C_{quat}), 144.6 (C_{quat}), 145.0 (C_{quat}). MALDI-TOF MS: m/z 452.9 $[M]^+$. IR (ATR): $\tilde{\nu}$ 627 cm^{-1} (w), 642 (w), 669 (w), 692 (s), 758 (w), 810 (m), 833 (m), 845 (m), 883 (w), 905 (w), 997 (m), 1016 (w), 1043 (w), 1059 (w), 1078 (w), 1098 (w), 1180 (w), 1225 (w), 1279 (m), 1333 (w), 1350 (w), 1377 (m), 1406 (m), 1459 (m), 1508 (s), 1537 (w), 1570 (w), 1611 (w), 2853 (w), 2924 (m), 2953 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 237 nm (sh, 12 400), 300 (12 700), 355 (sh, 2950), 420 (sh, 1900). HRMS (ESI) calcd for $C_{24}H_{23}NS_4$: 453.07133, found: 453.07097.

*4-(4-Hexylphenyl)-2-(pyridin-4-yl)-4H-dithieno[2,3-b:3′,2′-e]-[1,4]thiazin (**6c**).* According to the GP2 and after flash chromatography on silica gel (*n*-hexane–ethyl acetate 5 : 1 with 2% of triethylamine), compound **6c** (105 mg, 47%) was obtained as a red oil.

R_f (*n*-hexane–ethyl acetate 5 : 1): 0.19. ^{1}H NMR (300 MHz, acetone-d_6–CS_2 5 : 1): δ 0.96 (t, ^3J = 7.1 Hz, 3 H), 1.34–1.47 (m, 6 H), 1.73 (p, ^3J = 7.6 Hz, 2 H), 2.70–2.77 (m, 2 H), 6.10 (d, J = 5.5 Hz, 1 H), 6.60 (s, 1 H), 7.15 (d, J = 5.5 Hz, 1 H), 7.24–7.27 (m, 2 H), 7.32–7.37 (m, 2 H), 7.39–7.43 (m, 2 H), 8.43–8.46 (m, 2 H). ^{13}C NMR (75 MHz, acetone-d_6–CS_2 2 : 1): δ 14.8 (CH_3), 23.7 (CH_2), 30.0 (CH_2), 32.4 (CH_2), 32.7 (CH_2), 36.5 (CH_2), 102.8 (C_{quat}), 106.8 (C_{quat}), 118.0 (CH), 119.2 (CH), 120.6 (CH), 124.8 (CH), 129.3 (CH), 131.3 (CH), 138.8 (C_{quat}), 140.7 (C_{quat}), 141.7 (C_{quat}), 143.7 (C_{quat}), 144.3 (C_{quat}), 145.7 (C_{quat}), 151.2 (CH). MALDI-TOF MS: m/z 448.2 $[M]^+$. IR (ATR): $\tilde{\nu}$ 627 cm^{-1} (w), 644 (w), 656 (m), 665 (w), 696 (m), 806 (s), 839 (m), 961 (w), 991 (m), 1000 (m), 1016 (w), 1061 (w), 1098 (w), 1117 (w), 1196 (w), 1217 (w), 1279 (m), 1325 (w), 1377 (m), 1404 (s), 1431 (s), 1458 (w), 1491 (s), 1508 (m), 1526 (m), 1545 (w), 1566 (m), 1591 (s), 2853 (w), 2924 (m), 2951 (w), 3028 (w). UV/Vis (CH_2Cl_2): λ_{max} (ε) 238 nm (sh, 9750), 292 (13 250), 367 (1900), 449 (2150). Anal. calcd for $C_{25}H_{24}N_2S_3 \cdot \frac{1}{3}\ CH_3CO_2C_2H_5$ (448.7 + 29.4): C 66.17, H 5.62, N 5.86, S 20.12, found: C 66.23, H 5.44, N 5.84, S 20.48.

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Notes and references

1 For a monograph, see *e.g. Functional Organic Materials – Syntheses Strategies, and Applications*, ed. T. J. J. Müller and U. H. F. Bunz, Wiley-VCH, Weinheim, 2007.

2 For excellent reviews, see *e.g.* M. Farinola and R. Ragni, *Chem. Soc. Rev.*, 2011, **40**, 3467; L. Hu and G. Xu, *Chem. Soc. Rev.*, 2010, **39**, 3275; G. Qian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, Z. Y. Wang and D. Ma, *Adv. Mater.*, 2009, **21**, 111; J. Shinar and R. Shinar, *J. Phys. D: Appl. Phys.*, 2008, **41**, 133001; J. A. G. Williams, A. J. Wilkinson and V. L. Whittle, *Dalton Trans.*, 2008, 2081; *Organic Light Emitting Devices: Synthesis, Properties and Applications*, ed. K. Müllen and U. Scherf, Wiley-VCH, Weinheim, 2006; J. G. C. Veinot and T. J. Marks, *Acc. Chem. Res.*, 2005, **38**, 632; G. Hughes and M. R. Bryce, *J. Mater. Chem.*, 2005, **15**, 94; C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.

3 For excellent reviews, see *e.g.* X. Huang, S. Han, W. Huang and X. Liu, *Chem. Soc. Rev.*, 2013, **42**, 173; M. Liang and J. Chen, *Chem. Soc. Rev.*, 2013, **42**, 3453; C. W. Schlenker and M. E. Thompson, *Chem. Commun.*, 2011, 3702; J. L. Delgado, P.-A. Bouit, S. Filippone, M. A. Herranz and N. Martin, *Chem. Commun.*, 2010, **46**, 4853; A. Mishra, M. K. R. Fischer and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2009, **48**, 2474; Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868; B. C. Thompson and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2008, **47**, 58; S. Günes, H. Neugebauer and N. S. Sariciftci, *Chem. Rev.*, 2007, **107**, 1324; *Organic Photovoltaics: Concept and Realization*, C. J. Brabec, ed., Springer, Berlin, 2003; P. Peumans, A. Yakimov and S. R. Forrest, *J. Appl. Phys.*, 2003, **93**, 3693.

4 For excellent reviews, see *e.g.* W. Wu, Y. Liu and D. Zhu, *Chem. Soc. Rev.*, 2010, **39**, 1489; H. Klauk, *Chem. Soc. Rev.*, 2010, **39**, 2643; H. Dong, C. Wang and W. Hu, *Chem. Commun.*, 2010, **46**, 5211; J. E. Anthony, *Angew. Chem., Int. Ed.*, 2008, **47**, 452; A. L. Briseno, S. C. B. Mannsfeld, S. A. Jenekhe, Z. Bao and Y. Xia, *Mater. Today*, 2008, **11**, 38; A. Facchetti, *Mater. Today*, 2007, **10**, 28; A. R. Murphy and J. M. J. Fréchet, *Chem. Rev.*, 2007, **107**, 1066; M. Mas-Torrent and C. Rovira, *Chem. Soc. Rev.*, 2008, **37**, 827; M. Mas-Torrent and C. Rovira, *Mater. Chem.*, 2006, **16**, 433; Y. Sun, Y. Liu and D. Zhu, *J. Mater. Chem.*, 2005, **15**, 53; C. D. Dimitrakopoulos and P. R. L. Malenfant, *Adv. Mater.*, 2002, **14**, 99; G. Horowitz, *Adv. Mater.*, 1998, **10**, 365.

5 J. R. Sheats, *J. Mater. Res.*, 2004, **19**, 1974; D. J. Gundalch, J. A. Nichols, I. Zhou and T. N. Jackson, *Appl. Phys. Lett.*, 2002, **80**, 2925; A. Hepp, N. von Malm, R. Schmechel and H. von Seggern, *Synth. Met.*, 2003, **138**, 201.

6 For reviews on molecular wires, see *e.g.* D. K. James and J. M. Tour, *Top. Curr. Chem.*, 2005, **257**, 33; N. Robertson and C. A. McGowan, *Chem. Soc. Rev.*, 2003, **32**, 96.

7 For reviews on unimolecular electronics, see *e.g.* R. M. Metzger, *J. Mater. Chem.*, 2008, **18**, 4364; S. R. Forrest, *Nature*, 2004, **428**, 911; R. L. Carroll and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2002, **41**, 4379; J. M. Tour, *Acc. Chem. Res.*, 2000, **33**, 791.

8 C. Dostert, C. Wanstrath, W. Frank and T. J. J. Müller, *Chem. Commun.*, 2012, **48**, 7271.
9 S. Gronowitz and A. B. Hörnfeldt, *Thiophenes (Best Synthetic Methods)*, Elsevier Academic Press, Oxford, 1st edn, 2004; D. J. Chadwick and C. Willbe, *J. Chem. Soc., Perkin Trans. 1*, 1977, 887; B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon, Oxford, 1974; J. M. Mallan and R. L. Bebb, *Chem. Rev.*, 1969, **69**, 693; H. Gilman and D. Shirley, *J. Am. Chem. Soc.*, 1949, **71**, 1870.
10 C. Muschelknautz, C. Dostert and T. J. J. Müller, *Synlett*, 2010, 415.
11 C. Dostert, D. Czajkowski and T. J. J. Müller, *Synlett*, 2014, 371.
12 For recent reviews, see: P. Knochel, M. I. Calaza, E. Hupe, E.-I. Negishi and F. Liu, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. de Meijere and F. Diederich, Wiley-VCH, Weinheim, 2004, p. 619; E.-I. Negishi, X. Zeng, Z. Tan, M. Qian, Q. Hu and Z. Huang, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. A. de Meijere and F. Diederich, Wiley-VCH, Weinheim, 2004, p. 815; E. Negishi, *Acc. Chem. Res.*, 1982, **15**, 340; E. Negishi, Q. Hu, Z. Huang, M. Qiang and G. Wang, *Aldrichimica Acta*, 2005, **38**, 71; E. Negishi, in *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. E. Negishi, Wiley-Interscience, New York, 2002, vol. 2, p. 229.
13 D. Cai, D. L. Hughes and T. R. Verhoeven, *Tetrahedron Lett.*, 1996, **37**, 2537.
14 M. J. Frisch, *et al.*, *Gaussian 03, Revision D.01*, Gaussian, Inc., Wallingford CT, 2004.
15 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, Oxford, 1989.
16 R. Ditchfield, R. W. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724.
17 C. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
18 L. Michaelis, *Chem. Rev.*, 1935, **16**, 243.