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Dithienoquinazolines – A Convenient Synthesis by the Oxidative Photocyclization of 4,5-Dithienyl-Substituted Pyrimidines and Their Photophysical Properties

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A convenient synthetic route to novel thienoacene systems bearing a fused pyrimidine ring has been advanced. The commercially available 5-bromopyrimidine was used as the starting material to obtain various dithienoquinazoline systems through nucleophilic aromatic substitution of hydrogen (the S_N^H reaction), Suzuki cross-coupling, and oxidative photocyclization. The redox and optical properties of some of the new compounds have been investigated. The data obtained show the potential of dithienoquinazoline systems in organic electronic applications.

Introduction

Fused polycyclic aromatic compounds are considered to be at the forefront of research into organic semiconductors (OSC) due to their unique characteristics, including high charge mobility. Indeed, organic semiconductors have undergone significant developments during the past two decades due to their potential applications in future-generation ultrathin, large-area and/or flexible devices, including organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs). Compounds of the thienoacene family[1–3] have emerged as high-performance OSCs due to their high charge mobility as compared with acenes such as pentacene[4] and rubrene.[5] A great number of thienoacenes with diverse molecular structures have been synthesized and elucidated as promising organic semiconductors. In particular, acenedithiophenes, in which two thiophene rings are fused to a benzene ring, for example, linear benzodithiophenes (**BDT-1** and **-2**) and their angular isomers (**BDT-3**–**5**; Figure 1), proved to have many advantages over other classes of compounds owing to their ease of functionalization at the α positions of the thiophene subunits, thus providing access to a wide range of organic semiconductors with p- to n-type characteristics, including polymeric materials.[6,7] Meanwhile, data concerning the effects of nitrogen incorporation into thienoacene systems are scarce in the literature. Only a few examples have been reported that deal with angular benzodithiophenes bearing a fused pyrazine ring, for example, dithieno[3,2-*f*:2′,3′-*h*]quinoxalines (**QDT**s) and quinoxalino[6,5-*b*:7,8-*b*′]bis([1]benzothiophene)s (**DTNQ**s; see Figure 1), to modulate effectively HOMO and LUMO energies.[2,8] In addition, **QDT** derivatives have been used as "weak donor" moieties for the fabrication of bulk heterojunction (BHJ) polymer solar cells,[8] whereas in the case of **DTNQ**, a p-type field effect was observed.[2]

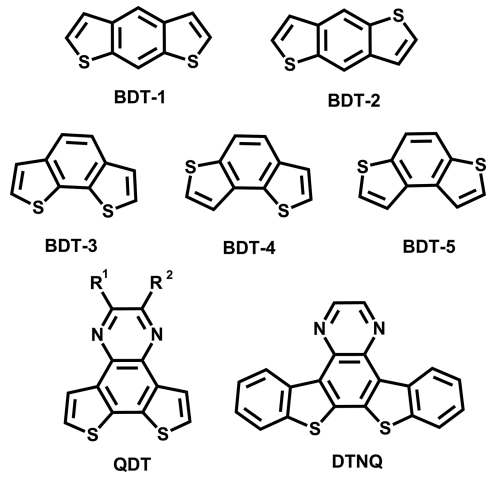

Figure 1. Chemical structures of benzodithiophenes (**BDT**s) and their derivatives containing the fused pyrazine ring.

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In this paper we wish to report the synthesis and characterization of four novel thienoacene systems (see Figure 2) that incorporate a fused pyrimidine ring: dithieno[2,3-*f*:3′,2′-*h*]quinazoline (**DTQ-1**), dithieno[3,2-*f*:3′,2′-*h*]quinazoline (**DTQ-2**), [1]benzothieno[2,3-*f*]thieno[3,2-*h*]quinazoline (**BTTQ-1**), and [1]benzothieno[3,2-*f*]thieno[3,2-*h*]quinazoline (**BTTQ-2**).

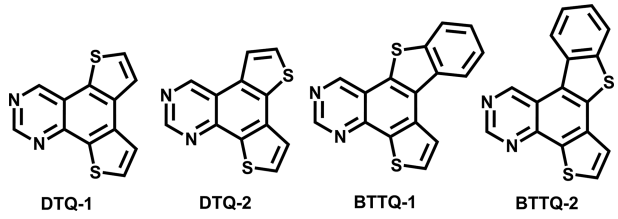


Figure 2. Chemical structures of dithienoquinazolines (**DTQ**s) and [1]benzothienothienoquinazolines (**BTTQ**s).

Results and Discussion

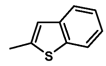
Synthesis

It has previously been shown that 5-bromo-2-(hetero)-arylpyrimidines react with a variety of (hetero)aryl-substituted boronic acids under Pd-catalyzed microwave-assisted conditions.[9,10] 4,5-Dithienyl-substituted pyrimidines **3a**–**d**, employed as the key synthetic intermediates in the preparation of dithienoquinazoline systems (**DTQ** and **BTTQ**), were generated by using a sequence that is initiated by the conversion of readily available[9] 5-bromo-4-(thien-2-yl)pyrimidine (**2**) into 5-(hetero)aryl-4-(thien-2-yl)pyrimidines **3a**–**d** in dioxane/H_2O (3:4), which is similar to the above-mentioned microwave-assisted Suzuki cross-coupling reaction (Scheme 1, Table 1). The structures of the 4,5-dithienylpyrimidines **3a**–**d** were established unequivocally by X-ray crystallography analysis, performed for compound **3b** (Figure 3).

Compounds **3a**–**d** were subjected to oxidative photocyclization by the action of iodine in toluene in the presence of an excess of propylene oxide as the scavenger of hydrogen iodide. The reaction mixtures were irradiated at room temperature with a UV lamp to yield the dithienoquinazolines **DTQ** and **BTTQ** in moderate yields (Scheme 2, Table 2).

Note that the yields of the [1]benzothienothienoquinazolines (**BTTQ**s) were lower than those of the dithienoquinazolines (**DTQ**s). This can be explained by the poor solubility in toluene of both the starting pyrimidines **3b**,**d** and the products **4b**,**d**, as well as radical-mediated side-reactions.[12]

Table 1. Yields of 4,5-dithiophenylpyrimidines **3a**–**d**.

Entry	Het	Pyrimidine	Yield (%)
1		**3a**	ref.[9]
2		**3b**	78
3		**3c**	72
4		**3d**	77

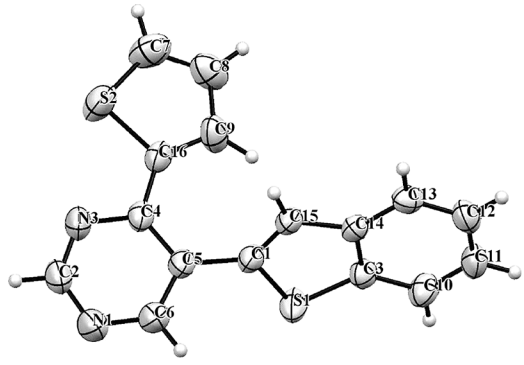
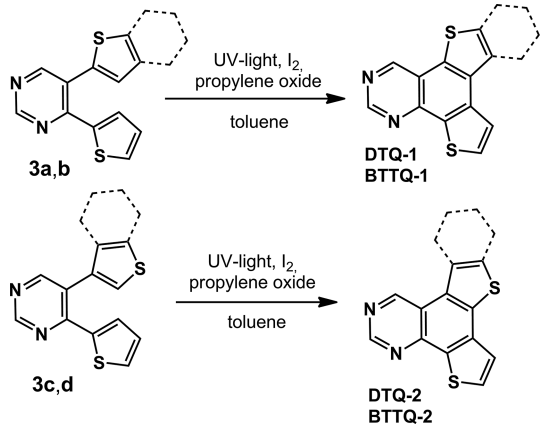
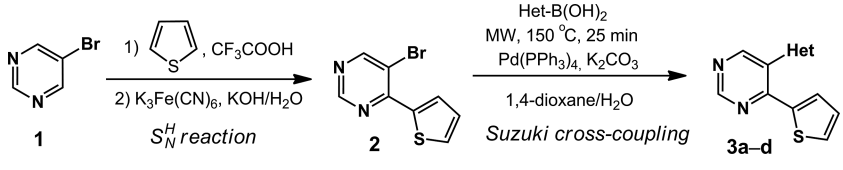


Figure 3. Mercury[11] representation of the X-ray crystal structure of **3b** with thermal ellipsoids drawn at the 50% probability level.

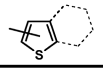
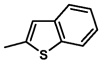


Scheme 2.



Scheme 1.

Table 2. Yields of dithienoquinazolines (**DTQ**s) and [1]benzothienothienoquinazolines (**BTTQ**s).

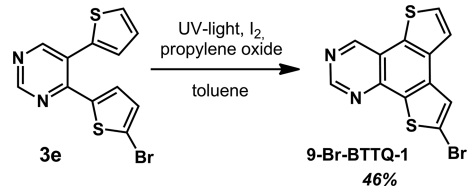
Entry	Pyrimidine		Dithienoquinazoline	Yield (%)
1	**3a**		**DTQ-1**	64
2	**3b**		**BTTQ-1**	38
3	**3c**		**DTQ-2**	47
4	**3d**		**BTTQ-2**	22

To explore the reactivity of the novel dithienoquinazoline systems and their further functionalization, we investigated the reactions of dithienoquinazolines (**DTQ**s) with an excess (5 equiv.) of *N*-bromosuccinimide (NBS) at room temperature for 24 h in DMF. In the case of dithieno[2,3-*f*:3′,2′-*h*]quinazoline (**DTQ-1**), the reaction resulted in a mixture of mono- and dibromo-substituted compounds (Scheme 3) that could not be separated. Under similar conditions, only 9-bromodithieno[3,2-*f*:3′,2′-*h*]quinazoline (**9-Br-DTQ-2**) was obtained in 61% yield from the reaction of dithieno[3,2-*f*:3′,2′-*h*]quinazoline (**DTQ-2**) (Scheme 3). All the reaction mixtures were analyzed by GC–MS and several by-products were identified (Table 3).

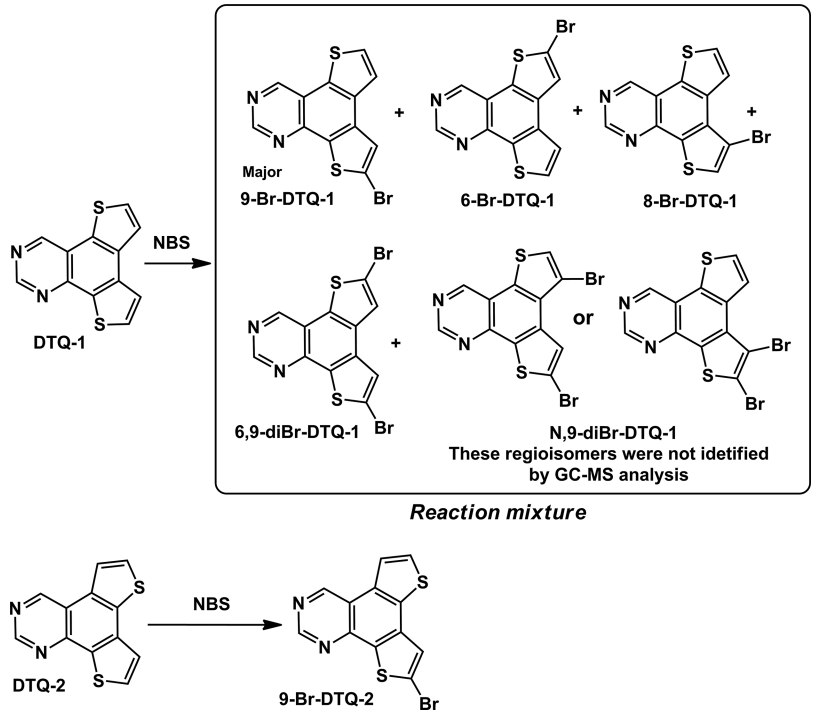
Table 3. Composition of the reaction mixtures obtained from dithienoquinazolines (**DTQ**s) and *N*-bromosuccinimide.

Entry	Dithieno-quinazoline	Product	Yield [%] Reaction mixture GC–MS	Isolated yield
1	**DTQ-1**	**6-Br-DTQ-1**	41.7	not isolated
		8-Br-DTQ-1	9.7	
		9-Br-DTQ-1	8.8	
		6,9-diBr-DTQ-1	16.4	
		***N*,9-diBr-DTQ-1**	23.3	
2	**DTQ-2**	**DTQ-2**	24.1	
		9-Br-DTQ-2	75.9	61

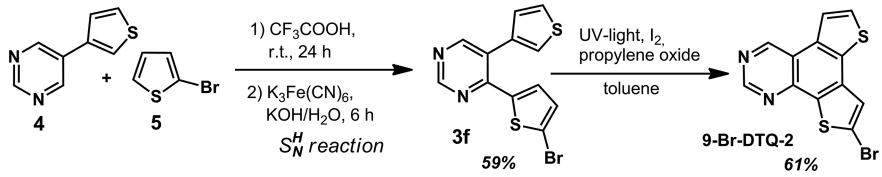
To prove the structure of the by-product **9-Br-DTQ-1**, the targeted synthesis of 9-bromodithieno[2,3-*f*:3′,2′-*h*]-quinazoline (**9-Br-DTQ-1**) was carried out by photocyclization of 4-(5-bromothien-2-yl)-5-(thien-2-yl)pyrimidine[9] (**3e**; Scheme 4). Moreover, the structure of **9-Br-DTQ-1** was established unequivocally by an X-ray diffraction study (see Figure 4).



Scheme 4.



Scheme 3.



Scheme 5.

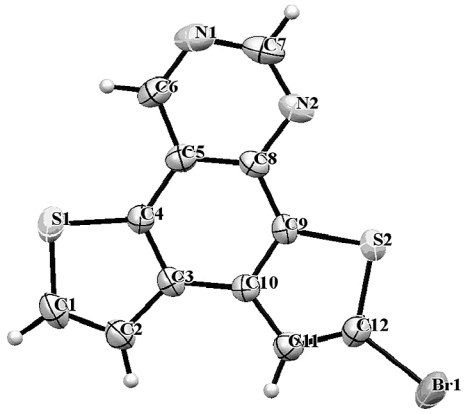


Figure 4. Mercury[11] representation of the X-ray crystal structure of **9-Br-DTQ-1** with thermal ellipsoids drawn at the 50% probability level.

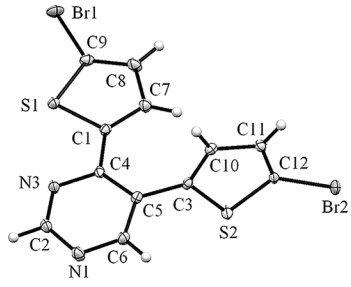
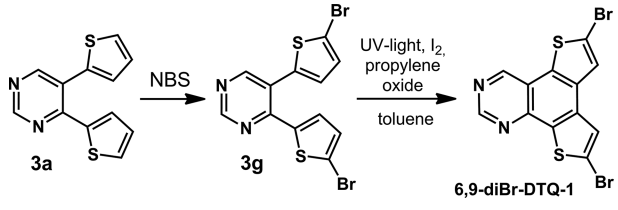


Figure 5. Mercury[11] representation of the X-ray crystal structure of **3g** with thermal ellipsoids drawn at the 50% probability level.

The structure of **9-Br-DTQ-2** was also determined unequivocally by the targeted synthesis of **9-Br-DTQ-2** by the S_N^H reaction[9,10] of 5-(thien-3-yl)pyrimidine (**4**) followed by oxidative photocyclization of the intermediate 4-(5-bromothien-2-yl)-5-(thien-3-yl)pyrimidine (**3f**; Scheme 5). The retention time (GC–MS) for compound **9-Br-DTQ-2** proved to coincide with that for the product derived from the reaction of **DTQ-2** with NBS.

Finally, we prepared 6,9-dibromodithieno[2,3-*f*:3′,2′-*h*]-quinazoline (**6,9-diBr-DTQ-1**) in 55% yield by the bromination of **3a** and subsequent UV irradiation of the resulting 4,5-bis(5-bromothien-2-yl)pyrimidine (**3g**) under similar conditions (Scheme 6).



Scheme 6.

The structure of the intermediate 4,5-bis(5-bromothien-2-yl)pyrimidine (**3g**) was established unequivocally by X-ray diffraction (see Figure 5).

Unfortunately, the bromination of novel dithienoquinazolines has proved to be a nonselective process leading to rather complicated mixtures of products, whereas mono- and dibromo-substituted dithienoquinazolines can be obtained simply by direct photocyclization of the corresponding bromo-substituted 4,5-dithienylpyrimidines.

Photophysical and Electrochemical Properties

Cyclic voltammetry was performed on the four basic dithienoquinazolines (**DTQ**s) and [1]benzothienothienoquinazolines (**BTTQ**s) to determine their redox potentials. Unfortunately, in the accessible range[13] of potentials [0–2.5 V, analogously[2] to quinoxalino[6,5-*b*:7,8-*b*′]bis[1]benzothiophene (**DTNQ**) in THF], no oxidation or reduction peaks were determined for any of the compounds.

The UV/Vis absorption and photoluminescent spectra of **DTQ-1**, **DTQ-2**, **BTTQ-1**, and **BTTQ-2** were recorded, and the results are summarized in Table 4 and Figures S1–S4 in the Supporting Information. All four compounds show several maxima in the UV spectra resulting from vibronic coupling of the π–π* transition. This behavior is common for rigid thienoacenes, which have limited conformational disorder as a result of their fused structures.[14] The optical band gaps (E_g^{opt}) of **DTQ-1**, **DTQ-2**, **BTTQ-1**, and **BTTQ-2** have been estimated from the long-wavelength absorption edge and are summarized in Table 4. Although the electrochemical studies have not enabled the HOMO and LUMO levels to be determined, the optical band gap values of 3.16–3.36 eV for **DTQ** and **BTTQ** appear to be typical of similar semiconducting thienoacenes (e.g., the optical band gap is 3.29 eV for DTNQ).[2] In addition, it has been found that the optical band gaps (E_g^{opt}) and quantum yields of

Table 4. Photophysical properties of dithienoquinazolines (**DTQ**s) and [1]benzothienothienoquinazolines (**BTTQ**s).

	E_g^{opt}[a]	Absorbance		Fluorescence			
	[eV]	λ_{abs}^{exp} [nm]	ε [L mol^{-1} cm^{-1}]	λ_{ex}^{exp} [nm]	λ_{em}^{exp} [nm]	Stokes shift [cm^{-1}]	Φ[b]
DTQ-1	3.32	361.0	4143	363	388	1928	1.8
		344.0	4661	346			
		328.5	4640	285			
		285.0	48009				
DTQ-2	3.36	350.5	6540	338	395	3174	3.7
		335.0	7319	284			
		278.0	27157				
		248.5	34516				
BTTQ-1	3.16	373.0	5058	374	417	2757	2.8
		356.0	5927	355			
		336.5	7763	336			
		304.0	38808	307			
		273.5	25474				
		253.5	26903				
BTTQ-2	3.20	373.5	8303	373	406	2107	4.1
		355.0	8211	340			
		339.5	9700	277			
		273.5	43859				

[a] E_g^{opt} is the energy gap estimated from the onset of the absorption spectra recorded in THF solution. [b] Φ is the quantum yield of photoluminescence.

photoluminescence for **DTQ-1** and **BTTQ-1** are less than those for **DTQ-2** and **BTTQ-2** as a result of longer conjugation lengths in **DTQ-1** and **BTTQ-1** and higher intramolecular charge transfer (ICT). On the other hand, the quantum yields of photoluminescence proved to be lower for **DTQ-1** and **DTQ-2** than for **BTTQ-1** and **BTTQ-2**, whereas the values of E_g^{opt} were higher due to the effect of benzannulation. This finding suggests that an increase in conjugation in structurally similar compounds could lead to smaller band gaps and may be a useful strategy for the design of semiconductors.

Conclusions

A convenient synthetic route to novel thienoacene systems with a fused pyrimidine ring has been advanced. A commercially available 5-bromopyrimidine was used to synthesize various dithienoquinazoline systems through a sequence of reactions involving nucleophilic aromatic substitution of hydrogen (the S_N^H reaction), Suzuki coupling, and oxidative photocyclization. The X-ray diffraction data have been obtained for a number of new dithienoquinazolines and intermediate pyrimidines.

It is legitimate to say that the compounds studied herein have potential as organic semiconductors, but additional modifications are required to achieve this. Future research will be directed at creating push–pull systems with stronger donor and acceptor groups attached to the opposite ends of the oligothiophene motif.

Experimental Section

General: All reagents and solvents were obtained from commercial sources and dried by using standard procedures before use. 5-Bromo-4-(thien-2-yl)pyrimidine (**2**), 4,5-di(thien-2-yl)pyrimidine (**3a**), 4-(5-bromothien-2-yl)-5-(thien-2-yl)pyrimidine (**3e**) and 5-(thien-3-yl)pyrimidine (**4**) were prepared according to the earlier reported method.[9,10] The solvents (1,4-dioxane and H_2O) for the microwave-assisted Suzuki cross-coupling reactions were deoxygenated by bubbling argon for 1 h.

^{1}H and ^{13}C NMR spectra were recorded with Bruker DRX-400 and AVANCE-500 spectrometer using Me_4Si as an internal standard. Elemental analysis was carried with a Eurovector EA 3000 automated analyzer. Melting points were determined on Boetius combined heating stages.

GC–MS analysis was carried out by using an Agilent GC 7890A MS 5975C Inert XL EI/CI GC–MS spectrometer with a quadrupole mass-spectrometric detector with electron ionization (70 eV) and scan over the total ionic current in the range m/z = 20–1000 and a quartz capillary column HP-5MS (30 m × 0.25 mm, film thickness 0.25 mm). Helium served as the carrier gas, the split ratio of the flow was 1:50, and the consumption through the column was 1.0 mL min^{-1}; the initial temperature of the column was 40 °C (storage 3 min), the heating rate was 10 °C min^{-1} to 290 °C (storage 20 min), the temperature of the evaporator was 250 °C, the temperature of the source was 230 °C, the temperature of the quadrupole was 150 °C, and the temperature of the transition chamber was 280 °C. Solutions of the samples at a concentration of 3–4 mg mL^{-1} were prepared in THF and 1 mL of the solutions was analyzed.

Flash column chromatography was carried out by using Lancaster silica gel 0.040–0.063 mm (230–400 mesh), eluting with ethyl acetate/hexane. The progress of the reactions and the purity of compounds were checked by TLC on Sorbfil plates (Russia); the spots were visualized with UV light (λ = 254 or 365 nm).

Microwave experiments were carried out in a Discover unimodal microwave system (CEM, USA) with a working frequency of 2.45 GHz and the power of the microwave radiation ranged from 0 to 300 W. The reactions were carried out in a 10 mL reaction tube fitted with hermetic Teflon cork. The temperature of the reaction was monitored by using an IR sensor at the external surface of the reaction vessel.

The light source used for the photochemical reactions was a Hanovia medium-pressure mercury lamp (PC 451050/805221).

A suitable crystal of **3g** was selected and X-ray analysis was performed with an Xcalibur E diffractometer by following a standard procedure (Mo-K_α graphite-monochromated irradiation, ω scanning with steps of 1). The crystal was kept at 120.00(10) K during data collection and empirical absorption correction was applied. By using Olex2,[15] the structure was solved by using the Superflip[16] structure solution program using Charge Flipping and refined with the SHELX[17] refinement package by using the full-matrix least-squares on F^2 method with anisotropic approximation for non-hydrogen atoms. X-ray analyses of crystals of **3b** and **9-Br-DTQ-1** were performed with an Xcalibur S diffractometer following a standard procedure (Mo-K_α graphite-monochromated irradiation, ω scanning with steps of 1°). The crystals were kept at 295(2) K during data collection. For compound **9-Br-DTQ-1**, empirical absorption correction was applied. By using the SHELX program package,[17] the structures were solved by direct methods and refined by the full-matrix least-squares on F^2 method with anisotropic approximation for non-hydrogen atoms. Crystal data and data collection parameters are summarized in Table S5 in the Supporting Information.

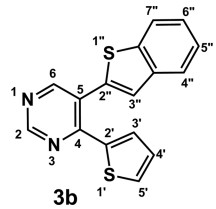
CCDC-1018352 (for **3b**), -1018351 (for **3g**), and -1018350 (for **9-Br-DTQ-1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Cyclic voltammetry was carried out with a Metrohm Autolab PGSTAT128N potentiostat with a standard three-electrode configuration. Typically, a three-electrode cell equipped with a glass carbon (and platinum) working electrode, an $Ag/AgNO_3$ reference electrode, and a glass carbon rod counter electrode was employed. The measurements were performed in anhydrous THF solution containing the compound (2 mM) and tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte under argon at a scan rate of 100 $mV\,s^{-1}$. The potential of the $Ag/AgNO_3$ reference electrode was calibrated by using the ferrocene/ferrocenium redox couple (Fc/Fc+), which has a known oxidation potential of +4.8 eV.

UV/Vis spectra were recorded for 1×10^{-5} M dichloromethane solutions with a Shimadzu UV-2401PC spectrophotometer. Photoluminescent spectra were recorded as 1×10^{-6} M THF solutions with a Varian Cary Eclipse fluorescence spectrophotometer. Quantum yields (Φ) were estimated by using a 1 N H_2SO_4 solution of quinine bisulfate ($\Phi = 0.55$) as a reference.[18]

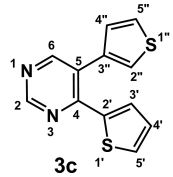
IR spectra of samples (solid powders) were recorded with a Spectrum One Fourier transform IR spectrometer (Perkin–Elmer) equipped with a diffuse reflectance attachment (DRA) in the frequency range 3500–450 cm^{-1}. Spectrum processing and band intensity determination were carried out by using the special software supplied with the spectrometer.

General Procedure for the Microwave-Assisted Suzuki Cross-Coupling Reactions: A solution of K_2CO_3 (346 mg, 2.5 mmol) in H_2O (4 mL) was added to a mixture of 5-bromo-4-(thien-2-yl)pyrimidine (**2**; 0.5 mmol), (benzo[*b*]thien-2-yl)boronic acid [or 3-thienylboronic acid or (benzo[*b*]thien-3-yl)boronic acid] (107 mg, 0.6 mmol) and $[Pd(PPh_3)_4]$ (29 mg, 5 mol-%) in THF (3 mL). The resulting mixture was irradiated in a microwave oven at 150 °C (250 W) for 25 min. Then the solvent was distilled off in vacuo and the residue purified by flash column chromatography (hexane/ethyl acetate, 1:3) to afford the desired cross-coupling products (**3b**–**3d**).



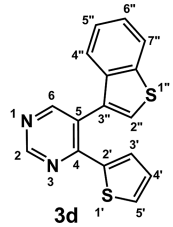
3b

5-Benzo[*b*]thien-2-yl-4-(thien-2-yl)pyrimidine (3b): Yield 78%, pale-yellow solid; m.p. 156–158 °C. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 7.03 (dd, J = 5.0, 3.9 Hz, 1 H, 4′-H), 7.14 (dd, J = 3.9, 1.0 Hz, 1 H, 4′-H), 7.43–7.50 (m, 2 H, benzo[*b*]thienyl), 7.68 (s, 1 H, 3′′-H), 7.79 (dd, J = 5.0, 1.0 Hz, 1 H, 5′-H), 7.95 (dd, J = 6.6, 2.2 Hz, 1 H, benzo[*b*]thienyl), 8.05–8.08 (m, 1 H, benzo[*b*]thienyl), 8.85 (s, 1 H, 6-H), 9.20 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]-DMSO): δ = 122.16, 123.23, 124.12, 124.85, 124.96, 127.86, 128.32, 130.11, 131.00, 131.66, 137.44, 139.54, 140.79, 156.30, 157.76, 159.45 ppm. GC: t_R = 27.58 min. MS: m/z (%) = 294 (100) $[M]^+$. $C_{16}H_{10}N_2S_2$ (294.40): calcd. C 65.28, H 3.42, N 9.52; found C 64.94, H 3.58, N 9.45.



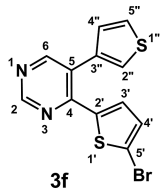
3c

5-(Thien-3-yl)-4-(thien-2-yl)pyrimidine (3c): Yield 72%, off-white solid; m.p. 95–97 °C. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 6.89 (d, J = 3.7 Hz, 1 H, thienyl), 7.03 (dd, J = 4.7, 4.1 Hz, 1 H, thienyl), 7.16 (dd, J = 4.7, 1.5 Hz, 1 H, thienyl), 7.76–7.78 (m, 3 H, thienyl), 8.66 (s, 1 H, 6-H), 9.11 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 125.53, 125.93, 127.70, 128.31, 128.33, 130.10, 131.39, 135.74, 141.24, 156.61, 157.14, 158.45 ppm. GC: t_R = 22.99 min. MS: m/z (%) = 244 (100) $[M]^+$. $C_{12}H_8N_2S_2$ (244.34): calcd. C 58.99, H 3.30, N 11.46; found C 58.65, H 3.49, N 11.30.



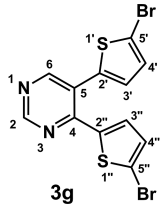
3d

5-(Benzo[*b*]thien-3-yl)-4-(thien-2-yl)pyrimidine (3d): Yield 77%, pale-yellow solid; m.p. 99–101 °C. ^1H NMR (500 MHz, [D$_6$]DMSO): δ = 6.78 (dd, J = 4.1, 0.6 Hz, 1 H, 3′-H), 6.88 (dd, J = 4.8, 4.1 Hz, 1 H, 4′-H), 7.23–7.33 (m, 1 H, benzo[*b*]thienyl), 7.39–7.45 (m, 1 H, benzo[*b*]thienyl), 7.68 (dd, J = 4.8, 0.6 Hz, 1 H, 5′-H), 8.05 (s, 1 H, 2′′-H, benzo[*b*]thienyl), 8.13 (s, J = 8.2 Hz, 1 H, 7′′-H), 8.75 (s, 1 H, 6-H), 9.24 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 122.14, 123.21, 124.10, 124.81, 124.91, 127.75, 128.32, 130.08, 130.99, 131.66, 137.44, 139.54, 140.79, 156.30, 157.76, 159.40 ppm. GC: t_R = 27.04 min. MS: m/z (%) = 294 (100) $[M]^+$. $C_{16}H_{10}N_2S_2$ (294.40): calcd. C 65.28, H 3.42, N 9.52; found C 65.01, H 3.50, N 9.43.



3f

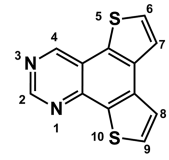
Synthesis of 4-[5-Bromo(thien-2-yl)]-5-(thien-3-yl)pyrimidine (3f): 2-Bromothiophene (**5**; 387 μL, 4 mmol) was added to a solution of 5-(thien-3-yl)pyrimidine (**4**; 324 mg, 2 mmol) in CF_3COOH (5 mL). The reaction mixture was stirred at room temperature for 24 h and the solvents evaporated. A solution of KOH (449 mg, 8.0 mmol, 4 equiv.) and $K_3[Fe(CN)_6]$ (1.317 g, 4.0 mmol, 2 equiv.) in water (15 mL) was added to the residue. The resulting mixture was stirred for 6 h at room temperature, and the precipitate formed was filtered, washed with H_2O, and air-dried. The residue was purified by flash column chromatography (hexane/ethyl acetate, 1:1) to afford the desired 4-[5-bromo(thien-2-yl)]-5-(thien-3-yl)pyrimidine (**3f**), yield 381 mg, 59%, off-white crystalline powder; m.p. 168–170 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.67 (d, J = 4.1 Hz, 1 H, 3′-H), 7.17 (d, J = 4.1 Hz, 1 H, 4′-H), 7.19 (dd, J = 4.5, 1.7 Hz, 1 H, 3′′-H), 7.78–7.81 (m, 2 H, thienyl), 8.68 (s, 1 H, 6-H), 9.11 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 117.80, 125.78, 125.88, 128.02, 128.26, 130.76, 131.80, 135.12, 143.00, 154.47, 157.16, 158.72 ppm. GC: t_R = 25.35 min. MS: m/z (%) = 322 (100) [M]$^+$ for ^{79}Br, 324 (100) [M]$^+$ for ^{81}Br. $C_{12}H_7BrN_2S_2$ (323.23): calcd. C 44.59, H 2.18, N 8.67; found C 44.65, H 2.29, N 8.73.



3g

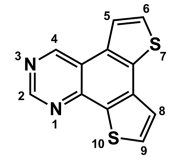
Synthesis of 4,5-Bis[5-bromo(thien-2-yl)]pyrimidine (3g): NBS (219 mg, 1.23 mmol) was added to a solution of 4,5-di(thien-2-yl) pyrimidine (**3a**; 100 mg, 0.41 mmol) in DMF (5 mL) at room temperature. Then the mixture was stirred for 24 h at room temperature. The reaction mixture was diluted with H_2O and the precipitate formed was filtered, washed with H_2O, and air-dried. The residue was purified by flash column chromatography (hexane/ethyl acetate, 1:1). The product **3g** was isolated as a dark-yellow powder (125 mg, 76%), m.p. 168–170 °C. ^{1}H NMR (500 MHz, [D$_6$]-DMSO): δ = 6.90 (d, J = 4.1 Hz, 1 H, 3′′-H), 7.20 (d, J = 3.7 Hz, 1 H, 3′-H), 7.25 (d, J = 4.1 Hz, 1 H, 4′′-H), 7.40 (d, J = 3.7 Hz, 1 H, 4′-H), 8.76 (s, 1 H, 6-H), 9.15 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 113.74, 118.39, 122.60, 130.44, 131.36, 131.44, 132.08, 136.92, 142.15, 155.20, 158.02, 159.59 ppm. GC: t_R = 27.11 min. MS: m/z = 401 [M]$^+$ for ^{79}Br, 403 [M]$^+$ for ^{81}Br. $C_{12}H_6Br_2N_2S_2$ (402.13): calcd. C 35.84, H 1.50, N 6.97; found C 35.68, H 1.44, N 6.84.

General Procedure for the Oxidative Photocyclization Reactions: Iodine (0.037 g, 0.14 mmol) and excess propylene oxide (ca. 5 mL) was added to a solution of 5-(het)aryl-4-(thien-2-yl)pyrimidine **3a**–**3g** (1 mmol) in toluene (150 mL). The reaction mixture was irradiated at room temp. with a UV lamp. After 20 h of irradiation, the toluene layer was washed with aqueous $Na_2S_2O_3$, water, and brine, dried with anhydrous $MgSO_4$, and the solvents evaporated. The residue was purified by flash column chromatography using EtOAc/hexane (from 1:3 to 1:1) as eluent to afford the desired dithienoquinazoline system.



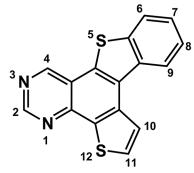
DTQ-1

Dithieno[2,3-*f*:3′,2′-*h*]quinazoline (DTQ-1): Yield 64%, pale-brown solid; m.p. 224–226 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.14–8.18 (m, 3 H, 6-H, 7-H, 9-H), 8.29 (d, J = 5.2 Hz, 1 H, 8-H), 9.37 (s, 1 H, 4-H), 9.87 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 118.32, 123.23, 123.92, 129.51, 131.74, 132.86, 133.36, 134.73, 138.80, 145.46, 155.00, 155.14 ppm. IR (DRA): $\tilde{\nu}$ = 513, 577, 628, 643, 691, 726, 738, 764, 801, 851, 908, 963, 1010, 1098, 1115, 1149, 1201, 1218, 1229, 1250, 1271, 1327, 1357, 1385, 1413, 1440, 1478, 1487, 1556, 1576, 1658, 3008, 3061, 3077, 3098 cm^{-1}. GC: t_R = 25.87 min. MS: m/z (%) = 242 (100) [M]$^+$. $C_{12}H_6N_2S_2$ (242.32): calcd. C 59.48, H 2.50, N 11.56; found C 59.22, H 2.31, N 11.57.



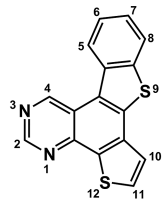
DTQ-2

Dithieno[3,2-*f*:3′,2′-*h*]quinazoline (DTQ-2): Yield 47%, pale-brown solid; m.p. 238–240 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.93 (d, J = 5.3 Hz, 1 H), 8.10 (d, J = 5.3 Hz, 1 H), 8.32 (d, J = 5.3 Hz, 1 H), 8.45 (d, J = 5.3 Hz, 1 H), 9.38 (s, 1 H, 4-H), 10.15 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 118.11, 122.62, 123.06, 127.83, 132.36, 132.54, 133.69, 133.71, 137.41, 145.90, 154.89, 156.16 ppm. IR (DRA): $\tilde{\nu}$ = 478, 568, 630, 657, 687, 731, 756, 803, 862, 895, 920, 1012, 1064, 1101, 1129, 1205, 1333, 1366, 1416, 1425, 1440, 1470, 1494, 1555, 1583, 3058, 3078 cm^{-1}. GC: t_R = 25.89 min. MS: m/z (%) = 242 (100) [M]$^+$. $C_{12}H_6N_2S_2$ (242.32): calcd. C 59.48, H 2.50, N 11.56; found C 59.63, H 2.47, N 11.34.



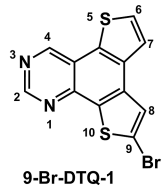
BTTQ-1

[1]Benzothieno[2,3-*f*]thieno[3′,2′-*h*]quinazoline (BTTQ-1): Yield 38%, pale-brown solid; m.p. 281–284 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.69–7.77 (m, 2 H, 7-H, 8-H), 8.33 (d, J = 7.7 Hz, 1 H, 9-H), 8.48 (d, J = 5.6 Hz, 1 H, 10-H), 8.71 (d, J = 5.6 Hz, 1 H, 11-H), 8.90 (d, J = 7.7 Hz, 1 H, 6-H), 9.47 (s, 1 H, 4-H), 9.94 (s, 1 H, 2-H) ppm. IR (DRA): $\tilde{\nu}$ = 638, 691, 707, 722, 762, 800, 869, 910, 963, 1013, 1022, 1103, 1119, 1147, 1163, 1207, 1265, 1307, 1342, 1380, 1408, 1433, 1448, 1483, 1546, 1579, 1661, 3046, 3109 cm^{-1}. GC: t_R = 31.52 min. MS: m/z (%) = 292 (100) [M]$^+$. $C_{16}H_8N_2S_2$ (292.38): calcd. C 65.73, H 2.76, N 9.58; found C 65.52, H 2.61, N 9.39. The ^{13}C NMR spectra of **BTTQ-1** could not be obtained due to the poor solubility of this compound in deuteriated solvents.



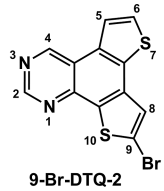
BTTQ-2

[1]Benzothieno[3,2-*f*]thieno[3′,2′-*h*]quinazoline (BTTQ-2): Yield 22%, pale-brown solid; m.p. 280–283 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.64–7.72 (m, 2 H, 6-H, 7-H), 8.00 (d, J = 5.2 Hz, 1 H, 10-H), 8.31 (dd, J = 8.0, 0.8 Hz, 1 H, 5-H), 8.39 (d, J = 5.2 Hz, 1 H, 11-H), 9.09 (d, J = 8.0 Hz, 1 H, 8-H), 9.45 (s, 1 H, 4-H), 10.65 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 119.36, 123.46, 123.87, 124.89, 125.89, 126.00, 126.32, 134.22, 134.82, 135.11, 135.17, 137.33, 138.33, 146.18, 154.19, 154.85 ppm. IR (DRA): $\tilde{\nu}$ = 425, 482, 513, 567, 636, 688, 728, 742, 758, 802, 867, 918, 933, 1011, 1029, 1094, 1122, 1165, 1177, 1204, 1252, 1295, 1311, 1336, 1353, 1377, 1412, 1446, 1466, 1484, 1545, 1574, 3033, 3060, 3097 cm^{-1}. GC: t_R = 31.56 min. MS: *m/z* (%) = 292 (100) [M]$^+$. $C_{16}H_8N_2S_2$ (292.38): calcd. C 65.73, H 2.76, N 9.58; found C 65.59, H 2.68, N 9.45.



9-Br-DTQ-1

9-Bromodithieno[2,3-*f*:3′,2′-*h*]quinazoline (9-Br-DTQ-1): Yield 46%, beige solid; m.p. 224–226 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.08 (d, J = 5.3 Hz, 1 H, 7-H), 8.16 (d, J = 5.3 Hz, 1 H, 6-H), 8.36 (s, 1 H, 8-H), 9.34 (s, 1 H, 4-H), 9.83 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 118.23, 119.91, 123.13, 127.45, 129.84, 132.39, 133.68, 134.11, 138.61, 144.22, 155.10, 155.38 ppm. IR (DRA): $\tilde{\nu}$ = 466, 513, 542, 572, 626, 691, 749, 782, 828, 838, 908, 931, 963, 990, 1013, 1080, 1113, 1199, 1235, 1247, 1318, 1347, 1383, 1409, 1440, 1473, 1487, 1554, 1578, 3012, 3069, 3111 cm^{-1}. GC: t_R = 27.99 min. MS: *m/z* (%) = 320 (100) [M]$^+$ for ^{79}Br, 322 (100) [M]$^+$ for ^{81}Br. $C_{12}H_5BrN_2S_2$ (321.22): calcd. C 44.87, H 1.57, N 8.72; found C 44.63, H 1.33, N 8.57.



9-Br-DTQ-2

9-Bromodithieno[3,2-*f*:3′,2′-*h*]quinazoline (9-Br-DTQ-2): Yield 61%, dark-yellow solid; m.p. 243–244 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.92 (d, J = 5.3 Hz, 1 H, 8-H), 8.33 (d, J = 5.3 Hz, 1 H, 9-H), 8.68 (s, 1 H, 5-H), 9.39 (s, 1 H, 4-H), 10.11 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 114.46, 117.24, 123.00, 126.09, 132.33, 133.12, 134.06, 134.66, 136.41, 145.78, 155.23, 156.48 ppm. GC: t_R = 27.97 min. MS: *m/z* (%) = 320 (100) [M]$^+$ for ^{79}Br, 322 (100) [M]$^+$ for ^{81}Br. $C_{12}H_5BrN_2S_2$ (321.22): calcd. C 44.87, H 1.57, N 8.72; found C 44.83, H 1.70, N 8.67.

6,9-diBr-DTQ-1

6,9-Dibromodithieno[2,3-*f*:3′,2′-*h*]-quinazoline (6,9-diBr-DTQ-1): Yield 55%, beige solid; m.p. 264–266 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 8.33 (s, 1 H, 7-H), 8.35 (s, 1 H, 8-H), 9.37 (s, 1 H, 4-H), 9.83 (s, 1 H, 2-H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ = 116.35, 117.48, 120.18, 126.48, 127.39, 133.34, 133.56, 134.74, 137.58, 143.99, 155.34, 155.66 ppm. IR (DRA): $\tilde{\nu}$ = 470, 511, 561, 572, 642, 659, 692, 709, 791, 818, 828, 916, 962, 971, 999, 1019, 1114, 1196, 1215, 1238, 1297, 1315, 1342, 1409, 1444, 1477, 1552, 1582, 1669, 3016, 3043, 3080 cm^{-1}. GC: t_R = 30.11 min. MS: *m/z* (%) = 399 (100) [M]$^+$ for ^{79}Br, 401 (100) [M]$^+$ for ^{81}Br. $C_{12}H_4Br_2N_2S_2$ (400.21): calcd. C 36.02, H 1.01, N 7.00; found C 36.29, H 0.82, N 6.81.

Supporting Information (see footnote on the first page of this article): UV/Vis and ^{1}H and ^{13}C NMR spectra of the new compounds, crystal structural data for compounds **3b**, **3g**, and **9-Br-DTQ-1**.

Acknowledgments

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[1] K. Takimiya, S. Shinamura, I. Osaka, E. Miyazaki, *Adv. Mater.* **2011**, *23*, 4347, and references cited therein.
[2] H. T. Black, S. Liu, V. S. Ashby, *Org. Lett.* **2011**, *13*, 6492.
[3] I. Osaka, S. Shinamura, T. Abe, K. Takimiya, *J. Mater. Chem. C* **2013**, *1*, 1297.
[4] O. D. Jurchescu, J. Baas, T. T. M. Palstra, *Appl. Phys. Lett.* **2004**, *84*, 3061.
[5] T. Hasegawa, J. Takeya, *Sci. Technol. Adv. Mater.* **2009**, *10*, 024314.
[6] a) S. Yoshida, M. Fujii, Y. Aso, T. Otsubo, F. Ogura, *J. Org. Chem.* **1994**, *59*, 3077; b) E. Fischer, J. Larsen, J. B. Christensen, M. Fourmigué, H. G. Madsen, N. Harrit, *J. Org. Chem.* **1996**, *61*, 6997; c) J. G. Laquindanum, H. E. Katz, A. J. Lovinger, A. Dodabalapur, *Adv. Mater.* **1997**, *9*, 36; d) I. Akimoto, K. Kan'no, H. Osuga, K. Tanaka, *J. Lumin.* **2005**, *112*, 341; e) J. L. Brusso, O. D. Hirst, A. Dadvand, S. Ganesan, F. Cicoira, C. M. Robertson, A. Oakley, F. Rosei, D. F. Perepichka, *Chem. Mater.* **2008**, *20*, 2484; f) R. Rieger, D. Beckmann, A. Mavrinskiy, M. Kastler, K. Müllen, *Chem. Mater.* **2010**, *22*, 5314; g) A. A. Leitch, A. Mansour, K. A. Stobo, I. Korobkov, J. L. Brusso, *Cryst. Growth Des.* **2012**, *12*, 1416; h) R. Søndergaard, M. Manceau, M. Jørgensen, F. C. Krebs, *Adv. Energy Mater.* **2012**, *2*, 415; i) Q. Peng, S.-L. Lim, I. H.-K. Wong, J. Xu, Z.-K. Chen, *Chem. Eur. J.* **2012**, *18*, 12140; j) Y. Chen, H. Chang, H. Tian, C. Bao, W. Li, D. Yan, Y. Geng, F. Wang, *Org. Electron.* **2012**, *13*, 3268.

[7] a) M. Dueggeli, R. Rieger, K. Muellen, N. Chebotareva, D. Beckmann, WO Patent 2011120951, **2011**; b) M. Dueggeli, R. Rieger, K. Muellen, N. Chebotareva, D. Beckmann, U.S. Patent 20110240973, **2011**.
[8] a) H. Zhou, L. Yang, S. Liu, W. You, *Macromolecules* **2010**, *43*, 10390; b) H. Zhou, L. Yang, S. C. Price, K. J. Knight, W. You, *Angew. Chem. Int. Ed.* **2010**, *49*, 7992; *Angew. Chem.* **2010**, *122*, 8164.
[9] E. V. Verbitskiy, E. M. Cheprakova, P. A. Slepukhin, M. I. Kodess, M. A. Ezhikova, M. G. Pervova, G. L. Rusinov, O. N. Chupakhin, V. N. Charushin, *Tetrahedron* **2012**, *68*, 5445.
[10] E. V. Verbitskiy, G. L. Rusinov, V. N. Charushin, O. N. Chupakhin, E. M. Cheprakova, P. A. Slepukhin, M. G. Pervova, M. A. Ezhikova, M. I. Kodess, *Eur. J. Org. Chem.* **2012**, 6612.
[11] *Mercury*, v. 3.3, available from http://www.ccdc.cam.ac.uk/mercury/.
[12] F. B. Mallory, C. W. Mallory, *Photocyclization of Stilbenes and Related Molecules*, in: *Organic Reactions*, Wiley, Hoboken, NY, **1984**, vol. 30.
[13] C. K. Mann, *Nonaqueous solvents for electrochemical use*, in: *Electroanalytical Chemistry*, vol. 3 (Ed.: A. J. Bard), Marcel Dekker, New York, **1969**, p. 57.
[14] R. S. Sánchez-Carrera, M. C. R. Delgado, C. C. Ferrón, R. M. Osuna, V. Hernandez, J. T. L. Navarrete, A. Aspuru-Gazik, *Org. Electron.* **2010**, *11*, 1701.
[15] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
[16] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **2007**, *40*, 786.
[17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
[18] A. M. Brouwer, *Pure Appl. Chem.* **2011**, *83*, 221.

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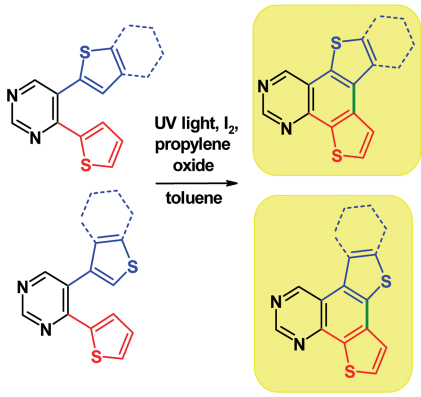
Thieno-aza-acenes

A convenient route to a new class of thienoacene systems bearing a fused pyrimidine ring is presented along with their optoelectronic properties. The photophysical and electrochemical properties of these newly developed thieno-aza-acenes have been investigated by UV/Vis absorption and photoluminescence spectrophotometry and cyclic voltammetry, and some crystal structures have also been determined.



Synthesis, electochemical and optical properties

Keywords: Photocyclization / Nucleophilic substitution / UV/Vis spectroscopy / Luminescence / Nitrogen heterocycles / Fused ring systems

