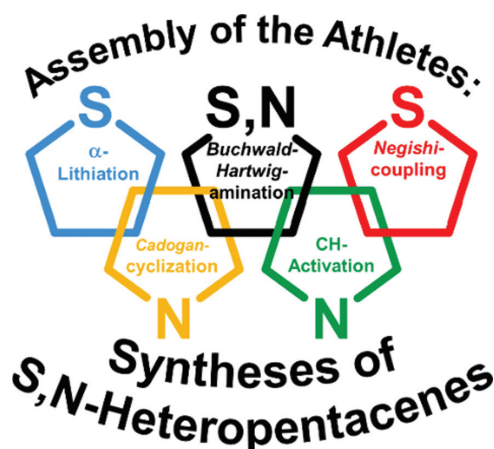


S,N-Heteropentacenes – Syntheses of Electron-Rich Anellated Pentacycles

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Dedicated to Prof. Dr. Peter Bäuerle on the occasion of his 65th birthday.



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Abstract This review summarizes syntheses of S,N-heteropentacenes, i.e. electron-rich sulfur and nitrogen-embedding pentacycles, and briefly highlights selected applications in molecular electronics. Depending on the annellation mode and the number of incorporated heteroatoms, electron density can be raised by increasing nitrogen incorporation and polarizability is manifested by the sulfur content. In comparison to triacene analogues, the conjugation pathways of S,N-heteropentacenes are increased and the favorable acene-typical crystallization behavior allows for diverse application in organic electronics. Furthermore, substitution patterns allow fine-tuning the electronic properties, extending the π -systems, and supplying structural elements for further application.

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Key words heteroacenes, cross-coupling, condensations, cyclizations, modular syntheses, optoelectronics, energy conversion, materials

1 Introduction

Over many years, organic heterocycles have attracted considerable interest as functional molecules in academia and industry. Besides numerous medicinal applications, as impressively emphasized by recent reports on antibiotic, anti-viral, or anti-cancer drugs,¹ they found increasing entry as functional molecular components in optoelectronics. Often heterocyclic structures ideally feature high polarizability and high propensity for charge separation, a prerequisite in organic photovoltaics (OPVs).² In addition, increased polarizability and favorable redox properties enable hole mobility, a crucial feature for application as semiconductive functional molecules in organic field effect transistors (OFETs)³ or organic light emitting diodes (OLEDs).⁴ Hole mobility relies on crystalline packing and morphology of the electron-rich molecular entities with short intermolecular distances.⁵ This calls for planar fused systems with improved crystallinity of folded structures.⁶ Sulfur-containing π -systems inherently gain electron density and substantial polarizability.⁷ Among these sulfur heterocycles, thiophenes and congeners are extensively explored due to their rich reactivity patterns and stability.⁸ The increase of electron density by sulfur atoms can be even enhanced by combination with nitrogen atoms, where lone pairs can more effectively overlap with orbitals in conjugated π -systems, thereby enhancing the delocalization.⁹ Therefore, integration of both heteroatoms increases both polarizability and electron density, making S,N-heterocyclic systems ideal candidates for applications in organic electronics. Many tricyclic S,N-heterocycles are reported in the literature and applications in OPV are well documented.¹⁰ While five-membered heterocycles such as

Biosketches



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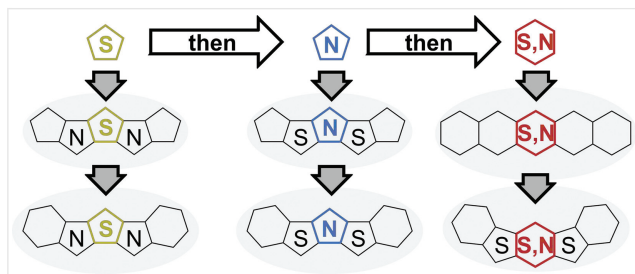
Thomas J. J. Müller was born in Würzburg, Germany, in 1964 and studied chemistry at Ludwig-Maximilians-Universität München (LMU) from 1984 to 1989. He obtained his diploma in 1989 and completed his PhD in 1992 with Prof. R. Gompper on novel cyanine systems as models for optical switches and molecular metals. After a post-doctoral stay with Prof. B. M. Trost at Stanford University, USA, in 1993 and 1994 working on ruthenium-catalyzed Alder-Ene reactions, he returned to

Germany. In 1994, as a Liebig scholar he began his independent research at Technical University Darmstadt, moved to LMU as a DFG scholar in 1997, to obtain his habilitation and was appointed to Privatdozent in 2000. From 2002 to 2006 he was an associate professor of organic chemistry at Ruprecht-Karls-Universität Heidelberg. Since 2006 he is a full professor and holds the chair of organic chemistry at Heinrich-Heine-Universität Düsseldorf. In 2016 he received a call to a chaired professor-

ship at Ruprecht-Karls-Universität Heidelberg, which he declined. Since 2019 he is the spokesman of the DFG-funded Research Training Group 2482 (Modulation of Intersystem Crossing - ModISC). His research interests encompass synthetic heterocyclic chemistry, functional chromophores, and the design of novel multi-component and domino reactions. He is an author of more than 290 journal articles and book chapters.

thiophenes and pyrroles and their congeners tend to crystallize easily, 1,4-thiazine-based structures typically adopt butterfly-like structures that can hamper efficient crystallization.¹¹ Tetra- and hexacyclic fused systems are more challenging synthetic targets and symmetry-based synthetic approaches are often difficult.¹² Higher homologues like octa- and decacenes were efficiently synthesized by Bäuerle and coworkers.¹³ For the synthesis of pentacyclic fused structures, symmetry-based approaches enable broader accessibility. While this synthesis-based reasoning also holds true for heptacyclic systems, synthetic effort has considerably increased even for highly symmetrical systems.¹⁴ Conceptually challenging remains minimization of the molecular size with simultaneously meeting optoelectronic requirements, such as excitation and emission within the visible spectrum at shortest possible conjugation length. Interestingly, pentacyclic fused systems present a good tradeoff between molecular size for crystallization, photophysical properties, and synthetic feasibility. They additionally possess comparably low molecular weights and open avenues for functionalization and fine-tuning of important physical parameters, such as crystallization, solubility, and electronic properties. In addition, syntheses can take advantage of the tunable reactivity of easily accessible building blocks such as thiophenes. For instance, regioselective α -lithiation opens a broad array of selective functionalization at 2-

position.⁸ Furthermore, by regioselective electrophilic bromination, the adjacent β -position can be addressed, opening all avenues for unsymmetrical functionalization and intermediates en route to pentacyclic systems. Ultimately, thiophenes as starting materials prove to be almost abundant, commercially available ideal building blocks. Otherwise, pyrroles and their scaffolds as starting materials are significantly more electron-rich, yet, syntheses, workups, and handlings might become complicated.¹⁵ Therefore, pyrroles are generally better formed in the final synthetic steps. Cadogan-type cyclizations of nitrobiaryls¹⁶ or transition-metal-catalyzed C–N-couplings of dibromides with amines have become general solutions.¹⁷ The latter approach is particularly attractive for generating substance libraries in a modular fashion. Starting from privileged building blocks (thiophenes and benzothiophenes) and versatile methodologies, a broad range of novel *S,N*-pentacyclic condensed systems became feasible. This review exclusively focuses on the syntheses of symmetrical pentacyclic fused *S,N*-topologies based upon the central cores: thiophene, pyrrole, and thiazine (Scheme 1). Therefore, the synthetic concepts are developed from bottom-up anellation starting from the central heterocycle (thiophenes) or leading to late-stage anellation furnishing the central heterocycle (pyrroles, thiazines). Some representative electronic properties are briefly presented and highlighted.



Scheme 1 Conceptual structure of this review based on the central heterocyclic cores thiophene, pyrrole, and thiazine, where various symmetrical pentacyclic fused *S,N*-topologies are accessible.

2 Thiophene-Centered *S,N*-Heteropentacenes

In the context of photonic or electronic molecular materials, fused *S*-heterocycles can be either five- or six-membered. Although five-membered rings in contrast to six-membered systems cause an angular kink, they are equally regarded as linear topologies (Figure 1). Therefore, dipyrrolo-fused and diindolo-fused thiophenes are considered.

2.1 Dipyrrolo-Fused Thiophenes

For dipyrrolo-fused thiophenes (DPTP) and their pentacenes, the electron density as well as the conjugation considerably increases in comparison to all-thieno-fused systems. The synthesis is feasible from thiophene (**1**) in five steps (Scheme 2). Starting with the synthesis of tetrabromothiophene (**2**) from thiophene and with in situ prepared thienylzinc chloride **3**, two required building blocks are obtained to give tetrabrominated terthiophene **4** upon Negishi cross-coupling. By cyclizing through Buchwald–Hartwig coupling with aniline (**5a**), the fused system **6a** is finally formed (Scheme 2).¹⁸ Employing various amines **5** allows a broad variation of the *N*-substituent pattern.

Most advantageously, terminal thiophene moieties can be easily functionalized by α -lithiation as well as electrophilic substitution reactions such as Vilsmeier–Haack formylation. Thus, difunctionalized (via **7**, see Scheme 3) and even unsymmetrically substituted structures (via **9**, see Scheme 4) are feasible. Employing this strategy in a symmetrical approach from aliphatic substrate **6b** gives dialdehyde **7**. Concluding Knoevenagel condensation furnishes the symmetrically

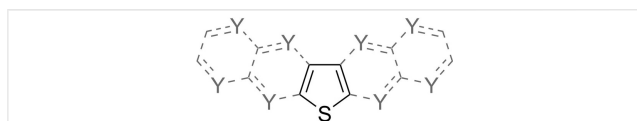
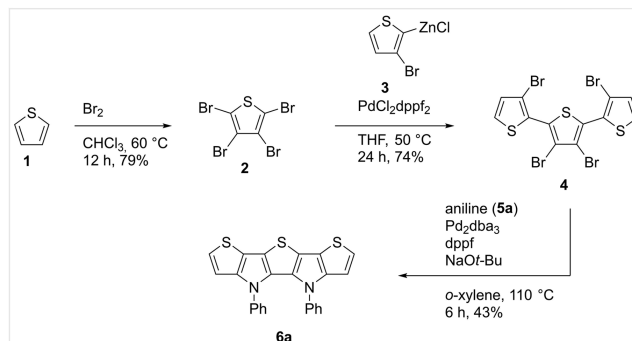


Figure 1 Doubly fused thiophenes.

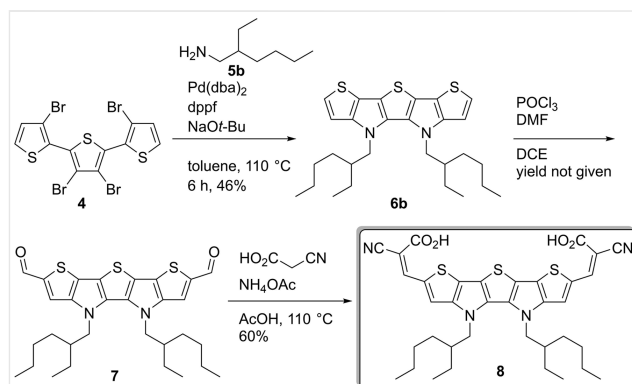


Scheme 2 Synthesis of a generic parent building block **6** for various dipyrrolo-fused thiophene compounds, depicted for the synthesis of **6a**.

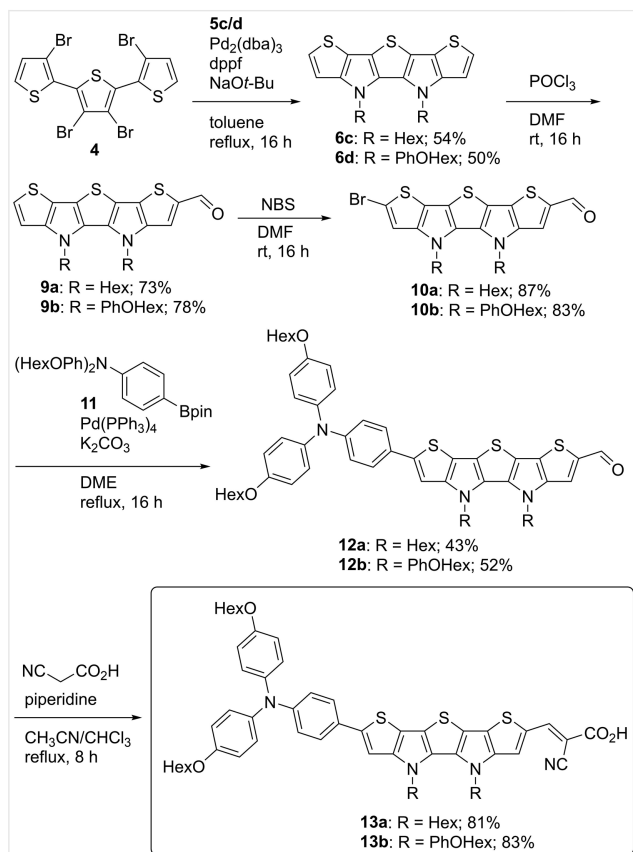
acceptor-substituted derivative **8** was successfully employed in DSSC (dye-sensitized solar cell) dyes (Scheme 3).¹⁹

Compound **8** features an overall incident photon-to-current efficiency (IPCE) of 5.01%, which is quite high for these relatively small molecules. The photocurrent production of this material amounts to $J_{SC} = 12.9 \text{ mA/cm}^2$ with an open-circuit voltage of $V_{OC} = 580 \text{ mV}$. By employing malononitrile as the condensation partner, Bäuerle and coworkers furthermore reported bulk-heterojunction type solar cell dyes with efficiencies between 4 and 6%. Interestingly, the solar cell efficiencies were influenced by the chain lengths of the aliphatic *N*-alkyl substituents with even numbered chain lengths exhibiting the best performances.²⁰

By a desymmetrization approach, efficiencies of this structure can be further enhanced (Scheme 4). Starting from the base structures **6** the unsymmetrical aldehydes **7** can be obtained by singular Vilsmeier–Haack formylation. Having only one side of the molecule **9** decorated, the other counterpart region can be addressed by electrophilic bromination with NBS to give **10**, which opens reactivity towards cross-coupling reactions. Exploiting this with strong donor fragments like **11** to give **12** and final



Scheme 3 Synthesis of an acceptor-substituted dipyrrolo-fused thiophene **8** by twofold Vilsmeier–Haack formylations followed by Knoevenagel condensation reactions.

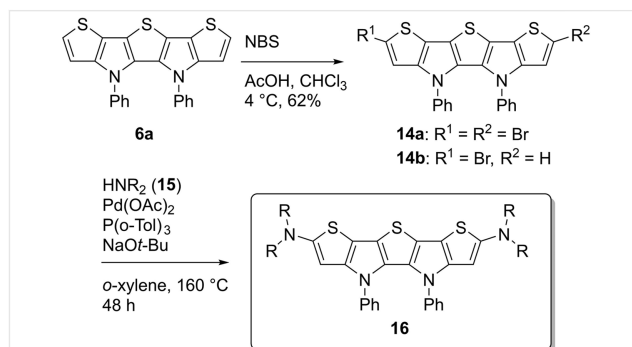


Scheme 4 Synthesis of the unsymmetrical counterparts **13a** and **13b** by single Vilsmeier–Haack formylation, followed by electrophilic bromination and subsequent Suzuki cross couplings and Knoevenagel condensations.

Knoevenagel condensation leads to **13** as target structures. Depending on the employed amine **5** in the cyclization reaction towards **6**, two differently substituted structures **13a** and **13b** were obtained in the literature. Interestingly, the nature of the pyrrole substituent exerts a significant effect on the dye's performance. Aromatic substituents are apparently more favorable than purely aliphatic side chains. The *p*-hexyloxyphenyl-substituted donor–acceptor type DSSC dye **13b** (Scheme 4) reaches an IPCE of 6.6% with $J_{\text{SC}} = 11.6 \text{ mA/cm}^2$ and $V_{\text{OC}} = 800 \text{ mV}$. The hexyl-substituted dye **13a**, however, does not exceed 4.4% with $J_{\text{SC}} = 8.6 \text{ mA/cm}^2$ and $V_{\text{OC}} = 710 \text{ mV}$.²¹

Decoration of compound **6a** with amino donor substituents via the brominated derivative **14** by twofold Buchwald–Hartwig coupling with secondary amines **15** furnishes electron-enriched systems **16** that can be applied as a hole-transport material in electroluminescent devices like OLED (Scheme 5).

The synthesis is eased by the reactivity of the terminal thiophene moieties of **6** towards even mild reagents like NBS to afford **14**.



Scheme 5 Electronically enriched derivatives **16** synthesized by electrophilic bromination of **6a** and Buchwald–Hartwig amination employing various arylamines **15**.

A broad substituent pattern has been reported in the patent literature of this motif with phenyl, naphthyl, and other aromatic groups.¹⁸

Molecules **16** exceed current efficiencies η_{L} of 20–30 cd/A for some red-light emitting dyes with luminances L_{V} of 3000–3500 cd/m² for representative blue-light emitters. Four generic syntheses of both symmetrical and unsymmetrical substances are reported. The substitution patterns and reactions yields of the amination step are depicted in Figure 2. More distinctly substituted compounds are described as applied in devices however, demonstrating the diversity of the reactions.¹⁸

Furthermore, DPTP can be employed as useful building blocks in synthetic strategies towards higher ladder-type heteroacenes as reported by Bäuerle (Scheme 6).²² The selectivity of reactions including lithiation at any step could here be addressed by silylation of one of the two opposite facing α -thienyl regions. By single deprotonation of **17** and nucleophilic substitution with triisopropylsilylic chloride, monosilylated DPTP **18** was feasible. Bromination with NBS on the remaining thienyl moiety leads to α -brominated **19**, which is employed in a “halogen dance” rearrangement reaction²³ to warrant the correct regioisomers to be formed in the following sequence of reactions. De novo α -deprotonation of **20** and oxidative homo-coupling with copper(II)chloride, followed by a Pd-catalyzed C–S-coupling with potassium thioacetate, forms a focal thieno-ring with two heteropentaceno-anellands. Final fluoride-mediated desilylation furnishes *S,N*-heteroundecacene **21**. Its pronounced absorption with extinction coefficient of $\epsilon = 98000 \text{ L mol}^{-1} \text{ cm}^{-1}$ combined with a red-shifted

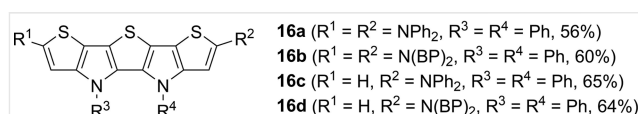
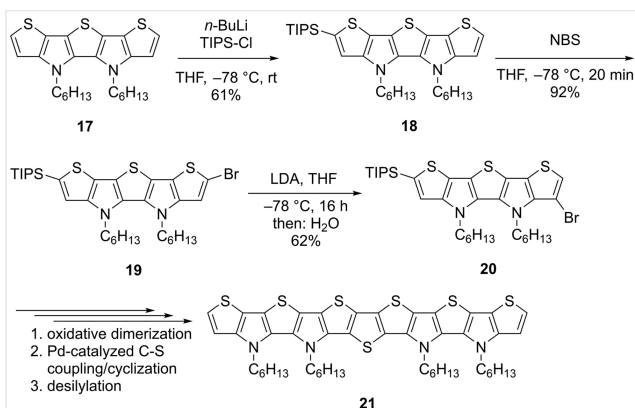


Figure 2 Representative bis(thienopyrrolo)thiophenes **16** for OLED applications (BP = [1,1'-biphenyl]-4-yl).

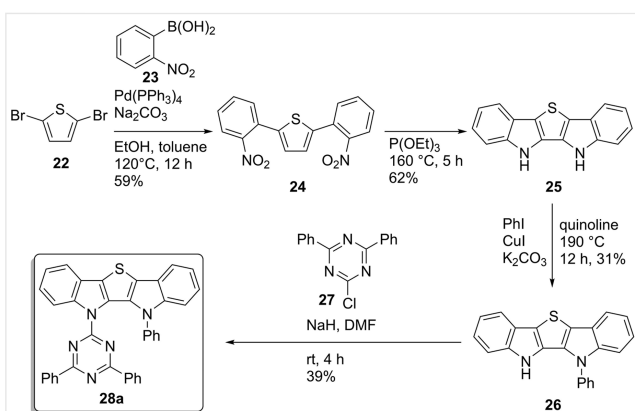


Scheme 6 Synthesis of higher ladder-type heteroacenes by utilization of DTP-type heteropentacene **20** as the functional building block.

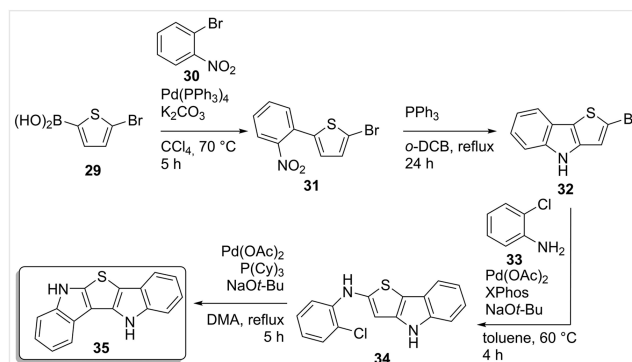
absorption at $\lambda_{\text{max,abs}} = 453$ nm and a HOMO energy level of as high as $E_{\text{HOMO}} = -4.84$ eV presents *S,N*-heteroundecacene **21** and its congeners as very promising candidates for optoelectronic applications.²²

2.2 Diindolo-Fused Thiophenes

Compared to their thieno-fused congeners bis[1]benzo-thieno-thiophenes, indolo-fused systems feature higher electron density, similarly to thienopyrrolothiophenes **6** (Scheme 5), and open application in electroluminescent devices, and here some derivatives have already been patented.²⁴ Diindolothienophenes can be designed as three regioisomers, depending on the mode of fusing. Here, only *anti,anti*- or *syn,anti*-derivatives are considered (Schemes 7 and 8). A synthetic approach to this class of compounds is achieved with relatively simple reactants. For instance,



Scheme 7 Synthesis of pivotal diindolothienophene **25** from 2,5-dibromothiophene **22** and subsequent cyclization, followed by Ullmann-type arylation and S_NAr furnishing an unsymmetrically bis(*N*-arylated) diindolothienophene **28a**.



Scheme 8 Synthesis of sickle-shaped NH-diindolothienophene **35** by Suzuki coupling, Cadogan-type cyclization, Buchwald–Hartwig amination, and CH-activation reaction.

dibromothiophene **22** and 2-nitrophenylboronic acid (**23**) react by a Suzuki-coupling and dinitro product **24** is then transformed in a Cadogan-type cyclization¹⁶ reaction to give the pivotal *anti,anti*-diindolothienophene **25**. Subsequent copper-catalyzed Ullmann-type couplings of compound **25** form the *N*-phenyl derivative **26**, which is transformed by nucleophilic aromatic substitution with chlorotriazine **27** to finally furnish product **28a** (Scheme 7). This and related compounds have been published in the patent literature as red-light-emitting dyes for use in OLED devices. Likewise five novel compounds **28** were synthesized according to this route and their OLED performances were reported (Figure 3).²⁴

Not only linear *anti,anti*-fused systems based on **28**, but also sickle-shaped *syn,anti*-derivatives like **35** (Scheme 8) can be employed as OLED emitters. Likewise, starting from Suzuki-coupling of thiophene **29** and *o*-nitroarene **30** to form **31**, Cadogan-type cyclization gives thienoindeole **32**, which is then coupled with aniline **33** under Buchwald conditions (Scheme 8). Finally, intramolecular CH-activation of intermediate **34** forms the pivotal structure **35**. Buchwald–Hartwig amination of compound **35** leads to an immense variety of more than 30 sickle-shaped derivatives.²⁵ Performance measurements with these compounds at a luminance of 1000 cd/m² show operating voltages of 5.3–5.6 V with efficiencies of 13–22 cd/A.

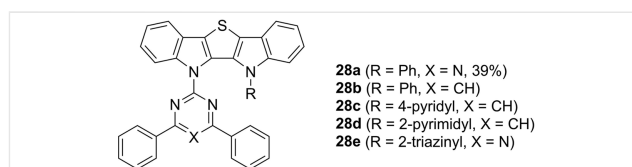


Figure 3 Synthetic examples of diindolothienophenes **28**.

3 Pyrrole-Centered *S,N*-Heteropentacenes

Azoles possess a higher electron density and, thus, lower redox potentials than their sulfur analogues. It is not surprising that nitrogen-containing heterocycles have therefore received particular attention in technical applications. The most dominant structure with this respect is pyrrole (Figure 4) with only few publications on pyrazines, however, none of them as *S,N*-heteropentacenes. In this context, dithieno-fused and bis[1]benzothieno-fused pyrroles are considered.

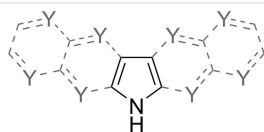


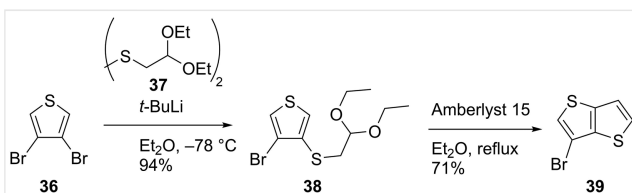
Figure 4 Doubly fused pyrroles.

3.1 Dithieno-Fused Pyrroles

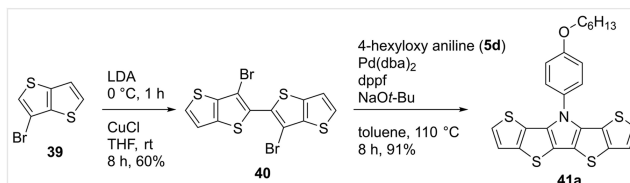
Multiple thieno-fused pyrroles have been reported and applications range from OLED emitters to DSSC dyes, or, if incorporated into polymer chains, as organic semiconductors. Syntheses mostly aim to assemble the basic structure, followed by subsequent functionalization, by either bromination or lithiation reactions. Unlike for thiophene congeners, the central pyrrole unit does not appear as a main building block for annellation. A major reason is the sensitivity of pyrroles against oxidation. Therefore, the central pyrrole unit is rather formed in the terminal step, exploiting the relative electroneutrality and low reactivity as well as the good functionalizability of thiophene-based building blocks. Syntheses thus start from brominated thienothiophene **39**, which can be obtained from dibromothiophene **36** by monolithiation and reaction with an acetal-decorated disulfide **37** to form thienyl alkylacetalsulfide **38** (Scheme 9). Under acidic conditions, this intermediate forms thienothiophene **39** by cyclizing condensation using the acidic polymeric catalyst amberlyst 15®.

Compound **39** is then oxidatively dimerized²⁶ to intermediate **40** prior to conclusion by cyclizing Buchwald–Hartwig amination to form **41a** (Scheme 10).^{26,27}

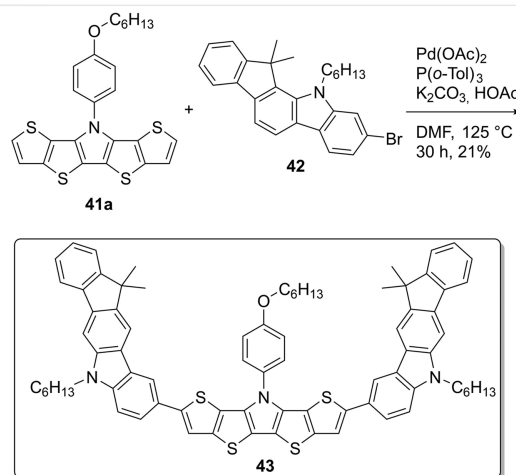
Compound **41a** can be further transformed via Pd-catalyzed CH-activation at the α -position by coupling an



Scheme 9 Two-step synthesis of 3-bromothiopheno[3,2-*b*]thiophene (**39**) starting from 3,4-dibromothiophene (**36**).



Scheme 10 Synthesis of the generic building block **41a** by oxidative dimerization of **39** and ring-closing Buchwald–Hartwig amination of **40**.

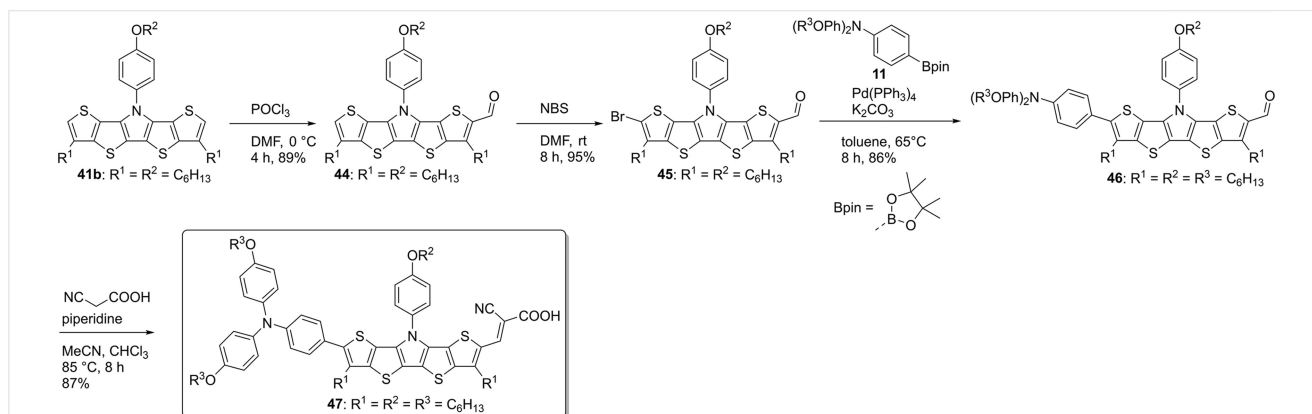


Scheme 11 Synthesis of indenocarbazole-substituted derivative **43** by CH-activation.

aryl bromide, e.g., **42**, to open entry to large, expanded π -systems (Scheme 11). In 2017 scientists of the Huaiyin Institute of Technology patented a tetrathienopyrrole-based hole-transport material **43** for use in perovskite solar cells, decorated with expanded carbazole substituents.²⁸ This system reaches a $V_{OC} = 1.118$ V with a current production of $J_{SC} = 23.9$ mA/cm². The overall conversion efficiency was determined to be 21%.

Besides perovskite-based solar cells, DSSC dyes were studied as well. The general donor–acceptor architectures can be either symmetrical or unsymmetrical. For instance, an unsymmetrical approach furnishes donor–acceptor dye **47** (Scheme 12).^{27a} Starting from bis-hexyl-substituted tetrathienopyrrole **41b**, formyl derivative **44** was obtained by single Vilsmeier formylation. After α -bromination, Suzuki coupling with the triphenylamine donor boronate **11** forms compound **46**. The acceptor moiety and required linker for binding to the anode material is obtained by Knoevenagel condensation of the formyl group with cyanoacetic acid, leading to compound **47**.

The solar cell system with dye **47** ($R_1 = R_2 = R_3 = n$ -hex) reaches an open circuit voltage of $V_{OC} = 826$ mV, with a short-circuit current J_{SC} of 16.5 mA/cm². The filling factor accounts to 0.69, which gives an IPCE η_L of 9.4%.^{27a}



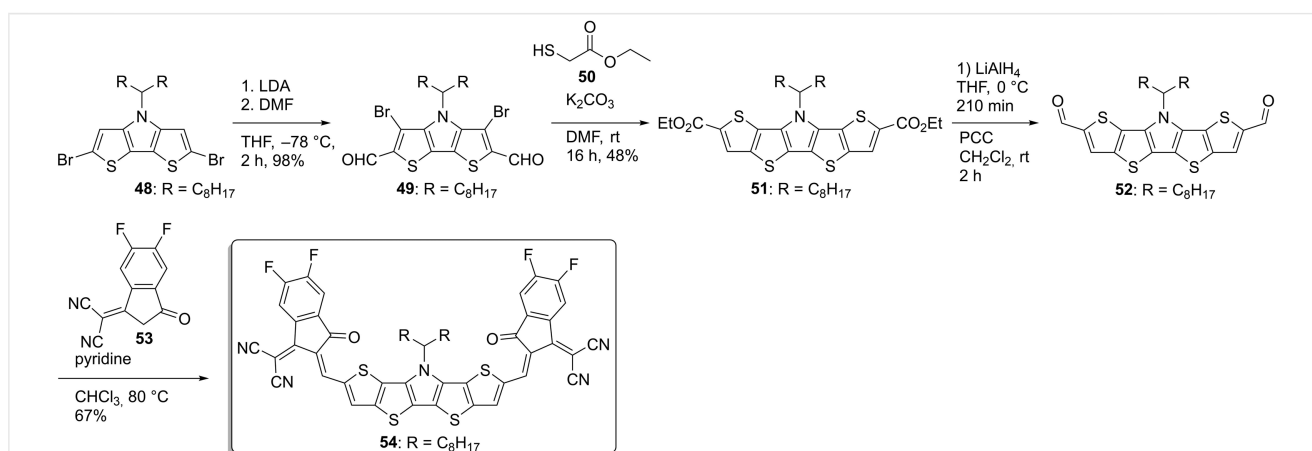
Scheme 12 Synthesis of the unsymmetrical solar cell dye **47** by a two-step Vilsmeier–Haack formylation–electrophilic bromination sequence concluded by cross-coupling and Knoevenagel condensation.

A symmetrical DSSC dye based on tetrathienopyrrole was published in 2019 by Chen et al., comprising an indenonylidene-acceptor fragment **53** (Scheme 13).²⁹

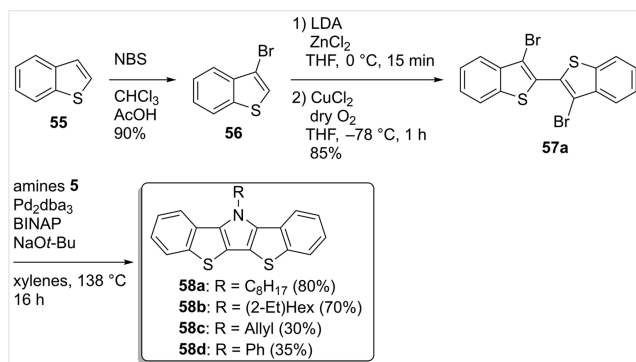
The synthetic approach to the formulated intermediate **52** was considerably different from the aforementioned process. Here, a dibrominated dithienopyrrole **48** was first isomerized, then formylated to give dialdehyde **49**. This was then employed in a nucleophilic aromatic substitution using ethyl 2-mercaptoacetate (**50**), which in situ cyclized to form the pentacene **51**. After that, correcting the oxidation state of the substituent is necessary to obtain the dialdehyde **52**. Condensation with the acceptor component **53** then leads to DSSC dye **54**. The compound was not explicitly examined in DSSC measurements, however, with another dye as a coadditive.

3.2 Bis[1]benzothieno-Fused Pyrrole

Analogously to indolo-fused thiophenes shown in Section 2.2, also pyrroles have been fused with two heteroindeno systems, i.e. benzothienopyrroles. The resulting bis[1]benzothienopyrroles have found various applications in organic electronics. However, synthetic approaches to these two compound classes are orthogonal. While the favored route for most bis(benzothieno)pyrroles is the formation of the central pyrrole ring in the last step of the synthesis (Scheme 14), diindolothiophenes are rather established from an existing thiophene moiety (Scheme 7). Rasmussen's group reported on the synthesis and properties of a series of bis(benzothieno)pyrroles **58** with varying *N*-substituents from aliphatic to aromatic and also allylic moieties (Scheme 14).³⁰ The route resembles the synthesis of bis(benzothieno)thiophenes,³¹ and



Scheme 13 Synthetic pathway to DSSC dye **54** from dithienopyrrole **48** via dialdehyde **52** and concluding Knoevenagel condensation.



Scheme 14 Synthesis of bis[1]benzothienopyrroles **58** by concluding cyclizing two-fold Buchwald–Hartwig amination of benzothiophene dimer **57a**.

also starts from benzo[b]thiophene (**55**), which is brominated using NBS towards **56** and then oxidatively dimerized to give **57a**, but from that instead of lithiation and nucleophilic S-cyclization rather Buchwald–Hartwig amination proceeds to form the central pyrrole moiety in the products **58**.

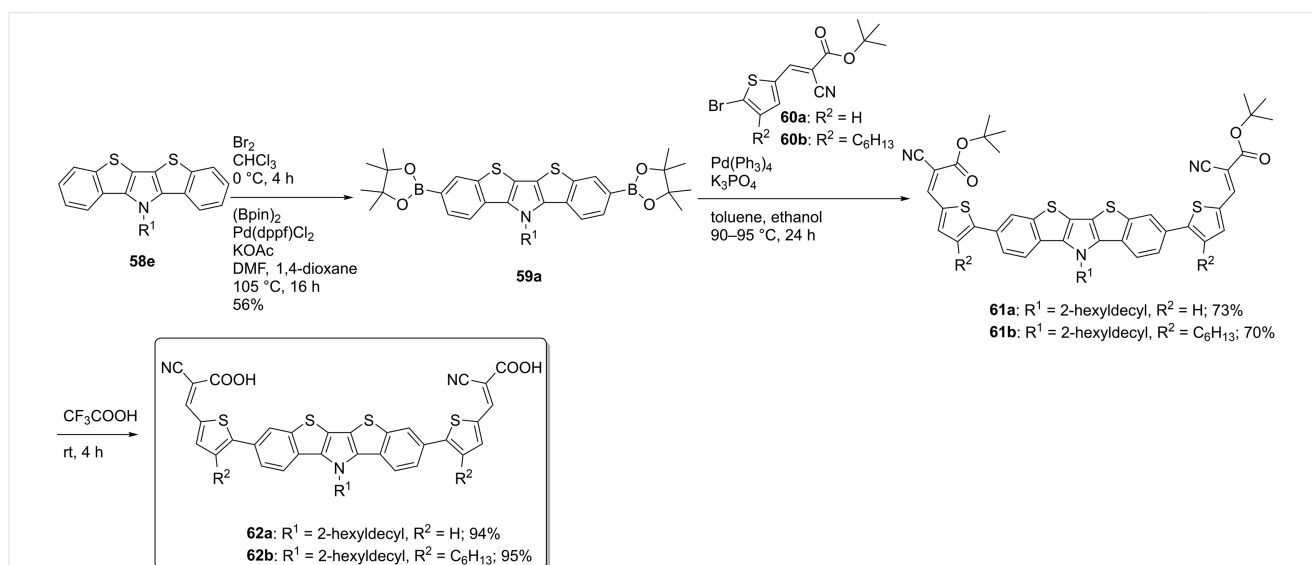
Rasmussen examined these products and a Korean research group proceeded with the functionalized derivative **59a**³² and synthesized donor–acceptor dyes for DSSC application (Scheme 15).³³ Compound **59a** was obtained by electrophilic bromination of aliphatically substituted precursor **58e**, with a subsequent Miyaura borylation to give the diboronic acid **59a**. The acceptor moiety was introduced by Suzuki coupling with acceptor-substituted thienylbromides **60**.

The intermediate diboronic acid **59** also acts as a copolymer building block for low-bandgap conjugated polymers as reported by Yoon et al. in 2015.³² Using the

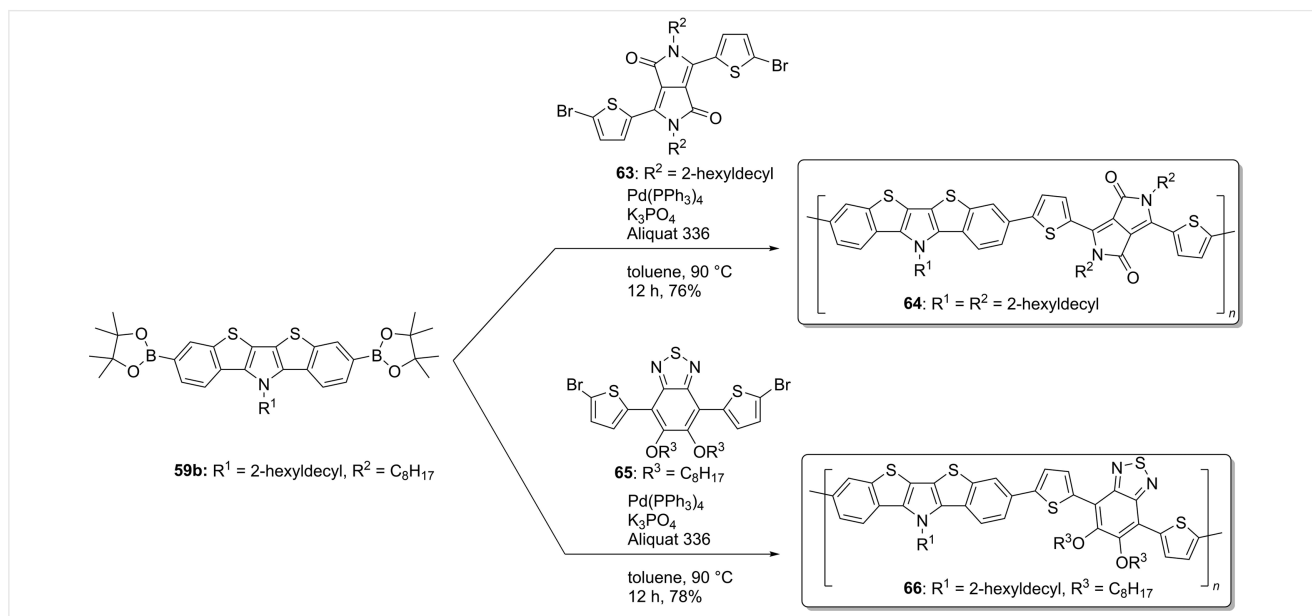
diboronic acid **59b**, which bears long chiral aliphatic chains to increase solubility, multiple polymeric structures **64** and **66** were readily feasible. Polymerization proceeded via Suzuki coupling using the electron-poor dibromo arene linker units **63** and **65** (Scheme 16).

The polymers with molecular weights of up to 74800 (**64**) and 50300 (**66**) were examined in bulk-heterojunction-type solar cells, where they display significantly enhanced properties compared to their triacene analogues. For instance, polymer **64** exhibits an open circuit voltage V_{OC} of 0.66 V with a short-circuit current J_{SC} of 15.8 mA/cm^2 amounting to an efficiency η_{L} of 6.8%. The dithienopyrrole as a direct triacene-based analogue only features an open-circuit voltage V_{OC} of 0.38 V, with $J_{\text{SC}} = 14.9 \text{ mA}/\text{cm}^2$, and an overall IPCE η_{L} of only 2.7%. As often seen, extension of the π -conjugation by benzannellation vastly improves the systems' performance.³²

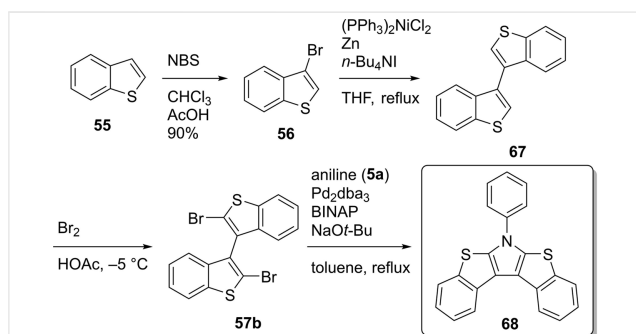
By 3,3'-ligation of the two benzothiophene moieties, the arch-typed *syn,syn*-bis(benzothieno)pyrroles are formed. Their syntheses were reported by Mu et al. in 2018 (Scheme 17). Starting from benzo[b]thiophene (**55**) after electrophilic bromination towards **56** using NBS a Nickel catalyzed reductive homo-coupling to form 3,3'-bis(benzothieryl) **67** was utilized. The second electrophilic bromination furnished the starting material for the concluding cyclizing Buchwald–Hartwig amination to give **68**. Interestingly, transitioning from linear (compound **59**, see Scheme 14) to arch-shaped *syn,syn*-derivatives **68**, especially, the *N*-aryl-substituted molecules exhibit a highly ordered crystal packing in perfectly parallel alignments. In particular, for OFET applications, this morphology is a key prerequisite. Unsurprisingly, arch-shaped structures featuring a very favorable crystallization behavior with a hole mobility μ_{h} of



Scheme 15 Modular approach to bis[1]benzothienopyrrole-based donor–acceptor systems **62** by electrophilic bromination, Miyaura borylation, and Suzuki coupling followed by acidic deprotection.



Scheme 16 Synthesis of polymeric donor–acceptor dyes **64** and **66** for use in solar cell application.



Scheme 17 Synthesis of arch-shaped bis[1]benzothienopyrroles **68**.

0.037 cm²/Vs can greatly exceed far less organized crystallizing linear structures with μ_h of only 1.310^{−6} cm²/Vs.³⁴

4 Fused 1,4-Thiazines

As *S,N*-heterocycles, only 1,4-thiazines (Figure 5) are considered in this review article since 1,2-thiazines do not generate linearly fused systems. Also, higher homologous systems, such as thiazepines or thiazocines, are not discussed here. Therefore, in this context dinaphtho-fused and bis[1]benzothieno-fused 1,4-thiazines are considered.

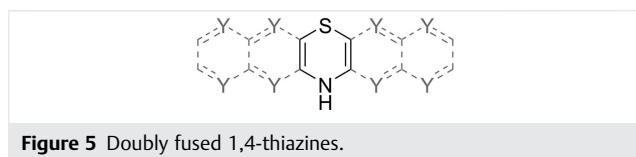
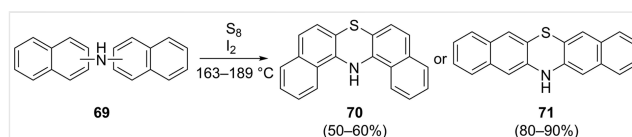


Figure 5 Doubly fused 1,4-thiazines.

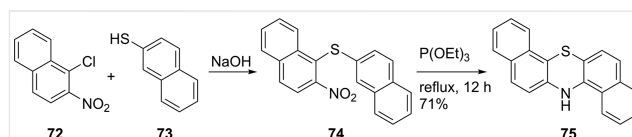


Scheme 18 Syntheses of dinaphthothiazines **70** and **71** by Bernthsen thiation.

4.1 Dinaphtho-Fused 1,4-Thiazines

Some scattered examples of naphtho-fused thiazines are reported in the literature. Syntheses date back to the 1910s (Scheme 18)³⁵; however, recent publications only appeared in the patent literature from 2016 (Scheme 19).³⁶ Apparently, this compound class experiences a comeback. First syntheses by Knoevenagel in 1914 started from dinaphthylamines **69** and utilized Bernthsen thiation to form fused thiazines **70** or **71** in dependence of the substrate, utilizing significantly high temperatures. Such harsh conditions are a challenge for the synthesis of substituted derivatives.

Contemporary syntheses utilize less forceful reactions conditions, such as Cadogan-type cyclization leading to dibenzo[*a,h*]pheno-thiazine **75** (Scheme 19). Starting



Scheme 19 Synthesis of dinaphthothiazine **75** by Cadogan-type cyclization.

from 1-chloro-2-nitronaphthalene (**72**) and naphthalene-2-thiole (**73**), intermediate **74** is formed by nucleophilic aromatic substitution.³⁷ Cadogan cyclization with triethyl phosphite gives dinaphthothiazine **75** in good yield.

Using Buchwald–Hartwig amination, several arylated dibenzo[*a,h*]phenothiazines **76** can be generated that are employed as an emissive layer in OLED devices with good device performance.³⁶ Selected examples of reported compounds **76** showing a wide range of products are depicted in Figure 6.

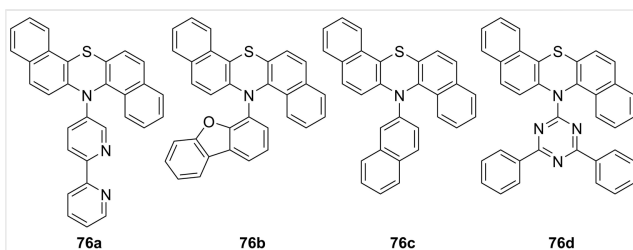


Figure 6 Synthetic examples of dibenzo[*a,h*]phenothiazines **76**.

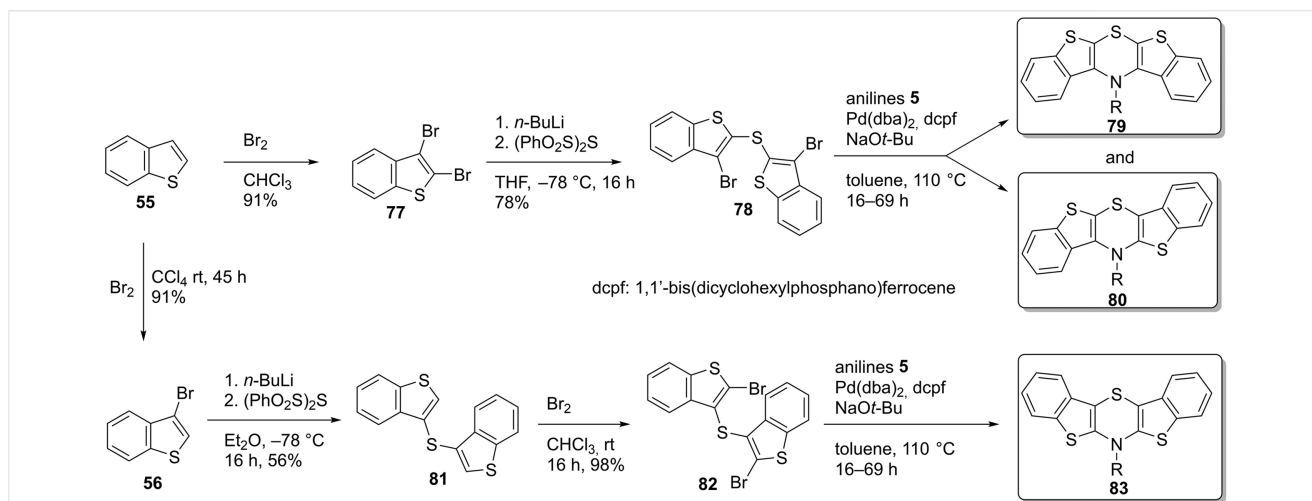
4.2 Bis[1]benzothieno-Fused 1,4-Thiazines

As an evolutionary heir of phenothiazines and dithienothiazines, di(benzothieno)-fused thiazines were first reported by Schneeweis et al. in 2018.^{11c} These electron-rich fused systems are synthesized starting from benzo[*b*]thiophene (**55**) via bromination to give dibromobenzo[*b*]thiophene **77** and thioetherification to form **78**, which is finally employed in a twofold Buchwald–Hartwig coupling to form the ring-closed *syn,syn*-bis(benzothieno)thiazine (BBTT) **79** (Scheme 20). Interestingly, depending on the conditions, not only the symmetrical *syn,syn*-BBTT **79** is

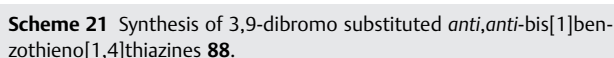
formed, but also the unsymmetrical *syn,anti*-BBTT **80** is formed. In a similar fashion, the symmetrical *anti,anti*-BBTT **83** can be generated. Here, the thioether formation takes place on C3 of the bromobenzothiophene **56** with subsequent bromination at C2 to form substrate **82**. Finally, twofold cyclizing Buchwald–Hartwig coupling furnishes *anti,anti*-BBTT **83**.^{11c}

Unexpectedly, compounds **83** are essentially planarized. Usually, fused 1,4-thiazines are neither planar in solution nor in the solid state, but exhibit angled bent, butterfly-like structures. This stereoelectronic feature is caused by the formal antiaromaticity of the planar 8 π -electron system. Therefore, puckering from coplanarity into a nonaromatic, boat-conformation-like butterfly structure circumvents the antiaromatic energetic bias. For *anti,anti*-BBTTs **83**, however, the steric bias of the *N*-substituent obviously overrides the antiaromatic bias, assisted by delocalization of the thiazine π -electrons into the benzo extensions. Furthermore, planarized *anti,anti*-BBTTs **83** exhibit some additional significant electronic deviations from their butterfly counterparts. While *syn,syn*-BBTTs **79** are nonluminescent in solution and in the solid state, only weak emission can be observed. However, a significant increase of emission is detected for partially planarized *anti,anti*-derivatives **83**. Their longest wavelength absorption bands are bathochromically shifted against **79** and **80** by about 8500 cm⁻¹.

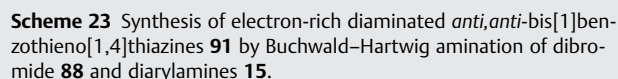
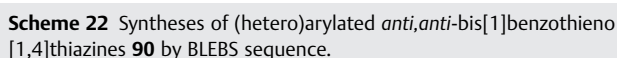
By introducing substituents on the benzo[*b*]thiophene structure at the outset of the synthesis of BBTT, substituted derivatives are feasible, which are not accessible by functionalization of the parent system. For example, bromination neither proceeded with bromine nor with other electrophilic bromination agents due to oxidation to stable radical cations instead. For the brominated structure **88**, the synthetic route starts with bromination of benzo[*b*]



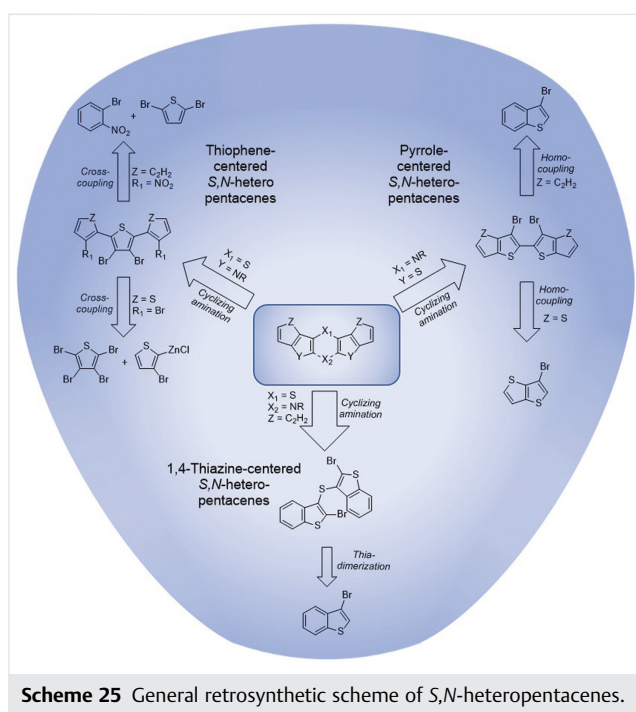
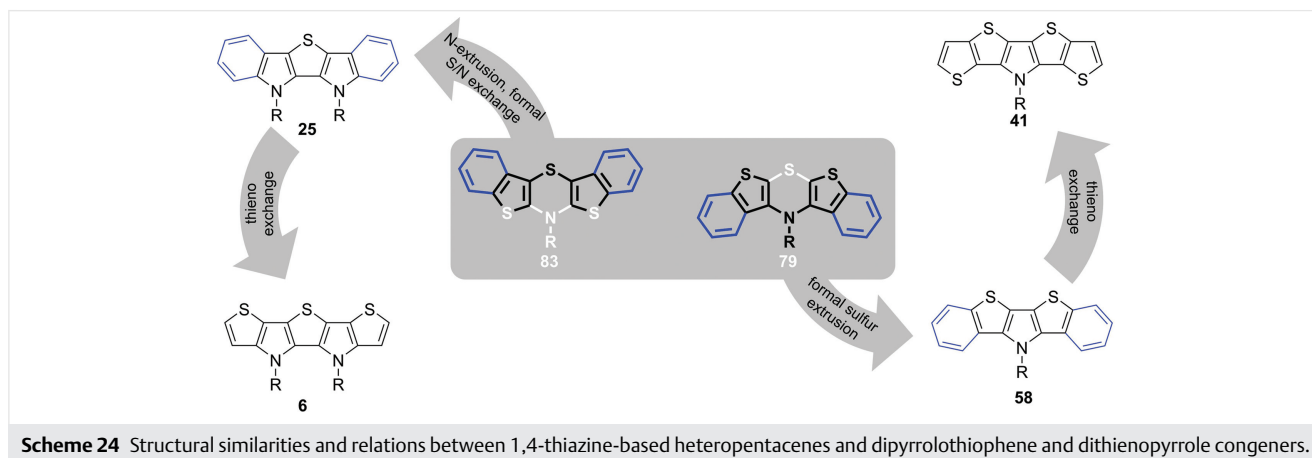
Scheme 20 Synthetic pathways to the three isomeric bis[1]benzothieno[1,4]thiazines **79**, **80**, and **83** utilizing cyclizing Buchwald–Hartwig coupling as a key step.



Taking into account the structural similarity of this class to those reported in Sections 2.1, 2.2, 3.1, or 3.2, *anti,anti-*



Formal ring contraction by sulfur extrusion directly correlates *syn,syn*-bis[1]benzothienothiazines **75** (Scheme 24, right path) to bis[1]benzothienopyrroles **59**, which has found application as solar cell dyes (Scheme 15). Further thieno exchange leads to dithienothienopyrroles **41**, again featuring wide applicability in DSSC or perovskite-based solar cell devices. Likewise, formally *anti,anti*-bis[1]benzothieno[1,4]thiazines **83** (Scheme 24, left path) can by formal N-extrusion be traced back to bis[1]benzothienothiophenes as all-S heteropentacenes (not shown). However, *N*-analogous diindolothiophenes **25** through *S/N*-exchange and their ring-contracted congeners dithienopyrrolothiophenes **6** are *S,N*-heteropentacenes and find application in OLED devices (Scheme 5) or solar cells (Scheme 4).



side reactions, and their stability makes them well-to-handle materials. Another factor advocating for thiophenes as building blocks also lies within their well addressable reactivity. Halogens, as precursors for cross-coupling reactions but also for bromo–lithium-exchange methodologies, help in building up fused systems as substrates for final cyclizing Buchwald–Hartwig couplings to form pyrrole units. In addition, α -lithiation of thiophenes opens avenues to beneficial side-chain modification, e.g. in OPV dye compounds. More challenging with this respect are pyrroles, which easily tend to oxidize, especially when halogenated. Finally, also fused 1,4-thiazines, formed by (5 + 1)-Buchwald–Hartwig cyclizations from bromo-

benzothiophenes, provide access to a quite novel class of particularly electron-rich *S,N*-heteropentacenes, some with considerable antiaromatic character with concomitant high stability.

In summary, as a consequence of their concise syntheses, tunability of the molecular electronic properties as well as solid-state morphology, ranging from amorphous to highly ordered crystallinity, *S,N*-heteropentacenes are promising electronic molecular building blocks for functional organic materials in the highly vibrant, rapidly developing field of molecular electronics and photonics. Novel structures based on these scaffolds are literally waiting to be unraveled, disclosed, and conceived in the near future.

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