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Benzo[*c*][1,2,5]thiadiazole doubly fused with thieno[2′,3′:4,5]thieno[3,2-*b*]pyrroles as a key building block for non-fullerene acceptors of Y6 series

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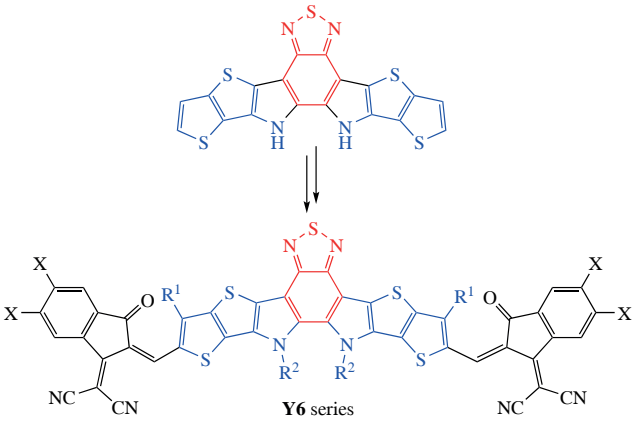
Organic solar cells have attracted much attention nowadays due to their great advantages such as lightweight, mechanical flexibility, semitransparency, and indoor applicability as next generation renewable energy devices. The most promising types of organic solar cells at the moment are cells with a bulk heterojunction, in which the key components are non-fullerene acceptors. The title building block, more strictly named as 12,13-dihydro[1,2,5]thiadiazolo[3,4-*e*]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-*g*]thieno[2′,3′:4,5]thieno[3,2-*b*]indole, is most commonly used in the design of non-fullerene acceptors in organic bulk heterojunction solar cells. This review presents data on the synthesis of this polycycle and its transformations into organic functional materials including components of highly efficient solar cells.



Keywords: 12,13-dihydro[1,2,5]thiadiazolo[3,4-*e*]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-*g*]thieno[2′,3′:4,5]thieno[3,2-*b*]indole, benzo[*c*][1,2,5]thiadiazoles, thieno[2′,3′:4,5]thieno[3,2-*b*]pyrroles, (inden-1-ylidene)malononitriles, chemical reactivity, heterocycles, heterocyclic synthesis, non-fullerene acceptors, organic bulk heterojunction solar cells.

Introduction

Among alternative energy sources, solar energy is the most promising, as it has inexhaustible (at least for the next billion years) potential and maximum power. Silicon thin-film elements are leaders in the world market: their share reached about 80% of the sales volume of solar cells. However, organic solar cells, which began to be obtained in the mid-1980s, have a number of advantages over silicon batteries.[1–3] The production of organic photovoltaic devices is cheaper and much simpler. The ability of organic photovoltaic materials to form nanocomposites allows achieving the required morphology of the active layer and greater adaptability to the shape and dimensions of the photovoltaic device. No less important is the relative ease with which the structure and chemical composition of organic compounds can be changed, which allows for targeted optimization of their properties depending on the specific application of the final material. One of the most efficient technologies of organic solar cells is bulk heterojunction cells, in which donor and acceptor fragments are located in the same photoactive layer. As a rule, polymeric materials act as donors, and at an early stage, fullerene derivatives acted as acceptors. Recently, the development of replacing fullerene and its derivatives with high-performance non-fullerene acceptors (NFA) has dramatically increased the power conversion efficiency of a single cell by more than 19%.[4–6]

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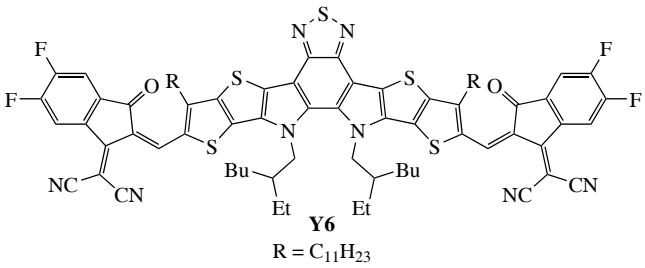


Y6

R = $C_{11}H_{23}$

Figure 1 The structure of non-fullerene acceptor **Y6**.

This success was achieved in 2019 by obtaining one of the key compounds, 2,2′-{(2*Z*,2′*Z*)-[(12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro[1,2,5]thiadiazolo[3,4-*e*]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-*g*]thieno[2′,3′:4,5]thieno[3,2-*b*]indole-2,10-diyl)bis(methaneylylidene)]bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene)}dimalononitrile (**Y6**), which had such unique properties as dominant face-on orientation, high electron mobility, and low energy loss with high electroluminescent quantum efficiency (Figure 1).[7] The **Y6** molecule has an acceptor–donor–acceptor (A–D–A) structure in which moiety of benzo[*c*][1,2,5]thiadiazole doubly fused with thieno[2′,3′:4,5]thieno[3,2-*b*]pyrroles (namely, 12,13-dihydro[1,2,5]thiadiazolo[3,4-*e*]thieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-*g*]thieno[2′,3′:4,5]thieno[3,2-*b*]indole, DTPI) acts as the donor component, and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile parts serve as electron-withdrawing end-fragments; the alkyl substituents in the core are solubilizing groups. The physical parameters of solar cells have been discussed in detail in a number of reviews,[8–11] while there are no reviews in the literature devoted to the synthetic capabilities of the DTPI fragment. This review should fill this gap.

Synthesis of DTPI core

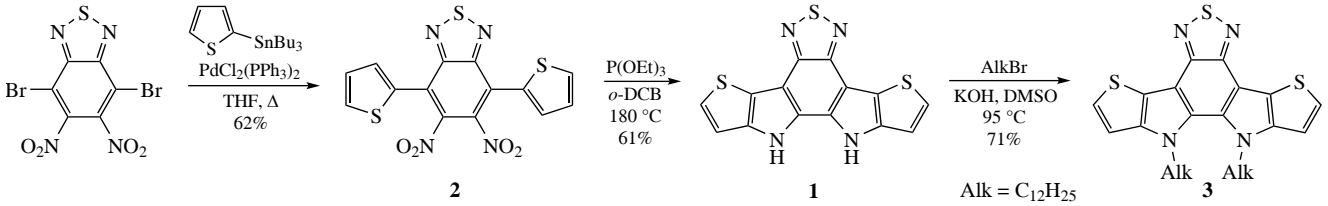
The strategy for the synthesis of 10,11-dihydro[1,2,5]thiadiazolo[3,4-*e*]thieno[2′,3′:4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*]indole **1** starting from 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole was first proposed by Hsu in 2011.[12] It was Stille-coupled with tributyl(thiophen-2-yl)stannane to yield 5,6-dinitro-4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **2**. Its double intramolecular Cadogan reductive cyclization[13,14] in the presence of $P(OEt)_3$ successfully furnished the fused polycycle **1** in 61% yield whose final alkylation gave dialkyl derivative **3** (Scheme 1). Later Nakamura showed that PPh_3 could be successfully used in the Cadogan cyclization step affording polycycle **1** in near to quantitative yield (97%).[15]

This method was successfully applied to the synthesis of DTPI **4** and its 3,9-dialkyl derivatives. Tributyl(thieno[3,2-*b*]thiophen-2-yl)stannane[16,17] and its 5-alkyl derivatives were used as the thiophene arylating agents, and $P(OEt)_3$[18–21] or PPh_3[22–26] were used as the cyclizing agents (Scheme 2). Final alkylation at the nitrogen atom of the pyrrole ring completes the formation of the DTPI core **4**.

Reactions of DTPI at positions 2 and 8

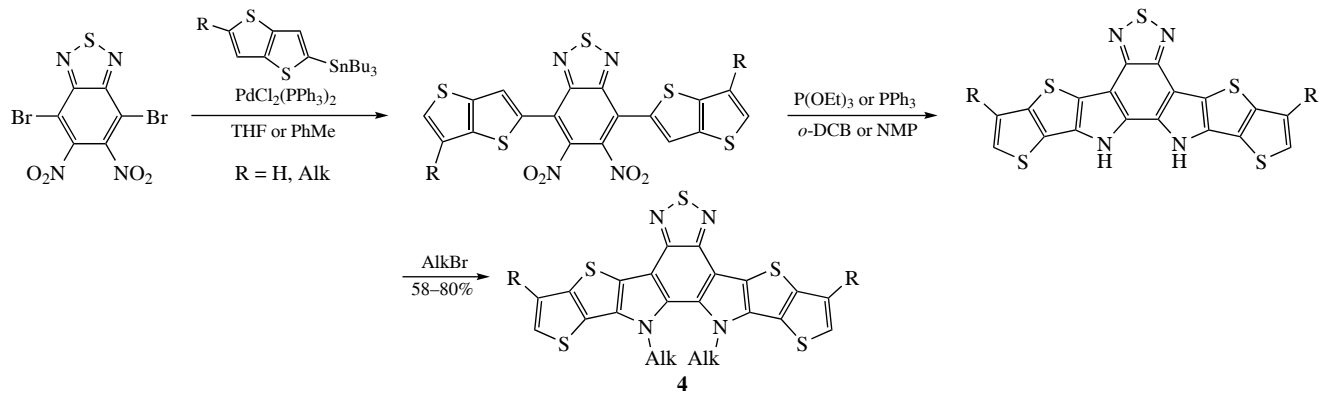
The most frequently studied reaction for this heterocyclic system is the Vilsmeier–Haack formylation followed by the Knoevenagel reaction with 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitriles (Scheme 3). The standard formylation includes treatment of DTPI with the DMF/$POCl_3$ system at 80–85 °C for several hours.[19,27] Compound **5**, precursor of NFA **Y6**, can be alternatively prepared by the unusual reaction with Bu^nLi and DMF at room temperature.[7] Knoevenagel reaction was performed in the presence of pyridine in $CHCl_3$ at room temperature[28–30] or by heating at 65 °C.[7,19,27] Compound **Y6** [$R^1 = C_{11}H_{23}$, R^2 = 3,4-F_2, Alk = $CH_2CH(Et)Bu$],[7] the first and the most studied among the NFAs **6** for organic bulk heterojunction solar cells was synthesized in this way (see Scheme 3).

The synthesis of **Y6** analogs containing non-symmetrical (oxodihydroindenylidene)malononitrile side groups was achieved by treatment of diformyl derivatives **5** with subsequent addition of 2-(3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile or its 5-bromo derivative in the presence of pyridine in $CHCl_3$ at room temperature (Scheme 4).[31] The compounds obtained were employed further to undergo dimerization under the Stille–Kelly conditions with $Pd(PPh_3)Cl_2$ as catalyst and Me_6Sn_2 as reducing agent to give **Y6** dimeric products **7** in moderate yields (44–66%). Under the same conditions condensation of dibromo non-fullerene acceptor **6′b** with monobromo derivative **6a** afforded trimeric **Y6** analogs, while self-condensation of dibromide **6′c** gave polymeric NFA in high yield (91%). To enhance a solubility of NFA, a series of



2 **1** **3**

Scheme 1 Synthesis of 10,11-dihydro[1,2,5]thiadiazolo[3,4-*e*]thieno[2′,3′:4,5]pyrrolo[3,2-*g*]thieno[3,2-*b*]indole **1**.



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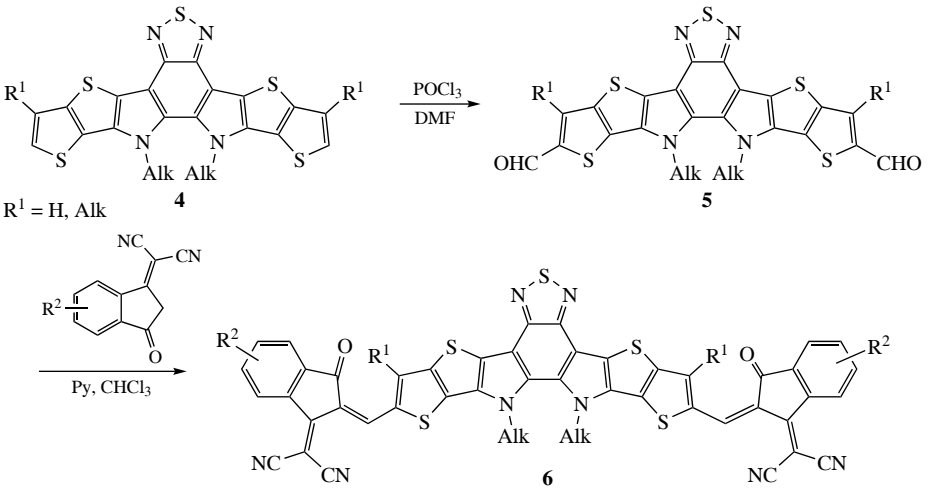
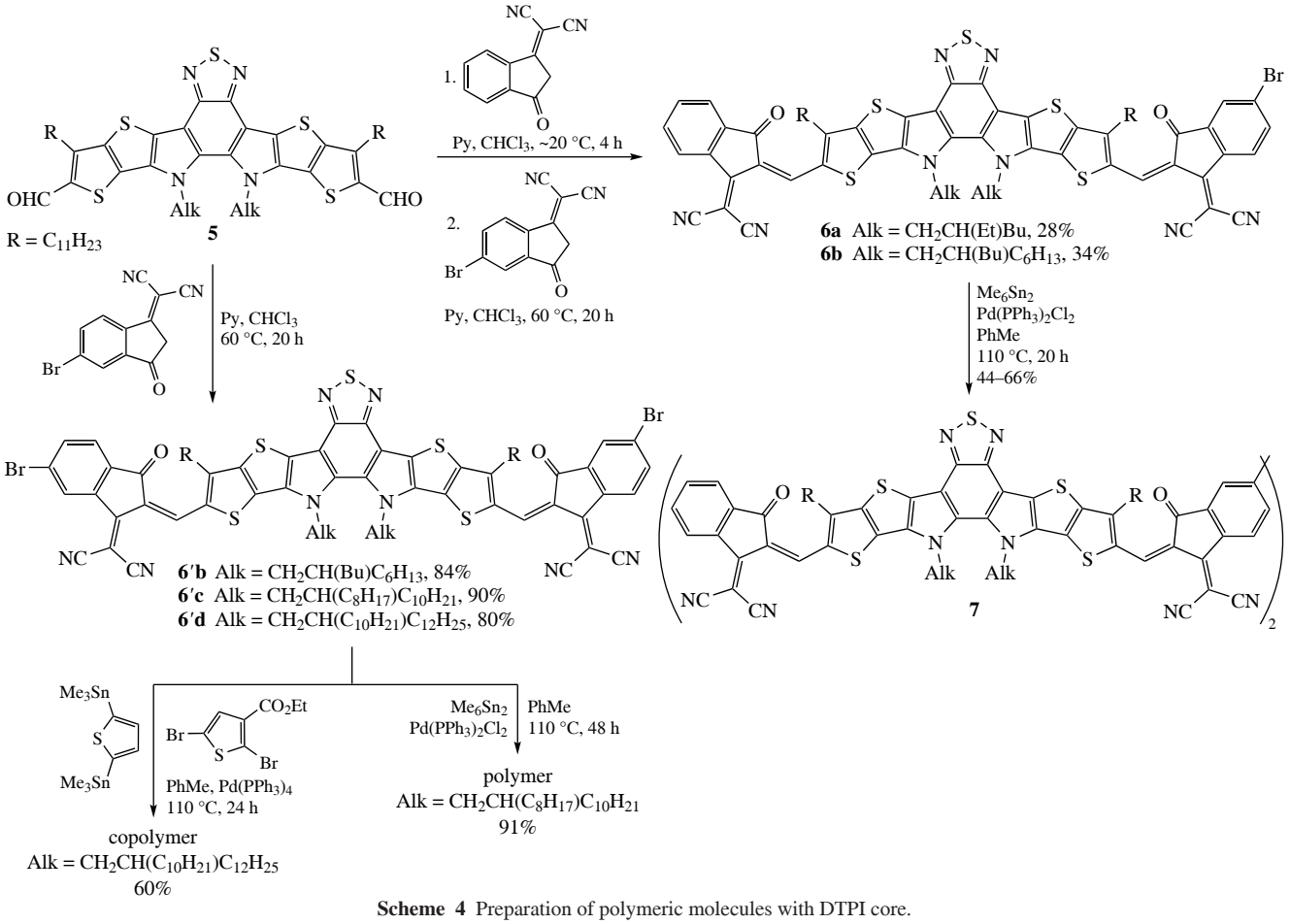
Scheme 2 General route for DTPI compounds.



Scheme 3 Synthesis of NFA of **Y6** series.



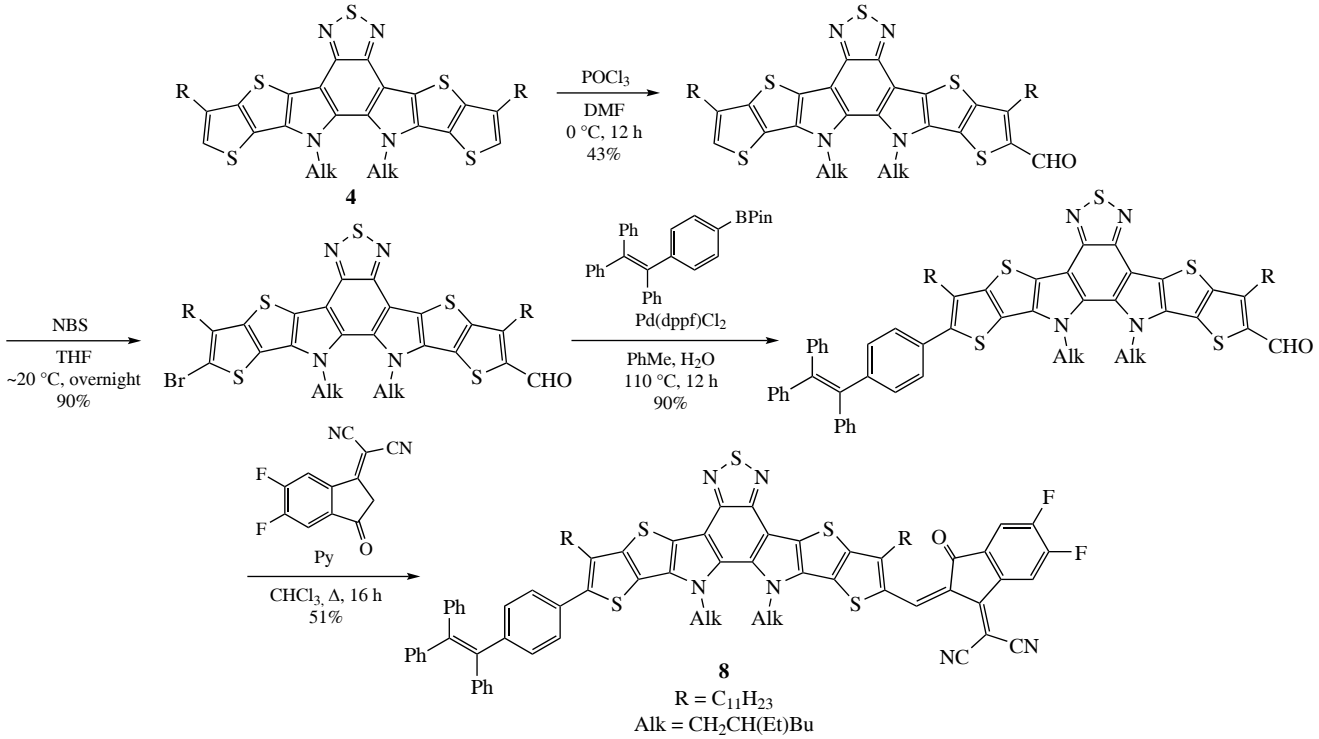
Scheme 4 Preparation of polymeric molecules with DTPI core.

copolymers were synthesized by the Stille cross-coupling polymerization of brominated **Y6** acceptor **6′d** (R = Br) with 2,5-bis(trimethylstannyl)thiophene and ethyl 2,5-dibromothiophene-3-carboxylate.[32]

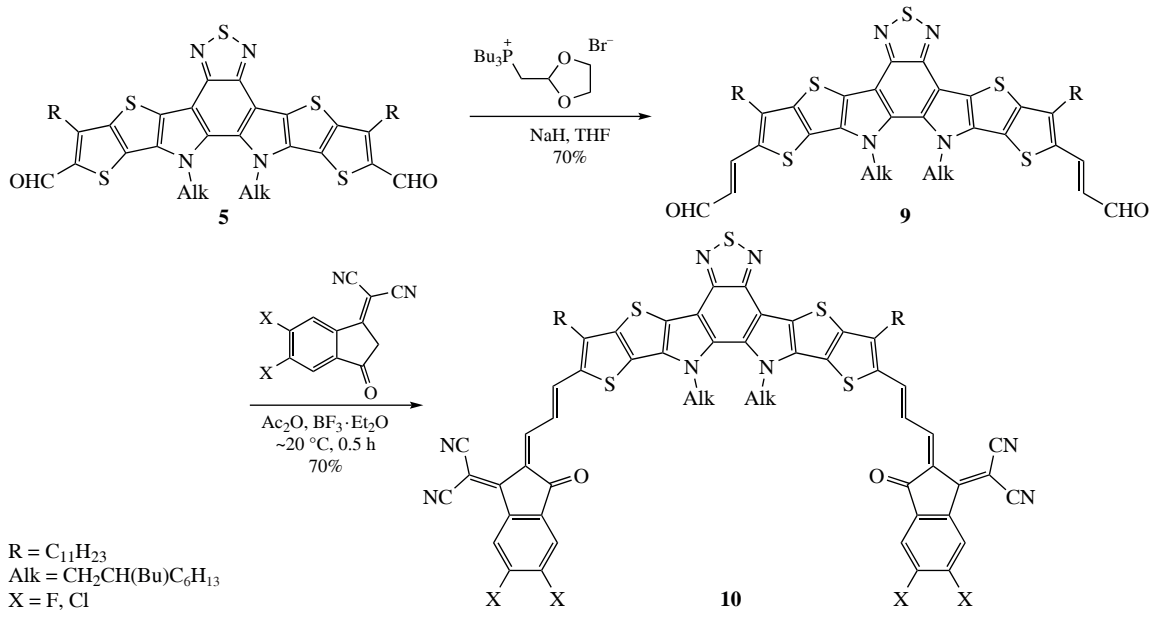
Lin succeeded in synthesizing a non-symmetrical **Y6** analog of D–D–A type by replacing one acceptor terminal dicyanomethylenindene group with a donor tetraphenylethylene group by monoformylation of the starting ring in DTPI followed by bromination with NBS. The final Suzuki and Knoevenagel reactions carried out under standard conditions gave unsymmetrical non-fullerene acceptor **8** in moderate yield (Scheme 5).[33]

Diformyl DTPI derivative **5** was used to increase conjugation with the diene system. For this purpose, the Wittig oxopropenylation with tributyl(1,3-dioxolan-2-ylmethyl)phosphonium bromide in the presence of NaH in THF was used to access novel bis-acrolein derivative **9**. Dialdehyde **9** was subjected to the Knoevenagel reaction with the indanone counterpart under unusual conditions ($Ac_2O/BF_3 \cdot Et_2O$ system) to give compound **10** being the NFA **Y6** vinylog (Scheme 6).[34]

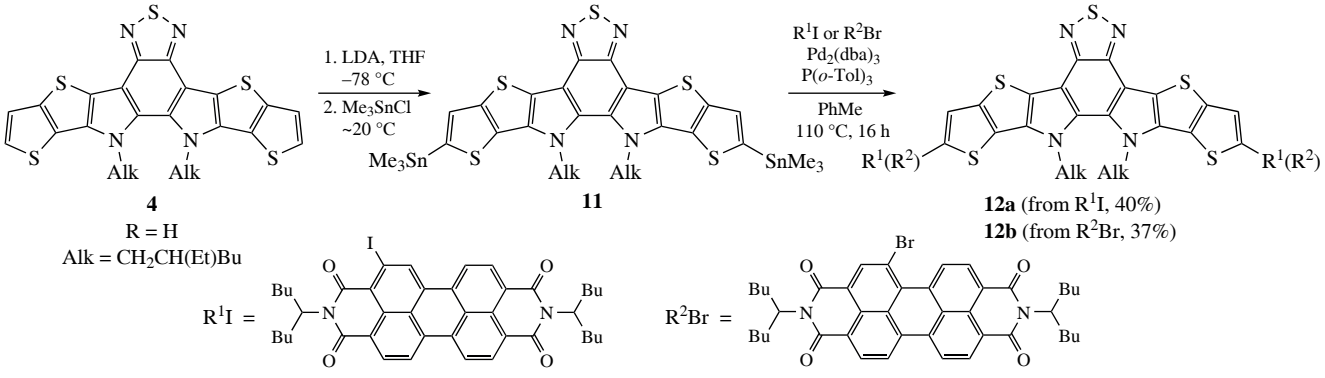
Another possibility for introducing an acceptor fragment into α-positions of anchoring thiophene rings in DTPI **4** is their stannylation. Bis(trimethylstannyl) derivative **11** was obtained by the reaction of DTPI **4** (R = H) with lithium diisoprorylamide and Me_3SnCl. The Stille coupling with 4-iodoperylene or isomeric 5-bromoperylene produced target NFA **12** in moderate yield (Scheme 7).[35]



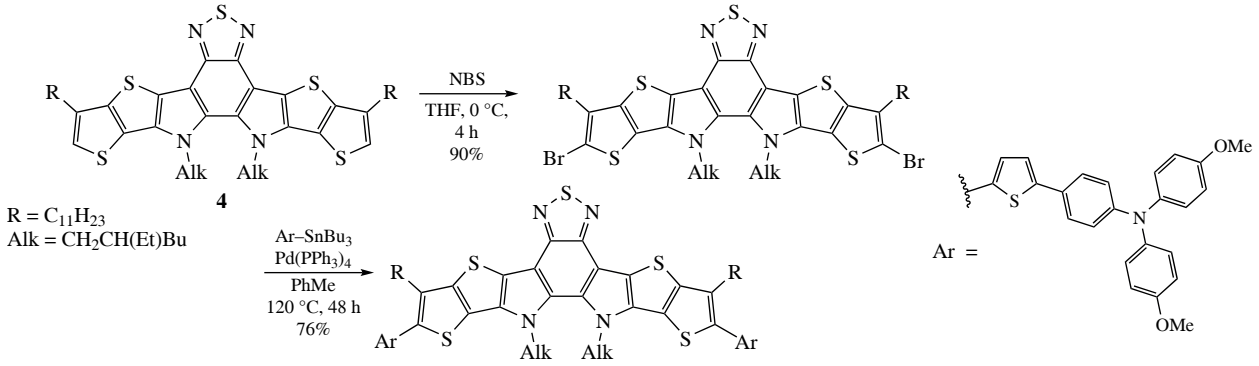
Scheme 5 Synthesis of unsymmetrical **Y6** analog of D–D–A type.



Scheme 6 Preparation of NFA **Y6** analog **10** with additional double bond π-spacers.



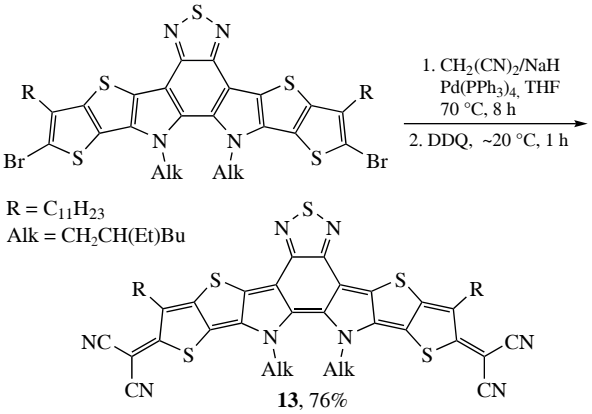
Scheme 7 Introducing anchor perylene fragments into DTPI molecule.



Scheme 8 Introducing donor fragments into DTPI molecule.

Donor fragments can be introduced into positions 2 and 10 of DTPI **4** by the bromination reaction followed by replacement of the bromine atoms for triarylamine residues employing the Stille coupling (Scheme 8).[36]

The unique quinonoid structure **13** with enhanced π-electron delocalization and bond lenght uniformity was synthesized from dibromo DTPI by coupling with malononitrile followed by DDQ oxidation (Scheme 9).[37]



Scheme 9 Synthesis of quinonoid structure **13**.

Transformations of the [1,2,5]thiadiazole ring in DTPI

Several types of transformation of the [1,2,5]thiadiazole ring with the formation of valuable intermediates, diamino and diketo derivatives, are known. The reduction is usually carried out with $LiAlH_4$ in THF, and the resulting diamine **14** is introduced into the next reaction without isolation. Pyrazine derivatives **15** are most often obtained by reaction of diamine **14** with the corresponding diketones in EtOH or $CHCl_3$ (Scheme 10).[38–42]

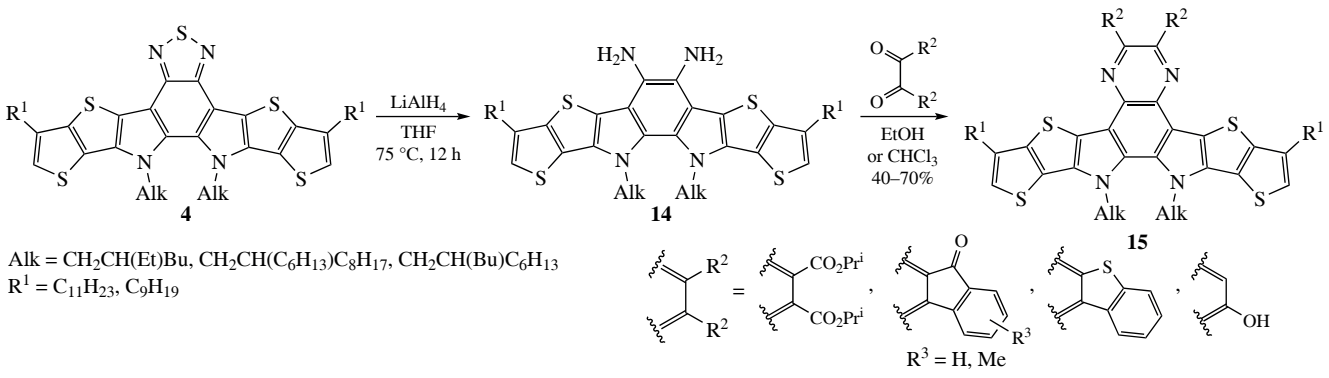
Much attention has been given to the synthesis of fused pyrazines from DTPI **4** through intermediate 11,12-dialkylthieno[2″,3″:4′,5′]thieno[2′,3′:4,5]pyrrolo[3,2-*g*]thieno[2′,3′:4,5]thieno[3,2-*b*]indole-5,6(11*H*,12*H*)-dione **17**.[43–49] Y. Chen proposed an interesting method for converting the thiadiazole ring into a pyrazine one.[43] The first step involves reducing the 1,2,5-thiadiazole in DTPI **4** to diamine **14**, which is then oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), presumably to the corresponding diimine **16**. The latter reacts *in situ* with *o*-arylenediamines under unexpectedly mild conditions (6 h at room temperature) to form pyrazine **15** (Scheme 11).[43–47] Y. Chen showed that pyrazine **15** could be obtained by more rational method converting diimine **16** into diketone **17** by hydrolysis in HCl, followed by heating with *o*-arylenediamines in AcOH.[48,49] However, the yields in this case are not higher, and the procedure for obtaining pyrazine **15** is longer.

Imidazole derivatives **18a**,**b** can be obtained in the reaction of diamine **14** with CF_3CO_2H or by direct reduction of DTPI **4** with Zn in AcOH with subsequent cyclization (Scheme 12).[50]

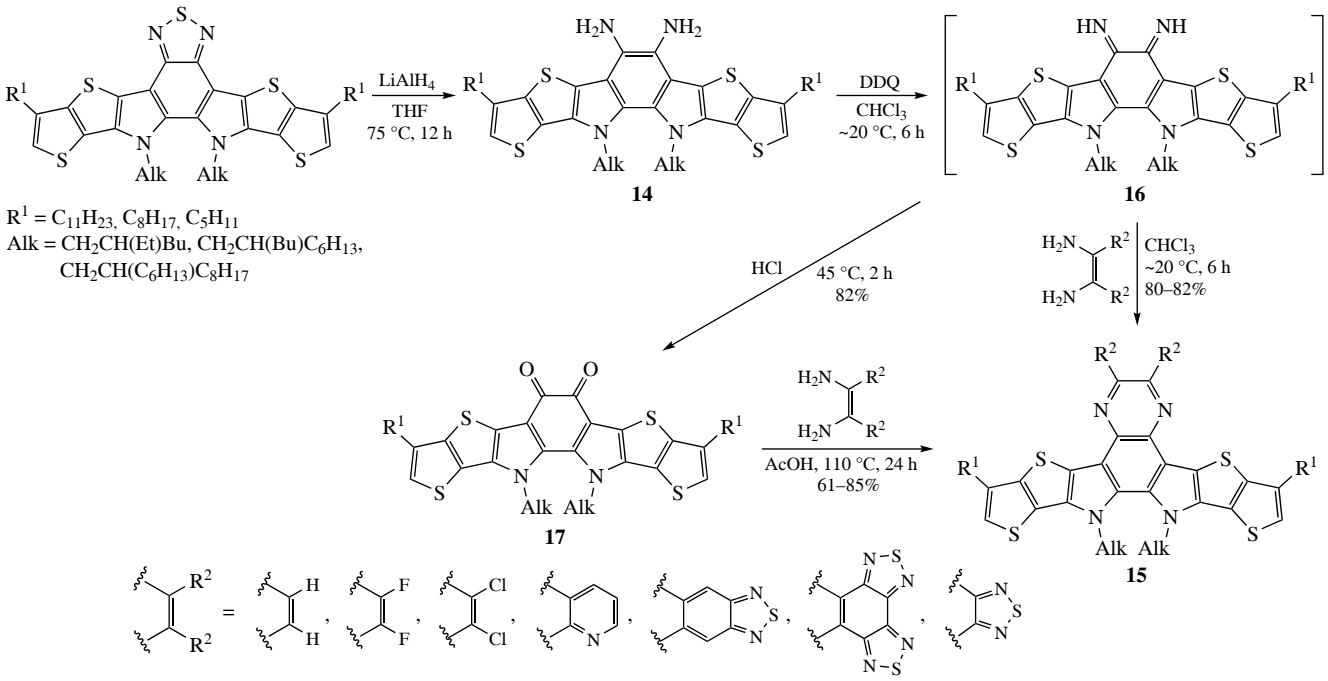
Selenium analogs of DTPI

The selenium analogs of DTPI are much less studied. They can contain selenium atoms both in the central electron-accepting core and in five-membered selenophene rings on the periphery. The selenium analog of DTPI **19** can be prepared by two methods: from 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]selenadiazole **20** *via* the Cadogan reaction[51–53] or by reduction of DTPI **4** with $LiAlH_4$ to diamine **14** followed by cyclization to 1,2,5-selenadiazole derivatives **19** in the reaction with SeO_2 in a mixture of EtOH/H_2O (Scheme 13).[54] The yield in the latter case is much lower, which may be due to insufficiently thorough development of the conditions for cyclization of the 1,2,5-selenadiazole ring.[55]

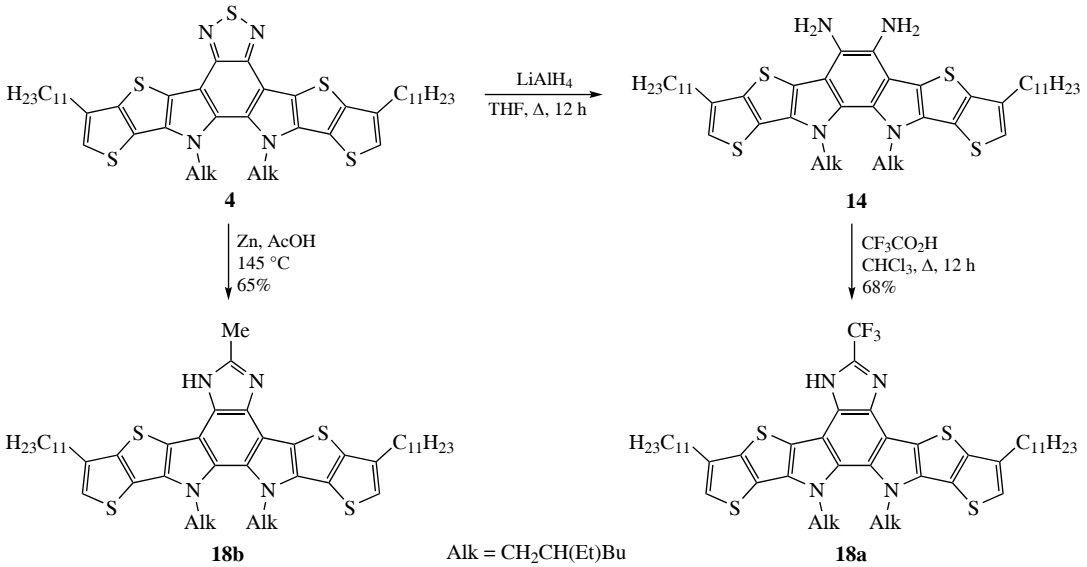
Two isomeric analogs of DTPI **21** and **22** were prepared by a well-established strategy in the reaction of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]thiadiazole with trimethyl(5-alkylselenopheno[3,2-*b*]thiophen-2-yl)stannanes[18,56–59] or trimethyl(2-alkylselenopheno[3,2-*b*]thiophen-5-yl)stannanes



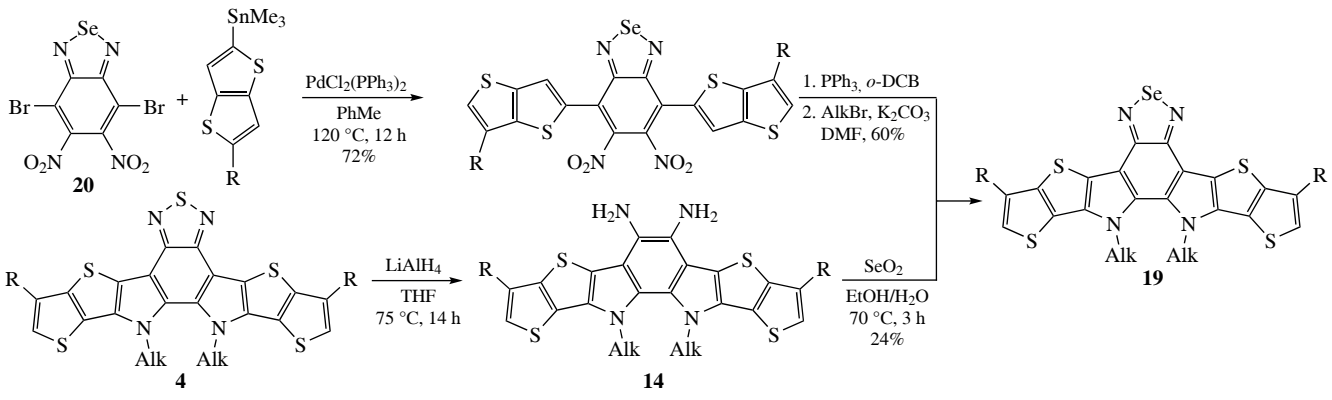
Scheme 10 Formation of the pyrazine in the DTPI molecules to from 1,2,5-thiadiazole ring *via* 1,2-diamines.



Scheme 11 Formation of the pyrazine in the DTPI molecules from 1,2,5-thiadiazole ring *via* 1,2-diketones.



Scheme 12 Formation of fused imidazoles.



Scheme 13 Synthesis of [1,2,5]selenadiazole analogs of DTPI.

(Figure 2).[51] Non-symmetrical DTPI **23** was obtained by sequential reaction of 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]-thiadiazole with tributyl(6-undecylthieno[3,2-*b*]thiophen-2-yl)-stannane and tributyl(5-undecylselenopheno[3,2-*b*]thiophen-2-yl)stannane followed by double intramolecular Cadogan reductive cyclization in the presence of $P(OEt)_3$ in 1,2-di-

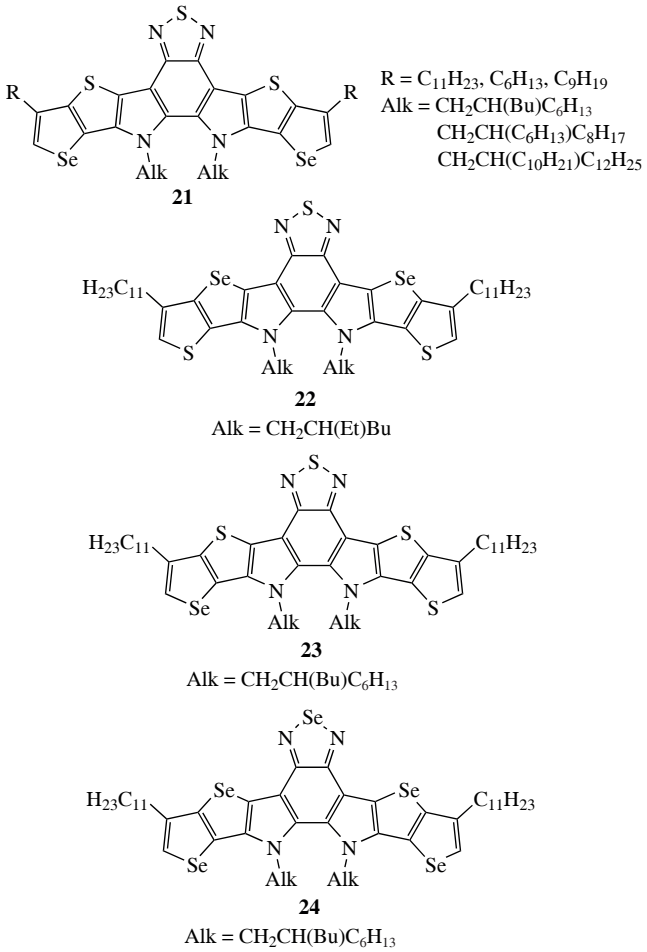


Figure 2 Structure of selenium-containing heterocycles **21**–**24**.

chlorobenzene.[60] All-selenium DTPI **24** was also prepared starting from 4,7-dibromo-5,6-dinitrobenzo[*c*][1,2,5]selenadiazole **20** and tributyl(5-undecylselenopheno[3,2-*b*]selenophen-2-yl)stannane.[61]

Applications of DTPI in the materials construction

In 2019, Zou reported on the preparation of a promising NFA **Y6** molecule with a unique electron-deficient polycyclic center, which provided not only the traditional terminal–terminal stacking but also the center–terminal stacking between acceptor molecules, thereby forming a unique three-dimensional interpenetrating network to effectively enhance the exciton diffusion length and carrier transport efficiency.[7] The presence of side chains effectively tuned the crystallinity and increased the solubility of **Y6** molecules, and the introduction of 2-(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)-malononitrile helped to reduce the LUMO energy level of the molecules and to significantly extend the absorption range to 930 nm. Even though the donor material (**PM6**, poly[[4,8-bis[5-(2-ethylhexyl)-4-fluoro-2-thienyl]benzo[1,2-*b*:4,5-*b′*]-dithiophene-2,6-diyl]-2,5-thiophenediyl-[5,7-bis(2-ethylhexyl)-4,8-dioxo-4*H*,8*H*-benzo[1,2-*c*:4,5-*c′*]dithiophene-1,3-diyl]-2,5-thiophenediyl]) was not optimally selected, the device efficiency of **PM6**:**Y6**-based OPV reached 15.7%. By optimizing the alkyl chain of the **Y6** molecule, Hou was able to construct a single-junction organic photovoltaic device with an efficiency approaching 18% in 2020.[28] Further numerous attempts to optimize the **Y6** molecule by increasing conjugation in the central polycycle, introducing halogen atoms, and using more suitable donor components in solar cells made it possible to increase the photovoltaic efficiency of single-junction devices to 19%,[43,62–64] and ternary devices to more than 19.5%.[65–67] Compounds containing DTPI heterocyclic system have been studied as non-doped hole transporting materials in perovskite solar cells.[36,68] Efficient high-speed near-infrared organic photodetector has been constructed using a narrow-bandgap non-fullerene acceptor BTPSV-4Cl with DTPI core.[34] Chiral **Y6-R** isomers (with enantiopure *R*-chiral alkyl side chain) showed enhanced catalytic activity and were employed as nanoparticle photocatalysts in photocatalytic hydrogen evolution under simulated solar light[69,70] and for self-suspending sacrificial hydrogen production from seawater.[71] Compounds with DTPI structure demonstrated remarkable electron transport capability ($1.1\ cm^2\ V^{-1}\ s^{-1}$) in organic field-effect transistor devices.[72] Glycolated **Y6**-type compounds exhibited mixed ion-electron transport in both conventional and vertical organic electrochemical transistor architectures.[73]

Conclusions

The chemistry of DTPI and the creation of NFA based on them is a rapidly developing area. The main attention is currently paid to the creation of molecules and solar cells based on them, which have high values of photovoltaic efficiency, thermal and photostability. The main direction of research development in this area is the complication of NFA structures, in particular, to produce dimers,[74–76] giant trimer star-shape structures[77] or polymer[78,79] structure or development of terminal anchor groups.[80,81] At present, photovoltaic efficiency values above 20% have been achieved,[82] and the struggle is for hundredths of a percent with the obligatory maintenance of the stability of the device. To achieve enhanced properties, it is necessary to develop not only high values of physical properties, but also to design new highly efficient molecules. This review contributes to a decision of the latter task.

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