

# Heterotetracenes: Flexible Synthesis and *in Silico* Assessment of the Hole Transport Properties

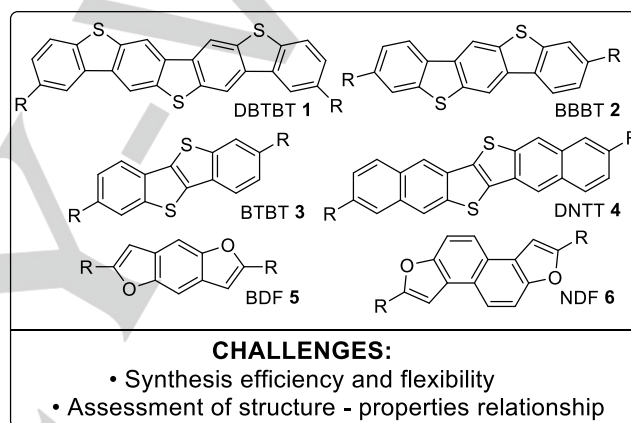
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**Abstract:** Thienoacenes and furoacenes are among the most frequent molecular units found in organic materials. The efficient synthesis of morphologically different heteroacenes and the rapid determination of their solid-state and electronic properties are still challenging tasks, which slow down progress in the development of new materials. Herein, we report a flexible and efficient synthesis of unprecedented heterotetracenes based on a platinum- and gold-catalyzed cyclization-alkynylation domino process using EthynylBenziiodoXole (EBX) hypervalent iodine reagents as key step. The proof-of-principle *in silico* estimation of the synthesized tetracenes' charge transport properties reveals their strong dependence on both the position and nature of the heteroatoms in the ring system. A broad range of mobilities is predicted, with some compounds displaying performance potentially comparable to that of state-of-the-art electronic organic materials.

## Introduction

Acenes and heteroacenes are important compounds in material science.<sup>[1]</sup> Among them, thienoacenes and furoacenes were intensively studied due to their easily tuned electronic properties depending on their conjugation topology.<sup>[2]</sup> Especially successful examples are dibenzo[*b,b'*]thieno[2,3-*f5,4-f'*]bis[1]benzothiophene (DBTBT, **1**),<sup>[2b]</sup> benzo[1,2-*b:4,5-b'*]bis[1]benzothiophene (BBBT, **2**),<sup>[2c]</sup> [1]benzothieno[3,2-*b'*]benzothiophene (BTBT, **3**),<sup>[2e-f]</sup> dinaphtho[2,3-*b:2',3'-f'*]thieno[3,2-*b'*]thiophene (DNNT, **4**),<sup>[2g-h]</sup> benzodifuran (BDF, **5**),<sup>[2j]</sup> and naphtho[2,1-*b:6,5-b'*]difuran (NDF, **6**)<sup>[2k]</sup> (Figure 1). Systematic studies of the influence of the sulfur and oxygen heteroatoms on the electronic properties in dependence on their position in the ring systems are limited.<sup>[1h,3]</sup> This is surprising, when considering that a broad diversity of building blocks and a good understanding of their electronic properties will be essential for the development of new organic materials. One possible reason for this lack of diversity is that a rapid and flexible synthesis of novel and morphologically diverse building blocks remains difficult. To address this challenge, we

envisioned a new synthesis of heterotetracenes derived from either dibenzofuran or dibenzothiophene starting from broadly available iodo- and alkynyl arenes in four steps only (Scheme 1, goal 1). This approach allows varying systematically the central and the last ring of the conjugated system to study their effect on the hole transport properties and to introduce selectively either an oxygen or a sulfur heteroatom at the desired position. It is interesting to note that despite their relative simplicity, most of the targeted compounds have not yet been reported.



**Figure 1.** Thieno- and furo- acenes building blocks for organic materials

Improved synthesis methods are necessary but alone not sufficient for the development of new materials. Indeed, analyzing the relationship between structure and electronic properties is also required to guide the synthetic effort. Since measuring the hole transport properties under conditions relevant for the material applications can be highly resource and time-consuming, rapid computational pre-screening is valuable for identifying the most promising structures for subsequent experimental testing. Admittedly, highly accurate estimates of charge mobility require rigorous multiscale simulations, based on experimental crystal structures.<sup>[4]</sup> In the absence of the latter in this study we retreat to a much more limited and computationally inexpensive approach of applying the Marcus hopping model of the charge transport to the model dimers.<sup>[5]</sup> This approach ignores the crucial effects of disorder and specificity of crystal packing, but allows isolating the role of the nature and position of the heteroatoms in the  $\pi$ -conjugated cores (*via* the reorganization energy) and the extent of orbital overlap between them (*via* the transfer integral, see Scheme 1, goal 2), providing a hypothetical estimate of the core's charge transport capacity.

Overall, herein we present a method for the synthesis and assessment of heterotetracene building blocks with potential for applications in organic materials. A highly efficient synthetic

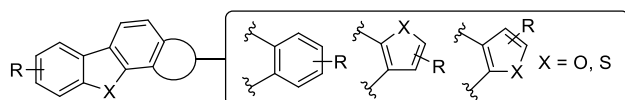
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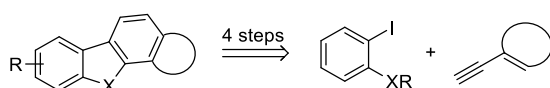
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approach based on a platinum-catalyzed domino cyclization-alkynylation process is first presented. Computational evaluation of the charge transport properties of the synthesized tetracenes indicates that several of them can potentially compete with the current state-of-the-art organic semiconducting materials.

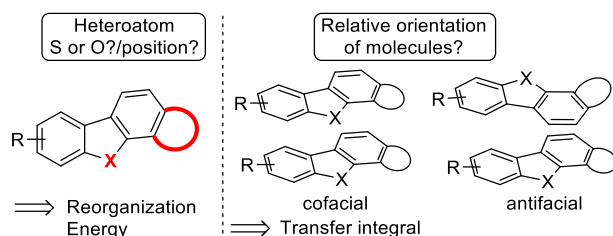
#### Targeted tetracenes



#### Goal 1: Flexible synthesis



#### Goal 2: Estimation of the hole mobility properties by computation



**Scheme 1.** Targeted tetracenes: flexible synthesis and hole mobility prediction.

## Results and Discussion

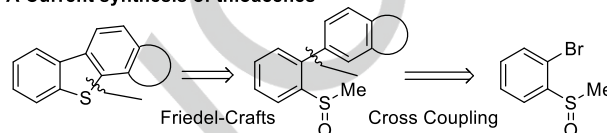
### Synthesis of Heterotetracenes

Most of the past efforts in the synthesis of heterotetracenes have focused on the synthesis of thioacenes bearing an external thiophene ring.<sup>[6]</sup> Only a few reports dealt with the installation of an internal thiophene ring. One of the most efficient approaches was introduced by Müllen and co-workers based on the intermolecular cross coupling with an aryl sulfoxide followed by a Friedel-Crafts annulation (Scheme 2, **A**).<sup>[2b]</sup> This convenient transformation has been limited so far to the introduction of only one heteroaryl ring into the  $\pi$ -conjugation system and cannot be used for the synthesis of benzofuran derivatives. Only a few methods were reported for furoacene synthesis.<sup>[2j-k]</sup> An improved approach to construct heteroaryl fused thienoacenes and furoacenes in a rapid way is consequently required to reach our goal of systematic structure modification.

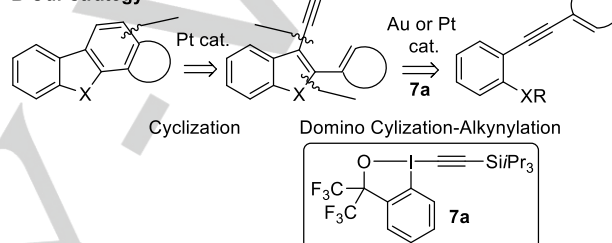
In view of developing a more general synthesis, we envisaged to form the benzene ring of heterotetracenes using a platinum-catalyzed cyclization as the last step instead of forming the C-X bond (Scheme 2, **B**).<sup>[7]</sup> This disconnection leads to 2,3-disubstituted 3-alkynyl benzothiophenes and benzofurans as starting materials, which needed to be efficiently synthesized. Usually, a multi-step synthesis is employed to access these substrates, such as halogenation at C3 position starting from C2 substituted precursors, followed by functional group transformations.<sup>[8]</sup> In the last two decades, C-H functionalization has been developed as a more efficient method to introduce substituents to heterocycle rings, but it takes place at the C2

position for benzothiophenes and benzofurans or requires the introduction of directing groups.<sup>[9]</sup> To improve synthetic efficiency and allow functionalization at less reactive positions, domino reactions constitute an attractive strategy.<sup>[10]</sup> For example, the formation of the heterocycle and another C-C bond at C3 position was employed to synthesize alkenyl-, aryl- or alkyl- C3-substituted benzofurans via Pd,<sup>[11]</sup> or Rh<sup>[12]</sup> catalysis, and C3 alkyl or aryl benzothiophenes and benzofurans via Au/Pt,<sup>[13]</sup> or Pd<sup>[14]</sup> catalysis. To our surprise, a cyclization-alkynylation domino process was unprecedented.<sup>[15,16]</sup>

#### A Current synthesis of thioacenes



#### B Our strategy



**Scheme 2.** Current synthesis of thioacenes (**A**) and our new strategy for the synthesis of heterotetracenes (**B**).

Recently, we developed cyclization-alkynylation domino reactions to access functionalized furans<sup>[17]</sup> and indoles<sup>[18]</sup> based on the use of ethynylbenziodoxole (EBX) hypervalent iodine reagents. We therefore envisaged that these reagents could be used to develop the unprecedented domino cyclization alkynylation process. Herein, we report the first intermolecular domino reactions to synthesize 2,3-disubstituted 3-alkynyl benzothiophenes and benzofurans, easily obtained via Sonogashira coupling of the corresponding iodo- and alkynyl-aryls, via gold- or platinum- catalyzed domino reactions using EBX reagent **7a** (Scheme 2, **B**).

We started our investigations on the cyclization-alkynylation domino reaction with 2-alkynyl phenol **8a**<sup>[11d]</sup> as substrate (Table 1). The conditions reported for Lautens's domino reaction<sup>[12]</sup> or Hashmi's benzofuran formation<sup>[19]</sup> didn't give any desired product, independently of the hypervalent iodine reagent used (Table 1, entries 1-6). PtCl<sub>2</sub><sup>[18]</sup> was not efficient for this domino process (Table 1, entry 7). When we turned our attention to Au(III) catalysts, we were pleased to observe the formation of the desired product with benziodoxole **7a** (Table 1, entries 8-10). Other hypervalent iodine reagents were not successful in this transformation (results not shown). AuCl<sub>3</sub> gave a better yield (83%) when compared to dichloro(pyridine-2-carboxylato)gold(III) (PicAuCl<sub>2</sub>) and pyridine gold(III) trichloride (PyAuCl<sub>3</sub>). The influence of the solvents was then examined, demonstrating that THF was optimal (Table 1, entries 11-12).

We continued our investigation with 2-ethynyl thioanisole **10a** (Table 2).<sup>[20]</sup> An iodide salt was added to the reaction, as it has been reported to promote demethylation.<sup>[16c]</sup> The conditions optimized for the cyclization-alkynylation of **8a** were not successful: neither AuCl<sub>3</sub> nor AuBr<sub>3</sub> could be used as catalyst (Table 2, entries 1-2). On the other hand, AuCl could promote the desired transformation in 41% yield (Table 2, entry 3). The yield was improved to 61% when PtCl<sub>2</sub> was used (Table 2, entry 4). The effect of solvents was then examined. 41%, 28% and 19% of benzothiophene **11a** were obtained in toluene, ether and DCM respectively (Table 2, entries 5-7). 2-Phenyl benzothiophene was isolated as by-product in toluene and DCM. Initially, we used basic conditions to prevent proto-demetalation. However, as no proton is generated during the reaction, we wondered if the use of a base was really required. Indeed, in the absence of the base the yield could even be increased to 77% (Table 2, entry 8). This result is consistent with our previous observation with a platinum catalyst.<sup>[18]</sup> The reaction did not occur without NaI (Table 2, entry 9). The use of 2.0 equiv. of **7a** did not improve the yield (Table 2, entry 10). Under the optimized reaction conditions, it was therefore possible to obtain the desired 3-alkynyl benzo-furan and thiophene **9a** and **11a** at room temperature using open flasks, resulting in a highly practical procedure.

**Table 1.** Optimization of the Domino Cyclization- Alkynylation Reaction of 2-Alkynyl Phenol **8a**.

entry	catalyst	reagent	temp	solvent	yield <sup>[a]</sup>
1	[Rh(cod)OH] <sub>2</sub>	<b>7a</b>	90 °C	dioxane	<5%
2	[Rh(cod)OH] <sub>2</sub>	<b>7b</b>	90 °C	dioxane	<5%
3	[Rh(cod)OH] <sub>2</sub>	<b>7c</b>	90 °C	dioxane	<5%
4	IPrAuCl/AgOTf	<b>7a</b>	rt	THF	<5%
5	IPrAuCl/AgOTf	<b>7b</b>	rt	THF	<5%
6	IPrAuCl/AgOTf	<b>7c</b>	rt	THF	<5%
7	PtCl <sub>2</sub>	<b>7a</b>	rt	THF	<5%
8	PyAuCl <sub>3</sub>	<b>7a</b>	rt	THF	53%
9	PicAuCl <sub>2</sub>	<b>7a</b>	rt	THF	53%
10	AuCl <sub>3</sub>	<b>7a</b>	rt	THF	83%
11	AuCl <sub>3</sub>	<b>7a</b>	rt	DCM	53%
12	AuCl <sub>3</sub>	<b>7a</b>	rt	toluene	<5%

[a] Reaction conditions: **8a** (0.10 mmol), catalyst (10 mol%), **7** (0.12 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.12 mmol), 0.1 M, overnight. Isolated yields after column chromatography.

We then explored the scope of the domino reaction for the synthesis of benzofurans (Scheme 3, **A**). The reaction was easily scaled up to 0.3 mmol. Phenyl and tolyl substituted alkynes gave the domino products **9a** and **9b** in 85% and 66% yield respectively. A cyclopropyl group was well tolerated (product **9c**). Benzofurans **9d** and **9e** bearing a C2- and C3-substituted thiophene substituent respectively could also be obtained in good yields.

**Table 2.** Optimization of the Domino Cyclization- Alkynylation Reaction of 2-Alkynyl Thioanisole **10a**.

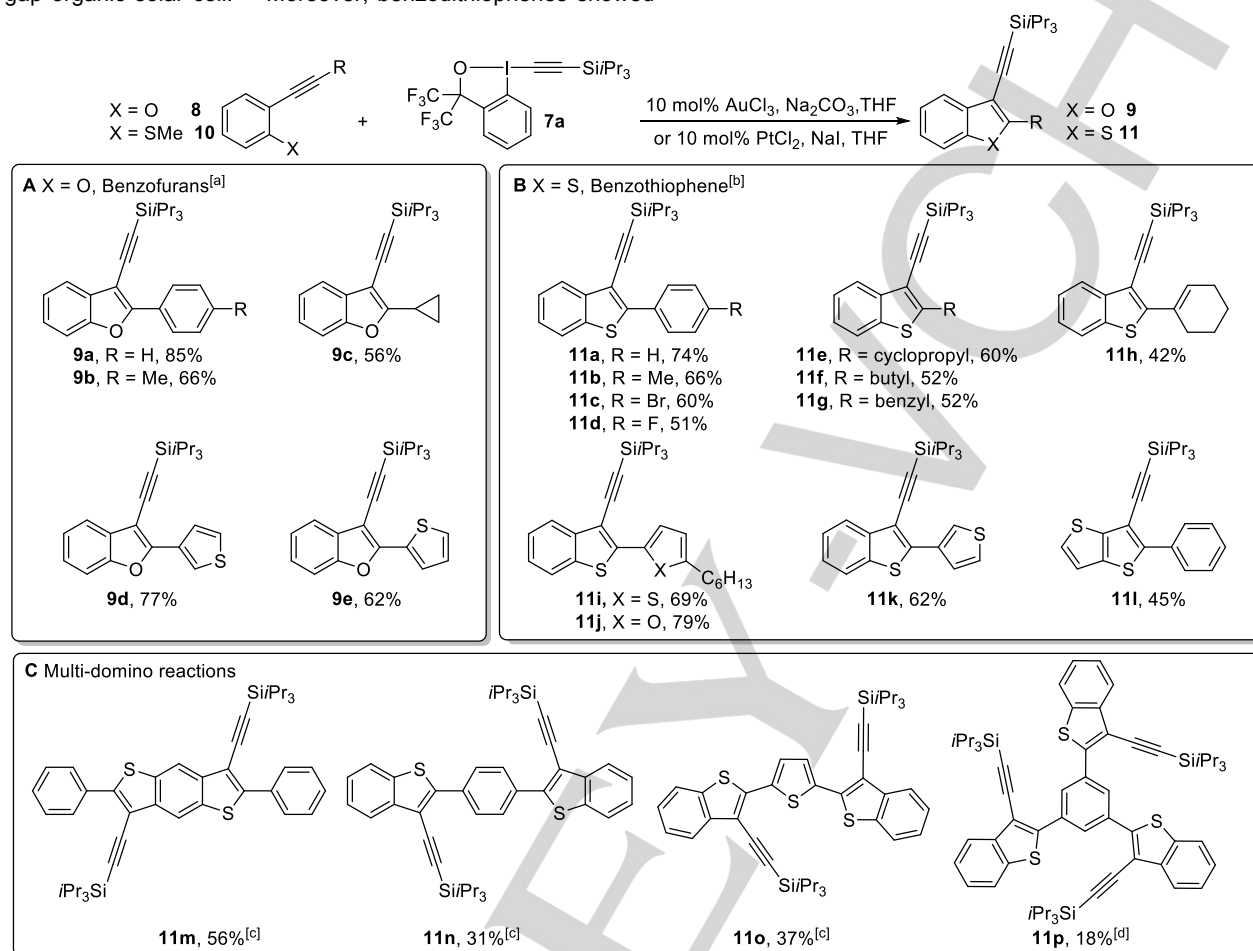
entry	catalyst	additive	base	solvent	yield <sup>[a]</sup>
1	AuCl <sub>3</sub>	NaI	Na <sub>2</sub> CO <sub>3</sub>	THF	<5%
2	AuBr <sub>3</sub>	NaI	Na <sub>2</sub> CO <sub>3</sub>	THF	<5%
3	AuCl	NaI	Na <sub>2</sub> CO <sub>3</sub>	THF	41%
4	PtCl <sub>2</sub>	NaI	Na <sub>2</sub> CO <sub>3</sub>	THF	61%
5	PtCl <sub>2</sub>	NaI	Na <sub>2</sub> CO <sub>3</sub>	toluene	41% <sup>[b]</sup>
6	PtCl <sub>2</sub>	NaI	Na <sub>2</sub> CO <sub>3</sub>	Et <sub>2</sub> O	28%
7	PtCl <sub>2</sub>	NaI	Na <sub>2</sub> CO <sub>3</sub>	DCM	19% <sup>[c]</sup>
8	PtCl <sub>2</sub>	NaI	-	THF	77%
9	PtCl <sub>2</sub>	-	Na <sub>2</sub> CO <sub>3</sub>	THF	<5%
10 <sup>[d]</sup>	PtCl <sub>2</sub>	NaI	-	THF	54%

[a] Reaction conditions: **10a** (0.10 mmol), catalyst (10 mol%), **7a** (0.12 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.12 mmol), NaI (0.10 mmol), 0.1 M, overnight. Isolated yields after column chromatography. [b] 19% of 2-phenyl benzothiophene was isolated. [c] 11% of 2-phenyl benzothiophene was isolated [d] 0.20 mmol **7a** was used.

The synthesis of benzothiophene derivatives is then proposed in Scheme 3, **B**. A methyl, a bromide and a fluoride substituent were well tolerated on the phenyl ring linked to the alkyne (products **11b-11d**). C2 alkylated benzothiophenes **11e-g** could also be accessed using our method, as well as cyclohexene substituted product **11h**. The reaction conditions were also applicable to substrates bearing furan or thiophene heterocycles (**11i-k**). Disubstituted thienothiophene **11l** was obtained in 45% yield. Even though the yield is moderate, it is usually challenging to synthesize C3-substituted thienothiophenes as the C2 position is more reactive.<sup>[11]</sup> Gratifyingly, double and triple domino reactions also took place (Scheme 3, **C**). Symmetric 2,3,5,6-tetrasubstituted benzodithiophene **5m** was synthesized in 56% yield. The multi domino reaction could also be performed when the thioanisoles units were linked by a benzene or a thiophene ring (products **5n-p**). The overall yields were moderate, but the yield for each domino reaction remains between 56% and 75%. Both thienothiophenes and

benzodithiophenes are important building blocks in organic material science. They are used as donor fragments for small gap organic solar cell.<sup>[21]</sup> Moreover, benzodithiophenes showed

remarkable properties for applications as field-effect transistors, such as high hole mobility and excellent on/off ratio.<sup>[2e]</sup>



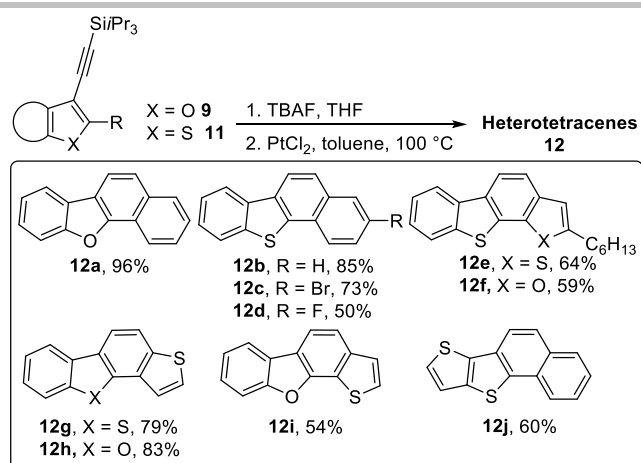
**Scheme 3.** Scope of 3-alkynylated benzofurans and 3-alkynylated benzothiophenes.

With a series of 3-alkynylated benzofurans and benzothiophenes in hand, we then performed the envisaged sequence of transformations involving desilylation promoted by TBAF followed by PtCl<sub>2</sub> catalyzed cyclization to obtain the desired heterotetracenes **12** (Scheme 4).

Naphtho[1,2-b]benzofuran (**12a**) and naphtho[1,2-b]benzothiophene (**12b**) were obtained in excellent yields -96% and 85% respectively. When a halogen was introduced on the phenyl group, the cyclization step still occurred but with a decrease in yield (products **12c** and **12d**). Heteroacene **12c** can be further functionalized via conventional cross coupling methods. Notably, 3-halogenated naphtho[1,2-b]benzothiophenes such as **12c** are highly challenging to synthesize via Friedel-Crafts halogenation, as it usually takes place on the more nucleophilic *para*-position to the sulfur atom.<sup>[22]</sup> Two heteroatom-containing heteroacenes **12e-j**, which could not be yet synthesized using conventional approaches,<sup>[2b]</sup>

were smoothly accessed with diverse and unprecedented morphologies. Heteroacenes **12e** and **12f** containing S,S and S,O heteroatoms *ortho* to each other and **12g** and **12h** containing S,S and S,O heteroatoms *meta* to each other were obtained in 59-83% yield.

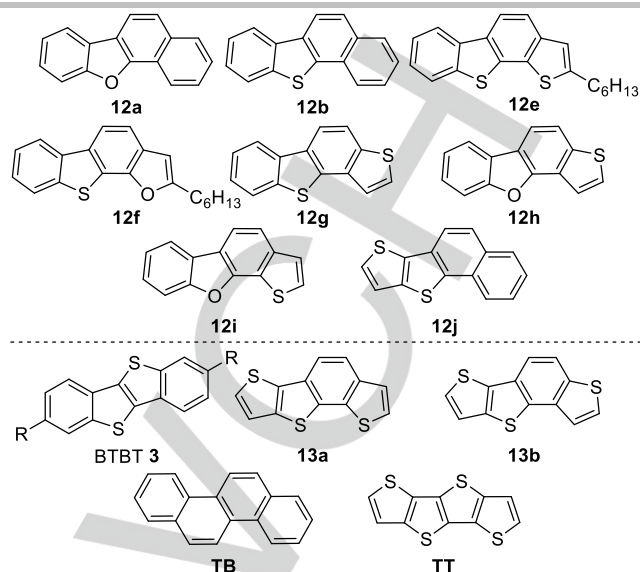




The structure of **12h** was further confirmed by X-ray analysis.<sup>[23]</sup> Heteroacene **12i** with an *ortho* O,S substitution was formed in 54% yield. Finally, the synthesis of naphtho[2,1-*b*]thienothiophene **12j** was also possible.<sup>[24]</sup>

#### Assessment of the hole mobility properties

In order to assess the potential of the novel heterotetracenes in molecular electronics applications, we have estimated their hole transport properties. Details of the computations<sup>[25]</sup> can be found in the Supporting Information. The following substrates were investigated: **12a**, **12b**, **12e** and **12f** (a C<sub>6</sub>H<sub>13</sub> group was replaced with a hydrogen atom in the calculations to facilitate the computational effort), **12g**, **12h**, **12i** and **12j** (Figure 2). In order to have a more complete analysis of the influence of introducing thiophene rings in the tetracene, we also examined compounds **13a** and **13b** (3 S atoms), as well as tetrabenzene (**TB**) and tetrathiophene (**TT**) (0 and 4 S atoms respectively). As a further reference point we have chosen a  $\pi$ -conjugated heteroaromatic core, namely the [1]benzothieno[3,2-*b*][1]benzothiophene (BTBT, **3**, also computed without substituent). This substrate has been shown to yield superior organic field effect transistor (OFET) characteristics, with experimentally measured mobilities in the range of 1.0-3.0 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.<sup>[1h]</sup>



**Figure 2.** Tetracenes selected for *in silico* pre-screening.

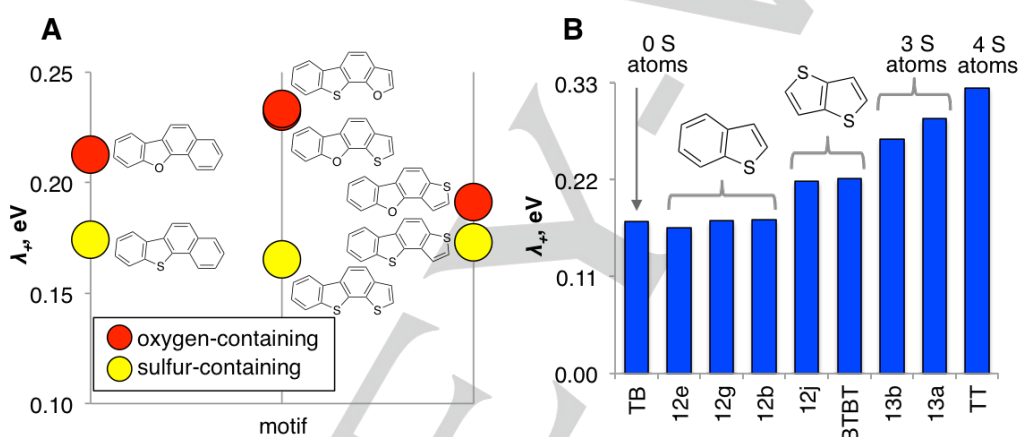
To estimate the hole transport rates we utilise the Marcus-Hush theory for the hopping charge mechanism,<sup>[26]</sup> which affords an excellent agreement with the experimental results for various acene- and thiophene-based systems.<sup>[27]</sup> It relies upon two main parameters: the reorganization energy  $\lambda_+$  of the monomer and the electronic coupling  $t_+$  (hole transfer integral) in the dimer. Our results indicate the dependence of the reorganization energies  $\lambda_+$  (evaluated as the energy difference between the charged and the neutral counterparts) on the type, number and mutual arrangement of the heteroatoms. Substitution of sulfur with oxygen in either the central or terminal ring (compare compounds **12a** with **12b**, **12f** with **12e**, **12h** with **12g** and **12i** with **12e**) generally impedes the ionization and thus leads to higher  $\lambda_+$  since smaller, less polarizable and more electronegative O atoms are less effective in stabilizing the positive charge (Figure 3, **A**). Adding more sulfur atoms tends to increase the reorganization energy. A clear correlation is also observed between  $\lambda_+$  and the structural pattern of the heterocycles (Figure 3, **B**): species with the benzothiophene motif have the lowest reorganization energies, while molecules, which also comprise the thienothiophene moiety, have higher  $\lambda_+$ . Compounds with lower reorganization energies are expected to afford better charge transport properties. In this case, simple tetrabenzene (**TB**) should have a significant charge transfer rate. However, reorganization energies alone are insufficient to predict material properties – charge transport rates depend greatly on the crystallinity of the material, the extent of structural and energetic disorder, the type of crystal packing, etc.<sup>[4,5,28]</sup>

Reliable computational prediction of the charge transport properties is challenging<sup>[29]</sup> and necessitates (i) more sophisticated computational techniques, e.g. involving molecular dynamics and kinetic Monte-Carlo simulations,<sup>[30]</sup> and (ii) the pre-existing knowledge of the crystal structure. Since the determination of the crystal structure for each compound studied

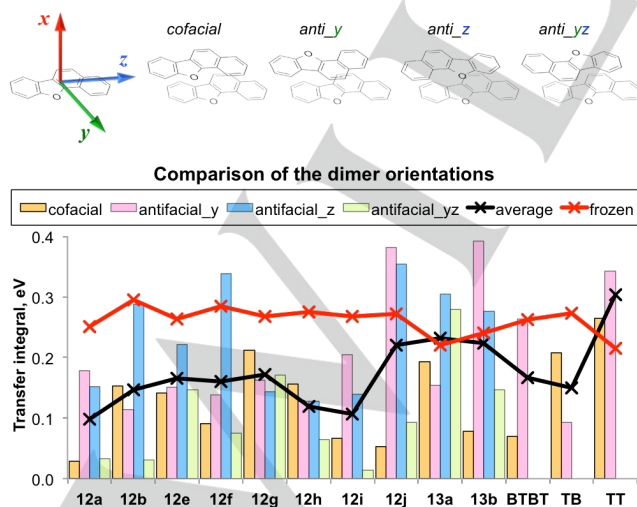
here is experimentally challenging and very time-consuming, we retreat to simplistic models based on  $\pi$ -stacked dimers. Such approach admittedly ignores the disorder and packing effects and the influence of substituents,<sup>[31]</sup> however it provides an insight into the range of transfer integrals that can potentially be expected in the materials comprising the investigated heterotetracene cores.<sup>[32]</sup> Furthermore, while in general the latter tend to favour the herringbone crystal packing,<sup>[33]</sup>  $\pi$ -stacking can be enforced via side-chain modification.<sup>[34]</sup>

Initially, we consider coplanar cofacial dimers in what we call a 'frozen' geometry, *i.e.* the geometry with fixed zero longitudinal and transversal shifts (as well as any rotations) and energetically optimal interplanar separation (at SAPT0/jun-cc-pVDZ level of theory)<sup>[35]</sup>. Their computed transfer integrals (red line in Figure 4) are fairly similar, in the range of 0.22-0.30 eV. However, once allowed to fully relax, such dimers tend to contract (interplanar distance decreasing from 3.7-3.8 Å to ~3.3 Å) and undergo lateral and/or transversal shifting and even minor rotations disturbing

the cores' coplanarity (See Table S2 in the Supporting Information), leading to a much broader range of  $t_+$  values. This range expands even further when non-cofacial mutual core orientations (antifacial, *i.e.* various disorderers,<sup>[36,37]</sup> Figure 4 top panel) are accounted for, and many more transfer integral values can be achievable for herringbone and other types of dimer assemblies. This complex behaviour of the electronic coupling is caused by an interplay of several factors, including the frontier orbital symmetries, proximity of the heteroatoms, mutual orientation of the monomers within a given crystal packing, contribution of exchange and charge penetration effects to their interaction energies, etc.<sup>[38]</sup> On average for the optimized  $\pi$ -stacked dimers (black line in Figure 4), we observe somewhat higher  $t_+$  for sulfur-containing cores (vs. oxygen) and for systems with more heteroatoms (3- and 4- S atom cores vs. 0-2 S atoms).



**Figure 3.** Reorganization energies depending of the type (A), number and mutual arrangement (B) of the heteroatoms in the core.

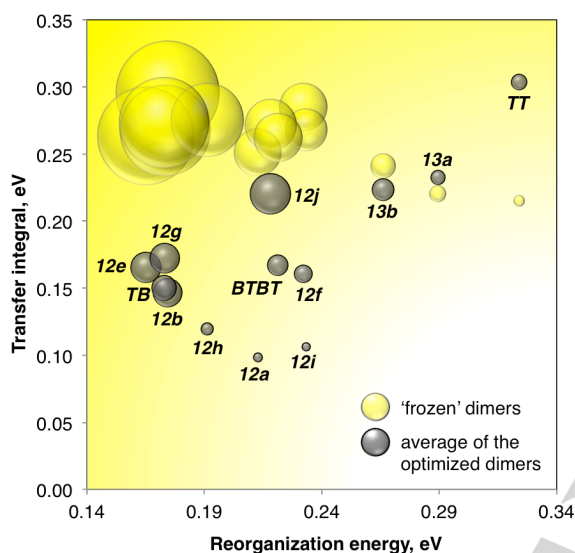


**Figure 4.** Various dimer geometries depending on the mutual orientation of two monomer cores (disorderer, illustrated here for 12a) and the computed

transfer integrals for the model 'frozen' and optimized dimers ('average' corresponds to the average value for the optimized disorderers).

The resulting hole mobilities, computed for the studied dimers, are shown in Figure 5. Generally, higher mobilities are expected for systems with lower monomer reorganization energies and higher transfer integrals. Since the  $t_+$  values in the 'frozen' model dimers are fairly similar, their mobilities are largely defined by their  $\lambda_+$ . Regarding the optimized dimers, the two "extreme" (from the reorganization energy perspective) compounds **TB** and **TT** give moderate mobilities: **TB** because of its average transfer integral, and **TT** because of its high  $\lambda_+$ . The chosen reference core, BTBT **3**, with its average  $t_+$  and  $\lambda_+$  displays a moderate computed mobility of  $3.3 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .<sup>[39]</sup> Several heterotetracenes bearing 1-3 sulfur atoms – **12b**, **12e**, **12g**, **12j** and **13b** – display comparable ( $\mu_+ > 3.0 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) hole transport characteristics. Considering various disorderers, the antifacial dimers afford the highest mobilities (See Table S3 in the Supporting Information), consistent with experimental

observations.<sup>[36,40]</sup> Our results, based on a crude dimer model, illustrate the potential of the new heterotetracenes to achieve mobilities, comparable to or better than those already reported, and reveal that these properties depend on the type and arrangement of the heteroatoms within the monomer frame. As noted above, more sophisticated modelling based on the experimental crystal structures and, ultimately, experimental testing of these compounds in real life devices is necessary to exhaustively evaluate their performance in the molecular electronics applications.



**Figure 5.** Computed hole mobilities (bubble sizes) for 'frozen' dimers and average between the optimized disorderers, plotted against the corresponding reorganization energies and transfer integrals. For each core, the average mobility bubble is labelled.

## Conclusions

In conclusion, we have developed efficient gold- and platinum-catalyzed domino reactions to synthesize 3-alkynylated benzofurans and benzothiophenes based on the use of EBX hypervalent iodine reagents. Heterotetracenes containing two O, two S, or one O and one S heteroatoms were accessed in only four steps. Subsequent proof-of-principle computations suggest that some of the synthesized compounds and other heterotetracenes can potentially afford hole mobilities, comparable or superior to current state-of-the-art organic materials, provided they are not hampered by the crystal packing and disorder effects. The results confirmed that both the identity and position of the heteroatom in the conjugated system strongly affect the hole mobility. Our study combining improved synthetic methodologies and *in silico* analysis of the electronic structure leads to a better understanding of the relationships between the structure and charge transport properties of the heteroacenes. Further effort can now be focused on other factors (e.g. crystallization techniques, substitution patterns) that

influence both the solid-state structure and the material performances of the most promising cores.<sup>[41]</sup>

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**Keywords:** Acenes • Domino Reactions • Hole Mobility  
Computation • Organic Materials • Hypervalent Iodine

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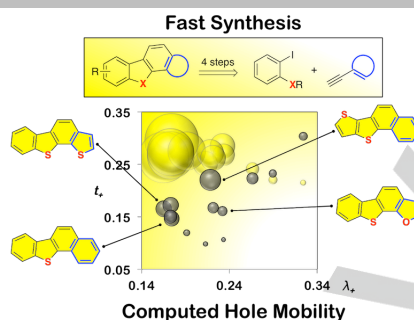


Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Thienoacenes and furoacenes are among the most frequent molecular units found in organic materials. Herein, we report a flexible and efficient synthesis of heterotetracenes based on a platinum- and gold- catalyzed cyclization-alkynylation domino process using EthynylBenziodoXole (EBX) hypervalent iodine reagents as key step, as well the *in silico* estimation of the synthesized tetracenes' charge transport



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**Heterotetracenes: Flexible Synthesis and *in Silico* Assessment of the Hole Transport Properties**