



Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Adv. Synth. Catal. 10.1002/adsc.202001123

Link to VoR: https://doi.org/10.1002/adsc.202001123

DOI: 10.1002/adsc.202001123

Gold Catalysis Meets Materials Science – A New Approach to π -Extended Indolocarbazoles

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201#######.((Please delete if not appropriate))

Abstract. Herein we describe a modular, convergent synthesis of substituted benzo[*a*]benzo[6,7]-indolo[2,3-*h*]carbazoles (BBICZs) using a bidirectional gold-catalyzed cyclization reaction as a key step. A building block strategy enabled the easy variation of substituents at different positions of the core structure and a general analysis of substitution effects on the materials properties of the target compounds. All BBICZs were fully characterized and their optical and electronic properties were studied experimentally as well as by computational methods. Organic thin-film transistors based on eight selected derivatives were fabricated by vacuum deposition and charge-carrier mobilities up to 1 cm²/Vs were measured.

Keywords: Materials science; gold catalysis; indolocarbazoles; organic semiconductors; modular synthesis; thin-film transistors

Introduction

Small-molecule organic semiconductors are of interest for a variety of electronic devices, including organic thin-film transistors (TFTs).^[1] Among the large number of molecular motifs that have been explored for the fabrication of organic p-channel (ICZs).^[2,3] TFTs are the indolocarbazoles Indolocarbazoles are typically characterized by good solubility in common organic solvents and good air stability, which can be attributed to their low-lying HOMO-energy level. While the performance of the first ICZ-based TFTs was quite disappointing, with a carrier mobility of 0.001 cm²/Vs,^[4] the performance of ICZ-based TFTs has been continuously and significantly improved, mainly through strategic

substitutions at the various positions of the molecular core. For example, Ong *et al.* introduced a 4-octylphenyl substituent and reported a TFT mobility of 0.14 cm²/Vs.^[5] Bao and Leclerc synthesized 3,9-di(*p*-octylbenzene)-5,11-dihydroindolocarbazole and measured a carrier mobility of 0.22 cm²/Vs.^[6]

The fact that even small modifications to the molecular structure can have significant effects on the electronic properties was demonstrated by the introduction of chloro-substituents at the 2- and 8-positions of *N*-alkylated ICZs, which led to a carrier mobility of 0.5 cm²/Vs in single-crystal transistors.^[7] In 2013, Sung *et al.* reported on the synthesis of 7-ring π -extended indolocarbazoles (Scheme 1), so called benzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazoles (BBICZs), with alkyl substituents ranging in chain length from C5 to C16.^[8] The π -extension led to a

carrier mobility of 1.5 cm²/Vs for transistors based on a C12-BBICZ single-crystal. C12-BBICZ and its non-alkylated derivative have also been used as a hole-transporting material in perovskite solar cells^[9] and as a donor in solution-processed organic semiconductors.^[10]



Scheme 1. π -Extension of indolocarbazoles.

What is currently lacking is a systematic analysis of the effects of the substitution patterns on the material properties of π -extended indolocarbazoles. This is in part due to the fact that the traditional synthesis involves a double Fischer indole reaction of 3,4-dihydronaphthalen-1(2H)-one and Cbz-protected 1,4-dihydrazineylbenzene that is characterized by rather harsh conditions and requires precursors with limited commercial availability (Scheme 2). In order to conduct a deeper study on the effect of substitution manipulations on the electronic properties of BBICZs, as a missing link to the already mentioned current research on ICZs, we envisioned that a modular approach using a gold-catalyzed key step might contribute to a further evolution of this promising substrate class.^[11]



Scheme 2. Previous approach towards BBICZs and our strategy.

Results and Discussion

In contrast to the established approaches to indolocarbazoles, we reasoned an entirely new approach for the synthesis of BBICZs.^[12] Numerous publications during the past decade impressively demonstrated gold catalysis as an effective tool for the formation of extended π -systems.^[13] In this context, cascade cyclizations turned out to be

especially effective in which polyynes serve as starting materials.^[14] As an example, the well-known gold-catalyzed indole synthesis from Utimoto et al. served as a first step of a cascade reaction, in which this nucleophilic unit was further transferred to a larger π -system by one or more additional alkyne moieties that react in a nucleophilic cascade towards the extended π -systems.^[15] Additionally, bidirectional approaches and cascade cyclizations can be combined, which has already been demonstrated by Yamamoto et al. and our group.^[16] In the present study, we present a new access to π -extended indolocarbazoles by a gold-catalyzed bidirectional tandem cyclization as crucial step. Tetraynes 1a-g, which serve as starting materials for the subsequent gold-catalyzed step, were made accessible by a modular building block principle which opens up a highly variable, convergent synthetic approach towards differently substituted derivatives of the target molecules (Scheme 3).



Scheme 3. Building block principle for the BBICZ-synthesis.

The diamine building block **A** was synthesized through a modified literature procedure from Lepoittevin *et al.* in three steps starting from *p*-diaminobenzene in excellent yield (scheme 4).^[17] This building block acts as the inner core and is therefore part of all BBICZs.



Scheme 4. Synthesis of building blocks A and B.

The diyne-building block **B** was derived from different commercially available 2bromobenzaldehydes (**Ba**) and terminal alkynes (**Bb**). A Sonogashira cross-coupling, followed by a Seyferth-Gilbert homologation with the BestmannOhira reagent or a Corey-Fuchs strategy (for $R^1 = TMS$) delivered this subunit (overall 7 examples). By using the chlorinated 2-bromo-4chloro-benzaldehyde, it was also possible to introduce a hexyl substituent as an example for an alkyl chain at the R²-position through a Suzuki reaction with hexylboronic acid. Based on the availability of many different alkynes and 2bromobenzaldehydes in combination with mild reaction conditions, building block **B** turned out to be the most variable one in our strategy. In accordance with already reported procedures, the R³ substituent from building block C was introduced by a late stage modification of the N-unprotected molecules. Alkyl groups with different chain lengths turned out to be the most suitable units.

By combining the two building blocks **A** and **B** via a bidirectional Sonogashira reaction, tetraynes **1a-g** were achieved in reasonable to excellent yields from 51-88% (scheme 5). Only in the case of **TMS-If** ($R^1 = TMS$, $R^2 = Cl$), the yield dropped down to 27%. Owing to their amino-functionality and their moderate solubility, purification of these π -extended alkyne systems was challenging at first, but simple filtration over a short pad of silica gel and subsequent recrystallisation/precipitation from EA or an EA/PEmixture turned out to be a simple way to furnish the compounds in high purity



Scheme 5. Combination of building blocks A and B via a bidirectional Sonogashira reaction. For **1a** Pd(PPh₃)₄ was used instead of PdCl₂(PPh₃)₂.

The tetraynes themselves might appear as promising materials as well.^[17] Analyzing the optical properties (absorption and emission spectroscopy) of the respective compounds revealed fluorescence quantum yields of up to 68%, indicating potential applicability in organic devices (for absorption and emission spectra see SI). Scheme 6 shows the crucial gold-catalyzed cyclization step of tetraynes 1a-g to Boc-BBICZs 2a-g. In general, 5 mol% of the commercially available IPrAuNTf₂ served as catalyst in 1,2-dichloroethane at 60 °C over night. Overall, 6 new bonds are formed during the reaction in a single step. Products 2a-g were either isolated via common flash column chromatography or, for compounds 2c-f which precipitate due to the formation of the large planar π -system causing low solubility, by simple filtration of the product from the reaction mixture.



Scheme 6. Gold-catalyzed conversion of tetraynes 1a-g. For 1a and 1b 10 mol% IPrAuNTf₂ were used. For TMS-1c, 29% of deprotected 2c was obtained.

It is noteworthy, that it was also possible to synthesize BBICZs with $R^1 = H$ (2c) via the cyclization of the corresponding terminal alkynes. These are of particularly interest, because cross-couplings like Sonogashira reaction are once more feasible at this stage of the sequence. To demonstrate this approach, **1a** was synthesized by a Sonogashira reaction from **1c** with 2 eq of iodobenzene in 74% yield (scheme 7).



Scheme 7. Gold-catalyzed conversion of tetrayne **1c** an further Sonogashira-modification.

Interestingly, the TMS-protected tetrayne **TMS-1c** furnished the desilylated BBICZ **2c** in 29% yield after the gold-catalyzed step. The reason for this fact can be explained by the isolobal-analogy of LAu⁺ and a proton combined by the use of non-dry solvents for the gold catalysis.^[19,20] To cleave the Boc-protection group, which was introduced for synthetic reasons at the beginning of the synthesis, we applied a modified procedure of Cava and Bergman.^[21] This thermal deprotection worked quantitatively under vacuum at temperatures above 200 °C without any solvent. Usually no further purification was needed (scheme 8). Other attempts using more classic deprotection methods like acidic cleavage with TFA or HCl indioxane resulted in difficult workup or low conversion.

The work by Sung *et al.* already demonstrated a dependence of the product solubility from the length of the alkylchain.^[8] In this study, the dodecyl chain gave the best results, hence all synthesized BBICZs were alkylated analogously following Sung's protocol with aqueous NaOH and dodecylbromide in anhydrous DMSO. For **4a**, **4b** and **4e**, THF was used as solvent due to higher solubility of the corresponding starting materials. **3d**, **3f** and **3g** were alkylated using KO'Bu instead of a NaOH solution as

base. Following the same strategy it was also possible to introduce a methyl-group (**4h**). Remarkably, R¹ seems to be crucial for the solubility of **3a-g** as well. For R¹ = Ph and ^{*i*}Pr (**3a**, **3d**), the products are soluble in common organic solvents such as chloroform or dichloromethane, whereas all other non-alkylated BBICZs were only soluble in THF or DMSO. In contrast, all alkylated BBICZs showed a decent solubility in chloroform and dichloromethane. Overall 15 different BBICZs were synthesized in good to excellent yields.

X-Ray structures for BBICZs 3a, 3b, 3d and the alkylated 4a and 4f were obtained.^[22] The solid state molecular structures are in excellent agreement with expected bond lengths and angles.^[8] It should be noted that for the non alkylated **3a-g** in most cases a solvent molecule is part of the determined solid state structure (except for 3d). For 3a the molecules show π - π -stacking of the naphthyl ends between each other, which leads to one-dimensional chains in direction of the molecule plane (Figure 1). In between there is one solvent molecule (DCM). For 3b and 3d no π stacking was observed in the solid state structure. 3b forms parallel columns, but one solvent molecule (DMSO) and the alkylchains prevent decent π stacking. 3d also forms columns; however, molecules are strongly laterally shifted against each other so that there is hardly any π -contact. The alkylated **4a** forms one-dimensional columns perpendicular to the molecular plane with significant π -stacking. 4f shows a similar behaviour.



Figure 1. X-ray structure with π - π -stacking of the naphthyl ends of **3a.** Left: top view, right: side view.



Figure 2. Absorption and emission spectra of **3a-g** (left, in THF) and **4a-h** (right, in DCM). All emission spectra were normalized to the maximum emission signal.



Scheme 8. Boc-deprotection to the final BBICZs 3a-g and alkylation methods to get 4a-h. Method A: aqueous NaOH, benzyltriethylammonium chloride (25 mol%), DMSO; method B: KOtBu (4 eq), DMSO.

Starting material	\mathbb{R}^1	\mathbb{R}^2	Yield of the gold catalysis	Method of alkylation	Yield of the alkylation	
1a	Ph	Н	54%	А	92%	
1b	Hexyl	Н	82%	А	68%	
TMS-1c	TMS	Н	29% ^{a)}	/	/	
1c	Н	Н	74%	А	77%	
				B ^{b)}	60% ^{b)}	
1d	ⁱ Pr	Н	78%	В	88%	
1e	Cyclopentyl	Н	53%	A ^{c)}	58%	
1f	Н	Cl	82%	В	75%	
1g	Н	Hexyl	73%	В	85%	

Table 1. Yields of gold cyclization and final alkylation.

^{a)} 29% of **2c** was obtained. ^{b)} methyl (=4h) by using MeI instead of dodecylbromide. ^{c)} THF was used due to better solubility.

Our next efforts concentrated on the evaluation of the optical and redox properties of the obtained BBICZs **3a-g**, the alkylated BBICZs **4a-h** and the Boc-protected derivatives (2, see Supporting Information). Among themselves, **3a-g** and **4a-h** show quite similar absorption spectra with maxima of

395-406 nm and 417-425 nm, respectively (Figure 2). It is striking that while a hexyl substitution at the 3,11-position of derivatives **3g/4g** leads to the most hypsochromice shift, the same substituents attached to the 6,14-position only have a minor influence on the absorption signal maximum. A similar effect was observed for the fluorescence quantum yields (QY). All 6,14-substituted BBICZs show similar quantum yields varying between 33-37% for **3a-g** and 24-36% for **4a-h**. However, 3,11-substitution has a notable greater influence. **3f/4f** with the electron-withdrawing chloro substituent show the lowest QY (15% for **3f**, 14% for **4f**), while the hexyl-substituent led to the highest yield with 58% (**3g**) and 44%, respectively (**4g**).

Cyclic voltammograms were recorded for all dichloromethane soluble compounds, namely **3a**, **3d** and all alkylated **4a-h** (see Supporting Information for more details). All compounds show two reversible oxidation potentials. For **3a** and **3d**, the second oxidation potential is almost the same (774 mV vs. 739 mV), but a big difference in the first oxidation potential can be detected (125 mV vs. 317 mV). The alkylated compounds **4a-h** show greater differences between both potentials. **4f** and **4a** with an electron-withdrawing chloro, respectively an aryl substituent, have similar and high values for both oxidation states (321-333 mV; 919-934 mV). In contrast the values of the alkyl-substituted (**4b**, **4d**, **4e**, **4g**) vary much stronger (11-240 mV; 646-981 mV).

In order to get a better understanding of substitution effects on optical and electronic properties, theoretical calculations (computational

details see SI) of selected compounds were conducted next, followed by device fabrications of the most notable compounds. Calculation of the optical properties using time dependent density functional theory (TDDFT) illuminated the character of the emitting excited state being mainly unchanged and derived from the parent molecule 3c. Thus, in the case of **3c**, a bright π - π * transition (oscillator strength) of 0.23) constitutes the first excited singlet state, classified as typical the Ls state of Nheteropolycyles,^[23] exhibiting a strongly correlated electron-hole pair (exciton) with a pronounced correlation coefficient of 0.56. The excitation energy (optical gap) for 3c of 3.93 eV is in the UV-A region. The effect of alkylation at the carbon skeleton (e.g. for **3b**) on the photophysical properties is only marginal, except a change in oscillator strength with 3g exhibiting an almost twice as large oscillator strength of the first excited singlet state (0.28)compared to 3b (0.14). The difference in the coupling of the S1 and S0 states is in line with the experimental findings of an increased quantum yield for the 3,11-substitution pattern in contrast to the 6,14-position. The addition of additional π -systems as substituents, i.e. in **3a**, results mainly in the reduction of the exciton binding energy (difference between fundamental and optical gap) from 2.15 eV (3c) to 1.99 eV. An alkyl substituent (3d) shows the same trend, but less pronounced, with an exciton binding energy of 2.04 eV. Generally, the alkylation of the amino groups (4a and 4d) leads to a decreased exciton binding energy (1.95 eV and 1.98 eV) as well. as a smaller optical gap (3.78 eV and 3.80 eV).

Table 2. Overview of quantum yield (QY), photophysical and electrochemical properties of **3a-g** and **4a-h**, including theoretical and device properties of selected BBICZs. $\lambda_{abs, max} = maximum$ of the longest absorption wavelength; $\lambda_{em} = maximum$ of the shortest emission wavelength, $E_{g,cal} =$ calculated optical Gap, $IP_{cal} =$ calculated ionization potential, $EA_{cal} =$ calculated electron affinity, $\lambda_{cal} =$ reorganization energy, $FG_{cal} =$ fundamental gap, $\mu^{h} =$ hole transport mobility.

Compound	$\lambda_{abs,max}$	λ_{em}	E _{g,opt}	QY	Ox-pot.	E _{g,cal}	$_{\rm l}$ IP _{cal} / $\lambda_{\rm cal}$ FG _{cal} $\mu^{\rm h}$ [cm		μ ^h [cm ² /Vs	5]	
	[nm]	[nm]	[eV] ^{a)}		[mV] ^{b)}	[eV]	EA _{cal} [eV]	[meV]	[eV]	Silicon substrate	PEN substrate
3a	404	414	2.99	37%	317/774	3.89	6.32/0.43	100.94	5.88	3×10 ⁻⁵	No field effect
3b ^{c)}	405	413	2.95	36%		3.93	6.36/0.34	93.42	6.02	0.1	0.01
3c	397	403	2.99	15%		3.93	6.44/0.37	100.52	6.07	1	0.5
3d	406	413	2.98	34%	125/739	3.91	6.33/0.38	96.48	5.95	0.003	0.008
3e	406	414	2.98	33%							<u> </u>
3f	404	413	2.99	24%							
3g ^{c)}	395	400	3.06	58%		3.94	6.32/0.29	116.23	6.03	0.1	0.05
4a ^{c)}	425	434	2.82	36%	333/934	3.78	6.11/0.38	84.17		0.2	0.02
4b	423	430	2.83	24%	11/646						
4c ^{c)}	420	420	2.88	36%						0.02	0.002
4d ^{c)}	423	425	2.83	30%	240/650	3.80	6.16/0.38	96.30		No field effect	0.001
4e	424	431	2.82	33%	195/875						
4f	422	429	2.86	14%	321/919						
4g	417	425	2.91	44%	130/981						
4h	418	425	2.87	41%							

^{a)} from onset of the absorption spectra. ^{b)} from cyclic voltammographic measurements. ^{c)} alkyl chains were simplified using a methyl group.

The calculations provide an additional puzzle piece to understand structure-property relationships and therefore assist to uncover the potential of deliberate tuning of desired electronic and optical properties. The fundamental gap (single-molecule band gap), being the difference of non-adiabatic (vertical) ionization potential and electron affinity, gives an indication of the energetic barrier of charge transport (creating and eliminating a charge carrier). Therefore, a smaller fundamental gap should have a positive effect on the charge carrier mobility. Furthermore, a decreasing reorganization energy, as defined within Marcus theory (see SI), leads to an acceleration of an electron transfer process. While the fundamental gap turned out to be invariant from the substitution pattern of compounds 3b and 3g (3,11- vs. 6,14-hexyl substitution, Table 3), a significant effect on the reorganization energy was calculated. While the 3,11derivative showed a higher reorganization energy (116.23 meV) compared to 3c (100.52 meV), the 6,14-derivative showed a lower one (93.42 meV). The type of substituent on the 6,14-position with either being an alkyl **3b** or an aryl type substituent **3a**, influences mainly the electron affinity (0.43 eV for **3a** and 0.34 eV for **3b**) leading to a decrease in the fundamental gap in the case of 3a (5.88 eV). The difference in reorganization energy is relatively marginal in comparison with **3b** exhibiting slightly smaller reorganization energy (93.42 meV) compared to **3a** (100.94 meV). Varying the type of alkyl substituent (3b compared to 3d) has insignificant influence on electronic properties indicating the steric load being responsible for varying measured charge carrier mobilities. The most notable change happens in the case of alkylation (methylation) of the amino group, with the **4a** derivative showing a significantly lower reorganization energy (84.17 meV) compared to its non-alkylated counterpart **3a** (100.64 meV). In addition, the ionization potential decreases from 6.32 eV to 6.11 eV which consequently leads to a smaller fundamental gap of 5.73 eV. The same trend can be observed for the alkylated substituents (3d compared to 4d). However, the steric hindrance due to the bulkiness of the 'Pr group (3d/4d) should again be the predominant factor in resulting thin film morphologies and subsequently measured mobilities. Consequently, the substitution pattern of 4a should have the most positive influence, as both, the fundamental gap as well as the reorganization energy are the lowest calculated and the ability for π stacking in aggregation should remedy the increased sterics due the aryl substituent.

To investigate the charge-transport properties of BBICZ **3c** and its alkylated and non-alkylated derivatives **3a**, **3b**, **3d**, **3g**, **4a**, **4c** and **4d**, we fabricated TFTs in the inverted staggered (bottomgate, top-contact) device architecture on heavily doped silicon substrates^[24] and on flexible polyethylene naphthalate (PEN) substrates^[25] (Figure 3). The organic semiconductors were deposited by thermal sublimation in vacuum (for more details see the Supporting Information). All TFTs operate as pchannel transistors. The best TFT performance was obtained for the parent compound BBICZ 3c, which showed effective charge-carrier mobilities of 1 cm²/Vs in TFTs fabricated on a silicon substrate and 0.5 cm²/Vs in TFTs fabricated on flexible PEN. These mobilities are larger compared to the literature value of 0.21 cm²/Vs reported previously for this compound.^[10e] In contrast to the theoretical calculations, which predict carrier mobilities larger than that of 3c for some of the derivatives, our measurements of TFTs based on 3a, 3b, 3d, 3g, 4a, 4c and 4d all yielded mobilities smaller than that of **3c**. For example, hexyl substitution at the carbon skeleton led to a mobility of 0.1 cm²/Vs, regardless of the position of the substituents (3b and 3g). Especially for **3g** we expected a higher value, based on previous results on similar substituted DNTTs (dinaphtho[2,3-b:2,3'-f]thieno[3,2-b]thiophenes).^[26] However, the morphology of the formed layer and so the obtained value are dependent on the fabrication process, which might be improved further.

Phenyl (3a) or isopropyl (3d) substitution at the 6,14-positions of the N-unsubstituted compounds produced mobilities below 0.01 cm²/Vs. Interestingly, a phenyl substitution at the 6,14-positions in combination with a dodecyl substitution at the nitrogen atoms (4a) led to carrier mobilities of $0.2 \text{ cm}^2/\text{Vs}$ on silicon and $0.02 \text{ cm}^2/\text{Vs}$ on flexible PEN substrates. The fact that these mobilities are larger than those of the *N*-unalkylated counterparts (3a and 3d) is consistent with the theoretical predictions which indicate a beneficial effect of Nalkylation. In contrast, this effect was not observed for the isopropyl derivate (4d), which completely falls out of the series with a carrier mobility of just 0.001 cm²/Vs on PEN and without yielding a field effect on a silicon substrate.



Figure 3. Above: Schematic cross-section of organic TFTs fabricated on silicon substrates. Below: Schematic cross-section of organic TFTs fabricated on polyethylene naphthalate (PEN) substrates.

For the previously reported 4c we measured a mobility of $0.02 \text{ cm}^2/\text{Vs}$, which is substantially

smaller compared to the value of 1.5 cm²/Vs reported by Sung *et al.* for a transistor based on solutiongrown single-crystals of this compound.^[8] These results serve as a reminder that the specific crystal packing for which theory may predict a large carrier mobility is not always identical to the crystal packing obtained in thin films, especially when these are prepared by vacuum deposition, which typically provides less control over the crystallization process than some solution-based deposition methods. In other words, while vacuum deposition can yield high mobilities for molecules with a simple rod-like shape (such as 3c), it is often less suitable for molecules with sterically demanding substituents, which means that some of the BBICZ derivatives presented here might perform better if processed using an optimized solution-based protocol. Nevertheless, the fact that we measured carrier mobilities between 0.1 and 1 cm²/Vs for four different compounds (**3b**, **3c**, **3g**, **4a**) confirms that BBICZ is indeed an interesting molecular motif for future device-fabrication efforts.



Scheme 9. Overview of BBICZs used for fabrication of TFTs.

Conclusion

We present a new highly modular, bidirectional synthetic strategy to π -extended indolocarbazoles via a variable building block principle. The starting materials for this route are easily accessible by wellknown procedures. Bidirectional Sonogashira crosscoupling, followed by gold catalysis as a key step and a final quantitative thermal deprotection, provides access to BBICZs in very good yields. In total, 13 new BBICZ derivatives were synthesized, and their optical, electronic and redox properties were studied. The solid-state structures of some of the compounds were also obtained. Based on these BBICZs, we analyzed a number of potentially useful structureproperty relationships. The effects of different substitution patterns on the electronic properties of the molecules were studied theoretically and by fabricating TFTs, in which we measured carrier mobilities up to $1 \text{ cm}^2/\text{Vs}$. The measurements confirmed some of the trends predicted by the theoretical calculations regarding the effect of certain substitution patterns on the charge-carrier mobility, such as the beneficial effect of N-alkylation. In general, however, we measured smaller carrier mobilities in the substituted BBICZs compared to the unsubstituted parent compound 3c, which is partly in contradiction to the results of the theoretical analysis. This might be due to the fact that certain substitution patterns make it difficult, if not impossible, to obtain favorable thin-film morphology by vacuum а

deposition. Such compounds may provide better performance when processed into single-crystals or from solution, much like TIPS pentacene for which the best mobilities obtained by solution processing are significantly larger than the best mobilities obtained by vacuum deposition. More importantly, the modular synthetic approach presented here will greatly accelerate the rapid screening of this class of compounds for materials science. Further screenings of this class of compounds is ongoing in our laboratories.

Experimental Section

General Procedure for the Gold Catalysis

1.00 eq of the corresponding alkyne was dissolved in DCE. 5 mol% IPrAuNTf₂ were added and the mixture was stirred at given temperature for the given time until TLC showed full conversion. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography.

General Procedure for the thermal Boc deprotection

In a flask with vacuum-connection the Boc-protected BBICZ was heated up to 200-220 °C on a vacuum of $5*10^{-3}$ mbar for 3-5 h. The progress of the reaction could be determined by colour change and meantime decrease of the applied vacuum.

Di-tert-butyl 6,14-diphenylbenzo[*a*]benzo[6,7]indolo[2,3-*h*]carbazole-8,16-dicarboxylate (2a): According to the general procedure, 1.00 eq of the corresponding tetrayne (100 mg, 141 μ mol) was dissolved in 20 mL DCE and 10 mol% IPrAuNTf₂ (12.2 mg, 14.1 μ mol) were added to the solution. After stirring over 3 d at 60 °C, the mixture was treated according to general procedure (silica gel, PE:EA = 50:1). A beige solid was obtained (54.0 mg, 76.2 μ mol, 54%).

Mp.: decomp. >192 °C; R_f: 0.27 (silica gel, PE:EA = 10:1); IR (ATR): $\hat{\nu}$ [cm⁻¹] = 3056, 2979, 2932, 1731, 1495, 1438, 1392, 1368, 1339, 1286, 1254, 1144, 1122, 1065, 878, 852, 832, 784, 864, 742, 698, 643, 617; ¹H NMR (CD₂Cl₂, 600.2 MHz): δ [ppm] = 1.49 (s, 18H), 7.52-7.57 (m, 4H), 7.62-7.64 (m, 6H), 7.67 (s, 2H), 7.72-7.74 (m, 4H), 7.97 (d, ³J_{H-H} = 7.6 Hz, 2H), 8.18-8.19 (m, 4H); ¹³C NMR (CD₂Cl₂, 150.9 MHz): δ [ppm] = 28.0 (q, 6C), 84.8 (s, 2C), 107.8 (d, 2C), 122.1 (s, 2C), 123.0 (s, 2C), 125.2 (d, 2C), 125.4 (d, 2C), 125.5 (s, 2C), 126.1 (d, 2C), 126.5 (d, 2C), 128.5 (d, 2C), 152.0 (d, 2C), 129.2 (d, 4C), 129.7 (d, 4C), 133.3 (s, 2C), 152.0 (s, 2C); HRMS (MALDI+): C₄₈H₄₀N₂O₄⁺, calculated: 708.2983 [M⁺], observed: 708.2983 [M⁺]; UV/VIS (DCM, 2.20 µg/mL): λ[nm] (logε) = 238 (4.87), 272 (4.79), 298 (4.71), 335 (4.74), 348 (4.79), 365 (4.62), 380 (4.43); Fluorescence (DCM): λ_{Anr} = 380 nm, λ_{max} = 394 nm; Quantum yield: Φ = 52.5%.

6,14-Diphenyl-8,16-dihydrobenzo[a]benzo[6,7]-

indolo[2,3-*h***] carbazole 3a:** According to the general procedure, the Boc-protected BBICZ (137 mg, 193 μ mol) was heated up to 200 °C for 4 h. The deprotected BBICZ was obtained as yellow solid in quantitave yields (98.2 mg, 193 μ mol).

Mp.: >300 °C; IR (ATR): \hat{v} [cm⁻¹] = 3429, 3052, 3027, 1566, 1520, 1493, 1452, 1398, 1370, 1343, 1309, 1280, 1225, 1152, 1103, 1072, 1027, 935, 911, 838, 782, 766, 740, 701, 670, 615; ¹H NMR (CD₂Cl₂, 600.2 MHz): δ [ppm] = 7.49 (s, 2H), 7.55-7.57 (m, 4H), 7.60-7.63 (m, 4H), 7.65-7.67 (m, 4H), 7.77-7.79 (m, 4H), 8.01 (d, ³J_{H-H} = 8.0 Hz, 2H), 8.16 (d, ³J_{H-H} = 8.0 Hz, 2H), 8.88 (s, 2H); ¹³C NMR (CD₂Cl₂, 150.9 MHz): δ [ppm] = 102.7 (d, 2C), 116.4 (s, 2C), 120.5 (s, 2C), 120.6 (d, 2C), 120.9 (d, 2C), 123.2 (s, 2C), 125.8 (d, 2C), 129.8 (d, 4C), 132.5 (s, 2C), 135.1 (s, 2C), 136.9 (s, 2C), 137.2 (s, 2C), 141.8 (s, 2C); HRMS (DART+): C₃₈H₂₅N₂⁺, calculated: 509.2012 [M⁺+H], observed: 509.2005 [M⁺+H]; UV/VIS (THF, 6.10 µg/mL): λ[nm] (logε) = 238 (4.69), 274 (4.72), 320 (4.57), 342 (4.74), 355 (4.77), 391 (4.16), 410 (4.10); Fluorescence (DCM): λ_{Anr} = 400 nm, λ_{max} = 414 nm, 439 nm, 464 nm; Quantum yield: Φ = 36.8%.

Acknowledgements

The authors are grateful to funding by the DFG (SFB 1249- N- Heteropolyzyklen als Funktionsmaterialien).

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