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# Azaindolo[3,2,1-*jk*]carbazoles: New Building Blocks for Functional Organic Materials.

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Abstract: The preparation and characterization of twelve azaindolo[3,2,1-jk]carbazoles is being presented. Ring closing C-H activation allowed for the convenient preparation of six mono and six twofold nitrogen substituted indolo[3,2,1-jk]carbazole derivatives whereupon ten of the materials have not been described in literature The detailed photophysical and before. electrochemical characterization of the developed materials revealed a significant impact of the incorporation of pyridine like nitrogen into the fully planar indolo[3,2,1-jk]carbazole backbone. Furthermore, the nitrogen position decisively impacts intermolecular hydrogen bonding and thus the solid state alignment. Ultimately, the versatility of the azaindolo[3,2,1-jk]carbazoles scaffold suggests this class of materials as an attractive new building block for the design of functional organic materials.

## Introduction

The development of π-conjugated small molecules with tailored molecular properties has been one of the major driving forces for the rapid development of the field of organic electronics over the last decades.<sup>1-2</sup> In particular small to medium sized polycyclic (hetero)aromatic molecules with a defined molecular structure are of tremendous importance.<sup>2-6</sup> Accordingly, many materials based on these building blocks have been developed for applications in Organic Light Emitting Diodes (OLEDs), 2.7-12 Organic Field Effect Transistors (OFETs), 1-2,6-7,13-15 Organic Photovoltaics (OPVs),<sup>2,16-19</sup> and sensing technology<sup>11,20-22</sup> to name a few. As a consequence, there is an ongoing quest for novel fused aromatic moieties to fulfill the particular requirements of the respective technological application.<sup>2-3,12</sup> Recently we have introduced indolo[3,2,1-jk]carbazole (ICz) as new building block for optoelectronic materials.<sup>23-26</sup> ICz can be considered a fully planarized derivative of triphenylamine (TPA). Although arylamines are widely employed as electron donating moieties, reports on the application of ICz have been scarce for a long time,27-29 owing to the elaborate preparation of the planarized scaffold (e.g. vacuum flash pyrolysis).<sup>30-31</sup> However, a

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new synthetic strategy based on modern C-H activation renders the wider application of this building block possible.23,32 Compared to TPA and phenylcarbazole (PCz) ICz is a weaker electron donor (Chart 1). Owing to the increasing planarization, the electron donating power of the triarylamines significantly decreases from TPA to PCz and ICz. This gradual decrease of donor strength is due to the contribution of the lone pair of the nitrogen to the aromaticity of the pyrroles formed by planarization. Therefore, the lone pair is tighter bound to the arylamine core and less prone to be delocalized in a donoracceptor molecule.<sup>24</sup> Effectively, the ICz moiety can exhibit light acceptor properties itself as evidenced in bipolar host materials.<sup>23,33</sup> Furthermore, the ICz building block has been utilized as weak electron acceptor in thermally activated delayed fluorescent (TADF) emitters.<sup>34</sup> Increasing the electron accepting strength by substitution of the ICz scaffold with electron withdrawing cyano groups enabled the preparation of pure blue TADF emitters.35

Based on these results and the growing interest regarding the application of the indolo[3,2,1-jk]carbazole as building block for optoelectronic materials, we set out to further expand the concept of planarization to intrinsically modulate the acceptor strength by incorporation of electron withdrawing pyridine like nitrogen atoms into the ICz moiety (Chart 1; henceforth the atoms in the nitrogen substituted ICzs (NICzs) will be numbered according to the original numbering of ICz, whereby the numbers specify the positions of nitrogen atoms). The concept of heteroatom doping is widely employed in silicon based semiconductor technology. Analogously, the incorporation of heteroatoms into polycyclic aromatic scaffolds has been demonstrated to effectively modify the photophysical and electrochemical properties of the parent material.<sup>36-37</sup> In particular nitrogen incorporation into acenes has been successfully realized to induce *n*-type charge transport properties in materials for OFET applications.38-40 Moreover, carbolines, which contain an electron deficient pyridine unit, were successfully employed as electron transporting units in host materials for efficient phosphorescent OLEDs.<sup>41-42</sup> Notably, the exact position of the nitrogen atom within the carboline scaffold significantly impacted the molecular properties of the materials and the device efficiency.42-43

Besides the electronic effects, also the structure directing potential of nitrogen atoms by means of weak CH…N hydrogen bonds can be employed to induce intra-<sup>44-45</sup> or intermolecular<sup>46-47</sup> interactions in order to control optical or electronic properties of the organic materials.<sup>48</sup>

Consequently, the NICzs are an interesting class of materials. A reliable synthetic access to this scaffold would allow for the intriguing possibility to fine-tune the molecular properties of optoelectronic materials by the subtle variation of nitrogen

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Chart 1. Schematic representation of the concept of planarization of the triarylamine framework and nitrogen incorporation to control donor and acceptor strength.

position and content of the NICz building block. Notably, three NICz derivatives have already been prepared, namely **5NICz**, **7NICz**, and **7,9NICz**, which are accessible as single regioisomers by vacuum flash pyrolysis.<sup>49</sup> However, all other NICzs are unknown to literature.

In this work we present a comprehensive synthetic approach towards all possible mono-, as well as six twofold substituted NICzs employing a convenient C-H activation reaction. This strategy allows control of the substitution pattern of the NICz by choice of substrate as well as the regioselectivity of the ring closing reaction by electronic manipulation of the nitrogen atom by oxidation. Ultimately, our approach enables the preparation of a full set of NICz building blocks with tunable photophysical and electrochemical properties.

### **Results and Discussion**

#### **Precursor synthesis**

Compared to plain ICz, the preparation of the substrates for C-H activation towards NICz proved to be more challenging, owing to altered reactivity, stability, and availability of the required substituted pyridines. Furthermore, the issue of regioselectivity during the ring closing step arises as a result of the

desymmetrization of the ICz scaffold by nitrogen incorporation. Therefore, we opted to investigate different approaches for the synthesis of these precursors (Scheme 1). These different strategies allow not only for the convenient synthesis of the required precursors but also pave the way for the future preparation of substituted NICzs as well as for the incorporation of the NICz moiety into larger  $\pi$ -conjugated systems. The pursued approaches can be divided into two groups and the results of the respective reactions towards NICz precursors are summarized in Table 1.

The first strategy relies on the establishment of a carbazole unit attached to a halogen substituted pyridine. Notably, the outcome of the cyclization reaction for these precursors is solely determined by the substitution pattern of the pyridine. Accordingly, this strategy allows for the preparation of NICzs with the nitrogen atom incorporated in the peripheral benzene unit of the ICz scaffold (position 4-7). The most straightforward preparation of the respective precursors is a nucleophilic aromatic substitution of a properly substituted dihalogenated pyridine (Scheme 1). Following this approach the bromoprecursors bromo-**5PCz** and bromo-**7PCz** were obtained in 69 and 37% yield by heating the according bromochloropyridines and carbazole in the presence of a base (Table 1). The two remaining carbazole precursors bromo-**4PCz** and bromo-**6PCz**,



Scheme 1. Synthetic approaches towards precursors for C-H-activation; carbazole and carboline strategy<sup>a</sup>.

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precursor	method <sup>[a]</sup>	halogen	yield
	condensation	X=Br	52%
	Buchwald-Hartwig	X=Br	-
X 4PCz	substitution	X=Br	[b]
Ň	substitution	X=CI	69%
	condensation	X=Br	32%
N N	Buchwald-Hartwig	X=Br	81%
X 5PCz	substitution	X=Br	69%
N	substitution	X=CI	95%
	condensation	X=Br	-
N N	Buchwald-Hartwig	X=Br	67%
x 6PCz	substitution	X=Br	_[c]
Ň	substitution	X=CI	57%
	condensation	X=Br	39% <sup>[d]</sup>
N N	Buchwald-Hartwig	X=Br	4%
X 7PCz	substitution	X=Br	37%
	substitution	X=CI	94%
X X X X X X X X X X X X X X X X X X X	substitution	X=Br	86%
X SPCb	substitution	X=Br	82%
	substitution	X=Br	92%
X X X X X X X X X X X X X X X X X X X	substitution	X=Br	34%

 Table 1. Synthesis of the precursors for C-H activation towards mono substituted NICzs

[a] Reaction conditions: condensation: 2,5-dimethoxytetrahydrofuran (4 eq.), AcOH, reflux; Buchwald-Hartwig amination: 2,2'-diiodo-1,1'-biphenyl (1 eq.), NaOtBu (6 eq.), Pd<sub>2</sub>(dba)<sub>3</sub> (2 mol%), dppf (4 mol%), toluene, reflux; nucleophilic aromatic substitution towards PCzs: dihalogenated pyridine (1 eq.), Cs<sub>2</sub>CO<sub>3</sub> (1.1 eq.), DMF, 130 °C, and nucleophilic substitution towards PCbs: 1-bromo-2-fluorobenzene (2 eq.), Cs<sub>2</sub>CO<sub>3</sub> (2 qc.), DMF, 130 °C. [b] Chloro-**7PCz** was isolated with a yield of 35%. [c]Chloro-**5PCz** was isolated with a yield of 37%. [d] Containing inseparable byproducts.

however, could not be prepared using this method. Instead, nucleophilic substitution occurred in the more activated 2 and 4 positions of the pyridines, yielding chloro-**7PCz** and chloro-**5PCz** in low yields. Therefore, we employed brominated aminopyridines as alternative substrates (Scheme 1) and bromo-**4PCz** could be obtained by condensation of 3-amino 2bromopyridine and three molecules of 2,5dimethoxytetrahydrofuran<sup>50</sup> with a yield of 52%. In the case of bromo-**6PCz** the carbazole moiety was formed by a Pd catalyzed Nozaki type Buchwald-Hartwig amination.<sup>51</sup> Notably, the condensation reaction did not yield bromo-**6PCz** and the Nozaki approach failed in the preparation of bromo-**4PCz**. To fully explore the accessibility of the carbazole precursors we employed these two methods also for the preparation of bromo-**5PCz**, which was obtained in good yields from both reactions, as well as bromo-**7PCz**, which could not be successfully prepared following these approaches.

The second strategy employs the four different carboline derivatives as starting materials (Scheme 1). The corresponding four carboline-based NICz precursors (PCbs) could be prepared by nucleophilic aromatic substitution of 1-bromo-2fluorobenzene and were obtained in excellent yields (82-92%) with the exception of bromo-7PCb (34%; Table 1). In contrast to the PCz precursors, the unsymmetrical nature of the carbolines entails two possible sites at which ring closure may occur in the case of 4PCb, 5PCb and 6PCb. Whereas reactions at the benzene unit of the carbolines would yield the same products, which are available through the carbazole strategy, ring closure at the pyridine unit would give the two remaining NICz derivatives. Notably, the site selectivity and ratio of product is determined by the electronic demand of the ring closing reaction and thus may be significantly influenced by the nitrogen position. Furthermore, we aimed to explore the substrate scope of the C-H activation. Accordingly, the chloro-PCz precursors were prepared starting from carbazole and the corresponding chlorofluoropyridines. In contrast to the bromo-precursors all of the chloro-derivatives could be obtained by nucleophilic aromatic substitution in acceptable to excellent yield (57-95%; Table 1).

### **C-H** activation

During initial experiments regarding the ring closing reaction by C-H activation, we encountered difficulties with reproducibility of reaction time and yields of the reactions. Thus, we decided to revisit the reaction conditions of this Pd-catalyzed key step on the example of the reaction towards **4NICz** starting from bromo-**4PCz** (Scheme 2, Table 2).



Scheme 2. Model system for the optimization of the reaction conditions; molecular structure of (NHC)Pd(allyl)Cl.

First, various catalytic systems (10 mol%) were investigated applying a catalyst based on an *N*-heterocyclic carbene ligand  $((NHC)Pd(allyl)Cl)^{52-53}$  (Scheme 2) as well as different phosphine ligands, which have been previously applied in the preparation of **ICz**<sup>23,32</sup> or other intramolecular arylation reactions.<sup>54-56</sup> Yields were determined using GC (FID). As depicted in Figure 1,

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Figure 1. C-H activation of bromo-4PCz towards 4NICz applying different catalysts. Reactions conditions: bromo-4PCz (0.025 mmol),  $K_2CO_3$  (2 eq.), catalyst (10 mol%) and ligand (12 mol%: NHC, dppf; 22 mol%: PPh<sub>3</sub>, PCy<sub>3</sub>\*HBF<sub>4</sub>, JohnPhos), DMA, 130 °C.

(NHC)Pd(allyl)Cl provides by far the best results with over 90% yield within 90 minutes. In comparison, the use of phosphine based catalysts resulted in longer reaction times and lower yields (47-68%) due to increased formation of dehalogenated byproduct (Figure S63, supporting information). Notably, also the precursor salt of the ligand, (1,3-bis(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium chloride), could directly be applied in combination with Pd(OAc)<sub>2</sub><sup>26</sup> to give the product in 76% yield

after 120 min. Variations of base (Figure S64, support information) and solvent decreased the reaction rate. In addition, the reactivity of (NHC)Pd(allyl)Cl towards the chlorine precursor chloro-**4PCz** was investigated to explore the scope of the reaction. Notably, **4NICz** was obtained in 68% yield after 180 min. In contrast, starting from chloro-**4PCz** PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> gave **4NICz** with a yield of only 10% after 180 min (Figure S65, supporting information), highlighting the importance of the NHC ligand. Accordingly, the combination of (NHC)Pd(allyl)Cl and K<sub>2</sub>CO<sub>3</sub> in DMA represents the optimum reaction conditions. Hence, we decreased the catalyst loading to establish the final reaction conditions with a catalyst loading of 5 mol% (Figure S66, supporting information).

First experiments on the 1 mmol scale were performed using the carbazole precursors (Table 3). To our delight, the conversion of the bromo-substrates smoothly delivered all four NICz derivatives (4NICz, 5NICz, 6NICz, 7NICz) in excellent yields of 80-96% after reasonable reaction times (4-8 h). Inspired by this initial success we investigated the reactivity of the respective chloro precursors. Surprisingly, the results obtained for the chloro substrates in these quantitative experiments exceeded those of the bromo precursors. This finding is in opposition to previous results, which suggest a lower reactivity of chloro substrates in the C-H activation step towards ICz.23 Nevertheless, 4NICz, 5NICz, 6NICz and 7NICz were obtained from the corresponding chloro-PCzs in excellent yields between 92 and 98% after a short reaction time of 4 h (Table 3). In a next step we investigated the reactivity of the carboline precursors (PCbs, Table 4). In contrast to the carbazole strategy, two.

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entry	catalyst	ligand	base <sup>[a]</sup>	solvent <sup>[b]</sup>	temperature [°C]	time [min] <sup>[c]</sup>	yield [%] <sup>[d]</sup>
1	Pd(OAc) <sub>2</sub> <sup>[e]</sup>	NHC•HCI <sup>[f]</sup>	K <sub>2</sub> CO <sub>3</sub>	DMA	130	120 (91%)	76
2	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>[e]</sup>	-	K <sub>2</sub> CO <sub>3</sub>	DMA	130	60	68
3	Pd(OAc) <sub>2</sub> <sup>[e]</sup>	PPh <sub>3</sub> <sup>[g]</sup>	K <sub>2</sub> CO <sub>3</sub>	DMA	130	60	59
4	Pd(OAc) <sub>2</sub> <sup>[e]</sup>	dppf <sup>[f]</sup>	K₂CO₃	DMA	130	35	50
5	Pd(OAc) <sub>2</sub> <sup>[e]</sup>	PCy <sub>3</sub> •BF <sub>4</sub> <sup>[g]</sup>	K <sub>2</sub> CO <sub>3</sub>	DMA	130	120 (65%)	47
6	Pd(OAc) <sub>2</sub> <sup>[e]</sup>	JohnPhos <sup>[g]</sup>	K <sub>2</sub> CO <sub>3</sub>	DMA	130	120	47
7	Pd(OAc) <sub>2</sub> <sup>[e]</sup>	-	K <sub>2</sub> CO <sub>3</sub>	DMA	130	120 (71%)	36
8	(NHC)Pd(allyl)Cl <sup>[e]</sup>	-	K <sub>2</sub> CO <sub>3</sub>	DMA	130	60	93
9	(NHC)Pd(allyl)Cl <sup>[e]</sup>		Na <sub>2</sub> CO <sub>3</sub>	DMA	130	180	94
10	(NHC)Pd(allyl)Cl <sup>[e]</sup>		K <sub>3</sub> PO <sub>4</sub>	DMA	130	60	84
11	(NHC)Pd(allyl)Cl <sup>[e]</sup>	-	Et <sub>3</sub> N	DMA	130	1200 (76%)	10
12	(NHC)Pd(allyl)Cl <sup>[e]</sup>	-	K <sub>2</sub> CO <sub>3</sub>	toluene	110	150 (6%)	3
13	(NHC)Pd(allyl)Cl <sup>[e]</sup>	-	K <sub>2</sub> CO <sub>3</sub>	dioxane	100	150 (4%)	1
14	(NHC)Pd(allyl)Cl <sup>[h]</sup>		K <sub>2</sub> CO <sub>3</sub>	DMA	130	360	73
15	(NHC)Pd(allyl)Cl <sup>[i]</sup>	-	K <sub>2</sub> CO <sub>3</sub>	DMA	130	1200 (93%)	52
16 <sup>[j]</sup>	(NHC)Pd(allyl)Cl <sup>[e]</sup>	-	$K_2CO_3$	DMA	130	180 (72%)	68
17 <sup>[j]</sup>	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>[e]</sup>	-	K <sub>2</sub> CO <sub>3</sub>	DMA	130	180 (47%)	10

Table 2. Screening of the reaction conditions for the ring closure towards 4NICz employing bromo-4PCz (entry 1-15) or chloro-4PCz (entry 16-17).

[a] 2 eq.; [b] the water content of DMA was adjusted to 3000 ppm; [c] reaction time until ≥97% conversion unless noted otherwise in bracket; [d] determined by GC-FID analysis; [e] 10 mol%; [f] 12 mol%; [g] 22 mol%; [h] 5 mol%; [i] 2 mol%; [j] starting from chloro-4PCz.

precursor	product	halogen	time	yield
		X=Br	6 h	93%
4PCz	4NICz	X=CI	4 h	98%
		X=Br	4 h	96%
5PCz	5NICz	X=CI	4 h	97%
		X=Br	4 h	80%
6PCz	6NICz	X=CI	4 h	92%
		X=Br	8 h	84%
7PCz	7NICz	X=CI	4 h	96%

 Table 3. C-H activation towards mono substituted NICzs starting from carbazole precursors.

possible products can be formed in the C-H activation step from the PCbs. While the formation of a product mixture is a clear disadvantage, 1NICz and 2NICz are only accessible via this strategy. Precursors 4PCb, 5PCb and 6PCb were all converted towards ring-closed NICzs. In contrast, hardly any conversion of 7PCb was observed and starting material along with small amounts of dehalogenated byproduct was recovered even after prolonged reaction times of 96 h. We assume that the ortho nitrogen of **7PCb** can stabilize the initially formed Pd-complex and thus prevents productive ring-closure. Analyzing the products formed in the C-H activation, we determined that ring closure regioselectively occurred at the 4 and 3 position of the pyridine ring in the case of 4PCb and 5PCb, respectively. Accordingly, 1NICz and 4NICz were obtained from 4PCb in a ratio of 3:1 after separation, whereas 5PCb yielded 2NICz and 5NICz in a ratio of 6.9:1. Notably, the separation of the regioisomers was achieved by simple column chromatography. Thus, the two missing NICz regioisomers could be indeed prepared using the carboline strategy. In the case of 6PCb, ring closure on the benzene ring of the carboline was preferred, presumably owing to the highly electron poor alternative 2 position of the pyridine. Therefore, 1NICz and 6NICz were formed in a ratio of 1:3.9.

Inspired by these results, we wondered if we could control the regioselectivity of the C-H activation by manipulation the electron density of the pyridine unit. Thus, we oxidized the nitrogen atom of the pyridine to increase the electron density of the aromatic ring applying mCPBA yielding the corresponding N-oxides in good to excellent yields (61-90%). Employing these N-





[a] Overall yield of ring-closed products (ratio determined by <sup>1</sup>H NMR) and isolated yields in bracket. For reactions starting from N-oxides yields over two steps (C-H activation and reduction) are given; [b] not determined owing to overlapping signals from small amounts of dehalogenated byproduct.

oxides we indeed observed an increased tendency for the ringclosure to occur on the now more electron rich pyridine rings (Table 4), while high yields (between 89 and 92%) were retained. Reduction of the N- oxides was smoothly accomplished using Fe powder in AcOH with yields ranging from 76 to 97%. In the case of **4PCb** the ratio of isolated **1NICz** to **4NICz** could be significantly shifted towards **1NICz** upon starting form **4PCb-Ox** (3:1 vs. 19.3:1), whereat the ratio of the products remained roughly the same for **5PCb** and **5PCb-Ox**. Most strikingly, however, the regioselectivity could be inverted for **6PCb**. While **6NICz** is the favored product starting from **6PCb**, predominately **1NCz** is formed from **6PCb-Ox** (**1NICz:6NICz=**4.4:1). This

Table 5. C-H activation towards twofold substituted NICzs.



<sup>[</sup>a] Overall yield of ring-closed products (ratio determined by 1H NMR) and isolated yields in bracket. For reactions starting from N-oxides yields over two steps (C-H activation and reduction) are given; [b] not determined owing to overlapping signals from small amounts of dehalogenated byproduct.

remarkable result underlines the impact of the electronic layout of the carboline systems on the outcome of the ring closing step. Notably, this oxidation-reduction sequence was established as a powerful tool to control the regioselectivity of the C-H activation reaction, which is of particular interest for the synthesis of more complex and/or extended annulated systems (see section 2.1.3).

#### Diazaindolo[3,2,1-jk]carbazoles

Inspired by the successful preparation of all mono substituted NICz regioisomers, we explored the potential to further increase the electron deficiency of the ICz scaffold by twofold pyridine incorporation. Owing to the numerous possibilities to position two nitrogen atoms in the annulated system we limited these investigations to substrates that can yield symmetrically substituted products 4,12NICz, 5,11NICz and 6,10NICz (Table 5). The according precursors 4,12PyCb, 5,11PyCb and 6,10PyCb were prepared by nucleophilic substitution of suitably substituted dihalogenated pyridines with the respective carbolines. To our delight also these precursors underwent smooth ring-closure under the optimized conditions, giving the twofold substituted NICzs in high overall yields. In analogy to the mono substituted compounds, ring-closure occurred on the pyridine ring in the case of 4,12PyCb and 5,11PyCB, preferentially yielding unymmetric 1,4NICz and 2,5NICz, respectively (Table 5). Separation of the regioisomers was accomplished by HPLC on the preparative scale with an acceptable product loss. In contrast 6,10PyCb yielded symmetric 6,10NICz as the major product. Compared to the mono substituted precursor 6PCb the electron deficient 2position of the pyridine ring was disfavored more pronouncedly in 6,10PyCb as symmetric 6,10NICz and unymmetric 1,10NICz were obtained in a ratio of 15.2:1. To control the regioselectivity of the C-H activation we again employed the oxidation-reduction strategy. Indeed, the selectivity could be inverted and 1,10NICz was the preferred product starting from 6,10PyCb-Ox (6,10NICz:1,10NICz=1:12.7). The complete inversion of the regioselectivity decisively underlines the potential of the N-oxide methodology to control the outcome of the ring-closing step.

### Characterization

With all six possible mono substituted NICzs and three symmetric twofold substituted NICzs as well as their respective unsymmetric congeners isolated we investigated the molecular properties of the new building blocks.

### **Photophysical properties**

To investigate the effects of the nitrogen incorporation on the photophysical properties of the synthesized building blocks UV-Vis absorption and fluorescence spectra in dichloromethane (Figure 2), as well as low temperature phosphorescence spectra (Figure 3) were recorded (Table 6). Molar attenuation coefficients are given in Table S1. Plain **ICz** shows a distinct absorption peak at 285 nm which can be attributed to a  $\pi$ - $\pi$ <sup>\*</sup> transition of the conjugated molecular scaffold.<sup>25-26</sup> This peak disappears almost completely with the incorporation of nitrogen in the twofold annulated central benzene ring in **1NICz** and

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**2NICz.** The lowest energy transition of **ICz** can be observed as clear peak at 363 nm with a shoulder at shorter wavelength. In contrast, **1NICz** and **2NICz** show rather broad and weak absorption at longer wavelengths. While **ICz** and **2NICz** have nearly the same absorption onset at approximately 375 nm, the absorption onset of **1NICz** is clearly redshifted to 400 nm.

The isomers with a nitrogen in one peripheral benzene ring show distinct peaks between 280-300 nm. Analogously to ICz, 5NICz and 6NICz exhibit a sharp absorption peak at about 285 nm. 7NICz and 4NICz feature peaks at 286 nm and 290 nm, respectively, but those two compounds also feature additional further redshifted absorption peaks at 297 nm. At longer wavelengths the absorption of 5NICz and 6NICz resemble that of ICz with a distinct peak with a shoulder towards shorter wavelengths and absorption onsets at 359 and 386 nm, respectively. In contrast, 7NICz and 4NICz exhibit broader and weaker absorption with onsets at 366 nm and 375 nm. Notably, nitrogen incorporation and the altered substitution position significantly impacts the electronic layout and thus absorption behavior of the NICz building blocks. Accordingly, the optical bandgap of the mono substituted NICz, which is an important characteristic for practical applications, can be tuned over a range of 0.35 eV from 359 to 400 nm solely by choice of nitrogen position.

The absorption characteristics of unsymmetrically twofold derivatives 1,4NICz and 1,10NICz as well as 2,5NICz clearly resemble those of 1NICz and 2NICz, respectively. This result is in line with the finding that compounds 4-7NICz more closely resemble plain ICz. Thus, nitrogen substitution in the central benzene ring is the decisive factor determining the absorption properties of the twofold substituted derivatives. Notably, the distinct absorption band of 4NICz at 295 nm is also observed for 1,4NICz. The onset of absorption of unsymmetric 1,4NICz is identical to that of 1NICz at 400 nm, while the broad lowest energy transition of 1,10NICz is shifted to longer wavelengths with an absorption onset of 410 nm. In contrast, the absorption onset of unsymmetric isomer 2,5NICz at 353 nm is shifted towards higher energy compared to 2NICz (373 nm). Accordingly, the optical bandgaps of the unsymmetrically twofold substituted derivatives span a larger range of 0.49 eV compared to the mono substituted NICzs.

Symmetric building blocks **4,12NICz**, **5,11NICz** and **6,10NICz** exhibit absorption properties similar to their respective mono substituted congeners. The absorption onset of **4,12NICz** and **5,11NICz** are slightly blueshifted compared to **4NICz** and **5NICz**, while the onset of **6,10NICz** is shifted to somewhat longer wavelength compared to **6NICz**.

**1NICz** and **2NICz** exhibit similar fluorescence characteristics as **ICz**. Analogously to the absorption onset, the emission maximum of **2NICz** displays the same emission maximum at 375 nm as **ICz**, while **1NICz** is distinctly redshifted to 407 nm. In contrast, all isomers with nitrogen substitution in the peripheral benzene ring exhibit a sharper peak maximum as well as a redshifted shoulder. The nitrogen position influences the emission maximum which follow the same order as the absorption onset from **5NICz** (354 nm) to **7NICz** (364 nm), **4NICz** (375 nm) and **6NICz** (384 nm).

The unsymmetric twofold substituted isomers **1,4NICz**, **2,5NICz** and **1,10NICz** all show one broad emission peak. The emission maxima of **1,4NICz** and **1,10NICz** are similar to **1NICz** rather redshifted at 410 nm and 416 nm, respectively. In contrast, **2,5NICz** exhibits an emission maximum at 361 nm, which is blueshifted to that of **2NICz** and closer to the emission of peripheral substituted **5NICz**. Analogously to the absorption properties, **5,11NICz** and **6,10NICz** feature similar emission properties as their respective mono substituted derivatives. Notably, **5,11NICz** exhibits the highest energy emission of the investigated materials with an emission maxima at 345 nm. Unlike the other derivatives, the emission characteristic of **4,12NICz** clearly differs from that of **4NICz**. While the emission maximum of **4,12NICz** is redshifted to 392 nm compared to **4NICz** an additional high energy band at 372 nm emerges.



Figure 2. UV-Vis absorption (full lines) and normalized fluorescence spectra (dotted lines) of ICz and the synthesized NICz building blocks. All spectra recorded as  $5 \,\mu$ M solutions in DCM.

The triplet energy, corresponding to the highest energy phosphorescent transition, of building blocks for organic electronics is a decisive factor in particular for applications in OLEDs.<sup>10</sup> Therefore, phosphorescence spectra of the developed building blocks were recorded. All compounds exhibit vibronically resolved phosphorescence. The phosphorescence

spectra of the NICz isomers with the nitrogen in the peripheral ring are similar to the spectrum of ICz. While the highest energy maximum of 5NICz at 436 nm is the same compared to ICz, this transition is slightly redshifted for 7NICz (439 nm), 4NICz (443 nm) and 6NICz (446 nm). Notably, this redshift occurs in the same order as for the fluorescence. In contrast, 1NICz and 2NICz show clearly different phosphorescence. The first maximum is blueshifted to 428 nm in the case of 2NICz, but redshifted to 445 nm for 1NICz. The spectra of the unsymmetric twofold NICz isomers are clearly impacted by the nitrogens in the central benzene ring, as they show great similarity to the spectra of 1NICz and 2NICz. While 1,4NICz and 1,10NICz have highest energy maxima at 456 nm and 455 nm, 2,5NICz is blueshifted to 429 nm. The spectra of the symmetric twofold isomers are similar to the peripheral mono substituted derivatives. Accordingly, the highest energy vibronic transitions of **5,11NICz** and **4,12NICz** are located at about the same energy as those of 5NICz and 4NICz at 432 nm respectively 442 nm. In contrast, in the case of 6.10NICz this transition (436 nm) is slightly blueshifted compared to 6NICz. Notably, the triplet energies of the NICz derivatives are located between 2.90 and 2.72 eV and therefore suitable for the development of functional



Figure 3. Normalized low temperature phosphorescence spectra (77 K) of ICz and the synthesized NICz building blocks.

organic materials for applications in blue and even deep blue phosphorescent and TADF based OLEDs.  $^{\rm 57}$ 

Summarizing, clear trends for the impact of the different nitrogen substitution positions are found. Substitution of one of the peripheral benzene rings (position 4-7) results in photophysical properties similar to those of plain ICz, whereby the exact energetic localization (blueshift, redshift) of absorption and emission is dependent on the substitution position. Derivatives with symmetric, twofold substitution of the peripheral rings follow these tendencies, albeit the resulting shifts are generally more pronounced. In contrast, substitution of the central benzene ring (position 1 or 2) significantly alters the photophysical behavior, whereby nitrogen incorporation at position 1 leads to a shift towards lower and incorporation at position 2 towards higher energies. In the case of the unsymmetric twofold substituted derivatives with one pyridine like nitrogen in the central and one in a peripheral benzene ring, the effect of the nitrogen in the central benzene ring clearly dominates and those derivatives feature similar properties as 1NICz and 2NICz, respectively.

Table	6.	Electrochemical	and	photophysical	data	of	the	developed
materia	als.							

	- All					
	opt. [eV]	BG <sup>[a]</sup>	λ <sub>max</sub> <sup>[b]</sup> [nm]	<i>Ε</i> <sub>7</sub> <sup>[c]</sup> [eV]	HOMO <sup>[d]</sup> [eV]	LUMO <sup>[d]</sup> [eV]
ICz	3.30		375	2.84	-5.78	-2.27
1NICz	3.10		407	2.79	-6.22	-2.68
2NICz	3.33		375	2.90	-6.28	-2.43
4NICz	3.30		375	2.80	-6.22	-2.57
5NICz	3.45		354	2.84	-6.32	-2.42
6NICz	3.21		384	2.78	-6.23	-2.62
7NICz	3.38		364	2.82	-6.00	-2.46
1,4NICz	3.10		410	2.72	-6.28	-2.84
2,5NICz	3.51		361	2.89	-6.48	-2.58
1,10NICz	3.03		416	2.72	-6.31	-2.85
4,12NICz	3.37		392	2.81	-6.35	-2.70
5,11NICz	3.56		345	2.87	-6.42	-2.54
6,10NICz	3.18		387	2.84	-6.44	-2.75

[a] Optical bandgap determined from the absorption onset measured in DCM solutions (5  $\mu$ M) at room temperature; [b] emission maximum measured in DCM solutions (5  $\mu$ M) at room temperature; [c] determined from the highest vibronic transition in solid solutions of toluene/EtOH (9/1; 0.5 mg/ml) at 77 K; [d] calculated from the onset of the oxidation and reduction peak observed during cyclic voltammetry.

#### **Electrochemical properties**

The exact energetic alignment of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of organic materials is of tremendous importance regarding charge transport in and charge injection into electronic devices. Therefore, cyclic voltammetric measurements were conducted to explore the effects of nitrogen incorporation and the impact of nitrogen position on the frontier molecular orbitals (Figure S67-S73, supporting information). All NICz derivatives exhibited irreversible oxidation, as typically observed for 9*H*-

carbazole and ICz derivatives, owing to the instability of the formed oxidation products.  $^{25,58}$ 

The determined energy values of the HOMOs and LUMOs of the developed NICzs are summarized in Table 6 and selected energy levels are depicted in Figure 4. In general nitrogen incorporation decreased the energy of both orbitals of all compounds compared to **ICz** (HOMO: -5.78 eV; LUMO: -2.27), whereat the effect is slightly more pronounced for the HOMO levels. The HOMO levels of the mono substituted NICzs were decreased by 0.22-0.54 eV, while the LUMO energy levels are lowered by 0.15-0.41 eV. In the case of the twofold substituted NICzs, HOMO and LUMO levels are decreased by 0.50-0.70 and 0.27-0.58 eV, respectively. Notably, the magnitude of this effect is dependent on the exact position of the pyridine nitrogen in the **ICz** scaffold.

For the mono substituted NICz the biggest impact on the HOMO levels is observed for compounds 2NICz (-6.28 eV) and 5NICz (-6.32 eV) with the pyridine nitrogen in para position to the central nitrogen atom. Notably, the effect on the LUMO levels of these two compounds is distinctly weaker and thus 2NICz (-2.43 eV) and 5NICz (-2.42 eV) feature the highest LUMO levels of the mono substituted series. In contrast, the overall effect of nitrogen incorporation is least pronounced for ortho substituted 7NICz. Therefore, within this series 7NICz exhibits the highest HOMO energy of -6.00 eV corresponding to a 0.22 eV decrease compared to ICz and a LUMO level at -2.46 eV. Compounds 1NICz, 4NICz and 6NICz with a meta substitution pattern display similar electrochemical behavior. The LUMO levels of these three compounds are impacted the most by nitrogen incorporation and are decreased to -2.68, -2.57 and -2.62 eV, respectively, while their HOMO levels are located in a narrow range of -6.22 to -6.23 eV between those of the *ortho* and *para* substituted materials.

The influence of the nitrogen position on the electrochemical properties can be rationalized by the exploration of the spatial distribution of the HOMO and the LUMO of the investigated derivatives (Figure 5 and Figure S74-S75, supporting information). HOMO and LUMO levels of the materials were calculated employing density functional theory. As can be seen in Figure 5 significant electron density of the HOMO level of ICz is located on the central nitrogen, as well as C2, C5 and C11 which are located para to the central nitrogen. Analogously, hardly any electron density is located on C1, C3, C6 and C10 which are all located meta to the central nitrogen atom. The distribution of the electron density explains why para nitrogen substitution influences the energetic location of the HOMO levels the most. Indeed, the HOMO level of 2NICz is strongly distorted compared to ICz (Figure 5). The concentration of the electron density on the two benzene rings and the reduction of the spatial extension of the molecular orbital decrease the orbital energy of the HOMO of 2NICz. In contrast, the shape of the HOMO of 1NICz is highly similar to that of ICz and in the case of the meta substituted NICz the decreased orbital energy can be explained by a general inductive effect of the pyridine nitrogen. The electron density of the LUMO of ICz is located virtually exclusively on carbon atoms located meta to the central nitrogen and the annulation positions. This finding explains the significantly decreased energy of the LUMOs of 1NICz, 4NICz and 6NICz. Analogously to the HOMO of 2NICz, a similar distortion of the shape of the LUMO of 1NICz is observed. However, the restriction of the LUMO is less pronounced which is in agreement with the finding that the LUMO energy levels are generally influenced to a slightly lower degree by the nitrogen



Figure 4. Schematic representation of the energy levels of HOMOs and LUMOs of selected materials.



Figure 5. Spatial distribution of the HOMO and LUMO levels of ICz, 1NICz and 2NICz.

incorporation. As expected, the energy levels of the HOMOs and LUMOs are further lowered by the introduction of a second pyridine ring. Compared to ICz the HOMO levels of the twofold substituted NICzs were decreased by 0.50-0.70 eV and the LUMO energy levels are lowered by 0.27-0.58 eV. The same trends as for the mono substituted derivatives were observed. Accordingly, para substituted 2,5NICz exhibits the lowest HOMO energy level among the developed compounds at -6.48 eV while the HOMO level of 5,11NICz is located slightly higher at -6.42 eV. Analogously to 2NICz and 5NICz, the LUMO levels of the twofold substituted derivatives are located at -2.58 and -2.54 eV and thus significantly higher compared to the LUMOs of the meta substituted compounds. The meta substituted derivatives can be divided into two groups. Unsymmetric 1,4NICz and 1,10NICz feature a smaller electrochemical bandgap compared to symmetric 4,12NICz and 6,10NICz. Accordingly, 1,4NICz and 1,10NICz exhibit the lowest LUMO energy levels of -2.84 and -2.85 eV among the developed materials.

#### **Crystal packing**

The arrangement and  $\pi$ - $\pi$  interactions of individual molecules in the solid state can significantly impact the macroscopic photophysical and electronic properties of thin films of organic materials.<sup>59</sup> In particular, CH...N hydrogen bonds can be employed to induce or control specific interactions between molecules and influence their alignment.46-47 Hence, we were interested in the packing of the newly developed NICz molecules as the incorporation of the pyridine like nitrogen atom into the molecular scaffold entails the potential to induce CH---N hydrogen bonding. Therefore, single crystals suitable for X-ray structure determination were grown by recrystallization of 2NICz, 5NICz, 6NICz, 7NICz, 2,5NICz and 6,10NICz. Crystals of 1NICz were only obtained as the acetonitrile solvate. 2NICz, 5NICz and 2,5NICz featured temperature-dependent polymorphism and twinning, which is beyond the scope of this contribution and will be detailed elsewhere.<sup>60</sup> Atoms were labeled as outlined in Chart 1. In the case of more than one crystallographically unique molecules (Z=2), prime characters are added to the atom names.

The molecular packing in the solid state is generally determined by non-classical C-H···N hydrogen bonding.61-62 In these kind of non-classical hydrogen bonds electrostatic interactions are more prominent than covalent bonding.61 Their influence on the structure is not as pronounced as in the case of strong hydrogen bonds. Notably, some of the interactions reported herein feature H...N distances longer than the sum of the van-der-Waals radii [2.75 Å]. If possible, the lone pairs of the N atoms connect to the Hs in 7 and 9 position (Table S2). In a few exceptions, the H atom in 2 position acts as donor. From a topological point of view, the hydrogen-contacts form one-dimensional chains, which usually are connected by  $\pi$ - $\pi$  interactions to layers. The layers in turn are stacked to give the final crystal structure. A more detailed description of the molecular arrangements will be given first for the molecules with N-substitution para to the central N8 atom (2NICz. 5NICz. 2.5NICz), then meta (1NICz. 1.10NICz. 6NICz, 6,10NICz) and finally ortho (7NICz).

**para-N**: The hydrogen bonding of **2NICz** and **2,5NICz** molecules forms straight chains as shown in Figure 6. In both cases, the molecules are located on a (pseudo-)twofold rotation axis. This (pseudo-)symmetry is the crucial feature of the phase transitions described elsewhere.<sup>60</sup> The mutual inclination of adjacent molecules with respect to this axis is determined by the crystal packing: In **2NICz**, the least squares (LS) planes defined by the C and N atoms of the individual aromatic planes of two adjacent molecules are inclined by 63.4°. **2,5NICz**, on the other hand, exists as two polymorphs. The first is isostructural with **2NICz**, whereas in the second, adjacent molecules are perfectly coplanar (adjacent molecules related by a **b+c** lattice translation). In both **2,5NICz** polymorphs, the molecule is 1:1 disordered with respect to the N5 atom which is not involved in hydrogen bonding.



Figure 6. Chains of (a) 2NICz and (b) 2,5NICz molecules, second polymorph, connected by non-classical C—H···N hydrogen bonding. C (grey) and N (blue) atoms are represented by ellipsoids drawn at the 50% probability levels; H atoms by white spheres of arbitrary radius. The hydrogen bonds are indicated by dotted lines.

The chains are in all cases connected to layers by  $\pi$ - $\pi$  interactions. Adjacent chains within these layers are related by an **a** (**2NICz**, **2,5NICz** first polymorph) or a **b** (**2,5NICz**, second polymorph) lattice translation. The distances between the least squares planes of individual molecules of neighboring chains are 3.45 Å in all cases. Neighboring chains of two adjacent layers feature different propagation directions for the two structures

(Figure 7). In the crystals of **2NICz** and the first polymorph of **2,5NICz** the chains are parallel and extend in opposite directions. In contrast, in the second polymorph of **2,5NICz** neighboring interlayer chains are inclined by 42.71° but propagate in the same direction. No notable inter-layer C—H…  $\pi$  interactions are observed in either of the structures.



Figure 7. Packing of chains of 2NICz (a) and 2,5NICz second polymorph (b). Color codes as in Figure 6.

For **5NICz**, analogous chains form in the solid state (Figure 8a). Here, the hydrogen bond acceptor N5 is located off the molecular axis (C2-N8). Accordingly, the H7...N5 and H9...N5 contacts and the molecular axis form angles of approximately 90° and the formed molecular chains adopt a zig-zag pattern. Adjacent molecules in these chains are related by a  $2_1$  screw rotation and are nearly coplanar [angle between LS planes:  $3.55^{\circ}$ ].



Figure 8. a) Chain of **5NICz** molecules in the solid state. b) Packing of **5NICz**. Color codes as in Figure 6.

Again, the chains are connected by  $\pi$ - $\pi$  interactions, whereby adjacent chains are related by inversion symmetry (Figure 8b). The distance between connected molecules is approximately 3.55 Å (a precise value cannot be given because the connected molecules are not perfectly coplanar). The thus formed layers are stacked along [100]. In principle, nitrogen atoms in 2 and 5 position are capable of forming similar C—H…N hydrogen bonds with the Hs in 7 and 9 position. Yet, only N2 is involved in

hydrogen bonding in **2,5NICz**, indicating that this interaction is preferred.

**meta-N**: Concerning the *meta* substituted **1NICz**, only acetonitrile solvate crystals were formed, whereby the N-electron lone pair is directed towards the solvent filled voids of the structure (Figure S76, supporting information). This is a first indication that forming a hydrogen-bond network is more difficult in these cases. The **1NICz** molecules are connected via  $\pi$ - $\pi$  interactions to rods extending along the [100] direction [Adjacent molecules related by an **a** lattice translation; distance of LP planes: 3.41 Å]. These rods are located around the solvent filled voids.

Crystals of **1,10NICz**, on the other hand, consist of two crystallographically independent molecules. These molecules are connected by H2···N10' and H9'···N1 contacts, each molecule of the pair acting as donor and acceptor (Figure 9a). Adjacent molecules are related by a pseudo- $b_{10011}$  glide reflection [the  $P2_1$  structure has pseudo- $Pc2_1b$  symmetry] forming chains extending in the [010] direction. The two crystallographically independent molecules are nearly coplanar [angle between LS planes: 3.65°]. Analogously to **2NICz** and **2,5NICz**, the chains are connected to layers by  $\pi$ - $\pi$ 



Figure 9. Packing of chains of 1,10NICz (a) and side view of chains of 1,10NICz (b) and 2,5NICz (c). Color codes as in Figure 6.

interactions [adjacent chains related by an a lattice translation; distance of LS planes 3.47 Å in both cases]. Notably, the arrangement of the 1,10NICz chains closely resembles the structure formed by 2,5NICz (second polymorph). Chains in neighboring layers propagate in the same direction and are inclined by 56.41° (Figure 9b and 9c). The hydrogen bonding networks in meta substituted 6NICz is complex. Crystals of 6NICz contain two crystallographically independent 6NICz molecules (Z'=2). In contrast to 1,10NICz these molecules are also not related by pseudo-symmetry. Molecules of the first kind are connected by C-H...N hydrogen bonding, whereby each molecule connects to two others, acting as hydrogen-bond donor and acceptor, respectively. Since the donor (H7, H9) and acceptor (N6) atoms are in close vicinity, this is only possible owing to a strong twisting of the two connecting molecules [angle between LS planes: 77.8°; Figure 10a]. The two molecules connecting as donor and acceptor to one twisted

molecule are coplanar (related by a b lattice translation) and their LS planes are spaced by only 3.26 Å, indicating a strong interaction of the  $\pi$  systems (Figure 10b). These fragments form chains extending along the [010] direction. Notably,  $\pi$ - $\pi$  stacking does not occur between adjacent chains but between two molecules of the same chain, which are connected by a third 6NICz molecule, which acts as a hydrogen donor and acceptor for the stacked molecules, respectively (Figure 10a). Therefore, in contrast to the previous cases, the  $\pi$ - $\pi$  interaction does not connect adjacent chains to two-dimensional layers but forms one-dimensional rods extending along [010] by intra-chain  $\pi$ - $\pi$ interaction. For the second kind of 6NICz molecule, a rather short C-H···N contact to a H2 atom is observed. The observed C-H···N angle of 135° indicates a rather weak interaction, which is probably not structure-directing. These weak interactions form chains extending in the [001] direction (Figure 10c). Analogously to **2NICz**, these chains are connected by  $\pi$ - $\pi$ interactions to layers by a b lattice translation with a distance of the LS planes of 3.31 Å.



Figure 10. a) Three 6NICz molecules (molecule 1) connected via C—H…N contacts to a chain fragment and (b) resulting chain. c) Chain of 6NICz molecules (molecule 2) connected via non-structure directing C—H…N contacts. Color codes as in Figure 6.

Thus, in the case of **6NICz**, the  $\pi$ - $\pi$  interaction between the planar molecules results in different packing features for the two crystallographically independent molecules. While intrachain stacking yields one-dimensional rods, interchain stacking leads to two-dimensional layers.

Finally, the whole **6NICz** crystal is built of a stacking of an alternation of two layers of which the first corresponds to the layer formed by the  $\pi$ - $\pi$  stacking of chains of molecule 2 and the second is made of neighboring rods of molecule 1 which are packed by van-der-Waals interactions (Figure S77, supporting information).

In **6,10NICz**, only one of the N atoms is involved in hydrogen bonding. As with **6NICz**, the connected molecules [related by a  $2_1$  screw rotation] are distinctly non-coplanar [angle between LS planes: 53.0°]. In the resulting chains (Figure S78, supporting information), pairs of molecules are again connected by intrachain  $\pi$ - $\pi$  interactions [distance between LS planes: 3.41 Å] forming rods along [100]. Thus, even though topologically (considering hydrogen bonding and  $\pi$ - $\pi$  interactions) the chains are related to one of the **6NICz** chains, the actual geometry of the chains is distinctly influenced by packing effects. The chains are packed in a checkerboard pattern connected only by Vander-Waals interactions (Figure 11).



 $\otimes$  chain direction  $\odot$  chain direction  $\otimes$ 

Figure 11. Packing of 6,10NICz. Each 6,10NICz molecule connects as hydrogen bond donor and hydrogen bond acceptor to two different adjacent 6,10NICz molecules. Color codes as in Figure 6.

*ortho*-N: Finally, in **7NICz**, no notable intermolecular hydrogenbonding interactions are observed, owing to steric shielding of the N in 7-position. Instead, molecules are connected by  $\pi$ - $\pi$  interactions to rods [adjacent molecules related by an **a** lattice translation; distance of LS planes: 3.30 Å]. The rods are packed by van-der-Waals interactions (Figure S79, supporting information).

In summary, the investigated NICzs exhibited a rich crystallization behavior whereat  $\pi$ - $\pi$  stacking and non-classical C-H...N hydrogen bonds proofed to be structure determining factors. While all compounds featured  $\pi$ - $\pi$  stacking of the planar aromatic scaffolds, hydrogen bonds were not formed between molecules of 1NICz and 7NICz. Notably, the sole pyridine like nitrogen of these two compounds is located next to the annulation position and thus not effectively available for hydrogen bonding due to steric reasons. Although the interactions between isolated molecules of the developed compounds are similar, the position of the nitrogen has a decisive impact on the exact packing of the crystals. Thus, depending on the nitrogen position one- or two-dimensional supramolecular arrangements are formed. Compounds lacking hydrogen bonds are organized in rods by  $\pi$ - $\pi$  stacking, which are packed by van-der Waals interactions (1NICz, 7NICz). If hydrogen bonding is possible, chains will be formed which are connected to neighboring chains by  $\pi$ - $\pi$  stacking to form layers (2NICz, 5NICz, 2,5NICz, 1,10NICz). Notably, the propagation direction of chains in adjacent layers is dependent on the nitrogen position. If a linear propagation of the chains in direction of the molecular axis (C2-N8) is not possible owing to the geometrical requirements of the hydrogen bonds, twisted chains will be formed and  $\pi\text{-}\pi$  stacking occurs between molecules of

the same chain (6NICz, 6,10NICz). In such a way the chains are arranged to one-dimensional rods.

## Conclusions

We have described the convenient synthesis of all six possible mono substituted azaindolo[3,2,1-jk]carbazoles as well as three symmetric twofold substituted derivatives and their unsymmetric regioisomers. Notably, the presented C-H activation approach not only allows for the preparation of the azaindolo[3,2,1*ik*]carbazole congeners described in this work but the developed oxidation-reduction strategy enables to control the regioselectivity of the ring closing C-H activation step. Therefore, numerous further twofold substituted regioisomers are accessible employing this method and additional nitrogen incorporation could be realized. We investigated the photophysical and electrochemical properties as well as the solid state interaction of the developed materials and revealed the impact of nitrogen incorporation in different positions of the indolo[3,2,1-jk]carbazole scaffold. Ultimately, we provide synthetic chemists with a toolbox full of NICz building blocks. The established structure properties relationship and the possibility to tune their molecular properties and to control the supramolecular arrangement of individual molecules predestines the class of azaindolo[3,2,1-jk]carbazoles as a novel molecular platform and will guide material scientists in the design of functional organic materials with tailored properties.

## **Experimental Section**

All reagents and solvents were obtained commercially and used without further purification. Anhydrous solvents were prepared by filtration through drying columns. The water content of purchased DMA was determined by Karl Fischer titration using a Mitsubishi CA-21 Moisture Meter and corrected to 3000 ppm for C-H activation screening reactions. As further experiments indicated no significant impact of the water content on the reaction outcome large scale experiments were conducted using unmodified DMA with roughly 100 ppm H<sub>2</sub>O. Screening reactions were performed in glass vials under argon atmosphere in a controlled heating block using argon degassed substrate solutions including 1-methylnaphthalene as internal standard as well as a catalyst solution. All screening experiments were performed three times independently. The depicted results represent the mean of these experiments. Yields of the screening reactions were determined by GC using a Thermo Scientific TRACE 1310 gas chromatograph with dual configuration consisting of two AS 1310 autosamplers, Thermo Scientific TR-5MS columns and FID detectors. Absorption and photoluminescence measurements were conducted using a Perkin Elmer Lambda 750 spectrometer and a PerkinElmer LS 55 fluorescence spectrometer, respectively. DCM solutions (5 µM) were employed for solution measurements while phosphorescence spectra were recorded at 77 K using solid solutions of the materials in toluene/EtOH (9/1; 0.5 mg/ml) with a

delay of 1 ms. Cyclic voltammetry was measured using a three electrode configuration consisting of a Pt working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode and a PGSTAT128N potentiostat provided by Metrohm Autolab B.V. The measurements were carried out in a 0.5 mM solution in HPLC-grade ACN employing Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M) as supporting electrolyte. Prior to the measurements, the solutions were purged with nitrogen for approximately 15 minutes. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction peaks, respectively. The onset potential was determined by the intersection of two tangents drawn at the background and the rising of the oxidation and reduction peaks. Synthetic details are described in the Supporting Information.

**General procedure for C-H activation:** A glass vial was charged with the corresponding halogenated precursor (1 eq.),  $K_2CO_3$  (2 eq.) and (NHC)Pd(allyl)Cl (5 mol%) and flushed with argon. After addition of 10 ml/mmol degassed DMA, the reaction was stirred under argon atmosphere until full conversion at 130 °C (4 h - 8 h). After cooling, the reaction mixture was poured into water and repeatedly extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography.

**Computational details:** DFT calculations were performed using the Gaussian 09 package<sup>63</sup> applying the Becke three-parameter hybrid functional with Lee–Yang–Perdew correlation (B3LYP)<sup>64-65</sup> in combination with Pople basis sets 6-311G(d,p).<sup>66</sup> Geometry optimizations were performed in the gas phase and without symmetry constraints. Orbital plots were generated using GaussView.<sup>67</sup>

crystal diffraction: X-ray diffraction Sinale data of  $1 \text{NICz} \cdot \text{xCH}_3\text{CN}, \quad 2 \text{NICz}, \quad 5 \text{NICz}, \quad 6 \text{NICz}, \quad 7 \text{NICz}, \quad 1,10 \text{NICz},$ 2,5NICz and 6,10NICz (CCDC 1864321-1864328) were collected at T = 100-270 K in a dry stream of nitrogen on a Bruker Kappa APEX II diffractometer system using graphitemonochromatized Mo-Ka radiation ( $\lambda = 0.71073$  Å) and fine sliced  $\varphi$ - and  $\omega$ -scans. Data were reduced to intensity values with SAINT and an absorption correction was applied with the multi-scan approach implemented in SADABS or TWINABS.68 The structures were solved by the dual-space approach implemented in SHELXT^{69} and refined against  $\textit{F}^{2}$  with JANA2006.<sup>70</sup> Non-hydrogen atoms were refined anisotropically. The H atoms connected to C atoms were placed in calculated positions and thereafter refined as riding on the parent atoms. Contributions of disordered solvent molecules to the intensity data were removed for 1NICz using the SQUEEZE routine of the PLATON<sup>71</sup> software suite. 2NICz, 5NICz and 1,10NICz crystallize as twins by pseudo-merohedry. 7NICz forms twins with non-overlapping reflections and was refined against HKLF5 data with information on reflection overlap. The absolute structure of non-centrosymmetric crystals (1NICz·xCH<sub>3</sub>CN, 1,10NICz, 2,5NICz and 6,10NICz) was not determined owing to a lack of resonant scatterers. Molecular graphics were generated with the program MERCURY.72

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Thomas Kader, Berthold Stöger, Johannes Fröhlich, and Paul Kautny\*

Page No. – Page No.

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Page No. – Page No. Title

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