BOOK OF ABSTRACTS

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Modification of Planarized Triarylamines via Nitrogen Incorporation

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Arylamines are widely used electron donating moieties in organic optoelectronic materials. We recently introduced novel bipolar host materials for Phosphorescent Organic Light Emitting Diodes (PhOLEDs) based on oxadiazole electron acceptors and planarized triarylamines as donors. Planarization of the arylamines allowed for the control of the donor properties as increased planarization significantly decreased the donor strength (figure 1, left). Additionally, our investigations also unveiled that beside its decreased donor strength fully planarized indolo[3,2,1-*jk*]carbazole (ICz) possesses weak acceptor character.[1] Furthermore, we investigated ICz based host materials for PhOLEDs with high triplet energies (E_T >2.8eV).[2]
Our current research focuses on the incorporation of additional nitrogen atoms into the ICz framework (figure 2, right) in order to integrate electron poor pyridine into the scaffold to further enhance the acceptor strength. Results from theoretical calculations revealed that incorporation of nitrogen into the scaffold significantly lowers both HOMO and LUMO levels, indicating increased acceptor strength of these derivatives.
A comprehensive synthetic approach towards different nitrogen containing ICz derivatives, as well as results from photophysical and electrochemical characterization as well as theoretical calculations will be presented within this contribution.

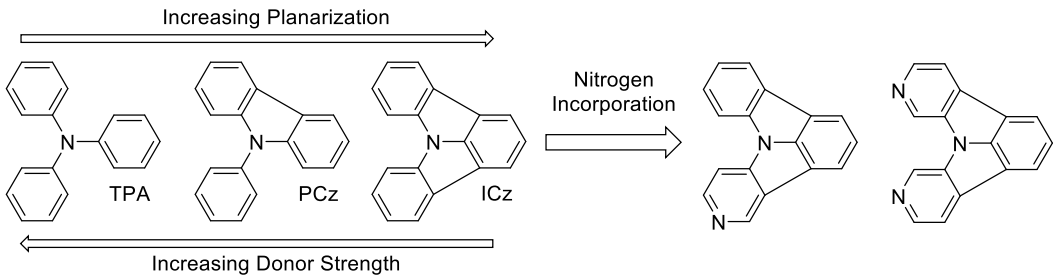

Figure 1: Concept of donor strength modulation in triarylamines by planarization (left) and examples for different nitrogen containing ICz derivatives (right).

References

1 P. Kautny, D. Lumpi, Y. Wang, A. Tissot, J. Bintinger, E. Horkel, B. Stöger, C. Hametner, H. Hagemann, D. Ma, J. Fröhlich, *J. Mater. Chem. C*. **2014**, 11, 2069-2081.
2 P. Kautny, Z. Wu, J. Eichelter, E. Horkel, B. Stöger, J. Chen, D. Ma, J. Fröhlich, D. Lumpi, *Organic Electronics* **2016**, 34, 237-245.

Modification of Planarized Triarylamines *via* Nitrogen Incorporation

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Motivation

Recently, our investigations on planarized arylamines as electron donating moieties unveiled, that **increased planarization** leads to a **decreased donor strength**. Fully planarized indolo[3,2,1-*jk*]carbazole (ICz) exhibited also weak acceptor character.[1] The aim of this work was the incorporation of additional **pyridine**-like **nitrogen atoms** into the ICz scaffold to further **increase the acceptor strength**. This gradual modification of donor and acceptor strength by planarization and nitrogen content allows for the specific adjustment of the electrochemical properties of the triarylamine building block.

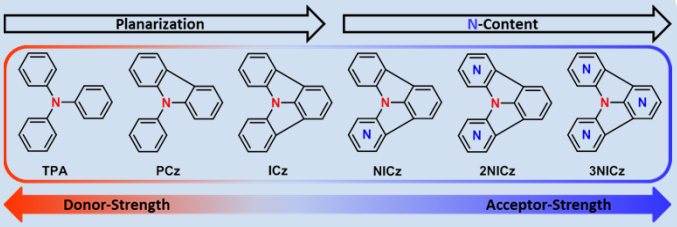


Figure 1. Concept of modulation of donor and acceptor strength in triarylamines by planarization and nitrogen incorporation.

Synthesis

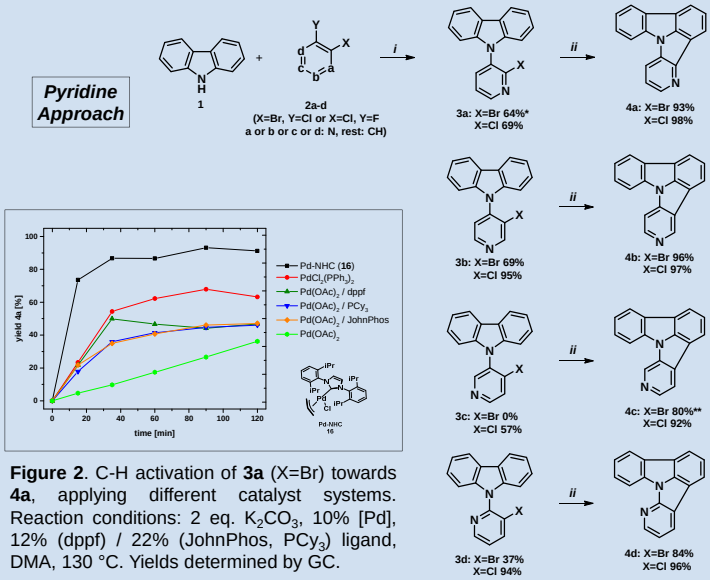
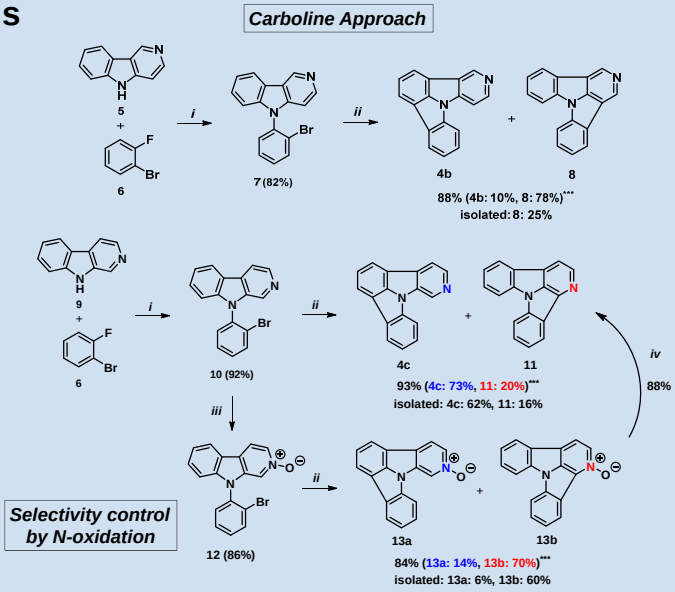
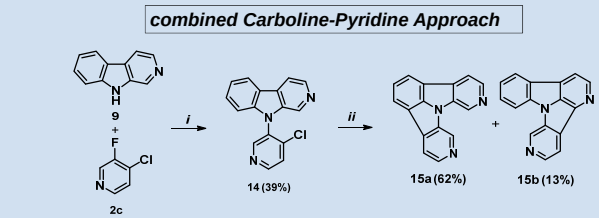


Figure 2. C-H activation of **3a** (X=Br) towards **4a**, applying different catalyst systems. Reaction conditions: 2 eq. K_2CO_3, 10% [Pd], 12% (dppf) / 22% (JohnPhos, PCy_3) ligand, DMA, 130 °C. Yields determined by GC.



Scheme 1. Synthetic approach towards various N substituted ICz derivatives. i: Cs_2CO_3, DMF, 130 °C. ii: Pd-NHC (16), K_2CO_3, DMA, 130 °C. iii: mCPBA, CH_2Cl_2, 0 °C. iv: iron powder, AcOH, 60 °C.
*Starting from 2-bromo-3-fluoropyridine. **Precursor synthesized by Buchwald-Hartwig amination of 3-amino-4-bromopyridine and 2,2'-diiodo-1,1'-biphenyl. ***Determined by ^{1}H-NMR.



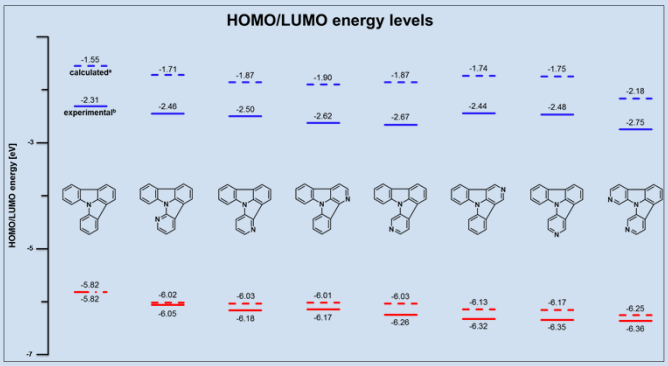


Figure 3. Experimental determination and theoretical calculation of HOMO and LUMO energy levels. [a]Calculated from the onset of the oxidation respectively reduction peak from CV-measurements in acetonitrile. [b]Calculated applying density functional theory (B3LYP/6-311G(d,p)).

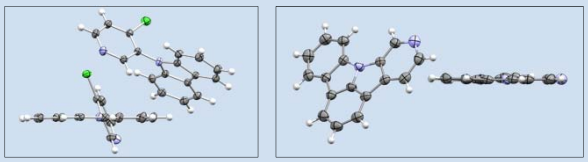


Figure 4. Molecular structures of **3c** (X=Cl, left) and **4c** (right). C, N and Cl atoms are represented by gray, blue and green ellipsoids drawn at 70% probabiliy levels, H atoms by spheres of arbitrary radius.

Results and Outlook

A reliable synthetic protocol for the incorporation of pyridine into the ICz moiety was established. According to both experimental data and theoretical calculations these molecular modification significantly lowers both HOMO and LUMO levels (figure 3). Notably, the degree of the decrease depends on the nitrogen position in the ring, thus allowing to tune the energy levels.

Our current research focuses on the functionalization of the NICz moiety for implementation in functional organic materials.

[1] P. Kautny, D. Lumpi, Y. Wang, A. Tissot, J. Bintinger, E. Horkel, B. Stöger, C. Hametner, H. Hagemann, D. Ma, J. Fröhlich; J. Mater. Chem. C. 2014, 2, 11, 2069-2081.

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