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## COMMUNICATION

## **Diindenopyrazines: Electron-Deficient Arenes**

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**Abstract:** We report the syntheses, properties and application of air stable, electron acceptors, the diindenopyrazines **4a-g**. We demonstrate introduction of functional aryl groups in 6,12-position. The targets are accessible on the hundred milligrams to the gram scale. The structure of the aryl groups in **4a-g** modulate the solubility, redox potentials and optical properties. Introduction of electron poor aryl groups to the electron poor diindenopyrazine backbone reduces the electron affinity to -4 eV, attractive as n-semiconductors. A simple organic field-effect transistor - without optimization - of **4e** shows electron transport with a mobility of up to 0.037 cm<sup>2</sup>/Vs.

Diindenoacenes<sup>[1-3]</sup> are quinoidal systems<sup>[4,5]</sup> with the possibility of diradical (-oid) character.<sup>[6-8]</sup> Such diradicals display attractive magnetic,<sup>[9]</sup> optical<sup>[10]</sup> and theoretical properties.<sup>[11]</sup> The diradical character is prominent, when the central core is an anthracene.<sup>[12]</sup> Indenofluorene 1 is a quinoidal closed shell system, as the aromatization energy of benzene - around 21 kcal/mol - is not sufficient to enforce the diradical character,<sup>[13]</sup> while diindenoanthracene 2 displays a diradical ground state (Figure 1a).<sup>[12]</sup> N-Heterocyclic indenofluorenes are sparsely investigated and only recently, Wang et al. described compounds of the type 3 and 4d.<sup>[14]</sup> Their electron affinity is increased in comparison to that of 1. 3 is a triplet diradical while 4d is a closed-shell singlet, easily understood, as 3 gains two Clar sextet upon "radicalization", while 4d, analogously to indenofluorene will only gain one of them (Figure 1b).



Figure 1. a) Previous work from Haley *et. al.*<sup>[12,13]</sup> b)Previous work from Pei *et al.*<sup>[14]</sup> c) Reactants for the synthesis of 1 (from 5a), 3 (from 5b), and 4d (from 6).

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So far, diradicaloid<sup>[12]</sup> and closed shell indenofluorene-type compounds<sup>[13,15]</sup> were applied in organic field effect transistors as ambipolar charge transport systems.<sup>[16]</sup>

**1**, **3** and **4d** were prepared from **5a,b** or **6** (Figure 1c) by double addition of an aryl Grignard followed by reductive deoxygenation of the intermediate biscarbinol with SnCl<sub>2</sub>. While this is a time-tested method, the yields are variable and for the synthesis of **4d** did not exceed 20%. We are interested in structures of the type **4** and present three different routes that lead to **4** featuring seven different phenyl-substituents. Reaction of **7** with an excess of lithium bis(trimethylsilyl)amide and reaction of the dianion with fluorobenzene, hexafluorobenzene or 4-flurobenzonitrile gave the



**Scheme 1.** Synthesis of diindenopyrazines **4a-g**. i) LHMDS, F-**Ar**<sup>a,e,g</sup> in THF, r.t., 16 h. ii) one pot synthesis: LHMDS, F-**Ar**<sup>a,e,g</sup>, chloranil in THF, r.t., 16 h. iii) Pd<sub>2</sub>(dba)<sub>3</sub>, DavePhos, Br-**Ar**<sup>a,b,c,d</sup>, Cs<sub>2</sub>CO<sub>3</sub> in DMAc, 80°C, 16 h. iv) PPA, 120 °C, 4 h. v) DDQ in PhMe, 100°C, monitored by thin layer chromatography or KO'Bu, chloranil in THF, r.t. 1 h.

compounds **9a,e,g** after aqueous workup. Instead of quenching the *in situ* generated dianions of **9a,e,g** with water, addition of chloranil forms **4a,e,g** in a one pot synthesis in in 30-45% yield as stable crystalline materials without diradical character. For **e** and **g** the S<sub>N</sub>Ar-mechanism is probably addition-elimination i.e. associative. For fluorobenzene, an elimination-addition-mechanism cannot be excluded. **b,c** and **f** gave inseparable mixtures of compounds, probably due to the presence of an eliminationaddition reaction, which gives mixtures of stereoisomers,<sup>[17]</sup> whereas **d** did not react at all.

Direct arylation via C-H activation of the diindenopyrazine works well for Br-Ar<sup>a-d</sup> in the presence of a Pd<sup>0</sup> source and the biphenylbased ligand DavePhos giving **9a-d** in yields between 25% and 65%. The reaction does not work well with electron deficient arylbromides, probably due to competing C-H activation of the aryl bromide. Oxidation of **9a-g** with DDQ in toluene at reflux gave

## COMMUNICATION

moderate yields of **4a-g**. The dianions of **9a-g**, generated *in situ* by the addition of KO*t*Bu, were oxidized by DDQ in yields > 85%. The third method employs the 2,5-dialdehyde of *para*-diphenylpyrazine. Addition of an aryl Grignard reagent followed by dehydration of the carbinol by polyphosphoric acid gives **9** in 40-70% yield. The. S<sub>N</sub>Ar and C-H activation allow the introduction of aryl substituents that do not survive Grignard formation, necessary to transform **5** or **6** into **1**,**3** or **4**.

On a scale above 50 mg **4** and **9** were purified by crystallization (exception **4c**, **9c**); but we also note that **5** the starting material used by Pei *et.al.* is synthesized by oxidation of **7**, which we use directly.<sup>[14]</sup>



Figure 2. Normalized UV-Vis spectra of 4a-g in DCM.



Figure 3. DFT- Calculated FMO levels (B3LYP/def2TZVP) of the compounds **4a-4g**. Dashed lines represent the FMOs of the indenofluorenes **1a,b,d-f**, taken from [12].

Non-fluorescent compounds **4a-g** absorb visible light up to 700 nm, with their absorption maxima  $\lambda_{max}$  ranging between 537 nm (opt. gap 2.31 eV) for **d** and 586 nm (opt. gap 1.92 eV) for **b**, **c**. (Figure 2, Table 1). The mesityl and the perfluorophenyl-substituted diindenopyrazines display the most blue-shifted features in their absorption spectra, due to the twisting of the

phenyl rings with respect to the diindenopyrazine. The other phenyl-substituents display more planar geometries, i.e. enlarge the  $\pi$ -system. The pyrazine ring allows for a larger degree of planarization, as the peri-hydrogens of the indenofluorenes are absent. The observed red-shift – when compared to the indenofluorenes 1 – is a result of the decreased torsion angle but also due to an electronic effect of the pyrazine. Compared to 1, HOMO and LUMO levels of 4 are stabilized by the electron poor pyrazine core (Figure 3).

We obtained single crystalline specimen from **4c** and **4d** (Figure 4); **4c** displays a torsion angle of only 28°, while mesityl substituted **4d** displays an angle of 63°. The larger twist compared to **4c** is caused by steric pressure of the *ortho*-methyl groups and weakens the conjugation of the backbone to the aryl groups (see above). This leads to the already mentioned blue-shift of **4d**, as well as larger HOMO-LUMO / IP-E<sub>A</sub> gaps (Table 1). The crystal structure of **4d** has been reported.<sup>[14]</sup>



Figure 4. Single crystal structure a,c) and packing b,d) of 4c and 4d, respectively.

Both the single crystal structures but also the quantum chemical calculations confirm the quinoidal and non-diradical character of derivatives of **4**. The molecules of **4c** pack in one-dimensional oblique stacks with  $\pi$ -contacts between parallel diindenopyrazine units, the attached phenyl rings however are oriented perpendicular to those of the adjacent molecules, thus showing CH- $\pi$ -contacts among each other. In contrast, the two independent centrosymmetric molecules of **4d** show no parallel

## COMMUNICATION

stacking motif in the crystal lattice. In **4c** the distance between the  $\pi$ -systems is 3.2 and 3.5 Å, i.e. below the van der Waals radius.



Figure 5. a) drop-casted film of 4e from chloroform (0.38 mg/mL), 50x darkfield microscopy; b) schematic device architecture c) transfer characteristics of bottom-gate/top-contact FET ( $V_{ds} = 50 V$ ) d) output characteristics.

We built a transistor with a bottom gate top contact geometry of 4e, due to its sufficient solubility and thus good film forming properties. We used a silicon substrate with successive layers of 100 nm thermally grown silica, solution processed alumina and 12-cyclohexyldodecylphosphonic acid (CDPA) as a selfassembled monolayer to modify the dielectric.<sup>[18]</sup> A solution of 4e was drop-cast on the substrate from chloroform (0.38 mg/mL) resulting in a crystalline thin-film (Figure 5a). 40 nm silver was evaporated through a shadow mask to form the contact electrodes. Figure 5b) shows the schematic device architecture. 4e displays low hysteresis in the transfer curves and is without hysteresis in the output curves, with a top mobility of  $\mu_{max} = 0.037$ cm<sup>2</sup>/Vs (Figure 5c,d). The average mobility is 0.022 cm<sup>2</sup>/Vs (6 channels, 2 substrates). Compared to the literature known 1e, which displays ambipolar behaviour with  $\mu_{Max}^+ = 7x10^{-4} \text{ cm}^2/\text{Vs}$ ,  $\mu_{Max}$  = 3x10<sup>-3</sup>cm<sup>2</sup>/Vs as single crystal transistor the mobility of 4e is an order of magnitude higher.[13]

Reaction of **4d** with SbCl<sub>5</sub> or NOSbF<sub>6</sub> in dichloromethane/ acetonitrile quantitatively gave the protonated species **4d**H<sub>2</sub><sup>2+</sup>, identified by X-ray single crystal structure and UV-Vis spectrum (Figure 6). **4d**H<sub>2</sub><sup>2+</sup> was obtained by reaction of **4d** with HBF<sub>4</sub>. Addition of water to **4d**H<sub>2</sub><sup>2+</sup> re-forms **4d** quantitatively. Oxidation into the radical cation or the dication of **4d** did not occur, probably due to the instability of fluorenyl cation in addition to the destabilizing pyrazine-core and lack of conjugation into the mesityl substituents. For a quinoidal diindenonaphthalene derivative, Haley *et. al.* suggested a higher degree of delocalization of the positive charge compared to that of the negative charge, localized at the fluorenyl-position.<sup>[19]</sup>



Figure 6. Synthesis, UV-Vis and single crystal structure of  $4dH_2{}^{2+}$  with  ${\rm SbCl}_6{}^{-}$  as counterion.

We investigated the reduction of **4e** with potassium anthracenide. The radical anion formed easily; its EPR spectrum is in good agreement with the simulated spectrum (Supporting Information) and the UV-Vis spectrum displays an absorption at 1103 nm (Figure 7). In air, the signal disappears after 90 minutes.



Figure 7. Reduction of 4e with potassium anthracenide in THF (top) and UV-Vis spectrum of 4e<sup>••</sup> (bottom).

## COMMUNICATION

In conclusion, we present three efficient routes towards diindenopyrazines using  $S_NAr$ , C-H activation and ring closure reactions. Compounds **4**, lacking diradical character, yet display attractive properties. Particularly **4e** is an n-channel semiconductor, which even in un-optimized proof of concept transistors display mobilities of up to 0.037 cm<sup>2</sup>/Vs.

compound	λ <sub>max, abs</sub> [nm] (DCM) <sup>[a]</sup>	Opt.gap [eV] <sup>[b]</sup>	E <sup>Ox</sup> [V] <sup>[c]</sup>	E <sup>Red</sup> [V] <sup>[c]</sup>	IP [eV] <sup>[c]</sup>	E <sub>A</sub> [eV] <sup>[c]</sup>	HOMO [eV] <sup>[d]</sup>	LUMO [eV] <sup>[d]</sup>	HOMO-LUMO gap [eV]
а	576	1.98	0.76	-1.12	-5.56	-3.68	-5.37	-3.43	1.94
b	584	1.92	0.81	-1.18	-5.61	-3.62	-5.28	-3.30	1.98
с	586	1.92	0.85	-1.18	-5.65	-3.62	*	*	*
d	537	2.31	0.93	-1.30	-5.73	-3.50	-5.53	-3.32	2.21
е	550	2.12	_[e]	-0.88	_[e]	-3.92	-6.23	-3.98	2.25
f	577	1.98	_[e]	-0.87	_[e]	-3.93	-6.05	-4.10	1.95
g	586	1.94	_[e]	-0.90	_[e]	-3.90	-5.99	-4.02	1.97

Table 1. Experimental and calculated properties of 4a-g

[a] Measurements were performed in DCM. [b] Calculated from  $\lambda_{onset, abs.}$  [c] Oxidation  $E_{1/2}^{Ox}$  and reduction  $E_{1/2}^{Red}$  half-wave potentials measured by cyclic voltammetry (CV) in DCM with Bu<sub>4</sub>NPF<sub>6</sub> as the electrolyte against Fc/Fc<sup>+</sup> as the internal standard (-4.80 eV) at 0.2 V s<sup>-1</sup>. IP and E<sub>A</sub>

estimated from cyclovoltammetric (CV) measurements [IP/E<sub>A CV</sub>=  $-4.80 \text{ eV} - E_{\text{OV/Red}}$ ]. [d] Obtained from quantum-chemical calculations with DFT/B3LYP/def2-TZVP. <sup>[e]</sup> Not in the accessible stability window of the solvent. It is not expected, that the longer alkyl group of **4c** compared to **4b** has a significant influence on the geometry or energy levels. Therefore, no separate calculation was performed.

#### **Experimental Section**

#### Gram scale synthesis of 4e:

6,12-dihydrodiindeno[1,2-b:1',2'-e]pyrazine (7) (1.50 g, 5.85 mmol, 1.00 eq.) was dissolved in dry THF (500 mL) and LHMDS (1 M in THF, 35.1 mL, 35.1 mmol, 6.00 eq.) and hexafluorobenzene (4.36 g, 23.4 mmol, 4.00 eq.) was added slowly. The reaction was stirred for 16 h at room temperature and afterwards chloranil (8.63 g, 35.1 mmol, 6.00 eq.) was added. Recrystallization from chlorobenzene gave **4e** as a dark purple solid. Yield 1.10 g, 1.88 mmol, 32%. <sup>1</sup>H NMR (Tetrachloroethane-d<sub>2</sub>, 400 MHz):  $\delta$  = 7.59 (m, 2H), 7.23 (m, 2H), 7.18 (m, 2H), 6.96

(m, 2H) ppm. <sup>13</sup>C NMR (Tetrachloroethane-d<sub>2</sub>, 125 MHz):  $\delta$  = 165.1, 142.2, 141.8, 138.0, 133.2, 129.7, 129.5, 128.5, 126.3, 123.3, 122.7, 120.2 ppm. IR:  $\tilde{\nu}$  = 2960, 2920, 2851, 1659, 1632, 1459, 1439, 1425, 1259, 1089, 1060, 1017, 850, 798, 778, 744, 736, 719, 704, 683, 669, 661 cm<sup>-1</sup>.  $\lambda_{max, abs}$  = 550 nm,  $\lambda_{onset, abs}$  = 586 nm. HR-MS (DART+): m/z: [M+H]<sup>+</sup>: calcd. for C<sub>30</sub>H<sub>8</sub>F<sub>10</sub>N<sub>2</sub><sup>+</sup>: 587.0528; found 587.0596, correct isotope distribution.

#### Crystallographic data

Deposition Numbers CCDC 2058078 (for 4c), CCDC 2058079 (for 4d), and CCDC 2058080 (for  $4dH_2^{2+}$ ) </ur><br/>lementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service <ur>

## COMMUNICATION

href="https://www.ccdc.cam.ac.uk/structures/?">www.ccdc.cam. ac.uk/structures</url

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#### **Conflict of Interests**

The authors declare no conflict of interests.

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## COMMUNICATION

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

Layout 1:

## COMMUNICATION

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Page No. – Page No.

Diindenopyrazines: Electron-Deficient Arenes