

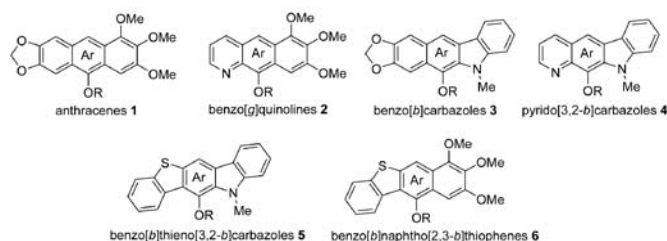
# A new tool for synthesis of organic optoelectronic materials

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Last decades have revealed new applications for organic compounds with spatially developed system of  $\pi$ -conjugated bonds as semiconducting materials useful in electronics and optoelectronics. They have been successfully applied and commercialized in electronic elements and devices involving organic light emitting diodes (OLED) and to a lesser extent in organic field-effect transistors (OFET). Organic photovoltaic cells (OPV) still suffer from a low efficiency preventing their broader application in solar batteries. They require better organic energy converting materials and auxiliary devices, such as solar concentrators, what makes a challenge for organic chemists.

In the present mini review, we demonstrate the results of our investigations on a new reaction of synthesis of polycyclic, fused aromatic and heteroaromatic hydrocarbons, fulfilling the condition to possess a system of many  $\pi$ -conjugated bonds. This new synthetic tool is based on a novel modification of the Friedel-Crafts type intramolecular cyclization reaction involving *O*-protected *ortho*-acetal diarylmethanols as a new type of reactants which enabled synthesis of a series of polycyclic aromatic and heteroaromatic hydrocarbons, such as: hexahydroxylated anthracene systems **1** [1a,1c, benzo[*b*]carbazoles **2** [1b], benzo[*g*]quinolines **3** [3b], pyrido[3,2-*b*]carbazoles **4** [1b], benzo[*b*]thieno[3,2-*b*]carbazoles **5** and benzo[*b*]naphtho[2,3-*b*]thiophenes **6** (Fig. 1).

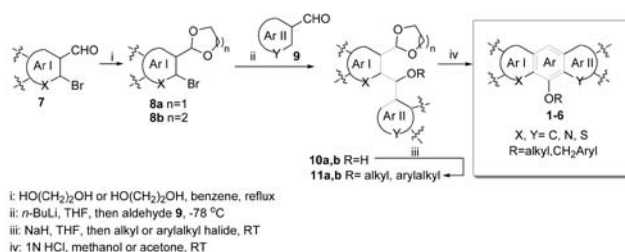


**Fig. 1. Structures of compounds 1-6 with newly formed 6-membered rings Ar, synthesized via a new modification of the Friedel-Crafts type intramolecular cyclization reaction**

The characteristic feature of these systems is a presence of central, six-membered aromatic ring Ar, built on two Ar(I) and Ar(II) rings of two independent aromatic aldehydes, used as substrates (Scheme 1). The general strategy for this synthesis involves:

i) protection of aldehyde group in the *ortho*-bromo aldehyde **7** with 1,2-ethanediol or 1,3-propanediol to give acetals **8a** or **8b**, respectively, ii) the Br/Li exchange reaction in **8a,b** followed by condensation with the second aromatic aldehyde **9** to afford **10a,b**, ii) protection of hydroxyl group in **10a,b** with alkyl or arylalkyl halide to obtain protected diarylmethanols **11a** or **11b**, iii) acid-promoted cyclization of **11a,b** to the corresponding polycyclic aromatic or heteroaromatic hydrocarbon systems **1-6** (Scheme 1). The last, key step (iii) of the new approach constitutes aromatic, electrophilic substitution reaction of the Friedel-Crafts type (developed in 1877) and resembles its later intramolecular extension (1940), known as the Bradsher reaction of *ortho*-acyl diarylmethanes [2a÷c]. Our

modification is identified by the presence of two functional groups: acetal and dibenzyl alkoxy, which, have never coexisted together during cyclisation and the presence of the OR substituent in the product. The presence of the latter functional group, makes the substrate more demanding to reaction conditions than the original versions and gives rise to unique OR-substituted polycyclic fused aromatic compounds that have not been available so far.

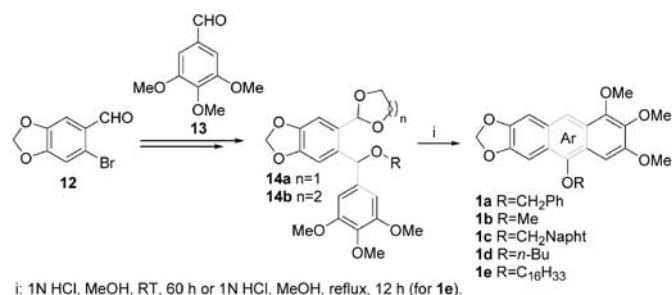


**Scheme 1. General strategy for synthesis of polycyclic, fused (hetero)aromatic hydrocarbons of type 1-6 via a new intramolecular electrophilic cyclisation reaction (bonds involved in the intramolecular cyclization are depicted in grey color)**

## Synthesis, crystal structure and optoelectronic properties of hexahydroxylated 10-O-R substituted anthracenes

Anthracene derivatives are tested as emitting materials in OLEDs [3] since usually these derivatives possess good solubility enabling their technological processing from solutions in organic solvents, high fluorescence quantum yields and good thermal stability. Recently, anthracene-based compounds have also been intensively studied as donor materials for bulky heterojunction solar cells [4]. Hexahydroxylated anthracenes possessing 10-O-R substituents, a subject of the present investigations, were unknown until 2006 [1a]

According to our new approach, the synthesis of 10-O-R substituted anthracene derivatives **1a-e** was based on transformation of 10-O-protected *ortho*-acetal diarylmethanols **14a** and **14b**, obtained from 6-bromopiperonal **12** and 3,4,5-trimethoxybenzaldehyde **13** (Scheme 2) [1a, 1c÷e]. Both physicochemical and optoelectronic properties of the obtained anthracenes were investigated in solution, crystal and solid film.



**Scheme 2. Synthesis of blue-light emitting 10-O-R derivatives of hexahydroxylated anthracenes 1a-e (bonds involved in the intramolecular cyclization are depicted in grey color)**

In Figure 2, crystal structures of anthracenes **1b**, **1d** and **1a** (Figs 2a÷c) with slipped  $\pi$ -stacking (partially parallel arrangement) has been compared with the herringbone arrangement of unsubstituted anthracene (Fig. 2d) and the monosubstituted 9-methoxyanthracene (Fig. 2e). Bearing in mind that arrangements with substantial spatial overlap of planar arene rings in the solid state (crystal or film) are particularly attractive as materials for organic field-effect transistors possessing high charge carrier mobilities [5a, b], the group of hexahydroxylated anthracenes, especially **1b** with the charge lifetime of 200  $\mu$ s, might constitute a new and useful group of arenes for this purpose.

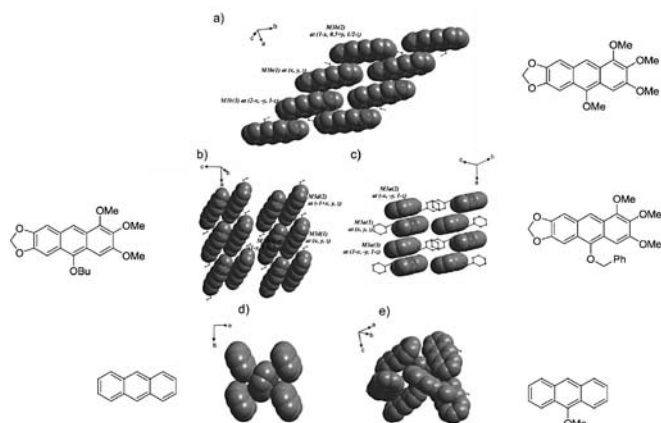


Fig. 2. a), b) and c) Columnar stacks of **1b**, **1d** and **1a**, respectively; d) and e) Herringbone packing diagram of anthracene and 9-methoxyanthracene

The quantum yields of fluorescence ( $\Phi_F$ ,  $\text{CH}_2\text{Cl}_2$ ) calculated for methoxy **1b**, butoxy **1d**, heksadecyloxy **1e** and benzyloxy **1a** anthracene derivatives oscillated around the 0.3 value (Table I) and were comparable with the values determined for the unsubstituted anthracene ( $\Phi_F = 0.27$  [6a]) and 1,4,5,8-tetraalkylsubstituted anthracenes ( $\Phi_F = 0.25$ -0.36 [6b]). UV-Vis absorption and fluorescence spectra of anthracene derivatives **1a**, **1b**, **1d**, **1e** are depicted in Figure 3a and Figure 3b, respectively.

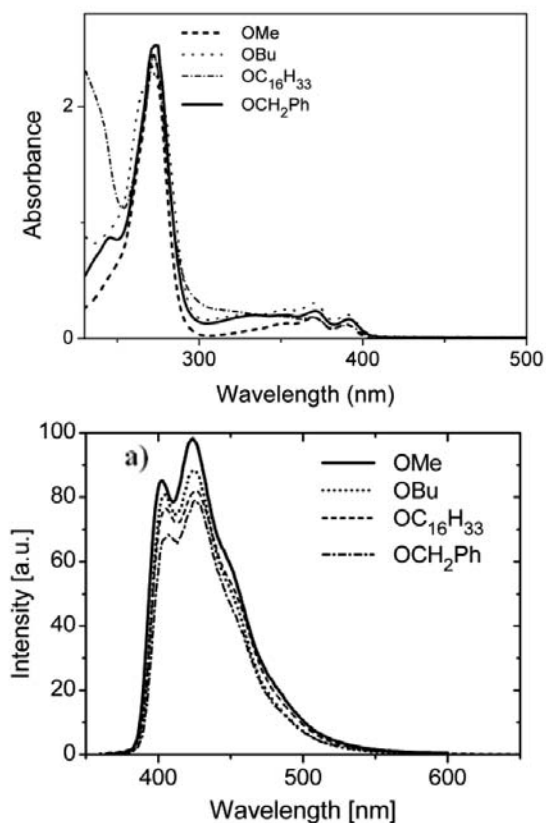


Fig. 3. Absorbance (a) and fluorescence (b) of anthracenes **1a**, **1b**, **1d**, **1e** in  $\text{CH}_2\text{Cl}_2$  solution

Application of organic compounds in molecular electronics requires, in most cases, preparation of thin films. Such films of compounds **1a**, **1b** and **1d** have been prepared using vacuum evaporation technique ( $10^{-5}$  Torr), on glass, spin casting and drop casting. Films of the O-Me derivative **1b** crystallized within 2÷48 hours depending on the film thickness. Progress of crystallization of a 2  $\mu$ m thick film is shown in Figure 4.

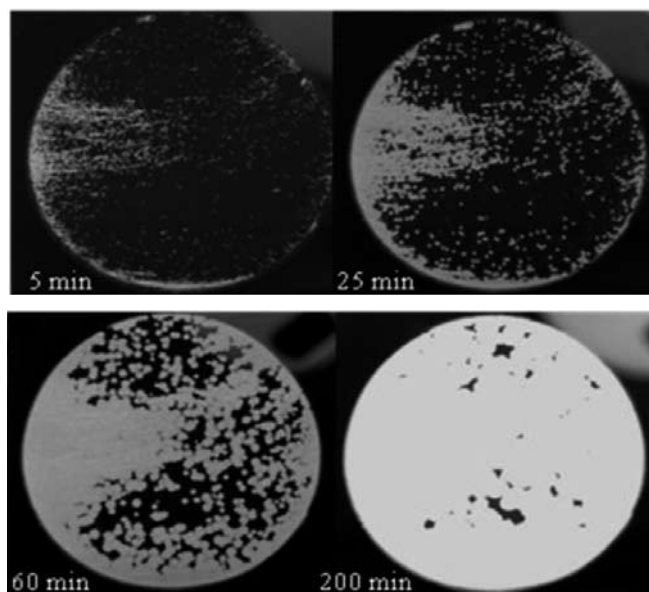


Fig. 4. Progress in crystallization of a 2  $\mu$ m-thick film of the O-Me derivative **1b**

Figure 5 shows a typical AFM (atomic force microscope) image of the thin film prepared from **1b** and the surface height profile (z-direction).

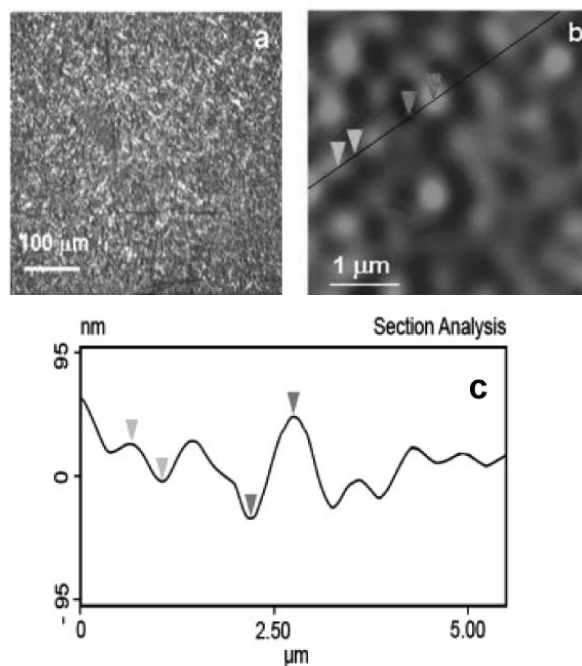


Fig. 5. Polarized optical microscope picture of evaporated layer of **1b** (a), AFM image (b), and its section analysis along the line indicated on the image (c)

Films of **1d** form several polymorphic crystalline structures, not suitable for optoelectronic applications. Films of **1a** were obtained by both drop casting and vacuum evaporation, in amorphous form. Such layers are stable for at least a couple of weeks but crystallize very slowly, forming after a few months big spherulites with good crystallite orientation and the classical maltese cross image observed under crossed polarizers (Fig. 6).

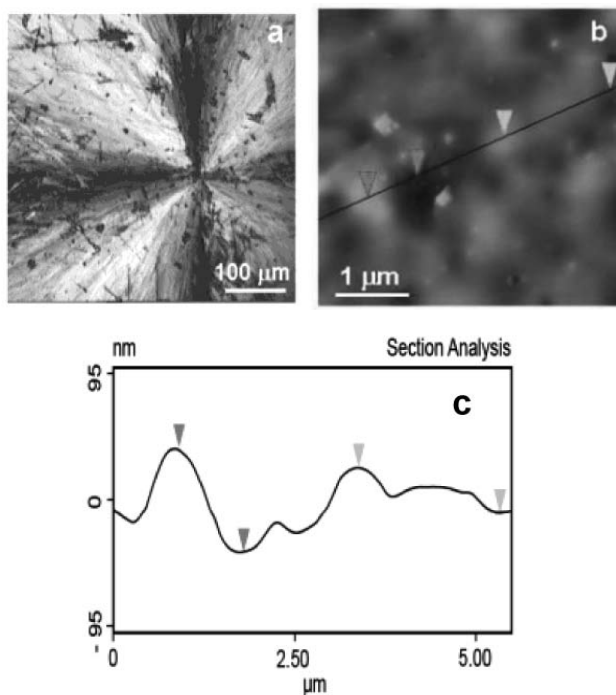


Fig. 6. Polarized optical microscope picture of 1a layer (a), AFM image (b) and its section analysis along the line indicated on the image (c)

The electrical properties investigated for thin films obtained by vacuum deposition of methoxy **1b** and benzyloxy **1a** substituted anthracenes on glass (Fig. 7) showed that transient currents decay was much slower in case of the methoxy derivative **1b**. It was in accordance with the observation that the lifetime of charge carriers were 25 times longer for the material with the methoxy substituent **1b**. Summarizing, it was found that the compound **1b** with the best  $\pi$ -stacking had also the most promising electrical properties.

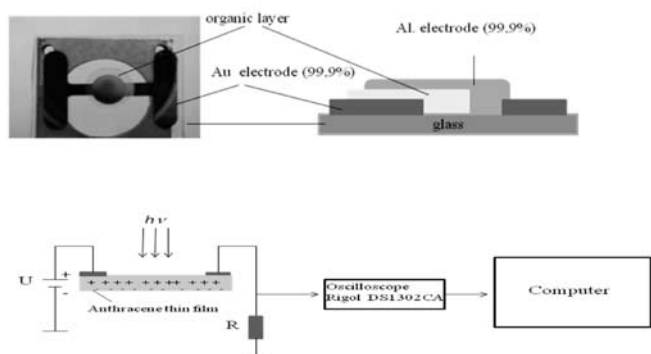
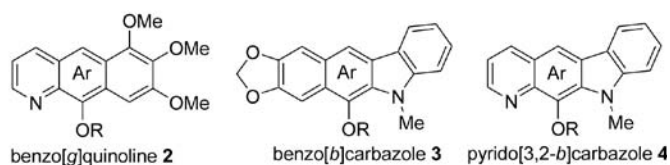


Fig. 7. A photograph, pictorial and circuit diagrams of the sandwich device for investigation of electrical properties of anthracene thin films

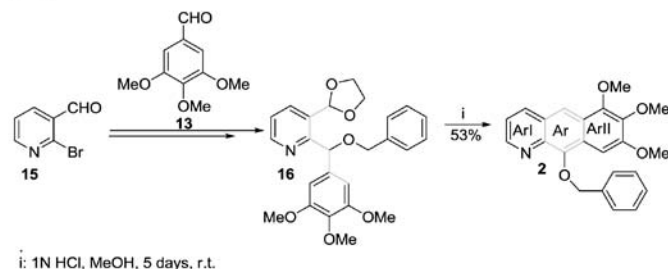
### Synthesis, crystal structure and optical properties of nitrogen containing polycyclic, fused aromatic hydrocarbons

Our new modification of the Friedel-Crafts type cyclization reaction was also utilized in synthesis of nitrogen containing polycyclic, fused aromatic hydrocarbons: benzo[*g*]quinoline **2**, benzo[*b*]carbazole **3**, pyrido[3,2-*b*]carbazole **4**.



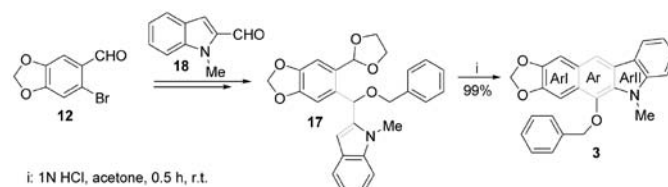
These new systems contain nitrogen atoms in Ar(I) and/or Ar(II) aromatic rings according to the general Scheme 1. Over the past few years, nitrogen containing fused aromatic systems have been a subject of interest in several areas from new materials for optoelectronic application [7] to biologically active substances [8]. Especially, carbazole containing molecules, have been widely used as materials for construction of high-mobility organic field-effect transistors (OFETs) [9] and organic light emitting diodes (OLEDs) [10], while 2,2'-bispyridyl derivatives found application in luminescent solar concentrators (LSCs).

In the synthesis of benzo[*g*]quinoline derivative **2**, containing nitrogen atom in Ar(I), the key diarylmethanol was obtained from *o*-bromoaldehyde **15** and 3,4,5-trimethoxybenzaldehyde **13**. Cyclization of the benzyl derivative **16** in presence (30 eq) of 1N HCl, afforded the desired benzoquinoline system **2** in satisfactory yield (Scheme 3) [1b].



Scheme 3. Synthesis of the greenish emitting benzo[*g*]quinoline derivative **2** (bonds involved in the intramolecular cyclization are depicted in grey color)

In the approach to nitrogen containing fused aromatics with nitrogen atom in the Ar(II) aromatic ring, the unknown 1,3-dioxabenzob[*b*]carbazole system **3** has been synthesized in almost 100% purity, starting from two aromatic aldehydes: the protected 6-bromopiperonal **12** and *N*-methylindole-2-carboxaldehyde **18** via the diarylmethanol derivative **17** (Scheme 4).



Scheme 4. Synthesis of the bluish benzo[*b*]carbazole derivative **3** (bonds involved in the intramolecular cyclization are depicted in grey color)

In Figure 8, the crystal structure of **3** has been compared with the crystal structure of unsubstituted carbazole. Modification of molecular structure of the latter, having a herringbone arrangement (Fig. 8a), by substitution of C-H and N-H hydrogen atoms by benzyloxy and *N*-methyl groups, respectively, led to a change of ring arrangement to a more parallel in **3** (Fig. 8b) as a result of replacement of intermolecular interactions of type  $\text{NH}\cdots\pi(\text{arene})$  by  $\text{CH}\cdots\text{O}$  interactions. Although, thin film investigations are underway, one can suppose that **3** may be a promising material for the device applications in the area of organic field effect transistors (OFETs).

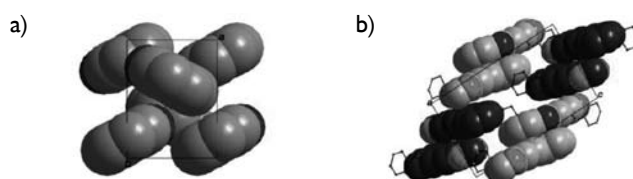
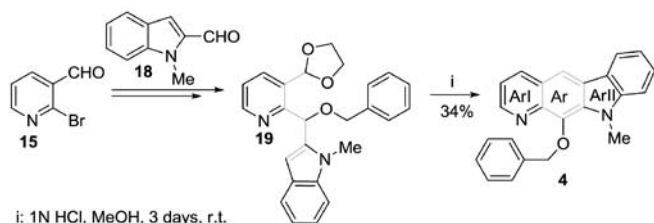


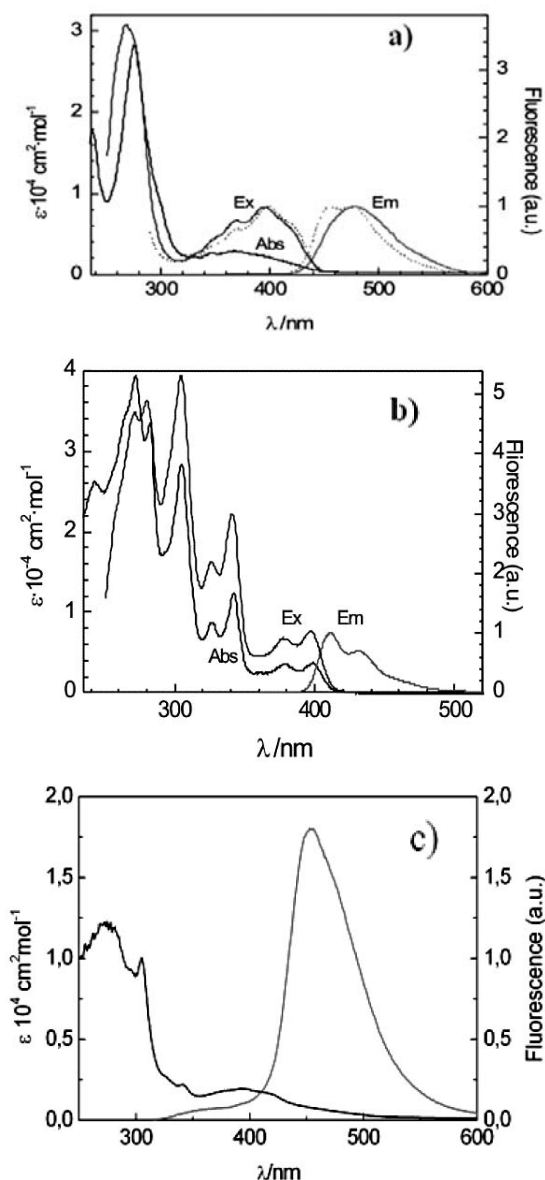
Fig. 8. a) Herringbone packing of the unsubstituted carbazole; b) Columnar stacks of 1,3-dioxabenzob[*b*]carbazole **3**

A combination of two nitrogen containing aldehydes: protected pyridinecarboxyaldehyde **15** and *N*-methylindolecarboxyaldehyde **18**, afforded the diarylmethanol derivative **19**, a key substrate in synthesis of the pyrido[3,2-*b*]carbazole **4**, as example of the system containing two nitrogen atoms in Ar(I) and Ar(II) aromatic rings (Scheme 5).



i: 1N HCl, MeOH, 3 days, r.t.

**Scheme 5. Synthesis of the greenish pyrido[3,2-*b*]carbazole derivative **4** (bonds involved in the intramolecular cyclization are depicted in grey color)**



**Fig. 9. a) Plots of absorption (Abs), fluorescence excitation (Ex) and fluorescence emission (Em) spectra of **2** in chloroform (solid lines) and toluene (dotted lines); b) Plots of absorption (Abs), fluorescence excitation (Ex) and fluorescence emission (Em) spectra of **3** in chloroform; c) Plots of absorption and fluorescence emission spectra of **4** in chloroform**

The compounds **2**, **3** and **4** revealed very interesting photophysical properties and spectacular fluorescence (Fig. 9). The compounds **2** and **3** strongly emitted greenish ( $\lambda_{\text{max}}=479$  nm) and bluish ( $\lambda_{\text{max}}=410$  nm)

fluorescence with quantum yields of 0.24 and 0.21, respectively. In comparison to **2**, the compound **4** revealed much more intensive green fluorescence at  $\lambda_{\text{max}}=453$  nm at the same concentrations of  $1.5\text{--}1.7 \cdot 10^{-4}$  mol·L<sup>-1</sup> in chloroform (Fig. 9c).

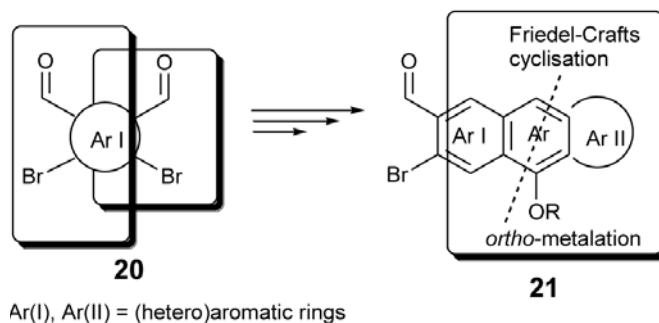
The Stokes shift, is significantly distinct for **3** and **4** (Figs. 10a,b). The Stokes shift for the carbazole derivative **4** amounted just 860 cm<sup>-1</sup> while for the pyridine derivative **3** had an exceptionally high value of 4500 cm<sup>-1</sup>, indicating that the ground and fluorescence states might have different geometries. A further contribution to the longer emission wavelength of **3** might result from the bulky methoxy substituents distorting dielectric properties of a solvent. The Stokes shift for **5** also revealed high value of 3435 cm<sup>-1</sup>. Both compounds with high Stokes shifts constitute excellent base materials for further structure optimization towards luminescent solar concentrators<sup>11</sup>, which require large values of both the Stokes shift and quantum yields, and which significantly reduce the costs of photovoltaic power generation by decreasing the required surface area of expensive silicon photovoltaic cells.

Investigation on synthesis and optoelectrical properties of **5** and **6** containing ring sulfur as well as ring sulfur and nitrogen atoms are underway in our laboratory.

### A new project for synthesis of polycyclic, fused (hetero) aromatic hydrocarbons.

Heteroaromatic and aromatic aldehydes play an important role as intermediates in pharmaceutical industry and organic synthesis in general. So far, *o*-bromo (hetero)aromatic aldehydes with one or two fused rings were utilized as powerful reagents to construct various heterocyclic and carbocyclic ring systems [12]. *O*-bromo aldehydes with more than two fused aromatic rings are so far unknown.

In the new project which is currently carried out in our laboratory, we realize a further expansion of our methodology towards such systems **21** (Scheme 6). *o*-Bromo aldehydes are replaced by dibromodialdehydes **20** and the whole concept of synthesis of new fused benzene ring Ar is applied for one pair of bromo and formyl substituents. The methodology covers diacetalisation, *ortho*-bromometalation, OH-diprotection and finely electrophilic cyclisation under acidic conditions. In this extension, syntheses of isomeric (hetero)aromatic bromo aldehydes as reagents with potential applications in organic synthesis and material chemistry may be achieved.



Ar(I), Ar(II) = (hetero)aromatic rings

**Scheme 6. An extension of the basic concept to synthesis of polycyclic, fused (hetero)aromatic hydrocarbons using dibromodialdehydes**

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