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## A Friedländer route to 5,7-Diazapentacenes

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A route to compounds with a 5,7-diazapentacene skeleton has been established involving a Friedländer reaction. A diaminodiketone **8** has been made by a novel method and reacted with cyclohexanone to prepare an octa-hydro-5,7-diazapentacene **7a** and with tetralone to produce a dibenzotetrahydro-5,7-diazapentacene **7b**. Reaction of the diaminodiketone with a diarylethanone followed by oxidation gave a tetrabenzo-5,7-diazapentacene **18b**. Compound **7b** undergoes solid-state dimerization during single-crystal X-ray analysis. These materials possess lower frontier orbitals than pentacene and show strong absorption and fluorescence which is affected by the presence of acid. In particular **18b** shows a remarkable colour change in solution upon addition of acid. These results suggest that suitably functionalised 5,7-diazapentacenes could be promising candidates for optoelectronic applications.

## Introduction

Acenes<sup>1</sup> are one of the most heavily investigated classes of organic semiconductors, in part because of the exceptionally high (>10 cm<sup>2</sup>/Vs) charge carrier mobilities measured in single crystals of acenes such as pentacene (**1**) and rubrene (**2**).<sup>2</sup> Charge carrier mobilities above 1 cm<sup>2</sup>/Vs have also been measured in field effect transistors (FETs) using thin films of solution processable pentacene derivatives such as TIPS-pentacene (**3**).<sup>3</sup> While these acenes are p-type materials, the incorporation of nitrogen atoms into the aromatic core of acenes such as pentacene increases their electron affinity and lowers the frontier molecular orbital energies, making them better electron acceptors and transporters. As a result **4**, a tetraazapentacene analogue of TIPS-pentacene is an n-type semiconductor.<sup>4</sup> Thus, pyrazinacenes such as **4** which contain pyrazine rings have become widely studied materials due to their potential application as n-type semiconductors in OFETs and other organic electronic devices,<sup>1,5</sup> and there exist well developed procedures for their synthesis.<sup>6</sup> However, some nitrogen doped acenes, which could be important for elucidating structure-property relations such as 5,7-diazapentacene (quinolino[3,2-b]acridine) (**5**), have never been synthesized, and, thus, studied. The only reported attempt to synthesize **5** was unsuccessful.<sup>7</sup> The authors

obtained a mixture of products with secondary amino groups instead of the target molecule with pyridine rings.

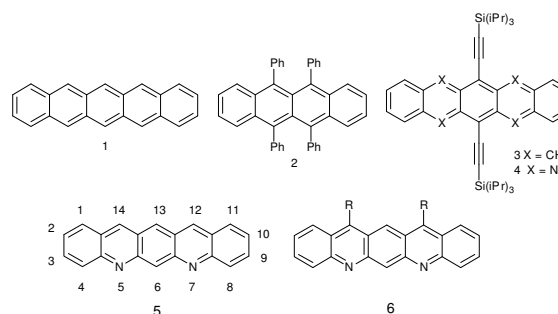


Figure 1 Structures of previously known acenes and tetrazaacenes and of the new diazapentacenes

We now report our attempts to obtain molecules containing a 12,14-disubstituted 5,7-diazapentacene framework **6**, as well as optical and electrochemical properties of the obtained 5,7-diazapentacene precursors and derivatives.

## Experimental

Reagents were purchased from Sigma-Aldrich and used as received. Chromatographic purification was performed as flash chromatography with silica gel (40–65 μm) and solvents indicated as eluent with 0.1–0.5 bar pressure. For quantitative flash chromatography, technical grades solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 μm F254 TLC glass plates. Visualization was accomplished with UV light.

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## ARTICLE

Journal Name

Uv-visible spectroscopy was performed on a Shimadzu UV-2700 spectrophotometer. Fluorescence spectra were measured on a Cary Eclipse spectrophotometer. Quantum yields ( $\Phi$ ) were obtained by the absolute method<sup>8</sup> using Quantum Efficiency Measurement System QE-2000 (Otsuka Electronics Co., Ltd.). The given  $\Phi$  values for solutions in chloroform are average values of three independent measurements.

Proton and carbon nuclear magnetic resonance spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were recorded on Bruker AVANCE 400 MHz spectrometers with solvent resonances as the internal standard (<sup>1</sup>H NMR: 400 MHz, CDCl<sub>3</sub> at 7.26 ppm; <sup>13</sup>C NMR: 100 MHz, CDCl<sub>3</sub> at 77.0 ppm). The accurate mass analyses were run in ESI mode on a double focusing magnetic sector mass spectrometer at a mass resolution of 10 000 using PFK (perfluorokerosene) as an internal calibrant or in ESI mode using a hybrid linear ion trap/orbitrap tandem mass spectrometer.

Cyclic voltammetry was performed using a CHI 604E Electrochemical Analyzer. Glassy carbon (diameter: 1.6 mm; area 0.02 cm<sup>2</sup>) was used as working electrode, platinum wires were used as counter electrode and reference electrode, respectively. nBu<sub>4</sub>NPF<sub>6</sub> (0.1M) was used as supporting electrolyte. Potential was recorded in an anhydrous DCM solution and the scanning rate was 50 mV/s. Fc<sup>+</sup>/Fc (HOMO = -4.80 eV) was used as an external standard.

## Results and discussion

### Synthesis of a precursor to the 5,7-diazapentacene framework

In order to obtain the diazapentacene framework, we decided to utilize an approach based on a double Friedländer condensation<sup>9</sup> between one molecule of diaminodiketone **8** and two molecules of cyclohexanone **9** giving a derivative of pyrido[3,2-g]quinoline **7** (Figure 2) followed by oxidation to produce the desired diazapentacene **6**. We anticipated that alkyl chains in the 12 and 14 position of the diazapentacene framework **6** would stabilize the target molecule as well as improve its solubility, thus, we decided to attach hexyl chains onto the framework.

A new approach was implemented to synthesize the compound **8** (Figure 3). First, nitration of *m*-dibromobenzene (**10**) gave 1,5-dibromo-2,4-dinitrobenzene (**11**),<sup>10</sup> which was then subjected to Sonogashira coupling with 1-heptyne in THF using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst and Et<sub>3</sub>N as a base.

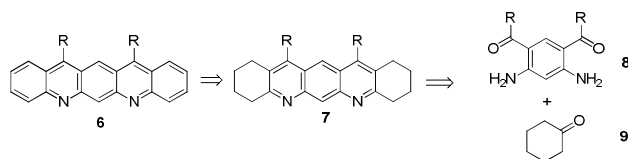


Figure 2. Retrosynthetic analysis of **6**.

The reaction was complete within 8 hours at room temperature, giving the product **12** in 80% yield, but did not give the compound **12** if performed at higher temperatures. If the reaction mixture was kept for longer than 8 hours, the yield started to decrease gradually. Tandem reduction of nitro groups and hydrolysis of triple bonds of **12** using SnCl<sub>2</sub><sup>11</sup> gave **8** in 60% overall yield, which is good for a four step process. A reported procedure for synthesis of monoaminophenones that utilizes tin in acidic conditions<sup>12</sup> failed to give the desired product, although the starting material was completely consumed. Given the good yields and mild conditions, our new procedure is a convenient way to prepare **8**. We have not yet tested to see if it is a general reaction but see no reason why it should not work equally well to produce other similar molecules.

For the synthesis of the pentacene precursors **7**, we conducted screening of conditions for the Friedländer reactions including acid, base and Lewis acid catalyzed conditions as shown in Table 2 to investigate the extent of reactions for each type. It was discovered that the desired reaction does not take place in basic conditions nor when Lewis acids were used, with the starting material being recovered and no indication of **7a** having been formed. The reaction in acidic conditions in refluxing AcOH was successful, but the yield of 12% obtained was not satisfactory. It was observed that lowering the temperature was effective in producing **7a** in 45% yield with a conversion rate of 98.4%. When using ethanolic HCl as a catalyst, we found the reaction had a much higher yield of 73% and took less time than in case of acetic acid and so these conditions were selected as the initial conditions for all future Friedländer reactions.

To test that these optimized conditions were generally applicable a variety of pyrido[3,2-g]quinolone derivatives **7b-e** were synthesized using these conditions (Table 2). Remarkably, 1,3-cyclohexanedione gave only the product of monoaddition even when a significant excess of the reactant was used, while acetophenone did not react.

We then attempted to obtain the corresponding pentacene derivatives **6** by means of dehydrogenation of **7a** and **7b** using Pd/C. Unfortunately, we did not succeed despite attempting the reaction at different temperatures, i.e. 200 °C and 170 °C and utilizing different solvents (*p*-cymene, nitrobenzene, diphenyl ether). The complex mixture of oligomers formed in the reaction may be evidence for the desired products having low stability under the reaction conditions. We are investigating further the dehydrogenation of **7a** and **7b** to see if it is possible to convert them to the desired compounds **6**. We are also investigating alternative routes to **6**.

Because of the unsuccessful dehydrogenation of **7a** and **7b**, we decided upon incorporation of additional benzene rings, as represented by the structure **13**, to stabilize the 5,7-diazapentacene (**2**) framework. We expected to obtain **13** by oxidation of **14**, which could be obtained by a Friedländer reaction between **8** and **15** (Figure 4).

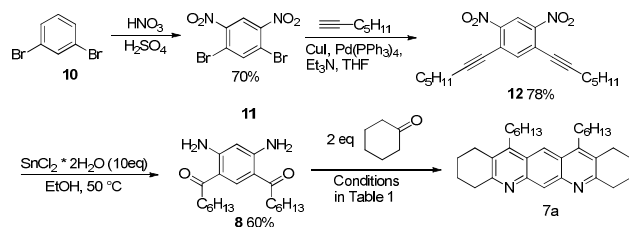


Figure 3 Synthesis of 7a.

Entry	Reagents	Amount of catalyst	Conditions	Yield
1	Bi(OTf) <sub>3</sub> , EtOH	20 mol %	75 °C, 48h	-
2	FeCl <sub>3</sub> , EtOH	20 mol %	75 °C, 24h	-
3	LiOH, MeCN	50 mol %	75 °C, 24h	-
4	KOH, EtOH	50 mol %	75 °C, 48h	-
5	TsOH * H <sub>2</sub> O	2.1 eq	80 °C, 2h	-
6	AcOH	Solvent	110 °C, 48h	12%
7	AcOH	Solvent	85 °C, 60h	45%
8	HCl, EtOH	2 eq	75 °C, 20h	73%

Table 1. Conditions screening for the reaction between 8 and cyclohexanone

We found that **8** and **16a-c** did not react using the conditions used to make **7a-e**. Instead, we found that **16a-c** reacted with **8** under solvent free conditions using *p*-toluenesulfonic acid (TsOH) as a catalyst at 105 °C giving **17a-c** in good to moderate yields (Figure 5). **16b,c** were synthesized using known procedures involving Friedel-Crafts reactions.<sup>13</sup>

We found that among **17a-c** only **17b** could be converted to the desired product **18b** using BF<sub>3</sub>\*Et<sub>2</sub>O / [Bis(trifluoroacetoxy)iodo]benzene (PIFA)<sup>14</sup> as oxidant, though the yield was only 28%. **17a** did not react in these conditions, while **17c** gave a complex mixture of oligomeric products. Other oxidants tested such as DDQ and FeCl<sub>3</sub> also did not convert **17a-c** to the desired products.

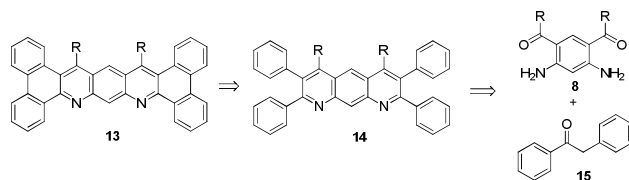


Figure 4. Synthetic strategy for making 13

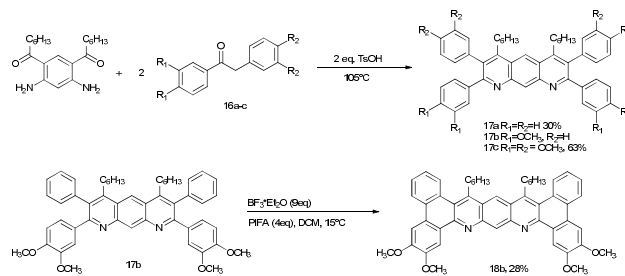


Figure 5. Synthesis of 17a-c and 18b.

Reactant	Product	Time	Yield
		16h	60%
		48h	51%
		24h	32%
		48h	49%

Table 2. Reaction of various ketones with 8 under optimized conditions.

### Single crystal X-Ray diffraction results

To investigate the packing of the molecules, single crystals of **7a** and **7b** were grown and subjected to single crystal X-ray diffraction (SCXRD) analysis. SCXRD was performed on **7a** on a Bruker D8 Quest with a Photon II detector using Mo K $\alpha$  of wavelength 0.71073 Å and a multilayer mirror monochromator at 100 K. The frames were integrated using Bruker SAINT software package, absorption corrections were applied using the program SADABS. SHELXT and SHELXL were used for structural solution and refinement respectively.

The final refinement yielded a  $R_1 = 6.05\%$ , a  $wR_2 = 17.08\%$  and a *goodness-of-fit* factor of 1.018. The final structure was solved in the monoclinic space group  $P2_1/c$  with the unit cell  $a = 16.6840(7)$  Å,  $b = 9.5024(6)$  Å,  $c = 18.4451(8)$  Å,  $\beta = 113.6951(16)^\circ$  and  $V = 2677.7(2)$  Å<sup>3</sup> (CCDC 1583758).

The refined structure is made up of single units (Figure 6, left) that display  $\pi$ - $\pi$  stacking through the aromatic backbone with a  $\pi$ - $\pi$  stacking distance of 3.68 Å (Figure 6 right), each neighbouring stack alternates between two orientations at 90° to each other. This  $\pi$ - $\pi$  stacking distance is appreciably greater than the values of 3.43 Å reported for TIPS-pentacene,<sup>3a</sup> or of 3.30-3.35 Å reported for TIPS-1-aza-pentacene derivatives.<sup>15</sup>

## ARTICLE

## Journal Name

This is due to the less planar nature of **7a** resulting from the nonaromatic rings, and we anticipate that fully aromatised 5,7-diazapentacenes would pack more closely.

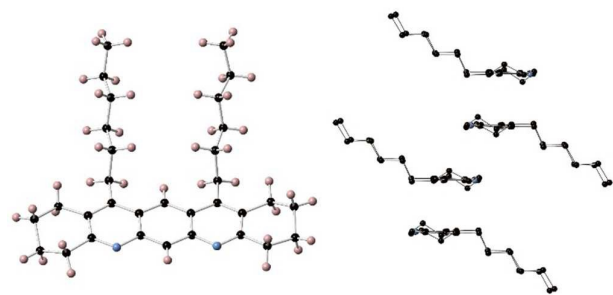


Figure 6: Left shows a single monomer unit and right depicts the  $\pi$ - $\pi$  stacking of the monomer units that are separated by 3.68 Å. Black, blue and pink spheres represent carbon and nitrogen and hydrogen respectively.

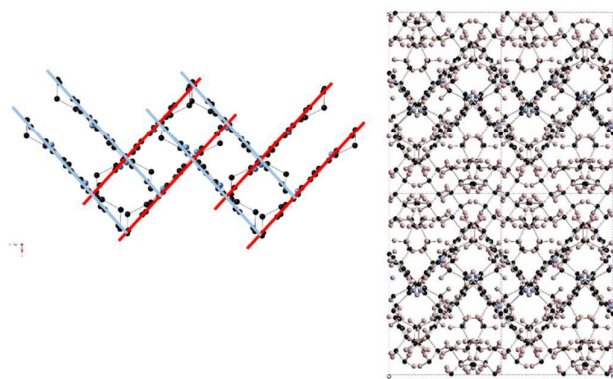


Figure 7: A structural view down the z-axis showing the alternating stacks of the monomeric unit alternated at 90° to each other (shown left as red and blue lines) and how those zig-zag units connect through the extension of their  $C_6H_{13}$  units (right). Black, blue and pink spheres represent carbon and nitrogen and hydrogen respectively.

When viewed down the z-axis this creates a zig-zag pattern of interlinking 'layers' of the aromatic backbones with the interlayer region made up of the extended  $C_6H_{13}$  chains interacting through van der Waals forces (Figure 7).

Single-crystal X-ray crystallography was also performed on **7b**. A Bruker SMART APEX-II was used with a Mo  $K_{\alpha}$  wavelength 0.71073 Å and a graphite monochromator at room temperature. The frames were integrated using Bruker SAINT software package, absorption corrections were applied using the program SADABS and the space group assigned using the program XPREP. SHELXT and SHELXL were used for structural solution and refinement respectively. The final refinement yielded a  $R_1 = 6.23\%$ , a  $wR_2 = 13.91\%$  and a *goodness-of-fit* factor of 1.046. The final structure was solved in the triclinic space group *P*-1 with the unit cell  $a = 8.8518(19)$  Å,  $b = 12.613(3)$  Å,  $c = 14.689(3)$  Å,  $\alpha = 89.365(2)^\circ$ ,  $\beta = 86.918(2)^\circ$ ,  $\gamma = 74.577(2)^\circ$  and  $V = 1578.6(6)$  Å<sup>3</sup> (CCDC 1583759).

The final structure seen in the X-ray structure is in fact a dimer of the initially targeted compound (Figure 8). The structure of

**7b** remains intact apart from a dimerization reaction across the central ring, this yields an X-shaped molecule, whose long  $C_6H_{13}$  groups extend out and interact with each other to cause stacking of the dimerised units along the y-axis.

For both newly synthesised and recrystallized **7b**, we see proton shifts in the NMR spectrum (see ESI) for the protons on the central ring in the aromatic region, rather than at ca.  $\delta 4.5$  as would be expected for the bridgehead protons in the dimer, and no ions corresponding to the dimer are seen in the mass spectra. Since both the NMR and mass spectra are consistent with the monomeric rather than dimeric structure, we tentatively conclude that a dimerization has occurred during the X-ray measurements, either during handling of the crystal or upon X-ray irradiation. **7b** appears to be stable in the solid as no change in the NMR spectrum was seen in crystals that been left exposed to light for several weeks. We also found that the irradiation of **7b** in solution with 325 nm laser light for 5 hours did not lead to any detectable dimerization.

Attempts to produce good quality single crystals of **18b** suitable for SCXRD analysis have to date proven unsuccessful

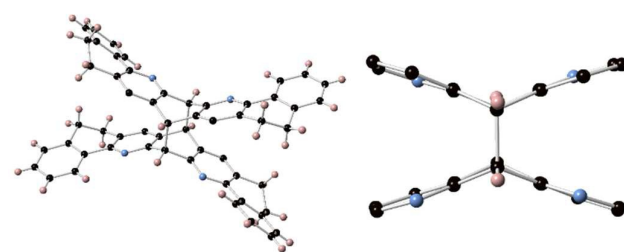


Figure 8: the X-shaped dimer of **7b**. Left shows one dimer molecule where the  $C_6H_{13}$  groups that normally extend out from the para position from each nitrogen have been omitted for clarity. Right shows the connection between each monomeric unit to form the X-shaped dimer. It should be noted that each  $N_2C_{40}H_{44}$  half of the dimer connects through the central ring at 180° to each other such that each monomeric units'  $C_6H_{13}$  groups extend in opposite directions. Black, blue and pink spheres represent carbon, nitrogen and hydrogen respectively.

### Electrochemical properties

As shown in Figure 9, both **7a** and **7b** demonstrate two reversible reductive and oxidative peaks in CV using  $FeCp_2/FeCp_2^+$  as internal standard from which their HOMO and LUMO energy levels were calculated using the following equations:

$$E(HOMO) = -(E_{ox}^{onset}(vs. FeCp_2/FeCp_2^+) + 4.80)$$

$$E(LUMO) = -(E_{red}^{onset}(vs. FeCp_2/FeCp_2^+) + 4.80)$$

They show very similar oxidation potentials of 0.9 and 0.8 V corresponding to HOMO energies of -5.7 and -5.6 eV respectively, and identical reduction potentials of -1.3 V corresponding to a LUMO energy value of -3.5 eV. As also shown in Figure 9, compound **18b** demonstrates a smaller lower oxidation potential than **7a,b** of 0.4 V, but an identical reduction potential of -1.3 V (versus  $FeCp_2/FeCp_2^+$ ) corresponding to HOMO and LUMO energies of -5.2 and -3.5 eV, and a smaller bandgap ( $E_g$ ) of 1.7 eV compare with 2.2

	E <sub>ox</sub> onset (V) vs Fc/Fc <sup>+</sup>	E <sub>red</sub> onset (V) vs Fc/Fc <sup>+</sup>	HOMO level (eV)	LUMO level (eV)	E <sub>g</sub> from CV (eV)	E <sub>g</sub> optical (eV)
7a	0.9	-1.3	-5.7	-3.5	2.2	3.0
7b	0.8	-1.3	-5.6	-3.5	2.1	3.0
7e	0.8	-1.3	-5.6	-3.5	2.1	2.7
18b	0.4	-1.3	-5.2	-3.5	1.7	2.3

and 2.1 eV for 7a and 7b respectively. This is to be expected given the more extended  $\pi$ -system in **18b** compared with **7a,b**. For all three compounds the optical bandgaps calculated from UV and PL spectra (see below) were larger by 0.6-0.9 eV. The electrochemical data and calculated frontier orbital energies and bandgaps for these molecules are tabulated in Table 3. These compare with reported values for pentacene of -5.00 and -3.20 eV,<sup>16</sup> and -5.40 and -3.40 eV for an inseparable mixture of 1,8- and 1,11-diazapentacenes.<sup>15</sup> It is also reported in patent literature that a 5,12-diazapentacene has calculated HOMO and LUMO energy levels 0.54 eV and -0.41 eV respectively lower than those of pentacene corresponding to values of -5.54 and -3.20 eV.<sup>17</sup> These experimental and theoretical results confirm that introduction of nitrogen 'dopant' atoms into pentacene lowers the frontier orbital

energies.

While solution cast thin films of **18b** appear to be of good quality, attempts to obtain charge carrier mobilities from FETs based them on them have to date proved unsuccessful suggesting this material may be amorphous, which is also suggested by our inability to grow good quality single crystals for X-ray analysis

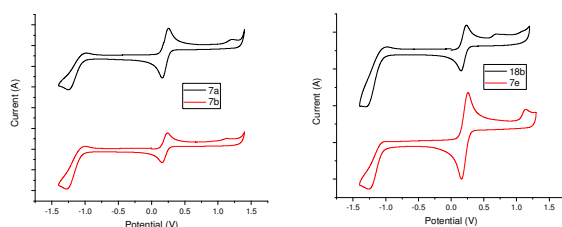


Figure 9. CV plots for 7a,b (left), and 7e, 18b (right)

Table 3 Electrochemical data for compounds **7a**, **7b** and **18b**.

### Optical properties

Since azaacenes have been reported to show strong absorption and fluorescence<sup>18</sup> we studied the absorption and

emission properties of our new materials. All the molecules showed strong absorption in the UV and/or violet and strong green or yellow fluorescence, suggesting they may have potential for use as emissive materials, e.g. in LEDs. The absorption and emission maxima for **7a-d**, **17a-c** and **18b** in chloroform solution ( $5 \times 10^{-5}$  M) are tabulated in Table 4.

Figure 10 shows the UV Vis absorption and PL emission spectra of **7a**, **7b** and **7e**. The peaks of **7b** in the visible part of the spectra are shifted to longer wavelengths comparing to **7a**, as would be expected given the longer conjugation length in **7b** due to the extra benzene rings. The absorption peaks for **7b** also demonstrate higher intensity than the peaks for **7a**. In the UV part of the spectra, **7b** shows several peaks (324nm, 311nm, 298nm, 290nm, 266nm) which are significantly red-shifted comparing to the single broad peak for **7a** at 265nm. The photoluminescence spectra also display a similar red shift between **7a** and **7b**. Thus, the additional benzene ring enlarges the aromatic system, which leads to the red shift of the **7b** spectra compared to **7a**.

The absorption spectra of **7e**, whose structure is isoelectronic to septacene, demonstrates four absorption peaks with the maximum intensity at 400 nm. The emission spectra has three distinctive peaks with the maximum intensity at 460 nm, which corresponds to a Stokes shift of 60 nm. Since the aromatic system of **7e** is even larger than that of **7b**, an even larger red shift compared to **7a** is observed.

	$\lambda_{\max}$ (abs) (nm)	$\lambda$ onset (nm)	$\lambda_{\max}$ (em) (nm)	Stokes Shift (nm)	$\epsilon$ (L M <sup>-1</sup> cm <sup>-1</sup> )	$\Phi$
<b>7a</b>	370	415	438	45	16380	0.42
<b>7b</b>	407	419	456	49	28600	0.10
<b>7e</b>	400	464	460	60	7620	0.30
<b>17a</b>	382	405	463	81	24480	0.08
<b>17b</b>	398	430	467	37	20200	0.17
<b>17c</b>	403	437	467	30	19300	0.23
<b>18b</b>	462	542	579	37	31120	0.27

Table 4 optical properties of **7a,b,e**, **17a-c**, and **18b** in chloroform solution

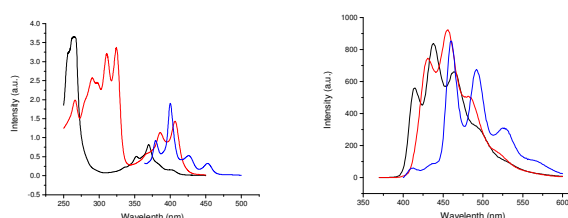


Figure 10. UV Vis (left) and photoluminescence (right) spectra of **7a** (black), **7b** (red), and **7e** (black) in solution ( $10^{-5}$  M in chloroform).

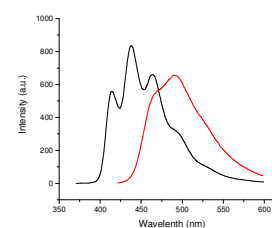


Figure 11. UV Vis (left) and photoluminescence (Right) spectra of **7a** (black) and a mixture of **7a** with 1 equivalent of CF<sub>3</sub>COOH (5 x 10<sup>-5</sup> M in chloroform)

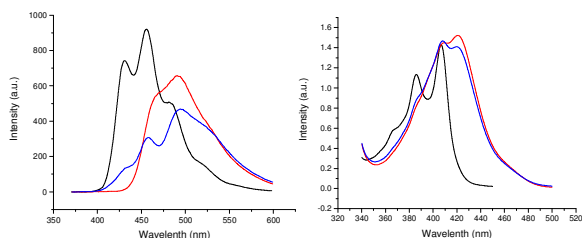


Figure 12. UV Vis (left) and photoluminescence (right) spectra of **7b** (black), a mixture of **7b** with 1 equivalent of CF<sub>3</sub>COOH (red), a mixture of **7b** with 2 equivalents of CF<sub>3</sub>COOH (red) (5x10<sup>-5</sup> M in chloroform)

Since the nitrogen atoms in **7a,b** are weakly basic the effects of acid upon the absorption and emission spectra of these compounds were studied. Addition of 1 equivalent of trifluoroacetic acid to a solution of **7a** in chloroform led to a significant red shift in both UV-Vis and fluorescence spectra, and change of the peaks pattern as well (Figure 11). This significant change in both UV-Vis and PL spectra is related to the protonation of a nitrogen, which leads to changes in the molecules' electronic structure. Further addition of the acid has not led to any further change in the spectra. This combined with the presence of only one isosbestic point, leads us to the conclusion that only one nitrogen is protonated in this range of acid concentrations.

For compound **7b**, addition of 1 eq. CF<sub>3</sub>COOH leads to significant changes in both the UV-Vis and photoluminescence spectra, but the value of the absorption maximum is not changed significantly. Addition of one more equivalent of CF<sub>3</sub>COOH leads to decreased intensity of the peak at 408 nm and an increase of the peak at 421 nm. In the emission spectra, two distinct peaks become visible upon addition of 2 equivalents of CF<sub>3</sub>COOH.

Compounds **17a-c** demonstrate similar patterns in both UV-Vis and PL spectra but with lower absorption in UV part of the spectra for **17b**. (See Figures 14-16 and combined spectra in Supporting Information)

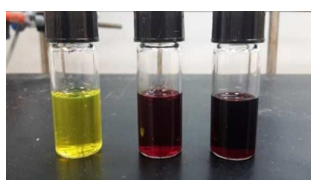
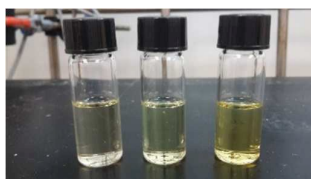


Figure 13. The solutions of **17a** (left), **17b** (middle) and **17c** (right) in chloroform before (top picture) and after the addition of trifluoroacetic acid (bottom picture).

The colour of the solutions containing **17a-c** significantly changes upon addition of 10 equivalents of acid, as shown in Figure 13.

No change in either UV Vis or PL spectra was observed upon addition of 1 and 2 eq of CF<sub>3</sub>COOH to a solution of **17a** in chloroform (Figure 14). However, 10 eq of CF<sub>3</sub>COOH leads to the appearance of a broad peak in UV Vis spectra with a maximum at 396 nm and a shift of the maximum to 502 nm in PL spectra.

By contrast as shown in Figures 15 and 16, the spectra of **17b** and **17c** change upon addition of 1 eq. of CF<sub>3</sub>COOH. The peak at 397nm starts to disappear and the peak at 449nm becomes more intense upon increase of the concentration of the acid. Unlike for **17a**, fluorescence quenching is observed for **17b** and **17c** upon addition of acid.

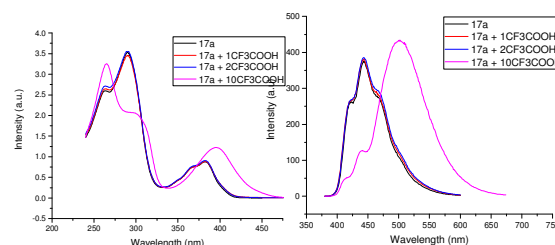
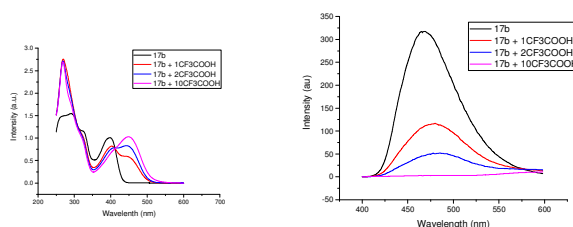


Figure 14. UV Vis (left) and photoluminescence (right) spectra of **17a**, and mixtures of **17a** with 1 equivalent, 2 equivalents, and 10 equivalents of CF<sub>3</sub>COOH



(5 x 10<sup>-5</sup> M in chloroform)

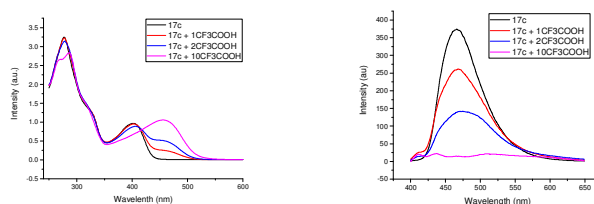


Figure 15. UV Vis (left) and photoluminescence (Right) spectra of **17b**, and mixtures of **17b** with 1 equivalent, 2 equivalents, and with 10 equivalents of CF<sub>3</sub>COOH (5 x 10<sup>-5</sup> M in chloroform)

Figure 16. UV Vis (left) and photoluminescence (right) spectra of **17c**, and mixtures of **17c** with 1 equivalent, 2 equivalents, and 10 equivalents of  $\text{CF}_3\text{COOH}$  ( $5 \times 10^{-5}$  M in chloroform)

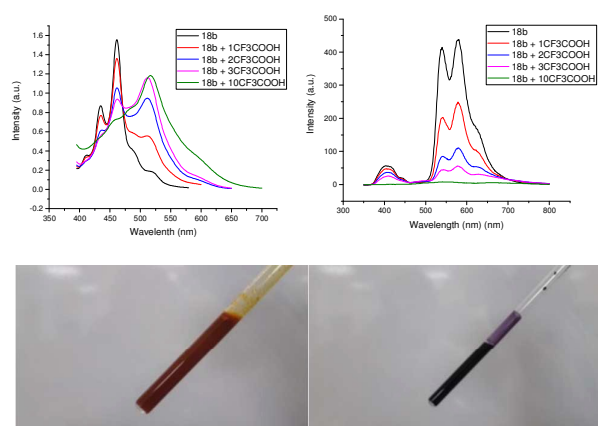


Figure 17. UV Vis (above left) and photoluminescence above (right) spectra of **18b**, and mixtures of **18b** with 1 equivalent, 2 equivalents, and 10 equivalents of  $\text{CF}_3\text{COOH}$  ( $10^{-5}$  M in chloroform). Solutions of **18b** in  $\text{CHCl}_3$  before (bottom left) and after (bottom right) addition of 10 equivalents of  $\text{CF}_3\text{COOH}$ .

Thus, the protonation of the compounds **17b** and **17c** occurs more easily than for **17a**. This is explained by the electron density, and thus the basicity, of the aromatic system in **17b** and **17c** being increased by the electron donating methoxy substituents in these molecules. This enrichment of the aromatic core electron density also explains the red shift in spectra with increasing number of methoxy groups from **17a** to **17c**.

Considering that the changes that occur in the UV-Vis spectra of **17a-c** upon the addition of acid are quite similar to the ones observed for **7a,b** (the intensity of one peak decreases, and the intensity of another gradually increases), and the presence of only one isosbestic point in the spectra (333nm for **17a**, 414nm for **17b**, and 412nm for **17c**), we again conclude that only one nitrogen is protonated in this range of acid concentrations.

Compound **18b** displays (Figure 17) two peaks in UV absorption spectrum at 435 and 462 nm and two peaks in the photoluminescence spectrum, at 540 and 581 nm (Stokes shift of 117nm). The onset of absorption is at 542 nm, which corresponds to an optical bandgap of 2.3 eV. Since the aromatic system of **18b** is larger than that of **17a-c**, a larger red shift is observed. A significant change in the absorption spectra is observed upon addition of trifluoroacetic acid. Upon addition of 10 eq. of trifluoroacetic acid, the mixture demonstrates a broad absorption with the maximum intensity at 516 nm which shows as a change in colour from red to purple (Figure 21 inset), which is similar to the colour change seen with indicators such as litmus. Again it can be concluded from the pattern of the change in UV-Vis spectra upon the acid addition, that as for all the previously mentioned compounds only one nitrogen protonates upon addition of the acid in the

studied range of concentrations. Quenching of fluorescence is observed upon addition of the acid, as was also seen for **17b** and **17c**.

This extreme change in optical properties suggests that compounds based on the diazapentacene framework may have potential for use in sensors. Unlike tetrazapentacenes whose solutions have been shown to undergo colour charges upon addition of anions such as fluoride due to a charge transfer process,<sup>6c</sup> no change in absorption or emission spectra were observed upon adding fluoride or cyanide anions to solutions of **18b**. This is because the lower number of nitrogen atoms in the diazapentacenes make them less able to accept an electron through charge transfer. Studies are underway into the effect of adding metal ions to solutions of **7a-d**, **17a-c** and **18b**.

## Conclusions

A convenient and general 4 step procedure for synthesis of various derivatives of pyrido[3,2-g]quinoline including an octahydro- (**7a**) and a tetrahydro-dibenzo-5,7-diazapentacene (**7b**), via Friedlander condensation has been developed. Although we have not yet succeeded in converting these molecules to fully aromatized 5,7-diazapentacene by means of dehydrogenation, we have synthesized a tetrabenzo-5,7-diazapentacene by employing a double Friedlander reaction followed by oxidation. Electrochemical measurement show that the effect of the nitrogen atoms is to lower the HOMO and LUMO energies of our new materials compared to pentacene. The materials show strong absorbance in the UV and violet regions of the spectrum, and strong fluorescence, suggesting they may have potential as emissive materials. We also found that the solutions of some of our compounds show significantly altered UV Vis absorption and photoluminescence spectra upon exposure to acids, which suggests they may have applications in sensing for acids. The measured optical and electrical properties of our 5,7-diazapentacene derivative and precursors suggest that suitably functionalized 5,7-diazapentacenes may be suitable for application in organic electronic devices.

## Conflicts of interest

There are no conflicts to declare.

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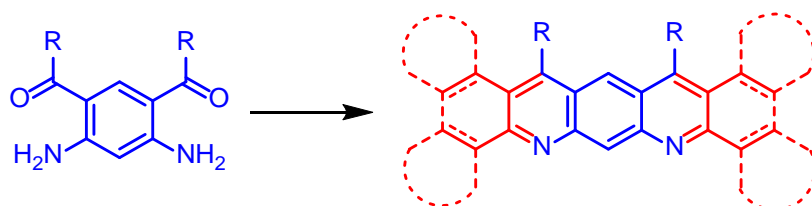
## A Friedländer route to 5,7-Diazapentacenes

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New 5,7-diazapentacene-based materials have been made by means of a Friedländer reaction, which could be promising candidates for optoelectronic applications.