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# The reductive aromatization of naphthalene diimide: A versatile platform for 2,7-diazapyrenes

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The reductive aromatization of naphthalene diimide provides tetrapivaloxy-2,7-diazapyrene, which serves as a versatile platform toward peripherally substituted 2,7-diazapyrenes. Timeresolved microwave conductivity measurements demonstrated that the intrinsic electron mobility of 2,7-diazapyrene is significantly higher than that of the corresponding pyrene.

Modification of the inner and outer regions in polycyclic aromatic hydrocarbons (PAHs) is a promising prospect for tuning their intrinsic properties leading to organic electronic materials.<sup>1</sup> The introduction of peripheral substituents in PAHs also modulates their electronic and photophysical properties, as well as their solubility and aggregation behaviour in the solid state. Consequently, the development of methods for the peripheral functionalization of PAHs is an important topic in current organic chemistry.<sup>2-6</sup>

The incorporation of heteroatoms into the core of PAHs also dramatically alters their electronic properties.<sup>7</sup> Specifically, the replacement of benzene rings in PAHs with pyridine rings is an efficient method for the modulation of their electronic properties, as the high electronegativity of the nitrogen atoms can lower the energy level of the LUMO of the PAHs.<sup>8-16</sup> Furthermore, nitrogen-doped PAHs should find applications as acid-responsive materials and as supporting ligands in supramolecular structures due to the ability of the nitrogen atom on the pyridine ring to coordinate protons and various metals.<sup>10, 12, 14</sup>

Pyrenes are simple and fundamental motifs in PAHs, which have attracted considerable attention as luminescent dyes and fluorescent probes in material and biological science.<sup>5,17</sup> Photophysical properties of pyrene derivatives have been extensively investigated to date. Considering the excellent

properties and functions of pyrenes, 2,7-diazapyrenes 1, a nitrogen-doped analogue of pyrene, should have versatile utilities in a wide range of areas. However, studies on 1 remain limited to those of the parent 2,7-diazapyrene (1a), due to the lack of efficient synthetic routes to other 2,7-diazapyrene derivatives.<sup>14-17</sup>



Scheme 1 Synthesis of 2,7-diazapyrenes.

The synthesis of 1a is based on the reduction of carbonyl groups and the oxidative aromatization of naphthalene diimides 2 (Scheme 1a).<sup>14, 18</sup> However, the low solubility of 1a hinders further transformations. Sachdev has reported the formation of 1,3,6,8-tetrakis(trimethylsiloxy)-2,7-diazapyrene from the reaction of 2a with butyllithium and trimethylsilyl chloride.<sup>16</sup> Unfortunately, the transformation of the siloxy groups was unsuccessful due to the low reactivity of the C-O bonds and the hydrolysis of the Si-O bonds. Herein, we report the reductive aromatization of 2a to 1,3,6,8-tetrapivaloxy-2,7diazapyrene 1b. The latter serves as a platform for the synthesis of a variety of substituted derivatives (1) via Nicatalysed cross-coupling reactions (Scheme 1b).<sup>19,20</sup> The highly planar and rigid structure, as well as the incorporation of the pyridinic nitrogen atoms endow 1 with intriguing photophysical properties and high electron mobility.

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The synthetic route to diazapyrenes **1b-1f** is shown in Scheme 2. Treatment of naphthalene diimide (2a) with 16 equiv of zinc powder and 16 equiv of pivalic anhydride (Piv<sub>2</sub>O) in 1,4-dioxane at 120 °C for 24 h afforded 1,3,6,8tetrapivaloxy-2,7-diazapyrene (1b) in 85% yield, which was then successfully transformed into tetraaryl-2,7-diazapyrenes 1c-f via Ni-catalysed cross-coupling reactions with arylboronic acids.<sup>20</sup> The reaction of **1b** with 4-*tert*-butylphenylboronic acid in the presence of Ni(cod)<sub>2</sub> (cod: 1,5-cyclooctadiene), tricyclohexylphosphine (PCy<sub>3</sub>), and K<sub>3</sub>PO<sub>4</sub> in toluene at 60 °C for 18 h afforded the corresponding diazapyrene (1c) in 59% yield. A variety of arylboronic acids were applicable to this reaction system, and 1d-1f were obtained in moderate yields. Unfortunately, attempts to use alkylboronic acids for the introduction of alkyl groups were not successful. However, we were able to prepare 1g in 77% yield from the desulfurization of the thiophene rings of 1f using Raney nickel (Scheme 3). Diazapyrenes 1b-g are readily soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and toluene, while **1g** is soluble even in hexane and cyclohexane. The present synthetic route is simple, but should be useful and promising to solve the difficulties in the preparation of various functionalized 2,7diazapyrenes and tuning their prosperities (vide infra).



Scheme 2 Synthesis of 1 via the reductive aromatization of naphthalene diimide (2a). a) Zn (16 equiv),  $Piv_2O$  (16 equiv), 1,4-dioxane, 120 °C, 24 h; b) ArB(OH)<sub>2</sub> (16 equiv), Ni(cod)<sub>2</sub> (40 mol%), PCy<sub>3</sub> (80 mol%), K<sub>3</sub>PO<sub>4</sub> (16 equiv), toluene, 60 °C, 18 h



Scheme 3 Desulfurization of 1f into 1g.

Recrystallization of **1c** (toluene/acetonitrile) and **1g** (acetonitrile) afforded single crystals suitable for X-ray diffraction analyses. The mean plane deviation of the diazapyrene core in **1c** is 0.079 Å, reflecting the highly planar conformation of the diazapyrene core (Fig. 1a). The dihedral angles (~32–33°) between the pyridine moieties and the 4-*tert*-buthylphenyl groups in **1c** are smaller than those in 1,3,6,8-tetra(4-*tert*-buthylphenyl)pyrene (51–55°).<sup>21</sup> This result clearly shows that the replacement of the C–H moieties at the 2 and 7 positions in pyrene with nitrogen atoms reduces the steric repulsion between the central core and the peripheral aryl groups. The dihedral angles (~15-18°) in **1f** are smaller than

those of **1c** (Fig. S1). These dihedral angles in **1c** and **1f** indicate the effective expansion of  $\pi$ -conjugation.

The packing structure of **1g** is different from those of **1c** and **1f** (Fig. 1d). While  $\pi$ -stacking between the diazapyrene cores was not observed for molecules of **1c** and **1f**, those of **1g** are stacked in a face-to-face manner with an interplanar distance of 3.406 Å.



Fig. 1 Molecular structures of 1c and 1g. (a) Top and (b) side views of 1c. (c) Molecular structure and (d) packing structure of 1g. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Thermal ellipsoids are set to 50% probability.

Fig. 2a shows the electronic absorption spectra of 1c, 1f and 1g in  $CH_2CI_2$ . In order to clarify the features of the electronic spectra, time-dependent density functional theory (TDDFT) calculations were carried out at the B3LYP/6-31G+(d,p) level of theory on 1a (as a model for 1g) and 1c. The simulated absorption spectrum of 1a was consistent with the experimental one of 1g (Fig. S2). According to the TDDFT calculations, the lowest energy band of 1g consists of two similar transitions, which were assigned to a combination of the HOMO-4→LUMO and HOMO→LUMO+1 transitions, and to a combination of the HOMO-4→LUMO+1 and HOMO→LUMO transitions. On the other hand, the lowest energy band of 1c was assigned to the HOMO→LUMO transition.

In CH<sub>2</sub>Cl<sub>2</sub>, diazapyrenes **1c–1g** exhibit fluorescence ( $\Phi = 0.13 \sim 0.47$ ) spectra, which are the mirror images of the corresponding absorption spectra (Fig. 2b and S10). The introduction of peripheral aryl groups also exhibits a bathochromic shift of emission bands: The colours of emission were changed dramatically based on effective  $\pi$ -conjugation of the aryl groups (Fig. 3b, 3c and S10). Furthermore, solid samples of **1c–1g** emit fluorescence ( $\Phi = 0.01 \sim 0.41$ ) (Fig. S10). Interestingly, a new emission band at ~500 nm was observed with increasing concentration of **1g** (Fig. 3a, 3d-e). The lifetime measured in dilute solution ( $1.0 \times 10^{-6}$  M) at 425 nm was 7.6 ns, while it was 19.4 ns when measured at 500 nm in a

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concentrated solution ( $1.0 \times 10^{-2}$  M). Based on these results, the new emission at ~500 nm was assigned to the excimer emission.



**Fig. 2** (a) Absorption spectra of **1c** (red), **1f** (black) and **1g** (blue) in CH<sub>2</sub>Cl<sub>2</sub>. (b) Absorption (black solid line: in CH<sub>2</sub>Cl<sub>2</sub>; red solid line: in 2,2,2-trifluoroethanol) and fluorescence (black dashed line: in CH<sub>2</sub>Cl<sub>2</sub>; red dashed line: in 2,2,2-trifluoroethanol) spectra ( $\lambda_{ex}$  = 360 nm) of **1g**.



**Fig. 3** (a) Fluorescence spectra of **1g** in methylcyclohexane at various concentrations (normalized at 425 nm). (b) Photo of cuvette containing **1c** in CH<sub>2</sub>Cl<sub>2</sub> (4.9 × 10<sup>-5</sup> M) under illumination ( $\lambda_{ex}$  = 365 nm). (c) Photo of cuvette containing **1f** in CH<sub>2</sub>Cl<sub>2</sub> (6.9 × 10<sup>-5</sup> M) under illumination ( $\lambda_{ex}$  = 365 nm). Photos of cuvettes containing **1g** in methylcyclohexane under illumination ( $\lambda_{ex}$  = 365 nm) at (d) 1.0 × 10<sup>-6</sup> M and (e) 1.0 × 10<sup>-2</sup> M.

We also discovered that the use of protic solvents induces significant changes in the photophysical properties of 1g. When we measured the absorption spectrum of 1g in 2,2,2trifluoroethanol, a new absorption band was observed at ~420 nm (Fig. 3a). In addition, the emission spectrum was bathochromically shifted. In sharp contrast, such a change was not observed for 1,3,6,8-tetrapentylpyrene (3). In order to investigate the potential of 1g to serve as an acid-responsive material, protonation experiments of 1g in CH<sub>2</sub>Cl<sub>2</sub> were carried out (Fig. 4). The addition of trifluoroacetic acid (TFA) to a CH<sub>2</sub>Cl<sub>2</sub> solution of **1g** resulted in the appearance of a new absorption band at 427 nm (Fig. 4a). The observation of isosbestic points supports the direct transformation of 1g into the monoprotonated species A (Fig. 4c). After 2.5 equiv of TFA had been added, the absorption band bathochromically shifted to 444 nm (Fig. 4b). For the sake of comparison, we prepared the diprotonated compound 4 (OTs = p-toluenesulfonate), which exhibited a similar absorption band at 441 nm; this result confirms that the absorption band at 444 nm in Fig. 4b originates from the diprotonated species B. Similar changes were also observed in the fluorescence spectra of 1g upon protonation (Fig. S13).

The electrochemical properties of **1g** and **3** were examined by cyclic voltammetry (Fig. S6–S9). Diazapyrene **1g** exhibits one reversible reduction potential (–2.56 V; vs  $[Fc]/[Fc]^+$ ), while a reduction peak was not observed for pyrene **3** up to –3.0 V,





Fig. 4 Spectral changes in the absorption spectra of 1g in  $CH_2Cl_2~(2.7\times10^{-5}$  M) upon addition of TFA (a) (0–2.5 equiv) and (b) (2.5–1132 equiv). (c) Stepwise protonation of 1g.

The low LUMO level motivated us to evaluate the electron mobility of 1g in the hope to find a new n-type semiconducting material. In order to minimize the effects of contact resistance on the electrodes and focus on its intrinsic properties, 1g was analysed using field-induced time-resolved microwave conductivity (FI-TRMC) measurements.<sup>22</sup> Using FI-TRMC, the intrinsic carrier mobility at semiconductor-insulator interfaces was evaluated by monitoring microwaves reflected by a simple metal-insulator-semiconductor (MIS) device that contains the target semiconductor materials. Here, a hexane solution of 1g was spin-coated onto poly(methyl methacrylate)/SiO<sub>2</sub> layers to form a thin film, and gold electrodes were deposited to inject charge carriers. A powder X-ray diffraction analysis revealed that 1g exhibits a lamellar periodicity of 14.4 Å (Fig. S14), suggesting that the 2,7-diazapyrene cores form 2D  $\pi$ -electron layers parallel to the substrate. Upon applying a gate bias to the MIS devices, current flows were observed (Fig. S15), indicating that the injection of electrons into the 1g layer and the reflected microwave power changed simultaneously (Fig. S16). The number of charge carriers  $(N_e)$  was estimated from integration of the flow current, while the the pseudoconductivity ( $N_e\mu_e$ ) was calculated from the reflected microwave power.<sup>22a</sup> The  $N_e$  and  $N_e\mu_e$  values were plotted as a function of the gate bias, and the slope of the resulting plots describes the electron mobility (Fig. 5a). For 1g, an electron mobility of  $\mu_{\rm e}$  = 0.6 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was estimated. In sharp contrast, pyrene 3 showed little microwave response for both holes and electrons, i.e., the mobilities were below the instrument detection limit (<  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) (Fig. 5b and S17). This clear contrast suggests that nitrogen-doping PAHs dramatically alters their electronic properties, inducing e.g. electron mobility in the solid state. It should be noted that the devices were prepared by spin-coating from a nonhalogenated solvent, the use of which has not been

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demonstrated for common n-type materials such as arylene diimides.



Fig. 5 Correlation between the pseudo-electrical conductivity ( $N\mu$ ) and the number of injected electrons (N) in MIS devices using (a) **1g** and (b) **3**.

In summary, we have developed a novel protocol for the synthesis of various 2,7-diazapyrenes using a combination of a reductive aromatization of naphthalene diimide and Nicatalysed cross-coupling reactions. We have also discovered that 1g exhibits an excimer emission in concentrated solution as well as acid-responsive changes in the absorption and fluorescence spectra. The electrochemical studies of 1 confirmed that the electronegativity of the nitrogen atoms lowers the LUMO level. Furthermore, FI-TRMC measurements clearly demonstrated a higher electron mobility for 1g compared to pyrene, suggesting that diazapyrenes 1 may become promising n-type organic semiconductors.<sup>23</sup> The present method is potentially applicable for the synthesis of  $\pi$ extended pyridine-doped PAHs by the reductive aromatization of various arylene diimides. Consequently, this protocol will open up a new field of larger nitrogen-doped PAHs based on precise control of structure and electronic nature. Further investigations into the synthesis of new pyridine-annulated PAHs using reductive aromatization are currently in progress in our group.

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### **Conflicts of interest**

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There are no conflicts to declare.

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