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Synthesis and crystal packing structures of 2,7-diazapyrenes with various alkyl groups at 1,3,6,8-positions

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We have developed the synthesis of 1,3,6,8-tetramethoxy-2,7-diazapyrene through reductive aromatization of naphthalene diimide. The methoxy groups were readily converted to a variety of alkyl groups through Ni-catalyzed cross-coupling reaction with alkyl Grignard reagents. The peripheral substituents significantly influenced the packing structures of 2,7-diazapyrenes in the solid state.

Keywords: Diazapyrene, Reductive aromatization, Cross-coupling

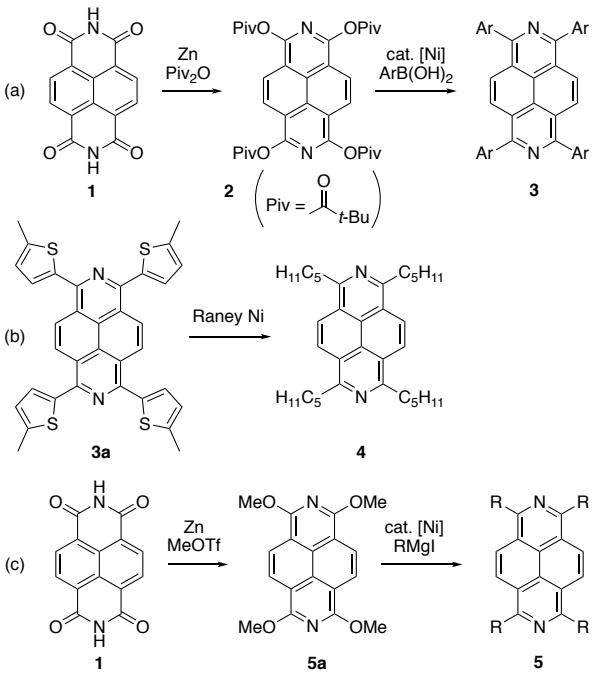
Polycyclic aromatic hydrocarbons (PAHs) are widely investigated for organic electronic materials.[1-5] To modulate the electronic and photophysical properties of PAHs, introduction of heteroatoms to the PAHs flameworks is an effective strategy.[6] Nitrogen is an attractive element to be doped into PAHs flameworks because of its high electro-negativity.[7-9] Consequently, nitrogen-doped PAHs are often examined for n-type semiconductors.[10-12,15,17]

Pyrene is one of the representative PAHs. Numerous pyrene derivatives have been synthesized and widely explored in various fields such as photo-, electro- and bio-chemistry.[13] Nitrogen-doped pyrenes have also been prepared.[14-16] However, the studies on nitrogen analogous of pyrene have largely lagged behind those of pyrenes because of the lack in their efficient synthetic methods.

Recently, we have synthesized 1,3,6,8-tetra(pivaloxy)-2,7-diazapyrene **2** by reductive aromatization of naphthalene diimide **1** (Scheme 1a).[17a] This strategy enables efficient introduction of various aryl groups to 2,7-diazapyrenes to afford tetraaryl-2,7-diazapyrene **3**. Unfortunately, however, tetraalkyl-2,7-diazapyrenes **5** were not accessible because no coupling reaction of **2** with alkylboronic acids proceeded. Alkylation of **2** with alkyl Grignard reagents was also not successful because of the nucleophilic attack of Grignard reagents to the pivaloxy groups.

Desulfurization of the thienyl groups of **3a** with Raney nickel allowed the indirect introduction of alkyl groups to the peripheral positions of 2,7-diazapyrene (Scheme 1b). Field-induced time-resolved microwave conductivity (FI-TRMC) measurements[18] revealed a good electron mobility for **4**,[17a] demonstrating that tetraalkyl-2,7-diazapyrenes are promising candidates for n-type semiconductors. To investigate the potential of 2,7-diazapyrenes for electron transporting materials, their solid state structures should be engineered by the proper peripheral alkyl groups.[19] However, the desulfurization strategy is not straightforward to synthesize 2,7-diazapyrenes with various alkyl groups. Furthermore, desulfurization only provides 2,7-diazapyrenes with alkyl groups longer than a butyl group.

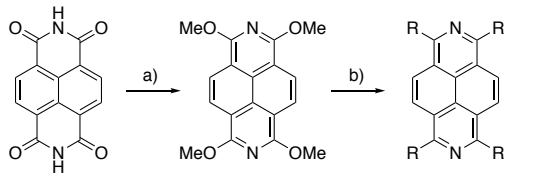
To overcome the shortcomings, we have developed a more efficient method for the introduction of various alkyl groups at the peripheral position of 2,7-diazapyrenes. Herein we disclose the reductive aromatization of naphthalene diimide **1** into 1,3,6,8-tetramethoxy-2,7-diazapyrene **5a** (Scheme 1c). Furthermore, we have demonstrated the transformation of the methoxy groups to alkyl groups via cross-coupling reaction with alkyl Grignard reagents.[20-22]



Scheme 1. (a) Synthesis of 2,7-diazapyrene derivatives via reductive aromatization of **1**. (b) Desulfurization of **3a** into **4**. (c) This work.

Scheme 2 shows the synthetic procedure of diazapyrenes **5a**–**5d**. The reaction of naphthalene diimide (**1**) with 6 equiv of methyl triflate (MeOTf) in the presence of 16 equiv of zinc powder in 1,4-dioxane at 60 °C for 24 h afforded tetramethoxy-2,7-diazapyrene **5a** in 41% yield. The methoxy groups in **5a** were readily converted to various alkyl groups through the cross-coupling reaction with alkyl Grignard reagents to provide tetraalkyl-2,7-diazapyrenes **5b**–**5d**.[21e] Treatment of **5a** with methylmagnesium iodide in the presence of catalytic amounts of $Ni(cod)_2$ (cod: 1,5-cyclooctadiene) and bis(dicyclohexylphosphino)ethane (dcype) afforded tetramethyldiazapyrene **5b** in 37% yield.

The use of ethyl and propyl Grignard reagents furnished tetraethyldiazapyrene **5c** and tetrapropyldiazapyrene **5d** in 16% and 12% yields, respectively. Unfortunately, the introduction of longer alkyl groups was sluggish under the optimized conditions. Diazapyrenes **5a**–**5d** are readily soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, and toluene.



Scheme 2. Synthesis of tetralkyldiazapyrenes. (a) Zn (16 equiv), MeOTf (6 equiv), 1,4-dioxane, 60 °C, 24 h; (b) RMgI (6 equiv), $Ni(cod)_2$ (40 mol%), dcype (40 mol%), toluene, 80 °C, 24 h.

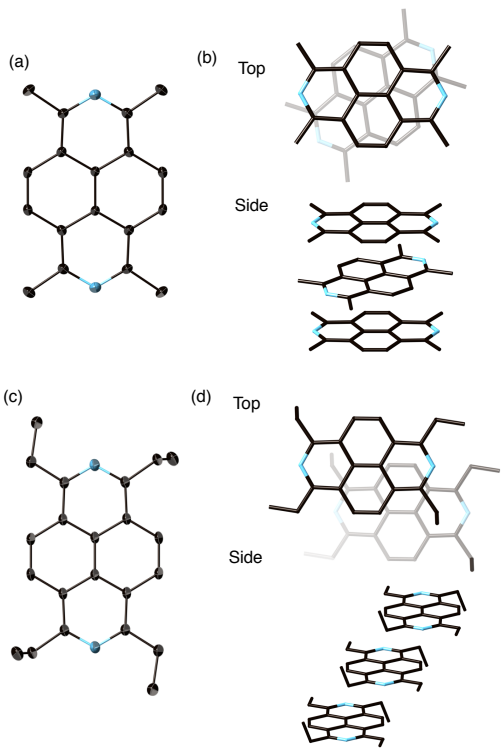


Figure 1. (a) Molecular structure and (b) packing structure of **5b** and (c) molecular structure and (d) packing structure of **5c**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 50% probability.

We successfully obtained single crystals of **5a** (dichloroethane/hexane), **5b** ($CHCl_3$/hexane), and **5c** ($CHCl_3$/acetonitrile) suitable for X-ray analysis (Figures 1 and S1). The diazapyrene core in **5a**, **5b**, and **5c** adopts highly planar conformation. Each molecule of **5c** is arranged in a slipped stacking manner in the one-dimensional columnar structure. The distance between π-planes is 3.364 Å (Figure 1d). This packing structure is similar to that of **4**. In sharp contrast, **5b** forms face-to-face stacking in the crystal with an interplanar distance of 3.385 Å (Figure 1b). A brickwork packing structure was observed in **5a** (Figure S1b). The distance between π-planes in **5a** (3.448 Å) is longer than those of **5b** and **5c** having alkyl groups. It is noteworthy that such small differences in peripheral substituents dramatically changed the morphology of the solid state.

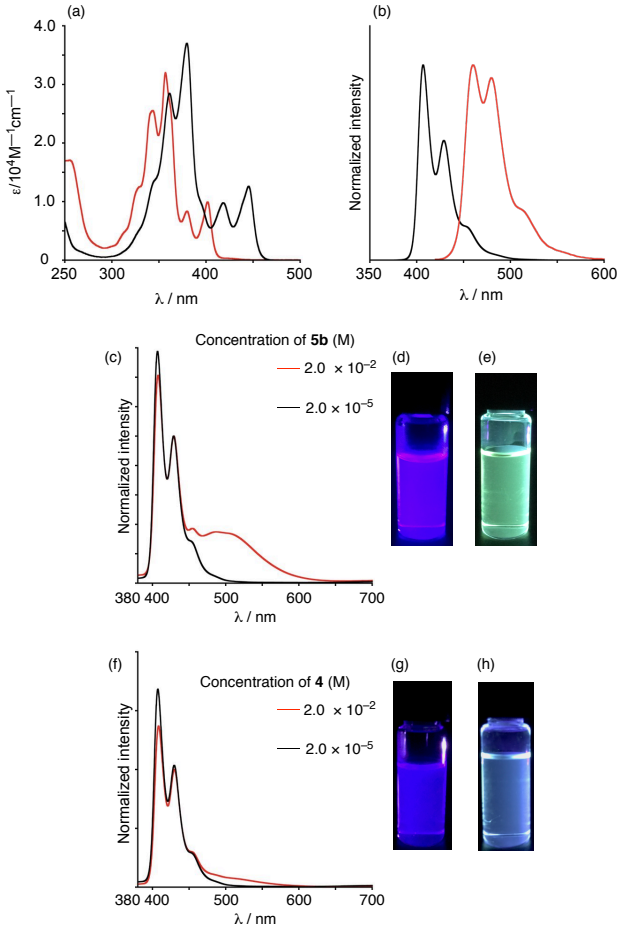


Figure 2. (a) UV-vis absorption spectra of **5a** (black line) and **5b** (red line) in CH_2Cl_2. (b) Fluorescence spectra of **5a** (black line) and **5b** (red line) in CH_2Cl_2. (c) Emission spectra of **5b** in CH_2Cl_2. Photo images of **5b** in CH_2Cl_2 (2.0×10^{-5} M) under excitation (λ_{ex} = 360 nm) at (d) 2.0×10^{-5} M and (e) 2.0×10^{-2} M. (f) Emission spectra of **4** in CH_2Cl_2. Photo images of **4** in CH_2Cl_2 under excitation (λ_{ex} = 360 nm) at (g) 2.0×10^{-5} M and (h) 2.0×10^{-2} M.

Figure 2a and Figure S7 show UV-vis absorption spectra of **5a**–**5d** in CH_2Cl_2. While the change of the alkyl groups did not alter the absorption spectra of tetraalkyldiazapyrene **5b**–**5d**, bathochromic shift was observed in tetramethoxydiazapyrene **5a**. Diazapyrenes **5a**–**5d** show fluorescence (Φ = 0.28–0.49) in CH_2Cl_2. In accordance with the absorption spectra, the emission band of **5a** also bathochromically shifted compared to **5b**–**5d** (Figures 2b and S7). As the concentration increased, a new emission band was observed around 500 nm in **5b** (Figure. 2c).[23] The fluorescence lifetime measured at 425 nm in a

dilute solution was 6.5 ns, while the lifetime measured at 500 nm in a concentrated solution was 26 ns. These results clearly suggest that the newly observed emission was the excimer emission. Interestingly, the stronger excimer emission of **5b** was observed than that of **4** (Figure. 2f). This result clearly indicates that **5b** readily forms an excimer because of the smaller steric hindrance of the methyl group than the pentyl group.

The electrochemical properties of **5a**–**5d** were investigated by cyclic voltammetry and differential-pulse voltammetry (Table 1). Diazapyrene **5b** exhibits one reversible reduction potential (–2.58 V; vs $[Fc]/[Fc]^+$), which is similar to those of **5c** and **5d**. While no reduction wave was observed in **5a** up to –3.0 V. This result indicates that the introduction of methoxy groups to the diazapyrene core raises the LUMO level. The first oxidation potential of **5a** was also observed at a lower potential (0.16 V) than those of **5b**–**5d**.

Table 1. Redox potentials of **5a**–**5d**.[a]

Diazapyrene	E_{ox}^1 (V)	E_{red}^1 (V)
5a	0.16	–
5b	0.81[b]	–2.58
5c	0.83	–2.56
5d	0.83	–2.56

[a]Solvent: CH_2Cl_2 (oxidation) or THF (reduction); supporting electrolyte: Bu_4NPF_6 (0.1 M); working electrode: glassy carbon electrode; counter electrode: platinum wire; reference electrode: Ag/Ag^+. All potentials are referenced to the potential of ferrocene/ferrocenium couple. [b]Determined by differential-pulse voltammetry.

The unique face-to-face packing structure of **5b** in its single crystal stimulated us to investigate its conductivity. The field-induced time-resolved microwave conductivity (FI-TRMC) technique was employed to investigate the local-scale charge transport properties for both positive (hole) and negative (electron) carriers.[18] A $CHCl_3$ solution of **5b** was spincoated to form a thin film on polyimide-coated SiO_2 insulating layers on gold electrode-patterned quartz substrate. A top gold electrode was deposited on the **5b** layer to fabricate the metal–insulator–semiconductor (MIS) device. The MIS device, placed in the resonant cavity, was monitored by microwave spectroscopy. With a square wave gate bias applied to the MIS devices, current flows were appeared (Figure. S8a), indicating the injection of electrons to the **5b** layer. By integrating the flow current, the profiles of the number of accumulated charges were obtained (Figure. S8b). The number of injected charge carriers (N_{inj}) was calculated from the saturated values in each bias voltage. Accordingly, the reflected microwave power changed in response to the accumulated charges (Figure. S8c). The pseudoconductivity ($\Delta N\mu_e$) was calculated from the saturated reflected microwave power.[18a] As the N_{inj} and $\Delta N\mu_e$ values were plotted at each gate bias, the slope of the resulting plots represents electron mobility (Figure. S8d), yielding $\mu_e = 0.07$ cm^2 V^{-1} s^{-1} for the film of **5b**. Similarly, the charge carrier mobility of a spincoated film of **5c** was evaluated by the FI-TRMC method, recording $\mu_e = 0.06$ cm^2 V^{-1} s^{-1} (Figure. S9). These values are almost same as the electron mobility of **4** measured under the similar conditions ($\mu_e = 0.09$ cm^2 V^{-1} s^{-1}) (Figure. S10). Powder X-ray diffraction (PXRD) measurements of the spincoated film of **5b** revealed that the packing structure in the film was close to that of the single crystal (Figure. S11a). On the other hand, the patterns obtained from the spincoated film and simulation from the single crystal data were different for **5c** (Figure. S11b). Control of the packing structures and the degree of crystallinity in the film state are worthy of further investigation. Nevertheless, the comparable electron mobility values evaluated for **5b** and **5c** suggests that the overlaps of low LUMOs of the 2,7-diazapyrene derivatives contribute to the observed high electron mobility for **5b** and **5c**.

In summary, we have developed the synthesis of 1,3,6,8-tetramethoxy-2,7-diazapyrene **5a** through reductive aromatization of naphthalene diimide. The methoxy groups were converted to a variety of alkyl groups through Ni-catalyzed cross-coupling reaction with alkyl Grignard reagents. The X-ray crystallographic analysis of **5** elucidated that the length of the alkyl groups dramatically affected their packing structures in the solid state. Tetramethyl-2,7-diazapyrene **5b** exhibited more distinct excimer emission as compared to tetrapentyl-2,7-diazapyrene **4**, indicating that the length of the alkyl groups modulates the intermolecular interactions in solution. Furthermore, FI-TRMC measurements clearly revealed the intrinsic high electron mobility of **5b** and **5c**. Further investigations for the application of 2,7-diazapyrenes to OFETs are currently in progress in our group.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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23 Triangular fluorescence cell (T-81 TOSOH QUARTS) was used for the measurement of the excimer emission.