



A concise method to prepare linear 2,3-diazaoligoacene derivatives



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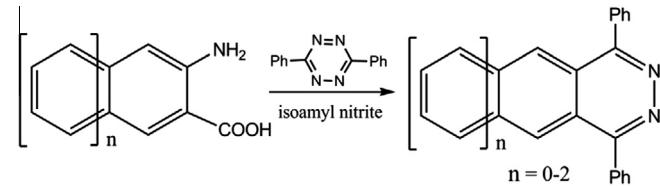
Cycloaddition reaction

Crystal packing

ABSTRACT

In this Letter, we demonstrate that linear 2,3-diazanaphthalene (**1**), 2,3-diazaanthracene (**2**), and 2,3-diazatetracene (**3**) can be easily prepared through [4+2] cycloaddition reaction between 3,6-diphenyl-1,2,4,5-tetrazine as the diene and arynes as dienophiles, generated *in situ* from *ortho*-aminoarylcarboxylic acids. The physical properties and crystal packing of the prepared compounds **1–3** were fully investigated. In addition, the experimental data (e.g., band gap and band position) are further confirmed by theoretical studies.

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Scheme 1. The synthetic method toward 2,3-diazaacenes.

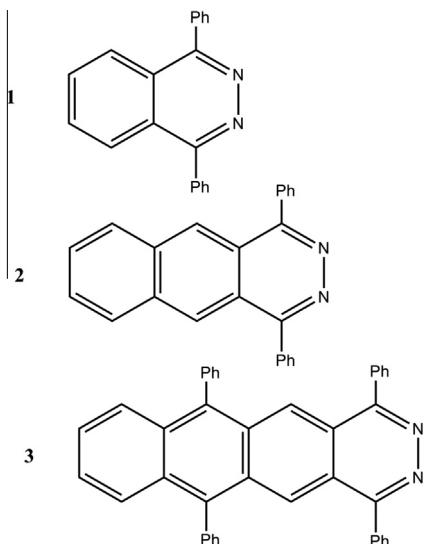
(CV), crystal structures, and theoretical studies, except UV-vis absorption] are reported here for the first time.

1,4-Diphenyl-2,3-diazanaphthalene (**1**), 1,4-diphenyl-2,3-diazaanthracene (**2**), and 1,4,6,11-tetraphenyl-2,3-diazatetracene (**3**) (Scheme 2) have been synthesized through [4+2] reactions between 3,6-diphenyl-1,2,4,5-tetrazine and the corresponding aryne precursors [2-aminobenzoic acid (for **1**, yield 58%), 3-amino-2-naphthoic acid (for **2**, yield 63%), and 3-amino-9,10-diphenylanthracene-2-carboxylic acid¹¹ (for **3**, yield 40%)]. The compounds prepared were fully characterized by ¹H NMR, ¹³C NMR, and high-resolution mass spectrometry (HRMS). Moreover, the structures of compounds **1–3** were further confirmed by single crystal structure analysis (CCDC numbers for **1–3** are 998769, 998770 and 993356, respectively).

The crystal structures and the crystal packing arrangements of compounds **1–3** are shown in Figure 1. Compound **1** possesses an orthorhombic space group, Cmc₂1 (36), and its unit cell data are as follows: *a* = 20.1791(10) Å, *b* = 10.7017(6) Å, *c* = 8.2409(3) Å, $\alpha = \beta = \gamma = 90(0)$. The molecules of compound **1** are stacked with an offset head-to-head mode due to the spatial hindrance of the phenyl

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**Scheme 2.** Molecular structures of compounds **1–3**.

groups. There are weak π – π stacking interactions (~ 3.75 Å) between the pyridazine unit and benzene groups. Compound **2** has a monoclinic space group, $C12/c1$ (15), and its unit cell data are: $a = 20.4657(5)$ Å, $b = 10.6386(3)$ Å, $c = 7.6951(2)$ Å, $\beta = 96.16(0)$ °. Being different from compound **1**, compound **2** shows an offset head-to-tail stacking and the distance between the two naphthalene units is nearly 3.86 Å, indicating a very weak π – π stacking interactions between the molecules. Compound **3** possesses a triclinic space group, $p1$ (2), with unit cell data of $a = 10.0261(4)$ Å, $b = 13.2546(4)$ Å,

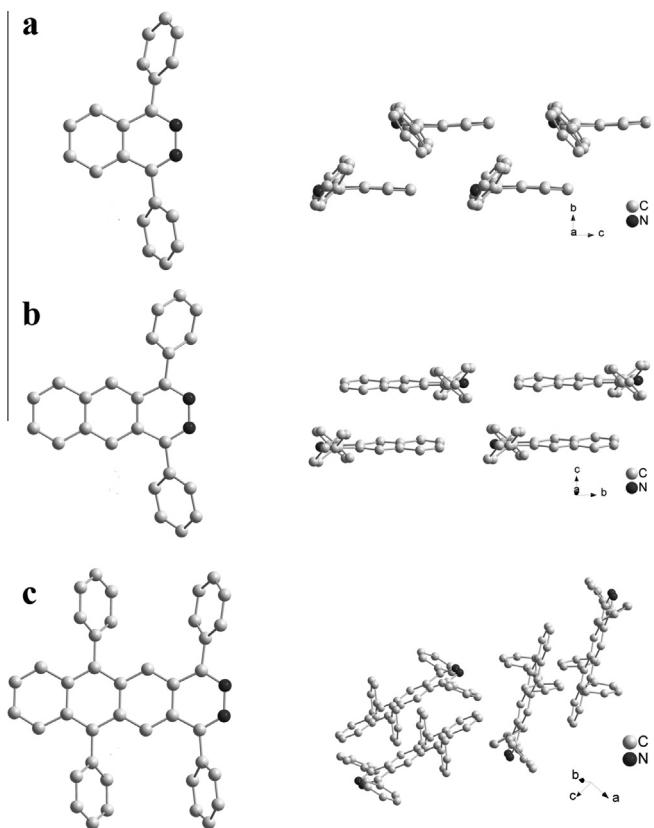
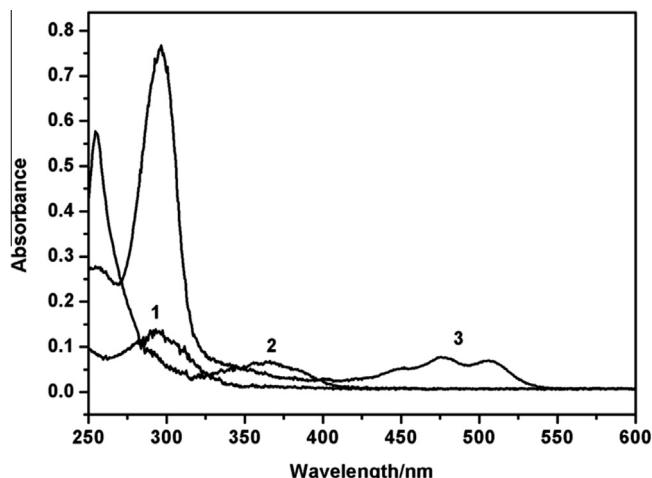
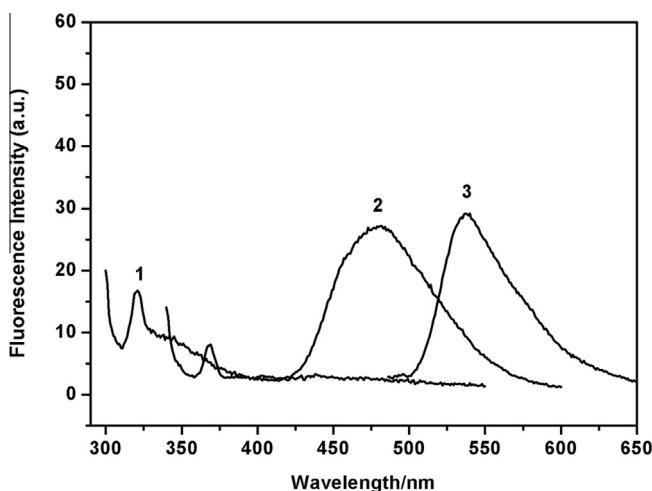
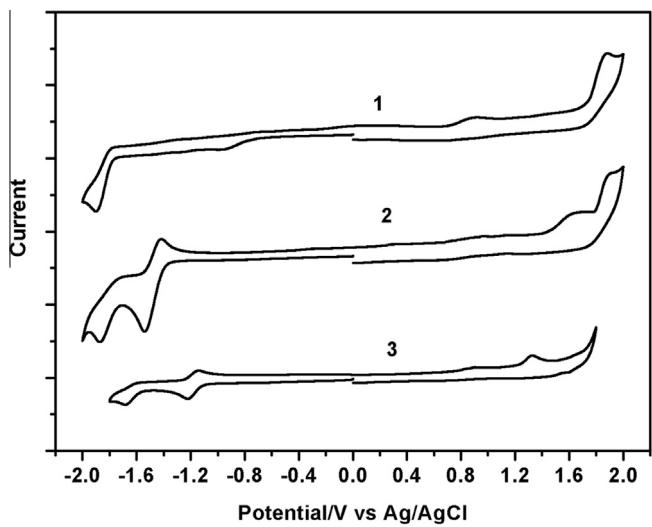
**Figure 1.** Crystal structures of compounds **1–3** (hydrogen atoms are omitted) and Crystal packing arrangements.**Figure 2.** UV-vis spectra of compounds **1–3** (1×10^{-5} M) in CH_2Cl_2 .**Figure 3.** Fluorescence spectra of compounds **1–3** (1×10^{-5} M) in CH_2Cl_2 .**Figure 4.** Cyclic voltammetry curves of compounds **1–3** in CH_2Cl_2 solution containing 0.1 M TBAP electrolyte. Scanning rate: 100 mV/s.

Table 1Electrochemical data and calculated HOMO–LUMO gaps of compounds **1–3**

| Compound | $E_{\text{onset}}^{\text{red}} \text{ (V)}$ | $E_{\text{onset}}^{\text{ox}} \text{ (V)}$ | $E_{\text{gap}} \text{ (eV)}$ | LUMO ^c (eV) | HOMO ^d (eV) | $E_{\text{gap}}/\lambda_{\text{onset}} \text{ [(eV)/nm]}$ | LUMO ^f (eV) | HOMO ^f (eV) | $E_{\text{gap}} \text{ (eV)}$ |
|----------|---|--|-------------------------------|------------------------|------------------------|---|------------------------|------------------------|-------------------------------|
| 1 | −1.76 | 1.66 | 3.42 | −2.64 | −6.06 | 3.71/334 | −1.78 | −6.07 | 4.29 |
| 2 | −1.37 | 1.40 | 2.77 | −3.03 | −5.80 | 3.05/406 | −2.23 | −5.75 | 3.52 |
| 3 | −1.11 | 1.23 | 2.34 | −3.29 | −5.63 | 2.33/533 | −2.47 | −5.19 | 2.72 |

^a Obtained from cyclic voltammograms in CH_2Cl_2 . Reference electrode: Ag/AgCl.^b $E_{\text{gap}} = E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$.^c Calculated from cyclic voltammograms.^d Calculated according to the formula $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{gap}}$.^e Optical band gap, $E_{\text{gap}} = 1240/\lambda_{\text{onset}}$.^f Obtained from theoretical calculations.

$c = 23.7718(8) \text{ \AA}$, $\alpha = 100.86(0)^\circ$, $\beta = 99.16(0)^\circ$, $\gamma = 106.94(0)^\circ$. There are two different stacking columns in the crystal of compound **3** and both columns show head-to-tail packing. However, as shown in Figure 1c, the left column shows face-to-face packing with a stacking distance of 3.92 \AA (very weak π - π interactions), while in the right column, molecules have a large offset stacking, where the main force for this type of packing might be induced by the CH- π stacking effect between the phenyl groups and backbone of the tetracenes. Moreover, all the molecules in the two columns are arranged in a herringbone motif.

Figure 2 shows the UV-vis spectra of 1,4-diphenyl-2,3-diazanaphthalene (**1**), 1,4-diphenyl-2,3-diazaanthracene (**2**), and 1,4-diphenyl-2,3-diazatetracene (**3**) in CH_2Cl_2 . As the length of the acene increases, the maximum absorption peak is red-shifted from 293 nm to 362 nm to 506 nm . Moreover, compounds **1–3** display no (for compound **1**) or very weak fluorescence (for compounds **2** and **3**) (Fig. 3). The fluorescence quantum yields (Φ_f) of compounds **2** and **3** were calculated as 0.0075 and 0.0071 , respectively, with 9,10-diphenylanthracene ($\Phi_f = 0.95$ in ethanol)¹² and rubrene ($\Phi_f = 0.96$ in CH_2Cl_2)¹³ as the reference standards, which indicates

that inserting N atoms at positions 2 and 3 can strongly quench the fluorescence, which might be attributed to the intersystem crossing effect.¹⁴

The electrochemical properties of compounds **1–3** were investigated by CV in anhydrous CH_2Cl_2 (Fig. 4 and Table 1). Compound **1** shows one irreversible oxidation peak and one irreversible reduction peak. The onset oxidative and onset reductive potentials are at 1.66 V and $−1.76 \text{ V}$, respectively. With increasing length of the azaacene, the onset oxidation potentials were reduced from 1.66 V (for **1**) to 1.40 V (for **2**) and 1.23 V (for **3**), respectively. Meanwhile, the onset reductive potentials were increased from $−1.76 \text{ V}$ (for **1**) to $−1.37 \text{ V}$ (for **2**) and $−1.11 \text{ V}$ (for **3**), respectively. Results show that with increasing length, the prepared compounds become much easier to oxidize and more difficult to reduce.

The molecular geometries of compounds **1–3** were optimized using density functional theory (DFT) at the B3LYP/6-31G* level.¹⁵ The ground state frontier molecular orbitals of the optimized molecules were also calculated at the same level. As shown in Figure 5, for compound **1**, the highest occupied molecular orbitals (HOMO) were mainly localized on the pyridazine ring but the lowest unoccupied molecular orbitals (LUMO) were localized on the whole molecule including the phenyl groups. For compounds **2** and **3**, the HOMO and LUMO orbitals are mainly localized on the backbones of the molecules. The calculated HOMO, LUMO, and band gap values of compounds **1–3** are slightly different to those obtained by cyclic voltammetry, which maybe because the simulation was performed in the gas phase (Table 1). However, the variation tendencies of the calculated results are consistent with experimental data.

In summary, using the classical [4+2] cycloaddition reaction between 3,6-diphenyl-1,2,4,5-tetrazine as the diene and in situ generated arynes as dienophiles, three oligoazaacenes have been successfully synthesized. The physical properties and crystal packing of compounds **1–3** have been studied and compared. Meanwhile, the data from DFT calculations were in accordance with experimental results. Our method should offer a useful strategy to prepare challenging oligoazaacenes.

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Supplementary data

Supplementary data (experimental details, the cif files, NMR, MALDI-TOF, FTIR, and TGA of compounds **1–3**) associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tlet.2014.06.033>.

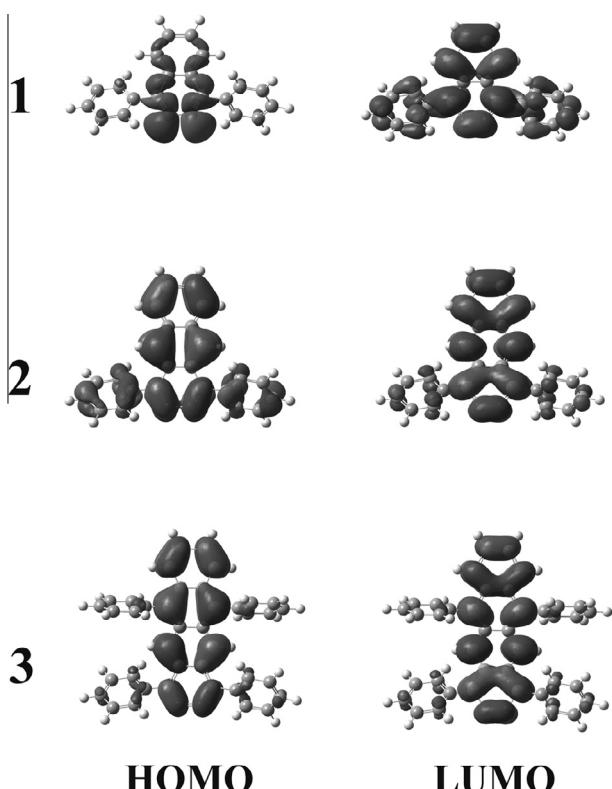


Figure 5. HOMO and LUMO wave functions of compounds **1–3**.

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