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## A julolidine-fused anthracene derivative: synthesis, photophysical properties, and oxidative dimerization†

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We describe the synthesis and characterization of a julolidine-fused anthracene derivative **J-A**, which exhibits a maximum absorption of 450 nm and a maximum emission of 518 nm. The fluorescent quantum yield was determined to be 0.55 in toluene. **J-A** dimerizes in solution *via* oxidative coupling. Structure of the dimer was characterized using single crystal X-ray diffraction.

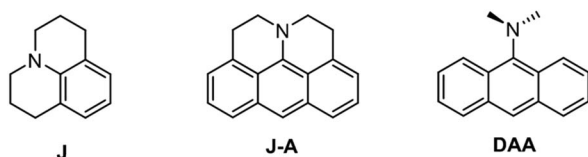
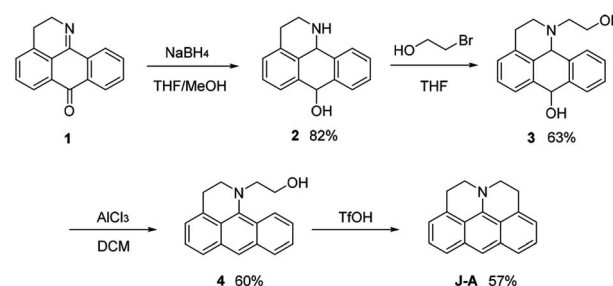
Julolidine<sup>1</sup> is a popular structural subunit in various fluorescent dyes (Chart 1).<sup>2</sup> The restricted motion and strong electron-donating capability of the fused julolidine moiety are quite effective for improving the photophysical properties. For instance, julolidine-fused fluorophores normally display desirable photophysical characteristics, such as high quantum yield, red-shifted absorption and emission, and good photostability. Recently, julolidine derivatives have been widely exploited in various applications such as sensing,<sup>3</sup> imaging,<sup>4</sup> and nonlinear optical materials.<sup>5</sup> Several julolidine dyes have been used in dye-sensitized solar cells due to their large  $\pi$ -conjugated system and the promising electron donating property.<sup>6</sup>

In this paper, we report a julolidine-fused anthracene derivative **J-A**, which exhibits attractive photophysical properties not observed in **DAA**, a dimethyl-amino substituted analogue. Both the absorption and emission of **J-A** show a dramatic red-shift (*ca.* 74 and 131 nm, respectively), compared with the unmodified anthracene (Fig. 2). The fluorescence quantum yield of **J-A** was determined to be 0.55 in toluene, while the emission of **DAA** was completely quenched. The observed spectral properties were rationalized by DFT

calculations. In addition, we found that **J-A** was stable in the solid state, but reactive in solution. **J-A** dimer was formed through oxidative coupling at the para-position of the N-atom in a dichloromethane solution under air atmosphere. The structure of the dimerized product was characterized using single crystal X-ray diffraction, which unambiguously reveals the structural feature of the julolidine-fused anthracene compound. Preparation of **J-A** is shown in Scheme 1. Detailed synthesis and characterizations are provided in the ESI.†

<sup>1</sup>H-NMR signals of **J-A** shift to the high-field significantly, compared with **DAA** (Fig. 1), which indicates that the fused structure of **J-A** facilitates electron delocalization from the nitrogen atom to the anthracene moiety, and thus resulting in a stronger shielding effect. In the case of **DAA**, however, electron delocalization from the dimethyl amino group to the anthracene core is essentially inhibited due to steric hindrance, which will explain the fact that it displays a spectral feature similar to that of the unmodified anthracene.

Fusing with julolidine will exert significant effects on the photophysical properties of anthracene. The absorption and fluorescence spectra of **J-A**, **DAA**, and anthracene are shown in Fig. 2. The maximum absorption of **J-A** is 450 nm, which displays a red-shift of about 70 nm compared with the unmodified anthracene. **J-A** emits green light ( $^{\text{max}}\lambda_{\text{em}} = 518$  nm,  $\Phi = 0.55$ ), while anthracene emits blue light ( $^{\text{max}}\lambda_{\text{em}} = 380$  nm,

Chart 1 The structure of julolidine, **J-A** and **DAA**.Scheme 1 Synthetic route of **J-A**.

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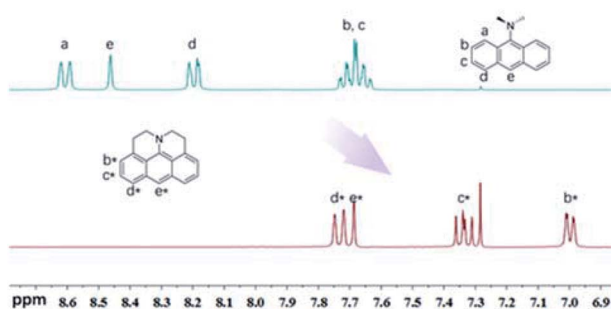


Fig. 1 Comparison of the  $^1\text{H}$ -NMR spectrum between **J-A** and **DAA** in  $\text{CDCl}_3$ . Partial resonance signals in aromatic region are shown.

$\Phi = 0.22$ ). In contrast, the absorption of **DAA** essentially overlaps with that of anthracene, with only a minor red shift of *ca.* 10 nm, but its fluorescence is quenched significantly (Fig. 2). This spectral feature indicates that the dimethyl amino group is electronically separated from the anthracene moiety in the ground state, a result in good accordance with the  $^1\text{H}$ -NMR data shown above. The quenched fluorescence of **DAA** may result from the photo-induced electron transfer<sup>7</sup> from the lone pair of the nitrogen atom to the anthracene moiety in the excited state.

The observed photophysical properties of **J-A** were reproduced by DFT calculations. The HOMO and LUMO orbitals are evenly distributed over the anthracene moiety and the N-atom in the julolidine, indicating the existence of a conjugated structure. The HOMO–LUMO transition ( $f = 0.10$ ) corresponds

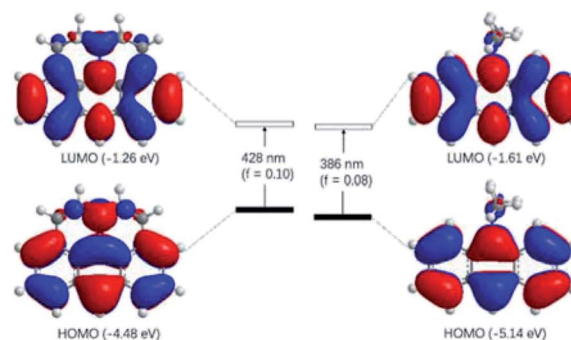


Fig. 3 Molecular orbitals of **J-A** and **DAA** calculated at the B3LYP/6-31G(d) level of theory (iso value = 0.02). Orbital energies were given in parentheses. Excitation energies were computed by TD-DFT at the same level. Values in parentheses represent the oscillator strengths ( $f$ ).

to the absorption band at 450 nm. The sharper absorption at 390 nm can be assigned to the HOMO to LUMO + 1 transition. In contrast, the HOMO and LUMO orbitals of **DAA** resemble those of anthracene, because the dimethyl-amino group is orthogonal to the conjugated  $\pi$ -system (Fig. 3).

**J-A** is stable in the solid state, but reactive in solution. The cyclic voltammetry (CV) diagram of **J-A** shows an irreversible oxidation potential at 0.007 V (vs.  $\text{Fc}/\text{Fc}^+$ ), indicating that **J-A** is easy to be oxidized (Fig. S3†). Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of a dichloromethane solution of **J-A** under air atmosphere. To our surprise, instead of **J-A**, X-ray data discloses the formation of a dimeric product (Scheme 2) of **J-A**. We hypothesized that the dimeric compound **5** formed *via* oxidative coupling reaction, a mechanism well-documented for the dimerization of the dimethylaniline compounds.<sup>8</sup> The  $^1\text{H}$ -NMR spectrum of **5** is distinct from that of **J-A**. All protons of the anthracene part ( $b'$ – $d'$ ) appear as a group of multiplet resonance signals (6.93–7.04 ppm) (Scheme 2). In addition, mass spectrometric analysis indicates that two hydrogen atoms were removed after the dimerization of **J-A**. Compound **5** exhibits a maximum absorption at 460 nm and a very weak emission ( $\lambda_{\text{em}}^{\text{max}} = 530$  nm,  $\Phi = 0.03$ , Fig. S1†). Two quasi-reversible oxidation waves were identified in the CV diagram of **5** at  $-0.010$  V and  $0.135$  V (vs.  $\text{Fc}/\text{Fc}^+$ ), respectively (Fig. S5†).

X-ray structure of **5** is shown in Fig. 4. The two connected anthracene planes are found to be orthogonal to each other with a dihedral angle of  $90.17^\circ$ , as a result of steric repulsion. Specifically, the bond length of N–C3 is  $1.389$  Å, which is similar to those of the other reported julolidine compounds ( $1.359$ – $1.393$  Å), while significantly shorter than that of the dimethyl-amino anthracene ( $1.433$  Å).<sup>9</sup> This result testifies the presence

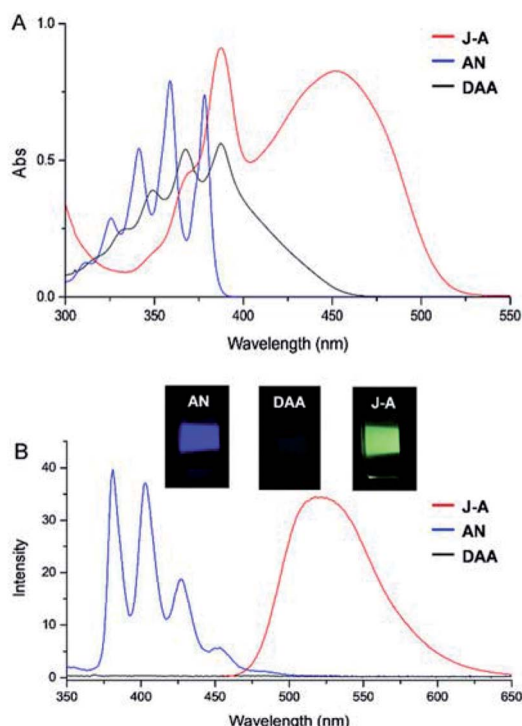
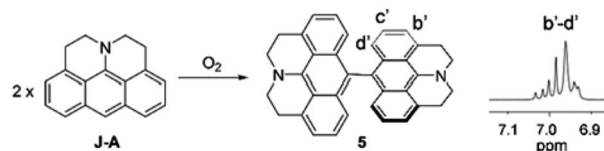


Fig. 2 (A) Absorption spectra of **J-A**, **AN**, and **DAA** ( $1 \times 10^{-4}$  mol  $\text{L}^{-1}$  in dichloromethane); (B) emission spectra of **J-A**, **AN**, and **DAA** ( $1 \times 10^{-5}$  mol  $\text{L}^{-1}$  in dichloromethane). Excitation wavelength: 350 nm. 1 cm cuvette was used in both of the experiments. Inset: visualized fluorescence in solution was shown.



Scheme 2 Oxidative dimerization of **J-A**. Inset: partial  $^1\text{H}$ -NMR of **5** is shown.



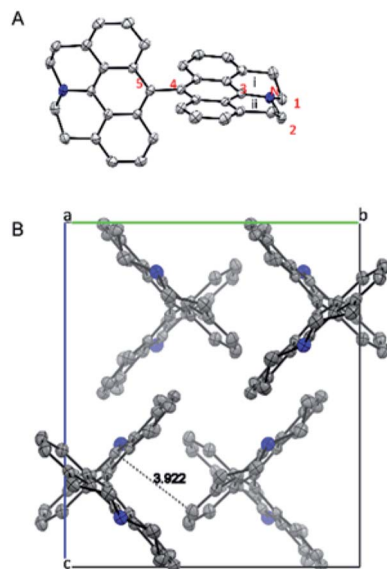


Fig. 4 (A) Single crystal X-ray structure of **5**. (B) View along *a*-axis.

of electron delocalization between the fused julolidine nitrogen and the anthracene  $\pi$ -plane, which is in good agreement with the DFT calculations (Fig. 3). However, the two anthracene  $\pi$ -planes connected by the single bond (C4–C5, 1.489 Å) might not exhibit electron delocalization because of the orthogonal conformation. The fused julolidine ring-i and -ii are symmetric to each other, and both of them adopt an “envelope” conformation. The fused julolidine is nonplanar (bond angle, C3–N–C2, 115.73°, C3–N–C1, 115.92°, C1–N–C2, 113.81°). **5** is closely packed in the crystal (Fig. 4B), and no intercalated solvent molecules were observed. The closest distance between two adjacent anthracene planes is 3.922 Å, indicating a weak  $\pi$ – $\pi$  stacking. Detailed crystal data are summarized in Table S5.†

In summary, we report the synthesis and characterizations of a julolidine-fused anthracene derivative **J-A**, which demonstrates significantly red-shifted absorption ( $\lambda_{\text{ab}}^{\text{max}} = 450$  nm) and emission ( $\lambda_{\text{em}}^{\text{max}} = 518$  nm,  $\Phi = 0.55$ ), compared with the unmodified anthracene. The photophysical properties of **J-A** also contrast dramatically with a dimethyl-amino analogue **DAA**, which were rationalized by DFT calculations. In addition, **J-A** could be transformed into **5**, a dimeric product, whose single crystal X-ray structure unambiguously confirmed the structural feature of the julolidine-fused anthracene.

## Conflicts of interest

There are no conflicts to declare.

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