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## COMMUNICATION

# Preparation and Photoelectrochemical Behavior of 1,4,6,8,11,13-Hexazapentacene (HAP)

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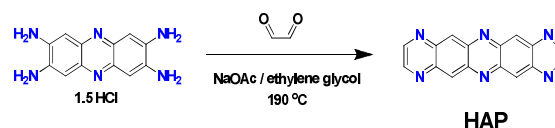
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**Photoelectrochemical study demonstrated that 1,4,6,8,11,13-hexazapentacene (HAP) exhibited active n-type semiconductor behavior under visible light ( $\lambda > 400$  nm) illumination.**

During the past decades, significant progress has been witnessed in the preparation of larger acenes (including heteroacenes) due to their unique properties like low fabrication cost, lightweight, flexibility, and solution processability, and their interesting electro-optical properties and potential applications, including organic electronics<sup>1-3</sup> such as organic field effect transistors (OFET),<sup>4</sup> memories,<sup>5</sup> organic light-emitting diodes, (OLED)<sup>6</sup> and organic photovoltaic devices (OPVs).<sup>7</sup> Acenes can be classified as electron (n-type) or hole (p-type) transporting materials, strongly depending upon the nature of their charge transport. Among these materials, the majority of them are p-type with hole mobility as high as  $5.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ,<sup>8,9</sup> while the research on n-type acenes is relatively slower.<sup>10</sup> Generally, N-type acenes can be realized through modifying known p-type oligoacenes with electron-withdrawing groups or inserting heteroatoms (e.g. N atoms) into the backbone of oligoacenes.<sup>11</sup> If  $sp^2$  N atoms are employed to replace CH groups in the backbone of oligoacenes, the as-prepared compounds are called oligoazaacenes. Up to now, great progress in synthesis and applications of oligoazaacenes has been witnessed: for example, Bunz group firstly reported a soluble, solution-processable and stable silylethynylated tetraazapentacene<sup>12a</sup> and the synthesis of the longest azacene tetraazahexacene through palladium-catalyzed amination following by subsequent oxidation<sup>12b</sup> while Miao group demonstrated silylethynylated tetraazapentacene with an electron mobility of up to  $3.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>13</sup> Our group also investigated the synthesis and applications of several larger azacenes.<sup>11b-11d</sup> In order to further understand the physical properties of azaacenes, photoelectrochemical devices could be a useful tool to investigate these materials. To the best of our knowledge, no study of azacenes using photoelectrochemical cells has been carried out. Herein, we report the synthesis, characterization and photoelectrochemical behaviors of a new compound 1,4,6,8,11,13-hexazapentacene (HAP).

As shown in Scheme 1, compound HAP was synthesized in high yield by reacting 2,3,7,8-Phenazinetetramine hydrochloride<sup>14</sup> with

glyoxal solution in ethylene glycol (EG) containing NaOAc at 190 °C for 48 h. The as-prepared HAP has been fully characterized by <sup>1</sup>HNMR, <sup>13</sup>CNMR, FT-IR, high resolution mass spectroscopy (HRMS), and TGA (see supporting information). As shown in Fig. 1, <sup>1</sup>HNMR spectroscopy of HAP showed the characteristic singlet at 8.97 and 8.00 ppm corresponding to Ha and Hb protons, whereas <sup>13</sup>CNMR spectroscopy displayed the characteristic peaks at 140.09, 139.19, 135.69, and 104.21 ppm for four carbons (supporting information). HAP only slightly dissolved in strong-polar aprotic organic solvent, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP).



Scheme 1. Synthetic route for compound HAP.

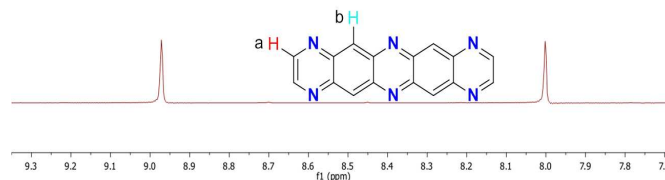
Fig. 1 <sup>1</sup>H NMR (400 MHz, CF<sub>3</sub>COOD) spectrum of HAP.

Fig. 2 shows the optical properties of neutral and protonated HAP. UV-Vis absorption of HAP in NMP solution has maxima peak at 491 nm ( $\epsilon = 9359 \text{ M}^{-1} \text{ cm}^{-1}$ ) with a shoulder at 462 nm ( $\epsilon = 6098 \text{ M}^{-1} \text{ cm}^{-1}$ ). After excitation at the maximum absorption wavelength (491 nm), HAP emits a weak red fluorescence with maximum emission wavelength at 560 nm, the fluorescence quantum yield (0.12) of HAP in NMP solution was measured using quinine sulfate as standard ( $\phi_f = 0.546$ ).<sup>14a</sup> The UV-Vis absorption is significantly red-shifted when UV-Vis spectrum was recorded in trifluoroacetic acid

(TFA), its maximum absorption appeared at 599 nm ( $\epsilon = 9247 \text{ M}^{-1}\text{cm}^{-1}$ ), the bathochromic-shift phenomenon may be attributed from the enhanced intramolecular charge transfer (ICT) absorption through protonation of central nitrogen atom.<sup>14b</sup>

The electrochemical property of **HAP** was studied in dry NMP solution through cyclic voltammetry (CV). The electron-deficient nature of **HAP** was reflected by reduction peaks in negative region (Fig. 3). **HAP** displayed quasi-reversible half-wave reduction potential at  $-1.18 \text{ V}$  relative to  $\text{Fc}/\text{Fc}^+$ , where the LUMO level was estimated to be  $-3.62 \text{ eV}$  according to the equation of  $E_{\text{LUMO}} = -4.8 \text{ eV} - E_{\text{red}}^{1/2}$ .<sup>15</sup> The optical bandgap of **HAP** was estimated to be  $2.52 \text{ eV}$  from the maximum absorption peaks, which was obviously larger than that of pentacene ( $2.1 \text{ eV}$ ).<sup>3b</sup> The HOMO energy level of **HAP** was calculated to be  $-6.14 \text{ eV}$  from the formula of  $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{gap}}$ .

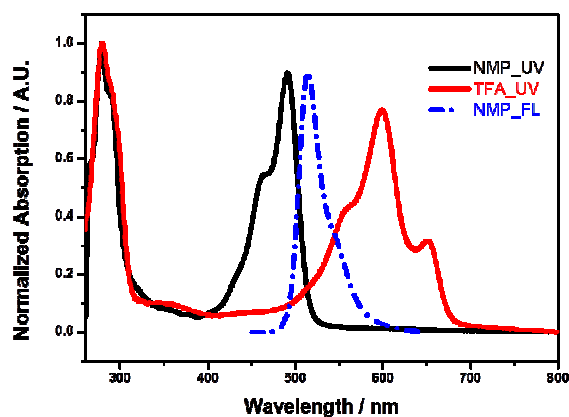


Fig. 2 UV-Vis spectrum of compound **HAP** in NMP and TFA solutions.

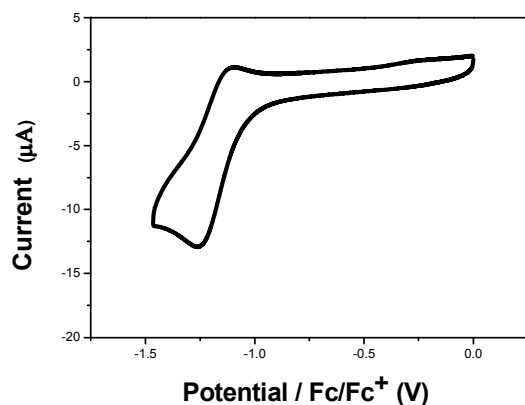


Fig. 3 Cyclic voltammetry curves of compound **HAP** in NMP solutions.

Electronic structure of **HAP** is theoretically investigated through quantum chemistry calculations performed with Gaussian09.<sup>16</sup> The molecular geometries of **HAP** in ground state was optimized using density functional theory (DFT) at the B3LYP/6-31G\* level and the frontier molecular orbitals of **HAP** were shown in supporting information (Fig. S5). The HOMO and LUMO orbitals of **HAP** are all delocalized on the hexazapentacene backbones. The calculated HOMO, LUMO and bandgap are  $-6.29 \text{ eV}$ ,  $-3.97 \text{ eV}$  and  $2.32 \text{ eV}$ , respectively, which are close to the experimental results.

As shown in Fig. S7, the photoelectrochemical tests of **HAP** were performed in a 22.5 ml ES (extrasil) quartz cell filled with 0.5 M sodium phosphate buffer solution ( $\text{pH}=7$ ), using an electrochemical workstation (CHI 760E). Prior to each measurement, the electrolyte was deaerated by purging with argon continuously for 30 minutes. A 300 W xenon lamp (Newport) coupled to an AM 1.5G filter was used as the standard light source, and the illumination intensity on the surface of the photoelectrode was  $\sim 100 \text{ mW}/\text{cm}^2$ , calibrated using a standard silicon photodiode.

Three-electrode set-up, with a platinum plate ( $1 \times 2 \text{ cm}^2$ ) and a saturated calomel electrode (SCE, in 3 M KCl) as the counter and reference electrodes, respectively, was used to study the photovoltage response (illuminated open circuit potential). The photocurrent tests were carried out using a two-electrode set-up, in which the working electrode was connected with **HAP**/FTO, while both counter and reference electrodes were connected with Pt plate counter electrode (Fig. S8). The photocurrent responses were recorded using amperometric technique under zero-biased (short-circuited) condition. The distance between **HAP**/FTO and Pt plate was fixed at 1.0 cm in all photoelectrochemical measurements.

Fig. 4 shows the photocurrent profile of **HAP**/FTO electrode recorded under zero-bias (two-electrode, short-circuit) conditions, indicating that **HAP** is active under visible light ( $\lambda > 400 \text{ nm}$ ) illumination. The repeatable anodic (positive) photocurrent of about  $40 \text{ nA}/\text{cm}^2$  suggests that **HAP** is an n-type semiconductor. As shown in the inset of Fig. 4, **HAP**/FTO cells also showed highly repeatable photovoltage (illuminated open-circuit potential) responses of about 10 mV during the on-off cycles of illumination throughout the measurement.

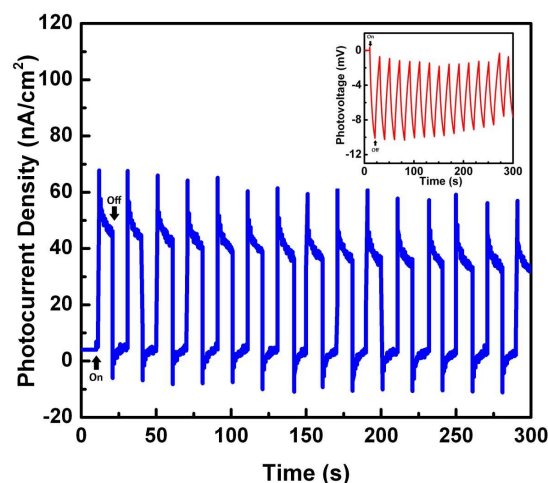


Fig. 4 Zero-bias photocurrent response of **HAP** as electrode upon chopped AM 1.5G light illumination, inset is the photovoltage (illuminated open-circuit potential) responses.

To further reveal the conductivity and flat band potential of **HAP**, the Mott-Schottky measurement was performed in 0.5 M  $\text{Na}_3\text{PO}_4$  aqueous solution. As shown in Fig. S9, the positive slope indicates n-type behavior of **HAP**, consistent with our previous photoelectrochemical analysis. Besides the n-type behavior, the Mott-Schottky measurement also gives the flat-band potential of **HAP** at  $0.37 \text{ V}$  vs. RHE.

In conclusion, 1,4,6,8,11,13-hexazapentacene (**HAP**) has been successfully synthesized and characterized. The

photophysical properties were studied in NMP solutions, revealing a maximum visible absorption band at 491 nm and maximum emission band at 560 nm. The HOMO and LUMO energy levels calculated at the DFT level and estimated from experimental data are very close. The photoelectrochemical properties were investigated using HAP/FTO as working electrode, indicating HAP presents a n-type semiconductor response under visible light ( $\lambda > 400$  nm) illumination.

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## Notes and references

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<sup>c</sup>Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, College of Chemistry, Beijing Normal University, 100875 Beijing, China Electronic Supplementary Information (ESI) available: [Experimental details, <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectra, HRMS spectra, TGA spectra of compound HAP and digital photo of the actual set-up for photoelectrochemical measurements.]. See DOI: 10.1039/c000000x/

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