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Supporting Information

Aromaticity and Tautomerism of a 4n π Electrons Dihydrohexaazapentacene

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1. Molecule synthesis and characterization

Synthesis: Pyridine-2,3-diamine and 2,5-dihydroxy-1,4-benzoquinone were mixed by sufficient grinding, then heated for 1 hour at 180 °C under an inert atmosphere. After cooling down, the mixture was filtrated and the residue was washed by water and acetone for several times. Finally, a dark purple metallic solid was obtained (35%).[1] dihydro-1,5,7,8,12,14-hexaazapentacene (**DHHAP**) is slightly soluble in strong polar solvents, such as DMF and DMSO.

General Instrument: ^{1}H NMR and ^{1}H-^{1}H COSY NMR were recorded on a Bruker ADVANCE 400MHz and 600MHz spectrometer. UV–Vis absorption spectra were measured using a T6 UV–Vis spectrometer.

The obtained **DHHAP** was fully characterized by ^{1}H NMR spectra：

b-DHHAP: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.50 (d, 1H, J = 7.2 Hz), 6.62 (s, 2H), 6.77 (d, 1H, J = 7.2 Hz), 7.26 (d, 1H, J = 5.2 Hz), 7.46 (d, 1H, J = 4.0Hz), 8.10 (d, 1H, J = 8.0 Hz), 8.78 (s, 1H), 10.44 (s, 1H), 10.49 (s, 1H).

q-DHHAP: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.45 (s, 2H), 6.64 (d, 2H, J = 7.6Hz), 6.82 (d, 2H, J = 7.2 Hz), 7.50 (d, 2H, J = 3.6 Hz), 10.03 (s, 1H), 10.09 (s, 1H).

The **elemental analysis** found: C: 63.19, H: 3.91, N: 27.64. Calculated for $C_{16}H_{10}N_6 \cdot H_2O$: C: 63.15, H: 3.97, N: 27.62

ESI-HRMS: $C_{16}H_{10}N_6$ $[M+H]^+$ Calculated: 287.0995, Found: 287.1041.

Oxidization of **DHHAP** to 1,5,7,8,12,14-hexaazapentacene (**HAP**) was carried out with CuOAc and pyridine with yield of about 30%.[2] Compound HAP is a dark powder and almost insoluble in any solvents, so the exact structure couldn't be further confirmed. The elemental analysis found: C: 67.72, H: 2.81, N: 29.47. Calculated for $C_{16}H_8N_6$: C: 67.6, H: 2.84, N: 29.56.

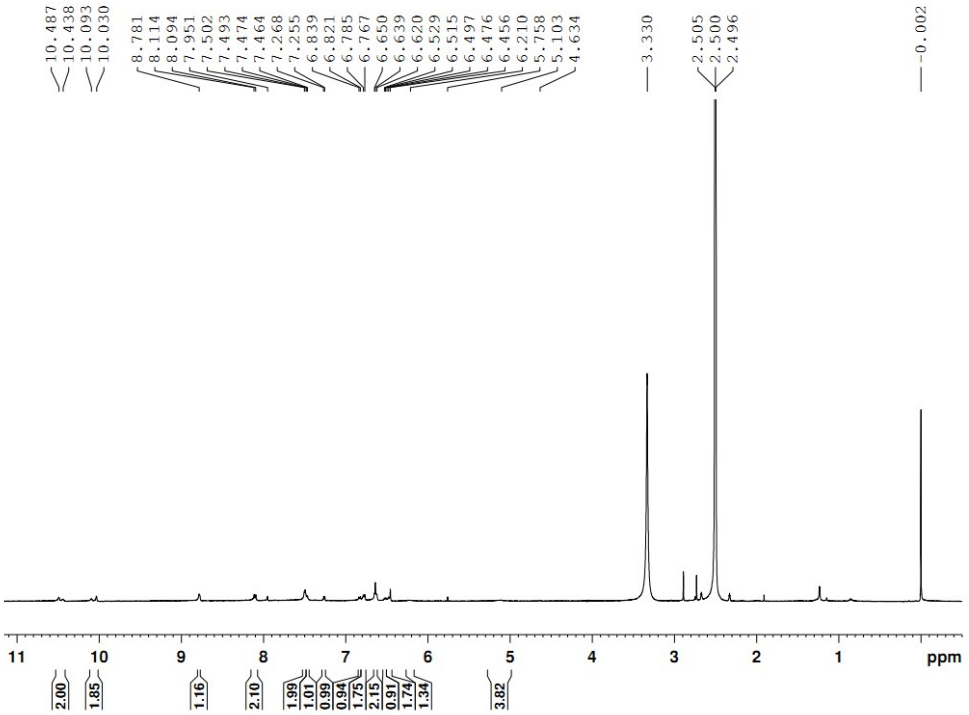

Figure S1 ^{1}H NMR full spectra of **DHHAP** in DMSO-d_6 (400MHz)

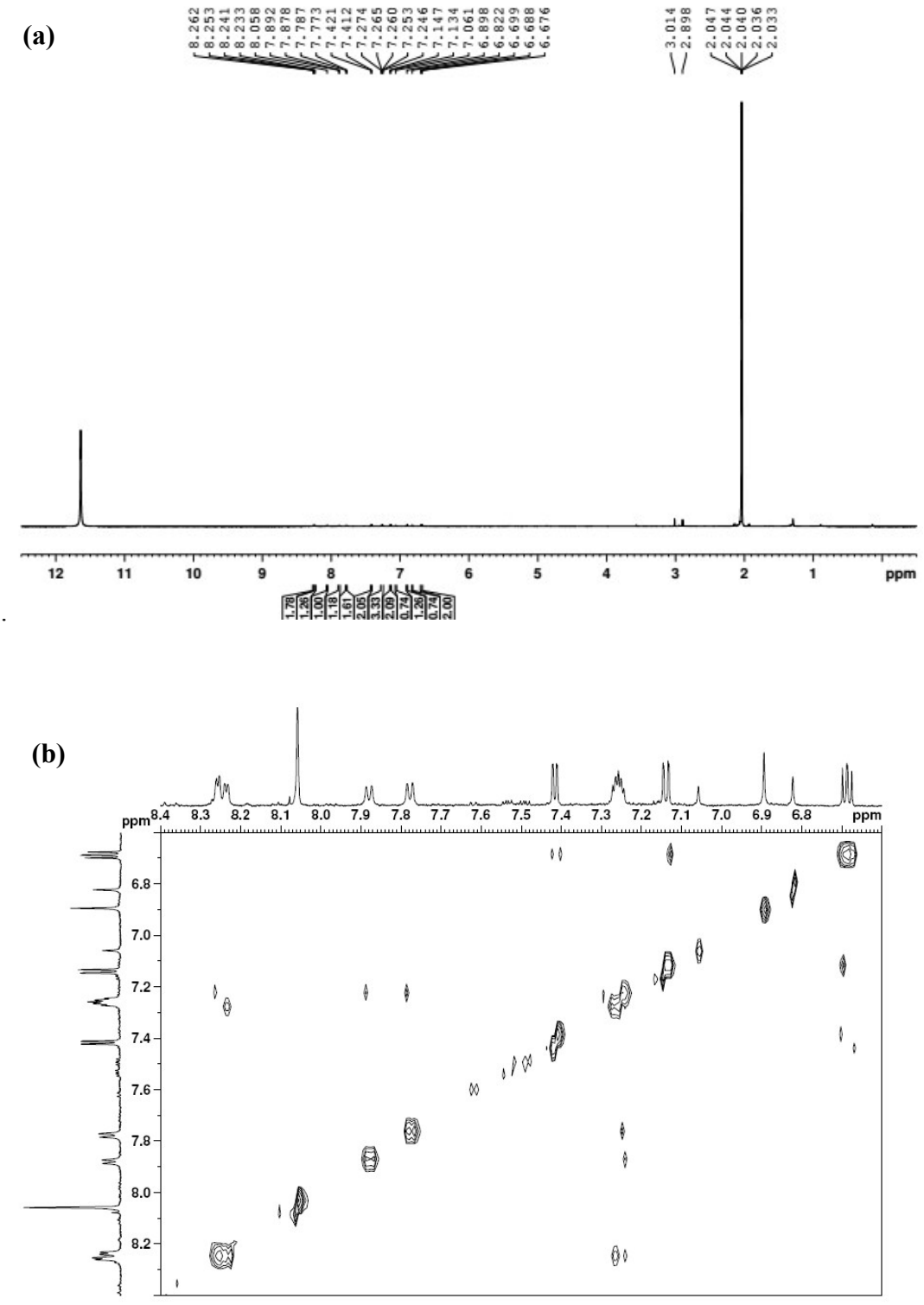

Figure S2 (a) ^{1}H NMR full spectrum and (b)^{1}H-^{1}H COSY spectra of **DHHAP** in CD_3COOD (600MHz)

2. The time-resolved fluorescence spectra

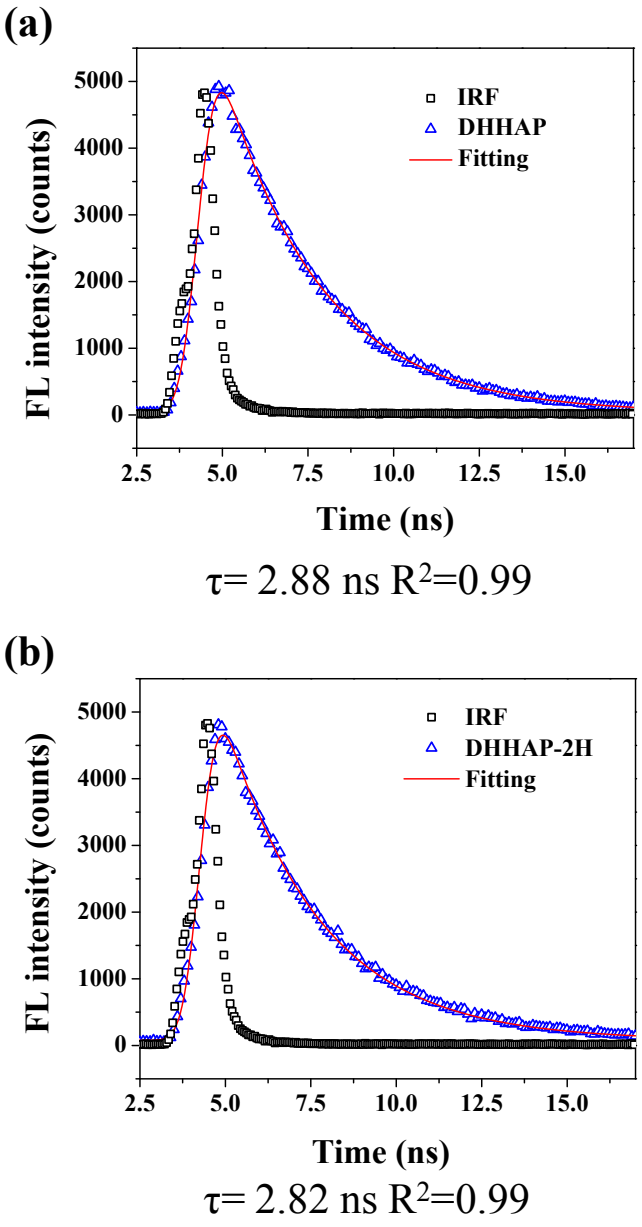

Figure. S3. The time-resolved fluorescence spectra of **DHHAP** (a) in DMF solutions, (b) added excess HCl acid. The scatter dot presents the experiment fluorescence decay curves, and the black curves show the fitting line. The life of fluorescence (τ) and coefficient of determination (R^2) are provided with each chart.

3. Nucleus independent chemical shift (NICS) calculation

All geometries were optimized at the DFT/B3LYP/6-311++G(d,p) level and NICS were computed for the Gauge-Independent Atomic Orbital (GIAO) method at some level as implemented in Gaussian09.[3, 4]

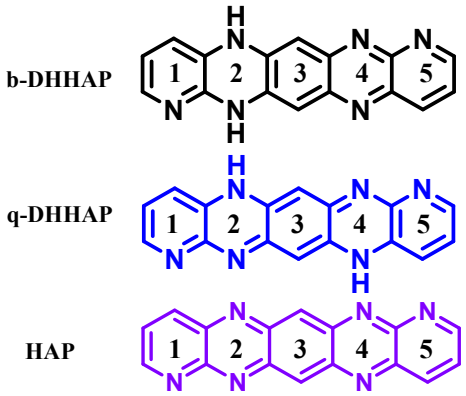

Table S1. Calculated NICS values (in ppm) of different rings in **DHHAP** and **HAP** (purple). NICS values correspond to the rings from left to right as drawn in the structures, The black and red number show diatropic (aromatic) and paratropic (antiaromatic) NICS, respectively.

Molecule	NICS(X)	R-1	R-2	R-3	R-4	R-5	Total
	NICS(0.0)	-3.9333	7.9235	-4.3269	-4.7500	-5.5221	-10.6088
	NICS(0.5)	-5.4306	7.0558	-5.6967	-7.6992	-7.8802	-19.6509
	NICS(1.0)	-5.8589	5.1949	-5.7638	-9.0177	-8.8646	-24.3101
b-DHHAP	NICS(1.5)	-4.2693	3.2530	-3.8751	-6.9544	-6.8578	-18.7036
	NICS(2.0)	-2.6460	1.7465	-2.3054	-4.7811	-4.6675	-12.6535
	NICS(2.5)	-1.5801	0.8056	-1.4878	-3.3087	-3.1543	-8.7253
	NICS(3.0)	-0.9626	0.2942	-1.0771	-2.3621	-2.1955	-6.3031
	NICS(0.0)	-4.8147	4.6957	-0.9282	4.6985	-4.8417	-1.1904
	NICS(0.5)	-6.7091	2.5406	-2.8487	2.4898	-6.7566	-11.284
	NICS(1.0)	-7.3066	0.3063	-3.5769	0.2486	-7.3348	-17.6634
q-DHHAP	NICS(1.5)	-5.4096	-0.3170	-2.0946	-0.3451	-5.4154	-13.5817
	NICS(2.0)	-3.4887	-0.4857	-0.9453	-0.4974	-3.4900	-8.9071
	NICS(2.5)	-2.2289	-0.5424	-0.5159	-0.5476	-2.2296	-6.0644
	NICS(3.0)	-1.4694	-0.5303	-0.3874	-0.5326	-1.4697	-4.3894
	NICS(0.0)	-3.4953	-8.2410	-11.9472	-8.2307	-3.5967	-35.5109
	NICS(0.5)	-6.0773	-11.2027	-13.8522	-11.2170	-6.2379	-48.5871
	NICS(1.0)	-7.6068	-11.9134	-13.4911	-11.9281	-7.6980	-52.6374
HAP	NICS(1.5)	-6.1465	-8.9693	-9.8709	-8.9647	-6.1446	-40.096
	NICS(2.0)	-4.3362	-6.1899	-6.6268	-6.1771	-4.3035	-27.6335
	NICS(2.5)	-3.0374	-4.3605	-4.6088	-4.3487	-3.0035	-19.3589
	NICS(3.0)	-2.1868	-3.1875	-3.3860	-3.1788	-2.1592	-14.0983

4. Thermochemistry simulation

$$M+2H^{+}=MH^{2+}$$
$$\Delta G_{protonation}=G(MH^{2+})-2G(H^{+})$$

Table S2.The free energies of different structures of **HAP**, **DHHAP** and possible diprotoned **DHHAP** derivatives after Zero-Point Energy (ZPE) corrections (DFT/B3LYP/6-311++G(d,p), at 298.150 Kelvin and 1.00 Atm), and the $G(H^{+})$ is about 6.3 kcal/mol.[5]

Compound	Free Energy (kcal/mol)	Protonation energy	Compound	Energy (kcal/mol)	protonation energy
TAP	-571642.09507	--	**HAP**	-591786.17698	--
b-DHHAP	-592546.37209	--	**q-DHHAP**	-592557.05670	--
a-2-1	-592954.86855	-421.09646	**b-2-1**	-592962.59446	-418.13775
a-2-2	-592962.59446	-428.82236	**b-2-2**	-592948.08391	-403.62721
a-2-3	-592965.22686	-431.45477	**b-2-3**	-592970.08128	-425.62457
a-2-4	-592957.24681	-423.47472	**b-2-4**	-592954.86855	-410.41185
a-2-5	-592951.20954	-417.43745	**a-2-6**	-592948.08391	-414.31182

5. The femtosecond transient absorption (fs TA) kinetics decay curve fitting for DHHAP

Table S3. The kinetics decay curve fitting data at representative wavelength of **DHHAP** solution and the solution added with hydrochloric acid

DHHAP			**DHHAP treated with acid**		
λ	τ_1	τ_2	λ	τ_1	τ_2
503	2681(120)	230(55)	518	699(616)	1.755(180)
536	2800(37.7)	1.6(-133)	587	0.034(-906)	692(-2.3)
577	1.0(-405)	0.2(285)	641	1091(-28.9)	700(-106)
604	19.4(16)	4104(-262)			
654	19.4(211)	2378(-341)			

The λ present the representative wavelength (nm), τ_1 and τ_2 present two fitting lifetime (ps) by the bi-exponential fitting model and the pre-exponential factor number (a.u.) shown in parentheses.

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