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Synthesis, crystal structure and photophysical properties of 1,4-bis(1,3-diazaazulene-2-yl)-benzene: a new π building block

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S1. Synthetic details

S1.1. General Methods

All reagents were purchased from *J&K* (China) and used as received unless other mentioned. Trifluoroacetic acid (99.5%) was purchased from Sigma-Aldrich. Dichloromethane (spectral grade) was purchased from *J&K* (China) for UV-vis experiments. All reagents were weighed and handled in room temperature. Flash column chromatography was performed over silica gel 200-300.

S1.2. Instrumentation

^{1}H NMR spectra were recorded on Bruker 400 or 600 MHz and the chemical shifts were reported in parts per million (δ) relative to the internal solvent signals (7.26 ppm for $CDCl_3$, 4.79 ppm for D_2O and 3.31 ppm for CD_3OD). ^{13}C NMR spectra were obtained at Bruker 100 or 150 MHz and referenced to the internal solvent signals (central peak 77.0 ppm for $CDCl_3$). The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants are reported in Hertz (HZ). APEX II (Bruker Inc.) was used for ESI-MS.

UV-vis absorption spectra were recorded on Varian Cary 50 UV-vis spectrophotometer with dichloromethane as solvent.

^{1}H NMR protonation titration spectra were recorded on Bruker 400 MHz with $CDCl_3$:MeOD (3:1) as solvent.

S1.3. Synthetic details

2-Methoxy tropone (2): 2-Methoxy tropone was obtained as a light yellow oil (room temperature) according to the literature (Chen, 1999). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.15 (m, 1H), 7.03 (t, J = 10.3 Hz, 1H), 6.84-6.78 (m, 1H), 6.69 (d, J = 9.9 Hz, 1H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):

δ 180.55, 165.42, 136.90, 136.68, 132.78, 127.94, 112.45, 77.48, 77.36, 77.16, 76.84, 56.32; HRMS (ESI): calcd for [$C_8H_9O_2$+H^+], *m/z* 137.0597; found, *m/z* 137.0597.

Benzene-1,4-dicarboximidamide hydrochloride (4): The synthetic route was according to previous report (Song *et al.*, 2010). ^{1}H NMR (400 MHz, D_2O): δ 7.96 (s, 1H); ^{13}C NMR (101 MHz, D_2O): δ 165.87, 132.90, 128.7;. HRMS (ESI): calcd for [$C_8H_{10}N_4$+H^+], *m/z* 163.09782; found, *m/z* 163.09713.

S2. Solvent effect

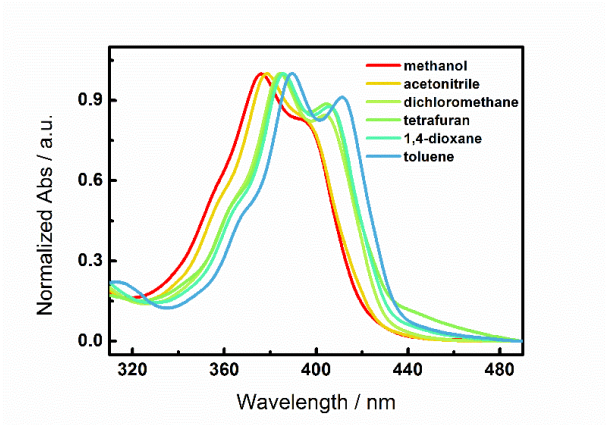

Figure S1 Normalized absorbance of (I) in different solvents (all in a concentration of 1 × 10^{-5} mol/L).

S3. Lifetime of (I)

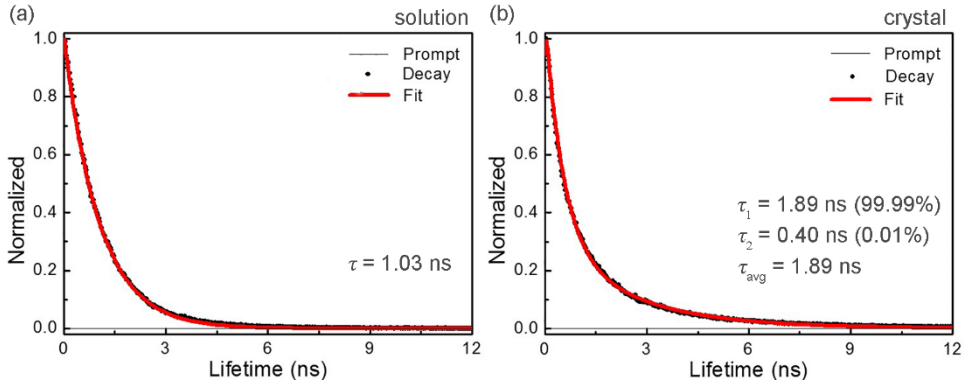

Figure S2 Lifetime of (I). Fittings of the (a) emission of (I) in dichloromethane solution (1 × 10^{-5} mol L^{-1}) at ~480 nm (τ = 1.03 ns) and (b) emission of (I) in crystal at ~650 nm (τ_{avg} = 1.89 ns).

S4. Theoretical calculation

S4.1. TD-DFT calculation

Table S1 TD-DFT calculation results of (I).

λ/ nm	Oscillator Strength	Transition	Amplitude
421.29	1.2592	LUMO←HOMO	0.70137
394.39	0.0041	LUMO←HOMO−1	0.54357
391.03	0.0000	LUMO←HOMO−2	0.57226

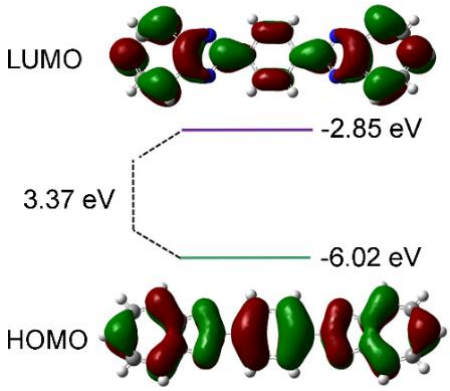

Figure S3 Calculated molecular frontier orbitals based on the (I) crystal coordinates.

S4.2. Second-order nonlinear optical calculation

Polarizability (α): $\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$;

Polarizability anisotropy: $\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]^{1/2}$;

Hyperpolarizability (β): $\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$; $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{xxy}$, $\beta_z = \beta_{xxz} + \beta_{yyz} + \beta_{zzz}$.

Table S2 Calculated values of polarizability (× 10^{-24} esu) and hyperpolarizability (× 10^{-30} esu) parameters using DFT/B3LYP/6-311G(d,p) method for (I).

Polarizability parameters	Value (esu)	Hyperpolarizability parameters	Value (esu)
α_{xx}	28.28	β_{xxx}	0.00
α_{xy}	-11.00	β_{xxy}	0.00
α_{yy}	45.71	β_{xyy}	0.00

α_{xz}	-30.79	β_{yyy}	0.00
α_{yz}	24.08	β_{xxz}	0.00
α_{zz}	86.87	β_{xyz}	0.00
α	53.62	β_{yyz}	0.00
$\Delta\alpha$	87.52	β_{xzz}	0.00
		β_{yzz}	0.00
		β_{zzz}	0.00
		β	0.00

S5. ^{1}H NMR and ^{13}C NMR spectra

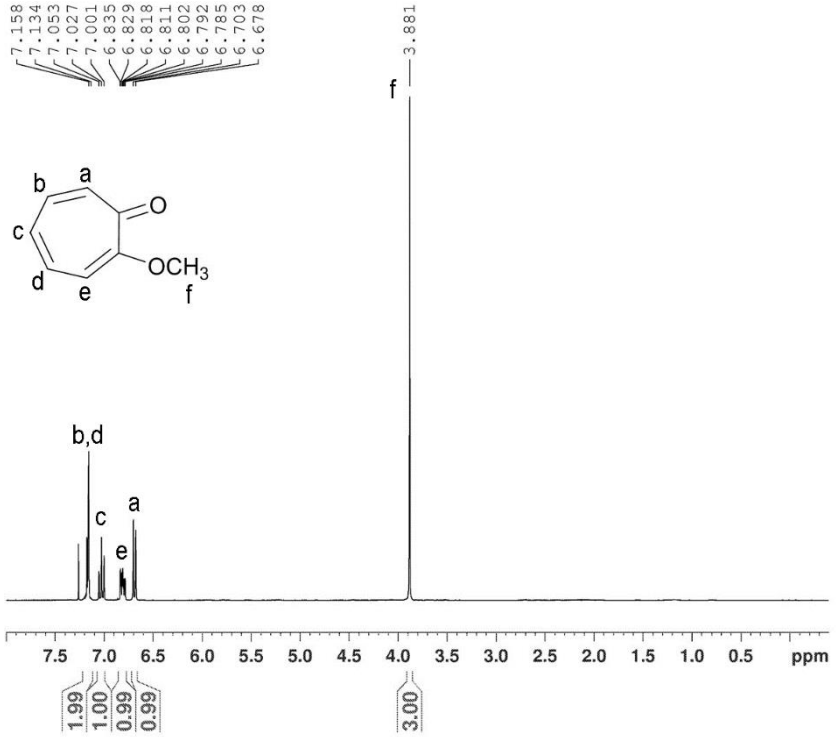

Figure S4 ^{1}H NMR of compound 2-methoxy tropone (**2**, measured in $CDCl_3$).

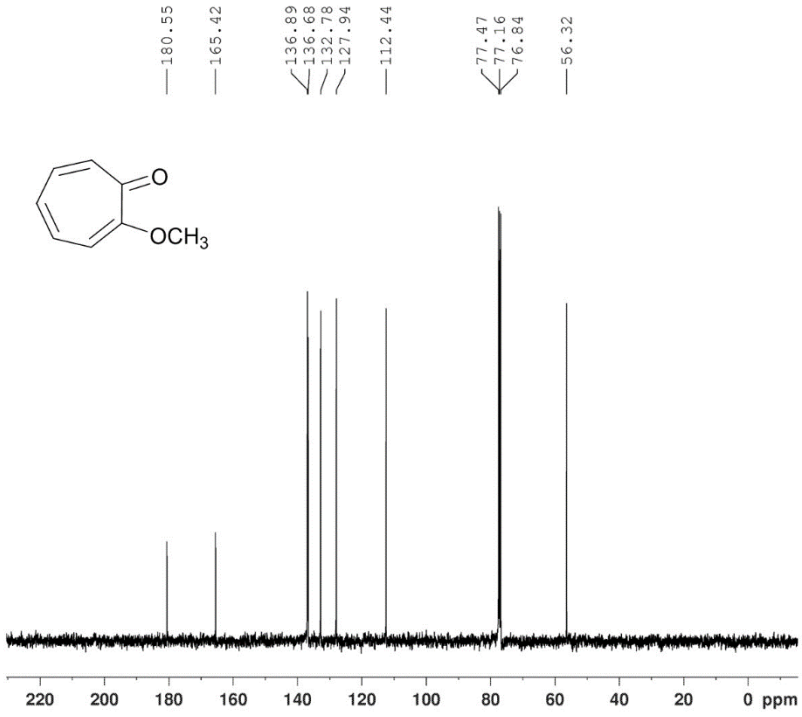

Figure S5 ^{13}C NMR of compound 2-methoxy tropone (**2**, measured in $CDCl_3$).

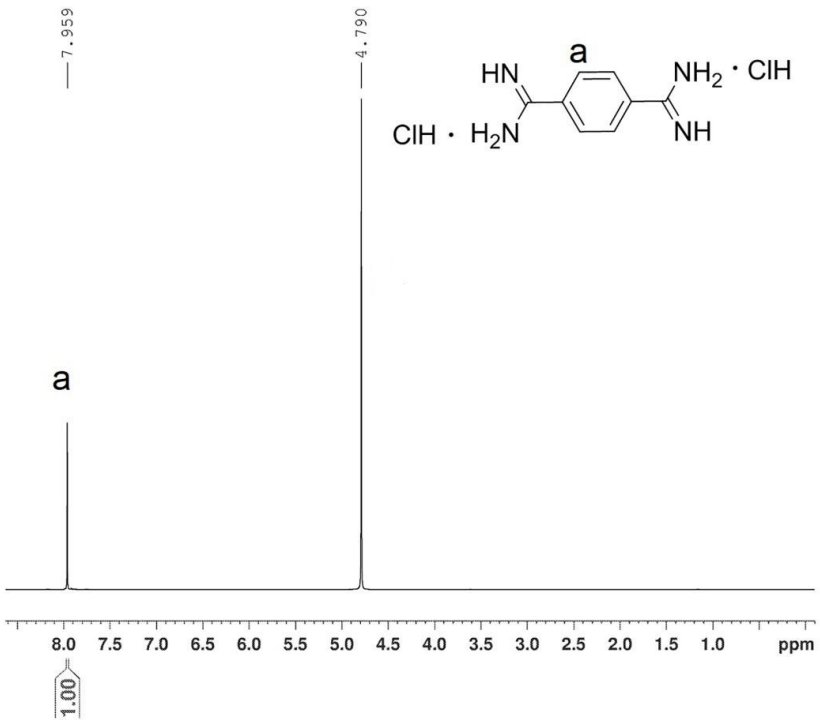

Figure S6 ^{1}H NMR for compound Benzene-1,4-dicarboximidamide hydrochloride (**4**, measured in D_2O).

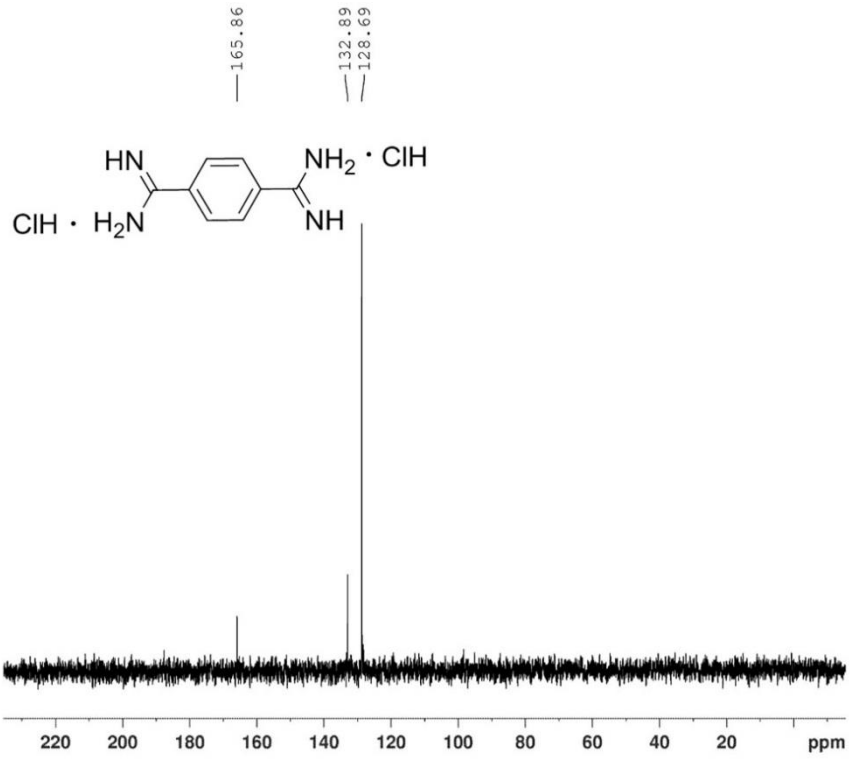

Figure S7 ^{13}C NMR for compound Benzene-1,4-dicarboximidamide hydrochloride (**4**, measured in D_2O).

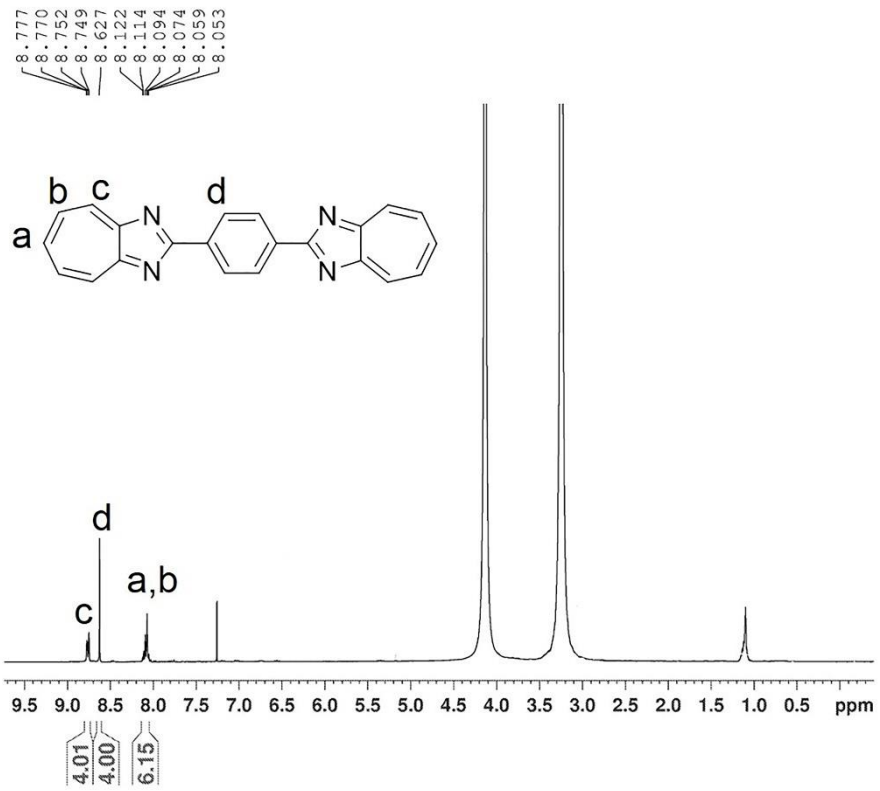

Figure S8 ^{1}H NMR for compound (I) (solvent: $CDCl_3$:MeOD (3:1)).

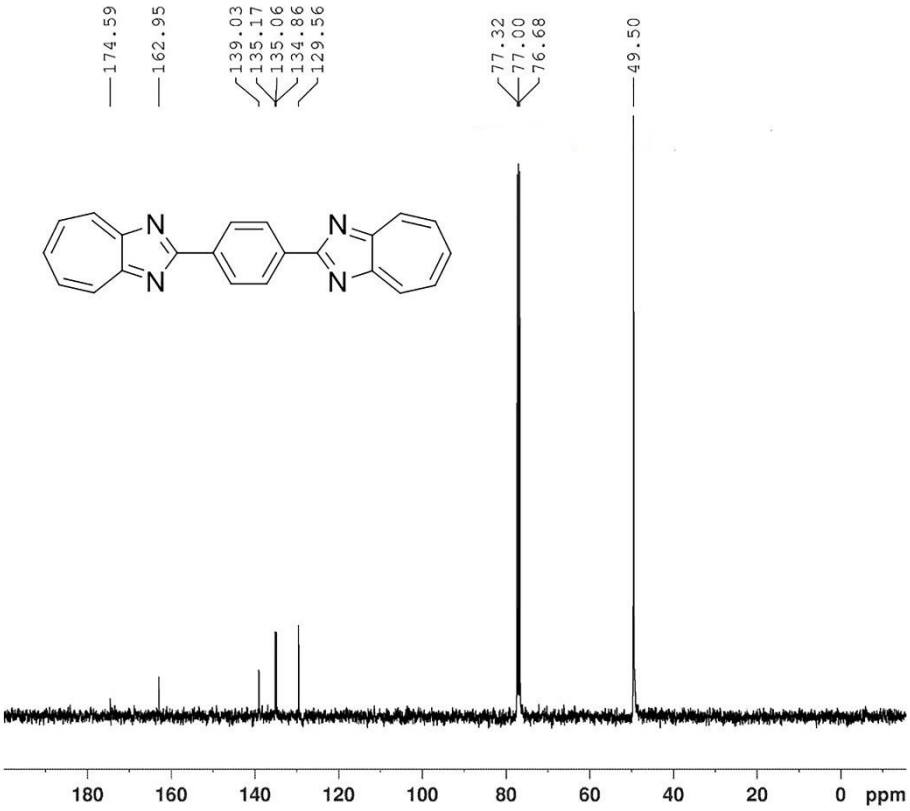

Figure S9 ^{13}C NMR for compound (I) (solvent: $CDCl_3$:MeOD (3:1)).

References

Chen, A. H. (1999). *J. Chin. Chem. Soc.* **46**, 35-39.

Song, G.-L., Zhu, H.-J., Chen, L., Liu, S. & Luo, Z.-H. (2010). *Helv. Chim. Acta* **93**, 2397-2405.