Supporting Information

for

The Excited-State Intramolecular Proton Transfer in the Kinetic-Control Regime

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Contents

Experimental section

Synthesis and Characterization.

All solvents were distilled freshly according to standard procedure. Commer-cially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC. Column chromatography was performed using silica gel from Merck (230–400 mesh). ^{1}H and ^{13}C NMR spectra were rec-orded on a Varian Unity 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts (δ) are recorded in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). Mass spectra were recorded on a VG70-250S mass spectrometer.

Synthesis of 2,11-dihydro-1*H*-cyclopenta[*de*]indeno[1,2-*b*]quinolin-7-amine (**CPIQ-NH₂**). 7-amino-1-indanone (**7AI**, 200 mg, 1.4 mmol) was added to ethanol (15 mL). Sulfuric acid (0.2 mL, 3.7 mmol) was then added dropwise over 1 min. The mixture was stirred for 30 min at room temperature under a nitrogen atmosphere, and then heated at 80 °C for 20 h. After concentrating under reduced pressure, the reaction mixture was digested with methylene chloride, the solution washed with dilute aqueous sodium carbonate, dried, and concentrated. The crude product was purified by silica gel column chromatography with eluent ethyl acetate/*n*-hexane (1/8) to afford **CPIQ-NH₂** (322 mg, 92%), ^{1}H NMR ($CDCl_3$, ppm) δ 7.77 (d, J = 8.0 Hz, 1H), 7.59 (dd, J_1 = 8.0, J_2 = 1.0 Hz, 1H), 7.18–7.28 (m, 2H), 6.87 (dd, J_1 = 8.0, J_2 = 1.0 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.01 (s, 2H), 3.74 (s, 2H), 3.40 (m, 2H), 3.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm)) δ 165.2, 148.6, 145.9, 145.8, 145.6, 145.5, 132.5, 130.5, 130.1, 128.1, 123.7, 122.8, 118.8, 113.5, 112.5, 32.4, 30.5, 29.1; MS (EI, 70 eV): m/z (relative intensity) 258 (M^+, 100); HRMS calcd. for $C_{18}H_{14}N_2$ 258.1157, found 258.1159. Colorless parallelepiped-shaped crystals suitable for the crystallographic studies reported here were isolated over a period of four weeks by slow evaporation from a dichloromethane solution.

Synthesis of *N*-methyl-2,11-dihydro-1*H*-cyclopenta[*de*]indeno[1,2-*b*]quinolin-7-amine (**CPIQ-NHMe**). A mixture of a solution of **CPIQ-NH₂** (100 mg, 0.39 mmol), K_2CO_3 (75 mg, 0.54 mmol) and THF (15 mL) was stirred at room temperature for 30 min. Methyl iodide (55 mg, 0.39 mmol) was then added, and the resulting mixture was heated at 60 °C for 6 h. Following the addition of water (100 mL), the mixture was extracted with CH_2Cl_2 (20 mL), and the combined organic layers were washed with water (3 times) and dried over Na_2SO_4 to yield the crude product. The crude product was purified by silica gel column chromatography with eluent ethyl acetate/n-hexane (1/8) to afford **CPIQ-NHMe** (98 mg, 93%). ^{1}H NMR ($CDCl_3$, ppm) δ 7.96 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.56 (dd, J_1 = 8.0, J_2 = 1.0 Hz, 1H), 7.26–7.34 (m, 1H), 7.21 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 3.66 (s, 2H), 3.32 (d, J = 3.4 Hz, 2H), 3.22 (d, J = 3.4 Hz, 2H), 3.09 (d, J = 2.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.4, 148.2, 147.8, 145.9, 145.4, 132.3, 131.0, 130.0, 128.0, 122.7, 122.5, 118.6, 111.8, 106.7, 32.3, 30.4, 29.5, 29.0; MS (EI, 70 eV): m/z (relative intensity) 272 (M^+, 100); HRMS calcd. for $C_{19}H_{16}N_2$ 272.1313, found 272.1317. Yellow parallelepiped-shaped crystals suitable for the crystallographic studies reported here were isolated over a period of five weeks by slow evaporation from a dichloromethane solution.

Synthesis of *N*-(2,11-dihydro-1*H*-cyclopenta[*de*]indeno[1,2-*b*]quinolin-7-yl)acetamide (**CPIQ-NHAc**). A mixture of **CPIQ-NH₂** (100 mg, 0.39 mmol) and acetic anhydride (0.11 mL, 1.0 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. After the solvent was removed, the crude product was purified by silica gel column

chromatography with eluent ethyl acetate/*n*-hexane (1/6) to afford **CPIQ-NHAc** (110 mg, 95%). ^{1}H NMR ($CDCl_3$, ppm) δ 12.04 (s, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.62–7.68 (m, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 2H), 3.46 (m, 2H), 3.35 (m, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 169.3, 163.6, 150.1, 145.8, 144.9, 144.8, 137.4, 132.8, 130.8, 130.7, 128.1, 125.7, 122.6, 119.5, 119.5, 116.8, 32.2, 30.5, 29.3, 25.0; MS (EI, 70 eV): m/z (relative intensity) 300 (M^+, 100); HRMS calcd. for $C_{20}H_{16}N_2O$ 300.1263, found 300.1254. Yellow parallelepiped-shaped crystals suitable for the crystallographic studies reported here were isolated over a period of four weeks by slow evaporation from a dichloromethane solution.

Synthesis of *N*-(2,11-dihydro-1*H*-cyclopenta[*de*]indeno[1,2-*b*]quinolin-7-yl)-4-methylbenzenesulfonamide (**CPIQ-NHTs**). A mixture of **CPIQ-NH$_2$** (100 mg, 0.39 mmol) and tosyl chloride (145 mg, 0.76 mmol) in pyridine (10 mL) was stirred at room temperature for 20 h. Aqueous HCl was added and the mixture was extracted with CH_2Cl_2, and the combined organic layers were washed with water (3 times) and dried over Na_2SO_4 to yield the crude product. The crude product was purified by silica gel column chromatography with eluent ethyl acetate/n-hexane (1/6) to afford **CPIQ-NHTs** (138 mg, 86 %). ^{1}H NMR ($CDCl_3$, ppm) δ 11.81 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.83 (m, 2H), 7.73 (m, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.10 (m, 2H), 3.82 (s, 2H), 3.46 (m, 2H), 3.36 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 163.6, 155.6, 148.7, 148.2, 145.6, 137.0, 134.7, 134.2, 133.7, 133.1, 130.5, 130.15, 129.8, 128.9, 127.9, 126.3, 123.8, 115.9, 113.2, 33.1, 31.3, 31.0, 21.5; MS (EI, 70 eV): m/z (relative intensity) 412 (M^+, 100); HRMS calcd. for $C_{25}H_{20}N_2O_2S$ 412.1245, found 412.1249. Colorless parallelepiped-shaped crystals suitable for the crystallographic studies reported here were isolated over a period of five weeks by slow evaporation from a dichloromethane solution.

Synthesis of 2,11-dihydro-1*H*-cyclopenta[*de*]indeno[1,2-*b*]quinolin-7-ol (**CPIQ-OH**). A solution of 7-hydroxy-1-indanone (**7HI**, 100 mg, 0.67 mmol) and 7-amino-1-indanone (**7AI**, 100 mg, 0.67 mmol) in ethanol (30 mL) was stirred under nitrogen at room temperature for 30 min. Sulfuric acid (0.2 mL, 9.3 mmol) was then added dropwise over 1 min, and the mixture was heated at 80 °C for 12 h. After concentrating under reduced pressure, the reaction mixture was digested with methylene chloride, the solution washed with dilute aqueous sodium carbonate, dried, and concentrated. The crude product was purified by silica gel column chromatography with eluent ethyl acetate/*n*-hexane (1/6) to afford **CPIQ-OH** (96 mg, 55%), ^{1}H NMR ($CDCl_3$, ppm) δ 11.85, 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (m, 1H), 7.31 (m, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 2H), 3.45 (m, 2H), 3.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) 164.1, 155.6, 150.1, 145.7, 145.1, 144.9, 132.8, 131.2, 130.7, 127.4, 124.9, 122.0, 119.2, 116.3, 113.2, 32.6, 30.4, 29.1; MS (EI, 70 eV): m/z (relative intensity) 259 (M^+, 100); HRMS calcd. for $C_{18}H_{13}NO$ 259.0997, found 259.0991.

X-ray Structure Analysis.

Single-crystal X-ray diffraction data were acquired on a Bruker SMART 1000CCD diffractometer using λ (Mo-Kα) radiation (λ = 0.71073 Å). The data collection was executed using the SMART program. Cell refinement and data reduction were carried out with the SAINT program. The structure was determined using the SHELXTL/PC program and refined using full-matrix least squares. All non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were placed at calculated positions and included in the final stage of refinements with fixed parameters.

Steady-State and Time-Resolved Fluorescence Spectroscopy.

Steady-state absorption and emission spectra were collected by U3310 spectrophotometer (Hitachi) and FLS980 fluorometer (Edinburgh), respectively. Both excitation and emission response of FLS980 fluorometer were care-fully calibrated.

Briefly speaking for the time-resolved spectroscopic measurements, the subnanosecond to nanosecond lifetime measurements were performed by a time-correlated single photon counting (TCSPC) system (OB-900L lifetime spectrometer, Edinburgh) with the excitation light source from second harmonic generation (SHG) of 380 nm and third harmonic generation (THG) of 310 nm of pulse-selected femtosecond laser pulses at 780 nm and 930 nm (tsunami, Spectra-Physics), respectively. The sample emission was collected at an angle of 90o with respect to the pump beam path. The pump beam then passed through a polarizer, which is set at 54.7° (the magic angle) with respect to the pump polarization, located in front of the detector to eliminate the anisotropic effect. The temporal resolution, after removing the instrument broadening partially, is about 20 ps. The ultrafast time-resolved spectroscopic studies were recorded by a FOG100 femtosecond up-conversion system (CDP) pumped by both SHG and THG of the same femtosecond pulse laser. In the experiment, the sample emission generated from a rotating sample cell and the interrogation gate pulse at designated de-lay time were focused on a BBO crystal with respect to the pump pulse for frequency summation. A $\lambda/2$ plate was used to set polarization at magic angle of 54.7° between pump and gate pulse to avoid fluorescence anisotropy. The femtosecond time-resolved data were fitted to the sum of exponential functions convoluted with the IRF, which is fitted to 150 fs determined by Raman scattering signal.

Computational Methodology.

All the computational results were performed by the Gaussian 09 program. The ground-state (S_0) and first excited-state (S_1) geometry optimization for CPIQ series in acetonitrile in combination with a polarizable continuum solvation model (PCM) were performed using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) under 6-31+G(d,p) basis set, respectively. PBE1PBE[1], M062X[2] and B3LYP[3] hybrid functions are used in this study for comparison. The first excited-state structures were optimized by time-dependent DFT using the same hybrid functional. The absorption energies are calculated by the linear response approach under the corresponding ground state geometries.

The charge transfer ratio (ω_{CT})[4] is calculated by the sum of off-diagonal elements of the $S_0 \rightarrow S_1$ transition density matrix (TDM) divided by the sum of all the elements of the same matrix. (eq. 1)

$$\omega_{CT} = \frac{1}{\Omega} \sum_{A \neq B} \Omega_{AB} \qquad (1)$$

,where Ω denotes the sum of all the elements of TDM and Ω_{AB} represents the each element in TDM.

The charge transfer lengths (Δr)[5] are calculated by the change in charge centroids of the orbitals involved in the excitation, which can be expressed as eq. 2:

$$\Delta r = \frac{\sum_{i,a} K_{ia}^2 |\langle \varphi_a | r | \varphi_a \rangle - \langle \varphi_i | r | \varphi_i \rangle|}{\sum_{i,a} K_{ia}^2} \qquad (2)$$

,where K denotes the configuration coefficient corresponding to a selected orbital transition $a \leftarrow i$. φ_i and φ_a represent the initial and final orbital wavefunction, respectiviely.

NMR spectra

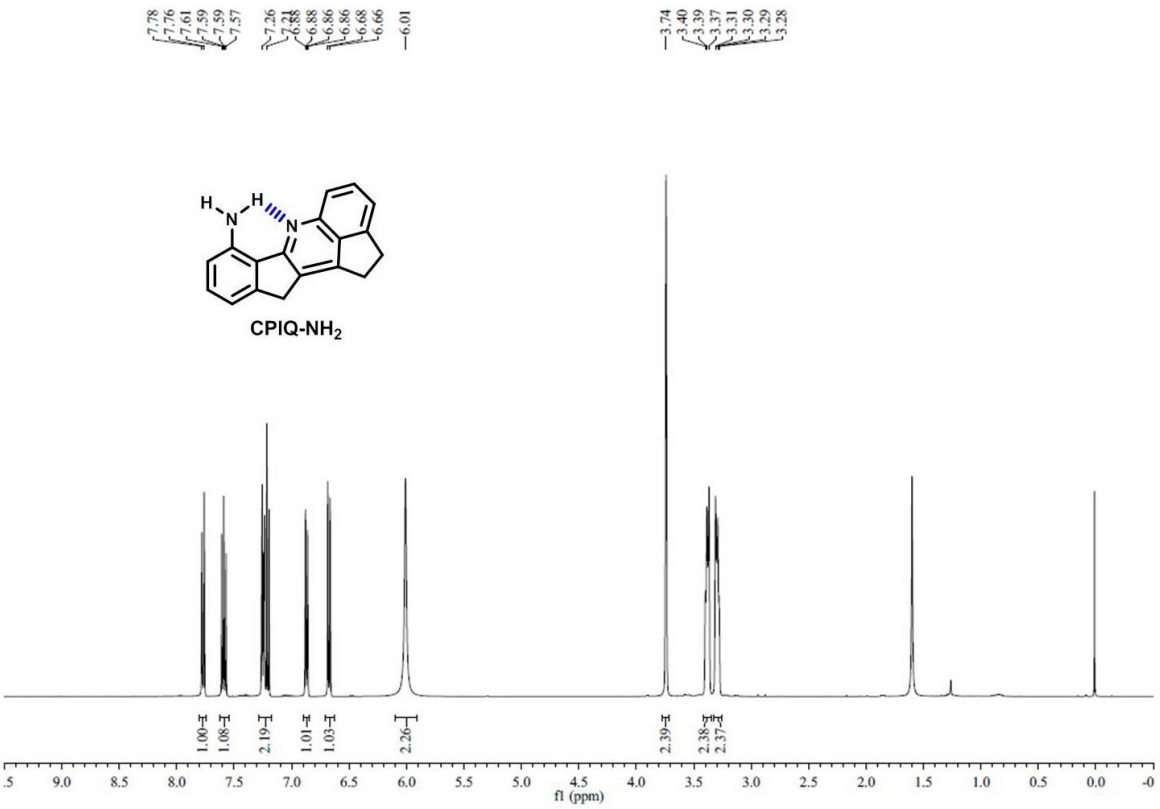


Figure S1. ^{1}H NMR spectrum of **CPIQ-NH$_2$**.

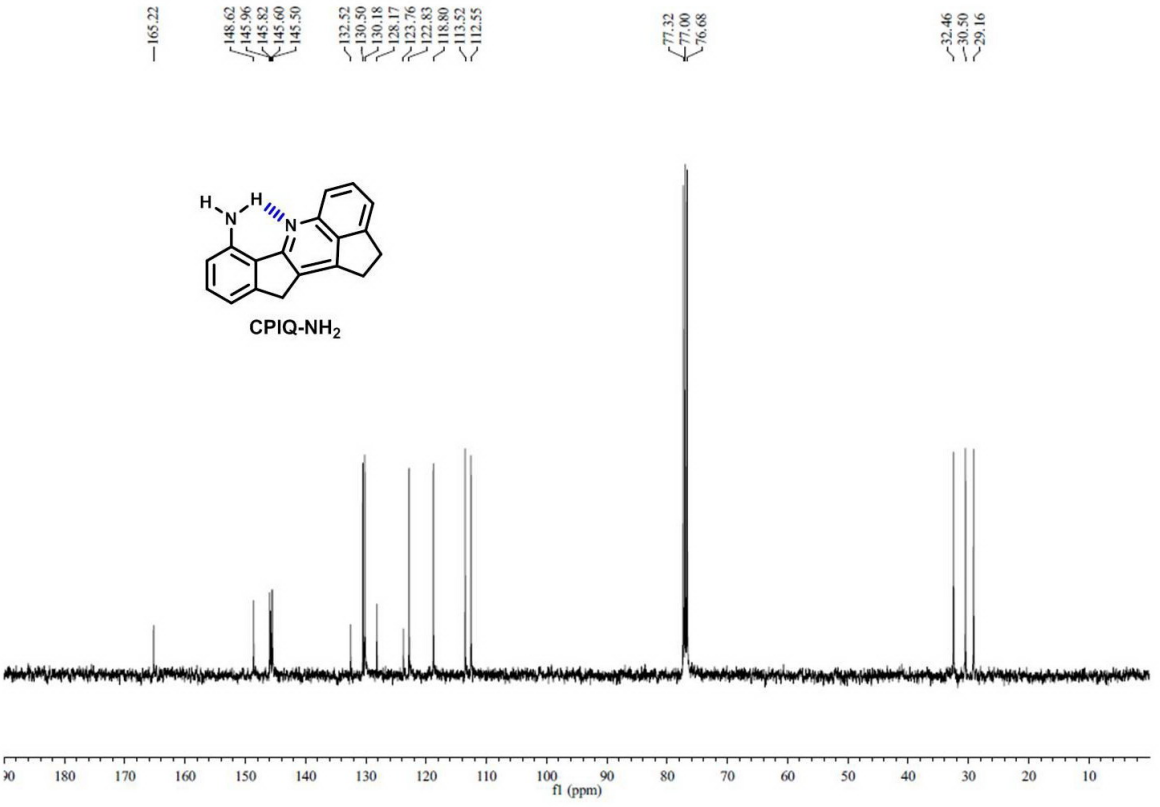


Figure S2. ^{13}C NMR spectrum of **CPIQ-NH$_2$**.

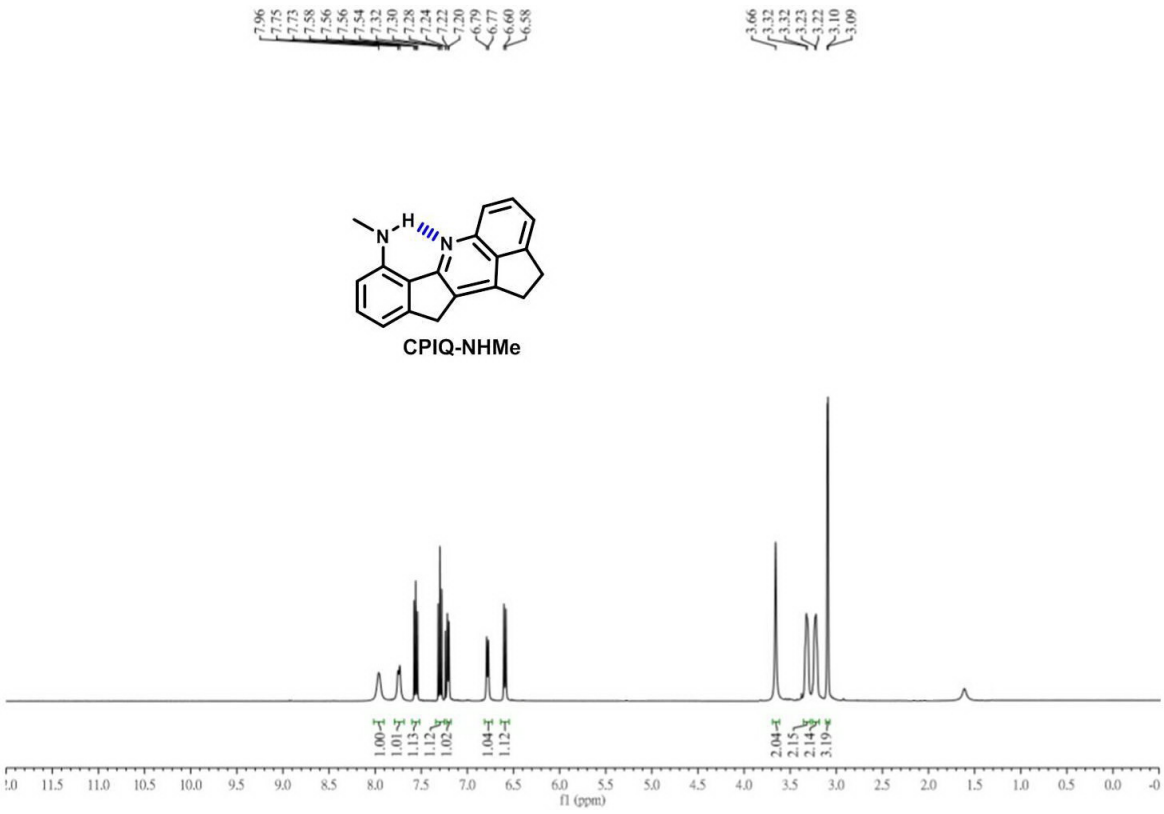


Figure S3. ^{1}H NMR spectrum of **CPIQ-NHMe**.

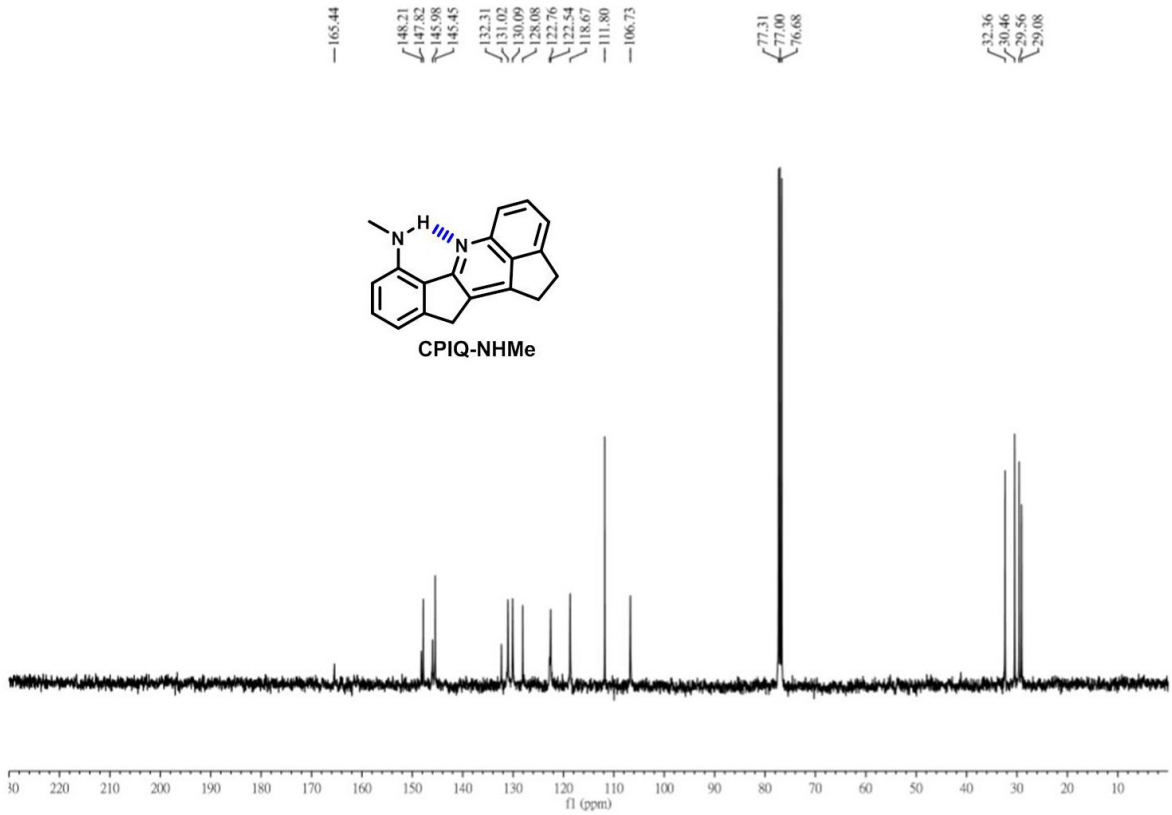


Figure S4. ^{13}C NMR spectrum of **CPIQ-NHMe**.

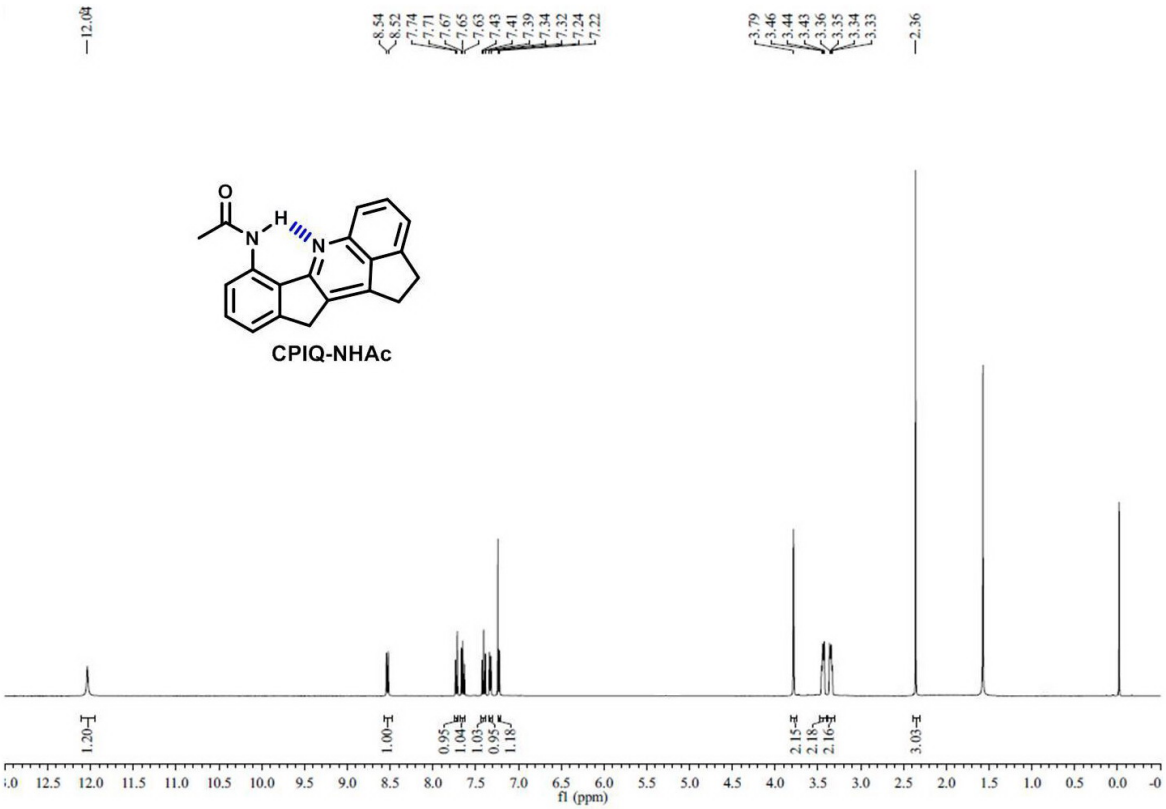


Figure S5. [1]H NMR spectrum of **CPIQ-NHAc**.

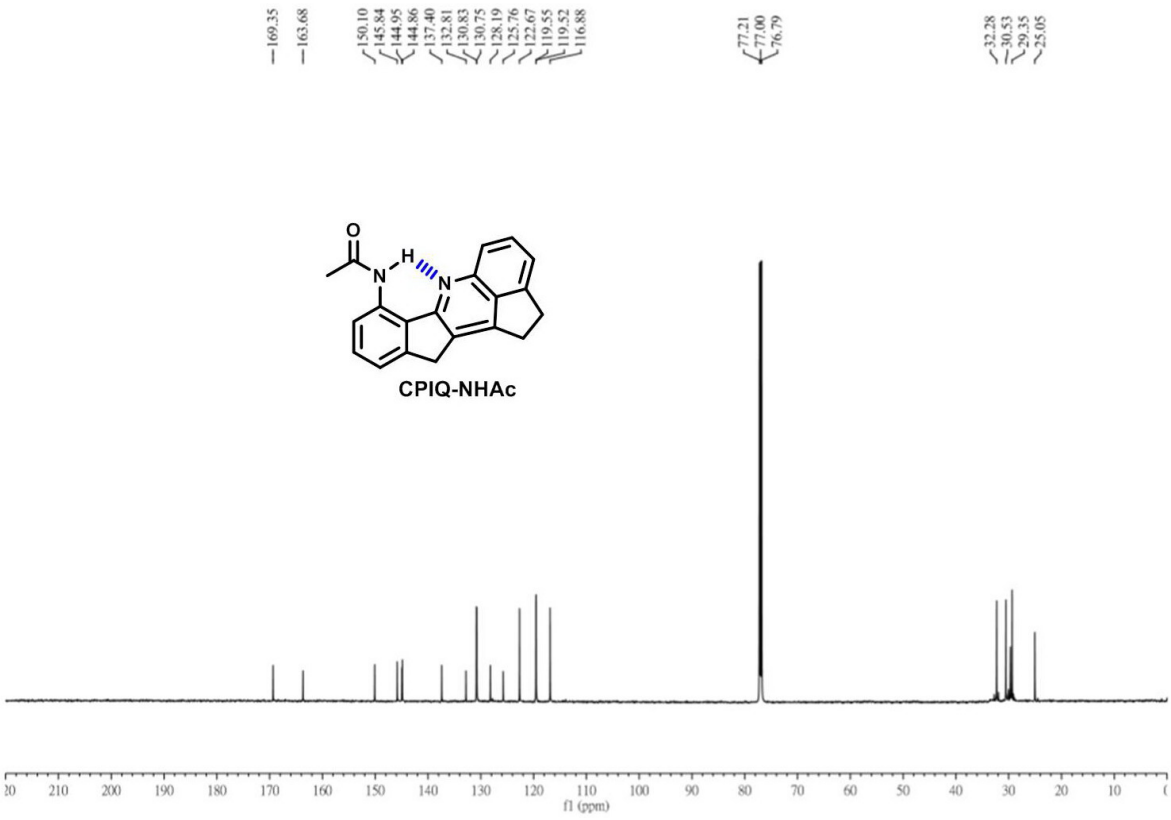


Figure S6. [13]C NMR spectrum of **CPIQ-NHAc**.

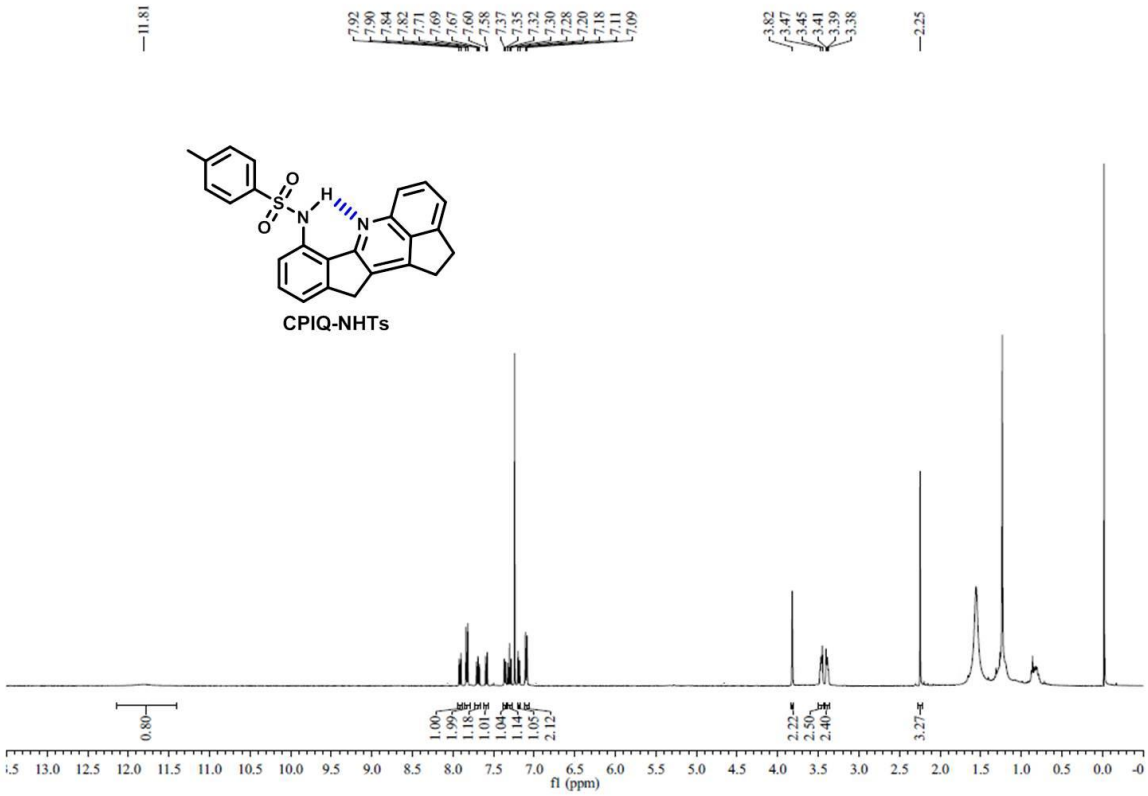


Figure S7. ^{1}H NMR spectrum of **CPIQ-NHTs**.

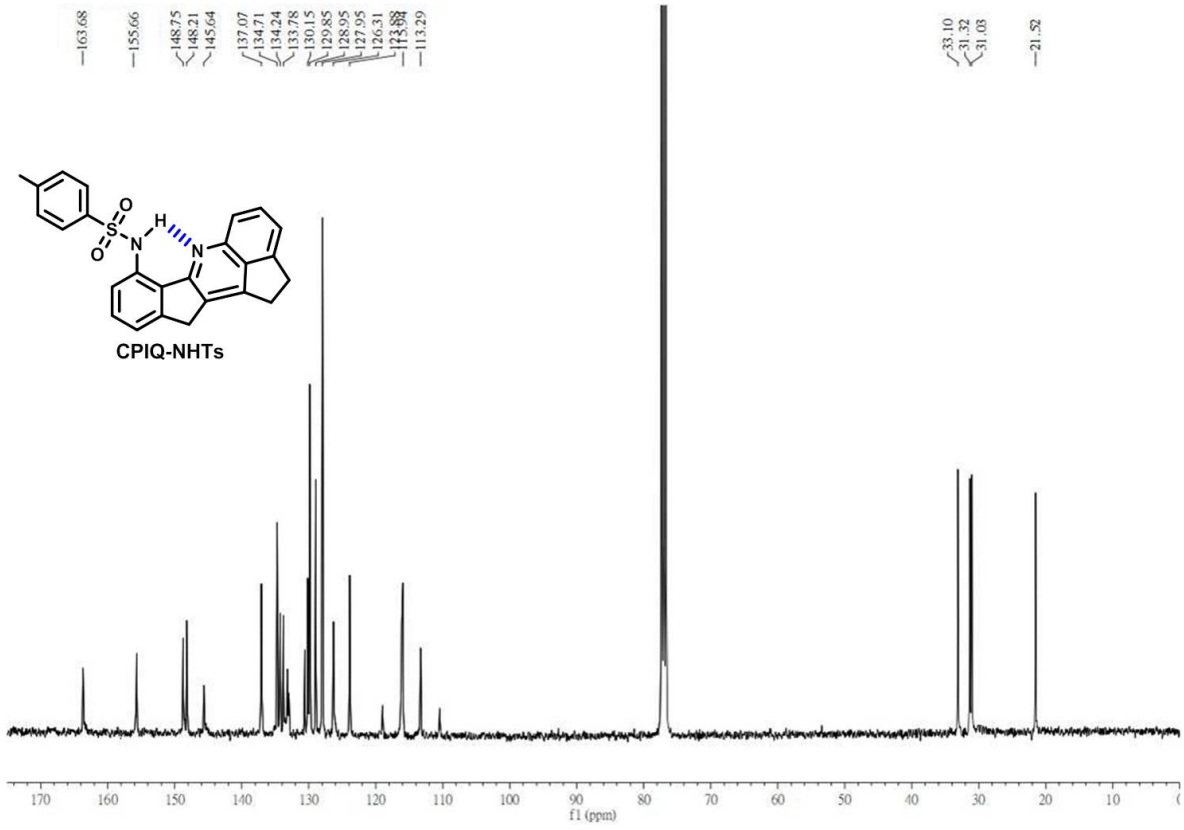


Figure S8. ^{13}C NMR spectrum of **CPIQ-NHTs**.

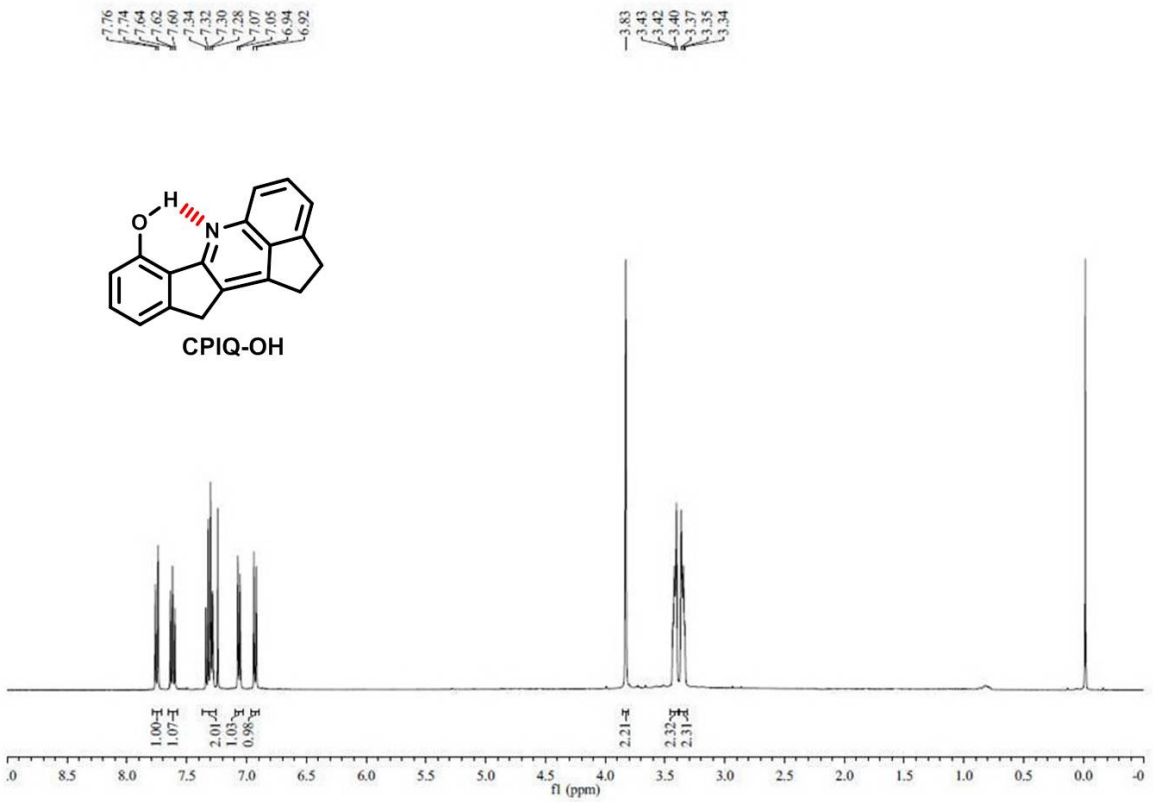


Figure S9. [1]H NMR spectrum of **CPIQ-OH**.

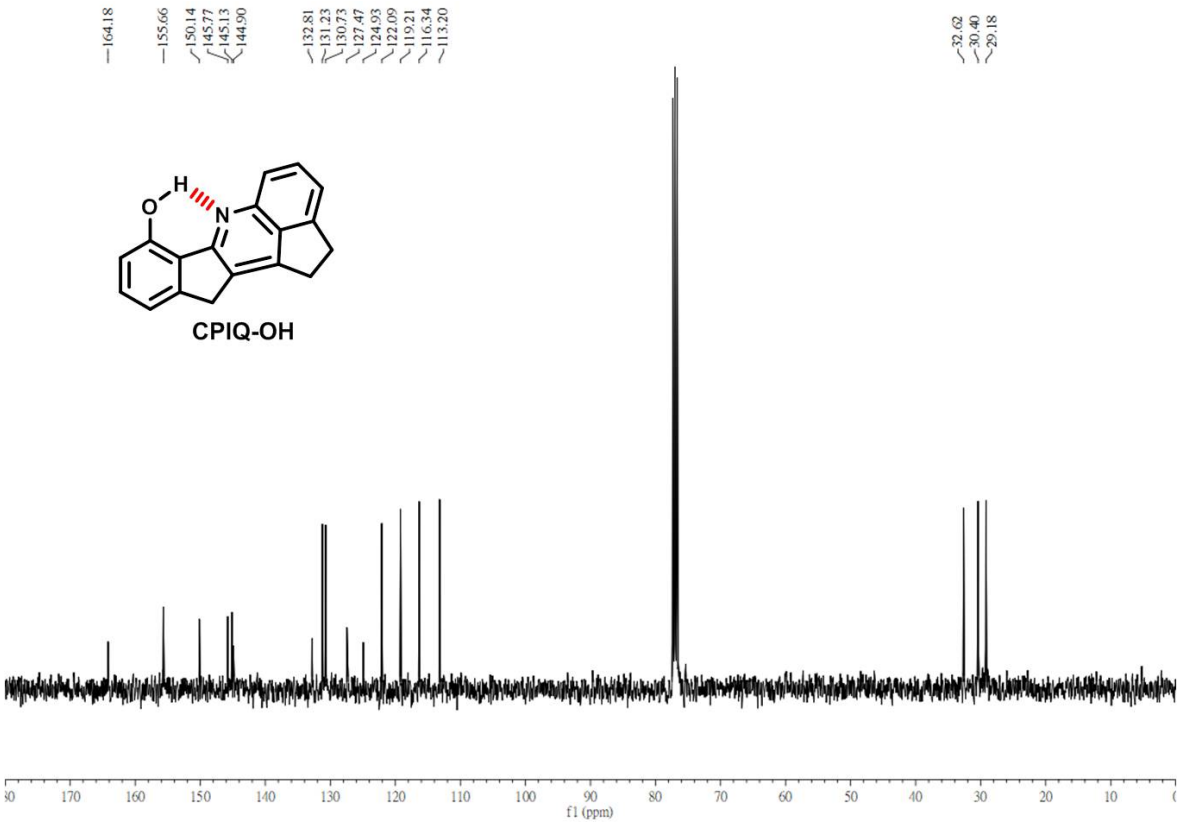


Figure S10. [13]C NMR spectrum of **CPIQ-OH**.

X-ray Crystallography

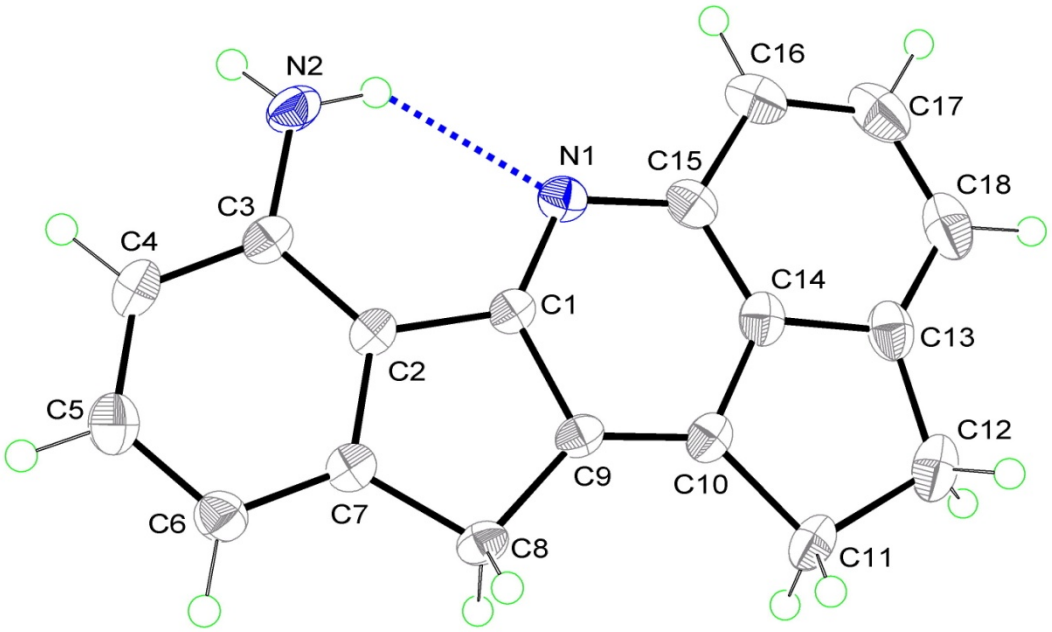


Figure S11. Structure of **CPIQ-NH$_2$** showing the labelling scheme; the displacement ellipsoids are drawn at the 50% probability level, and the H atoms are drawn as spheres of arbitrary radii. The blue dashed line denotes the intramolecular N–H···N hydrogen bond.

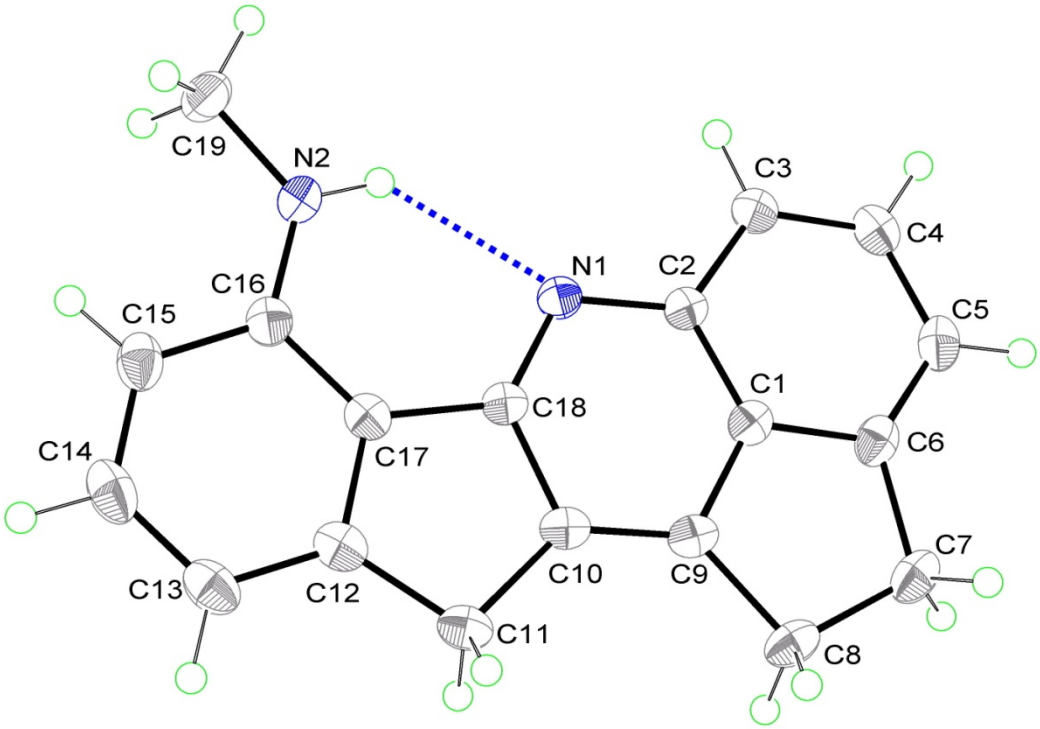


Figure S12. Structure of **CPIQ-NHMe** showing the labelling scheme; the displacement ellipsoids are drawn at the 50% probability level, and the H atoms are drawn as spheres of arbitrary radii. The blue dashed line denotes the intramolecular N–H···N hydrogen bond.

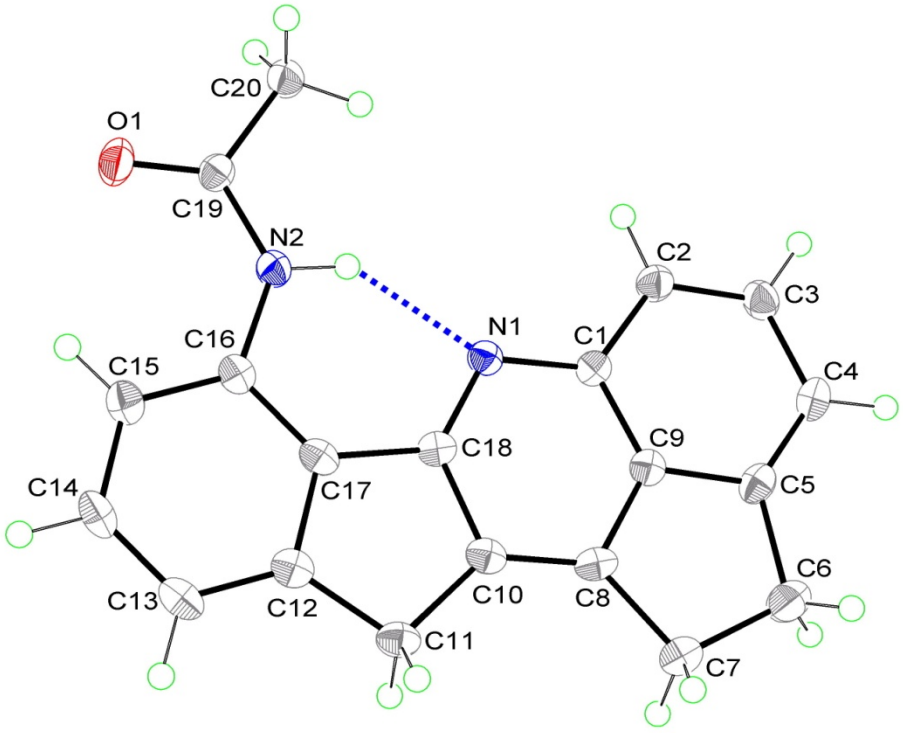


Figure S13. Structure of **CPIQ-NHAc** showing the labelling scheme; the displacement ellipsoids are drawn at the 50% probability level, and the H atoms are drawn as spheres of arbitrary radii. The blue dashed line denotes the intramolecular N–H···N hydrogen bond.

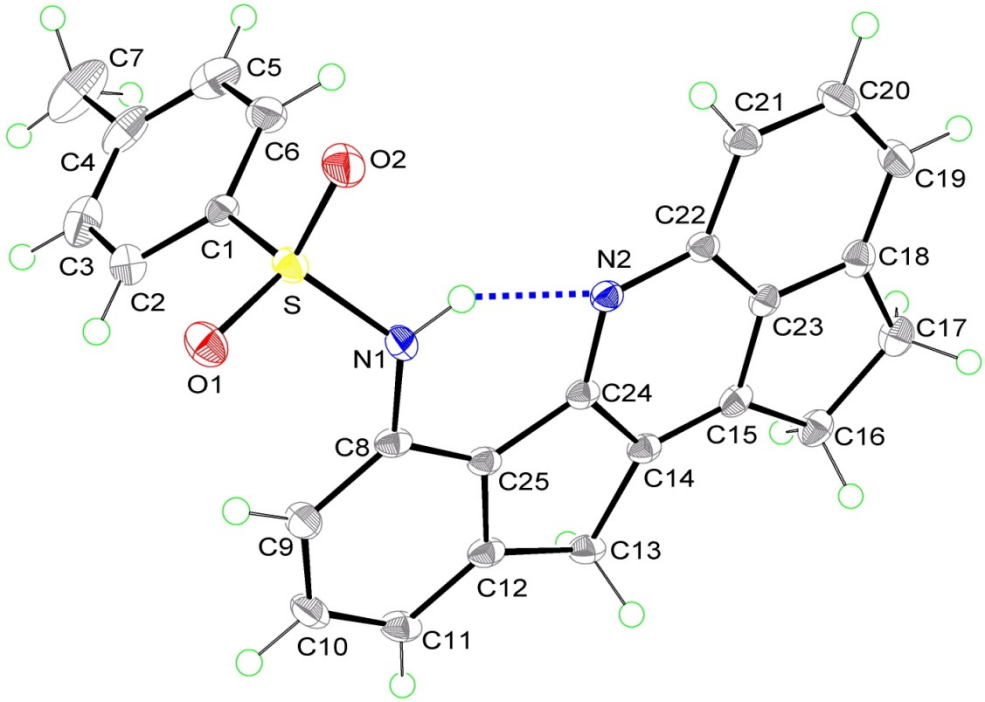


Figure S14. Structure of **CPIQ-NHTs** showing the labelling scheme; the displacement ellipsoids are drawn at the 50% probability level, and the H atoms are drawn as spheres of arbitrary radii. The blue dashed line denotes the intramolecular N–H···N hydrogen bond.

Table S1. Crystal data and structure refinement for **CPIQ-NH$_2$**.

Empirical formula	$C_{18}H_{14}N_2$	
Formula weight	258.31	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.1263(4) Å	α= 67.0568(19)°.
	b = 13.1296(8) Å	β= 82.3572(19)°.
	c = 15.5168(9) Å	γ = 75.4351(19)°.
Volume	1293.02(13) Å^3	
Z	4	
Density (calculated)	1.327 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	544	
Crystal size	0.410 x 0.130 x 0.090 mm^3	
Theta range for data collection	3.059 to 26.403°.	
Index ranges	-8<=h<=8, -16<=k<=16, -19<=l<=19	
Reflections collected	25951	
Independent reflections	5284 [R(int) = 0.0436]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9281 and 0.7836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5284 / 0 / 369	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0835, wR2 = 0.2189	
R indices (all data)	R1 = 0.1049, wR2 = 0.2387	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.001 and -0.477 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **CPIQ-NHMe**.

Empirical formula	$C_{19}H_{16}N_2$	
Formula weight	272.34	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 6.9216(4) Å	α= 90°.
	b = 15.8745(9) Å	β= 103.530(3)°.
	c = 12.8437(8) Å	γ = 90°.
Volume	1372.06(14) $Å^3$	
Z	4	
Density (calculated)	1.318 Mg/m^3	
Absorption coefficient	0.078 mm^{-1}	
F(000)	576	
Crystal size	0.430 x 0.420 x 0.260 mm^3	
Theta range for data collection	3.263 to 27.107°.	
Index ranges	-8<=h<=8, -20<=k<=20, -16<=l<=16	
Reflections collected	25175	
Independent reflections	3004 [R(int) = 0.0424]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9281 and 0.8825	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3004 / 0 / 194	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.1100	
R indices (all data)	R1 = 0.0460, wR2 = 0.1193	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.277 and -0.229 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **CPIQ-NHAc**.

Empirical formula	$C_{20}H_{16}N_2O$	
Formula weight	300.35	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 18.6355(8) Å	α= 90°.
	b = 7.0763(2) Å	β= 90°.
	c = 22.0296(9) Å	γ = 90°.
Volume	2905.05(19) $Å^3$	
Z	8	
Density (calculated)	1.373 Mg/m^3	
Absorption coefficient	0.086 mm^{-1}	
F(000)	1264	
Crystal size	0.600 x 0.240 x 0.090 mm^3	
Theta range for data collection	2.863 to 27.176°.	
Index ranges	-23<=h<=23, -9<=k<=8, -28<=l<=28	
Reflections collected	33227	
Independent reflections	6405 [R(int) = 0.0413]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9281 and 0.8598	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6405 / 1 / 423	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1055	
R indices (all data)	R1 = 0.0560, wR2 = 0.1147	
Absolute structure parameter	0.3(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.232 and -0.297 $e.Å^{-3}$	

Table S4. Crystal data and structure refinement for **CPIQ-NHTs**.

Empirical formula	$C_{25}H_{20}N_2O_2S$	
Formula weight	412.49	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1962(10) Å	α= 82.486(4)°.
	b = 9.1505(10) Å	β= 87.536(5)°.
	c = 14.0898(19) Å	γ = 68.336(4)°.
Volume	973.6(2) $Å^3$	
Z	2	
Density (calculated)	1.407 Mg/m^3	
Absorption coefficient	0.192 mm^{-1}	
F(000)	432	
Crystal size	0.290 x 0.170 x 0.040 mm^3	
Theta range for data collection	2.674 to 27.109°.	
Index ranges	-10<=h<=10, -11<=k<=9, -17<=l<=17	
Reflections collected	17881	
Independent reflections	4127 [R(int) = 0.0565]	
Completeness to theta = 25.242°	96.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9281 and 0.8640	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4127 / 0 / 275	
Goodness-of-fit on F^2	1.113	
Final R indices [I>2sigma(I)]	R1 = 0.0515, wR2 = 0.1266	
R indices (all data)	R1 = 0.0731, wR2 = 0.1345	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.388 and -0.500 $e.Å^{-3}$	

Table S5. The proton donor-acceptor (N(2)-N(1) and/or O-N) distance in crystal and the 1H chemical shift of NH and/or OH proton.

	^{1}H NMR (amino and/or hydroxy H) (ppm)	D---N(1) distance (X-ray) (Å)
CPIQ-NHMe	7.96	2.931
CPIQ-NH2	6.01	2.917
CPIQ-NHAc	12.04	2.818
CPIQ-NHTs	11.81	2.811
CPIQ-OH	11.85	2.826[a]

[a]The value in ref. 50 in the text.

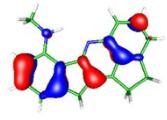
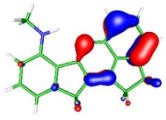
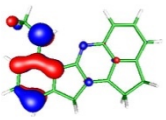
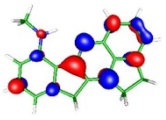
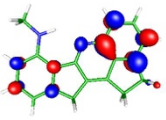
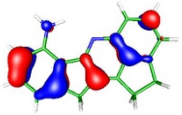
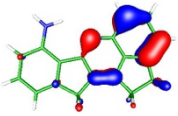
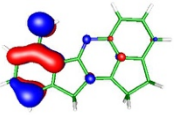
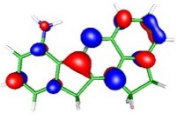
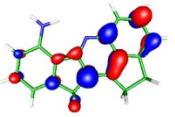
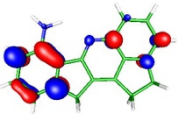
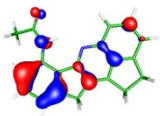
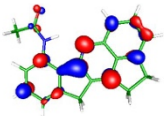
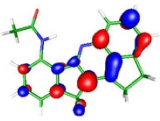
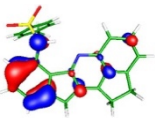
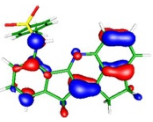
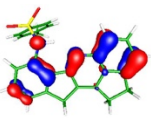
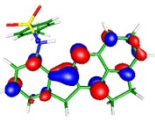
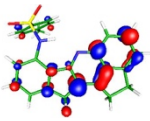
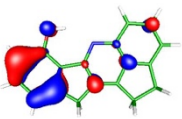
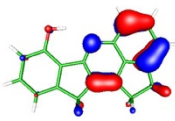
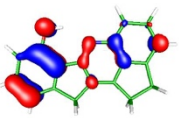
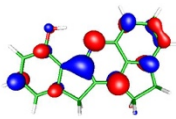
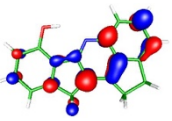
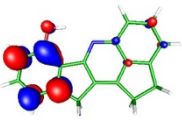
Photophysical Section

Table S6. The calculated wavelength (λ), oscillator strength (*f*) and orbital transition assignments for titled compounds at PBE0/6-31+G(d,p) level.

	Transition	λ (nm)	*f*	Assignments	Weight
CPIQ-NHMe	$S_0 \rightarrow S_1$	371.9	0.3636	HOMO→LUMO	98%
	$S_0 \rightarrow S_2$	307.09	0.0115	HOMO-2→LUMO	6%
				HOMO-1→LUMO	18%
				HOMO→LUMO+1	72%
	$S_0 \rightarrow S_3$	298.16	0.0942	HOMO-1→LUMO	76%
				HOMO→LUMO+1	14%
	$N^* S_1 \rightarrow S_0$	414.63	0.566	LUMO→HOMO	98%
	$T^* S_1 \rightarrow S_0$	616.79	0.5033	LUMO→HOMO	99%
CPIQ-NH$_2$	$S_0 \rightarrow S_1$	355.66	0.3495	HOMO→LUMO	97%
	$S_0 \rightarrow S_2$	301.98	0.0373	HOMO-2→LUMO	5%
				HOMO-1→LUMO	61%
				HOMO→LUMO+1	30%
	$S_0 \rightarrow S_3$	295.1	0.0687	HOMO-2→LUMO	17%
				HOMO-1→LUMO	33%
				HOMO-1→LUMO+1	6%
				HOMO→LUMO+1	37%
	$N^* S_1 \rightarrow S_0$	397	0.5753	LUMO→HOMO	98%
	$T^* S_1 \rightarrow S_0$	591.78	0.467	LUMO→HOMO	99%
CPIQ-NHAc	$S_0 \rightarrow S_1$	326.58	0.4255	HOMO-1→LUMO	4%
				HOMO→LUMO	91%
	$S_0 \rightarrow S_2$	311.67	0.0597	HOMO-1→LUMO	90.%
				HOMO→LUMO	4%
	$S_0 \rightarrow S_3$	291.13	0.0714	HOMO-2→LUMO	75%
				HOMO-1→LUMO+1	8%
				HOMO→LUMO+1	9%
	$N^* S_1 \rightarrow S_0$	374.68	0.7143	LUMO→HOMO	97%
	$T^* S_1 \rightarrow S_0$	543.53	0.4506	LUMO→HOMO	99%
CPIQ-NHTs	$S_0 \rightarrow S_1$	319.01	0.4132	HOMO-1→LUMO	65%
				HOMO→LUMO	29%
	$S_0 \rightarrow S_2$	311.75	0.0735	HOMO-1→LUMO	29%
				HOMO→LUMO	67%
	$S_0 \rightarrow S_3$	288.64	0.0415	HOMO-2→LUMO	76%
				HOMO→LUMO+2	13%
	$N^* S_1 \rightarrow S_0$	373.56	0.7045	LUMO→HOMO	97%

	T* $S_1 \rightarrow S_0$	514.84	0.4671	LUMO→HOMO	99%
CPIQ-OH	$S_0 \rightarrow S_1$	318.64	0.4224	HOMO-1→LUMO	7%
				HOMO→LUMO	86%
	$S_0 \rightarrow S_2$	305.27	0.0764	HOMO-1→LUMO	86%
				HOMO→LUMO	8%
	$S_0 \rightarrow S_3$	285.92	0.0297	HOMO-2→LUMO	73%
				HOMO-1→LUMO+1	8%
				HOMO→LUMO+1	12%
	N* $S_1 \rightarrow S_0$	361.76	0.7917	LUMO→HOMO	96%
	T* $S_1 \rightarrow S_0$	528.74	0.4368	LUMO→HOMO	99%

Table S7. The frontier orbitals for titled compounds.

Compounds	HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
CPIQ-NHMe						
CPIQ-NH_2						
CPIQ-NHAc						
CPIQ-NHTs						
CPIQ-OH						

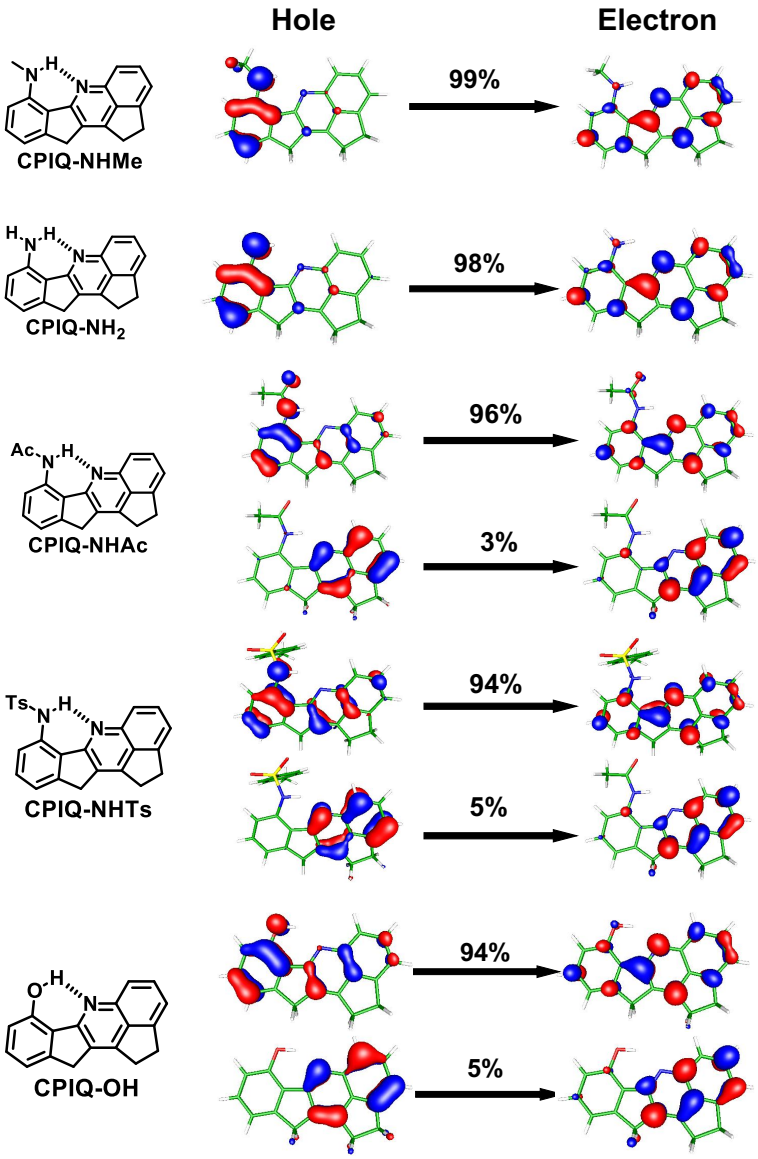


Figure S15. The computed natural transition orbitals for titled compounds, which are involved in S_1 transition.

Table S8. The charge transfer ratio (ω_{CT}) and charge transfer length (Δr) of S_1 transition for title compounds

Compounds	ω_{CT}	Δr (Å)
CPIQ-NHMe	0.944	2.756
CPIQ-NH$_2$	0.940	2.636
CPIQ-NHAc	0.949	1.709
CPIQ-NHTs	0.896	0.525
CPIQ-OH	0.937	1.575

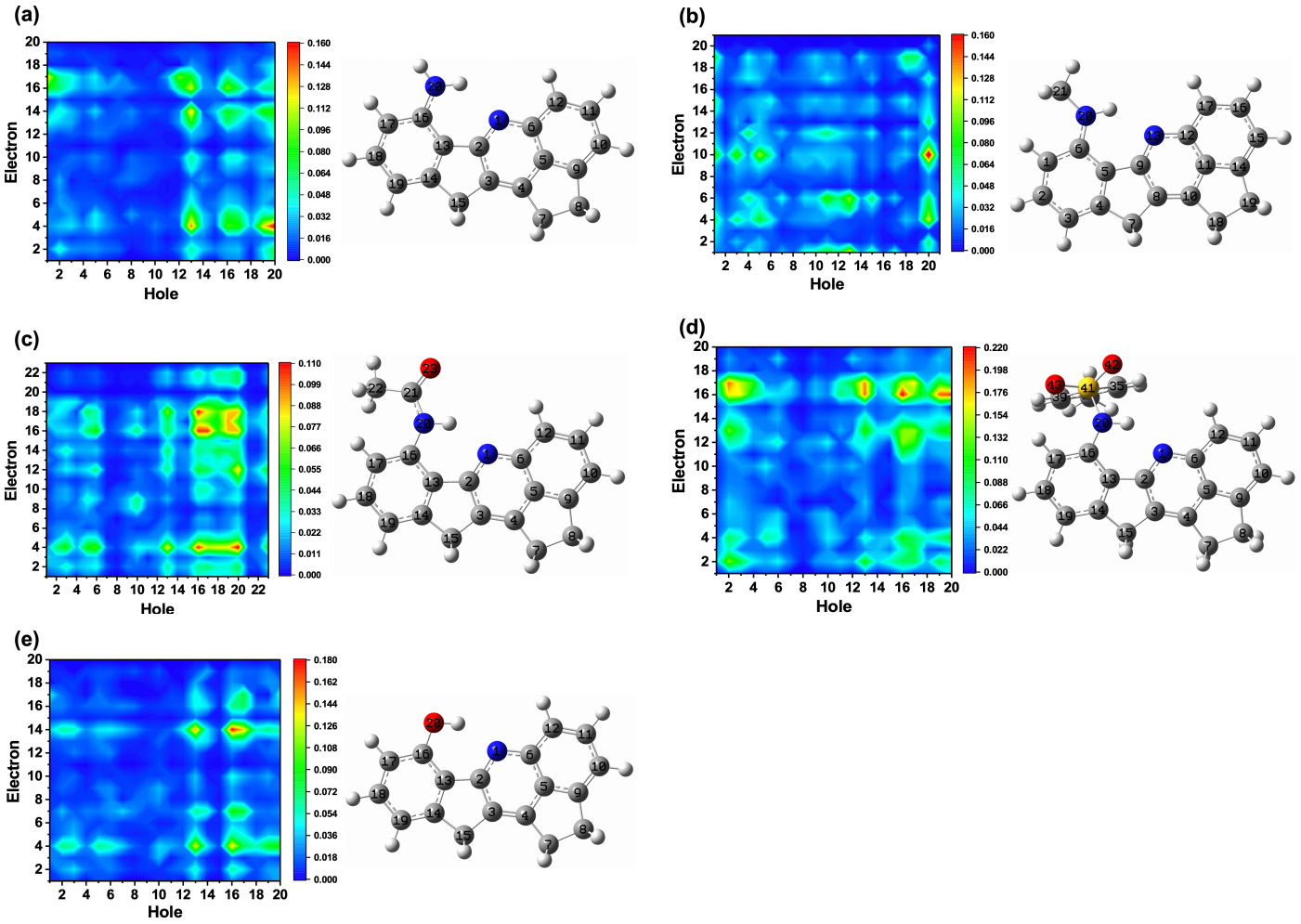


Figure S16. The contour plot of transition density matrix of $S_0 \rightarrow S_1$ transition for (a) **CPIQ-NH$_2$**, (b) **CPIQ-NHMe**, (c) **CPIQ-NHAc**, (d) **CPIQ-NHTs** and (e) **CPIQ-OH**.

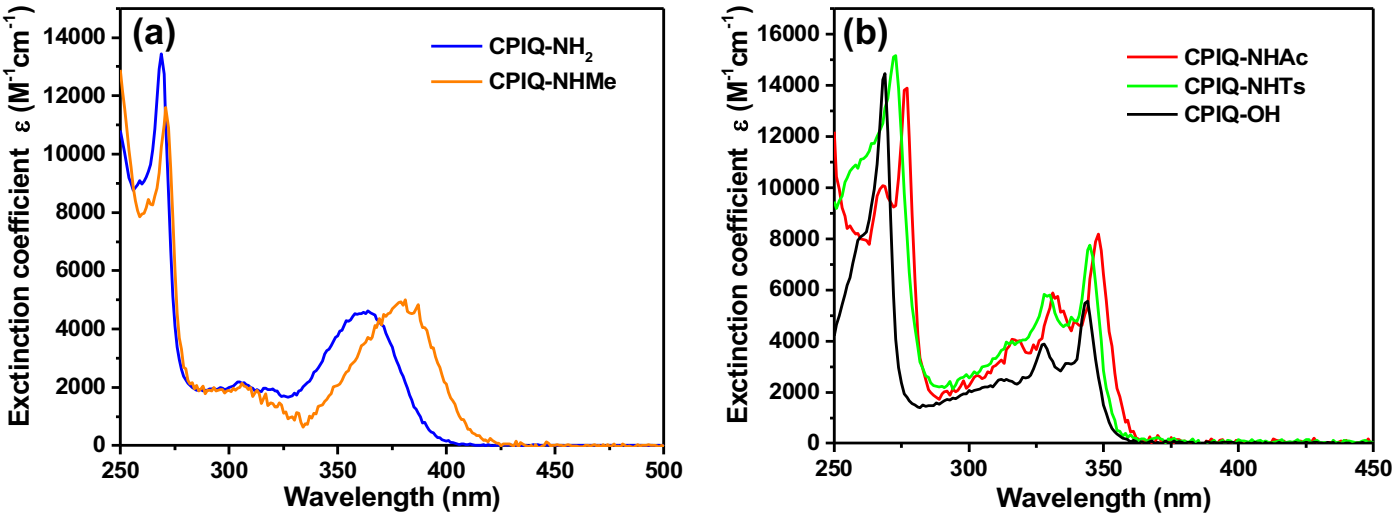


Figure S17. The extinction coefficient of (a) **CPIQ-NH$_2$** (blue) and **CPIQ-NHMe** (orange) and (b) **CPIQ-NHAc** (red), **CPIQ-NHTs** (green) and **CPIQ-OH** (black) in acetonitrile at 298K.

Table S9. The computed absorption and emission wavelength.

	B3LYP		M062X		PBE1PBE	
	λ_{abs}/nm (f)	λ_{em}/nm (f)	λ_{abs}/nm (f)	λ_{em}/nm (f)	λ_{abs}/nm (f)	λ_{em}/nm (f)
CPIQ-NHMe	389 (0.3407)	N*: 425 (0.2909) T*: 658 (0.3079)	335 (0.4920)	N*: 370 (0.5431) T*: 548 (0.4651)	372 (0.3636)	N*: 415 (0.5660) T*: 617 (0.5033)
CPIQ-NH$_2$	372 (0.3256)	N*: 407 (0.2713) T*: 644 (0.2684)	322 (0.4855)	N*: 357 (0.5504) T*: 527 (0.4448)	356 (0.3495)	N*: 397 (0.5753) T*: 592 (0.4670)
CPIQ-NHAc	342 (0.3740)	N*: 376 (0.3963) T*: 629 (0.2393)	300 (0.5142)	N*: 344 (0.6037) T*: 504 (0.4396)	327 (0.4255)	N*: 375 (0.7143) T*: 543 (0.4506)
CPIQ-NHTs	337(0.3935)	T*: 616 (0.2382)	292 (0.3610)	N*: 342 (0.5840) T*: 480 (0.4562)	319 (0.4132)	N*: 374 (0.7045) T*: 515 (0.4671)
CPIQ-OH	335 (0.3883)	N*: 374 (0.3089) T*: 629 (0.2014)	296 (0.5289)	N*: 346 (0.9828) T*: 485 (0.4348)	319 (0.4224)	N*: 362 (0.7917) T*: 529 (0.4368)

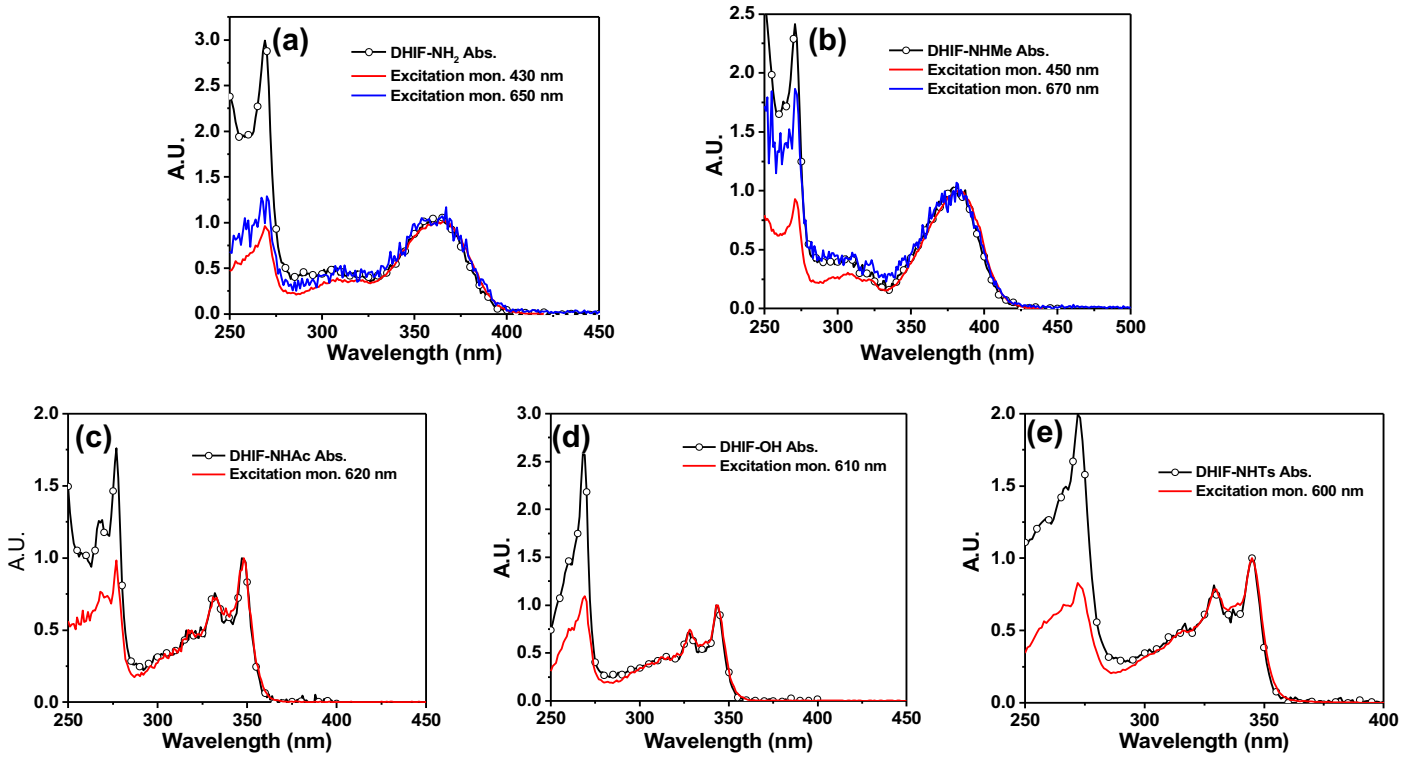


Figure S18. The excitation spectra for (a) **CPIQ-NH$_2$**, (b) **CPIQ-NHMe**, (c) **CPIQ-NHAc**, (d) **CPIQ-OH** and (e) **CPIQ-NHTs** in acetonitrile at 298K.

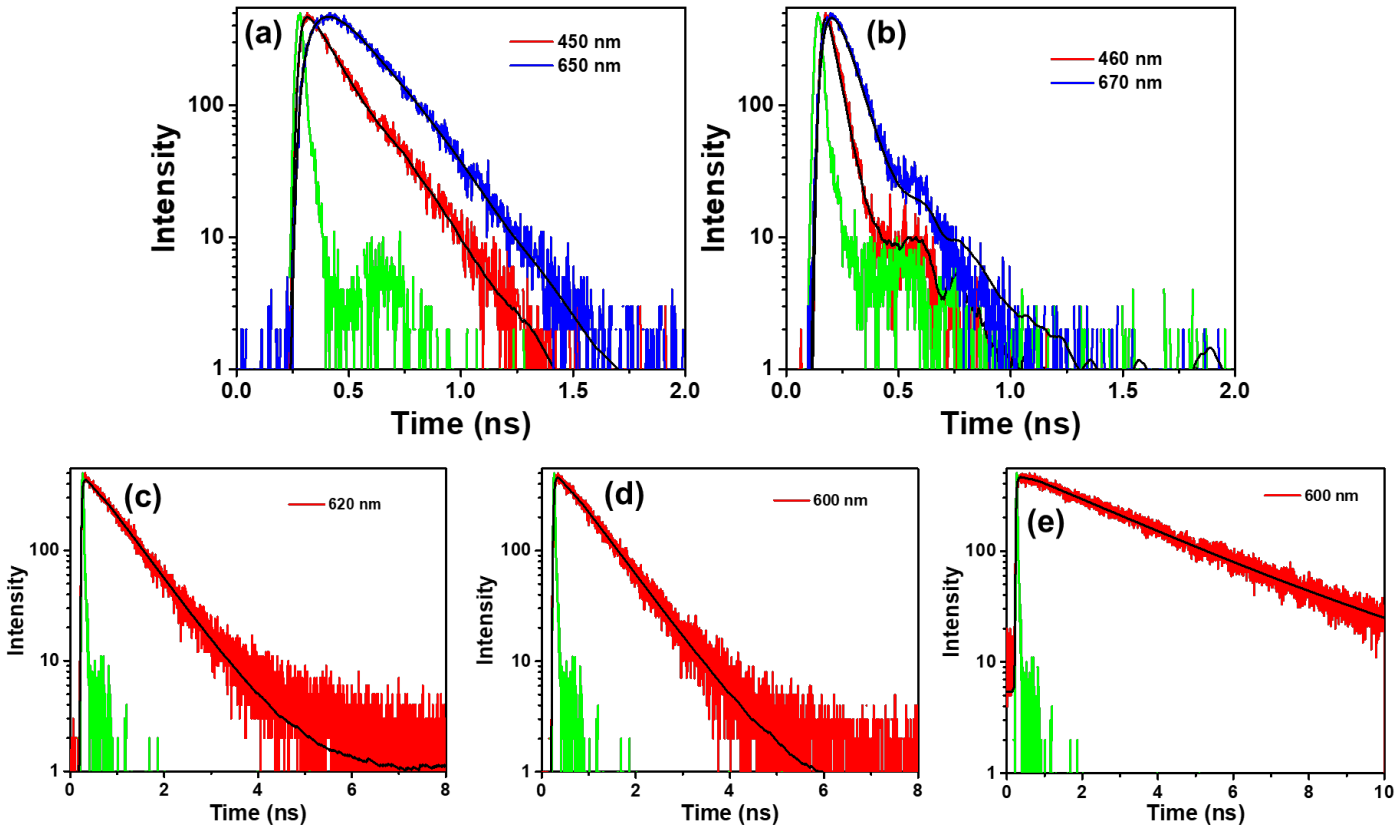


Figure S19. The time-resolved spectra for (a) **CPIQ-NH$_2$**, (b) **CPIQ-NHMe**, (c) **CPIQ-NHAc**, (d) **CPIQ-OH** and (e) **CPIQ-NHTs** obtained by TCSPC in acetonitrile at 298K. λ_{ex}=380 nm for (a) and (b) and 310 nm for (c), (d) and (e), respectively.

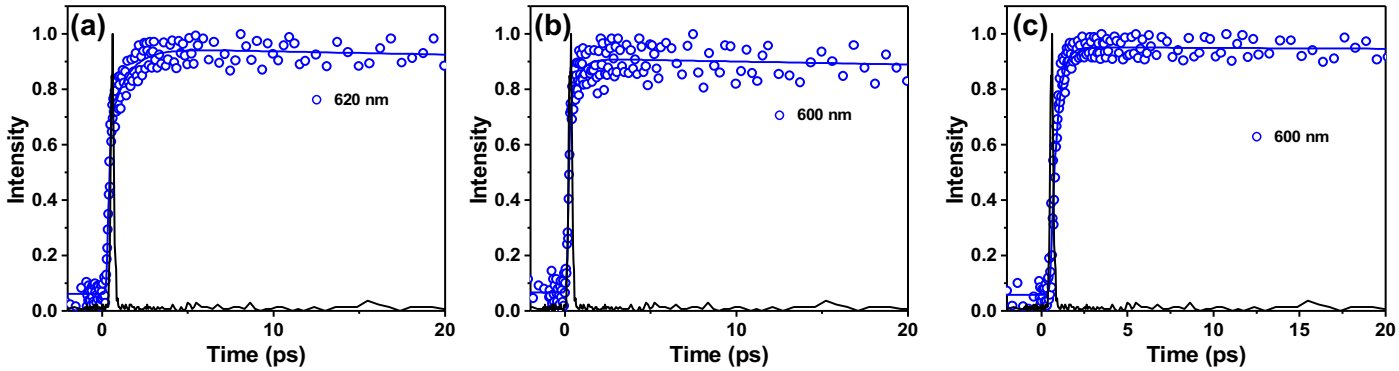


Figure S20. The early-stage kinetic traces for (a) **CPIQ-NHAc**, (b) **CPIQ-OH** and (c) **CPIQ-NHTs** acquired by fluorescence up-conversion measurements in acetonitrile at 298K. The black line represents the instrument response function. λ_{ex}=310 nm.

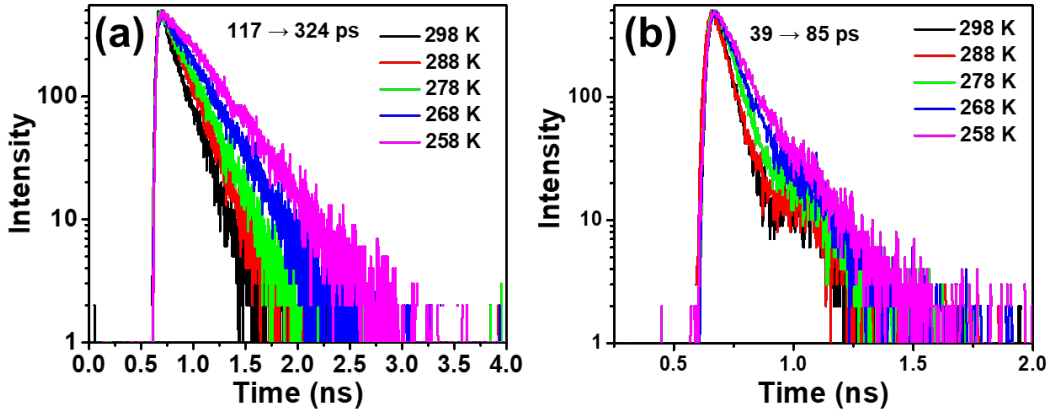


Figure S21. The temperature-dependent time-resolved spectra monitored at normal form emission (450 nm) for (a) **CPIQ-NH$_2$** and (b) **CPIQ-NHMe**, respectively. λ_{ex}= 380 nm.

Table S10. The computed H-bond distance (HBD) at S_1 state and energy difference between N* and T* ($\Delta E_{T^*-N^*}$).

	B3LYP		M062X		PBE1PBE	
	HBD (Å)	$\Delta E_{T^*-N^*}$ (kcal/mol)	HBD (Å)	$\Delta E_{T^*-N^*}$ (kcal/mol)	HBD (Å)	$\Delta E_{T^*-N^*}$ (kcal/mol)
CPIQ-NHMe	2.006	-1.76	2.027	-2.19	1.965	-1.73
CPIQ-NH$_2$	2.073	-4.14	2.073	-3.53	2.151	-3.66
CPIQ-NHAc	1.896	-10.87	1.920	-8.88	1.854	-9.99
CPIQ-NHTs	-[a]	-[a]	1.925	-17.28	1.832	-18.45
CPIQ-OH	1.847	-20.86	1.896	-16.60	1.800	-19.59

[a]We failed to obtain the optimized normal-form geometry under B3LYP functional.

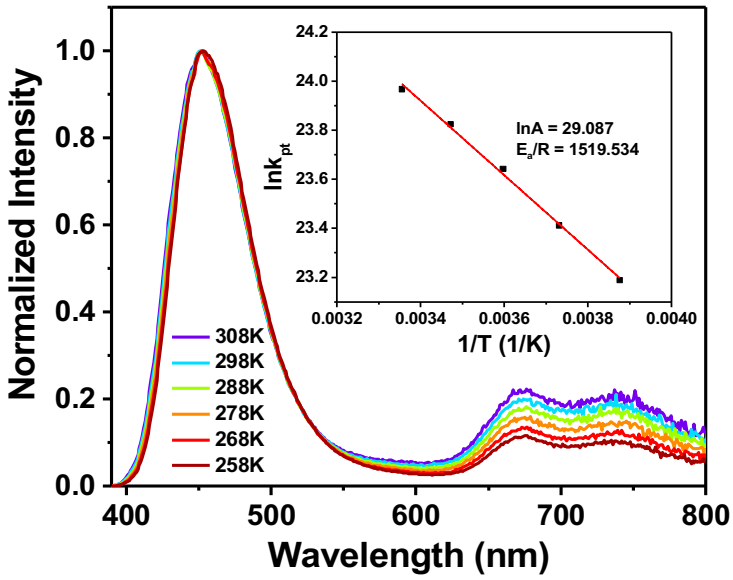


Figure S22. The temperature-dependent emission spectra for **CPIQ-NHMe** in acetonitrile. The inset: The Arrhenius plots for **CPIQ-NHMe**, which is plotted by using the corresponding time-resolved data.

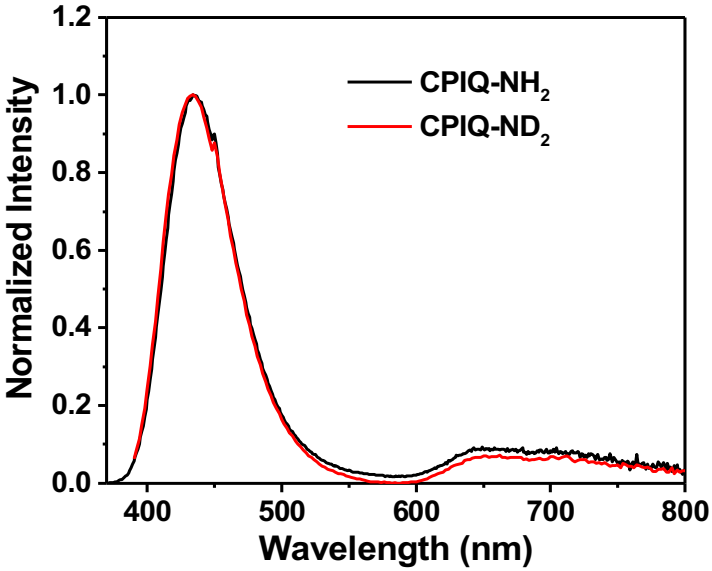


Figure S23. The steady-state emission spectra of **CPIQ-NH$_2$** (black) and **CPIQ-ND$_2$** (red) in acetonitrile at 298K.

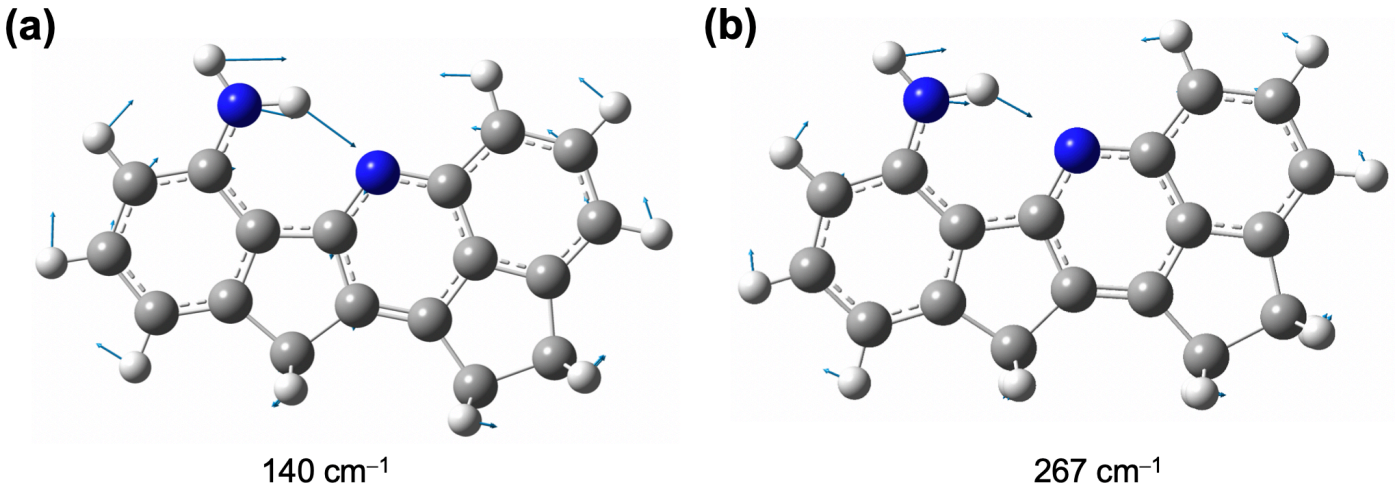


Figure S24. The calculated possible low-frequency vibration motion for **CPIQ-NH$_2$**, which is associated with the changes of H-bonds in distance and/or angle. The arrows represent the displacement vector.

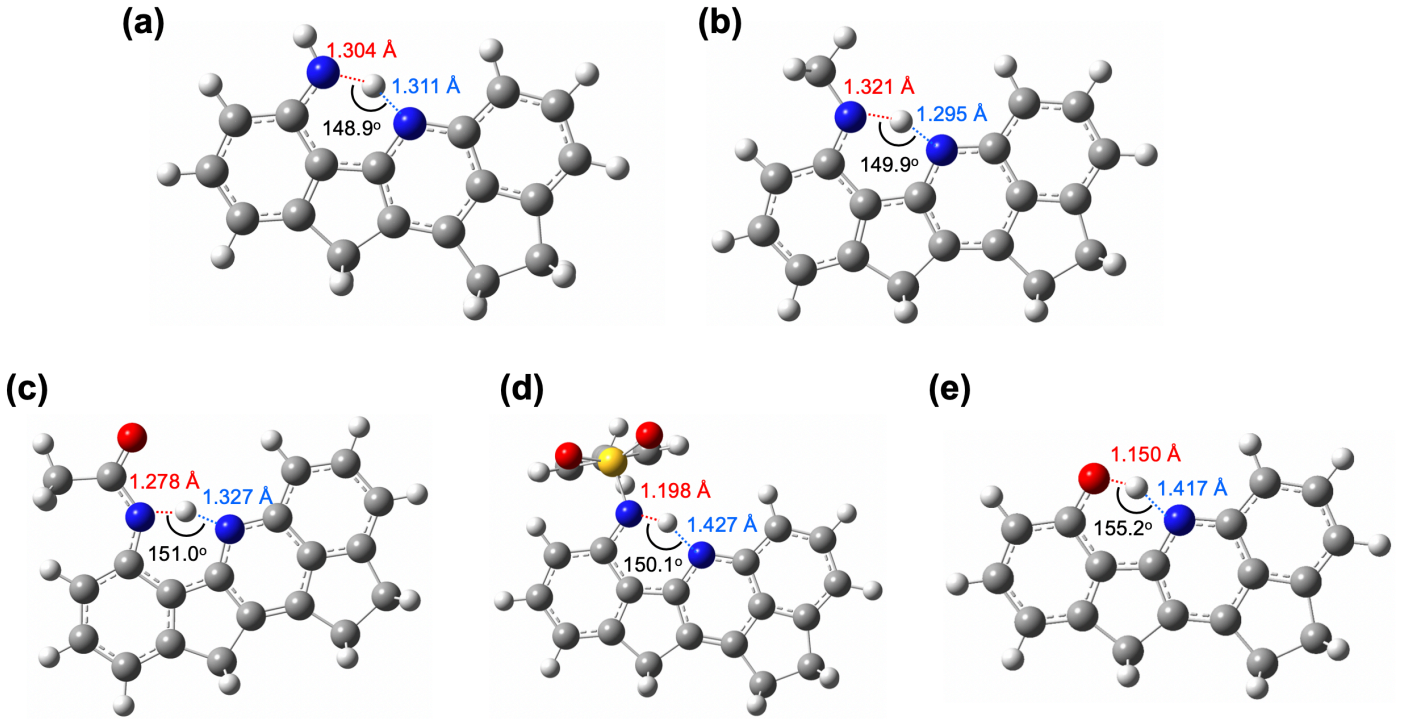


Figure S25. The transition state geometries for (a) **CPIQ-NH$_2$**, (b) **CPIQ-NHMe**, (c) **CPIQ-NHAc**, (d) **CPIQ-NHTs** and (e) **CPIQ-OH** optimized at PBE0/6-31+G(d,p) level.

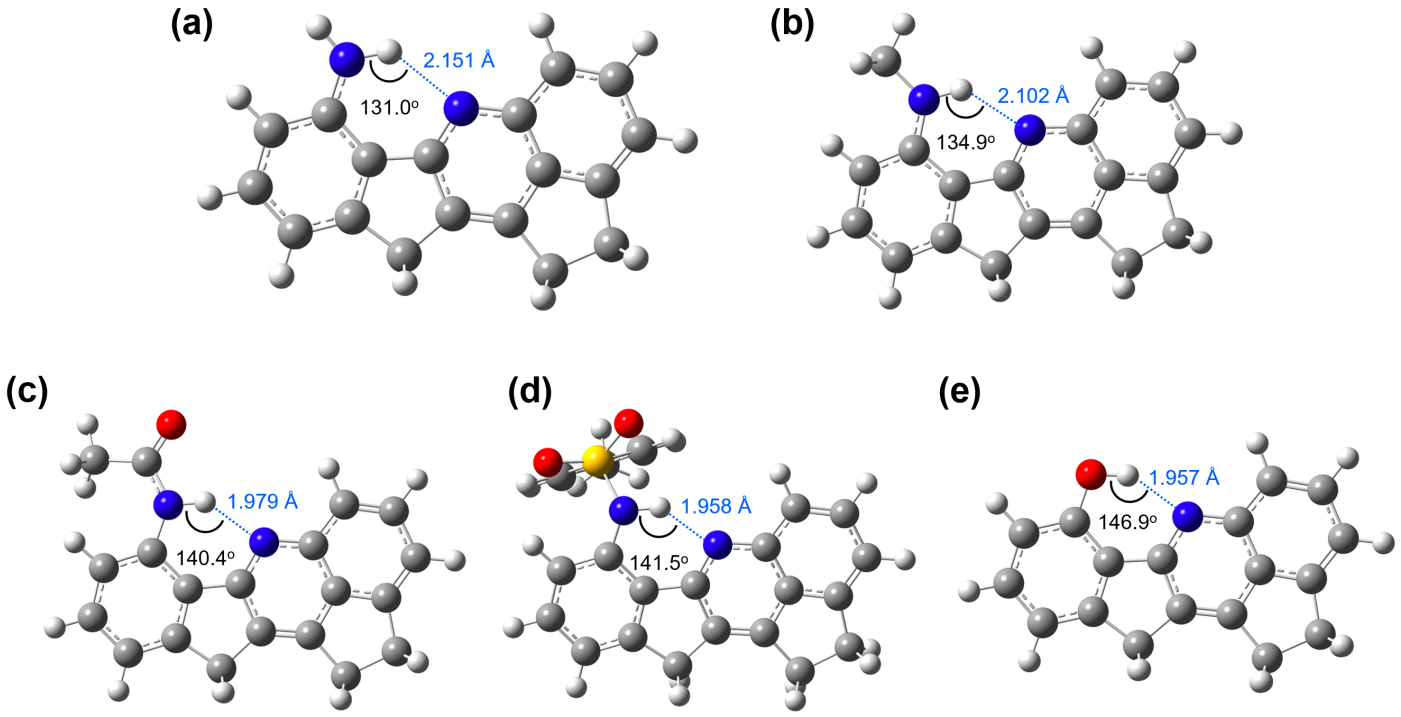


Figure S26. The ground state geometries for (a) **CPIQ-NH$_2$**, (b) **CPIQ-NHMe**, (c) **CPIQ-NHAc**, (d) **CPIQ-NHTs** and (e) **CPIQ-OH** optimized at PBE0/6-31+G(d,p) level.

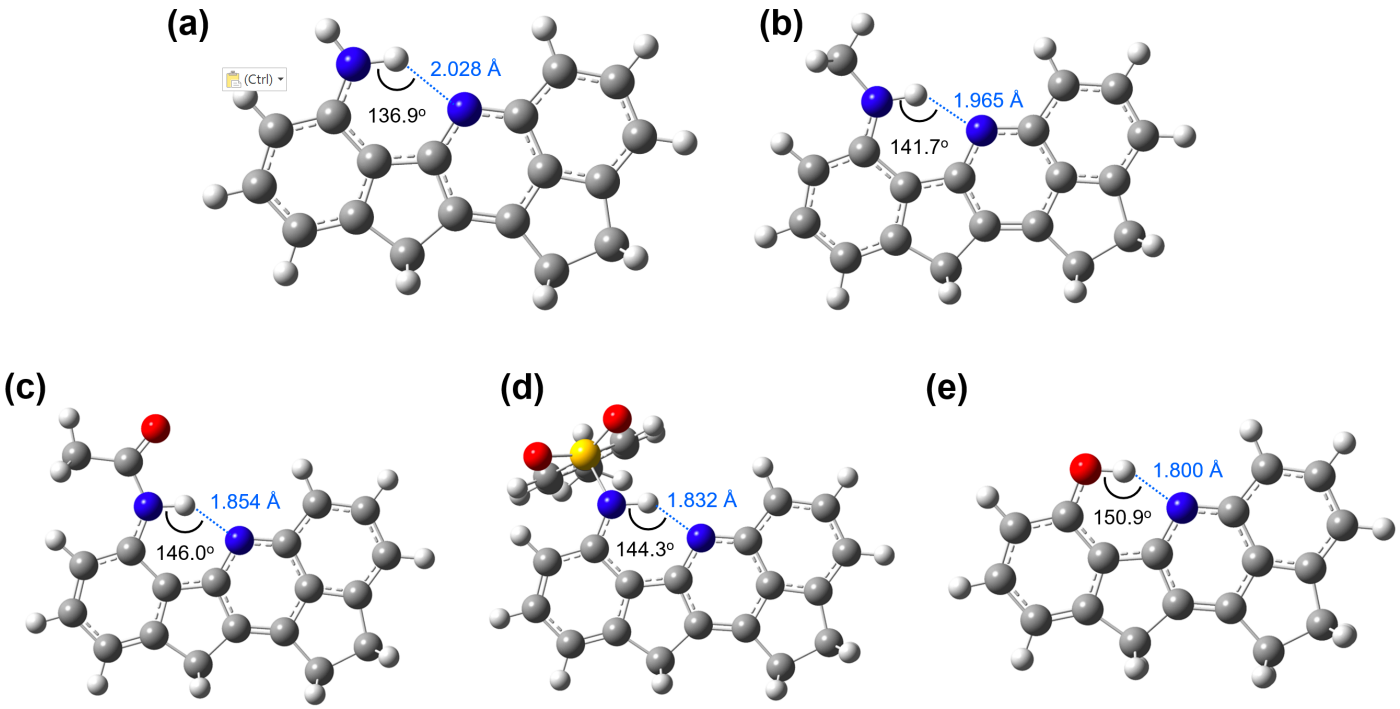


Figure S27. The normal form S_1 state geometries for (a) **CPIQ-NH$_2$**, (b) **CPIQ-NHMe**, (c) **CPIQ-NHAc**, (d) **CPIQ-NHTs** and (e) **CPIQ-OH** optimized at PBE0/6-31+G(d,p) level.

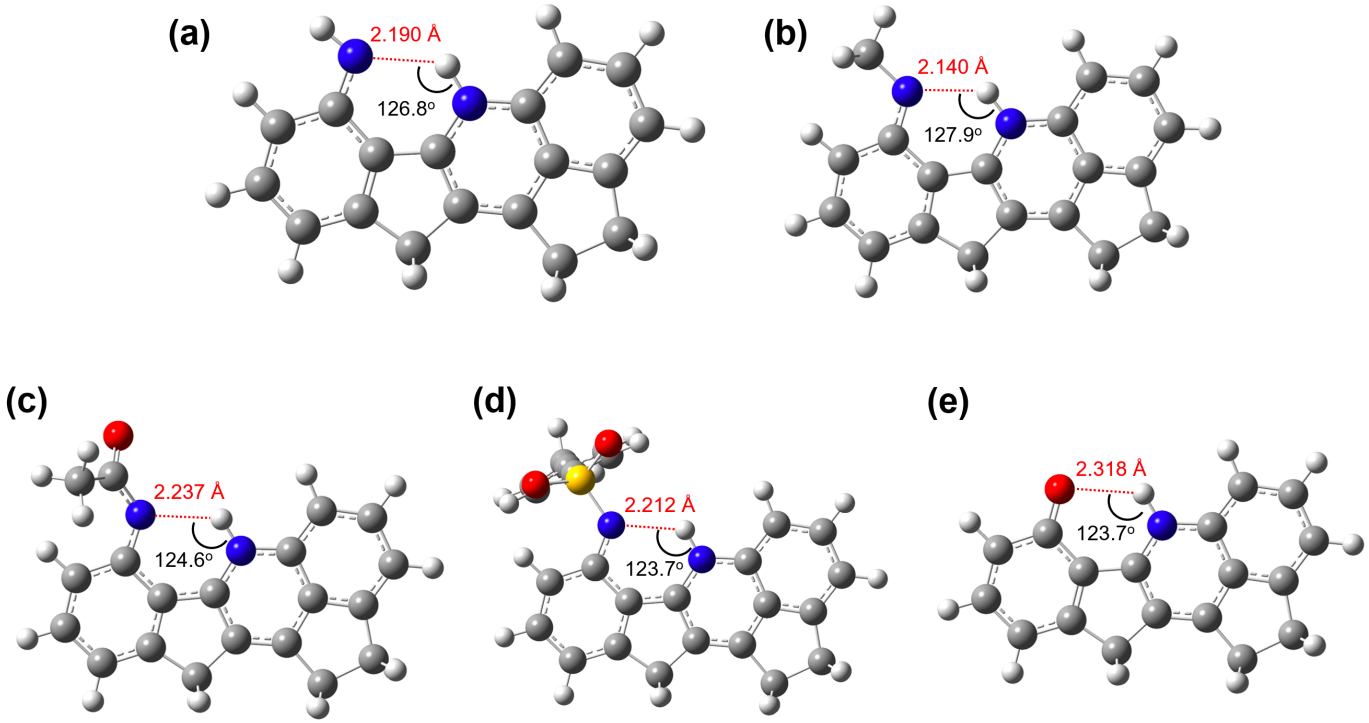


Figure S28. The tautomeric form S_1 state geometries for (a) **CPIQ-NH$_2$**, (b) **CPIQ-NHMe**, (c) **CPIQ-NHAc**, (d) **CPIQ-NHTs** and (e) **CPIQ-OH** optimized at PBE0/6-31+G(d,p) level.

Table S11. The Cartesian coordinates of optimized geometry for **CPIQ-NHAc** at PBE0/6-31+G(d,p).

	S_0 geometry			N* geometry			T* geometry			TS* geometry		
	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
N	-0.324282	0.917284	-0.095848	0.302316	0.930248	-0.000043	0.406784	0.93706	-0.145117	0.2357	0.8407	0.0185
C	-0.003145	-0.365839	-0.036171	-0.018252	-0.401303	-0.000048	-0.012312	-0.366554	-0.089282	-0.0618	-0.4899	0.0082
C	-0.903208	-1.4822	0.041747	0.894921	-1.508618	0.00003	0.867815	-1.451636	0.010959	0.8261	-1.5853	-0.0031
C	-2.243855	-1.205301	0.068664	2.24122	-1.231025	0.000084	2.23567	-1.203775	0.065707	2.1799	-1.2889	-0.0077
C	-2.601945	0.158815	0.011635	2.587996	0.147755	0.000029	2.635824	0.152965	0.013787	2.5124	0.0965	-0.0009
C	-1.66047	1.203246	-0.072342	1.624793	1.205684	0.000045	1.74929	1.245773	-0.090099	1.5635	1.1608	0.0116
C	-3.498199	-2.036255	0.143751	3.506309	-2.050077	0.000639	3.463314	-2.06582	0.177505	3.4516	-2.0944	-0.0198
C	-4.66559	-1.003534	0.130225	4.660617	-0.998442	-0.000692	4.658164	-1.061144	0.184074	4.5963	-1.0336	-0.0195
C	-3.994319	0.348873	0.041005	3.970349	0.349068	-0.000096	4.027259	0.30963	0.077625	3.8971	0.3085	-0.0071
C	-4.479665	1.638221	-0.014214	4.462629	1.650504	-0.000029	4.56231	1.590137	0.036268	4.3853	1.6105	-0.001
C	-3.553176	2.709779	-0.098703	3.536171	2.719401	0.000127	3.68618	2.684932	-0.067643	3.4629	2.6737	0.0112
C	-2.18166	2.517677	-0.128282	2.158737	2.523231	0.000138	2.294406	2.532533	-0.130665	2.0791	2.4704	0.0175
C	1.360854	-0.891085	-0.058443	-1.339863	-0.915362	-0.000052	-1.377792	-0.844955	-0.121584	-1.399	-0.9622	0.0084
C	1.308407	-2.291713	-0.014187	-1.316134	-2.330746	0.000022	-1.355745	-2.232955	-0.050848	-1.4193	-2.3576	0.0013
C	-0.122702	-2.764421	0.066552	0.119599	-2.796945	0.000159	0.065527	-2.723727	0.044173	0.0115	-2.8606	-0.0083
C	2.584892	-0.196821	-0.12537	-2.599915	-0.200616	-0.000105	-2.605251	-0.113682	-0.188565	-2.5779	-0.1437	0.0141
C	3.754151	-0.965672	-0.191908	-3.789329	-0.960718	-0.000202	-3.797393	-0.886785	-0.248589	-3.8209	-0.8326	0.025
C	3.688511	-2.360398	-0.145257	-3.732861	-2.345199	-0.000196	-3.766428	-2.28223	-0.19726	-3.8385	-2.2226	0.0209
C	2.475657	-3.043387	-0.047929	-2.490853	-3.045095	-0.00006	-2.552964	-2.968501	-0.088633	-2.6492	-3.0013	0.0073
N	2.506106	1.197634	-0.162763	-2.46874	1.160083	0.000008	-2.512477	1.229899	-0.251185	-2.2628	1.1798	0.012
C	3.408486	2.199122	0.071223	-3.356079	2.22833	-0.000006	-3.527463	2.09845	0.024397	-3.0594	2.3061	-0.0078
C	4.823429	1.878671	0.461833	-4.833883	1.999583	0.000302	-4.481803	1.824632	1.170035	-4.5555	2.2128	-0.0786
O	3.026848	3.36735	-0.02977	-2.863475	3.354285	-0.000202	-3.610462	3.17109	-0.589669	-2.4861	3.3979	0.0293
H	-3.506624	-2.650529	1.050815	3.559994	-2.706947	-0.876013	3.535821	-2.772816	-0.658613	3.5075	-2.7453	-0.9014
H	-3.557517	-2.730374	-0.701863	3.560236	-2.704637	0.879038	3.444543	-2.675037	1.090149	3.5173	-2.7565	0.8528
H	-5.278727	-1.081974	1.034342	5.305553	-1.114722	-0.879374	5.341887	-1.248903	-0.651451	5.2388	-1.1394	-0.9013
H	-5.336756	-1.169584	-0.719063	5.307861	-1.114745	0.876259	5.25348	-1.154412	1.099344	5.2484	-1.1503	0.8538
H	-5.545342	1.849531	0.004486	5.52946	1.857983	-0.000101	5.634806	1.758774	0.082646	5.4522	1.8176	-0.0055
H	-3.93924	3.724857	-0.142266	3.917347	3.737776	0.000216	4.09832	3.689535	-0.100243	3.8379	3.6941	0.0159
H	-1.501849	3.362443	-0.193968	1.478515	3.37053	0.000217	1.650092	3.403313	-0.209176	1.3979	3.3165	0.0269
H	-0.305502	-3.341834	0.981904	0.346944	-3.41365	-0.87903	0.319742	-3.392526	-0.788432	0.2182	-3.4773	-0.8924
H	-0.381436	-3.420984	-0.773865	0.346795	-3.413263	0.879668	0.238333	-3.295167	0.965407	0.2259	-3.489	0.8657
H	4.724165	-0.500393	-0.299433	-4.758028	-0.482375	-0.000314	-4.750414	-0.380202	-0.360412	-4.7624	-0.3014	0.0381
H	4.617375	-2.921506	-0.196383	-4.659851	-2.909275	-0.000295	-4.697351	-2.837809	-0.250802	-4.7968	-2.7318	0.029
H	2.450444	-4.128507	-0.012471	-2.487595	-4.131423	-0.000032	-2.536659	-4.053647	-0.046554	-2.7212	-4.0852	0.0038
H	1.545574	1.542526	-0.265216	-1.471718	1.467458	-0.000047	-0.315325	1.647667	-0.222595	-0.9948	1.3366	0.0191

H	4.873048	1.09314	1.22005	-5.147682	1.441361	-0.887313	-5.495507	1.686096	0.779078	-4.8754	1.6425	-0.9562
H	5.399132	1.552071	-0.410233	-5.147177	1.440634	0.887632	-4.208246	0.952269	1.765734	-4.958	1.7209	0.813
H	5.276992	2.791228	0.848629	-5.324918	2.972233	0.000808	-4.501616	2.711695	1.809209	-4.9624	3.222	-0.1391

Table S12. The Cartesian coordinates of optimized geometry for **CPIQ-NHMe** at PBE0/6-31+G(d,p).

	S_0 geometry			N* geometry			T* geometry			TS* geometry		
	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
C	-4.189298	0.108495	0.000007	-4.223359	0.156457	0.00004	-4.228422	0.185063	0.000035	4.175209	0.329715	-0.000006
C	-4.391314	-1.271122	0.000044	-4.457509	-1.217717	0.000044	-4.466536	-1.199599	0.000033	4.498513	-1.036785	-0.000006
C	-3.329852	-2.183729	0.000034	-3.382697	-2.135918	0.000023	-3.422563	-2.122679	0.000022	3.516116	-2.045087	-0.000006
C	-2.039046	-1.668848	-0.000003	-2.071512	-1.666931	0.000004	-2.098186	-1.632886	0.000013	2.160215	-1.675991	-0.000006
C	-1.815409	-0.284598	-0.00004	-1.810793	-0.290127	0.000004	-1.857552	-0.267389	0.000016	1.852011	-0.326692	-0.000106
C	-2.883672	0.644424	-0.000052	-2.897631	0.646758	0.000014	-2.904371	0.713595	0.000027	2.813508	0.722411	-0.000006
C	-0.721071	-2.408101	0.000004	-0.757709	-2.411627	-0.000011	-0.791337	-2.389489	-0.000001	0.860317	-2.463995	-0.000006
C	0.291777	-1.298167	-0.000013	0.263524	-1.302887	-0.000012	0.240113	-1.291407	-0.000006	-0.204286	-1.381498	-0.000006
C	-0.385065	-0.026345	-0.000039	-0.398289	-0.039936	-0.000002	-0.423407	-0.059825	0.000005	0.436411	-0.135196	-0.000106
C	1.658321	-1.283335	0.000002	1.642745	-1.305403	-0.000019	1.634153	-1.29245	-0.000019	-1.595586	-1.358502	-0.000006
C	2.270746	-0.008888	-0.000009	2.264653	-0.028168	-0.000016	2.271346	-0.032418	-0.000019	-2.199289	-0.070703	-0.000006
C	1.54314	1.19697	-0.000027	1.537638	1.198918	0.000002	1.594577	1.207406	-0.000005	-1.486193	1.162399	-0.000006
N	0.174992	1.176142	-0.000044	0.181123	1.196216	0.000012	0.219511	1.142787	0.000006	-0.118993	1.105302	-0.000106
C	3.672867	-0.088209	0.000005	3.660386	-0.11206	-0.000027	3.672126	-0.130389	-0.000033	-3.599789	-0.138307	0.000094
C	4.39694	1.08648	0.000007	4.410565	1.062331	-0.000019	4.426001	1.03488	-0.000033	-4.338393	1.041391	0.000094
C	3.691202	2.316456	-0.000008	3.722064	2.291909	0.000001	3.759881	2.274024	-0.000018	-3.650196	2.266592	-0.000006
C	2.306873	2.388385	-0.000025	2.327837	2.37755	0.000011	2.361048	2.377065	-0.000005	-2.250196	2.342796	-0.000006
C	2.73394	-2.339414	0.000042	2.713384	-2.366473	-0.00002	2.6877	-2.365911	-0.000024	-2.680083	-2.402505	0.000094
C	4.076129	-1.546323	0.000008	4.059435	-1.57316	-0.000054	4.045876	-1.596068	-0.000054	-4.015385	-1.593709	0.000094
N	-2.620956	1.977137	-0.000148	-2.56395	1.950949	-0.000011	-2.533011	2.000748	0.000028	2.261805	1.950109	-0.000006
C	-3.638801	2.994334	0.000136	-3.495172	3.045487	0.000027	-3.57496	2.986583	0.00003	3.068402	3.134411	-0.000006
H	-5.047451	0.772737	0.000018	-5.056576	0.851432	0.000056	-5.075809	0.863091	0.000045	4.966107	1.073217	-0.000006
H	-5.412846	-1.643491	0.000084	-5.47784	-1.58662	0.000063	-5.493483	-1.555146	0.000039	5.545214	-1.325682	-0.000006
H	-3.514797	-3.25384	0.000064	-3.588456	-3.202999	0.000024	-3.623891	-3.189959	0.000019	3.817619	-3.088886	-0.000006
H	-0.619815	-3.057353	0.879269	-0.658605	-3.062471	0.87891	-0.697216	-3.040101	0.879201	0.781019	-3.116795	-0.878906
H	-0.61982	-3.057375	-0.879245	-0.658621	-3.062457	-0.878946	-0.697231	-3.040095	-0.879209	0.781019	-3.116795	0.878894
H	5.483615	1.089147	0.000018	5.497556	1.046858	-0.000027	5.512538	1.007354	-0.000044	-5.425392	1.029687	0.000094
H	4.262341	3.241373	-0.000006	4.299263	3.213933	0.000009	4.346783	3.188299	-0.000017	-4.221199	3.191591	-0.000006
H	1.800342	3.349685	-0.000038	1.835605	3.346822	0.000026	1.880984	3.351259	0.000006	-1.751599	3.308198	-0.000106
H	2.645122	-2.98913	0.877706	2.633872	-3.021036	0.877155	2.593853	-3.019582	0.876719	-2.607981	-3.059005	-0.876706
H	2.64512	-2.989221	-0.877552	2.633845	-3.021074	-0.877164	2.593826	-3.019609	-0.876745	-2.607981	-3.059005	0.876894
H	4.684065	-1.789055	-0.878221	4.668321	-1.821807	-0.877601	4.649846	-1.852465	-0.877918	-4.626984	-1.83431	0.877694
H	4.684117	-1.789051	0.8782	4.668384	-1.82183	0.877442	4.649897	-1.852483	0.877769	-4.627084	-1.83431	-0.877506
H	-1.640343	2.235931	0.000009	-1.547724	2.129602	0.000002	-0.393762	1.961151	0.000014	0.944805	1.843605	-0.000106
H	-4.281325	2.9318	0.888671	-4.138333	3.013263	0.888092	-4.235001	2.908829	0.882697	3.721301	3.181013	-0.884806
H	-3.155299	3.972229	0.000052	-2.937686	3.981086	-0.000119	-3.134731	3.987277	0.000012	2.422399	4.01411	-0.000006

H	-4.281717	2.93186	-0.888114	-4.138563	3.013125	-0.887863	-4.235029	2.908807	-0.882614	3.721201	3.181013	0.884894

Table S13. The Cartesian coordinates of optimized geometry for **CPIQ-NH$_2$** at PBE0/6-31+G(d,p).

	S_0 geometry			N* geometry			T* geometry			TS* geometry		
	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
N	0.125928	1.357241	-0.000238	0.137729	1.3813	0.000154	-0.164086	1.320397	-0.000106	-0.078406	1.301399	-0.000104
C	-0.581076	0.235361	-0.000366	-0.586798	0.22222	0.00004	0.618624	0.201824	-0.00003	0.611395	0.1283	-0.000004
C	-0.070796	-1.112005	-0.000229	-0.082934	-1.111667	-0.000084	0.110507	-1.098105	0.000092	0.117595	-1.181801	0.000096
C	1.286761	-1.270241	-0.000071	1.286589	-1.283003	-0.00013	-1.276122	-1.270592	0.000147	-1.269205	-1.318501	0.000096
C	2.055269	-0.083735	0.000026	2.05754	-0.090593	-0.000071	-2.059143	-0.097504	0.00007	-2.013105	-0.107102	0.000096
C	1.485646	1.204408	-0.000003	1.483303	1.216957	0.000073	-1.538299	1.216243	-0.00006	-1.443306	1.199999	-0.000004
C	2.219883	-2.454097	0.000128	2.220358	-2.466238	-0.000191	-2.19134	-2.464175	0.000233	-2.228504	-2.478402	0.000396
C	3.651545	-1.837298	0.000159	3.652493	-1.841318	-0.000309	-3.632504	-1.863632	0.000299	-3.646404	-1.824802	0.000096
C	3.436253	-0.339906	0.000219	3.433269	-0.342589	-0.000132	-3.438865	-0.363144	0.000131	-3.397805	-0.331802	0.000096
C	4.302613	0.733977	0.000406	4.319618	0.732665	-0.000041	-4.327483	0.702263	0.000054	-4.264505	0.757097	0.000096
C	3.75778	2.043385	0.000393	3.784962	2.037132	0.000105	-3.816789	2.013298	-0.000079	-3.719306	2.052498	-0.000004
C	2.393748	2.289877	0.000193	2.411539	2.291237	0.000162	-2.439898	2.28396	-0.000136	-2.336406	2.285898	-0.000004
C	-2.033386	0.158204	-0.000427	-2.017743	0.142764	0.000041	2.069448	0.170048	-0.000067	2.038995	0.0969	-0.000104
C	-2.430081	-1.18888	-0.000096	-2.44362	-1.19179	-0.000064	2.471763	-1.154378	0.000029	2.499795	-1.2061	-0.000004
C	-1.214677	-2.086639	-0.000161	-1.229875	-2.088721	-0.000157	1.266878	-2.063091	0.000138	1.298096	-2.1365	0.000096
C	-2.975104	1.209361	-0.000451	-2.985772	1.203943	0.000144	2.99317	1.268616	-0.000183	2.873494	1.253501	-0.000204
C	-4.336229	0.844191	0.000297	-4.363117	0.874524	0.000215	4.373482	0.89335	-0.000196	4.275394	1.016101	-0.000204
C	-4.713736	-0.495688	0.000683	-4.760212	-0.456947	0.000148	4.776689	-0.446755	-0.000103	4.751695	-0.298999	-0.000104
C	-3.773895	-1.535868	0.000406	-3.800959	-1.5	0.000002	3.845828	-1.486827	0.000011	3.889396	-1.416599	-0.000004
N	-2.556481	2.503344	-0.001982	-2.516902	2.45894	0.000085	2.501464	2.508197	-0.000265	2.187794	2.4026	-0.000304
H	2.04921	-3.08734	-0.877465	2.062241	-3.106389	-0.877379	-2.019836	-3.102085	0.876986	-2.083604	-3.122702	0.877396
H	2.04909	-3.087075	0.877894	2.062379	-3.106324	0.877074	-2.019938	-3.1021	-0.876531	-2.083504	-3.123202	-0.876304
H	4.22389	-2.155203	-0.878007	4.226673	-2.162021	-0.877903	-4.200883	-2.191563	0.878141	-4.227504	-2.133003	0.877396
H	4.223934	-2.155319	0.878251	4.226927	-2.162219	0.877043	-4.201061	-2.191761	-0.877352	-4.227104	-2.133003	-0.877504
H	5.380948	0.599619	0.000564	5.396773	0.585895	-0.000081	-5.402665	0.543001	0.000095	-5.343305	0.622897	0.000096
H	4.441372	2.888591	0.000544	4.469935	2.882143	0.000177	-4.509714	2.84997	-0.000142	-4.391206	2.907097	-0.000004
H	2.012673	3.307438	0.000184	2.040349	3.312999	0.000276	-2.080608	3.309002	-0.00024	-1.949907	3.301298	-0.000104
H	-1.19533	-2.74353	-0.879384	-1.211002	-2.746898	-0.87906	1.25536	-2.72062	0.879239	1.295296	-2.7942	0.878996
H	-1.195211	-2.743532	0.879053	-1.210982	-2.747088	0.878603	1.255312	-2.720767	-0.878852	1.295296	-2.7943	-0.878604
H	-5.095592	1.622217	0.000436	-5.098481	1.673922	0.000301	5.122748	1.681877	-0.000282	4.968894	1.852402	-0.000304
H	-5.774004	-0.736106	0.001212	-5.817172	-0.70183	0.000203	5.838108	-0.678708	-0.000118	5.824395	-0.467198	-0.000204
H	-4.093178	-2.573896	0.0007	-4.134	-2.534211	-0.000054	4.169553	-2.523263	0.000085	4.309396	-2.418399	-0.000004
H	-1.561958	2.69056	0.00146	-1.497367	2.58044	0.000219	0.331735	2.212039	-0.000193	0.905194	2.1685	-0.000204
H	-3.215104	3.263037	0.003454	-3.133891	3.258439	0.000398	3.264567	3.186424	-0.000336	2.718093	3.267701	-0.000304

Table S14. The Cartesian coordinates of optimized geometry for **CPIQ-OH** at PBE0/6-31+G(d,p).

	S_0 geometry			N* geometry			T* geometry			TS* geomtry		
	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
N	-0.105302	1.341865	-0.000084	0.096748	-1.355333	-0.000008	0.171344	-1.334447	-0.000046	0.0525	-1.305793	-0.000001
C	0.584392	0.211342	0.000019	-0.602374	-0.172228	-0.00001	-0.615289	-0.21344	-0.000024	-0.612002	-0.112794	-0.000001
C	0.08515	-1.133242	0.00005	-0.097784	1.161243	0.000001	-0.113316	1.086258	-0.000003	-0.116204	1.203107	-0.000001
C	-1.27555	-1.282455	0.000056	1.273705	1.3124	0	1.273918	1.269918	0.000015	1.269296	1.331309	-0.000001
C	-2.036076	-0.089461	-0.000013	2.023847	0.101148	-0.000001	2.060657	0.097652	0.000002	1.997498	0.10681	-0.000001
C	-1.466743	1.200696	-0.000093	1.43887	-1.211448	-0.000003	1.547717	-1.219006	-0.00003	1.4129	-1.20199	-0.000001
C	-2.215198	-2.459712	0.000087	2.229862	2.476171	0.000001	2.184513	2.466827	0.000038	2.241794	2.479511	-0.000001
C	-3.6426	-1.835358	0.00007	3.648918	1.824818	0.000013	3.627422	1.869599	0.000049	3.650595	1.807913	-0.000001
C	-3.418975	-0.339805	-0.000011	3.400939	0.331837	0.000003	3.438812	0.368286	0.00002	3.383797	0.318413	-0.000001
C	-4.281168	0.736851	-0.00008	4.271707	-0.75639	0.000002	4.333602	-0.691851	0.00001	4.240699	-0.776786	-0.000001
C	-3.733654	2.04495	-0.000157	3.725332	-2.060823	-0.000002	3.830005	-2.005333	-0.000022	3.683601	-2.070887	-0.000001
C	-2.369576	2.28892	-0.000165	2.354294	-2.299991	-0.000004	2.454577	-2.280915	-0.000045	2.303201	-2.293989	-0.000001
C	2.030843	0.149604	0.000055	-2.008364	-0.117543	-0.000009	-2.065198	-0.185014	-0.000032	-2.019102	-0.080896	-0.000001
C	2.451411	-1.186284	-0.000024	-2.470198	1.215603	0.000023	-2.472405	1.135208	-0.000008	-2.502104	1.223503	-0.000001
C	1.242958	-2.098843	0.000042	-1.260045	2.128076	0.000017	-1.272173	2.047245	-0.000016	-1.299606	2.156305	-0.000001
C	2.930725	1.218531	0.000089	-2.908641	-1.231752	-0.000025	-2.99762	-1.284639	-0.000068	-2.8335	-1.254497	-0.000001
C	4.295747	0.925423	-0.000042	-4.286551	-0.97857	0.00001	-4.388572	-0.907133	0.000035	-4.235801	-1.061699	-0.000001
C	4.713651	-0.408599	-0.000139	-4.730554	0.341183	0.000045	-4.790244	0.427942	0.000051	-4.728703	0.2398	-0.000001
C	3.809355	-1.479285	-0.000114	-3.828453	1.449981	0.000047	-3.849472	1.463894	0.00001	-3.882604	1.392501	-0.000101
O	2.483183	2.493226	0.000328	-2.396878	-2.454924	-0.000081	-2.600314	-2.488142	0.000019	-2.204098	-2.399396	0.000099
H	-2.04631	-3.093156	0.87777	2.083036	3.117868	0.877513	2.013467	3.104672	0.876921	2.104993	3.124811	0.877199
H	-2.04631	-3.093198	-0.877566	2.083047	3.117856	-0.877521	2.013487	3.104689	-0.876837	2.104893	3.124911	-0.877101
H	-4.216646	-2.149448	0.878327	4.229475	2.131554	0.877825	4.19519	2.198744	0.877766	4.235495	2.107214	0.877599
H	-4.216666	-2.149543	-0.878138	4.229498	2.131566	-0.87778	4.195216	2.198775	-0.87764	4.235495	2.107214	-0.877601
H	-5.359706	0.605172	-0.000084	5.350184	-0.621789	0.000005	5.407729	-0.525958	0.000024	5.320499	-0.652184	-0.000001
H	-4.415242	2.89158	-0.000216	4.404081	-2.910053	-0.000003	4.526234	-2.839113	-0.000032	4.350202	-2.929586	-0.000001
H	-1.98562	3.305116	-0.000224	1.967817	-3.315377	-0.000007	2.100059	-3.307728	-0.00007	1.907703	-3.30589	-0.000101
H	1.229995	-2.755337	0.87935	-1.244869	2.784979	0.879145	-1.26522	2.705553	0.878781	-1.296007	2.813805	0.878799
H	1.229947	-2.755366	-0.879243	-1.244884	2.784994	-0.879099	-1.265216	2.705552	-0.878815	-1.295907	2.814005	-0.878601
H	5.020217	1.734287	-0.000016	-4.986416	-1.808073	0.000001	-5.123741	-1.707078	0.000089	-4.904299	-1.9166	0.000099
H	5.78017	-0.617111	-0.000208	-5.798191	0.538081	0.000067	-5.849308	0.668269	0.000106	-5.803403	0.392898	-0.000001
H	4.169988	-2.503657	-0.000173	-4.229971	2.459261	0.000071	-4.170116	2.501185	0.000034	-4.337406	2.378901	-0.000101
H	1.499672	2.462165	0.000615	-1.392075	-2.366438	-0.000158	-0.296283	-2.234278	-0.000062	-1.079499	-2.157594	-0.000201

Table S15. The Cartesian coordinates of optimized geometry for **CPIQ-NHTs** at PBE0/6-31+G(d,p).

	S_0 geometry			N* geometry			T* geometry			TS* geometry		
	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
N	1.404047	-0.310087	-0.886407	1.372397	-0.372737	-0.74665	1.570457	-0.496285	-0.62301	1.291001	-0.327398	-0.6342
C	1.338254	0.839933	-0.233591	1.441758	0.840088	-0.117745	1.548173	0.76939	-0.091934	1.478301	0.886402	-0.0398
C	2.34706	1.433621	0.595618	2.542522	1.372355	0.629958	2.648443	1.342881	0.561091	2.620401	1.369202	0.6419
C	3.518762	0.739955	0.741571	3.677236	0.601236	0.728698	3.820427	0.605565	0.682352	3.707301	0.515402	0.7146
C	3.606106	-0.492217	0.056781	3.628657	-0.656457	0.066625	3.810314	-0.695969	0.123344	3.541902	-0.752598	0.0863
C	2.569253	-1.010803	-0.744474	2.489531	-1.129932	-0.658564	2.705124	-1.274744	-0.53493	2.354302	-1.178798	-0.5826
C	4.805443	0.975386	1.488476	5.023463	0.75199	1.388327	5.17174	0.858468	1.293099	5.086001	0.584902	1.3156
C	5.684499	-0.273344	1.177899	5.785305	-0.566194	1.042992	5.977116	-0.454587	1.038681	5.741502	-0.788398	0.9698
C	4.839175	-1.133563	0.265725	4.815362	-1.379996	0.213404	5.02862	-1.366558	0.292436	4.684902	-1.553598	0.2031
C	5.056812	-2.348644	-0.348671	4.916862	-2.636236	-0.374809	5.162125	-2.655013	-0.208249	4.681102	-2.827498	-0.3544
C	4.029342	-2.892998	-1.161952	3.807814	-3.131107	-1.099677	4.06645	-3.239338	-0.867226	3.519102	-3.266198	-1.0193
C	2.815454	-2.257677	-1.365929	2.623371	-2.415759	-1.246801	2.845901	-2.571699	-1.037216	2.374502	-2.473598	-1.1394
C	0.188383	1.736455	-0.246528	0.398464	1.796158	-0.108103	0.444853	1.704714	-0.098672	0.477201	1.884901	-0.0287
C	0.468358	2.858827	0.545401	0.771872	2.93704	0.636577	0.85034	2.864652	0.551311	0.913801	3.022202	0.6561
C	1.854188	2.747238	1.135861	2.17679	2.735224	1.155721	2.274914	2.725512	1.017096	2.331201	2.770802	1.1346
C	-1.036703	1.593737	-0.912534	-0.905425	1.711596	-0.718701	-0.878288	1.570998	-0.633888	-0.826899	1.774501	-0.6119
C	-1.986754	2.608648	-0.768273	-1.790494	2.800085	-0.570669	-1.746826	2.689449	-0.4789	-1.696399	2.884801	-0.4843
C	-1.704153	3.71622	0.035779	-1.397256	3.906517	0.164389	-1.325078	3.846428	0.174639	-1.255499	4.011801	0.1979
C	-0.482302	3.860006	0.698386	-0.110765	3.983653	0.779496	-0.030125	3.949377	0.695924	0.045401	4.096601	0.775
N	-1.198931	0.454239	-1.725746	-1.136014	0.55449	-1.4078	-1.128464	0.379334	-1.225245	-1.006399	0.571501	-1.2246
H	4.619567	1.087655	2.562201	4.925443	0.887532	2.472231	5.093865	1.081941	2.364594	5.043501	0.747802	2.3998
H	5.283695	1.903625	1.157021	5.557064	1.634325	1.014894	5.663609	1.726335	0.835856	5.663501	1.421502	0.9033
H	5.951676	-0.811742	2.093457	6.083086	-1.105172	1.949785	6.305768	-0.909872	1.97977	6.043902	-1.326498	1.8756
H	6.625699	0.009796	0.694876	6.707872	-0.360123	0.488052	6.883687	-0.260516	0.454517	6.650001	-0.656898	0.3705
H	5.989107	-2.892943	-0.225396	5.818964	-3.236124	-0.288601	6.088387	-3.21293	-0.100699	5.546702	-3.481198	-0.2863
H	4.205135	-3.850487	-1.645327	3.884122	-4.112803	-1.560959	4.163872	-4.246823	-1.261842	3.510102	-4.261398	-1.457
H	2.051509	-2.704006	-1.996193	1.792096	-2.830175	-1.810603	2.022171	-3.057301	-1.552591	1.496602	-2.847398	-1.6589
H	1.828518	2.758231	2.232922	2.217034	2.776498	2.251886	2.358941	2.837228	2.105995	2.411501	2.846102	2.2267
H	2.494289	3.584396	0.82955	2.859128	3.513311	0.7898	2.922091	3.494559	0.575446	3.034001	3.505102	0.7203
H	-2.936897	2.538906	-1.285441	-2.763866	2.771382	-1.045404	-2.744401	2.639621	-0.8978	-2.683999	2.860001	-0.9287
H	-2.459938	4.490202	0.135635	-2.08238	4.741598	0.268728	-2.013527	4.679497	0.273925	-1.922899	4.862601	0.2898
H	-0.286888	4.734311	1.312417	0.156452	4.869696	1.348321	0.289278	4.855588	1.202015	0.336201	5.003501	1.2975
C	-3.070509	-0.927162	-0.217634	-3.240871	-0.822437	-0.318456	-3.411374	-0.720312	-0.3533	-3.199598	-0.763199	-0.3553
H	-0.384496	-0.178328	-1.671669	-0.326392	-0.116168	-1.381737	0.722191	-0.822502	-1.074824	-0.038299	-0.125299	-1.1118
C	-2.422129	-2.030982	0.339119	-2.829199	-2.099862	0.080206	-3.102922	-2.01108	0.08565	-2.805098	-2.035399	0.0731
C	-2.748808	-2.422398	1.630767	-3.264221	-2.591877	1.30126	-3.698195	-2.492818	1.243501	-3.360598	-2.554399	1.2329

C	-3.713178	-1.729891	2.377954	-4.094518	-1.830393	2.140271	-4.597317	-1.705949	1.97924	-4.299198	-1.824499	1.9803
C	-4.343332	-0.626022	1.793812	-4.481245	-0.552342	1.717427	-4.885505	-0.415989	1.518221	-4.672299	-0.553599	1.5267
C	-4.029735	-0.216865	0.50022	-4.061132	-0.037217	0.496239	-4.298749	0.084938	0.359381	-4.128299	-0.012199	0.3662
C	-4.075129	-2.183915	3.76213	-4.57055	-2.389127	3.448168	-5.247992	-2.249765	3.21763	-4.881698	-2.402499	3.2361
S	-2.624743	-0.399	-1.851366	-2.623342	-0.153522	-1.819379	-2.597388	-0.08532	-1.795919	-2.445699	-0.072099	-1.7908
O	-2.26443	-1.572698	-2.64651	-2.234765	-1.235745	-2.716723	-2.32036	-1.214519	-2.693099	-2.021898	-1.153999	-2.6761
O	-3.660312	0.5183	-2.324169	-3.50046	0.921407	-2.269864	-3.407149	1.022943	-2.331673	-3.286399	1.010701	-2.2993
H	-1.679542	-2.579205	-0.232523	-2.188071	-2.693935	-0.563298	-2.411832	-2.627128	-0.480936	-2.084198	-2.607499	-0.5023
H	-2.248756	-3.283005	2.067323	-2.956297	-3.586601	1.612193	-3.464065	-3.498323	1.583694	-3.065598	-3.546199	1.5652
H	-5.093488	-0.076682	2.356277	-5.126876	0.0491	2.35155	-5.583865	0.206593	2.071173	-5.405499	0.021001	2.0859
H	-4.530861	0.632999	0.049277	-4.380931	0.947041	0.170806	-4.542022	1.080908	0.003752	-4.435699	0.967101	0.0144
H	-3.189586	-2.504322	4.318512	-3.756421	-2.883263	3.987033	-4.51924	-2.758333	3.856179	-4.102898	-2.550099	3.9925
H	-4.572285	-1.39058	4.325642	-4.987955	-1.608454	4.088452	-5.725764	-1.457956	3.799624	-5.647698	-1.749199	3.6601
H	-4.758581	-3.039966	3.718325	-5.351456	-3.140941	3.283382	-6.017826	-2.985488	2.957129	-5.331898	-3.381999	3.044

Reference

1. Ernzerhof, M.; Scuseria, G. E., Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional. *J. Chem. Phys.* **1999,** *110*, 5029-5036.
2. Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008,** *120*, 215-241.
3. Becke, A. D., A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993,** *98*, 1372-1377.
4. Plasser, F.; Bappler, S. A.; Wormit, M.; Dreuw, A., New tools for the systematic analysis and visualization of electronic excitations. II. Applications. *J. Chem. Phys.* **2014,** *141*.
5. Guido, C. A.; Cortona, P.; Mennucci, B.; Adamo, C., On the Metric of Charge Transfer Molecular Excitations: A Simple Chemical Descriptor. *J Chem Theory Comput* **2013,** *9*, 3118-3126.