Electronic Supporting Information

Fluorescent pH sensor constructed from a heteroatom-containing luminogen with tunable AIE and ICT characteristics

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Experimental section

Materials

Tetrahydrofuran (THF) was distilled from sodium benzophenone immediately prior to use. Chloroform was distilled over calcium hydride. Bromobenzene was purchased from Acros. 4-Iodobenzyl bromide was provided by Int. Lab. Other chemicals were purchased from Sigma-Aldrich and used as received without further purification. Diethyl 4-iodobenzylphosphonate was prepared according to the literature procedures.[1] Buffer solutions with pH 1 to 12 were purchased from Merck, Riedel-de Haen or Sigma-Aldrich. Mixtures of CP_3E in THF/water with various pH values were prepared by adding THF stock solutions into buffer solutions with specific pH values.

Instruments

^1H NMR and ^{13}C NMR spectra were measured on a Bruker ARX 300 NMR spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS, $\delta = 0$ ppm) as internal reference. UV spectra were recorded on a Milton Ray Spectronic 3000 array spectrophotometer. Photoluminescence spectra were taken on a Perkin-Elmer LS 55 spectrofluorometer. Theoretical calculation were performed on Gaussian 03 with B3LYP/6-31+G** as basis set. High-resolution mass spectra (HRMS) were obtained from a GCT Premier CAB 048 mass spectrometer operated in MALDI-TOF or Cl-TOF mode. Elemental analysis was carried out on an Elementary Vario Micro

Cube. Particle sizes of the nano-aggregates were determined on a Zeta-plus potential Analyzer. Morphologies of the nano-aggregates were studied on a JEOL 100CX transmission electron microscope. Single crystals of CP$_3$E were grown from its hexane/ethyl acetate mixture (3:1 v/v) at room temperature. X-ray diffraction intensity data were collected at 100 K on a Bruker-Nonices Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Processing of the intensity data was conducted using the SAINT and SADABS routines, and the structure and refinement were carried out using the SHELTL suite of X-ray programs (version 6.10).

Synthesis

*4-Pyridophenone (**2**).* Compound **2** was synthesized according to a modified procedure reported previously.[2] To a dry THF solution of bromobenzene (1.57 g, 10 mmol) at −78 °C was added *n*-butyllithium (10 mmol) dropwise under stirring. After stirring at −78 °C for 2 h, 4-cyanopyridine (1.04 g, 10 mmol) in dry THF was slowly added. The mixture was gradually warmed to room temperature and allowed to stir for another 12 h. After hydrolysis by addition of water, the mixture was extracted with chloroform. The organic layer was separated and dried over magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica gel chromatography using hexane/ethyl acetate (3:1 v/v) as eluent to give 1.65 g (90%) of **2** as a white powder. ^{1}H NMR (300 MHz, CDCl$_3$), δ (TMS, ppm): 8.83 (d, 2H), 7.82 (d, 2H), 7.61–7.69 (m, 3H), 7.50–7.55 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$), δ (CDCl$_3$, ppm): 195.1, 150.3, 144.3, 135.8, 133.5, 130.1, 128.6, 122.8. HRMS (CI-TOF): *m*/*z* 184.0765 [(M+H)$^+$, calcd 184.0762].

*1-(4-Pyridinyl)-1-phenyl-2-(4-iodophenyl)ethene (**4**).* Into a round-bottom flask equipped with condenser were added **2** (1.65 g, 9 mmol) and **3** (3.54 g, 10 mmol) in dry THF. Catalytic amount of potassium *t*-butoxide was then added into the solution. The reaction mixture was refluxed at 70 °C for 20 h and cooled down to room temperature. During reflux, additional catalyst was added until the reaction went to completion. The reaction was terminated by addition of water and the mixture was extracted with chloroform. The organic layer was separated and dried over magnesium sulfate. After filtration and solvent evaporation, the crude product was purified by silica gel column chromatography using hexane/ethyl acetate (4:1 v/v) as eluent to give 2.82 g (74%) of **4** as yellow-brown powder. ^{1}H NMR (300 MHz,

$CDCl_3$), *δ* (TMS, ppm): 8.58 (d, 2H), 7.49 (d, 2H), 7.32–7.34 (m, 3H), 7.23–7.27 (m, 2H), 7.12 (dd, 2H), 6.94 (s, 1H), 6.76 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), *δ* ($CDCl_3$, ppm): 149.9, 148.7, 141.5, 140.8, 137.4, 137.3, 135.8, 131.4, 131.1, 130.7, 129.9, 129.2, 128.8, 128.5, 128.4, 128.3, 127.5, 125.4, 93.1. HRMS (CI-TOF): *m*/*z* 384.0253 $[(M+H)^+$, calcd 384.0249].

1-(4-Pyridinyl)-1-phenyl-2-(9-carbazoyl)ethene (CP_3E). Into a round-bottom flask were added **3** (1.91 g, 5 mmol), carbazole (1.25 g, 7.5 mmol), K_2CO_3 (2.76 g, 20 mmol), copper powder (0.64 g, 10 mmol) and catalytic amount of 18-crown-6 (0.13 g, 0.5 mmol) in 100 mL of *o*-dichlorobenzene. The mixture was then heated to reflux for 22 h. After cooling to room temperature, the mixture was filtrated and extracted with dichloromethane. The organic layers were collected and after solvent evaporation, the crude product was purified by silica gel column chromatography using hexane/dichloromethane (6:1 v/v) as eluent to give 0.95 g (45% yield) of CP_3E as a light yellow powder. ^1H NMR (300 MHz, $CDCl_3$), *δ* (TMS, ppm): 8.645 (d, 2H), 8.13 (d, 2H), 7.36–7.40 (m, 9H), 7.24–7.34 (m, 8H), 7.14 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), *δ* ($CDCl_3$, ppm): 150.3, 148.4, 141.6, 140.6, 140.4, 136.6, 135.3, 130.8, 128.7, 128.5, 128.2, 127.5, 126.4, 125.9, 123.4, 120.3, 120.0, 109.7. HRMS (MALDI-TOF): *m*/*z* 423.1471 $[(M+H)^+$, calcd 423.1861]. Elemental analysis for $C_{31}H_{22}N_2$: C, 88.12; H, 5.25; N, 6.63. Found: C, 88.12; H, 5.25; N, 6.60.

Preparation of nano-aggregates

9 mL THF/water mixtures with appropriate water fractions were prepared. Under vigorous stirring, 1 mL of THF solution of CP_3E (0.1 mM) was added dropwise into the above mixtures to furnish 10 μM solutions with defined fractions of water (f_w = 0–90 vol %). For mixtures with 95 and 99 vol % water fractions, 0.1 mL of THF solution of CP_3E with a concentration of 1 mM was used. Water acidified with hydrochloric acid (pH ~1) was used to prepare aqueous mixtures of CP_3EH^+.

Table S1. Crystal data and structure refinement for CP$_3$E.

Empirical formula	C31 H22 N2	
Formula weight	422.51	
Temperature	173.00(14) K	
Wavelength	1.5418 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 9.72420(10) Å	= 90°.
	b = 17.6641(2) Å	= 90°.
	c = 25.6425(2) Å	= 90°.
Volume	4404.59(8) Å^3	
Z	8	
Density (calculated)	1.274 Mg/m^3	
Absorption coefficient	0.572 mm^{-1}	
F(000)	1776	
Crystal size	0.38 x 0.18 x 0.04 mm^3	
Theta range for data collection	5.01 to 67.50°.	
Index ranges	-11<=h<=7, -21<=k<=20, -29<=l<=30	
Reflections collected	25386	
Independent reflections	3908 [R(int) = 0.0286]	
Completeness to theta = 66.50°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.85877	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3908 / 0 / 298	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0320, wR2 = 0.0835	
R indices (all data)	R1 = 0.0355, wR2 = 0.0865	
Largest diff. peak and hole	0.134 and -0.178 e.Å^{-3}	

Table S2. Bond lengths [Å] and angles [°] for CP$_3$E.

N(1)-C(2)	1.4014(14)	C(3)-C(4)-C(5)	122.12(12)
N(1)-C(13)	1.4008(14)	C(6)-C(5)-C(4)	120.60(11)
N(1)-C(14)	1.4209(14)	C(5)-C(6)-C(7)	118.75(12)
C(2)-C(3)	1.3959(16)	C(2)-C(7)-C(8)	107.10(10)
C(2)-C(7)	1.4085(16)	C(6)-C(7)-C(2)	119.90(11)
C(3)-C(4)	1.3849(17)	C(6)-C(7)-C(8)	132.91(11)
C(4)-C(5)	1.3944(19)	C(9)-C(8)-C(7)	133.24(11)
C(5)-C(6)	1.3800(19)	C(9)-C(8)-C(13)	119.74(10)
C(6)-C(7)	1.3998(16)	C(13)-C(8)-C(7)	106.97(10)
C(7)-C(8)	1.4422(16)	C(10)-C(9)-C(8)	118.92(11)
C(8)-C(9)	1.3964(16)	C(9)-C(10)-C(11)	120.75(11)

C(8)-C(13)	1.4052(15)	C(12)-C(11)-C(10)	121.56(11)
C(9)-C(10)	1.3757(18)	C(11)-C(12)-C(13)	117.57(11)
C(10)-C(11)	1.3972(17)	N(1)-C(13)-C(8)	109.10(9)
C(11)-C(12)	1.3827(17)	C(12)-C(13)-N(1)	129.39(10)
C(12)-C(13)	1.3925(16)	C(12)-C(13)-C(8)	121.41(10)
C(14)-C(15)	1.3914(16)	C(15)-C(14)-N(1)	120.85(10)
C(14)-C(19)	1.3936(15)	C(15)-C(14)-C(19)	119.48(10)
C(15)-C(16)	1.3846(16)	C(19)-C(14)-N(1)	119.66(10)
C(16)-C(17)	1.3983(15)	C(16)-C(15)-C(14)	119.76(10)
C(17)-C(18)	1.3990(16)	C(15)-C(16)-C(17)	121.50(10)
C(17)-C(20)	1.4709(15)	C(16)-C(17)-C(18)	117.83(10)
C(18)-C(19)	1.3804(16)	C(16)-C(17)-C(20)	120.52(10)
C(20)-C(21)	1.3435(16)	C(18)-C(17)-C(20)	121.53(10)
C(21)-C(22)	1.4951(14)	C(19)-C(18)-C(17)	121.07(10)
C(21)-C(28)	1.4905(15)	C(18)-C(19)-C(14)	120.33(10)
C(22)-C(23)	1.3884(15)	C(21)-C(20)-C(17)	127.86(10)
C(22)-C(27)	1.3914(15)	C(20)-C(21)-C(22)	122.03(9)
C(23)-C(24)	1.3851(16)	C(20)-C(21)-C(28)	121.06(10)
C(24)-N(25)	1.3330(16)	C(28)-C(21)-C(22)	116.82(9)
N(25)-C(26)	1.3391(15)	C(23)-C(22)-C(21)	122.30(9)
C(26)-C(27)	1.3821(16)	C(23)-C(22)-C(27)	116.67(10)
C(28)-C(29)	1.4009(16)	C(27)-C(22)-C(21)	120.98(9)
C(28)-C(33)	1.3933(16)	C(24)-C(23)-C(22)	119.47(10)
C(29)-C(30)	1.3846(17)	N(25)-C(24)-C(23)	124.30(11)
C(30)-C(31)	1.380(2)	C(24)-N(25)-C(26)	115.87(10)
C(31)-C(32)	1.3788(19)	N(25)-C(26)-C(27)	124.03(10)
C(32)-C(33)	1.3862(17)	C(26)-C(27)-C(22)	119.65(10)
		C(29)-C(28)-C(21)	121.24(10)
C(2)-N(1)-C(14)	126.68(9)	C(33)-C(28)-C(21)	121.06(10)
C(13)-N(1)-C(2)	107.97(9)	C(33)-C(28)-C(29)	117.70(10)
C(13)-N(1)-C(14)	125.23(9)	C(30)-C(29)-C(28)	120.73(11)
N(1)-C(2)-C(7)	108.84(9)	C(31)-C(30)-C(29)	120.65(12)
C(3)-C(2)-N(1)	129.75(10)	C(32)-C(31)-C(30)	119.32(11)
C(3)-C(2)-C(7)	121.38(10)	C(31)-C(32)-C(33)	120.42(12)
C(4)-C(3)-C(2)	117.24(11)	C(32)-C(33)-C(28)	121.12(11)

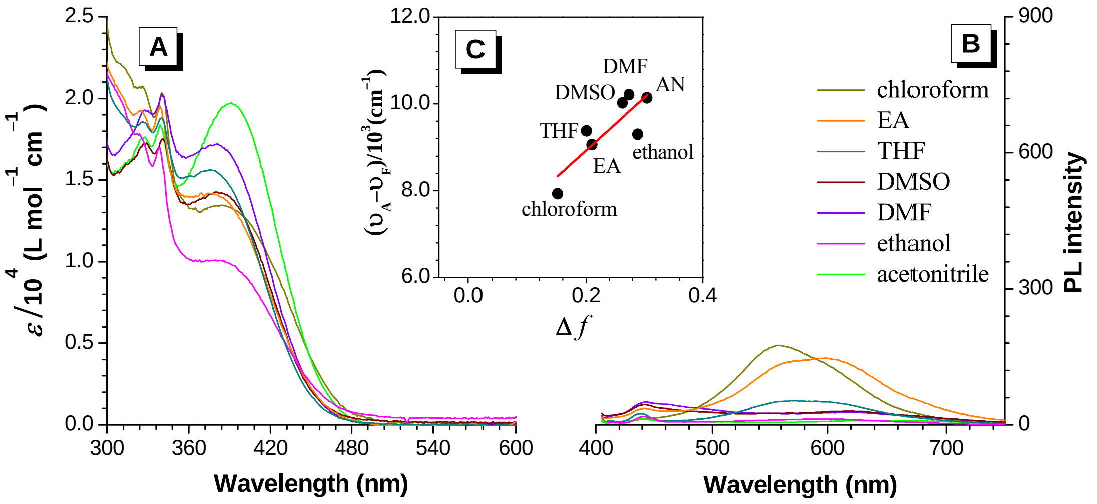

Fig. S1 (A) UV and (B) PL spectra and (C) Lippert–Mataga plot of CP_3EH^+ in solvents acidified with 100 μL of TFA (pH ~1) with different polarities. Concentration: 10 μM; excitation wavelength: absorption maximum. Abbreviation: EA = ethyl acetate, THF = tetrahydrofuran, DMSO = dimethylsulfoxide, DMF = dimethylformamide, AN = acetonitrile. υ_A = absorption wavenumber, υ_F = emission wavenumber, and Δf = orientation polarizability = $(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$, where ε = dielectric constant and n = refractive index.

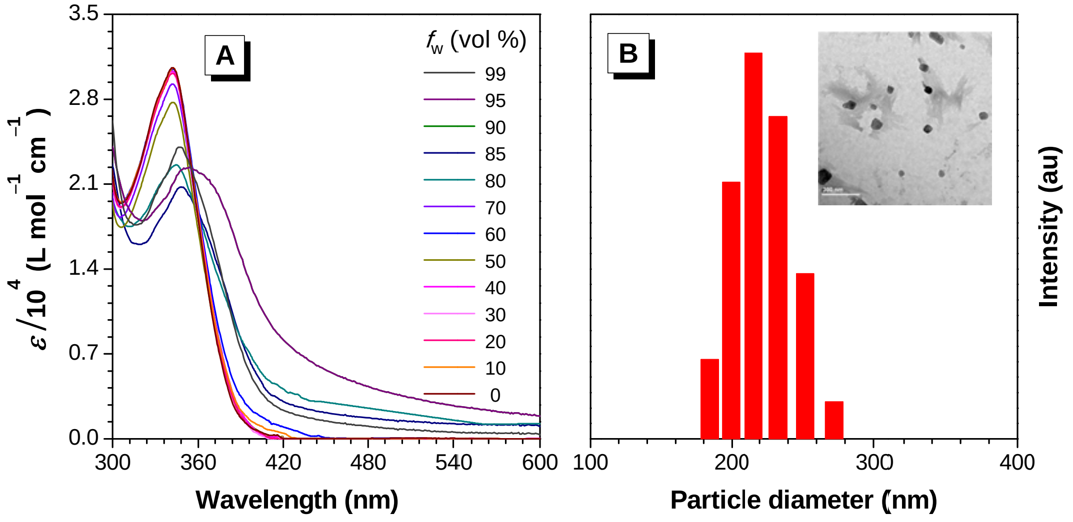

Fig. S2 (A) UV spectra of CP_3E in THF/water mixtures with different water fractions (f_w). Concentration: 10 μM. (B) Particles size distribution of nano-aggregates of CP_3E formed in THF/water mixtures with 99% water fraction. Inset: TEM image of the nano-aggregates.

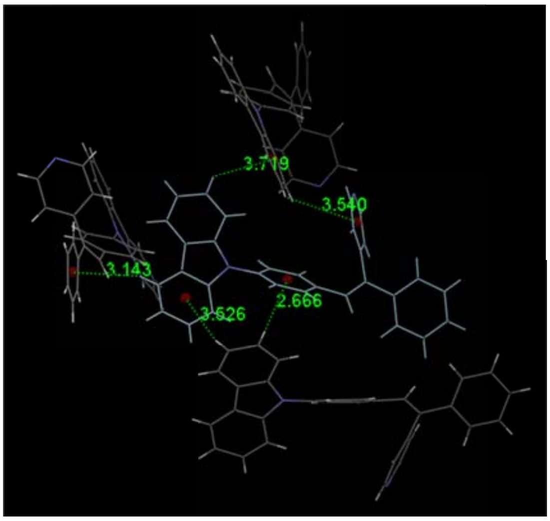

Fig. S3 C–H···π hydrogen bonds formed between adjacent molecules of CP_3E in the crystal state.

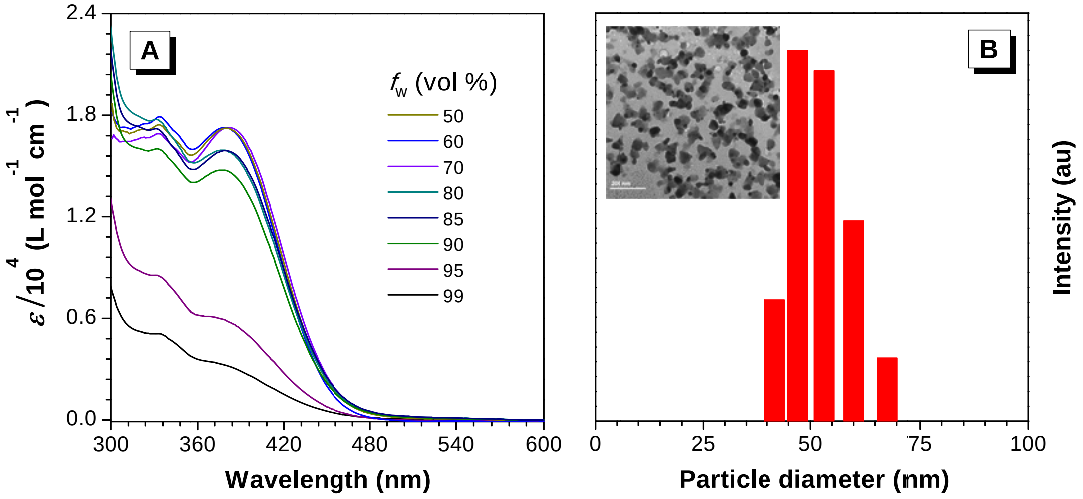

Fig. S4 (A) UV spectra of CP_3EH^+ in THF/water mixtures with different water fractions (f_w) acidified with hydrochloric acid (pH ~1). Concentration: 10 μM. (B) Particles size distribution of nano-aggregates of CP_3EH^+ formed in THF/water mixture with 99% water fraction. Inset: TEM image of the nanoparticles.

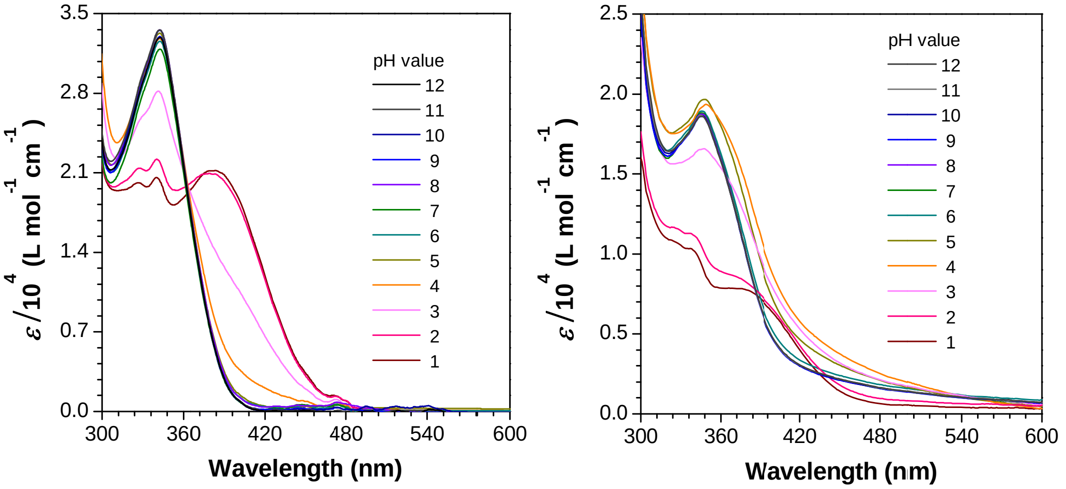

Fig. S5 Effect of pH on the UV spectra of CP_3E in THF/water mixtures with volume ratios of (A) 3:7 and (B) 1:9. Concentration: 10 μM.

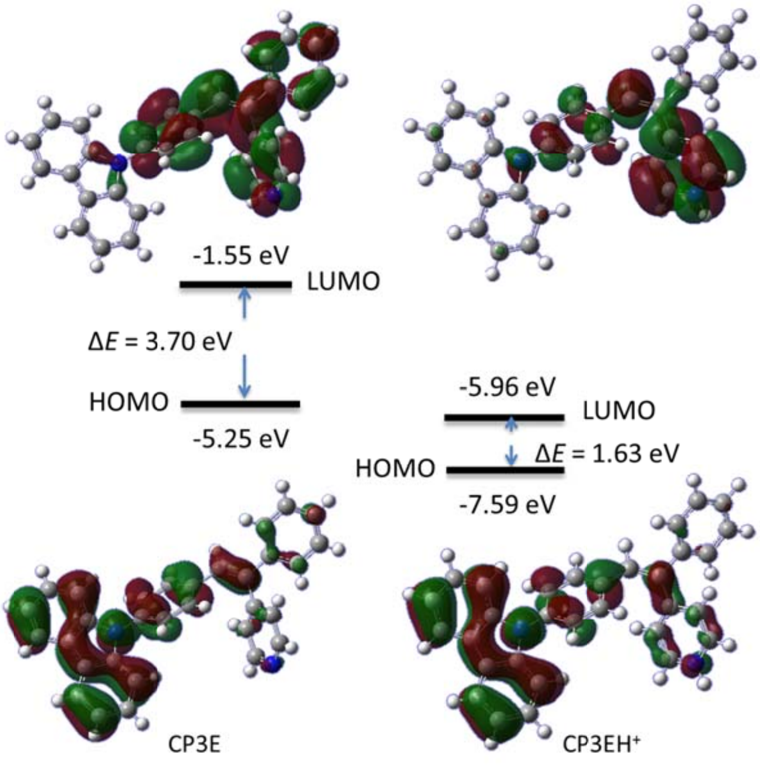

Fig. S6 Molecular orbital amplitude plots of (upper) LUMO and (lower) HOMO of CP_3E and CP_3EH^+.

Table S3 Structural parameters for single crystals of CP_3E and CP_3EH^+ calculated using Gaussian 03, B3LYP/6-31+G** basis set.

Structural parameter	CP_3E	CP_3EH^+
Bond length (Å)		
C17-C20	1.4709	1.4495
C20-C21	1.3435	1.3764
C21-C22	1.4951	1.4604
Dihedral angle (°)		
C20-C21-C22-C27	51.7	34.2
C21-C20-C17-C18	40.8	26.6

References

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2. S. Ghosh, S. R. Batten, D. R. Turner and P. S. Mukherjee, *Organometallics*, 2007, **26**, 3252.