Supplementary materials

Phosphorescent Pt(II) complexes of C^N^N type tridentate ligands augmented for liquid crystallinity

Yulia A. Yakovleva[a], Vladislav M. Abramov[a], Oleg S. Eltsov[a]

[a]*Ural Federal University, Mira 19, 620002, Ekaterinburg, Russia*

Content

Synthesis and characterisation

All reagents used were commercially available and were used without further purification (Sigma Aldrich, Merck, TCI). IR spectra were recorded on a Bruker IR spectrometer Alpha in KBr. Melting points were determined in open capillaries on a Stuart SMP3 apparatus. Column chromatography was performed with Silica gel 60 (40–63 μm). The reaction progress and purity of the obtained compounds were controlled by TLC method on Sorbfil UV-254 plates, using visualisation under UV light. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHNS / O analyzer. ^{1}H, ^{13}C ^{19}F and ^{195}Pt NMR spectra were acquired from solutions in DMSO-d_6 and $CDCl_3$ on a Bruker AVANCE NEO (600 MHz) NMR spectrometer. Chemical shifts were referenced to the residual peaks of solvents as an internal standard. EI-MS spectra was recorded on Shimadzu «GCMS-QP2010 Ultra» instrument.

6-phenyl-4-(3,4,5-trimethoxyphenyl)-2,2'-bipyridine (3)

6.35g 3,4,5-trymetoxychalconoid **1** (21,3 mmol), 6.95g 1-[2-Oxo-2-(2-pyridyl)ethyl]pyridinium Iodide **2** (21,3 mmol, 1 eq) and 7.70g ammonium acetate (100 mmol, 4.7 eq) were heated under reflux in acetic acid (65 ml) for 15h. After cooling to room temperature, the reaction mixture was diluted with water (200 ml), precipitate was washed with acetone (20 ml). Reaction mixture was heated with coal in methanol and filtered while hot. After precipitate was formed, it was dissolved in $CHCl_3$, filtered and solvent was evaporated under reduced pressure. Yield (5.09g 60%). Grey crystals. MP=94 ℃ **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.2 Hz, 1H), 8.69 (d, *J* = 7.9 Hz, 1H), 8.58 (d, *J* = 1.4 Hz, 1H), 8.20 (d, *J* = 7.3 Hz, 2H), 7.92 (d, *J* = 1.4 Hz, 1H), 7.88 (td, *J* = 7.8, 1.7 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 6.99 (s, 2H), 3.99 (s, 6H), 3.93 (s, 3H). IR (cm^{-1}) KBr: *ν* 1089, 1585, 2963 Found, %: C 75,54; H 5,38; N 7,16. $C_{25}H_{22}N_2O_3$. Calculated, %: C 75,36; H 5,57 N; 7,03. EI-MS(+): m/z 356 $[M]^+$

6-phenyl-4-(3,4,5-trihydroxyphenyl)-2,2'-bipyridine (4)

4.06g 6-phenyl-4-(3,4,5-trimethoxyphenyl)-2,2'-bipyridine **3** (10,2 mmol, 1 eq) and 29.46g Pyridinium chloride (255 mmol, 25 eq) were heated at 200 ℃ under nitrogen atmosphere. Reaction mixture was diluted with water (150ml) and NH_4OH (1 ml), grey residue was filtered and washed with small amount of hot ethanol. Yield (3.23g 89%). Light-grey crystals. MP=80 ℃ **^{1}H NMR** (600 MHz, DMSO-*d6*) δ 8.85 (d, *J* = 5.3 Hz, 1H), 8.81 (d, *J* = 8.5 Hz, 1H), 8.55 (d, *J* = 1.6 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 2H), 8.17 (s, 1H), 7.76 (s, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 6.99 (s, 2H). IR (cm^{-1}) KBr: *ν* 3067, 1537, 1147. Found, %: C 74,02; H 4,41; N 7,96. $C_{22}H_{16}N_2O_3$. Calculated, %: C 74,15; H 4,53; N 7,86. EI-MS(+): m/z 356 $[M]^+$

6-phenyl-4-(3,4,5-tridodecyloxyphenyl)-2,2'-bipyridine (5)

1.78g 6-phenyl-4-(3,4,5-trihydroxyphenyl)-2,2'-bipyridine **4** (5 mmol, 1 eq), 6.21g potassium carbonate (2.3 g, 45 mmol, 9 eq) and 3.96ml 1-Bromododecan (16.5 mmol, 3.3 eq) were heated under nitrogen atmosphere in acetonitrile (100 ml) for 14h. Solvent was evaporated under reduced pressure. The product was obtained after column chromatography (silica gel, Petroleum ether/ethyl acetate = 3/1). Yield (2.76g 64%). Light-grey crystals. MP=46 ℃ **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.69 (d, *J* = 8.0 Hz, 1H), 8.56 (s, 1H), 8.23 – 8.16 (m, 2H), 7.91 (d, *J* = 1.3 Hz, 1H), 7.87 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.35 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.96 (s, 2H).), 4.17 (t, *J* = 6.4 Hz, 4H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.91 (p, *J* = 6.7 Hz, 4H), 1.83 (p, *J* = 6.8 Hz, 2H), 1.56 (q, *J* = 8.4, 7.4 Hz, 8H), 1.50 – 1.09 (m, 47H), 0.91 (q, *J* = 6.7 Hz, 8H). IR (cm^{-1}) KBr: *ν* 2936, 2869, 1584, 1116, 1030. Found, %: C 80,62; H 10,44; N 3,10. $C_{58}H_{88}N_2O_3$. Calculated, %: C 80,88; H 10,30; N 3,25. EI-MS(+): m/z 860 $[M]^+$

Platinum (II) 6-phenyl-4-(3,4,5-tridodecyloxyphenyl)-2,2'-bipyridine chloride (6)

1.22g 6-phenyl-4-(3,4,5-tridodecyloxyphenyl)-2,2'-bipyridine **5** (1,5 mmol, 1eq) was dissolved in acetic acid (25ml) and 0,62g $K_2[PtCl_4]$ (1,5 mmol, 1 eq) in water (0,5 ml) was added. Reaction mixture was heated under reflux and nitrogen atmosphere for 19 h. After cooling to room temperature the precipitate was filtered off and washed with water (10 ml), methanol (10 ml). Yield (0.92g 56%). Orange crystals. MP=116 ℃ **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.2 Hz, 1H), 7.89 (d, *J* = 7.9 Hz, 1H), 7.85 (t, *J* = 7.7 Hz, 1H), 7.56 (s, 1H), 7.55 (s, 1H), 7.35 – 7.31 (m, 1H), 7.30 (s, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.04 (p, *J* = 7.1 Hz, 2H), 6.97 (s, 2H), 4.17 (t, *J* = 6.4 Hz, 4H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.91 (p, *J* = 6.7 Hz, 4H), 1.83 (p, *J* = 6.8 Hz, 2H), 1.56 (q, *J* = 8.4, 7.4 Hz, 8H), 1.50 – 1.09 (m, 47H), 0.91 (q, *J* = 6.7 Hz, 8H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.85, 157.21, 157.20, 154.09, 153.83, 151.43, 148.45, 146.49, 146.47, 142.43, 140.03, 138.65, 135.07, 135.05, 132.95, 130.70, 126.80, 123.95, 123.71, 123.69, 122.69, 116.96, 116.37, 106.13, 77.23, 77.02, 76.81, 73.66, 69.74, 69.72, 31.98, 31.96, 31.95, 30.43, 29.81, 29.79, 29.76, 29.74, 29.73, 29.71, 29.67, 29.54, 29.46, 29.43, 29.40, 26.22, 26.20, 22.71, 14.15. **^{195}Pt NMR** (129 MHz, $CDCl_3$) δ -3508.94. IR (cm^{-1}) KBr: *ν* 3435, 2921, 2851, 1612, 1117. Found, %: C 63,59; H 8,18; N 2,50. $C_{58}H_{87}ClN_2O_3Pt$. Calculated, %: C 63,68; H 8,04; N 2,57.

Platinum (II) 6-phenyl-4-(3,4,5-tridodecyloxyphenyl)-2,2'-bipyridine phenylacetylene (7)

0.11g Platinum (II) 6-phenyl-4-(3,4,5-tridodecyloxyphenyl)-2,2'-bipyridine chloride **6** (0,1mmol, 1eq), 0,083 ml Triethylamine (0,6 mmol, 6eq) and 0,01g Copper(I) iodide (0,05 mmol, 0.5 eq)

were dissolved in DCM. Corresponding Phenylacetylene (0,63mmol, 6.3eq) was added, Reaction mixture was heated under reflux and nitrogen atmosphere for 12 h and then solvent was evaporated under reduced pressure. The product was obtained after column chromatography (silica gel, DCM). Yield (0.042g 36%). Orange crystals. MP=114 °C **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.22 (d, *J* = 5.2 Hz, 0H), 8.10 – 8.00 (m, 1H), 7.62 – 7.56 (m, 1H), 7.54 (t, *J* = 6.5 Hz, 0H), 7.44 (d, *J* = 7.6 Hz, 0H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.28 (s, 2H), 7.23 – 7.18 (m, 0H), 7.18 – 7.12 (m, 0H), 7.08 (t, *J* = 7.4 Hz, 0H), 6.85 (s, 1H), 4.08 (dt, *J* = 15.1, 6.5 Hz, 2H), 1.91 – 1.78 (m, 2H), 1.57 (s, 2H), 1.56 – 1.51 (m, 2H), 1.42 – 1.37 (m, 1H), 1.34 (d, *J* = 22.0 Hz, 7H), 1.29 (s, 11H), 0.91 (td, *J* = 6.9, 4.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.47, 158.12, 154.44, 153.87, 153.87, 152.19, 151.85, 146.73, 142.04, 140.22, 140.20, 138.56, 133.08, 131.76, 131.47, 127.92, 127.88, 127.52, 123.72, 116.46, 116.03, 106.04, 77.23, 77.02, 76.81, 69.67, 31.97, 31.95, 30.41, 29.80, 29.78, 29.74, 29.74, 29.69, 29.65, 29.50, 29.43, 29.39, 26.18, 22.71, 14.14. **^{195}Pt NMR** (129 MHz, $CDCl_3$) δ -3749.68. IR (cm^{-1}) KBr: *ν* 2923, 2852, 2147, 1117. Found, %: C 68,42; H 7,96; N 2,53. $C_{66}H_{92}N_2O_3Pt$. Calculated, %: C 68,54; H 8,02; N 2,42.

Platinum (II) 6-phenyl-4-(3,4,5-tridodecyloxyphenyl)-2,2'-bipyridine (3,5-Bis(trifluoromethyl)-phenylacetylene (8)

Same procedure as (7). Yield (0.061g 47%). Dark-red crystals. MP=115 **°C ^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.28 – 9.25 (m, 0H), 8.14 (td, *J* = 7.8, 1.6 Hz, 0H), 8.04 (d, *J* = 8.0 Hz, 0H), 7.97 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.72 (dd, *J* = 11.0, 1.4 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.51 (dd, *J* = 7.5, 1.4 Hz, 0H), 6.86 (s, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 1H), 1.89 (p, *J* = 6.6 Hz, 2H), 1.82 (dt, *J* = 14.3, 6.7 Hz, 1H), 1.56 (s, 2H), 1.54 (s, 2H), 1.40 (q, *J* = 7.2, 6.2 Hz, 2H), 1.36 – 1.24 (m, 16H), 0.91 (td, *J* = 7.0, 4.5 Hz, 4H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.27, 158.05, 154.41, 153.89, 152.34, 151.70, 146.74, 141.60, 140.37, 138.75, 138.34, 132.77, 131.53, 131.50, 131.37, 131.28, 131.06, 130.83, 127.62, 126.26, 124.47, 124.45, 124.42, 123.90, 123.88, 122.70, 122.65, 122.64, 120.84, 117.98, 116.38, 116.01, 112.56, 112.53, 106.03, 105.98, 103.73, 77.24, 77.03, 76.82, 73.72, 69.67, 31.98, 31.95, 31.94, 30.42, 29.80, 29.78, 29.74, 29.70, 29.66, 29.50, 29.43, 29.40, 26.19, 22.74, 22.71, 14.14. **^{195}Pt NMR** (129 MHz, $CDCl_3$) δ -3765.58. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.97. IR (cm^{-1}) KBr: *ν* 2921, 2852, 2132, 1606, 1128 Found, %: C 63,02; H 8,91; N 2,09. $C_{68}H_{90}F_6N_2O_3Pt$. Calculated, %: C 63,19; H 8,82; N 2,17.

Spectroscopic studies

Optical spectroscopy. The steady state photophysical measurements were performed on solutions of the complexes **6**, **7** and **8** in spectroscopic grade dichloromethane. The UV-Vis absorption spectra were measured with a Varian Cary 300 double beam spectrometer. The emission and excitation spectra were measured with a Horiba Jobin Yvon Fluorolog-3 steady-state fluorescence spectrometer. The emission decay times were measured with a PicoBright PB-375 pulsed diode laser (λ_{exc} = 378 nm, pulse width 100 ps) used as the excitation source, and the PL signal was detected with a cooled photomultiplier attached to a FAST ComTec multichannel scalar PCI card with a time resolution of 250 ps. The PL quantum yields were determined with a Hamamatsu C9920-02 system equipped with a Spectralon® integrating sphere. Solid state fluorescence of the sample was measured using a Hitachi F-7000 spectrophotometer.

Mesophase investigations. Optical textures were recorded using an Olympus BX50 polarising microscope equipped with a Linkam scientific LTS350 heating stage, Linkam LNP2 cooling pump and Linkam TMS92 controller. DSC was performed on a Mettler DSC822e fitted with an autosampler operating with Mettler Star-E software and calibrated before use against an indium standard (onset = 156.55 ± 0.2°C, ΔH = 28.45 ± 0.40 J g^{-1}), with all runs performed under an atmosphere of dry nitrogen. Small angle X-ray scattering was recorded using a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. Cu-Kα (λ = 0.154056 nm) radiation was used, generated from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048 × 2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small angle and wide angle scattering data. Samples were measured in 1 mm capillary tubes in a magnetic field of ca. 1 T.

Computations. All calculations were carried out with the Gaussian 09 package [1] utilizing the DFT approach with the M06 functional [2] and the def2-SVP basis set [3] including ECPs for the Pt(II) ion. Geometry optimisations were conducted with "tight" criteria. The C-PCM solvation model [4] applied with solvent parameters of dichloromethane.

Table S1. Composition of selected MOs of **6'** in optimised T_1 geometry according to Mulliken's population analysis.

Orbitals	Energy, eV	Contribution, % (Mulliken)		
		Pt	**C^N^N**	**Cl**
LUMO+1	−1.880	1	99	0
LUMO	−2.642	6	93	1
HOMO	−5.784	16	78	7
HOMO−1	−6.256	37	63	0
HOMO−2	−6.442	43	17	40
HOMO−3	−6.460	31	40	29
HOMO−4	−6.702	87	6	7

Table S2. Composition of selected MOs of **7'** in optimised T_1 geometry according to Mulliken's population analysis.

Orbitals	Energy, eV	Contribution, % (Mulliken)		
		Pt	**C^N^N**	**phenylacetylene**
LUMO+1	−1.934	2	97	1
LUMO	−2.794	5	91	4
HOMO	−5.693	21	10	70
HOMO−1	−6.199	30	11	59
HOMO−2	−6.360	34	66	0
HOMO−3	−6.630	1	94	5
HOMO−4	−6.790	87	8	5

Table S3. Composition of selected MOs of **8'** in optimised T_1 geometry according to Mulliken's population analysis.

Orbitals	Energy, eV	Contribution, % (Mulliken)		
		Pt	**C^N^N**	**phenylacetylene**
LUMO+1	−1.908	1	97	1
LUMO	−2.675	4	92	4
HOMO	−5.786	13	72	15
HOMO−1	−6.252	16	35	49
HOMO−2	−6.322	35	65	0
HOMO−3	−6.451	38	15	48
HOMO−4	−6.770	88	5	7

Table S4. TD-DFT calculated lowest triplet and singlet states of **6'** in the T_1 state geometry

State, energy (eV)	*f* (oscillator strength)	Contributing transition coefficients*	Character**
triplets			
T_1, 1.760	(triplet)	HOMO→LUMO (0.64) HOMO→LUMO+1 (−0.18)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT/\ XL^{C\wedge N\wedge N}CT$
T_2, 2.371	(triplet)	HOMO−1→LUMO (0.67)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT$
T_3, 2.515	(triplet)	HOMO−3→LUMO (0.55) HOMO→LUMO+1 (0.30)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT/\ XL^{C\wedge N\wedge N}CT$
singlets			
S_1, 2.514	0.4594	HOMO→LUMO (0.68) HOMO−3→LUMO (0.13)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT/\ XL^{C\wedge N\wedge N}CT$
S_2, 2.586	0.0020	HOMO−1→LUMO (0.70)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT$
S_3, 2.736	0.0008	HOMO−2→LUMO (0.67) HOMO−4→LUMO (0.15)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT$
S_4, 2.891	0.0026	HOMO−4→LUMO (0.68) HOMO−2→LUMO (−0.14)	$M^{Pt}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}$
S_5, 3.056	0.1748	HOMO−3→LUMO (0.64) HOMO→LUMO+1 (0.17)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT/\ XL^{C\wedge N\wedge N}CT$

*Square of the coefficient multiplied by two gives percentage contribution of the transition to formation of the excited state.

**MLCT – Metal (M) to Ligand (L) Charge Transfer. XLCT- Halide to ligand Charge Transfer. LC-Ligand Centered. LLCT – Ligand to Ligand Charge Transfer.

Table S5. TD-DFT calculated lowest triplet and singlet states of **7'** in the T_1 state geometry

State, energy (eV)	*f* (oscillator strength)	Contributing transition coefficients*	Character**
triplets			
T_1, 1.847	(triplet)	HOMO→LUMO (0.67)	$L^{phac}L^{C\wedge N\wedge N}CT/\ M^{Pt}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}$
T_2, 2.298	(triplet)	HOMO−2→LUMO (0.65)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT$
T_3, 2.612	(triplet)	HOMO−1→LUMO (0.70)	$L^{phac}L^{C\wedge N\wedge N}CT/\ M^{Pt}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}$
singlets			
S_1, 2.198	0.3309	HOMO→LUMO (0.70)	$L^{phac}L^{C\wedge N\wedge N}CT/\ M^{Pt}L^{C\wedge N\wedge N}CT\ /LC^{C\wedge N\wedge N}$
S_2, 2.409	0.0002	HOMO−1→LUMO (0.70)	$L^{phac}L^{C\wedge N\wedge N}CT/M^{Pt}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}$
S_3, 2.552	0.0156	HOMO−2→LUMO (0.69)	$LC^{C\wedge N\wedge N}/M^{Pt}L^{C\wedge N\wedge N}CT$
S_4, 2.831	0.0036	HOMO−4→LUMO (0.70)	$M^{Pt}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}$
S_5, 3.031	0.2027	HOMO→LUMO+1 (0.69)	$L^{phac}L^{C\wedge N\wedge N}CT/\ M^{Pt}L^{C\wedge N\wedge N}CT\ /LC^{C\wedge N\wedge N}$
S_6, 3.213	0.1704	HOMO−3→LUMO (0.70)	$LC^{C\wedge N\wedge N}$

*Square of the coefficient multiplied by two gives percentage contribution of the transition to formation of the excited state.

**MLCT – Metal (M) to Ligand (L) Charge Transfer. LC-Ligand Centered. LLCT – Ligand to Ligand Charge Transfer.

Table S6. TD-DFT calculated lowest triplet and singlet states of **8'** in the T_1 state geometry

State, energy (eV)	*f* (oscillator strength)	Contributing transition coefficients*	Character**
triplets			
T_1, 1.801	(triplet)	HOMO→LUMO (0.62) HOMO→LUMO+1 (−0.18)	$LC^{C\wedge N\wedge N}/L^{dtfmphac}L^{C\wedge N\wedge N}CT/M^{Pt}L^{C\wedge N\wedge N}CT$
T_2, 2.426	(triplet)	HOMO−2→LUMO (0.63) HOMO−1→LUMO (0.17)	$LC^{C\wedge N\wedge N}/ M^{Pt}L^{C\wedge N\wedge N}CT$
T_3, 2.457	(triplet)	HOMO−1→LUMO (0.55) HOMO−2→LUMO (−0.22)	$L^{dtfmphac}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}/ /M^{Pt}L^{C\wedge N\wedge N}CT$
singlets			
S_1, 2.309	0.7530	HOMO→LUMO (0.68) HOMO−1→LUMO (0.15)	$LC^{C\wedge N\wedge N}/L^{dtfmphac}L^{C\wedge N\wedge N}CT/ M^{Pt}L^{C\wedge N\wedge N}CT$
S_2, 2.653	0.0009	HOMO−2→LUMO (0.69)	$LC^{C\wedge N\wedge N}/ M^{Pt}L^{C\wedge N\wedge N}CT$
S_3, 2.780	0.0010	HOMO−3→LUMO (0.69)	$L^{phac}L^{C\wedge N\wedge N}CT/M^{Pt}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}$
S_4, 2.921	0.0337	HOMO−1→LUMO (0.67) HOMO→LUMO (−0.16)	$L^{dtfmphac}L^{C\wedge N\wedge N}CT/LC^{C\wedge N\wedge N}/ /M^{Pt}L^{C\wedge N\wedge N}CT$
S_5, 2.988	0.0045	HOMO−4→LUMO (0.70)	$M^{Pt}L^{C\wedge N\wedge N}CT$

*Square of the coefficient multiplied by two gives percentage contribution of the transition to formation of the excited state.

**MLCT – Metal (M) to Ligand (L) Charge Transfer. LC-Ligand Centered. LLCT – Ligand to Ligand Charge Transfer.

Table S7. Iso-surface contour plots (iso-value=0.05) of selected MOs' of **6'** at optimised T_1 state geometry. Hydrogens are omitted for clarity.

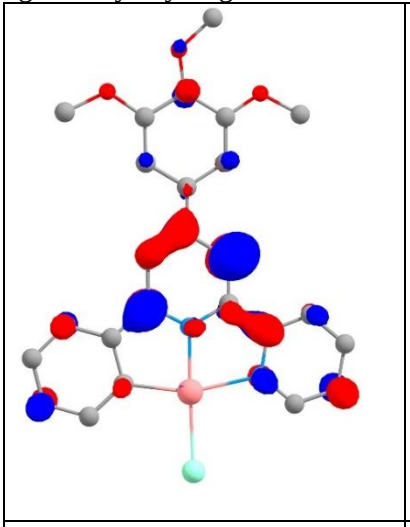
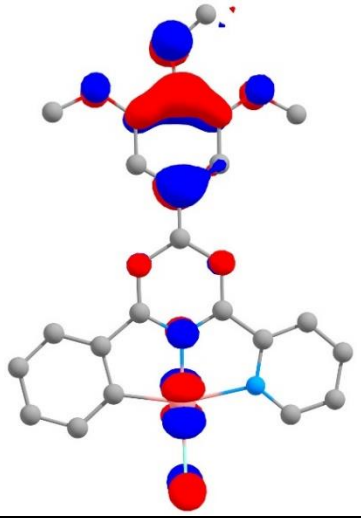
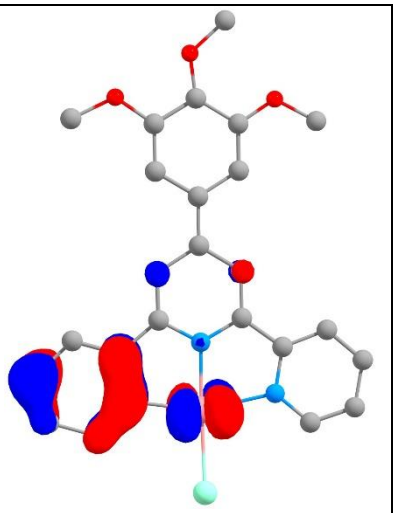
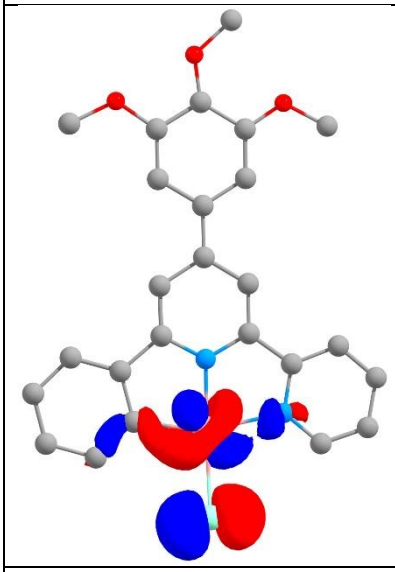
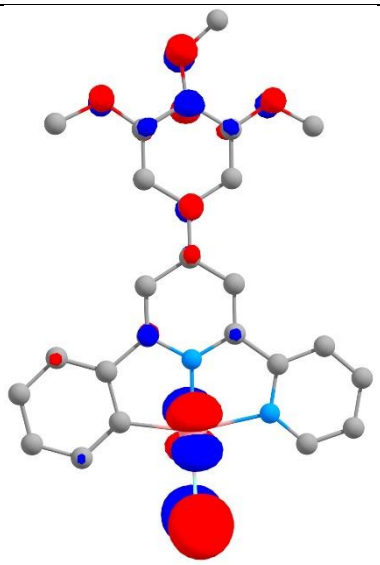
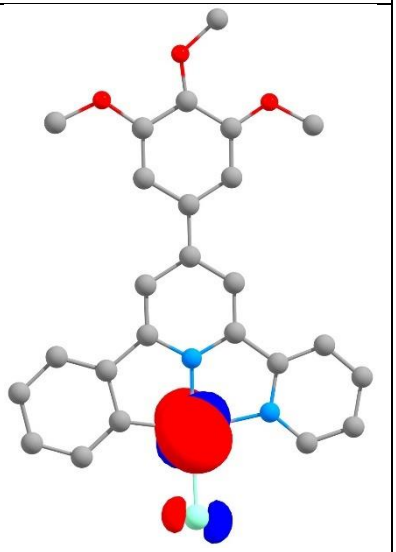
		
LUMO	**HOMO**	**HOMO−1**
		
HOMO−2	**HOMO−3**	**HOMO−4**

Table S8. Iso-surface contour plots (iso-value=0.05) of selected MOs' of **7'** at optimised T_1 state geometry. Hydrogens are omitted for clarity.

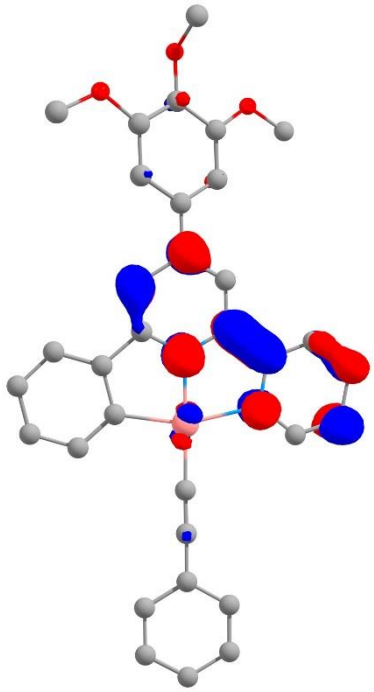
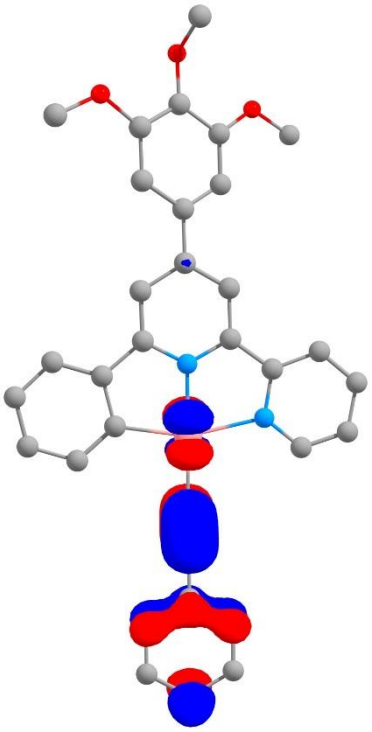
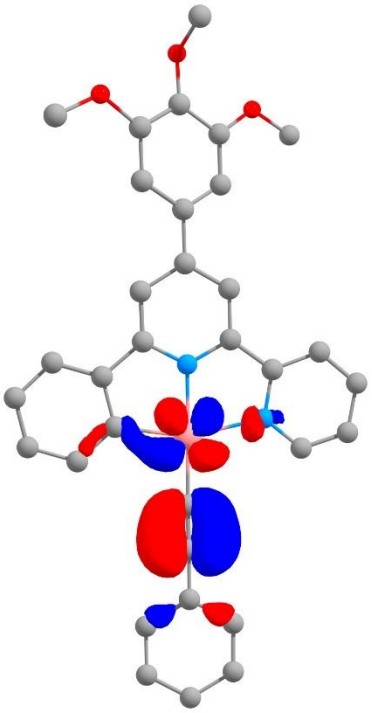
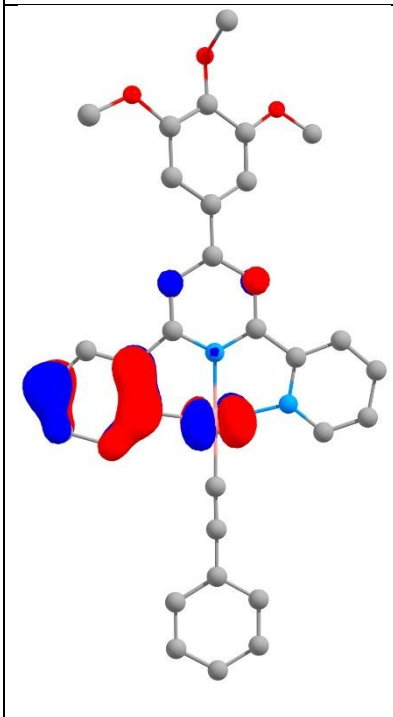
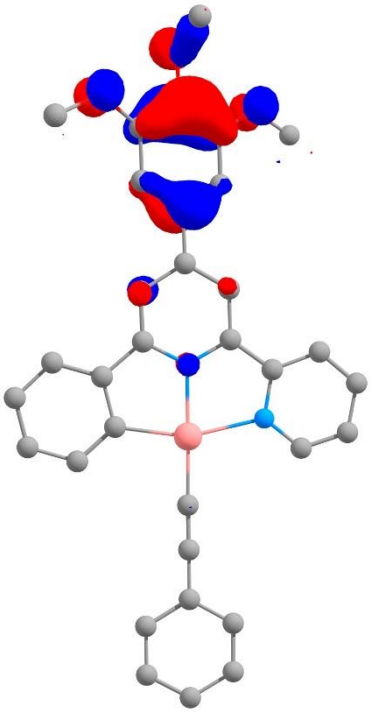
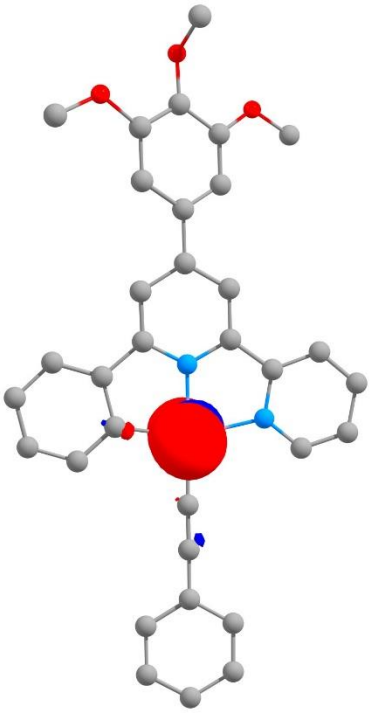
		
LUMO	**HOMO**	**HOMO−1**
		
HOMO−2	**HOMO−3**	**HOMO−4**

Table S9. Iso-surface contour plots (iso-value=0.05) of selected MOs' of **8'** at optimised T_1 state geometry. Hydrogens are omitted for clarity.

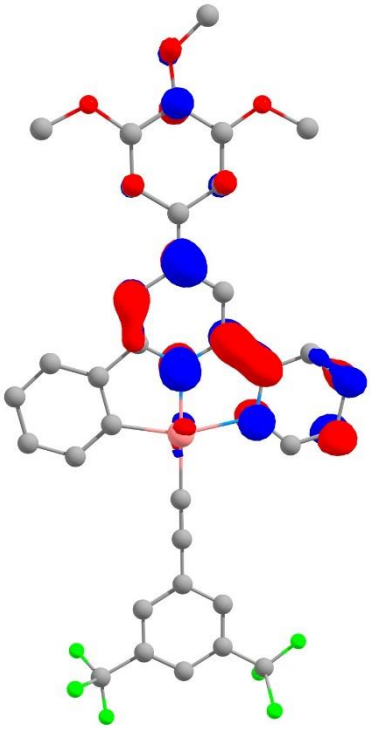
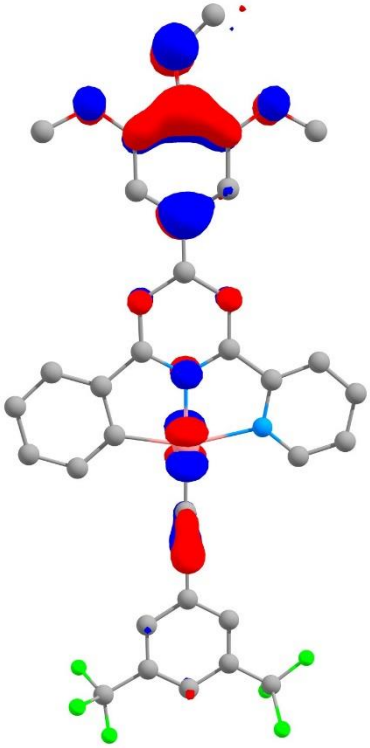
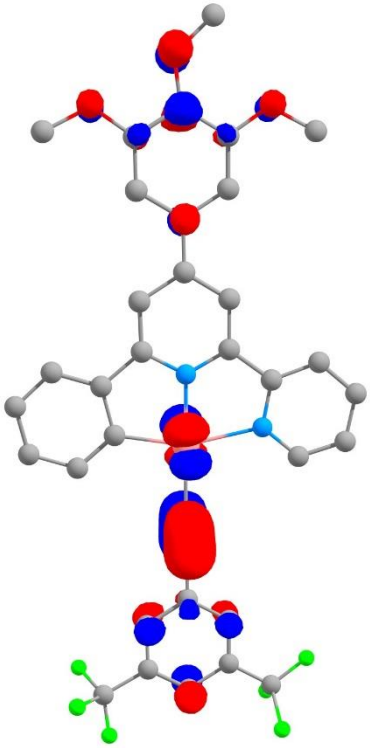
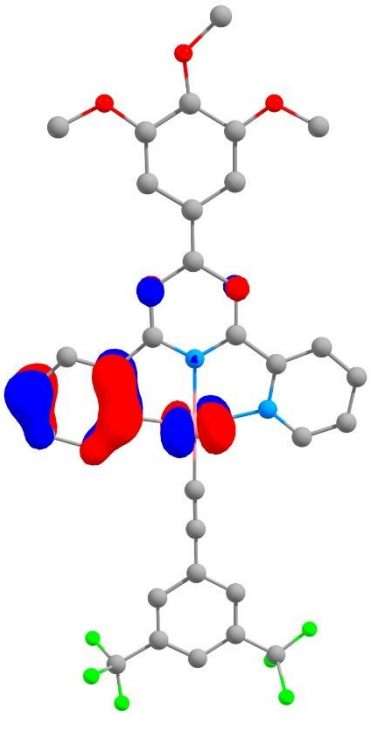
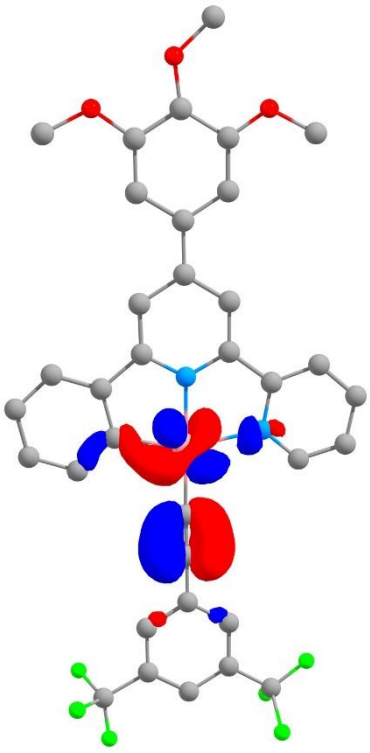
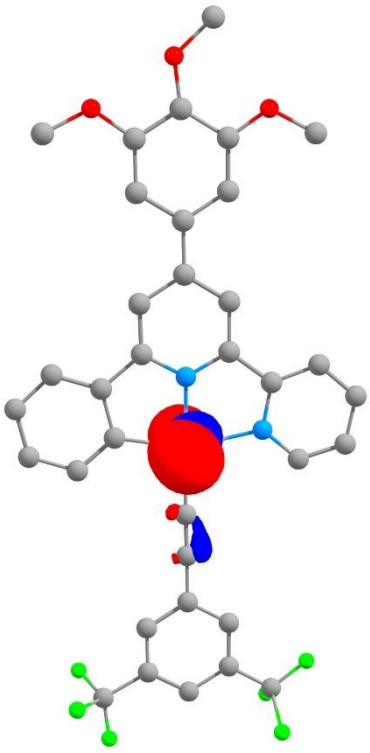
		
LUMO	**HOMO**	**HOMO−1**
		
HOMO−2	**HOMO−3**	**HOMO−4**

Table S10. DFT optimised ground state (S_0) and T_1 state geometry of **6'** in cartesian (XYZ) coordinates

State S_0				State T_1			
C	0.967027000	-1.226020000	0.217409000	C	-0.931060000	1.286857000	0.037720000
C	-0.425677000	-1.190349000	0.190087000	C	0.438692000	1.234341000	0.038386000
C	1.708546000	-0.045929000	0.076031000	C	-1.721137000	0.072993000	0.022153000
C	1.013050000	1.164131000	-0.090719000	C	-1.000241000	-1.153893000	0.006023000
C	-0.375876000	1.162684000	-0.114053000	C	0.375884000	-1.178623000	-0.001875000
N	-1.044588000	0.001514000	0.025214000	N	1.074052000	0.017302000	0.016304000
C	-1.365093000	-2.306639000	0.324870000	C	1.396729000	2.346777000	0.059809000
C	-0.961392000	-3.633305000	0.512540000	C	1.023042000	3.694943000	0.091031000
C	-1.913457000	-4.640543000	0.632573000	C	1.994544000	4.690826000	0.110920000
C	-3.270627000	-4.318932000	0.564491000	C	3.346415000	4.339455000	0.099596000
C	-3.683839000	-2.998479000	0.377078000	C	3.730612000	2.997919000	0.067704000
C	-2.750119000	-1.965417000	0.253248000	C	2.775254000	1.976303000	0.046686000
C	-1.236949000	2.353481000	-0.292193000	C	1.218267000	-2.369673000	-0.031168000
N	-2.573331000	2.125046000	-0.292753000	N	2.564938000	-2.149961000	-0.044408000
C	-3.425328000	3.137608000	-0.447482000	C	3.415101000	-3.181304000	-0.069679000
C	-2.993359000	4.449931000	-0.612522000	C	2.987678000	-4.499645000	-0.083371000
C	-1.625639000	4.701635000	-0.613644000	C	1.610004000	-4.746853000	-0.070133000
C	-0.735881000	3.643532000	-0.451650000	C	0.724272000	-3.683162000	-0.044228000
C	3.184786000	-0.071781000	0.097842000	C	-3.149372000	0.107915000	0.016825000
Pt	-3.027032000	-0.006449000	-0.016648000	Pt	3.023703000	-0.012723000	-0.004384000
C	3.869980000	-1.172545000	-0.430746000	C	-3.855218000	1.348765000	-0.049888000
C	3.895879000	1.001957000	0.647509000	C	-3.929543000	-1.090855000	0.078184000
C	5.293752000	0.974560000	0.673252000	C	-5.306005000	-1.071650000	0.070093000
C	5.984716000	-0.135400000	0.158064000	C	-6.009417000	0.179250000	-0.011727000
C	5.267673000	-1.198864000	-0.416247000	C	-5.229940000	1.390314000	-0.066443000
O	6.063996000	1.951579000	1.183777000	O	-6.073271000	-2.165401000	0.142307000
O	7.338271000	-0.181447000	0.214527000	O	-7.316738000	0.359986000	-0.033269000
O	6.014166000	-2.195532000	-0.923102000	O	-5.959993000	2.502668000	-0.138267000
Cl	-5.388042000	0.051162000	-0.089266000	Cl	5.388310000	-0.118408000	-0.055666000
H	1.477020000	-2.179232000	0.376091000	H	-1.408496000	2.266911000	0.062059000
H	1.563580000	2.096461000	-0.231940000	H	-1.531127000	-2.106652000	-0.014760000
H	0.103087000	-3.884971000	0.566214000	H	-0.036854000	3.972177000	0.100169000
H	-1.598348000	-5.677180000	0.779690000	H	1.698319000	5.743504000	0.135267000
H	-4.019924000	-5.111638000	0.659121000	H	4.111301000	5.122913000	0.115224000
H	-4.751573000	-2.761319000	0.325660000	H	4.793737000	2.734313000	0.057392000
H	-4.488139000	2.869880000	-0.436491000	H	4.478496000	-2.914175000	-0.078643000
H	-3.721361000	5.253700000	-0.736871000	H	3.714903000	-5.313455000	-0.103399000
H	-1.247334000	5.718737000	-0.740038000	H	1.230887000	-5.771981000	-0.079572000
H	0.340768000	3.823840000	-0.449358000	H	-0.352853000	-3.863723000	-0.032755000
H	3.309453000	-1.987485000	-0.892846000	H	-3.302358000	2.284370000	-0.104899000
H	3.354495000	1.843591000	1.084104000	H	-3.429146000	-2.054785000	0.150086000
C	5.366730000	-3.304685000	-1.493883000	C	-5.304385000	3.748031000	-0.203636000
C	7.989614000	0.387286000	-0.901861000	C	-8.299817000	-0.662973000	-0.069805000
C	5.444266000	3.091154000	1.723863000	C	-5.465392000	-3.433463000	0.232067000
H	4.750744000	-3.016698000	-2.364040000	H	-4.667801000	3.819596000	-1.102120000
H	4.725911000	-3.824887000	-0.760332000	H	-4.684183000	3.922615000	0.692077000
H	6.150329000	-3.995119000	-1.830167000	H	-6.085528000	4.515598000	-0.255043000
H	7.739607000	1.457712000	-1.010097000	H	-8.278011000	-1.270062000	0.845756000
H	7.719388000	-0.139254000	-1.834530000	H	-8.160677000	-1.317462000	-0.941677000
H	9.072305000	0.291272000	-0.742398000	H	-9.261828000	-0.142046000	-0.146618000
H	4.797221000	2.836576000	2.581756000	H	-4.846935000	-3.517093000	1.141832000
H	4.841018000	3.625536000	0.968797000	H	-4.838685000	-3.640286000	-0.651963000
H	6.244234000	3.756651000	2.071741000	H	-6.276004000	-4.169914000	0.279006000

Table S11. DFT optimised ground state (S_0) and T_1 state geometry of **7'** in cartesian (XYZ) coordinates

State S_0				State T_1			
C	2.011930000	-1.219477000	0.221359000	C	-1.985418000	-1.237457000	-0.191972000
C	0.618215000	-1.174197000	0.204294000	C	-0.612561000	-1.193641000	-0.172519000
C	2.755915000	-0.039937000	0.079527000	C	-2.743104000	-0.022000000	-0.088025000
C	2.066907000	1.176154000	-0.075194000	C	-2.047868000	1.182838000	0.034976000
C	0.677086000	1.175275000	-0.085347000	C	-0.648832000	1.207734000	0.057428000
N	0.010137000	0.019245000	0.052594000	N	0.025977000	0.008155000	-0.048350000
C	-0.329630000	-2.289621000	0.336564000	C	0.336082000	-2.313933000	-0.274824000
C	0.085349000	-3.614360000	0.512629000	C	-0.065152000	-3.646431000	-0.418359000
C	-0.853479000	-4.634156000	0.632099000	C	0.881365000	-4.662721000	-0.510168000
C	-2.213313000	-4.326571000	0.574508000	C	2.239860000	-4.348687000	-0.457469000
C	-2.639481000	-3.008453000	0.398548000	C	2.654276000	-3.022701000	-0.313344000
C	-1.721160000	-1.961019000	0.275787000	C	1.724794000	-1.983534000	-0.219640000
C	-0.192150000	2.364541000	-0.249065000	C	0.196743000	2.363856000	0.187393000
N	-1.530674000	2.136766000	-0.240164000	N	1.559311000	2.131028000	0.181951000
C	-2.377748000	3.156402000	-0.383832000	C	2.408745000	3.161895000	0.297981000
C	-1.943892000	4.468408000	-0.545574000	C	1.993208000	4.473951000	0.425483000
C	-0.576160000	4.717147000	-0.555807000	C	0.607366000	4.734090000	0.432834000
C	0.309781000	3.654482000	-0.405702000	C	-0.280110000	3.686954000	0.314113000
C	4.232689000	-0.072641000	0.087129000	C	-4.212964000	-0.053923000	-0.099807000
Pt	-2.023179000	0.003222000	0.022846000	Pt	2.021653000	0.010123000	-0.016522000
C	4.908055000	-1.173121000	-0.454500000	C	-4.898078000	-1.212421000	0.303217000
C	4.954040000	0.995108000	0.635123000	C	-4.950819000	1.069098000	-0.511821000
C	6.351996000	0.962313000	0.645515000	C	-6.346261000	1.038322000	-0.513135000
C	7.033100000	-0.147491000	0.117131000	C	-7.029025000	-0.128388000	-0.125266000
C	6.305712000	-1.205128000	-0.454820000	C	-6.294652000	-1.246124000	0.305475000
O	7.131505000	1.933923000	1.152480000	O	-7.129360000	2.067618000	-0.889667000
O	8.387094000	-0.198765000	0.158401000	O	-8.385035000	-0.175438000	-0.168939000
O	7.042779000	-2.202200000	-0.974670000	O	-7.028218000	-2.304715000	0.699790000
C	-3.995993000	-0.026396000	-0.014192000	C	3.938771000	-0.017093000	0.020121000
H	2.522781000	-2.173762000	0.370096000	H	-2.494276000	-2.194396000	-0.325048000
H	2.622638000	2.105376000	-0.216806000	H	-2.598112000	2.120188000	0.148434000
H	1.152588000	-3.855488000	0.557962000	H	-1.131094000	-3.894437000	-0.459719000
H	-0.525093000	-5.667885000	0.770341000	H	0.558703000	-5.701575000	-0.623316000
H	-2.954883000	-5.126503000	0.668244000	H	2.986974000	-5.145589000	-0.529490000
H	-3.711200000	-2.787544000	0.355824000	H	3.725482000	-2.796262000	-0.273823000
H	-3.443213000	2.902207000	-0.368068000	H	3.474515000	2.904718000	0.286822000
H	-2.671886000	5.273532000	-0.660535000	H	2.728027000	5.275909000	0.517172000
H	-0.195487000	5.733594000	-0.680054000	H	0.236398000	5.757600000	0.531973000
H	1.387236000	3.829943000	-0.410489000	H	-1.357007000	3.872752000	0.317831000
H	4.339568000	-1.983330000	-0.915142000	H	-4.334846000	-2.075613000	0.661214000
H	4.420770000	1.836594000	1.081862000	H	-4.427833000	1.960630000	-0.861915000
C	6.384919000	-3.306625000	-1.542649000	C	-6.365159000	-3.468851000	1.120542000
C	9.028025000	0.372189000	-0.962843000	C	-9.020904000	0.256624000	1.014370000
C	6.522077000	3.074642000	1.701731000	C	-6.522222000	3.267470000	-1.293568000
H	5.760560000	-3.013002000	-2.404925000	H	-5.736933000	-3.285584000	2.010365000
H	5.750154000	-3.827272000	-0.804155000	H	-5.731328000	-3.890532000	0.320382000
H	7.162167000	-3.998706000	-1.890123000	H	-7.138538000	-4.202552000	1.381096000
H	8.780121000	1.443765000	-1.064416000	H	-8.772970000	1.308602000	1.243157000
H	8.746103000	-0.149984000	-1.894511000	H	-8.734895000	-0.372575000	1.876338000
H	10.112096000	0.272341000	-0.815536000	H	-10.106044000	0.174617000	0.861898000
H	5.882667000	2.820661000	2.565502000	H	-5.890582000	3.126346000	-2.188569000
H	5.913430000	3.613432000	0.954151000	H	-5.904285000	3.705441000	-0.489568000
H	7.328304000	3.735939000	2.043131000	H	-7.329385000	3.968961000	-1.539961000
C	-5.228612000	-0.004958000	-0.043368000	C	5.194487000	-0.004430000	0.047508000
C	-6.656694000	-0.001362000	-0.073928000	C	6.595265000	-0.005600000	0.074137000
C	-7.384649000	-1.194721000	0.099820000	C	7.315242000	-1.222550000	-0.039136000
C	-8.775143000	-1.192255000	0.070504000	C	8.699232000	-1.218812000	-0.013518000
C	-9.473873000	-0.001745000	-0.132774000	C	9.393676000	-0.011767000	0.124732000
C	-8.767553000	1.188808000	-0.306702000	C	8.699895000	1.198291000	0.237999000
C	-7.376923000	1.191639000	-0.277900000	C	7.315937000	1.208074000	0.213617000
H	-6.835862000	-2.128500000	0.259127000	H	6.756103000	-2.156314000	-0.146736000
H	-9.321048000	-2.130545000	0.207884000	H	9.250068000	-2.158660000	-0.101456000
H	-10.567458000	-0.001846000	-0.155573000	H	10.486972000	-0.014089000	0.144339000
H	-9.307574000	2.126945000	-0.466710000	H	9.251384000	2.135715000	0.345716000
H	-6.822812000	2.125769000	-0.414173000	H	6.757572000	2.144320000	0.300729000

Table S12. DFT optimised ground state (S_0) and T_1 state geometry of **8'** in cartesian (XYZ) coordinates

State S_0				State T_1			
C	3.549183000	-1.230188000	0.134107000	C	-3.530883000	1.275671000	0.005109000
C	2.155535000	-1.180191000	0.124480000	C	-2.156855000	1.227641000	0.000605000
C	4.295504000	-0.045689000	0.065537000	C	-4.309919000	0.058632000	-0.019892000
C	3.609345000	1.179524000	-0.011064000	C	-3.582573000	-1.164798000	-0.054632000
C	2.219795000	1.182694000	-0.018244000	C	-2.204502000	-1.169942000	-0.065215000
N	1.550582000	0.021828000	0.048884000	N	-1.520812000	0.020916000	-0.036616000
C	1.205028000	-2.299067000	0.193585000	C	-1.205047000	2.349998000	0.036484000
C	1.616920000	-3.633175000	0.283636000	C	-1.606000000	3.690419000	0.069771000
C	0.675528000	-4.655738000	0.347039000	C	-0.659699000	4.709792000	0.103291000
C	-0.683505000	-4.341486000	0.319732000	C	0.698983000	4.389053000	0.103397000
C	-1.106802000	-3.013614000	0.229415000	C	1.111954000	3.056083000	0.070173000
C	-0.185687000	-1.963973000	0.164233000	C	0.184273000	2.008565000	0.035915000
C	1.354106000	2.382765000	-0.103705000	C	-1.342677000	-2.352069000	-0.101676000
N	0.014850000	2.160118000	-0.100958000	N	0.003011000	-2.119146000	-0.092831000
C	-0.828482000	3.190029000	-0.175914000	C	0.857620000	-3.148317000	-0.122934000
C	-0.389841000	4.507859000	-0.258651000	C	0.439608000	-4.469003000	-0.163981000
C	0.978787000	4.751207000	-0.262138000	C	-0.935015000	-4.726827000	-0.173950000
C	1.860952000	3.677625000	-0.183602000	C	-1.826260000	-3.667519000	-0.142794000
C	5.772021000	-0.081473000	0.070718000	C	-5.739775000	0.083644000	-0.006724000
Pt	-0.483257000	0.012757000	0.033056000	Pt	0.481417000	0.021740000	-0.022266000
C	6.445680000	-1.142511000	-0.546320000	C	-6.455488000	1.322693000	-0.035771000
C	6.494266000	0.944085000	0.693013000	C	-6.510921000	-1.125051000	0.038688000
C	7.892088000	0.907649000	0.703000000	C	-7.885309000	-1.116733000	0.058955000
C	8.571830000	-0.163370000	0.098337000	C	-8.601416000	0.134248000	0.031481000
C	7.843346000	-1.176637000	-0.547966000	C	-7.828870000	1.355383000	-0.020541000
O	8.672813000	1.839074000	1.278524000	O	-8.645321000	-2.213871000	0.107162000
O	9.925529000	-0.219893000	0.138596000	O	-9.907436000	0.305804000	0.048025000
O	8.579158000	-2.135602000	-1.136517000	O	-8.568946000	2.459845000	-0.051038000
C	-2.452524000	-0.014395000	0.013218000	C	2.454723000	0.031428000	0.004674000
H	4.057902000	-2.193135000	0.221895000	H	-4.016395000	2.251209000	0.043243000
H	4.167269000	2.114458000	-0.094083000	H	-4.106648000	-2.120977000	-0.081034000
H	2.683654000	-3.879507000	0.305321000	H	-2.671791000	3.943890000	0.068889000
H	1.001517000	-5.696966000	0.417895000	H	-0.981293000	5.754930000	0.128850000
H	-1.427011000	-5.143478000	0.369486000	H	1.446928000	5.188323000	0.129341000
H	-2.178319000	-2.788430000	0.208953000	H	2.182482000	2.823077000	0.070065000
H	-1.895063000	2.940746000	-0.169390000	H	1.921374000	-2.885195000	-0.112692000
H	-1.115027000	5.321409000	-0.318811000	H	1.174002000	-5.276223000	-0.187417000
H	1.363239000	5.771802000	-0.325679000	H	-1.307285000	-5.753890000	-0.206083000
H	2.939143000	3.848330000	-0.184641000	H	-2.902447000	-3.853506000	-0.150408000
H	5.875975000	-1.917546000	-1.062711000	H	-5.909437000	2.262654000	-0.081893000
H	5.961931000	1.753134000	1.197177000	H	-6.001760000	-2.086418000	0.069609000
C	7.920182000	-3.193232000	-1.786466000	C	-7.927288000	3.714417000	-0.102397000
C	10.570208000	0.427283000	-0.938293000	C	-10.887335000	-0.720190000	0.113506000
C	8.064904000	2.937138000	1.910369000	C	-8.031125000	-3.482942000	0.140825000
H	7.297550000	-2.834512000	-2.625032000	H	-7.312725000	3.811814000	-1.013355000
H	7.283551000	-3.766763000	-1.089971000	H	-7.288821000	3.873034000	0.783107000
H	8.696764000	-3.858700000	-2.183805000	H	-8.717582000	4.473880000	-0.117929000
H	10.325200000	1.504022000	-0.964008000	H	-10.777590000	-1.314689000	1.031082000
H	10.288897000	-0.026905000	-1.905074000	H	-10.824601000	-1.384750000	-0.759214000
H	11.653686000	0.314325000	-0.796321000	H	-11.853416000	-0.201687000	0.118620000
H	7.424239000	2.620865000	2.752390000	H	-7.396199000	-3.594502000	1.035853000
H	7.457971000	3.531126000	1.204376000	H	-7.420188000	-3.653829000	-0.761438000
H	8.872030000	3.569743000	2.300503000	H	-8.838533000	-4.223289000	0.176193000
C	-3.685250000	0.005031000	-0.002629000	C	3.689639000	-0.000699000	0.016186000
C	-5.108977000	0.006398000	-0.019458000	C	5.111400000	-0.017865000	0.023361000
C	-5.836461000	-1.179158000	0.167874000	C	5.851512000	1.175030000	-0.018181000
C	-7.230369000	-1.171660000	0.150103000	C	7.244992000	1.151418000	-0.015270000
C	-7.934778000	0.008295000	-0.054070000	C	7.938333000	-0.051999000	0.030277000
C	-7.218359000	1.193084000	-0.241993000	C	7.210196000	-1.244085000	0.073105000
C	-5.831332000	1.199583000	-0.225667000	C	5.823414000	-1.235075000	0.069557000
H	-5.294934000	-2.117022000	0.329145000	H	5.319138000	2.131092000	-0.054126000
C	-7.942704000	-2.475026000	0.361178000	C	7.969976000	2.463899000	-0.063429000
H	-9.027827000	0.011954000	-0.068026000	H	9.031329000	-0.068767000	0.032691000
C	-8.000550000	2.453846000	-0.462501000	C	7.980536000	-2.530241000	0.116162000
H	-5.282220000	2.132802000	-0.373388000	H	5.265065000	-2.173982000	0.102266000
F	-7.639155000	-3.006265000	1.548625000	F	7.647038000	3.235217000	0.978203000
F	-7.590521000	-3.375246000	-0.560544000	F	7.651371000	3.153804000	-1.162004000
F	-9.266262000	-2.347336000	0.308493000	F	9.292717000	2.316746000	-0.055196000
F	-8.813306000	2.705647000	0.567763000	F	8.799296000	-2.569513000	1.171414000
F	-8.777662000	2.358062000	-1.545253000	F	8.750346000	-2.669485000	-0.967390000
F	-7.221049000	3.519571000	-0.624663000	F	7.191771000	-3.599270000	0.183937000

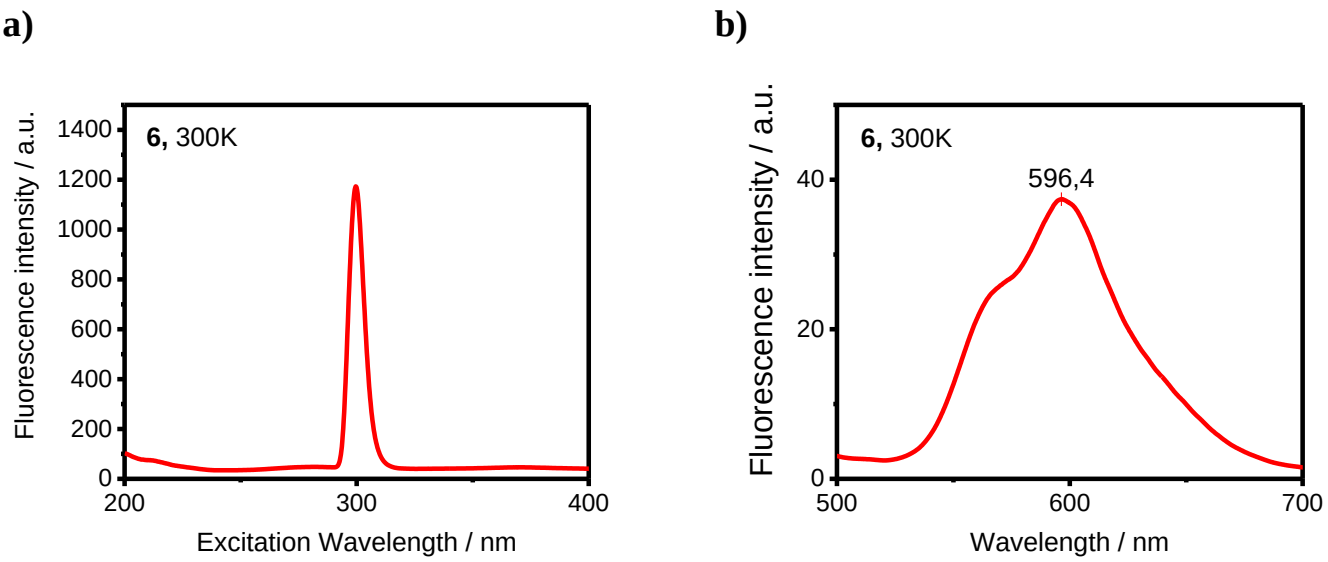


Figure S1. Solid state spectroscopy data (Excitation spectrum a, Emission spectrum b) measured in solid state for substance **6** at room temperature (300 K).

[1] Frisch MJ, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li X, Caricato M, Marenich A, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, Ortiz JV, Izmaylov AF, Sonnenberg JL, Williams-Young D, Ding F, Lipparini F, Egidi F, Goings J, Peng B, Petrone A, Henderson T, Ranasinghe D, Zakrzewski VG, Gao J, Rega N, Zheng G, Liang W, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Throssell K, Montgomery Jr. JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Keith T, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Millam JM, Klene M , Adamo C, Cammi R, Ochterski JW, Martin RL, Morokuma K, Farkas O, Foresman JB, Fox DJ. Gaussian 09 [CD-ROM]. Revision A.02. Wallingford CT: Gaussian, Inc.; 2016.

[2] Zhao Y, Truhlar DG. 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(1):215-241.

[3] Weigend F, Ahlrichs R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. PCCP. 2005;7(18):3297-3305.

[4] Cossi M, Rega N, Scalmani G, Barone V. Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. J Comput Chem. 2003;24(6):669-681.