Supporting Information

Phosphorescent Cu(I) Complexes based on Bis(pyrazol-1-yl-methyl)-pyridine Derivatives for Organic Light-Emitting Diodes

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1. Experimental Section

1.1. Instrumentation and spectroscopic methods

NMR spectra were recorded on a Bruker Ultrashield 400 Plus NMR spectrometer. The NMR chemical shifts for ^{1}H and ^{31}P were referenced to tetramethylsilane (δ = 0.00 ppm) and external 85% H_3PO_4. High-resolution mass spectra, reported as *m/z*, were obtained on a Bruker Autoflex MALDI-TOF mass spectrometer. The electronic absorption spectra in the UV/Vis region were recorded with a Hewlett Packard 8453 UV/Vis spectrophotometer. Luminescence properties of the complexes in degassed dichloromethane solution and in spin-coated poly (methyl methacrylate) (PMMA) films (≈ 20 wt % of the complex) were investigated at ambient temperature. Steady-state visible fluorescence and PL-excitation spectra were measured with a Photon Technology International (PTI) Alphascan spectrofluorimeter. Visible-decay spectra were recorded with a pico-N_2 laser system (PTI Time Master) with λ_{ex} = 337 nm. Photoluminescence quantum yields (Φ_{PL} or PLQY) in solution were obtained from corrected spectra on a wavelength scale (nm) and measured according to the approach described by Demas and Crosby[1] using air-equilibrated $[Ru(bpy)_3][Cl]_2$ water solution (Φ_{PL} = 0.028) as the standard.[2] Solid-state Φ_{PL} values were determined using a Hamamatsu system for absolute PL quantum yield measurements (type C9920-02)

equipped with an integrating sphere with Spectralon inner surface coating. The samples were carefully degassed by at least five freeze-pump-thaw cycles.

Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer thermal analyzer. Cyclic voltammetry measurements were conducted on a CHI660C electrochemical workstation, using a polished Pt plate as the working electrode, Pt mesh as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode, at a scan rate of 0.1 V/s. Cyclic voltammograms were recorded using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Solutions were purged with N_2 for 10 min to remove dissolved O_2.

1.2. DFT calculation procedure

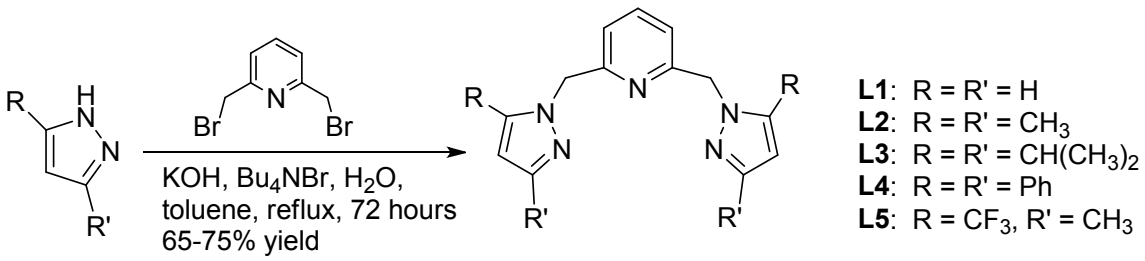
The density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations were performed with Gaussian 09 [3] at the Université de Sherbrooke with the Mammouth supercomputer supported by Le Réseau Québécois De Calculs Hautes Performances. The DFT geometry optimisations as well as TD-DFT calculations [4-12] were carried out using the B3LYP method. A 6-31g* basis set was used for C, H, N, P, and F atoms.[13-18] VDZ (valence double ζ) with SBKJC effective core potentials were used for all Cu and Br atoms.[13-18] Geometry optimisations and TDDFT calculations were carried out in the absence of solvent effects. In order to verify the nature of the stationary points that of both the singlet and triplet state geometry optimization calculations a frequency calculation was performed. The results of the frequency calculations showed no imaginary frequencies for all singlet ant triplet optimized structures. The lack of imaginary frequencies indicates clearly that the optimised structures are a true minimum. Spin density distributions were also calculated for the each of the examined compounds. The results of the spin density calculations support the notion of mixed MLCT (Cu(I) to bis(pyrazol-1-yl)-pyridine) and LLCT (phosphine to bis(pyrazol-1-yl)-pyridine) and are shown further in the supporting information. The calculated absorption spectra were obtained from GaussSum 2.1.[19]

1.3. Device fabrication and measurements

PEDOT-PSS (CH8000) was purchased from H.C. Stark. PYD2 and DPEPO were synthesized using the following procedures described previously.[20,21] Before device fabrication, PYD2 and DPEPO were purified by sublimation after recrystallization from dichloromethane/methanol and dichloromethane/ether admixtures, respectively.

A 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) layer was spin-coated at 3000 rpm onto a pre-cleaned ITO glass substrate, followed by drying at 200 °C for 10 min. Subsequently, a 30 nm thick doped film of Cu(I) complex in PYD2 was spin-coated at 1500 rpm onto the PEDOT layer from a filtered 5.5 mg mL^{-1} CH_2Cl_2 solution. After the film was dried under a vacuum for 1 h at room temperature, a 50 nm thick electron-transport layer (DPEPO) was deposited in an inert chamber under a pressure of $< 4 \times 10^{-4}$ Pa. Finally, the cathode was fabricated by thermal evaporation of a LiF layer (0.5 nm) followed by an Al layer (100 nm). The intersection of the ITO and the metal electrodes gives an active device area of 4 mm^2. The current density, voltage, and brightness characteristics of the OLEDs were measured in ambient air with a semiconductor parameter analyzer (E5273A, Agilent) and an optical power meter (1930C, Newport). The EL spectra were recorded using a multi-channel spectrometer (UBS2000, Ocean Optics).

1.4. Synthesis of ligands (L1–L5)



Scheme S1 The synthetic routes for the Cu(I) complexes **P1**–**P5**.

In a 50 mL Schlenk flask equipped with a reflux condenser, pyrazole (20.5 mmol), potassium hydroxide (2.31 g, 41.2 mmol), tetrabutylammonium bromide (0.212 g, 0.63 mmol), and water (1 mL) were stirred at room temperature for 25 min. Then 2,6-

bis(bromomethyl)pyridine (2.55 g, 9.6 mmol) and toluene (25 mL) were added and the mixture was heated to reflux for 72 hours. The resulting mixture was treated with water and the combined organic layers were dried with magnesium sulphate, concentrated, and purified by column chromatography on silica gel (hexane-dichloromethane as eluent) to afford the desired white solid.

2,6-Bis(pyrazol-1-ylmethyl)-pyridine (**L1**). (Yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 5.45 (s, 4H, CH_2), 6.33 (t, 2H, *J*(HH) = 2.2 Hz, H4-pz), 6.83 (d, 2H, *J*(HH) = 8.0 Hz, H3- pz),7.52 (d, 2H, *J*(HH) = 2.0 Hz, H5-pz) and 7.54-7.57 (m, 3H, H-py). MALDI-TOF MS: $[M]^+$ Calcd for $[C_{13}H_{13}N_5]^+$, 239.1136, Found: 239.3415.

2,6-Bis(3,5-dimethylpyrazol-1-ylmethyl)-pyridine (**L2**). (Yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 2.17 (s, 6H, Me5- pz), 2.25 (s, 6H, Me3-pz), 5.30 (s, 4H, CH_2), 5.87 (s, 2H, H4-pz), 6.61 (d, 2H, *J*(HH) = 8.0 Hz, H3-py) and 7.50 (t, 1H, *J*(HH) = 8.0 Hz, H4-py). MALDI-TOF MS: $[M]^+$ Calcd for $[C_{17}H_{21}N_5]^+$, 295.1827, Found: 295.5741.

2,6-Bis(3,5-diisopropylpyrazol-1-ylmethyl)-pyridine (**L3**). (Yield 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 1.14 (d, 12H, *J*(HH) = 6.8 Hz, Me5-pz), 1.28 (d, 12H, *J*(HH) = 6.8Hz,Me3-pz), 2.84 (m, 2H,CH-5-pz), 2.98-3.02 (m, 2H,CH-3-pz), 5.38 (s, 4H, CH_2), 5.93 (s, 2H, H4-pz),6.50 (d, 2H, *J*(HH) = 8.0 Hz, H3-py) and 7.48 (t, 1H, *J*(HH) = 8.0 Hz, H4-py). MALDI-TOF MS: $[M]^+$ Calcd for $[C_{25}H_{37}N_5]^+$, 407.3121, Found: 407.3123.

2,6-Bis(3,5-diphenylpyrazol-1-ylmethyl)-pyridine (**L4**). (Yield 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 5.47 (s, 4H, CH_2), 6.68 (s, 2H, H4-pz), 6.88 (d, 2H, *J*(HH) = 8.0 Hz, H3-py), 7.34-7.37 (m, 16H, *o*,*m*-Ph), 7.57 (t, 1H, *J*(HH) = 8.0 Hz, H4-py), 7.83-7.86 (m, 4H, *p*-Ph). MALDI-TOF MS: $[M]^+$ Calcd for $[C_{37}H_{29}N_5]^+$, 543.2495, Found: 543.2512.

2,6-Bis(3-methyl-5-trifluoromethylpyrazol-1-ylmethyl)-pyridine (**L5**). (Yield 65%). ^{1}H NMR (400 MHz,$CDCl_3$): δ/ppm 2.18 (s, 6H, Me3-pz), 5.38 (s, 4H, CH_2), 6.31 (s, 2H, H4-pz),6.92 (d, 2H, *J*(HH) = 8.0 Hz, H3-py), 7.63 (t, 1H, *J*(HH) = 8.0 Hz, H4-py). MALDI-TOF MS: $[M]^+$: Calcd for $[C_{17}H_{15}F_6N_5]^+$, 403.1253, Found: 403.2362.

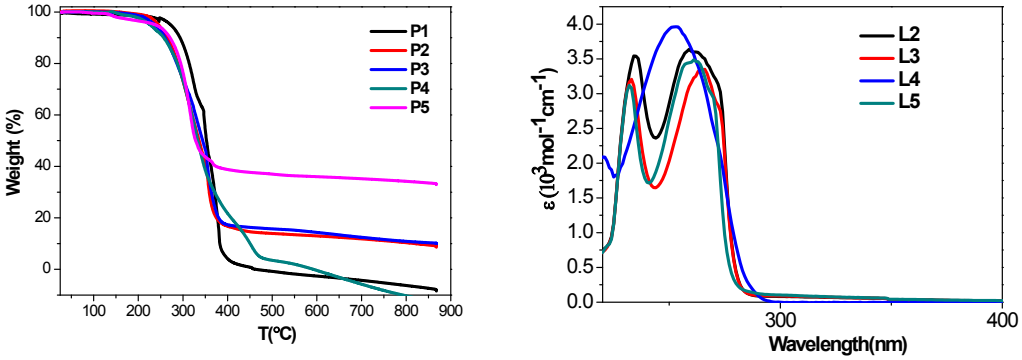


Fig. S1 Left: TGA traces of complexes **P1–P5;** Right: Absorption spectra of the ligands in CH_2Cl_2.

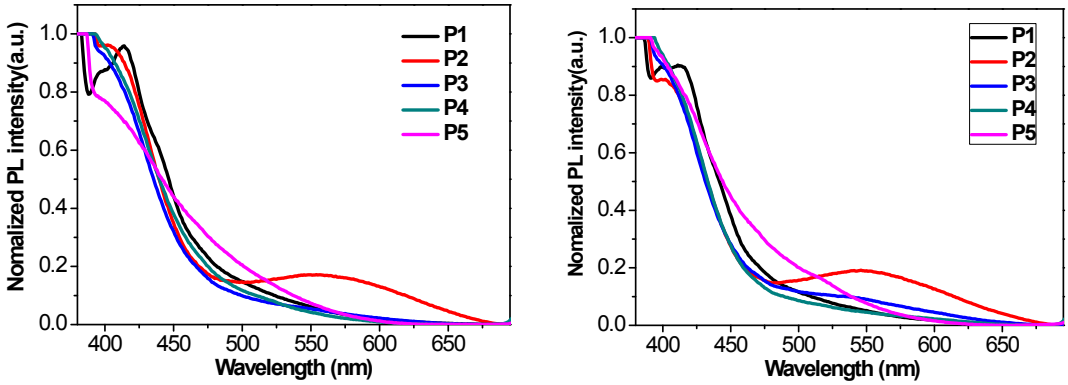


Fig. S2 Left: Emission spectra of the Cu (I) complexes in CH_3CN; Right: Emission spectra of the Cu (I) complexes in MeOH.

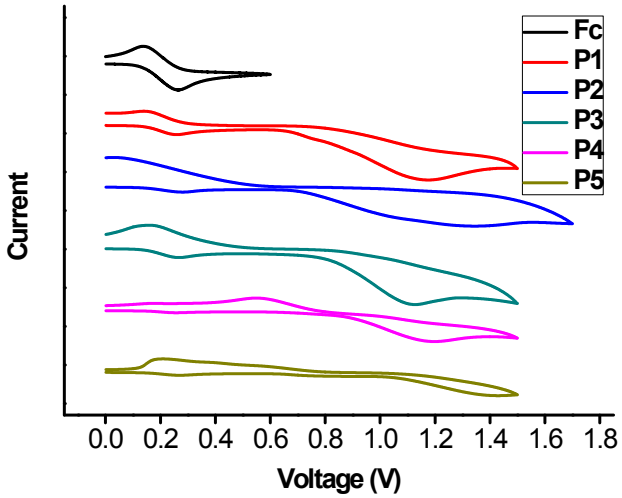


Fig. S3 Cyclic voltammograms of the Cu(I) complexes and the reference.

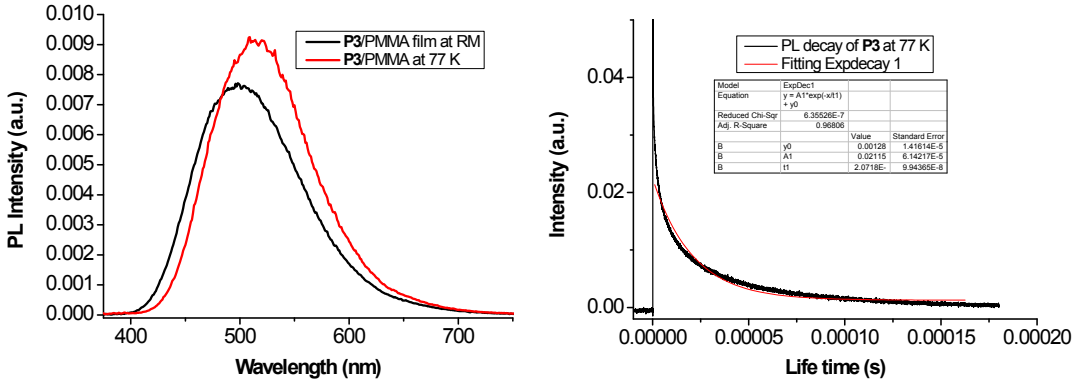


Fig. S4. (a) PL of P3 at 77 K and room temperature; (b) PL decay of P3 at 77 K.

2. DFT and TDDFT calculation results

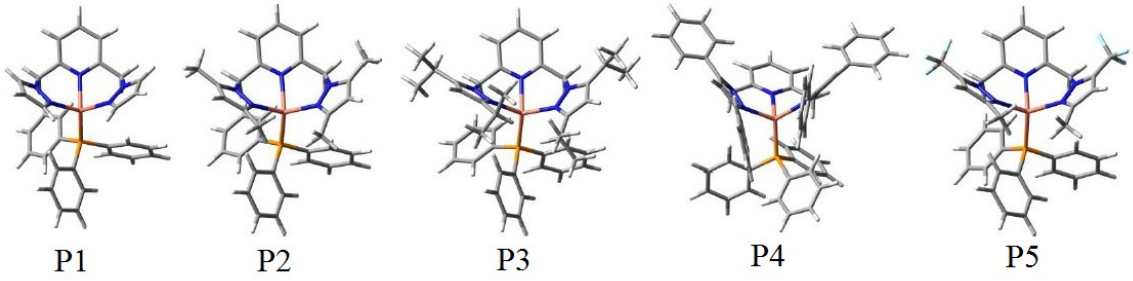


Fig. S5 Optimized geometries of compounds **P1** to **P5** obtained by DFT using the G09/B3LYP method.

2.1 DFT calculation results for P1

Images of the molecular orbitals of complex **P1** (including the orbital energies), a table describing the molecular orbital contributions function of molecular fragments, a side view image of the spin density distribution for **P1** showing the mixed MLCT and LLCT**,** a graphical representation of the calculated UV-Visible absorption spectrum and a table comparing the molecular geometry about the copper atom of **P1** in the it S_0 and t_1 states are provided in the main text of this work. A detailed conformational analysis comparing the bond length, bond angles and dihedral angles is provided here. The table below provided the 100 calculated transitions for compound **P1**.

Table S1 Calculated positions of the 100 first electronic transitions, oscillator strength (F) and major contributions to these electronic transitions for **P1**.

Wavelength (nm)	Osc. Strength	Major contributors (%)

391.5	0.0368	HOMO→LUMO (97%)
371.0	0.0045	H-1→LUMO (97%)
356.6	0.0024	H-2→LUMO (99%)
333.9	0.0055	HOMO→L+1 (98%)
312.4	0.0001	H-1→L+1 (98%)
308.0	0.0003	H-6→LUMO (96%)
302.9	0.0091	H-9→LUMO (10%), H-7→LUMO (39%), H-5→LUMO (27%), H-4→LUMO (13%)
299.6	0.0004	H-2→L+1 (97%)
284.9	0.0079	H-9→LUMO (10%), H-7→LUMO (14%), H-4→LUMO (39%), H-3→LUMO (23%)
282.7	0.0007	H-4→LUMO (11%), H-3→LUMO (73%)
282.2	0.0082	H-5→LUMO (50%), H-4→LUMO (20%), HOMO→L+2 (20%)
281.7	0.0481	HOMO→L+2 (59%), HOMO→L+3 (22%)
280.7	0.075	HOMO→L+2 (17%), HOMO→L+3 (73%)
272.4	0.0019	H-8→LUMO (86%)
270.4	0.0536	HOMO→L+4 (87%)
269.0	0.0125	H-10→LUMO (17%), H-9→LUMO (49%), H-7→LUMO (27%)
266.3	0.0002	H-10→LUMO (72%), H-9→LUMO (22%)
263.6	0.0006	H-6→L+1 (95%)
263.1	0.0078	H-7→L+1 (15%), H-5→L+1 (12%), HOMO→L+5 (15%), HOMO→L+6 (33%)
262.6	0.0026	H-11→LUMO (12%), H-7→L+1 (22%), H-5→L+1 (14%), HOMO→L+5 (11%), HOMO→L+6 (19%)
260.9	0.0056	H-11→LUMO (71%), HOMO→L+5 (15%)
260.5	0.0085	H-11→LUMO (12%), HOMO→L+5 (36%), HOMO→L+6 (35%)
259.2	0.0027	H-12→LUMO (94%)
258.5	0.0026	H-1→L+3 (73%)
257.3	0.0288	H-1→L+2 (81%)
255.4	0.0051	H-2→L+2 (83%)
253.9	0.0141	H-1→L+4 (63%), H-1→L+5 (17%)
252.8	0.0012	H-7→L+1 (13%), H-4→L+1 (32%), H-3→L+1 (30%)
251.3	0.014	H-2→L+3 (21%), H-2→L+4 (31%), H-2→L+5 (11%), HOMO→L+7 (16%)
251.1	0.0015	H-4→L+1 (11%), H-3→L+1 (64%)
250.7	0.0052	H-5→L+1 (47%), H-4→L+1 (21%)
250.4	0.0036	H-4→L+1 (13%), H-2→L+3 (10%), H-2→L+4 (19%), HOMO→L+7 (30%)
248.0	0.0393	H-2→L+3 (40%), HOMO→L+7 (31%)
246.1	0.0012	H-1→L+5 (11%), H-1→L+6 (73%)
245.0	0.013	H-13→LUMO (84%)
244.1	0.0036	HOMO→L+8 (43%), HOMO→L+9 (14%)
243.5	0.002	HOMO→L+8 (18%), HOMO→L+9 (47%)
243.0	0.001	H-8→L+1 (83%)
240.4	0.0033	H-2→L+6 (65%)
240.4	0.0005	H-10→L+1 (17%), H-9→L+1 (48%), H-7→L+1 (29%)

239.2	0.0006	H-1→L+4 (20%), H-1→L+5 (54%), H-1→L+6 (10%)
238.0	0.002	H-10→L+1 (71%), H-9→L+1 (23%)
236.4	0.0065	H-14→LUMO (90%)
236.3	0.0036	H-2→L+4 (23%), H-2→L+5 (50%)
233.4	0.0019	H-12→L+1 (57%), H-3→L+2 (12%)
233.3	0.0031	H-12→L+1 (31%), H-3→L+2 (22%)
233.1	0.0222	H-11→L+1 (95%)
231.2	0.0085	H-5→L+3 (18%), H-4→L+2 (18%)
229.5	0.0008	H-5→L+3 (13%), H-3→L+3 (11%), H-1→L+7 (11%), HOMO→L+8 (11%)
228.9	0.003	H-1→L+7 (57%)
228.4	0.0249	H-15→LUMO (20%), H-6→L+2 (25%)
228.0	0.0227	H-15→LUMO (33%), H-6→L+2 (39%)
227.3	0.0071	H-6→L+2 (18%), H-6→L+3 (24%)
227.2	0.0045	H-7→L+2 (10%), H-5→L+2 (17%), H-4→L+2 (11%), H-4→L+3 (12%)
226.5	0.0074	H-6→L+3 (15%), H-5→L+2 (15%), H-3→L+2 (11%), H-3→L+3 (18%)
226.3	0.0057	H-6→L+3 (20%), H-3→L+3 (25%), H-2→L+7 (17%)
225.7	0.0028	H-4→L+3 (12%), H-2→L+7 (38%)
224.7	0.0137	H-7→L+3 (17%), H-4→L+3 (29%), H-3→L+2 (14%)
224.1	0.0132	H-7→L+2 (35%), H-5→L+2 (12%), H-4→L+2 (12%)
223.6	0.0145	H-6→L+4 (42%), H-6→L+5 (11%)
222.7	0.0218	H-7→L+4 (25%), H-5→L+4 (11%)
222.2	0.007	H-8→L+3 (16%), H-7→L+3 (24%), H-5→L+3 (21%)
221.0	0.0071	H-1→L+8 (43%), H-1→L+9 (15%)
220.6	0.0017	H-13→L+1 (92%)
220.3	0.0015	H-8→L+2 (17%), H-1→L+8 (33%), H-1→L+9 (25%)
220.1	0.0126	H-8→L+2 (23%), H-5→L+2 (11%), H-2→L+9 (12%), H-1→L+9 (10%)
219.8	0.0044	H-2→L+9 (53%), H-1→L+8 (13%)
218.7	0.0044	H-10→L+2 (21%), H-9→L+2 (31%), H-8→L+2 (10%)
217.7	0.0021	H-9→L+3 (24%), H-8→L+3 (18%), H-3→L+4 (27%)
217.4	0.0152	H-6→L+6 (14%), H-2→L+8 (57%), H-2→L+9 (10%)
216.6	0.0133	H-7→L+6 (20%), H-6→L+6 (22%)
216.5	0.0314	HOMO→L+10 (49%)
216.0	0.0014	H-6→L+6 (22%)
215.0	0.0347	H-9→L+3 (19%), H-4→L+4 (26%), H-3→L+4 (15%)
214.5	0.0287	H-10→L+2 (13%), H-10→L+3 (23%), H-4→L+4 (13%)
213.7	0.038	H-10→L+2 (25%), H-4→L+4 (22%)
213.2	0.0012	H-14→L+1 (89%)
212.4	0.0039	H-6→L+4 (21%), H-6→L+5 (50%), H-6→L+6 (10%), H-6→L+7 (11%)
212.2	0.0489	H-10→L+3 (15%), H-5→L+4 (12%)
211.5	0.0052	H-10→L+3 (10%), H-7→L+4 (12%), H-7→L+5 (18%)
210.4	0.03	H-5→L+4 (14%), H-3→L+7 (15%)
209.7	0.0086	H-4→L+7 (10%), H-3→L+5 (19%)
209.2	0.0047	H-20→LUMO (15%), H-16→LUMO (53%)

208.6	0.0157	H-3→L+5 (34%), H-3→L+7 (19%)
208.4	0.0074	H-4→L+5 (24%), H-4→L+6 (13%), H-3→L+6 (35%)
208.2	0.0046	H-8→L+4 (22%), H-5→L+7 (12%), H-4→L+7 (12%)
207.4	0.0022	H-7→L+5 (13%), H-5→L+5 (32%), H-3→L+6 (12%)
206.8	0.0054	H-4→L+6 (33%), H-3→L+5 (10%)
206.4	0.0074	H-4→L+5 (28%), H-3→L+6 (41%)
206.1	0.0212	H-9→L+4 (28%)
204.6	0.0131	H-10→L+4 (22%), H-9→L+4 (10%), H-4→L+7 (16%)
204.2	0.0027	H-6→L+7 (64%)
203.9	0.0089	H-8→L+5 (11%), H-5→L+6 (41%)
203.4	0.0182	H-7→L+7 (13%), H-5→L+7 (10%)
203.1	0.021	H-2→L+10 (12%), H-1→L+10 (36%)
202.9	0.0127	H-2→L+10 (60%)
202.1	0.0387	H-10→L+4 (18%), H-1→L+10 (12%)
201.7	0.0024	H-8→L+5 (19%), H-7→L+7 (21%)
201.2	0.02	H-9→L+5 (16%), H-8→L+5 (10%), HOMO→L+13 (10%)
200.7	0.0007	H-9→L+5 (25%), H-8→L+5 (10%), H-7→L+7 (15%), H-3→L+9 (12%)

Table S2 Conformational analysis comparing the optimized structures of the singlet and triplet states of **P1**.

Atom ID					Singlet State			Triplet State			Conformation change		
Tag	Symbol	NA	NB	NC	X	Y	Z	X	Y	Z	Δ Bond	Δ Angle	Δ Dihedral
1	C				-2.946	-1.146	-1.297	2.478	-1.155	1.491			
2	C	1			-4.147	-1.182	-2.008	3.454	-1.132	2.461	-0.02		
3	C	2	1		-4.756	0.021	-2.361	3.895	0.085	3.027	0.02	2.31	
4	C	3	2	1	-4.156	1.220	-1.978	3.345	1.277	2.503	0.02	-1.76	4.30
5	C	4	3	2	-2.954	1.175	-1.269	2.369	1.246	1.534	-0.02	2.33	-4.37
6	N	5	4	3	-2.357	0.013	-0.952	1.864	0.029	1.056	0.06	-0.97	-1.89
7	H	3	2	1	-5.688	0.025	-2.918	4.649	0.106	3.803	0.00	0.87	-358.50
8	H	2	1	6	-4.594	-2.133	-2.279	3.889	-2.075	2.783	0.00	-1.76	-358.23
9	H	4	3	2	-4.610	2.174	-2.226	3.692	2.243	2.859	0.00	-0.58	355.58
10	C	1	6	5	-2.232	-2.412	-0.860	2.007	-2.426	0.853	-0.02	6.52	-0.95
11	H	10	1	6	-1.187	-2.381	-1.188	0.917	-2.539	0.932	0.00	1.84	-73.07
12	H	10	1	6	-2.705	-3.293	-1.297	2.473	-3.290	1.330	0.00	-0.14	167.07
13	C	5	4	3	-2.250	2.435	-0.801	1.779	2.494	0.950	-0.02	0.34	358.52
14	H	13	5	4	-2.730	3.323	-1.217	2.174	3.375	1.459	0.00	-0.36	12.73
15	H	13	5	4	-1.204	2.423	-1.127	0.685	2.512	1.039	0.00	1.89	252.89
16	N	13	5	4	-2.268	2.576	0.653	2.080	2.673	-0.488	0.02	1.11	-226.42
17	C	16	13	5	-2.920	3.501	1.403	2.852	3.608	-1.084	-0.01	0.51	224.80
18	C	16	13	5	-1.806	2.097	2.691	2.071	2.196	-2.590	0.01	-0.24	-127.97
19	C	17	16	13	-2.643	3.225	2.730	2.867	3.339	-2.446	0.01	0.44	-357.49
20	H	17	16	13	-3.513	4.279	0.943	3.326	4.389	-0.507	0.00	-0.22	3.44

21	H	18	16	13	-1.353	1.556	3.510	1.819	1.649	-3.488	0.00	-0.01	-6.76
22	H	19	17	16	-2.990	3.766	3.597	3.379	3.894	-3.217	0.00	0.00	-358.80
23	N	10	1	6	-2.253	-2.587	0.591	2.336	-2.511	-0.586	0.02	0.86	46.19
24	C	23	10	1	-2.915	-3.525	1.316	3.198	-3.337	-1.217	-0.01	0.88	-223.49
25	C	24	23	10	-2.661	-3.269	2.651	3.214	-2.986	-2.561	0.01	0.41	355.14
26	H	24	23	10	-3.498	-4.296	0.834	3.728	-4.108	-0.676	0.00	-0.18	-5.85
27	C	25	24	23	-1.828	-2.137	2.643	2.325	-1.910	-2.657	-0.01	0.07	-0.82
28	H	25	24	23	-3.020	-3.824	3.504	3.787	-3.447	-3.351	0.00	-0.02	358.66
29	H	27	25	24	-1.392	-1.605	3.478	2.042	-1.332	-3.526	0.00	0.16	-0.02
30	N	27	25	24	-1.582	-1.725	1.394	1.789	-1.626	-1.457	0.01	-0.46	0.69
31	N	18	16	13	-1.581	1.704	1.433	1.591	1.795	-1.400	0.01	-0.29	-5.62
32	Cu	31	18	16	-0.703	0.001	0.535	0.847	0.011	-0.588	-0.18	-15.69	334.14
33	P	32	31	18	1.475	0.008	-0.091	-1.421	-0.046	0.070	0.10	-15.33	195.19
34	C	33	32	31	2.092	1.631	-0.713	-2.112	1.588	0.523	-0.01	-0.43	-46.72
35	C	34	33	32	2.975	1.747	-1.797	-2.947	1.758	1.638	0.00	-0.98	278.62
36	C	34	33	32	1.662	2.797	-0.055	-1.801	2.699	-0.283	0.00	0.60	-82.64
37	C	35	34	33	3.419	3.004	-2.213	-3.466	3.019	1.938	0.00	-0.25	358.46
38	H	35	34	33	3.317	0.859	-2.320	-3.194	0.912	2.271	0.00	0.10	-1.58
39	C	36	34	33	2.115	4.050	-0.468	-2.330	3.954	0.018	0.00	-0.28	-357.70
40	H	36	34	33	0.979	2.720	0.787	-1.152	2.583	-1.147	0.00	0.48	1.46
41	C	37	35	34	2.992	4.156	-1.550	-3.161	4.116	1.130	0.00	0.00	-0.41
42	H	37	35	34	4.101	3.081	-3.055	-4.112	3.141	2.802	0.00	-0.05	-0.08
43	H	39	36	34	1.783	4.943	0.054	-2.091	4.805	-0.614	0.00	-0.05	358.98
44	H	41	37	35	3.341	5.132	-1.875	-3.569	5.095	1.365	0.00	-0.05	-359.75
45	C	33	32	31	1.854	-1.172	-1.460	-1.816	-1.185	1.446	-0.02	2.01	197.22
46	C	45	33	32	2.927	-2.072	-1.414	-2.918	-2.053	1.389	0.00	-1.28	264.98
47	C	45	33	32	1.015	-1.171	-2.589	-1.010	-1.160	2.598	0.00	0.55	-95.87
48	C	46	45	33	3.156	-2.953	-2.475	-3.208	-2.884	2.473	0.00	-0.38	-0.93
49	H	46	45	33	3.586	-2.089	-0.552	-3.548	-2.082	0.506	0.00	0.26	-0.88
50	C	47	45	33	1.253	-2.044	-3.651	-1.310	-1.989	3.679	0.00	-0.62	1.72
51	H	47	45	33	0.180	-0.476	-2.641	-0.148	-0.500	2.646	0.00	0.31	1.41
52	C	48	46	45	2.323	-2.940	-3.594	-2.407	-2.853	3.617	0.00	-0.11	-0.48
53	H	48	46	45	3.991	-3.647	-2.425	-4.062	-3.553	2.422	0.00	0.04	359.89
54	H	50	47	45	0.604	-2.024	-4.523	-0.685	-1.963	4.566	0.00	-0.23	359.10
55	H	52	48	46	2.506	-3.624	-4.418	-2.637	-3.501	4.458	0.00	-0.17	-359.76
56	C	33	32	31	2.644	-0.447	1.257	-2.366	-0.625	-1.390	-0.01	-7.71	75.57
57	C	56	33	32	3.927	0.111	1.367	-3.504	0.047	-1.866	0.00	-0.14	276.17
58	C	56	33	32	2.230	-1.399	2.203	-1.919	-1.782	-2.056	0.00	-0.09	-83.80
59	C	57	56	33	4.779	-0.280	2.401	-4.185	-0.439	-2.983	0.00	-0.23	-0.65
60	H	57	56	33	4.261	0.855	0.650	-3.862	0.941	-1.366	0.00	0.14	-0.62
61	C	58	56	33	3.087	-1.795	3.231	-2.607	-2.264	-3.168	0.00	-0.18	-358.69
62	H	58	56	33	1.236	-1.833	2.133	-1.038	-2.311	-1.701	0.00	0.44	0.63
63	C	59	57	56	4.362	-1.234	3.332	-3.740	-1.592	-3.634	0.00	0.08	-0.08

64	H	59	57	56	5.769	0.161	2.478	-5.068	0.083	-3.342	0.00	-0.08	0.14
65	H	61	58	56	2.758	-2.535	3.954	-2.258	-3.161	-3.671	0.00	-0.08	359.29
66	H	63	59	57	5.027	-1.536	4.136	-4.274	-1.965	-4.503	0.00	-0.04	359.97

2.2. DFT calculation results for P2

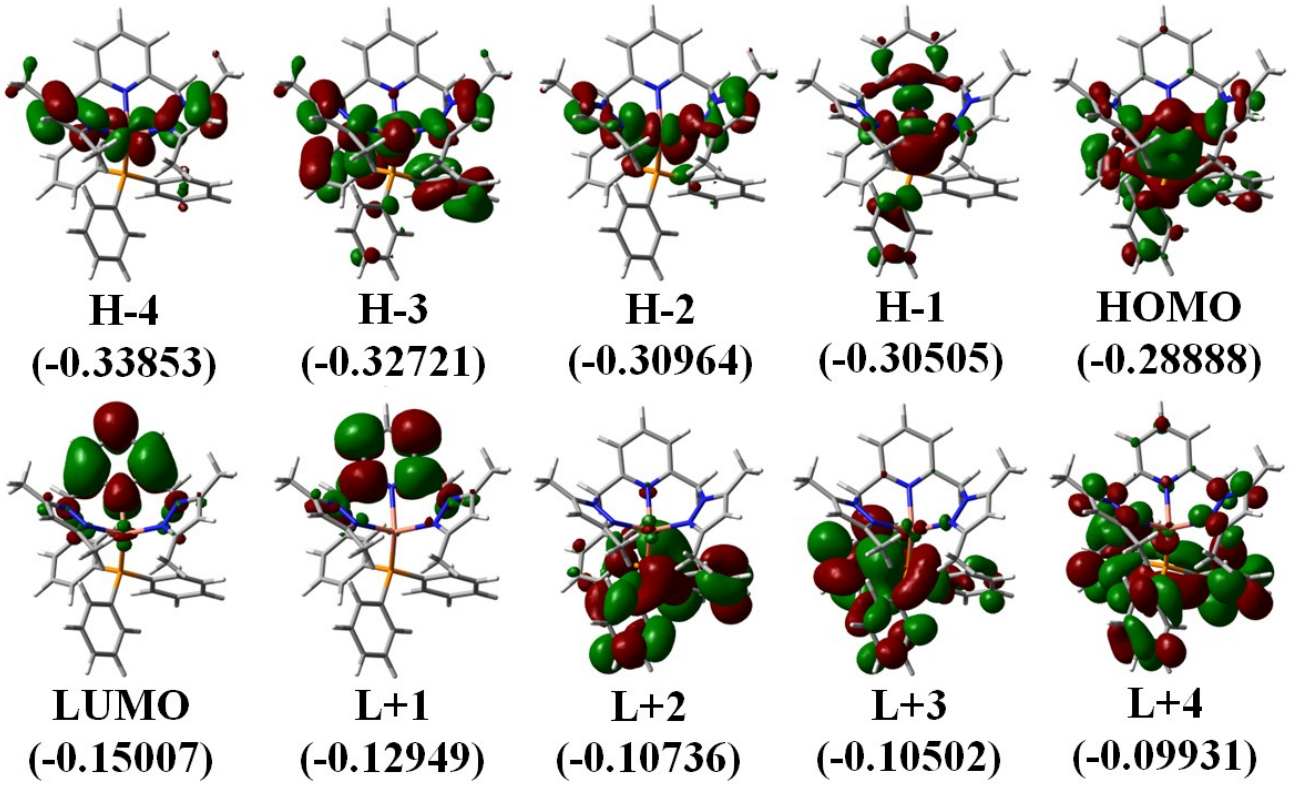


Fig. S6 Representations of the frontier MOs for **P2**. The MO energies are in a.u..

Table S3 Relative atomic contributions (in %) of the frontier MOs of compound **P2** separated by fragments. The grey boxes indicate the major contributions. (H = HOMO, L = LUMO)

Molecular Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Pyridine	1.01	1.46	0.41	17.96	1.24	**84.38**	**86.63**	1.77	1.71	5.50
Pyrazole groups	20.11	17.32	25.23	7.33	13.10	10.18	11.43	1.02	1.36	10.76
Copper	**75.11**	**50.81**	**69.19**	**68.24**	**44.02**	2.02	0.71	1.65	1.74	7.62
Triphenylphosphine	1.71	28.72	3.58	6.00	**40.85**	1.78	0.83	**94.39**	**94.49**	**72.12**
Methyl groups	1.47	1.69	1.60	0.47	0.79	1.65	0.41	1.17	0.71	4.01

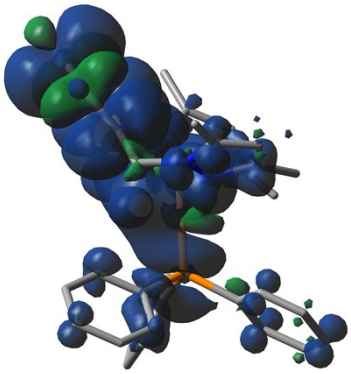


Fig. S7 Side view image of the spin density distribution for **P2** showing the mixed MLCT and LLCT

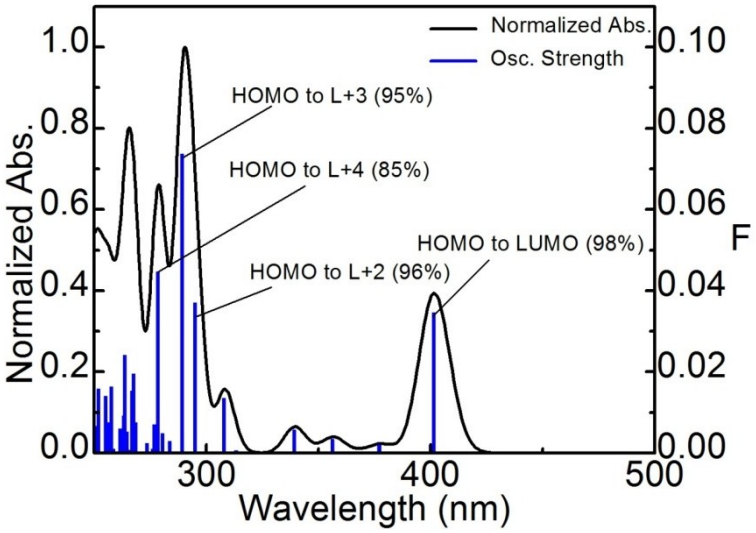


Fig. S8 Bar graph representing the positions of the first hundred electronic transitions (blue) for **P2**. Calculated spectrum by applying a thickness of 1000cm^{-1} to each bar (black). There is no vibronic component in these transitions. The assignments of the most intense transitions are provided.

Table S4 Calculated positions of the 100 first electronic transitions, oscillator strength (F) and major contributions to these electronic transitions for **P2**.

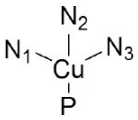
Wavelength (nm)	Osc. Strength	Major contributors (%)
401.3	0.0346	HOMO→LUMO (98%)
377.0	0.002	H-1→LUMO (98%)
356.3	0.0035	H-2→LUMO (99%)
339.1	0.0057	HOMO→L+1 (98%)
314.7	0	H-1→L+1 (98%)
313.2	0.0006	H-4→LUMO (91%)
307.8	0.0135	H-7→LUMO (17%), H-3→LUMO (75%)
298.3	0	H-2→L+1 (98%)

294.8	0.0371	HOMO→L+2 (96%)
289.1	0.0737	HOMO→L+3 (95%)
283.6	0.0029	H-8→LUMO (29%), H-7→LUMO (37%), H-6→LUMO (18%)
280.3	0.0049	H-8→LUMO (29%), H-7→LUMO (28%), H-6→LUMO (15%), H-3→LUMO (10%)
278.4	0.0447	HOMO→L+4 (85%)
276.7	0.007	H-11→LUMO (14%), H-10→LUMO (14%), H-9→LUMO (55%), H-5→LUMO (10%)
276.0	0.0011	H-6→LUMO (16%), H-5→LUMO (71%)
273.5	0.0024	H-11→LUMO (19%), H-8→LUMO (22%), H-6→LUMO (43%), H-5→LUMO (12%)
268.3	0.0076	HOMO→L+5 (55%), HOMO→L+6 (18%)
267.4	0.0196	H-13→LUMO (29%), H-12→LUMO (17%), H-1→L+2 (21%)
266.8	0.0154	H-4→L+1 (18%), H-1→L+2 (54%)
266.6	0.0003	H-4→L+1 (72%), H-1→L+2 (15%)
265.8	0.0008	H-7→L+1 (14%), H-3→L+1 (61%)
265.1	0.0003	H-11→LUMO (39%), H-10→LUMO (41%)
264.4	0.0052	H-1→L+3 (69%), HOMO→L+5 (10%)
263.6	0.0241	HOMO→L+5 (12%), HOMO→L+6 (49%), HOMO→L+7 (16%)
263.0	0.0092	H-12→LUMO (23%), H-11→LUMO (20%), H-10→LUMO (17%), H-9→LUMO (22%)
261.5	0.006	H-2→L+2 (81%)
258.3	0.001	H-13→LUMO (49%), H-12→LUMO (37%)
257.5	0.0163	H-2→L+3 (14%), HOMO→L+6 (17%), HOMO→L+7 (52%)
256.1	0.0075	H-14→LUMO (60%), H-1→L+4 (21%)
255.0	0.014	H-14→LUMO (32%), H-2→L+3 (10%), H-1→L+4 (44%)
251.7	0.0158	H-2→L+3 (47%), HOMO→L+7 (11%), HOMO→L+8 (17%)
251.1	0.004	H-8→L+1 (10%), H-7→L+1 (13%), HOMO→L+8 (42%)
250.8	0.0066	H-8→L+1 (20%), H-7→L+1 (21%), H-6→L+1 (12%), HOMO→L+8 (22%)
249.4	0.0095	H-2→L+4 (26%), H-1→L+5 (14%), H-1→L+6 (10%), HOMO→L+9 (26%)
248.4	0.0044	H-2→L+4 (43%), H-1→L+5 (22%), H-1→L+6 (12%)
247.8	0.002	H-8→L+1 (22%), H-7→L+1 (28%), H-6→L+1 (10%), H-3→L+1 (10%), HOMO→L+9 (13%)
247.3	0.0093	H-1→L+5 (12%), HOMO→L+9 (44%)
245.7	0.0041	H-11→L+1 (15%), H-10→L+1 (13%), H-9→L+1 (56%), H-5→L+1 (12%)
244.8	0.0033	H-6→L+1 (14%), H-5→L+1 (70%)
243.3	0.0029	H-6→L+1 (17%), H-1→L+6 (13%), H-1→L+7 (27%)
242.9	0.0046	H-11→L+1 (11%), H-8→L+1 (16%), H-6→L+1 (28%), H-1→L+7 (16%)
240.8	0.0134	H-2→L+4 (10%), H-2→L+5 (52%), H-2→L+6 (13%)
237.8	0.0045	H-13→L+1 (14%), H-2→L+6 (16%), H-2→L+7 (27%)
237.2	0.0138	H-13→L+1 (20%), H-12→L+1 (14%), H-10→L+1 (23%)
236.6	0.0001	H-5→L+2 (14%), H-1→L+6 (24%), H-1→L+7 (29%)
236.4	0.0006	H-11→L+1 (16%), H-10→L+1 (13%), H-4→L+2 (35%), H-3→L+2 (10%)

236.2	0.003	H-11→L+1 (26%), H-10→L+1 (13%), H-4→L+2 (25%)
235.0	0.0037	H-4→L+2 (10%), H-3→L+2 (29%)
234.6	0.0001	H-12→L+1 (30%), H-11→L+1 (13%), H-10→L+1 (14%), H-9→L+1 (17%)
234.2	0.0035	H-5→L+2 (20%), H-1→L+7 (10%)
233.4	0.0096	H-4→L+3 (20%), H-3→L+2 (13%), H-3→L+3 (28%)
233.0	0.0102	H-7→L+3 (10%), H-3→L+3 (23%)
231.6	0.0019	H-4→L+3 (41%)
231.4	0.0186	H-15→LUMO (16%), H-13→L+1 (15%), H-12→L+1 (13%)
230.7	0.0042	H-2→L+6 (10%), H-2→L+7 (24%)
229.5	0.0115	H-15→LUMO (21%), H-14→L+1 (30%), H-13→L+1 (26%), H-12→L+1 (11%)
229.0	0.0017	H-6→L+3 (13%), H-2→L+6 (15%), H-2→L+7 (15%)
227.0	0.0208	H-7→L+2 (19%), H-1→L+8 (43%)
226.8	0.0127	H-15→LUMO (28%), H-14→L+1 (53%)
226.0	0.0261	H-7→L+2 (32%), H-1→L+8 (24%)
225.8	0.0227	H-4→L+4 (57%), H-4→L+5 (10%)
225.1	0.004	H-1→L+9 (55%)
224.5	0.0038	H-6→L+2 (19%), H-5→L+3 (55%)
224.0	0.0147	H-7→L+3 (17%), H-5→L+3 (13%), H-3→L+4 (10%), H-1→L+9 (17%)
223.5	0.0073	H-7→L+3 (35%), H-3→L+4 (13%)
223.2	0.0007	H-2→L+8 (72%), H-2→L+9 (15%)
221.8	0.0106	H-10→L+3 (16%), H-6→L+2 (17%), H-6→L+3 (10%)
221.4	0.0081	H-9→L+2 (10%), H-6→L+3 (13%), H-5→L+2 (10%)
220.5	0.0016	H-2→L+8 (11%), H-2→L+9 (44%)
220.0	0.0069	H-4→L+5 (30%), H-4→L+6 (14%), H-2→L+9 (23%)
220.0	0.0027	H-11→L+2 (13%), H-10→L+2 (28%), H-3→L+5 (10%)
219.4	0.0095	H-10→L+2 (16%), H-3→L+5 (15%), H-3→L+6 (14%)
218.3	0.0179	HOMO→L+10 (64%)
217.0	0.0032	H-9→L+3 (15%), H-8→L+2 (19%), H-5→L+4 (19%)
216.4	0.0031	H-9→L+3 (12%), H-4→L+7 (16%)
216.3	0.0118	H-8→L+2 (15%), H-4→L+7 (13%)
215.2	0.0209	H-8→L+2 (14%), H-5→L+4 (13%)
214.9	0.032	H-4→L+7 (10%), H-3→L+7 (18%)
214.4	0.0256	H-12→L+2 (11%), H-9→L+2 (20%), H-6→L+4 (34%)
214.0	0.0113	H-8→L+3 (60%)
213.6	0.0143	H-11→L+2 (30%), H-9→L+2 (19%), H-7→L+4 (13%)
212.8	0.0301	H-12→L+2 (23%), H-11→L+2 (15%), H-8→L+2 (10%), H-7→L+4 (14%)
212.2	0.043	H-12→L+3 (21%)
210.8	0.0022	H-9→L+4 (10%), H-8→L+4 (10%), H-3→L+6 (18%), H-3→L+7 (12%)
210.4	0.0027	H-12→L+3 (17%), H-7→L+4 (12%)
209.9	0.0035	H-4→L+5 (12%), H-4→L+6 (30%), H-4→L+7 (33%)
209.4	0.0015	H-11→L+3 (22%), H-10→L+3 (21%), H-9→L+3 (42%)
209.2	0.0086	H-11→L+3 (12%), H-10→L+4 (18%), H-5→L+6 (13%)

208.7	0.0064	H-20→LUMO (32%), H-16→LUMO (48%)
208.0	0.0094	H-8→L+4 (38%)
207.5	0.0027	H-9→L+4 (18%), H-7→L+5 (10%), HOMO→L+11 (10%)
207.2	0.0043	H-13→L+2 (59%)
207.2	0.006	H-13→L+3 (11%), H-12→L+3 (13%), H-11→L+4 (11%)
206.2	0.0182	H-9→L+4 (27%), H-7→L+5 (15%)
206.2	0.0667	H-11→L+4 (22%), H-10→L+4 (20%)
205.8	0.009	H-7→L+5 (14%), H-5→L+5 (11%), HOMO→L+11 (34%)
205.6	0.039	H-6→L+5 (21%), H-5→L+5 (32%), H-3→L+8 (10%)
205.2	0.0025	H-13→L+3 (21%), H-12→L+4 (15%), H-6→L+6 (16%), H-5→L+5 (11%)
204.6	0.0003	H-4→L+8 (32%), H-4→L+9 (10%)
204.2	0.0225	H-4→L+8 (23%), H-3→L+8 (13%), HOMO→L+11 (13%)

Table S5 Geometric parameters about the Cu atom for compound **P2** in the S_0 and T_1 states.



Geometric Parameter		Singlet State	Triplet State	Difference
Bond Length (Å)	P-Cu	2.2917	2.4562	0.1645
	N_1-Cu	2.1685	2.0505	0.118
	N_2-Cu	2.2118	1.9678	0.244
	N_3-Cu	2.1321	2.0555	0.0766
Bond Angle (°)	P-Cu-N_1	115.7127	100.2039	15.5088
	P-Cu-N_2	120.7304	136.9787	16.2483
	P-Cu-N_3	118.2728	104.6745	13.5983
	N_1-Cu-N_2	88.0893	92.7585	4.6692
	N_2-Cu-N_3	91.4159	96.2704	4.8545
	N_3-Cu-N_1	116.5384	131.6441	15.1057

Table S6 Conformational analysis comparing the optimized structures of the singlet and triplet states of **P2**.

Atom ID					Singlet State			Triplet State			Conformation Change		
Tag	Symbol	NA	NB	NC	X	Y	Z	X	Y	Z	Δ Bond	Δ Angle	Δ Dihedral
1	C				-2.510	-1.381	-1.562	-2.940	-1.350	-1.153			
2	C	1			-3.658	-1.603	-2.323	-4.166	-1.533	-1.750	-0.02		
3	C	2	1		-4.405	-0.507	-2.752	-4.998	-0.435	-2.059	0.02	2.17	
4	C	3	2	1	-3.980	0.774	-2.405	-4.479	0.850	-1.787	0.02	-2.16	3.11
5	C	4	3	2	-2.816	0.917	-1.647	-3.248	1.008	-1.194	-0.02	2.12	-3.25
6	N	5	4	3	-2.096	-0.142	-1.239	-2.454	-0.079	-0.810	0.05	0.42	-0.81
7	H	3	2	1	-5.302	-0.649	-3.347	-5.968	-0.569	-2.521	0.00	1.05	-359.33

8	H	2	1	6	-3.957	-2.615	-2.578	-4.479	-2.544	-1.999	0.00	-1.54	0.27
9	H	4	3	2	-4.535	1.650	-2.724	-5.039	1.738	-2.070	0.00	-0.61	-4.32
10	C	1	6	5	-1.652	-2.519	-1.046	-2.010	-2.501	-0.919	-0.02	5.47	3.89
11	H	10	1	6	-0.602	-2.324	-1.287	-1.059	-2.360	-1.452	0.00	1.77	168.72
12	H	10	1	6	-1.941	-3.460	-1.516	-2.456	-3.433	-1.266	0.00	0.12	167.78
13	C	5	4	3	-2.270	2.281	-1.277	-2.619	2.361	-1.084	-0.02	-0.96	-6.54
14	H	13	5	4	-2.847	3.062	-1.773	-3.322	3.131	-1.400	0.00	0.29	13.78
15	H	13	5	4	-1.231	2.359	-1.618	-1.729	2.430	-1.731	0.01	1.41	12.91
16	N	13	5	4	-2.294	2.563	0.154	-2.167	2.717	0.266	0.01	0.49	13.94
17	C	16	13	5	-2.944	3.580	0.796	-2.563	3.745	1.057	-0.01	1.29	1.14
18	C	16	13	5	-1.520	2.543	2.171	-0.824	2.679	1.974	0.01	0.18	-8.44
19	C	17	16	13	-2.471	3.582	2.095	-1.720	3.741	2.161	0.01	0.29	-3.66
20	H	19	17	16	-2.768	4.255	2.886	-1.749	4.429	2.993	0.00	0.01	359.70
21	N	10	1	6	-1.775	-2.691	0.396	-1.680	-2.677	0.501	0.01	0.31	-192.17
22	C	21	10	1	-2.335	-3.733	1.077	-2.093	-3.635	1.366	-0.01	1.06	-5.27
23	C	22	21	10	-2.210	-3.422	2.419	-1.658	-3.239	2.625	0.01	0.34	8.41
24	C	23	22	21	-1.569	-2.169	2.478	-1.004	-2.012	2.455	-0.01	0.29	0.76
25	H	23	22	21	-2.536	-4.027	3.253	-1.804	-3.772	3.553	0.00	0.03	-0.01
26	N	24	23	22	-1.304	-1.725	1.239	-1.011	-1.678	1.146	0.01	-0.88	-0.98
27	N	18	16	13	-1.420	1.922	0.987	-1.108	2.051	0.811	0.01	-0.45	7.63
28	Cu	27	18	16	-0.550	0.091	0.326	-0.772	0.120	0.191	-0.16	-11.53	-7.36
29	C	22	21	10	-2.925	-4.938	0.415	-2.869	-4.843	0.947	0.00	-0.39	7.41
30	H	29	22	21	-3.288	-5.629	1.179	-3.058	-5.475	1.817	0.00	0.17	-0.56
31	H	29	22	21	-3.775	-4.683	-0.230	-3.838	-4.569	0.514	0.00	-0.65	-0.48
32	H	29	22	21	-2.189	-5.477	-0.195	-2.327	-5.444	0.207	0.00	-0.06	-0.96
33	C	24	23	22	-1.218	-1.386	3.704	-0.419	-1.138	3.519	0.00	0.11	-2.63
34	H	33	24	23	-0.235	-0.916	3.613	0.613	-0.854	3.296	0.00	0.54	-10.65
35	H	33	24	23	-1.954	-0.596	3.893	-1.009	-0.223	3.644	0.00	-0.20	-9.96
36	H	33	24	23	-1.205	-2.041	4.580	-0.423	-1.667	4.476	0.00	-0.37	-10.31
37	C	18	16	13	-0.669	2.156	3.340	0.323	2.286	2.853	0.00	0.67	8.52
38	H	37	18	16	-0.160	3.036	3.748	1.034	3.116	2.942	0.00	-0.14	-10.08
39	H	37	18	16	-1.267	1.724	4.150	-0.017	2.044	3.866	0.00	-0.38	-10.49
40	H	37	18	16	0.089	1.428	3.044	0.862	1.423	2.459	0.00	1.11	-10.21
41	C	17	16	13	-3.944	4.474	0.132	-3.696	4.658	0.713	0.00	-0.25	-3.51
42	H	41	17	16	-4.776	3.908	-0.305	-4.625	4.103	0.543	0.00	-0.47	-0.71
43	H	41	17	16	-4.364	5.161	0.870	-3.866	5.356	1.536	0.00	0.12	-0.51
44	H	41	17	16	-3.493	5.080	-0.664	-3.488	5.250	-0.187	0.00	-0.16	-0.25
45	P	28	27	18	1.676	0.081	-0.216	1.632	0.035	-0.303	0.16	18.71	-17.48
46	C	45	28	27	2.341	1.666	-0.884	2.370	1.545	-1.051	0.00	0.87	110.60
47	C	46	45	28	3.360	1.713	-1.849	3.440	1.438	-1.957	0.00	-2.34	-0.84
48	C	46	45	28	1.815	2.871	-0.389	1.893	2.818	-0.701	0.00	2.12	-0.34
49	C	47	46	45	3.841	2.941	-2.307	4.022	2.584	-2.496	0.00	-0.09	0.76
50	H	47	46	45	3.777	0.794	-2.247	3.816	0.461	-2.245	0.00	0.04	0.72

51	C	48	46	45	2.304	4.097	-0.843	2.481	3.963	-1.243	0.00	-0.21	-0.49
52	H	48	46	45	1.021	2.847	0.352	1.061	2.915	-0.015	0.00	0.38	-0.98
53	C	49	47	46	3.316	4.134	-1.805	3.544	3.848	-2.140	0.00	-0.09	0.02
54	H	49	47	46	4.629	2.965	-3.055	4.847	2.490	-3.195	0.00	0.00	359.87
55	H	51	48	46	1.893	5.022	-0.448	2.104	4.943	-0.967	0.00	-0.10	359.59
56	H	53	49	47	3.694	5.088	-2.162	3.998	4.740	-2.563	0.00	0.03	-0.20
57	C	45	28	27	2.117	-1.155	-1.518	1.798	-1.227	-1.634	-0.01	-8.75	116.47
58	C	57	45	28	3.084	-2.153	-1.329	2.761	-2.247	-1.618	0.00	0.43	-9.98
59	C	57	45	28	1.429	-1.100	-2.744	0.935	-1.117	-2.740	0.00	-0.76	-6.46
60	C	58	57	45	3.355	-3.076	-2.343	2.855	-3.141	-2.687	0.00	-0.21	-356.58
61	H	58	57	45	3.629	-2.212	-0.393	3.443	-2.344	-0.780	0.00	0.30	3.12
62	C	59	57	45	1.710	-2.015	-3.758	1.038	-2.008	-3.808	0.00	-0.20	356.95
63	H	59	57	45	0.680	-0.329	-2.911	0.188	-0.327	-2.774	0.00	0.33	-3.23
64	C	60	58	57	2.672	-3.009	-3.558	1.996	-3.024	-3.781	0.00	-0.01	-0.10
65	H	60	58	57	4.107	-3.843	-2.182	3.606	-3.925	-2.664	0.00	-0.02	-0.11
66	H	62	59	57	1.179	-1.952	-4.705	0.371	-1.907	-4.660	0.00	-0.10	-0.32
67	H	64	60	58	2.890	-3.724	-4.347	2.076	-3.719	-4.612	0.00	-0.08	0.10
68	C	45	28	27	2.781	-0.329	1.202	2.784	-0.473	1.035	-0.01	4.85	-242.54
69	C	68	45	28	3.993	0.336	1.440	3.803	0.380	1.486	0.00	-1.43	18.77
70	C	68	45	28	2.380	-1.350	2.082	2.610	-1.722	1.660	0.00	1.31	16.47
71	C	69	68	45	4.787	-0.014	2.535	4.637	-0.012	2.535	0.00	-0.04	-1.91
72	H	69	68	45	4.318	1.130	0.775	3.953	1.346	1.016	0.00	0.05	-2.59
73	C	70	68	45	3.181	-1.705	3.167	3.454	-2.113	2.700	0.00	-0.16	-358.07
74	H	70	68	45	1.441	-1.870	1.913	1.823	-2.394	1.329	0.00	0.35	2.20
75	C	71	69	68	4.385	-1.035	3.397	4.468	-1.258	3.141	0.00	0.02	-0.16
76	H	71	69	68	5.721	0.512	2.709	5.424	0.656	2.872	0.00	-0.06	359.52
77	H	73	70	68	2.864	-2.501	3.835	3.319	-3.085	3.166	0.00	-0.14	0.31
78	H	75	71	69	5.006	-1.306	4.247	5.122	-1.563	3.952	0.00	0.04	-0.31

2.3. DFT calculation results for P3

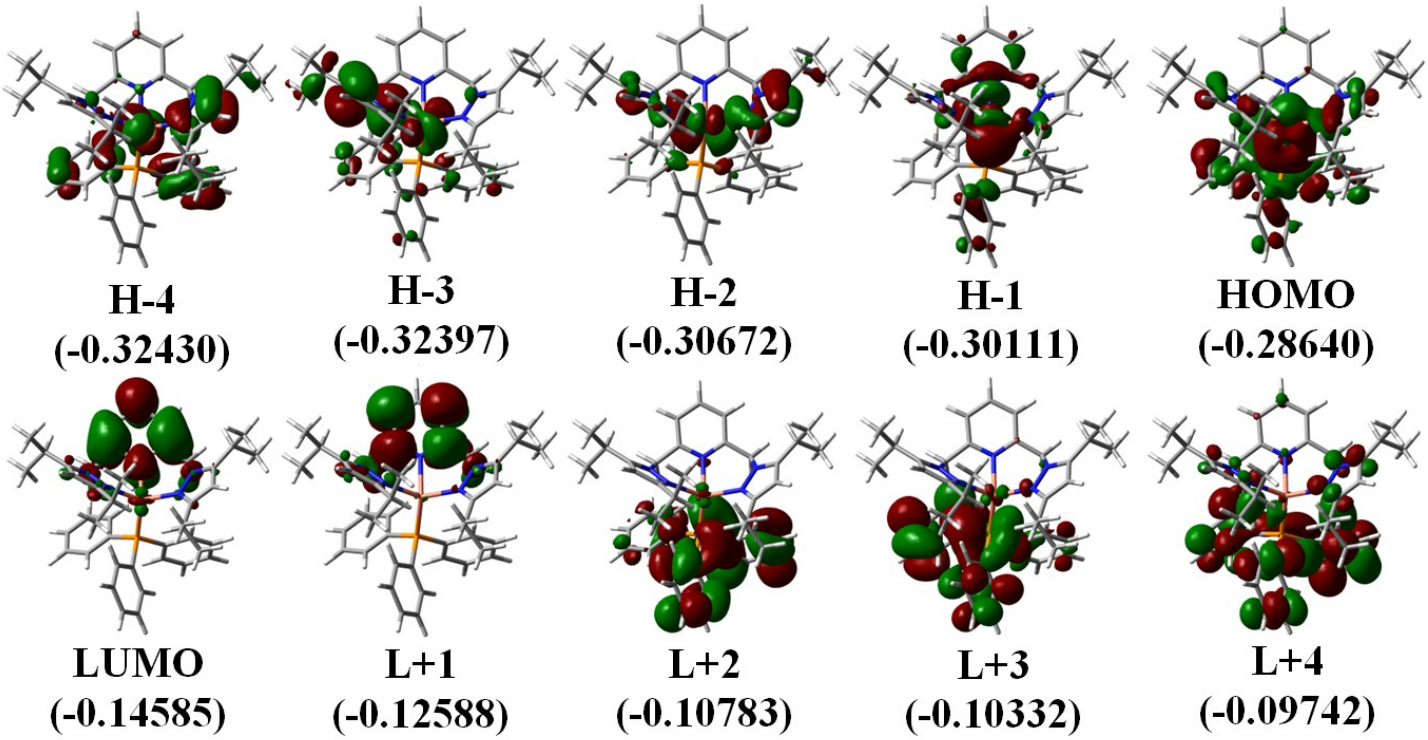


Fig. S9 Representations of the frontier MOs for **P3**. The MO energies are in a.u.

Table S7 Relative atomic contributions (in %) of the frontier MOs of compound **P3** separated by fragments. The grey boxes indicate the major contributions. (H = HOMO, L = LUMO)

Molecular Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Pyridine	1.94	1.08	0.44	18.42	1.22	**84.05**	**86.50**	1.24	1.80	6.06
Pyrazole groups	13.42	28.38	25.55	7.31	13.56	10.04	11.21	0.68	1.65	5.32
Copper	**70.18**	**59.61**	**68.43**	**67.82**	**45.49**	2.44	0.54	2.05	3.51	5.58
Triphenylphosphine	12.73	7.51	3.16	5.67	**38.55**	1.54	0.87	**95.44**	**92.45**	**78.26**
Isopropyl groups	1.73	3.42	2.42	0.78	1.17	1.92	0.88	0.59	0.59	4.78

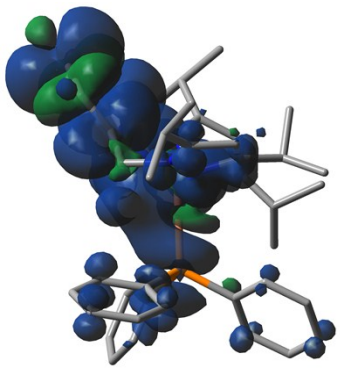


Fig. S10 Side view image of the spin density distribution for **P3** showing the mixed MLCT and LLCT

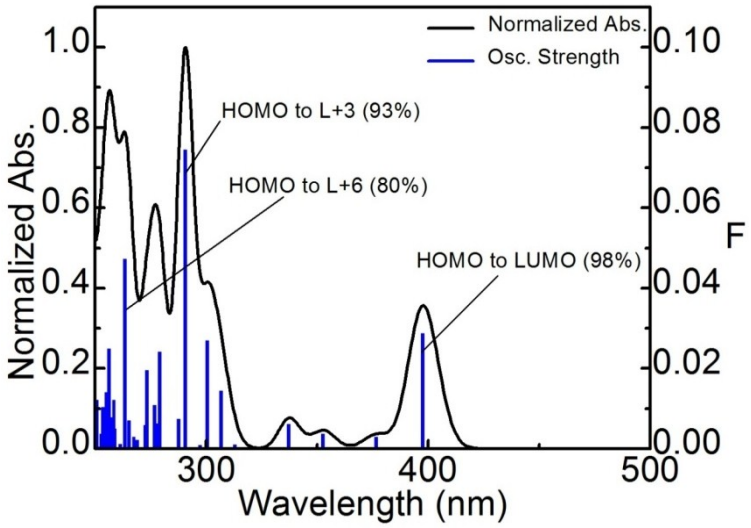


Fig.S11 Bar graph representing the positions of the first hundred electronic transitions (blue) for **P3**. Calculated spectrum by applying a thickness of 1000cm^{-1} to each bar (black). There is no vibronic component in these transitions. The assignments of the most intense transitions are provided.

Table S8 Calculated positions of the 100 first electronic transitions, oscillator strength (F) and major contributions to these electronic transitions for **P3**.

Wavelength (nm)	Osc. Strength	Major contributors (%)
397.3	0.0288	HOMO→LUMO (98%)
376.4	0.0029	H-1→LUMO (98%)
352.5	0.0037	H-2→LUMO (98%)
337.2	0.0062	HOMO→L+1 (98%)
315.9	0.0001	H-1→L+1 (98%)
312.8	0.0011	H-4→LUMO (21%), H-3→LUMO (69%)
306.7	0.0145	H-4→LUMO (66%), H-3→LUMO (17%)
300.3	0.0269	HOMO→L+2 (96%)
297.1	0.0009	H-2→L+1 (98%)
290.4	0.0744	HOMO→L+3 (93%)
287.4	0.0074	H-5→LUMO (86%)
279.0	0.0242	HOMO→L+4 (89%)
278.1	0.0063	H-9→LUMO (53%), H-8→LUMO (33%)
276.7	0.0109	H-9→LUMO (33%), H-8→LUMO (12%), H-7→LUMO (19%)
273.1	0.0196	H-1→L+2 (84%)
272.6	0.0059	HOMO→L+5 (73%)
270.6	0.0004	H-12→LUMO (11%), H-6→LUMO (72%)
268.8	0.0022	H-8→LUMO (32%), H-7→LUMO (39%)
268.0	0.0014	H-1→L+3 (71%)

267.8	0.0002	H-4→L+1 (52%), H-3→L+1 (22%)
267.3	0.003	H-13→LUMO (14%), H-12→LUMO (28%), H-6→LUMO (12%), H-3→L+1 (24%)
266.1	0.0003	H-4→L+1 (32%), H-3→L+1 (37%), H-2→L+2 (11%)
265.1	0.0071	H-2→L+2 (72%)
263.4	0.0473	HOMO→L+6 (80%)
261.1	0.0012	H-10→LUMO (73%), H-7→LUMO (10%)
258.6	0.005	H-11→LUMO (88%)
258.3	0.0122	H-14→LUMO (60%), H-2→L+3 (10%), HOMO→L+7 (12%)
257.7	0.0078	H-14→LUMO (21%), H-2→L+3 (12%), H-1→L+4 (23%), HOMO→L+7 (18%)
256.2	0.0249	H-2→L+3 (16%), H-1→L+4 (45%), HOMO→L+7 (10%)
254.9	0.0141	H-5→L+1 (83%)
254.4	0.0039	H-2→L+3 (18%), H-1→L+5 (41%), HOMO→L+7 (10%)
253.4	0.0104	H-13→LUMO (11%), H-2→L+3 (19%), H-1→L+5 (13%), HOMO→L+7 (27%)
252.6	0.0037	H-13→LUMO (50%), H-12→LUMO (22%)
251.7	0.0005	H-1→L+5 (10%), HOMO→L+8 (77%)
250.7	0.0122	HOMO→L+9 (65%)
247.8	0.0119	H-9→L+1 (15%), H-2→L+4 (63%)
247.5	0.0081	H-9→L+1 (49%), H-8→L+1 (21%), H-2→L+4 (20%)
245.6	0.0021	H-9→L+1 (23%), H-8→L+1 (21%), H-7→L+1 (26%)
244.7	0.0212	H-4→L+2 (10%), H-2→L+5 (62%)
242.2	0.0044	H-4→L+2 (11%), H-1→L+6 (56%)
241.2	0.0054	H-12→L+1 (10%), H-6→L+1 (77%)
240.5	0.0094	H-4→L+2 (17%), H-3→L+2 (30%), H-1→L+6 (15%), H-1→L+7 (10%), H-1→L+9 (10%)
240.3	0.0061	H-3→L+2 (39%), H-1→L+7 (13%), H-1→L+9 (13%)
240.0	0.0022	H-8→L+1 (27%), H-7→L+1 (38%)
238.5	0.0034	H-13→L+1 (19%), H-12→L+1 (46%), H-6→L+1 (13%)
238.4	0.0012	H-4→L+2 (28%), H-1→L+7 (18%), H-1→L+9 (11%)
236.7	0.0014	H-6→L+2 (34%), H-1→L+8 (10%)
235.7	0.0013	H-4→L+3 (59%)
235.2	0.0019	H-7→L+2 (10%), H-3→L+3 (19%), H-2→L+6 (17%)
235.0	0.0131	H-3→L+3 (18%), H-2→L+6 (35%)
234.3	0.0071	H-10→L+1 (11%), H-3→L+3 (22%)
233.9	0.0038	H-10→L+1 (56%)
232.1	0.0017	H-11→L+1 (10%), H-2→L+7 (22%), H-2→L+9 (22%)
232.0	0.0055	H-14→L+1 (10%), H-11→L+1 (65%)
231.3	0.0104	H-1→L+8 (19%)
231.0	0.0079	H-15→LUMO (10%), H-14→L+1 (55%), H-11→L+1 (13%)
229.6	0.0006	H-1→L+7 (42%), H-1→L+9 (46%)
229.1	0.0148	H-1→L+8 (36%)

228.1	0.0254	H-15→LUMO (39%), H-14→L+1 (11%), H-13→L+1 (10%), H-12→L+1 (12%)
227.9	0.0338	H-7→L+2 (12%), H-5→L+2 (25%)
226.7	0.0098	H-4→L+4 (31%), H-3→L+4 (21%), H-3→L+5 (10%)
226.3	0.0133	H-15→LUMO (13%), H-14→L+1 (12%), H-13→L+1 (47%), H-12→L+1 (14%)
225.9	0.0058	H-4→L+4 (29%), H-4→L+5 (16%), H-3→L+5 (21%)
225.2	0.0015	H-3→L+4 (15%), H-2→L+8 (64%)
224.6	0.0252	H-4→L+5 (15%)
224.4	0.0127	H-4→L+5 (15%), H-3→L+4 (15%), H-3→L+5 (22%)
224.2	0.0065	H-7→L+2 (13%), H-5→L+2 (12%), H-3→L+4 (15%), H-2→L+8 (11%)
223.6	0.0128	H-7→L+3 (12%), H-4→L+5 (10%), H-2→L+7 (14%)
223.0	0.0059	H-2→L+7 (27%), H-2→L+9 (34%)
222.7	0.0067	H-10→L+2 (15%), H-7→L+3 (19%), H-6→L+3 (21%)
222.3	0.0018	H-10→L+2 (27%), H-6→L+3 (37%)
221.3	0.0053	H-8→L+3 (10%), H-5→L+3 (21%)
220.5	0.0013	H-11→L+2 (15%), H-9→L+2 (32%)
219.8	0.0015	H-9→L+2 (42%), H-8→L+2 (16%), HOMO→L+10 (22%)
219.5	0.0006	H-8→L+3 (40%), H-5→L+3 (32%)
218.7	0.0156	H-11→L+2 (18%), HOMO→L+10 (42%)
216.4	0.0057	H-12→L+2 (17%), H-11→L+2 (18%), H-11→L+3 (12%)
215.8	0.0049	H-12→L+2 (20%), H-11→L+3 (13%), H-6→L+4 (10%)
215.4	0.0038	H-4→L+6 (21%), H-3→L+6 (26%)
215.0	0.0199	H-10→L+3 (20%), H-7→L+4 (15%), H-4→L+6 (17%)
214.1	0.0045	H-4→L+7 (14%), H-4→L+9 (12%), H-3→L+6 (29%)
213.8	0.0385	H-12→L+2 (15%), H-12→L+3 (11%), H-5→L+4 (22%)
213.5	0.016	H-4→L+6 (24%)
213.0	0.0027	H-9→L+3 (78%)
212.5	0.016	H-12→L+3 (21%), H-7→L+4 (33%)
212.3	0.0194	H-12→L+3 (14%), H-8→L+4 (14%), H-5→L+4 (14%)
211.9	0.0204	H-3→L+7 (30%), H-3→L+9 (20%)
211.7	0.0092	H-13→L+2 (43%)
210.2	0.0281	H-9→L+4 (64%)
210.1	0.0138	H-13→L+2 (13%), H-8→L+4 (14%), H-6→L+5 (26%), H-6→L+6 (12%)
209.7	0.0121	H-10→L+4 (24%), H-7→L+5 (14%)
209.6	0.0064	H-13→L+3 (11%), H-12→L+3 (10%), H-10→L+4 (17%)
208.9	0.0152	H-11→L+4 (11%), H-5→L+5 (33%)
208.2	0.0015	H-16→LUMO (11%), H-14→L+2 (46%)
207.8	0.0115	H-14→L+2 (23%), H-4→L+8 (12%)
207.6	0.0049	H-16→LUMO (17%), H-11→L+4 (10%), H-5→L+5 (15%)
207.2	0.0098	H-4→L+8 (38%), H-3→L+8 (22%)
207.0	0.0102	H-13→L+3 (26%), H-11→L+4 (12%), H-3→L+8 (24%)
206.8	0.0059	H-8→L+5 (17%), H-7→L+5 (16%), H-5→L+5 (14%), H-3→L+8 (14%)

206.5	0.0015	H-5→L+6 (20%), H-4→L+8 (17%), H-3→L+8 (10%)

Table S9 Geometric parameters about the Cu atom for compound **P3** in the S_0 and T_1 states.

Geometric Parameter		Singlet State	Triplet State	Difference
Bond Length (Å)	P-Cu	2.3017	2.4816	0.1799
	N_1-Cu	2.1948	2.0514	0.1434
	N_2-Cu	2.2004	1.9616	0.2388
	N_3-Cu	2.1393	2.065	0.0743
Bond Angle (°)	P-Cu-N_1	116.9162	99.9871	16.9291
	P-Cu-N_2	120.3971	135.1859	14.7888
	P-Cu-N_3	115.7171	104.3478	11.3693
	N_1-Cu-N_2	86.6203	91.148	4.5277
	N_2-Cu-N_3	92.6067	97.064	4.4573
	N_3-Cu-N_1	118.6491	135.276	16.6269

Table S10 Conformational analysis comparing the optimized structures of the singlet and triplet states of **P3**.

Atom ID					Singlet State			Triplet State			Conformation Change		
Tag	Symbol	NA	NB	NC	X	Y	Z	X	Y	Z	Δ Bond	Δ Angle	Δ Dihedral
1	C				1.075	-2.018	-2.260	0.968	-2.671	-1.797			
2	C	1			1.129	-3.079	-3.166	0.989	-3.856	-2.495	-0.02		
3	C	2	1		-0.059	-3.561	-3.710	-0.208	-4.498	-2.877	0.02	2.15	
4	C	3	2	1	-1.262	-2.965	-3.335	-1.414	-3.819	-2.589	0.02	-2.11	3.94
5	C	4	3	2	-1.236	-1.901	-2.432	-1.409	-2.631	-1.896	-0.02	2.02	-4.13
6	N	5	4	3	-0.087	-1.440	-1.907	-0.232	-2.050	-1.417	0.05	0.33	-1.10
7	H	3	2	1	-0.048	-4.385	-4.418	-0.202	-5.437	-3.416	0.00	1.00	-359.21
8	H	2	1	6	2.085	-3.514	-3.440	1.951	-4.283	-2.769	0.00	-1.50	0.30
9	H	4	3	2	-2.205	-3.312	-3.744	-2.363	-4.214	-2.943	0.00	-0.57	-5.53
10	C	1	6	5	2.317	-1.455	-1.600	2.225	-1.920	-1.482	-0.02	5.99	3.86
11	H	10	1	6	2.286	-0.362	-1.630	2.193	-0.902	-1.891	0.00	1.52	167.73
12	H	10	1	6	3.214	-1.784	-2.123	3.093	-2.424	-1.906	0.00	0.13	166.98
13	C	5	4	3	-2.499	-1.162	-2.041	-2.647	-1.799	-1.793	-0.02	-0.73	-7.17
14	H	13	5	4	-3.334	-1.516	-2.644	-3.500	-2.344	-2.194	0.00	0.38	14.73
15	H	13	5	4	-2.366	-0.094	-2.249	-2.534	-0.874	-2.381	0.01	1.26	13.79
16	N	13	5	4	-2.882	-1.297	-0.637	-3.006	-1.371	-0.433	0.01	0.42	14.91
17	C	16	13	5	-4.062	-1.771	-0.131	-4.155	-1.596	0.255	-0.01	1.01	0.58
18	C	16	13	5	-2.880	-0.704	1.445	-2.885	-0.089	1.324	0.01	0.74	-7.75

19	C	17	16	13	-4.077	-1.410	1.206	-4.097	-0.790	1.387	0.01	0.30	-3.44
20	H	19	17	16	-4.855	-1.631	1.921	-4.844	-0.720	2.163	0.00	0.00	-0.40
21	N	10	1	6	2.429	-1.882	-0.210	2.456	-1.797	-0.033	0.01	0.69	-192.93
22	C	21	10	1	3.340	-2.736	0.347	3.382	-2.414	0.747	-0.01	0.77	-2.78
23	C	22	21	10	2.936	-2.915	1.659	2.984	-2.205	2.062	0.01	0.43	7.77
24	C	23	22	21	1.763	-2.149	1.824	1.787	-1.473	2.011	-0.01	0.27	0.64
25	H	23	22	21	3.424	-3.524	2.404	3.491	-2.553	2.949	0.00	-0.08	-0.20
26	N	24	23	22	1.457	-1.518	0.681	1.482	-1.211	0.723	0.01	-1.01	-1.23
27	N	18	16	13	-2.150	-0.646	0.321	-2.213	-0.455	0.207	0.01	-0.34	6.72
28	Cu	27	18	16	-0.103	-0.186	-0.099	-0.193	-0.496	-0.221	-0.18	-10.30	-6.84
29	C	22	21	10	4.550	-3.270	-0.382	4.594	-3.123	0.195	0.00	-0.50	6.84
30	C	29	22	21	5.084	-4.547	0.285	5.203	-4.079	1.232	0.00	0.04	-2.39
31	C	29	22	21	5.658	-2.198	-0.480	5.648	-2.111	-0.308	0.00	-0.05	-2.55
32	H	29	22	21	4.248	-3.540	-1.404	4.270	-3.731	-0.661	0.00	-0.46	-2.40
33	H	30	29	22	4.311	-5.319	0.356	4.468	-4.808	1.589	0.00	-0.02	0.14
34	H	30	29	22	5.919	-4.951	-0.296	6.038	-4.628	0.787	0.00	-0.09	-0.08
35	H	30	29	22	5.455	-4.341	1.295	5.593	-3.531	2.098	0.00	0.10	-0.06
36	H	31	29	22	5.311	-1.288	-0.983	5.243	-1.437	-1.070	0.00	-0.05	0.40
37	H	31	29	22	6.004	-1.914	0.520	6.015	-1.497	0.522	0.00	0.05	0.53
38	H	31	29	22	6.515	-2.589	-1.039	6.503	-2.641	-0.741	0.00	-0.12	0.41
39	C	24	23	22	0.915	-2.044	3.064	0.869	-1.134	3.157	0.00	0.42	-5.88
40	C	39	24	23	1.733	-1.549	4.271	1.644	-0.692	4.409	0.00	0.54	-14.81
41	C	39	24	23	0.244	-3.398	3.374	-0.030	-2.351	3.472	0.00	-1.02	-14.29
42	H	39	24	23	0.128	-1.311	2.855	0.225	-0.305	2.840	0.00	0.82	-14.17
43	H	40	39	24	2.217	-0.587	4.064	2.306	0.155	4.202	0.00	0.27	-0.33
44	H	40	39	24	1.086	-1.425	5.146	0.947	-0.396	5.200	0.00	-0.18	-0.29
45	H	40	39	24	2.519	-2.265	4.538	2.259	-1.509	4.803	0.00	-0.01	-0.65
46	H	41	39	24	-0.386	-3.730	2.541	-0.641	-2.631	2.607	0.00	0.10	-1.02
47	H	41	39	24	0.995	-4.175	3.560	0.579	-3.219	3.749	0.00	-0.42	-1.17
48	H	41	39	24	-0.382	-3.321	4.270	-0.698	-2.130	4.311	0.00	0.03	358.79
49	C	18	16	13	-2.457	0.003	2.709	-2.403	0.981	2.273	0.00	1.27	5.60
50	C	49	18	16	-2.691	-0.863	3.958	-2.581	0.566	3.745	0.00	-0.08	2.09
51	C	49	18	16	-3.191	1.355	2.843	-3.143	2.310	2.006	0.00	-0.06	2.81
52	H	49	18	16	-1.385	0.218	2.620	-1.336	1.148	2.086	0.00	0.80	1.93
53	H	50	49	18	-2.192	-1.834	3.881	-2.091	-0.387	3.963	0.00	0.08	-0.13
54	H	50	49	18	-2.313	-0.352	4.850	-2.159	1.332	4.404	0.00	-0.21	-0.14
55	H	50	49	18	-3.760	-1.048	4.116	-3.642	0.462	4.000	0.00	-0.01	-0.17
56	H	51	49	18	-2.997	2.004	1.983	-3.011	2.650	0.974	0.00	0.32	0.48
57	H	51	49	18	-4.274	1.207	2.921	-4.218	2.199	2.190	0.00	-0.28	0.32
58	H	51	49	18	-2.854	1.879	3.744	-2.763	3.092	2.672	0.00	-0.10	0.19
59	C	17	16	13	-5.104	-2.494	-0.951	-5.246	-2.528	-0.215	0.00	-0.28	-3.41
60	C	59	17	16	-6.107	-1.503	-1.579	-6.236	-1.798	-1.149	0.00	-0.08	2.05
61	C	59	17	16	-5.836	-3.553	-0.108	-5.982	-3.165	0.975	0.00	-0.05	2.01

62	H	59	17	16	-4.592	-3.026	-1.764	-4.774	-3.341	-0.782	0.00	-0.32	1.92
63	H	60	59	17	-5.611	-0.754	-2.208	-5.737	-1.362	-2.021	0.00	-0.02	0.20
64	H	60	59	17	-6.833	-2.038	-2.201	-6.998	-2.496	-1.511	0.00	-0.20	0.00
65	H	60	59	17	-6.658	-0.968	-0.798	-6.745	-0.988	-0.614	0.00	0.15	-0.08
66	H	61	59	17	-5.136	-4.270	0.332	-5.290	-3.691	1.641	0.00	0.03	0.33
67	H	61	59	17	-6.407	-3.090	0.704	-6.518	-2.412	1.563	0.00	0.10	0.59
68	H	61	59	17	-6.544	-4.105	-0.735	-6.721	-3.887	0.613	0.00	-0.11	0.55
69	P	28	27	18	0.410	2.054	-0.231	0.434	1.893	-0.459	0.18	19.47	-26.56
70	C	69	28	27	-0.850	3.101	-1.080	-0.692	2.836	-1.564	-0.01	-1.87	106.77
71	C	70	69	28	-0.514	4.265	-1.791	-0.237	3.975	-2.253	0.00	-1.90	-3.55
72	C	70	69	28	-2.202	2.731	-0.984	-2.027	2.430	-1.721	0.00	1.67	-4.44
73	C	71	70	69	-1.510	5.039	-2.391	-1.106	4.696	-3.072	0.00	-0.14	-0.39
74	H	71	70	69	0.525	4.566	-1.883	0.795	4.297	-2.155	0.00	0.09	-0.44
75	C	72	70	69	-3.196	3.511	-1.579	-2.893	3.155	-2.544	0.00	-0.21	0.73
76	H	72	70	69	-2.474	1.832	-0.438	-2.387	1.549	-1.202	0.00	0.26	0.45
77	C	75	72	70	-2.851	4.665	-2.285	-2.435	4.287	-3.218	0.00	0.03	-0.29
78	H	73	71	70	-1.235	5.936	-2.939	-0.745	5.575	-3.597	0.00	0.03	359.75
79	H	75	72	70	-4.238	3.216	-1.491	-3.923	2.831	-2.659	0.00	-0.07	359.57
80	H	77	75	72	-3.623	5.270	-2.752	-3.108	4.849	-3.860	0.00	-0.05	0.11
81	C	69	28	27	1.964	2.428	-1.161	2.044	1.959	-1.355	0.00	-6.83	112.98
82	C	81	69	28	3.114	2.934	-0.539	3.240	2.368	-0.750	0.00	0.43	0.56
83	C	81	69	28	2.013	2.129	-2.536	2.067	1.540	-2.700	0.00	-0.63	1.96
84	C	82	81	69	4.285	3.138	-1.275	4.435	2.361	-1.475	0.00	-0.16	1.42
85	H	82	81	69	3.100	3.177	0.518	3.247	2.710	0.279	0.00	0.32	0.79
86	C	83	81	69	3.180	2.344	-3.269	3.261	1.542	-3.421	0.00	-0.18	-1.22
87	H	83	81	69	1.129	1.746	-3.041	1.148	1.235	-3.194	0.00	0.27	-0.96
88	C	84	82	81	4.322	2.846	-2.638	4.450	1.948	-2.808	0.00	0.01	-0.19
89	H	84	82	81	5.167	3.535	-0.779	5.353	2.690	-0.996	0.00	-0.04	-0.34
90	H	86	83	81	3.196	2.123	-4.333	3.261	1.229	-4.461	0.00	-0.10	-0.16
91	H	88	84	82	5.231	3.013	-3.209	5.379	1.952	-3.371	0.00	-0.06	-0.03
92	C	69	28	27	0.652	2.859	1.410	0.654	2.922	1.049	-0.01	5.59	-247.64
93	C	92	69	28	0.279	4.186	1.673	0.057	4.184	1.190	0.00	-0.72	13.92
94	C	92	69	28	1.235	2.098	2.438	1.425	2.409	2.109	0.00	0.67	12.60
95	C	93	92	69	0.492	4.740	2.937	0.239	4.922	2.362	0.00	-0.07	359.00
96	H	93	92	69	-0.183	4.788	0.897	-0.548	4.596	0.389	0.00	0.10	-1.53
97	C	94	92	69	1.456	2.659	3.697	1.612	3.156	3.272	0.00	-0.08	-359.04
98	H	94	92	69	1.518	1.067	2.248	1.887	1.430	2.020	0.00	0.38	1.34
99	C	95	93	92	1.082	3.981	3.949	1.017	4.413	3.402	0.00	0.08	-0.14
100	H	95	93	92	0.195	5.768	3.129	-0.227	5.899	2.456	0.00	-0.11	359.59
101	H	97	94	92	1.913	2.063	4.481	2.219	2.754	4.078	0.00	-0.07	0.36
102	H	99	95	93	1.247	4.416	4.931	1.160	4.992	4.310	0.00	0.05	-0.20

2.4 DFT calculation results for P4

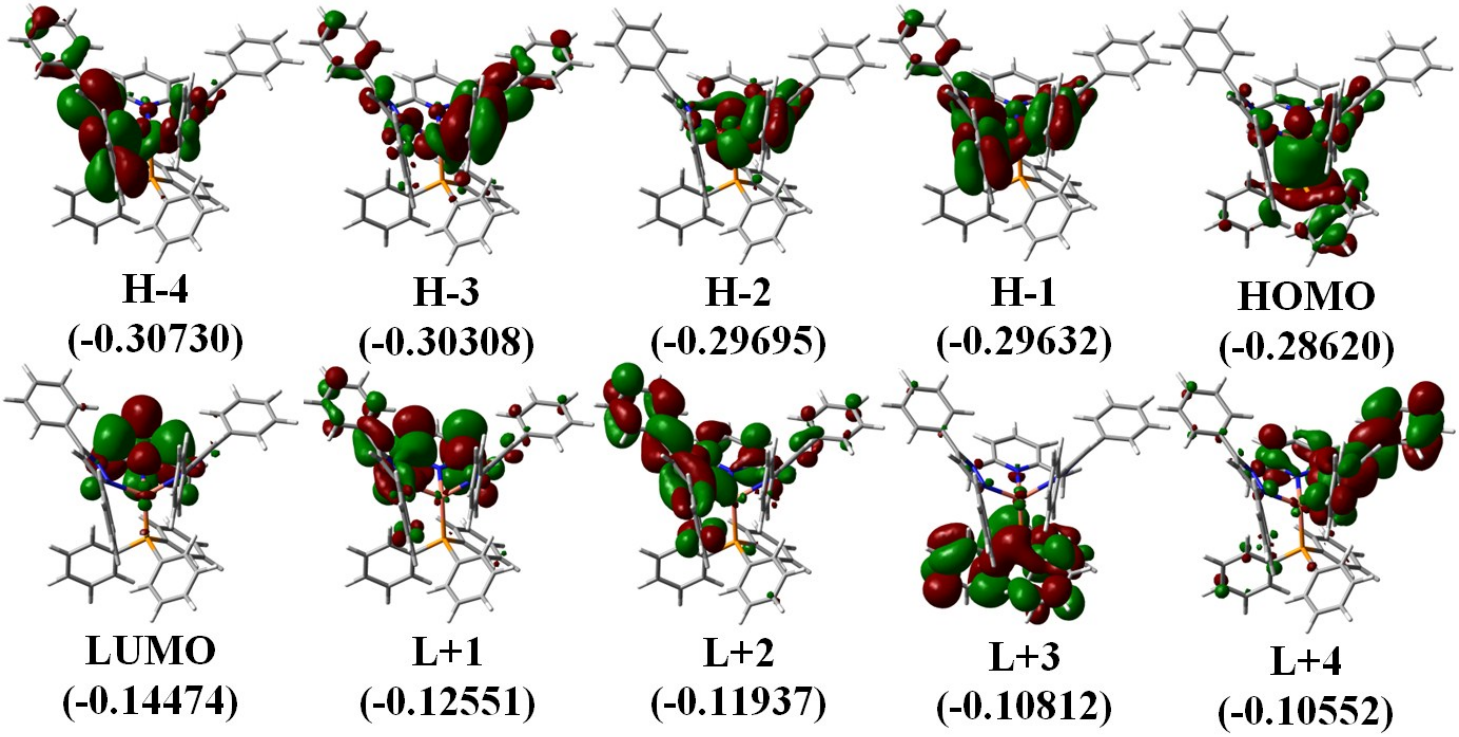


Fig. S12 Representations of the frontier MOs for **P4**. The MO energies are in a.u.

Table S11 Relative atomic contributions (in %) of the frontier MOs of compound **P4** separated by fragments. The grey boxes indicate the major contributions. (H = HOMO, L = LUMO)

Molecular Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Pyridine	3.65	2.59	13.41	3.77	2.89	**82.69**	**69.98**	16.46	2.10	12.83
Pyrazole groups	33.15	28.83	16.19	**29.54**	11.09	9.59	15.47	**40.46**	1.09	**36.89**
Copper	15.24	28.36	**58.92**	**28.10**	**43.40**	1.53	1.64	2.20	2.01	0.90
Triphenylphosphine	2.62	3.23	2.27	1.19	**37.94**	2.62	2.19	5.30	**91.85**	5.10
Phenyl groups	**45.34**	**36.99**	9.21	**37.40**	4.69	3.56	10.72	**35.58**	2.95	**44.28**

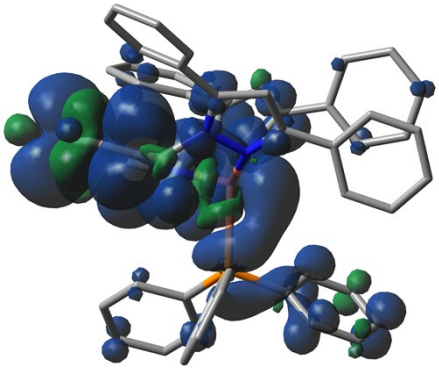


Fig. S13 Side view image of the spin density distribution for **P4** showing the mixed MLCT and LLCT.

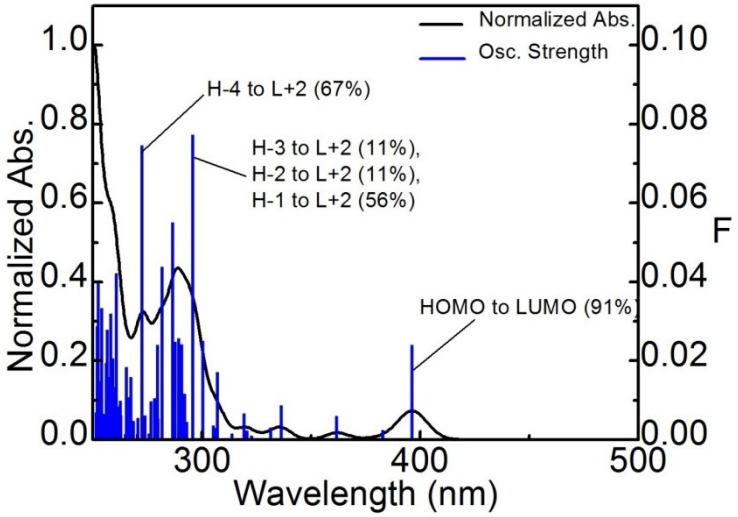


Fig.S14 Bar graph representing the positions of the first hundred electronic transitions (blue). Calculated spectrum by applying a thickness of 1000cm^{-1} to each bar (black). There is no vibronic component in these transitions. The assignments of the most intense transitions are provided.

Table S12 Calculated positions of the 100 first electronic transitions, oscillator strength (F) and major contributions to these electronic transitions for **P4**.

Wavelength (nm)	Osc. Strength	Major contributors (%)
396.1	0.024	HOMO→LUMO (91%)
382.8	0.0025	H-2→LUMO (80%)
361.6	0.006	H-3→LUMO (20%), H-1→LUMO (66%)
336.2	0.0087	HOMO→L+1 (98%)
331.4	0.0031	H-3→LUMO (68%), H-1→LUMO (19%)
322.6	0.0011	H-2→L+1 (50%), HOMO→L+2 (37%)

320.4	0.0023	H-2→L+1 (32%), HOMO→L+2 (55%)
319.2	0.0067	H-4→LUMO (79%)
313.7	0.0015	H-10→LUMO (17%), H-8→LUMO (32%), H-7→LUMO (28%), H-6→LUMO (12%)
306.9	0.0171	H-2→L+2 (22%), H-1→L+1 (40%)
306.4	0.003	H-9→LUMO (10%), H-6→LUMO (15%), H-2→L+2 (47%)
305.2	0.0036	H-9→LUMO (14%), H-8→LUMO (13%), H-6→LUMO (14%), H-1→L+1 (27%)
300.4	0.025	HOMO→L+3 (91%)
295.6	0.0773	H-3→L+2 (11%), H-2→L+2 (11%), H-1→L+2 (56%)
292.9	0.0045	H-6→LUMO (16%), H-5→LUMO (58%)
292.0	0.0116	H-6→LUMO (10%), H-5→LUMO (31%), HOMO→L+4 (35%)
290.5	0.0242	H-9→LUMO (16%), H-6→LUMO (20%), HOMO→L+4 (27%)
289.2	0.0257	H-3→L+1 (73%), H-1→L+1 (10%)
287.6	0.0248	H-10→LUMO (59%), H-7→LUMO (10%)
286.4	0.055	HOMO→L+4 (16%), HOMO→L+5 (75%)
281.5	0.0438	H-4→L+1 (65%), H-3→L+2 (14%)
279.7	0.0054	H-9→LUMO (10%), H-8→LUMO (31%), H-7→LUMO (45%)
279.6	0.0057	H-2→L+3 (63%), H-1→L+3 (10%)
279.4	0.024	H-4→L+1 (19%), H-3→L+2 (52%)
278.1	0.0105	H-2→L+4 (67%)
276.6	0.0097	HOMO→L+6 (79%)
275.6	0.0016	H-12→LUMO (14%), H-11→LUMO (57%)
273.9	0.0061	H-3→L+3 (14%), H-1→L+3 (62%)
272.4	0.0746	H-4→L+2 (67%)
270.5	0.0055	H-2→L+5 (57%)
270.3	0.0014	H-8→L+1 (29%), H-7→L+1 (22%), H-6→L+1 (13%), H-2→L+5 (12%)
268.4	0.0048	H-16→LUMO (10%), H-12→LUMO (34%), H-6→L+1 (18%)
267.9	0.0008	H-13→LUMO (84%)
267.6	0.0035	H-12→LUMO (21%), H-9→L+1 (12%), H-8→L+1 (10%), H-6→L+1 (25%)
267.2	0.0159	H-14→LUMO (10%), H-1→L+4 (42%)
266.1	0.0107	H-14→LUMO (57%)
265.3	0.0184	HOMO→L+7 (81%)
264.8	0.0014	H-15→LUMO (82%)
262.7	0.0062	H-5→L+1 (11%), H-1→L+5 (22%), HOMO→L+8 (25%)
262.6	0.0099	H-5→L+1 (40%), H-5→L+2 (13%), HOMO→L+8 (15%)
261.9	0.0084	H-10→L+2 (11%), H-8→L+2 (21%), H-7→L+2 (15%), H-6→L+2 (11%), H-5→L+1 (21%)
261.5	0.0015	H-16→LUMO (58%), H-12→LUMO (15%)
260.6	0.0421	H-1→L+5 (31%), HOMO→L+8 (22%)
259.8	0.0133	H-6→L+2 (10%), H-2→L+6 (51%)
259.1	0.0206	H-7→L+1 (13%), H-5→L+2 (10%), H-3→L+4 (12%)
259.0	0.0084	H-9→L+2 (13%), H-6→L+2 (15%), H-2→L+6 (18%)

258.1	0.032	H-17→LUMO (11%), H-3→L+4 (35%)
258.0	0.0042	H-3→L+3 (47%), H-1→L+3 (10%)
257.9	0.0159	H-17→LUMO (57%)
256.5	0.0278	H-9→L+1 (24%), H-6→L+1 (13%)
256.1	0.0194	HOMO→L+9 (19%), HOMO→L+12 (42%)
255.4	0.0018	H-7→L+1 (11%), H-7→L+2 (22%), H-5→L+2 (32%)
254.5	0.0065	H-10→L+1 (10%), H-1→L+6 (44%)
253.9	0.0334	H-10→L+1 (43%), HOMO→L+9 (12%)
253.7	0.0148	H-18→LUMO (24%), HOMO→L+9 (16%)
253.4	0.0026	H-18→LUMO (56%), H-10→L+1 (11%)
252.3	0.0399	H-4→L+3 (47%), H-2→L+7 (18%)
251.9	0.0288	H-4→L+3 (26%), H-2→L+7 (46%)
251.4	0.0018	HOMO→L+13 (64%)
251.3	0.0069	H-19→LUMO (84%)
249.7	0.1864	H-2→L+7 (19%), H-1→L+7 (52%)
249.1	0.0062	H-3→L+5 (68%)
248.5	0.0297	H-4→L+4 (62%)
248.3	0.0037	H-15→L+1 (10%), H-15→L+2 (14%), HOMO→L+10 (15%)
247.9	0.0222	H-8→L+1 (15%), H-7→L+1 (19%), H-7→L+2 (19%)
246.1	0.0046	H-11→L+1 (32%), H-2→L+8 (22%)
245.9	0.0009	H-11→L+1 (25%), H-2→L+8 (35%)
245.5	0.0295	H-9→L+2 (19%), H-6→L+2 (22%), HOMO→L+11 (12%)
245.2	0.0009	H-5→L+4 (14%), HOMO→L+11 (33%)
245.1	0.0151	H-9→L+2 (13%), H-5→L+4 (21%)
244.2	0.0015	HOMO→L+10 (68%)
243.7	0.0126	H-10→L+3 (13%), H-8→L+3 (23%), H-7→L+3 (21%)
242.4	0.071	H-2→L+8 (10%), H-1→L+8 (21%)
242.4	0.0005	H-4→L+5 (52%)
242.3	0.0295	H-10→L+2 (41%)
242.1	0.0064	H-3→L+6 (10%), H-2→L+9 (38%)
241.7	0.008	H-3→L+6 (34%), H-1→L+8 (32%)
241.4	0.0025	H-13→L+1 (42%), HOMO→L+11 (21%)
241.3	0.0055	H-20→LUMO (44%), H-13→L+1 (11%)
241.0	0.0319	H-20→LUMO (30%), H-8→L+4 (12%), H-7→L+4 (11%), H-3→L+7 (12%)
240.7	0.0066	H-3→L+7 (59%)
240.5	0.0126	H-20→LUMO (12%), H-9→L+3 (12%), H-6→L+3 (14%), H-2→L+12 (14%)
240.1	0.0064	H-12→L+1 (56%), H-11→L+1 (11%)
239.6	0.0599	H-1→L+9 (53%)
239.0	0.0079	H-16→L+1 (15%), H-14→L+1 (44%)
238.7	0.0102	H-9→L+4 (15%), H-8→L+4 (10%), H-6→L+4 (15%)
238.3	0.0023	H-5→L+3 (58%)
238.0	0.0008	HOMO→L+14 (22%)

237.6	0.0059	HOMO→L+14 (23%)
237.1	0.0088	H-4→L+6 (13%), H-1→L+12 (12%)
236.6	0.0015	H-15→L+1 (48%), H-14→L+1 (10%), H-1→L+10 (13%)
236.2	0.0024	H-11→L+2 (15%), H-4→L+6 (18%), H-4→L+7 (13%)
236.0	0.0074	H-11→L+2 (18%), H-4→L+6 (29%)
236.0	0.0095	H-10→L+5 (10%), H-8→L+5 (25%), H-7→L+5 (20%)
235.8	0.0058	H-11→L+2 (12%), H-4→L+7 (10%), HOMO→L+14 (13%)
235.4	0.0021	H-16→L+1 (19%)
235.3	0.0014	H-16→L+1 (15%), H-13→L+1 (12%)
235.0	0.0175	H-2→L+10 (14%), H-2→L+13 (22%)
234.6	0.0123	H-4→L+7 (12%), H-1→L+12 (20%)
234.3	0.0287	H-21→LUMO (44%)

Table S13 Geometric parameters about the Cu atom for compound **P4** in the S_0 and T_1 states.

Geometric Parameter		Singlet State	Triplet State	Difference
Bond Length (Å)	P-Cu	2.3088	2.4296	0.1208
	N_1-Cu	2.1705	2.1728	0.0023
	N_2-Cu	2.2246	1.9359	0.2887
	N_3-Cu	2.1981	2.1104	0.0877
Bond Angle (°)	P-Cu-N_1	118.4592	110.3491	8.1101
	P-Cu-N_2	112.2002	100.7926	11.4076
	P-Cu-N_3	119.5786	121.6644	2.0858
	N_1-Cu-N_2	92.316	100.4184	8.1024
	N_2-Cu-N_3	87.5256	95.5447	8.0191
	N_3-Cu-N_1	116.8825	121.0389	4.1564

Table S14 Conformational analysis comparing the optimized structures of the singlet and triplet states of **P4**.

Atom ID					Singlet State			Triplet State			Conformation Change		
Tag	Symbol	NA	NB	NC	X	Y	Z	X	Y	Z	Δ Bond	Δ Angle	Δ Dihedral
1	C				0.923	1.996	-2.195	0.271	1.698	-2.357			
2	C	1			1.813	2.667	-3.037	0.931	2.438	-3.310	-0.02		
3	C	2	1		3.129	2.216	-3.122	2.335	2.343	-3.472	0.02	2.42	
4	C	3	2	1	3.520	1.129	-2.341	3.026	1.511	-2.565	0.02	-2.03	-1.79
5	C	4	3	2	2.576	0.521	-1.511	2.354	0.785	-1.608	-0.02	2.33	1.97
6	N	1	2	3	1.297	0.935	-1.463	0.958	0.815	-1.519	0.06	-0.78	-0.85

7	H	3	2	1	3.840	2.709	-3.777	2.856	2.908	-4.235	0.00	0.98	-0.57
8	H	2	1	6	1.476	3.522	-3.615	0.347	3.094	-3.950	0.00	-1.77	358.70
9	H	4	3	2	4.539	0.757	-2.368	4.110	1.431	-2.607	0.00	-0.63	1.94
10	C	1	6	5	-0.535	2.394	-2.119	-1.222	1.711	-2.250	-0.02	4.95	-353.93
11	H	10	1	6	-1.145	1.612	-2.587	-1.648	0.739	-2.537	0.00	1.96	179.14
12	H	10	1	6	-0.696	3.321	-2.670	-1.635	2.466	-2.918	0.00	-0.01	-181.86
13	C	5	4	3	2.927	-0.646	-0.611	3.054	-0.072	-0.599	-0.02	0.70	0.90
14	H	13	5	4	3.975	-0.921	-0.731	4.133	-0.051	-0.753	0.00	0.27	-0.53
15	H	13	5	4	2.311	-1.512	-0.873	2.723	-1.118	-0.651	0.00	2.13	-1.65
16	N	13	5	4	2.713	-0.344	0.798	2.802	0.375	0.780	0.01	-0.17	-0.71
17	C	16	13	5	3.663	-0.115	1.756	3.639	1.018	1.641	-0.01	1.57	0.58
18	C	16	13	5	1.606	-0.097	2.636	1.647	0.658	2.598	0.01	-1.04	-7.91
19	C	17	16	13	2.975	0.044	2.945	2.919	1.203	2.817	0.01	0.27	-3.18
20	H	19	17	16	3.409	0.219	3.918	3.283	1.657	3.726	0.00	0.00	-0.41
21	N	10	1	6	-1.052	2.598	-0.767	-1.757	1.992	-0.902	0.02	0.28	-181.58
22	C	21	10	1	-1.565	3.766	-0.261	-2.571	3.021	-0.526	-0.01	1.34	1.37
23	C	22	21	10	-2.347	3.407	0.822	-3.175	2.630	0.662	0.01	0.17	0.56
24	C	23	22	21	-2.286	1.999	0.914	-2.694	1.340	0.952	-0.01	0.06	0.30
25	H	23	22	21	-2.902	4.081	1.457	-3.889	3.206	1.230	0.00	-0.08	-359.30
26	N	24	23	22	-1.482	1.510	-0.051	-1.810	0.961	0.000	0.01	-0.33	0.08
27	N	18	16	13	1.448	-0.332	1.318	1.574	0.153	1.340	0.01	-0.33	6.52
28	Cu	26	24	23	-0.142	-0.191	-0.194	0.058	-0.143	-0.098	-0.23	-12.73	28.58
29	C	22	21	10	-1.302	5.100	-0.821	-2.741	4.271	-1.283	0.00	0.24	0.51
30	C	29	22	21	-0.005	5.502	-1.188	-1.647	4.932	-1.869	0.00	-0.01	3.58
31	C	29	22	21	-2.360	6.015	-0.954	-4.019	4.848	-1.381	0.00	-0.14	3.81
32	C	30	29	22	0.222	6.785	-1.687	-1.833	6.136	-2.547	0.00	-0.17	0.27
33	H	30	29	22	0.829	4.821	-1.049	-0.649	4.512	-1.774	0.00	0.11	1.12
34	C	31	29	22	-2.128	7.298	-1.448	-4.199	6.053	-2.058	0.00	-0.04	-0.19
35	H	31	29	22	-3.366	5.711	-0.679	-4.871	4.340	-0.939	0.00	0.12	-0.34
36	C	32	30	29	-0.838	7.685	-1.819	-3.108	6.698	-2.644	0.00	0.08	-0.04
37	H	32	30	29	1.230	7.087	-1.956	-0.979	6.640	-2.989	0.00	-0.12	0.24
38	H	34	31	29	-2.955	7.994	-1.548	-5.193	6.485	-2.131	0.00	0.02	-0.13
39	H	36	32	30	-0.659	8.684	-2.204	-3.250	7.637	-3.172	0.00	-0.01	0.13
40	C	24	23	22	-3.082	1.159	1.827	-3.182	0.447	2.016	0.00	0.52	1.35
41	C	40	24	23	-3.564	1.700	3.030	-3.818	0.985	3.147	0.00	0.17	1.49
42	C	40	24	23	-3.483	-0.137	1.465	-3.152	-0.950	1.866	0.00	-0.12	0.89
43	C	41	40	24	-4.435	0.973	3.838	-4.427	0.153	4.084	0.00	0.00	-0.88
44	H	41	40	24	-3.250	2.693	3.339	-3.835	2.061	3.295	0.00	-0.03	-0.57
45	C	42	40	24	-4.351	-0.866	2.276	-3.754	-1.782	2.808	0.00	0.13	0.68
46	H	42	40	24	-3.140	-0.565	0.530	-2.691	-1.388	0.987	0.00	0.11	0.19
47	C	43	41	40	-4.838	-0.310	3.461	-4.404	-1.234	3.915	0.00	-0.08	0.12
48	H	43	41	40	-4.801	1.410	4.763	-4.922	0.589	4.947	0.00	-0.02	0.28
49	H	45	42	40	-4.656	-1.864	1.972	-3.729	-2.859	2.664	0.00	0.00	-0.16

50	H	47	43	41	-5.527	-0.872	4.086	-4.890	-1.880	4.640	0.00	0.09	358.08
51	C	18	16	13	0.516	-0.061	3.627	0.586	0.557	3.613	0.00	-0.54	10.64
52	C	51	18	16	0.603	0.837	4.704	0.339	1.652	4.459	0.00	0.15	1.12
53	C	51	18	16	-0.543	-0.980	3.594	-0.077	-0.656	3.856	0.00	-0.45	2.59
54	C	52	51	18	-0.340	0.808	5.730	-0.546	1.533	5.529	0.00	-0.12	1.22
55	H	52	51	18	1.413	1.562	4.734	0.846	2.595	4.274	0.00	-0.08	0.99
56	C	53	51	18	-1.479	-1.013	4.625	-0.955	-0.773	4.934	0.00	-0.09	-1.27
57	H	53	51	18	-0.613	-1.689	2.777	0.129	-1.518	3.230	0.00	0.04	-0.45
58	C	56	53	51	-1.380	-0.123	5.697	-1.188	0.317	5.773	0.00	-0.06	-0.06
59	H	54	52	51	-0.259	1.509	6.556	-0.727	2.387	6.175	0.00	0.01	-0.01
60	H	56	53	51	-2.288	-1.736	4.590	-1.452	-1.720	5.120	0.00	0.14	0.20
61	H	58	56	53	-2.109	-0.156	6.502	-1.867	0.220	6.616	0.00	-0.08	0.10
62	C	17	16	13	5.120	-0.100	1.511	5.036	1.389	1.355	0.00	0.50	-2.97
63	C	62	17	16	5.707	0.805	0.611	5.381	2.158	0.230	0.00	0.05	-5.19
64	C	62	17	16	5.947	-0.973	2.236	6.041	1.020	2.266	0.00	-0.24	-5.78
65	C	63	62	17	7.090	0.823	0.429	6.707	2.535	0.017	0.00	-0.19	-0.60
66	H	63	62	17	5.081	1.516	0.079	4.606	2.483	-0.457	0.00	0.08	-0.89
67	C	64	62	17	7.330	-0.951	2.053	7.364	1.398	2.046	0.00	-0.07	0.41
68	H	64	62	17	5.500	-1.672	2.936	5.780	0.427	3.137	0.00	0.15	0.67
69	C	67	64	62	7.904	-0.056	1.147	7.701	2.153	0.920	0.00	0.07	-0.31
70	H	65	63	62	7.535	1.534	-0.262	6.961	3.137	-0.851	0.00	-0.14	-0.09
71	H	67	64	62	7.958	-1.633	2.618	8.133	1.101	2.754	0.00	0.00	0.21
72	H	69	67	64	8.981	-0.039	1.007	8.733	2.448	0.752	0.00	-0.01	-359.87
73	P	28	26	24	-0.904	-2.108	-1.229	-0.291	-2.302	-1.156	0.12	-17.67	0.55
74	C	73	28	26	0.401	-2.980	-2.216	1.148	-2.894	-2.130	-0.02	0.47	-101.79
75	C	74	73	28	0.857	-4.273	-1.925	1.797	-4.109	-1.857	0.00	-1.02	4.33
76	C	74	73	28	0.977	-2.286	-3.297	1.595	-2.100	-3.203	0.00	0.38	1.98
77	C	75	74	73	1.867	-4.858	-2.695	2.876	-4.519	-2.643	0.00	-0.33	357.62
78	H	75	74	73	0.423	-4.834	-1.105	1.461	-4.738	-1.040	0.00	0.14	-2.51
79	C	76	74	73	1.978	-2.875	-4.068	2.669	-2.520	-3.986	0.00	-0.53	-357.84
80	H	76	74	73	0.628	-1.288	-3.549	1.107	-1.156	-3.425	0.00	0.39	3.41
81	C	77	75	74	2.430	-4.164	-3.766	3.313	-3.728	-3.706	0.00	-0.14	0.05
82	H	77	75	74	2.206	-5.863	-2.459	3.369	-5.462	-2.425	0.00	0.07	-0.11
83	H	79	76	74	2.403	-2.331	-4.907	3.004	-1.899	-4.812	0.00	-0.21	0.73
84	H	81	77	75	3.210	-4.623	-4.366	4.151	-4.051	-4.316	0.00	-0.16	-0.26
85	C	73	28	26	-2.239	-1.883	-2.484	-1.721	-2.455	-2.297	-0.01	0.92	-106.89
86	C	85	73	28	-2.474	-2.838	-3.489	-1.695	-3.360	-3.372	0.00	-0.65	-6.89
87	C	85	73	28	-3.048	-0.737	-2.434	-2.879	-1.690	-2.073	0.00	0.31	-8.57
88	C	86	85	73	-3.499	-2.649	-4.416	-2.809	-3.499	-4.200	0.00	-0.23	-1.71
89	H	86	85	73	-1.853	-3.726	-3.550	-0.808	-3.955	-3.564	0.00	0.20	-1.44
90	C	87	85	73	-4.076	-0.553	-3.362	-3.991	-1.837	-2.904	0.00	-0.24	1.72
91	H	87	85	73	-2.874	0.013	-1.667	-2.913	-0.979	-1.254	0.00	0.44	1.92
92	C	90	87	85	-4.302	-1.507	-4.355	-3.958	-2.740	-3.968	0.00	0.06	-0.05

93	H	88	86	85	-3.669	-3.395	-5.188	-2.777	-4.202	-5.028	0.00	-0.10	0.03
94	H	90	87	85	-4.697	0.337	-3.309	-4.881	-1.242	-2.720	0.00	-0.10	0.14
95	H	92	90	87	-5.098	-1.363	-5.079	-4.822	-2.850	-4.616	0.00	-0.06	0.05
96	C	73	28	26	-1.546	-3.394	-0.074	-0.564	-3.547	0.168	-0.01	-6.37	256.26
97	C	96	73	28	-2.800	-4.003	-0.228	-1.674	-4.406	0.174	0.00	-0.72	-1.35
98	C	96	73	28	-0.752	-3.748	1.032	0.361	-3.615	1.228	0.00	0.42	-1.69
99	C	97	96	73	-3.246	-4.947	0.700	-1.849	-5.321	1.214	0.00	-0.19	-0.59
100	H	97	96	73	-3.432	-3.745	-1.071	-2.397	-4.367	-0.634	0.00	-0.04	-0.19
101	C	98	96	73	-1.194	-4.702	1.949	0.187	-4.539	2.258	0.00	-0.25	0.36
102	H	98	96	73	0.217	-3.275	1.177	1.223	-2.952	1.244	0.00	0.28	-0.08
103	C	99	97	96	-2.445	-5.302	1.786	-0.920	-5.392	2.254	0.00	-0.03	0.29
104	H	99	97	96	-4.220	-5.410	0.567	-2.707	-5.986	1.204	0.00	0.01	-359.49
105	H	101	98	96	-0.565	-4.970	2.793	0.914	-4.590	3.064	0.00	0.00	-0.24
106	H	103	99	97	-2.793	-6.040	2.503	-1.056	-6.109	3.059	0.00	-0.07	0.05

2.5. DFT calculation results for P5

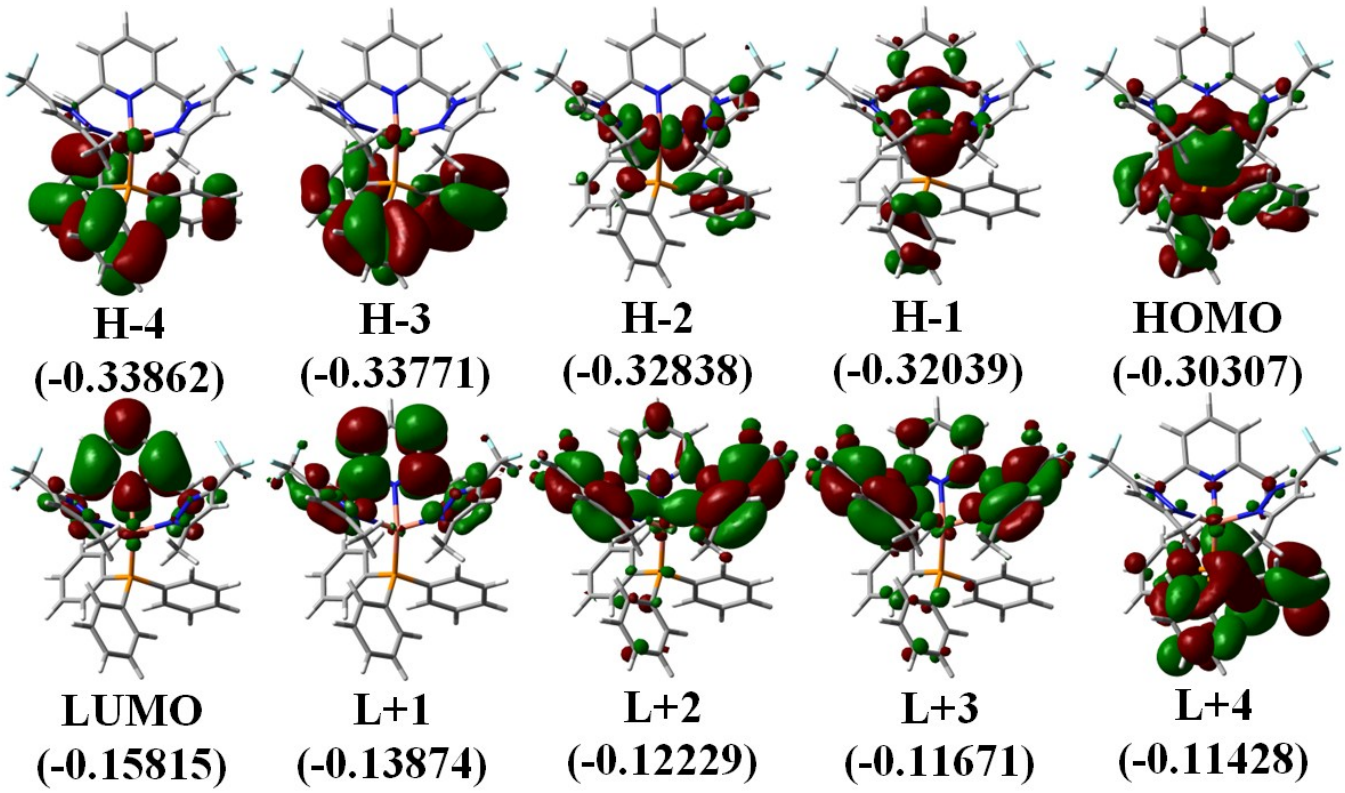


Fig. S15 Representations of the frontier MOs for **P5**. The MO energies are in a.u.

Table S15 Relative atomic contributions (in %) of the frontier MOs of compound **P5** separated by fragments. The grey boxes indicate the major contributions. (H = HOMO, L = LUMO)

Molecular Fragment	H-4	H-3	H-2	H-1	HOMO	LUMO	L+1	L+2	L+3	L+4
Pyridine	1.04	0.62	0.38	17.48	1.50	**82.21**	**78.24**	11.84	16.22	1.16
Pyrazole groups	1.43	0.63	17.94	7.25	8.54	12.83	18.57	**68.03**	**65.34**	2.33
Copper	5.10	3.02	**74.33**	**68.91**	40.57	2.15	0.80	3.43	1.07	1.11
Triphenylphosphine	**91.71**	**95.41**	6.43	6.02	**48.88**	2.05	0.95	5.86	6.80	**94.35**
CF_3 and CH_3 groups	0.71	0.32	0.92	0.33	0.51	0.76	1.44	10.84	10.58	1.05

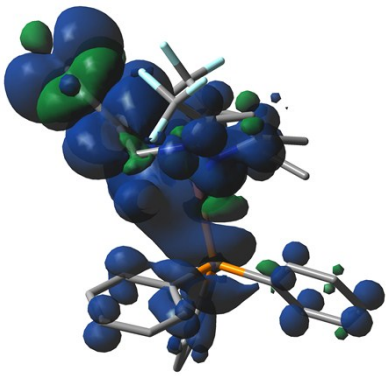


Fig. S16 Side view image of the spin density distribution for **P5** showing the mixed MMCT and LLCT.

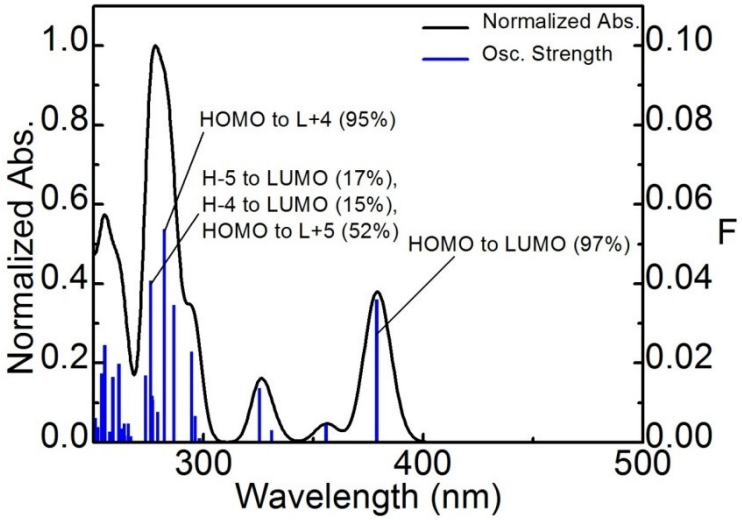


Fig. S17 Bar graph representing the positions of the first hundred electronic transitions (blue). Calculated spectrum by applying a thickness of 1000cm^{-1} to each bar (black). There is no vibronic component in these transitions. The assignments of the most intense transitions are provided.

Table S16 Calculated positions of the 100 first electronic transitions, oscillator strength (F) and major contributions to these electronic transitions for **P5**.

Wavelength (nm)	Osc. Strength	Major contributors (%)
378.7	0.036	HOMO→LUMO (97%)
355.7	0.0045	H-1→LUMO (97%)
331.0	0.0031	H-2→LUMO (96%)
325.5	0.0137	HOMO→L+1 (96%)
302.1	0.0001	H-1→L+1 (97%)
298.1	0.001	H-8→LUMO (27%), H-7→LUMO (64%)
296.1	0.0066	H-9→LUMO (15%), H-6→LUMO (13%), H-5→LUMO (13%),

		HOMO→L+2 (37%)
294.5	0.0229	H-5→LUMO (14%), HOMO→L+2 (55%)
286.5	0.0346	HOMO→L+3 (93%)
282.0	0.0538	HOMO→L+4 (95%)
281.6	0.0002	H-2→L+1 (84%)
279.1	0.0077	H-4→LUMO (29%), H-3→LUMO (41%)
276.7	0.0108	H-4→LUMO (34%), H-3→LUMO (22%), HOMO→L+5 (30%)
276.5	0.0118	H-5→LUMO (33%), H-3→LUMO (27%), HOMO→L+5 (13%)
275.9	0.0407	H-5→LUMO (17%), H-4→LUMO (15%), HOMO→L+5 (52%)
273.5	0.0169	H-1→L+2 (87%)
266.7	0.0015	H-8→LUMO (30%), H-6→LUMO (50%)
265.8	0.0048	H-1→L+3 (89%)
264.1	0.0017	H-9→LUMO (64%), H-8→LUMO (16%)
263.9	0.0047	HOMO→L+6 (88%)
263.0	0.0035	H-10→LUMO (72%)
261.4	0.0198	H-2→L+2 (87%)
258.7	0.0165	H-11→LUMO (60%)
257.3	0.0027	H-11→LUMO (24%), H-9→L+1 (10%), H-7→L+1 (25%), H-5→L+1 (21%)
256.3	0.0001	H-8→L+1 (34%), H-7→L+1 (35%), H-6→L+1 (11%)
255.0	0.0245	H-2→L+3 (14%), H-1→L+4 (77%)
253.4	0.0174	H-12→LUMO (93%)
251.7	0.0039	H-2→L+3 (17%), H-1→L+5 (70%)
250.7	0.0061	H-2→L+3 (45%), H-1→L+5 (23%), HOMO→L+7 (16%)
249.0	0.0016	H-4→L+1 (28%), H-3→L+1 (41%)
247.9	0.0193	H-2→L+4 (14%), HOMO→L+7 (53%)
246.9	0.002	H-4→L+1 (21%), H-3→L+1 (42%), H-2→L+4 (19%)
246.8	0.0131	H-5→L+1 (11%), H-2→L+4 (50%), HOMO→L+7 (11%)
246.5	0.0013	H-5→L+1 (45%), H-4→L+1 (29%)
244.8	0.0009	HOMO→L+8 (64%)
242.7	0.0003	HOMO→L+9 (63%)
240.5	0.0408	H-2→L+5 (71%)
239.6	0.0011	H-1→L+6 (89%)
239.1	0.0015	H-8→L+2 (31%), H-7→L+2 (53%)
239.0	0.0004	H-8→L+1 (31%), H-6→L+1 (51%)
237.8	0.0021	H-9→L+2 (16%), H-7→L+2 (12%), H-6→L+2 (13%), H-5→L+2 (12%), H-2→L+5 (12%)
236.9	0.0023	H-9→L+1 (63%), H-8→L+1 (15%)
235.9	0.0038	H-10→L+1 (74%)
233.9	0.0011	H-13→LUMO (75%)
233.5	0.0013	H-13→LUMO (17%), H-9→L+3 (11%), H-7→L+3 (22%), H-5→L+3 (13%)
232.6	0.0084	H-4→L+5 (10%), H-3→L+4 (26%)
231.5	0.0114	H-3→L+2 (13%)
231.0	0.0096	H-11→L+1 (51%), H-2→L+6 (17%)

230.8	0.007	H-11→L+1 (12%), H-2→L+6 (59%)
230.7	0.0126	H-11→L+1 (13%), H-8→L+3 (22%), H-7→L+3 (25%)
229.7	0.0016	H-3→L+2 (59%)
229.0	0.0102	H-15→LUMO (22%), H-12→L+1 (45%)
228.9	0.0113	H-14→LUMO (42%), H-5→L+2 (17%)
228.3	0.0114	H-12→L+1 (27%), H-4→L+5 (15%)
228.0	0.0159	H-14→LUMO (31%), H-4→L+2 (22%)
227.5	0.0363	H-15→LUMO (22%), H-14→LUMO (15%), H-12→L+1 (16%)
226.8	0.0092	H-8→L+4 (12%), H-4→L+2 (25%)
226.6	0.0168	H-8→L+4 (14%), H-7→L+4 (26%), H-5→L+2 (12%)
225.9	0.0011	H-7→L+4 (11%), H-5→L+2 (11%), H-5→L+4 (11%), H-4→L+4 (11%), H-1→L+7 (15%)
225.4	0.001	H-4→L+4 (24%), H-3→L+5 (10%), H-1→L+7 (39%)
224.7	0.0018	H-3→L+3 (12%), H-3→L+5 (21%), H-1→L+7 (25%)
223.8	0.0174	H-5→L+4 (12%), H-5→L+5 (19%)
223.2	0.0109	H-5→L+3 (13%), H-5→L+5 (33%), H-3→L+5 (12%)
222.9	0.0033	H-3→L+3 (16%)
222.3	0.0091	H-8→L+2 (11%), H-5→L+3 (20%)
222.2	0.0093	H-6→L+5 (25%), H-4→L+3 (13%), H-3→L+5 (11%)
221.8	0.0006	H-8→L+5 (11%), H-7→L+5 (20%), H-4→L+3 (20%), H-3→L+3 (16%)
221.3	0.0038	H-8→L+5 (11%), H-7→L+5 (27%), H-3→L+3 (21%)
220.7	0.0055	H-8→L+4 (17%), H-8→L+5 (14%), H-4→L+3 (13%)
220.3	0.0015	H-9→L+2 (22%), H-7→L+5 (11%), H-6→L+2 (17%), H-4→L+3 (13%)
219.4	0.0082	H-9→L+5 (24%), H-1→L+8 (11%)
219.1	0.0043	H-9→L+2 (11%), H-8→L+2 (20%), H-5→L+3 (10%), H-3→L+3 (11%)
218.7	0.0002	H-6→L+2 (20%), H-6→L+4 (18%)
217.8	0.004	H-9→L+4 (11%), H-2→L+7 (11%), H-1→L+8 (36%)
217.6	0.0065	H-10→L+2 (25%), H-10→L+4 (10%), H-2→L+7 (23%), H-1→L+8 (19%)
217.3	0.0051	H-1→L+9 (76%)
217.0	0.0016	H-10→L+2 (22%), H-2→L+7 (45%)
215.9	0.0142	H-9→L+5 (18%), H-8→L+5 (10%), H-4→L+6 (11%)
215.6	0.0102	H-10→L+4 (14%), H-6→L+3 (10%), H-3→L+6 (15%), HOMO→L+11 (10%)
214.6	0.0181	H-8→L+3 (11%), H-6→L+3 (10%), HOMO→L+10 (12%), HOMO→L+11 (15%)
214.4	0.0059	H-10→L+2 (12%), H-8→L+3 (11%), H-6→L+3 (29%)
213.6	0.0067	H-9→L+6 (14%), H-7→L+6 (15%), H-5→L+6 (25%), H-4→L+6 (10%)
213.5	0.0055	H-9→L+3 (42%), H-6→L+3 (10%)
213.1	0.0115	H-7→L+6 (18%), H-2→L+8 (23%)
212.7	0.0119	H-8→L+6 (10%), H-7→L+6 (19%), H-2→L+8 (33%), H-2→L+9 (13%)
212.4	0.0501	H-8→L+6 (12%), H-6→L+5 (10%), H-3→L+6 (12%)
211.6	0.0045	H-13→L+1 (59%), H-11→L+2 (10%), H-10→L+3 (16%)
211.5	0.0318	H-10→L+3 (10%), H-10→L+4 (10%)

211.3	0.034	H-10→L+3 (22%), H-4→L+6 (10%)
210.7	0.0306	H-11→L+2 (12%), H-10→L+3 (17%), H-10→L+5 (20%), H-8→L+6 (12%)
210.3	0.0048	H-13→L+1 (15%), H-11→L+2 (48%)
209.8	0.019	H-2→L+8 (13%), H-2→L+9 (32%)
208.9	0.0436	H-12→L+2 (25%), HOMO→L+10 (15%), HOMO→L+11 (18%)
208.3	0.0169	H-6→L+6 (19%), H-5→L+6 (13%), H-5→L+7 (11%), H-2→L+9 (18%)
207.6	0.0086	H-9→L+6 (11%), H-6→L+6 (18%), H-3→L+7 (12%)
206.9	0.0001	H-14→L+1 (84%)
206.8	0.0033	H-20→LUMO (17%), H-16→LUMO (32%)
206.5	0.0099	H-10→L+5 (10%), H-5→L+6 (12%)
205.9	0.0121	H-12→L+2 (10%), H-11→L+3 (31%), HOMO→L+12 (21%)
205.2	0.047	H-12→L+2 (36%), HOMO→L+10 (19%), HOMO→L+11 (15%)

Table S17 Geometric parameters about the Cu atom for compound **P5** in the S_0 and T_1 states.

Geometric Parameter		Singlet State	Triplet State	Difference
Bond Length (Å)	P-Cu	2.2886	2.436	0.1474
	N_1-Cu	2.2048	2.0809	0.1239
	N_2-Cu	2.2094	1.9598	0.2496
	N_3-Cu	2.1758	2.0761	0.0997
Bond Angle (°)	P-Cu-N_1	116.4014	101.2761	15.1253
	P-Cu-N_2	122.8421	138.8836	16.0415
	P-Cu-N_3	117.2576	104.8318	12.4258
	N_1-Cu-N_2	88.3602	92.0548	3.6946
	N_2-Cu-N_3	90.9027	95.7959	4.8932
	N_3-Cu-N_1	115.5492	129.1627	13.6135

Table S18 Conformational analysis comparing the optimized structures of the singlet and triplet states of **P5**.

Atom ID					Singlet State			Triplet State			Conformation Change		
Tag	Symbol	NA	NB	NC	X	Y	Z	X	Y	Z	Δ Bond	Δ Angle	Δ Dihedral
1	C				0.242	-2.437	-1.609	0.741	-2.636	-1.412			
2	C	1			-0.139	-3.591	-2.296	0.634	-3.872	-2.008	-0.02		
3	C	2	1		-1.477	-3.748	-2.656	-0.627	-4.428	-2.300	0.02	2.09	
4	C	3	2	1	-2.388	-2.747	-2.319	-1.759	-3.635	-2.012	0.02	-1.95	2.87

5	C	4	3	2	-1.927	-1.621	-1.637	-1.624	-2.403	-1.415	-0.02	2.09	-3.17
6	N	5	4	3	-0.638	-1.473	-1.283	-0.381	-1.884	-1.040	0.05	0.12	-0.75
7	H	3	2	1	-1.804	-4.636	-3.187	-0.724	-5.402	-2.763	0.00	0.98	0.15
8	H	2	1	6	0.598	-4.351	-2.530	1.545	-4.409	-2.262	0.00	-1.40	-0.02
9	H	4	3	2	-3.439	-2.836	-2.573	-2.754	-3.980	-2.279	0.00	-0.81	355.08
10	C	1	6	5	1.667	-2.198	-1.164	2.071	-1.992	-1.180	-0.02	5.98	3.70
11	H	10	1	6	1.964	-1.171	-1.396	2.122	-0.996	-1.639	0.00	1.57	169.91
12	H	10	1	6	2.357	-2.874	-1.665	2.881	-2.595	-1.586	0.00	0.10	168.87
13	C	5	4	3	-2.846	-0.483	-1.257	-2.793	-1.483	-1.279	-0.02	-1.05	-7.45
14	H	13	5	4	-3.809	-0.573	-1.758	-3.705	-1.960	-1.631	0.00	-0.17	16.33
15	H	13	5	4	-2.397	0.471	-1.551	-2.639	-0.565	-1.867	0.01	1.01	15.86
16	N	13	5	4	-3.101	-0.417	0.183	-3.045	-1.031	0.102	0.01	1.27	16.41
17	C	16	13	5	-4.272	-0.607	0.848	-4.135	-1.210	0.885	-0.01	1.08	-4.46
18	C	16	13	5	-2.702	0.100	2.244	-2.686	0.119	1.914	0.01	-0.41	-8.29
19	C	17	16	13	-4.057	-0.288	2.172	-3.943	-0.492	2.052	0.00	0.34	-1.45
20	H	19	17	16	-4.781	-0.322	2.972	-4.624	-0.419	2.886	0.00	-0.01	0.14
21	N	10	1	6	1.819	-2.395	0.278	2.342	-1.803	0.257	0.01	0.18	-190.78
22	C	21	10	1	2.475	-3.388	0.934	3.175	-2.489	1.075	-0.01	0.91	-5.19
23	C	22	21	10	2.333	-3.154	2.286	2.892	-2.116	2.377	0.00	0.32	11.12
24	C	23	22	21	1.554	-1.982	2.380	1.837	-1.196	2.285	-0.01	0.38	0.53
25	H	23	22	21	2.742	-3.743	3.093	3.382	-2.465	3.273	0.00	-0.02	0.01
26	N	24	23	22	1.241	-1.533	1.152	1.516	-1.007	0.983	0.01	-0.79	-1.03
27	N	18	16	13	-2.129	0.004	1.032	-2.147	-0.225	0.722	0.01	-0.43	3.70
28	Cu	27	18	16	-0.089	-0.007	0.277	-0.185	-0.263	0.044	-0.22	-12.56	-4.63
29	C	22	21	10	3.200	-4.491	0.232	4.193	-3.465	0.568	0.00	-0.14	10.63
30	C	24	23	22	1.102	-1.292	3.628	1.109	-0.537	3.413	0.00	0.00	-2.99
31	H	30	24	23	1.050	-0.210	3.486	1.090	0.551	3.309	0.00	0.81	-19.69
32	H	30	24	23	0.113	-1.646	3.939	0.076	-0.897	3.474	0.00	-0.26	-19.19
33	H	30	24	23	1.797	-1.499	4.447	1.600	-0.777	4.360	0.00	-0.46	-19.41
34	C	18	16	13	-1.956	0.604	3.439	-2.023	1.056	2.874	0.00	0.68	3.22
35	H	34	18	16	-2.531	1.387	3.943	-2.657	1.933	3.046	0.00	-0.09	-10.08
36	H	34	18	16	-1.781	-0.193	4.170	-1.861	0.580	3.847	0.00	-0.35	-10.50
37	H	34	18	16	-0.991	1.023	3.145	-1.060	1.407	2.499	0.00	1.04	-10.26
38	C	17	16	13	-5.524	-1.076	0.175	-5.314	-2.038	0.472	0.00	0.14	-2.17
39	F	29	22	21	3.729	-5.342	1.116	4.920	-3.942	1.586	0.00	-0.41	355.55
40	F	29	22	21	2.365	-5.187	-0.583	3.607	-4.506	-0.063	-0.01	0.23	-4.44
41	F	29	22	21	4.193	-4.015	-0.553	5.029	-2.886	-0.322	0.00	-0.29	-3.97
42	F	38	17	16	-5.316	-2.241	-0.486	-4.950	-3.304	0.187	-0.01	0.26	2.62
43	F	38	17	16	-6.496	-1.265	1.072	-6.223	-2.064	1.454	0.00	-0.52	2.68
44	F	38	17	16	-5.959	-0.184	-0.745	-5.900	-1.535	-0.638	0.00	-0.40	2.01
45	P	28	27	18	0.863	2.018	-0.203	0.419	2.079	-0.250	0.15	21.63	-16.25
46	C	45	28	27	-0.300	3.300	-0.835	-0.893	3.133	-0.984	-0.01	-0.14	110.24
47	C	46	45	28	0.083	4.257	-1.789	-0.565	4.142	-1.906	0.00	-1.85	3.98

48	C	46	45	28	-1.611	3.328	-0.330	-2.234	2.965	-0.601	0.00	1.66	5.03
49	C	47	46	45	-0.829	5.219	-2.227	-1.561	4.967	-2.429	0.00	-0.11	1.23
50	H	47	46	45	1.090	4.249	-2.194	0.465	4.285	-2.218	0.00	0.14	1.07
51	C	48	46	45	-2.517	4.297	-0.764	-3.226	3.794	-1.126	0.00	-0.15	-0.96
52	H	48	46	45	-1.921	2.591	0.406	-2.504	2.185	0.101	0.00	0.36	-1.46
53	C	49	47	46	-2.128	5.242	-1.716	-2.892	4.794	-2.041	0.00	-0.15	0.05
54	H	49	47	46	-0.522	5.952	-2.967	-1.296	5.743	-3.140	0.00	-0.03	359.83
55	H	51	48	46	-3.527	4.311	-0.363	-4.260	3.655	-0.824	0.00	-0.10	359.62
56	H	53	49	47	-2.835	5.993	-2.058	-3.665	5.436	-2.453	0.00	-0.02	-0.29
57	C	45	28	27	1.693	2.799	1.245	1.097	3.020	1.171	-0.01	6.01	-242.66
58	C	57	45	28	1.515	4.147	1.587	0.496	4.208	1.618	0.00	-1.33	9.88
59	C	57	45	28	2.530	1.997	2.041	2.225	2.524	1.852	0.00	1.24	8.72
60	C	58	57	45	2.164	4.682	2.703	1.020	4.889	2.720	0.00	-0.06	-0.84
61	H	58	57	45	0.872	4.783	0.987	-0.372	4.610	1.106	0.00	0.12	-1.44
62	C	59	57	45	3.186	2.537	3.147	2.748	3.215	2.945	0.00	-0.16	-359.11
63	H	59	57	45	2.677	0.951	1.786	2.705	1.608	1.521	0.00	0.41	1.19
64	C	60	58	57	3.000	3.881	3.483	2.145	4.398	3.382	0.00	0.04	-0.15
65	H	60	58	57	2.017	5.727	2.959	0.548	5.809	3.053	0.00	-0.07	359.60
66	H	62	59	57	3.839	1.910	3.747	3.628	2.830	3.453	0.00	-0.15	0.21
67	H	64	60	58	3.506	4.301	4.347	2.553	4.933	4.235	0.00	0.02	-0.18
68	C	45	28	27	2.171	1.935	-1.503	1.733	2.043	-1.536	-0.01	-9.71	116.66
69	C	68	45	28	3.437	2.519	-1.352	2.968	2.692	-1.397	0.00	0.41	1.08
70	C	68	45	28	1.874	1.257	-2.699	1.454	1.345	-2.727	0.00	-0.68	2.23
71	C	69	68	45	4.385	2.424	-2.374	3.909	2.639	-2.429	0.00	-0.19	1.05
72	H	69	68	45	3.687	3.050	-0.439	3.199	3.248	-0.495	0.00	0.28	0.48
73	C	70	68	45	2.818	1.173	-3.722	2.394	1.302	-3.757	0.00	-0.20	-0.83
74	H	70	68	45	0.893	0.806	-2.836	0.496	0.848	-2.860	0.00	0.42	-0.72
75	C	71	69	68	4.079	1.753	-3.559	3.626	1.946	-3.607	0.00	0.02	-0.13
76	H	71	69	68	5.362	2.880	-2.243	4.861	3.149	-2.312	0.00	-0.05	359.71
77	H	73	70	68	2.571	0.655	-4.645	2.164	0.769	-4.674	0.00	-0.12	-0.13
78	H	75	71	69	4.817	1.684	-4.353	4.359	1.911	-4.408	0.00	-0.06	-0.01

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