

Electronic Supplementary Information

Outstanding luminescence from neutral copper(I) complexes with pyridyl-tetrazolate and phosphine ligands

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Experimental section

General. Solvents and chemicals used were purchased from commercial suppliers and used without further purification. 2-(Tetrazol-5-yl)pyridine (PyrTetH) and 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene (PTEPhos) were synthesized according to literature methods.^[1,2] ¹H and ³¹P NMR spectra were recorded on Bruker DRX 250. MS FAB (fast atom bombardment mass spectrometry) was carried out on a Finnigan MAT 90 (70 eV). The abbreviation P refers to the used phosphine ligand and P[^]P refers to the used bis(phosphine), respectively, while L refers to the neutral or deprotonated form of PyrTetH. Elemental analyses were performed with an elemental analyser by Elementar vario Micro.

Warning! Nitrogen-rich compounds such as tetrazole derivatives are used as components for explosive mixtures.^[3] In this lab, the reactions described here were run on only a few grams scale, and no problems were encountered. However, great caution should be exercised when handling or heating compounds of this type.

Synthesis. *General Procedure for neutral complexes 1a–4a.* The corresponding cationic complex **1b–4b** (1.00 equiv.) and KOH (2.50 equiv.) were suspended in dry methanol under nitrogen atmosphere and stirred overnight. The solvent was evaporated and the residue extracted with dichloromethane, possible residuals were filtered off. The complex was purified by precipitation in diethyl ether, collected by filtration, washed with diethyl ether and dried in vacuum.

General Procedure for cationic complexes 1b–4b. [Cu(CH₃CN)₄]BF₄ salt (1.00 equiv.), PyrTetH (1.00 equiv.) and PPh₃ (2.00 equiv.) or bis(phosphine) (1.00 equiv.), respectively, were suspended in a solvent mixture of dry CH₂Cl₂/EtOH (3/1) under nitrogen atmosphere. After stirring for 12 h at room temperature the solvents were evaporated and the residue dissolved in little dichloromethane, possible residuals were filtered off. The solution was precipitated in diethyl ether (100 mL), the solid filtered off and washed with diethyl ether. The complex was further purified by repeated washing in water and diethyl ether, followed by drying in vacuum.

[Cu(PPh₃)₂(PyrTet)] (1a). Purification of **1a** was difficult due to ligand exchange reactions during precipitation and stirring in diethyl ether,^[4] which resulted in the reproducible formation of the cluster [Cu₂(PPh₃)₂(PyrTet)₂]. Therefore, complex **1a** had to be obtained by reaction of the cationic species **1b** with a KOH, evaporation of the solvent, extraction with dichloromethane and evaporation of dichloromethane. Small impurities of **1a** with PPh₃ were not preventable with this method. Yield: 113 mg, 0.14 mmol, 70%, white powder. ¹H NMR

(250 MHz, CDCl₃): δ = 8.20 (br, 1H, PyrTet), 7.84 (br, 1H, PyrTet), 7.65–7.56 (m, 1H, PyrTet), 7.48–7.36 (m, 1H, PyrTet), 7.25–7.10 (m, 30H, PPh₃). ³¹P NMR (100 MHz, CDCl₃): δ = –0.5 ppm. MS (FAB), *m/z* (%): 1742 (<1) [P⁴Cu₄L₃], 1530 (<1) [P⁴Cu₃L₂], 1271 (<1) [P³Cu₃L₂], 1218 (<1), 1098 (<1), 1061 (1) [P³Cu₂L], 1008 (3) [P²Cu₃L₂], 956 (<1) [P²Cu₄L₂ – 2N₄], 891 (<1) [P²Cu₃L₂ – 2N₄], 799 (14) [P²Cu₂L], 746 (1) [P²Cu₂L – N₄], 706 (2) [P²CuL – N₂], 691 (2) [P²CuL – N₃], 681 (2) [P²Cu₃L – N₄], 588 (58) [P²Cu], 473 (18) [P¹CuL], 327 (80) [P¹Cu], 264 (100) [P¹]. Anal. calcd. for C₄₈H₃₉CuN₅P_{2.3} (*i.e.*, [Cu(PPh₃)₂(PyrTet)]×0.33PPh₃): C, 70.16; H, 4.78; N, 8.52%. Found: C, 70.22; H, 4.75; N, 8.38%.

[Cu(PPh₃)₂(PyrTetH)]BF₄ (1b). Yield: 575 mg, 0.70 mmol, 70%, white powder. ¹H NMR (250 MHz, CDCl₃): δ = 8.37 (d, *J* = 8.0 Hz, 1H, PyrTetH), 8.08 (d, *J* = 5.4 Hz, 1H, PyrTetH), 7.98 (t, *J* = 7.6 Hz, 1H, PyrTetH), 7.36–7.27 (m, 7H, PPh₃), 7.19–7.12 (m, 24H, PPh₃, PyrTetH). ³¹P NMR (100 MHz, CDCl₃): δ = 3.3 ppm. MS (FAB), *m/z* (%): 1532 (<1) [P⁴Cu₃L₂], 1322 (<1), 1272 (<1) [P³Cu₃L₂], 1216 (<1), 1159 (<1), 1060 (1) [P³Cu₂L], 1007 (2) [P²Cu₃L₂], 896 (1) [P²Cu₃L₂ – 2N₄], 799 (43) [P²Cu₂L], 741 (2) [P²Cu₂L – N₄], 735 (2) [P²CuL], 588 (82) [P²Cu], 473 (18) [P¹CuL], 327 (50) [P¹Cu], 264 (15). Anal. calcd. for C₄₂H₃₅BCuF₄N₅P₂: C, 61.36; H, 4.29; N, 8.52%. Found: C, 61.53; H, 4.31; N, 8.45%.

[Cu(DPEPhos)(PyrTet)] (2a). Yield: 203 mg, 0.27 mmol, 68%, white powder. ¹H NMR (250 MHz, CDCl₃): δ = 8.23 (d, *J* = 8.0 Hz, 1H, PyrTet), 7.84 (br, 1H, PyrTet), 7.71 (t, *J* = 7.6 Hz, 1H, PyrTet), 7.08–7.18 (m, 19H, DPEPhos, PyrTet), 6.81–6.90 (m, 8H, DPEPhos), 6.61–6.68 (m, 2H, DPEPhos). ³¹P NMR (100 MHz, CDCl₃): δ = –12.8 ppm. MS (FAB), *m/z* (%): 2096 (<1) [P³Cu₃L₂], 1559 (1) [P²Cu₃L₂], 1350 (6) [P²Cu₂L], 1139 (2) [P²Cu], 812 (1) [P¹Cu₂L], 749 (4) [P¹CuL], 691 (3) [P¹CuL – N₄], 602 (100) [P¹Cu]. Anal. calcd. for C₄₂H₃₂CuN₅OP₂: C, 67.42; H, 4.31; N, 9.36%. Found: C, 67.26; H, 4.36; N 9.28%.

[Cu(DPEPhos)PyrTetH][Cu(DPEPhos)(PyrTet)]BF₄ (2b). Complex **2b** was obtained as cationic and neutral species in the ratio 1:1 linked via a hydrogen bonding, as confirmed by elemental analysis and crystal structure. The crystal structure of **2b** contains PF₆[–] as counterion instead of BF₄[–] and was obtained by using [Cu(CH₃CN)₄]PF₆ salt. Yield: 300 mg, 0.36 mmol, 57%, light yellow powder. ¹H NMR (250 MHz, CDCl₃): δ = 8.48 (d, *J* = 7.8 Hz, 1H, PyrTetH), 8.04 (br, 1H, PyrTetH), 7.95 (t, *J* = 7.8 Hz, 1H, PyrTetH), 7.13–7.23 (m, 21H, DPEPhos, PyrTetH), 6.81–6.90 (m, 6H, DPEPhos), 6.61–6.68 (m, 2H, DPEPhos). ³¹P NMR (100 MHz, CDCl₃): δ = –13.2 ppm. MS (FAB), *m/z* (%): 2097 (<1) [P³Cu₃L₂], 1559 (1) [P²Cu₃L₂], 1350 (18) [P²Cu₂L], 1139 (<1) [P²Cu], 812 (4) [P¹Cu₂L], 749 (1)

[P⁺PCuL], 691 (1) [P⁺PCuL – N₄], 602 (100) [P⁺PCu]. Anal. calcd. for C₈₄H₆₇BCu₂F₄N₁₀O₃P₄ (i.e., [Cu(DPEPhos)PyrTetH][Cu(DPEPhos)(PyrTet)]BF₄·xH₂O): C, 62.27; H, 4.29; N, 8.64%. Found: C, 62.27; H, 4.31; N 8.11%.

[Cu(Xantphos)(PyrTet)] (3a). Yield: 62 mg, 0.08 mmol, 37%, yellowish white powder. ¹H NMR (250 MHz, CDCl₃): δ = 8.37 (br, 1H, PyrTet), 7.84 (br, 2H, PyrTet), 7.63–7.59 (d, *J* = 6.4 Hz, 2H, Xantphos), 7.29–7.06 (m, 23H, Xantphos, PyrTet), 6.64–6.55 (br, 2H, Xantphos), 1.76 (s, 6H, Xantphos). ³¹P NMR (100 MHz, CDCl₃): δ = –14.1 ppm. MS (FAB), *m/z* (%): 1431 (<1) [P⁺P₂Cu₂L], 1020 (<1), 886 (1) [P⁺PCu₂L₂ – 2N₄], 788 (1) [P⁺PCuL], 732 (1) [P⁺PCuL – N₄], 664 (2), 642 (6) [P⁺PCu], 604 (6), 578 (2) [P⁺P], 341 (2), 309 (15). Anal. calcd. for C₄₅H₃₆CuN₅OP₂: C, 68.56; H, 4.60; N 8.88%. Found: C, 68.45; H, 4.74; N, 8.57%.

[Cu(Xantphos)(PyrTetH)]BF₄ (3b). Yield: 270 mg, 0.31 mmol, 77%, yellow powder. ¹H NMR (250 MHz, CDCl₃): δ = 8.49 (br, 1H, PyrTetH), 8.01 (br, 2H, PyrTetH), 7.52–7.55 (d, *J* = 6.9 Hz, 2H, Xantphos), 7.04–7.26 (m, 23H, Xantphos, PyrTetH), 5.58 (br, 2H, Xantphos), 1.64 (s, 6H, Xantphos). ³¹P NMR (100 MHz, CDCl₃): δ = –12.6 ppm. MS (FAB), *m/z* (%): 2217 (<1) [P⁺P₃Cu₃L₂], 1641 (2) [P⁺P₂Cu₃L₂], 1430 (10) [P⁺P₂Cu₂L], 958 (<1) [P⁺PCu₂L₂ – N₃], 851 (<1) [P⁺PCu₂L], 789 (1) [P⁺PCuL], 732 (2) [P⁺PCuL – N₄], 658 (2), 642 (100) [P⁺PCu], 627 (7) [P⁺PCu – CH₃], 442 (2), 309 (10). Anal. calcd. for C₄₅H₃₇BCuF₄N₅OP₂: C, 61.69; H, 4.26; N 7.99%. Found: C, 61.92; H, 4.31; N, 7.59%.

[Cu(PTEPhos)(PyrTet)] (4a). Yield: 33 mg, 0.04 mmol, 61 %, white powder. ¹H NMR (250 MHz, CDCl₃): δ = 8.36 (br, 1H, PyrTet), 7.75–7.89 (m, 2H, PyrTet), 6.98–7.23 (m, 19H, PTEPhos, PyrTet), 6.86–6.91 (m, 3H, PTEPhos), 6.71–6.75 (m, 3H, PTEPhos), 6.38 (br, 2H, PTEPhos), 1.99 (s, 6H, PTEPhos). ³¹P NMR (100 MHz, CDCl₃): δ = –11.9 ppm. MS (FAB), *m/z* (%): 2181 (<1) [P⁺P₃Cu₃L₂], 1617 (<1) [P⁺P₂Cu₃L₂], 1554 (<1) [P⁺P₂Cu₂L₂], 1406 (2) [P⁺P₂Cu₂L], 1197 (<1) [P⁺PCu₃L₃], 840 (<1) [P⁺PCu₂L], 778 (3) [P⁺PCuL], 720 (2) [P⁺PCuL – N₄], 630 (55) [P⁺PCu], 382 (2), 309 (30). Anal. calcd. for C₄₄H₃₆CuN₅OP₂: C, 68.08; H, 4.67; N, 9.02%. Found: C, 67.88; H, 4.74; N 8.81%.

[Cu(PTEPhos)(PyrTetH)]BF₄ (4b). Yield: 100 mg, 0.12 mmol, 46%, yellow powder. ¹H NMR (250 MHz, CDCl₃): δ = 8.64 (d, *J* = 6.5 Hz, 1H, PyrTetH), 8.18–8.08 (m, 2H, PyrTetH), 7.42–7.20 (m, 19H, PTEPhos, PyrTetH), 7.07–7.03 (m, 3H, PTEPhos), 6.89–6.84 (br, 3H, PTEPhos), 6.59 (br, 2H, PTEPhos), 2.15 (s, 6H, PTEPhos). ³¹P NMR (100 MHz, CDCl₃): δ = –12.0 ppm. MS (FAB), *m/z* (%): 2071 (<1), 1616 (3) [P⁺P₂Cu₃L₂], 1505 (<1), 1406 (10) [P⁺P₂Cu₂L], 839 (8) [P⁺PCu₂L], 720 (2) [P⁺PCuL – N₄], 630 (100) [P⁺PCu], 567 (1) [P⁺P], 490 (5), 383 (13). Anal. calcd. for C₄₄H₃₇BCuF₄N₅OP₂: C, 61.16 ; H, 4.32; N, 8.10%. Found: C, 61.10; H, 4.35; N, 7.84%.

X-ray Crystallography.

All single-crystal X-ray diffraction studies were carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K (**1b**, **2a**, **2b**, **3a**, **4a**), or a Bruker-Nonius APEXII at 123(2) K (**1a**) using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Direct Methods (SHELXS-97^[5]) were used for structure solution (for **1a** and **2a** Patterson Methods were used) and refinement was carried out using SHELXL-97^[5] (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference electron density determination and refined using a riding model H(N) free. Semi-absorption corrections were applied for all structures. In **2b** the H(N) is disordered about the two molecules with the occupancy of 0.5 (due to the crystallographic C_i -symmetry). The content of the unit cell is a neutral and the protonated molecule linked by a hydrogen bond (Fig. S1), one PF₆ anion and two solvent molecules. In **1a** one phenyl group is disordered. Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 922230 (**1a**), CCDC 922231 (**1b**), CCDC 922232 (**2a**), CCDC 922233 (**2b**), CCDC 922234 (**3a**), and CCDC 922235 (**4a**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

DFT calculations.

All complexes were studied using density functional theory (DFT). For complexes **1a–4a** and **1b**, initial geometries were obtained from single-crystal X-ray diffraction data. The other initial structures of cationic complexes **2b–4b** were generated by adding a hydrogen atom to the neutral complex. These structures were optimized in the ground state and in the lowest triplet state using the BP86^[6,7] functional with the resolution-of-identity (RI)^[8–10] approximation. Analytical harmonic vibrational frequency calculations were performed to verify that the optimized structures are minima on the potential energy surface. Excitation and phosphorescence energies were calculated as energy differences between the closed-shell singlet ground-state and the lowest (unrestricted) triplet state. In all calculations, the def2-SV(P) basis set^[11,12] and the m4 grid for numerical integration were employed. All calculations were performed with the Turbomole program package version 6.4.^[13]

Photophysical measurements. UV-vis absorption spectra were measured on a Thermo Scientific Evolution 201 UV-vis spectrometer. Emission and excitation spectra were recorded on a Horiba Scientific FluoroMax-4 spectrofluorometer. Emission lifetimes were measured on the same system using the TCSPC method. For this, a flashlight was used as excitation source

($\lambda = 250\text{--}2000$ nm, 3 μs pulse). Decay curves were analysed with the software DAS-6 and DataStation provide by Horiba Yvon Jobin. PL quantum yields were measured with Hamamatsu Photonics C9920-02G. All solvents used were of spectrometric grade.

Electrochemical measurements. Cyclic voltammetry was recorded with a Model 600D Series Electrochemical Analyzer with Workstation (CH Instruments) with a scan rate of 100 mV s^{-1} . Measurements were carried out at room temperature, under argon with a three-electrode configuration consisting of glassy carbon working electrode, a platinum wire counter electrode and a platinum wire reference electrode, calibrated against a ferrocene/ferrocenium couple. **2a** was dissolved in dried and argon purged CH_2Cl_2 , the supporting electrolyte was $0.1\text{ M NBU}_4\text{PF}_6$. Oxidation and reduction potentials were corrected using ferrocene as internal standard versus SCE. ^[14]

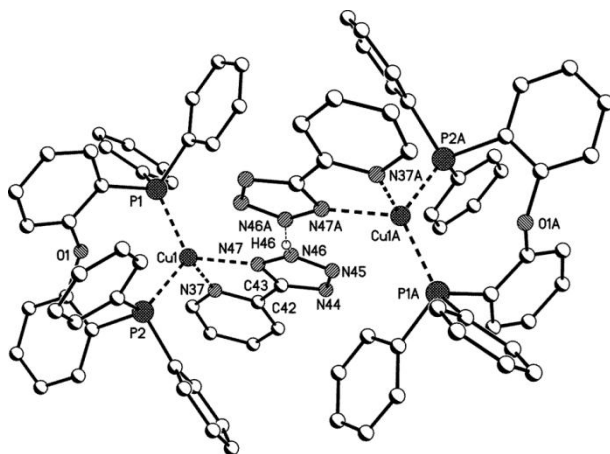


Fig. S1 Crystal structure of **2b**. Counterion, hydrogen atoms (only H46 is shown) and solvent molecules are omitted for clarity.

Table S1. Selected bond lengths and angles of complexes **1a–4a** and **1b, 2b**.

Complex	1a	2a	3a	4a	1b	2b
Distances [Å]						
Cu1–N1	2.0428(4)	2.0400(15)	2.0206(12)	2.0614(14)	2.0794(14)	2.095(2)
Cu1–N11	2.1184(4)	2.0818(16)	2.1138(12)	2.1024(14)	2.1396(14)	2.046(3)
Cu1–P1	2.2397(16)	2.2493(5)	2.2405(4)	2.2844(5)	2.2342(5)	2.245(8)
Cu1–P2	2.2508(15)	2.2262(5)	2.2510(4)	2.2436(5)	2.2724(5)	2.200(9)
Bond Angles [°]						
N1–Cu1–N11	79.816(16)	80.525(6)	81.077(5)	80.264(5)	79.010(5)	79.99(10)
P1–Cu1–P2	121.21(6)	114.42(2)	116.125(15)	114.812(17)	129.93(19)	115.43(3)
φ^a	83.379	84.306	79.110	87.913	85.214	87.647
N1–C5–C6–N11	5.561(7)	8.290(3)	6.519(19)	10.151(2)	2.009(2)	7.324(4)

^a Dihedral angle between N–Cu–N and P–Cu–P planes.

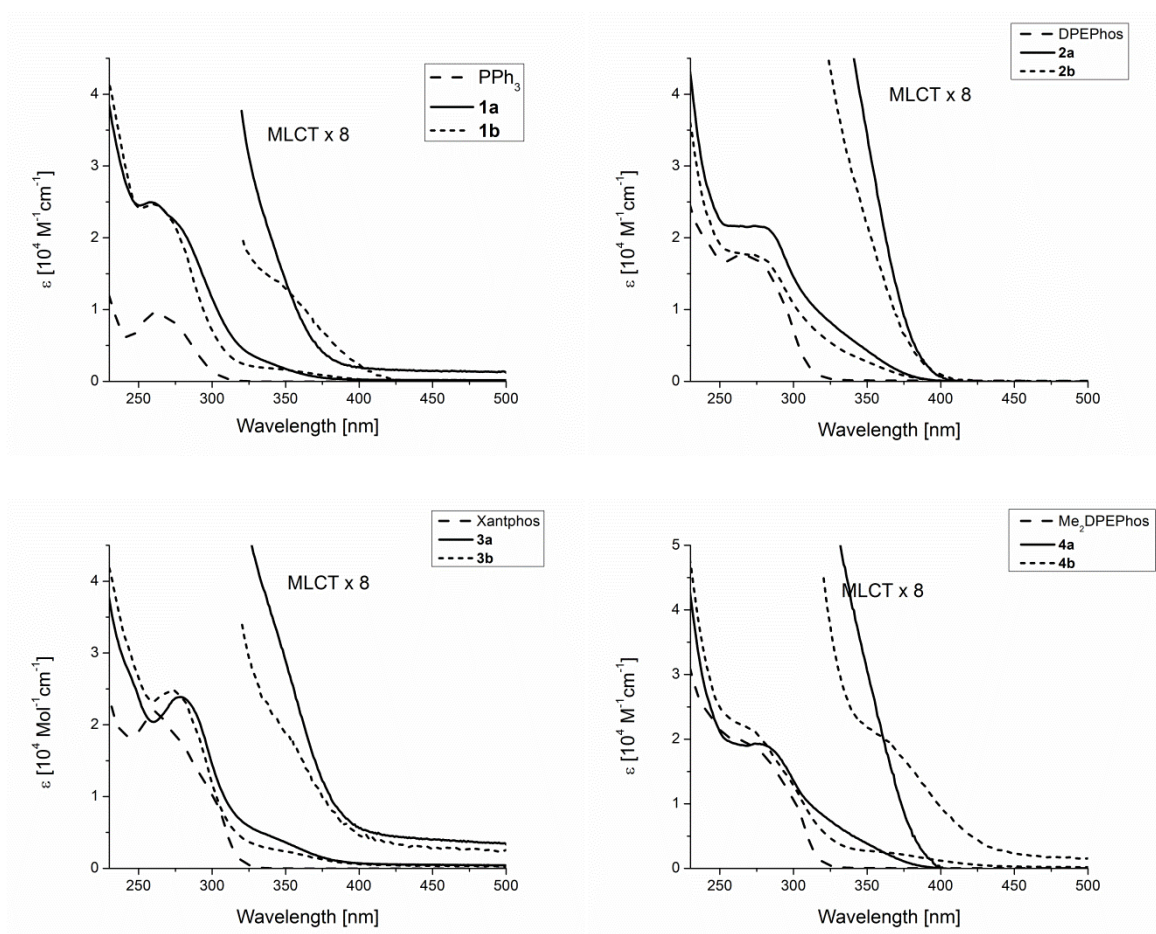


Fig. S2 Absorption spectra of complexes **1a–4a**, **1b–4b** in dichloromethane at room temperature.

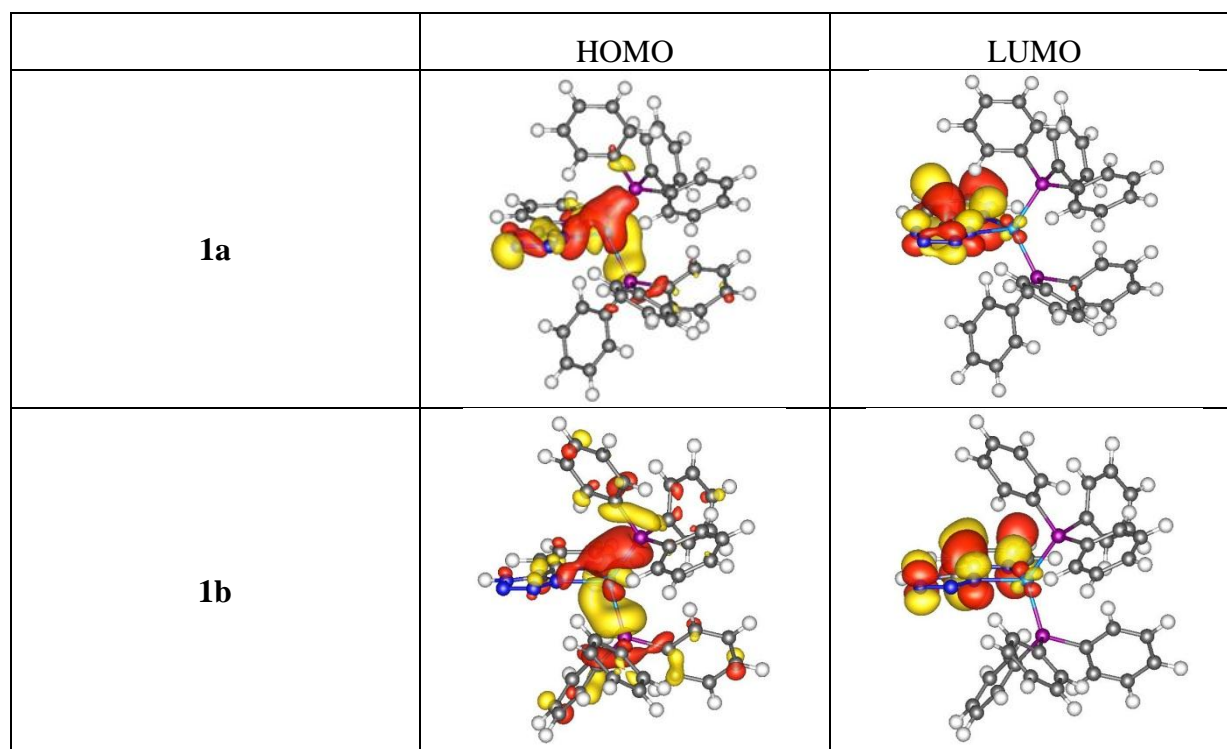


Fig. S3 HOMO and LUMO of the neutral complex **1a** and the cationic complex **1b** as calculated by DFT.

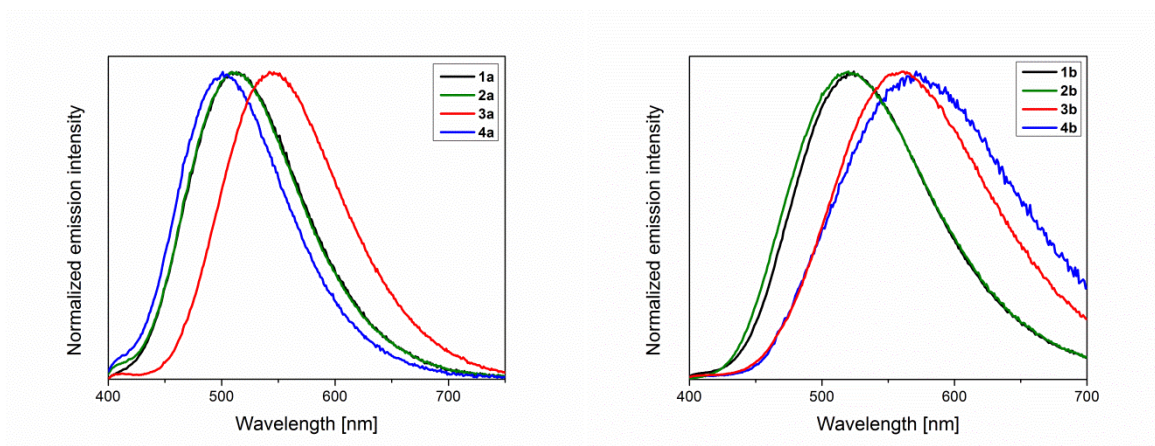


Fig. S4 Powder emission spectra of complexes **1a–4a**, **1b–4b** at room temperature.

Table S2. Excitation and phosphorescence energies calculated as energy differences at the optimized ground state and triplet geometries, respectively. For the cationic complexes, both isomers with the hydrogen in 2 and in 4 position of the tetrazole ring were studied.

Triplet excitation energies [eV] (nm ^c)				
	1	2	3	4
a	2.93 (355)	2.92 (356)	- ^a	2.93 (356)
b (N2) ^b	2.37 (424)	2.76 (374)	2.74 (376)	2.69 (381)
b (N4)	2.82 (367)	2.35 (427)	2.32 (431)	2.32 (431)
Phosphorescence energies [eV] (nm ^c)				
	1	2	3	4
a	1.85 (515)	1.93 (499)	1.85 (515)	1.92 (500)
b (N2)	1.67 (556)	1.57 (469)	1.59 (576)	1.54 (590)
b (N4)	1.82 (521)	1.32 (658)	1.30 (668)	1.31 (663)

^a No convergence. ^b For assignment of the numbers see fig. 2. ^c Before conversion into nm the calculated values were corrected by adding 0.56 eV for comparison with experimental data.

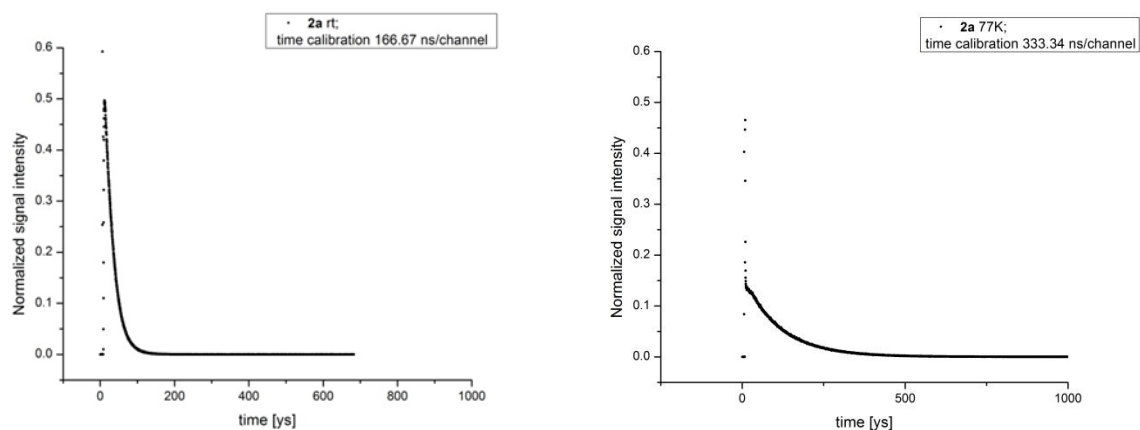


Fig. S5 Decay curves of **2a** in solid state.

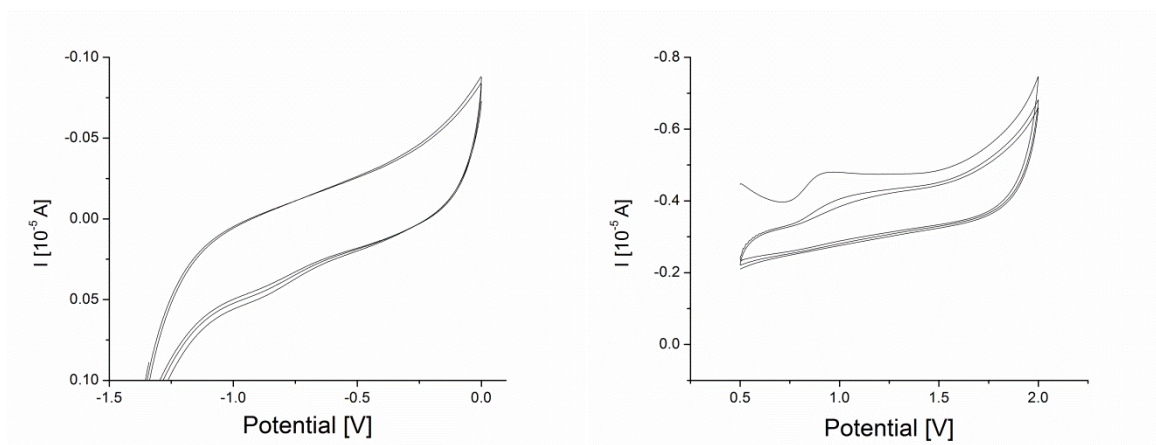


Fig. S6 Electrochemical data of **2a**, uncorrected. For comparison of oxidation and reduction potentials the values were corrected using ferrocene as the internal standard versus SCE.

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