Supporting information

Transition metal complexes of the PPO/POP ligand: variable coordination chemistry and photo-luminescence properties

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1. Representative NMR spectra

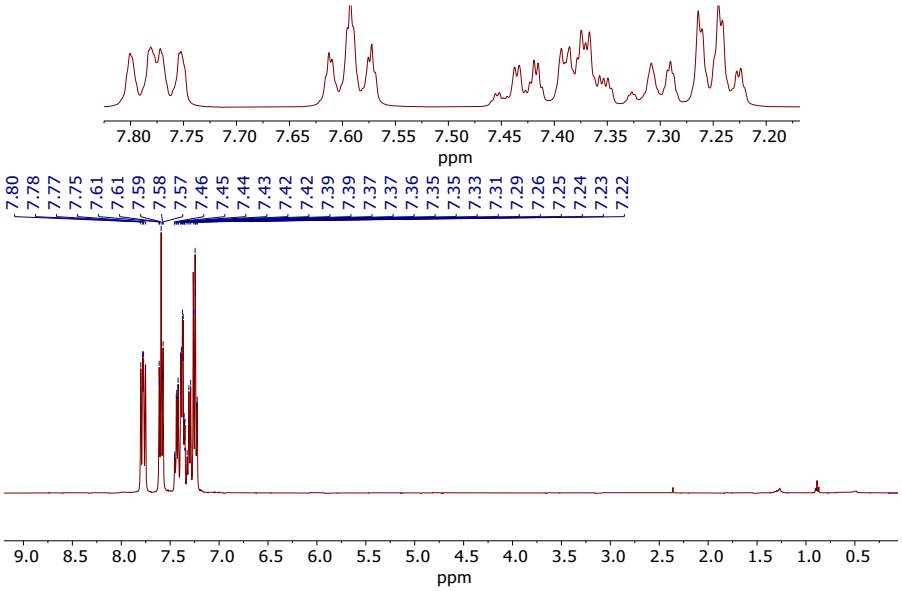


Figure S1: *^{1}H NMR (298 K, $CDCl_3$, 400 MHz) spectrum of the PPO/POP ligand.*

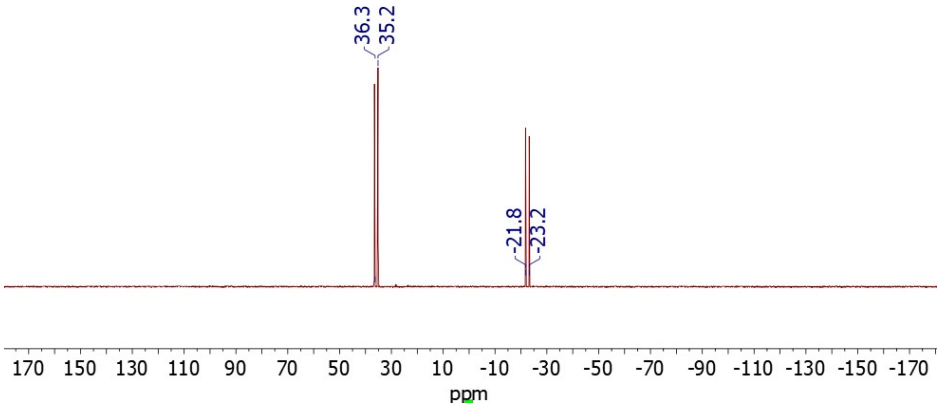


Figure S2:*^{31}P{^{1}H} NMR (298 K, $CDCl_3$, 162 MHz) spectrum of the PPO/POP ligand.*

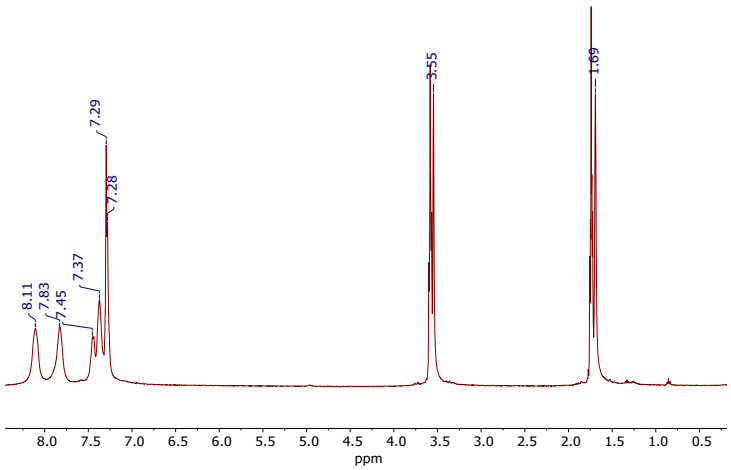


Figure S3: *^{1}H NMR (298 K, D_8-THF, 400 MHz) spectrum of $[YCl_3(THF)_2(PPO)]\cdot 0.5THF$ (**2**·0.5THF). Note: the solvent residual peaks of THF overlaps with the signals of the coordinated THF molecules.*

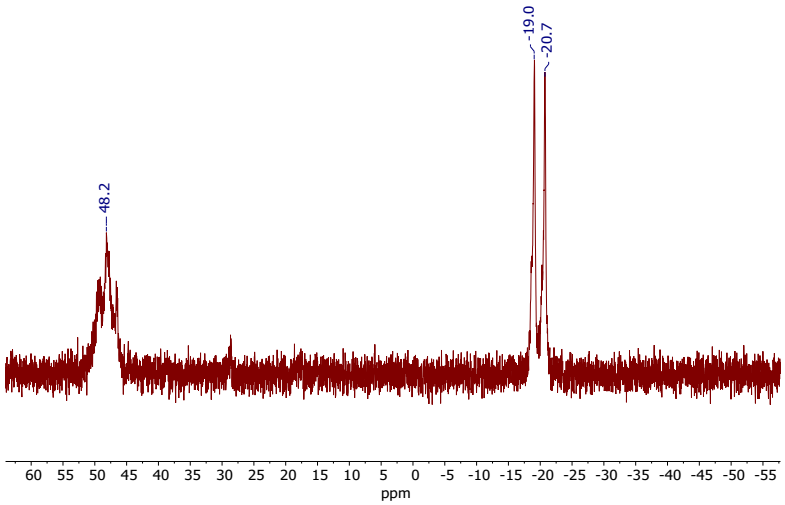


Figure S4: *$^{31}P\{^{1}H\}$ NMR (298 K, D_8-THF, 162 MHz) spectrum of $[YCl_3(THF)_2(PPO)]\cdot 0.5THF$ (**2**·0.5THF).*

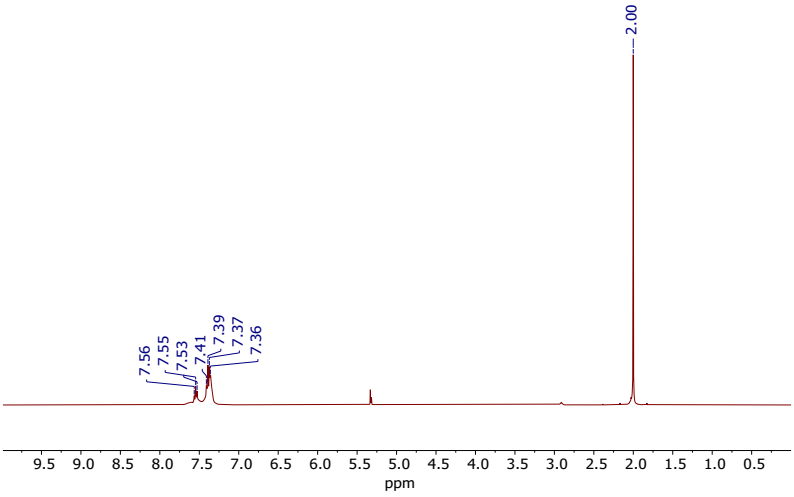


Figure S5: *^{1}H NMR (298 K, CD_2Cl_2, 400 MHz) spectrum of $[Cu_2(MeCN)_4(\mu_2\text{-}POP)_2](PF_6)_2$ (**3**).*

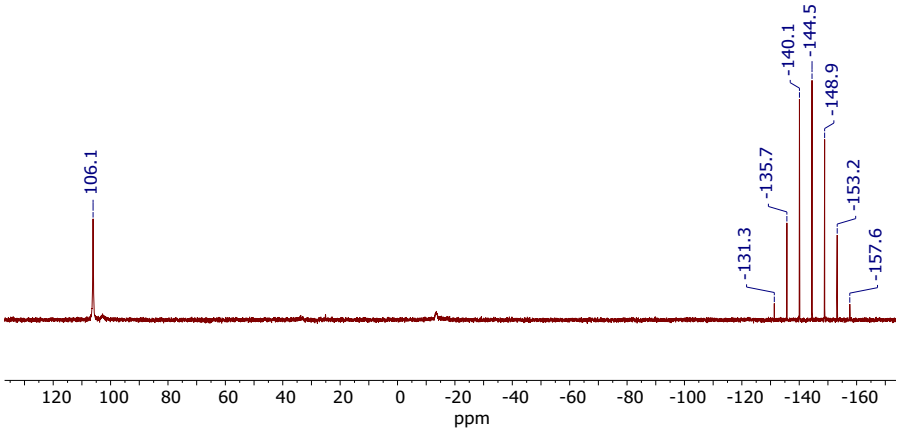


Figure S6: *$^{31}P\{^{1}H\}$ NMR (298 K, CD_2Cl_2, 162 MHz) spectrum of $[Cu_2(MeCN)_4(\mu_2\text{-}POP)_2](PF_6)_2$ (**3**).*

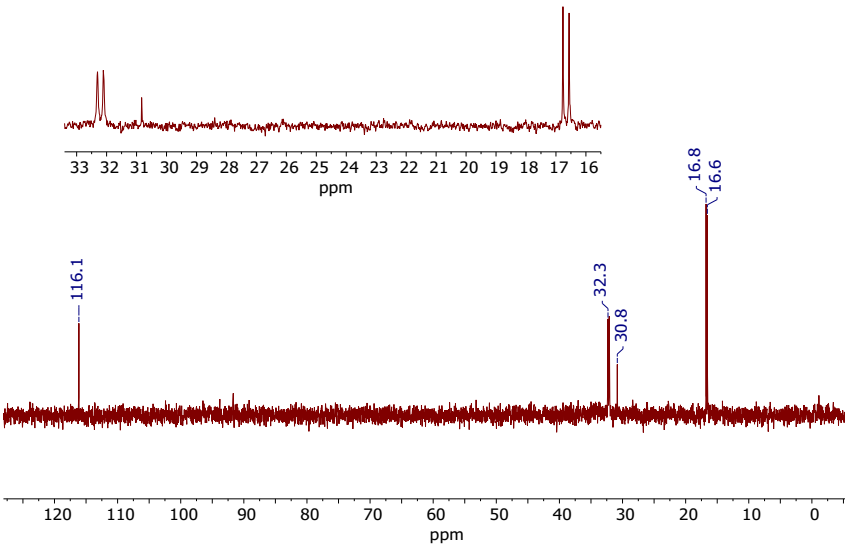


Figure S7: *$^{31}P\{^{1}H\}$ NMR (298 K, $CDCl_3$, 162 MHz) spectrum of $[Au_2Cl_2(\mu_2\text{-POP})]$ (**4**) and [AuCl(PPO)] (**4'**). Note: a small amount of impurities (30.8 ppm) was observed, since **4** is readily hydrolyzed.*

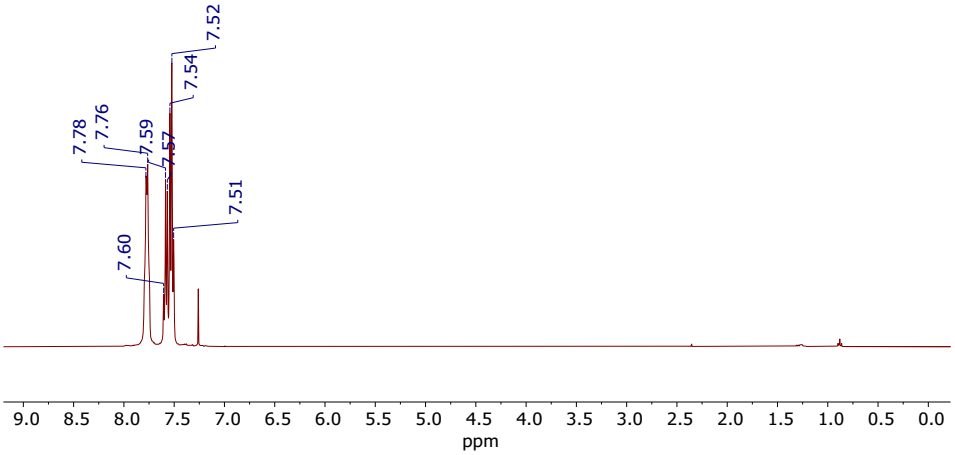


Figure S8: *^{1}H NMR (298 K, $CDCl_3$, 400 MHz) spectrum of $[Au_2(\mu_2\text{-POP})_2](OTf)_2\cdot 2.3DCM$ (**5**·2.3DCM).*

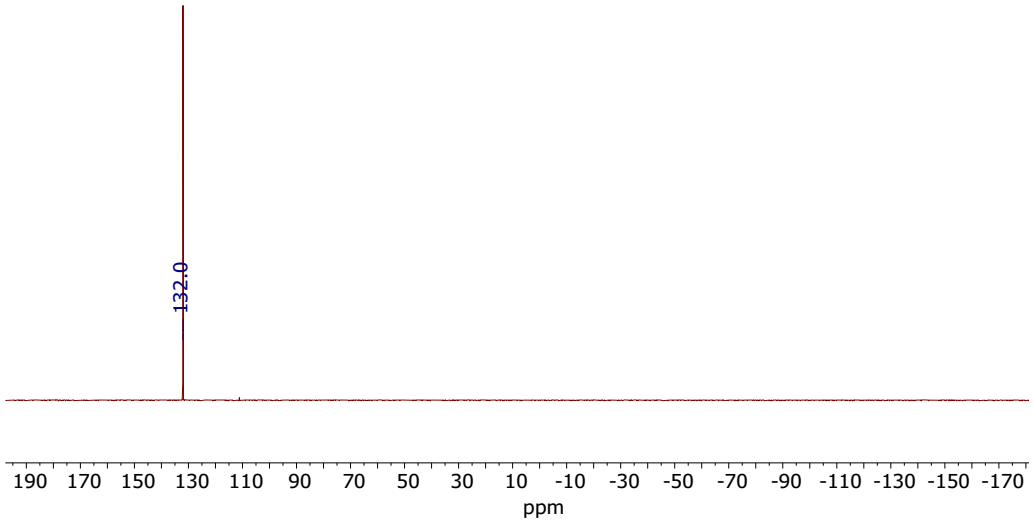


Figure S9: *$^{31}P\{^{1}H\}$ NMR (298 K, $CDCl_3$, 162 MHz) spectrum of $[Au_2(\mu_2\text{-POP})_2](OTf)_2\cdot 2.3DCM$ (**5**·2.3DCM).*

2. Single-crystal X-ray crystallography

Complex 2·0.5THF: A co-crystallized THF molecule is disordered about an inversion center.

Complex 3: The complex crystallized on an inversion center. The second acetonitrile molecule (N2) must have an occupancy of 50% because of its vicinity to an inversion center does not allow a full occupancy. In fact, the model refines well with this. An additional disorder related to the former is observed for the Cu atom which splits to two positions corresponding to two different coordination environments: One for a coordination by three (P1,P2,N1) donor atoms and one for the a coordination of four (P1,P2,N1,N2) donor atoms. Because the Cu site with four instead of three donor atoms is caused by the coordination of the second acetonitrile (N2) and thus its occurrence is linked to the presence of the latter, the occupancies of this Cu position and in turn also the one of the second one were fixed to 50%.

Complex 5·2.3DCM: When modeling the DCM molecule which is disordered about a twofold rotation axis (C54), very large thermal ellipsoids as well as large regions of negative electron density around the atoms were observed which suggest only a partial occupancy. For this reason, its occupancy was set free and refined indeed satisfactorily.

Table S1: *Crystallographic parameters of the complexes **1**–**5**.*

Compound	**1**	**2**·0.5THF	**3**	**4**	**5**·2.3DCM
CCDC No.	2163970	2163971	2163973	2163972	2163974
Formula	C48 H40 Cl2 Fe O2 P4	C34 H40 Cl3 O3.50 P2 Y	C54 H49 Cu2 F12 N3 O2 P6	C24 H20 Au2 Cl2 O P2	C52.28 H44.56 Au2 Cl4.56 F6 O8 P4 S2
Formula weight	899.43	761.86	1312.86	851.17	1658.48
Crystal system	orthorhombic	triclinic	triclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
T [K]	100	100	100	100	150
a [Å]	18.2692(8)	10.0759(11)	10.708(6)	8.9878(11)	20.9822(6)
b [Å]	10.0180(4)	10.3953(13)	12.106(8)	16.301(2)	15.6904(3)
c [Å]	23.2815(8)	16.487(2)	12.285(4)	16.7718(18)	35.7489(10)
α [°]	90	87.021(11)	112.48(4)	90	90
β [°]	90	86.896(10)	96.83(4)	102.113(9)	102.180(2)
γ [°]	90	81.16(4)	104.09(4)	90	90
V [Å^3]	4261.0(3)	1702.2(4)	1386.8(13)	2402.6(5)	11504.3(5)
Z	4	2	1	4	8
Radiation type	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
Temp. [K]	100	100	100	100	150
$\rho_{(calcd)}$ [g·cm^{-3}]	1.402	1.486	1.572	2.353	1.915
μ [mm^{-1}]	0.669	2.078	1.025	12.569	5.563
F(000)	1856	784	666	1576	6430
Cryst. size [mm^3]	0.118 x 0.112 x 0.052	0.179 x 0.130 x 0.080	0.208 x 0.164 x 0.080	0.308 x 0.241 x 0.122	0.776 x 0.473 x 0.276
θ range [°]	2.213-30.321	2.048-31.836	1.846-32.049	2.318-31.574	1.634-25.576
Limiting indices	-23<=h<=25 -12<=k<=13 -32<=l<=32	-14<=h<=13 -15<=k<=15 -21<=l<=22	-15<=h<=15 -18<=k<=17 -17<=l<=17	-10<=h<=13 -16<=k<=21 -22<=l<=22	-25<=h<=25 -19<=k<=17 -43<=l<=43
Reflections collected/unique[a]	46568 / 11147 [R(int) = 0.0491]	20687 / 9113 [R(int) = 0.0647]	17633 / 7480 [R(int)= 0.0808]	14860 / 6619 [R(int) = 0.0264]	66001 / 10752 [R(int) = 0.0312]

Data/restraints/ param	11147 / 1 / 514	9113 / 0 / 410	7480 / 0 / 364	6619 / 0 / 280	10752 / 3 / 698
Completeness to $\theta = 25.242°$ [%]	100.0	99.8	99.9	99.8	100.0
Max. and min. transmission	0.9607 and 0.5372	0.8501 and 0.3293	0.9043 and 0.4873	0.1555 and 0.0471	0.2271 and 0.0662
Final R indices ($I > 2\sigma(I)$)[b]	$R_1 = 0.0380$, $wR_2 = 0.0784$	$R_1 = 0.0751$, $wR_2 = 0.1715$	$R_1 = 0.0553$, $wR_2 = 0.1440$	$R_1 = 0.0297$, $wR_2 = 0.0698$	$R_1 = 0.0360$, $wR_2 = 0.0901$
R indices (all data)	$R_1 = 0.0544$, $wR_2 = 0.0850$	$R_1 = 0.1143$, $wR_2 = 0.2175$	$R_1 = 0.0857$, $wR_2 = 0.1596$	$R_1 = 0.0379$, $wR_2 = 0.0731$	$R_1 = 0.0469$, $wR_2 = 0.0958$
Absolute Structure Parameter	-0.024(9)	n/a	n/a	n/a	n/a
Goodness of fit[c] on F^2	1.016	1.035	1.054	1.025	1.058
Largest diff. peak and hole [$Å^{-3}$]	0.479 and -0.346	1.504 and -1.856	1.195 and -0.602	1.404 and -1.712	2.535 and -1.194

[a] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, [c] GooF $= \{S/(n - p)\}^{1/2} = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

3. Photo-luminescence spectroscopy

Table S2: *Overview of the photo-luminescence studies concerning the PPO ligand and complexes* ***2****,* ***3****,* ***4*** *and* ***5****.*

Compound	**T [K]**	**λ_{ex} [nm]**	**λ_{em} [nm]**	**Lifetime [µs]**	**Quantum yield [%]**
PPO ligand	77	367	456	5.7	n.d.
	298	367	456	5.9	2
2·0.5THF	77	352	414	5.8	n.d.
	298	352	414	5.9	1
3	77	373	483	215.3, 66.7	n.d.
	298	400	440	4.6	0
4	77	361	499	7.2	n.d.
	298	387	470	5.5	0
5·2.3DCM	77	350	445	6.8	n.d.
	298	364	452	5.9	2

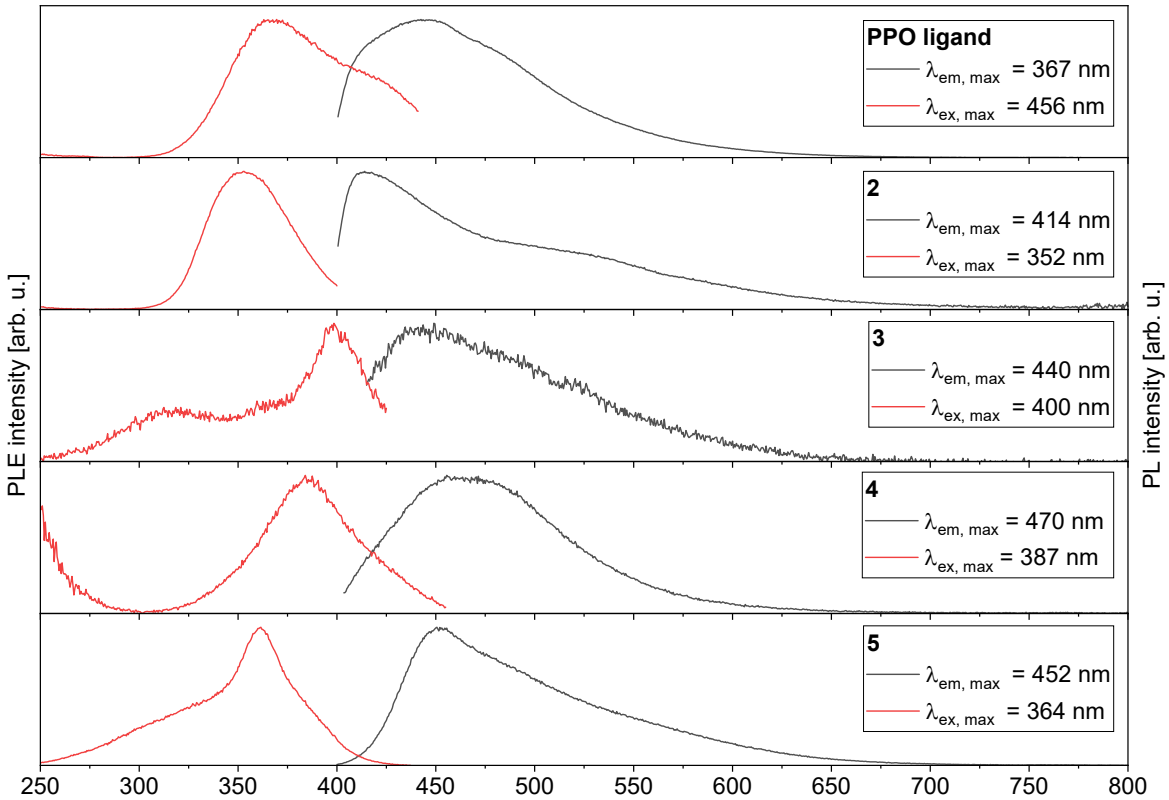
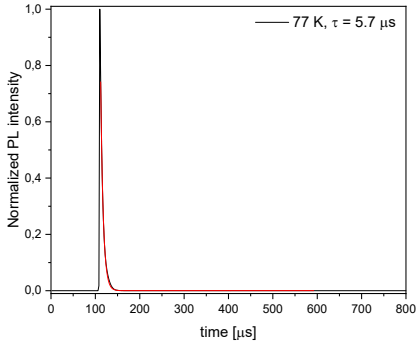
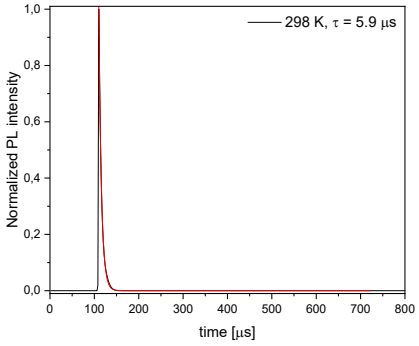
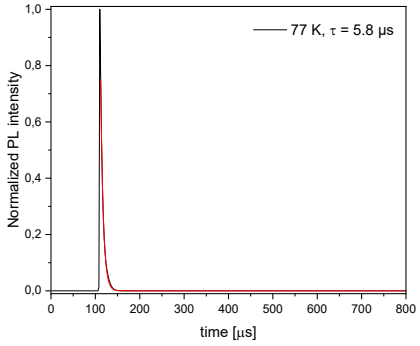
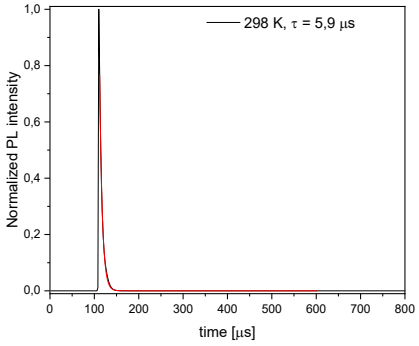
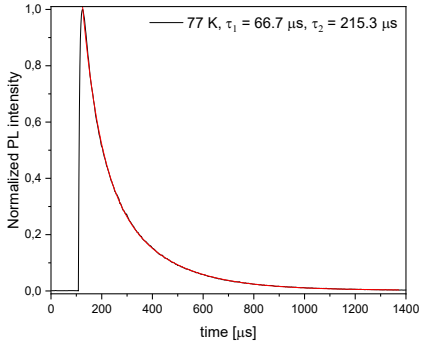
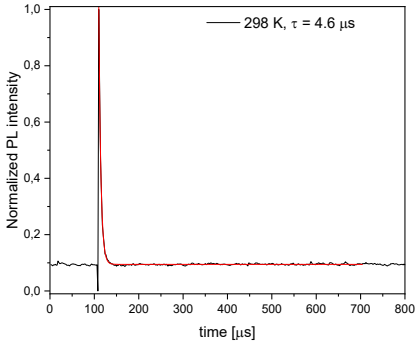
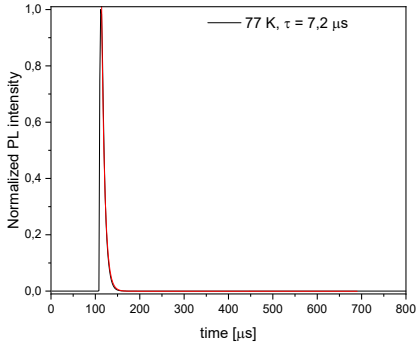
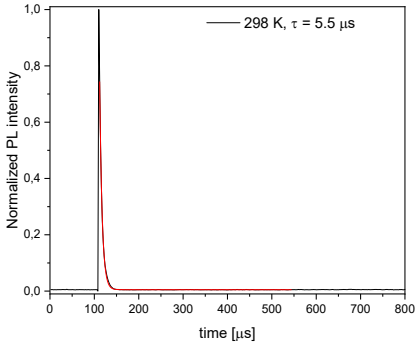
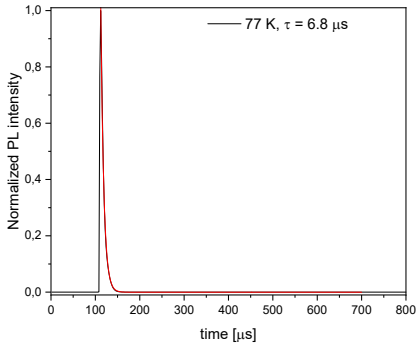
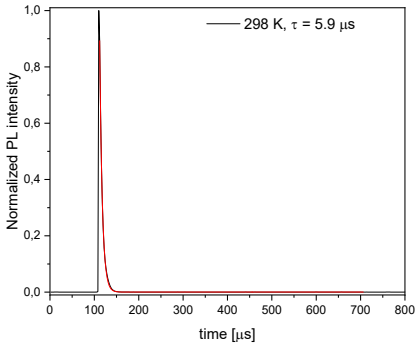


Figure S10: *Photo-luminescence emission (PL) and excitation (PLE) spectra of the PPO ligand and complexes* ***2****–****5*** *at ambient temperature.*

Table S2: *Emission decay traces (black) of the PPO ligand and complexes* ***2****–****5*** *at 77 K and 298 K excited using a PTI XenonFlash™ with a pulse number of 10.000. The red lines indicate decay fits with monoexponential and biexponential curves.*

	77 K	298 K
PPO ligand		
2·0.5THF		
3		
4		

5·2.3DCM	 77 K, τ = 6.8 μs Normalized PL intensity time [μs]	 298 K, τ = 5.9 μs Normalized PL intensity time [μs]