Supporting Information

Bright photo- and triboluminescence of centrosymmetric Eu(III) and Tb(III) complexes with phosphine oxides containing azaheterocycles

Yuliya A. Bryleva*, Alexander V. Artem'ev, Ludmila A. Glinskaya, Mariana I. Rakhmanova, Denis G. Samsonenko, Vladislav Yu. Komarov, Maxim I. Rogovoy, Maria P. Davydova

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3, Academician Lavrentiev Avenue, Novosibirsk 630090, Russian Federation

*Corresponding author

E-mail address: bryleva@niic.nsc.ru (Yu. A. Bryleva)

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Table S1. Selected crystal, data collection and refinement parameters for complexes **1**, **3**, and **5**.

Compound	**1**	**3**	**5**
Empirical formula	$C_{49}H_{31}EuF_{18}N_2O_8P_2$	$C_{47}H_{29}EuF_{18}N_4O_8P_2$	$C_{47}H_{29}EuF_{18}N_4O_8P_2$
Formula weight	1331.66	1333.64	1333.64
T (K)	100(2)	150(2)	150(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/c$	$P2_1/c$
a (Å) b (Å) c (Å)	12.7089(5) 17.7622(7) 20.0802(10)	12.2249(2) 22.3649(2) 19.3523(2)	12.6533(5) 13.3458(5) 30.1222(15)
α (º) β (º) γ (º)	81.090(2) 88.144(2) 88.268(2)	108.084(1)	90.640(4)
Volume (Å^3)	5142.8(4)	5029.7(1)	5086.4(4)
Z	4	4	4
Calculated density (g cm^{-3})	1.720	1.761	1.742
μ (mm^{-1})	1.402	1.44	1.42
Crystal size	0.17 × 0.13 × 0.05	0.22 × 0.17 × 0.13	0.22 × 0.19 × 0.07
T_{min}/T_{max}	0.660/ 0.746	0.841/ 1.0	0.949/ 1.000
Reflections collected	94520 [R(int) = 0.038]	37209 [R(int) = 0.018]	22730 [R(int) = 0.024]
Independent reflections	32502	11316	10992
Observed reflections [$I > 2\ \sigma(I)$]	24970	10084	9383
Number of parameters refined	1459	990	892
Goodness-of-fit on F^2	1.01	1.04	1.11
Final R indices [$I \geq 2\sigma(I)$]	R_1 = 0.0378	R_1 = 0.023	R_1 = 0.038
R indices (all data)	$w\ R_2$ = 0.0745	$w\ R_2$ = 0.057	$w\ R_2$ = 0.080
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.15/ –1.35	0.60/ –0.30	0.97/ –0.70

Table S2. Selected bond lengths and angles for complexes **1**, **3**, and **5**.

1				**3**		**5**	
Bond	Bond lengths (Å)	Bond	Bond lengths (Å)	Bond	Bond lengths (Å)	Bond	Bond lengths (Å)
Eu1–O1	2.338(2)	Eu2–O3	2.338(2)	Eu1–O1	2.366(1)	Eu1–O1	2.325(2)
Eu1–O2	2.330(2)	Eu2–O4	2.316(2)	Eu1–O2	2.381(1)	Eu1–O2	2.321(2)
Eu1–O11	2.412(2)	Eu2–O41	2.407(2)	Eu1–O11	2.501(1)	Eu1–O11	2.389(2)
Eu1–O12	2.407(2)	Eu2–O42	2.441(2)	Eu1–O12	2.399(1)	Eu1–O12	2.425(2)
Eu1–O21	2.387(2)	Eu2–O51	2.366(2)	Eu1–O21	2.426(1)	Eu1–O21	2.404(2)
Eu1–O22	2.431(2)	Eu2–O52	2.439(7)	Eu1–O22	2.377(1)	Eu1–O22	2.410(2)
Eu1–O31	2.402(2)	Eu2–O61	2.412(2)	Eu1–O31	2.517(1)	Eu1–O31	2.430(2)
Eu1–O32	2.418(2)	Eu2–O62	2.400(2)	Eu1–O32	2.409(1)	Eu1–O32	2.381(2)
				Eu1–N12	2.822(2)		
P1 –O1	1.500(2)	P3 –O3	1.498(2)	P1 –O1	1.495(1)	P1 –O1	1.494(2)
P1 –C101	1.807(3)	P3 –C301	1.805(3)	P1 –C101	1.816(2)	P1 –C101	1.802(4)
P1 –C105	1.804(3)	P3 –C306	1.799(3)	P1 –C105	1.793(2)	P1 –C105	1.793(3)
P1 –C112	1.798(2)	P3 –C312	1.804(3)	P1 –C111	1.791(2)	P1 –C111	1.797(3)
P2 –O2	1.501(2)	P4 –O4	1.500(2)	P2 –O2	1.489(2)	P2 –O2	1.489(2)
P2 –C201	1.799(3)	P4 –C401	1.796(3)	P2 –C201	1.822(2)	P2 –C201	1.822(2)
P2 –C206	1.800(3)	P4 –C406	1.795(3)	P2 –C205	1.799(2)	P2 –C205	1.799(2)
P2 –C212	1.807(2)	P4 –C412	1.806(3)	P2 –C211	1.797(2)	P2 –C211	1.797(2)
Angle	Angle size (º)	Angle	Angle size (º)	Angle	Angle size (º)	Angle	Angle size (º)
O1–Eu1–O2	145.70(6)	O3–Eu2–O4	145.00(6)	O1–Eu1–O2	85.93(5)	O1–Eu1–O2	145.53(8)
O1–Eu1–O11	141.02(6)	O3–Eu2–O41	71.98(6)	O1–Eu1–O11	147.57(4)	O1–Eu1–O11	72.20(8)
O1–Eu1–O12	72.32(6)	O3–Eu2–O42	140.36(6)	O1–Eu1–O12	134.57(4)	O1–Eu1–O12	139.39(8)
O1–Eu1–O21	81.67(6)	O3–Eu2–O51	85.35(6)	O1–Eu1–O21	133.09(5)	O1–Eu1–O21	113.03(8)
O1–Eu1–O22	80.10(6)	O3–Eu2–O52	77.83(6)	O1–Eu1–O22	81.89(5)	O1–Eu1–O22	73.10(8)
O1–Eu1–O31	72.78(6)	O3–Eu2–O61	73.64(6)	O1–Eu1–O31	70.54(5)	O1–Eu1–O31	78.66(8)
O1–Eu1–O32	111.31(6)	O3–Eu2–O62	109.30(6)	O1–Eu1–O32	73.62(4)	O1–Eu1–O32	83.07(8)
O2–Eu1–O11	72.96(6)	O4–Eu2–O41	142.77(6)	O2–Eu1–O11	74.25(5)	O2–Eu1–O11	141.62(8)
O2–Eu1–O12	141.38(6)	O4–Eu2–O42	73.98(6)	O2–Eu1–O12	85.31(5)	O2–Eu1–O12	74.35(8)
O2–Eu1–O21	106.73(6)	O4–Eu2–O51	101.90(6)	O2–Eu1–O21	139.12(5)	O2–Eu1–O21	77.80(9)
O2–Eu1–O22	72.05(6)	O4–Eu2–O52	72.64(6)	O2–Eu1–O22	72.05(6)	O2–Eu1–O22	80.71(8)
O2–Eu1–O31	80.40(6)	O4–Eu2–O61	79.85(6)	O2–Eu1–O31	140.92(5)	O2–Eu1–O31	72.22(8)
O2–Eu1–O32	78.26(6)	O4–Eu2–O62	82.33(6)	O2–Eu1–O32	75.08(5)	O2–Eu1–O32	103.69(8)

Table S3. Quantum yields (Φ_{TOT}), wavelengths of kinetics registration (λ_{reg}), lifetimes (τ_i), and relative contribution of exponents to the number of emitted photons $N(\%) = 100 \times A_i\tau_i / \sum_i A_i\tau_i$ at the fitting of the kinetics (Fig. S10) in the two-exponential approximation for $Ph_2P(O)Py$, $Ph_2P(O)Pym$, and $Ph_2P(O)Pyr$ in the solid state at 300 K (λ_{ex} = 350 nm).

Compound	Φ_{TOT}, %	λ_{reg}, nm	τ_1, ns	N_1, %	τ_2, ns	N_2, %
$Ph_2P(O)Py$	8.5	400	4.7	–	–	–
		500	8.7	99.8	113	0.2
$Ph_2P(O)Pym$	7	400	7.8	–	–	–
		500	11.9	99.96	3.1	0.04
$Ph_2P(O)Pyr$	7	400	4.1	–	–	–
		500	71.2	99.98	5.8	0.02

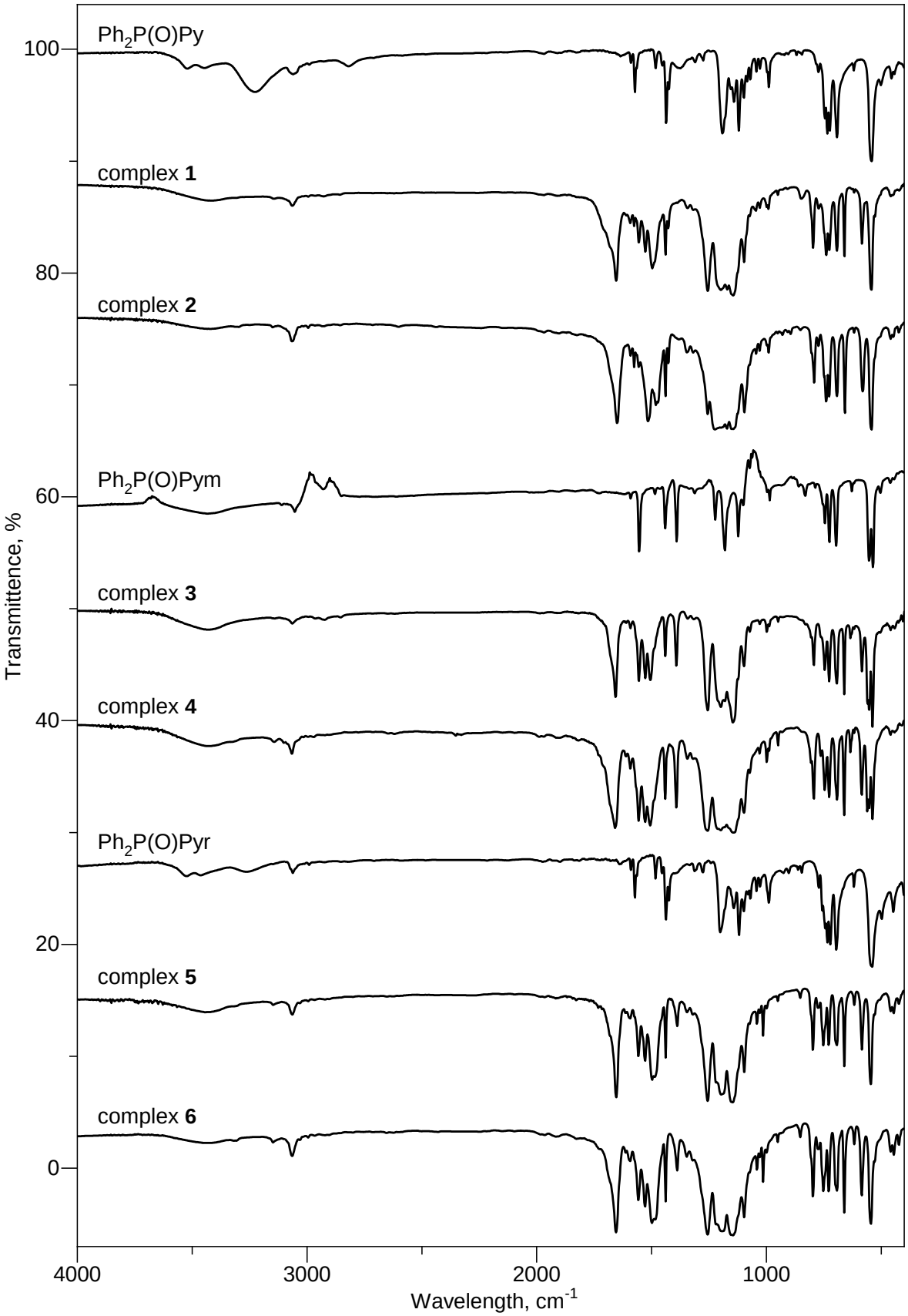
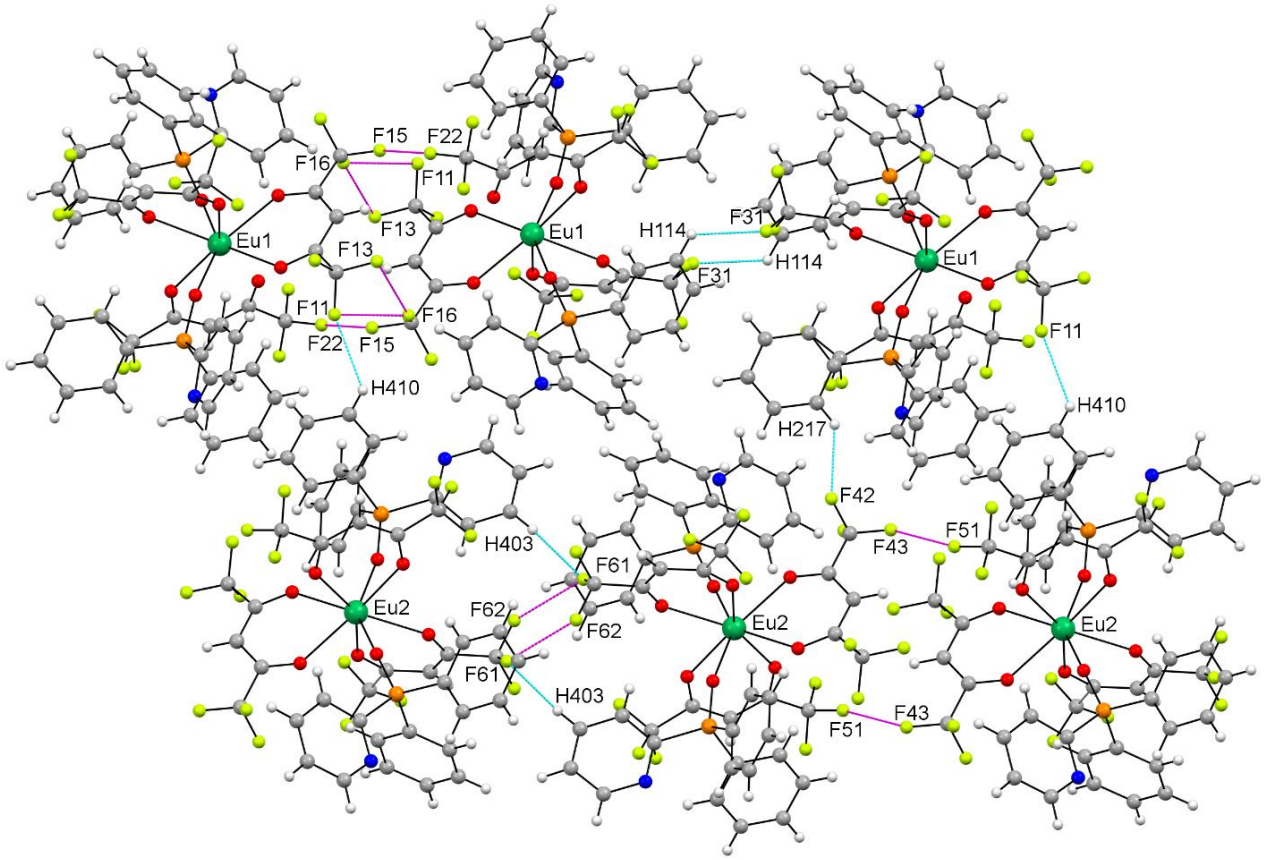


Figure S1. FT-IR spectra of $Ph_2P(O)Py$, $Ph_2P(O)Pym$, $Ph_2P(O)Pyr$ and complexes **1**–**6**.

(*a*)



(*b*)

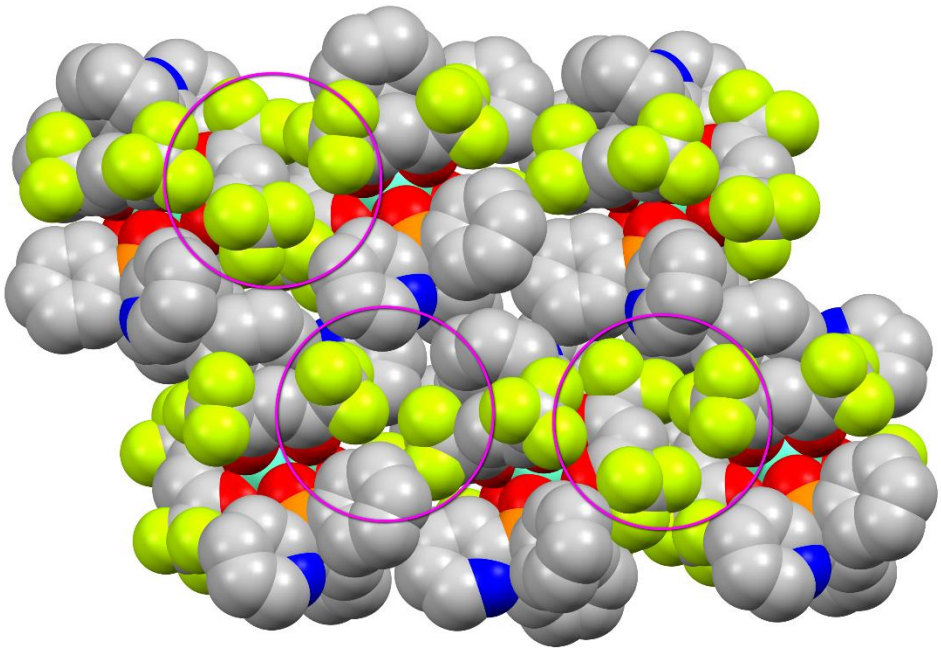
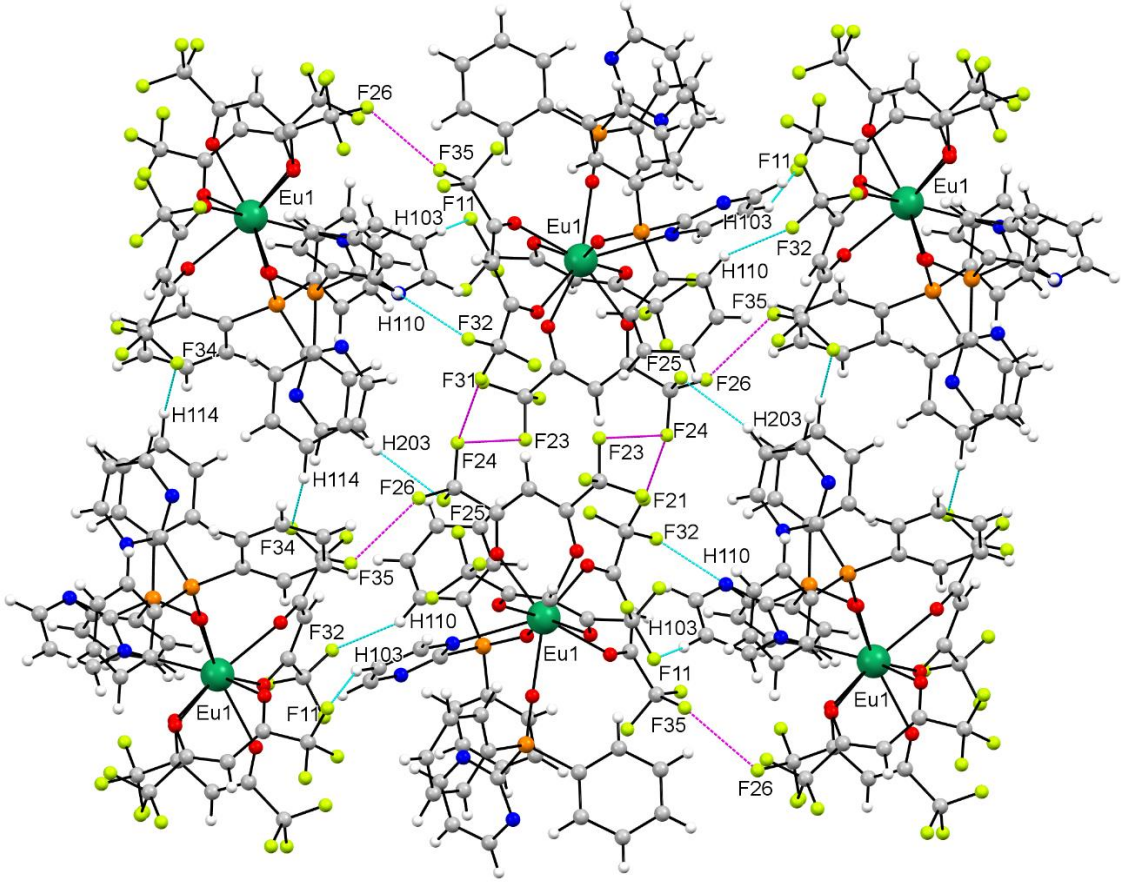


Figure S2. (*a*) Crystal structure of complex **1** focused on intermolecular C–H..F (cyan) and F…F (magenta) contacts, disordered atom positions are omitted for clarity; (*b*) space filling model focused on the intermolecular CF_3 arrangement in **1** (disordered atom positions and hydrogen atoms are omitted).

(*a*)



(*b*)

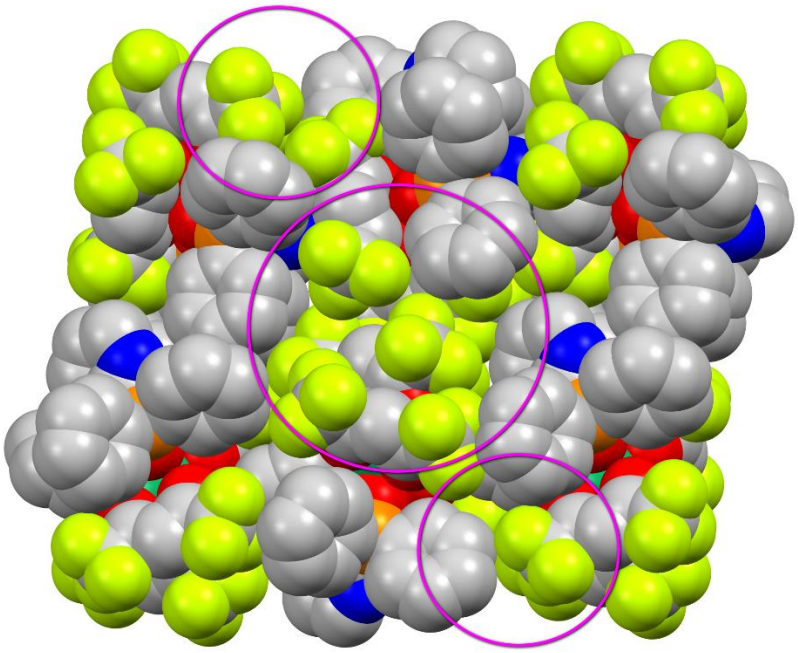
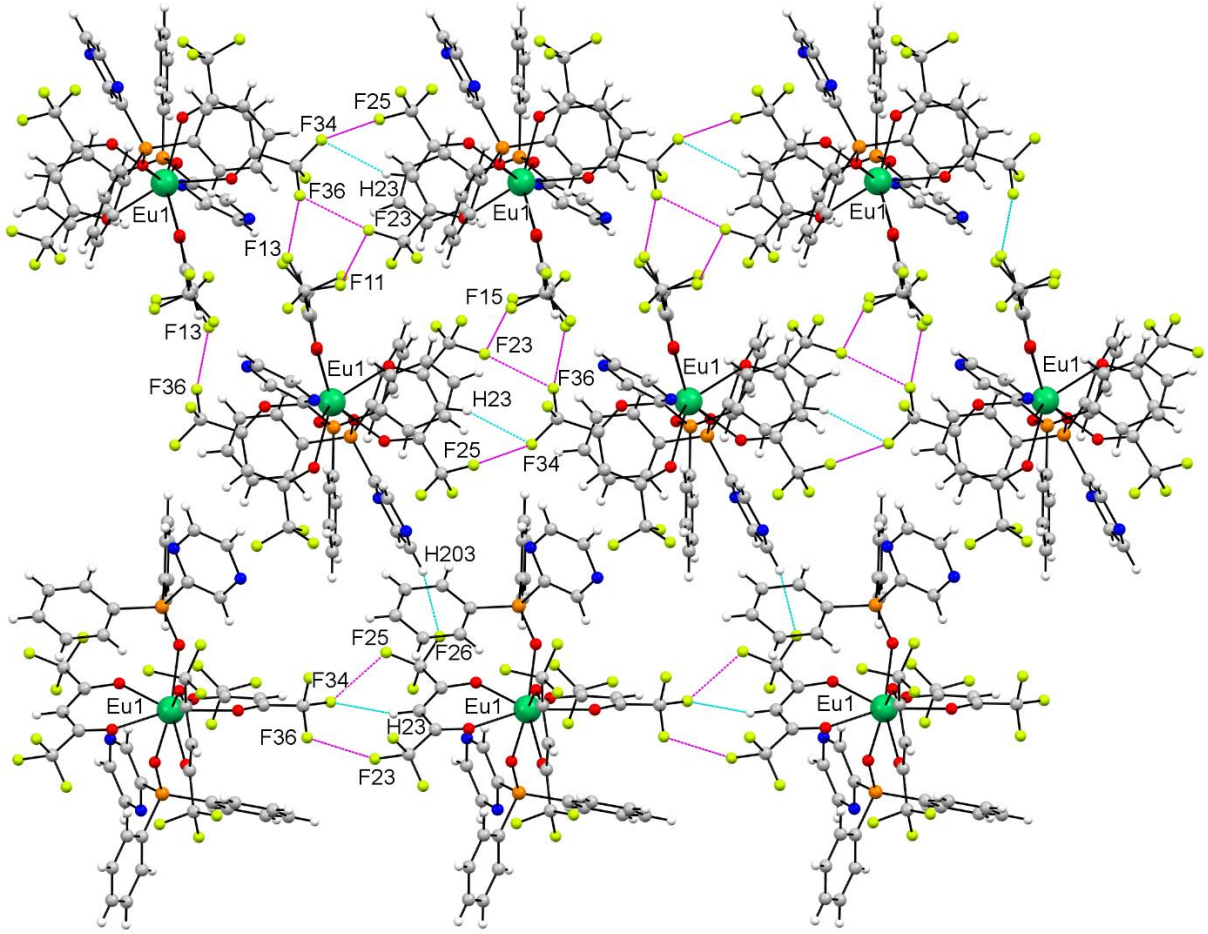


Figure S3. (*a*) Crystal structure of complex **3** focused on intermolecular C–H..F (cyan) and F…F (magenta) contacts, disordered atom positions are omitted for clarity; (*b*) space filling model focused on the intermolecular CF_3 arrangement in **3** (disordered atom positions and hydrogen atoms are omitted).

(*a*)



(*b*)

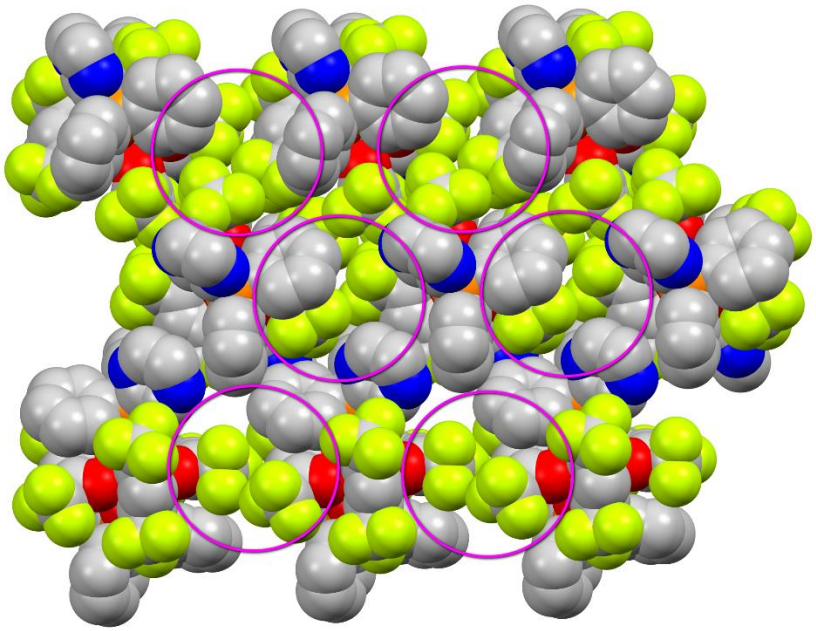


Figure S4. (*a*) Crystal structure of complex **5** focused on intermolecular C–H..F (cyan) and F…F (magenta) contacts, disordered atom positions are omitted for clarity; (*b*) space filling model focused on the intermolecular CF_3 arrangement in **5** (disordered atom positions and hydrogen atoms are omitted).

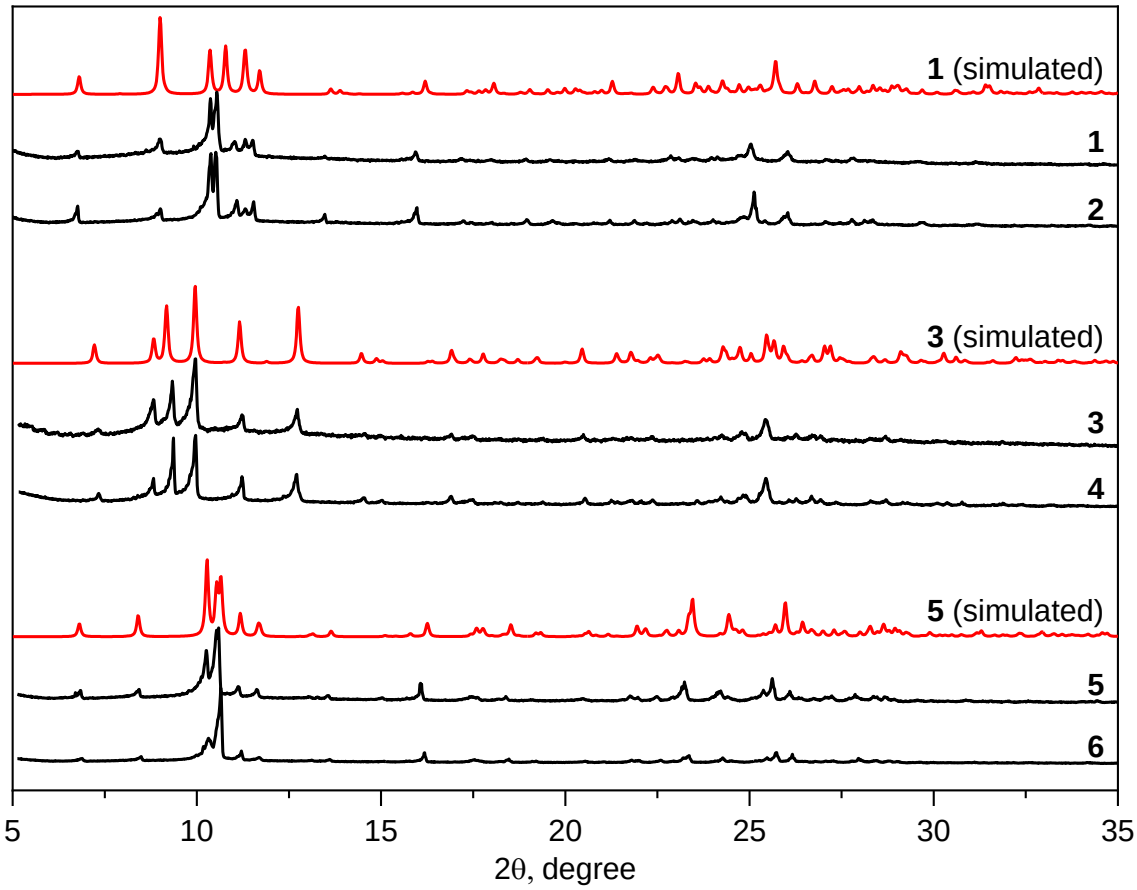


Figure S5. Simulated XRPD pattern of **1**, **3**, and **5** (red), and experimental ones of complexes **1**−**6** (black).

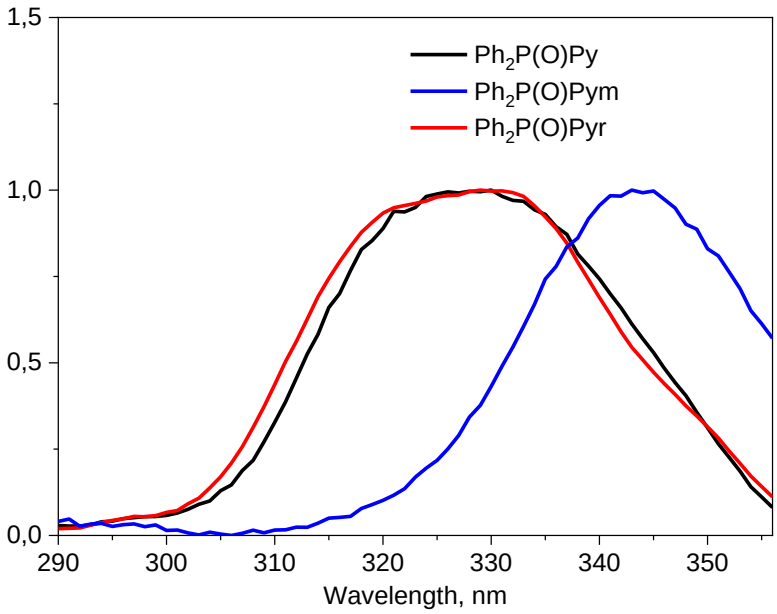


Figure S6. Normalized photoluminescence excitation spectra of $Ph_2P(O)Py$, $Ph_2P(O)Pym$, and $Ph_2P(O)Pyr$ at λ_{em} = 370 nm.

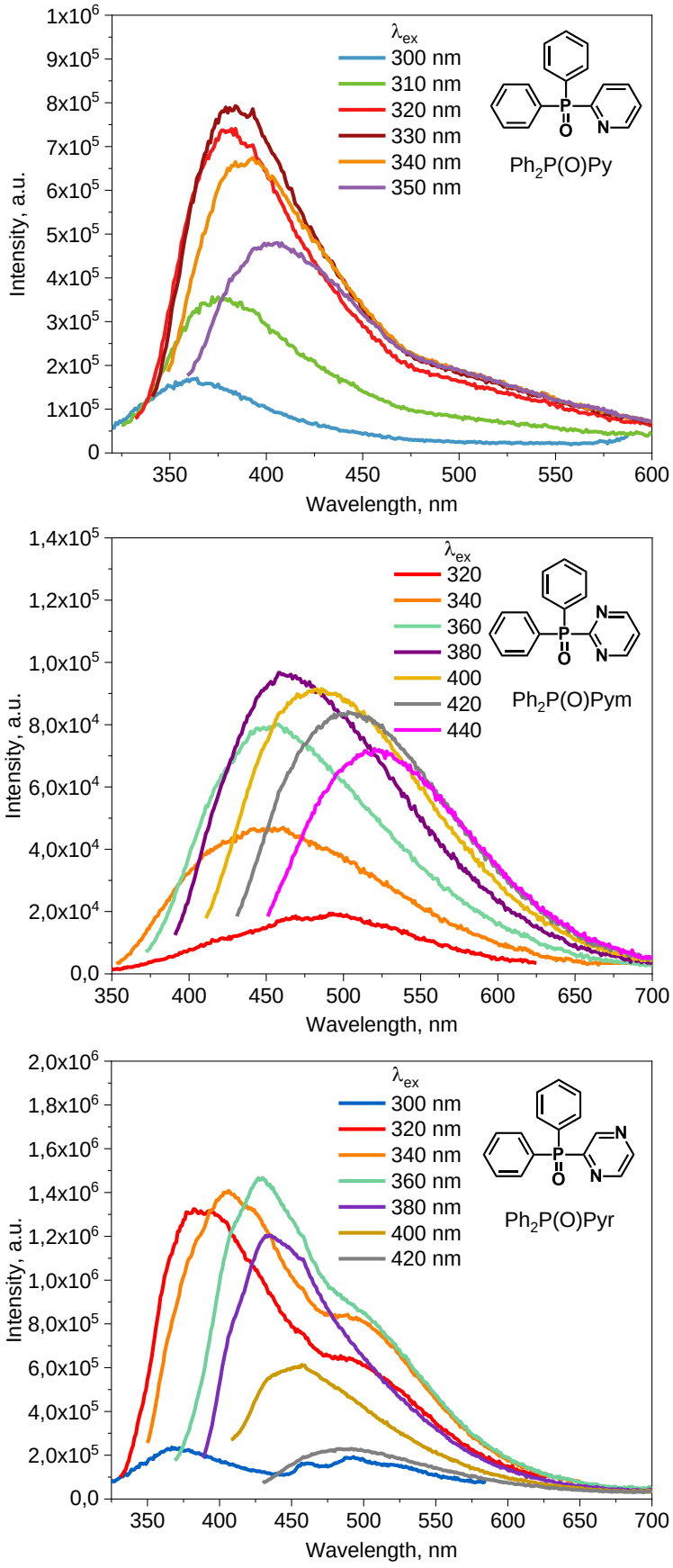


Fig. S7. Photoluminescence spectra of $Ph_2P(O)Py$, $Ph_2P(O)Pym$, and $Ph_2P(O)Pyr$ recorded at different excitation wavelengths (λ_{ex}) in the solid state at 300 K.

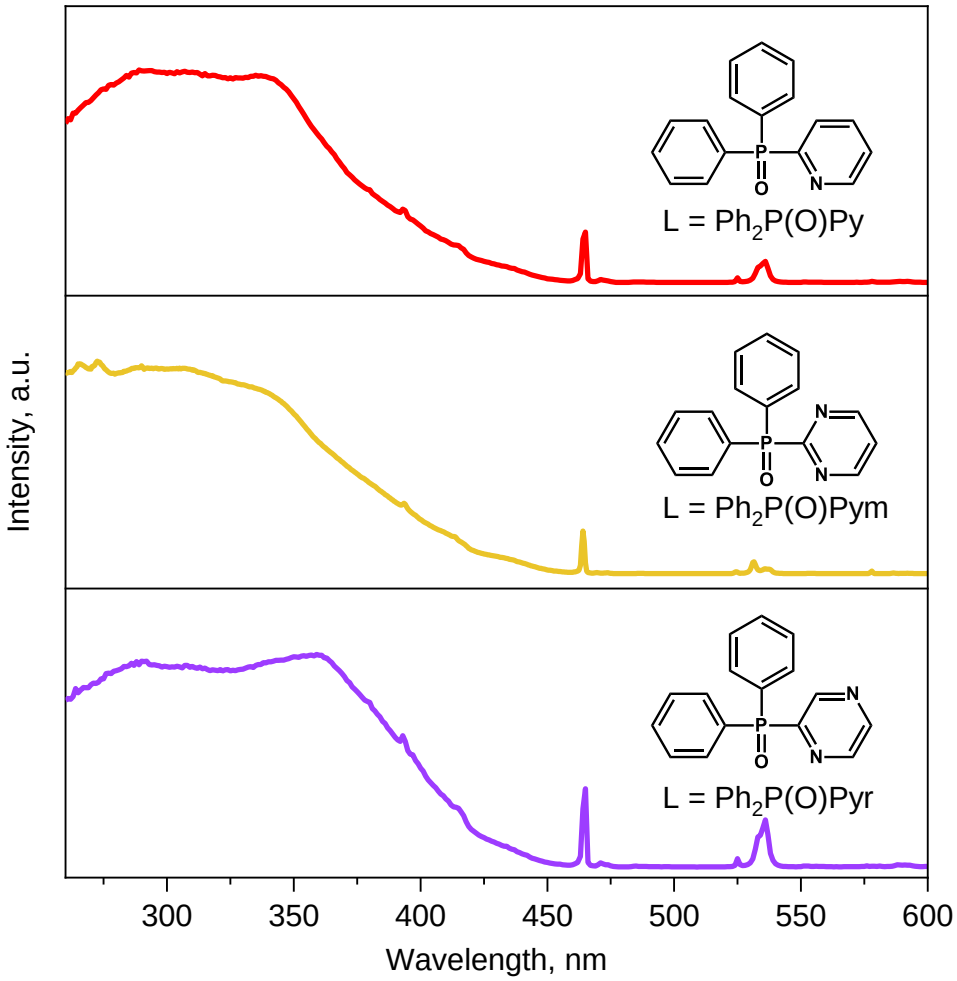


Figure S8. Normalized photoluminescence excitation spectra of the complexes $[EuL_2(hfac)_3]$, where L is $Ph_2P(O)Py$ (**1**), $Ph_2P(O)Pym$ (**3**), or $Ph_2P(O)Pyr$ (**5**).

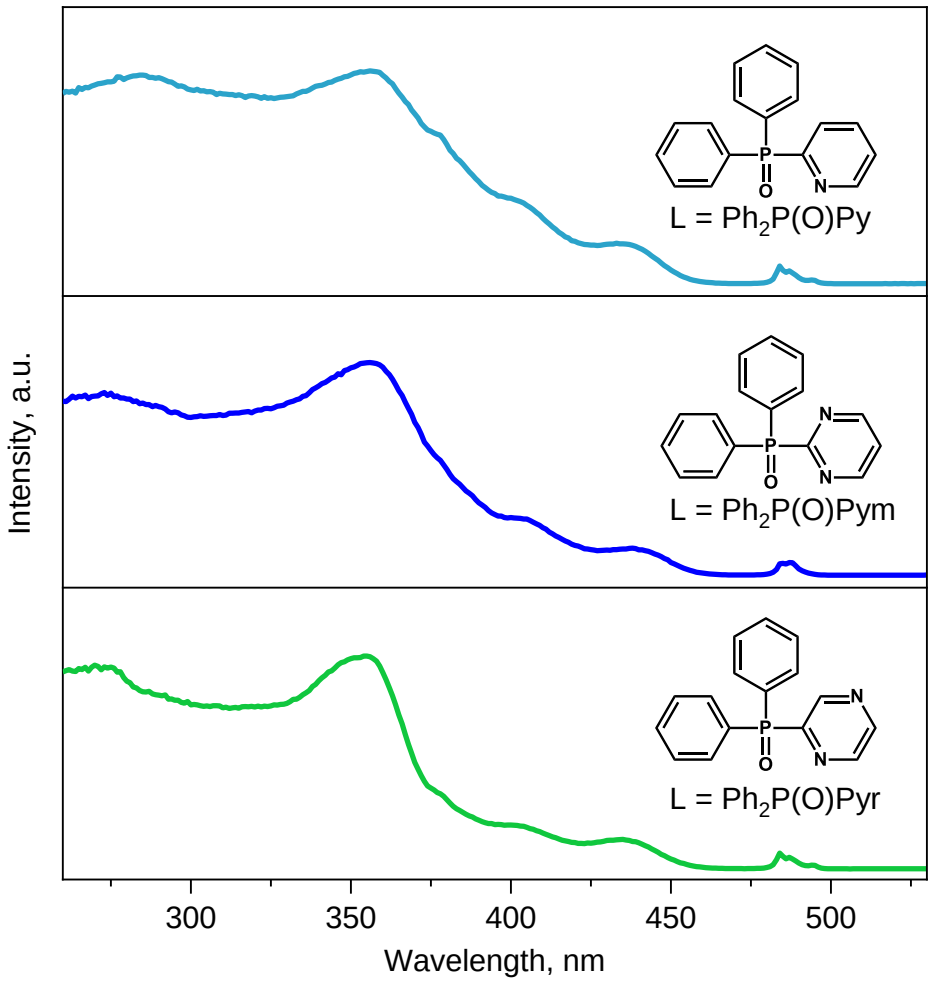


Fig. S9. Normalized photoluminescence excitation spectra of the complexes $[TbL_2(hfac)_3]$, where L is $Ph_2P(O)Py$ (**2**), $Ph_2P(O)Pym$ (**4**), or $Ph_2P(O)Pyr$ (**6**).

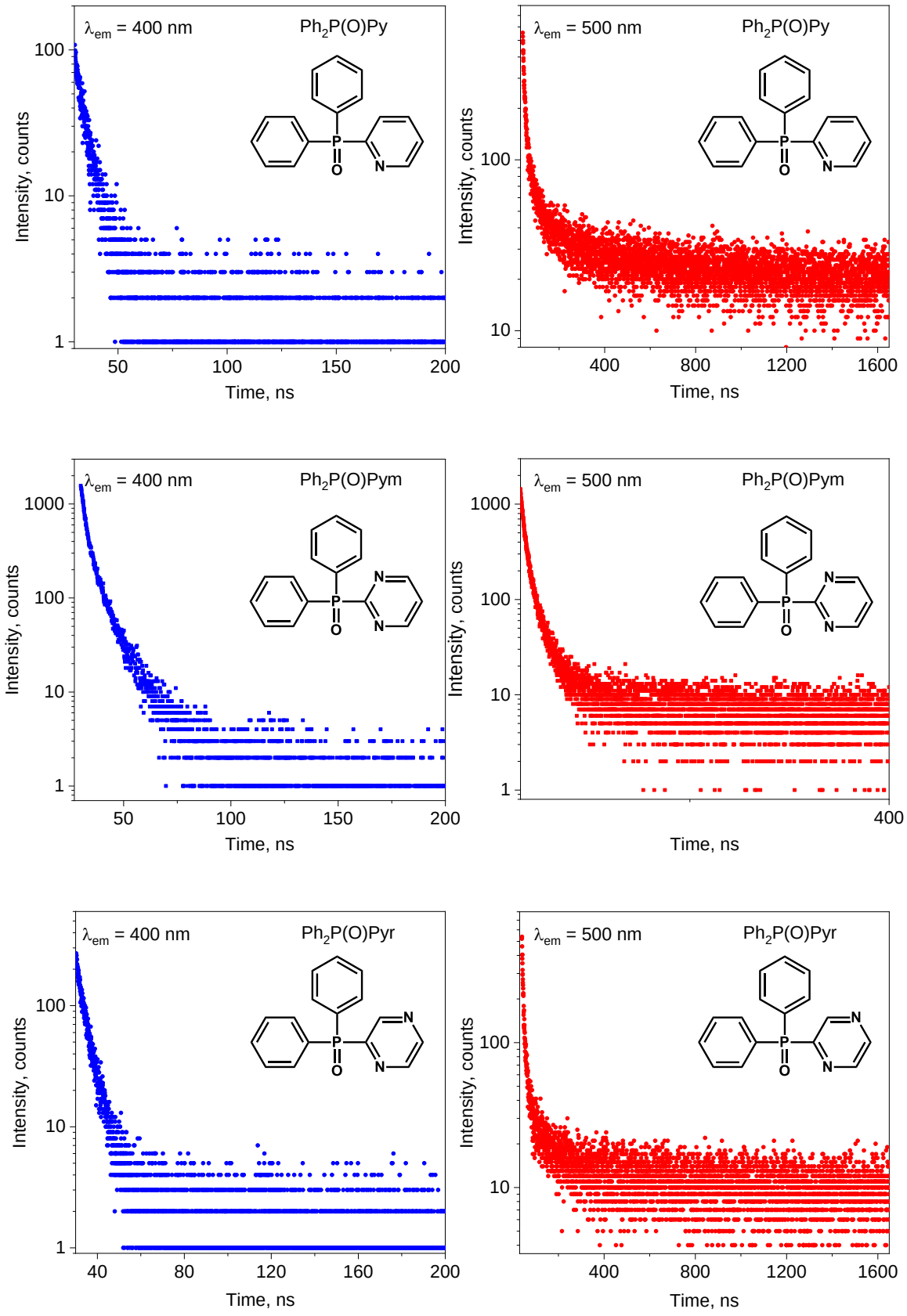


Fig. S10. Kinetics of photoluminescence decay of $Ph_2P(O)Py$, $Ph_2P(O)Pym$, and $Ph_2P(O)Pyr$ at λ_{em} = 400 and 500 nm in the solid state at 300 K (λ_{ex} = 350 nm).