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Tris[(pyridin-4-yl)methyl]phosphine, its *P*-oxide and CuI-based 1D polymer thereof

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§1. Materials and Instrumentation

4-Methylpyridine ("for synthesis", Sigma-Aldrich), *n*-butyllithium solution (2.5 M in hexanes, Sigma-Aldrich), chlorotrimethylsilane (TMSCl, "for synthesis", Sigma-Aldrich), phosphorus trichloride ("for synthesis", Sigma-Aldrich), acetone (Vekton), 30% aqeous H_2O_2 (Vekton), methanol (Vekton), hexane (ANT), and acetonitrile (Cryochrom) were commercially purchased and used as received. Tetrahydrofuran (Vekton) and diethyl ether (Cryochrom) were absolutized by boiling over sodium and subsequent distillation. FT-IR spectra were recorded on a Bruker Vertex 80 spectrometer at ambient temperature. The microanalyses were performed on a MICRO cube analyzer. ^{1}H and ^{31}P{^{1}H} NMR spectra were registered using a Bruker AV-500 spectrometer at 500.13 and 202.46 MHz, respectively. Chemical shifts were reported in δ (ppm) relative to $CDCl_3$ and DMSO-d$_6$ (for ^{1}H) as internal standard or 85% H_3PO_4/D_2O (for ^{31}P) as an external standard. The microanalyses were performed on a MICRO cube analyzer.

4-[(Trimethylsilyl)methyl]pyridine. *n*-Buthyllithium (30.0 mL, 75 mmol, 2.5 M in hexanes) was added to a stirred solution of 4-methylpyridine (7.40 mL, 6.98 g, 75 mmol) in THF (75 mL) at −50 °C. After stirring for 1 h at −20 °C, chlorotrimethylsilane (9.50 mL, 75 mmol) was added dropwise. The cooling was then removed, and the reaction mixture was stirred overnight at ambient temperature. The resulting solution was concentrated in vacuum, an obtained residue was washed with hexane (50 mL) and dried in vacuum. The yellow oil was distilled at 40 °C under reduced pressure (0.1 mm Hg) to give colorless liquid. Yield: 5.3 g (51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48–8.34 (m, 2H, Py), 6.98–6.85 (m, 2H, Py), 2.12 (s, 2H, CH_2), 0.04 (s, 9H, CH_3). Anal. Calc., %: C 65.4; H 9.1; N 8.5. $C_9H_{15}NSi$. Found, %: C 65.2; H 9.2; N 8.6.

Tris(pyridin-4-ylmethyl)phosphine (1). Phosphorus trichloride (0.87 mL, 1.37 g, 10 mmol) was added dropwise to a stirred solution of 4-[(trimethylsilyl)methyl]pyridine (5.30 g, 32 mmol) in absolute THF (30 mL) at −30 °C. Then the cooling was removed, and the reaction mixture was stirred overnight at ambient temperature. The resulting solution was concentrated in vacuum. The residue was extracted with absolute diethyl ether (200 mL). The ether was removed in vacuum to give 1.00 g (30%) of beige powder. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55–8.49 (m, 6H, Py), 7.10–7.02 (m, 6H, Py), 2.77 (s, 6H, CH_2). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ −11.10. Anal. Calc., %: C 70.3; H 5.9; N 13.7. $C_{18}H_{18}N_3P$. Found, %: C 70.3; H 6.0; N 13.5.

Tris(4-pyridin-4-ylmethyl)phosphine oxide (2). Aqueous H_2O_2 (30%, 100 µL, 1 mmol) was added to a solution of phosphine **1** (310 mg, 1 mmol) in acetone (10 mL). After stirring for 30 min, the volatiles were removed in vacuum, and the residue was dried at room temperature to leave white powder. Yield: 290 mg (89%). ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.41 (t, *J* = 4.4 Hz, 6H, Py), 7.22–7.13 (m, 6H, Py), 3.26 (d, *J* = 14.0 Hz, 6H, CH_2). ^{31}P{^{1}H} NMR (202 MHz, DMSO-*d*$_6$) δ 37.49. FT-IR (KBr, cm^{-1}): 496, 546, 562, 593, 618, 657, 669, 699, 794, 827, 854, 884, 963, 991, 1035, 1070, 1130, 1180, 1218, 1245, 1258, 1341, 1364, 1415, 1450, 1488, 1506, 1557, 1599, 1637, 1669, 1685, 1705, 1716, 1943, 2914, 2949, 3025, 3051. Anal. Calc., %: C 66.9; H 5.7; N 13.2. $C_{18}H_{18}N_3OP$. Found, %: C 66.9; H 5.6; N 13.0. Crystals of compound **2** were grown by slow evaporation of solution of **2** in methanol for 48 h at room temperature.

$[Cu_4I_4L_2]_n$·4MeCN (**3**·4MeCN). A mixture of **2** (8 mg, 0.025 mmol) and CuI (9 mg, 0.05 mmol) was suspended in MeCN (1 mL) and then was kept at 80 °C for 24 h. After slow cooling, the precipitated yellow crystals were manually separated. Yield: 5 mg (27%). Anal. Calc. for $C_{44}H_{48}Cu_4I_4N_{10}O_2P_2$, %: C 33.6; H 3.1; N 8.9. Found, %: C 33.5; H 3.2; N 8.7

§2. Single crystal X-ray crystallography

Table S1. X-Ray crystallographic data for **2** and **3**·4CH_3CN.

Parameter	**2**	**3**·4CH_3CN
CCDC number	2312478	2312479
Chemical formula	$C_{18}H_{18}N_3OP$	$C_{22}H_{24}Cu_2I_2N_5OP$
M_r	323.32	786.31
Crystal system, space group	Trigonal, *R*3	Triclinic, $P\bar{1}$
Temperature (K)	150	150
a, *b*, *c* (Å)	16.5575(6), 5.1041(3)	10.2693(2), 11.1017(2), 12.6897(3)
α, β, γ (°)	–	88.950(1), 73.962(1), 79.294(1)
V (Å^3)	1211.82(11)	1365.37(5)
Z	3	2
μ (mm^{-1})	0.18	3.90
Crystal size (mm)	0.19 × 0.04 × 0.03	0.13 × 0.1 × 0.06
T_{min}, T_{max}	0.684, 0.746	0.600, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4768, 1296, 1261	15788, 6744, 5763
R_{int}	0.028	0.021
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.667	0.667
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.028, 0.066, 1.10	0.024, 0.054, 1.03
No. of reflections	1296	6744
No. of parameters	70	300
No. of restraints	1	–
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.19	0.67, −0.67

§3. NMR spectra

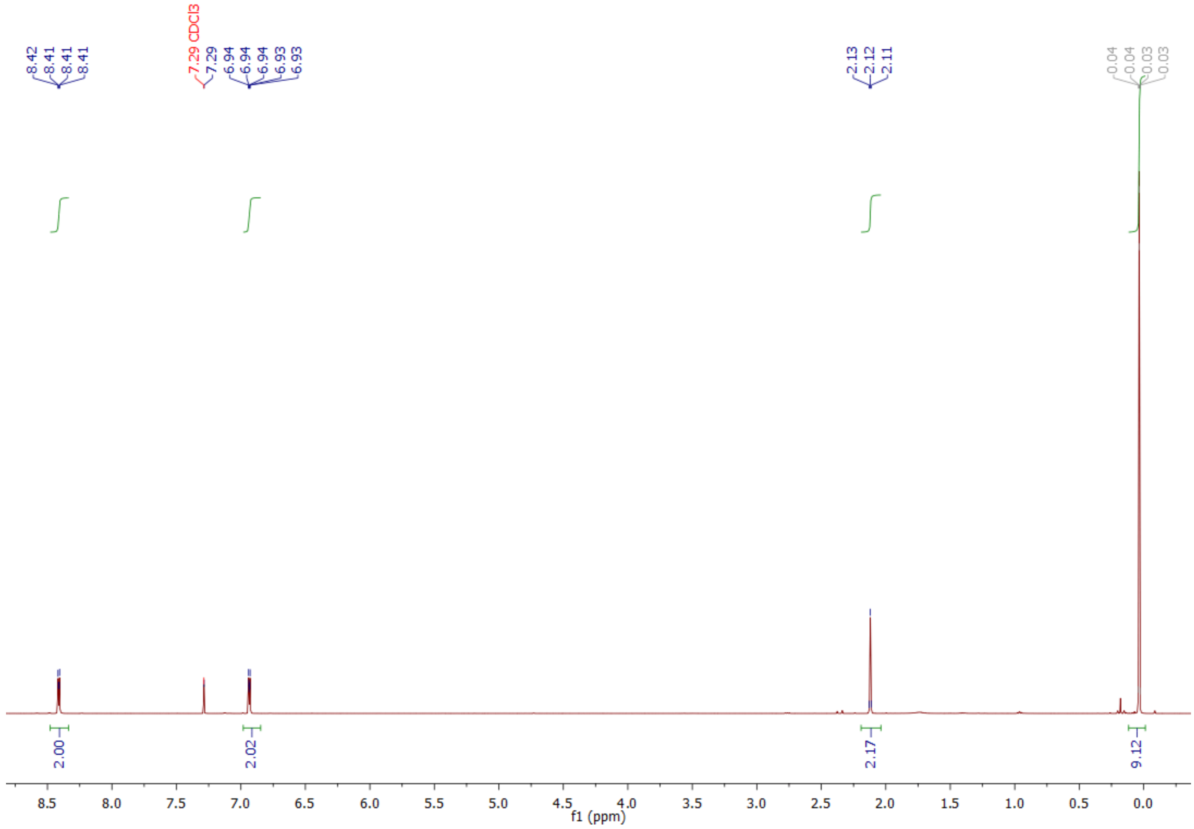

Figure S1. ^{1}H NMR spectrum of 4-[(trimethylsilyl)methyl]pyridine ($CDCl_3$).

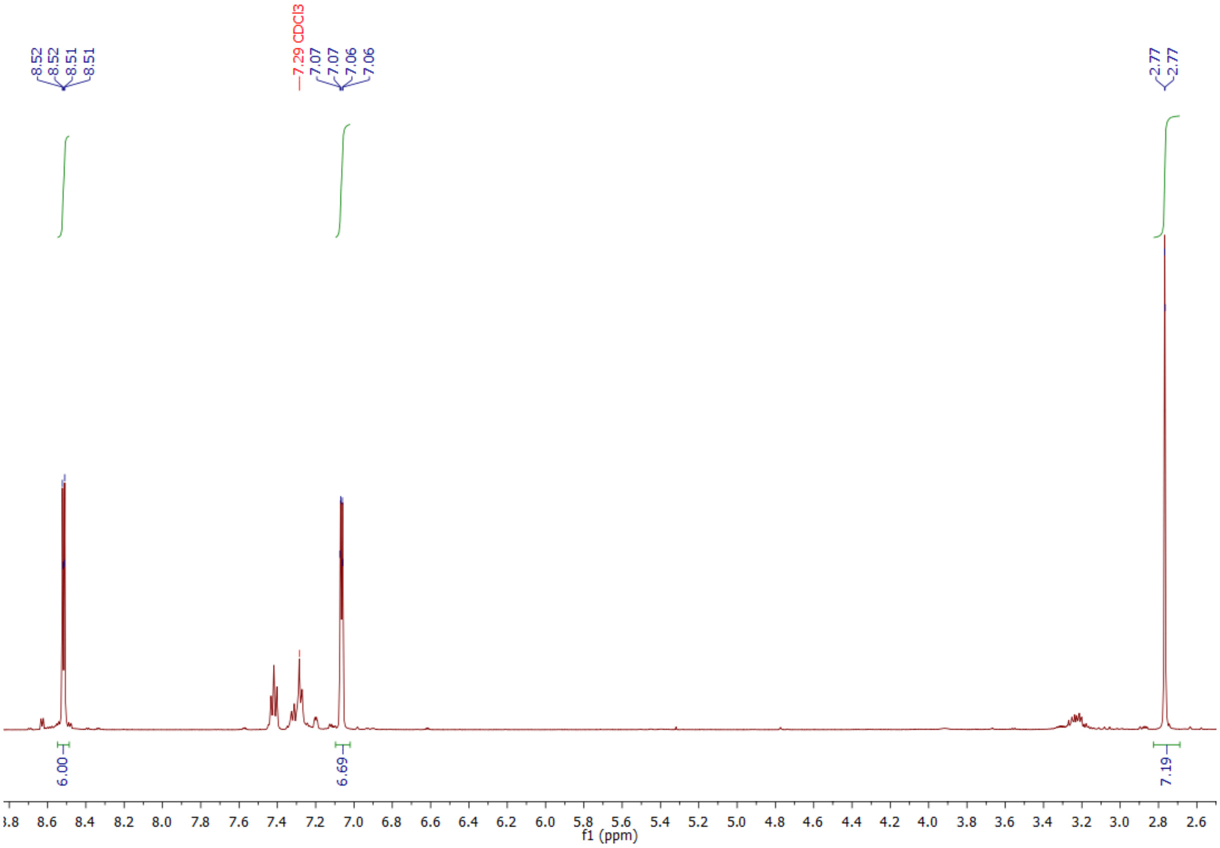

Figure S2. ^{1}H NMR spectrum of tris(pyridin-4-ylmethyl)phosphine **1** ($CDCl_3$).

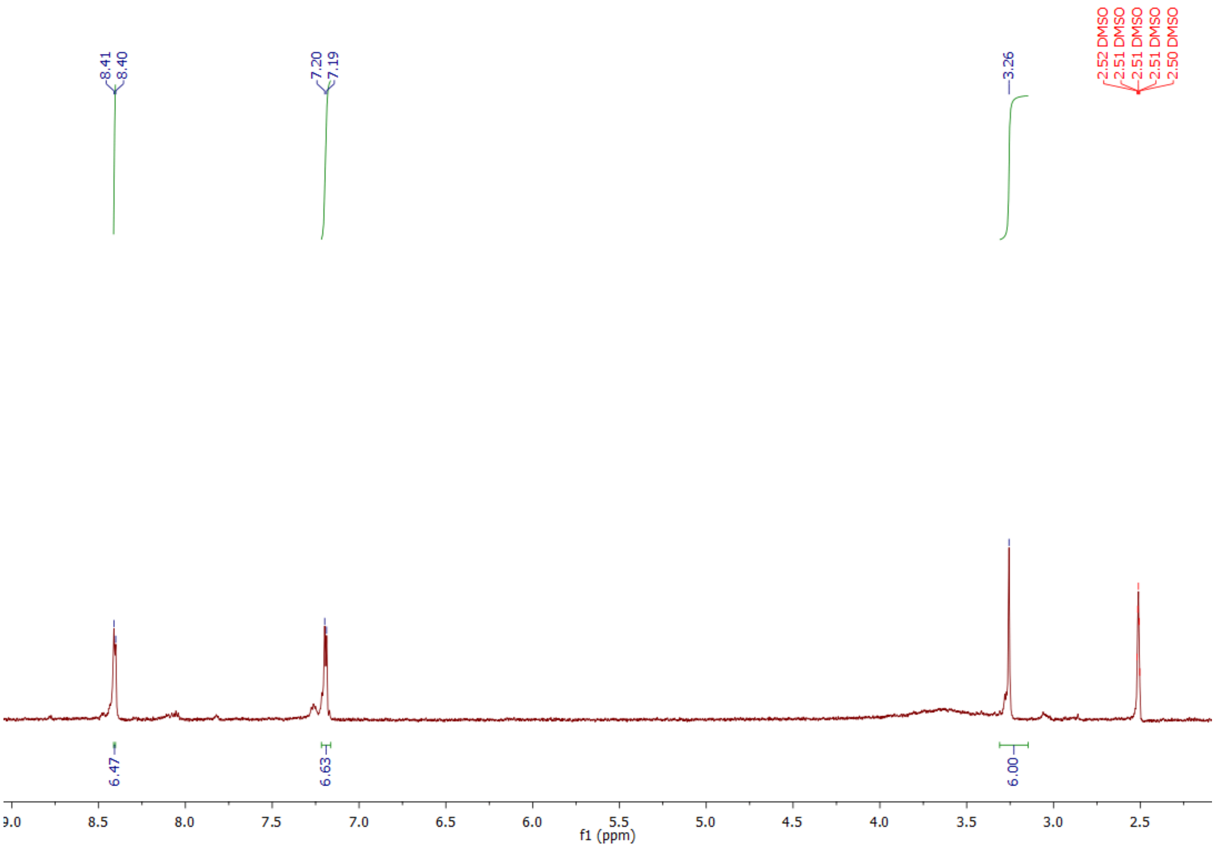

Figure S3. ^{1}H NMR spectrum of tris(4-pyridin-4-ylmethyl)phosphine oxide **2** (DMSO-d_6).

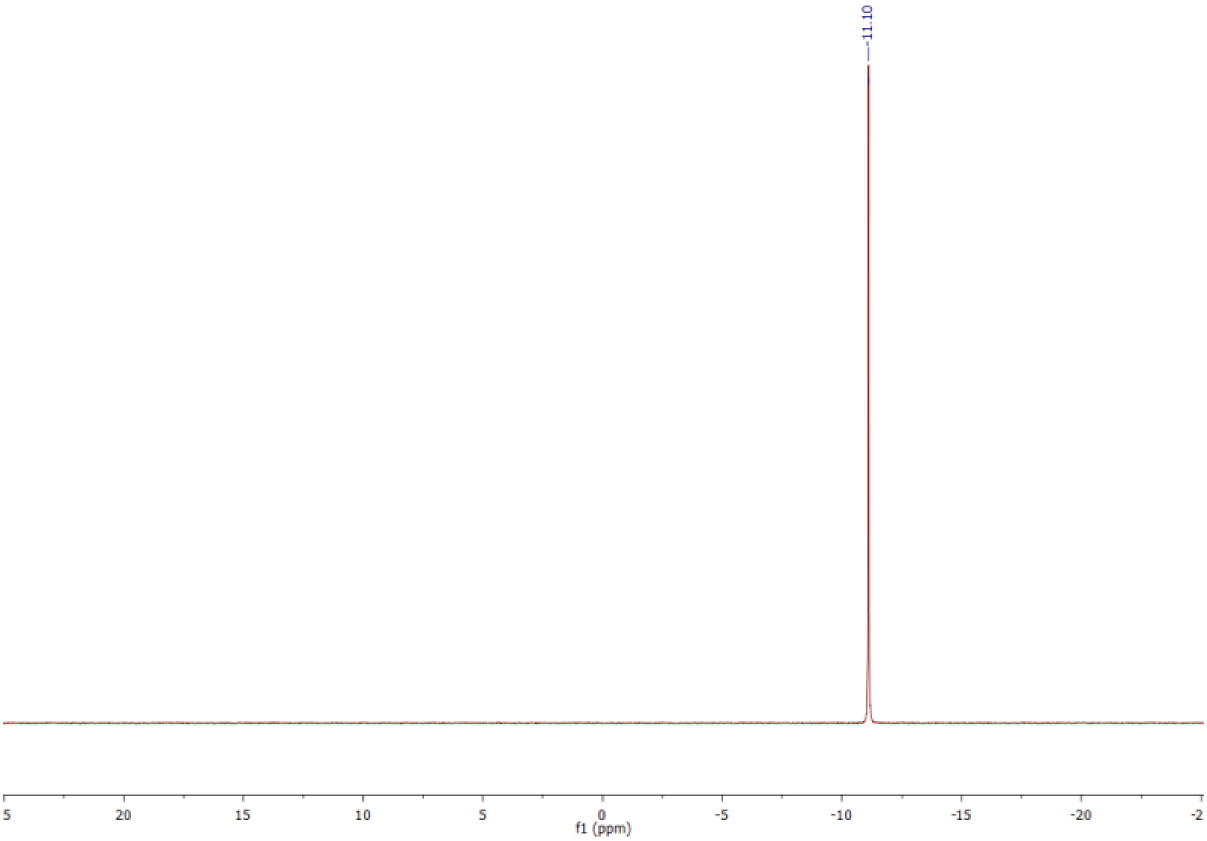

Figure S4. ^{31}P{^{1}H} NMR spectrum of tris(pyridin-4-ylmethyl)phosphine **1** (CDCl$_3$).

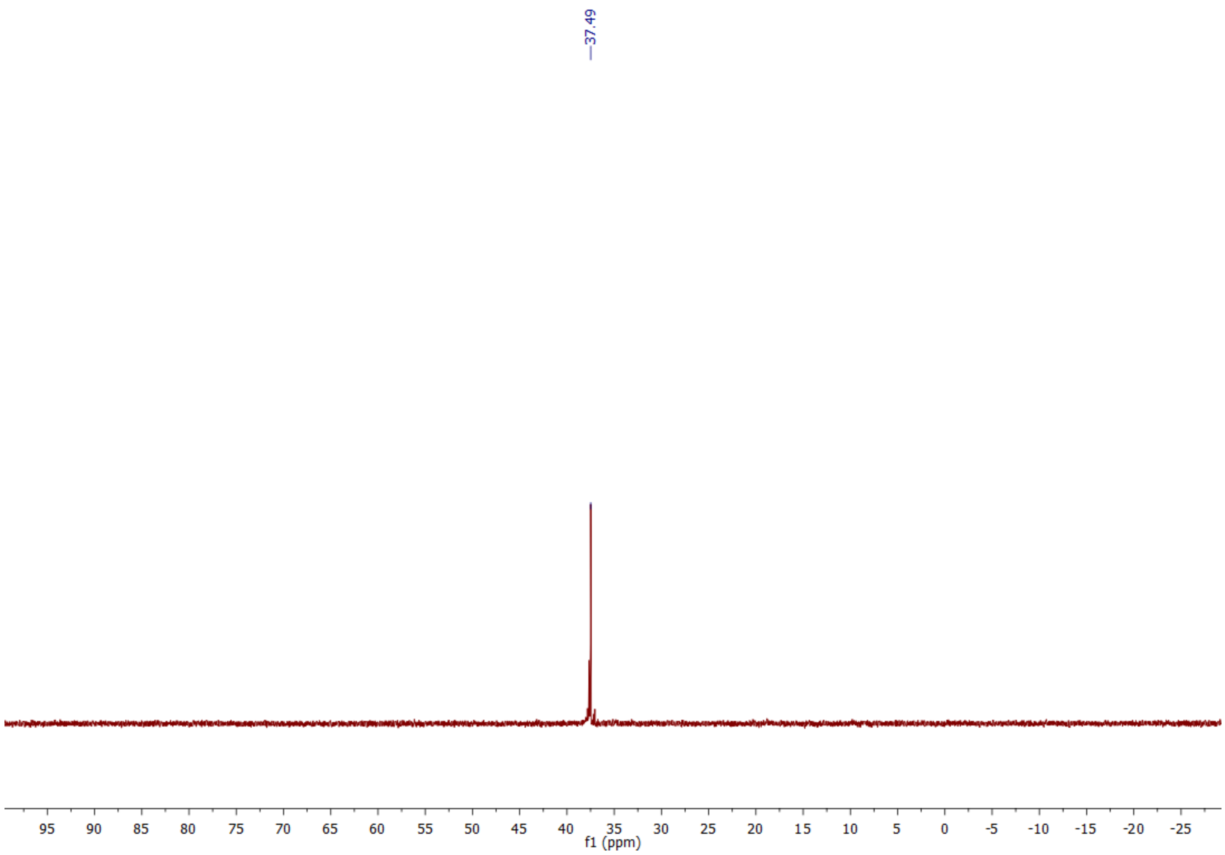

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of tris(4-pyridin-4-ylmethyl)phosphine oxide **2** (DMSO-d_6).

§6. Excitation and emission spectra

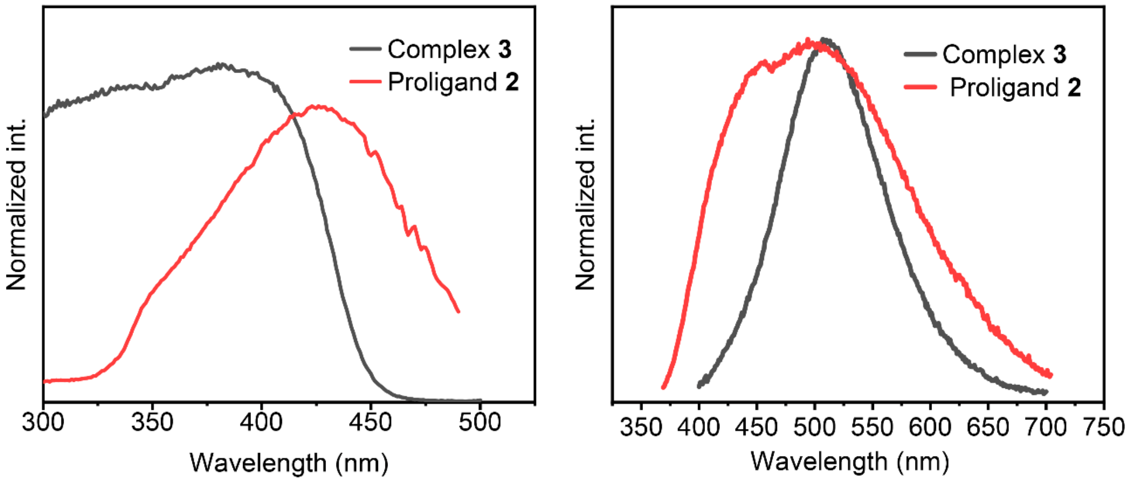

Figure S6. Excitation and emission (λ_{ex} = 360 nm) spectra of polycrystalline samples of phosphine oxide **2** and polymer **3**$\cdot$4CH_3CN (measured at ambient temperature).