Excited-State Characteristics of Tetracyanidonitridorhenium(V) and -technetium(V) Complexes with N-heteroaromatic Ligands

Hayato Ikeda,[†] Akitaka Ito,[‡] Eri Sakuda,[‡,§] Noboru Kitamura,[‡,§] Tsutomu Takayama,[⊥] Tsutomu Sekine,[∥] Atsushi Shinohara[†], and Takashi Yoshimura[,#]*

[†]Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka 560-0043, Japan
[‡]Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan
[§]Department of Chemical Sciences and Engineering, Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0810, Japan
[⊥]Department of Chemistry, Daido University, Nagoya 457-8530, Japan
[∥]Center for the Advancement of Higher Education, Tohoku University, Sendai 980-8576, Japan
[#]Radioisotope Research Center, Osaka University, Suita 565-0871, Japan

Supporting Information

Preparation of the Complexes. $(PPh_4)_2[ReN(CN)_4(dmap)]$ (Re-dmap). $(PPh_4)_2[ReN(CN)_4]$ (39.5 mg, 0.0402 mmol) and dmap (169.5 mg, 1.387 mmol) were dissolved in 3 mL of acetonitrile, and then, 7 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether and left for 1 h in *vacuo*. Yield of **Re-dmap**: 39.4 mg (86.6%). Anal. Calcd for $C_{59}H_{50}N_7P_2Re\cdot CH_2Cl_2$: C, 62.40; H, 4.11; N; 6.72. Found: C, 62.52; H, 4.29; N, 6.69. ^{1}H NMR in $CDCl_3$: δ 8.30 – 8.23 (m, 2H, H_o of dmap), 7.91 – 7.61 (m, 40H, phenyl of PPh_4), 6.42 – 6.34 (m, 2H, H_m of dmap), 2.96 (s, 6H, -CH_3 of dmap). UV-vis in the solid state: 415 nm. IR (KBr pellet): 2129 ($\nu_{C\equiv N}$), 2120 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1609 ($\nu_{ring(dmap)}$), 1531 ($\nu_{ring(dmap)}$), 1385 ($\delta_{C-H(dmap)}$), 1234 ($\delta_{C-H(dmap)}$), 1070 ($\delta_{C-H(dmap)}$), 1051 ($\delta_{C-H(dmap)}$), 950 ($\delta_{ring(dmap)}$), 810 ($\gamma_{ring(dmap)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(lut)]$ (Re-lut). $(PPh_4)_2[ReN(CN)_4]$ (97.5 mg, 0.0992 mmol) and lut (400 μL, 3.51 mmol) were dissolved in 2 mL of dichloromethane, and then, the solution was evaporated slowly. The solution was left for several hours to form yellow crystals. The crystals collected were washed with diethyl ether and left for 1 h in *vacuo*. Yield of **Re-lut**: 100.0 mg (92.5%). Anal. Calcd for $C_{59}H_{49}N_6P_2Re$: C, 65.00; H, 4.53; N; 7.71. Found: C, 65.12; H, 4.46; N, 7.77. ^{1}H NMR in $CDCl_3$: δ 8.58 (s, 2H, H_o of lut), 7.90 – 7.61 (m, 40H, phenyl of PPh_4), 7.21 (s, 1H, H_p of lut), 2.24 (s, 6H, -CH_3 of lut). UV-vis in the solid state: 417 nm. IR (KBr pellet): 2127 ($\nu_{C\equiv N}$), 2116 ($\nu_{C\equiv N}$), 2107 ($\nu_{C\equiv N}$), 1646 ($\nu_{ring(lut)}$), 1636 ($\nu_{ring(lut)}$), 1383 ($\delta_{C-H(lut)}$), 1063 ($\delta_{ring(lut)}$), 866 ($\gamma_{ring(lut)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(pic)]$ (Re-pic). $(PPh_4)_2[ReN(CN)_4]$ (141.4 mg, 0.1438 mmol) and pic (1000 μL, 10.3 mmol) were dissolved in 1 mL of dichloromethane, and then, the solution was evaporated slowly. The solution was left for several hours to form yellow crystals. The crystals collected were washed with dichloromethane and left for 1 h in *vacuo*. Yield of **Re-pic**: 70.2 mg (42.1%). Anal. Calcd for $C_{58}H_{47}N_6P_2Re\cdot CH_2Cl_2$: C, 61.03; H, 4.25; N; 7.24. Found: C, 61.18; H, 4.26; N, 7.39. ^{1}H NMR in $CDCl_3$: δ 8.50 – 8.47 (m, 2H, H_o of pic), 7.90 – 7.61 (m, 40H, phenyl of PPh_4), 7.21 (m, 2H, H_m of pic), 2.33 (s, 3H, -CH_3 of pic). UV-vis in the solid state: 416 nm. IR (KBr pellet): 2127 ($\nu_{C\equiv N}$), 2117 ($\nu_{C\equiv N}$), 2108 ($\nu_{C\equiv N}$), 1615 ($\nu_{ring(pic)}$), 1604 ($\nu_{ring(pic)}$), 1073 ($\delta_{ring(pic)}$), 1064 ($\delta_{ring(pic)}$), 1003($\delta_{ring(pic)}$), 812 ($\gamma_{ring(pic)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(ppy)]$ (Re-ppy). $(PPh_4)_2[ReN(CN)_4]$ (36.0 mg, 0.0366 mmol) and ppy (134.6 mg, 0.8673 mmol) were dissolved in 2 mL of acetonitrile, and then, 8 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals, and the crystals collected were washed with diethyl ether. Yield of **Re-ppy**: 36.3 mg (79.8%). Anal. Calcd for $C_{63}H_{49}N_6P_2Re\cdot CH_2Cl_2\cdot H_2O$: C, 61.93; H, 4.30; N; 6.77. Found: C, 61.85; H, 4.28; N, 6.86. ^{1}H NMR in CD_3CN: δ 8.69 – 8.65 (m, 2H, ppy), 7.96 – 7.40 (m, 47H, phenyl of PPh_4 and ppy). UV-vis in the solid state: 421 nm. IR (KBr pellet): 2130 ($\nu_{C\equiv N}$), 2115 ($\nu_{C\equiv N}$), 2104 ($\nu_{C\equiv N}$), 1601 ($\nu_{ring(ppy)}$), 1412 ($\nu_{ring(ppy)}$), 1287 ($\delta_{C-H(ppy)}$), 1230 ($\delta_{C-H(ppy)}$), 1065 ($\delta_{ring(ppy)}$), 835 ($\gamma_{C-H(ppy)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(py)]$ (Re-py). $(PPh_4)_2[ReN(CN)_4]$ (66.2 mg, 0.0673 mmol) was dissolved in 5 mL of py, and then, 15 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals which were collected and washed with diethyl ether. Yield of **Re-py**: 75.3 mg (95.8%). Anal. Calcd for $C_{57}H_{45}N_6P_2Re \cdot C_5H_5N \cdot 1.5H_2O$: C, 63.74; H, 4.57; N; 8.39. Found: C, 63.56; H, 4.51; N, 8.39. ^{1}H NMR in $CDCl_3$: δ 8.68 – 8.64 (m, 4H, H_o of py), 7.92 – 7.58 (m, 42H, phenyl of PPh_4 and H_p of py), 7.24 – 7.19 (m, 4H, H_m of py). UV-vis in the solid state: 414 nm. IR (KBr pellet): 2127 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1594 ($\nu_{ring(py)}$), 1224 ($\delta_{C-H(py)}$), 1151 ($\nu_{ring(py)}$), 1135 ($\delta_{C-H(py)}$), 1064 ($\delta_{C-H(py)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(3bzpy)]$ (Re-3bzpy). $(PPh_4)_2[ReN(CN)_4]$ (30.0 mg, 0.0305 mmol) and 3bzpy (183.0 mg, 0.999 mmol) were dissolved in 3 mL of dichloromethane, and then, 10 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals, the crystals collected were washed with diethyl ether. Yield of **Re-3bzpy**: 31.1 mg (87.5%). Anal. Calcd for $C_{64}H_{49}N_6OP_2Re \cdot 0.4CH_2Cl_2$: C, 64.45; H, 4.18; N; 7.00. Found: C, 64.65; H, 4.36; N, 6.81. ^{1}H NMR in CD_3CN: δ 8.96 (s, 1H, H_o of 3bzpy), 8.82 (d, 1H, H_o of 3bzpy), 8.08 (m, 1H, H_p of 3bzpy), 7.53 – 7.93 (m, 45H, phenyl of PPh_4 and 3bzpy), 7.47 (m, 1H, H_m of 3bzpy). UV-vis in the solid state: 410 nm. IR (KBr pellet): 2100 ($\nu_{C\equiv N}$), 1652 ($\nu_{C=O(3bzpy)}$), 1286 ($\nu_{ring(3bzpy)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(bpy)]$ (Re-bpy). $(PPh_4)_2[ReN(CN)_4]$ (41.5 mg, 0.0422 mmol) and bpy (448.7 mg, 2.873 mmol) were dissolved in 4 mL of acetonitrile, and then, 6 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals, and the crystals collected were washed with diethyl ether. Yield of **Re-bpy**: 36.9 mg (73.0%). Anal. Calcd for $C_{62}H_{48}N_7P_2Re \cdot 0.5CH_3CN \cdot 2H_2O$: C, 63.28; H, 4.51; N; 8.78. Found: C, 63.28; H, 4.54; N, 8.82. ^{1}H NMR in DMSO-d_6: δ 8.72 – 8.66 (m, 4H, bpy), 8.00 – 7.58 (m, 44H, phenyl of PPh_4 and bpy). UV-vis in the solid state: 425 (sh) nm. IR (KBr pellet): 2128 ($\nu_{C\equiv N}$), 2102 ($\nu_{C\equiv N}$), 1532 ($\nu_{ring(bpy)}$), 1409 ($\nu_{ring(bpy)}$), 1222 ($\delta_{C-H(bpy)}$), 1079 ($\delta_{ring(bpy)}$), 1066 ($\delta_{ring(bpy)}$), 1028 ($\delta_{ring(bpy)}$), 817 ($\gamma_{C-H(bpy)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(pz)]$ (Re-pz). $(PPh_4)_2[ReN(CN)_4]$ (53.6 mg, 0.0545 mmol) and pz (624.0 mg, 7.791 mmol) were dissolved in 2 mL of dichloromethane, and then, 8 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether and left for 1 h in *vacuo*. Yield of **Re-pz**: 44.8 mg (74.1%). Anal. Calcd for $C_{56}H_{44}N_7P_2Re \cdot 2.5H_2O$: C, 60.69; H, 4.46; N; 8.85. Found: C, 60.55; H, 4.35; N, 8.92. ^{1}H NMR in $CDCl_3$: δ 8.58 (s, 4H of pz), 7.91 – 7.60 (m, 40H, phenyl of PPh_4). UV-vis in the solid state: 408 nm. IR (KBr pellet): 2128 ($\nu_{C\equiv N}$), 2117 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1417 ($\nu_{ring(pz)}$), 1151 ($\nu_{ring(pz)}$), 1135 ($\delta_{C-H(pz)}$), 1070 ($\delta_{C-H(pz)}$), 1033 ($\delta_{ring(pz)}$), 797 ($\gamma_{C-H(pz)}$) cm^{-1}.

$(PPh_4)_2[ReN(CN)_4(cpy)]$ (Re-cpy). $(PPh_4)_2[ReN(CN)_4]$ (54.9 mg, 0.0558 mmol) and cpy (478.7 mg, 4.598 mmol) were dissolved in 3 mL of dichloromethane, and then, 7 mL of diethyl ether was layered on the solution. The solution was left for several days to form orange crystals which were collected and washed with diethyl ether and left for 1 h in *vacuo*. Yield of **Re-cpy**: 36.9 mg (52.7%). Anal. Calcd for

$C_{58}H_{44}N_7P_2Re \cdot 2CH_2Cl_2$: C, 57.33; H, 3.85; N; 7.80. Found: C, 57.43; H, 3.91; N, 7.95. ^{1}H NMR in $CDCl_3$: δ 8.95 – 8.92 (m, 2H, H_o of cpy), 7.91 – 7.58 (m, 40H, phenyl of PPh_4) 7.39 – 7.36 (m, 2H, H_m of cpy). UV-vis in the solid state: 402, 465 (sh) nm. IR (KBr pellet): 2137 ($\nu_{C\equiv N(cpy)}$), 2125 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1599 ($\nu_{ring(cpy)}$), 1543 ($\nu_{ring(cpy)}$), 1415 ($\nu_{ring(cpy)}$), 1407 ($\nu_{ring(cpy)}$),1077 ($\delta_{C-H(cpy)}$), 1067 ($\delta_{C-H(cpy)}$), 831 ($\gamma_{C-H(cpy)}$) cm^{-1}.

$(PPh_4)_2$[ReN(CN)$_4$(4bzpy)] (Re-4bzpy). $(PPh_4)_2[ReN(CN)_4]$ (40.6 mg, 0.0413 mmol) and bzpy (189.1 mg, 1.032 mmol) were dissolved in 2 mL of dichloromethane, and then, 8 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether. Yield of **Re-4bzpy**: 43.7 mg (87.7%). ^{1}H NMR in $CDCl_3$: δ 8.81 – 8.77 (m, 2H, 4bzpy), 7.99 – 7.52 (m, 47H, phenyl of PPh_4 and 4bzpy). UV-vis in the solid state: 460 (sh) nm. IR (KBr pellet): 2123 ($\nu_{C\equiv N}$), 2108 ($\nu_{C\equiv N}$), 2101 ($\nu_{C\equiv N}$), 1664 ($\nu_{C=O(4bzpy)}$), 1409 ($\nu_{ring(4bzpy)}$), 1280 ($\nu_{ring(4bzpy)}$), 1222 ($\delta_{C-H(4bzpy)}$), 1077 ($\delta_{C-H(4bzpy)}$), 1063 ($\delta_{C-H(4bzpy)}$), 1007 ($\delta_{ring(4bzpy)}$), 945 ($\delta_{ring(4bzpy)}$), 935 ($\gamma_{C-H(4bzpy)}$), 799 ($\gamma_{C-H(4bzpy)}$) cm^{-1}.

$(PPh_4)_2$[TcN(CN)$_4$(dmap)] (Tc-dmap). $(PPh_4)_2[TcN(CN)_4]$ (6.12 mg, 6.83 μmol) and dmap (124.17 mg, 1.0164 mmol) were dissolved in 1 mL of acetonitrile, and then, 4 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether. Yield of **Tc-dmap**: 5.08 mg (73.1%). UV-vis in the solid state: 413 nm. IR (KBr pellet): 2129 ($\nu_{C\equiv N}$), 2120 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1609 ($\nu_{ring(dmap)}$), 1531 ($\nu_{ring(dmap)}$), 1385 ($\delta_{C-H(dmap)}$), 1234 ($\delta_{C-H(dmap)}$), 1070 ($\delta_{C-H(dmap)}$), 1051 ($\delta_{C-H(dmap)}$), 950 ($\delta_{ring(dmap)}$), 810 ($\gamma_{ring(dmap)}$) cm^{-1}.

$(PPh_4)_2$[TcN(CN)$_4$(lut)] (Tc-lut). $(PPh_4)_2[TcN(CN)_4]$ (7.67 mg, 8.56 μmol) and lut (100 μL, 0.876 mmol) were dissolved in 100 μL of dichloromethane. The solution was evaporated slowly. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether. Yield of **Tc-lut**: 3.31 mg (38.6%). UV-vis in the solid state: 410 nm. IR (KBr pellet): 2127 ($\nu_{C\equiv N}$), 2116 ($\nu_{C\equiv N}$), 2107 ($\nu_{C\equiv N}$), 1646 ($\nu_{ring(lut)}$), 1636 ($\nu_{ring(lut)}$), 1383 ($\delta_{C-H(lut)}$), 1063 ($\delta_{ring(lut)}$), 866 ($\gamma_{ring(lut)}$) cm^{-1}.

$(PPh_4)_2$[TcN(CN)$_4$(pic)] (Tc-pic). $(PPh_4)_2[TcN(CN)_4]$ (3.10 mg, 3.46 μmol) and pic (50 μL, 0.51 mmol) were dissolved in 50 μL of dichloromethane. The solution was evaporated slowly. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether. Yield: 1.54 mg (45.1%). UV-vis in the solid state: 421 nm. IR (KBr pellet): 2127 ($\nu_{C\equiv N}$), 2117 ($\nu_{C\equiv N}$), 2108 ($\nu_{C\equiv N}$), 1615 ($\nu_{ring(pic)}$), 1604 ($\nu_{ring(pic)}$), 1073 ($\delta_{ring(pic)}$), 1064 ($\delta_{ring(pic)}$), 1003($\delta_{ring(pic)}$), 812 ($\gamma_{ring(pic)}$) cm^{-1}.

$(PPh_4)_2$[TcN(CN)$_4$(py)] (Tc-py). $(PPh_4)_2[TcN(CN)_4]$ (4.40 mg, 4.91 μmol) was dissolved in 0.75 mL of py, and then, 4 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether. Yield of **Tc-py**: 4.53 mg (94.7%). UV-vis in the solid state: 415 nm. IR (KBr pellet): 2127 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1594 ($\nu_{ring(py)}$), 1224 ($\delta_{C-H(py)}$), 1151 ($\nu_{ring(py)}$), 1135 ($\delta_{C-H(py)}$), 1064 ($\delta_{C-H(py)}$) cm^{-1}.

$(PPh_4)_2[TcN(CN)_4(pz)]$ (Tc-pz). $(PPh_4)_2[TcN(CN)_4]$ (10.05 mg, 11.22 μmol) and pz (162.95 mg, 2.0346 mmol) were dissolved in 1 mL of dichloromethane, and then, 4 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether. Yield of **Tc-pz**: 10.69 mg (97.6%). UV-vis in the solid state: 420 nm. IR (KBr pellet): 2128 ($\nu_{C\equiv N}$), 2117 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1417 ($\nu_{ring(pz)}$), 1151 ($\nu_{ring(pz)}$), 1135 ($\delta_{C-H(pz)}$), 1070 ($\delta_{C-H(pz)}$), 1033 ($\delta_{ring(pz)}$), 797 ($\gamma_{C-H(pz)}$) cm^{-1}.

$(PPh_4)_2[TcN(CN)_4(cpy)]$ (Tc-cpy). $(PPh_4)_2[TcN(CN)_4]$ (9.14 mg, 10.2 μmol) and cpy (161.68 mg, 1.5530 mmol) were dissolved in 1 mL of dichloromethane, and then, 4 mL of diethyl ether was layered on the solution. The solution was left for several days to form yellow crystals. The crystals collected were washed with diethyl ether. Yield of **Tc-cpy**: 9.52 mg (80.6%). UV-vis in the solid state: 407 nm. IR (KBr pellet): 2237 ($\nu_{C\equiv N(cpy)}$), 2125 ($\nu_{C\equiv N}$), 2109 ($\nu_{C\equiv N}$), 1599 ($\nu_{ring(cpy)}$), 1543 ($\nu_{ring(cpy)}$), 1415 ($\nu_{ring(cpy)}$), 1407 ($\nu_{ring(cpy)}$), 1077 ($\delta_{C-H(cpy)}$), 1067 ($\delta_{C-H(cpy)}$), 831 ($\gamma_{C-H(cpy)}$) cm^{-1}.

Table S1. Crystallographic Data of **Re-dmap**, **Re-lut**, **Re-pic**, **Re-ppy**, **Re-py**, and **Re-3bzpy**

	Re-dmap	**Re-lut**	**Re-pic**	**Re-ppy**	**Re-py**	**Re-3bzpy**
Formula	$C_{63}H_{56}N_9OP_2Re$	$C_{61}H_{53}Cl_4N_6P_2Re$	$C_{59}H_{49}Cl_2N_6P_2Re$	$C_{65}H_{53}N_6Cl_4P_2Re$	$C_{62}H_{50}N_7OP_2Re$	$C_{64}H_{49}N_6O_2P_2Re$
F.W.	1203.34	1260.10	1161.14	1308.14	1157.28	1182.28
Space group	*P*-1	*C*c	$P2_1/a$	$Pna2_1$	*P*nma	*P*-1
a/Å	11.017(2)	28.4518(6)	17.6081(2)	17.8025(18)	17.3282(6)	14.2377(3)
b/Å	11.119(2)	12.2466(4)	13.5650(2)	13.3672(14)	23.0629(6)	14.7409(2)
c/Å	24.848(4)	20.5026(5)	22.8090(5)	25.167(4)	13.5233(4)	15.8576(5)
α/deg	80.171(7)					108.5155(6)
β/deg	80.257(6)	120.4628(6)	101.7600(5)			99.8394(6)
γ/deg	76.629(6)					114.9721(6)
V/Å^3	2891.0(9)	5745.4(3)	5333.66(16)	5989.1(12)	5404.4(3)	2674.75(12)
Z	2	4	4	4	4	2
T/	-103.0	-103.0	-103.0	-103.0	-103.0	-103.0
ρ_{calc}/gcm^{-3}	1.382	1.457	1.446	1.451	1.422	1.468
μ/mm^{-1}	2.207	2.401	2.483	2.307	2.357	2.384
*R*1	0.0996	0.0609	0.0278	0.0815	0.0365	0.0351
*wR*2	0.2632	0.1731	0.0657	0.2556	0.0770	0.0965
GOF	1.173	1.043	1.065	1.056	0.848	1.094

Table S2. Crystallographic Data of **Re-bpy**, **Re-pz**, **Re-cpy**, **Re-4bzpy**, and **Tc-cpy**

	Re-bpy	**Re-pz**	**Re-cpy**	**Re-4bzpy**	**Tc-cpy**
Formula	$C_{62}H_{47}N_7O_3P_2Re$	$C_{57.5}H_{47}Cl_3N_7P_2Re$	$C_{60}H_{48}Cl_4N_7P_2Re$	$C_{66}H_{52}N_7OP_2Re$	$C_{60}H_{48}Cl_4N_7P_2Tc$
F.W.	1186.25	1190.56	1257.05	1207.34	1167.85
Space group	$P2_1/c$	P-1	P-1	P-1	P-1
a/Å	14.0874(3)	12.6241(2)	13.9026(3)	12.8223(3)	13.9373(3)
b/Å	22.1900(7)	12.7121(2)	14.1565(3)	14.4774(3)	14.1798(4)
c/Å	18.1072(5)	33.8633(5)	16.0409(5)	18.3372(5)	16.0434(5)
α/deg		80.4592(5)	110.4661(8)	68.6593(6)	110.5469(11)
β/deg	105.8863(7)	85.2153(5)	90.2934(8)	81.9011(8)	90.2077(9)
γ/deg		82.1026(5)	107.0898(6)	62.2832(7)	107.3319(7)
V/Å^3	5444.1(3)	5298.11(15)	2806.58(13)	2805.13(12)	2813.29(14)
Z	4	4	2	2	2
T/	-103.0	-103.0	-103.0	-103.0	-103.0
ρ_{calc}/gcm^{-3}	1.447	1.492	1.487	1.429	1.379
μ/mm^{-1}	2.345	2.551	2.458	2.274	0.545
$R1$	0.0673	0.0307	0.0386	0.0589	0.0590
$wR2$	0.1554	0.0774	0.1061	0.1576	0.1652
GOF	1.037	1.091	1.180	1.069	1.086

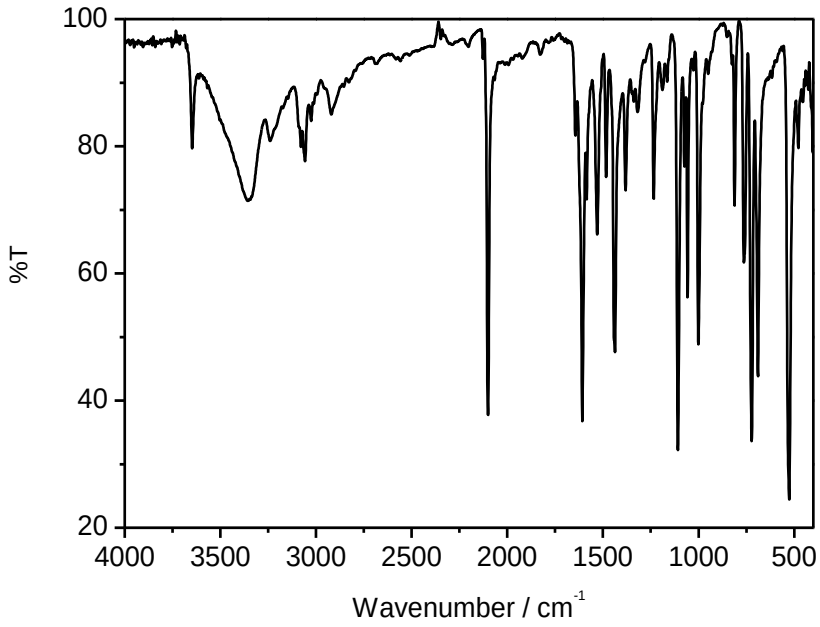

Figure S1. IR spectrum of **Re-dmap** in the solid state.

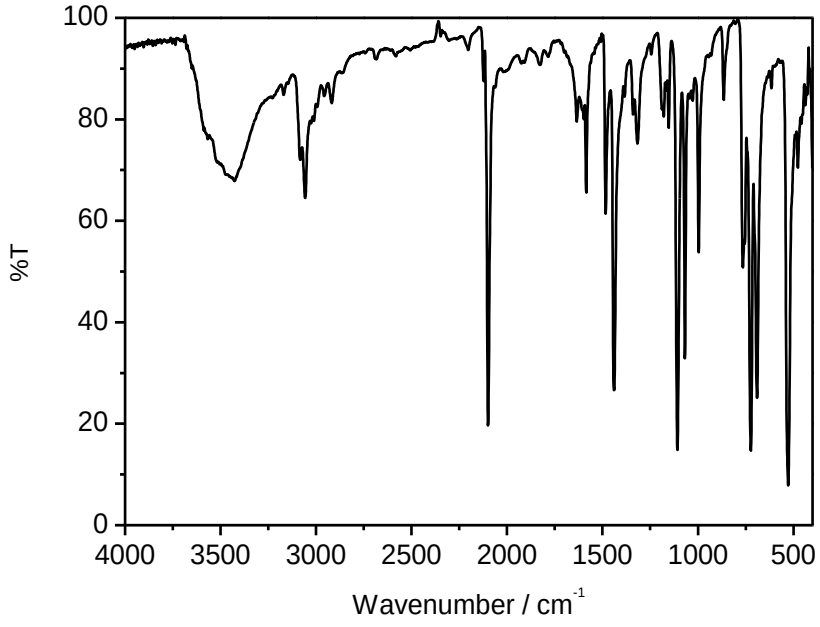

Figure S2. IR spectrum of **Re-lut** in the solid state.

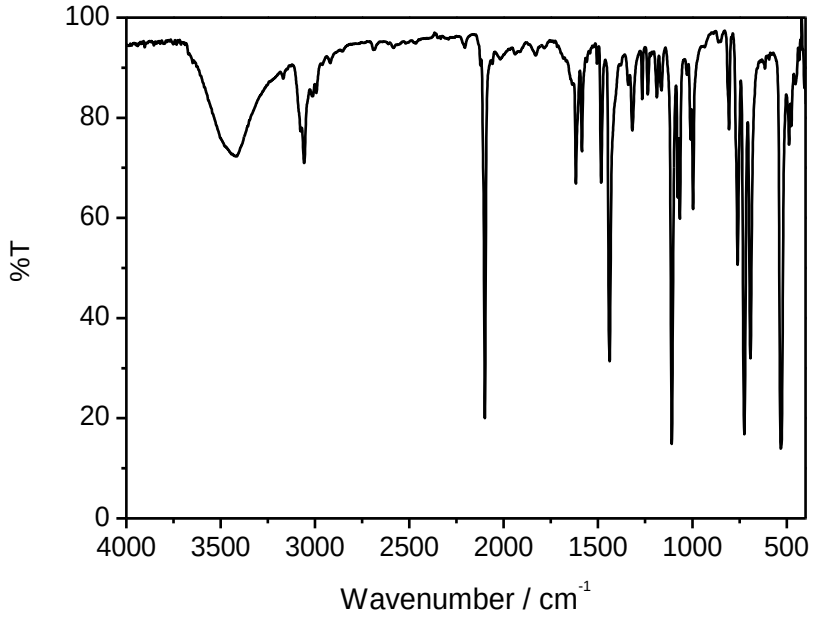

Figure S3. IR spectrum of **Re-pic** in the solid state.

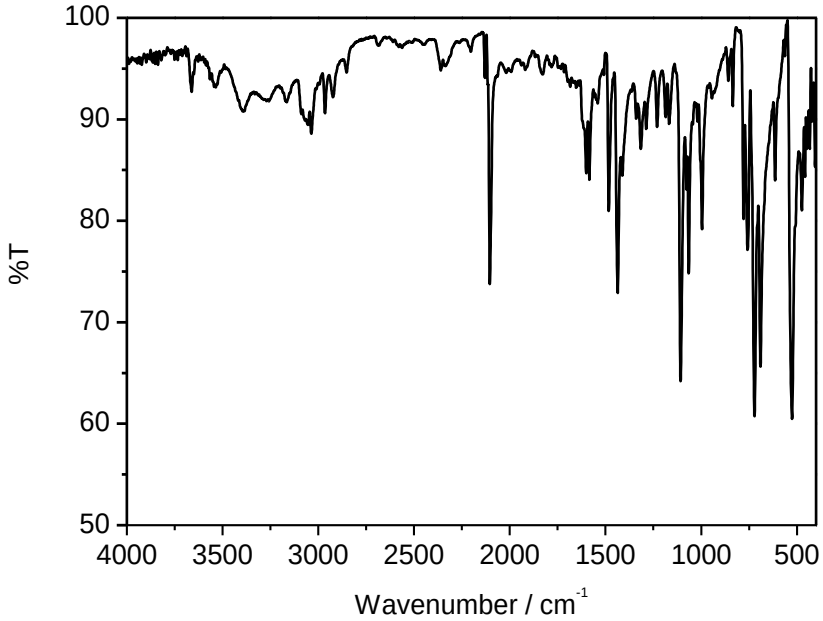

Figure S4. IR spectrum of **Re-ppy** in the solid state.

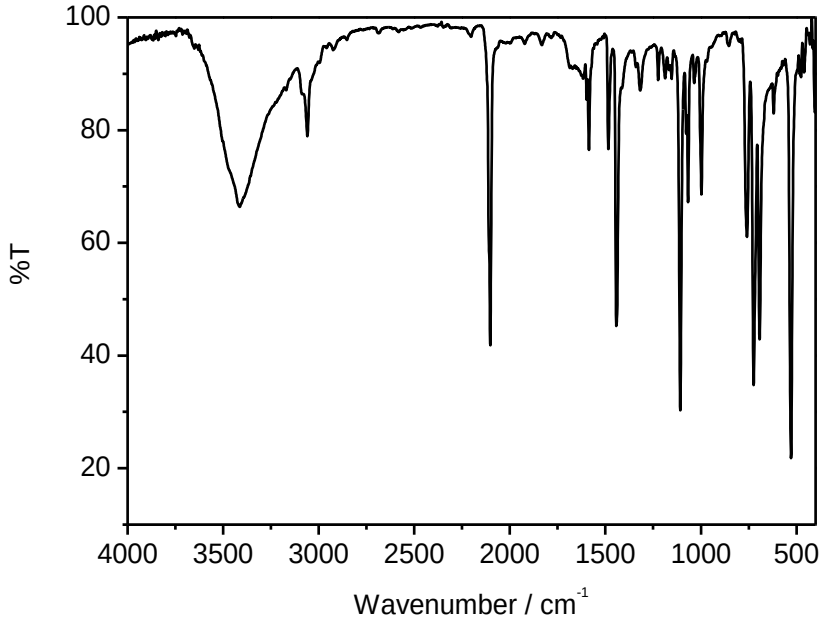

Figure S5. IR spectrum of **Re-py** in the solid state.

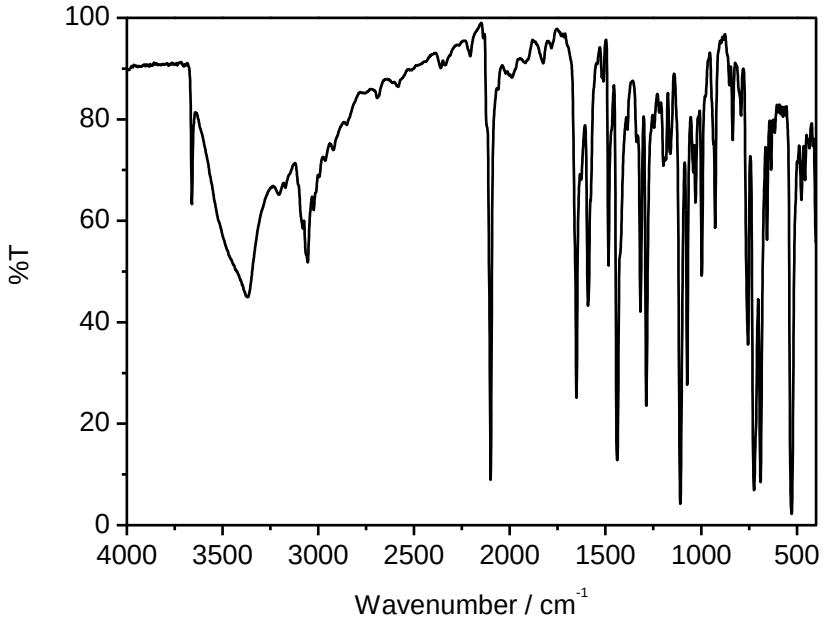

Figure S6. IR spectrum of **Re-3bzpy** in the solid state.

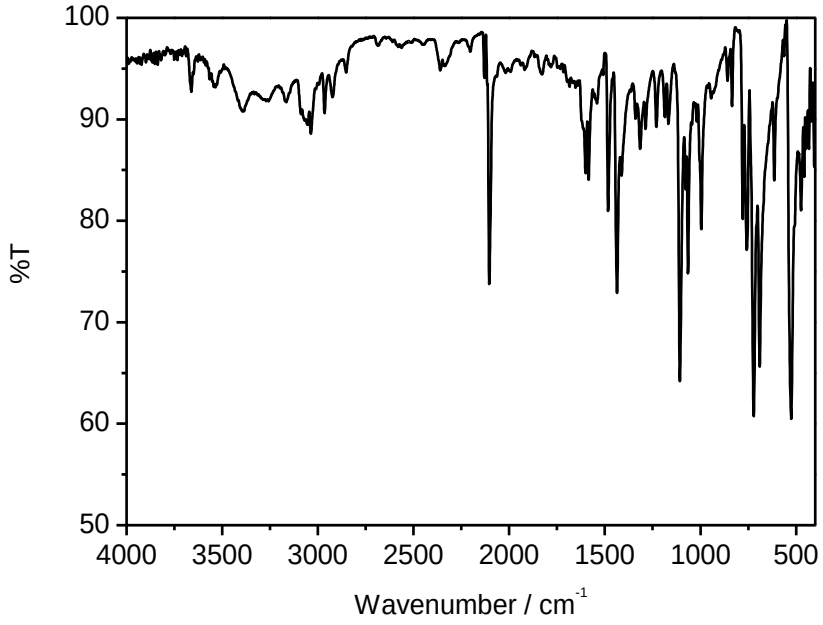

Figure S7. IR spectrum of **Re-bpy** in the solid state.

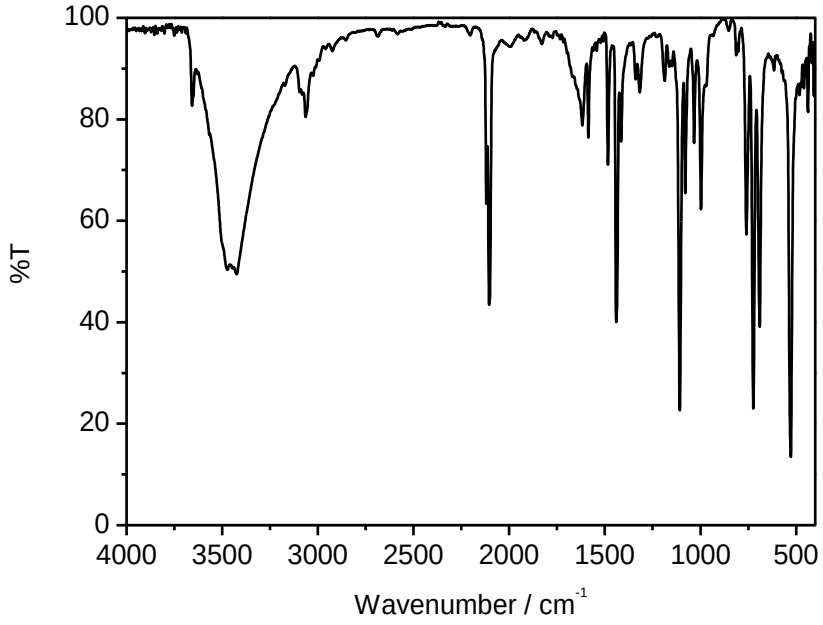

Figure S8. IR spectrum of **Re-pz** in the solid state.

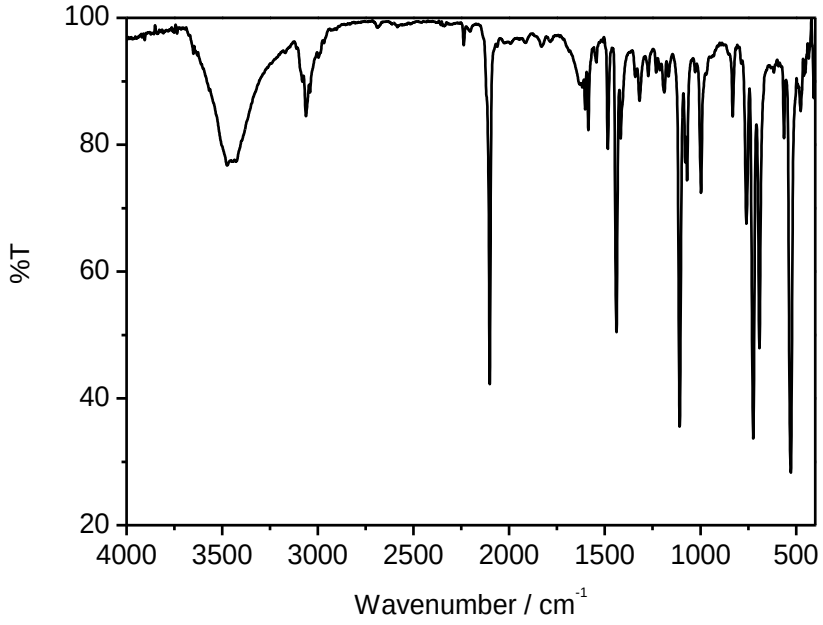

Figure S9. IR spectrum of **Re-cpy** in the solid state.

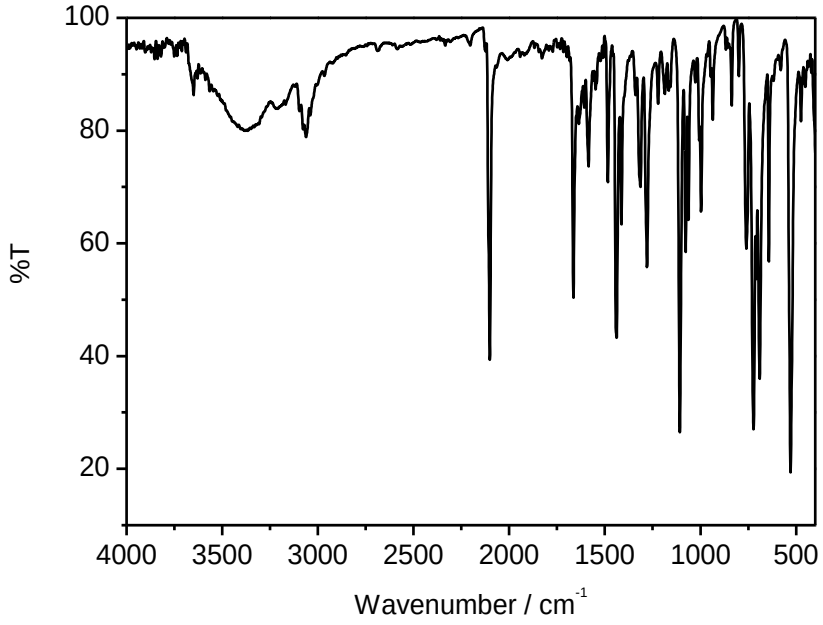

Figure S10. IR spectrum of **Re-4bzpy** in the solid state.

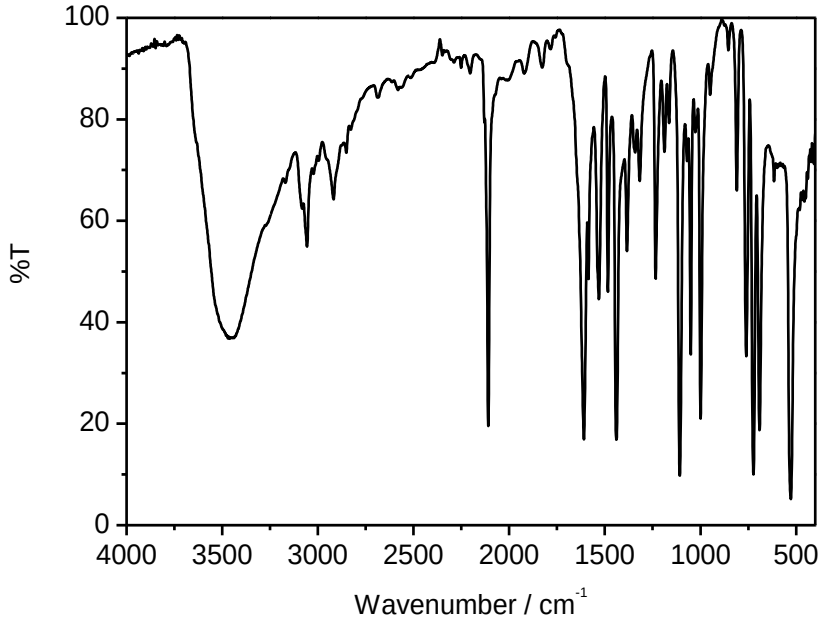

Figure S11. IR spectrum of **Tc-dmap** in the solid state.

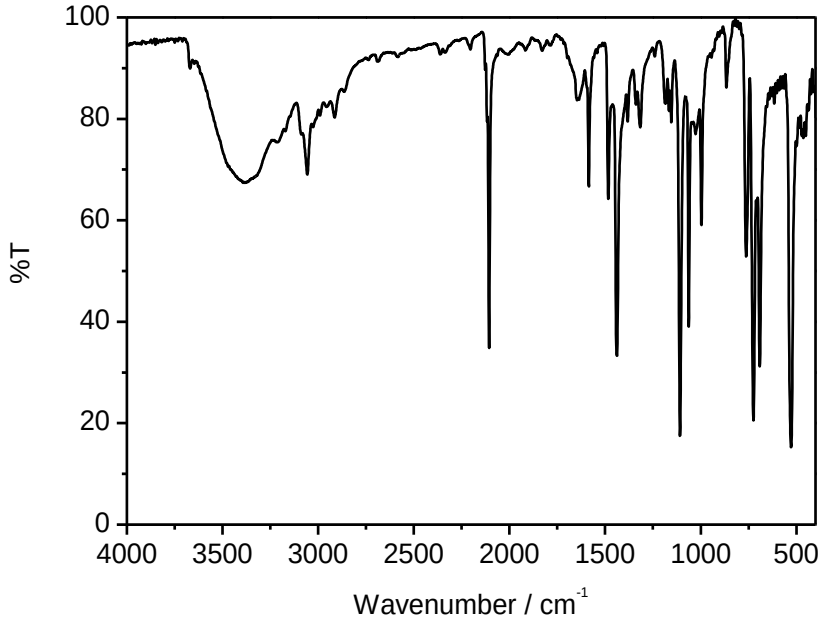

Figure S12. IR spectrum of **Tc-lut** in the solid state.

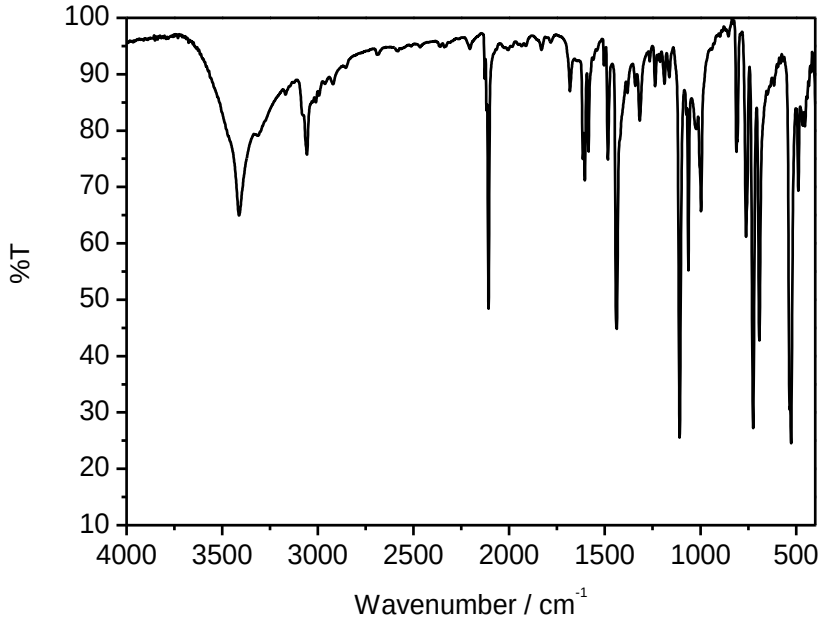

Figure S13. IR spectrum of **Tc-pic** in the solid state.

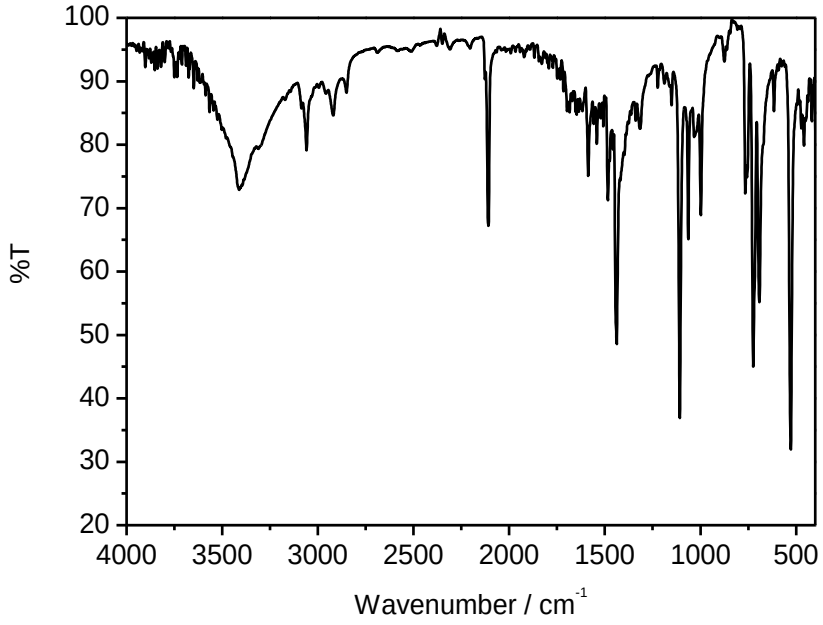

Figure S14. IR spectrum of **Tc-py** in the solid state.

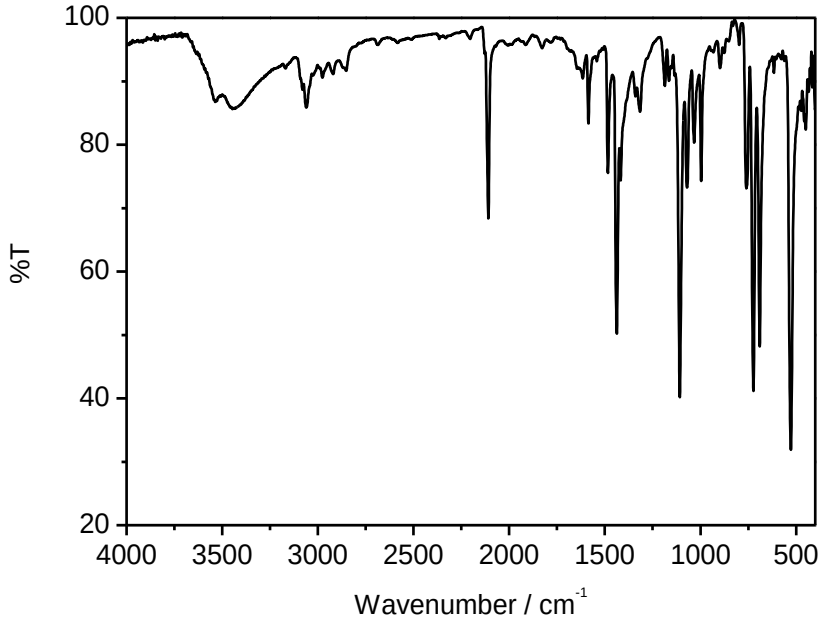

Figure S15. IR spectrum of **Tc-pz** in the solid state.

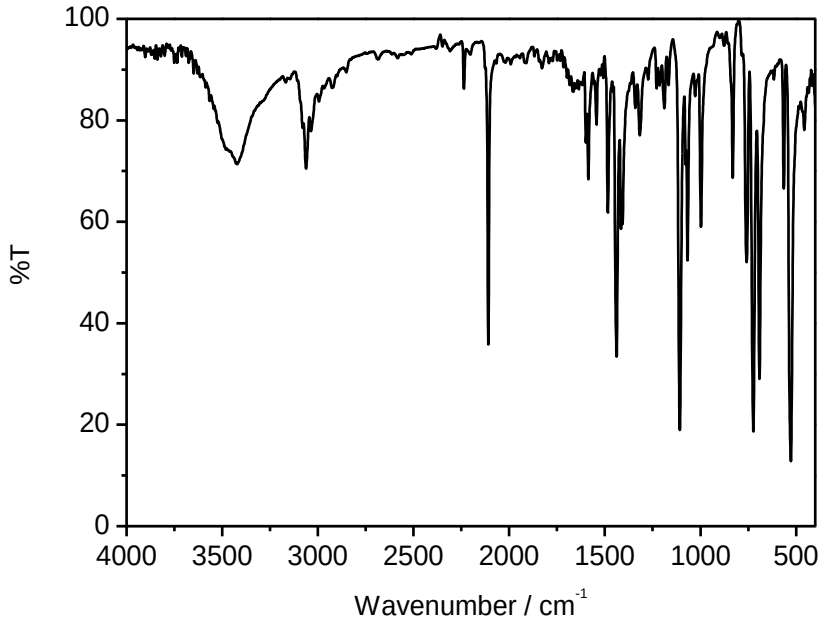

Figure S16. IR spectrum of **Tc-cpy** in the solid state.

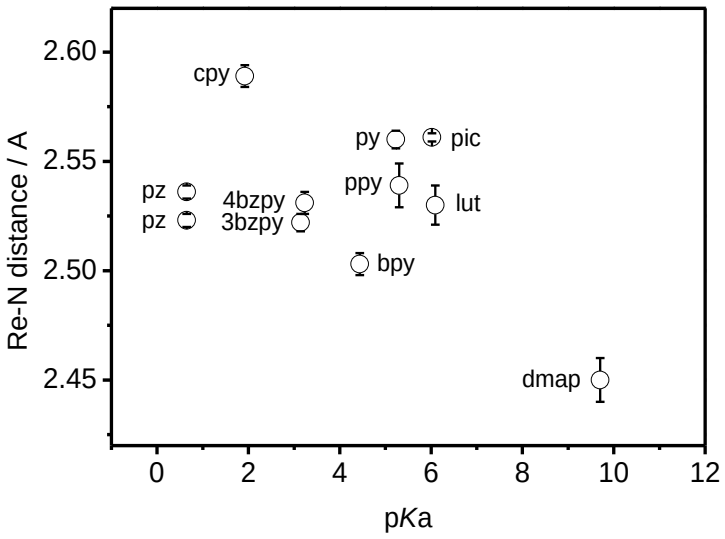

Figure S17. Plot of pK_a of free ligand against the Re-N bond distance (Å). Two **Re-pz** anions exist in the asymmetric unit of the crystal lattice.

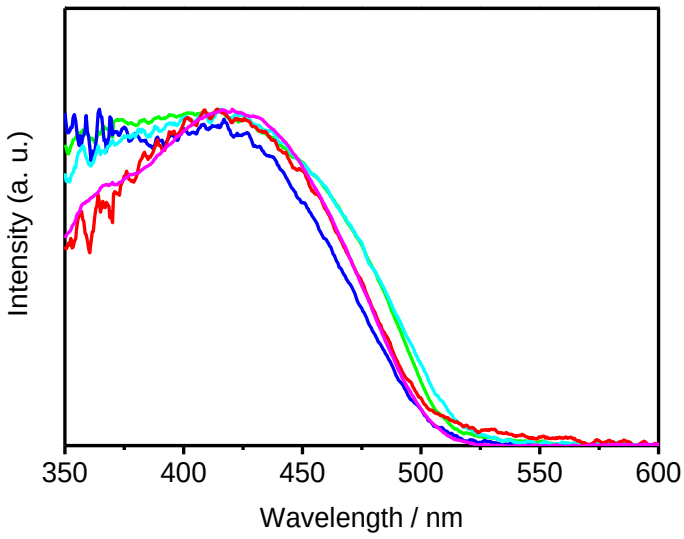

Figure S18. UV-vis reflectance spectra of **Re-dmap** (lime green), **Re-lut** (blue), **Re-pic** (cyan), **Re-ppy** (magenta), and **Re-py** (red) in the solid state.

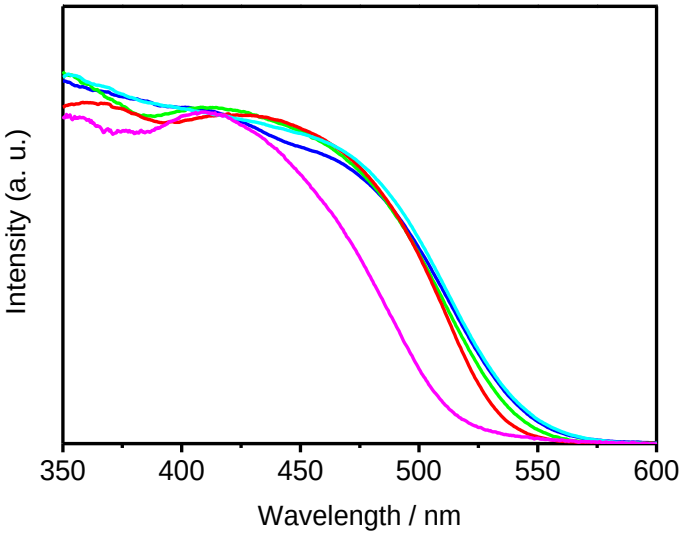

Figure S19. UV-vis reflectance spectra of **Re-3bzpy** (magenta), **Re-bpy** (red), **Re-pz** (lime green), **Re-cpy** (blue), and **Re-4bzpy** (cyan) in the solid state.

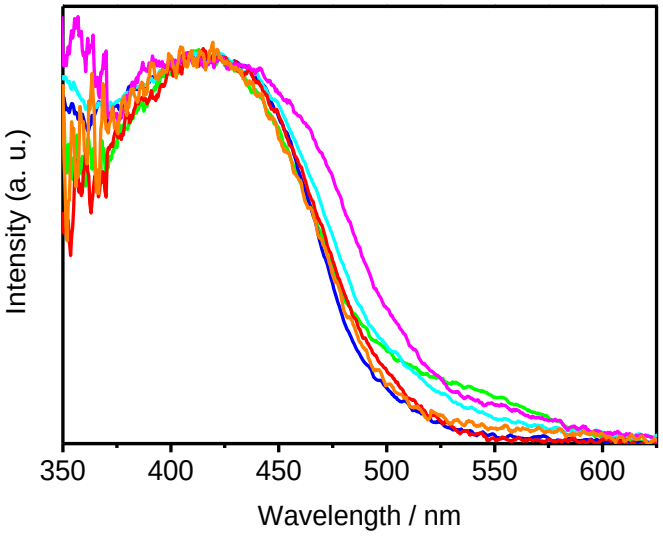

Figure S20. UV-vis reflectance spectra of **Tc-dmap** (lime green), **Tc-lut** (blue), **Tc-pic** (cyan), **Tc-py** (red), **Tc-pz** (magenta), and **Tc-cpy** (orange) in the solid state.