Electronic Supporting Information

Spectroscopic study on the coordination and solution structures for the interaction systems between biperoxidovanadate complexes and the pyrazolylpyridine-like ligands

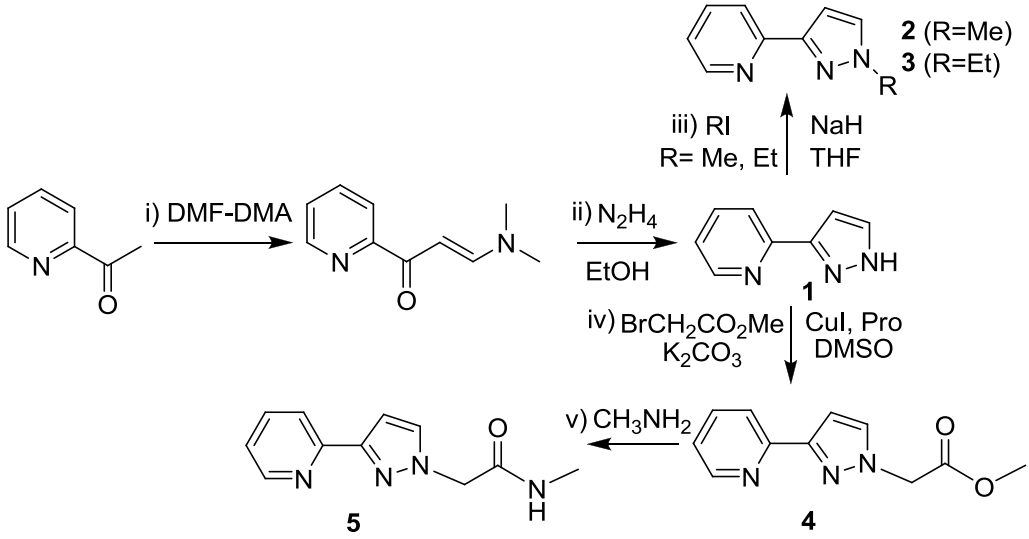
Xian-Yong Yu,*[a] Lin Deng,[a] Baishu Zheng,[a] Bi-Rong Zeng,[c] Pinggui Yi,*[a] and Xin Xu*[b]

[a] *Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan Province College Key Laboratory of QSAR/QSPR, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, P.R. China*

[b] *Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, MOE Laboratory for Computational Physical Science, Department of Chemistry, Fudan University, Shanghai, 200433, China; State Key Laboratory of Physical Chemistry of Solid Surfaces; College for Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China*

[c] *Department of Materials Science and engineering, Key Laboratory for Fire Retardant Materials of Fujian Province, Xiamen University, Xiamen 361005, China*

1. The syntheses rout of the organic ligands:

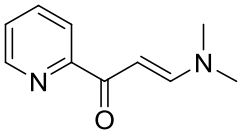


Scheme S1. The syntheses rout of pyrazolylpyridine-like ligands. i) DMF-DMA, 110 °C; ii) $N_2H_4 \cdot H_2O$, EtOH, 85 °C; iii) RI (R=Me, Et), NaH, THF, 65 °C; iv) $BrCH_2CO_2Me$, K_2CO_3, Pro, DMSO, 80 °C; v) CH_3NH_2, RT.

2. The synthesis of the organic ligands (1 ~ 5):

Synthesis of 3-dimethylamino-1-pyridin-2-yl-propan-1-one

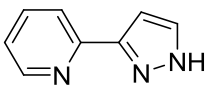
A mixture of 2-acetyl-pyridine (250 mL) and *N*,*N*-dimethylformide dimethyl acetal (500 mL) was heated at 110 °C for 1.5 h, shown in **Scheme S1**. The mixture was cooled to room temperature and refrigerated overnight. The yellow solid was filtered, washed with petroleum ether and dried. Yield: 260 g (66 %).



Synthesis of 2-(1*H*-pyrazol-3-yl)pyridine (pzpy, 1)

The ligand 2-(1*H*-pyrazol-3-yl)pyridine **1** (190 g) was prepared according to the following methods: (1) F. Wang and A. W. Schwabacher, *Tetrahedron. Lett.*, 1999, **40**, 4779-4782; (2) J. S. Uber, Y. Vogels, D. van den Helder, I. Mutikainen, U. Turpeinen, W. T. Fu, O. Roubeau, P. Gamez and J. Reedijk, *Eur. J. Inorg. Chem.* 2007, **26**, 4197-4206.

pzpy: white solid, 89% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 6.82(s, 1H, Pz-**H**), 7.24(t, *J*=5.9 Hz, 1H, Py-**H**), 7.68(s, 1H, Pz-**H**), 7.71-7.80(m, 2H, Py-**H**), 8.69(d, *J*=4.4 Hz, 1H, Py-**H**), 10.73(br, 1H, N-**H**); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 149.4, 144.9, 137.3, 137.0, 137.0, 122.7, 120.2, 103.4; FT-IR (KBr, cm^{-1}): ν 3170, 1594, 1567, 1465, 1419, 1356, 1050, 925, 766.

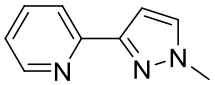


Synthesis of 2-(1-methyl-1*H*-pyrazol-3-yl)pyridine (2-Me-pzpy, 2), 2-(1-ethyl-1*H*-pyrazol-3-yl)pyridine (2-Et-pzpy, 3)

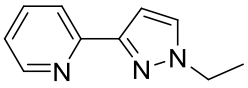
The ligand **2** and **3** were prepared according to the following method: W. R. Thiel, M.

Angstl and T. Priermeier, *Chem. Ber.*, 1994, **127**, 2373-2379.

2-Me-pzpy: yellow oil, 45% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.94(s, 3H, C**H**$_3$), 6.84(d, *J*=2.1 Hz, 1H, Pz-**H**), 7.15(dd, *J*=7.2, 4.9 Hz, 1H, Py-**H**), 7.38(d, *J*=2.1 Hz, 1H, Pz-**H**), 7.67(td, *J*=7.7, 1.3 Hz, 1H, Py-**H)**, 7.88(d, *J*=7.9 Hz, 1H, Py-**H**), 8.59(d, *J*=4.9 Hz, 1H, Py-**H**); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 152.1, 151.6, 149.3, 136.6, 131.6, 122.3, 119.9, 104.4, 39.1; FT-IR (KBr, cm^{-1}): ν 2930, 1592, 1496, 1458, 1392, 1232, , 922, 764.



2-Et-pzpy: yellow oil, 53% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.55(t, *J*= 7.3 Hz, 3H, C**H**$_3$), 4.27(q, *J*= 7.3 Hz, 2H, C**H**$_2$), 6.89(s, 1H, Pz-**H**), 7.20(dd, *J*=7.2, 5.1 Hz, 1H, Py-**H**), 7.47(d, *J*=2.1 Hz, 1H, Pz-**H**), 7.72(t, *J*=7.6 Hz, 1H, Py-**H**), 7.93(d, *J*= 7.9 Hz, 1H, Py-**H**), 8.64(d, *J*=4.6 Hz, 1H, Py-**H**); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 152.3, 151.3, 149.3, 136.5, 129.7, 122.2, 119.9, 104.2, 47.3, 15.6; FT-IR (KBr, cm^{-1}): ν 2924, 2853, 1593, 1493, 1458, 1401, 1227, 1048, 760.

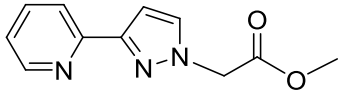


Synthesis of methyl 2-(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)acetate (2-Ester-pzpy, 4)

The ligand **4** was prepared according to the following method: H. Zhang, Q. Cai and D. W. Ma, *J. Org. Chem.*, 2005, **70**, 5164-5173.

2-Ester-pzpy: white solid, 75% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 3.78(s, 3H, C**H**$_3$), 5.00(s, 2H, C**H**$_2$), 6.97(d, *J*=2.2 Hz, 1H, Pz-**H**), 7.21(dd, *J*=7.3, 5.0 Hz, 1H, Py-**H**), 7.54(d, *J*=2.2 Hz, 1H, Pz-**H**), 7.72(td, *J*=7.7, 1.1 Hz, 1H, Py-**H**), 7.92(d, *J*=7.9 Hz, 1H, Py-**H**), 8.63(d, *J*=4.6 Hz, 1H, Py-**H**); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 168.1, 152.2, 151.7, 149.3, 136.6, 132.2, 122.6, 120.2, 105.4, 53.2, 52.7; FT-IR

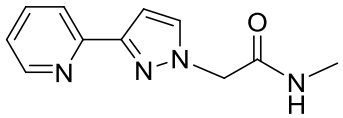
(KBr, cm^{-1}): ν 1751, 1593, 1492, 1401, 1363, 1237, 1218, 991, 767.



Synthesis of *N*-methyl-2-(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)acetamide(2-Amide-pzpy, 5)

The CH_3NH_2 (1.5 mL, 40%) solution was added to Methyl 2-(3-(pyridin-2-yl)-1*H*-pyrazol-1-yl)acetate (**4,** 300 mg) in ethanol. The mixture was reacted at room temperature for 3 h, shown in **Scheme S1.** Progress of the reaction was monitored by TLC. The solvent was evaporated in vacuum. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate as eluent to afford the corresponding product.

2-Amide-pzpy: white solid, 62% yield; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.79(d, *J*=4.9 Hz, 3H, C**H**$_3$), 4.89(s, 2H, C**H**$_2$), 6.20(s, 1H, N-**H**), 6.97(d, *J*=2.0 Hz, 1H, Pz-**H**), 7.24-7.28(m, 1H, Py-**H**), 7.54(d, *J*=2.0 Hz, 1H, Pz-**H**), 7.76(t, *J*=7.7 Hz, 1H, Py-**H**), 7.93(d, *J*=7.9 Hz, 1H, Py-**H**), 8.66(d, *J*=4.6 Hz, 1H, Py-**H**); ^{13}C NMR ($CDCl_3$, 125 MHz) δ:167.6, 153.5, 151.4, 149.5, 136.8, 132.7, 122.9, 120.3, 105.5, 55.4, 26.2; FT-IR (KBr, cm^{-1}): ν 3298, 1667, 1594, 1566, 1402, 1361, 1236, 1052, 765.



3. The detailed spectroscopic characterization of $NH_4[OV(O_2)_2(pzpy]\cdot 6H_2O$ (6):

$NH_4[OV(O_2)_2(pzpy]\cdot 6H_2O$: ^{1}H NMR ($D_2O$, 500 MHz): **Isomer A:** 6.62(d, *J*=2.3 Hz, 1H, Pz-**H**), 6.80(t, *J*=6.2 Hz, 1H, Py-**H**), 7.33(d, *J*=7.8 Hz, 1H, Py-**H**), 7.39(t, *J*=7.7 Hz, 1H, Py-**H**), 7.54(d, *J*=4.9 Hz, 1H, Py-**H**), 7.66(d, *J*=2.3 Hz, 1H, Pz-**H**); **Isomer B:** 6.35(s, 1H, Pz-**H**),

7.14(s, 1H, Pz-**H**), 7.18(t, *J*=6.1 Hz, 1H, Py-**H**), 7.51-7.57(m, 1H, Py-**H**), 7.71(t, *J*=7.4 Hz, 1H, Py-**H**), 8.95(d, *J*=4.5 Hz, 1H, Py-**H**); ^{13}C NMR (D_2O, 125 MHz): **Isomer A:** 149.3, 145.9, 145.6, 138.3, 133.8, 123.9, 120.0, 103.1; **Isomer B:** 153.3, 149.9, 145.7, 140.9, 130.5, 124.3, 121.9, 102.4; IR (KBr): *v* = 3158 vs, 1595 w, 1568 w, 1401 s, 948 s (V=O), 885 m $(O-O)_{peroxo}$, 866 s $(O-O)_{peroxo}$, 772 m, 619 s $(V-O)_{peroxo}$ cm^{-1}.

4. Detailed structural data (bond distances and angles) of complex 6:

Table S1 Bond lengths [Å] and angles [º] around the vanadium center in $NH_4[OV(O_2)_2(pzpy]\cdot 6H_2O$ (**6**)

Bonds	Bond-lengths	Angles	Bond-angles	Angles	Bond-angles
V(1)-O(5)	1.597(3)	O(5)-V(1)-O(2)	103.03(16)	O(1)-O(2)-V(1)	69.52(17)
V(1)-O(2)	1.865(3)	O(5)-V(1)-O(3)	103.60(15)	O(2)-O(1)-V(1)	65.44(17)
V(1)-O(3)	1.877(3)	O(2)-O(1)-V(1)	65.44(17)	O(3)-O(4)-V(1)	65.86(18
V(1)-O(1)	1.920(3)	O(2)-V(1)-O(3)	87.90(14)	O(4)-O(3)-V(1)	69.09(18)
V(1)-O(4)	1.922(3)	O(5)-V(1)-O(1)	99.94(15)	C(8)-N(1)-C(4)	118.1(4)
V(1)-N(2)	2.086(4)	O(2)-V(1)-O(1)	45.04(13)	C(8)-N(1)-V(1)	126.8(3)
V(1)-N(1)	2.370(4)	O(3)-V(1)-O(1)	131.18(14)	C(4)-N(1)-V(1)	115.0(3)
O(2)-O(1)	1.451(4)	O(5)-V(1)-O(4)	101.14(16)	C(1)-N(3)-N(2)	110.9(4)
O(4)-O(3)	1.456(4)	O(2)-V(1)-O(4)	131.05(14)	C(7)-C(6)-C(5)	119.3(5)
N(1)-C(8)	1.325(6)	O(3)-V(1)-O(4)	45.05(14)	C(1)-C(2)-C(3)	104.7(4)
N(1)-C(4)	1.329(6)	O(1)-V(1)-O(4)	158.70(13)	C(3)-N(2)-N(3)	105.9(4)
N(3)-C(1)	1.324(6)	O(5)-V(1)-N(2)	93.40(16)	C(3)-N(2)-V(1)	123.8(3)
N(3)-N(2)	1.338(5)	O(2)-V(1)-N(2)	131.43(14)	N(3)-N(2)-V(1)	130.3(3)
C(6)-C(7)	1.360(8)	O(3)-V(1)-N(2)	132.28(15)	N(2)-C(3)-C(2)	110.1(4)
C(6)-C(5)	1.365(7)	O(1)-V(1)-N(2)	87.50(14)	N(2)-C(3)-C(4)	116.4(4)
C(2)-C(1)	1.359(7)	O(4)-V(1)-N(2)	88.30(14)	C(2)-C(3)-C(4)	133.5(4)
C(2)-C(3)	1.389(6)	O(5)-V(1)-N(1)	164.15(15)	C(6)-C(5)-C(4)	118.7(5)
N(2)-C(3)	1.333(6)	O(4)-V(1)-N(1)	78.70(13)	N(3)-C(1)-C(2)	108.4(4)
C(3)-C(4)	1.457(6)	O(2)-V(1)-N(1)	88.36(14)	N(1)-C(4)-C(5)	122.5(4)
C(5)-C(4)	1.373(6)	O(3)-V(1)-N(1)	87.59(13)	N(1)-C(4)-C(3)	114.0(4)
C(8)-C(7)	1.377(7)	O(1)-V(1)-N(1)	80.20(13)	C(5)-C(4)-C(3)	123.5(4)
		N(2)-V(1)-N(1)	70.75(14)	N(1)-C(8)-C(7)	122.6(5)

5. Detailed NMR results for the interaction systems of bpV and the pzpy-like ligand:

Table S2 NMR results for the interaction systems of bpV and the pzpy-like ligands.

Systems	Species	Chemical shifts		
		^{1}H (ppm)	^{13}C (ppm)	^{51}V (ppm)
6 + **1** [a]	$[OV(O)_2(pzpy)]^-$ (**Isomer A**)	6.59(s, 1H, Pz-**H**), 6.79(t, *J*=5.9 Hz, 1H, Py-**H**), 7.26-7.32(m, 1H, Py-**H**), 7.37(t, *J*=7.7 Hz, 1H, Py-**H**), 7.53(d, *J*=4.2 Hz, 1H, Py-**H**), 7.64(s, 1H, Pz-**H**)	149.3, 145.9, 145.6, 138.2, 133.8, 123.9, 120.0, 103.1	−745
	$[OV(O)_2(pzpy)]^-$ (**Isomer B**)	6.33(s, 1H, Pz-**H**), 7.12(s, 1H, Pz-**H**), 7.14-7.19(m, 1H, Py-**H**), 7.48-7.52(m, 1H, Py-**H**), 7.66-7.72(m, Py-**H**), 8.90-8.97(m, 1H, Py-**H**)	153.3, 149.8, 145.7, 140.9, 130.5, 124.3, 121.9, 102.3	−783
	pzpy (**1**)	6.33(s, 1H, Pz-**H**), 6.91(t, *J*=5.9 Hz, 1H, Py-**H**), 7.25-7.34(m, 2H, Pz-**H**, Py-**H**), 7.40-7.45(m, 1H, Py-**H**), 7.98-8.01(m, 1H, Py-**H**)	147.6, 145.6, 138.5, 138.5, 138.2, 123.3, 120.6, 103.5	
bpV + **2** [b]	$[OV(O)_2(2\text{-Me-pzpy})]^-$ (**Isomer A**)	3.88(s, 3H, C**H**$_3$), 6.52(s, 1H, Pz-**H**), 6.82(s, 1H, Py-**H**), 7.20-7.28(m, 1H, Py-**H**), 7.36-7.41(m, 1H, Py-**H**), 7.54(s, 1H, Pz-**H**), 7.60-7.69(m, 1H, Py-**H**)	149.9, 145.3, 144.8, 137.8, 136.8, 123.4, 119.2, 102.9, 38.5	−743
	$[OV(O)_2(2\text{-Me-pzpy})]^-$ (**Isomer B**)	3.33(s, 3H, C**H**$_3$), 6.29(s, 1H, Pz-**H**), 7.02(s, 1H, Pz-**H**), 7.12-7.16(m, 1H, Py-**H**), 7.41-7.48(m, 1H, Py-**H**), 7.60-7.69(m, 1H, Py-**H**), 8.93(s, 1H, Py-**H**)	152.7, 149.3, 144.6, 140.3, 132.6, 123.6, 121.1, 102.6, 36.8	−775
	2-Me-pzpy (**2**)	3.41(s, 3H, C**H**$_3$), 6.20(s, 1H, Pz-**H**), 6.87-6.93(m, 1H, Py-**H**), 7.11(s, 1H, Pz-**H**), 7.20-7.28(m, 1H, Py-**H**), 7.36-7.41(m, 1H, Py-**H**); 7.94(s, 1H, Py-**H**)	148.6, 148.4, 146.6, 138.3, 132.6, 122.7, 119.8, 103.6, 37.5	
bpV + **3** [a]	$[OV(O)_2(2\text{-Et-pzpy})]^-$ (**Isomer A**)	1.17(s, 3H, C**H**$_3$), 4.32(s, 2H, C**H**$_2$), 6.50(s, 1H, Pz-**H**), 6.80(s, 1H, Py-**H**), 7.20-7.23(m, 1H, Py-**H**), 7.31-7.38(m, 1H, Py-**H**), 7.56-7.69(m, 2H, Pz-**H**, Py-**H**)	149.9, 145.3, 144.8, 137.7, 135.2, 123.2, 119.1, 103.1, 46.5, 15.0	−741

	$[OV(O)_2$(2-Et-pzpy)$]^-$ (**Isomer B**)	0.92(t, *J*= 6.7 Hz, 3H, C**H**$_3$), 3.63-3.72(m, 2H, C**H**$_2$), 6.29(s, 1H, Pz-**H**), 7.09(s, 1H, Pz-**H**), 7.10-7.13(m, 1H, Py-**H**), 7.42(d, *J*= 7.2 Hz, 1H, Py-**H**), 7.63(t, *J*=8.0 Hz, 1H, Py-**H**); 8.93(d, *J*=3.7 Hz, 1H, Py-**H**)	152.7, 149.4, 144.2, 140.2, 130.4, 123.5, 121.0, 102.7, 45.5, 13.8	−773
	2-Et-pzpy (**1**)	0.98(t, *J*= 7.1 Hz, 3H, C**H**$_3$), 3.63-3.72(m, 2H, C**H**$_2$), 6.17(s, 1H, Pz-**H**), 6.85(t, *J*=6.0 Hz, 1H, Py-**H**), 7.15(s, 1H, Pz-**H**), 7.19(d, *J*=7.7 Hz, 1H, Py-**H**), 7.35(t, *J*=7.4 Hz, 1H, Py-**H**), 7.92(d, *J*= 4.2 Hz, 1H, Py-**H**)	148.7, 148.5, 146.8, 138.0, 131.0, 122.6, 119.7, 103.4, 46.1, 14.2	
bpV + **4** [b]	$[OV(O)_2$(2-Ester-pzpy)$]^-$ (**Isomer A**)	3.35(s, 3H, C**H**$_3$), 5.24(s, 2H, C**H**$_2$), 6.65(s, 1H, Pz-**H**), 6.79-6.85(m, 1H, Py-**H**), 7.26-7.32(m, 1H, Py-**H**), 7.36-7.40(m, 1H, Py-**H**), 7.61(s, 1H, Py-**H**), 7.70(s, 1H, Pz-**H**)	169.2, 151.0, 145.0, 144.9, 137.9, 137.9, 123.7, 119.6, 103.7, 52.3, 51.7	−737
	$[OV(O)_2$(2-Ester-pzpy)$]^-$ (**Isomer B**)	3.35(s, 3H, C**H**$_3$), 4.60(s, 2H, C**H**$_2$), 6.37(s, 1H, Pz-**H**), 7.13(s, 1H, Pz-**H**), 7.17(t, *J*=6.2 Hz, 1H, Py-**H**), 7.50(d, *J*=7.7 Hz, 1H, Py-**H**), 7.69(t, *J*=7.7 Hz, 1H, Py-**H**), 8.94(d, *J*= 4.7 Hz, 1H, Py-**H**)	169.2, 152.7, 148.9, 145.4, 140.4, 133.4, 124.0, 121.4, 103.0, 52.1, 50.7	−761
	2-Ester-pzpy (**4**)	3.38(s, 3H, C**H**$_3$), 4.68(s, 2H, C**H**$_2$), 6.34(s, 1H, Pz-**H**), 6.92(t, *J*=6.1 Hz, 1H, Py-**H**), 7.28(s, 1H, Pz-**H**), 7.26-7.32(m, 1H, Py-**H**), 7.42(t, *J*=7.6 Hz, 1H, Py-**H**), 7.97(d, *J*=4.5 Hz, 1H, Py-**H**)	169.8, 149.6, 148.2, 146.6, 138.5, 133.5, 123.1, 120.2, 104.4, 52.3, 51.7	
bpV + **5** [b]	$[OV(O)_2$(2-Amide-pzpy)$]^-$ (**Isomer A**)	2.30-2.32(s, 3H, C**H**$_3$), 5.13(s, 2H, C**H**$_2$), 6.67(s, 1H, Pz-**H**), 6.82(s, 1H, Py-**H**), 7.23-7.28(m, 1H, Py-**H**), 7.30(s, 1H, Py-**H**), 7.59-7.63(s, 1H, Py-**H**), 7.70(s, 1H, Pz-**H**)	168.6, 151.1, 145.0, 145.0, 138.1, 137.8, 123.7, 119.6, 103.8, 52.8, 25.3	−740
	$[OV(O)_2$(2-Amide-pzpy)$]^-$ (**Isomer B**)	2.29(s, 3H, C**H**$_3$), 4.38(s, 2H, C**H**$_2$), 6.37(s, 1H, Pz-**H**), 7.12(s, 1H, Pz-**H**), 7.15(t, *J*=6.0 Hz, 1H, Py-**H**), 7.47(d, *J*=7.2 Hz, 1H, Py-**H**), 7.67(t, *J*=7.2 Hz, 1H, Py-**H**), 8.94(d, *J*=4.7 Hz, 1H, Py-**H**)	168.6, 152.8, 148.7, 145.6, 140.4, 132.8, 124.1, 121.5, 103.6, 52.8, 25.1	−760
	2-Amide-pzpy (**5**)	2.33(s, 3H, C**H**$_3$), 4.49(s, 2H, C**H**$_2$), 6.32(s, 1H, Pz-**H**), 6.87(t, *J*=6.0 Hz, 1H, Py-**H**), 7.23-7.28(m, 2H, Pz-**H,** Py-**H**), 7.35(t, *J*=7.7 Hz, 1H, Py-**H**), 7.97(d, *J*=4.5 Hz, 1H, Py-**H**)	169.1, 150.7, 148.9, 147.4, 137.5, 133.5, 122.9, 120.0, 104.2, 53.0, 25.1	

[a] The molar ratio between complex **6** and the pzpy ligand is 1:0.2;

[b] The molar ratio between bpV and other pzpy-like ligand is 1:1.5.