Supplementary Data

An Evidence of Proton-Coupled Mixed-Valency by Electrochemical Behavior on Transition Metal Complex Dimers Bridged by two Ag^+ Ions

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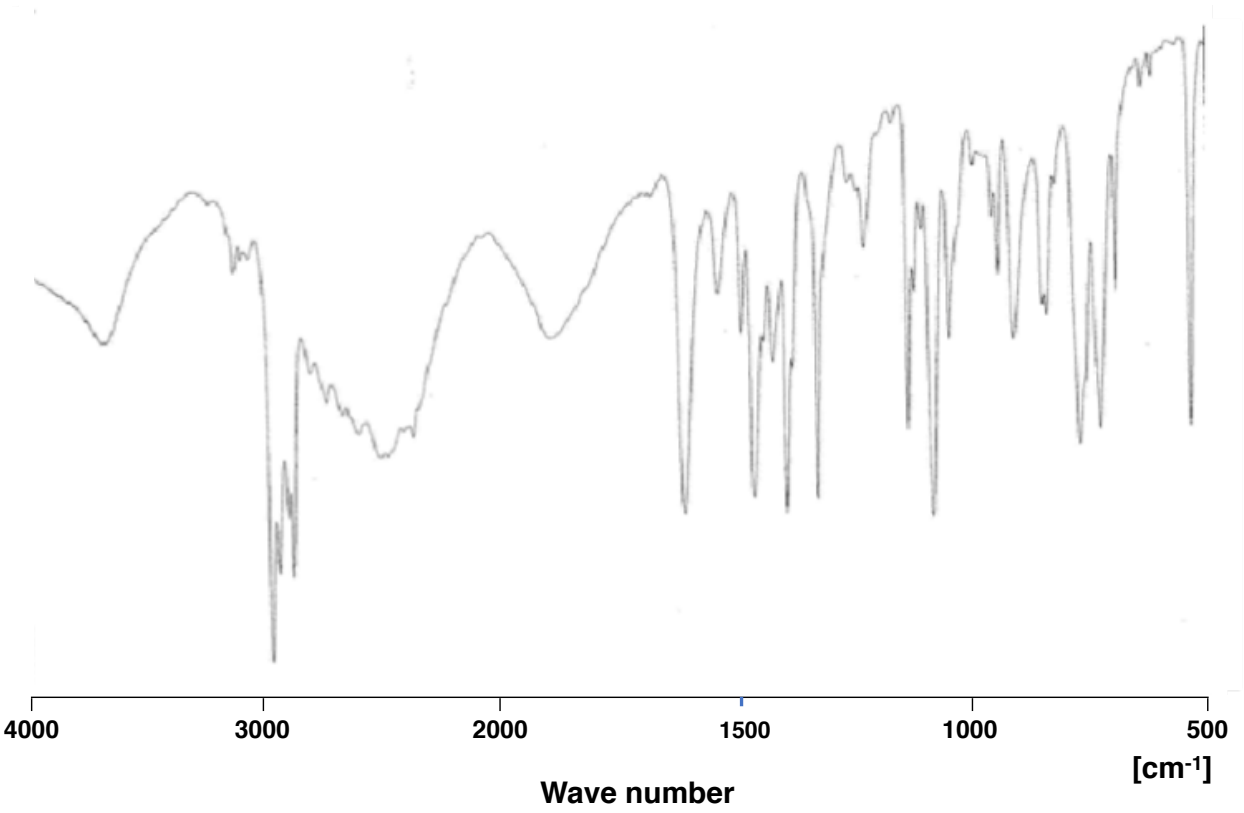

Figure S1

IR spectrum of $[Re^{III}Cl_2(P^nPr_3)_2(Hbim)]_2$(2)

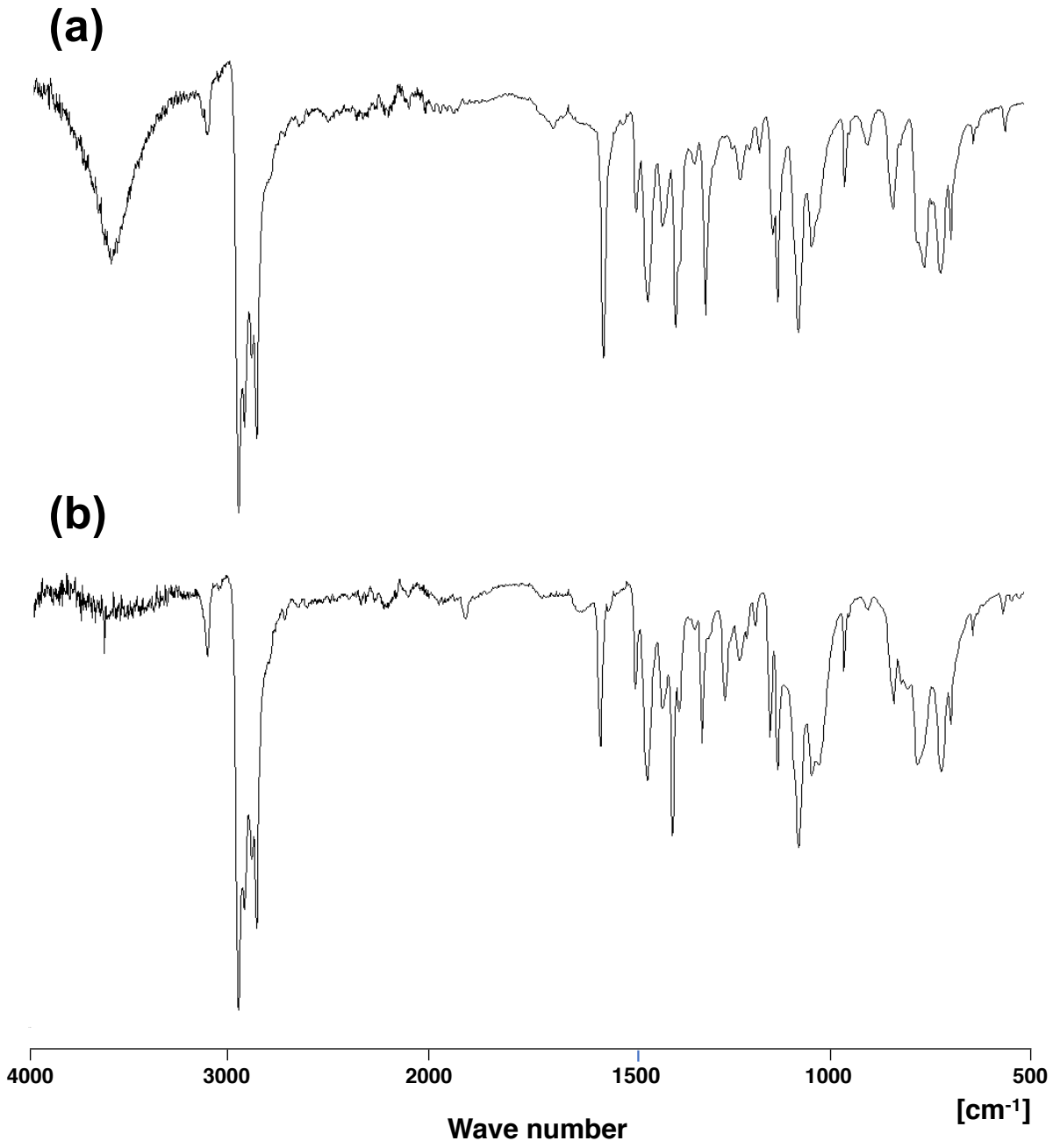

Figure S2

IR spectra of (a) $[Re^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(4) and (b) $[Os^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(5)

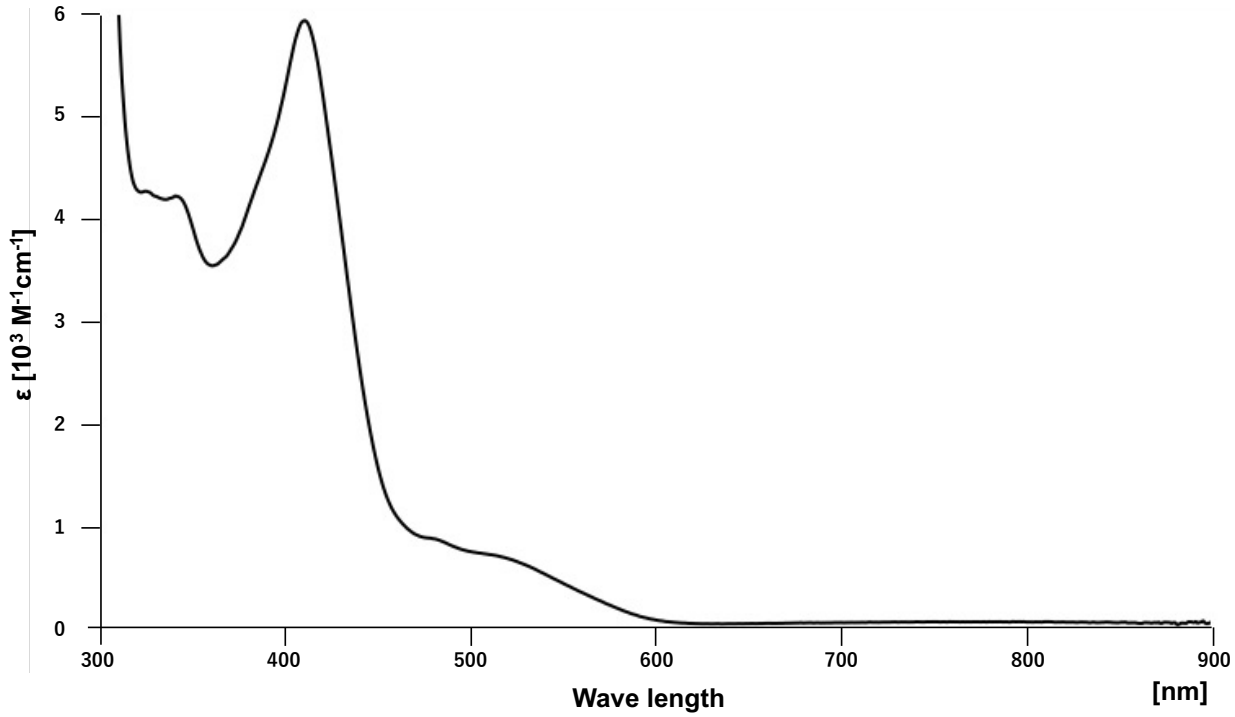

Figure S3

UV-*vis* absorption spectrum of $[Re^{III}Cl_2(P^nPr_3)_2(Hbim)]_2$ (2) in CH_2Cl_2

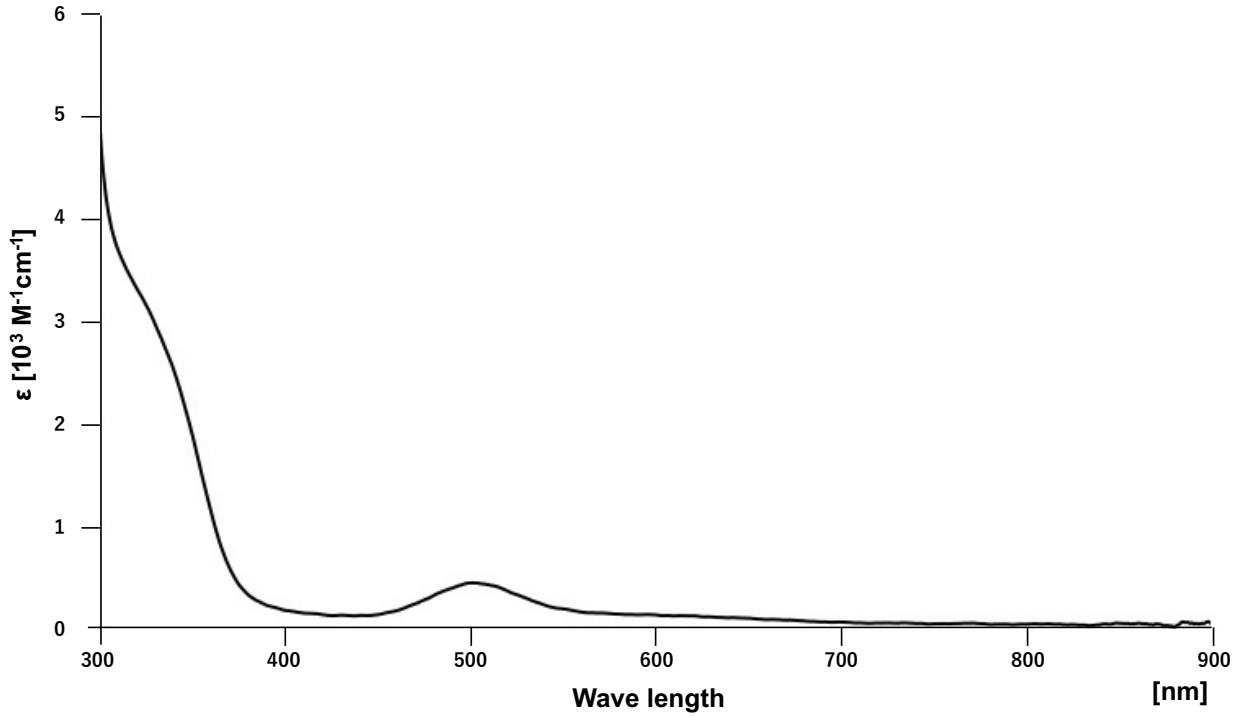

Figure S4

UV-*vis* absorption spectrum of $[Os^{III}Cl_2(P^nPr_3)_2(Hbim)]_2$(3) in CH_2Cl_2

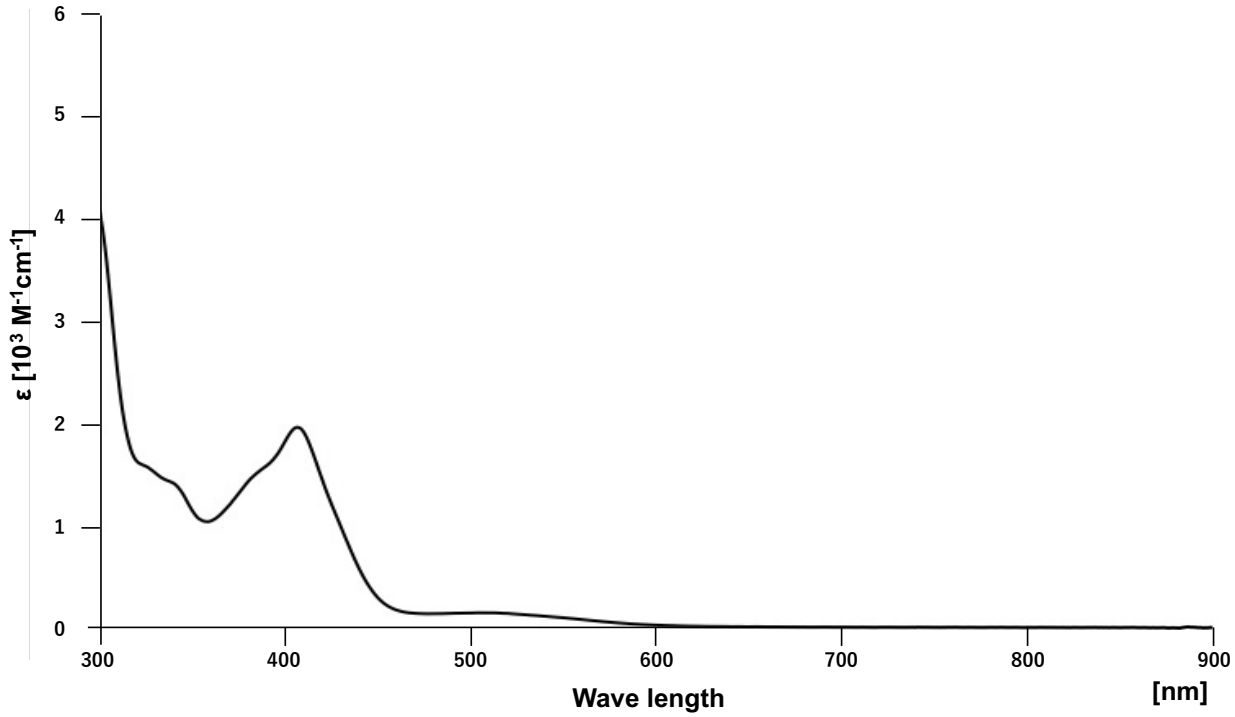

Figure S5

UV-*vis* absorption spectrum of $[Re^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(4) in CH_2Cl_2

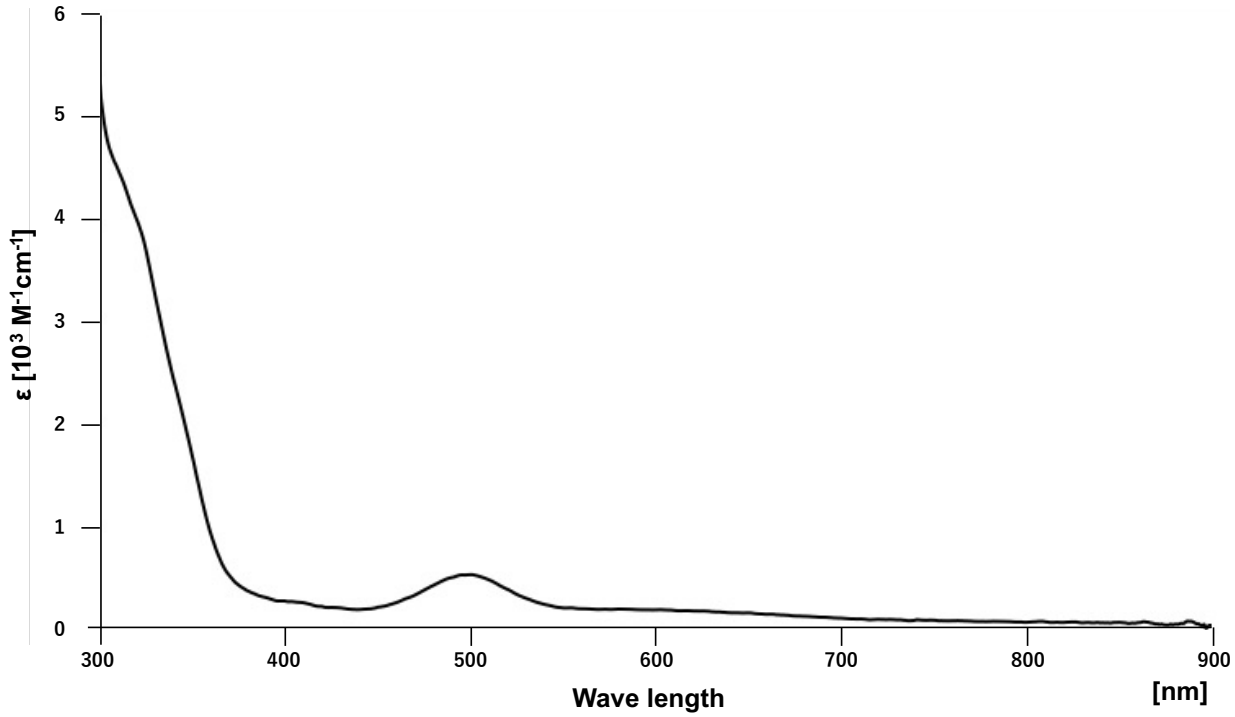

Figure S6

UV-*vis* absorption spectrum of $[Os^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(5) in CH_2Cl_2

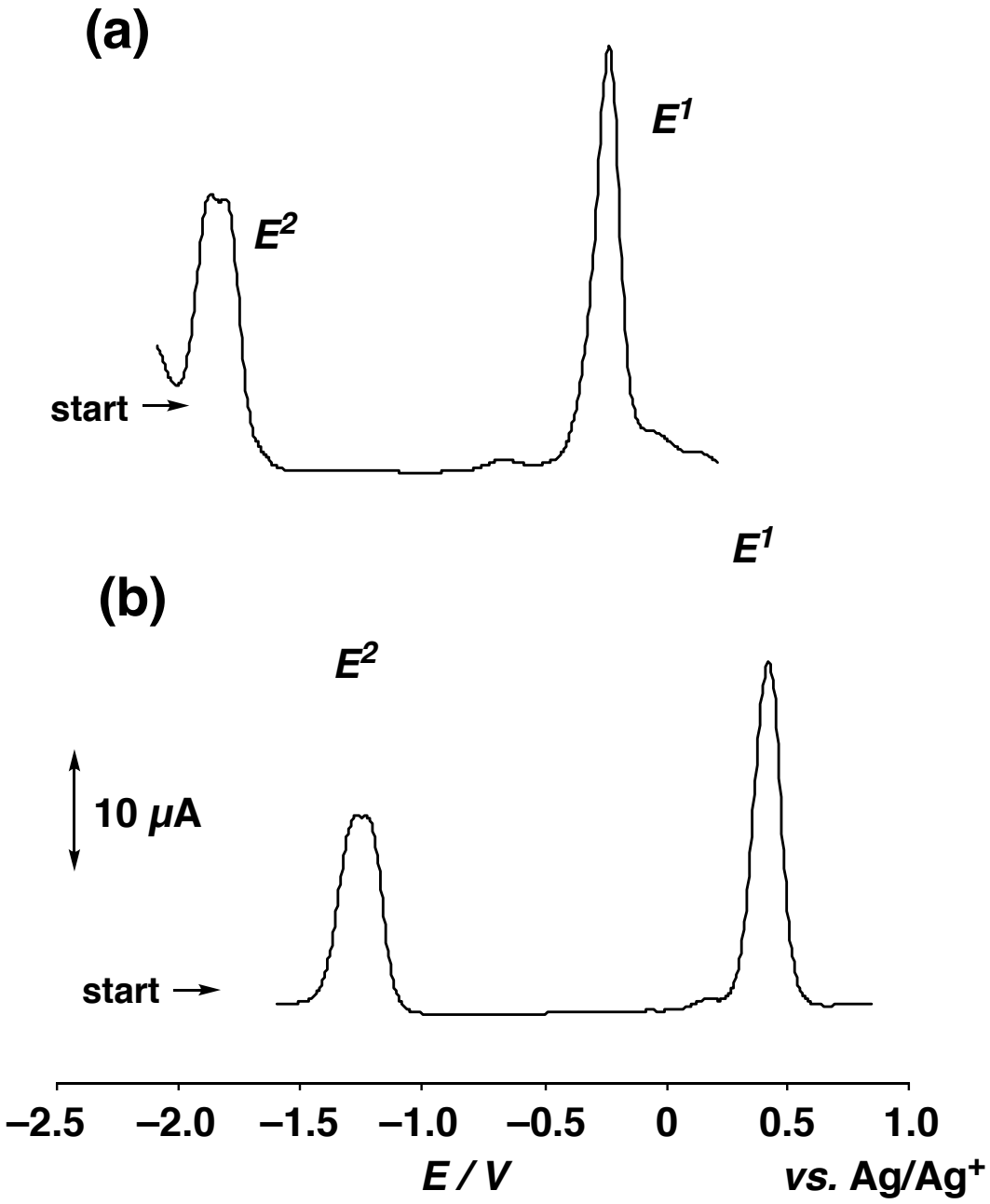

Figure S7

The results of DPV measurements (a) $[Re^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(4) (b) $[Os^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(5) in CH_2Cl_2

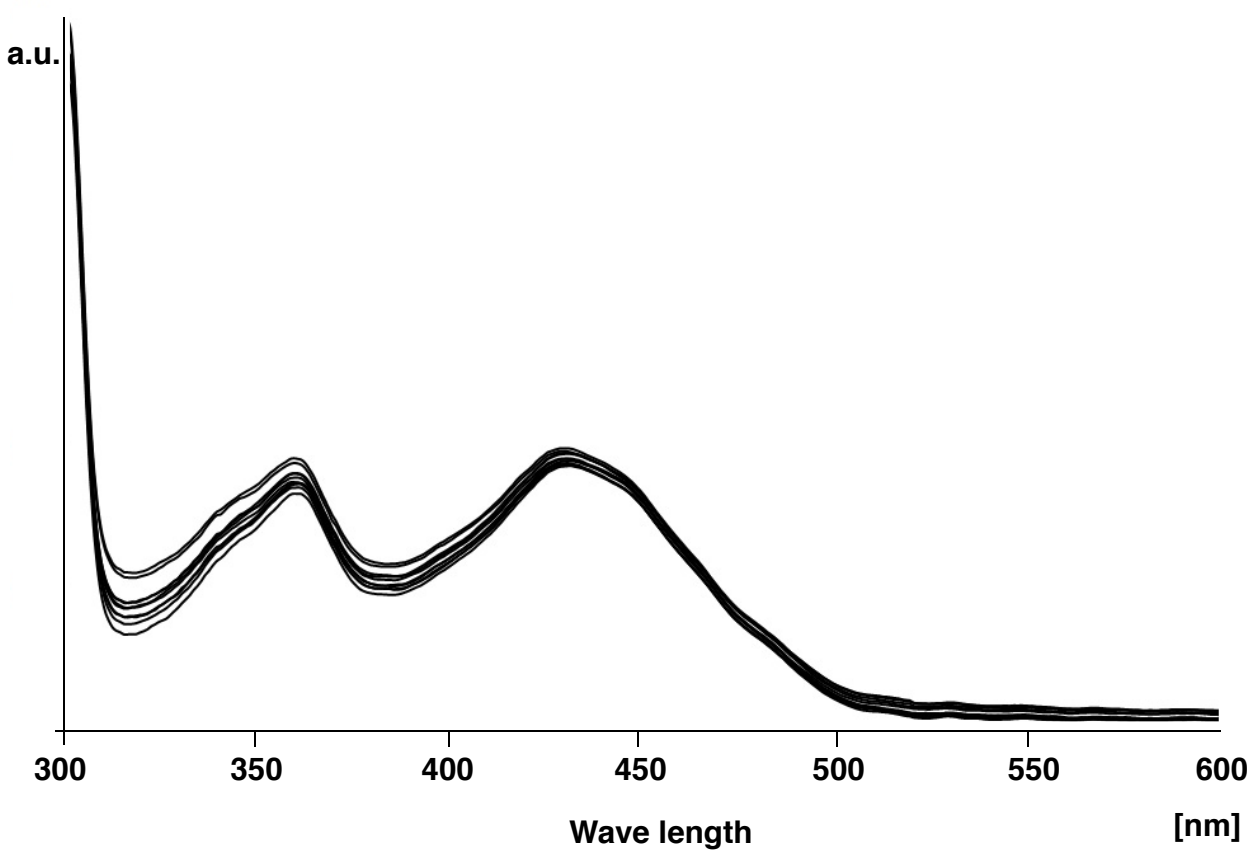

Figure S8

UV-*vis* absorption spectra at pH = 2.37～4.22 of $[Re^{III}Cl_2(P^nPr_3)_2(H_2bim)]Cl$ for Pourbaix Diagram.

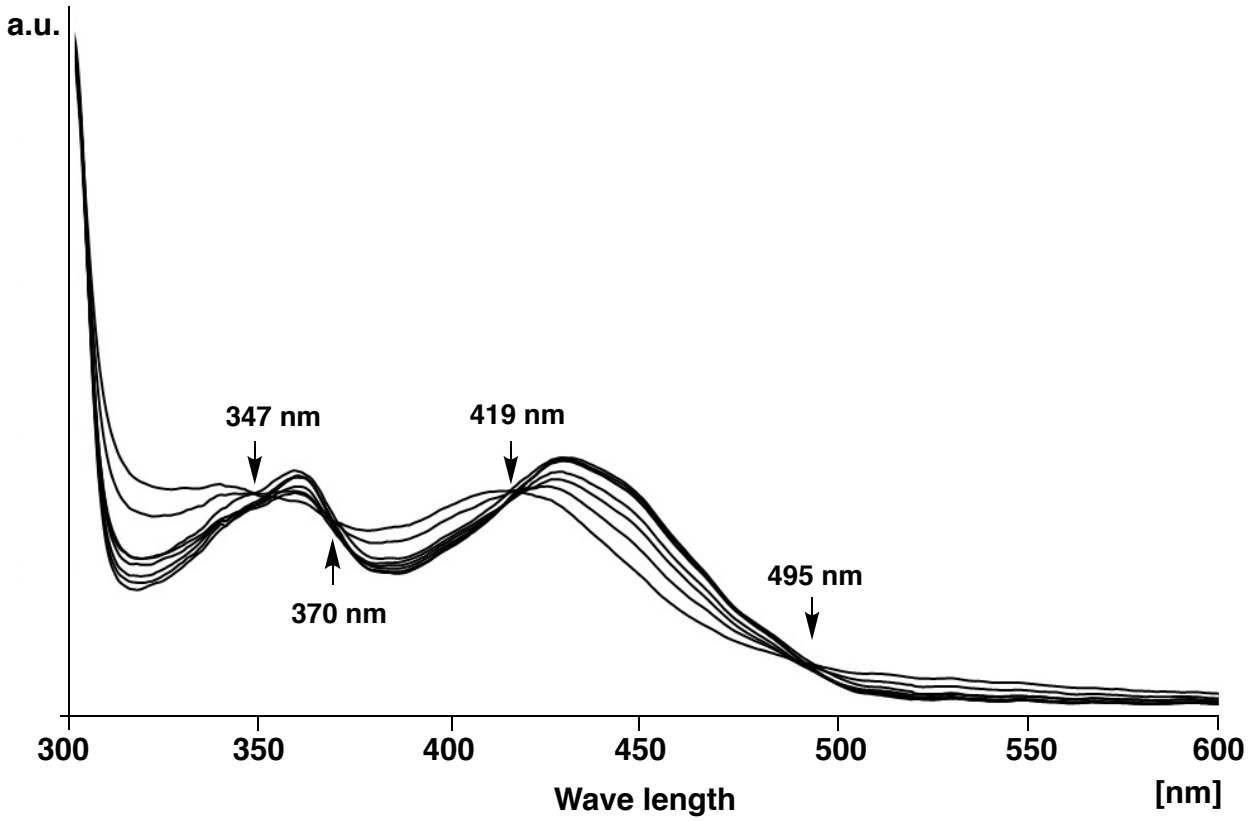

Figure S9

UV-*vis* absorption spectra at pH = 4.40～6.22 of $[Re^{III}Cl_2(P^nPr_3)_2(H_2bim)]Cl$ for Pourbaix Diagram. Four isosbestic points were observed at 347 nm, 370 nm, 419 nm, and 495 nm.

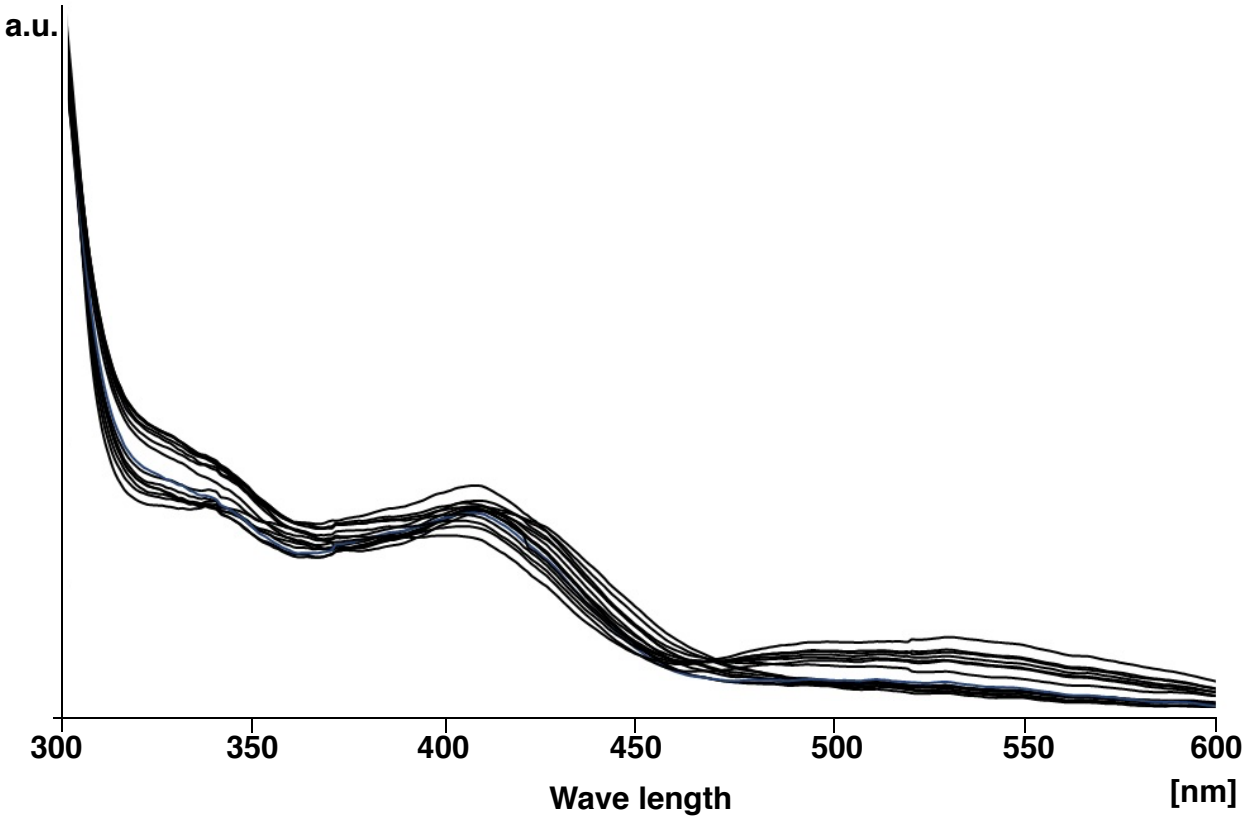

Figure S10

UV-*vis* absorption spectra at pH = 6.39～9.45 of $[Re^{III}Cl_2(P^nPr_3)_2(H_2bim)]Cl$ for Pourbaix Diagram.

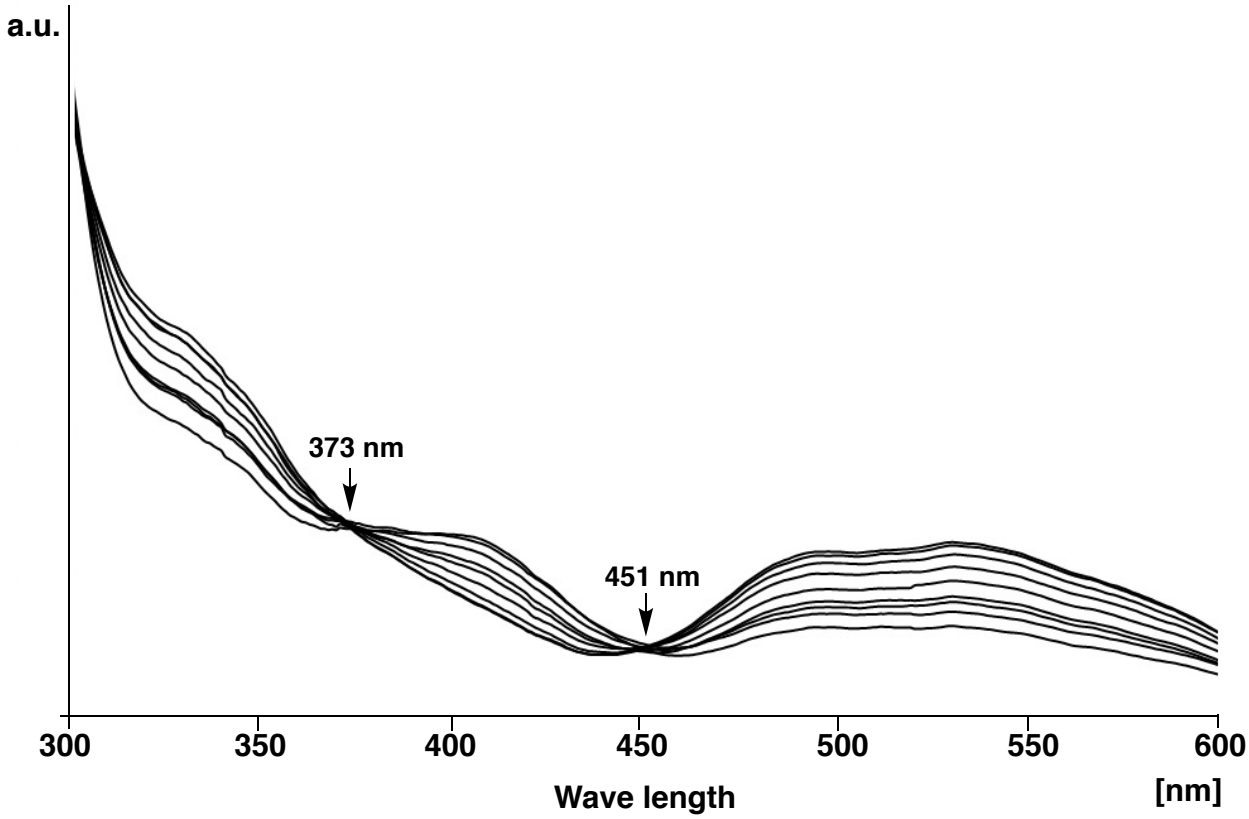

Figure S11

UV-*vis* absorption spectra at pH = 9.61～11.43 of [$Re^{III}Cl_2(P^nPr_3)_2(H_2bim)$]Cl for Pourbaix Diagram. Two isosbestic points were observed at 373 nm, and 451 nm.

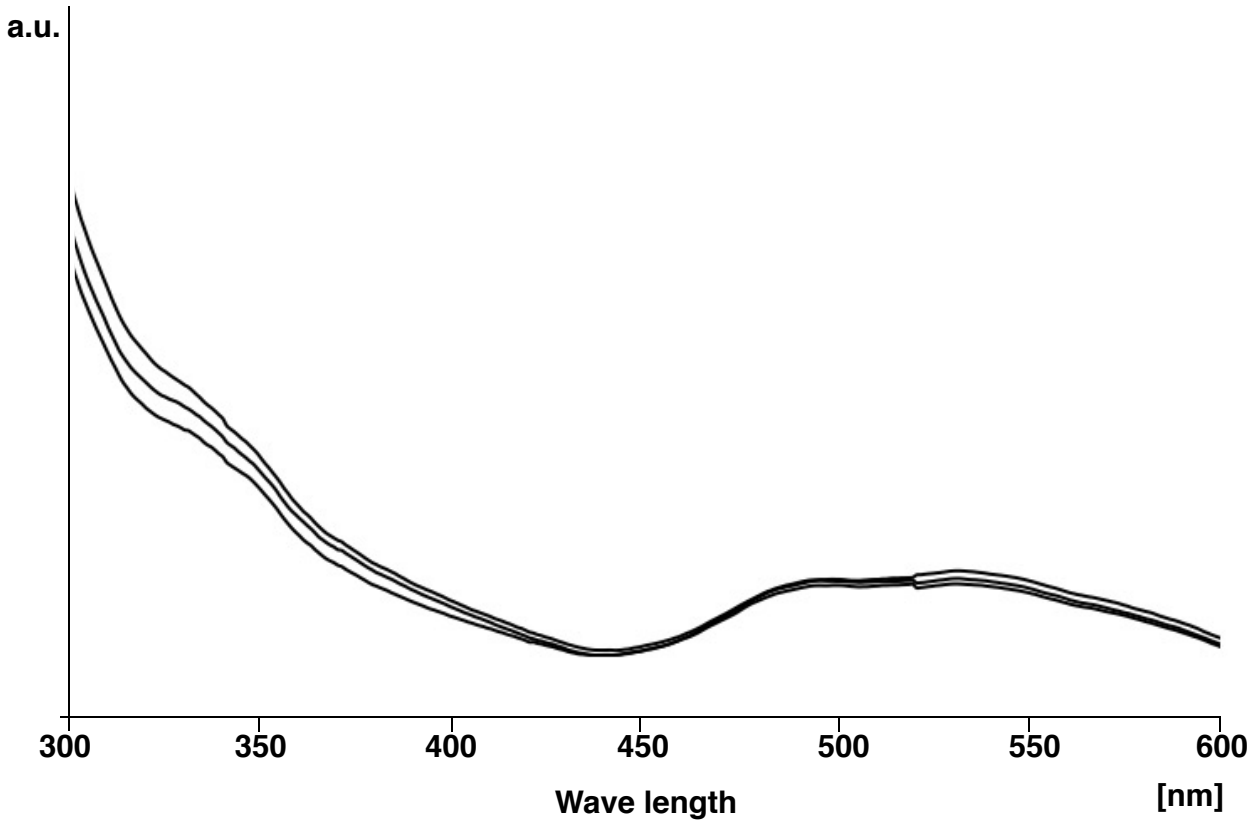

Figure S12

UV-*vis* absorption spectra at pH = 11.60～12.00 of [$Re^{III}Cl_2(P^nPr_3)_2(H_2bim)$]Cl for Pourbaix Diagram.

Table S1. Bond distances (Å) and angles (°) around metal coordination of $[Re^{III}Cl_2(P^nPr_3)_2(Hbim)]_2$(**2**)

Re(1)–Cl(1)	2.3742(9)	Re(1)–P(2)	2.4566(10)
Re(1)–Cl(2)	2.3833(9)	Re(1)–N(1)	2.111(3)
Re(1)–P(1)	2.4638(9)	Re(1)–N(3)	2.091(3)
Cl(1)–Re(1)–Cl(2)	100.94(3)	Cl(2)–Re(1)–N(3)	92.06(8)
Cl(1)–Re(1)–P(1)	89.98(3)	P(1)–Re(1)–P(2)	178.38(3)
Cl(1)–Re(1)–P(2)	91.28(3)	P(1)–Re(1)–N(1)	87.42(8)
Cl(1)–Re(1)–N(1)	91.26(8)	P(1)–Re(1)–N(3)	91.93(8)
Cl(1)–Re(1)–N(3)	166.88(8)	P(2)–Re(1)–N(1)	93.57(8)
Cl(2)–Re(1)–P(1)	89.31(3)	P(2)–Re(1)–N(3)	87.07(8)
Cl(2)–Re(1)–P(2)	89.46(3)	N(1)–Re(1)–N(3)	75.87(10)
Cl(2)–Re(1)–N(1)	167.37(8)		

Table S2. Bond distances (Å) and angles (°) around metal coordination of $[Os^{III}Cl_2(P^nPr_3)_2(Hbim)]_2$(**3**)

Os(1)–Cl(1)	2.360(2)	Os(4)–Cl(7)	2.363(2)
Os(1)–Cl(2)	2.367(2)	Os(4)–Cl(8)	2.370(2)
Os(1)–P(1)	2.396(2)	Os(4)–P(7)	2.386(3)
Os(1)–P(2)	2.396(2)	Os(4)–P(8)	2.402(2)
Os(1)–N(1)	2.067(7)	Os(4)–N(13)	2.069(7)
Os(1)–N(3)	2.078(6)	Os(4)–N(15)	2.089(7)
Os(2)–Cl(3)	2.366(2)	Os(5)–Cl(9)	2.368(2)
Os(2)–Cl(4)	2.365(3)	Os(5)–Cl(10)	2.352(3)
Os(2)–P(3)	2.385(3)	Os(5)–P(9)	2.396(3)
Os(2)–P(4)	2.402(3)	Os(5)–P(10)	2.392(3)
Os(2)–N(5)	2.064(7)	Os(5)–N(17)	2.072(8)
Os(2)–N(7)	2.082(7)	Os(5)–N(19)	2.070(7)
Os(3)–Cl(5)	2.366(2)	Os(6)–Cl(11)	2.362(2)
Os(3)–Cl(6)	2.362(3)	Os(6)–Cl(12)	2.376(2)
Os(3)–P(5)	2.387(2)	Os(6)–P(11)	2.384(3)
Os(3)–P(6)	2.382(3)	Os(6)–P(12)	2.393(3)
Os(3)–N(9)	2.070(7)	Os(6)–N(21)	2.071(7)
Os(3)–N(11)	2.080(7)	Os(6)–N(23)	2.074(7)
Cl(1)–Os(1)–Cl(2)	96.19(8)	P(2)–Os(1)–N(1)	91.0(2)
Cl(1)–Os(1)–P(1)	90.30(9)	P(2)–Os(1)–N(3)	88.9(2)
Cl(1)–Os(1)–P(2)	89.24(9)	N(1)–Os(1)–N(3)	77.2(3)
Cl(1)–Os(1)–N(1)	171.60(18)	Cl(3)–Os(2)–Cl(4)	99.85(9)
Cl(1)–Os(1)–N(3)	94.4(2)	Cl(3)–Os(2)–P(3)	86.44(10)
Cl(2)–Os(1)–P(1)	89.48(8)	Cl(3)–Os(2)–P(4)	89.68(9)
Cl(2)–Os(1)–P(2)	89.39(8)	Cl(3)–Os(2)–N(5)	90.3(2)
Cl(2)–Os(1)–N(1)	92.21(18)	Cl(3)–Os(2)–N(7)	167.5(2)
Cl(2)–Os(1)–N(3)	169.2(2)	Cl(4)–Os(2)–P(3)	89.38(10)
P(1)–Os(1)–P(2)	178.73(8)	Cl(4)–Os(2)–P(4)	88.77(10)
P(1)–Os(1)–N(1)	89.6(2)	Cl(4)–Os(2)–N(5)	169.9(2)
P(1)–Os(1)–N(3)	92.4(2)	Cl(4)–Os(2)–N(7)	92.7(2)

Table S2. Bond distances (Å) and angles (°) around metal coordination of $[Os^{III}Cl_2(P^nPr_3)_2(Hbim)]_2$(**3**) (*continued* 1)

P(3)–Os(2)–P(4)	175.36(9)	P(7)–Os(4)–N(13)	90.9(2)
P(3)–Os(2)–N(5)	91.7(2)	P(7)–Os(4)–N(15)	92.71(19)
P(3)–Os(2)–N(7)	93.3(2)	P(8)–Os(4)–N(13)	91.5(2)
P(4)–Os(2)–N(5)	90.8(2)	P(8)–Os(4)–N(15)	92.54(19)
P(4)–Os(2)–N(7)	91.1(2)	N(13)–Os(4)–N(15)	76.7(3)
N(5)–Os(2)–N(7)	77.2(3)	Cl(9)–Os(5)–Cl(10)	98.00(10)
Cl(5)–Os(3)–Cl(6)	97.90(9)	Cl(9)–Os(5)–P(9)	88.62(10)
Cl(5)–Os(3)–P(5)	87.88(8)	Cl(9)–Os(5)–P(10)	88.87(9)
Cl(5)–Os(3)–P(6)	90.31(10)	Cl(9)–Os(5)–N(17)	90.7(2)
Cl(5)–Os(3)–N(9)	91.38(18)	Cl(9)–Os(5)–N(19)	167.0(2)
Cl(5)–Os(3)–N(11)	167.5(2)	Cl(10)–Os(5)–P(9)	87.94(11)
Cl(6)–Os(3)–P(5)	86.61(9)	Cl(10)–Os(5)–P(10)	87.48(10)
Cl(6)–Os(3)–P(6)	89.06(10)	Cl(10)–Os(5)–N(17)	171.0(2)
Cl(6)–Os(3)–N(9)	170.25(18)	Cl(10)–Os(5)–N(19)	94.7(2)
Cl(6)–Os(3)–N(11)	94.6(2)	P(9)–Os(5)–P(10)	174.43(10)
P(5)–Os(3)–P(6)	175.03(9)	P(9)–Os(5)–N(17)	90.0(2)
P(5)–Os(3)–N(9)	90.80(18)	P(9)–Os(5)–N(19)	94.6(2)
P(5)–Os(3)–N(11)	93.8(2)	P(10)–Os(5)–N(17)	95.0(2)
P(6)–Os(3)–N(9)	93.87(19)	P(10)–Os(5)–N(19)	89.0(2)
P(6)–Os(3)–N(11)	88.9(2)	N(17)–Os(5)–N(19)	76.7(3)
N(9)–Os(3)–N(11)	76.2(3)	Cl(11)–Os(6)–Cl(12)	96.93(9)
Cl(7)–Os(4)–Cl(8)	97.71(9)	Cl(11)–Os(6)–P(11)	89.21(9)
Cl(7)–Os(4)–P(7)	86.62(9)	Cl(11)–Os(6)–P(12)	86.86(9)
Cl(7)–Os(4)–P(8)	88.45(8)	Cl(11)–Os(6)–N(21)	93.9(2)
Cl(7)–Os(4)–N(13)	92.5(2)	Cl(11)–Os(6)–N(23)	170.71(19)
Cl(7)–Os(4)–N(15)	169.09(18)	Cl(12)–Os(6)–P(11)	87.27(9)
Cl(8)–Os(4)–P(7)	90.26(9)	Cl(12)–Os(6)–P(12)	90.14(8)
Cl(8)–Os(4)–P(8)	88.24(9)	Cl(12)–Os(6)–N(21)	169.1(2)
Cl(8)–Os(4)–N(13)	169.8(2)	Cl(12)–Os(6)–N(23)	92.33(19)
Cl(8)–Os(4)–N(15)	93.19(18)	P(11)–Os(6)–P(12)	175.00(9)
P(7)–Os(4)–P(8)	174.61(10)	P(11)–Os(6)–N(21)	91.3(2)

Table S2. Bond distances (Å) and angles (°) around metal coordination of $[Os^{III}Cl_2(P^nPr_3)_2(Hbim)]_2$(**3**) (*continued* 2)

P(11)–Os(6)–N(23)	92.0(2)	P(12)–Os(6)–N(23)	92.4(2)
P(12)–Os(6)–N(21)	92.0(2)	N(21)–Os(6)–N(23)	76.9(3)

Table S3 Bond distances (Å) and angles (°) around metal coordination of $[Re^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(**4**)

Re(1)–Cl(1)	2.369(5)	Re(3)–N(11)	2.095(12)
Re(1)–Cl(2)	2.399(5)	Re(4)–Cl(7)	2.372(4)
Re(1)–P(1)	2.459(6)	Re(4)–Cl(8)	2.390(4)
Re(1)–P(2)	2.440(6)	Re(4)–P(7)	2.482(6)
Re(1)–N(1)	2.056(16)	Re(4)–P(8)	2.423(6)
Re(1)–N(3)	2.087(14)	Re(4)–N(13)	2.093(12)
Re(2)–Cl(3)	2.393(4)	Re(4)–N(15)	2.051(13)
Re(2)–Cl(4)	2.367(5)	Ag(1)–Ag(2)	2.9855(19)
Re(2)–P(3)	2.459(6)	Ag(1)–N(2)	2.037(12)
Re(2)–P(4)	2.425(6)	Ag(1)–N(6)	2.083(15)
Re(2)–N(5)	2.100(13)	Ag(2)–N(4)	2.089(13)
Re(2)–N(7)	2.112(12)	Ag(2)–N(8)	2.069(13)
Re(3)–Cl(5)	2.389(4)	Ag(3)–Ag(4)	2.9815(18)
Re(3)–Cl(6)	2.362(5)	Ag(3)–N(10)	2.083(12)
Re(3)–P(5)	2.448(5)	Ag(3)–N(14)	2.095(13)
Re(3)–P(6)	2.451(5)	Ag(4)–N(12)	2.116(14)
Re(3)–N(9)	2.101(12)	Ag(4)–N(16)	2.084(13)
Cl(1)–Re(1)–Cl(2)	100.76(17)	P(1)–Re(1)–N(3)	86.2(4)
Cl(1)–Re(1)–P(1)	90.1(2)	P(2)–Re(1)–N(1)	87.8(5)
Cl(1)–Re(1)–P(2)	89.8(2)	P(2)–Re(1)–N(3)	94.2(4)
Cl(1)–Re(1)–N(1)	92.4(5)	N(1)–Re(1)–N(3)	76.8(6)
Cl(1)–Re(1)–N(3)	168.3(4)	Cl(3)–Re(2)–Cl(4)	100.59(17)
Cl(2)–Re(1)–P(1)	89.96(17)	Cl(3)–Re(2)–P(3)	88.87(19)
Cl(2)–Re(1)–P(2)	88.81(19)	Cl(3)–Re(2)–P(4)	90.92(18)
Cl(2)–Re(1)–N(1)	166.4(5)	Cl(3)–Re(2)–N(5)	90.7(4)
Cl(2)–Re(1)–N(3)	90.4(4)	Cl(3)–Re(2)–N(7)	166.8(4)
P(1)–Re(1)–P(2)	178.70(19)	Cl(4)–Re(2)–P(3)	92.8(2)
P(1)–Re(1)–N(1)	93.5(5)	Cl(4)–Re(2)–P(4)	88.3(2)

Table S3 Bond distances (Å) and angles (°) around metal coordination of $[Re^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(**4**) (*continued* 1)

Cl(4)–Re(2)–N(5)	168.4(4)	P(5)–Re(3)–N(11)	88.5(4)
Cl(4)–Re(2)–N(7)	92.5(4)	P(6)–Re(3)–N(9)	89.3(4)
P(3)–Re(2)–P(4)	178.9(2)	P(6)–Re(3)–N(11)	92.9(4)
P(3)–Re(2)–N(5)	90.0(5)	N(9)–Re(3)–N(11)	74.8(5)
P(3)–Re(2)–N(7)	88.6(3)	Cl(7)–Re(4)–Cl(8)	98.13(16)
P(4)–Re(2)–N(5)	88.9(5)	Cl(7)–Re(4)–P(7)	88.1(2)
P(4)–Re(2)–N(7)	91.3(3)	Cl(7)–Re(4)–P(8)	90.57(17)
N(5)–Re(2)–N(7)	76.4(5)	Cl(7)–Re(4)–N(13)	94.1(4)
Cl(5)–Re(3)–Cl(6)	101.71(16)	Cl(7)–Re(4)–N(15)	169.5(4)
Cl(5)–Re(3)–P(5)	88.92(18)	Cl(8)–Re(4)–P(7)	87.1(2)
Cl(5)–Re(3)–P(6)	89.70(16)	Cl(8)–Re(4)–P(8)	93.6(2)
Cl(5)–Re(3)–N(9)	90.9(3)	Cl(8)–Re(4)–N(13)	167.4(4)
Cl(5)–Re(3)–N(11)	165.4(4)	Cl(8)–Re(4)–N(15)	92.3(4)
Cl(6)–Re(3)–P(5)	90.62(19)	P(7)–Re(4)–P(8)	178.6(2)
Cl(6)–Re(3)–P(6)	89.29(17)	P(7)–Re(4)–N(13)	90.3(4)
Cl(6)–Re(3)–N(9)	167.3(4)	P(7)–Re(4)–N(15)	91.2(5)
Cl(6)–Re(3)–N(11)	92.7(4)	P(8)–Re(4)–N(13)	89.2(4)
P(5)–Re(3)–P(6)	178.56(19)	P(8)–Re(4)–N(15)	90.0(5)
P(5)–Re(3)–N(9)	91.1(4)	N(13)–Re(4)–N(15)	75.4(5)

Table S4. Bond distances (Å) and angles (°) around metal coordination of $[Os^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(**5**)

Os(1)–Cl(1)	2.3749(19)	Os(3)–N(11)	2.082(7)
Os(1)–Cl(2)	2.370(2)	Os(4)–Cl(7)	2.3729(19)
Os(1)–P(1)	2.379(2)	Os(4)–Cl(8)	2.370(2)
Os(1)–P(2)	2.379(2)	Os(4)–P(7)	2.369(3)
Os(1)–N(1)	2.064(6)	Os(4)–P(8)	2.365(3)
Os(1)–N(3)	2.055(6)	Os(4)–N(13)	2.079(6)
Os(2)–Cl(3)	2.370(2)	Os(4)–N(15)	2.071(6)
Os(2)–Cl(4)	2.382(2)	Ag(1)–Ag(2)	2.9712(9)
Os(2)–P(3)	2.383(2)	Ag(1)–N(2)	2.075(7)
Os(2)–P(4)	2.377(3)	Ag(1)–N(6)	2.073(7)
Os(2)–N(5)	2.062(6)	Ag(2)–N(4)	2.071(7)
Os(2)–N(7)	2.064(6)	Ag(2)–N(8)	2.075(6)
Os(3)–Cl(5)	2.368(2)	Ag(3)–Ag(4)	2.9710(10)
Os(3)–Cl(6)	2.3800(19)	Ag(3)–N(10)	2.086(6)
Os(3)–P(5)	2.383(2)	Ag(3)–N(14)	2.071(6)
Os(3)–P(6)	2.384(2)	Ag(4)–N(12)	2.086(6)
Os(3)–N(9)	2.061(6)	Ag(4)–N(16)	2.085(7)
Cl(1)–Os(1)–Cl(2)	96.54(7)	P(1)–Os(1)–N(3)	88.7(2)
Cl(1)–Os(1)–P(1)	89.38(8)	P(2)–Os(1)–N(1)	90.63(19)
Cl(1)–Os(1)–P(2)	89.82(8)	P(2)–Os(1)–N(3)	92.1(2)
Cl(1)–Os(1)–N(1)	93.21(19)	N(1)–Os(1)–N(3)	76.9(3)
Cl(1)–Os(1)–N(3)	169.96(19)	Cl(3)–Os(2)–Cl(4)	96.18(7)
Cl(2)–Os(1)–P(1)	90.65(8)	Cl(3)–Os(2)–P(3)	91.15(8)
Cl(2)–Os(1)–P(2)	89.26(9)	Cl(3)–Os(2)–P(4)	91.04(9)
Cl(2)–Os(1)–N(1)	170.25(19)	Cl(3)–Os(2)–N(5)	93.99(18)
Cl(2)–Os(1)–N(3)	93.34(19)	Cl(3)–Os(2)–N(7)	171.02(19)
P(1)–Os(1)–P(2)	179.17(9)	Cl(4)–Os(2)–P(3)	89.36(8)
P(1)–Os(1)–N(1)	89.60(19)	Cl(4)–Os(2)–P(4)	89.79(8)

Table S4 Bond distances (Å) and angles (°) around metal coordination of $[Os^{III}Cl_2(P^nPr_3)_2(Agbim)]_2$(**5**) (*continued* 1)

Cl(4)–Os(2)–N(5)	169.70(19)	P(5)–Os(3)–N(11)	89.6(2)
Cl(4)–Os(2)–N(7)	92.78(18)	P(6)–Os(3)–N(9)	91.2(2)
P(3)–Os(2)–P(4)	177.72(9)	P(6)–Os(3)–N(11)	89.0(2)
P(3)–Os(2)–N(5)	88.8(2)	N(9)–Os(3)–N(11)	76.8(3)
P(3)–Os(2)–N(7)	89.5(2)	Cl(7)–Os(4)–Cl(8)	97.86(7)
P(4)–Os(2)–N(5)	91.6(2)	Cl(7)–Os(4)–P(7)	89.27(8)
P(4)–Os(2)–N(7)	88.5(2)	Cl(7)–Os(4)–P(8)	89.64(8)
N(5)–Os(2)–N(7)	77.1(3)	Cl(7)–Os(4)–N(13)	92.09(18)
Cl(5)–Os(3)–Cl(6)	96.87(7)	Cl(7)–Os(4)–N(15)	168.5(2)
Cl(5)–Os(3)–P(5)	90.91(8)	Cl(8)–Os(4)–P(7)	88.89(9)
Cl(5)–Os(3)–P(6)	90.53(9)	Cl(8)–Os(4)–P(8)	88.92(11)
Cl(5)–Os(3)–N(9)	93.42(19)	Cl(8)–Os(4)–N(13)	170.05(18)
Cl(5)–Os(3)–N(11)	170.22(19)	Cl(8)–Os(4)–N(15)	93.5(2)
Cl(6)–Os(3)–P(5)	89.45(8)	P(7)–Os(4)–P(8)	177.40(10)
Cl(6)–Os(3)–P(6)	90.27(8)	P(7)–Os(4)–N(13)	91.6(2)
Cl(6)–Os(3)–N(9)	169.58(19)	P(7)–Os(4)–N(15)	89.2(2)
Cl(6)–Os(3)–N(11)	92.90(18)	P(8)–Os(4)–N(13)	90.8(2)
P(5)–Os(3)–P(6)	178.56(9)	P(8)–Os(4)–N(15)	92.3(2)
P(5)–Os(3)–N(9)	88.8(2)	N(13)–Os(4)–N(15)	76.6(3)

Table S5. Redox potential at each pH of $[Re^{III}Cl_2(P^nPr_3)_2(H_2bim)]Cl$ for Pourbaix Diagram

pH	$E_c(Re^{II}/Re^{III})$	$E_c(Re^{III}/Re^{IV})$	$E_a(Re^{III}/Re^{IV})$	$E_{1/2}(Re^{III}/Re^{IV})$
2.4	-0.93	0.314	0.501	0.408
2.5	-0.928	0.306	0.497	0.402
2.61	-0.927	0.301	0.49	0.396
2.72	-0.926	0.293	0.489	0.391
2.8	-0.922	0.287	0.484	0.386
2.9	-0.919	0.283	0.472	0.378
3	-0.918	0.281	0.465	0.373
3.1	-0.91	0.276	0.461	0.369
3.19	-0.909	0.275	0.445	0.36
3.29	-0.907	0.272	0.438	0.355
3.39	-0.899	0.269	0.427	0.348
3.49	-0.906	0.261	0.419	0.34
3.6	-0.899	0.254	0.422	0.338
3.71	-0.901	0.25	0.414	0.332
3.79	-0.895	0.248	0.405	0.327
3.99	-0.9	0.241	0.394	0.318
4.09	-0.893	0.236	0.393	0.315
4.22	-0.898	0.227	0.384	0.306
4.32	-0.893	0.22	0.377	0.299
4.40	-0.897	0.214	0.369	0.292
4.53	-0.891	0.209	0.361	0.285
4.62	-0.894	0.205	0.361	0.283
4.71	-0.891	0.198	0.351	0.275
4.86	-0.894	0.194	0.344	0.269
4.99	-0.89	0.19	0.34	0.265
5.1	-0.895	0.184	0.33	0.257

[V] (*vs*. F_c/F_c^+)

Table S5 Redox potential at each pH of $[Re^{III}Cl_2(P^nPr_3)_2(H_2bim)]Cl$ for Pourbaix Diagram (*continued* 1)

pH	$E_c(Re^{II}/Re^{III})$	$E_c(Re^{III}/Re^{IV})$	$E_a(Re^{III}/Re^{IV})$	$E_{1/2}(Re^{III}/Re^{IV})$
5.29	-0.898	0.176	0.321	0.249
5.39	-0.898	0.171	0.309	0.24
5.49	-0.905	0.166	0.304	0.235
5.59	-0.922	0.16	0.333	0.247
5.7	-0.913	0.162	0.296	0.229
5.79	-0.928	0.157	0.297	0.227
5.9	-0.921	0.148	0.265	0.207
6.01	-0.947	0.152	0.243	0.198
6.13	-0.931	0.147	0.238	0.193
6.23	-0.957	0.14	0.237	0.189
6.32	-0.945	0.135	0.237	0.186
6.4	-1	0.128	0.227	0.178
6.51	-0.965	0.122	0.225	0.174
6.62	-0.983	0.117	0.199	0.158
6.72	-0.972	0.112	0.196	0.154
6.8	-0.983	0.107	0.193	0.15
6.94	-0.984	0.101	0.189	0.145
7	-0.99	0.091	0.184	0.138
7.12	-0.994	0.09	0.179	0.135
7.21	-1.006	0.085	0.175	0.13
7.3	-1.007	0.078	0.171	0.125
7.41	-1.014	0.071	0.165	0.118
7.5	-1.021	0.066	0.159	0.113
7.62	-1.028	0.06	0.153	0.107
7.7	-1.036	0.052	0.151	0.102

[V] (*vs*. F_c/F_c^+)

Table S5 Redox potential at each pH of $[Re^{III}Cl_2(P^nPr_3)_2(H_2bim)]Cl$ for Pourbaix Diagram (*continued* 2)

pH	$E_c(Re^{II}/Re^{III})$	$E_c(Re^{III}/Re^{IV})$	$E_a(Re^{III}/Re^{IV})$	$E_{1/2}(Re^{III}/Re^{IV})$
7.8	-1.043	0.049	0.143	0.096
7.9	-1.052	0.044	0.139	0.092
8	-1.059	0.037	0.131	0.084
8.13	-1.071	0.032	0.125	0.079
8.24	-1.078	0.026	0.12	0.073
8.35	-1.089	0.021	0.114	0.068
8.43	-1.093	0.012	0.103	0.058
8.69	-1.112	0.01	0.095	0.053
8.8	-1.12	0	0.085	0.043
9	-1.131	-0.006	0.074	0.034
9.15	-1.145	-0.01	0.064	0.027
9.22	-1.149	-0.016	0.059	0.022
9.38	-1.159	-0.022	0.054	0.016
9.44	-1.162	-0.028	0.049	0.011
9.57	-1.175	-0.034	0.051	0.009
9.72	-1.179	-0.046	0.029	-0.009
9.8	-1.189	-0.052	0.033	-0.010
9.92	-1.195	-0.054	0.022	-0.016
10.02	-1.203	-0.06	0.025	-0.018
10.12	-1.205	-0.067	0.019	-0.024
10.2	-1.217	-0.078	0.011	-0.034
10.3	-1.217	-0.081	0.004	-0.039
10.42	-1.23	-0.089	0.008	-0.041
10.5	-1.234	-0.092	0.001	-0.046
10.6	-1.246	-0.103	-0.005	-0.054

[V] (*vs*. F_c/F_c^+)

Table S5 Redox potential at each pH of $[Re^{III}Cl_2(P^nPr_3)_2(H_2bim)]Cl$ for Pourbaix Diagram (*continued* 3)

pH	$E_c(Re^{II}/Re^{III})$	$E_c(Re^{III}/Re^{IV})$	$E_a(Re^{III}/Re^{IV})$	$E_{1/2}(Re^{III}/Re^{IV})$
10.71	-1.249	-0.103	-0.015	-0.059
10.79	-1.265	-0.109	-0.023	-0.066
10.89	-1.262	-0.118	-0.026	-0.072
10.99	-1.286	-0.123	-0.031	-0.077
11.12	-1.286	-0.129	-0.036	-0.083
11.2	-1.31	-0.137	-0.045	-0.091
11.31	-1.321	-0.143	-0.047	-0.095
11.41	-1.321	-0.146	-0.05	-0.098
11.5	-1.339	-0.153	-0.059	-0.106
11.61	-1.345	-0.155	-0.062	-0.109
11.72	-1.356	-0.161	-0.064	-0.113
11.8	-1.367	-0.164	-0.066	-0.115
11.89	-1.367	-0.167	-0.068	-0.118
12.01	-1.369	-0.172	-0.069	-0.121

[V] (*vs*. F_c/F_c^+)