Supporting Information

Constructions of Metallamacrocycles Using Half-Sandwich Ru^{II}₂ Precursors: Synthesis,

Molecular Structures and Self-Selection for a Single Linkage Isomer

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Figure S1. Infra-red spectra of the macrocycles **2a-2b** and **3-5**.

Figure S2. ^1H NMR spectrum of tetranuclear molecular rectangle **2a** recorded in CD_3CN .

Figure S3. ^1H NMR spectrum of tetranuclear molecular tweezers **3** recorded in $\text{CD}_3\text{OD}-\text{CDCl}_3$.

Figure S4. ^1H NMR spectrum of binuclear macrocycle **4** recorded in CD_3OD .

Figure S5. ^1H NMR spectrum of binuclear macrocycle **5** recorded in CD_3OD .

Figure S6. ^{31}P NMR of binuclear macrocycle **5** recorded in CD_3OH .

Figure S7. ESI-MS spectra of macrocycle **2a** analyzed in acetonitrile and (inlet) the experimentally observed isotopic distribution for the peak $[2a^{2+}-2O_3SCF_3]^-$ ion.

Figure S8. ESI-MS spectra of macrocycle **2b** analyzed in acetonitrile and (inlet) the experimentally observed isotopic distribution for the peak $[2b^{2+}-2O_3SCF_3]^-$ ion.

Figure S9. ESI-MS spectra of macrocycle **3** analyzed in acetonitrile and (inlet) the experimentally observed isotopic distribution for the peak $[3^{2+}-2O_3SCF_3]^-$ ion.

Figure S10. ESI-MS spectra of macrocycle **4** analyzed in acetonitrile and (inset) the experimentally observed isotopic distribution for the peak $[4^+-\text{O}_3\text{SCF}_3]^-$ and $[4^{2+}-2\text{O}_3\text{SCF}_3]^-$ ion.

Figure S11. ESI-MS spectra of macrocycle **5** analyzed in acetonitrile and (inlet) the experimentally observed isotopic distribution for the peak $[5^+-\text{O}_3\text{SCF}_3]^-$ and $[5^{2+}-2\text{O}_3\text{SCF}_3]^-$ ion.

Figure S12. Solid state packing of **2a** viewed along crystallographic *b* axis (hydrogen atoms are removed for clarity).

Figure S13. Solid state packing of **2b** viewed along crystallographic *b* axis (hydrogen atoms are removed for clarity).

Figure S14. Solid state packing of **3** viewed along crystallographic *b* axis (hydrogen atoms are removed for clarity).

Figure S15. Solid state packing of **4** viewed along crystallographic *a*-axis (hydrogen atoms are removed for clarity).

Figure S16. Electronic absorption spectra of macrocycle **3** recorded in methanol (5.0×10^{-7} M).

Figure S17. Emission spectra of macrocycle **3** recorded in methanol (5.0×10^{-7} M).

Table S1: Selected Bonds Distances (Å) and Angles (°) for **2a** and **2b**.

2a					
Ru(1)-O(1)	2.105(7)	Ru(1)-O(2)	2.115(7)	Ru(1)-N(1)	2.136(8)
Ru(1)-C(28)	2.152(13)	Ru(1)-C(31)	2.178(13)	Ru(1)-C(32)	2.188(14)
Ru(1)-C(29)	2.193(15)	Ru(1)-C(27)	2.208(13)	Ru(1)-C(30)	2.216(14)
Ru(2)-O(4)	2.109(6)	Ru(2)-N(4)	2.108(9)	Ru(2)-O(3)	2.123(7)
Ru(2)-C(41)	2.151(12)	Ru(2)-C(42)	2.158(11)	Ru(2)-C(37)	2.176(10)
Ru(2)-C(40)	2.175(11)	Ru(2)-C(39)	2.176(10)	Ru(2)-C(38)	2.195(11)
O(1)-Ru(1)-O(2)	78.5(3)			O(1)-Ru(1)-N(1)	85.5(2)
O(2)-Ru(1)-N(1)	83.0(2)			O(1)-Ru(1)-C(28)	142.4(5)
O(2)-Ru(1)-C(28)	138.0(5)			N(1)-Ru(1)-C(28)	90.5(4)
O(1)-Ru(1)-C(31)	102.6(4)			O(2)-Ru(1)-C(31)	103.9(5)
N(1)-Ru(1)-C(31)	170.2(4)			C(28)-Ru(1)-C(31)	79.7(6)
O(1)-Ru(1)-C(32)	88.3(5)			O(2)-Ru(1)-C(32)	135.6(5)
N(1)-Ru(1)-C(32)	138.5(5)			C(28)-Ru(1)-C(32)	70.4(6)
C(31)-Ru(1)-C(32)	37.9(6)			O(1)-Ru(1)-C(29)	170.6(3)
O(2)-Ru(1)-C(29)	105.1(5)			N(1)-Ru(1)-C(29)	103.5(3)
C(28)-Ru(1)-C(29)	36.6(5)			C(31)-Ru(1)-C(29)	68.2(5)
C(32)-Ru(1)-C(29)	83.1(7)			O(1)-Ru(1)-C(27)	105.8(5)
O(2)-Ru(1)-C(27)	171.6(4)			N(1)-Ru(1)-C(27)	104.4(4)
C(28)-Ru(1)-C(27)	39.5(6)			C(31)-Ru(1)-C(27)	68.3(6)
C(32)-Ru(1)-C(27)	39.0(6)			C(29)-Ru(1)-C(27)	69.5(7)

O(1)-Ru(1)-C(30)	135.5(4)	O(2)-Ru(1)-C(30)	89.8(4)
N(1)-Ru(1)-C(30)	135.9(4)	C(28)-Ru(1)-C(30)	66.7(6)
C(31)-Ru(1)-C(30)	38.8(5)	C(32)-Ru(1)-C(30)	70.5(6)
C(29)-Ru(1)-C(30)	37.2(5)	C(27)-Ru(1)-C(30)	82.1(6)
O(4)-Ru(2)-N(4)	84.1(2)	O(4)-Ru(2)-O(3)	78.2(3)
N(4)-Ru(2)-O(3)	82.7(2)	O(4)-Ru(2)-C(41)	126.3(4)
N(4)-Ru(2)-C(41)	92.1(4)	O(3)-Ru(2)-C(41)	154.4(4)
O(4)-Ru(2)-C(42)	165.0(3)	N(4)-Ru(2)-C(42)	99.2(3)
O(3)-Ru(2)-C(42)	116.6(3)	C(41)-Ru(2)-C(42)	39.4(4)
O(4)-Ru(2)-C(37)	147.4(3)	N(4)-Ru(2)-C(37)	126.7(3)
O(3)-Ru(2)-C(37)	94.1(3)	C(41)-Ru(2)-C(37)	69.1(5)
C(42)-Ru(2)-C(37)	36.4(4)	O(4)-Ru(2)-C(40)	96.1(3)
N(4)-Ru(2)-C(40)	113.6(4)	O(3)-Ru(2)-C(40)	162.4(4)
C(41)-Ru(2)-C(40)	37.9(4)	C(42)-Ru(2)-C(40)	69.1(4)
C(37)-Ru(2)-C(40)	81.7(5)	O(4)-Ru(2)-C(39)	89.6(3)
N(4)-Ru(2)-C(39)	150.2(4)	O(3)-Ru(2)-C(39)	124.5(4)
C(41)-Ru(2)-C(39)	68.4(5)	C(42)-Ru(2)-C(39)	80.2(4)
C(37)-Ru(2)-C(39)	68.5(5)	C(40)-Ru(2)-C(39)	38.1(5)
O(4)-Ru(2)-C(38)	110.4(3)	N(4)-Ru(2)-C(38)	165.4(3)
O(3)-Ru(2)-C(38)	98.4(3)	C(41)-Ru(2)-C(38)	80.7(5)
C(42)-Ru(2)-C(38)	67.2(5)	C(37)-Ru(2)-C(38)	38.7(4)
C(40)-Ru(2)-C(38)	67.6(5)	C(39)-Ru(2)-C(38)	36.6(4)

Ru(1)-O(2)	2.061(15)	Ru(1)-N(1)	2.107(17)	Ru(1)-C(40)	2.09(4)
Ru(1)-O(2)	2.086(6)	Ru(1)-O(1)	2.099(7)	Ru(1)-N(1)	2.111(7)
Ru(1)-C(27)	2.138(10)	Ru(1)-C(30)	2.152(11)	Ru(1)-C(29)	2.152(12)
Ru(1)-C(26)	2.164(11)	Ru(1)-C(28)	2.188(11)	Ru(1)-C(40)	2.194(12)
Ru(2)-O(3)	2.073(6)	Ru(2)-O(4)	2.095(6)	Ru(2)-N(2)	2.130(8)
Ru(2)-C(25)	2.147(11)	Ru(2)-C(21)	2.150(11)	Ru(2)-C(35)	2.188(11)
Ru(2)-C(22)	2.184(12)	Ru(2)-C(24)	2.174(12)	Ru(2)-C(20)	2.153(11)
O(2)-Ru(1)-O(1)	77.2(2)			O(2)-Ru(1)-N(1)	86.6(3)
O(1)-Ru(1)-N(1)	82.5(3)			O(2)-Ru(1)-C(27)	90.7(3)
O(1)-Ru(1)-C(27)	139.6(4)			N(1)-Ru(1)-C(27)	135.8(4)
O(2)-Ru(1)-C(30)	167.6(5)			O(1)-Ru(1)-C(30)	104.6(5)
N(1)-Ru(1)-C(30)	105.8(5)			C(27)-Ru(1)-C(30)	80.0(5)
O(2)-Ru(1)-C(29)	144.1(5)			O(1)-Ru(1)-C(29)	137.5(4)
N(1)-Ru(1)-C(29)	89.6(4)			C(27)-Ru(1)-C(29)	67.9(4)
C(30)-Ru(1)-C(29)	38.1(5)			O(2)-Ru(1)-C(26)	100.6(4)
O(1)-Ru(1)-C(26)	105.2(4)			N(1)-Ru(1)-C(26)	170.4(4)
C(27)-Ru(1)-C(26)	38.7(4)			C(30)-Ru(1)-C(26)	67.1(5)
C(29)-Ru(1)-C(26)	80.9(5)			O(2)-Ru(1)-C(28)	108.4(4)
O(1)-Ru(1)-C(28)	172.9(4)			N(1)-Ru(1)-C(28)	101.8(4)
C(27)-Ru(1)-C(28)	38.2(4)			C(30)-Ru(1)-C(28)	68.9(6)
C(29)-Ru(1)-C(28)	38.0(5)			C(26)-Ru(1)-C(28)	70.0(5)
O(2)-Ru(1)-C(40)	130.3(5)			O(1)-Ru(1)-C(40)	91.2(5)
N(1)-Ru(1)-C(40)	140.3(5)			C(27)-Ru(1)-C(40)	67.3(5)

C(30)-Ru(1)-C(40)	38.2(5)	C(29)-Ru(1)-C(40)	69.0(6)
C(26)-Ru(1)-C(40)	35.9(5)	C(28)-Ru(1)-C(40)	81.9(6)
O(3)-Ru(2)-O(4)	76.3(3)	O(3)-Ru(2)-N(2)	85.4(3)
O(4)-Ru(2)-N(2)	85.3(3)	O(3)-Ru(2)-C(25)	91.9(4)
O(4)-Ru(2)-C(25)	144.4(5)	N(2)-Ru(2)-C(25)	127.7(5)
O(3)-Ru(2)-C(21)	160.2(5)	O(4)-Ru(2)-C(21)	99.4(4)
N(2)-Ru(2)-C(21)	113.7(5)	C(25)-Ru(2)-C(21)	80.4(5)
O(3)-Ru(2)-C(35)	115.6(5)	O(4)-Ru(2)-C(35)	167.4(4)
N(2)-Ru(2)-C(35)	99.3(4)	C(25)-Ru(2)-C(35)	37.0(5)
C(21)-Ru(2)-C(35)	68.0(5)	O(3)-Ru(2)-C(22)	122.6(6)
O(4)-Ru(2)-C(22)	89.9(4)	N(2)-Ru(2)-C(22)	149.5(6)
C(25)-Ru(2)-C(22)	68.2(6)	C(21)-Ru(2)-C(22)	37.6(5)
C(35)-Ru(2)-C(22)	80.2(4)	O(3)-Ru(2)-C(24)	95.3(5)
O(4)-Ru(2)-C(24)	108.0(4)	N(2)-Ru(2)-C(24)	166.4(5)
C(25)-Ru(2)-C(24)	38.8(5)	C(21)-Ru(2)-C(24)	67.3(6)
C(35)-Ru(2)-C(24)	68.2(5)	C(22)-Ru(2)-C(24)	36.8(5)
O(3)-Ru(2)-C(20)	152.5(5)	O(4)-Ru(2)-C(20)	131.1(5)
N(2)-Ru(2)-C(20)	93.8(4)	C(25)-Ru(2)-C(20)	67.0(5)
C(21)-Ru(2)-C(20)	37.3(5)	C(35)-Ru(2)-C(20)	37.4(5)
C(22)-Ru(2)-C(20)	67.2(5)	C(24)-Ru(2)-C(20)	79.4(5)

Table S2: Selected Bonds Distances (Å) and Angles (°) for **3**.

3					
Ru(3)-C(56)	2.07(3)	Ru(3)-N(1)	2.073(19)	Ru(3)-O(3)	2.102(13)
Ru(3)-C(55)	2.10(3)	Ru(3)-O(4)	2.136(14)	Ru(3)-C(60)	2.15(3)
Ru(3)-C(57)	2.14(3)	Ru(3)-C(59)	2.17(3)	Ru(3)-C(58)	2.17(3)
C(56)-Ru(3)-N(1)	92.6(10)			C(56)-Ru(3)-O(3)	156.5(18)
N(1)-Ru(3)-O(3)	83.8(6)			C(56)-Ru(3)-C(55)	38.9(13)
N(1)-Ru(3)-C(55)	115.9(15)			O(3)-Ru(3)-C(55)	158.4(15)
C(56)-Ru(3)-O(4)	124.5(17)			N(1)-Ru(3)-O(4)	84.3(7)
O(3)-Ru(3)-O(4)	78.4(5)			C(55)-Ru(3)-O(4)	94.2(12)
C(56)-Ru(3)-C(60)	68.0(13)			N(1)-Ru(3)-C(60)	153.3(16)
O(3)-Ru(3)-C(60)	121.3(14)			C(55)-Ru(3)-C(60)	37.9(12)
O(4)-Ru(3)-C(60)	91.7(9)			C(56)-Ru(3)-C(57)	38.3(13)
N(1)-Ru(3)-C(57)	98.4(15)			O(3)-Ru(3)-C(57)	119.2(13)
C(55)-Ru(3)-C(57)	68.9(13)			O(4)-Ru(3)-C(57)	162.4(12)
C(60)-Ru(3)-C(57)	78.1(12)			C(56)-Ru(3)-C(59)	79.2(12)
N(1)-Ru(3)-C(59)	159.0(13)			O(3)-Ru(3)-C(59)	96.0(11)
C(55)-Ru(3)-C(59)	68.9(12)			O(4)-Ru(3)-C(59)	116.3(10)

C(60)-Ru(3)-C(59)	38.4(11)	C(57)-Ru(3)-C(59)	63.4(15)
C(56)-Ru(3)-C(58)	68.6(13)	N(1)-Ru(3)-C(58)	125.4(15)
O(3)-Ru(3)-C(58)	94.7(10)	C(55)-Ru(3)-C(58)	81.2(12)
O(4)-Ru(3)-C(58)	149.0(13)	C(60)-Ru(3)-C(58)	65.9(13)
C(57)-Ru(3)-C(58)	36.8(14)	C(59)-Ru(3)-C(58)	33.6(11)

Table S3: Selected Bonds Distances (Å) and Bond Angles (°) for **4** and **5**.

4

Ru(3)-C(56)	2.07(3)	Ru(3)-N(1)	2.073(19)	Ru(3)-O(3)	2.102(13)
C(45)-Ru(3)	2.17(3)	N(4)-Ru(3)	2.143(18)	C(44)-Ru(3)	2.17(3)
C(46)-Ru(3)	2.16(3)	C(43)-Ru(3)	2.13(2)	C(41)-Ru(3)	2.16(2)
Ru(3)-O(8)	2.092(14)	Ru(3)-O(7)	2.140(16)	Ru(3)-C(42)	2.19(2)
C(46)-C(45)-Ru(3)	71.4(16)			C(44)-C(45)-Ru(3)	70.9(15)
C(43)-C(44)-Ru(3)	69.4(14)			C(45)-C(44)-Ru(3)	70.7(15)
C(49)-C(44)-Ru(3)	130.5(12)			C(45)-C(46)-Ru(3)	72.2(18)
C(41)-C(46)-Ru(3)	71.1(14)			C(42)-C(43)-Ru(3)	74.2(10)
C(44)-C(43)-Ru(3)	72.4(14)			C(46)-C(41)-Ru(3)	71.0(16)
C(42)-C(41)-Ru(3)	71.9(9)			C(47)-C(41)-Ru(3)	127.0(14)

C(30)-N(4)-Ru(3)	123.3(12)	C(26)-N(4)-Ru(3)	120.2(12)
O(5)-Ru(1)-N(3)	86.6(7)	O(8)-Ru(3)-O(7)	77.1(6)
O(8)-Ru(3)-N(4)	84.4(5)	O(7)-Ru(3)-N(4)	84.2(5)
O(8)-Ru(3)-C(43)	90.4(6)	O(7)-Ru(3)-C(43)	129.6(6)
N(4)-Ru(3)-C(43)	143.7(8)	O(8)-Ru(3)-C(41)	141.4(7)
O(7)-Ru(3)-C(41)	92.4(7)	N(4)-Ru(3)-C(41)	131.9(9)
C(43)-Ru(3)-C(41)	67.8(10)	O(8)-Ru(3)-C(46)	167.5(9)
O(7)-Ru(3)-C(46)	114.3(9)	N(4)-Ru(3)-C(46)	101.3(9)
C(43)-Ru(3)-C(46)	78.3(11)	C(41)-Ru(3)-C(46)	37.9(9)
O(8)-Ru(3)-C(44)	99.8(6)	O(7)-Ru(3)-C(44)	167.9(7)
N(4)-Ru(3)-C(44)	107.4(8)	C(43)-Ru(3)-C(44)	38.3(8)
C(41)-Ru(3)-C(44)	82.8(9)	C(46)-Ru(3)-C(44)	68.0(11)
O(8)-Ru(3)-C(45)	133.5(7)	O(7)-Ru(3)-C(45)	148.4(7)
N(4)-Ru(3)-C(45)	90.7(8)	C(43)-Ru(3)-C(45)	67.3(9)
C(41)-Ru(3)-C(45)	68.2(10)	C(46)-Ru(3)-C(45)	36.4(9)
C(44)-Ru(3)-C(45)	38.4(9)	O(8)-Ru(3)-C(42)	106.9(8)
O(7)-Ru(3)-C(42)	101.3(7)	N(4)-Ru(3)-C(42)	168.2(6)

C(43)-Ru(3)-C(42)	36.1(7)	C(41)-Ru(3)-C(42)	38.3(7)
C(46)-Ru(3)-C(42)	67.0(7)	C(44)-Ru(3)-C(42)	68.1(6)
C(45)-Ru(3)-C(42)	79.1(7)		

5

Ru(3)-C(56)	2.07(3)	Ru(3)-N(1)	2.073(19)	Ru(3)-O(3)	2.102(13)
Ru(1)-O(1)	2.093(9)	Ru(1)-O(2)	2.157(10)	Ru(1)-C(39)	2.221(3)
Ru(1)-C(44)	2.224(3)	Ru(1)-C(40)	2.237(2)	Ru(1)-C(41)	2.2333(15)
Ru(1)-C(43)	2.255(3)	Ru(1)-C(42)	2.283(3)	Ru(1)-P(1)	2.381(4)
O(1)-Ru(1)-O(2)	77.5(4)	O(1)-Ru(1)-C(39)	161.5(3)		
O(2)-Ru(1)-C(39)	97.6(3)	O(1)-Ru(1)-C(44)	153.6(3)		
O(2)-Ru(1)-C(44)	128.4(3)	C(39)-Ru(1)-C(44)	37.64(5)		
O(1)-Ru(1)-C(40)	123.0(3)	O(2)-Ru(1)-C(40)	88.4(3)		
C(39)-Ru(1)-C(40)	38.51(4)	C(44)-Ru(1)-C(40)	69.07(8)		
O(1)-Ru(1)-C(41)	95.3(3)	O(2)-Ru(1)-C(41)	108.2(3)		
C(39)-Ru(1)-C(41)	68.99(6)	C(44)-Ru(1)-C(41)	82.04(8)		
C(40)-Ru(1)-C(41)	37.84(3)	O(1)-Ru(1)-C(43)	113.2(3)		
O(2)-Ru(1)-C(43)	169.1(3)	C(39)-Ru(1)-C(43)	71.55(8)		
C(44)-Ru(1)-C(43)	41.28(5)	C(40)-Ru(1)-C(43)	83.68(8)		

C(41)-Ru(1)-C(43)	69.61(7)	O(1)-Ru(1)-C(42)	89.0(3)
O(2)-Ru(1)-C(42)	142.4(3)	C(39)-Ru(1)-C(42)	84.21(8)
C(44)-Ru(1)-C(42)	72.81(8)	C(40)-Ru(1)-C(42)	69.72(5)
C(41)-Ru(1)-C(42)	37.65(4)	C(43)-Ru(1)-C(42)	40.12(5)
O(1)-Ru(1)-P(1)	85.2(3)	O(2)-Ru(1)-P(1)	88.5(3)
C(39)-Ru(1)-P(1)	112.73(10)	C(44)-Ru(1)-P(1)	90.00(9)
C(40)-Ru(1)-P(1)	150.07(11)	C(41)-Ru(1)-P(1)	163.11(12)
C(43)-Ru(1)-P(1)	94.62(9)	C(42)-Ru(1)-P(1)	125.64(10)