Supporting Information

for

Synthesis and Photophysical Properties of Neutral Luminescent Rhenium-Based Molecular Rectangles

T. Rajendran,[†] Bala. Manimaran,[†] Rong-Tang Liao,[†] Ren-Jay Lin,[§] P. Thanasekaran,[†] Gene-Hsiang Lee,[¶] Shie-Ming Peng,[¶] Yen-Hsiang Liu,[†] I-Jy Chang,[*,§] S. Rajagopal,[*,†,‡] and Kuang-Lieh Lu[*,†]

[†]*Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan*

[§]*Department of Chemistry, National Taiwan Normal University, Taipei 117, Taiwan*

[¶]*Department of Chemistry, National Taiwan University, Taipei 107, Taiwan*

[‡]*School of Chemistry, Madurai Kamaraj University, Madurai, 625 021, India*

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Table T1. Crystal Data and Structure Refinement for **1**.

Identification code	ic6486
Empirical formula	$C_{58}H_{60}Br_4N_8O_{18}Re_4$
Formula weight	2221.58
Temperature	150(1) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.0890(2) Å alpha = 90° b = 24.2982(2) Å beta = 107.923(1)° c = 12.8721(2) Å gamma = 90°
Volume, Z	3597.57(9) $Å^3$, 2
Density (calculated)	2.051 Mg/m^3
Absorption coefficient	8.998 mm^{-1}
F(000)	2096
Crystal size	0.35 x 0.18 x 0.12 mm
θ range for data collection	1.68 to 26.37°
Limiting indices	$-15 \le h \le 14$, $-30 \le k \le 30$, $-11 \le l \le 16$
Reflections collected	18370
Independent reflections	7285 (R_{int} = 0.0402)
Absorption correction	empirical used sadabs
Max. and min. transmission	0.4921 and 0.2767
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7285 / 0 / 451
Goodness-of-fit on F^2	1.174
Final R indices [I>2σ(I)]	R1 = 0.0356, wR2 = 0.0693
R indices (all data)	R1 = 0.0488, wR2 = 0.0724
Extinction coefficient	0.00040(4)
Largest diff. peak and hole	1.195 and -0.838 $eÅ^{-3}$

Table T2. Atomic Positional Parameters for **1**.

Table Atomic coordinates [x 10^4] and equivalent isotropi displacement parameters [$Å^2$ x 10^3] for 6486. U(eq) is defined a one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Re(1)	533(1)	-2631(1)	-1061(1)	20(1)
Re(2)	3246(1)	-552(1)	-3458(1)	19(1)
Br(1)	-1130(1)	-2603(1)	-2872(1)	28(1)
Br(2)	5132(1)	-662(1)	-1838(1)	32(1)
C(3)	1824(23)	-2645(13)	251(22)	53(8)
O(3)	2658(10)	-2629(7)	1002(12)	50(4)
C(6)	1832(12)	-489(7)	-4646(14)	28(3)
O(6)	1002(12)	-430(7)	-5400(11)	48(5)
Br(1')	2205(5)	-2596(3)	646(5)	35(2)
Br(2')	1343(5)	-450(2)	-5005(4)	30(2)
C(3')	-606(34)	-2634(13)	-2377(34)	51(9)
O(3')	-1490(26)	-2681(12)	-3273(28)	67(11)
C(6')	4639(27)	-618(11)	-2418(29)	38(7)
O(6')	5639(23)	-687(10)	-1545(22)	50(8)
N(1)	1407(4)	-1996(2)	-1758(4)	20(1)
N(2)	2456(4)	-1196(2)	-2698(4)	18(1)
N(3)	-277(4)	-1919(2)	-493(4)	22(1)
N(4)	2561(4)	-3(2)	-2422(4)	21(1)
C(1)	-245(5)	-3166(3)	-424(6)	31(2)
C(2)	1248(5)	-3236(2)	-1576(5)	26(1)
C(4)	3800(5)	-1052(2)	-4341(5)	27(1)
C(5)	3949(5)	44(3)	-4014(5)	30(1)
C(7)	2530(5)	-2016(2)	-1686(5)	23(1)
C(8)	3054(5)	-1623(2)	-2150(5)	23(1)
C(9)	1326(5)	-1167(2)	-2755(5)	24(1)
C(10)	815(5)	-1557(2)	-2290(5)	23(1)
C(11)	406(5)	-1543(2)	186(5)	30(2)
C(12)	-54(5)	-1144(2)	688(6)	31(2)
C(13)	-1235(5)	-1099(2)	487(5)	22(1)
C(14)	-1944(5)	-1456(2)	-263(5)	26(1)
C(15)	-1439(5)	-1858(2)	-719(5)	22(1)
C(16)	1874(5)	424(2)	-2862(5)	29(1)
C(17)	1424(5)	778(2)	-2263(5)	31(2)
C(18)	1699(5)	708(2)	-1134(5)	23(1)
C(19)	2402(5)	260(2)	-678(5)	26(1)
C(20)	2806(5)	-83(2)	-1345(5)	27(1)
O(1)	-706(4)	-3489(2)	-55(4)	40(1)
O(2)	1685(4)	-3598(2)	-1875(4)	40(1)
O(4)	4140(4)	-1347(2)	-4875(4)	43(1)
O(5)	4375(4)	404(2)	-4327(4)	43(1)
O(7)	751(6)	461(4)	2052(8)	121(3)
O(8)	6861(4)	1164(3)	-377(5)	69(2)
O(9)	14715(8)	2664(4)	6140(12)	201(7)
C(21)	1758(7)	437(4)	2606(7)	58(2)
C(22)	2448(8)	-76(3)	2613(9)	71(3)
C(23)	2359(9)	883(4)	3271(9)	86(3)
C(24)	6019(6)	1186(3)	-1176(6)	39(2)
C(25)	4884(7)	944(4)	-1161(8)	75(3)
C(26)	6028(7)	1449(4)	-2211(7)	58(2)
C(27)	14221(7)	2410(4)	5347(14)	98(5)
C(28)	13445(6)	1950(3)	5412(8)	63(3)
C(29)	14393(10)	2499(7)	4296(16)	195(12)

Table T3. Bond Lengths (Å) and Angles (°) for **1**.

Re(1)-C(3')	1.83(4)	Re(1)-C(3)	1.92(2)
Re(1)-C(2)	1.922(6)	Re(1)-C(1)	1.929(7)
Re(1)-N(1)	2.212(5)	Re(1)-N(3)	2.221(5)
Re(1)-Br(1')	2.487(5)	Re(1)-Br(1)	2.5694(14)
Re(2)-C(6')	1.81(4)	Re(2)-C(6)	1.917(14)
Re(2)-C(4)	1.919(6)	Re(2)-C(5)	1.924(7)
Re(2)-N(2)	2.212(4)	Re(2)-N(4)	2.218(5)
Re(2)-Br(2')	2.549(5)	Re(2)-Br(2)	2.5873(13)
C(3)-O(3)	1.16(3)	C(6)-O(6)	1.17(2)
C(3')-O(3')	1.31(5)	C(6')-O(6')	1.38(4)
N(1)-C(7)	1.332(7)	N(1)-C(10)	1.347(7)
N(2)-C(8)	1.337(7)	N(2)-C(9)	1.346(7)
N(3)-C(15)	1.352(7)	N(3)-C(11)	1.354(7)
N(4)-C(20)	1.340(8)	N(4)-C(16)	1.340(7)
C(1)-O(1)	1.146(7)	C(2)-O(2)	1.153(7)
C(4)-O(4)	1.153(7)	C(5)-O(5)	1.149(7)
C(7)-C(8)	1.380(8)	C(9)-C(10)	1.366(8)
C(11)-C(12)	1.376(8)	C(12)-C(13)	1.375(8)
C(13)-C(14)	1.381(8)	C(13)-C(18)#1	1.484(8)
C(14)-C(15)	1.376(8)	C(16)-C(17)	1.374(8)
C(17)-C(18)	1.398(9)	C(18)-C(19)	1.395(8)
C(18)-C(13)#1	1.483(8)	C(19)-C(20)	1.387(8)
O(7)-C(21)	1.208(10)	O(8)-C(24)	1.205(8)
O(9)-C(27)	1.18(2)	C(21)-C(23)	1.432(12)
C(21)-C(22)	1.498(11)	C(24)-C(26)	1.480(11)
C(24)-C(25)	1.498(10)	C(27)-C(29)	1.45(2)
C(27)-C(28)	1.479(12)		

C(3')-Re(1)-C(2)	88.2(11)	C(3)-Re(1)-C(2)	87.7(10)
C(3')-Re(1)-C(1)	93.7(11)	C(3)-Re(1)-C(1)	89.1(10)
C(2)-Re(1)-C(1)	87.8(3)	C(3')-Re(1)-N(1)	86.8(11)
C(3)-Re(1)-N(1)	90.5(10)	C(2)-Re(1)-N(1)	94.1(2)
C(1)-Re(1)-N(1)	178.0(2)	C(3')-Re(1)-N(3)	91.4(11)
C(3)-Re(1)-N(3)	92.6(10)	C(2)-Re(1)-N(3)	178.6(2)
C(1)-Re(1)-N(3)	93.6(2)	N(1)-Re(1)-N(3)	84.5(2)
C(3')-Re(1)-Br(1')	174.9(11)	C(2)-Re(1)-Br(1')	90.1(2)
C(1)-Re(1)-Br(1')	91.0(3)	N(1)-Re(1)-Br(1')	88.6(2)
N(3)-Re(1)-Br(1')	90.2(2)	C(3)-Re(1)-Br(1)	177.3(10)
C(2)-Re(1)-Br(1)	90.9(2)	C(1)-Re(1)-Br(1)	93.2(2)
N(1)-Re(1)-Br(1)	87.21(12)	N(3)-Re(1)-Br(1)	88.67(12)
C(6')-Re(2)-C(4)	88.1(9)	C(6)-Re(2)-C(4)	88.1(6)
C(6')-Re(2)-C(5)	85.7(9)	C(6)-Re(2)-C(5)	91.8(6)
C(4)-Re(2)-C(5)	88.9(3)	C(6')-Re(2)-N(2)	92.3(9)
C(6)-Re(2)-N(2)	90.5(5)	C(4)-Re(2)-N(2)	95.3(2)
C(5)-Re(2)-N(2)	175.3(2)	C(6')-Re(2)-N(4)	92.5(9)
C(6)-Re(2)-N(4)	91.5(5)	C(4)-Re(2)-N(4)	177.6(2)
C(5)-Re(2)-N(4)	93.5(2)	N(2)-Re(2)-N(4)	82.4(2)
C(6')-Re(2)-Br(2')	176.7(10)	C(4)-Re(2)-Br(2')	89.7(2)
C(5)-Re(2)-Br(2')	91.9(2)	N(2)-Re(2)-Br(2')	90.3(2)
N(4)-Re(2)-Br(2')	89.8(2)	C(6)-Re(2)-Br(2)	178.4(5)
C(4)-Re(2)-Br(2)	91.8(2)	C(5)-Re(2)-Br(2)	89.8(2)
N(2)-Re(2)-Br(2)	87.91(11)	N(4)-Re(2)-Br(2)	88.65(12)
O(3)-C(3)-Re(1)	174(3)	O(6)-C(6)-Re(2)	176(2)
O(3')-C(3')-Re(1)	173(3)	O(6')-C(6')-Re(2)	174(2)
C(7)-N(1)-C(10)	115.8(5)	C(7)-N(1)-Re(1)	123.3(4)
C(10)-N(1)-Re(1)	120.9(4)	C(8)-N(2)-C(9)	116.4(5)
C(8)-N(2)-Re(2)	123.1(4)	C(9)-N(2)-Re(2)	120.5(4)
C(15)-N(3)-C(11)	116.9(5)	C(15)-N(3)-Re(1)	123.3(4)
C(11)-N(3)-Re(1)	119.6(4)	C(20)-N(4)-C(16)	117.3(5)

C(20)-N(4)-Re(2)	122.1(4)	C(16)-N(4)-Re(2)	120.6(4)
O(1)-C(1)-Re(1)	179.0(6)	O(2)-C(2)-Re(1)	179.3(5)
O(4)-C(4)-Re(2)	179.2(5)	O(5)-C(5)-Re(2)	178.8(6)
N(1)-C(7)-C(8)	122.5(5)	N(2)-C(8)-C(7)	121.3(5)
N(2)-C(9)-C(10)	121.9(5)	N(1)-C(10)-C(9)	122.0(5)
N(3)-C(11)-C(12)	121.6(5)	C(13)-C(12)-C(11)	120.9(5)
C(12)-C(13)-C(14)	117.9(5)	C(12)-C(13)-C(18)#1	119.6(5)
C(14)-C(13)-C(18)#1	122.3(5)	C(15)-C(14)-C(13)	118.9(5)
N(3)-C(15)-C(14)	123.6(5)	N(4)-C(16)-C(17)	123.3(6)
C(16)-C(17)-C(18)	119.9(5)	C(19)-C(18)-C(17)	116.9(5)
C(19)-C(18)-C(13)#1	123.4(6)	C(17)-C(18)-C(13)#1	119.7(5)
C(20)-C(19)-C(18)	119.5(6)	N(4)-C(20)-C(19)	123.1(5)
O(7)-C(21)-C(23)	123.3(9)	O(7)-C(21)-C(22)	120.2(9)
C(23)-C(21)-C(22)	116.5(8)	O(8)-C(24)-C(26)	123.3(7)
O(8)-C(24)-C(25)	120.5(8)	C(26)-C(24)-C(25)	116.2(7)
O(9)-C(27)-C(29)	123.3(13)	O(9)-C(27)-C(28)	120(2)
C(29)-C(27)-C(28)	116.2(13)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Table T4. Anisotropic Thermal Parameters [$Å^2 \times 10^3$] for **1**.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Re(1)	24(1)	17(1)	22(1)	0(1)	12(1)	2(1)
Re(2)	23(1)	18(1)	20(1)	0(1)	10(1)	1(1)
Br(1)	31(1)	27(1)	25(1)	-5(1)	6(1)	1(1)
Br(2)	24(1)	35(1)	34(1)	4(1)	4(1)	0(1)
C(3)	60(18)	28(8)	91(24)	3(14)	54(14)	-1(11)
O(3)	43(8)	47(6)	54(9)	6(6)	9(6)	6(6)
C(6)	43(9)	25(5)	20(10)	0(6)	15(8)	0(7)
O(6)	49(9)	59(6)	29(9)	9(6)	3(6)	8(5)
Br(1')	42(5)	30(2)	38(5)	6(3)	21(3)	5(4)
Br(2')	36(4)	31(2)	24(5)	1(3)	9(3)	1(3)
N(1)	25(2)	19(2)	15(3)	1(2)	6(2)	0(2)
N(2)	21(2)	16(2)	19(3)	-2(2)	8(2)	0(2)
N(3)	22(2)	24(2)	22(3)	1(2)	9(2)	2(2)
N(4)	24(2)	18(2)	20(3)	0(2)	4(2)	2(2)
C(1)	29(3)	29(3)	39(4)	-2(3)	15(3)	6(3)
C(2)	25(3)	28(3)	25(4)	1(3)	7(3)	-3(2)
C(4)	32(3)	25(3)	24(4)	-2(3)	9(3)	-1(2)
C(5)	32(3)	29(3)	25(4)	2(3)	7(3)	6(3)
C(7)	24(3)	21(3)	24(3)	3(3)	8(3)	5(2)
C(8)	22(3)	24(3)	23(3)	4(3)	7(3)	2(2)
C(9)	24(3)	21(3)	27(4)	4(3)	6(3)	4(2)
C(10)	20(3)	24(3)	26(3)	0(3)	7(2)	5(2)
C(11)	22(3)	36(3)	35(4)	-10(3)	12(3)	-2(3)
C(12)	24(3)	28(3)	39(4)	-14(3)	8(3)	-5(2)
C(13)	32(3)	19(3)	19(3)	0(2)	13(3)	3(2)
C(14)	22(3)	34(3)	25(4)	1(3)	12(3)	6(2)
C(15)	22(3)	27(3)	17(3)	-2(2)	5(2)	-4(2)
C(16)	43(4)	27(3)	19(3)	2(3)	11(3)	11(3)
C(17)	41(4)	29(3)	22(4)	3(3)	9(3)	19(3)
C(18)	22(3)	20(3)	27(4)	-2(2)	9(3)	-1(2)
C(19)	33(3)	29(3)	16(3)	1(3)	7(3)	7(3)
C(20)	33(3)	25(3)	21(4)	4(3)	6(3)	8(2)
O(1)	47(3)	31(2)	53(3)	11(2)	31(3)	-2(2)
O(2)	51(3)	28(2)	47(3)	-8(2)	22(2)	12(2)
O(4)	50(3)	40(3)	48(3)	-8(2)	29(3)	6(2)
O(5)	49(3)	37(3)	48(3)	12(2)	22(2)	-11(2)
O(7)	60(4)	147(8)	131(8)	15(6)	-8(5)	22(5)
O(8)	36(3)	107(5)	51(4)	19(4)	-6(3)	-8(3)
O(9)	97(7)	94(7)	327(18)	-44(9)	-59(9)	-48(5)
C(21)	44(5)	75(6)	50(6)	14(5)	9(4)	8(4)
C(22)	70(6)	49(5)	107(9)	6(5)	47(6)	-6(4)
C(23)	85(7)	95(8)	64(7)	-13(6)	2(6)	35(6)
C(24)	36(4)	36(4)	44(5)	1(3)	11(3)	-2(3)
C(25)	52(5)	96(7)	74(7)	8(6)	17(5)	-34(5)
C(26)	50(5)	84(6)	46(5)	-7(5)	23(4)	-13(4)
C(27)	27(4)	52(6)	187(14)	15(7)	-9(6)	3(4)
C(28)	43(4)	51(5)	88(8)	3(5)	11(5)	-1(4)
C(29)	61(7)	240(18)	297(24)	239(19)	72(11)	54(9)

Table T5. Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(7A)	2987(5)	-2313(2)	-1300(5)	28
H(8A)	3857(5)	-1658(2)	-2079(5)	28
H(9A)	872(5)	-867(2)	-3130(5)	29
H(10A)	18(5)	-1518(2)	-2344(5)	28
H(11A)	1223(5)	-1556(2)	317(5)	36
H(12A)	451(5)	-895(2)	1182(6)	37
H(14A)	-2766(5)	-1424(2)	-459(5)	31
H(15A)	-1935(5)	-2106(2)	-1221(5)	27
H(16A)	1688(5)	484(2)	-3626(5)	35
H(17A)	928(5)	1070(2)	-2616(5)	37
H(19A)	2603(5)	189(2)	83(5)	32
H(20A)	3278(5)	-388(2)	-1023(5)	32
H(22A)	1953(8)	-351(3)	2133(9)	106
H(22B)	2733(8)	-221(3)	3358(9)	106
H(22C)	3110(8)	10(3)	2352(9)	106
H(23A)	1827(9)	1194(4)	3204(9)	129
H(23B)	3019(9)	995(4)	3029(9)	129
H(23C)	2642(9)	764(4)	4035(9)	129
H(25A)	4974(7)	782(4)	-443(8)	112
H(25B)	4643(7)	658(4)	-1723(8)	112
H(25C)	4292(7)	1234(4)	-1308(8)	112
H(26A)	6807(7)	1592(4)	-2132(7)	87
H(26B)	5466(7)	1751(4)	-2385(7)	87
H(26C)	5817(7)	1176(4)	-2801(7)	87
H(28A)	13389(6)	1927(3)	6155(8)	94
H(28B)	13760(6)	1605(3)	5230(8)	94
H(28C)	12670(6)	2014(3)	4896(8)	94
H(29A)	14919(10)	2811(7)	4345(16)	293
H(29B)	13644(10)	2577(7)	3749(16)	293
H(29C)	14734(10)	2168(7)	4083(16)	293

Table T6. Luminescence Quenching Rate Constants of Molecular Rectangles **2**, **3** and **4** with Electron Donors and Acceptors at 298 K

Quencher	E_{red} and E_{ox}	k_q, $M^{-1}s^{-1}$		
		2	**3**	**4**
4-fluoronitrobenzene	– 1.13	5.1×10^9	1.9×10^9	3.0×10^7
2,4-dinitrotoluene	–1.00	6.0×10^9	1.7×10^9	1.3×10^9
1,3-dinitrobenzene	– 0.90	6.8×10^9	6.3×10^8	8.6×10^8
1,4-naphthaquinone	–0.68	3.8×10^{10}	9.2×10^9	7.6×10^9
1,4-benzoquinone	– 0.50	6.6×10^9	2.8×10^9	9.6×10^9
tetracyanoquinodimethane	– 0.30	2.1×10^{11}	6.2×10^{11}	1.5×10^{11}
1,2-chloranil	0.0	2.2×10^{10}	1.8×10^{10}	1.7×10^{10}
N,N-diethylaniline	0.72	8.1×10^9	1.5×10^{10}	5.6×10^9
1,4-phenylenediamine	0.18	2.0×10^{10}	2.2×10^{10}	2.1×10^{10}

```
[ Theoretical Ion Distribution ]
Molecular Formula : Re2 Br2 H8 N2 O8 C18
                    (m/z   911.7763, MW   912.4921, U.S. 16.0)
Base Peak :   911.7724, Averaged MW :   912.4909(a),   912.4954(w)

    m/z       INT.
  907.7707    9.5612 ******
  908.7739    2.0250 *
  909.7717   50.9657 ******************************
  910.7749   10.7641 ******
  911.7724  100.0000 ************************************************************
  912.7755   21.0189 ************
  913.7727   86.0918 ************************************************
  914.7757   17.9204 **********
  915.7728   28.4754 *****************
  916.7757    5.7642 ***
  917.7778    0.9892 *
  918.7803    0.1242
  919.7826    0.0133
  920.7850    0.0012
```

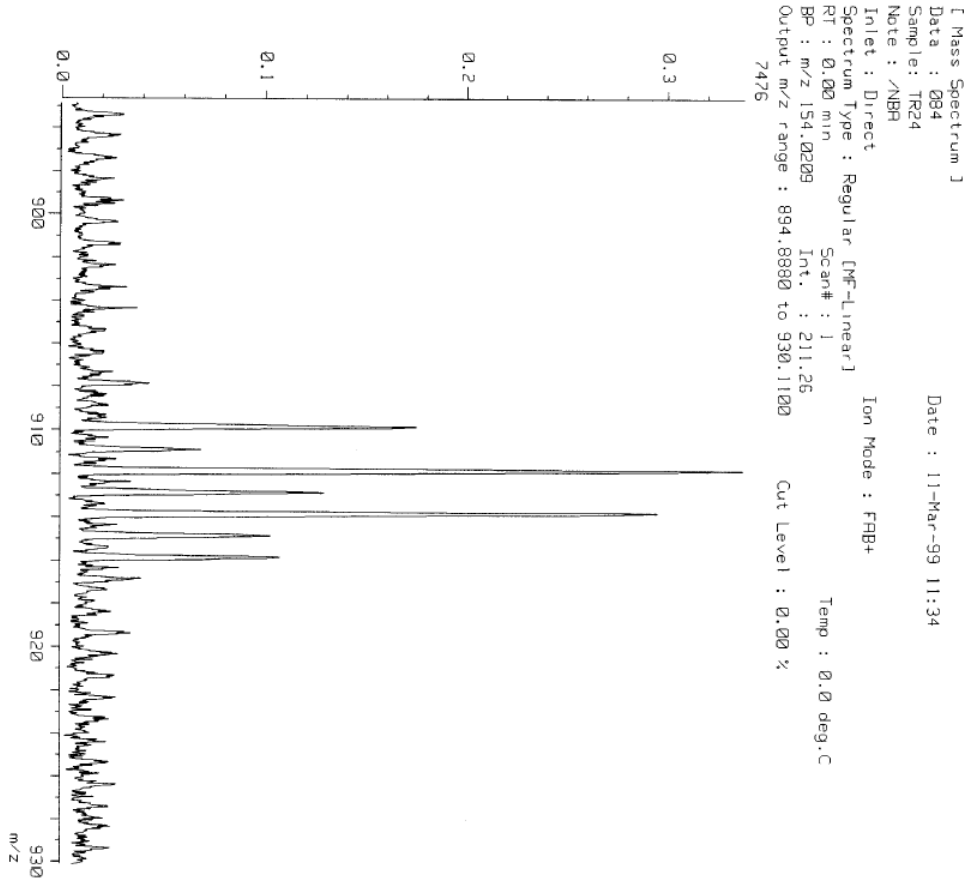


Figure F1. Calculated and observed isotopic distribution patterns of the M^+ peaks for $\{Re(CO)_4Br\}_2(\mu\text{-bpy})$.

```
[ Theoretical Ion Distribution ]
Molecular Formula : Re4 Br4 C40 H24 N8 O12
                    (m/z  1871.6478, MW  1873.1210, U.S. 33.0)
Base Peak :  1873.6405, Averaged MW :  1873.1193(a),  1873.1238(w)

    m/z        INT.
 1863.6366    0.4285
 1864.6396    0.2067
 1865.6377    4.5949 ***
 1866.6407    2.2008 *
 1867.6386   21.4247 ***********
 1868.6415   10.1659 ******
 1869.6394   56.8170 *********************************
 1870.6422   26.6256 ***************
 1871.6400   94.0142 ********************************************************
 1872.6428   43.3043 ************************
 1873.6405  100.0000 ************************************************************
 1874.6432   44.9180 *************************
 1875.6410   67.6797 ***************************************
 1876.6434   29.2195 *****************
 1877.6416   27.6279 ****************
 1878.6437   11.1156 ******
 1879.6428    5.9940 ***
 1880.6443    2.0636 *
 1881.6464    0.5179
 1882.6487    0.1024
 1883.6510    0.0168
 1884.6534    0.0024
 1885.6557    0.0003
```

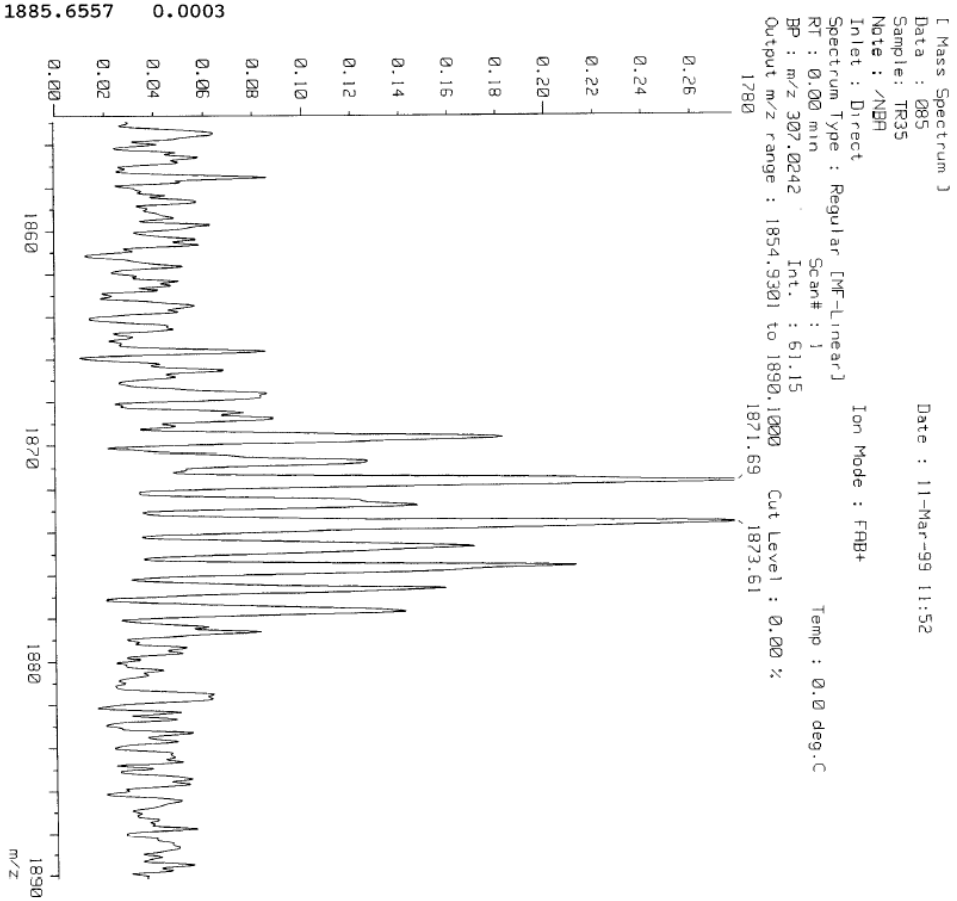


Figure F2. Calculated and observed isotopic distribution patterns of the M^+ peaks for **1**.

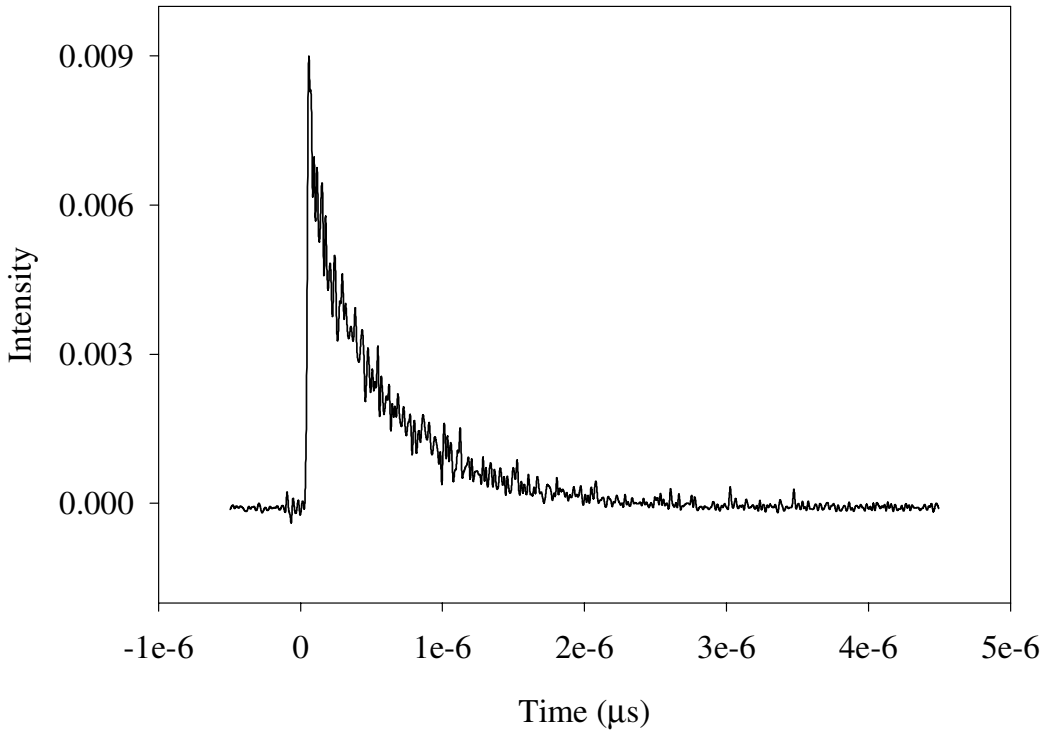


Figure F3. Decay profile recorded for the emission from rectangle **4** in deoxygenated dichloromethane at 298 K following laser excitation at 355 nm.

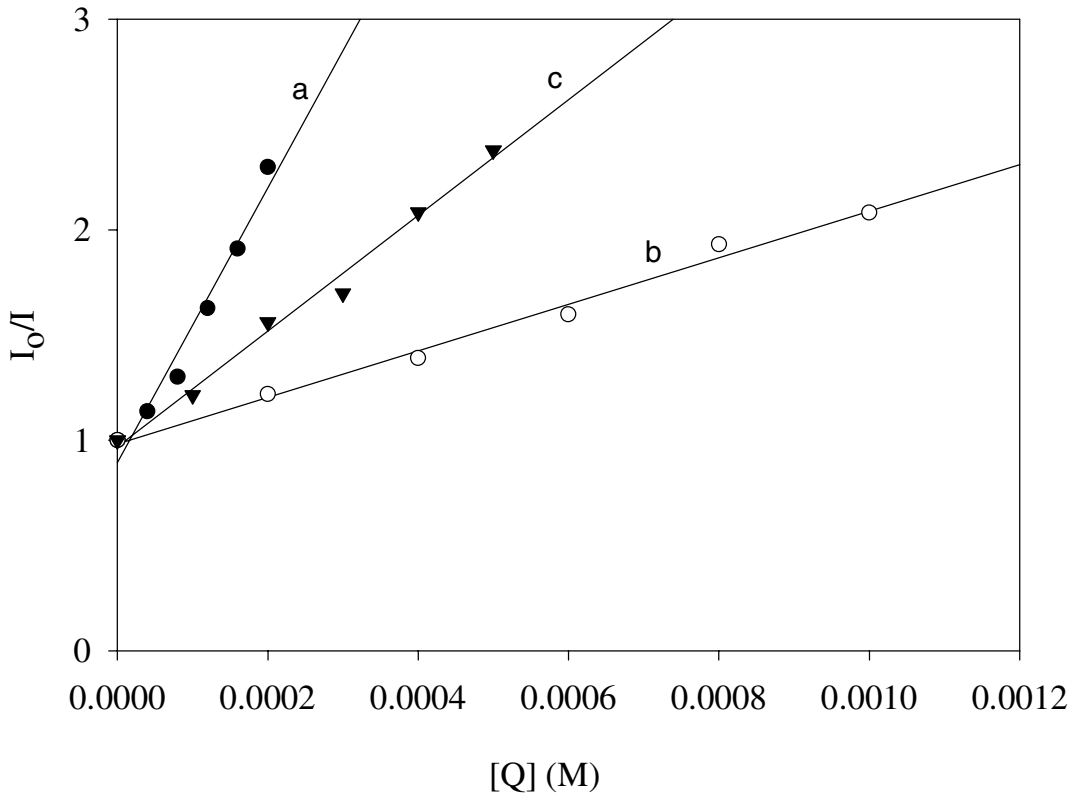
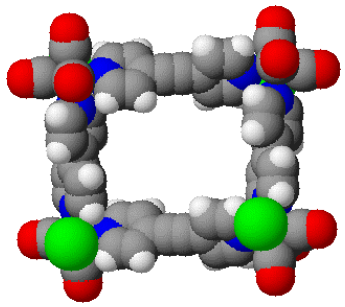
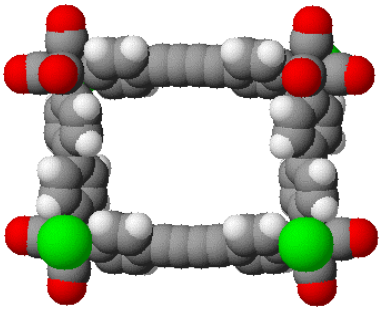


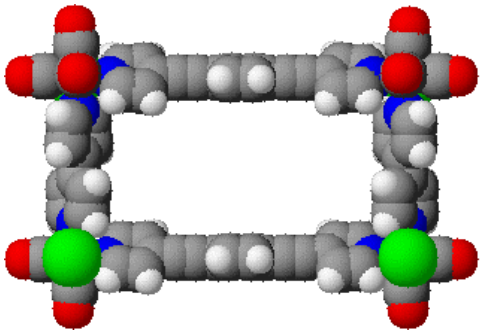
Figure F4. Stern-Volmer plot for the quenching of rectangle **4** with (a) 1,4-naphthaquinone, (b) 2,4-dinitrotoluene and (c) N,N-diethylaniline in dichloromethane.



2



3



4

Figure F5. Molecular modeling diagram of molecular rectangles **2**, **3** and **4** using MM2 simulation.