ESI:

Molecular and Electronic Structures and Photophysical Properties of Quadruply Bonded Dimetal Complexes (M = Mo or W) Supported by trans-Arylethynylcarboxylate Ligands where aryl = p-tolyl or 9-anthrancenyl

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Table S1. Crystallographic details for **1a**

Molecular formula	C68 H92 Mo2 O12	
Formula weight	1293.30	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.9166(1) Å	α= 78.634(1)°
	b = 11.6291(1) Å	β= 84.373(1)°
	c = 13.4313(2) Å	γ = 76.304(1)°
Volume	1621.77(3) $Å^3$	
Z	1	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.446 mm^{-1}	
F(000)	680	
Crystal size	0.08 x 0.15 x 0.23 mm^3	
Theta range for data collection	2.53 to 27.52°	
Index ranges	-14<=h<=14, -15<=k<=15, -17<=l<=17	
Reflections collected	42565	
Independent reflections	7415 [R(int) = 0.043]	
Completeness to theta = 27.52°	99.4 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7415 / 0 / 376	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0368, wR2 = 0.0925	

R indices (all data)	R1 = 0.0516, wR2 = 0.0987
Largest diff. peak and hole	0.792 and -0.739 e/Å^3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7135(2)	3326(2)	5557(2)	26(1)
C(2)	8226(2)	2409(2)	5901(2)	31(1)
C(3)	9106(2)	1632(2)	6216(2)	30(1)
C(4)	10155(2)	696(2)	6596(2)	27(1)
C(5)	10952(2)	889(2)	7267(2)	34(1)
C(6)	11951(3)	-22(3)	7638(2)	38(1)
C(7)	12196(2)	-1144(2)	7347(2)	36(1)
C(8)	11419(3)	-1316(2)	6670(2)	37(1)
C(9)	10406(3)	-426(2)	6305(2)	33(1)
C(10)	13269(3)	-2138(3)	7785(3)	57(1)
C(11)	3822(2)	3990(2)	6717(2)	24(1)
C(12)	3176(2)	3406(2)	7640(2)	26(1)
C(13)	1888(2)	3855(2)	7835(2)	31(1)
C(14)	1266(3)	3237(3)	8657(2)	40(1)
C(15)	1913(3)	2199(3)	9271(2)	45(1)
C(16)	3198(3)	1809(3)	9069(2)	44(1)
C(17)	3854(3)	2382(2)	8263(2)	34(1)
C(18)	1175(3)	4953(2)	7143(2)	37(1)
C(19)	349(3)	5868(3)	7735(2)	46(1)
C(20)	414(3)	4590(3)	6413(3)	59(1)
C(21)	1259(4)	1459(4)	10145(3)	65(1)
C(22)	-127(4)	1675(4)	10084(3)	91(2)
C(23)	1655(4)	1624(3)	11169(3)	74(1)
C(24)	5253(3)	1898(3)	8025(2)	42(1)
C(25)	6016(3)	1491(3)	8977(3)	62(1)
C(26)	5437(3)	891(3)	7422(3)	61(1)
C(27)	7369(3)	6957(3)	6240(3)	55(1)
C(28A)	7869(4)	8019(5)	5801(7)	44(2)*
C(28B)	7895(9)	7825(10)	5393(13)	38(3)*
C(29)	6869(3)	8789(3)	5096(3)	65(1)

C(30)	5672(3)	8464(2)	5586(2)	41(1)
C(31)	2755(6)	4818(5)	150(4)	107(2)
C(32)	3792(6)	4075(6)	757(5)	127(2)
C(33)	3967(6)	4860(6)	1451(4)	117(2)
C(34)	2769(6)	5710(6)	1475(4)	112(2)
Mo	5241(1)	5583(1)	5418(1)	21(1)
O(1)	6923(2)	4331(1)	5858(1)	25(1)
O(2)	3586(2)	6905(1)	5032(1)	25(1)
O(3)	4333(2)	4849(1)	6764(1)	23(1)
O(4)	6174(2)	6397(1)	4111(1)	24(1)
O(5)	6039(2)	7228(2)	6088(1)	33(1)
O(6A)	1984(5)	5484(5)	796(4)	124(2)*
O(6B)	2593(19)	6073(19)	412(16)	113(6)*

*Refined isotropically. The occupancy factor for C(28A) refined to 0.68(2), which restricted the occupancy factor for C(28B) to 0.32(2). The occupancy factors for O(6A) and O(6B) were fixed at 0.8 and 0.2, respectively.

Table S3. Bond lengths [Å] and angles [°] for **1a**.

C(1)-O(1)	1.274(3)
C(1)-O(2)#1	1.274(3)
C(1)-C(2)	1.443(3)
C(2)-C(3)	1.198(3)
C(3)-C(4)	1.436(3)
C(4)-C(9)	1.394(4)
C(4)-C(5)	1.395(4)
C(5)-C(6)	1.383(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.392(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.375(4)
C(7)-C(10)	1.510(4)
C(8)-C(9)	1.378(4)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-O(3)	1.269(3)
C(11)-O(4)#1	1.278(3)
C(11)-C(12)	1.490(3)
C(12)-C(13)	1.397(4)
C(12)-C(17)	1.406(4)
C(13)-C(14)	1.403(4)
C(13)-C(18)	1.518(4)
C(14)-C(15)	1.398(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.386(4)
C(15)-C(21)	1.535(4)
C(16)-C(17)	1.386(4)
C(16)-H(16)	0.9500
C(17)-C(24)	1.523(4)
C(18)-C(19)	1.522(4)
C(18)-C(20)	1.522(4)
C(18)-H(18)	1.0000

C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.481(6)
C(21)-C(23)	1.541(5)
C(21)-H(21)	1.0000
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(26)	1.516(4)
C(24)-C(25)	1.528(4)
C(24)-H(24)	1.0000
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-O(5)	1.438(3)
C(27)-C(28A)	1.463(6)
C(27)-C(28B)	1.529(11)
C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900
C(27)-H(27C)	0.9900
C(27)-H(27D)	0.9900
C(28A)-C(29)	1.515(6)
C(28A)-H(28A)	0.9900
C(28A)-H(28B)	0.9900
C(28B)-C(29)	1.410(10)
C(28B)-H(28C)	0.9900
C(28B)-H(28D)	0.9900
C(29)-C(30)	1.500(4)

C(29)-H(29A)	0.9900
C(29)-H(29B)	0.9900
C(29)-H(29C)	0.9900
C(29)-H(29D)	0.9900
C(30)-O(5)	1.442(3)
C(30)-H(30A)	0.9900
C(30)-H(30B)	0.9900
C(31)-O(6A)	1.369(7)
C(31)-C(32)	1.460(7)
C(31)-O(6B)	1.53(2)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(31)-H(31C)	0.9900
C(31)-H(31D)	0.9900
C(32)-C(33)	1.480(7)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.442(7)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-O(6A)	1.411(7)
C(34)-O(6B)	1.43(2)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(34)-H(34C)	0.9900
C(34)-H(34D)	0.9900
Mo-O(3)	2.103(2)
Mo-Mo#1	2.1043(4)
Mo-O(2)	2.109(2)
Mo-O(1)	2.110(2)
Mo-O(4)	2.112(2)
Mo-O(5)	2.617(2)
O(2)-C(1)#1	1.274(3)
O(4)-C(11)#1	1.278(3)

O(1)-C(1)-O(2)#1	122.5(2)
O(1)-C(1)-C(2)	118.9(2)
O(2)#1-C(1)-C(2)	118.6(2)

C(3)-C(2)-C(1)	177.6(3)
C(2)-C(3)-C(4)	179.7(3)
C(9)-C(4)-C(5)	118.3(2)
C(9)-C(4)-C(3)	121.0(2)
C(5)-C(4)-C(3)	120.7(2)
C(6)-C(5)-C(4)	120.2(3)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(5)-C(6)-C(7)	121.4(3)
C(5)-C(6)-H(6)	119.3
C(7)-C(6)-H(6)	119.3
C(8)-C(7)-C(6)	117.9(2)
C(8)-C(7)-C(10)	121.6(3)
C(6)-C(7)-C(10)	120.5(3)
C(7)-C(8)-C(9)	121.7(3)
C(7)-C(8)-H(8)	119.2
C(9)-C(8)-H(8)	119.2
C(8)-C(9)-C(4)	120.6(3)
C(8)-C(9)-H(9)	119.7
C(4)-C(9)-H(9)	119.7
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(3)-C(11)-O(4)#1	122.0(2)
O(3)-C(11)-C(12)	120.2(2)
O(4)#1-C(11)-C(12)	117.8(2)
C(13)-C(12)-C(17)	121.6(2)
C(13)-C(12)-C(11)	118.8(2)
C(17)-C(12)-C(11)	119.5(2)
C(12)-C(13)-C(14)	118.3(2)
C(12)-C(13)-C(18)	120.4(2)
C(14)-C(13)-C(18)	121.2(2)
C(15)-C(14)-C(13)	121.1(3)
C(15)-C(14)-H(14)	119.4
C(13)-C(14)-H(14)	119.4

C(16)-C(15)-C(14)	118.5(3)
C(16)-C(15)-C(21)	118.6(3)
C(14)-C(15)-C(21)	122.9(3)
C(15)-C(16)-C(17)	122.6(3)
C(15)-C(16)-H(16)	118.7
C(17)-C(16)-H(16)	118.7
C(16)-C(17)-C(12)	117.9(3)
C(16)-C(17)-C(24)	121.5(2)
C(12)-C(17)-C(24)	120.6(2)
C(13)-C(18)-C(19)	112.4(2)
C(13)-C(18)-C(20)	110.9(2)
C(19)-C(18)-C(20)	111.4(2)
C(13)-C(18)-H(18)	107.3
C(19)-C(18)-H(18)	107.3
C(20)-C(18)-H(18)	107.3
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(15)	114.3(3)
C(22)-C(21)-C(23)	113.4(3)
C(15)-C(21)-C(23)	109.4(3)
C(22)-C(21)-H(21)	106.4
C(15)-C(21)-H(21)	106.4
C(23)-C(21)-H(21)	106.4
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5

H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(26)-C(24)-C(17)	110.6(3)
C(26)-C(24)-C(25)	111.0(3)
C(17)-C(24)-C(25)	112.8(3)
C(26)-C(24)-H(24)	107.4
C(17)-C(24)-H(24)	107.4
C(25)-C(24)-H(24)	107.4
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
O(5)-C(27)-C(28A)	108.9(3)
O(5)-C(27)-C(28B)	104.5(4)
O(5)-C(27)-H(27A)	109.9
C(28A)-C(27)-H(27A)	109.9
O(5)-C(27)-H(27B)	109.9
C(28A)-C(27)-H(27B)	109.9
H(27A)-C(27)-H(27B)	108.3
O(5)-C(27)-H(27C)	110.9
C(28B)-C(27)-H(27C)	110.9
O(5)-C(27)-H(27D)	110.9
C(28B)-C(27)-H(27D)	110.9
H(27C)-C(27)-H(27D)	108.9
C(27)-C(28A)-C(29)	104.2(4)

C(27)-C(28A)-H(28A)	110.9
C(29)-C(28A)-H(28A)	110.9
C(27)-C(28A)-H(28B)	110.9
C(29)-C(28A)-H(28B)	110.9
H(28A)-C(28A)-H(28B)	108.9
C(29)-C(28B)-C(27)	106.1(7)
C(29)-C(28B)-H(28C)	110.5
C(27)-C(28B)-H(28C)	110.5
C(29)-C(28B)-H(28D)	110.5
C(27)-C(28B)-H(28D)	110.5
H(28C)-C(28B)-H(28D)	108.7
C(28B)-C(29)-C(30)	108.9(5)
C(30)-C(29)-C(28A)	103.3(3)
C(30)-C(29)-H(29A)	111.1
C(28A)-C(29)-H(29A)	111.1
C(30)-C(29)-H(29B)	111.1
C(28A)-C(29)-H(29B)	111.1
H(29A)-C(29)-H(29B)	109.1
C(28B)-C(29)-H(29C)	109.9
C(30)-C(29)-H(29C)	109.9
C(28B)-C(29)-H(29D)	109.9
C(30)-C(29)-H(29D)	109.9
H(29C)-C(29)-H(29D)	108.3
O(5)-C(30)-C(29)	105.5(2)
O(5)-C(30)-H(30A)	110.6
C(29)-C(30)-H(30A)	110.6
O(5)-C(30)-H(30B)	110.6
C(29)-C(30)-H(30B)	110.6
H(30A)-C(30)-H(30B)	108.8
O(6A)-C(31)-C(32)	105.3(5)
C(32)-C(31)-O(6B)	104.2(9)
O(6A)-C(31)-H(31A)	110.7
C(32)-C(31)-H(31A)	110.7
O(6A)-C(31)-H(31B)	110.7
C(32)-C(31)-H(31B)	110.7
H(31A)-C(31)-H(31B)	108.8
C(32)-C(31)-H(31C)	110.9
O(6B)-C(31)-H(31C)	110.9

C(32)-C(31)-H(31D)	110.9
O(6B)-C(31)-H(31D)	110.9
H(31C)-C(31)-H(31D)	108.9
C(31)-C(32)-C(33)	103.4(5)
C(31)-C(32)-H(32A)	111.1
C(33)-C(32)-H(32A)	111.1
C(31)-C(32)-H(32B)	111.1
C(33)-C(32)-H(32B)	111.1
H(32A)-C(32)-H(32B)	109.1
C(34)-C(33)-C(32)	103.9(4)
C(34)-C(33)-H(33A)	111.0
C(32)-C(33)-H(33A)	111.0
C(34)-C(33)-H(33B)	111.0
C(32)-C(33)-H(33B)	111.0
H(33A)-C(33)-H(33B)	109.0
O(6A)-C(34)-C(33)	108.5(5)
O(6B)-C(34)-C(33)	99.9(9)
O(6A)-C(34)-H(34A)	110.0
C(33)-C(34)-H(34A)	110.0
O(6A)-C(34)-H(34B)	110.0
C(33)-C(34)-H(34B)	110.0
H(34A)-C(34)-H(34B)	108.4
O(6B)-C(34)-H(34C)	111.8
C(33)-C(34)-H(34C)	111.8
O(6B)-C(34)-H(34D)	111.8
C(33)-C(34)-H(34D)	111.8
H(34C)-C(34)-H(34D)	109.5
O(3)-Mo-Mo#1	92.65(4)
O(3)-Mo-O(2)	91.16(6)
Mo#1-Mo-O(2)	91.81(5)
O(3)-Mo-O(1)	88.52(6)
Mo#1-Mo-O(1)	91.70(5)
O(2)-Mo-O(1)	176.48(6)
O(3)-Mo-O(4)	176.61(6)
Mo#1-Mo-O(4)	90.73(4)
O(2)-Mo-O(4)	88.45(6)
O(1)-Mo-O(4)	91.66(6)
C(1)-O(1)-Mo	117.00(15)

C(1)#1-O(2)-Mo	116.88(15)
C(11)-O(3)-Mo	116.73(15)
C(11)#1-O(4)-Mo	117.84(15)
C(27)-O(5)-C(30)	108.3(2)
C(31)-O(6A)-C(34)	106.9(5)
C(34)-O(6B)-C(31)	97.9(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S4. Torsion angles [°] for **1a**.

O(1)-C(1)-C(2)-C(3)	92(7)
O(2)#1-C(1)-C(2)-C(3)	-88(7)
C(1)-C(2)-C(3)-C(4)	23(60)
C(2)-C(3)-C(4)-C(9)	66(55)
C(2)-C(3)-C(4)-C(5)	-114(55)
C(9)-C(4)-C(5)-C(6)	-0.8(4)
C(3)-C(4)-C(5)-C(6)	179.3(2)
C(4)-C(5)-C(6)-C(7)	0.7(4)
C(5)-C(6)-C(7)-C(8)	0.6(4)
C(5)-C(6)-C(7)-C(10)	-178.2(3)
C(6)-C(7)-C(8)-C(9)	-1.7(4)
C(10)-C(7)-C(8)-C(9)	177.1(3)
C(7)-C(8)-C(9)-C(4)	1.6(4)
C(5)-C(4)-C(9)-C(8)	-0.2(4)
C(3)-C(4)-C(9)-C(8)	179.6(2)
O(3)-C(11)-C(12)-C(13)	90.7(3)
O(4)#1-C(11)-C(12)-C(13)	-88.5(3)
O(3)-C(11)-C(12)-C(17)	-92.7(3)
O(4)#1-C(11)-C(12)-C(17)	88.0(3)
C(17)-C(12)-C(13)-C(14)	-1.8(4)
C(11)-C(12)-C(13)-C(14)	174.7(2)
C(17)-C(12)-C(13)-C(18)	-179.3(2)
C(11)-C(12)-C(13)-C(18)	-2.8(4)
C(12)-C(13)-C(14)-C(15)	0.1(4)
C(18)-C(13)-C(14)-C(15)	177.5(3)
C(13)-C(14)-C(15)-C(16)	2.0(5)

C(13)-C(14)-C(15)-C(21)	-176.9(3)
C(14)-C(15)-C(16)-C(17)	-2.4(5)
C(21)-C(15)-C(16)-C(17)	176.5(3)
C(15)-C(16)-C(17)-C(12)	0.7(4)
C(15)-C(16)-C(17)-C(24)	-176.8(3)
C(13)-C(12)-C(17)-C(16)	1.5(4)
C(11)-C(12)-C(17)-C(16)	-175.0(2)
C(13)-C(12)-C(17)-C(24)	179.0(2)
C(11)-C(12)-C(17)-C(24)	2.5(4)
C(12)-C(13)-C(18)-C(19)	-133.2(3)
C(14)-C(13)-C(18)-C(19)	49.4(4)
C(12)-C(13)-C(18)-C(20)	101.3(3)
C(14)-C(13)-C(18)-C(20)	-76.1(3)
C(16)-C(15)-C(21)-C(22)	-159.7(4)
C(14)-C(15)-C(21)-C(22)	19.2(5)
C(16)-C(15)-C(21)-C(23)	71.9(4)
C(14)-C(15)-C(21)-C(23)	-109.2(4)
C(16)-C(17)-C(24)-C(26)	81.6(4)
C(12)-C(17)-C(24)-C(26)	-95.9(3)
C(16)-C(17)-C(24)-C(25)	-43.3(4)
C(12)-C(17)-C(24)-C(25)	139.2(3)
O(5)-C(27)-C(28A)-C(29)	-17.5(7)
C(28B)-C(27)-C(28A)-C(29)	65.8(11)
O(5)-C(27)-C(28B)-C(29)	22.5(12)
C(28A)-C(27)-C(28B)-C(29)	-81.5(13)
C(27)-C(28B)-C(29)-C(30)	-10.1(13)
C(27)-C(28B)-C(29)-C(28A)	70.4(13)
C(27)-C(28A)-C(29)-C(28B)	-77.3(12)
C(27)-C(28A)-C(29)-C(30)	29.2(6)
C(28B)-C(29)-C(30)-O(5)	-5.9(9)
C(28A)-C(29)-C(30)-O(5)	-30.7(5)
O(6A)-C(31)-C(32)-C(33)	-34.4(7)
O(6B)-C(31)-C(32)-C(33)	10.8(10)
C(31)-C(32)-C(33)-C(34)	22.3(7)
C(32)-C(33)-C(34)-O(6A)	-3.4(7)
C(32)-C(33)-C(34)-O(6B)	-49.3(11)
O(2)#1-C(1)-O(1)-Mo	3.9(3)
C(2)-C(1)-O(1)-Mo	-175.51(17)

O(3)-Mo-O(1)-C(1)	90.86(17)
Mo#1-Mo-O(1)-C(1)	-1.74(16)
O(2)-Mo-O(1)-C(1)	175.7(10)
O(4)-Mo-O(1)-C(1)	-92.52(17)
O(3)-Mo-O(2)-C(1)#1	-94.80(17)
Mo#1-Mo-O(2)-C(1)#1	-2.12(16)
O(1)-Mo-O(2)-C(1)#1	-180(36)
O(4)-Mo-O(2)-C(1)#1	88.56(17)
O(4)#1-C(11)-O(3)-Mo	-1.7(3)
C(12)-C(11)-O(3)-Mo	179.07(16)
Mo#1-Mo-O(3)-C(11)	1.08(15)
O(2)-Mo-O(3)-C(11)	92.95(16)
O(1)-Mo-O(3)-C(11)	-90.55(16)
O(4)-Mo-O(3)-C(11)	176.2(9)
O(3)-Mo-O(4)-C(11)#1	-174.8(9)
Mo#1-Mo-O(4)-C(11)#1	0.40(15)
O(2)-Mo-O(4)-C(11)#1	-91.39(16)
O(1)-Mo-O(4)-C(11)#1	92.12(16)
C(28A)-C(27)-O(5)-C(30)	-1.8(5)
C(28B)-C(27)-O(5)-C(30)	-26.6(8)
C(29)-C(30)-O(5)-C(27)	20.7(3)
C(32)-C(31)-O(6A)-C(34)	32.9(7)
O(6B)-C(31)-O(6A)-C(34)	-61.7(11)
O(6B)-C(34)-O(6A)-C(31)	67.1(12)
C(33)-C(34)-O(6A)-C(31)	-18.4(7)
O(6A)-C(34)-O(6B)-C(31)	-52.6(9)
C(33)-C(34)-O(6B)-C(31)	53.7(11)
O(6A)-C(31)-O(6B)-C(34)	57.3(10)
C(32)-C(31)-O(6B)-C(34)	-40.2(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table S5:Solvent dependence of absorption and emission of **1a**, **2a**, **1b**, **2b**.

Compound	Absorbance (λ_{max})				
	$CHCl_3$ nm, cm^{-1}	CH_2Cl_2 nm, cm^{-1}	C_6H_6 nm, cm^{-1}	THF nm, cm^{-1}	DMSO nm, cm^{-1}
1a	419, 23866	420, 23810		440, 22727	462, 21645
2a	492, 20325	507, 19724		520, 19231	540, 18519
1b	542, 18450	576, 17361	584, 17123	616, 16234	637, 15698
2b	679, 14728	*a*	692, 14450	762, 13123	807, 12392
	Emission (Fl) (λ_{max})				
	$CHCl_3$ nm, cm^{-1}	CH_2Cl_2 nm, cm^{-1}	C_6H_6 nm, cm^{-1}	THF nm, cm^{-1}	DMSO nm, cm^{-1}
1a	523, 19120	545, 18349		570, 17544	570, 17544
2a	636, 15723	665, 15038		717, 13947	*b*
1b	628, 15923	632, 15823	636, 15723	674, 14837	~702, 14245
2b				800-830,	980, 10204
	Emission (Ph) (λ_{max})				
		CH_2Cl_2 nm, cm^{-1}	THF nm, cm^{-1}	2-MeTHF (77) nm, cm^{-1}	DMSO nm, cm^{-1}
1a		1060, 9434	1080, 9259		
2a		1070, 9346	1080, 9259		
1b				875, 11429[c]	~870, 11494

[a] not appreciably soluble in CH_2Cl_2, [b] not detectable due to instrument limitations [c] emission not observed at room temperature in THF, only at 77K in 2-MeTHF

Table S6: Calculated orbital contributions of transitions of singlet ground state of (1a) Mo2(O2CH)2(O2CC≡CTolyl)2
(2a) Mo2(O2CH)2(O2CC≡CAnthryl)2 (1b) W2(O2CH)2(O2CC≡CTolyl)2 (2b) W2(O2CH)2(O2CC≡CAnthryl)2

	λ_{calc} / nm major transitions (contribution)
(1a)	461.19 H → L (0.672)
	306.28 H → L+6 (0.678)
	284.18 H-2 → L (0.610), H-1 → L+2 (0.163), H → L+10 (0.231)
	270.54 H-4 → L+2 (-0.196), H-2 → L (0.273), H-1 → L+2 (0.551), H → L+10 (0.275)
	258.62 H-1 → L+2 (-0.302), H → L+10 (0.585)
(2a)	574.45 H → L (0.673)
	426.03 H-2 → L (0.503), H-1 → L+1 (0.389), H → L+3 (0.146)
	361.98 H → L+3 (0.667)
(1b)	533.23 H → L (0.647)
	344.94 H → L+4 (0.664)
	297.93 H-4 → L (0.434), H-3 → L +1 (0.159), H → L+11 (0.527)
(2b)	677.89 H → L (0.655)
	443.07 H-2 → L (0.551), H-1 → L+1 (-0.202), H → L+3 (0.345)
	349.19 H → L+6 (0.665)
	320.56 H-6 → L+1 (-0.180), H-5 → L (0.405), H-2 → L+7 (0.229), H-1 → L+8 (0.243), H → L+7 (0.428)