Electronic Supplementary Information (ESI) for

Stepwise Formation of Organometallic Macrocycles and Triangular Prisms Containing 2,2'-bisbenzimidazole ligands

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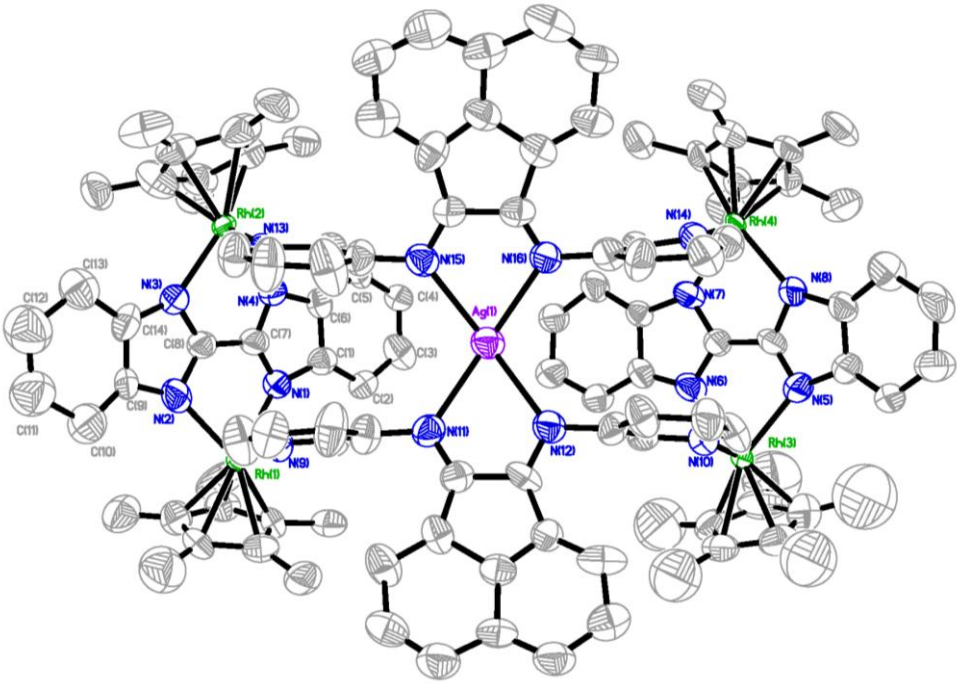

Fig. S1 Complex cation of **3b** with thermal ellipsoids drawn at the 30% level. (Ir, green; N, blue; C, gray; Ag, purple; O, red). All hydrogen atoms, anions, and solvent molecules are omitted for clarity. Selected bonds (Å) and angles (°). Rh(1)-N(9), 2.117(14), Rh(1)-N(2), 2.187(17); Rh(1)-N(1), 2.194(12). Ag(1)-N(11), 2.440(15). Ag(1)-N(12), 2.418(14). Ag(1)-N(15), 2.462(15). Ag(1)-N(16), 2.409(13). N(9)-Rh(1)-N(2), 84.1(6); N(9)-Rh(1)-N(1), 85.8(5); N(2)-Rh(1)-N(1), 78.4(5). N(16)-Ag(1)-N(12), 104.6(4). N(16)-Ag(1)-N(11), 153.6(5). N(12)-Ag(1)-N(11), 68.4(5). N(16)-Ag(1)-N(15), 69.8(5). N(12)-Ag(1)-N(15), 151.3(5). N(11)-Ag(1)-N(15), 103.6(5). O(1)-Ag(1)-N(16), 118.7(5). O(1)-Ag(1)-N(12), 117.7(5). O(1)-Ag(1)-N(11), 85.7(5), O(1)-Ag(1)-N(15), 88.0(5)

Data of complex **3b**: ^{1}H NMR (400 MHz, [D_6]-DMSO, ppm): 1.71 (s, 60H, Cp*), 8.63 (s, 8H, pyrazine), 7.79 (q, 8H, Ar-H), 7.40 (q, 8H, Ar-H); IR (KBr disk, cm-1): v = 1616 (m, Ar), 1354 (m, C=N); elemental analysis calcd (%) for $C_{117}H_{106}AgF_{15}N_{16}O_{16}Rh_4S_5$: C, 47.52; H, 3.61; N, 7.58. Found: C, 47.41; H, 3.60; N, 7.62. ^{13}C NMR ([D_6]-DMSO, ppm): 8.62 (CH_3, Cp*), 94.78 (Cp*), 101.31, 121.01, 122.4, 126.29, 128.08 , 130.77, 155.50 (pyrazine), 169.44(C=N, 3-pyridyl-bian), 177.12.

Table 1 Crystallographic Data and Structure Refinement Parameters for **2a–c**, **3a–3b**, **4a.**

	2a	**2b**	**2c**	**3a**	**3b**	**4a**
Chemical Formula	$C_{168}H_{192}F_{24}Ir_8N_{24}O_{28}S_8$	$C_{95.60}H_{128.40}F_{12}N_{12}O_{18.60}Rh_4S_4$	$C_{102}H_{126}F_{12}Ir_4N_{12}O_{19}S_4$	$C_{129}H_{136}AgF_{15}Ir_4N_{16}O_{19}S_5$	$C_{117}H_{106}AgF_{15}N_{16}O_{16}Rh_4S_5$	$C_{202}H_{219}F_{18}Ir_6N_{24}O_{27}S_6$
F_W	5245.54	2511.18	2949.19	3536.51	2956.99	5102.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	C2/m	P2(1)/m	P2(1)	Pccn	Pccn	P2(1)/c
a/Å	27.431(2)	13.3751(8)	12.8163(8)	33.945(2)	34.2162(8)	22.1957(19)
b/Å	17.7844(14)	32.7892(18)	25.5882(14)	25.8578(18)	25.9800(5)	33.541(3)
c/Å	20.7641(17)	14.0292(8)	17.7677(10)	28.822(2)	28.8348(6)	29.504(3)
α/°	90	90	90	90	90	90
β/°	112.1960(10)	116.6330(10)	110.4360(10)	90	90	110.164(2)
γ/°	90	90	90	90	90	90
V/Å^3	9379.0(13)	5499.8(5)	5460.1(5)	25298(3)	25632.3(9)	20618(3)
Z	2	2	2	8	8	4
D_c (Mg / m^3)	1.857	1.515	1.794	1.857	1.533	1.644
$\mu(M_o\text{-}K_\alpha)$(mm^{-1})	5.837	0.754	5.027	4.525	6.802	4.007
F(000)	5104	2420	2908	13952	11920	10140
θ range (°)	1.06–27.53	1.24–27.95	1.22–27.50	0.99–25.01	2.58–67.50	0.95–26.01
Reflections collected	35364	42053	40168	148971	124155	134029
Independent reflections	11142	13354	20032	22279	22619	40344
R_{int}	0.1387	0.0442	0.0467	0.1129	0.1029	0.0759
Completeness to θ	99.8 %	99.3 %	99.2 %	99.9 %	97.9 %	99.4 %
Data/restraints/param.	11142/ 185/ 756	13354/ 10/ 657	20032/ 265/ 1191	22279/ 130/ 1522	22619/ 105/ 1351	40344/ 401/ 2061
Goodness-of-fit on F^2	0.969	1.058	1.059	1.000	0.970	0.936
R_1[a],wR_2[a] [I>2σ(I)[a]]	0.0537/0.1395	0.0496/0.1281	0.0541/0.1421	0.0723/0.1869	0.0976/0.2603	0.0794, 0.2123
R_1, wR_2 (all data)	0.0880/0.1573	0.0773/0.1395	0.0664/0.1497	0.1257/0.2118	0.1392/0.2919	0.1456, 0.2423

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = [\Sigma w(F_o^2\text{-}F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.