Supplementary Material (ESI) for Chemical Communications

Polynuclear cyanoruthenate chromophores based on hexaaza-triphenylene containing up to twelve cyanides: photophysical and structural properties

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Supporting information

Table S1: Analytical, ^{1}H-NMR and IR spectroscopic data for the Ru_x-HAT complexes

Complex	Elem analysis (%C, %H, %N)[a]	1H-NMR (D_2O) δ(ppm)	Principal IR spectral peaks (cm^{-1})[c]
$Na_2[Ru(C_{12}N_6H_6)(CN)_4].4H_2O$	33.9 (34.4) 2.3 (2.5) 25.0 (25.1)	9.18 (2H, s) 9.25 (2H, d, J 2.75 Hz) 9.74 (2H, d, J 2.75 Hz)	3431, 2105, 2073, 2062, 1629, 1384
$PPN_2[Ru(C_{12}N_6H_6)(CN)_4].5H_2O$[b]	65.6 (65.8) 4.5 (4.7) 10.3 (10.5)	7.55 (60H, multiplet) 9.02 (2H, d, J 2.85Hz) 9.21 (2H, s) 10.00 (2H, d, J 2.9Hz)	3435, 2099, 2071, 1639, 1438, 1289, 1265, 1115, 724, 693, 548, 534
$Na_4[Ru_2(C_{12}N_6H_6)(CN)_8].8H_2O$	26.2 (27.2) 2.4 (2.51) 21.9 (22.2)	9.33 (2H, d, J 2.75Hz) 9.64 (2H, s) 9.77 (2H, d, J 2.75Hz)	3436, 2099, 2068, 2057, 1632, 1387
$PPN_4[Ru_2(C_{12}N_6H_6)(CN)_8].14H_2O$[b]	64.6 (64.5) 4.8 (5.1) 8.22 (8.26)	7.55 (120H, multiplet) 8.90 (2H, d, J 2.75Hz) 9.60 (2H, s) 9.93 (2H, d, J 2.75Hz)	3435, 2097, 2069, 1636, 1437, 1262, 1115, 724, 694, 549, 533
$Na_6[Ru_3(C_{12}N_6H_6)(CN)_{12}].12H_2O$	23.0 (23.94) 2.4 (2.51) 20.0 (20.94)	9.66 (6H,s)	3436, 2102, 2070, 1630, 1390
$PPN_6[Ru_3(C_{12}N_6H_6)(CN)_{12}].10H_2O$[b]	67.6 (67.6) 4.9 (4.8) 8.1 (7.9)	7.55 (180H,multiplet) 9.54 (6H, s)	3434, 2093, 2068, 1634, 1437, 1263, 1114, 723, 692, 548, 534

[a] calculated figures are in parentheses.

[b] PPN salts are hygroscopic, elemental analysis have been done on samples which had attained a final steady weight in air

[c] PPN bands are in red.

Table S2: UV-vis absorption spectra of Ru_x-HAT derivates

Sodium salts				
Compounds	H_2O		CH_3OH	
	λ (nm)	ε x 10^{-3} (M^{-1} cm^{-1})	λ (nm)	ε x 10^{-3} (M^{-1} cm^{-1})
$Na_2[Ru(C_{12}N_6H_6)(CN)_4].4H_2O$	443	8.2	482	8.8
$Na_4[Ru_2(C_{12}N_6H_6)(CN)_8].8H_2O$	478 516 (sh)	14.1 13.7	520 571 (sh)	15.9 13.9
$Na_6[Ru_3(C_{12}N_6H_6)(CN)_{12}].12H_2O$	524	28.0	575	28.3

PPN salts						
Compounds	CH_3CN		DCM		DMF	
	λ (nm)	ε x 10^{-3} (M^{-1} cm^{-1})	λ (nm)	ε x 10^{-3} (M^{-1} cm^{-1})	λ (nm)	ε x 10^{-3} (M^{-1} cm^{-1})
$PPN_2[Ru(C_{12}N_6H_6)(CN)_4].5H_2O$	527 578(sh)	11.7 8.5	523 579(sh)	11.4 8.1	546 618(sh)	11.3 7.1
$PPN_4[Ru_2(C_{12}N_6H_6)(CN)_8].14H_2O$	576 657(sh) 780sh	21.1 14.1 5.7	572 644(sh) 744(sh)	22.2 14.2 6.1	596 692 805	22.8 12.6 6.4
$PPN_6[Ru_3(C_{12}N_6H_6)(CN)_{12}].10H_2O$	602sh 666 739sh	27.2 34.8 21.1	593sh 632 705sh	26.4 32.6 21.1	610sh 692 762sh	26.3 36.4 20.95

Table S3: Bond lengths in the crystal structure of $Nd_2[\{Ru(CN)_4\}_3(\mu^3–HAT)$ •$23H_2O$

Nd(1)-O(55')	2.425(17)
Nd(1)-O(51)	2.482(8)
Nd(1)-O(54)	2.496(6)
Nd(1)-N(34)#1	2.515(8)
Nd(1)-O(55)	2.518(14)
Nd(1)-N(46)#2	2.525(9)
Nd(1)-O(53)	2.528(7)
Nd(1)-N(44)	2.555(7)
Nd(1)-N(48)#3	2.571(9)
Nd(1)-O(52)	2.59(3)
Nd(1)-O(52')	2.62(2)
Ru(2)-C(33)#4	1.970(9)
Ru(2)-C(33)	1.970(9)
Ru(2)-C(35)	2.022(15)
Ru(2)-C(31)	2.032(17)
Ru(2)-N(15)#4	2.104(7)
Ru(2)-N(15)	2.104(7)
Ru(3)-C(45)	1.975(10)
Ru(3)-C(43)	1.978(9)
Ru(3)-C(47)	1.998(10)
Ru(3)-C(41)	2.040(10)
Ru(3)-N(22)	2.111(8)
Ru(3)-N(12)	2.115(7)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z-1 #2 -x+2,-y+1,-z+1 #3 x+1,y,z

#4 x,-y+1/2,z #5 x-1,y,z+1 #6 x-1,y,z #7 -x+2,-y+1,-z+2