Supplementary Information for

Ionic liquid mediated routes to polydentate oxygen-donor adducts of cerium(III) bromide

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1) Experimental Section

General Procedures: All syntheses and manipulations were carried out under argon inside a Vacuum Atmospheres glove box. Anhydrous solvents were purchased from either Sigma Aldrich or Acros and stored over 4 Å molecular sieves. $CeBr_3$ (99.999%) was purchased from Sigma Aldrich and used without further purification. [BMP][$N(Tf)_2$] was synthesized according to literature procedure.[1] The $CeBr_3$/IL paste was prepared as previously reported.[2] Elemental Analysis was performed by Midwest Microlab, LLC. A Photon Technologies International Timemaster® photoluminescence spectrophotometer was used for all optical characterizations. Continuous wave spectra were excited by a Xenon lamp and lifetime measurements were excited by a tunable nitrogen laser. All complexes were analyzed as fine suspensions in their respective coordinating solvent. X-ray diffraction data were collected by mounting crystals under Paratone on glass fiber loops on a Bruker Apex II system fitted with an Oxford nitrogen cryostream. Structure solution and refinement against F^2 were performed using SHELX97. FTIR spectra were collected using a Bruker Vertex 80v infrared spectrometer. A. Samples were mounted onto an ATR plate with a diamond window in an inert atmosphere glovebox, covered with a mylar film then sealed with a powder holder.

Preparation of [$CeBr_2$(diglyme)$_2$][$CeBr_4$(diglyme)] (**1**): $CeBr_3$ (0.100 g, 0.263 mmol) was suspended in THF (5 mL) and stirred at 50°C for 10 minutes. The solvent was removed in vacuo and diglyme (5 mL) and [BMP][NTf_2] (0.15 g) were added to the white powder. The resulting suspension was stirred at 125°C for 10 minutes, during which time the solution went transparent. The mixture was filtered hot and the resulting clear, colorless solution was stored at ambient temperature for 3 days resulting in a large crop of colorless crystals. The mother liquor was decanted and the resulting crystals washed sequentially with diglyme (5 mL) and Et_2O (10 mL) and dried in vacuo. (0.121 g, 0.104 mmol, 79% yield). Anal. calcd for $C_{18}H_{42}O_9Ce_2Br_6$: C, 18.61 H, 3.62. Found: C, 18.91 H, 3.74. Ce-Br stretches via FTIR (bold is most intense); **162 cm^{-1}**, 146 cm^{-1}, 124 cm^{-1}.

Alternatively, **1** can also be prepared by the above method without inclusion of [BMP][NTf$_2$], resulting in a small crop of crystalline material. Matching of the unit cell of one of the crystals to that of **1** provided confirmation of the identity of the material**.** (0.010 g, 0.0092 mmol, 7% yield).

Preparation of [BMP][CeBr$_4$(diglyme)] (**2**): Diglyme (5 mL) was added to CeBr$_3$/IL (1.00 g) and the mixture stirred for 5 minutes. After permitting the undissolved solid to settle, the solution was filtered and the resulting clear, colorless solution was sealed and stored at room temperature for 2 days, affording a crop of colorless crystalline plates. The resulting crystals were washed with cold THF (5 mL) and dried under argon. Single crystal X-ray diffraction was performed on a random selection of several of the colorless plate-like crystals, indicating the presence of both **1** and **2**.

Preparation of [CeBr$_3$(dme)$_2$] (**3**): CeBr$_3$ (0.300 g, 0.790 mmol) was suspended in THF (5 mL) and stirred at 50°C for 10 minutes. The solvent was removed in vacuo and dimethoxyethane (7 mL) and [BMP][NTf$_2$] ((0.15 g) were added to the white powder. The resulting suspension was stirred at 70°C for 10 minutes, during which time the solution went transparent. The mixture was filtered hot and the resulting clear, colorless solution was stored at ambient temperature overnight resulting in a crop of colorless crystals. The mother liquor was decanted and the resulting crystals washed sequentially with dimethoxyethane (5 mL) and Et$_2$O (10 mL) and dried in vacuo. (0.321 g, 0.573 mmol, 72% yield). Anal. calcd for $C_8H_{20}O_4CeBr_3$: C, 17.16 H, 3.57. Found: C, 16.92 H, 3.39. Ce-Br stretches via FTIR (bold is most intense); **175 cm^{-1}**, 142 cm^{-1}.

Preparation of [CeBr$_3$(tetraglyme)$_n$] (4): CeBr$_3$ (1.00 g, 2.63 mmol) was suspended in THF (5 mL) and stirred at 50°C for 10 minutes. The solvent was removed in vacuo and tetraglyme (7 mL) and [BMP][NTf$_2$] (1.25 g) were added to the white powder. The resulting suspension was stirred at 150°C for 10 minutes, during which time the solution went transparent and faintly yellow. The mixture was filtered hot and the resulting clear solution was cooled to room temperature slowly over the course of 24 hours resulting in a crop of colorless needles. The mother liquor was decanted and the resulting crystals washed sequentially with tetraglyme (5 mL) and Et$_2$O (10 mL) and dried in vacuo. (1.110 g, 1.894 mmol, 70% yield). Anal. calcd for $C_{10}H_{22}O_5CeBr_3$: C, 20.00 H, 3.61. Found: C, 20.17 H, 3.69. Ce-Br stretches via FTIR (bold is most intense); **167 cm^{-1}**, 129 cm^{-1}.

2) X-ray Data Tables

Table 1. Crystal data for compounds **1-4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{18}H_{42}Br_6Ce_2O_9$	$C_{15}H_{34}Br_4CeNO_3$	$C_8H_{20}O_4CeBr_3$	$C_{10}H_{22}O_5CeBr_3$
M	1162.22	739.19	560.09	586.13
T/K	140(1)	140(1)	140(1)	140(1)
Color	Colorless	Colorless	Colorless	Colorless
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P 2_1/c	P 2_1/c	P2_1/n	P2_1/n
a/Å	9.1670(6)	15.7138(11)	10.021(4)	7.493(2)
b/Å	24.8802(15)	10.3798(7)	13.135(6)	19.263(5)
c/Å	15.4087(9)	15.0842(11)	12.733(6)	12.710(3)
β/°	99.275(1)	103.6910(10)	97.358(5)	103.926(3)
U/Å^3	3468.4(4)	2390.4(3)	1675.7(5)	1780.6(8)
Z	4	4	4	4

Dc/Mg m^{-3}	2.226	2.046	2.220	2.186
μ/mm^{-1}	9.540	8.603	9.867	9.291
Crystal size/mm	0.18x0.18x0.18	0.26x0.18x0.10	0.28x0.22x0.08	0.18x0.02x0.02
Reflections collected	37881	25357	18332	17540
R(int)	0.0543	0.0488	0.0275	0.0639
Data/restraints/parameters	7583 / 0 / 322	5153 / 20 / 196	3937 / 6 / 168	3402 / 0 / 174
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical
*R*1 [*I* > 2 (*I*)]	0.0290	0.0436	0.0227	0.0316
*w*R2 (all data)	0.0696	0.1204	0.0485	0.0743
Largest peak, hole / e Å^{-3}	1.199, -0.664	2.770, -2.181	1.191, -0.804	0.733, -0.825

Table 2. Bond distances for compounds **1-4**.

	1	**2**	**3**	**4**
Ce-Br1	2.8673(5)	2.8959(7)	2.8828(6)	2.9206(10)
Ce-Br2	2.8924(5)	2.8972(8)	2.8907(6)	2.9205(9)
Ce-Br3	2.9036(5)	2.8975(8)	2.8764(5)	2.9102(9)
Ce-Br4	2.9283(5)	2.8640(8)		
Ce-Br5	2.8759(5)			
Ce-Br6	2.8509(5)			
Ce-O1	2.563(3)	2.621(4)	2.519(2)	2.618(4)
Ce-O2	2.490(3)	2.567(4)	2.520(2)	2.600(4)
Ce-O3	2.560(3)	2.623(4)	2.544(2)	2.540(4)
Ce-O4	2.565(3)		2.522(2)	2.620(4)
Ce-O5	2.561(3)			2.613(4)
Ce-O6	2.527(3)			
Ce-O7	2.569(3)			

Ce-O8	2.586(3)			
Ce-O9	2.624(3)			

References

1 A. K. Burrell, R. E. Del Sesto, S. N. Baker, T. M. McCleskey and G. A. Baker, *Green Chem.*, 2007, **9**, 449-454.

2 K. V. Vasudevan, N. A. Smith, B. L. Scott, E. A. McKigney, M. W. Blair, J. C. Gordon and R. E. Muenchausen, *Inorg. Chem.*, 2011, **50**, 4627.