Supplementary Material (ESI) for Journal of Materials Chemistry

Polymer Nanoencapsulated Rare Earth Aerogels: Chemically Complex but Stoichiometrically Similar Core-Shell Superstructures with Skeletal Properties of Pure Compounds

Nicholas Leventis[*,1], Plousia Vassilaras[2], Eve Fabrizio[2] and Amala Dass[3]

1. NASA Glenn Research Center, 21000 Brookpark Road, Cleveland, OH 44135
2. Ohio Aerospace Institute, 22800 Cedar Point Road, Cleveland, OH 44142
3. Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409

Supporting Information

Table S1. Physical characterization data for rare earth sol-gel materials made using epichlorohydrin as deprotonation agent.

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Figure S1. CP MAS ^{13}C NMR spectra of samples as shown.

Figure S2. Photoluminescence data for Eu and Tb aerogels.

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[*] Current address: Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65409. Tel.: 573-341-4391, Fax: 573-341-6033, E-mail: leventis@umr.edu

Table S1. Physical characterization data for rare earth sol-gel materials made using epichlorohydrin as deprotonation agent.

Sample [a]	Diameter, mm	Density, g cm^{-3} Bulk [b]	Skeletal [c]	% Porosity, v/v	BET Surface Area, m^2 g^{-1} [d]	Force at Rupture, kg [e]	Modulus, MPa [e]	Susceptibility, emu g^{-1}×10^6 [f]
Sc-xero	2.69±0.06	1.20±0.03			478(2.51)			$-0.2\pm0.0_4$
Sc-aero	6.12±0.28	0.12±0.03			592(6.16)			-0.6±0.3
Sc-aeroX	7.98±0.53	0.21±0.04	1.15±0.01	81.7	242(6.62)	1.53±0.14	6.2±3.1	-0.6±0.1
Y-xero	3.31±0.10	1.49±0.09			431(2.76)			$-0.2\pm0.0_3$
Y-aero	8.57±0.14	0.12±0.01	2.39±0.19	94.9	528(6.25)			-0.3±0.1
Y-aeroX	8.33±0.02	0.36±0.01	$1.36_1\pm0.00_3$	73.5	144(8.10)	5.67	22.0	-0.4±0.1
La-xero					208(5.37)			$-0.3\pm0.0_3$
La-aero					128(6.57)			$-0.1\pm0.0_4$
La-aeroX	9.84±0.68	0.13±0.02	1.51±0.02	91.4	70(7.85)	0.25±0.05	16.0±0.9	-0.4±0.1
Pr-xero	3.48±0.04	1.56±0.19			296(2.75)			21.2±0.2
Pr-aero	7.88±0.42	0.18±0.03	2.82±0.16	93.6	186(6.94)			17.8±2.2
Pr-aeroX	8.37±0.65	0.38±0.13	1.41±0.03	73.0	130(6.70)	7.09±0.08	15.1±0.4	5.9±0.1
Nd-xero	3.38±0.01	2.09±0.10			307(2.60)			20.3±0.5
Nd-aero	7.73±0.24	0.19±0.02	3.14±0.41	93.9	384(8.54)			17.9±1.3
Nd-aeroX	8.71±0.43	0.46±0.06	1.39±0.01	66.9	144(12.3)	19.09 ±4.03	36.4±6.4	4.2±0.2
Sm-xero	3.41±0.01	2.04±0.01			257(2.65)			3.9±0.1
Sm-aero	7.52±0.17	0.22±0.02	2.97±0.12	92.6	383(7.09)			5.1±0.4
Sm-aeroX	8.45±0.30	0.39±0.05	1.39±0.01	71.9	168(8.36)	13.43±0.80	25.9±2.6	$0.7\pm0.0_2$
Eu-xero	3.20±0.05	2.11±0.05			300(2.65)			18.5±0.4
Eu-aero	7.61±0.32	0.20±0.02	2.47±0.14	91.9	379(6.17)			16.6±1.5
Eu-aeroX	7.70±0.68	0.53±0.08	1.42±0.03	62.7	144(8.54)	14.34	13.6	5.2±0.2
Gd-xero	3.38±0.02	2.02±0.02			294(2.63)			101.6±3.7

Gd-aero	8.04±0.36	0.18±0.02	3.14±0.24	94.3	383(5.80)			90.8±1.3
Gd-aeroX	8.17±0.21	0.44±0.01	1.40±0.03	68.6	171(8.47)	10.90±2.26	28.5±5.2	30.6±0.3
Tb-xero	3.48±0.02	1.96±0.02						145.3±2.1
Tb-aero	7.65±0.38	0.20±0.01	3.32±0.31	94.0	365(7.06)			130.5±5.9
Tb-aeroX	8.30±0.14	0.42±0.03	1.40±0.01	70.0	160(8.34)	6.30±0.73	29.6±7.5	43.6±0.4
Dy-xero	3.44±0.06	2.00±0.12			295(2.67)			181.7±3.2
Dy-aero	8.02±0.09	0.18±0.01	3.02±0.13	94.0	366(6.75)			167.6±3.5
Dy-aeroX	8.16±0.06	0.46±0.06	1.44±0.01	68.1	176(6.69)	2.62±0.28	20.5±3.2	59.2±3.1
Ho-xero	3.39±0.12	2.13±0.04			278(2.63)			167.5±4.5
Ho-aero	7.57±0.18	0.21±0.01	2.47±0.22	91.5	358(8.16)			139.1±7.0
Ho-aeroX	8.35±0.20	0.42±0.03	1.41±0.02	70.2	177(14.9)	6.57±1.31	19.3±1.3	54.8±3.4
Er-xero	3.43±0.02	2.04±0.05			299(2.67)			133.2±4.2
Er-aero	8.36±0.25	0.16±0.01	3.28±0.26	95.1	368(6.87)			104.5±5.4
Er-aeroX	8.41±0.34	0.40±0.05	1.14±0.01	64.9	157(6.36)	13.65±1.41	16.4±2.8	43.9±0.3
Tm-xero	3.38±0.02	1.96±0.09			312(2.73)			84.5±4.2
Tm-aero	8.63±0.57	0.14±0.02	3.17±0.12	95.6	349(6.91)			66.2±1.7
Tm-aeroX	8.59±0.04	0.34±0.01	1.44±0.01	76.4	170(13.6)	5.65±0.75	9.8±1.4	31.1±1.1
Yb-xero	3.53±0.03	1.73±0.15			323(2.71)			28.1±0.2
Yb-aero	8.43±0.08	0.15±0.01	3.25±0.16	95.4	345(6.33)			31.2±1.9
Yb-aeroX	8.38±0.12	0.38±0.01	1.49±0.01	74.5				10.9±0.4
Lu-xero	3.49±0.03	1.96±0.05						0.08±0.04
Lu-aero	—		—		214(8.17)			0.1±0.3
Lu-aeroX	8.35±0.07	0.39±0.02	1.49±0.02	73.8	120(6.97)	7.25±0.30	18.7±5.1	0.9±0.0$_4$

a. "X" stands for polymer crosslinked samples; b. from the sample volume and weight; c. by He pycnometry; d. by N_2 sorption porosimetry (numbers in parentheses are average pore diameters in nm by the BJH-desorption method); e. by a short beam three-point flexural bending test method; aerogels were to weak to test accurately, xerogels were too short; f. using a Johnson Matthey Mark I magnetic susceptibility balance with tightly packed powders of the samples.

Table S2. Elemental analysis data for RE xerogels, aerogels and polymer crosslinked aerogels.[a]

Sample (% water)[b]	**Elemental Analysis (%w/w)**[c,d]					
	C	**H**	**N**	**Metal**	**CO_3^{2-}**	**Cl_{Total} (Chloride)**
Sc-xero	17.71	3.32	1.69	34.4±0.3	2.0	5.2 (3.0)
Sc-aero (14.1)				32.6	4.4	3.9
Sc-aeroX				8.2	3.6	
Y-xero	11.88	2.77	0.91	46.4±0.2	2.6	8.0±0.2 (4.1)
Y-aero (10.3)				44.9	12.8	7.6 (6.8)
Y-aeroX				13.0	5.3	
La(PO)-xero	3.59	1.26	0.36	59.3	2.61	14.2 (7.7)
La(PO)-aero	16.39	2.82	4.70	45.4	2.18	8.6 (6.1)
La-aeroX				31.0	1.69	
Pr-xero	8.28	1.83	0.63	57.2±1.7	2.8±1.1	9.2±0.6 (8.0)
Pr-aero (7.9)				54.8±0.5	13.0	8.5±0.5 (6.0)
Pr-aeroX				18.3	5.70	
Nd-xero	8.40	1.85	0.86	58.1±1.3	2.5±0.6	7.9±0.5 (7.3)
Nd-aero (7.45)				56.2±0.6	10.8	7.2±0.2 (6.4)
Nd-aeroX				20.1	4.20	
Sm-xero	8.11	1.93	0.79	56.4±0.2	2.3±0.8	6.8±0.2 (4.9)
Sm-aero (8.01)				55.2±0.9	10.4	6.2±0.1 (5.9)
Sm-aeroX				18.1	5.2	
Eu-xero	5.17	1.51	0.43	62.1±2.9	4.3±0.3	7.3±0.6 (3.4)

Eu-aero (8.55)				56.7	11.3	5.6 (5.2)
Eu-aeroX				19.0	2.29	

Table S2 (continued)

Sample (% water)[b]	**Elemental Analysis (%w/w)**[c,d]					
	C	**H**	**N**	**Metal**	**CO_3^{2-}**	**Cl_{Total} (Chloride)**
Gd-xero	8.87	1.92	0.73	59.4±0.5	4.6±0.5	6.2±0.4 (3.5)
Gd-aero (7.81)				59.1±0.5	9.6	5.5±0.3 (5.1)
Gd-aeroX				20.6	5.79	
Tb-xero	9.12	1.94	0.81	57.1±0.9	2.8±0.4	5.8±0.1 (3.3)
Tb-aero (9.12)				55.3±2.2	8.97	5.3±0.1 (4.6)
Tb-aeroX				19.1	3.90	
Dy-xero	4.41	1.51	0.38	63.1±2.9	4.6±0.6	5.8±0.9 (3.3)
Dy-aero (6.29)				59.2±0.1	7.42	4.9±0.3 (4.1)
Dy-aeroX				21.0	4.72	
Ho-xero (1.45)	4.93	1.51	0.36	59.7±2.3	2.5±1.1	5.1±1.0 (2.6)
Ho-aero (6.94)				57.5	9.63	4.3
Ho-aeroX				20.6	4.28	
Er-xero	8.27	1.87	0.53	60.9±1.3	5.2±0.5	5.7±0.0 (3.2)
Er-aero (5.88)				59.9±0.2	7.50	4.8±0.2 (4.0)
Er-aeroX				22.4	5.34	
Tm-xero	6.93	1.81	0.29	61.1±0.8	2.4±1.3	4.8±0.4 (2.7)
Tm-aero (6.61)				59.5±1.3	6.43	4.7±0.2 (4.0)
Tm-aeroX				21.8	4.75	

Yb-xero	7.49	1.82	0.49	63.3±1.7	6.0±2.2	4.9±0.6 (2.8)
Yb-aero (5.39)				62.1±2.2	9.06	4.6±0.1
Yb-aeroX				21.9	1.96	

Table S2 (continued)

Sample (% water)[b]	Elemental Analysis (%w/w)[c,d]					
	C	H	N	Metal	CO_3^{2-}	Cl_{Total} (Chloride)
Lu-xero	4.45	1.56	0.55	63.0±2.8	2.9±0.1	4.9±0.6 (2.3)
Lu-aero (10.35)				60.2	4.03	4.4
Lu-aeroX				23.7	3.03	

Table 1S footnotes

a. RE analysis: Samples were prepared by dissolving 50 mg of sol-gel material in 1:1 HNO_3 under mild heating, followed by dilution to 100 mL with DI water. The RE element was determined on multiple emission lines using an Inductively Coupled Plasma Emission Spectrometer (Varian Vista-Pro). Carbonate analysis was conducted gravimetrically by NSL Analytical Inc. (7650 Hub Parkway, Cleveland, OH 44125) according to ASTM-D 460 Section 61-64 (Modified).
b. Numbers in parentheses is the % w/w water lost by heating at 105 ^{o}C for 24 h.
c. On a dry basis.
d. Wherever there is error information, analysis was conducted twice with different samples processed 6-9 months apart from one another.

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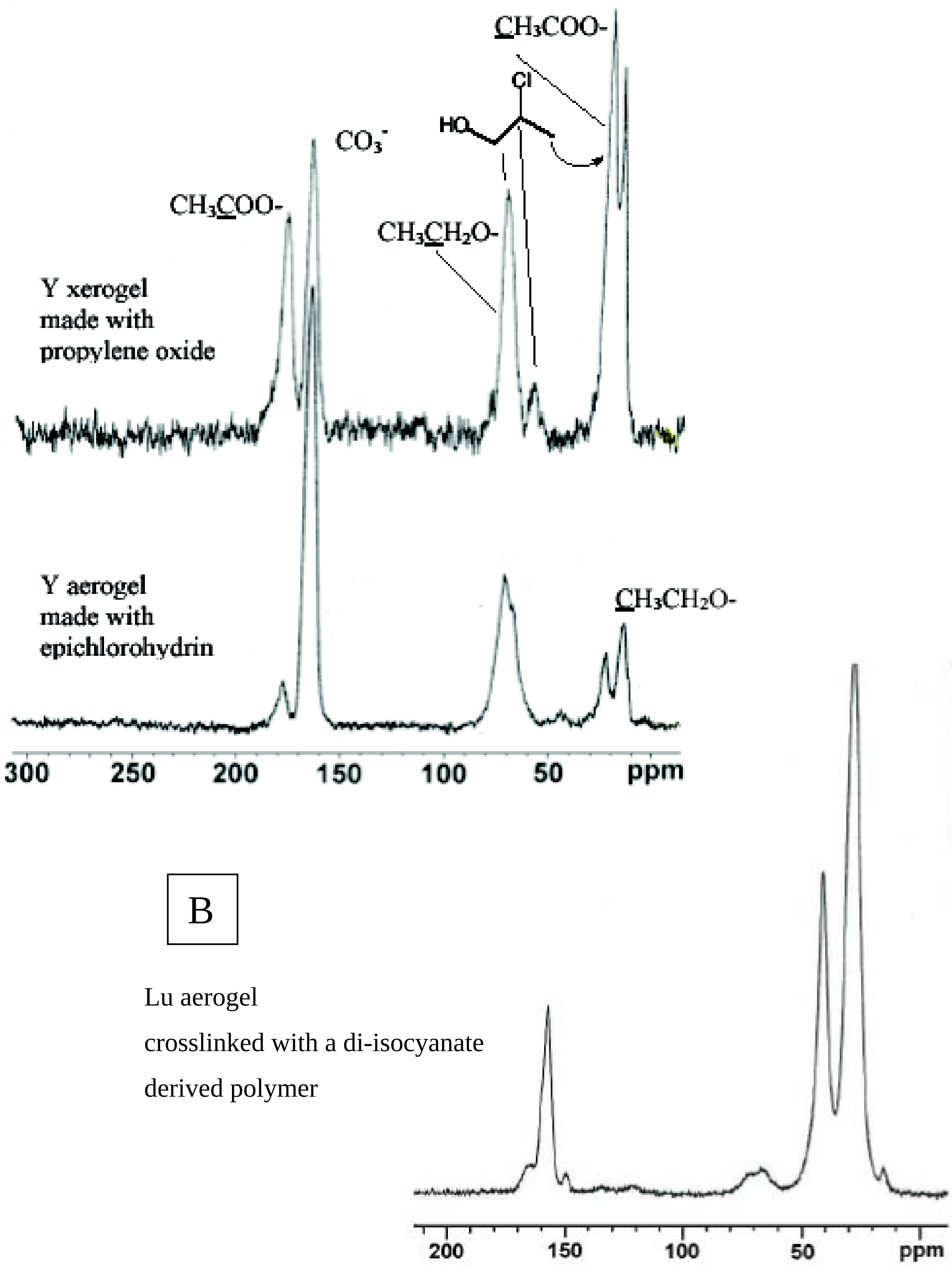
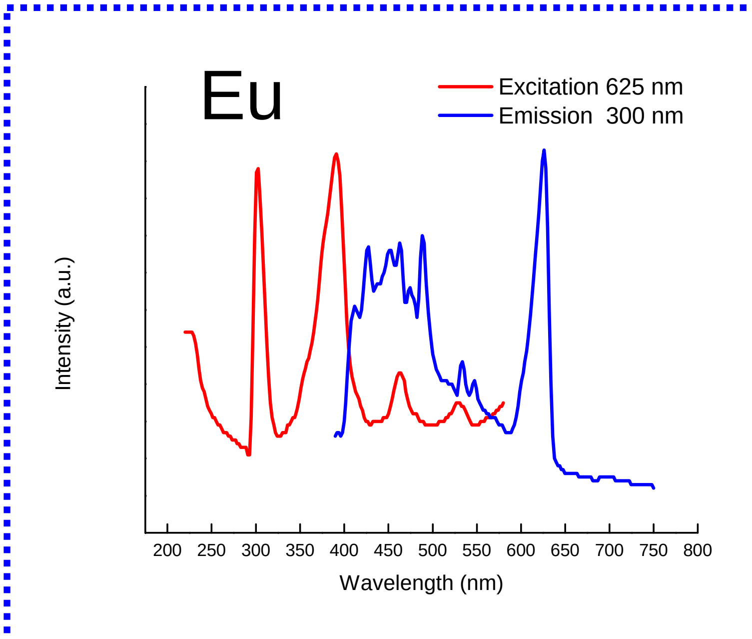


Figure S1. CP MAS ^{13}C NMR spectra of samples as shown.



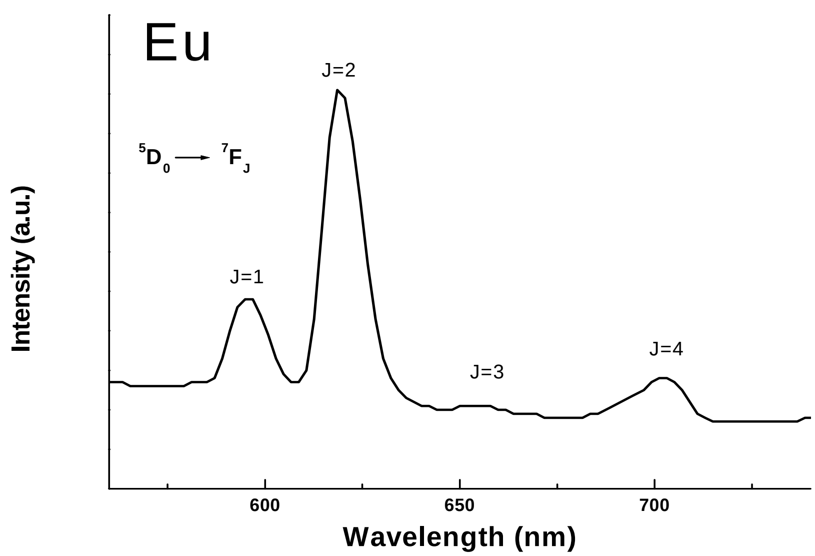


Figure S2-A. Photoluminescence data for Eu aerogels. <u>Top</u>: In red, excitation spectrum with λ_{em}=625 nm. Two major maxima are identified at 300 nm and at 390 nm. In blue, emission spectrum with excitation at 300 nm. <u>Bottom</u>: Emission spectrum with excitation at 390 nm.

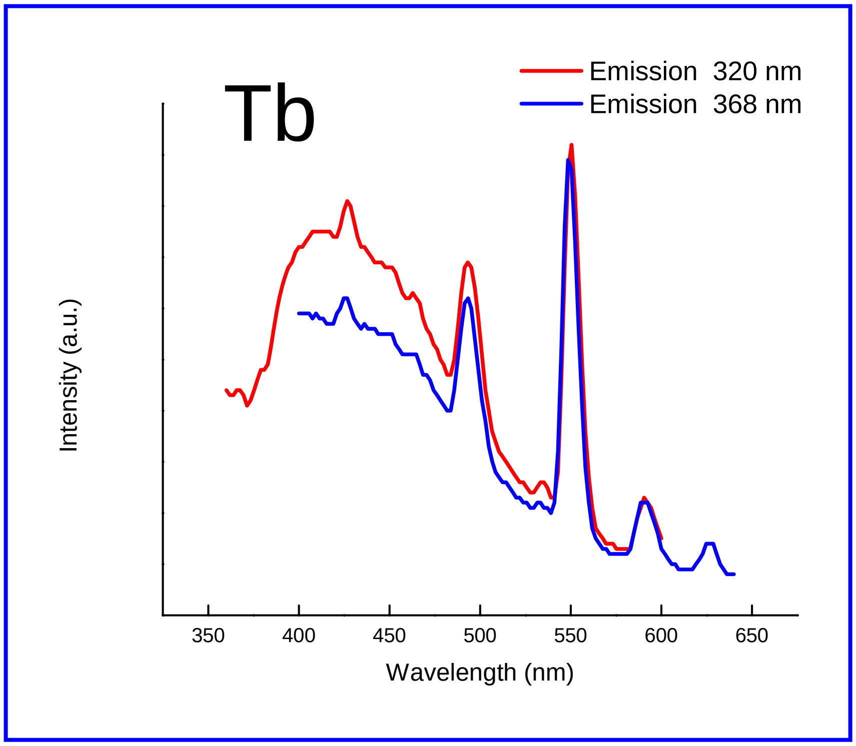


Figure S2-B. Photoluminescence data for Tb aerogels. Emission spectra (both colors) after excitation at the wavelengths indicated.