SUPPORTING INFORMATION

Multiscale investigations of europium(III) complexation with tetra-*n*-octyl diglycolamide confined in porous solid supports

Erin R. Bertelsen,[a] Nolan C. Kovach,[a] Benjamin J. Reinhart,[b] Brian G. Trewyn,[a,c] Mark R. Antonio[d] and Jenifer C. Shafer[a,e*]

[a.] Department of Chemistry, Colorado School of Mines, Golden, CO 80401, USA
[b.] Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA
[c.] Material Science Program, Colorado School of Mines, Golden, CO 80401, USA
[d.] Chemical Sciences & Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA
[e.] Nuclear Science and Engineering Program, Colorado School of Mines, Golden, CO 80401, USA
[*] Corresponding author email: jshafer@mines.edu

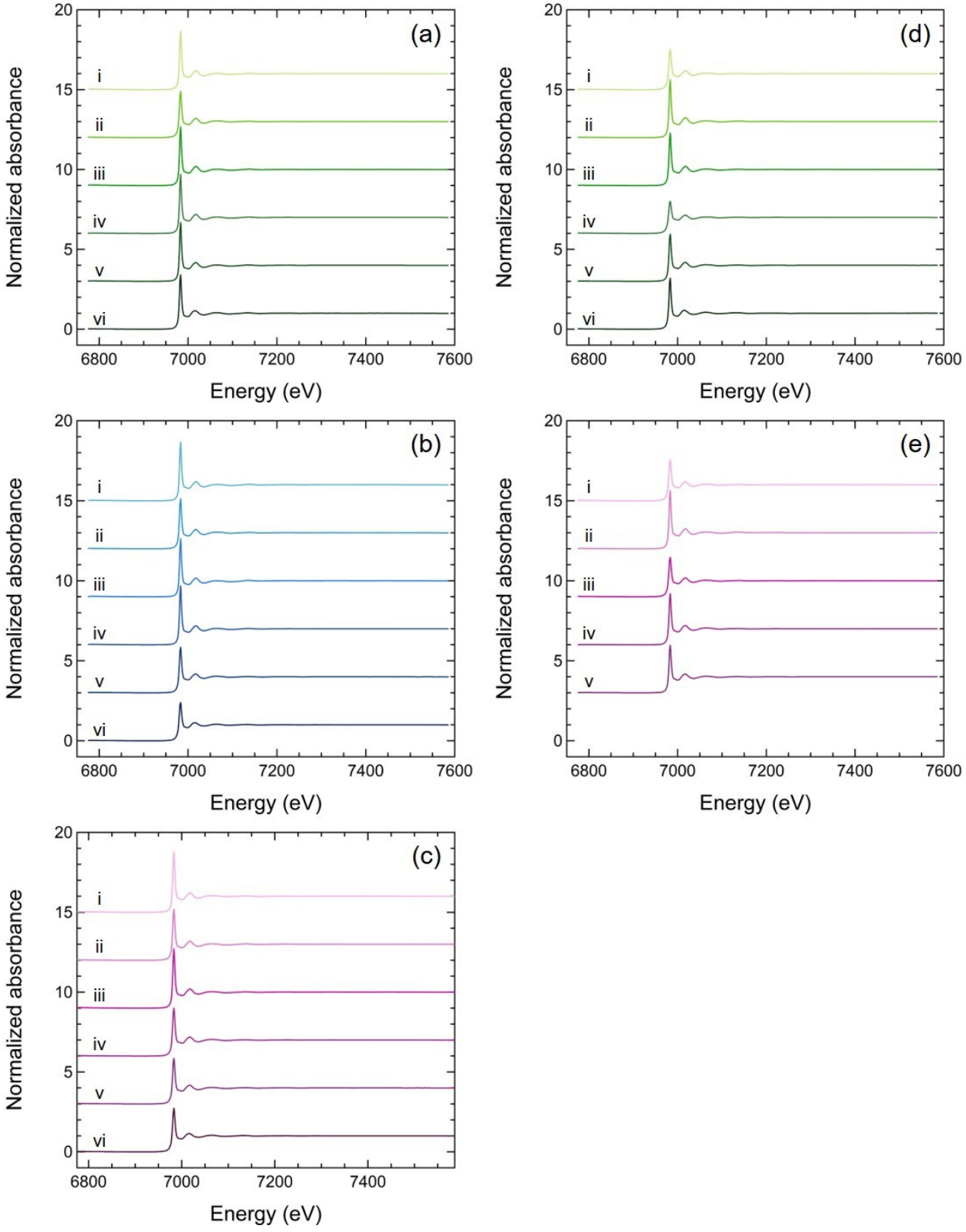

Figure S1. Normalized transmittance ($\ln(I_0/I_t)$) or fluorescence (I_f/I_0) absorbance spectrums for (a) 34 wt% TODGA OMC, (b) 22 wt% TODGA/4 wt% 2-octanol OMC, (c) 16 wt% TODGA/8 wt% 2-octanol OMC, (d) 40 wt% TODGA resin, and (e) 24 wt% TODGA/16 wt% 2-octanol resin. Roman numerals correspond to EXAFS and O phase-shift-corrected Fourier transform (FT) data (Figures 6 and 7 in the text) for each Eu^{3+} loading concentration.

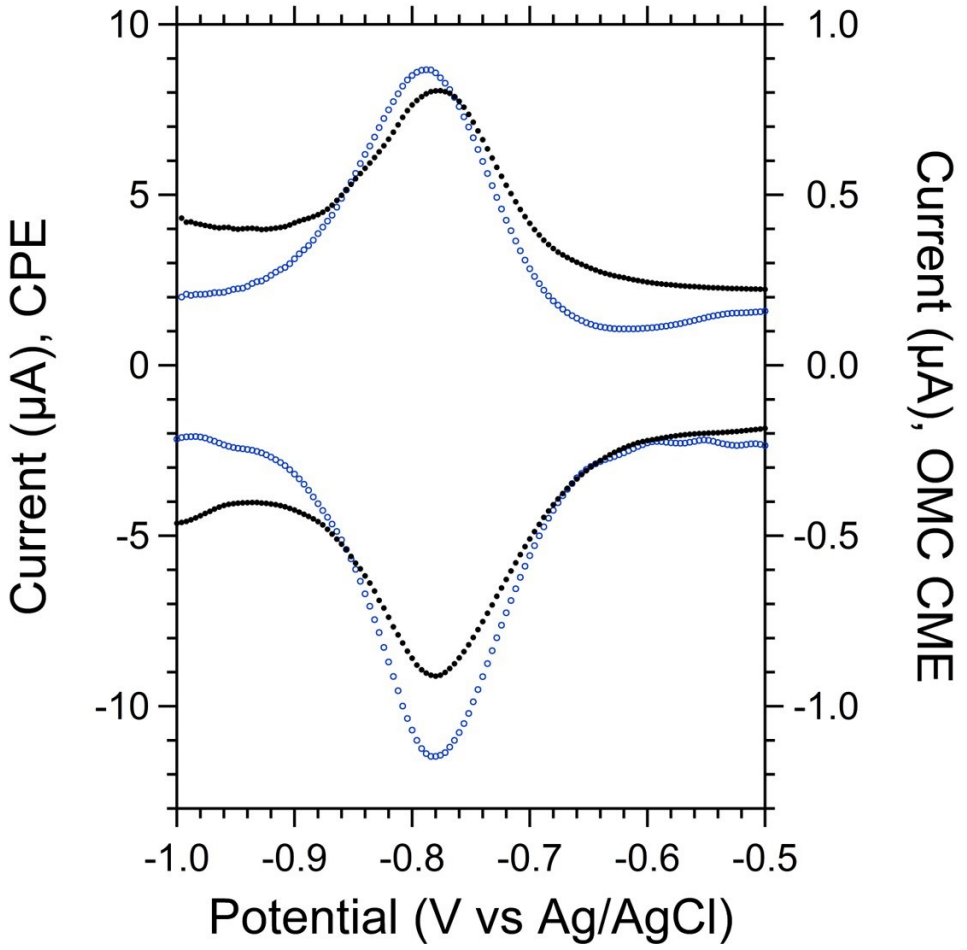

Figure S2. Differential pulse voltammograms for $Eu(TODGA)_3^{3+}$ complexes. Blue (open circles): $Eu(TODGA)_3(BiCl_4)_3$ in 3 M $LiNO_3$ using a carbon paste electrode (CPE). The $E_{1/2}$ is –0.782 V. Black (filled circles): 16 wt% TODGA/8 wt% 2-octanol OMC carbon microelectrode (CME) contacted with 0.100 M $Eu(NO_3)_3$/1 M HNO_3 in 1 M $LiNO_3$. The $E_{1/2}$ is –0.777 V.[1]

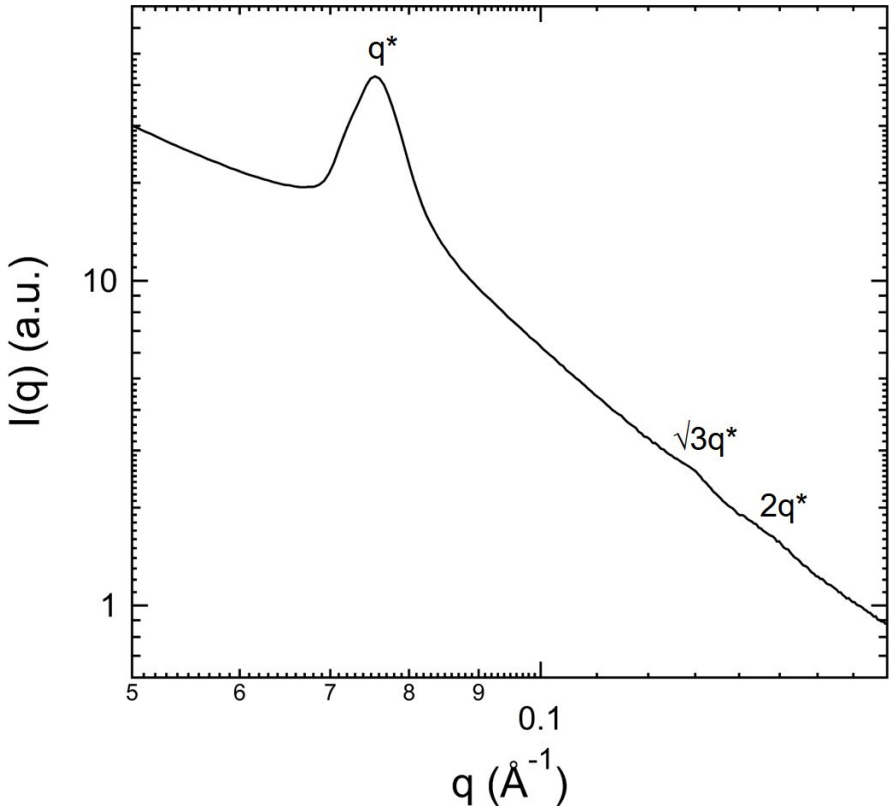

Figure S3. Enlarged SAXS profile for OMC material with a prominent peak at 0.0756 $Å^{-1}$ (100) and two poorly defined features at 0.130 (110) and 0.150 $Å^{-1}$ (200), indicative of a 2D hexagonal pore arrangement (refer to Figure 2a).[2]

Table S1. SAXS peaks unfunctionalized OMC and Amberchrom CG-71 (refer to Figure 2).

OMC, *q* (Å)	Amberchrom CG-71, *q* (Å)
0.0756	0.0797
	0.159
	1.29
1.64	

Table S2. SAXS peaks for 34 wt% TODGA OMC (refer to Figures 2–5). Diffraction peaks are indicated by italics.

	34 wt% TODGA OMC, *q* (Å)							
Eu^{3+} (mg g^{-1}):	0.0	1.1	12.2	15.0	10.0	28.6	73	460
Eu^{3+} to TODGA		1:81	1:7	1:6	1:9	1:3	1:1	5:1
	0.0745	0.0740	0.0740	0.0742	0.0742	0.0743	0.0743	0.0744
								0.289
				0.314		*0.310*	*0.316*	*0.310*
	0.370	0.353	0.341	0.330	0.344	0.342		*0.354*
								0.394
								0.398
								0.464
								0.499
								0.527
								0.537
								0.559
								0.562
								0.577
								0.588
								0.609
				0.628			*0.633*	*0.614*
								0.620
								0.669
								0.682
								0.690
								0.709
								0.726
								0.785
								0.786
								0.795
								0.803
								0.808
								0.844
								0.847
	1.49	1.50	1.48	1.50	1.49	1.50	1.49	1.56

Table S3. SAXS peaks for 22 wt% TODGA/4 wt% 2-octanol OMC (refer to Figures 2–5). Diffraction peaks are indicated by italics.

	22 wt% TODGA/4 wt% 2-octanol OMC, *q* (Å)							
Eu^{3+} (mg g^{-1}):	0.0	1.1	7.3	9.0	14.5	16.6	80	670
Eu^{3+} to TODGA		1:53	1:8	1:6	1:4	1:3	1:1	12:1
	0.0742	0.0740	0.0743	0.0744	0.0742	0.0743	0.0740	0.0744
								0.289
						0.317	*0.310*	*0.310*
	0.367	0.353	0.333	0.337	0.338	0.335	0.337	
							0.354	*0.354*
							0.393	*0.393*
							0.398	*0.398*
							0.465	*0.465*
							0.499	*0.498*
							0.527	*0.528*
							0.537	*0.537*
							0.558	*0.558*
							0.562	*0.562*
								0.578
							0.587	*0.586*
							0.609	*0.609*
							0.614	*0.613*
							0.620	*0.620*
							0.668	*0.668*
							0.689	*0.689*
							0.708	*0.709*
							0.726	*0.727*
							0.785	
							0.789	*0.787*
							0.795	*0.796*
							0.803	*0.803*
							0.817	*0.806*
							0.846	*0.846*
	1.49	1.52	1.50	1.50	1.51	1.51	1.51	1.54

Table S4. SAXS peaks for 16 wt% TODGA/8 wt% 2-octanol OMC (refer to Figures 2–5). Diffraction peaks are indicated by italics.

	16 wt% TODGA/8 wt% 2-octanol OMC, *q* (Å)							
Eu^{3+} (mg g^{-1}):	0.0	1.0	7.0	11.1	13.2	37.1	147	530
Eu^{3+} to TODGA		1:43	1:6	1:4	1:3	1:1	4:1	13:1
	0.0746	0.0741	0.0742	0.0745	0.0744	0.0745	0.0742	0.0744
								0.289
						0.309	*0.310*	*0.310*
	0.366	0.354	0.334	0.337	0.335	0.336	0.337	
							0.354	*0.354*
							0.394	*0.391*
							0.398	*0.398*
							0.464	*0.465*
							0.499	*0.498*
							0.527	*0.527*
							0.537	*0.537*
							0.559	*0.558*
							0.561	*0.562*
								0.576
							0.587	*0.587*
							0.609	*0.608*
							0.614	*0.613*
							0.620	*0.620*
							0.668	*0.668*
								0.681
							0.689	*0.689*
							0.708	*0.708*
							0.726	*0.726*
							0.785	*0.785*
							0.789	*0.788*
							0.794	*0.795*
							0.802	*0.803*
							0.808	*0.807*
							0.846	*0.846*
	1.51	1.51	1.49	1.50	1.49	1.49	1.51	1.52

Table S5. SAXS peaks for 40 wt% TODGA Resin and 24 wt% TODGA/16 wt% 2-octanol Resin (refer to Figures 2–5). Diffraction peaks are indicated by italics.

				40 wt% TODGA Resin, *q* (Å)				
Eu^{3+} (mg g^{-1}):	0.0	1.0	20.3	22.5	22.3	52	89	480
Eu^{3+} to TODGA		1:105	1:5	1:5	1:5	1:2	1:1	5:1
	0.0797	0.0782	0.0775	0.0782	0.0783	0.0784	0.0785	0.0779
	0.164	0.163	0.164	0.165	0.163	0.164	0.163	0.165
								0.293
		0.361	0.350	0.346	0.346	0.352	0.349	0.329
	1.29	1.34	1.36	1.35	1.36	1.37	1.36	1.38
				24 wt% TODGA/16 wt% 2-octanol Resin, *q* (Å)				
Eu^{3+} (mg g^{-1}):	0.0	1.0	17.5	20.5	25.7	43	52	580
Eu^{3+} to TODGA		1:62	1:4	1:3	1:2	2:3	1:1	9:1
								0.0086
	0.0792		0.0784	0.787	0.0776	0.0773	0.0787	0.0805
	0.163			0.166		0.166	0.164	
		0.358	0.343	0.341	0.342	0.342	0.341	0.345
	1.31	1.31	1.33	1.33	1.32	1.33	1.34	1.34

Table S6. SAXS slope analysis using selected scattering vector regions for OMC materials (refer to Figures 2–5).

	Eu^{3+} (mg g^{-1})	q ($Å^{-1}$)	Slope	q ($Å^{-1}$)	Slope
OMC	0.0	0.003–0.012	–3.18	0.085–0.200	–3.65
34 wt% TODGA OMC	0.0	0.004–0.012	–3.6	0.087–0.150	–3.94
	1.1	0.003–0.012	–3.90	0.085–0.150	–3.95
	122	0.003–0.012	–3.76	0.085–0.150	–3.97
	15	0.003–0.012	–3.69	0.085–0.150	–3.93
	10.0	0.003–0.012	–3.90	0.085–0.150	–3.89
	28.6	0.003–0.012	–3.81	0.085–0.150	–3.94
	73	0.003–0.012	–3.72	0.085–0.150	–3.87
	460	0.003–0.012	–3.74	0.085–0.150	–3.84
22 wt% TODGA/4 wt% 2-octanol OMC	0.0	0.003–0.012	–3.78	0.085–0.150	–3.93
	1.1	0.003–0.012	–3.82	0.085–0.150	–3.85
	7.3	0.003–0.012	–3.90	0.085–0.150	–3.84
	9.0	0.003–0.012	–3.92	0.085–0.150	–3.95
	14.5	0.003–0.012	–3.83	0.085–0.150	–3.86
	16.6	0.003–0.012	–3.88	0.085–0.150	–3.89
	80	0.003–0.012	–3.76	0.085–0.150	–3.90
	670	0.003–0.012	–3.69	0.085–0.150	–3.70
16 wt% TODGA/8 wt% 2-octanol OMC	0.0	0.003–0.012	–3.85	0.085–0.150	–4.17
	1.0	0.003–0.012	–3.86	0.085–0.150	–3.86
	7.0	0.003–0.012	–3.80	0.085–0.150	–3.84
	11.1	0.003–0.012	–3.86	0.085–0.150	–3.87
	13.2	0.003–0.012	–3.88	0.085–0.150	–3.89
	37.1	0.003–0.012	–3.83	0.085–0.150	–3.97
	147	0.003–0.012	–3.85	0.085–0.150	–3.86
	530	0.003–0.012	–3.84	0.085–0.150	–3.82

Table S7. SAXS slope analysis using selected scattering vector regions for Resin materials (refer to Figures 2–5).

	Eu^{3+} (mg g^{-1})	q ($Å^{-1}$)	Slope	q ($Å^{-1}$)	Slope
Amberchrom CG-71	0.0	0.006–0.012	–2.727	0.020–0.070	–3.053
40 wt% TODGA Resin	0.0	0.006–0.012	–3.063	0.020–0.070	–3.877
	1.0	0.006–0.012	–3.557	0.020–0.070	–3.810
	20.3	0.006–0.012	–3.567	0.020–0.070	–3.885
	22.5	0.006–0.012	–3.44	0.020–0.070	–3.934
	22.3	0.006–0.012	–3.29	0.020–0.070	–3.957
	52	0.006–0.012	–3.28	0.020–0.070	–3.968
	89	0.006–0.012	–3.25	0.020–0.070	–3.982
	480	0.006–0.012	–3.41	0.020–0.070	–4.021
24 wt% TODGA/16 wt% 2-octanol	0.0	0.005–0.012	–3.04	0.020–0.070	–3.871
	1.0	0.004–0.012	–3.51	0.020–0.070	–2.945
	17.5	0.004–0.012	–3.56	0.020–0.070	–3.214
	20.5	0.004–0.012	–3.49	0.020–0.070	–3.615
	25.7	0.004–0.012	–3.59	0.020–0.070	–3.408
	43	0.004–0.012	–3.52	0.020–0.070	–3.527
	52	0.003–0.012	–3.44	0.020–0.070	–3.310
	580	0.003–0.012	–3.32	0.020–0.070	–3.178

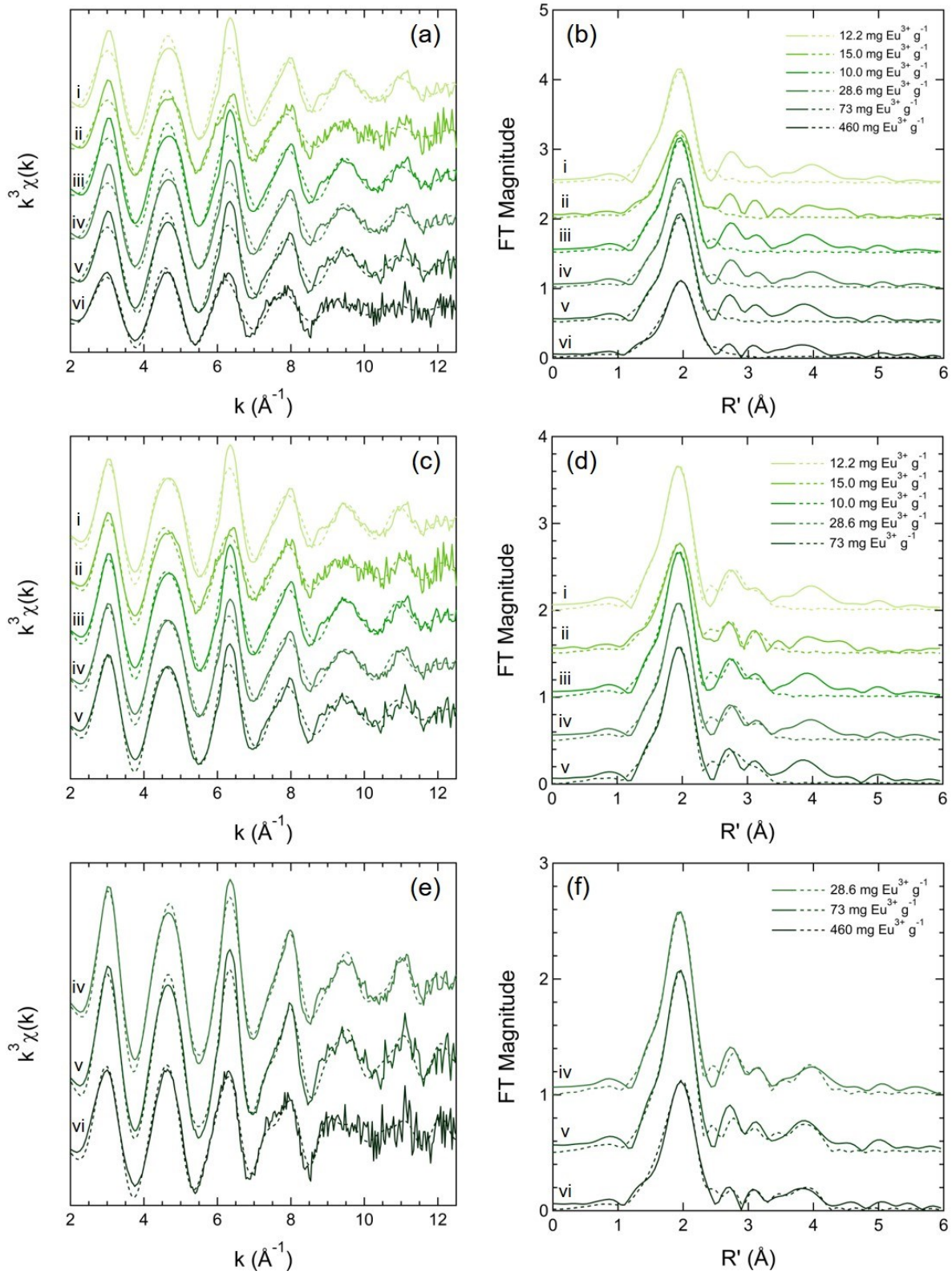

Figure S4. Eu L_3-edge $k^3\chi(k)$ EXAFS data (left) and the corresponding Fourier transform (FT) data (right) for 34 wt% TODGA OMC and the corresponding fits (dashed lines) for (a,b) a single-shell fit using a fixed O coordination number of 9, (c,d) a three-shell fit using fixed coordination numbers of 9 O, 6 C_a, and 6 C_b, and (e,f) a four-shell fit using a fixed coordination number of 9 O and fixing the coordination numbers for C_a and C_b after initial refinement, and floating coordination number for the fourth shell (Z = C or Eu). Eu^{3+} concentrations increase from (i) to (vi). EXAFS data are arbitrarily offset for clarity.

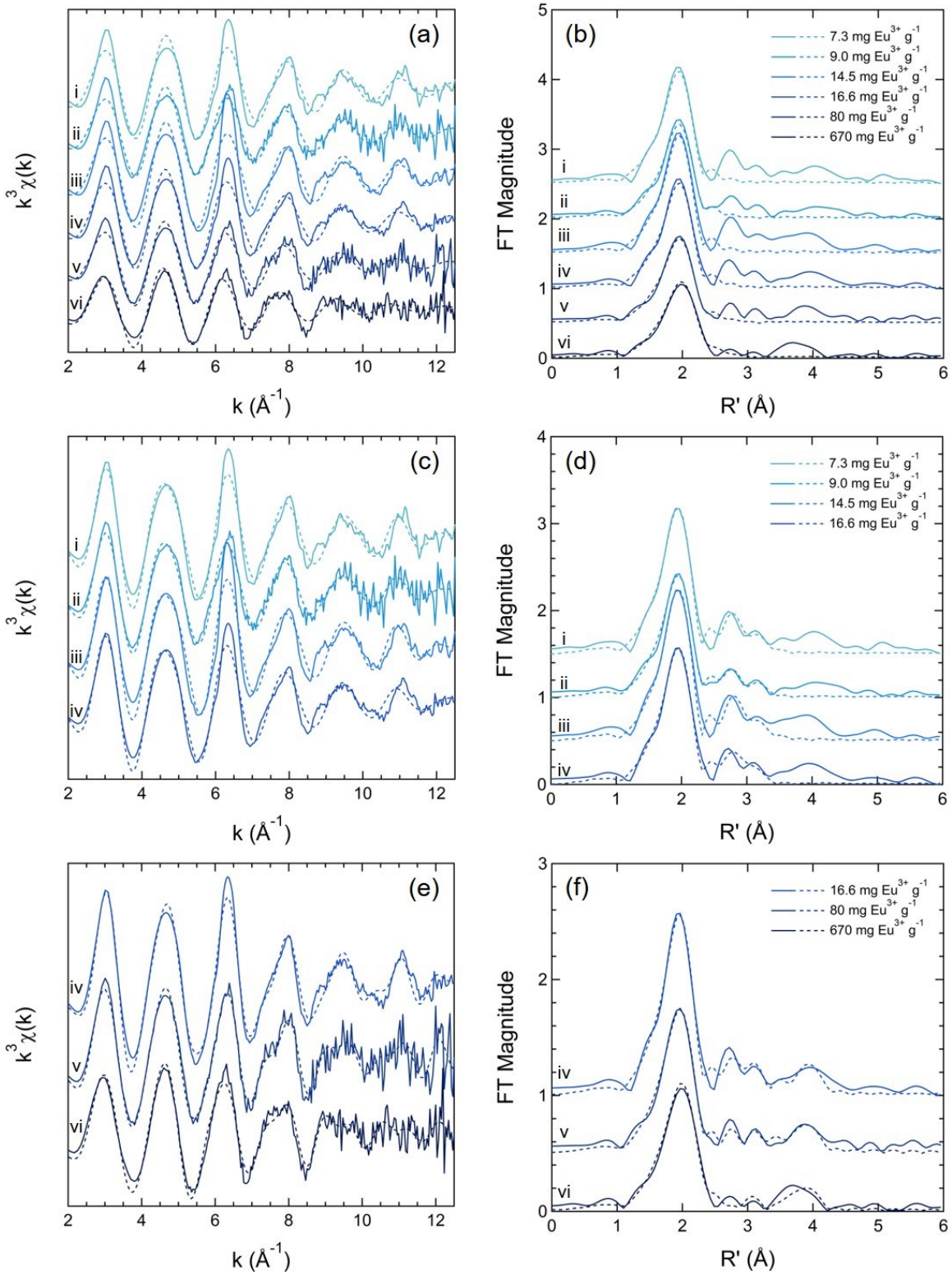

Figure S5. Eu L_3-edge $k^3\chi(k)$ EXAFS data (left) and the corresponding Fourier transform (FT) data (right) for 22 wt% TODGA/4 wt% 2-octanol OMC and the corresponding fits (dashed lines) for (a,b) a single-shell fit using a fixed O coordination number of 9, (c,d) a three-shell fit using fixed coordination numbers of 9 O, 6 C_a, and 6 C_b, and (e,f) a four-shell fit using a fixed coordination number of 9 O and fixing the coordination numbers for C_a and C_b after initial refinement, and floating coordination number for the fourth shell (Z = C or Eu). Eu^{3+} concentrations increase from (i) to (vi). A second carbon shell could not be fit for the highest Eu^{3+} concentration; therefore, the four-shell fit shown uses three shells (Eu–O, Eu–C, and Eu–Eu; see text for details). EXAFS data are arbitrarily offset for clarity.

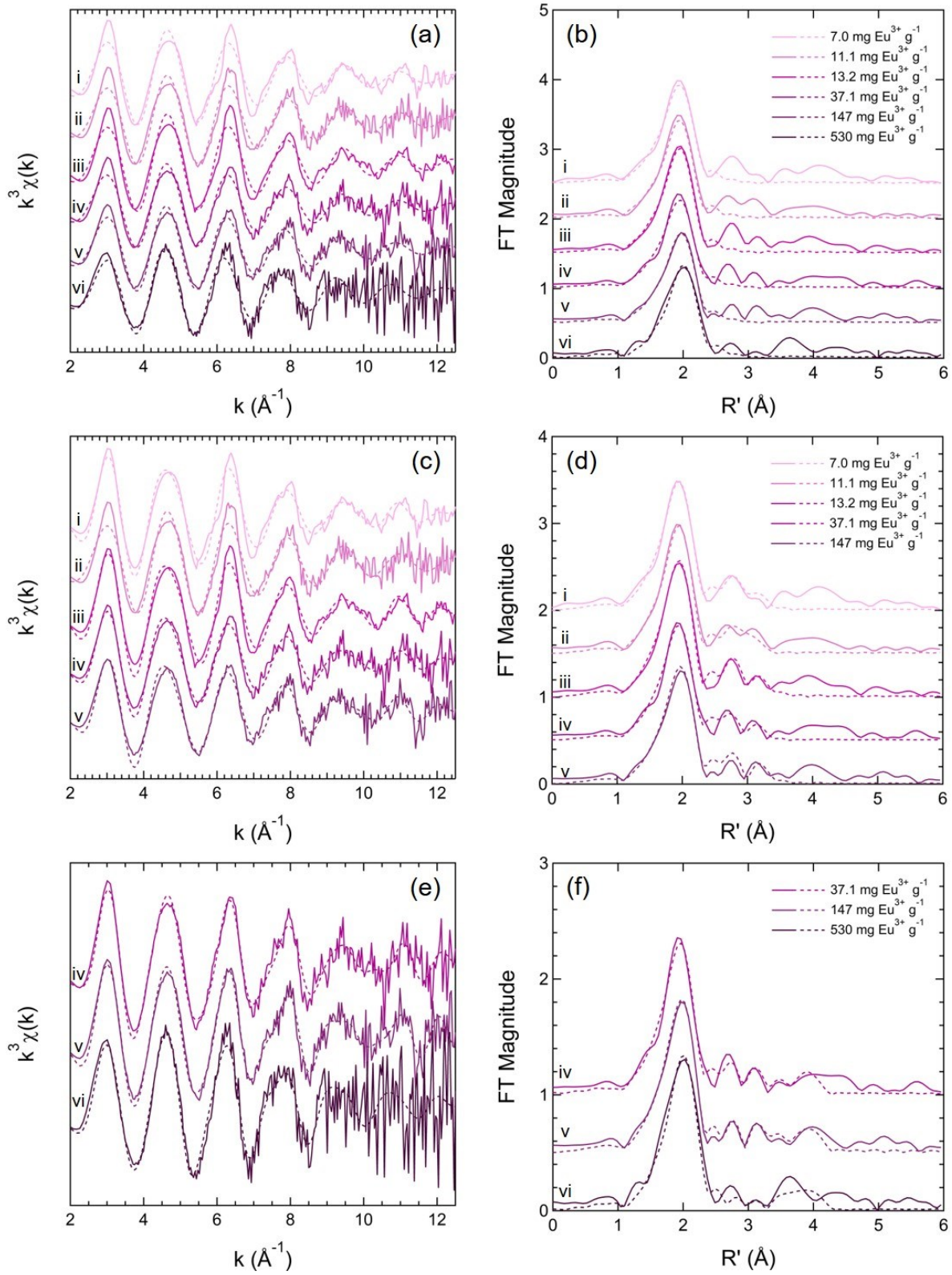

Figure S6. Eu L_3-edge $k^3\chi(k)$ EXAFS data (left) and the corresponding Fourier transform (FT) data (right) for 16 wt% TODGA/8 wt% 2-octanol OMC and the corresponding fits (dashed lines) for (a,b) a single-shell fit using a fixed O coordination number of 9, (c,d) a three-shell fit using fixed coordination numbers of 9 O, 6 C_a, and 6 C_b, and (e,f) a four-shell fit using a fixed coordination number of 9 O and fixing the coordination numbers for C_a and C_b after initial refinement, and floating coordination number for the fourth shell (Z = C or Eu). Eu^{3+} concentrations increase from (i) to (vi). EXAFS data are arbitrarily offset for clarity.

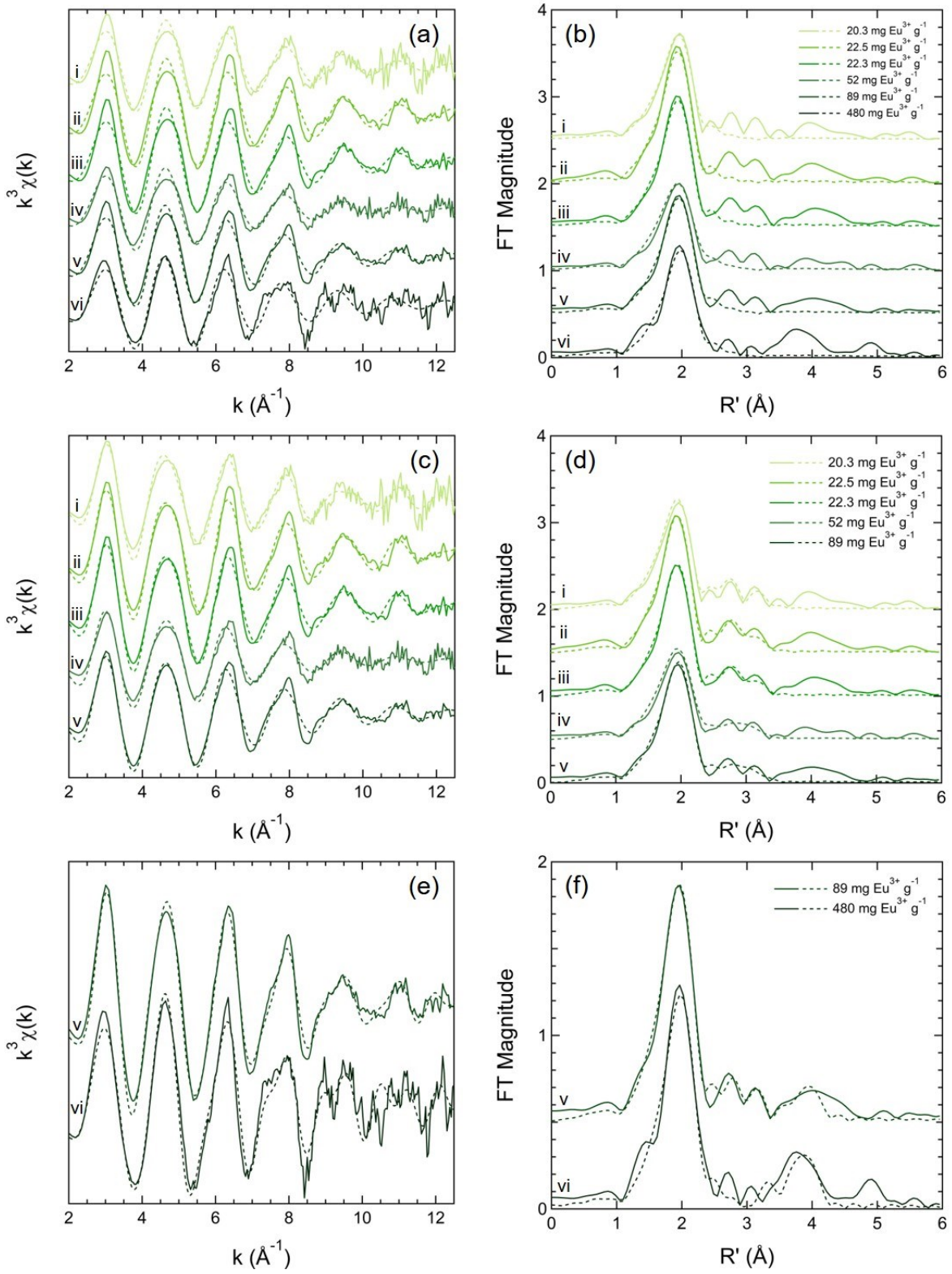

Figure S7. Eu L_3-edge $k^3\chi(k)$ EXAFS data (left) and the corresponding Fourier transform (FT) data (right) for 40 wt% TODGA resin and the corresponding fits (dashed lines) for (a,b) a single-shell fit using a fixed O coordination number of 9, (c,d) a three-shell fit using fixed coordination numbers of 9 O, 6 C_a, and 6 C_b, and (e,f) a four-shell fit using a fixed coordination number of 9 O and fixing the coordination numbers for C_a and C_b after initial refinement, and floating coordination number for the fourth shell (Z = C or Eu). Eu^{3+} concentrations increase from (i) to (vi). No carbon shells could not be fit for the highest Eu^{3+} concentration; therefore, the four-shell fit shown uses two shells (Eu–O and Eu–Eu; see text for details). EXAFS data are arbitrarily offset for clarity.

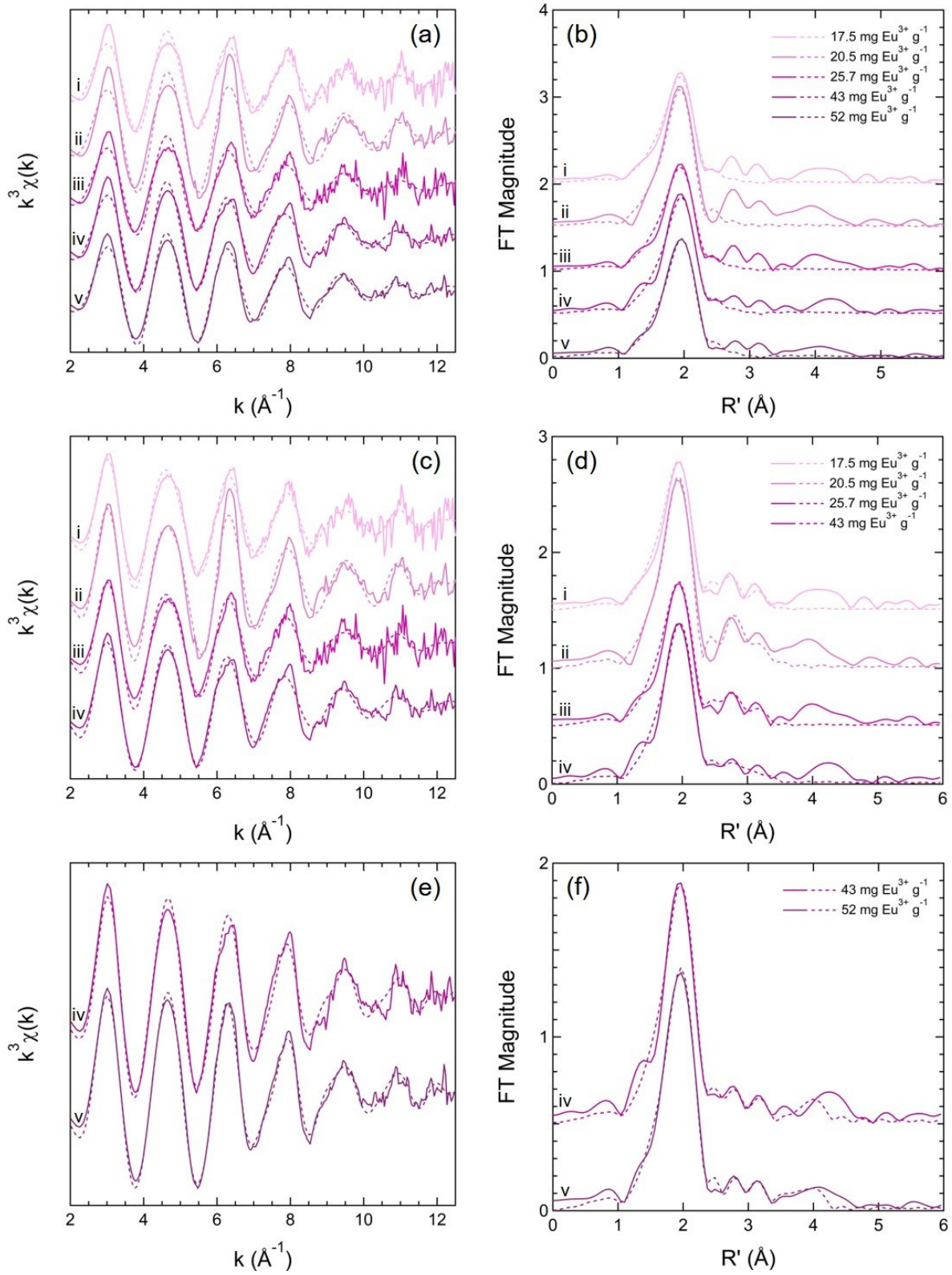

Figure S8. Eu L_3-edge $k^3\chi(k)$ EXAFS data (left) and the corresponding Fourier transform (FT) data (right) for 24 wt% TODGA/16 wt% 2-octanol resin and the corresponding fits (dashed lines) for (a,b) a single-shell fit using a fixed O coordination number of 9, (c,d) a three-shell fit using fixed coordination numbers of 9 O, 6 C_a, and 6 C_b, and (e,f) a four-shell fit using a fixed coordination number of 9 O and fixing the coordination numbers for C_a and C_b after initial refinement, and floating coordination number for the fourth shell (Z = C or Eu). Eu^{3+} concentrations increase from (i) to (v). EXAFS data are arbitrarily offset for clarity.

References

1. E. R. Bertelsen, N. C. Kovach, B. G. Trewyn, M. R. Antonio and J. C. Shafer, *Journal of Materials Chemistry C*, 2020, **8**, 6689-6700.
2. M. Joglekar, S. Pylypenko, M. M. Otting, J. S. Valenstein and B. G. Trewyn, *Chemistry of Materials*, 2014, **26**, 2873-2882.