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Kinetic and thermodynamic sorption studies of Fe(III) and Zr(IV) by DFO@Purolite, a desferrioxamine B based chelating resin

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Supplementary Information

Contents

I. Infrared spectroscopy

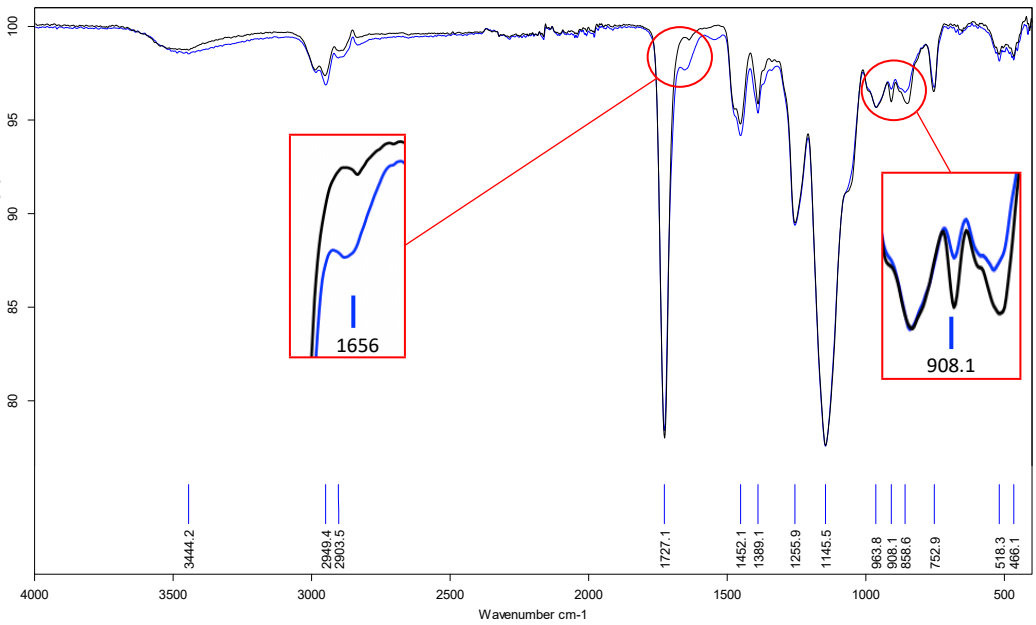

Figure S1. ATR FT-MIR spectra of pristine Purolite® ECR8209 (black line) and DFO@Purolite (red line) recorded at a resolution of 4 cm^{-1}.

II. Thermogravimetric analyses (TGA)

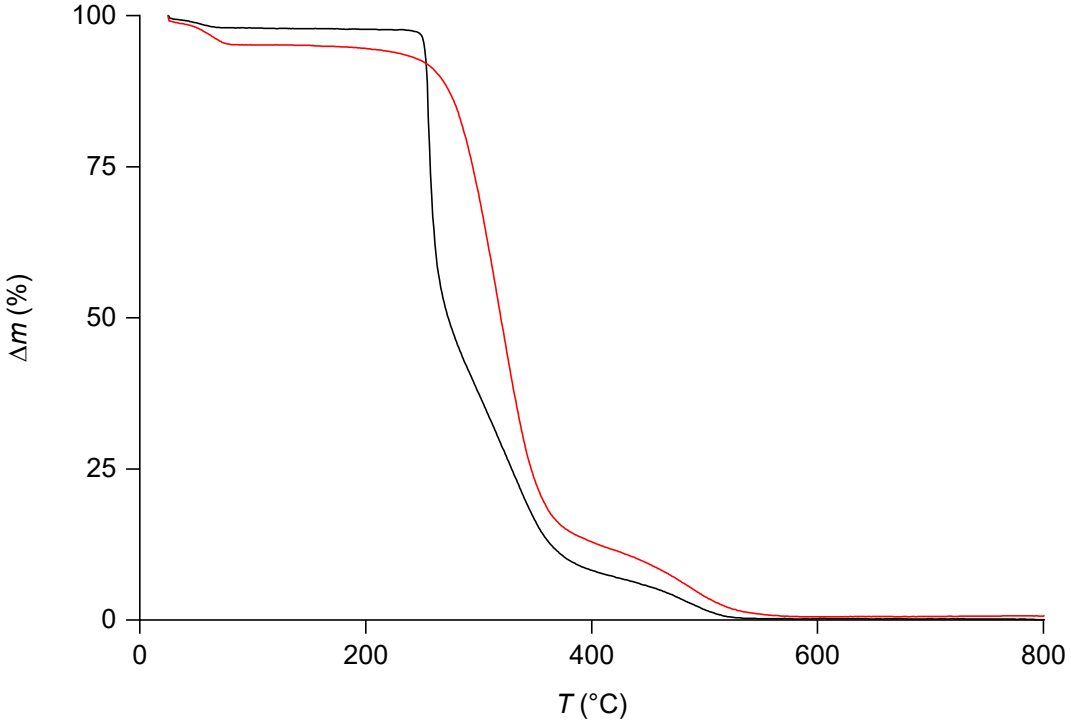

Figure S2. Thermograms of pristine Purolite® ECR8209 (black line) and DFO@Purolite (red line) recorded under a N_2 (30 mL min^{-1})/O_2 (10 mL min^{-1}) gas stream at a heating rate of 10 °C min^{-1}.

III. Scanning electron microscopy (SEM)

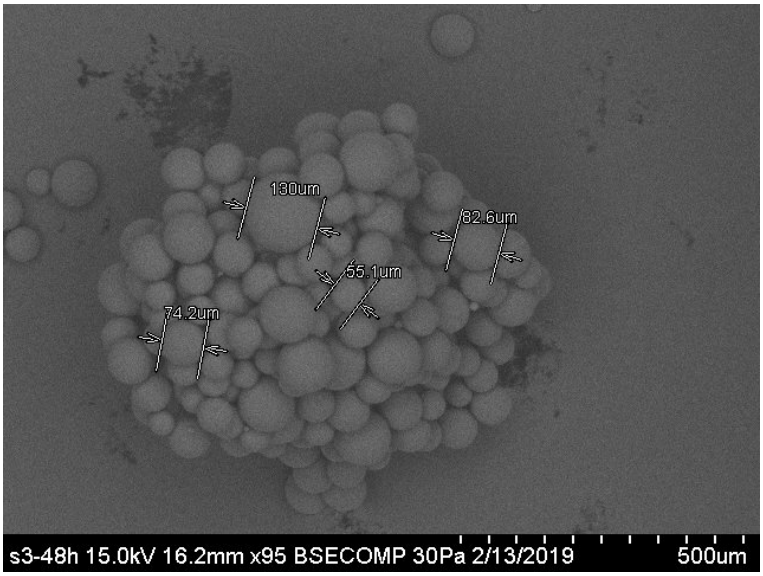

Figure S3. SEM image of gold-sputtered Purolite® ECR8209 resin. Magnification: ×95, working distance: 16.2 mm, acceleration voltage: 15.0 kV, vacuum: 30 Pa.

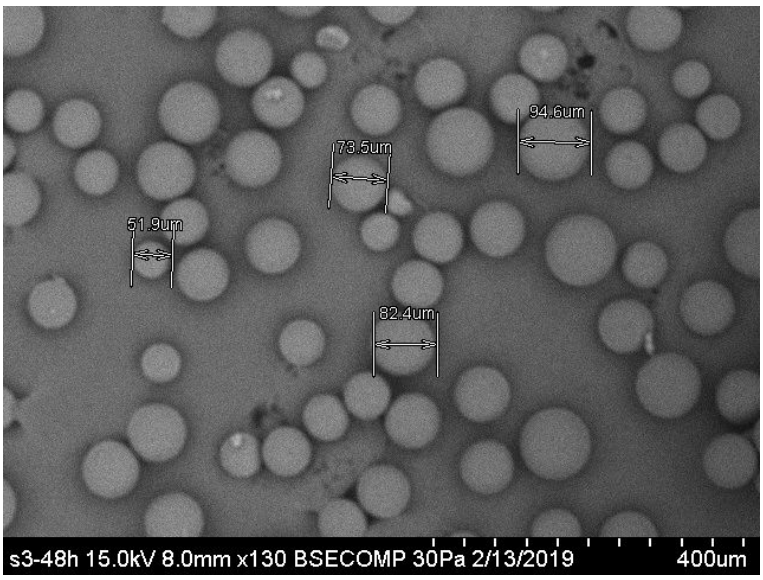

Figure S4. SEM image of gold-sputtered DFO@Purolite resin. Magnification: ×130, working distance: 8.0 mm, acceleration voltage: 15.0 kV, vacuum: 30 Pa.

IV. Luminescence emission spectroscopy

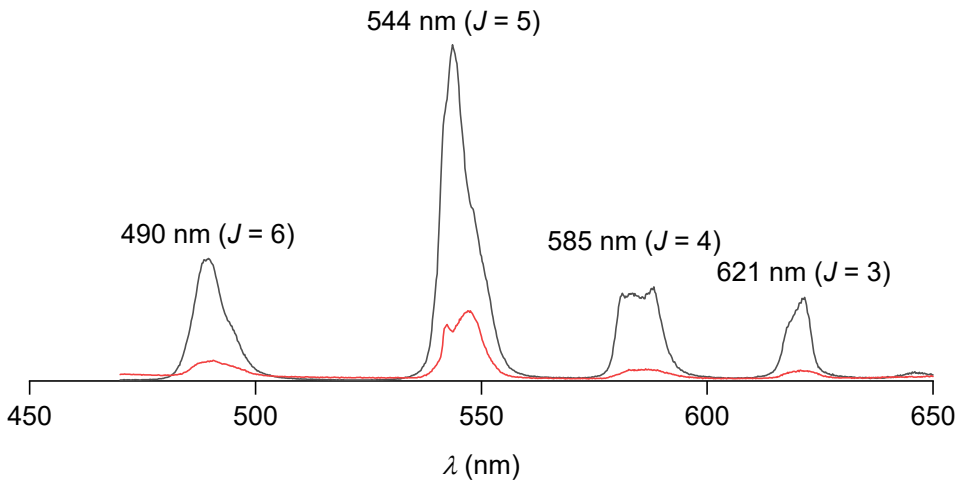

Figure S5. Emission spectra of a 0.015 M $Tb(NO_3)_3$ solution in 0.01 M HNO_3 showing the $^5D_4 \rightarrow {}^7F_J$ transitions (black line) and of $[Tb(DFO)H]^+$ at pH 9.6 (red line). λ_{ex} = 355 nm.

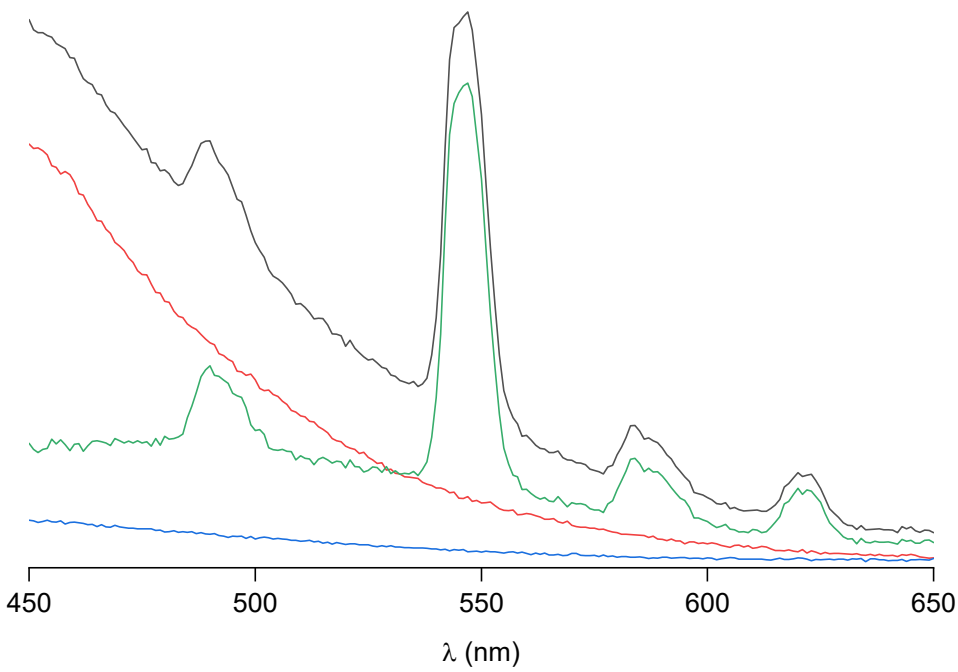

Figure S6. Emission spectra of pristine Purolite® ECR8209 (blue line), DFO@Purolite (red line), and Tb(DFO)@Purolite (black line) resins. The green line corresponds to the Tb(DFO)@Purolite spectrum after subtraction of the DFO@Purolite contribution. λ_{ex} = 355 nm, entrance and exit slit bandpass: 2 nm.

V. Two-photon microscopy

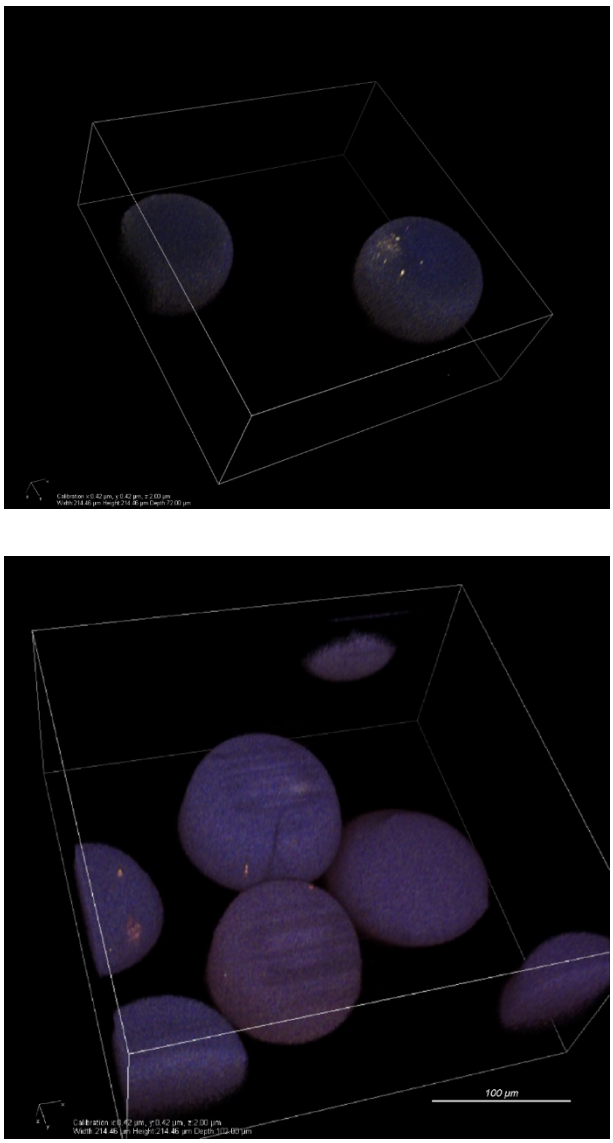

Figure S7. Two-photon microscopy images of DFO@Purolite (top) and Tb(DFO)@Purolite (bottom) beads showing the autofluorescence of DFO and luminescence of Tb(III), respectively, upon excitation at 750 nm by a NIR laser. Pictures collected on each of the four detection channels (400–492, 500–550, 563–588, 601–657 nm) were merged without any other spectral selection. The 3D z-stack views were constructed by superimposing the resulting images scanned along the depth (100 µm) of the samples.

VI. Auxiliary equilibrium constants

Table S1. Values of the global protonation constants (β°_{01z}) of $EDTA^{4-}$, of the hydrolysis (β°_{x0z}) and complex formation constants (β°_{xyz}) with $EDTA^{4-}$ of Fe^{3+} and Zr^{4+} at infinite dilution retrieved from the database implemented in the MEDUSA software.[a]

	x	y	z	$\log \beta_{mlh}$
$HEDTA^{3-}$	0	1	1	11.24
H_2EDTA^{2-}	0	1	2	18.04
H_3EDTA^{-}	0	1	3	21.19
H_4EDTA	0	1	4	23.42
H_5EDTA^{+}	0	1	5	22.12
H_6EDTA^{2+}	0	1	6	21.62
$H_4EDTA_{(s)}$	0	1	4	27.22
$Fe(EDTA)^{-}$	1	1	0	27.8
$Fe(HEDTA)$	1	1	1	29.3
$Fe(EDTA)(OH)^{2-}$	1	1	–1	19.97
$Fe_2(EDTA)_2(OH)_2^{4-}$	2	2	–2	41.8
$Fe(OH)^{2+}$	1	0	–1	–2.19
$Fe(OH)_2^{+}$	1	0	–2	–5.67
$Fe(OH)_3$	1	0	–3	–12.56
$Fe(OH)_4^{-}$	1	0	–4	–21.6
$Fe_2(OH)_2^{4+}$	2	0	–2	–2.95
$Fe_3(OH)_4^{5+}$	3	0	–4	–6.3
$Fe(OH)_{3(am)}$	1	0	–3	–4.891
$Fe_2O_{3(cr)}$	2	0	–6	–0.408
$FeOOH_{(s)}$	1	0	–3	–1
$Zr(EDTA)$	1	1	0	31.1
$Zr(OH)^{3+}$	1	0	–1	0.3
$Zr(OH)_2^{2+}$	1	0	–2	–1.7
$Zr(OH)_3^{+}$	1	0	–3	–5.1
$Zr(OH)_4$	1	0	–4	–9.7
$Zr_3(OH)_4^{8+}$	3	0	–4	–0.6
$Zr_4(OH)_8^{8+}$	4	0	–8	6
$ZrO_{2(s)}$	1	0	–4	–1.9

[a] I. Puigdomenech, *MEDUSA – Chemical Equilibrium Diagrams Program*, (2010), Royal Institute of Technology: Stockholm, Sweden (https://www.kth.se/che/medusa/).