Electronic Supplementary Information for

Modulating extraction and retention of fluorinated β-diketonate metal complexes in perfluorocarbons through the use of non-fluorinated neutral ligands

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Experimental

All chemicals used were obtained from commercial sources and used without further purification. Perfluoro-15-crown-5 ether (PFCE) was obtained from Exfluor Research Corp. (Round Rock, Texas). **LH** was obtained from SynQuest Laboratories (Alachua, Florida). Metal salts used for aqueous phase preparation for all extractions are listed below. ^{19}F NMR spectroscopic measurements of metal-doped PFCE were taken with a coaxial insert filled with D_2O for locking purposes using an Agilent MR 400 NMR spectrometer at 376 MHz and room temperature. Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on a Varian 710 Series ICP-OES in the EWRE lab in the Department of Civil, Architectural and Environmental Engineering at the University of Texas at Austin. UV-Vis absorbance spectra were taken using a Agilent Cary 60 UV-Vis spectrophotometer.

Metal Ion	**Metal Salt Used**	**Supplier**
Li^+	$LiCl$	Fisher Scientific
Na^+	$NaCl$	Fisher Scientific
K^+	KCl	Fisher Scientific
Rb^+	$RbCl$	Fisher Scientific
Cs^+	$CsCl$	Fisher Scientific
Mg^{2+}	$MgCl_2$	Fisher Scientific
Ca^{2+}	$CaCl_2$	Fisher Scientific
Sr^{2+}	$SrCl_2•6H_2O$	Alfa Aesar
Ba^{2+}	$BaCl_2•2H_2O$	Fisher Scientific
Mn^{2+}	$MnCl_2•4H_2O$	Strem
Fe^{3+}	$FeCl_3•6H_2O$	Mallinckrodt
Co^{2+}	$CoCl_2•6H_2O$	Acros
Ni^{2+}	$NiCl_2•6H_2O$	Acros
Cu^{2+}	$CuCl_2•2H_2O$	Acros
Zn^{2+}	$Zn(OAc)_2•2H_2O$	Fisher Scientific
Zr^{4+}	$ZrOCl_2•8H_2O$	Aldrich
Ru^{3+}	$RuCl_3•XH_2O$	Sigma Aldrich
Rh^{3+}	$RhCl_3•3H_2O$	Pressure Chem
Pd^{2+}	$Pd(NO_3)_2$	Aldrich
Ag^+	$AgNO_3$	Sigma Aldrich
Cd^{2+}	$CdCl_2$	Sigma Aldrich
Ir^{3+}	$IrCl_3•3H_2O$	Sigma Aldrich
Pt^{2+}	K_2PtCl_4	Sigma Aldrich
Ga^{3+}	$Ga(NO_3)_3$	Alfa Aesar
In^{3+}	$InCl_3$	Strem
Pb^{2+}	$Pb(NO_3)_2$	Mallinckrodt
Sc^{3+}	$Sc(OTf)_3$	Alfa Aesar
Y^{3+}	$Y(NO_3)_3$	Lindsay Chemical Company
La^{3+}	$La(OTf)_3$	Sigma Aldrich
Nd^{3+}	$Nd(OTf)_3$	Sigma Aldrich
Eu^{3+}	$Eu(OTf)_3$	Sigma Aldrich
Gd^{3+}	$Gd(OTf)_3$	Sigma Aldrich
Tb^{3+}	$Tb(OTf)_3$	Sigma Aldrich
Dy^{3+}	$Dy(OTf)_3$	Sigma Aldrich
Yb^{3+}	$Yb(OTf)_3$	Sigma Aldrich
Lu^{3+}	$Lu(OTf)_3$	Sigma Aldrich
Th^{4+}	$Th(NO_3)_4$	Strem
UO_2^{2+}	$UO_2(OAc)_2•2H_2O$	JT Baker

Extraction of metal ions into the fluorous phase

For monovalent metal ions, a solution of **LH** in PFCE (400 µL, 10 mM) was added to an aqueous solution of the metal salt (400 µL, 10 mM, 100 mM MES pH 6) in a 1.5 mL Eppendorf tube. The biphasic mixture was mixed for 30 minutes using a Labquake Shaker Rotisserie. The biphasic mixture was then centrifuged (3,000 rcf, 3 min) to separate the aqueous and fluorous phases. The aqueous phase was diluted with 2% HNO_3 and the metal content was determined via ICP-OES. For M^{n+} ions the concentration of **LH** in PFCE was increased to n*10 mM. Due to precipitation of metal salts of Fe^{3+}, Ga^{3+}, and Ru^{3+} during aqueous phase preparation with pH 6 MES buffer, the following buffers were used for aqueous phase preparation of these ions: Fe^{3+} - 100 mM acetate buffer pH 5; Ga^{3+} 100 mM HEPES buffer pH 8; Ru^{3+} 100 mM acetate buffer pH 4.

Leaching of metal ions from fluorous phase with HNO_3

The fluorous phase from each forward extraction (125 µL) was added to 1M HNO_3 (2.5 mL) and mixed with a Benchmark Scientific H2024 incubator shaker at 40°C using the mix setting for 24 hrs. The biphasic mixture was then centrifuged (3,000 rcf, 3 min) to separate the aqueous and fluorous phases. The aqueous phase was diluted with 2% HNO_3 and the metal content was determined via ICP-OES. The same protocol was used for leaching of metal ions synergistically extracted with nitrogen donors.

Leaching of metal ions from fluorous phase with HEPES Buffer

A solution of $M^{n+}(L)_n$ in PFCE was synthesized using the same extraction procedure and standardized to 5 mM metal ion concentration in the fluorous phase. Metal-doped PFCE (500 µL) was added to 100 mM HEPES buffer (500 µL, pH 7.4, 100 mM NaCl) in a 1.5 mL Eppendorf tube. The biphasic mixture was mixed with a Benchmark Scientific H2024 incubator shaker at 37°C using the mix setting for 24 hrs. The biphasic mixture was then centrifuged (3,000 rcf, 3 min) to separate the aqueous and fluorous phases. The aqueous phase was diluted 100x with 2% HNO_3 and the metal content was determined via ICP-OES. The same protocol was used for leaching of metal ions synergistically extracted with nitrogen donors.

Leaching of metal ions from fluorous phase with EDTA

A solution of $M^{n+}(L)_n$ in PFCE was synthesized using the same extraction procedure and standardized to 5 mM metal ion concentration in the fluorous phase. Metal-doped PFCE (500 µL) was added to 100 mM HEPES buffer (500 µL, pH 7.4, 100 mM NaCl, 50 mM EDTA) in a 1.5 mL Eppendorf tube. The biphasic mixture was mixed with a Benchmark Scientific H2024 incubator shaker at 37°C using the mix setting for 24 hrs. The biphasic mixture was then centrifuged (3,000 rcf, 3 min) to separate the aqueous and fluorous phases. The aqueous phase was diluted with 2% HNO_3 and the metal content was determined via ICP-OES. The same protocol was used for leaching of metal ions synergistically extracted with nitrogen donors.

Synergistic extraction of metal ions with nitrogen donors

Extractions were carried out as described above with the addition of nitrogen donor ligands. The amount of nitrogen donor added to the extraction mixture was based on the number of expected open coordination sites of the metal ion and the denticity of the nitrogen donor. E.g., 1.5 equivalents of pyridine were added for each expected open coordination site, so 3 equivalents pyridine relative to Ni^{2+}. For bi- and tri-dentate nitrogen donors 1.5 equivalents was added relative to M^{n+}.

X-ray crystallography

X-ray diffraction experiments were performed in the University of Texas at Austin X-Ray Diffraction Laboratory. Single crystals were selected using a microscope, coated in Paratone oil and mounted on nylon loops.

Crystallographic data was acquired in an Agilent Supernova diffractometer equipped with an AtlasS2 CCD using collimating mirror monochromators with μ-focus CuKα radiation (λ= 1.5418 Å) or MoKα (λ= 0.71073 Å) radiation at 100 K, provided by an Oxford 700 series Cryostream device. Data was reduced and absorption corrected with the aid of the Agilent Technologies CrysAlysPro V 1.171.37.31 software.

Structures were solved using Olex2[1], by SHELXS[2] or SHELXT[3] and refined with full-matrix least-squares calculations on *F*2 by using SHELXL.[4] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the refinement using a riding model. ORTEP diagrams were created using Olex2.

Specific details regarding the refinement of each structure can be found in the corresponding .cif files. These files were deposited in the Cambridge Crystallographic Data Centre (deposition number 2091566 and 2091567). These files can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Luminescence lifetime measurements

Luminescence lifetimes of Eu^{3+}-doped PFCE solutions were obtained on a QuantaMaster 4 photon technology international (PTI) instrument. Luminescent decays of the 615 nm emission of Eu^{3+} was measured after excitation of the sample at 320 nm. Each decay was fitted as a single exponential decay with a χ^2 between 0.9 and 1.1.

Acquisition and Simulation of CW X-band EPR Spectra

Solutions of Cu(**L**)$_2$, Cu(**L**)$_2$(Py)$_2$, and Cu(**L**)$_2$TMEDA in PFCE were prepared using extraction procedures described above, loaded into 4 mm quartz EPR tubes, and then flash-frozen in liquid nitrogen. All spectra were obtained on a Bruker EMX EPR spectrometer equipped with an EMX

high-sensitivity probehead. All spectra were acquired using the parameters listed in Table S1. Spectra were simulated using the EasySpin software.[5] The specific parameters input for each simulation are given in Table S2.

Equations for extraction equilibria and distribution ratio calculations

The equilibrium for the extraction of neutral metal complexes with variable nuclearity assuming only anionic **L** ligands is given by Equation S1.

$$a\mathrm{M}^{n+} + n\mathbf{L}^{-} \rightleftharpoons$$

$$K_{ex} = [\mathrm{M}_a\mathbf{L}_{a*n}]_{\mathrm{fl}}/[\mathrm{M}^{n+}]^a[\mathbf{L}^{-}]^{a*n} \qquad \text{S1}$$

The distribution ratio, *D*, of the metal ion between the fluorous and aqueous phases is therefore given by Equation S2.

$$D = \frac{[\mathrm{M}^{n+}]_{fl,total}}{[\mathrm{M}^{n+}]_{aq,total}} = \frac{\sum_a a[\mathrm{M}_a\mathbf{L}_{a*n}]_{fl}}{\sum_b[\mathrm{M}\mathbf{L}_b^{a-b}]_{aq}} = \frac{\sum_a aK_{ex}[\mathrm{M}^{n+}]^{a-1}[\mathbf{L}^{-}]^{a*n}}{\sum_b \beta_b[\mathbf{L}^{-}]^b} \qquad \text{S2}$$

Where β_b is the stability constant given by Equation S3.

$$\beta_b = [\mathrm{M}\mathbf{L}_b^{n-b}]_{aq}/[\mathrm{M}^{n+}][\mathbf{L}^{-}]^b \qquad \text{S3}$$

Table S1. Experimental parameters for CW X-band EPR spectra.

Receiver Gain	2.00E+03
Phase	0 deg
Harmonic	1
Modulation Frequency	100.000 kHz
Modulation Amplitude	4.000 G
Conversion Time	9.000 ms
Time Constant	5.120 ms
Sweep Time	45.000 s
Microwave Frequency	9.40 GHz
Microwave Power	0.1262 mW
Resolution in x	5000
Center Field	3200.000 G
Sweep Width	2000.000 G
Temperature	115.0 K

Table S2. EasySpin parameters for simulated EPR spectra.

	CuL_2	**CuL_2+py**	**CuL_2+TMEDA**
S	1/2	1/2	1/2
g_x	2.055	2.113	2.092
g_y	2.055	2.113	2.092
g_z	2.293	2.273	2.278
Nucleus	Cu	Cu	Cu
A_x, MHz	55	12	37
A_y, MHz	55	12	37
A_z, MHz	498	564	525
g-strain$_x$	0.01	0.07	0.06
g-strain$_y$	0.01	0.07	0.06
g-strain$_z$	0.02	0.12	0.10
Microwave Frequency, GHz	9.42427	9.42427	9.42427
Temperature, K	115	115	115

Table S3. Structural parameters for Zn(**L**)$_2$(H$_2$O)$_2$, Zn(hfac)$_2$(H$_2$O)$_2$[6] and Zn(acac)$_2$(H$_2$O)$_2$[7]. The structural parameters of [Zn^{2+}(**L**)$_2$(H$_2$O)$_2$] resemble those of the known [Zn(acac)$_2$(H$_2$O)$_2$] and [Zn(hfac)$_2$(H$_2$O)$_2$].

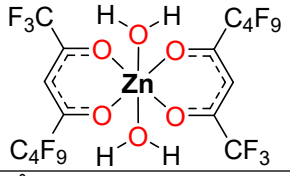
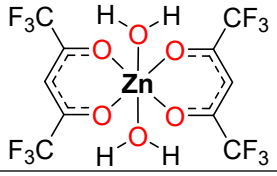
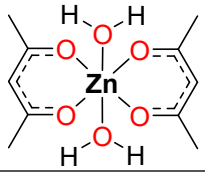
Compound	[Zn(**L**)$_2$(H$_2$O)$_2$]	Zn(hfac)$_2$(H$_2$O)$_2$[6]	Zn(acac)$_2$(H$_2$O)$_2$[7]
			
Bond Lengths (Å)			
Zn-O1	2.034(2)	2.052	2.0319(8)
Zn-O2	2.070(2)	2.061	2.0492(8)
Zn-OH$_2$	2.145(2)	2.099	2.1849(8)
Angles (°)			
∠O1-Zn-O2	88.58(9)	88.991	90.53(3)

Table S4. Magnetic parameters of Cu(**L**)$_2$, Cu(**L**)$_2$(Py)$_2$, Cu(**L**)$_2$TMEDA, and previously reported Cu(acac)$_2$ complexes determined by CW X-band EPR and simulations. Ligand abbreviations: acac = acetylacetonate, hfacac = hexafluoroacetylacetonate, bpy = 2,2'-bipyridine, en = ethylenediamine.

Compound	**g_{II}**	**$g_{\perp}$**	**A_{II}, MHz**	**$A_{\perp}$, MHz**
Cu(acac)$_2$[1]	2.285	2.060	520	35
Cu(hfacac)$_2$(bpy)[1]	2.299	2.056	486	77
Cu(acac)(en)[1]	2.184	2.033	621	77
Cu(**L**)$_2$	2.293	2.055	498	55
Cu(**L**)$_2$(Py)$_2$	2.273	2.113	546	12
Cu(**L**)$_2$TMEDA	2.278	2.092	525	37

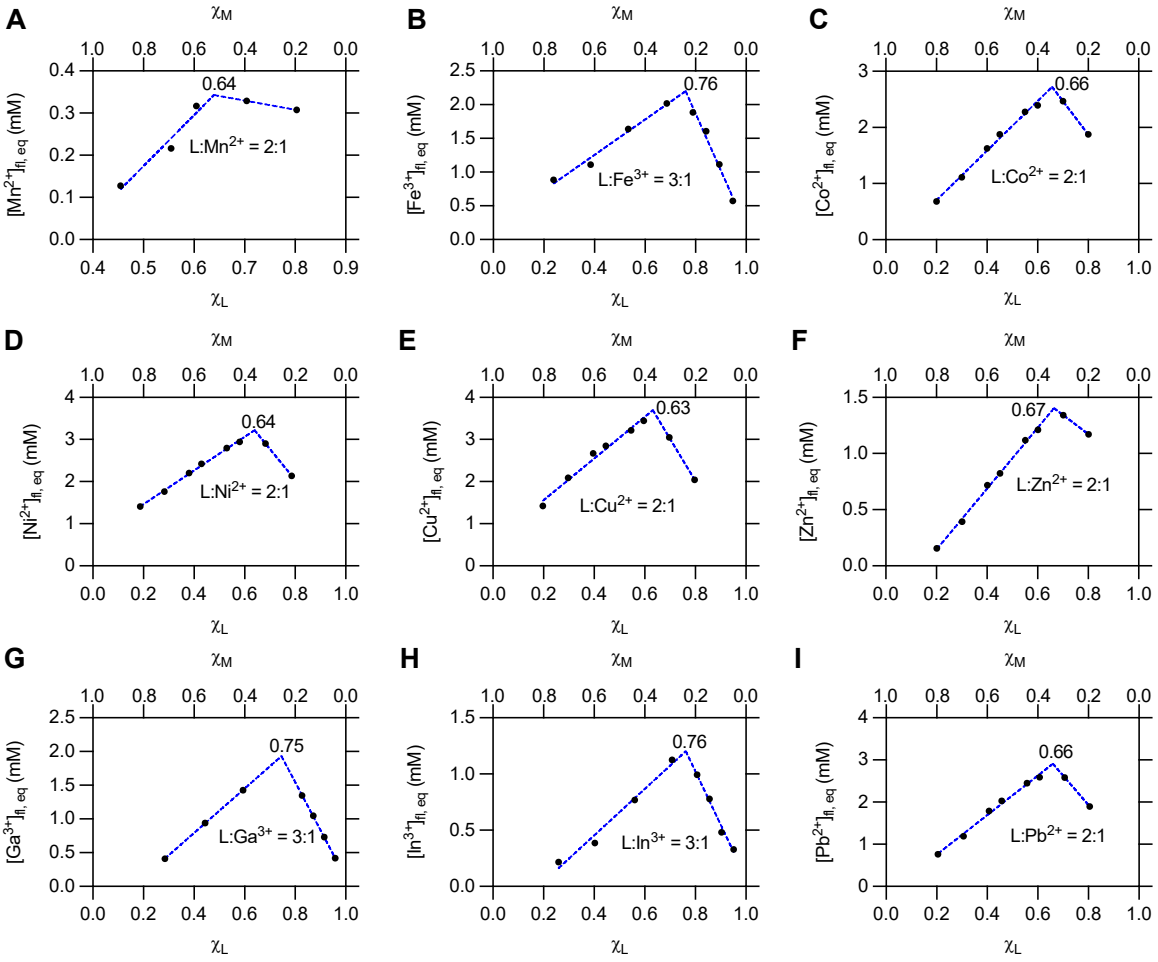


Figure S1. Job's continuous variance plots of for Mn^{2+} (A), Fe^{3+} (B), Co^{2+} (C), Ni^{2+} (D), Cu^{2+} (E), Zn^{2+} (F), Ga^{3+} (G), In^{3+} (H), and Pb^{2+} (I) with **LH**. $[\mathbf{LH}]_{fl,\,ini} + [M^{n+}]_{aq,\,ini}$ = 10 mM (100 mM MES buffer pH 6 for all metal ions except Fe^{3+} (100 mM acetate buffer pH 5) and Ga^{3+} (100 mM HEPES buffer pH 8)). Extraction time = 30 mins. Mole fractions of **LH** and M^{n+} indicated as χ_L and χ_M respectively.

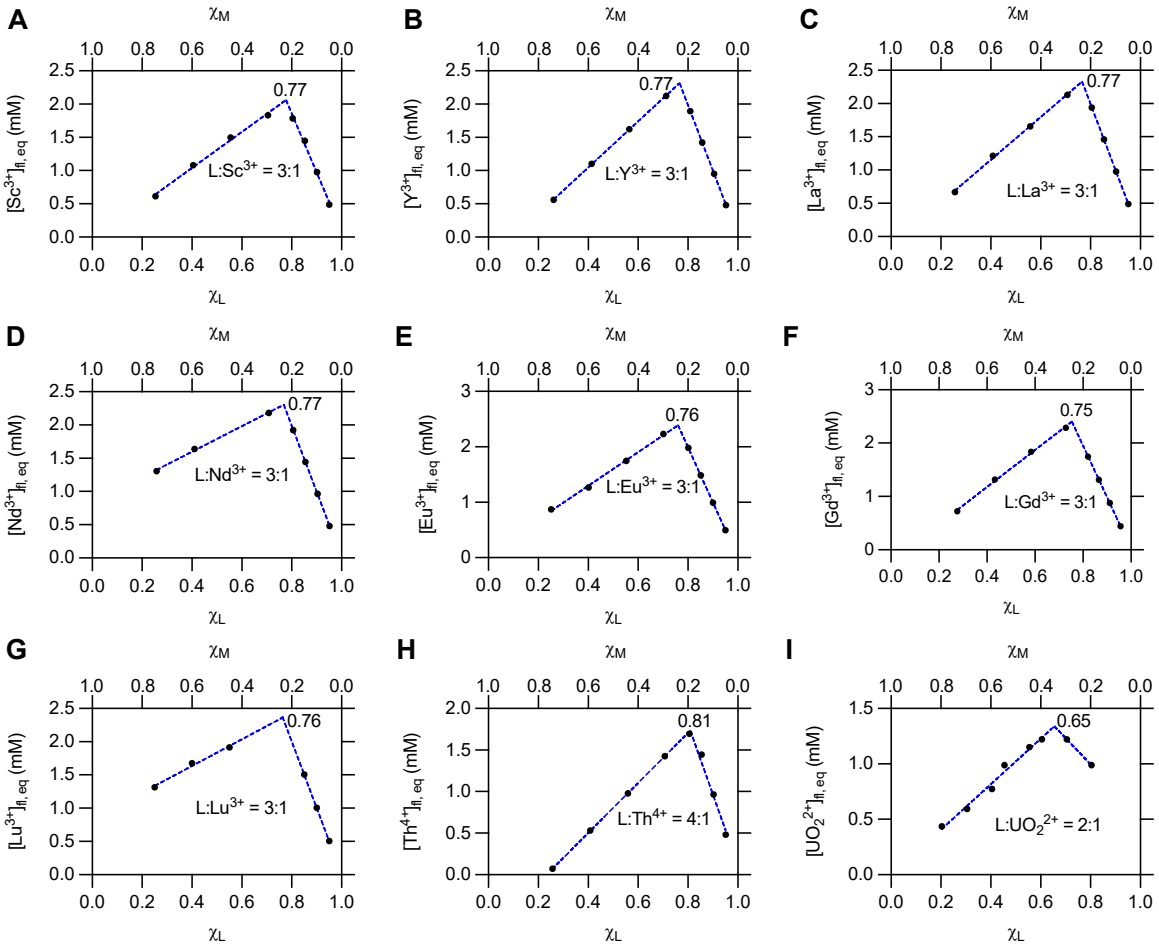


Figure S2. Job's continuous variance plots of for Sc^{3+} (A), Y^{3+} (B), La^{3+} (C), Nd^{3+} (D), Eu^{3+} (E), Gd^{3+} (F), Lu^{3+} (G), Th^{4+} (H), and UO_2^{2+} (I) with **LH**. $[\mathbf{LH}]_{fl,\ ini} + [M^{n+}]_{aq,\ ini}$ = 10 mM (100 mM MES buffer pH 6 for all metal ions). Extraction Time = 30 mins. Mole fractions of **LH** and M^{n+} indicated as χ_L and χ_M respectively.

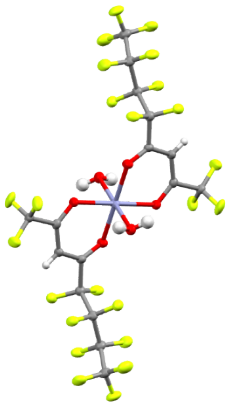


Figure S3. Crystal structure of $Zn(\mathbf{L})_2(H_2O)_2$. Thermal ellipsoid plots at 50 % probability are shown. Metal complex $[Zn^{2+}(\mathbf{L})_2(H_2O)_2]$ is octahedral and crystallizes as colorless crystalline planks in the P-1 space group. In the solid-state the aquo ligand are trans to each other while the two $\mathbf{L}^-$ ligands occupy the equatorial plane.

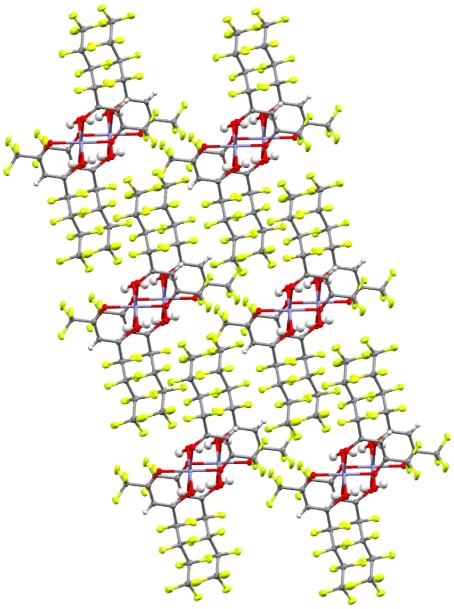


Figure S4. Packing of $Zn(\mathbf{L})_2(H_2O)_2$ showing segregation of perfluorinated C_4F_9 chains and ZnO_6 units. The packing of the $Zn(\mathbf{L})_2(H_2O)_2$ structure is characterized by assembly of the perfluorinated C_4F_9 chains while the Zn acac core forms a linear hydrogen bonded network enabled by the acac oxygens and the water ligands. Thermal ellipsoid plots at 50 % probability are shown.

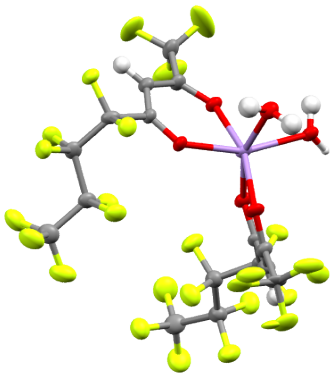


Figure S5. Crystal structure of Mn(**L**)$_2$(H_2O)$_2$. Thermal ellipsoid plots at 50 % probability are shown. Compound [Mn^{2+}(**L**)$_2$(H_2O)$_2$] forms yellow needles in the P-*1* space group. In this case, the aquo ligands are *cis* in the six-coordinate metal complex.

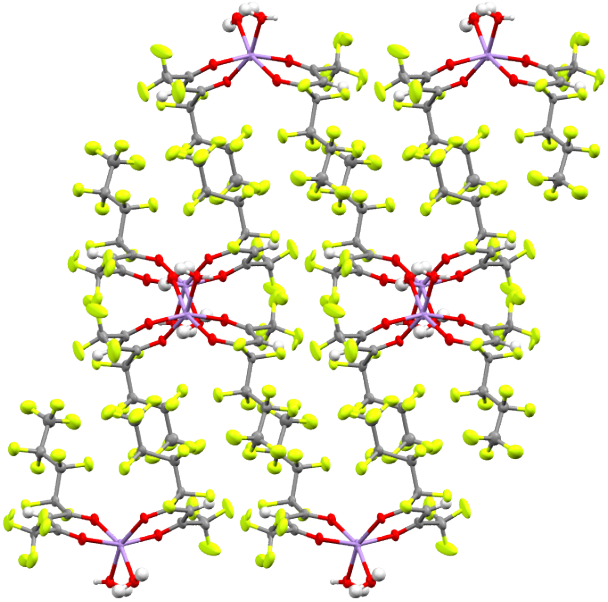


Figure S6. Packing of Mn(**L**)$_2$(H_2O)$_2$ showing segregation of perfluorinated C_4F_9 chains and MnO_6 units. The C_4F_9 substituents assemble together while the Mn acac coordination sphere is held in place by hydrogen bonding interactions with between alternating Mn acac units. Thermal ellipsoid plots at 50 % probability are shown.

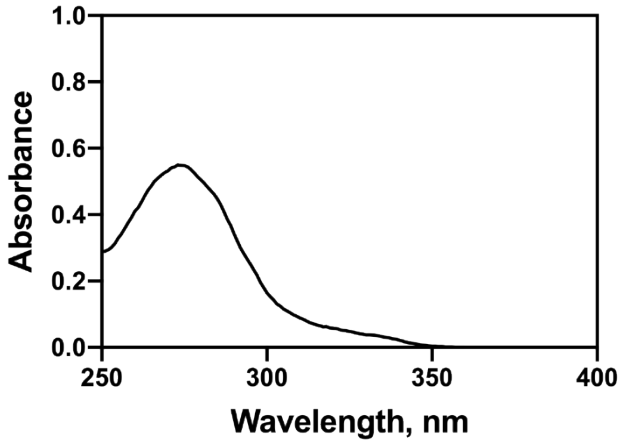


Figure S7. UV-vis absorbance spectrum of Ni(**L**)$_2$ in PFCE, [Ni^{2+}] = 10 μM.

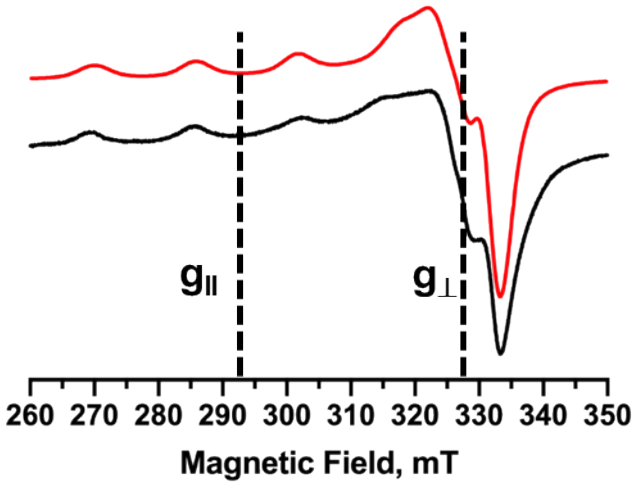


Figure S8. CW X-band EPR spectrum (black) of Cu(**L**)$_2$ acquired in frozen solution of PFCE (20 mM) at 115 K along with the simulated spectrum (red).

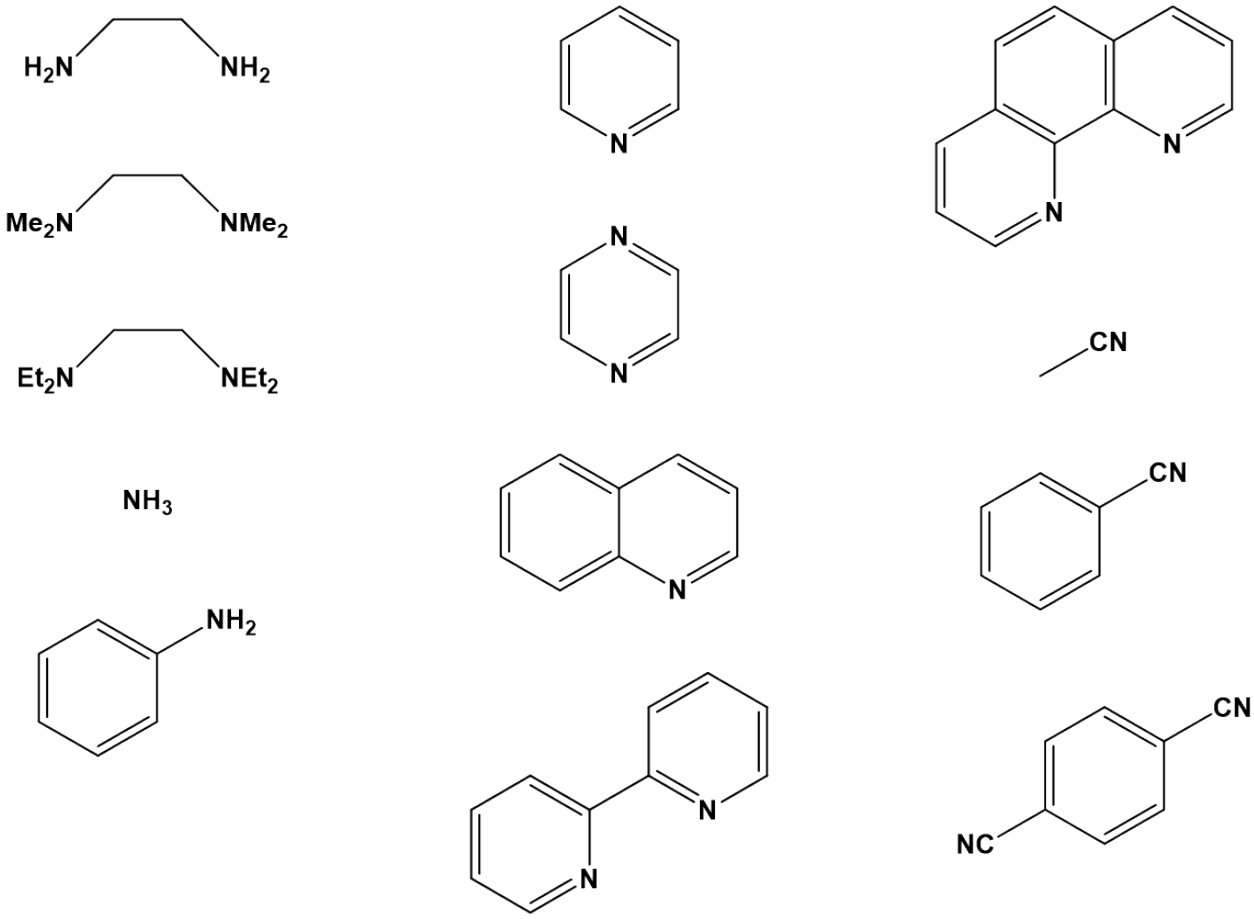


Figure S9. Nitrogen donor ligands (**A**) examined as synergistic extractants for Ni^{2+}.

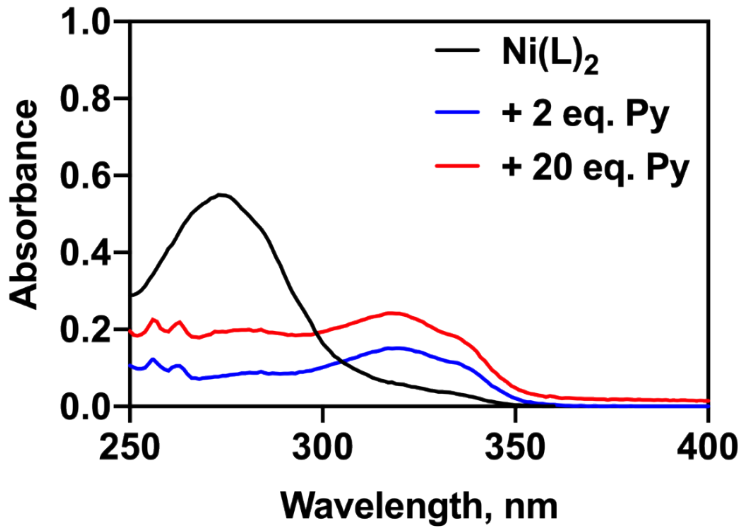


Figure S10. Absorbance spectra of Ni(**L**)$_2$ in PFCE with increasing amounts of pyridine (Py) added during extraction, [Ni^{2+}] = 10 μM.

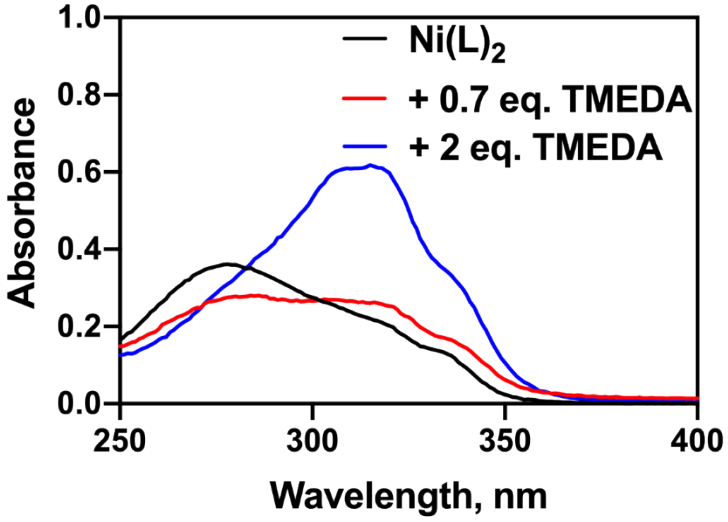


Figure S11. UV-vis absorbance spectra of Ni(**L**)$_2$ in PFCE with increasing amounts of tetramethylethylenediamine (TMEDA) added during extraction, [Ni^{2+}] = 10 μM.

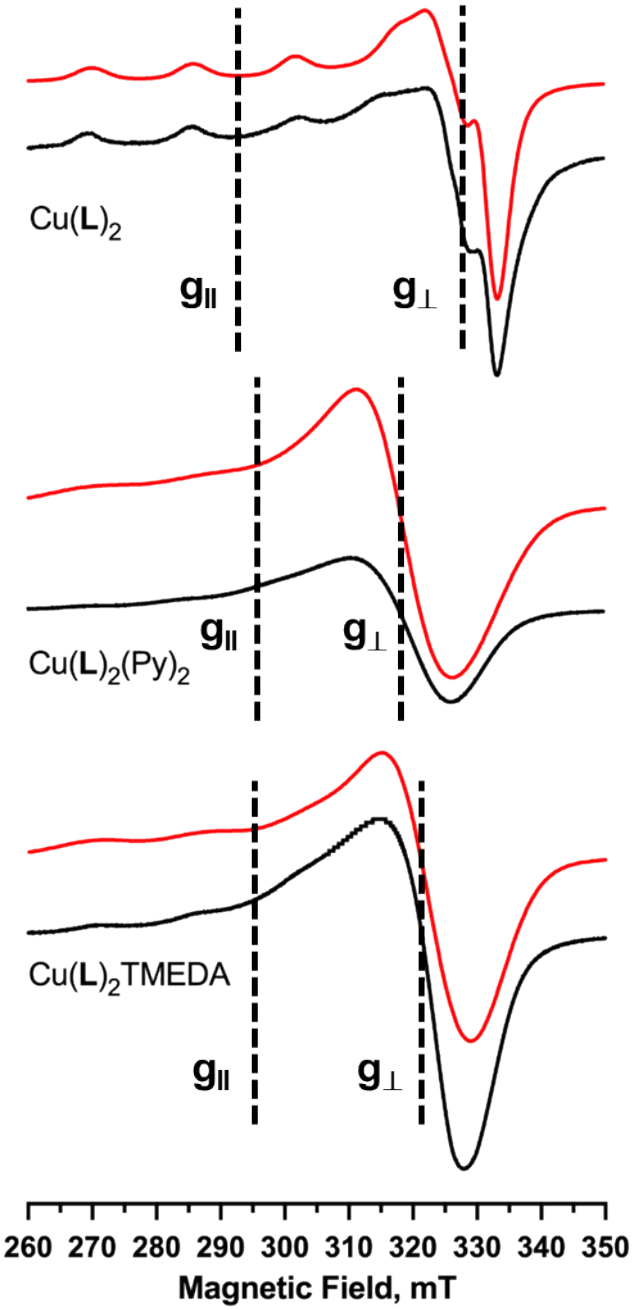


Figure S12. CW X-band EPR spectra (black) of Cu(**L**)$_2$, Cu(**L**)$_2$(Py)$_2$, and Cu(**L**)$_2$TMEDA acquired in frozen solution of PFCE (20 mM) at 115 K along with their respective simulated spectra (red).

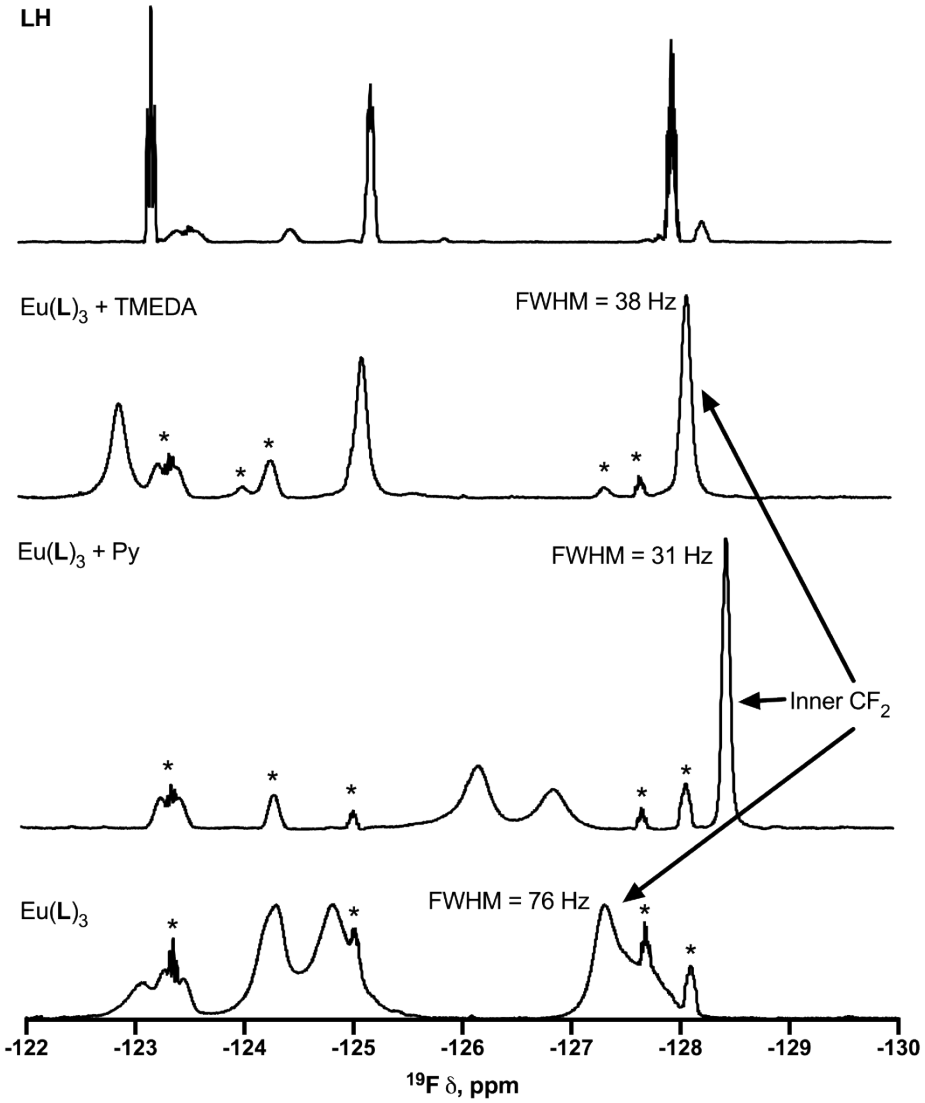


Figure S13. ^{19}F NMR spectrum (376 MHz, neat, 25°C) of **LH** in PFCE (10 mM) and the Eu(**L**)$_3$ species extracted with only **LH**, **LH** + 60 mM pyridine, and **LH** + 20 mM TMEDA. $[Eu^{3+}]_{fl}$ = 10 mM. Py = pyridine. TMEDA = tetramethylethylenediamine. Note, a coaxial insert filled with D_2O was used for solvent locking.

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