Metal loading of lanthanidopolymers driven by positive cooperativity.

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Supporting Information

Table S1 Exploration of Suzuki-type coupling reactions for the preparation of **L3**^{N} in different solvents at variable concentrations.[a]

Test	V_{tot} /mL	Solvent	Ratio	M_W (g/mol) [b]	M_n (g/mol) [c]	N_w [d]	I_p [e]
1	2	Dioxane	1	7512	5141	10	1.461
2	4	Dioxane/EtOH	3:1	8730	8440	11	1.03
3	2	Dioxane/EtOH	3:1	21437	17314	29	1.238
4	2	Dioxane/H_2O	3:1	9893	6161	13	1.606
5	2	THF/EtOH	3:1	18539	14336	25	1.293
6	2	THF/H_2O	3:1	9415	6035	13	1.56
7	2	Toluene/EtOH	3:1	19575	14965	27	1.308
8	2	Toluene/EtOH	1:1	16331	11254	22	1.451
9	2	Toluene/EtOH	7:3	19726	14092	27	1.400
10	2	Toluene/EtOH	9:1	16426	12765	22	1.287
11	4	Toluene/EtOH	3:1	18728	14140	26	1.324
12	2	CH_2Cl_2/EtOH	3:1	12204	8842	17	1.38

[a] 100 mg ($1.6\cdot10^{-4}$ mole) of 2,6-Bis-[1-(3-methylbutyl)-5-bromo-benzomidazol-2-yl)pyridine (**1**) mixed with 2,5-dihexyloxy-1,4-diboronic acid (**2,** 1.0 eq) in presence of $Pd(PPh_3)_4$ (0.1 eq) and CsF (10.0 eq).

[b] $M_w = M_0 \cdot \overline{DP}_w = \frac{\sum_i P_i \cdot DP_i \cdot M_0}{\sum_i P_i} = \frac{\sum_i P_i \cdot M_i}{\sum_i P_i} = \frac{\sum_i N_i \cdot M_i^2}{\sum_i N_i \cdot M_i} = \sum_i w_i \cdot M_i$ where DP is the degree of polymerization, M_0 is the molecular weight of a monomeric unit and w_i is the weight fraction of oligomer i in the mixture.

[c] $M_n = M_0 \cdot \overline{DP}_n = \frac{\sum_i N_i \cdot DP_i \cdot M_0}{\sum_i N_i} = \frac{\sum_i N_i \cdot M_i}{\sum_i N_i} = \sum_i x_i \cdot M_i$ where x_i is the mole fraction of oligomer i in the mixture. [d] $N_w = \frac{M_w - ew}{M_0}$ (eqn (6), see text). [e] Polydispersity index $I_P = \frac{M_w}{M_n} \geq 1.0$.

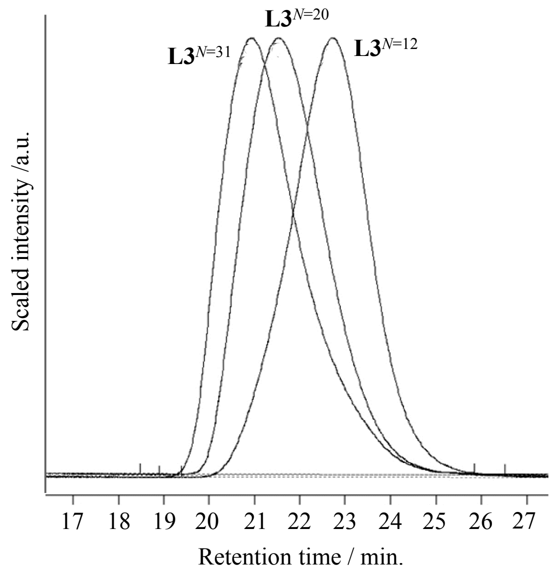

Figure S1 GPC traces for the polymers **L3**$^{N=12}$, **L3**$^{N=20}$ and **L3**$^{N=31}$ in THF at 303K (UV detector). A longer retention time is associated with a smaller molecular weight.

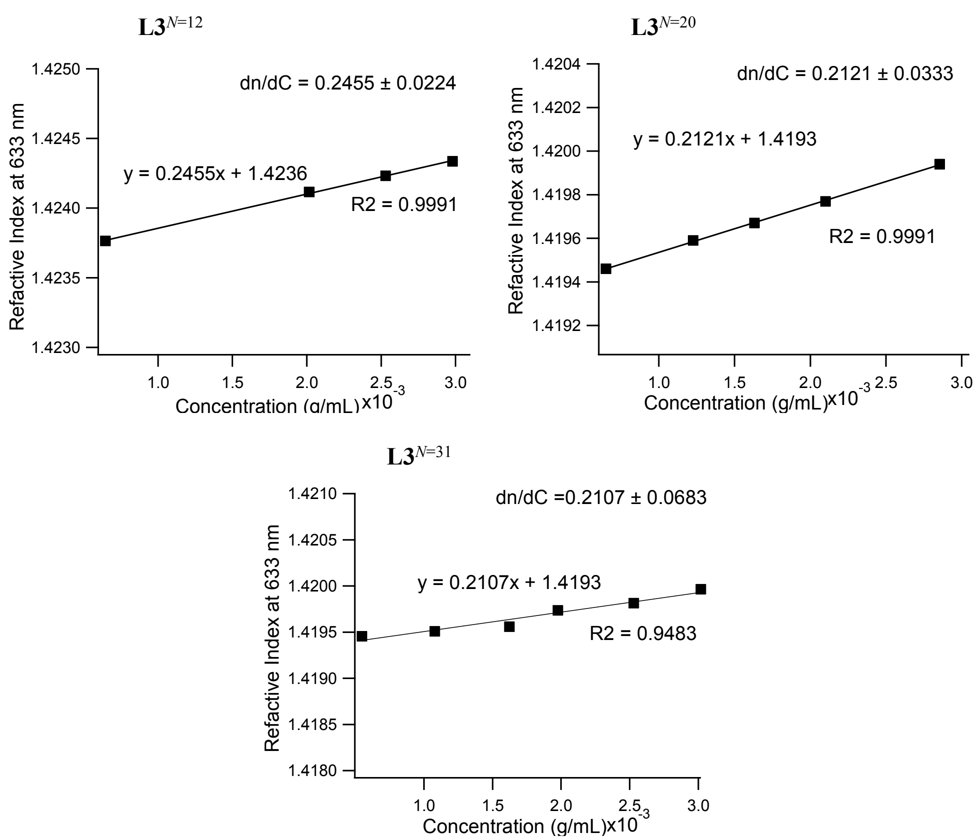

Figure S2 Concentration-dependent refractive indexes for the polymers **L3**$^{N=12}$, **L3**$^{N=20}$ and **L3**$^{N=31}$ in dichloromethane at 298K. The dn/dC values were used to calculate the optical constant K in the Debye plots in Fig. S3.

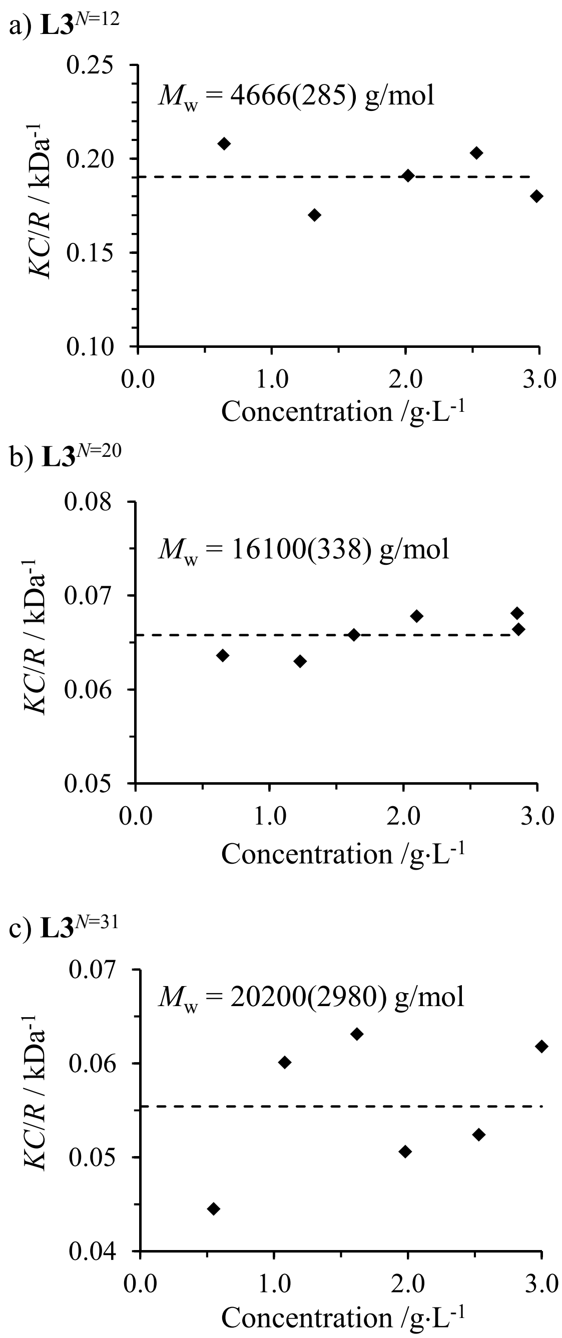

Figure S3 Debye plots for the polymers **L3**$^{N=12}$, **L3**$^{N=20}$ and **L3**$^{N=31}$ in dichloromethane at 298 K. The concentration dependence is expected to be negligible in this concentration range.

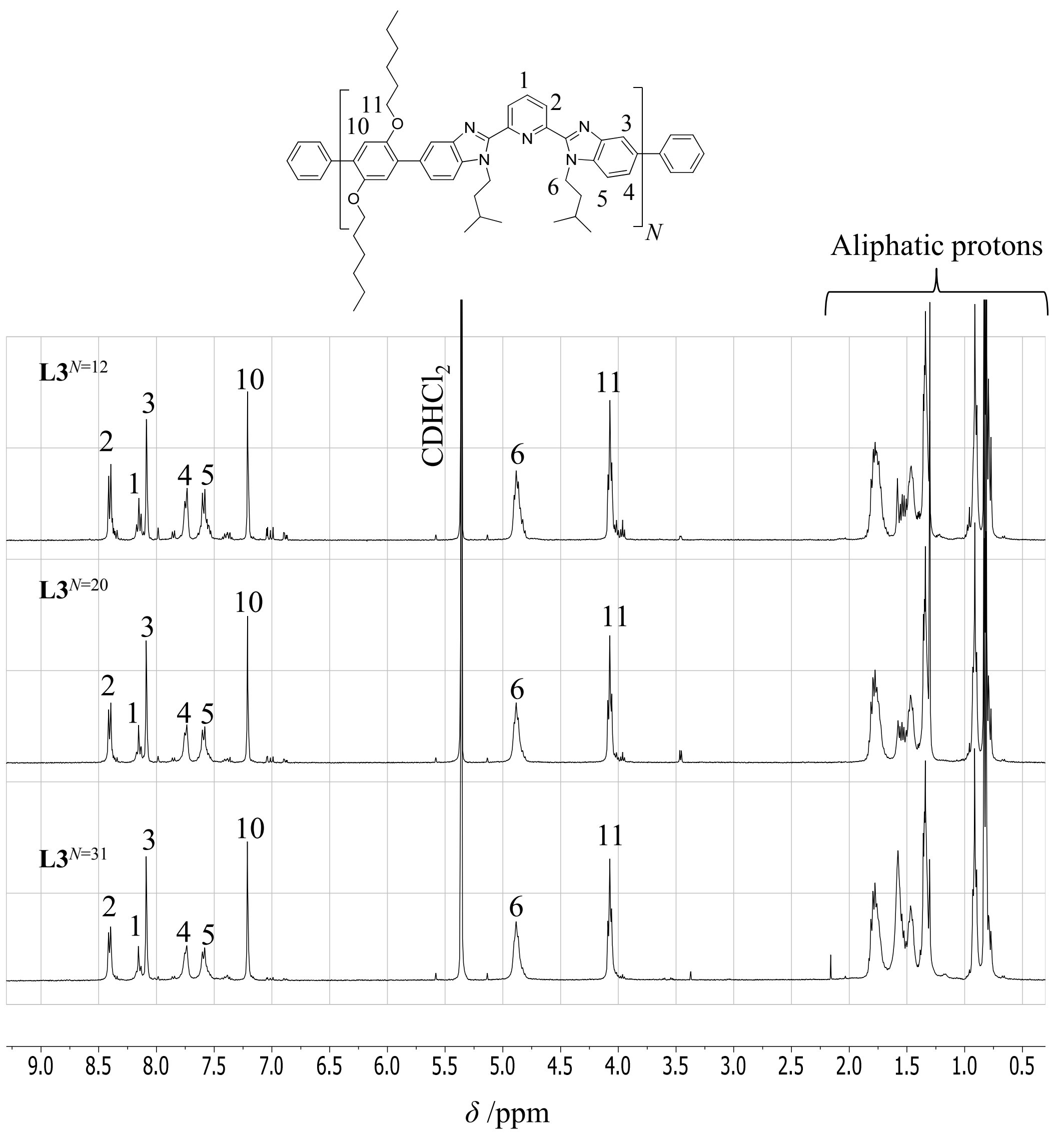

Figure S4 ^{1}H NMR spectra of the polymers **L3**$^{N=12}$, **L3**$^{N=20}$ and **L3**$^{N=31}$ (CD_2Cl_2, 293K).

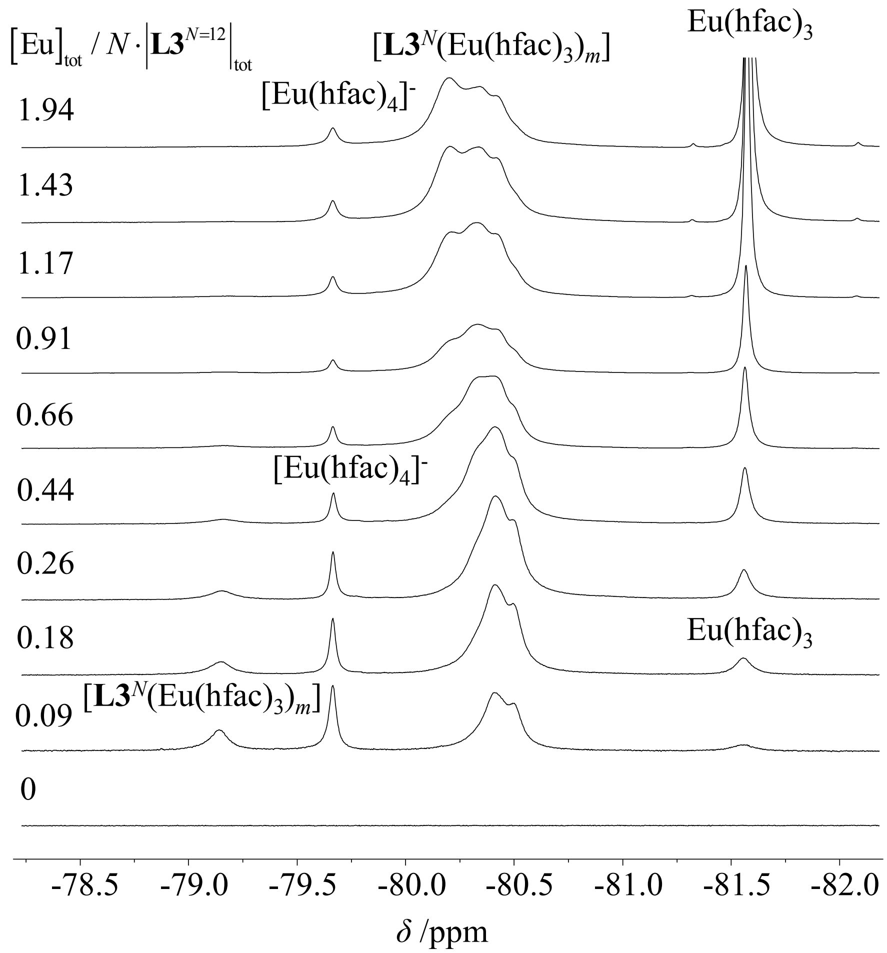

Figure S5 ^{19}F-NMR titration of **L3**$^{N=12}$ with [Eu(hfac)$_3$dig] (CD_2Cl_2 + 0.15 mol·dm^{-3} at 293K).

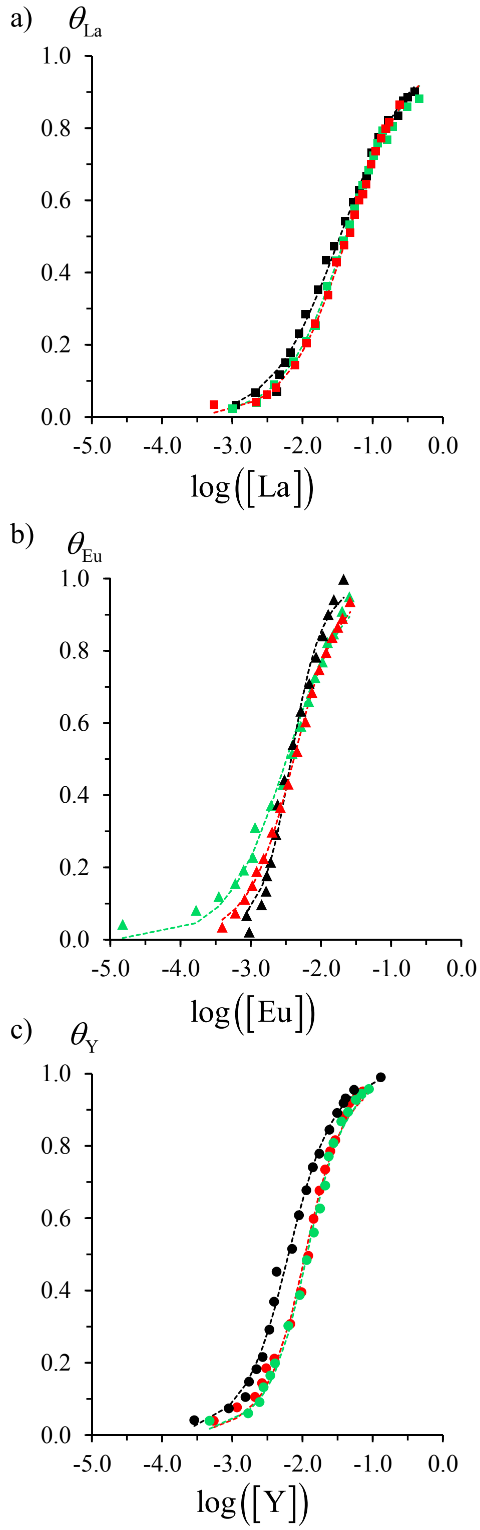

Figure S6 Experimental occupancy factors θ_{Ln} (markers) and fitted binding isotherms using eqns (9)-(10) (dotted traces) for the titrations of **L3**$^{N=12}$ (black), **L3**$^{N=20}$ (red) and **L3**$^{N=31}$ (green) with a) [La(hfac)$_3$dig], b) [Eu(hfac)$_3$dig] and c) [Y(hfac)$_3$dig] (CD_2Cl_2 + 0.15 mol·dm^{-3} diglyme at 293K).

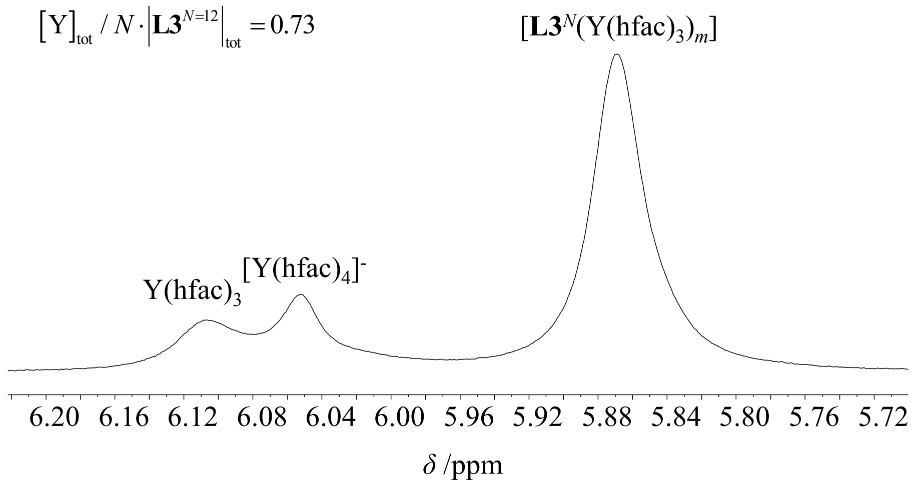

Figure S7 ^{1}H-NMR titration of **L3**$^{N=12}$ with [Y(hfac)$_3$dig] (CD_2Cl_2 + 0.15 mol·dm^{-3} at 293K).

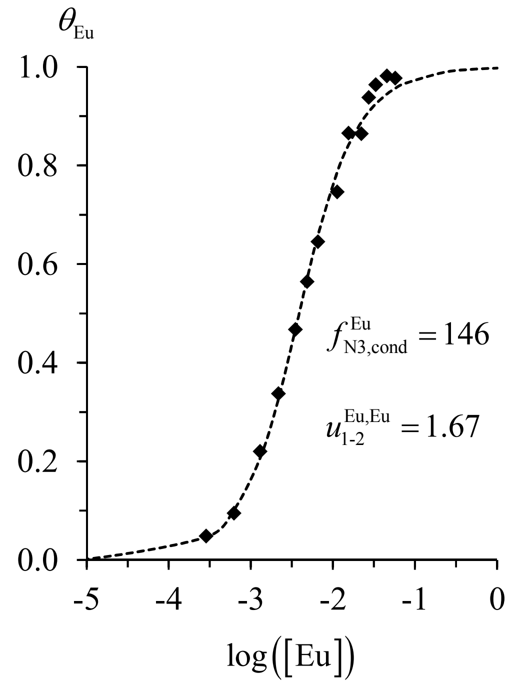

Figure S8 Corrected[35] occupancy factors θ_{Eu} (markers) and fitted binding isotherms using eqns (9)-(10) (dotted trace) for the titration of the polydisperse **L3**$^{3 \le N \le 18}$ polymer[14] with [Eu(hfac)$_3$dig] (CD_2Cl_2 + 0.15 mol·dm^{-3} diglyme at 293K).

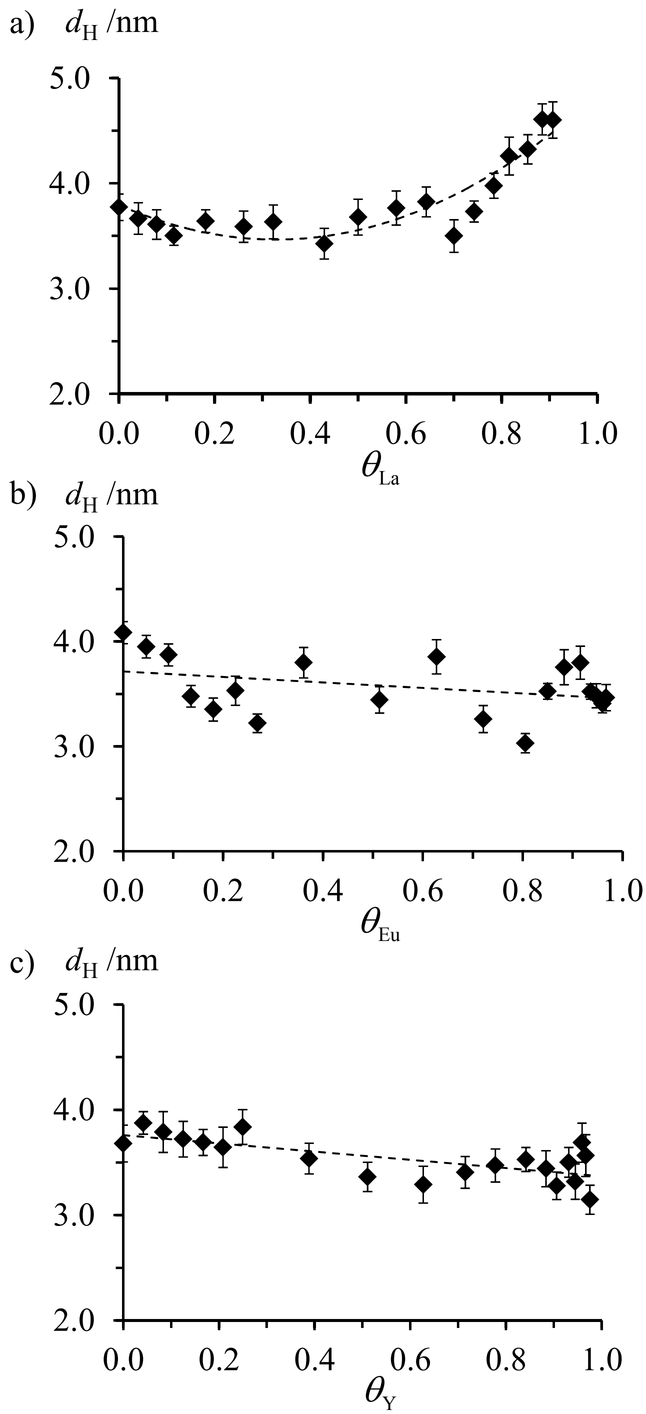

Figure S9 Hydrodynamic diameters ($d_H = 2R_H$) for the lanthanidopolymers [$\mathbf{L3}^{N=12}(Ln(hfac)_3)_m$] as a function of the occupancy factor θ_{Ln} for lanthanide loading with a) [$La(hfac)_3dig$], b) [$Eu(hfac)_3dig$] and c) [$Y(hfac)_3dig$] (CH_2Cl_2 + 0.15 mol·dm^{-3} at 293K). The trendlines are only guides for the eyes.

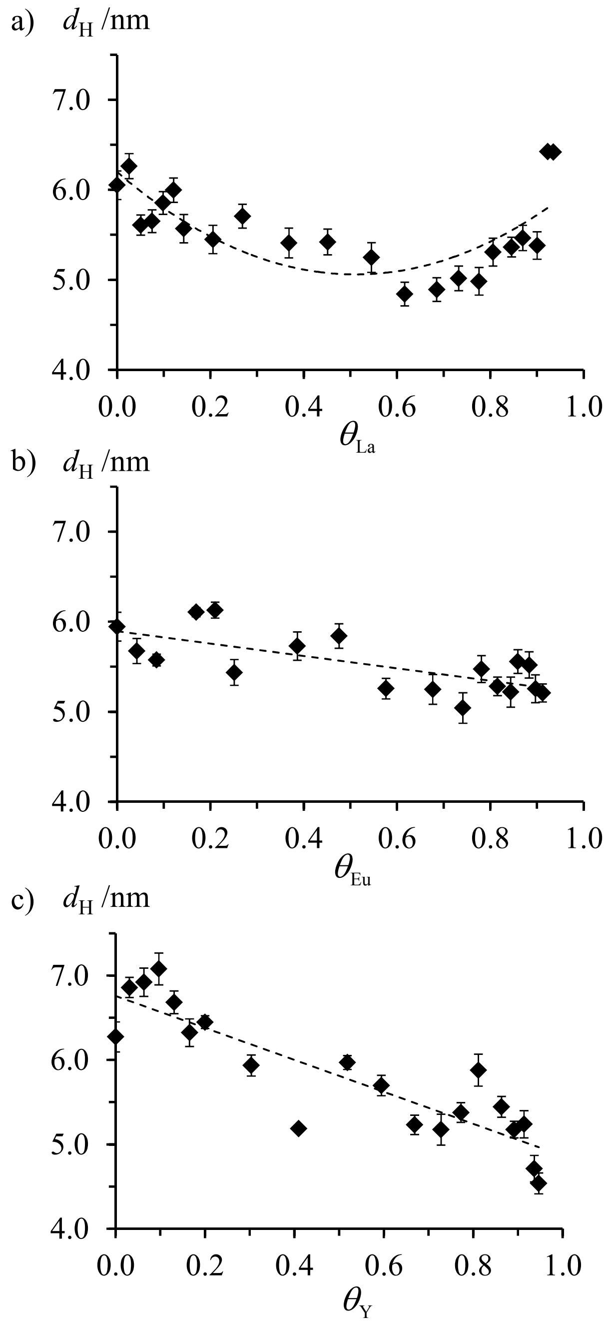

Figure S10 Hydrodynamic diameters ($d_H = 2R_H$) for the lanthanidopolymers [$\mathbf{L3}^{N=31}(Ln(hfac)_3)_m$] as a function of the occupancy factor θ_{Ln} for lanthanide loading with a) [$La(hfac)_3dig$], b) [$Eu(hfac)_3dig$] and c) [$Y(hfac)_3dig$] (CH_2Cl_2 + 0.15 mol·dm^{-3} at 293K). The trendlines are only guides for the eyes.

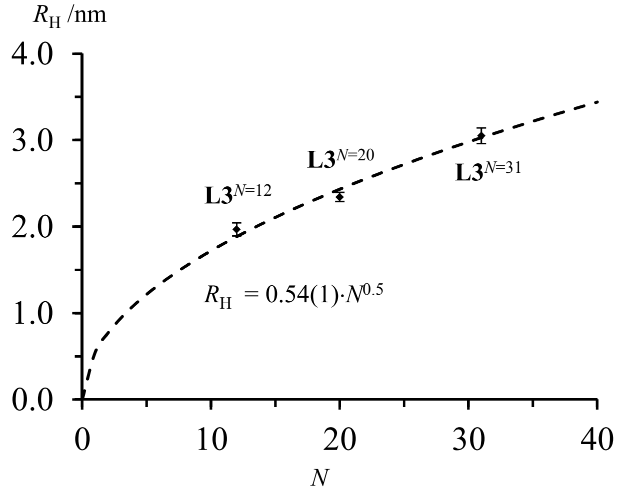

Figure S11 Hydrodynamic radii as a function of the number of binding units N for the polymers **L3**^{N}. The fitted trace corresponds to the best fit according to eqn (20).

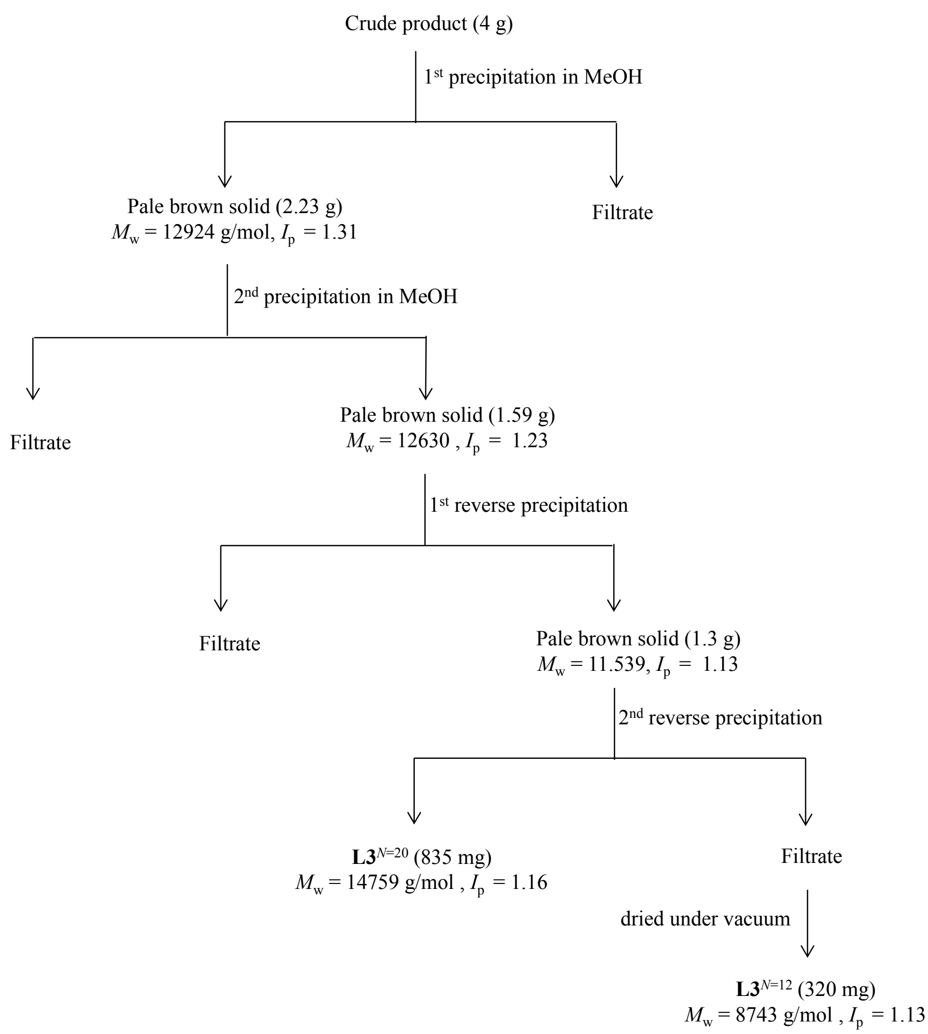

Figure S12 Purification of the polymers **L3**$^{N=12}$ and **L3**$^{N=20}$.