A new high-capacity metal ion-complexing gel containing cyclen ligands

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Supplementary Information
Fig. S1: $^1$H NMR (400 MHz, CDCl$_3$) of 2-(2-hydroxyethoxy)ethyl methacrylate.

Fig. S2: $^{13}$C NMR (100 MHz, CDCl$_3$) of 2-(2-hydroxyethoxy)ethyl methacrylate.
Fig. S3: $^1$H NMR (400 MHz, CDCl$_3$) of 2-(2-(2-bromoacetoxy)ethoxy)ethyl methacrylate 2.

Fig. S4: $^{13}$C NMR (100 MHz, CDCl$_3$) of 2-(2-(2-bromoacetoxy)ethoxy)ethyl methacrylate 2.
Fig. S5: $^1$H NMR (400 MHz, CDCl$_3$) of 10-(2-(2-(2-(methacryloyloxy)ethoxy)ethoxy)-2-oxoethyl)-1,4,7,10-tetraazacyclododecane-1,4,7-tricarboxylate 1.

Fig. S6: $^{13}$C NMR (100 MHz, CDCl$_3$) of 10-(2-(2-(2-(methacryloyloxy)ethoxy)ethoxy)-2-oxoethyl)-1,4,7,10-tetraazacyclododecane-1,4,7-tricarboxylate 1.
Fig. S7: $^1$H NMR (400 MHz, CDCl$_3$) of 3-Boc.

Fig. S8: $^1$H NMR (400 MHz, acetone-d$_6$) of 3.
Fig. S9: $^1$H NMR (400 MHz, CDCl$_3$) of 4-Boc.

Fig. S10: $^1$H NMR (400 MHz, CDCl$_3$) of 5-Boc.
Fig. S11: $^1$H NMR (400 MHz, acetone-d$_6$) of 5.

Fig. S12: $^1$H NMR (400 MHz, CD$_3$OD-d$_4$) of 5-PAMAM (G0).
Fig. S13: FTIR spectrum of Cu-crosslinked-PAMAM (G0) (top) and Cu-crosslinked-5-PAMAM (G0) (bottom).
Fig. S14: GPC analysis of 235K Dalton polystyrene standard.
Fig. S15: Example of GPC analysis; 4-Boc polymer.
Fig. S16: Dynamic light scattering analysis monitoring the self-assembly of the 3-ZnCl$_2$ metallopolyme aggregates upon the dropwise addition of a solution of ZnCl$_2$ (in methanol) to polymer 3 in methanol; (top) average particle size; (middle) turbidity measurement; and (bottom) relative population percentage versus ratio of zinc to cyclen moieties on the polymer chain.
Fig. S17: (Top) Average particle size and (bottom) turbidity measurement versus ratio of cobalt to cyclen moieties on the polymer chain, characterising the development of Co-metallopolymer aggregates $\text{3-CoCl}_2$ upon the dropwise addition of a solution of CoCl$_2$ to the homopolymer 3 solution in MeOH.
Fig. S18: Average particle size versus ratio of copper to cyclen moieties on the polymer chain, characterising the development of Cu-metallopolymer $3$-$\text{CuCl}_2$ aggregates upon the dropwise addition of a solution of CuCl$_2$ to the homopolymer 3 solution in MeOH.

Fig. S19: Picture showing the precipitate formation of Cu-metallopolymers (1) $3$-$\text{CuCl}_2$ and (2) $4$-$\text{CuCl}_2$ after centrifugation at 1,500 rpm for 20 min.
Fig. S20: Stacked XRD spectra of various polymers, metallopolymers and background.

Fig. S21: UV-Visible absorption spectra of copper metallopolymers $3$-$\text{CuCl}_2$ (black), $4$-$\text{CuCl}_2$ (red) and $\text{CuCl}_2$ (blue) in deionized water. Inset: magnified absorbance spectra of the visible region.
Fig. S22: Overlaid EPR spectra of polymer 3, copper-complexed metallopolymer 3-CuCl$_2$ and 4-CuCl$_2$, and CuCl$_2$.5H$_2$O solid samples.

Fig. S23: (left) SEM image and (right) EDS spectrum of 3-ZnCl$_2$ metallopolyme precipitate.
Fig. S24: SEM images (left) 3-CoCl$_2$ and (right) 3-CuCl$_2$ metallopolymers precipitates.

Fig. S25: EDS spectra of (left) 3-CoCl$_2$ and (right) 3-CuCl$_2$ metallopolymers precipitates.

Table S1: EDS results showing the relationship between the metal and Cl$^-$ anion for selected metallopolymers.

<table>
<thead>
<tr>
<th>Metallopolymers</th>
<th>Atomic % of Metal</th>
<th>Atomic % of Cl$^-$</th>
<th>Atomic Ratio (Metal:Cl$^-$)</th>
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</thead>
<tbody>
<tr>
<td>3-ZnCl$_2$</td>
<td>3.94</td>
<td>9.42</td>
<td>1 : 2</td>
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<tr>
<td>3-CoCl$_2$</td>
<td>1.99</td>
<td>7.46</td>
<td>1 : 3</td>
</tr>
<tr>
<td>3-CuCl$_2$</td>
<td>1.57</td>
<td>3.17</td>
<td>1 : 2</td>
</tr>
<tr>
<td>4-CuCl$_2$</td>
<td>4.43</td>
<td>8.08</td>
<td>1 : 2</td>
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</table>
Fig. S26: Pictures of (a) methanol solution and (b) dried Cu-crosslinked-PAMAM (G0) (left) and Cu-crosslinked-5-PAMAM (G0) (right).

Fig. S27: Solid state UV-visible spectrum of copper complexed networks Cu-crosslinked-PAMAM (G0) (black) and Cu-crosslinked-5-PAMAM (G0) (red).