

Supporting Information

Copper(II) binding to flexible triethanolamine-core PAMAM dendrimers: a combined experimental/*in silico* approach

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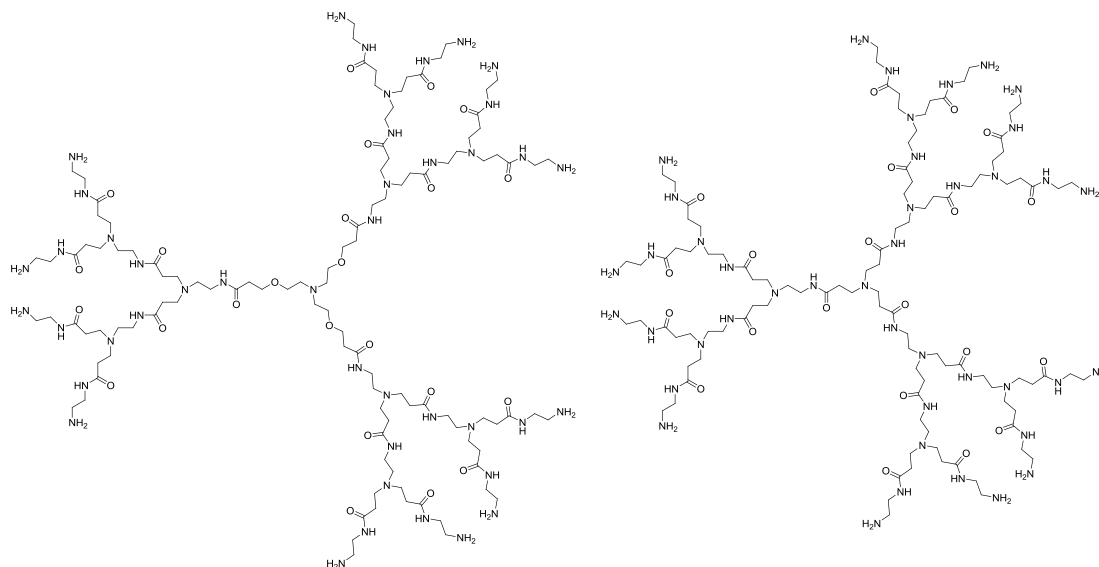


Figure S1. Structurally flexible triethanolamine (TEA)-core PAMAM dendrimer (left) and traditional amine (NH₃) core PAMAM dendrimer (right) of generation 2.

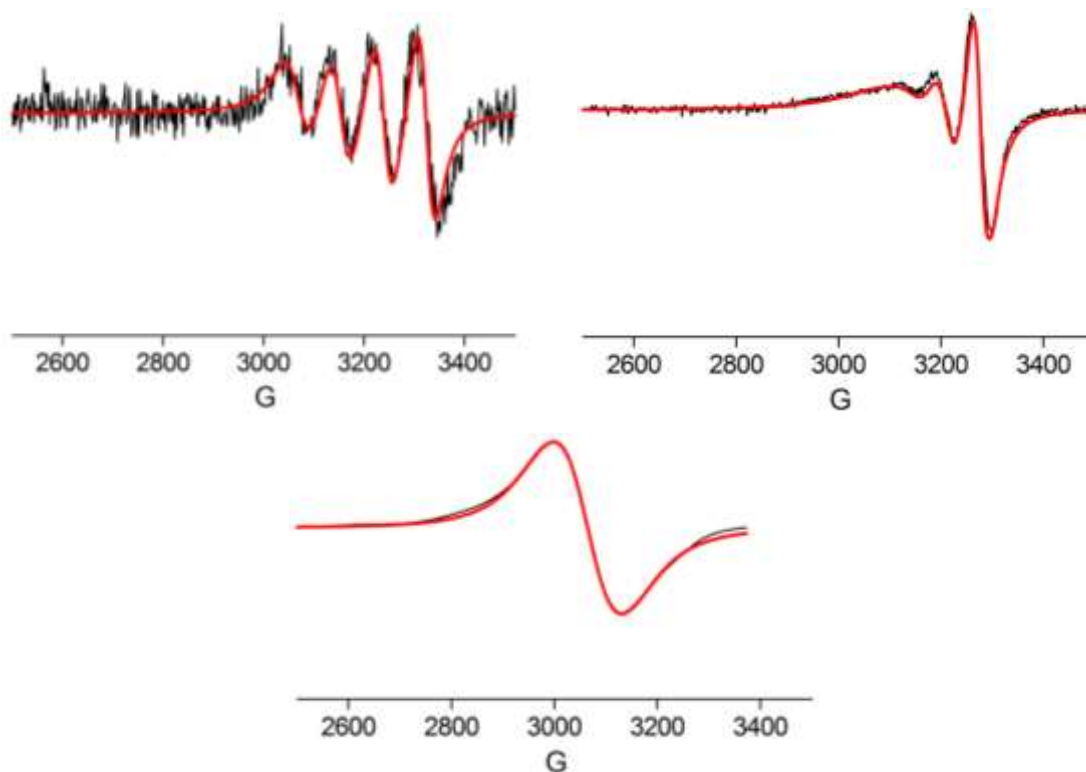


Figure S2. Experimental (black) and calculated (red) EPR signal 1 (top left), signal 2 (top right) and signal 3 (bottom) for TEA-core PAMAM dendrimer G2 at 298K. The parameters used in spectra calculations were the following: Signal 1: [Cu(II)] = 0.0025 M; $g_{xx} = 2.055$; $g_{yy} = 2.06$; $g_{zz} = 2.231$, $A_{xx} = 30$ G; $A_{yy} = 35$ G; $A_{zz} = 190$ G; $\tau = 42$ ps; Signal 2: [Cu(II)] = 0.05 M; $g_{xx} = 2.062$; $g_{yy} = 2.09$; $g_{zz} = 2.300$, $A_{xx} = 25$ G; $A_{yy} = 25$ G; $A_{zz} = 159$ G; $\tau = 0.2$ ns; Signal 3: [Cu(II)] = 0.5 M; $g_{xx} = 2.07$; $g_{yy} = 2.07$; $g_{zz} = 2.28$, $A_{xx} = 5$ G; $A_{yy} = 5$ G; $A_{zz} = 125$ G; $\tau = 0.07$ ns; Heisenberg exchange frequency,

$$W_{\text{ex}}=1 \times 10^8 \text{ s}^{-1}.$$

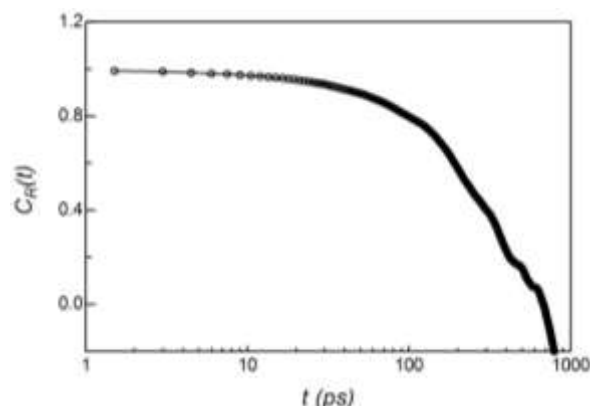


Figure S3. Autocorrelation function $C_R(t)$ of the squared radius of gyration for the G2/Cu²⁺ complex. $C_R(t)$ is given by the following relationship: $C_R(t) = \frac{\langle (R^2(t) - \langle R^2 \rangle)(R^2(0) - \langle R^2 \rangle) \rangle}{\langle R^4 \rangle - \langle R^2 \rangle^2}$. The corresponding relaxation time is the time at which $C_R(t) = 1/e$. For this complex, the estimated relaxation time is 0.32 ns. This value has several, important implications: 1) it is quite small, implying a high mobility/flexibility of the corresponding dendrimeric structure, 2) it is exceedingly small comparable with the overall simulation time, meaning that the trajectory of the relevant molecular complex sampled enough independent configurations for sufficient averaging of the structural properties, and 3) it is comparable to the correlation time obtained from EPR for the same complex.

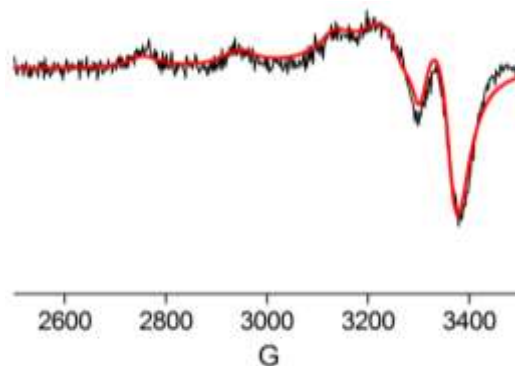


Figure S4. Experimental (black) and calculated (red) EPR signal 1 for TEA-core PAMAM dendrimer G2 at 150K. The parameters used in spectra calculation were the following: [Cu(II)] = 0.0025 M; $g_{xx} = 2.055$; $g_{yy} = 2.06$; $g_{zz} = 2.231$, $A_{xx} = 30$ G; $A_{yy} = 35$ G; $A_{zz} = 190$ G; $\tau = 17$ ns.

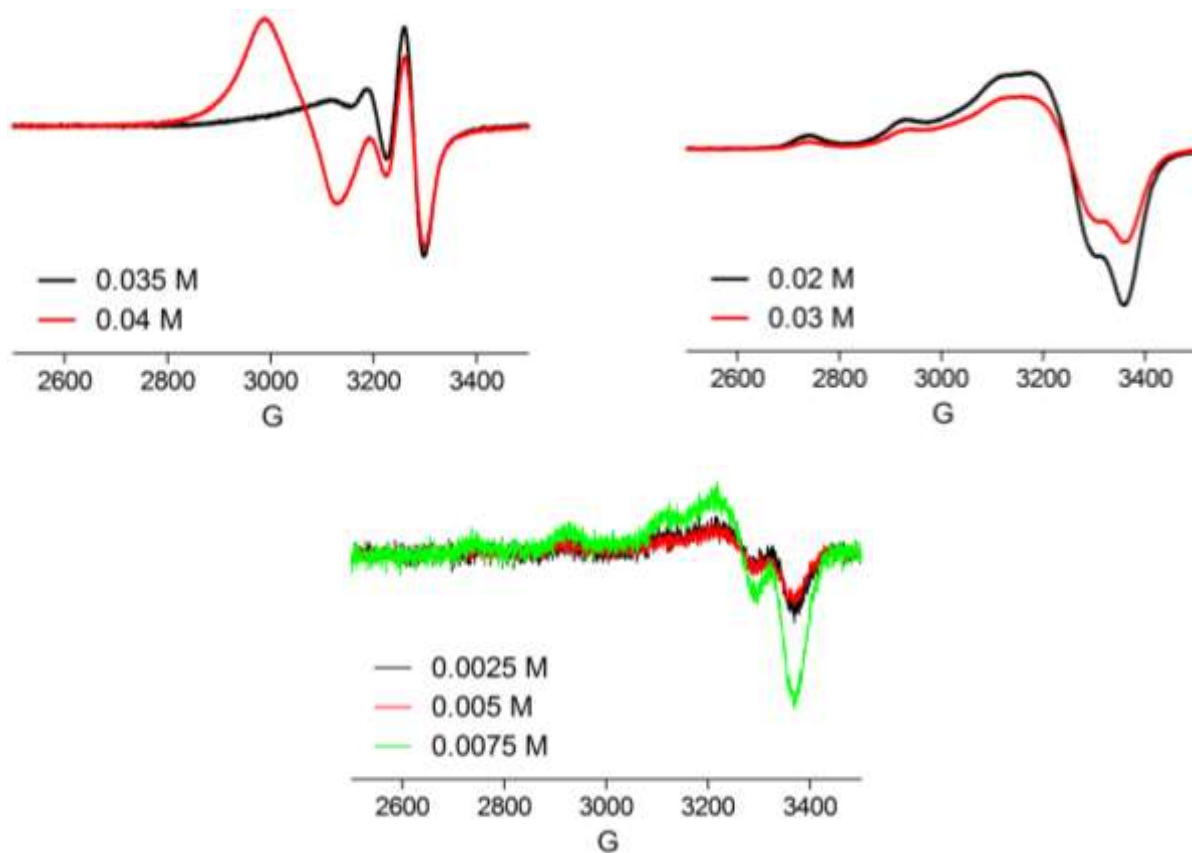


Figure S5. EPR experimental spectra for G0 at 298 K (top, left), G1 at 150 K (top, right) and G3 at 150 K (bottom) at Cu(II) concentrations corresponding to a Cu^{2+} /dendrimer molar ratio $\cong 1$.