ESI to accompany

When is a metallopolymer not a metallopolymer? When it is a metallomacrocycle.

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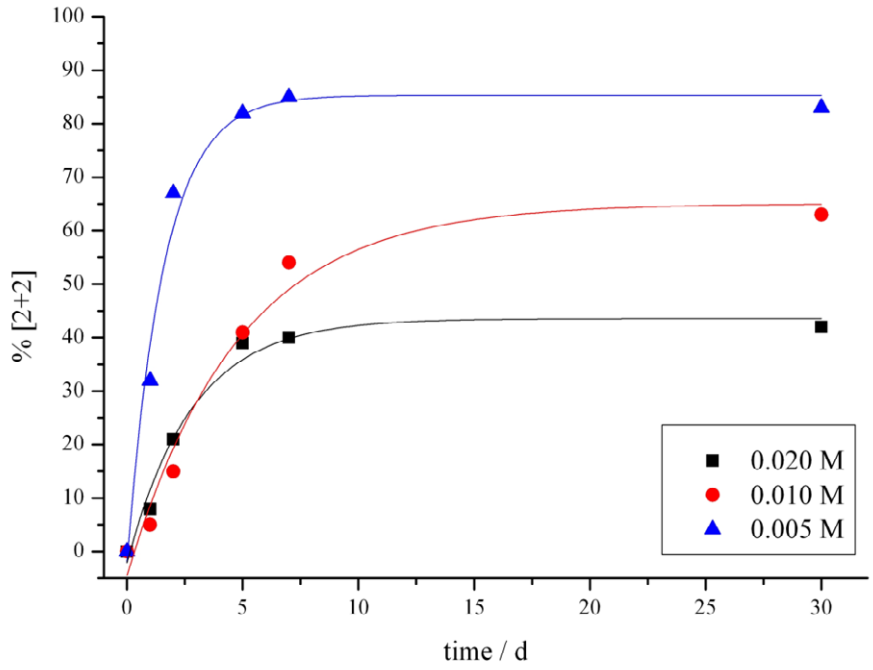


Fig. S1 Graph showing the relative proportions (determined by 250 MHz ^{1}H NMR spectroscopy of CD_3CN solutions) of the proposed $[Co_2(\mathbf{3})_2][PF_6]_4$ species present in mixtures formed in the reaction of **3** with $Co(OAc)_2{\cdot}4H_2O$ in $CHCl_3$/MeOH (9:1) followed by precipitation with NH_4PF_6.

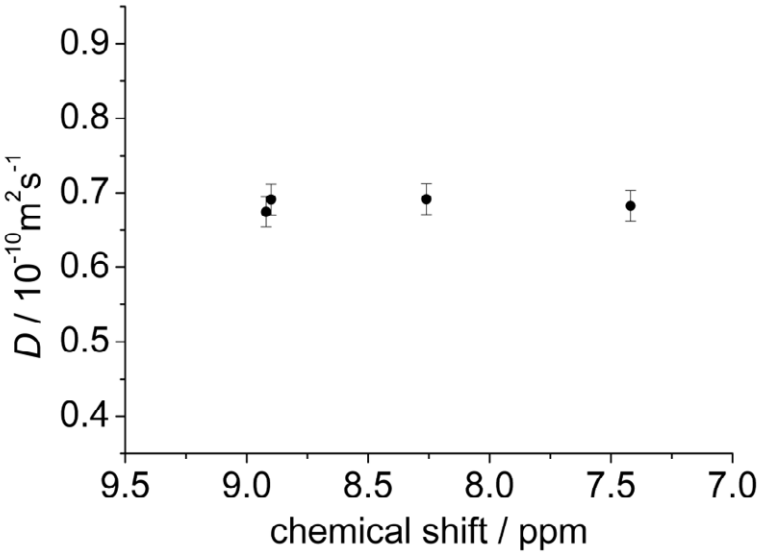
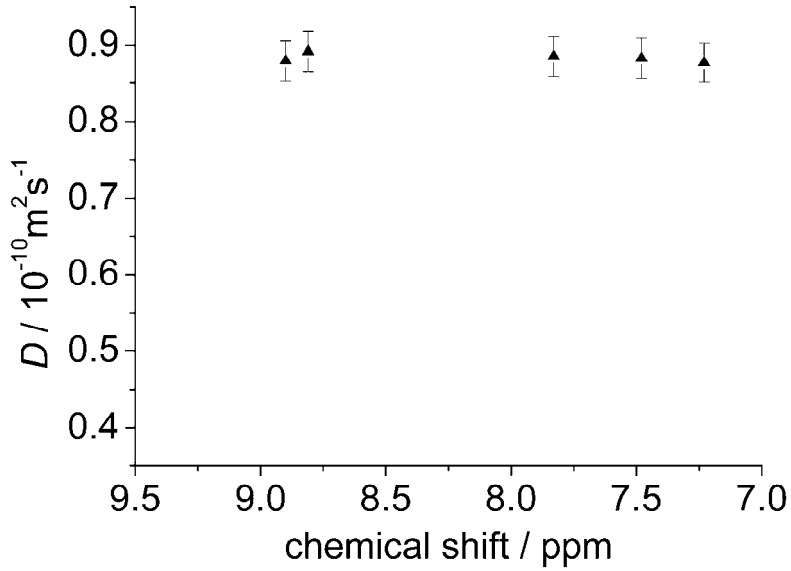


Fig. S2 ^{1}H DOSY-type plot (500 MHz, DMSO-d_6, 295 K) of an oxidized equilibrium mixture of $[Co_n(\mathbf{2})_n][PF_6]_3$ (Δ = 48.8 ms, δ = 11.0 ms).



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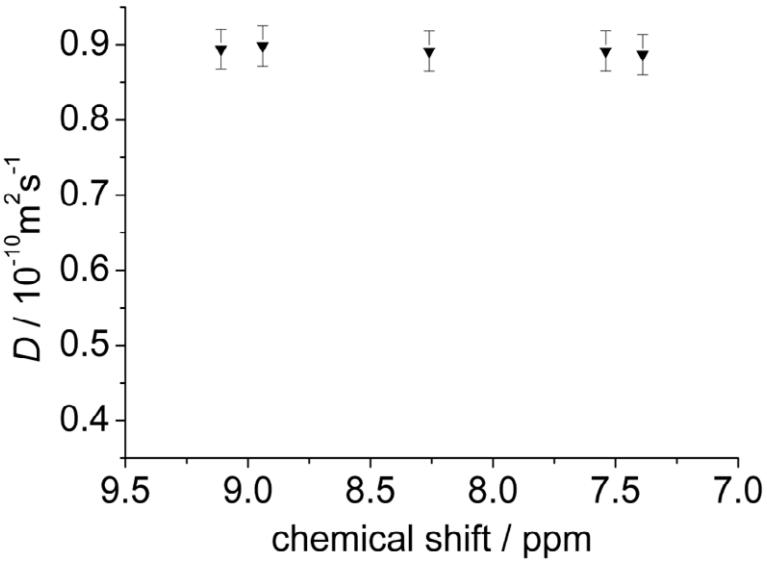

Fig. S4 ^{1}H DOSY-type plot (500 MHz, DMSO-d_6, 295 K) of an oxidized equilibrium mixture of $[Co_n(\mathbf{4})_n][PF_6]_3$ (Δ = 52.8 ms, δ = 9.0 ms).

Table S1 Calculated radii for models of the metallomacrocyclic complexes.[a]

Complex	r/ Å sphere	2α / Å	2β / Å	r_e,[d] / Å ellipsoid
$[Co_3(\mathbf{2})_3]^{9+}$	12.45	24.90	8.63	8.74[b]
$[Co_2(\mathbf{3})_2]^{6+}$	10.91	21.77	19.10	9.97[c]
$[Co_2(\mathbf{4})_2]^{6+}$	13.06	26.12	19.29	10.64[c]

[a]The length, 2α, of the major axis of both ellipsoids was taken as the longest distance across the metallomacrocycle in the crystal structure. The minor axis (length 2β) of the prolate ellipsoid was measured as the longest distance perpendicular to the major axis, and of the oblate ellipsoid was the longest distance between the H^{A4} protons of two tpy units coordinated to the same Co^{3+} ion, perpendicular to the major axis.

[b] Oblate ellipsoid model

[c] Prolate ellipsoid model

[d]r_e is calculated from 2α and 2β according to: K. E. v. Holde, W. C. Johnson and P. S. Ho, *Principles of Physical Biochemistry*, 2nd edn., Pearson Prentice Hall, Upper Saddle River, 2006.

Table S2 Correction factors[a] to the Stokes-Einstein equation for non-spherical model metallomacrocycles of molecular size f/f_0, for the shape of the molecule and c, taking into account the size of the molecule.

The relationship[b] used for the diffusion coeiffient was:

$$D = \frac{kT}{6\pi\eta rc(f/f_0)} \text{ where } c = \left[1 + 0.695\left(\frac{r_{solvent}}{r}\right)^{2.234}\right]^{-1}$$

Complex	$f/f_{0,\ ellipsoid}$[c]	$c_{ellipsoid}$	$c_{spherical}$
$[Co_3(\mathbf{2})_3]^{9+}$	1.11[d]	0.959[c]	0.981
$[Co_2(\mathbf{3})_2]^{6+}$	1.00[e]	0.969[c]	0.975
$[Co_2(\mathbf{4})_2]^{6+}$	1.01[e]	0.973[d]	0.983

[a] A. Macchioni, G. Ciancaleoni, C. Zuccaccia and D. Zuccaccia, *Chem. Soc. Rev.*, 2008, **37**, 479.

[b] E. Yumet, H. C. Chen and S. H. Chen, *AIChE J.*, 1985, **31**, 76; H. C. Chen and S. H. Chen, *J. Phys. Chem.*, 1984, **88**, 5118.

[c] K. E. v. Holde, W. C. Johnson and P. S. Ho, *Principles of Physical Biochemistry*, 2nd edn., Pearson Prentice Hall, Upper Saddle River, 2006.

[d] Oblate ellipsoid model

[e] Prolate ellipsoid model