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Supplementary Information for

Control of the Hierarchical Self-Assembly of Polyoxometalate-Based Metallomacrocycles by Redox Trigger and Solvent Composition

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Fig. S1. ^{31}P NMR (161 MHz) monitoring of the progressive addition of $[Co(H_2O)_6](NO_3)_2$ to a 1 mM solution of **1** in DMSO-*d*$_6$. (a) Before addition; (b) 0.33 equiv; (c) 0.66 equiv; (d) 1.0 equiv; (e) upon the addition of 1 equiv $TBABr_3$.
Fig. S2. ^{1}H NMR (400 MHz, selected peaks) temperature dependence of a solution of **1** (1 mM) in the presence of 1 equiv of $[Co(H_2O)_6](NO_3)_2$ in DMSO-*d*$_6$. (a) 300 K; (b) 310 K; (c) 320 K; (d) 330 K; (e) 340 K; (f) 350 K; (g) 300 K, one day after heating. The 9 coloured triangles and squares correspond to the signals of the trimer and tetramer repectively.
Fig. S3. T_2 measurements of ^{1}H signals (600 MHz) ranging from 8 to 15 ppm of a solution of **1** (1 mM) in the presence of 1 equiv of $[Co(H_2O)_6](NO_3)_2$ in DMSO-*d*$_6$).
Fig. S4. SAXS patterns of a solution of **1** (1 mM in DMSO-*d*$_6$, green), the resulting discrete supramolecular species in the presence of 1 equiv

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$[Co(H_2O)_6](NO_3)_2$ (blue) and the aggregated species after oxidation of the Co(II) with 1 equiv $TBABr_3$ (red) or by modification of the solvent composition (DMSO-d_6/CD_3CN 1:4, black).

Fig. S5. ^1H NMR (400 MHz) DMSO-d_6 solution containing (a) **1** (1 mM); (b) in the presence of 1 equiv of $[Co(H_2O)_6](NO_3)_2$; (c) after oxidation of the Co(II) with 1 equiv $TBABr_3$.

Fig. S6. (Top) Comparison of the experimental SAXS pattern of **1.Co^{III}** (red) in DMSO-d_6/H_2O (1:1, v/v) to the theoretical SAXS intensity (computed using SasView) of a flexible cylinder of 94 nm in length and 3.5 nm in radius (black).

Fig. S7. (Down) SAXS patterns of solutions of **1.Co^{II}** (c_{POM} = 1 mM) in DMSO-d_6/H_2O (1:1, v/v, blue) and DMSO-d_6/H_2O (1:4, v/v, orange). (Right) Comparison of the experimental SAXS pattern of **1.Co^{II}** (red) in DMSO-d_6/H_2O (1:4, v/v) to the theoretical SAXS intensity (computed using SasView) of a flexible cylinder of 76 nm in length and 3.0 nm in radius and a Kuhn length of 19 nm (black).

Fig. S8. TEM micrographs of worms-like supramolecular organizations of **1.Co^{II}** (a) and **1.Co^{III}** (b) from DMSO-d_6/H_2O (1:4, v/v) mixtures after deposition on a grid and rincing with H_2O.

Fig. S9. Absorption spectra recorded for solutions of **1.Co^{II}** (blue) and **1.Co^{III}** (red) in DMSO-d_6/H_2O mixtures (2:98, v/v).

Fig. S10. Absorption spectrum and molecular structure of 1-bromopyrene in DMSO.

Fig. S11. TEM micrographs of worms-like supramolecular organizations of **1.Co^{II}** (a) and **1.Co^{III}** (b) containing 1-bromopyrene in DMSO-d_6/H_2O mixtures.

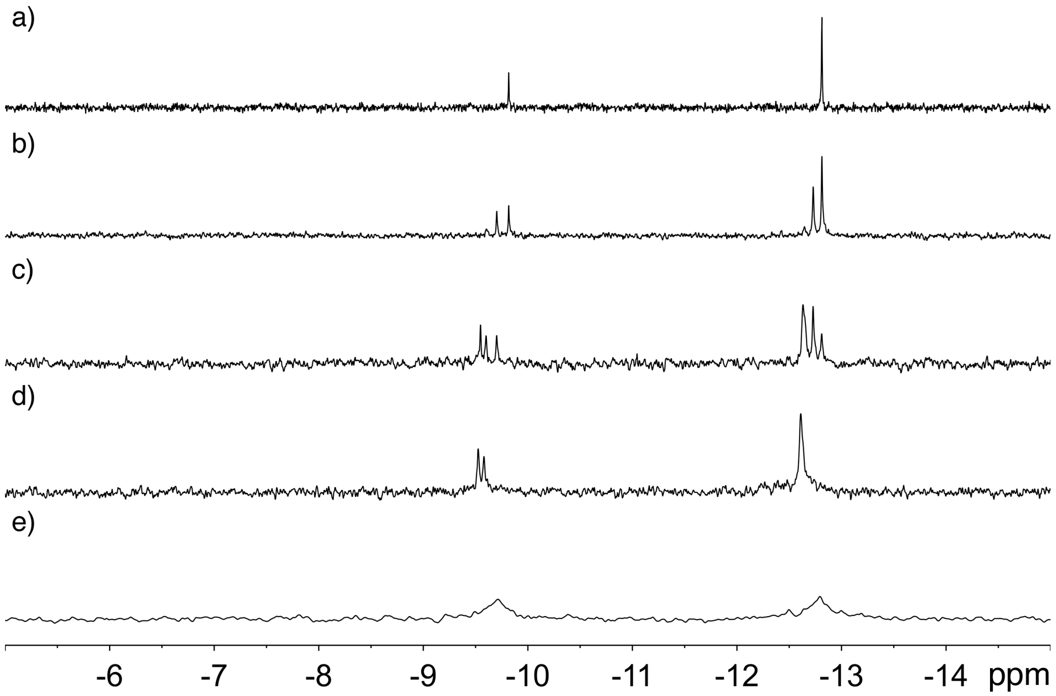
Generals Methods

NMR. NMR spectra were recorded on a Bruker Avance III nanobay 400 MHz spectrometer equipped with a BBFO probe head. ^{1}H chemical shifts are quoted as parts per million [ppm] relative to tetramethylsilane by using the solvent signals as secondary standard. ^{31}P chemical shifts are quoted relative to 85% H_3PO_4. T_2 NMR experiments were carried out without spinning at 600 MHz on a Bruker Avance III spectrometer equipped with a 5 mm BBFO probe head. T_2 was measured using a standard CPMG approach. Ten loop counter (2 - 200) were chosen for vclist and delay during echo time (d_{20}) was 500 µs. T_2 NMR spectrum was acquired with a spectral width of 12 kHz, an acquisition time of 2.73 s, a relaxation delay of 0.5 s and 2048 scans. The T_2 values were extracted from fitting the area of a given signal as a function of relaxation delays by using Dynamics center (Bruker software).

UV-visible spectra were recorded on a Jasco V-670 equipped with a ETC-717 Peltier module.

SAXS. SAXS experiments were performed at the SWING beamline of the SOLEIL synchrotron (Saint-Aubin, France). Measurements were carried out using a fixed energy of 12 or 8 keV. Samples were inserted in glass capillaries and scattering patterns were recorded on an AVIEX 170170 CCD camera formed by four detectors and radially averaged using beamline specific image treatement and data normalization.

TEM. TEM was carried out at “Plateforme de l’Institut des Matériaux de Paris Centre”, UPMC using two Jeol electron microscopes, JEM 2011 LaB6 and Jeol 2100 LaB6, operating at 200 kV accelerating voltage with 1.8 Å resolution, (equiped with EDX systeme for chemical analysis). Micrographs were recorded after deposition of a few drops of solutions of **1.Co$^{\mathbf{II}}$** or **1.Co$^{\mathbf{III}}$** (c_{POM} = 100 µM) on a Cu grid covered with an amorphous carbon film and several rinsing with the appropriate solvent (acetonitrile for DMSO-*d*$_6$/CD_3CN mixture and water for DMSO-*d*$_6$/H_2O mixtures).



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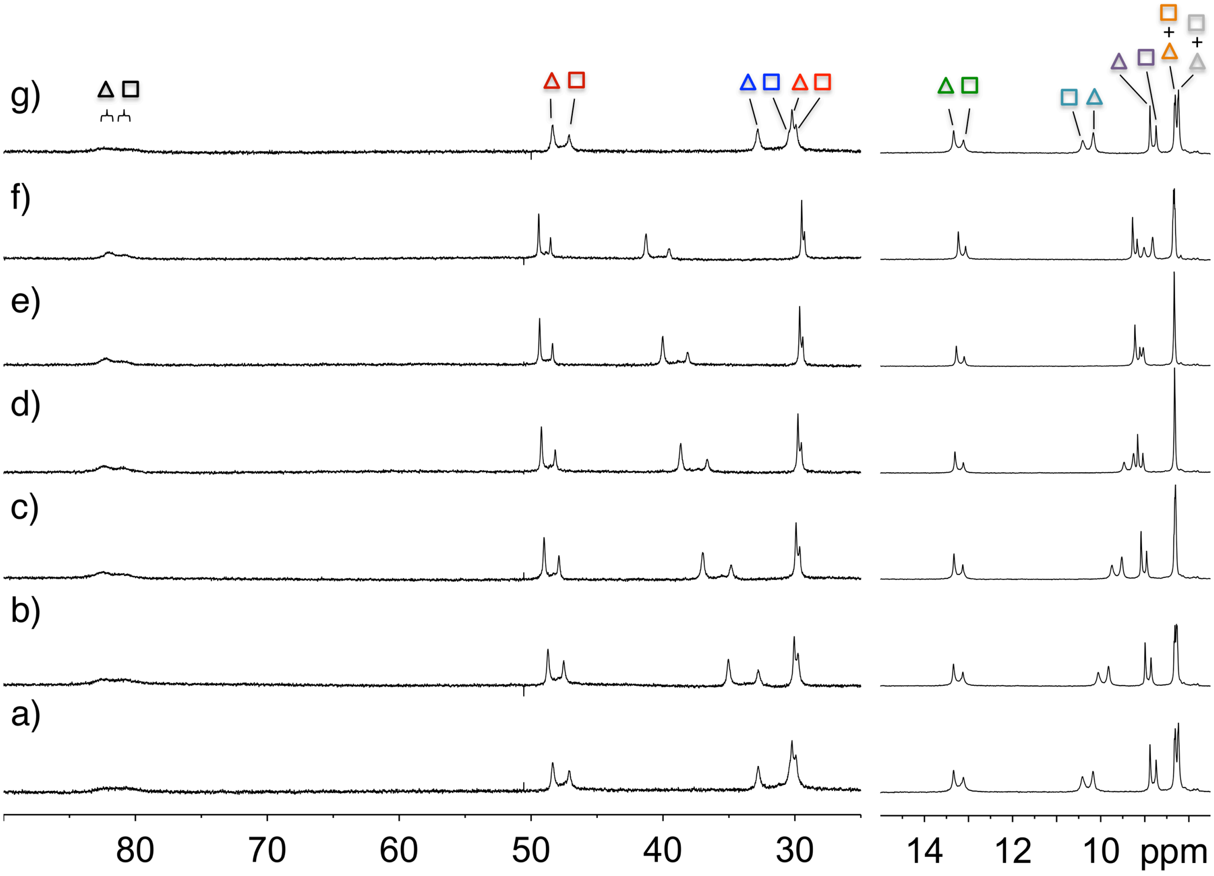
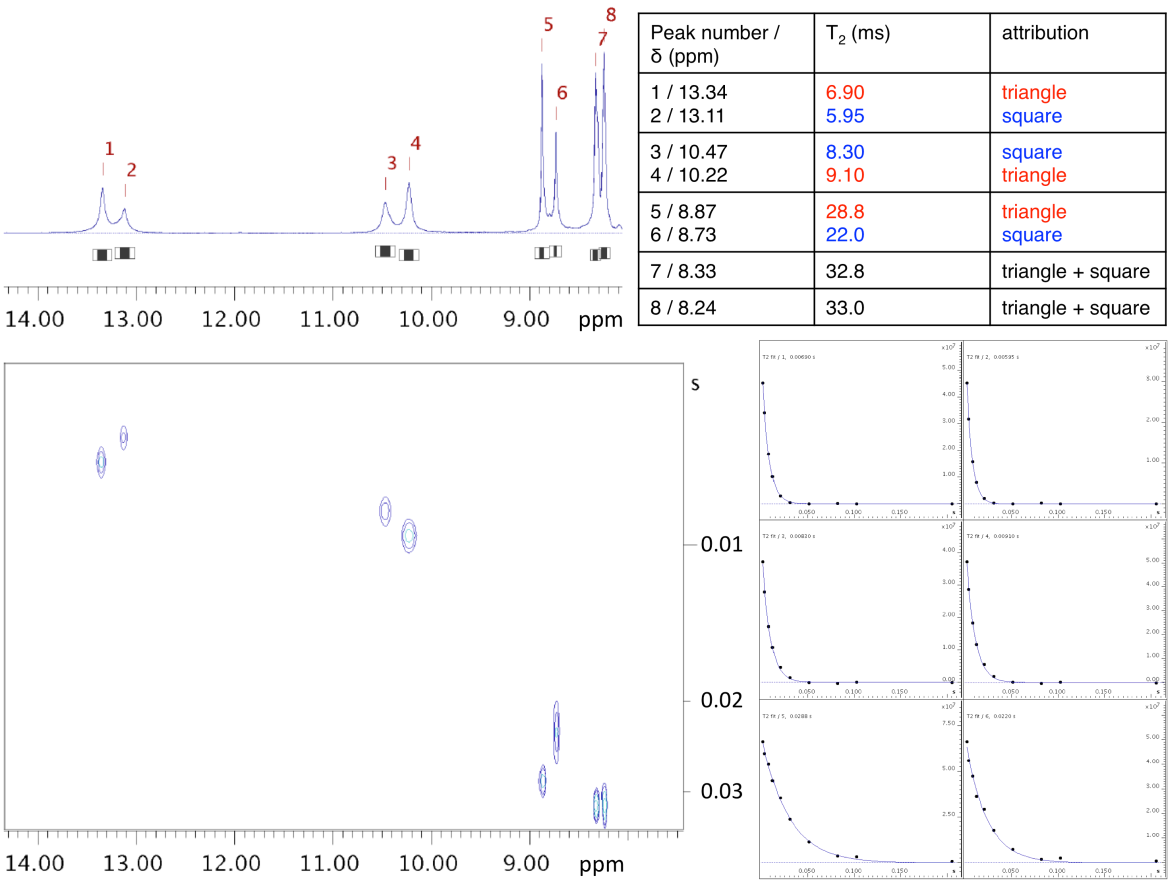


Fig. S2. ^{1}H NMR (400 MHz, selected peaks) temperature dependence of a solution of **1** (1 mM) in the presence of 1 equiv of $[Co(H_2O)_6](NO_3)_2$ in DMSO-d_6. (a) 300 K; (b) 310 K; (c) 320 K; (d) 330 K; (e) 340 K; (f) 350 K; (g) 300 K, one day after heating. The 9 coloured triangles and squares correspond to the signals of the trimer and tetramer repectively.



Peak number / δ (ppm)	T_2 (ms)	attribution
1 / 13.34 2 / 13.11	6.90 5.95	triangle square
3 / 10.47 4 / 10.22	8.30 9.10	square triangle
5 / 8.87 6 / 8.73	28.8 22.0	triangle square
7 / 8.33	32.8	triangle + square
8 / 8.24	33.0	triangle + square

Fig. S3. T_2 measurements of ^{1}H signals (600 MHz, selected peaks) of a solution of **1** (1 mM) in the presence of 1 equiv of $[Co(H_2O)_6](NO_3)_2$ in DMSO-d_6.

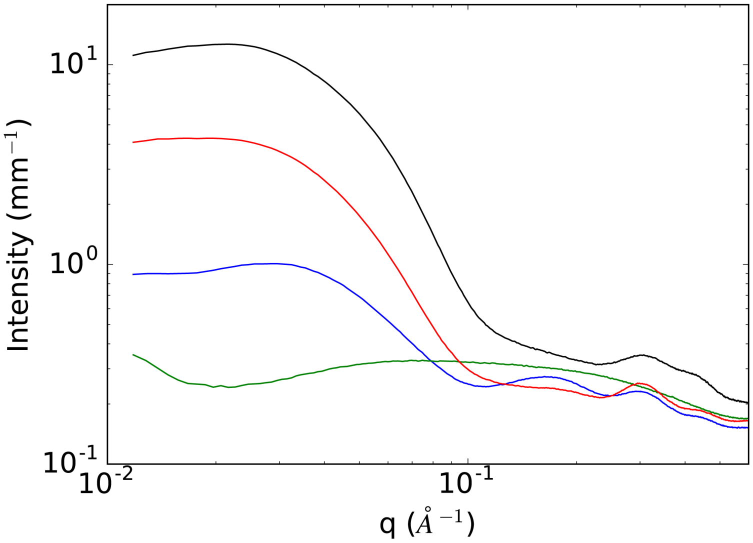
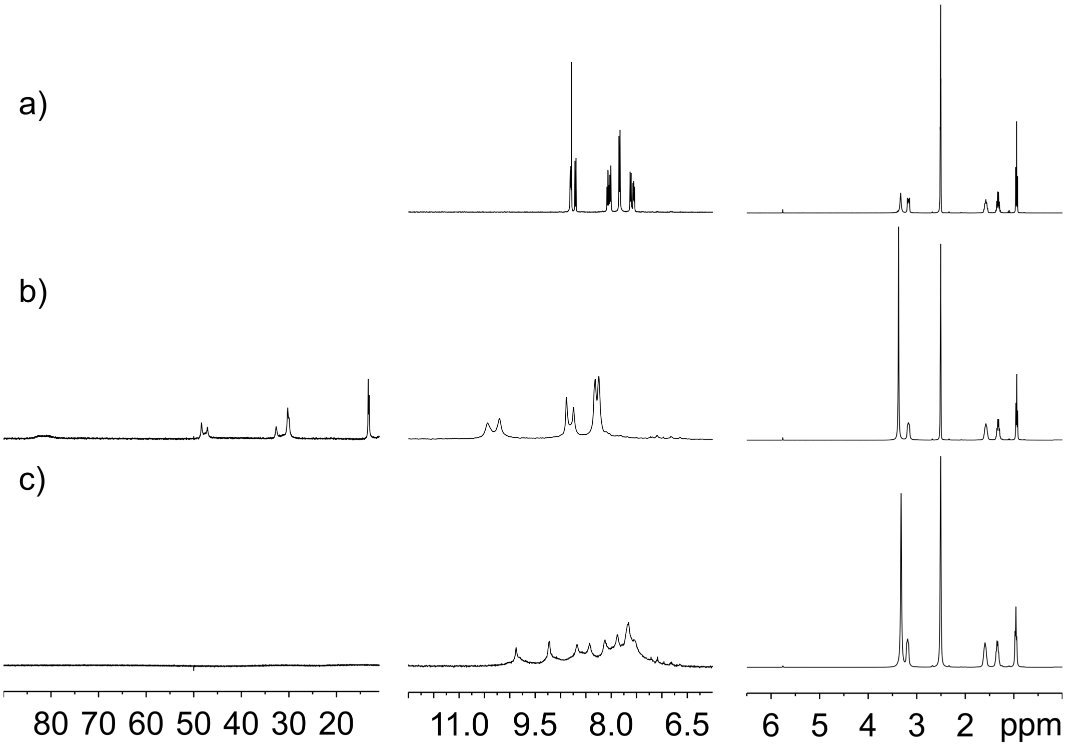


Fig. S4. SAXS patterns of a solution of **1** (1 mM in DMSO-*d*$_6$, green), the resulting discrete supramolecular species in the presence of 1 equiv $[Co(H_2O)_6](NO_3)_2$ (blue) and the aggregated species after oxidation of the Co(II) with 1 equiv $TBABr_3$ (red) or by modification of the solvent composition (DMSO-*d*$_6$/CD_3CN 1:4, black).



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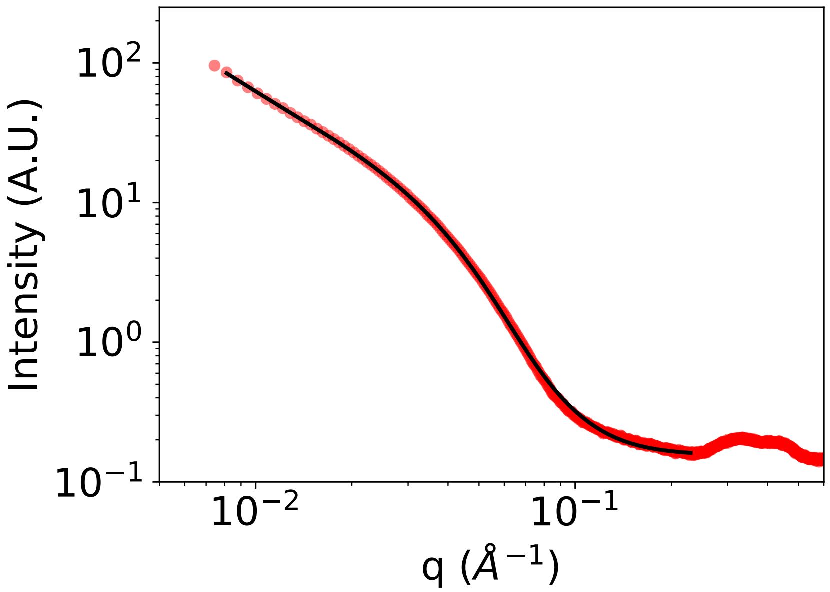
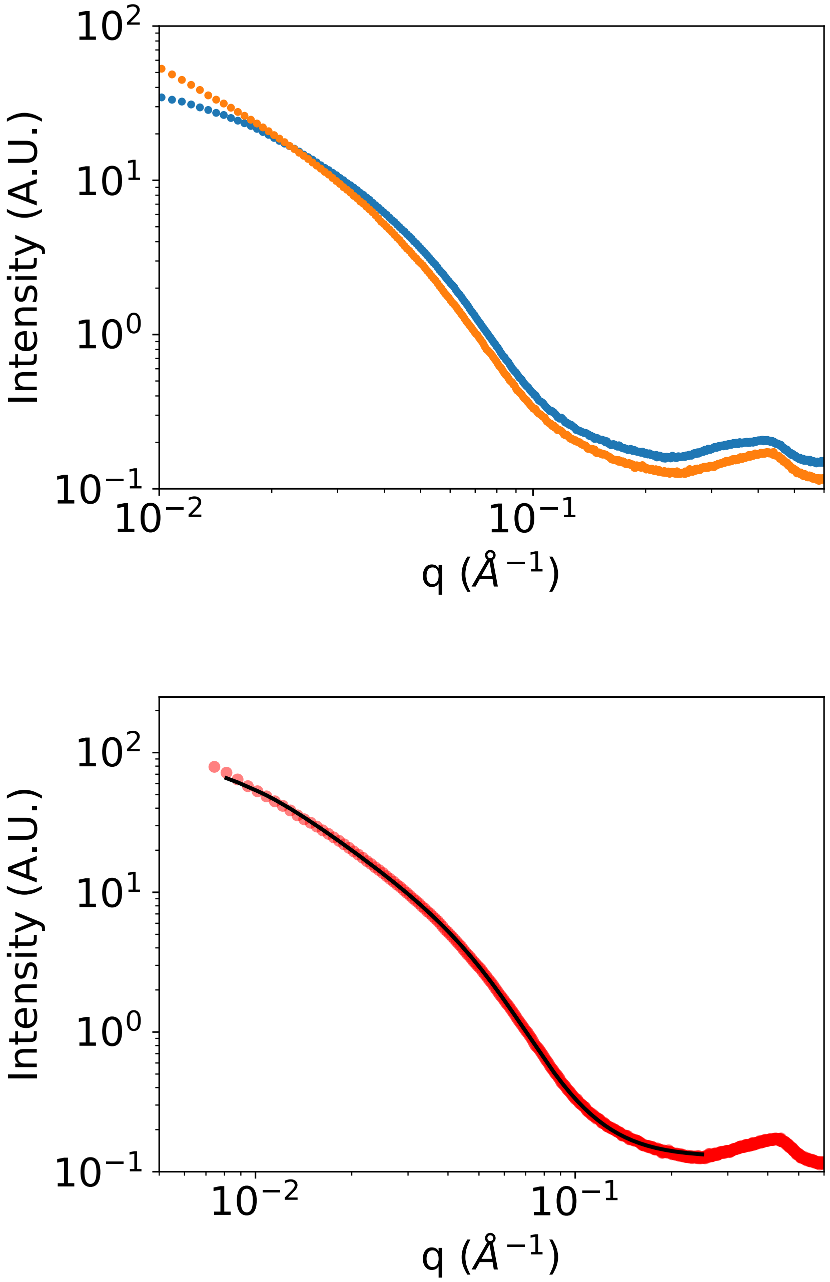


Fig. S6. Comparison of the experimental SAXS pattern of **1.Co^{III}** (red) in DMSO-d$_6$/H$_2$O (1:1, v/v, c$_{POM}$ = 1 mM) to the theoretical SAXS intensity (computed using SasView) of flexible cylinder of 260 nm in length and 3.6 nm in radius with a polydispersity of 44 % and a Kuhn length of 44 nm (black).



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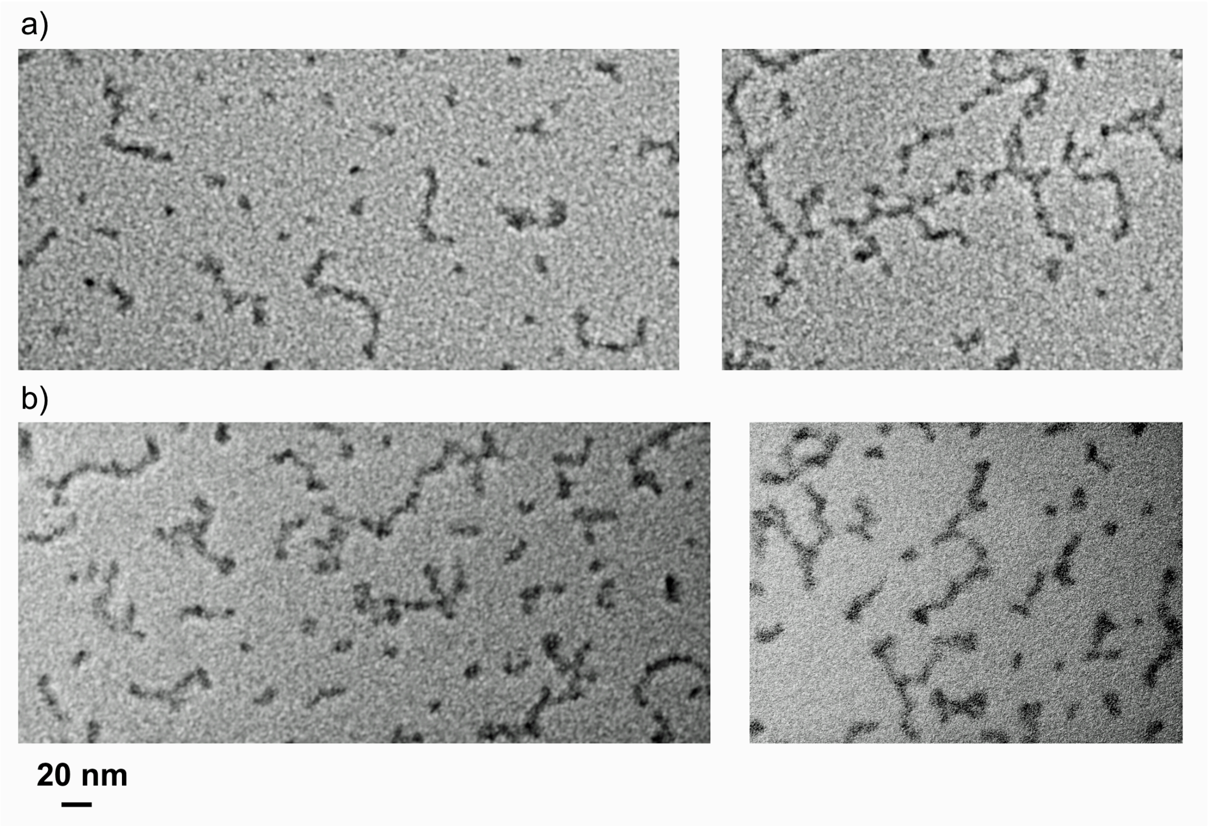

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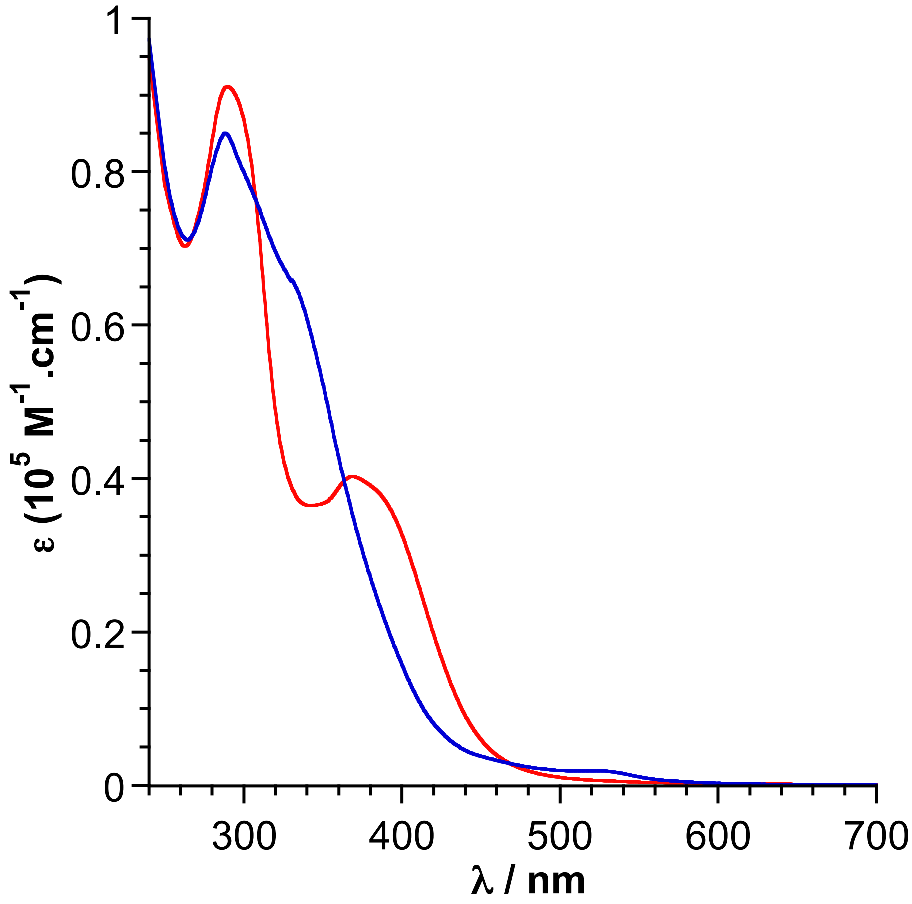
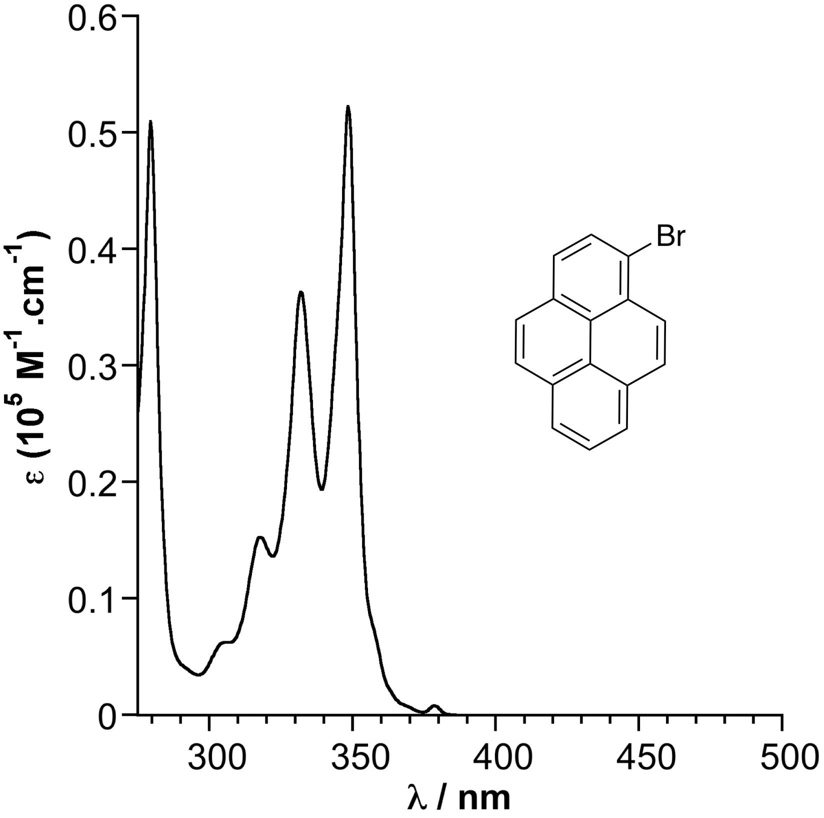


Fig. S9. Absorption spectra recorded for solutions of **1.Co^{II}** (blue) and **1.Co^{III}** (red) in DMSO-d_6/H_2O mixtures (2:98, v/v).



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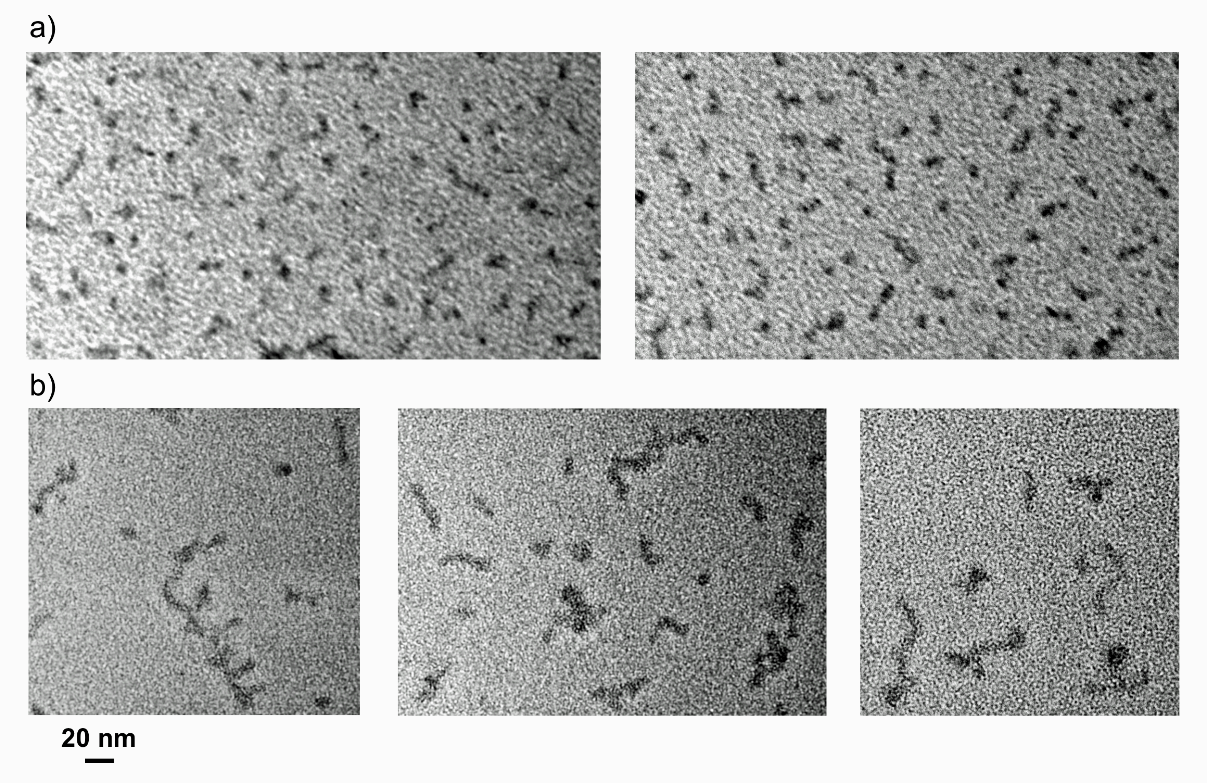

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