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Control of the light-response in supramolecular metallopolymeric gels by tuning the coordination metal

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Materials and Methods

General considerations

All reactions were carried out under inert atmosphere (Schlenk technique). All solvents were used as received from Aldrich or Fluka without any further purification. All chemicals were purchased and used as received. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ^{1}H NMR chemical shifts (δ) are given in ppm and referred to residual protons on the corresponding deuterated solvent. All deuterated solvents were used as received without any further purification. Elemental analyses were performed by the "Service d'analyse élémentaire" of the Faculty of Chemistry of the University of Strasbourg. Ligand **A**[1] and **B**[2] were synthesized by using the procedure reported elsewhere.

UV-vis characterization and titration experiments

Absorption spectra were measured on a Shimadzu 3600 double-beam UV-vis-NIR spectrophotometer and baseline corrected by using a standard Quartz Suprasil cuvette, optical path 1.00 cm. All solvents used were of spectrophotometric grade and purchased from Aldrich or VWR.

Rheological characterization

The rheological experiments have been carried out using a MCR302 rheometer from Anton Paar. Measurements have been performed under different modes using PP25 plates (diameter 25 mm). The MCR302 rheometer was equipped with a Peltier device and a high precision temperature control chamber in order to keep a constant measuring temperature. **Co-P** and **Fe-P** gel have been prepared and let rest for about 12 hours, then spread on the measuring cell while the space between the upper disposable measuring plate and the lower fixed plate was set to 0.25 mm.

G′ and G′′ measurements have been performed under the following experimental conditions:

- as a function of strain (from 0.1 to 100%) at a frequency of 1 Hz
- as a function of time at constant frequency (1 Hz) for two values of strain: 0.5% strain for 300 s and then switched to 200% of strain for 120 s.

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[1] T. Yutaka, M. Kurihara, H. Nishihara, *Mol. Cryst. Liq. Cryst.* **2000**, *343*, 193–198.

[2] A. Khatyr, R. Ziessel, *Tetrahedron Lett.* **1999**, 40, 5515–5518.

Synthetic procedures: polymer syntheses

Fe-P metallopolymer

Ligand **A** (38.7 mg, 0.06 mmol, 2 eq.) and **B** (28.9 mg, 0.03 mmol, 1 eq.) were dissolved in chloroform under an argon atmosphere and the mixture was heated at 60 °C. Then, $Fe(BF_4)_2{\cdot}6H_2O$ (30.4 mg, 0.09 mmol, 3 eq.) was added to the reaction and the resulting mixture was refluxed overnight. After cooling down to room temperature, the volatiles were removed under vacuum to give the polymeric material as a deep-violet powder. 1H NMR spectrum is displayed in Figure S2.

^{1}H NMR (DMSO-*d*$_6$, 400 MHz, 293 K) δ: 9.87, 9.47, 9.18, 8.96, 8.11, 7.58, 7.38–7.26, 4.35, 1.98–0.76. Analysis: Calcd. for **Fe-P** with stoichiometry 2 **A**: 1 **B** : 3 $Co(BF_4)_2$: C, 61.26%; H, 4.39%; N, 10.62%. Found: C, 65.16%; H, 6.75%; N, 7.29%.

Co-P metallopolymer

Ligand **A** (19.3 mg, 0.03 mmol, 2 eq.) and **B** (14.4 mg, 0.015 mmol, 1 eq.) were dissolved in chloroform under an argon atmosphere and the mixture was heated at 60 °C. Then, $Co(BF_4)_2{\cdot}6H_2O$ (15.3 mg, 0.045 mmol, 3 eq.) was added to the reaction and the resulting mixture was refluxed overnight. After cooling down to room temperature, the volatiles were removed under vacuum to give the polymeric material as an orange powder. Elemental Analysis: Calcd. for **Co-P** with stoichiometry 2 **A**: 1 **B** : 3 $Co(BF_4)_2$: C, 61.07%; H, 4.37%; N, 10.59%. Found: C, 59.62%; H, 5.41%; N, 8.47%.

Gel formation. Stock solutions of **Fe-P** or **Co-P** were prepared by dissolving the polymer in dry DMF (1 mg / 50 μL). Then, EtOH was added in the appropriate proportion (DMF:EtOH = 1:20 $^V/_V$ for 0.12 wt.%) and the mixture was left at room temperature for about 3 hours until gelation occurred (reverse vial test).

Titration experiments

Ligand **A** and **B** were titrated with the corresponding $M(BF_4)_2$ salt (where M is Fe(II), Co(II)) by using the following condition: a $1.0{\times}10^{-5}$ M solution of **A** and **B** in a mixture of $CH_3CN:CHCl_3$ (1:9 $^V/_V$) was titrated with 20 μL aliquots of a solution $2.5{\times}10^{-4}$ M in $M(BF_4)_2$ in the same solvent composition. The addition was done stepwise and the formation of M(II) supramolecular coordination polymer was monitored by UV-vis.

Figures

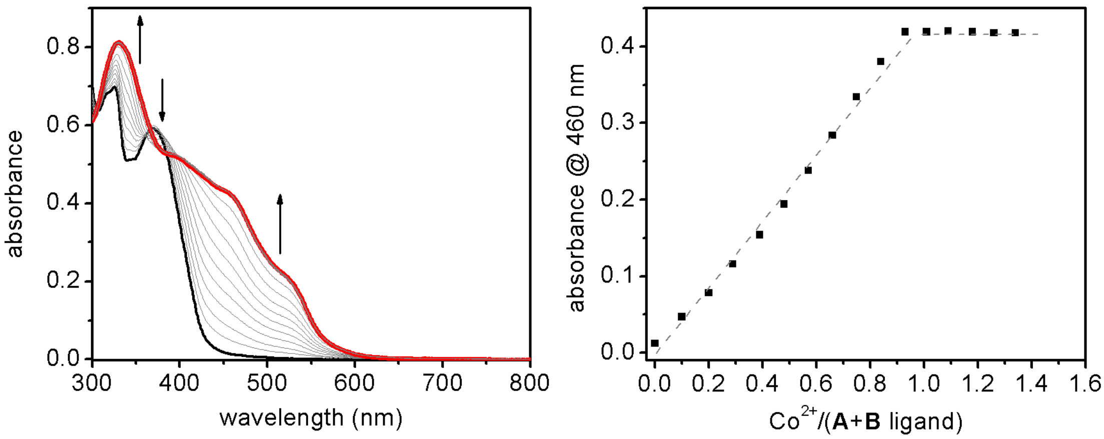

Figure S1. Titration of ligand **A** and **B** at concentration of 1×10^{-5} M in $CHCl_3$:CH_3CN 9:1 with $Co(BF_4)_2$ followed by UV-vis spectroscopy (*left*). The spectra corresponding to 0 and 1 eq. of Co^{2+} added are displayed as black and red trace, respectively. Black arrows indicate the variation of the spectra features upon addition of metal salt; plot of the absorbance variation recorded at 460 nm as function of $Co(BF_4)_2$ added (*right*). Dotted grey lines are only intended to guide the eye.

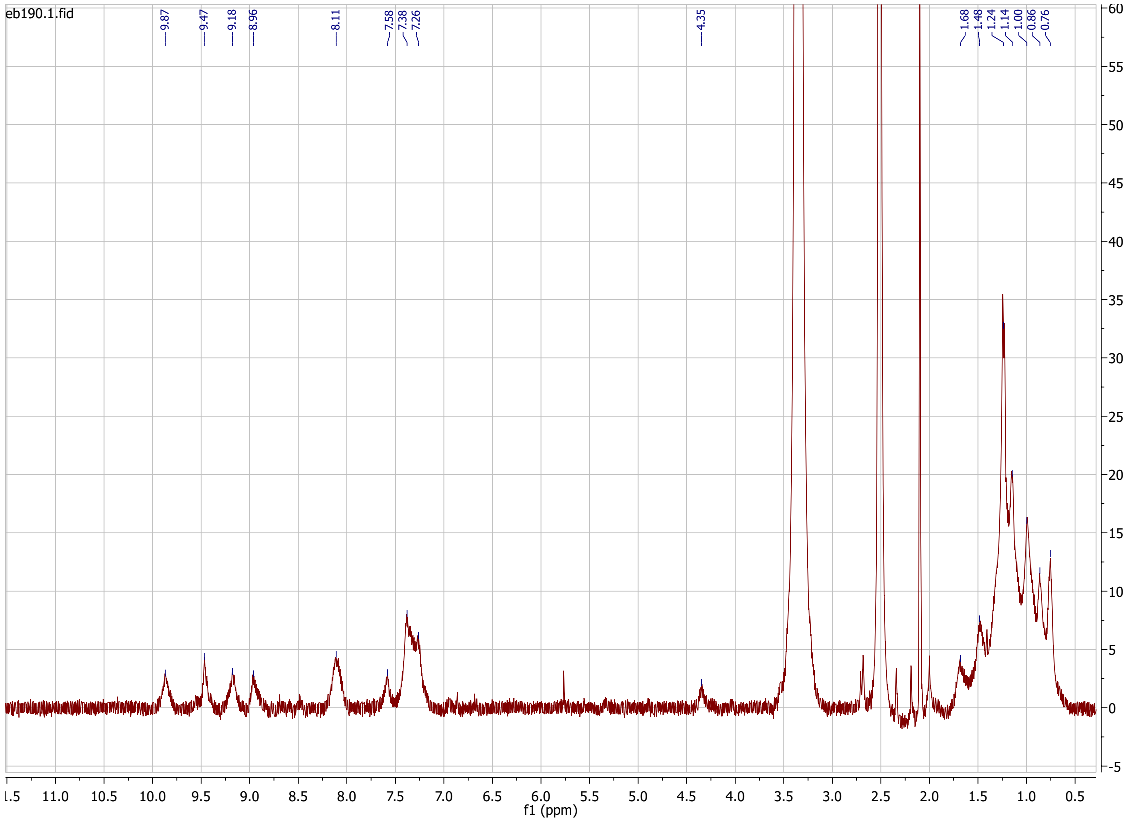

Fig. S2. ^{1}H NMR spectrum of **Fe-P** metallopolymer recorded in DMSO-d_6 at 293 K.

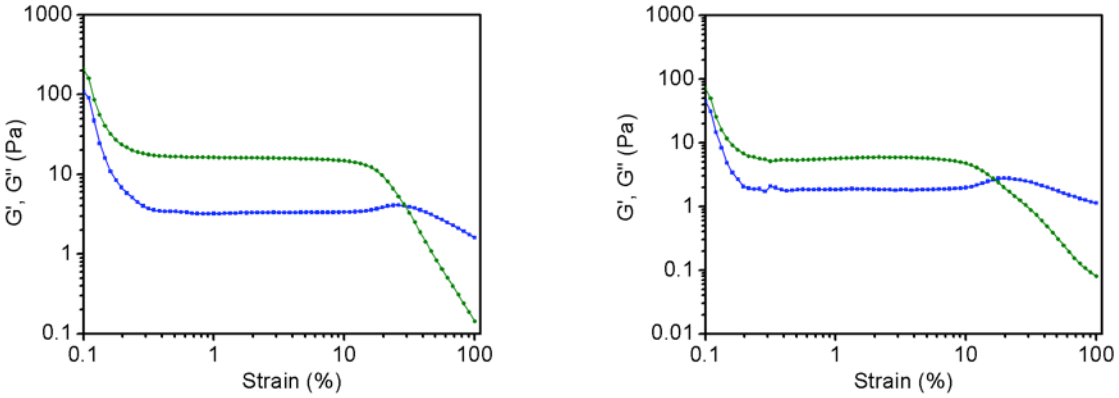

Figure S3. Dependency of the storage, G´ (green trace), and loss moduli, G´´ (blue trace), on strain recorded for **Co-P** (left box) and **Fe-P** (right box) gels. The gels were prepared at 0.5 wt.% in DMF:EtOH 1:5 v/v and measurements were carried out after about 12 hours to allow full gel formation. Applied frequency = 1 Hz, temperature = 25°C.

The storage and loss moduli dependencies over strain experiments for both **Co-P** and **Fe-P** systems allow to identify the critical strain level. Below this value (respectively 15% for **Co-P** system and 10% for **Fe-P** system), G' and G" are independant of the strain (linear-viscoelastic regime) and the structure of the gel is intact, which means the materials display a solid-like behaviour since G'>G", evidencing a significant structuration of the materials. Above this critical strain level, the behaviours of these materials are no longer linear and their storage modulus decreases significantly evidencing the disruption of the supramolecular network structure.

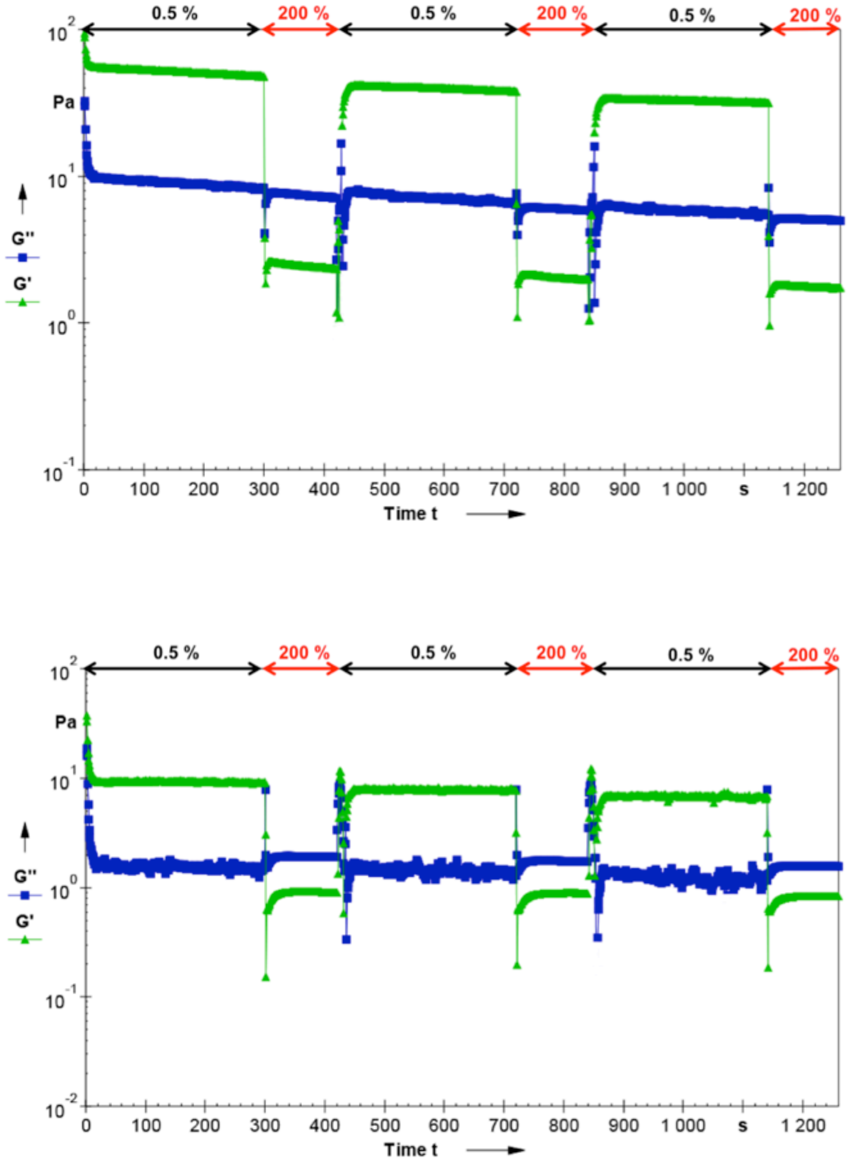

Figure S4. Rheological data monitoring the thixotropic properties of the **Co-P** (upper box) and **Fe-P** (lower box) gels using continuous step measurements upon application of small (0.5%) and large (200%) strain cycles. The corresponding applied strain is shown on the top of the plot. Storage, G′, and loss moduli G′′ are displayed as green and blue trace, respectively. The gels were prepared at 0.5 wt.% in DMF:EtOH 1:5 v/v and measurements were carried out after about 12 hours to allow full gel formation.