Electronic Supplementary Material (ESI) for Polymer Chemistry.

# Electronic Supporting Information

## The effect of metal ions on viscoelastic properties of thermosensitive sol-to-gel reversible metallo-supramolecular hydrogels

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### 1-Reagents

All chemicals products were purchased from Aldrich unless otherwise noted. *N,N*-dimethylformamide (DMF, 99.8 %), *N,N*-dimethylacrylamide (DMA, 99 %), 4,4'-azobis(4-cyanovaleric acid (ACPA, > 98 %), 1,4-dioxane (> 99.5 %), *N*-isopropylacrylamide (NIPAM, > 99%), diethyl ether (99.8 %, Carlo Erba) and 2,2'-azobis(2-methyl-propionamidine)dihydrochloride (V-50, 98 %) were used as received. Pure water was obtained from a Millipore Direct Q system and had a resistivity of 18.2 MΩ cm at 25°C. $FeCl_2,4H_2O$ (Aldrich, 99.99 %), $ZnCl_2$ (Aldrich, 99.99 %) and $NiCl_2,6H_2O$ (Aldrich, 99.99 %) were kept in a glove box and weighed under an argon atmosphere. Terpyridine-terminated trithiocarbonate chain transfer agent (Tpy-CTA) was synthesized following a reported procedure[1].

### 2-General Characterization

**Nuclear magnetic resonance (NMR) spectroscopy.** NMR spectra were recorded on a Bruker AC-400 spectrometer for $^1$H-NMR (400 MHz). Chemical shifts are reported in ppm relative to the deuterated solvent resonances.

**Size exclusion chromatography (SEC).** The average molar masses (number-average molar mass $\overline{M_n}$, weight-average molar mass $\overline{M_w}$) and dispersity (*Đ* = $\overline{M_w}/\overline{M_n}$) values were measured by SEC using *N,N*-dimethylformamide (with LiBr at 1 g.L$^{-1}$) as an eluent, and carried

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[1] S. Piogé, C.-A. Fustin and J.-F. Gohy, *Macromolecular Rapid Communications*, 2012, **33**, 534-539.

out using a system equipped with a guard column (Polymer Laboratories, PL gel 5 μm) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns) and with a Waters 410 differential refractometer (RI) and a Waters 481 UV detector operating at 309 nm and 285 nm. The instrument operated at a flow rate of 1.0 mL.min$^{-1}$ at 60°C and was calibrated with narrow linear polystyrene (PS) standards ranging in molar mass from 580 g.mol$^{-1}$ to 483 000 g.mol$^{-1}$. Molar mass and dispersities (Đ) were calculated using Waters EMPOWER software.

**Differential scanning calorimetry (DSC)**. DSC measurement was performed on a TA Instruments Q100 connected to a computer in aluminum pans. The DSC instrument was calibrated using an indium standard. Sample was heated under a static nitrogen atmosphere from 10°C to 50°C and then cooled to 10°C at a heating rate of 10 °C.min$^{-1}$ after an isotherm at 50°C during 2 minutes. Thermal transitions were read from the maximum of the endotherm (heating scan).

**Differential scanning calorimetry (DSC)**. DSC measurements were performed on a TA Instruments Q100 connected to a computer in aluminum pans under nitrogen otherwise noted. The DSC instrument was calibrated using an indium standard. Sample was heated from 15 °C to 50 °C at a heating rate of 10 °C.min$^{-1}$ and under a static nitrogen atmosphere, followed by cooling to 15°C at the same rate after an isotherm at 50°C during 2 minutes. Thermal transitions were obtained from the maximum of the endotherm (heating scan).

## 3-Synthesis of the terpyridine end-functionalized poly(*N*,*N*-dimethylacrylamide) PDMA macromolecular chain transfer agent (Tpy-PMDA-CTA)

A magnetic stirrer was charged to a Schlenk tube along with DMA (2.6593 g, 26.8 mmol), Tpy-CTA (0.1024 g, 0.150 mmol), ACPA (0.0054 g, 0.019 mmol) using the ratio of $[\mathrm{DMA}]_0/[\mathrm{Tpy\text{-}CTA}]_0/[\mathrm{ACPA}]_0 = 180/1/0.13$ with DMF (92 μL) used as internal standard and 1,4-dioxane (13.55 mL). The polymerization mixture was degassed with argon for 30 minutes and placed in a thermostated oil bath at 80 °C to initiate the polymerization. The immersion in the oil bath defines t=0 and a sample was removed using a deoxygenated syringe as a reference point. The polymerization was stopped and the reaction mixture was subjected to $^1$H-NMR spectroscopy to determine monomer conversion and to SEC analysis to determine molar mass and dispersity. DMA conversion was determined by comparing the integrals of vinylic protons from DMA at 5.55 ppm with the integral of $C\boldsymbol{H}O$ from DMF at 8 ppm. The monomer conversion mediated by Tpy-CTA was determined to be 45 % in 23 min. DMF and 1,4-dioxane were removed using a rotary evaporator and polymer was purified by a series of precipitations in cold ether, filtered and dried in a vacuum oven at 25 °C.

**SEC** (DMF-LiBr, 60°C) : $\overline{M_{n,SEC,\,Tpy\text{-}PDMA\text{-}CTA}}$ = 13800 g.mol$^{-1}$, $Đ_{Tpy\text{-}PDMA\text{-}CTA}$ = 1.23. **$^1$H-NMR** ($Tpy\text{-}PDMA_{82}\text{-}CTA$, 400MHz, $CDCl_3$), δ in ppm: 0.88 (t, $PDMA\text{-}S\text{-}C(=S)S\text{-}(CH_2)_{11}\text{-}C\boldsymbol{H}_3$); 1-2,7(m, $\text{-}OCH_2\text{-}C\boldsymbol{H}_2\text{-}C\boldsymbol{H}_2\text{-}C\boldsymbol{H}_2\text{-}$, $PDMA\text{-}S\text{-}C(=S)S\text{-}CH_2\text{-}(C\boldsymbol{H}_2)_{10}\text{-}CH_3$; $\text{-}C\boldsymbol{H}_2\text{-}CH\text{-}C(=O)\text{-}N(CH_3)_2$; $\text{-}C(C\boldsymbol{H}_3)_2\text{-}CO\text{-}NH\text{-}$; 2.7-3.2 (m, $\text{-}C\boldsymbol{H}\text{-}C(=O)\text{-}N(CH_3)_2$); $\text{-}O\text{-}(CH_2)_4\text{-}C\boldsymbol{H}_2\text{-}NH\text{-}$; $PDMA\text{-}S\text{-}C(=S)S\text{-}C\boldsymbol{H}_2\text{-}(CH_2)_{10}\text{-}CH_3$; $\text{-}N(C\boldsymbol{H}_3)_2$); 4.21 (t, 2H, $\text{-}OC\boldsymbol{H}_2\text{-}CH_2\text{-}$); 7.32 (ddd, 2H, $\text{-}C(N)=CH\text{-}C\boldsymbol{H}=$); 7.84 (dt, 2H, $=N\text{-}CH\text{-}CH\text{-}C\boldsymbol{H}\text{-}$); 8.00 (s, 2H, $\text{-}OC=C\boldsymbol{H}\text{-}$); 8.60 (dd, 2H, $\text{-}C(N)=C\boldsymbol{H}\text{-}$); 8.68 (dd, 2H, $=N\text{-}CH\text{-}C\boldsymbol{H}=$). $\overline{M_{n,NMR,Tpy\text{-}PDMA\text{-}CTA}}$ = 8800 g.mol$^{-1}$, $DP_{DMA}$=82.

## 4-RAFT copolymerization of NIPAM mediated by Tpy-PDMA-CTA in dispersed media

Dispersion copolymerization of NIPAM (2.09 g, 18.5 mmol) was performed in water at 70°C in the presence of $Tpy\text{-}PDMA_{82}\text{-}CTA$ (0.7997 g, 0.091 mmol), of initiator solution (0.099 g of a solution containing 0.0746 g of V50 and 1.0579 g of deionized water) and of deionized water (118.010 g) using the ratio of $[Tpy\text{-}PDMA_{82}\text{-}CTA]_0/[NIPAM]_0/[V50]_0=1/204/0.26$. The solution was purged with argon for 30 min in an ice bath and then placed in an oil bath thermostated at 70°C to initiate the polymerization. Twenty five minutes later the opalescence appeared and the reaction was continued for 240 min, quenched by immersion of the flask in iced water and then was lyophilized. The quasi complete monomer conversion (> 90%) was checked by $^1$H-NMR spectroscopy in $D_2O$ by the relative integration of the protons of DMF at 8 ppm and the vinylic protons of NIPAM between 5.9-6.3 ppm. The solution was dialyzed in water during 24 hours and lyophilized and the solid obtained was dried under vacuum on the presence of $P_2O_5$.

**SEC** (DMF-LiBr, 60°C) : $\overline{M}_{n,SEC,\ Tpy\text{-}PDMA\text{-}b\text{-}PNIPAM}$ = 52720 g.mol$^{-1}$, $Đ_{Tpy\text{-}PDMA\text{-}b\text{-}PNIPAM}$ = 1.46.

**$^1$H-NMR** (Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190}$, 400 MHz, $D_2O$), δ in ppm: 0,88-2,7 (m, PDMA-S-C(=S)S-$(CH_2)_{11}$-$C\boldsymbol{H}_{3;}$ PDMA-S-C(=S)S-$CH_2$-$(C\boldsymbol{H}_2)_{10}$-$CH_3$; -$C\boldsymbol{H}_2$-CH-CO-$N(CH_3)_2$; -$C(C\boldsymbol{H}_3)_2$-CO-NH-; -NH-$CH(C\boldsymbol{H}_3)_2$; -CH-CO-NH-$C(C\boldsymbol{H}_3)_2$-COOH; -C$\boldsymbol{H}$-CO-NH-$CH(CH_3)_{2;}$ -C$\boldsymbol{H}$-CO-NH-$C(CH_3)_2$-COOH; -$C\boldsymbol{H}_2$-CH-CO-NH-$CH(CH_3)_{2;}$ -$C\boldsymbol{H}_2$-CH-CO-NH-$C(CH_3)_2$-COOH; -C$\boldsymbol{H}$-CO-$N(CH_3)_2$); 2.7-3.2 (m, -O-$(CH_2)_4$-$C\boldsymbol{H}_2$-NH-; PDMA-S-C(=S)S-$C\boldsymbol{H}_2$-$(CH_2)_{10}$-$CH_3$; -$N(C\boldsymbol{H}_3)_2$; 4.00 (m, -NH-C$\boldsymbol{H}$$(CH_3)_2$); 7.32 (ddd, 2H, -C(N)=CH-C$\boldsymbol{H}$=); 7.84 (dt, 2H, =N-CH-CH-C$\boldsymbol{H}$-); 8.00 (s, 2H, -OC=C$\boldsymbol{H}$-); 8.60 (dd, 2H, -C(N)=C$\boldsymbol{H}$-); 8.68 (dd, 2H, =N-CH-C$\boldsymbol{H}$=). $\overline{M}_{n,NMR,\ Tpy\text{-}PDMA\text{-}b\text{-}PNIPAM}$ = 30270 g.mol$^{-1}$.

## 5-Figures

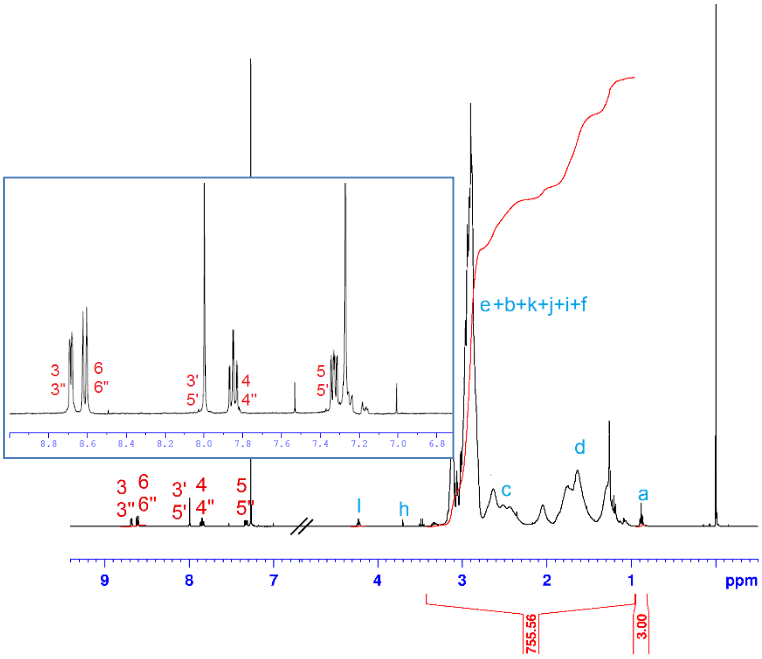

**Figure S1.** 1H-NMR spectrum (400 MHz, $CDCl_3$) of purified Tpy-PDMA-CTA.

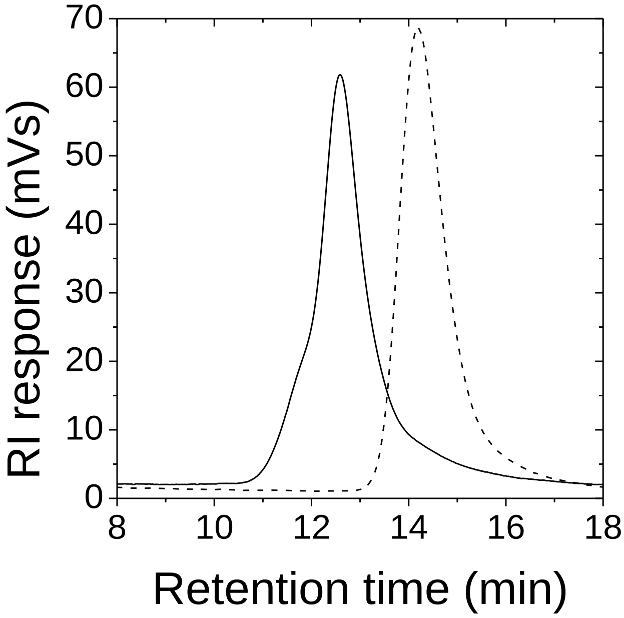

**Figure S2.** Overlaid SEC chromatograms of the purified Tpy-PDMA$_{82}$-CTA (---) and Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$ (—) using RI detection.

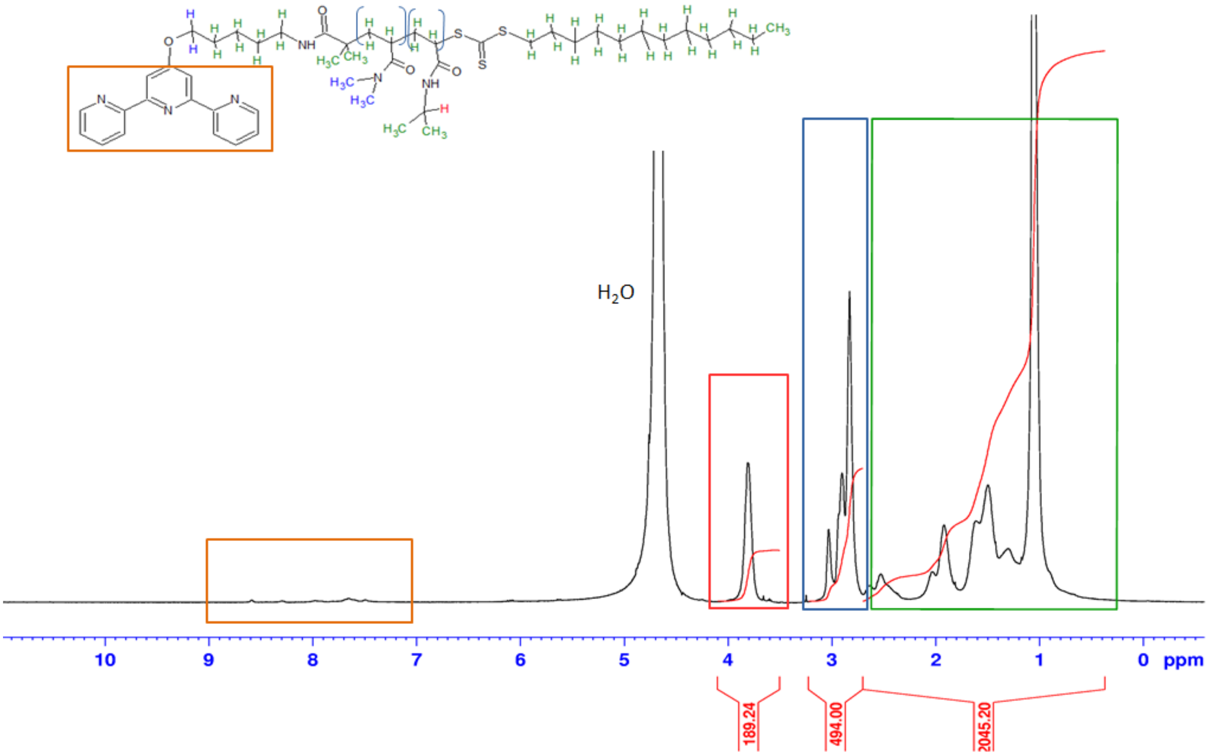

**Figure S3.** $^1$H-NMR spectrum (400 MHz, $D_2O$) of purified Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$.

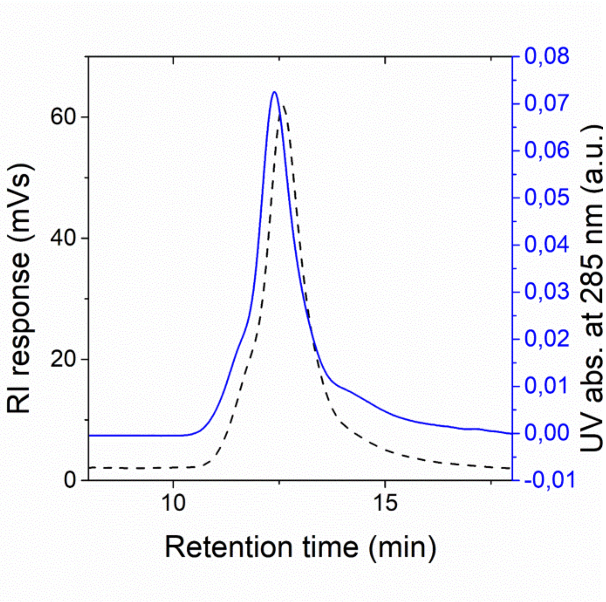

**Figure S4.** Overlay SEC chromatogram of the purified Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$ using RI (dashed line) and UV (solid line) detection at 285 nm.

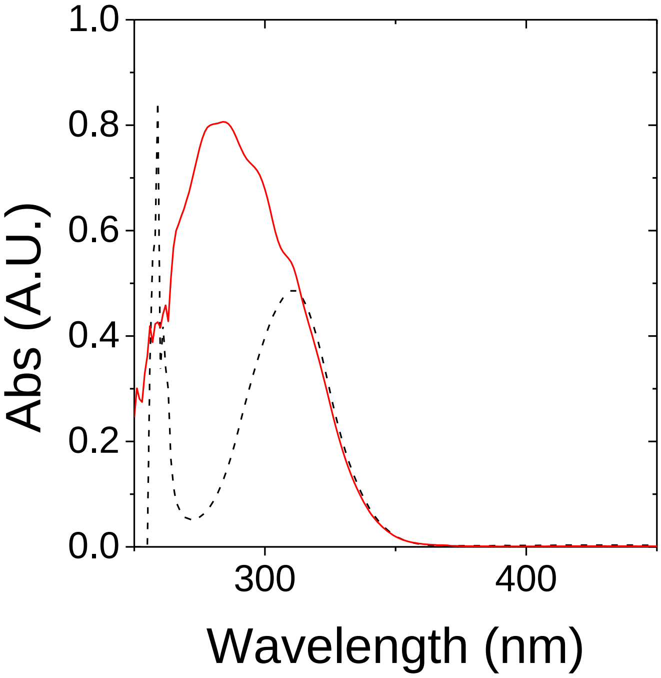

Figure **S5**. Overlay UV absorbance spectra (250 - 450 nm) of the Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$ (solid line) and HOOC-PDMA-*b*-PNIPAM (dashed line) detection at 285 nm.

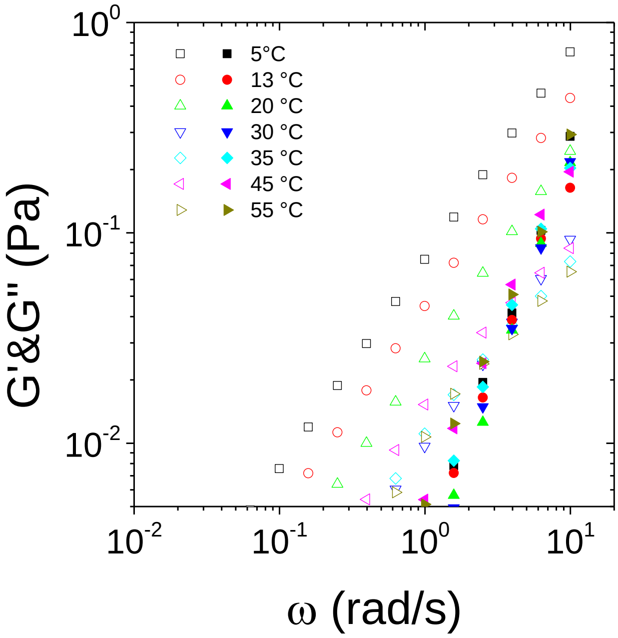

Figure **S6.** Frequency dependence of elastic G' (close symbols) and viscous G" (open symbols) moduli of (Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$)$_2$ in aqueous solution (8 % w/v) at different temperatures as indicated in the figure.

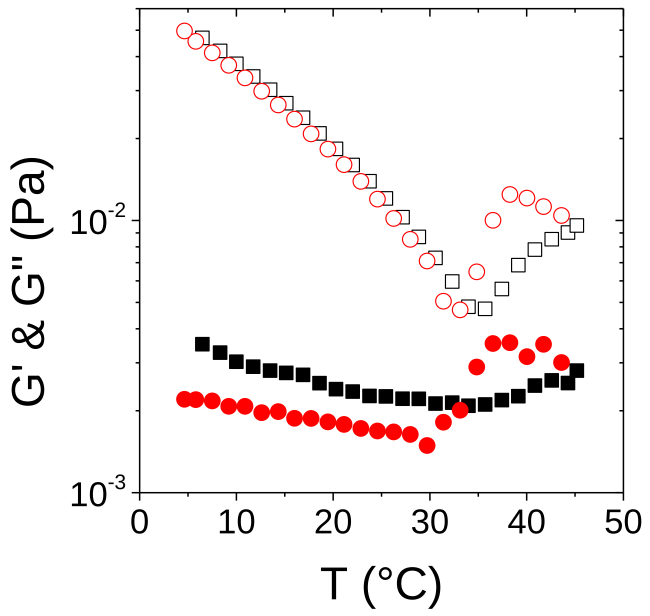

Figure **S7.** Temperature dependence of the storage G' and viscous G'' moduli, close and open symbols, respectively, of Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$ copolymers aqueous solution without metal ion (8 % w/v). The heating ramp was 5°C.min$^{-1}$. The frequency was fixed to 0.1 Hz and the strain to 1 %. Black square symbols are for the heating ramp and red circles symbols are for the cooling ramp.

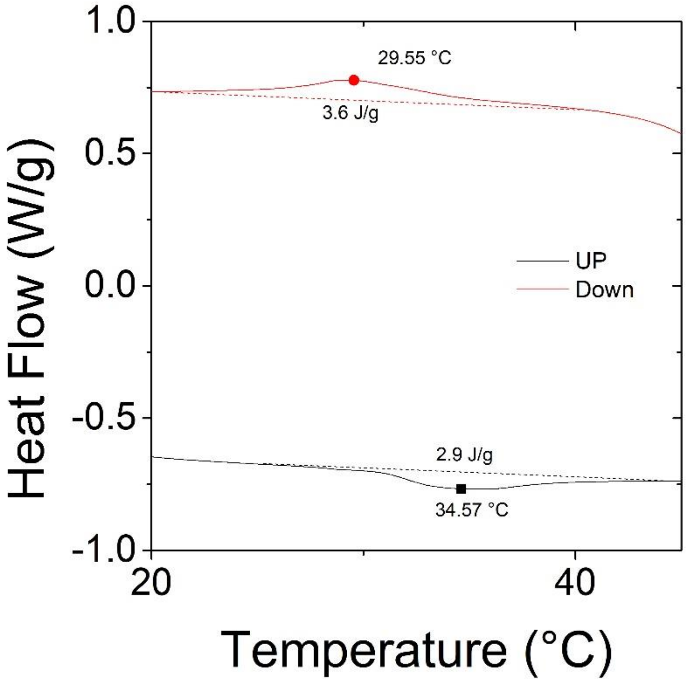

Figure **S8**. DSC thermogram of [0.5Fe(Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$)$_2$]$^{2+}$ complex.

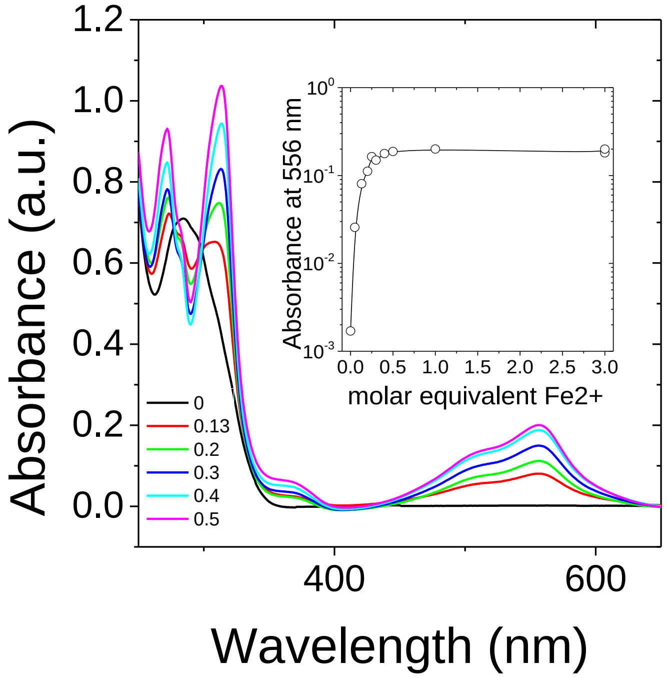

Figure **S9.** Effect of $Fe^{2+}$ molar equivalent on the absorption spectrum of Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$ in diluted aqueous media (0.15 % w/v) at 20°C. The inset shows the relationship between $Fe^{2+}$ molar equivalent with respect to terpyridine and the absorbance at 556 nm.

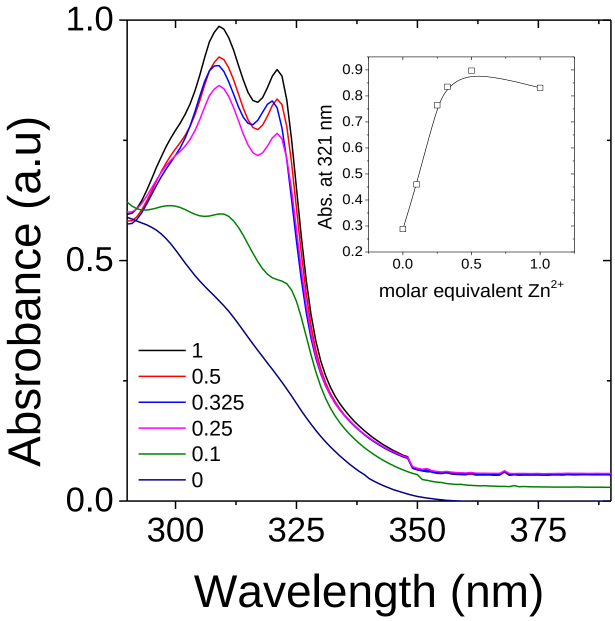

Figure **S10.** Effect of $Zn^{2+}$ molar equivalent on the absorption spectrum of Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$ in diluted aqueous media (0.15 % w/v) at 20°C. The inset shows the relationship between $Zn^{2+}$ molar equivalent with respect to terpyridine and the absorbance at 321 nm.

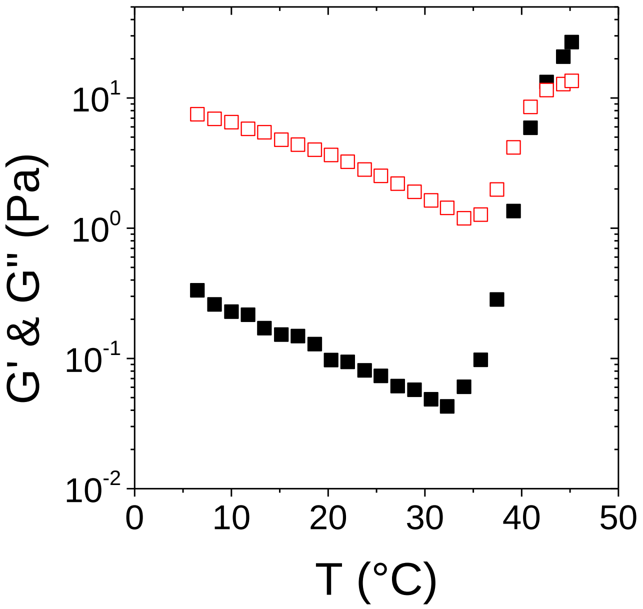

Figure **S11**. Temperature dependence of the viscoelastic moduli G’ and G”, close and open symbols, respectively, of $[0.5Ni(Tpy\text{-}PDMA_{82}\text{-}\textit{b}\text{-}PNIPAM_{190})_2]^{2+}$ aqueous solution at 8 % w/v. The heating ramp was 5°C.min$^{-1}$. The frequency and the strain were fixed to 0.1 Hz and 1 % respectively. The solid lines as just a guide for eyes.

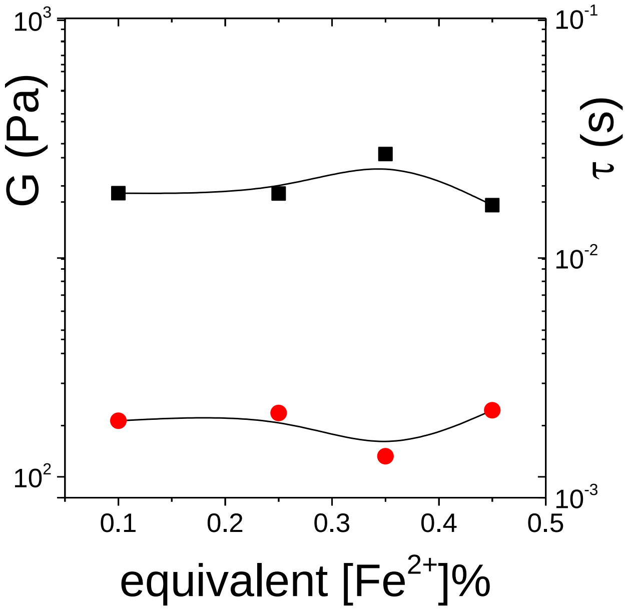

Figure **S12.** Influence of $Fe^{2+}/Zn^{2+}$ molar equivalent composition on the relaxation time τ (square) and the intersection modulus G (circle) of $[xFe/yZn(Tpy\text{-}PDMA_{82}\text{-}\textit{b}\text{-}PNIPAM_{190})_2]^{2+}$ (with x+y = 0.5) aqueous solution (8 % w/v) at 13 °C.

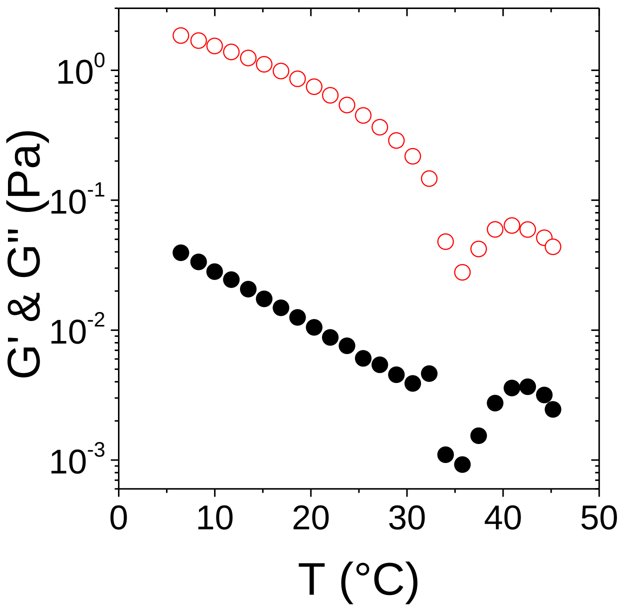

Figure **S13.** Temperature dependence of the viscoelastic moduli G’ and G”, close and open symbols, respectively, of [0.1Fe/0.4Zn(Tpy-PDMA$_{82}$-*b*-PNIPAM$_{190}$)$_2$]$^{2+}$ aqueous solution at 8 % w/v. The heating ramp was 5°C.min$^{-1}$. The frequency and the strain were fixed to 0.1 Hz and 1 % respectively.

Table **S1**. LCST determined by DSC for different hydrogels prepared from [xM(Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190})_2]^{2+}$

| Sample | Metal ion $M^{2+}$ | Molar equivalent[a] | LCST heating (°C)[b] | LCST cooling (°C)[c] |
|---|---|---|---|---|
| Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190}$ | - | - | 34.6 | 29.2 |
| [0.2Fe)(Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190})_2]^{2+}$ | Iron(II) | 0.2 | 34.3 | 29.4 |
| [0.5Fe(Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190})_2]^{2+}$ | Iron(II) | 0.5 | 34.5 | 29.6 |
| [3Fe(Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190})_2]^{2+}$ | Iron(II) | 3 | 34.9 | 29.0 |
| [0.5Zn(Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190})_2]^{2+}$ | Zinc(II) | 0.5 | 34.6 | 29.6 |
| [0.5Ni(Tpy-$PDMA_{82}$-*b*-$PNIPAM_{190})_2]^{2+}$ | Nickel(II) | 0.5 | 34.9 | 29.2 |

[a] The molar equivalent of $M^{2+}$ ions with respect to terpyridine. [b] LCST obtained from the maximum of the endotherm (heating scan) with heating rate of 10°C.$min^{-1}$. [c] LCST obtained from the maximum of the exotherm (cooling scan) with cooling rate of 10°C.$min^{-1}$.