

Triple stimuli responsive polymers with fine tuneable magnetic response

I. Chikh Alard,^{a,d} J. Soubhye,^b G. Berger,^b M. Gelbcke,^b S. Spassov,^c K. Amighi,^a J. Goole^a and F. Meyer^d

^a *Laboratory of Pharmaceutics and Biopharmaceutics, Faculty of Pharmacy, Université Libre de Bruxelles, 1050 Brussels, Belgium*

^b *Laboratory of Therapeutic Chemistry, Faculty of Pharmacy, Université Libre de Bruxelles, 1050 Brussels, Belgium.*

^c *Institut Royal Météorologique, Centre de Physique du Globe, 5670 Dourbes (Viroinval), Belgium.*

^d *Laboratory of Biopolymers and Supramolecular Nanomaterials, Faculty of Pharmacy, Université Libre de Bruxelles, 1050 Brussels, Belgium.*

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SQUID magnetization of magnetic polymers PXR

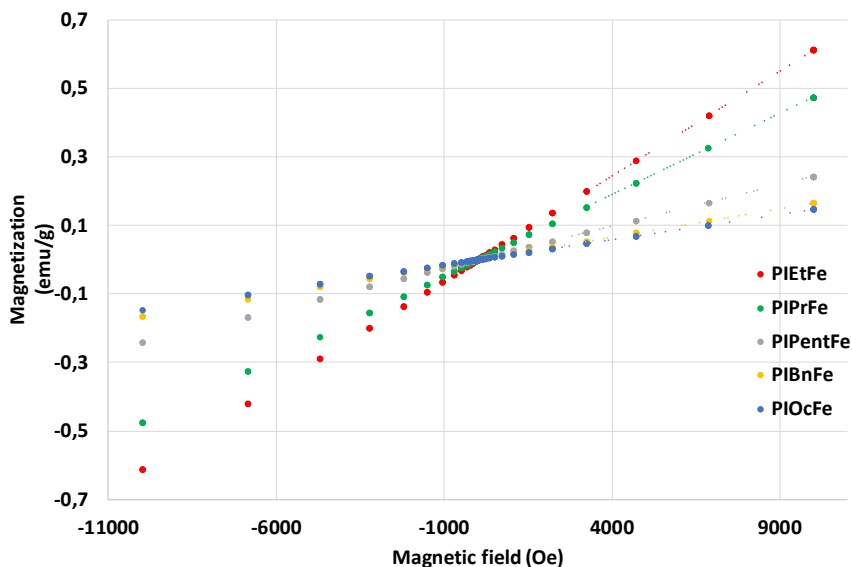


Figure S1. SQUID magnetization of magnetic polymers **PIRFe** with different appended R groups

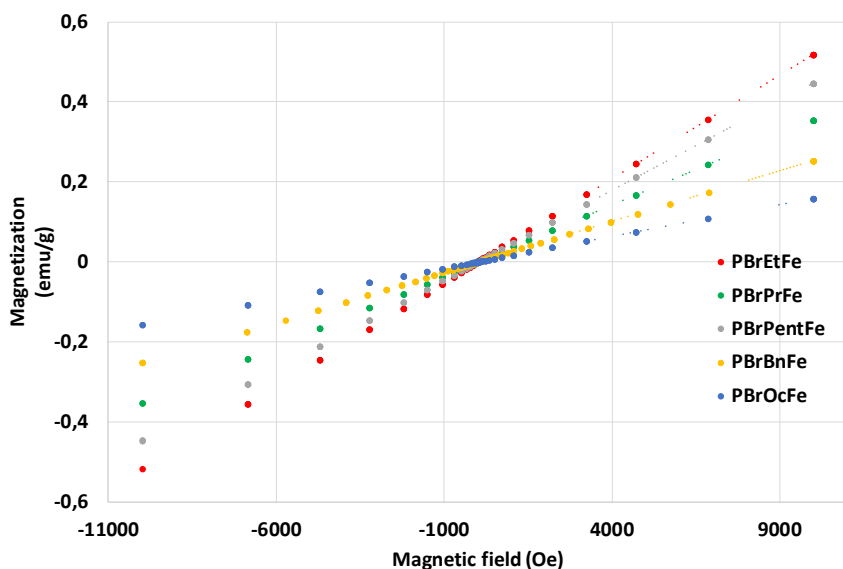


Figure S2. SQUID magnetization of magnetic polymers **PBrRFe** with different appended R groups

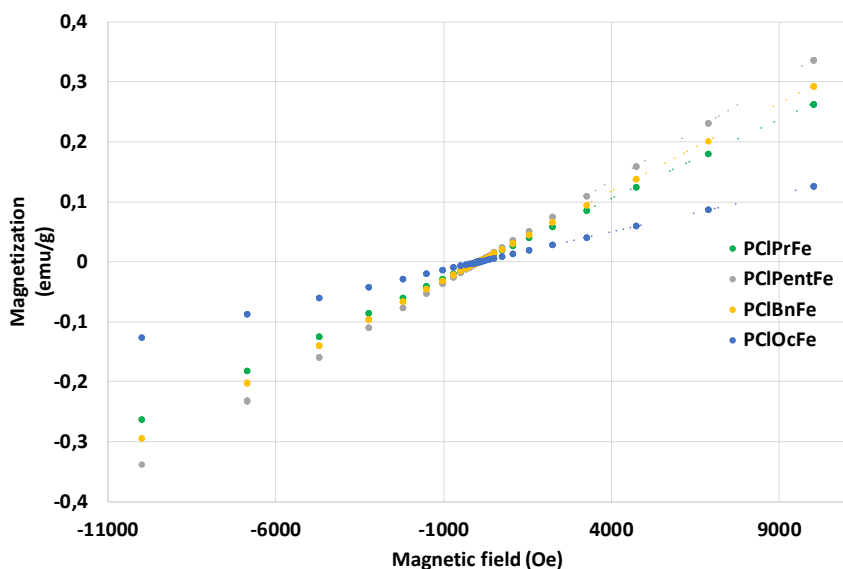


Figure S3. SQUID magnetization of magnetic polymers **PCIRFe** with different appended R groups

RAMAN spectra of magnetic polymers PXRFe

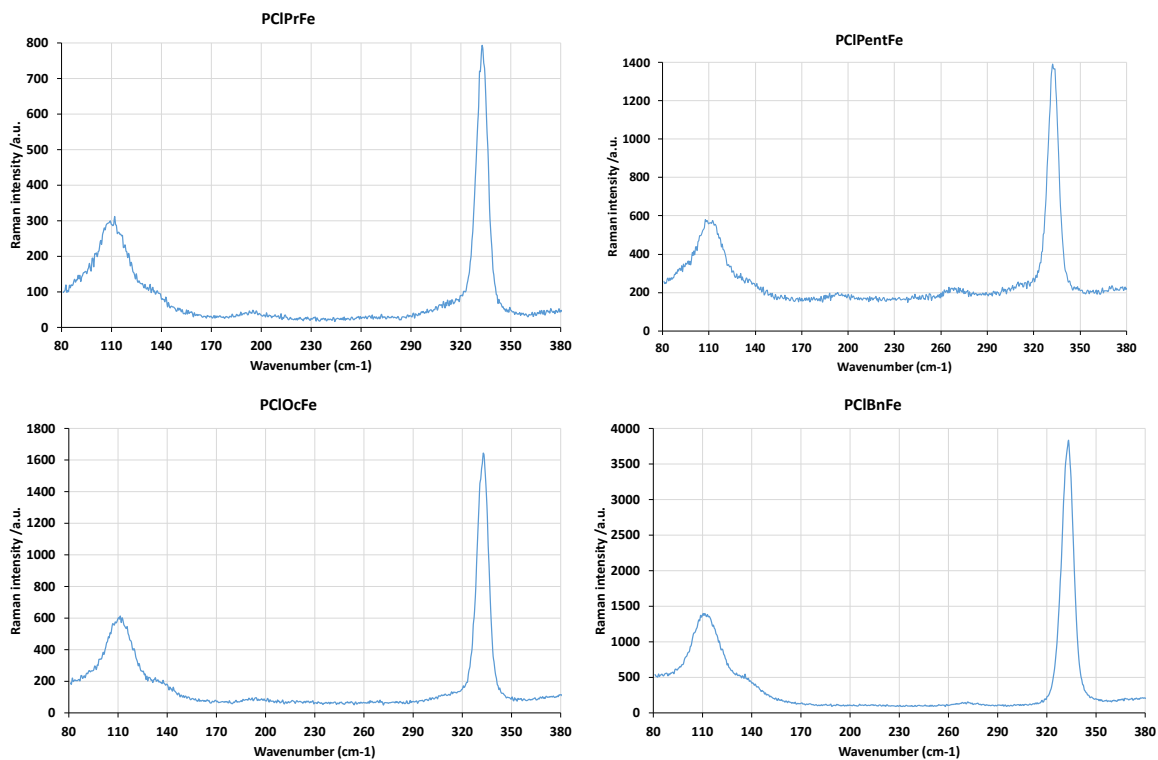
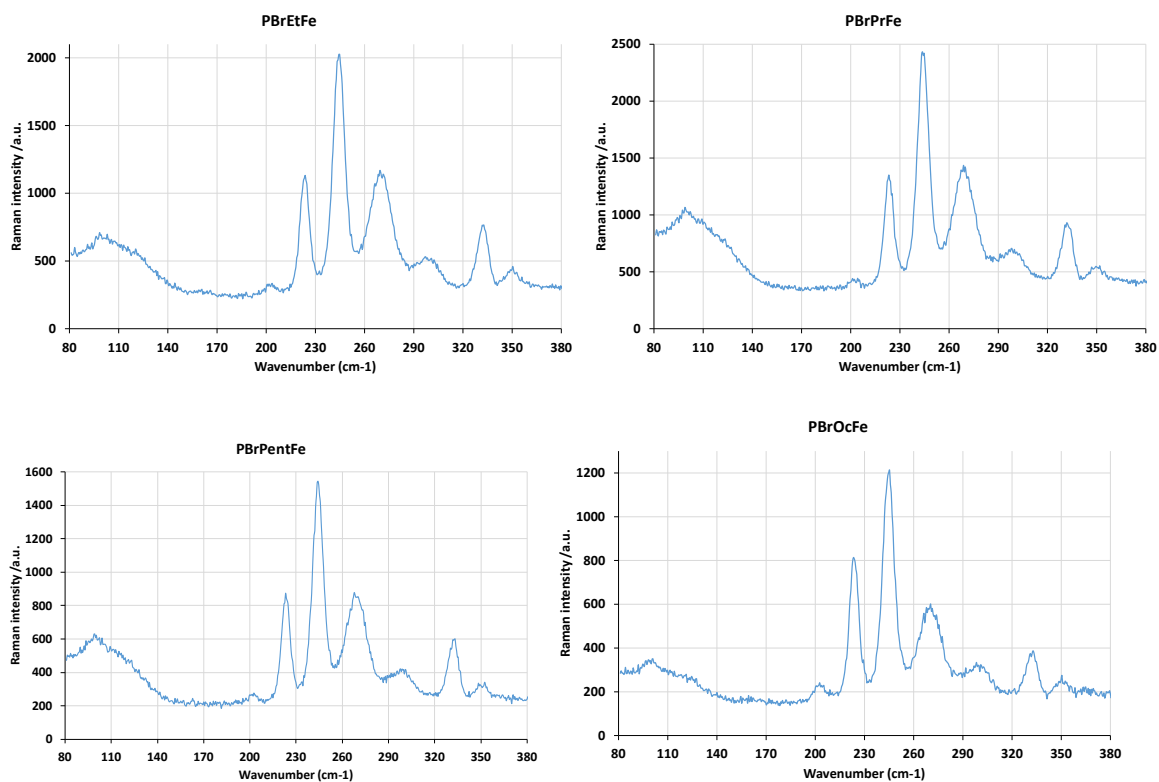


Figure S4. RAMAN spectra of magnetic polymers **PCIRFe** with different appended R groups



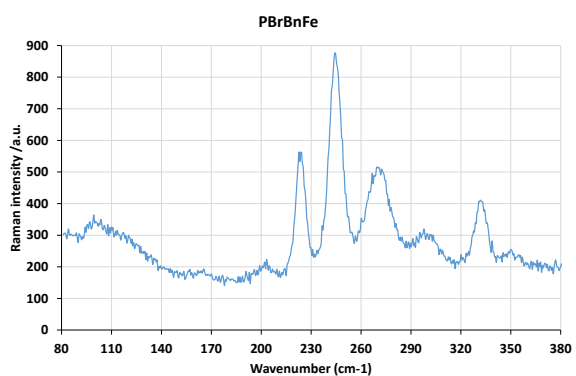


Figure S5. RAMAN spectra of magnetic polymers **PBRFe** with different appended R groups

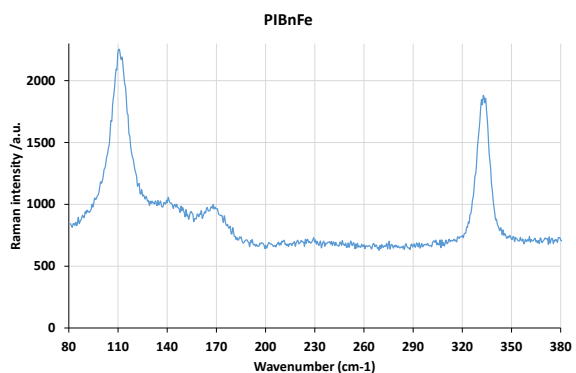
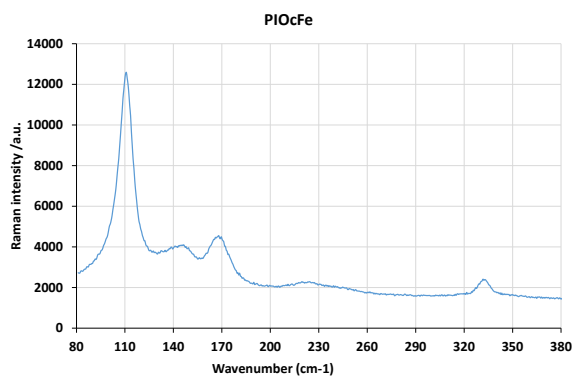
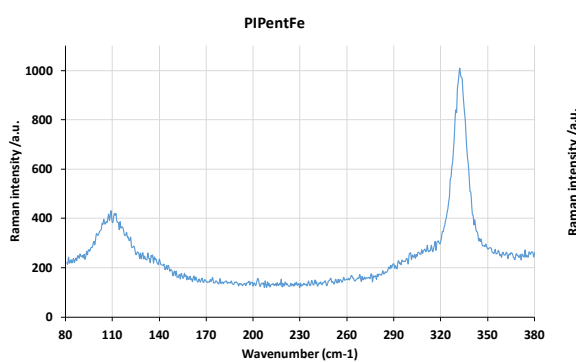
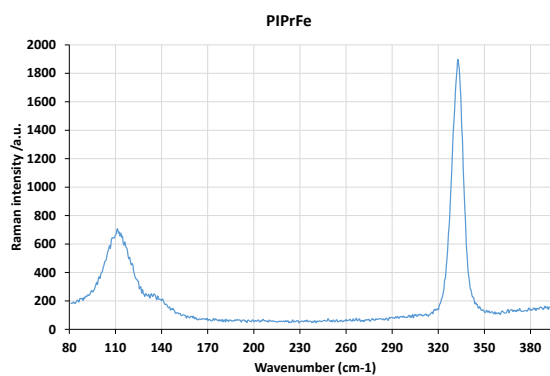
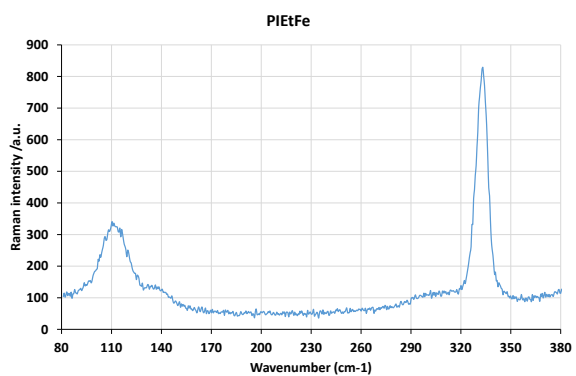


Figure S6. RAMAN spectra of magnetic polymers **PIRFe** with different appended R groups

Gel permeation chromatography of copolymers PDAX (X = 4, 6, 8)

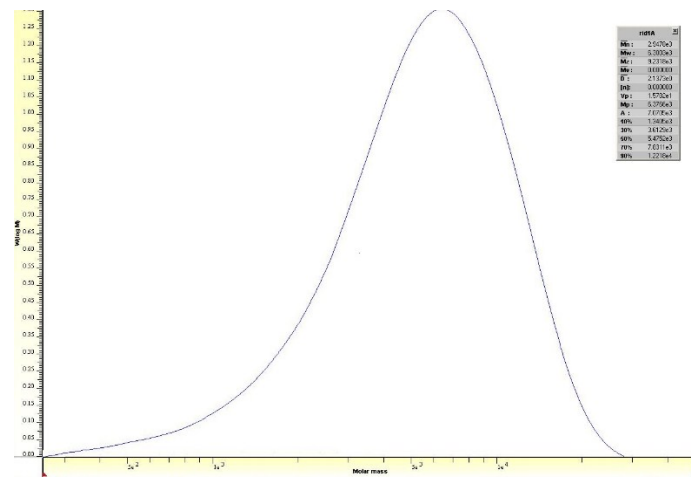


Figure S7. Gel permeation chromatography of copolymer **PDA4**

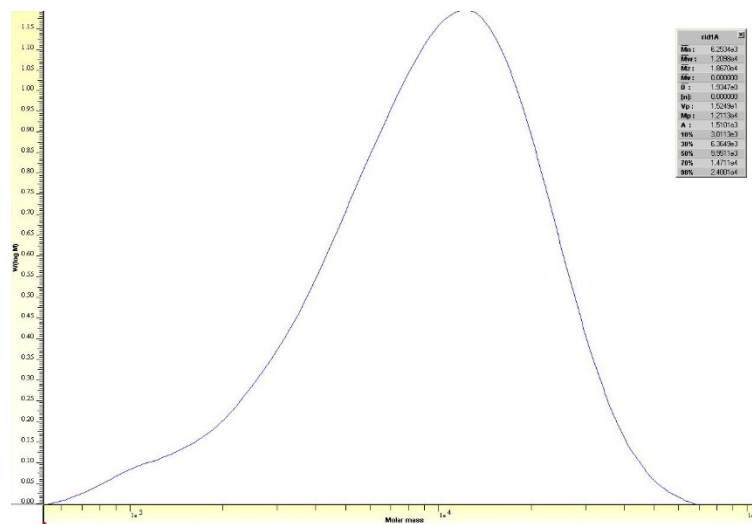


Figure S8. Gel permeation chromatography of copolymer **PDA6**

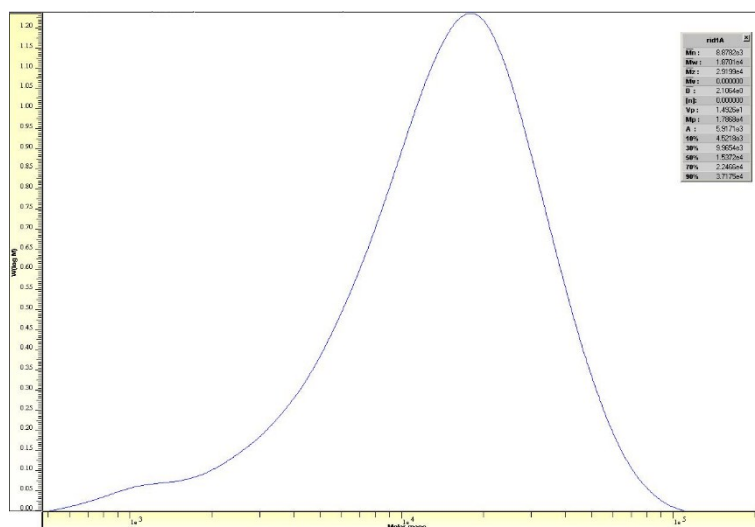


Figure S9. Gel permeation chromatography of copolymer **PDA8**

SQUID magnetization of magnetic copolymers PDAX/YF (X = 4, 6, 8 and Y = 10, 50, 100)

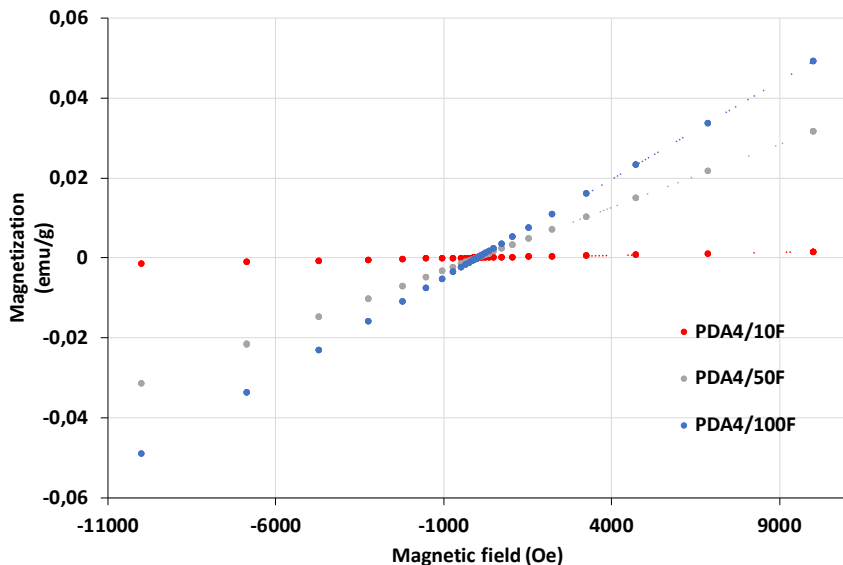


Figure S10. SQUID magnetization of magnetic polymers **PDA4/10F**, **PDA4/50F** and **PDA4/100F**.

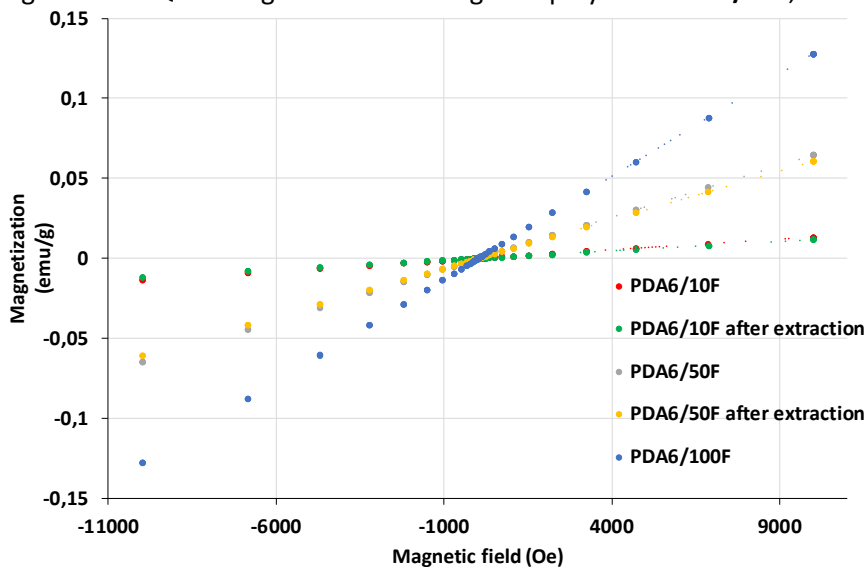


Figure S11. SQUID magnetization of magnetic polymers **PDA6/10F**, **PDA6/50F** and **PDA6/100F**. Measurements were performed after liquid-liquid extraction for **PDA6/10F** and **PDA6/50F**.

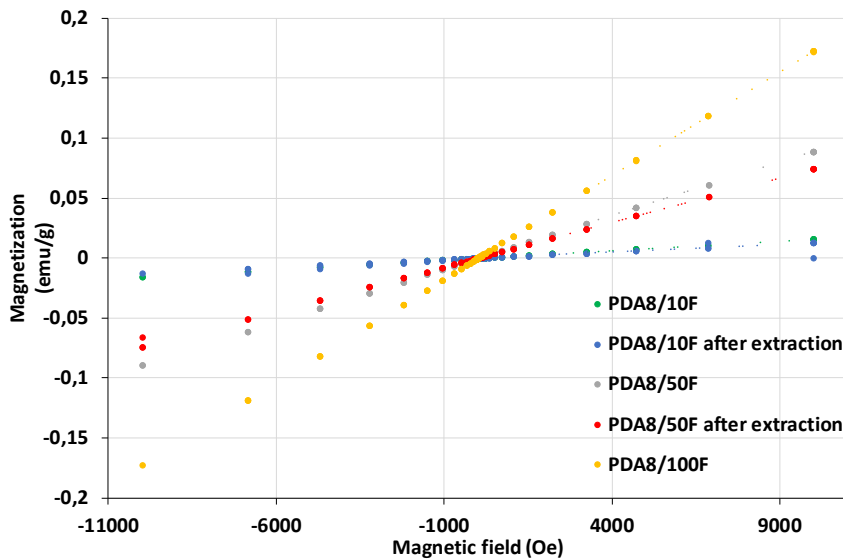


Figure S12. SQUID magnetization of magnetic polymers **PDA8/10F**, **PDA8/50F** and **PDA8/100F**. Measurements were performed after liquid-liquid extraction for **PDA8/10F** and **PDA8/50F**.

UV-Vis spectra of magnetic copolymers PDAX/YF (X = 4, 6, 8 and Y = 10, 50, 100)

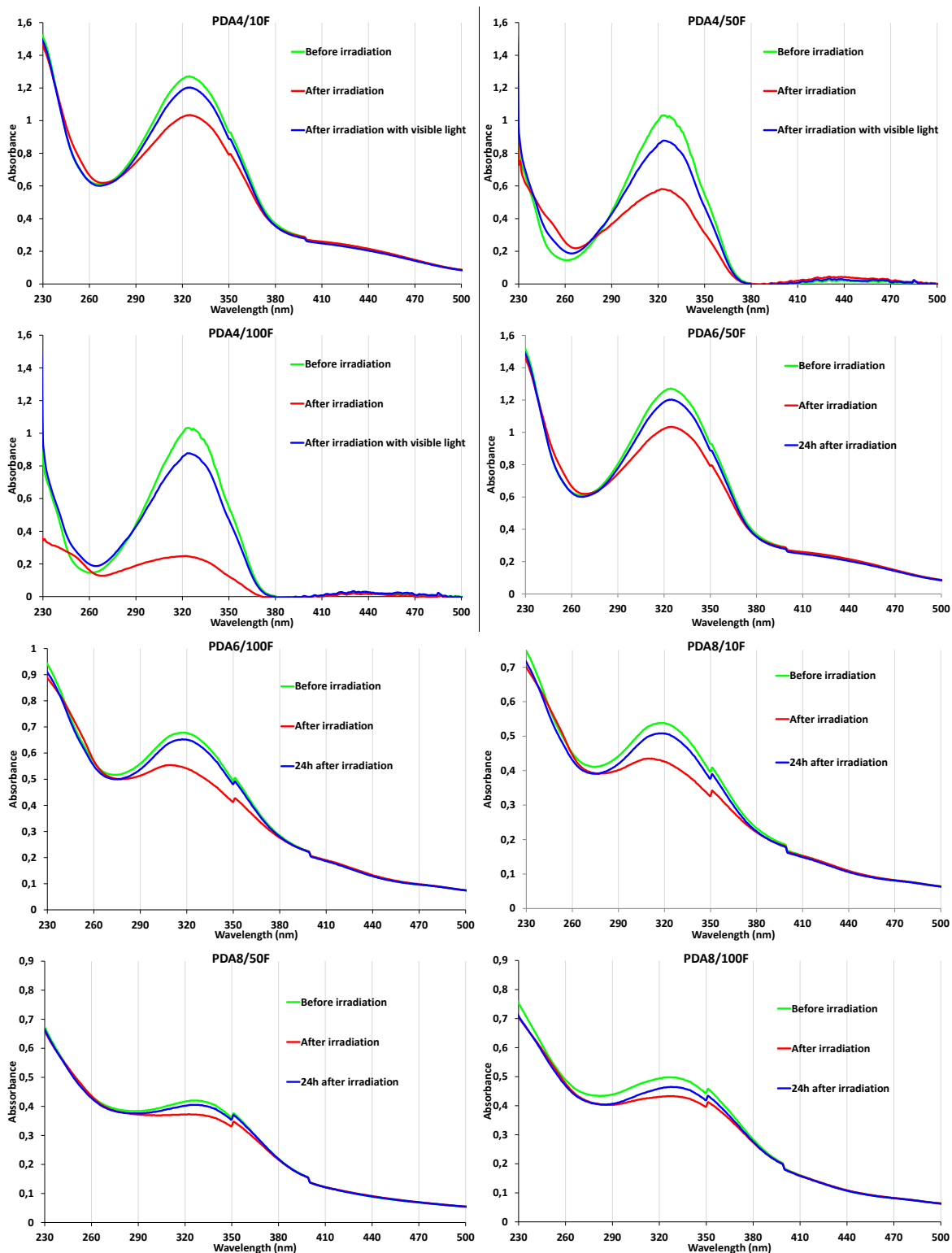


Figure S13. UV-Vis spectra for **PDAX/YF** (X = 4, 6, 8 and Y = 10, 50, 100) in dichloromethane solution before (green) and after (red) exposure to 365 nm light, and 24h after irradiation or exposure to visible light (blue).

Calculated Raman spectra

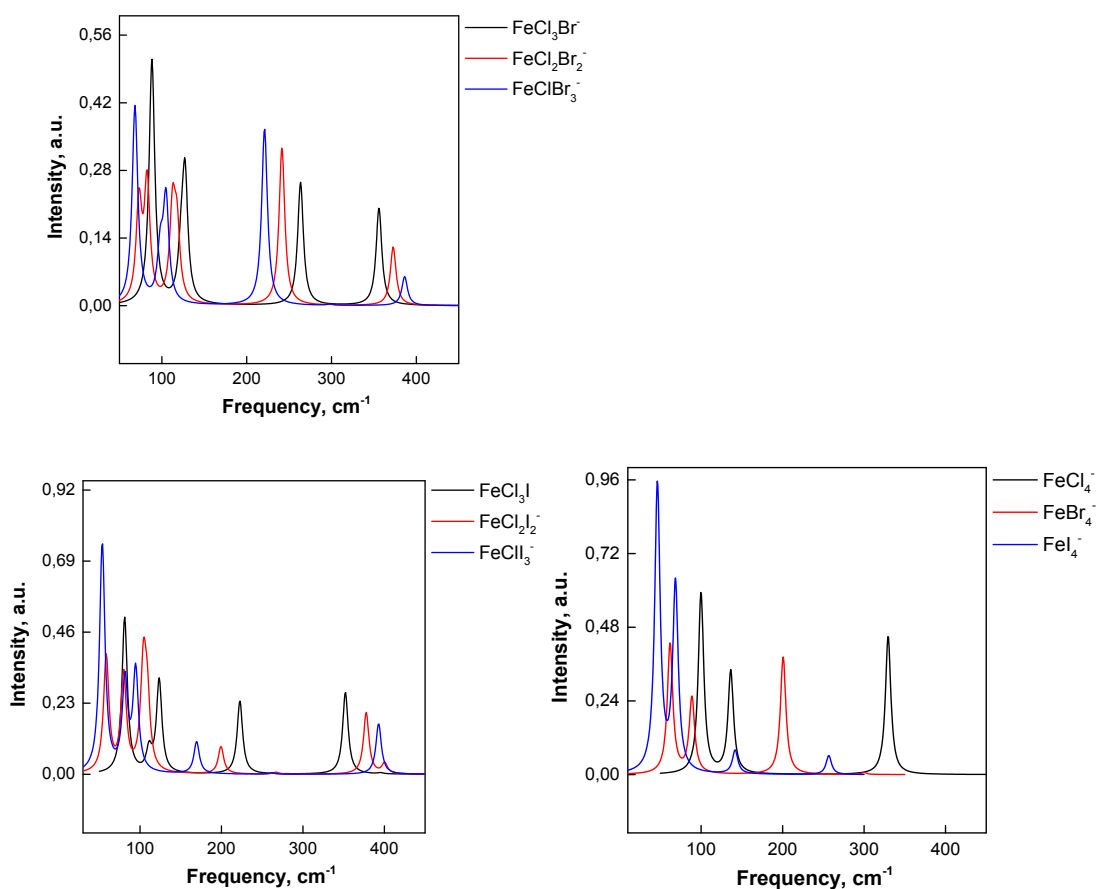


Figure S14. Calculated Raman spectra for magnetic ions $\text{FeCl}_m\text{Br}_{4-m}^-$ and $\text{FeCl}_m\text{I}_{4-m}^-$ ($m = 0$ to 4)

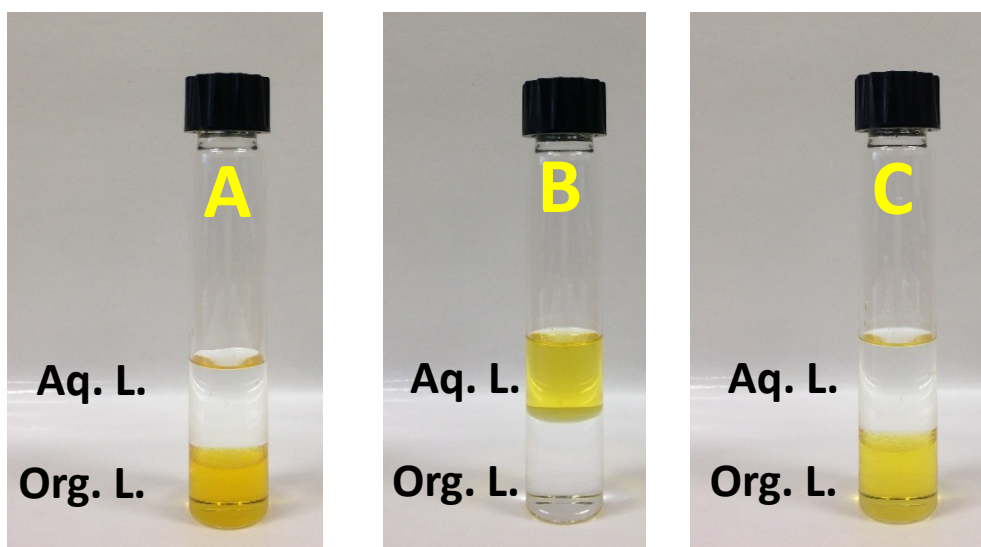


Figure S15. Liquid-liquid extraction using polymer **PDA8/10F**. Water (Aq. L.)/dichloromethane (Org. L.) bilayer before acidic extraction (A), after acidic extraction (B) and after alkaline treatment with NaHCO_3 (C).

pH sensitivity of PDA6/50F

The pH sensitivity of **PDA6/50F** was demonstrated through the comparison of FTIR spectra of **PDA6/50F**, trifluoroacetic acid (**TFA**) and the resulting salt **TFA-PDA6/50F**. **PDA6/50F** was stirred in TFA solution, filtrated and washed with CH_2Cl_2 . The FTIR spectra of **TFA-PDA6/50F** revealed a red-shift of the C=O stretching frequency for **TFA**, consistent with the presence of a carboxylate group due to the deprotonation by the free tertiary amine groups of the polymer.



Figure S16. FTIR spectra of **PDA6/50F**, trifluoroacetic acid (**TFA**) and the resulting salt **TFA-PDA6/50F** showing the red-shift of the C=O stretching frequency of **TFA** (top) and magnification of the region 1400-1900 cm^{-1} (bottom).

DSC diagrams of polymers PXRFe and PDAX/YF

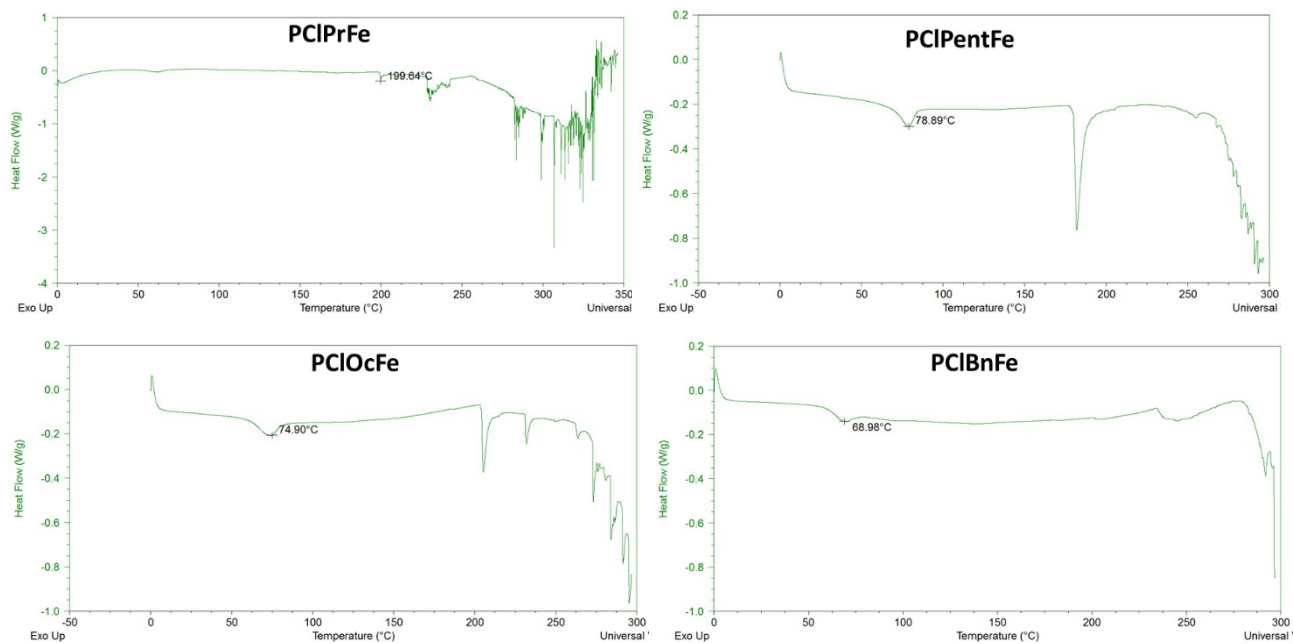


Figure S17. DSC diagrams of polymers **PCIRFe** with different appended R groups

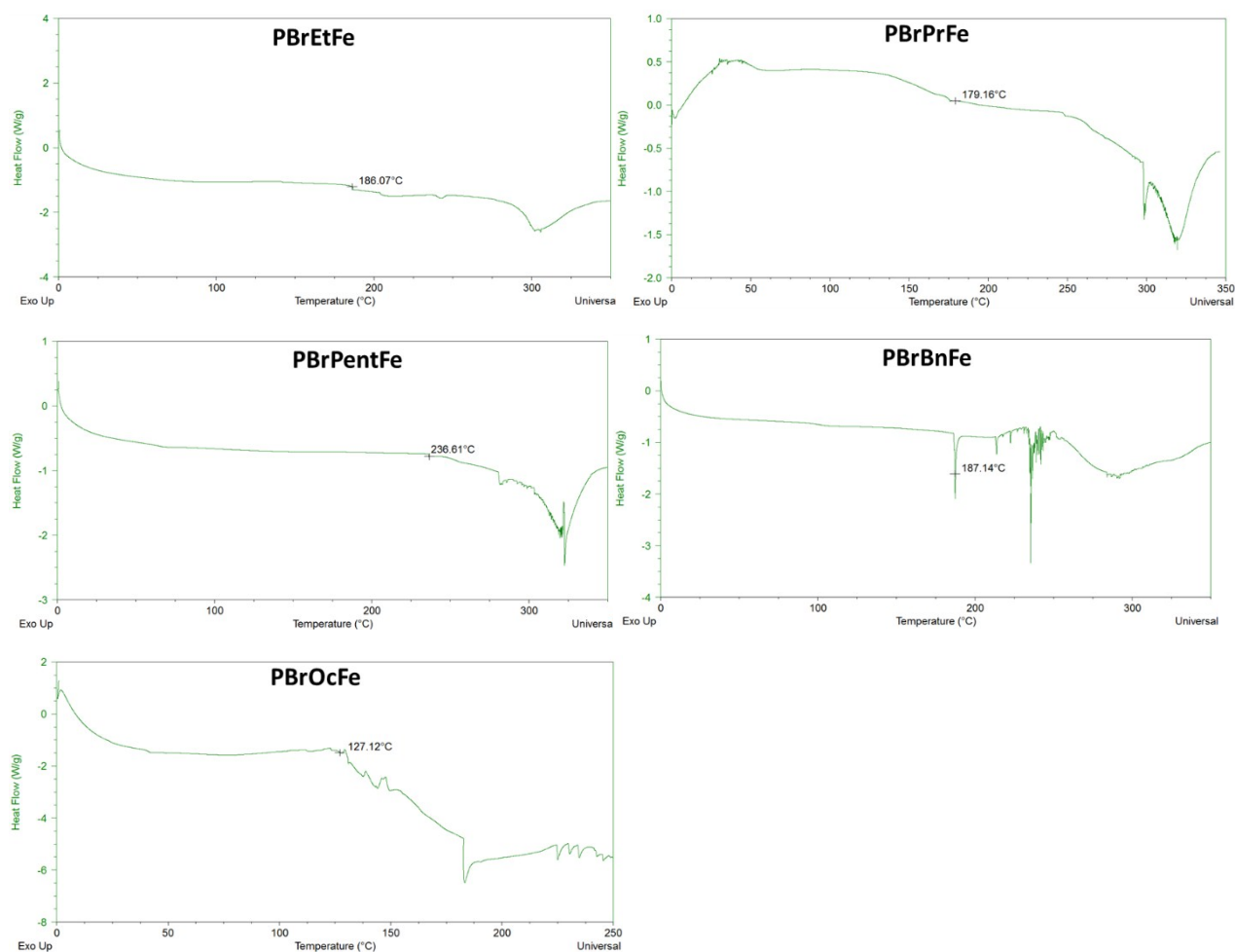


Figure S18. DSC diagrams of polymers **PBRFe** with different appended R groups

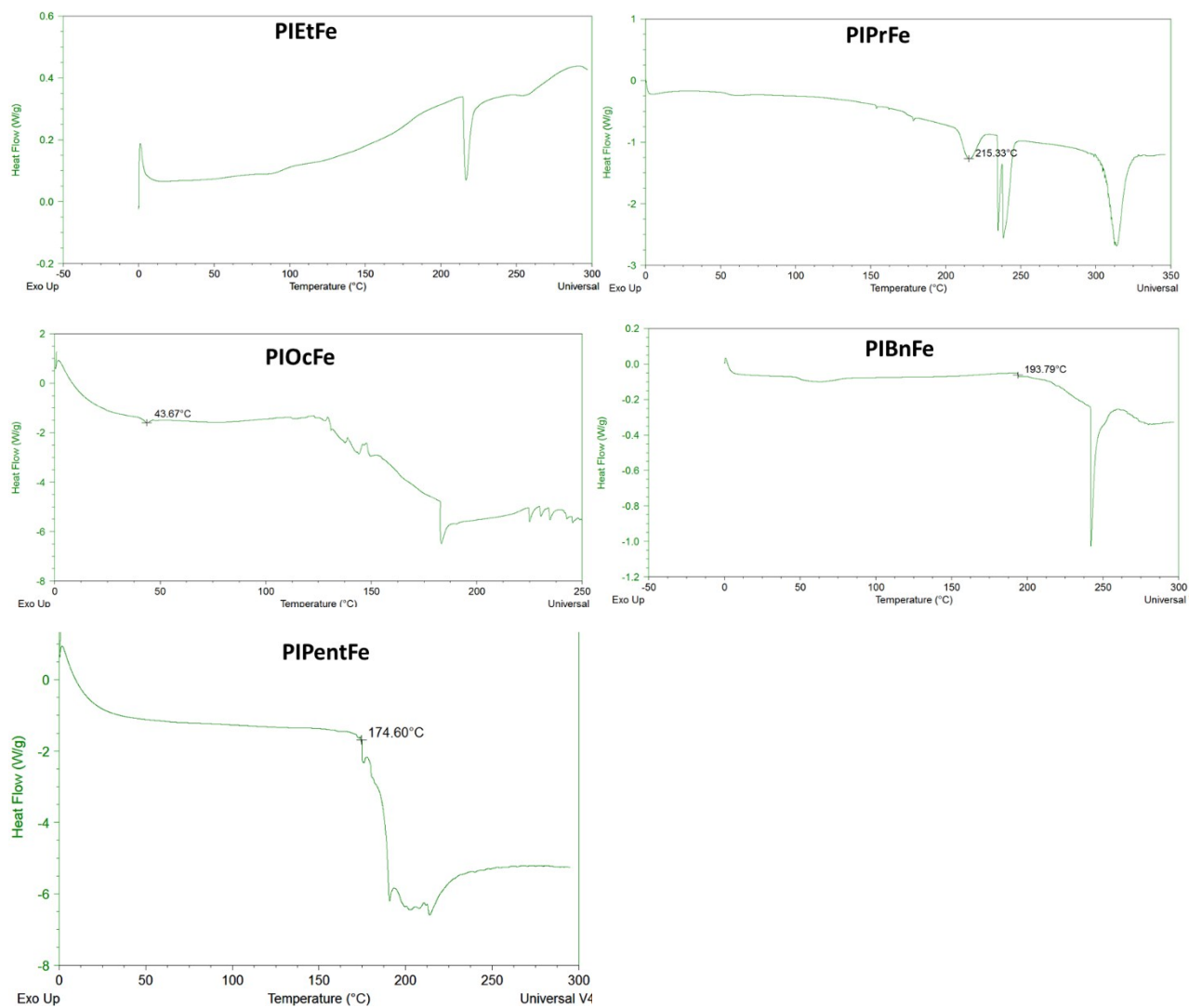


Figure S19. DSC diagrams of polymers **PIRFe** with different appended R groups

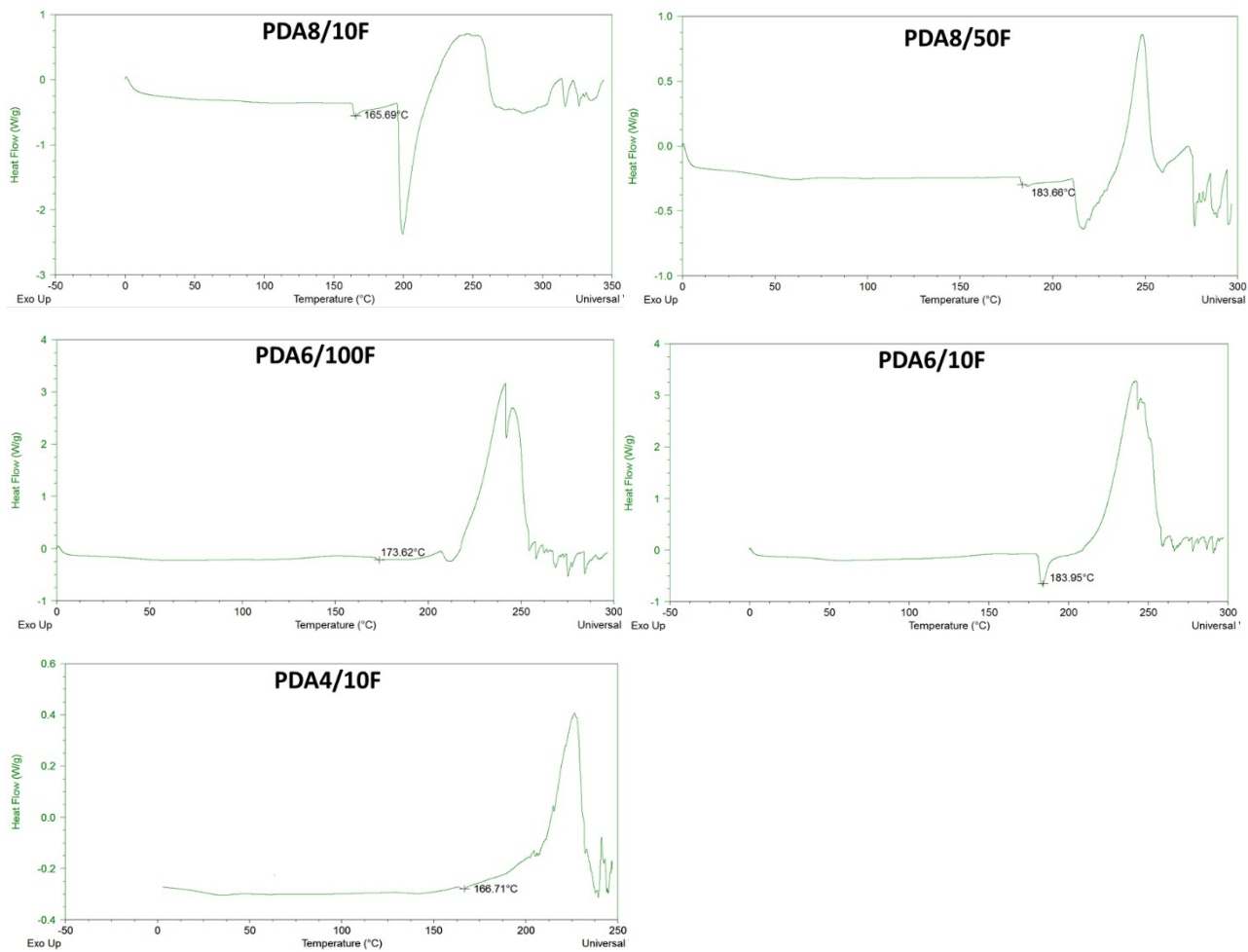
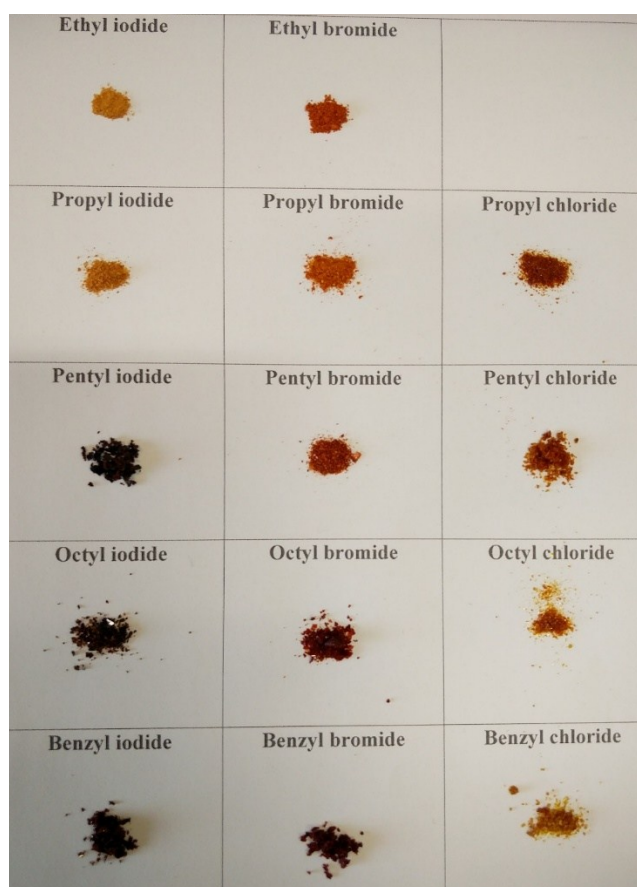


Figure S20. DSC diagrams of polymers **PDAX/YF**

Colors of magnetic polymers PXRFe

Table S1. Colours of magnetic polymers PXRFe

X	Alkyl and benzyl groups				
	Et	Pr	Pt	Oc	Bn
I	PIEtFe yellow	PIPrFe yellow	PIPentFe brown	PIOcFe brown	PIBnFe brown
Br	PBrEtFe orange	PBrPrFe orange	PBrPentFe orange	PBrOcFe red-brown	PBrBnFe red-brown
Cl	-	PCIPrFe orange- brown	PCIPentFe orange- brown	PCIOcFe yellow-orange	PCIBnFe yellow



Calculation of the effective magnetic moment of polymers PXRFe

The molecular weight (M_n) of starting PDMAEMA is 10500 g/mol that corresponds to approximately 67 units. Therefore, the molecular weight of each polymer was determined as $10500 + 67 \cdot (M_{RX} + M_{FeCl_3})$ where M_{RX} is the molecular weight of RX and M_{FeCl_3} is the molecular weight of $FeCl_3$. The effective magnetic moment was calculated using the equation $\mu_{eff} = 797.8 \sqrt{X_M T}$ where X_M is the molar magnetic susceptibility, T is the temperature in Kelvin and μ_B is the Bohr magneton.

Table S2. Magnetic susceptibility, molecular weight, molar susceptibility and effective magnetic moment of polymers PXRFe

Polymers	Susceptibility (m ³ /Kg)	Molecular weight (g/mol)	Molar susceptibility (m ³ /mol)	$X_M \cdot T^a$	μ_{eff} (μ_B)
PBrEtFe	6.52E-07	28690.5	1.87E-05	5.48E-03	59.1
PIEtFe	7.69E-07	31839.5	2.45E-05	7.18E-03	67.6
PCIPrFe	3.30E-07	26647	8.81E-06	2.58E-03	40.5
PBrPrFe	4.45E-07	29628.5	1.32E-05	3.86E-03	49.6
PIPrFe	5.96E-07	32777.5	1.95E-05	5.72E-03	60.3
PCIPentFe	4.23E-07	28523	1.21E-05	3.54E-03	47.5
PBrPentFe	5.62E-07	31504.5	1.77E-05	5.19E-03	57.4
PIPentFe	3.04E-07	34653.5	1.05E-05	3.09E-03	44.3
PCIBnFe	3.69E-07	29863	1.10E-05	3.23E-03	45.4
PBrBnFe	3.18E-07	32844.5	1.04E-05	3.06E-03	44.1
PIBnFe	2.09E-07	35993.5	7.51E-06	2.20E-03	37.4
PCIOcFe	1.58E-07	31337	4.96E-06	1.45E-03	30.4
PBrOcFe	1.99E-07	34318.5	6.81E-06	2.00E-03	35.6
PIOcFe	1.85E-07	37467.5	6.92E-06	2.03E-03	35.9

a Temperature was 293K

Table S3. Percentages of quaternized amines of random copolymers PDAX/Y

polymers	Targeted quaternized amines	Calculated quaternized amines*
PDA4/10	10%	14%
PDA4/50	50%	50%
PDA4/100	100%	100%
PDA6/10	10%	10%
PDA6/50	50%	50%
PDA6/100	100%	100%
PDA8/10	10%	9%
PDA8/50	50%	41%
PDA8/100	100%	100%

* Determined by ¹H NMR

Table S4. Susceptibility values and standard deviation referring to tables 2 and 5.

Polymers PXRFe	Susceptibility ($\times 10^{-6}$ emu/g)	STD	Polymer	Susceptibility ($\times 10^{-6}$ emu/g)	STD
PBrEtFe	51.9	3.1E-09	PDA4/10F	1.5	3.1E-09
PIEtFe	61.2	3.6E-09	PDA4/50F	3.2	7.3E-09
PCIPrFe	26.3	2.8E-09	PDA4/100F	4.9	1.5E-09
PBrPrFe	35.4	3.7E-09	PDA6/10F	1.3	2.4E-09
PIPrFe	47.4	3.8E-09	PDA6/10F ^b	1.2	1.50E-09
PCIPentFe	33.7	2.6E-09	PDA6/50F	6.5	2.6E-09
PBrPentFe	44.7	2.5E-09	PDA6/50F ^b	6.1	2.60E-09
PIPentFe	24.2	2.2E-09	PDA6/100F	12.8	1.8E-09
PCIBnFe	29.4	2.7E-09	PDA8/10F	1.6	1.2E-09
PBrBnFe	25.3	4.9E-09	PDA8/10F ^b	1.2	2.00E-09
PIBnFe	16.6	3.0E-09	PDA8/50F	8.9	1.0E-09
PCIOcFe	12.6	2.4E-09	PDA8/50F ^b	7.4	1.80E-09
PBrOcFe	15.8	2.9E-09	PDA8/100F	17.3	2.0E-09
PIOcFe	14.7	2.1E-09			

Materials

2-(*N,N*-Dimethylamino) ethyl methacrylate (DMAEMA) was filtered through aluminium oxide before use. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA), ethyl α -bromoisobutyrate (EBIB), CuBr, basic activated aluminum oxide Brockmann I, 2,2'-azobis(2-methylpropionitrile) 98% (AIBN), iodoethane, bromoethane, iodopentane, bromopentane, chloropentane, iodoctane, bromooctane, chlorooctane, benzylbromide, benzylchloride, benzyl iodide, 4-Phenylazophenol, sodium iodide, dichloromethane (DCM), 1,4-dioxane, dimethylformamide (DMF), D₂O, CDCl₃, CD₃OD, deuterated dimethyl sulfoxide-*d*₆, tetrahydrofuran (THF), were purchased from Sigma-Aldrich.

Iron(III) chloride hexahydrate, Diethyl ether (Et₂O), methanol, ethyl acetate (EtOAc) were purchased from VWR. Magnetic susceptibility values was determined using a SQUID Magnetometry which was performed with a MPMS 3 apparatus (Quantum Design, USA). Irradiation was done with a UV SBS instrument (Spain) and UV-vis spectra were made with UV-1800 SHIMADZU spectrophotometer (Japan).

¹H and ¹³C NMR spectra were taken on a Bruker Avance 300 MHz spectrometer (Wissemburg, France) at 293 K. Chemical shifts (δ) are given in parts per million (ppm) relative to tetramethylsilane (TMS), and the coupling constants are expressed in hertz. Gel permeation chromatography (GPC) was performed in THF + 2

wt% NEt_3 at 35 °C using a Polymer Laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate 1 mL min^{-1}), a Marathon autosampler (loop volume 100 mL, solution conc. 1mg/mL), a PLDRI refractive index detector and two columns: PL gel Mixed-B 10 mm columns. Poly(methyl methacrylate) standard was used for calibration. All reactions were followed by thin-layer chromatography (TLC) carried out on Fluka (Bornem, Belgium) PET foils silica gel 60, and compounds were visualized by UV and I_2 . Column chromatographies were performed with EchoChrom MP silica 63–200 from MP Biomedicals (Santa Ana, CA) or AlO_3 Sigma–Aldrich (Bornem, Belgium). Organic solutions were dried over Na_2SO_4 and concentrated with a Buchi rotatory evaporator (Flawil, Switzerland). Ferric contents were determined by TGA with a Q500 thermogravimetric analyzer (TA Instruments, New Castle, USA) and the Universal Analysis software v5.5.20 (TA Instruments, New Castle, USA). The parameters were as follow: weight sample: 5-10 mg, range: from 25 to 350 °C, ramp: 10 °C/min. Thermal properties were determined with a Q2000 Differential Scanning Calorimeter DSC (TA Instruments, New Castle, USA) equipped with a RCS90 Refrigerated Cooling System (TA Instruments, New Castle, USA) and calibrated with indium.

Synthesis of polymers

Poly(2-(*N,N*-Dimethylamino) ethyl methacrylate) PDMAEMA

DMAEMA (10 g, 63.6 mmol), HMTETA (575 mg, 2.5 mmol), EBIB (244 mg, 1.25 mmol) were stirred together in 22 ml dioxane at room temperature for 10 minutes. Then, CuBr (180 mg, 1.25 mmol) was added. The resulting mixture was heated at 100 °C for 12 hrs. The flask was evacuated and back-filled with argon three times. After 12 hrs, the obtained green solution was evaporated by rotary evaporator. THF was added in order to dissolve the mixture and filtered through Al_2O_3 column and finally evaporated and dried under vacuum to give yellowish gum.

^1H NMR (CDCl_3): δ 4.05 (CH_2O), 2.56 (CH_2N), 2.28 ($(\text{CH}_3)_2\text{N}$), 1.82 (CH_2), 0.98 (CH_3). M_n determined by GPC (relative PMMA calibration) = 10500 g mol^{-1} , PDI = 1.35.

Quaternization of PDMAEMA with alkyl and benzyl halides

Poly[2-(methacryloyloxy)ethyl] dimethyl-ethyl-ammonium iodide (PIEt) (procedure 1)

To a solution of **PDMAEMA** (1.5 g, 9.54 mmol) in 30 ml dioxane, iodoethane (7 ml, 87 mmol) was added. The solution was stirred at 70 °C overnight. Then, diethyl ether was added (25 ml) to insure complete precipitation and the suspension was filtered and dried under vacuum.

¹H NMR (DMSO-*d*₆): δ 4.41 (CH₂O), 3.87 (CH₂N), 3.61 (CH₂N), 3.24 ((CH₃)₂N), 1.90 (CH₂), 1.34 (CH₃), 0.88 (CH₃).

Poly[2-(methacryloyloxy)ethyl] dimethyl-ethyl-ammonium bromide (PBrEt)

The title compound was synthesized according to procedure 1.

¹H NMR (D₂O): δ 4.53 (CH₂O), 3.84 (CH₂N), 3.58 (CH₂N), 3.23 ((CH₃)₂N), 2.06 (CH₂), 1.45 (CH₃), 1.04 (CH₃).

Poly[2-(methacryloyloxy)ethyl] dimethyl-propyl-ammonium iodide (PIPr)

The title compound was synthesized according to procedure 1.

¹H NMR (D₂O): δ 4.56 (CH₂O), 3.90 (CH₂N), 3.50 (CH₂N), 3.28 ((CH₃)₂N), 1.71-2.23 (CH₂), 1.06 (CH₃).

Poly[2-(methacryloyloxy)ethyl] dimethyl-propyl-ammonium bromide (PBrPr)

The title compound was synthesized according to procedure 1.

¹H NMR (D₂O): δ 4.52 (CH₂O), 3.84 (CH₂N), 3.45 (CH₂N), 3.24 ((CH₃)₂N), 1.69-2.18 (CH₂), 1.03 (CH₃).

Poly[2-(methacryloyloxy)ethyl] dimethyl-pentyl-ammonium iodide (PIPent)

The title compound was synthesized according to procedure 1.

¹H NMR (DMSO-*d*₆): δ 4.39 (CH₂O), 3.90 (CH₂N), 3.56 (CH₂N), 3.25 ((CH₃)₂N), 1.36-1.76 (CH₂), 0.92 (CH₃).

Poly[2-(methacryloyloxy)ethyl] dimethyl-pentyl-ammonium bromide (PBrPent)

The title compound was synthesized according to procedure 1.

¹H NMR (DMSO-*d*₆): δ 4.41 (CH₂O), 4.00 (CH₂N), 3.59 (CH₂N), 3.29 ((CH₃)₂N), 1.34-1.74 (CH₂), 0.91 (CH₃).

Poly[2-(methacryloyloxy)ethyl] dimethyl-octyl-ammonium iodide (PIOc)

The title compound was synthesized according to procedure 1.

¹H NMR (DMSO-*d*₆): δ 4.40 (CH₂O), 3.88 (CH₂N), 3.58 (CH₂N), 3.25 ((CH₃)₂N), 1.27-1.75 (CH₂), 0.87 (CH₃)

Poly[2-(methacryloyloxy)ethyl] dimethyl-benzyl-ammonium iodide (PIBn)

The title compound was synthesized according to procedure 1.

¹H NMR (DMSO-*d*₆): δ 7.51-7.67 (H arom.), 3.99-4.93 (CH₂O, CH₂N, CH₂N), 3.17 ((CH₃)₂N), 1.91 (CH₂), 0.93 (CH₃).

Poly[2-(methacryloyloxy)ethyl] dimethyl-benzyl-ammonium bromide (PBrBn)

The title compound was synthesized according to procedure 1.

^1H NMR (DMSO- d_6): δ 7.49-7.68 (H arom.), 3.99-5.00 (CH_2O , CH_2N , CH_2N), 3.18 ($(\text{CH}_3)_2\text{N}$), 1.91 (CH_2), 0.93 (CH_3).

Poly[2-(methacryloyloxy)ethyl] dimethyl-octyl-ammonium bromide (PBrOc)

The title compound was synthesized according to procedure 1.

^1H NMR (DMSO- d_6): δ 4.44 (CH_2O), 4.02 (CH_2N), 3.61 (CH_2N), 3.28 ($(\text{CH}_3)_2\text{N}$), 1.27-1.72 (CH_2), 0.87 (CH_3).

Poly[2-(methacryloyloxy)ethyl] dimethyl-pentyl-ammonium chloride (PCIPent) (procedure 2)

PDMAEMA (1.5 g, 9.54 mmol) was dissolved in 30 ml of methanol and chloropentane (7 ml, 57.9 mmol) was added. Solution was stirred at 70 °C overnight. After cooling, diethyl ether was added to insure complete precipitation. This suspension was filtrated and dried under vacuum.

^1H NMR (DMSO- d_6): δ 4.37 (CH_2O), 3.96 (CH_2N), 3.52 (CH_2N), 3.25 ($(\text{CH}_3)_2\text{N}$), 1.28-1.72 (CH_2), 0.90 (CH_3).

Poly[2-(methacryloyloxy)ethyl] dimethyl-propyl-ammonium chloride (PCIPr)

The title compound was synthesized according to procedure 2.

^1H NMR (D_2O): δ 4.52 (CH_2O), 3.84 (CH_2N), 3.45 (CH_2N), 3.24 ($(\text{CH}_3)_2\text{N}$), 1.69-2.18 (CH_2), 1.03 (CH_3).

Poly[2-(methacryloyloxy)ethyl] dimethyl-octyl-ammonium chloride (PCIOc)

The title compound was synthesized according to procedure 2.

^1H NMR (DMSO- d_6): δ 4.40 (CH_2O), 3.88 (CH_2N), 3.58 (CH_2N), 3.25 ($(\text{CH}_3)_2\text{N}$), 1.27-1.75 (CH_2), 0.87 (CH_3).

Poly[2-(methacryloyloxy)ethyl] dimethyl-benzyl-ammonium chloride (PCIBn)

The title compound was synthesized according to procedure 2.

^1H NMR (CD_3OD): δ 7.53-7.69 (H arom.), 3.60-5.63 (CH_2O , CH_2N , CH_2N), 3.22 ($(\text{CH}_3)_2\text{N}$), 1.96 (CH_2), 1.14 (CH_3).

Complexation with iron

Poly[2-(methacryloyloxy)ethyl] dimethyl-pentyl-ammonium iodide. FeCl_3 PIPentFe (procedure 3)

PIPt (750 mg, 2.11 mmol) was dissolved in 30 ml methanol, and then a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (570 mg, 2.11 mmol) in 5 ml methanol was added and stirred at room temperature overnight. The solvent was filtrated and the solution was evaporated using rotary evaporator and dried under vacuum to give a brown powder.

Poly[2-(methacryloyloxy)ethyl] dimethyl-octyl-ammonium iodide.FeCl₃ (PIOcFe) and poly[2-(methacryloyloxy)ethyl] dimethyl-octyl-ammonium bromide.FeCl₃ (PBrOcFe) were synthesized according to procedure 3.

Poly[2-(methacryloyloxy)ethyl] dimethyl-ethyl-ammonium iodide.FeCl₃ (PIEtFe) (procedure 4)

PIEt (750 mg, 2.4 mmol) was dissolved in 30 ml water and a solution of FeCl₃.6H₂O (650 mg, 2.4 mmol) in 5 ml water was added and stirred at room temperature overnight. The solvent was filtrated and the solution was evaporated using rotary evaporator and dried under vacuum to give a yellow powder.

Poly[2-(methacryloyloxy) ethyl] dimethyl-ethyl-ammonium bromide.FeCl₃ (**PBrEtFe**), Poly[2-(methacryloyloxy)ethyl] dimethyl-propyl-ammonium iodide (**PIPrFe**), poly[2-(methacryloyloxy) ethyl] dimethyl-propyl-ammonium bromide (**PBrPrFe**), poly[2-(methacryloyloxy) ethyl] dimethyl-propyl-ammonium chloride (**PCIPrFe**), poly[2-(methacryloyloxy) ethyl] dimethyl-pentyl-ammonium bromide.FeCl₃ (**PBrPentFe**), poly[2-(methacryloyloxy) ethyl] dimethyl-pentyl-ammonium chloride.FeCl₃ (**PCIPentFe**), poly[2-(methacryloyloxy) ethyl] dimethyl-octyl-ammonium chloride.FeCl₃ (**PCIOcFe**), poly[2-(methacryloyloxy)ethyl] dimethyl-benzyl-ammonium iodide.FeCl₃ (**PIBnFe**), poly[2-(methacryloyloxy) ethyl] dimethyl-benzyl-ammonium bromide.FeCl₃ (**PBrBnFe**), and poly[2-(methacryloyloxy) ethyl] dimethyl-benzyl-ammonium chloride.FeCl₃ (**PCIBnFe**) were synthesized according to procedure 4.

poly[2-(methacryloyloxy)ethyl] dimethyl-benzyl-ammonium iodide.FeCl₃ (PIBnFe)

PIBn (750 mg, 2 mmol) was dissolved in 30 ml of boiled water, and then a solution of FeCl₃.6H₂O (540 mg, 2 mmol) in 5 ml water was added and stirred at room temperature overnight. The solvent was evaporated using rotary evaporator and dried under vacuum to give a brown powder.

Preparation of magnetic random copolymers

***Trans*-4-methacryloyloxyazobenzene (A)**

P-phenylazophenol (4 g, 20.1 mmol) and triethylamine (2.82 ml, 20.2 mmol) were dissolved in THF (100 ml). The mixture was stirred at room temperature under nitrogen gas. The solution was cooled to 0°C and methacryloyl chloride (1.95 ml, 22.2 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 48 h under a nitrogen atmosphere. The solvent was evaporated under vacuum, then the residue was dissolved in 60 mL of DCM. The mixture was washed with water, HCl 0.1 N, then NaHCO₃,

respectively. The organic layer was dried using anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel 60 with DCM and recrystallization from petroleum ether. Finally, the crystalline product **A** was dried under vacuum and isolated in 60% yield.

$^1\text{H NMR}$ (CDCl_3): δ 7.95 (m, 4H, H arom.), 7.50 (m, 3H, H arom.), 7.39 (m, 2H, H arom.), 6.38 (s, 1H, =CH₂), 5.79 (s, 1H, =CH₂), 2.04 (s, 3H, CH₃).

Syntheses of Poly(4-(phenyldiazenyl)phenyl-methacrylate-co-N,N-dimethylaminoethyl methacrylate) PDAX (X = 4, 6, 8)

Typical procedure

4-(phenyldiazenyl)phenyl methacrylate (**A**) (362 mg, 1.36 mmol) was dissolved in 25 ml of dioxane. To this solution, **DMAEMA** (500 mg, 3.18 mmol) was added. After heating the previous solution to 70 °C, (230 mg, 1.4 mmol) of azobisisobutyronitrile (AIBN) was added and the mixture was stirred overnight under inert atmosphere. Then, the product was precipitated from petroleum ether to give the co-polymer **PDA8**.

$^1\text{H NMR}$ (CDCl_3): δ 7.90-7.32 (H arom.), 4.20 (CH₂O), 2.65 (CH₂N), 2.30 ((CH₃)₂N), 1.85 (CH₂), 0.90 (CH₃).

Syntheses of quaternized copolymers PDAX/Y (X = 4, 6, 8 and Y = 10, 50, 100)

Typical procedure

PDA8 (0.88g, 2.01 mmol) was solubilized in 20ml of dioxane and iodomethane (22 μ l, 0.35 mmol) was added. The solution was stirred at 60 °C overnight. Then the solvent was evaporated and the residue was dried under vacuum to give **PDA8/10**.

$^1\text{H NMR}$ (CDCl_3): δ 7.91-7.33 (H arom.), 4.22 (CH₂O), 3.55 ((CH₃)₃N), 2.66 (CH₂N), 2.31 ((CH₃)₂N), 1.81 (CH₂), 0.90 (CH₃).

See table S3 for percentages of quaternized amines of copolymers PDAX/Y.

Syntheses of magnetic copolymers PDAX/YF (X = 4, 6, 8 and Y = 10, 50, 100)

Typical procedure

Co-polymer **PDA8/10** (0.69 g, 1.19 mmol) was dissolved in 30 ml methanol and a solution of (76 mg, 0.28 mmol) FeCl₃.6H₂O in 5 ml water was added and stirred at room temperature overnight. The solution was filtrated and evaporated using rotary evaporator and drying under vacuum to give **PDA8/10F**.

Computational details.

All quantum mechanical calculations have been achieved using either Gaussian09 revision D.01. Geometries were fully optimized at the spin-unrestricted Hartree-Fock level of theory followed by a Møller-Plesset perturbative correction, truncated at the second order¹ and using the frozen core approximation.

The balanced polarized triple-zeta basis set def2-TZVP from Ahlrichs and co-workers^{2,3} has been used for all atoms except iodine, for which the quasi-relativistic Stuttgart-Dresden core potential was used.⁴ Stationary points found upon optimization were confirmed by frequency calculations and free energies were corrected to account for the zero-point energy. Equilibrium geometries were verified as minima (*i.e.* zero imaginary frequencies). Accuracy of the MP2 method was confirmed by comparison to DFT (PBE0⁵/def2-TZVP) and both methods proved to deliver similar results.

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