Supplementary material

Detection of Fe^{3+} using a novel hyperbranched polymeric spectral sensor

Wenbo Guo[a], Tengxuan Tang [a], Shenzhou Lu [b], Dongmei Xu [a]*

[a]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, Jiangsu 215123, China

[b]College of Textile and Clothing Engineering, Soochow University, Suzhou, Jiangsu 215123, China

1. Synthesis of the sensor

1.1 Synthesis of rhodamine derivative (RTEA)

RB (0.05 g, 0.104 mmol) and TEA (160 μL, 1.154 mmol) were dissolved in 10 mL dichloromethane and added to a 100 mL three-necked flask. Then thiobisethylamine was added to the flask dropwise and stirred at 50 °C for 30 h under N_2 atmosphere. The solution was washed with water and the solvent of the separated organic layer was removed under reduced pressure. The residue was purified by silica column chromatography with methanol/trichloromethane/petroleum ether (1/12/2, v/v/v) as eluent. The solvent in the eluate was removed under reduced pressure. A yellow solid was obtained and dried in vacuum to give 0.0254 g RTEA (yield 44.5%). ^{1}H NMR (400 MHz, $CDCl_3$, δ /ppm): 7.89 (s, 1H, PhH), 7.49 (m, 2H, PhH), 7.05 (d, J=8.4 Hz, 1H, PhH), 6.43 (d, J=8.7 Hz, 2H, PhH), 6.37 (s, 2H, PhH), 6.27 (d, J=8.3 Hz, 2H, PhH), 3.42-3.21 (m, 10H, CH_3CH_2N and SCH_2CH_2N), 2.99-2.76 (m, 2H, $SCH_2CH_2NH_2$), 2.64-2.58 (t, J=6.4 Hz, 2H, SCH_2CH_2N), 2.26-2.15 (t, J=8.0 Hz, 2H, $SCH_2CH_2NH_2$), 1.21-1.10 (t, J=6.7 Hz, 12H, CH_3CH_2N) (Fig. S1). ESI-MS: $[M+H]^+$= 545.2959 (Fig. S2).

1.2 Synthesis of the inimer (MCP)

The inimer 2-(methacryloyloxy)ethyl-4-cyano-4-(phenylcarbonothioyl-thio)pentanoate (MCP) was prepared according to the reference.[1] 4-CPDB (1 g, 3.58 mmol) was dissolved in 50 mL dichloromethane and added to a 250 mL three-necked flask, followed by the addition of HEMA (0.5 g, 3.85 mmol) and DMAP (0.09 g, 0.74 mmol). The flask was immersed in an ice bath. DCC

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* Corresponding author. Tel.: 86 512 65882027; fax: 86 512 65880089; e-mail address: xdm.sd@163.com

(2 g, 9.71 mmol) was dissolved in 100 mL dichloromethane and added to the flask dropwise. The reaction mixture was stirred overnight at room temperature. The solution was washed with water. Then $MgSO_4$ was added to the separated organic layer and stirred overnight at room temperature. The mixture was filtered. The solvent was removed from the filtrate under vacuum. The crude product was further purified by silica column chromatography with ethyl acetate/petroleum ether (1/4, v/v) as eluent. The solvent in the eluate was removed under reduced pressure, and the residue was dried in vacuum to afford 0.9454 g MCP (yield 62.8%) as a red viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$, δ /ppm): 7.99-7.23 (m, 5H, Ph*H*), 5.61 and 6.14 (s, 2H, $C{=}C\mathit{H}_2$), 4.50-4.21 (t, J=6.8 Hz, 4H, $(CO)OC\mathit{H}_2C\mathit{H}_2O(CO)$), 2.77-2.64 (t, J=6.4 Hz, 2H, $C(CH_3)(CN)C\mathit{H}_2$), 2.64-2.36 (t, J=4.8 Hz, 2H, $C\mathit{H}_2(CO)O$), 1.95 (s, 3H, $CH_2{=}C(C\mathit{H}_3)COO$), 1.25 (s, 3H, $C(C\mathit{H}_3)(CN)$) (Fig. S3). ESI-MS: $[M+H]^+$=392.0988, $[M+Na]^+$=414.0835 (Fig. S4).

1.3 Synthesis of the hyperbranched polymer (MCPG)

MCPG was synthesized according to the reference.[2] MCP (0.2 g, 0.5 mmol), GMA (1.3 mL, 10 mmol), AIBN (16 mg, 0.10 mmol) and 10 mL dried dioxane were added to a 100 mL three-necked flask. The mixture was stirred at 70 °C for 12 h under N_2 atmosphere, followed by cooled down to room temperature, and then poured into 20 mL cold methanol. The red precipitation was dried in vacuum to obtained 0.9152 g MCPG with 55.9% conversion rate. FT-IR (KBr): 3000 (Ph), 2960, 2860 (CH_3, CH_2), 1720 (C=O), 1590, 1482, 1445 (Ph), 1148 (C-O-C), 908 (epoxy) cm^{-1} (Fig. S5a). Mn/PDI of MCPG was 14500/1.212 (Fig. S6a). ^{1}H NMR (400 MHz, $CDCl_3$, δ /ppm): 7.86-7.36(m, Ph*H*), 6.16 and 5.61(s, $C{=}C\mathit{H}_2$), 4.31 and 3.80 (s, $COOC\mathit{H}_2$ from GMA), 3.75-3.71 (t, J=6.4 Hz, $COOC\mathit{H}_2C\mathit{H}_2OCO$ from MCP), 3.35-3.16 (m, C*H* from GMA), 2.85 and 2.63 (s, $COC\mathit{H}_2$ from GMA), 1.97 (s, $C(CH_3)(COO)C\mathit{H}_2$from GMA), 1.90 (s, $C(CH_3)(COO)C\mathit{H}_2C(CN)(CH_3)$ from MCP) , 1.76-1.61 (t, J=6.8 Hz, $C(CN)(CH_3)CH_2C\mathit{H}_2COO$ from MCP), 1.50 (s, $CH_2{=}C\text{-}C\mathit{H}_3$from MCP), 1.41-1.20 (t, J=6.8 Hz, $C(CN)(CH_3)C\mathit{H}_2CH_2COO$ from MCP), 1.10 (s, $C(C\mathit{H}_3)COO$ from GMA), 0.93 (s, $C(C\mathit{H}_3)COO$ and $C(CN)(C\mathit{H}_3)$ from MCP) (Fig. S7).

1.4 Synthesis of the hyperbranched polymeric spectral sensor (MCPR)

MCPG (0.1545 g) and RTEA (0.0974 g, 0.174 mmol) were dissolved in 10 mL dry dioxane and added to a 100 mL three-necked flask. The solution was stirred at 70 °C for 10 h under N_2

atmosphere. Then, the mixture was cooled down to room temperature and added to 20 mL cold methanol. The emerging orange precipitation was collected, washed with cold methanol and dried in vacuum to give 0.1731 g MCPG with 69.5% yield. FT-IR (KBr): 3409 (OH, NH), 3000 (Ph), 2960, 2860 (CH_3, CH_2), 1720 (O=C-O), 1630 (O=C-NR_2), 1613, 1515, 1449 (Ph),1148(C-O-C), 908 (epoxy) cm^{-1} (Fig. S5b). Mn/PDI of MCPR was 18700/ 1.414 (Fig. S6b). ^1H NMR (400 MHz, $CDCl_3$, δ /ppm): 7.88-7.40 (m, PhH from MCPG and RTEA), 7.10 (m, PhH from RTEA), 6.37 and 5.62 (s, C=CH_2), 4.33 and 3.80 (s, COOCH_2 from GMA, COOCH_2CH(OH) from the reaction of MCPG and RTEA), 3.75-3.71 (t, J=6.4 Hz, COOCH_2CH_2OCO from MCP), 3.38-3.29 (m, NCH_2CH_2S from RTEA), 3.29-3.19 (m, CH from GMA, NHCH_2CH(OH) from the reaction of MCPG and RTEA), 2.85 and 2.64 (s, COC$H_2$from GMA, NHCH_2CH(OH) from the reaction of MCPG and RTEA), 2.0-0.8 (m, CH_3 and CH_2 except those listed above) (Fig. S8).

2. Characterization figures

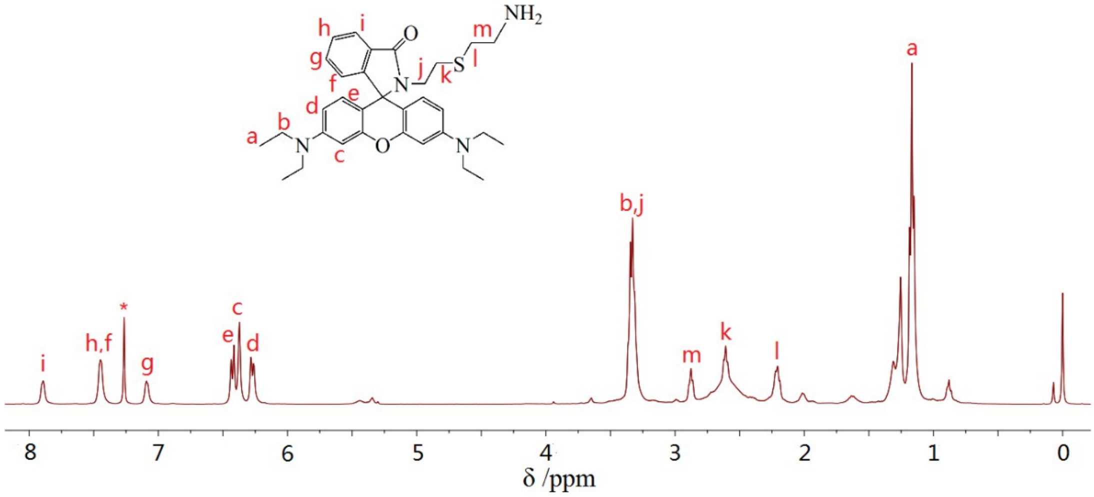

Fig. S1 ^1H NMR spectrum of RTEA in $CDCl_3$ (400 MHz)

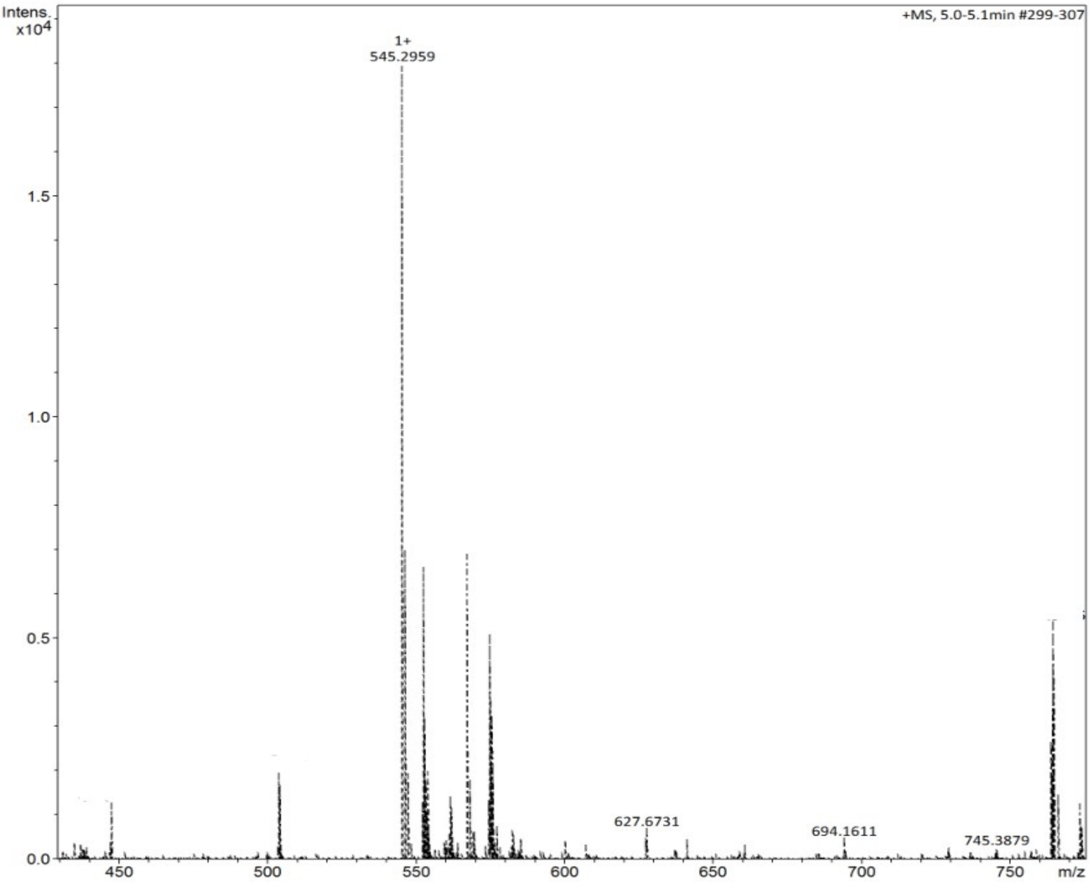

Fig. S2 LC-MS spectrum of RTEA

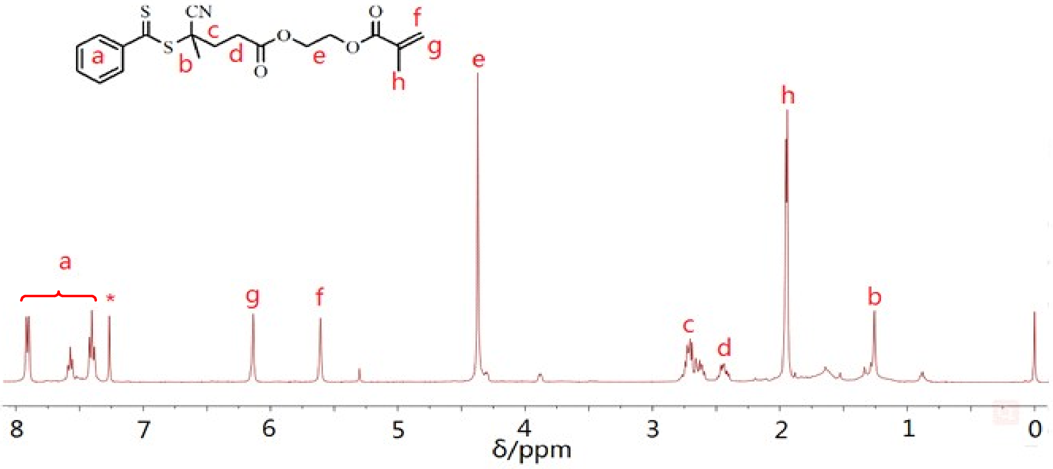

Fig. S3 ^{1}H NMR spectrum of MCP in $CDCl_3$ (400 MHz)

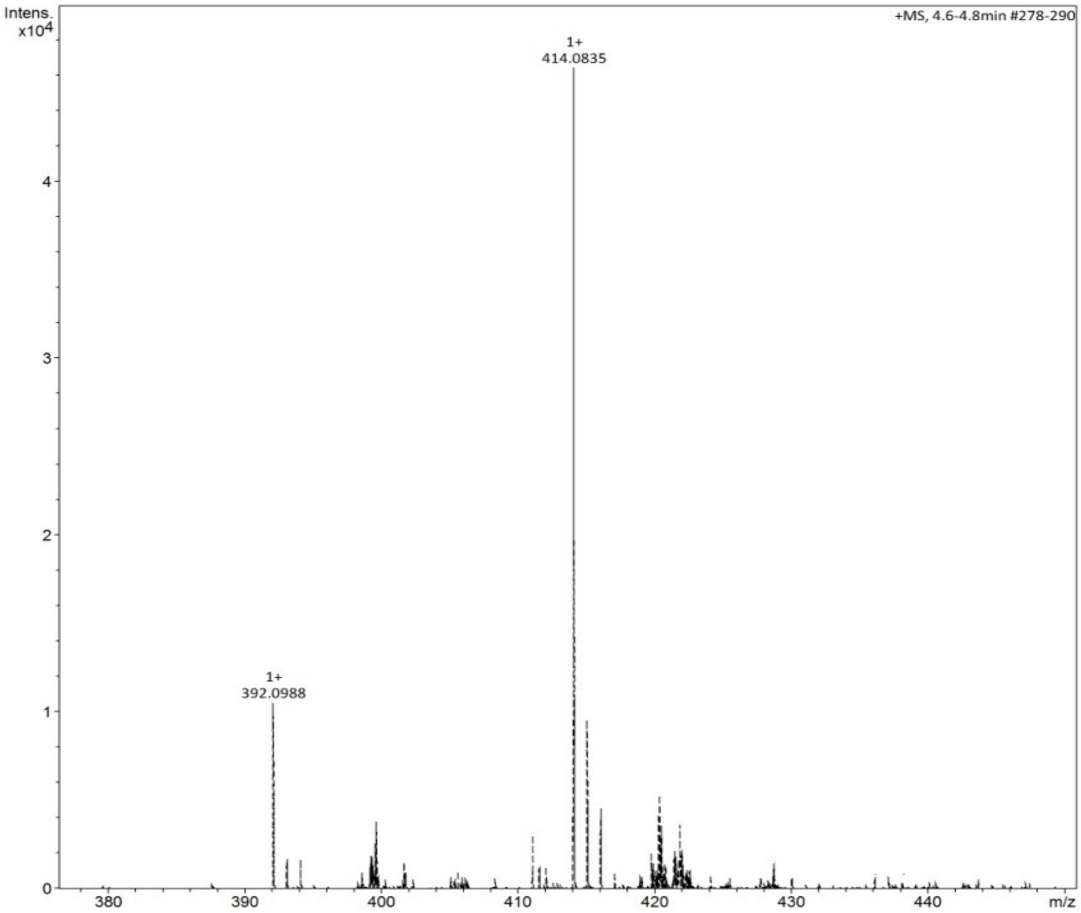

Fig. S4 LC-MS spectrum of MCP

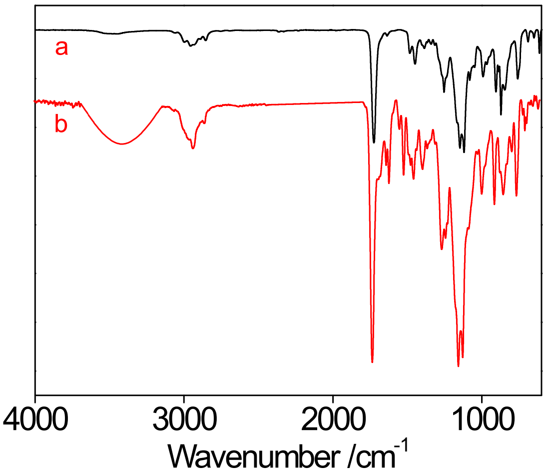

Fig. S5 IR spectra of MCPG (a) and MCPR (b)

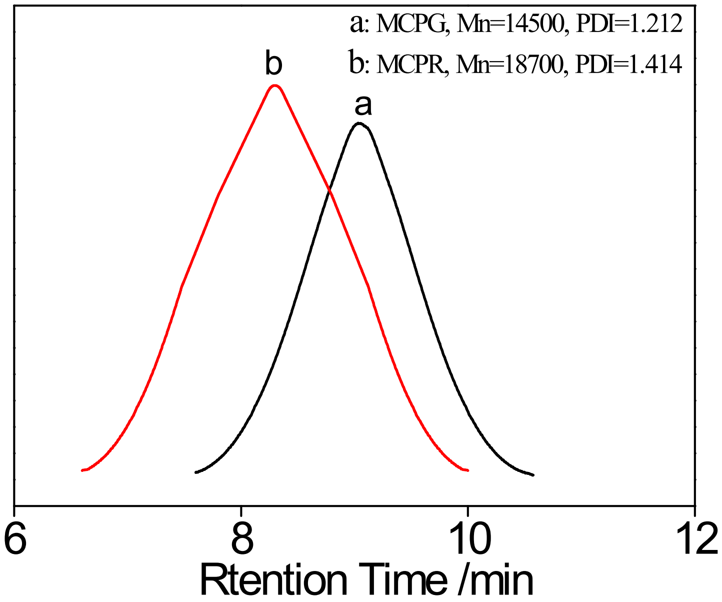

Fig. S6 GPC trace of MCPG (a) and MCPR (b)

3. Calculation of the structure parameters of MCPG and MCPR

Their structure parameters were estimated based on the characterization data according to the references.[2,3]

For MCPG, the degree of branching (DB) could be calculated by DB=(D+T)/(D+T+L), where D, T and L were specific data representing the branching, terminal and linear unit in the polymer, respectively. In the ^{1}H NMR spectrum of MCPG (Fig. S7), when the integral peak area at 7.86 ppm of the terminal phenyl proton was specified as 1, then the integral peak areas related to D, T and L were deduced to be 64.80 (g, h, i, j, k, l), 3.18 (a) and 92.42 (b, c, d, e, f) respectively which determined DB as 0.42.

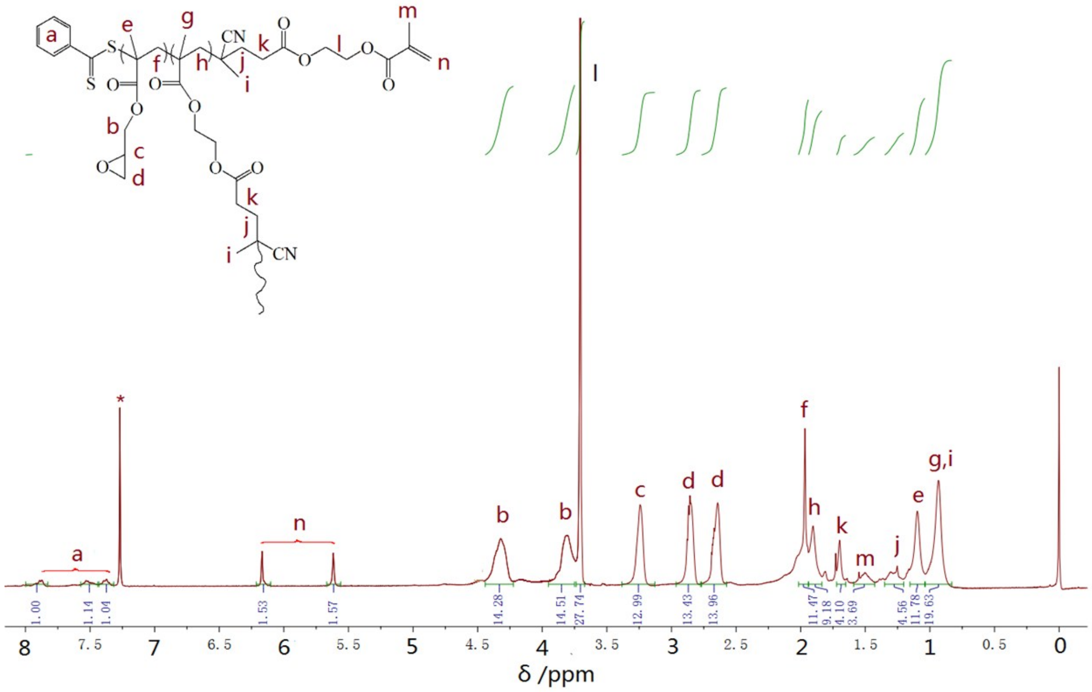

Fig. S7 ^{1}H NMR spectrum of MCPG in $CDCl_3$ (400 MHz)

Also from Fig. S7, the terminal phenyl signals appeared at 7.86, 7.45, 7.10, the remaining vinyl proton signals of MCP emerged at 6.16, 5.16 ppm ($C{=}CH_2$), and characteristic proton signals of GMA unit were at 4.31, 3.80 ($COOCH_2$), 3.23 (CH), 2.85 and 2.63 ppm (CH_2O). The number-average molecular weight (Mn) and polydispersity (PDI) of MCPG were 14500 and 1.212 (Fig. S6a). Based on these data, the number-average functionality (Fn) of the inimer MCP could be calculated as 3.54 according to the formula $Fn= Mn\times I_{7.86}/(MW_{MCP}\times I_{7.86}+2MW_{GMA}\times I_{3.23})$, where MW_{MCP} and MW_{GMA} were the molecular weight of MCP and GMA which are 391 and 142, respectively. $I_{7.86}$ and $I_{3.23}$ were the integral peak areas at 7.86 and 3.23 ppm, respectively. By comparing the integrated signal areas at 7.86 and 3.23 ppm, the molar ratio of GMA to MCP(R) was 25.98 ($R=2I_{3.23}/I_{7.86}$), and then each MCPG molecule comprised about 92 GMA units (Fn×R).

For MCPR, in its ^{1}H NMR spectrum (Fig. S8), the signals of aromatic protons were at 7.88, 7.45, 7.10 (Ph*H*) and the remaining vinyl protons were at 6.37 and 5.62 ($C{=}CH_2$). The signals of GMA units appeared at 4.33, 3.80 ($COOCH_2$), 3.24 (C*H*O of epoxy), 2.85 and 2.64 (CH_2O of epoxy). The characteristic signals of RTEA appeared at 3.33 (CH_2CH_2). Based on the integrated peak areas at 3.24 ppm, it was calculated by the equation $e=I_{3.33}/(8I_{3.24})$ that 12.5% of GMA units had participated in the epoxy ring-open reaction. Therefore, the number of GMA units involved in the epoxy ring-open reaction could be determined to be about 11 (12.5%×92), which was theoretically the number of RTEA grafted onto each MCPR.

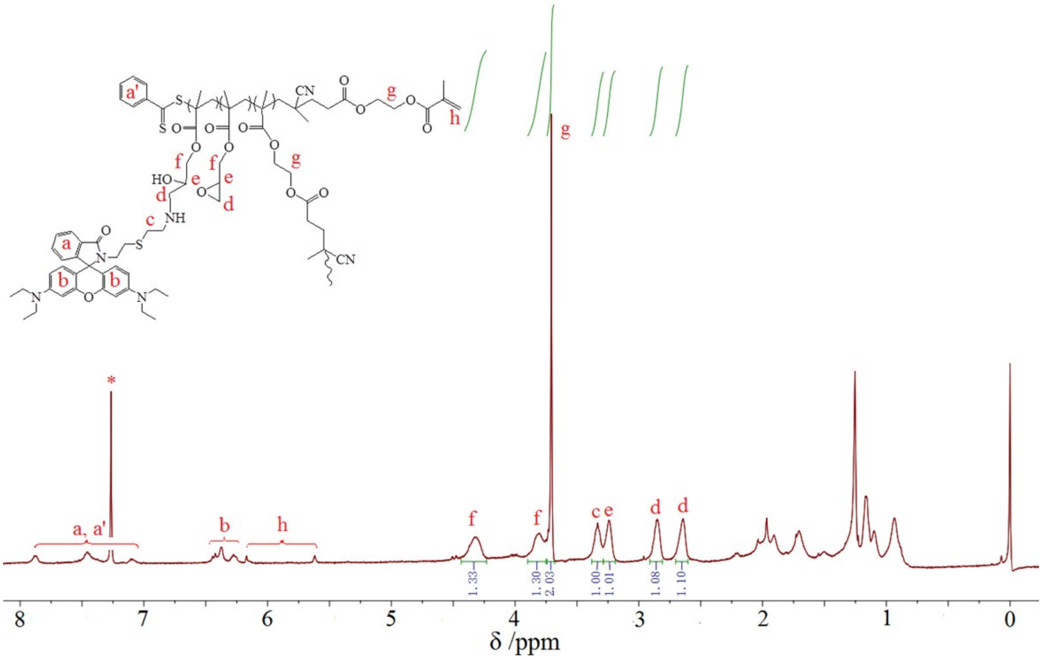

Fig. S8 ^{1}H NMR spectrum of MCPR in $CDCl_3$ (400 MHz)

Mn and PDI of MCPR were 18700 and 1.414 (Fig. S6b). By assuming that no GMA units were lost during the reaction, the number of RTEA in each MCPR was approximately 8 according to $(Mn_{MCPR}-Mn_{MCPG})/M_{RTEA}$, where Mn_{MCPR}, Mn_{MCPG} and M_{RTEA} were Mn of MCPR, MCPG and molecular weight of RTEA, respectively.

It can be found that the number of RTEA in each MCPR from ^{1}H NMR was greater than that from GPC. Besides the experimental errors in both ^{1}H NMR and GPC, the reason might be that some GMA units folded and wrapped in the long polymer chains were shielded, leading to the underestimation of them in ^{1}H NMR analysis. As a result, the amount of RTEA from ^{1}H NMR was on the high side.

4. Response of MCPR to Fe^{3+} in different media

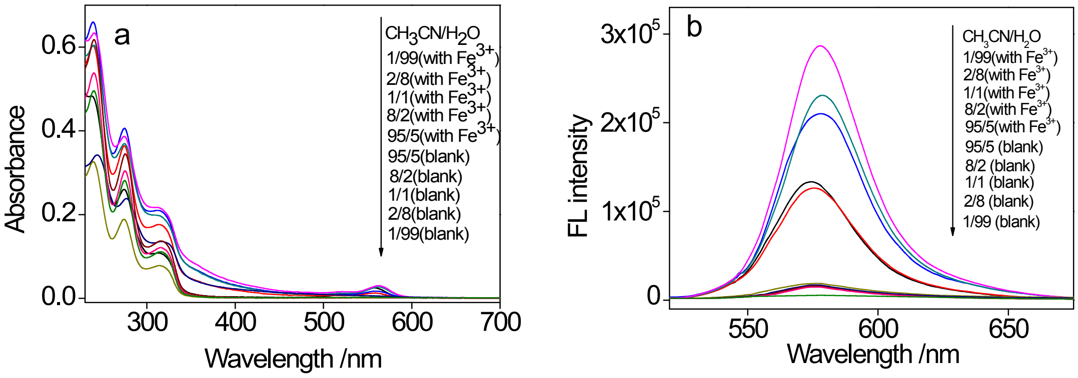

Fig. S9 UV-Vis absorption (a) and fluorescence (b) spectra of MCPR with and without Fe^{3+}. Solvent: CH_3CN/H_2O (95/5, 8/2, 5/5, 2/8, 1/99, v/v), concentration: 50 μg/mL for MCPR, 50 μM for metal ions. λ_{ex}: 467 nm, slit width: 5 nm.

5. Temperature effects on the sensing

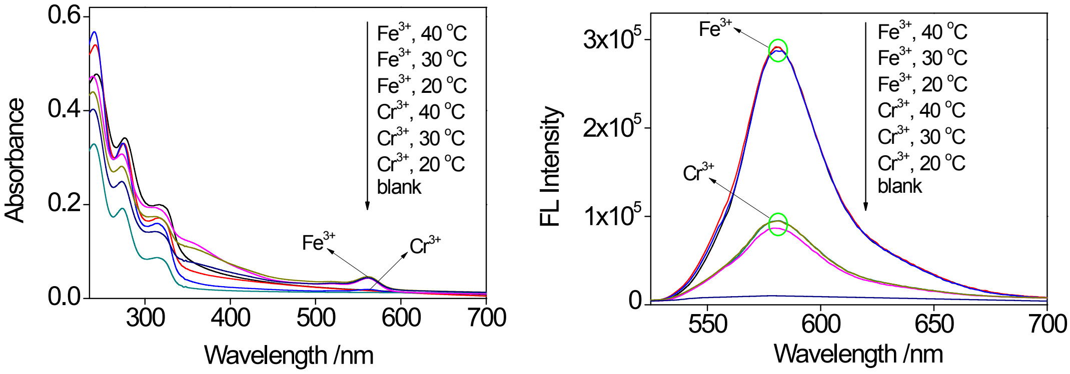

Fig. S10 UV-Vis absorption (left) and fluorescence (right) spectra of MCPR, MCPR-Fe^{3+} and MCPR-Cr^{3+} in different temperature. Solvent: CH_3CN/H_2O (1/99, v/v), concentration: 50 μg/mL for MCPR, 50 μM for Fe^{3+} and Cr^{3+}, temperature: 20, 30, 40 °C. λ_{ex}=467 nm, slit wide: 5 nm.

6. Retrievability of MCPR

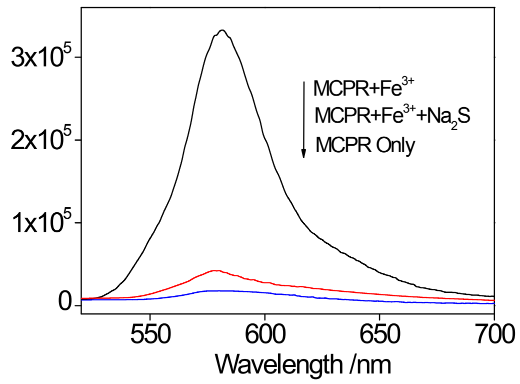

Fig. S11 Retrievability of MCPR as a fluorescent sensor for Fe^{3+}. Solvent: CH_3CN/H_2O (1/99, v/v), concentration: 50 μg/mL for MCPR, 50 μM for Fe^{3+}, 250 μM for Na_2S. λ_{ex}: 467 nm, slit width: 5 nm.

7. Materials for supporting sensing mechanism

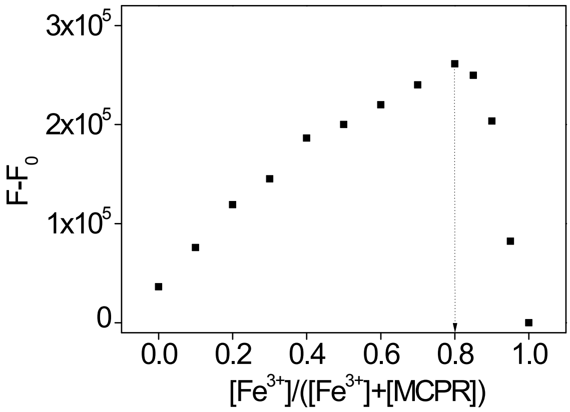

Fig. S12 Job's plots of MCPR and Fe^{3+}. Total concentration ([MCPR]+[Fe^{3+}]): 25 mM, F_0 and F: fluorescence maxima before and after addition of Fe^{3+} at 578 nm, respectively. λ_{ex}=467 nm, slit wide: 5 nm.

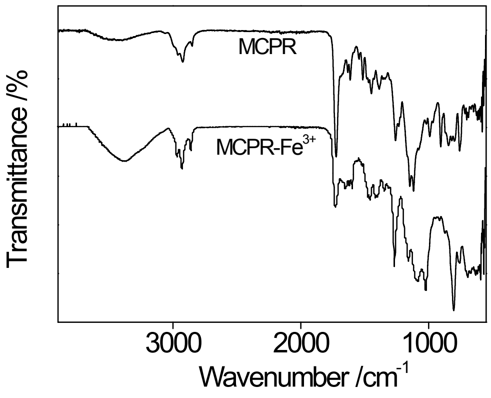

Fig. S13 FT-IR spectra of MCPR and MCPR-Fe^{3+}.

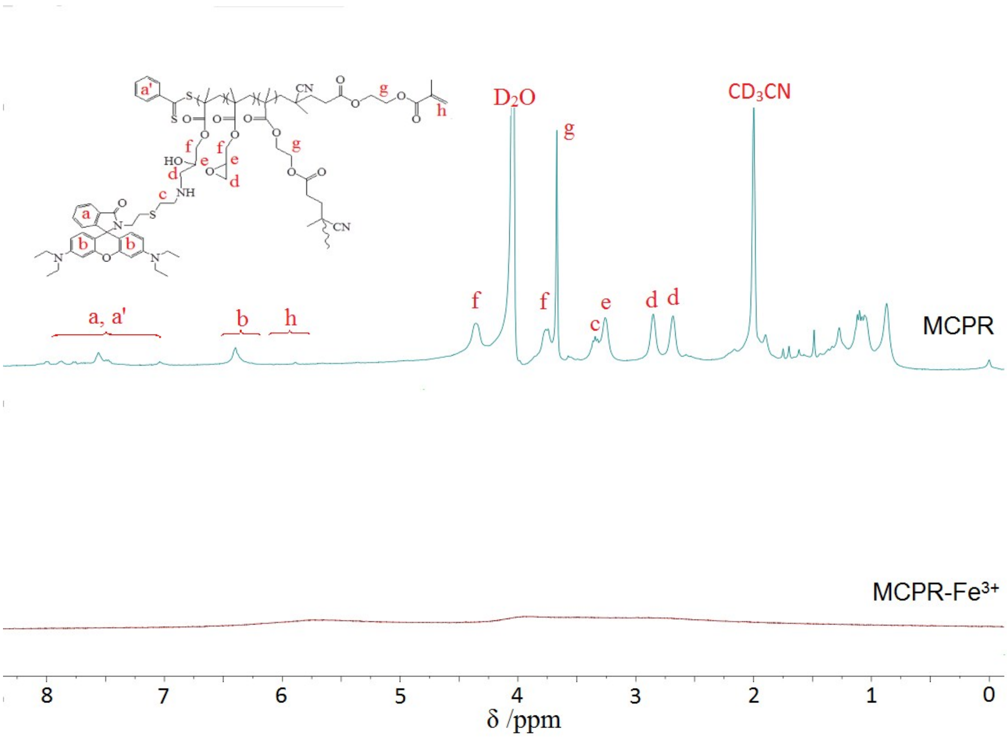

Fig. S14 ^{1}H NMR spectra of MCPR and MCPR-Fe^{3+} in CD_3CN-D_2O (1/1, v/v) (400 MHz).

References

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