Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Uracil-bearing Poly(2-isopropyl-2-oxazoline): Hg(II)-Selective Control of its Thermoresponsiveness

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Experimental Section

Materials and measurements

All commercially available reagents were reagent grade and used without further purification. Dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and acetonitrile were freshly distilled before each use. Recycling preparative size-exclusion chromatography (SEC) was performed on a LC-9201 (JAI, Tokyo, Japan) instrument equipped with JAIGEL-1H, JAIGEL-2H, and JAIGEL-3H columns using $CHCl_3$ as the eluent. Electronic absorption spectra were measured using a V-660 (JASCO, Tokyo, Japan) spectrophotometer equipped with a thermostatic cell holder coupled with a controller (ETCS-761, JASCO, Tokyo, Japan). ^1H, ^{13}C NMR spectra were recorded using a Bruker DPX 400 (400 MHz) spectrometer in $CDCl_3$ or DMSO-d_6. FT-IR spectra were recorded on Bruker Vertex 70 FT-IR spectrometer.

Determination of thermal transition temperature

The transmittance of the solution at 800 nm was measured using a spectrophotometer. The heating rate of the sample cells was adjusted to 2 °C min^{-1}. The cloud point temperature was taken as the temperature at which the transmittance reached 60% in the resulting transmittance versus temperature curves.

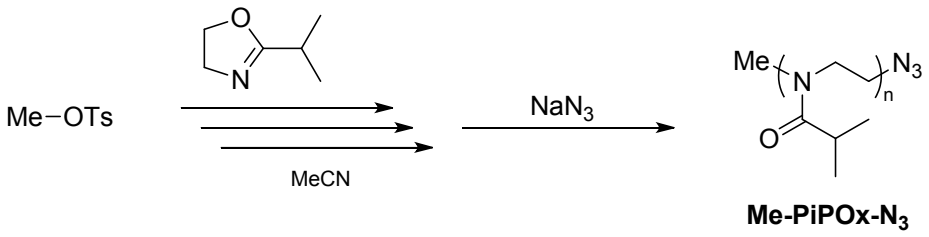
Synthesis

The synthetic route to U-PiPOx-U is outlined in Scheme 1. U-OH, U-Cl, U-N_3, and 2-isopropyl-2-oxazoline (iPOx) were synthesized to literature procedures.[1, 2]

Prop-PiPOx-Prop: A Schlenk flask was degassed under high vacuum and backfilled with N_2; this process was repeated three times. Propargyl *p*-toluenesulfonate (0.79 g, 0.65 mL, 3.76 mmol) in acetonitrile (15 mL) was placed in the Schlenk flask and 2-isopropyl-2-oxazoline (14.3 g, 15.0 mL, 126.4 mmol) was added. The mixture solution was stirred at 40 °C under N_2 atmosphere and the reaction was monitored by analytical SEC and MALDI-TOF-MS. Upon completion of the reaction, 0.401 g of N-methylpropargylamine (0.49 mL, 5.80 mmol) was poured into the reaction mixture, and then further stirred for 24 hr. The solution of PiPOx was purified via dialysis for 2 days against distilled water and poured into dichloromethane. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The combined organic layers were concentrated under reduced pressure then recovered by lyophilisation to afford Prop-PiPOx-Prop as white powder (12.3 g, 86%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 4.29–4.08 (m; initiation terminal N–CH_2–C≡), 3.65–3.26 (strong broad s; –CH_2–CH_2– on the polymer backbone), 2.98–2.52 (broad d; –CH– on the polymer side chain, α-terminal –C≡CH, ω-terminal –N–CH_2–C≡CH), 2.31 (broad s; terminal –N–CH_3), 1.09 (strong broad s; –CH_3 on the polymer side chain); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 178.24, 177.76, 73.66, 46.74, 45.91, 43.93, 30.25, 29.85, 19.87.

U-PiPOx-U: A mixture of **U-N_3** (251 mg, 1.50 mmol), **Prop-PiPOx-Prop** (1.00 g, 0.250 mmol), and copper(II) sulfate (399 mg, 2.50 mmol) in THF (40 mL) was placed in a round-bottom flask. Sodium ascorbate (495 mg, 2.50 mmol) was dissolved in H_2O (4 mL) and poured into the mixture. The mixture was refluxed for 2 days, and then the solution was cooled to room temperature and poured into CH_2Cl_2. The organic layer was

washed with brine and dried over anhydrous sodium sulfate. The combined organic layers were concentrated under reduced pressure. And then the residue was purified by recycling preparative SEC using $CHCl_3$ as the eluent and recovered by lyophilisation to afford U-PiPOx-U as white powder (748 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 11.01–9.50 (strong broad d; NH in uracil), 7.87–7.35 (m; N–CH=N in the triazole ring, N–CH=C in uracil), 5.19 (broad s; CH_2 between triazole ring and uracil), 4.68–4.52 (broad d; CH_2 from initiation terminal of PiPOx), 3.68 (s; CH_2 from termination terminal of PiPOx), 3.65–3.25 (strong broad s; –CH_2–CH_2– on the polymer backbone), 2.98–2.52 (broad d; –CH– on the polymer side chain, α-terminal –C≡CH, ω-terminal –N–CH_2–C≡CH), 2.31 (broad s; terminal –N–CH_3), 2.29 (broad t; terminal –N–CH_3), 1.09 (strong broad m; –CH_3 on the polymer side chain); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 178.47, 177.92, 164.03, 151.27, 107.75, 46.81, 45.91, 44.13, 30.41, 30.01, 20.00, 19.82.



Scheme S1. Synthesis of **Me-PiPOx-N_3**.

Me-PiPOx-N_3: A Schlenk flask was degassed under high vacuum and backfilled with N_2; this process was repeated three times. 0.45 g of methyl p-toluenesulfonate (0.36 mL, 2.4 mmol) in acetonitrile (15 mL) was placed in the Schlenk flask, and 9.50 g of iPOx (10.0 mL, 84.0 mmol) was added to it. The mixture solution was stirred at 40 °C under N_2 atmosphere and the reaction was monitored by analytical SEC and MALDI-TOF-MS. Upon completion of the reaction, 234 mg of sodium azide (3.60 mmol) was added to reaction mixture, and then further stirred for 36 h. The solution of PiPOx was purified via dialysis for 2 days against distilled water and poured into dichloromethane. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The combined organic layers were concentrated under reduced pressure then recovered by lyophilisation to afford Me-PiPOx-N_3 as white powder (7.91 g, 83%). ^1H NMR (400 MHz, CDCl3, 25 °C) δ (ppm): 3.77– 3.15 (strong broad d; –CH2–CH2– on the polymer backbone), 3.10–3.02 (t; CH3 from initiation terminal of PiPOx), 2.98–2.50 (broad d; –CH– on the polymer side chain), 1.07 (strong broad s; –CH– on the polymer side chain).

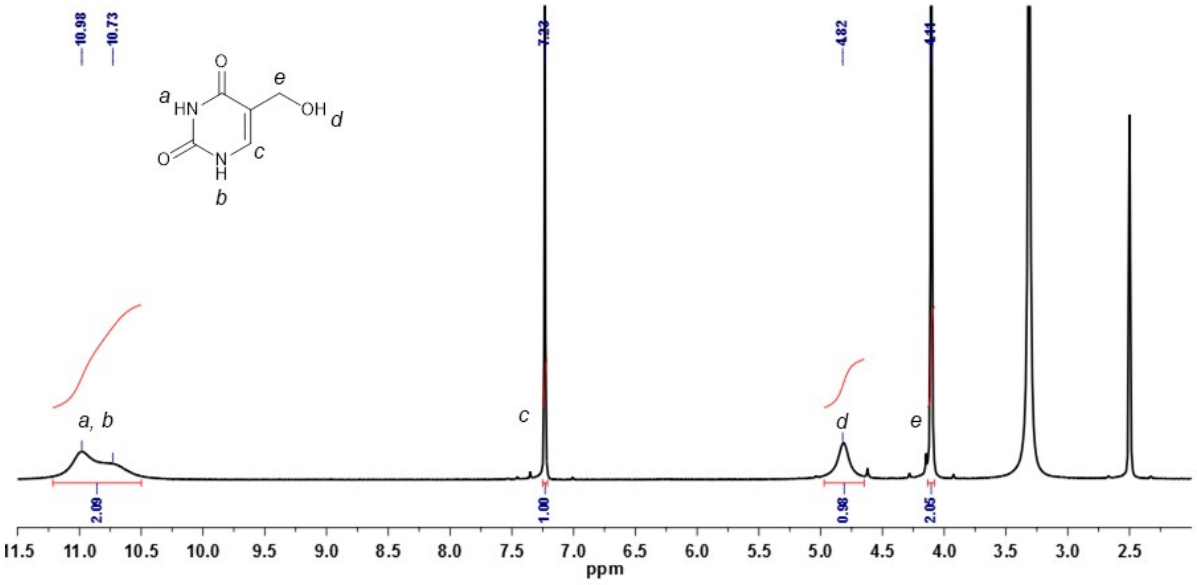


Figure S1. ^{1}H spectrum of **U-OH** in d_6-DMSO.

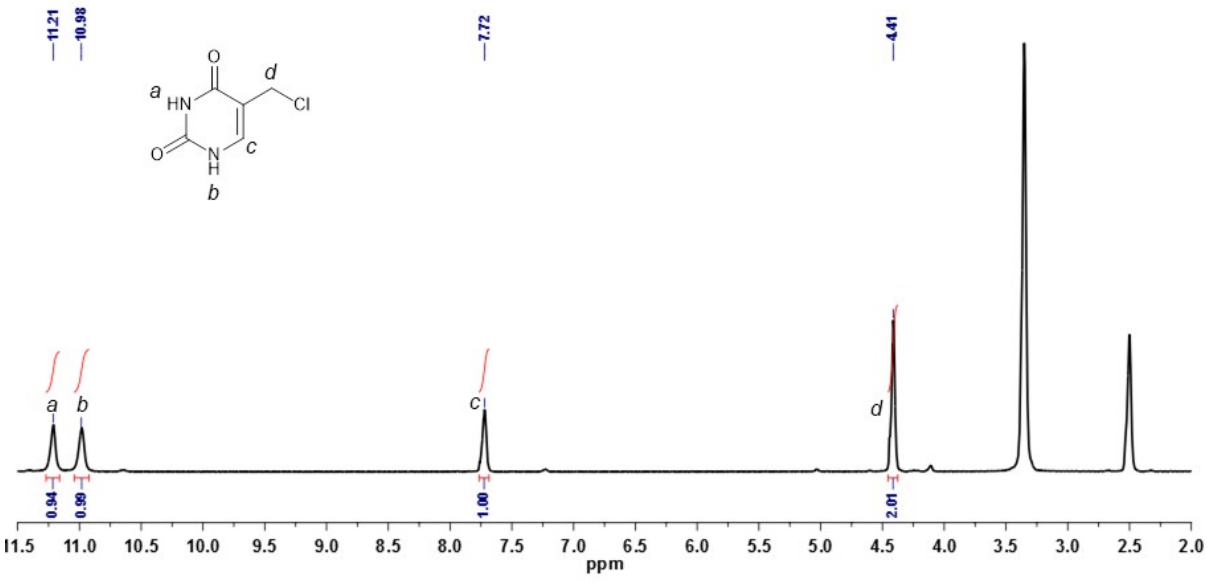


Figure S2. ^{1}H spectrum of **U-Cl** in d_6-DMSO.

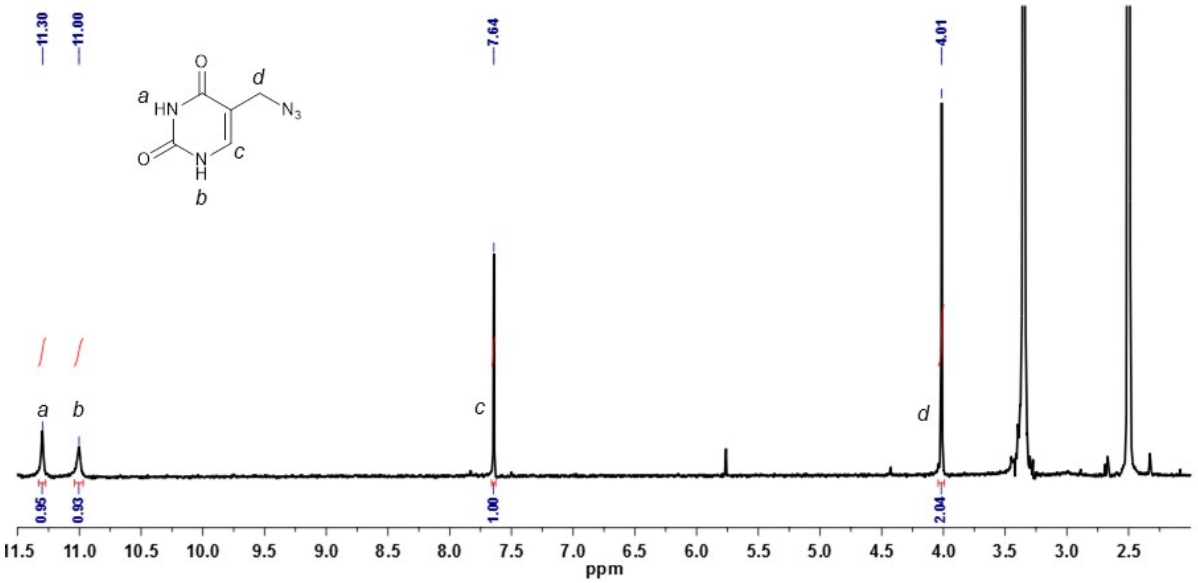


Figure S3. ^{1}H spectrum of **U-N$_3$** in d_6-DMSO.

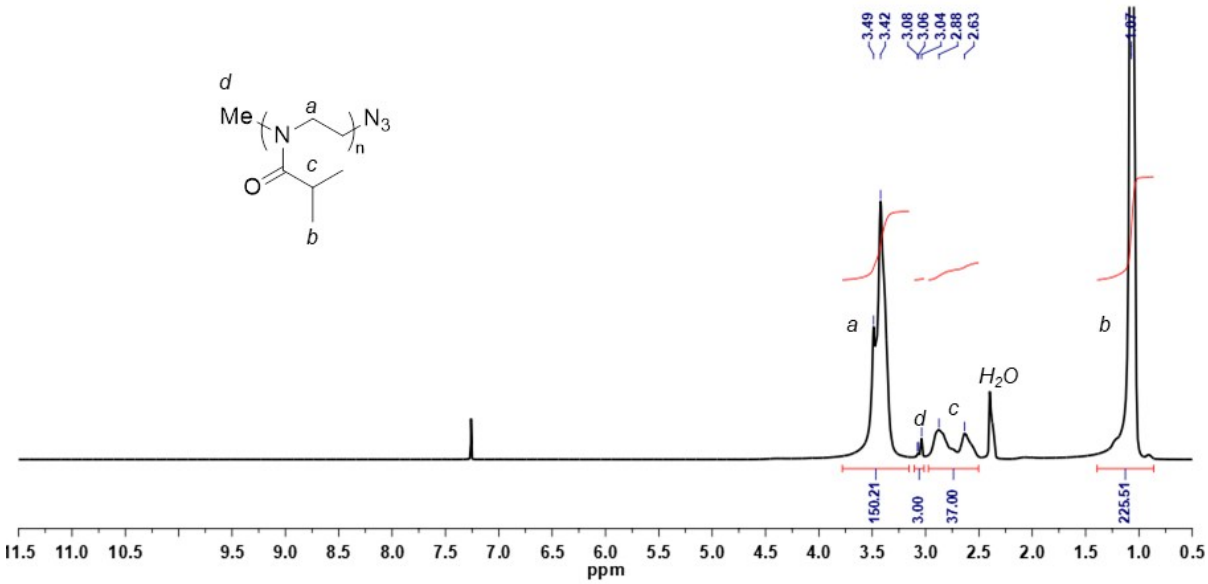


Figure S4. ^{1}H spectrum of **Me-PiPOx-N$_3$** in $CDCl_3$.

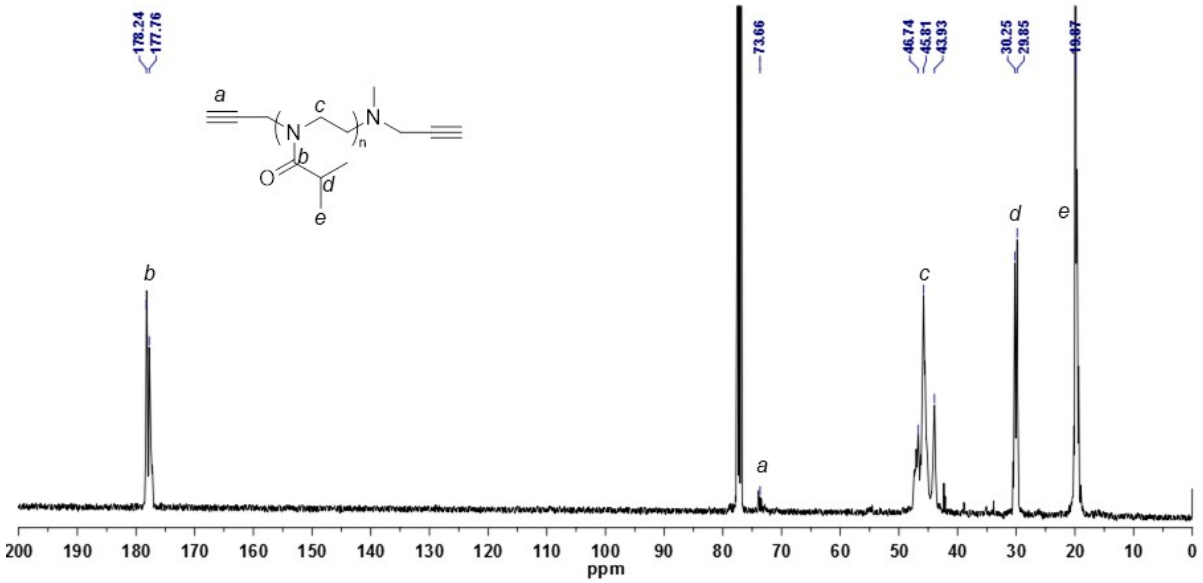


Figure S5. ^{13}C spectrum of **Prop-PiPOx-Prop** in $CDCl_3$.

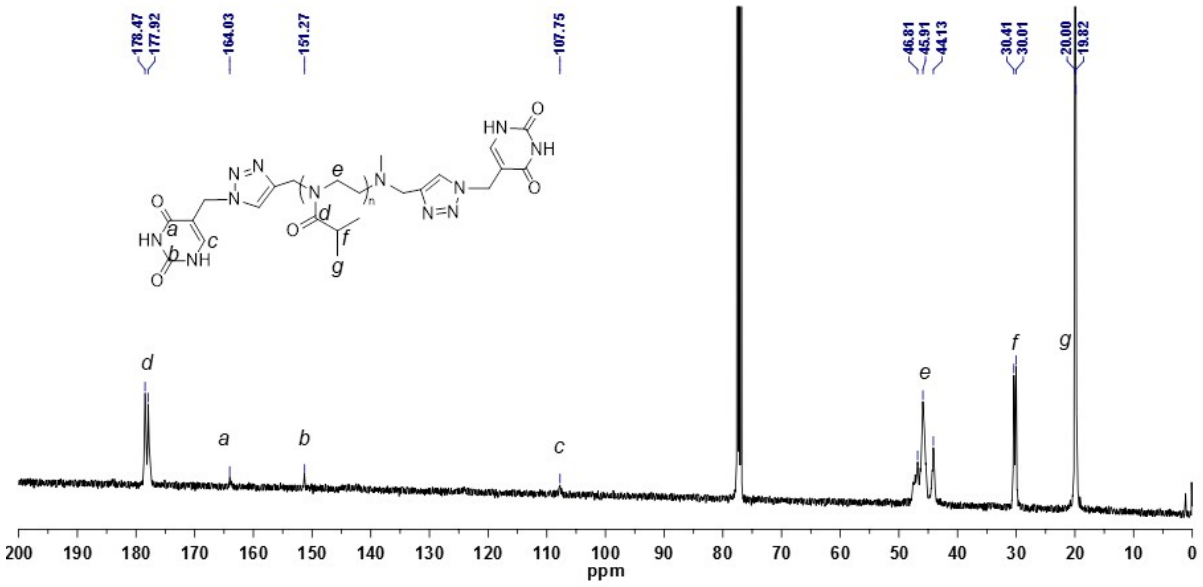


Figure S6. ^{13}C spectrum of **U-PiPOx-U** in $CDCl_3$.

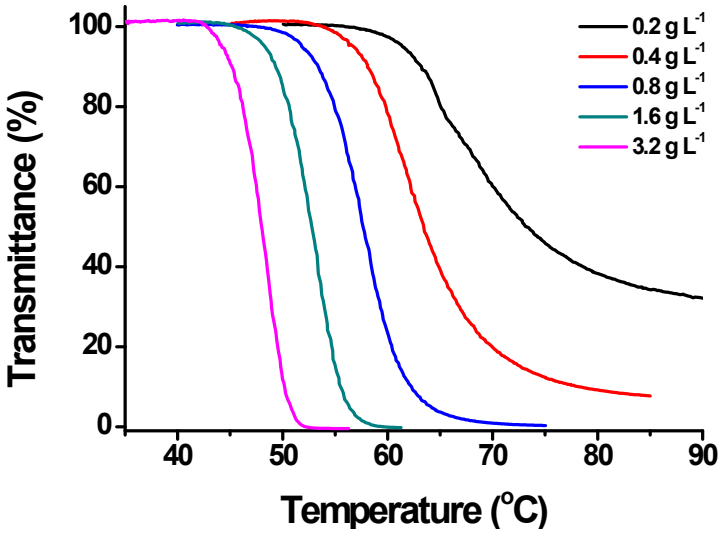


Figure S7. Temperature dependent transmittance changes of **U-PiPOx-U** aqua solutions with several concentrations.

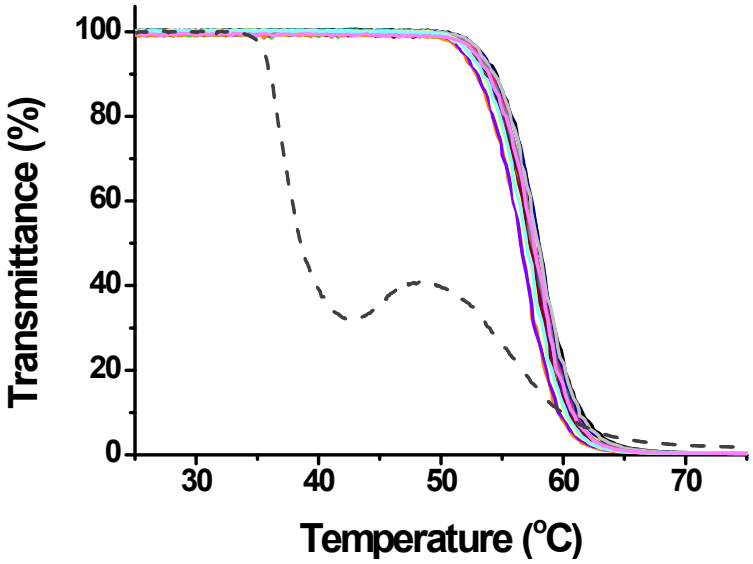


Figure S8. Temperature dependent transmittance changes of **U-PiPOx-U** aqua solution (0.8 g L^{-1}) upon addition of 0.50 eq. Hg^{2+} (dashed line) and Ag^{+}, Al^{3+}, Au^{+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Pt^{2+}, Rh^{2+}, Ru^{3+}, Zn^{2+} (solid lines).

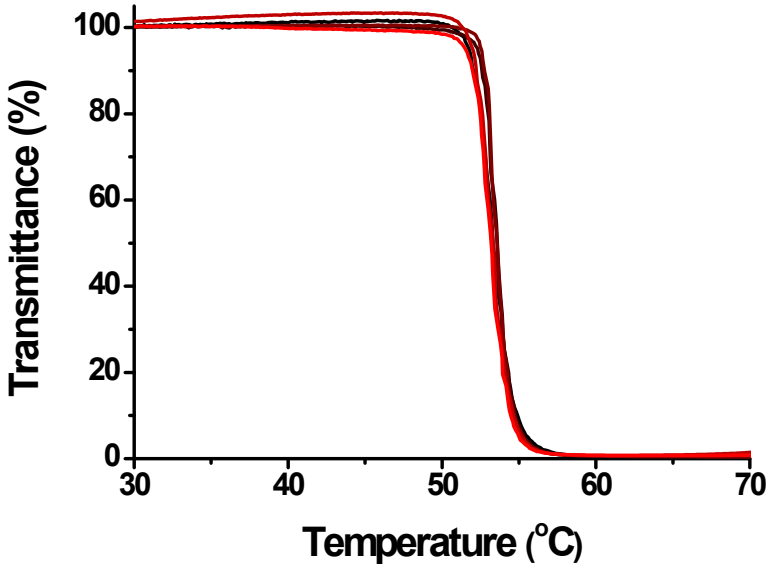


Figure S9. Temperature dependent transmittance changes of **Me-PiPOx-N_3** aqua solution (0.8 g L^{-1}) upon addition of 0.1 ~ 0.5 eq. Hg^{2+}.

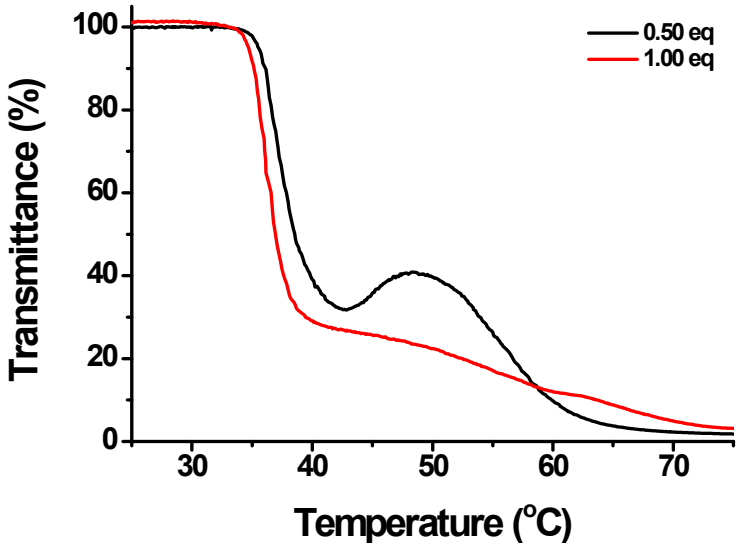


Figure S10. Temperature dependent transmittance changes of **U-PiPOx-U** aqua solution (0.8 g L^{-1}) upon addition of 0.50 eq. (black) and 1.00 eq. (red) Hg^{2+}.

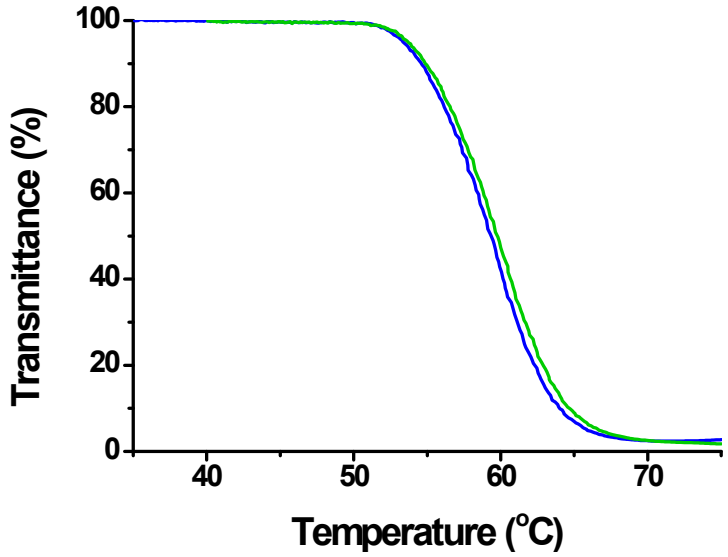


Figure S11. Temperature dependent transmittance changes of **U-PiPOx-U** aqua solution (0.8 g L^{-1}) upon addition of 0.5 eq. Ag^{+} at pH 10.0.

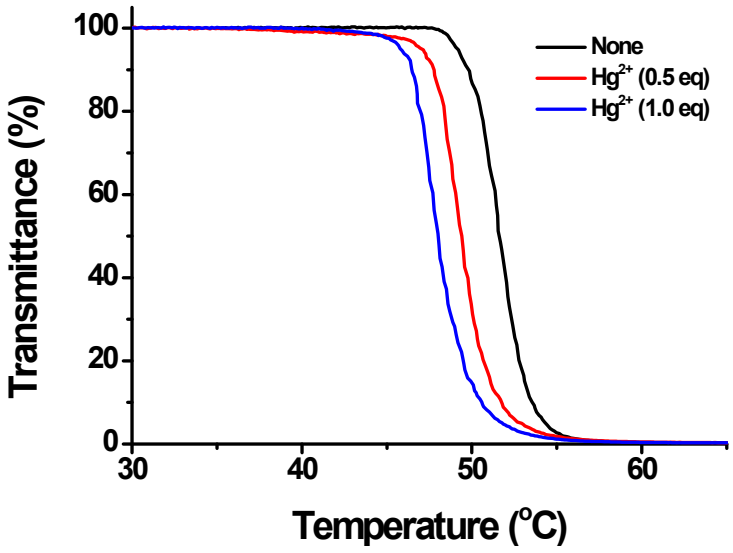


Figure S12. Temperature dependent transmittance changes of **Me-PiPOx-U** aqua solution (0.8 g L^{-1}) upon addition of 0.0 ~ 1.0 eq. Hg^{2+}.

References

1. M. Meyer and H. Schlaad, *Macromolecules*, 2006, **39**, 3967-3970.
2. E. Brognara, I. Lampronti, G. Breveglieri, A. Accetta, R. Corradini, A. Manicardi, M. Borgatti, A. Canella, C. Multineddu and R. Marchelli, *European journal of pharmacology*, 2011, **672**, 30-37.