Supporting Information

Ultraviolet-responsive self-assembled metallomicelles for photocontrollable catalysis of asymmetric sulfoxidation in water

Mengqiao Gao, Rong Tan, * Pengbo Hao, Yaoyao Zhang, Jiang Deng, Donghong Yin

Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education); National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Hunan Normal University, Changsha 410081 (P. R. China)

* Corresponding authors. Fax: +86-731-8872531. Tel: +86-731-8872576

E-mail: yiyangtanrong@126.com
1. Preparation and identity of the copolymers (PN_{422A_{25}-C}, PN_{427A_{10}-C}, and PN_{429A_{5}-C})

2. LCST determination of the copolymers

3. Identity of the obtained chiral sulfoxides
1. Preparation and identity of the copolymers (PN_{422}A_{25}-C, PN_{427}A_{10}-C, and PN_{429}A_{5}-C)

1.1 Preparation of the copolymers of PN_{422}A_{25}-C and PN_{429}A_{5}-C.

To regulate the LCST of copolymers close to room temperature (25 °C), various ratios of NIPAAm to azobenzene blocks have been modulated in the chiral salen Ti^IV^-containing amphiphiles. The synthetic procedure was similar to that of PN_{427}A_{10}-C excepted for the varied molar feeds of NIPAAm and N-azo-acrylamide.

During the procedure, monomers of NIPAAm and N-azo-acrylamide with different molar feed (9.8 mmol of NIPAAm and 0.49 mmol of N-azo-acrylamide for PN_{422}A_{25}-C, 39.2 mmol of NIPAAm and 0.49 mmol of N-azo-acrylamide for PN_{429}A_{5}-C), were dissolved in THF in a Schlenk tube. AIBN (0.051 mmol for PN_{422}A_{25}-C, and 0.199 mmol for PN_{429}A_{5}-C) and 2-aminoethanethiol hydrochloride (0.10 mmol for PN_{422}A_{25}-C, and 0.40 mmol for PN_{429}A_{5}-C), which acted as a radical initiator and chain transfer reagent, were then added into the solutions. The reaction mixtures were degassed by bubbling with nitrogen gas at room temperature for 30 min. Polymerizations were carried out at 60 °C for 24 h with nitrogen protection. The mixtures were then cooled to room temperature, and followed by treating with solid KOH to liberate the terminal amino group. The obtained solutions were concentrated under vacuum. The crude products were purified by repeated precipitating from diethyl ether and followed from THF to remove unreacted monomers. After drying under vacuum for 6 h at 40 °C, the copolymers of poly(NIPAAm-co-Azo) was obtained as yellow powders.

The obtained copolymers of poly(NIPAAm-co-Azo) (0.18 mmol), (R,R)-N- (3,5-di-tert-butylsalicylidene)-N’-(3-tert-butyl-5-chloromethyl-salicylidene)-1,2-cyclohexanediamine (0.25 mmol, 0.137 g) and triethylamine (0.2 mmol, 0.02 g) were mixed in dry toluene (30 mL) under
room temperature. The mixtures were refluxed for 48 h under nitrogen protection. After removal
of solvent, the residues were dissolved in tetrahydrofuran to remove the formed triethylamine
hydrochloride through filtration. Filtrates were concentrated in vacuo, and were treated with
Ti(O)iPr)₄ (0.25 mmol, 0.07 g) in dichloromethane (30 mL) for 12 h at room temperature. The
mixtures were concentrated under vacuum. Crude products were purified by repeatedly
precipitating from tetrahydrofuran using diethyl ether as precipitant. The resulting orange solids
were dissolved in chloroform (20 mL), and treated with water (2 mL) to remove any traces of TiO₂
by filtration. Filtrates were concentrated in vacuum and further dried in vacum at 40 °C overnight,
giving orange powder of poly(NIPAAm-co-Azo)-modified chiral salen Ti⁴⁺ catalyst, denoted as
PNₓAᵧ-C (where x represented the repeated units number of NIPAAM, and y represented the
repeated units number of N-azo-acrylamide in copolymers. The numbers were determined by ¹H
NMR spectra).

1.2 Identity of the PNₓAᵧ-C by ¹H NMR spectra

Given mass of PNₓAᵧ-C (PN₄₂₂A₂₅-C, PN₄₂₇A₁₅-C, and PN₄₂₉A₅-C) were placed in NMR tubes,
and the tubes were backfilled with N₂. In dark room, D-substituted solvent was added via syringe,
and the sample was carefully shaken until full dissolution was obtained. The solutions were
irradiated by visible light (λ= 410 nm) for 30 min, and then being kept in the dark for 72 h to give
dark-adapted samples for NMR determination.

PN₄₂₂A₂₅-C in DMSO-d₆: The structure and chemical composition of PN₄₂₂A₂₅-C were
identified by ¹H NMR spectrum carried out in DMSO-d₆ (see Fig. S1). ¹H NMR (500 MHz,
DMSO-d₆) δ (ppm): δ 7.91 (s, 2 H, Ph-H in Ti(salen)), 7.84 (m, 102 H, -N=N-Ph-H and Ph-H in
Ti(salen)), 7.55 (m, 50 H, -NH-Ph-H), 7.52 (m, 75 H, N=N-Ph-H), 7.19 (m, 447 H, O=C-NH-CH
and O=C-NH-Ph), 3.83 (m, 422 H, CH₂-Ch-Ch₂), 3.5 (m, 2 H, CH=NH-H), 2.96 (m, 2 H, NH-Ch₂-Ph), 2.63 (m, 2 H, S-Ch₂-Ch₂), 2.36 (m, 2 H, S-Ch₂-Ch₂), 2.17 (m, 2 H, CH₃-Ch-Ch₃ of ′PrO- in Ti(salen)), 1.96 (m, 447 H, CH₂-Ch- in NIPAAm and N-azo-acrylamide), 1.45 (s, 894 H, -CH₂-Ch- in NIPAAm and N-azo-acrylamide), 1.22 (m, 8 H, cyclohexyl-H), 1.18 (m, 39 H, -CH₃ of t-Bu and ′PrO- in Ti(salen)), 1.03 (s, 2532 H, CH₃-Ch-Ch₃).

![Fig. S1 ¹ H NMR spectrum of dark-adapted PN₄₂₂A₂₅-C in DMSO-d₆.](image)

PN₄₂₇A₁₀-C in DMSO-d₆: The structure and chemical composition of PN₄₂₇A₁₀-C were identified by ¹H NMR spectrum carried out in DMSO-d₆ (see Fig. S2). ¹H NMR (500 MHz, DMSO-d₆) δ (ppm): δ 9.97 (s, 2H, Ph-HC=N-), 7.90 (s, 2H, Ph-H in Ti(salen)), 7.84 (m, 42 H, N=N-Ph-H), 7.60-7.56 (m, 20 H, O=C-NH-Ph-H), 7.52 (m, 30 H, N=N-Ph-H), 7.29-7.20 (m, 437
H, O=C-NH-CH and O=C-NH-Ph), 3.83 (m, 427 H, CH₃-CH-CH₃ in NIPAAm), 3.17-3.16 (m, 2 H, cyclohexyl-H), 2.92-2.90 (m, 2 H, NH-CH₂-Ti(salen)), 2.63 (m, 2 H, S-CH₂-CH₂-NH), 2.36 (m, 2 H, S-CH₂-CH₂-NH), 2.17 (m, 2 H, CH₃-CH-CH₃ of t-PrO- in Ti(salen)), 1.95 (m, 437 H, CH₂-CH- in NIPAAm and N-azo-acylamide), 1.44 (s, 874 H, -C₆H₅-NH)-azo-acrylamide), 1.44 (s, 874 H, -C₆H₅-NH). 2.59 (m, 2 H, S-CH₂-C₆H₅-PrO- in Ti(salen)), 1.95 (m, 437 H, CH₂-CH- in NIPAAm and N-azo-acylamide), 1.22 (m, 8 H, cyclohexyl-H), 1.17 (m, 39 H, -C₆H₅ of t-Bu and t-PrO- in Ti(salen)), 1.03 (s, 2562 H, CH₃-CH-CH₃).

Fig. S2 ¹H NMR spectrum of dark-adapted PN₄₂₇A₁₀⁻C in DMSO-d₆.

PN₄₂₇A₁₀⁻C in D₂O: Self-assembly of PN₄₂₇A₁₀⁻C in aqueous system was demonstrated by ¹H NMR spectrum carried out in D₂O (see Fig. S3). ¹H NMR (500 MHz, D₂O) δ (ppm): 3.92 (m, 427 H, CH₃-CH-CH₃ in NIPAAm), 2.75 (m, 2 H, S-CH₂-CH₂-NH). 2.59 (m, 2 H, S-CH₂-CH₂-), 2.15-
2.04 (m, 427 H, CH2-CH- in NIPAAm), 1.74-1.60 (m, 854 H, -CH2-CH- in NIPAAm), 1.17 (s, 2562 H, CH3-CH-CH3 in NIPAAm).

Fig. S3 1H NMR spectrum of dark-adapted PN427A10-C in D2O.

PN429A5-C in DMSO-d6: The structure and chemical composition of PN429A5-C were identified by 1H NMR spectrum carried out in DMSO-d6 (see Fig. S4). 1H NMR (500 MHz, DMSO-d6) δ (ppm): 7.90 (s, 2 H, Ph-H in Ti(salen)), 7.84 (m, 22 H, -N=N-Ph-H and Ph-H in Ti(salen)), 7.55 (m, 10 H, -NH-Ph-H), 7.52 (m, 15 H, N=N-Ph-H), 7.19 (m, 434 H, O=C-NH-CH and O=C-NH-Ph), 3.84 (m, 429 H, CH3-CH-CH3 in NIPAAm), 3.57 (m, 2 H, cyclohexyl-H), 2.63 (m, 2 H, S-CH2-CH2-NH2), 2.36 (m, 2 H, S-CH2-CH2-NH), 2.17 (m, 2 H, CH3-CH-CH3 of PrO- in Ti(salen)) 1.96 (m, 434 H, CH2-CH-, CH2-CH- in NIPAAm and N-azo-acrylamide), 1.43-1.34 (s, 868 H, -CH2-CH- in NIPAAm and N-azo-acrylamide), 1.22 (m, 8 H, cyclohexyl-H), 1.17 (m, 39 H, -CH3 of t-Bu and PrO- in Ti(salen)), 1.04 (s, 2574 H, CH3-CH-CH3).
2. LCST determination of the copolymers (PN\textsubscript{422}A\textsubscript{25}-C, PN\textsubscript{427}A\textsubscript{10}-C, and PN\textsubscript{429}A\textsubscript{5}-C)

The LCST of these copolymers were measured via UV–visible spectrophotometry by determining the turbidity of corresponding aqueous solutions at various temperatures. The copolymer concentration was 0.8 mg. mL\textsuperscript{-1}, and the heating rate was 2 °C/min. The copolymer solution was stirred and kept at the same temperature for 1 min before each measurement. The turbidimetry curves was drawn by measuring the transmittance of the aqueous polymer solution (max = 440 nm) as a function of temperature, as shown in Fig. S5. Sharp decrease in transmittance pointed to the characteristic temperature of corresponding LCST. Therefore, the LCST of PN\textsubscript{422}A\textsubscript{25}-C, PN\textsubscript{427}A\textsubscript{10}-C, and PN\textsubscript{429}A\textsubscript{5}-C were determined as ca. 14, 26, and 28 °C. It was logical
that decreased hydrophobic block in PNIPAAm-based copolymer led to increase in the LCST.\[^1\]

Apparently, \textbf{PN}_{422}A_{25}-C\) with the LCST (14 °C) lower than room temperature (25 °C) couldn’t fulfill the demand of aqueous asymmetric sulfoxidation, since it would become hydrophobic and precipitate from the aqueous system at reaction temperature (25 °C). For \textbf{PN}_{429}A_{5}-C\), although its LCST (28 °C) fitted for the aqueous asymmetric sulfoxidation, few amount of photo-responsive azobenzene moiety in the copolymer was unfavorable to finely control the aqueous asymmetric sulfoxidation by UV light. With these points in mind, more azobenzene-containing \textbf{PN}_{427}A_{10}-C\) whose LCST (26 °C) was close to room temperature was chose as the suitable catalyst for photo-controlled catalysis of asymmetric sulfoxidation in water at room temperature (25 °C). The selected \textbf{PN}_{427}A_{10}-C\) indeed made the photo-controlled asymmetric catalysis in water come true, and also could be recovered for efficient reuse at mild temperature (slightly higher than room temperature).

**Fig. S5** Plot of changes in solution transmittance (at 440 nm) as a function of temperature for aqueous solutions of \textbf{PN}_{x}A_{y}-C\) (concentration: 0.8 mg mL\(^{-1}\)).

3. Identity of the obtained chiral sulfoxide.

**Methyl phenyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S6 and S7). $^1$H NMR (CDCl$_3$, 500 MHz) δ (ppm): 7.44-7.42 (m, 2 H, ArF), 7.29-7.27 (m, 3 H, ArF), 2.49 (s, 3 H, Me); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm): 43.1 (SCH$_3$), 122.8, 128.6, 130.3, 144.9 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL·min$^{-1}$, injector temperature and detector temperature were 250 °C, column temperature was programmed from 80 to 180 °C with 6 °C·min$^{-1}$, $t_{\text{methyl phenyl sulfoxide}}$ = 6.9 min; ee value was determined by HPLC ($i$-PrOH/n-hexane = 5: 5 (v/v)); flow rate = 1.0 mL·min$^{-1}$; 25 °C; λ = 254 nm; major enantiomer $t_R = 4.4$ min, minor enantiomer $t_S = 5.2$ min (see Fig. S8, S9 and S10).

![Fig. S6 $^1$H NMR of methyl phenyl sulfoxide.](image-url)
Fig. S8 HLPC of methyl phenyl sulfoxide obtained over PN$_{427}$A$_{10}$C after 60 s of UV irradiation (ee value = 99%).
**Ethyl phenyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S11 and S12). $^1$H NMR (CDCl$_3$, 500 MHz) δ (ppm): 7.59-7.53 (m, 2 H, Ar$H$), 7.52-7.47 (m, 3 H, Ar$H$), 2.92-2.72 (m, 2 H, -C$H_2$), 1.19-1.16(m, 3 H, Me); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ (ppm): 5.91 (CH$_3$), 50.24 (SCH$_2$), 124.13, 129.09, 130.88, 143.25 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL min$^{-1}$, the injector temperature and the detector temperature were 250 °C, the column temperature was 180 °C, $t_{ethyl}$ phenyl sulfoxide = 2.5 min; ee value was determined by HPLC (i-PrOH/ n-hexane = 2: 8 (v/ v)); flow rate = 1.0 mL min$^{-1}$; 25 °C; $\lambda$ = 254 nm; major enantiomer $t_R$ = 6.4 min and minor enantiomer $t_S$ =8.2 min (see Fig. S13, S14 and S15).
Fig. 11 $^1$H NMR of ethyl phenyl sulfoxide.

Fig. 12 $^{13}$NMR of ethyl phenyl sulfoxide.
Fig. 13 HPLC of ethyl phenyl sulfoxide obtained over PN_{427}A_{10}^C after 60 s of UV irradiation (ee value = 97%).

Fig. 14 HPLC of ethyl phenyl sulfoxide obtained over dark-adapted PN_{427}A_{10}^C (ee value = 97%).
Methyl p-methoxyphenyl sulfoxide: The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S16 and S17). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ (ppm): 7.60-7.57 (d, 2 H, ArH), 7.03-7.01 (d, 2 H, ArH), 3.84 (s, 3 H, OCH$_3$), 2.69 (s, 3 H, SCH$_3$); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ (ppm): 43.9 (SCH$_3$), 55.5 (OCH$_3$), 114.8, 125.4, 136.6, 162.0 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL·min$^{-1}$, injector temperature and detector temperature were 250 °C, the column temperature was programmed from 80 to 180 °C with 6 °C·min$^{-1}$, $t_{methyl \ p\text{-methoxyphenyl sulfoxide}} = 11.7$ min; ee value was determined by HPLC ($i$PrOH/n-hexane = 4: 6 (v/v)); flow rate = 1.0 mL·min$^{-1}$; 25 °C; $\lambda = 254$ nm; major enantiomer $t_R = 5.5$ min and minor enantiomer $t_S = 6.6$ min (see Fig. S18, S19, and S20).
Fig. S16 $^1$H NMR of methyl $p$-methoxyphenyl sulfoxide.

Fig. S17 $^{13}$C NMR of methyl $p$-methoxyphenyl sulfoxide.
**Fig. S18** HLPC of methyl $p$-methoxyphenyl sulfoxide obtained over PN$_{427}$A$_{10}$-C after 60 s of UV irradiation (ee value = 97%)

**Fig. S19** HLPC of methyl $p$-methoxyphenyl sulfoxide obtained over dark-adapted PN$_{427}$A$_{10}$-C (ee value = 94%).

**Fig. S20** HLPC of methyl $p$-methoxyphenyl sulfoxide obtained over neat complex (ee value = 70%)
**Methyl o-methoxyphenyl sulfoxide:** The product has been identified by $^1$H and $^{13}$C NMR spectra (see Fig. S21 and S22). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ (ppm): 7.82-7.80 (m, 1 H, ArH), 7.46-7.42 (m, 1 H, ArH), 7.19-7.16 (m, 1 H, ArH), 6.92-6.90 (m, 1 H, ArH), 3.87 (s, 3 H, OCH$_3$), 2.76 (s, 3 H, SCH$_3$); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ (ppm): 41.16 (SCH$_3$), 55.64 (OCH$_3$), 110.53, 121.65, 124.58, 131.89, 133.07, 154.76 (ArC). Chemoselectivity was determined by GC, nitrogen was used as the carrier gas with a flow of 30 mL min$^{-1}$, injector temperature and detector temperature were 250 °C, the column temperature was 180 °C, $t_{\text{methyl o-methoxyphenyl sulfoxide}}$ = 9.8 min; ee value was determined by HPLC ($i$-PrOH/n-hexane = 5: 5 (v/v)); flow rate = 1.0 mL min$^{-1}$; 25 °C; $\lambda$ = 254 nm; major enantiomer $t_R$ = 4.8 min and minor enantiomer $t_S$ = 5.7 min (see Fig. S23, S24, and S25).

![Fig. S21 1 H NMR of methyl o-methoxyphenyl sulfoxide.](image-url)
Fig. S22 $^{13}$C NMR of methyl $o$-methoxyphenyl sulfoxide.

Fig. S23 HLPC of methyl $o$-methoxyphenyl sulfoxide obtained over $\text{PN}_{427}A_{10^{-6}}\text{C}$ after 60 s of UV irradiation (ee value > 99%).

Fig. S24 HLPC of methyl $o$-methoxyphenyl sulfoxide obtained over dark-adapted $\text{PN}_{427}A_{10^{-6}}\text{C}$ (ee value > 99%).
Fig. S25 HLPC of methyl o-methoxyphenyl sulfoxide obtained over neat complex (ee value = 76%).