

Electronic Supplementary Information (ESI)

Fluorescent thermometer based on quinolinemalononitrile copolymer with aggregation-induced emission characteristics

Jinfeng Yang,^{a,b} Kaizhi Gu,^a Chuanxing Shi,^a Meng Li,^c Ping Zhao,^{*a} and Wei-Hong Zhu^{*a}

^a Shanghai Key Laboratory of Functional Materials Chemistry, Key Laboratory for Advanced Materials and Institute of Fine Chemicals, Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, East China University of Science & Technology, Shanghai 200237, China.

^b School of Chemistry and Chemical Engineering, Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, North 4th Road, Shihezi, Xinjiang 832003, China..

^c Department of Environmental Science and Engineering, North China Electric Power University, Baoding 071003, China.

E-mail: whzhu@ecust.edu.cn, pzhao@ecust.edu.cn

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1. Experimental section

Materials and instruments

THF was distilled under argon atmosphere immediately prior to use. All other reagents were purchased commercially available in analytical grade without further purification. Nuclear magnetic resonance hydrogen (^1H NMR) and nuclear magnetic resonance carbon (^{13}C NMR) spectra in $\text{DMSO-}d_6$ or CDCl_3 were measured on a Bruker Avance III 400 MHz spectrometer with tetramethyl silane (TMS) as an internal standard. The high resolution mass spectra were recorded on a Waters LCT Premier XE spectrometer. Ultraviolet-visible (UV-Vis) spectra were obtained by using a Varian Cary 500 spectrophotometer (1 cm quartz cell). Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell). The solid fluorescence quantum yield was measured by the Horiba Fluoromax 4 integral sphere. The scanning electron microscope (SEM) was performed by a JEOL JSM-6360 instrument. Crystal data were collected on X-ray diffractometer (Rigaku RAXIS RAPID IP), using molybdenum target ($\lambda = 1.54178 \text{ \AA}$) at 133 K temperature.

Synthesis of compound 2

Compound 1 (117.6 mg, 0.5 mmol), 4-(piperazin-1-yl)benzaldehyde (167.3 mg, 0.88 mmol), piperidine (0.3 mL), and acetonitrile (30 mL) were successively added to a bottom flask under nitrogen atmosphere. The reaction mixture was refluxed for 8 h. After being filtered, the crude product was isolated by short chromatography on a silica gel column using a dichloromethane/petroleum ether (2/1, v/v) mixture as an eluent. Compound 1 was obtained in 39% yield. ^1H NMR (400 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 1.41$ (t, $J = 7.2$ Hz, 3H, $-\text{CH}_2\text{CH}_3$), 3.13 (t, $J = 4.8$ Hz, 4H, piperazine-H), 3.43 (t, $J = 4.8$ Hz, 4H, piperazine-H), 4.38 (q, $J = 7.2$ Hz, 2H, $-\text{CH}_2\text{CH}_3$), 7.02 (br, 2H, phenyl-H), 7.05 (s, 1H, quinoline-H), 7.33 (d, $J = 16.0$ Hz, 1H, alkene-H), 7.38 (d, $J = 16.0$ Hz, 1H, alkene-H), 7.61 (t, $J = 7.6$ Hz, 1H, phenyl-H), 7.72 (d, $J = 8.8$ Hz, 2H, phenyl-H), 7.92 (t, $J = 8.8$ Hz, 1H, phenyl-H), 8.08 (d, $J = 8.8$ Hz, 1H, phenyl-H), 8.92 (d, $J_1 = 8.4$ Hz, 1H, phenyl-H). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$, ppm): $\delta = 13.64, 43.14, 43.68, 45.44, 46.13, 106.38, 114.92, 116.57, 118.08, 120.06, 124.87, 125.08, 125.88, 129.57, 133.60, 137.85, 139.87, 149.65, 151.34, 151.98$. Mass spectrometry (ESI positive ion mode for $[\text{M} + \text{H}]^+$): Calcd. for $\text{C}_{26}\text{H}_{26}\text{N}_5$: 408.2188; found: 408.2188.

Synthesis of compound **EM**

Compound **2** (0.82 g, 2.0 mmol) was added in 20 mL dichloromethane of containing triethylamine (0.5 mL). When the mixture was completely dissolved, gradually added methyl-propionyl chloride (1.03 g, 9.85 mmol). The reactants were stirred for 24 h at the room temperature. After being filtered, the residue was purified by flash chromatography (dichloromethane/methanol = 200:1, v/v). Compound **EM** was obtained as orange solid in 60% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 1.57 (t, J = 7.2 Hz, 3H, -CH₂CH₃), 2.00 (s, 3H, -CH₃), 3.31 (br, 4H, piperazine-H), 3.78 (br, 4H, piperazine-H), 4.38 (q, J = 7.2 Hz, 2H, -CH₂CH₃), 5.10 (s, 1H, -C=CH₂), 5.27 (s, 1H, -C=CH₂), 6.89 (d, J = 16.0 Hz, 1H, alkene-H), 6.94 (d, J = 8.8 Hz, 2H, phenyl-H), 7.16 (s, 1H, quinoline-H), 7.29 (d, J = 16.0 Hz, 1H, alkene-H), 7.45 (t, J = 8.0 Hz, 1H, phenyl-H), 7.49 (d, J = 8.8 Hz, 2H, phenyl-H), 7.61 (d, J = 8.8 Hz, 1H, phenyl-H), 7.75 (t \times d, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1H, phenyl-H), 9.15 (d \times d, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1H, phenyl-H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 13.98, 20.56, 29.71, 43.87, 50.71, 107.46, 115.71, 115.86, 115.99, 116.02, 119.42, 120.47, 121.60, 124.57, 126.31, 127.03, 129.18, 133.13, 138.14, 140.09, 140.12, 148.34, 151.96, 153.40, 171.26. Mass spectrometry (ESI positive ion mode for [M + H]⁺): Calcd. for C₃₀H₃₀N₅O: 476.2450; found: 476.2451.

Synthesis of compound **P(NIPAM-co-EM)**

Compound **EM** (23.8 mg, 0.05 mmol), *N*-isopropyl acrylamide (0.56 g, 5.8 mmol), α , α' -azoisobutyronitrile (AIBN, 5.25 mg, 0.04 mmol) and anhydrous tetrahydrofuran (10 mL) were successively added to a Schlenk flask, and keeping the reaction temperature at -60 °C under nitrogen atmosphere. Then, the reaction mixture was refluxed at 70 °C for 48 h. After being cooled, the crude product was recrystallized from ether. **P(NIPAM-co-EM)** (0.20 g) was obtained as orange powder. ¹H NMR (400 MHz, CDCl₃, ppm): δ = 0.90-1.40 (m, -CH(CH₃)₂, -CH₃), 2.14 (br, -CCH₂), 3.10 (s, -COCH), 3.60-3.90 (m, piperazine-H), 3.99 (s, NHCH), 6.10-7.00 (br, NH), 7.10-7.80 (br, aromatic H), 9.15 (d, phenyl-H). GPC (THF): M_n 6956, M_w 11178, M_w/M_n 1.61.

2. ^1H NMR spectrum of EM

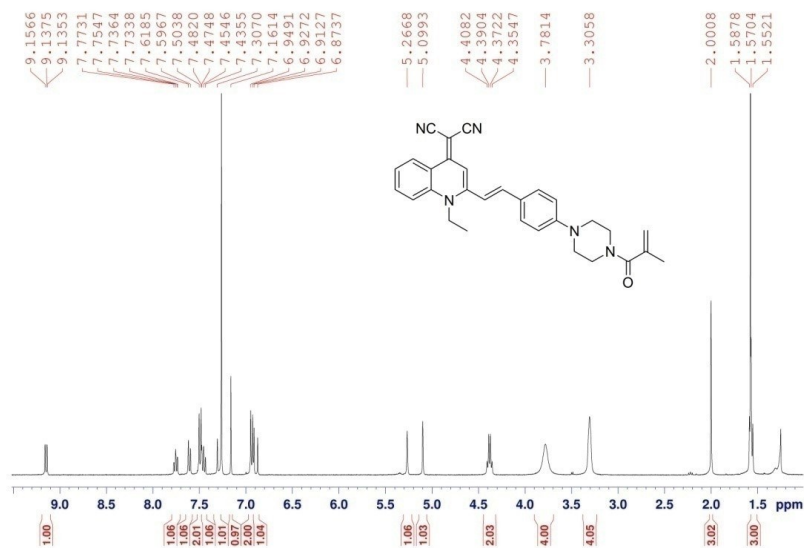


Fig. S1 ^1H NMR spectrum of EM in CDCl_3 .

3. GPC characterization of copolymer

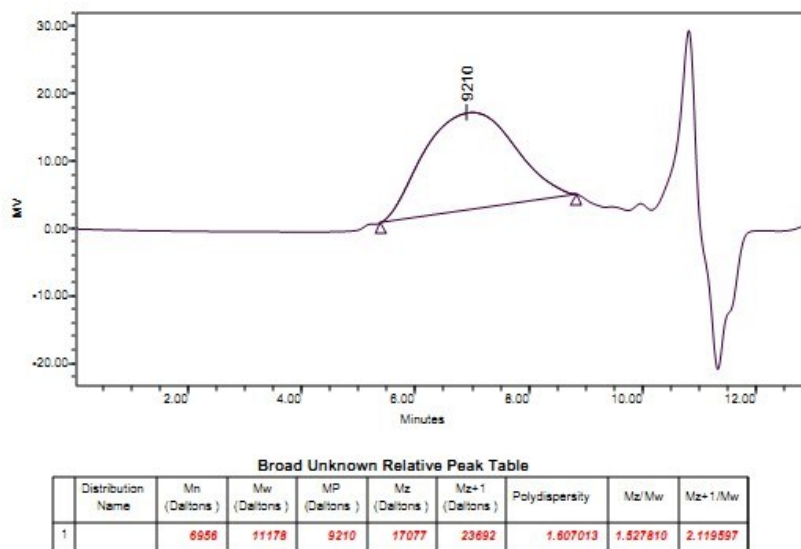


Fig. S2 GPC characterization of copolymer $\text{P}(\text{NIPAM-co-EPPM})$ in THF.

4. Single crystal data of EM

Table S1 Single crystal data of EM

Compound	EM
CCDC	1902267
Formula	C ₃₀ H ₂₉ N ₅ O
Formula weight	475.58
Temperature / K	133
Wavelength / Å	1.54178
Crystal system	Monoclinic
Space group	P 21/c
a / Å	22.0567(18)
b / Å	7.7405(6)
c / Å	15.5138(14)
α / deg	90
β / deg	102.762(7)
γ / deg	90
Volume	2583.2(4)
Z	4
Density / g cm ⁻³	1.223
Mu (mm ⁻¹)	0.602
F(000)	1008.0
h,k,l / max	25,9,18
Nref	4383
Tmin,Tmax	0.889,0.988
Data completeness	0.963
Theta (max)	66.490
R(reflections)	0.0772(2849)
S	1.022
Npar	325

5. Concentration effect on photophysical property

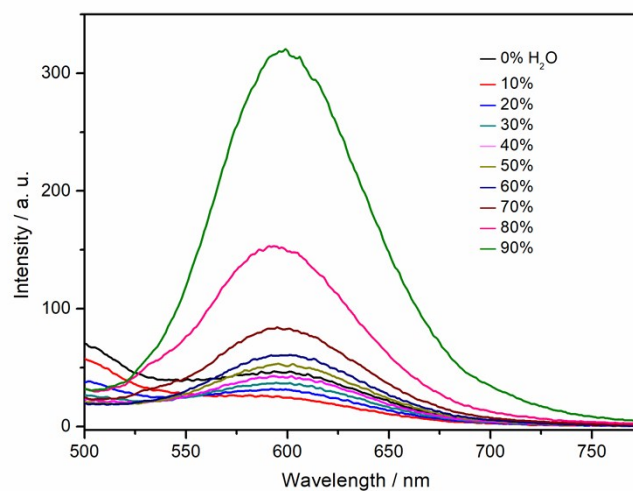


Fig. S3 Emission spectrum of copolymer **P(NIPAM-co-EPPM)** ($38 \mu\text{M}$) in THF/H₂O mixtures with different water fractions, $\lambda_{\text{ex}} = 430 \text{ nm}$.

6. Emission spectrum of copolymer

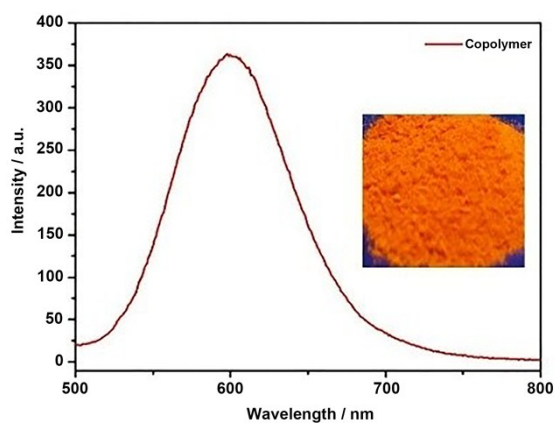


Fig. S4 Emission spectrum of copolymer **P(NIPAM-co-EPPM)** at solid state, $\lambda_{\text{ex}} = 450 \text{ nm}$.

7. Turbidity study upon cooling

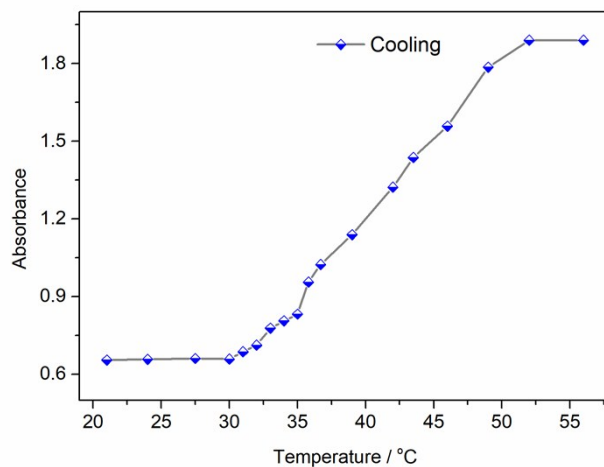


Fig. S5 Temperature-dependent absorption at 430 nm of P(NIPAM-co-EM) (14 μ M) in aqueous solution upon cooling.

8. Characterization of intermediates

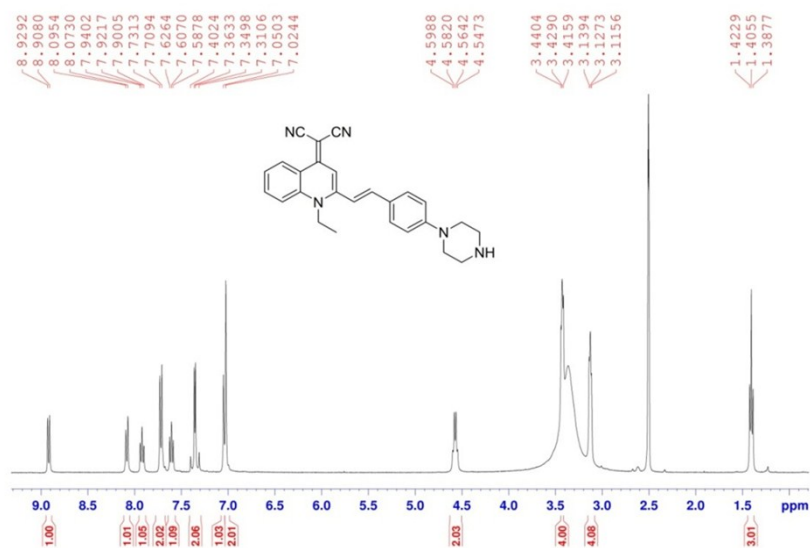


Fig. S6 ¹H NMR spectrum of intermediate 2 in DMSO-d₆.

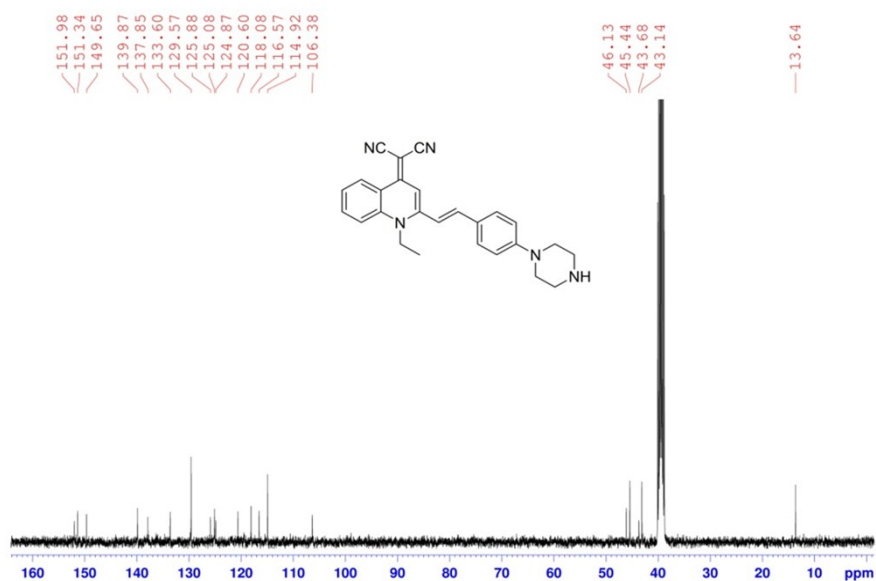


Fig. S7 ¹³C NMR spectrum of intermediate 2 in DMSO-*d*₆.

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

18 formula(e) evaluated with 3 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-49 H: 0-34 N: 0-5

WH-ZHU

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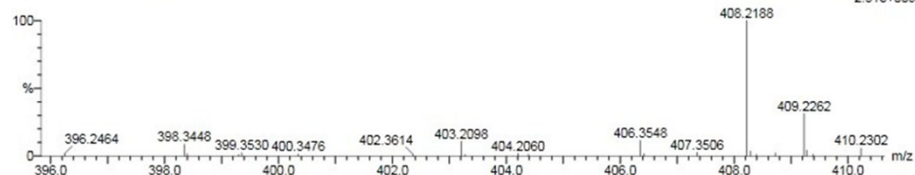
18-Apr-2012

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1: TOF MS ES+

2.31e+003

ZWH-SCX-100 47 (1.530) Cm (45:47)



Mass	Calc. Mass	mDa	PFM	DBE	i-FIT	i-FIT (Norm)	Formula
408.2188	408.2188	0.0	0.0	16.5	49.6	0.0	C26 H26 N5

Fig. S8 HRMS spectrum of intermediate 2.

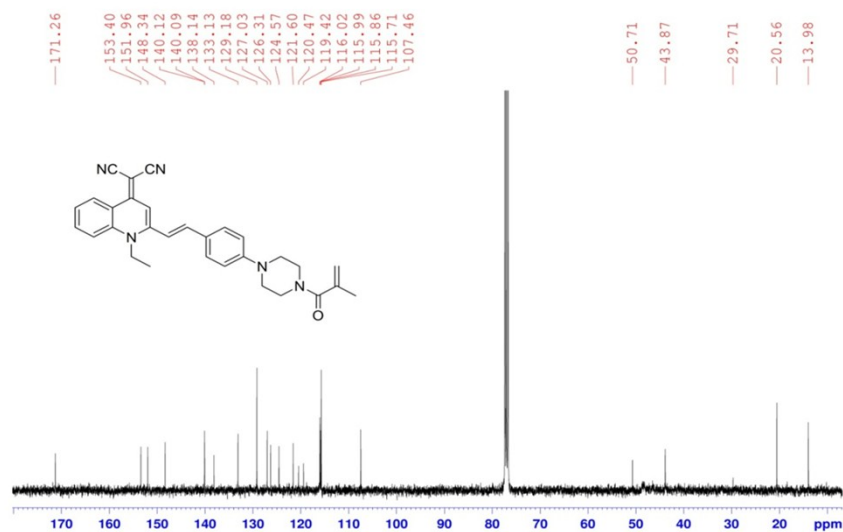


Fig. S9 ^{13}C NMR spectrum of EM in CDCl_3 .

Single Mass Analysis

Tolerance = 50.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

99 formula(e) evaluated with 9 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-62 H: 0-65 N: 0-5 O: 0-2

WH-ZHU

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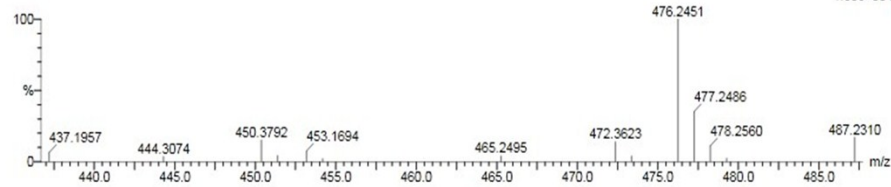
26-Apr-2012

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1.60e+004

ZW-SCX-P2 26 (0.889) Cm (8:27)



Minimum: -1.5
Maximum: 50.0 50.0 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
476.2451	476.2450	0.1	0.2	18.5	8.1	0.0	C30 H30 N5 O

Fig. S10 HRMS spectrum of EM.