## **Electronic Supplementary Information**

# Hyperbranched Polyester Nanorods with Pyrrolo[2,1a]isoquinoline End-Groups for Fluorescent Recognition of Fe<sup>3+</sup>

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#### 1. General information.

2,2-Bis(hydroxymethyl)propionic acid (DMPA) was purchased from Sigma-Aldrich Co. Ltd. and used without purification. Trimethylol propane (TMP) (>99% pure), p-toluene sulfonic acid (P-TSA), dicyclohexylcarbodiimide (DCC) were obtained from Energy Chemical Co. Ltd., China. DMSO (A. R. grade, Shanghai Chemical Reagent Co.) was refluxed with CaH<sub>2</sub> and distilled prior to use. All other solvents were AR grade.

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in DMSO- $d_6$  on a Bruker Avance DMX 300 spectrometers or a Bruker Avance 400 spectrometers at ambient temperature. FTIR spectra were recorded on a Nicolet Nexus 670 spectrometers using KBr pellets. The fluorescent spectra were recorded on Varian Cary Eclipse spectrometers. AFM images were recorded on a Agilent PICOPLUS (American). XRD spectra were recorded on Bruker D8 (Germany). The nanorods were examined with transmission electron microscopy (TEM, JEOL JEM 2010F, Japan).

Synthesis of 1-Cyano-Pyrrolo[2,1-a]isoquinoline-3-Carboxylic Acid (CICA)



Scheme S1. Synthetic route of CICA

*Preparation of compound B.* To a solution of isoquinoline (compound A, 6.46 g, 50 mmol) in ethyl acetate (30 mL), bromoacetonitrile (6.05 g, 50 mmol) was added. The mixture was stirred at room temperature for 24 hours. The resulting precipitate was collected by filtration, washed with ethyl acetate ( $3 \times 10$  mL), and dried under vacuum to give the compound **B** as a white solid (yield: 80%).

*Preparation of compound C.* Compound **B** (2.49 g, 10 mmol) was dissolved in DMF (30 mL), then triethylamine (10 mL, TEA), methyl acrylate (4.3 g, 50 mmol) and  $CrO_3$  (4.4 g, 44 mmol) were added stepwise. The reaction mixture was heated at 90 °C for 5 hours. The resulting solution was cooled, and then poured into a 5% HCl aqueous solution (100 mL) with stirring. The mixture was kept standing for an hour. The yellow precipitate was collected by filtration, and then purified

by column chromatography (silica gel, eluent: ethyl acetate/petroleum ether = 1:4) to give compound C as a yellow solid (yield: 85%).

*Preparation of CICA.* NaOH (10% in water, 20 mL) was added to a solution of compound C (1.25 g, 5 mmol) in 40 mL of ethanol. The mixture was heated at 80 °C for 2 hours, then cooled down to room temperature. The resulting solution was treated with 5% HCl solution to adjust pH to 2. A precipitate was formed and collected by filtration. The crude product was recrystallized in ethanol, and dried under vacuum to give CICA as a light blue solid (yield: 80%).

#### Synthesis of HBPE

All the reactions were carried out under nitrogen atmosphere. The second generation hyperbranched polyester with trimethylol propane as cores was prepared according to published procedures.<sup>S1</sup> Accordingly, as shown in Scheme 2, 2,2-Bis(hydroxymethyl)propionic acid (DMPA) and Trimethylol propane (TMP) were mixed in a ratio of 9:1, then heated at 140 °C in presence of catalytic amount of *p*-toluenesulfonic acid (0.3 mol%) as the catalyst for 2 hours. The resulting solution was distilled under vacuum for 2 hours, then the crude product was dissolved in acetone and precipitated by *n*-hexane, the precipitate was dried under vacuum, to give desired product with 12 terminal hydroxyl groups and a molecule weight of 1179 g/mol (as describe in the literature S1).

#### Synthesis of HBPE-CICA

To a solution of HBPE (0.12 g, 0.1 mmol) and CICA (0.31 g, 1.3 mmol) in DMSO (60 mL), N,N'-dicyclohexyl carbodimide (DCC, 0.29 g, 1.39 mmol)) was added. The mixture was heated at 85 °C under nitrogen for 20 hours, which was monitored with TLC. The resulting solution was evaporated, and the residue was poured into ethyl acetate (60 mL), then filtered. The filtrate was concentrated and subjected to column chromatography (silica gel, eluent: ethyl acetate/petroleum ether = 3/1). Two light blue products of HBPE-CICA<sub>6</sub> and HBPE-CICA<sub>2</sub> were obtained with yields of 30% and 50%, respectively.



Scheme S2. Synthetic route of HBPE-CICA<sub>6</sub> and HBPE-CICA<sub>2</sub>

#### Characterization of CICA, HBPE, HBPE-CICA2 and HBPE-CICA6 nanorods

The fourier transform infrared spectroscopy (FTIR) spectra were obtained with KBr pellets on a Bruker Tensor 27. The proton nuclear magnetic resonance (<sup>1</sup>H NMR, <sup>13</sup>C NMR) spectra were obtained by operating on a Bruker Advance DMX 300. <sup>1</sup>H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometers (Bruker, Germany) at room temperature. The measurements were carried out in DMSO solution at ambient temperature. The chemical shifts were referenced to a tetramethylsilane (TMS) standard. The nanorods were examined with transmission electron microscopy (TEM, JEOL JEM 2010F, Japan). For TEM measurement, in a typical experiment, one drop of DMSO dispersion of HBPE-CICA nanorods was introduced onto a copper grid with a microgrid carbon film. The droplet was allowed to dry under reduced pressure and then observed under TEM operating at an acceleration voltage of 100 kV. The

electrospray ionization mass spectrometry (ESI-MS) was obtain from mass spectrometer (LCQ/M/Z = 50-1850, Finnigan, U.S.) and micromass GCT.

CICA: IR vmax/cm<sup>-1</sup>: 3000, 2217, 1670, 1610, 1550, 1499, 1455, 620. <sup>1</sup>H NMR(DMSO-d<sub>6</sub>, 300

MHz),  $\delta$ (ppm): 9.27(d, 1H, J = 9 Hz), 8.73(d, 1H, J = 9 Hz), 7.96 (d, 1H, J = 9 Hz), 7.89(s, 1H), 7.76(m, 2H), 7.47(d, 1H, J = 9 Hz). ESI-MS (m/z): 235.05 (calculated, 236.2). HBPE: IR vmax/cm<sup>-1</sup>: 3426, 2946, 2890, 1635, 1523, 1431, 1342, 1234, 850, 743. <sup>1</sup>H NMR(DMSO-*d*<sub>6</sub>, 400 MHz), δ(ppm): 0.81(m, 3H, CH<sub>3</sub>CH<sub>2</sub>-), 1.08(m, 27H, CH<sub>3</sub>-CR<sub>3</sub>), 1.33(m, 2H, CH<sub>3</sub>CH<sub>2</sub>-), 3.42(m, 24H, CH<sub>2</sub>OH), 4.10 (m, 18H, R<sub>3</sub>C-CH<sub>2</sub>-OOC), 4.62 (6H, CH<sub>2</sub>OH), 4.94 (6H, CH<sub>2</sub>OH). ESI-MS (m/z), 1178.7(1201.67-Na<sup>+</sup>), calculated, 1179.2. HBPE-CICA<sub>6</sub>: IR vmax/cm<sup>-1</sup>: 3550, 3414, 3236, 2928, 2855, 2217, 1695, 1638, 1617, 1550, 1499, 1455, 1350, 1125, 621. <sup>1</sup>H NMR(DMSO-d<sub>6</sub>, 300 MHz), 1.14(m, 3H, CH<sub>3</sub>CH<sub>2</sub>-), 1.31 (m, 27H, CH<sub>3</sub>-CR<sub>3</sub>), 1.75 (m, 2H, CH<sub>3</sub>CH<sub>2</sub>-), 3.46 (m, 24H, CH<sub>2</sub>OH), 3.79 (m, 18H, R<sub>3</sub>C -CH<sub>2</sub>-OOC), 7.40-9.45(42H, Ar). <sup>13</sup>C NMR(75 MHz, DMSO-d6), 159.2(R<sub>3</sub>C-COO-CH<sub>2</sub>, Ar-COOCH<sub>2</sub>-), 127.7, 127.1, 128.9, 128.2, 125.3, 122.6, 114.8(Ar), 119.7(-CN), 82.9(R<sub>3</sub>C-CH<sub>2</sub>-OOC), 48.5(R<sub>3</sub>C-CH<sub>2</sub>-OH), 40.5(CR<sub>3</sub>-COO-), 32.7(CR<sub>3</sub>-CH<sub>3</sub>), 25.8(CR<sub>3</sub>-CH<sub>3</sub>). HBPE-CICA<sub>2</sub>: IR vmax/cm<sup>-1</sup>: 3550, 3414, 3236, 2928, 2855, 2217, 1695, 1638, 1617, 1550, 1499, 1455, 1350, 1158, 619. <sup>1</sup>H NMR(DMSO-d6, 300 MHz), 0.86(m, 3H, CH<sub>3</sub>CH<sub>2</sub>-), 1.12(m, 27H, CH3-CR3), 1.75(m, 2H, CH3CH2-), 3.42(m, 24H, CH2OH), 4.20 (m, 18H, R3C -CH2-OOC), 7.33-8.73 (m, 14H, Ar). <sup>13</sup>C NMR(DMSO-d6, 75 MHz), 159.2(R<sub>3</sub>C-COO-CH<sub>2</sub>, Ar-COOCH<sub>2</sub>-), 127.7, 127.1, 128.9, 128.2, 125.3, 122.6, 114.8(Ar), 119.7(-CN), 82.9(R<sub>3</sub>C-CH<sub>2</sub>-OOC), 48.5(R<sub>3</sub>C-*C*H<sub>2</sub>-OH), 40.5(*C*R<sub>3</sub>-COO-), 32.7(*C*R<sub>3</sub>-*C*H<sub>3</sub>), 25.8(*C*R<sub>3</sub>-*C*H<sub>3</sub>). ESI-MS(m/z):1614.15

(calculated, 1614.10).

S5



Fig. S1. The ESI-MS spectra of the HBPE-CICA<sub>2</sub>

Fig. S1 showed the real molecular weight of HBPE-CICA<sub>2</sub> is 1614.15, which is consistent with the theory molecular weight (1614.10). The main peak of 1614.15 and the minor peak 1412.15 possess a distance of 202, which corresponds to the part of the unit of CICA, as the green section as the illustration. The minor peaks 1412.15 and 1175.95 possess a distance of 236, which corresponds to the unit of CICA, as the black section as the illustration. The 1175.95 represent that HBPE (the real molecular weight, 1178.2) lose two H atoms, this further proved that the calculation of the grafting rate of HBPE-CICA<sub>2</sub> is accurate.



Fig. S3. The ESI-MS spectra of the HBPE

108 67

.67

sc

Relative Abundance

27 3.33

6 0 200



Chemical shift/ppm



Fig. S4. <sup>1</sup>H NMR spectra of HBPE in DMSO-d<sub>6</sub>

Fig. S5. <sup>13</sup>C NMR spectra of HBPE-CICA<sub>6</sub> (A) and HBPE-CICA<sub>2</sub> (B) in DMSO- $d_6$ 



**Fig. S6.** TEM images of HBPE-CICA<sub>2</sub> nanorods in ethyl acetate solution (0.010 mg/mL) stored at room temperature for 30 days

#### The fluorescent recognition of CICA and HBPE-CICA<sub>6</sub> nanorods

The fluorescent spectra were measured on a Varian Cary Edlipse spectrophotometer at slit width of 5nm/5nm. For all the samples, excitation and emission wavelength were 260 nm and 500 nm, respectively. The effect of metal cations on the fluorescence intensity was examined by addition of stock solution of the metal cations in water (less than 0.060 mL) to CICA or HBPE – CICA<sub>6</sub> sample in DMSO (3 mL).

Here, the influences of 10 metal cations (Fe<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup> and  $Mn^{2+}$ ) on the fluorescence intensity of the CICA have been investigated by fluorescent spectroscopy in DMSO solution with regard to its potential application as a sensor. The DMSO solution of the CICA is almost colorless with the maximum absorption at 260 nm and the strongest emission at 380 nm.



**Fig. S7.** Fluorescence decreasement factors (FD) of the CICA in the presence of different metal cations ( $c = 6.6 \times 10^{-5}$  M) in DMSO solution. The concentration of CICA in DMSO is  $c = 5.0 \times 10^{-5}$  M,  $\lambda ex = 260$  nm and  $\lambda em = 380$  nm.

The fluorescent response of CICA ( $5.0 \times 10^{-5}$  M) in the same DMSO solution to other metal cations of interest is investigated, and most of the tested metal cations such as Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup> and Mn<sup>2+</sup> ( $6.6 \times 10^{-5}$  M) do not alter the emission evidently, while Fe<sup>3+</sup> decreases the emission. The influences of metal cations on the fluorescence intensity of the CICA have been evaluated by a fluorescence decreasement (FD = I/I<sub>0</sub>) which is calculated by the ratio of the reduced fluorescence intensity in the presence of metal cations (I) and the fluorescence intensity without metal cations (I<sub>0</sub>). Fig.S7 shows that the calculated FD factors for Fe<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup>and Mn<sup>2+</sup> at the concentration of  $6.6 \times 10^{-5}$  M. As shown in Fig. S7, only the addition of Fe<sup>3+</sup> resulted in a prominent FD effect (FD = 0.71) of fluorescence, while other metal ions have a negligible effect (FD = 0.95 - 1.10).

The change of the fluorescent intensity of the CICA upon gradual titration with  $Fe^{3+}$  is plotted in Fig. S8. The addition of  $Fe^{3+}$  causes a strong decrease in the fluorescence intensity and the greatest effect on FD has been observed at  $\lambda_{em}$ = 380 nm, which implied that complexation existed between CICA and Fe<sup>3+</sup>.



Fig. S8. Fluorescence spectra of the CICA in DMSO solution (c =  $5.0 \times 10^{-5}$  M,  $\lambda ex = 260$  nm ) in the presence of Fe<sup>3+</sup> at a concentration of  $0 \sim 8.6 \times 10^{-4}$  M.

Possible interference from other cations in the spectrofluorometric response to  $Fe^{3+}$  was tested. A series of CICA solutions, each of which simultaneously contains the same concentration of  $Fe^{3+}$  and another tested cation type were used for testing. Fig.S9 shows the changes in the intensity of the emission peak (380 nm). The  $Fe^{3+}$ -induced fluorescent responses of the solution is not significantly interfered by the commonly coexistent metal ions, indicating the stable complexation between CICA and  $Fe^{3+}$ . As a result, the sensing measurement is appropriate even in the presence of high concentrations of competitive metal cations.



**Fig. S9.** Fluorescence responses of CICA ( $5.0 \times 10^{-5}$  M) in DMSO to  $6.6 \times 10^{-5}$  M Fe<sup>3+</sup> and  $6.6 \times 10^{-5}$  M different interference metal cations,  $\lambda ex = 260$  nm and  $\lambda em = 380$  nm.

The influences of different metal cations on the fluorescence intensity of the new HBPE-CICA<sub>6</sub> nanorods also have been investigated by fluorescent spectroscopy in DMSO solution. The DMSO solution of the HBPE-CICA<sub>6</sub> nanorods is almost colorless and has absorption maximum at  $\lambda_{ex}$ = 260 nm. The maximum emission wavelength of fluorescence is at 380 nm.



Fig. S10. Fluorescence decreasement factors (FD) of the HBPE-CICA<sub>6</sub> nanorods in the presence

of different metal cations (c =  $6.6 \times 10^{-5}$  M) in DMSO solution. The concentration of HBPE-CICA<sub>6</sub> in DMSO is c =  $5.0 \times 10^{-5}$  M,  $\lambda ex = 260$  nm and  $\lambda em = 380$  nm.

The influences of metal cations on the fluorescence intensity of the HBPE-CICA<sub>6</sub> nanorods also have been evaluated by a fluorescence decreasement (FD = I/I<sub>0</sub>). Fig. S10 shows the calculated FD factors for Fe<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup>and Mn<sup>2+</sup> at the concentration of  $6.6 \times 10^{-5}$  M. It is shown that Fe<sup>3+</sup> has obvious effect (FD = 0.72), while other metal ions have a negligible effect (FD = 0.98-1.10).



**Fig. S11.** Fluorescence decreasement factors (FD) of the HBPE-CICA<sub>2</sub> nanorods in the presence of different metal cations ( $c = 6.6 \times 10^{-5}$  M) in DMSO solution. The concentration of HBPE-CICA<sub>2</sub> in DMSO is  $c = 5.0 \times 10^{-5}$  M,  $\lambda ex = 260$  nm and  $\lambda em = 380$  nm.

The influences of metal cations on the fluorescence intensity of the HBPE-CICA<sub>2</sub> nanorods also have been evaluated by a fluorescence decreasement (FD = I/I<sub>0</sub>). Fig. S11 shows the calculated FD factors for Fe<sup>3+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Ag<sup>+</sup>, Al<sup>3+</sup>, Cd<sup>2+</sup>and Mn<sup>2+</sup> at the concentration of  $6.6 \times 10^{-5}$  M. It is shown that Fe<sup>3+</sup> has obvious effect (FD = 0.60), while other metal ions have a negligible effect (FD = 0.98-1.10).

#### References:

S1. E. Malmstrtjm, M. Johansson and A. Hult, Macromolecules, 1995, 28, 1698-1703.