Electronic Supplementary Material (ESI) for Polymer Chemistry

Poly(γ-benzyl-L-glutamate) decorated with cyanoferrate complex: synthesis, characterization and electrochemical properties

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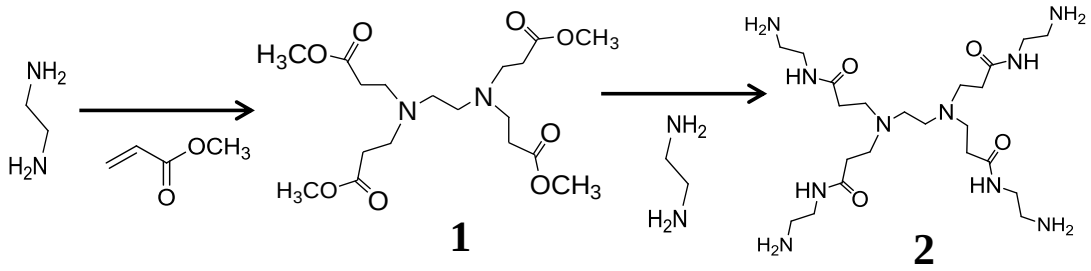
Materials. Ethanediamine, methyl acrylate, hydrobromic acid, L-glutamic acid, benzyl alcohol, pyridine, triphosgene, $NH_4Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$ and 4-(aminomethyl)pyridine were purchased from Sigma-Aldrich (China) and used without further purification unless otherwise indicated.

Synthesis.

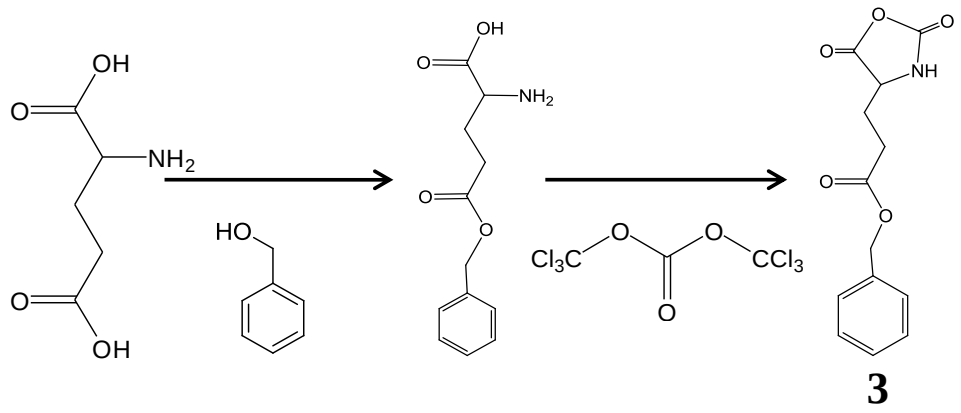


Scheme S1 Synthetic route of amidoamine initator **2**.

Synthesis of amidoamine initiator (2): The synthesis protocol for amidoamine initiator was adapted from previous literature procedures.[1,2] A typical run was shown as follows. A methanol solution (10 mL) of ethylenediamine (0.6 g, 10 mmol) was added dropwise into a methyl acrylate (5.16 g, 60 mmol) in methanol (20 mL) at 0 °C. The resulting reaction mixture was allowed to warm to room temperature and stirred for 2 days under N_2. Then the volatiles were removed under reduced pressure using a rotary evaporator and then in vacuum at 40 °C to give 3.8 g product (**1**) as slightly yellow oil (yield: 94%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.42 (m, 12 H, NC*H*$_2$), 2.72 (m, 8H, C*H*$_2$COOCH$_3$), 3.65 (m, 12H, COOC*H*$_3$). The ^{1}H NMR spectrum agreed with the literature data.[1,2]

A methanol solution (3 mL) of 1 (0.808 g, **2** mmol) was added dropwise into a round-bottomed flask containing ethylenediamine (1.202 g, 20mmol) and anhydrous methanol (7 mL) at 0 °C using an ice/water bath. The reaction mixture was allowed to warm to room temperature and stirred for 7 days under N_2 until complete disappearance of terminal methyl ester groups of **2**, monitored by ^{1}H NMR. Then the volatiles were removed using a rotary evaporator to get crude product. To the crude product was added 20 mL anhydrous methanol and then removed the solvent using a rotary evaporator. Repeat this cycle three times to remove un-reacted ethylenediamine, and finally residual volatiles were removed in vacuum at 40 °C overnight to give 0.986 g product (**2**) as viscous slightly yellow oil (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 2.34–2.44 (m, 12H, COC*H*$_2$ and NC*H*$_2$C*H*$_2$N), 2.64 (m, 8H, C*H*$_2$NH$_2$), 2.82 (m, 8H, NC*H*$_2$CH$_2$CO), 3.30 (m, 8H, CONHC*H*$_2$), 7.95 (br, 4H, CON*H*). The signal at 3.65

ppm derived from OCH_3 is neglectable. The ^{1}H NMR spectrum agreed with the literature data.[1,2]



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Scheme S2 Synthetic route of γ-Benzyl-L-glutamate carboxyanhydrides (BLG-NCA, **3**).

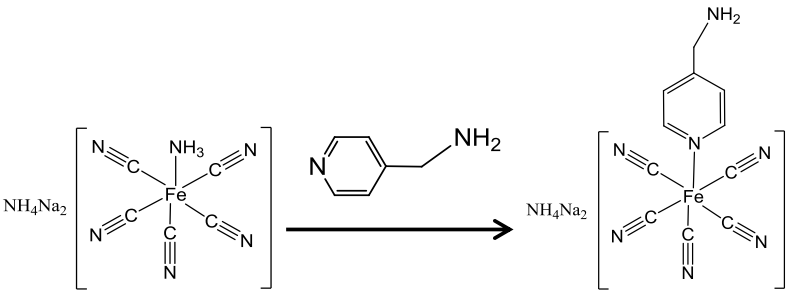
Synthesis of γ-Benzyl-L-glutamate carboxyanhydrides (BLG-NCA) (3): The preparation for BLG-NCA was adapted from literature procedures. [3-5] A typical run was shown as follows. 60 mL of 48% hydrobromic acid and 33 g L-glutamic acid were added to 220 mL benzyl alcohol. This mixture was heated at 70 °C with violently stirring until all glutamic acid was dissolved (ca. 1.5 hours). The reaction mixture was cooled to 30 – 40 °C, and then added to a solution of 33 mL pyridine in 220 mL 95% ethanol under stirring. Precipitation occurred upon cooling to 20 °C and the precipitation was allowed to continue at 3 °C for 12 h. The precipitate was then collected by filtration, washed with ethanol, then with ethyl ether and air-dried. The product was re-crystallized from 500 mL of 5% ethanol aqueous solution, followed by

adding sufficient sodium bicarbonate to keep the pH at 7. After filtration, the solution was cooled as rapidly as possible to 3 °C, and left for 12 h. The precipitate was collected by filtration, washed with water and adjusted to pH 7 with sodium bicarbonate, washed with distilled water, slurried with ethanol, filtered, washed with ethyl ether and air-dried, to yield 12.8 g white plates of γ-benzyl-L-glutamate (yield: 25.2%). ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 2.41 (m, 2H, $COCH_2CH_2$), 2.84 (t, 2H, $COCH_2CH_2$), 4.37 (t, 1H, $COCHNH_2$), 5.18 (s, 2H, $COOCH_2Ph$), 7.30–7.39 (m, 5H, $COOCH_2Ph$).

γ-Benzyl-L-glutamate (10 g) was suspended in 150 mL anhydrous THF and then triphosgene (4.5 g) was added under nitrogen. The mixture was stirred at 50 °C under N_2 until it turned into a transparent solution within 3 h. The product was precipitated by pouring the solution into 500 mL hexane, isolated by filtration, and purified by re-crystallizing three times from the THF/hexane mixed solution. The yield was 49%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 2.14 (m, 2H, $COCH_2CH_2$), 2.61 (t, 2H, $COCH_2CH_2$), 4.39 (t, 1H, $COCHNH$), 5.12 (br, 2H, $COOCH_2Ph$), 6.6 (s, 1H, $CONH$), 7.30–7.38 (m, 5H, $COOCH_2Ph$). The ^{1}H NMR spectrum agreed with the literature data.[5]

Synthesis of cyanoferrate complex (5): The protocol for cyanoferrate complex was adapted from literature procedures.[6] A typical run was shown as follows. $NH_4Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$ (1.0001 g, 3.3 mmol) was mixed with a tenfold excess of

4-(aminomethyl)pyridine (3.5602 g, 33 mmol) in 10 mL distilled water, and the mixture magnetically stirred at room temperature under nitrogen overnight. The product was precipitated by the addition of 100 mL ethanol, and was isolated through filtration. The crude product was washed with cold ethanol (100 mL × 3) and dried under vacuum to yield 0.9002 g $NH_4Na_2[Fe(II)(CN)_5Py]$ (**5**) as yellow powder. The yield is 66%. ^{1}H NMR (300 MHz, D_2O, 298 K): δ 4.08 (s, 2H, NH_2CH_2Py), 7.18 (d, 2H, *Py*), 8.95 (d, 2H, *Py*). The ^{1}H NMR spectrum agreed with the literature data.[6] ^{1}H NMR of 4-(aminomethyl)-pyridine was also carried out for purpose of comparison. ^{1}H NMR (300 MHz, D_2O, 298 K): δ 3.76 (s, 2H, NH_2CH_2Py), 7.27 (d, 2H, *Py*), 8.35 (d, 2H, *Py*). The product **5** showed a redox wave on a glassy carbon working electrode with $E_{1/2}$ of 0.20 V vs. Ag/AgCl in 0.1 M KCl solution under N_2.



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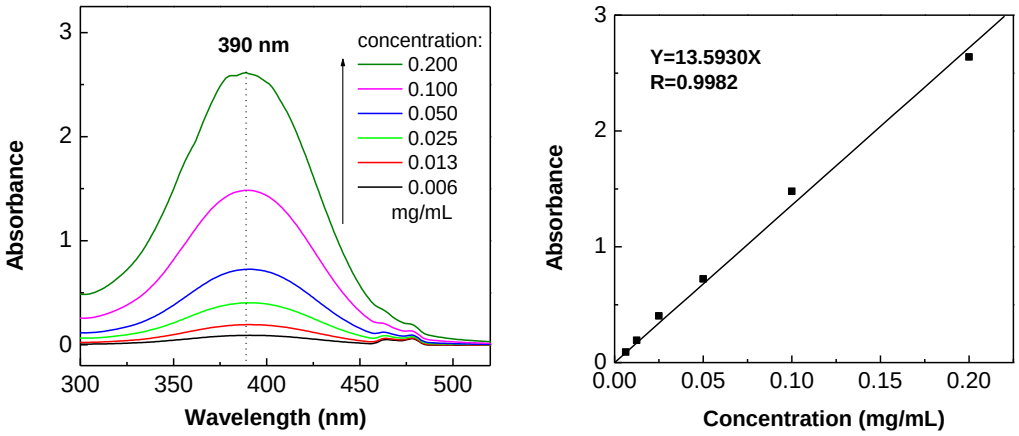
Scheme S3 Synthetic route of cyanoferrate complex ($NH_4Na_2[Fe(CN)_5NH_3]\cdot 2H_2O$, **5)**.

Table S1 Recipes for PBLG with various molecular weights.

Entry	Initiator **2** (mg)	BLG-NCA **3** (g)	[a][*M*]/[*I*]	PBLG (g)	Yield (%)
P1	103.2	3.16	60	2.783	88.2
P2	51.6	3.16	120	2.667	84.4
P3	25.8	2.63	200	2.333	88.7
P4	25.8	3.29	250	2.676	81.4

a[*M*]/[*I*] denotes molar ratio of monomer to initiator.

Calbration curve for determination of ferrate fractions of PBLG-Fe:



(a) (b)

Fig. S1 UV-vis spectra of ferrate complex (**5**) aqueous solutions at various concentrations (a) and plot of absorbance at 390 nm against ferrate complex concentration.

Electrochemical properties of PBLG-Fe with various molecular weights

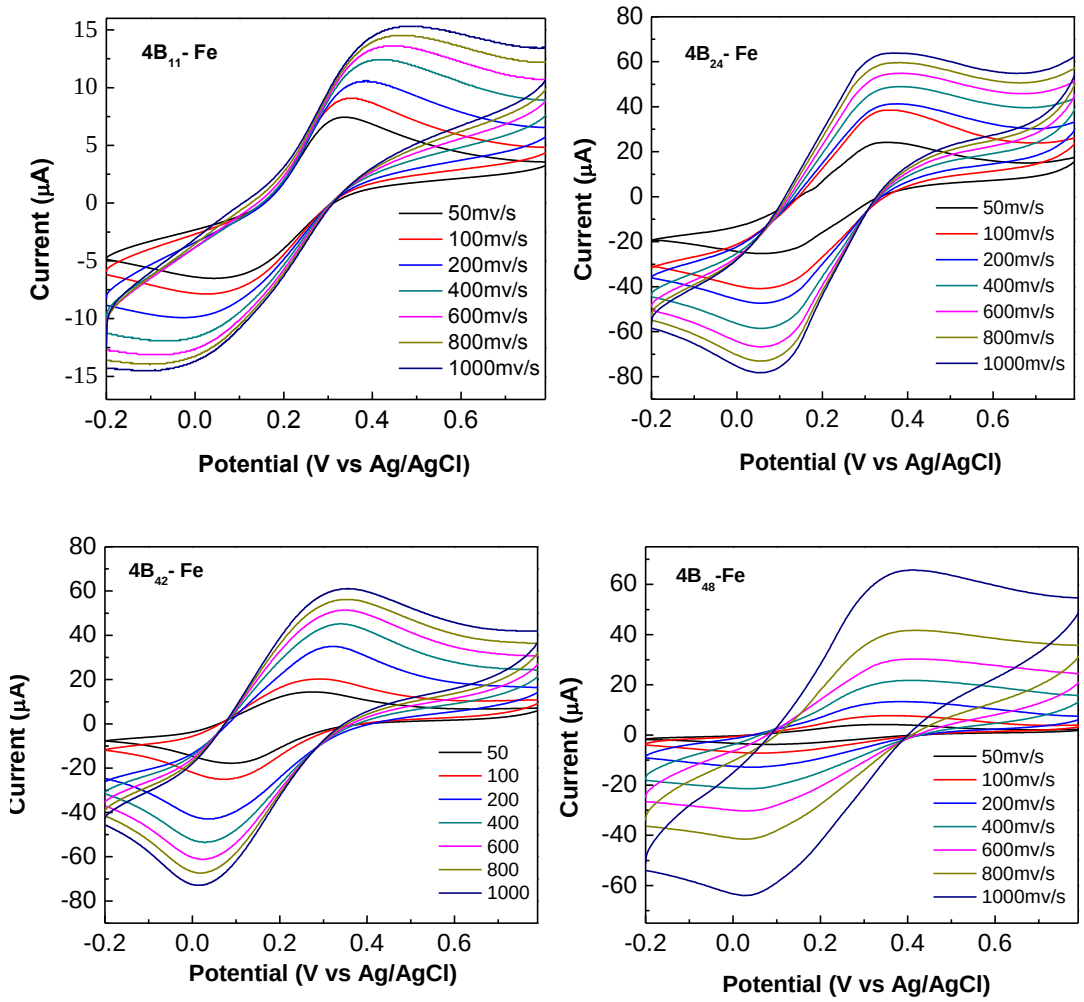


Fig. S2 CV curves of PBLG-Fe with various molecular weights at different scan rates.

Buffer: 0.1 M KCl, 3 mm glassy carbon electrodes, under N_2.

References

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