Electronic Supplementary Information

Ferrocene-based poly(aroxy carbonyl triazole)s: synthesis by metal-free click polymerization and precursors to magnetic ceramics

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**Experimental Section**

**General Information**

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl in an atmosphere of nitrogen immediately prior to use. Dichloromethane (DCM) was distilled under nitrogen over calcium hydride. *N,N*-Dimethylformamide (DMF) was extra-dry grade. Other solvents were purified by standard methods. 1,6-Hexanediol and 1,4-cyclohexanediol (cis- and trans-mixture) were obtained from Aladdin reagent Co., Ltd. (Shanghai, China). All other chemicals were purchased from Acros or Alfa, and used as received without further purification.
The $^1\text{H}$ and $^{13}\text{C}$ NMR spectra were recorded on a Bruker ADVANCE2B 300 or 400 NMR spectrometer in CDCl$_3$ or DMSO-$d_6$ using tetramethylsilane (TMS; $\delta = 0$) as internal reference. The IR spectra were measured on a Bruker Vector 22 spectrometer as thin films on KBr disks. The MALDI–TOF mass spectra were conducted on a GCT premier CAB048 mass spectrometer. Thermo-gravimetric analysis (TGA) measurements were performed on a Perkin-Elmer TGA 7 under dry nitrogen at 20 $^\circ$C/min. A TA Q 200 DSC was used to record the glass transition thermograms. The relative weight-average ($M_w$) and number-average ($M_n$) molecular weights of the polymers and their polydispersity indices (PDI, $M_w/M_n$) were estimated by a Waters 1515 gel permeation chromatography (GPC) system equipped with interferometric refractometer detector, using monodisperse poly(methyl methacrylate)s (PMMA) as calibration standards and DMF containing 0.05 M LiBr as the eluent at a flow rate of 1.0 mL/min. The cyclic voltammetry (CV) analysis of the polymers were conducted in an electrolyte of 0.1 M [(n-Bu)$_4$N]PF$_6$ in DCM at a scan rate of 100 mV/s at room temperature using a conventional three-electrode configuration. The working electrode was a platinum circular electrode. A Pt wire was used as the counter electrode and an Ag/AgNO$_3$ electrode was used as the reference electrode. The X-ray photoelectron spectroscopy (XPS) experiments were performed on a PHI 5600 spectrometer (Physical Electronics) and the core level spectra were measured using a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1386.6$ eV). The analyzer was operated at 23.5 eV pass energy and the analyzed area was 800 $\mu$m in diameter. Structures of the ceramics were investigated on a high-resolution transmission electron microscopy (HRTEM) JEOL 2010F TEM. The X-ray diffraction diagrams were obtained on a Philips PW 2830 powder diffractometer using monochromatized X-ray beam from a nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å). Magnetization curves were recorded on a Lake Shore 7037/9509-P vibrating sample magnetometer at room temperature.

**Monomer Preparation**

**Ferrocenedicarboxaldehyde** (4). Into a 500 mL two-necked round-bottom flask was placed 9.40 g (50 mmol) of ferrocene (3). The flask was evacuated under vacuum and
flushed with dry nitrogen three times for 1 h. After dry hexane (150 mL) and 
$N,N,N',N'$-tetramethylethlenediamine (TMEDA) (16.4 mL, 110 mmol) were injected, 
the mixture was stirred for 5 min at ambient temperature and subsequently 55 mL of 
n-butyllithium (2.0 M in hexane, 110 mmol) was added dropwise. After stirring at 
room temperature overnight, the solution was cooled to -78 °C and dry THF (75 mL) 
and DMF (8.56 mL, 110 mmol) were injected. The reaction mixture was then allowed 
to stir at room temperature for 1.5 h. Afterward, 30 mL of saturated brine was added 
to quench the reaction and the solution was extracted with DCM. The organic phase 
was separated and dried over MgSO$_4$ overnight. After filtration and solvent 
evaporation, the crude product was purified by a silica gel column using petroleum 
ether/ethyl acetate (2:1 by volume) as eluent. The dark red viscous oil of 4 was 
obtained in 52.0% yield (5.04 g). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 9.94 
(s, 2H), 4.88 (t, 4H), 4.67 (t, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 193.0, 
80.4, 74.3, 71.0.

**Ferrocenedimethanol (5).** In a 250 mL round-bottom flask was added 4 (3.63 g, 15 
mmol) in dry methanol (100 mL). The solution was cooled to 0 °C and 1.70 g (45 
mmol) of NaBH$_4$ was added portionwise. After the mixture was stirred at 0 °C for 
another 30 min and at room temperature for 2 h, acetic acid (2 mL) was added to 
quench the reaction. The reaction mixture was concentrated and then extracted with 
ethyl acetate. The organic phases were combined and dried over MgSO$_4$ overnight. 
The solvent was evaporated and the crude product was purified by a silica gel column 
using ether/ethyl acetate (2:1 by volume) as eluent. A yellow solid of 5 was obtained 
in 71.1% yield (2.62 g). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 4.38-4.30 (m, 
4H), 4.22-4.11 (m, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (TMS, ppm): 84.3, 70.1, 69.2, 
68.0, 60.5.

**1,1'-Bis(azidomethyl)ferrocene (2).** Into a 250 mL round-bottom flask were added 
1.65 g (5.3 mmol) of 5 and 4.11 g (63.2 mmol) of NaN$_3$ in glacial acetic acid (90 mL). 
The solution was heated at 50 °C for 3 h and then stirred at room temperature for 20 h. 
Afterward, the reaction mixture was diluted in 350 mL chloroform and washed with 
100 mL of a saturated aqueous solution of sodium bicarbonate. Solid sodium
bicarbonate was added portionwise until the solution reacted neutral. The reaction mixture was extracted and the organic phases were dried over MgSO₄ overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (30:1 by volume) as eluent. The yellowish-brown oil of 2 was obtained in 87.9% yield (1.75 g). IR (thin film), ν (cm⁻¹): 3093, 2925, 2862, 2097 (N₃ stretching), 1450, 1323, 1265, 1036. ¹H NMR (400 MHz, DMSO-d₆), δ (TMS, ppm): 4.29 (s, 4H), 4.24 (s, 4H), 4.21 (s, 4H). ¹³C NMR (100 MHz, DMSO-d₆), δ (TMS, ppm): 82.7, 69.8, 50.1. HRMS (MALDI-TOF), m/z calculated for C₁₂H₁₂FeN₆: 296.0473. Found: 296.0469.

Polymer Synthesis

Unless otherwise stated, all the polymerizations of dipropiolates 1 and ferrocene-containing diazide 2 were carried out under nitrogen using a standard Schlenk technique in a vacuum line system. Typical experimental procedures for the click polymerization of 1a with 2 are described below.

Into a 15 mL Schlenk tube with a stopcock in the side arm was placed 132.9 mg (0.4 mmol) of 1a and 118.4 mg (0.4 mmol) of 2. The tube was evacuated and refilled with dry nitrogen three times through the side arm. 2.4 mL of DMF was injected into the tube to dissolve the monomers. After stirring at 80 °C for 24 h, the reaction mixture was diluted with 20 mL of chloroform and added dropwise into 500 mL of hexane through a cotton filter under stirring. The precipitates were allowed to stand overnight and then collected by filtration. The polymer was washed with hexane and dried to a constant weight at ambient atmosphere.

**Characterization data for P3a.** Light yellow powder; 94.5% yield. Mₐ 13 400; Mₕ/Mₐ 1.51 (GPC, determined in DMF containing 0.05 M LiBr on the basis of PMMA calibration). F₁₄: 92.6%. IR (thin film), ν (cm⁻¹): 3138, 2966, 2927, 2862, 2097 (N₃ and C≡C stretching), 1747 (C=O stretching), 1669, 1501, 1360, 1201, 1039. ¹H NMR (400 MHz, DMSO-d₆), δ (TMS, ppm): 8.98, 8.50, 7.30, 7.17, 5.69, 5.47, 4.45, 4.24, 1.67. ¹³C NMR (100 MHz, DMSO-d₆), δ (TMS, ppm): 159.2, 148.2, 138.4, 129.8, 128.0, 121.7, 82.8, 70.0, 49.6, 42.4, 30.8.
**P3b.** The polymer was prepared from 1,6-hexanediol dipropionate 1b (88.9 mg, 0.4 mmol) and 1,1′-Bis(azidomethyl)ferrocene 2 (118.4 mg, 0.4 mmol) in 2.4 mL of DMF. Light yellow powder; 95.9% yield. $M_w 12 700$; $M_w/M_n 1.54$ (GPC, determined in DMF containing 0.05 M LiBr on the basis of PMMA calibration). $F_{1,4}$: 88.5 %. IR (thin film), $\nu$ (cm$^{-1}$): 3118, 2923, 2853, 2096 (N$_3$ and C≡C stretching), 1723 (C=O stretching), 1535, 1458, 1345, 1198, 1043. $^1$H NMR (400 MHz, DMSO-$d_6$), $\delta$ (TMS, ppm): 8.73, 8.24, 5.64, 5.41, 4.40, 4.29, 4.21, 1.65, 1.38. $^{13}$C NMR (100 MHz, DMSO-$d_6$), $\delta$ (TMS, ppm): 160.6, 139.2, 128.8, 82.9, 70.0, 64.7, 49.3, 28.4, 25.4.

**P3c.** The polymer was prepared from 1,4-cyclohexanediol dipropionate 1c (88.0 mg, 0.4 mmol) and 1,1′-Bis(azidomethyl)ferrocene 2 (118.4 mg, 0.4 mmol) in 2.4 mL of DMF. Light yellow powder; 96.9% yield. $M_w 12 700$; $M_w/M_n 1.59$ (GPC, determined in DMF containing 0.05 M LiBr on the basis of PMMA calibration). $F_{1,4}$: 87.7 %. IR (thin film), $\nu$ (cm$^{-1}$): 3134, 2925, 2853, 2097 (N$_3$ and C≡C stretching), 1724 (C=O stretching), 1538, 1450, 1369, 1197, 1042. $^1$H NMR (400 MHz, DMSO-$d_6$), $\delta$ (TMS, ppm): 8.77, 8.28, 5.66, 5.42, 5.03, 4.41, 4.30, 4.21, 1.84. $^{13}$C NMR (100 MHz, DMSO-$d_6$), $\delta$ (TMS, ppm): 160.0, 139.3, 128.9, 82.9, 70.7, 69.9, 49.4, 27.3.

**Pyrolytic Ceramization**

Ceramics C3a, C3b and C3a were fabricated from the precursors P3a, P3b and P3c by pyrolysis in a tube furnace with a heating capacity up to 1700 °C. In a typical ceramization experiment, 200 mg of P3a was placed in a porcelain crucible, which was heated to 1000 °C at a heating rate of 10 °C/min under a steam of nitrogen. The sample was sintered at 1000 °C for 1 h, and black ceramic C3a was obtained in 35.4% yield (70.7 mg) after cooling to room temperature.
**Scheme S1** Synthetic routes to ferrocene-containing diazide monomer 2.

**Fig. S1** FT-IR spectra of monomers 1a (A) and 2 (B) and their polymer P3a (C).
Fig. S2 $^{13}$C NMR spectra of monomers 1a (A) and 2 (B) and their polymer P3a (C) in DMSO-$d_6$. The solvent peaks are marked with asterisks.
**Fig. S3** FT-IR spectra of monomers 1b (A) and 2 (B) and their polymer P3b (C).

**Fig. S4** FT-IR spectra of monomer 1c (A) and 2 (B) and their polymer P3c (C).
Fig. S5 $^1$H NMR spectra of monomers 1b (A) and 2 (B) and their polymer P3b (C) in DMSO-$d_6$. The solvent and water peaks are marked with asterisks.
Fig. S6 $^1$H NMR spectra of monomers 1c (A) and 2 (B) and their polymer P3c (C) in DMSO-$d_6$. The solvent and water peaks are marked with asterisks.
Fig. S7 $^{13}$C NMR spectra of monomers 1b (A) and 2 (B) and their polymer P3a(C) in DMSO-$d_6$. The solvent peaks are marked with asterisks.
Fig. S8 $^{13}$C NMR spectra of monomers 1c (A) and 2 (B) and their polymer P3c (C) in DMSO-$d_6$. The solvent peaks are marked with asterisks.
**Fig. S9** TGA curves of P3a, P3b and P3c recorded under nitrogen at a heating rate of 20 °C/min.

**Fig. S10** DSC curves of P3a, P3b and P3c measured under nitrogen at a scanning rate of 10 °C/min.
**Fig. S11** HRTEM images of ceramics C3a (A–D), C3b (E) and C3c (F).
Fig. S12 XRD patterns of C3a, C3b and C3c.
Table S1 Electrochemical properties of the polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{pc}$ (V)$^a$</th>
<th>$E_{pa}$ (V)$^a$</th>
<th>$E_{1/2}$ (V)$^b$</th>
<th>$\Delta E_p$ (V)$^c$</th>
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<tbody>
<tr>
<td>P3a</td>
<td>0.690</td>
<td>0.832</td>
<td>0.761</td>
<td>0.142</td>
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<tr>
<td>P3b</td>
<td>0.735</td>
<td>0.875</td>
<td>0.805</td>
<td>0.140</td>
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<tr>
<td>P3c</td>
<td>0.750</td>
<td>0.904</td>
<td>0.827</td>
<td>0.154</td>
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</table>

$^a$ Determined by CV analysis, where $E_{pa}$ is the potential of the anodic peak current and $E_{pc}$ is the potential of the cathodic current.

$^b$ Formal redox potential $E_{1/2} = (E_{pa} + E_{pc})/2$.

$^c \Delta E_p = E_{pa} - E_{pc}$.

Table S2 Compositions of C3a–C3c estimated by XPS analyses

<table>
<thead>
<tr>
<th>Ceramics</th>
<th>C (%)</th>
<th>O (%)</th>
<th>N (%)</th>
<th>Fe (%)</th>
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</thead>
<tbody>
<tr>
<td>C3a</td>
<td>89.48</td>
<td>4.96</td>
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<td>C3b</td>
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<tr>
<td>C3c</td>
<td>88.28</td>
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<td>0.29</td>
<td>6.58</td>
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