

## Electronic Supplementary Information

### Synthesis and structure of a ferric complex of 2,6-di(1H-pyrazol-3-yl)pyridine and its excellent performance in the redox-controlled living ring-opening polymerization of $\epsilon$ -caprolactone

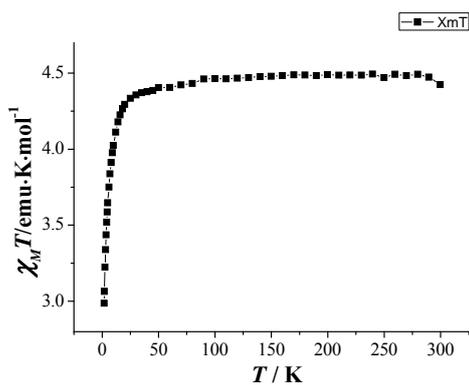
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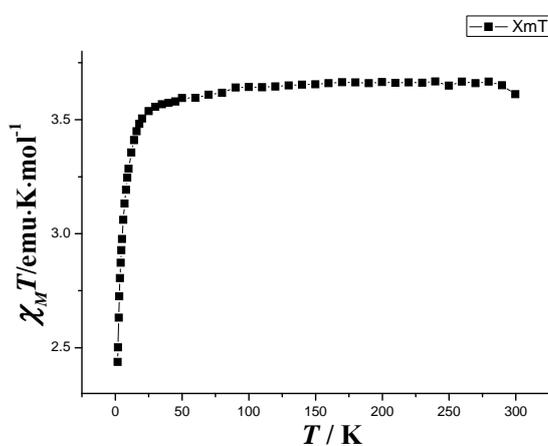
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(a)



(b)

Fig. S1. Variation of  $\chi_M T$  with temperature for **1** (a) and **2** (b).

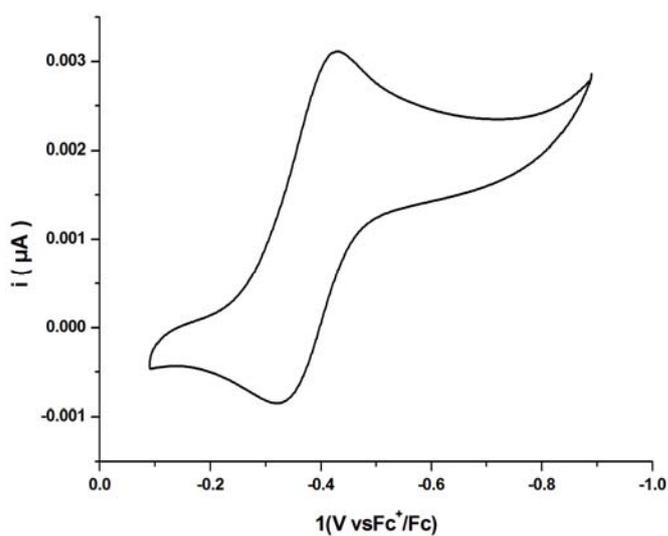
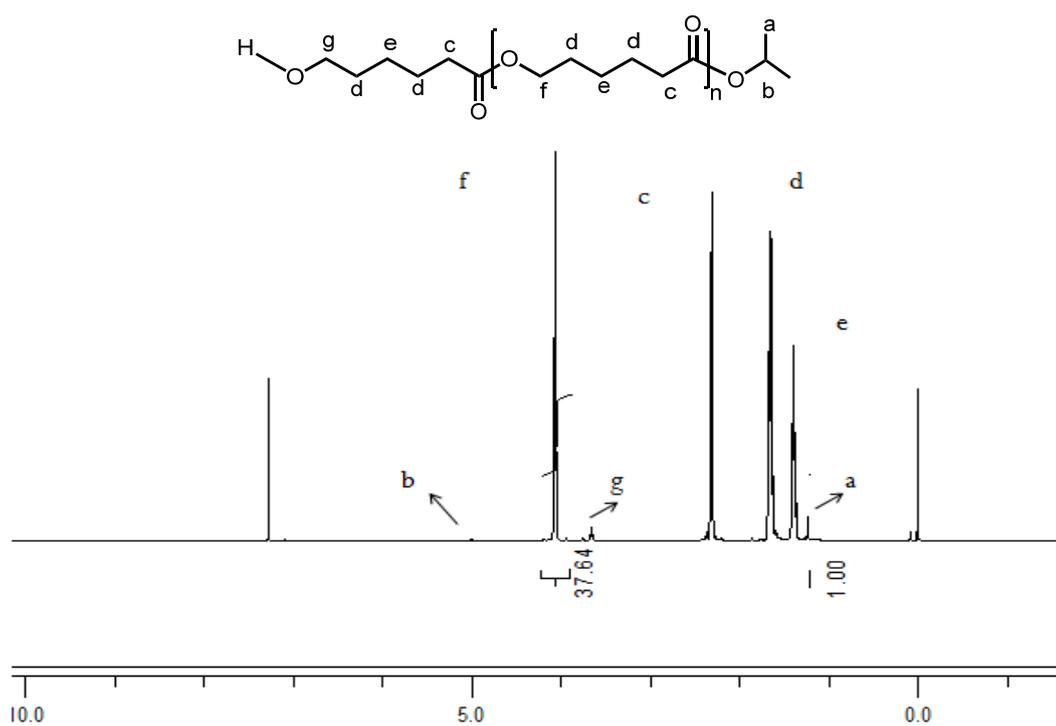
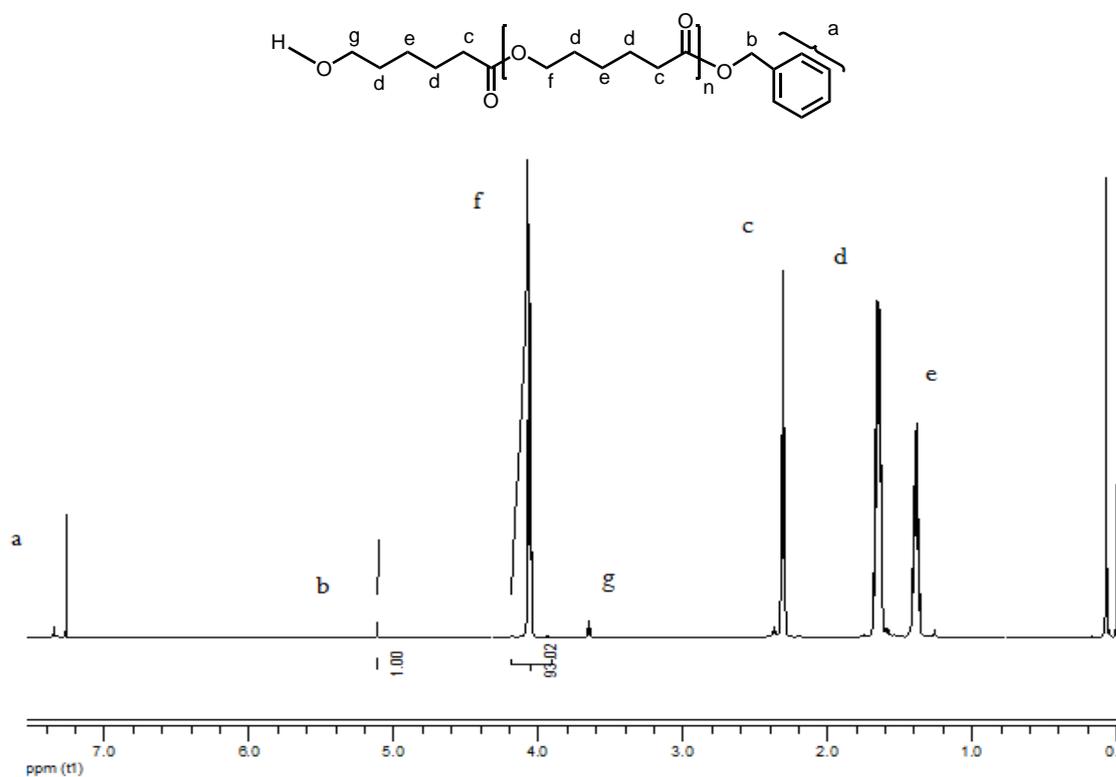


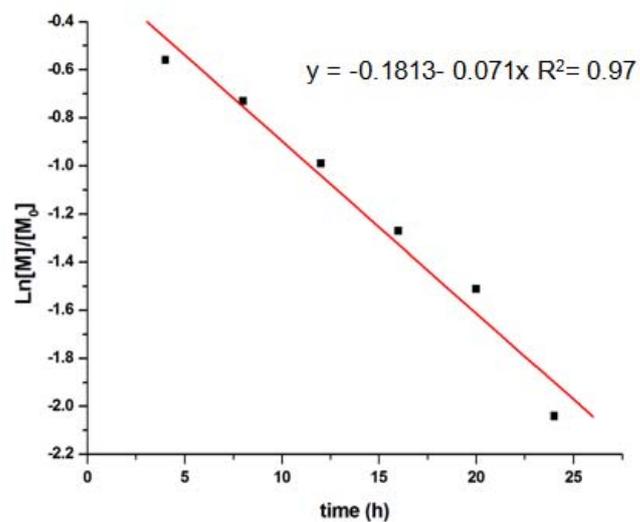
Fig. S2. Cyclic voltammogram of complex **1**. Conditions: 0.005 M acetonitrile solution of the analyte, 0.1M  $\text{Et}_4\text{NClO}_4$  as supporting electrolyte, platinum electrode as working electrode, platinum wire as counter electrode, scan rate of 50 mV/s.



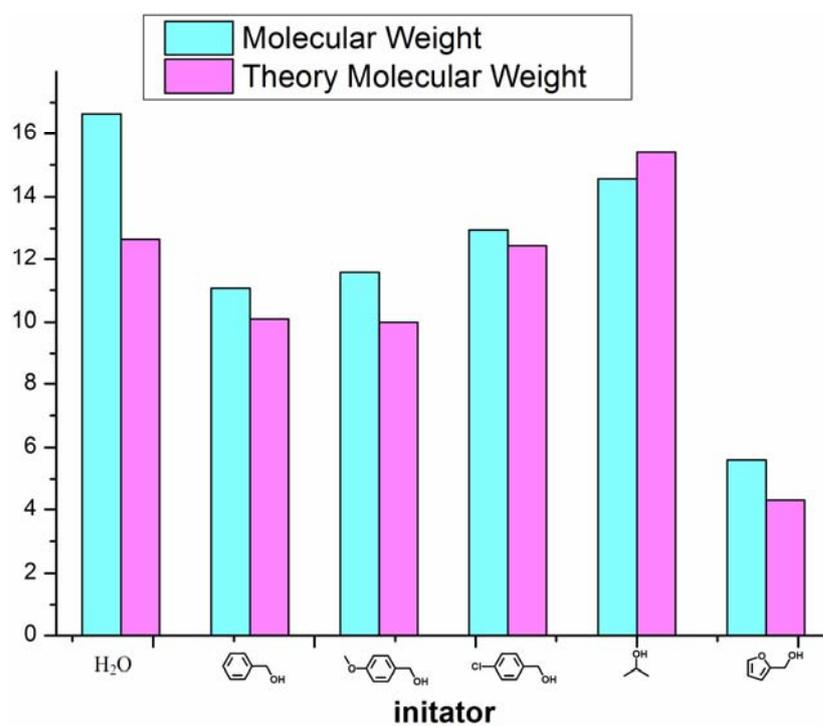
**Fig. S3.** The  $^1\text{H}$  NMR spectrum of PCL initiated by **1**/isopropanol with the molar ratio of **1**/isopropanol/CL being 1/2/300 (Table 2, entry 5).



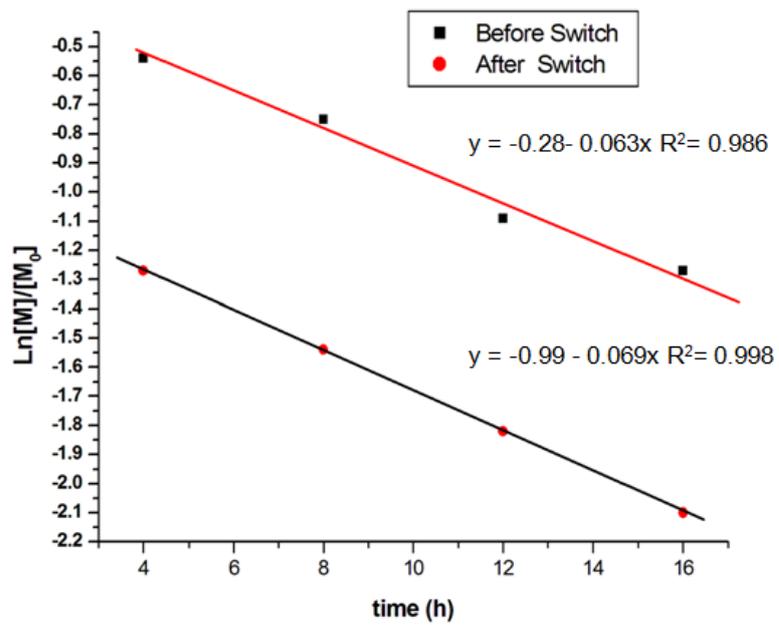
**Fig. S4.** The  $^1\text{H}$  NMR spectrum of PCL initiated by **1**/benzyl alcohol with the molar ratio of **1**/benzyl alcohol/CL being 1/2/300 (Table 2, entry 7).



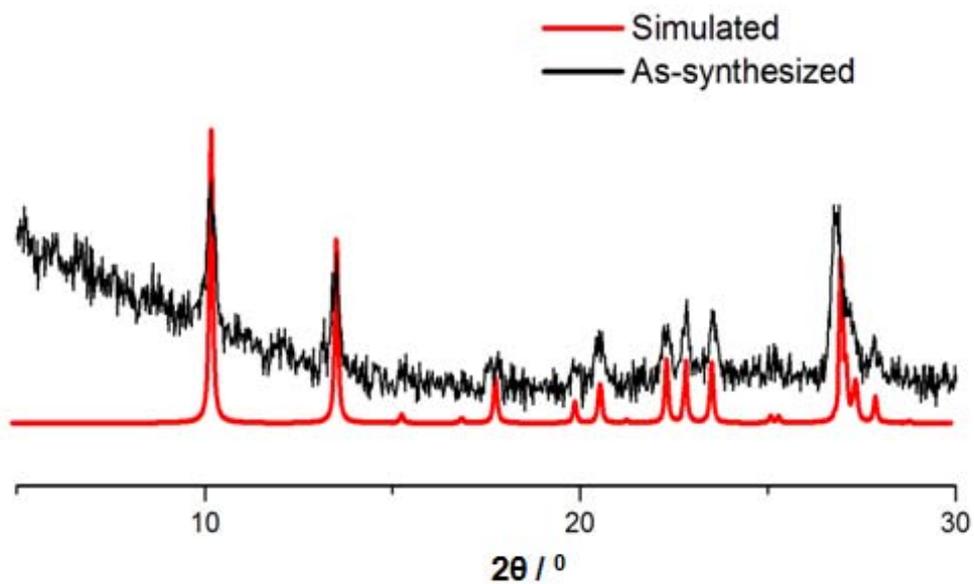
**Fig. S5.** Kinetic plot for the polymerization of  $\epsilon$ -CL initiated by 1/isopropanol without switching at 100 °C.



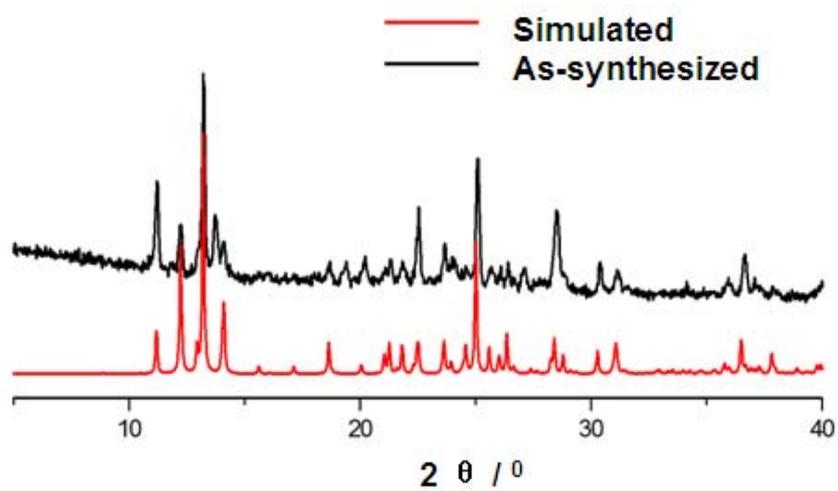
**Fig. S6.** Comparison of the experimental and theoretical molecular weights with two initiating alkoxides per iron center.



**Fig. S7.** Kinetic plot for the polymerization of  $\epsilon$ -CL initiated by 1/isopropanol with switching at 100 °C.



**Fig. S8.** PXRD patterns for **1**. Red line: simulated; Black line: a single-phase polycrystalline sample of **1**.



**Fig. S9.** PXRD patterns for **2**. Red line: simulated; Black line: a single-phase polycrystalline sample of **2**.