# *Supporting information*

## Immortal Ring-Opening Polymerization of ε-Caprolactone by a Neat Magnesium Catalyst System: An Approach to Block and Amphiphilic Star Polymers *In Situ*†

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Table S1. Selected bond lengths (Å) and angles (°) for complex **2**

| Bond length (Å) | | Angel (º) | |
|---|---|---|---|
| Mg(1)–O(1) | 1.8645(12) | O(1)–Mg(1)–O(1A) | 136.45(9) |
| Mg(1)–O(1A) | 1.8645(12) | O(1)–Mg(1)–O(2A) | 110.93(6) |
| Mg(1)–O(2A) | 2.0224(15) | O(1A)–Mg(1)–O(2A) | 97.64(5) |
| Mg(1)–O(2) | 2.0224(15) | O(1)–Mg(1)–O(2) | 97.64(5) |
| | | O(1A)–Mg(1)–O(2) | 110.93(6) |
| | | O(2A)–Mg(1)–O(2) | 97.32(10) |
| | | C(1)–O(1)–Mg(1) | 138.52(11) |

Table S2. Crystallographic data and refinement for complex **2**

| | **2** |
|---|---|
| Empirical formula | $C_{46}H_{46}MgO_4$ |
| Crystal colour | Colorless |
| formula weight | 687.14 |
| Crystal system | Monoclinic |
| space group | C2/C |
| *a* (Å) | 19.0981(16) |
| *b* (Å) | 9.6221(8) |
| *c* (Å) | 22.024(3) |
| *α*(deg) | 90 |
| *β* (deg) | 109.3890(10) |
| *γ* (deg) | 90 |
| *V* (Å$^3$) | 3817.8(6) |
| *Z* | 4 |
| Dcalcd (g/cm$^3$) | 1.195 |
| radiation (λ), Å | 0.71073 |
| *μ* (mm$^{-1}$) | 0.089 |
| F(000) | 1464 |
| *θ* range, (°) | 1.96–25.10 |
| No. of reflns collected | 29853 |
| No.of unique reflns (I>2σ(I)) | 9382 |
| no. of params refnd | 231 |
| Goodness of fit | 1.020 |
| Final *R*, $R_w$ (I>2σ(I)) | 0.04371,0.1079 |

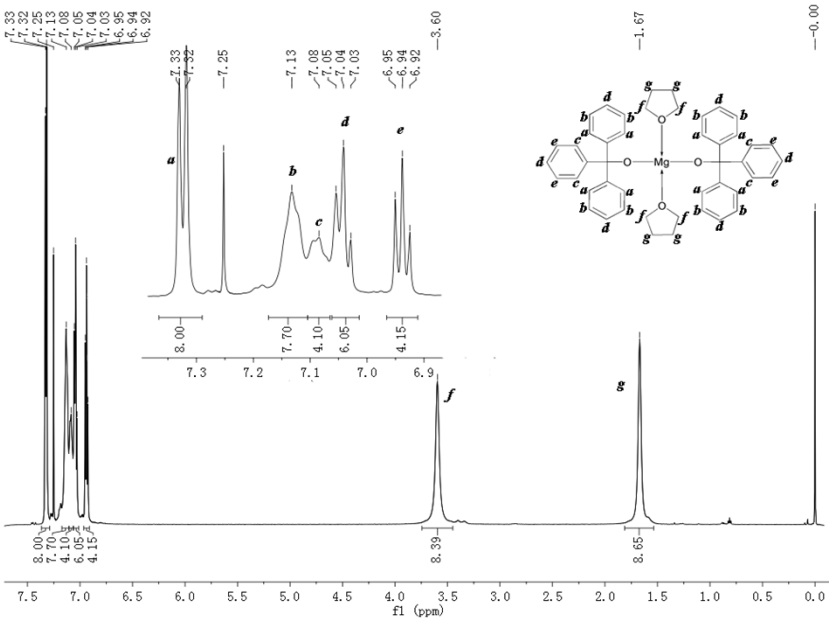

Figure S1. $^{1}H$ NMR in $CDCl_3$ of complex **2** (400 MHz, 25° C).

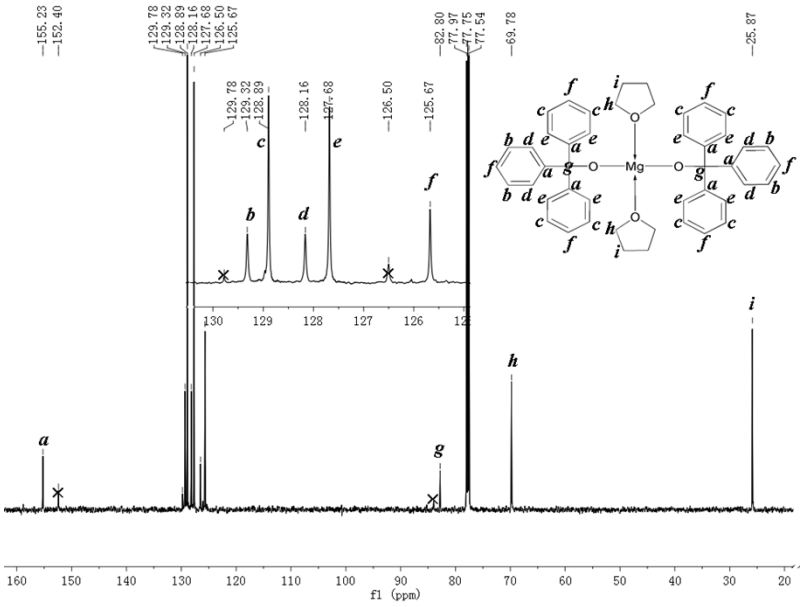

Figure S2. $^{13}C$ NMR in $CDCl_3$ of complex **2** (100 MHz, 25° C)

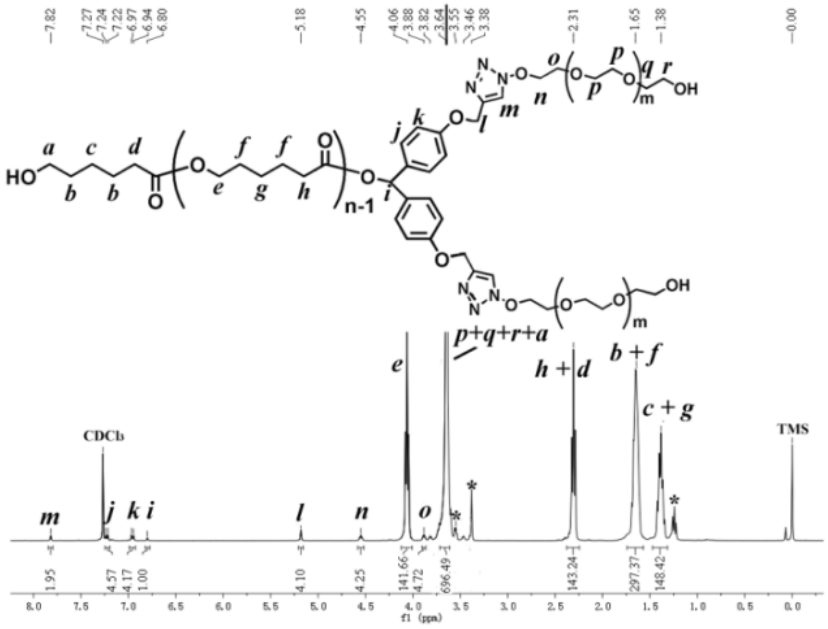


Figure S3. $^{1}H$ NMR in $CDCl_3$ of topologic Star-PCL-PEG (400 MHz).