## Electronic Supplementary Information

## A straightforward approach for one-pot synthesis of noncovalently connected graft copolymers with unique selfassembly nanostructures

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**Fig. S1** <sup>1</sup>H NMR spectra for (a) Ad-diene monomer, **1a**, (b) linear polymer, **1a**, and (c) supramolecular graft copolymer, **1a**. (\*\* CDCl<sub>3</sub>, \* DMSO- $d_6$  and H<sub>2</sub>O)



**Fig. S2** <sup>1</sup>H NMR spectra for (a) Ad-diene monomer, **1b**, (b) linear polymer, **1b**, and (c) supramolecular graft copolymer, **1b**. (\*\* CDCl<sub>3</sub>, \* DMSO-*d*<sub>6</sub> and H<sub>2</sub>O)



**Fig. S3** <sup>1</sup>H NMR spectra for (a) Ad-diene monomer, **1c**, (b) linear polymer, **1c**, and (c) supramolecular graft copolymer, **1c**. (\*\* CDCl<sub>3</sub>, \* DMSO- $d_6$  and H<sub>2</sub>O)



**Fig. S4** GPC traces of the Polymers via ADMET polymerization of Ad-diene monomers using **C3** as catalyst.

**Table S1** Conditions for ADMET polymerization of Ad-diene monomers and analytical data of the polymers<sup>a</sup>

Entry	Monomer	Catalyst	Yield	Т	$M_{ m n,GPC}^{ m c}$	$M_{ m w}/M_{ m n}^{ m c}$
			(%) <sup>b</sup>	(°C)		
1	1a	C1	_	60	_	_
2	1a	C2	87	60	2100	2.05
3	<b>1</b> a	C3	84	60	1600	1.70
4	<b>1</b> a	C3	90	80	1800	1.88
5	1b	C1	84	60	4300	1.65
6	1b	C2	75	60	7200	1.83
7	1b	C3	86	60	5700	1.66
8	1b	C3	86	80	6100	1.75
9	1c	C1	89	60	7500	1.58
10	1c	C2	82	60	11200	1.82
11	1c	C3	93	60	9300	1.64
12	1c	C3	91	80	10100	1.79

<sup>a</sup> Polymerizations were conducted at 60–80 °C for 24 h using  $[M/C]_0 = 50$ : 1.

<sup>b</sup> Isolated yield after precipitation, and obtained gravimetrically from the dried polymer.

<sup>c</sup> Determined by GPC in THF relative to monodispersed polystyrene standards.



**Fig. S5** <sup>1</sup>H NMR spectrum for alkyne-ended MPEG. (\*\* CDCl<sub>3</sub>)



Fig. S6 ATR–IR spectra for (a) azide-modified  $\beta$ -CD and (b) MPEG-substituted  $\beta$ -CD.



Fig. S7 GPC traces of supramolecular graft copolymer, 1c by ADMET polymerization using different ratios of M1c/MPEG- $\beta$ -CD.



**Fig. S8** Size and distribution of polymeric nanoparticles determined by means of DLS (a) SG-P1a, (b) SG-P1c, and (c) L-P1c.



Scheme S1 Schematic Illustration of Supramolecular Graft Copolymer via One-Pot ROMP and the Host–Guest Recognition.



Fig. S9 <sup>1</sup>H NMR spectra for (a) Ad-ROMP monomer and (b) supramolecular macromonomer. (\* DMSO- $d_6$  and H<sub>2</sub>O)



**Fig. S10** GPC traces of MPEG- $\beta$ -CD and polymer obtained by ROMP.