### Supporting Information

# **Self-Reporting Dynamic Covalent Polycarbonates Networks**

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## 1. <sup>1</sup>H NMR spectra of the prepared substances



Figure S1 <sup>1</sup>H NMR spectrum of PDT-OH in CDCl<sub>3</sub> at ambient temperature.



Figure S2 <sup>1</sup>H NMR spectrum of HDA-diol in DMSO-d6 at ambient temperature.



**Figure S3** <sup>1</sup>H NMR spectrum of **HDA-PC** in DMSO-d6 at ambient temperature. a' and b' relate to the hydrogens at the end-functionality of the polymer.



Figure S4  $^1\text{H}$  NMR spectrum of TriBr-linker in CDCl3 at ambient temperature.



Figure S5  $^{1}$ H NMR spectrum of TriCp-linker in CDCl<sub>3</sub> at ambient temperature.



Figure S6  $^{1}$ H NMR spectrum of HDA-triol in CDCl<sub>3</sub> at ambient temperature.

#### 2. ESI mass spectra of the HDA-diol and HDA-triol



Figure S7 ESI mass spectrum of the HDA-diol. The retro HDA products are formed during the ionization process due to the high temperatures (320 °C).

Tabel S1 Sum formula, the exact masses of the experimentally obtained data, theoretical m/z values and the deviation of
both for the HDA-diol and the products of the retro HDA reaction (rHDA1 and rHDA2).

Label	Sum formula	m/z <sub>exp</sub>	m/z <sub>theo</sub>	Δm/z
[HDA-diol+Na] <sup>+</sup>	$[C_{50}H_{72}NaO_{12}P_2S_4]^+$	1077.3289	1077.3274	0.0015
[rHDA1+Na]⁺	$[C_{15}H_{21}NaO_6PS_2]^+$	415.0414	415.0409	0.0005
[rHDA2+Na]⁺	$[C_{35}H_{51}NaO_6PS_2]^+$	685.7277	685.7257	0.0020



Figure S8 ESI mass spectrum of the HDA-triol. The retro HDA products are formed during the ionization process due to the high temperatures (320 °C).

**Tabel S2** Sum formula, the exact masses of the experimentally obtained data, theoretical m/z values and the deviation of both for the **HDA-triol** and the products of the retro HDA reaction (rHDA1, rHDA2 and rHDA3).

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Label	Sum formula	m/z <sub>exp</sub>	m/z <sub>theo</sub>	∆m/z
[HDA-triol+Na] <sup>+</sup>	$[C_{78}H_{99}NaO_{24}P_{3}S_{6}]^{+}$	1727.4114	1727.3956	0.0158
[rHDA1+Na]⁺	$[C_{15}H_{21}NaO_6PS_2]^+$	415.0411	415.0409	0.0002
[rHDA2+Na]⁺	$[C_{48}H_{57}NaO_{12}PS_2]^+$	943.2940	943.2921	0.0019
[rHDA3+Na]⁺	$[C_{63}H_{78}NaO_{18}P_2S_4]^+$	1335.3455	1335.3438	0.0017

#### 3. SEC analysis of the prepared linear polycarbonates (HDA-PC) P1 – P4

<b>Fable S3</b> SEC analysis of the prepared linear polycarbonates $P1 - P4$ . $M_n$ and $M_w$ in g mol <sup>-1</sup> .				
	<i>M</i> n	Mw	Ð	
P1	3.100	4.200	1.4	
P2	2.800	5.600	2.0	
Р3	7.500	16.000	2.4	
P4	7.600	20.000	2.7	

Table S4 SEC analysis of the degradation of P4 upon heating.  $M_n$  and  $M_w$  in g mol<sup>-1</sup>.

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	Mn	Mw	Ð
P4 (25 °C)	7.600	20.000	2.7
P4 (60 °C)	3.600	12.000	3.4
P4 (100 °C)	1.600	3.900	2.5
P4 (140 °C)	570	590	1.04

**Table S5** SEC analysis of the bonding/debonding behavior of P4.  $M_n$  and  $M_w$  in g mol<sup>-1</sup>. P4<sub>or</sub> is the original P4 polymer, P4<sub>deg</sub>, the degraded polymer at 120 °C and P4<sub>ref</sub>, the reformed polymer upon cooling.

		1, 1, 0	
	<b>M</b> n	Mw	Ð
P4 <sub>or.</sub> (25 °C	7.600	20.000	2.7
P4 <sub>deg.</sub> (120 °C)	1.300	1.700	1.4
P4 <sub>ref.</sub> (25 °C)	9.900	20.000	2.0

### 4. <sup>1</sup>H NMR spectra of the bonding/debonding behavior if P4



Figure S9 <sup>1</sup>H NMR spectra of the bonding/debonding behavior of the prepared linear polycarbonate P4 in DMSO- $d_6$ .