Electronic Supplementary Information

Structural Control of Self-Healing Silica-Poly(Tetrahydropyran)-Poly(ε-caprolactone) Hybrids

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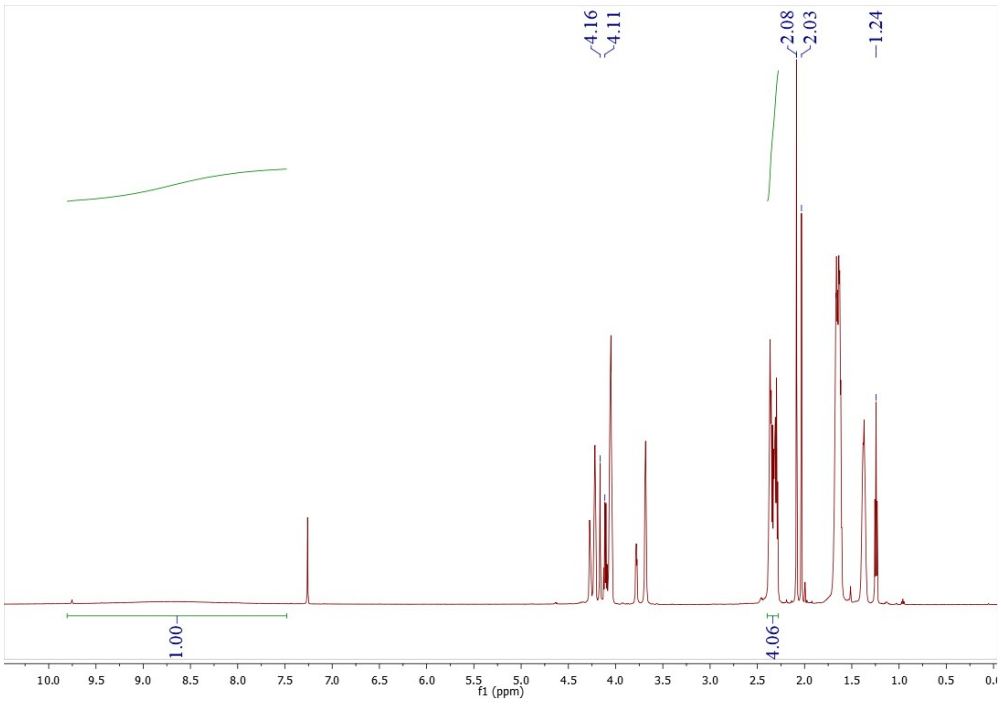


Fig. S1 ^{1}H-NMR spectrum of HOOC-PCL-COOH in $CDCl_3$.

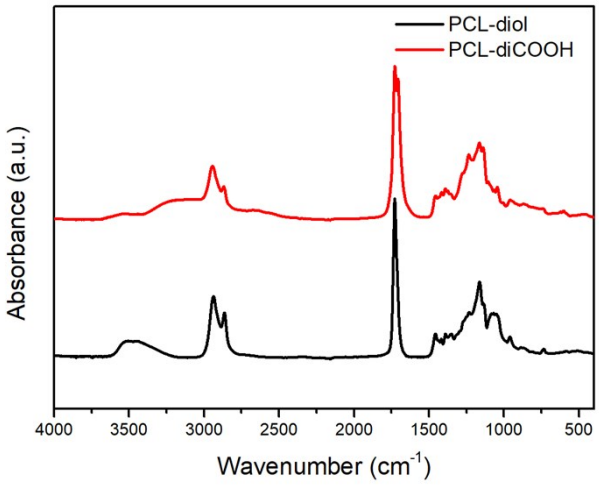
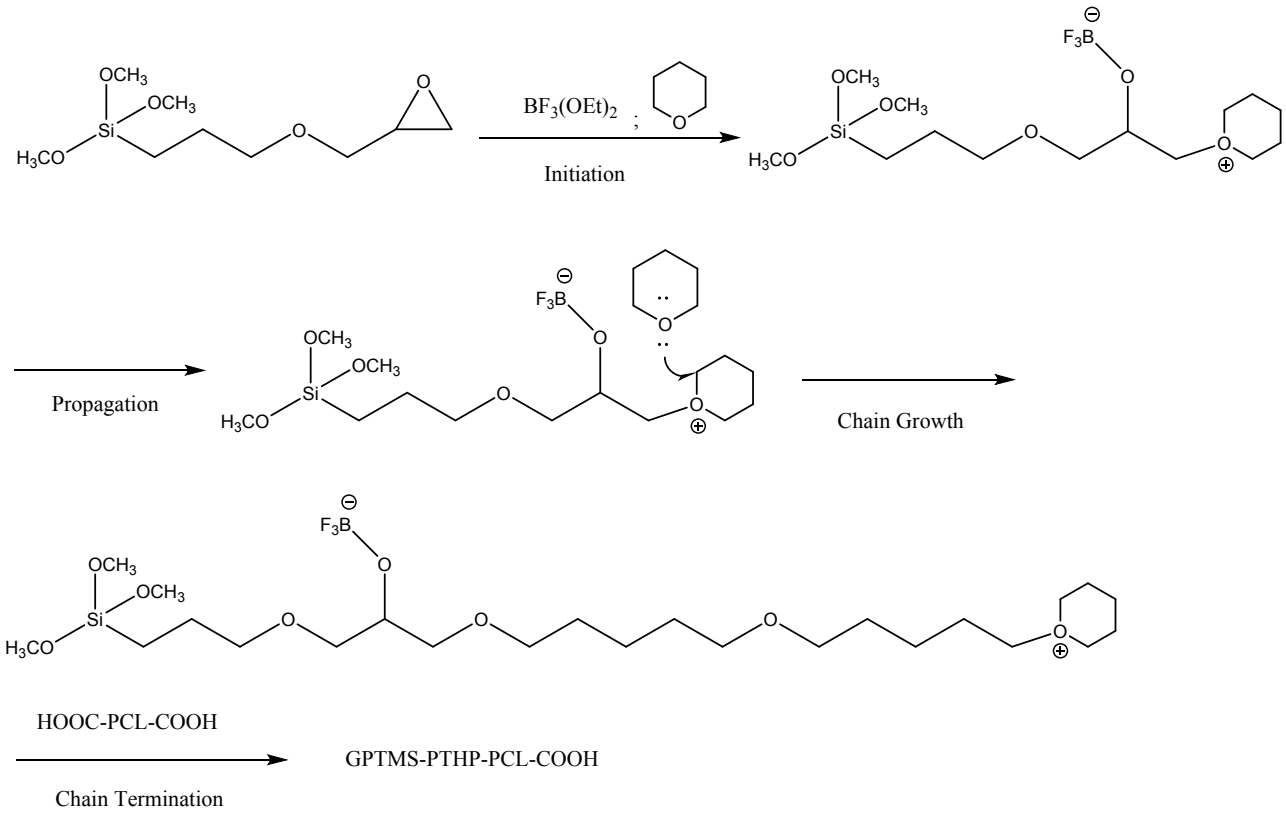


Fig. S2 FT-IR spectra HO-PCL-OH and HOOC-PCL-COOH.

(a) Step 1



(b) Step 2

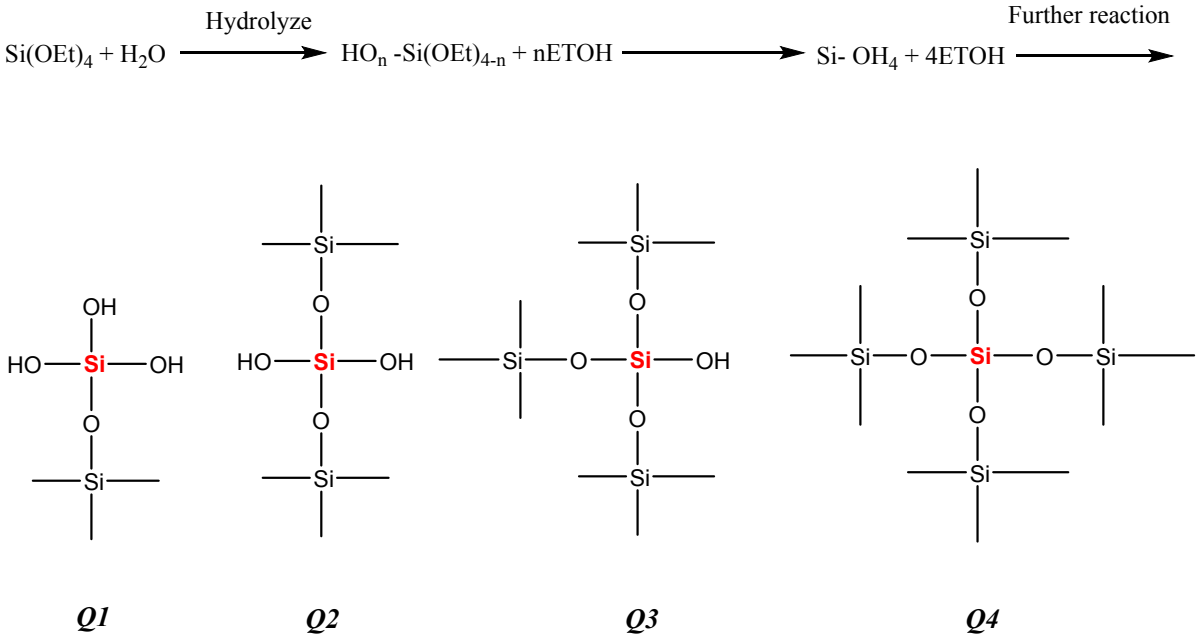


Fig. S3 Reaction mechanism of (a) THP cationic ring-opening polymerization; (b) hydrolysis of TEOS.

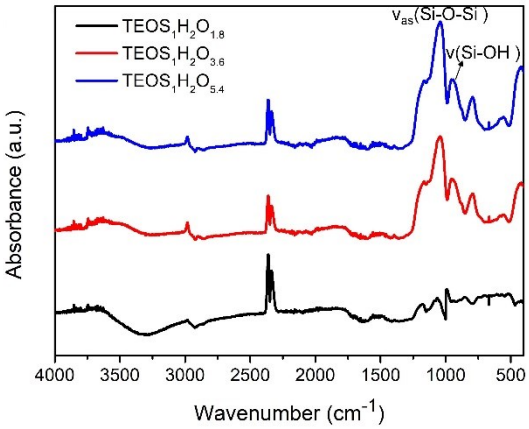


Fig. S4 Molecular structures of pure inorganic bulks compared through FTIR.

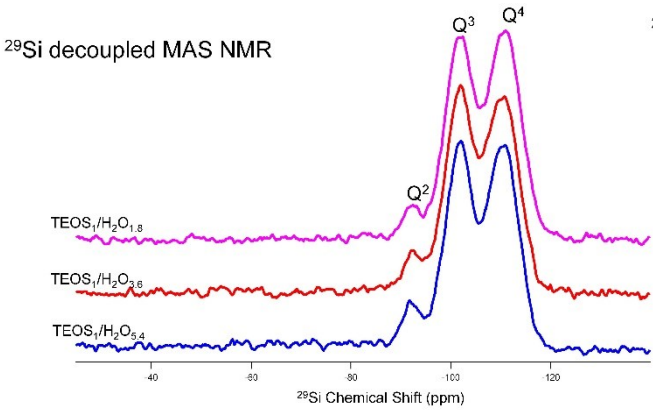


Fig. S5 ^{29}Si NMR spectra of inorganic bulks in different TEOS/H_2O molar ratios.

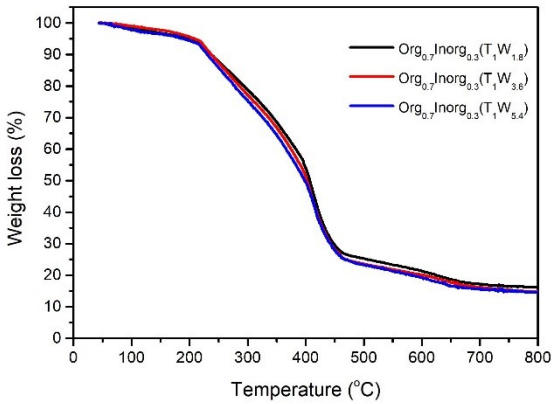


Fig. S6 TGA of hybrids with the same organic/inorganic compositions $Org_{0.7}Inorg_{0.3}$ with different silica structures.

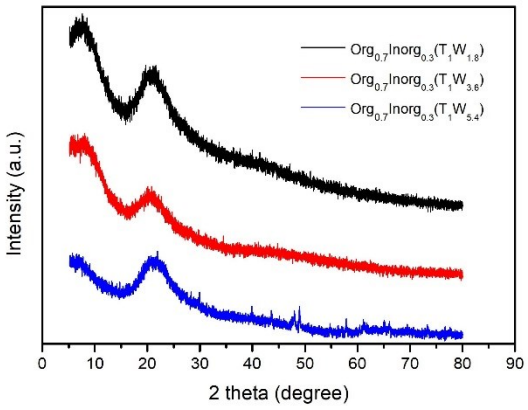


Fig. S7 XRD of hybrids with the same organic/inorganic compositions but different silica structures.

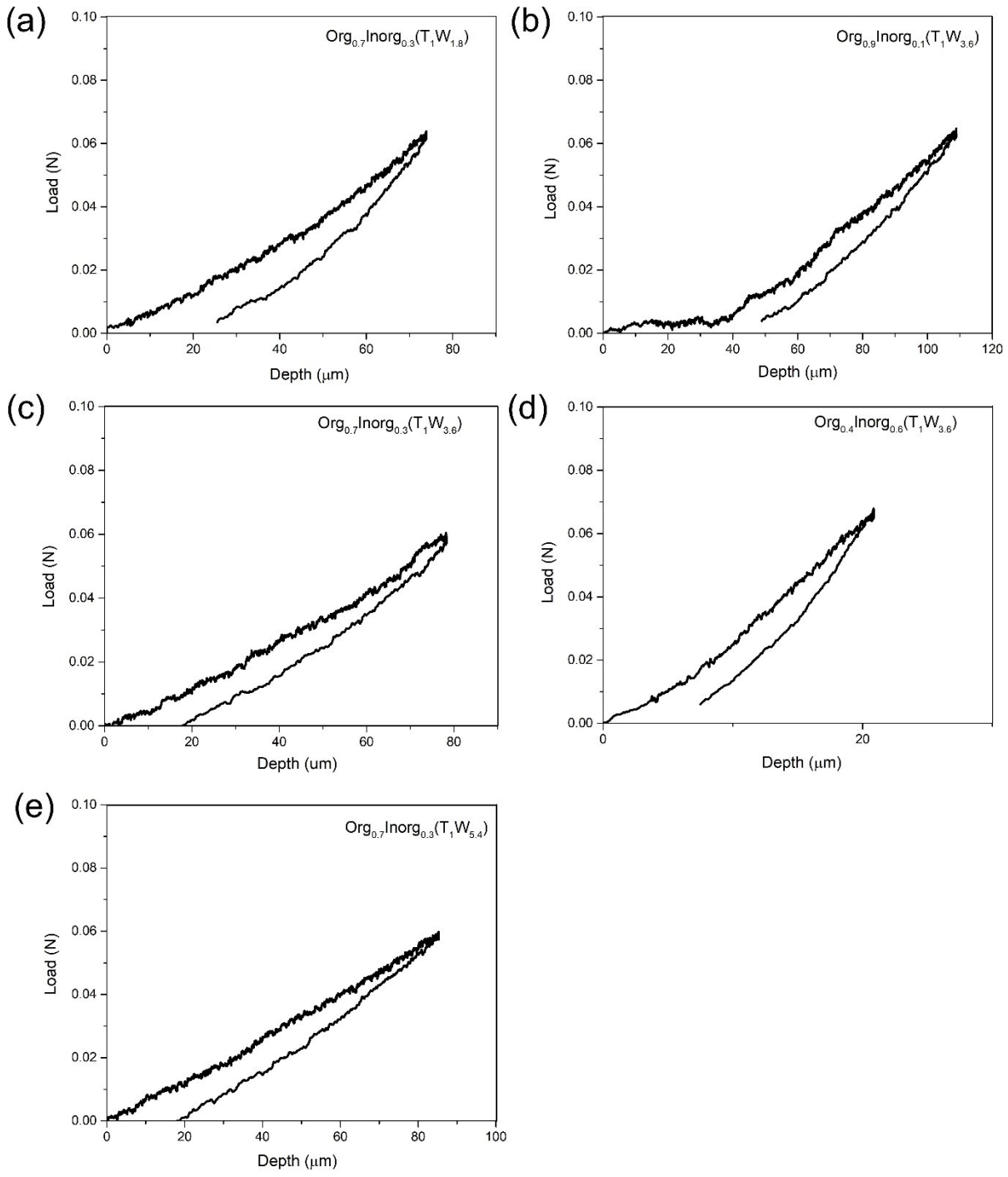


Fig. S8 Load-depth curves for the loading-unloading of the five hybrids as measured by micro-indentation.

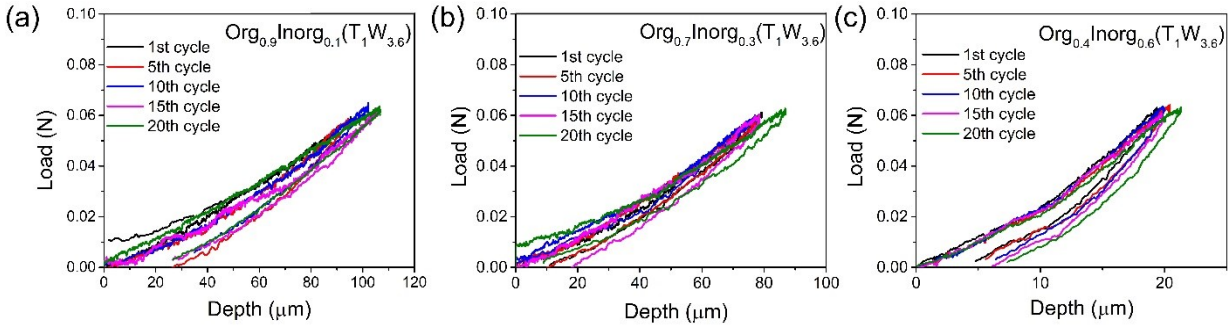


Figure S9. Indentation loading-unloading experiment of hybrids with different I/O ratios ($Org_{0.9}Inorg_{0.1}(T_1W_{3.6})$; $Org_{0.7}Inorg_{0.3}(T_1W_{3.6})$; $Org_{0.4}Inorg_{0.6}(T_1W_{3.6})$) for up to 20 cycles.

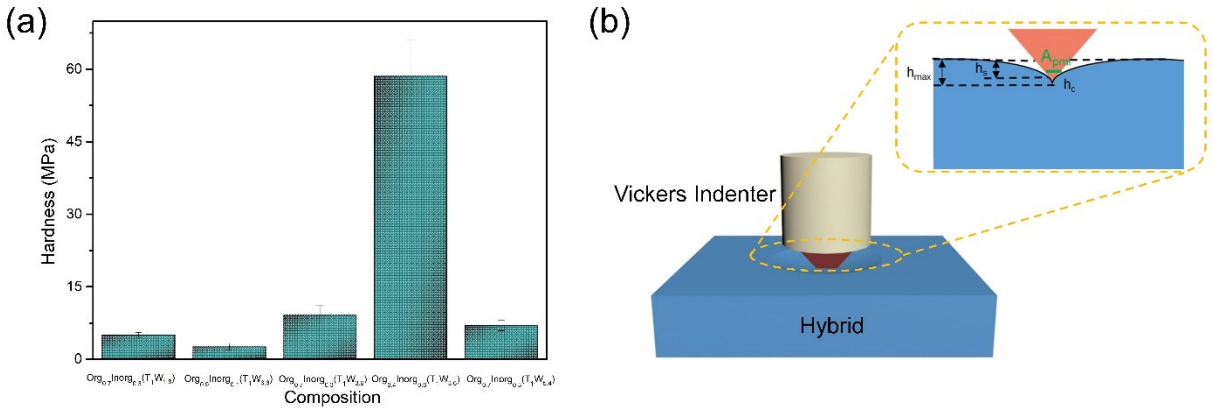


Fig. S10 (a) The hardness of five hybrids tested by micro-indentation method; (b) Elasto-plastic deformation of hybrids at the maximum load.

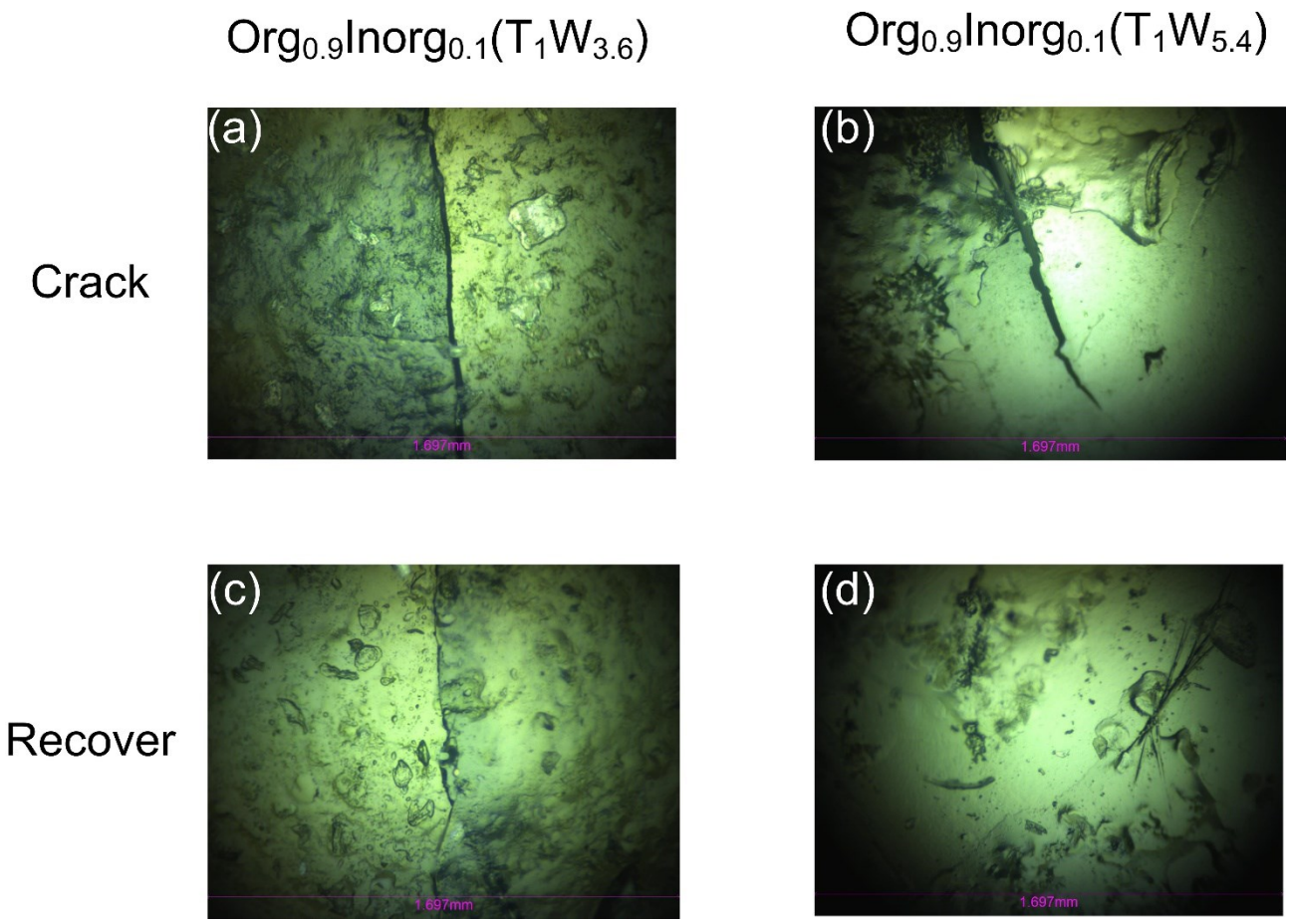


Fig. S11 Optical microscope images of four hybrid compositions after creation of a defect (top view): (a) $Org_{0.9}Inorg_{0.1}(T_1W_{3.6})$; (b) $Org_{0.9}Inorg_{0.1}(T_1W_{5.4})$. After self-healing for 24 hours: (c) $Org_{0.9}Inorg_{0.1}(T_1W_{3.6})$; (d) $Org_{0.9}Inorg_{0.1}(T_1W_{5.4})$.

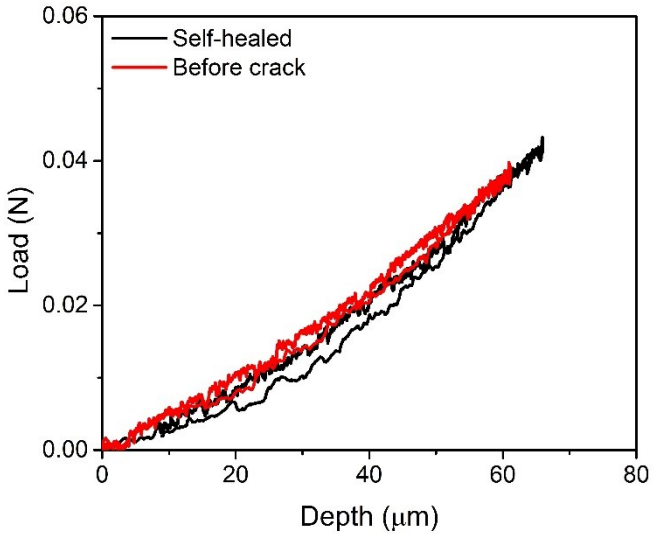


Fig. S12 Indentation test of hybrid $Org_{0.9}Inorg_{0.1}(T_1W_{1.8})$ before the induced crack (fresh samples) and after cracking and self-healing.

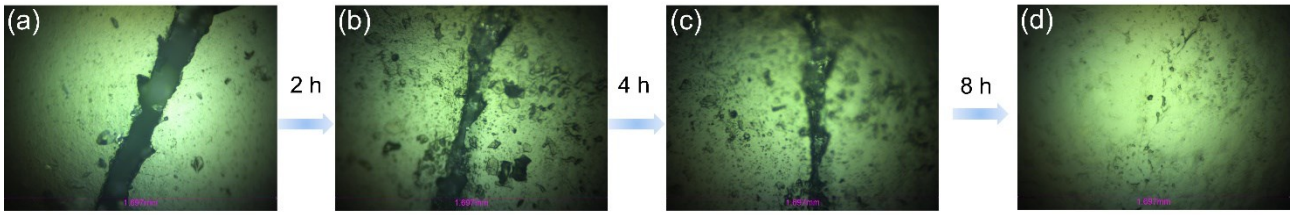


Fig. S13 Monitoring self-healing ability of hybrid $Org_{0.9}Inorg_{0.1}(T_1W_{1.8})$ at 37 ℃.

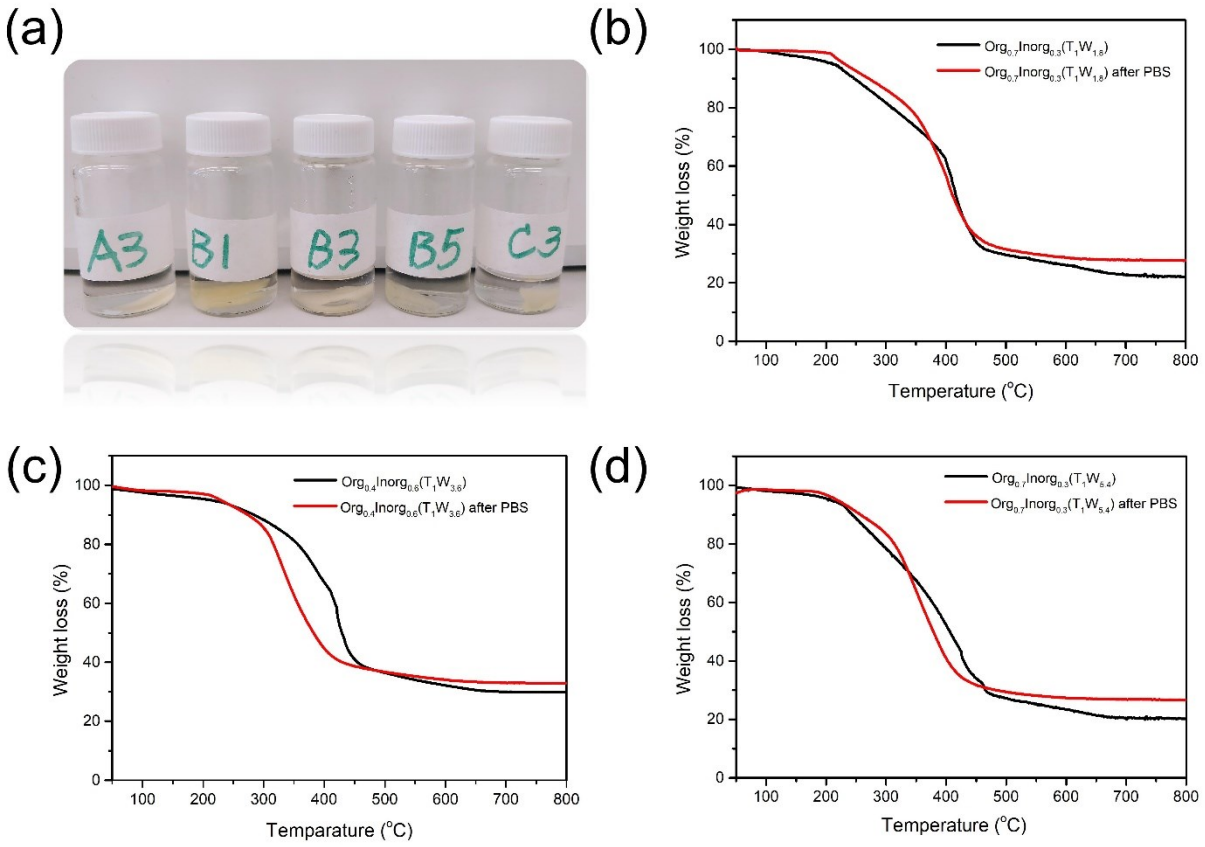


Fig. S14 (a) Pictures of hybrids after immersion (A3-C3 respresent hybrids $Org_{0.7}Inorg_{0.3}(T_1W_{1.8})$; (b) $Org_{0.9}Inorg_{0.1}(T_1W_{3.6})$; $Org_{0.7}Inorg_{0.3}(T_1W_{3.6})$; $Org_{0.4}Inorg_{0.6}(T_1W_{3.6})$; and $Org_{0.7}Inorg_{0.3}(T_1W_{5.4})$, respectively); TGA curves of hybrids (b) $Org_{0.7}Inorg_{0.3}(T_1W_{1.8})$; (c) $Org_{0.4}Inorg_{0.6}(T_1W_{3.6})$; (d $Org_{0.7}Inorg_{0.3}(T_1W_{5.4})$ before and after immersed in PBS solution.

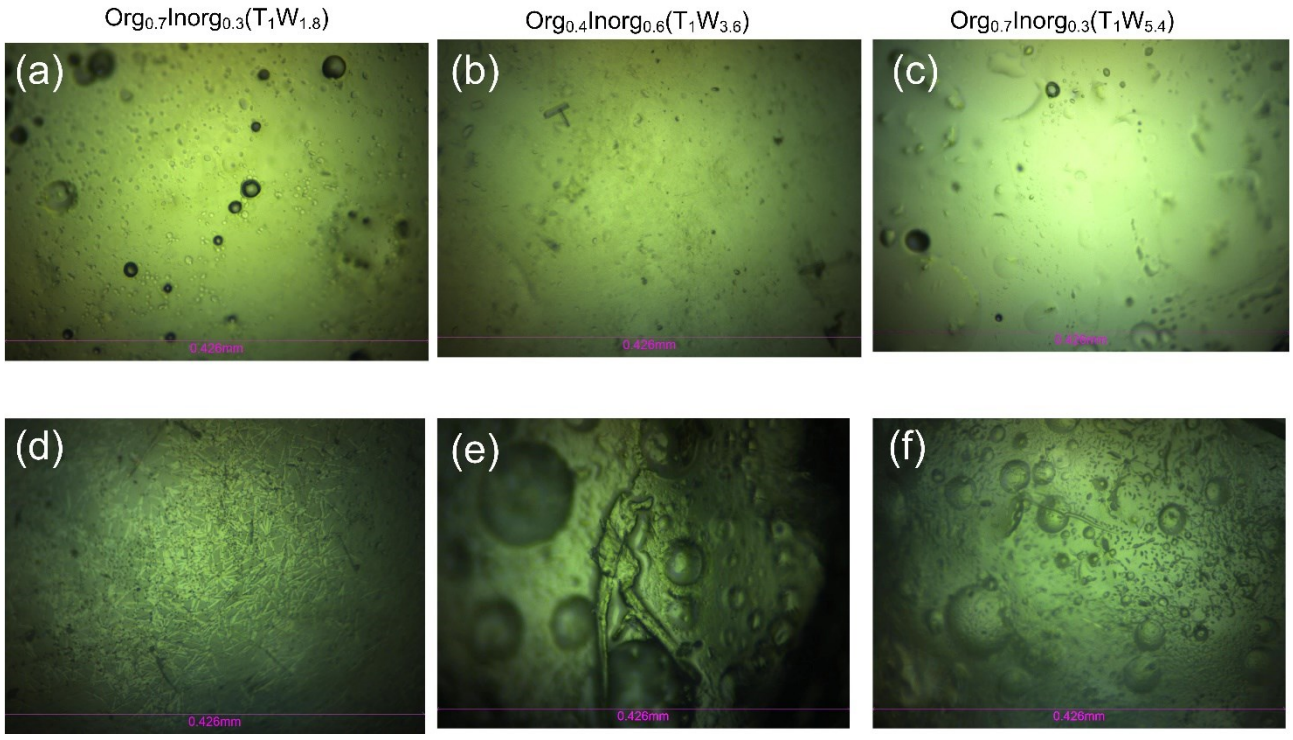


Fig. S15 Optical microscope images of hybrids before immersed in PBS (a) $Org_{0.7}Inorg_{0.3}(T_1W_{1.8})$; (b) $Org_{0.4}Inorg_{0.6}(T_1W_{3.6})$; (c) $Org_{0.7}Inorg_{0.3}(T_1W_{5.4})$; after immersed in PBS (d) $Org_{0.7}Inorg_{0.3}(T_1W_{1.8})$; (e) $Org_{0.4}Inorg_{0.6}(T_1W_{3.6})$; (f) $Org_{0.7}Inorg_{0.3}(T_1W_{5.4})$.

Table S1. Compositions of different hybrids.

Types	TEOS (mol)	H_2O (mol)	TEOS (wt %)	PCL-diCOOH (wt%)
$Org_{0.9}Inorg_{0.1}(T_1W_{1.8})$	1	1.8	10	90
$Org_{0.8}Inorg_{0.2}(T_1W_{1.8})$	1	1.8	20	80
$Org_{0.7}Inorg_{0.3}(T_1W_{1.8})$	1	1.8	30	70
$Org_{0.6}Inorg_{0.4}(T_1W_{1.8})$	1	1.8	40	60
$Org_{0.4}Inorg_{0.6}(T_1W_{1.8})$	1	1.8	60	40
$Org_{0.9}Inorg_{0.1}(T_1W_{3.6})$	1	3.6	10	90
$Org_{0.8}Inorg_{0.2}(T_1W_{3.6})$	1	3.6	20	80
$Org_{0.7}Inorg_{0.3}(T_1W_{3.6})$	1	3.6	30	70
$Org_{0.6}Inorg_{0.4}(T_1W_{3.6})$	1	3.6	40	60
$Org_{0.4}Inorg_{0.6}(T_1W_{3.6})$	1	3.6	60	40
$Org_{0.9}Inorg_{0.1}(T_1W_{5.4})$	1	5.4	10	90
$Org_{0.8}Inorg_{0.2}(T_1W_{5.4})$	1	5.4	20	80
$Org_{0.7}Inorg_{0.3}(T_1W_{5.4})$	1	5.4	30	70
$Org_{0.6}Inorg_{0.4}(T_1W_{5.4})$	1	5.4	40	60
$Org_{0.4}Inorg_{0.6}(T_1W_{5.4})$	1	5.4	60	40