Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Polysiloxane-Based Two-Photon Fluorescent Elastomers with Superior Mechanical and Self-healing Properties and Their Application in Bioimaging

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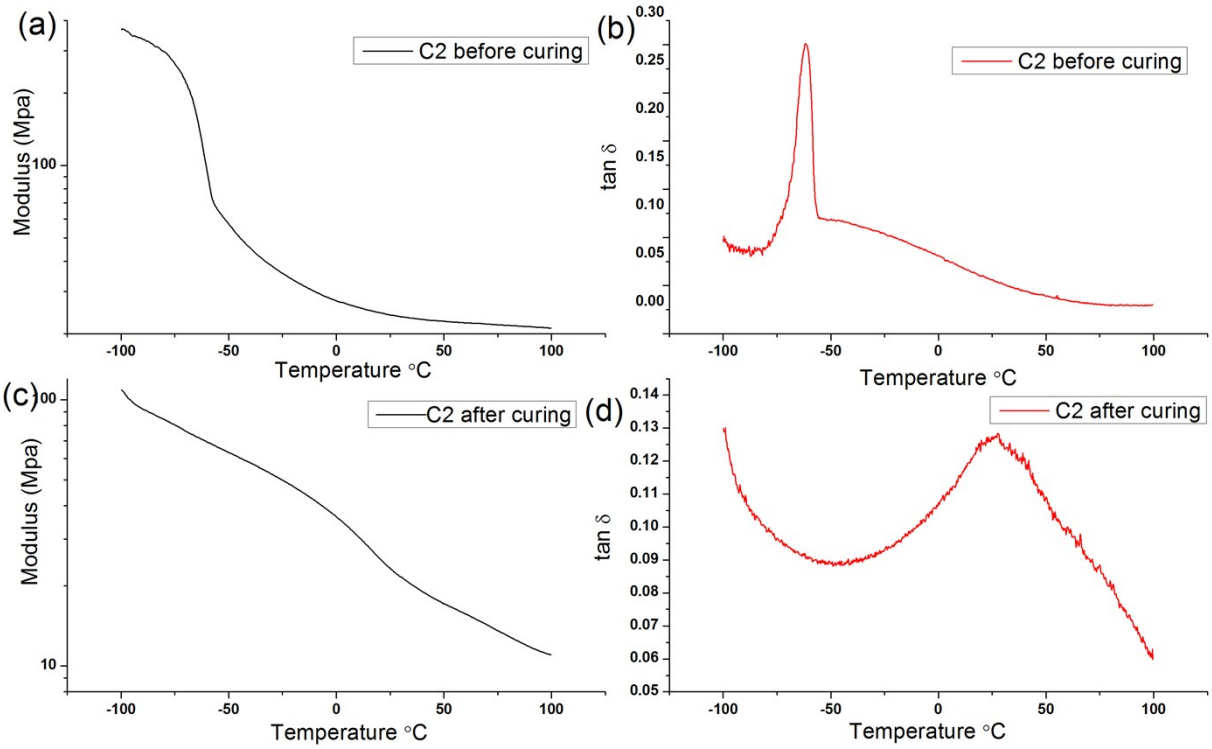


Figure S1. DMA curves of C2 before curing process and after curing, respectively. Modulus versus temperature [(a) and (c)] and Tan δ versus temperature [(b) and (d)].

Note:

The storage modulus of C2 decreased after curing step. The glass–transition temperature of C2 before curing is observed at –85 °C and tan δ is about 0.29, whereas after curing was found at 17 °C and 0.14. The glass-transition temperature increased dramatically after curing, however, the peak values of tan δ of C2 decreased. The DMA analysis demonstrated that the thermal curing process changed the cross-linking structure of C2 obviously. The concrete performance was the increasing of the cross-linking density.

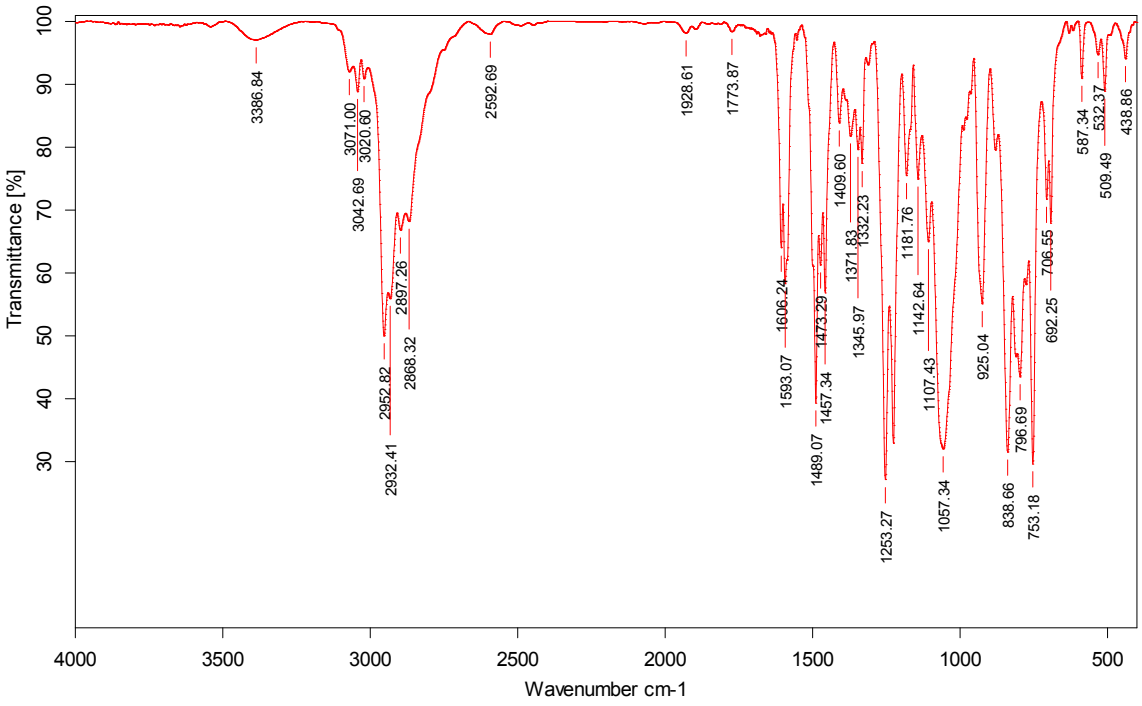


Figure S2. FT-IR spectral of **P1**.

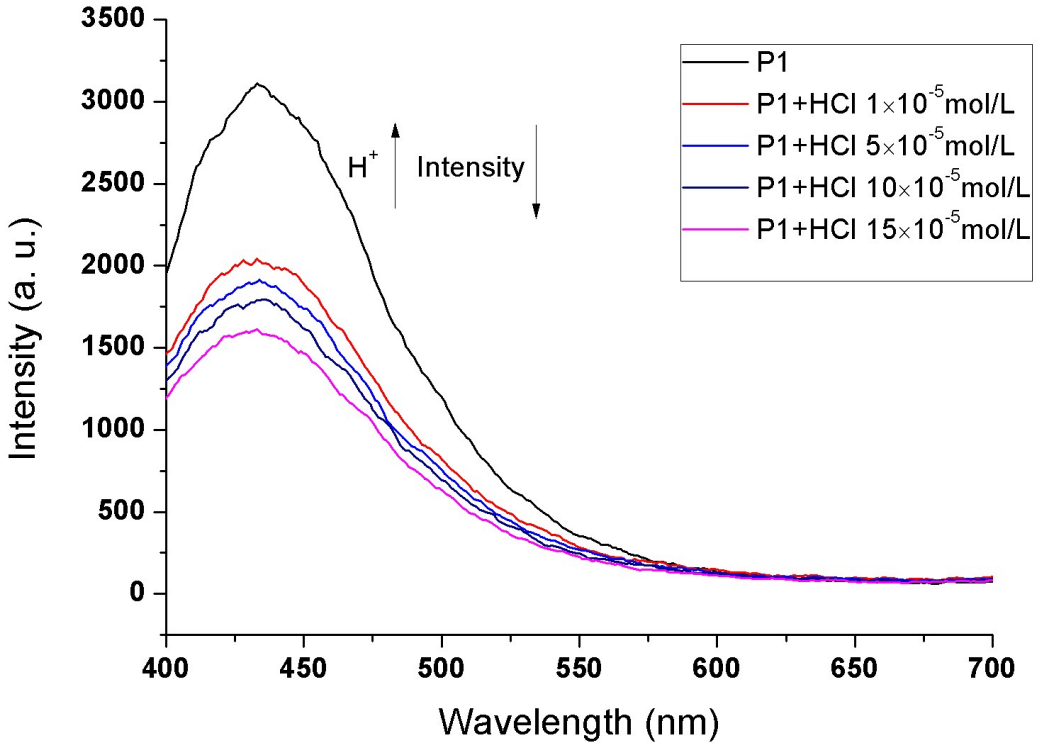


Figure S3. Fluorescence spectra of P1 (5 mg/mL) solution with HCl treated.

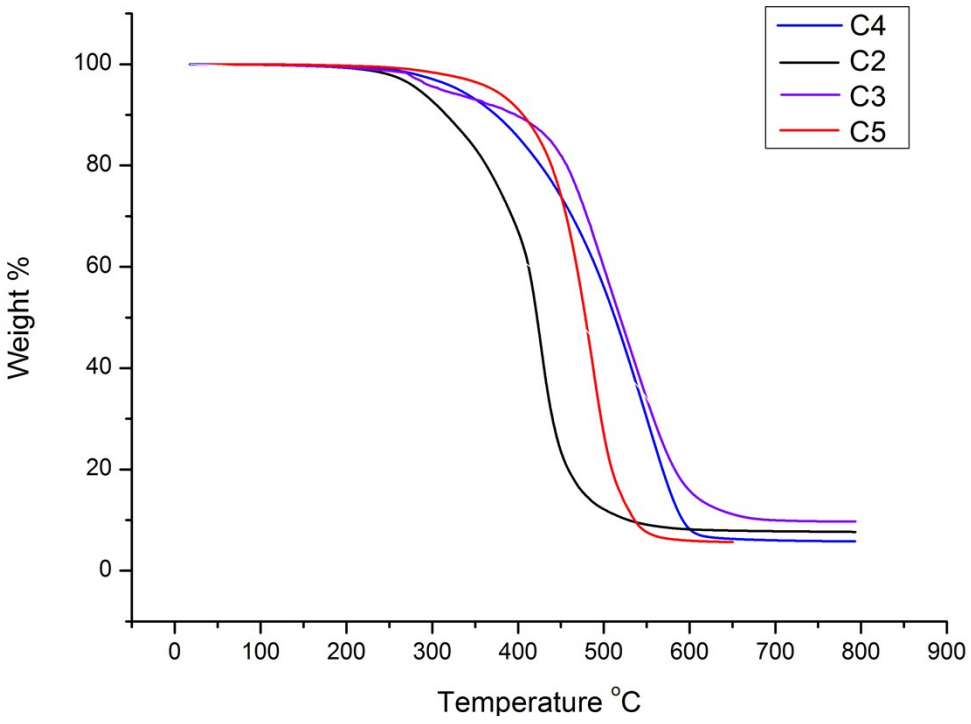


Figure S4. TGA curves of C2, C3, C4 and C5.

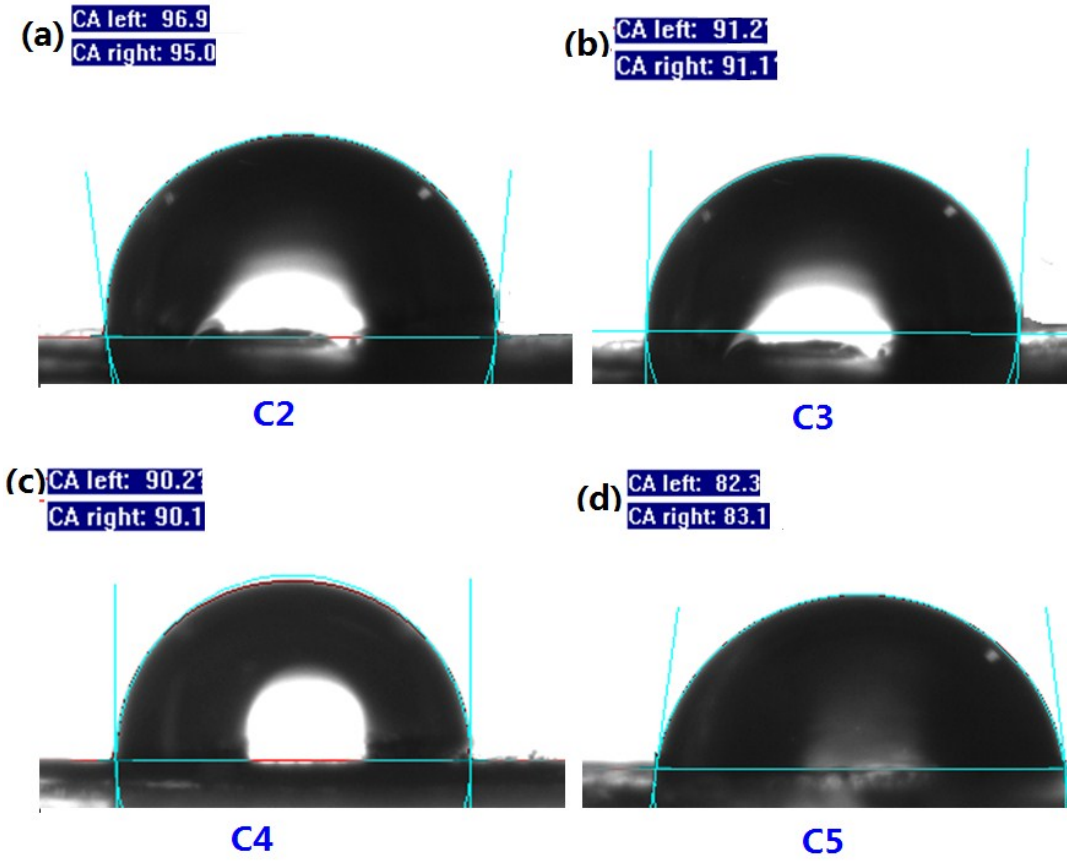


Figure S5. Contact angles of the samples C2 (a), C3 (b), C4 (c), and C5 (d).

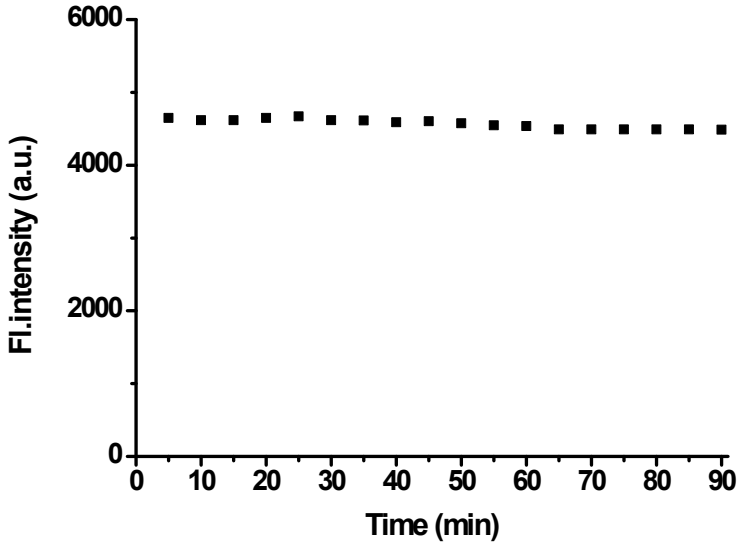


Figure S6. Photostability testing result for P1 in THF solution.

Note:

P1 is a potential platform for development of two photon fluorescent materials; thus, we decided to further evaluate its stability against photo. As shown in Figure S6, treatment of P1with ceaseless irradiation of 405 nm for 90 min induced no marked changes in the fluorescence intensity. The result indicated that P1 exhibited fine photostability.

The fluorescence quantum yields (FQY) of P1 was measured in THF solution using Quinine sulfate in 0.05 mol/L H_2SO_4 as the standard. The corrected fluorescent intensities were measured using quinine sulfate as standard.[1] The relative quantum yields was calculated in the equation below:

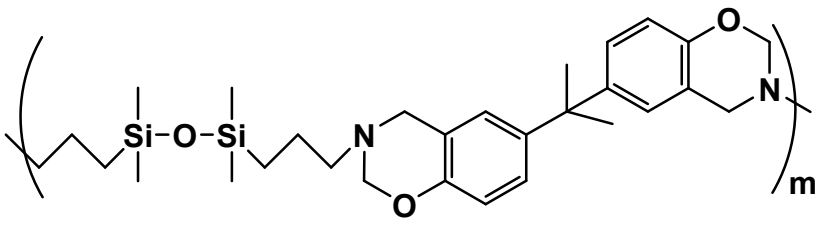
$$Q_x = Q_r(\frac{A_r}{A_x})(\frac{I_r}{I_x})(\frac{n_x^2}{n_r^2})(\frac{D_x}{D_r})$$

Q_x is the quantum yield of the testing solution, Q_r refers to the quantum yield of the standard solution, A was the absorbance intensity of the solution at the exciting wavelength, I represent the relative intensity of the exciting light, n was the average refractive index of the solution to the luminescence and *D* is the integrated area under the corrected emission spectrum.

Subscript X and r refer to the testing and standard solution, respectively. Ar= 0.05, λ_{ex}= 320 nm, Q_r= 0.508.[1,2]

The FQY of P1 determined in THF solution was about 0.107.

Model compound:



Scheme S1. The structure of model compound used for elemental analysis.

Elemental analysis for model compound:

Elemental Anal. Calc. for $C_{31}H_{50}N_2O_3Si_2$: C, 67.10; H, 9.08; N, 5.05, O, 8.65, Si, 10.12 %. Found: C, 67.11; H, 9.12; N, 5.04, O, 8.67, Si, 10.06 %.

The cross-linking density and Mc were calculated by the equations followed:

φ was obtained from Eq. (1):

$$\varphi = \frac{W_o / \rho_2}{\left[(W_t - W_o)/\rho_1 + W_o/\rho_1\right]} \quad (1)$$

where ρ_1 and ρ_2 were the densities of the toluene and the polysiloxane, respectively.

Mc was calculated by Eq. (2):

$$Mc = \frac{-\rho_2 V_0 \varphi^{1/3}}{\left[\ln(1-\varphi) + \varphi + \chi\varphi_2\right]} \quad (2)$$

where Mc was the average molecular weight between crosslink points, V_o represented the solvent volume, and χ denotes the Flory–Huggins interaction parameter 0.465.

Finally, crosslinking density (υ) was obtained using Eq. (3):

$$\upsilon = \frac{\rho_1}{Mc} \tag{3}$$

Table S1. **Crosslink densities, swelling ratio, and Mc of Cns**

Sample name	**Swelling (%)**	**φ**	**Crosslinking density ve×10⁴（mol/cm³）**	**Mc (g/mol)**
C1	870	0.060	0.51	20734
C2	778	0.068	0.55	19362
C3	790	0.067	0.54	19680
C4	752	0.070	0.52	16773
C5	797	0.066	0.55	19827

Note:

To investigate the H-bonding and π-π interactions, and Van der Waals force, we used the toluene swelling method to measure the crosslink density (v) and Mc as the data values for supramolecular interaction of the obtained silicone elastomers (Cns). The results of crosslinking density were shown in **Table S1**. Before thermal treating, the cross-linking density of Cns were about 0.50, the Mc between two cross-linking sites were about 20000 g/mol. The supramolecular interactions rendered physical cross-linking sites for P1.

Table S2. Distances of the benzene-polar H, N-H, H-H and benzene-benzene calculated at D-mol^3 program in MATERIAL STUDIO -optimized geometries

Polar π	**H-**	**Van**	**der**	**π-π**

	(benzene-polar H)	bonding (N-H)	Waals force (H-H)	（benzene-benzene）
Distance (Å)	2.776	2.205	2.392	2.679

Reference

1. J. Demas and G. Crosby, *J. Phys. Chem.*, 1971, **75**, 991–1024.

2. L. Li, S. Feng, and H. Liu, *RSC Adv.*, 2014, **4**, 39132-39139.