Electronic Supplementary Information (ESI)

# Roles of both amines and acid in supramolecular hydrogel formation of tetracarboxyl acids-appended calix[4]arene gelator

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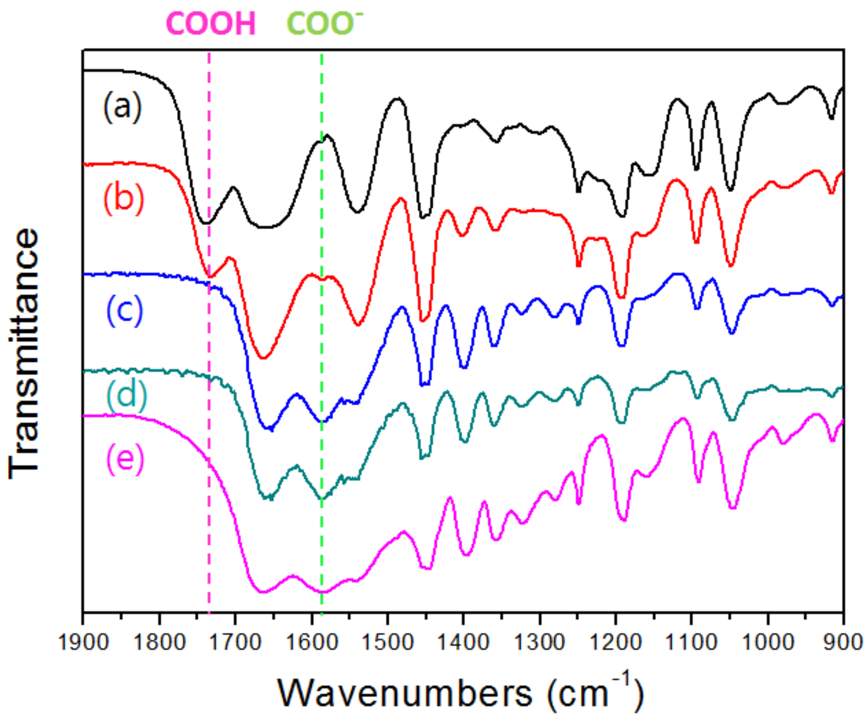


**Fig. S1** FT IR spectra of **1** (a) without and with (b) 1.0, (c) 2.0, (d) 3.0 and (e) 4.0 equivalents of diaminobutane.

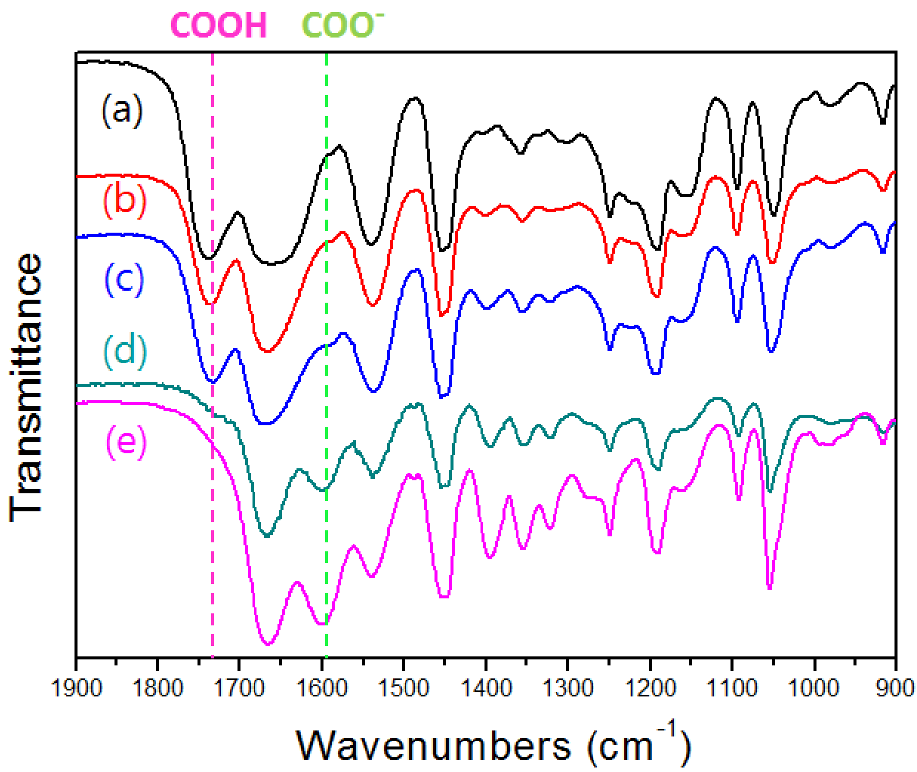


**Fig. S2** FT IR spectra of **1** (a) without and with (b) 1.0, (c) 2.0, (d) 3.0 and (e) 4.0 equivalents of monoaminobutane.

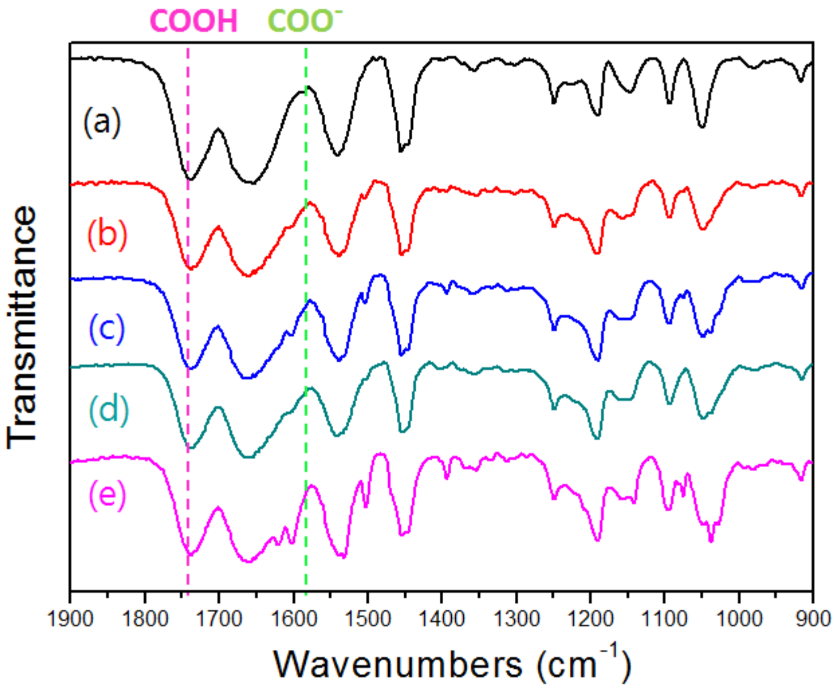


**Fig. S3** FT IR spectra of **1** without (a) and with (b-e) diaminobutane (b: 1 equiv., c: 2 equiv., d: 3 equiv. and e: 4 equiv.) in the presence of HCl (2 equiv.).

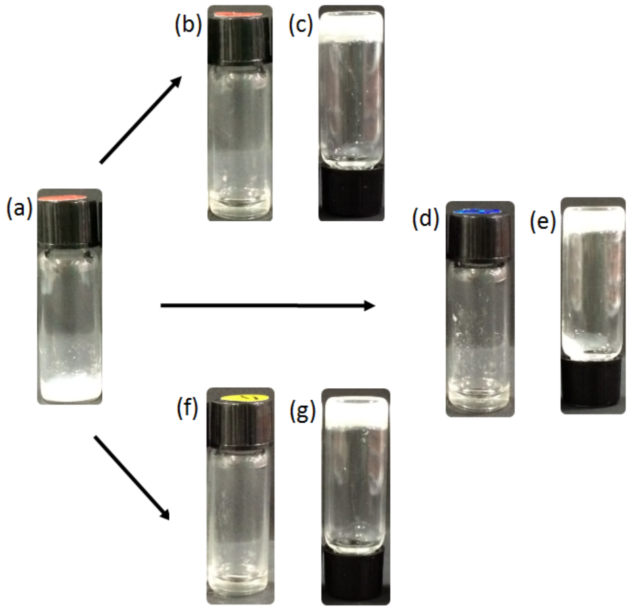


**Fig. S4** Photographs of (a) **1**, (b) **1**+DABCO (4 equiv.), (c) **1**+DABCO (4 equiv.)+HCl (2 equiv.), (d) **1**+N,N′-dimethylppiperazine (4 equiv.), (e) **1**+N,N′-dimethylppiperazine (4 equiv.)+HCl (2 equiv.), (f) **1**+TMEA (4 equiv.) and (g) **1**+TMEA (4 equiv.)+HCl (2 equiv.).

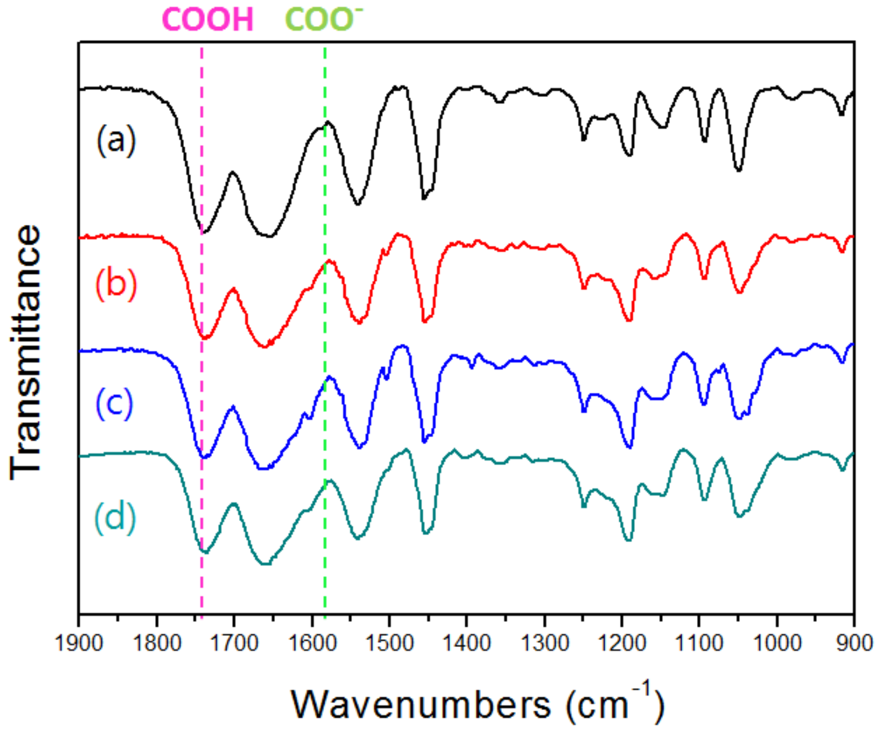


**Fig. S5** FT IR spectra of (a) **1**, (b) **1**+DABCO (4 equiv.)+HCl (2 equiv), (c) **1**+N,N´-dimethylppiperazine (4 equiv.)+HCl (2 equiv.) and (d) **1**+TMEA (4 equiv.)+HCl (2 equiv.).

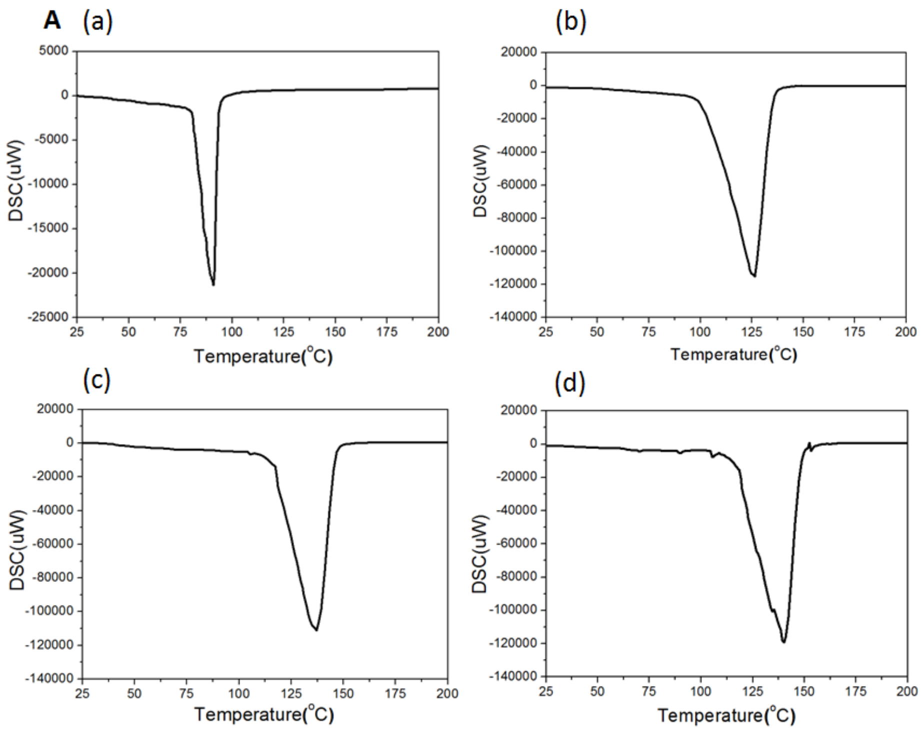


**Fig. S6** DSC thermograms of (a) **1+**diaminobutane (1 equiv.)+HCl (2 equiv.), (b) **1**+diaminobutane (2 equiv.)+HCl (2 equiv.), (c) **1**+diaminobutane (3 equiv.)+HCl (2 equiv.) and (d) **1**+diaminobutane (4 equiv.)+HCl (2 equiv.).

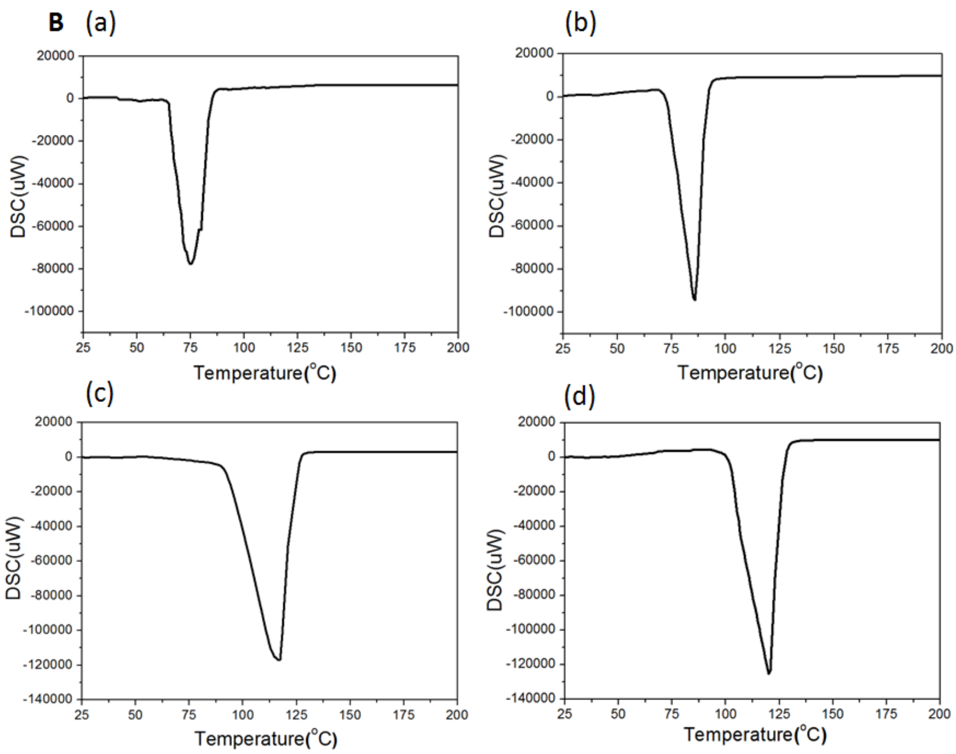


**Fig. S7** DSC thermograms of (a) **1+**monoaminobutane (1 equiv.)+HCl (2 equiv.), (b) **1**+monoaminobutane (2 equiv.)+HCl (2 equiv.), (c) **1**+monoaminobutane (3 equiv.)+HCl (2 equiv.) and (d) **1**+monoaminobutane (4 equiv.)+HCl (2 equiv.).

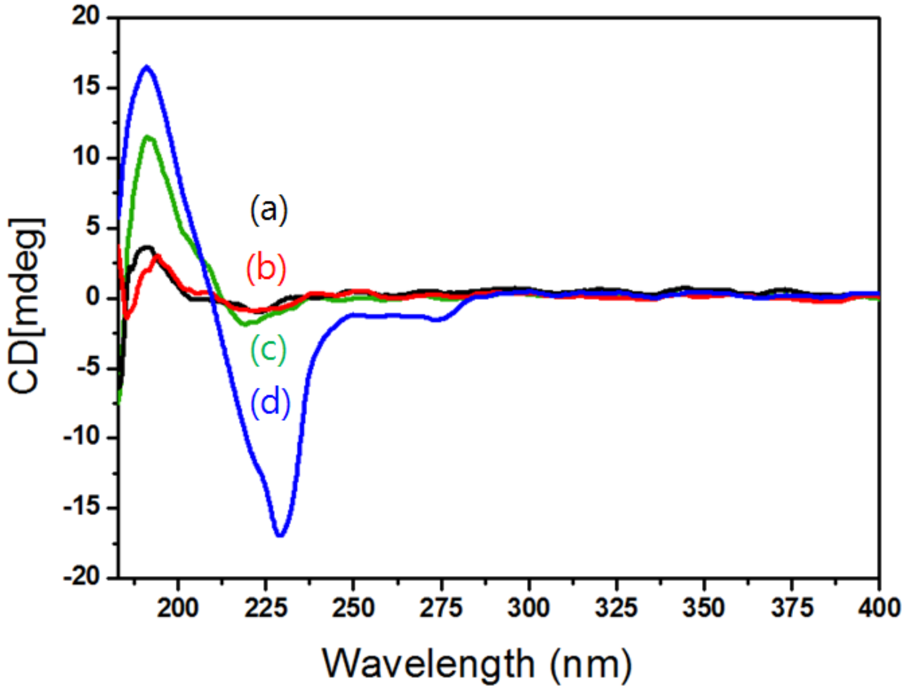


**Fig. S8** CD spectra of (a) **1**+diaminobutane (1 equiv.)+HCl (2 equiv.), (b) **1**+ diaminobutane (2 equiv.)+HCl (2 equiv.), (c) **1**+ diaminobutane (3 equiv.)+HCl (2 equiv.), (d) **1**+ diaminobutane (4 equiv.)+HCl (2 equiv.).

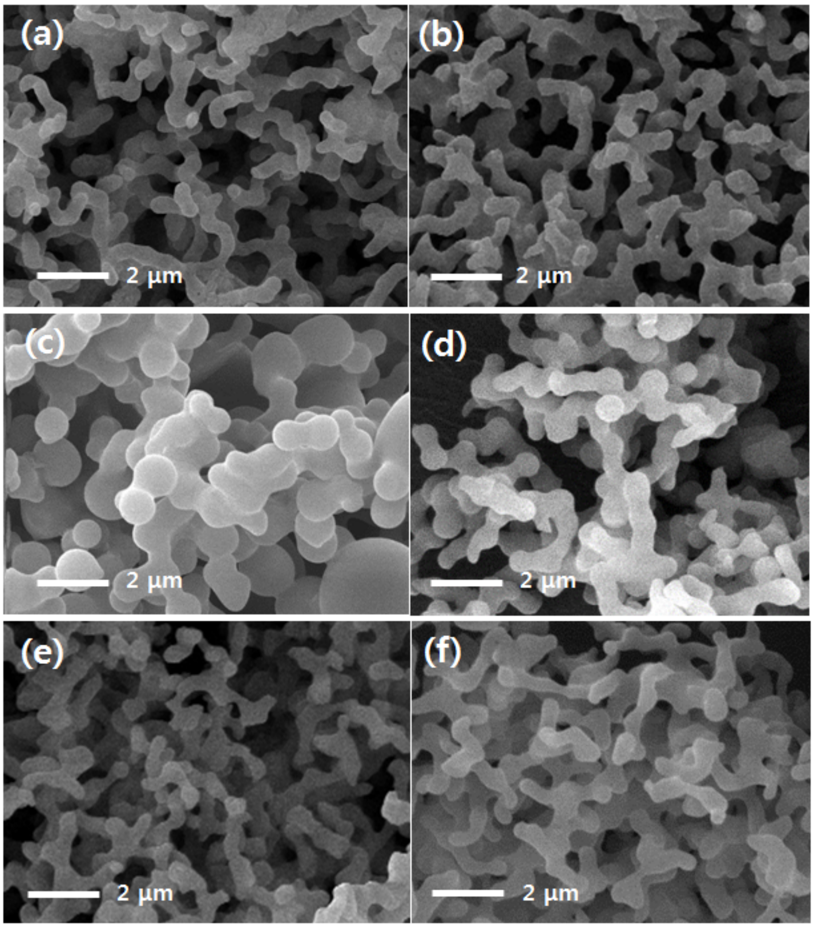


**Fig. S9** SEM images of (a) **1**+diaminobutane (2 equiv.)+HCl (2 equiv.), (b) **1**+ diaminobutane (3 equiv.)+HCl (2 equiv.), (c) **1**+ monoaminobutane (2 equiv.)+HCl (2 equiv.), (d) **1**+ monoaminobutane (3 equiv.)+HCl (2 equiv.), (e) **1**+ DABCO (2 equiv.)+HCl (2 equiv.) and (f) **1**+ DABCO (3 equiv.)+HCl (2 equiv.).

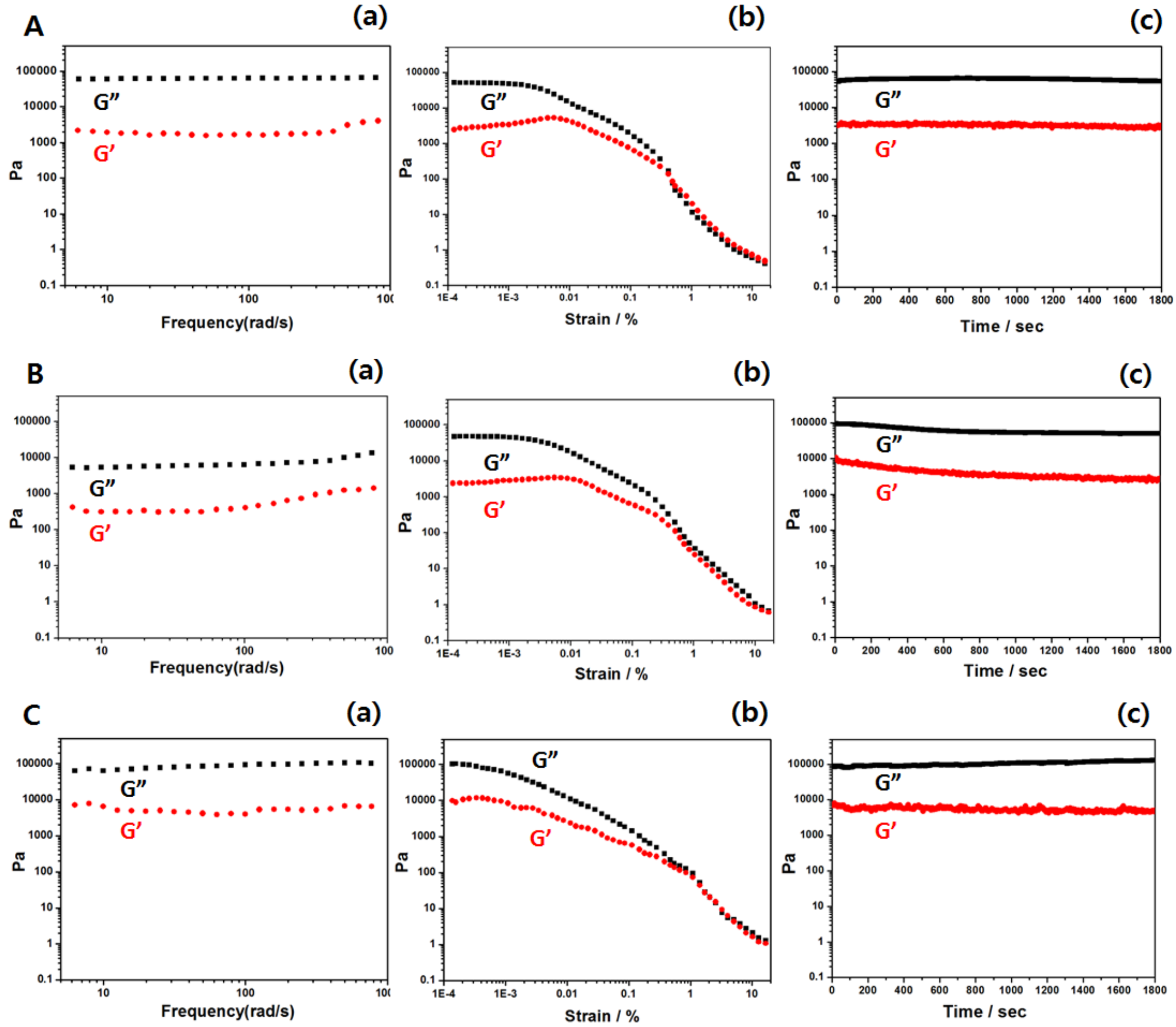


**Fig. S10** Rheological data. (A) hydrogel **1** with diaminobutane (4 equiv.) and HCl (2 equiv.), (B) hydrogel **1** with monoaminobutane (4 equiv.) and HCl (2 equiv.) and (C) hydrogel **1** with DABCO (4 equiv.) and HCl (2 equiv.). (a) Frequency dependences of elastic modulus (red line; G’) and viscous modulus (black line, G”), (b) Strain dependence of elastic modulus (red line; G’) and viscous modulus (black line, G”) at a frequency of 1 rads$^{-1}$ and (c) time dependence of elastic modulus (red line; G’) and viscous modulus (black line, G”) at the heating rate of 1 $^{o}$C min$^{-1}$, strain of 0.1 % and frequency of 1 rad s$^{-1}$.

**Table S1**. Amount of –COOH and $COO^{-}$ species of **1** in the different concentration of diaminobutane.

| diaminobutane | Sol **1** | |
|---|---|---|
| | $COO^{-}$ | COOH |
| 0 equiv. | 22 % | 78 % |
| 1 equiv. | 48 % | 52 % |
| 2 equiv. | 100 % | 0 |
| 3 equiv. | 100 % | 0 |
| 4 equiv. | 100 % | 0 |

**Table S2**. Amount of –COOH and $COO^{-}$ species of **1** in the different concentration of monoaminobutane.

| monoaminobutane | Sol **1** | |
|---|---|---|
| | $COO^{-}$ | COOH |
| 0 equiv. | 22 % | 78 % |
| 1 equiv. | 27 % | 73 % |
| 2 equiv. | 35 % | 65 % |
| 3 equiv. | 100 % | 0 |
| 4 equiv. | 100 % | 0 |

**Table S3**. Amount of –COOH and $COO^-$ species of **1** in the different concentration of DABCO.

| DABCO | Sol 1 | |
|---|---|---|
| | $COO^-$ | COOH |
| 0 equiv. | 22 % | 78 % |
| 1 equiv. | 52 % | 48 % |
| 2 equiv. | 100 % | 0 |
| 3 equiv. | 100 % | 0 |
| 4 equiv. | 100 % | 0 |