

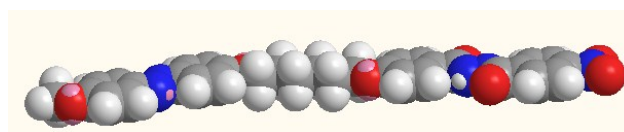
Supporting information

Multistimuli-responsive organogels based on hydrazide and azobenzene derivatives

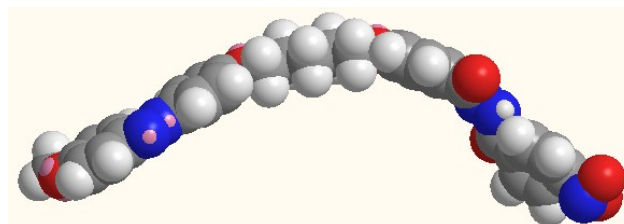
Table 1 Gelation properties of **E5**, **E6** and **E10** in various solvents

Solvent	E5	E6	E10
DMF	S	G (8)	G (11.5)
THF	S	S	S
DMSO	S	S	S
CHCl ₃	I	I	I

I: insoluble; G: stable gel formed at room temperature; S: soluble; Numbers in parentheses present the critical gel concentration (CGC, mg/mL).



(a)



(b)

Fig. S1 The molecular shapes of: (a) **E6**, an even; (b) **E5**, an odd numbered central spacer in the all-*trans* conformation (calculated by MM2).

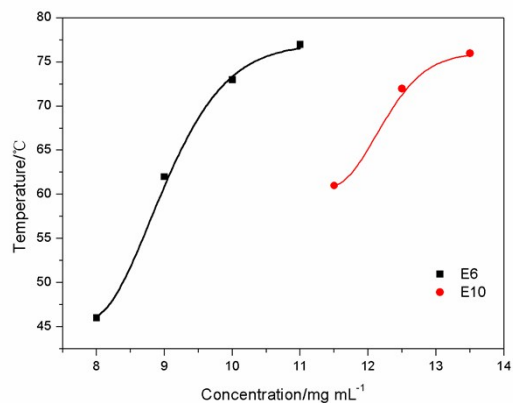


Fig.S2 Plots of T_{gel} versus the concentration of **E6** (■) and **E10** (●) in DMF.

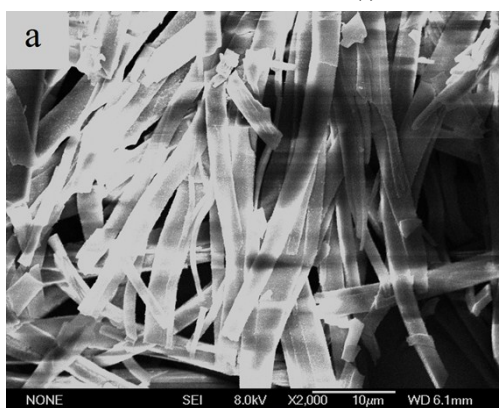


Fig. S3 SEM images of **E5** solution in DMF(25 mg/ml).

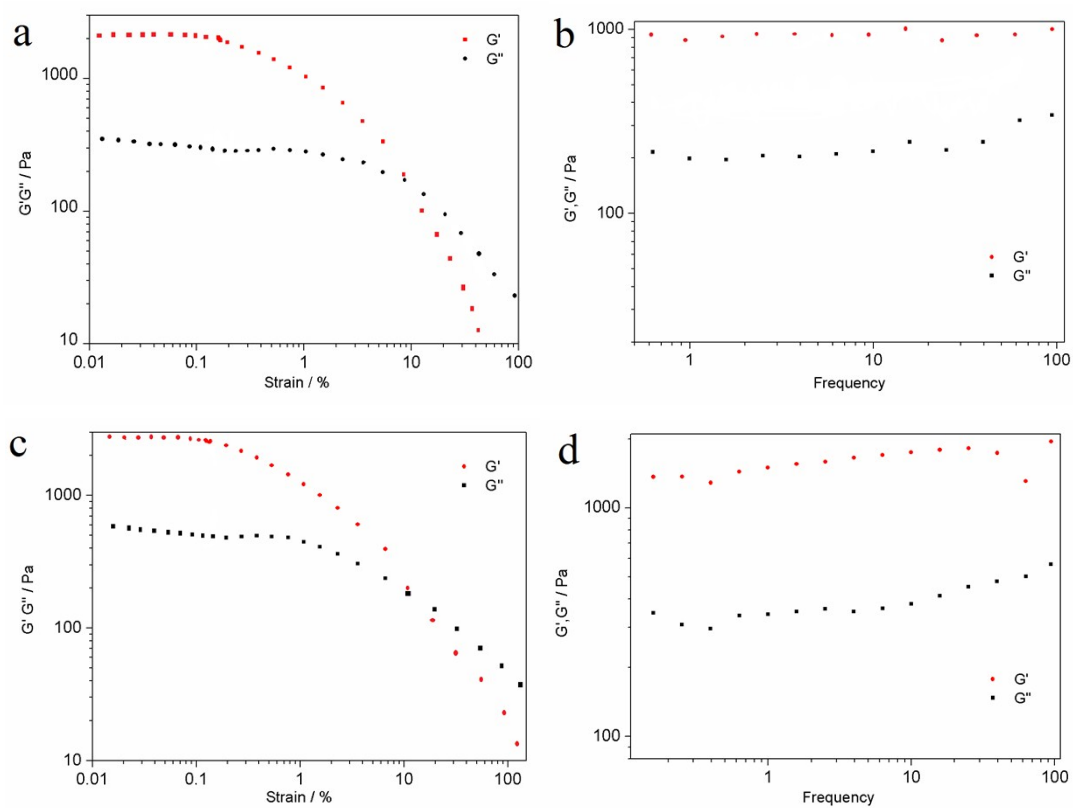


Fig. S4 (a) Amplitude dependencies and (b) Frequency dependency of storage modulus (G') and loss modulus (G'') of **E6** gel in DMF (12mg/ml). (c) Amplitude dependencies and (d) Frequency dependency of storage modulus (G') and loss modulus (G'') of **E10** gel in DMF (The frequency is 1 Hz and the strain is 0.1%, 12mg/ml).

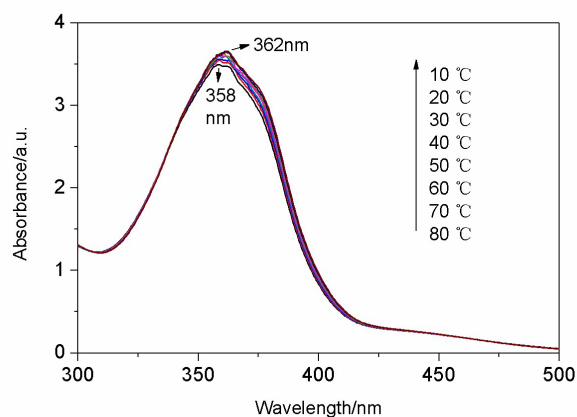


Fig. S5 Temperature-dependent UV-vis absorption spectra of **E6** solution (1×10^{-3} mol/L) in DMF

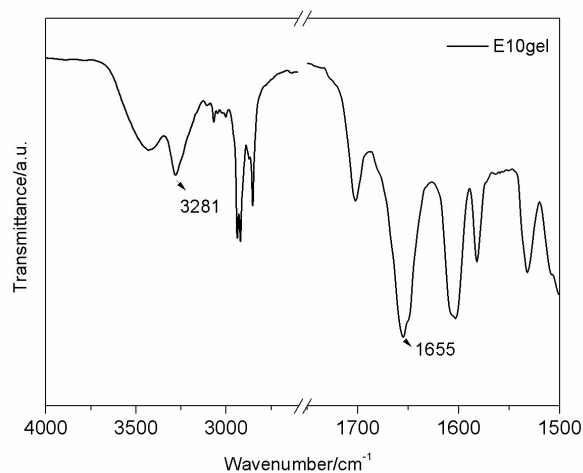


Fig. S6 FTIR spectra of **E10** xerogel (11mg/mL) in DMF.

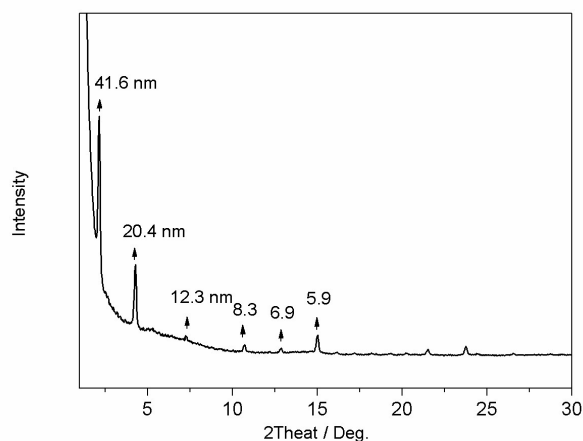


Fig. S7 X-Ray diffraction pattern of **E10** xerogel (11.5mg/ml) in DMF.

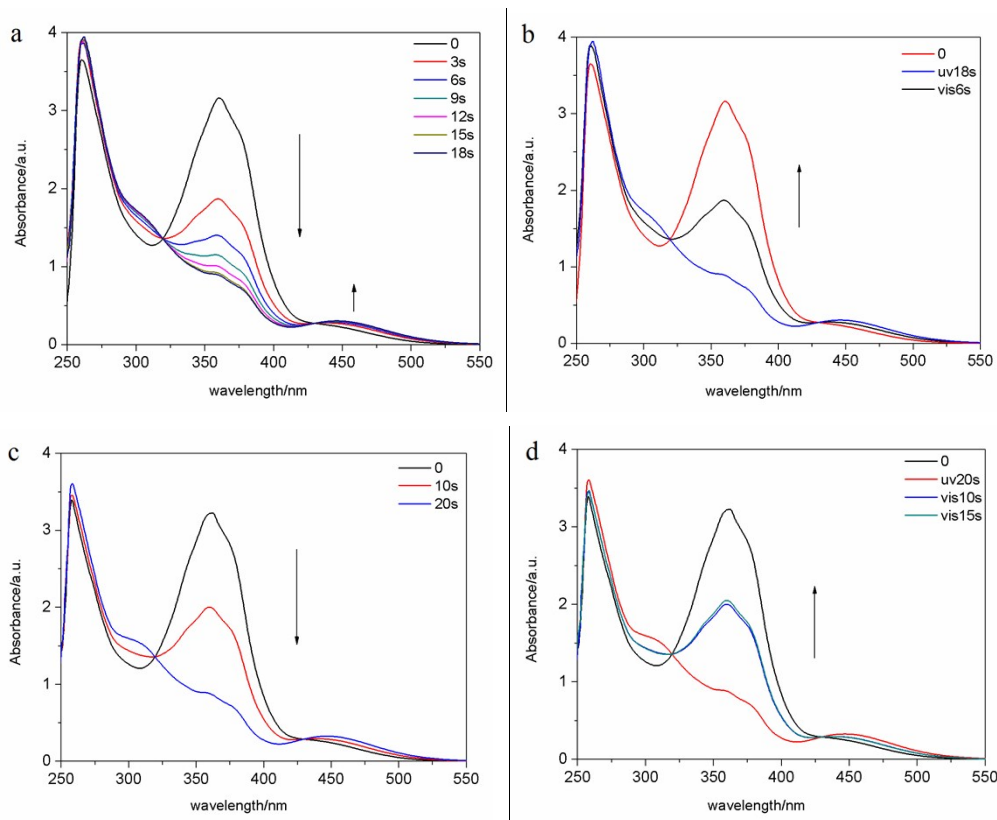


Fig. S8 UV-vis spectra of solution in DMF (1×10^{-3} mol/L) (a) **E5** under irradiation at UV light for 0-18s; (b) **E5** under visible light irradiation for 6s; (c) **E10** under irradiation at UV light for 20s; (d) **E10** under visible light irradiation for 15s.

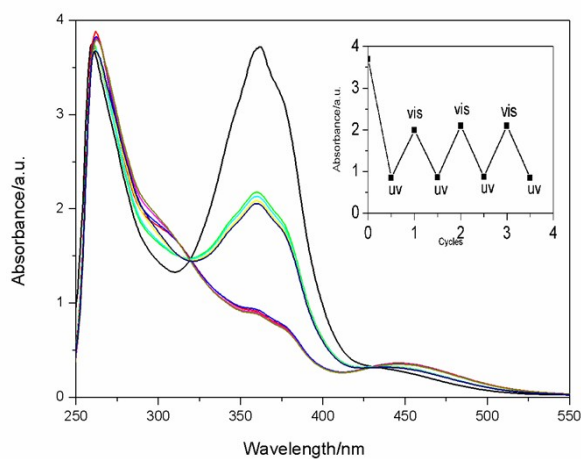


Fig. S9 UV-vis spectra of **E6** solution in DMF (1×10^{-3} mol/L) are irradiated multiple times by UV and vis light.

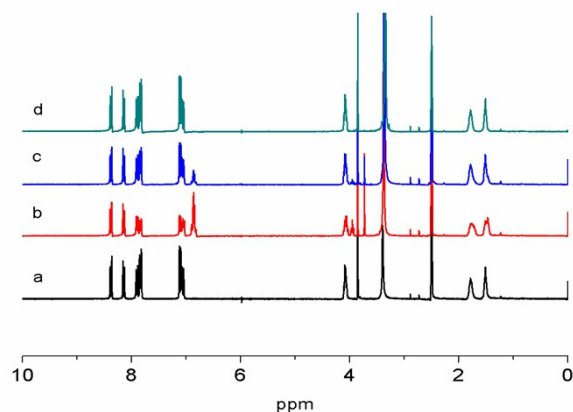


Fig. S10 Partial ^1H -NMR spectrum of **E6** upon alternating irradiation (a) none; (b) UV light for 1.5h ; (c) vis light for 1.5h ; (d) heat in $\text{DMSO-d}_6(1 \times 10^{-2} \text{mol/L})$.

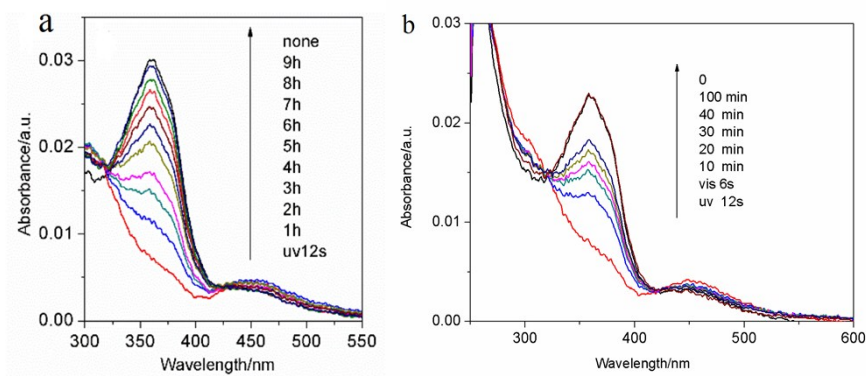


Fig. S11 The *trans*-azobenzene of **E₆** ($1 \times 10^{-5} \text{mol/L}$) be recovered by place in darkness (a) after UV light irradiation and then placed in darkness for 9h; (b) after UV light irradiation for 12s and vis light irradiation 6s, and then placed in darkness for 100min.

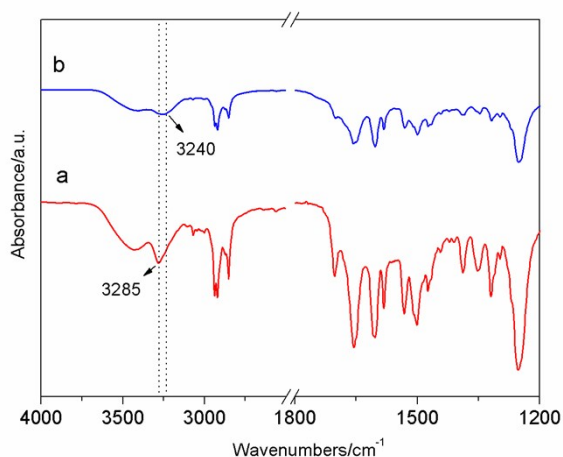


Fig. S12 FTIR spectra of (a) xerogel of **E10** gel in DMF; (b) the precipitate developed from the gel in DMF under the irradiation of 365 nm UV light.

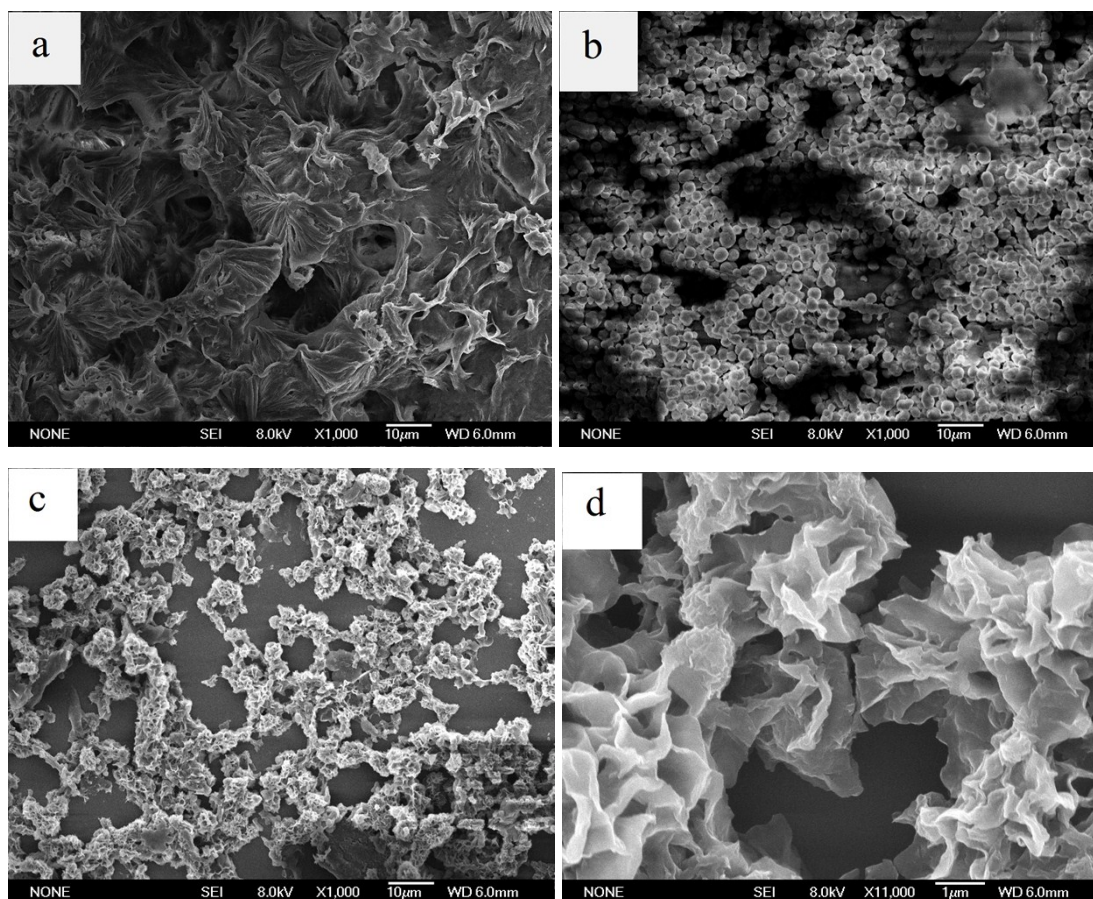
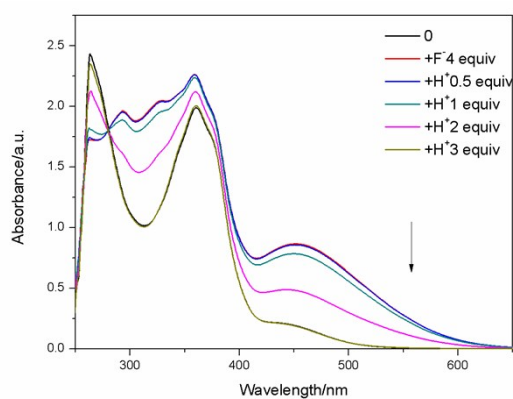


Fig. S13 SEM images of **E10**: (a) the precipitate from organogel in DMF under irradiation by 365 nm UV light for 9h ; (b) the solution of organogel in DMF under irradiation by 365 nm UV light for 9h. (c) (d) the solution after visible light irradiation. (11.5 mg/mL)



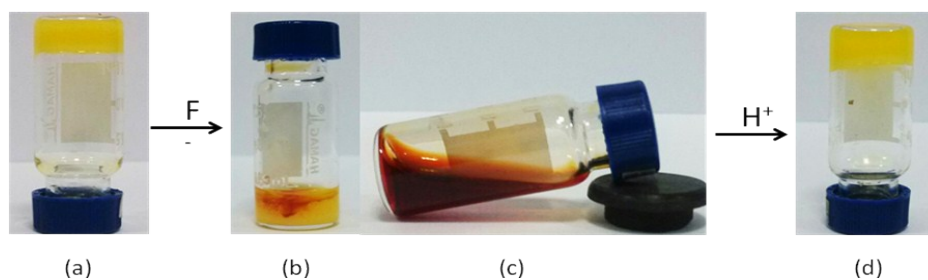


Fig. S14 (a) **E6** organogel (8mg/ml, in DMF); (b) immediately after addition of solid TBAF (10equiv); (c) after 1 min; (d) addition of H^+ .

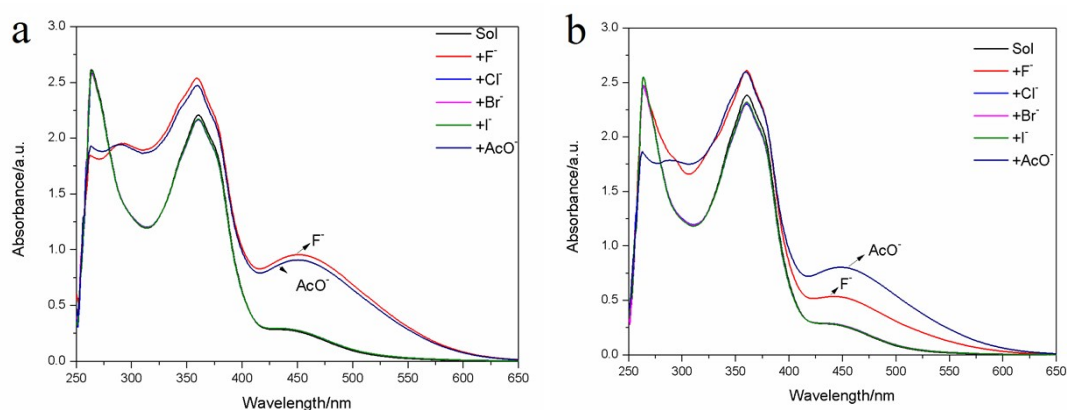
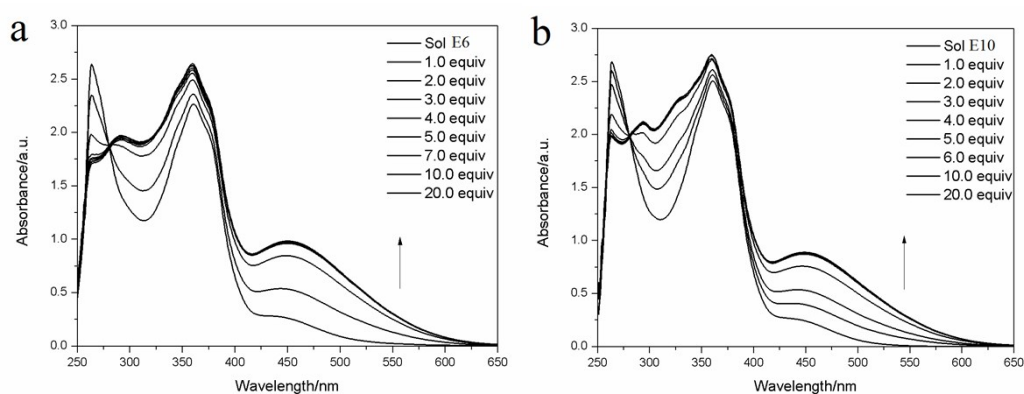


Fig. S15 UV-vis spectra of (a) **E5**; (b) **E10** (1×10^{-4} mol/L) in DMF upon addition of 10 equiv of various anions (F^- , Cl^- , Br^- , I^- , AcO^-).



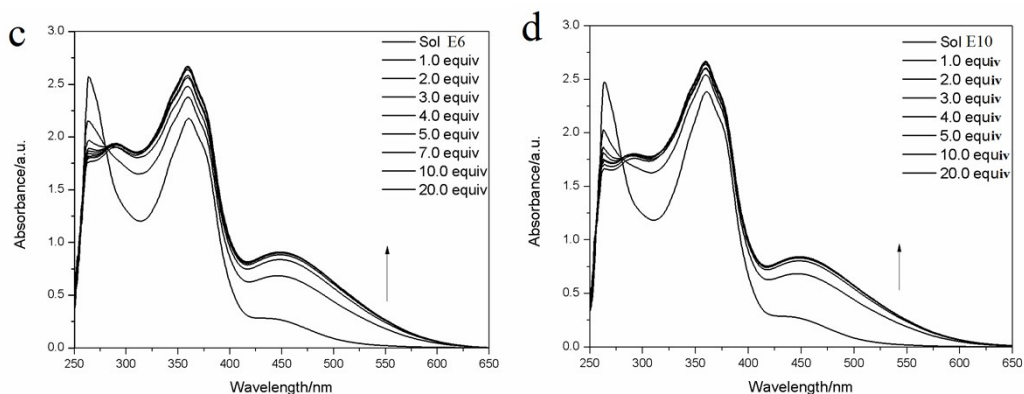


Fig. S16 UV-vis absorption spectra of **E6** and **E10** solution in the presence of F^- (a, b) and AcO^- (c, d) in DMF ($1 \times 10^{-4} \text{ mol/L}$).

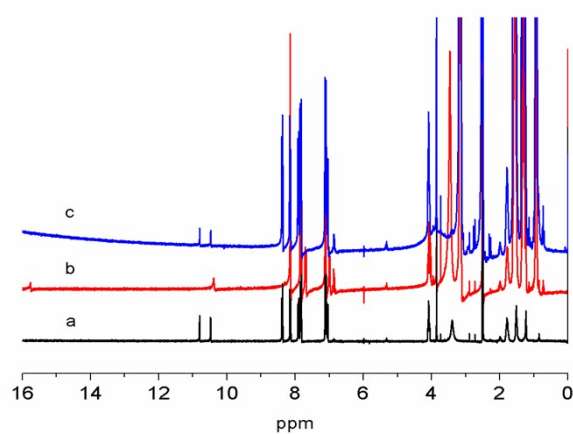


Fig. S17 Partial 1H -NMR spectra of **E6** in the addition of (a) none; (b) 5 equiv F^- ; (c) 10 equiv CF_3COOH in $DMSO-d_6$ ($1 \times 10^{-2} \text{ M}$).

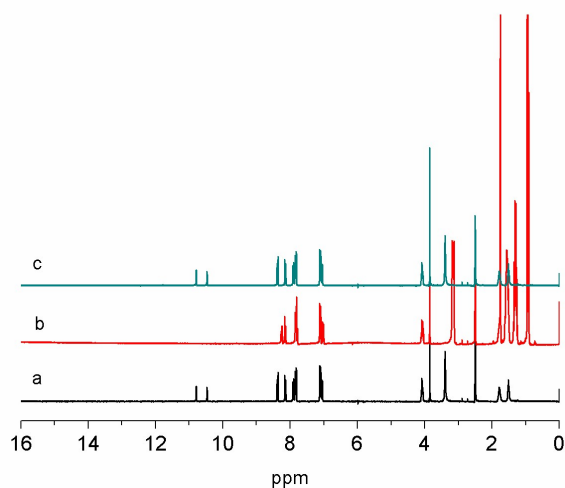


Fig. S18 Partial 1H -NMR spectra of **E6** in the addition of (a) none; (b) 3 equiv AcO^- ; (c) 10 equiv CF_3COOH in $DMSO-d_6$ ($1 \times 10^{-2} \text{ mol/L}$).

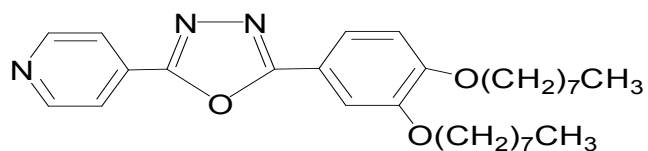


Fig. S19. Molecular structure of compound **4-poxd-B8**.

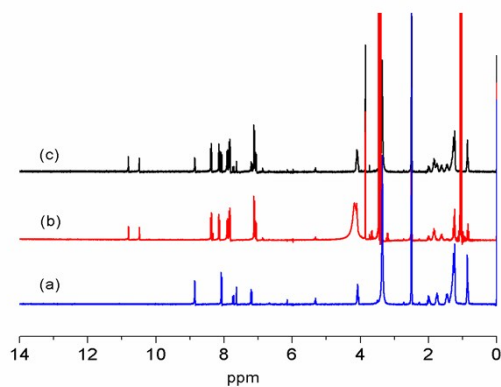


Fig. S20 Partial $^1\text{H-NMR}$ spectra of (a) **4-poxd-B8**, (b) **E5**, (c) two-components (**4-poxd-B8** : **E5**=1:1) in $\text{DMSO-}d_6$ ($3 \times 10^{-3} \text{ mol/L}$).

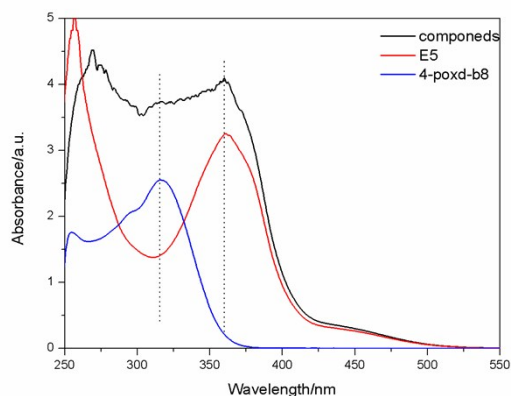
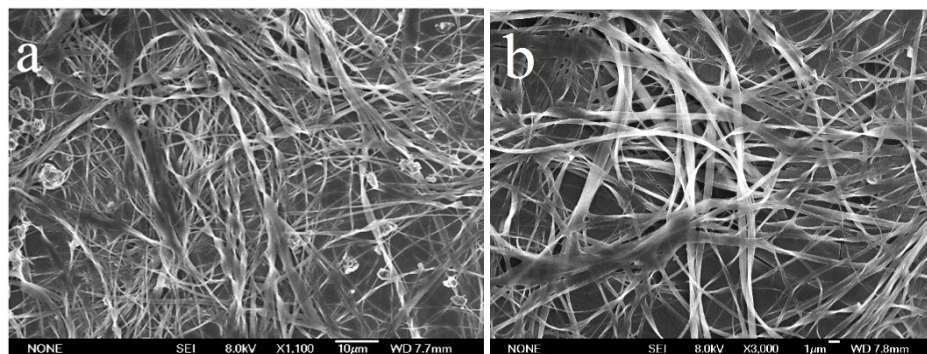


Fig. S21 UV-vis absorption spectra of **4-poxd-B8**, **E5** and two-components (**4-poxd-B8** : **E5**=1:1) in DMSO ($1 \times 10^{-4} \text{ mol/L}$).



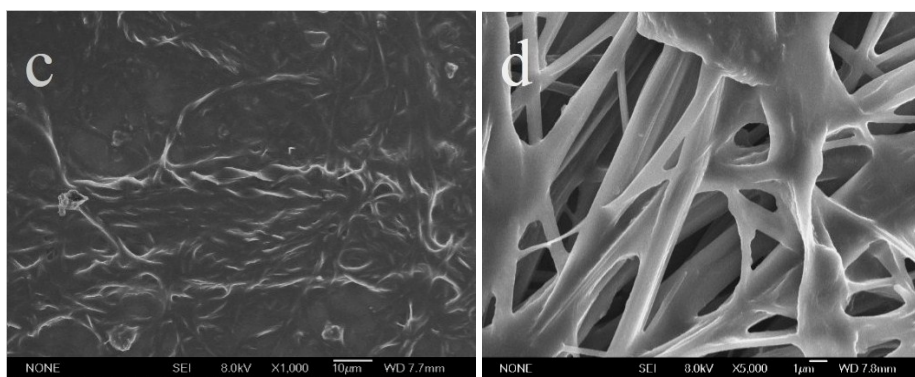


Fig. S22 SEM images of (a) **4-poxd-B8** xerogels in DMSO (5mg/ml); (b) two-components xerogels in DMSO (1:1); (c) two-components in the addition of 4 equiv F^- ; (d) two-components of addition 4 equiv CF_3COOH under (c).

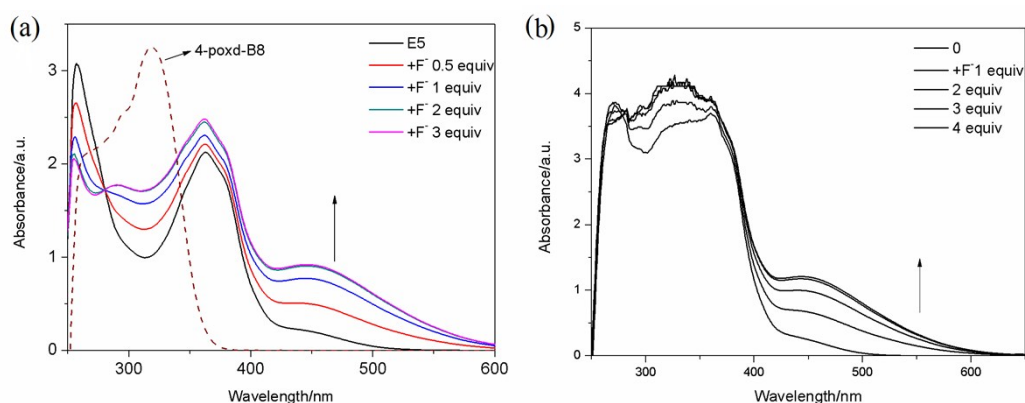


Fig. S23 UV-vis absorption spectra of (a) **4-poxd-B8** and **E5** solution in the DMSO (1×10^{-4} mol/L) in the presence of 0-3 equiv F^- ; (b) two-components (**4-poxd-B8** : **E5=1:1**) solution in the DMSO (1×10^{-4} mol/L, 1:1) in the presence of 0-4 equiv F^- .

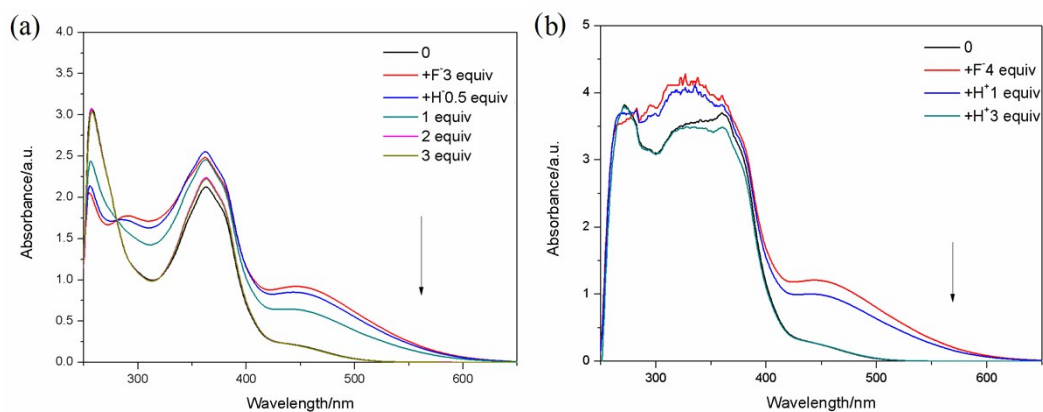


Fig. S24 UV-vis absorption spectra of (a) **E5** solution treated with 3equiv F^- , then added 0.5-3 equiv CF_3COOH ; (b) two-components (**4-poxd-B8** : **E5=1:1**) solution in the DMSO (1×10^{-4} mol/L, 1:1) in the presence of 4 equiv F^- , then added 1-3 equiv

CF₃COOH.

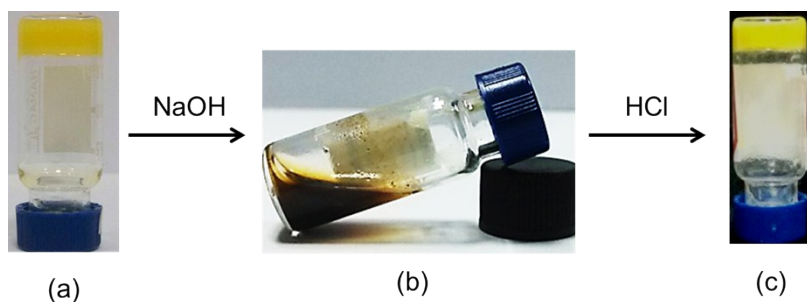


Fig. S25 (a) Organogel **E6** (8mg/ml, in DMF); (b) after addition of solid NaOH (20equiv) for 6h; (c) addition of HCl (20 equiv).

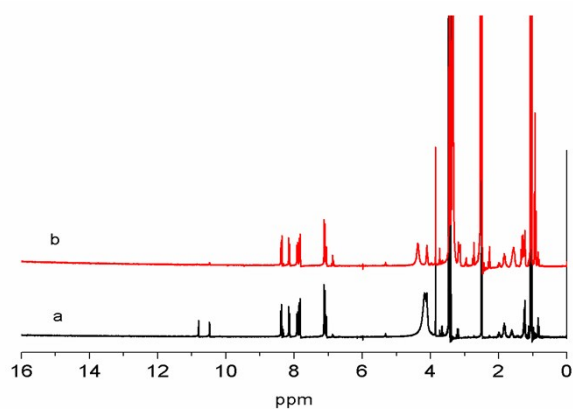


Fig. S26 Partial ¹H-NMR spectra of (a) **E5**; (b) addition 20 equiv NaOH.

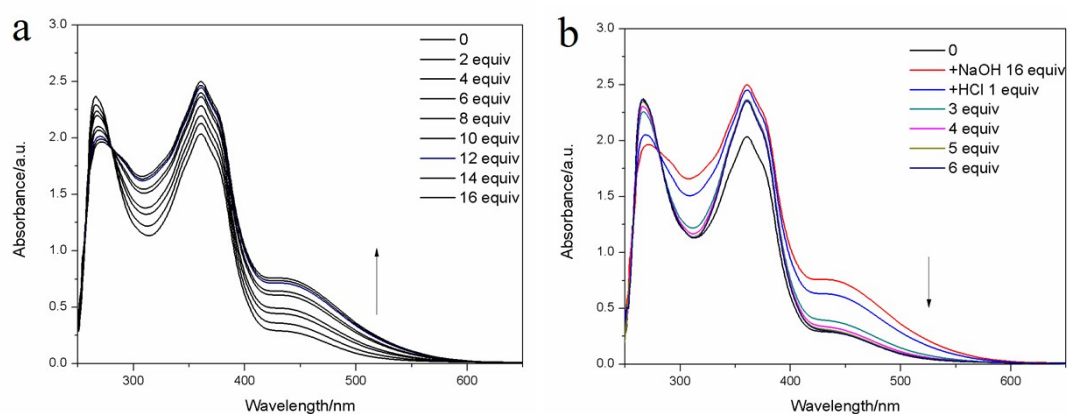


Fig. S27 UV-vis absorption spectra of E10 in the presence of (a) NaOH (0-16equiv.); (b) HCl in DMF (1×10^{-4} mol/L).