Supporting information

Multistimuli-responsive organogels based on hydrazide and azobenzene derivatives

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

<table>
<thead>
<tr>
<th>Solvent</th>
<th>E5</th>
<th>E6</th>
<th>E10</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF</td>
<td>S</td>
<td>G (8)</td>
<td>G (11.5)</td>
</tr>
<tr>
<td>THF</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>DMSO</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
</tbody>
</table>

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

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 $E_6$ (●) and $E_{10}$ (●) in DMF.

Fig. S3 SEM images of $E_5$ 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 ($1 \times 10^{-3}$ 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 $^1$H-NMR spectrum of E6 upon alternating irradiation (a) none; (b) UV light for 1.5h; (c) vis light for 1.5h; (d) heat in DMSO-d6($1\times10^{-2}$mol/L).

Fig. S11 The trans–azobenzene of E$_6$($1\times10^{-5}$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 (1×10⁻⁴mol/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 (1×10\(^{-4}\)mol/L).

Fig. S17 Partial \(^1\)H-NMR spectra of E6 in the addition of (a) none; (b) 5 equiv F\(^-\); (c) 10 equiv CF\(_3\)COOH in DMSO-\(d_6\)(1×10\(^{-2}\)M).

Fig. S18 Partial \(^1\)H-NMR spectra of E6 in the addition of (a) none; (b) 3 equiv AcO\(^-\); (c) 10 equiv CF\(_3\)COOH in DMSO-\(d_6\)(1×10\(^{-2}\)mol/L).
Fig. S19. Molecular structure of compound 4-poxd-B8.

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

Fig. S21 UV-vis absorption spectra of 4-poxd-B8, E5 and two-components (4-poxd-B8 : E5=1:1) in DMSO ($1 \times 10^{-4}$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 CF₃COOH 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 CF₃COOH; (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).