

Fig. S1 DSC curves of TC6 in the first heating run.



Fig. S2 Temperature-dependent FT-IR spectra of TC6 during first cooling run in the range of 3500-1200 cm<sup>-1</sup>.



**Fig. S3** <sup>1</sup>H NMR of TC6 ( $8 \times 10^{-3}$  mol L<sup>-1</sup>) in 20% DMSO-*d*<sub>6</sub>/CDCl<sub>3</sub> versus temperature (500 MHz; NH-1: near to alkoxyphenyl; NH-2: near to central phenyl; Ar-H: proton of phenyl).





Fig. S4. Partial proton <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>, 25 °C) of TC6 at different concentrations: (a) 26.58, (b) 7.59, (c) 2.17 and (d) 0.62 mM.



Fig. S5 Field emission scanning electron microscopic (FE-SEM) images of xerogels derived from benzene.



Fig. S6 XRD pattern of TC6 xerogel from benzene.



Fig. S7 UV-vis absorption spectra of gelling process of TC6 in 1,2-dichloroethane (0.23 wt %) at 50  $^\circ \!\!\! C$