SUPPORTING INFORMATION

SI1. Characterization data of intermediate compounds (1-4).

SI2. MicroTOF Mass Spectrometry of **Malt-Tz-C_{10}-Azo-OCH_3.**

SI3. Thermogravimetric analysis of peracetylated precursors and azo-glycolipids.

SI4. Microphotograph of **Malt-Tz-C_5-Azo-C_8.**

SI5. ^{1}H NMR experiments in DMSO-d_6 increasing water concentration from 6.00 to 3.00 ppm.

SI6. SEM and TEM images of the synthesized azo-glycolipids.

SI7. Absorption spectra of **Malt-Tz-Azo-C_{16}**, **Malt-Tz-C_5-Azo-C_8** and **Malt-Tz-C_{10}-Azo-OCH_3** in DMSO solution ($5x10^{-5}$ M).

SI8. CD and absorption spectra of **Malt-Tz-C_5-Azo-C_8** in a $4.5x10^{-5}$ M water solution.

SI9. Schematically design of a possible arrangement in **Gel I** and **Gel II**.

SI1. Characterization data of intermediate compounds.

Hepta-O-acetyl-β-maltosyl azide 1 ($C_{26}H_{35}N_3O_{17}$):

^{1}H NMR (500 MHz, $CDCl_3$, 25ºC, δ ppm): 1.99 (s, 3H), 2.01 (s, 3H) C*H*$_3$-CO-O-C3, C*H*$_3$-CO-O-C3´, 2.02 (s, 3H), 2.04 (s, 3H) C*H*$_3$-CO-O-C2, C*H*$_3$-CO-O-C4, 2.03 (s,3H), 2.10 (s, 3H), 2.15 (s,3H) C*H*$_3$-CO-O-C2, C*H*$_3$-CO-O-C6, C*H*$_3$-CO-O-C6´, 3.77 (ddd, 1H, $J_{5´,6´b}$= 2.5 Hz, $J_{5´,6´a}$=4.5 Hz, $J_{4´,5´}$=9.7 Hz, *H5´*), 3.94 (ddd, 1H, $J_{5,6b}$=2.4 Hz, $J_{5,6a}$=3.7 Hz, $J_{5,4}$=10.0 Hz, *H5*), 4.01 (ddd, 1H, $J_{3´,4´}$= 10.0 Hz, $J_{4´,5´}$= 9.7 Hz, *H4´*), 4.04 (dd, 1H, $J_{5,6b}$=2.4 Hz, $J_{6a,6b}$=12.5 Hz, *H6b*), 4.24 (dd, 1H, $J_{5,6a}$=3.7 Hz, $J_{6a,6b}$=12.5 Hz, *H6a*), 4.24 (dd, 1H, $J_{5´,6´a}$=4.5 Hz, $J_{6´a,6´b}$=12.2 Hz, *H6´a*), 4.50 (dd, 1H, $J_{5´,6´b}$=2.5 Hz, $J_{6´a,6´b}$=12.2 Hz, *H6´b*), 4.70 (d, 1H, $J_{1´,2´}$= 8.7 Hz, *H1´*), 4.78 (dd, 1H, $J_{1´,2´}$= 8.7 Hz, $J_{2´,3´}$= 9.0 Hz, *H2´*), 4.85 (dd, 1H, $J_{1,2}$=4.0 Hz, $J_{2,3}$= 10.5 Hz, *H2*), 5.05 (dd, 1H, $J_{3,4}$= 9.7 Hz, $J_{4,5}$= 10.0 Hz, *H4*), 5.25 (dd,1H, $J_{2´,3´}$= 9.0 Hz, $J_{3´,4´}$=10.0 Hz, *H3´*), 5.35 (dd, 1H, $J_{3,4}$= 9.7 Hz, $J_{2,3}$=10.5 Hz, *H3*), 5.40 (d, 1H, J_{1-2}= 4.0 Hz, *H1*).

^{13}C NMR (125 MHz, $CDCl_3$, 25ºC, δ ppm): 20.5, 20.6, 20.7, 20.8 (*C*H_3-CO-)$_7$, 61.5 *C6*, 62.5 *C6´*, 68.0 *C4*, 68.6 *C5*, 69.3 *C3*, 70.0 *C2*, 71.5 *C2´*, 72.4 *C4´*, 74.2 *C5´*, 75.1 *C3´*, 87.46 *C1´*, 95.7 *C1*, 169.4, 169.5 C2´-O-*C*O-, C4-O-*C*O-, 169.9, 170.1 C3-O-*C*O-, C3´-O-*C*O-, 170.1, 170.4, 170.5 C2-O-*C*O-, C6-O-*C*O, C6´-O-*C*O.

MALDI-TOF MS (DCTB): 684.2 $[M+Na]^+$.

IR (KBr, cm^{-1}): 2962, 2122, 1754, 1371, 1228, 1033, 896, 603.

Propargylamide derivative of HOOC-Azo-C$_{16}$ 2 ($C_{34}H_{49}N_3O_2$):

The product was partially soluble so the reaction was heated at 40ºC. The product was purified by recrystallization with ethyl acetate in 40% of yield.

^{1}H (300 MHz, $CDCl_3$, 25ºC, δ ppm): 0.91 (t, 3H, J=6.8 Hz, -C*H*$_3$), 1.17-1.56 (m, 26H, -CH_2-(C*H*$_2$)$_{13}$-CH_3), 1.76-1.89 (m, 2H, -O-CH_2-C*H*$_2$-), 2.30 (t, 1H, J=2.5 Hz, *H*C≡C-,)

4.06 (t, 2H, J=6.8 Hz, –O-C*H*$_2$-CH$_2$-), 4.30 (m, 2H, HC≡C-C*H*$_2$-NH), 6.26 (t, 1H, J=5.0 Hz, CH$_2$-N*H*-CO), 6.99-7.03 (m, 2H, *Har*), 7.87-7.97 (m, 6H, *Har*).

^{13}C (75 MHz, $CDCl_3$, 25ºC, δ ppm): 13.9 *C*H$_3$, 22.6, 25.9, 29.2, 29.3, 29.3, 29.5, 29.5, 29.6, 29.6, 29.9, 31.9 -(*C*H$_2$)$_{14}$-CH$_3$, ≡C-*C*H$_2$-NH, 68.5 O-*C*H$_2$-(CH$_2$)$_{14}$, 71.9 H*C*≡C-, 79.37 HC≡*C*, 114.8, 122.6, 125.1, 127.9 *C*Har x8, 134.9, 146.9, 154.8, 162.3, *C*ar, 166.4 NH-*C*O-Car.

ESI: 504.2 $[M+H]^+$, 526.1 $[M+Na]^+$.

IR (KBr, cm^{-1}): 3279, 3263, 2935, 2917, 2873, 2848, 1639, 1603, 1585, 1545, 1502, 1495, 1472, 1463, 1317, 1298, 1251, 1152, 1146, 1106, 1025, 858, 841, 823, 719, 680, 634, 553.

Propargylamide derivative of HOOC-C$_5$-Azo-C$_8$ 3 ($C_{29}H_{39}N_3O_3$):

The reaction was stirred at room temperature. The product was purified by flash chromatography with hexane/ethyl acetate 7:3 as eluent in 70% of yield.

^{1}H NMR (400MHz, DMSO-d$_6$, 25ºC, δ ppm): 0.90 (t, 3H, J= 6.5 Hz, –(CH$_2$)$_5$-C*H*$_3$), 1.35 (d, 3H, J=6.4 Hz, –CH-C*H*$_3$), 1.24-1.91 (m, 16H, -(C*H*$_2$)-), 2.21-2.30 (m, 3H, *H*C≡C-, –C*H*$_2$-CO), 4.00-4.12 (m, 4H, –O-C*H*$_2$-CH$_2$-, HC≡C-C*H*$_2$-NH), 4.46 (m, 1H, –O-C*H*-CH$_3$), 5.67 (s, 1H, CH$_2$-N*H*-CO), 6.94-7.04 (m, 4H, *Har*), 7.85-7.88 (m, 4H, *Har*).

^{13}C (100 MHz, DMSO-d$_6$, 25ºC, δ ppm): 14.0 CH$_2$-*C*H$_3$, 19.7 *C*H$_3$-O- 22.6, 25.2, 25.5, 25.7, 28.9, 29.2, 31.7, 36.2, 36.4, -(*C*H$_2$)-, ≡C-*C*H$_2$-NH, CO-*C*H$_2$-CH$_2$-, 67.9 O-*C*H$_2$-CH$_2$, 71.6 H*C*≡C-, 74.2 –O-*C*H-CH$_3$, 79.3 HC≡*C*, 114.6, 115.8, 124.2, 124.3 *C*Har x8, 146.8, 147.0, 160.3, 161.0 *C*ar, 172.1 NH-*C*O-Car.

ESI: 478.3 $[M+H]^+$, 500.2 $[M+Na]^+$, 516,2 $[M+K]^+$

IR (KBr, cm^{-1}): 3273, 2931, 2853, 1625, 1598, 1577, 1544, 1496, 1464, 1384, 1311, 1296, 1249, 1145, 1130, 1061, 971, 840, 550.

Propargylamide derivative of HOOC-C_{10}-Azo-OCH_3 4 ($C_{27}H_{35}N_3O_3$):

The reaction was stirred at room temperature. The product was purified by recrystallization with ethyl acetate in 40% of yield.

^{1}H (300 MHz, $CDCl_3$, 25ºC, δ ppm): 1.22-1.72 (m, 12H, -(C*H*$_2$)$_6$-), 1.76-1.89 (m, 2H, -O-CH$_2$-C*H*$_2$), 2.20 (t, 2H, J=7.0 Hz, –C*H*$_2$-CO), 2.24 (t, 1H, J=2.6 Hz, *H*C≡C-), 3.09 (s, 3H, -O-C*H*$_3$), 4.01-4.09 (m, 4H, -O-C*H*$_2$-CH$_2$-, HC≡C-C*H*$_2$-NH), 5.57 (s, 1H, CH$_2$-N*H*-CO), 6.97-7.05 (m, 4H, *Har*), 7.84-7.92 (m, 4H, *Har*).

^{13}C (100 MHz, $CDCl_3$, 25ºC, δ ppm): 25.5, 25.9, 29.1, 29.2, 29.2, 29.2, 29.3, 29.3, 29.4 -(*C*H$_2$)$_6$-, HC≡C-*C*H$_2$-NH, 36.4 –*C*H$_2$-CO, 55.6 -O-*C*H$_3$, 68.3 -O-*C*H$_2$-CH$_2$-, 71.5 H*C*≡C-, 79.7 HC≡*C*-, 11.4, 114.6, 124.3, 124.3 *C*Har, 146.9, 147.1, 161.2, 161.5 *C*ar, 172.6 NH-*C*O.

ESI: 450.3 $[M+H]^+$, 472.1 $[M+Na]^+$.

IR (KBr, cm^{-1}): 3290, 2935, 2917, 2849, 1643, 1602, 1583, 1546, 1497, 1470, 1463, 1421, 1318, 1296, 1249, 1152, 1107, 1029, 843, 823, 666, 640, 558.

SI2. MicroTOF Mass Spectrometry of **Malt-Tz-C_{10}-Azo-OCH_3**.

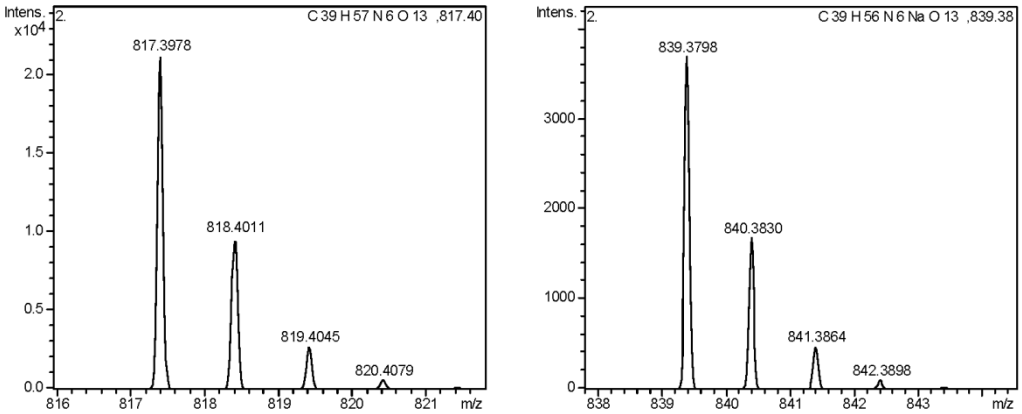

Figure SI2. MicroTOF Mass Spectrometry of **Malt-Tz-C_{10}-Azo-OCH_3**.

SI3. Thermogravimetric analysis of peracetylated precursors and azo-glycolipids.

Table SI3: Thermogravimetric analysis of peracetylated precursors and azo-glycolipids.

Compound	$T_{5\%}$	T_{onset}	T_{max}
OAc-Malt-Tz-azo-C_{16}	315ºC	320ºC	340ºC
OAc-Malt-Tz-C_5-azo-C_8	315ºC	320ºC	336ºC
OAc-Malt-Tz-C_{10}-azo-OCH_3	315ºC	320ºC	335ºC
Malt-Tz-azo-C_{16}	215ºC	240ºC	260ºC
Malt-Tz-C_5-azo-C_8	245ºC	273ºC	285ºC
Malt-Tz-C_{10}-azo-OCH_3	170ºC	218ºC	258ºC

$T_{5\%}$ = Temperatures at which 5% of the initial mass is lost. T_{onset} = onset of decomposition. T_{max} = Temperatures of maximum rate of weight loss.

SI4. Microphotograph of **Malt-Tz-C_5-Azo-C_8.**

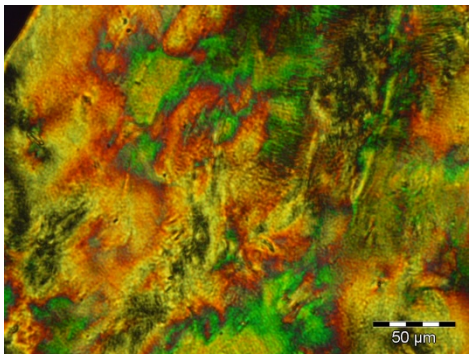

Figure SI4. Microphotograph of **Malt-Tz-C_5-Azo-C_8** taken at 130º C at first heating cycle.

SI5. ^{1}H NMR experiments in DMSO-d_6 increasing water concentration from 6.00 to 3.00 ppm.

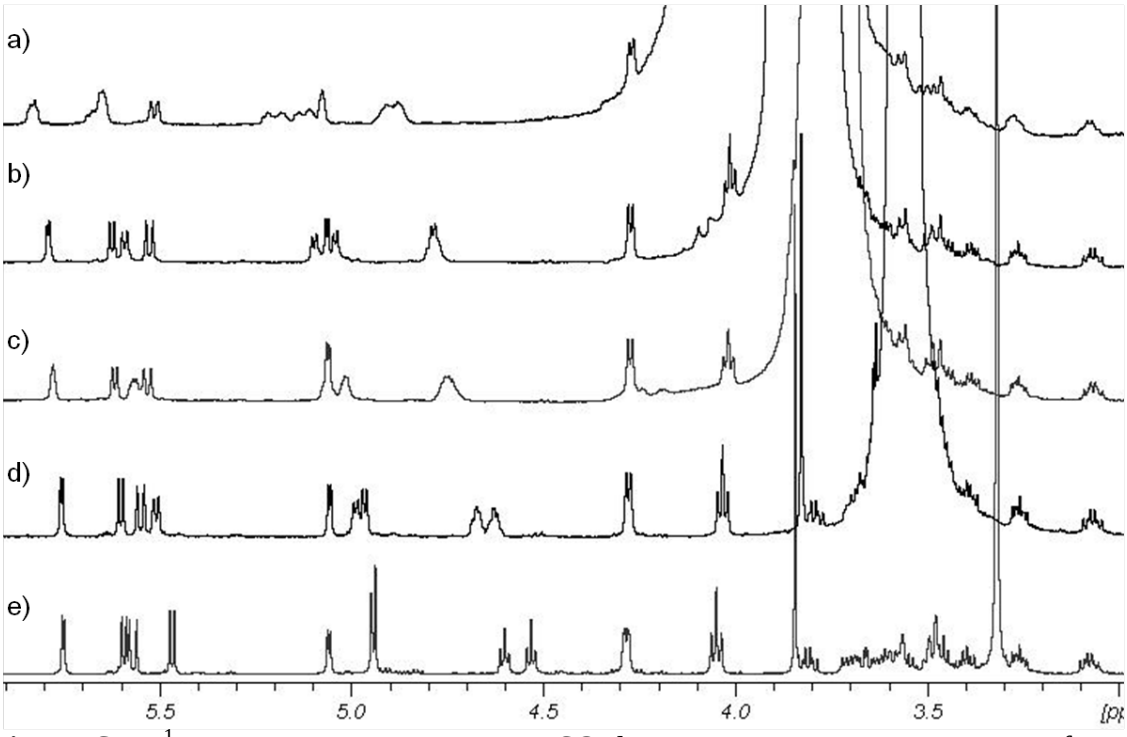

Figure SI5. ^{1}H NMR experiments in DMSO-d_6 increasing water concentration from 6.00 to 3.00 ppm. (a) 2.9 mg of **Malt-Tz-C_{10}-Azo-OCH_3** in 0.40 mL DMSO-d_6, (b) addition of 0.04 mL H_2O to **(a)** [1:0.1 DMSO/water], (c) addition of 0.08 mL H_2O to **(a)** [1:0.2 DMSO/water], **(**d) addition of 0.12 mL H_2O to **(a)** [1:0.3 DMSO/water], (e) addition of 0.16 mL H_2O to **(a)** [1:0.4 DMSO/water]**.**

SI6. SEM and TEM images of the synthesized azo-glycolipids.

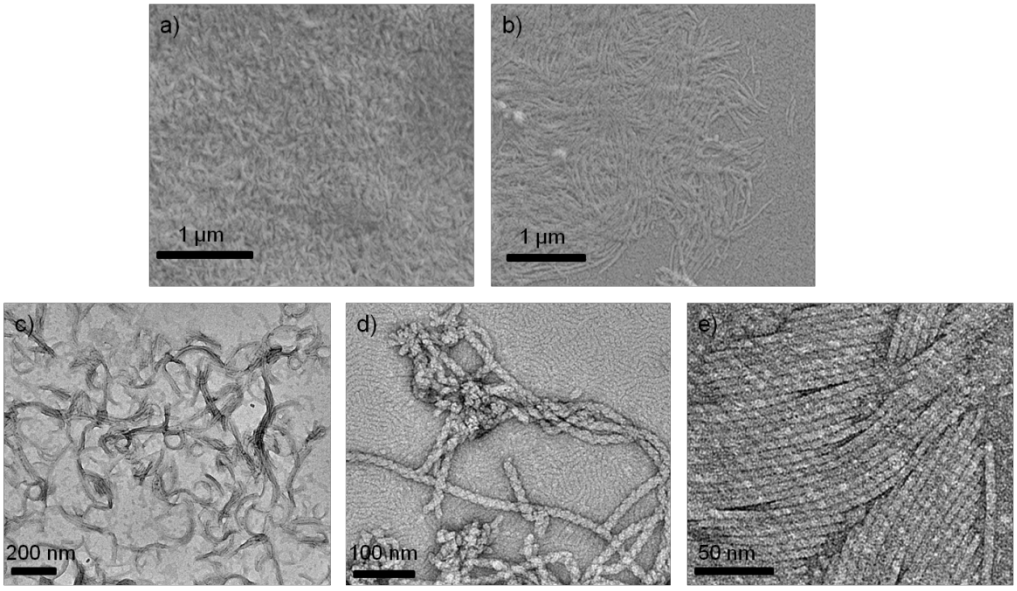

Figure SI6. (a) SEM image of **Malt-Tz-Azo-C_{16}** xerogel (5 wt % water), (b) SEM image of **Malt-Tz-Azo-C_{16}** xerogel (1.5 wt % DMSO/water 1:1 wt), (c) TEM image of **Malt-Tz-Azo-C_{16}** (0.1 wt % water), (d) TEM image of **Malt-Tz-Azo-C_{16}** (0.1 wt % DMSO/water 1:1 wt), (e) TEM image of **Malt-Tz-C_{10}-Azo-OCH_3** (0.1 wt % DMSO/water 1:1 wt).

SI7. Absorption spectra of **Malt-Tz-Azo-C_{16}**, **Malt-Tz-C_5-Azo-C_8** and **Malt-Tz-C_{10}-Azo-OCH_3** in DMSO solution ($5x10^{-5}$ M).

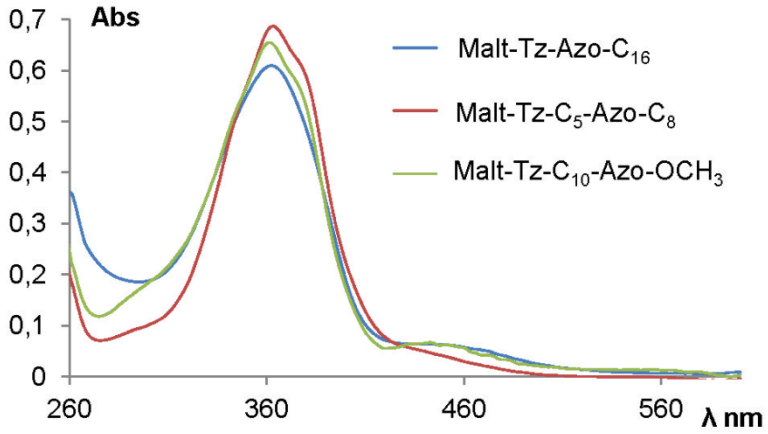

Figure SI7. Absroption spectra of **Malt-Tz-Azo-C_{16}**, **Malt-Tz-C_5-Azo-C_8** and **Malt-Tz-C_{10}-Azo-OCH_3** in DMSO solution ($5x10^{-5}$ M).

SI8. CD and absorption spectra of **Malt-Tz-C_5-Azo-C_8** in a $4.5x10^{-5}$ M water solution.

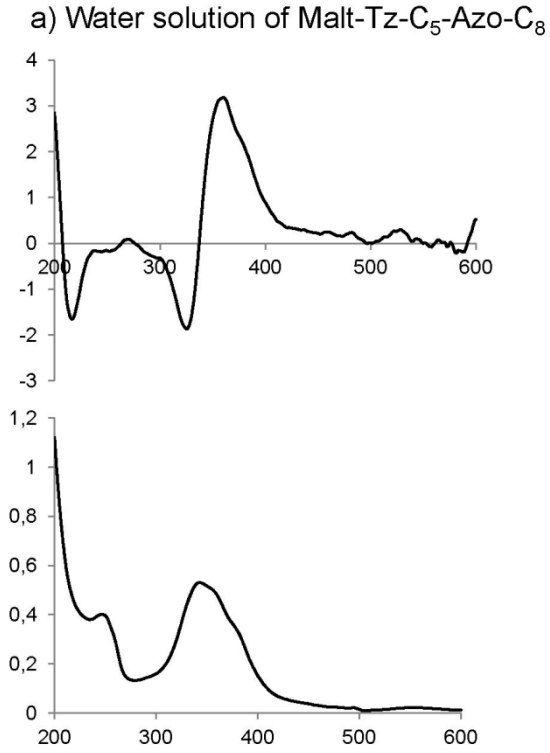

Figure SI8. CD and absorption spectra of a water solution of **Malt-Tz-C_5-Azo-C_8** ($4.5x10^{-5}$ M).

SI9. Schematically design of a possible arrangement in **Gel I** and **Gel II**.

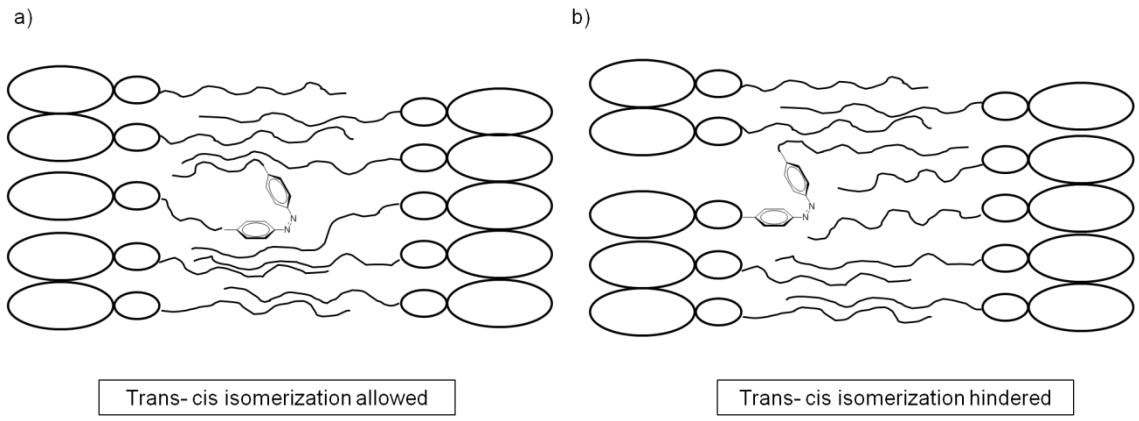

Figure SI9. Schematically design of a possible arrangement in (a) **Gel I** and (b) **Gel II**.