

Supporting Information

Monoglyceride-Based Organogelator for Broad-Range Oil Uptake with High Capacity

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Gelation method for gelators.

Typically, a given mass of gelator was added into required solvent (1mL) was heated until the solid was completely dissolved. The resulting solution was slowly cooled to room temperature even more to around 1 °C (for some low boil point organic liquids), and gelation was observed. All gels are thermally reversible. Above their gelation temperature, the gels dissolved in the solvent, however could be transformed to their original gel state via cooling.

The ^1H NMR data of gelators.

The ^1H NMR data of DGI (400 MHz, CDCl_3): δ 0.81 (t, 3H, CH_3), 1.19–1.27 (m, 18H, CH_2), 1.55(t, 2H, CH_2), 3.29 (s, 2H, CH_2), 3.52–3.65 (m, 2H, CH_2), 3.87–3.92 (m, 1H, CH), 4.02 (t, 2H, CH_2), 4.16–4.26 (m, 2H, CH_2), 5.66 (s, 1H, $=\text{CH}_2$), 6.30 (s, 1H, $=\text{CH}_2$).

The ^1H NMR data of HGI (400 MHz, CDCl_3): δ 0.81 (t, 3H, CH_3), 1.19–1.27 (m, 26H, CH_2), 1.55(t, 2H, CH_2), 3.29 (s, 2H, CH_2), 3.52–3.65 (m, 2H, CH_2), 3.87–3.92 (m, 1H, CH), 4.02 (t, 2H, CH_2), 4.16–4.26 (m, 2H, CH_2), 5.66 (s, 1H, $=\text{CH}_2$), 6.30 (s, 1H, $=\text{CH}_2$).

The ^1H NMR data of OGI (400 MHz, CDCl_3): δ 0.81 (t, 3H, CH_3), 1.19–1.27 (m, 30H, CH_2), 1.55(t, 2H, CH_2), 3.29 (s, 2H, CH_2), 3.52–3.65 (m, 2H, CH_2), 3.87–3.92 (m, 1H, CH), 4.02 (t, 2H, CH_2), 4.16–4.26 (m, 2H, CH_2), 5.66 (s, 1H, $=\text{CH}_2$), 6.30 (s, 1H, $=\text{CH}_2$).

The ^1H NMR data of HGM (400 MHz, CDCl_3): δ 0.88 (t, 3H, CH_3), 1.26–1.32 (m, 26H, CH_2), 1.66 (m, 2H, CH_2), 3.68 (m, 2H, CH_2), 3.84–4.06 (m, 1H, CH), 4.18 (t, 2H, CH_2), 4.33(m, 2H, CH_2), 6.23 (m, 1H, $=\text{CH}$), 6.36 (m, 1H, $=\text{CH}$).

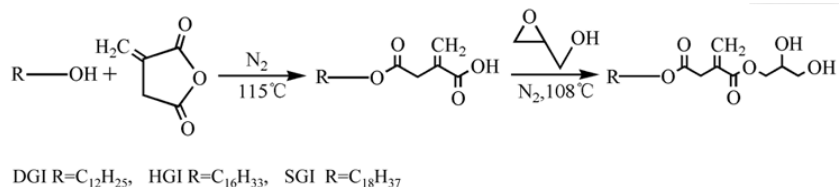


Figure S1. Synthesis of gelators (DGI, HGI, and OGI)

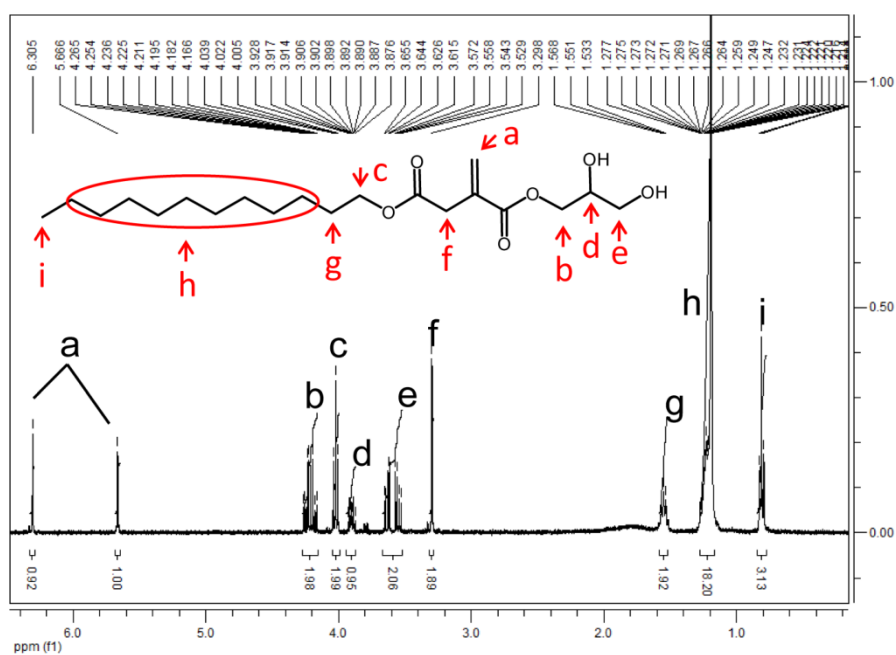


Figure S2. ^1H NMR spectrum of DGI

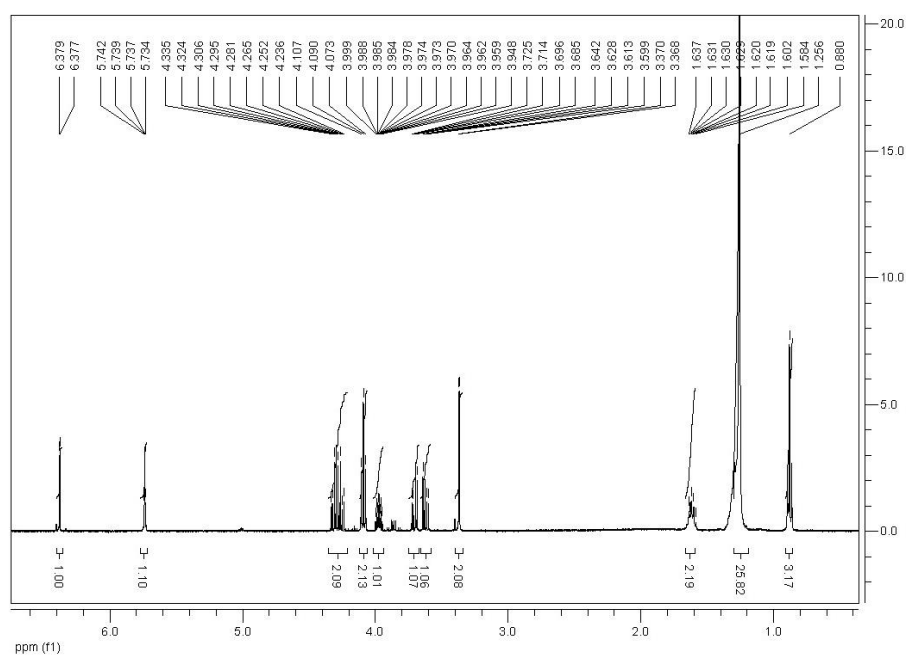


Figure S3. ^1H NMR spectrum of HGI

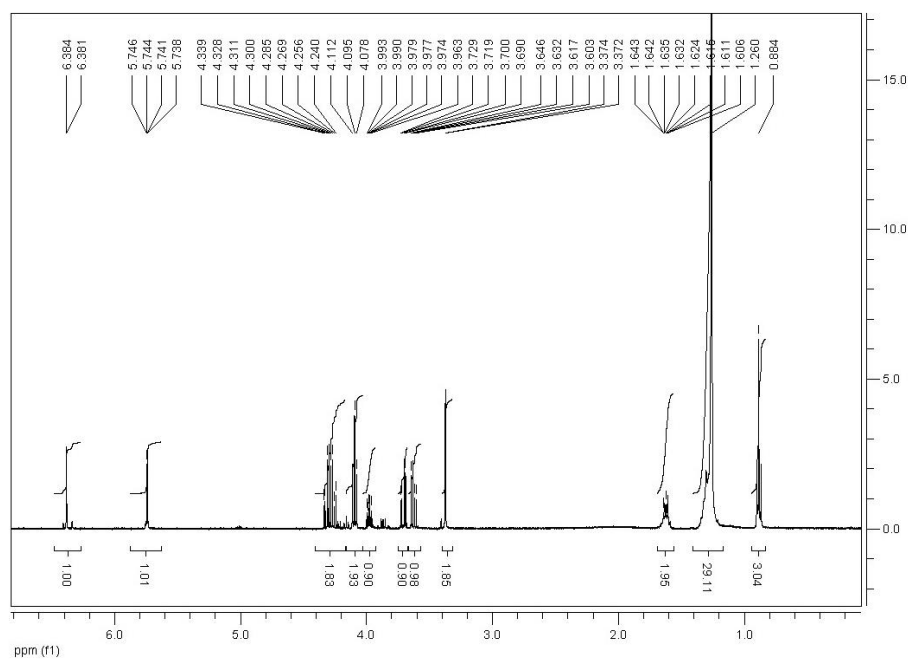


Figure S4. ^1H NMR spectrum of OGI

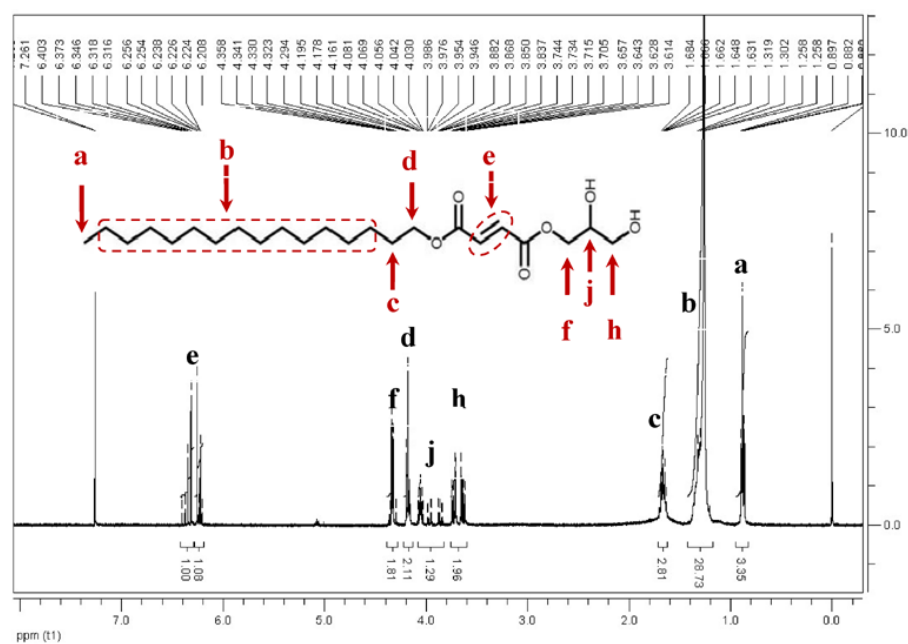


Figure S5. ^1H NMR spectrum of hexadecylglyceryl maleate (HGM)

XRD and IR spectra of HGM organogel

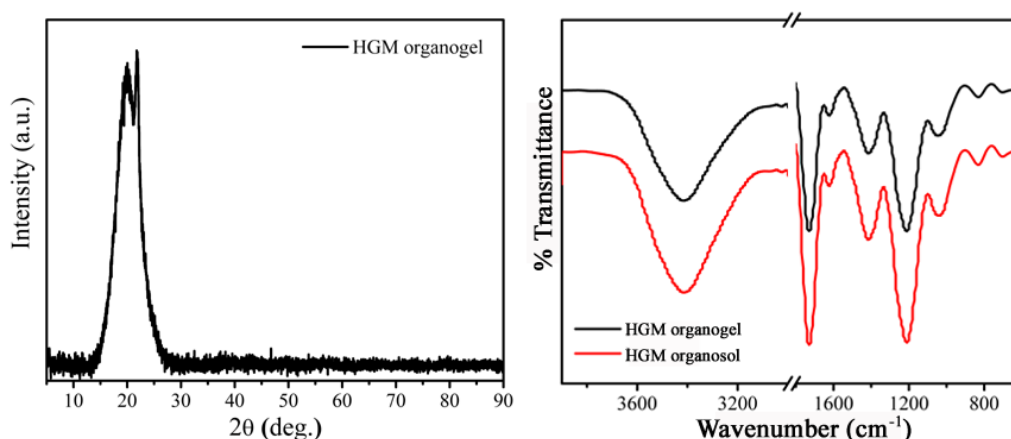


Figure S6. XRD (left) and IR (right) spectra of HGM organogel.

From XRD pattern, we cannot find out the existence of the periodic peaks, and do not form HGM fibers containing repeating layer structural units. The IR spectra indicate the -OH stretching band at 3413 cm^{-1} and >C=O stretching band at 1730 cm^{-1} of HGM in solution state has not shifted in the gel, which reveal HGM molecules cannot form strong hydrogen bonds network, in turns, to get stable L_{β} gels.

Analysis of gel-forming ability of HGI and HGM

To understand of relationship between the structure and the gel ability, we synthesized another amphiphilic molecule HGM by subtle modify the hydrophilic group of the HGI while keep its long alkyl chain intact. This modification was done to solve the question of whether the HGM can form gel under similar conditions or not. It is interesting to note that HGM cannot form any kind of gel, not only in fuel solvents also in other tested solvents. As we known, in the lipid-based organogels, below the Krafft temperature, the lamellar phase transforms into the α -crystalline phase (L_{α} gel) characterized by the hexagonal surfactant packing in layers with a single intermolecular spacing at 4.18 \AA . The initial α -crystalline gel readily transforms into the β -crystalline state (L_{β} , often called the “coagel”). It has a higher melting point and is characterized by several wide-angle X-ray reflecting short spacings in the unit cell, with the strongest line corresponding to $4.4\text{--}4.6\text{ \AA}$. The coagel state of surfactant molecular is believed to be due to hydrogen bonds being established between head groups in bilayers, which in turn lead to a further crystallization of aliphatic tails.

Based on the above analyzing, the XRD and IR data (see Figure S6, Supporting Information) indicate the HGI derived organogels are obviously located in the β -crystalline region while the HGM cannot form the stable gel. We simulated the way how the HGI and HGM molecular aligned in the middle-metastable L_α phase. It is interesting to find that compared to the HGI molecule, the area of the HGM head group is smaller than the distance between the neighboring molecules. Because the hydrogen bond is distance sensitive, so under this situation, the strength of hydrogen bonds maybe not strong enough to get the L_β gels. On the contrary, the head group of HGI is relatively large, the hydroxyl groups are easily contact each other and form the hydrogen bonding to promote the building of the stable organogel.

References

- [1] H. Qin, D. Wang, Z. Huang, D. Wu, Z. Zeng, B. Ren, K. Xu, J. Jin*, *J. Am. Chem. Soc.* **2013**, *135*, 12544–12547.