Supplementary Information

Self-assembly of Gelators Confined within the Nano-Scale Interlayer Space of Organo-Montmorillonite

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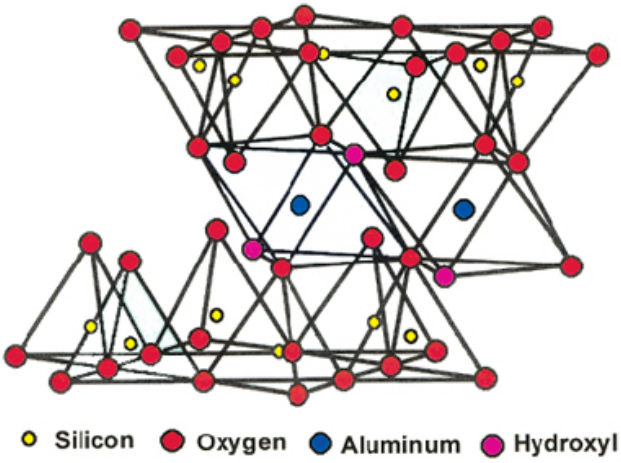
Experimental details

Experimental

Organo-montmorillonite (OMMT) was purchased from Zhejiang Huate Group, China.



Scheme S-1 Crystal structure of montmorillonite

Chlorobenzene (ArCl) and propylene carbonate (PC) were purchased from Sinopharm Chemical Reagent Co. and used as received.

Synthesis of the 1-methyl-2,4-bis(N'-n-octadecylureido)benzene (MBB18) and the 1-methyl-2,4-bis(N'-dodecylureido)benzene (MBB12) was described previously [Y. Xiong, Q. Liu, H. Wang

and Y. Yang, *J. Colloid and Interf. Sci.*, 2008, 318, 496–500; Y. Xiong, Q. Liu, Z. Li, H. Wang and Y. Yang, *Acta. Chimica. Sinica*, 2008, 66, 391-397].

MBB18: **m.p.** 174–176 °C. **FT–IR** (EQUINOX55, Bruker): 3319 (s, ν_{N-H}), 1634 (s, $\nu_{C=O}$, amide–I), 1575 (s, ν_{C-N}, amide–II). **^{1}H–NMR** (AV400, Bruker, [D_6]DMSO, 110 °C): δ 0.842–0.875 (t, J=13.2Hz, 6H), δ 1.261–1.289 (m, 60H), δ 1.417–1.466 (m, 4H), δ 2.089 (s, 3H), δ 3.057–3.087 (m, 4H), δ 5.727 (s, 1H), δ 6.085 (s, 1H), δ 6.895–6.917 (d, J=8.8Hz, 1H), δ 7.032–7.052 (d, J=8Hz, 1H), δ 7.200 (s, 1H), δ 7.617 (s, 1H), δ 7.851 (s, 1H). **MS** (APCI, Agilent 1100 LC/MSD Trap) m/z：calculated for MBB18 ($C_{45}H_{84}N_4O_2$): 713.2; found : 714.5 $[M+H]^+$.

MBB12: **m.p.** 178–179 °C. **FT–IR** : 3317 (s, ν_{N-H}), 1634 (s, $\nu_{C=O}$, amide–I), 1570 (s, ν_{C-N} amide–II). **^{1}H NMR** (AV400, Bruker, [D_6]DMSO, 110 °C) δ：0.839～0.873 (t, J=13.6Hz, 6H), 1.263～1.288 (m, 36H),1.411～1.444 (m, 4H), 2.086 (s, 3H), 3.055～3.079 (m, 4H), 5.747 (s, 1H), 6.132 (s, 1H), 6.895～6.916 (d, J=8.4Hz, 1H), 7.034～7.059 (d, J=10Hz, 1H), 7.232 (s, 1H), 7.626 (s, 1H), 7.894 (s, 1H). **MS**（APCI）m/z：calculated for MBB12 ($C_{33}H_{60}N_4O_2$): 544.8; found: 545.8 $[M+H]^+$.

Synthesis of the bis(4'-stearamidophenyl)methane (BSM18) was carried out according to the procedure described elsewhere [A.W. Ralston and M.R. Mccorkle, *J. Am. Chem. Soc.*, 1939, 61, 1604~1605], and the synthesis of the bis(4'-octanamidophenyl)methane (BOM8) was carried out similarly to that of BSM18, using octanoic acid instead of stearic acid.

Preparation of the Organo-montmorillonite powder: As a comparing experiment, 0.18 g of organo-montmorillonite was added in 6 g of chlorobenzene. The mixture was also sonicated for 3 h at 130 °C and then filtrated to obtain organo-montmorillonite powders.

Preparation of the MBB18/ArCl/OMMT gel: Dissolved 0.3 g of MBB18 in 6 g of hot chlorobenzene (ca. 5 wt %) and then 0.18 g of organo-montmorillonite was added in the mixture. The solution mixture was sonicated for 3 h at 130 °C and maintained for minutes to let the organo-montmorillonite precipitated. Then the solution mixture was allowed to cool to form chlorobenzene organogel with organo-montmorillonite at the bottom of the vessel.

Preparation of the MBB18/ArCl gel: 0.3 g of MBB18 was dissolved in 6 g of chlorobenzene. The solution was sonicated for 3 h at 130 °C, and then allowed to cool to form chlorobenzene organogel.

Preparation of the MBB12/ArCl/OMMT gel: The preparation process was similar with the preparation of MBB18/ArCl/OMMT gel. The concentration of gelator and organo-

montmorillonite was the same with the sample of MBB18/OMMT/ArC gel respectively.

Preparation of the MBB12/ArCl gel: The preparation process was similar with the preparation of MBB18/ArCl gel. The concentration of gelator and organo-montmorillonite was the same with the sample of MBB18/ArCl gel respectively.

Preparation of the BSM18/PC/OMMT gel: Dissolved 0.3 g of BSM18 in 6 g of hot propylene carbonate (ca. 5 wt %) and then 0.18 g of organo-montmorillonite was added in the mixture. The solution mixture was sonicated for 3 h at 180 °C and maintained for minutes to let the organo-montmorillonite precipitated. Then the solution mixture was allowed to cool to form propylene carbonate organogel with organo-montmorillonite at the bottom of the vessel.

Preparation of the BSM18/PC gel: 0.3 g of BSM18 was dissolved in 6 g of propylene carbonate. The solution was sonicated for 3 h at 180 °C, and then allowed to cool to form propylene carbonate organogel.

Preparation of the BOM8/PC/OMMT gel: The preparation process was similar with the preparation of BSM18/PC/OMMT gel. The concentration of gelator and organo-montmorillonite was the same with the sample of BSM18/PC/OMMT gel respectively.

Preparation of the BOM8/PC gel: The preparation process was similar with the preparation of BSM18/PC gel. The concentration of gelator and organo-montmorillonite was the same with the sample of BSM18/PC gel respectively.

Characterizations

Differential scanning calorimetry (DSC): The samples were placed in a sealed pan. Thermograms were measured on a differential scanning calorimeter (DSC 7, Perkin-Elmer) from 40 to 180 °C at a scan rate of 5 °C/min.

DSC data:

MBB18/ArCl gel (as shown in Fig. 1a): 59.909 °C and 129.542 °C.

MBB18/ArCl/OMMT gel (as shown in Fig. 1b): 59.916 °C, 123.333 °C and 139.750 °C.

Organo-montmorillonite powder (as shown in Fig. 1c): no thermal effect.

MBB12/ArCl gel (as shown in Fig. 1d): 96.416 °C and 133 °C.

MBB12/ArCl/OMMT gel (as shown in Fig. 1e): 95.083 °C, 125 °C and 143.75 °C.

BOM8/PC gel (as shown in Fig. 1f): 97.833 °C

BOM8/PC/OMMT gel (as shown in Fig. 1g): 97.583 °C and 147.166 °C.

BSM18/PC gel (as shown in Fig. 1h): 136.426 °C

BSM18/PC/OMMT gel (as shown in Fig. 1i): 136.083 °C and 148.426 °C

X-ray diffraction: Place the samples on a glass plate. After freeze-drying at -80 °C, a xerogel was obtained. X-ray diffraction were performed using a X' Pert PRO (PANalytical B.V.) powder diffractometer using CuKαX radiation (0.15406 Å) from 0.5° to 40° (2θ) in steps of 0.017°.

XRD data:

Organo-montmorillonite powder:

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]
3.9857	1157.65	0.8029	22.16931	100.00
7.9995	53.12	0.8029	11.05249	4.59
19.8320	62.66	0.2007	4.47687	5.41
20.8884	62.94	0.2007	4.25279	5.44
22.0750	27.73	0.4015	4.02681	2.40
26.7022	267.52	0.1338	3.33858	23.11
28.4286	14.57	0.8029	3.13964	1.26

MBB18/ArCl xerogel:

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]
2.1779	2079.70	0.4015	40.56513	100.00
6.7521	41.09	0.4684	13.09140	1.98
14.2395	3.67	0.8029	6.22005	0.18
20.1623	1.00	0.9368	4.40427	0.05
21.0805	9.39	0.9368	4.21447	0.45

MBB18/ArCl/OMMT xerogel:

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]
1.8391	144.36	0.2007	48.03865	30.23
2.1731	168.77	0.2635	40.65469	38.58
3.5861	477.54	0.9368	24.63911	100.00
7.9879	4.09	0.8029	11.06850	0.86
19.7172	42.29	0.2007	4.50267	8.86
26.5984	184.88	0.1171	3.35138	38.72
34.9699	3.17	0.8029	2.56589	0.66

BOM8/PC xerogel:

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]
3.1030	57063.32	0.1004	28.47362	100.00
6.1483	2579.10	0.1171	14.37559	4.52
9.1739	76.26	0.1338	9.64011	0.13
12.2734	886.07	0.1171	7.21168	1.55
15.3515	142.97	0.0669	5.77191	0.25
18.4306	200.77	0.2342	4.81400	0.35
19.3618	101.88	0.2342	4.58452	0.18
20.5345	395.84	0.1338	4.32527	0.69
20.8748	182.33	0.1338	4.25554	0.32
21.9277	348.05	0.2676	4.05352	0.61
22.1425	299.16	0.1338	4.01468	0.52
23.7997	157.68	0.1338	3.73875	0.28

24.6719	139.16	0.1171	3.60853	0.24
25.9279	27.24	0.2007	3.43650	0.05

BOM8/PC/OMMT xerogel:

Pos.[°2Th.]	Height[cts]	FWHM[°2Th.]	d-spacing[Å]	Rel.Int.[%]
1.0002	338.49	0.1673	88.32285	7.01
3.1254	4825.59	0.0669	28.26922	100.00
6.1994	504.45	0.0502	14.25711	10.45
9.4021	42.63	0.4015	9.40662	0.88
12.3108	94.24	0.1004	7.18990	1.95
15.4676	16.14	0.8029	5.72885	0.33
18.4967	53.26	0.2676	4.79695	1.10
20.5153	59.71	0.2007	4.32928	1.24
20.9043	76.90	0.1338	4.24959	1.59
22.0072	61.46	0.4015	4.03905	1.27
26.6749	221.46	0.1171	3.34194	4.59

Polarized optical microscope (POM) images

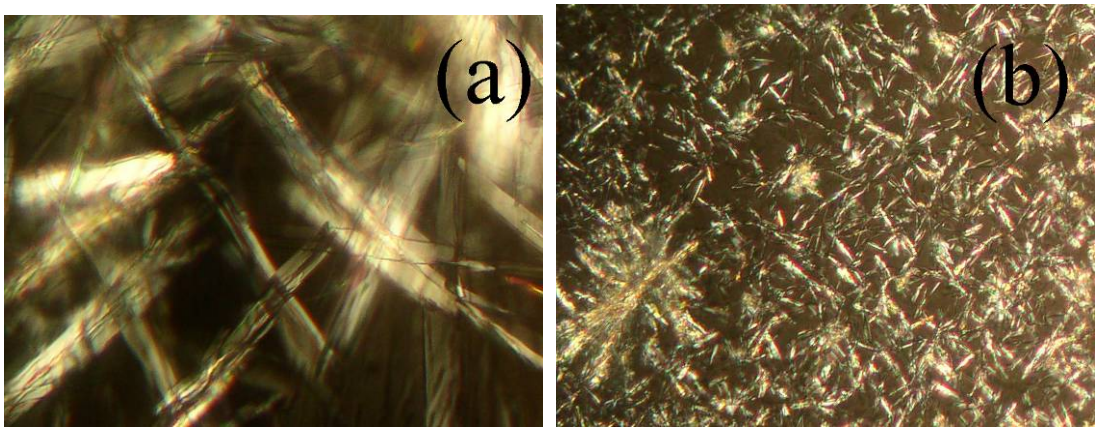


Figure S-1 Polarized optical microscope images of (a) BOM8 in propylene carbonate gel, (b) BSM18 in propylene carbonate gel

Molecular simulation: The energy-minimized structure of MBB18 molecules and aggregates (Figure 3 in manuscript) were simulated by Molecular Modeling Software HyperChem 7.5. The energy-minimized structure of MBB18 was shown as Figure S-2.

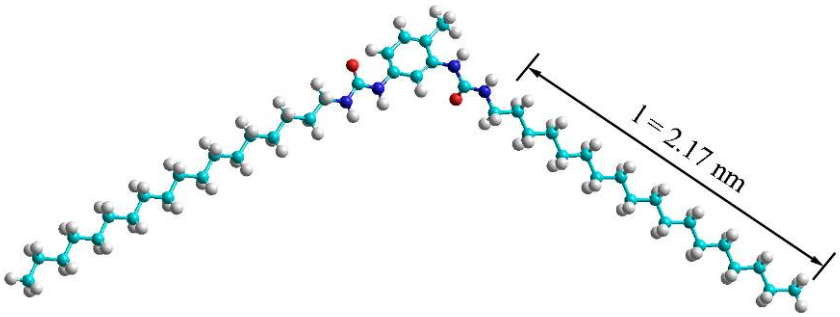


Figure S-2 The minimum energy structure of MBB18