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ARTICLE

Self-assembling supramolecular columnar organogels formed by wedge shaped cesium 3,4,5- alkyloxy benzene sulfonates

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Supplementary

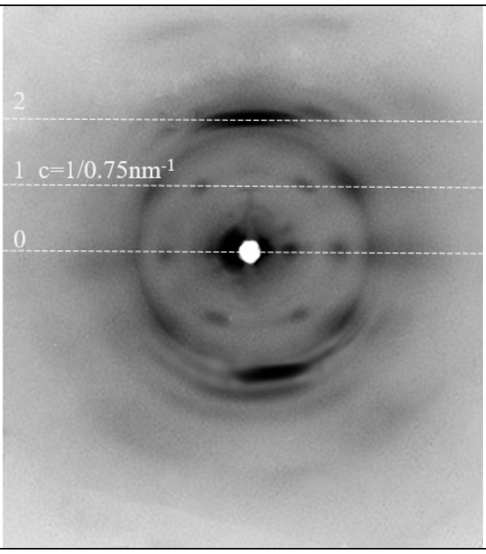

Figure S1. Fiber diagram for uniaxially oriented sample Cs12

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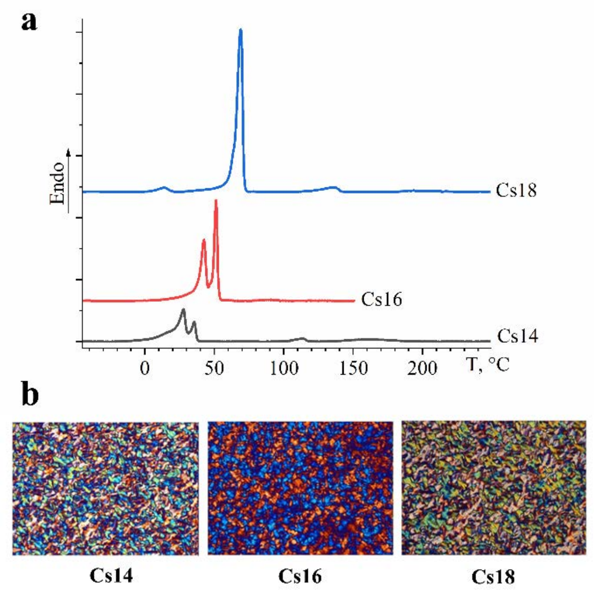

Figure S2. Second heating DSC thermograms for cesium 3,4,5-tris(alkyloxy)benzenesulfonates Cs14 – Cs18 (a). POM microphotographs of compounds Cs14 – Cs18 at 100°C 50°C and 100°C respectively (b).

EXPERIMENTAL SECTION

Materials

2-Ethylhexyl methacrylate (EHMA) (≥98%, Alfa Aesar), ethylene glycol dimethacrylate (EGDMA) (≥98%, Alfa Aesar), 2-hydroxyethyl methacrylate (HEMA) (≥97%, Alfa Aesar), n-hexyl methacrylate (HMA) (≥97%, Alfa Aesar), triethylene glycol dimethacrylate (TEGDMA) (99%, Sigma-Aldrich), benzene (≥99.7%, Sigma-Aldrich), N,N-dimethylformamide (DMF) (99.9%, Sigma-Aldrich), styrene (≥99.5%, Fluka), tetrahydrofuran (THF) (99.9%, Sigma-Aldrich), toluene (≥99.7 %, Fluka), acetone, methanol, n-hexane were used as received.

Synthesis

3,4,5-trihydroxybenzenesulfonic acid: Through 100mL of an aqueous solution of pyrogallol (10g, 0.08mol), Na_2SO_3 (25.2g, 0.2mol) and NaOH (3.3g, 0.08mol), air was strongly bubbled for 10h to form a dark solution. 50mL HCl (16%) were added and the mixture became continuously extracted with diethylether over 48h in a liquid-liquid extraction equipment. After addition of 51.2g (0.2mol) $Ba(OAc)_2$, dissolved in water, the precipitate was filtrated off and treated with sulfuric acid. The filtered solution was run subsequently over a pre-acidified ion-exchanger column (450g Amberlite IR 120 resin) to remove all metal ions. The strongly acidic solution was decolorized by boiling for 30min with 4g activated charcoal and the main amount of water was removed at reduced pressure on a rotary evaporator. After 3 times recrystallization from 100mL water at 0°C, the white crystals were dried over P_4O_{10} in vacuum for 48h to obtain a white powder.

Yield: 11.60g≌71% of theory ($C_6H_6O_6S$, 206.18 g/mol). M.p.: 39~40°C (by DSC). ^{1}H-NMR (D_2O, ppm): 6.911 (s, 2H, benzene-H); ^{13}C-NMR(D_2O, ppm): 106.19(2-benzene-C), 134.241(4-benzene–C), 135.742(1-benzene–C), 145.122(3- benzene –C).

Table 1. Synthetic conditions to prepare sulfonates **1a-1g** according to the general description.

Sulfonate	Formula	Mass (g/mol)	Time (h)	Tem.(°C)	Yield (%)
Cs6	$C_{24}H_{41}O_6SCs$	590.55	24	80	39.0
Cs8	$C_{30}H_{53}O_6SCs$	674.71	24	80	39.6
Cs10	$C_{36}H_{65}O_6SCs$	758.87	24	80	49.8
Cs12	$C_{42}H_{77}O_6SCs$	843.04	24	80	58.5
Cs14	$C_{48}H_{89}O_6SCs$	927.20	24	80	54.3
Cs16	$C_{54}H_{101}O_6SCs$	1011.36	36	100	54.2
Cs18	$C_{60}H_{113}O_6SCs$	1095.52	48	100	61.4

Procedure for synthesis of cesium 3,4,5-tris(alkyloxy)benzene sulfonates Cs6-Cs18:

3,4,5-Trihydroxybenzenesulfonic acid (1.04g, 5mmol) and Cs_2CO_3 (16.3g, 50mmol) were mixed with 60mL dried DMF in a 100mL three-necked flask with a magnetic stirrer under a nitrogen atmosphere. At 80°C, 30mmol of a solution of the 1-bromoalkane in 10 mL DMF was added dropwise, followed by 0.25g KI. The reaction mixture was stirred for 24h at 80°C. After reaction, almost all solvent was removed at reduced pressure upon a rotary evaporator. 300mL of acetone was added to the residuum to form a white precipitate. The precipitate was isolated by filtration and dried in vacuum for 24h. The crude product was recrystallized 3 times from 100mL MeOH to give a white solid. After filtration and freeze-drying from 20mL benzene, a white powder was obtained.

Cesium 3,4,5-tris(hexyloxy)benzene sulfonate (Cs6): Yield: 0.65g≌39.0% of theory. M.p.: 50.0°C (by DSC). TLC (MeOH/$CHCl_3$=1/6): R_f=0.42. ^{1}HNMR (500MHz, $CDCl_3$, 20°C, TMS): 0.882(overlapped peaks, 9H, CH_3-), 1.278, 1.310, 1.439, 1.743 (broad, 24H, $CH_3(CH_2)_4$), 4.073(m, 6H, OCH_2), 7.060(s, 2H, 2,6-benzene-H). ^{13}CNMR (125MHz, $CDCl_3$, 20°C, TMS): 14.029, 22.641, 29.272, 30.334, 31.888, 69.281, 73.481, 104.824, 140.942, 152.974. IR (cm^{-1}): 3408.11, 2912.47, 2855.45, 1588.68, 1502.81, 1427.22, 1379.06, 1320.90, 1235.25, 1190.89, 1112.76, 1053.50, 1001.32, 990.43, 834.60, 728.70, 720.75, 640.49, 599.52, 590.05, 545.23. Elemental analysis calculated(%):C 48.81 H 7.00 S 5.43; found(%): C 47.87 H 7.10 S 4.54

Cesium 3,4,5-tris(octyloxy)benzene sulfonate (Cs8): Yield: 1.08g≌39.6% of theory. M.p.: 59.0°C (by DSC). TLC (MeOH/$CHCl_3$ =1/6): R_f=0.46. ^{1}HNMR (500MHz, $CDCl_3$, 20°C, TMS): 0.894(overlapped peaks, 9H, CH_3-), 1.299, 1.435, 1.723(broad, 36H, $CH_3(CH_2)_6$), 3.948(m, 6H, OCH_2), 7.058(s, 2H, 2,6-benzene-H). ^{13}CNMR (125MHz, $CDCl_3$, 20°C, TMS): 14.029, 22.648, 29.550, 30.359, 31.845, 69.356, 73.415, 104.290, 139.772, 139.982, 153.004. IR (cm^{-1}): 3417.42, 2919.71, 2851.21, 1586.87, 1498.91, 1467.02, 1421.41, 1390.33, 1315.85, 1234.24, 1183.98, 1107.62, 1046.05, 1004.34, 984.24, 829.60, 722.65, 661.94, 637.97, 600.28, 583.78, 543.20. Elemental analysis calculated(%): C 53.40 H 7.92 S 4.75; found(%): C 53.25 H 7.96 S 4.49

Cesium 3,4,5-tris(decyloxy)benzene sulfonate (Cs10): Yield: 1.98g≌49.8% of theory. M.p.: 84.1°C (by DSC); TLC (MeOH/$CHCl_3$ =1/6): R_f=0.49. ^{1}HNMR (500MHz, $CDCl_3$, 20°C, TMS): 0.895(overlapped peaks, 9H, CH_3-), 1.278, 1.314, 1.442, 1.720, 1.749 (broad, 48H, $CH_3(CH_2)_8$), 3.945, 3.969 (t, 6H, OCH_2), 7.050(s, 2H, 2,6-benzene-H), ^{13}CNMR (125MHz, $CDCl_3$, 20°C, TMS): 14.067, 22.761, 26.173, 29.511, 29.649, 29.558, 31.923, 68.031, 69.375, 104.332, 139.114, 140.673, 153.515. IR (cm^{-1}): 3417.59, 2918.77, 2850.41, 1584.41, 1499.15, 1467.09, 1422.54, 1389.82, 1317.41, 1234.02, 1202.72, 1184.35, 1110.23, 1046.55, 1003.97, 829.08, 721.77, 66303, 638.06, 600.89, 584.13, 543.45. Elemental analysis calculated(%): C 56.98 H 8.63 S 4.22; found(%): C 56.34 H 8.55 S 3.97

Cesium 3,4,5-tris(dodecyloxy)benzene sulfonate (Cs12): Yield: 2.08g≌58.5% of theory. M.p.:79.7 °C (by DSC); TLC (MeOH/CHCl$_3$=1/6): R_f=0.51. ^{1}HNMR (500MHz, CDCl$_3$, 20°C, TMS): 0.887, 0.895(overlapped peaks, 9H, CH$_3$-), 1.243, 1.409, 1.679, 1.849 (broad, 60H, CH$_3$(CH$_2$)$_{10}$),, 3.924, 3.951(t, 6H, OCH$_2$), 7.050(s, 2H, 2,6- benzene-H). ^{13}CNMR (125MHz, CDCl$_3$, 20°C, TMS): 14.044, 22.663, 26,231, 29.377, 29.649, 29.739, 30.384, 31.923, 69.384, 73.429, 104.339, 139.765, 139.811, 153.015. IR (cm^{-1}): 3424.03, 2917.67, 2849.82, 1584.04, 1499.36, 1467.09, 1422.16, 1390.68, 1317.50, 1235.68, 1182.70, 1111.02, 1047.11, 997.12, 829.21, 721.25, 663.09, 637.81, 600.27, 543.55. Elemental analysis calculated(%): C 59.84 H 9.21 S 3.80; found(%): C 59.68 H 9.12 S 3.53

Cesium 3,4,5-tris(tetradecyloxy)benzene sulfonate (Cs14): Yield: 2.52g≌54.3% of theory. M.p.: 43.0°C (by DSC); TLC (MeOH/CHCl$_3$=1/6): R_f=0.56; ^{1}HNMR (500MHz, CDCl$_3$, 20°C, TMS) : 0.885(overlapped peaks, 9H, CH$_3$-), 1.281, 1.319, 1.448, 1.742, 1.797(broad, 72H, CH$_3$(CH$_2$)$_{12}$), 3.976, 4.011(t, 6H, OCH$_2$), 7.162(s, 2H, 2,6-benzene-H). ^{13}CNMR (125MHz, CDCl$_3$, 20°C, TMS): 14.088, 22.691, 26.253, 29.397, 29.592, 29.786, 30.404, 31.946, 69.334, 73.429, 104.326, 139.707, 139.851, 152.956. IR (cm^{-1}): 3419.24, 2956.42, 2917.37, 2850.11, 1585.25, 1497.16, 1466.48, 1421.46, 1388.76, 1316.60, 1235.05, 1109.83, 1045.30, 827.97, 720.94, 659.52, 637.64, 598.50, 542.99. Elemental analysis calculated(%): C 62.18 H 9.68 S 3.46; found(%): C 61.40 H 9.41 S 3.12

Cesium 3,4,5-tris(hexadecyloxy)benzene sulfonate (Cs16): Yield: 2.74g≌54.2% of theory. M.p.: 56.9°C (by DSC). TLC (MeOH/CHCl$_3$ =1/6): R_f=0.48. ^{1}HNMR 500MHz, CDCl$_3$, 20°C, TMS): 0.900 (overlapped peaks, 9H, CH$_3$-), 1.280, 1.304, 1.353, 1.694, 1.84(broad, 84H, CH$_3$(CH$_2$)$_{14}$), 3.929, 3.987(overlapped peaks, 6H, OCH$_2$), 7.164(s, 2H, 2,6-benzene-H). ^{13}CNMR (125MHz, CDCl$_3$, 20°C, TMS): 14.089, 22.686, 26.228, 29.227, 29.484, 29.788, 30.390, 31.938, 63.956, 68.031, 73.400, 104.413, 139.600, 139.979, 152.876, 155.457. IR (cm^{-1}): 2917.49, 2849.83, 1584.86, 1466.36, 1417.36, 1379.17, 1310.74, 1274.46, 1227.86, 1195.63, 1111.26, 1045.50, 960.43, 886.40, 791.31, 720.66, 659.92, 599.18, 540.38. Elemental analysis calculated(%): C 64.13 H 10.07 S 3.17; found(%): C 63.79 H 9.83 S 2.80

Cesium 3,4,5-tris(octadecyloxy)benzene sulfonate (Cs18): Yield: 3.36g≌61.4% of theory. M.p.: 71.7°C (by DSC); TLC (MeOH/CHCl$_3$ =1/6): R_f=0.58. ^{1}HNMR (500MHz, CDCl$_3$, 20°C, TMS): 0.898(overlapped peaks, 9H, CH$_3$-), 1.278, 1.432, 1.697, 1.740, 1.799(broad, 96H, CH$_3$(CH$_2$)$_{16}$), 3.927, 3.999 (overlapped peaks, 6H, OCH$_2$), 7.159(s, 2H, 2,6-benzene-H). ^{13}CNMR 125MHz, CDCl$_3$, 20°C, TMS): 14.057, 22.657, 26.151, 29.454, 29.701, 29.737, 63.980, 69.170, 76.981, 104.681, 139.317, 140.673, 152.662, 155.439. IR (cm^{-1}): 2915.88, 2849.16, 1585.16, 1469.25, 1419.53, 1383.56, 1317.34, 1230.74, 1187.30, 1105.62, 1047.24, 839.41, 718.38, 664.76, 603.49, 543.08. Elemental analysis calculated(%): C 65.78 H 10.40 S 2.93; found(%): C 65.87 H 10.46 S 2.62

Techniques

An optical polarizing microscope Zeiss AXIOPLAN 2, equipped with a Mettler FP-90 hot stage, was used for detecting thermo - optical properties of the formed gels at different concentrations. Micrographs were taken using a digital Zeiss AxioCam MRC4 camera with a resolution of 4 megapixels in combination with Zeiss AxioVision software.

Differential scanning calorimetry measurements were performed on a Netzsch DSC 204 'Phoenix' calorimeter to examine the phase transition behaviors of gels, and reported as the maximum or minimum temperatures of the respective endo- or exothermic signals. All measurements were performed using about 10mg gels, and the corresponding solvent as references. In all cases, the heating and cooling rates were 10°C/min. Indium and cyclohexane was used as calibration standards.

A Zeiss Evo ®50 Scanning Electron Microscope was applied to analyze the surface morphologies of dried gels. The SEM samples were prepared as follows: a tiny piece of the dried gel obtained by evaporation of the solvent in air was chipped off and mounted onto a stub using carbon paint dag. Subsequently the sample was sputtered with platinum on a Q150R rotary-pumped sputter coater (Quorum Technologies) for 3~5 min.

A Zeiss EM 902 A Transmission Electron Microscope was used to analyze the morphologies of dried gels. The TEM samples are prepared as follows: a dried gel, prepared by evaporation of the solvent in air, was laid horizontally on a glass plane, and a carbon-coated copper grid was dipped onto the gel surface and pressed slightly. Then the grid covered by a ultrathin film was stained in the gas phase with ruthenium tetroxide (RuO$_4$) freshly developed from mixing 100mg ruthenium trichloride hydrate (RuCl$_3$·xH$_2$O) in a 5mL sodium hypochloride solution (NaClO, assay of 6~14wt% active Cl)[28-30]. For a favorable contrast the section was stained for 5~8 minutes before the investigation by TEM.

Gel preparation

Gels were prepared by means of the following typical procedures:

(a) Spontaneous gelation: In a 5mL test vial with a screw cap, 400 mg of a solvent / sulfonate mixture (1wt%, 2wt%, 5wt%, 10 wt% sulfonate) was heated in an oil bath until a transparent solution was obtained. Subsequently the resulting solution was allowed to cool down spontaneously to the selected investigation temperature (+20°C, -5°C, -20°C, dT/dt ~ 10 K/min), and left untouched for at least 4h. Then the vial was turned upside down to examine the presence of viscous flow or a solid gel.

(b) Quench gelation: As described with procedure (a), 400 mg of the mixture of gelator and solvent was heated until the solid was completely dissolved, then the solution was immediately quenched with liquid nitrogen to -196°C to yield a clear glass (dT/dt ~ 100 K/min). The resulting solid was slowly thawed to the investigation temperature (20°C, -5°C and -20°C) and left for at least 4h. The gelling capability was evaluated qualitatively by optical inspection of the state of the samples.