Electronic Supplementary Information

Anion-directed self-organization of thermotropic liquid crystalline materials containing a guanidinium moiety

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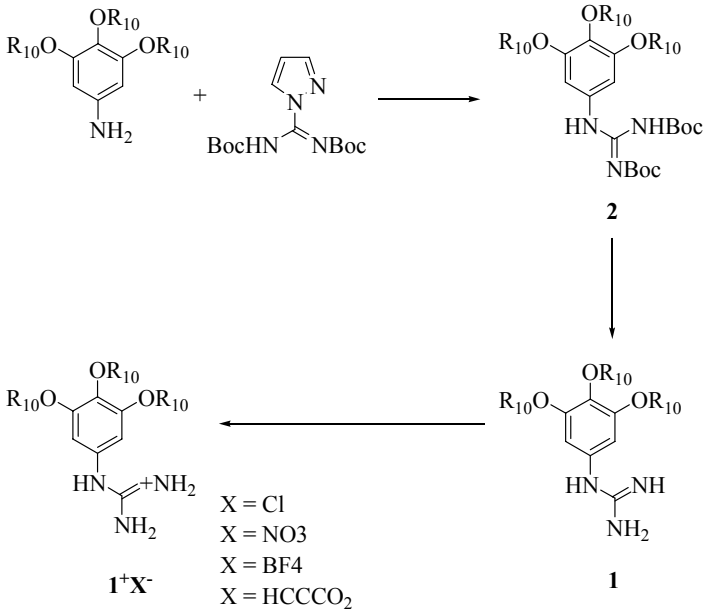

1. Experimental section

General Methods. ^{1}H NMR spectra and ^{13}C NMR spectra were taken on a Bruker DPX-300 or DRX-500 spectrometer. All chemical shifts are reported in parts per million downfield from internal TMS (tetramethylsilane). The optical textures of the mesophases were studied with a Zeiss JENALAB-pol polarizing microscope equipped with a Linkam LTS 350 hot stage, a TMS 93 temperature controller and SDC-460M CCD camera. Transition temperatures and enthalpies were measured with a Perkin-Elmer Pyris differential scanning calorimeter operated at a scanning rate of 10 °C/min. All chemicals were of reagent grade and were used without further purification except as noted below.

X-ray diffraction studies. The X-ray diffraction experiments were performed in a transmission mode with synchrotron radiation at the Pohang Accelerator Laboratory (Beamline 3C2). To investigate structural changes on heating, samples were held in an aluminum sample holder, which was sealed with 7μm thick Kapton films on both sides. The samples were heated with two cartridge heaters and the sample temperature was monitored by a thermocouple placed close to the samples.

1,2-Bis(*tert*-butyloxycarbonyl)-3-(3,4,5-tridecyloxyphenyl)-guanidine, 2

A solution of 3,4,5-tridecyloxyaniline[1] (520 mg, 1.68 mmol) and 1-*H*-pyrazole-1-(*N*,*N*'-bis(*tert*-butyloxycarbonyl))carboxamidine[2] (1.41g, 2.51 mmol) in $CHCl_3$ (20 mL) was stirred at room temperature for 60 h. The mixture was concentrated under a reduced pressure. The resulting oil was purified by chromatography on silica gel by eluting 10 % ethyl acetate in hexane to give **2** (1.02 g, 76.0 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 11.5 (s, 1H), 10.1 (s, 1H), 6.89 (s, 2H), 3.96 (t, 4H), 3.90 (t, 2H), 1.72 – 1.80 (m, 6H), 1.53 (s, 9H), 1.48 (s, 9H), 1.45 – 1.46 (m, 6H), 1.27 (m, 36H), 0.88 (t, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.61, 153.54, 153.40, 153.13, 135.47, 132.41, 101.50, 83.87, 79.48, 73.68, 69.30, 32.17, 32.14, 29.97, 29.90, 29.88, 29.84, 29.81, 29.62, 29.58, 29.53, 28.42, 28.32, 26.35, 26.28, 22.91, 14.33. MS (FAB, m/z), $[M+H]^+$ 804.63. Anal. Calc. for $C_{47}H_{85}N_3O_7$: C, 70.19; H, 10.65; N, 5.23. Found: C, 70.06; H, 10.95; N, 5.28.

3,4,5-Tridecyloxyphenylguanidine, 1

A solution of **2** (794 mg, 0.99 mmol) and trifluoroacetic acid (5 mL) in dichloromethane (5 mL) was stirred at room temperature for 10 h. The solvent was evaporated under a reduced pressure. The resulting mixture was dissolved in diethyl ether (10 mL) and washed with 25 % NaOH aqueous solution, water and brine, sequentially. The solvent was removed *in vacuo* and the resulting oil was recrystallized from acetonitrile at –4 ^{o}C to give **6** (1.07 g, 86 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.14 (s, 2H) 4.05 (br, 3H), 3.89 – 3.93 (m, 6H), 1.71 – 1.80 (m, 6H), 1.44 – 1.46 (m, 6H), 1.27 – 1.30 (m, 36H), 0.88 (t, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.79, 151.81, 144.75, 133.89, 101.78, 73.70, 69.18, 32.12, 30.55, 29.97, 29.86, 29.80, 29.64, 29.56, 26.37, 26.33, 22.89, 14.31. MS (FAB, m/z), $[M+H]^+$ 604.56. Anal. Calc. for $C_{37}H_{69}N_3O_3$: C, 73.58; H, 11.52; N, 6.96. Found: C, 73.15; H, 11.58; N, 6.82.

3,4,5-Tridecyloxyphenylguanidinium chloride, 1^+Cl^-

Aqueous HCl solution (35 %, 163 μL, 2.40 mmol) was added to a methanol solution (5 mL) of **1** (146 mg, 0.240 mmol) and the mixture was stirred at room temperature for 7 h. After cooling to –4^{o}C, the resulting waxy solid was filtered, washed with MeOH, MeOH-water (1:1) (50.2 mg, 32 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.52 (br s, 1H), 7.95 (br s, 4H), 6.42 (s, 2H), 3.90 – 3.95 (m, 6H), 1.53 – 1.82 (m, 6H), 1.46 (m, 6H), 1.27 (m, 36H), 0.88 (t, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 157.57, 154.32, 138.14, 128.49, 104.71, 73.77, 69.57, 32.13, 30.51, 29.96, 29.90, 29.85, 29.80, 29.61, 29.57, 29.47, 26.29, 22.90, 14.33. Anal. Calc. for $C_{37}H_{70}ClN_3O_3$: C, 69.39; H, 11.02; N, 6.56. Found: C, 69.05; H, 11.58; N, 6.41.

3,4,5-Tridecyloxyphenylguanidinium nitrate, $1^+NO_3^-$

This compound was prepared from **1** (154 mg, 0.250 mmol) and 61 % HNO_3 solution (101 μL, 2.50 mmol) by the same method as for $\mathbf{1^+Cl^-}$ (115 mg, 68 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.50 (br s, 1H), 8.02 (br s, 4H), 6.42 (s, 2H), 3.93 (m, 6H), 1.79 (m, 6H), 1.45 (m, 6H), 1.27 (m, 36H), 0.88 (t, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.90, 154.25, 137.76, 129.19, 104.27, 73.76, 69.47, 32.14, 32.11, 30.45, 29.95, 29.88, 29.83, 29.79, 29.58, 29.55, 29.45, 26.25, 22.88, 14.30. Anal. Calc. for $C_{37}H_{70}N_4O_6$: C, 66.63; H, 10.58; N, 8.40. Found: C, 67.05; H, 11.21; N, 8.25.

3,4,5-Tridecyloxyphenylguanidinium tetrafluoroborate, $1^+BF_4^-$

This compound was prepared from **1** (147 mg, 0.240 mmol) and , 48 % HBF_4 solution (226 μL, 2.40 mmol) by the same method as for $\mathbf{1}^+\mathbf{Cl}^-$ (80.5 mg, 48 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.01 (br s, 1H), 6.43 (s, 2H), 6.37 (br s, 4H), 3.90-3.95 (m, 6H), 1.70-1.81 (m, 6H), 1.46 (m, 6H), 1.27 (m, 36H), 0.88 (t, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 156.44, 154.29, 138.03, 128.45, 104.57, 73.85, 69.51, 32.14, 32.52, 29.97, 29.87, 29.83, 29.67, 29.59, 29.50, 29.32, 22.90, 14.31. Anal. Calc. for $C_{37}H_{70}BF_4N_3O_3 \cdot H_2O$: C, 62.61; H, 10.22; N, 5.92. Found: C, 62.91; H, 10.78; N, 5.84.

3,4,5-Tridecyloxyphenylguanidinium propiolate, $\mathbf{1}^+\mathbf{HCCCO_2}^-$

This compound was prepared from **1** (126 mg, 0.201 mmol) and propiolic acid (128 μL, 2.01 mmol) by the same method as for $\mathbf{1}^+\mathbf{Cl}^-$ (44.6 mg, 32 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.32 (s, 1H), 8.01 (br s, 4H), 6.40 (s, 2H), 3.90-3.95 (m, 6H), 2.46 (s, 1H), 1.70-1.81 (m, 6H), 1.46 (m, 6H), 1.27 (m, 36H), 0.88 (t, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.72, 157.51, 154.25, 137.83, 129.57, 104.59, 80.86, 73.77, 69.57, 68.18, 32.13, 30.53, 29.96, 29.90, 29.85, 29.62, 29.57, 29.52, 26.30, 22.90, 14.32. Anal. Calc. for $C_{39}H_{71}N_3O_2 \cdot H_2O$: C, 69.42; H, 10.63; N, 6.07. Found: C, 70.05; H, 10.63; N, 5.84.

References

1. Zinsou, A.; Veber, M.; Strzelecka, H.; Jallabert, C.; Fourre, P. *New. J. Chem*. **1993**, *17*, 309.
2. Bernatowicz, M. S.; Wu, Y.; Matsueda, G. R. *Tetrahedron Lett.* **1993**, *34*, 3389.

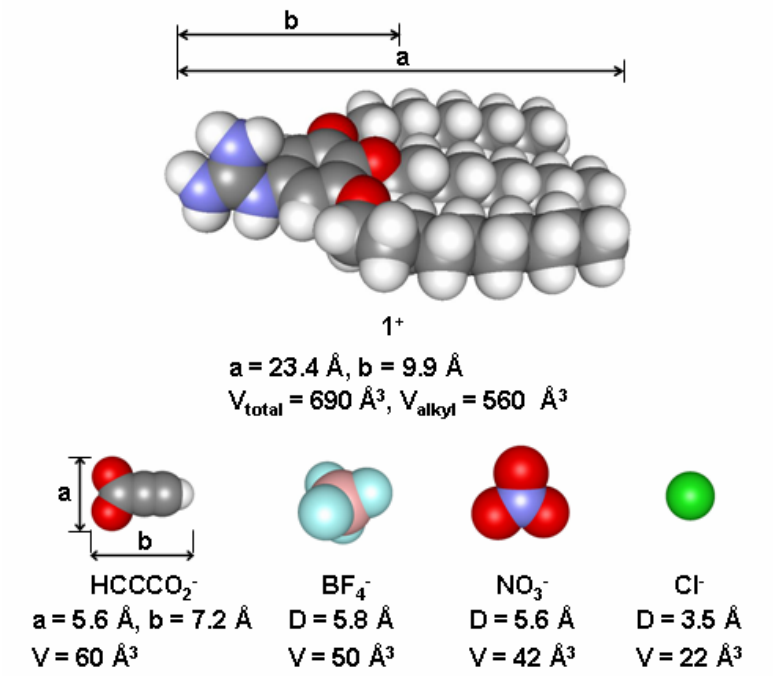

Fig. S1. Space-filling models of **1** and guest anions. Their size and volume were calculated using Cerius[2]