Supporting Information

Counterion effects on the mesomorphic and electrochemical properties of guanidinium salts

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1 Materials and Equipment

All chemicals were obtained from the supplier and used without further purification. Anhydrous tetrahydrofuran (THF) was prepared by distillation over potassium under a nitrogen atmosphere. Anhydrous dichloromethane was prepared by distillation over CaCl₂ under a nitrogen atmosphere. The eluents for chromatography hexanes (low boiling), ethyl acetate (EtOAc) and dichloromethane were distilled prior to use. When water was needed for reaction or work-up, demineralized water was always used. The degassed solvents acetonitrile (MeCN) and ethanol were prepared by channeling the respective gas (nitrogen or hydrogen) through the solvent. Dichloromethane (DCM) and ferrocene (Fc) used in the CV measurements were used as received. The supporting salt tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) was dried under vacuum overnight before measurements.

For thin-layer chromatography, TLC SiO₂ 60 F_{254} glass plates (layer thickness of 0.20 mm on aluminum, pore size 60 Å, fluorescence at 254 nm) from the company Merck were used. The identification of compounds with activity in the UV range was carried out by light irradiation of wavelengths 254 nm and 366 nm. In the case of UV-inactive compounds, staining reagents were used (KMnO₄, Seebach's reagent and phosphomolybdic acid).

Column chromatography was either carried out with silica gel (SiO₂, particle diameter of 40–63 μ m) from the company Macherey-Nagel. The silica gel used for the purification of ionic compounds was prepared by stirring SiO₂ with 6.0 M HCl for 30 min at room temperature, followed by filtration and washing with water as well as acetone until it was colourless.

¹*H NMR* (*and* ¹³*C NMR*) spectra were recorded using Bruker spectrometers Avance 300, Ascend 400, Avance 500 and Ascend 700 at 300 MHz (75 MHz), 400 MHz (101 MHz), 500 MHz (126 MHz) and 700 MHz (176 MHz), respectively. ¹⁹F NMR spectra were recorded at 376 MHz. Deuterated chloroform (CDCl₃, $\delta_{\rm H} = 7.26$ ppm, $\delta_{\rm C} = 77.2\pm0.1$ ppm) was used as solvent with tetramethyl silane (TMS, $\delta_{\rm H} = 0.00$ ppm, $\delta_{\rm C} = 0.0$ ppm) as reference for the chemical shift δ in ppm (parts per million). In some cases, deuterated dimethyl sulfoxide (DMSO-d6, $\delta_{\rm H} = 2.50$ ppm, $\delta_{\rm C} = 39.5\pm0.1$ ppm) was used instead. Coupling constants *J* were reported in Hertz (Hz) and signal multiplicities were abbreviated as follows: s (singlet), br. s (broad singlet), d (doublet), dd (doublet of doublets), dt (doublet of triplets), t (triplet), q (quartet), m (multiplet). Atom numbering can differ from the IUPAC nomenclature due to a better comparison of several compounds. ¹H- and ¹³C NMR spectra, COSY, HSQC and HMBC experiments were carried out to assign the NMR signals.

FT-IR spectra were recorded on a Bruker Vektor 22, equipped with a MKII Golden Gate Single Reflection Diamond ATR system. The intensity maxima were rounded to whole wave numbers

(cm⁻¹) and the relative absorption bands were indicated using the following abbreviations: w (weak), m (medium), s (strong), vs (very strong).

Mass spectra (MS) as well as high resolution mass spectra (HRMS) were recorded by electrospray ionisation (ESI) with a Bruker MicrOTOF-Q spectrometer, and electron ionisation (EI) with a Bruker Varian MAT 711 spectrometer.

Optical investigations were carried out with a polarising optical microscope Olympus BX 50, which could be heated via the hot plate LTS 350 from Linkam. Temperature was regulated with the control units TP93 and LNP from the company Linkam ($\Delta T = \pm 1$ K). Recorded images to capture occurring mesophase textures were taken over the digital camera Axiocam 105 Color from ZEISS, processed and archived using the software ZenCore v3 from ZEISS.

Differential scanning calorimetry (DSC) was performed on a DSC822e from the company Mettler Toledo. Therefore, sealed aluminum crucibles with heating and cooling rates of 5 K min⁻¹ were used. The phase transition temperatures of the extrapolated onset values were determined using the software STAR^e 14.0. A transition marked with '[–]' was observed at the appropriate temperature in the POM, but could not be reproduced in the DSC thermogram.

Melting points (M.p.) were determined either by investigation using the polarising optical microscope (heating rate 2–3 K) or by DSC measurements. The melting point was determined as the temperature at which the sample began to melt (liquid crystals) or was completely melted (for substances without mesophase).

X-ray diffractograms in the small (SAXS) and wide angle (WAXS) range were recorded on an AXS Nanostar C from Bruker. X-rays (nickel-filtered, monochromatic Cu-K α radiation, wavelength λ : 1.5406 Å) were generated in a Siemens X-ray tube with a power of 1500 W. Calibration was performed with silver behenate at 298 K. For the measurement of a sample to be examined, it was extruded, melted in a pith tube of the company Hilgenberg GmbH (outer diameter: 0.7 mm) and transferred into a heatable sample holder. Diffraction patterns were recorded using a HI-STAR detector from Bruker. The analysis of the measurement data was carried out with the software SAXS (version 4.1.51) of the company Bruker, that of the X-ray diffractograms with the programs Datasqueeze (version 2.2.8) and OriginPro 2021 (version 9.8.0.200) from OriginLab[®].

Cyclic voltammetry (*CV*) measurements were *performed* using the *three-electrode system* of a Metrohm Autolab PGSTAT204 and the TSC 70 closed measuring cell by rhd instruments. The CV cell consisted of platinum wires as working and reference electrode and a platinum crucible as counter electrode. Before measuring the ILC compounds were dried in-vacuo (10^{-2} mbar) overnight. Afterwards the samples were solved in dry dichloromethane (0.05 M) and the

solution deoxygenated by bubbling nitrogen through the solution. Ferrocene was utilized as internal standard ($5 \cdot 10^{-4}$ M) and tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆) as electrolyte (0.1 M). A scan rate of 0.1 V/s and three subsequent scans were used for all measurements. The ferrocene half wave potentials in the measurements of the ILC compounds ranged between 0.1 – 0.5 V and were subsequently normalized to a half wave potential of 0.0 V. For the analysis of the data the second scan of the measurements was used. For the reductive stability E_{cat} of the compounds a current cut-off at $1 \cdot 10^{-7}$ A was determined as stability limit, as most samples showed no real current peak that could be used in the investigated window. Two different approaches were, however, used for the oxidative stability E_{an} , as can be seen in table 3. For the first approach the current cut-off at $2 \cdot 10^{-7}$ A was determined as the limit and for the second approach the current maximum of the actual process peak(s). In contrast to the current did not return to a current baseline below $1 \cdot 10^{-7}$ A between ferrocene oxidation and oxidation of the sample. Therefore, a higher cut-off current had to be chosen.

Simultaneous thermogravimetric analysis-differential thermal analysis (TGA-DTA) experiments were done on a Mettler Toledo TGA/DSC 3+ Thermogravimetric Analyzer in a temperature range from 30 to 600 °C with a heating rate of 10 K/min in air in aluminium oxide crucibles.

2 Synthesis

2.1 Synthesis of Gua(n)X

Free amine $BzTyrC_nNH_2$ (n = 10, 12, 14), GuaCl, Gua(14)Cl were synthesized according to literature procedures.¹

Gua(14)Cl

Free amine **BzTyrC**₁₄**NH**₂ (414 mg, 5.67 mmol), sodium bicarbonate (4.70 g, 56.0 mmol), **GuaCl** (6.5 mL, 6.5 mmol, 1.0 M in CH₂Cl₂) was dissolved in dry CH₂Cl₂ (100 mL) and stirred for 1 h under reflux. After cooling to room temperature, the solid was filtered off, 50 mL conc. HCl was added to the organic phase and the solution stirred intensively for 10 min. Then, the aqueous phase was separated and the organic phase was washed with 2M aq. HCl (1 x 50 mL) and H₂O (1x 50 mL). Subsequently, the combined organic phases were dried over magnesium sulphate. After removing MgSO₄, HCl treated silica gel was added to the crude product (about 10 g) and the solvent was removed under reduced pressure. The crude product on the HCl silica gel was applied on a previously prepared silica gel column (about 60 g silica gel) and filtered off with 500 mL EtOAc. The organic phase was removed under reduced pressure and the crude product was purified by column chromatography (CH₂Cl₂ / MeOH = 10 : 1), followed by recrystallization from EtOAc (2x). **Gua(14)Cl** was isolated as a colorless solid (3.30 g, 3.82 mmol, 67 %).



¹H-NMR (500 MHz, CDCl₃): $\delta = 0.87$ (t, J = 6.9 Hz, 9H, CH₃), 1.25-1.32 (m, 60H, CH₂), 1.41-1.45 (m, 6H, CH₂), 1.67-1.79 (m, 6H, OCH₂CH₂), 2.96 (br s, 12H, N[CH₃]₂), 3.89 (t, J = 7.0 Hz, 2H, OCH₂), 3.93 (t, J = 6.4 Hz, 4H, OCH₂), 6.37 (s, 2H, 2-H), 12.02 ppm (s, 1H, NH); ¹³C-NMR (125 MHz, CDCl₃): $\delta = 14.2$ (CH₃), 22.8, 26.2, 29.48, 29.50, 29.6, 29.73, 29.76, 29.78, 29.83, 29.86, 30.4, 32.0 (CH₂), 40.7 (br s, N[CH₃]₂), 69.7, 73.6 (OCH₂), 100.4 (C-2), 133.3, 136.1 (C-1, C-4), 154.0 (C-3), 158.8 ppm (C-1[']). FT-IR (ATR): $\tilde{v} = 2922$ (s), 2853 (s), 2193 (w), 1621 (m), 1600 (m), 1560 (w), 1502 (w), 1466 (m), 1429 (w), 1310 (w), 1260 (m), 1231 (m), 1097 (s), 1014 (s), 907 (m), 798 (vs), 729 (vs), 641 (w) cm⁻¹ (m). Anal. calc. for C_{53H102}ClN₃O₃ (864,87): C 73.60, H 11.89, N 4.86; calc. for [M·0.15 H₂O]: C 73.38, H 11.89, N 4.84; found: C 73.43, H 11.92, N 4.84; MS (ESI): m/z (%) = 828.79 [M]⁺. HRMS (ESI): calcd. for $[C_{53}H_{102}N_3O_3]^+$ 828.7916, found 828.7910 [M]⁺. DSC, heating up: Cr₁ 34 °C [-36.5 kJ mol⁻¹] Cr₂ 72 °C [51.5 kJ mol⁻¹] Cr₃ 87 °C [-55.5 kJ mol⁻¹] I; cooling down: Cr 25 °C [36.7 kJ mol⁻¹] Col 89 °C [1.2 kJ mol⁻¹] I.

GP1: Anion Exchange of Gua(14)Cl to Gua(14)X

Guanidinium chloride Gua(14)Cl was dissolved in acetonitrile. Then, 5 equiv. of the corresponding salt was added to the suspension and refluxed for 0.5 h. After cooling to room temperature, the solvent was removed under reduced pressure and the reaction mixture was extracted with dichloromethane (3 x 75 mL), filtered through syringe filters, following by removing the solvent again on the rotary evaporator. Subsequent recrystallization gave the respective products Gua(14)X as colourless solids in 79%-91% yields

Gua(14)Br

According to GP1: **Gua(14)Cl** (163 mg, 0.188 mmol), 6 mL MeCN; KBr (274 mg, 2,30 mmol); recrystallization from EtOAc; yield: (88%, 0.151 g, 0.166 mmol)



¹H-NMR (500 MHz, CDCl₃): $\delta = 0.87$ (t, J = 6.9 Hz, 9H, CH₃), 1.25-1.32 (m, 60H, CH₂), 1.41-1.47 (m, 6H, CH₂), 1.68-1.79 (m, 6H, OCH₂CH₂), 2.96 (br s, 12H, N[CH₃]₂), 3.89 (t, J = 6.6 Hz, 2H, OCH₂), 3.94 (t, J = 6.4 Hz, 4H, OCH₂), 6.37 (s, 2H, 2-H), 11.67 ppm (s, 1H, NH); ¹³C-NMR (125 MHz, CDCl₃): $\delta = 14.2$ (CH₃), 22.8, 26.2, 29.5, 29.6, 29.74, 29.78, 29.80, 29.85, 29.88, 30.4, 32.1 (CH₂), 40.7 (br s, N[CH₃]₂), 69.6, 73.6 (OCH₂), 100.4 (C-2), 133.2, 136.1 (C-1, C-4), 154.0 (C-3), 158.8 ppm (C-1[']). FT-IR (ATR): $\tilde{v} = 3401$ (br w), 2916 (vs), 2849 (vs), 1629 (m), 1600 (m), 1559 (m), 1504 (m), 1467 (m), 1429 (m), 1403 (w), 1309 (w), 1232 (m), 1170 (w), 1116 (s), 1068 (w), 1010 (w), 906 (w), 831 (w), 721 (m); Anal. calc. for C₅₃H₁₀₂BrN₃O₃ (909.71): C 70.01, H 11.31, N 4.62; calc. for [M·0.8 H₂O]: C 68.91, H 11.30, N 4.55; found: C 68.82, H 11.38, N 4.66; MS (ESI): m/z (%) = 828.79 [M]⁺. HRMS (ESI): calcd. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, found 828.7910 [M]⁺. DSC, heating up: Cr₁ 34 °C [-32.4 kJ mol⁻¹] Col₁ 86 °C [-0.3 kJ mol⁻¹] Col₂ 93 °C [-1.0 kJ mol⁻¹]I; cooling down: Cr 25 °C [30.9 kJ mol⁻¹] Col 91 °C [-1.1 kJ mol⁻¹] I.

Gua(14)I

According to GP1: **Gua(14)Cl** (151 mg, 0.175 mmol), 6 mL MeCN; KI (280 mg, 1.69 mmol); recrystallization with EtOAc; yield: (91 %, 152 mg, 0.158 mmol).



¹H-NMR (500 MHz, CDCl₃): $\delta = 0.87$ (t, J = 6.9 Hz, 9H, CH₃), 1.25-1.35 (m, 60H, CH₂), 1.42-1.48 (m, 6H, CH₂), 1.69-1.80 (m, 6H, OCH₂CH₂), 3.03 (br s, 12H, N[CH₃]₂), 3.90 (t, J = 6.6Hz, 2H, OCH₂), 3.94 (t, J = 6.4 Hz, 4H, OCH₂), 6.42 (s, 2H, 2-H), 10.01 ppm (s, 1H, NH); ¹³C-NMR (125 MHz, CDCl₃): $\delta = 14.2$ (CH₃), 22.8, 26.3, 29.5, 29.6, 29.75, 29.79, 29.81, 29.83, 29.86, 29.89, 30.4, 32.1 (CH₂), 41.2 (br s, N[CH₃]₂), 69.7, 73.7 (OCH₂), 100.4 (C-2), 132.5, 136.3 (C-1, C-4), 154.1 (C-3), 158.4 ppm (C-1'). FT-IR (ATR): $\tilde{v} = 3451$ (br w), 2916 (vs), 2849 (s), 1626 (m), 1600 (m), 1558 (w), 1504 (w), 1467 (m), 1429 (w), 1308 (w), 1260 (m), 1232 (m), 1116 (s), 1010 (s), 906 (m), 722 (w) cm⁻¹ (m);); Anal. calc. for C₅₃H₁₀₂IN₆O₃ (956.36): C 66.57, H 10.75, N 4.39; found: C 66.87, H 10.94, N 4.33; MS (ESI pos.): m/z (%) = 828.79 [M]⁺. HRMS (ESI pos.): calcd. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, found. 828.7912 [M]⁺. MS (ESI neg.): m/z (%) = 126.91 (20) [I]⁻, 1082.60 (100) [M+2I]⁻. HRMS (ESI neg.): calcd. for [I]⁻ 126.9050, found 126.9058. DSC, heating up: Cr 34 °C [-33.8 kJ mol⁻¹] Col 100 °C [-1.0 kJ mol⁻¹] I; cooling down: Cr 25 °C [32.4 kJ mol⁻¹] Col 99 °C [1.0 kJ mol⁻¹] I.

Gua(14)BF4

According to GP1: **Gua(14)Cl** (292 mg, 0.337 mmol), 4 mL MeCN; KBF₄ (200 mg, 1.59 mmol); recrystallization from EtOAc; yield: (89 %, 274 mg, 0.299 mmol).



¹H-NMR (400 MHz, CDCl₃): $\delta = 0.87$ (t, J = 6.8 Hz, 9H, CH₃), 1.25-1.29 (m, 60H, CH₂), 1.41-1.45 (m, 6H, CH₂), 1.68-1.80 (m, 6H, OCH₂CH₂), 2.97 (br s, 12H, N[CH₃]₂), 3.88-3.94 (m, 6H, OCH₂), 6.29 (s, 2H, 2-H), 9.80 ppm (br s, 1H, NH); ¹³C-NMR (100 MHz, CDCl₃): $\delta = 14.2$ (CH₃), 22.8, 26.3, 29.5, 29.6, 29.76, 29.79, 29.81, 29.83, 29.86, 29.89, 30.4, 32.1 (CH₂), 40.5 (s, N[CH₃]₂), 69.6, 73.7 (OCH₂), 100.2 (C-2), 133.0, 136.1 (C-1, C-4), 154.1 (C-3), 158.9 ppm (C-1[']); ¹⁹F-NMR (375 MHz, CDCl₃): -151.7, -151.6 ppm. FT-IR (ATR): $\tilde{v} = 2916$ (vs), 2849 (vs), 1627 (m), 1600 (m), 1561 (m), 1504 (m), 1467 (m), 1430 (m), 1403 (w), 1310 (w), 1232 (m), 1170 (w), 1114 (s), 1054 (s), 908 (m), 833 (m), 722 (m); Anal. calc. for $C_{53}H_{102}BF_4N_3O_3$ (916.22): C 69.48, H 11.22, N 4.59; found: C 69.42, H 11.38, N 4.49; MS (ESI): m/z (%) = 828.79 [M]⁺. HRMS (ESI): calcd. for $[C_{53}H_{102}N_3O_3]^+$ 828.7916, found 828.7916 [M]⁺. MS (ESI neg.): m/z (%) = 87.00 [BF₄]⁻. HRMS (ESI neg.): calcd. for $[B_1F_4]^-$ 87.0035, found 87.0023. DSC, heating up: Cr 36 °C [-35.0 kJ mol⁻¹] Col 113 °C [-1.0 kJ mol⁻¹] I; cooling down: Cr 28 °C [33.7 kJ mol⁻¹] Col 112 °C [1.0 kJ mol⁻¹] I.

Gua(14)PF6

According to GP1: **Gua(14)Cl** (300 mg, 0.35 mmol), 6 mL MeCN; KPF₆ (322 mg, 1.75 mmol); recrystallization from EtOAc; yield: (90 %, 305 mg, 0.31 mmol).



¹H-NMR (400 MHz, CDCl₃): δ = 0.88 (t, *J* = 6.8 Hz, 9H, CH₃), 1.26-1.36 (m, 60H, CH₂), 1.42-1.45 (m, 6H, CH₂), 1.69-1.81 (m, 6H, OCH₂C*H*₂), 2.95 (br s, 12H, N[CH₃]₂), 3.89-3.94 (m, 6H, OCH₂), 6.21 ppm (s, 2H, 2-H); ¹³C-NMR (100 MHz, CDCl₃): δ = 14.3 (CH₃), 22.8, 26.25, 26.28, 29.49, 29.52, 29.6, 29.77, 29.80, 29.82, 29.87, 29.90, 30.5, 32.1 (CH₂), 40.3 (s, N[CH₃]₂), 69.6, 73.7 (OCH₂), 100.0 (C-2), 132.5, 136.3 (C-1, C-4), 154.3 (C-3), 158.8 ppm (C-1⁻); ¹⁹F-NMR (375 MHz, CDCl₃): -73.3, -71.4 ppm. FT-IR (ATR): \tilde{v} = 3375 (br w), 2917 (s), 2850 (s), 1632 (m), 1602 (m), 1560 (m), 1505 (m), 1467 (m), 1432 (w), 1404 (w), 1309 (w), 1233 (m), 1169 (w), 1117 (s), 1068 (w), 1011 (w), 907 (w), 840 (vs), 722 (w), 578 (m); Anal. calc. for C₅₃H₁₀₂F₆N₃O₃P (974.38): C 65.33, H 10.55, N 4.31; found: C 65.67, H 10.74, N 4.24; MS (ESI pos.): m/z (%) = 828.79 [M]⁺. HRMS (ESI pos.): calc. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, found 828.7916 [M]⁺. MS (ESI neg.): m/z (%) = 144.96 [PF₆]⁻. HRMS (ESI neg.): calcd. for [P₁F₆]⁻ 144.9647, found 144.9637. DSC, heating up: Cr₁ 34 °C [-36.8 kJ mol⁻¹] Cr₂ 39 °C [0.5 kJ mol⁻¹] Cr₃ 43 °C [-9.8 kJ mol⁻¹] Col 106 °C [-1.0 kJ mol⁻¹] I; cooling down: Cr 26 °C [34.4 kJ mol⁻¹] Col 106 °C [1.0 kJ mol⁻¹] I.

Gua(14)OMs

According to GP1: **Gua(14)Cl** 203 mg, 0.23 mmol), 6 mL MeCN; NaMes (250 mg, 2.12 mmol); recrystallization from EtOAc; yield: (79%, 171 mg, 0.18 mmol).



¹H-NMR (700 MHz, CDCl₃): $\delta = 0.87$ (t, J = 7.1 Hz, 9H, CH₃), 1.25-1.32 (m, 60H, CH₂), 1.42-1.47 (m, 6H, CH₂), 1.69-1.73 (m, 2H, OCH₂CH₂), 1.74-1.78 (m, 4H, OCH₂CH₂), 2.80 (s, 3H, S-CH₃), 2.93 (br s, 12H, N[CH₃]₂), 3.89 (t, J = 6.6 Hz, 2H, OCH₂), 3.93 (t, J = 6.3 Hz, 4H, OCH₂), 6.34 (s, 2H, 2-H), 11.62 ppm (br s, 1H, NH); ¹³C-NMR (175 MHz, CDCl₃): $\delta = 14.3$ (CH₃), 22.8, 26.3, 29.51, 29.52, 29.59, 29.75, 29.79, 29.81, 29.83, 29.86, 29.89, 29.91, 30.4, 32.1 (CH₂), 39.7 (S-CH₃), 40.6 (br s, N[CH₃]₂), 69.6, 73.3 (OCH₂), 100.3 (C-2), 133.4, 136.0 (C-1, C-4), 154.0 (C-3), 158.9 ppm (C-1'). FT-IR (ATR): $\tilde{v} = 3400$ (br w), 2917 (vs), 2850 (s), 1627 (m), 1600 (m), 1560 (m), 1504 (m), 1467 (m), 1429 (m), 1403 (w), 1383 (w), 1310 (w), 1230 (m), 1170 (m), 1116 (s), 1068 (w), 1041 (w), 1010 (w), 908 (m), 831 (w), 771 (w), 732 (s), 643 (w), 553 (w), 526 (w)); Anal. calc. for C₅₄H₁₀₅N₃O₆S (924.51): C 70.16, H 11.45, N 4.55, S 3.47; found: C 69.17, H 11.45.92, N 4.47, S 1.99; MS (ESI pos.): m/z (%) = 828.79 [M]⁺. HRMS (ESI pos.): calcd. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, gef. 828.7911 [M]⁺. MS (ESI neg.): m/z (%) = 94.98 [OMs]⁻. HRMS (ESI neg.): calcd. for [C₁H₃O₃S₁]⁻ 94.9808, found 94.9794. DSC, heating up: Cr 35 °C [-37.6 kJ mol⁻¹] Col 82 °C [-1.0 kJ mol⁻¹] I; cooling down: Cr 26 °C [35.3 kJ mol⁻¹] Col 112 °C [1.0 kJ mol⁻¹] I.

Gua(14)SCN

According to GP1: **Gua(14)Cl** 213 mg, 0.22 mmol), 5 mL MeCN; KSCN (256 mg, 2.63 mmol); recrystallization from EtOAc; yield: (84%, 185 mg, 0.21 mmol).



¹H-NMR (700 MHz, CDCl₃): $\delta = 0.87$ (t, J = 7.1 Hz, 9H, CH₃), 1.25-1.33 (m, 60H, CH₂), 1.43-1.47 (m, 6H, CH₂), 1.69-1.79 (m, 6H, OCH₂CH₂), 2.97 (br s, 12H, N[CH₃]₂), 3.89 (t, J = 6.5 Hz, 2H, OCH₂), 3.94 (t, J = 6.4 Hz, 4H, OCH₂), 6.24 (s, 2H, 2-H), 10.56 ppm (s, 1H, NH); ¹³C-NMR (175 MHz, CDCl₃): $\delta = 14.2$ (CH₃), 22.8, 26.2, 29.50, 29.51, 29.6, 29.74, 29.79, 29.80, 29.82, 29.85, 29.88, 29.90, 30.4, 32.1 (CH₂), 40.6 (s, N[CH₃]₂), 69.6, 73.7 (OCH₂), 100.1 (C-2), 133.1 (C-1), 133.3 (br s, SCN), 136.0 (C-4), 154.1 (C-3), 158.7 ppm (C-1′). FT-IR (ATR): $\tilde{v} = 2955$ (w), 2915 (vs), 2849 (vs), 2050 (s), 1628 (m), 1599 (m), 1559 (m), 1503 (m), 1467 (m), 1428 (m), 1401 (w), 1385 (w), 1309 (w), 1231 (m), 1168 (w), 1115 (s), 1067 (w), 1009 (w), 907 (w), 830 (w), 721 (m); Anal. calc. for $C_{54}H_{102}N_4O3S$ (887.50): C 73.08, H 11.58, N 6.31, S 3.61; calc. for [M·0.5 H₂O]: C 72.35, H 11.58, N 6.25, S 3.58; found: C 72.46, H 11.63, N 6.19, S 2.95; MS (ESI): m/z (%) = 828.79 [M]⁺. HRMS (ESI): calcd. for $[C_{53}H_{102}N_3O_3]^+$ 828.7916, found 828.7909 [M]⁺. DSC, heating up: Cr₁ 35 °C [-12.9 kJ mol⁻¹] Cr₂ 38 °C [17.6 kJ mol⁻¹] Cr₃ 55 °C [-51.2 kJ mol⁻¹] Col 77 °C [-0.8 kJ mol⁻¹] I; cooling down: Cr 30 °C [40.7 kJ mol⁻¹] Col 75 °C [0.8 kJ mol⁻¹] I.

Gua(14)N(CN)2

According to GP1: **Gua(14)Cl** 304 mg, 0.35 mmol), 6 mL MeCN; NaN(CN)₂ (156 mg, 1.75 mmol); recrystallization from EtOAc; yield: (89%, 278 mg, 0.31 mmol).



¹H-NMR (700 MHz, CDCl₃): $\delta = 0.87$ (t, J = 7.0 Hz, 9H, CH₃), 1.25-1.34 (m, 60H, CH₂), 1.44-1.48 (m, 6H, CH₂), 1.70-1.74 (m, 2H, OCH₂CH₂), 1.77-1.81 (m, 4H, OCH₂CH₂), 2.98 (br s, 12H, N[CH₃]₂), 3.91 (t, J = 6.6 Hz, 2H, OCH₂), 3.93 (t, J = 6.4 Hz, 4H, OCH₂), 6.16 (s, 2H, 2-H), 10.28 ppm (br s, 1H, NH); ¹³C-NMR (175 MHz, CDCl₃): $\delta = 14.3$ (CH₃), 22.8, 26.3, 29.50, 29.52, 29.53, 29.6, 29.76, 29.80, 29.82, 29.83, 29.87, 29.89, 29.91, 30.4, 32.1 (CH₂), 40.6 (s, N[CH₃]₂), 69.6, 73.7 (OCH₂), 100.0 (C-2), 120.0 (N-CN), 132.7, 136.3 (C-1, C-4), 154.2 (C-3), 158.7 ppm (C-1⁻). FT-IR (ATR): $\tilde{v} = 2916$ (vs), 2849 (vs), 2235 (m), 2198 (w), 2132 (vs), 1629 (m), 1600 (m), 1561 (m), 1467 (m), 1429 (m), 1401 (w), 1311 (m), 1231 (m), 1169 (w), 1116 (s), 1067 (w), 1010 (w), 908 (w), 829 (w), 722 (m); Anal. calc. for C₅₅H₁₀₂N₆O₃ (895.46): C 73.77, H 11.48, N 9.39; calc. for [M·0.9 H₂O]: C 72.46, H 11.48, N 9.22; found: C 72.40, H 11.50, N 9.07; MS (ESI): m/z (%) = 828.79 [M]⁺. HRMS (ESI): calcd. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, found 828.7912 [M]⁺.]⁺. MS (ESI neg.): m/z (%) = 66.0 [N(CN)₂]⁻. HRMS (ESI neg.): calcd. for [C₂N₃]⁻ 66.0098, found 66.0075. DSC, heating up: Cr 45 °C [-26.8 kJ mol⁻¹] Col 70 °C [-21.0 kJ mol⁻¹] I; cooling down: Cr 40 °C [51.5 kJ mol⁻¹] Col 70 °C [0.8 kJ mol⁻¹] I.

Gua(14)NO₃

According to GP1: **Gua(14)Cl** (194 mg, 0.22 mmol), 5 mL MeCN; NaNO₃ (191 mg, 2.25 mmol); recrystallization from EtOAc; yield: (89%, 177 mg, 0.20 mmol).



¹H-NMR (700 MHz, CDCl₃): $\delta = 0.87$ (t, J = 7.0 Hz, 9H, CH₃), 1.25-1.33 (m, 60H, CH₂), 1.42-1.48 (m, 6H, CH₂), 1.70-1.78 (m, 6H, OCH₂CH₂), 2.96 (br s, 12H, N[CH₃]₂), 3.89-3.92 (m, 6H, OCH₂), 6.24 (s, 2H, 2-H), 10.90 ppm (s, 1H, NH); ¹³C-NMR (175 MHz, CDCl₃): $\delta = 14.3$ (CH₃), 22.8, 26.25, 26.26, 29.50, 29.51, 29.52, 29.6, 29.75, 29.79, 29.81, 29.83, 29.86, 29.89, 29.90, 30.4, 32.1 (CH₂), 40.4 (s, N[CH₃]₂), 69.6, 73.7 (OCH₂), 100.0 (C-2), 133.4 (C-1), 136.0 (C-4), 154.1 (C-3), 159.2 ppm (C-1[°]). FT-IR (ATR): $\tilde{v} = 3466$ (br w), 2955 (w), 2916 (vs), 2849 (vs), 1632 (m), 1600 (m), 1561 (m), 1504 (m), 1467 (m), 1430 (m), 1378 (m), 1311 (s), 1232 (m), 1169 (w), 1115 (s), 1068 (w), 1009 (w), 908 (w), 830 (w), 722 (m), 645 (w)); Anal. calc. for C₅₃H₁₀₂N₄O₆ (891.42): C 71.41, H 11.53, N 6.29; found: C 71.19, H 11.74, N 6.14; MS (ESI): m/z (%) = 828.79 [M]⁺. HRMS (ESI): calcd. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, found 828.7914 [M]⁺. DSC, heating up: Cr₁ 20 °C [-12.2 kJ mol⁻¹] Cr₂ 35 °C [-2.4 kJ mol⁻¹] Cr₃ 57 °C [-11.2 kJ mol⁻¹] Col 105 °C [-1.0 kJ mol⁻¹] I; cooling down: Cr₁ 11 °C [10.7 kJ mol⁻¹] Cr₂ 20 °C [2.4 kJ mol⁻¹] Cr₃ 47 °C [11.7 kJ mol⁻¹] Col 104 °C [1.0 kJ mol⁻¹] I.

$Gua(14)NTf_2$

According to GP1: **Gua(14)Cl** (163 mg, 0.19 mmol), 4 mL MeCN; LiNTf₂ (579 mg, 2.02 mmol); recrystallization from EtOAc; yield: (90%, 188 mg, 0.17 mmol).



¹H-NMR (700 MHz, CDCl₃): $\delta = 0.88$ (t, J = 7.1 Hz, 9H, CH₃), 1.25-1.34 (m, 60H, CH₂), 1.43-1.48 (m, 6H, CH₂), 1.70-1.80 (m, 6H, OCH₂CH₂), 2.97 (br s, 12H, N[CH₃]₂), 3.91 (t, J = 6.5Hz, 6H, OCH₂), 6.18 (s, 2H, 2-H), 8.12 ppm (s, 1H, NH); ¹³C-NMR (175 MHz, CDCl₃): $\delta =$ 14.3 (CH₃), 22.8, 26.2, 26.3, 29.46, 29.52, 29.53, 29.57, 29.75, 29.79, 29.82, 29.84, 29.86, 29.90, 29.92, 30.4, 32.1 (CH₂), 40.4 (s, N[CH₃]₂), 69.6, 73.7 (OCH₂), 99.8 (C-2), 119.9 (q, J =321.0 Hz, CF₃), 132.4, 136.3 (C-1, C-4), 154.3 (C-3), 158.8 ppm (C-1′). FT-IR (ATR): $\tilde{v} =$ 3308 (br w), 2918 (vs), 2850 (s), 1629 (m), 1602 (m), 1561 (m), 1505 (m), 1467 (m), 1432 (m), 1404 (w), 1349 (s), 1228 (m), 1190 (vs), 1133 (s), 1118 (s), 1058 (s), 1011 (w), 908 (w), 831 (w), 789 (w), 737 (m), 653 (w), 616 (m), 601 (m), 571 (m), 512 (m)); Anal. calc. for C₅₅H₁₀₅F₆N₄O₇S₂ (1109.55): C 59.54, H 9.27, N 5.05, S 5.78; calc. for [M·1 H₂O]: C 58.59, H 9.30, N 4.97, S 5.69; found: C 58.61, H 9.06, N 4.87, S 5.74; MS (ESI pos.): m/z (%) = 828.79 [M]⁺. HRMS (ESI pos.): calcd. for $[C_{53}H_{102}N_3O_3]^+$ 828.7916, found 828.7913 [M]⁺. MS (ESI neg.): m/z (%) = 279.92 [NTf₂]⁻. HRMS (ESI neg.): calcd. for $[C_2F_6NO_4S_2]^-$ 279.9178, found 279.9176. DSC, heating up: Cr 56 °C [-105.5 kJ mol⁻¹] I; cooling down: Cr 28 °C [44.1 kJ mol⁻¹] I.

Gua(14)OTf

According to GP1: **Gua(14)Cl** (150 mg, 0.17 mmol), 6 mL MeCN; Kaliumtrifluormethansulfonate (175 mg, 0.93 mmol); recrystallization from diisopropylether; yield: (79%, 135 mg, 0.14 mmol).



¹H-NMR (700 MHz, CDCl₃): $\delta = 0.87$ (t, J = 7.0 Hz, 9H, CH₃), 1.25-1.33 (m, 60H, CH₂), 1.42-1.47 (m, 6H, CH₂), 1.70-1.79 (m, 6H, OCH₂CH₂), 2.95 (br s, 12H, N[CH₃]₂), 3.89-3.93 (m, 6H, OCH₂), 6.23 (s, 2H, 2-H), 9.28 ppm (br s, 1H, NH); ¹³C-NMR (175 MHz, CDCl₃): $\delta = 14.3$ (CH₃), 22.8, 26.22, 26.26, 29.48, 29.51, 29.52, 29.57, 29.75, 29.79, 29.81, 29.83, 29.86, 29.89, 29.90, 30.4, 32.1 (CH₂), 40.4 (s, N[CH₃]₂), 69.5, 73.7 (OCH₂), 99.8 (C-2), 120.7 (q, J = 319.8Hz, CF₃), 132.9, 136.0 (C-1, C-4), 154.2 (C-3), 158.8 ppm (C-1). FT-IR (ATR): $\tilde{v} = 3213$ (br w), 2917 (vs), 2850 (vs), 1633 (m), 1601 (m), 1561 (m), 1505 (m), 1467 (m), 1432 (m), 1404 (w), 1281 (m), 1245 (s), 1159 (m), 1117 (m), 1068 (w), 1030 (m), 908 (w), 830 (w), 722 (w), 638 (m), 574 (w), 517 (w); Anal. calc. for C₅₄H₁₀₂F₃N₃O₆S (978.48): C 66.29, H 10.51, N 4.26, S 2.59; found: C 66.45, H 10.71, N 4.30, S 2.53; MS (ESI pos.): m/z (%) = 828.79 [M]⁺. HRMS (ESI pos.): calcd. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, found 828.7913 [M]⁺. MS (ESI neg.): m/z (%) = 148.95 (69) [OTf]⁻, 1126.80 (100) [M+2OTf]⁻. HRMS (ESI neg.): calcd. for [C₁F₃O₃S₁]⁻ 148.9526, found 148.9529. DSC, heating up: Cr₁ 41 °C [-57.7 kJ mol⁻¹] Cr₂ 46 °C [71.2 kJ mol⁻¹] Cr₃ 64 °C [-74.6 kJ mol⁻¹] I; cooling down: Cr 37 °C [52.3 kJ mol⁻¹] I.

Gua(14)OTos

According to GPX: **Gua(14)Cl** (0.189 mg, 0.229 mmol), 6 mL MeCN; NaOTs (392 mg, 2.02 mmol); recrystallization from EtOAc; yield: (86%, 0.196 g, 0.196 mmol)



Gua(14)OTos C₆₀H₁₀₉N₃O₆S (1000.61)

¹H-NMR (700 MHz, CDCl₃): $\delta = 0.87$ (t, J = 7.1 Hz, 9H, CH₃), 1.25-1.31 (m, 60H, CH₂), 1.40-1.47 (m, 6H, CH₂), 1.69-1.75 (m, 6H, OCH₂CH₂), 2.33 (s, Tos-CH₃), 2.96 (br s, 12H, N[CH₃]₂), 3.82 (t, J = 6.4 Hz, 2H, OCH₂), 3.88 (t, J = 6.6 Hz, 4H, OCH₂), 6.21 (s, 2H, 2-H), 7.13 (d, J =8.0 Hz, 2H, 2⁻⁻H), 7.80 (d, J = 8.0 Hz, 2H, 3⁻⁻H), 10.75 ppm (br s, 1H, NH); ¹³C-NMR (175 MHz, CDCl₃): $\delta = 14.2$ (CH₃), 21.4 (Tos-CH₃), 22.8, 26.3, 29.50, 29.51, 29.53, 29.6, 29.78, 29.79, 29.81, 29.85, 29.87, 29.89, 30.4, 32.0 (CH₂), 40.5 (s, N[CH₃]₂), 69.4, 73.6 (OCH₂), 100.0 (C-2), 126.1 (2H, 2"-H), 128.7 (3"-H), 133.6 (br s, C-1), 135.7 (C-4), 139.4 (C-4"), 143.7 (C-1´´), 154.0 (C-3), 159.1 ppm (C-1´). FT-IR (ATR): $\tilde{v} = 3469$ (br w), 2916 (vs), 2849 (s), 1633 (m), 1601 (m), 1561 (m), 1504 (m), 1467 (m), 1430 (m), 1403 (w), 1310 (w), 1226 (s), 1176 (s), 1119 (s), 1068 (w), 1034 (m), 1011 (m), 908 (w), 818 (w), 722 (w), 681 (m), 567 (m); Anal. calc. for C₆₀H₁₀₉N₃O₆S (1000.61): C 72.02, H 11.58, N 6.31, S 3.20; calc. for [M·0.5 H₂O]: C 71.38, H 10.98, N 4.16, S 3.18; found: C 71.26, H 11.01, N 4.08, S 2.45; MS (ESI pos.): m/z (%) = 828.79 [M]⁺. HRMS (ESI pos.): calcd. for $[C_{53}H_{102}N_3O_3]^+$ 828.7916, found 828.7908 $[M]^+$. MS (ESI neg.): m/z (%) = 171.01 [OTos]⁻. HRMS (ESI neg.): calcd. for $[C_7H_7O_3S_1]^-$ 171.0121, found 171.0110. DSC, heating up: Cr 30 °C [-40.4 kJ mol⁻¹] I; cooling down: I 19 °C [36.2 kJ mol⁻¹] I.

Gua(14) as neutral species

Gua(14)Cl (0.189 mg, 0.229 mmol), was dissolved in 10 mL MeCN; NaCO₃ (214 mg, 2.02 mmol) was added. MeCN was removed under reduced pressure and the product was dissolved in CH_2Cl_2 , then filtered over celite to remove the remaining carbonate. The solvent was then removed under reduced pressure. The product was obtained as an off-white solid in 86 % yield.



1H-NMR (700 MHz, CDCl₃): $\delta = 0.87$ (t, J = 7.1 Hz, 9H, CH₃), 1.20–1.36 (m, 60H, CH₂), 1.39–1.49 (m, 6H, CH₂), 1.74 (m, 6H, CH₂), 2.70 (br s, 12H, N[CH₃]₂), 3.87 (t, J = 6.4 Hz, 2H, OCH₂), 3.91 (t, J = 6.6 Hz, 4H, OCH₂), 5.94 (s, 2H) ppm. ¹³C-NMR (176 MHz, CDCl₃) $\delta =$ 14.3 (CH₃), 22.8, 26.3, 26.4, 29.5, 29.5, 29.6, 29.6, 29.8, 29.8, 29.8, 29.9, 29.9, 29.9, 30.5, 32.1, 32.1 (CH₂), 69.1, 73.6, 77.0, 77.2, 77.4, 100.8, 132.4, 147.6, 153.4, 160.0 (C-1[^]) ppm. FT-IR (ATR): $\tilde{v} = 2920$ (vs), 2851 (s), 1577 (s), 1492 (m), 1465 (m), 1424 (w), 1374 (m), 1309 (w), 1221 (m), 1135 (m), 1114 (s), 1064 (w), 993 (w), 920 (w), 829 (w), 721 (m), 662 (m); Anal. calc. for C₅₃H₁₀₁N₃O₃ (828,41): C 76.84, H 12.29, N 5,07, found: C 76.62, H 12.39, N 4.99; MS (ESI pos.): m/z (%) = 827,79 [M]⁺. HRMS (ESI pos.): calcd. for [C₅₃H₁₀₂N₃O₃]⁺ 828.7916, found 828.7916 [M]⁺. DSC, heating up: Cr 16 °C [-54.5 kJ mol⁻¹] I.

The spectra are in good correlation with the literature.²

The synthesis of Gua(14)N₃, Gua(14)CN, Gua(14)OCN and Gua(14)OAc according to GP1 was not successful. Only the respective neutral species could be obtained in each case.

3 Gua-N-H shift in ¹H-NMR



Figure S1. Stacked sections of the ¹H-NMR spectra of Gua(14)X (CDCl₃).



Correlation between ion radius and N-H-proton shift



Concentration dependent N-H-proton shift in ¹H-NMR



Figure S3. Stacked sections of the ¹H-NMR spectra of the **Gua(14)Cl** at different concentration in CDCl₃ (400 MHz).



Figure S4. Stacked sections of the ¹H-NMR spectra of the **Gua(14)Cl** in different solvents CDCl₃, C₆D₆ and DMSO from top to bottom (400 MHz).

4 Polarising Optical Microscopy (POM)



Figure S5. POM images of **Gua(14)X.** After cooling from isotropic phase. Rate of 5 K \cdot min⁻¹.



Figure S6. POM images of Gua(14)X. After cooling from isotropic phase. Rate of 5 K \cdot min⁻¹.



5 Differential Scanning Calorimetry (DSC)

Figure S7. DSC curves of a) Gua(14)Cl, b) Gua(14)Br, c) Gua(14)I, d) $Gua(14)BF_4$, e) $Gua(14)PF_6$, f) Gua(14)OMs; Cr: crystalline; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K min⁻¹).



Figure S8. DSC curves of g) **Gua(14)SCN**, h) **Gua(14)NO₃**, i) **Gua(14)N(CN)₂**; Cr: crystalline; I: isotropic. H/C: heating/cooling (heating/cooling rates 5 K min⁻¹).

X	Cr ₁		Cr ₂		Smp			Ι			
Cl					•	34.44	(-34.74)	•	86.96	(-55.09)	$2^{nd}H$
					•	25.19	(32.09)	•	89.28	(1.18)	$2^{nd}C$
Br			34.44	(-31.94)	•	85.63	(-0.45)	•	93.11	(-1.03)	$2^{nd}H$
					•	25.22	(31.84)	•	91.43	(1.09)	$2^{nd}C$
Ι					•	33.89	(-33.90)	•	100.37	(-0.99)	$2^{nd}H$
					•	24.79	(32.86)	•	99.12	(0.99)	$2^{nd}C$
BF ₄					•	36.16	(-33.8)	•	112.30	(-1.0)	$2^{nd}H$
					•	27.85	(31.5)	•	112.04	(1.1)	$2^{nd}C$
PF ₆			34.16	(-32.96)	•	42.82	(-9.89)	•	106.18	(-1.02)	$2^{nd}H$
					•	25.76	(33.80)	•	105.92	(1.03)	$2^{nd}C$
OMs					•	35.01	(-37.15)	•	82.30	(-1.06)	$2^{nd}H$
					•	25.62	(35.3)	•	82.60	(1.02)	$2^{nd}C$
SCN	35.40	(-10.63)	38.02	(-16.37)	•	55.00	(-54.73)	•	76.59	(-0.85)	$2^{nd}H$
					•	30.15	(40.0)	•	75.02	(0.84)	$2^{nd}C$
N(CN)2					•	45.24	(-27.11)	•	70.59	(-22.87)	$2^{nd}H$
					•	40.14	(51.61)	•	70.33	(0.84)	$2^{nd}C$
NO ₃	11.13	(-10.47)	33.94	(-1.80)	•	57.17	(-12.03)	•	104.13	(-1.11)	$2^{nd}H$
	19.91	(8.61)	29.13	(1.94)	•	46.29	(11.95)	•	103.98	(1.02)	$2^{nd}C$

Table S1. Phase transition temperatures *T* in °C (-enthalpies ΔH in kJ·mol⁻¹, if available) of **Gua(14)X**. G: Glass-like; I: isotropic liquid; • observed in DSC; * observed in POM; – not observed. Values from DSC with cooling/heating rates of 5 K·min⁻¹.



6 X-Ray Scatterings and Diffraction Profiles (SAXS/WAXS)

Figure S9: X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of a) **Gua(14)Cl** at 65 °C, b) **Gua(14)Br** at 65 °C, c) **Gua(14)I** at 65 °C.



Figure S10: X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of d) **Gua(14)BF4** at 65 °C, e) **Gua(14)PF6** at 65 °C, f) **Gua(14)4OMs** at 65 °C



Figure S11: X-ray diffractograms (WAXS/SAXS) and 2D diffraction patterns (inset) of g) **Gua(14)SCN** h) **Gua(14)N(CN)**₂ i) **Gua(14)NO**₃ at 65 °C.

Gua(14)X	anion	mesophase	reflexes / Å	miller	lattice parameters /
	$\frac{(\emptyset / A)}{C^{1-}}$	$\frac{1}{C^{-1}} = \frac{1}{C^{-1}} = \frac{1}$	exp. (calc.)	(10)	A 29 29
Gua(14)CI	CI	Colh at 65 °C	<i>55,2400</i> 10,2020 (10,1011)	(10) (11)	a = 38,38
	2.62	pomm	19,2030 (19,1911)	(11) (20)	
	5.02		16,0100 (10,0200)	(20)	
Gu9(14)OMs	OMs ⁻	Column 65 °C	33 8517	(10)	a = 30.09
Gua(14)0113	01015	n6mm	19 5248 (19 5443)	(10) (11)	a 59,09
	3 77	pomm	16 9345 (16 9259)	(20)	
	5.77		4.53	halo	
Gua(14)Br	Br⁻	Col _b at 65 °C	33.2337	(10)	a = 38.38
0 4 4 (1 1) 2 1	21	p6mm	19,1818 (19,1875	(11)	<i>a c o</i> , <i>c o</i>
	3.92	1	16,5998 (16,6169)	(20)	
			4,56	Halo	
Gua(14)NO3	NO ₃ -	Col _h at 65 °C	34,0108	(10)	a = 39,27
		p6mm	19,7007 (19,6362)	(11)	
	4.00	-	17,0137 (17,0054)	(20)	
			4,59	Halo	
Gua(14)SCN	SCN ⁻	Col _h at 65 °C	32,882	(10)	a = 37,97
		p6mm	18,9647 (18,9845)	(11)	
	4.26		16,4744 (16,4411)	(20)	
			4,53	Halo	
Gua(14)I	I-	Col _h at 65 °C	29,8626	(10)	a = 34,48
		p6mm			
	4.40		4.50	TT 1	
$\mathbf{C} = (1 \mathbf{A}) \mathbf{N} (\mathbf{N} \mathbf{C})$	$\mathbf{N}(\mathbf{N}(\mathbf{C}))$ -	C_{1}	4,52	Halo	40.15
$Gua(14)N(NC)_2$	$N(NC)_2$	Col_h at 65 °C	34,/689	(10)	a = 40,15
	451	pomm	20,0814(20,0739) 17,2022(17,2845)	(11)	
	4.31		17,3932 (17,3643)	(20) Halo	
	BE ¹	Caluat 65 °	4, <i>52</i> 3/1.0633	(10)	a = 30.33
Gua(14)DF4	$\mathbf{D}\Gamma4$	n6mm	19 7721 (19 6665)	(10) (11)	a – 39,33
	4 64	pomm	17,0669 (17,0317)	(11) (20)	
	1.01		4.12	Halo	
Gua(14)PF6	PF_6^-	Col _b at 65 °C	33.1825	(10)	a = 38.32
)	0	p6mm	19,1647 (19,6665)	(11))-
	5.80	I	16,5998 (17,0317)	(20)	
			4,59	Halo	

Table S2: Summary of the XRD results of Gua(14)X derivatives.^{a,b}

^a anion diameters (except OMs, N(CN)₂) were taken from ref.³. ^b anion diameters of mesylate and biscyanamide were estimated from Chem3D ball & stick models.



7 Cyclic voltammetry (CV)

Figure S12: a) Cyclic voltammograms of DCM and Gua(14)I, b) original cyclic voltammograms of Gua(14)Br with and without Fc, c) all three CV cycles for Gua(14)NO₃.

8 Density functional theory (DFT) calculations

Table S3: HOMO and LUMO energies for the optimized structures of the guanidinium cations Gua(n) on the B3LYP/631G* level of theory. All energies are given in E_h .

method	cation	$\varepsilon_{ m HOMO}$	$\varepsilon_{ m LUMO}$
B3LYP/6-31G*			
	Gua(14)	-0.30359	-0.15109
	Gua(1)	-0.31333	-0.15695
	Gua(2)	-0.30892	-0.15405
	Gua(3)	-0.30723	-0.15307
	Gua(4)	-0.30848	-0.15147



Figure S13: Optimized structures for a) **Gua(2)** and b) **Gua(14)**, calculations on the B3LYP/6-31G* level of theory.

	B3LYP/DZ	B3LYP/TZ	M062X/DZ	PBE/DZ
Br	-0.65	-0.64	-0.59	-0.75
NO ₃	-0.56	-0.55	0.12	-1.25
PF ₆	3.09	3.03	4.12	2.13
Gua(1)	0.05	0.05	0.04	0.06
Gua(2)	0.00	0.00	0.00	0.00
Gua(3)	-0.04	-0.04	-0.04	-0.04
Gua(4)	0.07	0.07	0.08	0.08

Table S4 IP_X^{HOMO} , c.f. Eq. (2), derived from the HOMO energies of the optimized guanidinium cations **Gua(n)** and the anions **X**. All values are given in eV and relative to the IP of **Gua(2)**.

Table S5: IP_X^{vert} , c.f. Eq. 3, derived from Δ -SCF calculations. All values are given in eV and relative to the IP of **Gua(2)**.

	B3LYP/DZ	B3LYP/TZ	M062X/DZ	PBE/DZ
Br	-0.46	-0.50	-0.87	-0.25
NO ₃	-0.17	-0.18	-0.06	-0.45
PF ₆	3.43	3.37	4.08	2.65
Gua(1)	0.06	0.05	0.04	0.06
Gua(2)	0.00	0.00	0.00	0.00
Gua(3)	-0.04	-0.04	-0.04	-0.04
Gua(4)	0.08	0.08	0.09	0.07

	B3LYP/DZ	B3LYP/TZ	M062X/DZ	PBE/DZ	
Br	0.23	0.20	-0.10	0.36	
NO ₃	0.46	0.45	0.63	0.11	
PF ₆	4.09	4.03	3.56	3.25	
Gua(1)	0.06	0.06	0.04	0.06	
Gua(2)	0.00	0.00	0.00	0.00	
Gua(3)	-0.02	-0.02	-0.02	-0.03	
Gua(4)	0.10	0.09	0.18	0.08	

Table S6: IP_X^{adia} , c.f. Eq. 4, derived from Δ -SCF calculations. All values are given in eV and relative to the IP of **Gua(2)**.

Table S7: $-EA_X^{vert}$, c.f. Eq. 5, derived from Δ -SCF calculations. All values are given in eV and relative to the IP of **Gua(2)**.

	B3LYP/DZ	B3LYP/TZ	M062X/DZ	PBE/DZ
Br	0.71	0.69	0.47	0.73
NO ₃	0.87	0.88	1.13	0.42
PF6	4.54	4.49	0.99	3.59
Gua(1)	0.09	0.09	0.09	0.09
Gua(2)	0.00	0.00	0.00	0.00
Gua(3)	0.01	0.01	0.02	0.00
Gua(4)	0.06	0.04	0.20	0.03

9 Literature comparison of CV data

Table S8	Cyclic volt	ammetry data	of literature	compounds
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Compound		Struct	ural	characte	eristics	Limi	ts [V]	Potential reference	Ref.
	R	. ¹ R	2	R ³	X	anodic	cathodic		
$\begin{array}{c} NH_2 & O \\ I_+ & F_3C - \overset{O}{\overset{II}{\overset{O}}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}}{\overset{O}}{\overset{O}{\overset{O}{\overset{O}{\overset{O}}{\overset{O}}{\overset{O}{\overset{O}{\overset{O}{\overset{O}}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{\overset{O}{{}}}{\overset{O}{\\{O}}{\overset{O}{\\{O}}{\overset{O}{{}}}{\overset{O}{\overset{O}{\\{O}}{\\{O}}{{}}{\overset{O}{{}}{{}}{\overset{O}{{}}{{O}}{\overset{O}{{}}{\\{O}}{\\{O}}{\\{O}}{{}}{{O}}{\\{O}}{{\\{O}}{{O}}{\\{O}}{{}}{{$	0_					$\ge +0.8$	≥-1.2	vs. Pt.	4
	M	le E	Et	<i>n</i> Bu	TfO⁻	+0.6	-0.6		
N N	M	le E	Et	<i>n</i> Bu	Tf_2N^-	+1.0	-1.8		
$R^3_{>}$ $C^+_{>}$ $R^2_{>}$ χ	<u>с</u> Е	t nE	Bu	<i>n</i> Hex	Tf_2N^-	+0.8	-1.8	VS. $\Delta \alpha / \Delta \alpha C1$	5
	Ν	le E	Et	<i>n</i> Bu	$(NC)_2N^-$	+0.6	-1.5	Ag/AgCI	
R^3 R^2	E	t nE	Bu	<i>n</i> Hex	$(NC)_2N^-$	+0.6	-1.5		
1 1	N	le F	Et	nBu	Tf_2N^-	+1.0	-1.7		
R'R'	N	le M	le I	nBu	TfO^{-}	+1.0	-0.8		
	- E	10 IV.	2,,	и Цох	DE	11. 1	-0.0	ve Dt	6
			Ju	Die *	D1'4 T£ N-	+1.5	-1.5	vs. 1 t	
$\begin{vmatrix} 3 \\ B^3 \\ B^2 \end{vmatrix}$	IV.		*	Pip D: *	1121N	+1.5	-2.5		
	N	le Pi	р	Рір	$1f_2N$	+1./	-1.8		
$R^1 R^1$	M	le M	ſe	nHex	Tf_2N^-	+1.7	-1.8		
$R^{3} C^{+} R^{2} \chi$	ς Μ	le M	le	Pyr*	$\mathrm{Tf}_2\mathrm{N}^2$	+1.4	-1.2	vs. Ag/AgCl	7
$\begin{vmatrix} 1 \\ R^3 \\ R^2 \end{vmatrix}$	M	le M	ſe	nHex	BF ₄	+1.6	-2.2		
$R^2 R^3$	N	le M	ſe	nProp	Tf ₂ N ⁻	+4.9	+0.7		0
$R'_{N}C^{T}_{N}R'$	X							vs. Li/Li ⁺	0
$\begin{vmatrix} \mathbf{n} \\ \mathbf{n} \\ \mathbf{n} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{R} \\ \mathbf{R} $	Ν	le E	Et	Et	Tf_2N^-	+4.9	+0.7		
	N	le M	ſe	Et	Tf_2N^-	+2.1	-2.0		
	M	le M	ſe	nProp	Tf_2N^-	+2.2	-2.0		
R^2_{λ} R^3_{λ}	$R^2_{N} \sim R^3$ Me Me <i>n</i> Bu Tf ₂ N ⁻ +2.2 -2.0	-2.0							
Ň,	N	le E	Et	Et	Tf_2N^-	+2.1	-2.0		
	N	le E	Et	<i>n</i> Prop	Tf_2N^-	+2.2	-2.1	vs. Ag/Ag^+	9
Γ N N K	^ N	le E	ŝt	nBu	Tf_2N^-	+2.1	-2.1		
$\begin{vmatrix} & & & \\ & & & \\ & & & & \\ 1 & & & & 1 \end{vmatrix}$	N	$le nP_1$	rop	<i>n</i> Prop	Tt_2N^-	+2.2	-2.1		
R' R'	N	$n P_1$	rop	<i>n</i> Bu	Tt_2N	+2.2	-2.0		
	N.	n = n = 1	5U	nBu	I I2N TEN-	+2.2	-2.0		
	IV.	le E	2t	Ľι	1 121N	+1.3	-1./		

* Pip and Pyr representing piperidinium and pyridinium structures incorporating both R²s and R³s respectively

Compound	Stru	uctural	character	istics	Limi	ts [V]	Potential reference	Ref.
	\mathbb{R}^1	\mathbb{R}^2	\mathbb{R}^3	X	anodic	cathodic		
$R^2 R^3$	Me	Me	Et	Tf_2N^-	+2.0	-1.8		
$B^{1} \xrightarrow{C^{+}} B^{1} \xrightarrow{X^{-}}$	Me	Me	nProp	Tf_2N^-	+1.4	-1.7	vs. Ag/Ag ⁺	9
	Me	Et	Et	Tf_2N^-	+1.3	-1.7		
$ \begin{array}{c} $	Me	Me		Tf_2N^-	+1.66	-2.50	vs. Ag/AgNO ₃	10

Continuation Table S8: Cyclic voltammetry data of literature compounds.

Representative structure¹¹ of a guanidino-functionalized aromatic ligand for aromatic complexes as mentioned in references^{11–14}.

10 TGA analysis of the Gua(14)X derivatives

Gua(14)OMs

Gua(14)SCN

Gua(14)NO₃

Gua(14)N(CN)₂

Figure S14 TGA results for the mesomorphic Gua(14)X salts.

	T_{600} [%]	T _{on} [°C]
Gua(14)Cl	90.1	277.7
Gua(14)Br	91.2	278.7
Gua(14)I	91.1	278.5
Gua(14)BF ₄	91.8	271.3
Gua(14)PF6	88.3	298.6

91.6

83.5

82.7

89.9

277.0

281.6

304.9

240.4

Table S9: Thermal stability data for mesomorphic Gua(14)X salts.

 T_{on} : on-set decomposition temperature at 5 % weight loss; T_{600} : weight loss in % at 600 °C

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12 NMR spectra

Figure S15: ¹H NMR spectrum of Gua(14)Cl

Figure S16: ¹³C NMR spectrum of Gua(14)Cl

Figure S17: ¹H NMR spectrum of Gua(14)Br

Figure S18: ¹³C NMR spectrum of Gua(14)Br

Figure S19: ¹H NMR spectrum of Gua(14)I

Figure S20: ¹³C NMR spectrum of Gua(14)I

Figure S21: ¹H NMR spectrum of Gua(14)BF4

Figure S22: ¹³C NMR spectrum of Gua(14)BF₄

Figure S23: ¹H NMR spectrum of Gua(14)PF6

Figure S24: ¹³C NMR spectrum of Gua(14)PF₆

Figure S25: ¹H NMR spectrum of Gua(14)OMs

Figure S26: ¹³C NMR spectrum of Gua(14)OMs

Figure S27: ¹H NMR spectrum of Gua(14)SCN

Figure S28: ¹³C NMR spectrum of Gua(14)SCN

Figure S29: ¹H NMR spectrum of Gua(14)N(CN)₂

Figure S30: ¹³C NMR spectrum of Gua(14)N(CN)₂

Figure S31: ¹H NMR spectrum of Gua(14)NO₃

Figure S32: ¹³C NMR spectrum of Gua(14)NO₃

Figure S33: ¹H NMR spectrum of Gua(14)NTf₂

Figure S34: ¹³C NMR spectrum of Gua(14)NTf₂

Figure S35: ¹H NMR spectrum of Gua(14)OTf

Figure S36: ¹³C NMR spectrum of Gua(14)OTf

Figure S37: ¹H NMR spectrum of Gua(14)OTs

Figure S38: ¹³C NMR spectrum of Gua(14)OTs

Figure S39: ¹H NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaN₃

Figure S40: ¹³C NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaN₃

Figure S41: ¹H NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaOAc

Figure S42: ¹³C NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaOAc

Figure S43: ¹H NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaOAc.

Figure S44: ¹³C NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaOAc.

Figure S45: ¹H NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaOCN.

Figure S46: ¹³C NMR spectrum of Gua(14) out of the synthesis according to GP1 with NaOCN.

Figure S47: ¹³C NMR spectrum of Gua(14) out of the synthesis described for the neutral species.

Figure S48: ¹³C NMR spectrum of Gua(14) out of the synthesis described for the neutral species.