Electronic Supplementary Information

Li\textsuperscript{+} and K\textsuperscript{+} ionic conductivity in ionic nematic liquid crystals based on 18-diaza-crown ether substituted with six decylalkoxy-\textit{p}-cyanobiphenyl chains

Verónica Conejo-Rodríguez,\textsuperscript{a} Cristián Cuerva,\textsuperscript{b} Rainer Schmidt,\textsuperscript{c} Manuel Bardají,\textsuperscript{a,\*} and Pablo Espinet\textsuperscript{b,\*}

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E–47071 Valladolid, Spain.
\textsuperscript{b} Departamento de Química Inorgánica I, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, E-28040 Madrid, Spain.
\textsuperscript{c} GFMC. Departamento de Física Aplicada III, Universidad Complutense de Madrid, Ciudad Universitaria, E-28040 Madrid, Spain.

*Author to whom correspondence should be addressed. E-mail: espinet@qi.uva.es

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A. Synthesis and characterization of the compounds

*Synthesis of compounds 1 and 2*: Compound 3,4,5-tridecyloxybenzoic acid (0.9 g, 1.52 mmol) was dissolved in 15 mL of dry dichloromethane under argon atmosphere. After addition of oxalyl chloride (1.245 ml, 14 mmol) and DMF (catalytic amount), the mixture was stirred for 3h under reflux. The excess of oxalyl chloride and solvent were removed under vacuum. The acid chloride intermediate was then dried at 60 °C under vacuum for 24 h before being dissolved in 15 mL of dry THF. This solution was dropwise added to a 15 ml THF solution maintained at 0 °C and containing 1,4-diaza-18-crown-6 (0.19 g, 0.72 mmol) and triethylamine (0.3 ml, 2.13 mmol). The reaction mixture was allowed to warm up to room temperature and was stirred overnight. The crude obtained after THF evaporation was purified by column chromatography (silica gel, DCM/MeOH 95:5). The desired product was then dried at 45 °C under vacuum. Compound 1 was obtained as a waxy orange solid. Yield: 0.807 g, 79%. $^1$H NMR (500 MHz, CDCl$_3$): δ 6.56 (4H, s, H$_{arom}$), 3.94 (12H, t, J = 6.5 Hz, O-CH$_2$), 3.82-3.71 (m, 8H, CH$_2$-N), 3.69-3.52 (m, 16H, O-CH$_2$-CH$_2$-O) 1.81-1.69 (12H, m, O-CH$_2$-CH$_2$), 1.51-1.18 (84H, m, CH$_3$-(CH$_2$)$_7$), 0.88 (18H, t, J = 6.7 Hz, CH$_3$); IR (in solid cm$^{-1}$): 1634 (ν$_{c=o}$); MS (MALDI-TOF): m/z: calc (M = C$_{86}$H$_{154}$N$_2$O$_{12}$), (M + H)$^+$ 1408,16; found: 1408,3. Anal. calcd for C$_{86}$H$_{154}$N$_2$O$_{12}$: C 73.35, H 11.02, N 1.99; found C 73.43, H 11.29, N 1.99.

![Ligand 1](image)

**Figure ESI1.** $^1$H NMR spectrum of 1 in CDCl$_3$

*Synthesis of adducts 1a-1b*: KI (4.7 mg, 0.028 mmol) or, respectively, K$_2$[PtCl$_4$] (7.4 mg, 0.018 mmol) in 5 ml deoxygenated MeOH was stirred under ultrasound.
irradiation during 15 minutes and then added to a solution of macrocycle 1 (for 1a 40 mg, 0.028 mmol; for 1b 50 mg, 0.036 mmol in 5 ml diethyl ether under N₂.

The mixture was stirred overnight at 35 °C. The solution was filtered over celite and dried in vacuum. The products were obtained as waxy yellow (1a) or brown (1b) solids.

Yield of 1a: 40 mg, 89%. 1H NMR (400 MHz, CDCl₃): δ 6.57 (4H, s, H_arom), 3.94 (12H, t, J = 6.5 Hz, O-CH₂), 3.82-3.73 (8H, m, -CH₂-N), 3.69-3.51 (16H, m, CH₂-CH₂-O, CH₂-O) 1.82-1.69 (12H, m, O-CH₂-CH₂), 1.50-1.19 (84H, m, CH₂-(CH₂)7), 0.88 (18H, t, J = 6.6 Hz, CH₃); IR (in solid, cm⁻¹): 1634 (ν_c=o); MS (MALDI-TOF): m/z: calcd.(M = C₈₆H₁₅₄N₂O₁₂ macrocycle 1), calcd.(M + H)⁺: 1408,16; found: 1408,3; calcd.(M + Na)⁺: 1430,14; found: 1430,3; calcd.(M + K)⁺: 1446,11; found: 1446,1. Anal. calcd. for C₈₆H₁₅₄N₂IKO₁₂: C 65.62, H 9.86, N 1.78; found C 65.36, H 10.07, N 2.02.

Yield of 1b: 50 mg, 87%. 1H NMR (400 MHz, CDCl₃): δ 6.57 (4H, s, H_arom), 3.94 (12H, t, J = 6.5 Hz, O-CH₂), 3.82-3.72 (8H, m, -CH₂-N), 3.68-3.51 (16H, m, CH₂-CH₂-O, CH₂-O) 1.80-1.68 (12H, m, O-CH₂-CH₂), 1.51-1.18 (84H, m, CH₂-(CH₂)7), 0.88 (18H, t, J = 6.6 Hz, CH₃); IR (in solid, cm⁻¹): 1634 (ν_c=o); MS (MALDI-TOF): m/z: calcd.(M = C₈₆H₁₅₄N₂O₁₂ macrocycle 1), calcd.(M + H)⁺: 1408,16; found: 1408,3; calcd.(M + Na)⁺: 1430,14; found: 1429,4; calcd. (M + K)⁺: 1446,11; found: 1445,4. Anal. calcd. for C₁₇₂H₃₉₈N₄Cl₄K₂O₂₄Pt: C 63.93, H 9.61, N 1.73; found C 63.71, H 9.89, N 2.00.

Compound 2 was obtained as a yellow solid in a similar way to compound 1. Yield: 1.34 g, 61%. 1H NMR (500 MHz, CDCl₃): δ 7.70-7.58 (24H, m, H⁺+H⁻), 7.53-7.47 (12H, m, H), 7.01-6.93 (12H, m, H⁺), 6.57 (4H, s, -CH₂), 4.06-3.92 (24H, m, O-CH₂), 3.82-3.70 (8H, m, CH₂-N) 3.69-3.52 (16H, m, O-CH₂-CH₂-O), 1.85-1.70 (24H, m, O-CH₂-CH₂), 1.51-1.25 (72H, m, -CH₂). IR (in solid cm⁻¹): 2223 (ν_c≡N), 1623 (ν_c=o); MS (MALDI-TOF): m/z: calc (M = C₁₆₄H₁₉₆N₈O₁₈), (M + H)⁺ 2566,47; found: 2566,5. Anal. calcd for C₁₆₄H₁₉₆N₈O₁₈: C 76.72, H 7.69, N 4.36; found C 76.44, H 7.9, N 4.23.

**Ligand 2**

![Figure ESII. 1H NMR spectrum of 2 in CDCl₃.](image-url)
**Figure ESI3.** COSY spectrum of 2

**Figure ESI4.** ROESY spectrum of 2
Synthesis of adducts 2a-2f: MₐA (KI 4.8 mg, 0.029 mmol, K₂[PtCl₆] 7.0 mg, 0.017 mmol, K[AuCl₄] 10.5 mg, 0.028 mmol, K[AuCl₄] 5.3 mg, 0.014 mmol, K₂[Fe(CN)₆] 3.0 mg, 0.007 mmol, or LiI 3.4 mg, 0.025 mmol), respectively, in 5 ml dry dichloromethane was stirred under ultrasound irradiation during 15 minutes and then added to a solution of macrocycle 2 for 2a 75 mg, 0.029 mmol; for 2b 86.6 mg, 0.034 mmol; for 2c-2d-2e 72 mg, 0.028 mmol; for 2f 64 mg, 0.025 mmol) in 3 ml dichloromethane under N₂. The mixture was stirred overnight at 35 °C. The solution was filtered over celite and dried in vacuum. The products were obtained as beige (2a), light yellow (2b, 2e) grey (2c, 2d) or yellow (2f) solids.

Yield of 2a: 73 mg, 92%. ¹H NMR (500 MHz, CDCl₃): δ 7.70-7.59 (24H, m, H₂, H₂), 7.54-7.48 (12H, m, H₁), 7.00-6.94 (12H, m, H₁), 6.57 (4H, s, -CH₂), 4.06-3.92 (24H, m, O-CH₂), 3.82-3.71 (8H, m, -CH₂-N), 3.69-3.52 (16H, m, O-CH₂-CH₂-O), 1.85-1.70 (24H, m, O-CH₂-CH₂-), 1.51-1.25 (72H, m, (-CH₃)₃). IR (in solid cm⁻¹): 2224 (νCN), 1631 (νCO); MS (MALDI-TOF): m/z: calc (M = C₁₆₄H₁₉₆N₄O₁₈ macrocycle 2): 2586.47; found: 2586.46; calc (M + Na)⁺: 2588.5; 2604.43; found: 2604.5. Anal. calcd for C₁₆₄H₁₉₆N₄K₁O₁₈: C 72.06, H 7.23, N 4.10; found C 71.87, H 7.14, N 4.02.

Yield of 2b: 80 mg, 85%. ¹H NMR (500 MHz, CDCl₃): δ 7.71-7.58 (24H, m, H₂, H₂), 7.54-7.48 (12H, m, H₁), 7.00-6.93 (12H, m, H₁), 6.57 (4H, s, -CH₂), 4.03-3.91 (24H, m, O-CH₂), 3.83-3.71 (8H, m, -CH₂-N) 3.69-3.52 (16H, m, O-CH₂-CH₂-O), 1.84-1.68 (24H, m, O-CH₂-CH₂-), 1.51-1.18 (36H, m, (-CH₃)₃). IR (in solid cm⁻¹): 2224 (νCN), 1628 (νCO); MS (MALDI-TOF): m/z: calc (M = C₁₆₄H₁₉₆N₄O₁₈ macrocycle 2), calc (M + H)⁺ 2566.47; found: 2566.5; calc (M + Na)⁺: 2588.46; found: 2588.5; calc (M + K)⁺: 2604.43; found: 2604.5. Anal. calcd for C₁₆₄H₁₉₆N₄K₂O₁₈: C 70.99, H 7.12, N 4.04; found C 70.83, H 7.17, N 3.90.

Yield of 2c: 80 mg, 98%. ¹H NMR (500 MHz, CDCl₃): δ 7.79-7.58 (24H, m, H₂, H₂), 7.57-7.44 (12H, m, H₁), 7.03-6.91 (12H, m, H₁), 6.57 (4H, s, -CH₂), 4.09-3.88 (24H, m, O-CH₂), 3.82-3.71 (8H, m, -CH₂-N) 3.67-3.48 (16H, m, O-CH₂-CH₂-O), 1.83-1.69 (24H, m, O-CH₂-CH₂-), 1.60-1.22 (72H, m, (-CH₃)₃). IR (in solid cm⁻¹): 2223 (νCN), 1628 (νCO); MS (MALDI-TOF): m/z: calc (M = C₁₆₄H₁₉₆N₄O₁₈ macrocycle 2), calc (M + H)⁺ 2566.47; found: 2566.5; calc (M+Na)⁺: 2588.46; found: 2588.5; calc (M+K)⁺: 2604.43; found: 2604.5; calc (AuCl₄⁻): 338.33; found: 338.9. Anal. calcd for C₁₆₄H₁₉₆AuCl₄KN₃O₁₈: C 66.88, H 6.71, N 3.80; found C 67.11, H 7.00, N 3.69.

Yield of 2d: 71 mg, 93%. ¹H NMR (500 MHz, CDCl₃): δ 7.72-7.58 (24H, m, H₂, H₂), 7.55-7.48 (12H, m, H₁), 7.01-6.92 (12H, m, H₁), 6.57 (4H, s, -CH₂), 4.05-3.89 (24H, m, O-CH₂), 3.86-3.72 (8H, m, -CH₂-N) 3.71-3.49 (16H, m, O-CH₂-CH₂-O), 1.84-1.69 (24H, m, O-CH₂-CH₂-), 1.65-1.20 (72H, m, (-CH₃)₃). IR (in solid cm⁻¹): 2221 (νCN), 1631 (νCO); MS (MALDI-TOF): m/z: calc (M = C₁₆₄H₁₉₆N₄O₁₈ macrocycle 2), calc (M+H)⁺ 2566.47; found: 2567.5; calc (M+Na)⁺: 2588.46; found: 2588.5; calc (M+K)⁺: 2604.43; found: 2604.5. Anal. calcd for C₁₆₄H₁₉₆AuCl₄K₁N₃O₁₈: C 71.46, H 7.17, N 4.07; found C 71.66, H 7.26, N 3.98.

Yield of 2e: 70 mg, 93%. ¹H NMR (500 MHz, CDCl₃): δ 7.77-7.57 (24H, m, H₂, H₂), 7.57-7.46 (12H, m, H₁), 7.06-6.90 (12H, m, H₁), 6.57 (4H, s, -CH₂), 4.11-3.88 (24H, m, O-CH₂), 3.86-3.68 (8H, m, -CH₂-N) 3.68-3.48 (16H, m, O-CH₂-CH₂-O), 1.91-1.68 (24H, m, O-CH₂-CH₂-), 1.66-1.17 (72H, m, (-CH₃)₃). IR (in solid cm⁻¹): 2224, 2060 (νCN), 1628 (νCO); MS (MALDI-TOF): m/z: calc (M = C₁₆₄H₁₉₆N₄O₁₈ macrocycle 2), calc (M + H)⁺ 2566.47; found: 2566.5; calc (M+Na)⁺: 2588.46; found: 2588.5; calc (M+K)⁺: 2604.43; found: 2604.4. Anal. calcd for C₆₆₂H₇₈₆FeK₁₃₈N₃₈O₇₂: C 74.74, H 7.43, N 5.00; found C 74.52, H 7.60, N 4.84.

Yield of 2f: 67 mg, 97%. ¹H NMR (500 MHz, CDCl₃): δ 7.72-7.56 (24H, m, H₂, H₂), 7.54-7.45 (12H, m, H₁), 7.02-6.89 (12H, m, H₁), 6.57 (4H, s, -CH₂), 4.03-3.89 (24H,
m, O-CH₂), 3.88-3.75 (8H, m, -CH₂-N-) 3.73-3.51 (16H, m, O-CH₂-CH₂-O), 1.86-1.69 (24H, m, O-CH₂-CH₂-), 1.64-1.23 (72H, m, (-CH₂)₆). IR (in solid cm⁻¹): 2223 (ν C≡N), 1628 (ν C=O); MS (MALDI-TOF): m/z: calc (M = C₁₆₄H₁₉₀N₈O₁₈ macrocycle 2), calc (M + H)⁺ 2566,47; found: 2566,5; calc (M + Li)⁺: 2572,48; found: 2572,6; calc (M+Na)⁺: 2589,46; found: 2588,6. Anal. calcd for C₁₆₄H₁₉₀N₈LiO₁₈: C 72.92, H 7.31, N 4.15; found C 72.63, H 7.44, N 4.13.

B. Differential Scanning Calorimetry (DSC) thermograms for compounds 2-2f

![DSC thermogram](image)

Figure ESIS. DSC thermograms for 2
Figure ES16. DSC thermograms for 2a

Figure ES17. DSC thermograms for 2b

Figure ES18. DSC thermograms for 2c
**Figure ESI9.** DSC thermograms for 2d

**Figure ESI10.** DSC thermograms for 2e
Figure ESI11. DSC thermograms for 2f
C. **X-ray Powder Diffraction (XRD) patterns**

**Figure ESI12.** Powder XRD diffraction patterns for 2a at 40 °C (on heating at 2°C/min).

**Figure ESI13.** Powder XRD diffraction patterns for compound 2a at 90 °C (on heating at 2 °C/min).
Figure ESI14. Powder XRD diffraction patterns for compound 2a at 110 °C on heating at 2 °C/min (isotropic liquid).

Figure ESI15. Powder XRD diffraction patterns for 2f at 40 °C (on heating at 10 °C/min).
Figure ESI16. Powder XRD diffraction patterns for compound 2f at 90 °C (on heating at 10 °C/min).

Figure ESI17. Powder XRD diffraction patterns for compound 2f at 120 °C on heating at 10 °C/min (isotropic liquid).