Electronic Supplementary information for:

Templated nanoporous membranes based on hierarchically self-assembled materials

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Outline:

1. Synthetic details and characterisation of the promesogenic units and templates.
2. H-bonding formation: FTIR spectra.
3. Cross-linking of the mesophase and properties of the nanoporous materials.
4. Reference.
1. Synthetic details and characterisation of the promesogenic units and templates.

For the preparation of 2-acetamidoisonicotinic acid an adaptation of the procedure reported by Shen and Fan was followed.1

Synthesis of methyl 3,4,5-tris(10-undecenyloxy)benzoate (1)

A solution of DIAD (13.3 g, 65.2 mmol) in 40 mL of dry THF was added dropwise to a solution of methyl 3,4,5-trihydroxybenzoate (2.5 g, 13.6 mmol) and triphenylphosphine, PPh₃ (13.3 g, 50.9 mmol) in THF at 0°C and under inert (Ar) atmosphere. The reaction was stirred for 2 hours after which it was cooled to 15°C. After evaporation of THF, the aqueous phase was extracted with ether (3x100 mL). Organic fraction was washed with KOH 3M (50 mL) and H₂O (2x40 mL), and dried over MgSO₄. After partial evaporation of ethyl ether and cooling, OPPH₃ was filtered out. Pure product was purified by column chromatography on silica gel eluting with hexane to hexane/ethyl acetate (20:1). Yield 69% (6.02 g).

Synthesis of 3,4,5-tris(10-undecenyloxy)benzyl alcohol

A solution of the methyl ester (2.27 g, 0.56 mmol) in dry THF was added dropwise to a excess LiAlH₄ (400 mg, 10.5 mmol) at 0°C under inert (Ar) atmosphere. The reaction was stirred for 24 hours after which it was filtered over Celite® and washed with water (3x10 mL), washed with NaCl sat. and dried over MgSO₄. Partial evaporation of ethyl ether and cooling, OPPH₃ was filtered out. Pure product was purified by column chromatography on silica gel eluting with hexane to hexane/ethyl acetate (20:1). Yield 86% (2.78 g).

Synthesis of 3,4,5-tris(10-undecenyloxy)benzoic acid

A suspension of the methyl ester (3.30 g, 5.14 mmol) in water/methanol (3:1) was sapnfoled under reflux with DIAD (13.2 g, 65.2 mmol) in 40 mL of dry THF was added dropwise to a solution of methyl 3,4,5-trihydroxybenzoate (2.5 g, 13.6 mmol), 10-undecenol (8.1 g, 47.6 mmol) and triphenylphosphine, PPh₃ (13.3 g, 50.9 mmol) in THF at 0°C and under inert (Ar) atmosphere. The reaction was stirred for 24 hours after which it was filtered over Celite® and washed with water (3x10 mL), washed with NaCl sat. and dried over MgSO₄. After partial evaporation of ethyl ether and cooling, OPPH₃ was filtered out. Pure product was purified by column chromatography on silica gel eluting with hexane to hexane/ethyl acetate (20:1). Yield 69% (6.02 g).

Synthesis of 3,4,5-tris(10-undecenyloxy)benzyl 2-acetamidoisonicotinate (B3Py)

EDC·HCl (0.25 g, 1.62 mmol) was added to a suspension of 2-acetamidoisonicotinic acid (0.24 g, 1.36 mmol), PPh₃ (0.25 g, 1.62 mmol) and DMAP (0.03 g, 0.27 mmol) in dry CH₂Cl₂. Reaction was stirred until total consuption of the precipitate was observed (15 h). The crude reaction was extracted with water (3x10 mL), washed with NaCl sat. and dried over MgSO₄. The pure product was obtained as a white powder recrystallization from ethanol. Yield 65% (0.69 g).

**Experimental**

1H NMR (400 MHz, CDCl₃): δ 7.05 (s, 2H, ArH), 5.95 (ddt, J = 16.9, 10.2, 6.7 Hz, 3H, Csp²-H), 5.08–4.85 (m, 6H, C=CH₂), 4.58 (m, 2H, OCH₂), 4.05–3.84 (m, 6H, OCH₂), 2.14–1.91 (m, 6H, alCH₂), 1.60–1.21 (m, 30H, alCH₂). 13C NMR (100 MHz, CDCl₃): δ 172.01, 168.74, 164.89, 152.97, 151.38, 150.78, 146.26, 139.33, 137.71, 136.20, 114.27, 114.25, 110.50, 109.24, 94.39, 69.28, 69.24, 65.75, 63.19, 33.94, 32.93, 30.46, 29.80, 29.72, 29.71, 29.68, 29.60, 29.52, 29.41, 29.34, 29.30, 29.12, 29.09, 26.21, 26.18. FTIR v (NaCl, cm⁻¹): 3075, 2926, 2853, 1722, 1687, 1643, 1606, 1591, 1578, 1537, 1512. MS [MALDI-TOF] m/z: 775.5 [M+H]+, 797.6 [M+Na]+.
Synthesis of 4-benzyl oxyphenyl 2-acetamidoisonicotinate
A solution of EDC·HCl (1.65 g, 8.6 mmol) was added dropwise to a 0 °C cooled dry THF solution of 2-acetamidoisonicotinic acid (1.20 g, 6.6 mmol), 4-benzyl oxy phenol (1.72 g, 8.6 mmol) and DPTS (0.39 g, 1.3 mmol). After 6 hours, THF was evaporated and reaction crude redissolved in CH₂Cl₂. The organic solution was extracted with water (3x15 mL), washed with NaCl sat and dried over MgSO₄. The pure product was filtered out after recrystallization from pure methanol. Yield 68% (1.22 g).

H NMR (400 MHz, CDCl₃): δ 8.87 (s, 1H, PyH), 8.45 (d, J = 5.1 Hz, 1H, PyH), 8.06 (s, 1H, OCN-H), 7.72 (dd, J = 5.1, 1.5 Hz, 1H, PyH), 7.52–7.30 (m, 5H, ArH), 7.20–6.93 (m, 4H, ArH), 5.08 (s, 2H, OCH₂), 2.25 (s, 3H, OCCH₃). ¹³C NMR (100 MHz, CDCl₃): δ 164.06, 156.93, 152.38, 148.82, 144.36, 139.37, 136.89, 128.78, 128.21, 127.64, 122.41, 119.67, 115.73, 113.87, 70.62, 24.92. FTIR (KBr, cm⁻¹): 3192, 3038, 3929, 1739, 1673, 1570. M.p. 198–200 °C.

Synthesis of 4-hydroxyphenyl 2-acetamidoisonicotinate
A suspension of 4-benzyl oxyphenyl 2-acetamidoisonicotinate (1.0 g, 2.76 mmol) and Pd/C 10 % p. in dry THF was stirred for 24 hours under a hydrogen saturated atmosphere. The crude of reaction was filtered over Celite® and washed with abundant THF, acetone and ethanol. The pure product was obtained as a white powder by recrystallization from acetone. Yield 81% (0.63 g).

H NMR (400 MHz, MeOD): δ 8.78 (s, 1H, PyH), 8.51 (dd, J = 5.1, 0.9 Hz, 1H, PyH), 7.73 (dd, J = 5.1, 1.5 Hz, 1H, PyH), 7.10–6.80 (m, 4H, ArH), 6.62 (s, 1H, O-H), 2.21 (s, 3H, OCCH₃). ¹³C NMR (100 MHz, MeOD): δ 172.32, 165.52, 156.76, 150.21, 144.63, 103.27. 1H NMR (KBr, cm⁻¹): 3500-3100, 3040, 1736, 1690, 1626, 1606, 1573. MS (MALDI-TOF) m/z: 775.5 [M+H]⁺, 797.6 [M+Na]⁺. M.p. 236 °C (dec.).

Synthesis of 4-(3,4,5-tris(10-undecenyloxy)benzoxy)phenyl 2-acetamidoisonicotinate (A3Py)
A DCC (0.26 g, 1.28 mmol) solution in dry CH₂Cl₂ was added dropwise over a suspension of 4-hydroxyphenyl 2-acetamidoisonicotinate (0.35 g, 1.28 mmol), 3,4,5-tris(10-undecenyloxy)benzoic acid (0.67 g, 1.07 mmol) and DPTS (0.09 g, 0.31 mmol) in dry CH₂Cl₂. The suspension was filtered over Celite® after 18 hours of stirring at room temperature. The product was obtained as a white powder by recrystallization from pure methanol. Yield 80 % (0.76 g).

H NMR (400 MHz, CD₂Cl₂): δ 8.83 (s, 1H, PyH), 8.48 (dd, J = 5.1, 0.8 Hz, 1H, PyH), 8.16 (s, 1H, OCN-H), 7.73 (dd, J = 5.1, 1.5 Hz, 1H, PyH), 7.42 (s, 2H, ArH), 7.37–7.24 (m, 4H, ArH), 5.91–5.75 (m, 3H, Csp²-H), 5.09–4.83 (m, 6H, C=CH₂), 4.11 – 3.96 (m, 6H, OCH₂), 2.23 (s, 3H, OCCH₃), 2.12–1.96 (m, 6H, Csp²-CH₃), 1.91–1.78 (m, 4H, alCH₂), 1.78–1.68 (m, 2H, alCH₂), 1.54–1.43 (m, 6H, alCH₃), 1.43–1.19 (m, 30H, alCH₃). ¹³C NMR (100 MHz, CDCl₃): δ 169.25, 165.44, 164.34, 153.60, 153.13, 149.50, 149.48, 148.60, 143.54, 139.87, 139.52, 124.25, 123.48, 123.07, 119.70, 114.37, 113.83, 108.89, 74.08, 69.83, 34.38, 30.92, 30.24, 30.15, 30.11, 30.03, 29.96, 29.92, 29.79, 29.74, 29.59, 29.56, 26.66, 26.63, 25.13. FTIR (KBr, cm⁻¹): 3368, 3325, 3258, 3078, 2925, 2855, 1740, 1710, 1677, 1641, 1587, 1571, 1541. MS (MALDI-TOF) m/z: 881.6 [M+H]⁺, 903.6 [M+Na]⁺. Elemental Anal.: calculated for C₉₄H₇₅N₂O₆: C, 73.60; H, 8.69; N, 3.18. Experimental: C, 73.68; H, 8.26; N, 3.42. M.p. 85 °C.

Synthesis of tris(4-benzyl oxybenzyl) trimesatoate
A solution of trimesoyl trichloride (0.5g, 1.9 mmol) in dry CH₂Cl₂ was added dropwise to a solution of benzyl 4-hydroxybenzoate (1.42 g, 6.2 mmol), triethylamine (0.66 g, 6.8 mmol) and dimethylaminopyridine (0.02 g, 0.2 mmol) in dry CH₂Cl₂. The reaction was stirred for 72 hours at room temperature after which it is quenched by water addition. The organic phase was washed with NaHCO₃ sat. (3x10 mL) and dried over MgSO₄. The resulting oil was precipitated by ethanol addition. Yield 83% (1.30 g).

H NMR (400 MHz, CDCl₃): δ 9.24 (s, 1H, ArH), 8.28–8.17 (AA'BB', 2H, ArH), 7.50–7.38 (m, 5H, ArH), 7.38–7.34 (AA'BB', 2H, ArH), 5.39 (s, 2H, OCOCH₃). ¹³C NMR (101 MHz, CDCl₃): δ 165.60, 162.78, 154.23, 136.45, 135.98, 131.66, 131.14, 128.78, 128.49, 128.37, 121.74, 67.09. FTIR (KBr, cm⁻¹): 3701-3144, 3089, 3076, 3032, 2956, 2921, 2897, 2849, 1746, 1721, 1603, 1502. M.p. 151-152 °C.

Synthesis of 4,4',4''-tris(trimesoyloxy)benzoic acid (T2)
A suspension of tris(4-benzyl oxybenzyl) trimesatoate (0.075 g, 0.089 mmol) and Pd(OH)₂/C 20% in ethanol/cyclohexene (3:1) was refluxed for 20 hours under inert atmosphere. The product appears as a white precipitate during reaction. The crude of reaction was filtered over a Celite® pad, and afterwards, this pad washeased with abundant warm toluene/methanol (1:1) mixture. The product obtained was further purified by recrystallization from ethanol. Yield 55 % (0.028 g).

H NMR (400 MHz, DMSO-d₆): δ 9.07 (s, 1H, ArH), 8.14–8.05 (AA'BB', 2H, ArH), 7.58–7.52 (AA'BB', 2H, ArH). ¹³C NMR (100 MHz, DMSO-d₆): δ 166.52, 162.59, 153.70, 153.38, 130.98, 130.70, 128.94, 122.15. FTIR (KBr, cm⁻¹):
1): 3378, 3188-2737, 2671, 2545, 1754, 1729, 1710, 1698, 1685, 1602, 1588, 1504, 1429. **Elem. Anal.:** calculated for C$_{30}$H$_{18}$O$_{12}$: C, 63.16; H, 3.18. Experimental: C 63.03; H, 3.25. **M.p.** 230 °C (dec.).

2. **H-bonding formation: FTIR spectra.**

![FTIR spectra of the titration of T1 with A3Py.](image1)

*Figure S1.* FTIR spectra of the titration of T1 with A3Py.

![FTIR spectra of supramolecular system T1-B3Py. Inset: carbonyl stretching band area.](image2)

*Figure S2.* FTIR spectra of supramolecular system T1-B3Py. Inset: carbonyl stretching band area.
Figure S3. FTIR spectra of variable temperature experiments on supramolecular system T2-B3Py.
3. **Cross-linking of the mesophase and properties of the nanoporous materials.**

![Graph](image)

Figure S4. Photo-DSC curve of the curing process of T1-B3Py at a) 80 °C, and b) 20 °C.

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<th>Membrane</th>
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<th>mmemb (mg)</th>
<th>mads./mmemb (μg/mg)</th>
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$m_{\text{desor}}$: solution concentration after dye desorption,
$m_{\text{ads}}$: dye adsorbed mass,
$m_{\text{memb}}$: membrane mass.

Figure S5. FTIR spectra of the M(T1-B3Py) membrane before and after Ag⁺ coordination.

4. Reference