Electronic Supplementary information for:

Templated nanoporous membranes based on hierarchically selfassembled 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. <u>Synthetic details and characterisation of the promesogenic units and templates.</u>

For the preparation of 2-acetamidoisonicotinic acid an addaptation of the procedure reported by Shen and Fan was followed¹.

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

A solution of DIAD (13.2 g, 65.2 mmol) in 40 mL of dry THF was added dropwise to a solution of methyl 3,4,5trihydroxybenzoate (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 quenched with 100 mL of water. 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 cromatography on silica gel eluting with hexane to hexane/ethyl acetate (20:1). Yield 69% (6.02 g).

¹**H** NMR (400 MHz, CDCl₃): δ 7.25 (s, 2H, ArH), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 3H, Csp²-H), 5.07–4.87 (m, 6H, C=CH₂), 4.01 (m, 6H, OCH₂), 3.89 (s, 3H, OCH₃), 2.04 (m, 6H, Csp²-CH₂), 1.87–1.68 (m, 6H, alCH₂), 1.53–1.20 (m, 36H, alCH₂). ¹³**C** NMR (75 MHz, CDCl₃): δ 167.09, 152.94, 139.35, 124.79, 114.27, 108.09, 73.61, 69.28, 52.27, 33.97, 30.46, 29.80, 29.71, 29.69, 29.60, 29.51, 29.44, 29.35, 29.30, 29.12, 29.09, 26.21. FTIR $\tilde{\nu}$ (NaCl, cm⁻¹): 3075, 2926, 2853, 1718, 1651, 1637, 1588.

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 sapnofied under refux with KOH (2.02 g) for 2 hours. The product was collected after neutralization with HCl (1M). Yield 86% (2.78 g).

¹H NMR (400 MHz, CDCl₃): δ 7.32 (s, 2H, ArH), 6.02–5.67 (m, 3H, Csp²-H), 5.10–4.81 (m, 6H, C=CH₂), 4.04 (t, *J*= 6.6 Hz, 2H, OCH₂), 4.02 (t, *J*=6.6 Hz, 4H, OCH₂), 2.13–1.97 (m, 6H, Csp²-CH₂), 1.93–1.66 (m, 6H, alCH₂), 1.58–1.19 (m, 36H, alCH₂). ¹³C NMR (101 MHz, CDCl₃): δ 172.01, 152.97, 143.26, 139.33, 123.79, 114.27, 108.67, 73.67, 69.30, 33.98, 33.96, 30.47, 29.80, 29.71, 29.68, 29.60, 29.52, 29.41, 29.34, 29.30, 29.12, 29.09, 26.21, 26.18. FTIR \tilde{V} (NaCl, cm⁻¹): 3076, 2925, 2854, 1722, 1687, 1640, 1585. M.p. 36-37 °C.

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

A solution of the methyl ester (2.27 g, 0.56 mmol) in dry THF was added dropwise to a excess LiAlH₄ suspension in dry THF at 0 $^{\circ}$ C. The reaction was stirred for 1 hour, after which excess of LiAlH₄ was neutralized with MgSO₄·10 H₂O in an ice bath. The pure product was obtained as a colourless liquid after filtering over Celite[®] and evaporation. Yield 98% (2.11 g).

¹**H** NMR (400 MHz, CDCl₃): δ 6.55 (s, 2H, ArH), 5.81 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 3H, Csp²-H), 5.08–4.85 (m, 6H, C=CH₂), 4.58 (s, 2H, HOCH₂), 4.05–3.84 (m, 6H, OCH₂), 2.12–1.95 (m, 6H, Csp²-CH₂), 1.83–1.65 (m, 6H, alCH₂), 1.54–1.23 (m, 37H, alCH₂). ¹³C NMR (100 MHz, CDCl₃): δ 153.38, 139.31, 137.71, 136.20, 114.24, 114.23, 105.50, 73.54, 69.24, 65.75, 63.19, 33.96, 33.94, 32.93, 30.46, 29.80, 29.72, 29.71, 29.68, 29.59, 29.56, 29.52, 29.33, 29.28, 29.25, 29.11, 29.08, 29.06, 26.26, 26.22, 25.87. FTIR $\tilde{\nu}$ (NaCl, cm-1): 3428, 3077, 2926, 2854, 2120, 1640, 1589. M.p. Col_h 31 I.

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-acetamidoixonicotinic acid (0.24g, 1.36 mmol), 3,4,5-trix(10-undeneoxy)benzylic alcohol (1.02 g, 1.62 mmol) and DMAP (0.03 g, 0.27 mmol) in dry CH_2Cl_2 . 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).

¹**H** NMR (400 MHz, CDCl₃): δ 8.76 (s, 1H, PyH), 8.44 (s, 1H, OCN-H), 8.37 (dd, *J* = 5.1, 0.9 Hz, 1H, PyH), 7.61 (dd, *J* = 5.1, 1.5 Hz, 1H, PyH), 6.63 (s, 2H, ArH), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 3H, Csp²-H), 5.27 (s, 2H, OCCH₂), 5.08–4.87 (m, 6H, C=CH₂), 4.04–3.90 (m, 6H, OCH₂), 2.22 (s, 3H, OCCH₃), 2.09–1.97 (m, 6H, Csp²-CH₂), 1.87–1.69 (m, 6H, alCH₂), 1.57–1.42 (m, 6H, alCH₂), 1.42–1.23 (m, 30H, alCH₂). ¹³C NMR (100 MHz, CDCl₃): δ 168.74, 164.89, 153.38, 152.38, 148.33, 140.21, 139.31, 138.51, 130.35, 119.31, 114.24, 114.22, 113.84, 107.26, 73.55, 69.30, 67.95, 33.96, 33.93, 30.46, 29.80, 29.71, 29.67, 29.63, 29.58, 29.55, 29.54, 29.32, 29.28, 29.10, 29.07, 26.24, 26.22, 24.82. FTIR $\tilde{\nu}$ (KBr, cm⁻¹): 3330, 3268, 3225, 3124, 3079, 2922, 2850, 1728, 1697, 1643, 1606, 1591, 1578, 1537, 1512. MS (MALDI-TOF) m/z: 775.5 [M+H]⁺, 797.6 [M+Na]⁺. Elem. Anal.: calculado para C₄₈HH₇₄N₂O₆: C, 74.38; H, 9.62; N, 3.61. Experimental: C, 74.57; H, 9.35; N, 3.81. M.p. 63 °C.

Synthesis of 4-benzyloxyphenyl 2-acetamidoisonicotinate

A solution of EDC·HCl (1.65 g, 8.6 mmol) was added dropwise to a 0 $^{\circ}$ C cooled dry THF solution of 2acetamidoisonicotinic acid (1.20 g, 6.6 mmol), 4-benzyloxyphenol (1.72 g, 8.6 mmol) and DPTS (0.39 g, 1.3 mmol). After 6 hours, THF was evaporated and reaction crude redisolved 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).

¹**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, 139.57, 136.89, 128.78, 128.21, 127.64, 122.41, 119.67, 115.73, 113.87, 70.62, 24.92. **FTIR** $\tilde{\nu}$ (KBr, cm⁻¹): 3192, 3038, 3929, 1739, 1673, 1570. **M.p.** 198-200 °C.

Synthesis of 4-hydroxyphenyl 2-acetamidoisonicotinate

A suspension of 4-benzyloxyphenyl 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).

¹**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, 140.48, 123.27, 120.04, 116.78, 114.88, 24.01. FTIR $\tilde{\nu}$ (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)benzoyloxy)phenyl 2-acetamidoisonicotinate (A3Py)

A DCC (0.26 g, 1.28 mmol) solution in dry CH_2Cl_2 was added dropwise over a suspension of 4-hydroxyphenyl 2acetamidoisonicotinate (0.35 g, 1.28 mmol), 3,4,5-tris(10-undecenoxy)benzoic acid (0.67 g, 1.07 mmol) y DPTS (0.09 g, 0.31 mmol) in dry CH_2Cl_2 . The suspension was filtered over Celite[®] after 18 hours of stirring at room temperature. The pure product was obtained as a white powder by recrystallization from pure methanol. Yield 80 % (0.76 g).

¹**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-CH₂), 1.91–1.78 (m, 4H, alCH₂), 1.78–1.68 (m, 2H, alCH₂), 1.54–1.43 (m, 6H, alCH₂), 1.43–1.19 (m, 30H, alCH₂). ¹³**C NMR** (100 MHz, CD₂Cl₂): 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**^{$\tilde{\nu}$} (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]⁺. **Elem. Anal.:** calculated for C₅₄H₇₆N₂O₈: 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-benzoyloxybenzyl) trimesoate

A solution of trimesoyl trichloride (0.5g, 1.9 mmol) in dry CH_2CI_2 was added dropwise to a solution of benzyl 4hydroxybenzoate (1.42 g, 6.2 mmol), triethylamine (0.66 g, 6.8 mmol) and dimethylaminopyridine (0.02 g, 0.2 mmol) in dry CH_2CI_2 . The reaction was stirred for 72 hours at room temperature aftwer 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).

¹H 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, OCOCH₂). 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 $\tilde{\nu}$ (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-benzoyloxybenzyl) trimesoate (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 precipitation during reaction. The crude of reaction was filtered over a Celite® pad, and afterwards, this pad whased with abundant warm toluene/methanol (1:1) mixture. The product obtained was further purified by recrystrallization from ethanol. Yield 55 % (0.028 g).

¹H NMR (400 MHz, DMSO-*d*₆): 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-*d*₆): δ 166.52, 162.59, 153.70, 135.38, 130.98, 130.70, 128.94, 122.15. FTIR $\tilde{\nu}$ (KBr, cm⁻

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. <u>H-bonding formation: FTIR spectra</u>.



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



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.



b)



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

Membrane	Dye	Mdesor.	mads	mmemb	mads./mmemb
		(µmol L-	•	•	
		1)	(µg)	(mg)	(µg/mg)
М(Т1- ВЗРу)	TNPG	5.1	2.66	1.33	3.5
	RhB	0.5	0.46	0.55	0.83
	МО	1.4	0.93	0.69	1.35
М(T2- ВЗРу)	TNPG	6.4	3.32	1.02	3.4
	RhB	0.3	0.25	0.27	0.93

 Table S 1. Data collected from desorption experiments by UV-Vis analysis.



M_{desor}: solution concentration after dye desorption, m_{ads}.: dye adsorpted mass, m_{memb}.: membrane mass.



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

4. Reference

1. Xu, Y.; Qu, W.; Yang, Q.; Zheng, J.; Shen, Z.; Fan, X.; Zhou, Q. Synthesis and Phase Structures of Mesogen-Jacketed Liquid Crystalline Polyelectrolytes and Their Ionic Complexes. Macromolecules 2012, 45 (6), 2682–2689.