

A robust Ti(IV)-based mesogen constructed around a TiO₄N₂ core

L. Barloy, B. Heinrich, L. Douce, M. Henry, M. Scarpi-Luttenauer, N. Kyritsakas, P. Mobian

Supporting Information

Contents

| | |
|---|----|
| 1. Syntheses and Characterizations | 1 |
| 2. Thermal behaviour of [Ti(1b)(2) ₂] | 7 |
| 3. Mesomorphic properties of [Ti(1b)(2) ₂] | 8 |
| 4. Self-organization behaviour of [Ti(1b)(2) ₂] | 9 |
| 5. Indexation tables | 10 |
| 6. Experimental for the study of mesomorphic properties | 11 |

1. Syntheses and Characterizations

The following commercial reagents were used as received from TCI, Alfa Aesar or VWR : copper(II) sulfate pentahydrate, sodium *L*-ascorbate, ethylenediaminetetraacetic acid (EDTA), ammonia aqueous solution, [Ti(O^{*i*}Pr)₄]. For the synthesis of the ligands, CH₂Cl₂ and deionized water were previously degassed with argon. For coordination chemistry, CH₂Cl₂, CHCl₃, diethyl ether, toluene, *n*-heptane and pentane (Sigma-Aldrich) were dried with 4 Å molecular sieve before use. Column chromatography was carried out on aluminium oxide 90 standard or on silica gel 60 40-63 μm (Merck). 5-ethynyl-2,2'-bipyrimidine,¹ 5-(azidomethyl)-1,2,3-trimethoxybenzene,² and *cis*-[Ti(2)(HO^{*i*}Pr)₂]³ were synthesized following reported procedures. The synthesis and characterization of 5-(azidomethyl)-1,2,3-tris(hexadecyl-1-oxy)benzene has been reported recently,⁴ but we had rather prepared it through a procedure similar to the one described in ref. 2 (*vide supra*).

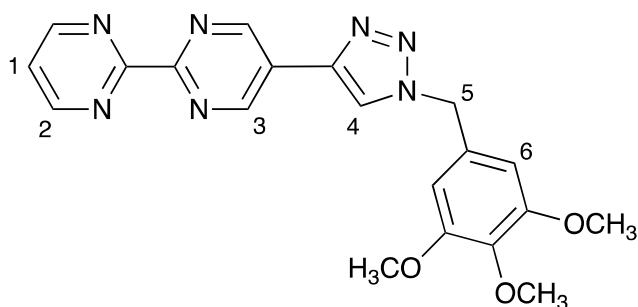
NMR spectra were recorded at room temperature on Bruker Avance spectrometers. ¹H NMR spectra were recorded at 500.13 MHz and referenced to SiMe₄. ¹³C{¹H} NMR spectra (broadband decoupled) were recorded at 125.77 MHz and referenced to SiMe₄. The NMR assignments were supported by 2D spectra: COSY, NOESY and/or ROESY for ¹H NMR, HSQC and HMBC for ¹³C{¹H} NMR. Chemical shifts are reported in ppm and coupling constants in Hz; the latter are proton-proton coupling constants. The ¹³C{¹H} signals are singlets. For the adopted numbering scheme, see Schemes 1 and 2 and Chart 1. Multiplicity: s = singlet, d = doublet, t = apparent triplet, m = multiplet. Mass spectrometry and elemental analyses were carried out by the corresponding facilities at the Institut de Chimie, Université de Strasbourg. The electrospray analyses were performed on a Micro-TOF (Bruker) apparatus equipped with an electrospray (ES) source. The MALDI mass spectra were acquired on a time-of-flight mass spectrometer (MALDI-TOF-TOF Autoflex II TOF-TOF, Bruker Daltonics) equipped with a nitrogen laser (λ = 337 nm). The elemental analyses were performed on a Flash 2000 apparatus (ThermoFischer Scientific) for C, H, and N elements.

¹ R. Ziessel and C. Stroh, *Tetrahedron Lett.*, 2004, **45**, 4051–4055.

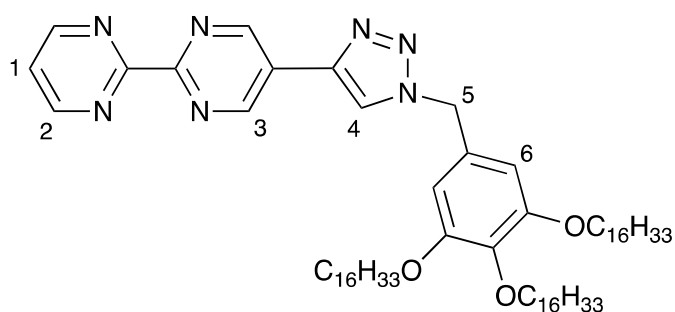
² K. Odlo, J. Fournier-Dit-Chabert, S. Ducki, O. A. B. S. M. Gani, I. Sylte and T. V. Hansen, *Bioorg. Med. Chem.*, 2010, **18**, 6874–6885.

³ C. Diebold, P. Mobian, C. Huguenard, L. Allouche and M. Henry, *Dalton Trans.*, 2009, 10178–10180.

⁴ R. Sekiya, Y. Uemura, H. Naito, K. Naka and T. Haino, *Chem. – Eur. J.*, 2016, **22**, 8198–8206.

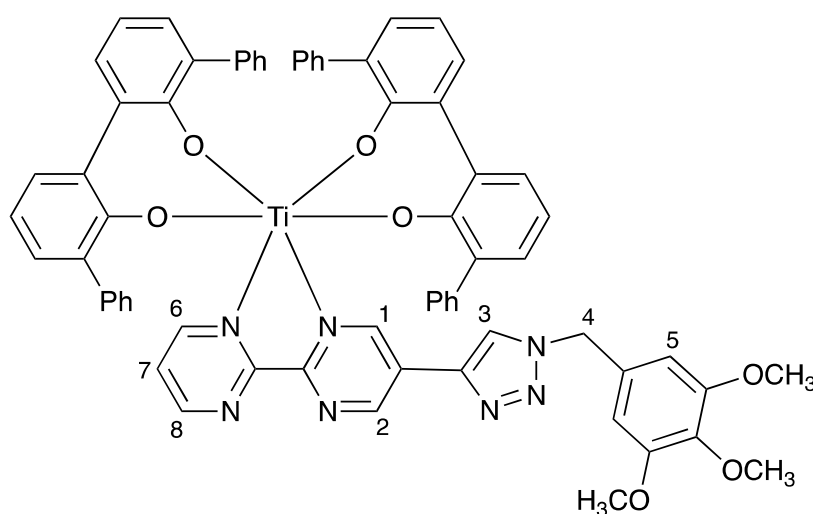


5-(1-(3,4,5-trimethoxybenzyl)-1H-1,2,3-triazol-4-yl)-2,2'-bipyrimidine (1a). In a vial filled with argon, 5-ethynyl-2,2'-bipyrimidine (27 mg, 0.148 mmol) and 5-(azidomethyl)-1,2,3-trimethoxybenzene (65 mg, 0.291 mmol) were dissolved in CH_2Cl_2 (1.6 mL). In another vial filled with argon, copper(II) sulfate pentahydrate (19 mg, 0.076 mmol) and sodium *L*-ascorbate (29 mg, 0.146 mmol) were dissolved in deionized water (1.6 mL), and the resulting aqueous suspension was added to the solution of reactants. The mixture was vigorously stirred at RT over 90 h, then added to a solution of EDTA (87 mg, 0.298 mmol) in aqueous ammonia (2 mL, 7%), and extracted with CH_2Cl_2 (3 X 50 mL). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The yellow crude product was chromatographed (alumina, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ 100:2) to obtain compound **1a** as an off-white solid (32 mg, 53%). Mp = 209 °C (from CH_2Cl_2). Anal. Calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_7\text{O}_3$: C, 59.25; N, 24.18; H, 4.72. Found C, 59.09; N, 23.83; H, 4.75. ^1H NMR (CDCl_3 , 500 MHz): δ 9.42 (2H, s, H3), 9.04 (2H, d, $^3J = 4.9$ Hz, H2), 7.95 (1H, s, H4), 7.45 (1H, t, $^3J = 4.9$ Hz, H1), 6.58 (2H, s, H6), 5.56 (2H, s, H5), 3.86 (6H, s, CH_3), 3.85 (3H, s, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz): δ 162.2, 161.5, 158.3, 154.9, 154.0, 142.0, 138.7, 129.5, 125.0, 121.7, 121.0, 105.5, 61.1, 56.4, 55.1. MS (ESI $^+$): m/z 406.16 ($[\text{M} + \text{H}]^+$, 84%), 428.14 ($[\text{M} + \text{Na}]^+$, 100%), 833.29 ($[\text{2M} + \text{Na}]^+$, 16%).

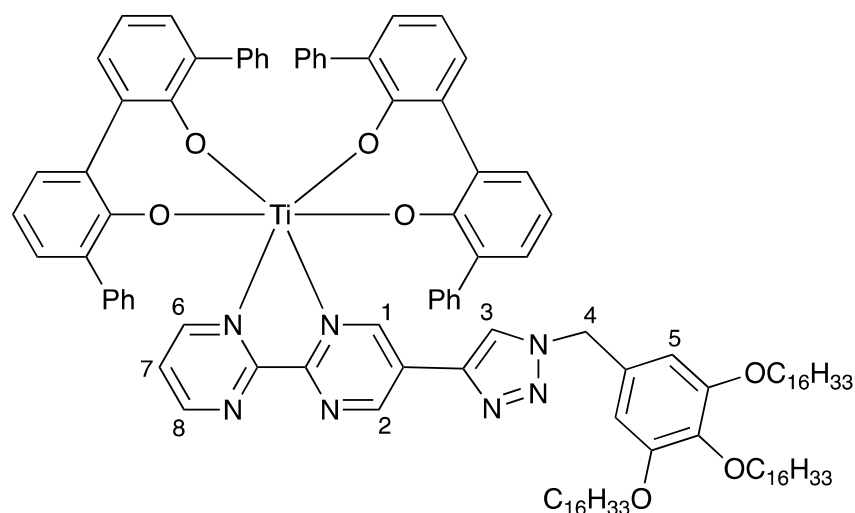


5-(1-(3,4,5-tris(hexadecyl-1-oxy)benzyl)-1H-1,2,3-triazol-4-yl)-2,2'-bipyrimidine (1b). In a vial filled with argon, 5-ethynyl-2,2'-bipyrimidine (48 mg, 0.263 mmol) and 5-(azidomethyl)-1,2,3-tris(hexadecyl-1-oxy)benzene (199 mg, 0.233 mmol) were dissolved in CH_2Cl_2 (1 mL). In another vial filled with argon, copper(II) sulfate pentahydrate (29 mg, 0.116 mmol) and sodium *L*-ascorbate (46 mg, 0.232 mmol) were dissolved in deionized water (1 mL), and the resulting aqueous suspension was added to the solution of reactants. The mixture was vigorously stirred at RT over 110 h, then added to a solution of EDTA (68 mg, 0.233 mmol) in aqueous ammonia (3 mL, 7%), and extracted with CH_2Cl_2 (3 X 50 mL). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure. The yellow crude product was

chromatographed (silica, CH₂Cl₂/CH₃OH 100:2), and then recrystallized in CH₂Cl₂/CH₃OH to obtain compound **1b** as an off-white solid (121 mg, 50%). Mp = 112 °C (from CH₂Cl₂). Anal. Calcd. for C₆₅H₁₀₉N₇O₃: C, 75.31; N, 9.46; H, 10.60. Found C, 74.82; N, 9.34; H, 10.30. ¹H NMR (CDCl₃, 500 MHz): δ 9.41 (2H, s, H3), 9.03 (2H, d, ³J = 4.8 Hz, H2), 7.91 (1H, s, H4), 7.44 (1H, t, ³J = 4.8 Hz, H1), 6.53 (2H, s, H6), 5.50 (2H, s, H5), 3.94 (6H, t, ³J = 6.4 Hz, OCH₂), 1.81-1.69 (6H, m, CH₂), 1.50-1.40 (6H, m, CH₂), 1.36-1.20 (72H, m, CH₂), 0.87 (9H, t, ³J = 7.0 Hz, CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz), selected data: δ 162.2, 161.5, 158.3, 154.8, 153.9, 141.9, 139.0, 128.9, 125.0, 121.7, 120.9, 107.0, 73.7, 69.5, 55.1, 32.1, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 26.2, 22.8, 14.3. MS (ESI⁺; addition of formic acid): *m/z* 1036.86 ([M + H]⁺, 100%), 1058.85 ([M + Na]⁺, 18%), 2095.70 ([2M + Na]⁺, 3%).



[Ti(1a)(2)₂]. Under Ar protection (glovebag), ligand **1a** (10.0 mg, 24.7 μmol) was added to a solution in a vial of *cis*-[Ti(2)₂(HO^{*i*}Pr)₂] (20.7 mg, 24.6 μmol) in CH₂Cl₂ (0.6 mL). After stirring for 5 minutes at RT, a layer of pentane was added and allowed to slowly diffuse into the solution. This led after several days to orange crystals of [Ti(1a)(2)₂] that were collected by filtration (20 mg, 72%). Single crystals suitable for X-ray analysis were obtained from a CHCl₃ solution of [Ti(2)₂(HO^{*i*}Pr)₂] instead of a CH₂Cl₂ solution. Anal. Calcd. for C₆₈H₅₁N₇O₇Ti•½CH₂Cl₂: C, 70.41; N, 8.39; H, 4.49. Found C, 70.53; N, 7.94; H, 4.56. ¹H NMR (CDCl₃, 500 MHz): δ 9.32 (1H, d, ⁴J = 2.5 Hz, H2), 8.69 (1H, dd, ³J = 4.7 Hz, ⁴J = 2.3 Hz, H8), 8.55 (1H, d, ⁴J = 2.6 Hz, H1), 8.52 (1H, dd, ³J = 5.3 Hz, ⁴J = 2.3 Hz, H6), 7.53 (1H, s, H3), 7.51-7.22 (8H, m, H_{arom}), 7.16-6.96 (9H, m, H_{arom}), 6.94-6.89 (3H, m, H_{arom}), 6.87 (1H, t, ³J = 5.1 Hz, H7), 6.84-6.59 (11H, m, H_{arom}), 6.58 (2H, s, H5), 6.22 (1H, t, ³J = 7.6 Hz, H_{arom}), 5.58 (1H, d, ²J = 14.6 Hz, H4), 5.44 (1H, d, ²J = 14.6 Hz, H4), 3.88 (3H, s, CH₃), 3.87 (6H, s, CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz): δ 160.7, 160.6, 160.4, 160.1, 159.9, 157.6, 156.5, 156.4, 156.3, 154.1, 152.0, 140.5, 138.9, 138.7, 138.5, 138.4, 138.2, 132.0, 131.7, 131.3, 130.9, 130.0 (2 signals), 129.9, 129.7, 129.6 (2 signals), 129.5 (3 signals), 129.4, 129.3, 129.2, 129.1 (2 signals), 129.0, 128.5, 128.2, 127.7, 127.6, 127.4, 127.2, 126.4, 126.3, 126.2, 125.2, 125.1, 122.6, 122.4, 122.3, 121.3, 120.0, 119.7, 105.8, 61.2, 56.7, 55.1. MS (ESI⁺): *m/z* 1126.34 ([M + H]⁺, 100%), 1148.32 ([M + Na]⁺, 65%).



[Ti(1b)(2)₂]. Under Ar protection (glovebag), ligand **1b** (28.4 mg, 27.4 μmol) was added to a solution in a vial of *cis*-[Ti(**2**)₂(HO^{*i*}Pr)₂] (23.0 mg, 27.4 μmol) in CH₂Cl₂ (0.7 mL). After stirring for 5 minutes at RT, a layer of pentane was added and allowed to slowly diffuse into the solution. This led after several days to an orange precipitate that was collected by removing the supernatant solution. The crude product was purified by column chromatography (alumina, CH₂Cl₂), and then recrystallized in CH₂Cl₂/pentane, yielding [Ti(**1b**)(**2**)₂] as an orange powder (35 mg, 73%). Anal. Calcd. for C₁₁₃H₁₄₁N₇O₇Ti•½CH₂Cl₂: C, 75.75; N, 7.95; H, 5.45. Found C, 76.00; N, 7.90; H, 5.49. ¹H NMR (CDCl₃, 500 MHz): δ 9.31 (1H, d, ⁴J = 2.6 Hz, H2), 8.69 (1H, dd, ³J = 4.7 Hz, ⁴J = 2.3 Hz, H8), 8.54 (1H, d, ⁴J = 2.6 Hz, H1), 8.51 (1H, dd, ³J = 5.3 Hz, ⁴J = 2.3 Hz, H6), 7.51 (1H, s, H3), 7.54-7.38 (4H, m, H_{arom}), 7.35-7.20 (4H, m, H_{arom}), 7.14-6.89 (12H, m, H_{arom}), 6.87 (1H, t, ³J = 5.1 Hz, H7), 6.82-6.57 (11H, m, H_{arom}), 6.53 (2H, s, H5), 6.20 (1H, t, ³J = 7.6 Hz, H_{arom}), 5.56 (1H, d, ²J = 14.6 Hz, H4), 5.38 (1H, d, ²J = 14.6 Hz, H4), 3.96 (6H, m, OCH₂), 1.85-1.70 (6H, m, CH₂), 1.52-1.40 (6H, m, CH₂), 1.40-1.15 (72H, m, CH₂), 0.87 (9H, m, CH₃). ¹³C{¹H} NMR (CDCl₃, 125 MHz), selected data: δ 160.6, 160.5, 160.3, 160.0, 159.8, 157.5, 156.4, 156.3, 156.2, 154.0, 151.9, 140.4, 139.0, 138.7, 138.4, 138.3, 138.1, 131.9, 131.6, 131.1, 130.9, 129.9, 129.8, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 128.4, 128.1, 127.6, 127.3, 127.1, 126.2, 126.1, 125.2, 122.4, 122.3, 121.2, 119.8, 119.7, 107.0, 73.7, 69.5, 55.1, 32.1, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.3, 26.2, 22.8, 14.3. MS (ESI⁺; addition of formic acid): *m/z* 1758.06 ([M + H]⁺, 100%), 1780.03 ([M + Na]⁺, 15%), 1796.01 ([M + K]⁺, 72%).

Crystallographic Details for [Ti(1a)(2)₂]. The X-ray diffraction data were collected at 173 K on a Bruker Smart CCD diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). The structures

were solved and refined using the Bruker SHELXTL Software Package using SHELXS-97 (Sheldrick, 2014) and refined by full matrix least-squares on F² using SHELXL-97 (Sheldrick, 2014) with anisotropic thermal parameters for all non-hydrogen atoms.⁵ The hydrogen atoms were introduced at calculated positions and not refined (riding model). We used the squeeze command because the solvents could not be identified.

Crystallography data: C₆₈H₅₁N₇O₇Ti, CHCl₃; *T* = 173(2)K; crystal size 0.050 X 0.060 X 0.060 mm; orthorhombic; space group P c c n; *a* = 23.6828(12) Å, *b* = 31.4643(16) Å, *c* = 18.0577(7) Å; *V* = 13455.9(11) Å³; *Z* = 8; *D*_{calcd.} = 1.230 g cm⁻³; reflections collected: 18797; *R*_{int} = 0.0871; *R*₁(*F*) (*I* > 2σ(*I*)) = 0.1013, w*R*₂(*F*²) (all data) = 0.3424; GOF(*F*²) = 1.132. CCDC number 1880954.

⁵ (a) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122; (b) G. M. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 2015, **71**, 3-8.

2. Thermal behaviour of [Ti(1b)(2)₂]

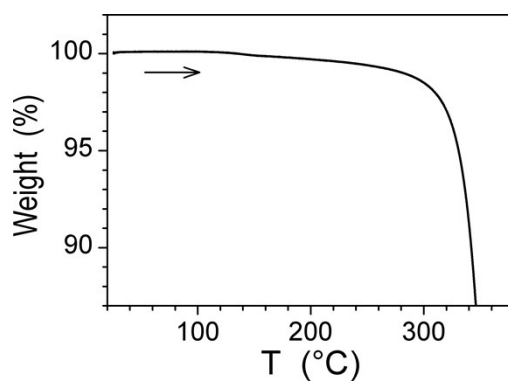


Figure S1 TGA curve of [Ti(1b)(2)₂] (conditions: 5°C.min⁻¹, air) showing significant weight loss from degradation above 230-240°C and 5% weight loss temperature of 330°C.

3. Mesomorphic properties of [Ti(1b)(2)₂]

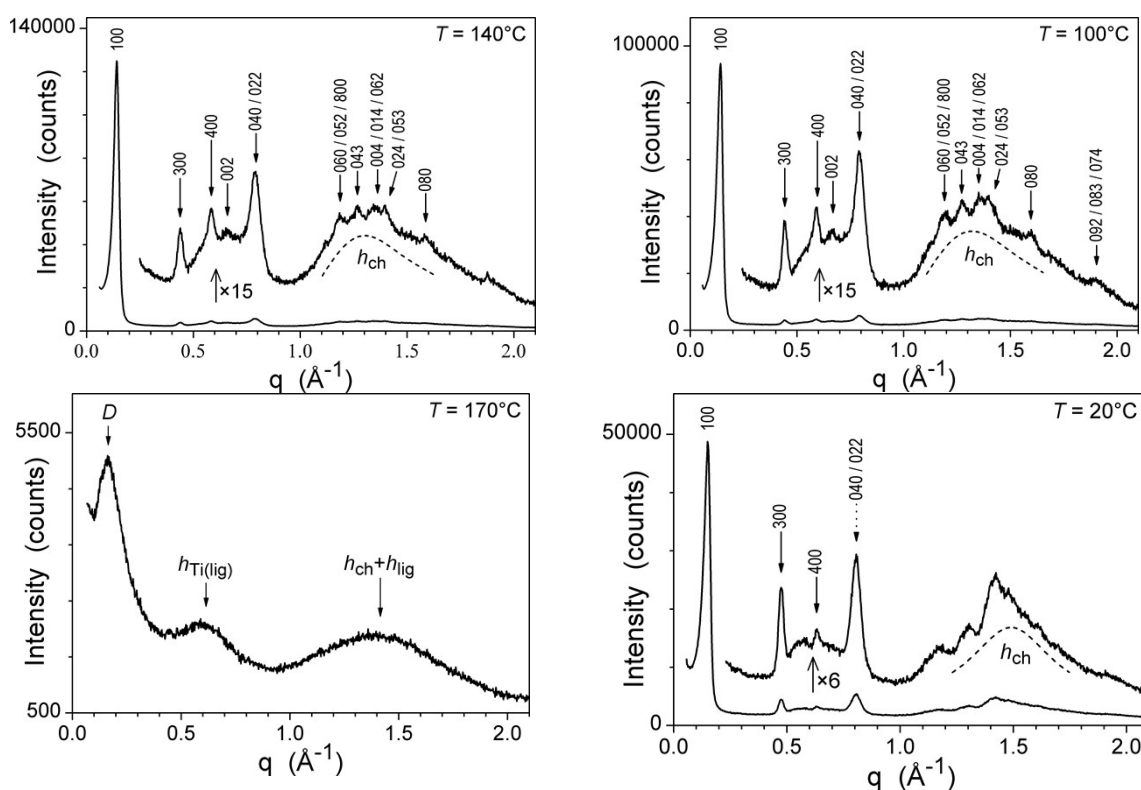


Figure S2: SAXS patterns of [Ti(1b)(2)₂], top: SAXS patterns at 140°C on heating and at 100°C on cooling, typical for a smectic-like mesophase, owing to the presence of the scattering signal of molten chains h_{ch} (≈ 4.7 Å; dashed line) and of the reflections of the lamellar periodicity formed by the alternation of complexes and molten chains ($h00$) series; smectic layer spacing: $d = d_{100} \approx 43$ Å); the mesophase was labelled Sm_{rec} due to the rectangular in-plane arrangement of complexes deduced from $(0kl)$ reflections, whose broadening corresponds to correlation lengths of 100-150 Å (from Scherrer equation with shape factor $K = 0.9$); bottom left: pattern at 170°C in the isotropic liquid state, that displays a local-range periodicity D from the nanosegregation of chains and complexes into strata ($D \approx 37$ Å; correlation length from Scherrer equation with $K = 0.9$: $\xi = 60$ Å), in addition to the scattering maximum from chains and ligand segments ($h_{ch}+h_{lig} \approx 4.5$ Å) and to a further scattering signal from lateral distances between entire complexes ($h_{Ti(lig)} \approx 10$ Å; $\xi = 25$ Å); bottom right: SAXS pattern of the crystallized state obtained on cooling from the mesophase, which preserves a lamellar structure close to the mesophase ($d \approx 40$ Å), but with even more disordered in plane-arrangement of complexes that blurs out the $(0kl)$ reflections. This high structural disorder is related to the crystallization of chains, as shown by the shift of the h_{ch} scattering maximum to 4.2 Å and the linked reduction of cross-sectional area: $\sigma_{ch} \approx (h_{ch}/0.9763)^2 = 18.5$ Å² [M. Marcos, R. Giménez, J. L. Serrano, B. Donnio, B. Heinrich, D. Guillon, *Chem. Eur. J.*, (2001), **7**(5), 1006-1013].

4. Self-organization behaviour of [Ti(1b)(2)₂]

| Compound ^a Phase T [°C] | d ; (N_{ML}) [Å] ^b b ; c [Å]; $\beta = 90^\circ$ ^c A (Z) [Å ²] ^d | A_{mol} [Å ²] ^e S_{ch} (τ) [Å ²] ^f q_{ch} ^g |
|---|---|---|
| [Ti(1b)(2) ₂] Sm _{rec} 140 | $d = 43.0$ ($N_{ML} = 2$) $b = 31.7$; $c = 18.9$ $A = 599$ ($Z = 4$) | $A_{mol} = 150$ $S_{ch} = 25.0$ ($\tau = 0$) $q_{ch} = 1.08$ |
| [Ti(1b)(2) ₂] Sm _{rec} 100 | $d = 42.7$ ($N_{ML} = 2$) $b = 31.6$; $c = 18.85$ $A = 596$ ($Z = 4$) | $A_{mol} = 149$ $S_{ch} = 24.8$ ($\tau = 0$) $q_{ch} = 1.10$ |
| [Ti(1a)(2) ₂] Cr -100 | $d = a = 23.6828$ ($N_{ML} = 2$) $b = 31.4643$; $c = 18.0578$ $A = 568.2$ ($Z = 4$) | $A_{mol} = 142.04$ |

Table S1: ^a geometrical and structural parameters of the molecular self-assembling for [Ti(1a,b)(2)₂] complexes at various temperatures T ; ^b lamellar periodicity d and number of molecular layers per lamella N_{ML} ; ^c parameters of the rectangular lattice formed by the lateral arrangement of complexes; ^d lattice area A and number of complexes per lattice Z ; ^e molecular area $A_{mol} = A/Z$; ^f area per chain $S_{ch} = (A_{mol}/N_{ch})/(2-\tau)$, where $N_{ch} = 3$ is the number of chains per molecule and τ is the bilayering ratio of the aliphatic layers, i.e. $\tau = 0$ for their intercalation into monolayer and $\tau = 1$ for their superposition into bilayer; ^g chain packing ratio $q_{ch} = S_{ch}/\sigma_{ch}$, where $\sigma_{ch} = 20.9 + 0.016 \times T$ Å² is the cross-sectional area of a molten chain at temperature T in °C [C. de Gracia Lux, B. Donnio, B. Heinrich, M. P. Krafft, *Langmuir*, (2013), **29**, 5325-5336].

5. Indexation tables

^{a,b}: measured scattering vectors and spacings; ^c: intensity (VS: very strong, S: strong, M: medium, W: weak, VW: very weak); ^d: Miller indices; ^{e,f}: calculated scattering vectors and spacings; curly brackets stand for reflections coincidences.

[Ti(1b)(2)₂], $T = 100^\circ\text{C}$, Sm_{rec} mesophase

| N° | $q_{\text{meas}} [\text{\AA}^{-1}]^a$ | $d_{\text{meas}} [\text{\AA}]^b$ | Intens ^c | hkl ^d | $q_{\text{calc}} [\text{\AA}^{-1}]^e$ | $d_{\text{calc}} [\text{\AA}]^f$ |
|-----------|---------------------------------------|----------------------------------|---------------------|------------------|---------------------------------------|----------------------------------|
| 1 | 0.143 | 43.9 | VS | 100 | 0.147 | 42.70 |
| 2 | 0.441 | 14.24 | M | 300 | 0.441 | 14.23 |
| 3 | 0.590 | 10.65 | W | 400 | 0.589 | 10.67 |
| 4 | 0.665 | 9.45 | VW | 002 | 0.667 | 9.43 |
| 5 | 0.794 | 7.917 | S | { 022 | 0.776 | 8.094 |
| | | | | { 040 | 0.795 | 7.900 |
| 6 | 1.192 | 5.270 | M | { 800 | 1.177 | 5.338 |
| | | | | { 060 | 1.193 | 5.267 |
| | | | | { 052 | 1.197 | 5.249 |
| 7 | 1.274 | 4.933 | W | 043 | 1.278 | 4.918 |
| 8 | 1.362 | 4.614 | W | { 004 | 1.333 | 4.713 |
| | | | | { 014 | 1.348 | 4.661 |
| | | | | { 062 | 1.367 | 4.598 |
| 9 | 1.400 | 4.487 | W | { 024 | 1.391 | 4.516 |
| | | | | { 053 | 1.410 | 4.456 |
| 10 | 1.59 | 3.945 | VW | 080 | 1.591 | 3.950 |
| 11 | 1.91 | 3.291 | VW | { 083 | 1.879 | 3.344 |
| | | | | { 092 | 1.910 | 3.290 |
| | | | | { 074 | 1.927 | 3.260 |

$a = 42.7 \text{ \AA}$; $b = 31.6 \text{ \AA}$; $c = 18.85 \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$; $V = 25.4 \cdot 10^3 \text{ \AA}^3$ ($Z=8$)

Table S2

[Ti(1b)(2)₂], $T = 140^\circ\text{C}$, Sm_{rec} mesophase

| N° | $q_{\text{meas}} [\text{\AA}^{-1}]^a$ | $d_{\text{meas}} [\text{\AA}]^b$ | Intens ^c | hkl ^d | $q_{\text{calc}} [\text{\AA}^{-1}]^e$ | $d_{\text{calc}} [\text{\AA}]^f$ |
|-----------|---------------------------------------|----------------------------------|---------------------|------------------|---------------------------------------|----------------------------------|
| 1 | 0.142 | 44.4 | VS | 100 | 0.146 | 43.00 |
| 2 | 0.438 | 14.34 | M | 300 | 0.438 | 14.333 |
| 3 | 0.583 | 10.78 | W | 400 | 0.585 | 10.750 |
| 4 | 0.665 | 9.45 | VW | 002 | 0.665 | 9.450 |
| 5 | 0.790 | 7.951 | S | { 022 | 0.774 | 8.117 |
| | | | | { 040 | 0.793 | 7.925 |
| 6 | 1.187 | 5.291 | M | { 800 | 1.169 | 5.375 |
| | | | | { 060 | 1.189 | 5.283 |
| | | | | { 052 | 1.193 | 5.265 |
| 7 | 1.271 | 4.943 | W | 043 | 1.274 | 4.932 |
| 8 | 1.348 | 4.661 | W | { 004 | 1.330 | 4.725 |
| | | | | { 014 | 1.345 | 4.673 |
| | | | | { 062 | 1.363 | 4.612 |
| 9 | 1.400 | 4.488 | W | { 024 | 1.388 | 4.528 |
| | | | | { 053 | 1.406 | 4.469 |
| 10 | 1.59 | 3.957 | VW | 080 | 1.586 | 3.962 |

$a = 43.0 \text{ \AA}$; $b = 31.7 \text{ \AA}$; $c = 18.90 \text{ \AA}$; $\alpha = \beta = \gamma = 90^\circ$; $V = 25.8 \cdot 10^3 \text{ \AA}^3$ ($Z=8$)

Table S3

6. Experimental for the study of mesomorphic properties

Optical textures were observed with a Leitz Orthoplan polarizing microscopy equipped with a Mettler FP82 hot stage and a FP80 unit. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a TA Instruments DSCQ1000 instrument operated at a scanning rate of $5^{\circ}\text{C min}^{-1}$ on heating and on cooling. The TGA measurements were carried out with a Q50 apparatus of TA Instruments, at a scanning rate of $5^{\circ}\text{C min}^{-1}$ and with air as purge gas. The SAXS patterns were obtained with a transmission Guinier-like geometry. A linear focalized monochromatic Cu $K_{\alpha 1}$ beam ($\lambda = 1.5405 \text{ \AA}$) was obtained using a sealed-tube generator (600 W) equipped with a bent quartz monochromator. The crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μm wall-thickness. The diffraction patterns were recorded with a curved Inel CPS120 counter gas-filled detector and on image plates scanned by Amersham Typhoon IP with 25 μm resolution. The sample temperature was controlled within $\pm 0.01^{\circ}\text{C}$, and exposure times were of 2 h.