

Modified Pyridine-Triazole and 2,2'-Bipyrimidine Ligands Generating Robust Titanium Complexes Constructed Around a TiO_4N_2 Core†

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Supporting Information

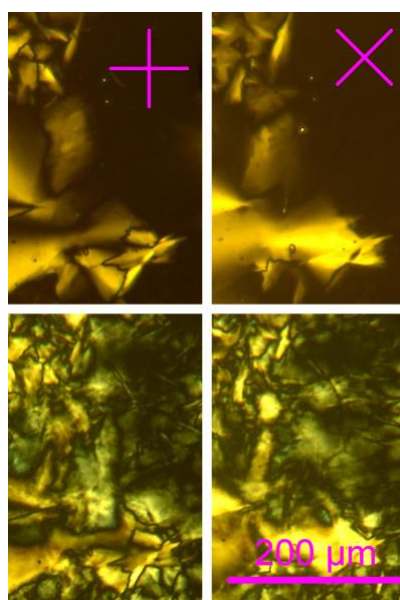


Fig. S1 Additional POM textures of ligand **3b** in mesophases $\text{Col}_{\text{hex}2}$ at 140°C (top) and $\text{Col}_{\text{hex}1}$ at 100°C (bottom), for different crossed polarizers directions (purple cross). On crossing $\text{Col}_{\text{hex}2}$ - $\text{Col}_{\text{hex}1}$ phase transition, the homeotropic areas are reversibly replaced by schlieren areas, which further confirms the changeover from an orthogonal to a tilted structure.

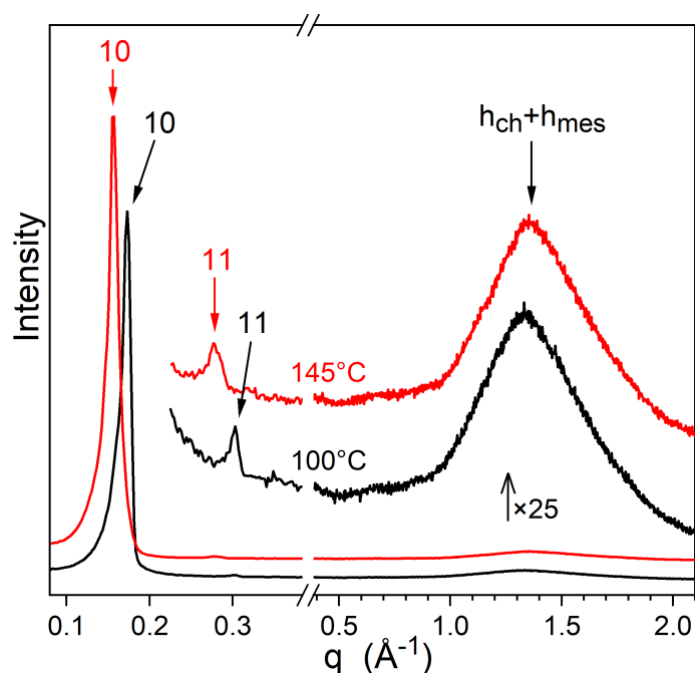


Fig. S2 SWAXS patterns of ligand **3b** in low- and high-temperature mesophases (black and red) that comply with col_{hex} structures of different lattice parameter, as indicated by the sharp reflections (10) and (11) with spacing ratio $d_{10}/d_{11} = \sqrt{3}$ and by the broad wide-angle scattering maximum $h_{\text{ch}}+h_{\text{mes}} \approx 4.7 \text{ \AA}$ from liquid-like lateral distances between molten chains and between mesogens. Therefore, lattice parameter is $a = (2/\sqrt{3}) \times d_{10} = 41.6 \text{ \AA}$ at 100°C and 45.2 \AA at 145°C ; columnar cross-sectional surface is $S_{\text{col}} = (\sqrt{3}/2) \times a^2 = 1770 \text{ \AA}^2$ at 100°C and 1500 \AA^2 at 145°C .

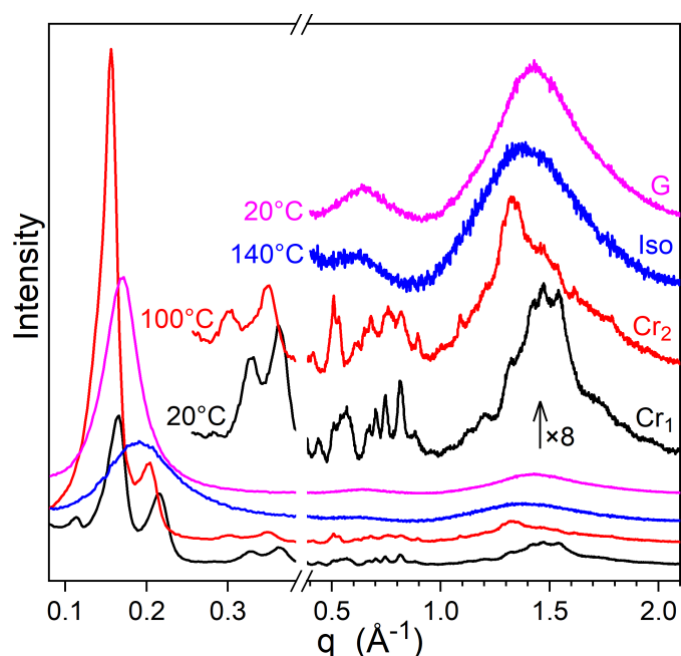


Fig. S3 SWAXS patterns of $[\text{Ti}(\mathbf{3b})(\mathbf{4})_2]$ in initial crystal 1 state (black), at 100°C in crystal 2 state (red), at 140°C in the isotropic liquid state (blue) and after cooling to 20°C in the glassy state (pink).

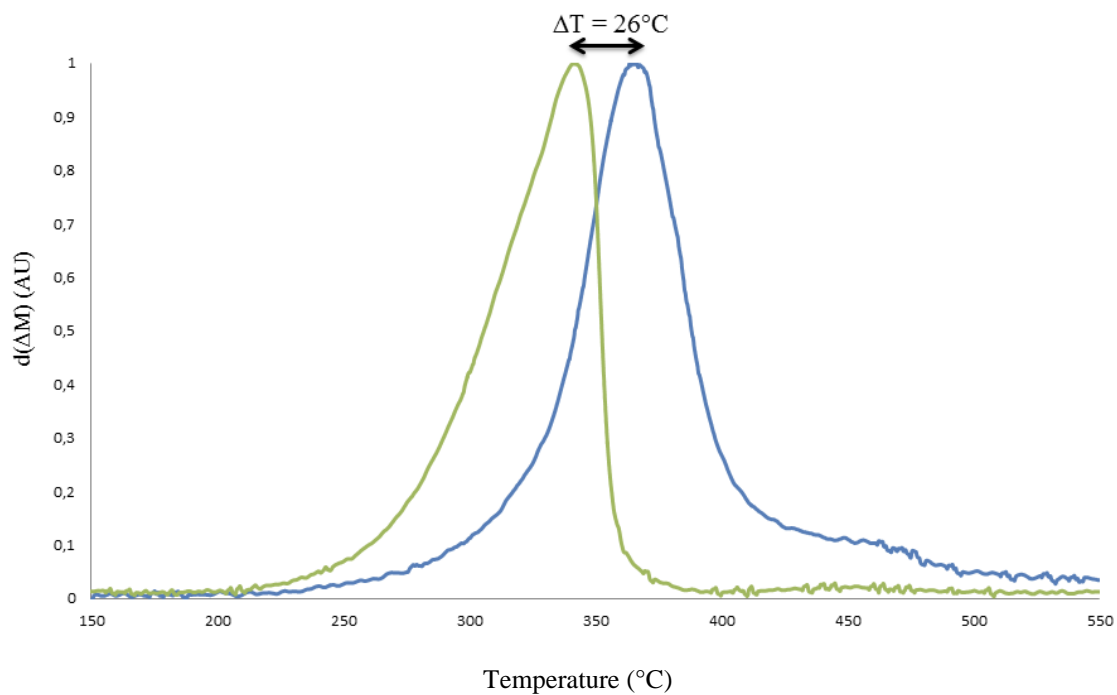


Fig. S4 Derived TGA thermogram of ligand **1b** (green) and complex $[\text{Ti}(\mathbf{1b})(\mathbf{4})_2]$ (blue), showing that the analyzed solid sample of the complex contains no free ligand. The thermogravimetric analysis was performed on a Pyris 6 (Perkin Elmer) apparatus.