

Electronic Supplementary Information

ESI.1 Schematic representations for (a) intercalated SmA (SmAc) and (b) interdigitated SmA (SmAd) structures.

ESI. 2 Binary phase diagrams for mixtures of **4-(6,9)** (**6PY9OCB**) and **4-(8,11)** (**8PY11OCB**); and an X-ray diffraction pattern for a mixture of **6PY9OCB** (75 wt%) and **8PY11OCB** (25 wt%) in the Mx phase.^{60(a)}

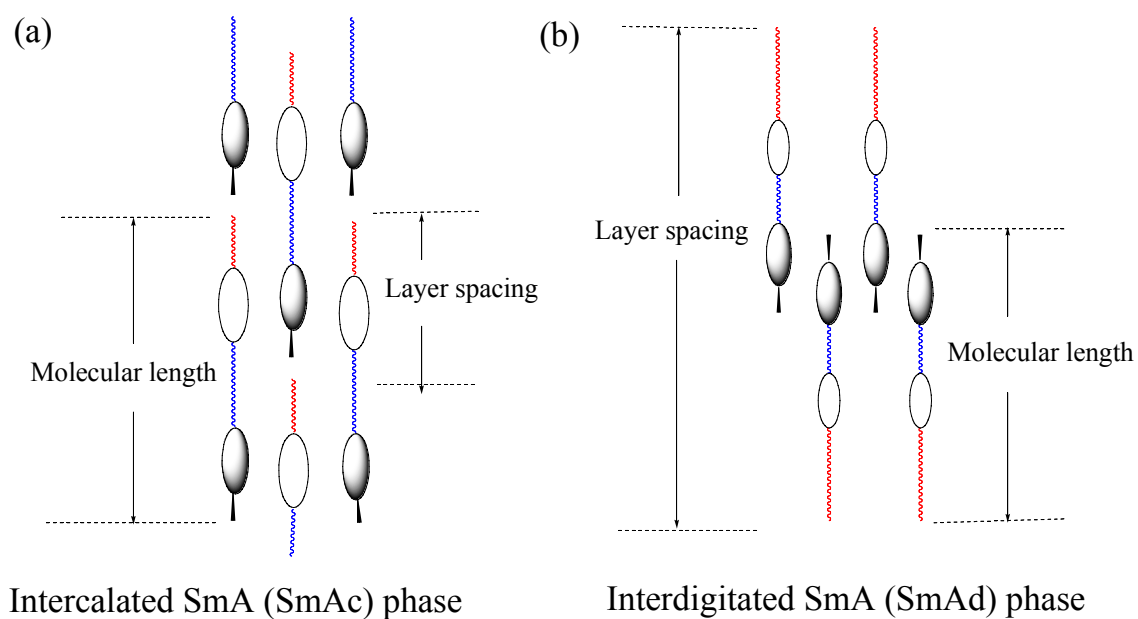
ESI. 3 Possible smectic structure for the interdigitated SmCanti phase induced in some mixtures between **4-(12,7)** and **4-(12,9)**.

ESI. 4 X-ray diffraction patterns of compound **11** in the SmAinc phase.

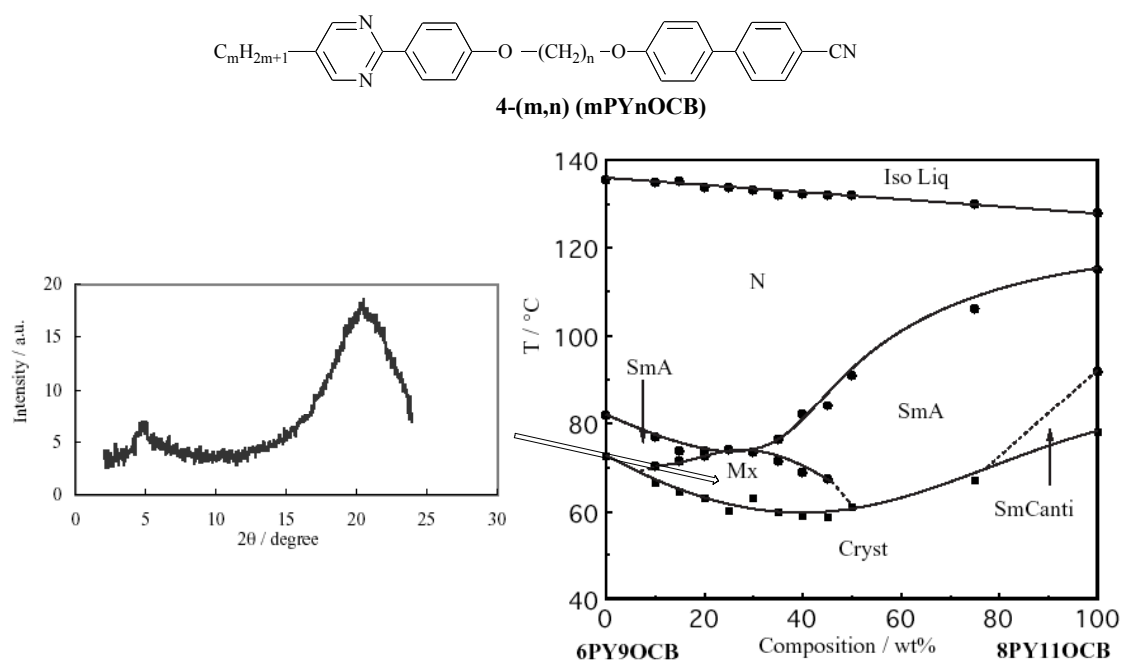
ESI. 5 A possible molecular arrangement for the interdigitated layer structure in the incommensurate SmA phase of compound **11**.

ESI. 6 MM2 models of (a) compound **19-6** with even-numbered spacers and (b) compound **19-7** with odd-numbered spacers.

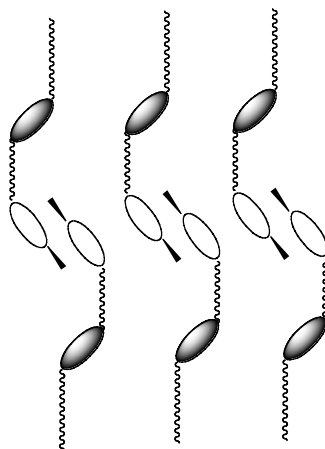
ESI. 7 Crystal structure of the T-shaped derivative.¹⁰²



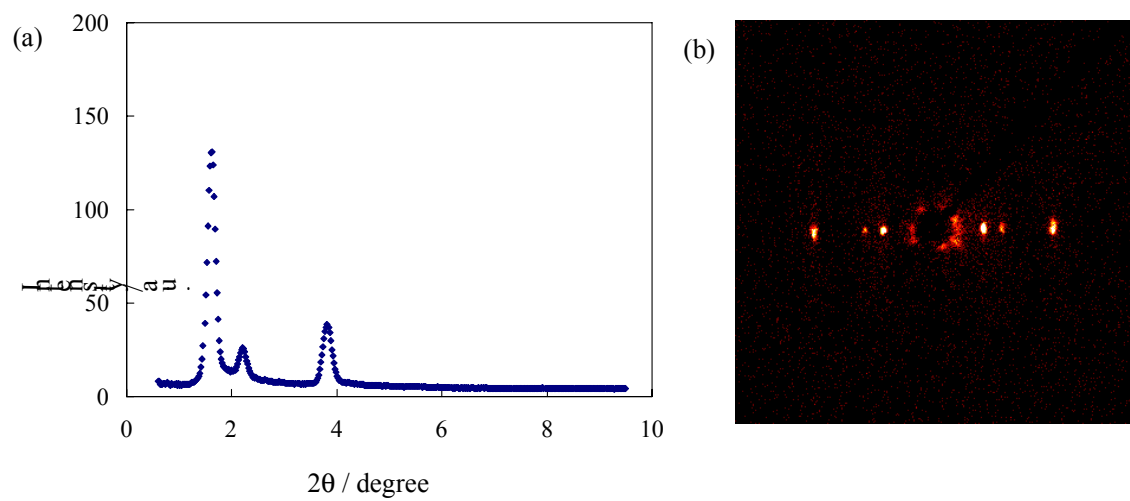
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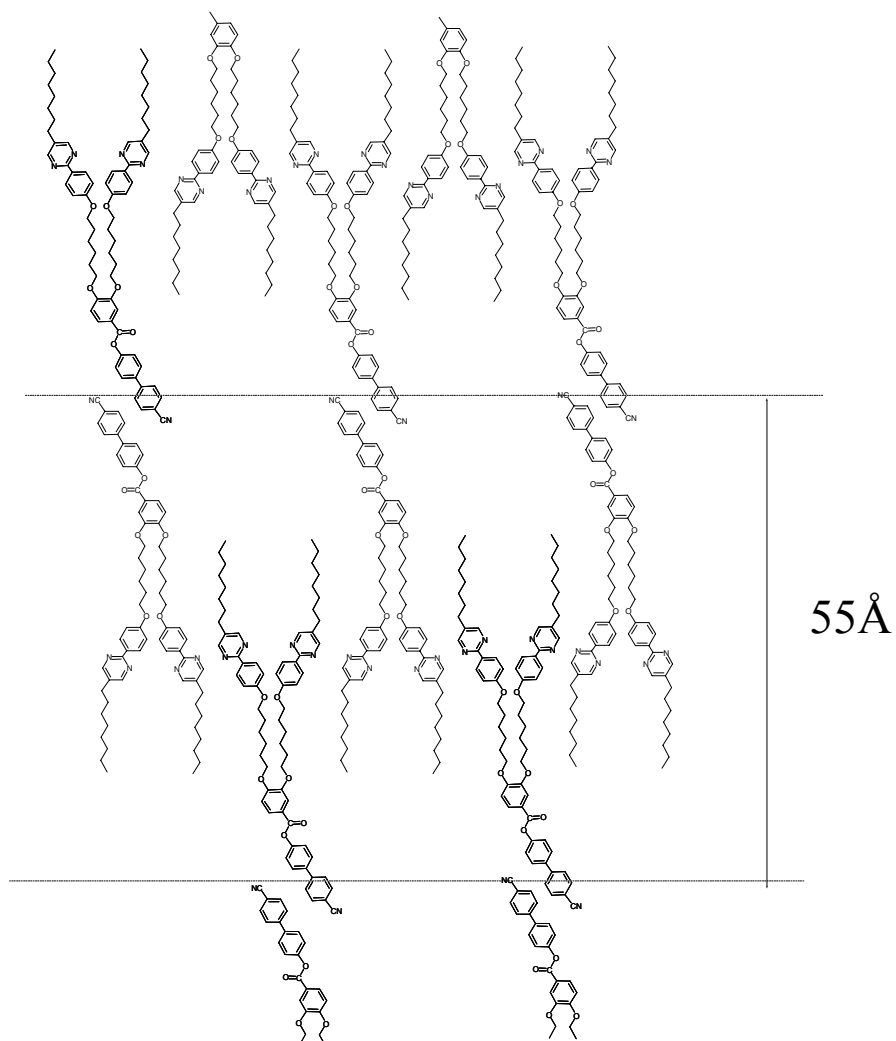
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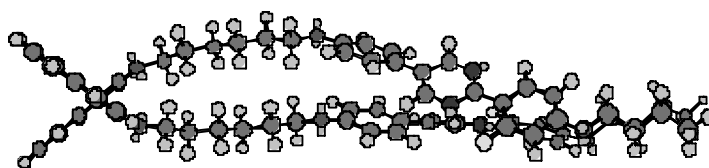


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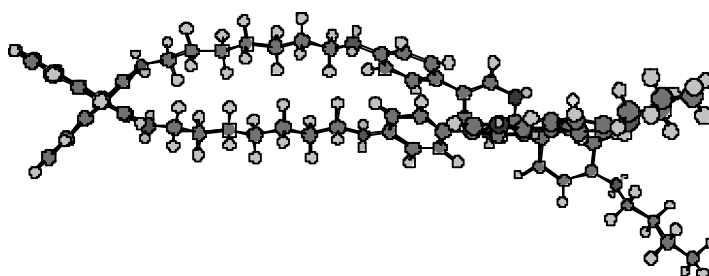


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(a)



(b)



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