

Supporting Information

Ferroelectric Nematic Droplets in their Isotropic Melt

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The scheme used for preparation of the RT11064 used in this study is provided in Figure S1. Commercial 3,4-dimethoxybenzoic acid is converted to its acid chloride using oxalyl chloride in dichloromethane (a). This acid chloride is reacted with 2-fluoro-4-hydroxybenzaldehyde with pyridine as base in dichloromethane solvent (b). This two-ring aldehyde is oxidized to the analogous carboxylic acid using Oxone in DMF (c). This two-ring carboxylic acid is converted to its respective acid chloride using oxalyl chloride in dichloromethane (d). Finally, this acid chloride is esterified with 2-fluoro-4-hydroxynitrobenzene with pyridine as base and dichloromethane as solvent to give the desired three-ring product RT11064 (e). The first three steps in this scheme (a-c) have already been described in detail and are not reproduced here.¹² The two-ring acid chloride obtained in the fourth step (e) is a new compound, but the method of preparation employed is routine. The final fifth step between this acid chloride and 2-fluoro-4-hydroxynitrobenzene with pyridine as base and dichloromethane as solvent gives RT11064. The yield in this final step of this specific prep was low but later preps of this same substance using a more careful chromatography provided a better yield. The RT11064 prepared by this route has spectroscopic properties very similar to the reported material prepared by an alternative route³. The final step of the synthesis was also attempted under Steglich and Mitsunobu conditions with low or no yield respectively. Details about the idiosyncrasies of this ester forming reaction will be described in more detail elsewhere.

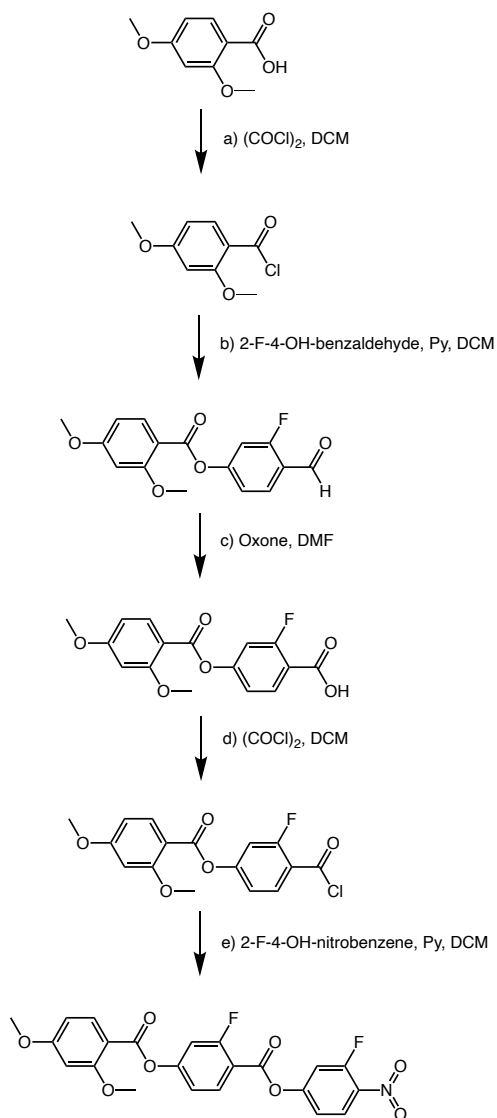
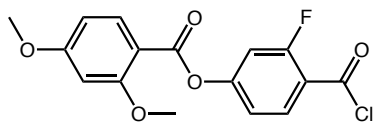


Figure S1. Five Step Synthesis Scheme Utilized for the Preparation of RT11064 Benzoic acid, 2,4-dimethoxy-, 3-fluoro-4-[(3-fluoro-4-nitrophenoxy)carbonyl]phenyl ester

Step (e)

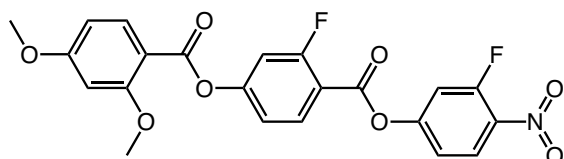
3-Fluoro-4-(chlorocarbonyl)phenyl 2,4-dimethoxybenzoate



In a 250 ml round bottom flask with fitted with stirbar and bubbler was placed the 3-fluoro-4-carboxyphenyl 2,4-dimethoxybenzoate (1.60 gm, 5.0 mmol) and dry dichloromethane (40 ml). The slurry was stirred in a cold water dimethylformamide. Gas evolution ensued and the mixture cleared and was allowed to warm and was stirred overnight. The next day the dichloromethane and excess acid chloride were removed by rotary evaporation. Dry dichloromethane (20 ml) was added, and the mixture was concentrated again. The acid chloride (1.75 gm, 100%) was used directly in the subsequent esterification.

Step (f) RT11064

Benzoic acid, 2,4-dimethoxy-, 3-fluoro-4-[(3-fluoro-4-nitrophenoxy)carbonyl]phenyl ester



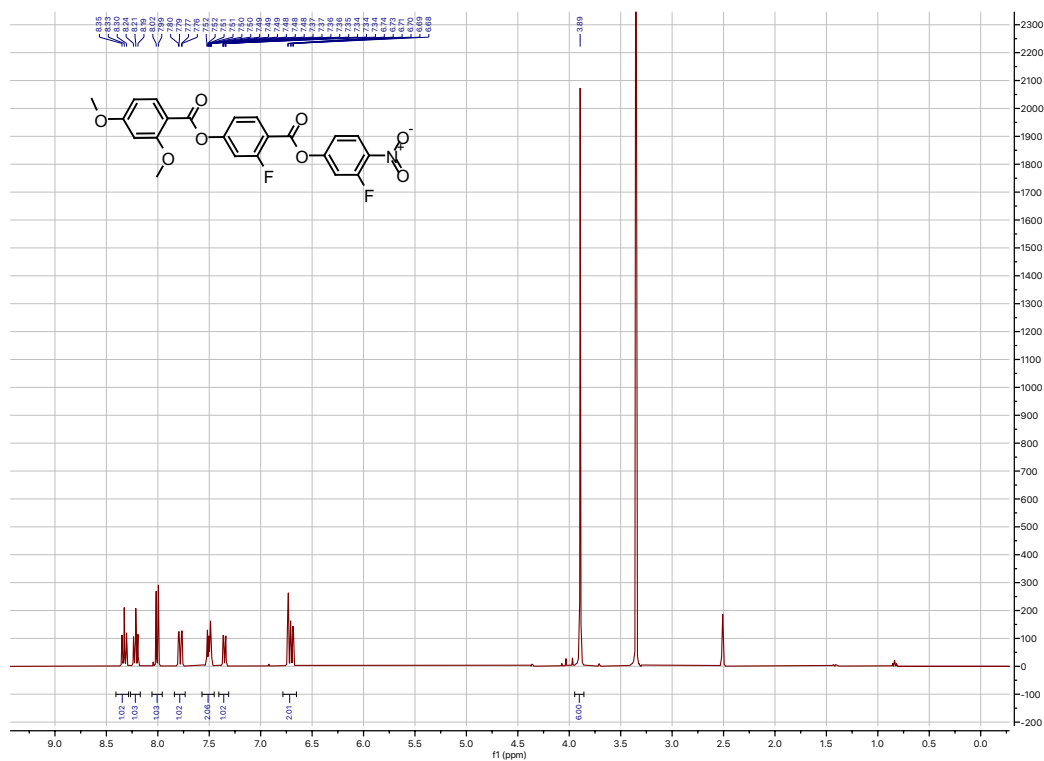
In a 500 ml recovery flask with stir bar was placed 3-fluoro-4-nitrophenol (1.17 gm, 7.50 mmol), and dry dichloromethane (40 ml). The mixture was stirred under nitrogen in an ice water bath and dry pyridine (2.40 gm, 30.0 mmol) was added all at once. The acid chloride (5.00 mmol) dissolved in dry dichloromethane (15 ml) was added dropwise and the resulting mixture was allowed to warm to room temperature and was stirred for 24 hr. The mixture was concentrated to about half its volume and applied to the top of a silica gel column (5 cm x 28 cm) made up with dichloromethane and eluted with dichloromethane. Analysis by TLC indicated that some intermediate fractions contained only pure product and they were combined, concentrated and the

solid obtained was recrystallized from 1-propanol (0.591 gm, 26%). Additional product was present in the other chromatography fractions but was not further pursued.

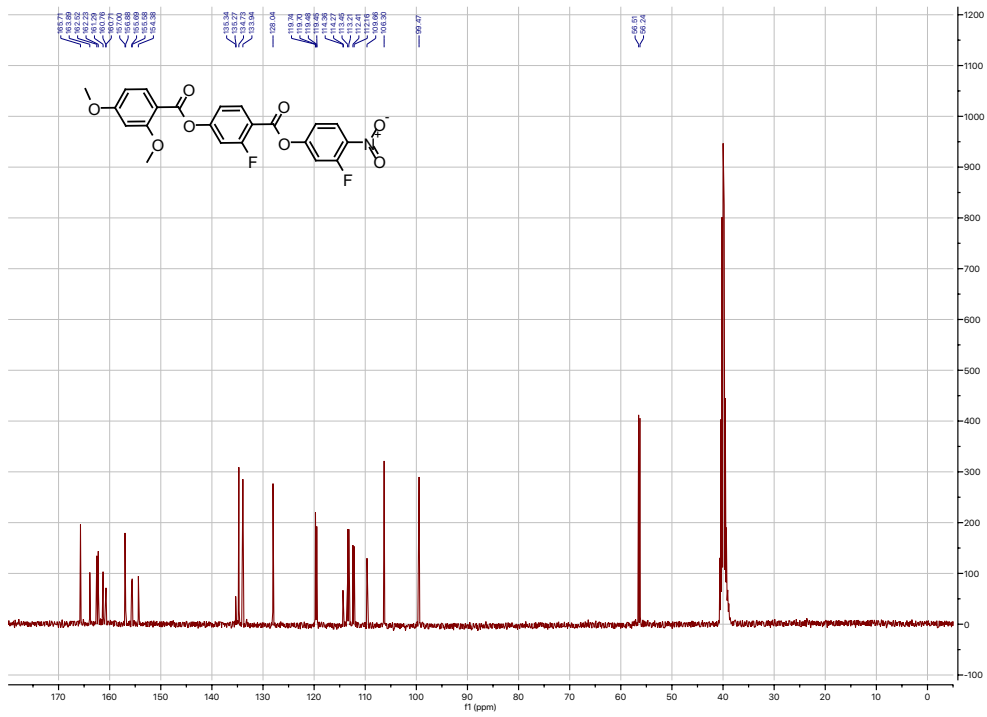
^1H NMR (400 MHz, DMSO) δ 8.33 (t, $J = 8.8$ Hz, 1H), 8.21 (t, $J = 8.5$ Hz, 1H), 8.01 (d, $J = 8.7$ Hz, 1H), 7.78 (dd, $J = 11.9, 2.4$ Hz, 1H), 7.57 – 7.45 (m, 2H), 7.35 (ddd, $J = 8.7, 2.3, 0.7$ Hz, 1H), 6.78 – 6.65 (m, 2H), 3.89 (s, 6H).

^{13}C NMR (100 MHz, DMSO) δ 165.71, 163.89, 162.52, 162.23, 161.29, 160.76, 160.71, 157.00, 156.88, 155.69, 155.58, 154.38, 135.34, 135.27, 134.73, 133.94, 128.04, 119.74, 119.70, 119.48, 119.45, 114.36, 114.27, 113.45, 113.21, 112.41, 112.16, 109.66, 106.30, 99.47, 56.51, 56.24.

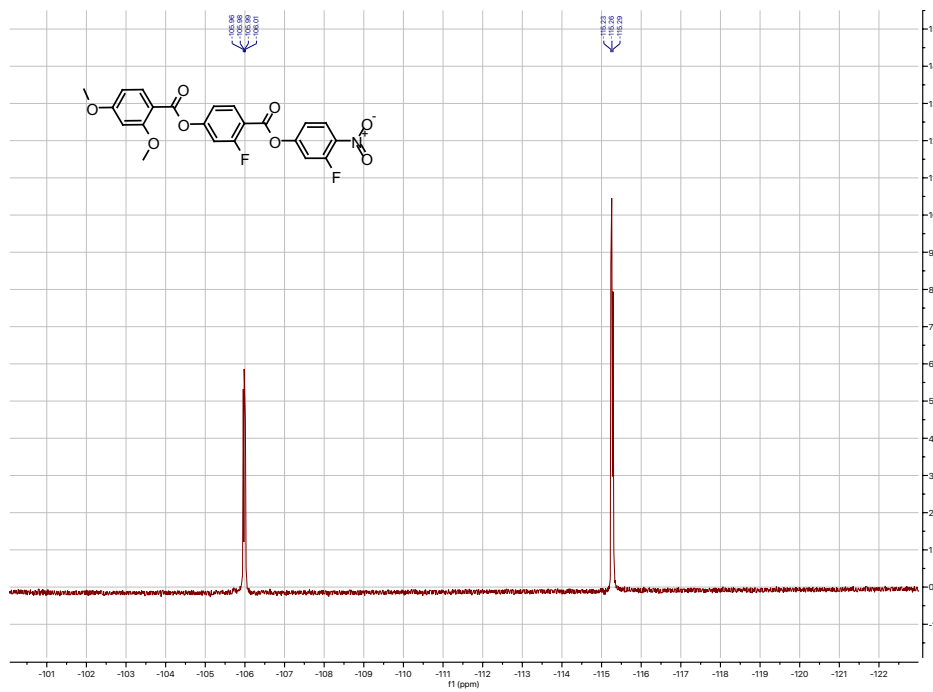
^{19}F NMR (376 MHz, DMSO) δ -105.98 (m, 1F), -115.26 (m, 1F).



^1H NMR of RT11064



¹³C NMR of RT11064



¹⁹F NMR of RT11064

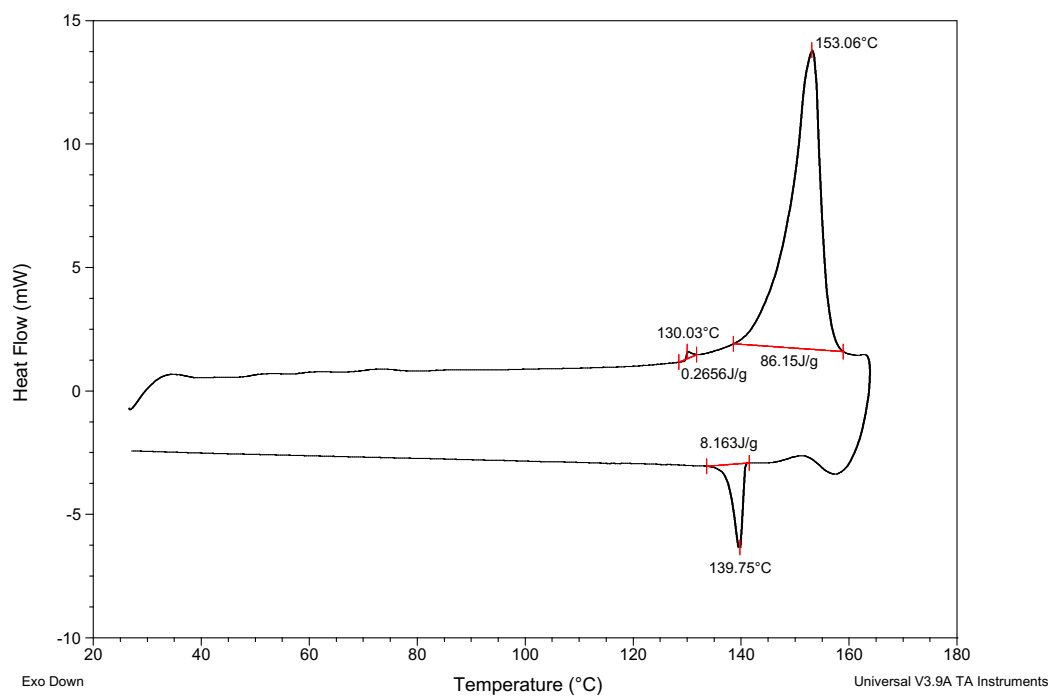


Figure S2: DSC of RT11064. First heating and cooling cycle (heating and cooling rate = 5 °C/min. Sample size = 5.567 mg).

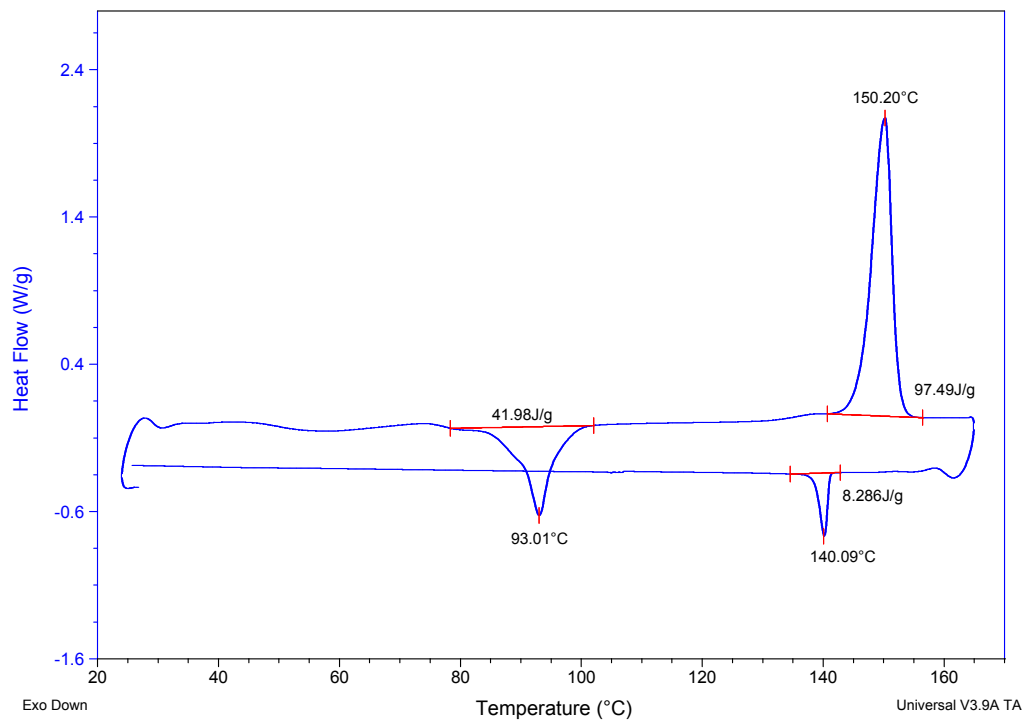


Figure S3: DSC of RT11064. Second heating and cooling cycle (heating and cooling rate = 5 °C/min. Sample size = 5.567 mg).

Video 1: Drift of the droplets along 0.5V DC electric voltage applied left (first part) and right (second part).

Video 2: Shape change of the droplets under 100 mHz, 1.5 V/mm electric field.

SI References

- (1) Saha, R.; Feng, C.; Hossain, S.; Gleeson, J. T.; Sprunt, S.; Twieg, R. J.; Jákli, A. Multiple Ferroelectric Nematic Phases of a Highly Polar Liquid Crystal Compound. *ArXiv* **2021**, 2104, 06520.
- (2) Saha, R.; Nepal, P.; Feng, C.; Hossain, M. S.; Fukuto, M.; Li, R.; Gleeson, J. T.; Sprunt, S.; Twieg, R. J.; Jákli, A. Multiple Ferroelectric Nematic Phases of a Highly Polar Liquid Crystal Compound. *Liq Cryst* **2022**. <https://doi.org/10.1080/02678292.2022.2069297>.
- (3) Brown, S.; Cruickshank, E.; Storey, J. M. D.; Imrie, C. T.; Pocięcha, D.; Majewska, M.; Makal, A.; Gorecka, E. Multiple Polar and Non-polar Nematic Phases. *ArXiv* **2021**, 2109.02299. <https://doi.org/10.1002/cphc.202100644>.