

Supplementary Information

Promotion Effects of Optical Antipodes on the Formation of Helical Fibrils: Chiral Perfluorinated Gelators

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1. Syntheses and NMR spectra of gelators:

^1H NMR spectra (400 MHz) were recorded on a JEOL ECX 400 spectrometer in acetonitrile- d_3 . ^{19}F NMR (470 MHz) spectra were recorded on a JEOL ECX 500 spectrometer in acetonitrile- d_3 . Chemical shifts (δ) were reported in ppm relative to tetramethylsilane or trichlorofluoromethane for ^1H and ^{19}F , respectively. Data are reported in the following order: multiplicity [(s) singlet; (d) doublet; (t) triplet; (q) quartet; (quint) quintet; (m) multiplet; (br) broad peak], coupling constants (Hz), number of protons.

Electrospray ionization (ESI) mass spectrometry was performed on a Thermo Scientific Exactive spectrometer in both negative and positive ionization modes.

SS-CF₈ was synthesized from pentadecafluorooctanoyl chloride (0.9 mL (3.6 mmol), Aldrich) and trans-(1*S*, 2*S*)-(+)-1,2-diaminocyclohexane (0.19 g, (1.7 mmol), Wako, Japan) in 73% yield.

$[\alpha]_{\text{D}}$ ($c = 0.1835$ g /100 ml in methanol) -18.37

^1H NMR (CD_3CN , 400 MHz): $\delta = 1.32$ (m, CH_2CHNH , 2H), 1.43 (m, CH_2CHNH , 2H), 1.76 (m, $\text{CH}_2\text{C}_2\text{H}_4\text{CH}_2$, 4H), 3.85 (m, CH_2CHNH , 2H), 7.66 (br, NHCO , 2H)

^{19}F NMR (CD_3CN , 470 MHz): $\delta = -126.6$, -123.2, -123.0, -122.5, -122.1 (s, 2F), -120.4 (d, $J = 272.1$ Hz), -119.6 (d, $J = 272.1$ Hz), -81.6 ppm (s, 3F)

HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{11}\text{O}_2\text{N}_2\text{F}_{30}$: 905.03360; found: 905.03406

IR (KBr, cm^{-1}): 3319, 1689, 1243, 1200, 1154

RR-CF₈ was synthesized from pentadecafluorooctanoyl chloride (0.9 mL (3.6 mmol), Aldrich) and trans-(1*R*, 2*R*)-(-)-1,2-diaminocyclohexane (0.19 g, (1.7 mmol), Tokyo Kasei, Ltd., Japan) in 94% yield.

$[\alpha]_{\text{D}}$ ($c = 0.1805$ g /100ml in methanol) +14.79

^1H NMR (CD_3CN , 400 MHz): $\delta = 1.34$ (m, CH_2CHNH , 2H), 1.46 (m, CH_2CHNH , 2H), 1.76 (m, $\text{CH}_2\text{C}_2\text{H}_4\text{CH}_2$, 4H), 3.87 (m, CH_2CHNH , 2H), 7.63 (br, NHCO , 2H)

^{19}F NMR (CD_3CN , 470 MHz): $\delta = -126.6$, -123.2, -123.0, -122.5, -122.1 (s, 2F), -120.4 (d, $J = 272.1$ Hz), -119.6 (d, $J = 272.1$ Hz), -81.6 ppm (s, 3F)

HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{11}\text{O}_2\text{N}_2\text{F}_{30}$: 905.03360; found: 905.03418

IR (KBr, cm^{-1}): 3312, 1689, 1242, 1200, 1153

Racemic-CF₈ was synthesized from pentadecafluorooctanoyl chloride (0.9 mL (3.6 mmol), Aldrich)

and trans-(±)-trans-1,2-diaminocyclohexane (0.19 g, (1.7 mmol), Aldrich) in 59% yield.

$[\alpha]_D$ (c = 0.075g/ 100 ml in methanol) 0.00

^1H NMR (CD_3CN , 400 MHz): δ = 1.35 (m, CH_2CHNH , 2H), 1.44 (m, CH_2CHNH , 2H), 1.77 (m, $\text{CH}_2\text{C}_2\text{H}_4\text{CH}_2$, 4H), 3.87 (m, CH_2CHNH , 2H), 7.62 (br, NHCO , 2H)

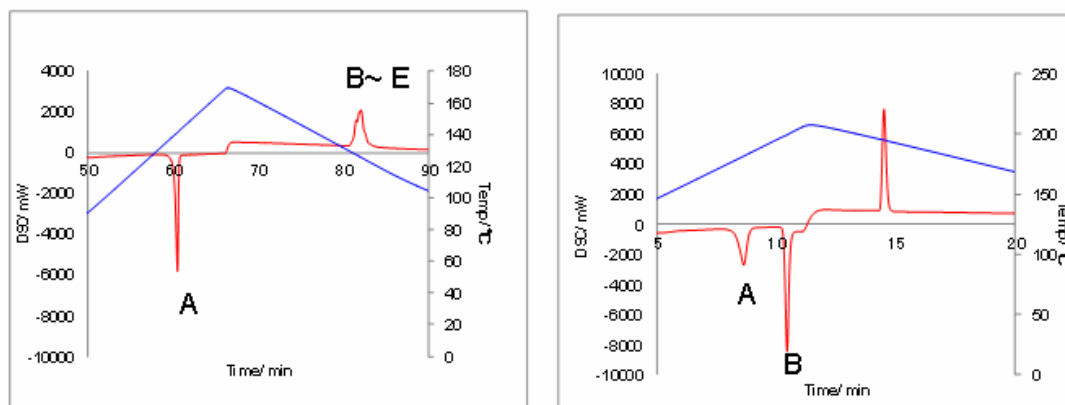
^{19}F NMR (CD_3CN , 470 MHz): δ = -126.6, -123.2, -123.1, -122.5, -122.1 (s, 2F), -120.4 (d, J = 272.1 Hz), -119.7 (d, J = 272.1 Hz), -81.6 ppm (s, 3F)

HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{11}\text{O}_2\text{N}_2\text{F}_3$: 905.03360; found: 905.03424

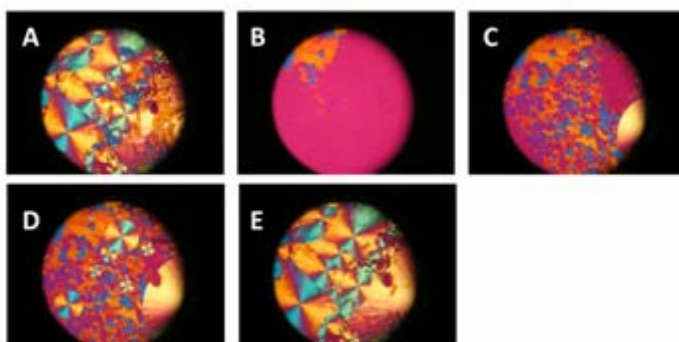
IR (KBr, cm^{-1}): 3300, 1697, 1240, 1206, 1150

2. DSC data of gelators:

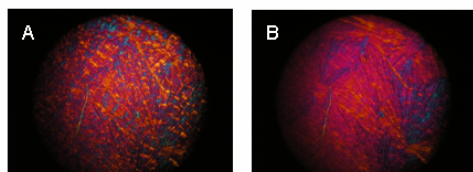
The DSC results (red) are presented as function of temperature (blue): *SS*-CF₈ (left) and racemic CF₈ (right).



Differential scanning calorimetry (DSC): DSC measurements were carried out with a DSC6200 (SEIKO, Japan). Heating and cooling runs were performed at a scan rate of 5 °Cmin⁻¹ and 3 °Cmin⁻¹ for enantiopure *SS*-CF₈, 10 °Cmin⁻¹ and 5 °Cmin⁻¹ for the racemic-CF₈, respectively. The corresponding optical microscope images are shown below.



SS-CF₈



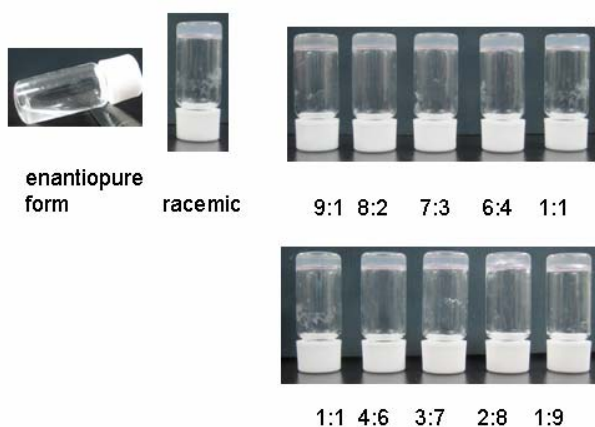
Racemic-CF₈

3. The critical concentrations of gelation for various solvents:

The critical concentration is given in terms of gL^{-1} for enantiopure $RR\text{-CF}_8$, $SS\text{-CF}_8$ and *racemic*- CF_8 as a gelator.

solvent	RR^*	SS^*	Racemic*
methanol	tv $s \rightarrow$ c	tv $s \rightarrow$ c	tg(8.5)
ethanol	tv $s \rightarrow$ c	tv $s \rightarrow$ c	tg(9.8)
2-propanol	tv $s \rightarrow$ c	tv $s \rightarrow$ c	cg(7.8)
1-butanol	tv s	tv s	tg(4.95)
2-butanol(racemic)	tv $s \rightarrow$ c	tv $s \rightarrow$ c	tg(2.8)
1-pentanol	tg(40.6)	tg(42)	tg(3.2)
2-pentanol	tg(43.4)	tg(41.8)	tg(5)
benzene	p	p	tg(11.3)
toluene	p	p	tv s
o-xylene	p	p	tv s
acetonitrile	c	c	tg(3.8)
cyclohexane	p	p	tv s
hexane	p	p	cg (11.2)

* The state of samples: c = crystal, p = solid precipitate, tg = turbid gel, cg = clear gel, tv s = turbid viscous solutions, tv $s \rightarrow$ c = from turbid viscous solutions to crystal



The photographic images of the samples at different RR/SS ratio dissolved in racemic 2-butanol. The sample at $e.e. = 1$ transformed gradually from turbid viscous solutions to crystal, while the samples at $e.e. = 0 \sim 0.8$ formed a gel.

4. The time-course of optical microscope images of the 2-butanol solutions containing the following gelators:

Enantiopure CFs (initial: turbid viscous solutions) (concentration 0.015M)



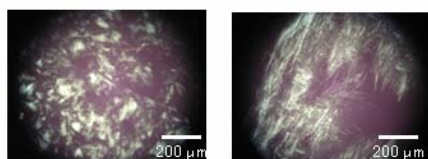
(a) 3 min

(b) 10 min

(c) 20 min

(d) 360 min

Racemic CFs (gel) (concentration 0.015M)



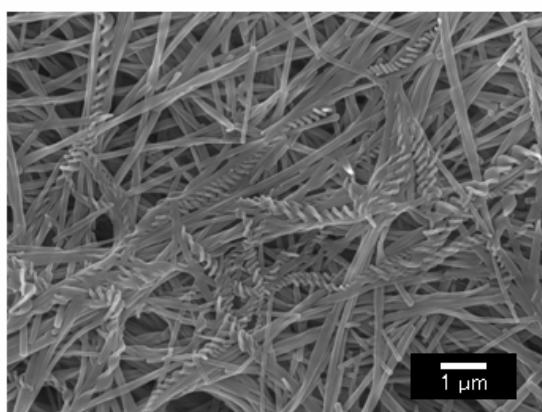
(a) 3 min

(b) 360 min

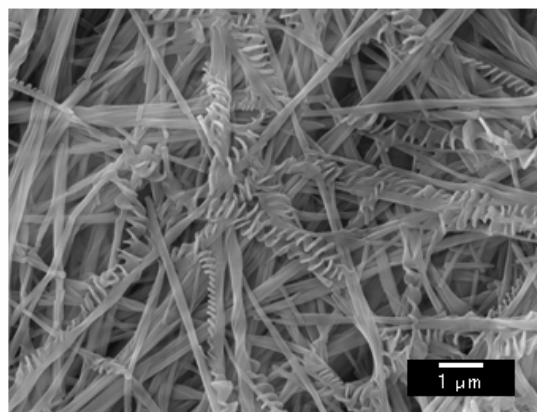
5. The SEM images of the freeze-dried racemic 2-butanols and 1-butanol samples containing chiral gelators at various ratios.

The ratio of *RR*-CF₈ to *SS*-CF₈ and the scale are indicated in each figure. The total concentration of a gelator was 0.015M.

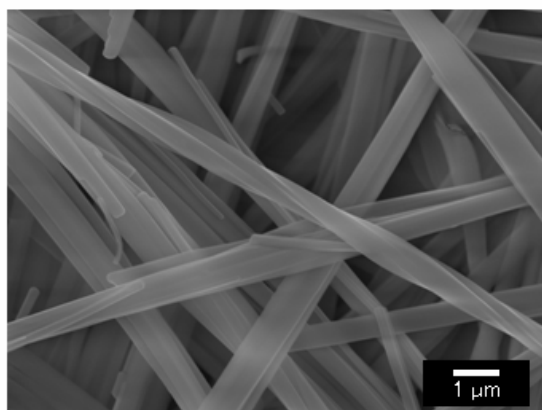
Racemic 2-butanol xerogels



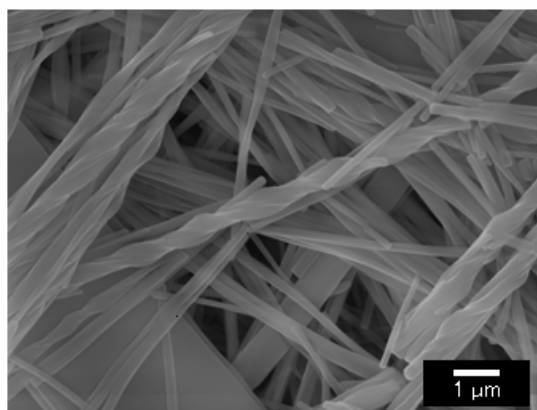
RR/SS 6:4



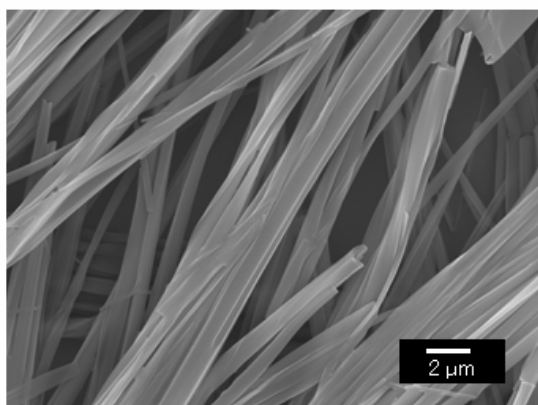
4:6



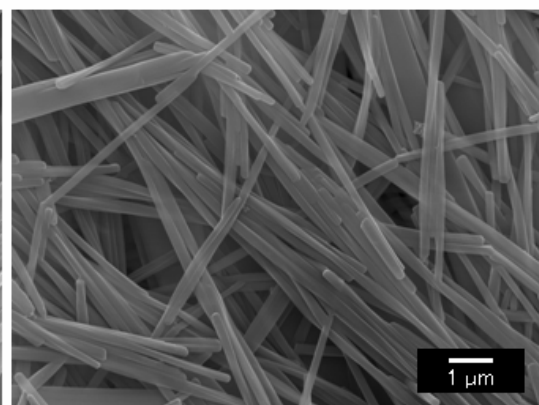
RR/SS 8:2



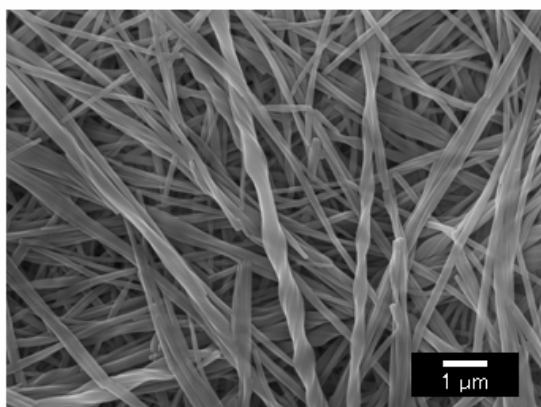
2:8



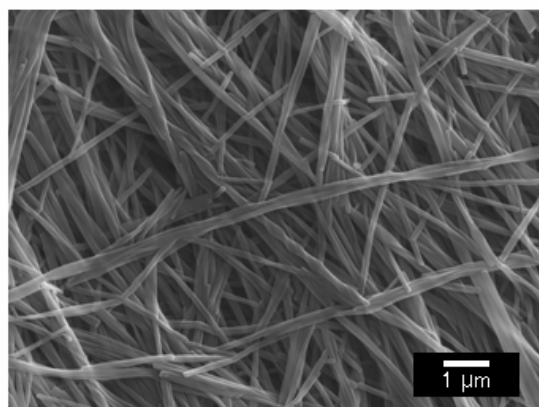
RR/SS 9:1



1:9

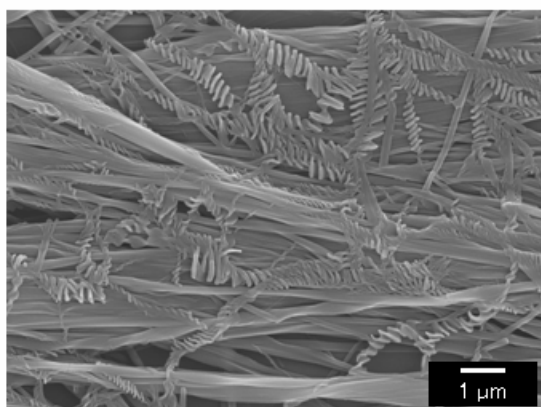


Racemic

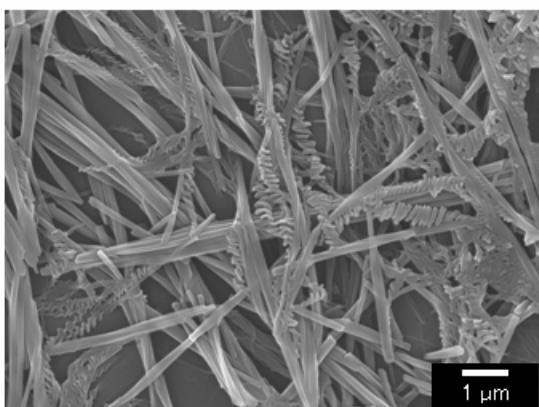


RR/SS 1:1

1-butanol xerogel

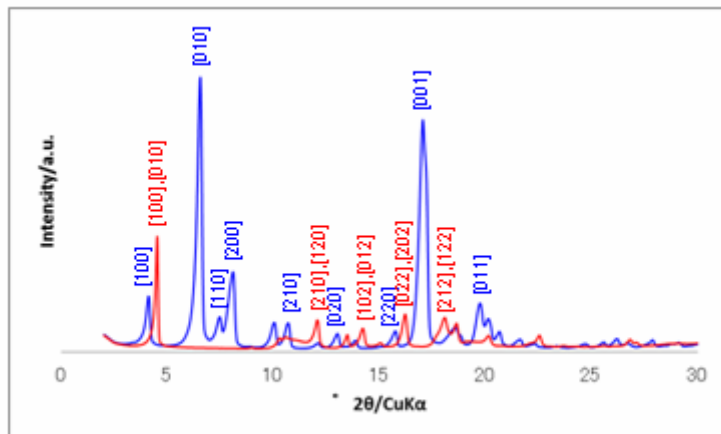


RR/SS 7:3



3:7

6. The XRD patterns of the solid crystal of enantiopure CF₈ (blue) and racemic CF₈ (red) at the wavelength of 0.154 nm from CuKα.

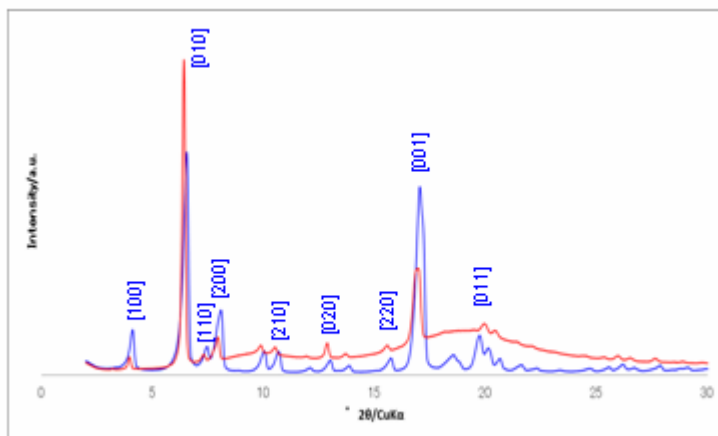


	crystal Enantiopure CF ₈	crystal Racemic CF ₈	xerogel racemic CF ₈
	monoclinic	hexagonal	hexagonal
a /nm	2.16	2.26	2.72
b /nm	1.36	2.26	2.72
c / nm	0.52	1.32	1.62
α /°	90.0	90.0	90.0
β /°	90.0	90.0	90.0
γ /°	95.0	120.0	120.0

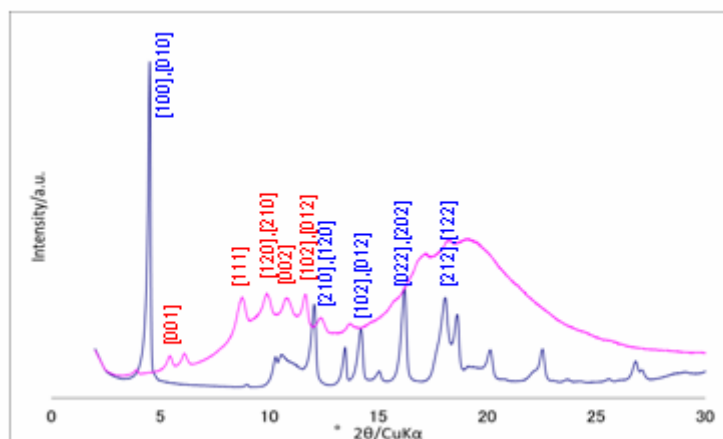
Conditions of PXRD measurements: The samples were subjected to X-ray diffraction measurements were performed with a PXRD (Ultima IV, Rigaku) under CuKα radiation ($\lambda = 0.15406$ nm) at the conditions of 40 kV, 40 mA, and 2θ 3°/min scanning. The temperature is kept at room temperature.

Here the analyses were made by use of the SFC and EDA program for the optimized unit cell size (Kogure, T. Journal of the crystallographic Society of Japan, (2003) 45, 391-395; http://www-gbs.eps.s.u-tokyo.ac.jp/kogure/EDANA/index_E.htm).

7. The XRD patterns of the solid crystals of enantiopure CF₈ (blue) and xerogel of enantiomeric CF₈ (red) at the wavelength of 0.154 nm from CuK α .



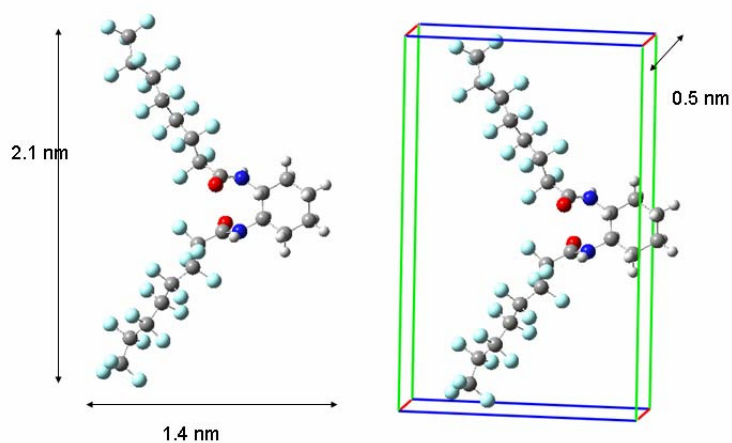
8. The XRD patterns of the solid crystals of racemic CF₈ (blue) and xerogel of racemic CF₈ (red) at the wavelength of 0.154 nm from CuK α .



9. Conditions of VCD experiment

The VCD spectra were measured using a spectrometer PRESTO-S-2007 (JASCO, Japan). Signals were accumulated for 5000 scans in about 1 hour at 4 cm^{-1} resolution, using a liquid nitrogen cooled MCT infrared detector equipped with ZnSe windows. After gels were warmed above the sol-gel transition temperature, about $50\text{ }\mu\text{L}$ of the samples were sandwiched between two CaF_2 plates with a $50\text{ }\mu\text{m}$ spacer.

10. The geometries of CF_8 molecules



11. An example of a hybrid associate proposed for a helical fibril

(Empty circle = major enantiomer; filled circle = minor enantiomer)

