SUPPORTING INFORMATION

Investigation of Solute-Fiber Affinity and Orientational Ordering of Norbornadiene Interacting with Two-polypeptide Chiral Liquid Crystalline Solvents by NAD NMR

Zeinab Serhan, Christie Aroulanda and Philippe Lesot*

RMN en Milieu Orienté, ICMMO, UMR CNRS 8182, Université de Paris Sud / Université Paris-Saclay, Bât. 410, F-91405 Orsay cedex, France.

Corresponding author: Philippe Lesot. E-mail: philippe.lesot@u-psud.fr. Phone: +33 (0)1 69 15 47 59 / Fax: +33 (0)1 69 15 81 05

Index of Electronic Supporting Information

I. FURTHER TABLES

I.1. General Tables

Table S1. Mass fraction (m/m%) of polypeptide and associated peptide unit fraction (x^{pu}%) used for Series I and II

Series[a]	m/m_T(PBLG) / %	m/m_T(PCBLL) / %	x^{up} (PBLG) / %[b]	x^{up} (PCBLL) / %[b]
I and II	0	100	0.000	100.000
I	25	75	28.509	71.491
I and II	50	50	54.470	45.530
I	75	25	78.209	21.791
I and II	100	0	100.000	0.000

[a]In Series I and II, the mass of solute is 100 and 10 mg, respectively. [b]The conversion from m/m_T(PBLG) to x^{up}(PBLG) is given in **Eq. 6**.

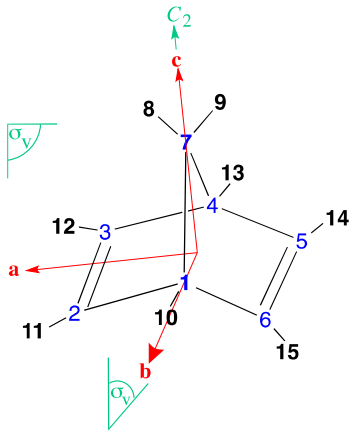

Table S2. Molecular atomic coordinates (Å) determined by Hyperchem 6.0, according to the atomic numbering chosen

	a	b	c
C1	+0.0000	+1.1319	+0.2792
C2	+1.2102	+0.6734	-0.5322
C3	+1.2102	-0.6734	-0.5322
C4	+0.0000	-1.1319	+0.2792
C5	-1.2102	-0.6734	-0.5322
C6	-1.2102	+0.6734	-0.5322
C7	+0.0000	+0.0000	+1.3634
H8	+0.8877	+0.0000	+2.0136
H9	-0.8877	+0.0000	+2.0136
H10	+0.0000	+2.1767	+0.6234
H11	+1.9038	+1.3600	-1.0084
H12	+1.9038	-1.3600	-1.0084
H13	+0.0000	-2.1767	+0.6234
H14	-1.9038	-1.3600	-1.0084
H15	-1.9038	+1.3600	-1.0084

I.2. Data relative to NBD (Series I – 100 mg)

Table S3. Experimental values (with sign) of RQC's of **NBD** and fit parameters (Series I)

^{2}H Sites[a] (δ decreasing)[b]	**$\Delta\nu_Q$ (in Hz) *versus* %m(PBLG)**[d]					**Fit parameters**	
	0%	**25%**	**50%**	**75%**	**100%**	**K**[e]	**R**[f]
C=C (11/14, 12/15)	+12 ± 2 (●)	+38 ± 2 (●)	+65 ± 2 (●)	+89 ± 2 (●)	+114 ± 2 (●)	0.87(9) ± 0.01	0.99993
C=C (12/15, 11/14)	+112 ± 2 (○)	+44 ± 2 (○)	-23 ± 2 (○)	-89 ± 2 (○)	-152 ± 2 (○)	0.87(7) ± 0.01	0.99994
C=C (aver)[c]	**+62 ± 2**	**+41 ± 2**	**+21 ± 2**	**0 ± 2**	**-19 ± 2**	**0.875 ± 0.004**	**0.99999**
Bridgehead (10/13)	-71 ± 2 (+)	-140 ± 3 (+)	-208 ± 2 (+)	-274 ± 3 (+)	-338 ± 3 (+)	0.87(9) ± 0.002	1.00000
Bridge (8/9)	+137 ± 2 (×)	+159 ± 3 (×)	+180 ± 2 (×)	+200 ± 3 (×)	+221 ± 3 (×)	0.86(9) ± 0.01	0.99994

[a]See **Figure 1a**. [b]The ^{2}H sites are ranked from deshielded to shielded ones (see **Figure 1b**). [c]Average of $\Delta\nu_Q$'s (associated to enantiotopic directions). This is the value that would be expected when recording NAD spectrum in the achiral mesophase «PBG/PCBL». [d]RQC's with negative sign are underlined. The labels in parenthesis correspond to those uses in plots of **Figure 2** and **Figures S2.** [e]K: Distribution coefficient (see **Eq. 3**). [f]R: Regression coefficient of fit.

Table S4. Experimental and back-calculated values of RQC's (in Hz) of **NBD** (Series I)

Sites[a]	**$\Delta\nu_Q$(exp) and $\Delta\nu_Q$(cal) *versus* %m(PBLG)**				
	0%	**25%**	**50%**	**75%**	**100%**
C=C (11/14)^{exp}	+12 ± 2	+38 ± 2	+65 ± 2	+89 ± 2	+114 ± 2
C=C (11/14)^{cal}	**18.2**	**42.7**	**67.8**	**90.2**	**113.8**
Symbol[c]	(●)	(●)	(●)	(●)	(●)
C=C (12/15)^{exp}	+112 ± 2	+44 ± 2	-23 ± 2	-89 ± 2	-152 ± 2
C=C (12/15)^{cal}	**+118.2**	**+48.7**	**-20.2**	**-87.7**	**-152.2**
Symbol	(○)	(○)	(○)	(○)	(○)
Bridgehead (10/13)^{exp}	-71 ± 2	-140 ± 3	-208 ± 2	-274 ± 3	-338 ± 3
Bridgehead(10/13)^{cal}	**-80.0**	**-146.7**	**-212.0**	**-275.8**	**-337.7**
Symbol	(+)	(+)	(+)	(+)	(+)
Bridge (8/9)^{exp}	+137 ± 2	+159 ± 3	+180 ± 2	+200 ± 3	+221 ± 3
Bridge (8/9)^{cal}	**+124.4**	**+149.6**	**+174.4**	**+197.5**	**+221.4**
Symbol	(×)	(×)	(×)	(×)	(×)
Rms[b]	**8.9**	**6.7**	**4.0**	**1.8**	**0.3**

[a]See **Figures 1a** and **SI-1a**. [b]Rms : root mean square obtained assuming QCC(sp^2) = 185 kHz, QCC(sp^3) = 170 kHz.
[c]The labels in parenthesis correspond to those used in **Figure 1** and **Figure SI-2.**

Table S5. Experimental values (with sign) of RQC's (in Hz) of **NBD** and fit parameters (Series II)

^{2}H Sites[a] (δ decreasing)[b]	**$\Delta\nu_Q$ *versus* %m(PBLG)**[d]			**Fit parameters**	
	0%	**50%**	**100%**	**K**[e]	**R**[f]
C=C (11/14, 12/15)	+14 ± 2 (●)	+71 ± 2 (●)	+126 ± 2 (●)	0.86(6) ± 0.01	1
C=C (12/15, 11/14)	+134 ± 2 (○)	-19 ± 2 (○)	-166 ± 2 (○)	0.87(0) ± 0.01	1
C=C (aver)[c]	**+74 ± 2**	**+26 ± 2**	**-20 ± 2**	**0.87(2) ± 0.01**	**1**
Bridgehead (10/13)	-43 ± 2 (+)	-207 ± 2 (+)	-365 ± 3 (+)	0.86(8) ± 0.01	1
Bridge (8/9)	+130 ± 2 (×)	+186 ± 2 (×)	+240 ± 3 (×)	0.86(7) ± 0.01	1

[a]See **Figure 1a**. [b]The ^{2}H sites are ranked from deshielded to shielded ones (see **Figure 5**). [c]Average of $\Delta\nu_Q$'s (relative to enantiotopic directions). This is the value that would be expected when recording NAD spectrum in the mesophase achiral «PBG/PCBL». [d]RQC's with negative sign are underlined. The labels in parenthesis correspond to those uses in plots of **Figures SI-4.** [e]K: Distribution coefficient (see **Eq. 3**). [f]R: Regression coefficient of fit. As only three experimental points are available, R = 1.

Table S6. Experimental and back-calculated values of RQC's (in Hz) of **NBD** in Hz and associated rms (Series II)

Sites[a]	**$\Delta\nu_Q$(exp) and $\Delta\nu_Q$(cal) *versus* %m(PBLG)**		
	0%	**50%**	**100%**
C=C (11/14)^{exp}	+14 ± 2	+71 ± 2	+126 ± 2
C=C (11/14)^{cal}	**+20.5**	**+74.2**	**+126.0**
Symbol	(●)[c]	(●)	(●)
C=C (12/15)^{exp}	+134 ± 2	-19 ± 2	-166 ± 2
C=C (12/15) ^{cal}	**+140.5**	**-15.8**	**-166.0**
Symbol	(○)	(○)	(○)
Bridgehead (10/13)^{exp}	-43 ± 2	-207 ± 2	-365 ± 3
Bridgehead (10/13)^{cal}	**-52.4**	**-211.6**	**-365.0**
Symbol	(+)	(+)	(+)
Bridge (8/9)^{exp}	+130 ± 2	+186 ± 2	+240 ± 3
Bridge (8/9)^{cal}	**+116.9**	**+179.5**	**+240.0**
Symbol	(×)	(×)	(×)
rms[b]	**9.3**	**4.6**	**0.01**

[a]See **Figures 1a** and **SI-1a**. [b]Rms : root mean square obtained assuming QCC(sp^2) = 185 kHz, QCC(sp^3) = 170 kHz.
[c]The labels in parenthesis correspond to those used in **Figure 5** and graphs of **Figures S4.**

II. FURTHER FIGURES

II.1. Figures relative to Series I (100 mg)

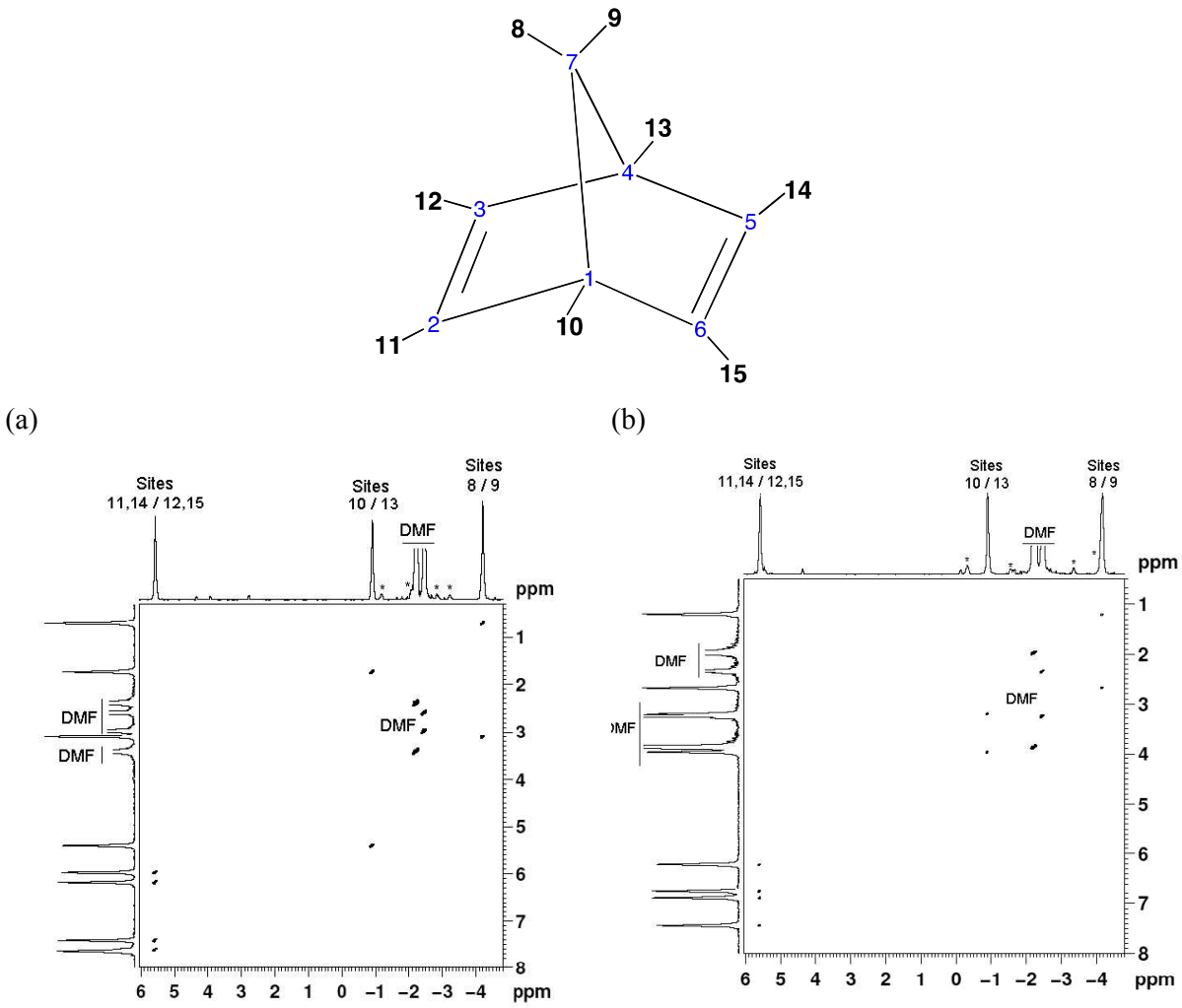

Figure S1. Tilted 92 MHz NAD 2D *Q*-COSY Fz map of **NBD** (Series I) in PBLG/DMF (a) and PCBLL/DMF mesophases (b) at 305 K. Peaks marked by an asterisk on F_2 projection are associated to residual NAD diagonal peaks of DMF. Scale of the horizontal axis (F_2) has no spectral meaning. Doublets of DMF were used to calibrate the 2D spectrum. As expected, the diastereotopic methyl groups of DMF leads to two quadrupolar doublets with slightly shifted chemical shifts.

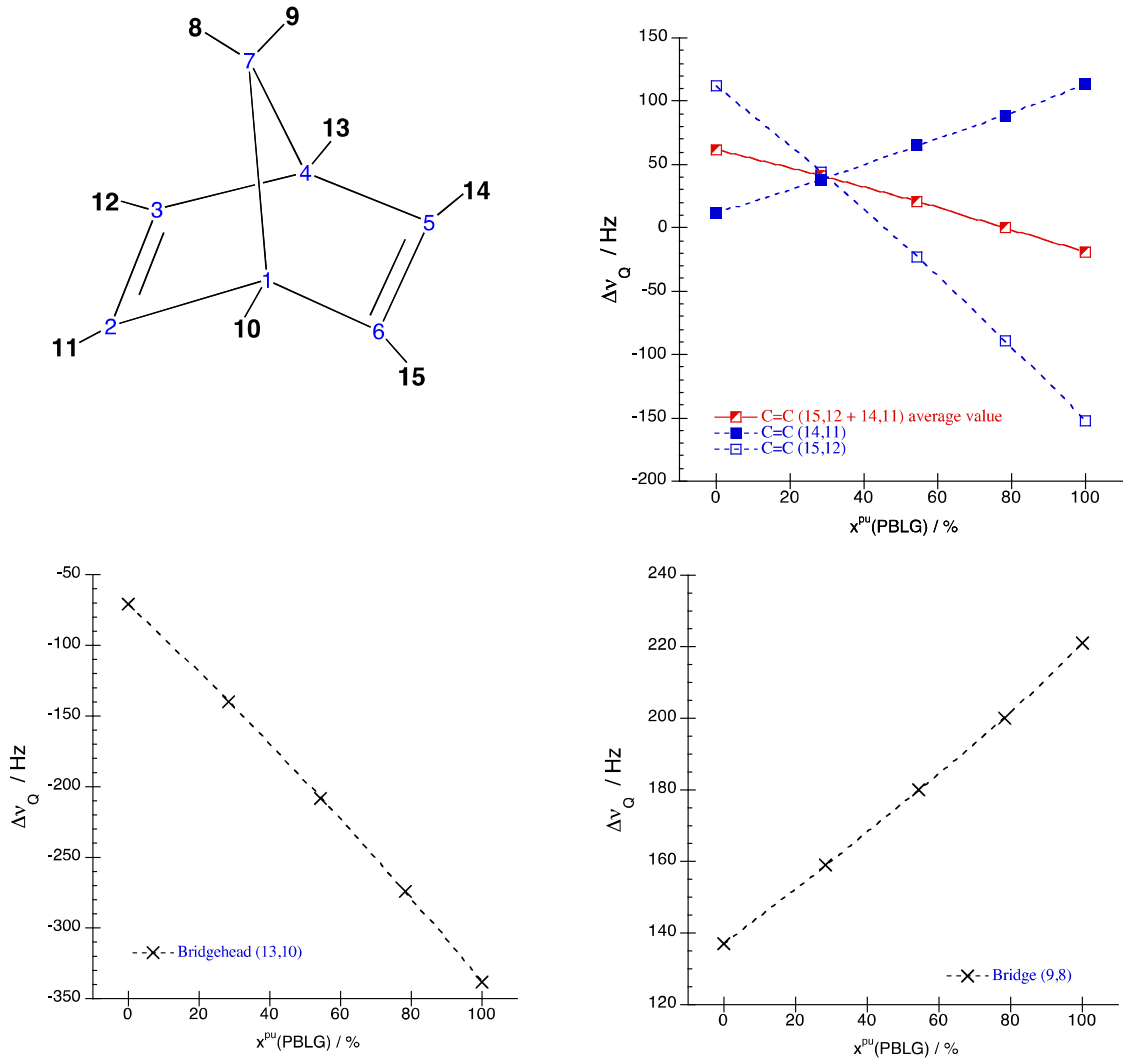

Figure S2. Variation of $\Delta\nu_Q$ *versus* x^{pu}(PBLG) (%) of all deuterium sites of **NBD** (Series I). Continuous lines correspond to the expected variation of RQC's for enantiotopic directions that would be obtained in the achiral system (PBG/PCBL). Open and black symbols using here correspond to the labels displayed in **Figure 1b**. Continuous lines show the expected variation of RQC's for enantiotopic directions that would be obtained in the achiral oriented system «PBG/PCBL».

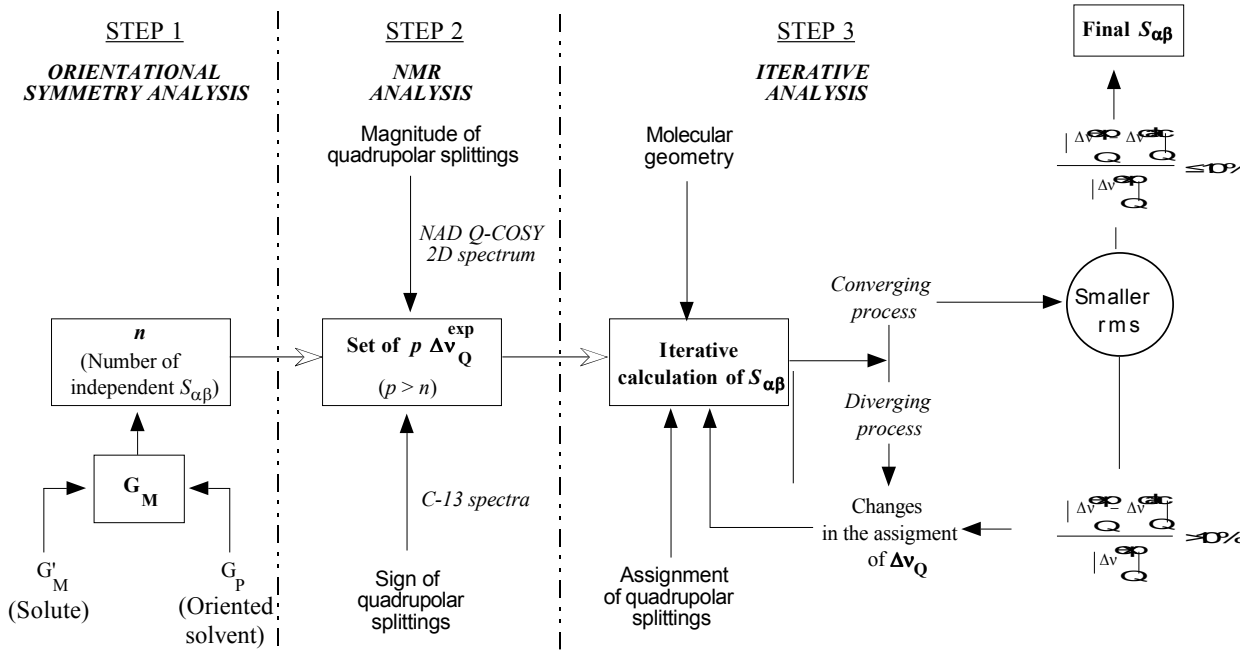

Figure S3. Flow chart showing the three-step analytical procedure adopted for the analysis of **NBD** dissolved in polypeptide mesophases through NAD 2D NMR. Signs of RQC are determined by comparison of proton coupled ^{13}C spectra recorded in isotropic and anisotropic solvents.

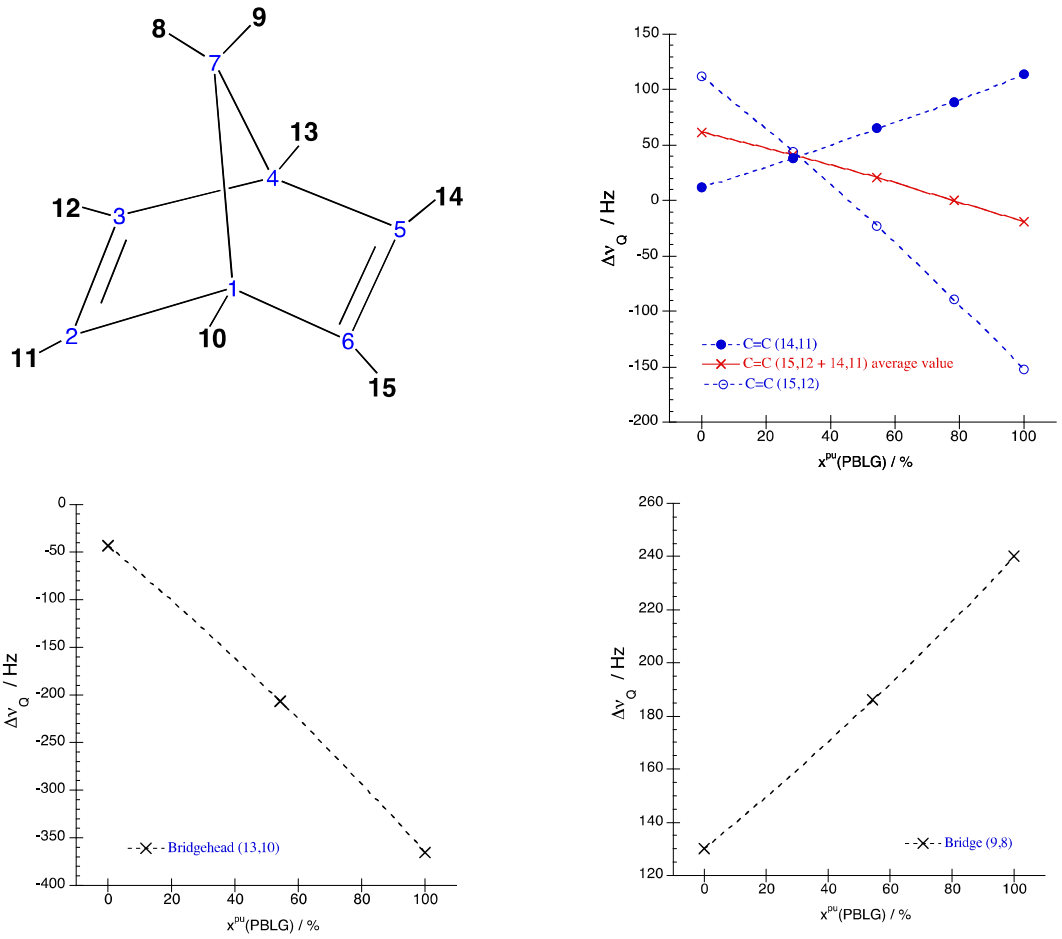

Figure S4. Variation of $\Delta\nu_Q$ *versus* x^{pu}(PBLG) (%) of all deuterium sites of **NBD** (Series II). Continuous lines correspond to the expected variation of $\Delta\nu_Q$ for enantiotopic directions that would be obtained in the achiral system (PBG/PCBL). Open and black circles used on graphs correspond to the labels displayed in **Figure 5**.