

Supporting Information

Designing Amphotropic Smectic Liquid Crystals Based on Phosphonium Salts for Partial Ordering of Solutes as Monitored by NMR Spectroscopy

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Table S1. Transition temperatures of various systems with **1PnA** phosphonium salts obtained by optical microscopy (K = crystal, LC = liquid crystalline, I = isotropic).

sample	molar ratio (solute:salt)	solute, wt%	transition temperatures (°C)			
			K ₁ → K ₂	K ₂ → I	LC → K	LC → I
[H(CH ₂) ₁₀] ₃ P ⁺ CD ₃ NO ₃ ⁻	neat				51.2 – 53.1	81.7 – 83.5
[H(CH ₂) ₁₄] ₃ P ⁺ CD ₃ NO ₃ ⁻	neat				40.1 – 42.6	98.1 – 99.6
[H(CH ₂) ₁₄] ₃ P ⁺ CD ₃ I ⁻	neat				63.4 – 65.7	112.3 – 113.5
[H(CH ₂) ₁₈] ₃ P ⁺ CD ₃ NO ₃ ⁻	neat				63.5 – 65.9	103.6 – 104.8
1P10NO ₃ •0.25CH ₃ OH	0.25 : 1	1.5			-24.3 – -33.9	45.7 – 50.4
1P10NO ₃ •0.6CH ₃ OH	0.6 : 1	3.5			-32.5 – -44.9	30.9 – 36.2
1P10NO ₃ •CH ₃ OH	1 : 1	5.7			-37.1 – -47.4	23.1 – 28.7
1P14NO ₃ •CH ₃ OH	1 : 1	4.4			25.1 – 27.2	54.8 – 57.3
1P18NO ₃ •CH ₃ OH	1 : 1	3.6			54.9 – 56.6	98.0 – 99.1
1P14NO ₃ •CH ₃ CN	1 : 1	5.5			27.8 – 30.1	49.1 – 53.6
1P18NO ₃ •CH ₃ CN	1 : 1	4.5			65.3 – 67.2	103.0 – 104.7
1P10NO ₃ •DMSO	1 : 1	12.8		-25.4 – -12.2		
1P10 NO ₃ •1-butanol	1 : 1	12.2			4.2 – -1.9	12.5 – 15.1
1P10 NO ₃ •1-hexanol	1 : 1	16.1			12.7 – 7.7	16.3 – 18.0
1P10NO ₃ •1-decanol	1 : 1	22.9			14.8 – 8.2	17.7 – 19.3
1P14NO ₃ •1-butanol	1 : 1	9.6			8.5 – 11.3	39.6 – 42.1
1P14NO ₃ •1-hexanol	1 : 1	12.7			29.1 – 31.2	41.5 – 42.7
1P18NO ₃ •1-butanol	1 : 1	7.9			62.1 – 64.3	98.5 – 100.9
1P18NO ₃ •1-hexanol	1 : 1	10.5		54.3 – 56.5		
1P18NO ₃ •DMSO	1 : 1	7.7			54.5 – 57.1	65.7 – 70.5
1P14Br•CH ₃ OH	1 : 1	4.2			49.7 – 54.9	76.6 – 82.5
1P18Br•CH ₃ OH	1 : 1	3.5		81.5 – 85.4		

1P14I• CD₃OD	1 : 1	4.0			27.5 – 30.4	67.7 – 71.8
1P14Cl• CH₃OH	1 : 1	4.5			59.6 – 64.9	75.7 – 81.5
1P18Cl• CH₃OH	1 : 1	3.7		79.3 – 84.6		
1P14Tf₂• CH₃OH	1 : 1	3.4		41.9 – 44.5		
1P14PF₆• CH₃OH	1 : 1	3.9	59.1 – 62.2	81.2 – 83.1		
1P18NO₃• CH₃CN	1 : 1	4.5			65.3 – 67.2	104.0 – 105.7
1P14BF₄• CH₃OH	1 : 1	4.2			51.7 – 53.7	94.1 – 95.2
1P14Br• CH₃CN	1 : 1	5.4	64.8 – 67.2	102.8 – 107.5		
1P18Tf₂• CH₃OH	1 : 1	2.9		60.5 – 62.3	–	–
1P18Br• CH₃CN	1 : 1	4.4	82.1 – 84.1	98.1 – 101.2		

Table S2. Sample compositions and LC temperature ranges, quadrupolar splittings of methyl group deuterons, and order parameters by NMR spectroscopy for various samples.

sample ^a	solute, wt%	<i>T</i> range (°C)	Δ (KHz)	<i>S_{CD}</i>	<i>S_{C3}</i>
1P14BF₄•CD₃OD	4.7	50.0 – 40.0	2.37 – 2.54	0.010 – 0.011	-0.031 – -0.034
1P10NO₃•CD₃OD	6.4	0 – -43.2	4.87 – 6.91	0.021 – 0.028	-0.065 – -0.092
1P14NO₃•CD₃OD	4.8	55 – 25	18.95 – 24.97	0.015 – 0.019	-0.045 – -0.057
1P18NO₃•CD₃OD	4.0	73 – 55	2.73 – 3.38	0.012 – 0.015	-0.036 – -0.048
1P14Cl•CD₃OD	5.1	50	4.23	0.0182	-0.056
1P14Br•CD₃OD	4.8	60 – 40	3.65 – 4.45	0.016 – 0.019	-0.048 – -0.060
1P14I•CD₃OD	4.5	60 – 25	3.26 – 4.37	0.014 – 0.019	-0.043 – -0.058
2P14OHBr•CD₃OD	4.6	30	4.68	0.0175	-0.054
1P14NO₃•1.5CD₃OD	7.2	35 – 21.2	3.56 – 3.96	0.015 – 0.017	-0.047 – -0.053
1P18NO₃•1.5CD₃OD	5.9	60 – 55	2.83 – 3.02	0.012 – 0.013	-0.038 – -0.040
2P14OHBr•0.22CD₃OD	1.0	75 – 45	3.69 – 4.94	0.016 – 0.021	-0.049 – -0.065

2P14OHBr•0.18CD₃CN	1.0	75 – 45	1.49 – 1.46	0.0067 – 0.0065
1P14NO₃•CD₃CN	5.9	40 – 25	1.20 – 1.00	0.0054 – 0.0042
1P18NO₃•CD₃CN	4.8	60 – 55	1.20 – 1.15	0.0054 – 0.0052
1P10NO₃•1-butanol	9.5	10 – 40	8.60 – 10.85	
1P10NO₃	0	80 – 57	9.21 – 10.62	
1P14NO₃	0	95 – 40	7.86 – 12.83	
1P18NO₃	0	97 – 60	7.94 – 12.14	
1P14I	0	95 – 65	8.63 – 10.34	

^a Molar ratio of salt to solute is 1:1 unless indicated otherwise.

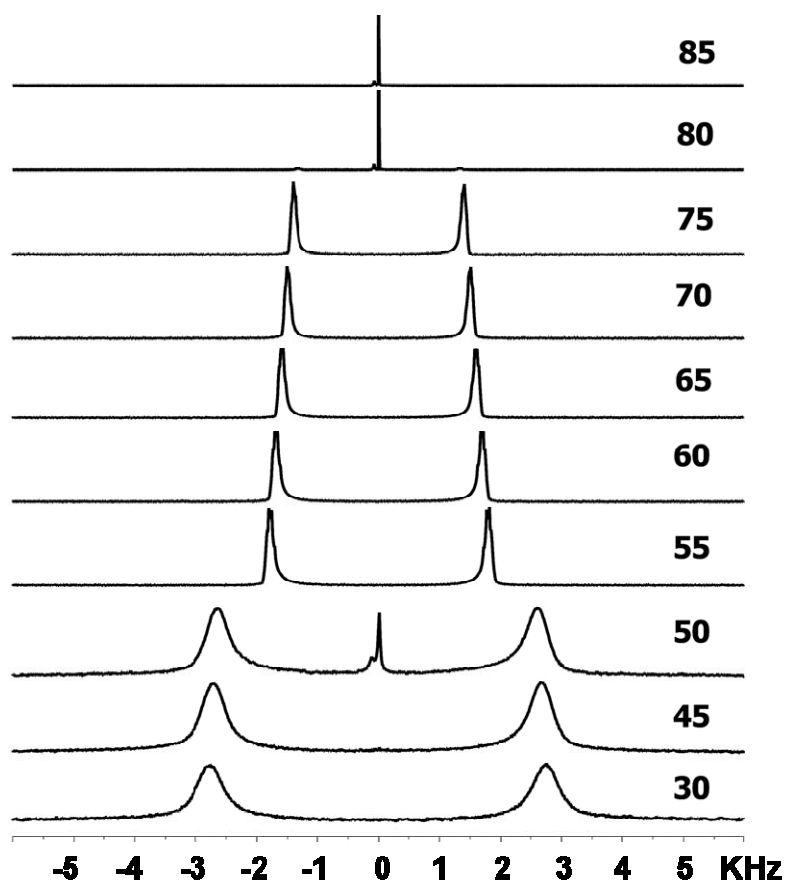


Figure S1. Stack plot of ^2H NMR spectra of $1\text{P18NO}_3\cdot\text{CD}_3\text{OD}$ at various temperatures ($^{\circ}\text{C}$).

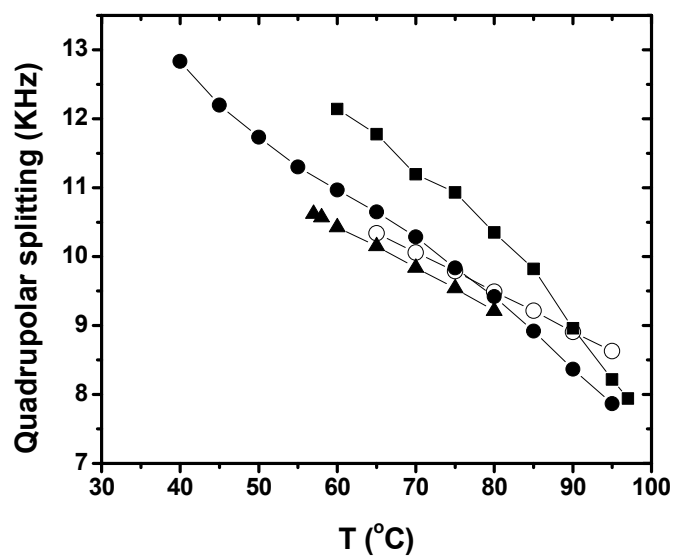


Figure S2. Quadrupolar splittings of methyl group deuterons in neat compounds ($[\text{H}(\text{CH}_2)_{14}]_3\text{P}^+\text{CD}_3\text{I}^-$ (○) and $[\text{H}(\text{CH}_2)_n]_3\text{P}^+\text{CD}_3\text{NO}_3^-$, with $n = 10$ (▲), 14 (●) and 18 (■) as a function of temperature within their liquid-crystalline phases.

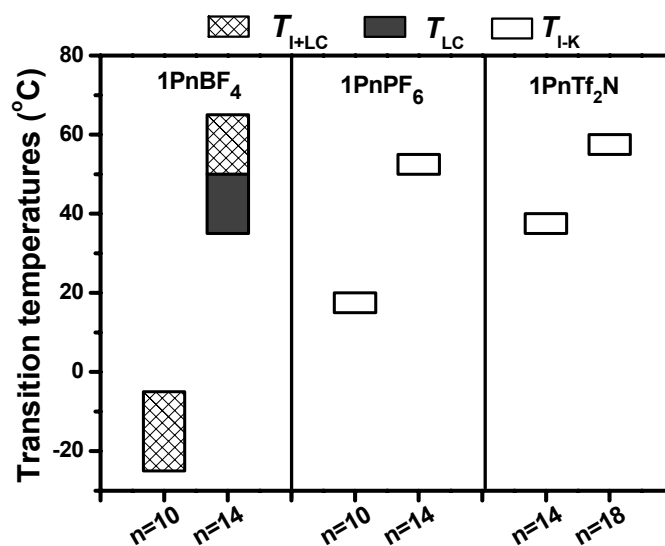


Figure S3. Transition temperatures of $1\text{P14A}\cdot\text{CD}_3\text{OD}$ systems with various n as determined by ^2H NMR measurements.

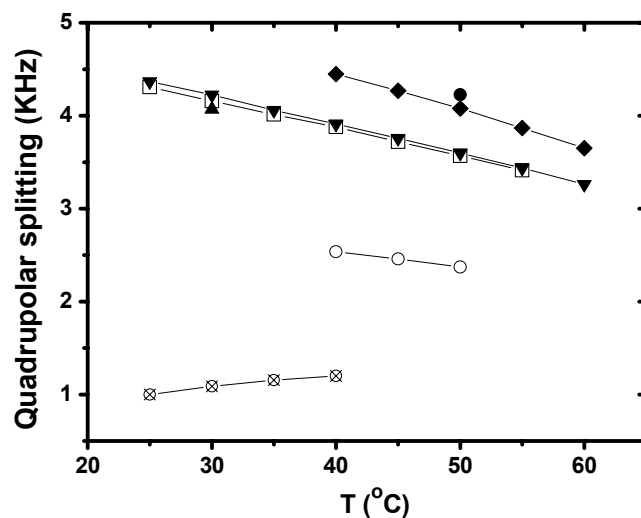


Figure S4. Temperature dependence of quadrupolar splittings of methyl group deuterons of solutes in $2\text{P14OHBr}\cdot\text{CD}_3\text{OD}$ (▲), $1\text{P14A}\cdot\text{CD}_3\text{OD}$ for $\text{A} = \text{Cl}^-$ (●), Br^- (◆), I^- (▼), BF_4^- (○), NO_3^- (□) and for $1\text{P14NO}_3\cdot\text{CD}_3\text{CN}$ (⊗).

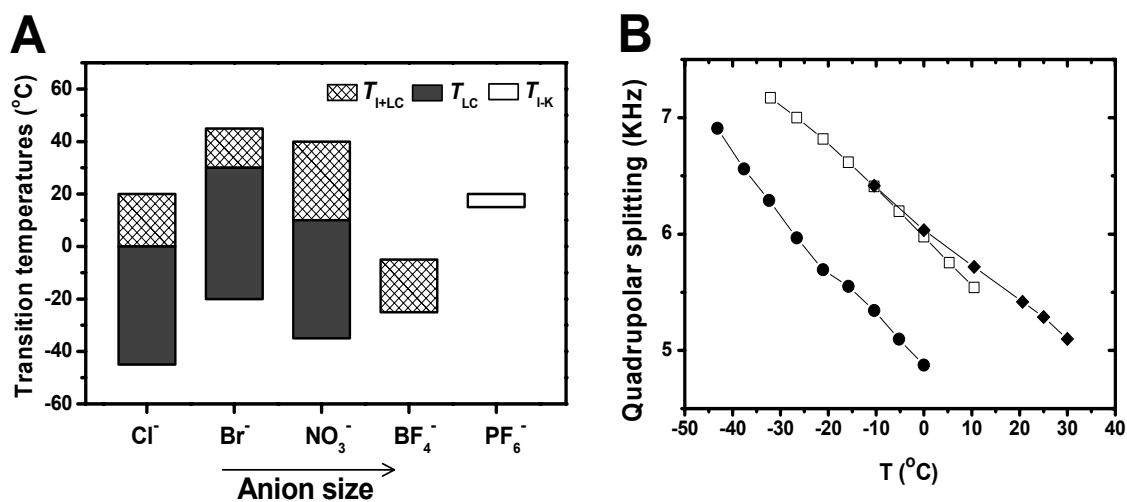


Figure S5. For **1P10A•CD₃OD** systems: (A) Transition temperatures observed for the LC phases from ²H NMR spectroscopy. (B) Temperature dependence of quadrupolar splittings of the CD₃ groups when **A** = Cl^- (●), Br^- (◆), NO_3^- (□).

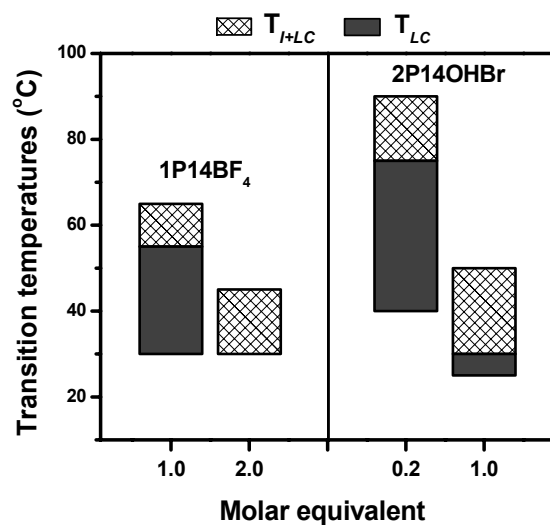


Figure S6. Transition temperatures of **1P14BF₄** and **2P14OHBr** systems with various concentrations of methanol as determined by ²H NMR measurements.

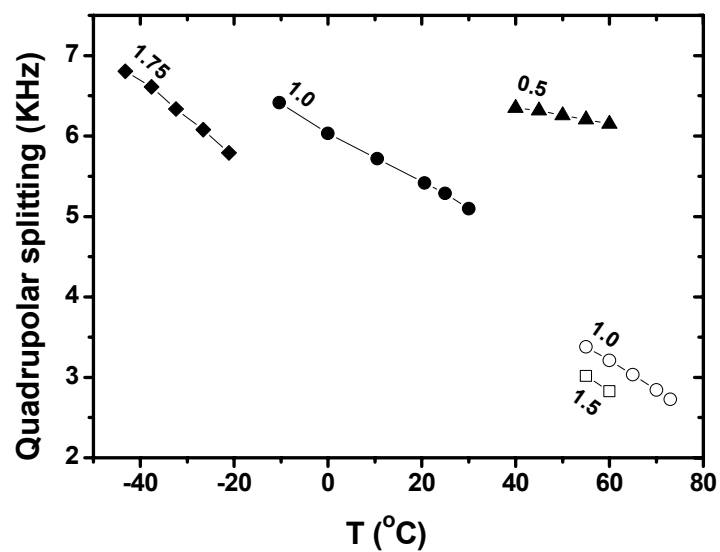


Figure S7. Quadrupolar splittings of methyl group deuterons of methanol- d_4 versus temperature in **1PnA•CD₃OD** systems. The molar equivalents of methanol- d_4 are shown next to each set of symbols for **1P10Cl** (filled symbols) and **1P18NO₃** (open symbols).

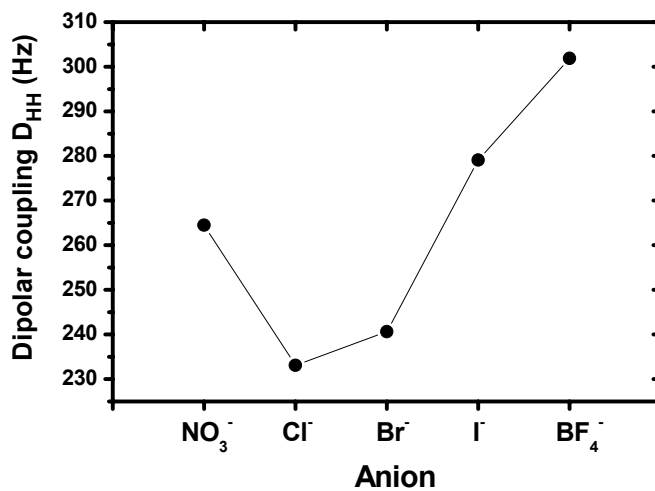


Figure S8. $|D_{HH}|$ absolute values of dipolar couplings of $^{13}\text{CH}_3\text{CN}$ in **1P14A•CD₃OD** systems with various anions at temperature $T = 50^\circ\text{C}$.

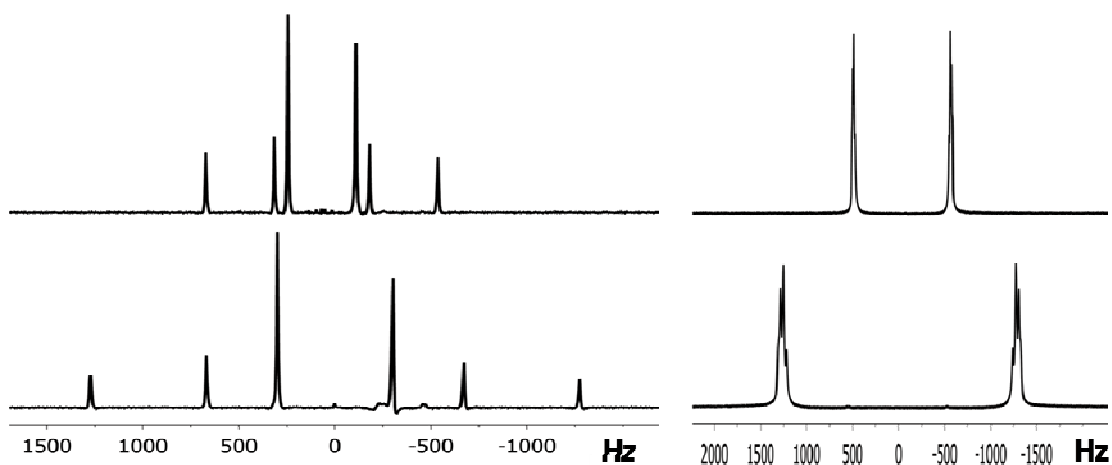


Figure S9. ^1H spectra of $^{13}\text{CH}_3\text{CN}$ in $1\text{P14NO}_3\cdot\text{CD}_3\text{CN}$ (top left) and in $1\text{P14BF}_4\cdot\text{CD}_3\text{OD}$ (bottom left), ^2H spectra of CD_3CN in $1\text{P14NO}_3\cdot\text{CD}_3\text{CN}$ (top right) and CD_3OD in $1\text{P14BF}_4\cdot\text{CD}_3\text{OD}$ (bottom right) (the deuteron signals of OD group are not shown) at 25 °C and 35 °C, respectively.

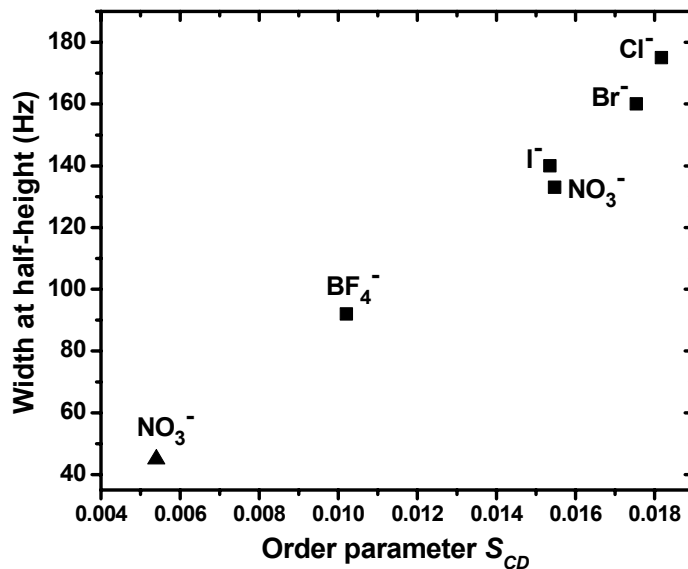


Figure S10. Dependence of width at half-height of multiplets in ^2H spectra of solutes in $1\text{P14A}\cdot\text{CD}_3\text{OD}$ (■) at $T = 50\text{ }^\circ\text{C}$ and for $1\text{P14NO}_3\cdot\text{CD}_3\text{CN}$ (▲) at $T = 40\text{ }^\circ\text{C}$ from S_{CD} , the order parameter along the CD bonds.

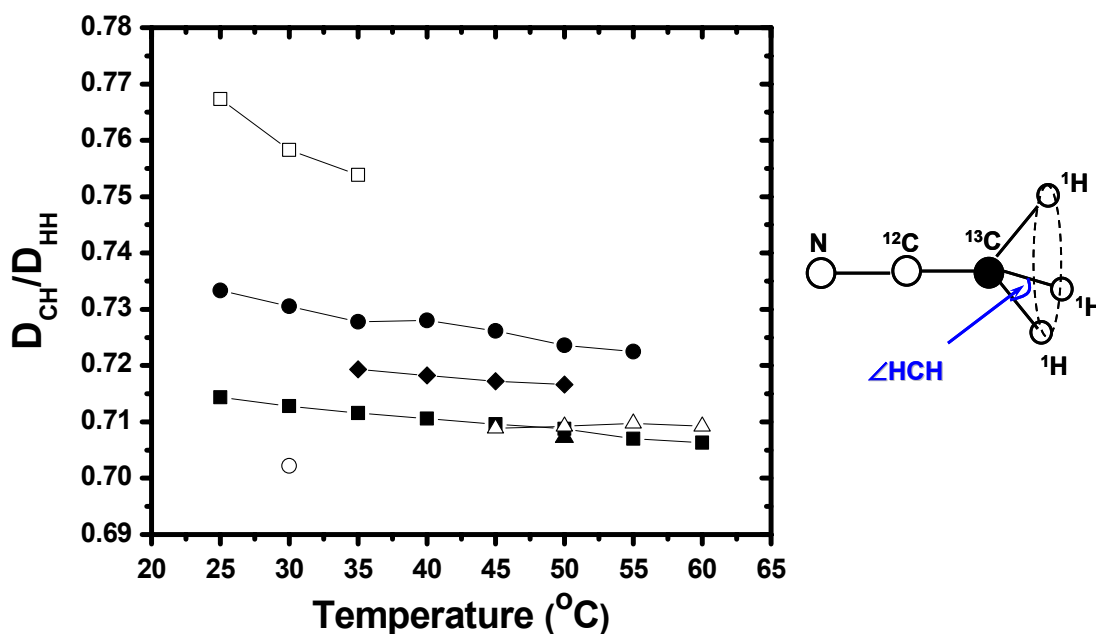


Figure S11. Dependence of the ratio of dipolar couplings (D_{CH}/D_{HH}) representing the HCH methyl angle of ^{13}C -acetonitrile as a function of temperature in the liquid-crystalline phases of **1P14NO₃•CD₃CN** (□), **1P14A•CD₃OD** (where A= Γ^- (■), Br^- (△), Cl^- (▲), NO_3^- (●), BF_4^- (◆)), and **2P14OHBr•CD₃OD** (○).

Application of analytical equations to determine the angle and the order parameter of the substituted methyls from the dipolar couplings.¹

$$S = \frac{8\pi^2}{h\gamma_H^2} r_{HH}^3 D_{HH} \quad (1)$$

r_{HH} is obtained from equation (2), taking $r_{CH} = 1.1044 \text{ \AA}$.

$$r_{HH} = 2r_{CH} \sin \frac{\angle(\text{HCH})}{2} \quad (2)$$

The dihedral angle of methyl group, $\angle(\text{HCH})$, is obtained from equation (3).

$$\frac{D_{CH}}{D_{HH}} = 16 \frac{\gamma_C}{\gamma_H} \sin^3 \frac{\angle(\text{HCH})}{2} \left(2 \sin^2 \frac{\angle(\text{HCH})}{2} - 1 \right) \quad (3)$$

γ_C and γ_H are the gyromagnetic ratios of the interacting carbon and hydrogen nuclei and D_{CH} and D_{HH} are the dipolar coupling constants in the methyl group. Vibrational corrections² were neglected because the correction factors for dipolar couplings for acetonitrile are $p_{HH} =$

1.0304 and $p_{CH} = 1.0621$.³ They lead to a very small change of the order parameters by a factor of 1.039 which, in our case, is a change in the order parameter of ≤ 0.001 . This change does not affect any of the correlations or conclusions derived in the text.

¹ Diehl, P.; Khetrpal, C. L. In *NMR Basic Principles and Progress*, Vol. 1; Diehl, P.; Fluck, E.; Kosfeld, R., Eds.; Springer-Verlag: New York, 1969.

² Khetrpal, C. L.; Kunwar, A. C. in *Advances in Magnetic Resonance*; Waugh, J. S. (Ed.); Academic Press: New York, 1977; Vol 9, pp 301-422.

³ Jokisaari, J.; Diehl, P.; Amrein, J.; Ijas, E. *J. Magn. Reson.* **1983**, 52, 193.