Supplementary information

Phase behaviour and applications of a binary liquid-liquid mixture of methanol and a thermotropic liquid crystal

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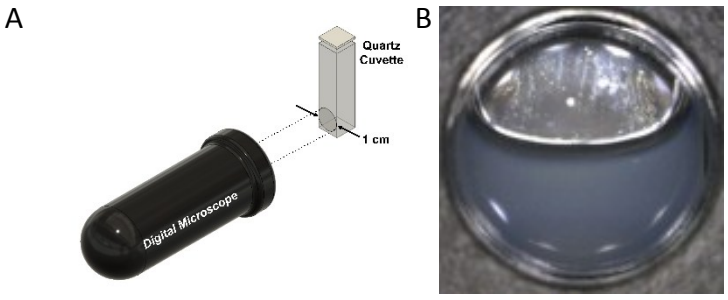
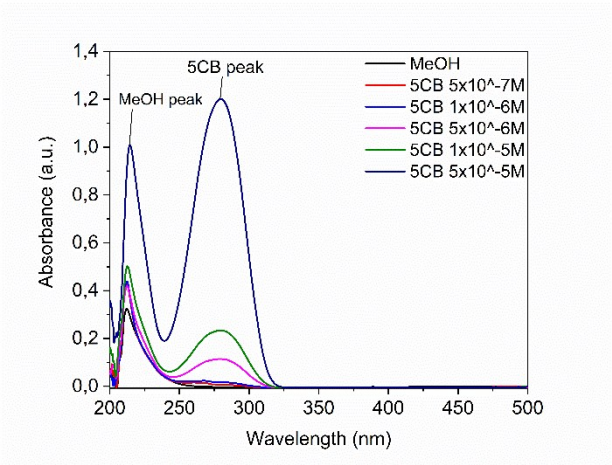


Figure S1: Scheme of the experimental setup for macroscopic observation. A) Temperature and stirring inside a quartz cuvette portion is controlled by a Peltier-regulated sample compartment. Macrographs in side-view are obtained by a digital microscope that is attached to the optical port of the compartment. B) Example of a macrograph (5CB, nematic phase, 35°C).

A



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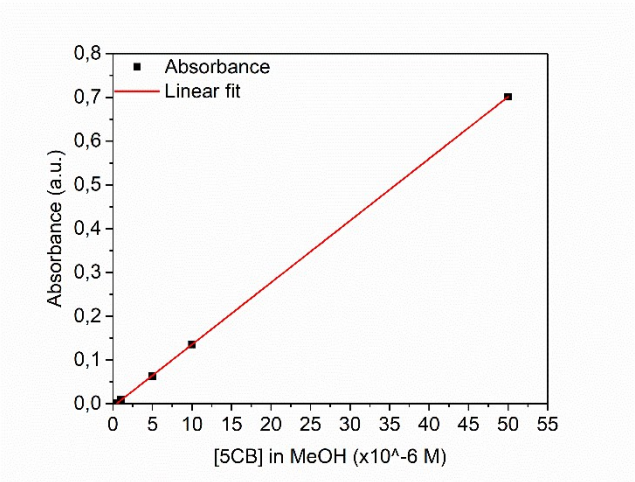

Figure S2: Absorbance spectra for different concentrations of 5CB in MeOH (top). Calibration curve using the absorbance at 297 nm (n=3) (bottom).

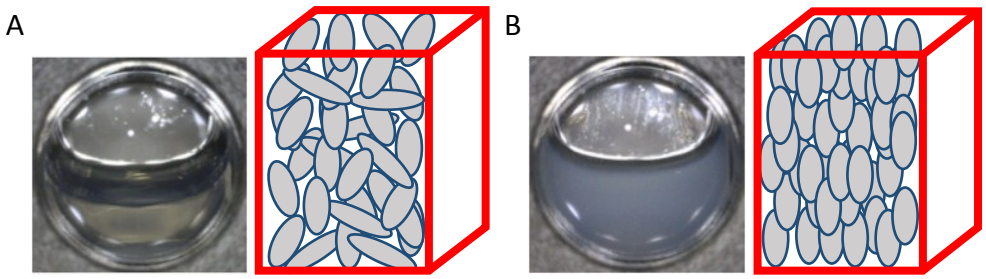

Figure S3: Thermotropic transformation of the liquid crystal 5CB. A) Isotropic phase at 36 °C, B) Nematic phase at 35 °C.

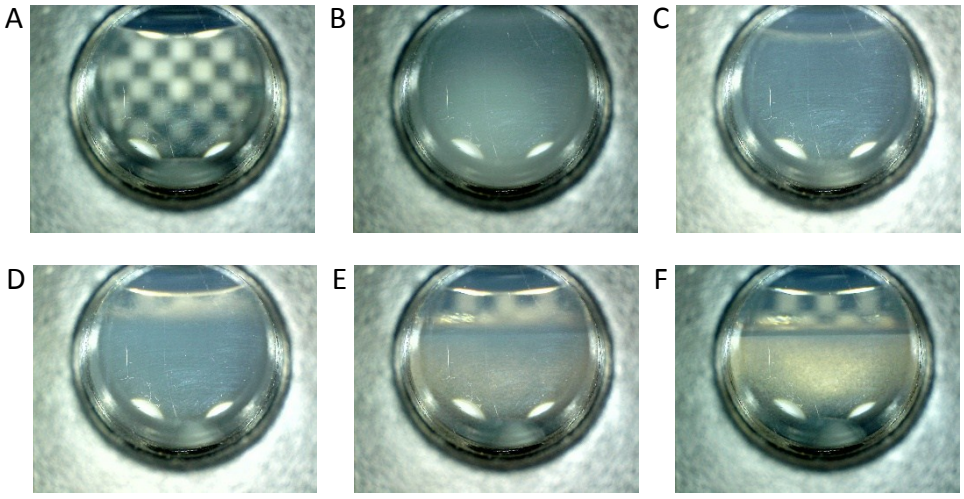

Figure S4: Kinetic study of the transient cloudification upon phase separation. Macrographs of a mixture of 50 vol% MeOH and 50 vol% 5CB. A chessboard type background was used to generate contrast. A) Mixture at 25°C under stirring exhibiting an isotropic transparent single phase. B) Mixture at 24°C where the cloud point was reached. The temperature was subsequently held constant at 24°C and the stirring was stopped to observe macroscopic phase separation with snapshots shown after 30 seconds (C), 60 seconds (D), 90 seconds (E), 120 seconds (F). Note that the top phase in the biphasic macrographs corresponds to the methanol-rich phase while the bottom phase corresponds to the 5CB-rich phase.

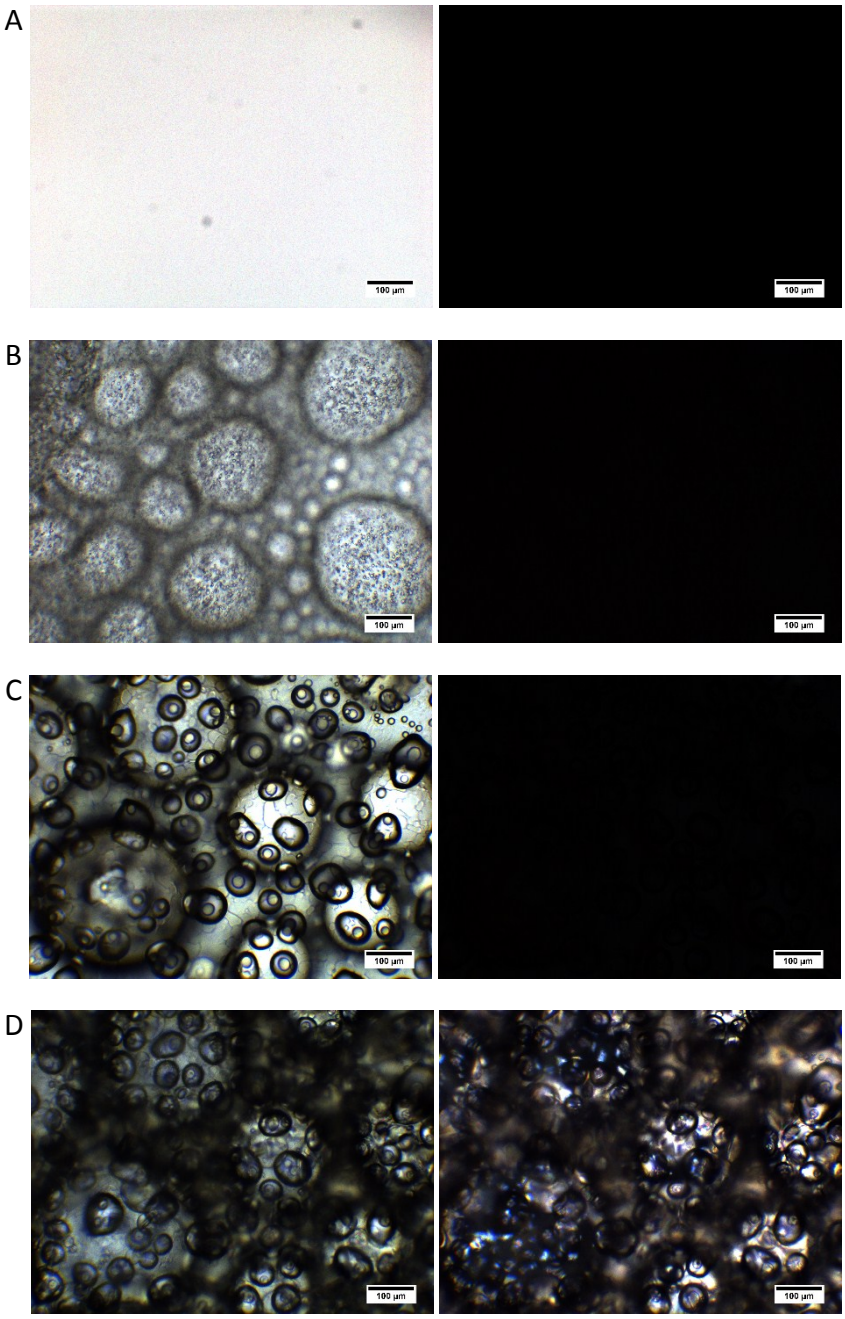

Figure S5: Microscopic observations of phase behaviour for a mixture of 50 vol% MeOH and 50 vol% 5CB in a sealed glass sandwich (60 um thickness). Left: bright field (exposition 0.4 ms). Right: Cross-polarised light (exposition 2 ms). A) At 25°, the mixture exhibited an isotropic single phase. B) At 24°C, phase separation was observed with a bilayer discernible in top-view. C) At 0°C, a similar configuration of two isotropic layers was found. D) At -1°C, the bottom 5CB-rich layer turned nematic as discernible under cross-polarised light. Note that no droplets were observed in macroscopic bulk experiments but rather a stratified bilayer configuration. We relate the prevalence of droplets after extended cooling times (even after one hour) to the spatial confinement in the sandwich configuration required for observation by optical microscopy.

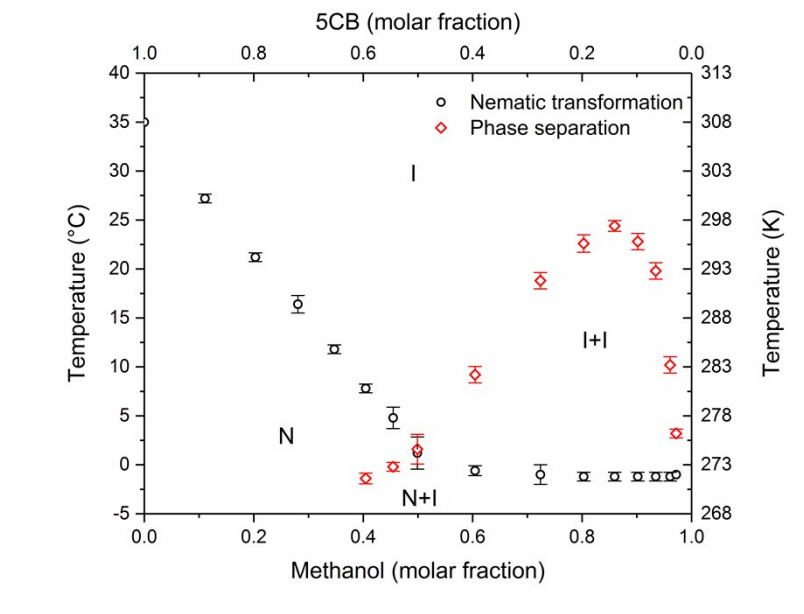

Figure S6: Phase diagram of 5CB–MeOH binary mixtures plotted in respective molar fractions. See Figure 2 in main manuscript for vol% representation.

5CB (%vol)	MeOH (%vol)	Phase separation (°C)			Isotropic-to-nematic transformation (°C)		
		n	$\bar{X}$	σ	n	$\bar{X}$	σ
100	0	-	-	-	5	35	0.0
98	2	-	-	-	5	27.2	0.4
96	4	-	-	-	5	21.2	0.4
94	6	-	-	-	5	16.4	0.9
92	8	-	-	-	5	11.8	0.4
90	10	5	-1.4	0.5	5	7.8	0.4
88	12	5	-0.2	0.4	5	4.8	1.1
86	14	5	1.6	1.5	5	1.2	1.6
80	20	5	9.2	0.8	5	-0.6	0.5
70	30	5	18.8	0.8	5	-1	1.0
60	40	5	22.6	0.9	5	-1.2	0.4
50	50	5	24.4	0.5	5	-1.2	0.4
40	60	5	22.8	0.8	5	-1.2	0.4
30	70	5	19.8	0.8	5	-1.2	0.4
20	80	5	10.2	0.8	5	-1.2	0.4
15	85	5	3.2	0.4	5	-1	0.0

Table S1: Phase separation and isotropic-to-nematic transformation temperatures obtained for a range of 5CB-MeOH mixtures.

Sample	Investigated	Separation	Expected values	Experimental results	Error

	phase	Temperature (°C)	from phase diagram						(%)
			5CB (%)	[5CB] (x10^{-5} M)	Abs.	[5CB] (x10^{-5} M)	5CB (ml)	5CB (%)	
1	5CB-rich	21	66.6	2.69	0.365	2.63	1.95	65.0	2.4
2	5CB-rich	24	55.0	2.22	0.295	2.13	1.05	52.5	4.5
3	5CB-rich	25	50.0	2.02	0.271	1.96	0.97	48.5	3.0
4	MeOH-rich	24	45.0	1.82	0.263	1.90	0.94	47.0	4.4

Table S2: Quantification of phase composition for an initial 50:50 v/v mixture of 5CB and MeOH. Expected values as based on applying the lever rule to the established phase diagram for a given separation temperature. Experimental results are based on the extraction of aliquots after separation and determination of 5CB via multiple dilution steps with MeOH (see Figure S5).

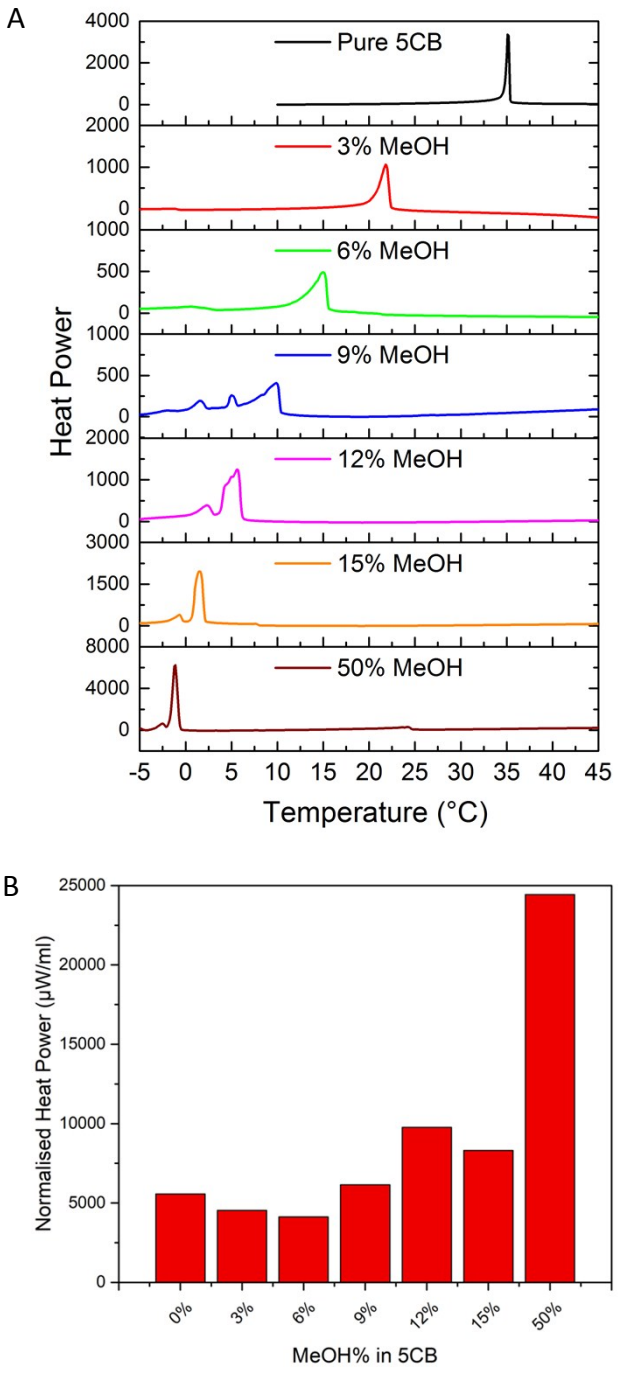

Figure S7: DSC characterisation of isotropic-to-nematic transition. A) Heat power versus temperature (°C) plots for cooling different 5CB-MeOH mixtures at 0.1 °C/min ramp rate. B) Normalised heat power obtained by peak integration.

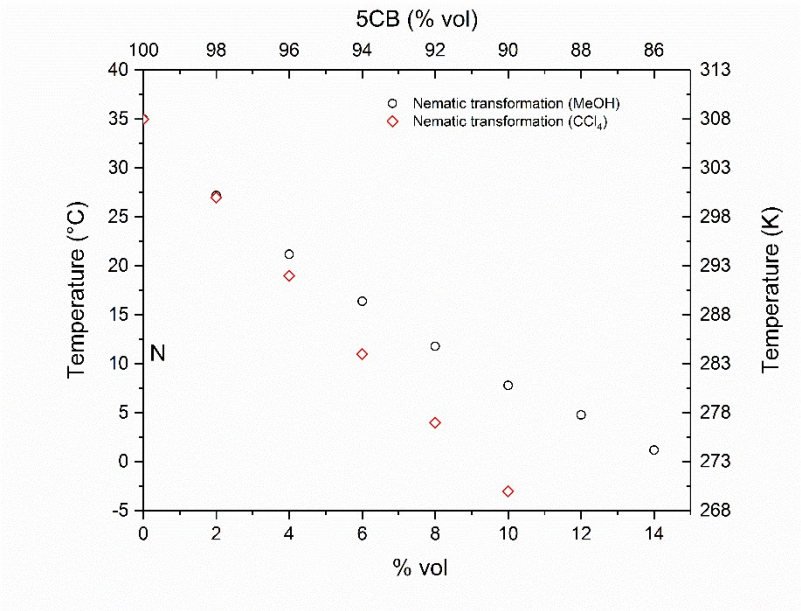

Figure S8: Effect of dilution with non-nematogenic species on the isotropic-to-nematic phase transition temperature of 5CB. Experiments were carried out with MeOH (black circles) and CCl4 (red diamonds).

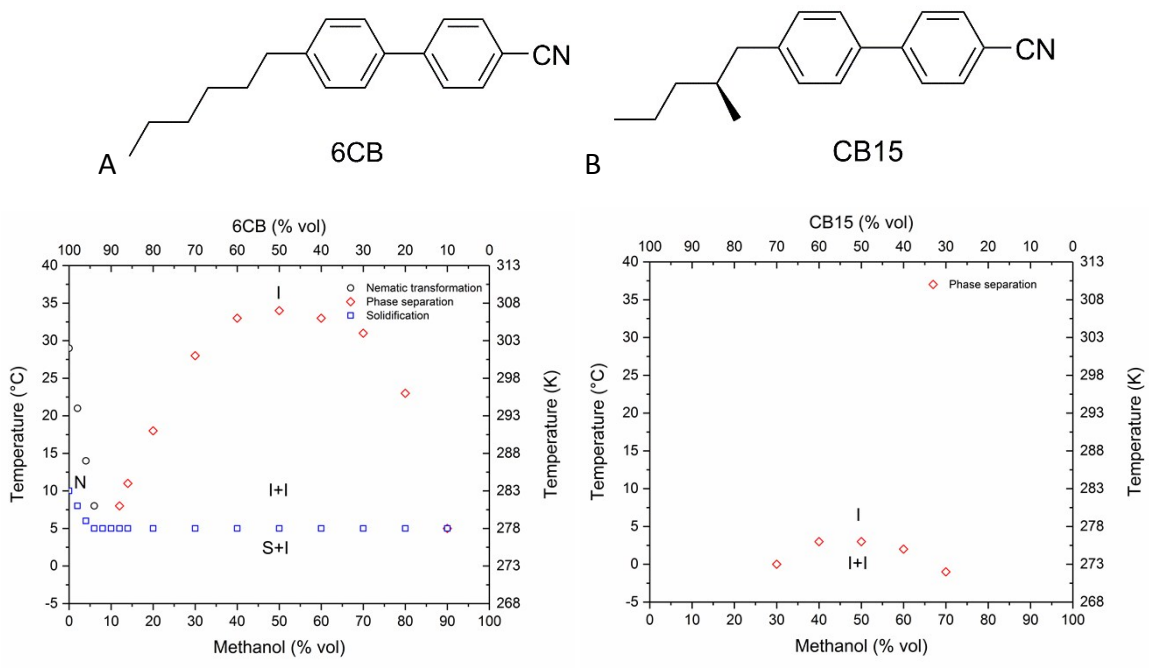

Figure S9: Phase diagrams for different binary liquid mixtures with respective molecular structure of the cyano-biphenyl compound. (A) 4-Cyano-4'-hexylbiphenyl (6CB, nematogenic) and MeOH. (B) (S)-4-Cyano-4´-(2-methylbutyl)biphenyl (CB15, non-nematogenic) and MeOH.

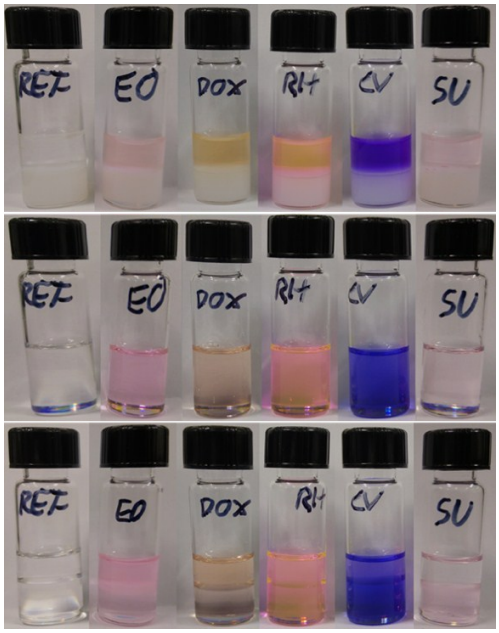

Figure S10: Photographs of 50:50 v/v mixtures of 5CB and MeOH containing the compounds presented in Figure 4 before phase mixing (top), after phase mixing (middle), and after phase separation (bottom).

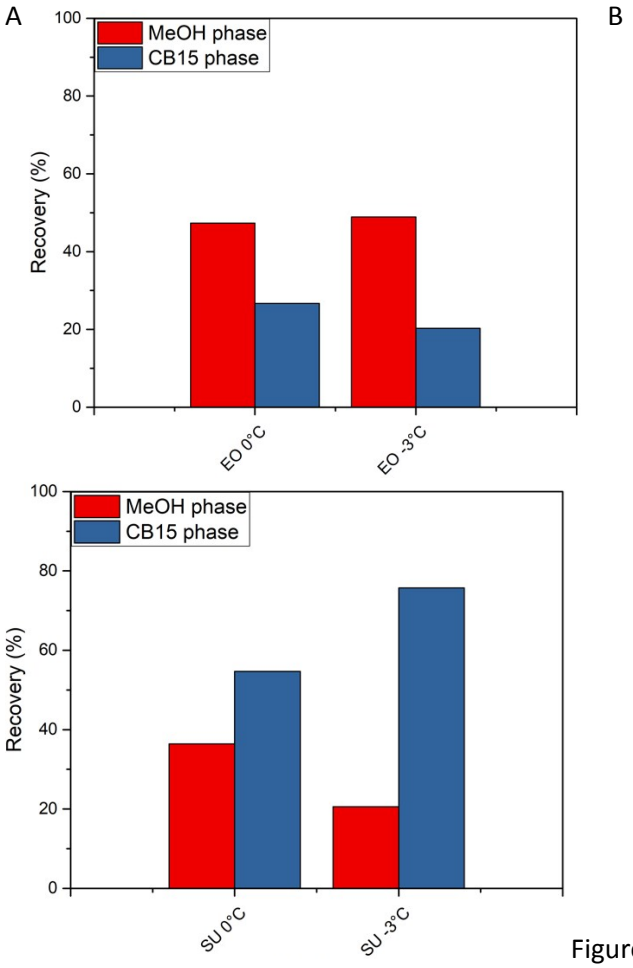

Figure S11: Temperature dependence of molecular partitioning for 50:50 v/v mixtures of CB15 and MeOH. Recovery into MeOH-rich (red) and 5CB-rich (blue) phase at different temperatures for Eosin Y (A) and Sudan IV (B).