

Improved electronic transport in ion complexes of crown ether based columnar liquid crystals.

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Supplementary Materials

1. Polarizing microscopy results

As shown by X-ray diffraction experiments all complexes formed glassy solids. Investigating the LC-to-crystal phase transition by polarizing microscopy provided further evidence of the absence of a crystalline solid state. Figure S1 shows the texture of **KI-2b** in the columnar state (*p2mg*) (left) and in the solid state *g* (right). No changes in texture could be observed during the phase transition which made it difficult to determine the transition temperature by polarizing microscopy. Most of the area is covered with **KI-2b**, the dark parts are not due to homeotropic alignment of the complex but to segregated neat **2b** as already seen in Figure 6 of the paper for **KSCN-2b**.

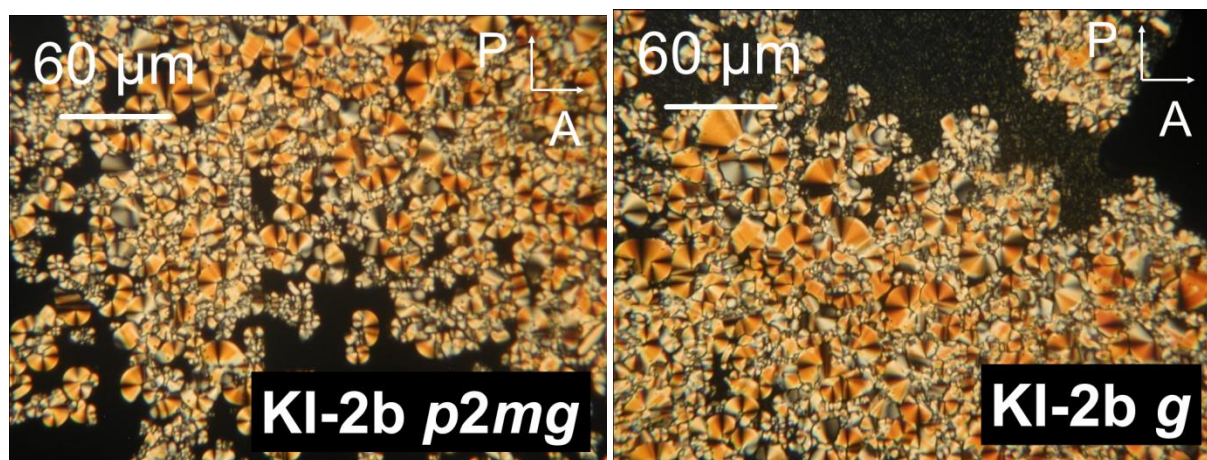


Figure S1: **KI-2b** in the columnar state (*p2mg*) (left) and in the solid state *g* (right). The texture shows no significant differences.

All the substances are still birefringent in the solid state which is the case if the structure is not completely amorphous but frozen into a glassy state.

2. Differential scanning calorimetry results

For DSC data of compounds **1** see reference [15], for DSC data of compounds **2** see reference [18].

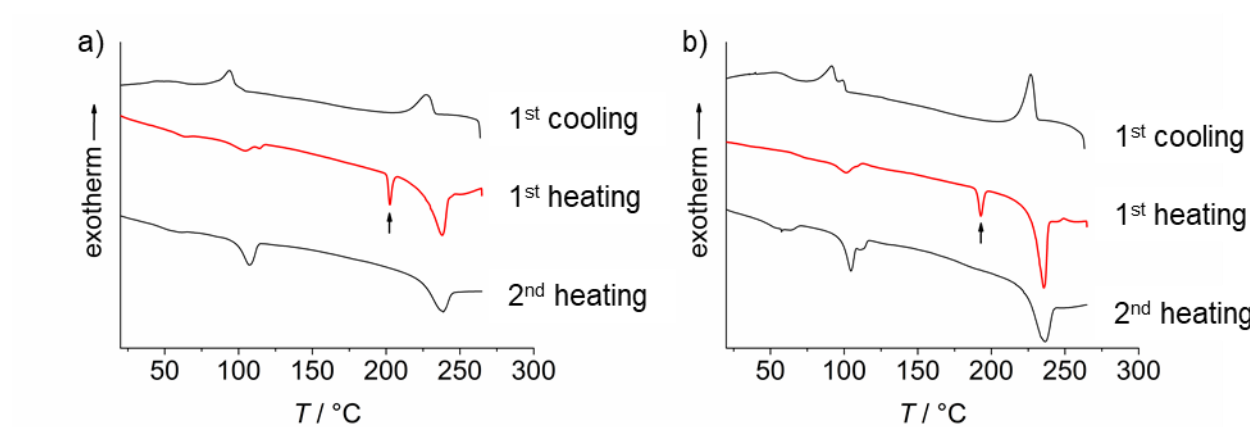


Figure S2: DSC curves of the complexes **KSCN-2b** (a) and **KSCN-2c** (b). Heating/cooling rate 10 K/min.

3. XRD results

The Small angle X-ray data for the two columnar phases of **KSCN-2b** are shown in Table S1.

Table S1: Small angle X-ray data of **KSCN-2b**. θ is the scattering angle, hk the Miller indices, d_{ob} and d_{cal} are the observed and calculated distances while a and b are the lattice constants for the rectangular unit cell.

structure	θ [°]	d_{ob} [Å]	hk	d_{cal} [Å]	lattice constants
col _r 2 (<i>p2mg</i>) (220°C)	1.16	38.24	10	38.24	$a = 64.1 \text{ Å}$ $b = 38.2 \text{ Å}$
	1.34	32.97	02	32.05	
	1.35	32.84	11	32.84	
	1.77	24.96	12	24.56	
	2.32	19.08	20	19.12	
	2.32	19.04	13	18.65	
	2.41	18.33	21	18.32	
	2.67	16.58	22	16.42	
	2.67	16.55	04	16.02	
	2.93	15.08	14	14.78	
	3.46	12.77	30	12.75	
	3.54	12.49	31	12.50	
	3.55	12.47	24	12.28	
	3.55	12.45	15	12.15	
	3.72	11.90	32	11.85	
col _r 1 (<i>p2gg</i>) (180°C)	1.25	35.34	11	35.34	$a = 53.1 \text{ Å}$ $b = 47.4 \text{ Å}$
	1.67	26.53	20	26.53	
	1.87	23.62	02	23.69	
	1.91	23.13	21	23.15	
	2.06	21.50	12	21.63	
	2.50	17.71	22	17.67	
	2.51	17.64	30	17.69	
	2.67	16.55	31	16.57	
	2.92	15.13	13	15.13	
	3.12	14.19	32	14.17	
	3.27	13.54	23	13.57	
	3.76	11.76	33	11.78	
	3.83	11.56	42	11.57	
	4.36	10.15	43	10.16	

Table S2: XRD data of **KSCN-2b** taken from ref. [1].

Structure	d_{obs} [Å]	hk	d_{calc} [Å]	lattice constants
Col _r ($p2gg$)	35.5	11	35.6	$a = 53.5$
(140°C)	26.8	20	26.8	$b = 47.7$
	23.6	02	23.8	
	21.9	12	21.8	
	17.8	22	17.8	
	16.7	31	16.7	
	15.3	13	15.2	
	14.3	32	14.3	
	13.7	23	13.7	
	12.9	41	12.9	
	11.7	14	11.6	
	10.2	43	10.2	
	4.4	halo		

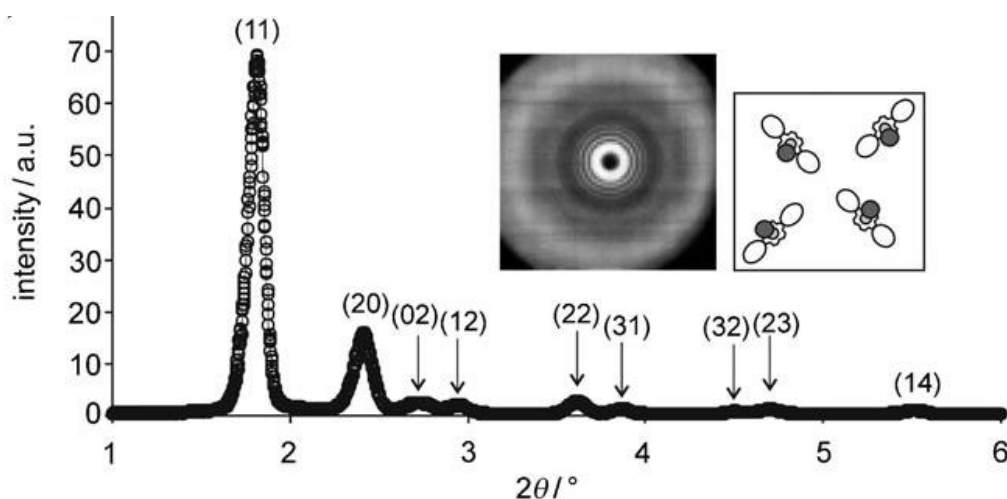


Figure S3: WAXS pattern of **KSCN-2b** taken from ref. [1].

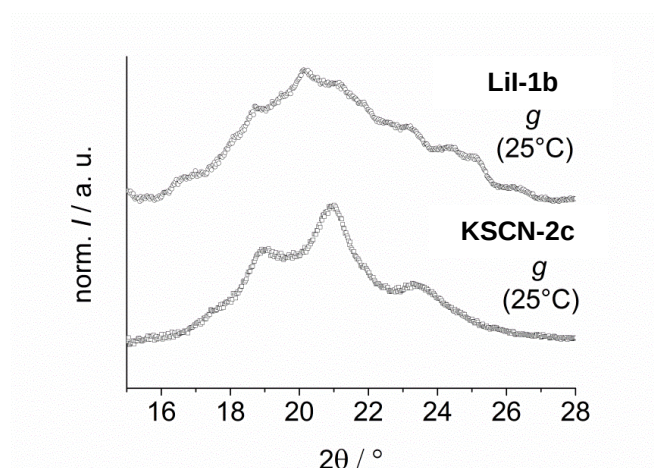


Figure S4: Wide angle diffraction pattern of **Lil-1b** (○) and **KSCN-2c** (□) in the solid state. Only diffuse smeared peaks can be observed indicating a low intra-columnar order.

4. UV-Vis Spectroscopy

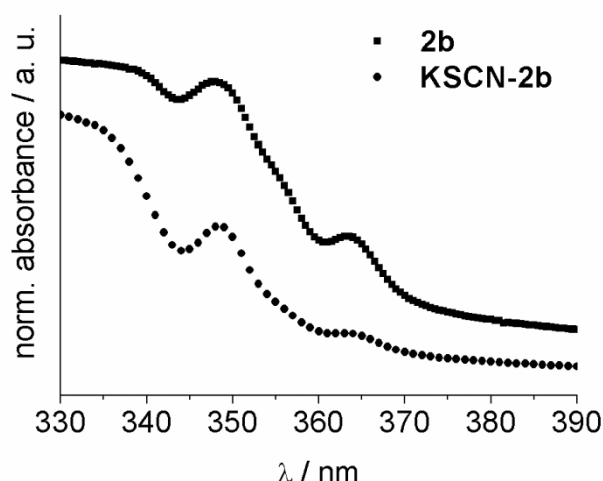


Figure S5: Absorbance spectrum of neat **2b** (■) and its KSCN-complex **KSCN-2b** (●) in the solid state.

5. Photoconductivity

Depending on the alignment of the two components present in the measurement cell (neat and complex compound) it was possible to observe either the measurement signal for the complex alone or the signal for both components. Usually the alignment of the complex was achieved by slow cooling from the isotropic phase while the parts of the sample covered by the segregated neat compound **2a,b** stayed isotropic until their clearing point was reached in the cooling process. Since the neat compound usually did align randomly on polyimide surfaces, it was more or less coincident if the homeotropically aligned part was large enough to produce a detectable signal. Since the insulating glassy solid states of the complexes do not contribute to the conductivity the whole low temperature part of the photoconductivity profile was dominated by the well conducting crystalline solid state of the neat compound.

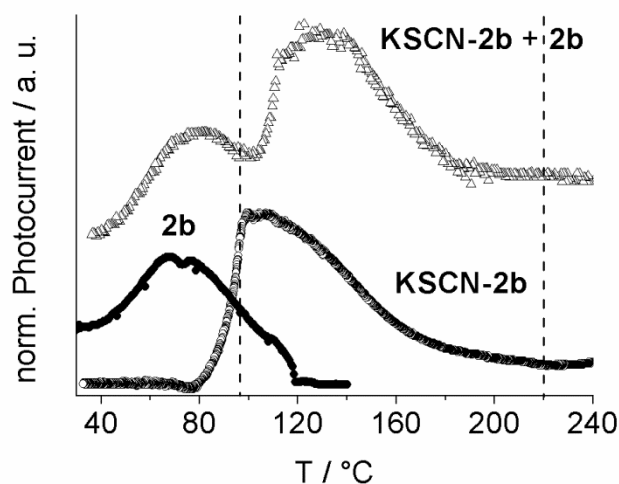


Figure S6: Photoconductivity profiles of a segregated sample of **KSCN-2b** (Δ) where both components contribute to the photocurrent in the respective temperature ranges. Furthermore, the profile of neat **2b** (●) and a **KSCN-2b** sample (○) where only the complex contributes are shown.

Figure S6 shows the photoconductivity profile of a segregated sample of **KSCN-2b** (Δ) where the signal of both components could be detected. Between 220 and 110 °C the signal of the

rectangular liquid crystal phases of **KSCN-2b** can be seen while below 110°C the homeotropically aligned parts of crystalline neat **2b** is visible. Furthermore the single response of a sample of neat **2b** (●) and a measurement of **KSCN-2b** (○) where the response of segregated **2b** was not observed are shown.

6. Ionic Transport

The conductivity was determined by modelling the impedance data as simple RC-circuits where R had to be replaced by a constant phase element due to the slightly depressed semicircles in the *Nyquist* plot. The bulk resistance was received from the intercept of the respective semicircle with the Z' -axis in the *Nyquist* diagram after fitting the data with the program *ZView*. The cell constant in cm^{-1} was determined by measuring the bulk resistance in Ohms of a drop of 1 mM KCl-solution with known ionic conductivity of 0.147 mS cm^{-1} covering the whole electrode structure.

The liquid crystal was put on the surface covered by a thin glass slide and heated to the columnar phase to equilibrate. Alignment of the material was achieved by shearing the liquid crystal mechanically either parallel or perpendicular to the electric field.

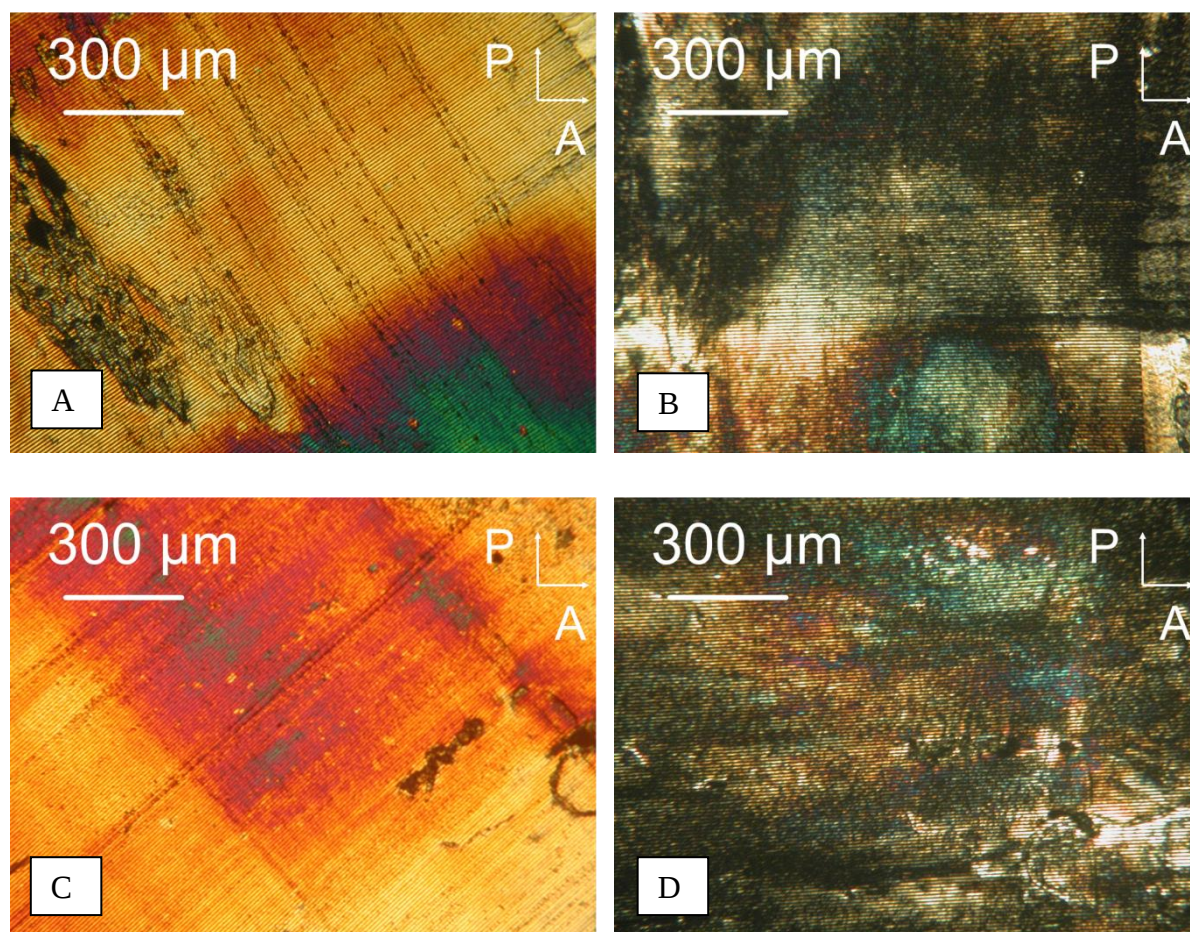


Figure S7: Large scale pictures of the aligned thin films of **KI-2b** between crossed polarizers in the bright state (left) and the dark state (right). The columns have been aligned parallel (A, B) and perpendicular (C, D) to the electric field.

The absolute ionic conductivity of the compounds only depended slightly on the film thickness. Well aligned films could be achieved by mechanical shearing of the substance in the columnar phase either parallel or perpendicular to the electric field. Figure S7 shows the good alignment of two thin films of **KI-2b** between crossed polarizers on a larger scale once

in the bright and once in the dark state depending on the angle between the optic axis of the material with respect to the crossed polarizers. The shearing direction can be seen in the pictures and is not indicated separately.

The film quality is quite good over the whole electrode structure. The average film thickness was estimated by the film colour and the respective retardation. The pictures were taken in reflexion which doubles the retardation and leads to an estimated film thickness of about 2–5 μm which is not enough to cover the whole stray field of the interdigitating electrodes. To overcome the influence of the film thickness the shearing method was applied to thicker films. The alignment quality however was much lower than in the thin films as expected (Figure S8).

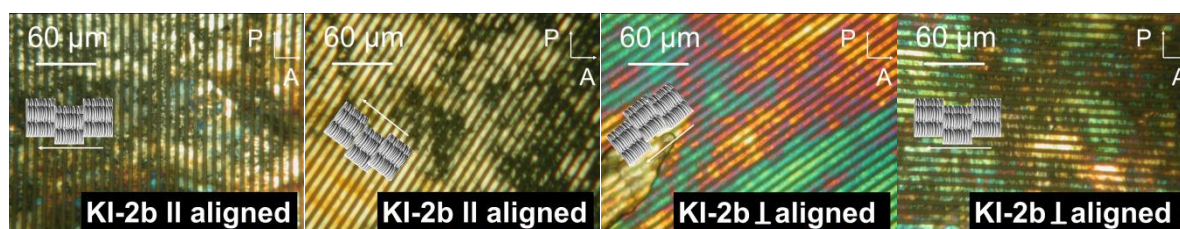
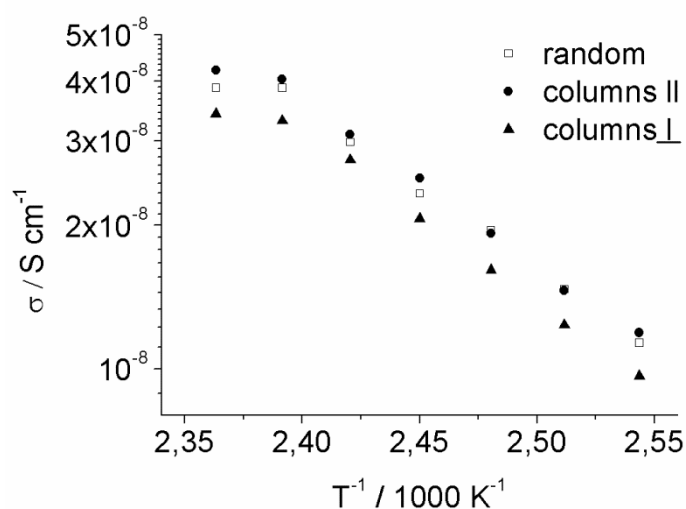


Figure S8: Temperature dependent ionic conductivity in thick films of **KI-2b** with columns aligned randomly ($\square$), parallel ($\bullet$) and perpendicular ($\blacktriangle$) to the electric field.

The observed conductivity of the films showed the same tendency as the thin films. The conductivity was reproducibly higher parallel to the columns than perpendicular to them while the randomly aligned film showed conductivity values between those measured for the aligned films (Figure S8). The anisotropy in fact was lower in all cases only about 1.2 – 1.3 affirming the observations made for the thin films.

References

- [1] Kaller, M.; Deck, C.; Meister, A.; Hause, G.; Baro, A.; Laschat, S. Counterion effects on the columnar mesophases of triphenylene-substituted 18crown-6 ethers: is flatter better? *Chem. Eur. J.* **2010**, *16*, 6326–6337.