Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary materials

# Molecular p-doping in organic liquid crystalline semiconductor: Influence of the charge transfer complex on the properties of mesophase and bulk charge transport

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# DSC thermograms

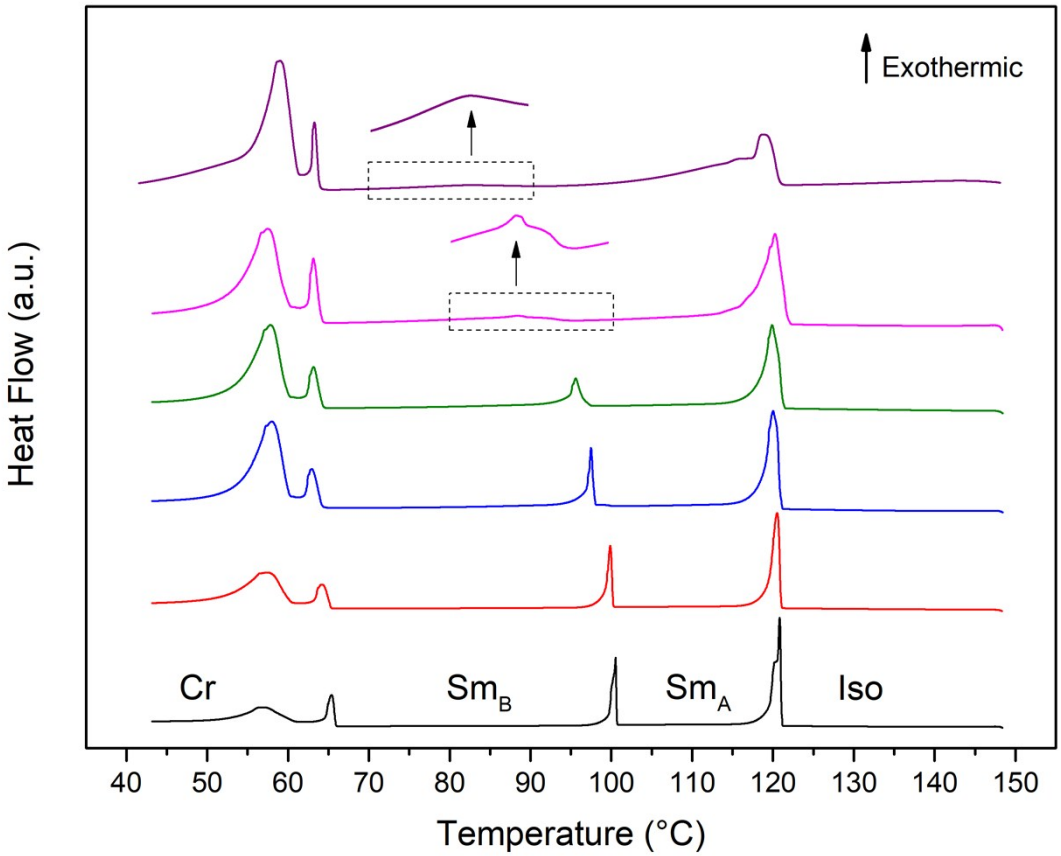
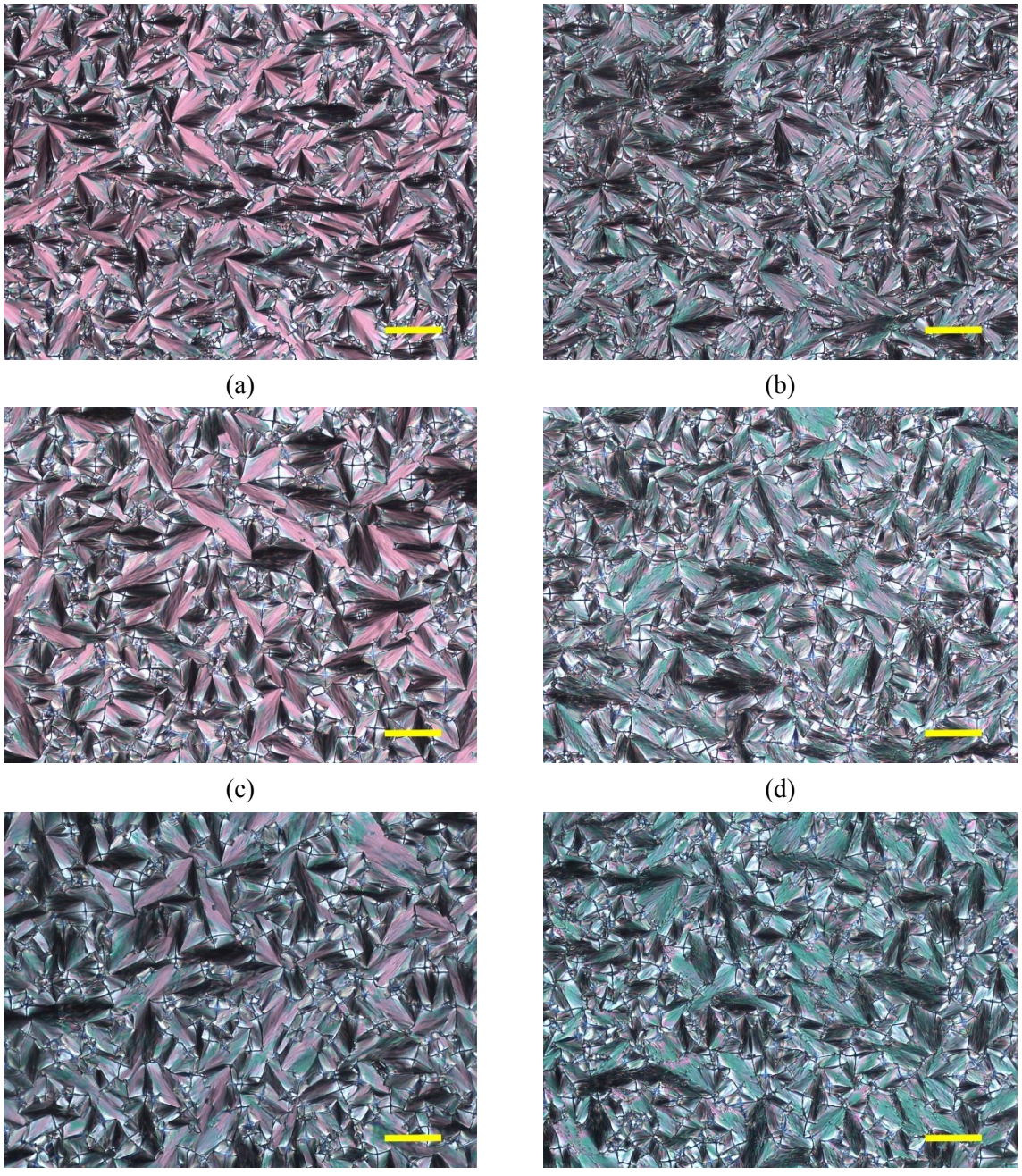



**Figure 1**. DSC plots for pure **8-PNP-O12** (black), **c1** (red), **c2** (blue), **c3** (green), **c4** (pink) composites obtained with 10°C min$^{-1}$ cooling program and **c5** (purple) composite obtained with 5°C min$^{-1}$ cooling program. Dashed rectangles denote the scaled part of the thermogram.

# Texture of prepared composites



(a) (b) (c) (d) (e) (f)

**Figure 2.1** Sample texture under crossed analyzer-polarizer: for pure **8-PNP-O12** (in $\mathbf{Sm_B}$ (a) and $\mathbf{Sm_A}$ (b) mesophase), **c1** (in $\mathbf{Sm_B}$ (c) and $\mathbf{Sm_A}$ (d) mesophase) and **c2** (in $\mathbf{Sm_B}$ (e) and $\mathbf{Sm_A}$ (f) mesophase). Scale bar represents 100μm.

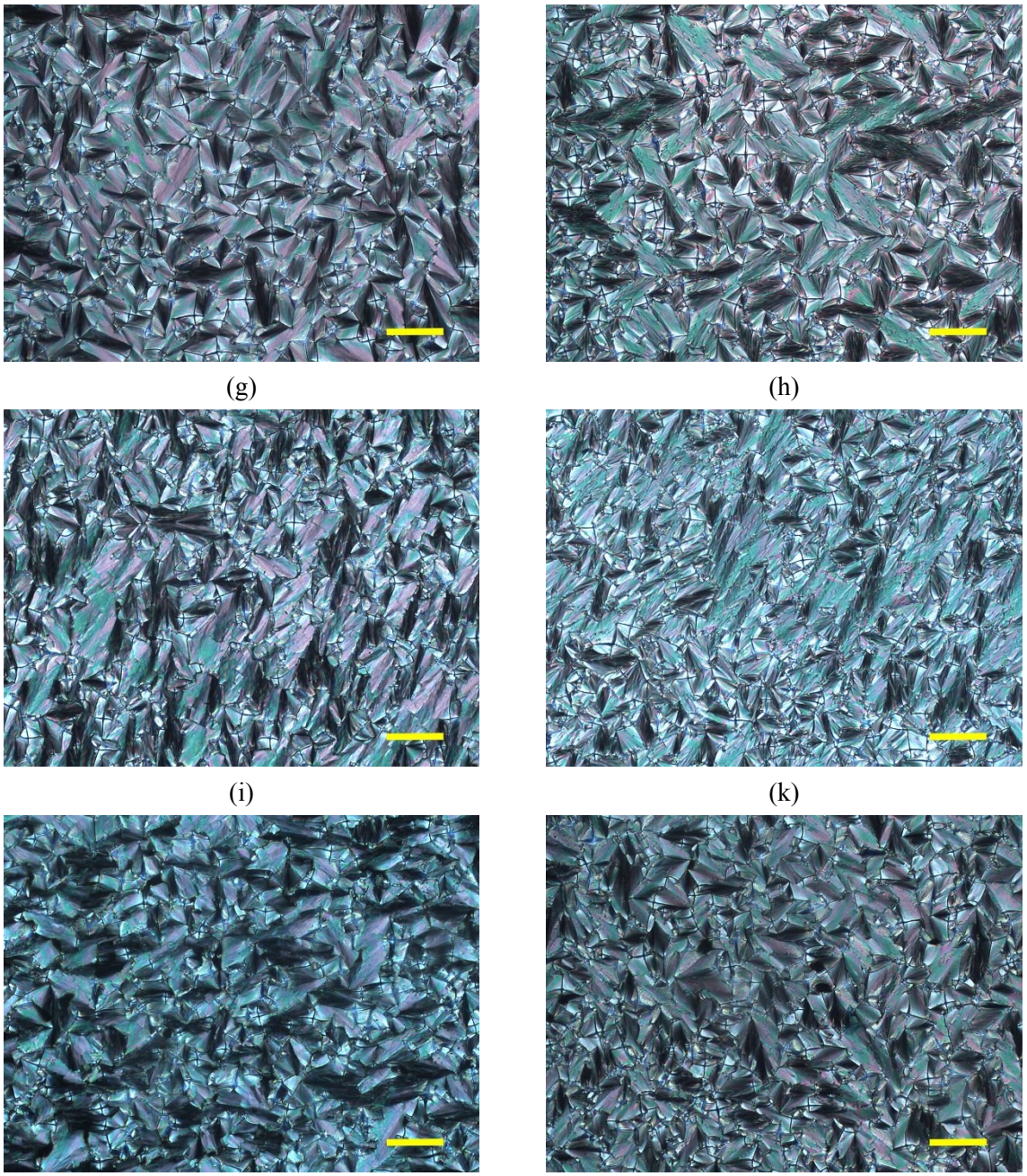



**Figure 2.2** Sample texture under crossed analyzer-polarizer: **c3** (in $\mathbf{Sm_B}$ (g) and $\mathbf{Sm_A}$ (h) mesophase), **c4** (in $\mathbf{Sm_B}$ (i) and $\mathbf{Sm_A}$ (k) mesophase), and **c5** (in $\mathbf{Sm_B}$ (l) and $\mathbf{Sm_A}$ (m) mesophase). Scale bar represents 100μm.

## Wide angle X-ray scattering data

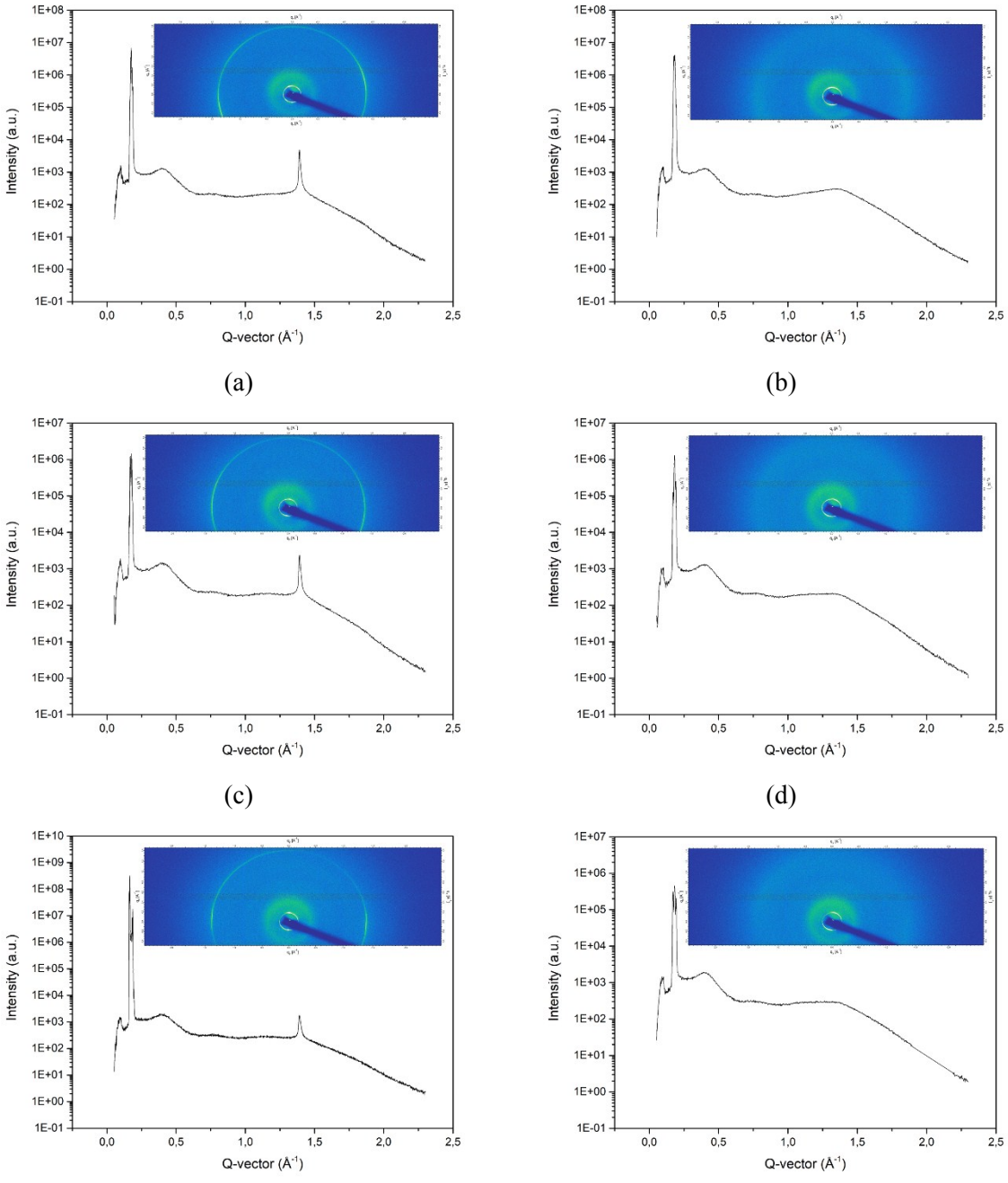



**Figure 3.1** 1D and 2D WAXS data: for pure **8-PNP-O12** (in $\mathbf{Sm_B}$ (a) and $\mathbf{Sm_A}$ (b) mesophase), **c1** (in $\mathbf{Sm_B}$ (c) and $\mathbf{Sm_A}$ (d) mesophase) and **c2** (in $\mathbf{Sm_B}$ (e) and $\mathbf{Sm_A}$ (f) mesophase). $\mathbf{Sm_B}$ is represented at 85°C, and $\mathbf{Sm_A}$ at 115°C.

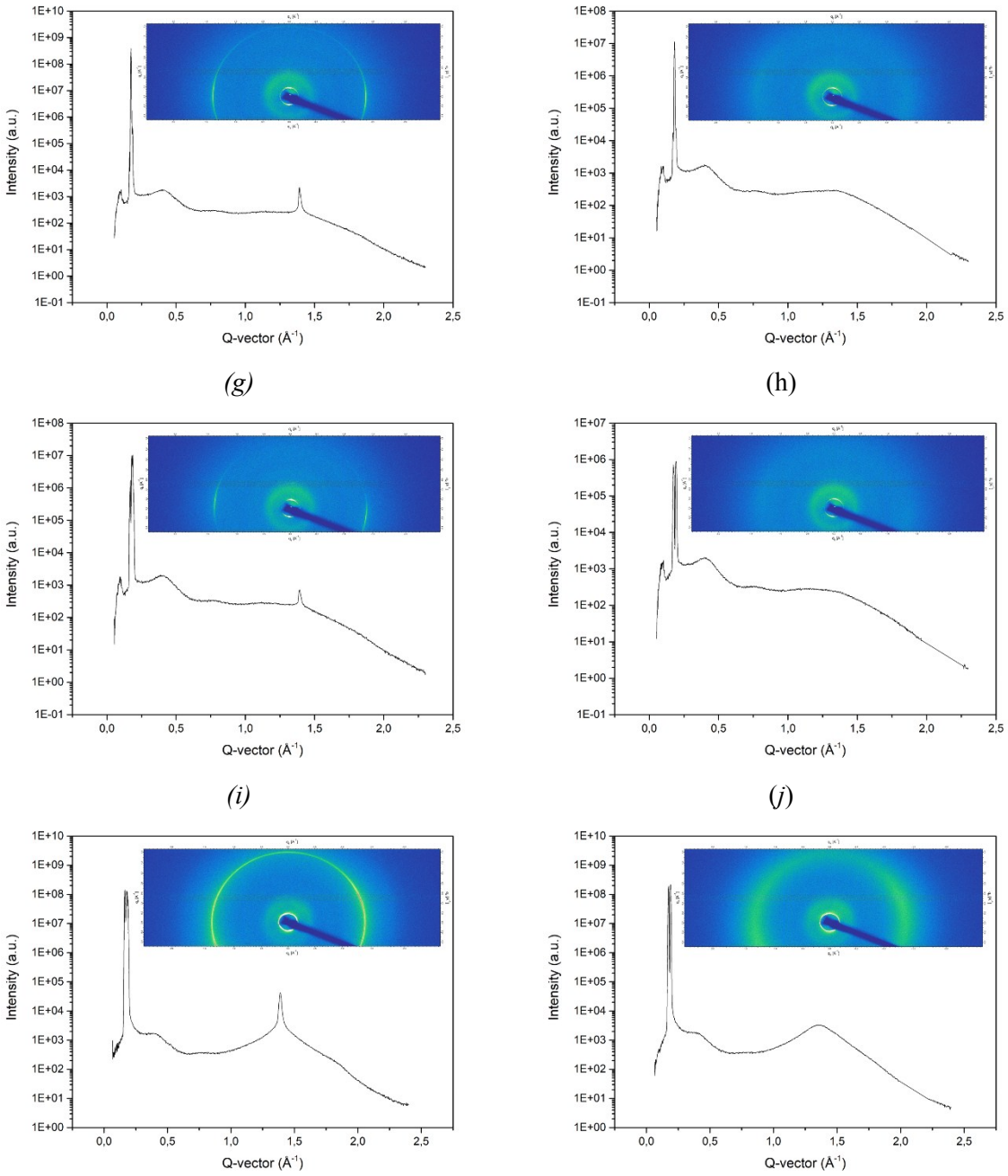



**Figure 3.2** 1D and 2D WAXS data: **c3** (in $\mathbf{Sm_B}$ (g) and $\mathbf{Sm_A}$ (h) mesophase), **c4** (in $\mathbf{Sm_B}$ (i) and $\mathbf{Sm_A}$ (j) mesophase), and **c5** (in $\mathbf{Sm_B}$ (k) and $\mathbf{Sm_A}$ (l) mesophase). $\mathbf{Sm_B}$ is represented at 85°C, and $\mathbf{Sm_A}$ at 115°C.

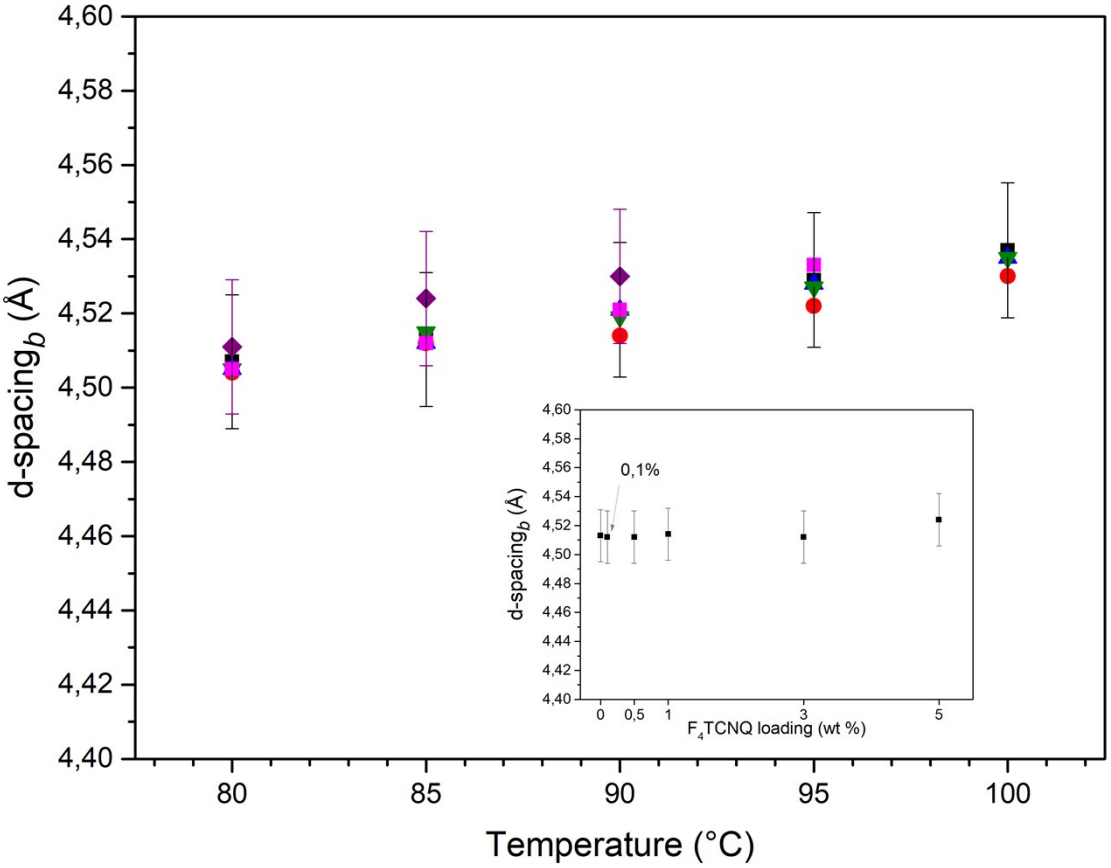



**Figure 3.3** Pseudo-hexagonal order spacing in $\mathbf{Sm_B}$ mesophase as a function of temperature. Black squares correspond to pure **8-PNP-O12**, red circles – **c1**, blue triangles – **c2**, green triangles – **c3**, magenta squares – **c4**, purple diamonds – **c5**, respectively. Inset: intermolecular $\mathbf{Sm_B}$ spacing as a function of $\mathbf{F_4TCNQ}$ content at 85°C.

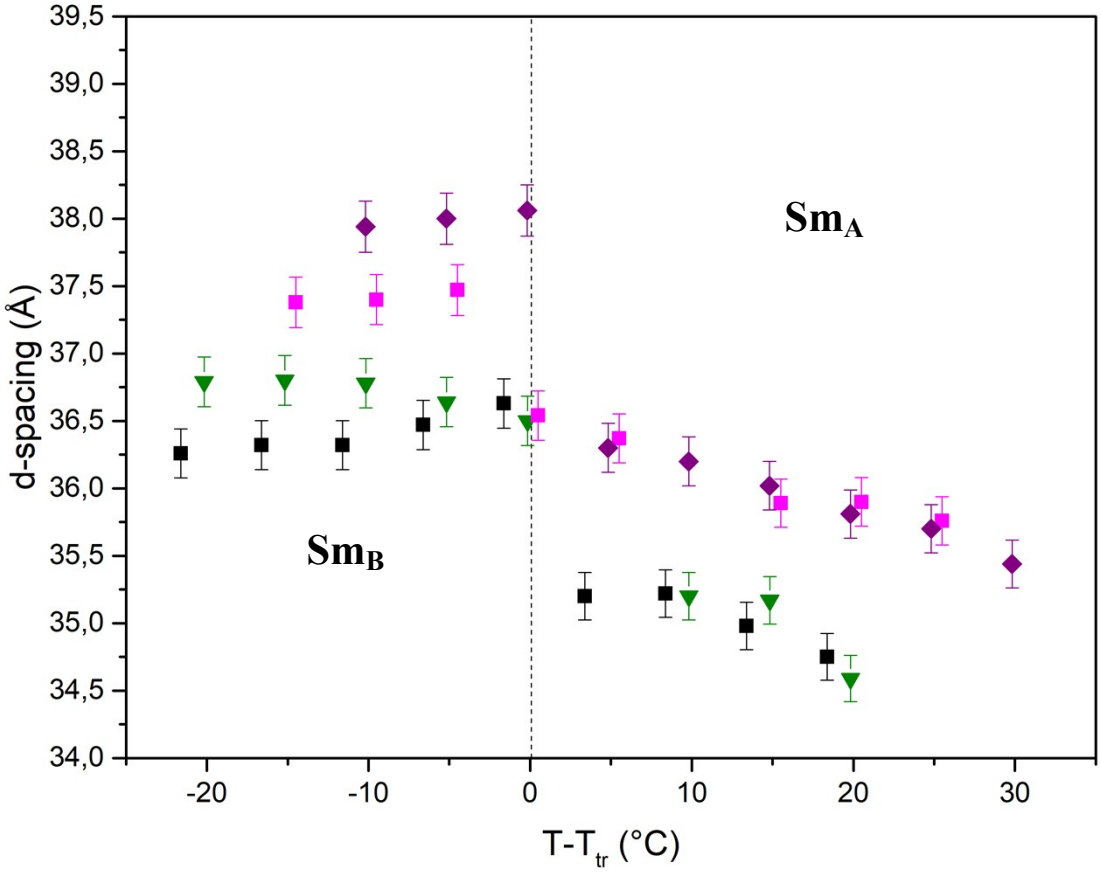



**Figure 3.4** Smectic layer spacing as a function of temperature relative in **$Sm_B$ and $Sm_A$** mesophases. Black squares correspond to pure **8-PNP-O12**, green triangles – **c3**, magenta squares – **c4**, purple diamonds – **c5**, respectively.

# Comparison of calculated bond lengths

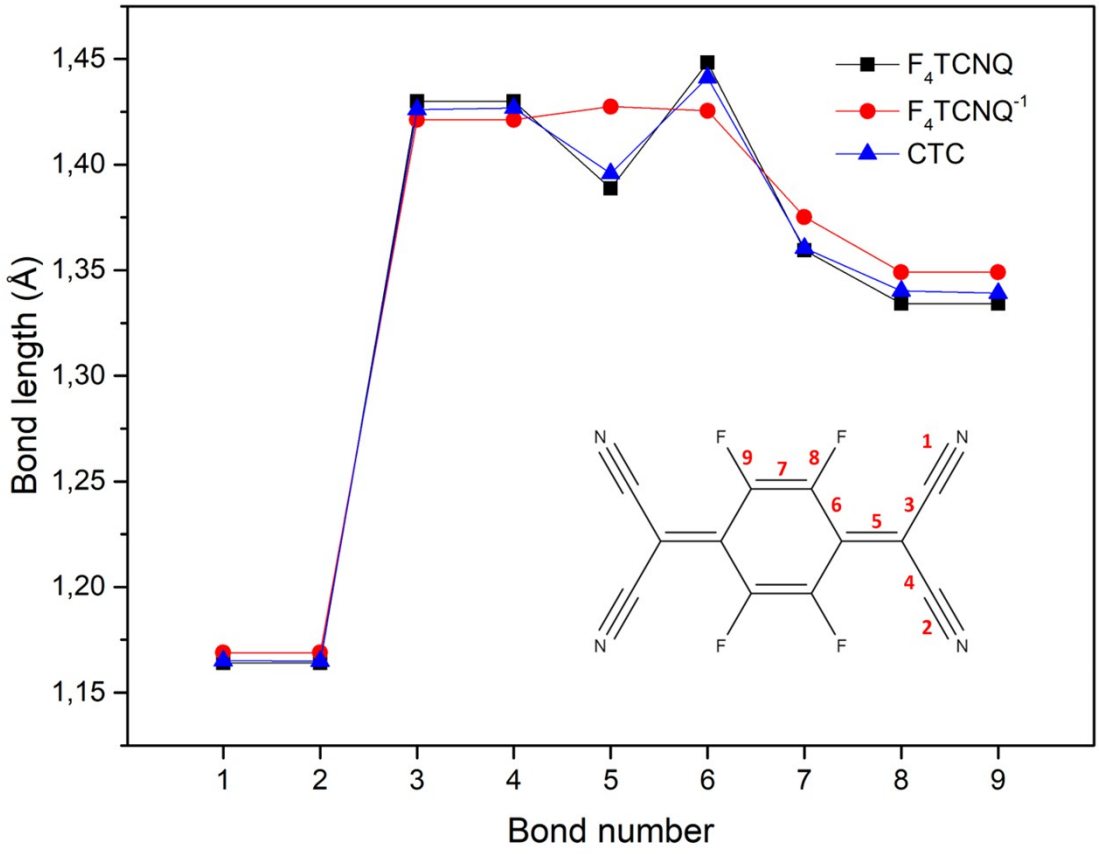



**Figure 4.1** Bond lengths calculated on B3LYP/6-31++G(d,p) level of theory for the isolated neutral **$F_4$TCNQ**, the anion **$F_4TCNQ^{-1}$** and the charge-transfer complex with **8-PNP-O12** (**CTC**).

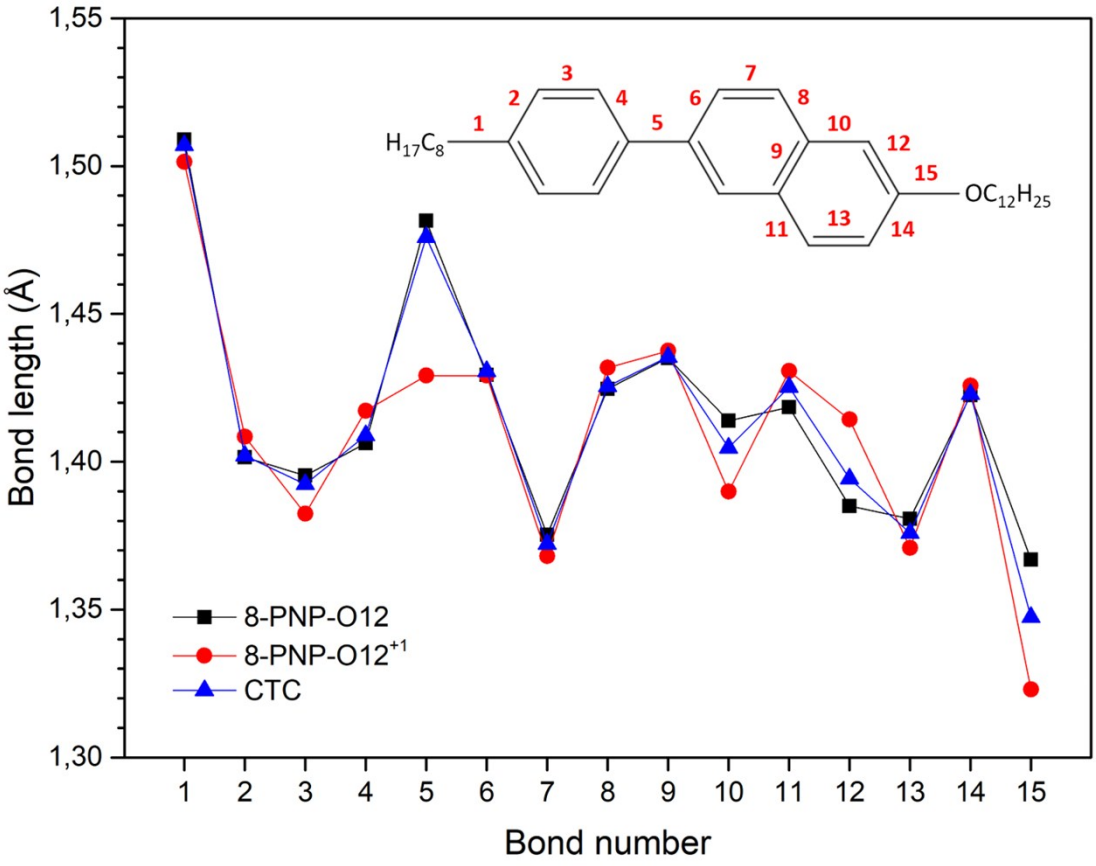



**Figure 4.2** Bond lengths calculated on B3LYP/6-31++G(d,p) level of theory for the isolated neutral **8-PNP-O12**, the cation **8-PNP-O12$^{+1}$** and the charge-transfer complex with **$F_4$TCNQ** (**CTC**).

# Comparison of Raman spectra before and after annealing

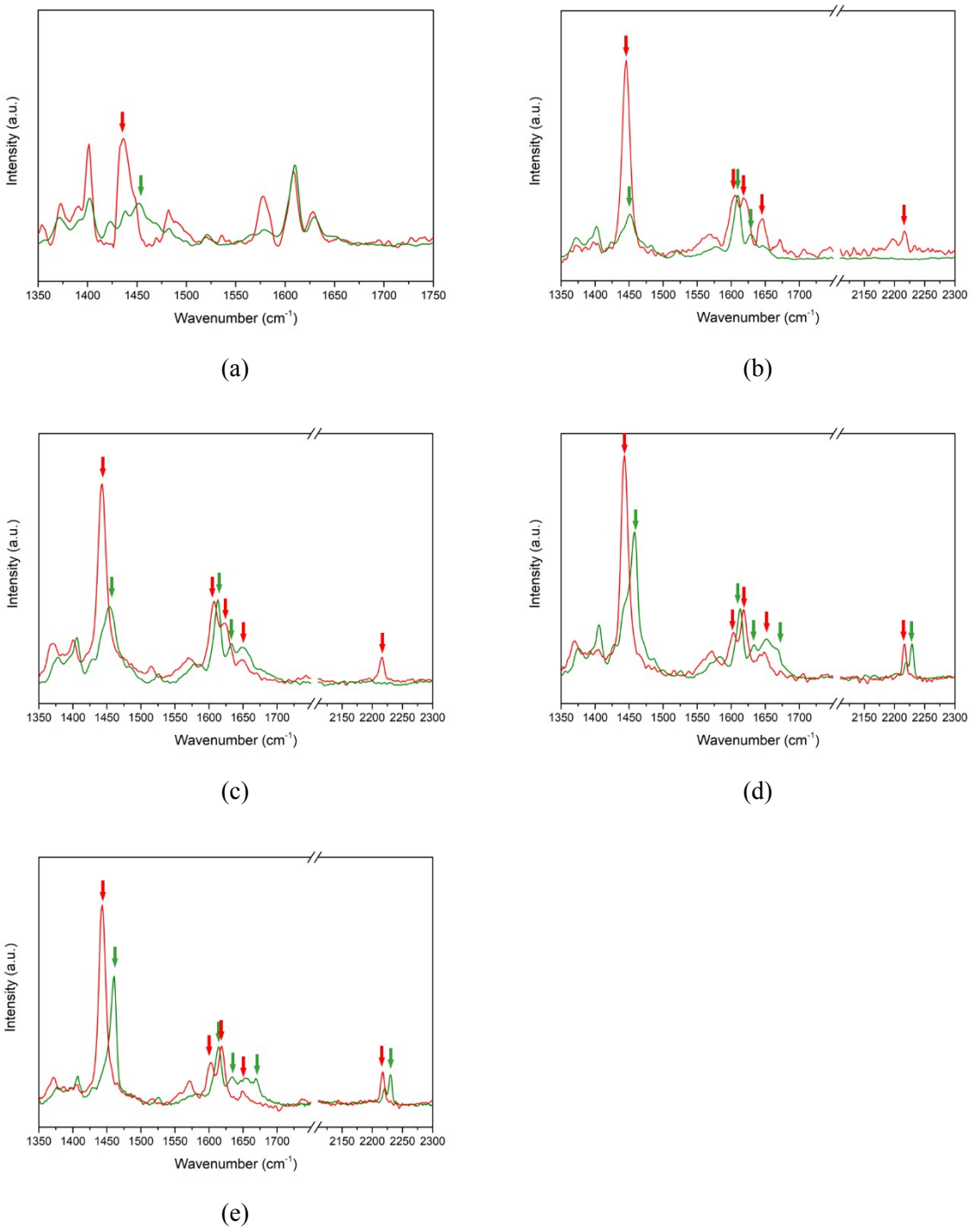



**Figure 5.** Room temperature Raman plots for as-prepared (green) and annealed (red) samples **c1** (a) **c2**(b), **c3** (c), **c4** (d) and **c5** (e). Green and red arrows indicate Raman bands shift for as-prepared and annealed samples, respectively.

# Transient photocurrent plots

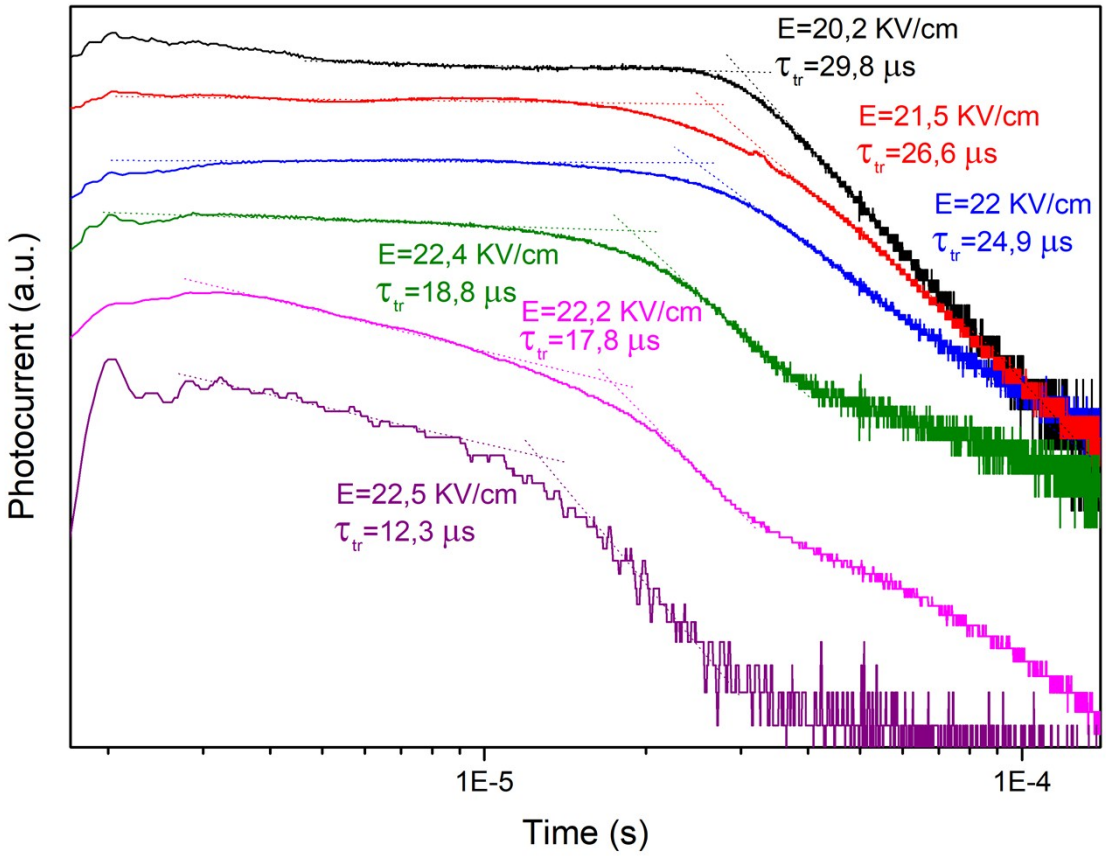



**Figure 6.1** Transient photocurrent plots recorded in $\mathbf{Sm_B}$ mesophase for pure **8-PNP-O12** (black), **c1** (red), **c2** (blue), **c3** (green), **c4** (pink) and **c5** (purple) composites.

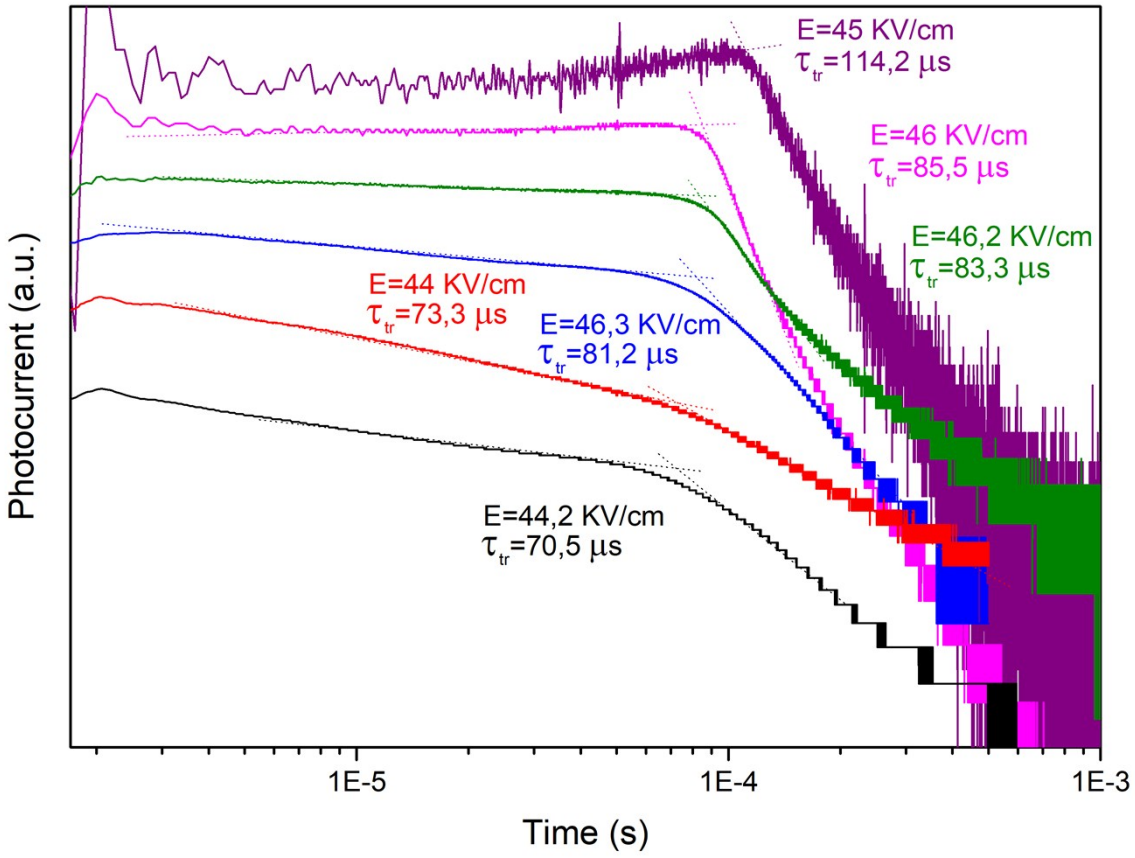



**Figure 6.2** Transient photocurrent plots recorded in $\mathbf{Sm_A}$ mesophase for pure **8-PNP-O12** (black), **c1** (red), **c2** (blue), **c3** (green), **c4** (pink) and **c5** (purple) composites.

# Current-voltage plot

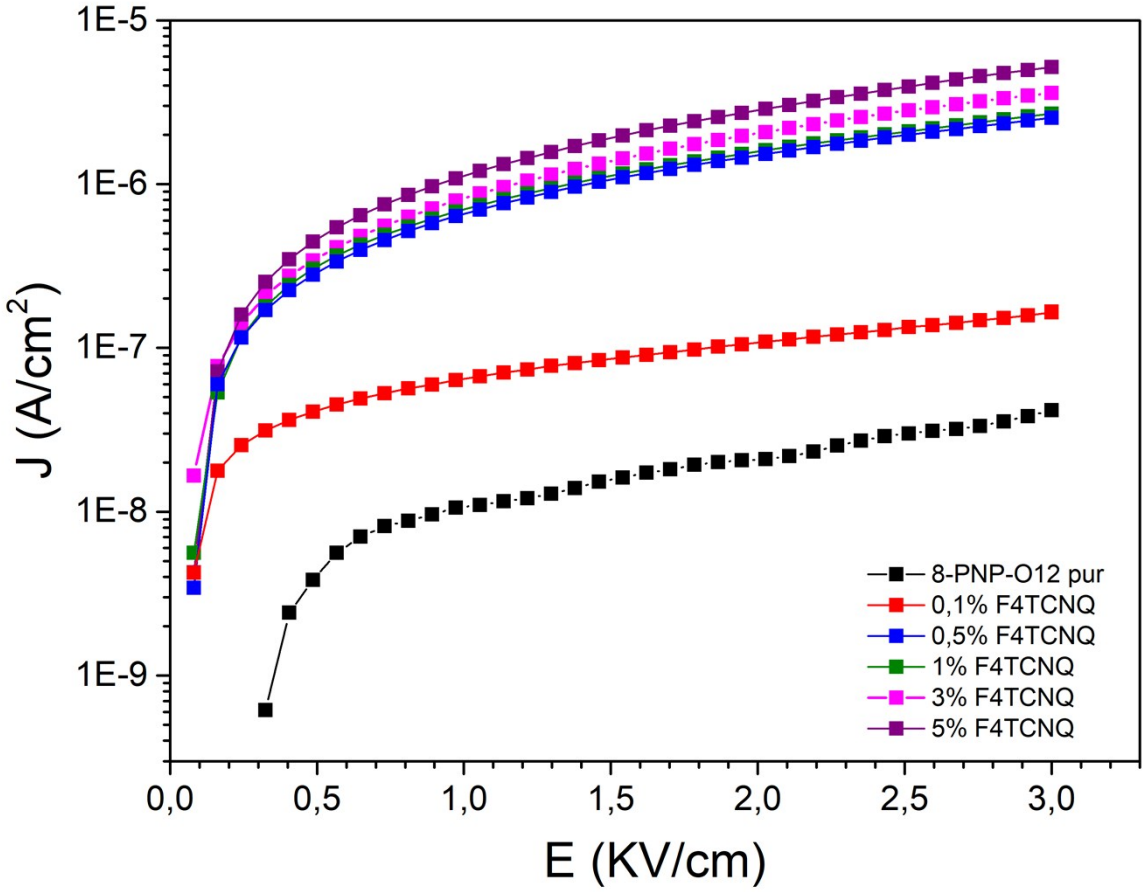



**Figure 7.1.** Current-voltage characteristic of composites sandwiched between **Au** and **ITO** electrodes recorded in crystalline phase for pure **8-PNP-O12** (black), **c1** (red), **c2** (blue), **c3** (green), **c4** (pink) and **c5** (purple) composites.

# Conductivity plot

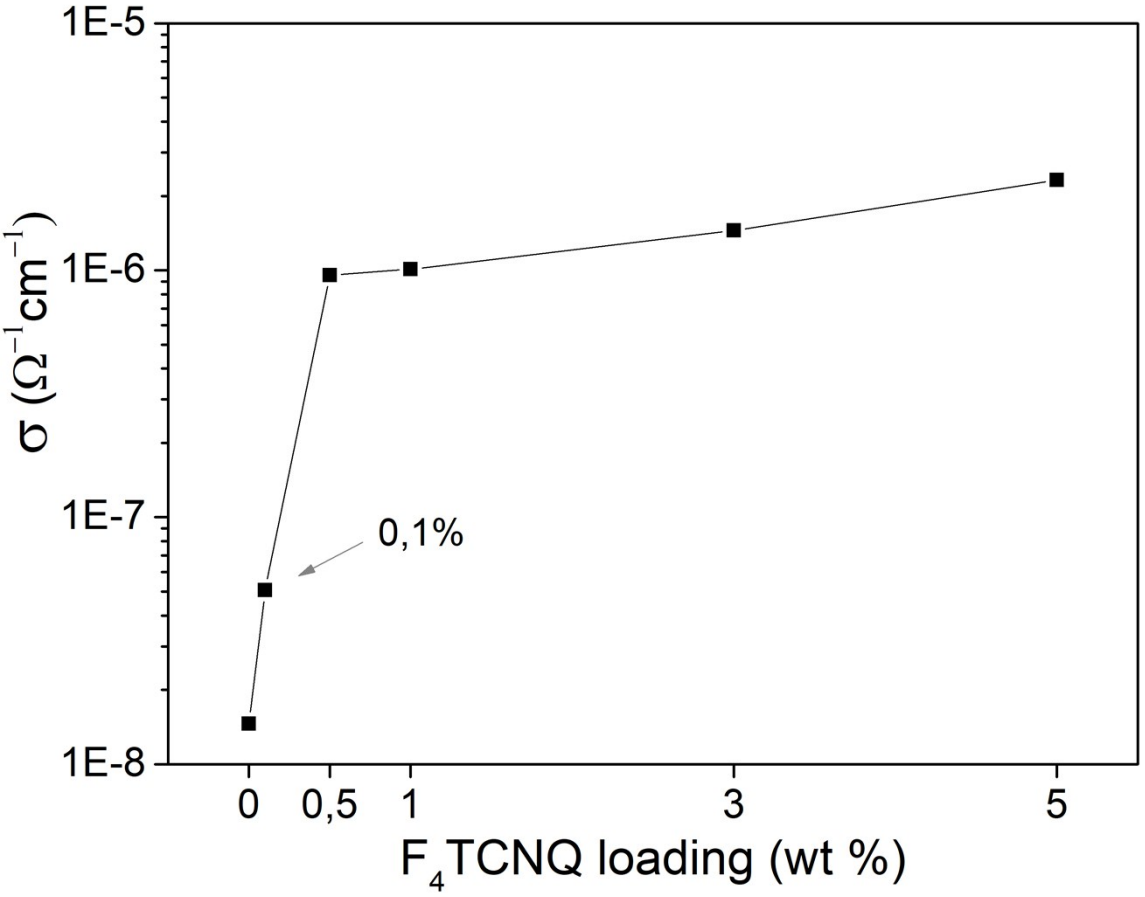



**Figure 7.2.** Conductivity of composites extracted from current-voltage plot at 85°C.

# Smectic layer with dopant

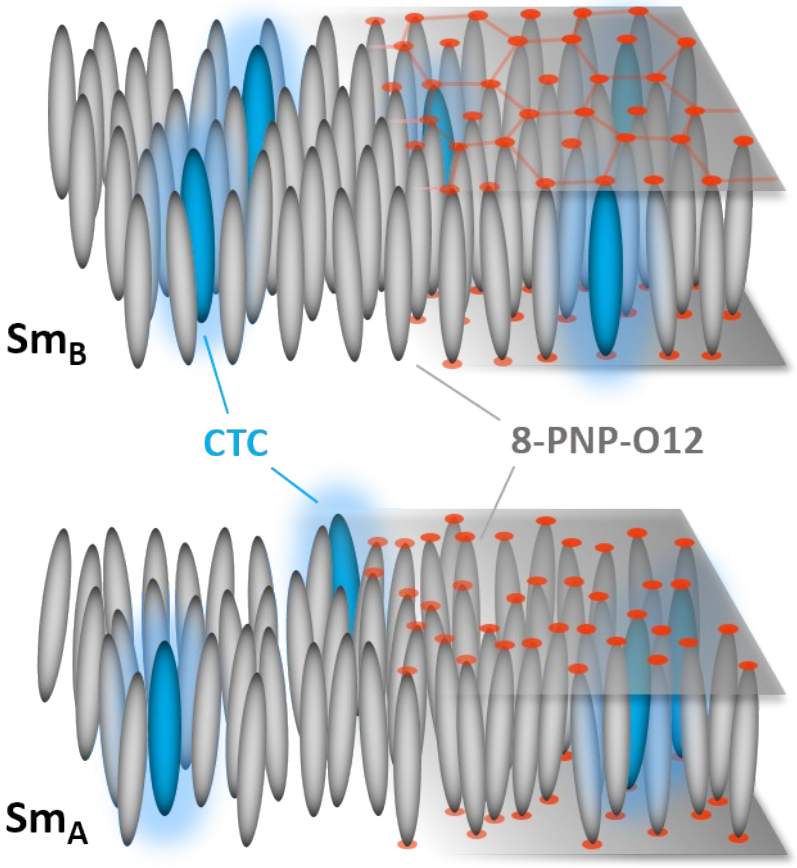



**Figure 8.** Schematic representation of possible **CTC** distribution in a smectic layer of corresponding mesophase of **8-PNP-O12**.