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Introduction and Objective

❖ Ferroelectric liquid crystals (FLCs), has emerged as a class of smart functional materials in the field of high-end applications ranging from tunable lasers, spatial modulators to fast electro optical switching devices. The design of such molecules has a profound impact both in terms of performance as well as their applicability in modern technological gadgets [1].

❖ Moreover, chiral molecules exhibiting the ferroelectric phase show advanced properties in relation to their fast switching speed and bistability. Therefore, it becomes imperative to deeply probe the static and dynamic aspects of such chiral molecules in relation to their *molecular structure-physical property* behaviour [2].

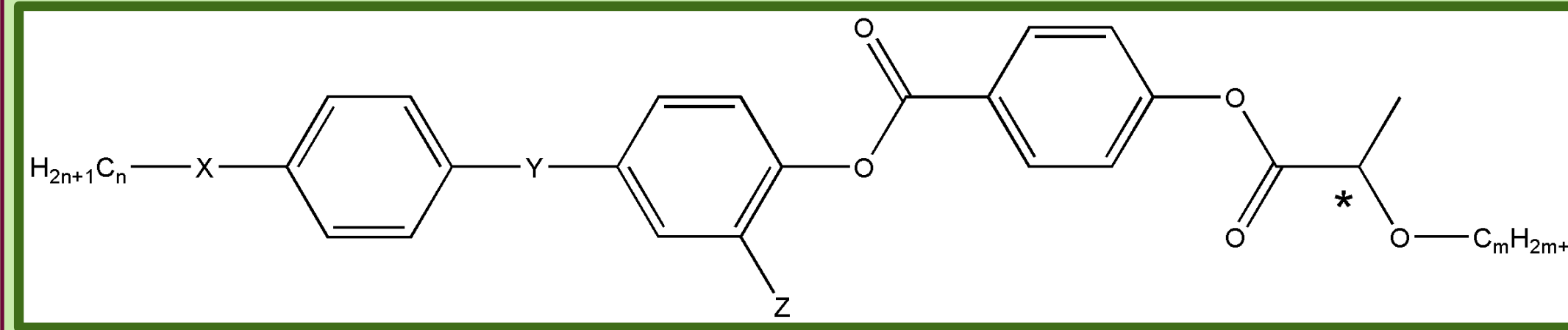
❖ The *main objective* of this work is to study some binary mixtures of chiral FLCs in order to contribute to better understanding of some *physical properties* which can be used for design of smart multifunctional liquid crystalline devices associated with optoelectronic and photonic applications.

❖ In order to accomplish the objective, the dielectric permittivity, dielectric anisotropy, electro-optical parameters like spontaneous polarisation, response time, torsional bulk viscosity and also the broad band dielectric spectroscopy of all the investigated **chiral FLC mixtures** has been measured and discussed. The activation energy of the studied samples and the nature of the phase transition have also been investigated [2,3].

Materials under investigation

❑ Materials of three structurally similar series, denoted as **QM n/m, E n/m** and **QVE n/m**, which were used as pure compound for the study (see Table 1).

Table 1. General structure of the investigated samples



| Compound | n | m | X | Y | Z |
|----------|----|----|-------|-------|------------------|
| QM 12/9 | 12 | 9 | -O- | -COO- | H |
| E 8/7 | 8 | 7 | -OCO- | -OCO- | H |
| E 6/10 | 6 | 10 | -OCO- | -OCO- | H |
| E 10/10 | 10 | 10 | -OCO- | -OCO- | H |
| E 8/12 | 8 | 12 | -OCO- | -OCO- | H |
| QVE 8/5 | 8 | 5 | -O- | -OCO- | OCH ₃ |

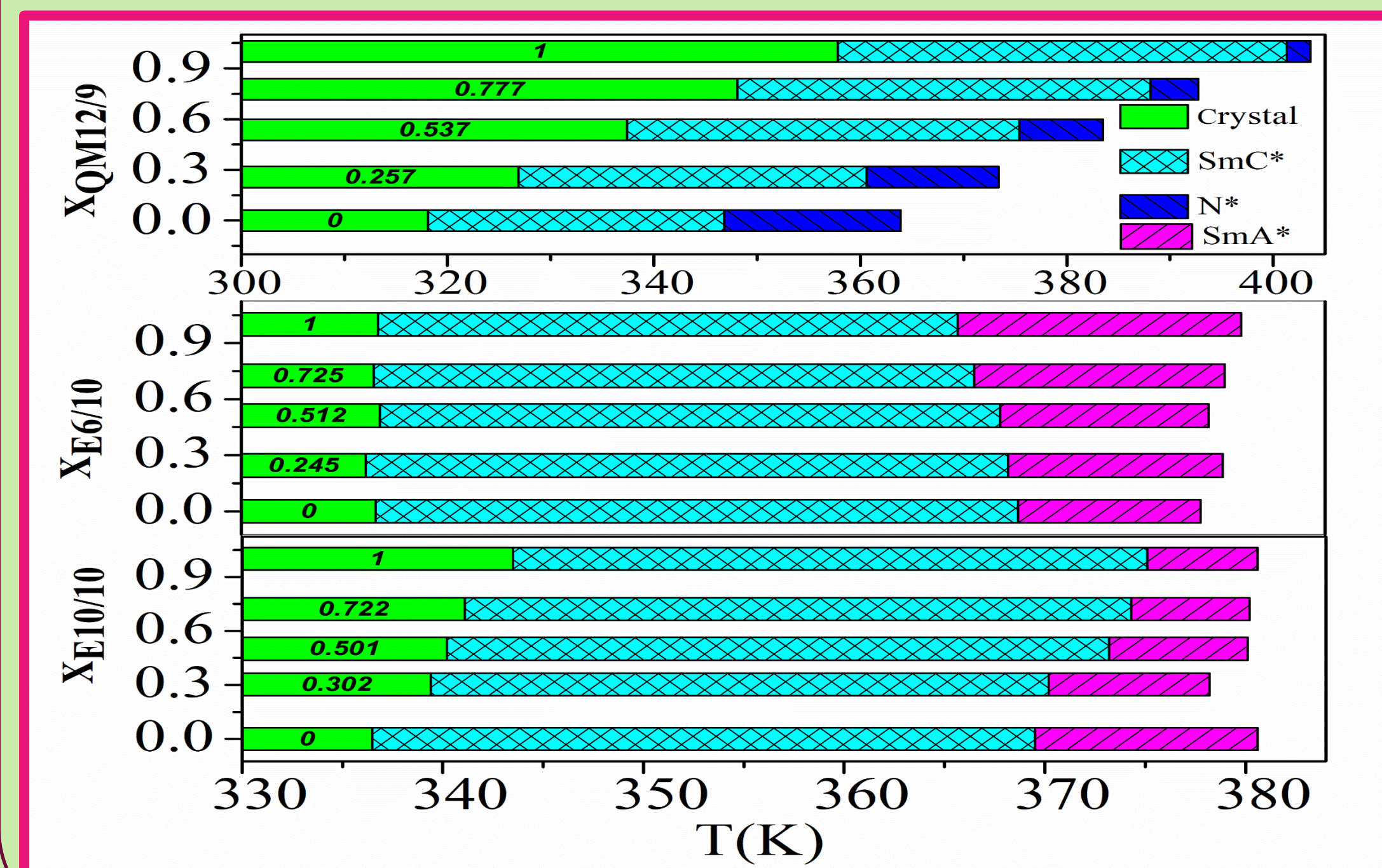
❑ The pure compounds differ in (i) their length of hydrocarbon chain in both chiral and non-chiral part (ii) the type of linking group in the core structure. In the molecular structure **n** represents the alkyl chain length in the non-chiral part and **m** denotes the alkoxy chain length associated with the chiral part, **X** denotes the linking group of the alkyl chain length with the first aromatic ring and **Y** is the linking group between the 1st and 2nd aromatic ring, the lateral substitution is denoted by **Z**. Total nine binary mixtures have prepared by using these pure chiral FLC compounds [2,3].

Results and discussions

➤ A polarising optical microscope (BANBROS) equipped with INSTEC HCS302 hot stage, the temperature of which was controlled by INSTEC mK 1000 Thermo system with an accuracy $\pm 0.001K$ has been used for observing the sequence of phases and their transition temperatures.

➤ A precision digital LCR bridge (Agilent 4294A) with a relative accuracy of $\pm 1\%$ and Indium Tin Oxide (ITO) coated cells (4.9 μm thick) supplied by AWAT company, Warsaw, Poland has been used for electro optic and dielectric measurements [2,3].

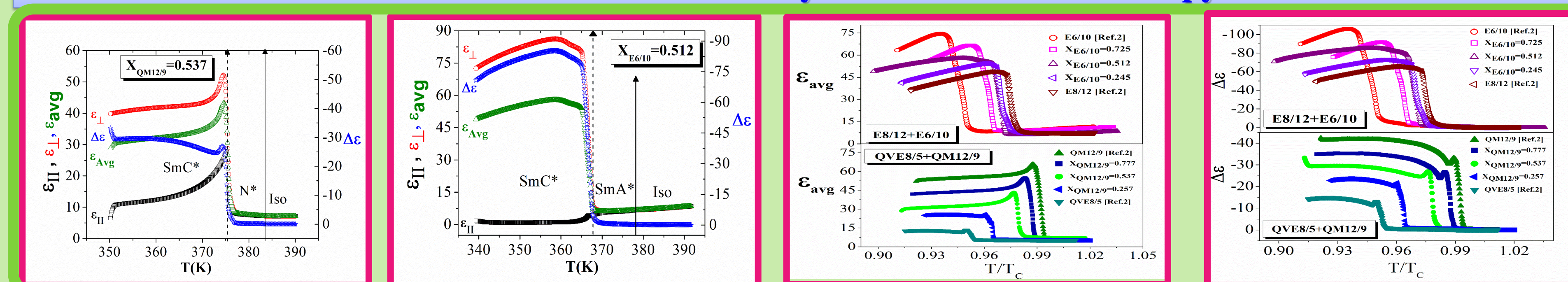
Table 2. Sequence of phases (Ph) and phase transition temperatures (K) measured on cooling; for all the studied mixtures



Experimental Results

Electro-optic properties

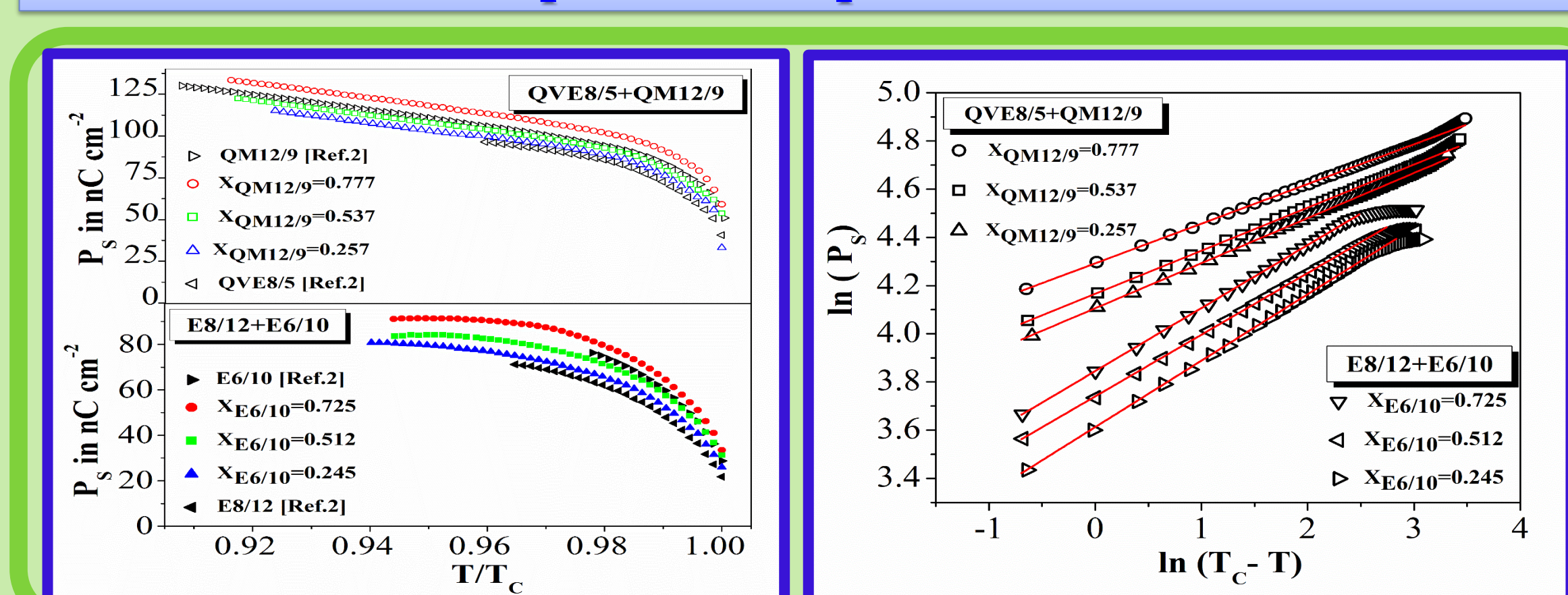
Static Dielectric Permittivity and Dielectric Anisotropy



❑ The temperature dependence of parallel and perpendicular components of static permittivities ($\epsilon_{||}$ and ϵ_{\perp}), their average values (ϵ_{avg}) and dielectric anisotropy ($\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp}$) for all the studied mixtures shows similar trend but possess different values.

❑ All the studied binary mixtures exhibit negative dielectric anisotropy with a considerable increase of ϵ_{\perp} with respect to $\epsilon_{||}$ near phase transition which may arise due to the transverse dipole moment of the polar linking ester groups which enhances the dielectric permittivity perpendicular to the molecular long axis.

Spontaneous polarisation



❖ The Spontaneous polarisation (P_s) values for all the studied mixtures shows similar nature as that of the pure compounds but with different values. From the Arrhenius plot, the values of the spontaneous polarisation critical exponent β has been determined from the slope of the first order polynomial fit of the plots. The β values clearly indicates the **second order nature** of the **SmA*-SmC*** and **N*-SmC*** phase transitions.

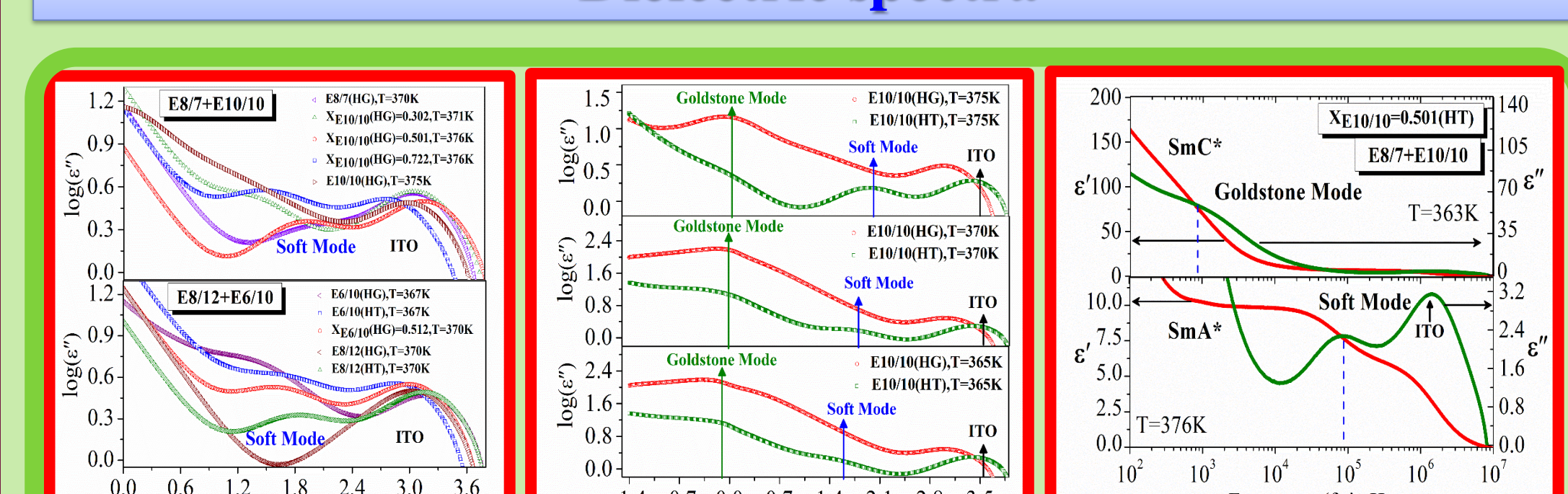
Table 3. Fitted parameters P_0 , T_c and exponent β of experimental spontaneous polarisation for all the investigated FLC mixtures

| $X_{QM12/9}$ (QVE8/5+QM12/9) | P_0 (nCcm ⁻²) | T_c (K) | exponent β |
|---------------------------------|-----------------------------|-----------|-------------------|
| 0.257 | 60.64 \pm 0.001 | 360.6 | 0.325 \pm 0.002 |
| 0.537 | 64.39 \pm 0.003 | 375.4 | 0.319 \pm 0.005 |
| 0.777 | 73.12 \pm 0.005 | 388.1 | 0.295 \pm 0.006 |

| $X_{E6/10}$ (E8/12+E6/10) | P_0 (nCcm ⁻²) | T_c (K) | exponent β |
|------------------------------|-----------------------------|-----------|-------------------|
| 0.245 | 37.04 \pm 0.002 | 368.2 | 0.320 \pm 0.005 |
| 0.512 | 42.09 \pm 0.005 | 367.8 | 0.322 \pm 0.002 |
| 0.725 | 46.75 \pm 0.003 | 366.5 | 0.299 \pm 0.001 |

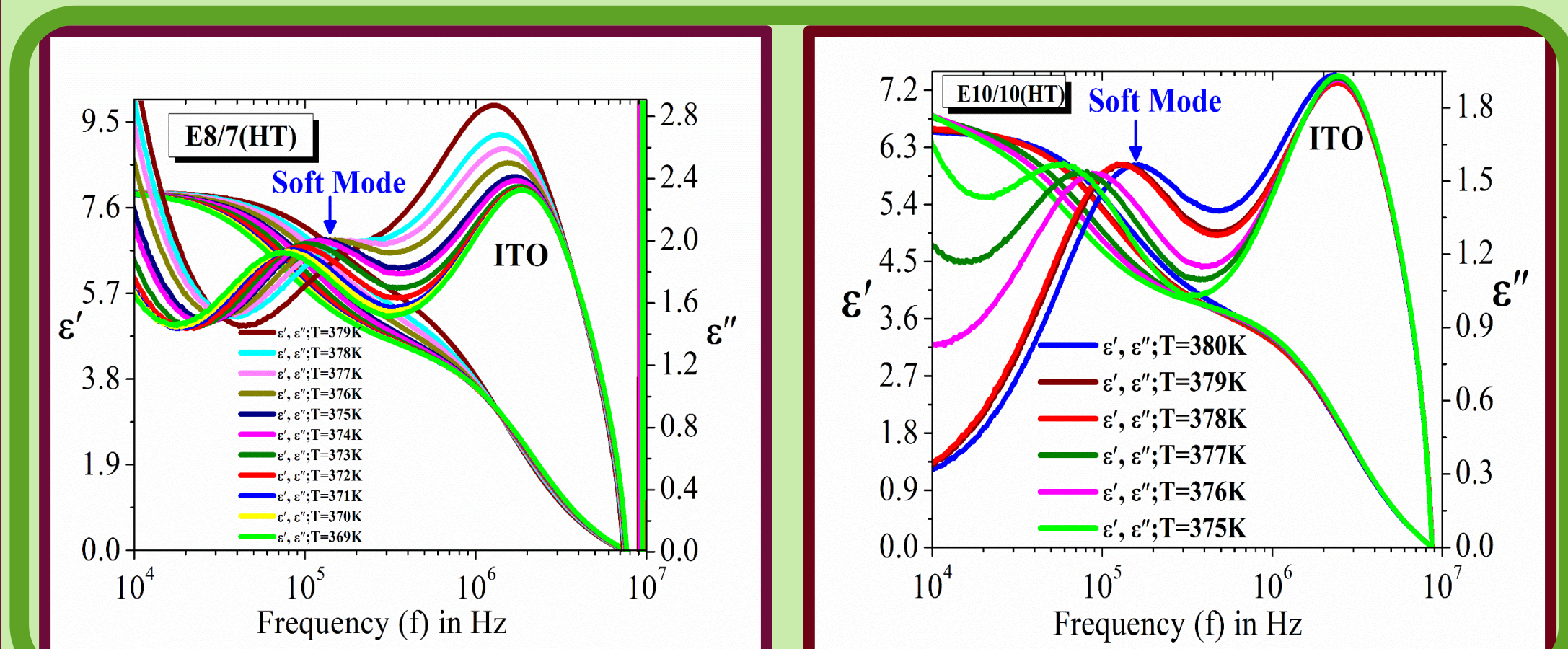
Dielectric properties

Dielectric spectra

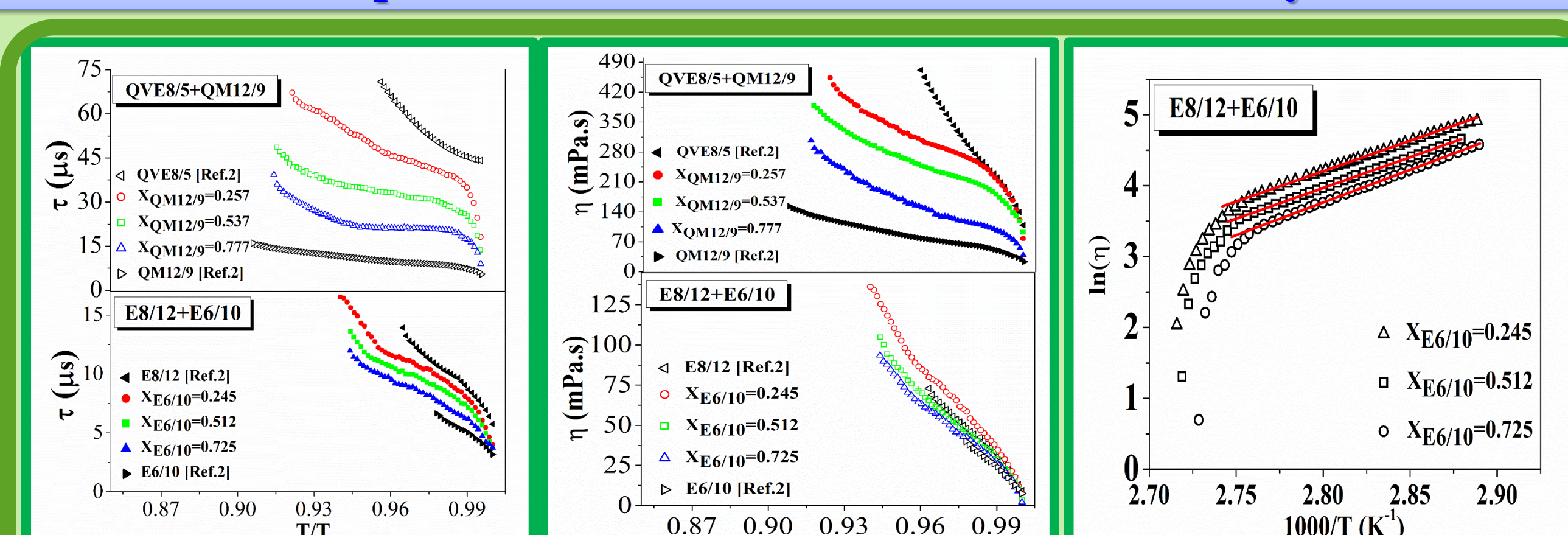


• The **Soft Mode** can be easily detectable by using the Homeotropically aligned (HT) cell for the studied samples. The **Goldstone Mode** is observed in the SmC* phase and the **Soft Mode** is observed in the SmA* phase.

• The strength of the **Goldstone Mode** in the SmC* phase is large enough as compared to the **Soft Mode** in the SmA* phase. The **Goldstone Mode** arises due to the tilt angle fluctuation in lower frequency region and the **Soft Mode** appears due to the director fluctuation in the high frequency regime. Another peak is observed in the high frequency (~few MHz) region due to the ITO effect of the cells.



Response Time and Torsional bulk viscosity

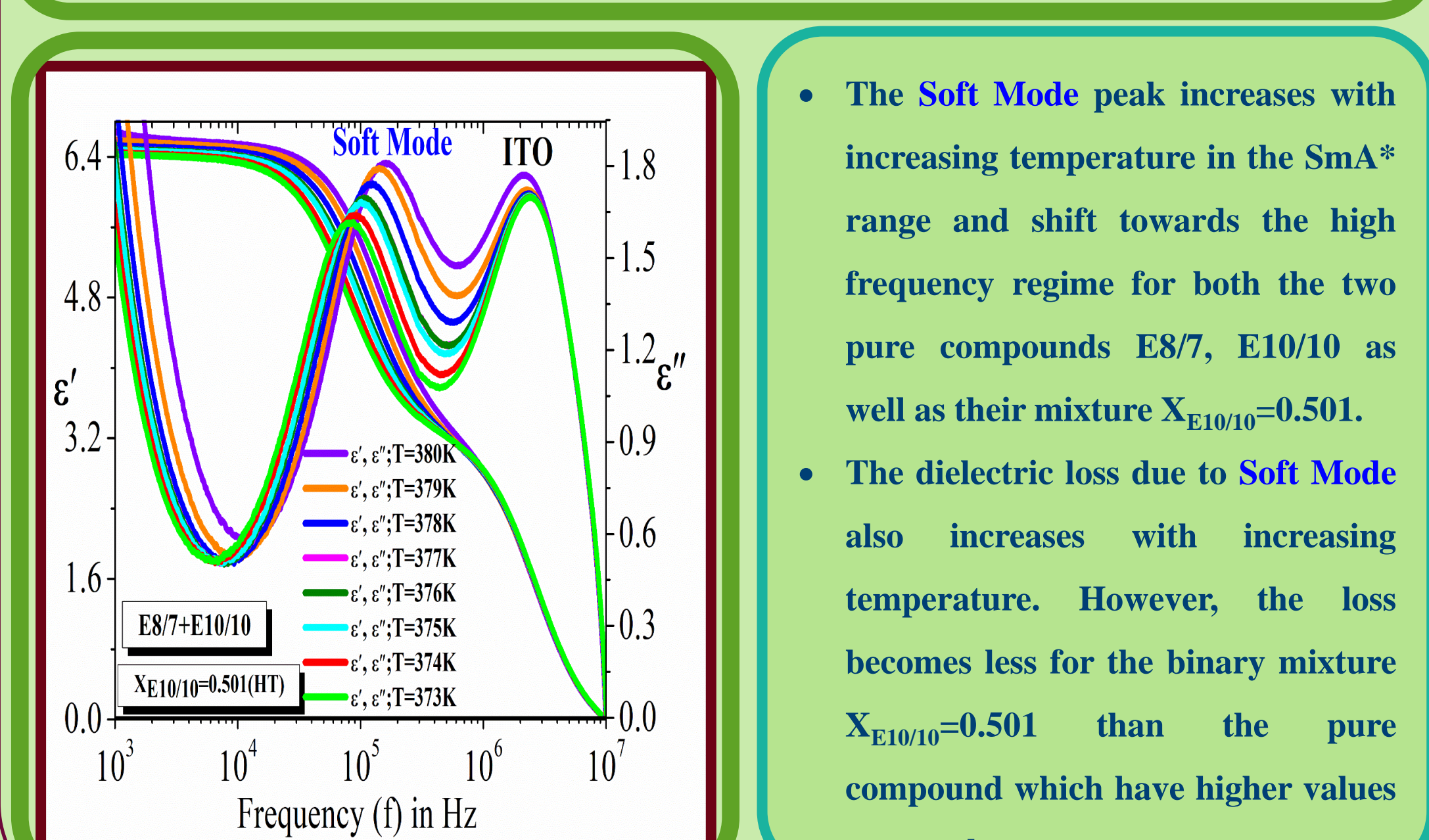


❖ The torsional bulk viscosity arises due to the twisting of the molecules, which plays an important role in understanding the dynamical behaviour of FLC systems. The activation energy of all the studied FLC mixtures has been determined from the best fitting of the Arrhenius plot. Response time (τ) is an important parameter responsible for the switching effect in FLC devices. The lower value of τ gives high speed electro-optic response which can be utilised to develop high-definition moving pictures. For all the investigated mixtures the response time lies in between **5-75 μs** ; which is useful for fast switching electro-optical devices.

Table 4. Activation energy of the investigated binary mixtures

| $X_{QM12/9}$ | Activation Energy (eV) |
|--------------|------------------------|
| 0.257 | 0.263 |
| 0.537 | 0.282 |
| 0.777 | 0.450 |

| $X_{E6/10}$ | Activation Energy (eV) |
|-------------|------------------------|
| 0.245 | 0.739 |
| 0.512 | 0.747 |
| 0.725 | 0.793 |



• The **Soft Mode** peak increases with increasing temperature in the SmA* range and shift towards the high frequency regime for both the two pure compounds E8/7, E10/10 as well as their mixture $X_{E10/10}=0.501$.

• The dielectric loss due to **Soft Mode** also increases with increasing temperature. However, the loss becomes less for the binary mixture $X_{E10/10}=0.501$ than the pure compound which have higher values among them.

CONCLUSIONS

❖ Relatively broad temperature range and high thermal stability of the ferroelectric SmC* phase and paraelectric SmA* phase, low viscosity, large spontaneous polarization, negative dielectric anisotropy and very low response time, for all the studied mixtures makes them as a promising candidate in the new smart multicomponent FLC mixtures for application in photonic as well as for fast switching Electro-Optic devices.

Acknowledgements

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References

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