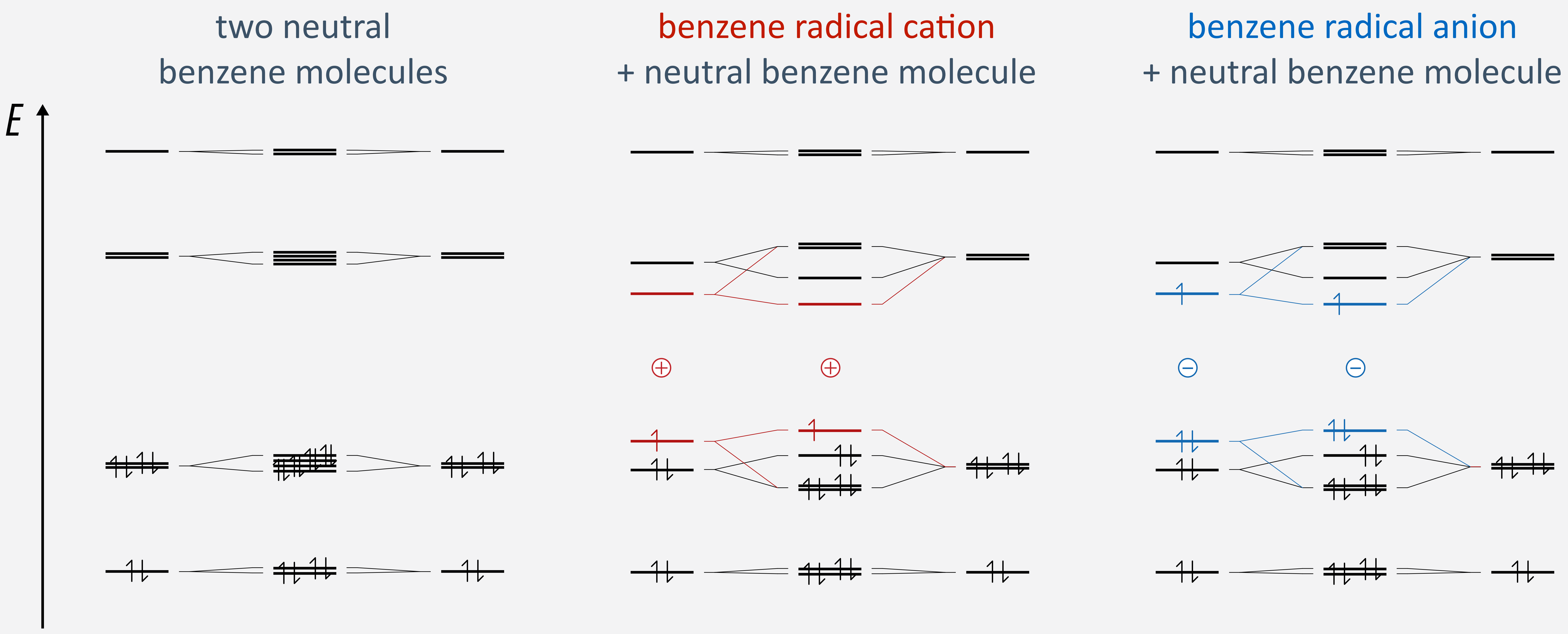
5.3 Charges in Organic Materials

Intermolecular Delocalization of a Polaron Defect

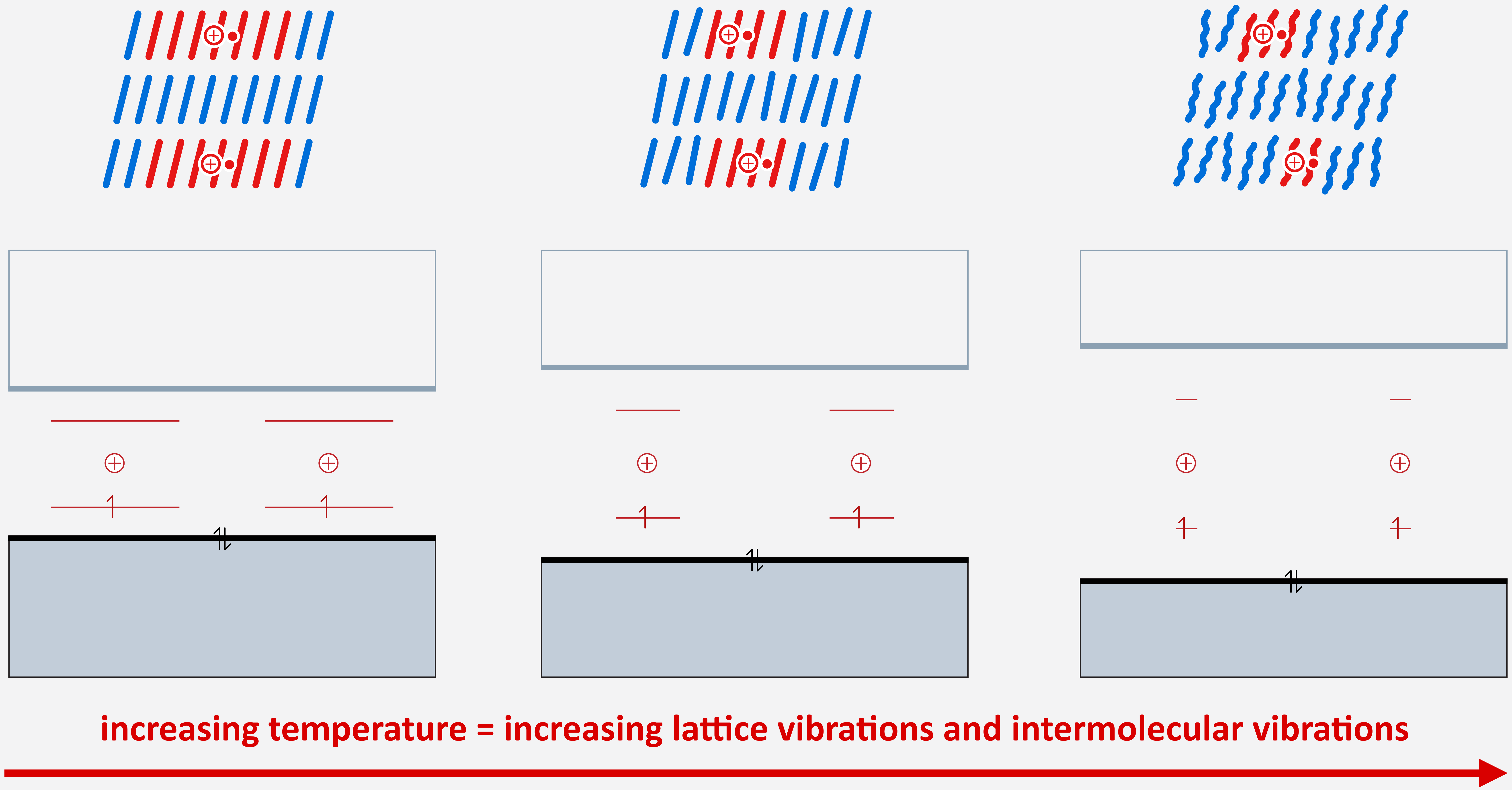
- π-π stacking between neutral molecules results in HOMO splitting and LUMO splitting
- overall electron energies increase, π–π stacking favorable due to other interactions



- **π-π stacking between polarons and neutral molecules has charge-transfer character**
- **electronic interactions energetically more favorable and stronger, higher correlation**
- **π-π stacking results in intermolecular delocalization of the charge over several molecules**

Delocalization and Dynamic Disorder in the Solid State

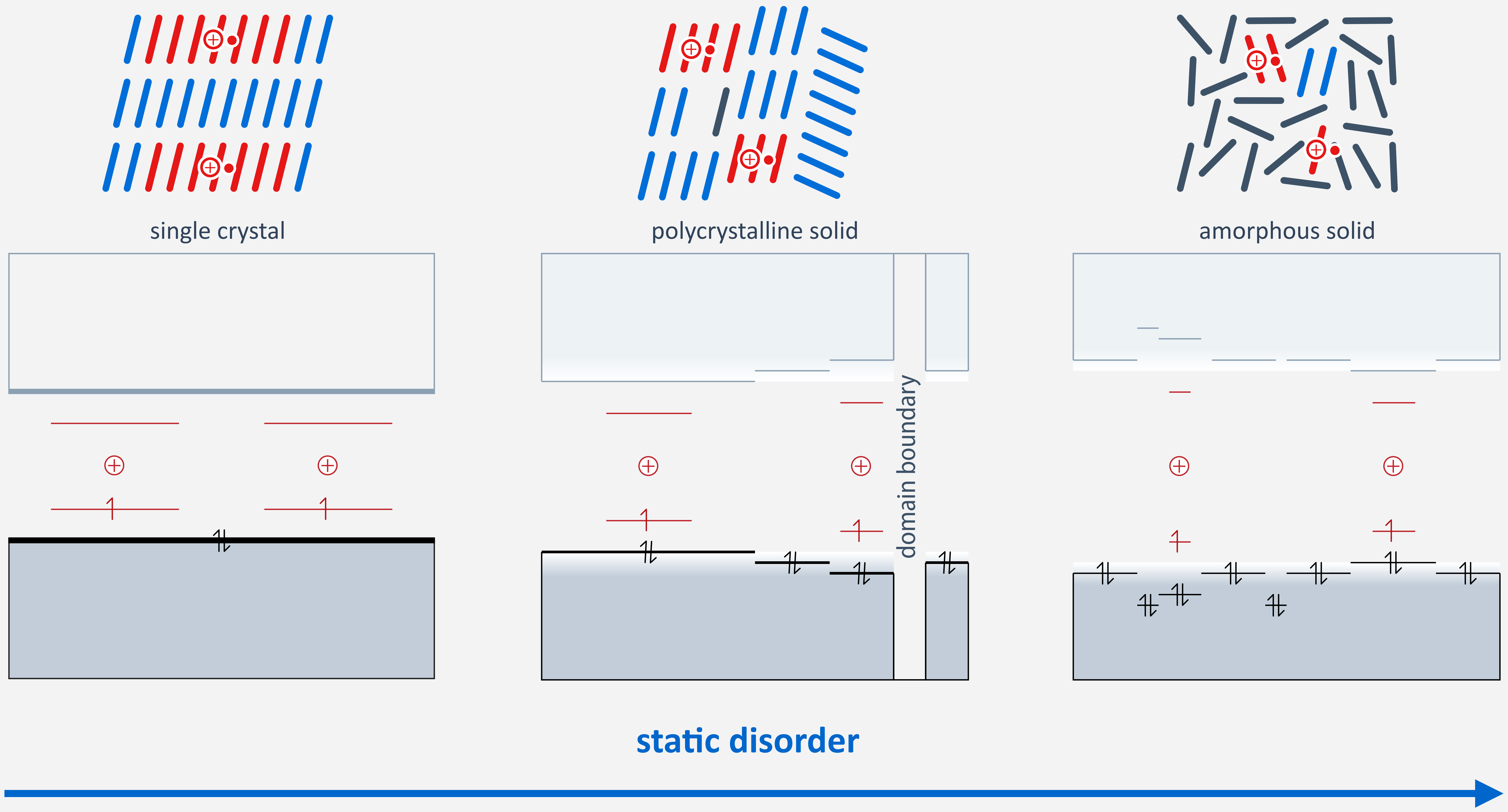
- intermolecular delocalization decreased by (supra)molecular motions in the solid state



- **dynamic disorder increases, charge carriers more localized with increasing temperature**
- **band gap and also distance between valence/conduction band and polaron levels increase**

Delocalization and Static Disorder in the Solid State (Crystals)

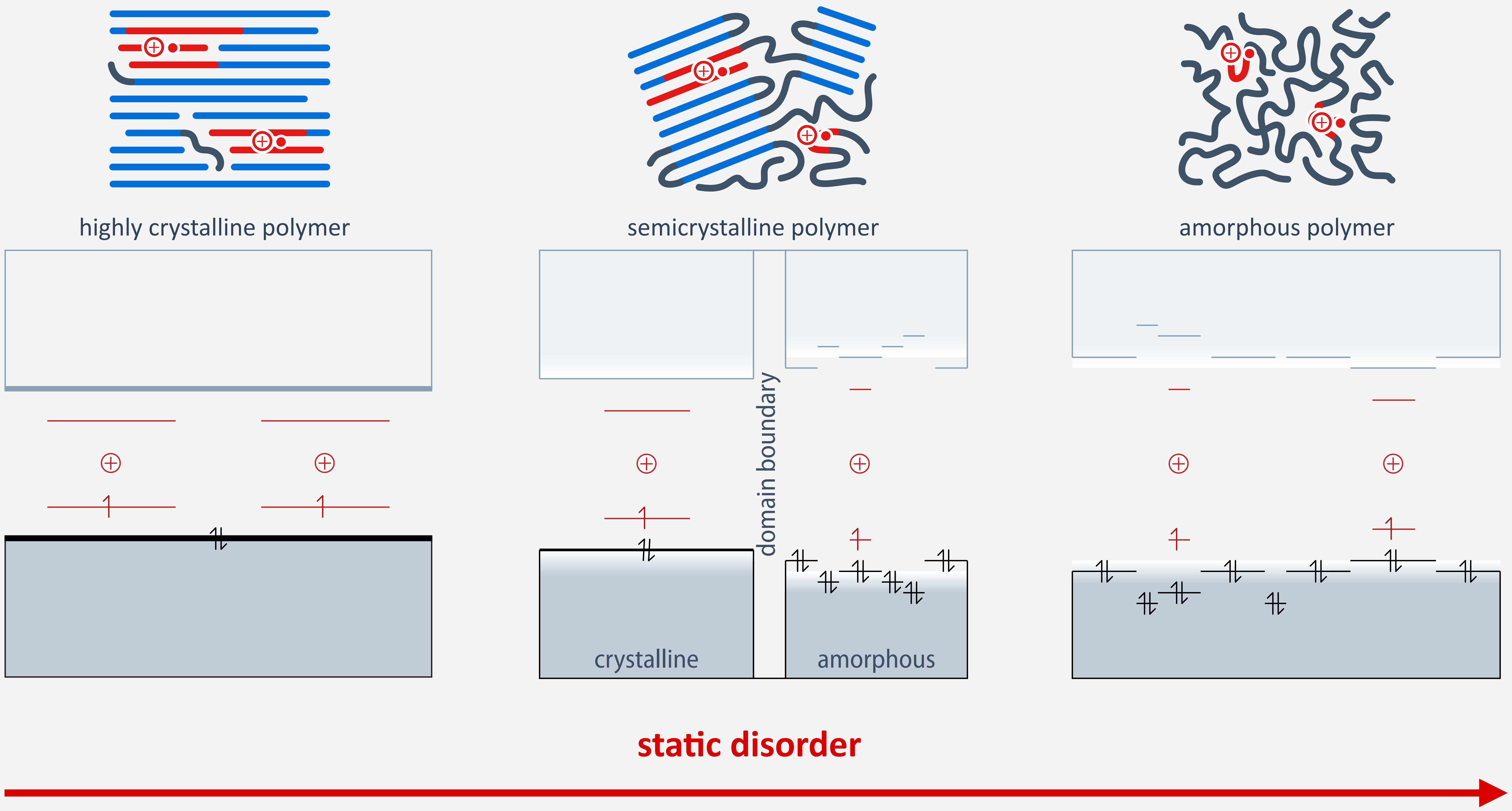
- intermolecular delocalization decreases with decreasing crystallinity and crystalline order



- **charge carriers more localized with increasing static disorder**
- **heterogeneity includes packing defects, lattice disorder, grain & domain boundaries, impurities, …**

Delocalization and Static Disorder in the Solid State (Polymers)

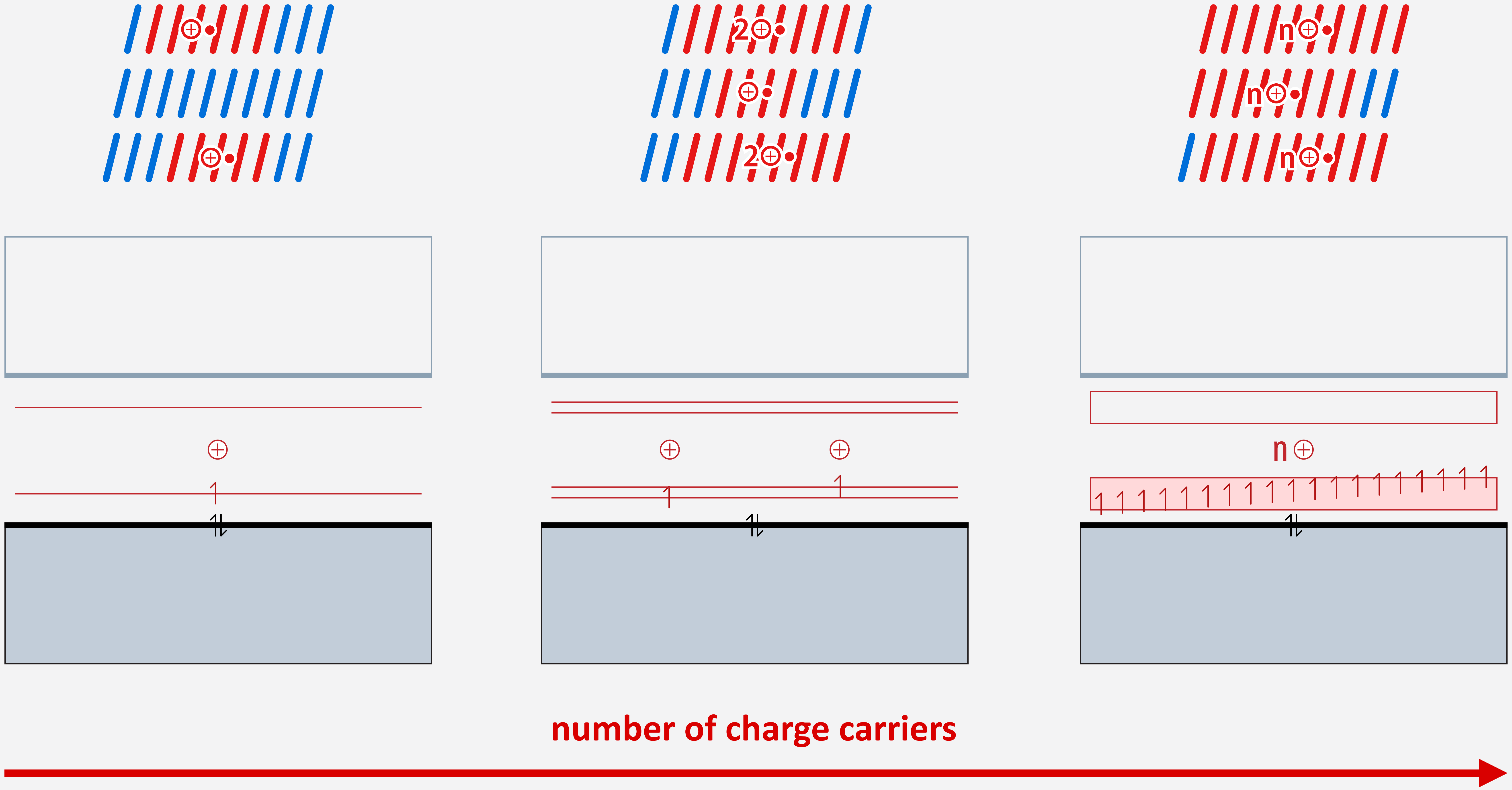
- intermolecular delocalization decreases with decreasing crystallinity and crystalline order



- **charge carriers more localized with increasing static disorder**
- **static disorder includes decreased size of crystalline domains, defects etc. in both phases**

Crystalline Organic Materials at High Charge Carrier Densities

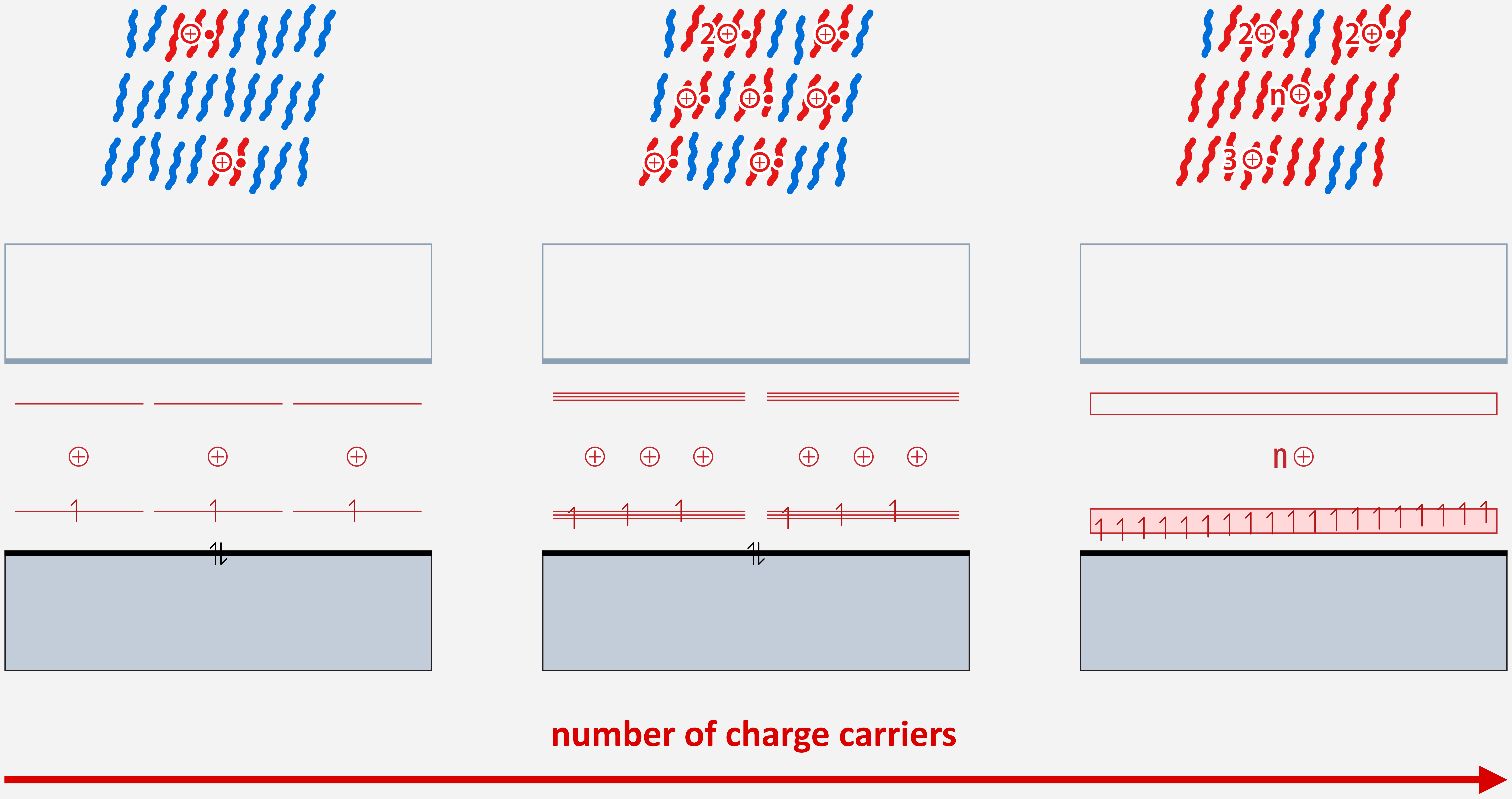
- at high doping levels, the polaron defect states start to interact with one another



- **at doping of >1/1000 molecules, polaron every 1/10 molecules along any lattice direction**
- **interaction of defect states results in MO splitting and formation of a narrow polaron band**

Effect of Disorder at High Charge Carrier Densities

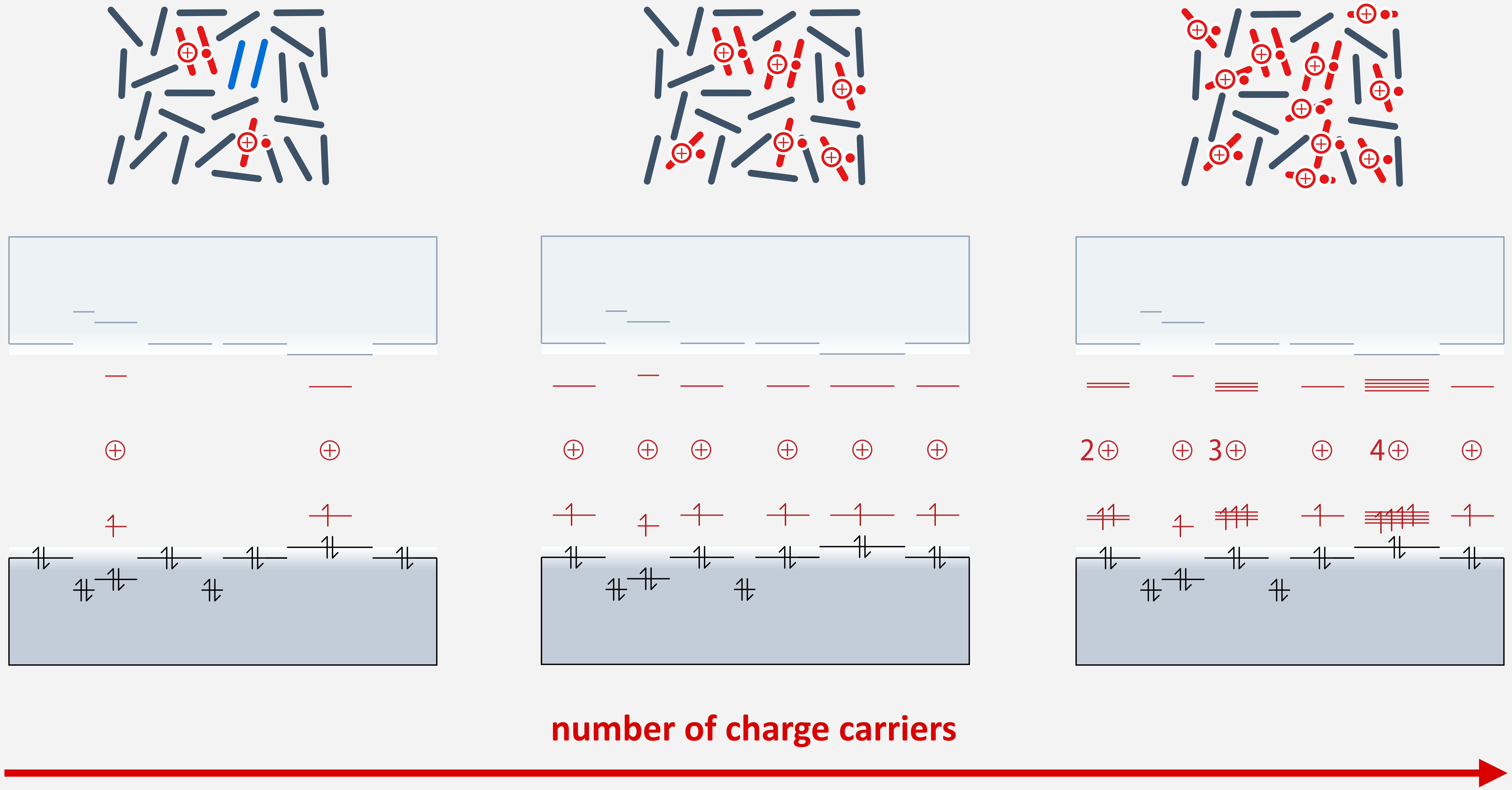
- threshold concentration increases in more disordered systems (e.g., at higher temperature)



- **increase above threshold will initially locally create more extended states**
- **the bandwidth of the final polaron band is lower than for highly ordered systems**

Highly Disordered Systems at High Charge Carrier Densities

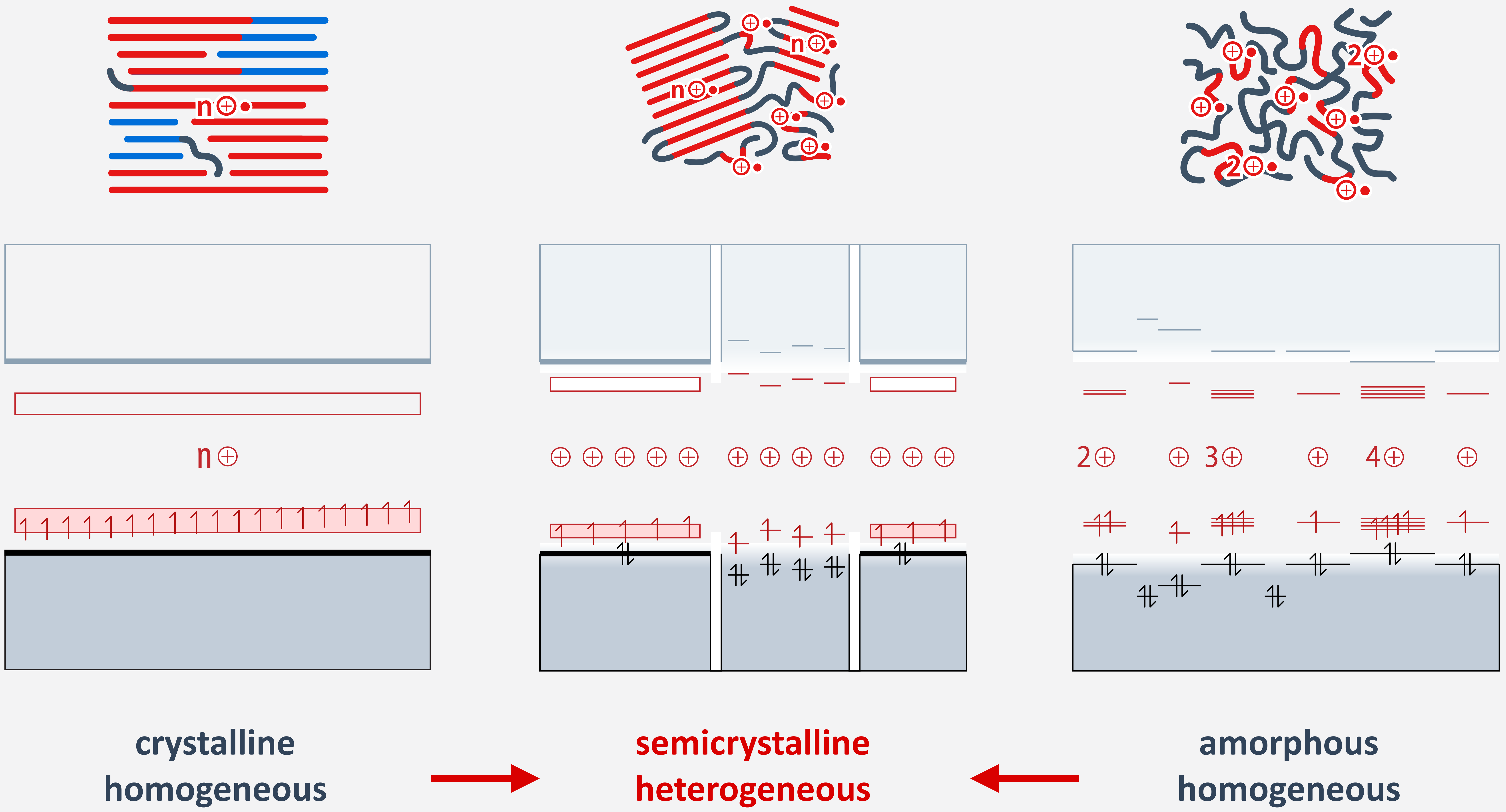
- no polaron bands even at high doping levels in highly disordered (amorphous) systems



- **even in amorphous solids, polaron defects can still locally start to interact with one another**
- **formation of more extended polaron defect states with limited delocalization**

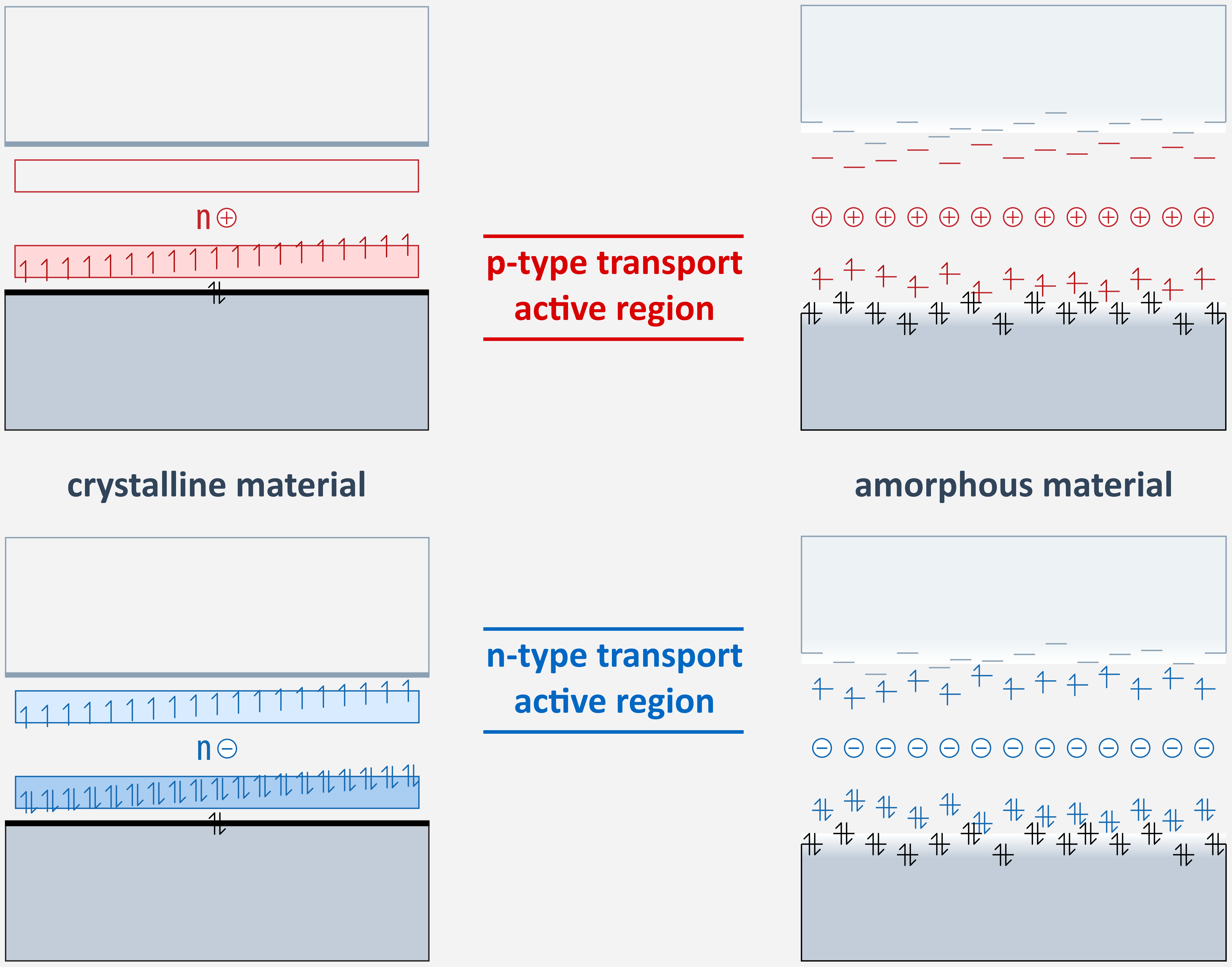
Heterogeneous Systems at High Charge Carrier Densities

- static/dynamic disorder increase from crystalline to semicrystalline to amorphous polymers



- **heterogeneous correlation length and energy levels of both neutral states and polarons**
- **all interactions and energy levels change abruptly at the crystalline/amorphous interfaces**

Active Regions in p-Type and n-Type Organic Semiconductors



Learning Outcomes

- **oxidation or reduction of π-conjugated systems generates charge carriers**
- **poly(acetylene) is an exception because it has degenerate ground states**
  - neutral solitons exist as defects at domain boundaries
  - spontaneous charge separation in an electric field possible
  - oxidation/reduction yields positive/negative soliton charge carriers
  - soliton charge carriers have a charge ($q = \pm e$), no spin ($s = 0$), plus a lattice defect
- **typical organic semiconductors do not have degenerate ground states**
  - spontaneous charge separation in an electric field is not observed
  - oxidation/reduction yields positive/negative polaron charge carriers
  - polarons have a charge ($q = \pm e$), a spin ($s = ½$), plus a lattice defect
- **delocalization of polaron charge carriers interacting with neutral neighbors**
  - delocalization depends on static / dynamic disorder, crystallographic direction
  - formation of narrow bands (≤0.1 eV) in ordered domains at high charge densities
  - abrupt changes of electronic levels at crystalline/amorphous interfaces
- **fuzzy band edge with neutral and polaronic states is active transport region**