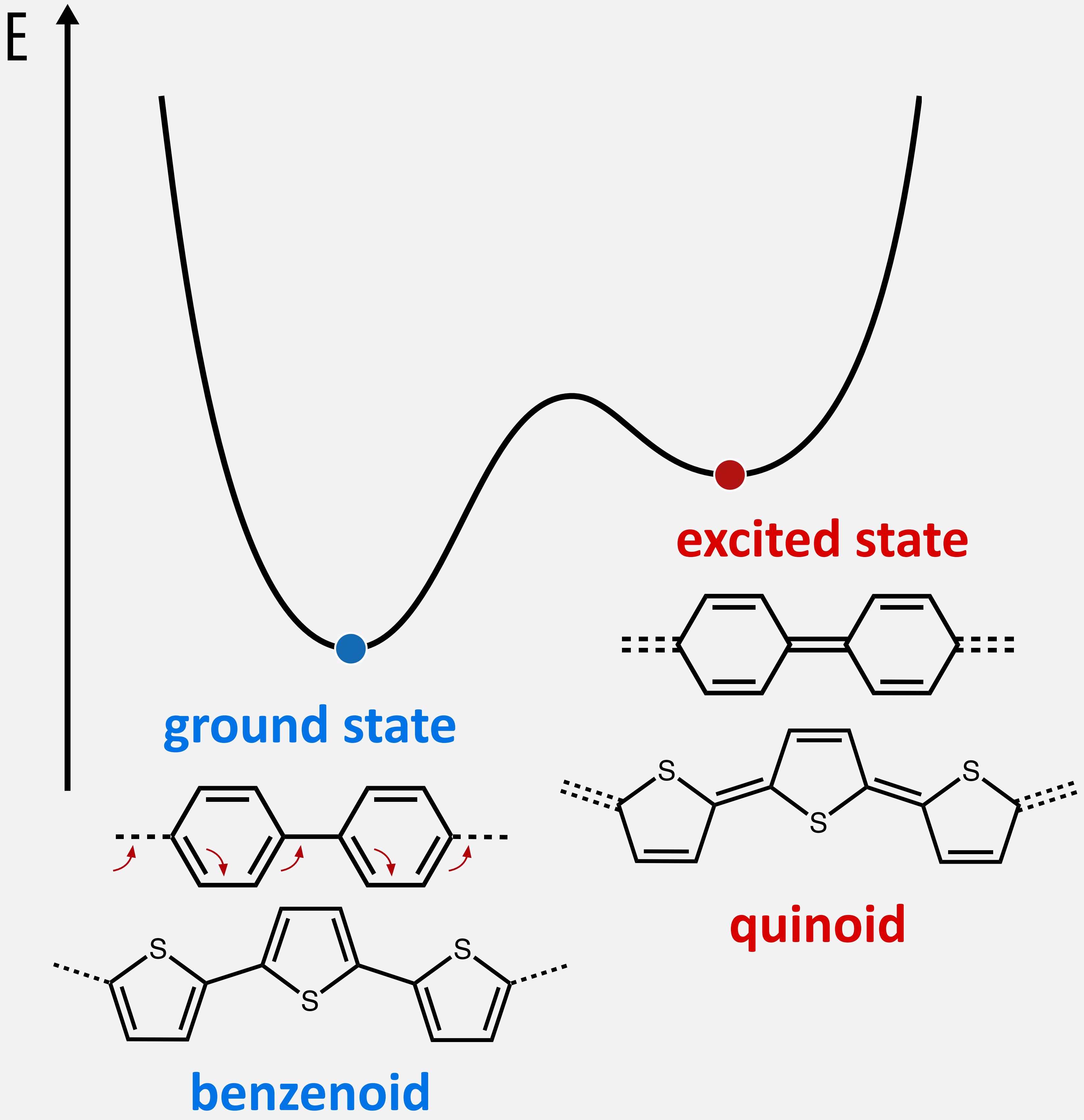
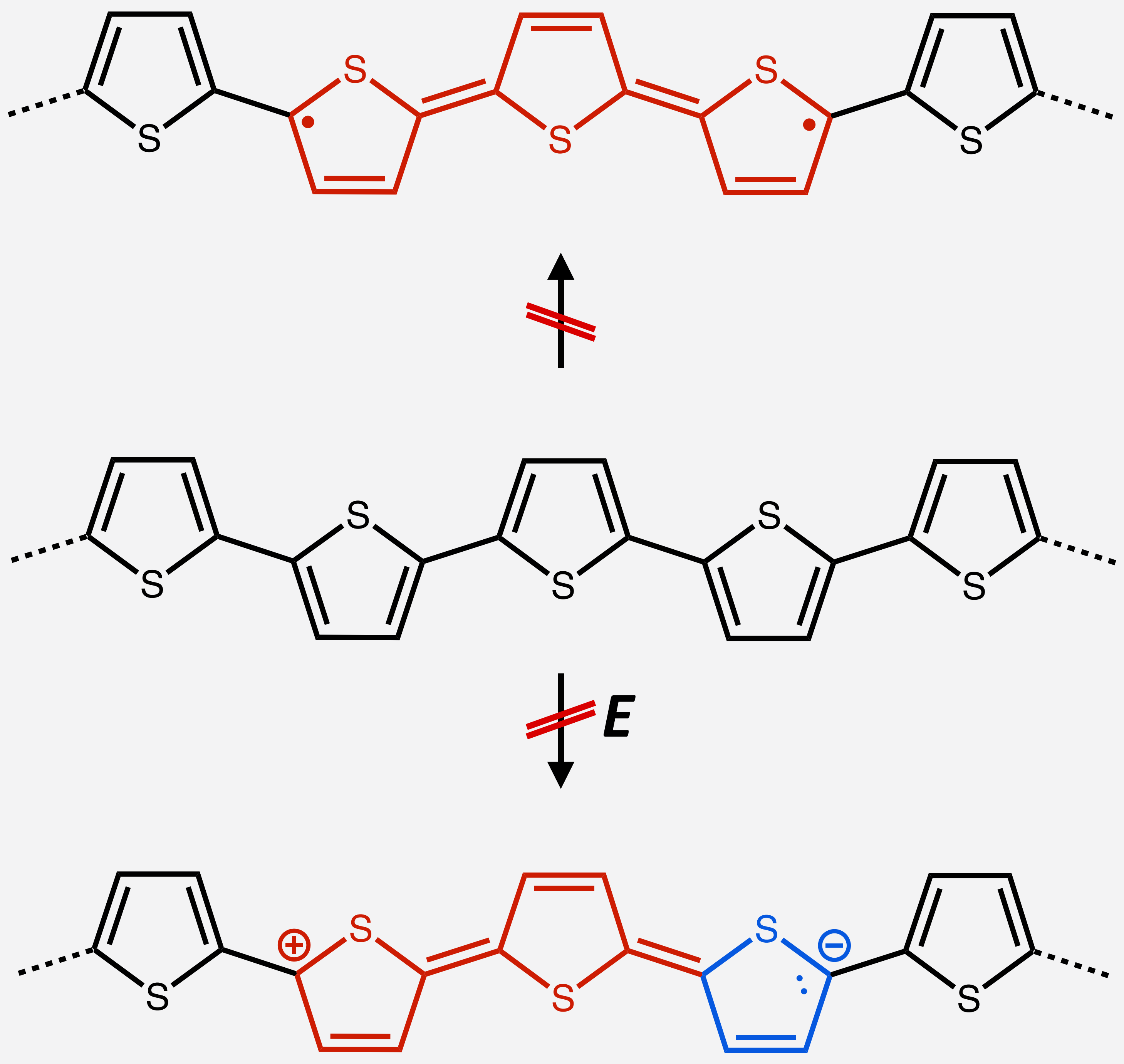
5.2 Polarons

Excitation in Polymers with Non-Degenerate Ground States

- energy difference “aromatic“ and “quinoid” state for typical π-conjugated polymers

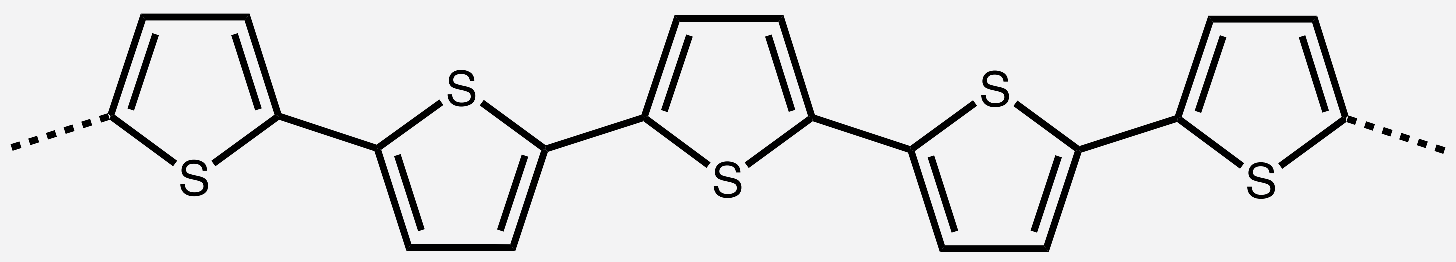




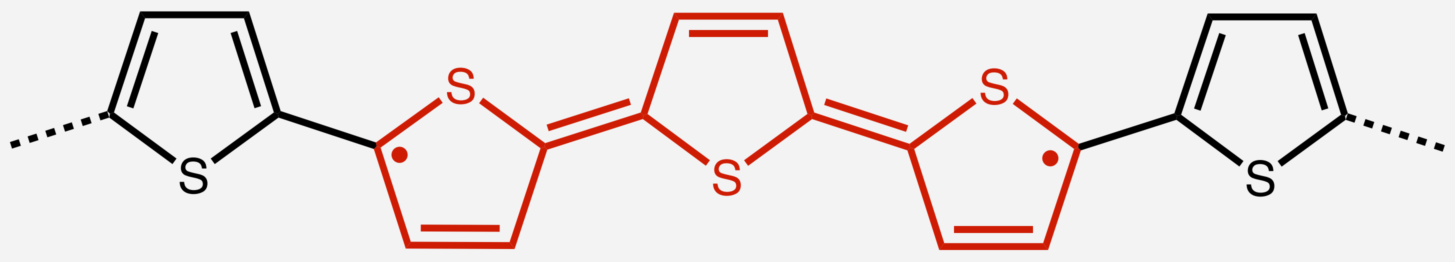
- **only poly(acetylene) has energetically/geometrically equivalent degenerate ground states**
- **all other π-conjugated polymers have “benzenoid” ground state and “quinoid” excited state**

Exciton Formation Upon Irradiation

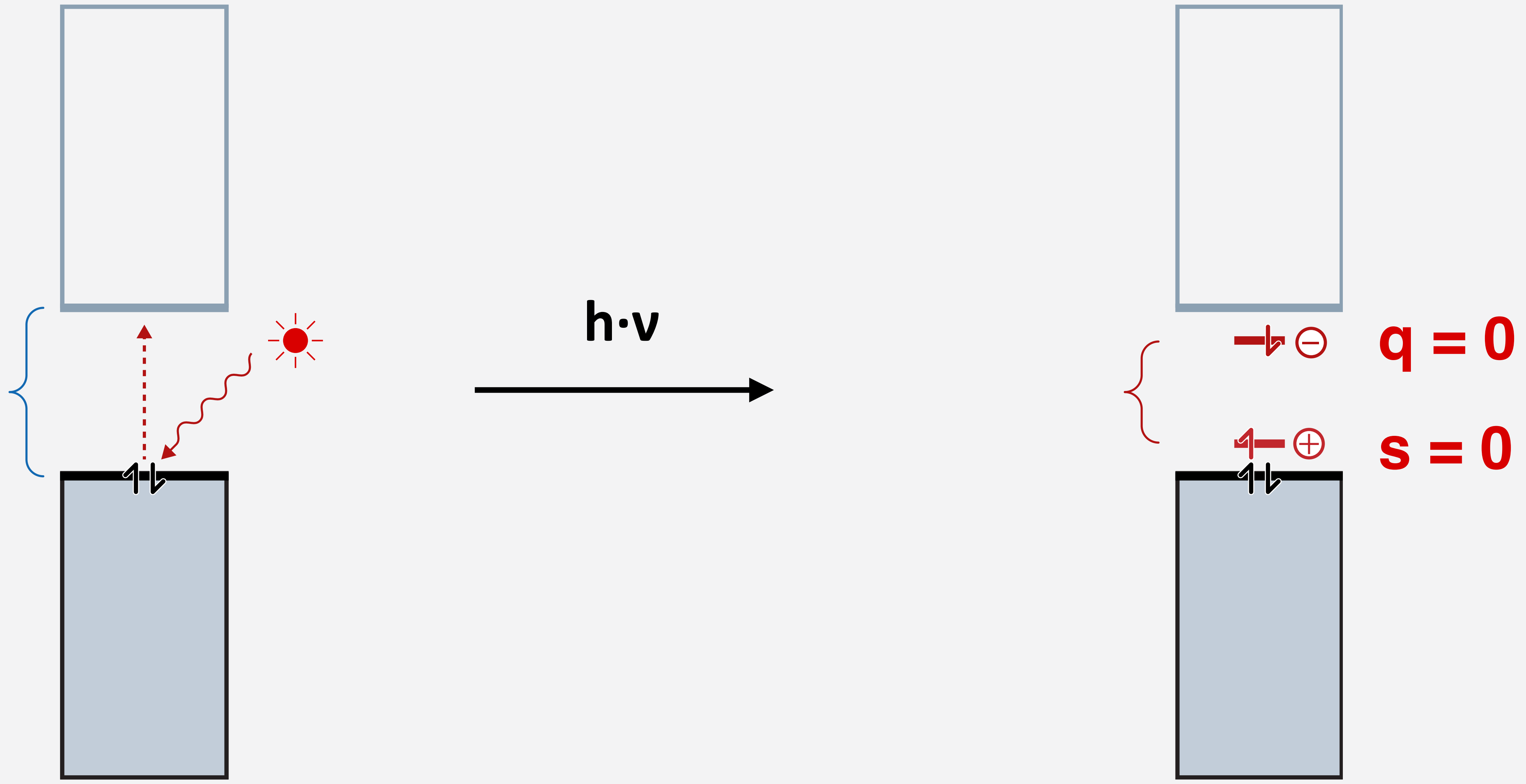
- Frenkel exciton formation by promotion of an electron from ground state S_0 to first excited state S_1



ground state



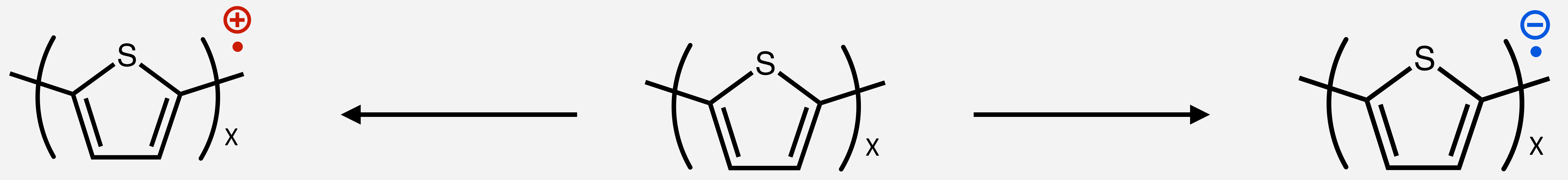
exciton



- **singlet excitons are neutral (q = 0), spin-less (s = 0) species associated with a lattice defect**
- **organic chemistry view: tightly bound radical cation/anion pairs with limited delocalization**
- **Frenkel excitons diffuse under geometry rearrangement, transport excitation energy, not charge**

Chemical Doping of Poly(thiophene)

- chemically doped poly(thiophene) in the solid state becomes semiconducting or even metallic



p-type doping

good semiconductor

I_2, AsF_5, SbF_5

oxidant

single electron acceptor

typical π-conjugated polymer

poor semiconductor

n-type doping

good semiconductor

Na, K, Li

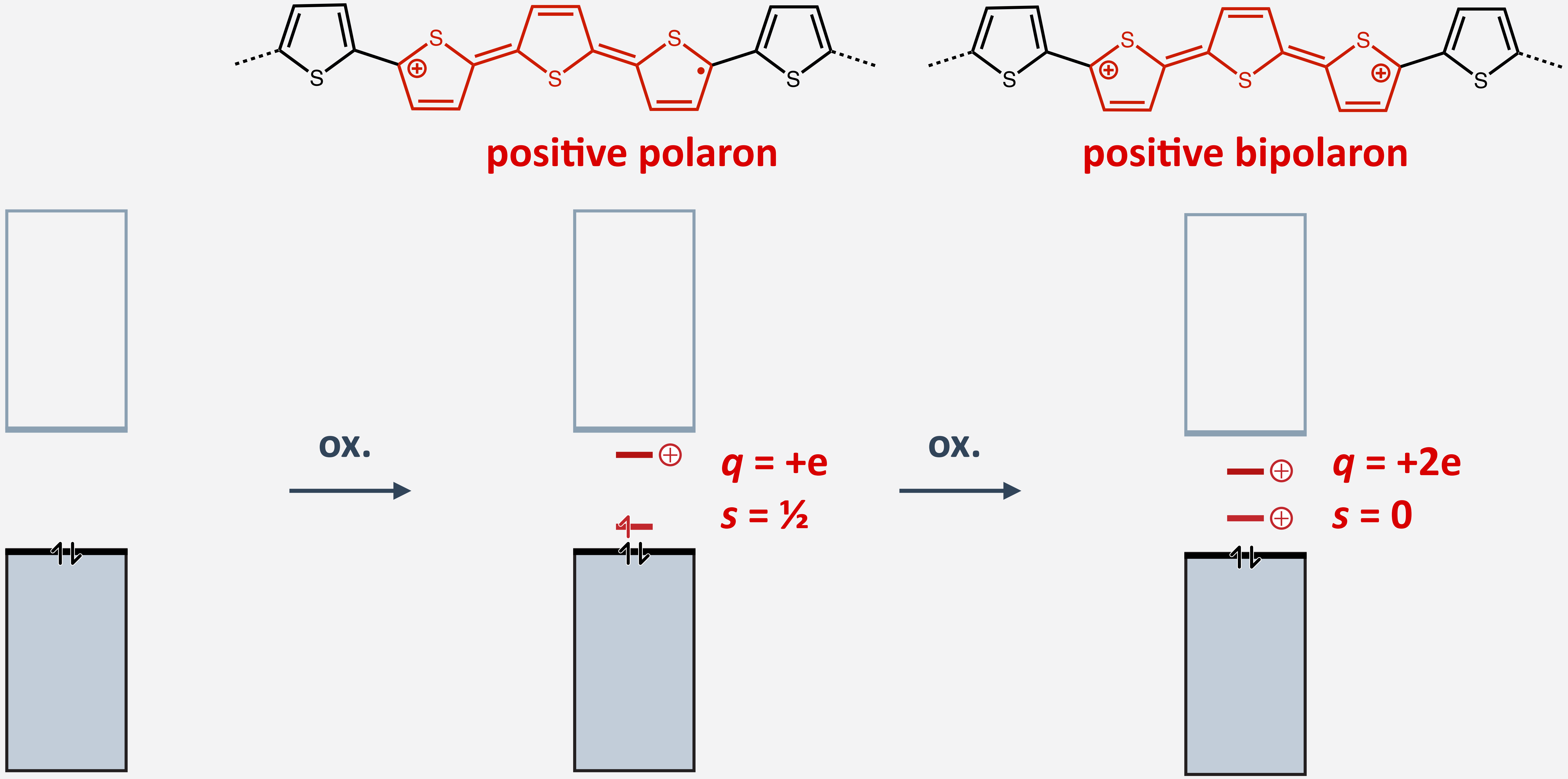
reductant

single electron donor

- **different from inorganic semiconductor “impurity doping” (at ppm concentrations)**
- **“single electron transfer” oxidant/reducant, but must not induce follow-up reaction**
- **dopant applied at high concentrations (0.1–10 mol%), strongly disturbs structure/geometry**
- **conductivity & mobility increased by several orders of magnitude by chemical doping**

Formation of Positive Polarons or Bipolarons

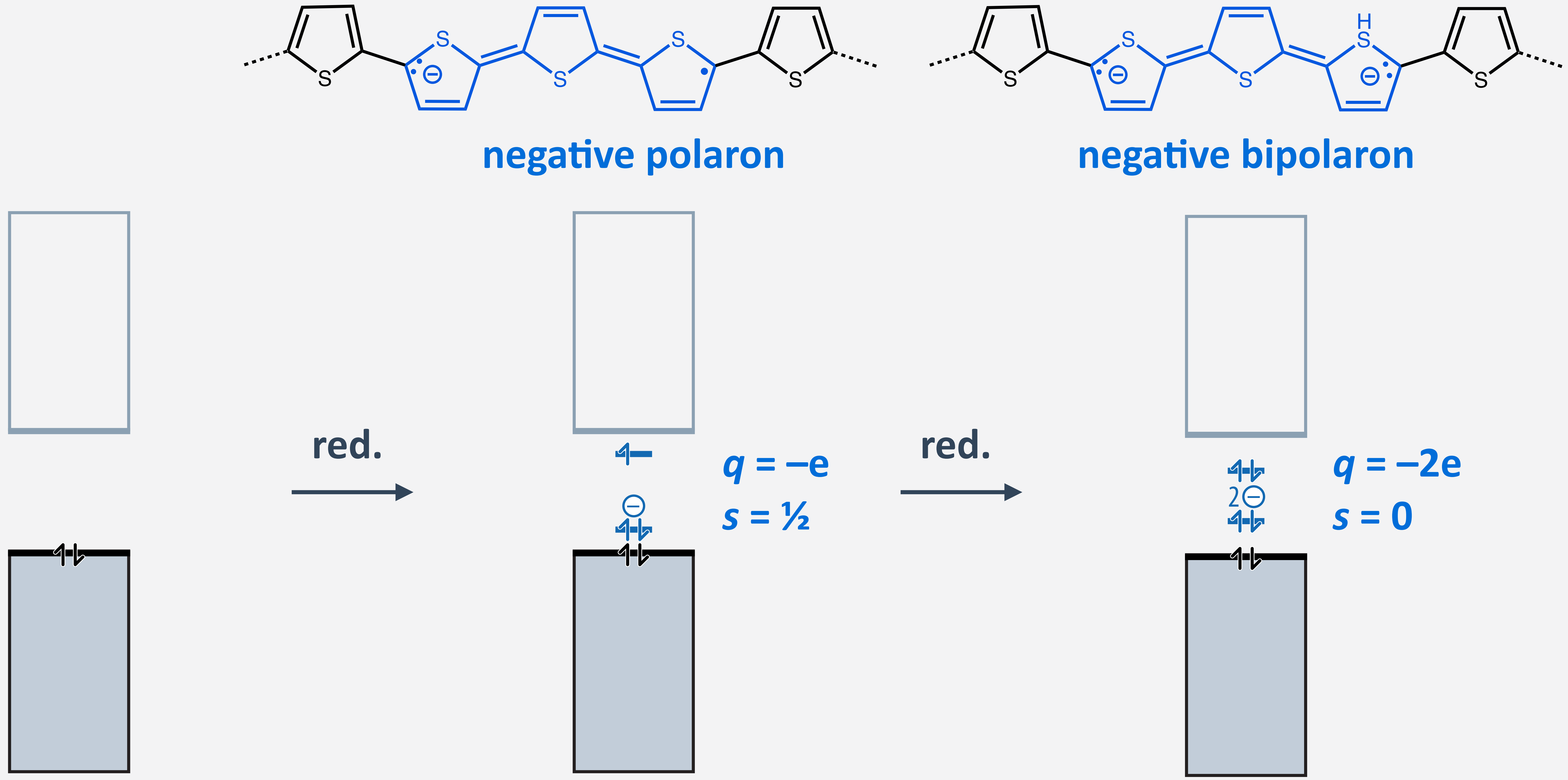
- chemical oxidation results in formation of positive polaron or bipolaron charge carriers



- **positive polarons: charge (*q* = +*e*) & spin (*s* = ½); delocalized radical cations & lattice defect**
- **positive bipolarons: charge (*q* = +2*e*), no spin (*s* = 0); delocalized dications & lattice defect**
- **(bi)polarons are one single species, correlation length = effective conjugation length**

Formation of Negative Polarons or Bipolarons

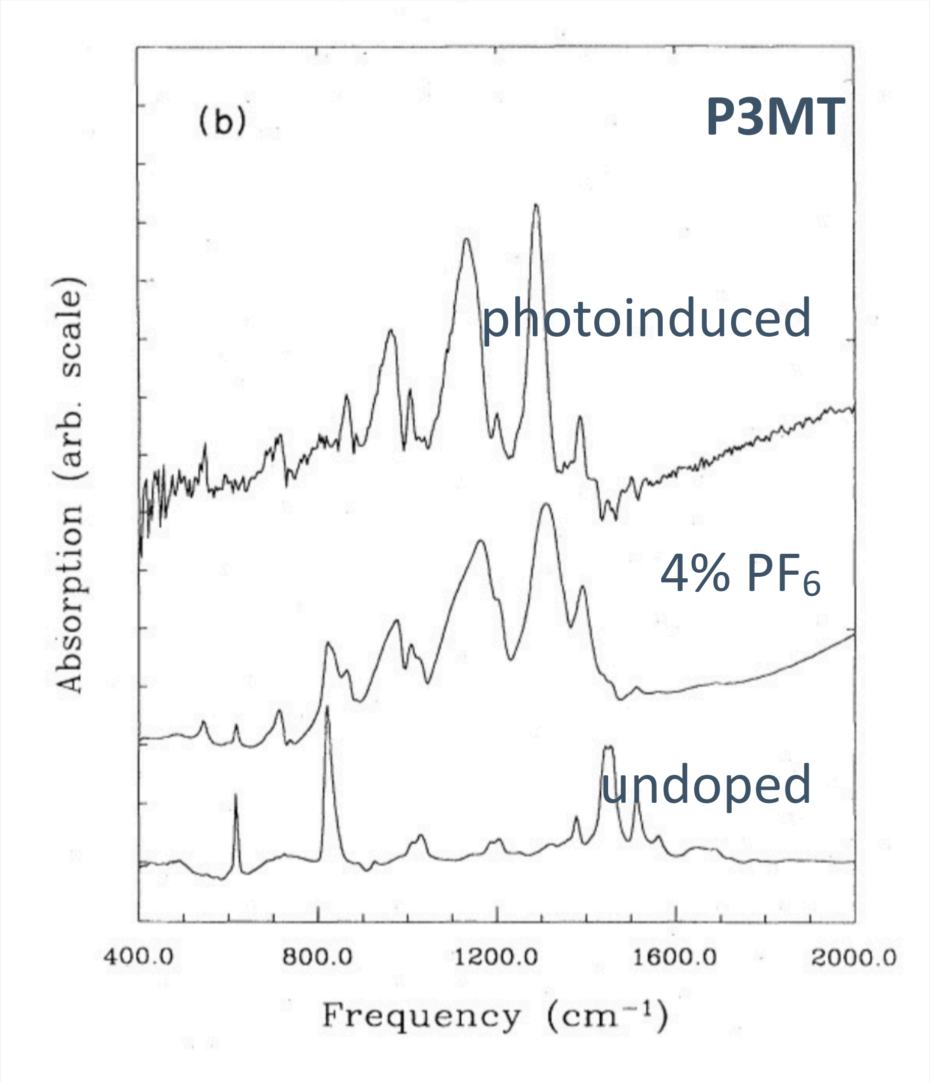
- chemical oxidation results in formation of negative polaron or bipolaron charge carriers



- **negative polarons: charge ($q = -e$) & spin ($s = ½$); delocalized radical cations & lattice defect**
- **negative bipolarons: charge ($q = -2e$), no spin ($s = 0$); delocalized dications & lattice defect**
- **(bi)polarons are one single species, correlation length = effective conjugation length**

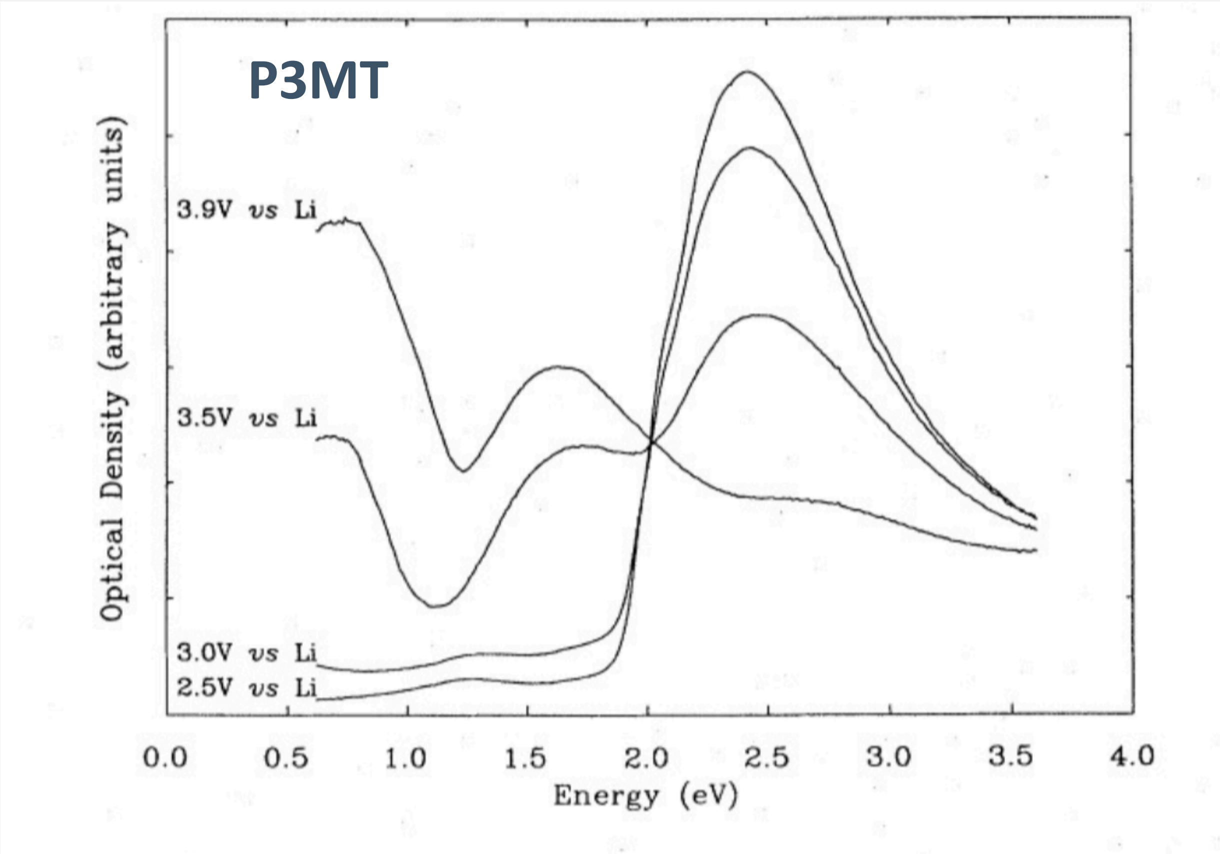
Evidence of Polarons and Bipolarons

IR Spectroscopy



appearance of additional vibrations assigned to charged distortions

UV-vis-NIR Spectroscopy

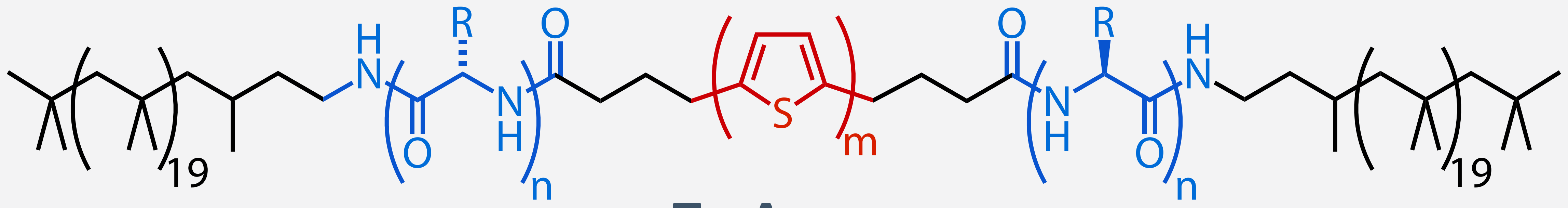


appearance of additional transitions assigned to mid-bandgap states

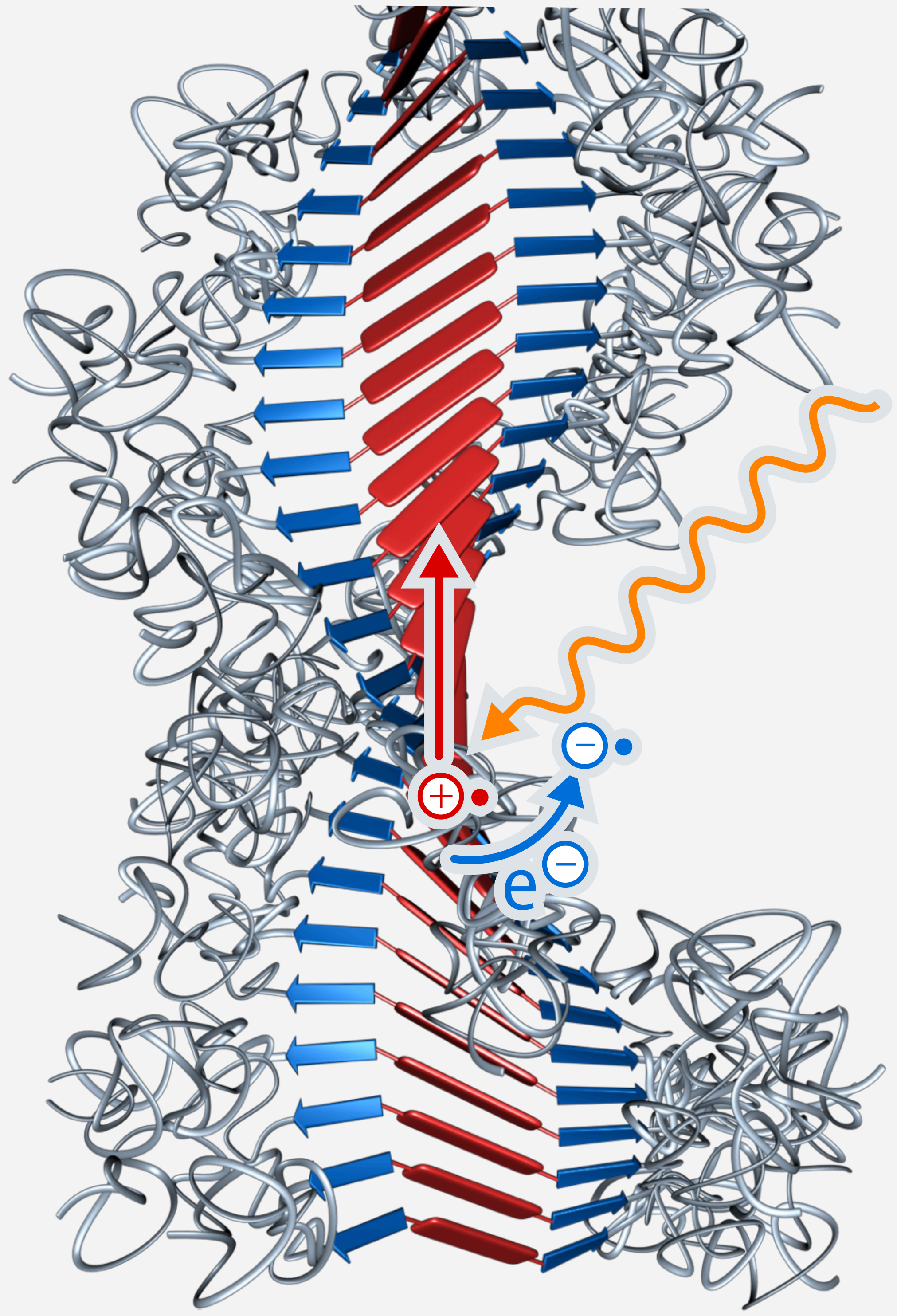
- **positive polarons: charge (*q* = +*e*) & spin (*s* = ½); delocalized radical cations & lattice defect**
- **positive bipolarons: charge (*q* = +2*e*), no spin (*s* = 0); delocalized dications & lattice defect**

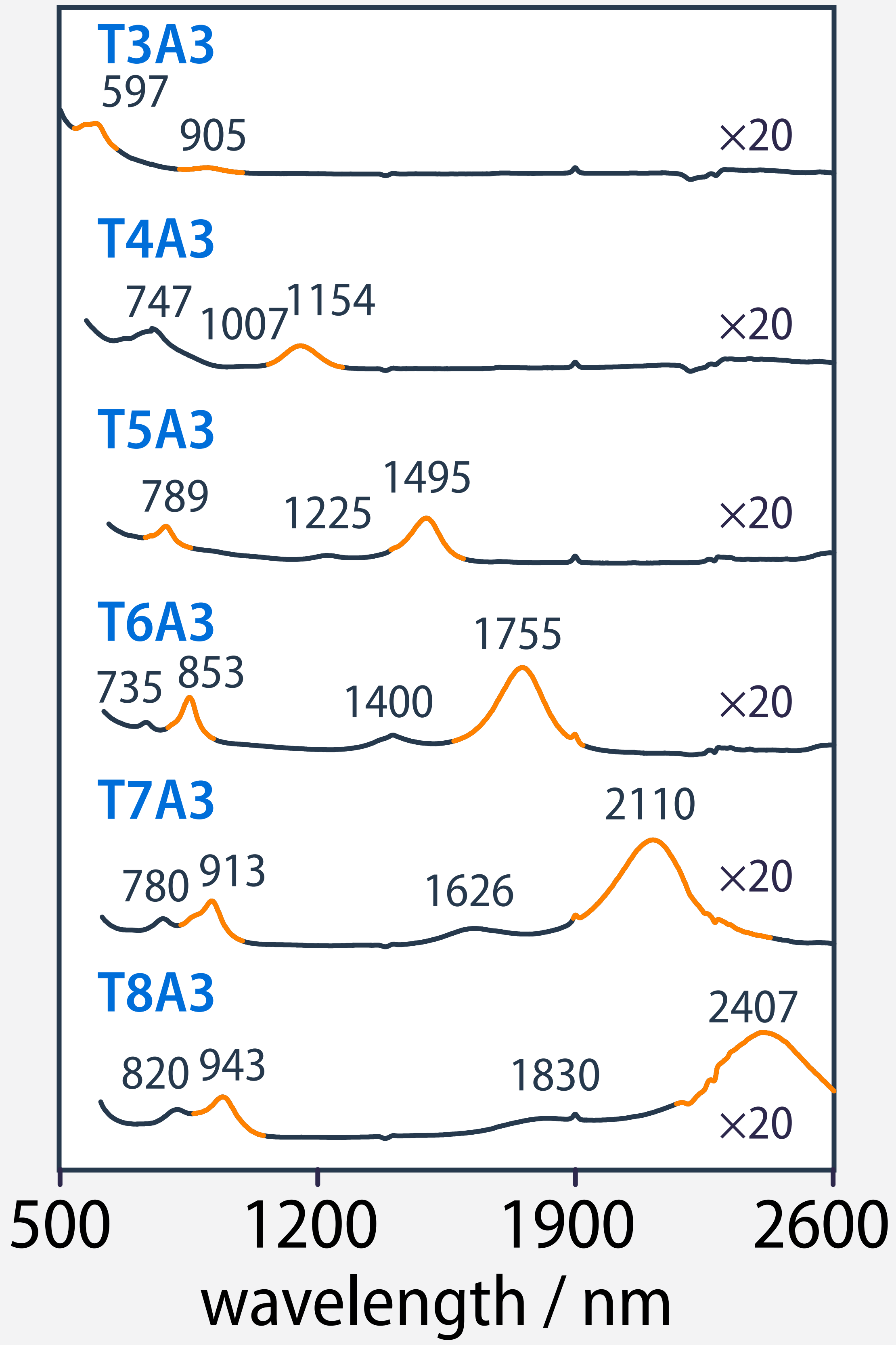
Kim 1987, Chen 1986, Harbeke 1985.

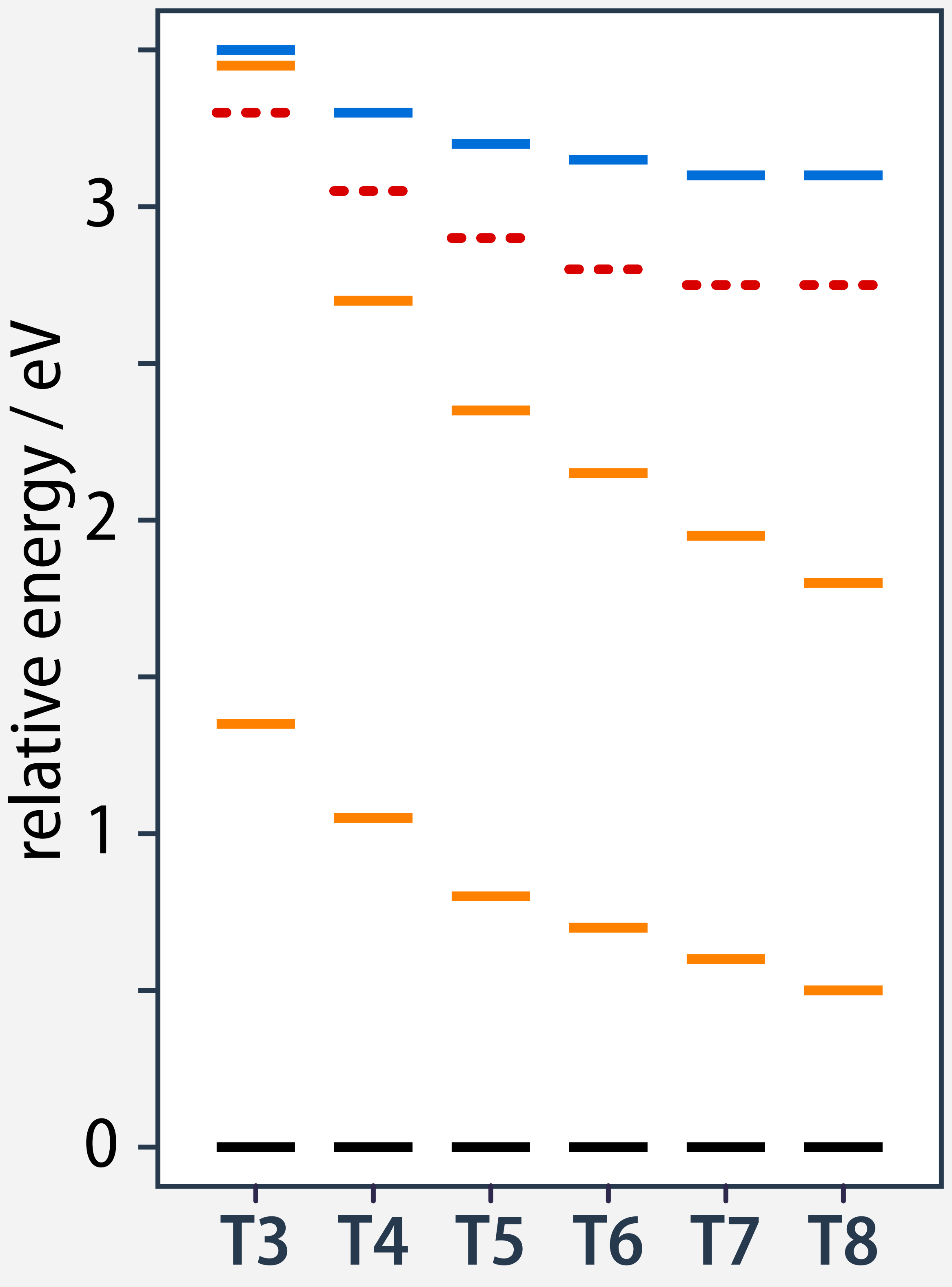
Spectroscopic Aggregates and Radical Cation Fomation



TmAn





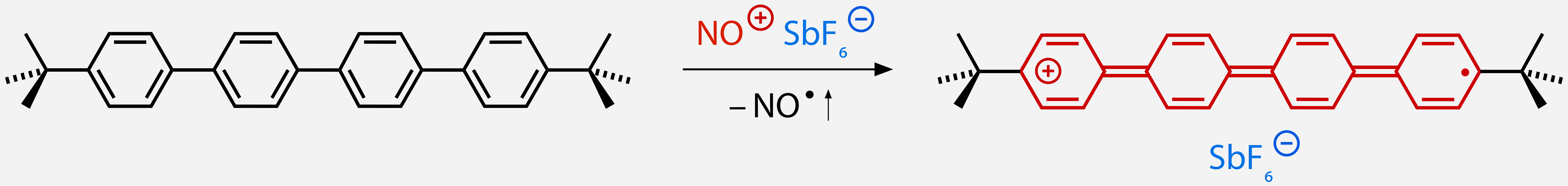


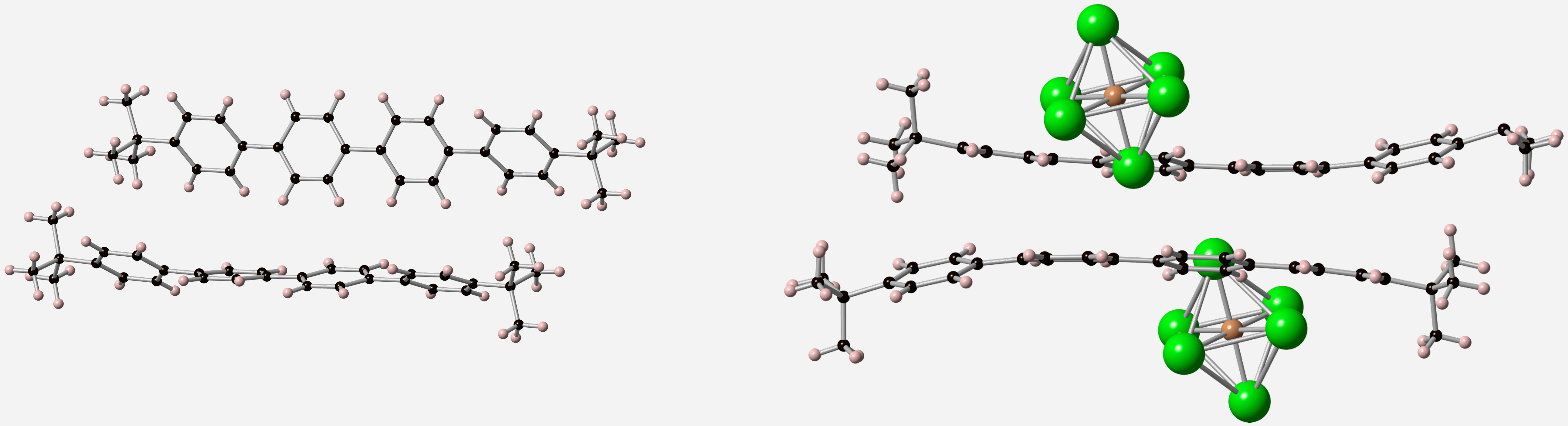
- **oligothiophenes T3A3–T8A3 form helical H aggregates and 'spontaneously' form radical cations**

Frauenrath et al., unpublished

Crystal Structure of the Quaterphenyl and its Radical Cation

- chemical oxidation can be used for quantitative polaron formation



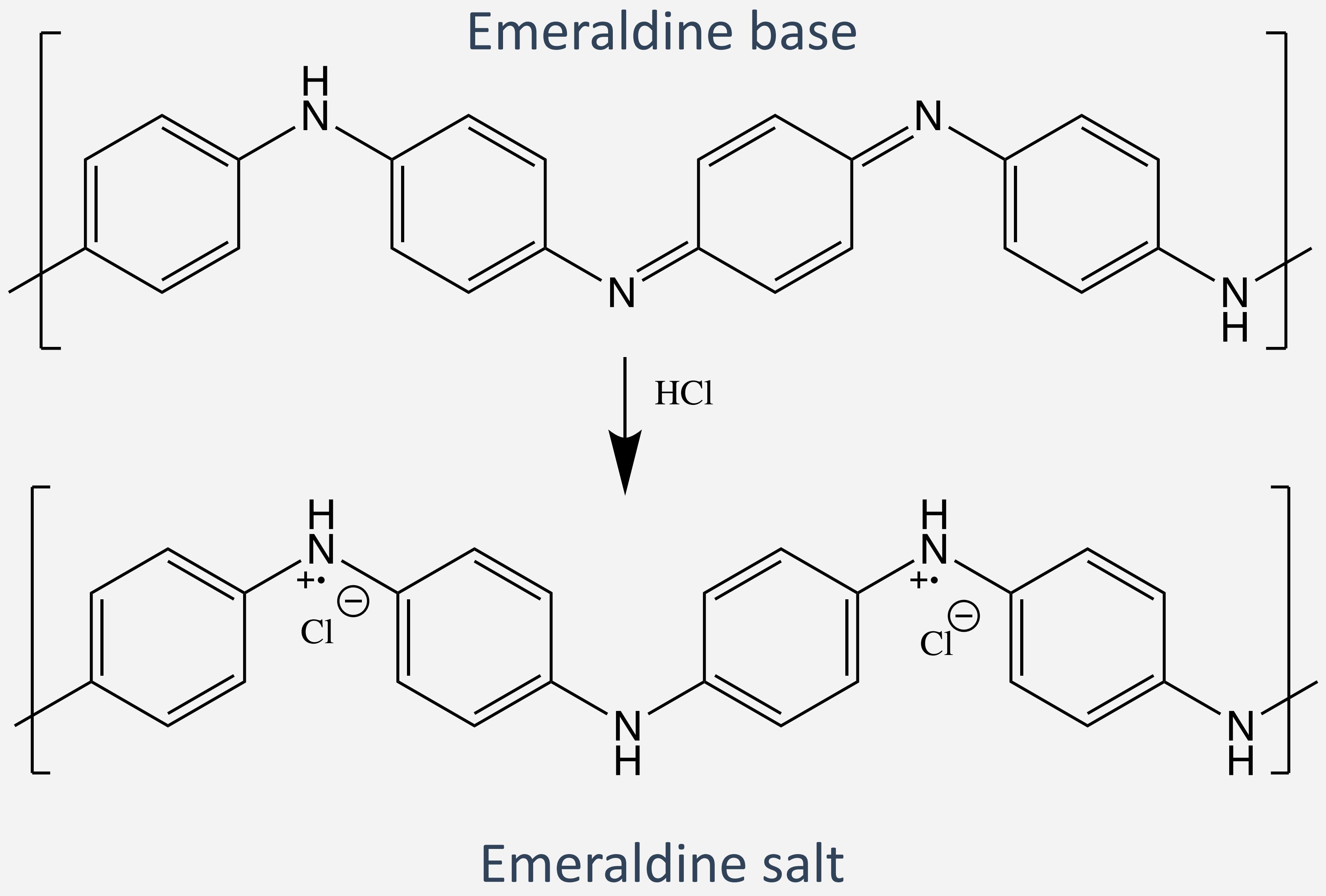


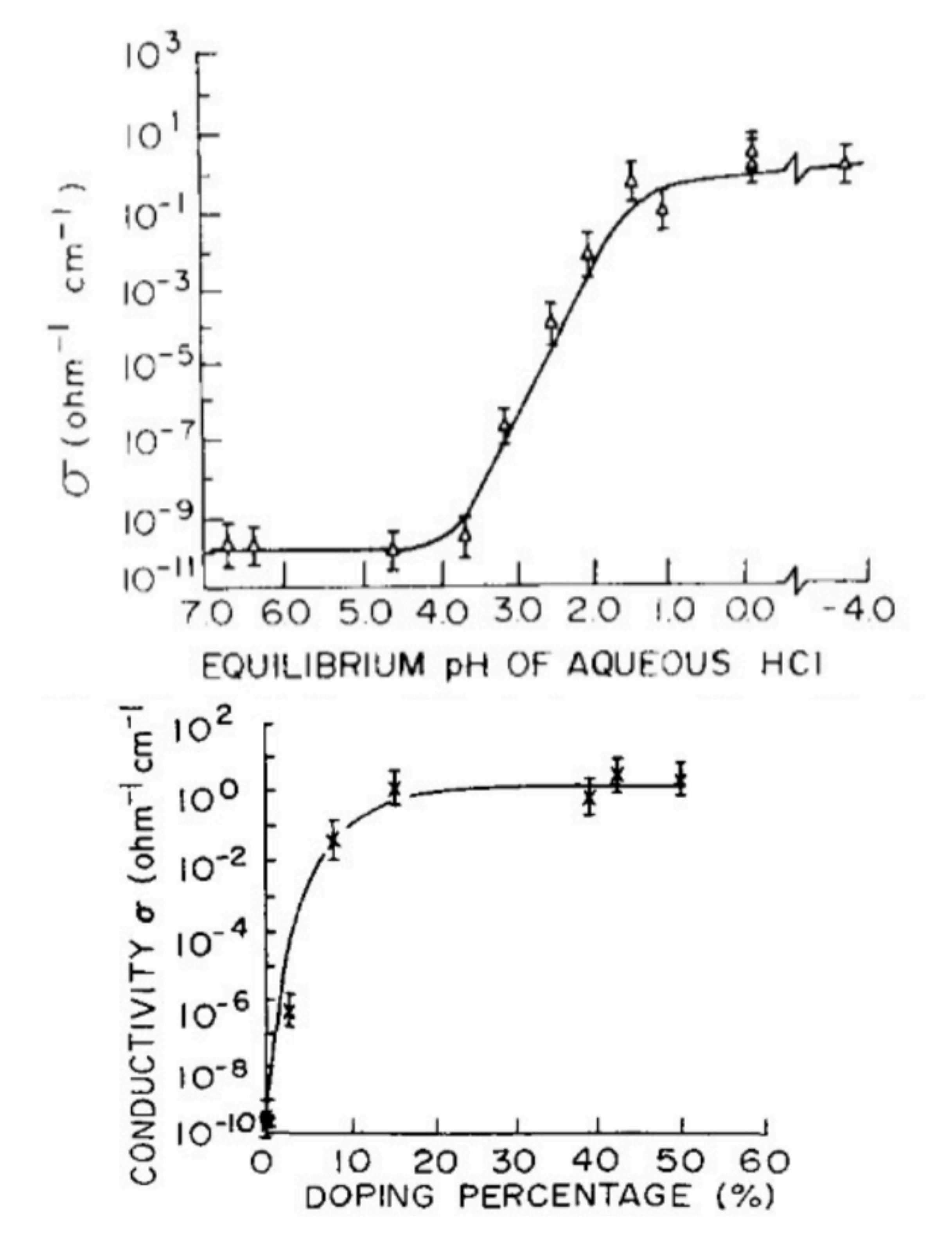
- **quinoidal structure of polaron requires planarization of molecular structure**
- **polaron structure is better delocalized than ground state, bond lengths become similar**

Rathore, *J. Am. Chem. Soc.* **2009**, 1780

Poly(aniline)

- poly(aniline) is a special case showing conductivity without oxidative/reductive doping
- 10-fold increase in conductivity through Brønsted acid doping



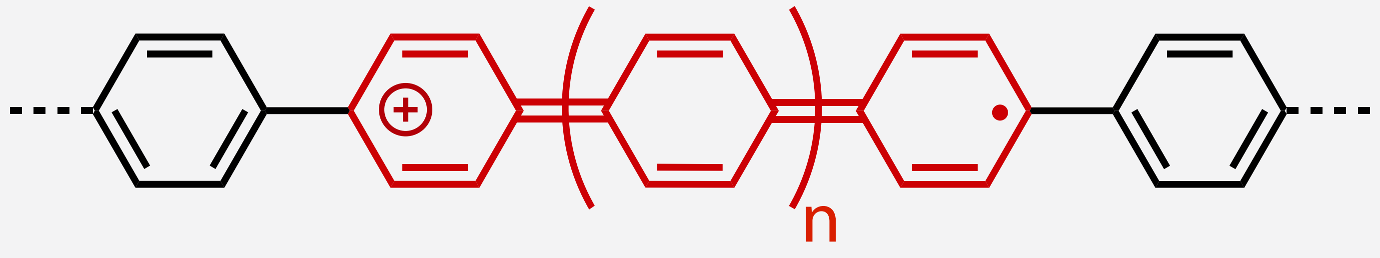


- **air-stable conducting polymer, stable towards oxygen (not the case with other doping types)**

Chiang, MacDiarmid, *Synth. Metals* 1986

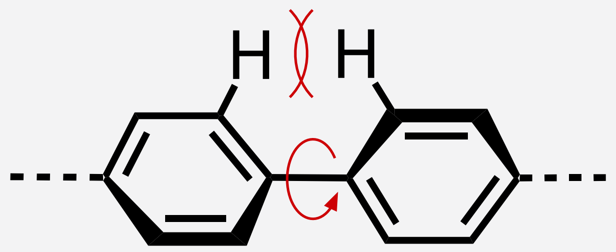
Effective Conjugation Length Revisited

- effective conjugation length is “correlation length” of the polaron/bipolaron wave package

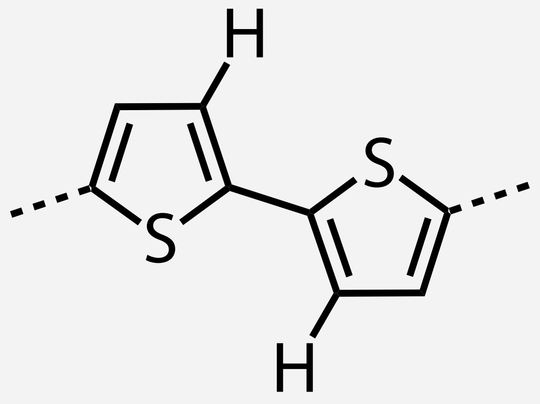


delocalized polaron

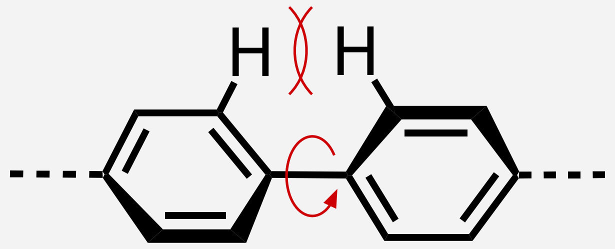
≈ 10–15° in solution



poly(phenylene) (solution)

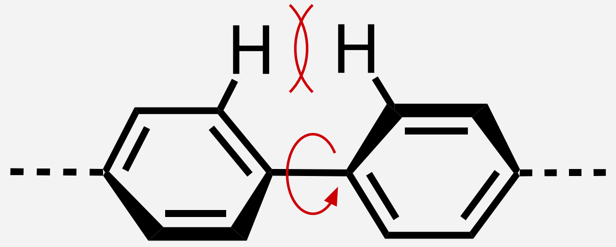


poly(thiophene) (amorphous)

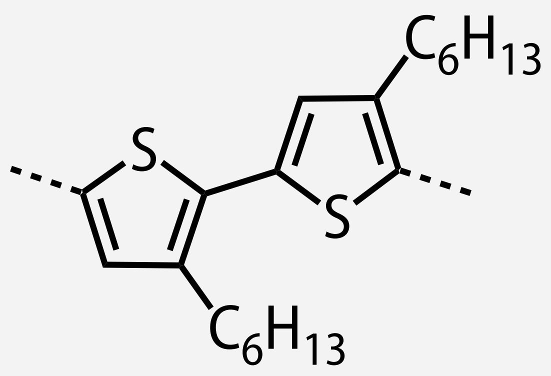


poly(phenylene)

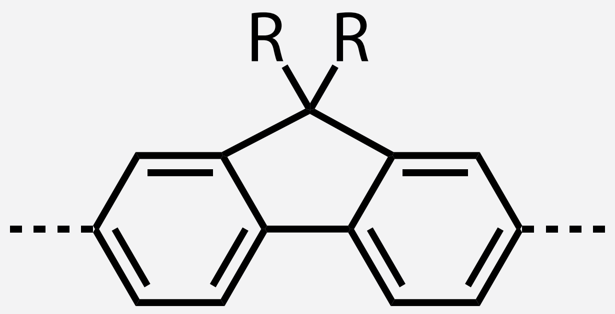
≈ 2–5° in crystal



poly(phenylene) (solid state)



P3HT (crystalline)



poly(fluorene)s

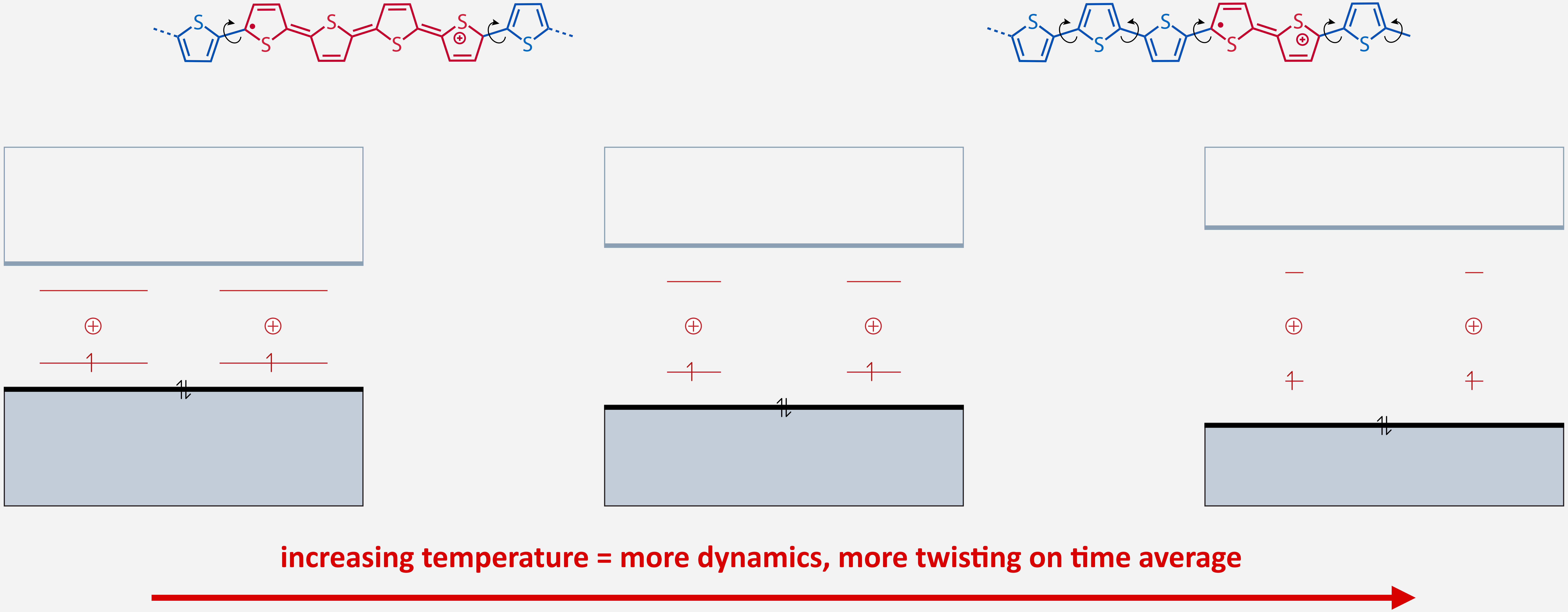
effective conjugation length
= polaron delocalization

- **chain twisting due to steric repulsion or structural dynamics decreases correlation length**
- **packing effects in the crystalline state increase correlation length**
- **correlation length drastically increased by enforced molecular rigidity and planarity**

Räder, *Macromolecules* **1999**, *32*, 1073.

Effect of Dynamic Disorder on the Molecular Level

- correlation length decreased by chain twisting due to structural (conformational) dynamics

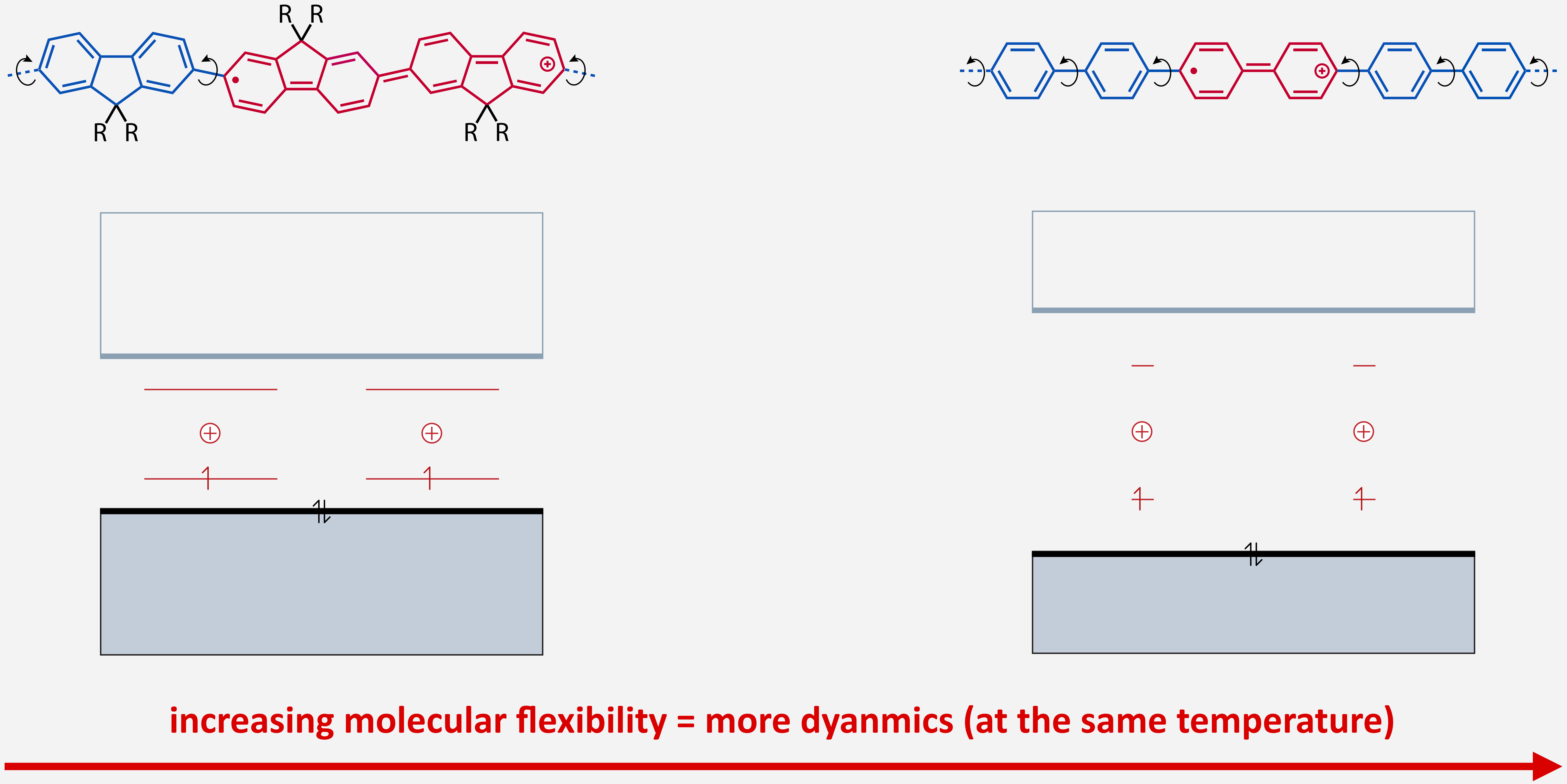


increasing temperature = more dynamics, more twisting on time average

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

Effect of Molecular Rigidity

- correlation length decreases with molecular flexibility and dynamics

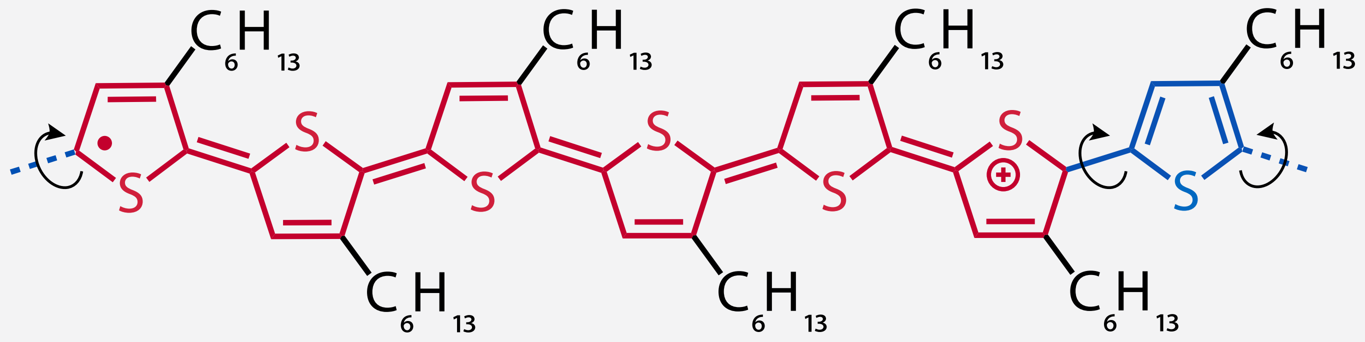


increasing molecular flexibility = more dyanmics (at the same temperature)

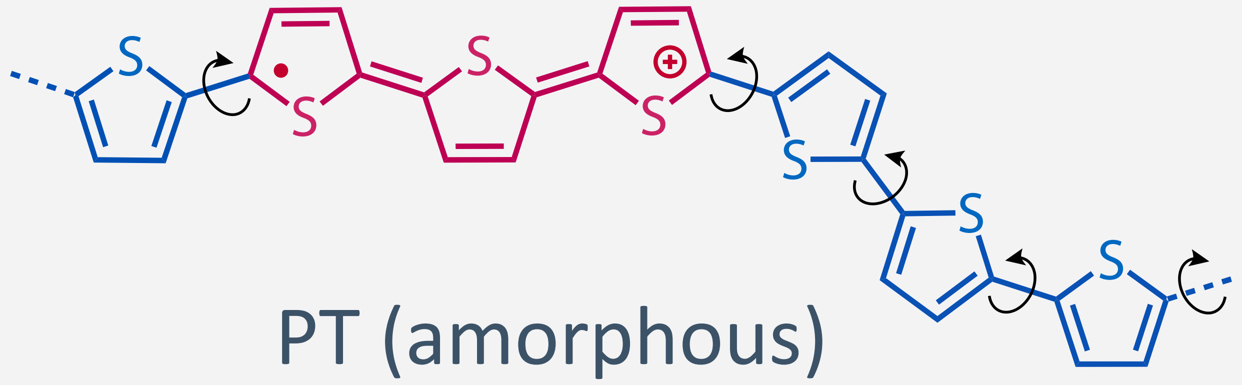
- **conformational freedom increases dynamic disorder, charge carriers more localized**
- **bandgap and also distance between valence/conduction band and polaron levels increase**

Effect of Packing Interactions on the Molecular Level

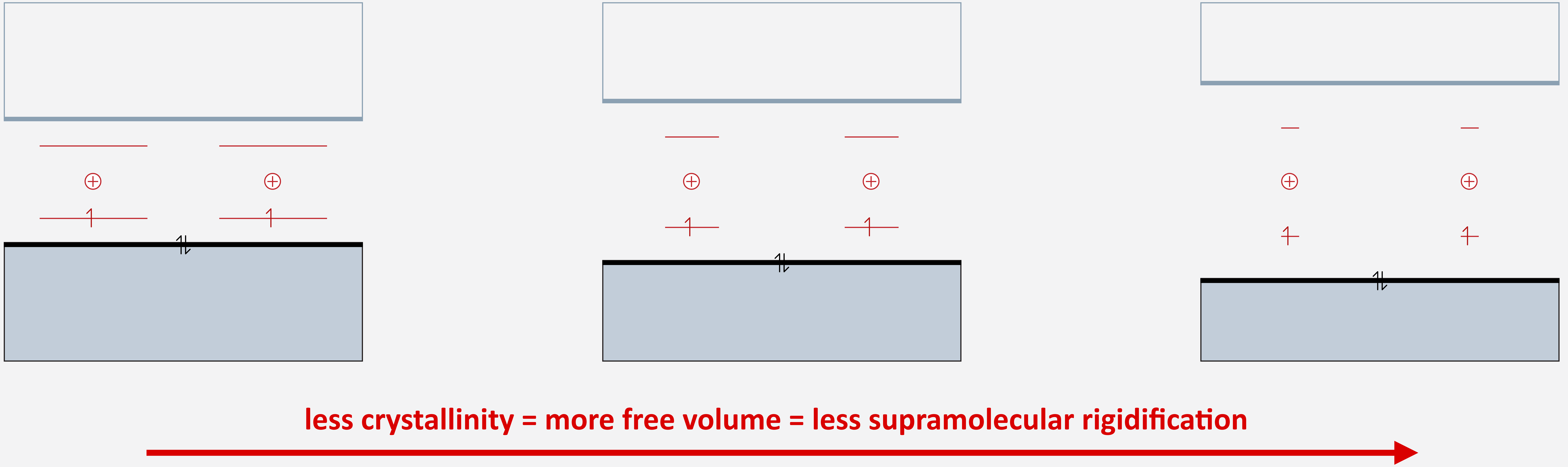
- correlation length decreased as structural dynamics are increased by less efficient packing



regioregular P3HT (crystalline)



PT (amorphous)

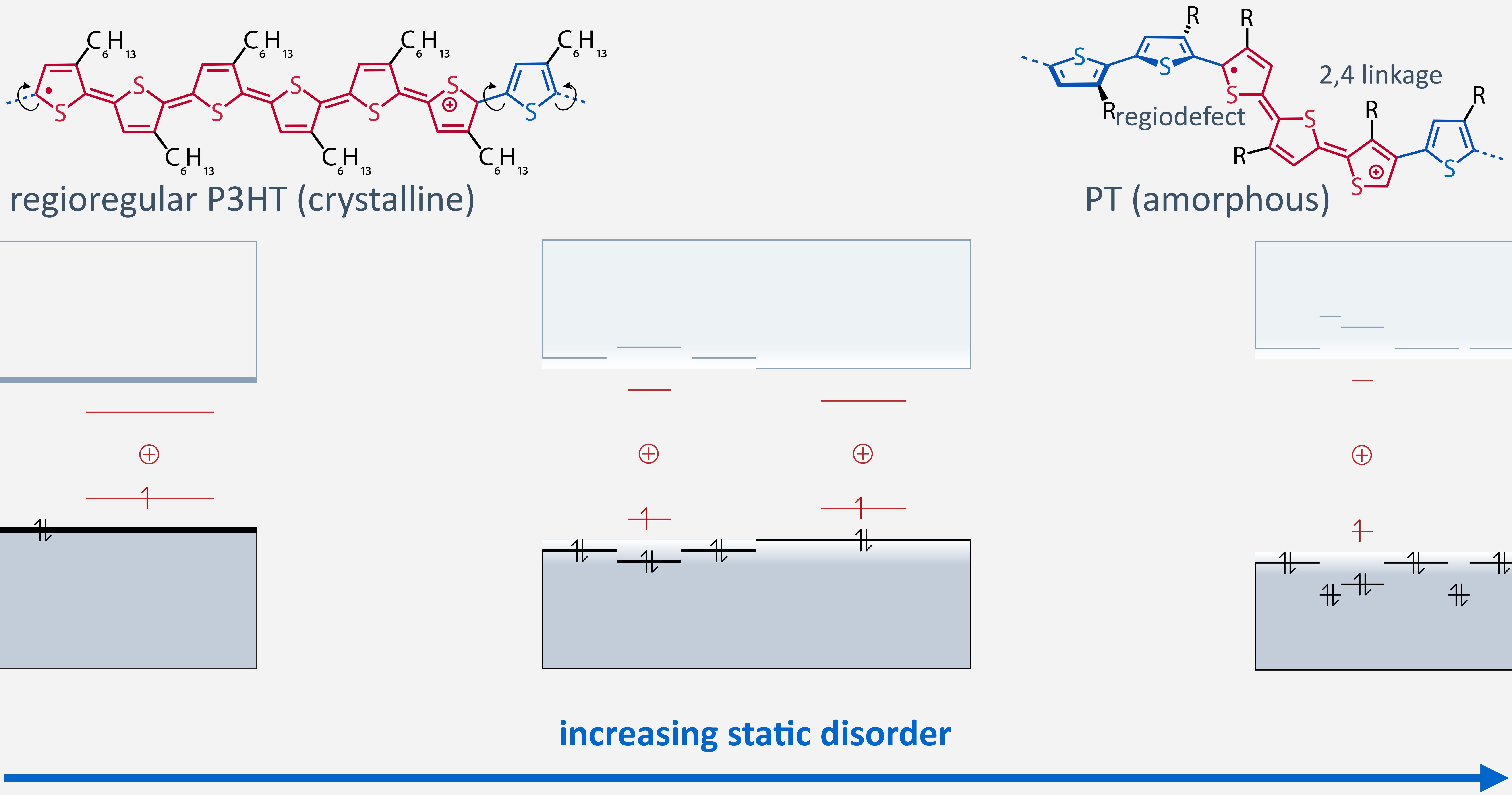


less crystallinity = more free volume = less supramolecular rigidification

- **dynamic disorder increases, charge carriers more localized with reduced crystalline packing**
- **bandgap and also distance between valence/conduction band and polaron levels increase**

Effect of Static Disorder on the Molecular Level

- correlation length decreases with increasing static disorder (structural defects)



- **static disorder breaks conjugation, charge carriers become more localized**
- **HOMO, LUMO, and polaron energy levels increase in heterogeneity due to structural variations**