Spectral shifts of solvatochromic dyes in ionic liquids – explicit solvent model

Andrzej Eilmes, Piotr Kubisiak

Jagiellonian University, Faculty of Chemistry

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motivation

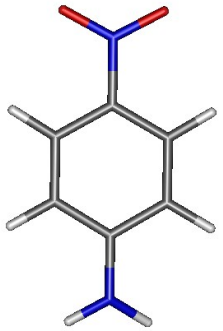
- Room-Temperature Ionic Liquids (RTILs) – organic salts liquid at room temperatures
- Considered as prospective solvents with unique properties („green chemistry”)

- ILs are composed of ions only, therefore electrostatic interactions are crucial for the properties of an IL
- ILs are different from typical molecular liquids
- Properties of molecular liquid and ionic liquid with similar static dielectric constant usually differ

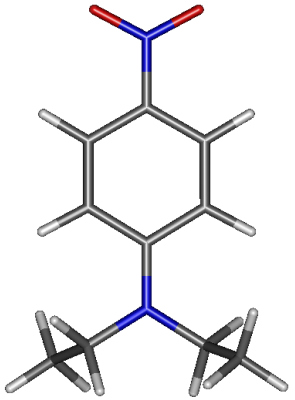
- Let us check the performance of an explicit solvent approach in modeling of solvatochromic effects

dyes in ILs – absorption spectra

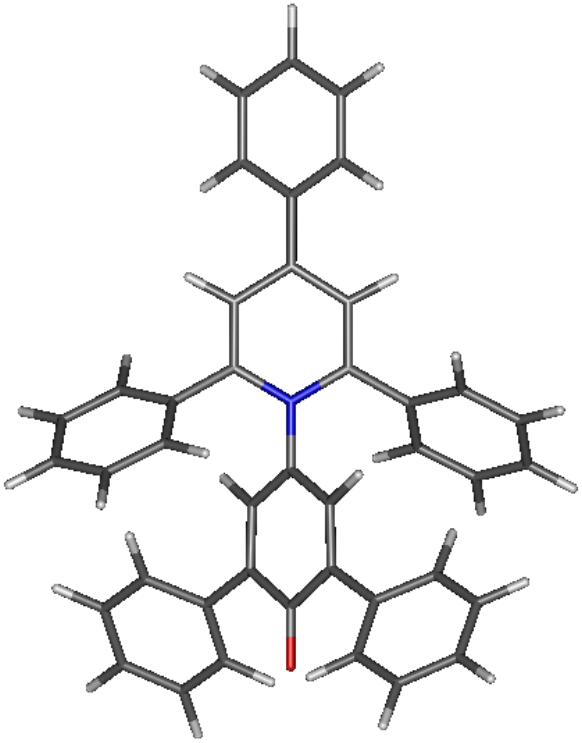
- ionic liquids induce solvatochromic shifts in absorption spectra of dissolved dye molecules
- commonly used solvent parameter scales are determined based on shifts of the maxima in absorption spectra of selected dyes used as probes



PNA



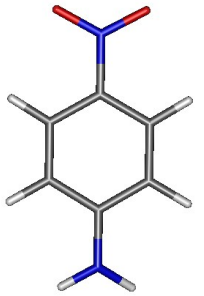
DEPNA



RD

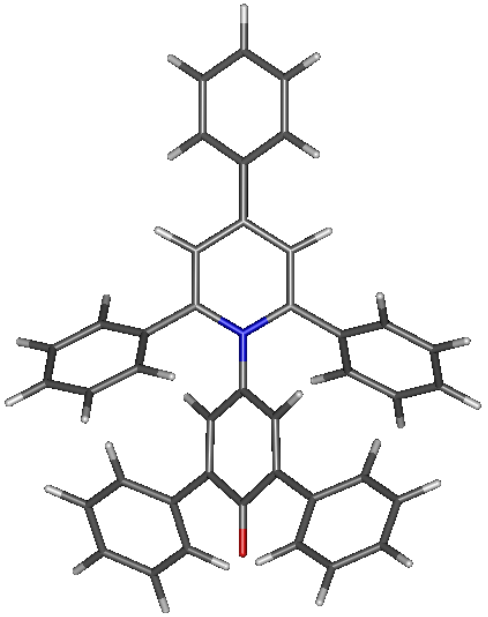
dyes in ILs – absorption spectra

• solavatochromic shifts in ILs are larger than expected from the dielectric constants of typical ILs (12-20) – similar to that measured in molecular liquids with ε = 30-40



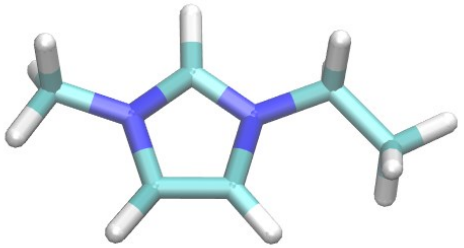
• several papers describing the use of limited explicit solvent model to ionic liquids:

V. Znamenskiy, M.N. Kobrak, J. Phys. Chem. B 108 (2004) 1072
C. Chiappe, C.S. Pomelli, Theor. Chem. Acc. 131 (2012) 1195



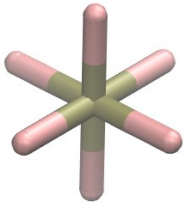
investigated systems

IL cation:



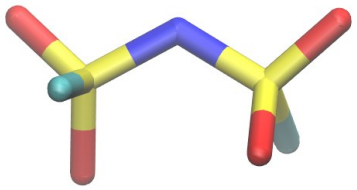
$EMIM^+$

4 different IL anions:

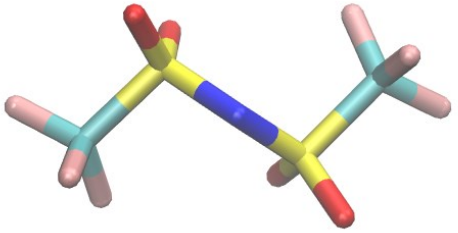


PF_6^-

BF_4^-

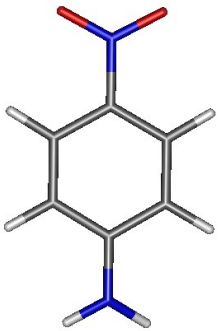


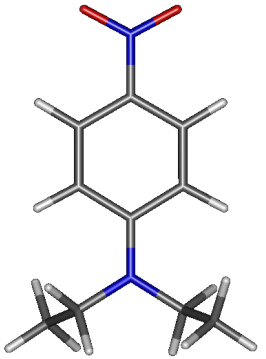
FSI^-

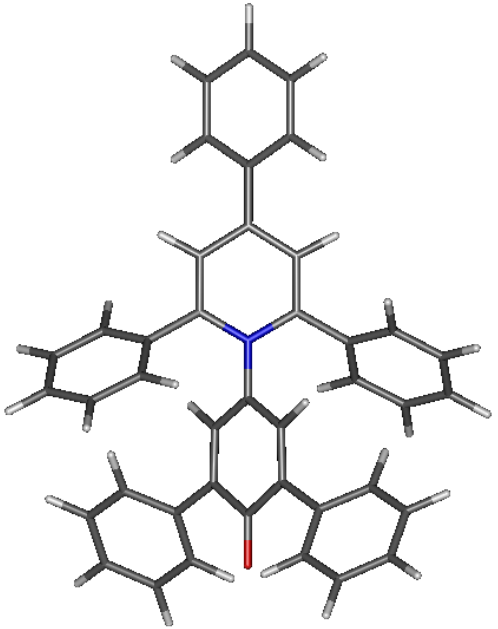


$TFSI^-$

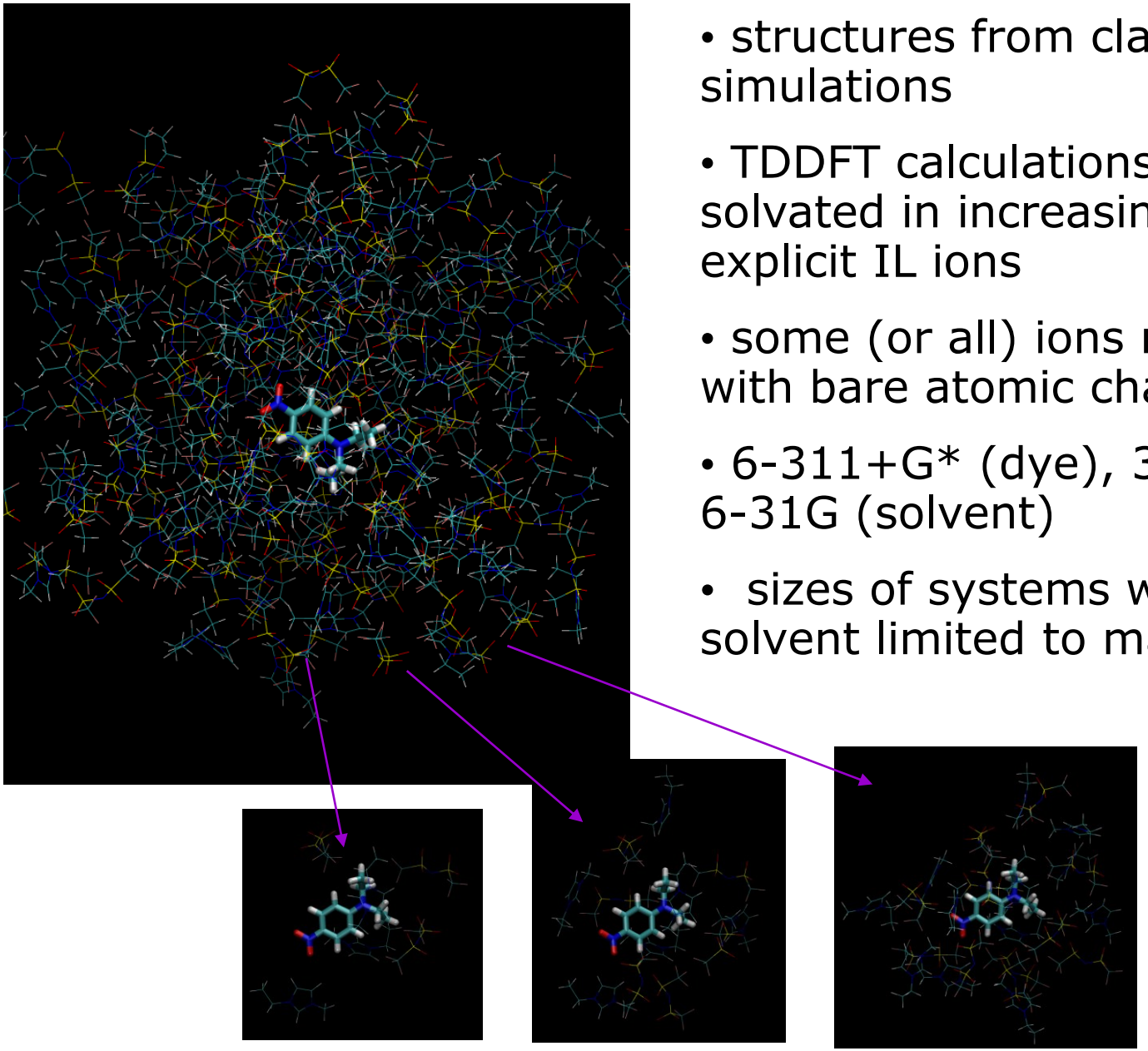
dyes:



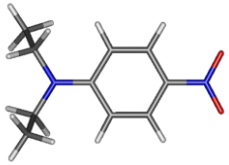




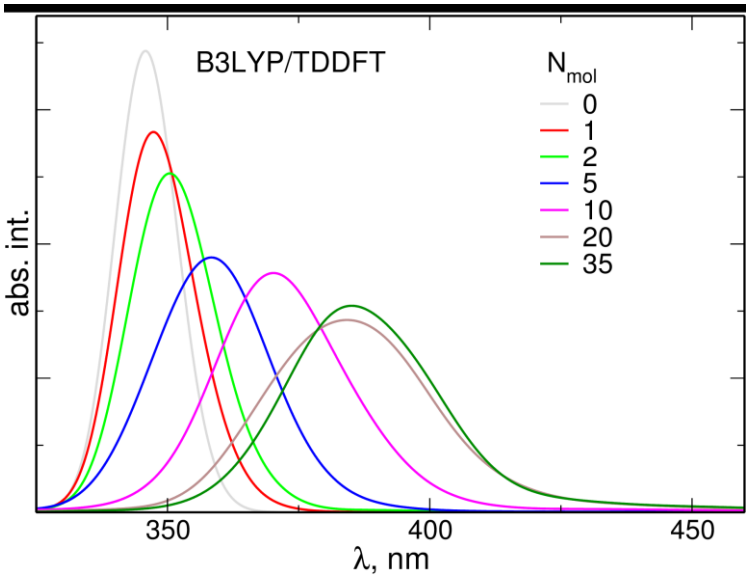
absorption spectra – explicit solvent

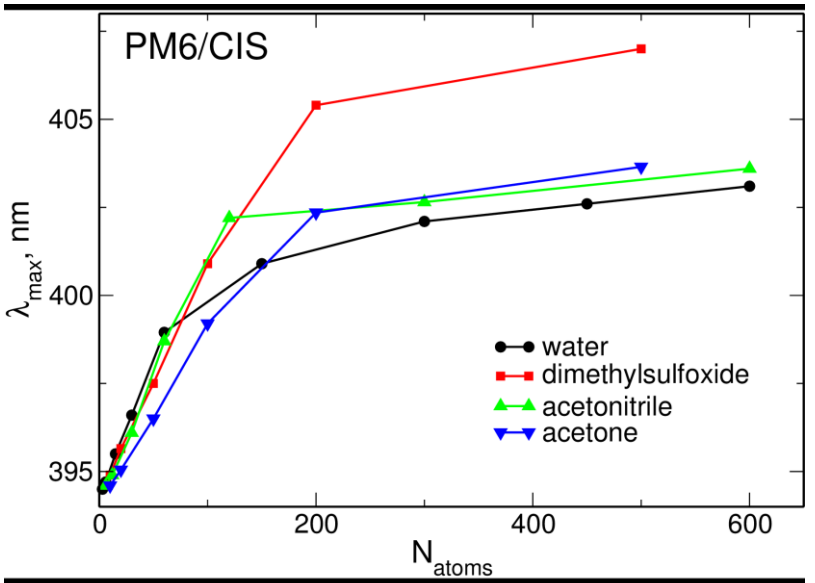


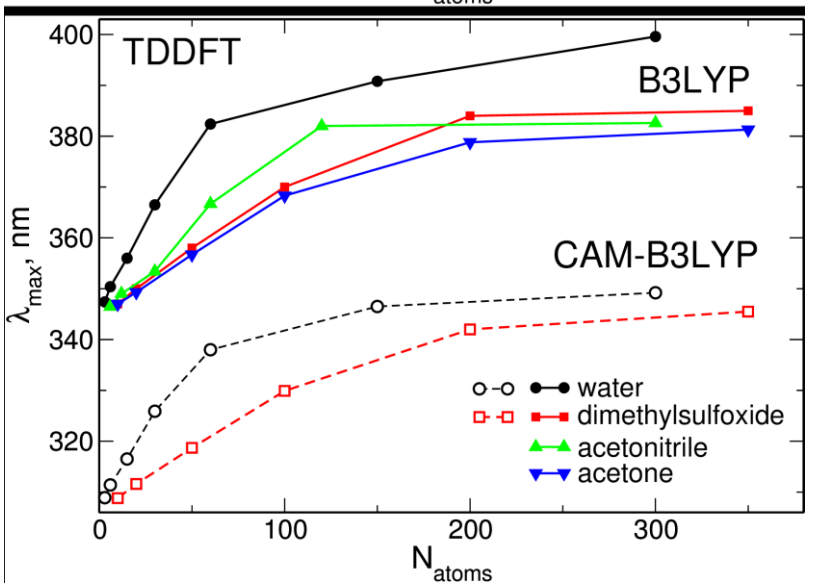
- structures from classical MD simulations
- TDDFT calculations for a dye solvated in increasing number of explicit IL ions
- some (or all) ions may be replaced with bare atomic charges
- 6-311+G* (dye), 3-21G or 6-31G (solvent)
- sizes of systems with fully explicit solvent limited to max. 9 ion pairs



DEPNA, molecular liquids





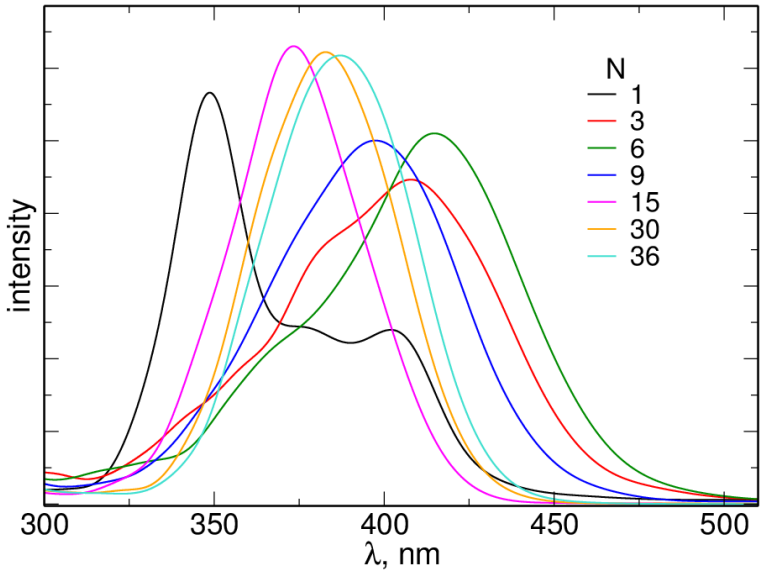


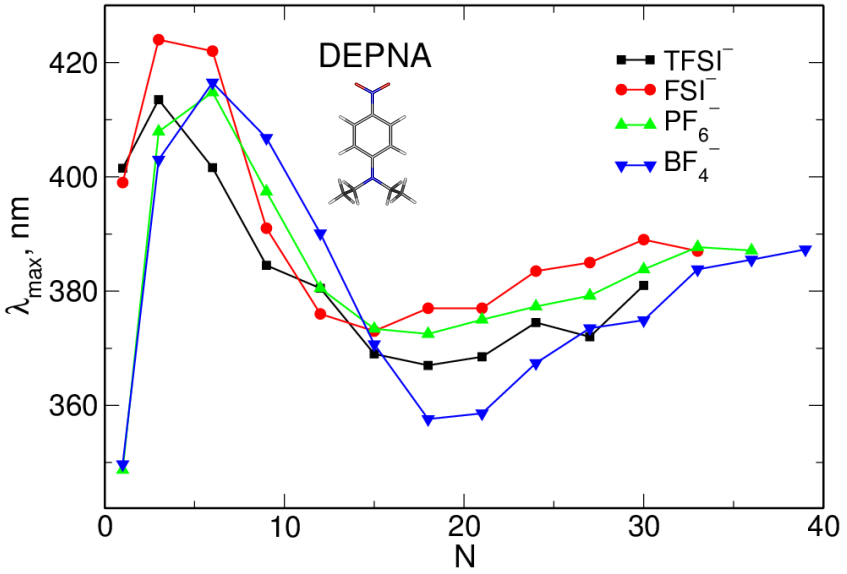
- absorption maximum shifts with increasing N
- TDDFT (B3LYP) results agree reasonably well with experimental data

A. Eilmes, Theor. Chem. Acc. (2014) 133:1538

absorption spectra – electrostatic embedding in ILs

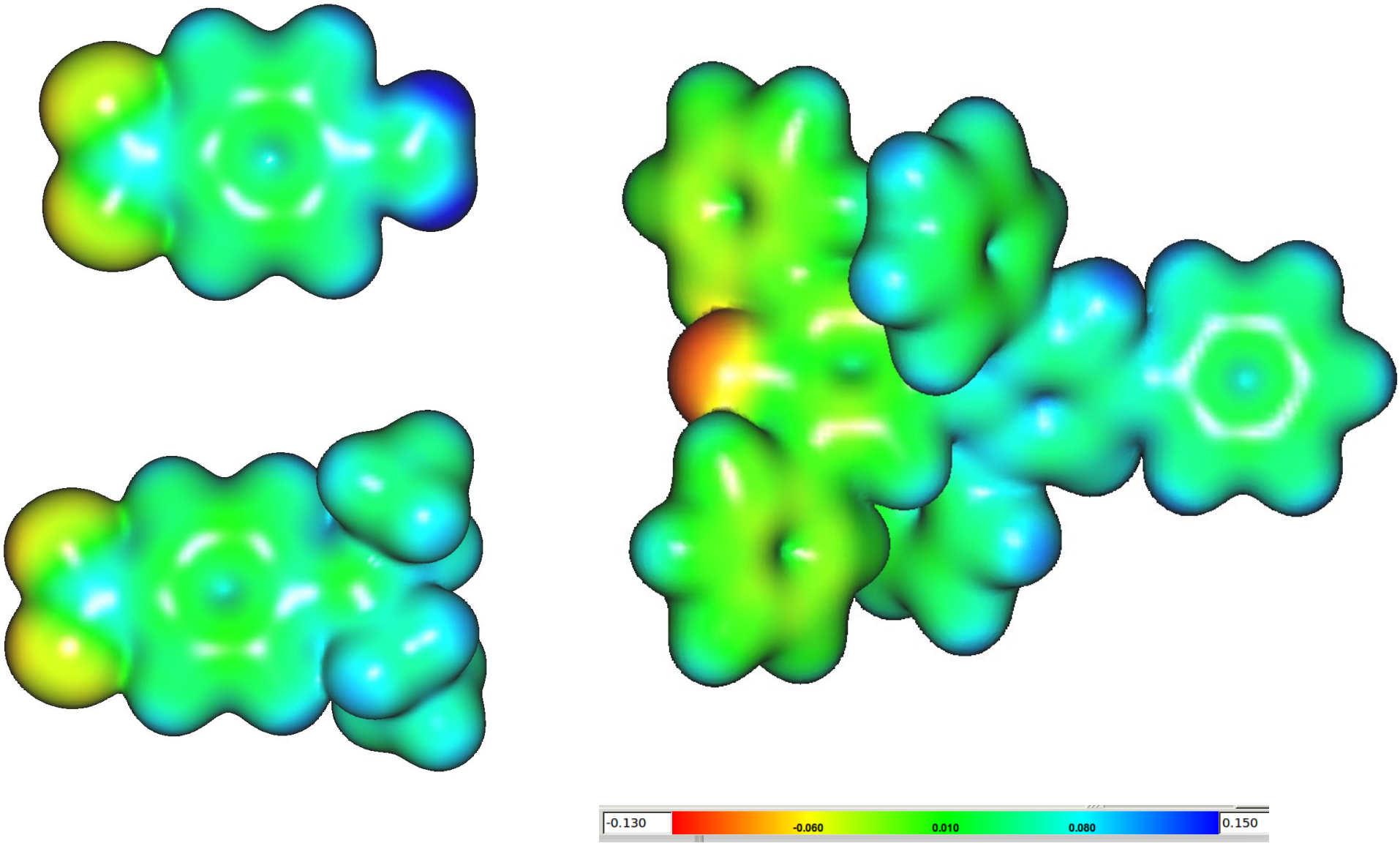
- TDDFT for the dye molecule in the electric field of point charges
- computational cost as for a lone dye molecule
- better convergence than in the case of fully explicit solvent – B3LYP may be used





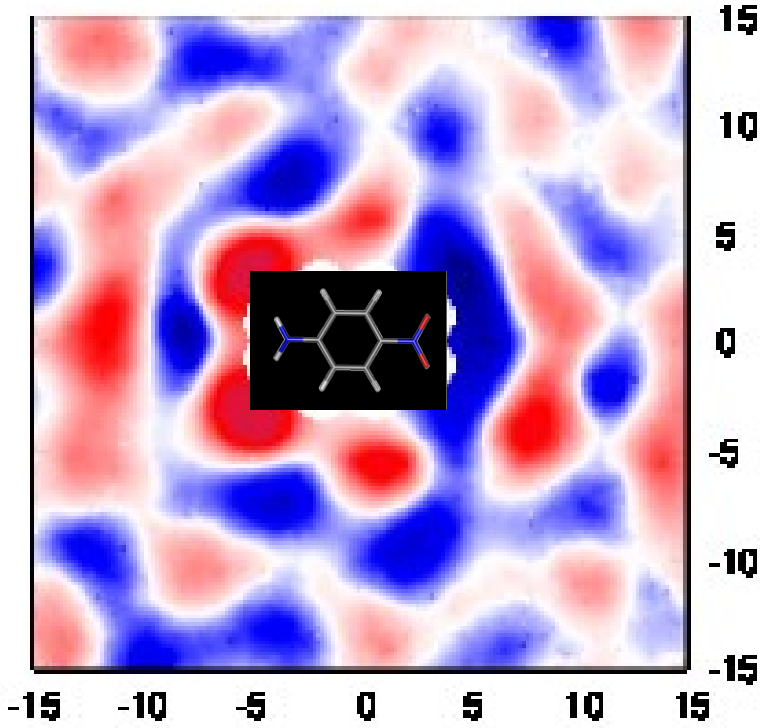
- good averaging may be achieved at low cost
- shifts comparable with experiment (max. at 405-410 nm)
- nonmonotonic shifts of absorption maximum with increasing N – a striking difference compared to molecular liquids

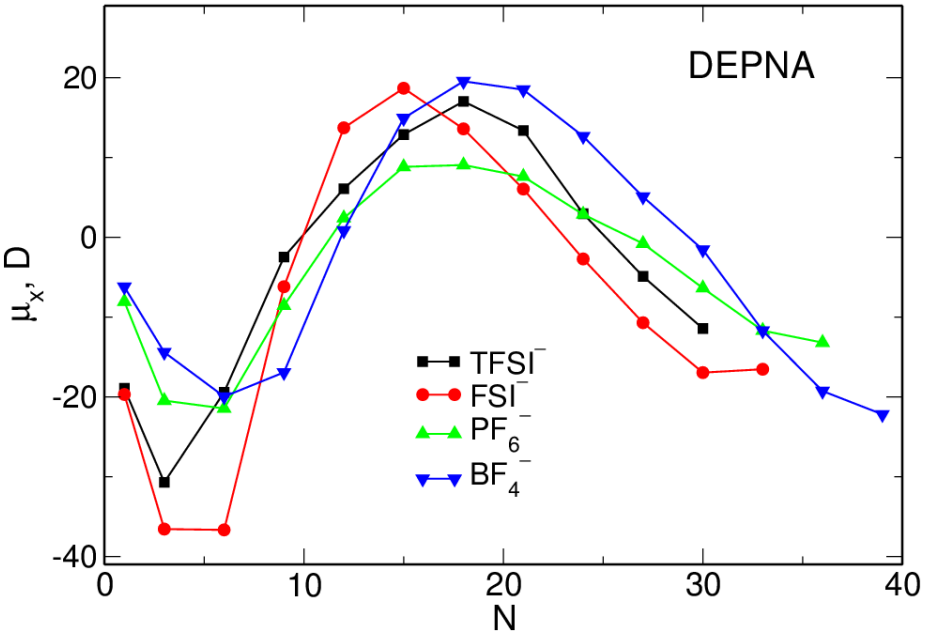
electrostatic potential of dye molecules

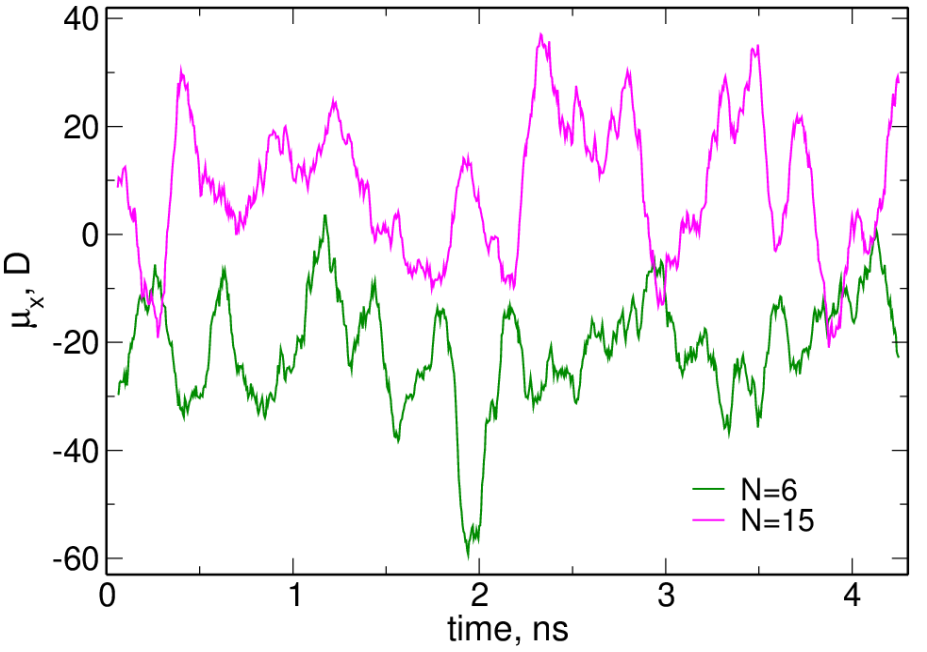


solvation shells of the dye

- electric field of the dipole moment of the dye induces reorganization of the solvent
- solvation shells give different contributions to the total dipole moment of the solvent

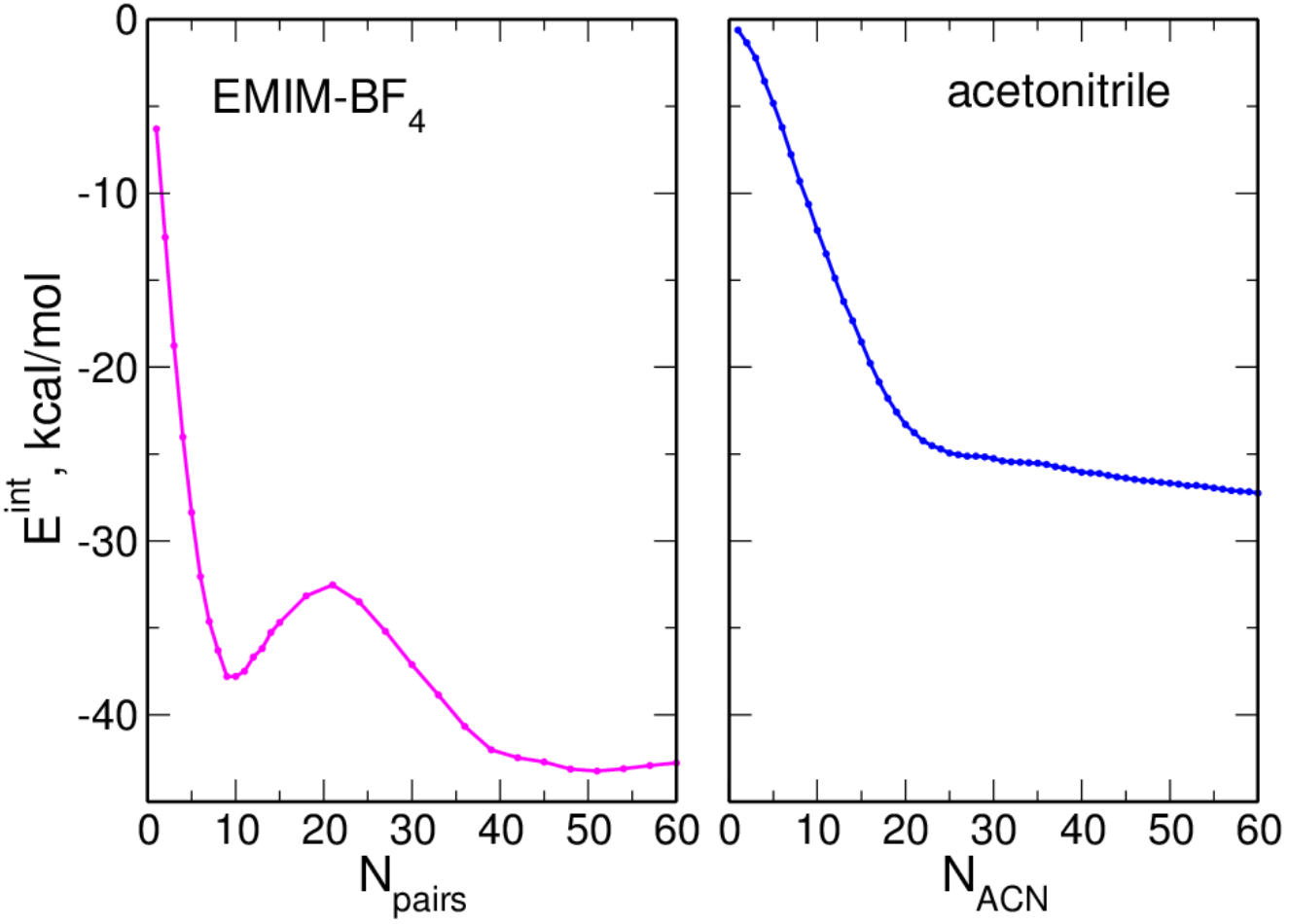






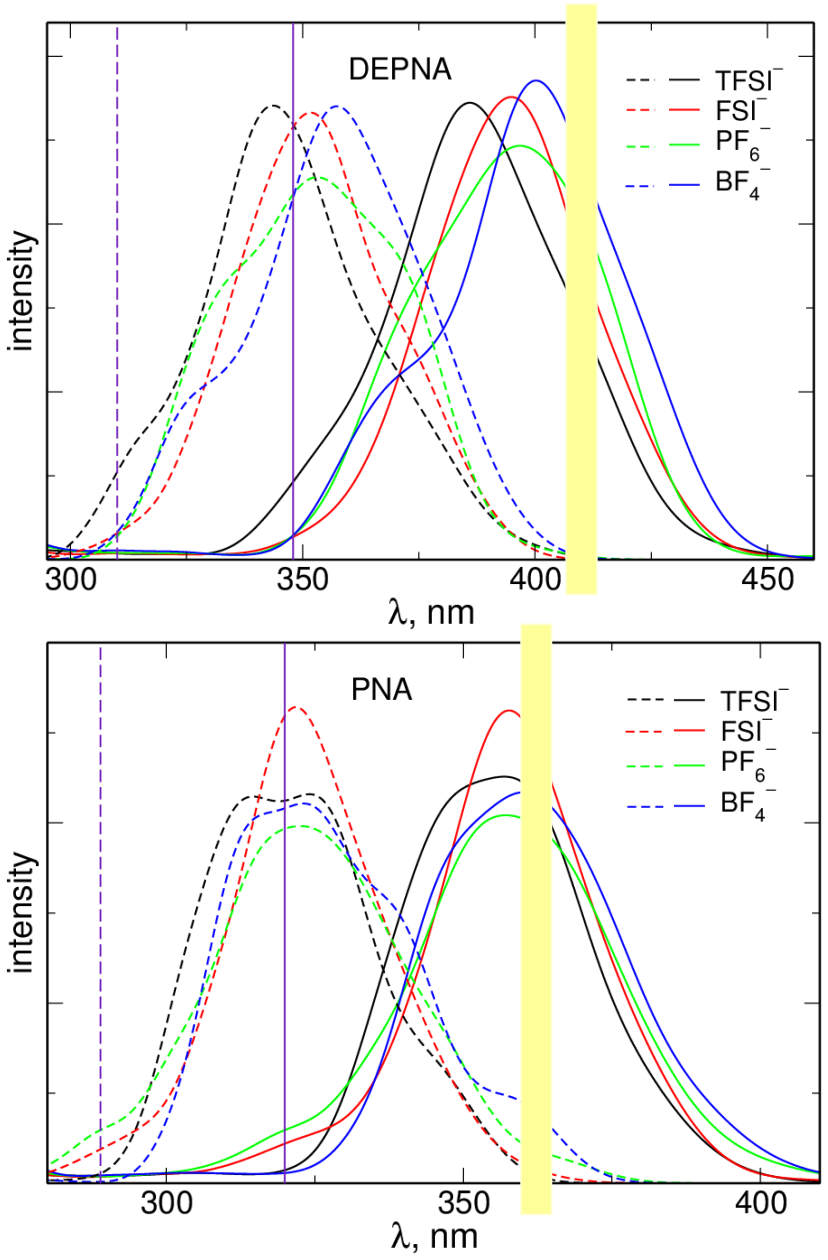
solute-solvent interaction

- shifts of the maximum in the absorption spectrum result from the structure of solvation shells
- in ionic liquids the effect is dominated by long-range electrostatic interactions



solute-solvent interaction energy in molecular and ionic liquid

absorption spectra of dyes in ILs



- mixed approach: a few (3-6) explicit IL ion pairs and about 30 ion pairs represented as partial charges
- for PNA and DEPNA B3LYP results (solid lines) are in better agreement with experimental data than CAM-B3LYP results (broken lines)
- for Reichardt's dye CAM-B3LYP performs better than B3LYP – possible reason: the dye is zwitterionic

summary

- strong interactions between solute and the ions of the ionic liquid result in structured solvation shells
- this affects calculated solvatochromic shifts
- long-range nature of electrostatic interactions means that much larger system sizes are needed in explicit solvent modeling of ILs
- mixed approach (explicit solvent/electrostatic embedding) seems to be the most effective

ackowledgments

Co-worker:

Dr Piotr Kubisiak

PL-Grid infrastructure was used in calculations

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