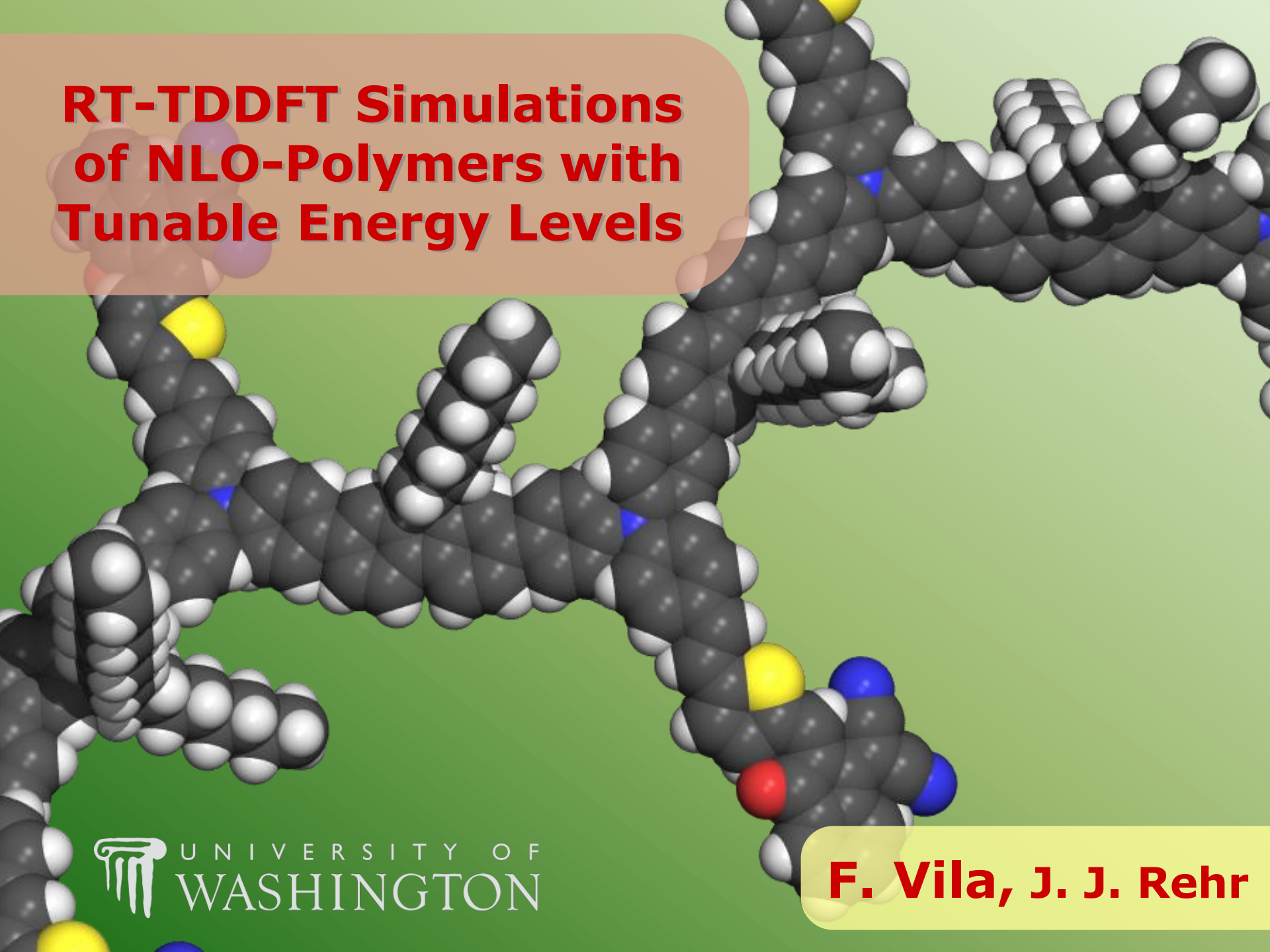
RT-TDDFT Simulations of NLO-Polymers with Tunable Energy Levels



UNIVERSITY OF WASHINGTON

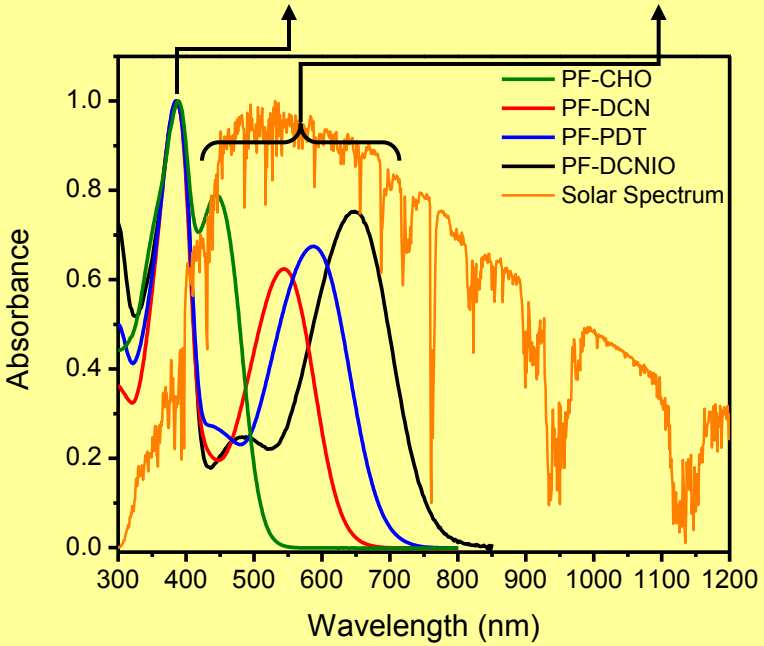
F. Vila, J. J. Rehr

New Polymer Design Concept

Cross-Conjugated Polymers for High Performance Solar Cells:

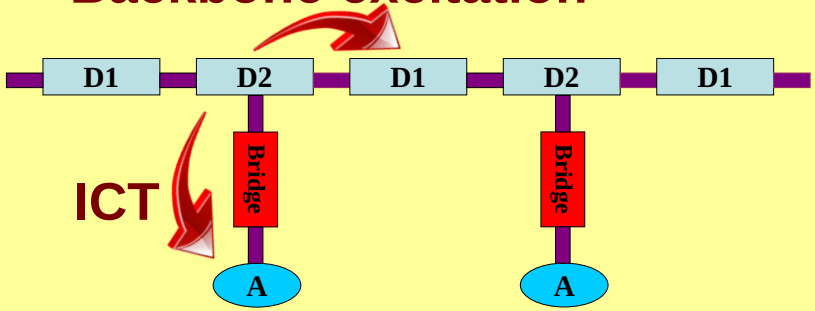
- Efficiency can be improved over donor of choice (P3HT)
- Absorption and gap can be controlled by tuning intramolecular charge transfer (ICT)
- Polymer backbone has high hole mobility

Backbone excitation ICT



Tunable energy levels and band gaps

Backbone excitation



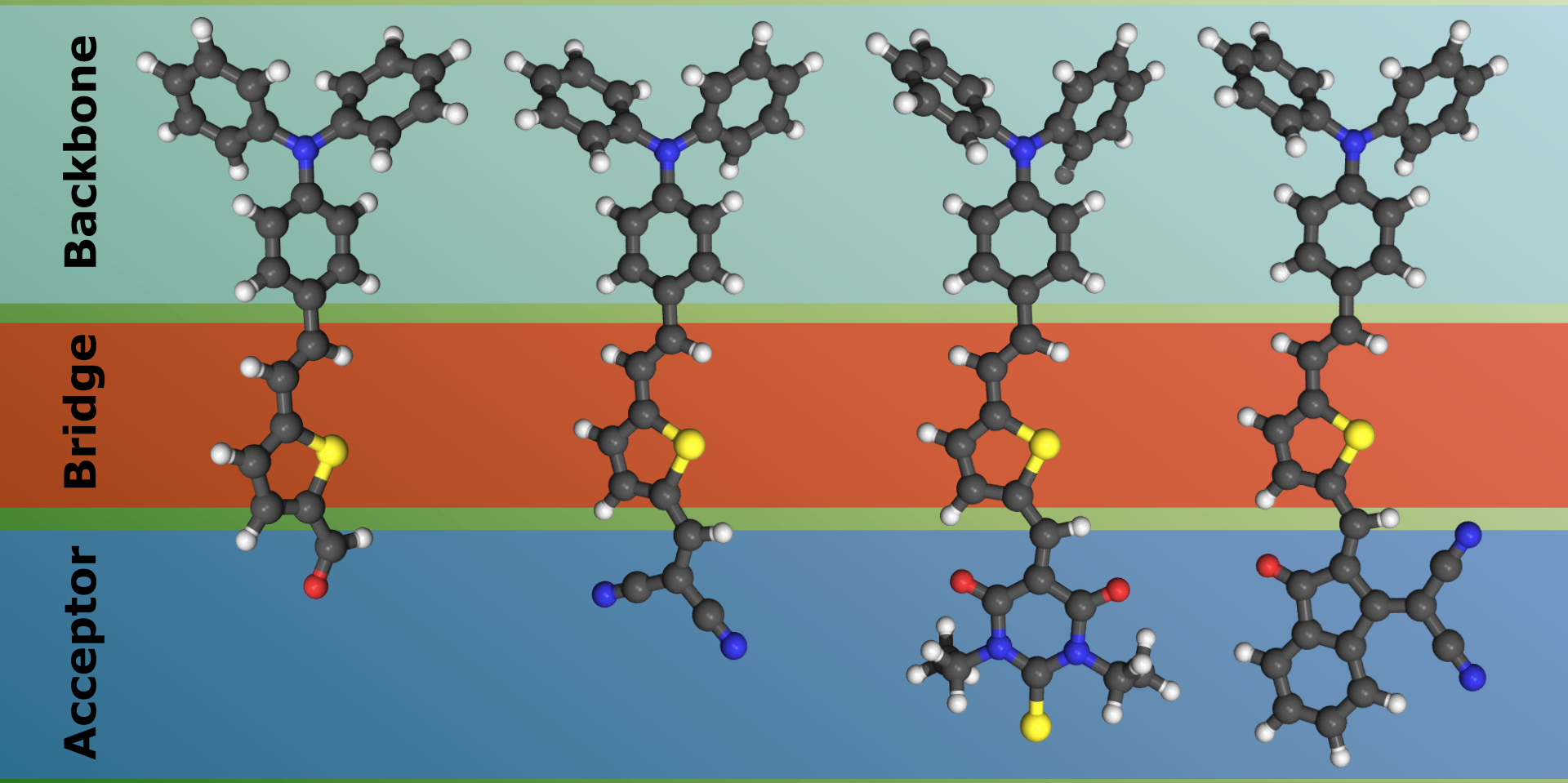
Copolymer backbone with donor-bridge-acceptor side chain

F. Huang *et al.*, JACS 131, 13886 (2009)

Objectives

1. Demonstrate New Developments in RT-TDDFT
2. Develop Models of NLO-Polymers
3. Study Accuracy of Different DFT Functionals
4. Study Theoretical Tunability of NLO-Polymers

B3LYP/6-31G(d,p) Optimized Models of NLO-Polymers



PF-CHO PF-DCN PF-PDT PF-DCNIO

Real-Time Time Dependent DFT

Direct numerical integration of the time-dependent Kohn-Sham equations in a time-dependent external electric field:

$$i\frac{\partial \Psi}{\partial t} = H(t)\,\Psi \qquad \Psi(t) = T\,\exp\left(-i\int_0^t H(t')dt'\right)\Psi(0)$$

$$H = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r},t) + V_H[\rho](\mathbf{r},t) + V_{xc}[\rho](\mathbf{r},t)$$

Optical properties are determined from the total dipole moment:

$$\mathbf{p}(t) = \int \rho(\mathbf{r},t)\,\mathbf{r}\,d^3\mathbf{r}$$

$$\underbrace{\chi^{(1)}_{ij}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega)}_{\text{Linear Response}} \qquad \underbrace{\sigma(\omega) \sim \omega\,\mathbf{Im}\,\langle\alpha(\omega)\rangle}_{\text{Absorption}}$$

Yabana and Bertsch, Phys. Rev. B 54, 4484 (1996)

Numerical Real-Time Evolution

Ground state density ρ_0, overlap S and Hamiltonian $H(t)$ evaluated at each time-step using our modified version of SIESTA:

$$i\frac{\partial c(t)}{\partial t} = S^{-1}H(t)\underbrace{c(t)}_{\text{Orbital coefficients}}$$

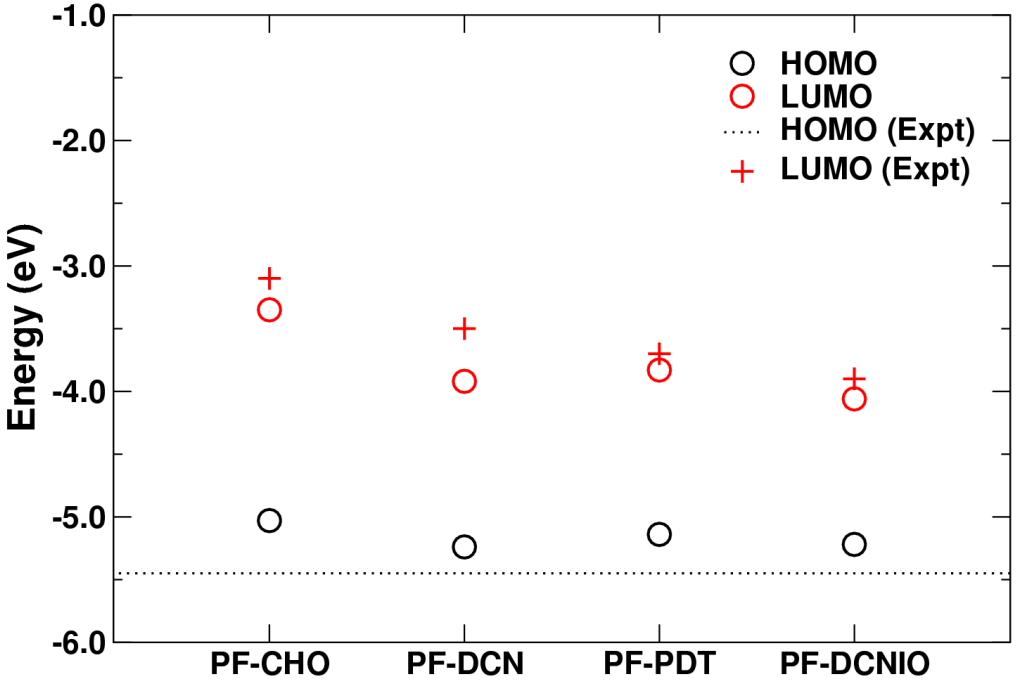
Soler *et al.* J. Phys.: Condens. Matter 14, 2745 (2002)

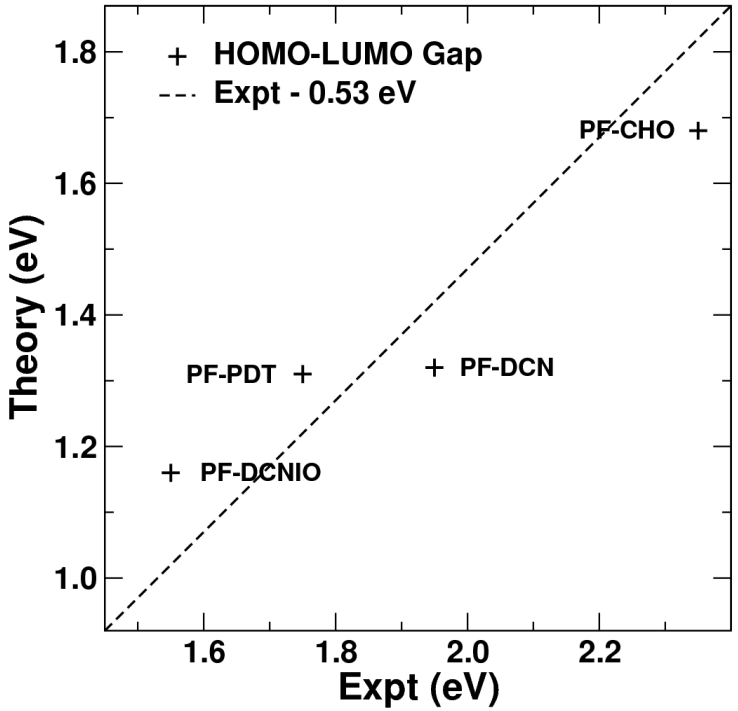
Accurate and stable time evolution achieved with recently implemented time-reversible Crank-Nicholson propagator:

$$c(t+\Delta t) = \frac{1 - iS^{-1}H(t+\Delta t/2)\Delta t/2}{1 + iS^{-1}H(t+\Delta t/2)\Delta t/2}\, c(t) + \mathcal{O}(\Delta t^2)$$

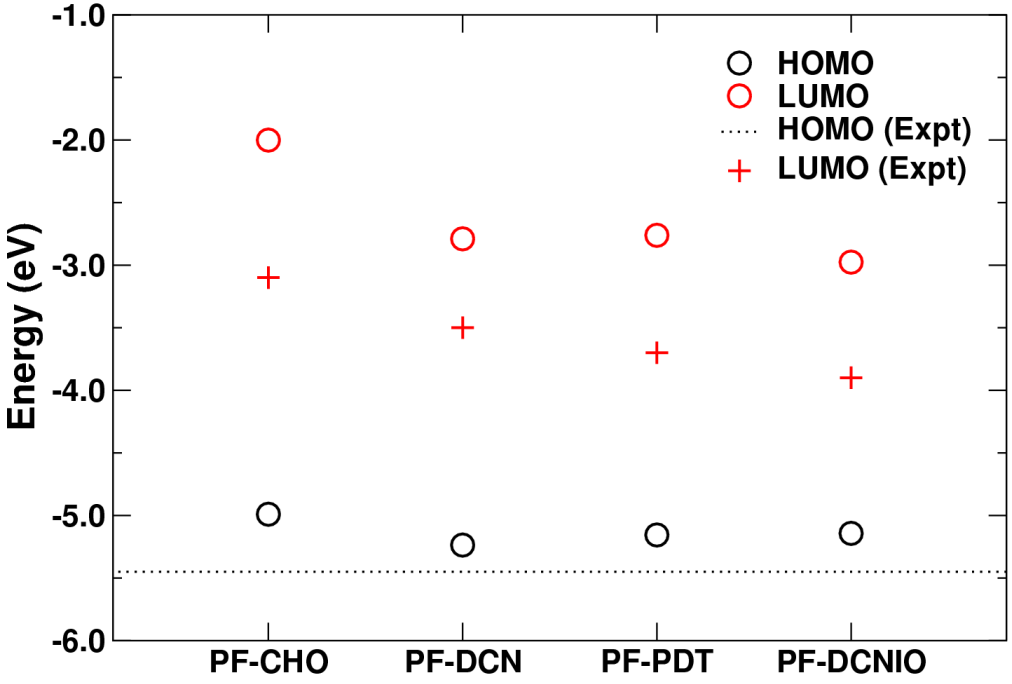
Takimoto *et al.* J. Chem. Phys. 127, 154114 (2007)

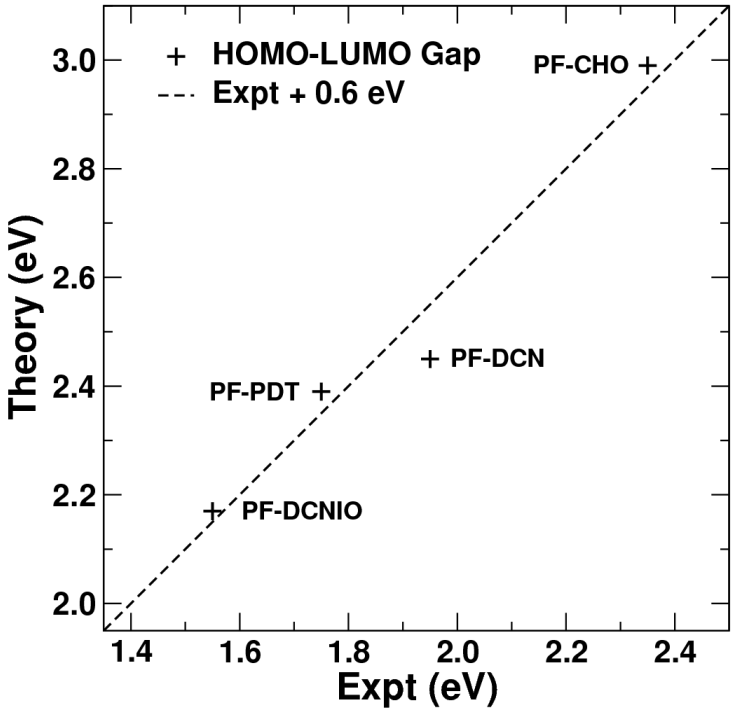
HOMO, LUMO and Gap Energies: PBE Functional



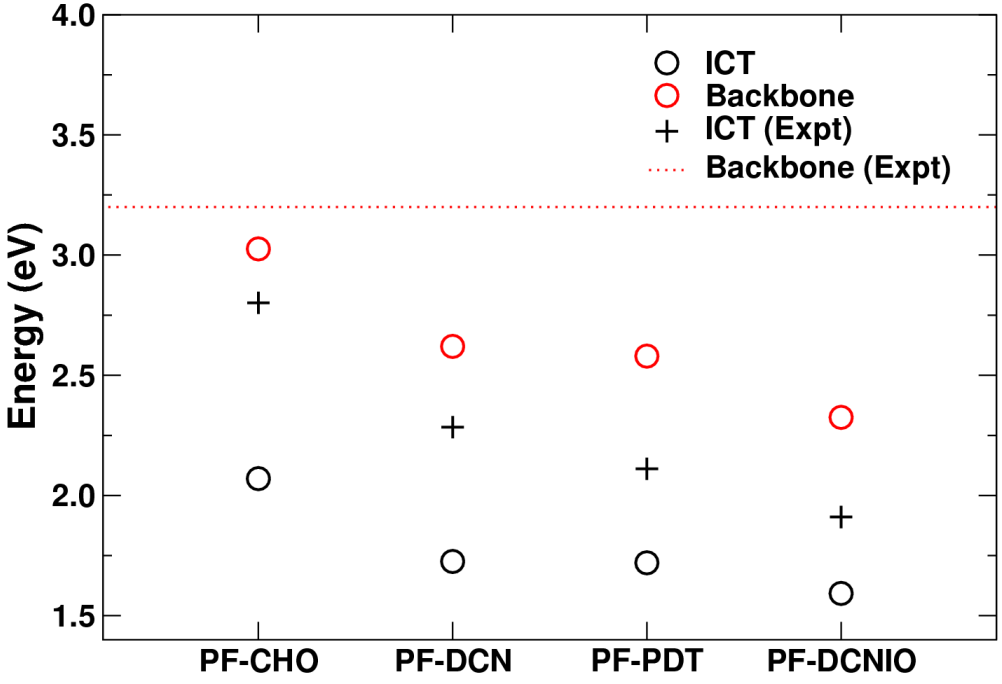


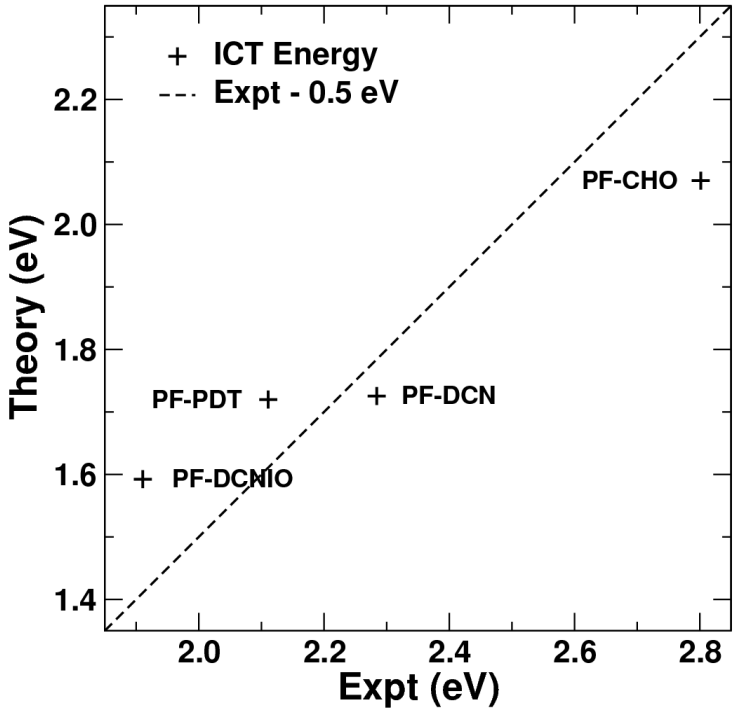
HOMO, LUMO and Gap Energies: B3LYP Functional



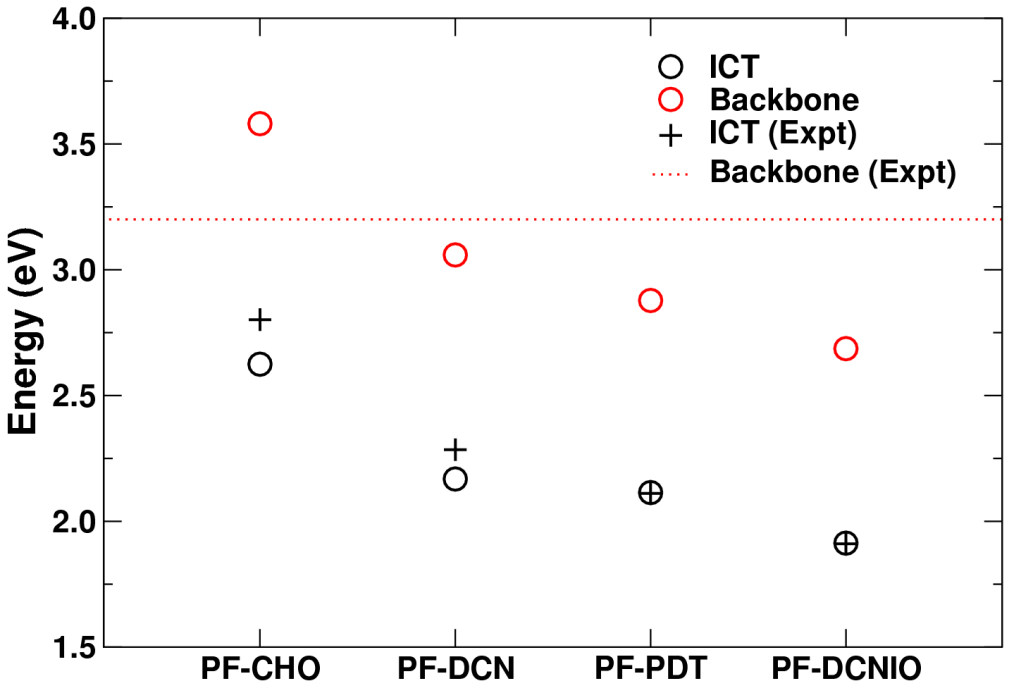


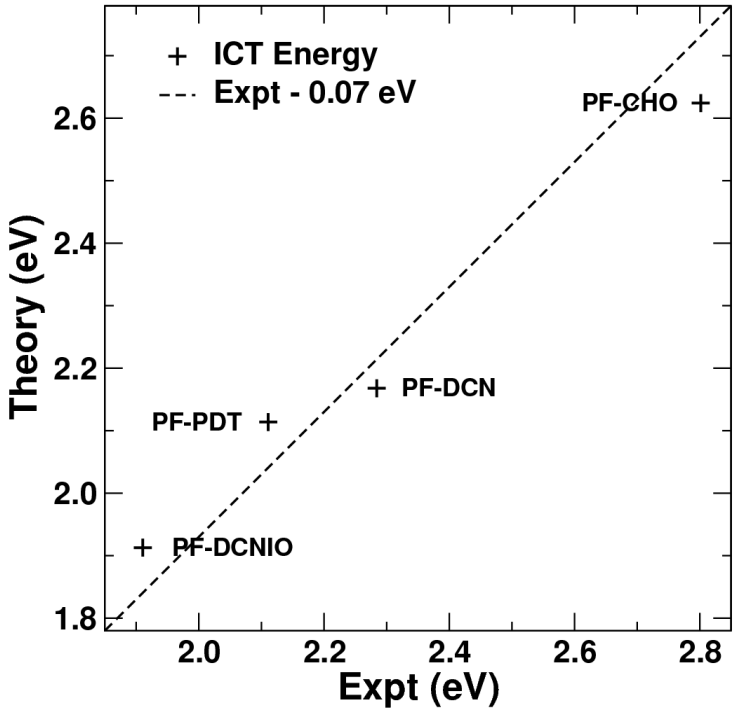
ICT and Backbone Energies: PBE Functional



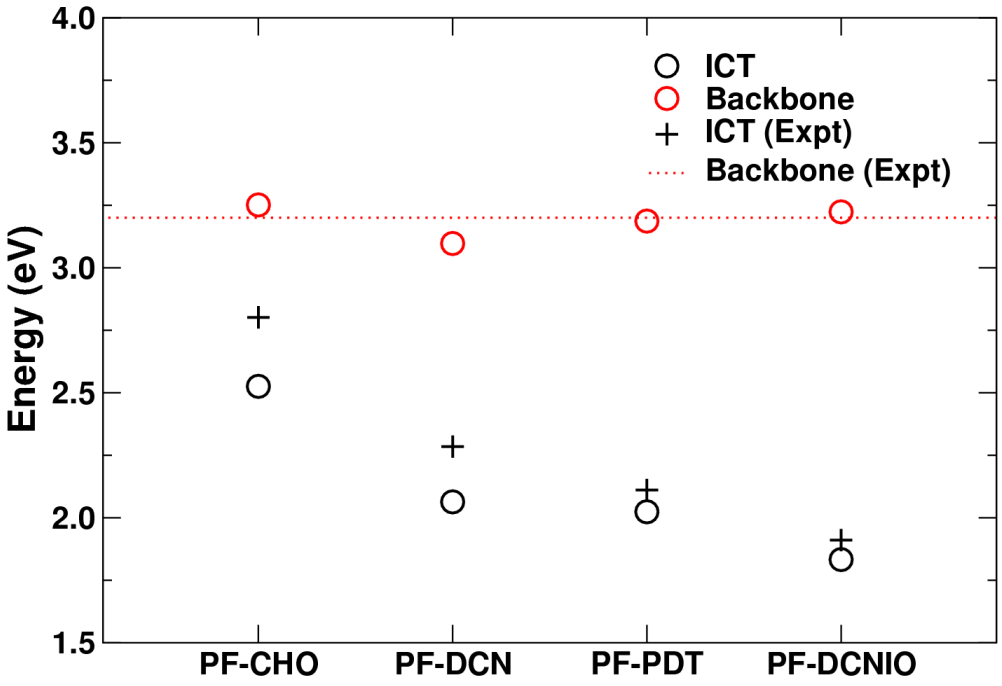


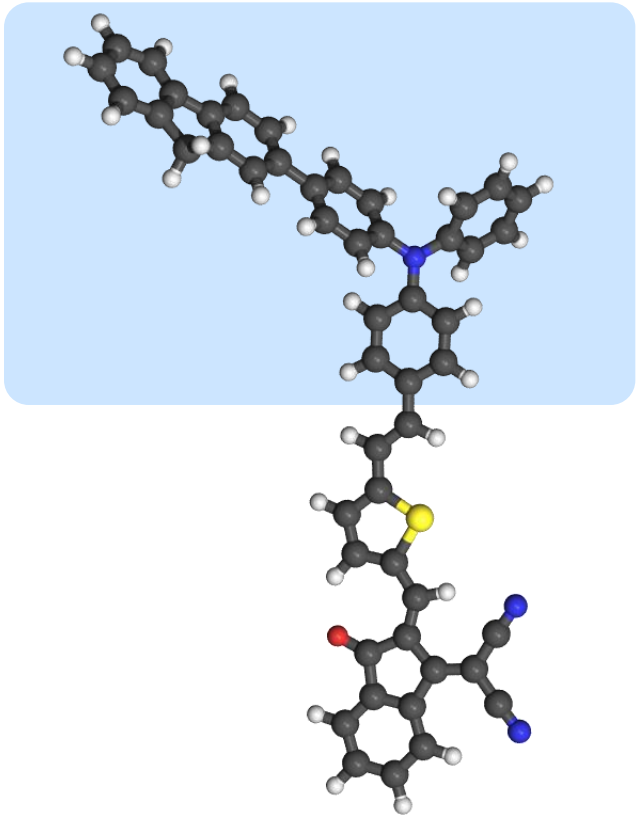
ICT and Backbone Energies: B3LYP Functional



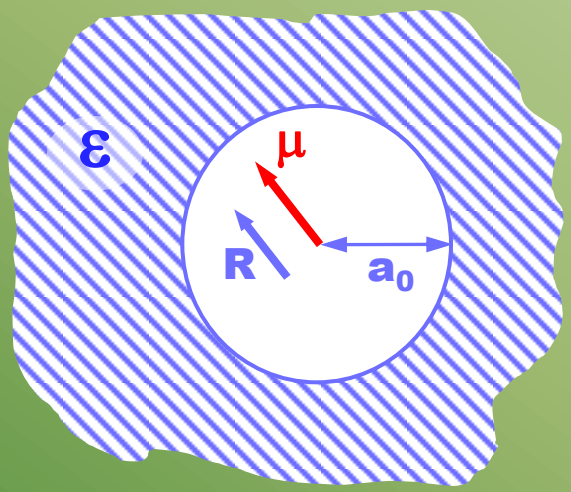


ICT and Backbone Energies: B3LYP Functional (Full Model)

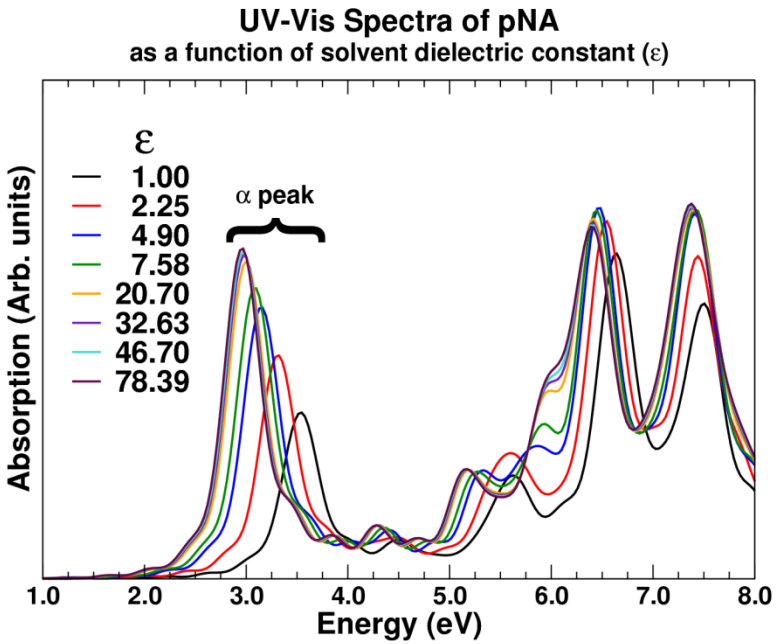


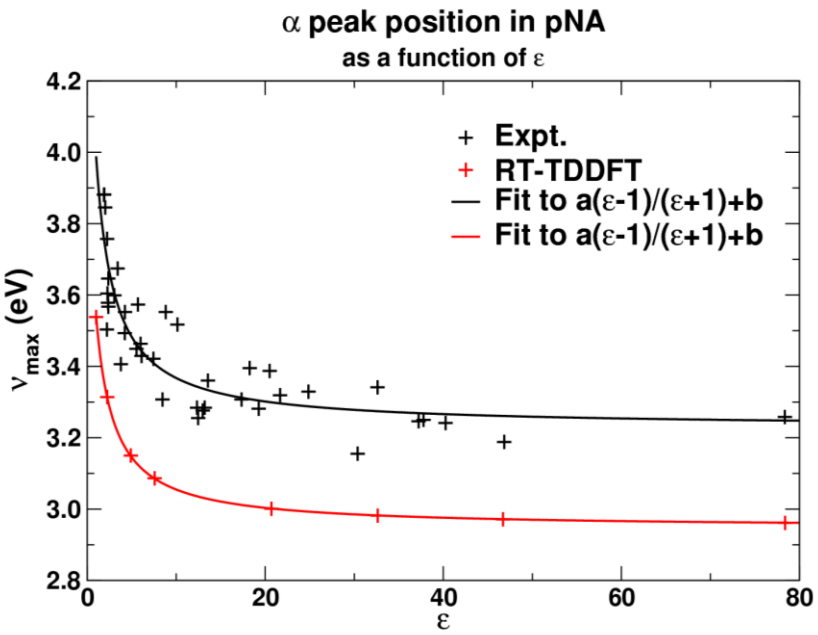


Onsager Solvation Model

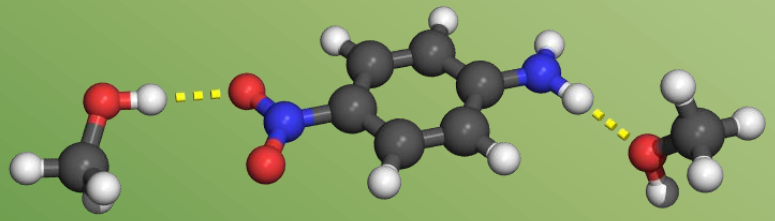


- Spherical cavity of radius a_0 in dielectric medium
- Computational effort equivalent to vacuum calculation

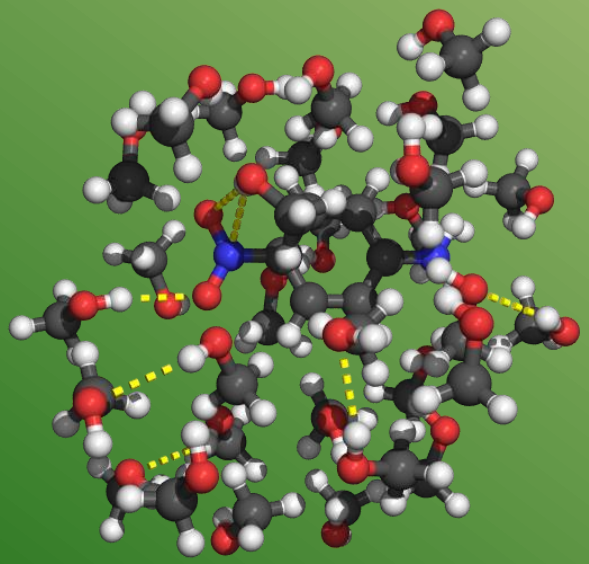




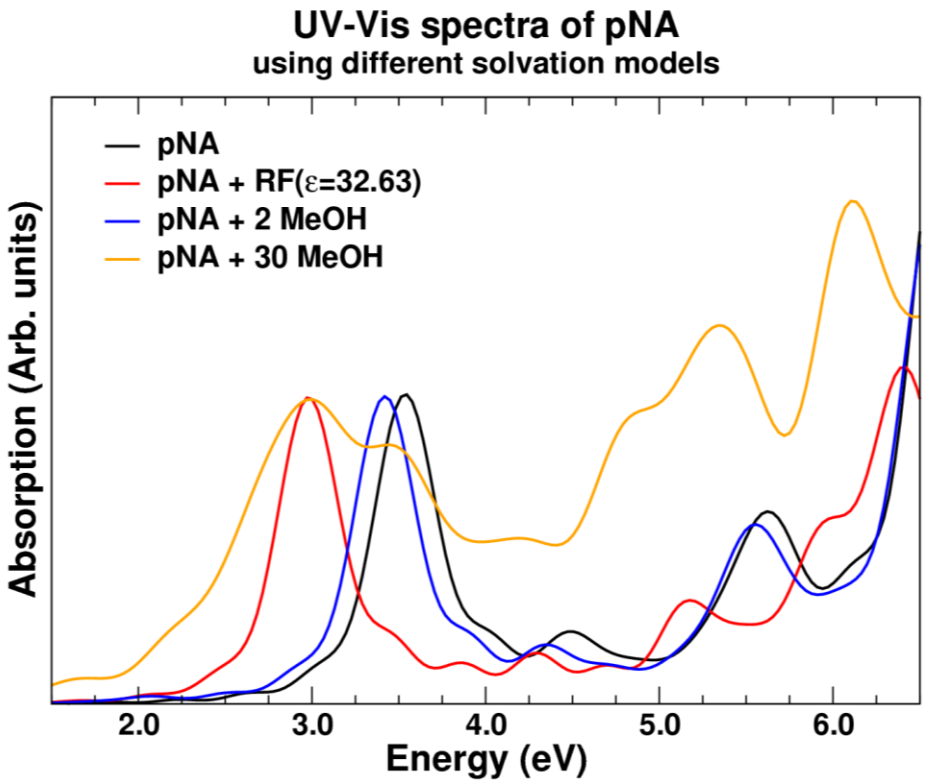
Explicit vs Reaction Field Solvation



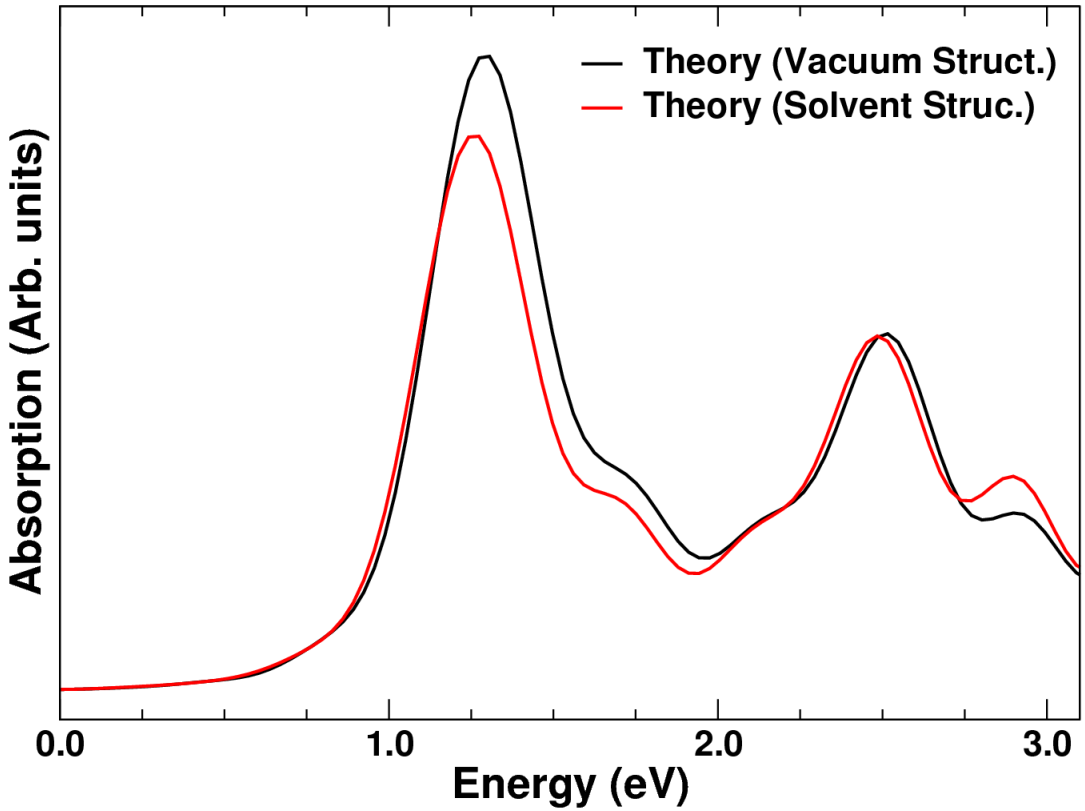
pNA + 2 MeOH



pNA + 30 MeOH



Solvent effect on structure

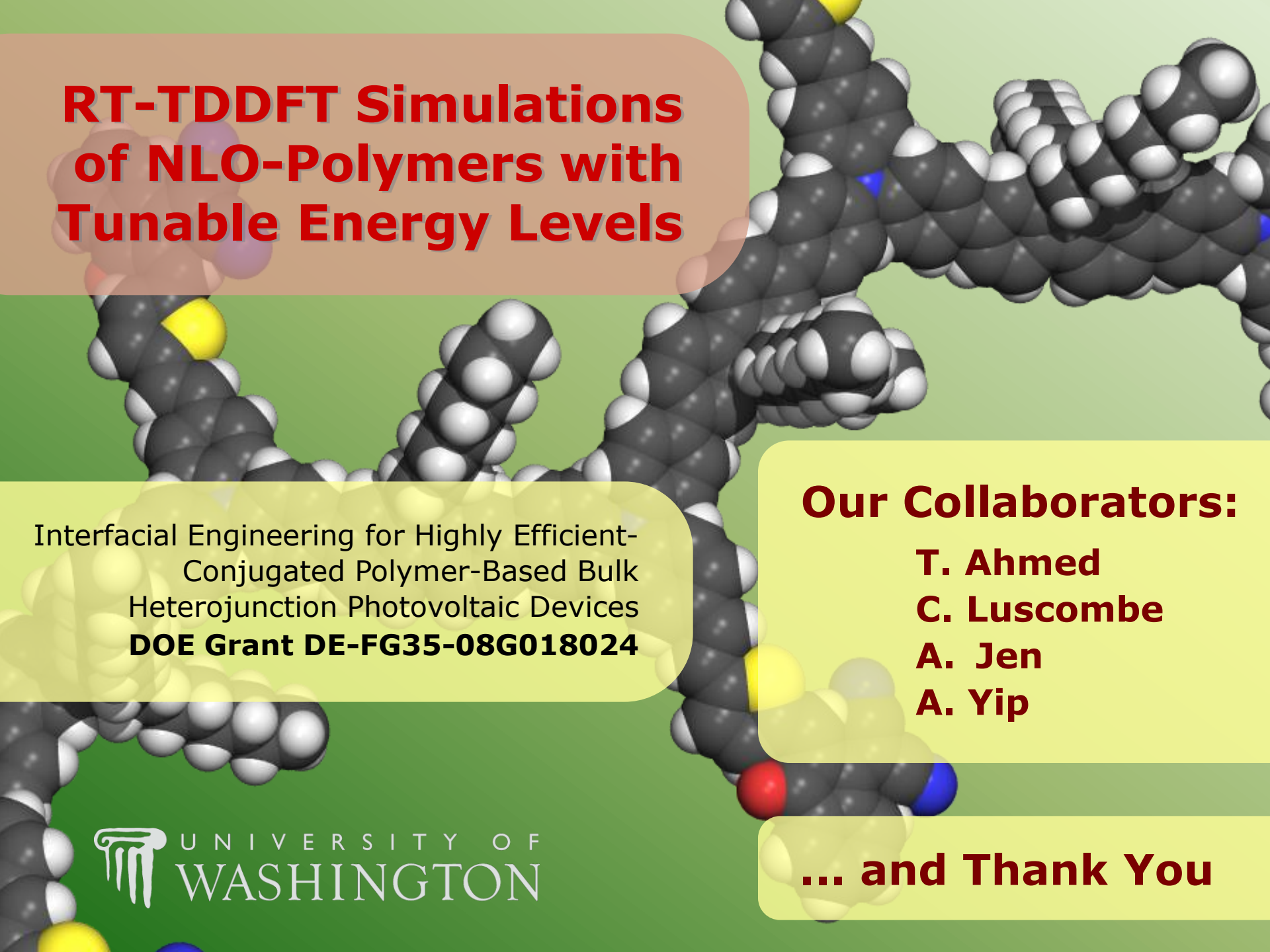


D. Strubbe, Session S1: Poster Session III 1:00 pm, Wed Mar 17th

Conclusions

1. New in RT-TDDFT: Predictor-Corrector Propagation, more accurate and efficient
2. New in RT-TDDFT: Onsager solvation model, more realistic modeling
3. Hybrid (Exact-exchange) functional gives good intramolecular charge transfer energies
4. Theoretical methods can be used to predict absorption maxima in NLO-polymers
5. Larger models needed to account for backbone excitations

RT-TDDFT Simulations of NLO-Polymers with Tunable Energy Levels



Interfacial Engineering for Highly Efficient-Conjugated Polymer-Based Bulk Heterojunction Photovoltaic Devices
DOE Grant DE-FG35-08G018024

Our Collaborators:

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A. Jen
A. Yip

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… and Thank You