SAND2010-2106C

Long-range-corrected DFT Methods for Materials Chemistry Applications

Bryan M. Wong

Joseph G. Cordaro, and Greg O'Bryan

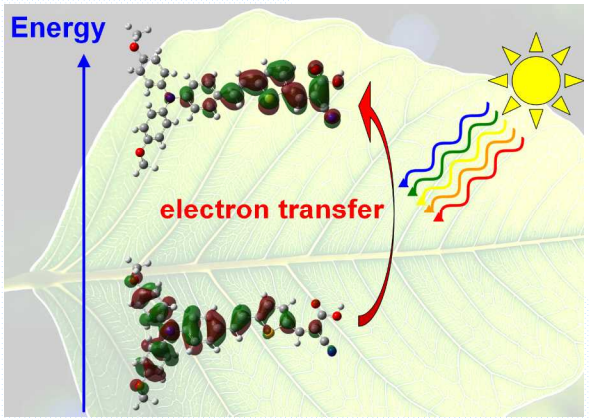
Materials Chemistry Department

Sandia National Laboratories, Livermore, CA

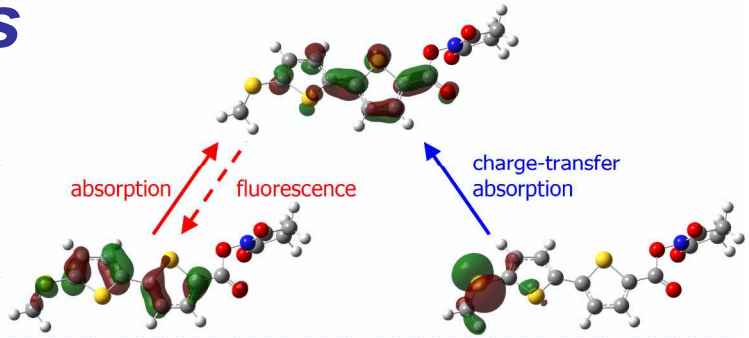
April 9, 2010

Road map

- ***Light-harvesting materials***
  - Can we accurately predict their optoelectronic properties?



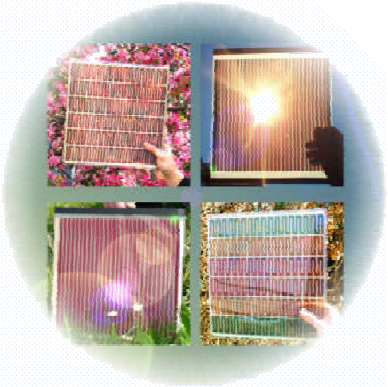
- ***Other types of excitations***
  - Can we describe different excitations on same footing?



- Overall theme: theory ***for*** experiments

Dye-sensitized solar cells

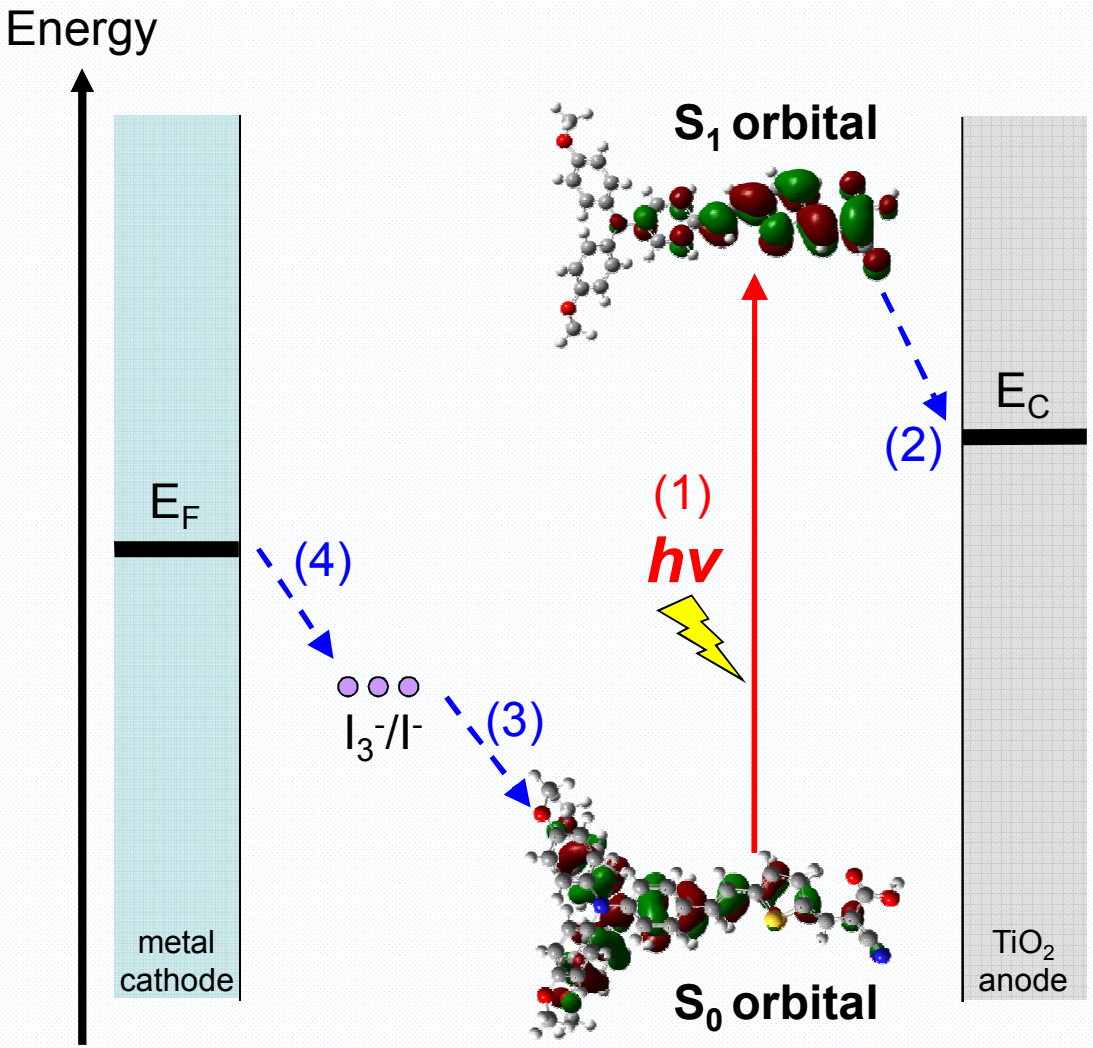
- Growing interest in converting *clean* solar energy to electricity at low cost
- Dye-sensitized solar cells (DSCs) efficient (Grätzel)
  (~ 11% for Ruthenium dyes)



commercial DSCs

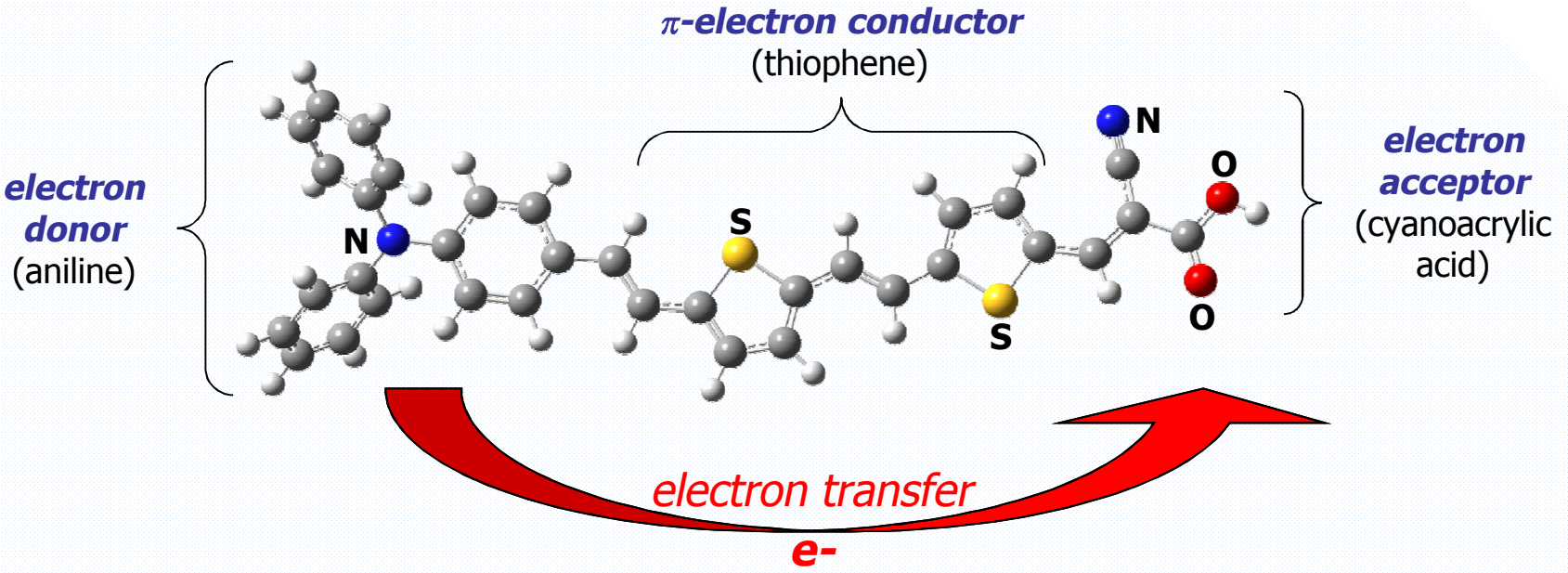
- Considerable progress in *organic sensitizers*
  - Lower cost than Ru
  - Lightweight compared to silicon
  - Easily *tune* absorption wavelengths

How do DSCs work?



Organic sensitizers

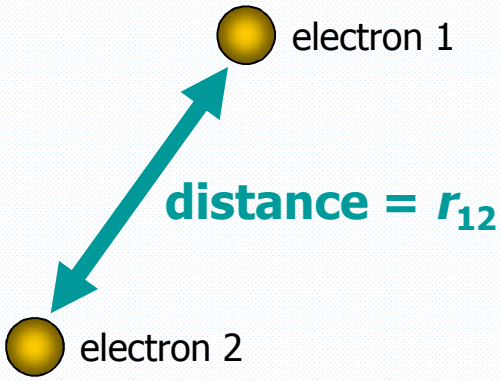
- Donor – π – Acceptor motif

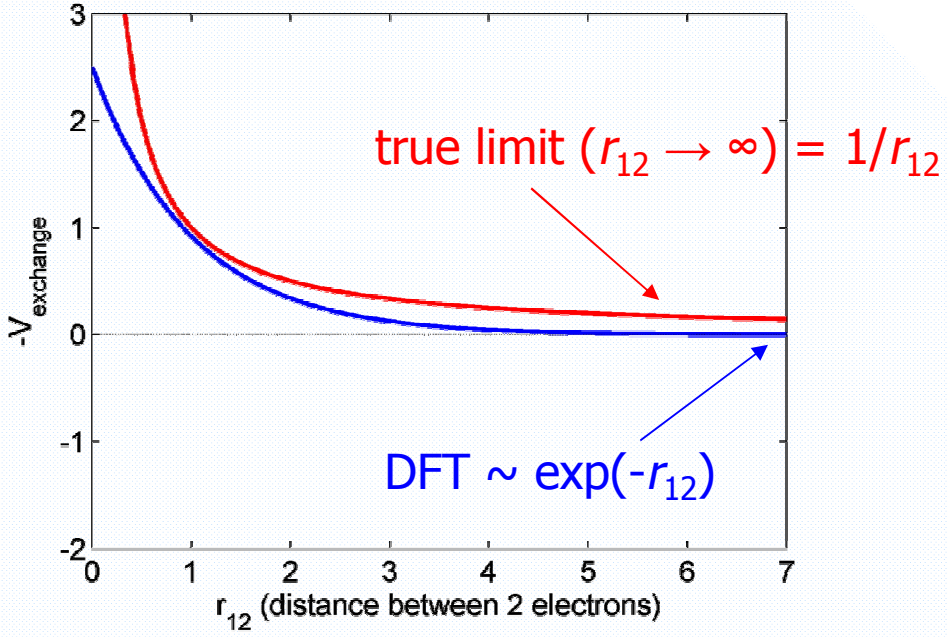


- Use *time-dependent DFT* to predict *excited-state properties* of solar dyes

Charge transfer in TDDFT

- Most DFT methods fail at describing *charge transfer*





- Wrong asymptotic behavior → *charge-transfer excitations severely underestimated*

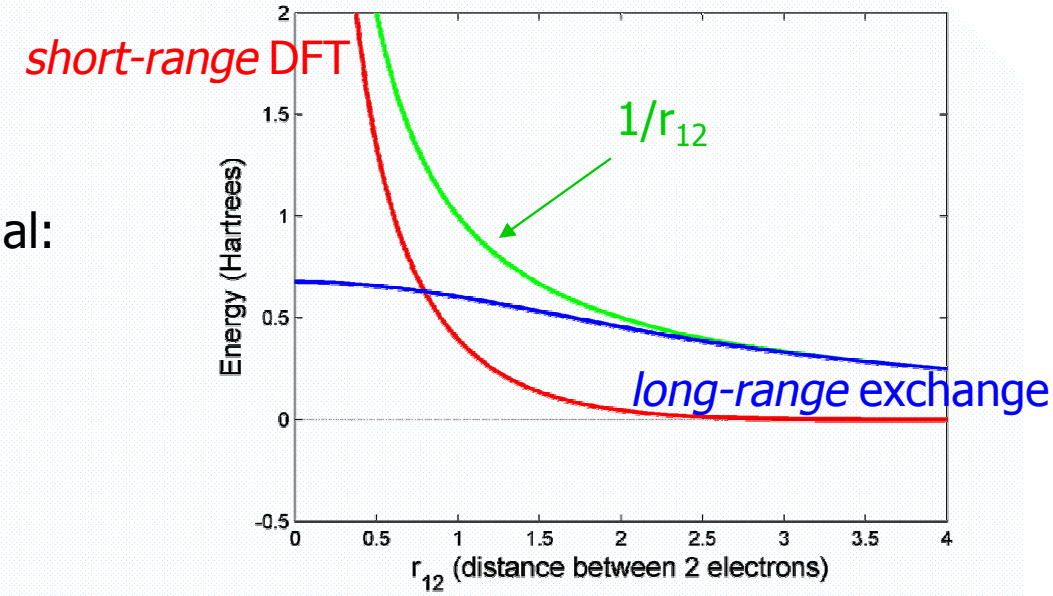
Modifying the exchange functional

- Replace incorrect DFT portion with *long-range nonlocal exchange*[1-5]

Splitting the Coulomb potential:

$$\frac{1}{\mathbf{r}_{12}} = \frac{1-\mathrm{erf}\left(\mu\cdot\mathbf{r}_{12}\right)}{\mathbf{r}_{12}} + \frac{\mathrm{erf}\left(\mu\cdot\mathbf{r}_{12}\right)}{\mathbf{r}_{12}}$$

short-range DFT **long-range exchange**



μ = range separation parameter
controls contributions of DFT and exchange

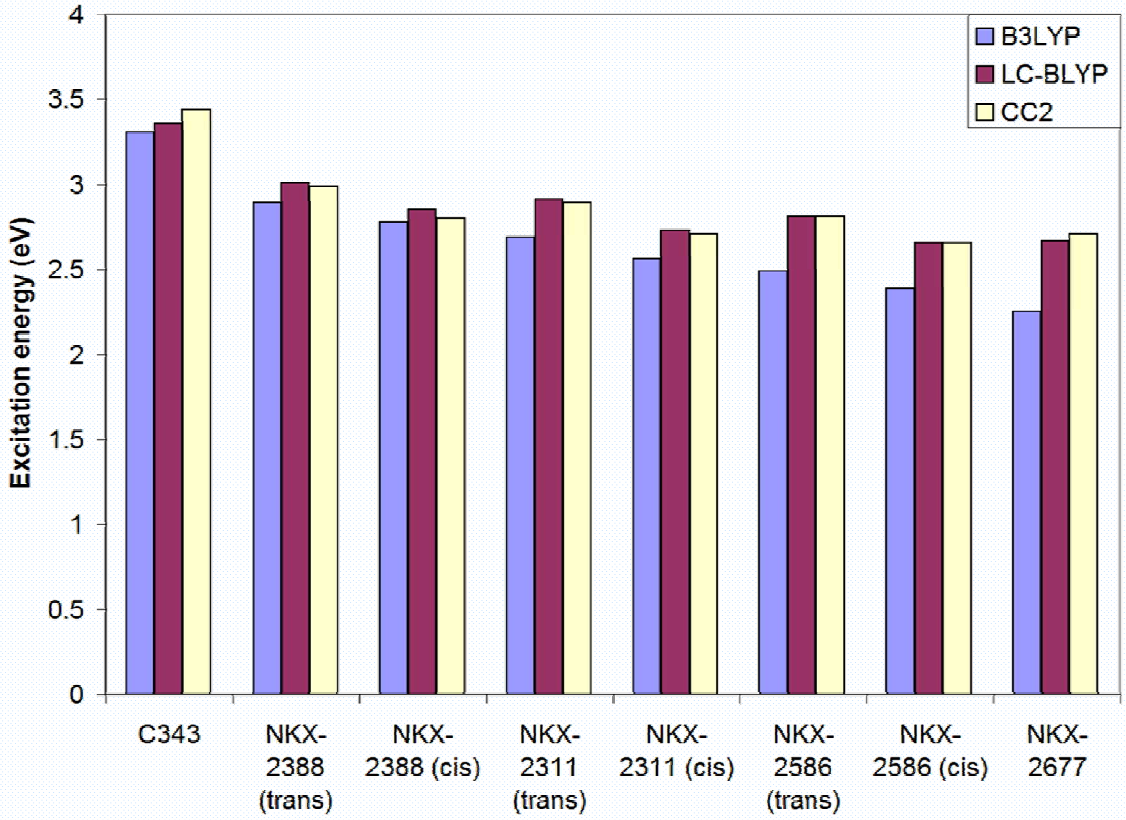
(1) K. Hirao, Univ. of Tokyo
(2) G. Scuseria, Rice Univ.
(3) M. Head-Gordon, UC Berkeley
(4) L. Kronik & R. Baer, Israel
(5) J. Herbert, Ohio State Univ.

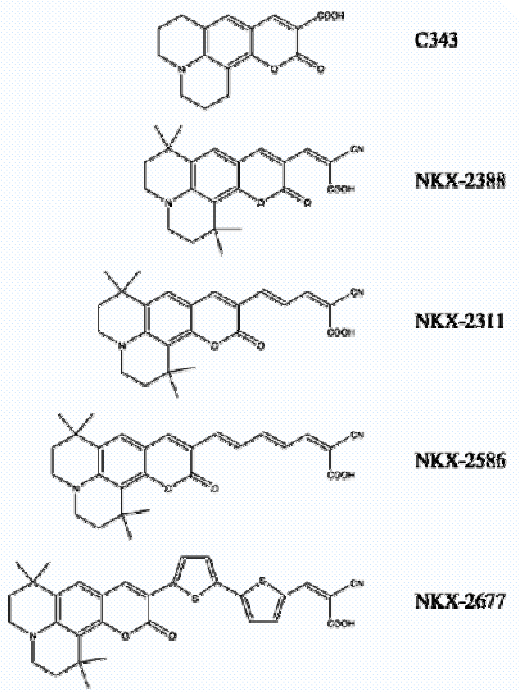
Benchmarking the *LC* method

- Need to compare against reliable benchmarks
- ***Coupled-cluster (CC2)*** wavefunction calculations reproduce experimental data well (extremely computationally demanding)
- Compare long-range corrections ***(LC-BLYP)*** against current popular functionals: ***B3LYP***
- Do we see any *general trends*?

Benchmarking the *LC Ansatz*

- Excitation energies

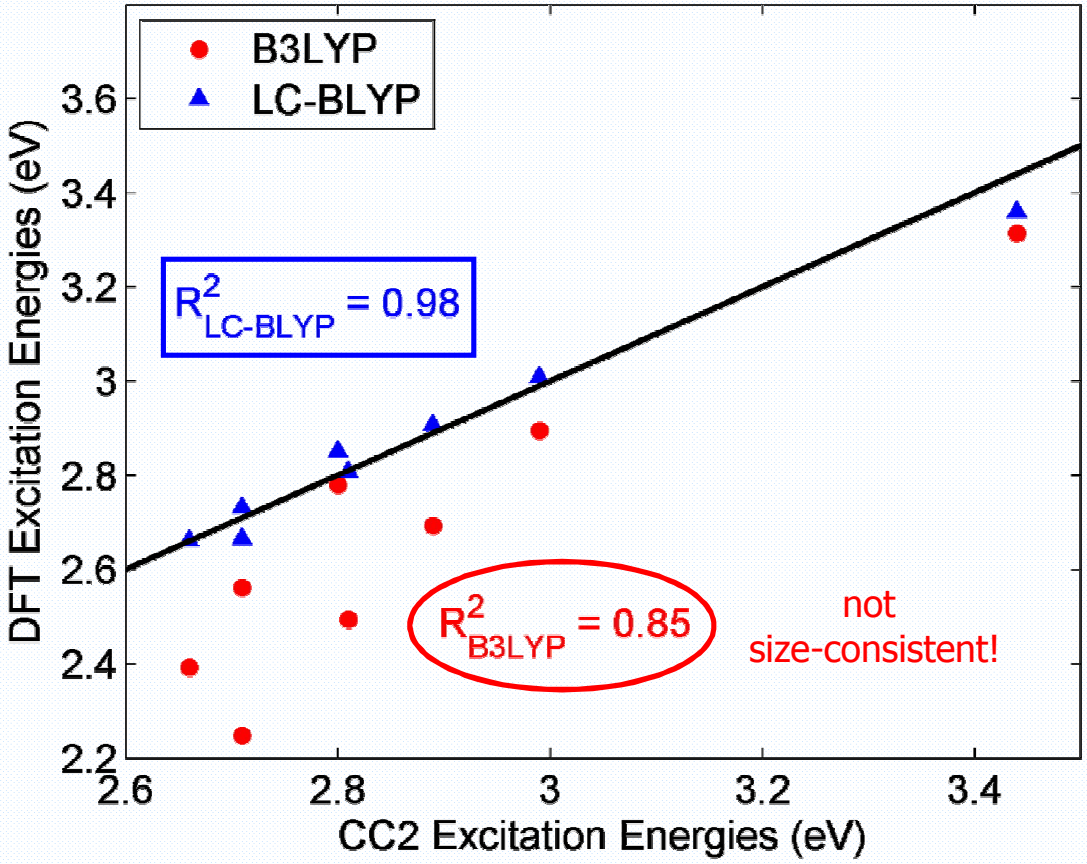


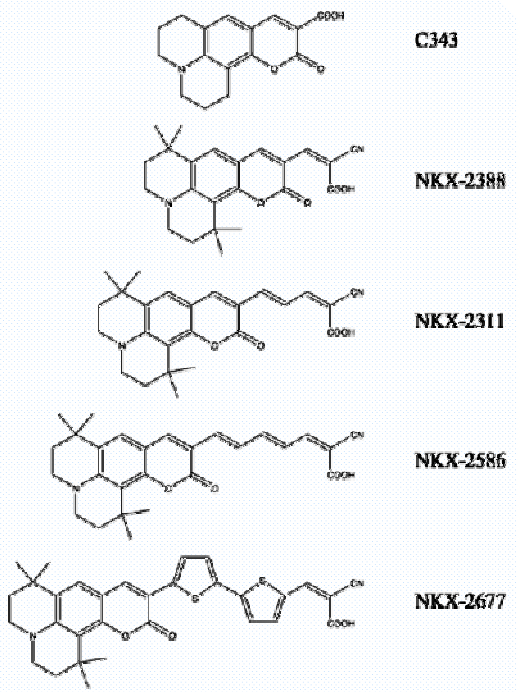


B.M. Wong & J.G. Cordaro, *J. Chem. Phys.* **129**, 214703 (2008)

Benchmarking the *LC Ansatz*

- Overall trends

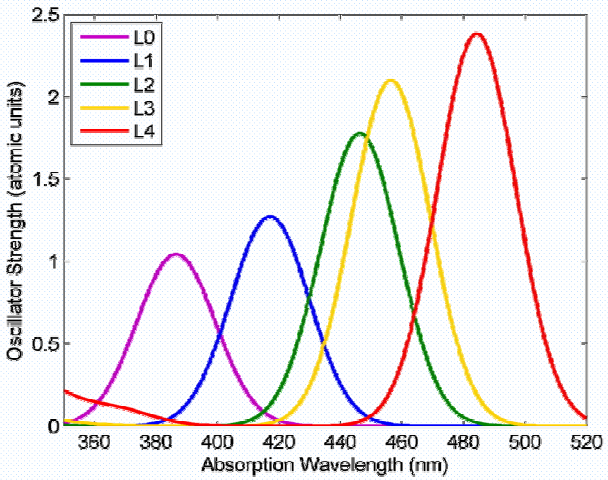


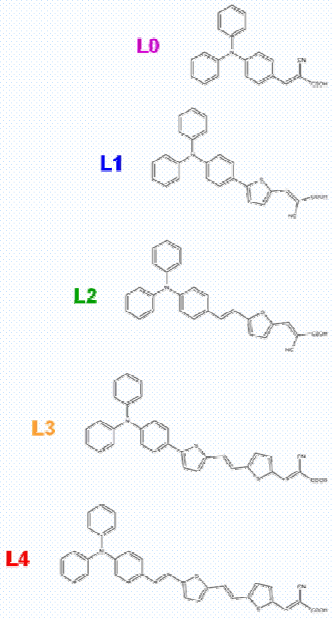


B.M. Wong & J.G. Cordaro, *J. Chem. Phys.* **129**, 214703 (2008)

Results from the *LC* formalism

- *Long-range exchange* vital for describing properties of solar cell dyes
- Knowing excitation energies/dipoles serve as guide for experimental synthesis

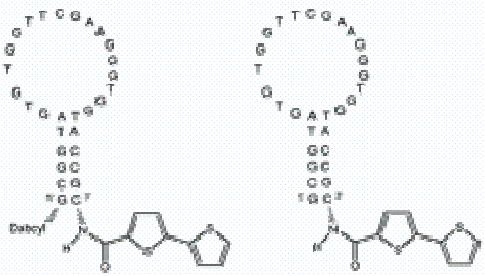




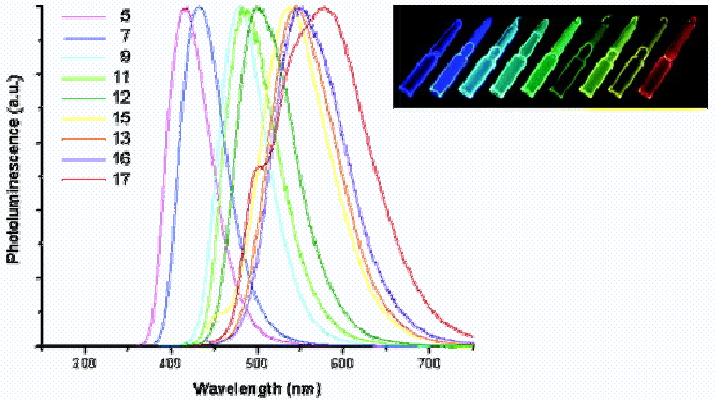
B.M. Wong & J.G. Cordaro, *J. Chem. Phys.* **129**, 214703 (2008)

A more extensive example

- ***Optical biomarkers***



Amino-terminated beacon sequence coupled to oligothiophene biomarker

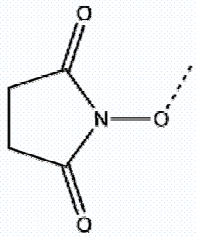


- ***Favorable binding*** to oligonucleotides and proteins
- ***Color tunability*** in the entire visible range
- ***High fluorescence efficiencies***

Chemical functionalization

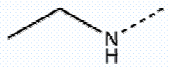
Chemical modifications result in different charge-transfer systems

X = NS:



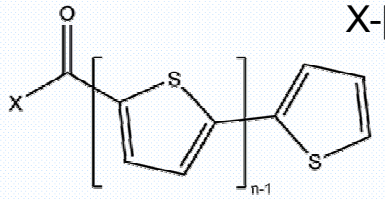
N-succinimidyl group

X = BC:



ethylamide group

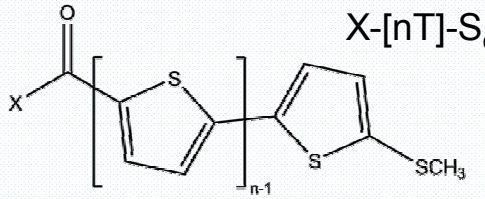
X-[nT]



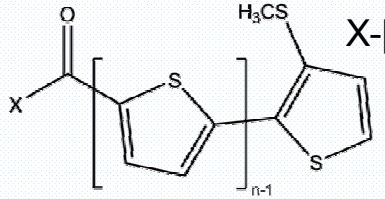
n = 2: bithiophene

n = 3: terthiophene

X-[nT]-S_α

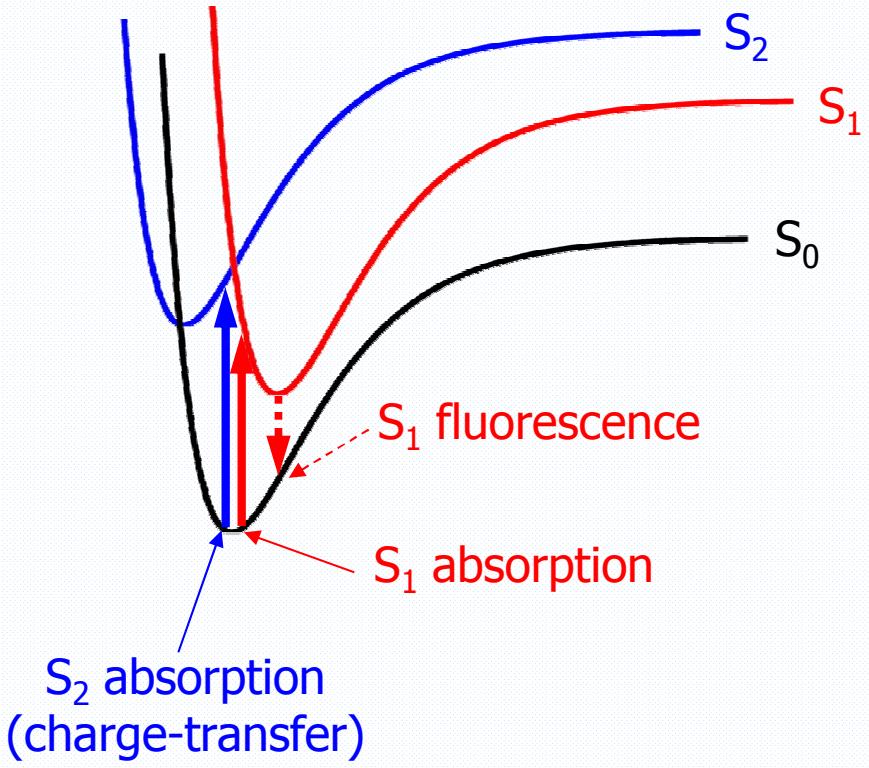


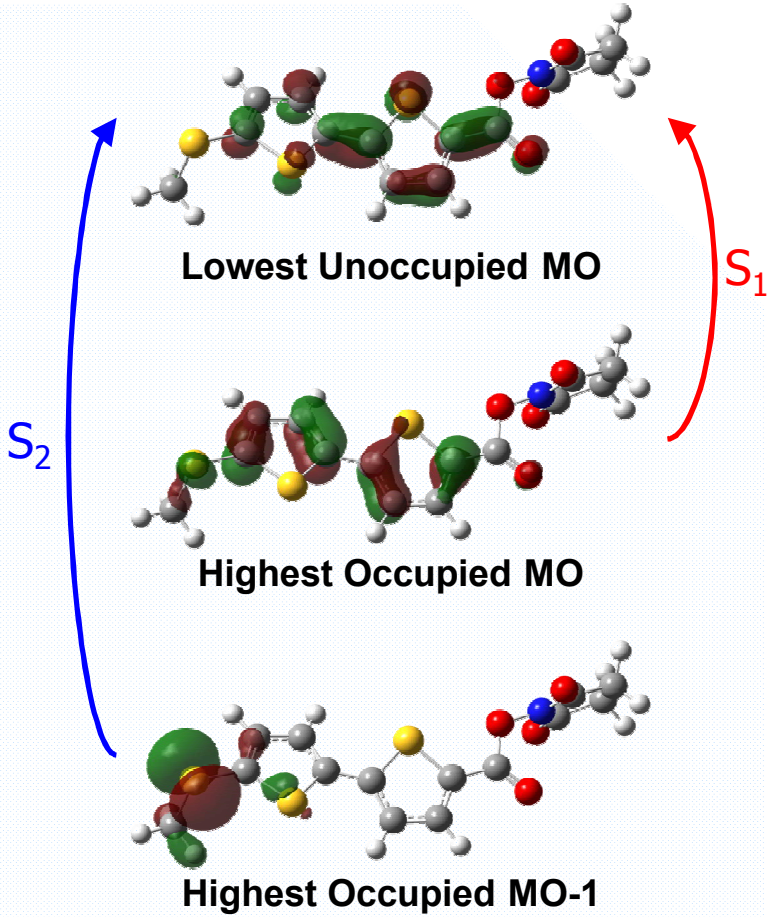
X-[nT]-S_β



Excited-state energetics

- Manifold of excited states





  - Can we describe ***all*** these processes accurately?

Diverse test set

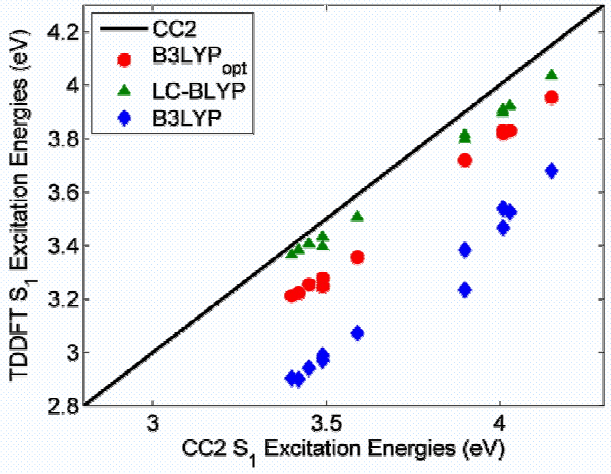
- *36 excitation energies* (12 $S_1 \leftarrow S_0$ absorptions, 12 $S_2 \leftarrow S_0$ absorptions, and 12 $S_1 \rightarrow S_0$ fluorescence de-excitations)

- Can ***simultaneous*** description of all excited states be predicted by TDDFT?

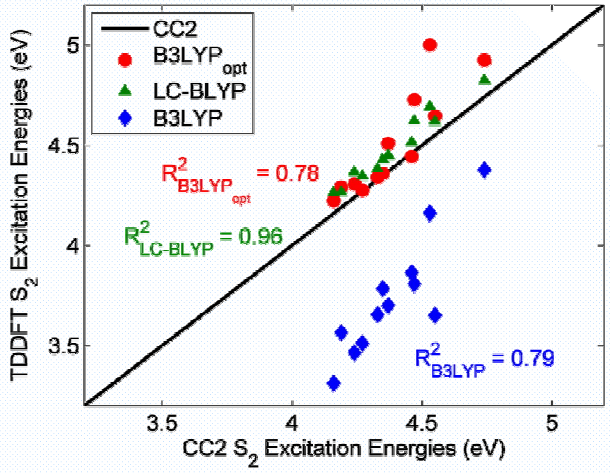
- *What role does HF exchange play?* Can we just re-optimize exchange in global hybrid (i.e. B3LYP) without using LC formalism?

Benchmarks

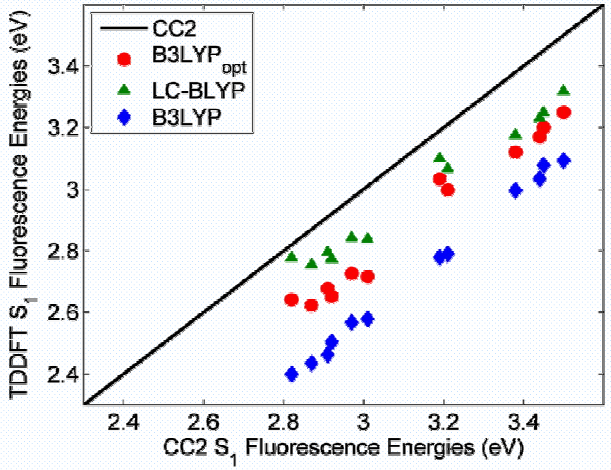
S_1 absorption



S_2 absorption



S_1 fluorescence



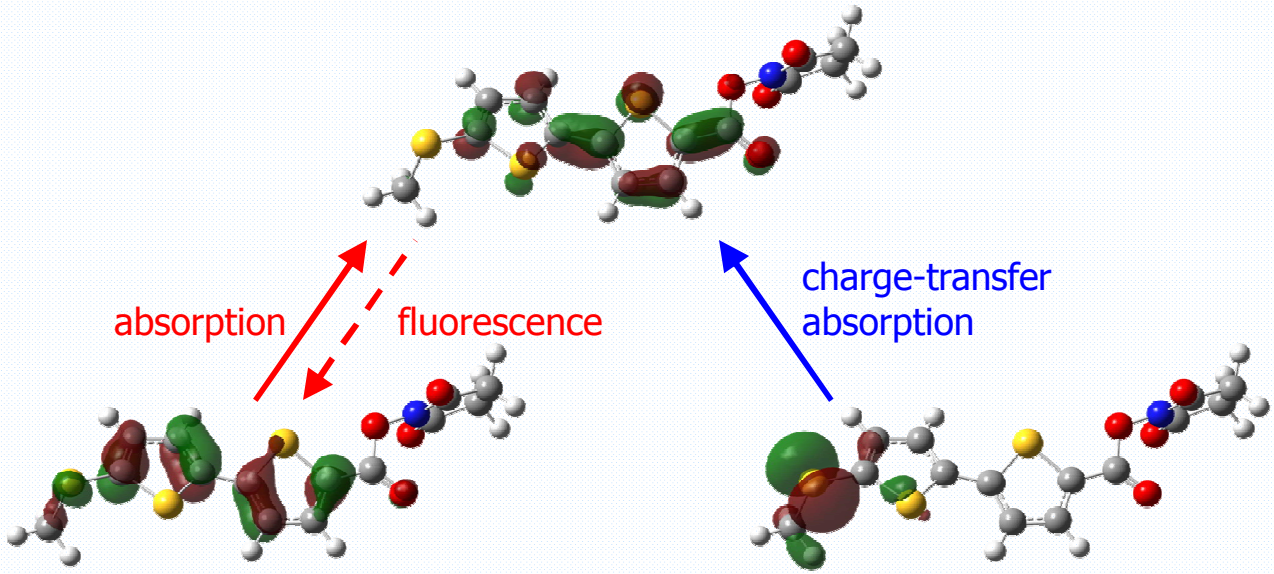
$B3LYP_{opt}$ = B3LYP with re-optimized exchange fraction

Impossible to describe all excited states accurately by adjusting fraction of exchange in B3LYP

B.M. Wong, M. Piacenza, & F. Della Sala, *Phys. Chem. Chem. Phys.* **11**, 4498 (2009)

Results from global and LC hybrids

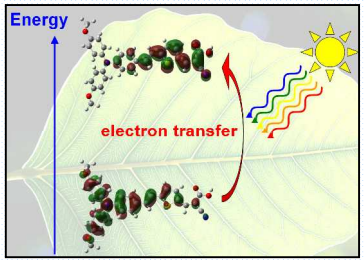
- *Distance-dependent exchange* provides consistent treatment for describing various excitations
- Conventional hybrids unable to capture trends *even if exchange fraction is optimized*

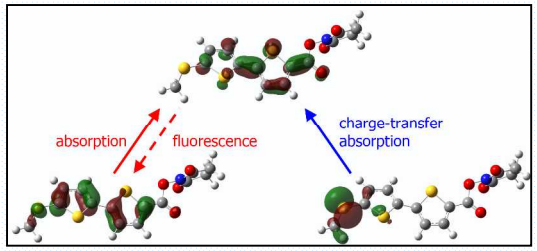


B.M. Wong, M. Piacenza, & F. Della Sala, *Phys. Chem. Chem. Phys.* **11**, 4498 (2009)

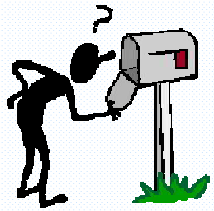
Conclusions

- *Long-range exchange* vital for describing excited states of organic photovoltaics
- Excellent *synergistic area* for theory and experiment





(1) B.M. Wong, J.G. Cordaro
J. Chem. Phys. **129**, 214703 (2008)
(2) B.M. Wong, M. Piacenza, F. Della Sala
Phys. Chem. Chem. Phys. **11**, 4498 (2009)

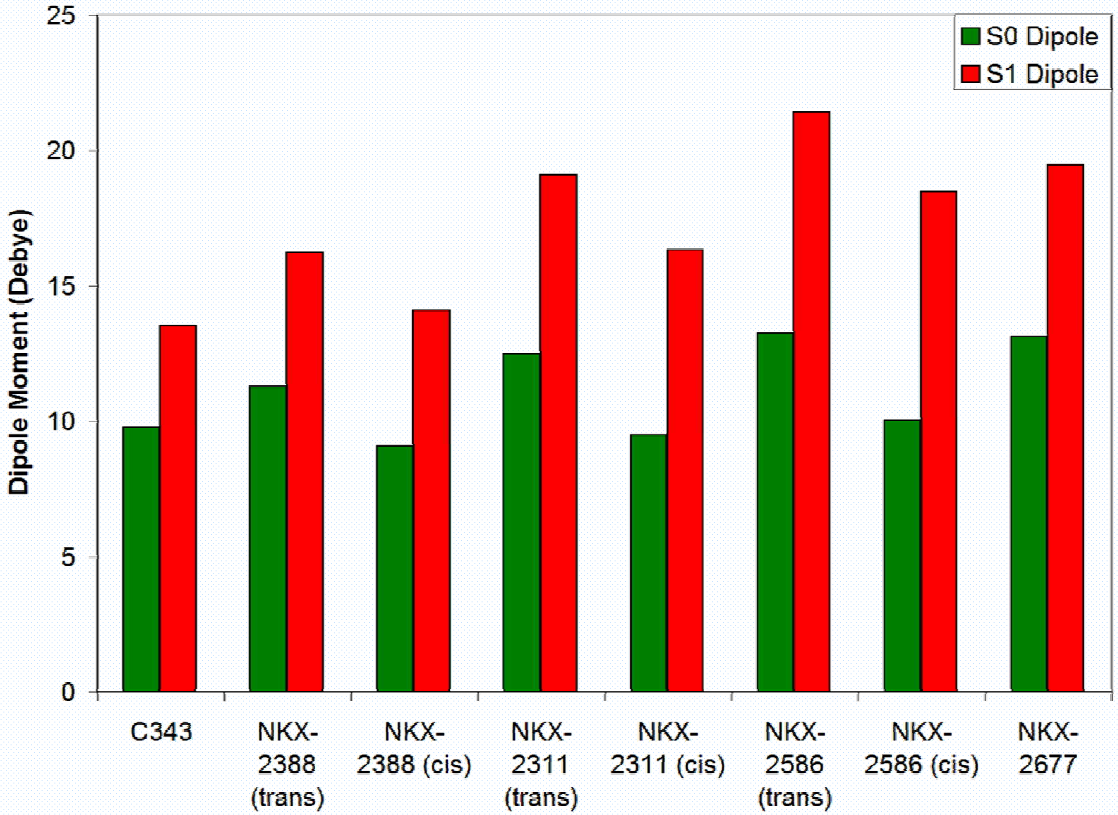


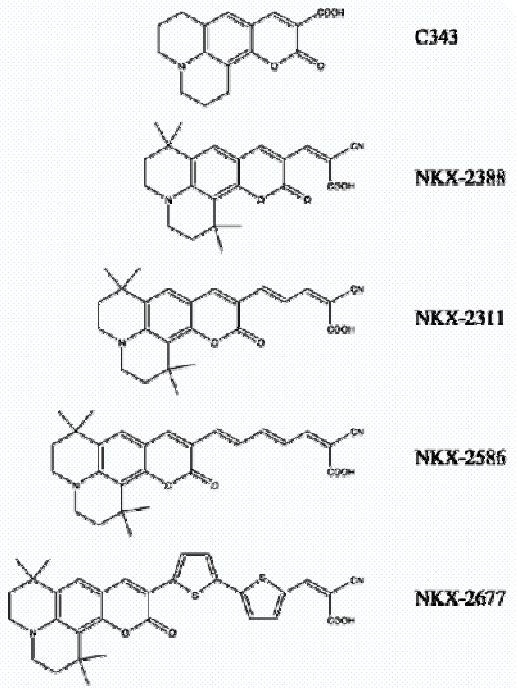
Bryan M. Wong
bmwong@sandia.gov

Sandia National Laboratories

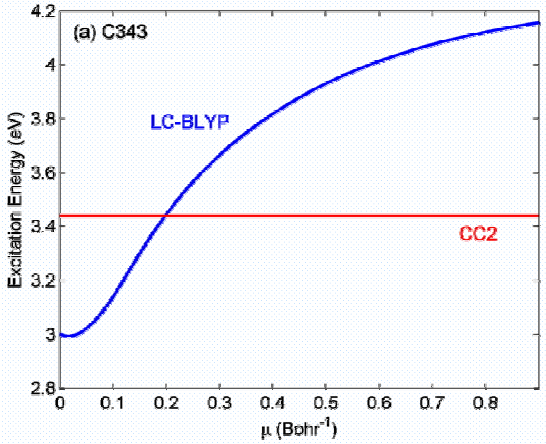
Electronic properties

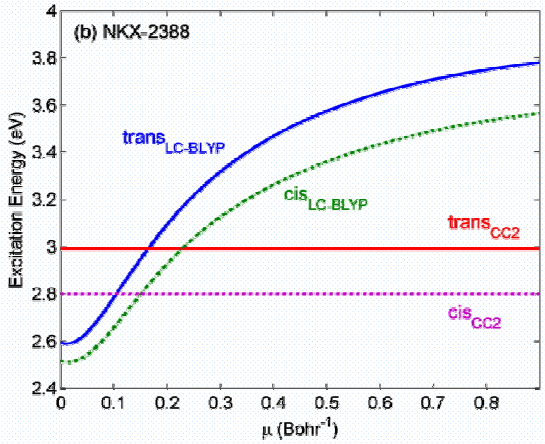
- Large S_1 dipole moments signify *charge transfer*

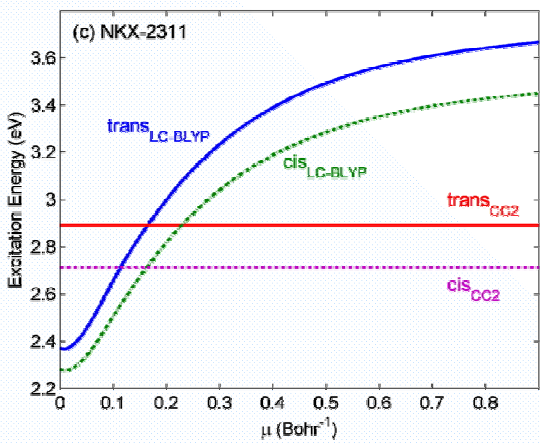


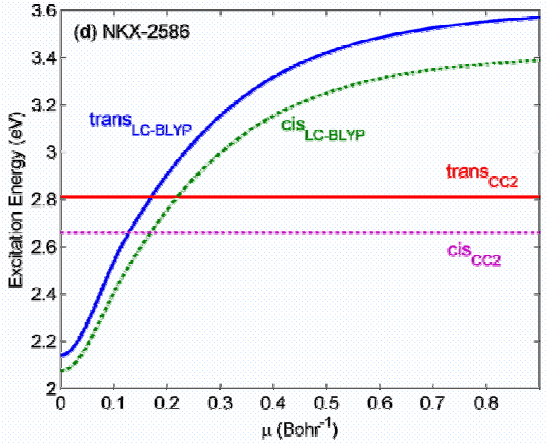


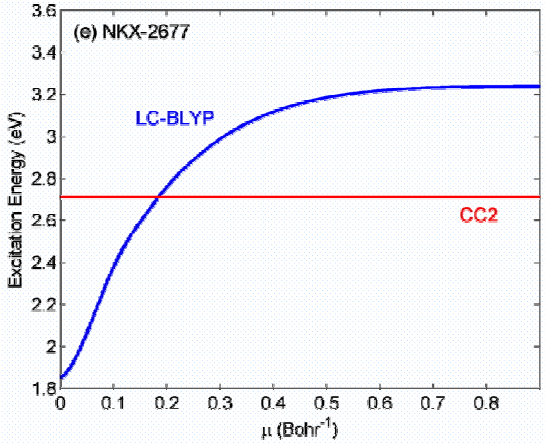
Optimizing the value of μ

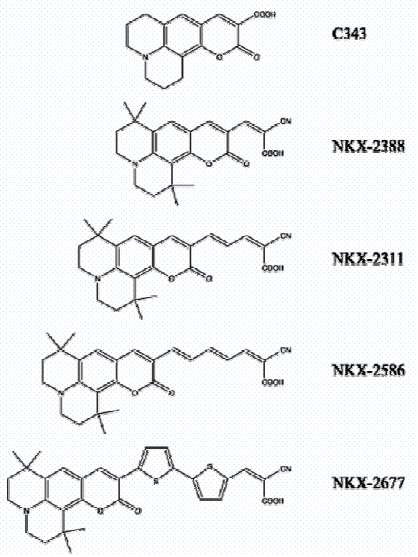






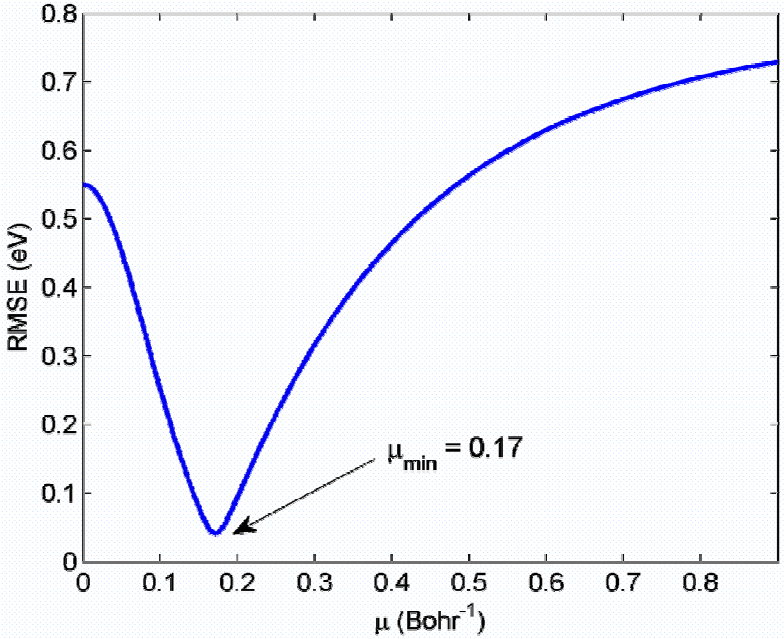




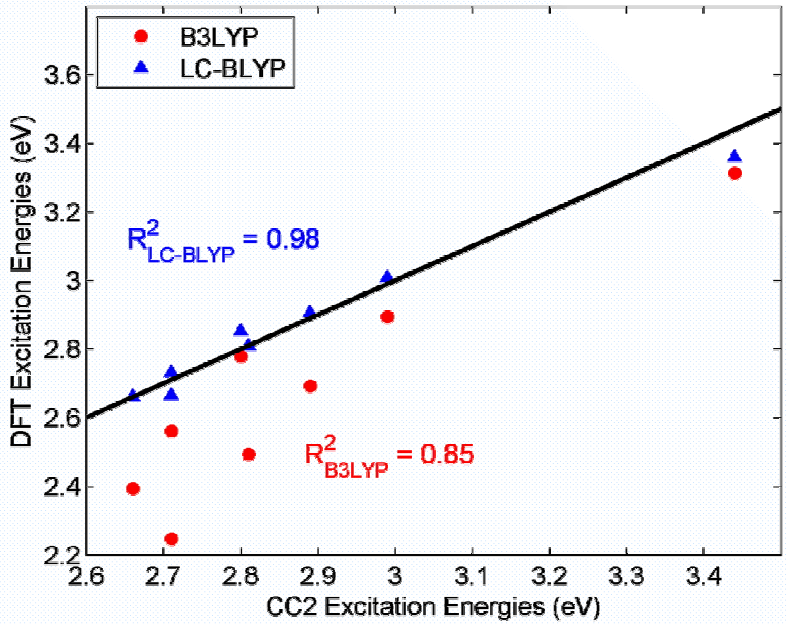


B.M. Wong & J.G. Cordaro, *J. Chem. Phys.* **129**, 214703 (2008)

Optimizing the value of μ



Total RMS error for all 8 dyes

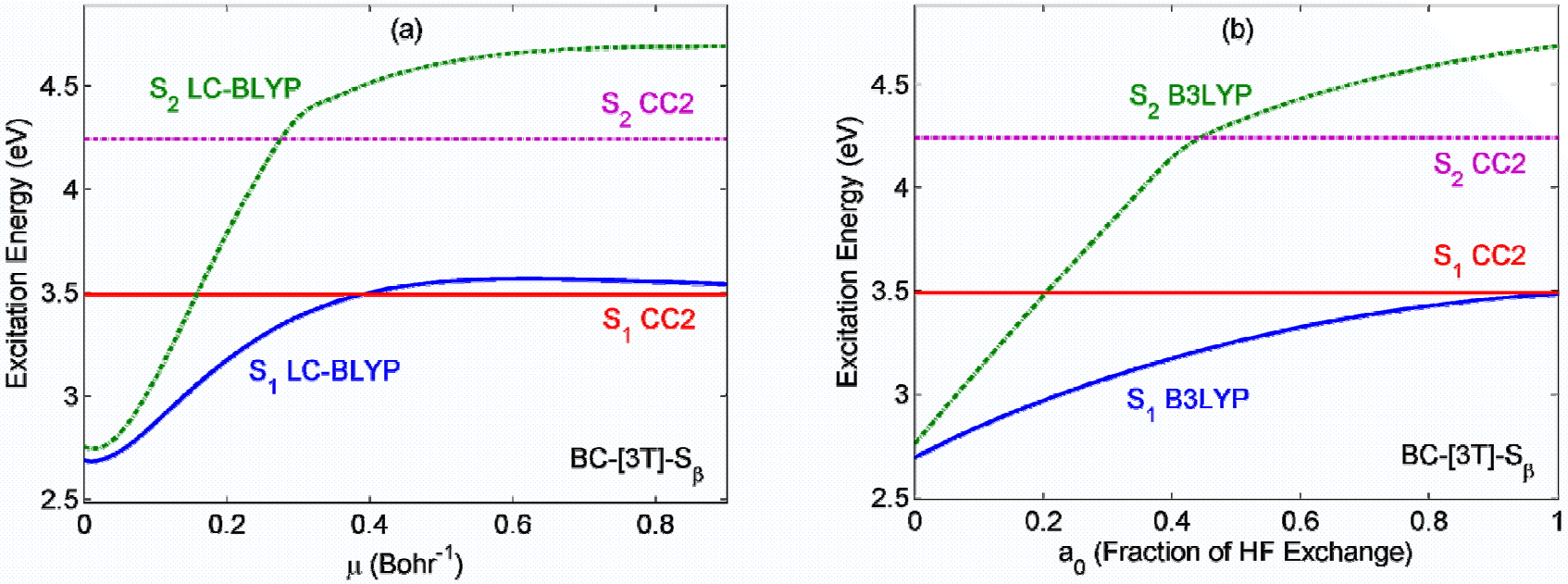


Impossible to *simultaneously* obtain both accurate energies and R^2 values by adjusting fraction of exchange in B3LYP

B.M. Wong & J.G. Cordaro, *J. Chem. Phys.* **129**, 214703 (2008)

Optimal values of μ vs. a_0

Vertical excitation energies for the BC-[3T]-S_β biomarker



LC-BLYP: both S_1 and S_2 excitation energies coincide at around *same range of μ*

B3LYP: *no single value of a_0* which gives reasonable accuracy for both S_1 and S_2

B.M. Wong, M. Piacenza, & F. Della Sala, *Phys. Chem. Chem. Phys.* **11**, 4498 (2009)