

Ab-Initio Studies of Exciton Interactions of Cyanine Dyes

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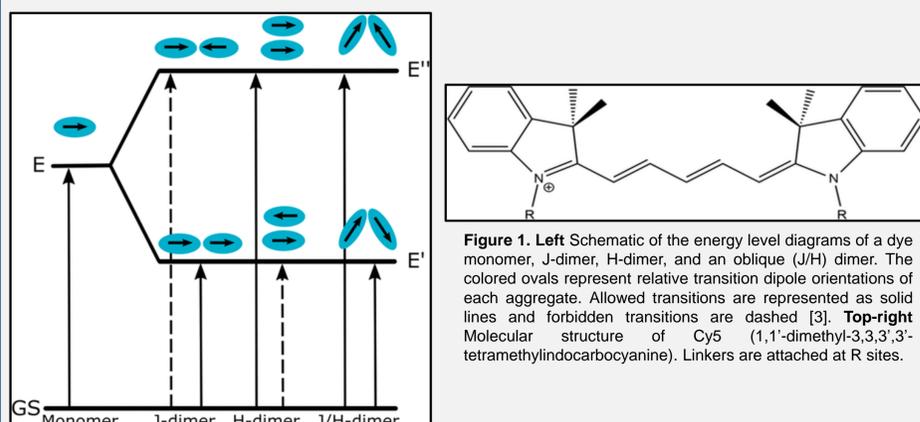
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Introduction and Motivation

Cyanine dyes covalently bound in DNA complexes have been studied for their exciton delocalization properties that include J and H-aggregate behavior and Davydov splitting [1,2]. The self assembly properties of DNA can bring dyes within distances (≤ 2 nm) that induce shifts in absorption maxima. Thus, DNA is used as a scaffold, allowing the manipulation of dyes.

- Dye dimer orientation determines allowed energetic transitions (shown in Fig. 1)
- Control of dye orientations is crucial for the viability of dye-DNA excitonic applications
- Density functional theory (DFT) can be used to optimize the structures of molecular systems and therefore perfect to explore dye orientations
- Proper choice of exchange-correlation (XC) functionals is necessary to model systems accurately

Goal of study: Determine XC-functional effects on ground state orientations and excited state properties of Cy5 dye molecules (shown in Fig. 1).



Computational Methods

- DFT and time-dependent DFT (TD-DFT) calculations were performed [4] using the Gaussian09 quantum chemistry package [5] and solvated in implicit water
- To obtain initial dimer orientations, absorption results [2] were fit with an in-house program based on theoretical work by Kühn, Renger, and May (KRM) [6]
- Monomer absorption spectra were calculated using TD-DFT and optimized at the first excited state
- Monomer and dimer solvation energies were calculated using Eq. 1 where E_T is the total energy of the solvated system and E_V is the total energy of the system in vacuum
- Dimer absorption spectra were calculated by inputting DFT-optimized structures back into the KRM program and the root-mean-squared error in relation to experiment was calculated using Eq. 2

$$E_{solv} = E_T - E_V \quad (1)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (y_{1i} - y_{2i})^2}{n}} \quad (2)$$

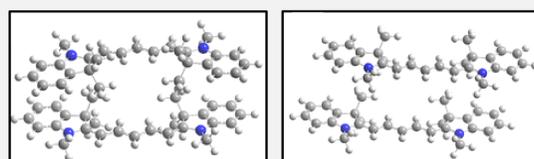


Figure 2. Top Initial input structure for H-dimer flipped solvation energy calculations. Bottom Initial structure for H-dimer stacked solvation energy calculations. N atoms are blue, C atoms are dark gray, and H atoms are light gray.

Monomer Results

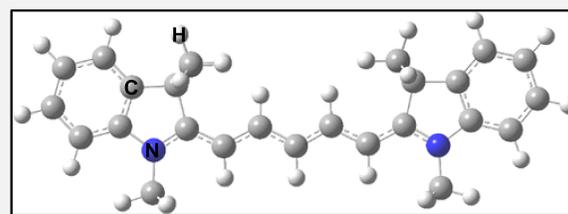


Figure 3. Ground state DFT optimized Cy5 structure using the ω B97XD XC-functional.

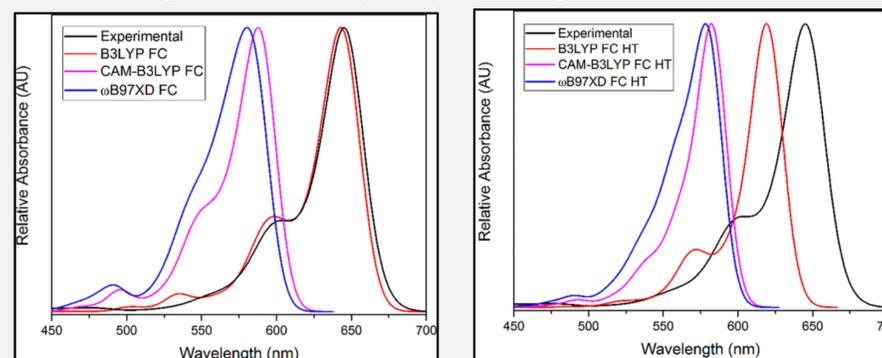


Figure 4. Cy5 monomer absorption spectra calculated using TD-DFT in implicit water solvent compared with experimental data (black). Left Absorption spectra calculated using the Franck-Condon (FC) approximation with B3LYP (red), CAM-B3LYP (pink), and ω B97XD (blue) XC-functionals. Right Absorption spectra calculated using both FC and Herzberg-Teller (HT) approximations with B3LYP (red), CAM-B3LYP (pink), and ω B97XD (blue) XC-functionals.

- CAM-B3LYP and ω B97XD XC-functionals underestimate max absorption wavelength due to inclusion of long-range interaction corrections
- B3LYP with Franck-Condon (FC) approximation accurately predicts max absorption wavelength and vibronic shoulder
- Inclusion of Herzberg-Teller (HT) approximation decreases accuracy of B3LYP absorption calculation

Table 1. Difference of calculated and experimentally observed max absorption wavelengths. $\Delta\lambda_{max}$ denotes the difference between calculated and experimentally measured max absorption wavelength.

XC-Functional	Approximation	$\Delta\lambda_{max}$ (eV)
B3LYP	FC	0.007
B3LYP	FC/HT	0.080
CAM-B3LYP	FC	0.188
CAM-B3LYP	FC/HT	0.207
ω B97XD	FC	0.215
ω B97XD	FC/HT	0.222

- B3LYP predicts $\Delta\lambda_{max}$ within 0.007 eV of experiment

Solvation Results

Table 2. Solvation energies of Cy5 monomer and Cy5 dimer structures calculated using Eq. 1 Flipped and stacked dimers refer to Fig. 2.

XC-Functional	Monomer Solvation Energy (eV)	H-Dimer Flipped Solvation Energy (eV)	H-Dimer Stacked Solvation Energy (eV)
B3LYP	-1.488	-4.234	-4.413
CAM-B3LYP	-1.501	-4.343	-4.638
ω B97XD	-1.506	-4.460	-4.690

- More negative solvation energy for dimers suggests that Cy5 dyes prefer to form dimer structures in polarizable solvents, such as water

Dimer Results

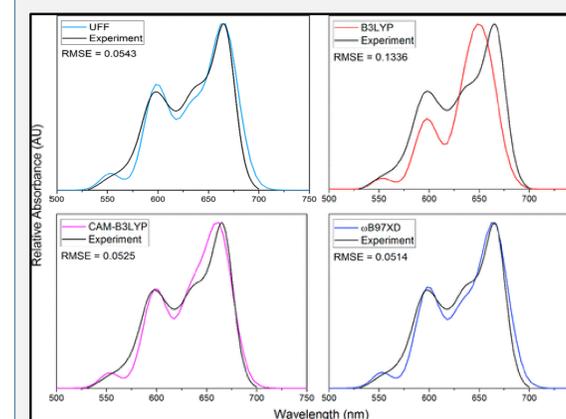


Figure 5. KRM calculated absorption spectra for Cy5 dimers compared to experimentally measured absorption (black). Differences between experimental and calculated results are given by RMSE values calculated using Eq. 2. Top-left Absorption of UFF optimized dimer (green). Top-right Absorption of B3LYP optimized dimer. Bottom-left Absorption of CAM-B3LYP optimized dimer. Bottom-right Absorption of ω B97XD optimized dimer.

- Absorption of UFF optimized dimer calculated using the KRM program is used as a baseline of comparison
- The B3LYP XC-functional yields a worse RMSE value compared to UFF
- Optimizing the dimer using CAM-B3LYP and ω B97XD improves the calculated absorption spectra compared to UFF due to long-range interaction corrections
- Unlike CAM-B3LYP, the ω B97XD XC-functional includes both long-range and damped empirical dispersion corrections which improve the RMSE value

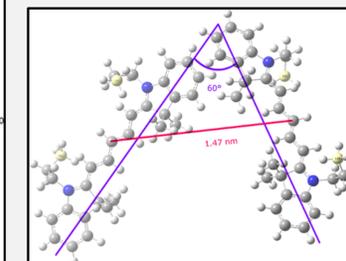


Figure 6. Ground state DFT optimized Cy5 dimer structure. The dye center-to-center separation is 1.47nm and the angle between the two dyes is 60° . N atoms are blue, C atoms are dark gray, and H atoms are light gray.

Conclusions

The effects of various XC-functionals on ground state orientations and excited state properties were explored using DFT calculations on Cy5 dye monomers and dimers. XC-functionals that include long-range or dispersion corrections overestimate the peak absorption energy of Cy5 monomers. XC-functionals that don't include such corrections, such as B3LYP, can accurately reproduce the absorption spectra of Cy5 monomers. For dimer systems, XC-functionals that account for long-range corrections improve KRM-calculated absorption spectra. Furthermore, the ω B97XD XC-functional yields the best KRM-calculated absorption spectra due to the consideration of damped empirical dispersion corrections.

References and Acknowledgments

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Acknowledgments

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