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Calculated photo-isomerization efficiencies of functionalized azobenzene derivatives in solar energy materials: azo-functional organic linkers for porous coordinated polymers

Amanda J Neukirch, Jinhee Park, Vladmir Zobac, Hong Wang, Pavel Jelinek, Oleg V Prezhdo, Hong-Cai Zhou and James P Lewis

1 Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627, USA
2 Creative and Fundamental Research Division, Korea Electrotechnology Research Institute, Changwon, 641-120, Republic of Korea
3 Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnicka 10, CZ-16200 Prague, Czech Republic
4 Department of Physics, West Virginia University, Morgantown, WV 26506-6315, USA
5 Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA
6 Department of Chemistry, Texas A&M University, College Station, TX 77842, USA

E-mail: ajneuk@pas.rochester.edu and james.lewis@mail.wvu.edu

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Abstract
Recently, we used a local orbital density functional theory code called FIREBALL, to study the photoisomerization process in azobenzene derivatives for solar energy materials. Azobenzene functional groups undergo photoisomerization upon light irradiation or application of heat. Zhou et al (2012 J. Am. Chem. Soc. 134 99–102) showed that these azobenzenes can then be introduced into metal–organic frameworks via an organic linker in order to create a reversible switch for CO2 adsorption. In this manuscript, we examined how the addition of organic linkers (isophthalic acid) changes the relaxation times, isomerization mechanism, and quantum yield for both the cis ↔ trans pathways. We then tuned these properties by substituting functional groups, finding an increase in quantum yield as well as improved optical properties.

Keywords: photoisomerization, azobenzene, metal–organic frameworks, molecular switches

(Some figures may appear in colour only in the online journal)

1. Introduction
Azobenzene and its derivatives undergo reversible ultrafast cis ↔ trans photoisomerization. Each isomer has distinct spectral and geometric properties that allow these molecules to serve as ideal model systems for molecular transducers in light-driven devices and optical switches [1, 2]. The scientific community has invested extensive effort optimizing the conversion of the molecular motion of these systems to the macroscopic scale. Applications range from optical storage devices [3, 4], charge transfer [5], regulating channels in the ligand-binding domain of proteins [6], photo-orientation of liquid crystals [7, 8], control of peptide conformations [9], modifying surface properties on oriented films [10–12], and the control of CO2 adsorption in porous metal–organic frameworks (MOFs) [13].

The azobenzene photoisomerization mechanism has been studied extensively with both theoretical and experimental
methods. It is well established that this isomerization reaction is ultrafast and can take place from either of the two lowest lying singlet excited states, $S_1$ and $S_2$. The quantum yield for both cis-to-trans and trans-to-cis isomerization is higher when the azobenzene is excited to $S_1$ (431 nm) compared to $S_2$ (320 nm). Experiments performed give trans-to-cis isomerization yields between 20% and 28% resulting from $S_1$ excitation, and 9% to 12% for $S_2$ excitation [14, 15]. The cis-to-trans process exhibits a quantum yield of between 40% and 69% from the $S_1$ state [14–20], and between 40% and 44% quantum yield form the $S_2$ state [20, 21]. In the present work, we focus on the more efficient $S_1$ pathway.

The $S_1$ state is associated with symmetry forbidden $n$–$\pi^*$ excitation in the visible region and is optically much weaker than the $S_2$ excitation in the ultraviolet region. Originally the $S_1$ isomerization was attributed to the in-plane inversion mechanism, where one N=N–C angle increases to 180° while the C–N=N–C dihedral angle remains fixed at 0° [22, 23]. The rotational pathway was later suggested as the way the reaction proceeds. In this mechanism the N=N $\pi$-bond ruptures to allow for free rotation around the N–N bond [16, 17, 24–26]. Rotation changes the C–N–N–C dihedral angle while the N–N–C angle remains close to 120°. According to the most recent mechanistic studies the driving force of the reaction is rotation of the N–N motif and not by large amplitude rotation of the phenyl rings [18, 27–30]. This latter mechanism was supported by our most recent work on the photoisomerization of cis-azobenzene [31].

While the computational community has invested a lot of effort on understanding the mechanisms in isolated azobenzene, to date, not much attention has been devoted to the study of $S_1$ isomerization mechanism in functionalized azobenzene. Many of the proposed stimuli-response applications require azobenzene to be embedded as a solar energy material into an extended matrix of some sort. One such application is the introduction of azobenzene into MOF via an organic linker in order to create a reversible switch for CO$_2$ adsorption [13]. It is therefore important to study how the addition of linkers changes the both the isomerization mechanism and quantum yield. In addition to studying how an extended system changes the underlying processes, the addition of substituents can also tune the optical and electronic properties. It is important to note that optimization of these azo-functional systems require looking at a couple of parameters to evaluate photo-efficiency. Firstly, having a solar sensitive switch is beneficial for many applications, and so any modification that either improves absorption into the $S_1$ state, or shifts the overall spectra to the red is advantageous. Secondly, it is important to not reduce efficiency in the isomerization process, as the azobenzene derivatives are functionalized.

In this work, we report both experimental and computational results in order to determine how the photoswitchable azobenzene will behave as it is modified for incorporation into a MOF structure with the addition of the organic linker, isophthalic acid, as shown in the top row of figure 1. In addition, the linker system is substituted with methyl, as illustrated in the bottom row of figure 1, as a proof of principle for assessing our ability to tune and optimize the optical and electronic properties of the photo-switch. The different azobenzene derivatives are synthesized in the trans form, and absorption spectra of each system are taken before and after irradiation UV irradiation in order to determine their optical properties. We then use nonadiabatic molecular dynamics with Tully’s fewest switches surface hopping algorithm to investigate how the above modifications to azobenzene change isomerization time scales, quantum yields, and mechanisms. We will examine the NNC angle,
CNNC dihedral angle, and active phonon modes in order to determine what the reaction pathway is in each azobenzene derivative, and correlate the quantum yield and relaxation time with the overall efficiency of the process.

2. Synthesis and spectra

In this report, the azobenzene derivatives with isophthalic acids were synthesized based on Mills reaction between nitrosobenzene and 2,5-dibromoaniline \[^{[32]}\] followed by Suzuki Coupling reaction between dibromoazobenzenes and borate \[^{[33]}\] as shown in scheme 1 and 2. The azobenzene derivatives with isophthalic acids can be used for preparation of photoresponsive MOFs. Adding additional methyl groups on the azobenzene moiety is able to increase the gas uptake difference between \textit{cis} and \textit{trans} isomers and to control light absorption properties of the MOFs derived from those ligands. \textit{Trans} to \textit{cis} isomerization of the azobenzene derivatives upon UV (365 nm) has been directly monitored by UV–vis spectroscopy. The UV exposure experiments for \textit{trans} to \textit{cis} isomerization were performed by UVLMS-38 EL Series 3 UV Lamp (8-watt). Feit Electric 13-Watt (60 W) Blue Twist CFL Light Bulb can be used as the light source for \textit{cis} to \textit{trans} isomerization. The results of the absorption spectra are shown in figure 2.

What we see with the addition of methyl in the para position is an increase of absorption in the visible region. This change in spectra shows that adding ligands can in fact tune optical properties toward desired outcomes. Now we will use computational methods in order to determine how the addition of organic ligands and linkers will change the overall time scale, efficiency and mechanism of the isomerization process.

3. Computational details

In this study, for each structure, we analyze the results from 500 NAMD trajectories beginning in the S\textit{i} state, and evolving in the microcanoical ensemble for up to a picosecond. It is important to point out that each trajectory of 4000 MD steps was completed in about 12 h on a single core. Over 99% of the trajectories had relaxed to the ground state (S\textit{g}) within the ps trajectory. We evaluate the \textit{cis}– or \textit{trans}-conformations by monitoring the central dihedral angle after relaxation into the ground state.

In order to model the nonadiabatic dynamics of the systems studied in this manuscript we used Tully’s fewest switches surface-hopping (FSSH) method to obtain the electronic occupations by averaging over an ensemble of initial conditions \[^{[34]}\]. FSSH uses a stochastic algorithm.
that generates trajectory branching and detailed balance \[35\] in order to define the effect of the quantum mechanical electron evolution on the classical nuclear motion. Trajectory branching mimics the splitting of quantum-mechanical nuclear wave-packets in correlation with different electronic states. Detailed balance ensures that population of electronic states satisfies a Boltzmann distribution at long times. At any given time the nuclei in any given trajectory are evolving classically on a single PES. The nonadiabatic coupling vectors are obtained by the method described in our previous works \[31, 36\]. At each integration time step, a decision is made as to whether an electronic transition will occur according to the probabilistic ‘fewest switches’ algorithm. Energy is conserved by re-scaling the nuclear velocities along the directions of the nonadiabatic coupling vectors (NACVs) of the nuclear time step was 0.25 fs and the electronic time step was 0.0025 fs during these simulations.

Our analysis uses a density functional theory approach, called FIREBALL, which is based on local orbitals within a nonlocal pseudopotential scheme \[41–43\]. FIREBALL is a molecular dynamics simulation technique which is based on a self-consistent functional \[44\], where the basis set consists of numerical orbitals. The ‘fireball’ orbitals, introduced by Sankey and Niklewski \[41\], are acquired by producing slightly excited atom-in-the-box states that smoothly vanish outside of a predetermined radius, \(r_c\). In this work, we use the Becke \[45\] exchange with Lee–Yang–Parr correlation \[46\]. We have adopted double numerical \(sp^3\) basis sets for C (cutoff radii of \(r_c(s) = 4.4\) a.u. and \(r_c(p) = 4.8\) a.u.) and N (cutoff radii of \(r_c(s) = 4.0\) a.u. and \(r_c(p) = 4.4\) a.u.); whereas we use a minimal basis set is used for H (cutoff radius of \(r_c(s) = 4.2\) a.u.).

We initially optimize the geometry of each molecular system, figure 1, so that it is in its lowest energy. Each system is then allowed to evolve at 300 K for 10 ps ground-state MD using a canonical ensemble \[47\]. Random coordinates are selected from the MD trajectory with an automated python script and we use these random configurations as the initial conditions for our MD simulations with electronic transitions. Proper preparation of the initial conditions is an important preliminary step in the simulations. The initial sampling of conformational space needs to be adequate in order to represent the equilibrated ensemble of molecules at a given set of thermodynamic conditions. The \(S_1\) state is defined using restricted self-consistent DFT calculations with one electron in the Kohn–Sham LUMO level and one hole in the HOMO level. The nuclear time step was 0.25 fs and the electronic time step was 0.0025 fs during these simulations.

4. Results and discussion

We have previously studied the \(cis \rightarrow trans\) isomerization for the azobenzene molecule from an ensemble of 400 trajectories \[31\]. Our results show a relaxation time of \(\sim 120\) fs with a 58\% quantum yield. At the time of electronic transition the dihedral angle averaged 94°. Here we repeat a similar investigation for the \(cis \rightarrow trans\) isomerization for azobenzene with organic linkers. Results of the time of electronic transition, and the dihedral angle are presented in figure 3.

We find that the average relaxation time decreased to 100 fs with a standard deviation of 79 fs; however the quantum yield also decreased to 43±2\%, and the average dihedral angle decreased to 85° with standard deviation of 11°. The decrease in dihedral angle can in part be explained by the higher percentage of trajectories that returned to their initial \(cis\)-configuration. However, the greatest difference between azobenzene and azobenzene with linkers is that the average dihedral at the time of electronic transition for systems that ended up in the \(trans\)-configuration went from 102° in unadulterated azobenzene to 91° with a standard deviation of 9° in azobenzene with added organic linkers. The fact that isomerization happens at a lower dihedral angle could very well explain the decrease in quantum yield. This decrease in
quantum efficiency shows the necessity of modeling molecular photoswitches within their application environments.

There is also a desire to see if the overall quantum yield can be tuned depending on how the system is modified. We examine the cis→trans isomerization of 2-methylazobenzene and 4-methylazobenzene with organic linkers to see how the quantum yields and mechanism changes. The quantum yield results are shown in figure 4. The results we obtain are somewhat surprising. We find that the quantum yield goes back up to 57±2% when the methyl is added to the ortho-(2) position, and decreases further to 31±2% if the methyl is added to the para-(4) position. The relaxation time for are 119 fs with a standard deviation of 90 fs for 4-methylazobenzene and 107 fs with a standard deviation of 104 fs for 2-methylazobenzene. Changing the position of the methyl substitute drastically changes the quantum yield, but does not change the relaxation time scale considerably.

The average dihedral angle at the time of electronic transition for methylated azobenzene with organic linkers is shown in figure 5. The average dihedral for 2-methylazobenzene with organic linkers is 87° with a standard deviation of 14° while the average angle for 4-methylazobenzene with organic linkers drops more significantly 83° with a standard deviation of 9°. The decrease in average dihedral angle at the time of electronic transition provides an explanation for the decrease in quantum yield, but to explore the decrease in quantum yield further we chose to examine another set of parameters.

The active phonon modes in the system with linkers were located at 235 cm⁻¹ (7 THz) and 601 cm⁻¹ (18 THz). The phonon modes for the 4-methylazobenzene are at 400 cm⁻¹ (12 THz) and 567 cm⁻¹ (15 THz). Finally, we found the phonon modes for the 2-methylazobenzene to be at 300 cm⁻¹ (9 THz), 500 cm⁻¹ (15 THz), and 700 cm⁻¹ (21 THz). Each of these sets of phonon modes is very similar to what we found in the system without the organic linker [31], and those frequencies correspond very well to experimentally identified modes at 275 cm⁻¹ (8.25 THz), 542 cm⁻¹ (16.25 THz) and 600 cm⁻¹ (18 THz) [48]. These modes are associated with torsion in the CCNN and CNNC angles respectively.
biggest differences are that the extended system without methyl substitutes is missing a mode at around 542 cm$^{-1}$ and the 4-methylazobenzene system does not have a mode near 275 cm$^{-1}$ and only one mode between 500 and 600 cm$^{-1}$. This begins to shed more light on why these two systems have a lower quantum yield.

We can elucidate the root cause of the pathway toward relaxation and isomerization by studying the projections of the nonadiabatic coupling vectors onto individual atoms in the molecular systems, table 1. In all cases we found that the central CNNC atoms, shown in figure 6, contribute the most to the nonadiabatic coupling terms, hence, they are the most influential atoms in this process.

In the three systems with organic linkers, the magnitudes of the coupling vectors are larger than those in the pure azobenzene system. In all four systems, we found that the nitrogen atoms possessed the nonadiabatic coupling vectors and terms with the largest magnitude. The greatest difference is that while the magnitude of the nitrogen coupling terms are about the same for all four systems, the magnitude of the nitrogen coupling vectors are much smaller in the pure azobenzene system. These results indicate that the velocities of nitrogen atoms in the non-linker system are either larger or are ‘more parallel’ (hence increasing the dot product) with the nonadiabatic coupling vectors. More aligned velocities will lead to a more concerted motion and potentially a higher quantum yield. We also observed that the least efficient 4-methylazobenzene case has very asymmetric contributions between both the two central nitrogen atoms and the two central carbon atoms perhaps explaining the decreased isomerization efficiency.

The results regarding quantum efficiency are more interesting when we look at what happens with trans- to cis isomerization in azobenzene with or without attached organic linkers. The results of the isomerization time and quantum yield for azobenzene and azobenzene with organic linkers are shown in figure 7.

Before any further analysis is discussed we first note that the results for trans $\rightarrow$ cis photosomerization are very different. After the organic linkers are added, the relaxation time slows from 260 fs with a standard deviation of 72 fs to 407 fs with a standard deviation of 136 fs and the quantum yield decreases from 47$\pm$2% to 23$\pm$2%. Previous studies have found a striking reduction in trans $\rightarrow$ cis quantum yield in when azobenzene is an organic solvent with respect to vacuum [19, 24, 49, 50]. In fact while the cis $\rightarrow$ trans pathway generally has a quantum yield above 40%, regardless of the surrounding environment, theoretical quantum yields for the trans $\rightarrow$ cis pathway in vacuum have been found to be 46% [17] and 52% [50]; both theoretical and experimental studies finding the range of quantum yield between 18% and 42% in solvents depending on polarity and viscosity [24]. Our results indicate that the addition of organic linkers plays a very similar role in reducing quantum yields as does the addition of an organic solvent. The resulting ensembles are significantly different, such as the shape of the distribution. For instance we observe multiple peaks in the case of azobenzene without linkers, but once the linkers are added the multiple transition times vanish and the transition time is closer to a chi-squared distribution. The vast difference in quantum yield is strong evidence that understanding the behavior of isolated azobenzene molecules may not be sufficient when working to optimize their properties for particular condensed matter applications, such as MOFs.

We continue our analysis by checking the dihedral angle at the time of electronic transition for photoexcited trans-azobenzene with and without organic linkers, as shown in figure 8. One of the greatest differences in the dihedral angle ensembles stems from the fact that the unreactive trajectories generally hop at slightly higher angles in systems with linkers compared to those without, averaging 110$^\circ$ with a standard
deviation of $12^\circ$ versus $107^\circ$, with a standard deviation of $14^\circ$, respectively. Another difference is that in the system with organic linkers there are many more trajectories that end up in the trans-conformation. Since the overall behavior of the dihedral is actually very similar between the two systems, indicating that in both systems rotation is a dominant mechanism.

Before discussing what could possibly be causing the drastic change in quantum yield, we will look at what happened to the relaxation distribution in a methyl substituted position, as shown in figure 9. The relaxation time remains similar to the linker system without the methyl substitution since both systems have a relaxation time around 410 fs with a standard deviations around 150 fs. More interestingly, is that the quantum yield increases from $23\pm2\%$ to $31.5\pm2\%$ and $28.5\pm2\%$, respectively. The multiple peak feature in the relaxation times that were present in simple azobenzene return in the case of 2-methylazobenzene, indicating that the change in mechanism caused by the addition of linkers is countered by the addition of the methyl.

Looking at the dihedral angle at the time of electronic transition, not much changes once the methyl is substituted, figure 10. The average dihedral angles for 4-methylazobenzene and 2-methylazobenzene are both about $103^\circ$. Therefore it appears as if the change in mechanism is not due to a change in the motion of the dihedral angle, but some other angular motion.

The cause root of the difference in the quantum yields between the system with and without organic linkers can be determined investigating which phonon modes are involved in the relaxation and isomerization. These modes are calculated from the relaxation dynamics by tracking the percentage of trajectories that are in the ground and excited state as a function of time. For trans-azobenzene without linkers, we found a single peak at 300 cm$^{-1}$ which corresponds to a rotation of the N$_2$ moiety out of the molecular plane and variations of the CNNC and CCNN dihedral angles [30]. These results for azobenzene with attached organic linkers are shown in figure 11. By taking the Fourier transform of the derivative of the population in the S$_0$ ground state as a function of time (left panel of figure 11), we are then able to obtain the active phonon modes shown in the right panel of figure 11.
Figure 9. Distribution of the transition times for 4-methyazobenzene (left) and 2-methylazobenzene (right) for the $\text{trans} \rightarrow \text{cis}$ photoisomerization. All trajectories start in the $\text{trans}$ configuration. Black cross bars represent all trajectories. Red slashed lines represent transitions that end in the $\text{cis}$-configuration. Blue slashed lines represent transitions that end in the $\text{trans}$-configuration.

Figure 10. Distribution of C–N=N–C dihedral angle at the time the electronic hop took place for the $\text{trans} \rightarrow \text{cis}$ photoisomerization for the 4-methylazobenzene without (left) and with 2-methylazobenzene (right) organic linkers. All trajectories start in the $\text{trans}$ configuration. Trajectories yielding the $\text{trans}$-configuration are in blue; while those in the $\text{cis}$-configuration are shown in red.

Figure 11. Left panel is the evolution of the ground an excited state populations for azobenzene with organic linkers. The right panel is the Fourier transform of the derivative of the $S_0$ population in azobenzene with attached organic linkers.
Figure 12. Schematic of trans-azobenzene indicating CNN angle 1 (left) and CNN angle 2 (right.)

Table 2. Trans→cis isomerization pathway classification for azobenzene, azobenzene with organic linkers, and 2-methylazobenzene with linkers. Results for CNN angle 1 are not in parentheses and results for angle 2 are in parentheses. As a reminder quantum yields for each system are put in parentheses after the name of each system.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Azo  (0.48)</th>
<th>Azo w/linkers (0.23)</th>
<th>4-methylazo w/linkers (0.315)</th>
<th>2-methylazo w/linkers (0.28)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation</td>
<td>0.67 (0.66)</td>
<td>0.77 (0.52)</td>
<td>0.79 (0.59)</td>
<td>0.82 (64)</td>
</tr>
<tr>
<td>Mixed</td>
<td>0.33 (0.33)</td>
<td>0.23 (0.42)</td>
<td>0.21 (0.38)</td>
<td>0.17 (34)</td>
</tr>
<tr>
<td>Inversion</td>
<td>0.00 (0.01)</td>
<td>0.00 (0.06)</td>
<td>0.00 (0.03)</td>
<td>0.02 (0.02)</td>
</tr>
</tbody>
</table>

Table 3. Ensemble Averages for values of modulus of projection on the central atoms CNC atoms of the nonadiabatic coupling vectors and absolute value of the nonadiabatic coupling terms between the HOMO and LUMO at time preceding electronic transition into the ground state of azobenzene, azobenzene with organic linkers, and 2-methylazobenzene with linkers.

<table>
<thead>
<tr>
<th></th>
<th>Azo w/linkers</th>
<th>4-methylazo w/linkers</th>
<th>2-methylazo w/linkers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$</td>
<td>d_{ij}</td>
<td>$ (Å$^{-1}$)</td>
</tr>
<tr>
<td>C1</td>
<td>7.9</td>
<td>41</td>
<td>7.41</td>
</tr>
<tr>
<td>N2</td>
<td>12.33</td>
<td>96</td>
<td>11.04</td>
</tr>
<tr>
<td>N3</td>
<td>12.64</td>
<td>71</td>
<td>11.75</td>
</tr>
<tr>
<td>C4</td>
<td>7.96</td>
<td>44</td>
<td>7.23</td>
</tr>
</tbody>
</table>

Azobenzene with linkers exhibits many peaks in the frequency domain. They appear at 9, 14, 17 and 22 THz. The extra modes are associated with C–N out of plane bending which indicate that the CNN angles, or the inversion mechanism, plays a greater role in isomerization. To verify this result we looked at what the evolution of the two CNN angles for 40 fs prior to and following the electronic transition into the ground state, and looked at the maximum angle achieved in each case. The results from this examination are presented in table 2. If the maximum angle is <140° the mechanism is deemed to be fully rotational. If the maximum angle is between 140° and 160° we consider the mechanism of mixed composition. Finally if the maximum angle reaches above 160° we consider the dominant mechanism to be inversion.

We found that in regular azobenzene two thirds of the reactive trajectories underwent pure rotation, and the mechanism for one third of the reactive trajectories had mixed contribution. Almost no reactive trajectories underwent inversion. It is important to note is that the behavior of the two CNN angles are symmetric. The symmetric behavior of the CNN angles in simple azobenzene is expected as simple azobenzene is symmetric around these coordinates. The results get more interesting as we look at azobenzene with the added organic linkers. We find that CNN angle 1 (the angle farthest from the linkers) has more reactive trajectories that undergo rotation as the sole mechanism. In the meantime, CNN angle 2 exhibits a large increase in the percentage of reactive trajectories that have a mixed isomerization mechanism, and even has a contribution from trajectories that isomerize by pure inversion. When the methyl is substituted the behavior of CNN angle 2 returns to be very similar to what it was for simple azobenzene. The rotational contribution is still larger for CNN angle 1 in the methyl substituted systems with linkers compared to simple azobenzene, showing that the system is still not symmetric, and that perhaps the more mobile half of azobenzene is compensating for the half ‘tied down’ by the organic linkers.

In table 3 we take a quick look at the coupling vector terms, we found that the azobenzene with organic linkers has contributions from the central nitrogen atoms that are very
asymmetric leading to an inefficient isomerization pathway. Once the methyl is added to the system the contribution from the nitrogen atoms is more symmetric. The nitrogen atoms in the 4-methylazobenzene system have the smallest vector magnitude, yet the largest average coupling term. Having the smallest NACV but largest coupling is an indication that the velocity is in the direction of the coupling vector and that the system will get a push toward rotating around each other. We also observe that the coupling contribution from the central carbon attached to the ‘free’ azobenzene ring is much higher in the 2-methylazobenzene system suggesting that it has more freedom to rotate and aide in the isomerization process leading to a higher quantum yield.

5. Conclusion

In this work, we investigated how the addition of the organic linkers, isophthalic acid, to the 2 and 5 positions on one of the azo-phenyl rings changes the isomerization mechanism and quantum yield compared to the regular azobenzene system. We found that the quantum yield decreased from 58% to 43% for the cis→trans pathway with the addition of the organic linkers. We found that both the optical properties and quantum yields could be tuned with the addition of methyl substitution. By synthesizing the azobenzene with organic ligands and methyl substitution and performing spectra we found that the addition of methyl shifts the absorption spectra into the visible region. By performing NAMD using the FSSH algorithm we found that substitution of a methyl in the para position returned the quantum yield up back up to 57%, while methyl substitution in the ortho-position caused the quantum yield to decrease to 31%.

When looking at the trans→cis pathway we found that the quantum yield decreased from 47% to 23% with the addition of linkers. The addition of linkers acts as a solvent and reduced the rotational efficiency of the photoisomerization process. Analysis of the NNC angle, CNNC dihedral angle, and active phonon modes suggest that in the trans→cis pathway the rotational pedal motion of the pure system is inhibited and the phonon modes suggest that in the

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