

Original Research Article

**Linear optical absorptions of  
photo/thermochromic organic molecules  
interacting with a gold nanoparticle**

## Abstract

We present linear optical absorptions of photo/thermochromic molecules interacting with a gold nanoparticle. The photo/thermochromic system is the dihydroazulene/vinylheptafulvene system and our aim is to study the effects of the interaction between the gold nanoparticle and the molecular systems. We consider the changes of the one-photon excitations of the dihydroazulene/vinylheptafulvene system as we increase the interactions between the molecules and the nanoparticle by decreasing the distance between them. We utilize a quantum mechanical/molecular mechanical method for investigating the photo/thermochromic molecular system interacting with the gold nanoparticle. The photo/thermochromic molecules are described quantum mechanically using density functional theory whereas the gold nanoparticle is represented as gold atoms with atomic polarizabilities using molecular mechanics. We observed that the optical properties of the photo/thermochromic systems are affected by the presence of the nanoparticle and the changes depend strongly on the conformer of the molecular system along with the relative orientation and distance between the photo/thermochromic molecules and the nanoparticle.

## Introduction

An alternative method for capturing and storing solar energy is to utilize MOlecular Solar Thermal (MOST) systems.<sup>1-17</sup> For this type of system, one utilizes that some molecules can undergo photoisomerization when they are excited by photons and end up in a meta-stable state. Thereby, one could ideally store the energy until it is needed, upon which the stored energy could be released through an isomerization back to the starting point. The advantage of the MOST systems compared to conventional solar cells is that the energy does not have to be utilized momentarily or stored externally.

The DHA/VHF system was initially synthesized in 1984 by Daub and co-workers<sup>1</sup> and it has since then been further investigated and modified for utilization and exploitation of

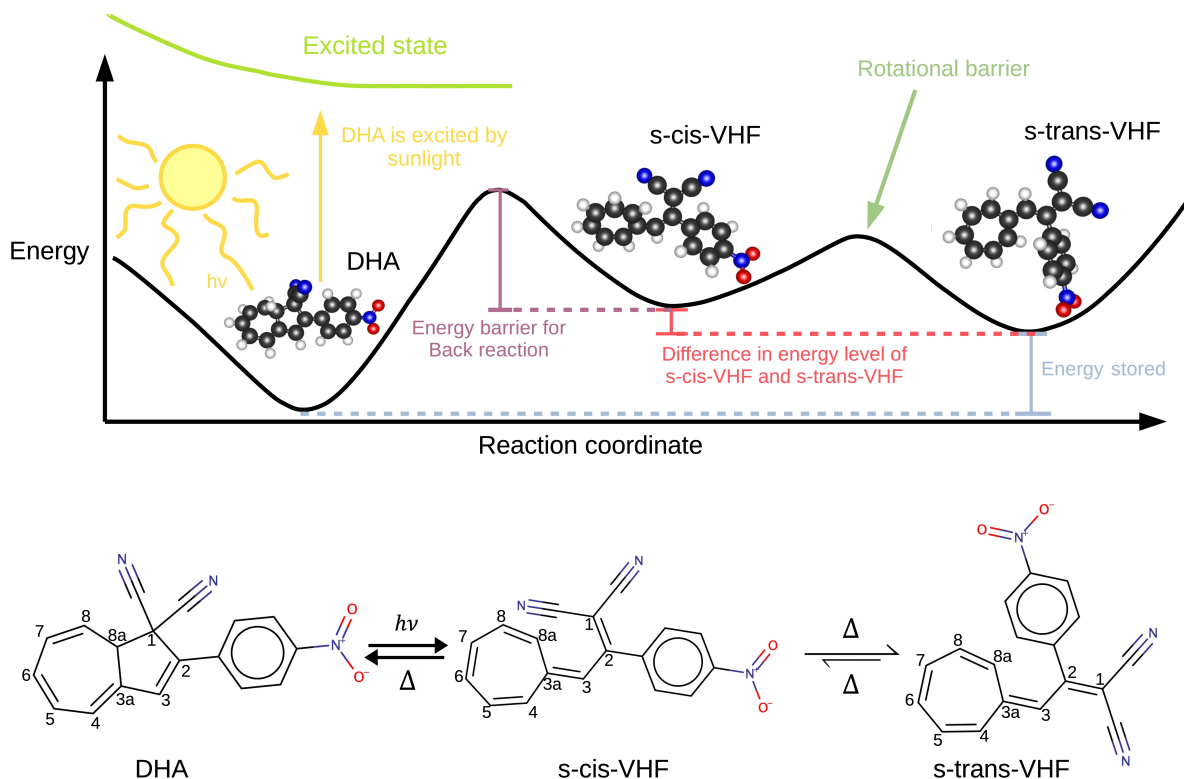
solar energy.<sup>2-19</sup>

Figure 1: Reaction scheme and energy level diagram for the photoinduced ring opening isomerization of DHA into the *s-cis* conformer of VHF and the thermal equilibrium between the *s-cis* and *s-trans* conformer of VHF. The *s-trans* conformer is more stable than the *s-cis* conformer, but it still lies higher in energy than DHA.

The DHA/VHF MOST system represents one of the promising systems for storing solar energy in this fashion.<sup>1-20</sup> DHA undergoes a ring-opening reaction after the photoexcitation and turns into *s-cis*-vinylheptafulvene (*s-cis*-VHF). Thereafter, a thermal equilibrium is established between *s-cis*-VHF and *s-trans*-vinylheptafulvene (*s-trans*-VHF). The stored energy can be released by the thermal backreaction to DHA (see Fig. 1).

The two isomers, DHA and VHF, have their respective absorption bands in different areas of the UV/Vis spectrum. DHA has an absorption band from 310-410 nm and VHF has one from 370-500 nm. This means that there is a small overlap where DHA competes with VHF for the same solar photons.<sup>1-20</sup> Presently, we wish to investigate if we are able to

change the positions of the absorption bands for DHA, *s-cis*-VHF and *s-trans*-VHF as the molecules are placed in close proximity of gold nanoparticles (NPs).

Several research groups have been investigating photo/thermochromic molecular systems since these systems are of interest concerning switches in molecular electronics, use in data storage, biological systems, and solar energy harvesting.<sup>21-33</sup> The utilization of NPs as anchors or electrodes requires investigations concerning the influence of the NPs on the optical and electronic properties and the photo/thermochromic properties of the molecular systems.<sup>34,34-39,39</sup>

We consider (8aS)-2-(4nitrophenyl)-1,8a-dihydroazulene-1,1-dicarbonitril which is a DHA molecule substituted with a nitro group in para position on the phenyl group. We are only considering one stereoisomer since the investigated properties are independent of stereoisomerism.<sup>12,18</sup> The VHF molecule has two conformers, namely *s-cis*-VHF and *s-trans*-VHF.

The main purpose of this investigation is to study how the absorption spectra change for DHA, *s-cis*-VHF and *s-trans*-VHF as the molecules interact with the gold NP.<sup>40-42</sup>

We wish to study how the absorption bands change with respect to (i) distance between the NP and the molecules, (ii) the conformations of the three molecules, and (iii) the relative orientations.

We have chosen to consider a DHA compound with a nitro group on the phenyl ring since this creates a large permanent dipole moment of the molecule.<sup>18,19</sup> A large permanent dipole moment of the molecular compounds will enable large interactions between the polarizable NP and the molecules. Thereby, we expect that the molecular properties of the investigated molecules will change significantly.

We wish to provide an atomistic description of the nanoparticle and thereby we go beyond a dielectric medium approach by assigning the individual gold atoms a polarizability and allowing each of them to have different induced dipoles. The photo/thermochromic system is attached to a planar surface of the nanoparticle and thereby we simulate how the DHA/VHF is physisorbed onto a very large nanoparticle. The present approach does not include the

absorption or frequency dependent polarizability of the nanoparticle which has previously been done through the use of dielectric medium approaches on other photo/thermochromic systems.<sup>43,44</sup>

## Computational approach

In order to investigate how the absorptions of the photo/thermochromic molecules DHA, *s-cis*-VHF og *s-trans*-VHF are affected by the interactions with a gold nanoparticle, we utilize a QM/MM method where the molecular systems are treated by quantum mechanics and the gold nanoparticle is given by molecular mechanics. The molecular systems are described by density functional theory using the functional CAM-B3LYP<sup>45</sup> and the basis set aug-cc-pVDZ.<sup>46</sup> The structures of the three molecules are geometry optimized in vacuum using Gaussian09<sup>47</sup> and the optimized structures were subsequently used in QM/MM and linear response calculations of the first 15 excitations and associated oscillator strengths carried out using Dalton.<sup>48</sup>

The present investigations do not include larger gold nanoparticles since we have previously shown that one photon absorptions do not change more than 5% when increasing the size of the nanoparticle.<sup>41,42</sup>

Each of the three molecules are placed at the nanoparticle in three different ways: 1) The NO<sub>2</sub> group points towards the nanoparticle. 2) The 7 membered ring points towards the nanoparticle. 3) The cyano group points towards the nanoparticle as displayed in Fig. 2-10.

Furthermore, we investigate the dependence of the excitation process on the distance between the photo/thermochromic molecules and the nanoparticle. We calculate the molecular properties at three different distances: 1) the shortest distance between the molecule and the nanoparticle which is given by the sum of the van der Waals radii between the atom of the molecule and the gold atom, that are closest to each other in the given relative orienta-

tion. 2) The other two distances are, respectively, 1.0 Å and 2.0 Å longer than the shortest distance. Previous investigations showed that the gold NP only has a minimal effect on the molecules for distances greater than 5 Å.<sup>40</sup>

The gold nanoparticle is formed as a hemisphere and the flat surface points towards the photo/thermochromic molecules. The gold surface is given by a fcc(111) surface since previous work has shown this to be the best description of how molecules are attached to gold nanoparticles.<sup>49,50</sup> The gold atoms are described by a static polarizability of 31.040 au.<sup>51</sup>

## Results and discussion

We present the calculated linear optical properties of the photo/thermochromic molecules for each of the relative orientations of the molecules with respect to the nanoparticle. The 15 obtained vertical excitations are presented in calculated UV/Vis spectra while the tables contain the wavelength and oscillator strength of the first 5 excitations for each molecule in all orientations and at all three distances. Our focus is on the first absorption band and the most intense transitions when the molecules are closest to the nanoparticle.

### The NO<sub>2</sub> orientation

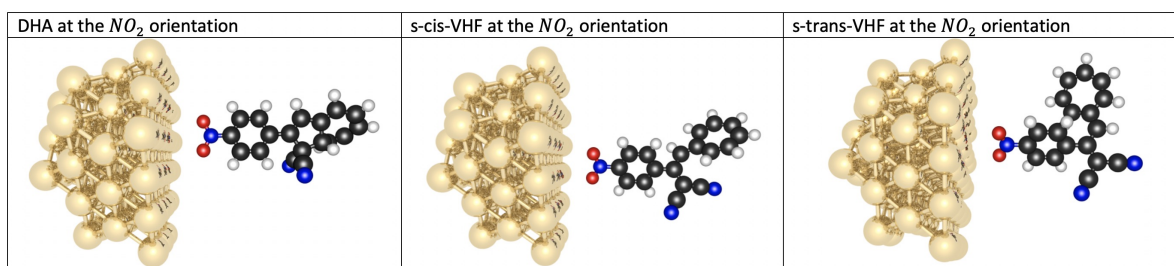


Figure 2: The NO<sub>2</sub> orientation of DHA, *s-cis*-VHF, and *s-trans*-VHF respectively.

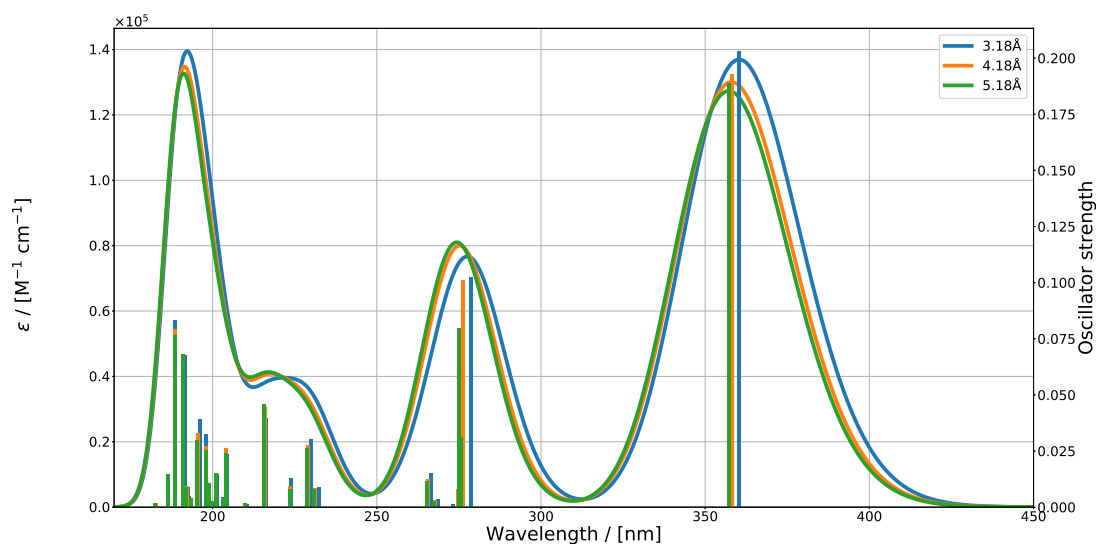


Figure 3: The UV/Vis spectra of DHA in the  $NO_2$  orientation with a molecule cluster separation of 3.18 Å, 4.18 Å, and 5.18 Å respectively.

For this orientation, the  $NO_2$  group of the three molecules points towards the nanoparticle (see Fig.2). In Fig. 3, we present the UV/Vis absorption spectrum of DHA and we observe an effect of the gold nanoparticle on the first absorption of DHA. We note that decreasing the distance between the molecule and the nanoparticle leads to a larger intensity and a longer wavelength of the first absorption band. This orientation gives rise to the largest change for the first absorption band of DHA and the shift is related to the interactions of the polar group with the nanoparticle. The change is not sufficiently large to shift the absorption of DHA into the part of the solar spectrum with the largest intensity. The two most intense transitions at the shortest distance for DHA are shifted by around 3nm and the intensities are increased by 7,4 and 230 percent as DHA gets closer to the nanoparticle (see Table 1).

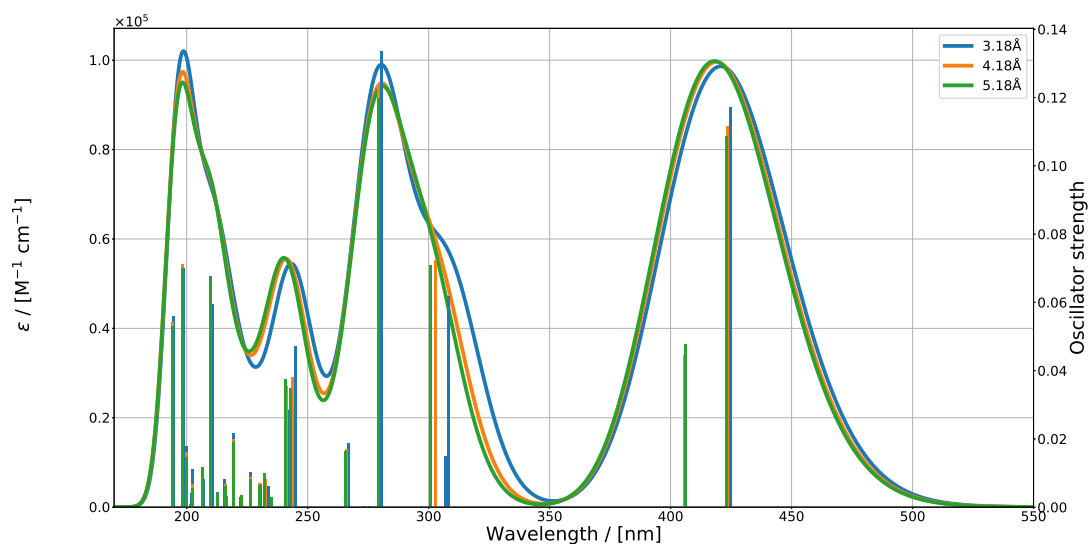


Figure 4: The UV/Vis spectra of *s-cis*-VHF in the  $\text{NO}_2$  orientation with a molecule cluster separation of 3.18 Å, 4.18 Å, and 5.18 Å respectively.

Generally, the first absorption band for *s-cis*-VHF is wider and lower compared to the spectra of DHA og *s-trans*-VHF. We note that the  $\text{NO}_2$  orientation leads to a small redshift and a minor decrease of the intensity for *s-cis*-VHF (see Fig. 4). For *s-cis*-VHF, we note that the wavelengths of the two most intense transitions have increased by 1.9 nm and 1.2 nm, respectively, as we decrease the distance between the molecule and the nanoparticle (see Table 1). Furthermore, the intensities for these two transitions increase by 7.3 and 11.7 percent as the distance between the molecule and the nanoparticle decreases (see Table 1). The huge increase of the intensity of excitation 3 relates to a forbidden excitation that becomes allowed as the molecule approaches the nanoparticle.

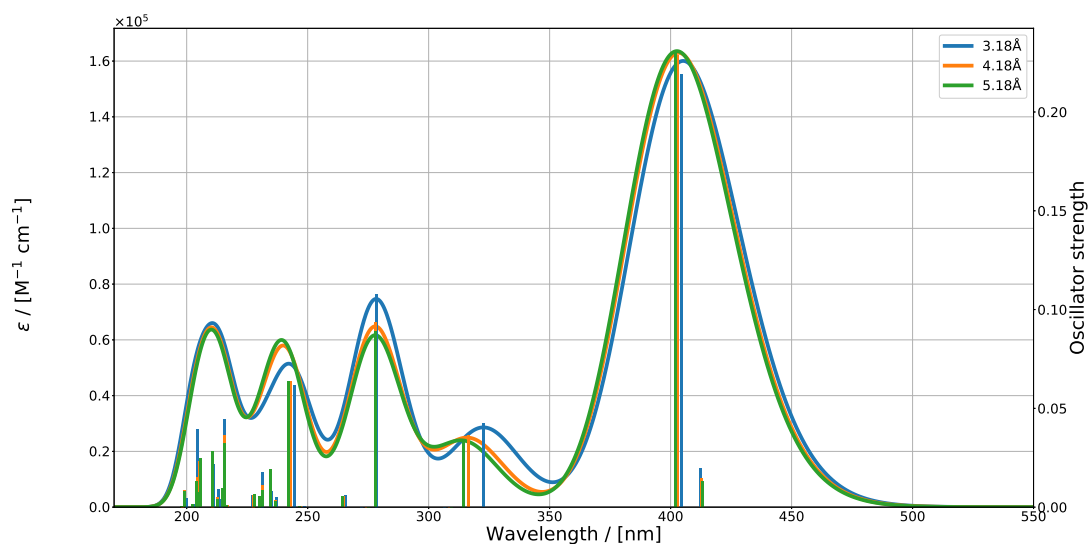


Figure 5: The UV/Vis spectra of *s-trans*-VHF in the  $NO_2$  orientation with a molecule cluster separation of 3.18 Å, 4.18 Å, and 5.18 Å respectively.

In the case of *s-trans*-VHF, the intensity of the first absorption band is significantly larger and the band is narrower compared to the spectrum for *s-cis*-VHF (see Fig. 5). We observe a slightly larger redshift for *s-trans*-VHF compared to *s-cis*-VHF. We note from Table 1 that the wavelengths of the two most intense transitions increase by 2.5 nm and 0.4 nm, respectively. For the most intense transition, there is a decrease of the intensity by about 5.2 percent as the molecule approaches the nanoparticle. For the second most intense transition we see an increase of 21 percent (see Table 1).

**Table 1: The wavelengths of excitation and associated oscillator strengths of the first five excitations for all three molecules in the NO2 orientation.**

<b>DHA</b>						
Ex. number	$\lambda_{3.18\text{\AA}} [nm]$	$f_{3.18\text{\AA}}$	$\lambda_{4.18\text{\AA}} [nm]$	$f_{4.18\text{\AA}}$	$\lambda_{5.18\text{\AA}} [nm]$	$f_{5.18\text{\AA}}$
1	360.4	0.203	358.1	0.193	357.2	0.189
2	307.8	2.20E-05	309.7	2.50E-05	310.4	2.60E-05
3	278.8	0.103	276.2	0.101	275.7	0.0311
4	273.2	0.00118	274.7	0.00811	274.9	0.0797
5	268.7	0.00350	267.8	0.00299	267.5	0.00263
<b>s-cis-VHF</b>						
Ex. number	$\lambda_{3.18\text{\AA}} [nm]$	$f_{3.18\text{\AA}}$	$\lambda_{4.18\text{\AA}} [nm]$	$f_{4.18\text{\AA}}$	$\lambda_{5.18\text{\AA}} [nm]$	$f_{5.18\text{\AA}}$
1	425.0	0.117	423.6	0.112	423.1	0.109
2	405.6	0.038	405.9	0.0445	406.0	0.0476
3	308.2	0.0618	309.4	0.000172	310.0	8.1E-05
4	307.1	0.0147	302.8	0.0723	300.9	0.0708
5	280.4	0.134	279.4	0.123	279.2	0.120
<b>s-trans-VHF</b>						
Ex. number	$\lambda_{3.18\text{\AA}} [nm]$	$f_{3.18\text{\AA}}$	$\lambda_{4.18\text{\AA}} [nm]$	$f_{4.18\text{\AA}}$	$\lambda_{5.18\text{\AA}} [nm]$	$f_{5.18\text{\AA}}$
1	412.4	0.0120	412.8	0.0145	413.0	0.0132
2	404.6	0.219	402.8	0.228	402.1	0.231
3	322.8	0.0422	316.7	0.0363	314.6	0.0345
4	306.4	7.10E-05	308.8	7.00E-05	309.4	9.50E-05
5	278.6	0.108	278.2	0.0936	278.2	0.0889

## The CN orientation

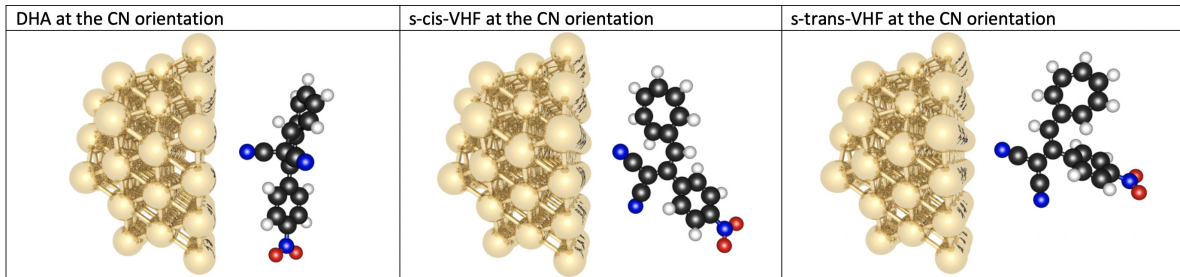


Figure 6: The CN orientation of DHA, *s-cis*-VHF, and *s-trans*-VHF respectively.

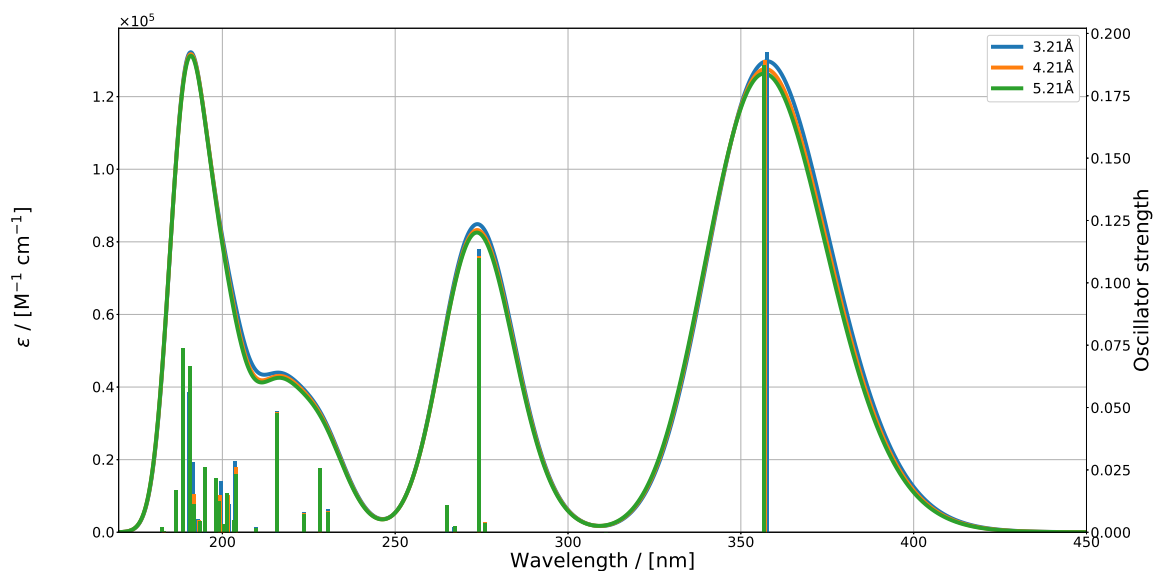


Figure 7: The UV/Vis spectra of DHA in the CN orientation with a molecule cluster separation of 3.21 Å, 4.21 Å, and 5.21 Å respectively.

For this molecular orientation, the cyano group (the other polar group) points towards the nanoparticle (see Fig. 6). In the case of DHA, there is hardly any redshift of the first absorption band but a small increase in the oscillator strength (see Fig. 7). For DHA, we observe an increase of the wavelength of 0.8nm for the most intense transition whereas the wavelength for the second most intense transition does not change as the molecule approaches the nanoparticle (see Table 2). For both transitions, the intensities are increased by about 3 percent as DHA gets closer to the nanoparticle (see Table 2).

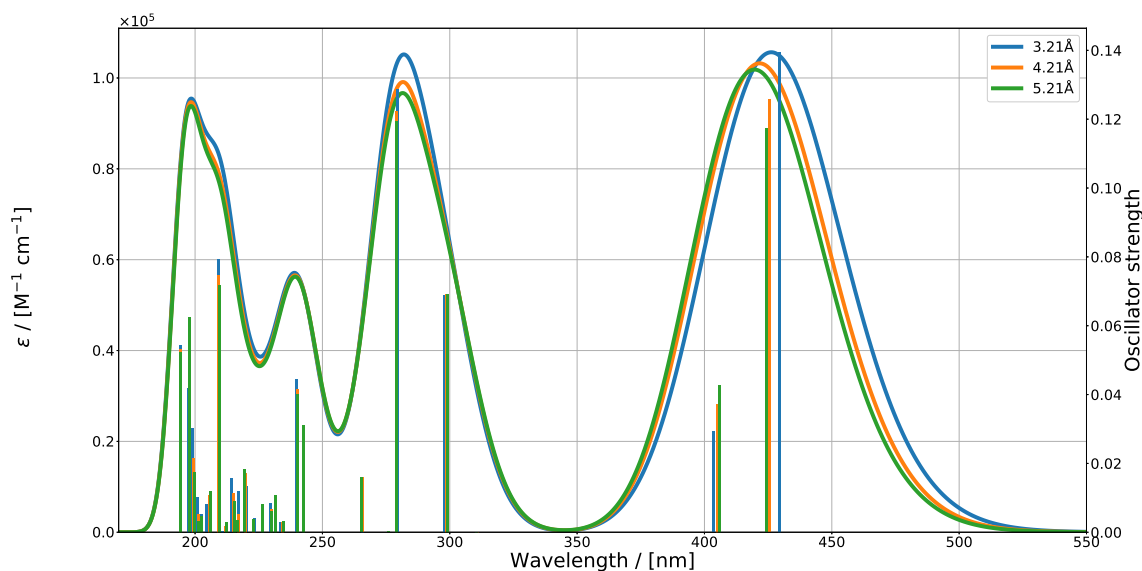


Figure 8: The UV/Vis spectra of *s-cis*-VHF in the CN orientation with a molecule cluster separation of 3.21 Å, 4.21 Å, and 5.21 Å respectively.

On the other hand, the effect of the nanoparticle on *s-cis*-VHF is substantially larger for the CN orientation than for the NO<sub>2</sub> orientation (see Fig. 8). The two most intense transitions for *s-cis*-VHF are the excitations numbered 1 and 5 (see Table 2). The wavelengths for these transitions increase 5.3nm and 0.4nm as the molecule gets closer to the nanoparticle. The corresponding intensities increase by 18.8 and 8.4 percent (see Table 2).

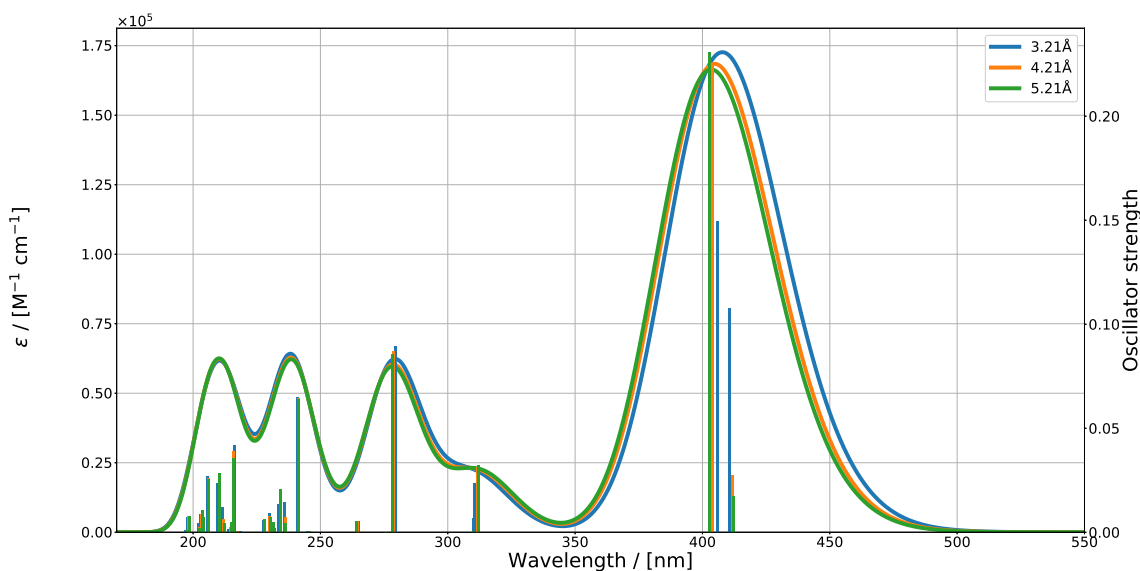


Figure 9: The UV/Vis spectra of *s-trans*-VHF in the CN orientation with a molecule cluster separation of 3.21 Å, 4.21 Å, and 5.21 Å respectively.

In the case of *s-trans*-VHF in the CN orientation, we observe significant effects in terms of a larger redshift and a larger intensity (see Fig. 9). It is clear that the VHF compounds are influenced significantly when the cyano group points towards to nanoparticle. We note from Table 2 that the second lowest transition has a decrease of the wavelength of 3.0 nm and its intensity decreases by 35 percent. For the first excitation the wavelength decreases by 1.6 nm and the corresponding intensity is increased by 5.2 percent (see Table 2).

**Table 2: The wavelengths of excitation and associated oscillator strengths of the first five excitations for all three molecules in the CN orientation.**

<b>DHA</b>						
Ex. number	$\lambda_{3.21\text{\AA}} [nm]$	$f_{3.21\text{\AA}}$	$\lambda_{4.21\text{\AA}} [nm]$	$f_{4.21\text{\AA}}$	$\lambda_{5.21\text{\AA}} [nm]$	$f_{5.21\text{\AA}}$
1	357.6	0.192	357.1	0.189	356.8	0.187
2	311.1	2.70E-05	311	2.70E-05	310.9	2.70E-05
3	276.1	0.00389	276	0.00399	276.0	0.00374
4	274.3	0.114	274.3	0.111	274.3	0.110
5	267.2	0.00187	267.2	0.00218	267.2	0.00225
<b>s-cis-VHF</b>						
Ex. number	$\lambda_{3.21\text{\AA}} [nm]$	$f_{3.21\text{\AA}}$	$\lambda_{4.21\text{\AA}} [nm]$	$f_{4.21\text{\AA}}$	$\lambda_{5.21\text{\AA}} [nm]$	$f_{5.21\text{\AA}}$
1	429.5	0.139	425.7	0.126	424.2	0.117
2	403.6	0.0292	405.2	0.0373	405.7	0.0427
3	311.0	5.30E-05	310.8	5.30E-05	310.7	5.20E-05
4	298.1	0.0689	298.7	0.0692	298.9	0.0693
5	279.5	0.129	279.2	0.122	279.1	0.119
<b>s-trans-VHF</b>						
Ex. number	$\lambda_{3.21\text{\AA}} [nm]$	$f_{3.21\text{\AA}}$	$\lambda_{4.21\text{\AA}} [nm]$	$f_{4.21\text{\AA}}$	$\lambda_{5.21\text{\AA}} [nm]$	$f_{5.21\text{\AA}}$
1	410.7	0.108	411.6	0.0273	412.3	0.0175
2	405.8	0.150	404.0	0.224	402.8	0.231
3	310.5	0.0235	311.8	0.0315	312.2	0.0321
4	310.3	0.00696	310.1	0.000338	310.0	0.000248
5	279.4	0.0895	278.7	0.0869	278.4	0.0858

## The 7 membered ring orientation

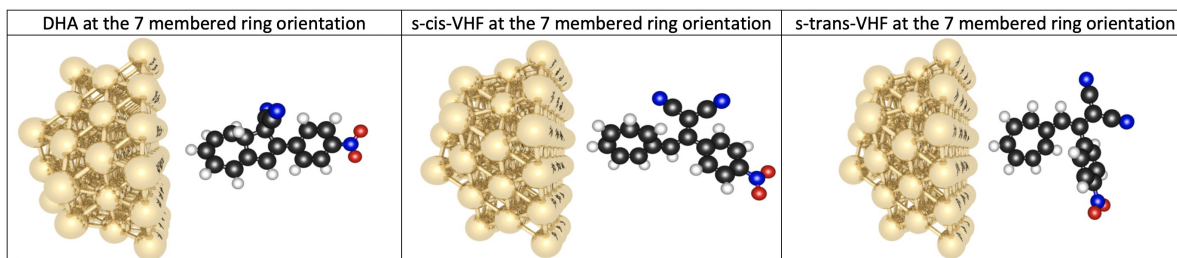


Figure 10: The 7 membered ring orientation of DHA, s-cis-VHF, and s-trans-VHF respectively.

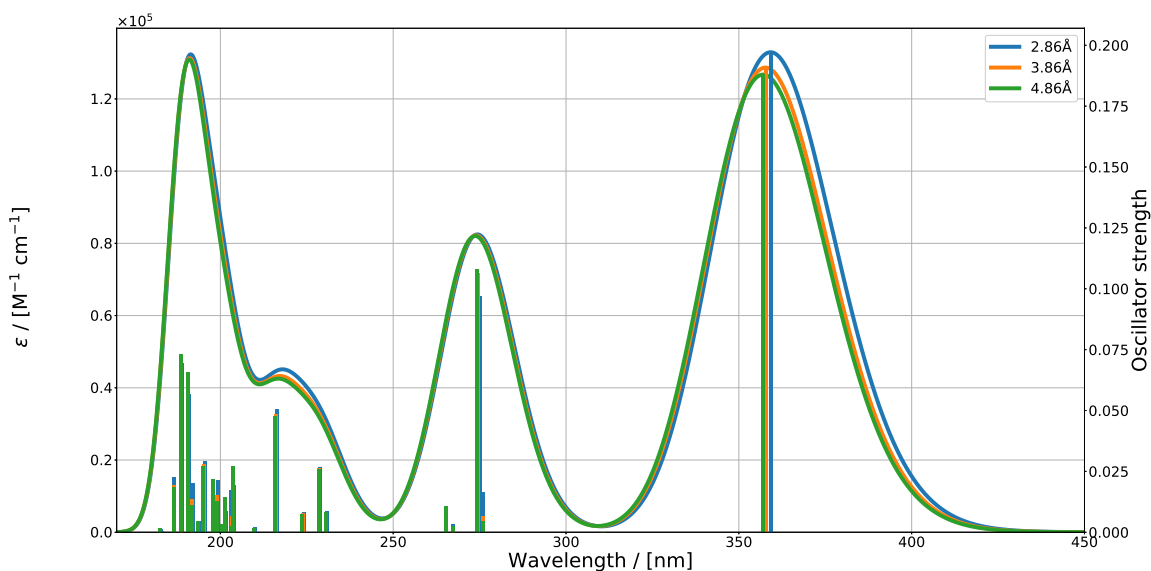


Figure 11: The UV/Vis spectra of DHA in the 7mem orientation with a molecule cluster separation of 2.86 Å, 3.86 Å, and 4.86 Å respectively.

This orientation of the three molecules is such that the 7 membered ring of the three molecules points towards the nanoparticle (see Fig. 10). For DHA in this orientation, we observe a larger effect than for the orientation where the CN group is pointed towards the cluster, but the redshift is smaller than that of DHA in the NO<sub>2</sub> orientation (see Fig. 11). Additionally, we observe that the two most intense transitions are the excitations numbered 1 and 4 (see Table 3). The intensity of transition 1/4 increases/decreases by 4.8/10.7 percent as the distance of the molecule and the nanoparticle gets smaller. The wavelength for the 1/4 excitation increase by 2.1nm/0.2nm (see Table 3).

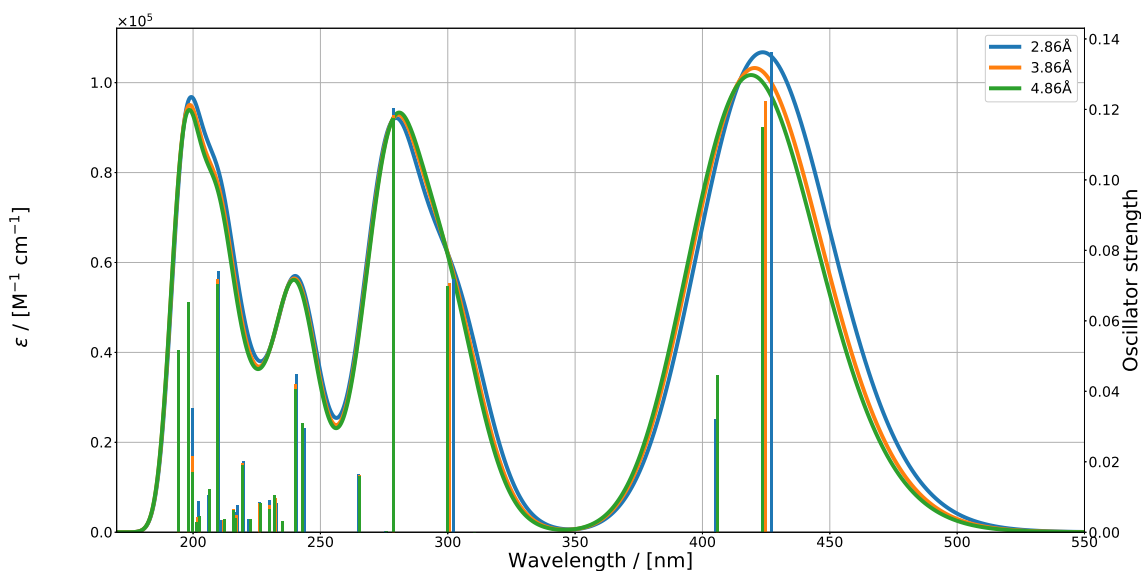


Figure 12: The UV/Vis spectra of *s-cis*-VHF in the 7mem orientation with a molecule cluster separation of 2.86 Å, 3.86 Å, and 4.86 Å respectively.

For *s-cis*-VHF, we find the same tendencies as *s-cis*-VHF with the CN orientation (see Fig. 12). We note from Table 3 that the excitations 1 and 5 are the most intense and the intensities increase by 18.3 and 2.6 percent, respectively, as *s-cis*-VHF approaches the nanoparticle. The corresponding wavelengths are increased and decreased by 3.3 nm and 0.3 nm, respectively.

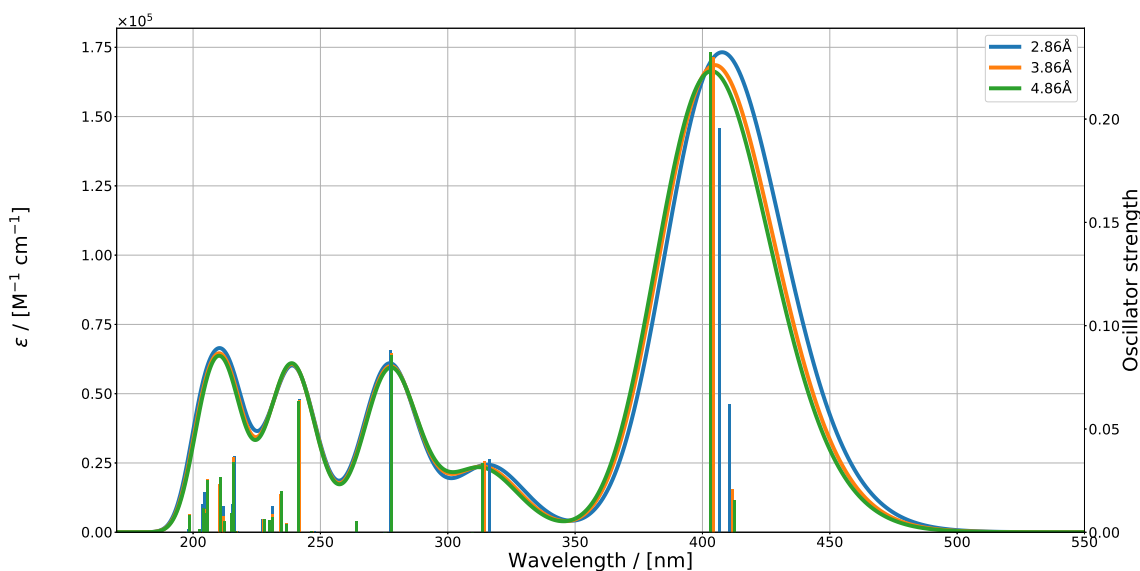


Figure 13: The UV/Vis spectra of *s-trans*-VHF in the 7mem orientation with a molecule cluster separation of 2.86 Å, 3.86 Å, and 4.86 Å respectively.

In the case of *s-trans*-VHF, we note that the trends are the same as for *s-trans*-VHF in the CN orientation (see Fig. 13). In the 7mem orientation, the *s-trans*-VHF molecule has an intense transition for excitation 2 where the wavelength increases by 3.8 nm and the intensity decreases by 15.5 percent as the molecule-particle separation is decreased (see Table 3). The second most intense transition hardly changes its intensity but the wavelength decreases by 0.4nm as the molecule gets closer to the nanoparticle.

**Table 3: The wavelengths of excitation and associated oscillator strengths of the first five excitations for all three molecules in the 7mem orientation.**

<b>DHA</b>						
Ex. number	$\lambda_{2.86\text{\AA}} [nm]$	$f_{2.86\text{\AA}}$	$\lambda_{3.86\text{\AA}} [nm]$	$f_{3.86\text{\AA}}$	$\lambda_{4.86\text{\AA}} [nm]$	$f_{4.86\text{\AA}}$
1	359.2	0.197	357.7	0.191	357.1	0.188
2	310.7	2.60E-05	310.8	2.60E-05	310.9	2.60E-05
3	275.9	0.0164	275.9	0.00643	275.9	0.00447
4	275.0	0.0968	274.6	0.106	274.4	0.108
5	267.4	0.00315	267.3	0.00258	267.2	0.00239
<b>s-cis-VHF</b>						
Ex. number	$\lambda_{2.86\text{\AA}} [nm]$	$f_{2.86\text{\AA}}$	$\lambda_{3.86\text{\AA}} [nm]$	$f_{3.86\text{\AA}}$	$\lambda_{4.86\text{\AA}} [nm]$	$f_{4.86\text{\AA}}$
1	427.0	0.136	424.6	0.122	423.7	0.115
2	405.0	0.0320	405.7	0.0398	406.0	0.0445
3	310.4	0.000138	310.5	7.80E-05	310.5	6.30E-05
4	302.3	0.0719	300.7	0.0705	299.9	0.0699
5	278.6	0.120	278.8	0.118	278.9	0.117
<b>s-trans-VHF</b>						
Ex. number	$\lambda_{2.86\text{\AA}} [nm]$	$f_{2.86\text{\AA}}$	$\lambda_{3.86\text{\AA}} [nm]$	$f_{3.86\text{\AA}}$	$\lambda_{4.86\text{\AA}} [nm]$	$f_{4.86\text{\AA}}$
1	410.7	0.0619	411.8	0.0210	412.4	0.0157
2	406.8	0.196	404.3	0.230	403.0	0.232
3	316.2	0.0355	314.5	0.0342	313.7	0.0336
4	309.7	6.50E-05	309.8	9.20E-05	309.8	0.000120
5	277.6	0.0880	277.9	0.0864	278.0	0.0856

The interactions between DHA and the gold nanoparticle are not sufficient for redshifting the first absorption band significantly and bringing the absorption closer to the maximum of solar irradiation. Redshifting the first absorption band would benefit the performance of the MOST system since there is a larger amount of photons in the area of 450-550 nm. It is clear that the obtained results give a valid representation of how the nanoparticle influences the absorption spectra in the DHA/VHF molecular system. We do observe a redshifting of the molecular spectra and the magnitude of the shift strongly depends on the orientation of the molecules and the distance between the nanoparticle and the photo/thermochromic molecular system. It is also clear that the distance between the nanoparticle and the respective polar groups is crucial for understanding how the absorption spectra change. The

polar groups are able to induce sizeable induced dipole moments in the nanoparticle which can then polarize the molecule even more. This effect can lead to a larger influence of the nanoparticle on the properties of the molecular system. Additionally, it is worth considering that the model used in this study does not include the frequency dependence of the properties of the nanoparticle. This effectively means that one discards the plasmonic effects which could create an even larger electrical field for the molecules to be perturbed by.

## Conclusion

In conclusion, we find that the resulting linear optical properties of the photo/thermochromic DHA/VHF system are promising with respect to the redshifting of the first absorptions of DHA and VHF. The redshifting of the absorption band is expected to potentially provide for an improved performance of the MOST system. Furthermore, we observe that the redshifts of the photo/thermochromic molecules depend substantially on the molecular orientation and the distance between the nanoparticle and the photo/thermochromic molecule.

The influence of the nanoparticle is larger on the optical properties of *s-trans*-VHF and *s-cis*-VHF than on the corresponding properties of the DHA molecule. It is also clear that we observe the largest changes when one of the two polar groups ( $\text{NO}_2$  or  $\text{CN}$ ) is oriented towards the nanoparticle. Generally, we observe that the excitation energies are redshifted as we decrease the molecule-cluster distance and we note that the stronger interaction of the *s-trans*-VHF and *s-cis*-VHF molecules with the nanoparticle provides a wider separation between the absorption peaks of DHA and VHF.

Experimentally,<sup>52</sup> it has been shown that the first excitation band of VHF is redshifted by about the same amount as calculated in the present investigation. The experiments involved complexes of VHF and Ag atoms along with complexes of DHA and Ag atoms. In the case of the complexes of DHA and Ag atoms there is no observed shifts of the first absorption.<sup>52</sup> Similar experimental results have been obtained for the DHF/VHF photo/thermochromic

system and Cu atoms.<sup>53</sup>

We have not included the optical properties of the nanoparticle in the presented calculations but it would be interesting to investigate how the excited states of the photo/thermochromic system are influenced by plasmonic modes of the nanoparticle using theoretical models that go beyond the dielectric models. Dielectric models have been utilized for investigating the effects of plasmons on photo/thermochromic systems.<sup>43,44</sup>

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