

# Adsorption of croconate dyes on TiO<sub>2</sub> anatase (101) surface: A periodic DFT study to understand the binding of diketo groups<sup>#</sup>

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**Abstract.** The adsorption of model croconate dyes on the stoichiometric TiO<sub>2</sub> anatase (101) surface has been studied by means of periodic density functional calculations to understand the adsorption of the diketo (-COCO-) groups. Past experimental and theoretical results have shown the strong binding ability of the acid group (-COOH) to the TiO<sub>2</sub> surface but here the theoretical studies predicts the binding strength of the diketo group to be also significant and comparable with that of the -COOH group. This may cause a competitive binding between the keto groups and the acid groups on the TiO<sub>2</sub> surface in the case of croconate dyes and cause a reduction in the efficiency of the DSSC.

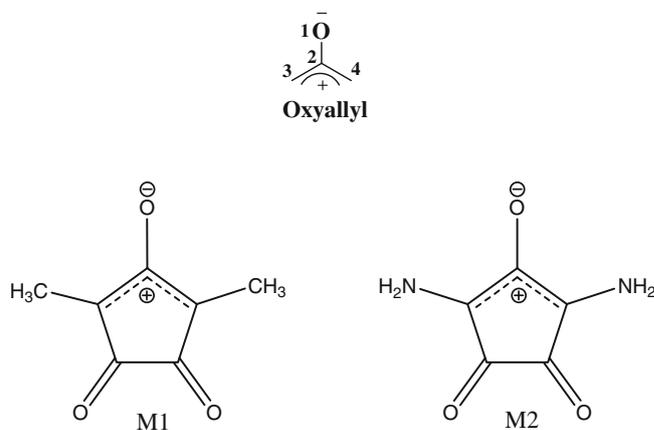
**Keywords.** DSSC; croconates; TiO<sub>2</sub>; adsorption; periodic DFT.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted a large amount of attention due to their potentially low-cost fabrication, easy production and flexibility compared to conventional photovoltaic cells and organic cells.<sup>1a</sup> Standard DSSCs are composed of a dye containing an anchoring group like carboxylic, sulphonic, or phosphonic acids grafted onto the surface of wide-bandgap semiconductors like NiO, ZnO or TiO<sub>2</sub> in contact with an electrolyte (typically I<sub>3</sub><sup>-</sup>/I<sup>-</sup> in an organic solvent) and closed by a counter electrode, usually made of Pt. Upon absorption of light, dye molecules promoted to an electronically excited state, can inject electrons into the conduction band of the semiconductor, typically an oxide. The oxidized dyes are regenerated by a reducing agent present in the electrolyte (usually I<sup>-</sup>), which is converted to the corresponding oxidized species (I<sub>3</sub><sup>-</sup>) and subsequently reduced at the counter electrode.<sup>1b</sup> Up to now, the best performances reported in the literature have been obtained with cells composed of a titania nanoparticulate thin film sensitized by a ruthenium polypyridine complex dye (N3 and other derivatives).<sup>2,3</sup> Unfortunately ruthenium dyes are very expensive due to the lack of natural abundance of ruthenium. Due to this, metal free sensitizers

such as organic dyes and natural dyes are being investigated as alternative sensitizers for DSSC applications.<sup>4</sup> Recent literature reports indicate achievement of efficiency of ~8% using organic dyes.<sup>5</sup> Several organic dyes such as coumarins,<sup>6–9</sup> merocyanine,<sup>10,11</sup> hemicyanine,<sup>12–14</sup> porphyrin,<sup>15–19</sup> phthalocyanine,<sup>20,21</sup> indoline,<sup>22,23</sup> squaraines<sup>24–26</sup> and croconates<sup>27</sup> have been reported.

The croconate and squaraine dyes are important class of organic ‘functional’ dyes of relatively short backbone containing the oxyallyl subgroup (scheme 1) which can be synthesized easily and possess features like flexibility, high interaction with light and broad absorption mainly localized in the red to near infrared



**Scheme 1.** Structures of the oxyallyl sub group and the two model croconate dyes (M1 and M2) investigated in this work.

<sup>#</sup>Dedicated to Prof. N Sathyamurthy on his 60th birthday

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(NIR) region.<sup>28,29</sup> The NIR absorption can be correlated to the biradical character (BRC) which is possessed by these molecules.<sup>30,31</sup> The absorption can be fine tuned by utilizing their property to undergo intermolecular interaction and produce H-type and J-type aggregates<sup>32–40</sup> or by varying substitution. These dyes can be used in solar cells as they can harvest low-energy photon that usually goes untapped.<sup>41</sup>

Geiger *et al.* have synthesized and characterized unsymmetrical squaraine dyes with carboxylic acid as the anchoring group.<sup>42</sup> They obtained a high efficiency of 5.4%. They attribute the high efficiency to small optical band gap. Another study by Burke *et al.* reports a squaraine dye with two carboxylic acid groups. They report efficiencies of 1.5% and 3.7%.<sup>43</sup> A recent report by Yum *et al.* indicate the efficient red sensitization of the TiO<sub>2</sub> film by the unsymmetrical squaraine dye. They obtain a 4.5% conversion efficiency.<sup>44</sup> More recently reports by Choi *et al.* indicate a overall efficiency of 5.2% for three new unsymmetrical squaraine dyes.<sup>45</sup> On the other hand, fewer reports are seen in the case of croconate dyes. Takechi *et al.* reports around 1.2% efficiency for the croconate dye which absorbs in the far infrared.<sup>27</sup> This reduced efficiency is intriguing as croconate dyes have an absorption maxima farther in the red compared to the corresponding squaraines. Takechi *et al.* have explained that the reduced efficiency could be due to net charge separation being poor.<sup>27</sup> From the structure of the croconate dyes it is also possible that the diketo groups may also have a competitive binding on the TiO<sub>2</sub> surface. Since binding energy is also a vital parameter for the efficiency of the cell a detailed understanding of this may throw some light on the performance of the dyes.<sup>46,47</sup> Keeping this in view we have undertaken the study of adsorption of diketo group of the model croconates shown in scheme 1 on the TiO<sub>2</sub> anatase (101) surface. M1 has methyl groups as the donors and these groups do not participate in the Valence bond (VB) resonance of the central structure. On the other hand, the donor groups in M2 are the NH<sub>2</sub> groups which can participate in the VB resonance.

## 2. Computational details

The results of calculations reported in this work have been obtained using the Gaussian 03 *ab initio*/DFT quantum chemical package.<sup>48</sup> The gas phase optimization of all the possible conformations of the two model croconate dyes in the scheme 1 have been carried out using the hybrid density functional-B3LYP and Pople's split valence basis set with polarization and diffuse

functions [6-311+G(d,p)] using the default integration grid as implemented in Gaussian 03. The theoretical singlet equilibrium structures were obtained when the maximum internal forces acting on all of the atoms and the stress were less than  $4.5 \times 10^{-4}$  eV/Å and  $1.01 \times 10^{-3}$  kbar, respectively and the most stable was selected for further studies. The minima were further confirmed by vibrational analysis. Only the low lying minima are reported.

As these molecules are known to possess BRC, calculation of the adiabatic singlet-triplet gap along with percentage BRC would give us an idea of the amount of BRC.<sup>30</sup> To obtain the singlet-triplet gap, the lowest singlet geometries have been considered as the initial geometries for calculating the lowest triplet state geometries at the UB3LYP/6-311+G(d,p) level of theory for the two modelled croconate dyes. The minimized singlet geometries obtained above are used for calculating the biradical character (BRC) and wave function stability. Several methods have been suggested for estimating the BRC. Wirz had suggested that a molecule can be said to be a biradical if the splitting between the singlet ( $S_0$ ) and triplet ( $T_1$ ) is around 2–24 kcal/mol.<sup>49</sup> On the other hand, the percent of BRC can also be estimated by using natural orbital occupation numbers method suggested by Nakano *et al.*<sup>50,51</sup> Here it is related to the HOMO- $i$  and LUMO+ $i$  and is defined as the weight of the doubly excited configuration in the MC-SCF theory and is formally expressed in the spin-projected UHF (PUHF) theory as.

$$C_D = \left( 1 - \frac{2S_i}{1 + S_i^2} \right) \times 100, \quad (1)$$

where  $S_i$  is the orbital overlap ( $\chi_{HOMO-i}$  and  $\eta_{HOMO-i}$ ) between the corresponding pairs,  $\chi_{HOMO-i} = \cos(\omega) \phi_{HOMO-i} + \sin(\omega) \phi_{LUMO+i}$  and  $\eta_{HOMO-i} = \cos(\omega) \phi_{HOMO-i} - \sin(\omega) \phi_{LUMO+i}$ .

Here  $\omega$  and  $\phi$  represent the UHF natural orbital (UNO) and orbital mixing parameter, respectively. The orbital overlap can be replaced by the occupation numbers ( $n_j$ ) of UNOs, which are obtained from the density matrix. This has been shown to be suitable for calculating the amount of biradicaloid character present in the molecule. The  $S_i$  can be expressed as  $S_i = \frac{n_{HOMO-i} - n_{LUMO+i}}{2}$ .

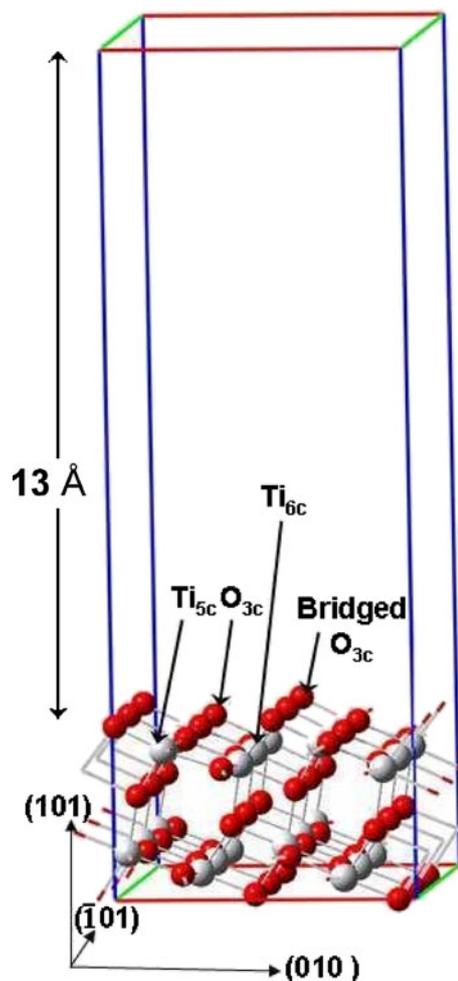
It has been reported in earlier studies that BRC estimated by the unrestricted DFT methods is underestimated whereas the *ab initio* UHF methods give reasonable BRC.<sup>52</sup> Hence we estimated this by using UHF at 6-311+G(d, p) level of the theory.

The minimized singlet geometries obtained above are also taken as starting points to carry out symmetry-

adapted cluster-configuration interaction (SAC-CI) calculations at 6-31G(d,p).<sup>53</sup> It is well known that for biradicaloid derivatives, double excited configurations in addition to the single excited configurations are also of importance for the description of the singlet ground state and its transitions.<sup>54</sup> This is due to the smaller energy differences between the orbitals which give rise to more contributing determinants to the state energy. Hence the Singles CI based on ZINDO and *ab initio*/CIS are not found suitable.<sup>55</sup> On the other hand, SAC/SAC-CI methods which take into consideration the singly and doubly excited states have been found reliable for studying molecular spectroscopy.<sup>56</sup> The detailed methodology of this is given elsewhere, but we give the salient features of our calculations in the relevant section.<sup>56</sup> SAC-CI is a cluster expansion method and it is usually found to converge rapidly than CI. It takes into consideration the singly and doubly excited states which mix up with the ground state and the targeted excited state

The adsorption of the croconate dyes over TiO<sub>2</sub> (101) anatase surface and density of states (DOS) studies have been carried out by employing PWscf code in quantum espresso suit.<sup>57</sup> For these calculations, we used the ultrasoft pseudopotentials proposed by Vanderbilt<sup>58</sup> and generated the Perdew-Wang 1991 (PW91)<sup>59</sup> exchange correlation functional with 18 electrons which include valence states of 2s and 2p shells for oxygen (six electrons) and 3s, 3p, 3d, and 4s shells for titanium (12 electrons). A kinetic energy cutoff of 25 Ry is chosen to describe the smooth part of the wave function in plane waves, while the augmented density cutoff is expanded up to 200 Ry. The Brillouin zone was sampled with  $1 \times 2 \times 2$  Monkhorst-Pack k-points<sup>60</sup> mesh to ensure convergence. For the relaxation of the isolated TiO<sub>2</sub> anatase (101) surface, single molecules, and the adsorbed complexes, the Broyden-Fletcher-Goldfrab-Shanno (BFGS)<sup>61</sup> algorithm has been used with the default convergence criteria.

To study the adsorption of diketo groups of the two model croconate dyes on the metal oxide surface, the anatase surface model used in the present calculations consists of a periodically repeated slab of  $3 \times 1 \times 2$  slabs with 24 [TiO<sub>2</sub>] units in the XY-plane and perpendicular to the Z-axis of the super cell. A vacuum space of 13 Å is considered in the Z-direction to ensure sufficient separation between the lowest and upper layer of the slab. To prevent the surface deformation, the lowest layer of the super cell is fixed in the calculation. Thus, the overall dimension of the super cell generated from the vacuum slab with dimensions of  $a = 10.24$ ,  $b = 11.35$ , and  $c = 18.86$ , are is shown in figure 1. The adsorption energy,  $E_{ads}$ , is calculated using the follow-



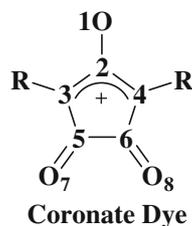
**Figure 1.** TiO<sub>2</sub> vacuum slab used for the adsorption studies of the croconate dyes.

ing expression,  $E_{ads} = E_{slab} + E_{molecule} - (E_{slab+molecule})$ , where  $E_{slab}$  represents the energy of the clean slab,  $E_{molecule}$  is the energy of the adsorbate in the gas phase, and  $E_{(slab+molecule)}$  is the total energy of the slab with adsorbate. A positive value of  $E_{ads} > 0$  indicates stable adsorption.

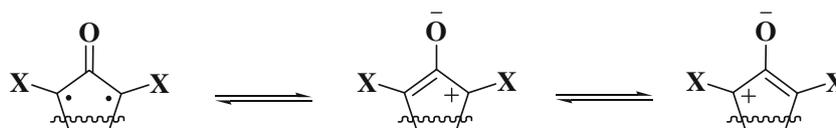
### 3. Results and discussions

#### 3.1 Geometries

The optimized geometry parameters of the two model croconate dyes investigated in this work is obtained using B3LYP/6-311+G(d,p) and given in table 1. The reliability of the DFT methods in reproducing the experimental geometry of the oxyallyl derivatives has been evaluated earlier; hence no further discussion of this is carried out here.<sup>53</sup> The C<sub>2</sub>-O<sub>1</sub> bond length of oxyallyl sub group is 1.226 Å in M1 and 1.236 Å in M2 which is longer when compared with the C<sub>5</sub>-O<sub>7</sub>/C<sub>6</sub>-O<sub>8</sub>

**Table 1.** Optimized geometrical parameters of the structures obtained at B3LYP/ 6-311+G(d,p) level.

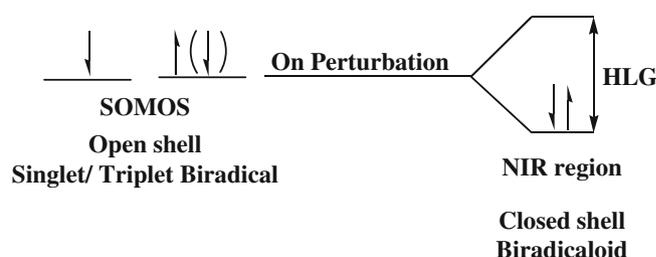
Molecules	$R_{ij}$ in Å				$\angle_{ijk}$ in Deg°	
	O <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub> /C <sub>2</sub> -C <sub>4</sub>	C <sub>3</sub> -R/C <sub>4</sub> -R	C <sub>5</sub> -O <sub>7</sub> /C <sub>6</sub> -O <sub>8</sub>	O <sub>1</sub> C <sub>2</sub> C <sub>3</sub> /O <sub>1</sub> C <sub>2</sub> C <sub>4</sub>	C <sub>3</sub> C <sub>2</sub> C <sub>4</sub>
M1	1.226	1.458	1.462	1.213	127.6	104.9
M2	1.236	1.446	1.319	1.218	128.0	104.1

**Figure 2.** Resonance structures of the oxyallyl subgroups.

which is 1.213 Å in M1 and 1.218 Å in M2. This indicates that the oxyallyl C=O has a smaller bond order or in other words has a larger single bond character. This is attributed to the resonance structures as shown in figure 2. In fact, this mixing of the biradical structure and the zwitterionic structure leads to very interesting properties (vide infra).<sup>30,62</sup>

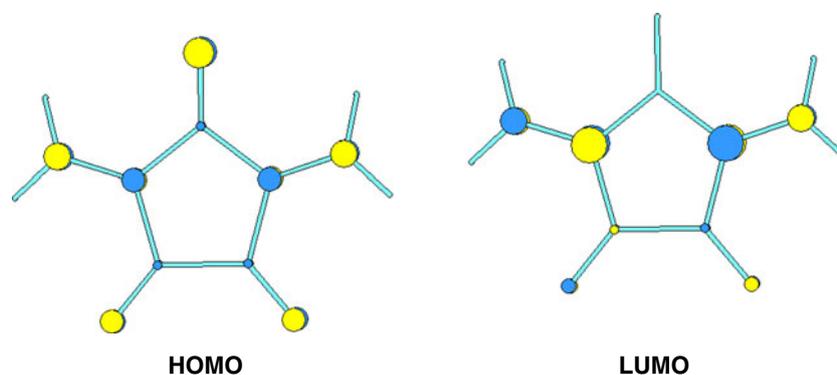
### 3.2 Biradical character (BRC)

Oxyallyl, a derivative of Trimethylenemethane (TMM), is a biradical species.<sup>63a</sup> Calculations predict that substitution of the oxygen of one methylene group in TMM should result in the lowest singlet (<sup>1</sup>A<sub>1</sub>) and triplet (<sup>3</sup>B<sub>2</sub>) states of oxyallyl being nearly isoenergetic<sup>63b</sup> and is also confirmed by experiments recently.<sup>62</sup> The BRC is reduced by geometric or electronegative perturbation with a heteroatom.<sup>63b</sup> The perturbation of the biradical to biradicaloids is shown in scheme 2. Alkyl substituents on the remaining two methylene groups of oxyallyl are unequivocally predicted to make <sup>1</sup>A<sub>1</sub> the ground state.<sup>63a</sup> Experimental results indicate that alkyl derivatives of oxyallyl do, indeed, have singlet ground states.<sup>64</sup> Fabian and Zahradnik had classified such dyes as biradicaloid dyes and attributed the larger wavelength absorption due to the biradicaloid nature, essentially indicating smaller HOMO LUMO gap (HLG).<sup>28,29</sup> The interesting nature of these molecules is that the non bonding orbitals of the oxyallyl subgroup make up the HOMO and the LUMO (figure 3).

**Scheme 2.** Representation of the perturbation of biradical to a biradicaloid.

The estimated BRC for these molecules are shown in table 2 along with the singlet–triplet gaps. It is observed that the dye M1 shows high BRC of 41% when compared to the dye M2 which shows only 14%. From the singlet triplet method one can see that the energy gap decrease in M1 is 2.2 kcal/mol while for M2 it is around 30.7 Kcal/mol and is in good agreement with the calculated BRC. The HLG given in the same table also indicates that the HLG for M1 is only 2.32 eV when compared to HLG of M2 which is around 3.13 eV.

To check the wave function stability of the molecules having high BRC, we carried out the wave function stability analysis proposed by Reinhart Ahlrichs.<sup>65</sup> The calculated stability eigen values are reported in table 2. We obtained positive eigen value for M2 0.02684 also we obtained a small negative eigen value for *B* matrix with magnitude of  $-0.01264$  indicating a mild external instability in the wave function due to the presence of high BRC (41%).



**Figure 3.** Frontier molecular orbital plots of M2. Drawn using MOPLOT.<sup>68</sup>

**Table 2.** HOMO–LUMO gap (HLG in eV), biradical character ( $Y_0$ ), singlet–triplet gap ( $\Delta E$  in kcal/mol) and Eigen value of the stability matrix of the two molecules.

Molecule	HOMO	LUMO	HLG <sup>a</sup>	$Y_0^b$	$\Delta E_{S-T}^d$	Eigen value <sup>c</sup>
M1	−7.20	−4.88	2.32	41	−2.23	−0.01264
M2	−6.38	−3.25	3.13	14	−30.7	0.02684

<sup>a</sup>HLG is taken from B3LYP/6-311+G(d,p) optimized geometries.

<sup>b</sup>Calculated at UHF/6-311+G(d,p) level.

<sup>c</sup>Calculated at RB3LYP/6-311+G(d,p) level.

<sup>d</sup> $\Delta E_{S-T} = E_{\text{Singlet}} - E_{\text{Triplet}} = -ve$  value indicates that singlet is stable.

### 3.3 Vertical electronic transitions

The symmetric, HF ground state wave function ( $A_1/A$ ) of all the molecules is improved by SAC and the configurations contributing to this state are shown in table 3. The number of linked operators before/after selection is in the order of  $10^6/10^4$  for SAC/SAC-CI methods. The contribution of the reference configuration for this state is 1.00 as per definition.<sup>56</sup> In addition to this, there exist

**Table 3.** Dimensions of the linked operator and configurations in the ground and first excited state from SAC/SAC-CI calculations at 6-31G(d,p) level.

Molecule	State <sup>a</sup>	Before <sup>b</sup>	After <sup>c</sup>	No. of configurations <sup>d</sup>
SAC				
M1	A	16367780	54827	7
M2	A1	3867960	60878	2
SAC-CI				
M1	A	16367780	150579	18
M2	B2	3864444	108345	21

<sup>a</sup>Number of solutions for SAC is one; for SAC-CI it is four.

<sup>b</sup>Number of linked operators before selection.

<sup>c</sup>Number of linked operators after selection.

<sup>d</sup>Number of configurations that have a CI coefficient larger than 0.03.

few more single and double configurations contributing to this state. Among them we present only the important double configuration coefficients for the ground state wave function which contributes reasonably ( $>0.04$ ) as shown in table 4, though they have contributions from singles ( $|c| \leq 30\%$ ). We also present the single and doubly excited configuration coefficients for the lowest first excited state ( $A/B_2$ ) which fairly contributes to the wave function ( $|c| \geq 0.10$ ) in table 4. It is observed that

**Table 4.** Weight of singles and doubles configuration for the ground and excited states, wave function obtained from SAC/SAC-CI at 6-31G(d,p) basis for all the molecules.

Molecule	Symmetry	Coefficients
M1 <sup>a</sup>	A	−0.078(36a–37a; 36a–37a) −0.049(36a–37a; 24a–37a)
M2 <sup>a</sup>	A1	−0.056(36b1–37a2; 36b1–37a2) −0.042(36b1–38b1; 36b1–38b1)
M1 <sup>b</sup>	A	0.931(36a–37a) 0.175(31a–37a) 0.154(36a–60a; 36a–37a) 0.107(36a–38a; 31a–37a)
M2 <sup>b</sup>	B2	−0.942(36b1–37a2) 0.115(33b2–37a2) −0.152(36b1–43a1; 36b1–37a2)

<sup>a</sup>Ground state:  $|c| \geq 0.040$

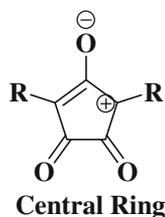
<sup>b</sup>Excited state:  $|c| \geq 0.10$

**Table 5.** Transition energy ( $\Delta E$  in eV), oscillator strength ( $f$ ), transition dipole moment ( $\mu_{ge}$ ), ground ( $\mu_g$ ) and excited ( $\mu_e$ ) state dipole moment in debye.

Molecule	$\Delta E$	$f$	$\mu_{ge}$	$\mu_g$	$\mu_e$
M1	2.16	0.194	4.87	-2.14	-3.95
M2	2.83	0.401	-6.11	3.14	4.24

in all these molecules, the major transitions are occurring from HOMO–LUMO ( $|c|=93\text{--}94\%$ ) in the singly excited state. In the case of these molecules, irrespective of substituents, a small contribution ( $|c|=11\text{--}15\%$ ) from the lower occupied orbitals to the higher unoccupied orbitals has been taking place and rest are all purely the transitions between the frontier orbitals.

The calculated electronic transition energies, transition dipole moments along with the oscillator strengths obtained by SAC/SAC-CI for B3LYP based geometries are shown in table 5. The absorption energies decrease with the BRC as expected. The absorption of M1 is only 2.2 eV when compared to 2.8 eV in M2. This correlation between the BRC with the absorption maximum in these dyes have already been reported.<sup>53a-c</sup> It is clear from the transition dipole moment that the direction of the charge transfer is dominantly on one axis of the molecule. The moments are reasonably large in magnitude. M2 has a larger transition dipole moment of 6.1 D compared to M1 having a value of 4.87 D. The oscillator strength of M1 is much smaller than M2 as expected due to the larger mixing of the biradical structure in its VB resonance picture. Ground and excited state dipole moments are given in the same table. The change in dipole moment in the case of M1 is around  $\sim 2$  D compared to only  $\sim 1$  D in M2. This indicates that M1 has a larger zwitterionic character in its excited state.

**Table 6.** Comparison of charge transfer (in e) from ground ( $S_0$ ) to first excited ( $S_1$ ) states of all the molecules obtained at SAC/SAC-CI/6-31G(d,p) level.

Molecule	Group	$(Q/e)_{Gr}$	$(Q/e)_{Ex}$	$(Q/e)$ Gain/Loss
M1	Central ring	-0.569	-0.490	-0.079
	2R- Group	0.569	0.490	0.079
M2	Central ring	-0.104	-0.215	0.111
	2R- Group	0.104	0.215	-0.111

**Table 7.** Optimized bond lengths and adsorption energies of water on  $\text{TiO}_2$  surface.

Bond lengths ( $r_{ij}$ )	in $\text{\AA}$	$E_{ads}$
Molecular adsorption of water molecule		
$\text{Ti}_{5c}\text{-O}_{\text{H}_2\text{O}}$	2.285	11.7 <sup>a</sup> , 11.5–16.1 <sup>b</sup>
$\text{O}_{\text{H}_2\text{O}}\text{-H-O}_{2c}$	2.355	14.3 <sup>c</sup>
$\text{O}_{\text{H}_2\text{O}}\text{-H}$	0.982	19.2 <sup>d</sup>
$\text{O}_{2c}\text{-Ti}_{6c}$	1.894	17.1 <sup>e</sup>

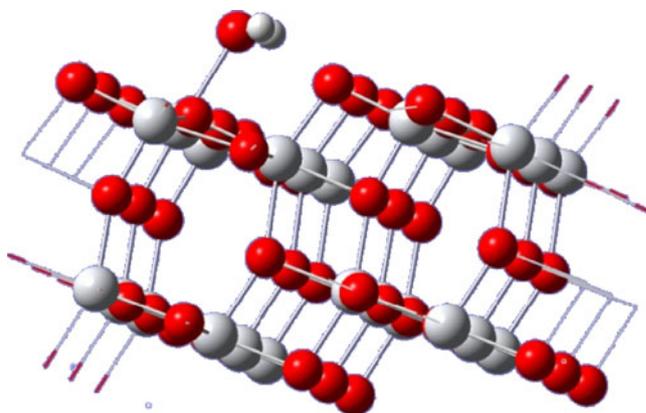
<sup>a</sup>This work, <sup>b</sup>66a, <sup>c</sup>66b, <sup>d</sup>67a, <sup>e</sup>67b

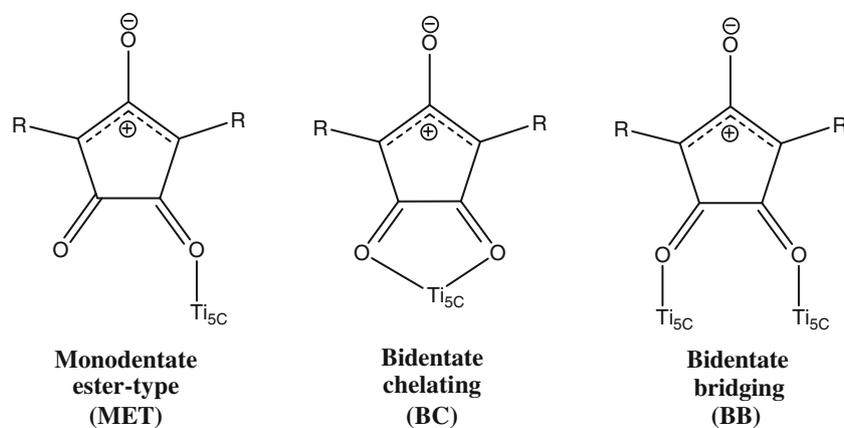
This correlation between BRC and the absorption maximum is further supported by Mulliken population analysis obtained at the SAC/SAC-CI level for the ground and the first excited state.<sup>53</sup> A comparison of charge transfer (CT) made in these molecules are given in table 6. It has been found that the CT from side substituents to the central part is more prominent in case of M2 i.e., 0.111e. In contrast, in the case of M1, CT from central part to side substituent's is only 0.079e.

### 3.4 Adsorption of dyes on the $\text{TiO}_2$ anatase (101) surface

First to check the consistency and reliability of our calculations, we compared the molecular adsorption energy of water on five-coordinated surface titanium ( $\text{Ti}_{5c}$ ) calculated here with the earlier results (table 7). The calculated molecular adsorption energy obtained here for water is 11.73 kcal/mol which is in good agreement with the experimental estimate of 11.53–16.14 kcal/mol.<sup>66,67</sup> Figure 4 shows the optimized structure of the water adsorption on the  $\text{TiO}_2$  surface.

The diketo groups of croconate dyes can bind the  $\text{TiO}_2$  surface. The various possible adsorption configurations are shown in figure 5. These are the monodentate ester type in which only one keto group is

**Figure 4.** Adsorption of water molecule on  $\text{TiO}_2$  surface.

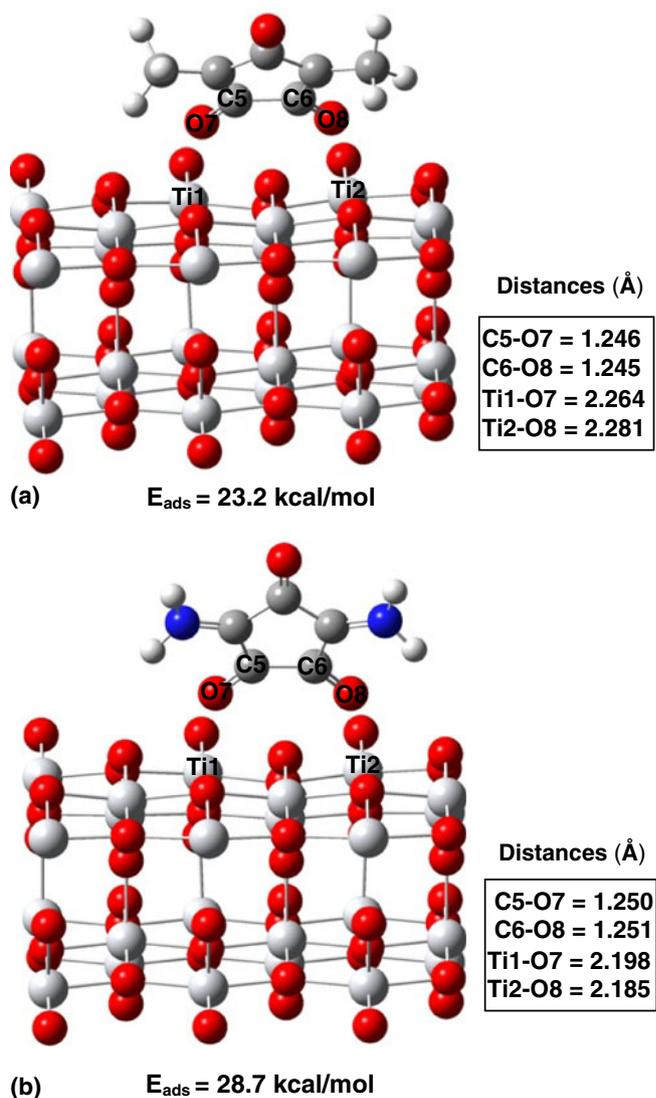


**Figure 5.** Possible adsorption configurations of diketo group.

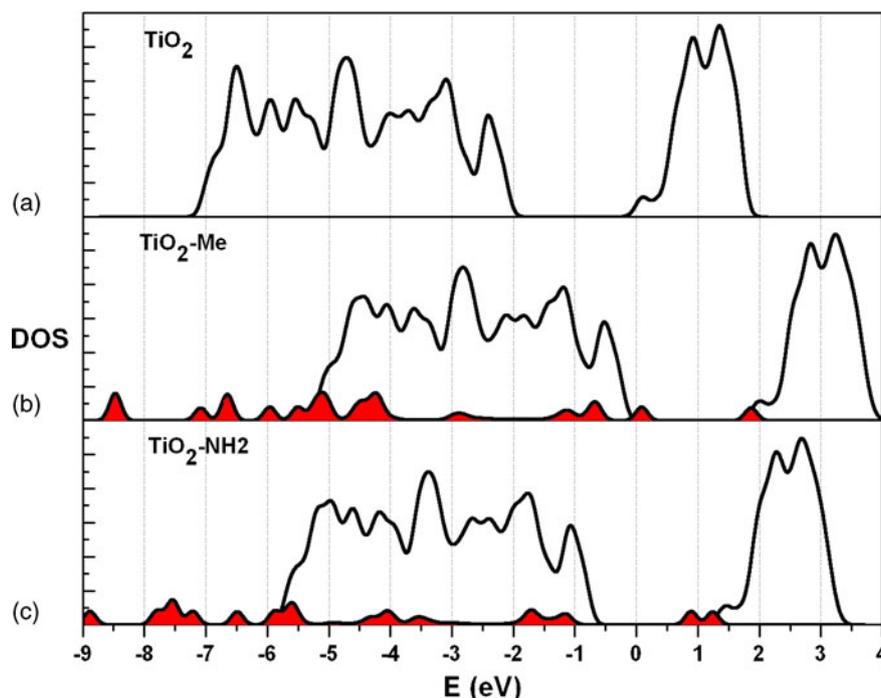
involved in the binding. The second configuration is the bidentate chelating in which only one Ti of the slab is involved with both the keto groups. The third possible configuration is the bidentate bridging, in which both the keto groups and both the five-coordinated Ti are involved. Earlier studies on carboxylic acid groups have shown that the latter configuration is the most stable one hence only this configuration is studied here.

Optimized structures of two model croconate dyes M1, M2 and TiO<sub>2</sub> slab are taken for the adsorption study and the complexes (TiO<sub>2</sub> slab + croconate dye) were relaxed with identical orientation. The relaxed structures with diketo interaction for M1 and M2 are shown in figure 6. The adsorption studies of M1 and M2 were carried out with bidentate bridging (BB) fashion. Small geometry changes in the C=O bond length is seen on binding. Prior to the adsorption the –C=O bond lengths of the diketo groups are relatively shorter that is for M1 it is 1.213 Å and after the adsorption on the TiO<sub>2</sub> it is increased to 1.246 Å and in case of for M2 before the adsorption the –C=O bond length of the diketo group is 1.218 Å but upon adsorption it is found to be 1.250 Å. In the latter case the lengthening is much smaller. In both the cases the –C=O bond lengths have increased, which indicate good interaction with TiO<sub>2</sub> surface. After the adsorption of the model croconate the bond lengths of the oxygens of the diketo and Ti of TiO<sub>2</sub> i.e., Ti1-O7 and Ti2-O8 for M1 are 2.264 Å and 2.281 Å and for M2 are 2.198 Å and 2.185 Å, respectively.

The binding energy is calculated to be 23.2 kcal/mol in the case of M1 binding to the surface while on the other hand in the case of M2 it has substantially increased to 28.7 kcal/mol. Here the binding energy can be correlated with the electron donating ability of the substituent over the croconate. It is found that the amine substituted croconate binds more strongly than that of methyl substituted croconate. It is clear that



**Figure 6.** (a) Adsorption of diketo group of M1 in BB fashion as shown in figure 5. (b) Adsorption of diketo group of M2 in BB fashion as shown in figure 5.



**Figure 7.** Total DOS (black) and the adsorbate-projected DOS (red) for (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-M1}$ , (c)  $\text{TiO}_2\text{-M2}$ .

the molecule with larger biradical nature has a lower binding energy. The binding energies of the M1 and M2 are comparable with that of the adsorption energy of -COOH group of 3-(anthracene-9-yl)-2-cyanoacrylic acid in BB mode which is 22.2 kcal/mol.<sup>46</sup> To understand the electronic structure, density of states (DOS) for the clean and the adsorbed complexes are presented in figure 7. The DOS contains broad surface valence and conduction bands separated by a wide band gap. After adsorption, the dyes introduce sharp occupied molecular energy levels in the band gap. From figure 7, it is clear that, when compared to the bare  $\text{TiO}_2$  DOS, the DOS of M1 adsorbed and M2 adsorbed  $\text{TiO}_2$  point out a shift of the conduction band edge of  $\text{TiO}_2$ , though the band gap remains almost the same.

#### 4. Conclusions

First-principles DFT has been used to systematically investigate the adsorption of the diketo groups of croconate dyes on anatase  $\text{TiO}_2$  (101) surface. The binding energy obtained clearly points out to large values of around 23.2 to 28.7 kcal/mol depending on the donor groups on the croconate ring. The molecule with larger biradical character also has a smaller binding energy. Thus, this study shows that the binding of the keto groups of the croconate dyes are competitive with the carboxylic acid groups.

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