SUPPORTING INFORMATION

QSPR STUDY OF THE EFFICIENCY OF DYE-SENSITIZED SOLAR CELLS UTILIZING CARBAZOLE-BASED DYES

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Trying to interpret the molecular descriptors

The interpretation of certain molecular descriptors – such as, for example, topological and electrotopological descriptors – can be a challenging task. In this context, for some best model's descriptors, we tried to establish correlations with chemically meaningful characteristics that are easier to interpret.

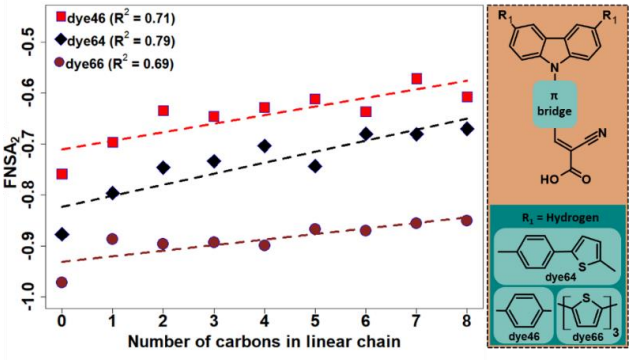
The descriptor $I_{434.46}$ is easily interpretable: dyes with strong absorptions in the 434 nm region tend to yield cells with higher PCEs. Thus, this descriptor reinforces the idea that sensitizers should absorb more intensely in the visible region to achieve higher PCEs [1,2]. While it strengthens a well-known property of sensitizers, this descriptor does not indicate structural characteristics that are favorable for improving efficiency. However, some structural aspects are suggested by the descriptor $FNSA_2$ (Fractional Negative Surface Area), as given by Eq. 1 – for further details, see [3].

$$FNSA_2 = \frac{Q^- \sum_{a^-} SA_a^-}{SASA} \quad (1)$$

Given that Q^- is the sum of all partial negative charges in the molecule, SA_a^- is the negative surface area on atom a accessible to the solvent, and $SASA$ corresponds to the solvent-accessible surface area. In this way, $FNSA_2$ indicates the fraction of the negatively charged molecule that the solvent can interact with. The structural information highlighted by this descriptor can be attributed to the effect of $SASA$. In other words, an increase in $SASA$ (Eq. 1) can reduce the absolute value of $FNSA_2$, which is associated with an increase in the predicted PCE. Then, some ways to increase the $SASA$ of the dye include, for example, elongating the π-bridge and/or introducing substitutions. In this regard, the literature reports the advantage of incorporating linear alkyl chains into sensitizers, as they reduce undesirable π-π interactions [4].

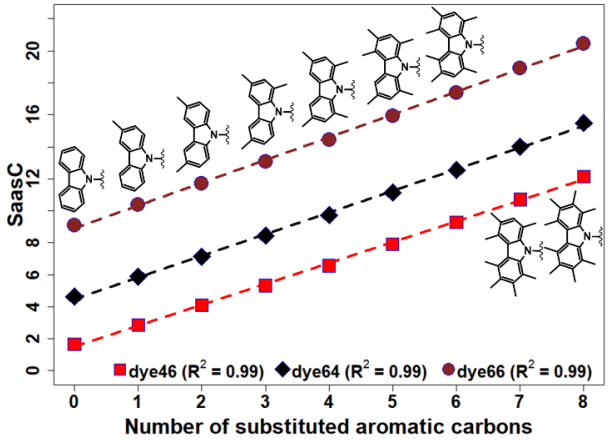
To observe the effect of altering the length of linear alkyl chains on the descriptor $FNSA_2$, we performed symmetrical substitutions on the donor group of three dyes (dye46, dye64, and dye66). In this way, it is possible to note the relationship between the increase in chain length and the descriptor $FNSA_2$ (Fig. 1), which supports the adoption of such chains for improving the efficiency of DSSCs [4].

Figure 1. Influence of the length of linear alkyl chains on $FNSA_2$.



Moreover, the model provides an indication of positions that may have a negative effect on the predicted PCE if substitutions are made. This is given by $SaasC$, an electrotopological descriptor related to substituted aromatic carbons. More specifically, it is defined as the sum of the so-called E-State values of the substituted aromatic carbons – for further details, see [5,6]. In general, since $SaasC$ is always a positive value, an increase in the number of substituted aromatic positions leads to a decrease in the predicted PCE. In fact, when we successively increase the number of substituents, for example, on the donor group of the dye46, dye64, and dye66, a strong linear relationship between the two variables is observed (Fig. 2). That is, this descriptor appears to indicate a relationship between substituents at aromatic positions – and likely the characteristics of these substituents, since the *E-State* is influenced by the electronegativity of neighboring groups [5,6] – and the efficiency of the DSSC.

Figure 2. Variation of the $SaasC$ descriptor as a function of the number of methyl groups present in the donor group of the dye46, dye64, and dye66 structures.



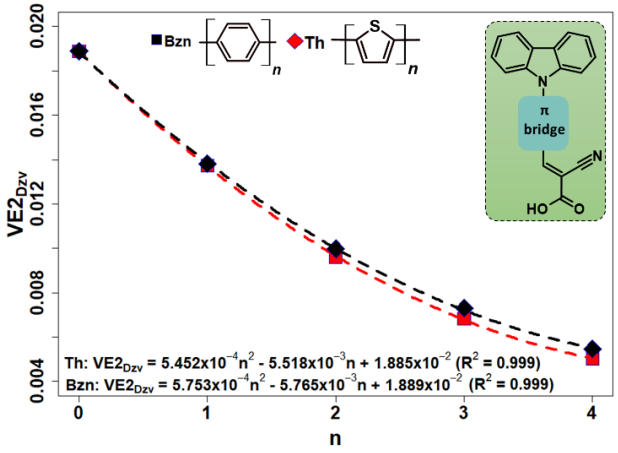
Two other electrotopological descriptors, minHBint8 and ndO, highlight the potential importance of electronegative species within the molecule and the modification of the dye's adsorption modes on the semiconductor surface, respectively. The

minHBint8 descriptor corresponds to the lowest E-state value among atoms that potentially form intramolecular hydrogen bonds at a distance of eight bonds. The influence of electronegativity arises from the tendency of E-state values to decrease when more electronegative species are present [5]. On the other hand, ndO represents the number of oxygen atoms with double bonds present in the molecule, which could result in an adsorption mode that reduces electron injection into the semiconductor's conduction band.

The autocorrelation descriptors ($ATS6m$, $ATSC6i$, $AATSC5s$, $MATS4s$, and $GATS7c$) indicate how a specific property (electronegativity, charge, mass, volume, etc.) is distributed across a molecule with N atoms [7]. In general, these descriptors highlight the importance of: 1) an increase in the mass/volume of the dye, which tends to elevate the predicted PCE, supporting the increase in solvent-accessible area; and 2) the presence of atoms with higher ionization energies or more electronegative characteristics.

Finally, the M-3 model presents four descriptors obtained through the eigenvalues of certain matrices ($VE2_{Dzv}$, $VE3_{Dt}$, $SpMin1_{Bhi}$, and $BCUTc_{1l}$) [8] Of this set, $VE2_{Dzv}$ is given by the average of the coefficients of the last eigenvector of the Barysz matrix weighted by van der Waals (vdW) volumes and shows a strong correlation with, for example, the number of rings present in the π-bridge (Fig. 3). In other words, $VE2_{Dzv}$ indicates that an increase in the π-bridge tends to elevate the PCE of the cell. On the other hand, $VE3_{Dt}$ – obtained by summing the coefficients of the last eigenvector of the detour matrix – shows identical values for similar structures, such as dye39 and dye40 (9.34), but experiences considerable variations when there is an increase in molecular branching, as seen with dye29 (-12.54), dye30 (-6.21), and dye87 (-6.38) and dye88 (-2.77).

Figure 3. Variation of the $VE2_{Dzv}$ descriptor as a function of the number of rings present in the π-bridge.



The $SpMin1_{Bhi}$ is obtained from the absolute value of the smallest eigenvalue of the Burden matrix weighted by the first ionization potential. Due to the property used in the weighting, it is expected that changes in the value of $SpMin1_{Bhi}$ are associated with the ionization potential of the molecule [7]. Finally, $BCUTc_{1l}$ – which corresponds to the first smallest eigenvalue of the Burden matrix weighted by partial charges – reinforces the idea presented by the set of autocorrelation descriptors.

De modo geral, o modelo M-3 apresenta um poder de predição similar aos modelos propostos por Krishnaa *et al.*[9] e, a partir da análise dos descritores realizada acima, também é possível notar certas semelhanças entre as características estruturais indicadas pelos modelos como, por exemplo, a presença de cadeias alquílicas para a redução de interações π-π. Todavia, o M-3 apresenta características não indicadas pelos modelos de Krishnaa, tais como: absorção na região do visível, substituição de carbonos aromáticos e comprimento da ponte π. Em suma, o nosso melhor modelo fornece um complemento de informações acerca de importantes características estruturais para um sensibilizador baseado carbazol atuar suficientemente bem em uma DSSC.

In general, the M-3 model demonstrates predictive power similar to the models proposed in the literature [9], and from the analysis of the descriptors presented above, it is also possible to observe certain similarities between the structural features indicated by the models, such as the presence of alkyl chains to reduce π-π interactions. However, the M-3 model introduces some new characteristics that were not previously indicated, such as absorption in the visible region, substitution of aromatic carbons, and the length of the π-bridge. In summary, our best model provides complementary information regarding important structural features for a carbazole-based sensitizer to perform adequately in a DSSC.

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