

## **Computational study of the influence of the $\pi$ -bridge conjugation order of novel molecular derivatives of coumarins for dye-sensitized solar cells using DFT**

Rody Soto-Rojo, Jesús Baldenebro-López, Daniel Glossman-Mitnik

### **Abstract**

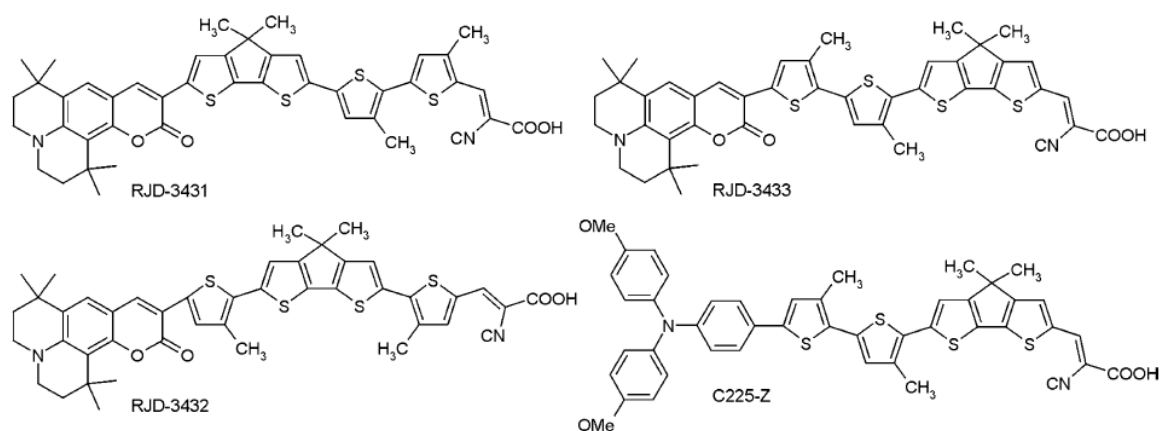
Three novel molecules derived from D- $\pi$ -A type coumarin were studied in order to be considered as potential dyes in dye-sensitized solar cells (DSSC), using density functional theory (DFT) and time-dependent density functional theory (TD-DFT). M06 and M06-2X density functionals were chosen and combined with the 6-31G(d) basis set. The effect of the  $\pi$ -bridge was studied using two units of methyl thiophene and one unit of dimethyl cyclopentadithiophene in different conjugation order. Geometry optimization, and the highest occupied molecular orbital and lowest unoccupied molecular orbital density and energy levels, and maximum absorption wavelength were calculated. Besides, certain chemical reactivity parameters, such as chemical hardness ( $\eta$ ), electrophilicity index ( $\omega$ ), electrodonating power ( $\omega^-$ ), and electroaccepting power ( $\omega^+$ ), were obtained. All these calculations were analyzed taking into account the potential application of the proposed molecular systems as photosensitizers in DSSC. The results suggest that the three proposed molecules are highly efficient dyes.

### **Introduction**

The dye-sensitized solar cells (DSSC) are devices that convert solar light to electricity with high conversion efficiency and low cost [1, 2]. The Ru bipyridyl

complexes were used in DSSC achieving up to 12 % of efficiency [3–5]. Organic sensitizers have been amply studied since they reach efficiencies compared with Ru derivatives, and show great advantages over them [6]. Recently, carbazole and indenoperylene-based organic dyes have been reported with a high conversion efficiency of the DSSC of 12.5 % [7, 8], 12.8 % with triphenylamine-based dye [9] and a cosensibilization using carbazole and coumarin-based dyes [10], and 14 % with co-sensibilization using carbazole and triphenylamine-based dyes [11]. In the above organic dyes, a redox electrolyte based on cobalt complexes was used. Organic dyes using  $I^-/I_3^-$  redox electrolyte have achieved conversion efficiencies of up to 10 % with triphenylamine-based dyes [12, 13] and 8 % with coumarin-based dyes [14]. Particularly, the research group of Arakawa and Hara [14–16], as well as Seo et al. [17, 18], has developed several donor- $\pi$ -bridge-acceptor (D- $\pi$ -A) molecules derived from coumarin, in which it can be observed that the extension of the bridge can have a positive effect on the conversion efficiency increase. Besides, Liu et al. [19] synthesized and evaluated extended bridge D- $\pi$ -A dyes based on triphenylamine: C225, C226, and C227, reaching efficiencies higher than 8 % with  $I^-/I_3^-$  electrolyte. This molecule was formed with the same electron-deficient groups in the  $\pi$ -bridge: two 3-methyl thiophene groups and one 4,4-dimethyl-4H-cyclopenta[2,1-b,3,4-b']dithiophene group with three different conjugations; the C225 and C226 molecules resulted more efficient (8.3 and 8.4 %, respectively) and C227 less efficient (6.9 %). Further, these dyes (C225, C226, and C227) were studied by Zhang et al. [20] through theoretical calculations, analyzing their molecular properties to predict which dye is more efficient. These theoretical results were

consistent with the reported experimental data, since C225 was chosen the best. In relation to above, the purpose of this research was the theoretical study of molecules based on the coumarin derivative donor with the extended  $\pi$ -bridge. In our proposal, three conjugations were studied using the same  $\pi$ -bridges, coumarin derivatives as the donor part, and cyanoacrylic acid was the acceptor group that serves as anchorage to TiO<sub>2</sub>. The new molecules were labeled RJD-3431, RJD-3432, and RJD-3433 (shown in Fig. 1) and were theoretically evaluated considering the ultraviolet–visible absorption spectra (UV–Vis) and the HOMO and LUMO energy levels, as other authors did [21–28]. Along with the aforementioned studies, the chemical reactivity parameters were calculated and analyzed in order to predict which molecule is the most efficient with a great capability to be used as a dye in DSSC. Additionally, theoretical calculations were carried out with the triphenylamine derivative molecule C225, which was reported by Liu et al. [19], labeled for this paper as C225-Z. The purpose of this study is to compare the molecular properties of this dye with the three coumarin derivatives proposed.



**Fig. 1** Molecular structure of the new coumarin derivative dyes RJD and the triphenylamine derivative molecule C225-Z

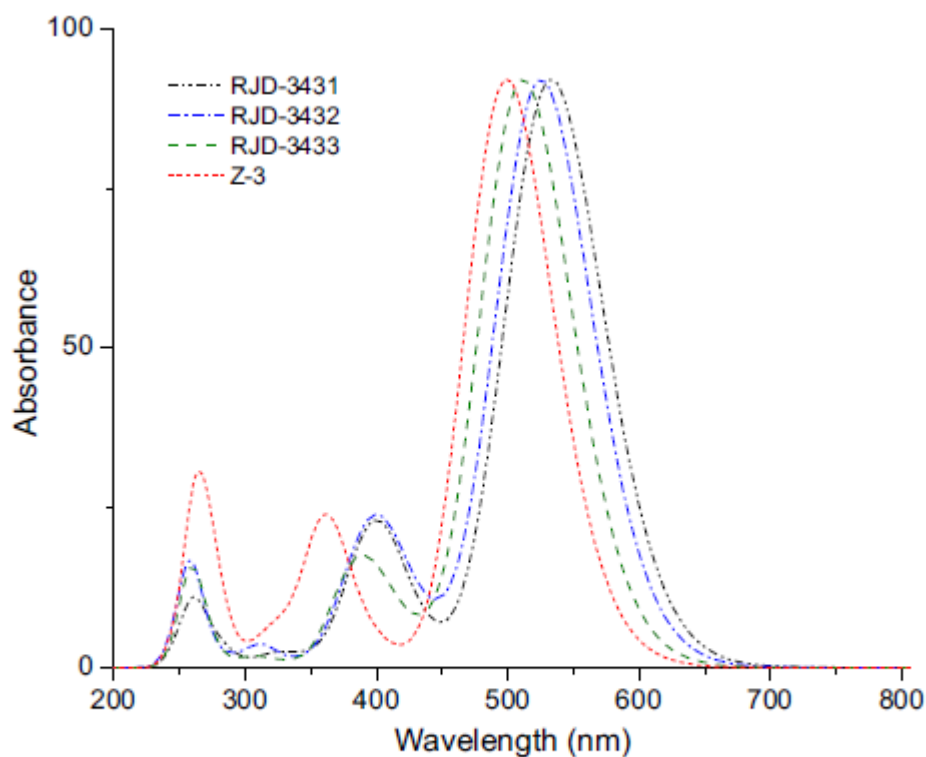
## Computational details

The density functional theory (DFT) was used to obtain the minimum energy molecular structure (geometry optimization), frequency calculation, chemical reactivity, and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels.

The analysis of frequencies was carried out to confirm that there are no imaginary frequencies; namely, the geometry is in a global minimum. The calculated chemical reactivity parameters were obtained using the formulae reported by Parr and Pearson [29] and Gázquez et al. [30] using the ionic and neutral states energy values. All above calculations were obtained by the M06 hybrid meta-GGA density functional [31] and the 6-31G(d) basis set [32, 33]. The vertical excitation energy, the oscillator strength, and the transitions all corresponding to the UV–Vis absorption spectra were obtained with time-dependent DFT (TD-DFT), using the M06-2X hybrid meta-GGA functional [31] with the above-mentioned basis set. The non-equilibrium calculation protocol [34, 35] was used for obtaining the UV–Vis spectrum; meanwhile, the considerations for the effect of the solvent (ethanol) were through integral equation formalism polarizable continuum model (IEF-PCM) [36]. The UV–Vis spectrum graphics, the oscillator strength, and the electronic transitions were processed using the SWizard software [37, 38] using the Gaussian model. Furthermore, the calculations were realized with the MIDIY basis set [39] and reported in Electronic Supplementary Material (ESM). All calculations were performed with Gaussian 09 Revision D.01 [40].

## Results

The maximum wavelength absorption ( $\lambda_{max}$ ), the oscillator strength ( $f$ ), and the HOMO and LUMO molecular orbital energy levels were employed to analyze the properties of the molecules with potential to be used as DSSC dyes and thus be able to infer which dye would be more efficient.



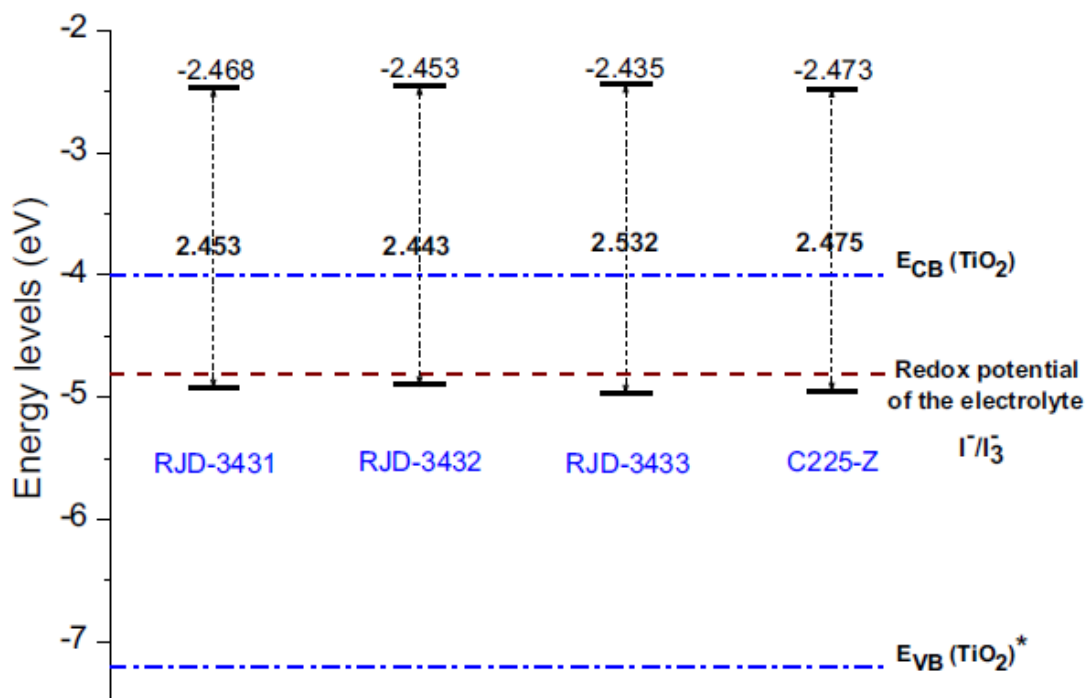
**Fig. 2** UV-Vis spectra of coumarin and triphenylamine derivative molecules using the M06-2X functional with the 6-31G(d) basis set

**Table 1** Absorption wavelengths ( $\lambda$ ), oscillator strengths ( $f$ ) and orbitals involved in the transitions of the coumarin derivatives and the C225-Z with M06-2X/6-31G(d)

Molecule	$\lambda$ (nm)	$f$	Transitions
RJD-3431	535	2.1747	H $\rightarrow$ L(66 %)
	408	0.3633	H $\rightarrow$ L+1(67 %)
	396	0.3721	H-1 $\rightarrow$ L(45 %) H $\rightarrow$ L(30 %)
	262	0.1047	H-5 $\rightarrow$ L(40 %)
RJD-3432	525	2.0858	H $\rightarrow$ L(64 %) H-1 $\rightarrow$ L(22 %)
	406	0.4315	H $\rightarrow$ L+1(68 %)
	389	0.3399	H-1 $\rightarrow$ L(42 %) H $\rightarrow$ L(34 %)
	258	0.2033	
RJD-3433	510	2.3694	H $\rightarrow$ L(58 %) H-1 $\rightarrow$ L(25 %)
	404	0.2171	H $\rightarrow$ L+1(59 %) H-1 $\rightarrow$ (25 %)
	384	0.4106	H $\rightarrow$ L(38 %) H-1 $\rightarrow$ L(30 %)
	258	0.1497	
C225-Z	497	2.0712	H $\rightarrow$ L(47 %) H-1 $\rightarrow$ L(39 %)
	363	0.5828	H $\rightarrow$ L+1(62 %)
	324	0.1131	H-2 $\rightarrow$ L(58 %)
	271	0.1742	H $\rightarrow$ L+6(75 %)
	263	0.1268	H-8 $\rightarrow$ L(32 %) H-12 $\rightarrow$ L(28 %)
	261	0.1589	H $\rightarrow$ L+8(24 %)

H  $\rightarrow$  HOMO; L  $\rightarrow$  LUMO

Furthermore, as an additional aspect to other published articles about coumarin-based sensitizers, we have considered to analyze the chemical reactivity parameters such as chemical hardness ( $\eta$ ), electrophilicity index ( $\omega$ ), electrodonating power ( $\omega^-$ ), and electroaccepting power ( $\omega^+$ ), in order to point out the best dye. All calculations in this paper are presented with 6-31G(d) basis set. Similar results were observed with MIDIY basis set shown in the ESM.



**Fig. 3** HOMO and LUMO energy levels of coumarin and triph-enylamine derivative molecules with the M06/6-31G(d) level of calculation

### Ultraviolet–visible absorption spectrum

According to the results reported by Dev et al. [41], the M06-2X functional was chosen to predict the UV–Vis spectra. Also, it was validated with the maximum absorption wavelength of the C225-Z molecule in chloroform: 2.28 eV experimental [19] versus 2.47 eV theoretical. The ultraviolet–visible (UV–Vis) spectra of the coumarins derivative systems RJD-3431, RJD-3432, and RJD-3433, as well as C225-Z dye, are shown in Fig. 2, where it can be observed that all molecules show a maximum wavelength of around 500 nm. This is a good result, since they are in the highest solar radiation zone [42]. RJD-3431 and RJD-3432 showed a slight redshift, which can mean a better conversion efficiency, as it has already been reported [25].

Moreover, a second absorption band around 400 nm, which shows a redshift for RJD-3431 and RJD-3432, can be observed. Its intensity is lower than that of the maximum wavelength, but it also contributes to solar energy harvesting. Table 1 shows the absorption wavelengths of RJD coumarins and the C225-Z, as well as their corresponding oscillator strength ( $f$ ) and the orbitals involved in the transitions. The contribution percentage from HOMO to LUMO is lower for the maximum absorption band in the C225-Z molecule than in the coumarins, from 10 to 20 percent. Further, the maximum absorption band is constituted by two transitions: from HOMO to LUMO and from HOMO-1 to LUMO. The second absorption band is constituted by a transition from HOMO to LUMO 1. The oscillator strength of the second absorption band is higher for C225-Z. However, the oscillator strength of the maximum absorption band is slightly lower in C225-Z than in the coumarins derivatives. Therefore, a better sunlight harvesting in coumarins derivatives can be inferred and a higher conversion efficiency in the cell in spite of the fact that the values are not significantly different among the four dyes



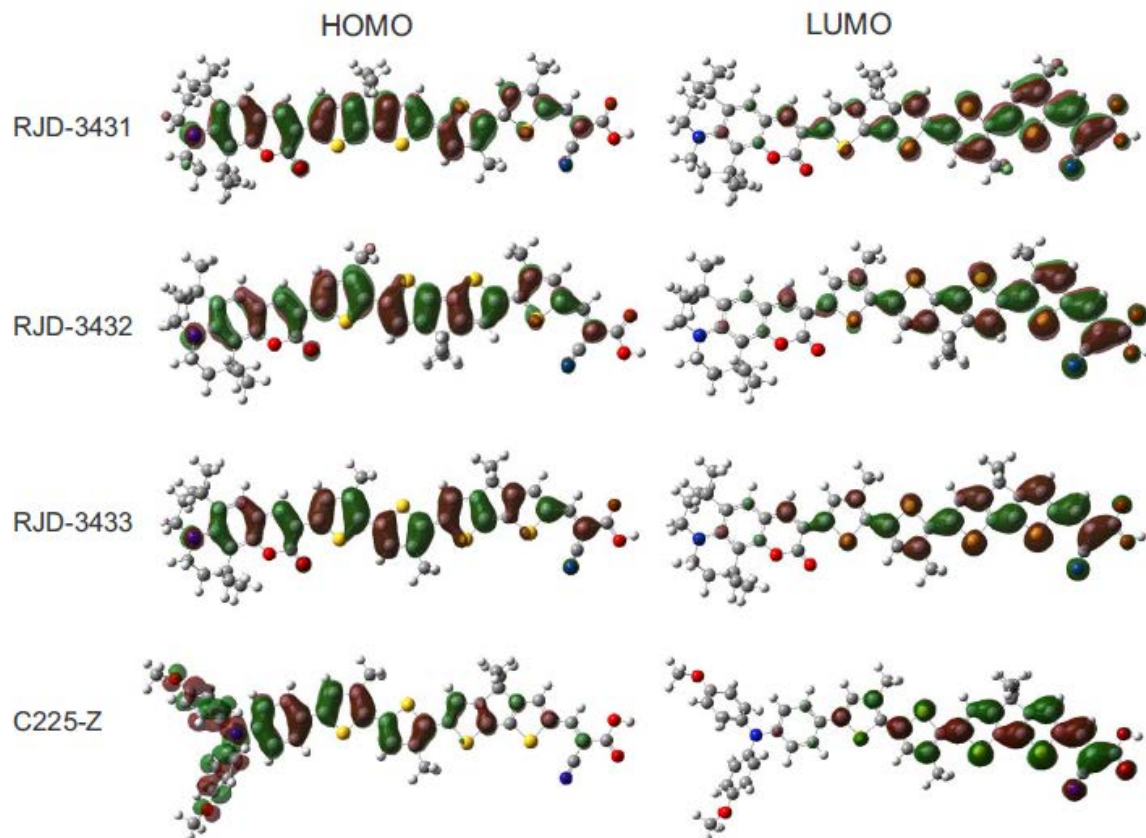


Fig. 4 HOMO and LUMO orbitals of coumarins and the C225-Z dye with M06/6-31G(d)

### Energy levels of HOMO and LUMO molecular orbitals

The frontier molecular orbital levels (HOMO and LUMO) were evaluated by the M06 functional. The choice of method is because it has been reported that functionals with long-range Hartree–Fock exchange tend to overestimate the energy gap [43]. Moreover, the geometry optimization calculation was carried out with the M06 functional. The energy levels of HOMO and LUMO molecular orbitals of the coumarins and the C225-Z molecule are shown in Fig. 3. The LUMO level was compared with the conduction band of the anatase phase of  $\text{TiO}_2$  because it is considered the most adequate phase for photovoltaic applications, and the measurements have shown that the lifetimes of photoexcited carriers are longer in

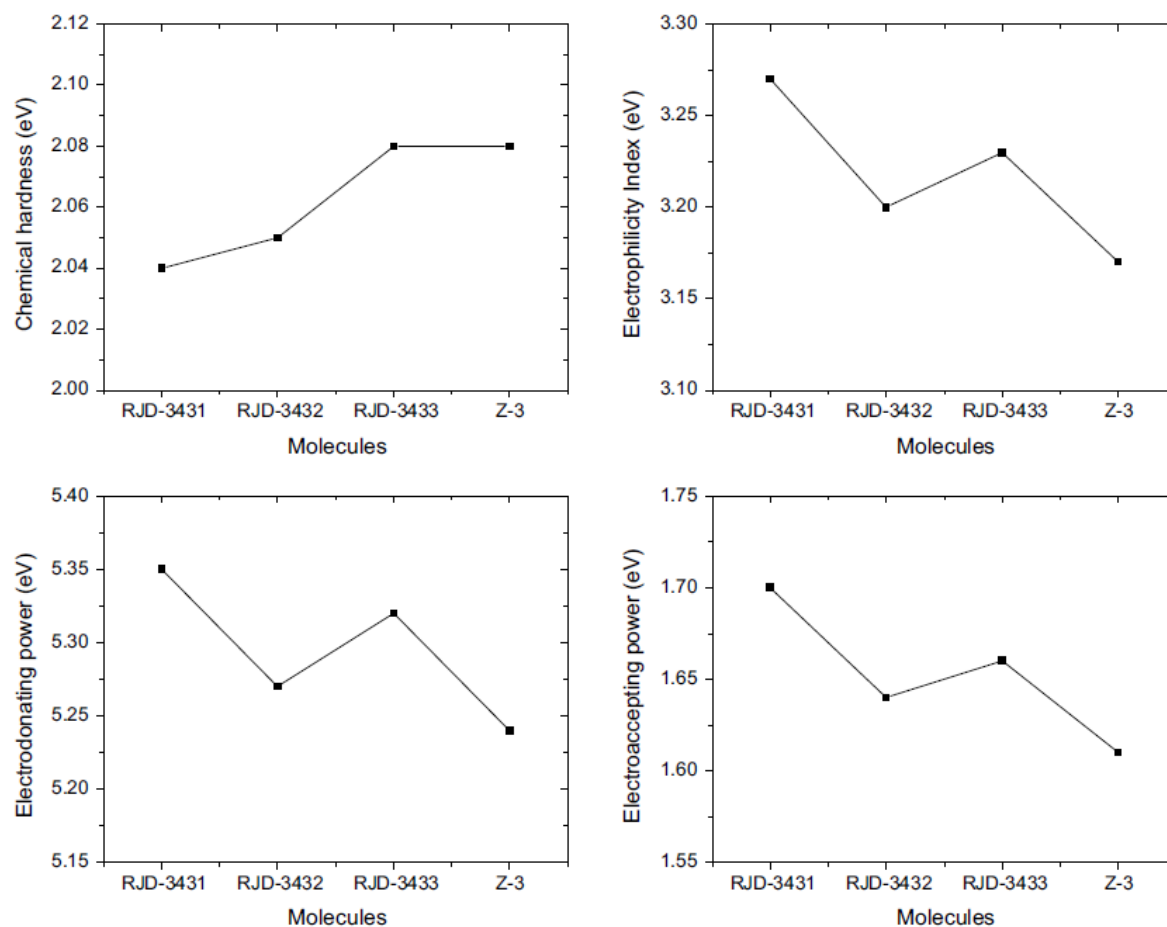
anatase [44]; according to experimental results, we have considered a conduction band of TiO<sub>2</sub> at -4.0 eV versus the vacuum level (this value is commonly accepted in the DSSC literature) [45–48]. The HOMO level is compared with the redox potential of an electrolyte;  $I^+/I_3^-$  has a favorable penetration ability into the porous semiconductor film, fast dye regeneration and relatively slow recombination with injected photoelectrons. Moreover,  $I^+/I_3^-$  is the only redox couple which has been proven to have long-term stability [49]. All the molecules

In this study, all the molecules have quite similar energy levels, and therefore, we cannot determine which one will present a better electron transfer to the oxide. However, we can remark that the RJD-3431 dye and the C225-Z are the closest to the TiO<sub>2</sub> conduction band with a LUMO of -2.47 eV. On the other hand, Fig. 4 shows the HOMO and LUMO molecular orbitals present in the transition of the maximum absorption band ( $\lambda_{max}$ ). Here, it can be observed that the four molecules present an intramolecular electron transfer that goes from the coumarin or triphenylamine donor part and the  $\pi$ -bridge to the final part of the bridge and up to the electron acceptor part, which serves as anchorage to TiO<sub>2</sub>. This is consistent with other high-performance dyes [13].

### **Chemical reactivity parameters**

Since the molecular properties addressed before are not enough to decide on a dye, it was proposed to study the chemical reactivity parameters and use that information to discriminate which dye will have more conversion efficiency in a DSSC. We have to consider that RJD coumarins are novel systems, and there are

no experimental results for comparison and validation of the proposals. However, there



**Fig. 5** Chemical hardness, electrophilicity index, electrodonating power and electroaccepting power of coumarin and triphenylamine derivative molecules with the M06/6-31G(d) level of calculation

are previous studies on NKX coumarins performed by our group (Phys. Chem. Chem. Phys., 2015,17, 14122–14129) that indicate the lower chemical hardness and higher electroaccepting power, the better short-circuit current density (JSC), and consequently a better light conversion efficiency. Based on the foregoing, in Fig. 5 we show the graphics of chemical hardness ( $\eta$ ), electrophilicity ( $\omega$ ), electrodonating power ( $\omega^-$ ), and electroaccepting power ( $\omega^+$ ) of the dyes in this study, compared to the dye molecule C225-Z, whose conversion efficiency has been

reported (8.3 %) [19]. In spite of a small difference among the chemical reactivity values we studied, these allow a deeper study of the electron properties of the dyes. Considering that chemical hardness measures the resistance of the molecule to intramolecular charge transfer [29, 52], it is logical to look for dyes with the lowest chemical hardness values. On the other hand, the electroaccepting power implies a higher capability to accept charge [30], and as it is observed in Fig. 4, the acceptor part is located in the group that anchors to TiO<sub>2</sub>. A higher electroaccepting power is wanted in order to attract the electrons from the donor fraction. If chemical hardness ( $h$ ) is observed, RJD-3431 has the lowest  $\eta$  (2.04 eV), followed by RJD-3432 (2.05 eV), and RJD-3433 and C225-Z with higher  $\eta$  (for both  $\eta=2.08$  eV). Therefore, RJD-3431 and RJD-3432 present lower resistance to intramolecular charge transfer. If we analyze now the electroaccepting power ( $\omega^+$ ), RJD-3431 has the highest  $\omega^+$  (1.70 eV) followed by RJD-3433 (1.66 eV), RJD-3432 (1.64 eV), and C225-Z (1.61 eV), and thus, RJD-3431 has the highest capability to attract electrons toward the acceptor fraction of the dye, from which a higher  $J_{sc}$  can be inferred. Also, electrophilicity ( $\omega$ ) shows results with a tendency similar to that of  $\omega^+$ , and so, RJD-3431 presents the highest energetic stability by acquiring electrons from the environment (saturation) [53]. Finally, the lower electrodonating power ( $\omega^-$ ) represents the higher capability of donating electrons [30], yet if we observe that coumarin derivatives RJD, they have different  $\omega^-$  despite their donor fraction being the same, with RJD-3432 being the one that has the highest donating capability among coumarins.

## Conclusions

In the studied coumarin derivatives, particularly in RJD-3431, a redshift of up to 0.18 eV in  $\lambda_{\text{max}}$  can be observed with transitions HOMO to LUMO and a contribution 19 % higher than that of the C225-Z sensitizer, and the oscillator strength is higher in the order of 0.1. The energy difference between the LUMO of the dyes and the TiO<sub>2</sub> conduction band is 1.53 eV for C225-Z and RJD-3431, whereas RJD-3432 and RJD-3433 have a higher difference of 0.02 and 0.03 eV, respectively. Furthermore, the representation of the HOMO and LUMO orbitals was very similar between RJD coumarins and C225-Z, showing a charge transfer from the coumarin-based or triphenylamine-based group (donor part) to the cyanoacrylic acid (electron withdrawing part). Finally, RJD-3431 represents the lowest chemical hardness, while the highest chemical hardness is achieved by C225-Z, with a difference of 0.04 eV. RJD-3431 had the highest electroaccepting power and C225-Z the lowest, with a 0.09 eV difference. It is clearly observed that there are no significant changes, but coumarins show slightly better properties than C225-Z. Therefore, RJD-3431 is expected to have a higher ability of conversion efficiency, though it cannot be said with certainty. However, in the search for better proposals, coumarins appear as potential sensitizers. Additionally, the RJD coumarin derivatives have very similar electronic properties among them, and there could not be a significant variation in the conversion efficiency achieved by any of them, and thus, they can be used as a mixture. It is advisable for experimentalists to perform the synthesis of the new RJD dyes proposed and test them in DSSC.

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## References

1. O'Regan B, Grätzel M (1991) *Nature* 353:737–740
2. Grätzel M (2003) *J Photochem Photobiol C Photochem Reviews* 4:145–153
3. Nazeeruddin MK, Kay A, Rodicio I, Humphry-Baker R, Mueller E, Liska P, Vlachopoulos N, Graetzel M (1993) *J Am Chem Soc* 115:6382–6390
4. Nazeeruddin MK, Pechy P, Grätzel M (1997) *Chem Commun* 18:1705–1706
5. Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B, Grätzel M (2005) *J Am Chem Soc* 127:16835–16847
6. Hagberg DP, Marinado T, Karlsson KM, Nonomura K, Qin P, Boschloo G, Brinck T, Hagfeldt A, Sun L (2007) *J Org Chem* 72:9550–9556
7. Kakiage K, Aoyama Y, Yano T, Otsuka T, Kyomen T, Unno M, Hanaya M (2014) *Chem Commun* 50:6379–6381
8. Yao Z, Zhang M, Wu H, Yang L, Li R, Wang P (2015) *J Am Chem Soc* 137:3799–3802
9. Zhang M, Wang Y, Xu M, Ma W, Li R, Wang P (2013) *Energy Environ Sci* 6:2944–2949
10. Kakiage K, Aoyama Y, Yano T, Oya K, Kyomen T, Hanaya M (2015) *Chem Commun* 51:6315–6317
11. Kakiage K, Aoyama Y, Yano T, Oya K, Fujisawa J-I, Hanaya M (2015) *Chem Commun* 51:15894–15897
12. Zeng W, Cao Y, Bai Y, Wang Y, Shi Y, Zhang M, Wang F, Pan C, Wang P (2010) *Chem Mater* 22:1915–1925
13. Hwang S, Lee JH, Park C, Lee H, Kim C, Park C, Lee M-H, Lee W, Park J, Kim K, Park N-G, Kim C (2007) *Chem Commun* 46:4887–4889
14. Wang Z-S, Cui Y, Dan-oh Y, Kasada C, Shinpo A, Hara K (2008) *J Phys Chem C* 112:17011–17017
15. Hara K, Tachibana Y, Ohga Y, Shinpo A, Suga S, Sayama K, Sugihara H, Arakawa H (2003) *Sol Energy Mater Sol Cells* 77:89–103
16. Hara K, Wang Z-S, Sato T, Furube A, Katoh R, Sugihara H, Dan-oh Y, Kasada C, Shinpo A, Suga S (2005) *J Phys Chem B* 109:15476–15482
17. Seo KD, Song HM, Lee MJ, Pastore M, Anselmi C, De Angelis F, Nazeeruddin MK, Grätzel M, Kim HK (2011) *Dyes Pigment* 90:304–310

18. Seo KD, Choi IT, Park YG, Kang S, Lee JY, Kim HK (2012) *Dyes Pigment* 94:469–474
19. Liu J, Zhou D, Wang F, Fabregat-Santiago F, Miralles SG, Jing X, Bisquert J, Wang P (2011) *J Phys Chem C* 115:14425–14430
20. Zhang J, Kan Y-H, Li H-B, Geng Y, Wu Y, Su Z-M (2012) *Dyes Pigment* 95:313–321
21. Sánchez-de-Armas R, Oviedo J (2011) San Miguel MÁ, Sanz JF. *J Phys Chem C* 115:11293–11301
22. Wang J, Li M, Qi D, Shen W, He R, Lin SH (2014) *RSC Adv* 4:53927–53938
23. Wang D, Zhang X, Ding W, Zhao X, Geng Z (2014) *Comput Theor Chem* 1029:68–78
24. Oprea C, Panait P, Cimpoesu F, Ferbinteanu M, Gîr u M (2013) *Materials* 6:2372–2392
25. Sanchez-de-Armas R, San Miguel MA, Oviedo J, Sanz JF (2012) *Phys Chem Chem Phys* 14:225–233
26. Sánchez-de-Armas R, San-Miguel MA, Oviedo J, Sanz JF (2012) *J Chem Phys* 136:194702
27. Feng J, Jiao Y, Ma W, Nazeeruddin MK, Grätzel M, Meng S (2013) *J Phys Chem C* 117:3772–3778
28. Agrawal S, Dev P, English NJ, Thampi KR, MacElroy JMD (2011) *J Mater Chem* 21:11101–11108
29. Parr RG, Pearson RG (1983) *J Am Chem Soc* 105:7512–7516
30. Gázquez JL, Cedillo A, Vela A (2007) *J Phys Chem A* 111:1966–1970
31. Zhao Y, Truhlar D (2008) *Theor Chem Acc* 120:215–241
32. Francl MM, Pietro WJ, Hehre WJ, Binkley JS, Gordon MS, DeFrees DJ, Pople JA (1982) *J Chem Phys* 77:3654–3665
33. Rassolov VA, Ratner MA, Pople JA, Redfern PC, Curtiss LA (2001) *J Comput Chem* 22:976–984
34. Cossi M, Barone V (2001) *J Chem Phys* 115:4708–4717
35. Improta R, Barone V, Scalmani G, Frisch MJ (2006) *J Chem Phys* 125:054103
36. Cancès E, Mennucci B, Tomasi J (1997) *J Chem Phys* 107:3032–3041
37. Gorelsky SI, Lever ABP (2001) *J Organomet Chem* 635:187–196
38. Gorelsky SI (2013) SWizard software, University of Ottawa, Ottawa, Canada
39. Lynch BJ, Truhlar DG (2004) *Theor Chem Acc* 111:335–344
40. Frisch MJ TG, Schlegel HB,, Scuseria GE RM, Cheeseman JR, Scalmani G, Barone V,, Mennucci B PG, Nakatsuji H, Caricato M, Li X,, Hratchian HP IAF, Bloino J, Zheng G, Sonnenberg, JL HM, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida, M NT, Honda Y, Kitao O, Nakai H, Vreven T,, Montgomery JA Jr PJ, Ogliaro F, Bearpark M, Heyd JJ,, Brothers E KK, Staroverov VN, Kobayashi R, Normand J,, Raghavachari K RA, Burant JC, Iyengar SS, Tomasi J,, Cossi M RN, Millam NJ, Klene M, Knox JE, Cross JB,, Bakken V AC, Jaramillo J, Gomperts R, Strat-mann RE,, Yazyev O AA, Cammi R, Pomelli C, Ochterski J W, Martin, RL MK, Zakrzewski VG, Voth GA, Salvador P,, Dannenberg JJ DS, Daniels AD, Farkas Ö, Foresman, JB OJ, Cioslowski J, Fox DJ (2009) Gaussian 09 software, Inc., Wallingford CT
41. Dev P, Agrawal S, English NJ (2012) *J Chem Phys* 136:224301

42. McEvoy A, Castaner L, Markvart T (2012) Solar cells: materials, manufacture and operation. Elsevier, Great Britain
43. Pastore M, Fantacci S, De Angelis F (2013) J Phys Chem C 117:3685–3700
44. Xu M, Gao Y, Moreno EM, Kunst M, Muhler M, Wang Y, Idriss H, Wöll C (2011) Phys Rev Lett 106:138302
45. Furube A (2013) In: Piotrowiak P (ed) Solar energy conversion: dynamics of interfacial electron and excitation transfer, 1st edn. RSC Publishing, New Jersey
46. oly D, Pelleja L, Narbey S, Oswald F, Meyer T, Kervella Y, Mal-divi P, Clifford JN, Palomares E, Demadrille R (2015) Energy Environ Sci 8:2010–2018
47. Nattestad A, Mozer AJ, Fischer MKR, Cheng YB, Mishra A, Bauerle P, Bach U (2010) Nat Mater 9:31–35
48. Pfeifer V, Erhart P, Li S, Rachut K, Morasch J, Brötz J, Reckers P, Mayer T, Rühle S, Zaban A, Mora Seró I, Bisquert J, Jaeger-mann W, Klein A (2013) J Phys Chem Lett 4:4182–4187
49. Cong J, Yang X, Kloo L, Sun L (2012) Energy Environ Sci 5:9180–9194
50. Cahen D, Hodes G, Grätzel M, Guillemoles JF, Riess I (2000) J Phys Chem B 104:2053–2059
51. Lu X, Wei S, Wu C-ML, Li S, Guo W (2011) J Phys Chem C 115:3753–3761
52. Martínez J (2009) Chem Phys Lett 478:310–322
53. Parr RG, Szentpály Lv, Liu S (1999) J Am Chem Soc 121:1922–1924