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Molecular design of electron-donor materials for fullerene-based organic solar cells

M. Spassova[1*], S. Angelova[1], M. Kandinska[2], A. Vasilev[2], S. Kitova[3], J. Dikova[3]

[1] *Institute of Organic Chemistry with Centre of Phytochemistry,*
Bulgarian Academy of Sciences, Sofia, 1113 Bulgaria

[2] *Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski", 1164 Sofia, Bulgaria*

[3] *Institute for Optical Materials and Technologies "Acad. J. Malinowski",*
Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

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A set of model symmetrical and unsymmetrically substituted squaraine and croconine dyes is designed as potential electron donor component in organic photovoltaic bulk heterojunction solar cell (BHJ) where [60]PCBM fullerene is set as acceptor. Ground-state geometries and electronic structures were investigated using density functional theory (DFT) and time-dependent (TD-DFT) density functional theory at the B3LYP/6-31+G(d,p) level. The effects of the electron-rich heterocycles on these squarilium/croconium based organic dyes are studied with respect to the electronic and transport properties of the systems. The estimated HOMO-LUMO gaps of all model dyes fall in the range of the typical organic semiconductors' gap of about 2 eV. The HOMO and LUMO energy levels of the dyes are compared with respect to the acceptor's and the rigorous conditions for an effective charge transfer is discussed. The calculated high values of the oscillator strengths for all proposed dyes are indicative for large absorption coefficient. Based on the optimized molecular geometries, relative positions of the frontier orbitals, absorption maxima and transport properties we propose some of these dyes as suitable components for optoelectronic devices.

Keywords: *squaraines, croconines, fullerene, DFT, transport properties*

INTRODUCTION

Organic Photovoltaics (OPVs) have recently attracted considerable attention as potentially cheap, lightweight, and flexible sources for renewable energy and are promising materials for harvesting solar energy. The ease of their processing and less environmental aggressiveness compared to inorganic solar cells make them objects of extensive elaboration. Exploring new organic materials by revealing relationship between molecular structure and optoelectronic properties is one of the paramount approaches to achieve high-performance OPVs. The performance of the OPVs crucially depends on the donor constituents which should satisfy requirements for large absorption coefficient, low bandgap, high charge mobility, environmental stability, suitable HOMO/LUMO level and solubility [1].

Although non-fullerene-based acceptors are recently in the focus of the search of new promising acceptor materials for bulk heterojunction (BHJ) solar cells (BHJ cells consist of a n-type highly conjugated electron acceptor with high electron affinity and a p-type electron donating part [2]), fullerene derivatives like [60] PCBM and [70] PCBM are, so far, the most widely used electron acceptors in organic photovoltaic cells [3]. Their unique spherical shape, molecular rigidity and large π-delocalization over the three-dimensional (3D) framework determine their low reorganization energy for electron transport [4] and the ultrafast charge transfer [2b]. BHJ solar cell where conjugated polymers or small organic molecules are blended with fullerenes represents an efficient way for rapid exciton dissociation [5].

Squarylium dyes (squaraines) are derivatives of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, quadratic acid), a condensation product of squaric acid and electron-rich aromatics or heterocycles. They are well-known as highly efficient absorbers for organic photovoltaics (OPV) applications [6, 7]. Squaraine dyes feature sharp and intense absorption, typically in the red to the near infrared (NIR) region. Squaraine film absorption is quite broad with large absorption coefficient, which is highly beneficial for sunlight absorption of the photoactive layer [8]. Many studies are addressed to the structural optimization of squaraine dyes for dye-sensitized solar cells. In order to improve their performance strategies like introduction of donors, acceptors, conjugated linkers, etc. aiming at tuning

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* To whom all correspondence should be sent.
E-mail: mspasova@orgchm.bas.bg

their HOMO, LUMO, HOMO-LUMO gap (HLG) and absorption were adopted [9-12]. Croconium dyes (croconines) are Knoevenagel condensation products of croconic acid (4,5-dihydroxycyclopent-4-ene-1,2,3-trione) and heterocyclic CH-acids and they have properties similar to those of the squaraines [13] with strong and broad absorption in infrared region and are also foreseen for application as electron donor in solution processed BHJ solar cells [14].

In this work, motivated by the promising results from the optical modelling of a symmetrical squaraine SQ1 (2-(5-(((2,2-diphenylhydrazono)methyl)-1-hexyl-1H-pyrrol-2-yl)-4-(5-(2,2-diphenyl-hydrazono)-ylidenemethyl)-1-hexyl-2H-pyrrol-1-ium)-3-oxocyclo-but-1-enolate) [7] we performed DFT and TDDFT calculations on the geometries, electronic structures and absorption spectra of a model set of three squaraine and croconine dyes. Quantum chemistry is an extremely powerful and low-cost tool for beforehand molecular designs of new efficient dyes. The computational methodologies based on density functional theory (DFT) and time-dependent DFT (TDDFT) provide reliable geometrical, electronic and spectroscopic properties for various dyes [15, 16]. The calculations of hole and electron reorganization energies, as well as exciton binding energies, aim at assessment of transport properties of the proposed dyes. The analysis of these quantities allows for rational design of more efficient electron-donor components which in conjunction with PCBM would satisfy the different criteria for OPV materials.

COMPUTATIONAL DETAILS

The reorganization energy (λ) is used to access crudely the electron-, and hole mobility of the proposed organic chromophores. The internal reorganization energies (for isolated molecules the external part is often neglected) for hole transport (λ^{+}) and electron transport (λ^{-}) are calculated following the so called "4-point model" [17] as:

$$\lambda^{\pm} = \lambda_1^{\pm} + \lambda_2^{\pm}$$

$$\lambda_1^{\pm} = E_{\pm}(Q_n) - E_{\pm}(Q_{\pm})$$

$$\lambda_2^{\pm} = E_n(Q_{\pm}) - E_n(Q_n)$$

where $E_{\pm}(Q_n)$, $E_{\pm}(Q_{\pm})$, $E_n(Q_{\pm})$ and $E_n(Q_n)$ are the total energies of the: charged state in the neutral geometry, charged state in the charged state geometry, neutral state in the charged state geometry, and neutral state in the neutral geometry, respectively.

Another indicator of optoelectronic performance is the exciton binding energy - the Coulomb interaction energy that stabilizes the exciton (bounded electron–hole pair) with respect to free electron and hole. Exciton binding energy is defined as difference between fundamental gap (E_g) and optical gap (E_{opt}) of a molecule $E_{bind}=E_g-E_{opt}$ where E_g is defined as the difference between the vertical ionization potential IP and vertical electron affinity EA E_g=IP-EA.

All calculations were carried out with Becke's three-parameter hybrid exchange-correlation functional B3LYP [18] with double-ζ polarized basis set, 6-31+G(d,p). It has been shown that this functional performs well in predicting molecular geometries and optical gaps [19] and gives results in good agreement with experiment for exciton binding energy of acene [15]. For the sake of the consistency the same functional (B3LYP) was used in molecular frontier orbital energy calculations although it is known that systematically underestimates the HLG by 0.2-0.3 eV [19, 22]. The Gaussian 09 program [20] is used for quantum chemical calculations and PyMOL molecular graphics software for generating the molecular graphics images [21].

RESULTS AND DISCUSSION

A set of 3 squaraines and 3 croconines with different substituents has been designed to screen dyes with desired properties (Figure 1). The DFT calculated frontier orbital energies, HOMO-LUMO gaps, as well as TDDFT obtained excitation energies and oscillator strengths of the model donor dyes and the acceptor [60]PCBM are listed in Table 1. The absolute position of HOMO and LUMO levels enables ranking of the substituents employed. The HOMO energy levels of both series (SQs and CRs) do not differ significantly. However, the LUMO levels of CR's are considerably lower (about 0.5 eV) which leads to a smaller HOMO-LUMO gap for CR's. Generally, the estimated HLG's of all model dyes are low enough, which is one of the inevitable requirement for a good donor constituents. They are in the ranges 1.8-2.02 eV and 1.37-1.53 eV for SQ's and CR's, respectively, and even accounting for the HLG's underestimation by B3LYP the most of the proposed structures HLG's are close to the typical organic semiconductors' gap of about 2 eV.

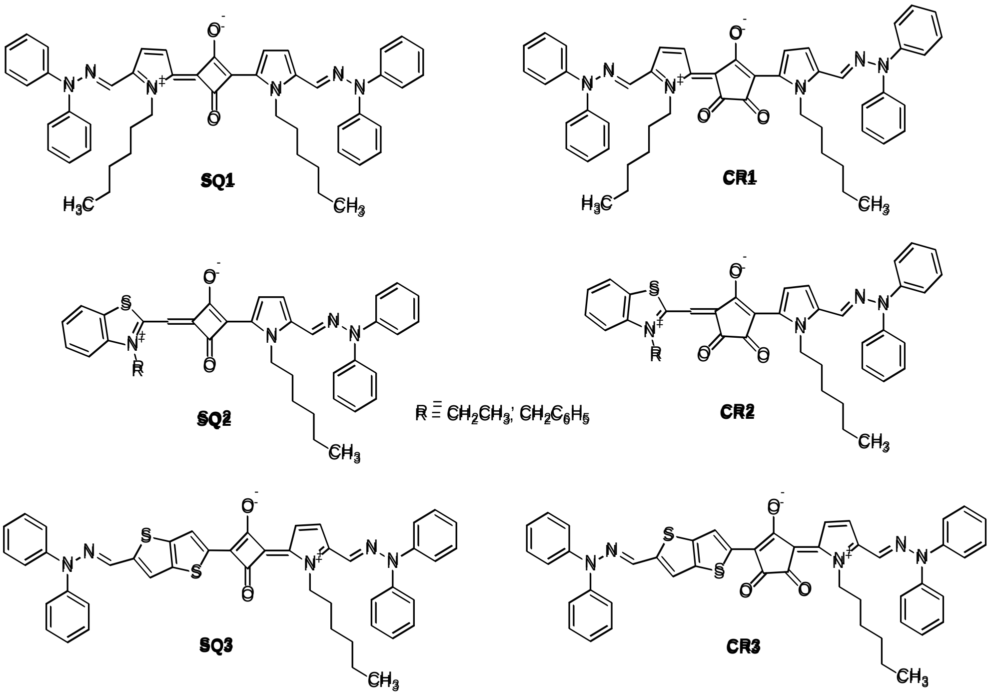

Figure 1. Structures of the proposed squaraines and croconines.

Table 1. B3LYP/6-31+G(d,p) calculated HOMO and LUMO energies, HOMO-LUMO gap (HLG), and excitation energies **E_{exc}** in eV, wavelengths λ_{max} in nm and oscillator strength *f*.

Compound	HOMO	LUMO	HLG	E_{exc}	λ_{max}	f
SQ1	-5.12	-3.19	1.93	1.877	660.7	1.63
SQ2_Et	-4.87	-2.85	2.02	1.970	629.3	1.25
SQ2_Bz	-4.87	-2.85	2.02	1.957	633.6	1.26
SQ3	-5.09	-3.29	1.80	1.794	691.0	2.23
CR1	-5.17	-3.74	1.43	1.522	814.9	1.24
CR2_Et	-4.94	-3.41	1.53	1.618	766.5	1.06
CR2_Bz	-4.93	-3.40	1.53	1.611	769.5	1.06
CR3	-5.14	-3.77	1.37	1.497	828.2	1.82
[60]PCBM	-6.06	-3.53	2.53	1.899	652.8	0.00

In fact, SQ's and CR's are inherent donor-acceptor-donor systems [23] and for such molecular architectures the growing interest is dictated by their efficient low bandgaps and wide spectral coverage [24]. The visualization of the spatial distribution of the frontier orbitals (Figure 2) allows for distinguishing the donor and acceptor units. The HOMO orbitals of all studied structures are spread over the whole conjugated chain lengths (which is one of the prerequisites for achieving high power conversion efficiency), whereas LUMO's are localized predominantly on the central four- and five membered rings (squaric and croconic cores). Neither HOMO nor LUMO are located at the ethyl and benzyl side-chain groups attached to the benzothiazole rings of SQ2 and CR2 because of the lack of conjugation with the backbone. Consequently, their presence does not affect the energy level positions. These solubilizing groups are proposed solely for achievement of good blend morphology.

In the view of an efficient OPV application frontier orbital energies of the donor (dyes) should satisfy many criteria. Along the requirements for absolute energies of HOMO and LUMO of the donor against the vacuum level [1] the rigorous condition for an effective charge transfer requires that the frontier orbitals of the donor must be 0.2-0.3 eV higher than the corresponding acceptor's orbitals.

The LUMO levels of CR1 and CR3 fall below the LUMO level of the fullerene [60]PCBM (Table 1). This means that these croconines cannot serve as donor in this blend. The LUMO levels of the unsymmetrical CR2's (with ethyl or benzyl group) are also very close to the LUMO of the acceptor system situated just 0.12 eV above. This small difference means that no efficient charge separation is expected. Contrary, SQ2's LUMO's are too high versus PCBM's which suggests that greater energy loss would be occurred in the BHJ. The LUMO levels of the SQs are properly positioned with respect to the acceptor's. However, the requirement for LUMO (donor) – LUMO (acceptor) > 0.2–0.3 eV is fulfilled only for SQ1 and SQ3. Nevertheless, in this respect, these dyes perform better than some newly proposed merocyanine dyes [25].

Absorption

DDFT/B3LYP/6-31+G(d,p) calculations of the excitation energies E_{exc} and corresponding wavelengths λ_{max} (Table 1) predict strong absorption in the red and NIR region of the spectrum. These results are in good agreement with the experimental findings for similar squarilium and croconium dyes [13]. The croconium dyes absorb at significantly longer wavelengths than the squarylium (Figure 3) as the difference for CR3 and SQ3 is about 0.30 eV and up to 0.35 eV for the rest of the molecules. Within the series SQ3 and CR3 are red-shifted with respect to SQ2 and CR2 by about 0.20 – 0.17 eV, respectively, and, in a lesser extend to SQ1 and CR1.

On the basis of the calculated high values of the oscillator strengths all proposed dyes fulfill the requirement for large absorption coefficient (especially for SQ3 and CR3) as SQ's absorb more intensively than CR's.

Transport properties

The assessment of the transport properties of the studied dyes is made by considering the internal reorganization energy λ and exciton binding energy E_{bind}. The small λ is precondition for high charge mobility; small E_{bind} is prerequisite for high charge separation efficiency which is needed for photovoltaic applications whereas high exciton binding energy is necessary for light-emitting devices.

According to the theoretical estimations the proposed systems are better hole than electron transport materials since the reorganization energy for hole transport λ^+ is smaller than for electron λ^- transport (Figure 6a). The ratio between these two energies λ^+/λ^- is lower than 1.0 for all chromophores, which evidences their p-type character. The smallest values of this ratio are found for the symmetrical SQ1 and CR1 dyes (0.58 and 0.61, respectively) which suggest that these chromophores should exhibit most clearly pronounced donor character. On the other hand their absolute values of λ^+ is the largest amongst the studied structures. SQ3 and CR3 have the smallest reorganization energies λ^+ and λ^- among the studied and they are the expected to have better hole transport properties. SQ2 and CR2 have larger values of the ratio (0.79 and 0.76, respectively) and closer to 1.0 which suggests enhanced ambipolar character.

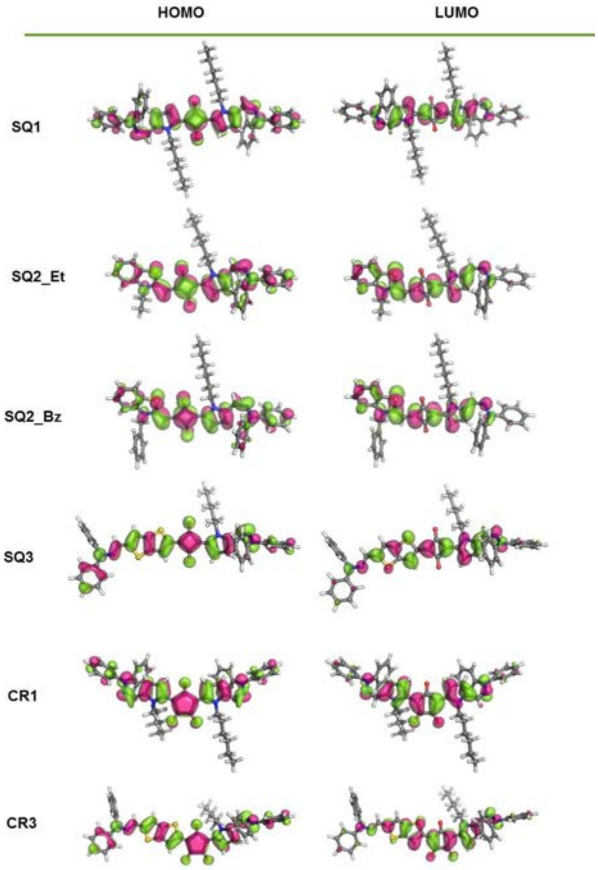

Figure 2. Frontier MO orbitals.

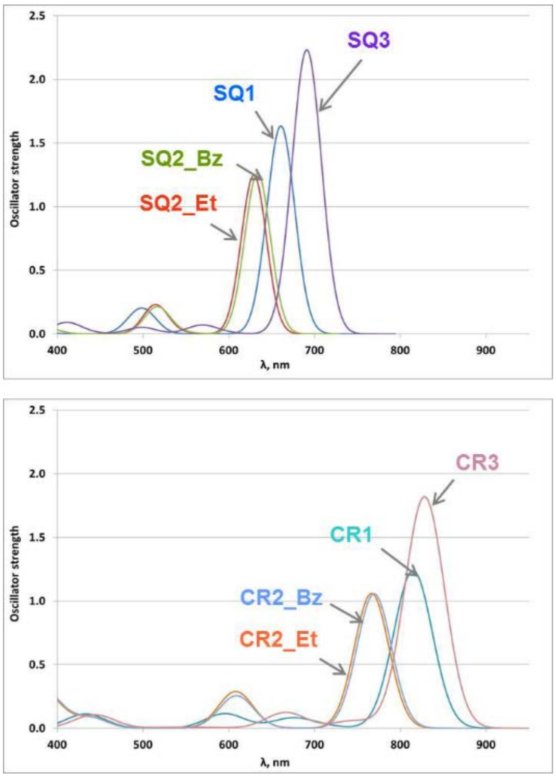

Figure 3. Simulated absorption spectra of: a) SQ's, b) CR's.

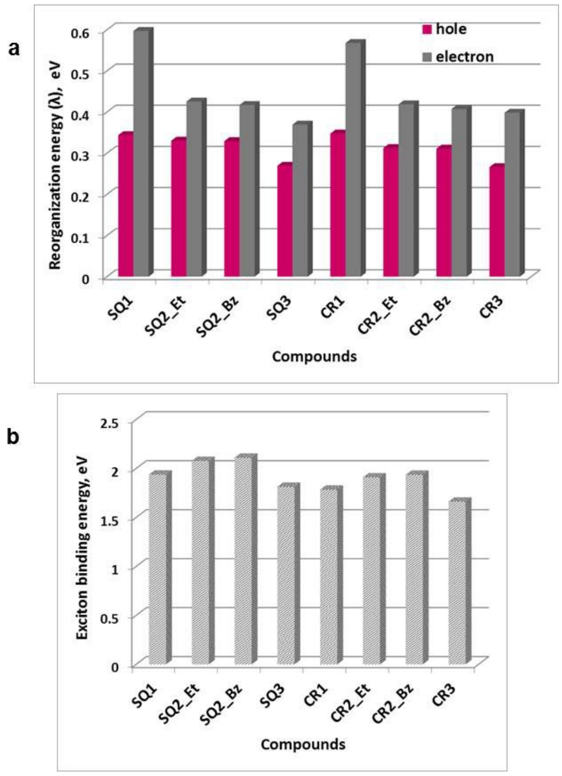

Figure 4. B3LYP/6-31+G(d,p) calculated: a) internal reorganization energies for hole and electron in eV, and, b) exciton binding energies for SQ' and CR's in eV.

Generally, the different substituents do not affect substantially the reorganization energies for electron and hole. The calculated values for λ are high in comparison of many other organic semiconductors [26] but comparable with values for some organic amines proposed for efficient organic electroluminescence (OLED) devices [27]. Also, there is no big difference between the corresponding dyes of the two series, i.e. the central acceptor fragments SQ or CR do not influence the reorganization energy. It might be helpful to propose new molecular architecture, ex. by increasing the extent of the electron delocalization which could lead to smaller reorganization energy.

The calculated exciton binding energies for the proposed dyes vary from 1.66 eV for CR3 to 2.11 eV for SQ2_Bz. These values are much higher than the reported for most of the organic semiconductors, ranging from 0 to 1.5 eV [28]. SQ2 and CR2 have largest exciton binding energies and are about 0.3 eV and 0.27 eV larger than E_{bind} for SQ3 and CR3, respectively.

CONCLUSIONS

Most of the proposed croconium and squarylium dyes satisfy the different criteria for efficient donor components for BHJ solar cell applications. The theoretical results predict low HLG's and intense red and NIR absorption. The estimated HLG's of all model dyes fall in the range of the typical organic semiconductors' gap of about 2 eV. The type of the central core fragment mainly affects the LUMO orbital energies. The replacement of central squaric fragment by croconic cores leads to a lower HLG and red shift in the absorption while the calculated oscillator strengths are lowered. Only SQ1's and SQ3's frontier orbitals satisfy all requirements for proper position with respect to HOMO and LUMO of the acceptor [60]PCBM. Due to the estimated smaller reorganization energy for hole than for electron these dyes are referred as p-type semiconductors which confirms their donor abilities. Considering the calculated reorganization energies λ and exciton binding energies E_{bind} the favorite structures are SQ3 and CR3.

Nevertheless, all dyes show comparatively high values of λ and E_{bind} which suggests moderate charge transport properties. These dyes can further be modified by adopting proper strategies toward reducing the reorganization energies and exciton binding energies in order to achieve more efficient charge mobility and charge separation.

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МОЛЕКУЛЕН ДИЗАЙН НА ЕЛЕКТРОН-ДОНОРНИ МАТЕРИАЛИ ЗА ФУЛЕРЕН-БАЗИРАНИ СЛЪНЧЕВИ КЛЕТКИ

М. Спасова[1], С. Ангелова[1], М. Къндинска[2], А. Василев[2], С. Китова[3], Ю. Дикова[3]

[1] Институт по органична химия с Център по фитохимия,
Българска академия на науките, София, 1113, България

[2] Факултет по химия и фармация, Софийски университет „Св. Климент Охридски“,
1164 София, България

[3] Институт по оптически материали и технологии „Акад. Йордан Малиновски”,
Българска академия на науките, София, 1113, България

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(Резюме)

Моделни симетрично и несиметрично заместени скуарилиеви и крокониеви багрила са предложени като потенциални донори на електрони в органични фотоволтаични слънчеви клетки с акцепторен компонент [60]PCBM фулерен. Геометриите и електронните структури в основно състояние са изследвани с помощта на теория на функционала на плътността (DFT) и зависещата от времето теория на функционала на плътността (TD-DFT) на ниво B3LYP/6-31+G(d,p). Ефектите на богатите на електрони хетероцикли върху скуарилиевите/крокониеви органични багрила са изследвани по отношение на електронните и транспортни свойства на системите. Очакваните забранени зони на всички моделни съединения са от порядъка на типичните за органичните полупроводници зони - около 2 eV. Енергиите на HOMO и LUMO орбиталите на багрилата са сравнени с тези на акцептора и са дискутирани стриктните условия за ефективен пренос на заряд. Изчислените високи стойности за силата на осцилатора за всички предложени съединения са показателни за голям коефициент на поглъщане. Въз основа на оптимизираните молекулни геометрии, относителните позиции на орбиталите, абсорбционните максимуми и транспортните свойства може да се заключи, че някои от багрилата, които предлагаме, са подходящи компоненти за оптоелектронни устройства.

Ключови думи: *скуарилиеви багрила, крокониеви багрила, фулерен, теория на функционала на плътността, транспортни свойства*