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# A Study of the Role Played by the Hartree–Fock Orbital Exchange in the Formation of the Energy of the First Singlet Charge-Transfer Excited State by the Example of JK-62 and JK-201 Sensitizing Dye Molecules

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**Abstract**—Based on the time-dependent density functional theory with the use of the functionals B3LYP, B97-2, BHandHLYP, BMK, MPWB1K, PBE1W, PBE1PBE,  $\tau$ -HCTHh, and TPSS in the 6-31G(d) basis set of atomic orbitals, we have performed a quantum-chemical investigation of electronic and spectral properties of JK-62 and JK-201 bis-dimethylfluorenyl dye sensitizers for Grätzel photoelectric converters. In terms of the Bader theory, we have done a complete analysis of the electron-density distribution function in the dye molecules under study, which proves the occurrence of intramolecular nonvalent interactions, which, in turn, stabilize a planar mutual arrangement of structural fragments of dye molecules. The role that the Hartree–Fock orbital exchange plays in the energy formation of the first and most intense electronic transition, which is responsible for the primary current generation in a solar cell, has been elucidated.

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## INTRODUCTION

Efficient conversion of solar radiation into electric power is an important problem, for solving of which various types of photoelectric converters are being actively developed. Among such devices are dye-sensitized solar cells, which have been designed by Grätzel in 1991 [1] and the principle of operation of which is based on photoelectrochemical transformation of light energy into electric current. A determining role in increasing the efficiency of dye-sensitized solar cells is played by the choice of a dye sensitizer with an intensive absorption in a wide spectral interval, which would cover maximally the visible and near-IR ranges [2]. These requirements are met by many organic dyes, in particular, JK-62 [3] and JK-201 [4] bis-dimethylfluorenyl dyes (Fig. 1), which are constructed according to the scheme donor–bridge–acceptor (D- $\pi$ -A). Elucidation of the nature of absorption of visible light by a dye is the direct problem of quantum chemistry, which can be solved by the method of time-dependent density functional theory (TD DFT) [5].

The basic problem in quantum-chemical modeling of absorption spectra of sensitizing dyes of the D- $\pi$ -A type by the TD DFT method is frequently related to a strong discrepancy between calculated and experimental data on the energy of the lowest  $S_1$  charge-transfer state, which is responsible for electron injection and electric-current generation in dye-sensitized solar cells. This problem is a characteristic drawback

of the TD DFT method for charge-transfer states [6–9], and it is known for many types of dyes; however, it manifests itself most strongly for triphenylamine [10–12] and bis-dimethylfluorenyl dyes [13, 14]. Thus, calculations with the use of the well-known B3LYP functional underestimate the energy of the  $S_1$  state by 0.4–1.0 eV compared to the experiment.

In this work, we present a system analysis of the contribution from a nonlocal Hartree–Fock orbital exchange to the exchange–correlation part of the functional for the correct quantitative and qualitative description of the  $S_1$  charge-transfer state by the example of two sensitizing dyes, JK-62 and JK-201.

## METHOD OF CALCULATION

Equilibrium geometrical parameters of the JK-62 and JK-201 dyes were calculated by the DFT/B3LYP method [15, 16] in the 6-31G(d) basis set of atomic orbitals [17]. For the equilibrium geometrical configuration of either molecule, we calculated 20 singlet excited states by the TD DFT method with the use of a series of functionals that contained different contributions of the Hartree–Fock orbital exchange to the exchange–correlation part. The excited states were calculated in terms of the PCM continual model [18] (ethanol and tetrahydrofuran were used as solvents for the JK-62 and JK-201 dyes, respectively, to detect their absorption spectra). For the equilibrium geometries, we also analyzed electron-density distribution

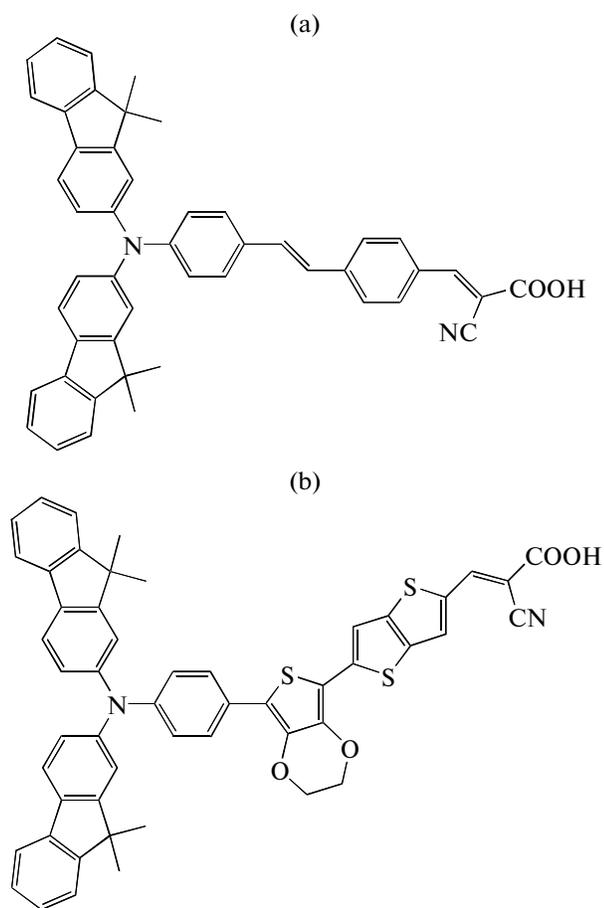


Fig. 1. Structures of (a) JK-62 and (b) JK-201 molecules.

function  $\rho(\mathbf{r})$  by the Bader method (QTAIM) [19], which yields useful data on intramolecular stabilization of molecules of sensitizing dyes. The energy of the found nonvalent interactions was calculated by the Espinosa formula [20, 21],

$$E_{\text{int}} = v(\mathbf{r})/2, \quad (1)$$

where  $E_{\text{int}}$  is the energy of the nonvalent contact (in au) and  $v(\mathbf{r})$  is the potential energy density at the corresponding critical point of the bond. By definition, the critical point corresponds to an extremum of the function  $\rho(\mathbf{r})$  in the interatomic space ( $\text{grad}\rho(\mathbf{r}) = 0$ ). The type of a critical point is determined by the number ( $\omega$ ) and algebraic sum of signs ( $\sigma$ ) of curvature elements ( $\lambda_i$ ) of the electron density at the critical point. For a chemical bond, the form of a critical point in the format ( $\omega, \sigma$ ) is given by (3, -1). Bader showed that the occurrence of critical point (3, -1) between atoms is a necessary and sufficient condition for the chemical bond to appear [19].

The profiles of the calculated electronic absorption spectra of the JK-62 and JK-201 dye molecule were approximated by the Gauss distribution function (with

a line halfwidth of  $3500 \text{ cm}^{-1}$ ) using the SWizard 4.6. program [22]. All calculations by the DFT and TD DFT methods were performed in terms of the Gaussian 03 software package [23] on a PDC supercomputer at the Royal Institute of Technology (Stockholm, Sweden). Topological analysis of the electron-density distribution function  $\rho(\mathbf{r})$  was performed by the QTAIM method using the AIMQB program, which was realized in terms of the AIMAll computer complex [24].

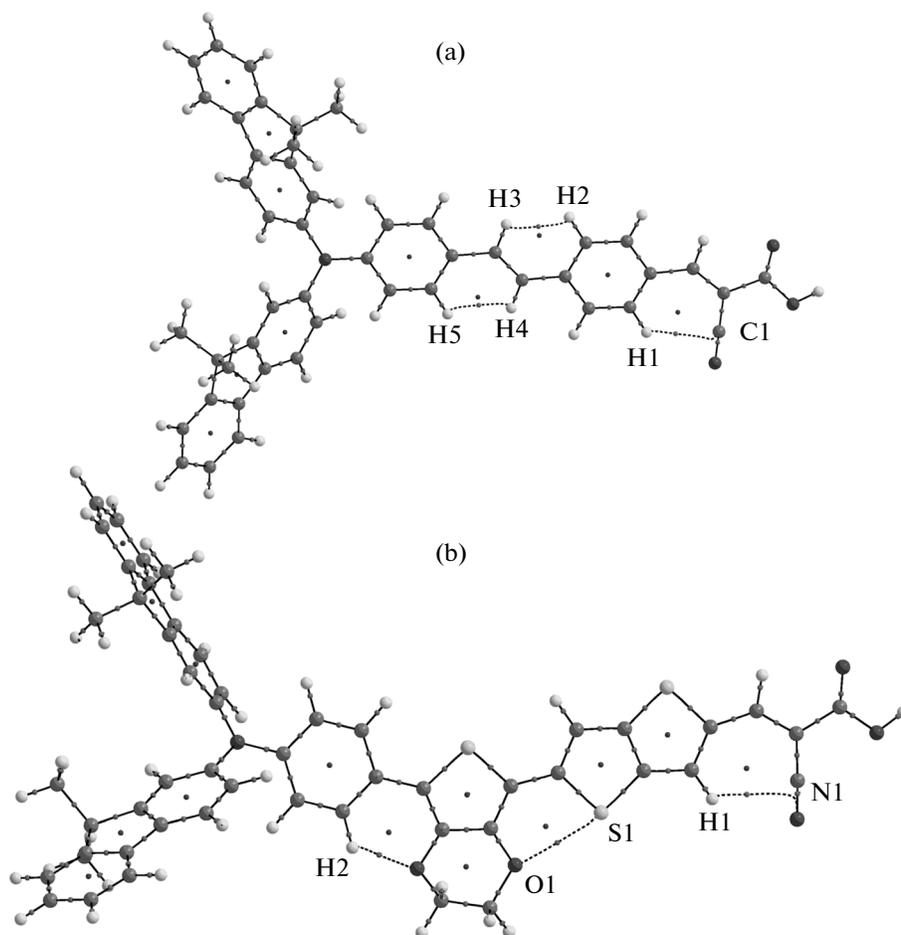
## RESULTS AND DISCUSSION

### *Analysis of the Structure of the JK-62 and JK-201 Dye Molecules*

Figure 2 presents graphs of the structure of the dye molecules that were obtained according to calculations by the QTAIM method. For these molecules, we analyzed the energy density and the sign of the Laplacian at the (3, -1) critical point and applied the Espinosa correlation dependence to find energies of nonvalent contacts (Table 1). A detailed analysis and determination of the energy of nonvalent interactions are very important, because it is precisely these weak intramolecular interactions that determine the conformational structure of dye molecules and, therefore, affect the dynamics of the electron transfer upon photoexcitation. In particular, Fukunishi et al. [25] showed that the mutual rotation of donor and acceptor groups of indoline dyes substantially affects the position and intensity of the first absorption band, which corresponds to the charge transfer, i.e., to the primary electric-current generation event in dye-sensitized solar cells. Therefore, the conformation of dye molecules “controls” the charge-transfer efficiency upon photoexcitation and directly determines the efficiency of dye-sensitized solar cells.

**$\text{O}^1\text{--S}^1$  and  $\text{H}^2\text{--O}^2$  interactions.** Two critical points of the (3, -1) type correspond to the  $\text{O}^1\text{--S}^1$  and  $\text{H}^2\text{--O}^2$  interactions in the JK-201 molecule. For these interactions. The values of electron-density Laplacian  $\nabla^2\rho(\mathbf{r})$  and electron-energy density  $h_e(\mathbf{r})$  are positive, which corresponds to the interaction of closed shells. The ellipticity values for these bonds are 0.10 and 0.17, respectively (Table 1), which indicates that these contacts are dynamically stable. The energies of the  $\text{O}^1\text{--S}^1$  and  $\text{H}^2\text{--O}^2$  bonds calculated by formula (1) are -3.01 and -3.20 kcal/mol, respectively (Table 1).

**$\text{H}^1\text{--C}^1$  and  $\text{N}^1\text{--H}^1$  interactions.** The  $\text{H}^1\text{--C}^1$  and  $\text{N}^1\text{--H}^1$  interactions in the JK-62 and JK-201 molecules, respectively, stabilize the planar mutual arrangement of the cyanoacrylic fragment and adjacent “bridge part.” The values of  $\nabla^2\rho(\mathbf{r})$  and  $h_e(\mathbf{r})$  are positive and small in magnitude, which corresponds the interaction of closed shells. The ellipticity values for the  $\text{H}^1\text{--C}^1$  and  $\text{N}^1\text{--H}^1$  bonds are 0.51 and 0.83, respectively, which indicates that these interactions



**Fig. 2.** Graph structures of (a) JK-62 and (b) JK-201 molecules: points in cycles show (3, +1) critical points and points on bonds represent (3, -1) critical points.

are considerably susceptible to the break with the cycle opening. The energies of the  $H^1-C^1$  and  $N^1-H^1$  bonds calculated by formula (1) are  $-2.20$  and  $-1.76$  kcal/mol, respectively (Table 1).

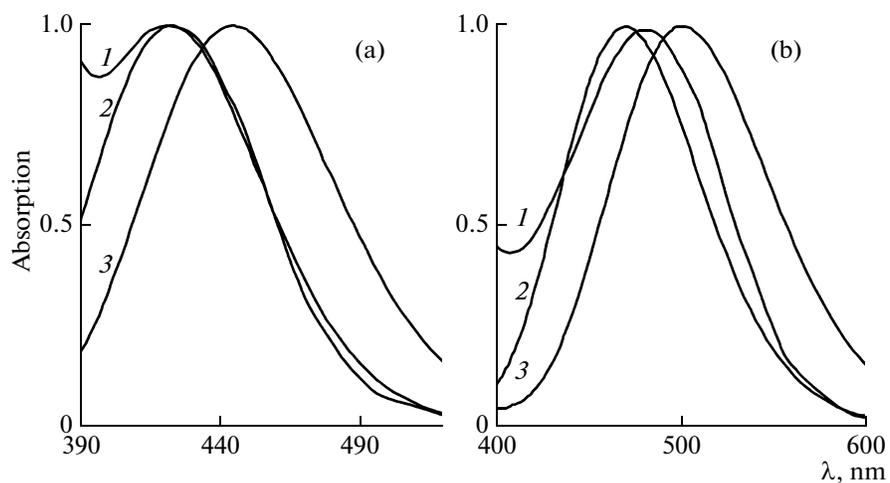
**$H^2-H^3$  and  $H^4-H^5$  interactions.** The interactions of the H–H type in the JK-62 dye molecule are rather strong for bonds of this type (Table 1); however, high ellipticity values for these bonds (0.88 and 1.02 for the  $H^2-H^3$  and  $H^4-H^5$  bonds, respectively) indicate that these interactions are susceptible to the break with the cycle opening.

#### *Electronic and Spectral Properties of the JK-62 and JK-201 Dyes*

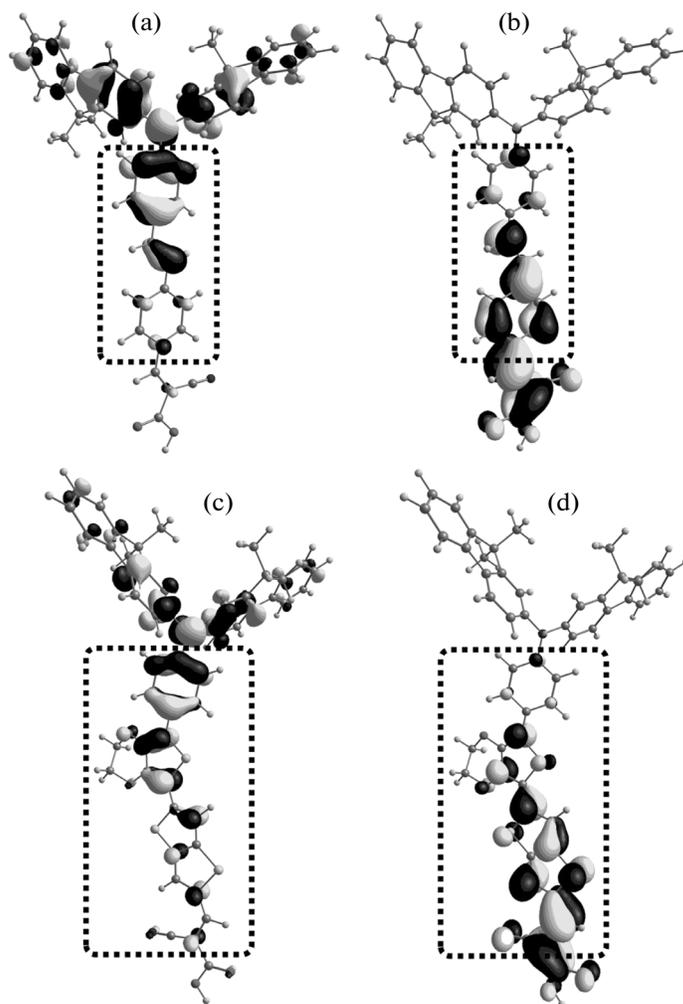
According to the experimental data, the electronic absorption spectra of the JK-62 and JK-201 dyes consist of two absorption bands each. Their long-wavelength bands lie in the range of 390–600 nm and are peaked at 421 and 481 nm for JK-62 and JK-201, respectively (Fig. 3). The short-wavelength bands are in the range of 300–390 nm with maxima at 374 and

371 nm for JK-62 and JK-201, respectively [3, 4] (they are not shown). Calculations by the TD DFT/BHandHLYP/6-31G(d) method [26] reproduce best this shape of the absorption spectra of the JK-62 and JK-201 dyes.

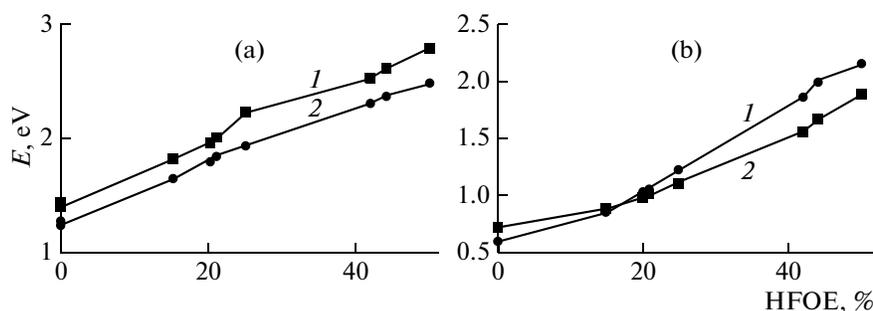
The calculation shows that the first absorption maximum at 421 (481) nm is caused by the singlet–singlet ( $S_0 \rightarrow S_1$ ) electronic transition of the  $\pi\pi^*$  type and corresponds to one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (Fig. 4.) From Fig. 4, it can be seen that this transition is accompanied by charge transfer from the donating fluorenylamine part of the dye molecule to the accepting cyanoacrylic fragment; i.e., charge separation takes place in the molecule, as a result of which a photoexcited electron is localized on the accepting part, whereas, on the donating triphenylamine fragment, a hole is formed. Importantly, this transition is the most intense in the spectrum and produces population of the first  $S_1$  state, which relaxes by injecting an electron to the conduction band of the semiconductor nanoc-



**Fig. 3.** (1) Experimental absorption spectra of the (a) JK-62 and (b) JK-201 dyes in comparison with their spectra calculated by the TD DFT/BHandHLYP/6-31G(d) method: (2) calculation in the vacuum approximation and (3) calculation taking into account the influence of the solvent.



**Fig. 4.** Shapes of frontier molecular orbitals of the (a, b) JK-62 and (c, d) JK-201 dye molecules (controlling value of the isosurface is 0.03 au): (a, c) HOMO and (b, d) LUMO.



**Fig. 5.** Dependences of the (a) energy of the  $S_1$  state, and (b) oscillator strength of the transition  $S_0 \rightarrow S_1$  on the contribution of the Hartree–Fock orbital exchange (HFOE) to the exchange–correlation part of the functional for the (1) JK-201 and (2) JK-62 dye molecules.

crystalline  $\text{TiO}_2$ . The relaxation efficiency of the  $S_1$  state is quantitatively determined by the coefficient of the photon–electric conversion, which has been measured experimentally [3, 4] to be about 90% at the absorption maxima of the two dyes adsorbed on the semiconductor surface (the absorption maxima of the dyes adsorbed on  $\text{TiO}_2$  are insignificantly bathochromically shifted with respect to their positions in the absorption spectra of the dyes in the solution). Higher excited states of the dyes manifest themselves in the near-UV range, the fraction of which constitutes about 3% in the solar emission spectrum. Therefore, under conditions of the dye-sensitized solar cell, higher excited states are almost not formed. However, even in the case of their formation, they rapidly relax to the  $S_1$  state, which is also useful for pumping of the conduction band of the semiconductor by electrons.

It can be seen from Fig. 4 that the HOMOs and LUMOs of the two dyes have rather vast “common” nonzero overlap regions (outlined by dotted rectangles), either of which is localized on the bridge part of the molecule of the JK-62 and JK-201 dyes. This indicates that the exchange interaction between these two orbitals is rather strong and should yield an apprecia-

ble contribution to the energy and intensity of the electronic transition between them by means of one-center exchange integrals. Indeed, increasing the part of the nonlocal Hartree–Fock orbital exchange by applying different exchange–correlation functionals leads to a linear increase in the energy of the  $S_1$  state (Fig. 5a; the coefficient of regression,  $R^2 = 0.99$ ; Table 2) and to a better agreement with experimental spectra. The oscillator strength of the first electronic transition also depends on linearly on the part of the Hartree–Fock orbital exchange in the exchange–correlation functional (Fig. 5b; the coefficient of regression,  $R^2 = 0.97$ ; Table 2) and increases proportionally with an increase in the contribution of the Hartree–Fock orbital exchange. These effects are determined by nonzero expansion coefficients of the wave functions of the HOMO and LUMO on common atoms of the bridge part of the dyes, with these coefficients increasing as the contribution of the Hartree–Fock orbital exchange increases. Their product appears in the expression for the exchange integral and transition electric-dipole moment and, correspondingly, yields large contributions to the transition energy and oscillator strength. It is important that, as the part of the Hartree–Fock orbital exchange increases to 100%,

**Table 1.** Parameters of nonvalent interactions in molecules of the JK-62 and JK-201 dyes

Bond	$d, \text{\AA}$	$\rho(\mathbf{r}), ea_0^{-3}$	$v(\mathbf{r}), \text{au}$	$h_e(\mathbf{r}), \text{au}$	$\nabla^2\rho(\mathbf{r}), ea_0^{-3}$	$\epsilon$	$E, \text{kcal/mol}$
JK-62							
H <sup>4</sup> –H <sup>5</sup>	2.152	0.0092	–0.0049	0.0024	0.0385	1.02	–1.54
H <sup>2</sup> –H <sup>3</sup>	2.127	0.0096	–0.0052	0.0024	0.0401	0.88	–1.63
H <sup>1</sup> –C <sup>1</sup>	2.438	0.0121	–0.0070	0.0019	0.0436	0.51	–2.20
JK-201							
N <sup>1</sup> –H <sup>1</sup>	2.586	0.0103	–0.0056	0.0019	0.0376	0.83	–1.76
O <sup>1</sup> –S <sup>1</sup>	2.932	0.0127	–0.0096	0.0007	0.0443	0.10	–3.01
H <sup>2</sup> –O <sup>2</sup>	2.313	0.0135	–0.0102	0.0012	0.0502	0.17	–3.20

$a_0$  is the Bohr radius, 0.529  $\text{\AA}$ .

**Table 2.** Energy and intensity of the transition  $S_0 \rightarrow S_1$  (calculated taking into account the influence of the solvent) in spectra of the JK-62 and JK-201 dyes in relation to the contribution of the Hartree–Fock orbital exchange (HFOE) to the exchange–correlation functional

Method	HFOE, %	JK-62			JK-201		
		$\lambda$ , nm	$E$ , eV	$f$	$\lambda$ , nm	$E$ , eV	$f$
TPSS	0	863	1.44	0.727	985	1.26	0.606
PBE1W	0	891	1.39	0.7061	1012	1.23	0.581
$\tau$ -HCTHh	15	687	1.81	0.881	752	1.65	0.855
B3LYP	20	634	1.96	0.973	690	1.80	1.014
B97-2	21	620	2.00	1.003	676	1.83	1.046
PBE1PBE	25	588	2.11	1.103	638	1.94	1.209
BMK	42	491	2.52	1.547	538	2.30	1.862
MPWB1K	44	474	2.62	1.656	524	2.37	1.984
BHandHLYP	50	445	2.79	1.887	501	2.47	2.158
Experiment	—	421	2.94	—	481	2.58	—

the charge-transfer state acquires the character of a local excitation, which has been demonstrated [27] by the example of a similar triphenylamine dye. Therefore, to correctly describe the  $S_1$  charge-transfer state, it is recommended to use functionals with a 40–60% fraction of the Hartree–Fock orbital exchange depending on the degree of coincidence of the energy of the state with the experimental spectrum.

## CONCLUSIONS

Our quantum-chemical calculations of the energy and intensity of the first electronic transition  $S_0 \rightarrow S_1$  in terms of the TD DFT method by the example of two bis-dimethylfluorenyl dyes, JK-62 and JK-201, have shown that they are highly sensitive to the contribution from the nonlocal Hartree–Fock orbital exchange to the exchange–correlation functional (Table 2). Functionals with a small contribution from the Hartree–Fock orbital exchange considerably underestimate the energy of the first  $S_1$  charge-transfer state, whereas an increase in the contribution of the Hartree–Fock orbital exchange improves the agreement between the data of calculations and experiment. We have shown that, for this class of sensitizing dyes, the BHandHLYP hybrid functional with a 50% contribution from the Hartree–Fock orbital exchange yields the best agreement with experiment.

Analysis of the conformational structure of molecules under study by the Bader method has shown that the planar mutual arrangement of structural fragments of dye molecules is stabilized by intramolecular bonds. Therefore, weak nonvalent interactions directly control the dynamics of the charge transfer over the flattened  $\pi$ -conjugated system upon photoexcitation.

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