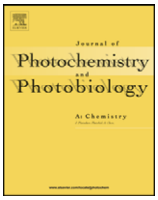
Journal of Photochemistry and Photobiology A: Chemistry 205 (2009) 139–144

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photoinduced intermolecular and intramolecular charge transfer in the mixed coaggregates of pyrazoline and dicyanonaphthalene

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ARTICLE INFO

Article history:
Received 24 December 2008
Received in revised form 26 March 2009
Accepted 22 April 2009
Available online 3 May 2009

Keywords:
Charge transfer
Excited state
2D site representation
3D cube representation
Transition dipole moment

ABSTRACT

Photoinduced charge transfer (CT) and excited state properties in the mixed coaggregates of 1,3,5-triphenyl-2-pyrazoline (TPP) and 1,4-dicyanonaphthalene (DCN) are investigated theoretically, using time-dependent density functional theory (TD-DFT) as well as the two-dimensional (2D) site (transition density matrix) and three-dimensional (3D) cube (transition density and charge difference density) representations. The calculated results indicate that a strong absorption band stems from the $S_0 \rightarrow S_4$ transition. There are electron–hole coherences between TPP and DCN monomers, which are shown by 2D site representation. Direct visual evidence revealed by 3D cube representations indicates that photoinduced CT mechanism for the mixed coaggregates of TPP and DCN is the mixture of intermolecular and intramolecular CT in the vertical absorption. Some phenyl group of TPP monomer not only serves as the electronic donor in the intramolecular CT, but also in the intermolecular CT process.

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1. Introduction

Photoinduced charge transfer (CT) from donor to acceptor is a primary step in photophysical, photochemical as well as photobiological processes [1–5]. The charge transfer process can be intermolecular CT in which an electron is transferred from electron-donating species (D) to electron-accepting species (A), producing the radical cation of donor and the radical anion of acceptor, or intramolecular CT, involving charge redistribution in the excited molecule which produces a very large excited state dipole moment. Much effort has been invested to understand the fine details of inter- and or intra-molecular CT processes [6–13]. Although a great variety of molecular systems (from directly linked D–A compounds to D–π–A compounds) have been elaborated [6–9], and although the covalently linked and hydrogen-bonded donor–acceptor coaggregates also exhibit excellent CT characteristics [10–13], photoinduced charge transfer for mixed coaggregates with electron-rich and electron-deficient components has been a little attention [14]. The possible mechanism of the reaction has not been investigated so far.

It is well known that photophysical properties of the organic molecules are determined predominantly by the low energy excited states. Knowledge of nature of excited states, and interplay of inter- and intra-molecular mechanism in the CT process, are becoming very important to develop the novel optoelectronic device. For mixed coaggregates, bimolecular interactions between an excited donor and a ground-state acceptor sometimes lead to the complex photophysical and or photochemical phenomena [15–19]. For example, those interactions give rise to the exciplex [17] and affect the emission spectra by developing a new structureless band at a longer wavelength region [18,19]. There are two possible pathways of electron transition to form exciplex: the first one is direct electronic transition from the HOMO of one entity to the LUMO of another entity; the other one is via the transition of one electron from the LUMO of one entity to the LUMO of another. The ground and excited ICT state of weak complex can be described in terms of wave function [20]:

$$\psi_g = a\psi_0(\mathrm{D, A}) + b\psi_1(\mathrm{D^+A^-}) \tag{1}$$

$$\psi_E = a^*\psi_1(\mathrm{D^+A^-}) - b^*\psi_0(\mathrm{D, A}) \tag{2}$$

where a and b describe the contribution of each structure to wave function. $\psi_0(\mathrm{D, A})$ is the configuration for the normal, weakly bound complex, and $\psi_1(\mathrm{D^+A^-})$ is the CT configuration. In Eq. (1), $\psi_0(\mathrm{D, A})$ make great contribution to the ground state because of very small resonance energy in the ionic structure $\psi_1(\mathrm{D^+A^-})$. For excited state, the ionic form becomes the predominant ($|a| \geq |b|$) because an electron is transferred from the donor to the acceptor. In this CT process, excited molecule should experience geometry modification in some segments of molecules (where the arrangement of electron–hole pairs occurs), exhibiting an obvious change of transition dipole moment (which can be approximated as $\mu_{eg} \approx a^* b\mu_{11} + aa^*\mu_{01}$ [21],

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doi:10.1016/j.jphotochem.2009.04.019

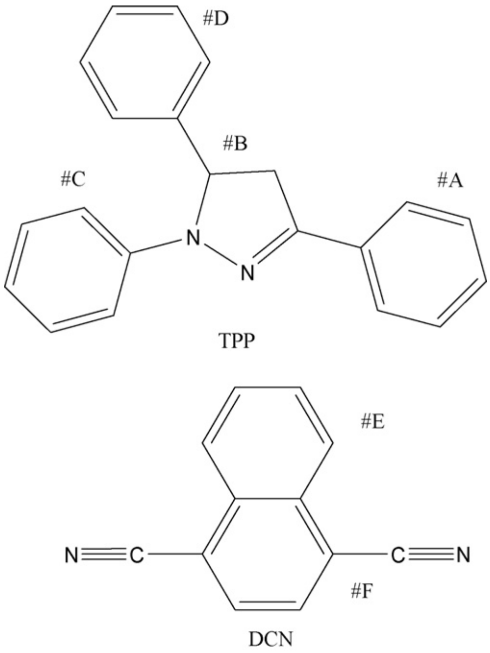

Fig. 1. Chemical structure of the TPP and DCN complex.

and μ_{11} is the static dipole moment and μ_{01} is the transition dipole, respectively).

To visualize all molecular orbitals involved in transitions to the excited state, several elaborate theoretical approaches have been developed. One is the 2D site representation of transition density matrix [22–24], which provides visual information of electron–hole coherence and the excitation delocalization region of conjugated molecule upon excitation. Another one is the 3D cube representation of transition density (TD) and charge difference density (CDD) [25–28], which has been employed to study CT process of several conjugated polymers.

In this paper, we perform quantum chemical calculation as well as two-dimensional (2D) site and three-dimensional (3D) cube studies on the mixed coaggregates with electron-rich 1,3,5-triphenyl-2-pyrazoline (TPP) and electron-deficient 1,4-dicyanonaphthalene (DCN) (see Fig. 1) [29], to provide a deeper insight into excited state properties and to reveal CT mechanism of the system. The article is organized as follows: Firstly, the nature of electronic state in absorption for TPP and DCN is examined in detail, respectively. Subsequently, we will describe a detailed analysis of the excited state properties and CT process for TPP and DCN complex with 2D site and 3D cube representations. The excited region and change of charge density, as the result of electronic orbital transition, can be employed as the useful evidence to explore the CT process for TPP and DCN complex in the vertical absorption.

2. Methods

Geometry optimizations of TPP, DCN and the TPP–DCN complex in the ground state were performed using density functional theory (DFT) [30], with Becke's three-parameter hybrid exchange functional (B3LYP) [31] at the 6-31G (d) basis set level. Vibration frequency calculation was conducted to confirm the stability of the optimized geometry. Electronic transition energies and oscillator strengths were calculated at these geometries using time-dependent density functional theory (TD-DFT) [32] at the same functional and basis set. All the calculations were done with Gaussian 03 suite [33].

To understand the nature of the excited states, we have used the result of the TD-DFT calculation to obtain two-dimensional (2D) electron–hole two-particle wave functions [22–24], which leads to a two-dimensional grid that – for each of the axes – runs over all the carbon sites:

$$\left|\Psi(x,y)\right|^2 = \sum_{q\in x}\sum_{r\in y}\left|\psi(q,r)\right|^2 \qquad (3)$$

For each data point (x, y) in two-dimensional grid, $|\psi(x,y)|^2$ gives the probability of finding one charged particle of the "exciton" in atomic orbital q on site x and the second in atomic orbital r on site y. These two-dimensional maps provide insight into the size of excitation delocalization along the diagonal part [22], the size of the exciton along the off diagonal part [23], and the amount of excited-state localization on the different parts of the model compounds [24].

In the 3D cube representation, the transition density (TD) from the ground state (S_0) to excited state (S_u) is described as [25–27]:

$$\rho_{u0}(\vec{r}) = \sum_{\substack{\alpha\in unoc\\ i\in occ}} C_{uai}\varphi_a(\vec{r})\varphi_i(\vec{r}) \qquad (4)$$

where C_{uai} represents the uth eigenvector of the configuration-interaction (CI) Hamiltonian based on the single excitations from the occupied Hartree–Fock molecular orbital $\varphi_i(\vec{r})$ to the unoccupied one $\varphi_a(\vec{r})$. Transition density (TD) determines the dipole transition moment (or transition dipole) [26,27], indicating the strength and the orientation for the interaction:

$$\vec{\mu}_{u0} = \int \vec{r}\rho_{\mu 0}(\vec{r})d^3\vec{r} \qquad (5)$$

The charge difference density (CDD) shows the orientation and results of the charge and energy transfer [24,26–28]:

$$\Delta\rho_{\mu\mu}(\vec{r}) = \sum_{\substack{a\in unocc\\ i,j\in occ}} C_{\mu aj}C_{\mu ai}\varphi_j(\vec{r})\varphi_i(\vec{r}) - \sum_{\substack{a,b\in unocc\\ i\in occ}} C_{\mu aj}C_{\mu ai}\varphi_b(\vec{r})\varphi_a(\vec{r}) \qquad (6)$$

The first and the second terms in Eq. (6) stand for hole and electron, respectively.

3. Results and discussion

3.1. Excited state properties of TPP

The calculated transition energies and oscillator strengths for TPP monomer are listed in Table 1. Within the considered energy range, there are three strong electronic transitions of sizable intensity ($f > 0.1$), corresponding to S_1, S_7 and S_9 excited states, respectively. The TD-DFT calculated transition energy ($S_0 \rightarrow S_1$) is found at 358.03 nm (Exp. 365 nm). This slight discrepancy between experiment and simulation can be contributed to the fact that solvent effect is not considered in the calculation. According to CI main coefficients, the S_1 state is composed of the HOMO → LUMO transition. As the result of molecular orbital transition, 3D cube representation of transition density and charge difference density reveals the nature of that characteristic electronic transition, as discussed below.

Photoinduced electron transfer results in charge redistribution, and thus molecules undergo obvious changes in dipole moment. To visualize the contribution of the molecular orbital to electronic transition, the 3D cube representation of transition density is investigated, which reveals the orientation and strength of the transition dipole moments. From transition density of S_1 state (see Fig. 2),

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