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Ab initio study for structure, electric properties and light emission of linear-trans-quinacridone

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Abstract. The structure, electric properties and emission rate of linear-trans-quinacridone are investigated within the density functional theory (DFT) calculations. We find the structure of the molecule to be planar with an energy gap of 3.06 eV. The emission lifetime from the lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO) of this material is found to be 24 ns, which is in good agreement with experimental results.

PACS. 31.70.Hq Time-dependent phenomena: excitation and relaxation processes, and reaction rates

Quinacridone pigments are fluorescent organic materials that have been considered for the fabrication of the organic light-emitting devices (OLED). Recent works have shown that quinacridone and its derivatives are good dopants in enhancing the electroluminescence of the tris (8–hydroxyquinoline) aluminum (Alq) emitter layer of OLED and enhancing the lifetime of the device as well [1,2]. Experimental studies show that this pigment exhibits high electroluminescence quantum efficiency, longer lifetime, good thermal and temporal stability [3,4].

One of the problems faced by experimentalists in the dye and pigment industry has been the identification of the crystal structure of the dye or pigment itself [5]. In fact, even the structure of a molecule of linear-trans-quinacridone (LTQ) (molecular formula = $C_{20}H_{12}O_2N_2$), the simplest type of quinacridone, is still under dispute. For instance, Koyama et al. proposed a "spiral staircase" structure, where the molecule is bent at the NH and CO groups which ran through the lattice in a stair-like fashion; whereas a flat-form structure was proposed by Lincke [5]. Knowing the crystal structure of the pigment will help elucidate the light absorption and scattering properties of the pigment.

As a first step of our investigations, despite the fact that it was postulated that the existence of a single molecule of LTQ is limited [5], we focus our study on the characterization of a molecule of this pigment. Based on density functional theory (DFT), we investigate its structure, electric properties and light emission rate. We obtain the one-electron wave function at the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels. Also, from the density of states (DOS) of this molecule, we obtain the energy gap, which describes its electric properties. Finally, we calculate the emission lifetime from LUMO to HOMO.

All calculations are based on DFT, employing the hybrid B3PW91 functional [6,7] and LANL2DZ basis set [8], as implemented in the Gaussian 03 suite of programs [9]. The choice of functional and or basis set has been used previously in the study of other organic systems and has shown to agree fairly well with experimental findings [10–13]. The structure of the molecule is optimized by performing a series of total energy calculation. The optimized structure gives the stable structure of the molecule and is shown in Figure 1. The O, C, N and H atoms are represented by red, green, blue, and white colors, respectively. Our result gives a planar molecule which is in agreement with the hypothesis of Lincke [5]. From this stable structure, we obtain the one-electron wave function at the HOMO and LUMO levels (Fig. 2 gives the representation of these molecular orbitals). From the coefficients of molecular orbital data, we find that both HOMO and LUMO are dominated by p_z orbitals from O, C and N atoms. C6, C14 and C15 atoms in HOMO built π bond of p_z orbitals as well as C5, C4 and C16.

Figure 3 shows the density of states (DOS) of the LTQ molecule. The first peak with energy around 1.5 eV below

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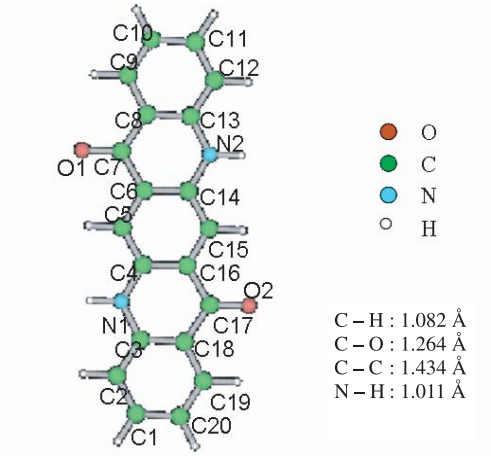

Fig. 1. Optimized structure of linear-trans-quinacridone. A colour version of the figure is available online at `http://www.eurphysj.orj`.

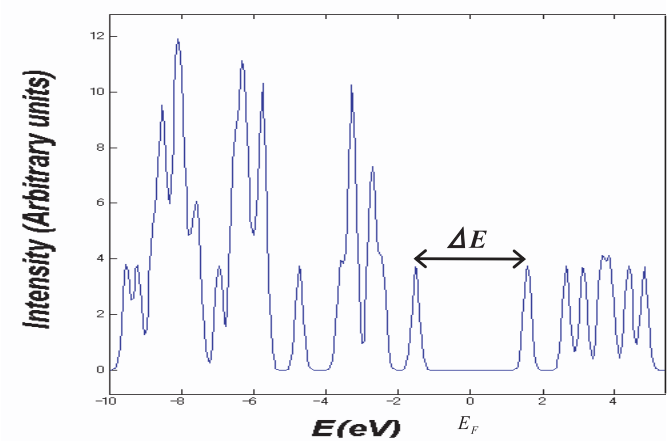

Fig. 3. Density of states (DOS) for linear-trans-quinacridone as a function of molecular orbital energy of the electrons (ΔE is the energy gap).

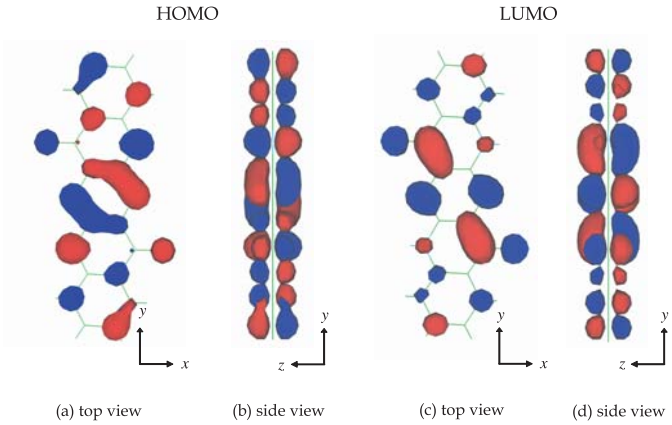

Fig. 2. HOMO and LUMO representation of linear-trans-quinacridone. A colour version of the figure is available online at `http://www.eurphysj.orj`.

the Fermi level describes HOMO while the peak at 1.5 eV above the Fermi level describes LUMO. The second and third peaks from HOMO with energies around 3 eV from the Fermi level contain molecular orbitals dominated by $2p_y$ orbitals of O, C and N atoms. The peaks with lower energy describe s orbitals of O, C and N atoms. The energy gap between HOMO and LUMO levels is 3.06 eV, indicating that this material is an insulator. Moreover, this energy difference translates to a violet color of fluoresce radiation, which is also observed in experiments [14,15]. We note, however, that, in here, the calculation is based from a single, isolated molecule of the compound and not from a crystal of it. Hence, inter-molecular interactions are not accounted for in the results.

The electron transition rate from the LUMO to HOMO is derived from the first-order time-dependent perturbation theory. The time-dependent coefficient is expressed by the following equation [16]

$$a_{mn}(t) \;=\; \frac{1}{i\hbar}\int_{t'=0}^{t'=t} \langle m|\, W\, |n\rangle \, \exp(i\omega_{mn}t')\, dt' \qquad (1)$$

where $|m\rangle$ and $|n\rangle$ are the one-electron wave functions at the LUMO and HOMO levels, respectively. W is the perturbation Hamiltonian which describes the interaction between the atomic dipole and oscillating electric field of a photon. The transition probability from LUMO to HOMO is

$$\begin{aligned} |a_{mn}(t)|^2 &= \left(\frac{e\left|\vec{E}_o\right|}{\hbar}\right)^2 |\langle m|\, r\, |n\rangle|^2\, \frac{\pi\, t}{2} \\ &= \frac{1}{3}\frac{\pi\, e^2 n_r^3}{\varepsilon_o \hbar^2}\, |\langle m|\, r\, |n\rangle|^2\, U(\omega)\, t, \end{aligned} \qquad (2)$$

where $\vec{E}_o$ is the oscillating electric field, $U(\omega) = (1/2)\varepsilon_o|\vec{E}_o|^2$ is the isotropic energy density, and n_r the refractive index. The emission lifetime is computed as

$$\tau \;=\; \frac{3\pi\varepsilon_o\hbar c^3}{e^2\omega^3 n_r^3}\frac{1}{|\langle m|\, r\, |n\rangle|^2}, \qquad (3)$$

which gives us a value of 24 ns. Previous study has shown that the fluorescence lifetime of quinacridone can be altered by chemical modification to produce a range of lifetime from 3 to 25 ns [17].

In summary, the structure, electric properties and light emission rate of linear-trans-quinacridone molecule were investigated. Based on density functional theory, we optimized the structure of the molecule and obtained the one-electron wave function at the HOMO and LUMO levels. From the DOS, it was shown that the energy gap is 3.06 eV. Finally, the emission lifetime of this material was calculated. The resulting fluorescence is in good agreement with experiments.

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