

Static (Hyper)Polarizability and Reorganization Energy of 4,5-Dicyanoimidazole Chromophores Derivate

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We have calculated the polarizability (α), the first hyperpolarizability, second hyperpolarizability (γ) and reorganization energy (λ) of 4,5-dicyanoimidazole chromophores derivate, in terms of gap energy HOMO-LUMO, at HF, DFT (CAM-B3LYP) and MP2 levels with 6-31+G(d,p) basis set. The $\langle \alpha \rangle$, β_{total} and $\langle \gamma \rangle$ values increase according to the donor electron groups sequence $-\text{H} < -\text{OCH}_3 < -\text{N}(\text{CH}_3)_2$. These properties enhance when the intra-molecular charge transference is increased due to the substitution of aromatic systems (Figure 1a). Moreover, the increase in the value of the (hyper)polarizability as accompanied by a decrease in the HOMO-LUMO energy difference, is in agreement with the Valence-Bond Charge-Transfer Model and sum-over-states (SOS) expressions (Figure 1b). The reorganization energy for electron transport (λ_e) and hole (λ_h) for structures **1** (D: $-\text{OCH}_3$), **2** (D: $-\text{H}$), **3** (D: $-\text{OCH}_3$) and **4** (D: $-\text{H}$) is very close to each other, suggesting that these molecules have good charge transport balance performance. Structure **2** (D: $-\text{H}$) holds the smallest λ_e and high λ_h , and thus, can be used as electron transfer material. On the other hand, structure **3** (D: $-\text{N}(\text{CH}_3)_2$) holds the smallest λ_h , and hence, can be used as hole transfer material. From NBO analysis, we observed that the total natural population was more localized on the nitrogen atom in the 4,5-dicyanoimidazole acceptor moiety, *i.e.*, the electron density in the nitrogen atom could be ionized more than the carbon π frame. The total natural population and natural charge are augmented as the donor character increases and, the smallest λ_h , is associated with the increase of donor character. Therefore, in the HOMO orbital, the energy release for the hopping hole can proceed from the 4,5-dicyanoimidazole acceptor moiety, when strength donor groups and large π -conjugated bridge are used.

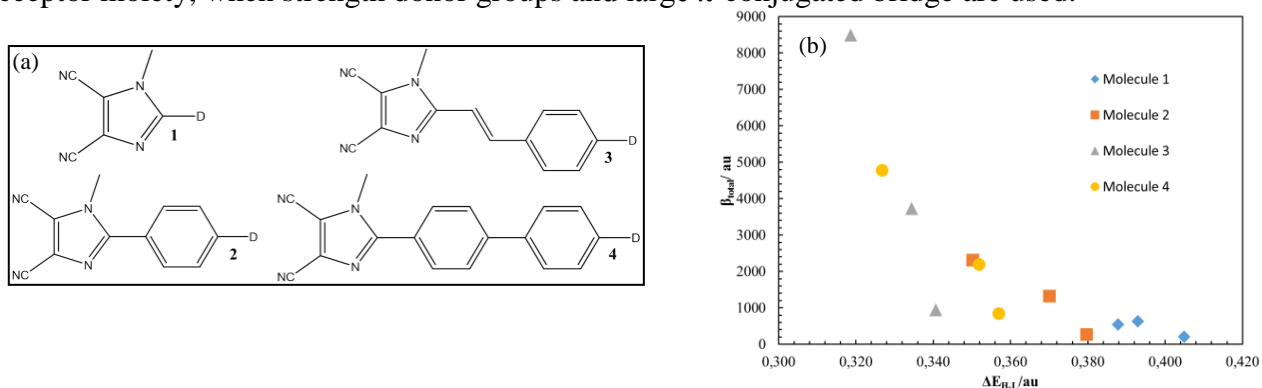


Figure 1: (a) 4,5-dicyanoimidazole molecules studied, where D: $-\text{H}$, $-\text{OCH}_3$, and $-\text{N}(\text{CH}_3)_2$. (b) β_{total} (au), as a function of gap energy HOMO-LUMO ($\Delta E_{\text{H-L}}$ /au), at MP2/6-31+G(d,p) level.