

2P099

共有結合性有機構造体の量子化学研究

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Quantum Chemical Investigation of Covalent Organic Frameworks

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A covalent organic framework (COF) is a crystalline porous polymer in which organic units are connected to each other by covalent bonds to form a 2D or 3D lattice structure. COFs have light weight, large pores and large surface area and can be applied for gas storage, gas separation, catalysis and so on. Especially, 2D-COF has a layered structure in which planar polymers are π -stacked, similar to graphite. Here we focus on a 2D-COF with donor and acceptor units, called DA-COF, developed by one of us.¹ In this structure, each of donors and acceptors stack precisely to form a column, like a segregated-stacked charge-transfer complex (Figure 1). The advantages of DA-COFs are atomically precise stacking and flexible units, allowing 2D and 3D structural design.² Furthermore, properties such as photo-induced electron transfer and photocurrent are expected.

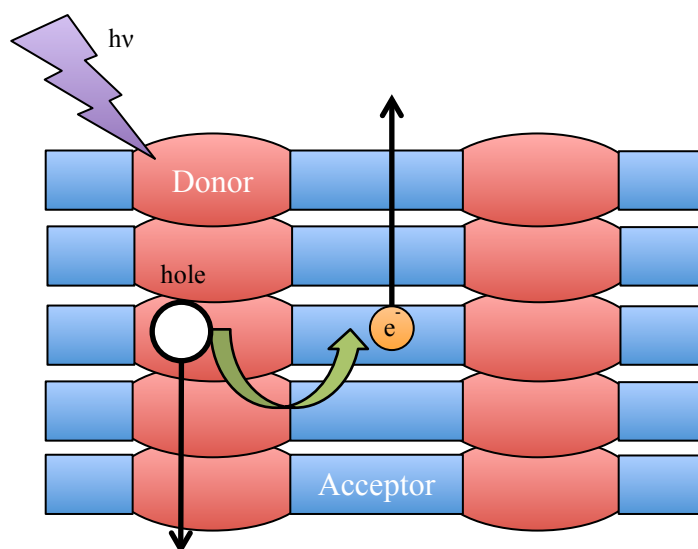


Figure 1: Image of a DA-COF with photo-induced electron transfer and photocurrent

In this work, we chose copper phthalocyanine-4-formylphenylboronic acid-zinc porphyrin (CuPc-FPBA-ZnP, Figure 2) as a sample DA-COF and performed the geometry optimization using the density-functional tight-binding (DFTB) method³ with self-consistent charge (SCC), including dispersion (UFF).⁴ First, we calculated the periodic monolayer structure by setting the c lattice parameter to 100 Å.

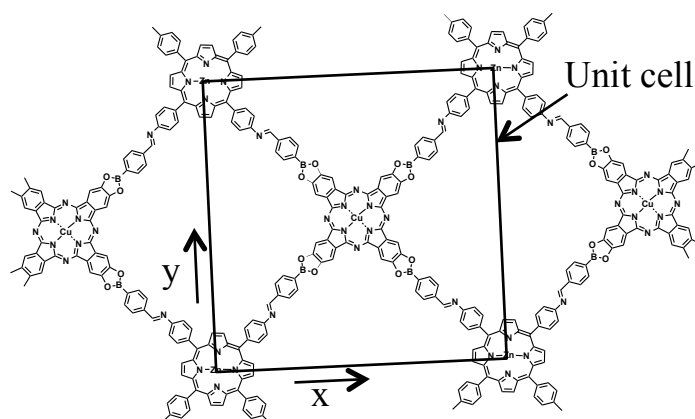


Figure 2: Molecular structure of CuPc-FPBA-ZnP

We investigated two possible rotamers of the phenyl groups (Ph) in ZnP, one with C_2 local point group and the other with C_4 . We calculated the periodic dimer structures, eclipsed AA, serrated AA, inclined AA, and staggered AB (called AA_e, AA_s, AA_i and AB), starting from the structures of the optimized monolayers. In the case of AA_s and AA_i, two slipping directions (x and xy) and three slipping lengths (1.0 Å, 1.5 Å and 2.0 Å) were tested. The initial distance between the layers was 3.5 Å. After the calculation, we obtained the stacking energies using

$$E_{stacking} = -(E_{dimer}/2 - E_{monolayer})$$

From the calculation result, the energy difference between C_2 and C_4 rotamer monolayers is very small, but the ones between the dimers are larger. In AA-type structures, C_2 dimers have lower energies than C_4 dimers, because in C_2 one layer can slip to avoid Ph-Ph repulsion while in C_4 when one layer slips in the same way it collides with another Ph of the neighboring layer. For the similar reason, serrated structures of C_2 are less stable than inclined structures. On the other hand, AB structures are much less stable because of the lack of π - π interactions.

In conclusion, we found that the slipped AA inclined structure with C_2 phenyl rotamers is most stable in CuPc-FPBA-ZnP. It is our goal for the future to calculate charge transfer and current conduction using this and other structures close in energy.

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