

PM7 Study on the Electronic Structure and Light Absorption of Some OPE (Oligo-Phenylene-Ethynylene Derivative)-RE₃N@C₈₀ Dyads

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Abstract: In this paper, we investigated the electronic structure and stability of some mesomorphic OPE-RE₃N@C₈₀ dyads from the oligo-phenylene-ethynylene derivatives (OPE) and the trimetallic nitride template endohedral fullerenes (TNT-EMFs) - RE₃N@C₈₀ (RE=Sc,Y,La) by using PM7, the updated version of the semi-empirical Hartree-Fock method. In OPE-RE₃N@C₈₀, the fullerene cages were modified to have the opened cage (fulleroid) structure by addition of OPE on the [6, 6] position of the fullerene cages. There was no considerable charge transfer between OPE and fullerene cage, but the fullerene cages had the remarkable minus charges mainly due to the electron transfer from RE₃N to the cage. The calculated electronic spectra showed that light absorption bands of OPE-C₈₀ were more red-shifted than that of OPE-RE₃N@C₈₀ and all of OPE-RE₃N@C₈₀ seem to have a couple of Vis-NIR absorption peaks.

Keywords: Endohedral Fullerene, Oligo-Phenylene-Ethynylene Derivatives, TNT-EMF, Quantum Chemistry, PM7

1. Introduction

Now it is well-known that fullerenes are not chemically inert and undergo various chemical reactions such as nucleophilic addition, Diel's-Alder reaction, 1,3-dipolar cycloaddition, radical addition, oxidation, reduction etc. [1, 2, 3] By chemical modifications of the fullerene cages there appeared a number of fullerene derivatives, which opened their potential application in practice. [4]

Many researches have been carried out for synthesis of the endohedral metallofullerenes (EMFs), the so-called "cluster-fullerene", containing metal atoms or clusters therein and for their application in manufacture of the useful nano-materials such as molecular devices and molecular medicines. [5] From the first preparation of La@C₈₂ in 1991, there made lots of advances in synthesis and application of the endohedral fullerenes with metal atoms or their nitride. [6]

Since the cluster fullerenes have peculiar properties useful in electronics, magnetics and photonics, they could enjoy the wider prosperity in many applications such as molecular

electronics and bio-technology. [7, 8] The recent reports showed the possibility of control of the stability, reactivity, solubility and function of the endohedral fullerenes by adding some organic compound on their surfaces. [9]

Especially, a variety of the trimetallic nitride template endohedral fullerenes (TNT-EMFs) such as RE₃N@C_n (RE = Sc, Y, La; n=78, 80, 82, ...) have been synthesized and modified for utilizing their functionalities in molecular electronics and bio-technology.[10] One of the most prosperous applications of RE₃N@C_n can be found in organic photovoltaics due to their excellent electron acceptor abilities. A recent research was carried out for synthesis of some π -conjugated system – fullerene dyads for photovoltaic applications, where the donor units were either oligo-phenylene-ethynylene (OPE) or oligo-phenylene-vinylene (OPV) derivatives and for the acceptor, C₆₀ or Y₃N@C₈₀ were used.[11] The liquid crystalline behavior, shown by the synthesized dyads was expected to improve the photovoltaic efficiency of the BHJ (block hetero-junction) organic solar cells by ambipolar charge transfer.

The rare earth elements (Sc, Y and lanthanides) have been attracting the interest of many research groups around the world due to their peculiar electronic, magnetic and biological characteristics including luminescence properties. Nowadays, increasing number of articles have been published every year on the synthesis of the functional materials containing the rare earth elements, but many of them could not be supported by the quantum chemical interpretation of their experimental results because of heavy cost of the theoretical computations. [12, 13]

To solve this problem, many researchers pay attention to MOPAC, the semi-empirical Hartree-Fock molecular orbital software package, which offers the most efficient quantum chemical calculations with the enhanced accuracy for a wide range of molecules, complexes, polymers, crystals, and TNT-EMFs. [12, 14] Especially, MOPAC2016, the latest version of MOPAC, has PM7 method and the Sparkle Models for lanthanides, and has wide application with other quantum chemical softwares such as LUMPAC [15] for design and preparation of the new series of the rare earth luminescence materials and supramolecular devices. [16]

In this paper, PM7 in MOPAC2016 was applied in the theoretical study on the electronic structure and stability of OPE-C₈₀ and OPE-RE₃N@C₈₀ dyads (RE = Sc, Y, La). There have been some reports on DFT (Density Functional Theory) study on RE₃N@C_n and their derivatives [5, 17], but still no research has been done on theoretical calculation of the electronic structures of the OPE-RE₃N@C₈₀ dyads.

2. Computational Models and Method

Here the quantum chemical study has been done on four OPE-FD dyads (OPE-C₈₀ and OPE-RE₃N@C₈₀), where FD

means C₈₀ and three kinds of RE₃N@C₈₀ (RE=Sc,Y,La).

For all the OPE-FDs, the geometry of C₈₀-I_h, one of the geometric isomers of C₈₀, was chosen as the fullerene cage, where I_h shows the geometric symmetry of the fullerene cage. (Figure 1)

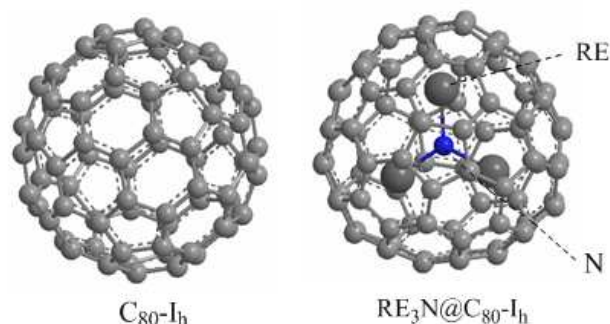


Figure 1. Models for FDs (RE=Sc,Y,La).

Figure 2 shows the chemical structures of the OPE-Y₃N@C₈₀ dyad, synthesized in the previous research. [11] According to that experimental research, the models for OPE-C₈₀ and OPE-RE₃N@C₈₀ dyad (RE=Sc, Y, La) were chosen as [6,6] adducts, where OPE was covalently linked to C₈₀ or RE₃N@C₈₀ just on the [6,6] addition site of the fullerene cage (the nearest site to RE atom in case of RE₃N@C₈₀). To simplify the task and avoid the overload in computation, the long alkyl chain R (-C₁₂H₂₅) in the OPE was shortened as -CH₃ in all the models for OPE-FDs.

The OPE-FDs can be separated as two individual subunits, OPE and FD, for comparing their electron donor – acceptor interaction. Here OPE₁ symbolizes a half part of OPE (Figure 3).

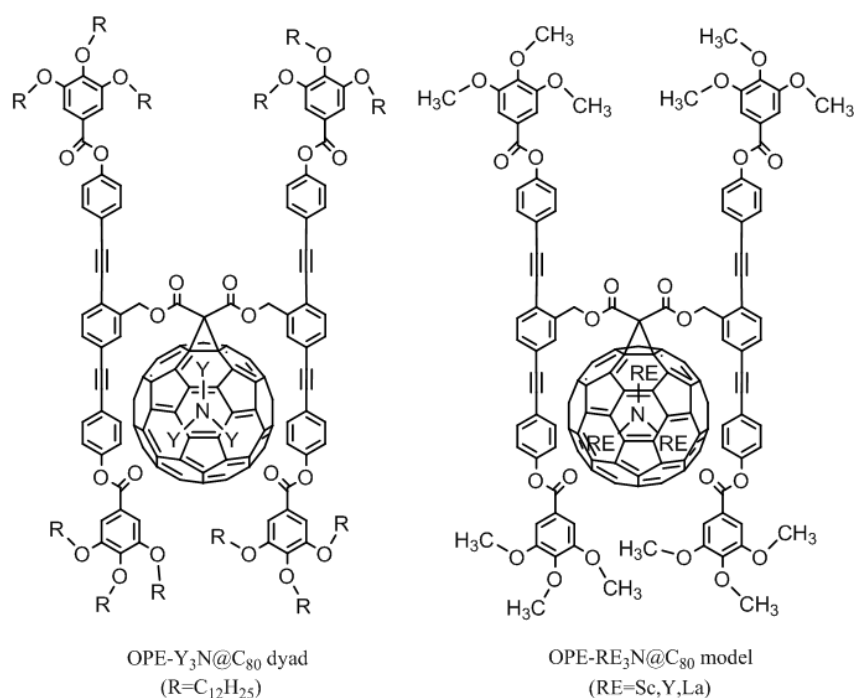


Figure 2. Models for OPE-FDs.

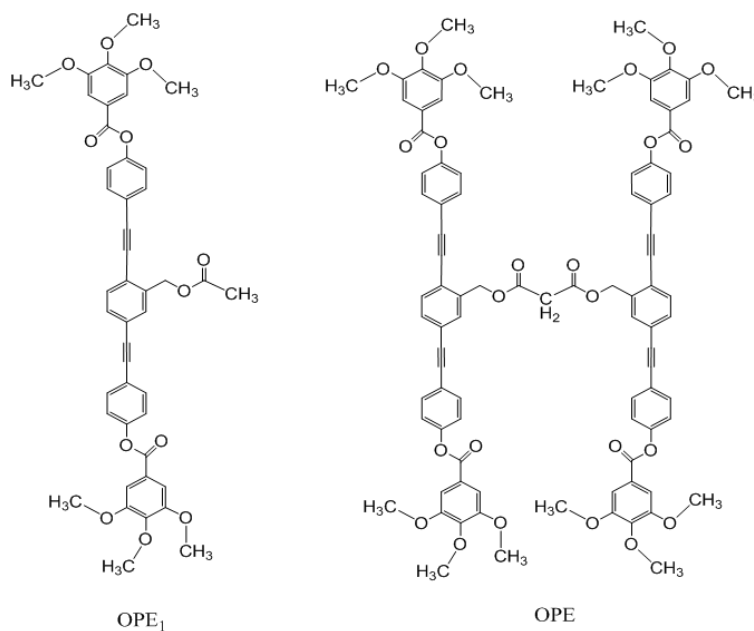


Figure 3. Models for OPE and OPE_l .

To consider the effect of RE_3N on the electronic structure of the $\text{OPE-RE}_3\text{N}@C_{80}$, the empty fullerene cage model without RE_3N was also calculated as OPE-C_{80} .

The geometric and electronic structures of the models were calculated by PM7 from MOPAC2016.

The first step of calculation was the geometry optimization by L-BFGS routine, which was followed by the configuration interaction (CI) calculation based on the single-point MO results. The configurations for the singlet electronic transitions were composed of 20 MOs near HOMO and LUMO (10 occupied MOs and 10 unoccupied MOs). The electronic spectra were drawn by using the Gaussian smoothing function based on the transition energies (mode positions) and the oscillator strengths (mode intensities).

Relative Stability of the OPE-FDs was evaluated by ΔE_t , the difference of total energies (E_t) between the resulting model (OPE-FD) and the separated subunits (OPE and FD).

3. Results and Discussion

1) *The geometric and electronic structures of the separated subunits (OPE and FDs)*

Figure 4 shows the optimized geometric structures of OPE and its one branch (OPE₁), where the phenylethynyl unit (-C₆H₄-C≡C-C₆H₄-C≡C-C₆H₄-) is arranged to form a straight line, but its three phenyl rings are not on the same plane, which prevents the formation of a larger π -conjugation plane in OPE.

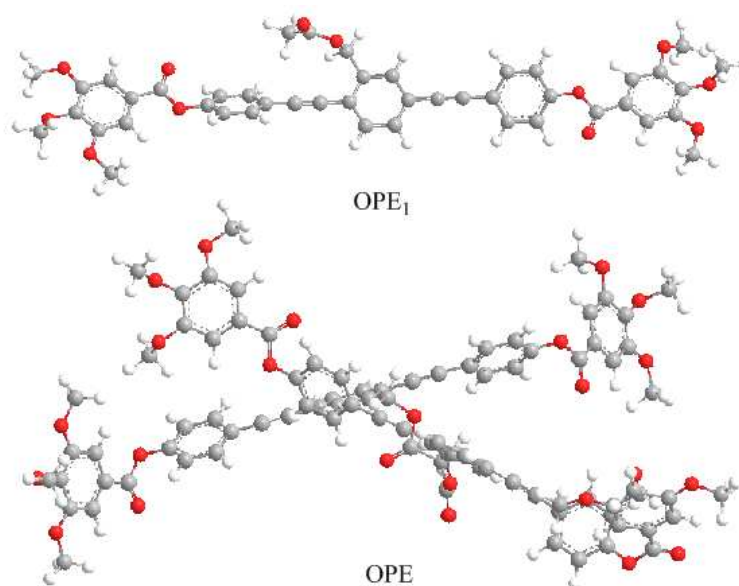


Figure 4. The optimized geometric structures of OPE and its one branch (OPE_1).

It can be seen from the optimized geometric structures of RE₃N@C₈₀ in Figure 5 that RE₃N (RE = Sc, La) has the planar form, but Y₃N has the pyramidal form, which resembles the previous XRD measurement of Gd₃N@C₈₀-I_h and DFT calculation of Y₃N@C₇₈-D_{3h}. [18, 19]

From the electronic structures of RE₃N@C₈₀ calculated

from their optimized geometry, it was found out that the positive charge of RE atoms was increased and the negative charge of N atom decreased in the cluster fullerene compared with those in free RE₃N, which shows that in RE₃N@C₈₀ more portion of electrons of RE atoms was transferred to the fullerene cage, not to N atom.

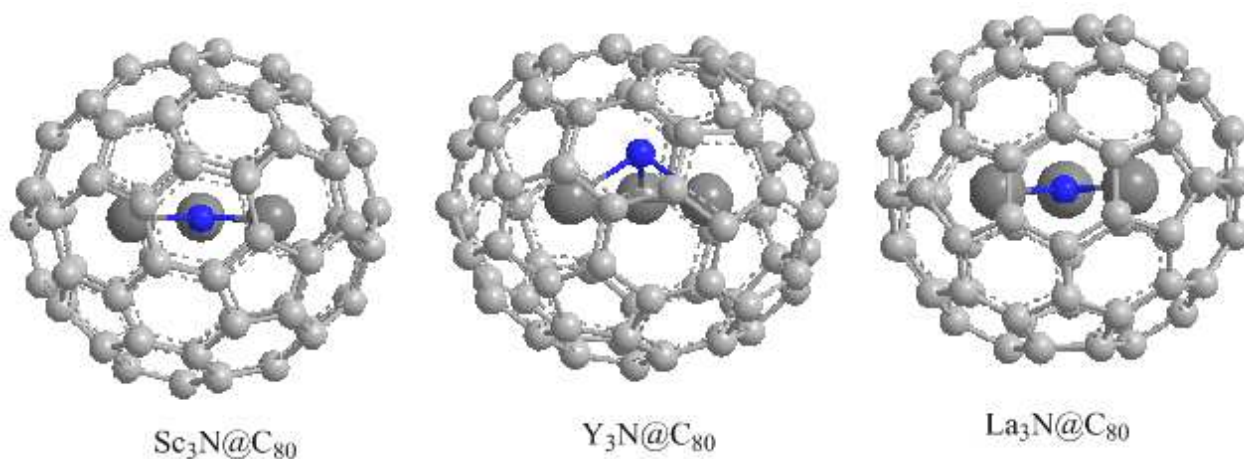


Figure 5. The optimized geometric structures of RE₃N@C₈₀.

Figure 6 shows that OPE₁ and OPE have the similar HOMO-LUMO levels, which means there can not be apparent π -conjugation between two phenylethynyl branches in OPE. All FDs (C₈₀ and RE₃N@C₈₀) have lower LUMO

levels than OPE, therefore they can accept electron from OPE. HOMO levels of RE₃N@C₈₀ are lower than that of the empty C₈₀. It can be explained as the result of stabilization of the C₈₀ cage by RE₃N incorporation. [20]

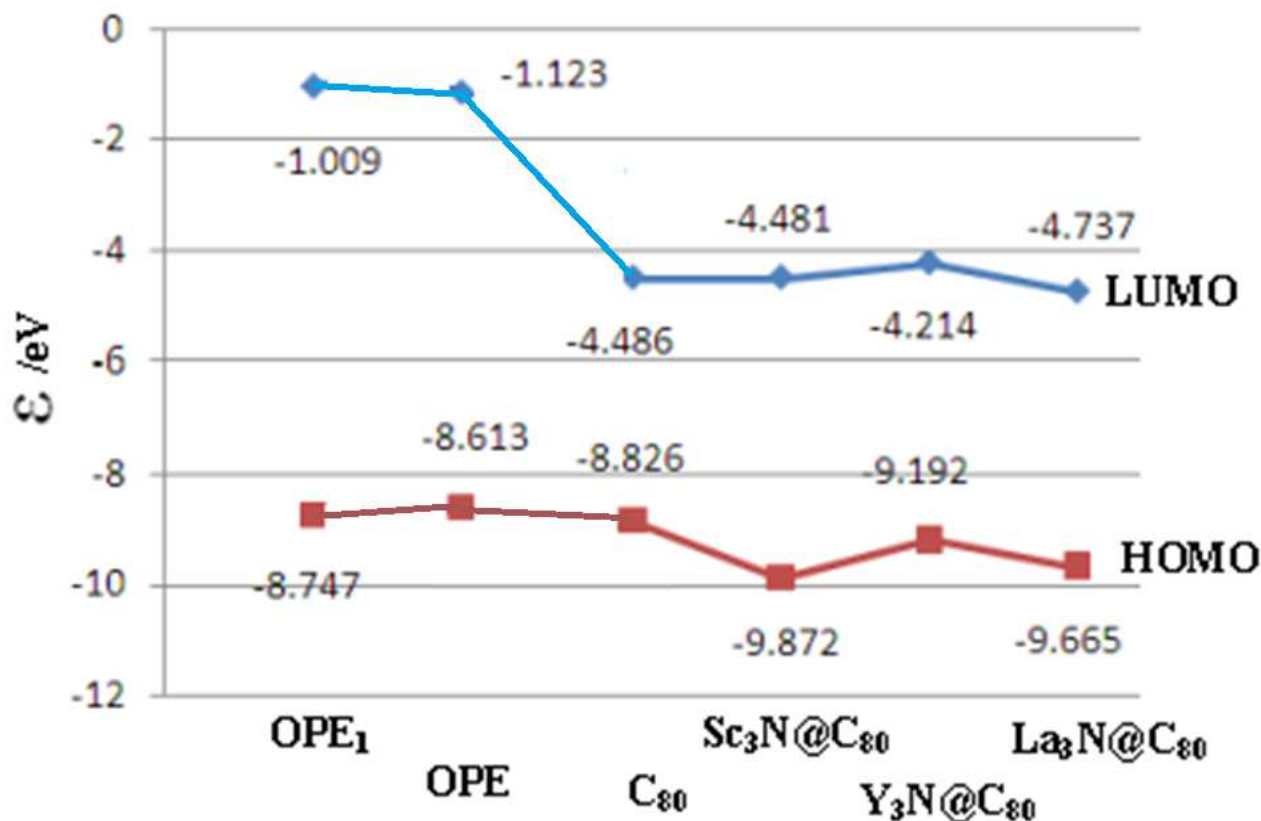


Figure 6. HOMO – LUMO energy levels of subunits of OPE-FDs.

From Figure 7, it can be seen that OPE has UV absorption, but FDs can interact with visible light or even with NIR. OPE has a long chain of phenylethynyl units, which makes it have more red-shifted peaks than FDs. The peak separation in UV range from $\text{Sc}_3\text{N}@C_{80}$ to $\text{La}_3\text{N}@C_{80}$ can be explained like that La (6s, 6p, 5d) has more diverse interaction with the fullerene cage than Sc (4s, 4p, 3d).

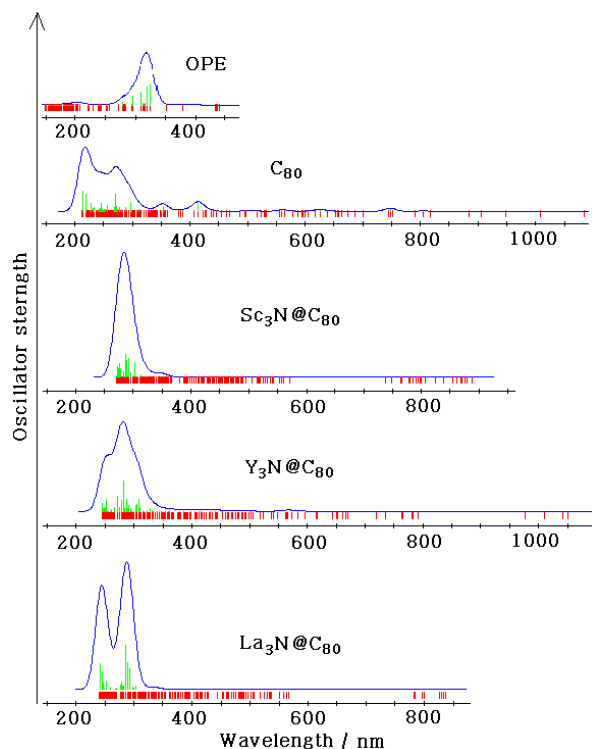


Figure 7. The electronic spectra of OPE and FDs (red: mode positions, green: mode intensities).

2) The geometric and electronic structures of OPE-FDs

Four models of the OPE-FDs discussed in this paper had the similar configurations after geometric optimization (Figure 8).

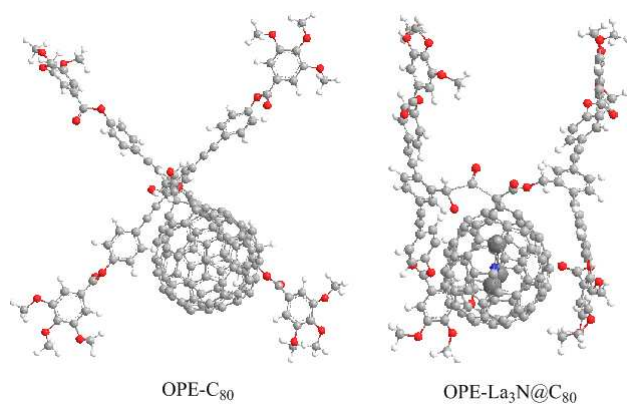


Figure 8. The different views of the optimized structures of OPE-FDs.

These configurations may be different from those of the real OPE-FD dyads [11] because these models have the shorten alkyl group ($-\text{CH}_3$) instead of the long chain ($-\text{C}_{12}\text{H}_{25}$) and can not express their well-assembled frameworks in the liquid crystalline phase.

From Figure 7, it can be seen that OPE has UV absorption, but FDs can interact with visible light or even with NIR. OPE has a long chain of phenylethynyl units, which makes it have more red-shifted peaks than FDs. The peak separation in UV range from $\text{Sc}_3\text{N}@C_{80}$ to $\text{La}_3\text{N}@C_{80}$ can be explained like that La (6s, 6p, 5d) has more diverse interaction with the fullerene cage than Sc (4s, 4p, 3d).

Figure 9 shows ΔE_t of the OPE-fullerenes calculated as the total energy difference of OPE-FD from its separated subunits (OPE and FD). OPE- C_{80} became to be unstable after the formation of the dyad and it can be considered as the result of structural deformation of the subunits, especially C_{80} due to the formation of the dyad. The most stable one was OPE- $\text{La}_3\text{N}@C_{80}$ and other OPE- $\text{RE}_3\text{N}@C_{80}$ were also more stable than OPE- C_{80} because all of $\text{RE}_3\text{N}@C_{80}$ had been stabilized by electron transfer from RE_3N to C_{80} .

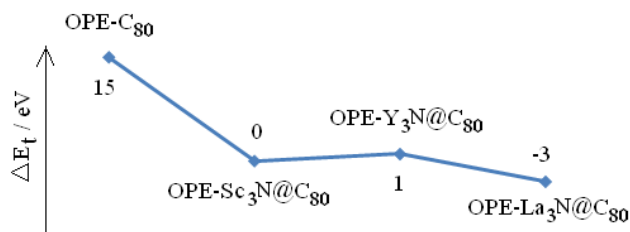


Figure 9. Relative stability (ΔE_t) of OPE-FDs.

In all of OPE-FDs, the fullerene cages were modified to have the open-up cage (fulleroid) structures. Table 1 shows the C-C distances at the [6, 6] OPE-addition sites of FDs and their increases (ΔR_{C-C}) after OPE-addition, where more stable OPE- $\text{La}_3\text{N}@C_{80}$ had the less ΔR_{C-C} and less stable OPE- C_{80} and OPE- $\text{Y}_3\text{N}@C_{80}$ had the larger ΔR_{C-C} .

Table 1. C-C distance at the [6,6] addition site of FDs (nm).

model	OPE- C_{80}	OPE- $\text{Sc}_3\text{N}@C_{80}$	OPE- $\text{Y}_3\text{N}@C_{80}$	OPE- $\text{La}_3\text{N}@C_{80}$
free FD	0.142	0.148	0.153	0.149
OPE-FD	0.235	0.239	0.247	0.234
ΔR_{C-C}	0.093	0.091	0.094	0.085

Table 2 shows the local charges of the subunits (OPE, C_{80} cage, RE_3N) in OPE-FDs, where there was no considerable charge transfer between OPE and FDs, but in OPE- $\text{RE}_3\text{N}@C_{80}$ the fullerene cages had the remarkable minus charges mainly due to the electron transfer from RE_3N to the cage. It seems that the more electrons were transferred from RE_3N to C_{80} , the more stable OPE- $\text{RE}_3\text{N}@C_{80}$ was formed.

Table 2. Local charges of the subunits in OPE-FDs (e).

model	OPE- C_{80}	OPE- $\text{Sc}_3\text{N}@C_{80}$	OPE- $\text{Y}_3\text{N}@C_{80}$	OPE- $\text{La}_3\text{N}@C_{80}$
OPE	0.012	0.071	0.037	0.069
C_{80} cage	-0.012	-4.454	-3.976	-4.471
RE_3N	-	4.383	3.939	4.402

From the electronic spectra of OPE-FDs (Figure 10), it can be found out that light absorption band of OPE- C_{80} was more red-shifted than that of OPE- $\text{RE}_3\text{N}@C_{80}$, but its maximum absorption intensity was far less than OPE- $\text{RE}_3\text{N}@C_{80}$, and all of OPE-FDs seem to have a couple of Vis-NIR absorption peaks.

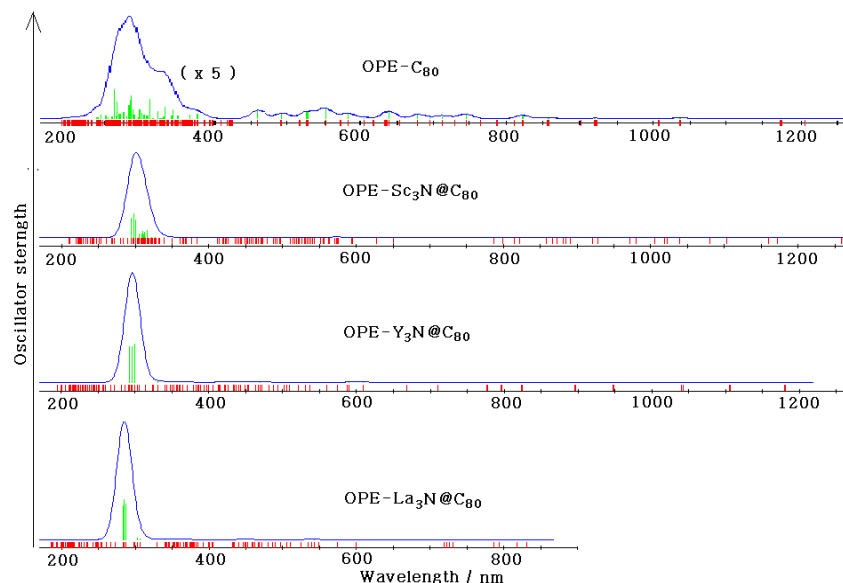


Figure 10. The electronic spectra of OPE-FDs (red: mode positions, green: mode intensities).

The red-shifted band of OPE-C₈₀ compared with OPE-RE₃N@C₈₀ can be considered as a result of larger bandgap between HOMO and LUMO: in case of OPE-C₈₀ it was 3.742eV, but OPE-La₃N@C₈₀ has 4.444eV. Moreover, In OPE-C₈₀ both of HOMO and LUMO were located on the fullerene cage, but in OPE-La₃N@C₈₀ HOMO was on the cage and LUMO was fixed on La₃N, which means the mechanisms of the electronic excitation in OPE-C₈₀ and OPE-RE₃N@C₈₀ can be different. (Figure 11, 12)

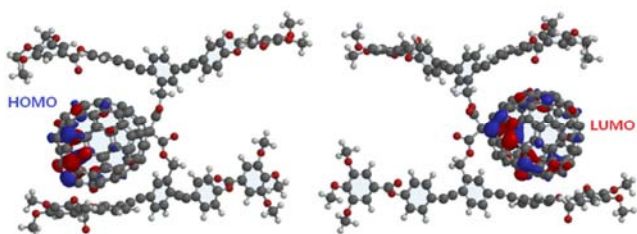


Figure 11. Location of HOMO and LUMO in OPE-C₈₀.

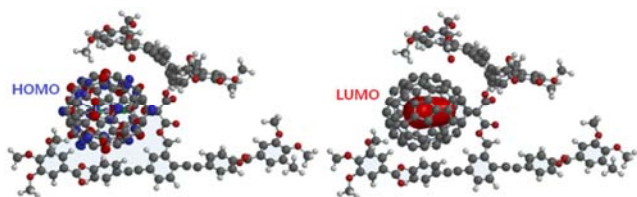


Figure 12. Location of HOMO and LUMO in OPE-La₃N@C₈₀.

4. Conclusion

PM7 calculations were carried out on four OPE-fullerene dyads (OPE-FDs) such as OPE-C₈₀ and OPE-RE₃N@C₈₀ (RE = Sc, Y, La).

In all of OPE-FDs, the fullerene cages were modified to have the open-up cage (fulleroid) structure by addition of OPE on the [6, 6] position of the fullerene cages. The C-C

distance at the [6, 6] addition site of the cages was less increased in the more stable OPE-FDs.

There was no considerable charge transfer between OPE and FDs, but in OPE-RE₃N@C₈₀ the fullerene cages had the remarkable minus charges mainly due to the electron transfer from RE₃N to the cage.

Light absorption bands of OPE-C₈₀ were more red-shifted than that of OPE-RE₃N@C₈₀ and all of OPE-FDs seem to have a couple of Vis-NIR absorption peaks.

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