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## Support information

# Orbital polarization dependent fragment twist-induced intra-molecular electric field driven charge transfer

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### S1. Method

#### S1.1. Dipole moments

Dipole moments are vital for analyzing local polarities. In this section, the dipole moment is obtained by quantum chemical. The formula for calculating the dipole moment vector of a fragment F composed of certain atoms in the system is (S1):

$$\mathbf{D}_F = \sum_{A \in F} \left[ Z_A \mathbf{R}_A - \int w_A(\mathbf{r}) \rho(\mathbf{r}) \mathbf{r} d\mathbf{r} \right] \quad (\text{S1})$$

Where R is the nuclear position, Z is the nuclear charge,  $\rho$  is the electron density, and  $w$  is the atomic weight function.

#### S1.2. Electrostatic potential

Electrostatic potential refers to the electrostatic interaction between a unit point charge at the  $\mathbf{r}$  position and the system. The formula for calculating the electrostatic potential in a molecular system is (S2):

$$V_{\text{Total}}(\mathbf{r}) = V_{\text{Nuc}}(\mathbf{r}) + V_{\text{Elec}}(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (\text{S2})$$

where Z and R represent the nuclear charge and nuclear position, respectively. Positive (negative) values indicate positions governed by nuclear (electron) charge.

#### S1.3. Polarity

To quantify molecular polarity, a molecular polarity index (MPI) [43-44] is defined, which is related to the  $\Pi$  index. The calculation formula of (MPI) is (S3):

$$\text{MPI} = (1/t) \sum_{k=1}^t |V(\mathbf{r}_k)| \equiv (1/A) \iint_S |V(\mathbf{r})| dS \quad (\text{S3})$$

where V is the molecular electrostatic potential, the integral is the integral over the molecular surface S, and A is the molecular surface area, and  $\Pi$  is the average deviation across the surface, regarded as an indicator of internal charge separation. MPI is a very reliable norm of molecular polarity, and the larger the index, the greater the polarity.

#### S1.4. Density of states

When calculating the DOS in quantum chemistry, the original total DOS (TDOS) of the isolated system can be written as (S4)

$$\text{TDOS}(E) = \sum_i \delta(E - \varepsilon_i) \quad (\text{S4})$$

where  $\{\varepsilon\}$  is the orbital energy and  $\delta_{is}$  is the Dirac function.

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The TDOS value has the same interval at each molecular orbital energy level point, and the TDOS plot is drawn as a series of vertical lines. The DOS curve cannot clearly show the density of states of the separated system, and the orbital distribution density of different energy regions cannot be analyzed intuitively, so the broadening function  $F(x)$  is used to replace  $\delta_{is}$ , and the broadened TDOS is obtained. The normalized Gaussian function is defined as:

$$G(x) = \frac{1}{c\sqrt{2\pi}} e^{-\frac{x^2}{2c^2}} \quad (S5)$$

$$c = \frac{FWHM}{2\sqrt{2\ln 2}} \quad (S6)$$

The larger the full width at half maximum (FWHM), the larger the peak of the curve, the smoother the DOS graph looks, and the more helpful for research. The curve that a specific segment contributes to TDOS is the local DOS. By defining the segment, this work studies the nature and bulk composition of orbitals in different energy intervals in the PDOS diagram. For example, define the PDOS of fragment A as formula (S7)  $\Theta_{i,A}$  where is the composition of fragment A in orbit i.

$$PDOS_A(E) = \sum_i \Theta_{i,A} F(E - \varepsilon_i) \quad (S7)$$

For such close structures, they have similar energies and roughly the same number of states. In the energy level range from -21.7 to -5.3 eV, the total density of states is dominated by the PX, PY and PZ orbitals. In the energy level range from -2.2 to 5.5 eV, the overall density of states is dominated by the PZ orbitals, which allows more electrons to remain in the PZ orbitals and be spin-polarized, which in turn enhances the local spin-polarization. The DOS between the two spikes flanking the Fermi level of O9H in the six figures is not zero and is broad. It shows that the covalent bond of the system is relatively strong at this time, and the smaller the electronegativity, the greater the polarization.

#### S1.5. Electrons and holes

The optical properties of molecules largely depend on the transition of electrons. According to the quantum theory of electronic transitions, the transition probability is related to the intrinsic dipole integral of the ground and excited states. The dipole moment can be seen as the electric dipole generating a local electric field so the modulation of the intramolecular electric field can affect the electronic transition. Expressions for electrons and holes for TDHF/TDDFT are (S8):

$$\begin{aligned} \rho^{\text{hole}}(\mathbf{r}) &= \rho_{(\text{loc})}^{\text{hole}}(\mathbf{r}) + \rho_{(\text{cross})}^{\text{hole}}(\mathbf{r}) \\ \rho_{(\text{loc})}^{\text{hole}}(\mathbf{r}) &= \sum_{i \rightarrow a} (w_i^a)^2 \varphi_i \varphi_i - \sum_{i \leftarrow a} (w_i^a)^2 \varphi_i \varphi_i \\ \rho_{(\text{cross})}^{\text{hole}}(\mathbf{r}) &= \sum_{i \rightarrow a} \sum_{j \neq i \rightarrow a} w_i^a w_j^a \varphi_i \varphi_j - \sum_{i \leftarrow a} \sum_{j \neq i \leftarrow a} w_i^a w_j^a \varphi_i \varphi_j \\ \rho^{\text{ele}}(\mathbf{r}) &= \rho_{(\text{loc})}^{\text{ele}}(\mathbf{r}) + \rho_{(\text{cross})}^{\text{ele}}(\mathbf{r}) \\ \rho_{(\text{loc})}^{\text{ele}}(\mathbf{r}) &= \sum_{i \rightarrow a} (w_i^a)^2 \varphi_a \varphi_a - \sum_{i \leftarrow a} (w_i^a)^2 \varphi_a \varphi_a \\ \rho_{(\text{cross})}^{\text{ele}}(\mathbf{r}) &= \sum_{i \rightarrow a} \sum_{i \rightarrow b \neq a} w_i^a w_i^a \varphi_a \varphi_b - \sum_{i \leftarrow a} \sum_{i \leftarrow b \neq a} w_i^a w_i^a \varphi_a \varphi_b \end{aligned} \quad (S8)$$

Where  $\mathbf{r}$  is the coordinate vector,  $\varphi$  is the orbital wave function,  $i$  or  $j$  is the occupied orbital label, and  $a$  or  $b$  is the empty orbital label.  $\sum i \rightarrow a$  represents the excited configuration of the cycle, and  $\sum i \leftarrow a$  represents the de-excited configuration of the cycle. The distribution of electrons and holes has local terms and cross terms. The dominant term is about the local term, which reflects the contribution of the configuration function, while the cross term can be ignored because it reflects the effect of the coupling between the configuration functions on the distribution of holes and electrons. TDM was used to analyze the photoelectron excitation properties. The transition density matrix is an effective tool for analyzing charge transfer between atoms. The core part of the transfer density matrix is to obtain the transfer density. It can be written in the basis function as (S9):

$$P_{\mu\nu}^{tran} = \sum_i^{occ} \sum_j^{vir} w_i^j C_{\mu i} C_{\nu j} \quad (S9)$$

where  $C_{\mu i}$  represents the expansion coefficient of the basis function  $\mu$  in molecular orbital  $i$ . And TDM in real space can be easily constructed by TDM in basis function representation.

$$T(\mathbf{r}; \mathbf{r}') = \sum_{\mu} \sum_{\nu} P_{\mu\nu}^{tran} \chi_{\mu}(\mathbf{r}) \chi_{\nu}(\mathbf{r}') \quad (S10)$$

The off-diagonal elements of the TDM essentially represent the coupling between various basis functions during electron excitation. The excitation can be perfectly expressed as an orbital transition, and the TDM can be written explicitly as (S11):

$$P_{\mu\nu}^{tran} = \begin{bmatrix} C_{vi} C_{\mu j} & C_{vi} C_{\nu j} \\ C_{\mu i} C_{\mu j} & C_{\mu i} C_{\nu j} \end{bmatrix} \quad (S11)$$

If the off-diagonal elements are large, this means that the basis functions contribute significantly to holes (occupant orbitals) and electrons (virtual orbitals), respectively. In this case, it can be said that the two basis set functions are strongly coupled in the excitation process. Since the transition density is contributed by different basis functions (those belonging to different atomic centers), the transitions represented by this transition density can be regarded as charge transfer excitations. The diagonal term also makes sense if the element has a larger magnitude, which means that the basis function must have a larger contribution to both holes and electrons. First of all, according to the numerical value of the elements on the diagonal, it can be judged where the electrons and holes have a significant distribution at the same time. For the electron-hole density map, the blue and red isosurfaces describe the electron and hole densities, respectively. In the TDM diagram, the diagonal part represents the local excitation and the off-diagonal part represents the charge transfer. The abscissa and ordinate correspond to the positions of holes and electrons, respectively. The position of electron-hole density change can intuitively reflect the increase and decrease regions of electron density in the transition of electrons from the ground state to the excited state, and can help to understand the internal characteristics of electronic excitation.

In this work, electron excitation characteristics are discussed by some quantitative numerical methods:

$$\begin{aligned}
S_r \text{ index} &= \int S_r(\mathbf{r}) d\mathbf{r} \equiv \int \min[\rho^{\text{hole}}(\mathbf{r}), \rho^{\text{ele}}(\mathbf{r})] d\mathbf{r} \\
S_r \text{ index} &= \int S_r(\mathbf{r}) d\mathbf{r} \equiv \int \sqrt{\rho^{\text{hole}}(\mathbf{r}) \rho^{\text{ele}}(\mathbf{r})} d\mathbf{r} \\
D \text{ index} &= \sqrt{(D_x)^2 + (D_y)^2 + (D_z)^2} \\
\sigma_{\text{hole},x} &= \sqrt{\int (x - X_{\text{hole}})^2 \rho^{\text{hole}}(\mathbf{r}) d\mathbf{r}} \\
\Delta\sigma \text{ index} &= |\sigma_{\text{ele}}| - |\sigma_{\text{hole}}| \\
H_\lambda &= (\sigma_{\text{ele}, \lambda} + \sigma_{\text{hole}, \lambda}) / 2 \quad \lambda = \{x, y, z\} \\
H_{CT} &= H \\
H \text{ index} &= (|\sigma_{\text{ele}}| + |\sigma_{\text{hole}}|) / 2 \\
t \text{ index} &= D \text{ index} - H_{CT}
\end{aligned} \tag{S12}$$

### S1.6. The transition dipole moment

The matrix element of the transition dipole moment matrix is defined as the product of the dipole moment integral between the corresponding TDM matrix element and the corresponding basis function. The transition dipole moment matrix has three components,  $X$ ,  $Y$ , and  $Z$ , such as the sum of all matrix elements of the  $X$  component matrix is exactly the  $X$  component of the system transition dipole moment. The transition dipole moment matrix can also be contracted into atom-based form, and the  $X$ ,  $Y$ , and  $Z$  components of the atomic transition dipole moment matrix are defined as (S13):

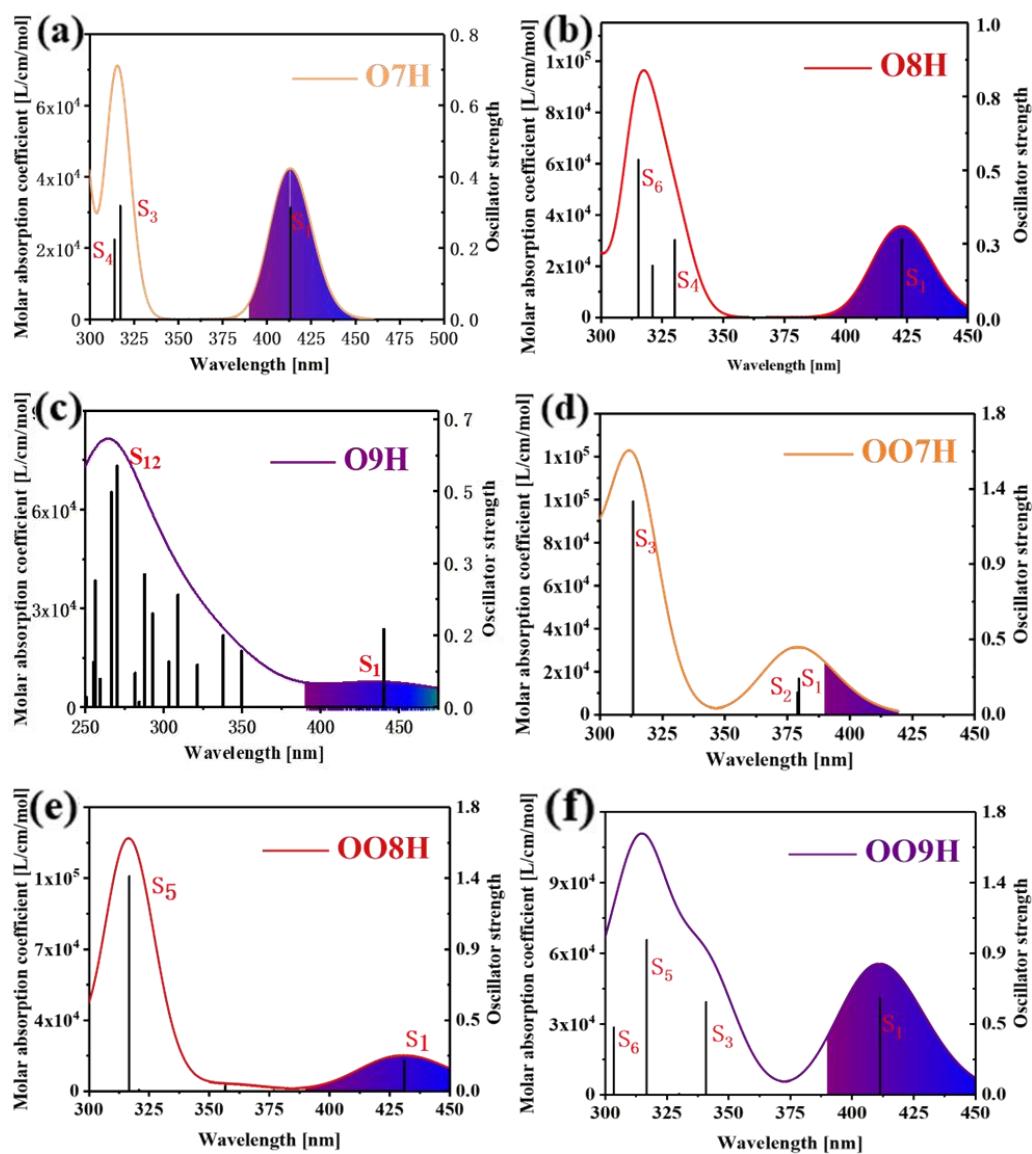
$$\begin{aligned}
D_{A,B}^X &= \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^{\text{tran}} \langle \chi_\mu | -x | \chi_\nu \rangle \\
D_{A,B}^Y &= \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^{\text{tran}} \langle \chi_\mu | -y | \chi_\nu \rangle \\
D_{A,B}^Z &= \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^{\text{tran}} \langle \chi_\mu | -z | \chi_\nu \rangle
\end{aligned} \tag{S13}$$

## S2. Figures, Tables

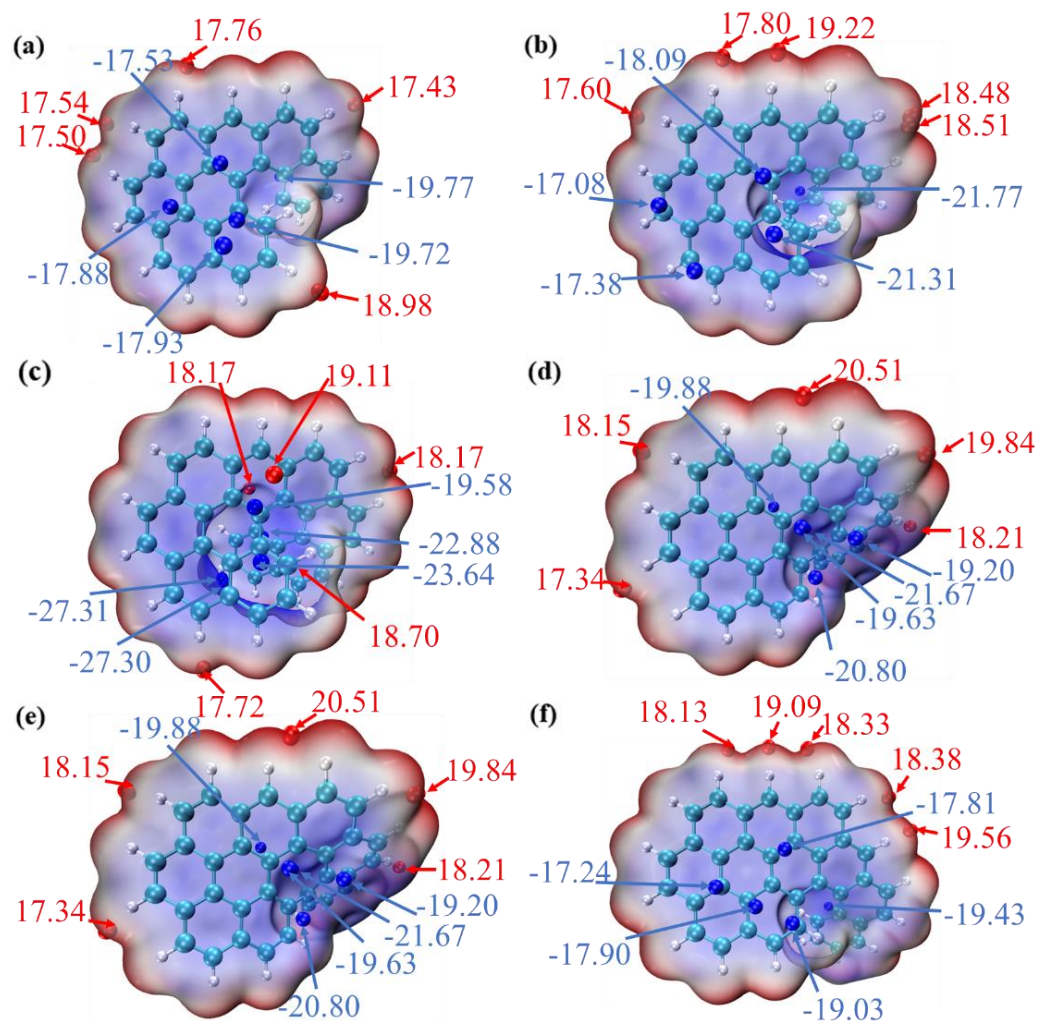
**Table S1.** The dipole moments and dipole moment components of benzo [ghi] perylene of the compound, the side and the whole system are shown in the table.

|     | a.u.               | dx      | dy      | dz      | total  |
|-----|--------------------|---------|---------|---------|--------|
| O7H | all                | -0.0308 | 0.0057  | -0.0007 | 0.0313 |
|     | benzo[ghi]perylene | 0.5891  | 0.0418  | -0.0958 | 0.5983 |
|     | side               | -0.6199 | -0.0361 | 0.0951  | 0.6282 |
| O8H | all                | -0.0768 | 0.0205  | -0.0188 | 0.0817 |
|     | benzo[ghi]perylene | 0.3668  | 0.5301  | -0.1215 | 0.6560 |
|     | side               | -0.6588 | 0.0993  | 0.0101  | 0.6663 |
| O9H | all                | -0.1120 | -0.0452 | 0.0060  | 0.1210 |
|     | benzo[ghi]perylene | 0.7325  | -0.1669 | -0.1155 | 0.7601 |

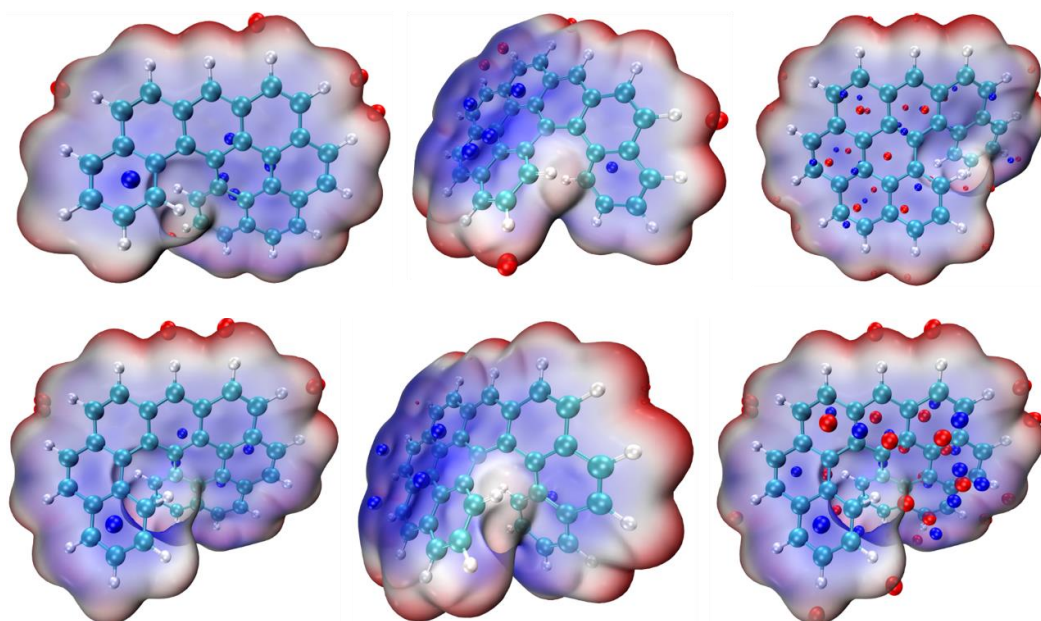
|      |                    |         |         |         |        |
|------|--------------------|---------|---------|---------|--------|
|      | side               | -0.8445 | -0.1217 | -0.1214 | 0.8618 |
|      | all                | 0.0065  | -0.0526 | 0.0000  | 0.0530 |
| OO7H | benzo[ghi]perylene | -0.9407 | -0.0832 | 0.0000  | 0.9444 |
|      | side               | 0.9472  | 0.0307  | 0.0000  | 0.9477 |
|      | all                | -0.0854 | 0.1855  | -0.0207 | 0.2053 |
| OO8H | benzo[ghi]perylene | 0.9260  | -0.2701 | -0.0807 | 0.9680 |
|      | side               | -0.9851 | 0.1882  | 0.0107  | 1.0030 |
|      | all                | -0.0410 | 0.0182  | 0.0038  | 0.0450 |
| OO9H | benzo[ghi]perylene | -2.0082 | 0.7801  | -0.2596 | 2.1699 |
|      | side               | -1.3918 | 0.2977  | 0.1819  | 1.4349 |



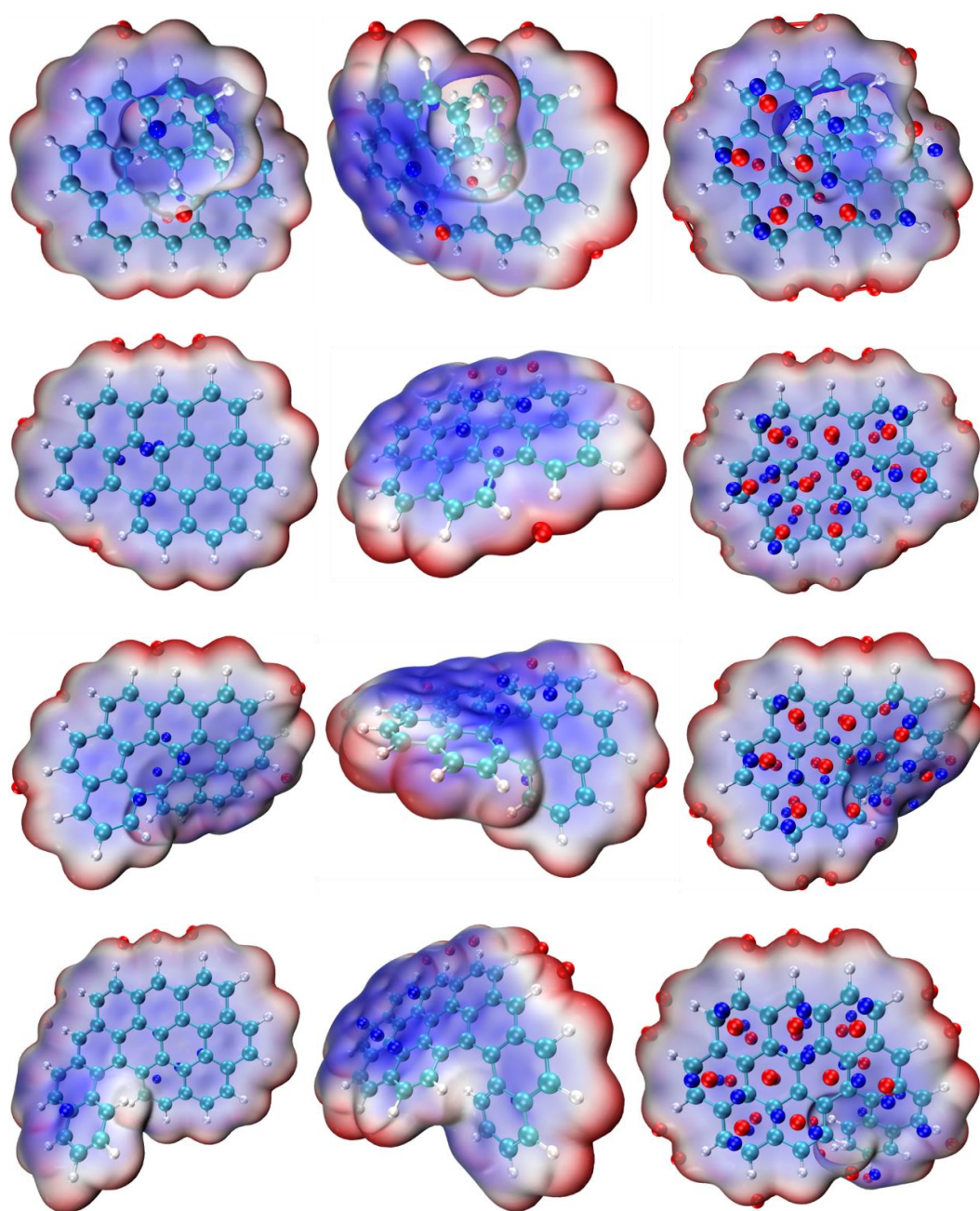
**Figure S1.** UV-Vis absorption spectra of 6 molecules: (a) O7H, (b) O8H, (c) O9H, (d) OO7H, (e) OO8H, (f) OO9H.



**Figure S2.** Electrostatic potential map of 6 molecules: (a) O7H, (b) O8H, (c) O9H, (d) OO7H, (e) OO8H, (f) OO9H.







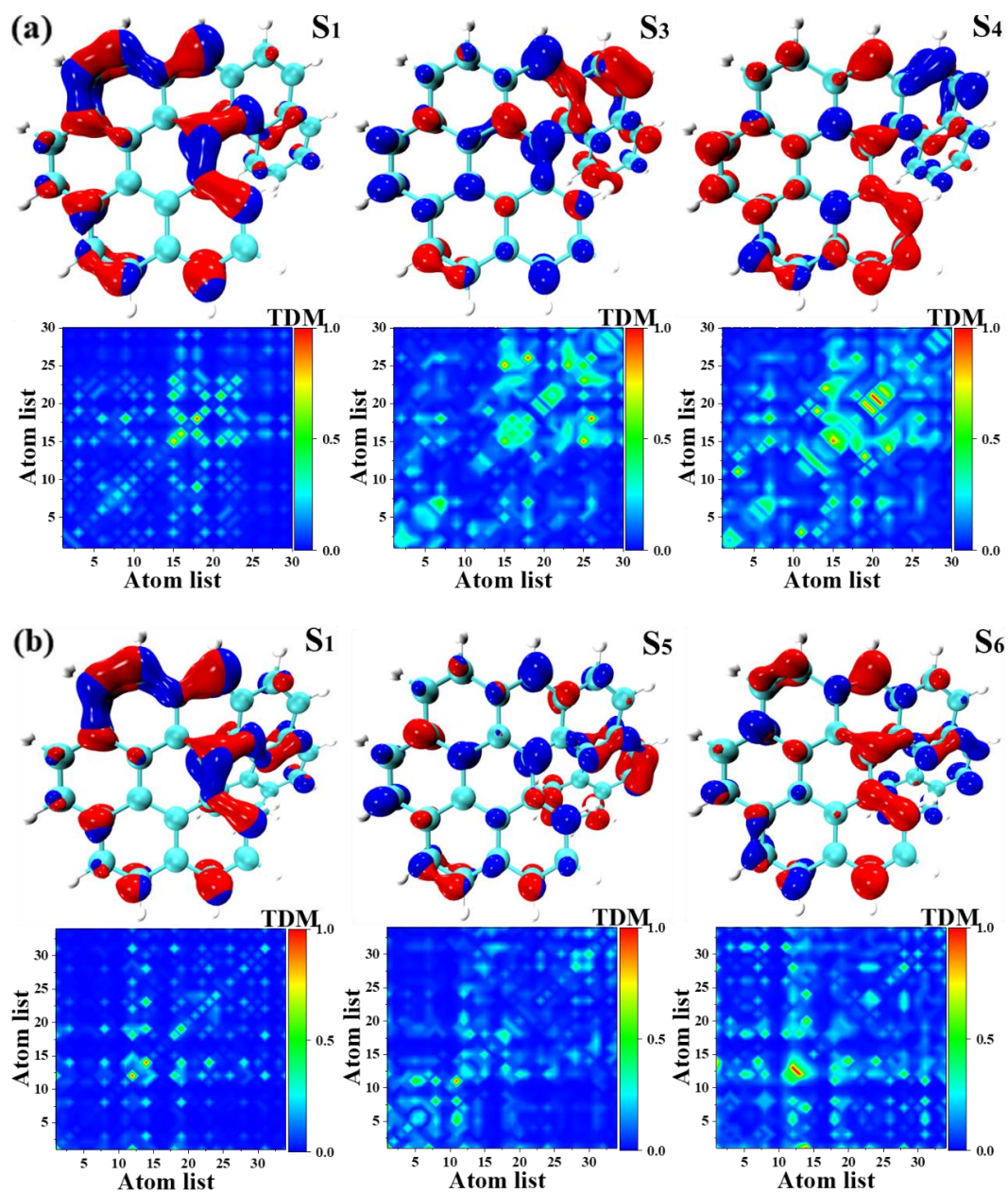
**Figure S3.** Electrostatic potential of 6 molecules from multiple angles.

**Table S2.** MPI values for 6 molecules.

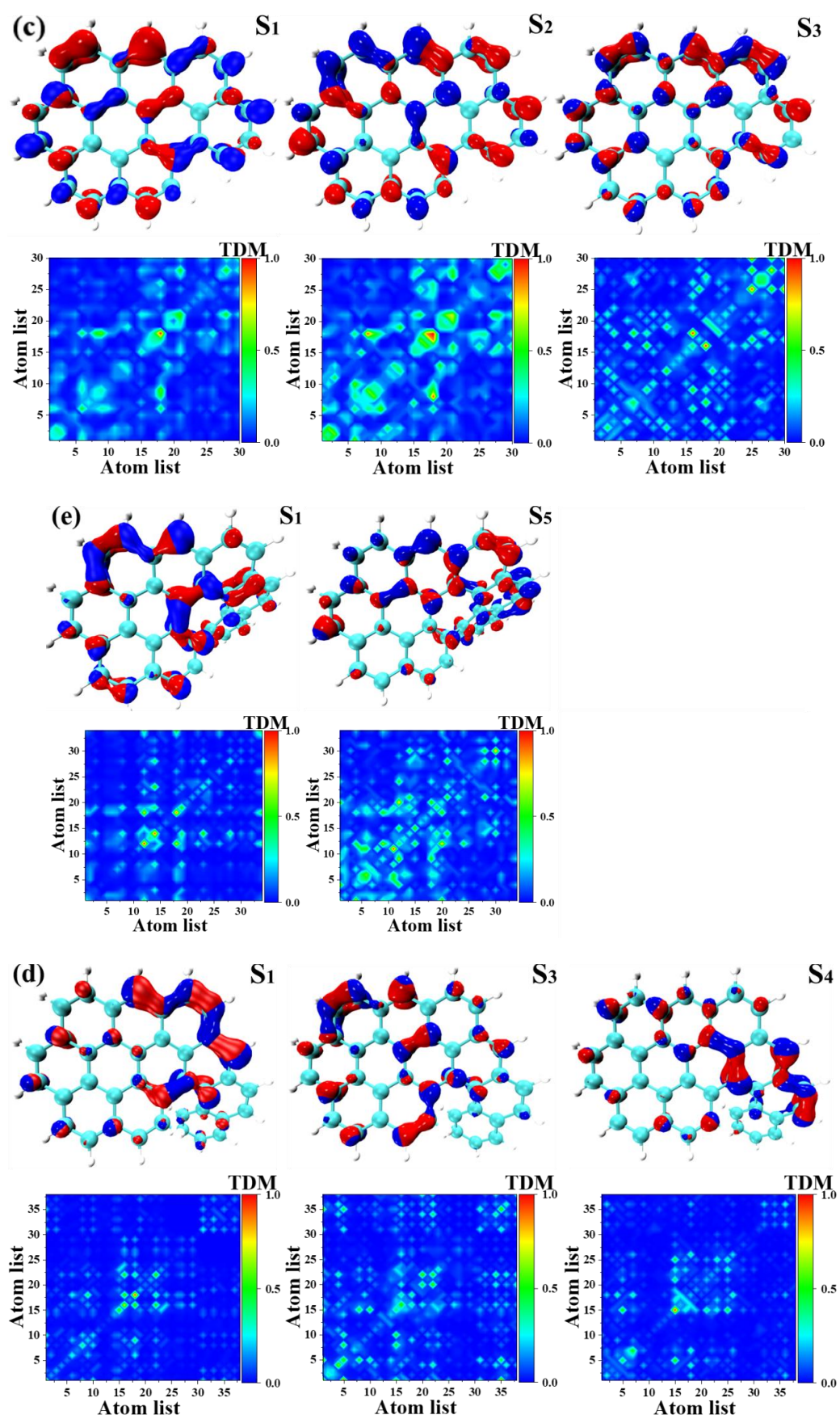
| Molecular | MPI(kcal/mol) |
|-----------|---------------|
| O7H       | 10.41235      |
| O8H       | 10.57574      |
| O9H       | 10.60316      |
| OO7H      | 11.49283      |
| OO8H      | 11.48095      |
| OO9H      | 10.79676      |

**Table S3.** Energy level and energy gap difference of 6-molecule HOMO-LUMO.

| Molecular | $E_{\text{HOMO}}(\text{eV})$ | $E_{\text{LUMO}}(\text{eV})$ | $\Delta E_{\text{gap}}(\text{eV})$ |
|-----------|------------------------------|------------------------------|------------------------------------|
| O7H       | -6.324892                    | -1.190331                    | 5.134561                           |
| O8H       | -6.286601                    | -1.243465                    | 5.043136                           |
| O9H       | -6.249785                    | -1.261893                    | 4.987892                           |
| OO7H      | -6.345477                    | -1.119999                    | 5.235478                           |
| OO8H      | -6.145297                    | -1.165988                    | 4.979309                           |
| OO9H      | -6.263892                    | -1.285898                    | 4.977995                           |







**Figure S4.** Electron-hole density map and transition density matrix of (a) O7H, (b) O8H, (c) OO7H, (e) OO8H, (d) OO9H.

**Table S4.** Electronic excitation characteristic parameters of the main excited states of the six molecules.

| <b>O7H</b>             | <b>S1</b> | <b>S3</b> | <b>S4</b> |
|------------------------|-----------|-----------|-----------|
| Sm                     | 0.67506   | 0.58833   | 0.62041   |
| Sr                     | 0.87763   | 0.86451   | 0.88506   |
| $\Delta\sigma$         | -0.003    | -0.083    | 0.141     |
| H index                | 3.5852    | 3.699     | 3.711     |
| D index                | 0.169     | 1.089     | 0.966     |
| t index                | -2.347    | -1.787    | -1.843    |
| Excitation energy (eV) | 3.001     | 3.913     | 3.954     |

| <b>O8H</b>             | <b>S1</b> | <b>S5</b> | <b>S6</b> |
|------------------------|-----------|-----------|-----------|
| Sm                     | 0.68206   | 0.61974   | 0.6109    |
| Sr                     | 0.88224   | 0.87835   | 0.87775   |
| $\Delta\sigma$         | 0.041     | -0.061    | 0.347     |
| H index                | 3.656     | 3.892     | 3.83      |
| D index                | 0.195     | 1.019     | 0.676     |
| t index                | -2.412    | -1.743    | -1.969    |
| Excitation energy (eV) | 2.933     | 3.936     | 4.188     |

| <b>O9H</b>             | <b>S1</b> | <b>S12</b> |
|------------------------|-----------|------------|
| Sm                     | 0.65921   | 0.68605    |
| Sr                     | 0.86917   | 0.91584    |
| $\Delta\sigma$         | 0.042     | -0.186     |
| H index                | 3.607     | 3.739      |
| D index                | 0.263     | 0.115      |
| t index                | -2.217    | -1.854     |
| Excitation energy (eV) | 2.816     | 4.589      |

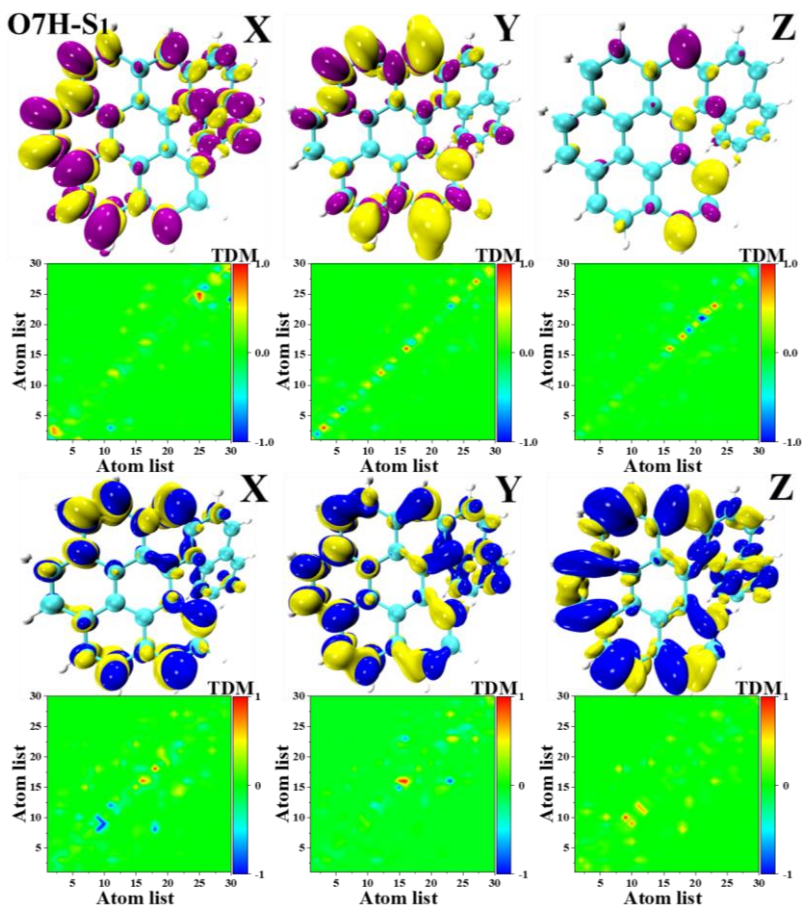
  

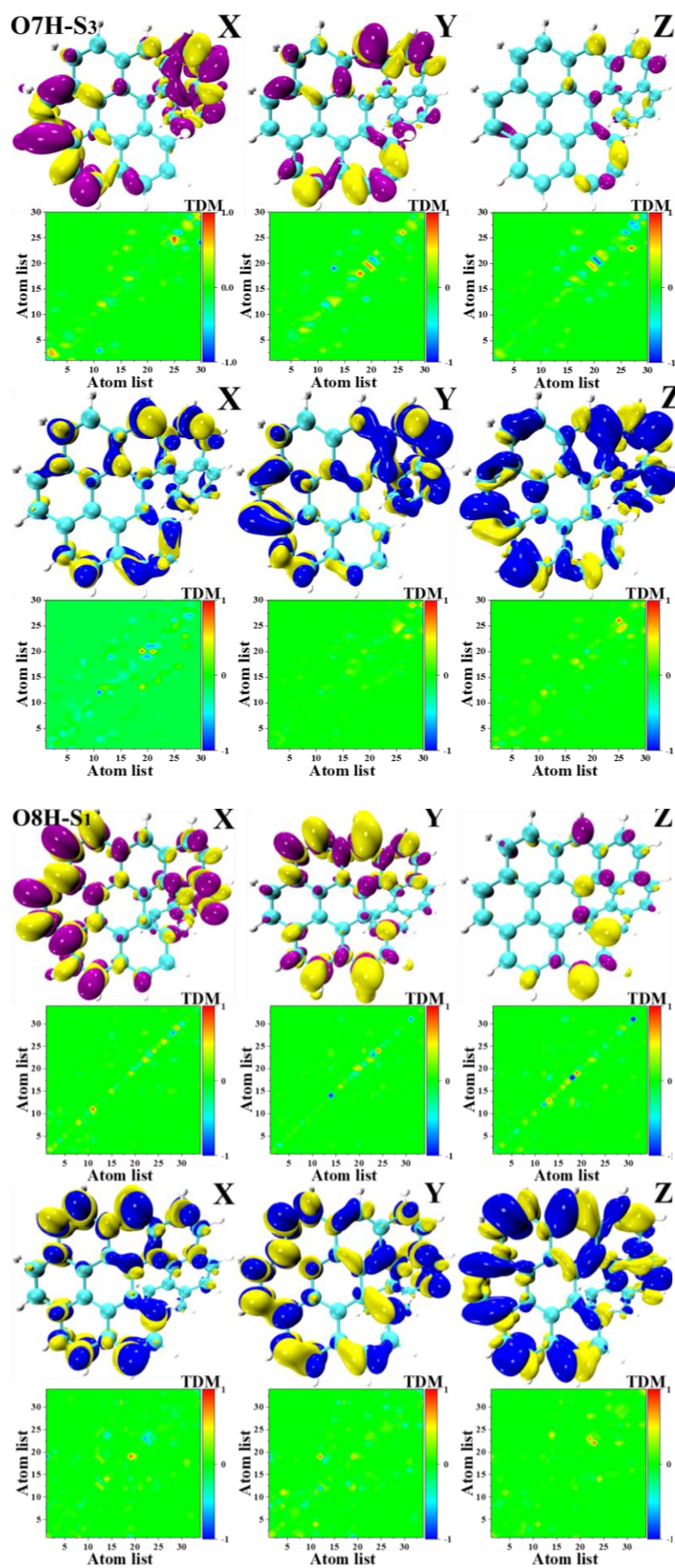
| <b>OO7H</b>            | <b>S1</b> | <b>S2</b> | <b>S3</b> |
|------------------------|-----------|-----------|-----------|
| Sm                     | 0.66711   | 0.68402   | 0.77925   |
| Sr                     | 0.9081    | 0.91657   | 0.9447    |
| $\Delta\sigma$         | 0.113     | -0.08     | 0.003     |
| H index                | 3.864     | 3.834     | 3.886     |
| D index                | 0.323     | 0.297     | 0.04      |
| t index                | -2.459    | -2.448    | -2.772    |
| Excitation energy (eV) | 3.269     | 3.274     | 3.961     |

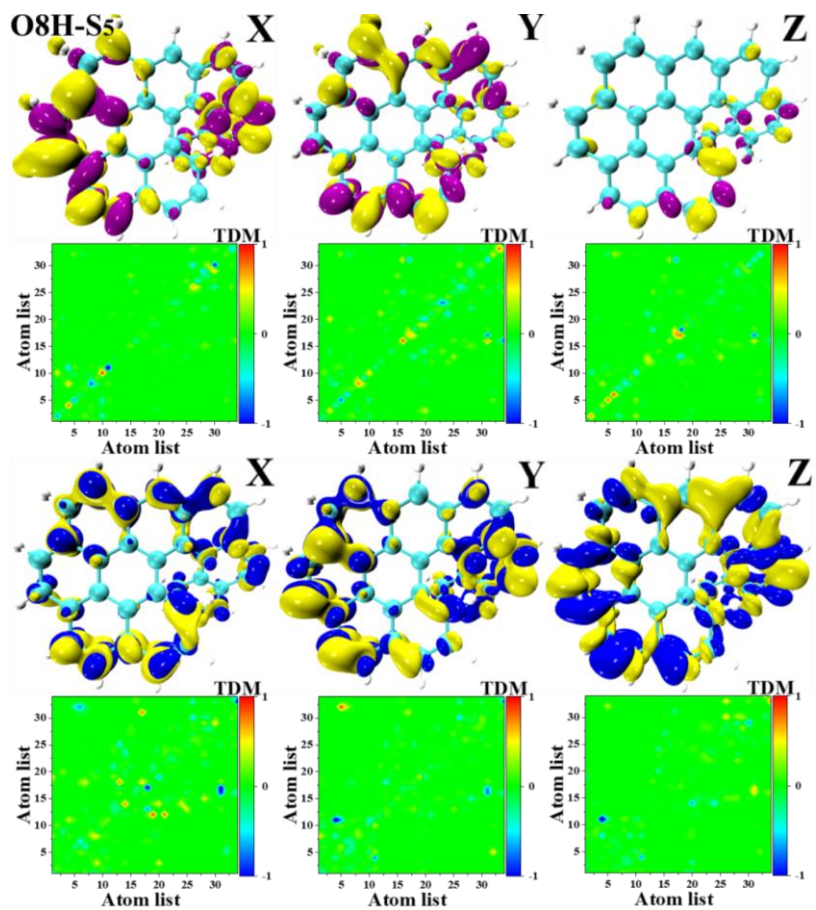
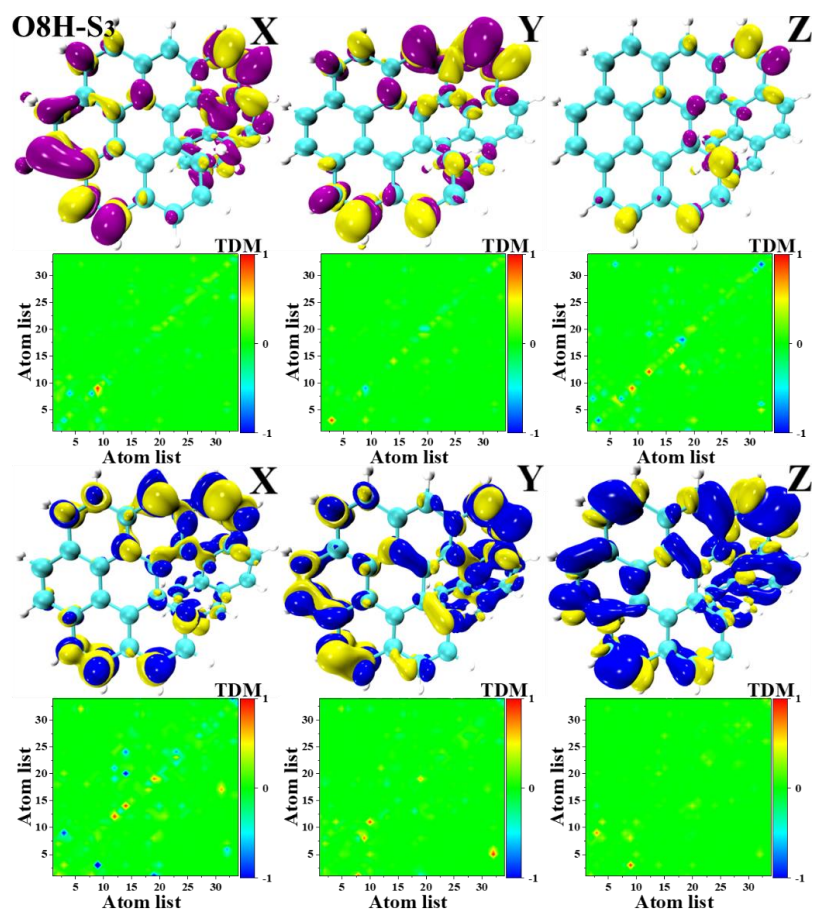
| <b>OO8H</b>    | <b>S1</b> | <b>S5</b> |
|----------------|-----------|-----------|
| Sm             | 0.60692   | 0.72533   |
| Sr             | 0.83661   | 0.92942   |
| $\Delta\sigma$ | -0.21     | 0.019     |
| H index        | 3.727     | 3.945     |
| D index        | 0.547     | 0.214     |
| t index        | -2.071    | -1.93     |

| Excitation<br>energy (eV)  | 2.879   |         | 3.917   |         |
|----------------------------|---------|---------|---------|---------|
| OO9H                       | S1      | S3      | S5      | S6      |
| Sm                         | 0.69532 | 0.74232 | 0.73626 | 0.73654 |
| Sr                         | 0.89955 | 0.92729 | 0.92762 | 0.92858 |
| $\Delta\sigma$             | 0.031   | 0.043   | -0.071  | -0.093  |
| H index                    | 4.11    | 4.08    | 4.178   | 4.138   |
| D index                    | 0.187   | 0.176   | 0.139   | 0.056   |
| t index                    | -2.875  | -2.76   | -2.813  | -1.312  |
| Excitation en-<br>ergy(eV) | 3.016   | 3.64    | 3.917   | 4.088   |

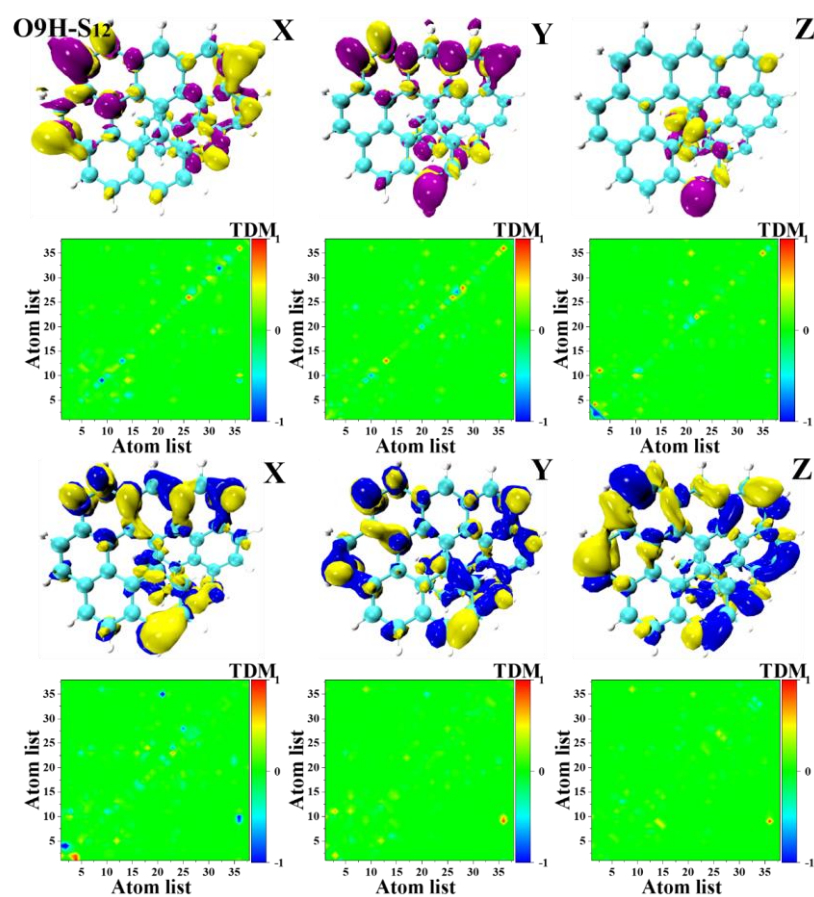
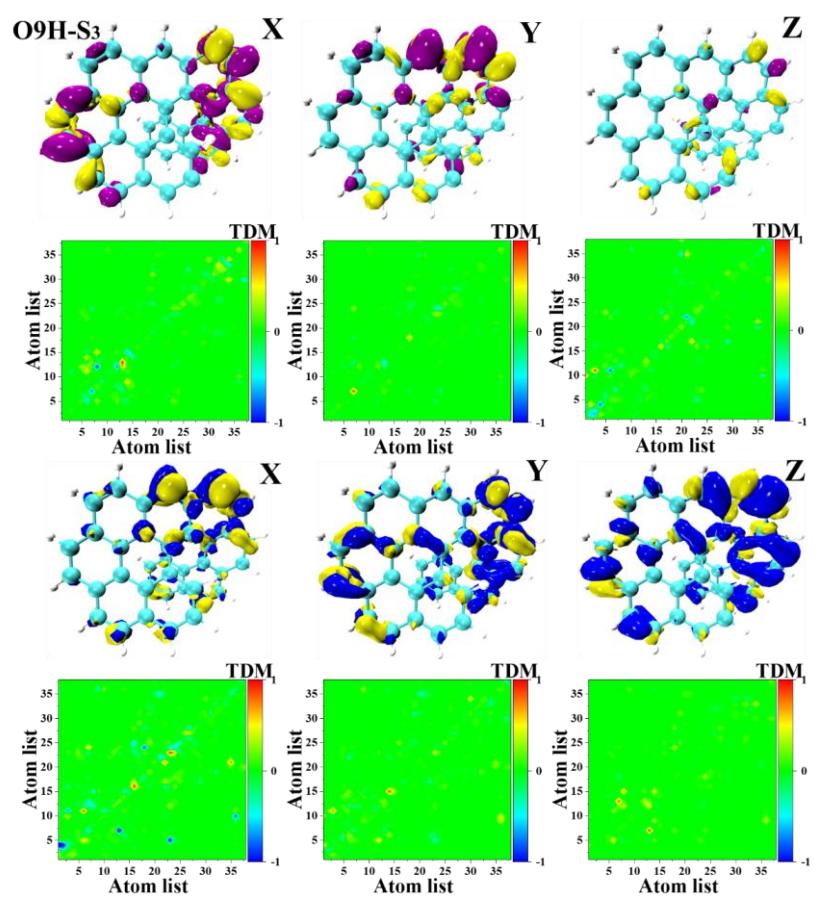








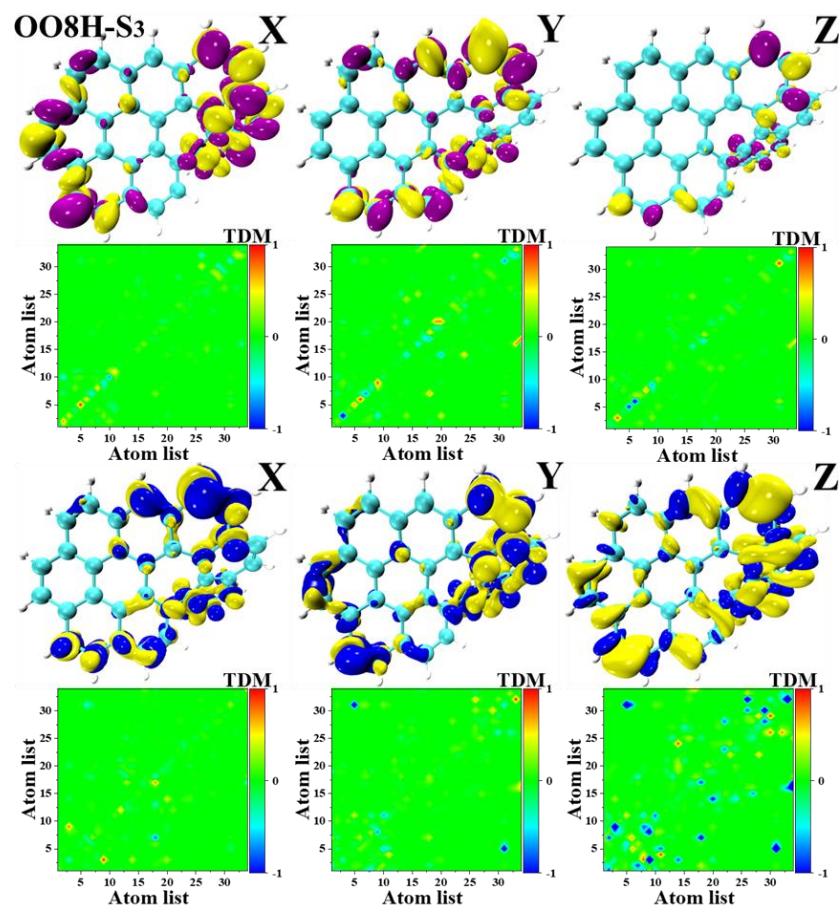
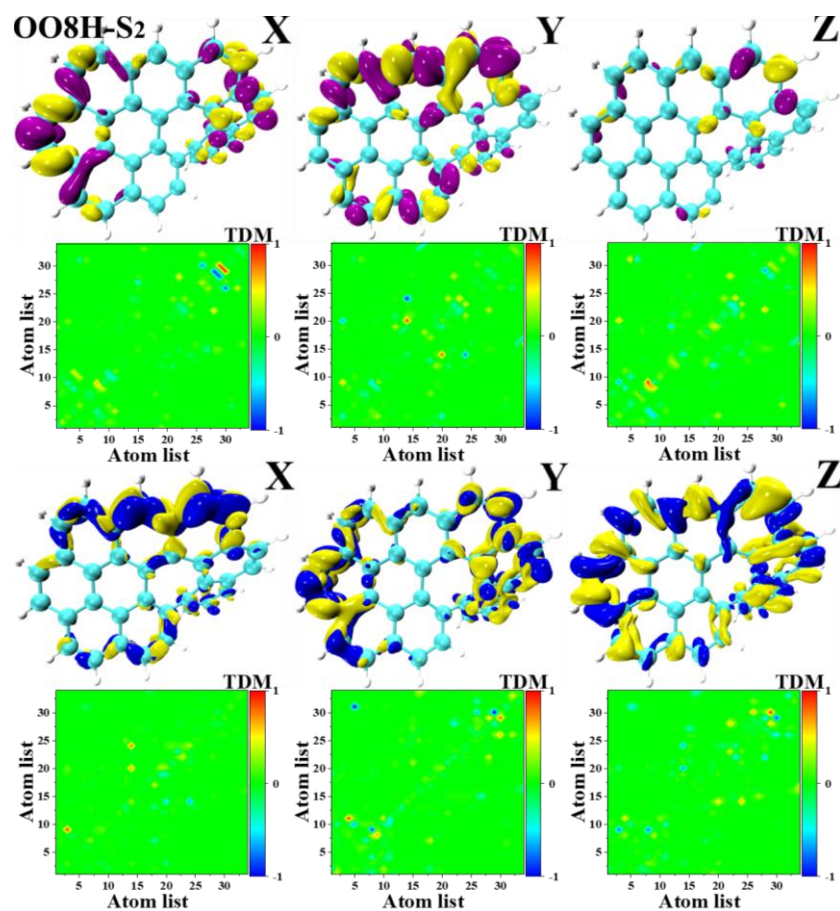




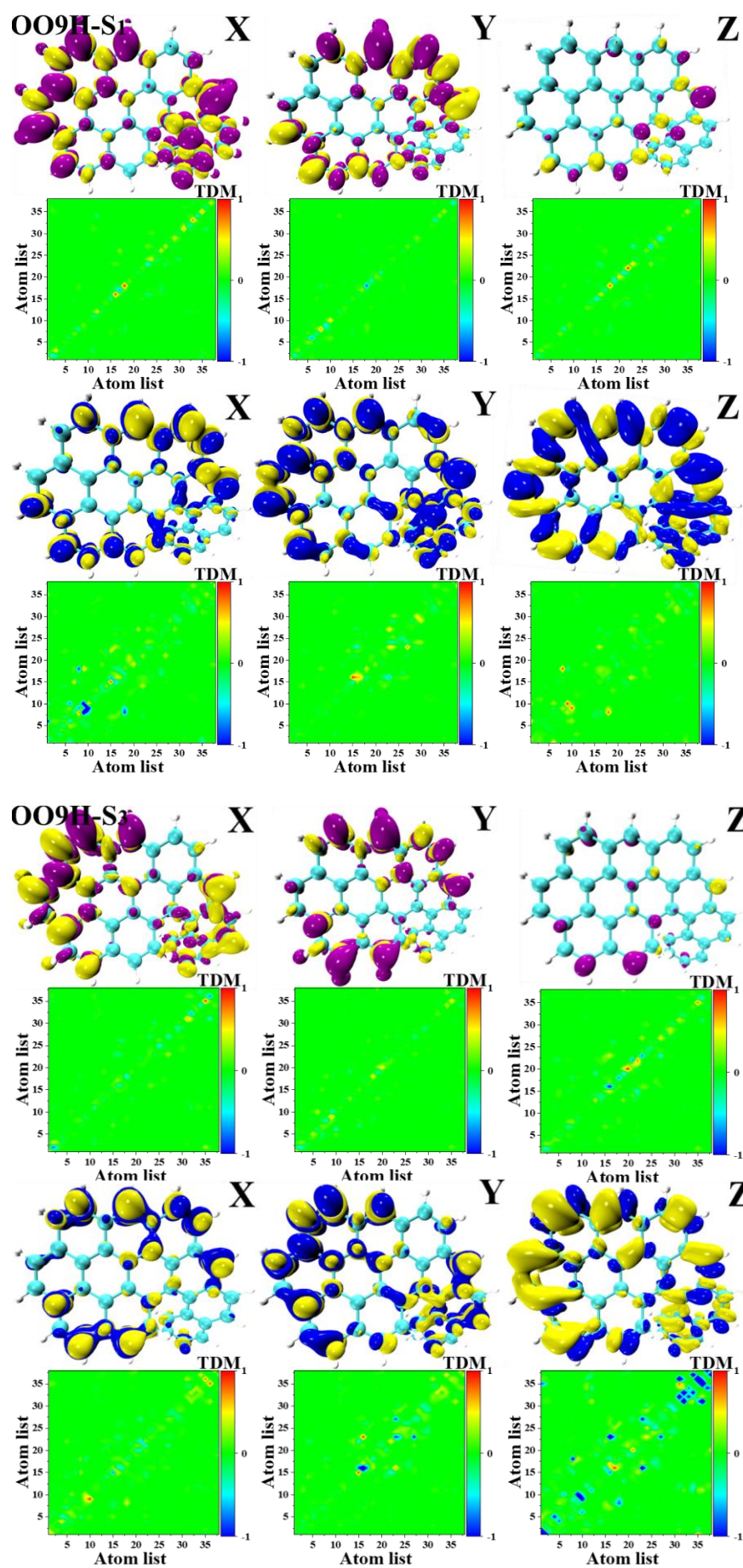




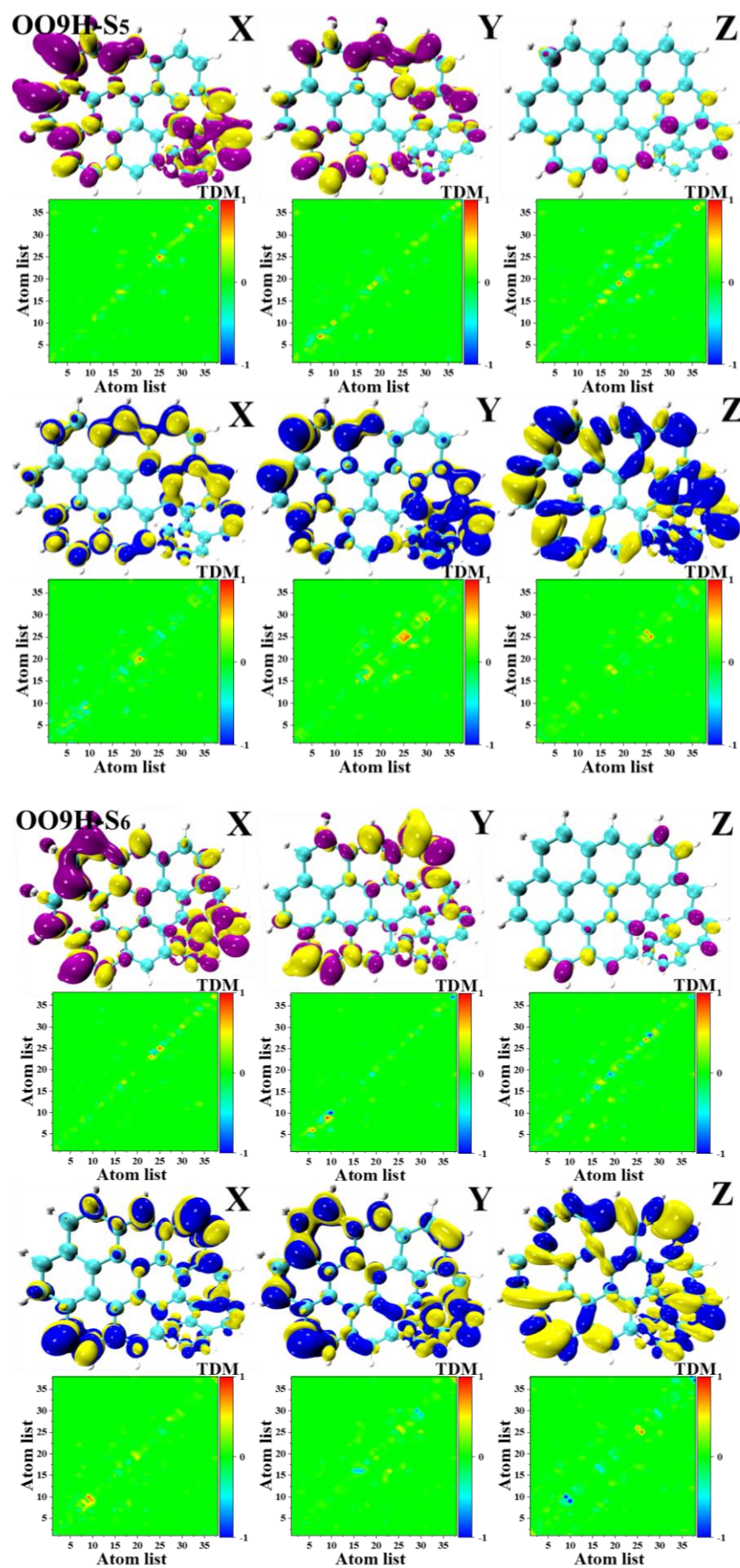




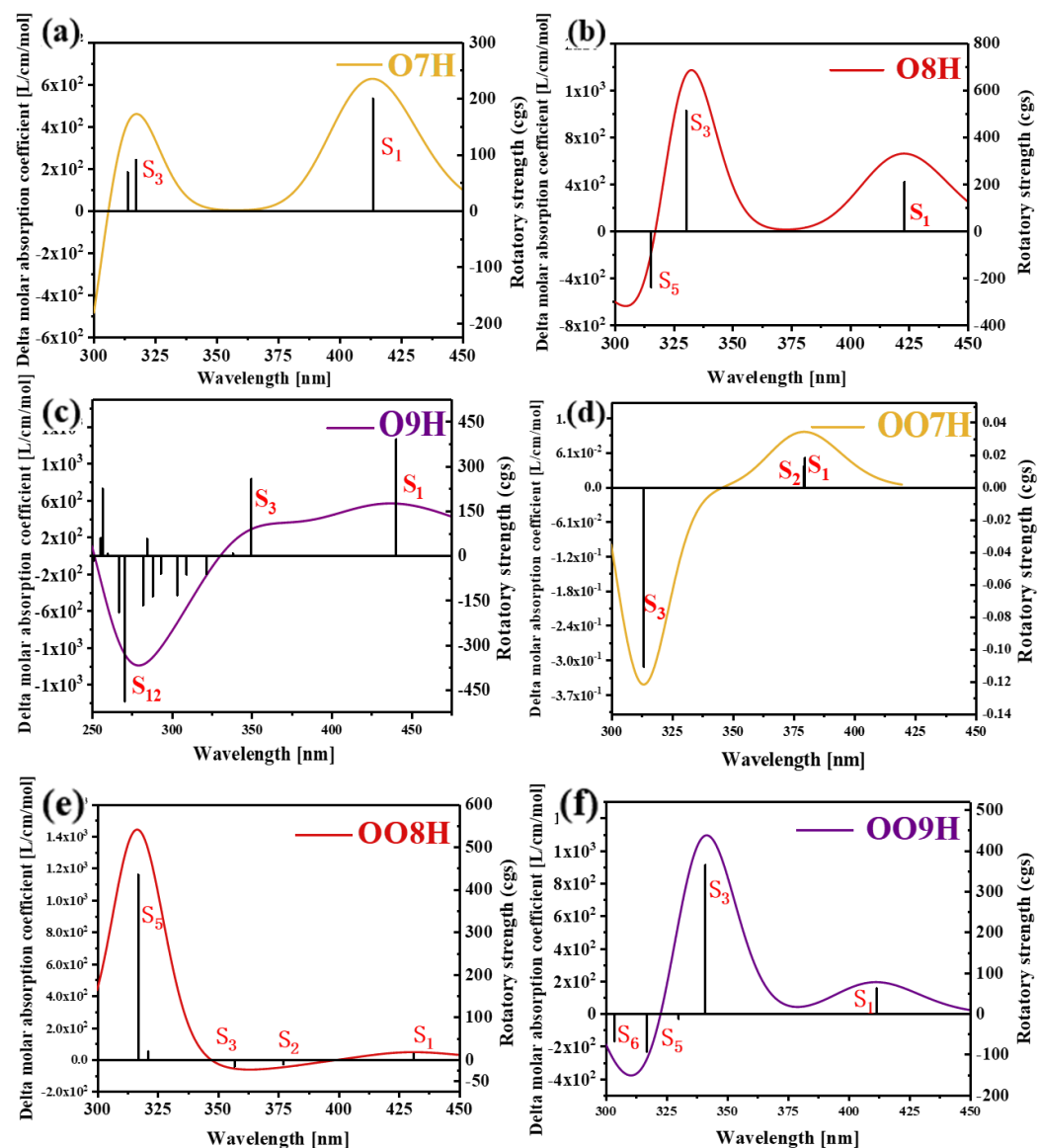




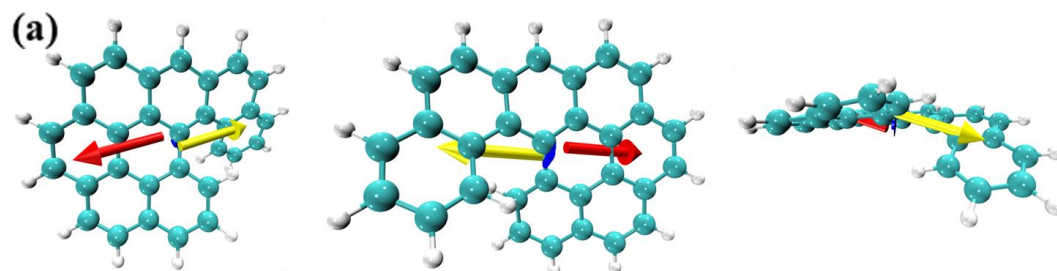


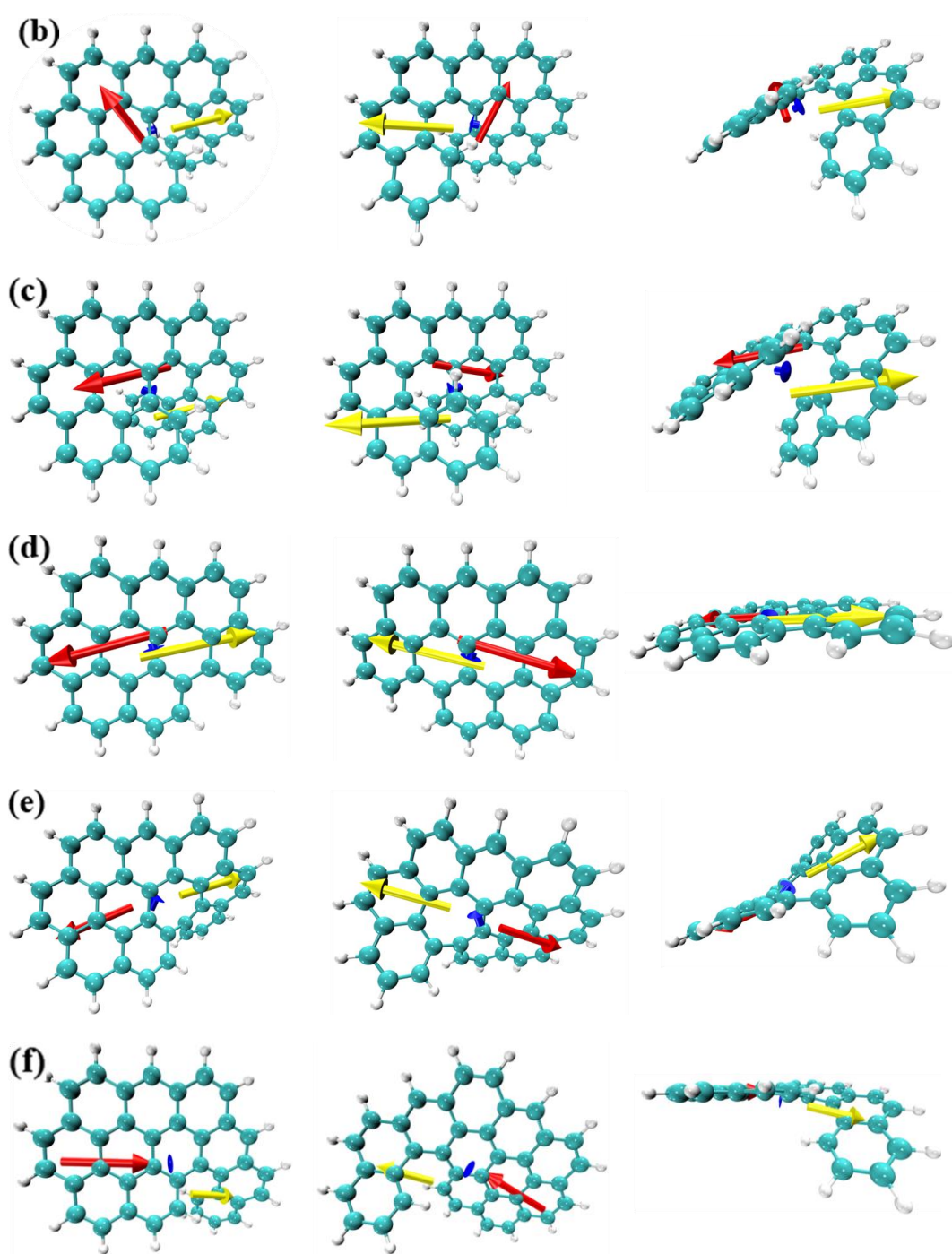


**Figure S5.** 3D and 2D diagrams of transition electric couple and magnetic dipole moment of O7H, O8H, O9H, OO7H, OO8H, OO9H.



**Figure S6.** Electron circular dichroism of each molecule: (a) O7H, (b) O8H, (c) O9H, (d) OO7H, (e) OO8H, (f) OO9H.





**Figure S7.** Front, back and bevel of dipole moments.: (a) O7H, (b) O8H, (c) O9H, (d) OO7H, (e) OO8H, (f) OO9H.