

Optical Transitions Dominated by Orbital Interactions in Two-Dimensional Fullerene Networks

Supplementary information

Principles and formulas of wave function analysis

1. The electron-hole overlap function (Sr) is defined as:

$$Sr = \int \sqrt{\rho^{ele}(r) \rho^{hole}(r)} d(r)$$

where ρ is the density of electron and hole at r . The larger the Sr, the higher the overlap of electron and hole.

The centroid (D) of electron and hole is defined as:

$$D_x = |X_{ele} - X_{hole}|$$

$$D_y = |Y_{ele} - Y_{hole}|$$

$$D_z = |Z_{ele} - Z_{hole}|$$

$$D = \sqrt{(D_x)^2 + (D_y)^2 + (D_z)^2}$$

where, such as X_{hole} represents the x-coordinate of the centroid of hole.

The overall distribution breadth (H) of electron and hole is defined as:

$$H = (|\sigma_{ele}| + |\sigma_{hole}|) / 2$$

where σ_{ele} and σ_{hole} are the distribution breadth of electron and hole, respectively.

The degree of separation (t) of electron and hole is defined as:

$$t = D - H_{CT}$$

$$H_{CT} = |H \cdot u_{CT}|$$

where H is the combined vector of H_x , H_y , and H_z , and u_{CT} is the unit vector in the direction of charge transfer (CT).

The hole delocalization index (HDI) and electron delocalization index (EDI) are defined as:

$$HDI = 100 \times \sqrt{\int [\rho^{hole}(r)]^2 dr}$$

$$EDI = 100 \times \sqrt{\int [\rho^{ele}(r)]^2 dr}$$

The smaller the HDI (EDI) value, the higher the degree of hole (electron) delocalization.

2. The van der Waals potential can be used to describe the van der Waals interaction dominated by the dispersive interaction in the system. For the van der Waals potential, described by the Lennard-Jones 12-6 potential (L-J potential) commonly used in molecular force fields, it can be

written as:

$$V^{vdW}(r) = V^{repul}(r) + V^{disp}(r) = \sum_A \varepsilon_{AB} \left(\frac{R_{AB}^0}{|R_A - r|} \right)^{12} + \sum_A \left[-2\varepsilon_{AB} \left(\frac{R_{AB}^0}{|R_A - r|} \right)^6 \right]$$

where V^{repul} and V^{disp} are the exchange mutual repulsion potential and the dispersion attractive potential in the van der Waals potential, respectively. A represents all atoms circulating, ε and R^0 are the L-J potential well depth and equilibrium distance between atoms, respectively, and R_A represents the nuclear coordinate of the A atom. In the van der Waals potential defined above, the B atom corresponds to the probe atom (the probe atom is the He atom in this work).

3. IGMH is a method that can visualize the interactions in chemical systems in a graphical way. It is defined as:

$$\delta g(r) = g^{IGM}(r) - g(r)$$

$$g(r) = \left| \sum_i \nabla \rho_i(r) \right|$$

$$g^{IGM}(r) = \sum_i |\nabla \rho_i(r)|$$

where g^{IGM} is the sum of the absolute values of the electron density gradients. g is the sum of the electron density gradients. ρ_i represents the electron density of the i atom. r is a coordinate vector. δg^{inter} and δg^{intra} are defined to reflect inter- and intra-fragment interactions.

$$\delta g^{inter}(r) = g^{IGM,inter}(r) - g^{inter}(r)$$

$$g^{inter}(r) = \left| \sum_A \sum_{i \in A} \nabla \rho_i(r) \right|$$

$$g^{IGM,inter}(r) = \sum_A \left| \sum_{i \in A} \nabla \rho_i(r) \right|$$

$$\delta g^{intra}(r) = \delta g(r) - \delta g^{inter}(r)$$

Table S1. The main contributing orbitals of each excited state in HLOPC60 (>10%).

excited states	MOs	contribution ratio
S ₃	HOMO→LUMO+2	95.9%
S ₁₉	HOMO-6→LUMO	92.0%
S ₇₀	HOMO-2→LUMO+6	65.4%
	HOMO-11→LUMO+2	11.6%
S ₈₂	HOMO→LUMO+11	69.3%
S ₁₄₄	HOMO-10→LUMO+8	31.0%
	HOMO-10→LUMO+6	20.7%
	HOMO-15→LUMO+4	15.3%

Table S2. The main contributing orbitals of each excited state in TLOPC60 (>10%).

excited states	MOs	contribution ratio
S ₂₉	HOMO-8→LUMO+2	57.0%
	HOMO-2→LUMO+3	29.6%
	HOMO-6→LUMO+1	12.1%
S ₅₀	HOMO-2→LUMO+3	57.9%
	HOMO-8→LUMO+2	16.0%
	HOMO-6→LUMO+1	12.1%
S ₁₃₄	HOMO-15→LUMO+4	96.5%
S ₁₅₂	HOMO-20→LUMO	95.1%
S ₁₇₆	HOMO-17→LUMO+5	90.4%

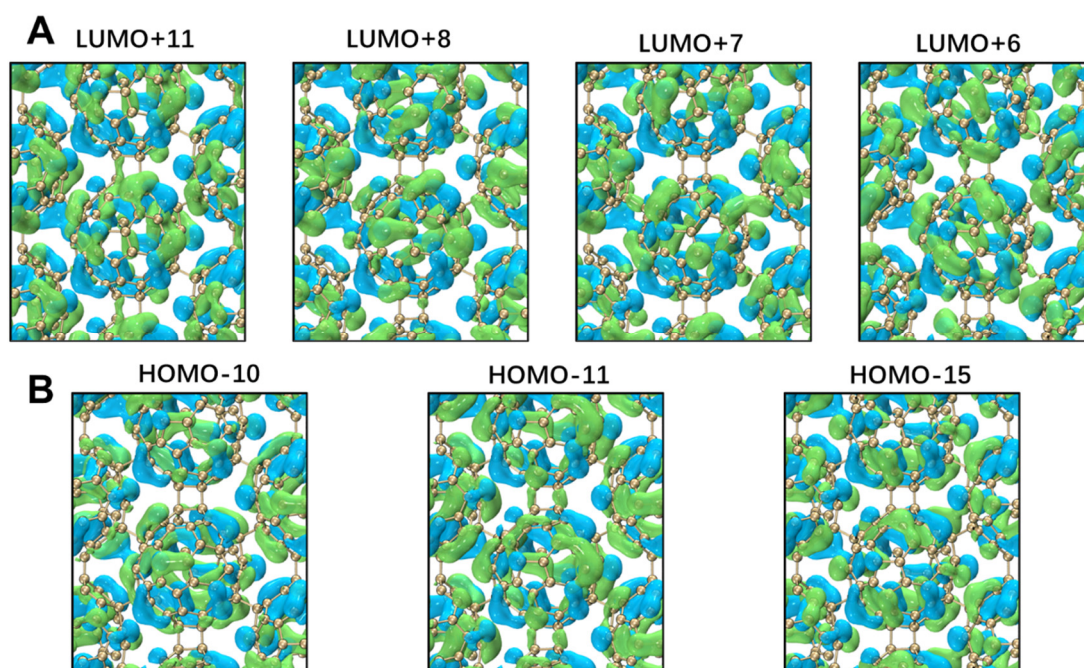


Figure S1. Empty orbitals (A) and occupied orbitals (B) that make major contributions in each excited state of HLOPC₆₀.

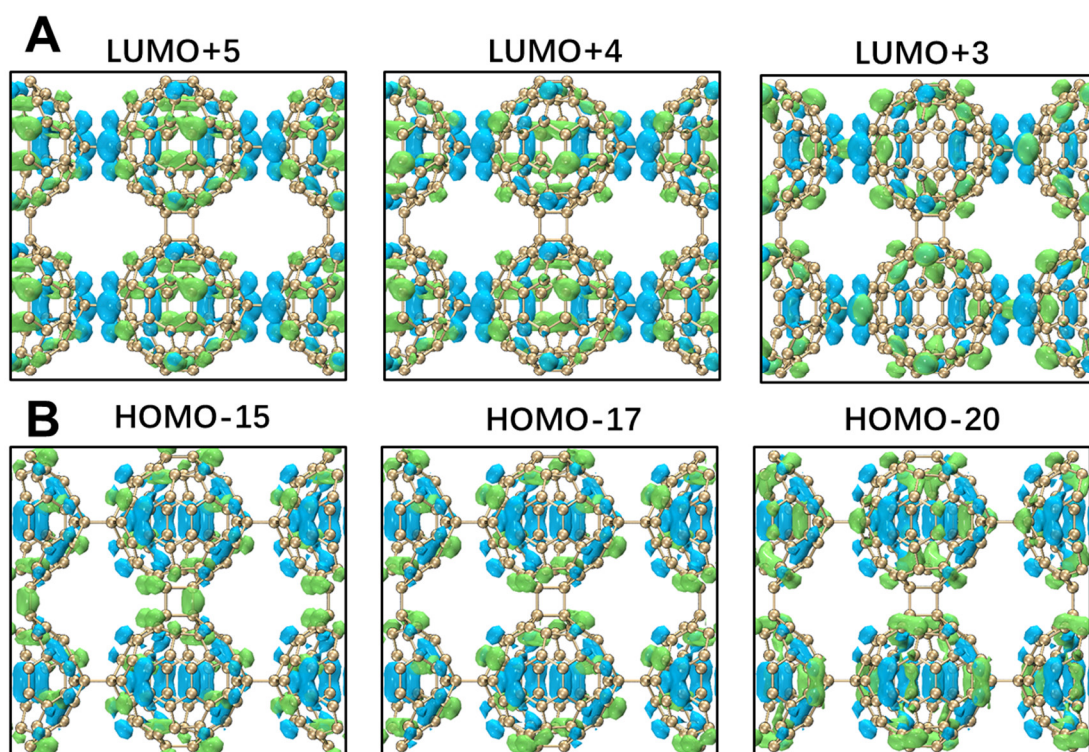


Figure S2. Empty orbitals (A) and occupied orbitals (B) that make major contributions in each excited state of TLOPC₆₀.