Effect of Conjugation Length on Fluorescence Characteristics of Carbon Dots

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Data availability. All data generated or analyzed during this study are included in this published article (and its Supplementary Information files). All relevant data are available from the authors.

Details of DFT calculation

Here's some computational details in Gaussian program.

(1) The convergence criteria for geometrical optimizations are set as: maximum force < 0.00045, mean square root of force < 0.0003, maximum displacement < 0.0018, and mean square root of displacement < 0.0012. Default ultrafine integration was used for computing the electronic integrals.

(2) The ultrafine integration requesting a pruned (99, 590) grid was used in this work. It is useful for optimizations of larger molecules, making such optimizations more reliable.

(3) The structural optimization was performed in default internal coordinates.

Details of Kuhn fit

Kuhn fit is a semiempirical extrapolation method and the formula is expressed as[1]:

$$E = E_0 \sqrt{1 + 2\frac{k^{'}}{k_0}cos\frac{\pi}{N + 1}}$$

where E is the fluorescence emission energy, E_0 is the minimum value of fluorescence emission energy, k_0 is the force constant of C=C double bonds, k' is the force constant when adjacent double bonds are coupled and N is the conjugation length. Usually, k'/k_0 is on the order of -0.45.
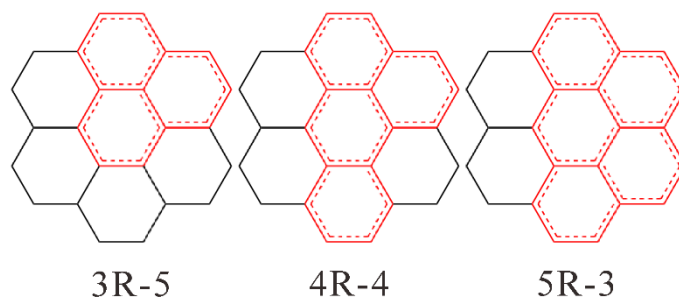

3R-5 4R-4 5R-3

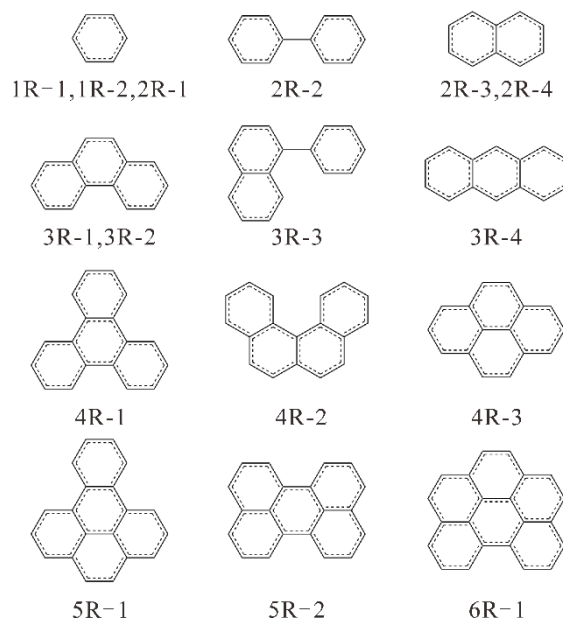**Figure S1.** Three structures with spin-triplet ground state.

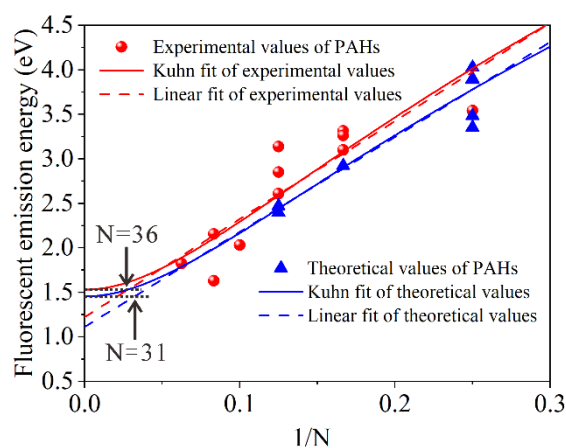**Figure S2.** The PAHs corresponding to coronene-like structures.

Figure S3. Experimental and theoretical values of PAHs fluorescent emission energy. Curves: Kuhn fit. Lines: linear fit. Experimental values are derived from the references.[2]

Theory of hole-electron distribution

Fluorescence emission is the process of releasing energy outward from the excited state to the ground state by electrons. According to the definition of "hole" and "electron" by Lu et al., the state where the electron leaves, which is defined as the

ground state, and treated as a hole; the state where the electron arrives, which is the excited state and treated as an electron. In order to further explore the excitation process of the CDs, the electron densities of the ground and excited states are calculated, and the distribution of electrons and holes can be obtained. Single-electron excitation can be described as the relative motion of a pair of hole and electron. In most cases, an electronic transition is expressed as the transition of multiple molecular orbital pairs with corresponding weight coefficients. Density distribution of hole and electron can be perfectly defined as: [3]

$$\rho^{hole}(r) = \sum_{i \to a}\left(w_i^a\right)^2 \varphi_i(r)\varphi_i(r) + \sum_{i \to a}\sum_{j \neq i \to a} w_i^a w_j^a \varphi_i(r)\varphi_j(r)$$

$$\rho^{ele}(r) = \sum_{i \to a}\left(w_i^a\right)^2 \varphi_a(r)\varphi_a(r) + \sum_{i \to a}\sum_{j \to b \neq a} w_i^a w_j^a \varphi_a(r)\varphi_a(r)$$

The overall distribution of hole and electron can be quantitatively characterized in following ways:

The total magnitude of charge transfer length is referred to D index:

$$X_i = \int x\rho^i(r)dr;(i = ele, hole)$$

$$D_i = \left|X_{ele} - X_{hole}\right|;(i = x,y,z)$$

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

where X is defined as centroid, x is the component of position vector r.

Overlapping extent of hole and electron S_r is defined as:

$$S_r(r) = \sqrt{\rho^{hole}(r)\rho^{ele}(r)}$$

The overall difference between root mean square error (RMSD) of electron and hole can be measured via $\Delta\sigma$ index:

$$\sigma_{i,x} = \sqrt{\int (x - X_i)^2 \rho^i(r)dr};(i = ele, hole)$$

$$\Delta\sigma = |\sigma_{ele}| - |\sigma_{hole}|$$

where $\sigma_{i,x}$ is defined as X component of RMSD of hole or electron.

H_i measures the average degree of spatial extension of hole and electron distribution in X/Y/Z direction, H_{CT} is that in charge transfer direction:

$$H_i = \frac{\sigma_{ele,i} + \sigma_{hole,i}}{2}; i = x,y,z$$

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

t index is designed to measure separation degree of hole and electron in CT direction:

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

If t <0, it implies that hole and electron is not substantially separated due to CT. Clear separation of hole and electron distributions must correspond to positive t index.

For the local excitation, there is no obvious difference in the distribution area of electrons or its distribution range covers the entire system when the electrons are excited. In general, the D index is small, S_r index is large, the t index is obviously negative, and the $\Delta\sigma$ index is small. The main distribution ranges of the excited hole and electron are very close, and the degree of overlap is large. The distributions of hole and electron are not significantly separated, and the distribution widths are similar. For the charge transfer excitation, the distribution area shifts significantly after the electrons are excited.

REFERENCES

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2. R. Rieger and K. Müllen, *Journal of Physical Organic Chemistry*, 2010, **23**, 315-325.

3. Z. Liu, T. Lu and Q. Chen, *Carbon*, 2020, **165**, 461-467.