

Supporting Information

# Luminescence Mechanism of Ligand-induced Interface States in Silicon Quantum Dots

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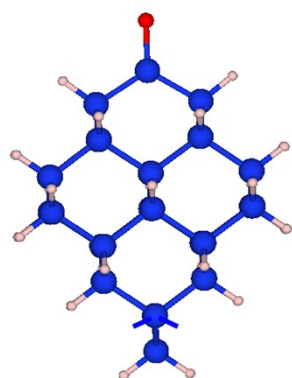
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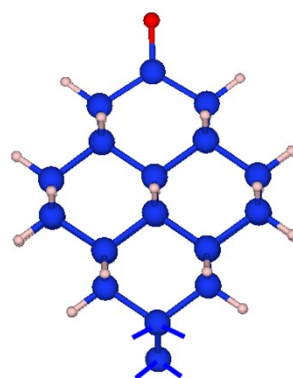
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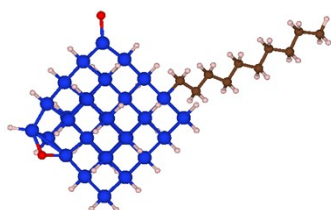


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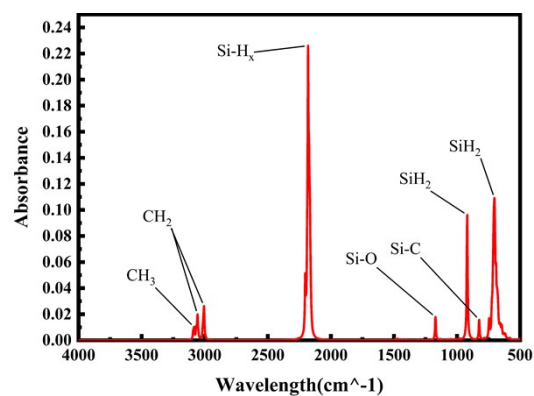


(b)1.1-O-4

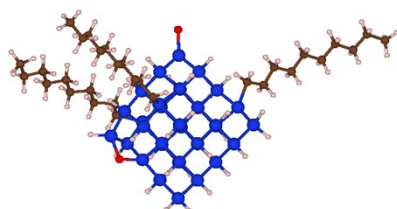
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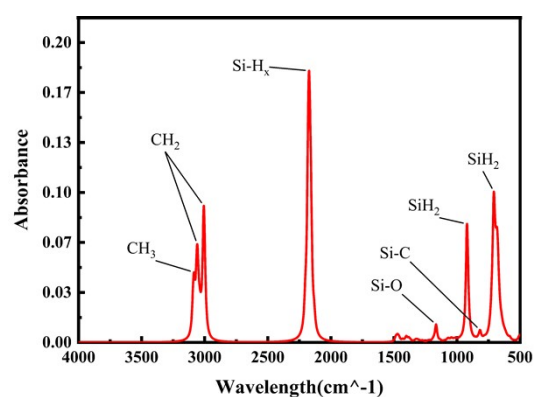
(a)



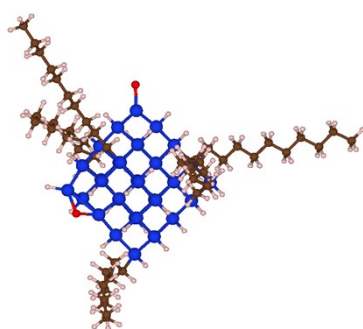
(b)



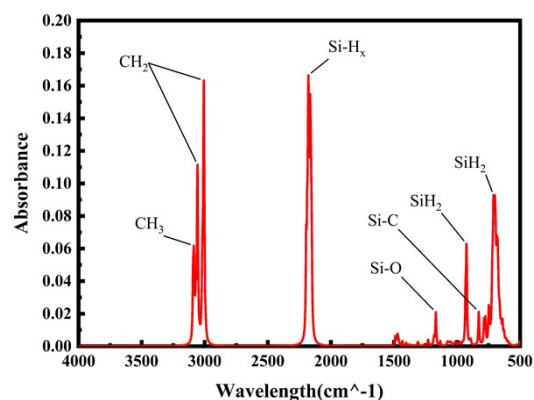
(c)



(d)

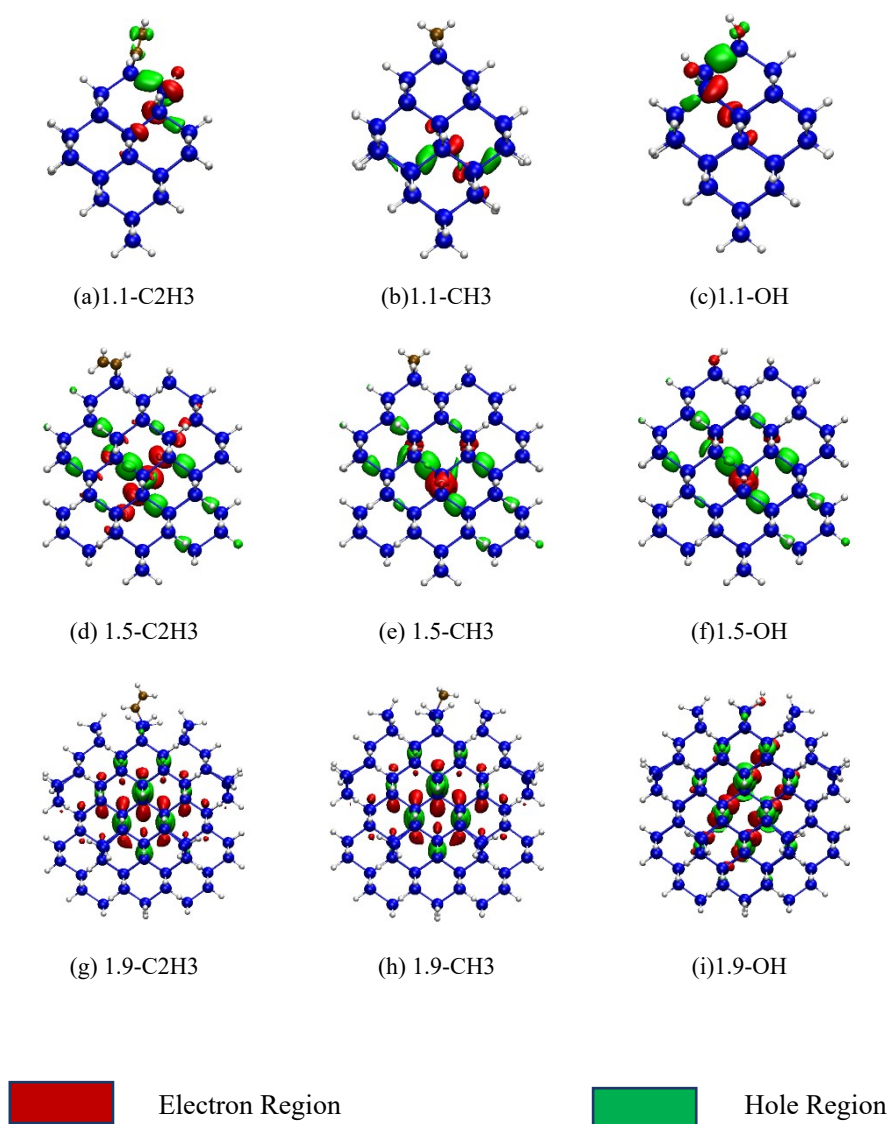


(e)

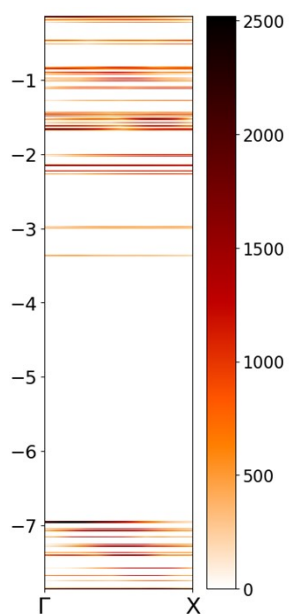


(f)

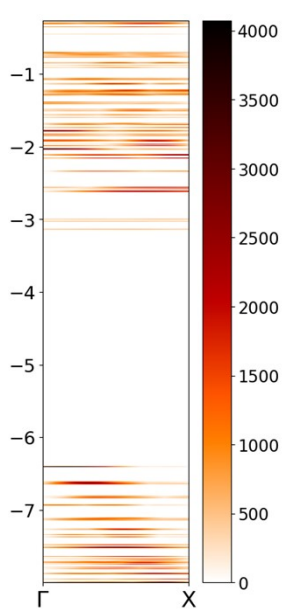
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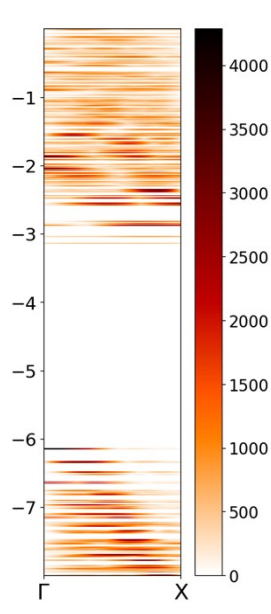
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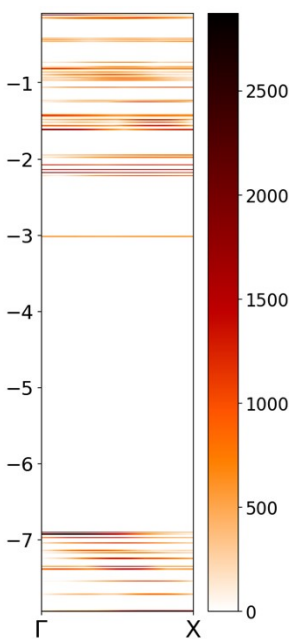
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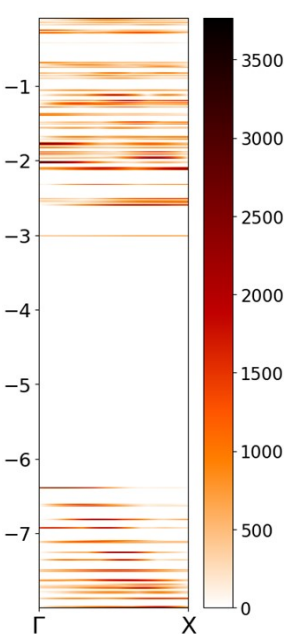
(b) 1.5-C7H7



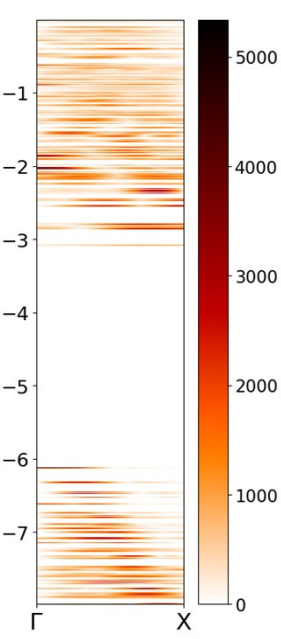
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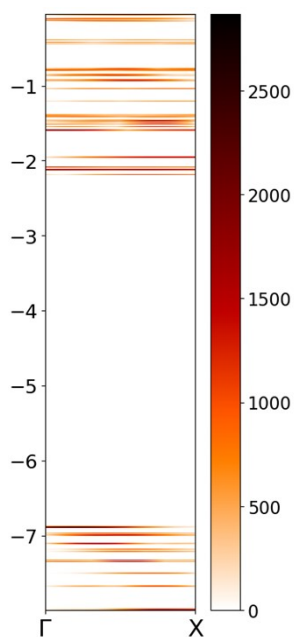
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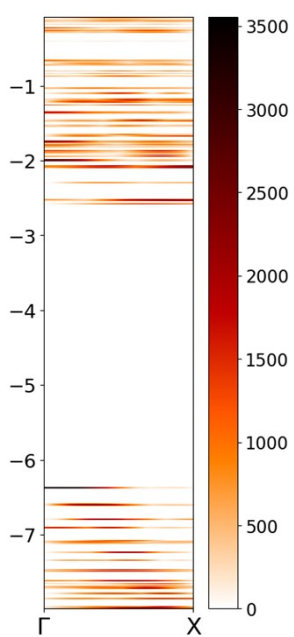
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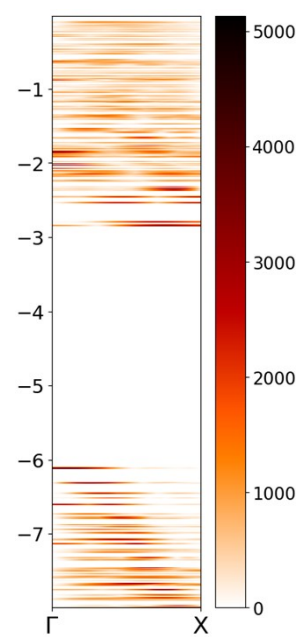
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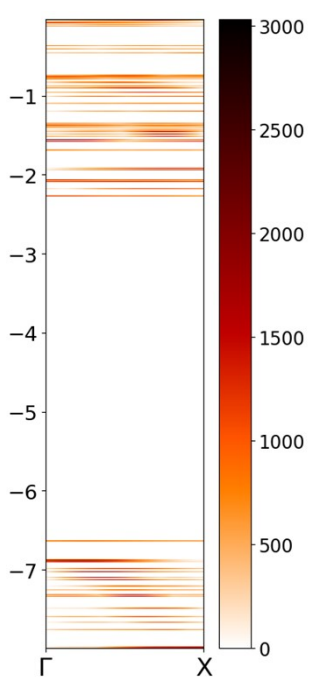
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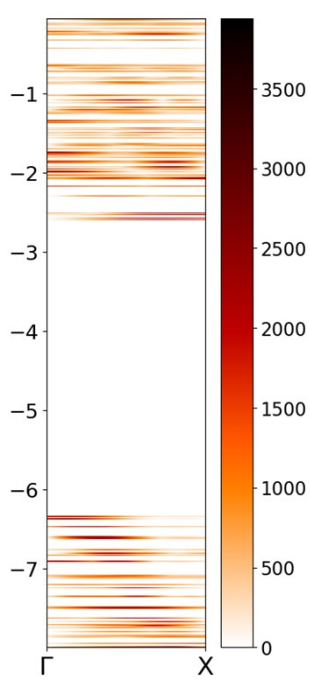
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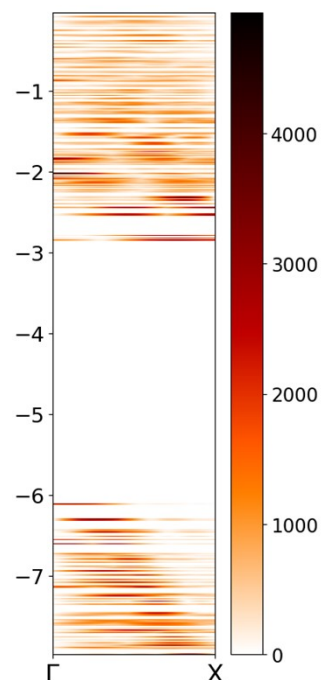
(i)1.9-CH3



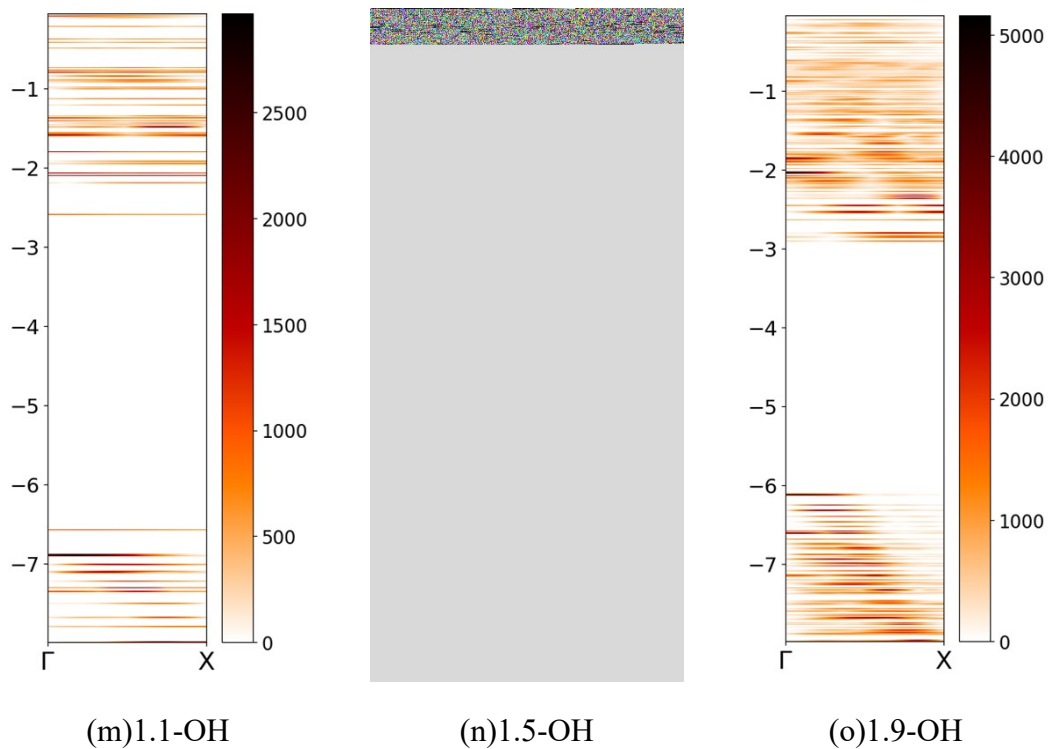
(j)1.1-NH2



(k)1.5-NH2



(l)1.9-NH2



**Figure S4.** Projection of molecular orbitals of Si-QDs of different sizes and terminated by different surface ligands in the  $\Gamma$ -X direction of the Brillouin zone. (a)–(c) 1.1, 1.5 and 1.9 nm silicon quantum dots terminated by toluene, (d)–(f) 1.1, 1.5 and 1.9 nm terminated by vinyl, (g)–(i) 1.1, 1.5 and 1.9 nm terminated by methyl, (j)–(l) 1.1, 1.5 and 1.9 nm terminated by amino, and (m)–(o) 1.1, 1.5 and 1.9 nm terminated by hydroxyl. The color bar is used to represent the density of the corresponding state, with a darker color indicating more electronic states.



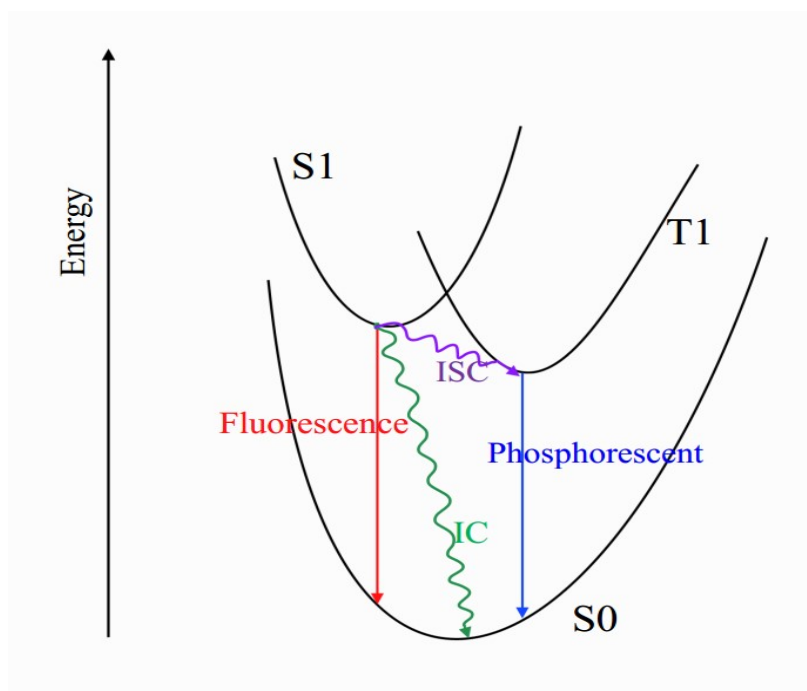
Calculate the details of non-radiative recombination:

The luminescence process of quantum dots is shown in Figure S1, and the calculation details of PLQY are as follows:

Photoexcited molecules form singlet excited state molecules, which may participate in the deactivation process of fluorescence emission, internal conversion, interstitial jumping and intermolecular interaction. Therefore, the total inactivation rate is the sum of the rates of the various inactivation processes it participates in.

$$k_{tot} = k_F + k_{IC} + k_{ISC} + k_q$$

Here,  $k_F$ ,  $k_{IC}$ ,  $k_{ISC}$  and  $k_q$  are the rate constants of fluorescence, internal conversion, intersystem crossing and intermolecular inactivation, respectively. The non-radiative recombination coefficient of S1 to S0 is called the internal transition rate, which describes the rate of the nonradiative process from the excited state S1 to the ground state S0. This process involves the recombination of excitons, usually including vibrational relaxation and intramolecular rotation. At the same time, the T1 state can also participate in this process, called interstitial jumping, but it is usually less involved than the S1 state, and the conversion rate is slower than internal conversion.



**Figure S5.** Transition orbit diagram

When we calculate the photoluminescence quantum yield of quantum dots, the inactivation of intermolecular interactions is temporarily ignored. Based on the Franck–Condon Principle and Kasha’s rule, the fluorescence emission and internal conversion from S1 to S0 and interstitial jumping from S1 to T1 are the most important. Therefore, we use the following formula to approximate the size of PLQY:

$$\Phi_F = \frac{k_F}{k_{tot}} \approx \frac{k_F}{k_F + k_{IC} + k_{ISC}}$$

The fluorescence rate constant is the reciprocal of the fluorescence lifetime.

$$k_F = \frac{1}{\tau}$$

Within the Born–Oppenheimer approximation, non-radiative transition between electronic states are impossible, and the potential energy surfaces represent impenetrable walls. To remove that artefact, the correlation of electronic and nuclear motions must be included explicitly in the Hamiltonian operator. These relatively small terms are introduced by time-dependent perturbation theory

$$k_{i \rightarrow f} = \frac{2\pi}{\hbar} V_{if}^2 \rho_f$$

The Fermi's Golden Rule formula<sup>[1]</sup> can be used to calculate the rate constants for internal conversion (IC) and intersystem crossing (ISC). The rate constant for a non-radiative transition between an initial and final state  $k_{i \rightarrow f}$  is thus proportional to the product of two factors, the density  $\rho_f$  of excited vibrational levels of the final state that match the energy of the initial state and the square of the vibronic coupling term between the initial and final BO state,  $V_{if} = \langle \psi_i | \hat{h} | \psi_f \rangle$ , where  $\hat{h}$  is a perturbation operator that couples nuclear with electronic motion to promote IC and couples electron spin with orbital angular momentum (spin–orbit coupling, SOC) to allow for ISC. As a result, the density of states is weighted by the square of the Franck–Condon integrals  $\langle \chi_i | \chi_f \rangle$ <sup>[2]</sup>. The Franck-Condon integrals are a set of integrals used in spectroscopy to describe the probability of a molecule undergoing a vertical electronic transition between two different electronic states. The integrals describe the overlap between the wave functions of the initial and final electronic states of the molecule, which

determines the degree of coupling between the electronic and nuclear motion. These integrals are named after James Franck and Edward Condon, who first described them in their 1926 paper on the theory of molecular spectra.

Quantitative calculations of rate constants  $k_{i \rightarrow f}$  are demanding, but empirical formulas based on the energy gap law can be used to roughly estimate nonradiative recombination coefficients.

The rate constants for IC and ISC exhibit exponential decrease with increasing energy difference  $\Delta E$  between the two electronic states<sup>[3]</sup>.

The empirical formula for internal conversion coefficient is as follows, where

$$\tilde{\Delta\nu} = \Delta E/hc$$

$$\log(k_{IC}/s^{-1}) \approx 12 - 2\tilde{\Delta\nu}/\mu m^{-1}$$

The rate of ISC is usually smaller than that of IC, and also follows the energy gap law.

$$\log(k_{ISC}/s^{-1}) \approx 7 - 2\tilde{\Delta\nu}/\mu m^{-1}$$

Here are the calculation results of PLQY. From the analysis of the results, we have determined that the main factor affecting PLQY is the pl rate. Therefore, it is reasonable for us to directly consider the emission intensity from the fluorescence lifetime.

Table 1 The lifetime, Internal conversion coefficient( $k_{IC}$ ), Intersystem crossing coefficient( $k_{ISC}$ ), Photoluminescence coefficient( $k_{PL}$ ), and PLQY of Si-QDs vary with different structures

| diameter | Ligand | Lifetime( $\mu$ s) | $k_{IC}$ | $k_{ISC}$ | $k_{PL}$   | PLQY(%) |
|----------|--------|--------------------|----------|-----------|------------|---------|
| 1.1      | -H     | 1.18               | 20007.00 | 229.30    | 845072.14  | 97.66   |
|          | -O     | 2.11               | 27955.35 | 28.75     | 474767.34  | 94.43   |
|          | -OH    | 4.46               | 333.97   | 237.24    | 224355.02  | 99.75   |
|          | -CH3   | 1.18               | 290.29   | 229.52    | 849182.95  | 99.94   |
|          | -C2H3  | 1.37               | 313.27   | 410.61    | 729567.32  | 99.90   |
|          | -C7H7  | 0.88               | 345.67   | 776.60    | 1137837.80 | 99.90   |
|          | -NH2   | 1.63               | 588.51   | 338.26    | 614557.37  | 99.85   |
| 1.5      | -H     | 487.64             | 753.35   | 1056.00   | 2050.69    | 53.13   |
|          | -O     | 1.58               | 4607.21  | 495.36    | 634634.92  | 99.20   |
|          | -OH    | 674.30             | 761.75   | 1059.35   | 1483.02    | 44.88   |
|          | -CH3   | 550.97             | 764.15   | 1067.98   | 1814.98    | 49.76   |
|          | -C2H3  | 204.58             | 760.95   | 85.54     | 4887.99    | 85.24   |
|          | -C7H7  | 285.97             | 768.46   | 1064.66   | 3496.90    | 65.61   |
|          | -NH2   | 48.34              | 900.29   | 1224.45   | 20688.26   | 90.69   |
| 1.9      | -H     | 66.09              | 1376.79  | 1121.89   | 15130.48   | 85.83   |
|          | -O     | 1.75               | 4699.96  | 511.25    | 572699.48  | 99.10   |
|          | -OH    | 50.03              | 1384.83  | 1082.15   | 19989.49   | 89.01   |
|          | -CH3   | 41.19              | 1362.90  | 1108.49   | 24276.10   | 90.76   |
|          | -C2H3  | 40.70              | 1390.10  | 1088.84   | 24572.73   | 90.84   |
|          | -C7H7  | 67.63              | 1410.30  | 1095.63   | 14786.20   | 85.51   |
|          | -NH2   | 72.94              | 1383.34  | 1075.29   | 13710.26   | 84.79   |

## References

- [1] Dirac P a M. The Quantum Theory of the Emission and Absorption of Radiation[J], 1927, 114: 243-265.
- [2] He R, Yang L, Zhu C, et al. Franck–Condon simulation of the A 1B2  $\rightarrow$  X 1A1 dispersed fluorescence spectrum of fluorobenzene and its rate of the internal conversion[J]. The Journal of Chemical Physics, 2011, 134(9): 094313.
- [3] A Crash Course in Photophysics and a Classification of Primary Photoreactions, Photochemistry of Organic Compounds, 2009: 25-72.