



Thermal Vibration Correlation Function Formalism for Molecular Excited State Decay Rates

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Cite this paper: *Chin. J. Chem.* 2020, 38, 1223–1232. DOI: 10.1002/cjoc.202000226

What is the most favorite and original chemistry developed in your research group?

MOMAP, abbreviated for MOlecular MAterials Property prediction package, wherein the key function is the thermal vibration correlation function (TVCF) formalism for excited state decay, allowing theoretical prediction of light-emitting quantum efficiency and carrier mobility. MOMAP starts to be popular after its first launch in 2015.

How do you get into this specific field? Could you please share some experiences with our readers?

I was trained with theoretical condensed matter physics in Fudan University. At that time, physicists have strong interests in low-dimensional system because the particular phenomenon has been predicted due to dimensionality. Conducting polymers have been quite a hot topic in the early 80's since exotic elementary excitations as soliton and polaron have been demonstrated in such systems. Then, the field more and more moved towards theoretical chemistry since the interest in physics was suddenly turned to high T_c superconductivity and fractional quantum Hall effect. My supervisor Prof. Xin Sun and I have kept the interests, ever since the beginning. So, after my PhD in Fudan university, I went to Belgium to work with Prof. Jean-Luc Bredas, a known theoretical chemist working in the same field. It should be noted that the basic concepts derived from conducting polymers such as spin-charge separation and fractional charge have been pivotal to understand the novel quantum phenomena such as strongly correlated electrons and topological excitations in novel quantum materials. But the field itself (organic and polymeric optoelectronics) has become interdisciplinary but predominantly chemistry research. And the theory part has expanded the theoretical chemistry scope. So, very naturally, I turned my self to be a theoretical chemist.

How do you supervise your students?

As for theoretical and computational chemistry group, it is imperial to develop their own computational methodology. Nevertheless, applicability is the value of methodology. Namely, the purpose of methodology is to be applied. Thus, it is equally important for the group to do application work, especially, to collaborate with experimental groups by using our own developed methods. So, all my students need to do computational work either to test the applicability of the methodology or to understand the structure-property for the newly discovered experimental findings, or to clarify some debates in understanding the mechanism/processes. Some of the students have interests in math and physics and in writing program codes. They are strongly encouraged to develop methodology. I am lucky that I do have some excellent students with both motivation and solid math/physics background. I believe they will

do better science than me in the future. And I hope they will also establish their own brand. I will be happy for that. But I am also very happy that the students coming to my group with little theory background but after a few years hard working, they can demonstrate important applications of quantum chemistry and lead to interesting findings by computational study, and they continue their academic career in computational chemistry.

What is the most important personality for scientific research?

Persistence! Chance will come (though only occasionally) to persistent people. Being smart is far from enough.

What's your hobbies? What's your favorite book(s)?

Swimming and music (Rock of the 60s). I like 《上帝掷骰子吗？量子物理史话》 by 曹天元 and all the books by Louis Cha (金庸).

How do you keep balance between research and family?

When you are young, say, before 40, you have to work very hard to establish yourself. Sacrificing family life seems inevitable. After that, it is easy to make a balance.

Who influences you mostly in your life?

My high school physics teacher influenced me most. At the time when GaoKao (高考) was not available, there was hardly any serious class education except my physics teacher. Under his guidance, I spent only 6 months to learn and master four years high school curriculum and got into college: in our school that time, less than 2% can get into college, let alone good university as Sun Yet-sen University. This changed my life.

What is your favorite journal(s)?

The Journal of Chemical Physics, *Physical Review B*, *the Journal of Physical Chemistry (Letters)*, and more and more, *Journal of Chemical Theory and Computation*. We theorists usually do not publish or recognize important work in general chemistry journal. Popular is not necessary important, especially for theoretical work. Most of the Nobel Prize works in physical or theoretical chemistry were published in *J. Chem. Phys.* or *Chem. Phys. Lett.* (with impact factors around 3).

Could you please give us some advices on improving Chinese Journal of Chemistry?

CJC is a general chemistry journal. Chemistry with broad interest should be the most important priority. Thus, methodology paper is usually of less audience unless it demonstrated broad applicability or possibilities to open new fields of applications.

If you have anything else to tell our readers, please feel free to do so.

Keeping in mind to do different science is the most important thing to do. "First" rather than "better" work is always the top priority.

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For submission: <https://mc.manuscriptcentral.com/cjoc>
For articles: <https://onlinelibrary.wiley.com/journal/16147065>



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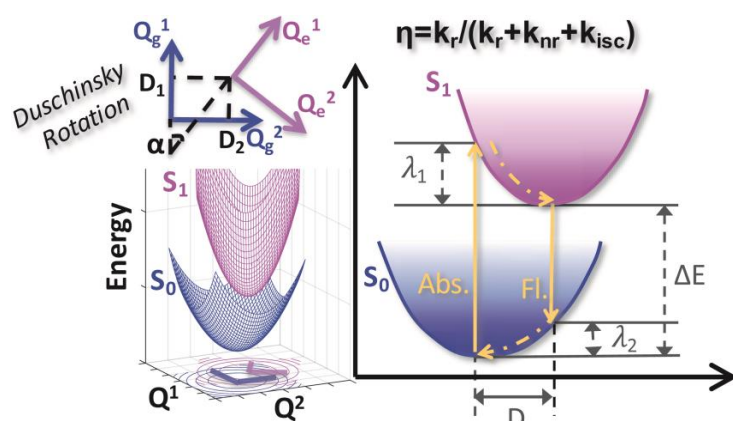
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Excited state decay for complex molecules consists of one of the most challenging issues for theoretical chemistry. By virtue of fast Fourier transformation we developed a highly efficient thermal vibration correlation function formalism for the excited state radiative and non-radiative decay rates, which transformed the conventional Fermi-Golden Rule into a time-dependent formalism and the time-consuming exponential scaling summation over vibrational states has been converted to an N^3 scaling matrix production algorithm combined with time integration. It allows vibration mode mixing (Duschinsky rotation) effect, pertinent for large and soft organic molecules. Another important feature is promoting-mode free, rendering this method quite general. By replacing the non-adiabatic coupling prefactor with intermolecular electronic coupling term, the same formalism can be applied to modeling the carrier mobility in organic semiconductors (which is not discussed in this work). It has been implemented in a portable computational program package MOMAP, which has been successfully applied by many groups for the investigations of organic functional materials,

for example, for fluorescent and phosphorescent emission, aggregation induced emission (AIE) phenomena, sensing process for biological and environmental processes, coordinate compounds, thermally activated delayed fluorescence, as well as organic room temperature phosphorescence.

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1. Introduction

A natural question one would ask is that from theoretical chemistry perspective, can we predict the light-emitting efficiency of a given molecule and molecular materials without any empirical parameters? In fact, this is a long-standing challenge. Even though there are hundreds of computational chemistry packages, so far none of them can address this question. Light-emission stems from the radiative decay from the electronic excited state, usually the lowest-lying one according to Kasha's rule, in competition with a number of radiationless decay processes. In fact, for the organic electroluminescence, which is important for novel display technology, the overall quantum efficiency can be written as a product of four factors: $\eta = \eta_1 \eta_2 \eta_3 \eta_4$, where the ratios are: (1)

No. of photons escaping from the device with respect to the total number of emitted photons from organic materials; (2) No. of emitted photons with respect to No. of singlet excitons; (3) No. of singlet exciton to electro-pumped excitons; (4) No. of electro-pumped exciton to injected carriers. The first factor is the optical out coupling for the photons to escape the device after reabsorption, which is device-structure dependent. Singlet exciton can decay radiatively (Einstein spontaneous emission) with rate denoted as k_r and non-radiatively with rate denoted as k_{nr} . $\eta_2 = k_r / (k_r + k_{nr})$. Quantitative prediction of η_2 is of primary importance for molecular design of OLEDs materials, as well as photovoltaic process, bio- and chemico-sensing. The Einstein spontaneous radiative decay rate is

$$k_r = \frac{8\pi^2 \nu_{fi}^3}{3\epsilon_0 \hbar c^3} \mu_{fi}^2 \approx \frac{f \nu_{fi}^2}{1.5},$$

where μ_{fi} is the electric transition dipole moment between the initial and the final electronic states, f is its (dimensionless) oscillator strength, and if the transition energy ν_{fi} is expressed in wavenumber, the dimension of k_r is in the unit of s^{-1} . The typical radiative decay rate for fluorescence is around 10^8 – $10^9 s^{-1}$ and for phosphorescence is 10^1 – $10^6 s^{-1}$. In fact, quite a large part of my scientific career has been devoted to the light-emitting problems. For instance, to understand the nature of emission from conjugated polymer modeled as a linear chain, we developed a density matrix renormalization group (DMRG) for Pariser-Parr-Pople model to study the ordering of the lowest-lying excited states. This happened to be the earliest application of DMRG in quantum chemistry.^[1] Conventional wisdom stated that for organic electroluminescence, η_3 is limited to 25% due to the spin statistics. Breaking such a limit has become the major task and the

center of interest for the past 20 years^[2-6] and the most successful attempt should be the proposition of using thermally activated delayed fluorescence (TADF) phenomena to convert electrically pumped triplets to singlets by Adachi *et al.*^[6] η_4 is related to charge transport and recombinations, which is close to 1 for the low mobility organic materials. Here, I like to talk more on our contributions to η_2 , without mentioning our work on η_3 . As we discussed above, the radiative decay time scale is ~ 10 ns, while the state-of-the-art excited state dynamics simulation is about 4 orders of magnitude shorter than the fluorescence, let alone phosphorescence. There have been quite large number of investigations on excited state dynamics in revealing the mechanisms for the absence of light-emitting, for instance, the well-known conical intersection (CI) for the ground state and the excited state crossing, occurring typically from femto to picosecond time scale if it occurs, much faster than the typical radiative decay process, defying any possibility for light-emitting. The only feasible theoretical approach for light-emitting efficiency prediction at the first-principles level is the rate formalism for both the radiative and the radiationless processes. In this regard, Kun Huang and his wife Avril Rhys are generally considered to be the first to formulate the radiationless rate, originally developed for the color-center in polar solid states, based on a displaced harmonic oscillator model and Fermi-Golden Rule by taking the nuclear motion as perturbation (Huang-Rhys theory), leading to the multiphonon relaxation process.^[7] Huang revisited this problem in the early 80's. His work aroused my strong interests through his series of lectures in the summer school of 1984 taking place in Huai Rou (precisely now the campus of the University of Chinese Academy of Sciences, UCAS) as well as by his progress review article.^[8] I was deeply impressed by Prof. Huang's clear physical picture and intuition, and the clarity in math. In early 1985, I attended a Winter School in Soochow University where I have learnt from Prof. Lu Yu of their extension of Huang's multiphonon relaxation theory to study the photoexcitation of soliton and polaron in polyacetylene, namely, the multiphonon relaxation processes of the nonlinear excitations.^[9] These early learnings during my graduate study have strong impact on my future academic career. In fact, in one of my postdoc work, I have used Su-Yu's approach to analyze the numerical results of the lattice relaxation for the $1B_u$ exciton in polyacetylene.^[10] Of course, a comprehensive study should take both the CI and the TVCF into considerations if the crossing point is not too high in potential energy surfaces.

Starting from early 2002, Prof. Yong Cao from South China University of Technology and I had the opportunity to coordinate a mega research plan (alias 973 program) on Organic Light-Emitting Materials. The team consisted of a number of major research groups in China in the field and I had the opportunity to learn the state-of-the-art and timely experimental discoveries in China. In one of the project meeting, around 2003, Prof. Ben Zhong Tang presented his work on the exotic aggregation induced emission (AIE) phenomena,^[11] which immediately caught my attention. Then, the long-standing question of quantitative evaluation of excited state radiationless decay came to my research project even till now. A number of aggregation effects on luminescence have been investigated through our theoretical and computational study.

Evidently, the first expert in the field of theoretical photochemistry coming to our mind to seek advisory opinion is Prof. Weihai Fang in Beijing Normal University. I have been lucky that Prof. Fang was very open for collaboration, whose expertise in photophysics and photochemistry had been very helpful to me. He introduced us the earlier work by Sheng-Hsien Lin on the displaced harmonic oscillator for molecules in 1966.^[12] Following that, in 2005, we were able to calculate the key molecular parameters such as the Huang-Rhys (HR) factor for each vibrational mode governing the electronic excited state decay through vibra-

tional relaxations. We noted that AIE chromophores possess large HR factors for the low-frequency modes, which largely helped to understand the mechanism, which was under controversy since the beginning. It is also worthwhile to mention that at that time, Prof. Yi Luo from Royal Institute of Technology in Stockholm, Sweden, was seeking collaborative opportunity in China. I happened to be his first bridge to the circle of Chinese theoretical and computational chemists. Yi Luo also showed his strong interest in AIE phenomena and made several constructive suggestions. Our first theoretical work on AIE was published in *Physical Review B* in 2006,^[13] with myself, Weihai Fang and Yi Luo as corresponding authors. This paper received quite strong interests with 100 citations now.

After that, I discussed this work with Prof. Eli Pollak from Weizmann Institute of Science, who was visiting Prof. Jiushu Shao at Institute of Chemistry, the Chinese Academy of Sciences. They both had been pivotal for the development of TVCF formalisms in my group, the main theme of this article. Eli pointed out the importance of mode-mixing effect for low-frequency modes. Jiushu introduced me the analytical solution of multi-dimensional Gaussian integration as well as operator derivatives with respect to vibration coordinate.

2. Methodology Development and Numerical Implementation

We started by considering that: (i) previous work has been almost exclusively focused on small molecules. More than often, the OLEDs/AIE molecules possess more than 30 atoms (which is considered as large system for excited state dynamics theory); (ii) many vibrational modes can contribute to the relaxation processes involving excited state; (iii) the low-frequency modes often dominate, leading to the mode-mixing as well as anharmonicity, and the previous work did not satisfy the above condition. Then we noted that (i) Duschinsky rotation effect (DRE) can take the mode-mixing effect into account and (ii) for large molecules, all the vibrational modes can be considered as so-called "promoting modes" originated from the atomic kinetic energy term, which can go beyond the displaced harmonic oscillator model, which assumes the same parabola for the ground and excited states. And after some tediously long mathematics, we found that by virtue of thermal vibration correlation function (TVCF) formalism, all the above considerations can be solved analytically. Here, I presents some of the key steps for deriving the formalism.

The non-adiabatic coupling term arising from one vibrational mode is given as:

$$R_i(f_i) = -\hbar^2 \left\langle \Phi_f \left| \frac{\partial}{\partial Q_i} \right| \Phi_i \right\rangle \quad (1)$$

where Φ represents the electronic state vector and Q is the vibration coordinate. I is the so-called "promoting mode" selected through chemical intuition. For small molecule, it is easy to identify one such important mode. However, for complex molecule, many modes could be equally important.

We formulate the rate formula as following:^[13]

$$W_{f \leftarrow i}(T) = \frac{2\pi}{\hbar} \sum_{l,k} R_{lk}^f \frac{1}{Z_{iv}} \sum_{v_i, v_f} e^{-\beta E_{iv_i}} \Omega_{lk}^f \delta(E_{fi} + E_{fv_f} - E_{iv_i}) \quad (2)$$

where Z is the partition function for the initial state parabola. The non-adiabatic coupling R now becomes a matrix with both l and k denoting modes instead of only one mode,

$$R_{lk}^f = \left\langle \Phi_f \left| \hat{P}_{fl} \right| \Phi_i \right\rangle \left\langle \Phi_i \left| \hat{P}_{fk} \right| \Phi_f \right\rangle \quad (3)$$

and Ω in Eq. (2) reads:

$$\Omega_{lk}^f = \left\langle \Theta_{fv_f} \left| \hat{P}_{fl} \right| \Theta_{iv_i} \right\rangle \left\langle \Theta_{iv_i} \left| \hat{P}_{fk} \right| \Theta_{fv_f} \right\rangle \quad (4)$$

where P is the nuclear momentum operator and Θ is the vibrational wavefunction. Thus, we had abandoned the traditional one promoting mode approximation by incorporating all the modes, as R-matrix appeared in the non-adiabatic coupling prefactor. Another effort was to introduce the Duschinsky rotation effect, which expresses the vibrational mode coordinates in the excited state potential as a linear combination of modes in the ground state:

$$Q_{ik} = \sum_l^{3n-6} S_{i \leftarrow f, kl} Q_{fl} + D_{i \leftarrow f, k} \quad (5)$$

where S is Duschinsky rotation matrix and D is the vibrational coordinate displacement vector appeared already in Huang-Rhys theory.

By virtue of Fourier transformation for the Dirac-delta function:

$$\delta(E_{fi} + E_{fv_j} - E_{iv_i}) = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\tau e^{-iE_{fi}\tau} e^{i(E_{iv_i} - E_{fv_j})\tau} \quad (6)$$

and inserting Eq. (6) into Eq. (2) and employing continuously the completeness relationship for the vibrational modes basis, and noting that the transformation between the ground state and the excited state parabola Eq. (5) is:

$$\langle \underline{x}' | \underline{x} \rangle = \delta[\underline{x}' - (S\underline{x} + \underline{D})] \quad (7)$$

and the nuclear momentum P matrix element is expressed as:

$$\langle x_k | \hat{P}_{jk} | y_k \rangle = -i\hbar \frac{\partial}{\partial x_k} \delta(x_k - y_k) \quad (8)$$

we finally obtained an analytical expression of rate as time integration of thermal vibration correlation function (TVCF) in the matrix products form, see Eqs. (27–48) in Ref. 14. Though the final formula looks complicated, the numerical computational cost scales simply as N^3 for each time step (N is the number of vibrational modes). And the time integration can be computed very efficiently by Fast Fourier Transformation (FFT) technique, which happened to have experienced a rapid development in the past years. Appeared in the final analytical formula, there are electronic excited state energy (both vertical and adiabatic), vibrational modes eigenvalues and eigenfunctions. The Duschinsky rotation matrix S and displacement vector D in Eq. (5) are calculated from the optimized ground state and excited state molecular structures plus first and second Eckart conditions. We found the Duschinsky rotation effect (DRE) expressed by S matrix plays an essential role for the aggregation-induced emission luminogens (AIEgens).^[15]

Before the publication of Ref. 14, I sent the preprint to Prof. Sheng-Hsien Lin, the pioneering figure for the excited state radiationless decay theory, for his advice. Here are some comments excerpted from his letter: "... the manuscript 'Promoting-mode free formalism for excited state radiation less decay process with Duschinsky rotation effect' ... deeply impressed, This is certainly a landmark paper in the field of excited state radiationless decay theory...". We are very much encouraged by his words and continue to work in this direction for more than 10 years.

Based on the TVCF, the intersystem crossing, optical absorption and emission now can be similarly re-formulated. The perturbation term for internal conversion is nuclear momentum (Eq. 1), and for intersystem conversion, it is the spin-orbit coupling constant, and for radiative decay, absorption, and emission, it is the transition electric dipole moment.^[16] All the necessary molecular parameters as input data to our formulae can be obtained through time-dependent density functional theory (TDDFT).

We note that the similar formalism can be applied to study the carrier hopping mobility for organic semiconductors. The difference lies in the prefactor appeared in Eq. (1). For inter-molecular charge transfer, the prefactor can be approximated by the

intermolecular electronic coupling.^[17] In addition, we have recently formulated an exciton transport theory based on TVCF, considering long-range intermolecular excitonic coupling and combining both rate process and optical spectra.^[18]

The TVCF method can be used to calculate the light-emitting quantum efficiency and carrier mobility for organic semiconductors. After a few years experiences, the computational results are found to be reasonably good compared with experiments. So we decided to implement the method into a program package, aiming to be used by other scientists, which I named it as MOMAP, for MOlecular MAterials Property Prediction Package.^[19] MOMAP allows starting from scratch to calculate the molecular photo-physics parameters such as radiative decay rate k_r , non-radiative decay k_{nr} , intersystem crossing rate k_{ISC} , absorption and emission spectra, in addition to carrier mobility. On top of that, we recently take the molecular aggregate effect into account through QM/MM approach, namely, the excited state process takes place in the quantum mechanics central part and the aggregate effects are modeled by molecular mechanics. MOMAP was launched in our own group website in the end of 2014. Within two years, the program was downloaded close to 3000 times. Very much encouraged by the success, we then made MOMAP a commercialized product in collaboration with HongZhiWei Technology (Shanghai) Inc. Since then, people have used this program to perform computational work and published more than 100 articles according to our incomplete statistics.

3. Applications of TVCF to Molecules and the Aggregates for the Excited State Processes

In this section, we give some examples of application of the TVCF, including the Duschinsky rotation effect on the excited state decay, quantitative understanding and mechanism of AIE, and photophysical parameters for the thermally activated delayed fluorescence (TADF) molecules.

3.1. Role of Duschinsky rotation effect for radiationless decay

We now first demonstrate the importance of Duschinsky rotation effect on the excited state non-radiative decay, by taking example of two isomeric compounds, *cis,cis*-1,2,3,4-tetraphenylbutadienes (**1**) and 1,1,4,4-tetraphenyl-butadiene (**2**) (Figure 1). It was found experimentally^[20] that at room temperature, **1** is dark in solution but strongly emissive in aggregation, while **2** is highly emissive in solution already. When lowering the temperature to 77 K, **1** starts to emit in solution. **1** is a typical AIEgen while **2** is just a normal chromophore with aggregation quenching behavior. The luminescence quantum efficiency increases about one thousand time from 300 K down to 70 K.

It is known that radiative decay rate as determined by Einstein spontaneous emission process is insensitive to temperature. Thus, it is the non-radiative decay process demonstrating large temperature effect. We compare the calculated non-radiative decay rate of $S_1 \rightarrow S_0$ by TVCF, within which the molecular parameters were evaluated at the TDDFT/B3LYP/6-31g level.

From Table 1, it can be seen DRE has a strong temperature dependence for non-radiative decay rate for **1** but not for **2**. Namely, for **1**, the decay rate increases about three orders of magnitudes from 70 to 300 K, accounting well the experimental findings. The effect can be explained as the mode-mixing of DRE caused electronic excited state energy spread out through vibrational modes, especially through the low-frequency twisting modes arising from phenyl side groups.

3.2. Quantitative characterization of AIE effect in siloles

Secondly, we look at the AIE effect. Molecular aggregate is modeled as a cluster consisting of ~100 molecules cut from crystal

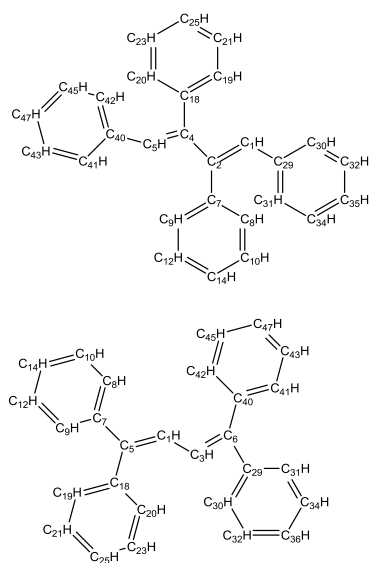


Figure 1 Molecular structures of *cis,cis*-1,2,3,4-tetraphenyl-butadienes (**1**, top) and 1,1,4,4-tetraphenyl-butadiene (**2**, bottom). Adapted with permission from the American Chemical Society (Ref. 15).

Table 1 Non-radiative decay rate (in s^{-1}) $S_1 \rightarrow S_0$ for **1** and **2** calculated at $T=70$ K and 300 K, with DRE in comparison with no DRE. The radiative decay rates for **1** and **2** are calculated to be 4.80×10^8 and 3.92×10^8 , respectively

T/K		1	2
70	DRE	1.12×10^7	1.26×10^5
	no DRE	1.80×10^8	2.24×10^5
300	DRE	1.09×10^{10}	1.86×10^6
	no DRE	1.23×10^9	5.33×10^5

structure, where the central molecule is calculated by TVCF and its surrounding molecules are treated by molecular mechanics, interacting the central part through electrostatic potential. We take hexaphenylsilole (HPS) as an example. Silole is the very first AIEgen. The molecular structure, computational model, and the Huang-Rhys factors for gas phase and aggregate are presented in Figure 2.^[21] Huang-Rhys factor measures the average vibrational quantum number released or absorbed during the excited state vibration relaxation process.

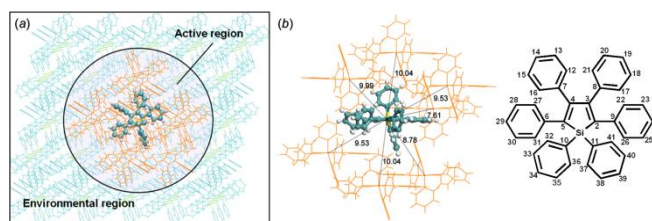


Figure 2 QM/MM model setup (a), active region structure (b), and the molecular structure of HPS (right). Adapted with permission from the American Chemical Society (Ref. 21).

From Table 2, it is noted that upon aggregation, the radiative decay increases a factor of 6 due to the planarization. At the same time, the non-radiative decay rate is reduced about four orders of magnitude. The numerical results are in support of the restriction of internal rotation mechanism proposed by Tang *et al.*^[22] It can be also seen from Figure 2 that the Huang-Rhys factors in aggregate state are deeply reduced in the low frequency regime, corresponding to the rotational motions of phenyl rings.

Table 2 Radiative and non-radiative decay rates for HPS at 300 K for both gas phase and aggregate, and for DRE and "no DRE"

	k_r/s^{-1}		k_{nr}/s^{-1}	
	DRE	No DRE	DRE	No DRE
Gas	1.05×10^7	4.76×10^7	3.76×10^{11}	6.65×10^5
Aggregate	6.56×10^7	6.53×10^7	2.06×10^7	9.36×10^5

Furthermore, we suggested two experimental schemas to verify the above mechanism, namely, through resonant Raman^[23] and isotope effect.^[24] The former is based on the fact that the resonant Raman intensity is proportional to the excited state vibrational mode relaxation energy. Thus, for AIEgens, upon molecular aggregation, there should occur decreased intensity for low-frequency modes and some overall blueshifts. But for non-AIEgens, there would not be any appreciable change. Such prediction is difficult to test because those vibrational modes responsible for AIE process are of quite low frequency (~ 50 cm^{-1} mostly phenyl ring twisting motions), quite difficult to probe. Our theory predicted that isotope effect on the non-radiative decay rate for non-AIEgens should be similarly large, but for AIEgens, it should be diminishingly small in solution phase but quite large at aggregate phase. This prediction is immediately confirmed in experiment which showed that for the typical AIEgen HPS, the isotope effect in solution is less than 1.9%, but can reach -63.6% in aggregation, while theory predicted -66.3% . Such nice agreement between theory and experiment indicates the reliability of the TVCF.

3.3. Mechanism and molecular design of organic room temperature phosphorescence

Recently, long after-glow organic room temperature phosphorescence (ORTP) has attracted great attentions for the potential application in optoelectronics and chemico-bio-sensors. It has been known for long that pure organic molecules possess very weak phosphorescence because of the weak spin-orbit coupling. However, recently there have been a number of experimental discoveries that some pure organic molecules can demonstrate remarkable phosphorescence in aggregate phase, especially in crystalline or co-crystal phase. Our quantum chemistry calculations demonstrated that the intermolecular interaction, specifically the electrostatic interaction (including hydrogen bond) can lead to change of spin-orbit coupling through modification of the ($n-\pi^*$) with respect to ($\pi-\pi^*$) compositions in the low-lying excited state S_1 and T_1 .^[25] Then the TVCF method is applied to investigate the radiative and non-radiative decay rates for the phosphorescent processes in solution and in aggregate phases.^[26] These theoretical approaches have been employed to explore a number of experiments to unravel the mechanism of ultralong lifetime and highly efficient ORTP compounds.^[27] Eventually, we proposed a set of the molecular descriptors for rational ORTP molecular design^[28] (see Figure 3).

3.4. TVCF to design TADF molecules

This part of the paper introduces the application of the TVCF method to design thermally activated delayed fluorescence (TADF) molecules by Prof. Lili Lin (a former visiting scholar) from Shandong Normal University, a successful user of MOMAP. TADF became the research focus of organic light-emitting diodes (OLEDs), because of the nearly 100% exciton utilization efficiency as light-emitting materials in OLEDs. The typical character of TADF molecules is that the energy gap between the first singlet excited state (S_1) and the first triplet excited state (T_1) is small enough that T_1 could effectively be up-converted to S_1 with thermal activation. Consequently, most of TADF molecules are composed of donors and acceptors to achieve small S_1 - T_1 energy gap by separating the electron distribution in the highest occupied molecular orbital

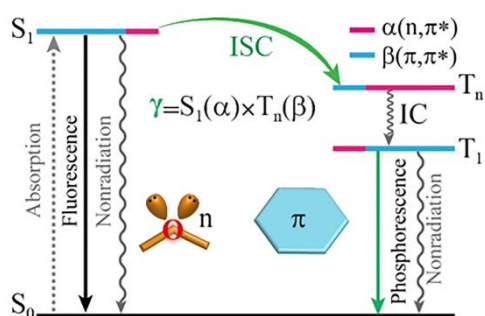
Descriptors (γ , β) in Organic RTP Materials

Figure 3 Four-state model (S_0 , S_1 , T_n , T_1) is most adequate to describe RTP: $S_1 \rightarrow T_n$ (descriptor γ) responsible for phosphorescence efficiency, $T_1 \rightarrow S_0$ (descriptor β) for life-time, where α is auxiliary for efficiency. Quantity (α , β , γ) can be easily obtained by quantum chemistry. Figure partly adapted from Ref. 27 with permission from the American Chemical Society.

(HOMO) and the lowest unoccupied molecular orbital (LUMO). Nevertheless, separated HOMO-LUMO could lead to small oscillator strength, or slow radiative rate, which is harmful for light-emitting. Although S_1 - T_1 energy gap, the radiative rate as well as the reverse intersystem crossing (RISC) rate could be measured experimentally, theoretical study could obtain some new insights on the TADF mechanisms. Several studies have found that there are more than one triplet states lying below S_1 for TADF molecules.^[29-32] Penfold *et al.* also stated that the spin vibronic-coupling effect may play an essential role for the reverse intersystem crossing processes, essential for TADF.^[32-34] Thermal vibration correlation function (TVCF) method, which could correctly predict

the decay rates of excited states, has been proven useful to reveal the mechanism of TADF molecules.^[29,35] As shown in Figure 4, two molecules DBT-BZ-PXZ and DBT-BZ-DMAC are found to have significant TADF phenomenon and minor modification in donor groups could induce different light-emitting efficiency and mechanism. Based on TD-DFT calculations, two triplet excited states are found lower in energy than S_1 for DBT-BZ-DMAC in solid state, while only one is found for DBT-BZ-PXZ. The TVCF calculated decay rates for both gas phase and solid state (QM/MM) are shown in Table 3.

It can be noted that the two triplet states lower than S_1 may be up-converted to S_1 for DBT-BZ-DMAC, although the S_1 - T_2 intersystem crossing (ISC) rate ($3.11 \times 10^7 \text{ s}^{-1}$) and RISC rate ($6.59 \times 10^5 \text{ s}^{-1}$) are a little larger than that between S_1 - T_1 ($5.62 \times 10^6 \text{ s}^{-1}$ and $2.50 \times 10^4 \text{ s}^{-1}$). For DBT-BZ-PXZ, only one triplet state is found to participate in the up-conversion with the RISC rate $2.82 \times 10^6 \text{ s}^{-1}$. It means that more channels are involved in the exciton harvest for DBT-BZ-DMAC. In addition, good agreement can be found

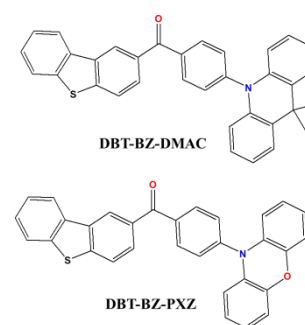


Figure 4 Molecular geometric structures of DBT-BZ-DMAC and DBT-BZ-PXZ.

Table 3 TVCF calculated radiative and nonradiative rates (s^{-1}) ($S_1 \rightarrow S_0$), intersystem crossing (ISC) and reverse ISC (RISC) rates (s^{-1}) ($S_1 \leftrightarrow T_1$). The theoretical prompt fluorescence efficiency (Φ_{PF}), ISC efficiency (Φ_{ISC}), TADF efficiency (Φ_{TADF}) and the total fluorescence efficiency (Φ_{F}) are also presented. Available experimental data are given with superscript 'exp'

	DBT-BZ-DMAC		DBT-BZ-PXZ	
	Gas	Solid	THF	Solid
$k_{\text{r}} (S_1 \rightarrow S_0)$	4.82×10^4	1.32×10^7	7.45×10^4	9.30×10^6
$k_{\text{nr}} (S_1 \rightarrow S_0)$	4.86×10^9	2.40×10^7	2.03×10^{10}	2.05×10^7
$k_{\text{ISC}} (S_1 \rightarrow T_1)$	1.44×10^4	5.62×10^6	1.75×10^5	3.55×10^7
$k_{\text{ISC}} (S_1 \rightarrow T_2)$	1.61×10^6	3.11×10^7	---	---
$k_{\text{RISC}} (T_1 \rightarrow S_1)$	1.84×10^4	2.50×10^4	1.87×10^5	2.82×10^6
$k_{\text{RISC}} (T_2 \rightarrow S_1)$	6.37×10^5	6.59×10^5	---	---
$k_{\text{ISC}}^{\text{cal}} (S \rightarrow T)$	1.60×10^6	2.72×10^7	1.75×10^5	3.55×10^7
$k_{\text{RISC}}^{\text{cal}} (T \rightarrow S)$	6.20×10^5	6.36×10^5	1.87×10^5	2.82×10^6
Φ_{PF}	0.001%	20.5%	0.0004%	14.2%
Φ_{ISC}	0.03%	42.2%	0.0009%	54.4%
Φ_{TADF}	0	15.0%	0	17.0%
Φ_{F}	0.001%	35.5%	0.0004%	31.2%
$k_{\text{r}}^{\text{exp}} (S_1 \rightarrow S_0)$	---	7.04×10^6	---	2.14×10^6
$k_{\text{nr}}^{\text{exp}} (S_1 \rightarrow S_0)$	---	1.74×10^6	---	3.48×10^6
$k_{\text{ISC}}^{\text{exp}} (S \rightarrow T)$	---	1.60×10^7	---	2.05×10^7
$k_{\text{RISC}}^{\text{exp}} (T \rightarrow S)$	---	7.76×10^5	---	9.95×10^6
$\Phi_{\text{PF}}^{\text{exp}}$	---	28.5%	---	8.2%
$\Phi_{\text{ISC}}^{\text{exp}}$	---	64.5%	---	78.5%
$\Phi_{\text{TADF}}^{\text{exp}}$	---	51.7%	---	29.9%
$\Phi_{\text{F}}^{\text{exp}}$	---	80.2%	---	38.1%

$$k_{\text{ISC}}^{\text{cal}} (S \rightarrow T) = \frac{k_{S_1-T_1}^2 + k_{S_1-T_2}^2}{k_{S_1-T_1} + k_{S_1-T_2}}, \quad k_{\text{RISC}}^{\text{cal}} (T \rightarrow S) = \frac{k_{T_1-S_1}^2 + k_{T_2-S_1}^2}{k_{T_1-S_1} + k_{T_2-S_1}}, \quad k_{\text{RISC}}^{\text{exp}} (T \rightarrow S) = \frac{k_{\text{TADF}}^{\text{exp}}}{1 - \frac{k_{\text{ISC}}^{\text{exp}}}{k_{\text{r}}^{\text{exp}} + k_{\text{nr}}^{\text{exp}} + k_{\text{ISC}}^{\text{exp}}}}$$

between theoretical calculation results and experimental values. The effective ISC and RISC rates calculated for DBT-BZ-DMAC are $2.72 \times 10^7 \text{ s}^{-1}$ and $6.36 \times 10^5 \text{ s}^{-1}$, respectively, and the experimental values are $1.60 \times 10^7 \text{ s}^{-1}$ and $7.76 \times 10^5 \text{ s}^{-1}$. For DBT-BZ-PXZ, the calculated decay rates also agree with experimental values well, and the calculated fluorescence efficiency (31.2%) is in good agreement with the experimental counterpart (38.1%). The calculated fluorescence efficiency (35.5%) for DBT-BZ-DMAC is also larger than that for DBT-BZ-PXZ, which is in accordance with experimental results. Theoretical study could not only confirm experimental results, but also provide some new insights on the TADF mechanism.

The theoretical calculation of decay rates can also help us to understand the light-emitting phenomenon. For example, by comparing the fluorescent efficiency of DBT-BZ-PXZ and DBT-BZ-DMAC in solution and in solid state (as shown in Table 3), we can see that the fluorescence efficiency of both molecules is enhanced in solid state, which proves that the two molecules have obvious AIE properties as discussed earlier. In some recent work, the analysis based on the decay rates calculated with TVCF methods also made great contribution in understanding which conformation of TADF molecules is favorable for emission, and why different intensity is found for the dual emission in TADF molecules as well as the light-emitting mechanism of the TADF molecules with excited-state intramolecular proton transfer.^[30,36,37]

3.5. Using TVCF for understanding the photochemical processes in environmental chemistry

Luminescent metal-organic framework (MOF) and crystalline covalent organic framework (COF) generally interact with environmental molecules through hydrogen bonding, which should account for the ultimate fluorescent quenching. Prof. Ce Hao *et al.* from Dalian University of Technology employed MOMAP in combination with density functional theory (DFT) and time-dependent density functional theory (TD-DFT) to investigate the hydrogen bond dynamics in the excited (S_1) states decay behavior for MOF and COF under the influences of hydrogen bonding. As shown in Table 4, MOMAP program was used to calculate the rate constants, which can reproduce the quenching process: the calculated fluorescent rate constants are low since the internal conversion (IC)

rate constant is enhanced for the hydrogen bonded MOF/COF complexes compared with free MOF/COF fragments.^[38,39]

Another example is trifluoromethyl-substituted cyclometalated platinum(II) (TSCP), which is useful for oxygen molecule detection and determination. The nature of oxygen sensing was explained by Hao and coauthors by calculating the rate constants (shown in Table 4) using MOMAP to figure out the quenching mechanism.^[40]

To obtain an in-depth understanding of photochemical reactions, the photophysical and photochemistry characteristics of the basic reactants and products are of great importance. Hao *et al.* studied the photodegradation of sulfapyridine in water,^[44] photodegradation of norfloxacin^[45] and CO_2 photoreduction^[46] through quantum chemical methods. The photophysical properties were revealed through calculation of the rate constants by MOMAP. In Figure 5, the competitions among the photophysical transitions and photochemical reaction paths indicate the intersystem crossing (ISC) from the S_1 state to T_1 state is the rate-limiting step in the aquatic photodegradation of norfloxacin. The study of photophysical processes is important and essential to have a comprehensive view of this kind of photochemical reactions.

Table 4 Calculated radiative rate constants (k_r) and internal conversion rate constants (k_{nr}) of luminescent fragments and their hydrogen bonded complexes

	k_r/s^{-1}	k_{nr}/s^{-1}
Zn(II)-MOF ^[39]	2.78×10^6	
Zn(II)-MOF•HCHO ^[39]	1.12×10^6	
PPy-COF ^[38]	7.64×10^6	
PPy-COF•HCHO ^[38]	2.26×10^3	
Ph-An-COF ^[41]	1.78×10^6	
Ph-An-COF•NH ₃ ^[41]	7.97×10^5	
TT-COF ^[42]	1.16×10^8	
TT-COF•HCHO ^[42]	1.45×10^3	
LCOF-BTT1 ^[43]	1.36×10^5	8.44×10^4
LCOF-BTT1•C ₆ H ₅ NO ₂ ^[43]	5.16×10^9	1.00×10^{11}
TSCP ^[40]	2.0×10^5	1.7×10^{-9}
TSCP•O ₂ ^[40]	6.1×10^2	1.6×10^{10}

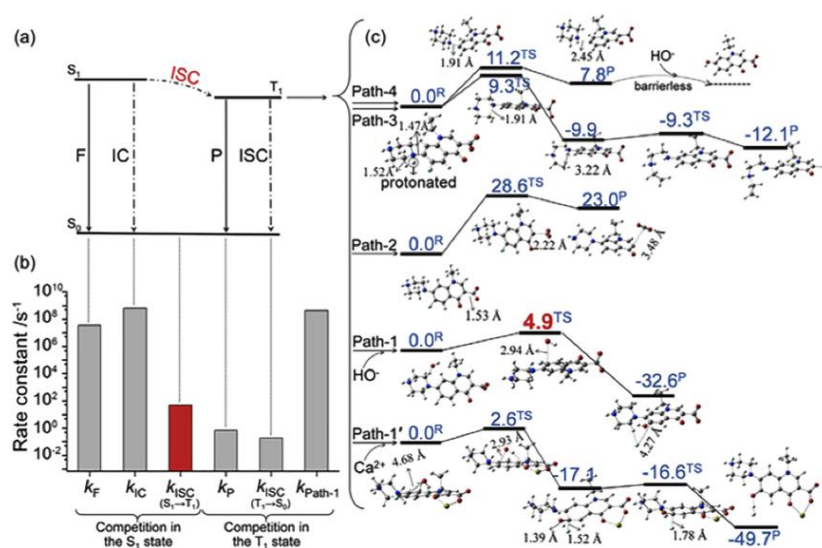


Figure 5 Photophysical and photochemical processes of the photodegradation of norfloxacin. (a) The photophysical transitions of norfloxacin. F: fluorescence emission, IC: internal conversion, ISC: intersystem crossing, P: phosphorescence emission. (b) Rate constants of the photophysical transitions and the reaction path with the lowest activation energy (Path-1). (c) The possible reaction paths and the corresponding activation energies. The blue number on each stationary point is the relative energy in the unit of kcal/mol. R: reactant, TS: transition state, P: product. Carbon: gray, nitrogen: blue, fluorine: cyan, oxygen: red, calcium: yellow. Adapted with permission from the American Chemical Society (Ref. 45).

3.6. TVCF for electrophosphorescence in organometallics

Harvesting triplet state emission is one major way to enhance the electroluminescence quantum efficiency. Through large spin-orbit coupling in organometallic compounds, the electro-pumped carriers can eventually form 100% triplet bound pairs for phosphorescence. Using the TVCF formalism by incorporating the spin-orbit coupling as the perturbation prefactor for non-radiative decay and its induced electric dipole transition from T_1 to S_0 , the phosphorescent quantum efficiency can also be evaluated.^[47] Such formalism was applied to answer the question why the efficiency drops drastically for blue emission in iridium compounds: blue-emitting compounds with large HOMO-LUMO gap can (i) manifest less d-orbital component in HOMO, reducing the metal contribution and decreasing the spin-orbit coupling related oscillator strength; (ii) and often could lead to larger non-radiative decay due to the stronger vibration relaxation in the ligands.^[48] It should be born in mind that in the iridium compound, the lowest triplet state is mostly of metal-ligand charge transfer (MLCT) excitation. Apart from a direct relaxation process from T_1 to S_0 , there exists another deactivation process through transition to the metal center (MC), see Figure 6.

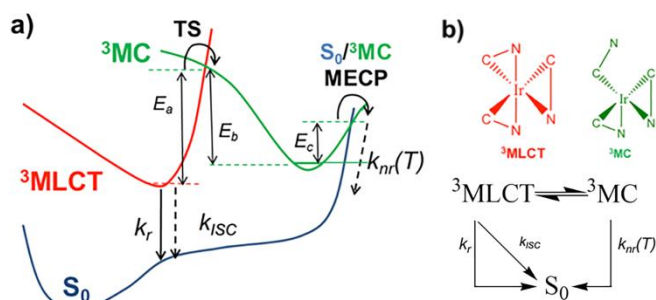
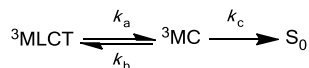


Figure 6 (a) Schematic representation of the potential energy surfaces to describe the competing excited state decay processes for Ir(III) complexes. (b) The kinetic model representation: metal-ligand charge transfer state versus metal center state. Figure adapted with permission from the American Chemical Society (ref. 49).

Thus, the phosphorescence quantum efficiency should be expressed as:

$$\Phi_p = \frac{k_r}{k_r + k_{ISC} + k_{nr}(T)}$$

where k_r and k_{ISC} can be readily calculated by TVCF, but k_{nr} involves the following multi-step reactions:



(see Figure 6)^[49] and it can be expressed as: $k_{nr}(T) = K_c K_a / (K_c + K_b)$, where each k 's can be expressed by thermal activation formalism, leading to the following equation:

$$k_{nr}(T) = \frac{A}{1 + \exp\left(\frac{E_c - E_b}{k_B T}\right)} \exp(-E_a / k_B T)$$

where the three energy barriers E 's are shown in Figure 6, and the prefactor A can be simulated by canonical variational transition state theory (CVT),^[50] the latter involves searching the relevant stationary points for the rate limiting step for ${}^3\text{MLCT} \rightarrow \text{TS} \rightarrow {}^3\text{MC}$, obtained by optimization and intrinsic reaction coordinate (IRC) calculation in both forward and backward directions at the B3LYP/6-31G(d,p)/LANL2DZ level.^[49]

The computational approach we devised should be a general protocol for organometallic compounds for the phosphorescence.

Taking *fac*-Ir($F_2\text{ppy}$)(ppz)₂, a blue-emitting system as an example, for which temperature-dependent phosphorescence has been extensively investigated by Thompson *et al.*,^[51] we depicted the experimental lifetime

$$\tau_p(T) = \frac{1}{k_r + k_{ISC} + k_{nr}(T)}$$

as a function of temperature compared with our theoretical results in Figure 7. It is seen that (i) both experiment and theory demonstrated a two-exponent decay behavior; (ii) theoretical magnitude of lifetime for the whole temperature range agrees nicely with the experiment; (iii) at low temperature, the decay is governed by the radiative plus ISC processes. However, as temperature increases, the transition state barrier (E_a) comes to play a role, the metal center involved deactivation process should be considered, which demonstrate a second (larger) decay exponent. And the even the theoretical transition temperature range is close to experiment.

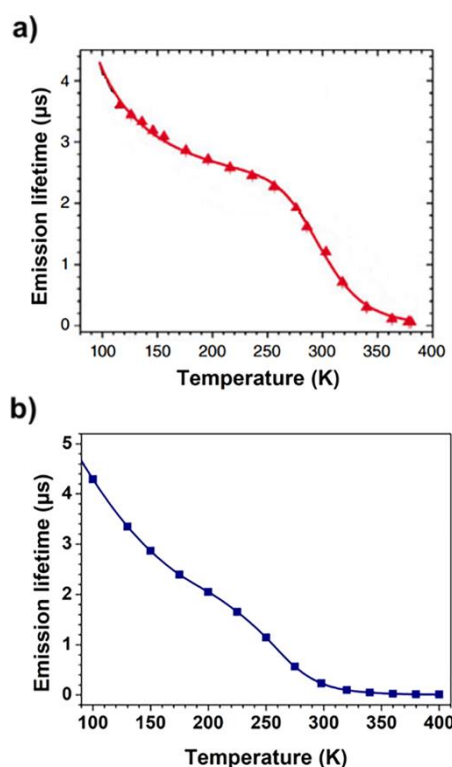


Figure 7 Experimental (a) and computed (b) temperature dependence of the phosphorescent emission lifetime for *fac*-Ir($F_2\text{ppy}$)(ppz)₂. Adapted with permission from the American Chemical Society (Ref. 49).

4. Perspective

So far, we presented the thermal vibration correlation function formalism we developed for the excited state rate processes, relevant for light-emitting and sensing properties. The original question that "can we predict the light-emitting efficiency of a given molecule and molecular materials without any empirical parameters?" is to certain extent answered with our development of TVCF as implemented in the MOMAP program package. It should be noted that the ultrafast conical intersection (CI) process is not considered in this approach. CI process is a necessary way to investigate the dark process, namely, CI occurs within hundreds fs to a few ps time scale, which is much faster than the radiative decay process (~10 ns). When light-emitting phenomena comes to play, it seems TVCF is the feasible theoretical approach. Upon (i) inclu-

sions of Duschinsky rotation effect, (ii) abandoning of “promoting-mode” approximation, and (iii) adding the metal center deactivation process for organometallics, TVCF can give quite quantitative predictions on the photophysical parameters without any empirical data. It is often commented that the non-harmonicity is essential for the photoexcitation relaxation process. Indeed, if you look at the potential energy surfaces of a diatomic molecule where only one degree of freedom (the bond vibration) can accept the electronic excitation energy (often large), the non-harmonicity should dominate the relaxation process. However, for modeling materials or for OLEDs molecules with 100 or so atoms, the degrees of freedom of nuclear coordinates are much more than the diatomic case and the electronic energy is much lower due to conjugation or size effect. Thus, the quantum number of vibrational modes for accepting the electronic energy is usually much less than that expected from diatomic molecule. This may justify the validity of the TVCF, as manifested by the 6 examples listed in the last section from different groups for different problems. Nevertheless, for the weakly fluorescent molecules, the CI process can come to play competitive role. Thus, combining the CI process with our TVCF should be a more comprehensive computational scheme for the light-emitting materials to cover a wider range of molecular parameters. Furthermore, the inclusion of non-harmonicity is certainly the necessary thing to do. These are now in active and promising progresses in our group with the help of the modern quantum chemistry, namely, the time-dependent density matrix renormalization group theory, which is powerful for both electronic structure and chemical dynamics for complex system.^[52]

Acknowledgement

This work was supported by the National Natural Science Foundation of China through the project “Science Center for Luminescence from Molecular Aggregates (SCELMA),” Grant No. 21788102, as well as by the Ministry of Science and Technology of China through the National Key R&D Plan, Grant No. 2017YFA0204501. The author is deeply in debt to Prof. Lili Lin and Miss Shiyun Lin for their kindly help in summarizing 3.4 and 3.5, respectively. The contributions from the following former students/postdocs are greatly acknowledged: Prof. Qian Peng, Prof. Yuanping Yi, Dr. Yingli Niu, Dr. Qunyan Wu, Dr. Huili Ma, Dr. Yuqian Jiang, Dr. Tian Zhang and more.

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Manuscript received: April 20, 2020

Manuscript revised: June 3, 2020

Manuscript accepted: June 4, 2020

Accepted manuscript online: June 8, 2020

Version of record online: XXXX, 2020