Promoting Intersystem Crossing of Fluorescent Molecule via Single Functional Group Modification

Ran Liu, Xing Gao, Mario Barbatti, Jun Jiang, Guozhen Zhang

Promoting Intersystem Crossing of Fluorescent Molecule via Single Functional Group Modification

Ran Liu,[a] Xing Gao,[b] Mario Barbatti,[*c] Jun Jiang,[a] Guozhen Zhang[*a]

[a] *Hefei National Laboratory for Physical Sciences at the Microscale, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: guozhen@ustc.edu.cn.*

[b] *Department of Chemistry, 930 N University Ave, University of Michigan, Ann Arbor, MI 48109, USA*

[c] *Aix Marseille Univ, CNRS, ICR, Marseille, France. E-mail: mario.barbatti@univ-amu.fr Website: www.barbatti.org*

Abstract: Pure light-atoms organic phosphorescent molecules have been under scientific scrutiny because they are inexpensive, flexible, and environment friendly. The development of such materials, however, faces a bottleneck problem of intrinsically small spin-orbit couplings (SOC), which can be addressed by seeking a proper balance between intersystem crossing (ISC) and fluorescence rates. Using N-substituted naphthalimides (NNI) as the prototype molecule, we applied chemical modifications with several electrophilic and nucleophilic functional groups, to approach the goal. The selected electron donating groups actively restrain the fluorescence, enabling an efficient ISC to the triplet manifold. Electron withdrawing groups do not change the luminescent properties of the parent species. The changes in ISC and fluorescence rates are related to the nature of the lowest singlet state, which changes from localized excitation into charge-transfer excitation. This finding opens an alternative strategy for designing pure light-atoms organic phosphorescent molecules for emerging luminescent materials applications.

TOC Graphic
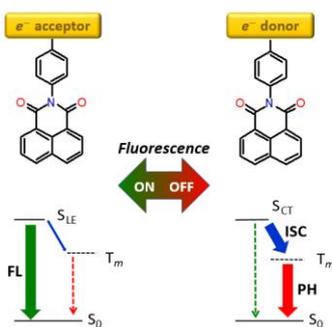
Molecular phosphorescence has a high potential in information processing applications, including sensors, biological imaging, and LEDs, which has promoted a vivid search for efficient, low-cost, and environment-friendly phosphorescent materials.[1-6] Naturally, a crucial point in this search is to develop molecules with efficient intersystem crossing (ISC), the nonradiative transition between electronic states with different spin multiplicity.[7-14] In organometallic LEDs, for instance, the interaction between the singlet metal-to-ligand charge transfer (^{1}MLCT) and the lowest triplet metal-to-ligand charge transfer (^{3}MLCT) states leads to robust ISC, resulting in high phosphorescence quantum yield.[15-16]

To date, many phosphorescent molecules are either organometallic molecules or organic molecules with halogen atoms.[17-18] Such dominance has two causes, both well-documented. First, heavy, occasionally magnetic metal ions help to strength the spin-orbit coupling (SOC), which is the root of ISC.[19-20] Secondly, charge transfer (CT) processes contribute to tuning the relevant excited energies favorably.[21-23] That is, the poor superposition of the orbitals from the metal center and ligand results in tiny singlet-triplet energy gap (ΔE_{ST}, the energy difference between the lowest singlet excited state and neighboring triplet state).[3] Thus, the ISC efficiency can be improved by either reducing ΔE_{ST} or enlarging the SOC matrix element[24-25] (see also eq. (1)).

2

It has been reported that small ΔE_{ST} led to efficient ISC and thereby strong phosphorescence in dibenzothiophene-*S,S*-dioxide and 2-biphenyl-4,6-bis(12-phenylindolo[2,3-a]carbazole-11-yl)-1,3,5-triazine complexes.[26-27] In suitable conditions, the metal-ligand compounds may emit phosphorescence thanks to the ligand-localized nature (^{3}IL* or $^3\pi$-π^*) of the lowest triplet state and the relaxation of ^{3}LMCT/^{3}MLCT to $^3\pi$LC*.[28] However, the risk of toxicity and instability of organometallic or halo-organic molecules limits their applications.[29]

By comparison, pure light-atoms organic molecules could be an alternative because of their low cost, potentially low toxicity, and high engineering flexibility. Recently, pure light-atoms organic materials have emerged as a promising type of phosphorescent materials. Their luminescent properties were modified through crystallization and aggregation-induced emission enhancement to reduce nonradiative losses.[29-33] Nevertheless, the designing of pure light-atoms organic phosphorescent chromophores has still been a significant challenge because of their tiny SOC, ranging from around 1 cm^{-1} in El-Sayed[34] forbidden transitions to typically 50 to 100 cm^{-1} in El-Sayed allowed transitions.[35-36] Such SOC values are truly too small compared to those above 500 cm^{-1} observed in organometallic systems,[37] especially considering that the ISC rate depends on their squared values.

Despite their tiny SOCs, specific chemical modification to pure light-atoms organic fluorescent molecules with functional groups have successfully activated phosphorescence. This is the case, for instance, of N-substituted naphthalimides (NNI), whose luminescent properties can be fundamentally altered when the functional group –OCH$_3$ is added, as reported by Chen et al.[3] Specifically, NNI is fluorescence active but phosphorescence inactive. By contrast, NNI–OCH$_3$ is phosphorescence active but fluorescence inactive (see Figure 1(a)). The proposed mechanism[3] explaining the phosphorescence activation in NNI–OCH$_3$ claims that both the first singlet excited state (S$_1$) and the closest triplet excited state of NNI–OCH$_3$ have charge-transfer (CT)

characters, reducing ΔE_{ST} and, consequently, enhancing the ISC rate (see Figure 1(b)).

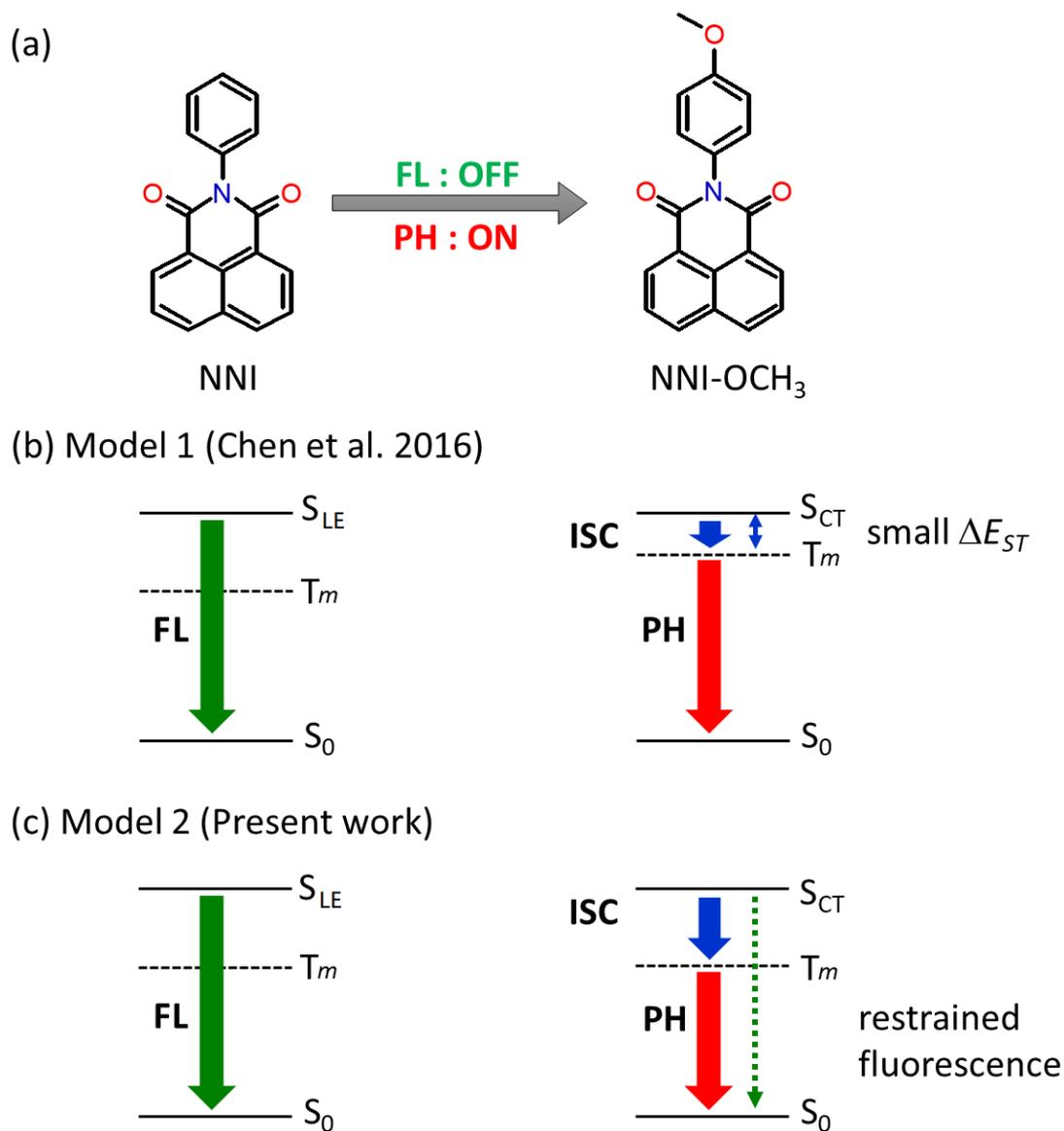Figure 1. (a) The luminescence properties of NNI and NNI–OCH$_3$. The addition of –OCH$_3$ turns the fluorescent NNI into a phosphorescent molecule. (b) A previously proposed mechanism to explain NNI–OCH$_3$ phosphorescence is based on a small ΔE_{ST} due to low-lying CT states.[3] (c) The mechanism proposed in this work is based on restrained fluorescence also caused by low-lying CT states.

These findings prompt us to investigate the photophysics of NNI from a theoretical standpoint, to learn how to control the luminescence behavior of a dye molecule through a delicate modification of its chemical structure. Here, we applied density functional theory (DFT) and time-dependent DFT (TD-DFT) to map electron-hole distributions and to estimate fluorescence and phosphorescence rates in NNI and NNI substituted with diverse functional groups. By studying functional groups that are either electron withdrawing (EWGs: –F and –COOH) or electron donating (EDGs: –OH and –OCH$_3$), we aimed to understand how these different classes of functional substitutions impact the luminescent properties.

We have found out that EDG substitutions strongly enhance the triplet population, while EWG substitutions have little effect compared to the parent system. As proposed by Chen et al.,[3] the CT character of the S$_1$ state in NNI-EDG is the crucial piece to understand the enhanced ISC in these systems. Nevertheless, the reason underlying the ISC enhancement is not a reduction of ΔE_{ST}, but rather a strongly-restrained fluorescence due to transition dipole moment reduction (Figure 1(c)), which compensates for the small SOCs.

Based on the semiclassical Marcus theory, the ISC rate, $k_{ISC} = \tau_{ISC}^{-1}$, from S$_1$ to a neighbor triplet state T$_m$ can be estimated as[38]

$$k_{ISC} = \frac{2\pi}{\hbar} \left|V_{SOC}\right|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{\left(\Delta G_{ST}^{v}\right)^2}{4\lambda k_B T}\right) \tag{1}$$

where V_{SOC} is the spin-orbit coupling (SOC) matrix element, λ is the reorganization energy, and ΔG_{ST}^{v} is the vertical free Gibbs energy variation. As usual, $\hbar$ is the reduced Planck constant, k_B is the Boltzmann constant, and T is the absolute temperature. The reorganization energy was approximated as $\lambda \approx E_{T_2}\left(\mathbf{R}_{\min S_1}\right) - E_{T_2}\left(\mathbf{R}_{\min T_2}\right)$ and the vertical free energy gap as

$\Delta G_{ST}^{v} \approx \Delta E_{ST} = E_{T_m}\left(\mathbf{R}_{\min S_1}\right) - E_{S_1}\left(\mathbf{R}_{\min S_1}\right)$. The SOC matrix elements of selected singlet-triplet channels were calculated at the optimized structure of S_1. They were evaluated adopting the Breit-Pauli (BP) spin-orbital Hamiltonian with effective-charge approximation,[39] using Casida's wavefunction Ansatz.[40] Given proper approximations (See details in the Supporting Information), the simplified rate model in Eq. (1) is supposed to deliver a qualitative estimate of the ISC rate. This limitation is not a major impediment for us, as the rates here are only needed for a qualitative comparison between different photophysical processes.

Meantime, the fluorescence rate, $k_{FL} = \tau_{FL}^{-1}$, was estimated as[41]

$$k_{FL} = \frac{e^2}{2\pi\varepsilon_0 m_e c^3 \hbar^2} \Delta E^2 f \qquad (2)$$

where ε_0 is the vacuum permittivity, m_e is the electron mass, e is the electron charge, c is the speed of light. $\Delta E = E_{S_0}\left(\mathbf{R}_{\min S_1}\right) - E_{S_1}\left(\mathbf{R}_{\min S_1}\right)$ and f are the S_1-S_0 energy gap and the oscillator strength calculated at the S_1 minimum.

The chemical structures of NNI and its four derivatives with single *para*-substitution are collected in the upper half of Figure 2. We first examined the ground states of all species. Intriguingly, regardless of the substituent added to NNI, the benzene and naphthalimide groups are always perpendicular to each other in optimized structures (See Cartesian coordinates in Supporting Information). Further, vertical excitation calculations based on optimized S_0 geometries show that the S_1 states of all species are almost the same (See Table S1 in Supporting Information). Thus, for NNI-OCH_3 and NNI-OH, there may be some configurational change during the relaxation of S_1 that can induce the change of its nature.

The electron-hole distributions of their respective S_1 and T_2 states based on optimized S_1 structures are collected in the lower half of Figure 2. Compared to the NNI molecule, the EDGs concerned in the work (–OH and –OCH_3) alter the nature of

S_1 and T_2 from locally excited states to charge-transfer (CT) states, with an electron transfer from the benzene to the naphtalimide group. Noticeably, this shift is closely related to the conformational change of S_1 and T_2. For NNI, the benzene and the naphthalimide groups are perpendicular to each other, while for NNI-X (X= –OH or –OCH$_3$), they are not. Also, the S_1 of NNI–OH and NNI–OCH$_3$ is a dark state because the two molecular orbitals involved in S_1 (see Table S2 in the Supporting Information) are poorly π-conjugated as the two corresponding molecular fragments appreciably deviated from co-planarity.[42] Meanwhile, the EWGs groups –F and –COOH left almost unchanged the nature of S_1 and T_2.
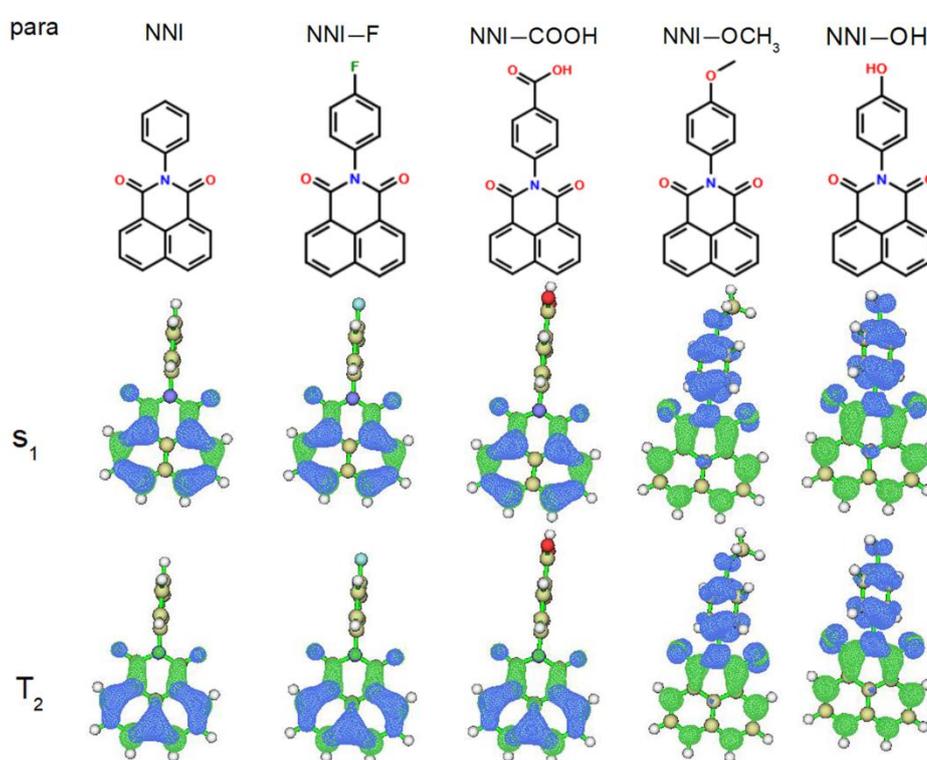

Figure 2.   Upper half: chemical structures; lower half: the electron-hole distribution of S_1 and T_2 of NNI and its *para*-substituted derivatives. (The blue and green regions represent the hole and electron, respectively.)

The occurrence of an S_1 state with CT character in NNI-EDG has major consequences for the photophysics of these molecules. While the $S_1 \rightarrow T_2$ ISC rate in the EWG substitutions is not significantly altered in relation to the parent NNI (Table 1), in the case of the EDGs, it shows an increase of three times for $-OCH_3$ and doubling for $-OH$. Thus, the ISC lifetime shortens from 23 - 26 ns in NNI and NNI-EWG to about 8 - 11 ns in NNI-EDG. The data in Table 1 also show that the ISC rate variation is caused by the increase of the V_{SOC}, from 0.5 to 1.3 cm^{-1} upon EDG substitution, which compensates the small but unfavorable growth of ΔE_{ST}.

Curiously, the reason V_{SOC} is so small in either NNI-EWGs or NNI-EDGs is not the same. In NNI-EWGs (and in the parent NNI), the singlet-triplet transition between $\pi\pi^*$ states is unfavorable by the El-Sayed rule.[34] In NNI-EDGs, V_{SOC} is tiny due to the local nature of the spin-orbit coupling Hamiltonian,[43] which tends to return vanishing elements for non-local transitions, as in CT states.

Table 1. S_1-T_2 energy gap (ΔE_{ST}) at the S_1 minimum, reorganization energy (λ), and SOC (V_{SOC}). ISC rate (k_{ISC}), ISC rate relative to that of NNI (k_{rel}), ISC lifetime (τ_{ISC}). All quantities calculated for NNI and its *para-* and *meta-*substituted derivatives with electron withdrawing (–F and –COOH) and electron donating ($-OCH_3$ and –OH) groups.

	ΔE_{ST} (eV)	λ (eV)	V_{SOC} (cm^{-1})	k_{ISC} (10^7 s^{-1})	k_{rel}	τ_{ISC} (ns)
NNI	-0.162	0.202	0.5	4.3	1	23
Para						
-F	-0.166	0.202	0.5	4.1	1	25
-COOH	-0.170	0.202	0.5	3.9	1	26
-OCH$_3$	-0.258	0.371	1.3	12.2	3	8
-OH	-0.265	0.320	1.3	8.8	2	11
Meta						
-F	-0.168	0.202	0.5	3.9	1	25.3
-COOH	-0.169	0.202	0.5	3.9	1	25.5
-OCH$_3$	-0.268	0.368	2.2	31.0	7	3.2
-OH	-0.286	0.406	2.2	27.7	6	3.6

Such modest changes in the ISC rates would not alone explain the fluorescence switch-on reported in Chen et al.'s work.[3] Nevertheless, the effect of the EDG substitutions on

the fluorescence is more impressive. In NNI and NNI-EWGs, the fluorescence rate is about 2×10^8 s^{-1} (Table 2). In NNI-EDGs, this value is strongly reduced by a factor ~35. Thus, the fluorescence lifetime is elongated from 5 ns in NNI and NNI-EWGs to about 180 ns in NNI-EDGs. This substantial shift in the fluorescence rates caused by the EDG substitutions is a direct result of the CT character of the S_1 state, which reduces the S_1-S_0 oscillator strength. In addition, large S_1-S_0 energy gaps at the S_1 minimum (Table 2) suggests that nonradiative decay of S_1 are not significant for these molecules, even though we have not explicitly investigated nonradiative decay pathways in this work.

Table 2. S_1-S_0 energy gap ΔE and oscillator strength f at the S_1 minimum. Fluorescence rate (k_{FL}), fluorescence rate relative to that of NNI (k_{rel}), and fluorescence lifetime (τ_{FL}). All quantities calculated for NNI and its *para-* and *meta-*substituted derivatives with electron withdrawing (–F and –COOH) and electron donating (–OCH$_3$ and –OH) groups.

	ΔE (eV)	f	k_{FL} (10^8 s^{-1})	k_{rel}	τ_{FL} (ns)
NNI	−3.444	0.367	1.89	1.00	5
Para					
-F	−3.444	0.367	1.89	1.00	5
-COOH	−3.442	0.389	2.00	1.06	5
-OCH$_3$	−3.306	0.011	0.05	0.03	185
-OH	−3.340	0.012	0.06	0.03	178
Meta					
-F	−3.444	0.368	1.89	1.00	5
-COOH	−3.443	0.378	1.90	1.03	5
-OCH$_3$	−3.049	0.007	0.03	0.02	340
-OH	−3.042	0.006	0.02	0.01	408

In short, we show that substitution of selected EDGs in NNI ~~results in the enhancement of ISC rate between its lowest singlet excited states and adjacent triplet excited states thanks to a larger SOC~~ induces discernable configuration change of the lowest singlet excited state, resulting in a larger SOC between S_1 and adjacent T_2 and ensuing enhancement of ISC rate. In contrast to the hypothesis in the experimental work which emphasizes the decisive role of reducing singlet-triplet gap to boost ISC, we

show that it follows an alternative mechanism for NNI species. Moreover, the dark nature of the S_1 state in the NNI-EDG, which also roots from the structural change of S_1, strongly elongates the fluorescence lifetime, making it slower than ISC and favoring the phosphorescence in these species. Thus, our theoretical results suggest the significance of configuration tuning of chromophores on their luminescent properties, casting new physical insight into the hypothesis proposed in the precedent work of Chen et al.[3]

To further exploit this design strategy, we studied the effect of substitutions in the *meta-* position. Our results, presented below, revealed the general relationship between the mechanism of intersystem crossing and the charge-transfer excited-state process.

Figure 3 shows the chemical structures of NNI and its four derivatives with single *meta*-substitution, and the electron-hole distributions of their S_1 and T_2. They are like their counterpart species of *para*-substitution in both geometric and electronic structures.
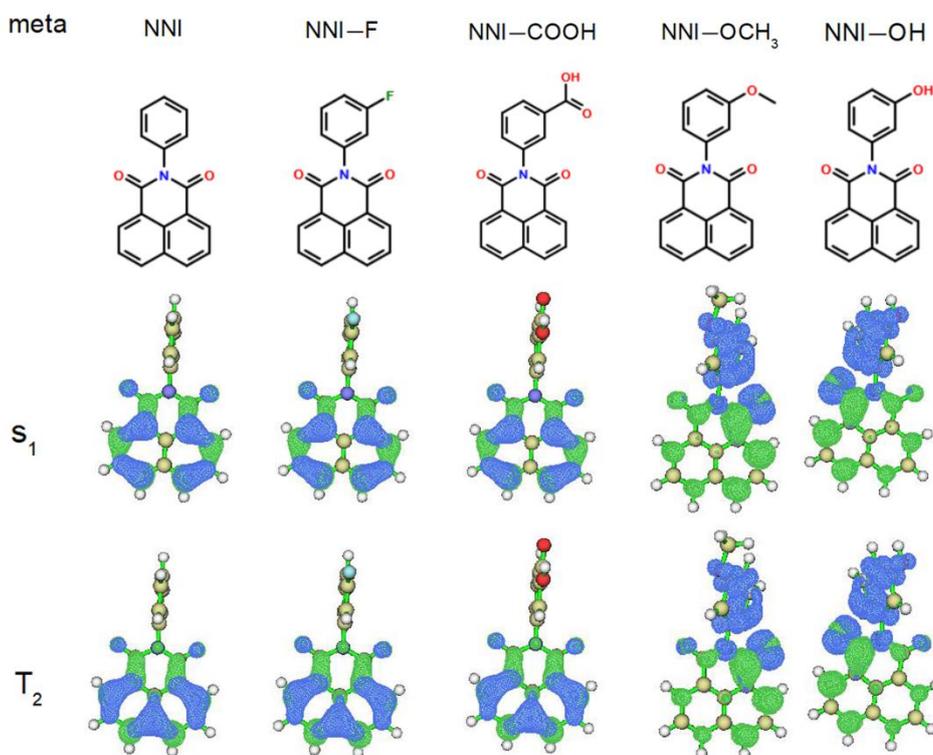
Figure 3.   Upper half: chemical structures; lower half: the electron-hole distribution of S_1 and T_2 of NNI and its meta-substitution derivatives.

The S_1-T_2 energy gaps of each *meta*-substituted species are almost invariant compared to their *para*-substituted counterpart, as seen from the data in Table 1 and Table 2. The natures of S_1 are barely changed as well. (See Table S2 and Table S3 in the Supporting Information). The main reason for the insensitivity to the substitution position on the excitation energy of S_1 lies in that the region the electron moves out during the $S_0{\rightarrow}S_1$ excitation does not directly involve the added group.

The effects of the substitutions on the ISC and fluorescence rates are also qualitatively the same as those observed in the *para*-substitutions. Nevertheless, there are some interesting quantitative variations.

The ISC rates of the *meta*-NNI-EDGs are about 6 to 7 times larger than that of NNI (Table 1). In the para-NNI-EDGs, this growth was no larger than 3. The reason for this additional enhancement is once again in V_{SOC}, which reaches 2.2 cm^{-1} in *meta*-NNI-EDGs against 0.5 cm^{-1} in NNI and 1.3 cm^{-1} in *para*-NNI-EDGs. Although all these values are within the error bar our methodology for V_{SOC} calculation,[35] we can speculate that the slightly larger value upon *meta*-substitutions are due to the asymmetry it introduces, helping to mix the singly-occupied orbitals in the singlet and triplet states.

The fluorescence rates are also more significantly impacted by the *meta*- than by the *para*-substitutions. While in the latter, they are reduced by a factor 35 compared to NNI, in upon a *meta*-substitution this reduction is between 64 and 77 times. Thus, the fluorescence lifetime is elongated up to 408 ns. Once more, the reduction of the fluorescence rates is due to the dark nature of S_1.

Efficient ISC is the prerequisite for photoinduced phosphorescence process. It is crucial to enhance ISC in molecular design towards organic phosphorescence.[14] In this theoretical study, we showed that for specific fluorescent molecules like NNI,

chemical modification by adding an electron donating group (EDG) could appreciably shift the balance between fluorescence and ISC, favoring the latter. In NNI and NNI with electron withdrawing group (EWG), ISC occurs within ~25 ns, while fluorescence is faster, occurring within 5 ns. Thus, these molecules tend to show strong fluorescence. In NNI-EDG, however, ISC becomes faster, between 3 and 11 ns, while fluorescence becomes much longer, between 185 and 408 ns. Therefore, these molecules efficiently populate the triplet manifold and, under adequate conditions, may become phosphorescent. It is encouraging to see that the EDG substitution enhances the transference from singlet to triplet states and enables phosphorescence, even in systems with very small spin-orbit couplings (~1 cm^{-1}), as it is often the case of pure light-atoms organic molecules.

The strong photophysical shift between NNI and NNI-EWG on the one hand and NNI-EDG on the other is related to the nature of the S_1 state. In the former molecules, the lowest singlet state has a localized character, while upon an EDG substitution it becomes a charge-transfer (CT) state in response to the configurational change of molecules. The CT state has a slightly stronger coupling to T_2. Although the spin-orbit coupling is still tiny, about 2 cm^{-1}, it is enough to enhance the ISC rate by up to a factor 7 compared to the parent NNI. Concerning fluorescence, while the localized S_1 state is strongly dipole-coupled to S_0, with oscillator strength near 0.4, the CT S_1 state has a vanishing coupling to S_0, with an oscillator strength not larger than 0.01. Therefore, the fluorescence rate reduces by up 77 times.

These are systematic findings observed in the comparison between the parent NNI and NNI functionalized by –F and –COOH EWGs and–OCH$_3$ and –OH EDGs. Substitution of these groups in either *para* or *meta* locations does not change the qualitative results, although the population of triplet states is even more favorable after a *meta*-substitution.

In short, we have shown that ISC can be promoted by restrained fluorescence due to low-lying CT singlet states. The triplet population formed in this way may

fluoresce as long as conventional conditions are met: nonradiative rates are small, and the chromophore is in an oxygen-depleted atmosphere. Restrained-fluorescence ISC turns out to be so efficient that it can deplete the singlet population even in systems with spin-orbit couplings as small as those in El-Sayed forbidden transitions.

This study cast new insight into the design of pure light-atoms organic phosphorescent molecules via chemical modifications of functional groups. By exploring more organic molecules using the same strategy and employing more comprehensive theoretical framework that can compute phosphorescent radiative decay rate,[44-45] we are on the way of rational design of new organic phosphorescent molecules.

AUTHOR INFORMATION

Corresponding Author

*(G.Z.) E-mail: guozhen@ustc.edu.cn.

*(M.B.) E-mail: mario.barbatti@univ-amu.fr.

ORCID

Guozhen Zhang: 0000-0003-0125-9666

Mario Barbatti: 0000-0001-9336-6607

Note

The authors declare no competing financial support.

Supporting Information Avaliable

The computational details, transition energies, transition related molecular orbitals and corresponding electron-hole distribution of the lowest singlet excited state, the energy level diagrams of low-lying excited states, the Cartesian coordinates of all optimized molecules.

References

1. He, Z.; Zhao, W.; Lam, J. W. Y.; Peng, Q.; Ma, H.; Liang, G.; Shuai, Z.; Tang, B. Z. White Light Emission from a Single Organic Molecule with Dual Phosphorescence at Room Temperature. *Nat Commun* **2017,** *8*, 416.

2. Zhao, W.; He, Z.; Lam, Jacky W. Y.; Peng, Q.; Ma, H.; Shuai, Z.; Bai, G.; Hao, J.; Tang, Ben Z. Rational Molecular Design for Achieving Persistent and Efficient Pure Organic Room-Temperature Phosphorescence. *Chem* **2016,** *1*, 592-602.

3. Chen, X., et al. Versatile Room-Temperature-Phosphorescent Materials Prepared from N-Substituted Naphthalimides: Emission Enhancement and Chemical Conjugation. *Angew Chem Int Ed Engl* **2016,** *55*, 9872-6.

4. Lee, J.; Chen, H. F.; Batagoda, T.; Coburn, C.; Djurovich, P. I.; Thompson, M. E.; Forrest, S. R. Deep Blue Phosphorescent Organic Light-Emitting Diodes with Very High Brightness and Efficiency. *Nat Mater* **2016,** *15*, 92-8.

5. Zhen, X.; Tao, Y.; An, Z.; Chen, P.; Xu, C.; Chen, R.; Huang, W.; Pu, K. Ultralong Phosphorescence of Water-Soluble Organic Nanoparticles for in Vivo Afterglow Imaging. *Adv. Mater.* **2017,** *29*.

6. Baryshnikov, G.; Minaev, B.; Agren, H. Theory and Calculation of the Phosphorescence Phenomenon. *Chem. Rev.* **2017,** *117*, 6500-6537.

7.   Kwon, M. S., et al. Suppressing Molecular Motions for Enhanced Room-Temperature Phosphorescence of Metal-Free Organic Materials. *Nat Commun* **2015,** *6*, 8947.

8.   Hedley, G. J.; Ruseckas, A.; Samuel, I. D. Ultrafast Intersystem Crossing in a Red Phosphorescent Iridium Complex. *J. Phys. Chem. A* **2009,** *113*, 2-4.

9.   Rothe, C.; King, S.; Monkman, A. Long-Range Resonantly Enhanced Triplet Formation in Luminescent Polymers Doped with Iridium Complexes. *Nat. Mater.* **2006,** *5*, 463-6.

10. Acharya, R.; Cekli, S.; Zeman, C. J. t.; Altamimi, R. M.; Schanze, K. S. Effect of Selenium Substitution on Intersystem Crossing in Pi-Conjugated Donor-Acceptor-Donor Chromophores: The LUMO Matters the Most. *J. Phys. Chem. Lett.* **2016,** *7*, 693-7.

11. Samanta, P. K.; Kim, D.; Coropceanu, V.; Bredas, J. L. Up-Conversion Intersystem Crossing Rates in Organic Emitters for Thermally Activated Delayed Fluorescence: Impact of the Nature of Singlet Vs Triplet Excited States. *J. Am. Chem. Soc.* **2017,** *139*, 4042-4051.

12. Lucenti, E.; Forni, A.; Botta, C.; Carlucci, L.; Giannini, C.; Marinotto, D.; Previtali, A.; Righetto, S.; Cariati, E. H-Aggregates Granting Crystallization-Induced Emissive Behavior and Ultralong Phosphorescence from a Pure Organic Molecule. *J. Phys. Chem. Lett.* **2017,** *8*, 1894-1898.

13. Bai, F. Q.; Nakatani, N.; Nakayama, A.; Hasegawa, J. Y. Excited States of a Significantly Ruffled Porphyrin: Computational Study on Structure-Induced Rapid Decay Mechanism Via Intersystem Crossing. *J. Phys. Chem. A* **2014,** *118*, 4184-94.

14. Ma, H.; Peng, Q.; An, Z.; Huang, W.; Shuai, Z. Efficient and Long-Lived Room-Temperature Organic Phosphorescence: Theoretical Descriptors for Molecular Designs. *J. Am. Chem. Soc.* **2019**.

15. Vlček, A.; Záliš, S. Modeling of Charge-Transfer Transitions and Excited States in D6 Transition Metal Complexes by Dft Techniques. *Coord. Chem. Rev.* **2007,** *251*, 258-287.

16. Thomas, R. A.; Tsai, C. N.; Mazumder, S.; Lu, I. C.; Lord, R. L.; Schlegel, H. B.; Chen, Y. J.; Endicott, J. F. Energy Dependence of the Ruthenium(Ii)-Bipyridine Metal-to-Ligand-Charge-Transfer Excited State Radiative Lifetimes: Effects of Pipi*(Bipyridine) Mixing. *J. Phys. Chem. B* **2015,** *119*, 7393-406.

17. Xu, H.; Chen, R.; Sun, Q.; Lai, W.; Su, Q.; Huang, W.; Liu, X. Recent Progress in Metal-Organic Complexes for Optoelectronic Applications. *Chem. Soc. Rev.* **2014,** *43*, 3259-302.

18. Mukherjee, S.; Thilagar, P. Recent Advances in Purely Organic Phosphorescent Materials. *Chem Commun (Camb)* **2015,** *51*, 10988-1003.

19. McClenaghan, N. D.; Leydet, Y.; Maubert, B.; Indelli, M. T.; Campagna, S. Excited-State Equilibration: A Process Leading to Long-Lived Metal-to-Ligand Charge Transfer Luminescence in Supramolecular Systems. *Coord. Chem. Rev.* **2005,** *249*, 1336-1350.

20. Yushchenko, O.; Licari, G.; Mosquera-Vazquez, S.; Sakai, N.; Matile, S.; Vauthey, E. Ultrafast Intersystem-Crossing Dynamics and Breakdown of the Kasha-Vavilov's Rule of Naphthalenediimides. *J. Phys. Chem. Lett.* **2015,** *6*, 2096-100.

21. Joo, B.; Kim, E. G. Model-Independent Determination of the Degree of Charge Transfer in Molecular and Metal Complexes. *Chem. Commun.* **2015,** *51*, 15071-4.

22. Niehaus, T. A.; Hofbeck, T.; Yersin, H. Charge-Transfer Excited States in Phosphorescent Organo-Transition Metal Compounds: A Difficult Case for Time Dependent Density Functional Theory? *RSC Advances* **2015,** *5*, 63318-63329.

23. Han, J.; Shen, L.; Chen, X.; Fang, W. Phosphorescent Mechanism for Single-Dopant White Oled of Fpt: Electronic Structure and Electron Exchange-Induced Energy Transfer. *Journal of Materials Chemistry C* **2013,** *1*, 4227.

24. Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Zhao, J.; Xu, J.; Chi, Z.; Aldred, M. P. Recent Advances in Organic Thermally Activated Delayed Fluorescence Materials. *Chem. Soc. Rev.* **2017,** *46*, 915-1016.

25. Yang, L.; Wang, X.; Zhang, G.; Chen, X.; Zhang, G.; Jiang, J. Aggregation-Induced Intersystem Crossing: A Novel Strategy for Efficient Molecular Phosphorescence. *Nanoscale* **2016,** *8*, 17422-17426.

26. Dias, F. B.; Bourdakos, K. N.; Jankus, V.; Moss, K. C.; Kamtekar, K. T.; Bhalla, V.; Santos, J.; Bryce, M. R.; Monkman, A. P. Triplet Harvesting with 100% Efficiency by Way of Thermally Activated Delayed Fluorescence in Charge Transfer Oled Emitters. *Adv. Mater.* **2013,** *25*, 3707-14.

27. Endo, A.; Sato, K.; Yoshimura, K.; Kai, T.; Kawada, A.; Miyazaki, H.; Adachi, C. Efficient up-Conversion of Triplet Excitons into a Singlet State and Its Application for Organic Light Emitting Diodes. *Appl. Phys. Lett.* **2011,** *98*, 083302.

28. Chabera, P., et al. A Low-Spin Fe(Iii) Complex with 100-Ps Ligand-to-Metal Charge Transfer Photoluminescence. *Nature* **2017,** *543*, 695-699.

29. Bolton, O.; Lee, K.; Kim, H. J.; Lin, K. Y.; Kim, J. Activating Efficient Phosphorescence from Purely Organic Materials by Crystal Design. *Nat Chem.* **2011,** *3*, 205-10.

30. An, Z., et al. Stabilizing Triplet Excited States for Ultralong Organic Phosphorescence. *Nat Mater* **2015,** *14*, 685-90.

31. Qian, Y.; Li, S.; Zhang, G.; Wang, Q.; Wang, S.; Xu, H.; Li, C.; Li, Y.; Yang, G. Aggregation-Induced Emission Enhancement of 2-(2'-Hydroxyphenyl)Benzothiazole-Based Excited-State Intramolecular Proton-Transfer Compounds. *J. Phys. Chem. B* **2007,** *111*, 5861-8.

32. Ravotto, L.; Ceroni, P. Aggregation Induced Phosphorescence of Metal Complexes: From Principles to Applications. *Coord. Chem. Rev.* **2017,** *346*, 62-76.

33. Mei, J.; Leung, N. L.; Kwok, R. T.; Lam, J. W.; Tang, B. Z. Aggregation-Induced Emission: Together We Shine, United We Soar! *Chem. Rev.* **2015,** *115*, 11718-940.

34. El-Sayed, M. A. Spin—Orbit Coupling and the Radiationless Processes in Nitrogen Heterocyclics. *J. Chem. Phys.* **1963,** *38*, 2834-2838.

35. Gao, X.; Bai, S.; Fazzi, D.; Niehaus, T.; Barbatti, M.; Thiel, W. Evaluation of Spin-Orbit Couplings with Linear-Response Time-Dependent Density Functional Methods. *J. Chem. Theory Comput.* **2017,** *13*, 515-524.

36. Dinkelbach, F.; Kleinschmidt, M.; Marian, C. M. Assessment of Interstate Spin–Orbit Couplings from Linear Response Amplitudes. *J. Chem. Theory Comput.* **2017,** *13*, 749-766.

37. Sayfutyarova, E. R.; Chan, G. K.-L. A State Interaction Spin-Orbit Coupling Density Matrix Renormalization Group Method. *J. Chem. Phys.* **2016,** *144*, 234301.

38. Bredas, J. L.; Beljonne, D.; Coropceanu, V.; Cornil, J. Charge-Transfer and Energy-Transfer Processes in Pi-Conjugated Oligomers and Polymers: A Molecular Picture. *Chem. Rev.* **2004,** *104*, 4971-5004.

39. Chiodo, S. G.; Russo, N. One-Electron Spin-Orbit Contribution by Effective Nuclear Charges. *J. Comput. Chem.* **2009,** *30*, 832-839.

40. Casida, M. E. Time-Dependent Density Functional Response Theory for Molecules. In *Recent Advances in Density Functional Methods*, Chong, D. P., Ed. World Scientific: Singapore, 1995; Vol. 1, pp 155-192.

41. Hilborn, R. C. Einstein Coefficients, Cross-Sections, F Values, Dipole-Moments, and All That. *Am. J. Phys.* **1982,** *50*, 982-986.

42. Gong, Z. Y.; Duan, S.; Tian, G.; Zhang, G.; Jiang, J.; Luo, Y. Optical Excitation in Donor-Pt-Acceptor Complexes: Role of the Structure. *J. Phys. Chem. A* **2016,** *120*, 3547-53.

43. Marian, C. M. Spin–Orbit Coupling and Intersystem Crossing in Molecules. *WIREs: Comp. Mol. Sci.* **2012,** *2*, 187-203.

44. Peng, Q.; Niu, Y.; Shi, Q.; Gao, X.; Shuai, Z. Correlation Function Formalism for Triplet Excited State Decay: Combined Spin-Orbit and Nonadiabatic Couplings. *J. Chem. Theory Comput.* **2013,** *9*, 1132-43.

45. Minaev, B.; Baryshnikov, G.; Agren, H. Principles of Phosphorescent Organic Light Emitting Devices. *Phys. Chem. Chem. Phys.* **2014,** *16*, 1719-1758.