

Accepted Article

- Title: Manipulating the Triplet Chromophore Stacking for Ultralong Organic Phosphorescence in Crystal
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201907572 Angew. Chem. 10.1002/ange.201907572

Link to VoR: http://dx.doi.org/10.1002/anie.201907572 http://dx.doi.org/10.1002/ange.201907572

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Manipulating the Triplet Chromophore Stacking for Ultralong Organic Phosphorescence in Crystal

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Abstract: Molecular packing has been of great importance for tailoring the ultralong organic phosphorescence (UOP) properties in crystal, whereas the underlying mechanism for the UOP properties is still unclear because of the complex influence factors on phosphorescence. Herein, we provide some deeper understanding, from the perspective of structural group, that the stacking between triplet chromophores really plays a critical role in UOP generation in crystal. Through adjusting the substitution positions of chlorine atoms, we found there was a UOP on and off variation from 24CPhCz to 35CPhCz. Remarkably, 24CPhCz with the strongest intermolecular coupling between carbazole units exhibited the most impressive UOP with a long lifetime of 1.06 s and a phosphorescence quantum yield of 2.5%. 34CPhCz showed UOP and TADF dual-emission with a moderately decreased phosphorescence lifetime of 770 ms, while 35CPhCz only displayed TADF owing to the absence of strong electronic coupling between triplet chromophores. This study will provide a clear understanding for explaining UOP generation in crystal and new guideline for obtaining UOP materials.

Ultralong organic phosphorescence (UOP), as a kind of novel long persistent luminescent phenomenon, is especially attractive in recent years,^[1] because materials with such a feature show great potential in sensing, displays, bioimaging and anticounterfeiting.^[2] To obtain UOP materials, tremendous efforts are mainly devoted to two prerequisites: one is the introduction of heavy halogen atoms, aromatic carbonyl groups or other substituents to accelerate intersystem crossing (ISC) between singlet and triplet excited states; the other is to provide a rigid molecular environment to suppress the non-radiation transitions for favoring UOP emission.^[3] Among the reported strategies, such as the polymerization, host-guest doping methods, etc.,[4] crystal engineering is indispensable to obtain UOP, because molecular motions can be efficiently restricted in the rigid crystal environment.^[5] In this context, the analysis of molecular packing in crystal is crucial for understanding the UOP generation.^[6]

Up to now, a plenty of investigations on the relationship between the UOP behaviors and the molecular packing have

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Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201YXXXXX. been reported.^[7] It was revealed that the molecular packing style in the solid state usually plays a vital role in tailoring the UOP lifetime,^[8] emission efficiency,^[9] luminescent color,^[10] and even realizing the unique dynamic UOP and mechano-induced persistent phosphorescence emission.^[11] Despite great success in studying the relationship between the phosphorescence properties and molecular packing styles, the underlying mechanism for the UOP properties is still unclear owing to the complex influence factors on phosphorescence. Therefore, a deeper understanding of the effective molecular packing is of great importance. Generally, each organic phosphor consists of several groups. In fact, not all the organic group coupling is effective for the UOP generation. The broad defined molecular packing involves the stacking between various groups. Some groups, such as carbazole,^[1a,5d,8a] phenothiazine,^[8b-c] etc., favoring for the triplet excited states could be regarded as triplet chromophores to manipulate phosphorescence generation, while the others can be seen as functional groups that may be inclined to manipulating molecular packing by tuning intermolecular interactions (Figure 1a). It is noteworthy to think that the stacking of which group is really essential for UOP generation in crystal.



Figure 1. a) Schematic illustration of different triplet chromophore stacking styles for tailoring UOP on and off behaviors. b) Chemical structures of three compounds and their luminescent properties.

Herein, we proposed a specific explanation that the stacking between triplet chromophores really plays a critical role in UOP generation in crystal. We designed three isomers to manipulate the triplet chromophore stacking by tiny modulation on the

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Figure 2. Photophysical properties of aromatic amide derivatives in the solid state. a) Steady-state photoluminescence (blue line) and phosphorescence (red line) spectra of 24CPhCz, 34CPhCz and 35CPhCz. Insets show photographs of 24CPhCz, 34CPhCz and 35CPhCz crystals under 365 nm UV light on and off. b) Excitation-phosphorescence mapping of 24CPhCz crystal under ambient conditions. c) Lifetime decay profiles of the ultralong phosphorescence bands of 24CPhCz and 34CPhCz at 532 and 537 nm, respectively. d) Lifetime decay profile of fluorescence band of 35CPhCz at 488 nm. e) Steady-state fluorescence spectra of 35CPhCz at different temperatures. The inset shows the luminescent intensity changes.

functional group (Figure 1b). With isomerization of chlorine atoms at phenyl unit, we found that there was an interesting UOP switching on-off behavior in these isomers. Remarkably, 24CPhCz exhibited an ultralong phosphorescence lifetime of up to 1.06 s, and 34CPhCz showed UOP (770 ms) and thermally activated delayed fluorescence (TADF, 1.9 μ s) dual-emission. For 35CPhCz, however, there displayed only TADF with a short lifetime of 2.7 μ s. Taken X-ray single crystal analysis and theoretical calculations together, we proposed that the intermolecular coupling between carbazole chromophores played a critical role in tailoring the two competing processes of UOP and TADF emission in crystal at room temperature.

In this work, the aromatic amide derivatives, namely, (9Hcarbazol-9-yl) (2,4dichlorophenyl) methanone (24CPhCz), (9Hcarbazol-9-yl) (3,4-dichlorophenyl) methanone (34CPhCz) and (9H-carbazol-9-yl) (3,5-dichlorophenyl) methanone (35CPhCz) were easily synthesized by one-step reaction with high yields of over 50% (Scheme S1). Their chemical structures were fully characterized by ¹H NMR, ¹³C NMR, elemental analysis, X-ray single-crystal diffraction analysis and high-resolution mass

spectra (Figure S1-6).

Firstly, the photophysical properties of these isomers were systematically investigated in dilute solution. As depicted in Figure S7, the absorption spectra in dichloromethane solution (DCM, 50 µM) of these molecules showed similar peaks at 300 and 315 nm. Accordingly, the steady-state photoluminescence (PL) spectra in DCM revealed splitting peaks at 340 and 353 nm, which might be attributed to locally excited states (Figure S8).^[12] Whereas the wide bands at around 533, 550 and 590 nm were ascribed to intramolecular charge transfer (ICT) states owing to their twisted D-A architectures, which was proved by the red-shift of the wide emission bands with the solvent polarity increased.^[13] Besides, these isomers all present similar phosphorescence profiles with peaks at 419 and 448 nm in dilute dimethyl tetrahydrofuran (50 µM) at 77 K, indicating the phosphorescence in single molecule state originated from the same chromophore (Figure S9). Interestingly, the PL and phosphorescence spectra were well-overlapped at 77 K, indicating a very high ISC efficiency of singlet excitons. Obviously, these compounds show the similar photophysical properties in dilute solution.

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In solid state, 24CPhCz, 34CPhCz, and 35CPhCz performed distinct emission features. As shown in Figure 2a, their emission colors in crystals are obviously tailored through altering the substitution positions of two chlorine atoms, displaying blue, green-white and green emission, respectively. Correspondingly, 34CPhCz and 35CPhCz presented a broad, structureless emission band at 454 and 488 nm in their PL spectra, respectively, which was different from the fine structural peaks with blue shift of 24CPhCz. Impressively, after removal of UV light, ultralong yellow phosphorescence for 24CPhCz and 34CPhCz was observed over 5 seconds with the naked eye, but it could not be observed for 35CPhCz crystal (SV1-SV3). With a delay time of 5 ms, it was found that 24CPhCz displayed two phosphorescent emission peaks at 532, 574 nm and a shoulder at around 620 nm, while 34CPhCz showed a major emission peaks at 537 nm and two shoulders at 582 and 636 nm. However, there was no emission signal detected for 35CPhCz at room temperature. The 3D-scanning of excitation-phosphorescence emission for

24CPhCz 34CPhCz demonstrated and unchanged emission position with the phosphorescence excitation wavelength changed from 260 to 460 nm (Figure 2b and Figure S10). The UOP properties were further demonstrated by the lifetime decay measurements and oxygen sensitivity experiments (Figure S11). As depicted in Figure 2c and Figure S12, 24CPhCz and 34CPhCz showed an ultralong lifetime of 1.06 s and 0.77 s with a phosphorescence efficiency (Φ_{Phos}) of 2.5% and 3.4%, respectively (Table S1). Different from 24CPhCz (Figure S13), the transient PL decay of 34CPhCz and 35CPhCz displayed a TADF feature with nanosecond-order (4.3 and 3.1 ns) prompt components and microsecond-order (1.9 and 2.7 µs) delayed components (Figure 2d, S14a and Table S2).[14] The TADF properties of 34CPhCz and 35CPhCz were further confirmed by the temperature dependent PL spectra changes in PL intensity (Figure 2e and S14b). With the temperature increased, the emission intensity of the structureless bands exhibited decrease first and then increased, demonstrating a typical TADF feature.



Figure 3. A probable explanation of ultralong organic phosphorescence in crystal state. Intermolecular interactions of a) 24CPhCz, b) 34CPhCz and c) 35CPhCz single molecules. The packing modes of d) 24CPhCz, e) 34CPhCz and f) 35CPhCz in crystals, respectively (The depth cue is to tell the spatial distance between two molecular groups not on the same plane).

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The initial decrease of the total emission intensity was attributed to the competing process between phosphorescence (Figure S15) and TADF emission with the temperature increase.^[15] In the amorphous films, however, characteristic phosphorescence emissions in crystal disappeared when dispersed in the PMMA matrix (Figure S16, S17 and Table S3). In a more rigidified Zeonex matrix, blue-green phosphorescence can only be detected in 24CPhCz/Zeonex film with main peak at 495 nm and a lifetime of 30.55 ms under N₂ atmosphere (Figure S18). For 34CPhCz and 35CPhCz/Zeonex films, structureless TADF emission bands were observed (Figure S19-S21).^[16] From these experimental results, we speculated that the distinct UOP behaviors in the three isomers were mainly attributed to their packing modes in crystal state rather than single molecules. To further ascertain the intermolecular interaction effect in crystal, we compared the photophysical properties of compounds in crystalline and amorphous states under ambient conditions (Figure S22 and S23). Note that the amorphous material is prepared by the treatment of fusing by heating and guick freezing at 77 K. It was found that the UOP of 34CPhCz disappeared in amorphous state, indicating the UOP generation was closely related to the special molecular packing in crystal state.

To gain a deep insight into the various UOP properties of these isomers, we carefully analyzed the intermolecular interactions and packing modes in their single crystal (Table S4). All of the three compounds showed a twisted molecular configuration with dihedral angle more than 60° between carbazole and benzene units (Figure S24). As shown in Figure 3a-3c, there exists plenty of intermolecular interactions in 24CPhCz crystal. The molecules were rigidly restricted by abundant interactions, including C-Cl…π (3.128~3.414 Å) and C-H…π (2.828, 2.887 Å), which contributes to restricting nonradiative transitions through molecular motions to prolong the UOP lifetime. In comparison, there are much fewer short contacts around 34CPhCz and 35CPhCz, meanwhile the individual interactions of the two compounds are almost equal. However, their luminescent properties are very different in crystal state, thereinto 34CPhCz displayed obvious UOP while 35CPhCz exhibited no phosphorescence emission. This finding indicates the molecular confinement effect is an important but not key factor to the UOP generation. From the perspective of the entire packing styles of these crystals, we found that 24CPhCz and 34CPhCz showed a similar stacking mode to carbazole in crystal (Figure S25),[17] which can't be observed in 35CPhCz crystal (Figure 3d-3f). More carefully analyzing the localized stacking modes between two adjacent carbazoles, it can be found that there existed very strong coupling between two adjacent carbazoles with C-H···π interactions (2.828 Å) in 24CPhCz crystal, which was slightly weaker in 34CPhCz with a longer distance between carbazoles (C-H···π=2.917) (Figure S26a and S26b). In contrast, for the TADF emitter 35CPhCz, there were only C-H···π (3.307 Å), C- $CI{\cdots}\pi$ (2.873 Å) and C-H ${\cdots}CI$ (2.892 Å) between benzene units or between benzene and carbazole (Figure S26c). Nevertheless, the coupling between carbazoles was very week, which may be mainly responsible for the exhaustive shut of UOP emission in 35CPhCz crystal. Based on these analyses, we speculated that the UOP generation is closely related to the stacking style between carbazole units in the three isomers.

In order to reveal the underlying reason of why strong C-H···π stacking between carbazoles could play such a critical role in UOP generation in these isomers, the density-functional theory (DFT) calculations were carried out (Figure S27). It was found that the natural transition orbitals (NTOs) of the lowest triplet state (T_1) were mainly distributed on carbazole units (Figure 4a), indicating carbazole acts as triplet chromophore for phosphorescence occurrence in this system. Therefore, the strong C-H···π stacking between carbazoles could stabilize the triplet excitons for ultralong phosphorescence emission (Figure 4b). To further verify our speculation, we made the independent gradient model (IGM) analysis to directly show the intermolecular weak interactions. From Figure 4c and S28, it is obvious that 24CPhCz displayed the largest isosurface between two carbazoles, which indicated the strongest weak interactions as well as the efficient electronic communications among triplet species. Meanwhile, the isosurface between benzene units was much more obvious in 35CPhCz. Besides, the isosurface displayed a gradual decreasing trend from 24CPhCz, 34CPhCz to 35CPhCz, which was in accordance with the UOP lifetime in the three compounds. Combining the experimental data and theoretical calculations, we provide a deeper understanding that the stacking between triplet chromophores really plays a critical role in UOP generation in crystal.



Figure 4. a) Natural transition orbitals (NTOs) for the lowest triplet state of 24CPhCz. b) The mechanism of the different emission behaviors in the three compounds. c) The calculated intermolecular weak interactions (green isosurface) in dimers of 24CPhCz, 34CPhCz and 35CPhCz (the isovalue is 0.007).

In summary, a new insight into ultralong organic phosphorescence in crystal was proposed in several aromatic amide derivatives. Through adjusting chlorine substitution positions, there was an interesting UOP switching on-off behavior in these isomers. Experimental and calculated results revealed that 24CPhCz with the strongest intermolecular coupling between carbazole chromophores exhibited the most impressive UOP emission with a long lifetime of 1.06 s and a Φ_{Phos} of 2.5%.

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34CPhCz was UOP and TADF dual-emissive with a moderately decreased phosphorescence lifetime of 770 ms and a Φ_{Phos} of 3.4%. However, the too weak coupling between triplet chromophores but strong coupling between benzene units resulted in the disappearance of UOP and only TADF emission with a luminescent lifetime of 2.7 µs for 35CPhCz. These results demonstrate it is the triplet chromophores stacking that really plays a critical role in UOP generation. Our viewpoint can provide some deeper understanding for the inherent mechanism of ultralong phosphorescence emission in purely organic compounds and new guideline for obtaining UOP materials.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (21875104, 51673095, 91833304 and 91833302), National Basic Research Program of China (973 Program, No. 2015CB932200), Natural Science Fund for Distinguished Young Scholars of Jiangsu Province (BK20180037). We are grateful to the High Performance Computing Center of Nanjing Tech University for supporting the computational resources.

Keywords: crystal engineering • triplet chromophore stacking • ultralong organic phosphorescence • intermolecular Interactions • thermally activated delayed fluorescence

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Ultralong organic phosphorescence can be controlled by manipulating the triplet chromophore stacking in crystal. The stronger coupling between carbazole chromophores favours the UOP generation of 24CPhCz and 34CPhCz, while the too weak coupling between triplet chromophores but strong coupling between benzene units resulted the disappearance of UOP and only TADF emission in 35CPhCz.



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