An Ingenious Strategy to Stereoscopically Enhance the Phosphorescence Properties of Guest-Host Materials: Adding Metal Ions to Form Coordination with the Guest

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Abstract

The host-guest doped strategy has been widely recognized as an effective method to construct room temperature phosphorescence materials. However, the advantage of the host in the doped system as a container that can hold the other components is ignored. Herein, benzophenone was selected as the host and seven phenylquinoline isomers were designed as guests to construct a phosphorescence doped system. Importantly, seven metal salts of the same period or the same main family (Al^{3+}, $Cu^{+/2+}$, Zn^{2+}, Ga^{3+}, Ag^{+}, Cd^{2+}, In^{3+}) are selected as the third component to coordinate with the nitrogen atom of the guests, thereby stereoscopically improving the phosphorescence performance of doped system. Metal ions can significantly increase the phosphorescence intensity, red-shift the emission wavelength and prolong the phosphorescence lifetime of the doped materials. Ag^{+} and Cd^{+} can greatly increase the emission intensity, up to 38 times, the highest phosphorescence quantum efficiency can reach 70%. Al^{3+}, Ga^{3+}, and In^{3+} can prolong the emission wavelength, and the phosphorescence wavelength can be red-shifted by up to 60 nm. And Cu^{2+}, Ga^{3+}, and In^{3+} can extend the phosphorescence lifetime by a maximum of 3.6 times. This is the first work to use metal ions to construct the multi-component doped system.

Introduction

Organic room temperature phosphorescence (RTP) materials with long afterglow phenomenon have unique advantages in anti-counterfeiting, biological diagnosis and treatment, optoelectronic devices and other fields.[1-10] Intersystem crossing (ISC) of excitons and stable triplet excitons are the prerequisites for the organic materials to have phosphorescence emission.[11-16] The guest-host doped strategy, as an emerging technology in recent years, has great advantages in the construction of organic RTP materials, which has attracted great attention and interest.[17-26] The host matrix can not only help the energy transfer of the guest excitons, but the rigid structure of the host can effectively limit the motion of the guest molecules, thereby stabilizing the triplet excitons.[27-36] In addition, the low content of the guest reduces the synthesis cost, the abundant varieties broaden the doped systems, and the special interaction of the host-guest can optimize and regulate the phosphorescence performance.[37-40] However, despite the rapid development of doped system RTP materials, these systems are basically two-component systems, and facing the shortcomings of low performance and single function.

A big difference from single-component RTP materials is that the content of guest as emitter in the doped system is extremely low, while the content of host reaches 99%-99.99%.[27-40] Actually, the host matrix is equivalent to a container in which guest molecules emit phosphorescence depending on the interaction with the container. Therefore, it is entirely possible to add a third or even fourth component to the host container, and use the interaction between the third component and the host or guest to control the phosphorescence lifetime, phosphorescence intensity and phosphorescence wavelength, or to construct the functional RTP materials. However, except for a few researchers who used water as the third component to construct the multi-component doped materials with strong phosphorescence emission by the formation of hydrogen bonds,[41-43] the advantage that the host can be used as a container is ignored. Organic matters, especially which containing heteroatoms such as nitrogen, sulfur, and phosphorus, are easily coordinated with various metal ions.[44-47] Therefore, the metal ions can affect or even regulate the luminescence properties of organic matters.

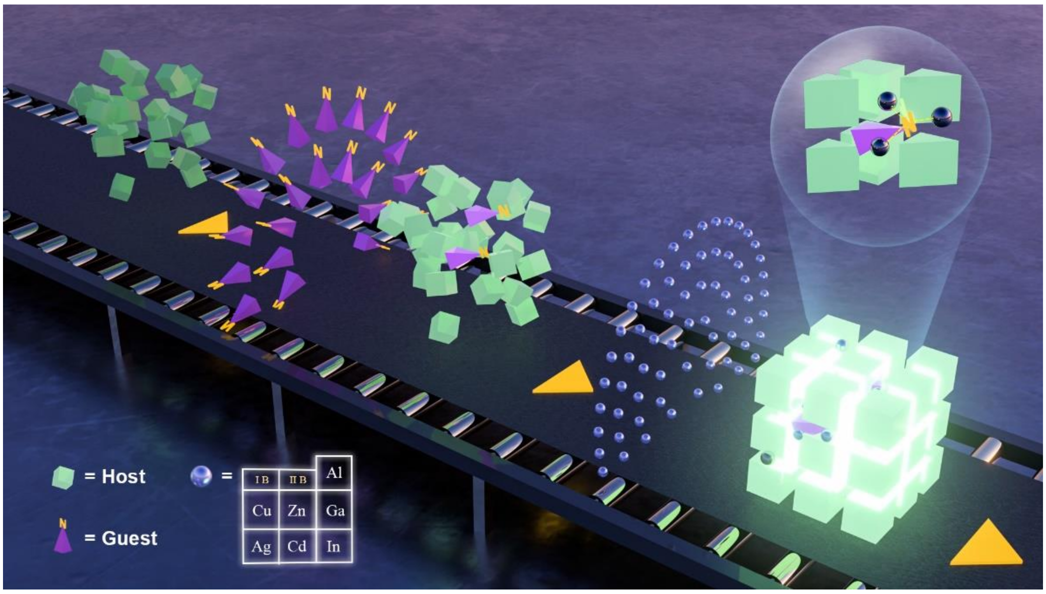

Figure 1. Design concept of the three-component doped system.

Based on the above ideas, seven phenylquinoline isomers (***n*-QL**) containing nitrogen atoms are designed as guests, and the benzophenone (**BPO**) with excellent crystallinity, lower melting point is selected as the host to construct a two-component doped system. Importantly, seven chloride salts of the same period or the same main family (Al^{3+}, Cu^{+}/Cu^{2+}, Zn^{2+}, Ga^{3+}, Ag^{+}, Cd^{2+}, In^{3+}) are selected as the third component to coordinate with the guests. The doped materials ***n*-QL/SDB** without the metal salts have only very weak green phosphorescence, but when the metal salts are added to the system, the phosphorescence performance of the three-component doped materials are significantly enhanced. More importantly, utilizing the difference in the coordination ability of each metal ions with the nitrogen atom and the difference in its own weight, the phosphorescence performance of the doped material can be selectively adjusted. Ag^{+} and Cd^{2+} can greatly enhance the phosphorescence emission through the heavy atom effect, the phosphorescence intensity can be increased by up to 38 times. The strong coordination ability of Al^{3+}, Ga^{3+}, $In^{3+}$and nitrogen atoms can significantly prolong the phosphorescence wavelength of the doped material, and the longest redshift can be 60 nm. And Cu^{2+}, Ga^{3+}, and In^{3+} can extend the phosphorescence lifetime by a maximum of 3.6 times.

Discussion

Photophysical properties of guest-host system. Seven guests ***n*-QL** was synthesized according to an established method (Figure 2a, Supplementary Figure 1). The molecular structure and purity were confirmed by single-crystal X-ray diffraction, NMR spectroscopy. The absorption spectra of the solution guests almost completely overlap, while the corresponding ones in the solid state are different (Supplementary Figure 2). This shows that the benzene rings at different positions have almost no effect on the energy levels of the molecules, but they will affect the arrangement of the molecules. But the guests have almost no emission activity at room temperature in the solution and solid state (Supplementary Figure 3). The host **BPO** is directly purchased commercially and purified by twice column chromatography. Because **BPO** has low melting point (66-71°C), the doped materials can be fabricated by the melt-casting method.[31,37] A series of the ***5*-QL/BPO** doped materials with different guest-host molar ratios (1:10-1:100000) are prepared to screen the materials with best phosphorescence properties. All the ***5*-QL/BPO** doped materials emit green phosphorescence with an emission wavelength of around 520 nm, and when the ratio is 1:1000, the material has the strongest emission intensity (Supplementary Figure 4), which is in line with our previous work.[29-32] Therefore, other six doped materials with a guest-host molar ratio of 1:1000 is selected as the research target.

Seven doped materials show different fluorescence and phosphorescence colors, the materials show cyan or green fluorescence under 365 nm UV light and exhibit green or yellow afterglow after removing the UV lamp (Figure 2b). From ***2*-QL/BPO** to ***8*-QL/BPO**, the maximum phosphorescence peaks are 490 nm (multi-peaks) - 560 nm (Figure 2c), the phosphorescence quantum efficiencies are 1.4% - 5.3%, and the phosphorescence lifetimes are 72 ms - 112ms (Figure 2d, Table 1). It is well known that in most doped systems the phosphorescence is actually emitted by guest molecules,[29-32] and the guest molecules are doped into the host matrix in an aggregated state or individually dispersed state. In this system, although the guest molecules in the solution state have almost the same absorption wavelength and phosphorescence emission wavelength/77K (Supplementary Figure 5), the phosphorescence properties of the doped materials are quite different. Therefore, guest molecules are present in the host in clusters rather than individually[32]. These results suggest that although different phenyl positions do not affect the energy levels of the guest molecules, they can affect the molecular arrangement, resulting in different phosphorescence properties of the doped materials. According to the previous works, the T_1 state of the host matrix can be the bridge between the S_1 and T_1 states of the guest,[37-40] so the excitons can transfer from S_1 state to T_1 state of the guest through the path of the T_1 state of the host. As shown in Figure 2e, the S_1 and T_1 states of ***5*-QL** are 4.05 eV and 2.69 eV, respectively, and the ΔE_{ST} is 1.36 eV. Such large energy gaps make it difficult for intersystem crossing (ISC) of excitons. However, the band gap between the S_1 state of **BPO** and the T_1 state of **BPO** is only 0.33 eV, which is very beneficial for ISC of excitons.

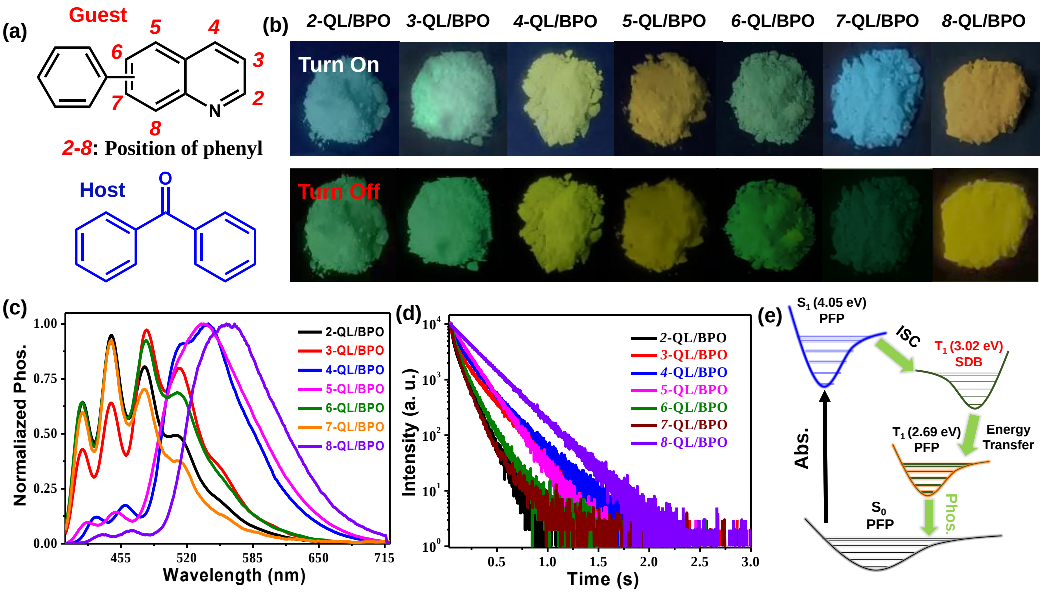

Figure. 2. | Photoluminescence properties of the two-component doped system. **a**, Molecular structures of the guest and host molecules. **b**, Fluorescence (top) and phosphorescence (down) images of the doped materials. **c**, Phosphorescence spectra of host-guest materials. Excitation wavelength: 380 nm; Delayed time: 0.5 ms. **d**, Phosphorescence decay curves of guest–host materials. Excitation wavelength: 380 nm. **e**, Proposed transfer path between guest and host.

Effects of Different Metal Salts on Phosphorescence Properties. Improving and enriching phosphorescence properties is a challenge that must be overcome for materials to realize practical applications. In most doped systems, the host matrix acts as a container to encapsulate the guest molecules, and the interaction of the two causes the guest to emit phosphorescence. However, people often ignore the fact that the host is equivalent to a container, which can encapsulate not only the guest but also the third component such as water, acid, initiator, and even metal salts. Therefore, in this work, a series of metal salts with empty orbitals (Al^{3+}, Cu^{+}/Cu^{2+}, Zn^{2+}, Ga^{3+}, Ag^{+}, Cd^{2+}, In^{3+}) were selected to be doped into the host as the third component to coordinate with the guests. Since the concentration of the third component have an impact on the phosphorescent activities of the materials, a series of **5-QL/PBO/CdI_2** and **5-QL/PBO/$InCl_3$** doped materials with different molar ratios (1:1000:0.1-1:1000:50) were prepared to optimize the luminescence activities. As shown in Figure S6, the **CdI_2** can greatly increase the phosphorescence intensity, while **$InCl_3$** can effectively increase the emission wavelength. And when the ratio is 1:1000:5 (Guest: Host: Metal salt), the three-component doped materials have the strongest phosphorescence intensity or longest phosphorescence. Compared with **5-QL/PBO**, the phosphorescence intensity of **5-QL/PBO/CdI_2** is enhanced by 11 times, and the phosphorescence wavelength is red-shifted by 7 nm. Corresponding, although the phosphorescence intensity of **5-QL/PBO/$InCl_3$** is only increased by a factor of 4.1, the wavelength is red-shifted by 28 nm. However, even if the ratio of metal ions is further increased to 1:1000:50, there is no obvious further change in the luminescence phenomenon of the doped materials. This may be that when the metal ions reach a certain amount, the coordination effect with the guest molecules reaches the maximum, so the effect on the doped materials will tend to be stable.[46,47] Furthermore, the low solubility of metal salts in the host also limits the maximum metal ion content that the doped system can contain. Therefore, other three-component doped materials with a guest-host-metal salt molar ratio of 1:1000:5 were prepared.

For the same cation salts, different anions have different effects on the coordination ability of metal ions and nitrogen atoms. Therefore, the effects of various metal salts on the phosphorescence properties of the doped system were first screened. Three three-component doped materials **5-QL/BPO/Al^{3+}** were prepared by selecting three aluminum salts $AlCl_3$, $Al(CF_3SO_3)_3$ and $Al(NO_3)_3$ as the third components, respectively. Compared with **5-QL/BPO**, the phosphorescence wavelength of **5-QL/BPO/Al^{3+}** is red-shifted by 35-41 nm, the phosphorescence intensity is enhanced by 1.17-1.41 times (Figure 3a), and the phosphorescence lifetime is slightly reduced to 85-92 ms (Figure 3f). From these results, it can be found that the main function of aluminum ions is to increase the phosphorescence wavelength of the materials, and among them, and $AlCl_3$ has the best effect (Figure 3k). Next, Seven monovalent and divalent copper salts ($Cu(CF_3SO_3)_2$, $CuSO_4$, $Cu(NO_3)_2$, $CuCl_2$, CuCl, CuBr, CuI, CuCN) were selected. The results show that the divalent copper salts can more effectively enhance the phosphorescence intensity of the doped materials than the monovalent copper salts (Figure 3b, 3l). This is because in general, the coordination ability of divalent copper ions is stronger than that of monovalent copper ions. Among them, $Cu(CF_3SO_3)_2$ can play the best effect, compared with **5-QL/BPO**, the phosphorescence intensity of **5-QL/BPO/$Cu(CF_3SO_3)_2$** is increased by 2.86 times, and the phosphorescence lifetime is also increased by 2.98 times to 301 ms (Figure 3f). But the copper salts have little effect on the phosphorescence wavelength, the red-shift is only 12 nm at most. For the four zinc salts ($ZnCl_2$, $Zn(NO_3)_2$, $Zn(CH_3CO_2)_2$, $Zn(CF_3SO_3)_2$), the highest phosphorescence intensity can be increased by 4.14 times (**5-QL/BPO/$ZnCl_2$**), the phosphorescence lifetime is slightly reduced to 88-95 ms (Figure 3c, 3h, 3m) . Similarly, zinc salts have little effect on the phosphorescence wavelength of the doped materials. Since silver and cadmium are heavy atoms, they can greatly improve the phosphorescence intensity of doped materials. Compared with **5-QL/BPO**, the phosphorescence intensities of **5-QL/BPO/CF_3CO_2Ag** and **5-QL/BPO/CdI_2** were increased by 11.7 and 13.8 times, respectively (Figure 3d, 3e). But different anion salts also show a huge difference in the effect on the phosphorescence properties. Among the six silver salts (CF_3SO_3Ag, Ag_2SO_4, AgCl, CF_3CO_2Ag, $AgNO_2$, $AgNO_3$) and three chromium salts ($CdCl_2$, $Cd(NO_3)_2$, CdI_2), the smallest phosphorescence intensity was only increased by a factor of 3.9 (**5-QL/BPO/Ag_2SO_4**) and 4.8 (**5-QL/BPO/$Cd(NO_3)_2$**), respectively (Figure 3d, 3e, 3n, 3o). And the phosphorescence lifetimes of **5-**

QL/BPO/Ag$^+$ and **5-QL/BPO/Cd^{2+}** are also slightly shortened to 33-86 ms and 43-92 ms, respectively (Figure 3i, 3j). It is worth pointing out that **5-QL/BPO/CF_3CO_2Ag** and **5-QL/BPO/CdI_2** have pure phosphorescence emission because the heavy atom effect of metals can effectively improve the intersystem crossing ability of excitons. As shown in Figure S7, the prompt spectra and the delayed spectra of the two doped materials almost completely coincide. And the time-resolved prompt emission decay curves shown that the emission intensity do not decay as quickly as ordinary fluorescence materials in the decay range of 200 ns (Supplementary Figure 8), which indicates that the nanosecond lifetime is almost nonexistent.[19] For the selection of gallium and indium salts, with $AlCl_3$ as the reference (Al, Ga, and In is an element of the same main group), $GaCl_3$ and $InCl_3$ were selected as the third components. Similar to $AlCl_3$, $GaCl_3$/$InCl_3$ can red-shift phosphorescence wavelengths by 36 nm and 31 nm, respectively (Figure 3p, Supplementary Figure 9). And the phosphorescence lifetime is increased to 120 ms and 135 ms, respectively. In addition, compared with **5-QL/BPO**, from **5-QL/BPO/ $AlCl_3$** to **5-QL/BPO/ $GaCl_3$** to **5-QL/BPO/$InCl_3$**, the phosphorescence intensity is improved by 1.72, 3.39 and 6.38 times, respectively (Supplementary Figure 10). This is because the increase in atomic mass from aluminum to indium improves the phosphorescence intensity of the materials. In summary, $AlCl_3$, $Cu(CF_3SO_3)_2$, $ZnCl_2$, $GaCl_3$, CF_3CO_2Ag, CdI_2, and $InCl_3$ are the seven salts with the best effect on improving the luminescence properties of doped materials. The main function of Ag$^+$ and Cd$^+$ is to greatly prove the phosphorescence intensity, the Al^{3+}, Ga^{3+}, and In^{3+} are to enhance the phosphorescence wavelength, and the Cu^{2+}, Ga^{3+}, and In^{3+} can increase the phosphorescence lifetime. In addition, to better quantify the extent of the influence of metal salts on the luminescence intensity, the phosphorescence quantum efficiencies of seven three-component doped materials were tested (**5-QL/BPO/$AlCl_3$**, **5-QL/BPO/$Cu(CF_3SO_3)_2$**, **5-QL/BPO/$ZnCl_2$**, **5-QL/BPO/$GaCl_3$**, **5-QL/BPO/CF_3CO_2Ag**, **5-QL/BPO/CdI_2**, **5-QL/BPO/$InCl_3$**), and the results are 6.6%, 12%, 18%, 17%, 61%, 70%, and 28%, respectively (Table 1). Compared with 4.5% of **5-QL/BPO**, the phosphorescence efficiency of the three-component doped materials is increased by a factor of 1.46 -11.66. It should be pointed out that the powders formed by the **5-QL** guest and metals also have no phosphorescence emission at room temperature (Supplementary Figure 11), which further indicates that the host matrix plays an indispensable role in the luminescence of the guests.

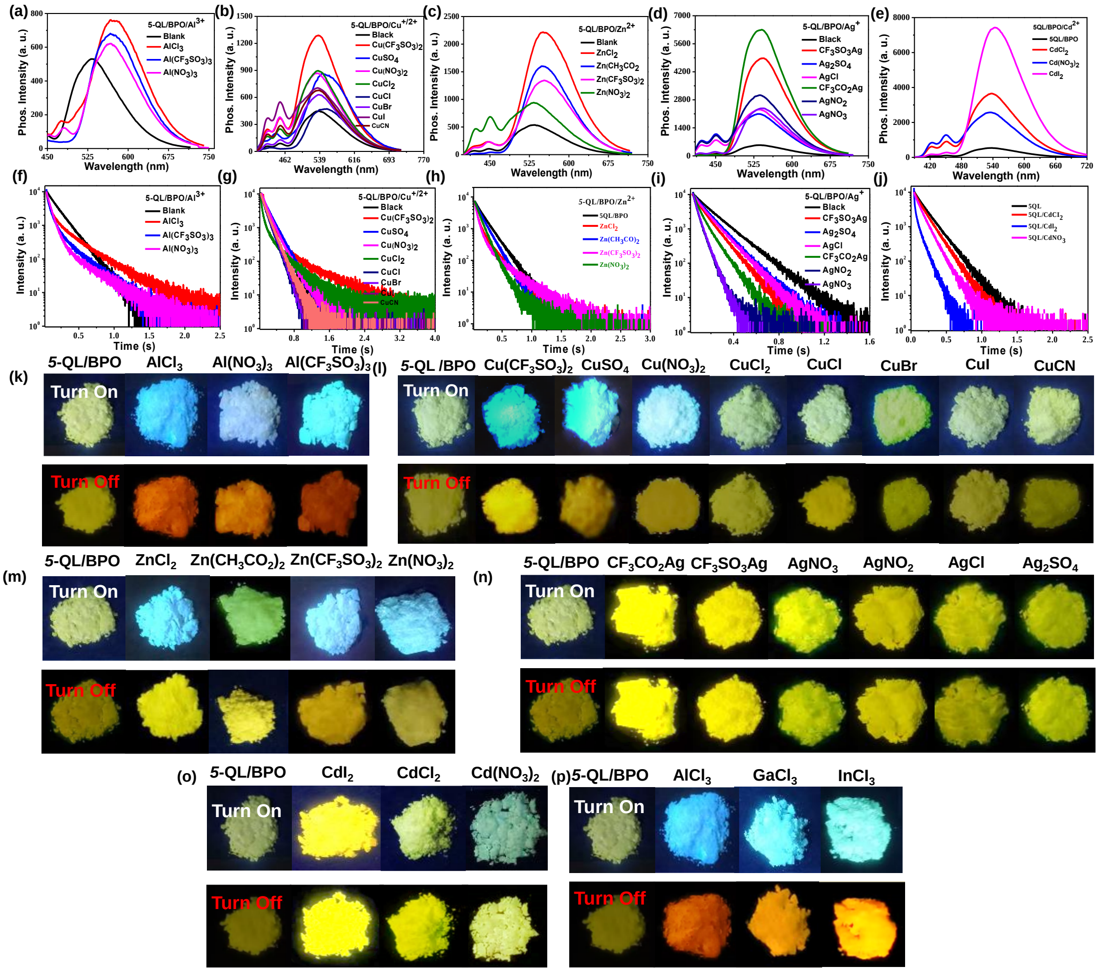

Figure. 3. | Photoluminescence properties of the three-component doped materials *5*-QL/BPO/M. a-e, Phosphorescence wavelengths of three-component doped materials composed of ***5*-QL/BPO** and various metal salts. Excitation wavelength: 380 nm; Delayed time: 0.5 ms. **f-j**, Phosphorescence decay curves of three-component doped materials composed of ***5*-QL/BPO** and various metal salts. Excitation wavelength: 380 nm. **k-p**, Fluorescence (top) and phosphorescence (down) images of three-component doped materials composed (**5-QL/BPO** and various metal salts).

Effects of Metal Salts on Phosphorescence Properties of Different Doped Materials. Next, the remaining six groups of three-component doped materials were prepared using the other seven guests, the host and the seven metal salts mentioned above. Compared with ***2*-QL/BPO** and ***8*-QL/BPO**, the phosphorescence properties of three-component doped materials ***2*-QL/BPO/M** and ***8*-QL/BPO/M** have no obvious change (Supplementary Figure 12). This may be due to the close spatial distance of the benzene ring at the 2- or 8-position from the nitrogen atom, which hinders the coupling of the metal ions to the nitrogen atom. For the doped materials ***3*-QL/BPO/M**, the main function of CF_3COOAg and CdI_2 is still to increase the phosphorescence intensity, compared with ***3*-QL/BPO**, the phosphorescence intensity is enhanced by a factor of

17 and 21, respectively, and the phosphorescence quantum efficiency reaches 55% and 62%, respectively, but the phosphorescence lifetime is also reduced to 36 ms and 32 ms (Figure 3a, 3k, Table 1). The $AlCl_3$, $GaCl_3$ and $InCl_3$ also play a role in significantly increasing the phosphorescence wavelength, and the three-component materials are red-shifted by 41-60 nm compared with the ***3*-QL/BPO** (Figure 3a, Table 1). Similar to ***5*-QL/BPO/M**, from $AlCl_3$ to $InCl_3$, with the increase of the metal ion quality, the phosphorescence intensity gradually increases (Figure 3a, Table 1). In addition, $AlCl_3$, $GaCl_3$ and $InCl_3$ can also increase the phosphorescence lifetime, from 108ms for ***3*-QL/BPO** to 227 -294 ms for the three components materials (Figure 3k, Table 1). Although $Cu(CF_3SO_3)_2$ and $ZnCl_2$ can improve the phosphorescence properties of doped materials, the effect is not obvious. But it is worth mentioning that $Cu(CF_3SO_3)_2$ can make the phosphorescence lifetime of the ***3*-QL/BPO/Cu(CF$_3$SO$_3$)$_2$** reach 313 ms (Figure 3k, Table 1). For the other three groups of three-component doped materials (***4*-QL/BPO/M**, ***6*-QL/BPO/M, *7*-QL/BPO/M)**. The main function of CF_3COOAg and CdI_2 is still to increase the phosphorescence intensity, compared with the two-component doped materials, the phosphorescence quantum efficiency of three-component doped materials reaches 54% - 63%. (Figure 3b-3d, Table 1). It is worth pointing out that the phosphorescence quantum efficiency increased from 1.4% of ***7*-QL/BPO** to 54% of ***7*-QL/BPO/CdI$_2$**, an increase of 38 times. The $AlCl_3$, $GaCl_3$ and $InCl_3$ also play a role in significantly increasing the phosphorescence wavelength, the three-component materials are red-shifted by 36-56 nm compared with the two-component materials (Figure 3b-3d, Table 1). Similarly, from $AlCl_3$ to $InCl_3$, with the increase of the metal ion quality, the phosphorescence intensity gradually increases (Table 1). In addition, $GaCl_3$, $InCl_3$, and $Cu(CF_3SO_3)_2$ can effectively prolong the phosphorescence lifetime of materials, especially $Cu(CF_3SO_3)_2$. Among them, the phosphorescence lifetime from 85 ms of ***6*-QL/BPO** to 304 ms of ***6*-QL/BPO/Cu(CF$_3$SO$_3$)$_2$**, an increase of 3.6 times (Figure 3f-3h, Table 1) . To sum up, the influence of the same metal ion on the phosphorescence properties of different doped materials is basically the same, but the influence of different metal ions on the phosphorescence properties of the same doped material is very different. These results also indicate that the different interactions between various metal ions and guests lead to the abundant phosphorescence phenomenon of doped materials.

Table 1. Phosphorescence properties of three-component doped materials

	Blank	Al^{3+}	Cu^{2+}	Zn^{2+}	Ga^{3+}	Ag^{+}	Cd^{2+}	In^{3+}
***3*-QL/BPO**	512^{a}	572^{a}	532^{a}	544^{a}	565^{a}	521^{a}	522^{a}	553^{a}
	3.3^{b}	5.4^{b}	8.3^{b}	15^{b}	12^{b}	53^{b}	67^{b}	19^{b}
	108^{c}	294^{c}	313^{c}	222^{c}	227^{c}	34^{c}	32^{c}	255^{c}
***4*-QL/BPO**	520^{a}	571^{a}	530^{a}	540^{a}	564^{a}	525^{a}	523^{a}	555^{a}
	5.3^{b}	6.2^{b}	10^{b}	18^{b}	16^{b}	55^{b}	59^{b}	22^{b}
	112^{c}	98^{c}	308^{c}	139^{c}	190^{c}	38^{c}	34^{c}	130^{c}
***5*-QL/BPO**	533^{a}	574^{a}	536^{a}	547^{a}	568^{a}	539^{a}	538^{a},	561^{a}
	4.5^{b}	6.6^{b}	12^{b}	18^{b}	17^{b}	61^{b}	70^{b}	28^{b}
	104^{c}	91^{c}	310^{c}	88^{c}	120^{c}	37^{c}	33^{c}	135^{c}
***6*-QL/BPO**	534^{a}	569^{a}	527^{a}	540^{a}	562^{a}	528^{a}	526^{a}	557^{a}
	2.8^{b}	4.5^{b}	7.1^{b}	11^{b}	13^{b}	60^{b}	64^{b}	23^{b}
	85^{c}	193^{c}	305^{c}	135^{c}	223^{c}	35^{c}	32^{c}	212^{c}
***7*-QL/BPO**	514^{a}	566^{a}	522^{a}	534^{a}	559^{a}	518^{a}	515^{a}	550^{a}
	1.4^{b}	2.8^{b}	6.4^{b}	7.4^{b}	9.2^{b}	48^{b}	54^{b}	13^{b}
	72^{c}	78^{c}	197^{c}	87^{c}	112^{c}	29^{c}	27^{c}	126^{c}

a: Phosphorescence emission wavelength (nm); b: Phosphorescence quantum efficiency (%); c: Phosphorescence lifetime (ms).

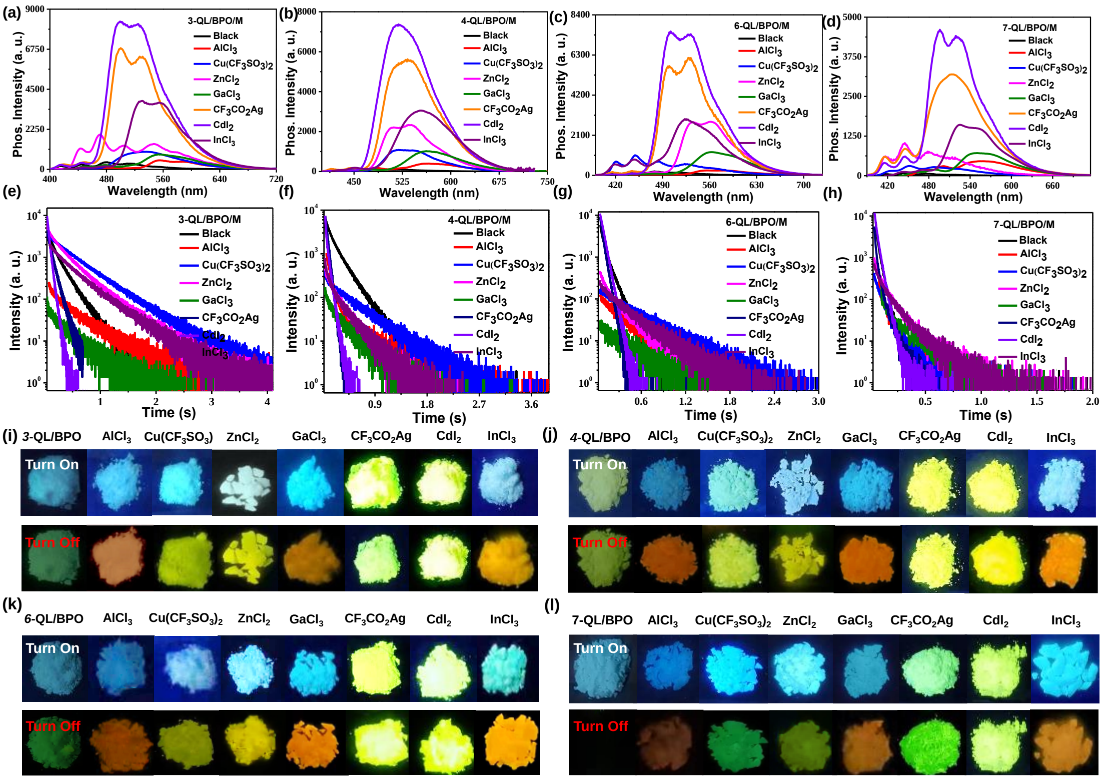

Figure. 4. | Photoluminescence properties of the three-component doped materials. a-d, Phosphorescence wavelengths of three-component doped materials composed of ***n*-QL/BPO** and

seven metal salts. Excitation wavelength: 380 nm; Delayed time: 0.5 ms. **e-h**, Phosphorescence decay curves of three-component doped materials composed of ***n*-QL/BPO** and seven metal salts. Excitation wavelength: 380 nm. **i-l**, Fluorescence (top) and phosphorescence (down) images of three-component doped materials composed of ***n*-QL/BPO** and seven metal salts.

Coordination of metal salt to guest. To further investigate whether it is the coordination of metal ions with guest molecules that enhances the phosphorescence properties of doped materials. First, seven metal salts were separately doped into the host matrix (Molar ratio of metal salts to host is 5:1000), and the results showed that these doped materials only had the phosphorescence of the host itself, which means that the metal salts do not emit phosphorescence in the host matrix (Figure 5a). The coordination of quinoline compounds with metals essentially means that the lone pair of electrons of the nitrogen atom occupies the empty orbital of the metal.[48]Therefore, if the lone pair of electrons of the nitrogen atom cannot interact with the empty orbital of the metal, the metal ions cannot coordinate with the quinoline compounds. Based on this, we salified **5-QL** to obtain hexafluorophosphate/**5-QL-PF$_6$**, as shown in Figure 5b, the salted nitrogen atoms no longer have lone pairs of electrons. The two-component doped material obtained by **5-QL-PF$_6$** and the host has bright yellow phosphorescence, and the quantum efficiency reaches 18% (Figure 5c). However, the phosphorescence properties of the three-component materials **5-QL-PF$_6$/BPO/CF$_3$COOAg** and **5-QL-PF$_6$/BPO/CdI$_2$** are almost unchanged compared with the two-component materials **5-QL-PF$_6$/BPO** (Figure 5d, 5e). This result indirectly confirms that metal ions enhance the phosphorescence properties of doped materials through coordination with nitrogen atoms in quinoline. Since AlCl$_3$ causes the most obvious red shift of the phosphorescence wavelength of the doped materials, the UV absorption wavelengths of **5-QL/BPO**, **AlCl$_3$/BPO** and **5-QL/BPO/AlCl$_3$** were tested. The results show that the absorption wavelength of **5-QL/BPO/AlCl$_3$** is significantly red-shifted compared to **5-QL/BPO** and **AlCl$_3$/BPO**, which also proves the formation of coordination reaction between the metal and the guest (Figure 5f). To further understand the effect of metal ions on the guest, theoretical simulations were first performed on the configurations of **5-QL-AlCl$_3$** and **5-QL-CdI$_2$** (Supplementary Figure 13). On this basis, the energy levels and spin-orbit coupling (SOC) constants of **5-QL-AlCl$_3$** and **5-QL-CdI$_2$** are calculated. The results show that compared with **5-QL**, **AlCl$_3$** reduces the excited state energy level of the molecule, the lowest triplet energy level/T$_1$ is reduced from 2.69 eV of **5-QL** to 2.41 eV of **5-QL- AlCl$_3$** (Figure 5g). And **CdI$_2$** can greatly increase the SOC values, the SOC is increased from 1.16 cm^{-1} of S$_1$-T$_1$ of **5-QL** to112.6 cm^{-1} of S$_1$-T$_1$of **5-QL- CdI$_2$** (Figure 5g). This is also consistent with the experimental results that **AlCl$_3$** extends the phosphorescence wavelength and **CdI$_2$** increases the phosphorescence intensity.

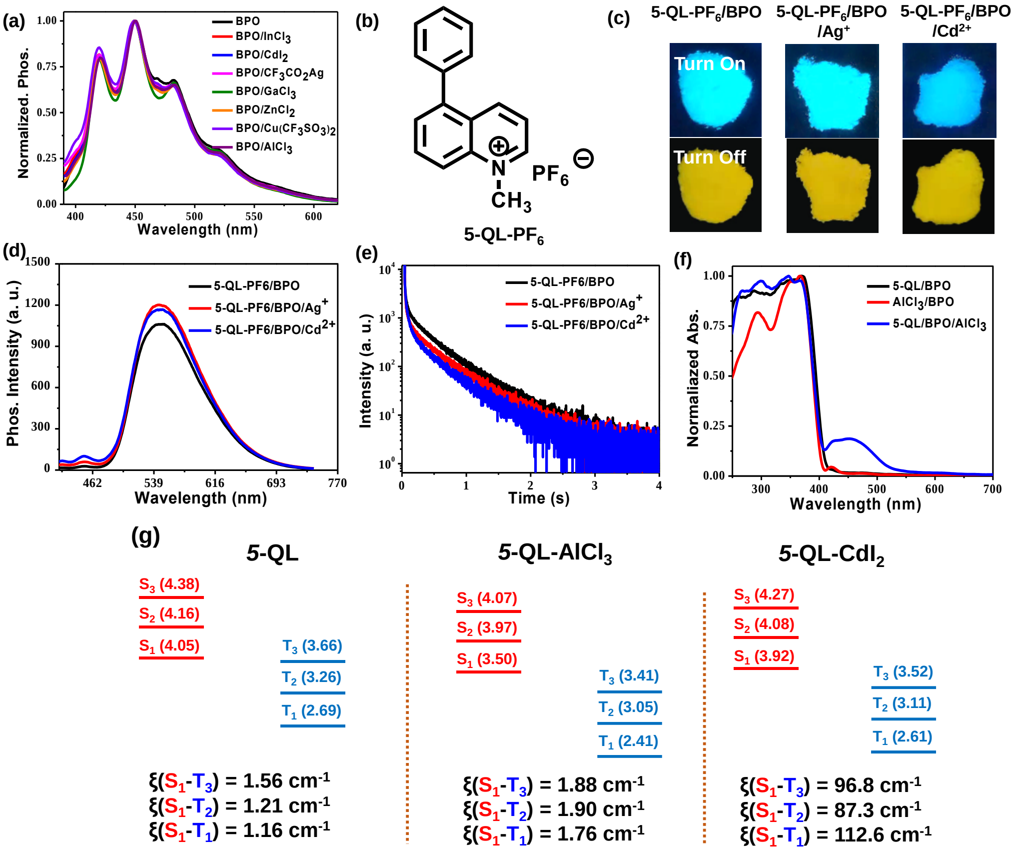

Figure. 5. | Coordination of guest to metal salt. a, Phosphorescence wavelengths of two-component doped materials **BPO/M**. Excitation wavelength: 380 nm; Delayed time: 0.5 ms. **b**, Molecular structure of guest **5-QL-PF$_6$**. **c**, Fluorescence (top) and phosphorescence (down) images of **5-QL-PF$_6$/BPO/CF$_3$COOAg**, **5-QL-PF$_6$/BPO/CdI$_2$**, and **5-QL-PF$_6$/BPO**. **d**, Phosphorescence wavelengths of **5-QL-PF$_6$/BPO/CF$_3$COOAg**, **5-QL-PF$_6$/BPO/CdI$_2$**, and **5-QL-PF$_6$/BPO**. Excitation wavelength: 380 nm; Delayed time: 0.5 ms. **e**, Phosphorescence decay curves of **5-QL-PF$_6$/BPO/CF$_3$COOAg**, **5-QL-PF$_6$/BPO/CdI$_2$**, and **5-QL-PF$_6$/BPO**. Excitation wavelength: 380 nm. **f**, UV absorption spectra of **5-QL/BPO**, **AlCl$_3$/BPO** and **5-QL/BPO/AlCl$_3$**. **g**, Energy levels and SOC values of **5-QL/BPO**, **5-QL-AlCl$_3$** and **5-QL-CdI$_2$**.

Discussion

In conclusion, we provide an ingenious idea to enhance the phosphorescence properties of doped materials: First, the nitrogen-containing heterocyclic compounds are used as the guests, then the third component/metal salts are added to the host-guest two-component doped system to form a three-component doped system. Metal ions affect the electronic properties of the guest by coordinating with the nitrogen atom of the guest, thereby ultimately improving the phosphorescence properties of the doped materials. Metal ions (Al^{3+}, $Cu^{+/2+}$, Zn^{2+}, Ga^{3+}, Ag^{+}, Cd^{2+}, In^{3+}) can stereoscopically enhance the phosphorescence properties of doped materials, among them, Ag^{+} and Cd^{+} can greatly increase the emission intensity, Al^{3+}, Ga^{3+}, and In^{3+} can prolong the emission wavelength, Cu^{2+}, Ga^{3+}, and In^{3+}can extend the phosphorescence lifetime. This work reminds people not to ignore the container advantage of host matrix, that is, not only the emitter/guest can be doped into the host, but also other third or even fourth components can be doped into the host. Ultimately, interactions between multiple components can enhance and enrich the phosphorescence properties of doped materials.

Methods.

Synthesis of pyrene derivatives. The mixture of *n*-bromoquinoline (10.0 mmol), boronic acid (12.0 or 24.0 mmol), $Pd(PPh_3)_4$ (5.0 mol%), and K_2CO_3 (5.0 mol%) were dissolved in THF (10.0 mL) and water (1.0 mL). The mixture was stirred for 12 h at 80°C under nitrogen atmosphere. The solvent was removed under reduced pressure and the residue were purified by column chromatography (petroleum ether: ethyl acetate = 1:100, v:v) to afford the pure seven compounds.

Preparation of doped materials. Put the corresponding amount of host, guest and ion salts together, and heat the mixture to 60 °C in air atmosphere. After the guests are completely dissolved in the molten hosts, the mixed systems are cooled to room temperature, and the mixed systems are crystallized to obtain the doped materials.

Code availability

No custom computer code is used in the manuscript.

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Author contributions

Y. L, Z. C. and X. H. designed the research work and revised the manuscipt. Y. G. synthesized the materials. G. Y, Y. L, K. C. carried out photophysical property measurements. Z. C. carried out density functional theory calculations. Y. L, Z. C. and X. H. wrote the manuscript. Z. H, X. L, M. L, H. W. and Y. D. edited the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.