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

Yan Guo  
Wenzhou University

Kaijun Cheng  
Wenzhou University

Zechen Hu  
Wenzhou University

Yunxiang Lei  
Wenzhou University

Xiaoqing Liu  
Wenzhou University

Miao-Chang Liu  
Wenzhou University

Zhengxu Cai  
Beijing Institute of Technology  
https://orcid.org/0000-0003-0239-9601

Huayue Wu  
Wenzhou University

Xiaobo Huang  
xiaobhuang@wzu.edu.cn  
Wenzhou University

Yuping Dong  
Beijing Institute of Technology  
https://orcid.org/0000-0001-7437-0678

Article

Keywords:

Posted Date: March 2nd, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1383745/v1

License: ☺️ ☐️ This work is licensed under a Creative Commons Attribution 4.0 International License. 
Read Full License
Abstract

The host–guest doped strategy has been widely recognized to be effective for preparing room-temperature phosphorescence materials. However, the advantage of the host in a doped system as a container that can hold the other components is ignored. In this study, benzophenone was selected as the host, and seven phenylquinoline isomers were designed as guests to construct a phosphorescence-doped system. Notably, seven metal salts of elements in the same period or in the same main group (e.g., Al$^{3+}$, Cu$^{+}$/2+, Zn$^{2+}$, Ga$^{3+}$, Ag$^+$, Cd$^{2+}$, and In$^{3+}$, respectively) are selected as the third component to coordinate with the nitrogen atom of the guests, thereby stereoscopically improving the phosphorescence performance of the doped system. Metal ions can significantly enhance the phosphorescence intensity, cause red-shift of the emission wavelength, and prolong the phosphorescence lifetime of doped materials. Ag$^+$ and Cd$^{2+}$ can considerably increase the emission intensity up to 38 times, and the highest phosphorescence quantum efficiency reaches 70%. Al$^{3+}$, Ga$^{3+}$, and In$^{3+}$ can prolong the emission wavelength, and the phosphorescence wavelength can be red-shifted up to 60 nm. Cu$^{2+}$, Ga$^{3+}$, and In$^{3+}$ can extend the phosphorescence lifetime by a maximum of 3.6 times.

Introduction

Organic room-temperature phosphorescence (RTP) materials with a long-afterglow phenomenon exhibit unique advantages in anti-counterfeiting, biological diagnosis and treatment, optoelectronic devices.$^{1–10}$ Intersystem crossing (ISC) of excitons and stable triplet excitons are prerequisites for organic materials to exhibit phosphorescence.$^{11–16}$ As an emerging technology in recent years, the guest–host doped strategy exhibits immense advantages in the construction of organic RTP materials, which has attracted considerable interest.$^{17–26}$ The host matrix can not only help the energy transfer of guest excitons, but also 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 synthesis costs, abundant varieties broaden doped systems, and the special interaction between the host and guest can optimize and regulate phosphorescence performance.$^{37–40}$ However, despite the rapid development of doped RTP materials, these systems are basically two-component systems, which are limited by low performance and limited functionality.

These materials are notably different from single-component RTP materials in that the content of guest as the emitter in the doped system is extremely low, while the content of the host is 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 into the host container and exploit the interaction between the third component and the host or guest to control the lifetime, intensity, and wavelength of phosphorescence or to construct new functional RTP materials. However, except for the use of water as the third component, successful example to construct multi-component doped materials was limited,$^{41–43}$ and the host can be used as a container has been clearly ignored. Organic compounds, especially those containing heteroatoms such
as nitrogen, sulfur, and phosphorus, are easily coordinated with various metal ions.\textsuperscript{44–47} Therefore, metal ions are excepted to affect or even regulate the luminescence properties of organic compounds (Fig. 1).

Based on the above ideas, seven phenylquinoline isomers (n-QL) are designed as guests, and benzophenone (BPO) with excellent crystallinity and a low melting point is selected as the host to construct a two-component doped system (Fig. 2a). Notably, seven chloride salts of the elements in the same period or in the same main group (e.g., Al\textsuperscript{3+}, Cu\textsuperscript{+}/Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Ga\textsuperscript{3+}, Ag\textsuperscript{+}, Cd\textsuperscript{2+}, and In\textsuperscript{3+}, respectively) are selected as the third component to coordinate with the guests. The two-component doped system n-QL/SDB without metal salts exhibit only extremely weak green phosphorescence, but when metal salts are added to the doped system, the phosphorescence performance of the three-component doped materials is significantly enhanced. More importantly, by exploiting the difference in the coordination ability of each metal ion with the nitrogen atom as well as its own weight, the phosphorescence performance of the doped material can be selectively adjusted. Ag\textsuperscript{+} and Cd\textsuperscript{2+} can considerably enhance phosphorescence emission via the heavy atom effect, and the phosphorescence intensity can be increased by up to 38 times. The strong coordination ability of Al\textsuperscript{3+}, Ga\textsuperscript{3+}, and In\textsuperscript{3+} with nitrogen atoms can significantly prolong the phosphorescence wavelength of the doped material, and the longest red-shift can reach 60 nm. Cu\textsuperscript{2+}, Ga\textsuperscript{3+}, and In\textsuperscript{3+} can extend the phosphorescence lifetime by a maximum of 3.6 times.

**Discussion**

**Photophysical properties of a guest–host system.** Seven guests n-QL were synthesized according to a published method (Figure 2a, Supplementary Figure 1). Absorption spectra of guests in solution almost completely overlap, while those in the solid state are different (Supplementary Figure 2), which means that the benzene rings at different positions affect arrangements of molecules but do not affect their energy levels. The guests have no emission activity at room temperature in the solution and solid state (Supplementary Figure 3). The melting point of BPO is low (66°C); thus, the doped materials can be fabricated by the melt-casting method.\textsuperscript{31,37} A series of the 5QL/BPO-doped materials with different guest–host molar ratios (1:10–1:100000) are prepared to screen materials with the best phosphorescence properties. All 5QL/BPO-doped materials emit green phosphorescence with an emission wavelength of ~520 nm, and the material exhibits the highest emission intensity at a ratio of 1:1000 (Supplementary Figure 4), which is in agreement with our previous study.\textsuperscript{29–32} Therefore, six other doped materials with a guest–host molar ratio of 1:1000 are selected as the research target.

Seven doped materials exhibit different fluorescence and phosphorescence colors. The materials exhibit cyan or green fluorescence under 365-nm UV light and exhibit green or yellow afterglow after removing the UV lamp (Figure 2b). From 2QL/BPO to 8QL/BPO, the maximum phosphorescence wavelengths are observed at 490 nm (multi-peaks) to 560 nm (Figure 2c), phosphorescence quantum efficiencies are 1.4% to 5.3%, and phosphorescence lifetimes are 72 ms–112 ms (Figure 2d, Table 1). In this doped system, although guest molecules in the solution state exhibit almost the same absorption wavelength and
phosphorescence emission wavelength at 77 K (Supplementary Figure 5), phosphorescence properties of the doped materials are quite different. Therefore, guest molecules are present in the host in clusters rather than individually.29-32 And different phenyl positions can affect the molecular arrangement, resulting in different phosphorescence properties of the doped materials. According to previous studies, the T_1 state of the host matrix can be the bridge between the S_1 and T_1 states of the guest, hence, the excitons can transfer from the S_1 state to T_1 state of the guest through the path of the T_1 state of the host (Supplementary Figure 6).37-40

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 their interaction causes the guest to emit phosphorescence. However, the host is equivalent to a container is often ignored, which can encapsulate not only the guest but also the third component. Therefore, in this study, a series of metal salts with empty orbitals (e.g., Al^{3+}, Cu^{+}/Cu^{2+}, Zn^{2+}, Ga^{3+}, Ag^{+}, Cd^{2+}, and In^{3+}) were selected to be doped into the host as the third component to coordinate with the guests. As the concentration of the third component affects the phosphorescent activities of the materials, a series of 5QL/PBO/CdI_2- and 5QL/PBO/InCl_3-doped materials with different molar ratios (1:1000:0.1–1:1000:50) were prepared to optimize luminescence activities. CdI_2 can considerably increase the phosphorescence intensity, while InCl_3 can effectively increase the emission wavelength (Supplementary Figure 7). At a ratio of 1:1000:5 (Guest:Host:Metal salt), the three-component-doped materials exhibit the best phosphorescence intensity or longest phosphorescence. Compared with 5QL/PBO, the phosphorescence intensity of 5QL/PBO/CdI_2 is enhanced by 11 times, and the phosphorescence wavelength is red-shifted by 7 nm. Correspondingly, although the phosphorescence intensity of 5QL/PBO/InCl_3 is only increased by a factor of 4.1, the wavelength is red-shifted by 28 nm. However, even with the further increase in the ratio of metal ions to 1:1000:50, no clear change in the luminescence of the doped materials is observed. This result may be related to the fact that when the metal ions reach a certain amount, the coordination effect with the guest molecules reaches the maximum; hence, the effect on doped materials tends to be stable.46,47 Furthermore, the low solubility of metal salts in the host also limits the maximum content of metal ion that can be contained in the doped system. Therefore, other three-component doped materials with a guest-host-metal salt molar ratio of 1:1000:5 are prepared.

For the same cation salts, different anions exert different effects on the coordination ability of metal ions and nitrogen atoms. Therefore, effects of various metal salts on phosphorescence properties of the doped system are first screened. Three-component doped materials 5QL/BPO/Al^{3+} were prepared by the selection of three aluminum salts, i.e., AlCl_3, Al(CF_3SO_3)_3, and Al(NO_3)_3, as the third components, respectively. Compared with 5QL/BPO, the phosphorescence wavelength of 5QL/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, the main role of
aluminum ions is to increase the phosphorescence wavelength of the materials, and AlCl$_3$ exhibits the best effect among three salts (Figure 3k). Next, seven monovalent and divalent copper salts (i.e., Cu(CF$_3$SO$_3$)$_2$, CuSO$_4$, Cu(NO$_3$)$_2$, CuCl$_2$, CuCl, CuBr, CuI, and CuCN, respectively) were selected. The results revealed that divalent copper salts can more effectively enhance the phosphorescence intensity of doped materials than monovalent copper salts (Figure 3b, 3l). This result is related to the fact that in general, the coordination ability of divalent copper ions is stronger than that of monovalent copper ions. Among them, Cu(CF$_3$SO$_3$)$_2$ exhibits the best effect. Compared with that of 5QL/BPO, the phosphorescence intensity of 5QL/BPO/Cu(CF$_3$SO$_3$)$_2$ is increased by 2.86 times, and the phosphorescence lifetime is increased by 2.98 times to 301 ms (Figure 3f). Different from aluminum salts, copper salts exhibit a negligible effect on the phosphorescence wavelength, and the red shift is only 12 nm at most. For the four zinc salts (i.e., ZnCl$_2$, Zn(NO$_3$)$_2$, Zn(CH$_3$CO$_2$)$_2$, and Zn(CF$_3$SO$_3$)$_2$, respectively), the highest phosphorescence intensity is increased by 4.14 times (5QL/BPO/ZnCl$_2$), and the phosphorescence lifetime is slightly reduced to 88–95 ms (Figure 3c, 3h, 3m). Similarly, zinc salts marginally affect the phosphorescence wavelength of doped materials. As silver and cadmium are heavy atoms, they can considerably improve the phosphorescence intensity of doped materials. Compared with that of 5QL/BPO/CF$_3$CO$_2$Ag and 5QL/BPO/CdI$_2$ are increased by 11.7 and 13.8 times, respectively (Figure 3d, 3e). However, different anion salts also exhibit a large difference in the effect on phosphorescence properties. Among the six silver salts (i.e., CF$_3$SO$_3$Ag, Ag$_2$SO$_4$, AgCl, CF$_3$CO$_2$Ag, AgNO$_2$, and AgNO$_3$, respectively) and three chromium salts (i.e., CdCl$_2$, Cd(NO$_3$)$_2$, and CdI$_2$, respectively), the phosphorescence intensity is enhanced by a factor of 3.9–13.8 (Figure 3d, 3e, 3n, 3o). In addition, phosphorescence lifetimes of 5QL/BPO/Ag$^+$ and 5QL/BPO/Cd$^{2+}$ are slightly shortened to 33–86 ms and 43–92 ms, respectively (Figure 3i, 3j). Notably, 5QL/BPO/CF$_3$CO$_2$Ag and 5QL/BPO/CdI$_2$ exhibit pure phosphorescence because the heavy atom effect of metals can effectively improve the ISC ability of excitons. Prompt spectra and delayed spectra of the two doped materials almost completely coincide (Supplementary Figure 8). Time-resolved prompt emission decay curves revealed that the emission intensity does not decay as rapidly as ordinary fluorescence materials in the decay range of 200 ns (Supplementary Figure 9), indicating that the nanosecond lifetime is almost nonexistent. For the selection of gallium and indium salts, with AlCl$_3$ as the reference (Al, Ga, and In are elements of the same main group), GaCl$_3$ and InCl$_3$ were selected as the third components. Similar to AlCl$_3$, GaCl$_3$ and InCl$_3$ can red-shift phosphorescence wavelengths by 36 nm and 31 nm, respectively (Figure 3p, Supplementary Figure 10). And the phosphorescence lifetimes correspondingly increases to 120 ms and 135 ms, respectively (Supplementary Figure 11). In summary, seven salts, i.e., AlCl$_3$, Cu(CF$_3$SO$_3$)$_2$, ZnCl$_2$, GaCl$_3$, CF$_3$CO$_2$Ag, CdI$_2$, and InCl$_3$, respectively, render the best effect on the improvement of luminescence properties of doped materials. The main roles of Ag$^+$ and Cd$^{2+}$ are to considerably improve the phosphorescence intensity, of Al$^{3+}$, Ga$^{3+}$, and In$^{3+}$ are to enhance the phosphorescence wavelength, and of Cu$^{2+}$, Ga$^{3+}$, and In$^{3+}$ are to increase the phosphorescence lifetime. In addition, to better quantify the extent of the effect of metal salts on the luminescence intensity, phosphorescence quantum efficiencies of seven three-component doped materials were investigated (5QL/BPO/AlCl$_3$, 5-
QL/BPO/Cu(CF$_3$SO$_3$)$_2$, 5QL/BPO/ZnCl$_2$, 5QL/BPO/GaCl$_3$, 5QL/BPO/CF$_3$CO$_2$Ag, 5QL/BPO/CdI$_2$, and 5QL/BPO/InCl$_3$, respectively), and their corresponding efficiencies are 6.6%, 12%, 18%, 17%, 61%, 70%, and 28% (Table 1). Compared with the phosphorescence efficiency of 5-QL/BPO (4.5%), the phosphorescence efficiencies of three-component doped materials are increased by a factor of 1.46–11.66. Notably, the powders formed by the 5QL guest and metals also do not exhibit phosphorescence at room temperature (Supplementary Figure 12), further indicating that the host matrix plays an indispensable role in the luminescence of the guests.

Table 1. Phosphorescence properties of three-component doped materials

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

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

Al$^{3+}$: AlCl$_3$, Cu$^{2+}$: Cu(CF$_3$SO$_3$)$_2$, Zn$^{2+}$: ZnCl$_2$, Ga$^{3+}$: GaCl$_3$, Ag$^{+}$: CF$_3$CO$_2$Ag, Cd$^{2+}$: CdI$_2$, In$^{3+}$: InCl$_3$.

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 six guests, the host, and seven metal salts mentioned above. Compared with phosphorescence properties of 2-QL/BPO and 8-QL/BPO, those of three-component doped materials 2-QL/BPO/M and 8-QL/BPO/M did not exhibit clear changes (Supplementary Figure 13). This result may be related 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$_3$COOAg and CdI$_2$ is still to increase the phosphorescence intensity, and the phosphorescence intensity is enhanced by factors of 17 and 21 compared with that of 3-QL/BPO, respectively. The phosphorescence quantum efficiencies reach 55% and 62%, respectively, but the phosphorescence lifetime is also reduced to 36 ms and 32 ms (Figure 4a, 4k, Table 1). 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 to 3-QL/BPO (Figure 4a, Table 1). Similar to 5QL/BPO/M, from AlCl$_3$ to InCl$_3$, with the increase in the metal-ion quality, the phosphorescence intensity gradually increases (Figure 4a, Table 1). In addition, AlCl$_3$, GaCl$_3$, and InCl$_3$ can also increase the phosphorescence lifetime, from 108 ms of 3-QL/BPO to 227–294 ms of the three-component materials (Figure 4k, Table 1). Although Cu(CF$_3$SO$_3$)$_2$ and ZnCl$_2$ can improve the phosphorescence properties of doped materials, the effect is not clear. However, notably, Cu(CF$_3$SO$_3$)$_2$ can make the phosphorescence lifetime of 3-QL/BPO/Cu(CF$_3$SO$_3$)$_2$ reach 313 ms (Figure 4k, Table 1). For the other three groups of three-component doped materials (i.e., 4QL/BPO/M, 6-QL/BPO/M, and 7-QL/BPO/M, respectively), the main function of CF$_3$COOAg and CdI$_2$ is still to increase the phosphorescence intensity. Compared with the phosphorescence quantum efficiencies of two-component doped materials, those of three-component doped materials reach 54%–63% (Figure 4b–4d, Table 1). Notably, the phosphorescence quantum efficiency increased from 1.4% of 7-QL/BPO to 54% of 7-QL/BPO/CdI$_2$, with an increase of 38 times. 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 36–56 nm in comparison to the two-component materials (Figure 4b–4d, Table 1). Similarly, from AlCl$_3$ to InCl$_3$, with the increase in the metal-ion quality, the phosphorescence intensity gradually increases (Table 1). In addition, GaCl$_3$, InCl$_3$, and Cu(CF$_3$SO$_3$)$_2$ can effectively prolong the phosphorescence lifetime of materials, especially Cu(CF$_3$SO$_3$)$_2$. Among them, the phosphorescence lifetime increases from 85 ms of 6-QL/BPO to 304 ms of 6-QL/BPO/Cu(CF$_3$SO$_3$)$_2$, with an increase by 3.6 times (Figure 4f–4h, Table 1). In summary, the effect of the same metal ion on phosphorescence properties of different doped materials is basically the same, but the effect of different metal ions on phosphorescence properties of the same doped material is different. These results also indicate that different interactions between various metal ions and guests lead to the abundant phosphorescence of doped materials.

**Coordination of metal salt to guest.** To further investigate whether the coordination of metal ions with guest molecules enhances the phosphorescence properties of doped materials, seven metal salts are first separately doped into the host matrix (Molar ratio of metal salts to host is 5:1000). The results reveal that these doped materials only exhibit phosphorescence of the host itself, indicating that the metal salts do not emit phosphorescence in the host matrix (Figure 5a). The coordination of quinoline compounds with metals essentially indicates 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 salifies 5QL to obtain hexafluorophosphate/5QL-PF$_6$ (Figure 5b). The nitrogen atoms of the salt no longer have lone pairs of electrons. The two-component doped material obtained by 5QL-PF$_6$ and the
host exhibit bright yellow phosphorescence, with a quantum efficiency reaching 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 in comparison with those of 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 via coordination with the nitrogen atoms in quinoline. As AlCl$_3$ causes the most obvious red-shift of the phosphorescence wavelength of doped materials, the UV absorption wavelengths of 5-QL/BPO, AlCl$_3$/BPO, and 5-QL/BPO/AlCl$_3$ are investigated. The results reveal that the absorption wavelength of 5-QL/BPO/AlCl$_3$ is significantly red-shifted in comparison with those of 5-QL/BPO and AlCl$_3$/BPO, also indicative of the formation of the coordination reaction between the metal and guest (Figure 5f). To further understand the effect of metal ions on the guest, theoretical simulations are first performed on the configurations of 5-QL-AlCl$_3$ and 5-QL-CdI$_2$ (Supplementary Figure 14). 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 reveal that AlCl$_3$ can reduce the excited-state energy level of the molecule, and the lowest triplet energy level or T$_1$ is reduced from 2.69 eV of 5QL to 2.41 eV of 5QL-AlCl$_3$ (Figure 5g). CdI$_2$ can considerably increase the SOC values: The SOC is increased from 1.16 cm$^{-1}$ of S$_1$-T$_1$ of 5QL to 112.6 cm$^{-1}$ of S$_1$-T$_1$ of 5QL-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.

**Discussion**

In conclusion, an ingenious idea to enhance phosphorescence properties of the doped materials is reported. First, nitrogen-containing heterocyclic compounds are used as the guests, and the third component/metal salts are then added to the host-guest two-component doped system to form a three-component doped system. Metal ions affect electronic properties of the guest by coordinating with the nitrogen atom of the guest, ultimately improving the phosphorescence properties of the doped materials. Metal ions (i.e., Al$^{3+}$, Cu$^{+/2+}$, Zn$^{2+}$, Ga$^{3+}$, Ag$^+$, Cd$^{2+}$, and In$^{3+}$) can stereoscopically enhance the phosphorescence properties of doped materials. Among them, Ag$^+$ and Cd$^{2+}$ can considerably increase the emission intensity, Al$^{3+}$, Ga$^{3+}$, and In$^{3+}$ can prolong the emission wavelength, while Cu$^{2+}$, Ga$^{3+}$, and In$^{3+}$ can extend the phosphorescence lifetime. In this study, it is crucial to note that the advantage of the host matrix as a container should not be ignored, that is, not only the emitter or guest can be doped into the host, but also the other third or even fourth component can be doped into the host. Ultimately, interactions between multiple components can enhance and enhance phosphorescence properties of doped materials.

**Methods**
Synthesis of quinoline derivatives. The mixture of bromoquinoline (10.0 mmol), boronic acid (12.0 or 24.0 mmol), Pd(PPh$_3$)$_4$ (5.0 mol%), and K$_2$CO$_3$ (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 = 100:1, v:v) to afford the pure $n$-QL 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.

References


28. 


**Declarations**

**Acknowledgements**

This work was supported by the National Natural Science Foundation of China (Nos 22105148 and 22071184) and the Zhejiang Provincial Natural Science Foundation of China (No LY20B020014). Thanks for the equipment support provided by the Analysis and Testing Center of Peking University, and thanks to Dr. Yan Guan for the technical support.
Author contributions

YL, ZC, and XH designed the research work and revised the manuscript. YG synthesized the materials. GY, YL, and KC carried out photophysical property measurements. ZC carried out density functional theory calculations. YL, ZC, and XH wrote the manuscript. ZH, XL, ML, HW, and YD edited the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Figures

Figure 1

Design concept of the three-component doped system.
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.
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 5QL/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 5QL/BPO and various metal salts. Excitation wavelength: 380 nm. k–p, Fluorescence (top) and phosphorescence (down) images of three-component doped materials composed of 5QL/BPO and various metal salts.
**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.
Figure 5

Coordination of the 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-PF₆. c, Fluorescence (top) and phosphorescence (down) images of 5-QL-PF₆/BPO/CF₃COOAg, 5-QL-PF₆/BPO/CdI₂, and 5-QL-PF₆/BPO. d, Phosphorescence wavelengths of 5-QL-PF₆/BPO/CF₃COOAg, 5-QL-PF₆/BPO/CdI₂, and 5-QL-PF₆/BPO. Excitation wavelength: 380 nm; Delayed time: 0.5 ms. e, Phosphorescence decay curves of 5-QL-PF₆/BPO/CF₃COOAg, 5-QL-PF₆/BPO/CdI₂, and 5-QL-PF₆/BPO. Excitation wavelength: 380 nm. f, UV absorption spectra of 5QL/BPO, AlCl₃/BPO, and 5QL/BPO/AlCl₃. g, Energy levels and SOC values of 5QL/BPO, 5QL-AlCl₃, and 5QL-CdI₂.

Supplementary Files
This is a list of supplementary files associated with this preprint. Click to download.

- NCSI.docx