

RESEARCH ARTICLE

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8, 2299Guest-boosted phosphorescence efficiency of a
supramolecular cage†Zhi-Yin Zhang,^a Dong-Qin Ye,^a Qi-Qi Gao,^a Zhi-Chun Shi,^a Mo Xie,^{ID a}
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Phosphorescent organic light emitting diodes (PhOLEDs) are required to achieve sufficiently high performance of devices; however, the synthesis of a phosphorescent emitter with high quantum efficiency and a short lifetime remains a great challenge. In this work, we synthesized a series of inclusion complexes composed of a phosphorescent Cu₆L₃ trigonal prismatic cage host and halobenzene guests. Interestingly, the quantum yield (QY) and emission lifetime of the inclusion complexes can be altered with the variation of halogen atoms in the guests due to the increment of spin-orbit coupling (SOC) and the promotion of intersystem crossing (ISC) processes *via* external heavy-atom effects (HAEs). For instance, on increasing the atomic number of the halogen from F to I, the QY enhanced six times (from 12.6 to 74.3%), while the lifetime reduced nearly two times (33.11 to 18.39 μs) at room temperature. Time-dependent density functional theory (TDDFT) calculations revealed that the encapsulation of iodobenzene guests can greatly promote the ISC processes, which are in good agreement with experimental results. Our studies demonstrated that a simple and efficient approach for designing promising phosphorescent emitters might be useful for PhOLED applications.

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Introduction

The discovery of novel luminescent materials and development of new strategies to tune the photoluminescence (PL) properties are crucial for fabricating organic light emitting diodes (OLEDs) with superior quantum efficiency, brightness, long-term stability and chromaticity.^{1–4} Compared with conventional organic fluorescent emitters with a maximum of 25% internal quantum efficiency (IQE), phosphorescent emitters with noble metals such as platinum and iridium could deliver 100% IQE and lead to outstanding performance of OLEDs.⁵ Therefore, phosphorescent OLEDs (PhOLEDs) are promising for commercial applications and are attracting much attention.^{6–8} To obtain efficient high-brightness PhOLEDs, a high quantum yield (QY) and a short emission lifetime (*e.g.*, in

the range of submicroseconds to microseconds) at room temperature (rt) are particularly desired.⁹ In principle, promoting the intersystem crossing (ISC) processes from singlet excited states to triplet states would be beneficial for enhancing the phosphorescence QY or shortening the lifetime.^{10–13}

Cyclic trinuclear complexes (CTCs) containing heavy metal atoms, such as Hg(I), Au(I), Ag(I) and Cu(I), are able to add organic aromatics *via* π-acid...base interactions and the phosphorescence of an organic luminophore can be triggered by CTCs due to the external heavy-atom effect (HAE) (Scheme 1a).^{14–16} In addition, Omary *et al.* have reported that the phosphorescence QY and emission lifetimes of CTC/organic arene adducts can be fine-tuned through the gradual increase of the size of halogen substituents (*i.e.*, from Cl and Br to I atoms) on the aromatics because of simultaneous external and internal HAEs.¹⁷ By utilizing these strategies, the highest phosphorescence QY of 70% with a long lifetime of 1.25 ms¹⁷ or the shortest lifetime of 29 μs with a low QY of 44%¹⁸ at rt can be achieved for CTC/organic arene adducts; so far, however, they are still far away from the ideal requirement for PhOLED applications. Moreover, the preparation of CTC/organic arene adducts is quite difficult and unpredictable; therefore, few examples have been reported.^{14–17}

A supramolecular coordination cage with a confined cavity is an excellent platform for the investigation of host-guest interactions and the encapsulation of the guest can readily affect the photophysical and photochemical properties of

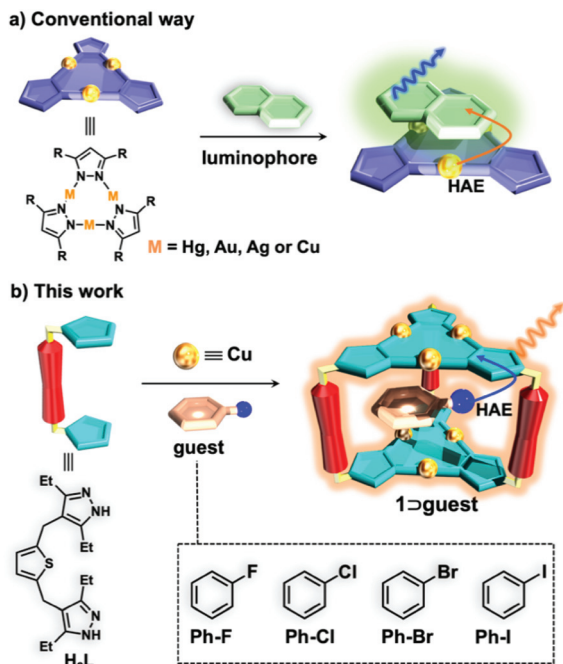
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Scheme 1 Conceptual representation of (a) triggering the phosphorescence of organic arenes utilizing the external HAEs of CTCs and (b) enhancing the phosphorescence of Cu₆L₃ cage **1** by the encapsulation of halogen aromatic guests.

inclusion complexes.^{19–24} Recently, our group synthesized a phosphorescent trigonal prismatic Cu₆L₃ cage **1** with two Cu(I) CTC units as the roof and floor (Scheme 1b).²⁵ By tailoring the ionization potential and volume occupancy of aromatic guests, the PL properties of **1** including the maximum emission peak and QY can be fine-tuned. However, only a very low QY of 14% has been demonstrated.²⁵ Inspired by the tunable phosphorescent cage host **1**, we envision that the inclusion of halogen aromatic guests could promote the ISC process of cage **1** *via* external HAEs (Scheme 1b), thereby enhancing the phosphorescence QY and reducing the emission lifetime.

Herein, we prepared four inclusion complexes composed of Cu₆L₃ cage host **1** and halogen aromatic guests and their structures were all confirmed by single X-ray crystallographic analyses. With the increment of the spin–orbit coupling constant (ζ) of halobenzene (*i.e.*, 272, 587, 2460 and 5060 cm⁻¹ for fluorobenzene (**Ph-F**), chlorobenzene (**Ph-Cl**), bromobenzene (**Ph-Br**), and iodobenzene (**Ph-I**), respectively),²⁶ the phosphorescence QY of the inclusion complexes is enhanced 6 times from 12.6% to 74.3% and the lifetimes are reduced 2 times from 30.11 to 18.39 μ s at rt, which provide potential for phosphorescent OLED applications. To the best of our knowledge, such a high phosphorescence QY with a microsecond lifetime has never been achieved in the field of metal–organic supramolecular cages (Table S1† and Fig. 2).^{25,27–30} More interestingly, the phosphorescence QY of the inclusion complexes exhibits a good linear relationship with the atomic number of the halogen atom. Furthermore, time-dependent density functional theory (TDDFT) calculations revealed that the encapsula-

tion of iodobenzene guests can greatly promote the ISC processes, which are in good agreement with experimental results. Our work demonstrated a new approach for great enhancement of the phosphorescence QY and the reduction of lifetimes by a simple alteration of guest molecules, which might be explored for other luminescent materials for fabricating PhOLEDs with high performance.

Results and discussion

To verify our hypothesis, a series of halobenzene guests (*i.e.*, **Ph-F**, **Ph-Cl**, **Ph-Br**, and **Ph-I**) have been chosen (Scheme 1b). According to our previous synthetic method,²⁵ single crystals of the inclusion complexes **1** ⊃ **Ph-X** (X = F, Cl, Br, and I) were obtained by the solvothermal reaction of **H₂L** and Cu₂O in acetonitrile/halobenzene for 72 h with high yields of up to 62% (see the ESI† for details). As expected, the ¹H-NMR spectra of the inclusion complexes in CD₂Cl₂ confirmed the 1 : 1 stoichiometry between host **1** and guests, which consisted of the crystal structures (Table S5 and Fig. S2–5†). In addition, the phase purity and thermal stability of the inclusion complexes were confirmed by powder X-ray diffraction (PXRD) analysis, elemental analysis, infrared spectroscopy and thermogravimetric analysis (TGA) (Fig. S6–8†).

The inclusion complexes of **1** ⊃ **Ph-Br** and **1** ⊃ **Ph-I** were crystallized in the triclinic space group of *P* $\bar{1}$, while **1** ⊃ **Ph-F** and **1** ⊃ **Ph-Cl** were crystallized in the monoclinic space group of *P*2₁/*c* and *P*2₁, respectively. The single crystal X-ray diffraction (SCXRD) analysis of these host–guest complexes revealed a similar hexanuclear prismatic cage **1** composed of two bending and distorted Cu(I) CTC units and three ligands (Fig. 1). The distance between the center of two Cu₃N₆ rings was changed in a range of 6.724 to 7.000 Å (Table S4†) with the alteration of guest molecules, showing no intertrimer Cu...Cu interaction within the cage.¹⁴ In addition, the cavity volume of cage **1** was changed in a range between 248.76 Å³ and 272.16 Å³ with the variation of guests due to the flexibility of host **1**. The halobenzene guests were encapsulated within the cavity of cage **1** to give a CTC–halobenzene–CTC structure and the distances between the plane of aromatic rings and the center of Cu₃N₆ rings ranged from 2.939 to 3.911 Å, suggesting strong Cu₃... π interactions (Fig. 1a–d).¹⁴ Moreover, cage **1** units in all inclusion crystals were stacked tightly to form an infinite column structure through supramolecular interactions including intermolecular Cu...Cu interactions, CH/ π interactions, and van der Waals force (Fig. 1a–d). Specifically, the shortest intermolecular Cu...Cu distance ($d_{\text{Cu}\dots\text{Cu}}$) between two neighboring cage units in **1** ⊃ **Ph-F** and **1** ⊃ **Ph-Cl** is 2.962 and 2.974 Å, respectively, which is significantly shorter than those in **1** ⊃ **Ph-Br** (3.155 Å) and **1** ⊃ **Ph-I** (3.151 Å). Such structural features suggest that **1** ⊃ **Ph-Br** and **1** ⊃ **Ph-I** exhibit weaker intermolecular Cu...Cu interactions compared to **1** ⊃ **Ph-F** and **1** ⊃ **Ph-Cl**. More importantly, short intermolecular Cu...X distances ($d_{\text{Cu}\dots\text{X}}$) (X = F, Cl, Br, and I) in a range from 3.496 to 3.775 Å are observed (Fig. 1e and f), which is close enough to

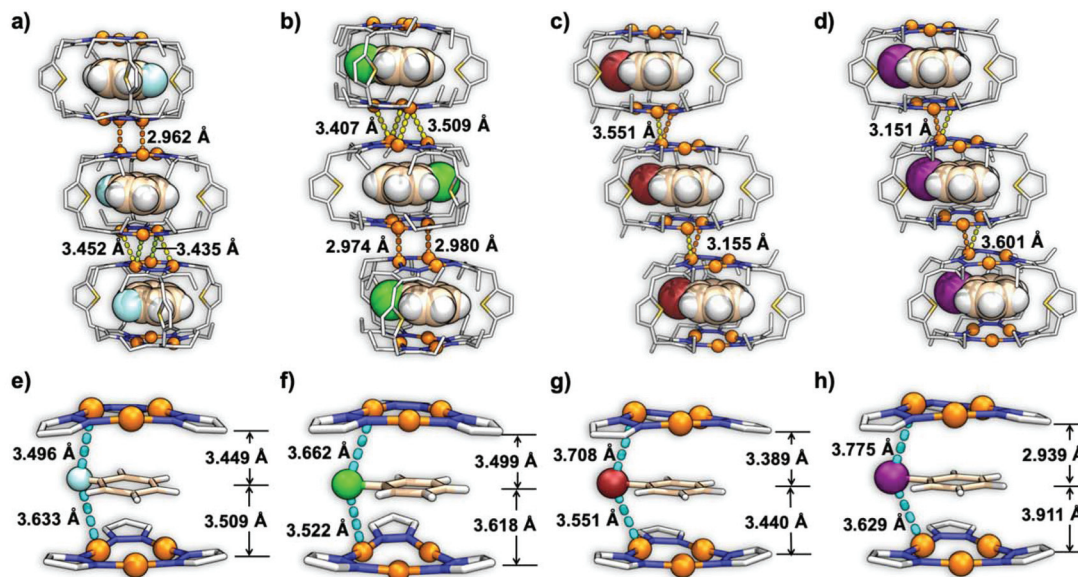


Fig. 1 Crystal structures of (a) $1 \supset \text{Ph-F}$, (b) $1 \supset \text{Ph-Cl}$, (c) $1 \supset \text{Ph-Br}$, and (d) $1 \supset \text{Ph-I}$, showing the Cu_3L_6 cage units in one packed column with intermolecular $\text{Cu}\cdots\text{Cu}$ distances of 2.962, 3.452 and 3.435 Å in $1 \supset \text{Ph-F}$, 3.407, 3.509, 2.974 and 2.980 Å in $1 \supset \text{Ph-Cl}$, 3.551 and 3.155 Å in $1 \supset \text{Ph-Br}$, and 3.151 and 3.601 Å in $1 \supset \text{Ph-I}$, respectively (Cu(i) ions, cage hosts 1, and halobenzene guests are shown as the ball, line and space-filling model, respectively; hydrogen atoms in cage hosts 1 are omitted for clarity; C, N, S, and Cu atoms in the cage are shown in gray, blue, yellow, and orange colours, respectively; C, H, F, Cl, Br and I atoms in the guests are shown in wheat, white, light cyan, green, brown and purple colours, respectively); CTC-guest-CTC structures of (e) $1 \supset \text{Ph-F}$, (f) $1 \supset \text{Ph-Cl}$, (g) $1 \supset \text{Ph-Br}$, and (h) $1 \supset \text{Ph-I}$, showing intermolecular $\text{Cu}\cdots\text{X}$ distances of 3.496 and 3.633 Å in $1 \supset \text{Ph-F}$, 3.662 and 3.522 Å in $1 \supset \text{Ph-Cl}$, 3.708 and 3.551 Å in $1 \supset \text{Ph-Br}$, and 3.775 and 3.629 Å in $1 \supset \text{Ph-I}$, respectively (Cu(i) ions, halogen atoms, CTC units, and guests are shown as the ball and line model, respectively).

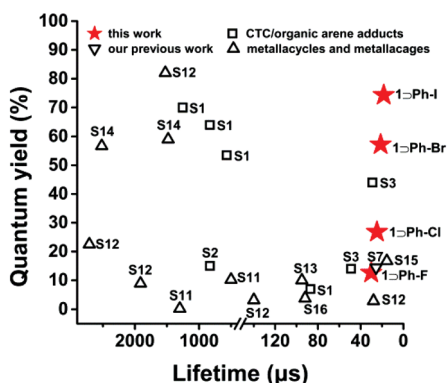


Fig. 2 A comparison of the phosphorescence quantum yield and emission lifetime for reported CTC complexes and coordination macrocycles and cages (S1 to S16 represent the reference S1–S16 in ESI†).

facilitate the ISC process of host 1 via external HAEs.³¹ The DFT-calculated electrostatic potential (ESP) of the inclusion complexes based on their crystal structures shows that the charges on the isosurface of $1 \supset \text{Ph-F}$ and $1 \supset \text{Ph-Cl}$ are relatively well distributed and indicate weak π -basicity (Fig. S18†). It is beneficial to reduce the electrostatic repulsion, thereby forming a more compact intermolecular $\text{Cu}\cdots\text{Cu}$ interaction in $1 \supset \text{Ph-F}$ and $1 \supset \text{Ph-Cl}$. The accommodation of Ph-Br and Ph-I guests significantly increases the electron density on cage

surfaces, resulting in strong π -basicity and weaker intermolecular $\text{Cu}\cdots\text{Cu}$ interactions.

The UV-vis absorption spectra (Fig. S9†) of all inclusion complexes in the solid state show strong absorption bands at 250 to 280 nm corresponding to π - π^* transitions of the ligand. The broad absorption bands appearing at 325 to 350 nm can be ascribed to metal-to-ligand charge-transfer (MLCT) transitions. All these inclusion complexes presented phosphorescence behavior at rt with lifetimes (τ) at the microsecond level. The solid-state photoluminescence (PL) spectrum of $1 \supset \text{Ph-I}$ at rt exhibits low-energy (LE) dominated broad emission bands at 640 nm attributed to metal-metal interaction based phosphorescence and weak high-energy (HE) structural emission bands in a range of 450–550 nm assigned to the ligand-centred (LC) emission, which are similar to those of the proligand (Fig. 3b). On increasing the excitation energy, LE bands gradually quenched concomitant with a slight enhancement of HE bands, as shown in the varied-excitation wavelength PL spectra (Fig. 3b). $1 \supset \text{Ph-F}$, $1 \supset \text{Ph-Cl}$, and $1 \supset \text{Ph-Br}$ show similar PL behaviors to $1 \supset \text{Ph-I}$, and display an LE dominated broad emission peak located at 672, 673, and 645 nm, respectively (Fig. 3a). It is worth mentioning that the red-shift emission of $1 \supset \text{Ph-F}$ and $1 \supset \text{Ph-Cl}$ compared with that of $1 \supset \text{Ph-Br}$ and $1 \supset \text{Ph-I}$ can be explained by cooperative effects between intermolecular $\text{Cu}\cdots\text{Cu}$ interactions and the ionization potential of guests, which have been demonstrated in our previous studies.²⁵ Furthermore, the emission intensity

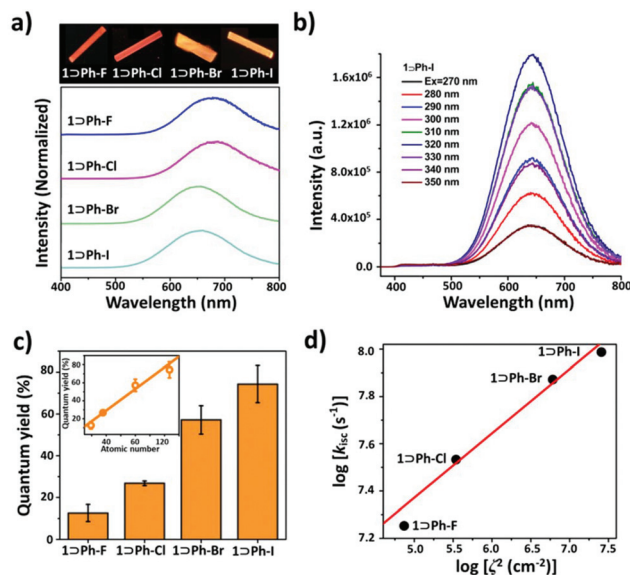


Fig. 3 (a) Luminescence photographs of inclusion crystals under 365 nm UV irradiation and emission spectra of the inclusion complexes; (b) excitation-energy-varied emission spectra of $1 \supset \text{Ph-I}$; (c) quantum yield of the inclusion complexes (inset: linear relationship between the quantum yield and atomic number of halogen in the guest); and (d) linear relationship between the logarithm of intersystem crossing rate constants ($\log(k_{\text{isc}})$) in the inclusion complexes and $\log \zeta^2$.

of $1 \supset \text{Ph-F}$, $1 \supset \text{Ph-Cl}$, $1 \supset \text{Ph-Br}$, and $1 \supset \text{Ph-I}$ slightly reduced with the increase of the temperature from 77 to 375 K.

The introduction of the halogen atom greatly affects the phosphorescence properties of cage **1**. By replacing one hydrogen atom with fluorine on benzene, the phosphorescence QY remains almost unchanged (12.6% for $1 \supset \text{Ph-F}$, and 14.4% for the inclusion complex accommodating benzene²⁵). However, the phosphorescence QY remarkably enhanced and followed the order of $1 \supset \text{Ph-Cl}$ (26.8%) < $1 \supset \text{Ph-Br}$ (57.2%) < $1 \supset \text{Ph-I}$ (74.3%) by utilizing heavier halogen atoms (Table 1). Interestingly, the phosphorescence QY of the inclusion complexes exhibits a linear relationship with the atomic number of halogen atoms (Fig. 3c). In addition, the QY can further increase with the decrease of temperature, especially, the QY of $1 \supset \text{Ph-I}$ can reach a near-unit QY of 97% (Table 1) at 77 K. More importantly, their lifetimes are also significantly reduced

from 30.11 to 18.39 μs at 298 K upon the change of halogen substituents on the benzene ring from F to I, which further confirms their phosphorescence nature. These results demonstrated that the phosphorescence QY and lifetime of the inclusion complexes can be fine-tuned with the alteration of halogen atoms on guests.

It has been proved that, in the case of external HAEs, the atomic number or SOC constant of the heavy atom is a crucial factor for strengthening ISC in the luminophore reported by Kasha.³² Thus, to better understand the mechanism, the ISC rate constants (k_{isc}) were calculated on the basis of the measured phosphorescence QY and lifetime.³³ The k_{isc} value of $1 \supset \text{Ph-I}$ ($9.71 \times 10^7 \text{ s}^{-1}$) increased 5.4 times than that of $1 \supset \text{Ph-F}$ ($1.79 \times 10^7 \text{ s}^{-1}$) (Table 1). As shown in Fig. 3d, the logarithm of k_{isc} of the inclusion complexes increases with the increment of $\log \zeta^2$, showing good linear correlation. Such results indicated that the SOC in the inclusion complexes was enhanced with the increment of the ζ values of guests; thus, ISC processes between singlet and triplet states were accelerated *via* external HAEs. In addition, the logarithm of the triplet radiative decay rate constants (k_{r}) and $\log \zeta^2$ also shows a linear relationship, suggesting that the transition from triplet excited states to ground states is remarkably promoted by the SOC in halobenzene guests (Fig. S16[†]). For instance, k_{r} increased almost 10 times from $4.18 \times 10^3 \text{ s}^{-1}$ to $4.04 \times 10^4 \text{ s}^{-1}$ and followed the order of $1 \supset \text{Ph-F}$ < $1 \supset \text{Ph-Cl}$ < $1 \supset \text{Ph-Br}$ < $1 \supset \text{Ph-I}$ (Table 1), implying that radiative decay processes from triplet excited states to ground states in the inclusion complexes are enhanced by external HAEs. In particular, $1 \supset \text{Ph-I}$ features the fastest ISC rate and radiative decay rate, resulting in the highest quantum efficiency of 74.3% and the shortest lifetime of 18.39 μs .

To further understand the mechanism of external HAEs, time-dependent density functional theory (TDDFT) calculations were performed to reveal the nature of singlet and triplet states of the inclusion complex $1 \supset \text{Ph-X}$. Generally, the small energy difference and matching transition components of singlet and triplet states are conducive to the ISC process.³⁴ As shown in Fig. 4, the inclusion complex $1 \supset \text{Ph-I}$ exhibited more than five triplet states (*e.g.*, T_{32} , T_{33} , T_{34} , T_{35} , and T_{36}) close to the energy of its S_1 , suggesting the presence of many potentially effective ISC channels in the excited state. In contrast, the potential ISC channels for $1 \supset \text{Ph-F}$ and $1 \supset \text{Ph-Cl}$

Table 1 Summary of crystal and photophysical parameters for the inclusion complexes in the solid state

Complexes	Shortest Cu...X distance (Å)	ζ^a /cm	λ_{ex} (nm)	λ_{em} (nm)	τ_{p}^b (μs)		τ_{F}^b (ns)	Φ^c (%)		$k_{\text{r}}^d \times 10^4$ (s^{-1})	$k_{\text{nr}}^e \times 10^4$ (s^{-1})	$k_{\text{isc}}^f \times 10^7$ (s^{-1})
					298 K	77 K		298 K	77 K			
$1 \supset \text{Ph-F}$	3.496	272	316	672	30.11	31.01	7.04	12.6	19.6	0.42	2.90	1.79
$1 \supset \text{Ph-Cl}$	3.522	587	310	673	24.75	24.49	7.86	26.8	46.9	1.08	2.96	3.41
$1 \supset \text{Ph-Br}$	3.551	2460	310	645	21.29	20.73	7.68	57.2	87.0	2.69	2.01	7.45
$1 \supset \text{Ph-I}$	3.629	5060	320	640	18.39	18.36	7.65	74.3	96.9	4.04	1.40	9.71

^a Spin-orbit coupling constant; see ref. 26. ^b τ_{p} is the average phosphorescence decay lifetime, and τ_{F} is the average fluorescence decay lifetime. ^c Φ is the average quantum yield measured at 298 K. ^d Radiative decay rate constant: $k_{\text{r}} = \Phi/\tau_{\text{p}}$. ^e Non-radiative decay rate constant: $k_{\text{nr}} = (1 - \Phi)/\tau_{\text{p}}$. ^f Intersystem crossing rate constant: $k_{\text{isc}} = \Phi/\tau_{\text{F}}$ the temperature effects did not consider here.

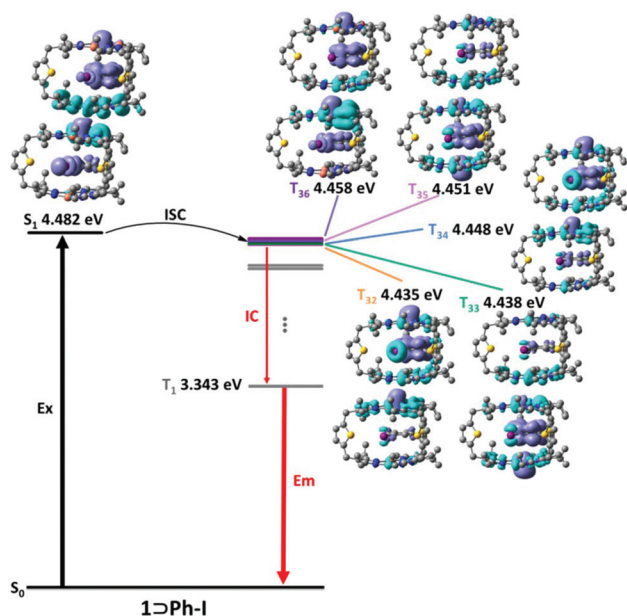


Fig. 4 Proposed intersystem crossing approaches for $1 \supset \text{Ph-I}$. The energy level and electron density difference (EDD) of the S_1 state and selected triplet states are illustrated.

are much less than those of $1 \supset \text{Ph-I}$ (Fig. S19–22[†]), further confirming that the promotion of the ISC processes followed the order of $1 \supset \text{Ph-F} < 1 \supset \text{Ph-Cl} < 1 \supset \text{Ph-Br} < 1 \supset \text{Ph-I}$. More importantly, the electron density difference (EDD) diagram between the excited state and the ground state (Tables S7–S14[†]) revealed that the guests **Ph-F** and **Ph-Cl** did not participate in the charge transfer transition of the triplet state (³XLCT), and the guest **Ph-Br** slightly participated in ³XLCT, while the guest **Ph-I** greatly contributed to ³XLCT, suggesting a great increment of the SOC and promotion of the ISC processes with the increase of the halogen atom size. Theoretical results further supported that the introduction of the halogen atom on the guests can accelerate the ISC processes in the excited state and enhance the efficiency of phosphorescence.

Conclusions

In summary, we designed four inclusion complexes by encapsulating halobenzene guests into a phosphorescent Cu_6L_3 prismatic cage. By mediating the halogen atom, the phosphorescence QY and lifetime of the inclusion complexes can be fine-tuned through external HAEs. More importantly, the linear relationship between the logarithm of ISC rate constants and $\log \zeta^2$ revealed that heavy atoms played an important role in the enhancement of QY and shortening of lifetime. For instance, the phosphorescence QY increased 6 times from 12.6% to 74.3%, while the lifetimes reduced 1.6 times from 30.11 to 18.39 μs for $1 \supset \text{Ph-F}$ and $1 \supset \text{Ph-I}$, respectively. To the best of our knowledge, $1 \supset \text{Ph-I}$ with such high phosphorescence QY and short lifetime has rarely been achieved in the

supramolecular cage. Furthermore, the TDDFT simulation suggested that the inclusion of iodobenzene guests can narrow the energy difference between the excited singlet and triplet states and allow more effective ISC channels, thus greatly promoting the ISC processes. By combining the experimental and theoretical approaches, we demonstrated a novel and simple way to tuning the PL properties of the phosphorescent emitter that might be suitable for PhOLED applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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