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External Heavy Atom Effect via Orbital Interactions Revealed by Single-Crystal X-Ray Diffraction

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ABSTRACT: Enhanced spin-orbit coupling through external heavy-atom effect (EHE) has been routinely used to induce room-temperature phosphorescence (RTP) for purely organic molecular materials. Therefore, understanding the nature of EHE, i.e., the specific orbital interactions between the external heavy atom and the luminophore, is of essential importance in molecular design. For organic systems, halogens (e.g., Cl, Br, and I) are the most commonly seen heavy atoms serving to realize the EHE-related RTP. In this report, we conduct an investigation on how heavy-atom perturbers and aromatic luminophores interact based on data obtained from crystallography. We synthesized two classes of molecular systems including *N*-haloalkyl-substituted carbazoles and quinolinium halides, where the luminescent molecules are considered as "base" or "acid" relative to the heavy-atom perturbers, respectively. We propose that electron

donation from a π molecular orbital (MO) of the carbazole to the σ^* MO of the C-X bond (π/σ^*) and n electron donation to a π^* MO of the quinolinium moiety (n/ π^*) are responsible for the EHE (RTP) in the solid state, respectively.

Introduction.

The external heavy atom effect (EHE) in the field of molecular spectroscopy has been extensively studied since the early 1950s.¹ The EHE is typically manifested as enhanced spinorbit coupling, which increases the rates of both intersystem crossing (ISC) and phosphorescence decay² of the excited state luminophore. It is considered that the EHE is executed through the orbital interactions between the heavy-atom perturber and the luminophore.³ Although the EHE has been routinely used to boost molecular phosphorescence^{4,5,6,7,8,9,10,11,12} for various applications,^{13,14,15} very few reports are focused on the mechanistic perspective.¹⁶

Here, we synthesized two types of organic aromatic molecules, carbazole and quinolinium derivatives (Chart 1), based on the relative energy-level of the HOMO (or basicity) / LUMO (or acidity) and combine them with heavy-atom perturbers to generate room-temperature phosphorescence (RTP)^{17,18} in the solid state. The orbital interactions can easily be revealed from single-crystal X-ray diffraction data, in addition to other complementary evidence such as optical and NMR spectroscopy. For the "basic" carbazole, we found that the π orbital interacts with the anti-bonding orbital (σ *) with the alkyl halide (C-X); whereas for the "acidic" quinolinium, its π * orbital interacts with filled p orbital from the counterion halide (X⁻) strongly to generate almost purely room-temperature phosphorescence (RTP). As can be expected, stronger EHE is observed for better orbital match in addition to the well-known factor of atomic number.



Chart 1. Representative structures of carbazole-based "n- σ *" and quinolinium-based "n- π *" organic luminescent molecules.

Results and Discussion.

The halogen-substituted *N*-alkyl carbazole derivatives (**CZ-nC-X**, n = 2, 4, 6; X = Cl, Br, I) were easily synthesized from carbazole and various end-substituted alkyl halides in the presence of a phase-transfer catalyst, tetrabutyl ammonium bromide. The reaction was conducted at 50 °C for 24 h and the crude product was purified by column chromatography (ethyl acetate/ petroleum ether = 1/20, v/v), yielding a colorless solid (Supporting Information, SI). The quinolinium salt (**Qs**) derivatives were synthesized via the $S_N 2$ substitution reaction between various quinolines and corresponding alkyl halides in acetone at room temperature for 24 h, and then the product was obtained by filtration and recrystallization. The structures of all compounds were analyzed with single-crystal x-ray diffraction (SC-XRD).

The steady-state photoluminescence emission spectra of *N*-alkyl carbazoles are shown in Figure 1a and Table 1, where all compounds are emissive in the solid state with the exception of *N*-substituted iodoethyl carbazole (**CZ-2C-I**). The higher energy band from 360 nm to 460 nm with distinct carbazole vibronic features is ascribed to fluorescence ($\tau = 0.56$ ns - 16.1 ns); the lower energy counterpart from 525 to 625 nm is contributed by RTP ($\tau = 32$ ms - 700 ms). Compared to carbazole emission in dilute solution,¹⁹ the relative intensity of the vibronic peaks varies significantly presumably due to coupled vibrational transitions in the aggregation state of the luminophores.²⁰ As expected, the EHE is the weakest for Cl-substitution and strongest for the iodo-substituted carbazole, based on the relative intensity between the fluorescence and RTP bands, which results in distinct color change from blue to orange to the naked eye under a UV lamp (Figure 1b). The Cl derivatives, **CZ-2C-Cl** and **CZ-4C-Cl**, exhibit very weak phosphorescence so that the RTP peak could only be observed in the amplified emission spectra from 530 nm to 600 nm (inset of Figure 1a). It is also expected that the shorter chain derivatives exhibit stronger EHE as well due to higher heavy-atom concentrations: e.g., for the Br derivatives, **CZ-6C-Br**, **CZ-4C-Br** and **CZ-2C-Br**: when the alkyl chain length is decreased, the RTP/fluorescence ratio gradually increases.

Other than these well-known general features of EHE, some interesting subtle spectroscopic features can also be observed from Figure 1a. In terms of the energy of fluorescence and RTP, the shorter chain derivatives exhibit more blue-shifted emissions (e.g., 371 nm and 373 nm in the fluorescence region and 544 nm and 555 nm in the RTP region for **CZ-2C-Br** and **CZ-4C-Br**, respectively). Representative fluorescence and RTP lifetime decays are shown in Figure 1c and 1d. In the fluorescence region, the lifetime is 16.1 ns, 5.97 ns and 0.56 ns for **CZ-4C-CI**, **CZ-4C-Br** and **CZ-4C-I**. In the RTP region, the measured lifetimes are 100 ms, 85 ms and 32 ms, respectively. The trend is obvious for both fluorescence and RTP: both exhibit drastically decreased lifetime values (e.g., fluorescence: from 11.86 ns to 0.56 ns; RTP: from 700 ms to 32 ms) for heavier-element substitution although the quantum yields do not decease as much (i.e., 10.8% to 3.6%, Table 1), which is ascribed to more pronounced EHE from the spin-orbit coupling. All fluorescence decays can be fitted with three exponents, which is possibly due to the

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formation of various aggregates in the ground state and/or in the solid state. Shorter-lived components are more prominent for Br- and I-containing derivatives as a result of the heavyatom quenching effect. For the RTP decays, however, the decay is much closer to singleexponential since triplet dimers or aggregates are less likely to form.



Figure 1. a) Normalized steady-state photoluminescence emission spectra of various N-alkyl carbazole derivatives. Inset, amplified emission spectra of **CZ-2C-Cl** and **CZ-4C-Cl** from 530 nm to 600 nm. b). Photos of **CZ-4C-Cl** (left), **CZ-4C-Br** (middle) and **CZ-4C-I** (right) crystals emission under 365-nm UV light. c) and d)Time-resolved fluorescence and room-temperature phosphorescence emission of **CZ-4C-Cl**, **CZ-4C-Br** and **CZ-4C-I** crystals.

	λ _{Fl} (nm) ^a	τ _{F11} (ns)/ (%)	τ _{Fl2} (ns)/ (%)	τ _{Fl3} (ns)/ (%)	$ au_{Fl0}^{\ \ b}$	λ _{RTP} (nm) ^c	τ _{RTP1} (ms)/ (%)	τ _{RTP2} (ms)/ (%)	τ _{RTP3} (ms)/ (%)	$ au_{RTP}^{\ \ d}$	$\Phi_{\rm Fl}(\%)^{ m e}$	Φ _{RTP} (%) ^e
CZ- 2C-Cl	406, 429	6.34/ 10.65	13.2/ 2.27	12.5/ 87.08	11.86	542	700/ 100			700	10.7	0.1
CZ- 4C-Cl	410, 438	20.2/ 5.42	15.8/ 92.78	19.1/ 1.80	16.10	551	100/ 100			100	9.1	<0.01
CZ- 2C- Br	371, 406	1.87/ 15.53	4.03/ 3.81	3.95/ 80.66	3.63	544, 592	180/ 64.19	310/ 35.81		230	5.0	1.8
CZ- 4C- Br	373	3.07/ 64.30	7.78/ 23.49	17.8/ 12.21	5.97	555, 604	85/ 100			85	4.4	0.8
CZ- 6C- Br	372	1.92/ 5.52	6.09/ 55.30	14.5/ 39.18	9.15	551, 604	410/ 100			410	4.5	0.5
CZ- 4C-I	372	1.13/ 12.63	0.12/ 81.37	5.40/ 6.00	0.56	556, 604	24/ 35.80	51 / 42.03	7.6 / 22.17	32	1.2	2.4

Table 1: Luminescent characterization of carbazole derivatives in solid state.

a. Fluorescence emission peak excited at excitation maxima.

b. Apparent pre-exponential weight-averaged lifetime at emission maximum.

c. RTP emission maximum excited at excitation maxima.

d. Apparent pre-exponential weight-averaged lifetime at emission maximum.

e. Absolute photoluminescence quantum yields under air at 298 K.



Figure 2. a) Normalized steady-state photoluminescence emission spectra of various quinolinium salts with PF₆ and halides as the counter-ions: non-substituted (**QPF**₆ and **QBr**), 6-methoxylsubsituted (**MeOQPF**₆ and **MeOQBr**) and 6-trifluoromethyl-substituted (**CF**₃**QBr** and **CF**₃**QI**) quinolinium salts. b). Photos of **QPF**₆ (left), **CF**₃**QBr** (middle) and **CF**₃**QI** (right) solid emission under 365 nm UV light. c) RTP decay profiles for **CF**₃**QBr** and **CF**₃**QI**.

	QPF ₆	QBr	MeOQPF ₆	MeOQBr	CF ₃ QBr	CF ₃ QI
$\lambda_{em}(nm)^{a}$	412	551	411	547	533	615
$ au_{1}$ / (%)	0.056 ns/ 2.40	84 μs/ 38.04	4.17 ns/ 58.87	173 μs/ 26.61	54 µs/ 29.14	1.44 μs/ 100
$ au_2$ / (%)	2.94 ns/ 13.87	467 μs/ 54.10	1.20 ns/ 11.12	433 μs/ 61.72	15 μs/ 58.52	
$\tau_{3}^{\prime}/(\%)$	12.9 ns/ 83.73	14 µs/ 7.86	11.3 ns/ 30.01	1505 μs/ 11.6	450 μs/ 12.34	
$ au^{\mathrm{b}}$	11.2 ns	286 µs	5.96 ns	490 μs	80.4 µs	1.44 µs

Table 2: Luminescent characterization of Qs in the solid state.

a. Photoluminescence emission peak excited at excitation maxima.

b. Apparent pre-exponential weight-averaged lifetime at emission maximum in the solid state.

We then performed the same experiments for all the quinolinium salts (**Qs**, Figure 2 and Table 2), where most **Qs** solids are emissive except for 1-ethylquinolin-1-ium iodide (**QI**) and 1-ethyl-6-methoxyquinolin-1-ium iodide (**MeOQI**). As shown in Figure 2a, we found that the counterion plays a significant role on the energy of the emission spectrum for the **Qs**, where the most blue-shifted emissions belong to the crystals with PF₆ counter-ions such as **QPF**₆ ($\lambda_{em} = 412 \text{ nm}$) and **MeOQPF**₆ ($\lambda_{em} = 411 \text{ nm}$). On the other hand, **Qs** with halides counter-ions have much redshifted emission peaks with the trifluoro-**Qs** iodide (**CF**₃**QI**) exhibiting the most red-shifted emission ($\lambda_{em} = 615 \text{ nm}$). The photoluminescence lifetimes of these **Qs** crystals were also measured. It was found that **Qs** with the PF₆ counter-ion have emission lifetimes in the ns range, e.g., **QPF**₆ ($\tau = 11.2 \text{ ns}$) and **MeOQPF**₆ ($\tau = 5.96 \text{ ns}$), which is typical of fluorescence; while those of **Qs** with the halide counter-ions are much longer-lived (µs-ms), which are ascribed to RTP. The results can be interpreted by a combination of charge-transfer (CT) transition and EHE. For **QPF**₆ and **MeOQPF**₆, there is no heavy atom perturbation nor significant CT involved; mostly the fluorescence emission characteristic π - π * arising from the quinolinium ring can be observed. For the **QsX** crystals, a combination of CT and EHE can result in the prominent emergence of triplet emissions. For instance, in the photoluminescence decay of **CF**₃**QBr**, a fast component in the µs domain and a slower one in the ms range are both present (Figure 2c and Table 2). Whereas for the iodide counterpart, a single-exponent decay with a fitted apparent lifetime of 1.44 µs was recorded. Since the bromide anion is a weaker electron donor compared to iodide, it is then possible that ³CT is slightly above the **Qs** ³ π - π * state, both µs and ms lifetimes corresponding to ³CT and ³ π - π * could be resolved. However, the **CF**₃**QI** ³CT is well below the **Qs** ³ π - π * state and thus a single exponent decay from ³CT is observed. The results are consistent with a previous report by Kosower et al,²¹ where the presence of multiple chargetransfer bands for pyridinium iodide is observed.



Figure 3. Molecular packing of CZ-2C-Cl, CZ-2C-Br, CZ-2C-I, CZ-4C-Cl, CZ-4C-Br, CZ-4C-I and CZ-6C-Br crystals (red dotted lines denote the weak interactions).

To further understand the structure-photoluminescence properties relationship in the crystalline state, single-crystal X-ray Diffraction (SC-XRD) measurements were performed for all the carbazole and **Os** compounds. The molecular packings of carbazole derivatives are presented in Figure 3. The nitrogen atom on the carbazone ring seems to be in close proximity with the C-X moiety, which is likely due to the π - σ * interaction. Specifically, from the aspect of the linker length, for the ethylene linker (CZ-2C-Cl, CZ-2C-Br, CZ-2C-I), the C-X "tail" all folds back onto the carbazole ring, which is a high-energy conformation because of the steric effect. It is possible that the stabilized energy from the intramolecular π - σ * interaction over compensates the energy rise from sterics. For the longer-linker derivatives (CZ-4C-Cl, CZ-4C-Br, CZ-4C-I, CZ-6C-Br), intermolecular contact via this π - σ * interaction is preferred since both orbital stabilization and sterics can both be achieved. In addition, for CZ-2C-Br, CZ-4C-Br and CZ-6C-Br, the distances between the nitrogen atom and bromine atom are 3.346 Å, 3.750 Å and 4.483 Å, respectively, indicating gradually weaker π - σ * interactions. The results are consistent with the spectroscopic data, where the RTP ratio decreases from CZ-2C-Br to CZ-**4C-Br** to **CZ-6C-Br**. On the other hand, for different halogen derivatives with the same linker length (4C), the distance between the halogen and nitrogen atom increases (3.694 Å, 3.750 Å and 3.950 Å for CZ-4C-Cl, CZ-4C-Br and CZ-4C-I). Considering the increasing atom radius of Cl (1.0 Å), Br (1.15 Å) and I (1.40 Å),²² the distance of ArC···HCH (another weak interaction denoted by the red dotted line) actually decreases from 2.859 Å to 2.830 Å to 2.791 Å from CZ-**4C-Cl** to **CZ-4C-Br** to **CZ-4C-I**, which could be related to the increasingly stronger π - σ^* interaction, given that the anti-bonding σ^* orbital primarily resides at the back of the carbon atom (the opposite side of the halogen atom).

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To further back the π - σ * interaction hypothesis, we studied the UV-Vis, fluorescence and ¹H-NMR spectroscopy of all the compounds in dilute solutions. For the UV-Vis absorption spectra, Figure 4 and Table 3, the three carbazole compounds with the ethylene linker, irrespective of the halogen type, exhibit the most blue-shifted absorption ($\lambda_{abs} = 326$ nm) at the lowest transition, followed by the counterparts with the butylene linker ($\lambda_{abs} = 330$ nm) and then the hexylene derivative ($\lambda_{abs} = 332$ nm). The fluorescence emission spectra exhibit the same trend with decreasing emission energy from C2 to C4 to C6-linker derivatives. A possible explanation is that the nearby nitrogen n orbital and C-X σ^* mixing can lead to decreased potential energy for the lone pair participating the conjugation and thus the π - π * transition is blue-shifted. However, the orbitals mixing between the p electrons on the halogen and the carbazole π^* may also result in increased energy for π^* . To further elucidate the interaction, ¹H-NMR spectra were investigated in CDCl₃ solution as well. The results in Figure 4c clearly indicate that the electron density is significantly depleted around the nitrogen atom as the proton closest to nitrogen atom (H_e) exhibits the biggest downfield shift from 4.32 ppm to 4.37 ppm to 4.69 ppm for C6, C4 and C2-linker derivatives. This non-linear decrease is unlikely to be from the induction effect from Br alone. Meanwhile the protons on the aromatic ring, Ha, Hb, Hc and Hd, also all show downfield chemical shift from C6 to C2 derivatives, indicating the electron density on the conjugated system (carbazole ring) decrease. Based on all the results above, we ascribe the orbital interaction more likely to be (N)n-(C-X) σ^* rather than (X)n-(CZ) π^* . Finally, we performed theoretical calculations for the lowest singlet transition states for both CZ-2C-Br and **CZ-4C-Br** (Figure 4d). Calculations were performed using wB97XD/cc-pVDZ with the X-ray CIF coordinates and a polarizable continuous medium (Tomasi) model solvent dichloromethane.^{23,24} From the calculations, it is clear that the 2C derivative has significant σ^*

participation but no such interaction is noted for the 4C counterpart. The calculations also indicate that the π orbital energy is indeed lower for the 2C derivative while the π^* is raised presumably due to the (CZ) π -(C-X) σ^* mixing.



Figure 4. a) and b). UV absorption spectra and steady-state emission spectra of various carbazole derivatives in dilute CH₂Cl₂ solution. c) ¹H-NMR spectra of **CZ-2C-Br**, **CZ-4C-Br** and **CZ-6C-Br**. d) Calculated main singlet transition state for **CZ-2C-Br** and **CZ-4C-Br** (orbital energy is given in Hartree).

Table 3: Luminescence	characterization	in dilute	CH ₂ Cl ₂	solution.
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	$\lambda_{abs} (nm)^{a}$	$\lambda_{_{FL}}(nm)^{b}$	$\tau_{_{\rm FL}}^{}$ (ns) ^c
CZ-2C-Cl	326, 339	343, 360	6.14
CZ-4C-Cl	330, 344	348, 365	5.79
CZ-2C-Br	326, 339	343, 360	4.96
CZ-4C-Br	330, 344	349, 365	6.02
CZ-6C-Br	332, 345	350, 367	9.32
CZ-2C-I	328, 341	346	6.13
CZ-4C-I	331, 345	348, 364	5.09

a. Lowest singlet transition.²⁵

b. Photoluminescence emission peak excited at excitation maxima.

c. Pre-exponent weight-averaged fluorescence lifetime.



Figure 5. Crystal packing of MeOQBr, MeOQI, MeOQPF₆, QBr, QI, QPF₆, CF₃QBr and CF₃QI.

The SC-XRD structures of the **Qs** derivatives are presented in Figure 5. From the crystal structures, two of the **Qs** include a water molecule in the crystals and the rest contain only the quinolinium ring and the halide counter ion. As can be seen, the "acidic" quinoline ring is in close proximity with filled p orbital from the counterion halide (X⁻), which is likely due to the much stronger (X⁻)n-(quinoline) π^* interaction, compared to that of π - σ^* for the carbazole derivatives based on calculations for some representative compounds (Table 4). Comparing the energies of the π^* orbital for **MeOQBr** and **MeOQPF**₆, the former shows a notable increase (-1.012 eV) vs. the latter (-1.143 eV), which is ascribed to the better mixing with bromide lone pairs. The calculated energy difference between the bromide lone pair and quinolinium π^* is 0.2418 hartrees (h); the difference between the conjugation-participating nitrogen lone pair with C-Br σ^* is 0.3611 h. From the calculated results, for **MeOQBr**, the lowest singlet transition state could be a CT one if the orbital overlap is reasonable in the solid state; for **MeOQPF**₆, however,

even in the solid state, the lowest singlet transition remains to be π - π *. The calculation results are consistent with spectroscopic data in Figure 2.

Table 4. Calculated orbita	l energies for Qs and	carbazole derivatives. ^a
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MeOQBr	MeOQPF6	CZ-2C-Br	
quinolinium π*: -0.0374 h	quinolinium π*: -0.0420 h	^b C-X σ*: +0.0681 h	
bromide lone pair: -0.2792 h	quinolinium π : -0.3238 h	CZ π*: +0.0269 h	
bromide lone pair: -0.2823 h	quinolinium π : -0.3564 h	^c CZ π: -0.2930 h	
quinolium π: -0.3207 h	fluorine lone pair: -0.4092h	${}^{d}CZ \pi$: -0.3381 h e bromide lone pair: -0.3645 h	

- a. Calculations were performed using wB97XD/cc-pVDZ with the X-ray CIF coordinates and a polarizable continuous medium (Tomasi) model solvent dichloromethane. Energy units are hartrees.
- b. Mostly σ^* with slight CZ π^* mixing.
- c. Mostly CZ π with N lone pair mixing.
- d. Mostly CZ π with slight bromide lone pair mixing.
- e. Mostly bromide lone pair with slight CZ π mixing.

Finally, we investigated the photoluminescence spectra of these carbazole and quinolinium salt derivatives in solution at 77 K. The emission spectra of dilute carbazole derivative solutions $(10^{-5} M)$ in methyltetrahydrofuran (mTHF) are shown in Figure 6a: in addition to the fluorescence band (~340-400 nm), the phosphorescence band (~410-500 nm with seconds-long "afterglow") could also be observed for each derivative. However, the relative intensity of the

phosphorescence band is the highest for CZ-2C-Br due to the strongest orbital mixing, which is consistent with the NMR spectra (Figure 4c). For the quinolinium derivatives (Figure 6b), however, no phosphorescence band is present from the spectra other than the high-energy fluorescence band from 300-350 nm (note that the hump in the spectra is probably from aggregates due to the poor solubility of the PF_6^- derivatives). The lack of phosphorescence for the quinolinium derivatives can be explained by the separation of the Qs π^* orbital and the counterion n orbital as a result of solvation.



Figure 6. Steady-state emission spectra of various carbazole (a, $\lambda_{ex} = 310$ nm) and quinolinium salt (b, $\lambda_{ex} = 280$ nm) derivatives in dilute mTHF solutions (10⁻⁵ *M*) at 77 K.

Conclusion

In conclusion, we synthesized two classes of organic aromatic molecules, carbazole and quinolinium derivatives with heavy-atom perturbers to investigate external heavy-atom induced RTP in the solid state. In the carbazole case, the heavy-atom perturber serves as an electron acceptor, or "acid", due to the presence of a low lying σ^* (C-X) orbital. The crystal structure suggests that both intramolecular and intermolecular mixings of the σ^* orbital with the carbazole π orbital are possible. In the quinolinium salts case, the heavy-atom perturber is an anion

(electron donor) and is likely to interact with the low-lying π^* orbital of the quinolinium ring. We thus conclude that regardless of electron acceptor or donor, the external heavy-atom effect can be realized as long as direct and matching orbital interactions are present.

Supporting Information. Materials, methods, syntheses of compounds, ¹H-NMR spectroscopy, supplementary figures and crystallographic data. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

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REFERENCES

⁽¹⁾ Kasha, M., Collisional Perturbation of Spin - Orbital Coupling and the Mechanism of Fluorescence Quenching. A Visual Demonstration of the Perturbation. *J. Chem. Phys.* **1952**, *20*, 71-74.

⁽²⁾ McGlynn, S.; Daigre, J.; Smith, F., External Heavy-Atom Spin-Orbital Coupling Effect. IV. Intersystem Crossing. *J. Chem. Phys.* **1963**, *39*, 675-679.

⁽³⁾ McGlynn, S.; Sunseri, R.; Christodouleas, N., External Heavy - Atom Spin - Orbital Coupling Effect. I. The Nature of the Interaction. *J. Chem. Phys.* **1962**, *37*, 1818-1824.

(4) Bolton, O.; Lee, K.; Kim, H.-J.; Lin, K. Y.; Kim, J., Activating Efficient Phosphorescence from Purely Organic Materials by Crystal Design. *Nat. Chem.* **2011**, *3*, 205-210.

(5) Kwon, M. S.; Yu, Y.; Coburn, C.; Phillips, A. W.; Chung, K.; Shanker, A.; Jung, J.; Kim, G.; Pipe, K.; Forrest, S. R. et al., Suppressing Molecular Motions for Enhanced Room-Temperature Phosphorescence of Metal-Free Organic Materials. *Nat. Commun.* **2015**, *6*.

(6) Ramamurthy, V.; Eaton, D.; Caspar, J., Photochemical and Photophysical Studies of Organic Molecules Included Within Zeolites. *Acc. Chem. Res.* **1992**, *25*, 299-307.

(7) d'Agostino, S.; Grepioni, F.; Braga, D.; Ventura, B., Tipping the Balance with the Aid of Stoichiometry: Room Temperature Phosphorescence versus Fluorescence in Organic Cocrystals. *Cryst. Growth Des.* **2015**, *15*, 2039-2045.

(8) Turro, N. J.; Kavarnos, G. J.; Cole Jr, T.; Scribe, P.; Dalton, J. C., Molecular Photochemistry. XXXIX. External Heavy-Atom-Induced Spin-Obital Coupling. Spectroscopic Study of Naphthonorbornanes. *J. Am. Chem. Soc.* **1971**, *93*, 1032-1034.

(9) Seybold, P. G.; White, W., Room Temperature Phosphorescence Analysis. Use of the External Heavy-Atom Effect. *Anal. Chem.* **1975**, *47*, 1199-1200.

(10) Zeng, Y.; Biczok, L.; Linschitz, H., External Heavy Atom Induced Phosphorescence Emission of Fullerenes: the Energy of Triplet C60. *J. Phys. Chem.* **1992**, *96*, 5237-5239.

(11) Ramamurthy, V.; Caspar, J.; Eaton, D.; Kuo, E. W.; Corbin, D., Heavy-Atom-Induced Phosphorescence of Aromatics and Olefins Included Within Zeolites. *J. Am. Chem. Soc.* **1992**, *114*, 3882-3892.

(12) Vo-Dinh, T.; Hooyman, J., Selective Heavy-Atom Perturbation for Analysis of Complex Mixtures by Room-Temperature Phosphorimetry. *Anal. Chem.* **1979**, *51*, 1915-1921.

(13) Zhang, D.; Duan, L.; Zhang, Y.; Cai, M.; Zhang, D.; Qiu, Y., Highly Efficient Hybrid Warm White Organic Light-Emitting Diodes Using a Blue Thermally Activated Delayed Fluorescence Emitter: Exploiting the External Heavy-Atom Effect. *Light Sci. Appl.* **2015**, *4*, e232.

(14) Yuan, W. Z.; Shen, X. Y.; Zhao, H.; Lam, J. W. Y.; Tang, L.; Lu, P.; Wang, C.; Liu, Y.; Wang, Z.; Zheng, Q. et al., Crystallization-Induced Phosphorescence of Pure Organic Luminogens at Room Temperature. *J. Phys. Chem. C* **2010**, *114*, 6090-6099.

(15) Yang, Z.; Mao, Z.; Zhang, X.; Ou, D.; Mu, Y.; Zhang, Y.; Zhao, C.; Liu, S.; Chi, Z.; Xu, J.; et al., Intermolecular Electronic Coupling of Organic Units for Efficient Persistent Room-Temperature Phosphorescence. *Angew. Chem. Int. Ed.* **2016**, *55*, 2181-2185.

(16) Chandra, A. K.; Turro, N. J.; Lyons, A. L.; Stone, P., The Intramolecular External Heavy Atom Effect in Bromo-, Benzo-, and Naphthonorbornenes. *J. Am. Chem. Soc.* **1978**, *100*, 4964-4968.

(17) Zhang, G.; Chen, J.; Payne, S. J.; Kooi, S. E.; Demas, J. N.; Fraser, C. L., Multi-Emissive Difluoroboron Dibenzoylmethane Polylactide Exhibiting Intense Fluorescence and Oxygen-Sensitive Room-Temperature Phosphorescence. *J. Am. Chem. Soc.* **2007**, *129*, 8942-8943.

(18) Zhang, G.; Palmer, G. M.; Dewhirst, M. W.; Fraser, C. L., A Dual-Emissive-Materials Design Concept Enables Tumour Hypoxia Imaging. *Nat. Mat.* **2009**, *8*, 747-751.

(19) Loiseau, F.; Campagna, S.; Hameurlaine, A.; Dehaen, W., Dendrimers Made of Porphyrin Cores and Carbazole Chromophores as Peripheral Units. Absorption Spectra, Luminescence Properties, and Oxidation Behavior. *J. Am. Chem. Soc.* **2005**, *127*, 11352-11363.

(20) Yang, Z.; Chi, Z.; Yu, T.; Zhang, X.; Chen, M.; Xu, B.; Liu, S.; Zhang, Y.; Xu, J., Triphenylethylene Carbazole Derivatives as a New Class of AIE Materials with Strong Blue Light Emission and High Glass Transition Temperature. *J. Mater. Chem.* **2009**, *19*, 5541-5546.

(21) Kosower, E. M.; Skorcz, J. A.; Schwarz Jr, W. M.; Patton, J. W., Pyridinium Complexes. I. the Significance of the Second Charge-Transfer Band of Pyridinium Iodides. *J. Am. Chem. Soc.* **1960**, *82*, 2188-2191.

(22) Slater, J. C., Atomic Radii in Crystals. J. Chem. Phys. 1964, 41, 3199-3204.

(23) Tomasi, J.; Mennucci, B.; Cammi, R., Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* **2005**, *105*, 2999-3094.

(24) Chai, J.-D.; Head-Gordon, M., Long-Range Corrected Hybrid Density Functionals with Damped Atom–Atom Dispersion Corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.

(25) Pan, B.; Wang, B.; Wang, Y.; Xu, P.; Wang, L.; Chen, J.; Ma, D., A Simple Carbazole-N-Benzimidazole Bipolar Host Material for Highly Efficient Blue and Single Layer White Phosphorescent Organic Light-emitting Diodes. *J. Mater. Chem. C* **2014**, *2*, 2466-2469.

