Suppression of Bimolecular Interactions via Bulky Blocking Groups in Tetradentate Pt(II) Complex for Efficient Organic Light-Emitting Diodes

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Abstract

Management of bimolecular interactions such as triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA) is crucial to reduce exciton loss for achieving high efficiency. Among several strategies, one approach is to use bulky blocking groups to increase the intermolecular distance. In this work, we investigated the correlation between the volume of blocking groups and bimolecular interactions in Pt complexes. It was found that the bulkiness of substituents is pivotal for maximizing quantum efficiency in these devices. An exciton dynamics study conducted during device operation quantitatively analyzed the contribution of substituents to the operational mechanism of device, demonstrating that complexes with bulky 2,6-diisopropylphenyl and tert-butyl substituents enhance exciton harvesting by suppressing TTA and TPA, thereby facilitating Förster energy transfer from Pt complexes to fluorescent dopant.

Author Keywords

organic light-emitting diodes; Pt complex; blocking group; bimolecular interaction; high efficiency

1. Objective and Background

The efficiency of organic light-emitting diodes (OLEDs) has been significantly enhanced by harvesting triplet excitons for light emission. One of the well-known methods is the use of heavy metal complexes that provide high radiative triplet decay rate by strong spin-orbit coupling (SOC) due to the heavy-atom effect. Therefore, commercial products are currently using red and green phosphorescent to meet the growing demand for highly efficient OLEDs.

The OLEDs based on metal complexes have demonstrated high efficiency and long lifetime.(1) In terms of Pt(II) complexes, it generally shows narrow emission spectrum favorable to color purity compared to Ir(III) complexes. However, intrinsic planar geometry of Pt(II) complexes reduces the intermolecular distance, leading to bimolecular interactions such as triplet-triplet annihilation (TTA) and triplet-polaron annihilation (TPA).

The triplet-involved processes degrade the electroluminescence (EL) efficiency and device operational stability because of exciton quenching and molecular dissociation. To reduce the bimolecular interactions as well as in Pt(II) complexes, numerous research groups have tried to prevent these issues by increasing the distance between molecules via introduction of bulky blocking groups.(2)

Herein, to investigate the relationship between bimolecular interactions and bulky blocking groups in phosphorescence, we selected three Pt(II) complexes, namely, platinum(II) [6-(1,3-dihydro-3-(3,5-di-*tert*-butylphenyl)−2*H*-imidazol-2-ylidene-*κ*C2)−1,2-phenylene-*κ*C1]-oxy[9-(4-*tert*-butylpyridin-2-yl-*κ*N) carbazole-1,2-diyl-*κ*C1] (Pt-1), platinum(II) [6-(1,3-dihydro-3-(3,5-di-*tert*-butylphenyl)−2*H*-imidazol-2-ylidene-*κ*C2)−1,2-phenylene-*κ*C1]-oxy[9-(4-*tert*-butylpyridin-2-yl-*κ*N)−6-*tert*-butylcarbazole-1,2-diyl-*κ*C1] (Pt-2), and platinum(II) [6-(1,3-dihydro-3-(3,5-di-*tert*-butylphenyl)−2*H*-imidazol-2-ylidene-*κ*C2)−1,2-phenylene-*κ*C1]-oxy[9-(4-*tert*-butylpyridin-2-yl-*κ*N)−6-(2,6-diisopropylphenyl)carbazole-1,2-diyl-*κ*C1] (Pt-3), with identical skeleton and varying ligand volumes due to various blocking groups.(3) In this study, a device structure was constructed using the phosphorescent materials as the host to minimize processes irrelevant to the bimolecular interactions.(4) Our studies demonstrated that bimolecular interaction processes were significantly mitigated by incorporating bulky blocking groups in Pt(II) complexes, leading to a 51% enhancement in maximum external quantum efficiency (EQE) compared to control device. In addition, quantitative analysis indicated that the rate coefficients of TTA and TPA in these complexes reduced by up to 59-fold and 3.5-fold, respectively, through rational ligand engineering.

2. Results and discussion

Figure 1(a) illustrates the molecular structures of Pt complexes and fluorescent dopant. We picked out the N9,N9,N10,N10-tetrakis(4-(2-phenylpropan-2-yl)phenyl)anthracene-9,10-diamine (PhtBuPAD) as a fluorescent dopant to minimize orbital overlap with adjacent molecules by its substantial aliphatic substituents of 2-phenylpropan-2-yl.(5) In terms of Pt-2 and Pt-3, *tert*-butyl and 2,6-diisopropylphenyl substituents were attached to the 3 position of carbazole embedded in the *N*-heterocyclic carbene based ligand, respectively. The distribution of frontier orbitals indicated that the molecular orbitals are confined to the main core, suggesting that the blocking groups influence the molecular geometry rather than the electronic characteristics.(3) In terms of energy transfer, excitons were generated by recombination of injected charges in Pt complex host. Subsequently, singlet excitons undergo rapid intersystem crossing to form triplet excitons, which then participate in the Förster energy transfer (FET) driven by effective SOC as shown in **Figure 1(b)**.

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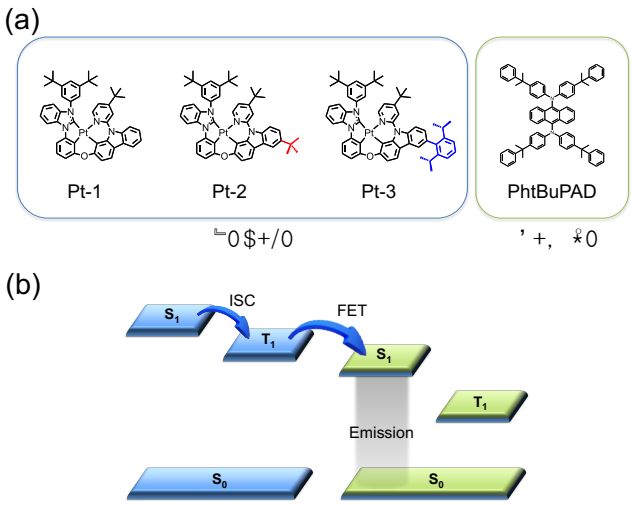

Figure 1. (a) Molecular structures of Pt complexes and fluorescent dopant. (b) Emission mechanism in Pt host.

To examine the effect of volume of blocking groups to EL properties, we fabricated devices doped with fluorescent dopant at 1 wt% as shown in **Figure 2(a)**. In current density (J)-voltage (V)-luminance (L) characteristics, all devices exhibited a low turn-on voltage of 2.5 V, corresponding to a luminance of 1 cd m^{-2}, via efficient charge injection. **Figure 2(b)** depicts EQE characteristics of devices. Maximum EQE (EQE_{max}) values were 8.3%, 10.5%, and 12.6% for Pt-1, Pt-2, and Pt-3 based devices, respectively. The enhanced EQE_{max} in the Pt-3 based device could be attributed to the suppressed bimolecular interactions facilitated by the bulky substituent in the Pt complex. All EL properties of devices are summarized in **Table 1**.

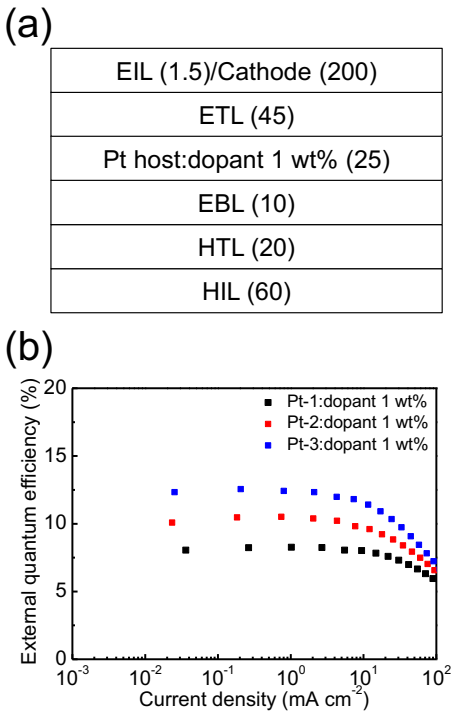

Figure 2. (a) Device structure. (b) EQE-J characteristics.

Table 1. Summarized EL properties.

Device	V_{on}	V_d	$\lambda_{emission}$	EQE_{max}
Pt-1:dopant 1 wt%	2.5 V	5.5 V	526 nm	8.3%
Pt-2:dopant 1 wt%	2.5 V	5.6 V	521 nm	10.5%
Pt-3:dopant 1 wt%	2.5 V	5.7 V	522 nm	12.6%

To quantitatively elucidate the impact of bulky blocking units to bimolecular interactions, we conducted transient EL (TREL) measurements and numerical modeling. While performing numerical fitting under EL conditions, the following equations were used:

$$\frac{dN(t)}{dt} = \frac{J}{ed} - \gamma N(t)^2 \qquad (2)$$

$$\frac{dT(t)}{dt} = \gamma N(t)^2 - (k_r + k_{nr} + k_{FET})T(t) - k_{TP}N(t)T(t) - \frac{1}{2}k_{TT}T(t)^2 \qquad (3)$$

where J, e, d, γ, and N(t) denote the current density, elementary charge, recombination zone width assumed as EML thickness, recombination coefficient, and polaron density over time, respectively. k_{TT}, k_{TP}, and k_{FET} represent rate coefficients of TTA, TPA, and FRET, respectively. In the TREL numerical fitting, γ, k_{TT}, and k_{TP} served as fitting parameters to assess the impact of bulky blocking units under EL conditions where polarons exist. The results of the TREL numerical fitting are summarized in **Table 2**.

Table 2. Parameter values determined by TREL fitting.

Device	γ	k_{TP}	k_{TT}
Pt-1:dopant 1 wt%	11.1×10^{-10} $cm^3\ s^{-1}$	46.2×10^{-13} $cm^3\ s^{-1}$	13.7×10^{-10} $cm^3\ s^{-1}$
Pt-2:dopant 1 wt%	9.81×10^{-10} $cm^3\ s^{-1}$	5.72×10^{-13} $cm^3\ s^{-1}$	5.81×10^{-9} $cm^3\ s^{-1}$
Pt-3:dopant 1 wt%	6.67×10^{-10} $cm^3\ s^{-1}$	0.78×10^{-13} $cm^3\ s^{-1}$	3.91×10^{-9} $cm^3\ s^{-1}$

Based on the TREL numerical fitting results, the plots of the fitted rate coefficients of TTA and TPA are exhibited in **Figure 3(a)**. Both rate coefficients of bimolecular interactions gradually decreased with the introduction of bulky blocking groups. For Pt-3 based device, the TTA and TPA rate coefficients were reduced by 59-fold and 3.5-fold relative to those of the Pt-1 based device, and by 7-fold and 1.5-fold compared to Pt-2 based device, respectively. The Pt-3 based device exhibited a reduction in bimolecular interactions, which could be attributed to the increased intermolecular distance facilitated by the bulky blocking units.

Figure 3(b) shows a comparison of the contributions of TPA and FET to triplet exciton consumption in the Pt host. The ratios of triplet exciton consumption by FET were 20.5% for Pt-1, 26.9% for Pt-2, and 30.5% for Pt-3 based devices. Moreover, the rates of triplet exciton consumption by FET were 1.17×10^{22} $cm^{-3}\ s^{-1}$ for Pt-1, 1.47×10^{22} $cm^{-3}\ s^{-1}$ for Pt-2, and 1.66×10^{22} $cm^{-3}\ s^{-1}$ for Pt-3 based devices. The Pt-3 based device exhibited the highest triplet exciton consumption ratio and rate by FET, indicating that minimizing triplet exciton quenching is crucial for effective triplet exciton harvesting in FET.

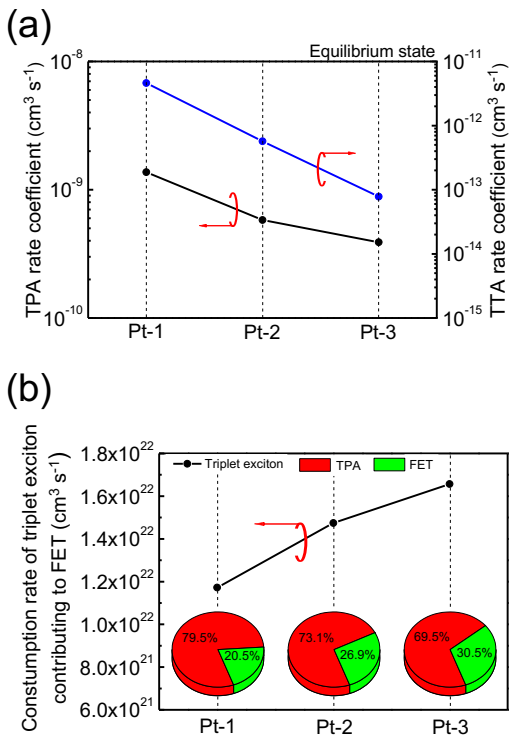

Figure 3. (a) Comparison of rate coefficients of bimolecular interactions determined by TREL numerical fitting. (b) Consumption ratios of triplet excitons for FET and TPA, alongside the consumption rate of triplet exciton contribution to FET.

3. Impact of Research

We studied the impact of bulky blocking groups in Pt complexes through exciton dynamics. It was demonstrated that bulky blocking units effectively suppressed the bimolecular interactions by increasing the distance between molecules. Consequently, Pt-3 based device exhibited a high EQE_{max} of 12.6%, benefiting from the attachment of bulky 2,6-diisopropylphenyl and *tert*-butyl units. The bulky blocking groups enhanced triplet exciton preservation by mitigating triplet-involved collision processes prior to their harvesting through FET, thereby increasing the number of triplet excitons available for luminescence and improving EL performance.

4. References

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