Phosphorescent Sensitizer Design for DET Suppression and Energy Transfer Analysis

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Abstract

Phosphor-sensitized fluorescence (PSF) is a well-established approach for optimizing the efficiency, lifetime, and color purity of organic light-emitting diodes (OLEDs). To fully utilize PSF system, it is crucial to suppress Dexter energy transfer (DET) and quantify its occurrence. In this study, we synthesized a novel platinum complex, Pt-BPS, incorporating bulky functional groups to PtON7-dtb reference molecule to minimize DET. We also developed an integrated energy transfer model to accurately quantify the rate constants of Förster resonance energy transfer (FRET) and DET using Monte Carlo simulations. Based on these findings, we fabricated PSF OLED devices using PtON7-dtb and Pt-BPS and the Pt-BPS-based PSF OLEDs demonstrated a significantly improved maximum external quantum efficiency (EQE_{max}) compared to PtON7-dtb PSF OLEDs. This research provides key insights into the design strategy of phosphor sensitizer for DET suppression in PSF systems, offering a deeper understanding of FRET and DET rate constants through an integrated energy transfer model.

Keywords

Phosphor-sensitized fluorescence; Organic light-emitting diodes; Dexter energy transfer; Förster resonance energy transfer; Monte Carlo simulation

1. Objective and Background

In an electrically-driven organic light emitting diodes (OLEDs), 25% singlet excitons and 75% triplet excitons are generated.(1) Since triplet excitons are forbidden transitions, their efficient utilization is essential for enhancing OLED performances such as efficiency and lifetime. Phosphor-sensitized fluorescence (PSF) is a promising approach that optimizes efficiency, lifetime, and color purity by harvesting triplet excitons through a phosphorescent sensitizer (PS).(2) This system ensures high device efficiencies by facile excitons consumption through Förster resonance energy transfer (FRET) from the PS to the terminal dopant (TD).(3) However, in PSF system, while FRET generates radiative singlet excitons in the TD, Dexter energy transfer (DET) leads to non-radiative triplet excitons, resulting in efficiency loss and device degradation.(4) Therefore, suppressing DET is critical, but to date, quantifying the extent of DET has been challenging. This difficulty arises from the shared triplet exciton decay pathways of FRET and DET, making it impossible to distinguish their respective rate constants (k_{FRET} and k_{DET}) by multiple solution problem. Furthermore, the DET process in PSF systems is not well understood, complicating the selection of PS materials that can effectively suppress DET.

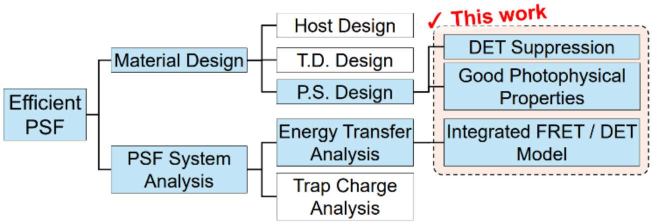

Figure 1. Schematic diagram of essential in achieving efficient PSF and the achievement of this paper.

In this study, we successfully suppressed DET by designing a novel PS molecule. We synthesized a platinum complex, Pt-B-PS, incorporating an electronically inert bulky group to effectively minimize DET to the TD. Additionally, for the first time, we established an integrated energy transfer model capable of precisely quantifying k_{FRET} and k_{DET} using distance correlated novel equations. Based on these findings, we fabricated PSF OLED devices using both Pt-BPS and the reference material PtON7-dtb as PS. The Pt-BPS-based device demonstrated improved maximum external quantum efficiency (EQE_{max}) of 12.7%, while PtON7-dtb PSF OLEDs showed 11.8%, by effectively suppressing DET, as validated by the proposed model through a significant reduction in the k_{DET}.

2. Results

2.1 Perfect-Fit Blue phosphor sensitizer design

In designing efficient PSF devices, a key strategy is selecting a PS that effectively form singlet exciton in TD via facile FRET process while suppressing triplet exciton formation to minimize DET process. Therefore, the need for designing PS with good photophysical properties (i.e. high photoluminescence quantum yield (PLQY), high k_r) along with electronically inert bulky

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functional group for isolating the DET process is demanding. We selected PtON7-dtb as a reference PS due to its good photophysical properties, but its lack of bulky structure increased DET.(5) As shown in Figure 2, to address this, we designed Pt-BPS by incorporating electronically inert bulky functional groups.

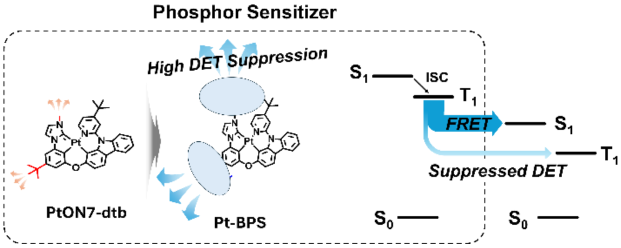


Figure 2. Molecular structure of PtON7-dtb and Pt-BPS and schematic diagram of suppressing DET in PSF device.

We successfully synthesized Pt-BPS and after thorough purification, we evaluated the intrinsic photophysical properties of PtON7-dtb and Pt-BPS at 77K in methylene chloride. Due to the adoption of electron-donating alkyl based bulky group, a slight red shifted λ_{MAX} of 447 nm in Pt-BPS is observed while that of PtON7-dtb was 445 nm. However, due to the strengthened rigidity in Pt-BPS, the full-width at half maximum (FWHM) decreased to 18.7 nm compared to that of 23.1 nm in PtON7-dtb by lowering the rotational freedom.(6) We measured PLQY and k_r by fabricating 20 wt% doped films. PtON7-dtb and Pt-BPS showed high PLQY of 100% and 95.6%, respectively. Pt-BPS demonstrated a high radiative rate constant (k_r) of 2.52 x 10^5 s^{-1} without compromising PLQY. This was attributed by careful control of metal-to-ligand charge transfer (MLCT) character by inducing deep lowest-unoccupied molecular orbital energy in Pt-BPS.(7) The good photophysical properties of Pt-BPS along with bulky functional groups are expected to yield good EL properties in PSF OLED.

Table 1. Photophysical properties of PtON7-dtb and Pt-BPS

	λ_{MAX}[a] / FWHM (nm)	T_1[a] (eV)	PLQY[b] (%)	k_r[b] (× 10^5 s^{-1})
PtON7-dtb	445 / 18.7	2.79	100	2.09
Pt-BPS	447 / 23.1	2.77	95.6	2.52

[a] Data measured at 77 K in methylene chloride.
[b] Data measured at 20 wt% doped in 3-CzPB host matrix.

2.2 Integrated Energy Transfer Model : Rational Quantification of FRET & DET

The precise quantification of k_{FRET} and k_{DET} is crucial for advanced PSF systems. However, quantifying the k_{DET} is challenging due to the arbitrary decay processes of FRET and DET resulting in multi-solution problem. To address the multi-solution problem in conventional energy transfer modeling, we developed an integrated model by focusing on common variables, distance (R), shared by both FRET and DET processes. As shown in *equations (1)* and *(2)*, both FRET and DET rate constants are influenced by R, stating both processes occur frequently at close range. (8, 9) τ_{rad}, R_0, K, J and L denote the radiative decay lifetime, FRET efficiency at 50%, experimental factor, spectral overlap, and van der Waals radius, respectively, and these factors are independent of distance and fixed for each PS. The Van der Waals radius was calculated through gaussian dimer state optimization. Therefore, k_{FRET} and k_{DET} can be divided into distance independent factor and distance related factor, respectively.

$$k_{FRET} = \frac{1}{\tau_{rad}}\left(\frac{R_0}{R}\right)^6 \cdots\cdots\cdots\cdots\cdots\cdots \ (1)$$

$$k_{DET} = KJe^{-\left(\frac{L}{2}\right)R} \cdots\cdots\cdots\cdots\cdots\cdots \ (2)$$

As a TD, we selected 2,5,8,11-tetra-tert-butylperylene (TBPe) for its good spectral overlap with Pt complexes and high PLQY. Using Monte Carlo simulations, we randomly distributed PS and TD in a cubic volume of 10^5 nm^3 and calculated the precise distances between PS and TD for varying TD concentration systems. (0.75, 1, 1.25, and 1.5 wt%) with 20% PS. For each TD doping concentration system, the ratios for $k_{FRET,x\%}$ and $k_{DET,x\%}$ were established based on $k_{FRET,0.75\%}$ and $k_{DET,0.75\%}$ accounting the distance related factor.

To access the experimental value for $k_{decay,x\%}$ we fabricated PSF films with 20% PS and varying TD concentrations (0.75, 1, 1.25, and 1.5 wt%) and measured time-resolved photoluminescence. The data was fitted accounting for exciton decay profiles with *equation (3)* and $k_{decay,x\%}$ ($k_{FRET,x\%}$ + $k_{DET,x\%}$) values were extracted for each film.

$$\frac{dT}{dt} = -T_{P.S.}\left(k_r + k_{decay,x\%}\right) - 0.5k_{TTA,x\%}T_{P.S.}^2 \qquad (3)$$

The $k_{FRET,x\%}$ and $k_{DET,x\%}$ were then fitted with the related ratios. The overall workflow is shown in **Figure 3 (a)** and the fitted values are depicted in **Figure 3 (b)**. The fitted values for k_{FRET} and k_{DET} are summarized in **Table 2**. For 20% PS with 1% TD, the fitted $k_{FRET,1\%}$ and $k_{DET,1\%}$ values for PtON7-dtb were 2.57 x 10^6 and 6.55 x 10^5 s^{-1}, respectively, while Pt-BPS exhibited similar $k_{FRET,1\%}$, 2.52 x 10^6 s^{-1} but a significantly lower $k_{DET,1\%}$, 1.77 x 10^5 s^{-1}. The results confirmed that Pt-BPS effectively reduced DET by incorporating bulky functional groups, increasing the physical distance from the TD. Incorporating the concept of distance, we well-organized the integrated energy transfer model which can rationalize k_{FRET} and k_{DET} solving multiple-solution problem.

Table 2. Summarized device datas of PtON7-dtb and Pt-BPS

	$k_{FRET,0.75\%}$ / $k_{DET,0.75\%}$ (× 10^5 s^{-1})	$k_{FRET,1\%}$ / $k_{DET,1\%}$ (× 10^5 s^{-1})	$k_{FRET,1.25\%}$ / $k_{DET,1.25\%}$ (× 10^5 s^{-1})	$k_{FRET,1.5\%}$ / $k_{DET,1.5\%}$ (× 10^5 s^{-1})
PtON7-dtb	16.3 / 6.1	25.5 / 6.9	43.0 / 8.0	58.3 / 8.7
Pt-BPS	15.9 / 1.6	25.2 / 1.8	42.7 / 2.1	56.7 / 2.2

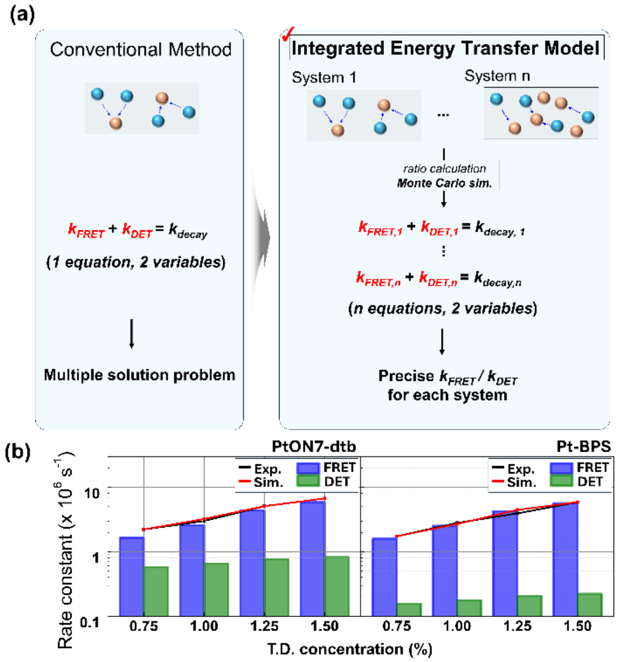
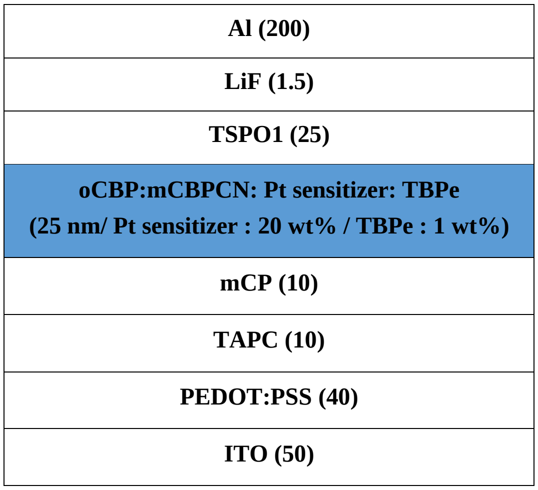


Figure 3. (a) The overall flow of integrated energy transfer model. (b) Fitted k_{FRET} and k_{DET} in PtON7-dtb and Pt-BPS.

Based on these findings, we fabricated PSF OLEDs with 20% PS and 1% TD for both PtON7-dtb and Pt-BPS in oCBP: mCBPCN host matrix. The device structure is shown in Figure 4. The detailed device structure is indium tin oxide (ITO, 50 nm)/ poly(3,4 ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, 40 nm)/ 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC, 10 nm)/ 1,3-bis(N-carbazolyl)benzene (mCP, 10 nm)/ oCBP: mCBP-CN: Pt sensitizer: TBPe (25 nm:40 wt%:20 wt%: 1 wt%)/ diphenyl 4-triphenylsilylphenyl-phosphine oxide (TSPO1, 25 nm)/ LiF (1.5 nm)/Al (200 nm).



Al (200)

LiF (1.5)

TSPO1 (25)

oCBP:mCBPCN: Pt sensitizer: TBPe
(25 nm/ Pt sensitizer : 20 wt% / TBPe : 1 wt%)

mCP (10)

TAPC (10)

PEDOT:PSS (40)

ITO (50)

Figure 4. Device structure of PSF device of PtON7-dtb and Pt-BPS.

The measured device data are summarized in **Table 3**. The measured current density-voltage-luminance, EQE-luminance and EL emission spectra are shown in Figure 5. The PSF device with PtON7-dtb and Pt-BPS showed EQE$_{max}$ of 11.8% and 12.7%, respectively. The suppression of DET by Pt-BPS by approximately one-third compared to PtON7-dtb led to better overall device performance.

Table 3. Summarized device datas of PtON7-dtb and Pt-BPS

	EQE[a] (%)	CE[a] (cd/A)	CIE (x, y)
PtON7-dtb PSF	11.8	16.2	(0.134, 0.170)
Pt-BPS PSF	12.7	17.7	(0.133, 0.173)

[a] Data measured at maximum value.

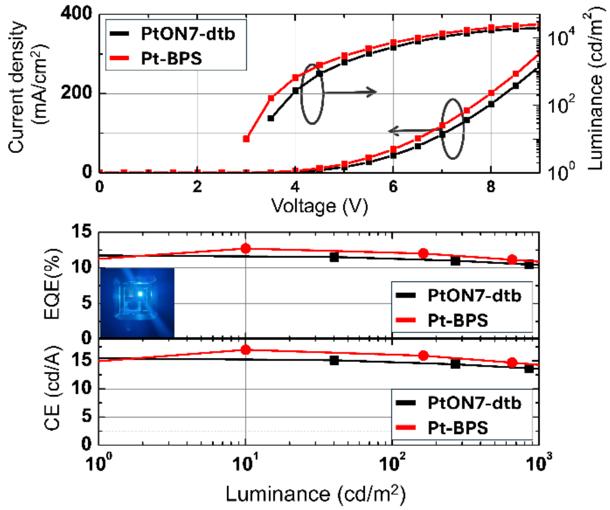


Figure 5. Measured J-V-L, EQE-luminance and current efficiency (CE)-luminance graphs of PtON7-dtb and Pt-BPS PSF devices.

3. Impact of Research

In this work, we successfully intrigued the suppression of DET in PSF OLED devices by designing a novel PS, Pt-BPS. Moreover, the k_{DET} is precisely quantified through integrated energy transfer model by focusing on common variable, R, which was impossible due to multi-solution problem. The quantified k_{DET} of Pt-BPS showed significantly lowered value compared to that of PtON7-dtb, which was benefited from the incorporation of bulky functional groups into the sensitizer. The Pt-BPS-based PSF device showed significant improvements in EQE compared to the PtON7-dtb-based device. Our findings highlight the importance of precisely quantifying k_{FRET} and k_{DET} for advancing PSF systems and demonstrate that the suppression of DET is key to enhancing overall OLED performance. This research provides a robust framework for future development of highly efficient PSF OLEDs.

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