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A Novel Bipolar Phosphorescent Host for Highly Efficient Deep-Red OLEDs at Wide Luminance Range of 1000-10000 cd m⁻²

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A novel phosphorescent host FPYPKA possessing the bipolar charge transporting ability realizes the most efficient deep-red PhOLED, which maintains very high-level EQEs of >23% at rather high and wide luminance range of 1000-10000 cd m⁻².

Phosphorescent organic light-emitting diodes (PhOLEDs) are considered the most promising technology for next generation flat panel display and/or solid-state lighting because of their merits of high energy efficiency, low power consumption and possible flexibility for large-scale ultrathin productions.¹ Among them, the deep-red electrophosphorescent emitting components that meet the standard of $\lambda_{\max}^{\text{EL}} \geq 610$ nm and the Commission Internationale de L'Eclairage (CIE_{x,y}) coordinates of $x \geq 0.65$ and $y \leq 0.35$, are very important in order to achieve highly efficient full-color and white OLEDs.² Although the deep-red PhOLEDs have been studied considerably, and the maximum external quantum efficiency (EQE) values of more than 20% were achieved, it is still a significant challenge to maintain such high efficiency at high-luminance level of 5000~10000 cd m⁻² that meets the requirement for solid-state lighting.³ Generally, the deep-red phosphors possessing relatively narrow energy gaps (E_g) between the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels, long life time and low triplet energy (T_1) level compared with the blue, green, yellow and orange cases, would cause noticeable differences between the organic fluorescent host molecules and the red phosphorescent dopant emitters in these optoelectronic properties above. Thus the resulting charge and exciton aggregation together with various nonradiative recombination would bring the unfavorable energy losses in the processes of both the created singlet and triplet excitons on the fluorescent host transferring to the triplets of red phosphorescent dopant, leading to the decline in the efficiency of red PhOLEDs at the high-luminance (corresponding to high-current) level. Hence, it is highly desirable to develop new-concept host-guest systems beyond the type of fluorescent host-phosphorescent guest for more efficient PhOLEDs. From this point of view, the phosphorescent iridium complexes with sufficient charge-transporting ability indeed have great potential as host materials, although research on this topic has been rather limited.⁴ Up until now, there is not a deep-red PhOLED that adopted the phosphor as the host has been reported.

In this work, we design and synthesize a novel class of heteroleptic Ir(III) complex (F₂ppy)₂Ir(dipcca) (FPYPKA)

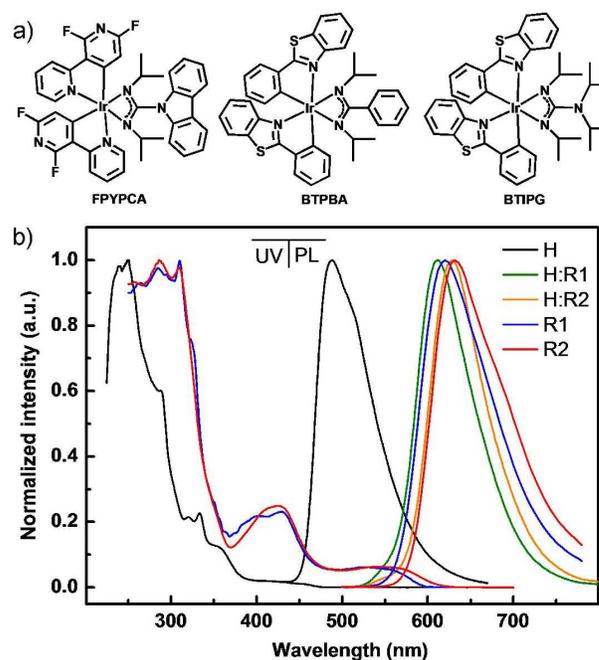


Fig. 1 a) Structural drawing of FPYPKA, BTPBA and BTIPG. b) UV-Vis absorption and PL spectra of FPYPKA (H), BTPBA (R1) and BTIPG (R2) in neat thin film, and PL spectra of BTPBA (R1) and BTIPG (R2) doped in FPYPKA (H) thin films with 10 wt% doping concentration.

bearing two cyclometalating 2',6'-difluoro-2,3'-bipyridyl (dfppy) chelates, which usually were used for building the complexes with large band gap and push the corresponding emission to shorter-wavelength region,⁵ and one ancillary ligand (dipcca) based on attaching electron donating carbazole substituent onto the N[^]N amidinate group (Fig. 1a).^{4c} This new complex is expected to have a high enough $T_1 \sim 2.5$ eV (phosphorescent emission of $\lambda_{\max} \sim 488$ nm) as a host to sensitize the emission of the red phosphors with the T_1 of less than 2.1 eV ($\lambda_{\max} > 600$ nm), while maintaining its inherent advantageous characteristics: narrow E_g as well as the comparable lifetime with the potential red dopant molecules. On the other hand, it is also important that FPYPKA possesses sufficient and balanced hole and electron mobilities ($\sim 10^{-3}$ cm² V⁻¹ s⁻¹). This ensures that both charge carrier species smoothly conduct by hopping between the adjacent FPYPKA molecules, leading to increased opportunity and broad zone for the hole/electron recombination. Series of new phosphor host-phosphor guest type (PPT) OLEDs were fabricated using FPYPKA as the host and two red phosphors of BTPBA and

BTIPG as the dopant. Due to the desirable bipolar property of host together with the excellent energy transfer in these PPT host-guest systems, the resulting PhOLEDs exhibited not only the deep-red electrophosphorescence with the CIE_{x,y} of (0.65,0.35)/(0.67,0.33), but very high EQEs of 26.3 and 22.8% coupled with rather high power efficiencies (PEs) of 18.8 and 11.4 lm/W respectively, at an illumination-relevant luminance of 1000 cd m⁻². Moreover, the high-level EQEs of >23 and 19% were retained at the extremely luminance of ~10000 cd m⁻². To our knowledge, these high efficiencies being realized at such high and wide luminance level, which is critical for the practical display and/or solid-state lighting, should be the best results for deep-red PhOLEDs with similar CIE coordinates.³

Three complexes FPYPCA, BTPBA and BTIPG were synthesized in high yields,^{4c,6} which exhibited good thermally stability (see the *Supporting Information-S.I.*), indicating the high morphologic stability of amorphous phase in their deposited films. Their UV/Vis absorption and photoluminescence (PL) spectra in the neat films and the doped films are shown in **Fig. 1b**. The apparent spectral overlap between the phosphorescence emission peak of FPYPCA ($\lambda=488$ nm) and the MLCT absorption band of BTPBA and BTIPG (480-570 nm), together with their triplet energy alignment: 2.5, 2.1 and 2.0 eV for T₁ of FPYPCA, BTPBA and BTIPG those estimated from the 0-0 band of their phosphorescence spectra respectively, suggested efficient triplet energy transfer from FPYPCA (host) to BTPBA and/or BTIPG (guest). This has been demonstrated in the PL spectra of doped FPYPCA: BTPBA and FPYPCA: BTIPG thin films with the concentration of 10 wt%, which show the emission only from BTPBA and BTIPG at λ_{\max} of ~610 and 630 nm with the quantum yields of 0.61±0.03 and 0.52±0.02, respectively. The phosphorescence lifetimes of FPYPCA, BTPBA and BTIPG in neat film were 0.15, 0.09 and 0.12 μ s (see **S-Fig. 4** in *S.I.*), respectively. Such short lifetime values are attributed to the high decay rates for the MLCT states of our phosphors. The more compact four-membered rings containing one Ir atom and N[^]N fragment of amidinate-based ancillary ligands led to the stronger involvement of the metal centre than those of the Ir complexes reported with other ancillary ligands, thus resulting in the larger spin-orbit coupling and consequently more efficient intersystem crossing from the singlet to triplet states in each complex.^{4b,c,7a} Moreover, such similar and short lifetimes are beneficial for decreasing the triplet exciton aggregation and reducing the roll-off in electroluminescent (EL) efficiency.^{7b,c}

Single crystal X-ray diffraction study on FPYPCA was executed to reveal the general structure of this complex. The molecule exhibits distorted octahedral geometries around the iridium center with the C,C-cis, N,N-trans chelate disposition (see **S-Fig. 5** in *S.I.*). Based on the molecule packing of FPYPCA, the theoretical simulation for the hopping transport model displayed the clear channels for conducting hole (red) and electron (blue) along with the respective stacking bedded columns as shown in **Fig. 2a**. In addition, from Marcus theory related to the mobility, two key parameters of reorganization

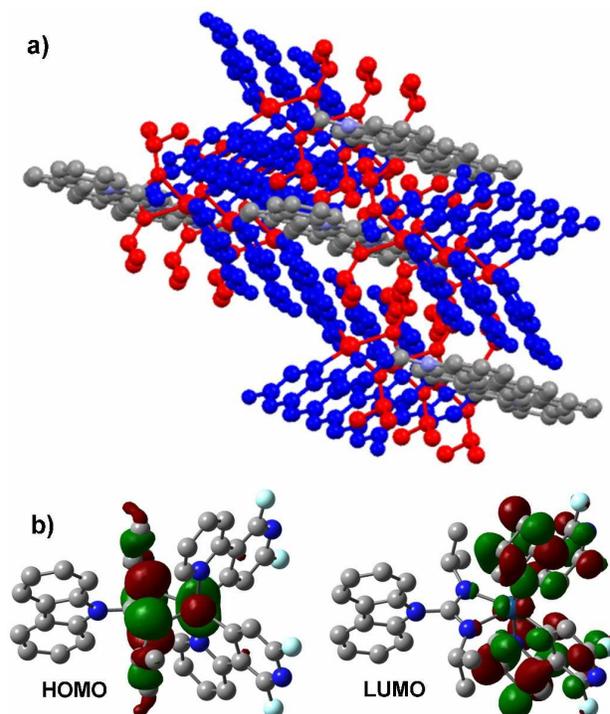


Fig. 2 a) Molecular packing diagram and transporting channel for holes (red) and electrons (blue) of FPYPCA. b) Contour plots of HOMO and LUMO in FPYPCA from DFT calculations.

reorganization energies are 0.28 and 0.23 eV, and electronic couplings are 2.34 and 7.14 meV for hole and electron, respectively. These results indicated that the FPYPCA solids should have well-balanced carrier-transporting abilities.⁸ On the other hand, the density functional theory (DFT) calculations gained more insight into the electronic structure of FPYPCA for supporting its bipolar nature. The HOMOs is mainly distributed on the *d*-orbitals of Ir atom and the N atoms of the ancillary ligand, while the LUMOs are largely located in the two main ligands (**Fig. 2b**). It is noticeably different from other d⁸ppy main ligand-based Ir(III) complexes reported,⁵ resulting from the introduction of our ancillary ligand (dipcca) that causes significant influence on the molecular orbitals of FPYPCA. This almost complete spatial separation of HOMO and LUMO energy levels of FPYPCA suggests that the HOMO-LUMO excitation would shift the electron density distribution from one side of the molecule as the donor to another side as the acceptor, leading to a polarized excited state. More importantly, such separated distributions of HOMO and LUMO can provides hole- and electron-transporting channel respectively, where both types of charges can realize intermolecular hopping smoothly along their respective pathways.^{4c,6c,9} Furthermore, the above hypothesis was strongly supported experimentally by Time-of-flight (TOF) technique (see **S-Fig. 6** in *S.I.*), which revealed the comparable hole and electron mobilities of 1.9×10^{-3} and 2.5×10^{-3} cm² V⁻¹ s⁻¹ respectively for FPYPCA. They are rather high levels for a phosphorescent emitter, even are similar to or much higher than those of the typical charge transport materials including NPB ($\sim 10^{-4}$ cm² V⁻¹ s⁻¹) and TPBi ($\sim 10^{-5}$ cm² V⁻¹ s⁻¹).¹⁰ This provides a direct proof for FPYPCA possessing the desirable bipolar character, which is

expected to be a host that plays the important role for conducting both hole and electron.

The energy levels (HOMO/LUMO) of three complexes were determined using cyclic voltammetry (CV) datas and their absorption edges of the UV-vis spectra. As shown in Fig. 3a, the HOMO/LUMO levels of these phosphors are well matched with those of common charge transport materials: 4,4'-bis(N-(1-naphthyl)-N-phenylamino)biphenyl (NPB) for holes and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) for electrons, which will be used below. Thus the HOMO/LUMO levels of FPYPCA are more suitable for both hole and electron injecting into the EML compared with the fluorescent host material 4,4'-N,N'-dicarbazolylbiphenyl (CBP).

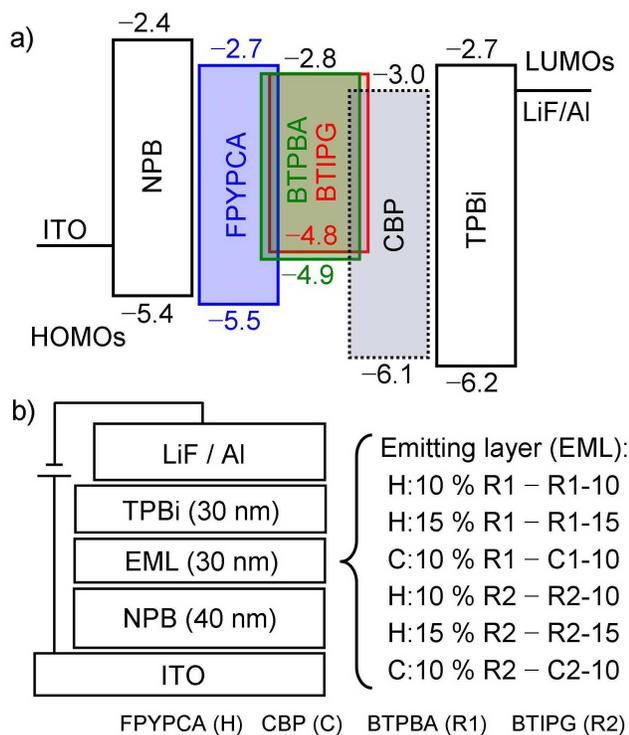


Fig. 3 a) Proposed energy diagram of the materials used in OLEDs. b) Schematic diagram of EL device configurations.

To explore the EL performance of the phosphor-phosphor type (PPT) OLEDs those employing FPYPCA as host, four devices were fabricated with the same configuration of [ITO/NPB (40 nm)/emitting layer (30 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al]. In each device, NPB served as the hole-transport layer (HTL) and TPBi as the electron-transport layer (ETL), with ITO (indium-tin oxide) anode and LiF/Al cathode. The devices using doped FPYPCA: BTPBA or FPYPCA: BTIPG (10 and 15wt%) films as the EMLs, which are denoted as R1-10, R1-15, R2-10 and R2-15, respectively. For comparison, two devices (C1-10 and C2-10) with the same configurations as the devices R1-10 and R2-10, respectively, were fabricated by using CBP as the host instead of FPYPCA. All the devices showed stable EL emission within the whole range of driving voltages, and no host emission is observed in the EL spectra. Deep-red EL with $\lambda_{\text{max}}^{\text{EL}}$ of 620-630 nm and the similar CIE coordinates of $x \geq 0.65$ and $y \leq 0.35$ of four PPT devices at a

luminance of 5000 cd m^{-2} were exhibited in Fig. 4a, where a photograph of R1-15 showed the well color purity intuitively.

Table 1. EL data of all the devices.

Device	$V_{\text{turn-on}}^a$ (V)	$L_{\text{max}}/\text{cd m}^{-2}$ (V at L_{max})	$PE^b/\text{lm W}^{-1}$	$EQE^b/\%$	$EL \lambda_{\text{max}}^c/\text{nm}$, CIE (x,y) ^c
R1-10	2.6	25970 (11.0)	23.3/17.1/9.0	24.8/24.6/19.7	620, (0.65, 0.35)
R1-15	2.6	29040 (11.0)	26.3/18.8/10.6	26.6/26.3/23.1	620, (0.65, 0.35)
C1-10	3.5	12190 (11.0)	20.6/8.4/2.5	13.0/9.3/4.4	612, (0.64, 0.36)
R2-10	2.6	20670 (11.0)	16.7/11.5/5.7	20.2/20.0/15.6	628, (0.66, 0.33)
R2-15	2.6	24530 (11.0)	15.1/11.4/6.3	23.0/22.8/19.1	632, (0.67, 0.33)
C2-10	3.5	9610 (11.0)	10.9/4.1/--	15.3/11.1/--	628, (0.66, 0.34)

^aRecorded at 1 cd m^{-2} . ^bIn the order of maximum, then values at 1000 and 10000 cd m^{-2} . ^cMeasured at 5000 cd m^{-2} .

The current density-voltage-luminance (J - V - L) and EL efficiency-luminance (PE/EQE- L) characteristics are shown in S-Fig. 7 (S.I.) and Fig. 4 respectively, and the EL data are summarized in Table 1. The turn-on voltages (V_{on} at 1 cd m^{-2}) of R1-10, R1-15, R2-10 and R2-15 are as low as 2.6 V, which are much lower than those of C1-10 and C2-10. Four PPT devices displayed the more rapidly increasing J - V and L - V curves after the onset than C1-10 and C2-10. Such ideal operating voltage in PPT devices can be partly attributed to the narrower energy gap (E_g) between the HOMO and LUMO of FPYPCA than that of CBP (Fig. 3a), which could lead to an enhanced charge injection into EMLs. Furthermore, desired EL efficiencies of our PPT devices, which are much higher than those of two reference CBP-based devices, have been realized on the base of high luminance values (Fig. 4b and Table 1). At the routinely practical luminance of 1000 cd m^{-2} , R1-10, R1-15, R2-10 and R2-15 show very high PE and EQE values of 17.1, 18.8, 11.5, 11.4 lm W^{-1} and 24.6, 26.3, 20.0, 22.8%, respectively. Moreover, the efficiency roll-off is low upon increasing the luminance and current density, where the respective EQE values as high as 19.7, 23.1, 15.6, 19.1% are maintained up to the extremely high luminance of $\sim 10000 \text{ cd m}^{-2}$, which is critical level for solid-state lighting.¹¹ To the best of our knowledge, these high efficiencies and remarkably low roll-off exceed any previously reported values for deep-red OLEDs with similar CIE coordinates.³ Such high and stable performance indicated that native triplet-triplet annihilation (TTA) processes, especially at high luminance levels, have been greatly reduced in these PPT devices, where bipolar FPYPCA molecules ensured the balanced and sufficient charge fluxes throughout the whole EMLs, effectively avoiding exciton/charge accumulation. Furthermore, the many inherent similarities between the host and guest molecules in the PPT doping systems such as the comparable energy levels, excited state lifetimes, and even the molecular morphologies, result in more efficient host-guest energy transfer than the doping cases with the fluorescent host CBP.⁴ These are the favorable factors for obtaining our highly efficient PPT OLEDs. Here, it is worth noting that R1-15/R2-15 showed noticeable EL efficiency enhancement compared to

R1-10/R2-10 respectively. This can be explained by that, in R1-15/R2-15 with the high doping concentration (15 wt%), the relatively high content of the guest molecules results in the more excitons formed on the dopant sites through direct charge recombination,^{6c,12} which is more efficient for the formation of excitons than host-guest energy transfer, because energy losses those exist in the host-guest energy transfer process can be avoided.

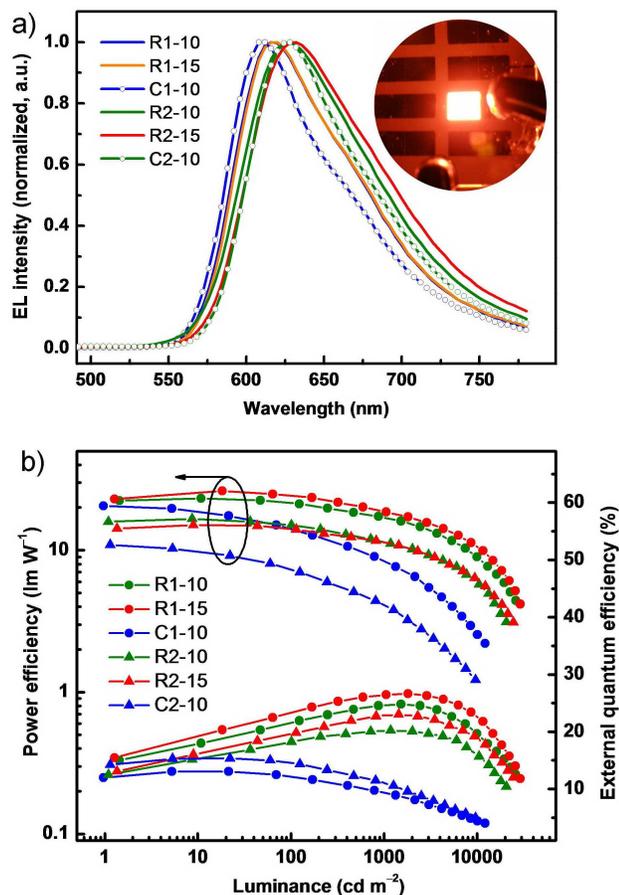


Fig. 4 a) EL spectra at the luminance of 5000 cd m^{-2} . Inset: photograph of R1-15 at the luminance of 5000 cd m^{-2} . b) Power efficiency-luminance-external quantum efficiency curves of all the PhOLEDs.

In summary, we demonstrated an effective molecular design strategy for a bipolar phosphorescent complex possessing narrow energy gap (E_g) coupled with high triplet energy (T_1), which is suitable as a host material for realizing efficient red PhOLEDs. These idealized phosphor-phosphor type (PPT) doped PhOLEDs exhibited stable deep-red emitting color and the constantly high EQE values of >23% at the rather high and wide luminance range of 1000-10000 cd m^{-2} . Such excellent EL performance demonstrated that designing a bipolar phosphor used as host, and then building the well-matched PPT emitting systems successfully, indeed have many advantages in terms of easily charge injecting, balanced charge fluxes and efficient host-guest energy transfer, compared with conventional emitting cases based on the fluorescent host such as CBP. Therefore, developing and employing the advanced multifunctional phosphorescent complexes as the hosts, is commonly believed to be an

effective way for realizing the exceptional-performance single-color PhOLEDs, even and the WOLEDs in future.

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Notes and references

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† Single crystals suitable for X-ray structural analysis were obtained by solvent diffusion (CCDC 1400002). For crystallographic data in CIF or other Electronic Supplementary Information (ESI) available: DOI: 10.1039/b000000x/

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