

# High Power Efficiency Solution-Processed Blue Phosphorescent Organic Light-Emitting Diodes Using Exciplex-Type Host with a Turn-on Voltage Approaching the Theoretical Limit

Xinxin Ban,<sup>†</sup> Kaiyong Sun,<sup>†</sup> Yueming Sun,<sup>\*,†</sup> Bin Huang,<sup>†</sup> Shanghui Ye,<sup>\*,‡</sup> Min Yang,<sup>‡</sup> and Wei Jiang<sup>\*,†</sup>

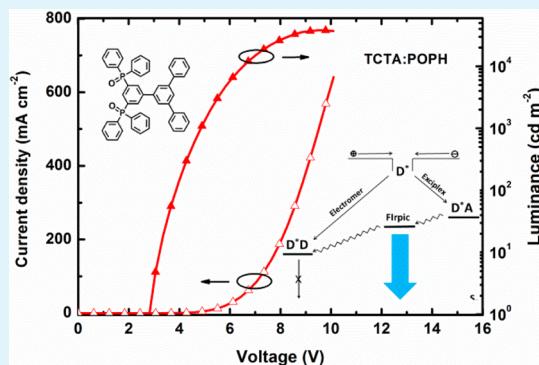
<sup>†</sup>School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu, P. R. China, 211189

<sup>‡</sup>National Synergistic Innovation Center for Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing, Jiangsu, P. R. China, 210023

## Supporting Information

**ABSTRACT:** Three solution-processable exciplex-type host materials were successfully designed and characterized by equal molar blending hole transporting molecules with a newly synthesized electron transporting material, which possesses high thermal stability and good film-forming ability through a spin-coating technique. The excited-state dynamics and the structure–property relationships were systematically investigated. By gradually deepening the highest occupied molecular orbital (HOMO) level of electron-donating components, the triplet energy of exciplex hosts were increased from 2.64 to 3.10 eV. Low temperature phosphorescence spectra demonstrated that the excessively high triplet energy of exciplex would induce a serious energy leakage from the complex state to the constituting molecule. Furthermore, the low energy electromer state, which only exists under the electro-excitation, was found as another possible channel for energy loss in exciplex-based phosphorescent organic light-emitting diodes (OLEDs). In particular, as quenching of the exciplex-state and the triplet exciton were largely eliminated, solution-processed blue phosphorescence OLEDs using the exciplex-type host achieved an extremely low turn-on voltage of 2.7 eV and record-high power efficiency of 22.5 lm W<sup>-1</sup>, which were among the highest values in the devices with identical structure.

**KEYWORDS:** exciplex, solution process, blue phosphorescence, turn-on voltage, power efficiency



## INTRODUCTION

Solution-processed organic light-emitting diodes (OLEDs) have attracted much scientific and industrial attention due to their promising applications to flexible displays and large area solid state lighting.<sup>1–4</sup> Although the use of the phosphorescent emitters has increased the internal quantum efficiency up to 100%, the excited states quenching induced by the triplet–triplet annihilation would extremely decrease the radiative decay of excitons.<sup>5–7</sup> Over the past decade, in order to enhance the performance of the solution-processed phosphorescent OLEDs (PHOLEDs), significant efforts have been made to develop suitable host materials to suppress triplet states quenching, balance charge transfer, and confine the excitons in the emitting layer (EML).<sup>8,9</sup>

Initial studies about the solution-processed PHOLEDs were focused on polymer-based hosts due to their high film density and low surface roughness, but the uncontrolled molecular weight and relatively poor purity of the polymeric materials made it difficult for them to be used in commercial active-matrix devices.<sup>10–17</sup> As an alternative, carbazole-based dendrimers were designed and used as universal solution-processable hosts for their exact molecular structures, tunable triplet energy, and high HOMO (highest occupied molecular

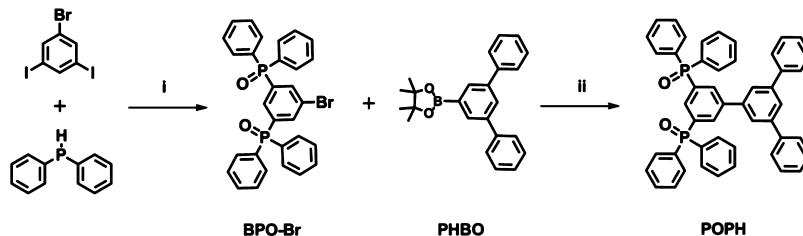
orbital) level.<sup>18–25</sup> After that, various solution-processable small molecular bipolar host materials were developed to balance the hole and electron in the emitting layer.<sup>26–33</sup> By doing so, the high performance and low efficiency roll-off of the red and green emitting PHOLEDs was successfully achieved. However, despite that the bipolar property facilitates charge transfer and broadens the recombination zone, a high operating voltage and a low power efficiency of solution-processed blue emitting PHOLEDs persisted.

Generally, the operating voltage of PHOLEDs is believed to be much higher than or equal to the energy gap ( $E_g$ ) of the host material, because electrical carrier injection takes place on the HOMO and LUMO (lowest unoccupied molecular orbital).<sup>34</sup> Thus, the small  $E_g$ , which corresponds to the excited singlet energy ( $E_s$ ), can lead to a lower operating voltage of the PHOLEDs. In addition, to design suitable hosts for confining exciton in the blue phosphorescent emitter, the triplet energy ( $E_T$ ) must be adequately high. As a result, the lower  $E_s$  and higher  $E_T$ , defined as the small  $\Delta E_{ST}$ , are essentially needed for

Received: July 16, 2015

Accepted: October 26, 2015

Published: October 26, 2015

Scheme 1. Synthetic Route of POPH<sup>a</sup>

<sup>a</sup>Conditions: (i)  $\text{Pd}(\text{OAc})_2$ ,  $\text{K}_3\text{PO}_4$ , toluene,  $\text{H}_2\text{O}_2$ ; (ii)  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{K}_2\text{CO}_3$ , 1,4-dioxane.

the design of effective hosts for devices with low operating voltage.<sup>35,36</sup> Xu and co-workers have developed a series of bipolar host materials with small  $\Delta E_{\text{ST}}$  by a ternary system to achieve a low driving voltage of 3.3 V in vacuum-deposition blue PHOLEDs.<sup>37</sup> However, the development of solution-processable bipolar hosts with small  $\Delta E_{\text{ST}}$ , especially for blue PHOLEDs, is extremely difficult due to many conflicts in molecular design. In addition to bipolar hosts, a new class of efficient small  $\Delta E_{\text{ST}}$  host material was recently demonstrated by Kim and co-workers through exciplex forming based on the intermolecular interaction between electron donor and electron acceptor molecules.<sup>38,39</sup> Similar to the bipolar host, an exciplex forming cohost exhibits a balanced charge transfer and a broad recombination zone. Furthermore, the exciplex host possesses an intrinsically small  $\Delta E_{\text{ST}}$  due to complete frontier orbital separation that is determined by the delocalized electron transfer from the LUMO of the acceptor to the HOMO of the donor. Using phosphorescence dopant as emitter and exciplex as host, Kido and co-workers reported the vacuum-deposition blue PHOLEDs with impressively high efficiencies and low operating voltages.<sup>40</sup> However, the exciplex-type mixed host structures developed for vacuum-deposition OLEDs may not be suitable for application in solution-processed OLEDs because of their undesirable film-forming ability concerning spin-coating. Furthermore, there has not been any report on using an exciplex host for the conventional solution-processed device architecture by far.

In this work, we have successfully used energy transferred from a suitable exciplex-type host to achieve high performance solution-processed blue PHOLEDs. Three exciplex hosts, TAPC:POPH, TCTA:POPH, and mCP:POPH, are designed by 1:1 molar ratio by mixing the common hole transporting materials, 1,1-bis[4-[*N,N*-di(*p*-tolyl)-amino]phenyl]-cyclohexane (TAPC), tris(4-carbazoyl-9-ylphenyl) amine (TCTA), and 1,3-di-9-carbazolylbenzene (mCP) with a newly synthesized electron-transporting molecule (*S*-Terphenyl-1,3-phenylene)bis(diphenylphosphine oxide) POPH, which possesses high thermal stability and good film-forming ability through the spin-coating technique. Particularly, by using energy transferred from the TCTA:POPH-based exciplex host, the solution-processed blue PHOLEDs demonstrated an extremely low turn-on voltage of 2.7 V, a high power efficiency of 22.5 lm W<sup>-1</sup>, and a very low efficiency roll-off, even with the luminance up to 10 000 cd m<sup>-2</sup>. To the best of our knowledge, this is the first time that the solution-processed device structure has ever been used to achieve the turn-on voltage of blue PHOLEDs below 3 V. In addition, the maximum luminance of 40 000 cd m<sup>-2</sup> and the small efficiency roll-off fully demonstrated a balanced charge transfer and an efficient exciton formation in such exciplex-type host material. More importantly, studies of the three exciplex-type host materials

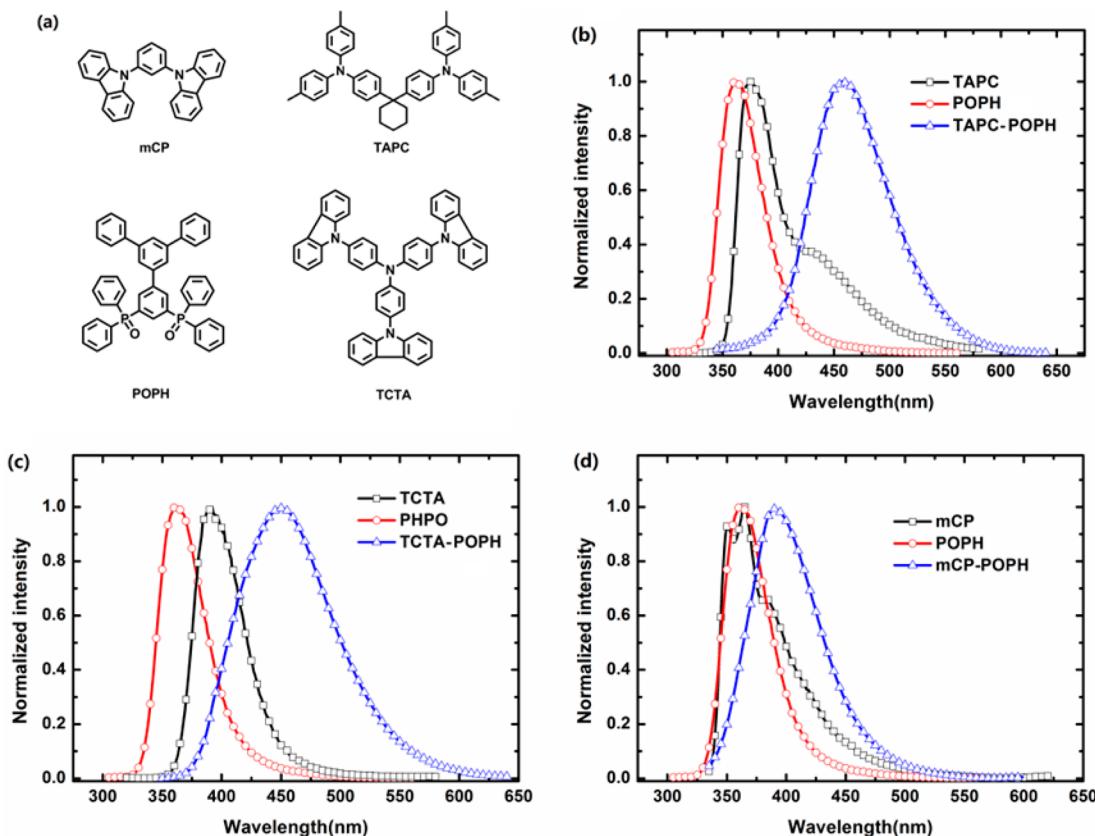
reveal that (a) given an exact acceptor molecule, the triplet energy of the exciplex host can be tunable by changing the HOMO level of the donor component; (b) the low energy electromer state in the exciplex-type host severely quenches the triplet excitons of FIrpic; (c) the exciplex and the electromer state will coexist and compete with each other in the local exciplex forming mechanism, and the ratio of the electromer emission can be extremely minimized by the rational choice of the constituent materials of the exciplex-type host.

## EXPERIMENTAL SECTION

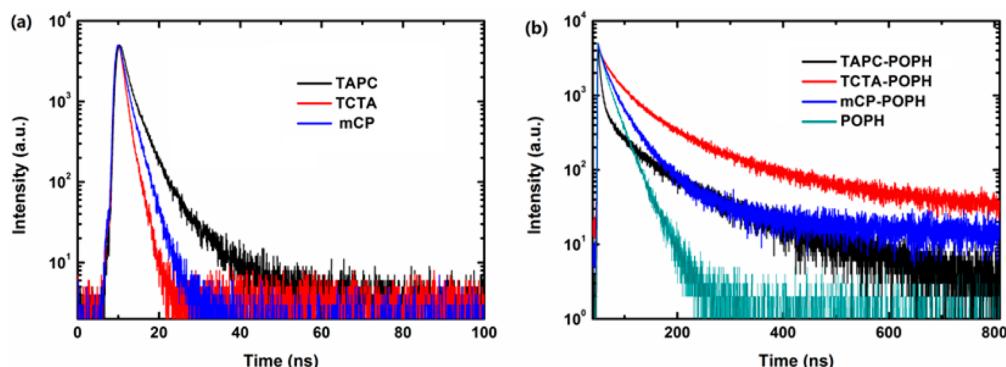
**General Information.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a BRUKER AMX 300-MHz instrument. Elemental analysis was determined by an Elementar Vario EL CHN elemental analyzer. Molecular masses were measured by a BRUKER DALTONICS Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS). The UV-vis absorption and photoluminescence emission spectra of the compounds were, respectively, measured by SHIMADZU UV-2450 and HORIBA FLUOROMAX-4. Phosphorescence spectra were measured at 77 K with a delayed time of  $\sim 1$  ms after photoexcitation, and liquid nitrogen was placed into the optical Dewar flask for the achievement of low temperature. Transient fluorescence decays and fluorescence quantum yield were measured with an HORIBA FM-4P-TCSPEC spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC) and DSC 2910 modulated calorimeter under a dry nitrogen gas flow at a heating rate of 10 °C min<sup>-1</sup>. Cyclic voltammetry (CV) was performed on a CHI750C voltammetric analyzer in a typical three-electrode cell with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. The optimized structure was calculated by Gaussian09 at the B3LYP functional with 6-31G basis sets.

**Device Fabrication and Measurement.** ITO-coated glass substrates with a sheet resistance of 10 Ω/cm<sup>-2</sup> were rinsed in deionized water and then ultrasonicated sequentially in acetone and ethanol for three times. Before device fabrication, the ITO substrate was treated in a UV-ozone oven for 15 min. Then, 25 nm of PEDOT:PSS as anode buffer layer was spin-coated onto the ITO substrate and dried at 200 °C for 10 min. After that, 35 nm of emissive layer materials was spin-coated on the PEDOT:PSS treated substrate. Finally, 35 nm of 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)-benzene (TPBI) was vacuum-deposited as an electron-transporting and hole-blocking layer, and Ca (10 nm) and Ag (100 nm) were deposited as the cathode. The thicknesses of the resulting films were measured by a Dektak surface profilometer. The current density–voltage characteristics and device luminance were recorded using a Keithley 2636A Sourcemeter coupled with Si-potodiodes calibrated with PR655. The EL spectra were collected with a Photo-Research PR-655 SpectraScan. All the device measurements were carried out in an inert gas glovebox with no protective encapsulation.

**Materials.** The synthetic procedure for POPH was illustrated in Scheme 1. All reactants and solvents used for the synthesis of the compounds, unless otherwise stated, were purchased from Aldrich and Acros and used without further purification. 1-Bromo-3,5-diiodoben-



**Figure 1.** Molecular structures and photoluminescence (PL) spectra of spin-coated films. (a) Molecular structures of mCP, TAPC, TCTA, and POPH. (b) PL spectra of TAPC, POPH, and TAPC:POPH, (c) TCTA, POPH, and TCTA:POPH, and (d) mCP, POPH, and mCP:POPH.



**Figure 2.** Transient fluorescence decays of films at 300 K. (a) TAPC, TCTA, and mCP. (b) TAPC:POPH, TCTA:POPH, mCP:POPH, and POPH.

zene was prepared following the reported procedure. 4,4',5,5'-Tetramethyl-2-[1,1':3',1"-terphenyl]-5'-yl-1,3,2-dioxaborolane (PHBO) was synthesized according to our previous method.

(5-Bromo-1,3-phenylene)bis(diphenylphosphine oxide) (*BPO-Br*). The mixture of 1-bromo-3,5-diiodobenzene (4.08 g, 10.0 mmol), diphenylphosphine (4.46 g, 24.0 mmol),  $\text{Pd}(\text{OAc})_2$  (0.22 g, 1.0 mmol),  $\text{K}_3\text{PO}_4$  (6.4 g, 30 mmol), and toluene (50 mL) was refluxed under an argon atmosphere for 4 h. After cooling to room temperature, the solvent was removed under vacuum. The crude material was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL) and to the solution was added 30% aqueous  $\text{H}_2\text{O}_2$  (15 mL). The mixed solution was stirred for 3 h at room temperature. The organic and aqueous portions in the mixed solution were separated, and the aqueous portion was extracted with dichloromethane two times; the combined organic layer was dried over  $\text{MgSO}_4$ . The product was then obtained by column chromatography on silica gel with petroleum ether and ethyl acetate as the eluent, to yield a white solid (2.82 g, 50.6%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.28 (d,  $J = 11.1$  Hz, 2H), 7.73 (s, 1H), 7.66 (s, 2H), 7.55

$\text{CDCl}_3$ ,  $\delta$ ): 8.06 (d,  $J = 12$  Hz, 2H), 7.58–7.50 (m, 13H), 7.43–7.33 (m, 8H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 140.59, 140.48, 139.64, 139.49, 138.34, 138.20, 136.26, 136.12, 135.98, 135.00, 134.98, 134.54, 134.40, 133.04, 131.40, 131.23, 126.86, 126.67, 126.48. MS (MALDI-TOF) [ $m/z$ ]: calcd for  $\text{C}_{30}\text{H}_{23}\text{BrO}_2\text{P}_2$ , 557.3; found, 557.4. Anal. Calcd for  $\text{C}_{30}\text{H}_{23}\text{BrO}_2\text{P}_2$ : C, 64.65; H, 4.16. Found: C, 64.60; H, 4.22.

(5-Terphenyl-1,3-phenylene)bis(diphenylphosphine oxide) (*POPH*). The mixture of *BPO-Br* (0.56 g, 1.0 mmol), PHBO (0.42 g, 1.2 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (0.1 g, 0.1 mmol) was dissolved in 1,4-dioxane (80 mL). After adding aqueous 2 N potassium phosphate solution (10 mL), the reaction mixture was heated at 100 °C for 12 h. The cooled crude mixture was poured into water and extracted with dichloromethane and dried over  $\text{MgSO}_4$ , filtered, and evaporated to yield a crude product. The product was then obtained by column chromatography on silica gel with petroleum ether and ethyl acetate as the eluent, to yield a white solid (0.50 g, 71%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.28 (d,  $J = 11.1$  Hz, 2H), 7.73 (s, 1H), 7.66 (s, 2H), 7.55

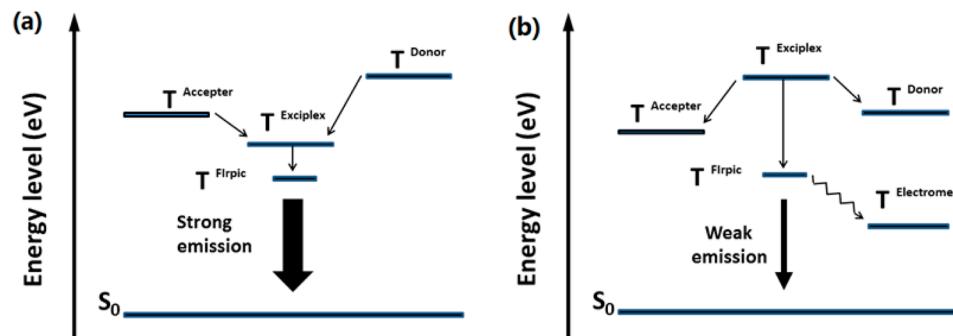


Figure 3. Triplet energy transfer diagrams with exciplex formation. (a) Energy confinement. (b) Energy leakage.

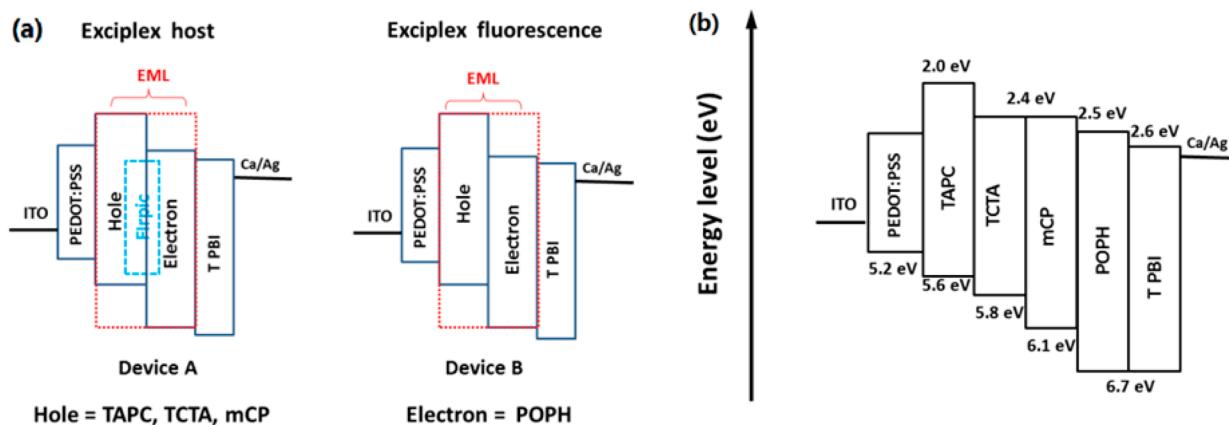


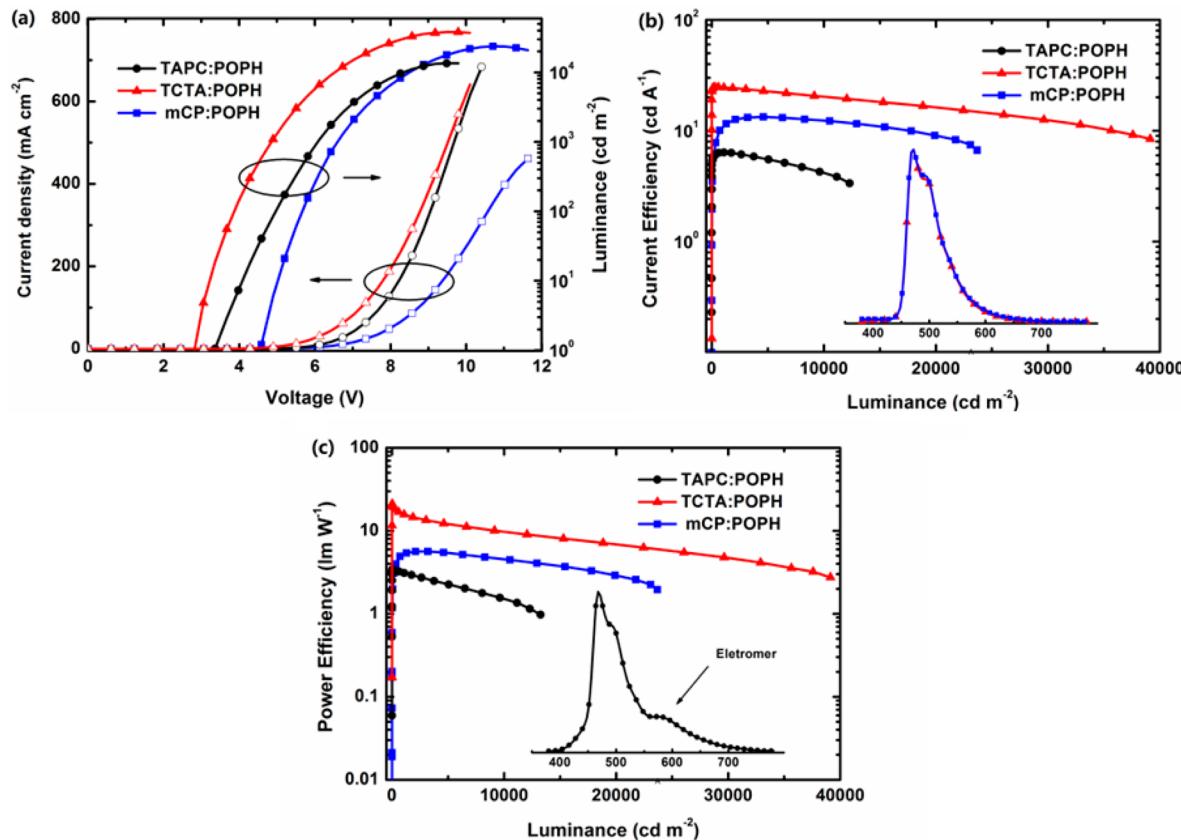
Figure 4. (a) Schematic diagram of the device structure. (b) Energy diagrams of the used materials.

$(t, J = 9.5 \text{ Hz}, 11\text{H}), 7.46 (d, J = 7.2 \text{ Hz}, 6\text{H}), 7.36 (\text{tt}, J = 14.3, 7.3 \text{ Hz}, 14\text{H})$ .  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 142.57, 140.38, 139.67, 134.00, 133.91, 131.94, 131.89, 131.77, 128.62, 128.51, 128.36, 127.52, 127.15, 125.97, 124.93. MS (MALDI-TOF) [ $m/z$ ]: calcd for  $\text{C}_{48}\text{H}_{36}\text{O}_2\text{P}_2$ , 706.7; found, 706.6. Anal. Calcd for  $\text{C}_{48}\text{H}_{36}\text{O}_2\text{P}_2$ : C, 81.57; H, 5.13. Found: C, 81.55; H, 5.12.

## RESULTS AND DISCUSSION

Figure 1 shows the molecular structures and the corresponding photoluminescence (PL) spectra of the constituting molecules and the exciplexes in solid film. The molar ratio of the two components in the blend film is 1:1. The emission spectra of TAPC:POPH, TCTA:POPH, and mCP:POPH are broad and red-shifted to 460, 448, and 392 nm compared with the 363, 375, 392, and 365 nm for POPH, TAPC, TCTA, and mCP, respectively. In addition, the broader fwhm (full width at half-maximum) and the unstructured emission spectra demonstrate that the new excited states in the mixed films can be attributed to exciplex formation through the intermolecular interaction between the excited state donor (or acceptor) and the ground state acceptor (or donor). The transient PL decay curves of the constituting pristine molecules show the lifetime of a few nanoseconds (Figure 2). On the other hand, the three mixed hosts exhibit long delayed components with lifetimes up to 0.13, 0.15, and 0.08  $\mu\text{s}$  for TAPC:POPH, TCTA:POPH, and mCP:POPH films, which correspond to the reversed intersystem crossing from the triplet state to the singlet state. Figure S1 shows the physical properties of the constituting material POPH. The single carrier devices clearly demonstrate the excellent electron-transporting property of POPH. The twisted space configuration of the molecule ensures a high triplet energy of 2.78 eV and good thermal stability with a high

glass-transition temperature of 138 °C, which would facilitate the achievement of morphological stability and uniform amorphous film through spin-coating. As a result, the root-mean-square (RMS) roughness values for POPH, TAPC:POPH, TCTA:POPH, and mCP:POPH are 0.41, 0.72, 0.33, and 0.65 nm, respectively (Figure S2). The LUMO level of POPH was estimated to be 2.5 eV according to the onset potential for reduction, while the HOMO level of 6.7 eV was calculated from the difference between the energy gap and the LUMO level. Figure S3 shows the fluorescence (PL) and phosphorescence (PH) spectra of the three blend films at 77K. The PL and PH spectra of TAPC:POPH and TCTA:POPH films have an identical single emission peak, while the mCP:POPH film shows the structured PH spectra with features from both the emission of exciplex and POPH. The triplet energy of the TAPC:POPH, TCTA:POPH, and mCP:POPH are determined at 2.64, 2.72, and 3.10 eV from their first peak of PH spectra, and the corresponding  $\Delta E_{ST}$  values are 0.059, 0.038, and 0.051 eV, respectively. As described in Figure 3, the POPH emission occurs in mCP:POPH film due to an energy leakage from the exciplex state to the  $T_1$  excited state of POPH, because the  $T_1$  of POPH is lower than that of mCP:POPH exciplex. All the physical properties are summarized in Table S1. The increased triplet energy can be explained by the enlarged difference between the LUMO of the acceptor and HOMO of the donor materials. Obviously, when given a special electron transport material, the triplet energy of the exciplex host can be tuned by choosing the particular donor component with the desired HOMO level, which seems beneficial for developing exciplex-type host material for blue emitters. Furthermore, the photoluminescence quantum yields of these three blend films doped with Flpiric are 0.72, 0.75, and



**Figure 5.** (a) Current density–voltage–luminance characteristics. (b) Current efficiency–luminance curves of the series of OLEDs. Inset: EL spectra of the FlIrpic doped TCTA:POPH- and mCP:POPH-based device. (c) Power efficiency–luminance curves of the series of OLEDs. Inset: EL spectra of the FlIrpic doped TAPC:POPH-based device.

**Table 1. Electroluminescent Data of the Devices<sup>a</sup>**

EML	$V_{\text{on}}^{\text{b}}$ [V]	$L_{\text{max}}^{\text{c}}$ [ $\text{cd m}^{-2}$ ]	$\text{CE}_{\text{max}}^{\text{d}}$ [ $\text{cd A}^{-1}$ ]	$\text{CE}^{\text{e}}$ [ $\text{cd A}^{-1}$ ]	$\text{PE}_{\text{max}}^{\text{d}}$ [ $\text{lm W}^{-1}$ ]	CIE ( $x, y$ )
TAPC:POPH:FlIrpic	3.4	13 000	6.3	6.2/5.5/3.8	3.4	(0.17, 0.38)
TCTA:POPH:FlIrpic	2.7	40 000	25.8	24.5/22.7/20.6	22.5	(0.15, 0.32)
mCP:POPH:FlIrpic	4.4	21 000	13.5	11.5/13.0/12.2	6.0	(0.15, 0.35)

<sup>a</sup>CE, current efficiency; PE, power efficiency; CIE, external quantum efficiency. <sup>b</sup>Turn-on voltages estimated at the luminance of 1  $\text{cd m}^{-2}$ .

<sup>c</sup>Maximum luminance. <sup>d</sup>Maximum efficiencies. <sup>e</sup>The current efficiency at the luminance of 1000, 5000, and 10000  $\text{cd m}^{-2}$ .

0.69 for TAPC:POPH, TCTA:POPH, and mCP:POPH, respectively. This suggests that the three exciplexes can serve as good hosts to prevent the triplet quenching of the phosphorescent emitter under the photoexcitation. However, whether these exciplexes, which possess higher triplet energy and extremely small  $\Delta E_{\text{ST}}$ , can achieve a desirable device performance with low operating voltage and high power efficiency needs to be further validated.

To evaluate the suitability of using exciplex as the host material for solution-processed blue PHOLEDs, FlIrpic was chosen as the dopant to prepare the PHOLEDs with the simple device structure: ITO/PEDOT:PSS (25 nm)/exciplexes:10 wt % FlIrpic (35 nm)/TPBI (35 nm)/Ca (10 nm)/Ag (Figure 4). Here, PEDOT:PSS and TPBI served as the hole injection and electron transporting layers, respectively. Figure 5 shows the current density–voltage–brightness ( $J$ – $V$ – $L$ ) characteristics and efficiencies as a function of brightness for the devices, and the electroluminescent (EL) data is summarized in Table 1. The TCTA:POPH-based device shows a low turn-on voltage of 2.7 V, a maximum power efficiency of 22.5  $\text{lm W}^{-1}$ , a maximum brightness of 40 000  $\text{cd m}^{-2}$ , and a very low efficiency roll-off

with the current efficiency of 24.5  $\text{cd A}^{-1}$  at 1000  $\text{cd m}^{-2}$ , 22.7  $\text{cd A}^{-1}$  at 5000  $\text{cd m}^{-2}$ , and 20.6  $\text{cd A}^{-1}$  at 10 000  $\text{cd m}^{-2}$ . Normally, the limit of turn-on voltage is generally believed to be equal to the energy gap ( $E_g$ ) between the HOMO and LUMO of the emitter molecule divided by the electron charge ( $e$ ). Considering the emission photon energy of FlIrpic (475 nm, 2.65 eV), the turn-on voltage value of 2.7 V has already reached the limitation of the FlIrpic-based devices and was lower than any reported blue PHOLEDs based on the solution process (Table 2). In addition, the power efficiency of 22.5  $\text{lm W}^{-1}$  and the brightness of 40 000  $\text{cd m}^{-2}$  of the TCTA:POPH-based device are among the highest values of solution-processed blue PHOLEDs, which has a commercial implication to energy-saving displays and general lighting. However, the performance of the mCP:POPH-based device is moderately relative to the TCTA:POPH-based one and turned-on at 4.4 V with the maximum values of 13.5  $\text{cd A}^{-1}$  and 21 000  $\text{cd m}^{-2}$  for the current efficiency and luminance, respectively. Even though the TAPC:POPH-based device shows a relatively low turn-on voltage of 3.4 V, the efficiency of 6.3  $\text{cd A}^{-1}$  and the maximum brightness of 13 000  $\text{cd m}^{-2}$  are extremely poor compared with

Table 2. Summary of Solution-Processed PHOLEDs with FIripic as Emitter

	host	$V_{on}^a$ [V]	$L_{max}^b$ [cd m $^{-2}$ ]	$PE_{max}^c$ [lm W $^{-1}$ ]	CIE ( $x, y$ )	
exciplex polymer	TCTA:POPH	2.7	40 000	22.5	(0.15, 0.32)	this work
	PVK	6.8	10 158	5.5	(0.19, 0.35)	ref 28
	PmPCz	10.0	2742	1.04	(0.16, 0.34)	ref 14
	PCzPO	6.0	1285	10.6	(0.17, 0.37)	ref 13
	PEPK	4.6	1687	5.07	(0.19, 0.32)	ref 15
	PVAK	5.4	1786	6.5	(0.21, 0.42)	ref 16
dendrimer	PmCPSi	5.8	6930	6.3	(0.15, 0.33)	ref 17
	H2	5.0	9000	15.4	(0.15, 0.34)	ref 21
	G3MP	5.3	9823	14.1	(0.15, 0.35)	ref 18
	36FCzG1	5.8	6302	8.1	(0.15, 0.31)	ref 22
	Cz-mCP	4.6	27 300	—/—	(0.15, 0.33)	ref 23
	BTCC-36	4.3	27 000	11.8	(0.15, 0.33)	ref 24
bipolar	Cz-TCB	4.9	20 000	13.0 <sup>d</sup>	(0.16, 0.33)	ref 25
	DOXDSiPA	7.6	1169	5.5	(0.16, 0.33)	ref 28
	(TPA-PO) <sub>3</sub>	6.0	11 500	9.0	—/—	ref 33
	p-TAZSiTPA	5.0	10 000	11.8	(0.15, 0.32)	ref 26
	CzPO2	5.8	9600	—/—	(0.16, 0.32)	ref 30
	PTC	4.9	2550	—/—	(0.16, 0.38)	ref 31
CP-QPBI	CzPPO	4.5	6498	4.97	(0.15, 0.35)	ref 29
	CP-QPBI	4.8	14 400	8.2	(0.16, 0.33)	ref 32

<sup>a</sup>Turn-on voltage. <sup>b</sup>Maximum luminance. <sup>c</sup>Maximum power efficiency. <sup>d</sup>General device configuration: ITO/PEDOT:PSS/Host:FIripic/ETL/Cathode.

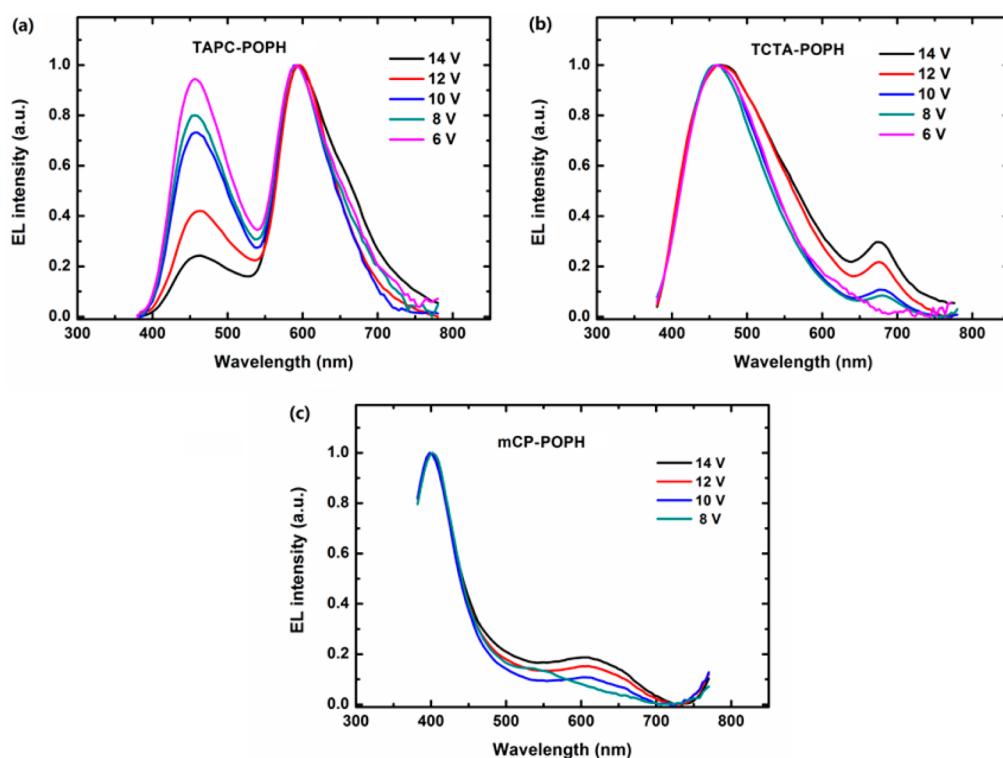


Figure 6. Electroluminescence spectra of the (a) TAPC-POPH-, (b) TCTA-POPH-, and (c) mCP-POPH-based devices at different voltages.

the devices based on TCTA:POPH or mCP:POPH. Obviously, a slight change in the donating component of the exciplex-forming cohost can significantly influence the device performance, which prompted us to further explore the internal reasons.

First, in terms of the TCTA:POPH- and mCP:POPH-based exciplexes, the triplet energies of mCP:POPH and TCTA:POPH films are both higher than that of FIripic, which may lead to a better confinement of the triplet excitons in the

phosphorescent emitter. However, in the mCP:POPH system, the  $T_1$  levels of the exciplex and the constituting molecules are in the order of mCP:POPH > mCP > POPH, which would induce the energy leakage from the exciplex state to mCP and POPH. Conversely, in the TCTA:POPH-based cohost, the  $T_1$  level of the exciplex is lower than that of the components, which means that triplet excitons of the exciplex have only one way to transfer to FIripic (Figure 3). Thus, on the basis of the energy transfer process in the two systems, high performance of

the TCTA:POPH host device seems to have been justified owing to its efficient energy transfer. As for the TAPC:POPH system, though the  $T_1$  level of the exciplex state is lower than the components and higher than Flpic, the performance of the device was extremely poor compared with TCTA:POPH and mCP:POPH films. This suggests that, besides the energy leakage from the exciplex state to the triplet state of the components, there might be other factors that affect the performance of the exciplex as an efficient host for PHOLEDs.

Figure S4 shows the EL spectra of these PHOLEDs at various applied voltages. By comparing the spectra of PHOLEDs using TCTA:POPH and mCP:POPH as the hosts, which have relatively stable electroluminescence independent of voltage, the EL spectra of TAPC:POPH-based PHOLED exhibit an additional peak at 580 nm. To understand the origin of such a long wavelength band, device B with the configuration of ITO/PEDOT:PSS/eExciplexes/TPBI/Ca/Ag was fabricated. All the devices showed the exact exciplex emissions corresponding to the wavelength under photoexcitation of the mixed films and no emission from the components was detected, which proved the effective exciplex state formation (Figure 6). However, in addition to the exciplex emissions, all the blend diodes showed long wavelength peaks, which only arose under electrical excitation and could not be found in the PL spectra. Furthermore, the intensity of these emission bands was sensitive to the increased applied voltage. All these phenomena demonstrated that the new red-shift emission bands were from the radiative transition of the electromer states, which were produced by the cross transition recombination of two molecules under electrical excitation. In particular, a strong electromer emission band at 580 nm was found in the TAPC:POPH film, which was equal to the redundant red-shift emission band in its corresponding PHOLEDs. The parasitic 580 nm red electroluminescence emission in the TAPC:POPH film could be mainly responsible for the poor device performance due to a serious energy leakage from Flpic to the electromer state.<sup>41,42</sup> To fully confine the triplet energy in the phosphorescent emitter, such long wavelength electromer emission must be eliminated. Unfortunately, the exciplex and electromer can coexist and compete with each other in one device under high electric field. Thus, an appropriate way to enhance the efficiency of exciplex-based blue PHOLEDs is to reduce the intensity of electromer emission in the EL spectra as much as possible. For this purpose, the formation mechanism of exciplex and electromer under electrical excitation should be understood.

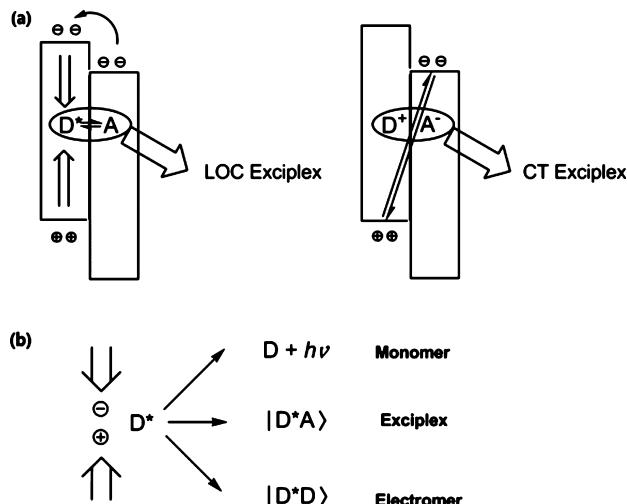
As we know, an exciplex, which can occur under both photoexcitation and electric field, is a bimolecular involving excited state complex that was formed at the interface of the donor and acceptor molecules.<sup>43,44</sup> Generally, an exciplex contains the quantum mechanical mixing of the local (LOC) exciplex and charge transfer (CT) exciplex configuration (Figure 7a), which can be described by the following functions:

$$\psi_{\text{ex}} = c_1|\text{DA}\rangle_{\text{LOC}}^* + c_2|\text{DA}\rangle_{\text{CT}}^* \quad (1)$$

$$|\text{DA}\rangle_{\text{LOC}}^* = a_1|\text{D}^*\text{A}\rangle + a_2|\text{DA}^*\rangle \quad (2)$$

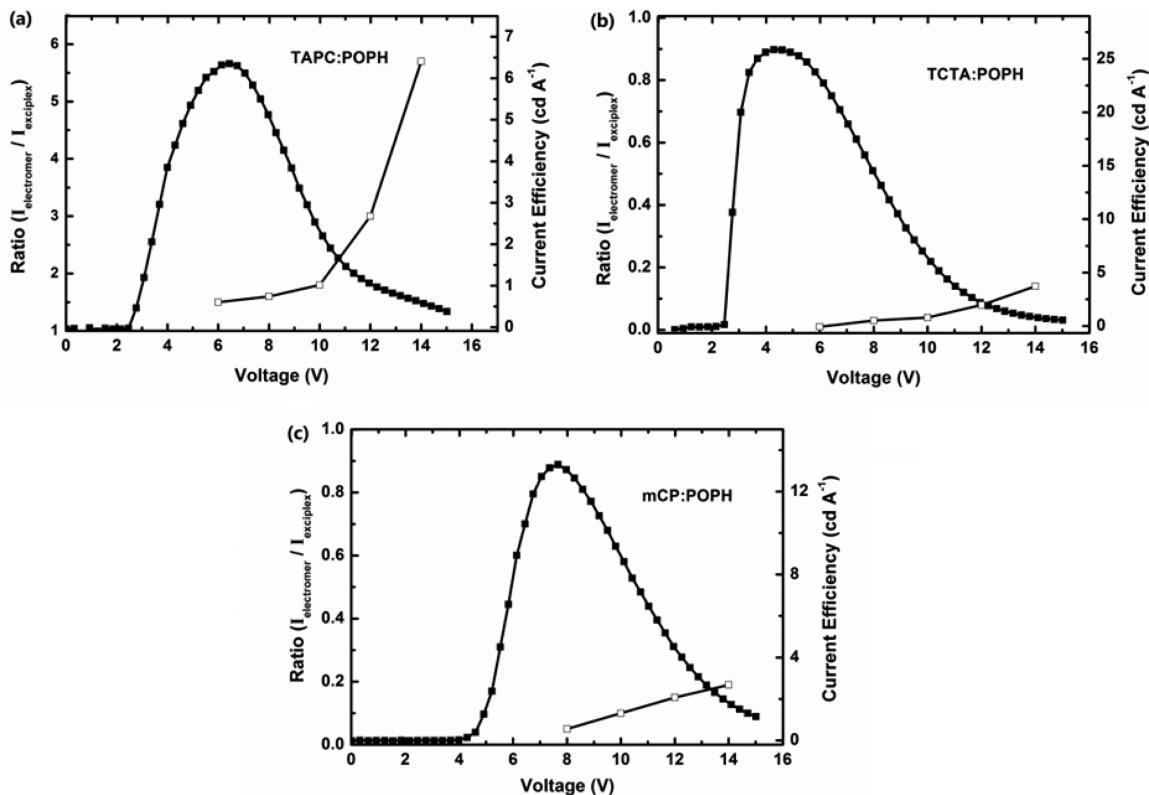
$$|\text{DA}\rangle_{\text{CT}}^* = b_1|\text{D}^+\text{A}^-\rangle + b_2|\text{D}^-\text{A}^+\rangle \quad (3)$$

where the coefficients  $a$ ,  $b$ , and  $c$  determine the contributions of the special configurations to the corresponding states.<sup>45</sup> Under photoexcitation, the exciton formation type was only LOC exciplex with the excitonic resonance between states  $|\text{D}^*\text{A}\rangle$  and



**Figure 7.** (a) The exciplex formation by LOC and CT recombination mechanisms. (b) The generation process of different excited species in the donor molecule.

$|\text{DA}^*\rangle$ , and excitation localized on the donor or acceptor can be tunable by changing the excitation light energy to activate the specific component.<sup>46</sup> As for electrical excitation, the formation probability of LOC and CT exciplex depends on the difference between HOMOs and LUMOs of the constituting molecules. The energy diagram of the three donor molecules TAPC, TCTA, and mCP and the acceptor POPH are shown in Figure 4. Comparing the HOMO differences (1.1, 0.9, and 0.6 eV for TAPC:POPH, TCTA:POPH, and mCP:POPH, respectively) and the LUMO differences (0.5, 0.1, and 0.1 eV for TAPC:POPH, TCTA:POPH, and mCP:POPH, respectively) of these three mixed hosts, the large hole-injection barriers will confine the holes at the interface of donor/POPH, while most of the electrons can effectively transfer to the LUMO of the donating component to form the excited state of  $\text{D}^*$ , which simultaneously combines with the unexcited counterpart A to form exciplex-type emission  $|\text{D}^*\text{A}\rangle$ . Even though the electron injection barrier was 0.5 eV in the TAPC:POPH system, no CT exciplex emission, corresponding to the charge transfer complex  $|\text{D}^+\text{A}^-\rangle$  by cross recombination of hole on charged donor ( $\text{D}^+$ ) and electron on charged acceptor ( $\text{A}^-$ ), was detected in the exciplex fluorescence device B. Therefore, under electrical excitation, the exciton formation type of  $|\text{D}^*\text{A}\rangle$  would govern the exciplex emission of the three mixed hosts mentioned above. However, such excited donor ( $\text{D}^*$ ) could take part in three decay pathways: (1) straight back to the ground state to result in the intrinsic light of monomer emission; (2) combination with the ground state donor to exhibit the electromer emission; or (3) interaction with the ground state acceptor to form the exciplex state. These three decay pathways strongly competed with each other under high electric fields (Figure 7b), and the main radiative decay scheme was determined by the molecular features of the donor itself. As the literature reported, the intense electromer emission band at 580 nm was observed in single-layer TAPC device and the PL spectra also showed the excimer emission, which meant the ground state TAPC had a strong interaction with the excited ( $\text{TAPC}^*$ ) to form the low energy electromer  $|\text{TAPC}^*\text{TAPC}\rangle$  state.<sup>47,48</sup> Fortunately, such a boring bimolecular interaction was weak in TCTA and mCP films, which led to a negligible electromer compared with the dominated exciplex emissions of



**Figure 8.** Ratio of emission intensity of electromer to that of exciplex ( $I_{\text{electromer}}/I_{\text{exciplex}}$ ) (hollow) and the current efficiency at different applied voltages (solid). (a) TAPC:POPH. (b) TCTA:POPH. (c) mCP:POPH.

|TCTA\*POPH⟩ and |mCP\*POPH⟩. Figure 8 shows the ratio of emission intensity of electromer to exciplex ( $I_{\text{electromer}}/I_{\text{exciplex}}$ ) and the current efficiency of the corresponding PHOLEDs at different applied voltages. Obviously, the exciplex governs the emission of TCTA- and mCP-based devices, while the electromer was predominant in the TAPC-based one. It is worthy to note that the high efficiencies were always obtained at the extremely small ratio of  $I_{\text{electromer}}/I_{\text{exciplex}}$ , which also demonstrates that the low energy electromer state was a serious exciton quenching channel, though it was ignored in the previous studies. The formation ability of electromer emission was strongly dependent on the chemical structure of the donor component, and the triphenylamine unit in the periphery of the molecule was tentatively considered to be the main reason for such unique species.<sup>49</sup> Although the vacuum-deposition technique can use a bilayer interface CT exciplex to minimize the electromer emission of the TAPC,<sup>40</sup> it is more challenging in the case of solution processing, because depositing one layer would dissolve the layer beneath it.<sup>50</sup> For designing an efficient exciplex-type host used for solution-processed blue PHOLEDs, such hole-transporting material like TAPC seems not to be a good candidate owing to its irreversible electromer formation under electrical excitation.

After detailed analysis of the exciplex exciton formation mechanism, we can easily understand the reason for the change of turn-on voltage of the devices based on these three exciplex-type hosts with small  $\Delta E_{\text{ST}}$ . Since the electron injection barriers (EIBs) of TCTA:POPH and mCP:POPH are both 0.1 eV, the turn on voltage should be dominated by the hole-injection barrier (HIB) from PEDOT:PSS to donor component. Indeed, the value of 2.7 V of the TCTA:POPH-based device was much lower than that of 4.2 V of the mCP:POPH-based one due to

its relatively small HIB. As for TAPC:POPH, the HIB was 0.2 eV lower than that of TCTA:POPH, while the EIB was 0.4 eV higher than TCTA:POPH. The relatively higher turn-on voltage of TAPC:POPH compared to TCTA:POPH may be attributed to the increased combined injection barrier of the exciplex exciton formation. However, the turn-on voltage of the TAPC:POPH-based device was much lower than that of the mCP:POPH-based one, which means that the strong electromer formation property of TAPC does not influence the turn-on voltage of the device in spite of its serious triplet exciton quenching effect. Although the direct carrier trapping on the guest and the charge transporting ability of the three different donor components may also have some influence, the minimized electron and hole injection barrier for the exciplex formation seems to play an important role for the low turn-on voltage.

## CONCLUSIONS

In conclusion, three exciplex-type cohost materials were designed by equal molar blending of the hole transporting molecule TAPC, TCTA, or mCP with a high triplet energy electron transporting material POPH. All the three cohosts exhibit broad and red-shift emissions compared with the constituted components, which distinctly prove the efficient exciplex formation under the photoexcitation. Particularly, the TCTA:POPH-based device has achieved a high power efficiency of  $22.5 \text{ lm W}^{-1}$ , a high luminescence of  $40\,000 \text{ cd m}^{-2}$ , and a very small efficiency roll-off. Moreover, an extremely low turn-on voltage of 2.7 eV of blue device is first achieved by the solution process, and such a value has approached the theoretical limit of the Flrpic-based device. When the three systems that we found were compared, though the triplet

energy of the exciplex state is tunable by manipulating the HOMO level of the electron-donating component, the excessively high energy of the exciplex states will induce a serious energy leakage to the components. In addition, the hole transporting molecule with a strong electromer formation property is not suitable for building the exciplex-type blending cohost used for blue PHOLEDs owing to its serious triplet exciton quenching effect. Finally, the turn-on voltage of the solution-processed PHOLEDs was mainly determined by the combined charge injection barrier of the exciplex state formation process, while the high efficiency can only be achieved by properly confining the triplet energy on the phosphorescent emitter. We expect that systematic investigations of the excited-state dynamics and the structure–property relationships will be beneficial for developing more efficient exciplex-type host materials that can be used for solution-processed OLEDs.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsami.5b06424](https://doi.org/10.1021/acsami.5b06424).

Physical properties of the electron-transporting material POPH, fluorescence and phosphorescence spectra of mixed films at 77 K, and electroluminescence spectra of the FIrpic-based devices at different voltages. ([PDF](#))

## AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: [jiangw@seu.edu.cn](mailto:jiangw@seu.edu.cn) (W.J.).

\*E-mail: [sun@seu.edu.cn](mailto:sun@seu.edu.cn) (Y.M.S.).

\*E-mail: [iamshye@njupt.edu.cn](mailto:iamshye@njupt.edu.cn) (S.H.Y.).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

We are grateful for the grants from the National Basic Research Program of China (2013CB932902) and National Natural Science Foundation of China (51103023, 21173042). We also are thankful for the support of the Research Fund for Graduate Innovation Project of Jiangsu Province (KYLX15\_0123), the Scientific Research Foundation of Graduate School of Southeast University (3260635700), and the Fundamental Research Funds for the Central Universities (3207045102).

## REFERENCES

- (1) Aizawa, N.; Pu, Y. J.; Chiba, T.; Kawata, S.; Sasabe, H.; Kido, J. Instant Low-Temperature Cross-Linking of Poly(N-Vinylcarbazole) for Solution-Processed Multilayer Blue Phosphorescent Organic Light-Emitting Devices. *Adv. Mater.* **2014**, *26*, 7543–7546.
- (2) Cho, Y. J.; Yook, K. S.; Lee, J. Y. High Efficiency in a Solution-Processed Thermally Activated Delayed-Fluorescence Device Using a Delayed-Fluorescence Emitting Material with Improved Solubility. *Adv. Mater.* **2014**, *26*, 6642–6646.
- (3) Muller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhirn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. Multi-Colour Organic Light-Emitting Displays by Solution Processing. *Nature* **2003**, *421*, 829–833.
- (4) Liaptsis, G.; Hertel, D.; Meerholz, K. Solution Processed Organic Double Light-Emitting Layer Diode Based on Cross-Linkable Small Molecular Systems. *Angew. Chem., Int. Ed.* **2013**, *52*, 9563–9567.

(5) Mondal, E.; Hung, W. Y.; Dai, H. C.; Wong, K. T. Fluorene-Based Asymmetric Bipolar Universal Hosts for White Organic Light-Emitting Devices. *Adv. Funct. Mater.* **2013**, *23*, 3096–3105.

(6) Han, C.; Zhu, L.; Li, J.; Zhao, F.; Zhang, Z.; Xu, H.; Deng, Z.; Ma, D.; Yan, P. Highly Efficient Multifluorenyl Host Materials with Unsymmetrical Molecular Configurations and Localized Triplet States for Green and Red Phosphorescent Devices. *Adv. Mater.* **2014**, *26*, 7070–7077.

(7) Li, Q.; Cui, L. S.; Zhong, C.; Jiang, Z. Q.; Liao, L. S. Asymmetric Design of Bipolar Host Materials with Novel 1,2,4-Oxadiazole Unit in Blue Phosphorescent Device. *Org. Lett.* **2014**, *16*, 1622–1625.

(8) Han, C.; Zhang, Z.; Xu, H.; Yue, S.; Li, J.; Yan, P.; Deng, Z.; Zhao, Y.; Yan, P.; Liu, S. Short-Axis Substitution Approach Selectively Optimizes Electrical Properties of Dibenzothiophene-Based Phosphine Oxide Hosts. *J. Am. Chem. Soc.* **2012**, *134*, 19179–19188.

(9) Jankus, V.; Monkman, A. P. Is Poly(Vinylcarbazole) a Good Host for Blue Phosphorescent Dopants in Pleds? Dimer Formation and Their Effects on the Triplet Energy Level of Poly(N-Vinylcarbazole) and Poly(N-Ethyl-2-Vinylcarbazole). *Adv. Funct. Mater.* **2011**, *21*, 3350–3356.

(10) Zou, J.; Wu, H.; Lam, C. S.; Wang, C.; Zhu, J.; Zhong, C.; Hu, S.; Ho, C. L.; Zhou, G. J.; Wu, H.; Choy, W. C.; Peng, J.; Cao, Y.; Wong, W. Y. Simultaneous Optimization of Charge-Carrier Balance and Luminous Efficacy in Highly Efficient White Polymer Light-Emitting Devices. *Adv. Mater.* **2011**, *23*, 2976–2980.

(11) Wu, H. B.; Zou, J. H.; Liu, F.; Wang, L.; Mikhailovsky, A.; Bazan, G. C.; Yang, W.; Cao, Y. Efficient Single Active Layer Electrophosphorescent White Polymer Light-Emitting Diodes. *Adv. Mater.* **2008**, *20*, 696–702.

(12) Yang, X.; Müller, D. C.; Neher, D.; Meerholz, K. Highly Efficient Polymeric Electrophosphorescent Diodes. *Adv. Mater.* **2006**, *18*, 948–954.

(13) Shao, S.; Ding, J.; Ye, T.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. A Novel, Bipolar Polymeric Host for Highly Efficient Blue Electrophosphorescence: A Non-Conjugated Poly(Aryl Ether) Containing Triphenylphosphine Oxide Units in the Electron-Transporting Main Chain and Carbazole Units in Hole-Transporting Side Chains. *Adv. Mater.* **2011**, *23*, 3570–3574.

(14) Liu, J.; Pei, Q. Poly(M-Phenylene): Conjugated Polymer Host with High Triplet Energy for Efficient Blue Electrophosphorescence. *Macromolecules* **2010**, *43*, 9608–9612.

(15) Dumur, F.; Beouch, L.; Peralta, S.; Wantz, G.; Goubard, F.; Gigmes, D. Solution-Processed Blue Phosphorescent OLEDs with Carbazole-Based Polymeric Host Materials. *Org. Electron.* **2015**, *25*, 21–30.

(16) Lessard, B. H.; Beouch, L.; Goubard, F.; Wantz, G.; Marić, M.; Gigmes, D.; Dumur, F. Poly(2-(N-Carbazolyl)Ethyl Acrylate) as a Host for High Efficiency Polymer Light-Emitting Devices. *Org. Electron.* **2015**, *17*, 377–385.

(17) Sun, D.; Zhou, X.; Liu, J.; Sun, X.; Li, H.; Ren, Z.; Ma, D.; Bryce, M. R.; Yan, S. Solution-Processed Blue/Deep Blue and White Phosphorescent Organic Light-Emitting Diodes (PhOLEDs) Hosted by a Polysiloxane Derivative with Pendant mCP (1,3-Bis(9-Carbazolyl)Benzene). *ACS Appl. Mater. Interfaces* **2015**, DOI: [10.1021/am507592s](https://doi.org/10.1021/am507592s).

(18) Wang, X.; Wang, S.; Ma, Z.; Ding, J.; Wang, L.; Jing, X.; Wang, F. Solution-Processible 2,2'-Dimethyl-Biphenyl Cored Carbazole Dendrimers as Universal Hosts for Efficient Blue, Green, and Red Phosphorescent OLEDs. *Adv. Funct. Mater.* **2014**, *24*, 3413–3421.

(19) Li, J. Y.; Zhang, T.; Liang, Y. J.; Yang, R. X. Solution-Processible Carbazole Dendrimers as Host Materials for Highly Efficient Phosphorescent Organic Light-Emitting Diodes. *Adv. Funct. Mater.* **2013**, *23*, 619–628.

(20) Zhang, B.; Tan, G.; Lam, C. S.; Yao, B.; Ho, C. L.; Liu, L.; Xie, Z.; Wong, W. Y.; Ding, J.; Wang, L. High-Efficiency Single Emissive Layer White Organic Light-Emitting Diodes Based on Solution-Processed Dendritic Host and New Orange-Emitting Iridium Complex. *Adv. Mater.* **2012**, *24*, 1873–1877.

- (21) Ding, J. Q.; Zhang, B. H.; Lu, J. H.; Xie, Z. Y.; Wang, L. X.; Jing, X. B.; Wang, F. S. Solution-Processable Carbazole-Based Conjugated Dendritic Hosts for Power-Efficient Blue-Electrophosphorescent Devices. *Adv. Mater.* **2009**, *21*, 4983–4986.
- (22) Qian, Y. B.; Cao, F.; Guo, W. P. High Thermal Stability 3, 6-Fluorene-Carbazole-Dendrimers as Host Materials for Efficient Solution-Processed Blue Phosphorescent Devices. *Tetrahedron* **2013**, *69*, 4169–4175.
- (23) Jiang, W.; Tang, J. N.; Yang, W.; Ban, X. X.; Huang, B.; Dai, Y. Q.; Sun, Y. M.; Duan, L.; Qiao, J.; Wang, L. D.; Qiu, Y. Synthesis of Carbazole-Based Dendrimer: Host Material for Highly Efficient Solution-Processed Blue Organic Electrophosphorescent Diodes. *Tetrahedron* **2012**, *68*, 5800–5805.
- (24) Jiang, W.; Duan, L.; Qiao, J.; Dong, G. F.; Zhang, D. Q.; Wang, L. D.; Qiu, Y. High-Triplet-Energy Tri-Carbazole Derivatives as Host Materials for Efficient Solution-Processed Blue Phosphorescent Devices. *J. Mater. Chem.* **2011**, *21*, 4918–4926.
- (25) Jiang, W.; Ge, Z. J.; Cai, P. Y.; Huang, B.; Dai, Y. Q.; Sun, Y. M.; Qiao, J.; Wang, L. D.; Duan, L.; Qiu, Y. Star-Shaped Dendritic Hosts Based on Carbazole Moieties for Highly Efficient Blue Phosphorescent OLEDs. *J. Mater. Chem.* **2012**, *22*, 12016–12022.
- (26) Gong, S.; Fu, Q.; Wang, Q.; Yang, C.; Zhong, C.; Qin, J.; Ma, D. Highly Efficient Deep-Blue Electrophosphorescence Enabled by Solution-Processed Bipolar Tetraarylsilane Host with Both a High Triplet Energy and a High-Lying HOMO Level. *Adv. Mater.* **2011**, *23*, 4956–4959.
- (27) Ge, Z.; Hayakawa, T.; Ando, S.; Ueda, M.; Akiike, T.; Miyamoto, H.; Kajita, T.; Kakimoto, M. A. Solution-Processible Bipolar Triphenylamine-Benzimidazole Derivatives for Highly Efficient Single-Layer Organic Light-Emitting Diodes. *Chem. Mater.* **2008**, *20*, 2532–2537.
- (28) Gong, S. L.; Zhong, C.; Fu, Q.; Ma, D. G.; Qin, J. G.; Yang, C. L. Extension of Molecular Structure toward Solution-Processable Hosts for Efficient Blue Phosphorescent Organic Light-Emitting Diodes. *J. Phys. Chem. C* **2013**, *117*, 549–555.
- (29) Lee, Y. T.; Chang, Y. T.; Lee, M. T.; Chiang, P. H.; Chen, C. T.; Chen, C. T. Solution-Processed Bipolar Small Molecular Host Materials for Single-Layer Blue Phosphorescent Organic Light-Emitting Diodes. *J. Mater. Chem. C* **2014**, *2*, 382–391.
- (30) Jiang, W.; Duan, L.; Qiao, J.; Dong, G. F.; Wang, L. D.; Qiu, Y. Tuning of Charge Balance in Bipolar Host Materials for Highly Efficient Solution-Processed Phosphorescent Devices. *Org. Lett.* **2011**, *13*, 3146–3149.
- (31) Jiang, W.; Duan, L.; Qiao, J.; Zhang, D. Q.; Dong, G. F.; Wang, L. D.; Qiu, Y. Novel Star-Shaped Host Materials for Highly Efficient Solution-Processed Phosphorescent Organic Light-Emitting Diodes. *J. Mater. Chem.* **2010**, *20*, 6131–6137.
- (32) Ban, X.; Jiang, W.; Sun, K.; Xie, X.; Peng, L.; Dong, H.; Sun, Y.; Huang, B.; Duan, L.; Qiu, Y. Bipolar Host with Multielectron Transport Benzimidazole Units for Low Operating Voltage and High Power Efficiency Solution-Processed Phosphorescent OLEDs. *ACS Appl. Mater. Interfaces* **2015**, *7*, 7303–7314.
- (33) Chen, K.; Zhao, H. R.; Fan, Z. K.; Yin, G.; Chen, Q. M.; Quan, Y. W.; Li, S. H.; Ye, S. H. Macrospirocyclic Oligomer Based on Triphenylamine and Diphenylphosphine Oxide as a Bipolar Host for Efficient Blue Electrophosphorescent Organic Light-Emitting Diodes (OLEDs). *Org. Lett.* **2015**, *17*, 1413–1416.
- (34) Sasabe, H.; Nakanishi, H.; Watanabe, Y.; Yano, S.; Hirasawa, M.; Pu, Y. J.; Kido, J. Extremely Low Operating Voltage Green Phosphorescent Organic Light-Emitting Devices. *Adv. Funct. Mater.* **2013**, *23*, 5550–5555.
- (35) Zhang, D. D.; Duan, L.; Zhang, D. Q.; Qiao, J.; Dong, G. F.; Wang, L. D.; Qiu, Y. Extremely Low Driving Voltage Electro-Phosphorescent Green Organic Light-Emitting Diodes Based on a Host Material with Small Singlet-Triplet Exchange Energy without P- or N-Doping Layer. *Org. Electron.* **2013**, *14*, 260–266.
- (36) Han, C.; Zhang, Z.; Xu, H.; Xie, G.; Li, J.; Zhao, Y.; Deng, Z.; Liu, S.; Yan, P. Convergent Modulation of Singlet and Triplet Excited States of Phosphine-Oxide Hosts through the Management of Molecular Structure and Functional-Group Linkages for Low-Voltage-Driven Electrophosphorescence. *Chem. - Eur. J.* **2013**, *19*, 141–154.
- (37) Yu, D.; Zhao, F.; Han, C.; Xu, H.; Li, J.; Zhang, Z.; Deng, Z.; Ma, D.; Yan, P. Ternary Ambipolar Phosphine Oxide Hosts Based on Indirect Linkage for Highly Efficient Blue Electrophosphorescence: Towards High Triplet Energy, Low Driving Voltage and Stable Efficiencies. *Adv. Mater.* **2012**, *24*, 509–514.
- (38) Lee, J. H.; Cheng, S. H.; Yoo, S. J.; Shin, H.; Chang, J. H.; Wu, C. I.; Wong, K. T.; Kim, J. J. An Exciplex Forming Host for Highly Efficient Blue Organic Light Emitting Diodes with Low Driving Voltage. *Adv. Funct. Mater.* **2015**, *25*, 361–366.
- (39) Shin, H.; Lee, S.; Kim, K. H.; Moon, C. K.; Yoo, S. J.; Lee, J. H.; Kim, J. J. Blue Phosphorescent Organic Light-Emitting Diodes Using an Exciplex Forming Co-Host with the External Quantum Efficiency of Theoretical Limit. *Adv. Mater.* **2014**, *26*, 4730–4734.
- (40) Seino, Y.; Sasabe, H.; Pu, Y. J.; Kido, J. High-Performance Blue Phosphorescent OLEDs Using Energy Transfer from Exciplex. *Adv. Mater.* **2014**, *26*, 1612–1616.
- (41) Kwon, S.; Wee, K.-R.; Pac, C.; Kang, S. O. Significance of Irreversible Formation of “Electromer” in 1-Bis[4-[N,N-Di(4-Tolyl)-Amino]Phenyl]-Cyclohexane Layer Associated with the Stability of Deep Blue Phosphorescent Organic Light Emitting Diodes. *Org. Electron.* **2012**, *13*, 645–651.
- (42) Matsumoto, N.; Adachi, C. Exciplex Formations at the Ht/Alq<sub>3</sub> interface in an Organic Light-Emitting Diode: Influence of the Electron–Hole Recombination Zone and Electric Field. *J. Phys. Chem. C* **2010**, *114*, 4652–4658.
- (43) Zhao, D.; Zhang, F.; Xu, C.; Sun, J.; Song, S.; Xu, Z.; Sun, X. Exciplex Emission in the Blend of Two Blue Luminescent Materials. *Appl. Surf. Sci.* **2008**, *254*, 3548–3552.
- (44) Lai, S. L.; Chan, M. Y.; Tong, Q. X.; Fung, M. K.; Wang, P. F.; Lee, C. S.; Lee, S. T. Approaches for Achieving Highly Efficient Exciplex-Based Organic Light-Emitting Devices. *Appl. Phys. Lett.* **2008**, *93*, 143301–143303.
- (45) Yang, S.; Zhang, X.; Hou, Y.; Deng, Z.; Xu, X. Charge Carriers at Organic Heterojunction Interface: Exciplex Emission or Electropole Emission? *J. Appl. Phys.* **2007**, *101*, 096101–096103.
- (46) Liu, X. K.; Chen, Z.; Zheng, C. J.; Liu, C. L.; Lee, C. S.; Li, F.; Ou, X. M.; Zhang, X. H. Prediction and Design of Efficient Exciplex Emitters for High-Efficiency, Thermally Activated Delayed-Fluorescence Organic Light-Emitting Diodes. *Adv. Mater.* **2015**, *27*, 2378–2383.
- (47) Yang, S.; Jiang, M. White Light Generation Combining Emissions from Exciplex, Excimer and Electromer in TAPC-Based Organic Light-Emitting Diodes. *Chem. Phys. Lett.* **2009**, *484*, 54–58.
- (48) Kalinowski, J.; Giro, G.; Cocchi, M.; Fattori, V.; Di Marco, P. Unusual Disparity in Electroluminescence and Photoluminescence Spectra of Vacuum-Evaporated Films of 1,1-Bis ((Di-4-Tolylamino) Phenyl) Cyclohexane. *Appl. Phys. Lett.* **2000**, *76*, 2352–2354.
- (49) Kulkarni, A. P.; Jenekhe, S. A. Blue-Green, Orange, and White Organic Light-Emitting Diodes Based on Exciplex Electroluminescence of an Oligoquinoline Acceptor and Different Hole-Transport Materials. *J. Phys. Chem. C* **2008**, *112*, 5174–5184.
- (50) Aizawa, N.; Pu, Y. J.; Watanabe, M.; Chiba, T.; Ideta, K.; Toyota, N.; Igarashi, M.; Suzuri, Y.; Sasabe, H.; Kido, J. Solution-Processed Multilayer Small-Molecule Light-Emitting Devices with High-Efficiency White-Light Emission. *Nat. Commun.* **2014**, *5*, 5756.