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Solution-Processed Bipolar Small Molecular Host Materials for Single-Layer Blue Phosphorescent Organic Light-Emitting Diodes

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Three new solution processable small molecular host materials based on bis-[3,5-di(9H-carbazol-9yl)phenyl] structural moiety have been developed for blue phosphorescence (FIrpic dopant) organic lightemitting diodes. All three host materials have been characterized for high glass transition temperatures ¹⁰ (T_g s), 155~175 °C, indicative of good morphological stability of their amorphous thin films prepared from solution process. Whereas N,N-bis-[3,5-di(9H-carbazol-9-yl)phenyl]methylamine (**CzPAMe**) has the highest solid state triplet energy gap (E_T) of 2.73 eV, tetrakis-[3,3',5,5'-(9H-carbazol-9-yl)] triphenylphosphine oxide (**CzPPO**) and N,N-bis-[3,5-di(9H-carbazol-9-yl)phenyl]pyrimidin-2-amine

(CzPAPm) are two host materials potentially being bipolar for charge transport due to the electron ¹⁵ deficient unit of phenylphosphine oxide and pyrimidine, respectively. Due to the insufficient E_T (2.56 eV) of CzPAPm, CzPPO or CzPAMe devices are significantly better than CzPAPm devices with or without 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) co-host. Particularly, having no OXD-7 co-host and no vacuum-thermal-deposited extra electron transporting layer, single-layer devices of CzPAPM surpassing CzPAMe devices reach current efficiency as high as 9.32 cd/A (or power efficiency

²⁰ of 4.97 lm/W), one of the highest efficiency among small molecular devices with the same fabrication process and same device configuration.

1. Introduction

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Small molecular host materials have attracted increasing attention in blue phosphorescence organic light-emitting diodes (OLEDs).¹

- ²⁵ Solution process instead of dry process (vacuum-thermal deposition) is better or more practical in terms of cost, speed, and size for OLED fabrication.² Materials wise, small molecular materials are superior to polymeric materials because of the easy synthesis and purification. However, it is very often that small ³⁰ molecular host materials have insufficiently high triplet energy gap (E_T) in solid state or they are prone to aggregate or crystallize in thin film state because of low glass transition temperature (T_g).³ It is less common for those solution processable small molecular host materials in the fabrication of single-layer blue ³⁵ phosphorescence OLEDs due to the usually poor
- electroluminescence (EL) efficiency.^{4,5} Regarding high EL efficiency, a vacuum-thermal-deposited triplet exciton-confining

(hole-blocking) or electron-transporting layer, such as 1,3,5tri(*m*-pyrid-3-yl-phenyl)benzene (TmPyPB),⁶ 3-(4-biphenyl)-4-

⁴⁰ phenyl-5-*tert*-butylphenyl-1,2,4-triazole (TAZ),⁷ diphenyl(4-(triphenylsilyl)phenyl)phosphine oxide (TSPO1),⁸ 4,7diphenylphenanthroline (BPhen),^{6f} 2.9-dimethyl-4,7diphenylphenanthroline (BCP),⁹ or 2,2',2"-(1,3,5-phenylene)tris[1-phenyl-1H-benzimidazole] (TPBI)^{4c,4d,4f,6c,10} is often 4s required for enhancing blue phosphorescence emission or charge balance of the device.

Recently, the molecular design of the host material prefers the bipolar charge transporting structure feature enabling charge balance of the light-emitting layer.^{1,11} Bipolar molecular hosts ⁵⁰ may eliminate the necessity of such extra layer fabricated by the vacuum-thermal-deposition fabrication process and the device fabrication keeps as simple as possible. On the other hand, a co-host material, usually a electron-transporting molecule like 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7),¹²

55 has been found effective in boosting EL efficiency of poly(9vinylcarbazole) (PVK) hosted single-layer blue phosphorescence OLEDs. We and Qiu et al. are two of the first research groups employing OXD-7 co-host in the solution processed small molecular hosted blue phosphorescence OLEDs.^{4a,4c,5a} In this

60 report, it will be demonstrated that both vacuum-thermaldeposited hole-blocking /electron-transporting layer and OXD-7 co-host material maybe not necessary in our newly designed bipolar small molecular hosted blue phosphorescence OLEDs.

The newly designed small molecular host materials are CzPAMe, 65 CzPPO, and CzPAPm (their chemical structures are shown in

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Scheme 1). These new host materials have been characterized with high $T_{\rm g}$ and high $E_{\rm T}$ in solid state and are suitable for solution process in the fabrication of blue phosphorescence iridium (III) bis(4,6-difluorophenylpyridinato)picolate (FIrpic) 5 OLEDs. Based on many known literature examples, pyrimidineand triphenylphosphine oxide-bearing CzPPO and CzPAPm, respectively, are potential to be bipolar charge transporting host materials. Herein, we report the synthesis and physical characterization of these newly prepared host materials. Without 10 vacuum-thermal-deposited hole-blocking/electron-transporting layer and without including OXD-7 co-host material, solution processed single-layer blue phosphorescence CzPPO OLEDs were found significantly better than others, including those of bis[3,5-di(9H-carbazol-9-yl)phenyl]diphenylsilane (SimCP2) 15 (Scheme 1), which has been demonstrated by us and others as an effective small molecular host materials suitable for solution process in the fabrication of single-layer blue phosphorescence OLEDs. 5,10b,13



Scheme 1 Molecular structures of SimCP2, CzPAMe, CzPPO, and CzPAPm. Their MM2 energy minimized structures (by Chem 3D) are shown in below correspondingly.

2. Results and discussion

2.1 Design and synthesis

SimCP2 is one of the very rare small molecular host materials that are suitable for blue phosphorescence OLEDs ³⁰ fabrication via either dry or solution process.^{10b} More recently, without including hole-blocking or electron-transporting layer, SimCP2 hosted blue phosphorescence OLEDs can exhibit relatively high EL efficiency (13.6 cd/A or 8 lm/W).^{5b} In this study, we have utilized two 3,5-di(9H-carbazol-9-yl)phenyl ³⁵ (mCP) units of SimCP2 in developing a new series of small molecular host materials CzPAMe, CzPPO, and CzPAPm.

Finishing with the oxidation reaction by hydrogen peroxide, reaction of dichlorophenylphosphine with lithiated 9,9'-(5-bromo-1,3-phenylene)bis(9*H*-carbazole) (BrmCP) affords **CzPPO** ⁴⁰ (Scheme 2). Both **CzPAMe** and **CzPAPm** were readily

synthesized from a common precursor, bis(3,5-di(9H-carbazol-9vl)phenvl)amine (CzPA), which was in turn synthesized from BrmCP and NH₂mCP (Scheme 2). Conducting a methylation by iodomethane and classical Ullmann reaction of 2-iodopyrimidine 45 on CzPA affords CzPAMe and CzPAPm, respectively (Scheme 2). Whereas BrmCP was synthesized according to a procedure reported in a patent,¹⁷ NH₂mCP is a previously unknown compound and we have developed a three-step synthetic procedure of it (Scheme 2). Starting from commercially available 50 2,6-diiodo-4-nitroaniline, the deamination reaction providing 1,3dijodo-5-nirtobenzene was readily achieved by a literature known procedure.¹⁸ Ullmann reaction with carbazole transformed 1,3diiodo-5-nirtobenzene to 9,9'-(5-nitro-1,3-phenylene)bis(9Hcarbazole) (NO₂mCP), and then a reduction of nitro group by 55 stannous chloride afforded NH₂mCP (see experimental section for synthetic details). All reactions conducted herein have satisfactory isolated yields (60~88%) and all new compounds were fully characterized by elemental analysis, MS, and ¹H NMR spectroscopies.



Scheme 2 Synthesis of CzPAMe, CzPPO, CzPAPm, NO₂mCP, and NH₂mCP.

65 2.2 Thermal and amorphousity characterization.

All four host materials exhibit pretty good thermal stability with thermal decomposition temperatures (T_{ds}) in the range of 466-536 °C (Figure 1). In addition to the solution process, such high thermal stability makes them potentially feasible for dry process 70 (vacuum-thermal-deposition) in device fabrication. Similar to the structure of **SimCP2**, the bulge dendron-like structure (see Chem 3D structures displayed in Scheme 1) of **CzPAMe**, **CzPPO**, and **CzPAPm** enables amorphous or semi-amorphous feature shown in DSC thermograms (Figure 2) and solution-casting thin film X-75 ray diffraction spectra (Figure 3).

All four host materials show discernible glass transition temperatures (T_{g} s) relatively high around 144-175 °C in all repeating scans. However, a stronger endothermic signal of melting temperature (T_{m}) was detected for **CzPAMe** and **CzPPO** ⁸⁰ at 292 and 328 °C, respectively, in the first heating scan. The thermal data (T_{d} , T_{g} , T_{m}) are summarized in Table 1. X-ray

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diffraction spectra of the solution-casting thin film of the four host materials confirm the amorphousity inferred from DSC thermograms. Except for few protruding signals in **CzPAMe** and **CzPPO** spectra, X-ray diffraction spectra of four host materials ⁵ are basically featureless broad halo, indicative of the amorphous nature of thin films.



Fig. 1 TGA thermograms of CzPAMe, CzPPO, CzPAPm, and 10 SimCP2.



Fig. 2 DSC thermograms of CzPAMe, CzPPO, CzPAPm, and 15 SimCP2.

2.3 Spectroscopic and energy level characterization.

Solid state HOMO energy levels of the host material were determined by a low-energy photoelectron spectrometer (Riken-

- ²⁰ Keiki AC-2). The AC-2 spectra are shown in Figure 4 and 6.01, 5.96, 5.84, and 5.88 eV are determined HOMO energy levels for SimCP2, CzPAMe, CzPPO, and CzPAPm, respectively. In spite of different central bridging unit, the HOMO energy level of four host materials shows moderate variation. Furthermore, those
- ²⁵ bipolar hosts (i.e., CzPPO, and CzPAPm) bearing electron deficient bridging unit tend to have shallower HOMO energy level. At first glance, this is somewhat contradictory to the general intuition. However, based on the electron density contour plots of the four host materials (Figure 5), there are little
- ³⁰ involvement of the central bridging unit in HOMO and HOMO-1. Therefore, we suggest that it is the molecular interaction of the host material in solid state that mainly decides the ground state energy level. Our suggestion is consistent with that bipolar CzPPO and CzPAPm have a stronger molecular interaction (i.e.,

35 dipolar interaction) than the non-bipoar SimCP2 and CzPAMe.



Fig. 3 X-ray diffraction spectra of the thin film samples 40 of CzPAMe, CzPPO, CzPAPm, and SimCP2 on quartz substrate.



Fig. 4 Low-energy photoelectron spectra (from AC-2) of 45 CZPAMe, CZPPO, CZPAPm, and SimCP2.

Absorption spectra (Figure 6) of solid state thin film of the host materials are used to acquire lowest photoexcitation state energy, i.e. LUMO energy gap. Once again, bipolar host ⁵⁰ materials **CzPPO** and **CzPAPm** tend to have smaller LUMO energy gap due to the stronger dipolar interaction in solid state. Accordingly, having determined HOMO energy level, LUMO energy level can thus be calculated as 2.44, 2.42, 2.35, and 2.34 eV, for **SimCP2, CzPAMe, CzPPO**, and **CzPAPm**, respectively ⁵⁵ (see data summarized in Table 1).

The order of these experimentally estimated LUMO energy levels is different from what anticipated from the structural feature of four host materials, i.e., electron deficient-bearing **CzPPO** or **CzPAPm** should have lower LUMO energy levels than that of **CzPAMe** or **SimCP2**. Our DFT calculation acquired LUMO energy levels are -1.11, -1.04, -1.32, and -1.36 eV for **SimCP2**, **CzPAMe**, **CzPPO**, **CzPAPm**, respectively. Such theoretically estimated order of LUMO energy levels fits better to he structural intuition based on electron deficient feature. Once 65 again, in condense phase, the stronger molecular interaction of bipolar host, either **CzPPO** or **CzPAPm**, alters the order of LUMO energy levels of the host materials, which are in the gas phase with isolated molecules in terms of theoretical estimation.

The Therman, Photophysical Data of SimCr2, CZPANie, CZPPO, and CZPAPin.									
Host	T_d^a	T _m ^b	T _g ^b	$\lambda_{\text{on set}}^{abs d}$	$\lambda_{\max}^{fl e}$	E_{T}^{f}	HOMO ^g	$LUMO^{h}$	T_1^i
materials	(°C)	(°C)	(°Č)	(nm, eV)	(nm)	(nm, eV)	(eV)	(eV)	(eV)
SimCP2	466	- ^c	144	347, 3.57	382	460, 2.70	6.01	2.44	3.31
CzPAMe	471	292	159	350, 3.54	405	454, 2.73	5.96	2.42	3.23
CzPPO	536	328	169	355, 3.49	408	458, 2.71	5.84	2.35	3.15
CzPAPm	473	- ^c	175	350, 3.54	426	466, 2.56	5.88	2.34	3.32

Table 1. The Thermal, Photophysical Data of SimCP2, CzPAMe, CzPPO, and CzPAPm.

^aObtained from TGA (5% weight loss). ^bObtained from DSC measurement. ^cNot observed in range of less than 350 oC ^dMeasured in thin film. ^fTriplet energy gap estimated from the highest-energy vibronic subband of emission spectra recorded in s thin film at ~10 K. ^gObtained from AC-2 low-energy photoelectron spectrometer. ^hDetermined as the lowest photoexcitation state energy from the on-set absorption energy (i.e., $\lambda_{on set}^{abs}$) in thin film absorption spectra and HOMO energy level. ⁱTriplet state energy level calculated from HOMO energy level and E_{T} .

Calculated electron density contour plots of LUMO of the host ${}_{\rm 10}$ materials are shown in Figure 7.

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Fig. 5 Calculated electron density contour plots of HOMO and ²⁰ HOMO-1 of the host materials.

Bipolar feature may be inferred from that more significant involvement of central bridging unit of CzPPO or CzPAPm than CzPAMe in LUMO. A bit surprise to us, SimCP2 possesses ²⁵ bipolar feature as well according to the substantial electron density found on the central bridging unit in the calculated LUMO contour plot (Figure 7). For SimCP2, the bipolar feature is consistent with our previous report that relatively close charge carrier mobility (i.e., hole and electron mobility) has been $_{\rm 30}$ determined by time-of-flight (TOF) tenique. 13a

With the time-gated, low temperature emission spectra acquiring (Figure 8), we are able to estimate the triplet energy gap (ET) of the host materials, which is vital for phosphorescence-based OLEDs. For blue phosphorescence ³⁵ dopant Firpic, the $E_{\rm T}$ of host materials has to be larger than





2.59 eV, which is the triplet energy gap of FIrpic based on our emission spectra (Figure 8). Particularly, the spectra were recorded on neat thin film samples instead of frozen solution. ⁴⁵ Because of the relatively high $E_{\rm T}$ of FIrpic, accurate and reliable $E_{\rm T}$ estimation can assure the sustainability of the host materials for blue phosphorescence dopant and that can be only achieved from the neat thin film sample rather than frozen solution. We have already demonstrated that there is always a red-shifting in 50 phosphorescence spectra of neat thin film compared with those of frozen solution (2-methyltetrahydrofuan is most common).³ As shown in our spectroscopic results (Figure 8 and Table 1), $E_{\rm T}$ of the four host materials is in range of 2.56 and 2.73 eV. Except for that of CzPAPm, they are all larger than 2.59 eV of blue 55 phosphorescence dopant FIrpic. Among four host materials, CzPAPm has the smallest $E_{\rm T}$ of 2.56 eV, which is very close to 2.59 eV of FIrpic and is most possible for impairing the EL efficiency of the OLEDs.

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⁵ Figure 7. Calculated electron density contour plots of LUMO of the host materials.

2.3 Solution Processed, Single-Layer, Blue Phosphorescence OLEDs.

- ¹⁰ To test the viability of four host material for solution processed, single-layer blue phosphorescent dopant FIrpic, we have fabricated a series of OLEDs: ITO/PEDOT:PSS(65 nm)/host:cohost:FIrpic (95-x:x:5, ~70 nm)/CsF(2 nm)/Al (100 nm), where x is four different weight ratio 0, 15, 30, and 50% of the OXD-7 co-
- ¹⁵ host for each of four host materials. Intentionally, we did not vacuum-thermal deposit a triplet exciton-confining (hole-blocking) or electron-transporting layer after the solution processed active single layer. In addition, by varying the co-host weight ratio from nil to 50%, we are able to quest the bipolar
 ²⁰ charge transport feature of the host materials. Table 2 summarizes the EL characteristics data; EL spectra and current
- density dependent EL efficiency (in unit of cd/A and lm/W) are plotted in Figure 9.
- In general, regardless of which host materials, all devices ²⁵ show an increasing trend on the EL efficiency (either cd/A or lm/W) in parallel with the weight ratio of OXD-7 co-host. Except for SimCP2, devices reach the highest maximum current efficiency of 9.2, 10.6, 12.2, 8.15 cd/A for SimCP2, CzPAMe, CzPPO, and CzPAPm, respectively, with OXD-7 co-host ratio
- ³⁰ of 50%. OXD-7 co-host weight ratio of 30% is the best condition for SimCP2 devices. In terms of reducing driving voltage, OXD-7 co-host is very effective for all host materials. Surveying our device data, it is easy to see that CzPPO devices are special because of relatively small variation of EL efficiency (both cd/A
- ³⁵ and lm/W) with varied weight ratio of OXD-7 co-host (Figure 9). With or without OXD-7 co-host, CzPPO devices outperform others in low turn-on voltage (Von) and high EL efficiency, either cd/A or lm/W (Table 2). Particularly, without OXD-7 cohost, CzPPO device is the best in terms of device brightness,
- ⁴⁰ current density, or low driving voltage (Figure 10). CzPPO is the only host material enables devices with driving voltage less than 15 V in achieving 1000 cd/m2 brightness without OXD-7 co-host in the active layer. Without OXD-7 co-host, current efficiency of CzPPO device reaches 9.32 cd/A, which is far better than
- ⁴⁵ 1.34~3.43 cd/A of devices based on the other three host materials. To the best of our knowledge, 9.32 cd/A (corresponding to 4.97

Im/W) is probably the best of FIrpic OLEDs that are fabricated with solution processed small molecular host without including OXD-7 co-host and no ETL after the active single layer. We so attribute such unique features of **CzPPO** devices mostly to the bipolar feature of **CzPPO** host material, which is an arylphosphine oxide-containing compound well known for the bipolar charge transport feature.





able 2. Electroluminescence Characteristics of Single-layer Firpic OLEDs Based on Four Host Materials.							
Host	OXD-7 ratio (%)	V_{on}, J, V (V, mA/cm ² , V) ^a	L_{max} , ^b Voltage at L_{max} (cd/m ² , V)	$\eta_{\rm C}^{\rm c}$ (cd/A)	η_P^d (lm/W)	CIE (x, y) ^e	
-	0	7.2, 35, 11.1	3293, 15.0	3.43, 3.52, 2.89	1.42, 1.24, 0.82	(0.15, 0.35)	
Sim CD2	15	5.7,47, 10.1	1582, 12.5	3.58, 3.58, 2.13	1.79, 1.6, 0.68	(0.15, 0.33)	
SIMCP2	30	5.0,11.7, 7.8	3775, 11.5	9.2, 5.64, 9.08	2.64, 2.8, 3.67	(0.14, 0.30)	
	50	5.0, 19.1, 9.0	1479, 12.5	6.29, 3.28, 5.55	3.85, 1.62, 1.98	(0.15, 0.33)	
	0	7.2, 65.7,12.8	1344, 15.0	1.34, 0.98, 0.69	0.56, 0.31, 0.19	(0.14, 0.30)	
C-DAMa	15	5.2, 22.7,8.8	2441, 11.5	6.61, 6.02, 4.72	3.07, 2.77, 1.68	(0.15, 0.34)	
CZFAMe	30	5.2, 11.6,8.2	3207, 11.5	8.80, 7.40, 8.61	3.45, 3.87, 3.30	(0.15, 0.34)	
	50	5.6, 12.7, 8.9	2839, 12.5	10.6, 10.02, 9.61	4.90, 4.81, 3.45	(0.16, 0.39)	
	0	4.5, 12.6, 7.1	6498, 11.5	9.32, 6.14, 9.02	4.97, 3.28, 3.98	(0.15, 0.35)	
CaDDO	15	5.0, 9.1, 7.5	4382, 11.5	10.4, 9.02, 9.64	5.13, 4.93, 3.98	(0.15, 0.34)	
CZITO	30	4.6, 9.6, 7.2	3803, 10.5	11.0, 9.28, 10.5	5.30, 4.91, 4.61	(0.15, 0.34)	
	50	4.6, 8.6, 8.3	3149, 12.5	12.2, 9.47, 11.46	5.38, 4.87, 4.30	(0.16, 0.39)	
	0	8.7, 54.8, 13.1	1814, 17.0	2.82, 2.75, 1.81	0.93, 0.82, 0.44	(0.15, 0.36)	
CaDADm	15	5.8, 23.8, 8.9	2344, 11.5	5.26, 4.72, 4.58	2.20, 2.13, 1.63	(0.15, 0.35)	
	30	5.1, 16.7, 8.0	3247, 10.5	6.70, 4.93, 6.52	3.12, 2.39, 2.60	(0.15, 0.34)	
	50	5.4, 12.8, 8.9	3162, 12.5	8.15, 2.61, 8.02	2.87, 1.21, 2.85	(0.17, 0.40)	

Т	able 2. Electr	oluminescence	Characteristics of S	ingle-layer F	Irpic OLEDs	Based on Four	Host Materials.

^aTurn-on voltage of 10 cd/m² (V_{on}); current density (J) and voltage at 1000 cd/m². ^bMaximum luminance. ^cMaximum current efficiency, current efficiency at 100 and 1000 cd/m², respectively. ^d Maximum power efficiency, power efficiency at 100 and 1000 cd/m², 5 respectively. ^e Measured at ~200 cd/m².



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Figure 9. Current density dependency of current efficiency and power efficiency of **CzPAMe**, **CzPPO**, **CzPAPm**, and **SimCP2** hosted devices with varied ratio of OXD-7 co-host. Corresponding EL spectra of each device were recorded at~200 cd/m².



Fig. 10 Voltage dependency of current density (top) and brightness (bottom) of **CzPAMe**, **CzPPO**, **CzPAPm**, and **SimCP2** hosted devices without OXD-7 co-host.

3. Conclusion

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By utilizing amorphous glass enabling bis-[3,5-di(9H-carbazol-9yl)phenyl] structural moiety of previously known, solution processable **SimCP2**, we have successfully developed three new 15 host materials, **CzPAMe**, **CzPPO**, and **CzPAPm**. We have physically characterized (by DSC and XRD) the amorphous feature of the host materials in thin film or solid state. Regarding the energy levels, particularly the solid state triplet energy gap was determined by time-gated, low temperature emission

- ²⁰ spectroscopy on thin film samples and they are 2.73, 2.71, and 2.56 eV for CzPAMe, CzPPO, and CzPAPm, respectively. Except for CzPAPm, they are all proper host materials for blue phosphorescence dopant FIrpic in the fabrication of OLEDs considering triplet energy gap. With or without OXD-7 co-host
- ²⁵ material, single-layer, CzPAMe, CzPPO, or CzPAPm hosted FIrpic OLEDs were successfully fabricated via solution process. In this study, SimCP2 hosted device was included for comparison. From the acquired device data, we have demonstrated that CzPPO outperforms other host materials with

³⁰ low turn-on voltage, high brightness, high current density, and high EL efficiency. We attribute the superior CzPPO OLED performance to the bipolar charge transport feature of CzPPO host material. Without OXD-7 co-host and without vacuumthermal deposited ETL, CzPPO OLED exhibits EL efficiency as ³⁵ high as 9.32 cd/A (~5 lm/W), which is one of the best among FIrpic devices, using small molecular host material, fabricated by solution process, without co-host material or ETL.

4. Experimental

40 4.1 General Information

¹H and ¹³C NMR spectra were recorded on a Bruker AV-400 MHz or AV-500 MHz Fourier transform spectrometer at room temperature. Elemental analyses (on a Perkin-Elmer 2400 CHN elemental analyzer), matrix-assisted laser desorption/ionization

- ⁴⁵ time-of-flight (MALDI-TOF), or fast atom bombardment (FAB) mass spectroscopy (MS) were performed by the Elemental Analyses and Mass Spectroscopic Laboratory, respectively, inhouse service of the Institute of Chemistry, Academic Sinica. Thermal decomposition temperatures (T_d 's) of the host materials
- ⁵⁰ were measured by thermogravimetric analysis (TGA) using Perkin-Elmer TGA-7 analyzer systems.Melting temperatures $(T_m$'s) and glass transition temperatures $(T_g$'s) of the host materials were measured by differential scanning calorimetry (DSC) using Perkin-Elmer DSC-6 analyzer systems. The x-ray
- ⁵⁵ diffraction measurement of solution-casting thin film was carried out by using the Philips X'Pert diffractometer equipped with an X'Celerator detector. The radiation used was a monochromatic Cu K α beam of wavelength $\lambda = 0.154$ nm. UV-visible absorption spectra were recorded on a Hewlett-Packard 8453 diode array ⁶⁰ spectrophotometer. Room temperature fluorescence spectra were
- ⁶⁰ spectrophotometer. Room temperature indorescence spectra were recorded on a Hitachi fluorescence spectrophotometer F-4500. The ionization potentials (or HOMO energy levels) of the host materials were determined by low energy photo-electron spectrometer (Riken-Keiki AC-2). To measure the triplet energy ⁶⁵ gap of a thin film sample, we established a system with a
- temperature control of Model 350 (LakeShore Company) as low as 10 K by Model 22C/350C Cryodyne Refrigerators (Janis Research Company) and a tunable laser with excitation wavelengths of 213, 266,355, 532, and 1064 nm (Brilliant B 70 laser, Quantel Company), which is couple to a time-delay controller of LP920 flash photolysis spectrometer (Edinburgh Instrument).

4.2 Computational studies.

The molecular structures of CzPAMe, CzPPO, CzPAPm, and SimCP2 were optimized by applying density functional theory (DFT) with the hybrid B3LYP functional and 6-31G* basis set. 5 With the optimized structure, calculations on the electronic ground states of CzPAMe, CzPPO, CzPAPm, and SimCP2 were processed using DFT with the hybrid B3LYP functional and 6-31G* basis set.¹⁴ The singlet excited states of the four host materials were studied with time-dependent density functional ¹⁰ theory (TDDFT) by using the hybrid B3LYP functional.¹⁵ All calculations were preformed with a developmental version of O-Chem.¹⁶

4.3 OLED Fabrication and EL Characterization.

- 15 The ITO substrate was purchased from Buwon with sheet resistance around 25 Ω /sq and thickness of 100 nm. The hole transport layer, Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) (CH8000), was purchased from Sigma-Aldrich. The OXD-7 electron transport 20 layer and FIrpic blue phosphorescent dopant were obtained commercially from either Sigma-Aldrich or Lumtec. The new small molecule hosts CzPAMe, CzPPO, and CzPAPm were synthesized according to a procedure reported herein. The indium tin oxide (ITO) substrates were pre-coated with the PEDOT:PSS 25 hole transporting layer (HTL) and baked in the air at 150 °C for 10 min. We would change ratios between each host (take one of hosts from SimCP2, CzPAMe, CzPPO, and CzPAPm) and
- OXD-7 to optimize hole and electron transport. The ratios of OXD-7 were x=0, 15, 30, and 50% and the hosts were (95-x)%, 30 respectively. Blends of host (SimCP2, CzPAMe, CzPPO, or CzPAPm), OXD-7, and FIrpic in chlorobenzene were spincoated on ITO/PEDOT:PSS. The active layer was then annealed
- at 90 °C for 30 min. After spin-coating active single-layer, an ultrathin CsF (2 nm) interfacial layer and then aluminum cathode 35 (100 nm) were vacuum- thermal deposited.

A surface profiler (Dektak 150 Veeco) was used for calibrating the thickness of HTL and active layer. After the deposition of cathode, the devices were hermetically sealed with glass and UV-cured resins in a glove box (O2 and H2O 40 concentration below 0.1 ppm). The device active area was 0.04 cm² was defined by self-made shadow mask applied in the cathode deposition. Current density and voltage characteristics were measured by a dc current/voltage source meter (Keithley 2400), and the device brightness (or electroluminance, cd/m^2), EL

45 spectra, corresponding 1931 $\text{CIE}_{x,y}$ chromaticity was monitored and recorded with a spectrophotometer (PR650; Photo Research).

4.4 Synthesis.

- All chemicals were purchased from Aldrich, Alfa Aesar, Acros, 50 and TCI Chemical Co., and they were used without further purifications. Solvents such as dichloromethane (CH₂Cl₂), chlorobenzene, terrahydrofuran (THF), N,N-dimethylformamide (DMF) and toluene and were distilled after drying with appropriate drying agents. The dried solvents were stored over 55 4Å molecular sieves before usage. 9,9'-(5-Bromo-1,3-
- phenylene)bis(9H-carbazole) (BrmCP) and 1,3-Diiodo-5nirtobenzene were synthesized by procedures reported

previously.^{17,18} 2-Iodopyrimidine was smoothly prepared from reacting 2-chloropyrimidine with 57% hydriodic acid.¹⁹

9,9'-(5-Nitro-1,3-phenylene)bis(9H-carbazole)

60 (NO₂mCP). 1,3-Diiodo-5-nirtobenzene (10.0 g, 26.7 mmol) was added to a dried DMF solution (100 mL) containing carbazole (9.8 g, 58.7 mmol), potassium carbonate (8.1 g, 58.7 mmol), copper(I) iodide (11.2 g, 58.7 mmol), and 18-crown-6 (1.4 g, 5.3 65 mmol). The mixture was heated to 155 °C for 24 hours under nitrogen atmosphere. After cooling, the reaction mixture was poured on ice and the resulting solid material was filtered. The solid was dissolved in dichloromethane and dried over anhydrous MgSO4. The solution was evaporated till dryness under reduced The product was subjected to flash column 70 pressure. chromatography (silica gel, dichloromethane/hexanes: 1/4) for purification. Yield: 78% (9.4 g). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 8.55 (d, J = 1.6 Hz, 2H), 8.19 (t, J = 2.0 Hz, 1H), 8.15 (d, J= 8.0 Hz, 4H), 7.54 (d, J = 8.4 Hz, 4H), 7.47 (t, J = 7.6 Hz, 4H), ⁷⁵ 7.35 (t, J = 7.6 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 150.86, 141.08, 140.37, 127.01, 124.49, 121.70, 121.122, 120.28, 110.91, 109.66. MALDI-MS: calcd MW, 453.15, m/e = 454.16 $(M+H)^{+}$.

3,5-Di(9H-carbazol-9-yl)aniline (NH2mCP). NO2mCP 80 (10.0 g, 22.1 mmol) was added to ethanol (200 mL) containing tin(II) chloride dihydrate (19.9 g, 88.4 mmol). The mixture was heated to reflux for 12 hours. After cooling, the reaction mixture was poured on ice and alkalized with sodium hydroxide solution 85 until basic conditions were reached. The basic solution was extracted with dichloromethane and dried over anhydrous MgSO₄. The solution was evaporated till dryness under reduced The product was subjected to flash column pressure. chromatography (silica gel, dichloromethane/hexanes: 2/3) for ⁹⁰ purification. Yield: 75% (7.0 g). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 8.12 (d, J = 7.7 Hz, 4H), 7.56 (d, J = 8.2 Hz, 4H), 7.42 (t, J = 7.8 Hz, 4H), 7.27 (t, J = 7.5 Hz, 4H), 7.16 (s, 1H), 6.96 (d, J = 1.2 Hz, 2H), 4.10 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 149.28, 140.82, 140.27, 126.24, 123.71, 120.56, 120.31, 115.35, 95 112.29, 110.22. MALDI-HRMS: calcd MW, 424.1814, m/e = 424.1818 (M+H)⁺.

Bis(3,5-di(9H-carbazol-9-yl)phenyl)amine (CzPA).

Under dry nitrogen atmosphere, a mixture of BrmCP (3.5 g, 7.2 100 mmol), NH₂mCP (3.0 g, 7.1 mmol), cesium carbonate (2.5 g, 7.8 mmol), palladium acetate (0.04 g, 0.18 mmol), P(t-Bu)₃ (0.17 mL, 0.71 mmol), and dry xylenes (40 mL) was heated at 120 °C for 20 hours. The reaction was quenched by an excess amount of saturated sodium chloride solution. The solution was extracted 105 with dichloromethane. The organic solution was dried over anhydrous MgSO₄. After the removal of drying agent, the solution was evaporated till dryness. The product was subjected to purification by flash column chromatography (silica gel, dichloromethane/hexanes: 2/3). Yield: 73% (4.3 g). ¹H NMR 110 (400 MHz, CDCl₃): δ [ppm] 8.16-8.12 (m, 8H), 7.56-7.52 (m, 12H), 7.44 (s, 2H), 7.29-7.23 (m, 16H), 6.35 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 145.04, 140.78, 140.61, 126.38, 123.84, (2×)120.60, 118.59, 115.17, 109.97. MALDI-HRMS:

calcd MW, 830.3283, $m/e = 830.3279 (M+H)^+$.

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Bis(3,5-di(9H-carbazol-9-yl)phenyl)(phenyl)phosphine

- oxide (CzPPO). To a dry THF solution (40 mL) containing BrmCP (2.0 g, 4.1 mmol) was added *n*-BuLi (1.8 mL, 4.5 mmol, 2.5 M in hexane) slowly at 78 °C. The mixture was stirred for 1 ⁵ hour under nitrogen atmosphere. After the slow addition of dichloro(phenyl)phosphine (0.36 g, 2.0 mmol), the reaction solution was kept at 78 °C for 1 hour. The reaction mixture was then warmed up to room temperature and stirred overnight. 2N HCl solution was added to the reaction solution. The solution was evaporated till dryness under reduced pressure. The solution was dissolved in dichloromethane (20 mL) and to the solution was added 30% aqueous H₂O₂ (6 mL). The mixed solution was then extracted for 6 hours at room temperature. The solution was then extracted
- ¹⁵ with dichloromethane, dried over MgSO₄. The solution was evaporated till dryness under reduced pressure. The product was subjected to flash column chromatography (silica gel, dichloromethane) for purification. Yield: 60% (1.1 g). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 8.20 (d, J = 1.6 Hz, 2H), 8.17 (d, J =
- ²⁰ 1.6 Hz 2H), 8.15-8.10 (m, 8H), 8.08 (s, 2H), 8.07-8.01 (m, 2H), 7.69-7.64 (m, 3H), 7.47-7.42 (m, 8H), 7.31-7.26 (m, 16H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 140.55 (d, J = 16.1 Hz, 4C), 140.29, 136.60 (d, $J_{PC} = 101.6$ Hz, 2C), 133.33, 132.22 (d, $J_{PC} =$ 9.9 Hz, 2C), 131.02 (d, $J_{PC} = 106.0$, 1C), 129.48 (d, $J_{PC} = 12.5$ ²⁵ Hz, 2C), 128.55, 128.48 (d, $J_{PC} = 10.3$ Hz, 4C), 126.62, 124.08, 121.10, 120.76, 109.59. MALDI-TOF MS: calcd MW, 938.3, m/e= 939.3 (M+H)⁺. Anal. Found (calcd) for C₆₆H₄₃N₄OP : C 84.34 (84.42), H 4.69 (4.62), N 5.85 (5.97).

30 **3,5-Di(9***H***-carbazol-9-yl)-N-(3,5-di(9***H***-carbazol-9-**

- yl)phenyl)-N-methylaniline (CzPAMe). CzPA (4.5 g, 5.4 mmol) was fully dissolved in dried N,N-dimethyl formamide (60 ml) under nitrogen atmosphere. Sodium hydride (0.24 g, 5.9 mmol, 60% dispersion in mineral oil) was slowly added, and the ³⁵ obtained mixture was stirred for 30 minutes at room temperature. Then, iodomethane (1.0 g, 7.0 mmol) was added and the reaction solution was heated at 60 °C for 2 hours. The solution was poured into ice water to terminate the reaction and any NaH left over. After filtration, the isolated product was subjected to purification ⁴⁰ by flash column chromatography (silica gel, diale.amethyle
- dichloromethane/hexanes: 1/5). Yield: 88% (4.0 g). ¹H NMR (400 MHz, CDCl₃): δ [ppm] 8.09 (d, 8H), 7.50 (sd, 4H), 7.47-7.45 (m, 8H), 7.41 (t, 2H), 7.25-7.20 (m, 16H), 3.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ [ppm] 150.90, (2×)140.66, 126.44,
- ⁴⁵ 123.87, 120.63, 120.61, 118.93, 117.88, 110.00, 41.04. MALDI-TOF MS: calcd MW, 843.34, m/e = 844.3 (M+H)⁺. Anal. Found (calcd) for C₆₁H₄₁N₅: C, 86.75 (86.81); H, 4.93 (4.90); N, 8.38 (8.30).

50 N,N-Bis(3,5-di(9H-carbazol-9-yl)phenyl)pyrimidin-2-

- **amine (CzPAPm).** CzPA (2.0 g, 2.4 mmol) was added to a dichlorobenzene solution (20 mL) containing 2-iodopyrimidine (0.65 g, 3.1 mmol), potassium carbonate (0.4 g, 2.9 mmol), copper powder (0.2 g, 3.1 mmol) and 18-crown-6 (0.13 g, 0.5 mmol). The mixture was heated to 180 eC for 24 hours under
- ⁵⁵ mmol). The mixture was heated to 180 oC for 24 hours under nitrogen atmosphere. After cooling to room temperature, the reaction solution was filtered. The resulting solid mixture was redissolved in dichloromethane and the filtration removed the

insoluble metal and inorganic salt. The dichloromethane solution was dried over anhydrous MgSO4. The solution was evaporated till dryness under reduced pressure and subjected to flash column chromatography (silica gel, dichloromethane/hexanes: 1/4) for purification. Yield: 65% (1.4 g). ¹H NMR (300 MHz, CDCl₃): δ [ppm] 8.59 (d, 2H), 8.06 (d, 8H), 7.72 (s, 4H), 7.68 (s, 2H), 7.57 65 (d, 8H), 7.30-7.20 (m, 16H), 6.93 (t, 1H). ¹³C NMR (100 MHz, CDCl₃) : δ [ppm] 162.04, 158.42, 146.73, 140.49, 140.12, 126.45, 123.93, 123.87, 121.71, 120.72, 120.65, 115.25, 110.12. MALDI-TOF MS: calcd MW, 907.34, *m/e* = 908.4 (M+H)⁺. Anal. Found (calcd) for C₆₄H₄₁N₇ : C 84.49 (84.65), H 4.52 (4.55), N 10.88 70 (10.80).

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