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Solution-Processed Thermal-Stable Amorphous Films of Small Molecular Hole Injection/Transport Bi-functional Materials and its Application in High Efficient OLEDs

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A series of novel triphenylamine-based small molecular hole transport materials (HTMs) are reported for solution processed organic light-emitting devices (OLEDs). The character of this series of HTMs, denoted as TPD(BTPA)_n (n=1,2,4) is connecting the flexible moieties of butadiene bridged triphenylamine (BTPA) to the *N*,*N*,*N'*,*N'*-tetraphenyl-[1,1'-biphenyl]-4,4'-diamine(TPD). The glass transition temperature and crystallization temperature (T_g and T_c) showed an proportional relationship with the number of BTPA moieties. The T_g of TPD(BTPA)₄ can be up to 125.5 °C, which is the higher than most of reported small molecular HTMs (T_g : 54°C-116°C). The TPD(BTPA)₄ spincoated film showed an outstanding thermal stability which maintained amorphous even annealed with 110°C, for 48 h. This indicated the break of planar molecular structure with BTPA moieties can suppress the intermolecular stacking. The solution processed OLEDs with 8-Hydroxyquinoline aluminum (Alq₃) as emission and electron transport layer showed high stability at high operation current density > 400 mA cm⁻²), which is higher than the maximum current efficiency of most evaporation and solution processing OLEDs in identical structure.

1 Introduction

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3 Organic light-emitting devices (OLEDs) are regarded as the
4 next generation flat-panel displays because of advantages,
5 such as portable, full colored, glare free, flexible, short
6 response time, wider viewing angles *etc.*¹⁻³

7 To date, there mainly are two issues need to be solved 8 about small molecular OLEDs. First, the ultra-thin films in 9 OLEDs are typically fabricated by vacuum evaporation (VE), 10 which has demerits of high energy consuming, waste of 11 materials and unfriendly to environment.⁴ Secondly, the 12 charge transfer and injection require homogeneous interface 13 and layer, which means that the organic semiconductor film 14 should be amorphous form.⁵

15 The first problem can be solved through solution 16 processing techniques such as layer-by-layer spin coating 17 and ink jet.⁶ While, those techniques are mainly applied in 18 the polymer materials. However, the research on structure-19 functional relationship of small molecular materials is more 20 mature than the polymers.⁷ Functional characteristics such

21 as energy level of the polymers depends on not only the unit
22 structure, but also the length of polymer chain which is not a
23 constant.⁸⁻¹⁰ It is believed that the design, synthesis and
24 purification of small molecular materials are more
25 convenient.

26 For the second problem, the crystallization of small 27 molecular materials during film-forming in the solution 28 process and operating at high temperature are main obstacles for its application in OLEDs.¹¹⁻¹⁴ The low glass 29 transition and crystallization temperatures (T_a and T_c) lead to 30 31 formation of polycrystalline in films resulting from thermal 32 stress.¹⁵ In the research reported by Douglas E Loy *et. al.*, the 33 OLED with *N*,*N*,*N*',*N*'-tetraphenyl-[1,1'-biphenyl]-4,4'-diamine 34 (TPD) and N,N'-diphenyl-N,N'-bis-(1-naphthyl)-1,1'-biphenyl-35 4,4'-diamine (NPD) as HTL showed irreversible failure when heated at 100 and 110 $^\circ C$ due to crystallization.¹⁶ As reported, 36 37 the T_q and T_c of organic semiconductor are determined by the molecular structure. Larger molecular volume resulted in 39 higher T_a .¹⁷⁻¹⁹



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1 In this work, we designed and synthesized three new 2 HTMs based on the TPD, which has a HOMO level of -5.30 eV 3 and a T_q of 69°C.^{20, 21} The TPD is modified with different 4 numbers of 4-(penta-1,3-dien-1-yl)-N,N-diphenylaniline 5 (BTPA) moieties (Fig. 1) to suppress the formation of crystal 6 in film through reducing the molecular rigidity and breaking 7 the molecular planarity. Comparing with triphenylamine, BTPA moieties can be introduced simply with witting-honor 8 9 reaction, which reaction condition is much milder than 10 Ullmann reaction or carbon-carbon coupling reaction.^{22, 23} In 11 addition, the BTPA moiety has larger volume than 12 triphenylamine, which are benefit for suppressing 13 intermolecular stacking in solid states. With considering 14 above reasons, we chose BTPA moieties to modify the TPD 15 The molecular structures are shown in Fig. 1 and denoted as 16 TPD(BTPA)_n (n=1,2,4). The crystallization during the spin-17 coating film forming process and the thermal stability of 18 these films are investigated by X-ray diffraction (XRD), 19 attenuated total reflectance fourier transform infrared 20 spectroscopy (ATR-FTIR) and differential scanning 21 calorimetry (DSC) measurements. The thermal stability 22 increases gradually with the increasing number of BTPA 23 moieties connected to the TPD. Notably, the spin-coating 24 film of TPD(BTPA)₄ can maintain amorphous even after 25 annealed at 110 $^{\circ}$ C for 48 h. At present, the reported HTM 26 films crystallized with annealing at < 95 °C for < 2 h, such as 27 N,N,N',N'-tetraphenylbenzidine (TPB), N,N,N',N'-tetra-p-28 tolyl-benzidine N,N'-di(naphthalene-1-yl)-N,N'-(TTB), 29 diphenyl-benzidine (NPB), 9,10-(2-naphthyl)anthracene (AND), 1,4-bis(phenyl-m-tolylamino) biphenyl (TPD), 1,4-30 bis(benzothiazole-vinyl) benzene (BT) et. al..²⁴⁻³⁰ 31



41 Fig. 1 Molecular structures of TPD(BTPA)_n compounds 42

43 The hole transport properties of as-synthesized HTMs 44 are evaluated in the solution processed OLEDs with the 45 structure of ITO/HTMs/Alq₃/LiF:Al. This structure with small 46 molecular HTMs (molecular weight < 6000 g mol⁻¹) has been 47 reported by many groups with maximum current efficiency 48 (*CE_{max}*) smaller than 5.7 cd A⁻¹, which are listed in **Table 5.**^{6, 11,} 49 ³¹⁻⁴⁴

50 In this work, the Device-TPD(BTPA)₄ can exhibit the 51 CE_{max} of 5.83 cd A⁻¹ at the operation current intensity larger 52 than 400 mA cm⁻². This CE_{max} is highest among the reported 53 small molecular OLED (molecular weight < 6000 g mol⁻¹) in 54 identical structure no matter fabricated with evaporation or 55 solution processing.^{6, 11, 31-44}

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57 Results and Discussions

58 Synthesis and Characterizations

60 The TPD(BTPA)_n (n=1,2,4) are synthesized by formylation and 61 Wittig-Honor reactions starting with TPD (**Scheme 1**).⁴⁵

62 The BTPA moieties were synthesized from 4-(di-p-63 tolylamino)benzaldehyde (Me-TPA-CHO) by formylation and 64 Wittig-Honor reactions. The total yield of 3-(4-(di-p-65 tolylamino)phenyl)prop-2-en-1-ol (Me-TPA-CH=CH-CH₂OH) was 92.0%. The aldehybe groups were introduced on the 66 67 TPD with different numbers. Then the BTPA moieties were 68 introduced on the $TPD(CHO)_n$ (n=1,2,4) by Witting-Honor 69 reaction. The yields were 72.3% (TPD(BTPA)₁), 68.2% 70 $(TPD(BTPA)_2)$ and 63.4% $(TPD(BTPA)_3)$, respectively. The 71 TPD(BTPA)_n(n=1,2,4) compounds are soluble in 72 methylbenzene, chlorobenzene, tetrahydrofuran and 73 chloroform, etc. The well-defined structures of all novel compounds are adequately verified by ¹H NMR, mass 74 75 spectrometry and IR spectroscopy (see details in the ESI).

The decomposition temperatures (T_d , which correspond 77 to 5% weight loss) of TPD(BTPA)_n (n=0-4), recorded by 78 thermal gravity analysis (TGA), are 411°C (TPD(BTPA)₁), 425°C 79 (TPD(BTPA)₂), and 448°C (TPD(BTPA)₄), respectively (**Fig. S10**, 80 Supporting Information). With the increase of *n* in 81 TPD(BTPA)_n, the T_d of as-synthesized HTMs increase 82 gradually.

84 Scheme 1 Synthetic routes of TPD(BTPA)_n (n=1,2,4).



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1 Photophysical and Electrochemical Properties

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3 UV-vis absorption spectra of TPD(BTPA)_n(n=0,1,2,4) are
4 shown in Fig. 2 and relative data are summarized in Table 1.
5 Cyclic voltammograms of TPD(BTPA)_n (n=0,1,2,4) are shown
6 in Fig. S11 (ESI).



16 Fig. 2 Normalized absorption spectra of TPD(BTPA)_n 17 (n=0,1,2,4) in chlorobenzene solution with concentration of 18 1.0×10^{-5} M (a) and spincoating films (b).

19 20 As shown in the **Fig. 2a**, the absorption peaks in the 21 wavelength region 280-310 nm can be assigned to the n- π 22 transition of the TPA moiety. The absorption peaks in the 23 region 375-450 nm can be assigned to the intramolecular 24 charge transfer (ICT) of π - π * transition. There is an obvious 25 red shift of ICT peaks and decrease of energy gap (E_g) with 26 the increasing number of BTPA moiety. The absorption 27 spectrum of each TPD(BTPA)_n compound in solid state film 28 reveals no red-shift compared to that in chlorobenzene 29 solution, indicating that no significant aggregation or 30 crystallization occurs in the films of TPD(BTPA)_n(n=1,2,4).⁴⁶

31 As shown in **Table 1**, with the increase of number *n* in 32 TPD(BTPA)_n, the HOMO level increases from -33 5.30eV(TPD(BTPA)₁) to -5.12eV(TPD(BTPA)₄), which exhibits 34 the HOMO level can be modified through changing the 35 number of BTPA moiety. The HOMO level of TPD(BTPA)₄ 36 matches the work function of ITO (-4.80 eV) quite well, 37 which could benefit the charge injection without the 38 assistant of the normally-used hole injection layer (HIL) 39 poly(3,4-ethylene-dioxythiophene) poly(styrene sulfonate) 40 (PEDOT:PSS).⁴⁷

58 Thermal Properties of TPD(BTPA)_n

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62 As shown in **Fig. 3**, the T_g , T_c and T_m of TPD(BTPA)_n 63 (n=0,1,2,4) increase gradually with the increasing number of 64 BTPA moieties (**n**). The T_g and T_c of TPD(BTPA)₄ are higher 65 than most of common used small molecular HTMs.²⁹⁻³⁴ The 66 corresponding enthalpies of crystallization are 41.51 Jg⁻ 67 ¹(TPD), 44.26 Jg⁻¹(TPD(BTPA)₁), 31.5 Jg⁻¹(TPD(BTPA)₂) and 68 28.26 Jg⁻¹(TPD(BTPA)₄), respectively. This indicates that the 69 TPD and TPD(BTPA)₁ have higher crystallization tendency 70 than TPD(BTPA)₂ and TPD(BTPA)₄.⁶ Apparently, the BTPA 71 moieties showed a capability for improving thermal stability, 72 while only one BTPA moiety was not enough for changing 73 crystallization property noticeably.



77 Fig. 3 DSC curves of TPD(BTPA)_n (n=0,1,2,4) selected from 78 the heating of second loop.

	T_{d}^{a}	T_g^{b}	T_{c}^{b}	T _m ^{b)}	$\lambda_{\text{ITC}}^{c)}$	$E_g^{(d)}$	HOMO ^{e)}	LUMO ^{e)}
	(°C)	(°C)	(°C)	(°C)	(nm)	(eV)	(eV)	(eV)
TPD	375	70.1	146.7	205.7	391	3.10	-5.30	-2.20
TPD(BTPA) ₁	411	95.9	17.4	230.5	399	2.94	-5.21	-2.27
TPD(BTPA) ₂	425	112.2	188.1	247.8	407	2.82	-5.16	-2.34
TPD(BTPA) ₄	448	125.5	201.8	260.7	415	2.73	-5.12	-2.39

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Table 1. The optical, thermal properties and energy levels of TPD(BTPA)_n (n=0,1,2,4)

^{a)} Measured by TGA at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. ^{b)} T_g glass transition temperature, T_c crystallization temperature, and T_m melt point measured by DSC according to the heat-cool-heat procedure (Fig. 3). ^{c)}

Intramolecular charge transfer peak of thin films. ^{d)} Optical energy gaps calculated from the absorption thresholds from UV Vis absorption spectra of chlorobezene solutions (1.0×10⁻⁵ M). ^{e)} Measured by cyclic voltammetry.

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1 Crystallization of Spincoated Films

2 3 The amorphous films can improve charge injection and 4 transfer between different layers.⁴⁸⁻⁵⁰ It is important to find 5 out when the crystallization occurs. Therefore, we measured 6 the crystallinity of spincoated films before and after 7 annealing though X-Ray Diffraction(XRD) and Attenuated 8 Total Reflectance-Fourier Transformed Infrared 9 Spectroscopy (ATR-FTIR).

10 The XRD spectra of TPD(BTPA)_n films are shown in **Fig. 4**. 11 When the TPD(BTPA)_n (n=0,1,2,4) were spincoated on the 12 ITO substrate, the XRD patterns in the region of 0<20<5.0° 13 were same as that of ITO substrate, which indicating that all 14 these spincoated films were amorphous. The diffraction 15 peaks $(2\vartheta \approx 1.5^{\circ})$ can be observed in TPD and TPD(BTPA)₁ 16 when these films were annealed at 70°C for 24 h. The 17 diffraction peaks $(2\vartheta \approx 1.5^{\circ})$ in TPD(BTPA)₂ and TPD(BTPA)₄ 18 films appeared at annealing temperature of 100°C and 120°C, 19 respectively. As shown in **Fig. 5(B)**, for the TPD(BTPA)₄ film, 20 the XRD pattern maintained unchanged even annealed at 21 110°C for 48 h.



22 Fig. 4 X-ray diffraction patterns of films on ITO glass 23 substrate annealed from 70-140 $^{\circ}$ C for 24 h (a); annealed at 24 110 $^{\circ}$ C for 0-48 h(b)

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The crystallinity were confirmed directly by ATR-FTIR measurement.⁵¹ As shown in **Fig. 5**, for spincoated films of

28 TPD and TPD(BTPA)₁, a broad band in the wavenumber region of 900-1200 cm⁻¹, and a small band in the 29 wavenumber region of 700-800 cm⁻¹ generated after 30 annealing. The broad band can be assigned to the in-plane 31 vibration of benzene.⁵² This phenomenon generate from the 32 change of optical property after crystallization. The change 33 of ATR-FTIR spectra for TPD(BTPA)₂ and TPD(BTPA)₄ films 34 before and after annealing at 100° C are unobvious, which 35 mean the TPD(BTPA)₂ and TPD(BTPA)₄ films maintained 36 37 amorphous. For most of reported small molecular HTMs, such as TPB, TTB, NPB, AND, TPD and BT, these films cannot 38 39 maintain amorphous form with annealing > 80° C less than 2 40 h.²⁹⁻³⁴



42 **Fig.5** ATR-FTIR spectra of TPD compounds before(a) and 43 after annealing(b).



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45 Fig. 6 Crystallization process in spincoated films.

47 All the results above indicate that the crystallization 48 capability is suppressed with BTPA moieties. The 49 crystallization process does not happen during spincoating 50 process. Instead, it occurs after the film-forming process. The 51 possible process is shown in **Fig. 6**.

52 All the spincoated films are amorphous before 53 annealing. As shown in Fig. 6, we discuss the two extreme 54 situations: TPD (crystalline) and TPD(BTPA)₄ (amorphous). In 55 the case of TPD, after spincoating the TPD molecules deposit 56 on the substrate randomly and the TPD film is amorphous 57 accordingly. While, the TPD molecule tends to stack because 58 of its planarity molecular structure, low T_g and T_c , as well as 59 the large change of enthalpies after crystallization. Then, the 60 orientated aggregation (crystallization) occurs, which will 61 break the homogenous TPD films.

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In the case of TPD(BTPA)₄, the film maintains 1 2 amorphous after annealing. Compared with TPD, the 3 molecular structure of $TPD(BTPA)_4$ is nonplanar. In addition, 4 the TPD(BTPA)₄ has higher T_g , T_c and smaller change of 5 enthalpies after crystallization. These prevent the orientated 6 aggregation (crystallization) in TPD(BTPA)₄ after annealing. 7 The crystallization property of TPD(BTPA)₁ and TPD(BTPA)₂ should be between that of TPD and TPD(BTPA)₄. 8

10 Molecular Geometry

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11 12 One of the most important roles of BTPA moiety is breaking 13 the planarity of TPD. In this work, the molecular geometry 14 was applied to estimate the change of planarity. First, the 15 molecular geometries of TPD(BTPA)_n (n=0,1,2,4) were 16 optimized with Gaussian 03 program.⁵³ Then the cartesian 17 coordinates of all the atoms in each molecule were obtained 18 from above step. We put the molecule into a regular 19 hexahedron as shown in Fig. 7.

20 The L, W, H and volume of regular hexahedron are listed 21 in Table 2. Apparently, the TPD molecule is much close to a 22 plate. With the increasing BTPA moieties, the molecules of 23 TPD(BTPA)_n (n=1,2,4) are approach to cubes. This indicated 24 that, beside increasing the molecular volume, the BTPA 25 moieties can break the molecular planar effectively. This 26 change of molecular geometry greatly affect the thermal 27 stability of TPD(BTPA),, which leads to the amorphous films 28 of TPD(BTPA)₄ even after annealing at 110 $^{\circ}$ C for 48 h. 29



30 Fig. 7 Molecular geometry of TPD(BTPA)_n (n=0,1,2,4) in a 31 regular hexahedron with length, width and height of L, W 32 and H, respectively.

33

34 Table 2. Geometry Parameters of TPD(BTPA)_n (n=0, 1, 2, 4)

	L ^{a)}	W . ^{a)}	H ^{a)}	Volume ^{b)}	L:W:H ^{c)}
TPD	15	6	16	1440	2.5:1.0:2.7
TPD(BTPA) ₁	14	16	25	5600	1.0:1.1:1.8
TPD(BTPA) ₂	14	21	36	10584	1.0:1.5:2.6
TPD(BTPA) ₄	38	25	36	34200	1.52:1.0:1.44

35^{a)} Estimated by the cartesian coordinates of all the atoms after 36 geometry optimized with Gaussian 03. ^{b)} Volume = $L \times W \times H$. ^{c)}

37 Normalized with minimum value of *L*, *W* and *H*; all the units are 38 a.u.,

40 Application in OLEDs

42 One role of BTPA moiety is increasing the molecular volume 43 to suppress crystallization in films and improve the thermal 44 stability. Another role is increasing the molecular 45 conjugation by introducing the butadiene units. As discussed 46 above, with the increasing number of BTPA moieties, the 47 HOMO levels of as-synthesized HTMs slightly increases.

48 As the HOMO levels of TPD(BTPA)_n (n=0-4) are in the 49 range of -5.12 \sim -5.40 eV which are very close to the HOMO 50 level of commonly-used hole injection material PEDOT:PSS (-5.00 eV), ⁵⁴ we fabricate double-layer OLEDs using 51 52 TPD(BTPA)_n as hole injection/transport double-functional layers, Alq_3 as electron transport and emission layers, with 53 54 the device structure: $ITO/TPD(BTPA)_n$ (200 nm)/Alq₃ (70 55 nm)/LiF (0.5 nm)/Al (120 nm). The current-voltage-56 luminance (J-V-L) characteristic curves and LE-J of these 57 OLEDs are shown in Fig. 8, the parameters are listed in Table 58 **3**.



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60 Fig. 8 OLED structures(a), *J-V-L* curves (b) and *J-η* curves(c)

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As shown in Fig. 8(b) and Table 3, the ture-on 1 2 voltage(V_{op}) of Device-TPD and Device-TPD(BTPA)₁ are the 3 same, despite the HOMO level of TPD(BTPA)₁ (-5.21eV) is 4 much closer to the work function of ITO (-4.80 eV) than TPD 5 (-5.40 eV). However, compared to Device-TPD, the V_{on} 6 reduces 28% (Device-TPD(BTPA)₂) and 38% (Device-7 TPD(BTPA)₄). This indicated the smaller difference between 8 ITO work function and HOMO level of TPD(BTPA), are 9 beneficial to hole injection. 10

11 Table 3. Electroluminescence characteristics of OLEDs 12

12					
Device	V _{on} a)	L _{max} ^{b)}	CD ^{b)}	CE ^{c)}	$\mu_{h}^{d)}$
	(V)	(cd m ⁻²)	(mA cm ⁻²)	(cd A ⁻¹)	(×10 ⁻⁵ cm V ⁻¹
TPD	5.0	8152	272	2.16	140
		(17.0 V)			
TPD(BTPA) ₁	5.0	9590	334	3.17	24
		(13.9 V)			
TPD(BTPA) ₂	3.6	12281	327	4.83	15
		(13.1 V)			
TPD(BTPA) ₄	3.1	14446	455	5.83	9
		(15.2 V)			

13 ^{a)} Turn-on voltage: the voltage at the brightness of 1 cd m^{-2} ;

14^{b)} Maximum brightness and corresponding voltage in the 15 bracket;

16^{c)} Maximum current efficiency;

20

17 $^{d)}$ Measured in hole-only devices (structure: ITO/HTMs (~1 18μ m)/Al (120 nm)). Hole mobilities are determined by time-19 of-fight (TOF) method²⁹, details see **ESI Fig. S12**.

21 From the Table 3, compared with Device-TPD, the 22 maximum brightness (Lmax) increase 20% (Device-23 TPD(BTPA)₁), 50% (Device-TPD(BTPA)₂) and 80% (Device-24 TPD(BTPA)₄); the maximum current efficiency (CE_{max}) 25 increase 50%, 120% and 170% , respectively. The LUMO 26 levels of TPD(BTPA)_n (n=0-4) are in the range of $-2.10^{-2.39}$ 27 eV, which are higher than the LUMO level of Alg_3 and it 28 means that the TPD(BTPA) $_n$ (n=0-4) layer can play the role of 29 electron blocking.

Hole mobilities of TPD(BTPA)_n (n=0,1,2,4) decreased 30 31 with increasing number of BTPA moieties n. This mainly 32 result from the suppression of crystallization by BTPA 33 moieties. The electron mobility (μ_e) of Alq₃ was reported to 34 be \sim 1.1-2.3 \times 10⁻⁵ cm V⁻¹S⁻¹.²⁹ The equilibrium of electron and 35 hole transport in device-TPD(BTPA)₄ resulted higher CE than 36 other OLEDs.

37 The most interesting phenomenon is that the CE 38 increases with higher operation current in the Device-39 TPD(BTPA)₁, Device-TPD(BTPA)₂, and Device-TPD(BTPA)₄. 40 This should result from the outstanding thermal stability of 41 the TPD(BTPA)_n (n=2,4) films which can maintain amorphous 42 even at high operation current.

43 To further investigate the hole injection/transport 44 properties of TPD(BTPA)₄, we compare the performance of 45 OLEDs with and without PEDOT:PSS layer, which are 46 denoted as Device-PP-TPD(BTPA)₄ (structure: ITO/PEDOT:PSS

47 (100nm)/TPD(BTPA)₄ (200 nm)/Alq₃ (70 nm)/LiF (0.5 nm)/Al (120 nm)and Device-TPD(BTPA)₄ (device structure: 48 49 ITO/TPD(BTPA)₄ (200 nm)/Alq₃ (70 nm)/LiF (0.5 nm)/Al (120 50 nm)), respectively. The device structures, current-voltage-51 Iuminance (J-V-L) characteristic curves and current-efficiency 52 (J-7) curves are shown in Fig. 9, parameters are listed in 53 Table 4.

54 As reported, the PEDOT:PSS normally applied to 55 improve hole injection because of its HOMO level closing to 56 the work function of ITO. However, the Device-PP-57 TPD(BTPA)₄ shows a higher V_{on} (3.1 V) and a lower CE_{max} 58 (4.48 cd A^{-1}) than Device-TPD(BTPA)₄. From Fig. 9 (c), it can 59 be found that with the increasing current intensity, the S_{0} efficiency of the Device-PP-TPD(BTPA)₄ reduces obviously. $\overline{61}$ On the contrary, the Device- TPD(BTPA)₄ remains stable.



63 Fig. 9 OLED structures(a), J-V-L curves(b) and J- 7 curves(c)

65 Table 4. Electroluminscence characteristics of OLEDs

	Dovico	V _{on} a)	L _{max} ^{b)}	CD ^{c)}	CE ^{d)}	
	Device	(∨)	(cd m⁻²)	(mA cm⁻²)	(cd A ⁻¹)	
		2.1	14446	455	E 00	
	IFD(BIFA) ₄	5.1	(15.2)	400	5.65	
		$(\mathbf{p}_{\mathbf{T}},\mathbf{p}_{\mathbf{A}})^{f} \rightarrow 0$		249	1 10	
PP- IPD(BIPA) ₄		5.0	(16.1)	540	4.48	

 66^{a} Turn-on voltage: the voltage at the brightness of 1 cd m⁻²; ^{b)}

67 Maximum brightness; ^{c)} Current efficiency at the maximum

68 brightness; ^{d)} Maximum current efficiency;

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58 Conclusions

60 In this work, the novel HTMs TPD(BTPA)_n (n=1,2,4) have been 61 designed and synthesized. The BTPA moieties are introduced 62 into TPD to improve thermal stability and suppress 63 crystallization in spincoated films. The thermal stability of 64 TPD(BTPA)_n (n=0,1,2,4) have been investigated by DSC, 65 which shows gradual increases of T_g , T_c and T_m with the 66 increasing number of TBPA moieties. The spincoated film of 67 TPD(BTPA)₄ maintained amorphous form even with 110° C, 68 48 h annealing which confirmed by XRD and ATR-FTIR. The 69 OLEDs with TPD(BTPA)_n (n=0,1,2,4) as HIL and HTL showed 70 an improvement of performance with increasing the number 71 of TBPA moieties. The BTPA moieties can improve the 72 stability of OLED operated with high current. The OLED with 73 TPD(BTPA)₄ showed the highest CE_{max} compared with 74 reported small molecular (Mw<6000) HTMs with identical 75 structure no mater solution processing or vacuum deposition.

It has been reported that during spin-coating the acidity 2 of PEDOT:PSS colloidal solution can corrode ITO to dissolve 3 some In^{3+} . The In^{3+} will make the PEDOT:PSS interface 4 unstable

- 5 and obstruct the hole injection, which will diffuse to emitting
- 6 layer to form a quenching center when devices operating at high current. This should be the reason for decrease of CE_{max} 7 at higher current density in Device-PP-TPD(BTPA)₄.⁵⁵⁻⁵⁹ 8

9 In Device-TPD(BTPA)₄, both the performance and the 10 stability at high current density of OLEDs have been 11 improved. The improvement of OLED performance at high 12 operation currents should be result from the combine effects 13 of outstanding thermal stability of hole transport layer and 14 balance of electron-hole transporting in device. This confirms 15 that the TPD(BTPA)_n (n>1) can be applied as hole 16 injection/transport di-functional material to improve the 17 performance and stability of OLEDs, as well as simplify the 18 fabrication process of solution-processing OLEDs. 19

The HTMs applied in solution-processing OLEDs with 76 20 identical structure are reported. ^{6, 11, 31-44} The molecular 77 78 21 formula (MF), molecular weight (MW), HOMO level, LUMO 79 22 level, energy gap of reported HTMs and corresponding 80 23 parameters of OLEDs are listed in Table 5. All the molecular 24 structure are listed in ESI Fig. S13. 81 25

Table 5. Reported HTMs for solution-processing OLEDs with identical structure

26					U					
27 28	Componds	MF	MW	HOMO (eV)	LUMO (eV)	E _g (eV)	Device Structure	V _{on} (V)	CE (cd A ⁻¹)	J _{90%} (mA cm ⁻²)
29	^{a)} DT2 ^[6]	$C_{432}H_{300}N_{22}$	5799	-5.22	-2.60	2.62	ITO/PEDOT:PSS/DT2/Alq3/LiF:Al	2.9	2.36	5
30	^{a)} G3F2 ^[34]	$C_{242}H_{212}N_{14}$	3316	-5.4	-2.19	3.21	ITO/PEDOT:PSS/G3F2/Alq3/LiF:Al	2.6	5.63	123
31 32	^{a)} TPD(BTPA)₄ ^{c)}	C123H112N6	1782	-5.12	-2.39	2.73	ITO/TPD(BTPA) ₄ /Alq3/LiF:Al	3.1	5.83	Unobservable
33	()4	125 112 0					ITO/PEDOT:PSS/TPD(BTPA) ₄ /Alq3/LiF:Al	3.8	4.48	168
34	^{a)} G3C ^[36]	$C_{97}H_{77}N_7$	1341	-5.37	-2.01	3.36	ITO/PEDOT:PSS/G3C/Alq3/LiF:Al	3	5.11	103
35	^{a)} T4C ^[35]	$C_{96}H_{85}N_5$	1309	-5.15	-1.91	3.24	ITO/PEDOT:PSS/T4C/Alq3/LiF:Al	2.5	5.07	160
36	a)FC ^[37]	$C_{85}H_{97}N_3$	1161	-5.21	-2.39	2.82	ITO/PEDOT:PSS/FC/Alq3/LiF:Al	5.6	3.2	155
37	^{b)} TECEB ^[31]	$C_{54}H_{45}N_3$	735	-5.20	-2.40	2.80	ITO/TECEB/Alq3/Mg:Ag	3.5	3.27	120
38	^{b)} FTPD7 ^[30]	$C_{53}H_{44}N_2$	708	-5.80	-2.12	3.68	ITO/FTPD7/Alq3/LiF:Al	6.5	2.18	١
39	^{a)} TPD ^[11]	$C_{36}H_{28}N_2$	488	-5.40	-2.10	3.30	ITO/TPD/Alq3/LiF:Al	2.0	3.67	200
10	,									

40 ^{a)} Spin-coated HTMs; ^{b)} Vacuum-deposited HTMs ; ^{c)} As-synthesized HTM in this work 41

42 43 As shown in Table 5, the Device-TPD(BTPA)₄ shows the 44 highest CE_{max} which is far beyond other reported small molecular HTMs (Mw< 6000) with identical structure no 100 Acknowledgements 45 46 matter fabircated by vacuum deposition or spin-coated.^{6, 11,} ³¹⁻⁴⁴ In addition, the efficiency roll-off is unobservable in 102 and Development Program of China (863 Program, 47 48 device applying TPD(BTPA)_n (n=1,2,4) 49 transport/injection bi-functional material, which confirmed 104 Tianjin (13ZCZDGX00900) for financial support of this 50 the outstanding operation stability even at large operation 105 research. 51 current. At present, only the 1,2,3,4,5,6-hexakis(9,9-dihexyl-52 9H-fluoren-2-yl)benzene T3(CE_{max} =6.45 cd A⁻¹) showed 53 slightly higher efficiency than Device-TPD(BTPA)₄.⁴⁰ However, 106 Notes and references

54 the MW of T3 is much larger than TPD(BTPA)₄ (>4 times). Not 107 1.

- 55 a mention the V_{on} of Device-T3 (5.5 V) is much higher than 108
- 56 Device-TPD(BTPA)₄ (3.1 V). ⁴⁰ 57

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TPD(BTPA)₄ can improve the stability of OLED operated with high current and can achieve the one of the highest CE_{max} (5.83 cd A⁻¹) compared with reported small molecular (Mw<6000) HTMs in OLEDs with identical structure no mater solution processing or vacuum deposition.