Supporting Information

Isomeric Fused Benzocarbazole as a Chromophore for Blue

Fluorescent Organic Light-Emitting Diodes

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Experimental section

General information

All the reagents and solvents were procured from the commercial sources and used without further purification. The chromatographic separations were performed using silica gel (200-300 nm). The purification of all the compounds was done by column chromatography and for the final products further purification was done by temperature gradient vacuum sublimation process. The final products were confirmed by ¹H, ¹³C nuclear magnetic resonance (NMR), and mass spectrometry. The ¹H and ¹³C NMR data of the final products were recorded on 500 and 300 MHz spectrometers by using deuterated chloroform (CDCl₃) as a solvent and chemical shift is expressed in parts per million (ppm), with tetramethylsilane (TMS) as an internal standard. The instrumental tools used are Fourier transform-nuclear magnetic resonance 500 MHz (Unity Inova), Fourier transform-nuclear magnetic resonance 300 MHz (Oxford 300 NMR), cyclic-voltammetry (CV) (Ivium Tech., Iviumstat), UV-Visible absorption spectroscopy (JASCO, V-730), fluorescence spectroscopy (PerkinElmer, LS-55), mass spectroscopy (Advion, Expresion^L CMS spectrometer in APCI mode), and thermogravimetric analyzer (TGA) [Seiko Exstar 6000 (TG/DTA6100)].

Device structure and fabrication

The optimized device structure was ITO (50 nm)/ DNTPD (10 nm)/ BPBPA (40 nm)/ TNPA (10 nm)/ α -ADN: emitter (30:2%)/ TNPT (5 nm)/ ZADN (20 nm)/ LiF (1.5 nm)/ Al (200 nm). Where, ITO (indium tin oxide) is an anode, DNTPD: N^{I} , $N^{I'}$ -([1,1'-biphenyl]-4,4'-diyl)bis(N^{I} phenyl- N^{4} , N^{4} -di-*m*-tolylbenzene-1,4-diamine) is a hole injection layer, BPBPA: N^{4} , N^{4} , $N^{4'}$, $N^{4'}$ tetra([1,1'-biphenyl]-4-yl)-[1,1'- biphenyl]-4,4'-diamine is a hole transport layer, TNPA (tris(4-(naphthalen-1-yl)phenyl)amine) is an electron blocking layer, α -ADN as host, α -ADN: **NIDPA-1**/ **NIDPA-2** is an emitting layer (EML), TNPT (2,4,6-tris(4-(naphthalen-1-yl)phenyl)-1,3,5-triazine) is a hole blocking layer, ZADN (2-(4-(9,10-di(naphthalen-2-yl)anthracen-2-yl)phenyl)-1-phenyl-1*H*-benzo[*d*]imidazole) is an electron transport layer. The emitting layer was the emitter doped α -ADN layer.

The OLED devices were fabricated by using a transparent glass substrate with 50 nm thick ITO. The cleaning of the ITO glass substrate was done using acetone and deionized water by ultrasonic treatment. The deposition of all the layers was carried out by vacuum thermal evaporation under the pressure of $3.0 \times 10-7$ torr. The deposition rates for the organic layers, LiF, and Al were controlled at 0.1, 0.01, and 0.5 nm/s, respectively. The encapsulation on glass was performed under the inert atmosphere (N₂ atmosphere) to protect the device from O₂. All the device measurements were performed at ambient temperature. The electrical and optical characterizations of the devices were carried out by using Keithley 2400 Source Meter and CS 2000 spectroradiometer, respectively.

Synthesis of target molecules

Synthesis of 7-(2-bromophenyl)-7*H*-benzo[*c*]carbazole (1)

In the three-neck round bottom flask, 7*H*-benzo[*c*]carbazole (**2**) (5 g, 23 mmol, 1 equiv.), 1-bromo-2-fluorobenzene (7.8 g, 46 mmol, 2 equiv.), cesium carbonate (Cs2CO3) (15 g, 46 mmol, 2 equiv.) were added in 20 mL of *N*,*N*-dimethyl formamide (DMF). The reaction was refluxed for 6 h and the progress of the reaction was monitored in TLC. After completion, the reaction mass was cooled to room temperature and poured into a mixture of 200 mL of water and 50 mL of DCM. After stirring for 30 min the organic phase was separated and the aqueous phase was further extracted in DCM (3 x 20 mL). All the organic layers were combined and washed with water (2 x 25 mL) and dried over anhydrous MgSO₄ and concentrated under vacuum. The crude product thus obtained was purified by column chromatography using hexane: DCM (95:5) to give the desired product (**1**) as white solid. Yield (8.2 g, 96%). MS- calcd. for C₂₂H₁₄BrN- 372.26; found- 373.13.

Synthesis of benzo[b]indolo[1,2,3-lm]carbazole [NI-1] and benzo[c]indolo[3,2,1-jk]carbazole [NI-2]

In the three-neck round bottom flask, 7-(2-bromophenyl)-7*H*-benzo[*c*]carbazole (1) (5 g, 13 mmol, 1 equiv.), palladium (II) acetate $[Pd(OAc)_2]$ (0.6 g, 2.7 mmol, 0.2 equiv.), triphenylphosphine (PPh₃) (1.4 g, 5.4 mmol, 0.4 equiv.), benzyl triethyl ammonium chloride (3.1 g, 13 mmol, 1 equiv.), potassium carbonate (K₂CO₃) (9.3 g, 67 mmol, 5 equiv.) were added in 25 mL of *N*,*N*-dimethyl acetamide (DMAc). The reaction mixture was refluxed for 6 h under nitrogen atmosphere. After complete consumption of (4), the reaction was cooled to room temperature and poured into a mixture of water: DCM (200 + 50 mL). The mixture was stirred for 30 min and the organic layer was separated from the aqueous phase. The aqueous layer was further extracted in (3 x 20 mL) of DCM. All the organic layers were combined and washed with water (2 x 25 mL) and dried over anhydrous MgSO₄. The solvent was removed under vacuum to give the crude product which was purified by column chromatography using hexane (100%) as eluent. The final product was obtained as a mixture of **NI-1** and **NI-2** chromophores which were difficult to separate. Therefore, we used it as a mixture to carry out further reactions. Yield (3.5 g, 89%). MS-calcd. for $C_{22}H_{13}N$ - 291.35; found- 292.22.

Synthesis of 6,12-dibromobenzo[b]indolo[1,2,3-*lm*]carbazole (2) and 10,13dibromobenzo[c]indolo[3,2,1-*jk*]carbazole (3)

A mixture of **NI-1** and **NI-2** chromophores (3.5 g, 12 mmol, 1 equiv.) and *N*-bromo succinimide (NBS) (5.3 g, 30 mmol, 2.5 equiv.) were stirred at room temperature in 20 mL of *N*, *N*-dimethyl formamide (DMF) for 24 h. The reaction mass was poured in 200 mL of water and stirred for 60 min at room temperature. The white residue obtained was filtered and washed with water (2 x 50 mL) and dried in the oven at 65 °C overnight. The dry crude product was used for the further reaction without purification. Yield (4.5 g, 83%). MS- calcd. for $C_{22}H_{11}Br_2N$ - 449.15; found- 451.33.

Synthesis of N^6 , N^6 , N^{12} , N^{12} -tetraphenylbenzo[*b*]indolo[1,2,3-*lm*]carbazole-6,12-diamine (NIDPA-1) and N^{10} , N^{10} , N^{13} , N^{13} -tetraphenylbenzo[*c*]indolo[3,2,1-*jk*]carbazole-10,13-diamine (NIDPA-2)

A mixture of 6,12-dibromobenzo[*b*]indolo[1,2,3-*lm*]carbazole (2) and 10,13dibromobenzo[*c*]indolo[3,2,1-*jk*]carbazole (3) (1.00 g, 2.22 mmol, 1 equiv.), diphenylamine (0.9 g, 5.34 mmol, 2.4 equiv.), and sodium *tert*. butoxide (0.9 g, 8.9 mmol, 4 equiv.) was stirred for 10 min in 10 mL of toluene at room temperature under nitrogen atmosphere. To this, a mixture of bis(dibenzylideneacetone) palladium (0) [Pd(dba)₂] (0.03 g, 0.044 mmol, 0.02 equiv.) and tri-tertbutylphosphine [P('Bu)₃] (0.018 g, 0.089 mmol, 0.04 equiv.) in 5 mL of toluene was added by syringe under nitrogen atmosphere. The reaction mass was heated to reflux for 12 h and the progress of the reaction was monitored on thin-layer chromatography (TLC). After completion of the reaction, the reaction mass was cooled to room temperature and diluted with DCM. The diluted reaction mass was filtered through the celite bed and washed with DCM (4 x 20 mL). The solvent was removed under vacuum and the crude product was purified by column chromatography using hexane: ethyl acetate (90:10) to get N^6 , N^{12} , N^{12} -tetraphenylbenzo[b]indolo[1,2,3-lm]carbazole-6,12-diamine (NIDPA-1) as yellow solid. Yield (0.21 g, 15%). ¹H NMR (500 MHz, CDCl₃) δ 8.50 (d, J = 8.3 Hz, 1H), 8.31 (s, 1H), 8.07 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 9.1 Hz, 2H), 7.87 (d, J = 9.1 Hz, 2Hz), 7.87 (d, J = 9.1 Hz), 7.87 (d, J = 9.1 Hz),8.6 Hz, 1H), 7.79 (s, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.38 (dd, J = 8.6, 2.1 Hz, 1H), 7.29 - 7.21 (m, 8H), 7.15 (t, J = 7.4 Hz, 8H), 6.99 (dt, J = 21.0, 7.3 Hz, 4H). ¹³C NMR (126 MHz, CDCl₃) δ 149.29 (s), 148.44 (s), 144.38 (s), 143.06 (s), 141.28 (s), 136.68 (s), 136.12 (s), 131.77 (s), 131.00 (s), 129.95 (s), 129.37 (t, J = 15.8 Hz), 128.57 (s), 127.57 (s), 125.47 (s), 124.38 (d, J = 2.2 Hz), 123.62 (s), 123.35 (s), 122.78 (s), 122.52 (s), 122.35 (s), 121.77 (s), 121.23 (s), 120.39 (s), 119.68 (d, J = 18.9 Hz), 113.11 (d, J = 13.8 Hz). MS- calcd. for C₄₆H₃₁N₃- 625.77; found- 626.13.

 N^{10} , N^{13} , N^{13} -tetraphenylbenzo[*c*]indolo[3,2,1-*jk*]carbazole-10,13-diamine (NIDPA-2) as yellow solid. (Yield 0.35 g, 25%). ¹H NMR (500 MHz, CDCl₃) δ 8.50 (s, 1H), 8.43 (d, *J* = 8.6 Hz, 1H), 8.29 (d, *J* = 1.7 Hz, 1H), 7.93 (s, 1H), 7.85 (s, 1H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.28 (dd, *J* = 14.4, 6.8 Hz, 5H), 7.20

(t, J = 6.5 Hz, 11H), 7.13 (t, J = 7.6 Hz, 1H), 7.02 (t, J = 7.3 Hz, 2H), 6.92 (d, J = 4.2 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 148.64 (s), 147.51 (s), 144.12 (s), 142.58 (s), 140.50 (s), 136.57 (s), 134.56 (s), 131.36 (s), 130.98 (s), 130.57 (s), 129.50 (d, J = 11.0 Hz), 128.56 (s), 128.32 (s), 127.18 (d, J = 7.3 Hz), 125.93 (s), 124.55 (d, J = 8.9 Hz), 123.95 (s), 123.27 (s), 122.54 (s), 122.25 (s), 122.01 (s), 121.49 (s), 121.18 (s), 119.09 (s), 113.14 (s), 111.90 (s), 110.38 (s). MS- calcd. for C₄₆H₃₁N₃- 625.77; found- 626.10.



Figure S1. The ¹H-NMR spectrum of NIDPA-1



Figure S2. The ¹³C-NMR spectrum of NIDPA-1



Figure S3. The ¹H-NMR spectrum of NIDPA-2



Figure S4. The ¹³C-NMR spectrum of NIDPA-2



Figure S5. The MS spectrum of NIDPA-1



Figure S6. The MS spectrum of NIDPA-2



Figure S7. Emission of NIDPA-1 emitter in different solvents with varying the polarity



Figure S8. Emission of NIDPA-2 emitter in different solvents with varying the polarity



Figure S9. TRPL curves of NIDPA-1 and NIDPA-2 emitters



Figure S10. TGA curves of NIDPA-1 and NIDPA-2 emitters



Figure S11. DSC curves of NIDPA-1 and NIDPA-2



Figure S12. The optimized device diagram of NIDPA-1 and NIDPA-2 devices



Figure S13. The quantum efficiency-current density diagram of NIDPA-1 and NIDPA-2 doped devices



Figure S14. Lippert Mataga plot for the **NIDPA-1** and **NIDPA-2** emitters in different solvents displaying the variation of Stokes' shift as a function of orientation polarizability of the solvents



Figure S14. The EL curves of NIDPA-1 doped devices with varying the voltage



Figure S15. The EL curves of NIDPA-2 doped devices with varying the voltage

NIDPA-1							
Singlet	E (N)	Triplet					
Excited state	$L_{g}(\mathbf{ev})$	Excited state	$L_{g}(ev)$				
S ₁	3.22	T ₁	2.65				
S ₂	3.75	T ₂	3.00				
S ₃	3.84	T ₃	3.31				
S ₄	3.99	T ₄	3.43				
S ₅	4.17	T ₅	3.51				
S ₆	4.26	T ₆	3.52				
S ₇	4.28	T ₇	3.53				
S ₈	4.31	T ₈	3.63				
S 9	4.33	T9	3.93				
S ₁₀	4.45	T ₁₀	3.97				
	NIDPA-2						
Singlet	$\mathbf{F}_{(\mathbf{a}\mathbf{V})}$	Triplet					
Excited state	$L_{g}(\mathbf{ev})$	Excited state	$L_{g}(ev)$				
S ₁	3.30	T ₁	2.82				
S ₂	3.49	T ₂	2.88				
S ₃	3.96	T ₃	3.18				
S ₄	4.12	T ₄	3.45				
S ₅	4.22	T ₅	3.51				
S ₆	4.30	T ₆	3.53				
S ₇	4.32	T ₇	3.63				
			2 =0				
S ₈	4.37	T ₈	3.78				
S ₈ S ₉	4.37 4.42	T ₈ T ₉	3.78				

 Table S1 The singlet and triplet excited states of NIDPA-1 and NIDPA-2 emitters

NIDPA-1								
Solvents	Absorption	Emission	Orientation polarizability	Stokes shift				
	(nm)	(nm)	(f)	(cm ⁻¹)				
Cyclohexane	427	459	-0.02	1633				
Toluene	427	472	0.014	2233				
Diethyl ether	421	470	0.167	2476				
<i>n</i> -butyl ether	426	467	0.096	2061				
Di-isopropyl ether	423	471	0.145	2409				
Dichloromethane	422	487	0.217	3163				
Dioxane	420	472	0.022	2623				
Chloroform	425	480	0.14	2696				
Ethyl acetate	419	478	0.19	2946				
Acetonitrile	416	501	0.305	4078				
THF	415	479	0.21	3220				
NIDPA-2								
Solvents	Absorption	Emission	Orientation polarizability	Stokes shift				
	(nm)	(nm)	(f)	(cm ⁻¹)				
Cyclohexane	433	471	-0.02	1863				
Toluene	435	487	0.014	2455				
Diethyl ether	431	493	0.167	2918				
<i>n</i> -butyl ether	433	485	0.096	2476				
Di-isopropyl ether	430	487	0.145	2722				
Dichloromethane	431	527	0.217	4227				
Dioxane	432	496	0.022	2987				
Chloroform	432	508	0.14	3463				
Ethyl acetate	430	514	0.19	3801				
Acetonitrile	428	553	0.305	5281				
THF	431	512	0.21	3671				

Table S2 Absorption, emission and Stokes shift data of the NIDPA-1 and NIDPA-2 emittersrecorded in different solvents for Lippert-Mataga model