Electronic Supplementary Information (ESI)

Asymmetric aggregation-induced emission materials with double

stable configurations toward promoted performance in non-doped

organic light-emitting diodes

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1. General Information

All chemical reagents were purchased from commercial channels and used without any pretreatment. ¹H-NMR and ¹³C-NMR spectra were obtained from a Bruker AVANCE HD 400 (400 MHz) spectrometer at room temperature. High resolution mass spectra (HRMS) were measured on a Thermo Fisher Q Exactive mass spectrometer. UV-vis absorption and photoluminescence spectra in solution state were recorded on an Ocean Optics QE Pro spectrometer. The SHIMADZU UV-2700 spectrophotometer was used to characterized the UV-vis absorption spectra of thin films. The photoluminescence spectra and fluorescence lifetimes of thin films as well as all the fluorescence quantum yields were determined on an Edinburgh FLS980 spectrometer, among which the last item was completed with the help of a calibrated integrating sphere system. TGA analyses were performed on a NETZSCH STA 409 PC simultaneous thermal analyzer and DSC curves were measured using a METTLER TOLEDO DSC 3 instrument under the nitrogen atmosphere at a heating rate of 10 °C·min⁻¹. CV data were collected from an Autolab PGSTAT 302N electrochemical workstation in a solution of tetra-*n*-butylammonium hexafluorophosphate (Bu₄NPF₆) (0.1 M) in acetonitrile. A three electrodes system including a Ag/Ag⁺ reference electrode, a platinum wire counter electrode and a glass carbon working electrode were used for the CV analyzation. The ferrocene/ferrocenium couple (Fc/Fc⁺) was used as the internal standard, whose oxidation potential is -4.8 V with respect to vacuum level while was determined to be -0.069 V under the preceding conditions. Therefore, the HOMO energy level can be obtained from the equation HOMO = $-e[E_{ox} + 0.069 + 4.8] eV$, among which the symbol "e" denotes electron charge quantity. The morphology analyzations of emission layers were carried out by a Keysight 5500 atomic force microscopy (AFM).

2. Material Synthesis and Characterization



Scheme 1. Synthetic routes of TriPE-PA, TriPE-α-NA, TriPE-β-NA.

Synthesis of 9-phenyl-10-(1,2,2-triphenylvinyl)anthracene (TriPE-PA)

Tetrakis(triphenylphosphine)palladium (116 mg, 0.10 mmol) was added to a mixture of bromotriphenylethylene (1.46 g, 4.36 mmol), (10-phenylanthracen-9-yl)boronic acid (1.00 g, 3.35 mmol) and K_2CO_3 (1.86 g, 13.46 mmol) in 40 mL 1,2-dimethoxyethane and 4 mL water under the nitrogen atmosphere, and the mixture was refluxed at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was poured into water and then extracted with DCM. The combined organic layers were washed with water and dried over with anhydrous MgSO₄. After filtration and evaporation, the crude product was purified by silica gel column

chromatography (eluent: PE/DCM = 9/1, v/v) to afford TriPE-PA as a yellow solid (yield = 1.09 g, 64%). ¹H-NMR (400 MHz, DMSO- d_6): δ (ppm) 8.50 (d, J = 8.8 Hz, 2H), 7.64 – 7.51 (m, 5H), 7.47 (d, J = 8.7 Hz, 2H), 7.36 (dd, J = 14.4, 8.1 Hz, 3H), 7.32 – 7.20 (m, 6H), 7.10 – 6.98 (m, 5H), 6.95 – 6.88 (m, 2H), 6.82 (d, J = 7.0 Hz, 3H). ¹³C-NMR (151 MHz, CDCl₃) δ (ppm): 144.71, 143.30, 143.14, 142.72, 139.08, 137.39, 137.24, 136.45, 131.47, 131.37, 131.27, 130.15, 129.92, 129.82, 128.97, 128.23, 128.19, 127.99, 127.72, 127.32, 127.22, 127.05, 126.89, 126.70, 126.50, 126.45, 125.46, 124.75. HRMS (m/z): [M+H]+ calculated for C₄₀H₂₈, 509.2264; found, 509.2263.

Synthesis of (P&M)-9-(naphthalen-1-yl)-10-(1,2,2-triphenylvinyl)anthracene (TriPE-α-NA)

TriPE- α -NA was Synthesized according to the similar procedure as for TriPE-PA but with (10-(naphthalen-1-yl)anthracen-9-yl)boronic acid (1.00 g, 2.87 mmol) instead of (10phenylanthracen-9-yl)boronic well the bromotriphenylethylene, acid as as tetrakis(triphenylphosphine)palladium and K₂CO₃ were decreased to 1.25 g (3.73 mmol), 99.6 mg (0.086 mmol) and 1.59g (11.49 mmol), respectively, yielding TriPE- α -NA as a light yellow solid (yield = 0.96 g, a 1:1 mixture of stereoisomers, 60%). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 8.48 (dd, J = 15.8, 8.8 Hz, 2H), 8.06 – 7.93 (m, 2H), 7.66 (dt, J = 12.9, 7.5 Hz, 1H), 7.58 (d, J = 6.8 Hz, 0.5 H), 7.49 - 7.33 (m, 5.5 H), 7.33 - 7.22 (m, 6H), 7.22 - 7.03 (m, 7.5 H), 6.93 (m, 7.5 H), 6.93 (m, 7.5 H), 7.33 - 7.22 (m, 6H), 7.22 - 7.03 (m, 7.5 H), 7.33 + 7.23 (m, 7.5 H),(d, J = 7.1 Hz, 1H), 6.89 – 6.71 (m, 4H), 6.57 (d, J = 8.5 Hz, 0.5H). ¹³C-NMR (151 MHz, CDCl₃) δ (ppm): 144.86, 144.81, 143.46, 143.32, 143.11, 142.86, 142.79, 142.47, 137.88, 137.79, 136.81, 136.76, 136.70, 136.48, 135.11, 134.79, 133.64, 133.59, 133.50, 131.38, 131.31, 130.66, 130.65, 130.18, 130.13, 129.91, 129.32, 129.01, 128.97, 128.75, 128.14, 128.08, 128.07, 128.01, 127.98, 127.96, 127.89, 127.82, 127.26, 127.09, 127.06, 127.00, 126.92, 126.83, 126.79, 126.72, 126.65, 126.63, 126.55, 126.53, 126.39, 126.31, 126.24, 126.03, 125.94, 125.82, 125.57, 125.45, 125.40, 125.00, 124.95. HRMS (m/z): [M+H]+ calculated for C₄₄H₃₀, 559.2420; found, 559.2418.

Synthesis of (P&M)-9-(naphthalen-2-yl)-10-(1,2,2-triphenylvinyl)anthracene (TriPE-β-NA)

TriPE-β-NA was Synthesized according to the similar procedure as for TriPE-α-PA but with (10-(naphthalen-2-yl)anthracen-9-yl)boronic acid (1.00 g, 2.87 mmol) instead of (10-(naphthalen-1-yl)anthracen-9-yl)boronic acid, yielding TriPE-β-NA as a yellow solid (yield = 1.31 g, a 1:1 mixture of stereoisomers, 82%). ¹H-NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.57 – 8.49 (m, 2H), 8.11 (dd, J = 19.2, 8.1 Hz, 2H), 8.04 – 7.96 (m, 1.5H), 7.89 (s, 0.5H), 7.57 (ddt, J = 39.2, 15.8, 7.7 Hz, 6.5H), 7.42 (d, J = 8.5 Hz, 0.5H), 7.32 (dd, J = 13.7, 5.6 Hz, 7H), 7.05 (s, 5H), 6.95 (s, 2H), 6.86 (d, J = 6.2 Hz, 3H). ¹³C-NMR (151 MHz, CDCl₃) δ (ppm): 144.75, 143.33, 143.16, 143.14, 142.73, 142.72, 137.58, 137.56, 137.02, 137.01, 136.62, 136.58, 136.43, 136.41, 133.33, 133.31, 132.67, 131.38, 130.25, 130.16, 130.09, 129.85, 129.83, 129.77, 129.61, 129.01, 128.06, 128.00, 127.84, 127.78, 127.73, 127.70, 127.28, 127.27, 127.15, 127.08, 126.91, 126.77, 126.77, 126.57, 126.55, 126.47, 126.36, 126.13, 125.51, 124.86. HRMS (m/z): [M+H]+ calculated for C₄₄H₃₀, 559.2420; found, 559.2421.

3. NMR and HRMS Spectra



Fig. S1. ¹H-NMR spectrum of TriPE-PA in DMSO-d₆.



Fig. S2. High resolution mass spectrum of TriPE-PA.



Fig. S3. ¹³C-NMR spectrum of TriPE-PA in CDCl₃.



Fig. S4. ¹H-NMR spectrum of TriPE-α-NA in CDCl₃.



Fig. S5. High resolution mass spectrum of TriPE-α-NA.



Fig. S6. ¹³C-NMR spectrum of TriPE-α-NA in CDCl₃.



Fig. S7. ¹H-NMR spectrum of TriPE- β -NA in DMSO- d_6 .



Fig. S8. High resolution mass spectrum of TriPE-β-NA.



4.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 fl (ppm)

Fig. S9. ¹³C-NMR spectrum of TriPE-β-NA in CDCl₃.

4. Theoretical Calculation

All theoretical calculations were carried out by using Gaussian 09 (Revision E.01) program¹. Both optimization calculations of ground states and energy calculations of excited state were performed based on single structures without consideration of solvation. No special keywords were used. Table S1 to S4 summarized the primary results of calculations, followed by the figures (Table S5 and S6) obtained from optimization and drawn by GaussView 5.0.

Molecule Structure ^{<i>a</i>}	HOMO/LUMO b (eV)	$E_{g}^{b}(eV)$	S_1^{c} (eV,nm)	f^c	Assignment ^c
TriPE-PA	-5.249/-1.921	3.328	2.930,423.2	0.1899	H→L (95.70%)
(P)-TriPE-α-NA	-5.268/-1.940	3.328	2.923,424.1	0.1951	H→L (95.68%)
(M)-TriPE-α-NA	-5.269/-1.940	3.329	2.925,423.9	0.2081	H→L (95.59%)
(P)-TriPE-β-NA	-5.259/-1.930	3.329	2.924,424.0	0.2192	H→L (95.61%)
(M)-TriPE-β-NA	-5.254/-1.937	3.316	2.914,425.5	0.2347	H→L (95.84%)

Table S1. Theoretical calculation results of all configurations

^{*a*} Molecule structures including different types of configurations. ^{*b*} HOMOs and LUMOs were carried out from energy calculations of optimized ground state structures by using DFT with B3LYP/6-311g(d)//B3LYP/6-31g(d) level. E_g =LUMO-HOMO. ^{*c*} First excitation energies (S₁), oscillator strengths (*f*) and dominant assignments of molecular orbitals with their electronic transition associated weights (inside the brackets) were carried out from energy calculation of excited state by using TD-DFT with B3LYP/6-311g(d) level.

Table S2. Total Energy	of optimized	structures and	transitional	structures
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	Total Energy ^{<i>a</i>} (Hartree)				
Compound —	Optimized		Transition State (TS)		
	P Type ^b	M Type ^b	Alkenyl (T) ^c	Aryl (A) ^c	
TriPE-PA	-1541.43479		-1541.37734	-1541.40231	
TriPE-α-NA	-1695.10626	-1695.10652	-1695.04883	-1695.04729	
TriPE-β-NA	-1695.10772	-1695.10769	-1695.05020	-1695.07564	

^{*a*} Total energies were calculated at B3LYP/6-311g(d) level based on the optimized structures. ^{*b*} Different types of optimized configurations in new compounds. ^{*c*} The transitional structures after rotations of triphenylethylene (T) group or aromatic (A) groups.

	Difference (kcal/mol)				
Compound	ΔE_{Oa}	$\Delta E_{\mathrm{TP}} b$	$\Delta E_{TM} b$	$\Delta E_{AP} c$	$\Delta E_{AM c}$
TriPE-PA	_	36.0	4883	20.3	7946
TriPE-α-NA	0.15877	36.19691	36.03815	37.16356	37.00479
TriPE-β-NA	0.01762	36.07248	36.09010	20.11101	20.12863

Table S3. Energy differences between different configurations or states

^{*a*} Energy differences between P and M type configurations, $\Delta E_{O} = |P - M|$. ^{*b*} Rotation barriers of aromatic groups, $\Delta E_{TP} = TS_T - P$, $\Delta E_{TM} = TS_T - M$. ^{*c*} Rotation barriers of triphenylethylene group, $\Delta E_{AP} = TS_A - P$, $\Delta E_{AM} = TS_A - M$. The meanings of letters in these formulae can be found in Table S2.

Table S4. Energy calculation results of excited state for all crystal structures

Molecule Structure	S_1^{a} (eV,nm)	f^a	Assignment ^a
$TriPE-PA(C)^b$	2.967,417.9	0.1944	H→L (95.96%)
(P)-TriPE- α -NA(C) ^b	2.975,416.7	0.1801	H→L (94.99%)
(P)-TriPE- β -NA(C) ^b	2.977,416.5	0.1938	H→L (95.37%)

^a Carried out from energy calculation of excited state by using TD-DFT with b3lyp/6-311g(d,p) level. ^b Crystal structures.

TriPE-PA

TriPE-α-NA

TriPE-β-NA



Fig. S10. Transitional structures after rotations of triphenylethylene groups (a) or aromatic groups (b). All transitional structures were collected by using Berny geometry optimization algorithm at B3LYP/6-31g(d) level.

5. Single Crystal X-ray Crystallography

Single crystal X-ray diffraction intensity data were collected at 200 K on a Bruker APEX II CCD diffractometer with the CuK α X-ray source.

All solving processes of structures were carried out on the Olex2 program.² The structures of TriPE-PA and (P)-TriPE- β -NA were solved with the olex2.solve structure solution program using Charge Flipping, while the structure of (P)-TriPE- α -NA was solved with the ShelXT structure solution program using Intrinsic Phasing.³ The structure of TriPE-PA was further refined with the olex2.refine refinement package using Gauss-Newton minimisation, and the other two were refined with the ShelXL refinement package using Least Squares minimization.⁴

Fig. S10 shows the disordered structures of TriPE- β -NA crystal. After compared with the theoretical calculation results, only the relatively reasonable structure was adopted and identified as P type configuration, which is shown in other figures. More details about crystallographic structures were summarized in the Table S6.



Fig. S11. The disordered structures of **TriPE-β-NA** crystal drawn with different kinds of models, and the hidden part is shown with dashed lines here.

Name of the structures	TriPE-PA	(P)-TriPE-α-NA	(P)-TriPE-β-NA
CCDC NO.	1903702	1903720	1903718
Empirical formula	$C_{40}H_{28}$	$C_{44}H_{30}$	C _{12.86} H _{9.14} Cl _{0.57}
Formula weight	508.62	558.68	183.89
Temperature/K	200.01(10)	200.00(10)	200.00(10)
Crystal system	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /c	P2 ₁ /c	P-1
a/Å	17.453(2)	9.2098(3)	9.0342(4)
b/Å	9.0614(4)	19.2806(6)	9.2974(4)
c/Å	19.864(5)	17.5985(7)	20.4306(13)
α/°	90	90	94.479(4)
β/°	116.382(13)	94.424(3)	97.557(5)
γ/°	90	90	91.137(4)
Volume/Å ³	2814.3(8)	3115.65(18)	1695.16(15)
Z	4	4	7
$\rho_{calc}g/cm^3$	1.200	1.191	1.261
µ/mm ⁻¹	0.514	0.510	1.952
F(000)	1072.0	1176.0	672.0
Crystal size/mm ³	$0.19 \times 0.18 \times 0.17$	$0.18 \times 0.17 \times 0.16$	$0.19 \times 0.18 \times 0.17$
Radiation	$CuK\alpha$ ($\lambda = 1.54184$)	$CuK\alpha$ ($\lambda = 1.54184$)	$CuK\alpha$ ($\lambda = 1.54184$)
20 range for data collection/°	8.99 to 132	6.812 to 131.97	8.762 to 131.992
In day non con	$-17 \le h \le 20, -10 \le k \le 9,$	$-10 \le h \le 3, -22 \le k \le 17,$	$\text{-10} \le h \le 10, \text{-8} \le k \le 11, $
Index ranges	$-23 \le l \le 23$	$-20 \le l \le 20$	$-22 \le l \le 24$
Reflections collected	10817	9146	8912
Independent reflections	4887	5362	5831
	$[R_{int} = 0.0511, R_{sigma} = 0.0494]$	$[R_{int} = 0.0427, R_{sigma} = 0.0577]$	$[R_{int} = 0.0408, R_{sigma} = 0.0561]$
Data/restraints/parameters	4887/0/361	5362/0/397	5831/108/526
Goodness-of-fit on F2	1.036	1.024	1.033
Final R indexes [I≥=2σ (I)]	$R_1 = 0.0733, wR_2 = 0.1890$	$R_1 = 0.0645, wR_2 = 0.1682$	$R_1 = 0.0731, wR_2 = 0.1927$
Final R indexes [all data]	$R_1 = 0.0919, wR_2 = 0.2161$	$R_1 = 0.0846, wR_2 = 0.1927$	$R_1 = 0.0885, wR_2 = 0.2149$
Largest diff. peak/hole / e Å-3	0.38/-0.28	0.32/-0.32	0.40/-0.80

Table S5. The crystallographic details of TriPE-PA, (P)-TriPE-α-NA and (P)-TriPE-β-NA

6. OLED Fabrications and EQE Curves

The new blue emission materials were further purified by sublimation before the fabrication of devices. The ITO glasses were cleaned with detergent, further underwent ultrasonic bath of deionized water, acetone, ethanol, and isopropanol each for 15 min. After it was dried under the nitrogen gas flow, oxygen plasma was used to treat the surfaces. The ammonium molybdate solution with concentration of 1.0 wt% was spin-coated onto the top of the ITO substrate at a speed of 2000 r·min⁻¹ for 30 s. Then the ITO glass with covering was heat treated at 80 °C for 2 h to prepare the MoO₃ thin film, further transferred to the vacuum deposition chamber. 40 nm of NPB layer, 20 nm of emission layer, 40 nm of TPBi layer, 1 nm of LiF layer and 100 nm of Al layer were evaporated onto the top of MoO₃ layer in sequence at a pressure of 10^{-4} Pa.

For the fabrications of PEDOT:PSS devices, a solution of PEDOT:PSS with concentration of 1.5 wt% was used in place of the ammonium molybdate solution, and the speed of spin-coating was increased to 5000 r·min⁻¹. The ITO substrate further dried at 120 °C for 45 min. Other fabricating procedures were as the same as those of MoO₃ devices.

The Photo Research PR-745 SpectraScan spectrophotometer was used to measure the EL spectra and brightness of devices. Other electrical characteristics were obtained from a Keithley 2400 SourceMeter. All the measurements were carried out at room temperature. The calculated EQE curves were shown in Figure S12 and S13.



Fig. S12. EQE versus brightness curves of MoO₃ hole-injection layer devices.



Fig. S13. EQE versus brightness curves of PEDOT:PSS hole-injection layer devices.

7. Additional Data



Fig. S14. UV-Vis absorption and PL spectra of **TriPE-PA**, **TriPE-\alpha-NA** and **TriPE-\beta-NA** in thin films.



Fig. S15. PL decay curves of TriPE-PA, TriPE-α-NA and TriPE-β-NA in thin films.

Reference

- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, G. Z. J. Bloino, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, Gaussian, Inc., Wallingford CT, Revision E.01 edn., 2013.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, 42, 339-341.
- 3. G. M. Sheldrick, Acta crystallographica. Section A, Foundations and advances, 2015, 71, 3-8.
- 4. G. M. Sheldrick, Acta crystallographica. Section C, Structural chemistry, 2015, 71, 3-8.