Facile Synthesis of 2-Aza-9,10-diphenylanthracene and the Effect of Precise Nitrogen Atom Incorporation on OLED Emitters Performance

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A. Materials and Methods.

Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of nitrogen and commercially obtained reagents were used as received. Anhydrous solvents were either freshly distilled or passed through activated alumina columns, unless otherwise stated. Trifluoroacetic acid was purchased from Oakwood chemical. Manganese dioxide was purchased from Strem Chemicals. Thin-layer chromatography (TLC) was conducted with EMD gel 60 F_{254} pre-coated plates (0.25 mm) and visualized using a combination of UV and potassium permanganate staining techniques. Silicycle Siliaflash P60 (particle size 40-63 µm) was used for flash column chromatography. ¹H NMR spectra were recorded on Bruker spectrometers (at 500 MHz) and are reported relative to residual solvent signals. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (125 MHz). DART-MS spectra were collected on a Thermo Exactive Plus MSD (Thermo Scientific) equipped with an ID-CUBE ion source and a Vapur Interface (IonSense Inc.). Both the source and MSD were controlled by Excalibur software version 3.0. The analyte was spotted onto OpenSpot sampling cards (IonSense Inc.) using CHCl₃ as the solvent. Ionization was accomplished using UHP He plasma with no additional ionization agents. The mass calibration was carried out using Pierce LTQ Velos ESI (+) and (-) Ion calibration solutions (Thermo Fisher Scientific). UV-Vis spectra were recorded using an JASCO C-770 UV-Visible/NIR spectrophotometer. Fluorescence spectra were recorded using a Horiba Instruments PTI Quanta Master Series Fluorometer. The UV-Vis and fluorescence spectra were recorded using a 1-cm quartz cuvette, with freshly distilled toluene. Quantum Yield measurements were recorded using a Horiba Fluoromax Spectrometer.

The materials for the hole transport/electron-blocking layer, N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) (purity: >98%), the active layer 9,10-diphenylanthracene (DPA) (purity: >98%), and electron transport/hole blocking layer 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) (purity: >98%) were all purchased from TCI America and used as received without further purification. LiF pieces (purity: >99.9%) and Aluminum pellets (purity: >99.99%) were both obtained from the Kurt J. Lesker Company.

B. Experimental Procedures and Characterization Data

 $\begin{array}{c} \begin{array}{c} \begin{array}{c} Ph \\ \\ BocN \\ \\ \end{array} \\ \begin{array}{c} 3 \\ Ph \end{array} \end{array} \end{array} \begin{array}{c} \begin{array}{c} 1. \text{ TFA: CH}_2 \text{Cl}_2 (1:5) \\ -78 \rightarrow 23 \text{ °C}, 1 \text{ h} \end{array} \\ \hline \begin{array}{c} 2. \text{ MnO}_2 (25.0 \text{ equiv}) \\ Ph \text{Me}, 110 \text{ °C}, 14 \text{ h} \end{array} \end{array} \begin{array}{c} \begin{array}{c} Ph \\ \\ \end{array} \\ \begin{array}{c} 2 \\ Ph \end{array} \end{array} \begin{array}{c} Ph \\ \end{array} \\ \begin{array}{c} 2 \\ Ph \end{array} \end{array}$

Synthesis of 2-aza-9,10-diphenylanthracene 2.

Aza-DPA 2. A 25 mL round-bottomed flask was equipped with a magnetic stir bar and charged with 3 (100.0 mg, 0.23 mmol, 1.0 equiv). Next, CH₂Cl₂ (5.0 mL) was added, and the solution was cooled to -78 °C via dry ice/acetone bath. At -78 °C, TFA (1.0 mL) was added dropwise over 5 minutes. The cooling bath was removed, and the mixture was stirred at 23 °C for an additional hour. After 1 hour, saturated aqueous sodium bicarbonate solution (20 mL) was slowly added to quench excess TFA. The contents of the reaction mixture were then transferred to a separatory funnel, where the aqueous layer was extracted 3 times with CH₂Cl₂ (20 mL). The combined organic phases were then washed with water (20 mL) and brine (20 mL) then dried over sodium sulfate, filtered, and concentrated. The resulting crude material was transferred to an 8dram vial equipped with a stir bar, and MnO₂ (500 mg, 5.75 mmol, 25.0 equiv) was then added. The vial was then brought into a nitrogen-filled glovebox where the solids were suspended in dry, degassed toluene (3.0 mL). The vial was then sealed with a Teflon-lined cap, removed from the glovebox, and heated to 110 °C for 14 hours. The mixture was cooled to 23 °C, and the contents of the reaction vial were filtered over Celite eluting with toluene. The eluate was concentrated under reduced pressure then purified by flash chromatography (9:1 benzene:Et₂O with 1% Et₃N) to yield Aza-DPA 2 (35.0 mg, 0.11 mmol, 46% yield). Aza-DPA 2: R_f: 0.60 (9:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃): δ 9.23–9.14 (s, 1H), δ 8.36–8.27 (d, J = 6.2, 1H), δ 7.85–7.75 (m, 2H), δ 7.76–7.56 (m, 6H), δ 7.54–7.50 (m, 2H), δ 7.49–7.39 (m, 5H); ¹³C NMR (125 MHz, CDCl₃):

153.8, 140.4, 139.3, 137.5, 136.8, 136.1, 132.4, 131.3, 131.2, 130.6, 130.4, 128.6, 128.5, 128.1, 127.9, 127.5, 127.0, 126.9, 125.7, 124.7, 118.4; IR (film): 3057, 1746, 1599, 1393, 1158 cm⁻¹; HRMS-APCI (m/z) $[M + H]^+$ calced for C₂₅H₁₈N⁺, 332.1434; found 332.1422. Spectral data matched those reported in the literature.¹

Sublimation Procedure: Prior to OLED fabrication, Aza-DPA **2** was further purified via sublimation. A sublimation chamber was charged with 50.0 mg of Aza-DPA **2** after flash chromatography. The chamber was evacuated (<1 mbar) and backfilled with nitrogen three times. Then, the chamber was placed under reduced pressure (<1 mbar), and the cold finger was cooled

with 23 °C water. Then, the sample was gently heated with a heat gun until a yellow solid collected on the cold finger. The chamber was then backfilled with nitrogen, and the cold finger removed. The yellow solid was then scraped off of the cold finger to give 35.0 mg of Aza-DPA **2** (mp: ~215 °C decomposes). This procedure was repeated two more times prior to OLED fabrication.



NMR Spectra.



¹³C NMR (125 MHz, CDCl₃) of compound **2** (pre-sublimation).



¹³C NMR (125 MHz, CDCl₃) of compound **2** (post-sublimation).

Cyclic Voltammetry Data.

Cyclic voltammograms were measured using a C-H Instruments CHI620E potentiostat. The analyte (5.00 mM) was dissolved in dry degassed 0.1 M NBu4PF6 in MeCN. Spectra were collected at a sweep rate of 100 mV/s at 23 °C. Ferrocene (Strem 99% purity; product number 26-1700) was added to each sample after each scan for reference. All spectra were collected using a glassy carbon working electrode (CH-Instruments product number CHI104), a platinum counter electrode (CH-Instruments product number CHI102), and a Ag/Ag+ reference electrode (CH-Instruments product number CHI112). The reference electrode was prepared with a 10 mM solution of AgNO3 (Strem 99.9% purity; product number 47-1325) in MeCN. The platinum wire was heated with a Bunsen burner until it glowed prior to each measurement. The glassy working electrode was polished to a mirror using 0.05 micron MicroPolish powder (CH-Instruments; product number CHI120) prior to each measurement.

Figure ESI1 DPA (1) oxidation vs Fc/Fc+.





Figure ESI2: DPA (1) reduction vs Fc/Fc+.





Figure ESI3: DPA (1) Full sweep vs Fc/Fc+.

9,10-diphenylanthracene vs Fc/Fc+



Figure ESI4: AzaDPA (2) oxidation vs Fc/Fc+.





Figure ESI5: AzaDPA (2) reduction vs Fc/Fc+.





Figure ESI6: AzaDPA (2) Full sweep vs Fc/Fc+.





Photophysical Data.

DPA (1) and Aza-DPA (2) solutions were prepared for photophysical measurements (data shown in Figure 4) as follows:

9,10-diphenylanthracene (1.30 mg, 3.92 μ mol, 1.00 equiv) was first dissolved in freshly distilled dry toluene (0.392 mL). This 10.0 mM solution was then diluted to 10.0 μ M solution by diluting 0.100 mL of the stock solution to a final volume of 10.0 mL. This solution was used to collect absorbance and emission data.

2-aza-9,10-diphenylanthracene (1.30 mg, 3.92 μ mol, 1.00 equiv) was first dissolved in freshly distilled dry toluene (0.392 mL). This 10.0 mM solution was then diluted to 10.0 μ M solution by diluting 0.100 mL of the stock solution to a final volume of 10.0 mL. This solution was used to collect absorbance and emission data.

The fluorescence quantum yield of Aza-DPA (2) in CH_2Cl_2 was measured as follows. A solution of 2 in CH_2Cl_2 (1 mg/mL) was prepared and diluted to a concentration of 0.1 mg/mL. The quantum yield was then measured at an excitation wavelength of 405 nm using an integrating sphere. The results of three measurements gave an average quantum yield value of 0.82 for 2 (run 1: 0.8203; run 2: 0.8202; run 3: 0.8205). The analogous procedure was used to measure the quantum yield of DPA (1) in CH_2Cl_2 , which gave a measured quantum yield of 0.99. This is in agreement with the literature value of $1.^2$

Figure ESI7: Solid state fluorescence of DPA (1) and AzaDPA (2) at 365 nm excitation.



OLED Device Fabrication.

OLED devices using 2-aza-9,10-diphenylanthracene and 9,10-diphenylanthracene as active layers were fabricated on ITO-coated glass substrates (10 Ohm/sq). ITO substrates were sequentially sonicated for 10 minutes each in a detergent solution, pure DI water, acetone, and isopropanol. These substrates were then dried under a nitrogen stream and plasma-treated for 10 minutes directly prior to device fabrication. The deposition of all layers was carried out in a NexDep thermal evaporator system at pressures $< 5.0 \times 10^{-6}$ Torr using a rotating substrate cooled to 12 °C with water. The deposition rate for all organic layers was monitored using a quartz crystal microbalance and maintained between 1.5-2.0 Å/s throughout the duration of each layer. The three organic layers were deposited sequentially without breaking vacuum, and the LiF/Al electrodes were deposited immediately after in a subsequent vapor deposition step.³ The thickness of the

deposited layers was calibrated prior to device fabrication by using the QCM to guide to a deposition of 100nm for each material. The actual thickness in the first recipe deviated from the target according to a tooling factor and the real value was measured using a surface profilometry. Subsequently, the tooling factor for the recipe was updated according to the following equation Q=(amount of material deposited on substrate)/(amount of material deposited on QCM)*100

Electroluminescence spectra were obtained inside an argon atmosphere using a fiber-optic-coupled Ocean Optics spectrometer. *J-V-L* traces were acquired inside an argon atmosphere using a LabVIEW-controlled Keithley 2400 and a Newport 818-UV-L photodiode.

Computational Section

Computational Methods. All calculations were carried out with the Gaussian 09 package.⁴ Geometry optimizations were performed at the B3LYP/6-31G(d) level of theory. Frequency analysis was conducted at the same level of theory to verify the stationary points as minima.

Frontier Molecular Orbitals of 1 and 2.

Figure ESI8: HOMO and LUMO orbital density maps for compounds 1 and 2.



HOMO and LUMO Energies.

Table S1: Computed HOMO and LUMO energies and HOMO/LUMO energy gaps for 1 and 2 (B3LYP/6-31G(d)).

Compound	HOMO Energy (eV)	LUMO Energy (eV)	ΔHOMO–LUMO Energy Gap (eV)
1	-5.10	-1.60	3.50
2	-5.39	-1.91	3.48

Cartesian Coordinates.



С	-4.68634	-0.44658 -3.31994
С	-3.90724	-0.78604 -2.25225
С	-3.80364	0.08031 -1.1157
С	-4.52764	1.31205 -1.12112
С	-5.33372	1.63359 -2.26125
С	-5.41045	0.78166 -3.3245
С	-3.01464	-0.25044 -0.00865
С	-4.43613	2.1702 -0.01991
С	-3.64768	1.8391 1.08748
С	-2.92519	0.60652 1.09371
С	-2.12371	0.28243 2.2363
Н	-1.57288	-0.67024 2.22915
С	-2.05047	1.13239 3.30141
С	-2.77086	2.36274 3.29485
С	-3.54418	2.70548 2.22396
Н	-4.77009	-1.11033 -4.1931
Н	-3.34382	-1.73118 -2.23622
Н	-5.88608	2.58534 -2.2532
Н	-6.02776	1.025 -4.20182
Н	-1.43677	0.88665 4.18062
Н	-2.68969	3.02474 4.1696
Н	-4.10523	3.65204 2.20636
С	-5.21662	3.49775 -0.02614
С	-4.53222	4.70876 -0.1334
С	-6.60773	3.48949 0.07533
С	-5.2388	5.91124 -0.1385
Н	-3.43544	4.71497 -0.2126
С	-7.31475	4.69219 0.06925
Н	-7.14732	2.5351 0.15969
С	-6.63055	5.90298 -0.0375
Н	-4.69937	6.86584 -0.22241
Н	-8.4116	4.68535 0.14885
Н	-7.18745	6.85121 -0.04161
С	-2.23446	-1.57818 -0.00302
С	-0.84368	-1.56952 0.10707
С	-2.91819	-2.7894 -0.10787
С	-0.13682	-2.77182 0.11161
Н	-0.30487	-0.61441 0.18894
С	-2.21134	-3.99221 -0.10235

Н	-4.01436	-2.79642	-0.19447
С	-0.82086	-3.9836	0.00723
Н	0.95947	-2.76505	0.19775
Н	-2.75074	-4.94707	-0.18462
Н	-0.26331	-4.93146	0.0109

	Ph I			
	$ \leq \$	1		
×∕∼		J		
2	 Ph			
С		-4.68634	-0.44658	-3.31994
С		-3.90724	-0.78604	-2.25225
С		-3.80364	0.08031	-1.1157
С		-4.52764	1.31205	-1.12112
С		-5.33372	1.63359	-2.26125
С		-5.41045	0.78166	-3.3245
С		-3.01464	-0.25044	-0.00865
С		-4.43613	2.1702	-0.01991
С		-3.64768	1.8391	1.08748
С		-2.92519	0.60652	1.09371
С		-2.12371	0.28243	2.2363
Η		-1.57288	-0.67024	2.22915
С		-2.77086	2.36274	3.29485
С		-3.54418	2.70548	2.22396
Η		-4.77009	-1.11033	-4.1931
Н		-3.34382	-1.73118	-2.23622
Η		-5.88608	2.58534	-2.2532
Η		-6.02776	1.025 ·	-4.20182
Н		-2.68969	3.02474	4.1696
Н		-4.10523	3.65204	2.20636
С		-5.21662	3.49775	-0.02614
C		-4.53222	4.70876	-0.1334
C		-6.60773	3.48949	0.07533
C		-5.2388	5.91124	-0.1385
Н		-3.43544	4.71497	-0.2126
C		-7.31475	4.69219	0.06925
H		-/.14/32	2.5351	0.15969
C		-6.63055	5.90298	-0.0375
H		-4.69937	6.86584	-0.22241
H		-8.4116	4.68535	0.14885
H		-/.18//45	6.85121	-0.04161
C		-2.23446	-1.5/818	-0.00302
C		-0.84368	-1.56952	0.10/0/
C		-2.91819	-2./894	-0.10787

C	0 12602	2 77102	0 1 1 1 6 1
C	-0.13082	-2.//182	0.11101
Н	-0.30487	-0.61441	0.18894
С	-2.21134	-3.99221	-0.10235
Н	-4.01436	-2.79642	-0.19447
С	-0.82086	-3.9836	0.00723
Н	0.95947	-2.76505	0.19775
Н	-2.75074	-4.94707	-0.18462
Н	-0.26331	-4.93146	0.0109
Ν	-2.05047	1.13239	3.30141

References

² A. Olesund, V. Gray, J. Mårtensson, B. Albinsson, J. Am. Chem. Soc., 2021, 143, 5745-5754.

³ a) S. W. Jung, K.-S. Kim, H.-u. Park, R. Lampande, S. K. Kim, J.-H. Kim, C.-W. Han, H.-C. Choi and J. H. Kwon, *Adv. Electron. Mater.* 2021, **7**, 2001101. b) M. Eritt, C. May, K. Leo, M. Toerker and C. Radehaus, *Thin Solid Films*, 2010, **518**, 3042–3045.

⁴ 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, J. Bloino, G. Zheng, 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., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, 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, 2009.

¹ M. R. Ramirez, E. R. Darzi, J. S. Donaldson, K. N. Houk and N. K. Garg, *Angew. Chem., Int. Ed.*, 2021, **60**, 18201–18208.