

Supporting Information

Insight into the mechanism and outcoupling enhancement of excimer-associated white light generation

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Experimental Section

Materials and Methods: 2-*tert*-Butyl-9,10-bis[4-(9-carbazolyl)phenyl]anthracene (**Cz⁹PhAnt**).

Synthesis of **Cz⁹PhAnt** was carried out according to previously reported procedure.¹

9,10-Bis[4-(9-carbazolyl)phenyl]anthracene (**Cz⁹PhAn**). A brief synthetic route of **Cz⁹PhAn** monomer is depicted in **Scheme 1**, and the synthetic procedures were modified according to a literature report.¹ Details are provided below.

Instruments: ¹H- and ¹³C-NMR spectra were recorded on a Varian Mercury 400. Mass spectra were obtained on a FINNIGAN LCQ mass Spectrometer. Chemical shifts (δ), quoted in parts per million (ppm), and coupling constants (J) were recorded in Hertz (Hz). All NMR spectra were recorded in deuterated 1,1,2,2-tetrachloroethane (C₂D₂Cl₄). DSC and TGA were performed using a SEIKOS Model SSC5200 unit at heating and cooling rates of 10 °C min⁻¹.

Synthesis of 9,10-Bis[4-(9-carbazolyl)phenyl]anthracene (Cz⁹PhAn): Under N₂ atmosphere and at -78 °C, *n*-BuLi (2.5 M in hexane, 2.0 mL) was added slowly over 1 h to a solution of 9-(4-bromo-phenyl)-9*H*-carbazole (1.61 g, 5.0 mmol) in dry THF (80 mL). After 1 h, a solution of anthraquinone (0.52 g, 2.5 mmol) in THF (20 mL) was then added dropwise to the reaction mixture at -78 °C. The resulting mixture was stirred overnight at room temperature. Then the reaction mixture was poured into cold water and extracted with dichloromethane (CH₂Cl₂). The combined organic fractions were dried (MgSO₄) and the solvent removed via rotary evaporation. The residue was added to a mixture of KI (1.66 g, 10.0 mmol), sodium hypophosphite monohydrate (2.13 g, 20.0 mmol), and AcOH (30 mL), after which the mixture was heated under reflux for 6 h. The resulting mixture was poured into cold water to precipitate the product. The yellowish crude product was purified through column chromatography (hexane/CH₂Cl₂ = 2:1) to offer a yellowish solid **Cz⁹PhAn** (1.2 g, 73%). *T_d*: 436 °C (Figure S7). ¹H NMR (C₂D₂Cl₄, 400 MHz, δ ppm): 8.24 (t, J = 7.2 Hz, 4H), 7.99 (d, J = 8.8 Hz, 2H), 7.91~7.86 (m, 6H), 7.79 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.57~7.50 (m, 6H), 7.41~7.35 (m, 8H). ¹³C NMR (C₂D₂Cl₄, 100 MHz, δ ppm): 143.84, 143.65, 141.10, 135.99, 133.06, 132.21, 129.86, 129.33, 128.67, 126.46, 123.55, 123.38, 113.16. HRMS calcd for C₅₀H₃₂N₂: 660.2565, found: 660.2541.

Spectroscopy Measurement. Steady-state UV-visible absorption and emission spectra were recorded by a Hitachi spectrophotometer (U-3310) and an Edinburgh fluorimeter (FS920), respectively. Both the wavelength-dependent excitation and the emission response of the fluorimeter were calibrated with the Rhodamine B spectrum and scattering light scans.

Time-resolved spectroscopic measurements were carried out by means previously reported elsewhere.^{2,3} In brief, time-resolved studies were performed using a time-correlated single photon counting (TCSPC) system (OB 900-L, Edinburgh) with the second harmonic generation (SHG, at 380 nm) of pulse-selected femtosecond laser centered at 760 nm (Tsunami and Model 3980 pulse picker, Spectra-Physics) as the photoexcitation light source. The photoluminescence of either solution or solid-film samples was collected with the right-angle geometry with respect to the pump beam direction and passed through a polarizer, which was located in front of the detector, and the polarization was set at the magic angle (54.7°) with respect to the pump laser polarization to eliminate any anisotropy. The temporal resolution, after deconvolution of the instrument time broadening function, was ~30 ps.

Quantum efficiency measurements were recorded with an integration sphere coupled with a photonic multi-channel analyzer (Hamamatsu C9920), which gave anthracene a quantum yield of 23%. The experimental values of HOMO levels were determined with a Riken AC-2 photoemission spectrometer (PES), and those of LUMO levels were estimated by subtracting the optical energy gap from the measured HOMO.

The variable angle spectroscopic ellipsometry (VASE) measurements for films of the materials on quartz substrates were performed using a spectroscopic ellipsometer (J. A. Woollam Co., Inc.). Ellipsometry measures the change in polarization of light as a function of incident angle and wavelength. VASE data were analyzed using WVASE32 (J. A. Woollam Co., Inc) software. The method used to determine the anisotropic optical constants is described in detail in the literature.⁴

Computational Methodology. All calculations were performed by the Gaussian 09 program package.⁵ The ground state structures of the titled molecule were first optimized with density functional theory (DFT) at the B3LYP/6-31G(d,p) level.⁶ The optimized structures were then used to calculate the lowest singlet energy optical excitations using the time-dependent density functional theory (TD-DFT) method. A polarizable continuum model (PCM)⁷ in Gaussian 09 was applied using CH₂Cl₂ as the solvent.

Time-of-flight (TOF) mobility measurements. We used terfluorene (E3) as the charge-generation layer (CGL)⁸ in the structure: ITO glass/ E3(0.1 μm)/ **Cz⁹PhAn** (1.55 μm) /Ag (200 nm), which were then placed inside a cryostat and kept under vacuum. The thicknesses of organic materials under testing were still set to be substantially greater than that of E3, so

that the total transit time was longer than the time resolution of the electronic system. Accordingly, the transit time across the E3 layer is negligible in comparison with the total transit time. The thickness of the organic film was monitored in situ with a quartz sensor and calibrated by a thin film thickness measurement (K-MAC ST2000). A pulsed nitrogen laser was used as the excitation light source through the transparent electrode (ITO) induced photogeneration of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Ag), and then recorded with a digital storage oscilloscope. In this method, depending on the polarity of the applied bias, selected carriers (holes or electrons) are swept across the sample with a transit time of t_T . With the applied bias V and the sample thickness D , the applied electric field E is V/D , and the carrier mobility is then given by $\mu = D/(t_T E) = D^2/(V t_T)$, in which the carrier transit time, t_T , can be extracted from the intersection of two asymptotes to the tail and plateau sections in double-logarithmic plots.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS): The GIWAXS experiments were conducted on a Bruker AXS NanoStar system, equipped with a rotating anode X-ray generator that emits an incident beam with a wavelength of 1.54 Å. The 2-D images of the diffraction patterns were taken on a Typhoon FLA 7000 image plate (GE Healthcare). The scattering intensities are reported as a function of wave vector q , where $q = (4\pi/\lambda) \sin (\theta/2)$, λ is the wavelength of incident X-rays, and θ is the scattering angle.

OLED device fabrication. All materials were purified by vacuum sublimation prior to use. The OLEDs were fabricated through direct vacuum deposition at 10^{-6} torr on ITO-coated glass substrates with a sheet resistance of $15 \Omega \text{ sq}^{-1}$. The ITO surface was ultrasonically cleaned in acetone, methanol, and deionized water in sequence, followed by a final treatment with air plasma. The deposition rate was kept at ca. $1 - 2 \text{ Å s}^{-1}$. Subsequently, LiF was deposited at 0.1 Å s^{-1} and then capped with Al metal (ca. 5 Å s^{-1}) through shadow masking without breaking the vacuum. The J - V - L characteristics of the devices were measured simultaneously in a glove-box using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si-photodiode. EL spectra were measured using a photodiode array (Ocean Optics USB2000+). Angle-dependent EL intensity were measured using the Keithley 2400 programmable source meter, a rotating stage, and a Photo Detector (Thorlabs DET210).

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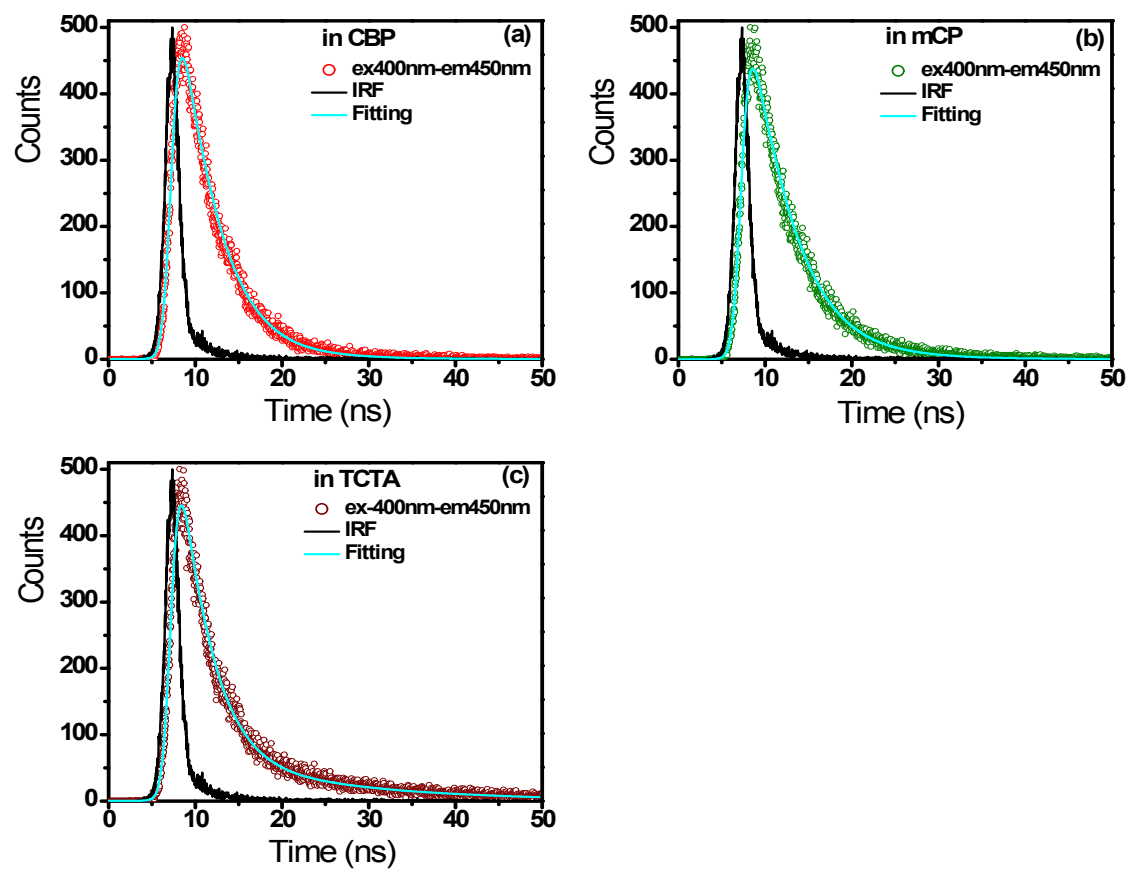


Figure S1. Time-resolved photoluminescence decay curves of a solid film in which Cz^9PhAn is doped in a host material (CBP, mCP and TCTA, see text for detail).

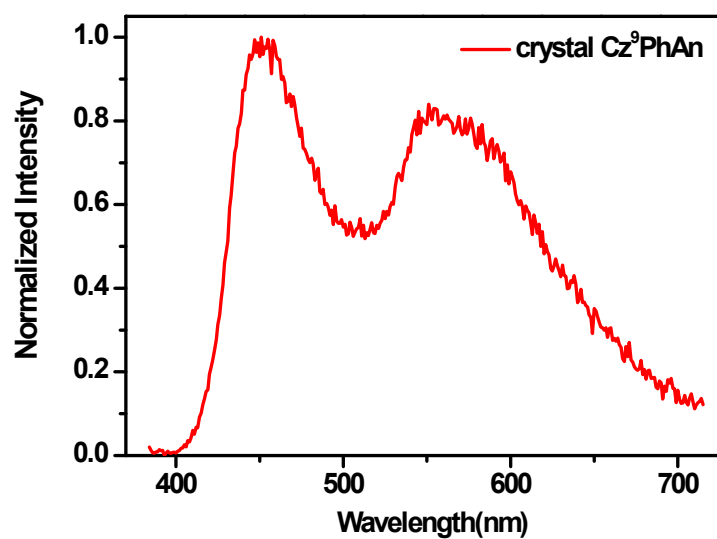


Figure S2. The emission spectrum of Cz^9PhAn in a single crystal.

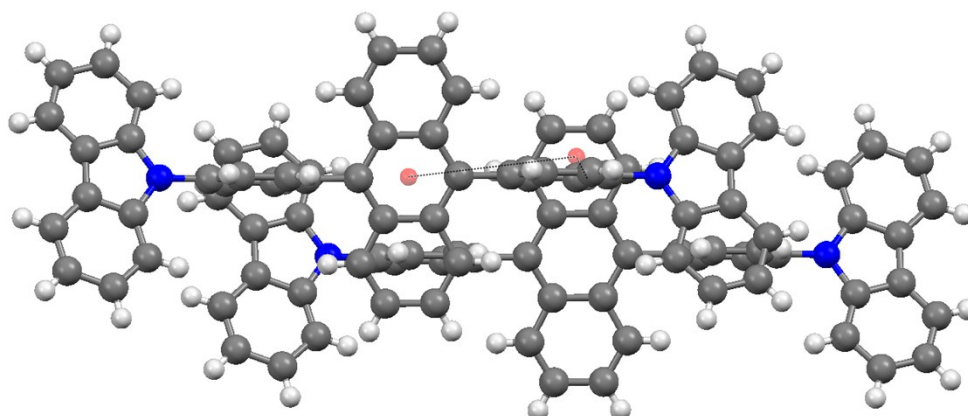
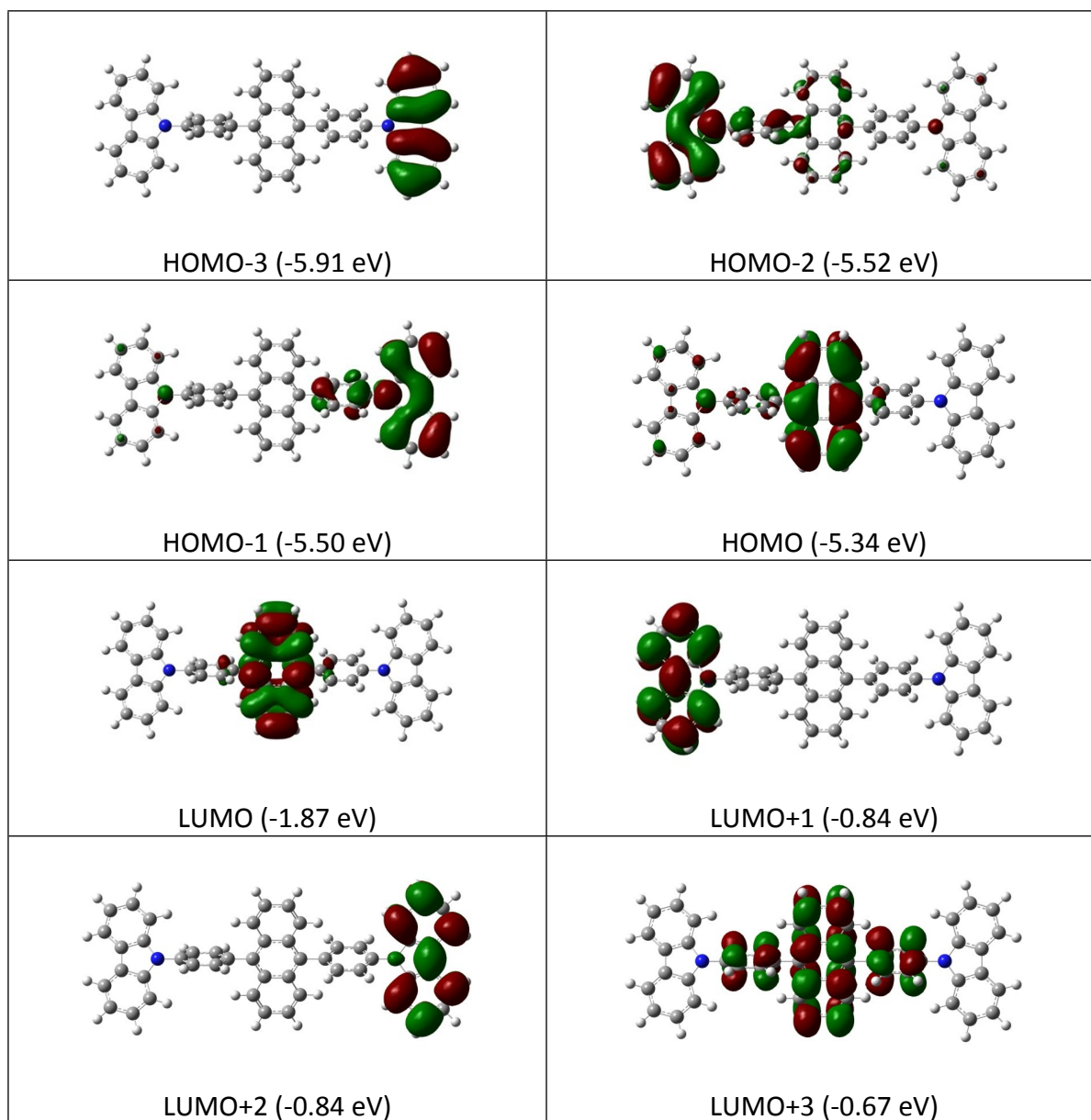
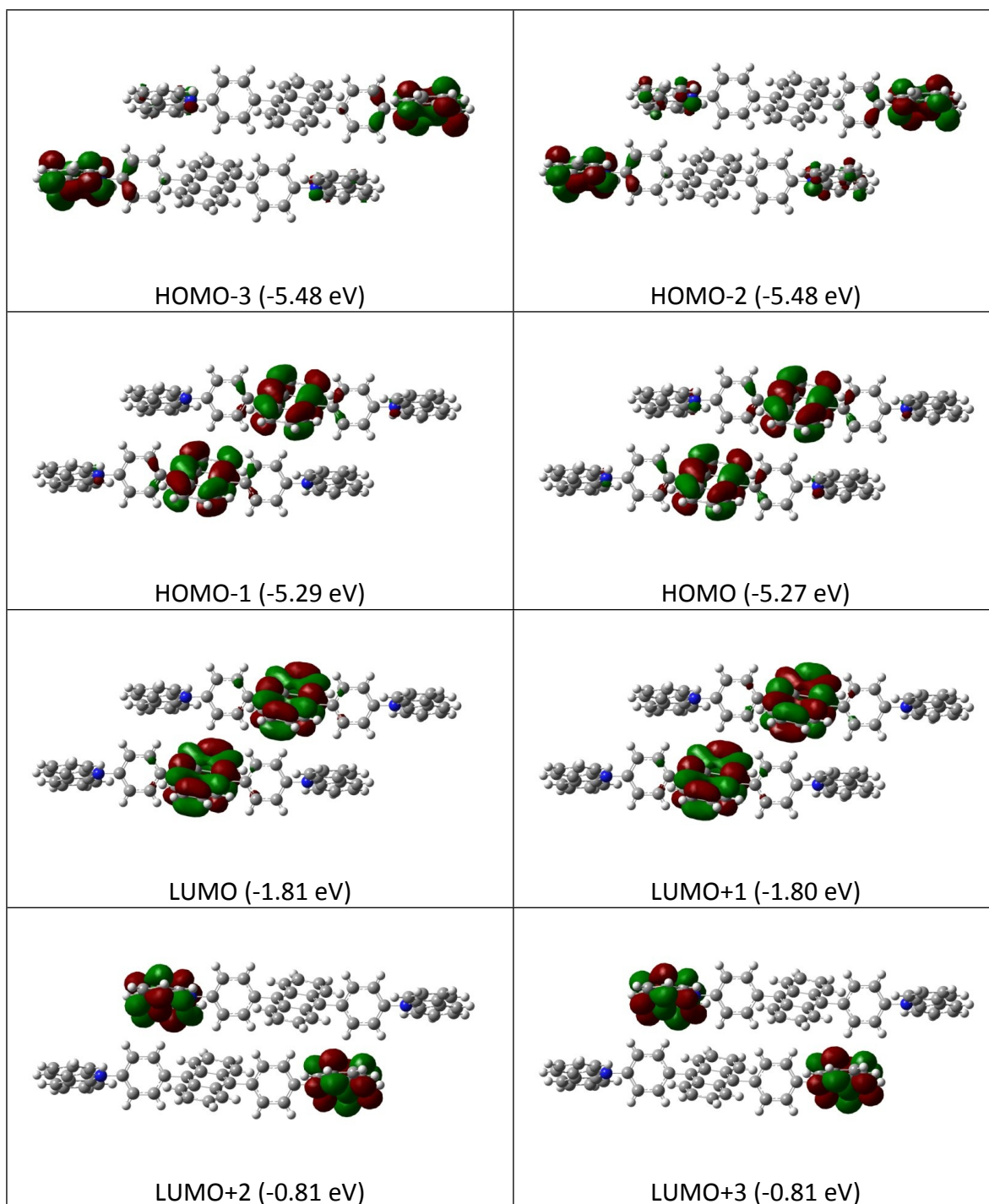


Figure S3. Molecular packing of **Cz⁹PhAn** from a top view.





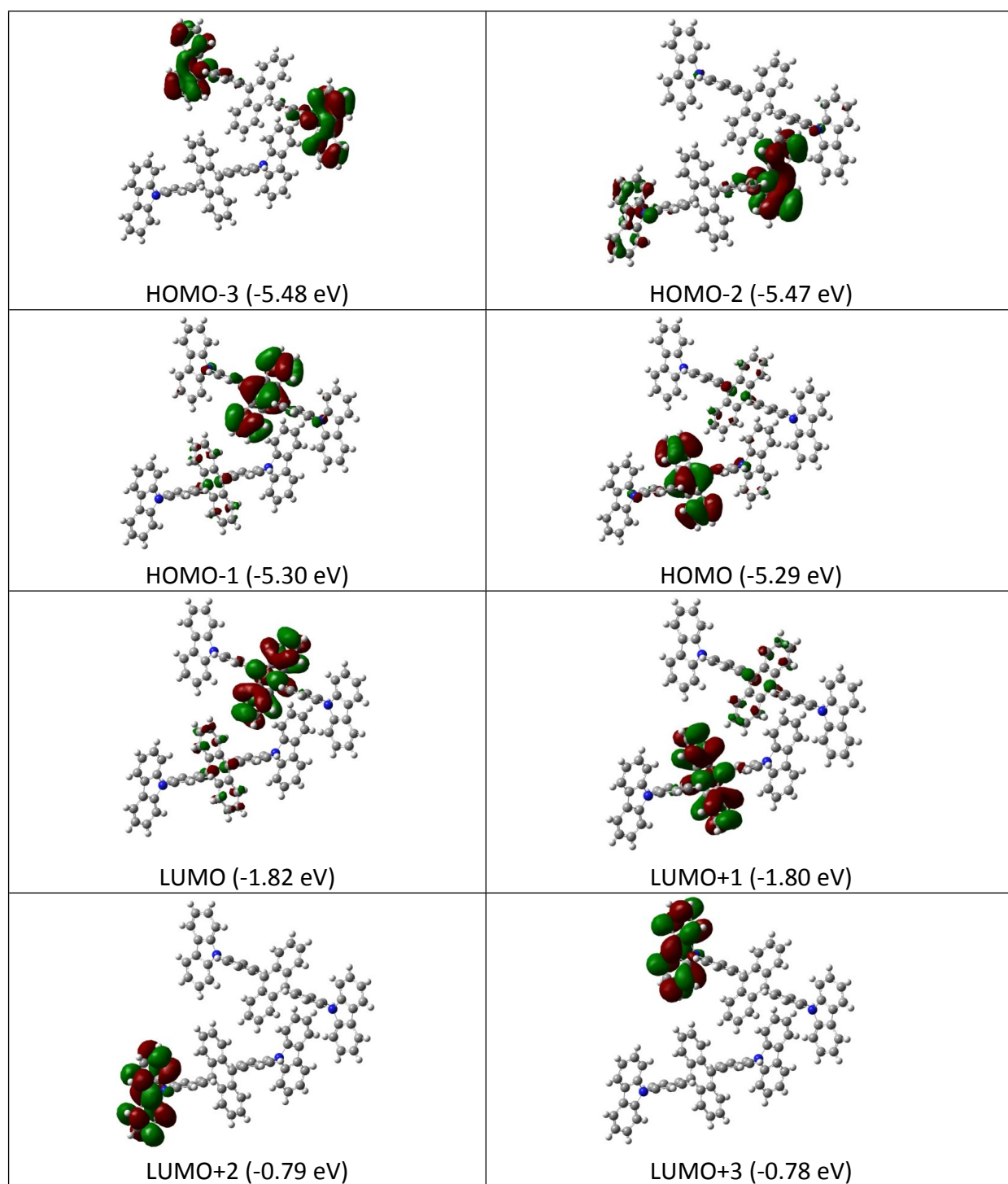


Figure S4. HOMO and LUMO frontier orbitals distribution for **Cz⁹PhAn** calculated using DFT methods (B3LYP 6-31G*).

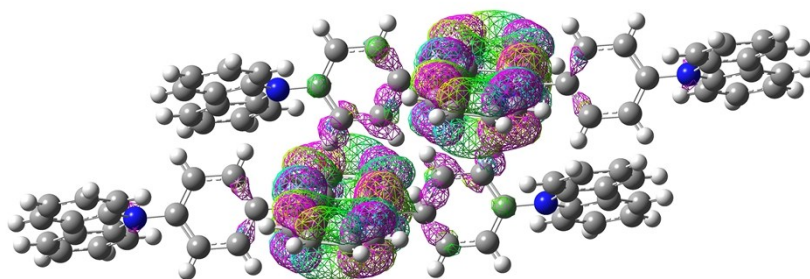


Figure S5. The side view of two truncated **Cz⁹PhAn** slabs. $S_0 \rightarrow S_1$ at 430 nm, $f = 0.1422$, HOMO (pink mesh) \rightarrow LUMO (green mesh) (98%). The distance between anthracenes is calculated to be 4.03 Å

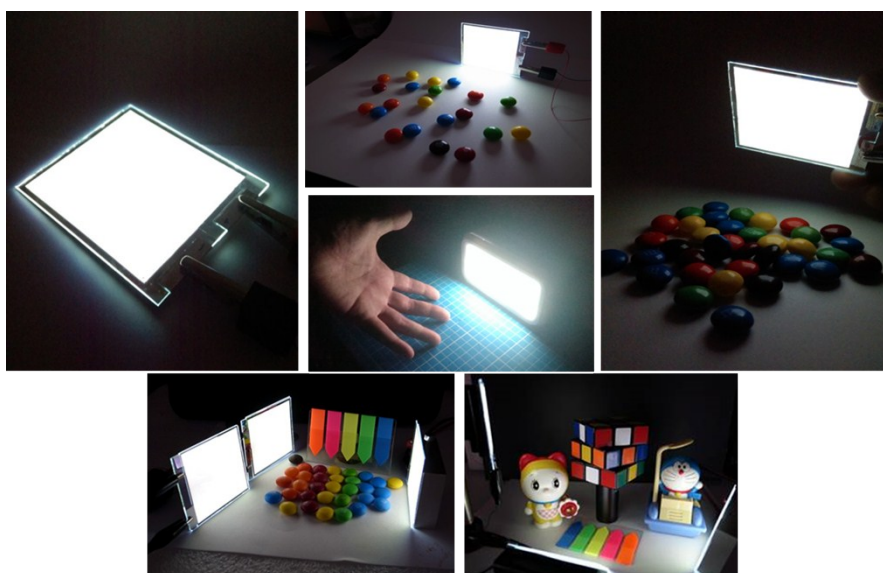


Figure S6. A prototype demonstration of our single molecule type WOLED lighting device based on **Cz⁹PhAn** with the size of $5 \times 10 \text{ cm}^2$ or $5 \times 5 \text{ cm}^2$.

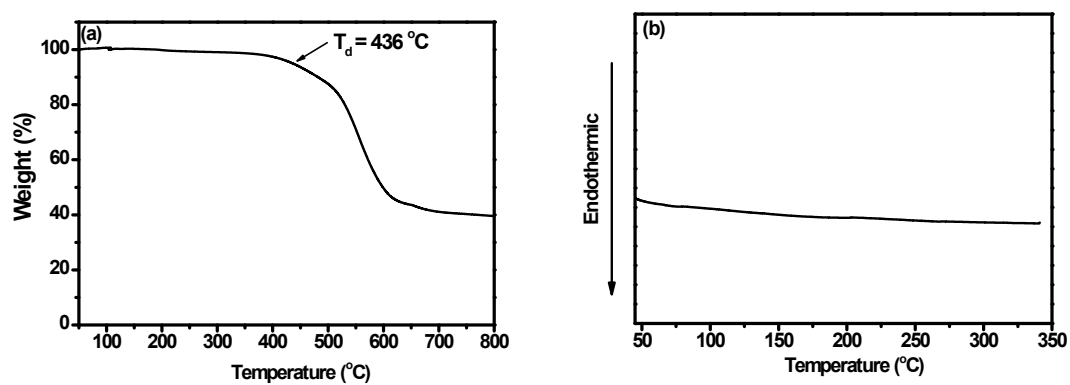


Figure S7. (a) TGA and (b) DSC spectra of **Cz⁹PhAn**.

Table S1. Crystal data and structure refinement details for **Cz⁹PhAn**.

CCDC no.	1008747	
Empirical formula	C ₅₀ H ₃₂ N ₂	
Formula weight	660.78	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.8317(4) Å	α = 90°.
	b = 7.8512(3) Å	β = 90.411(2)°.
	c = 17.4533(8) Å	γ = 90°.
Volume	1758.27(12) Å ³	
Z	2	
Density (calculated)	1.248 Mg/m ³	
Absorption coefficient	0.072 mm ⁻¹	
F(000)	692	
Crystal size	0.16 x 0.11 x 0.02 mm ³	
Theta range for data collection	2.33 to 25.00°.	
Index ranges	-15 ≤ h ≤ 15, -8 ≤ k ≤ 9, -20 ≤ l ≤ 20	
Reflections collected	10927	
Independent reflections	3090 [R(int) = 0.0794]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.998 and 0.961	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3090 / 0 / 235	
Goodness-of-fit on F ²	1.017	
Final R indices [I > 2σ(I)]	R1 = 0.0590, wR2 = 0.1219	
R indices (all data)	R1 = 0.1489, wR2 = 0.1587	
Largest diff. peak and hole	0.161 and -0.121 e.Å ⁻³	