Synthesis, Structure, Properties, and Application of a Carbazole-Based Diaza[7]helicene in a Deep-Blue-Emitting OLED

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Abstract: A carbazole-based diaza[7]helicene, 2,12-dihexyl-2,12-diaza[7]helicene (1), was synthesized by a photochemical synthesis and its use as a deep-blue dopant emitter in an organic light-emitting diode (OLED) was examined. Compound 1 exhibited good solubility and excellent thermal stability with a high decomposition temperature ($T_d = 372.1$ °C) and a high glasstransition temperature $(T_g, up to$ 203.0 °C). Single-crystal structural analysis of the crystalline clathrate (1)₂·cyclohexane along with a theoretical investigation revealed a non-planarfused structure of compound 1, which prevented the close-packing of molecules in the solid state and kept the molecule in a good amorphous state, which allowed the optimization of the properties of the OLED. A device with a structure of ITO/NPB (50 nm)/ CBP:5% 1 (30 nm)/BCP (20 nm)/ Mg:Ag (100 nm)/Ag (50 nm) showed saturated blue light with Commission

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Internationale de L'Eclairage (CIE) coordinates of (0.15, 0.10); the maximum luminance efficiency and brightness were $0.22 \text{ cd } A^{-1}$ (0.09 Lm W⁻¹) and 2365 cd m⁻², respectively. This new class of helicenes, based on carbazole frameworks, not only opens new possibilities for utilizing helicene derivatives in deep-blue-emitting OLEDs but may also have potential applications in many other fields, such as molecular recognition and organic nonlinear optical materials.

Introduction

Over the past couple of decades, organic light-emitting diodes (OLEDs) have been of great interest as promising candidates for applications in displays and solid-state lighting.^[1] To meet the requirement of full-color displays, suitable blue-light-emitting materials with saturated color purities, high solid-state photoluminescence (PL) quantum yields, and good stabilities still require further development to match the advancements in red- and green emitters.^[2] An ideal blue-light material would have CIE coordinates of (0.14, 0.08), as specified in the National Television System Committee (NTSC) standard. Until now, there have only

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been a few reported deep-blue emitters and the realization of highly efficient OLEDs remains a big challenge because blue light is generated from wide-gap excited states.^[3] It is well-known that the doping approach, which uses considerable amounts of blue-emitting dopants, is an effective strategy for improving device performance in terms of electroluminescence (EL) efficiency, pure emissive color, and operational lifetime.^[4] Moreover, to avoid current leakage from the device, a homogeneous film without grain boundaries or pin holes is required.^[5] To achieve this result, the introduction of suitable lengths of alkyl substituents onto organic molecules is a key approach that can also ensure the solubility of these molecules in solvents for the fabrication of devices in solution.^[6]

Helicene derivatives are a class of chiral helical molecules that are structurally characterized by their ortho-fusion of aromatic rings. Their unique structures and properties have led to them being extensively explored for use in various applications, such as asymmetric catalysis,^[7] enantioselective fluorescent sensors,^[8] chiral discotic liquid-crystalline materials,^[9] and organic materials that have nonlinear optical properties;^[10] however, their use as emitters in OLEDs has been rarely reported.^[11] Their twisted and non-coplanar helical configuration can prevent close-packing interactions, thereby effectively relieving excited-state quenching. Furthermore, their highly fused conjugated geometry could extend the π -system, which could balance the efficiency and charge-transport in OLEDs. Therefore, helicenes are promising candidates for emitting materials.

The carbazole group is a popular functional unit in conjugated systems owing to its good planarity and N–H bond, which can be easily substituted for other functional groups.^[12] Herein, by using carbazole as the starting material, we synthesized a nitrogenous helicene that was comprised of seven rings, namely 2,12-dihexyl-2,12-diaza[7]helicene (1), by using a traditional oxidative-photocyclization method (Scheme 1). Photocyclized compound 1 was ob-



Scheme 1. Synthesis of compound 1.

tained within a very short reaction time (about 10 min) in high yield (80.5%). Such an efficient and convenient reaction rendered it feasible to synthesize other carbazole-based diaza[7]helicene derivatives. We confirmed that compound 1 exhibited good solubility in common organic solvents, which overcame the formidable synthetic problem of long helicenes, which typically form highly rigid and annelated structures.^[13] Meanwhile, compound 1 showed excellent thermostability, with a decomposition temperature (T_d) of 372.1 °C and a high glass-transition temperature (T_g) of up to 203.0 °C. Single-crystal structure analysis and theoretical investigation revealed a non-planar-fused structure of compound 1, which decreased the close-packing arrangement and kept the molecule in a good amorphous state. These favorable properties enabled the optimization of the electroluminescent behavior of the OLED. An OLED device with the structure ITO/NPB (50 nm)/CBP:5% 1 (30 nm)/BCP (20 nm)/Mg:Ag (100 nm)/Ag (50 nm) was fabricated and emitted saturated blue light with CIE coordinates of (0.15, 0.10), which were quite close to the NTSC standard blue CIE coordinates, and maximum luminance efficiency and brightness of 0.22 cd A^{-1} (0.09 Lm W^{-1}) and 2365 cd m^{-2} , respectively. Moreover, by slow evaporation from a mixture of cyclohexane and CH₂Cl₂, we fortunately obtained the crystalline clathrate, that is, $(1)_2$ -cyclohexane, which has great potential in various supramolecular-chemistry applications, such as crystal engineering^[14] and molecular recognition.^[15] Carbazole-based helicenes may allow us to utilize helicene derivatives in deep-blue OLEDs and in many other fields, such as molecular recognition and organic nonlinear optical materials.

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Results and Discussion

Synthesis and characterization: The synthesis of compound 1 is shown in Scheme 1. First, compound 2 was formylated to give compound 3 by a Vilsmeier–Haack reaction with DMF and POCl₃. Then, compound 3 was subjected to a McMurry coupling reaction with TiCl₄, Zn powder, and pyridine in THF under an argon atmosphere to obtain compound 4. Finally, the target compound (1) was successfully achieved by oxidative photocyclization using compound 4, I₂, and propylene oxide in benzene under irradiation from a Hanovia high-pressure mercury lamp. The compounds were characterized by ¹H NMR, ¹³C NMR, and FTIR spectroscopy, MS, elemental analysis, and single-crystal X-ray diffraction.

Simple syntheses and satisfactory yields in each step would allow compound **1** to be synthesized on a large scale. Indeed, photocyclized compound **1** was obtained in an exceedingly short reaction time (about 10 min) and high yield (80.5%), which afforded us with an efficient and convenient route for synthesizing other diaza[7]helicene derivatives. Importantly, compound **1** was readily soluble in common organic solvents, owing to its hexyl substituents, as well as its non-coplanar helical structure. Such good solubility not only overcame the formidable synthetic problem of long helicenes, which typically form highly rigid and annelated structures,^[13] but also made it possible for us to afford homogeneous films^[5] and the fabrication of devices in solution.^[6]

Crystal-structure analysis: A yellow bulk crystal (see the Supporting Information, Figure S1) was obtained by crystallization of compound 1 from CH₂Cl₂/cyclohexane. The molecular structure and its packing arrangement are given in Figure 1. The crystal data and intensity collection parameters are summarized in Table 1. Unexpectedly, XRD showed that this sample was a host-guest complex with a 2:1 clathrate stoichiometry ((1)₂-cyclohexane), rather than a single crystal of compound 1 (Figure 1a). More specifically, a right-handed helicene interacted with a left-handed helicene through various short contacts to form a porous structure and molecules of cyclohexane were inserted into the holes (Figure 1b). This finding has important implication because clathrates have great potential in supramolecularchemistry applications, such as crystal engineering^[14] and molecular recognition.^[15] The dihedral angles between two planar carbazole segments in right-handed (containing N1, N2) and left-handed helicenes (containing N3, N4) were 27.4° and 30.1°, respectively. The non-coplanar-fused crystal structure of compound 1 impeded the close-packing arrangement and kept the molecule in a good amorphous state. Moreover, there were no classical hydrogen-bonding or classical face-to-face π - π interactions between the neighboring molecules owing to non-coplanar fused rings and a steric effect of the long substituted alkyl chains.

Thermal properties: Next, we investigated the thermal properties of the recrystallized clathrate of compound 1,

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Figure 1. a) Molecular structure of $(1)_2$ -cyclohexane; ellipsoids set at 30% probability. b) Crystal-packing diagram along the crystallographic *a* axis; hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data and structure refinement of $(1)_{2^{\circ}}$ cyclohexane.

(1)2	•cyclohexane
empirical formula	$(C_{38}H_{40}N_2)_2 \cdot C_6H_{12}$
formula weight	1133.63
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	8.3476(4)
$b\left[\mathring{A}\right]$	27.5396(14)
c [Å]	28.7473(15)
β[°]	93.4150(10)
$V[Å^3]$	6597.0(6)
Z	4
$ ho_{ m calcd} [m g cm^{-3}]$	1.138
$\mu (Mo_{Ka}) [mm^{-1}]$	0.065
F (000)	2436
crystal size [mm]	$0.50 \times 0.45 \times 0.10$
$2\theta_{\text{max}}$ [°] (completeness)	54.8 (99.4%)
total reflns	40277
unique reflns	14897 [R(int) = 0.0252]
data/restraints/parameters	14897/0/779
GOF, F^2	1.216
final R indices $[I > 2\sigma(I)]$	R1 = 0.0551, wR2 = 0.1669
R indices (all data)	R1 = 0.0803, wR2 = 0.1840
largest diff. peak/hole [e Å ⁻³]	0.747/-0.320

(1)₂-cyclohexane. Thermal transitions and stability were investigated by simultaneous TG-DSC. DSC scans were performed in the temperature range 25–240 °C for the first heating and cooling cycle, from 25–250 °C for the second cycle, and from 25–260 °C for the third cycle (see the Sup-



Figure 2. TG curve of $(1)_2$ -cyclohexane, recorded under a nitrogen atmosphere, in the temperature range 25–600 °C at a heating rate of 10 °C min⁻¹.

porting Information, Figure S10). A broad endothermic peak was observed at 96.0 °C, which corresponded to the desolvation of cyclohexane. Indeed, the observed mass-loss value of 7.42% (Figure 2) was in agreement with the calculated weight percentage of cyclohexane in $(1)_2$ -cyclohexane (7.43%). The desolvation temperature was much higher than the normal boiling point of cyclohexane (80.7 °C), which indicated that guest molecules were rather strongly held within the compact host lattice. This clathrate showed no melting point but instead showed a high glass-transition temperature at about 203.0 °C (T_g) from the first to the third heating processes. The TG curve showed that host molecule 1 possessed a high thermal-decomposition temperature $(T_d,$ corresponding to 5% weight loss) of 372.1 °C. It should be emphasized that a high T_d value is a great asset to OLED applications, because Joule heating occurs under typical operating conditions.^[16] These thermal analysis data confirmed that compound 1 was thermally stable and suitable for vacuum thermal sublimation for OLED fabrication.

Optical and electrochemical properties: The UV/Vis absorption and photoluminescence (PL) spectra of compound 1 in CH_2Cl_2 (1×10⁻⁵ M) and in the thin film are shown in Figure 3a. The UV/Vis spectra were characterized by several structured bands between 280 and 450 nm. Specifically, the absorption spectrum of compound 1 in CH₂Cl₂ contained two maxima (300 and 328 nm), one medium peak (313 nm), two shoulders (348 and 363 nm), and two minima (410 and 436 nm). Similar absorption behavior was found in the thin film except that the corresponding peaks and shoulders were red-shifted by about 5-8 nm. The main absorption peaks of compound 1 were blue-shifted compared with those of linear carbazole dimers 4 (see the Supporting Information, Figure S11) and with literature data.^[17] This shift suggested that the twisted and non-coplanar helical configuration prevented electron-delocalization to some extent. Compound 1 in CH_2Cl_2 emitted pure blue fluorescence with emission peaks at 444 and 471 nm and a shoulder peak at 498 nm. By comparison, the PL spectrum of the neat film showed only a small red-shift (about 8 nm), thereby indicating the formation of weak J-aggregates in the solid state. We concluded that neither specific nor additional intermolecular interactions that involved the π -systems occurred when the

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Figure 3. a) Normalized absorption and PL spectra of compound 1 in CH_2Cl_2 and in a thin film. b) Normalized absorption and PL spectra of compound 1 in different solutions $(1 \times 10^{-5} \text{ M})$. All of the PL emission spectra were excited at 325 nm.

film was formed because both the UV/Vis absorption and the PL spectra in the film state were identical to that in solution. Moreover, small Stokes' shifts (about 10 nm) and good mirror images between the absorption and fluorescence spectra revealed almost no conformational changes between the ground state and the excited state. Moreover, the absorption and PL emission spectra of compound 1 in different solvents exhibited solvent-polarity independence and PL quantum yields of 9-10% (Figure 3b; also see the Supporting Information, Table S12). Absorption at long wavelengths when the PL spectra were excited at 325 nmthereby generating intermolecular energy transfer-was determined to be the main reason for the low quantum yields. The LUMO/HOMO energy gap was estimated from the absorption edge of the optical absorption spectra.^[18] From the spectrum of the thin film, the optical band gap of compound 1 was 2.79 eV.

Cyclic voltammetry (CV) was used to identify the electrochemical behavior of compound **1** (Figure 4). A conventional three-electrode cell with a Pt working electrode, a Ag wire counter electrode, and a Ag/AgCl reference electrode was used. The potential of the Ag/AgCl reference electrode in CHCl₃ (0.1 M Bu₄NClO₄) was calibrated by using the ferrocene/ferrocenium (Fc/Fc⁺) redox system (-4.8 eV with respect to the vacuum level).^[19] In this arrangement, the halfwave potential of Fc/Fc⁺ ($E_{1/2,FOC}$) was 0.269 V versus Ag/ AgCl. The oxidation peaks of compound **1** were at 0.658 and 1.086 V and its onset oxidation potential of 0.53 V ($E_{onset(ox)}$) was adopted to determine the HOMO level. Thus, the HOMO level of compound **1** was estimated to be -5.06 eV by using the equation HOMO= $-e(E_{onset(ox)})-E_{1/2}$



Figure 4. CV of compound 1 in $CHCl_3~(0.1\,{\mbox{m}}~Bu_4NClO_4)$ at a scanning rate of $200~{\mbox{m}}V\,s^{-1}.$

 $_{2,FOC}$)-4.8 eV.^[20] Correspondingly, the energy of the LUMO level, as calculated by subtraction of the optical band gap (2.79 eV) from the HOMO level, was -2.27 eV.

Quantum-chemical calculations: To gain an insight into the electronic properties of compound **1**, quantum-chemical calculations were performed by using the Gaussian 09 program.^[21] The geometry was optimized by using density functional theory (DFT) with the B3LYP function and the 6-31G(d) basis sets. The optimized geometry, molecular orbitals, and energy diagrams are shown in Figure 5. As de-



Figure 5. a) Optimized geometry of compound 1. b) Molecular orbitals and energy diagrams [eV] of compound 1, calculated by using the B3LYP/6-31G(d) method.

scribed above, the molecular geometry was divided into two planar segments, containing five aromatic rings at one end and two at the other end, by the dihedral angle, and the distribution of the HOMO revealed that the delocalization of the electrons was on the main part of the five-membered plane owing to its extended π -electron system and good planarity, whilst the LUMO was spread over the whole condensed nucleus and exhibited limited delocalization.

Vertical electronic transitions for compound **1** were calculated by using TD-DFT methods at the B3LYP/6-31G(d) level. The transition energies, oscillator strength, and assignments for the most-relevant singlet excited states are listed in the Supporting Information, Table S13. The UV/Vis spectra were calculated by using the SWizard program, revision 4.6,^[22] with the Gaussian model. The half-bandwidths (D_{1/2,1})

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Figure 6. TD-DFT-calculated electronic spectrum of compound 1 compared with the experimental electronic spectrum (in CH_2Cl_2 , 10^{-5} M).

were taken to be equal to 3000 cm⁻¹ and the simulated spectrum (Figure 6) accurately reproduced the experimental data. These results indicated that the most-intense absorption band at 332 nm (30100 cm^{-1}) was mainly due to the HOMO \rightarrow LUMO+1 transition, whilst the HOMO \rightarrow LUMO transition at 409 nm (24500 cm⁻¹) was characteristic of a forbidden transition and possessed a small oscillator strength of 0.0320, which we believed to be unfavorable for efficient fluorescence. The absorptions with calculated absorption wavelengths 290 nm (34200 cm⁻¹) of and 359 nm (27900 cm^{-1}) corresponded to the HOMO-2 \rightarrow LUMO+1 and HOMO-1→LUMO electronic excitations, respectively.

Electroluminescence properties: The device properties of the blue material (1) were examined by doping compound 1 in a CBP host at a concentration of 5% with the following structure: ITO/NPB (50 nm)/CBP:5% 1 (30 nm)/BCP (20 nm)/Mg:Ag (100 nm)/Ag (50 nm); the device configuration and the energy diagram are shown in Figure 7. The EL properties are summarized in Table 2. The device emitted pure blue light ($\lambda_{max} = 446 \text{ nm}$), which was consistent with



Figure 7. a) Device configuration: ITO/NPB (50 nm)/CBP:5 % 1 (30 nm)/ BCP (20 nm)/Mg:Ag (100 nm)/Ag (50 nm). b) Energy-level diagram of the OLED components (relative to the vacuum energy level).

Table 2. EL properties of compound 1 based device.

$V_{\text{onset}}^{[a]}$ [V]	$B_{\rm max}^{~[{\rm b}]} [{\rm cd} { m m}^{-2}]$	$\eta_{\rm c,max}^{\rm [c]} [{\rm cd} {\rm A}^{-1}]$	$\eta_{\mathrm{p,max}}{}^{\mathrm{[d]}} [\mathrm{lm}\mathrm{W}^{-1}]$	$\operatorname{CIE}^{[e]}[x,y]$	$\lambda_{\max}^{[e]} [nm]$	$\eta_{\mathrm{ext,max}}^{\mathrm{[f]}}$ [%]
5.30	2365	0.22	0.09	(0.15, 0.10)	446	0.23

[a] V_{onset} : Turn-on voltage at a brightness of 1 cdm⁻²; [b] B_{max} : maximum brightness at 14.6 V; [c] $\eta_{\text{c,max}}$: maximum mum current efficiency at 11.8 V; [d] $\eta_{p,max}$: maximum power efficiency at 7.1 V; [e] CIE coordinates and λ_{max} values were obtained at the voltage of 8 V; [f] $\eta_{ext,max}$: maximum external quantum efficiency (EQE), calculated from the corresponding current efficiency.



als.^[23] However, the external quantum efficiency (EQE) of the device (0.23%) was inferior to those of a handful of deepblue-emitting OLEDs. For example, Bryce, Petty, and coworkers reported that, by using a carbazole moiety as the donor

1.0 ---- PL 8.0 <u>Is</u>it 9.0 Inter Normalized 7.0 0.0 350 400 450 500 550 600 650 a) Wavelength / nm 1.0 0.8 6V EL Intensity / a.u. 7\/ 0.6 0.4 0.2 0.0 b) 350 400 450 500 550 600 650 Wavelength / nm

Figure 8. a) EL spectrum of the device at 8 V compared with the PL spectrum in CH2Cl2. b) EL spectra of the device at different driving voltages.

the PL spectrum of compound 1 in CH_2Cl_2 (Figure 8). This result suggested that the host-guest CBP/1 system was just like a solid solution, thereby maintaining compound 1 in a good amorphous state. As shown in Figure 9, the corre-



Figure 9. CIE coordinates of the OLED along with the NTSC blue.

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Figure 10. a) Current-density-voltage-brightness (J-V-B) characteristics of the device. b) Current-efficiency-current-density-power-efficiency characteristics of the device.

group, an ambipolar molecule exhibited highly saturated deep-blue emission with a maximum EQE of 4.7% because of its balanced hole- and electron transport.^[4e] We suggested that the unbalanced carrier-transporting properties led to this non-excellent device performance. The low hole-injection barrier (0.37 eV) between NPB and the light-emitting layer facilitated hole transport, whilst a relatively high barrier (0.93 eV) hindered electrons transport from BCP to the light-emitting layer. The EL and thermal stability, and the interesting blue purity make carbazole-based helicene derivatives promising candidates for applications in modern displays. Further study on the structure of the device and full exploration of more carbazole-based helicene derivatives would improve the performances of these OLEDs.

Conclusion

A new carbazole-based diaza[7]helicene, namely, 2,12-dihexyl-2,12-diaza[7]helicene (1), was prepared by a photochemical synthesis and characterized by ¹H NMR, ¹³C NMR, and FTIR spectroscopy, HRMS, and X-ray diffraction. Its thermal, photophysical, electrochemical, and electroluminescent behavior, along with its single-crystal structure and electronic structure were also reported. Compound 1 exhibited good solubility and excellent thermal stability. Absorption and PL spectroscopic analysis, as well as a crystal structure of the crystalline clathrate (1)₂-cyclohexane, showed that the nonplanar conformation was beneficial for impeding the closepacking interactions and keeping the molecule in a good amorphous state. An OLED that incorporated compound 1 as the dopant emitter with the configuration ITO/NPB-(50 nm)/CBP:5% 1 (30 nm)/BCP (20 nm)/Mg:Ag (100 nm)/ Ag (50 nm) emitted saturated blue light with CIE coordinates of (0.15, 0.10). The device attained a brightness of 2365 cdm^{-2} and a maximum luminance efficiency of 0.22 cdA^{-1} (0.09 Lm W⁻¹). This class of carbazole-based helicenes is promising for the application of helicene derivatives in deep-blue-emitting OLEDs and in many other fields, such as molecular recognition and organic nonlinear optical materials.

Experimental Section

Chemicals and instruments: THF was distilled over sodium/benzophenone before use. Other reagents and chemicals were commercially available and used as received. Hexylcarbazole (2) was synthesized according to a literature procedure.^[24] Photocyclization was performed by using a Hanovia high-pressure mercury lamp (500 W). ¹H NMR and ¹³C NMR spectroscopy was performed on a Bruker Advance 300 spectrometer. FTIR spectra were recorded on a Thermo-Nicolet NEXUS 670 spectrometer (Thermo-Nicolet Company, USA). Matrix-assisted laser-desorption/ ionization time-of-flight (MALDI-TOF) MS were recorded on a Bruker Biflex III mass spectrometer that was equipped with a 337 nm nitrogen laser. HRMS spectra were recorded on a Q-TOF6510 spectrograph (Agilent). UV/Vis spectra were recorded on a U-4100 (Hitachi). Elemental analysis was performed on a German Vario EL III elemental analyzer. X-ray diffraction intensity data were collected at 130 K on a Bruker Smart Apex2 CCD area-detector diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Processing of the intensity data was carried out by using the Bruker SMART routine and the structure was solved by direct methods by using the SIR-97 program and refined by a full-matrix least-squares technique based on F² with the SHELXL-97 program.^[25]

CCDC-860240 (1)₂-cyclohexane contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

TG/DSC were measured on a SDT Q600 V8.0 Differential Scanning Calorimeter under a nitrogen atmosphere with heating and cooling rates of 10°C min⁻¹. UV-absorption spectroscopy was performed on a TU-1800 spectrophotometer and photoluminescence (PL) measurements were collected on a Hitachi F-4500 fluorescence spectrophotometer with a 150 W Xe lamp. The concentration of the solutions was 10⁻⁵ M and the neat film was prepared by using the spin-coating method. PL efficiencies were calculated by using quinine sulfate in $0.1\,\mathrm{M}$ H₂SO₄ as a reference.^[26] Cyclic voltammetry (CV) of compound 1 in 0.1 M [Bu₄N][ClO₄]CHCl₃ solution was carried out on a CHI660D electrochemical workstation. A conventional three-electrode cell with a Pt working electrode, a Ag wire counter electrode, and a Ag/AgCl reference electrode was employed. The experiment was corrected by using the ferrocene/ferrocenium (Fc/Fc⁺) redox system. DFT and TD-DFT calculations were performed by using the Gaussian 09 program. The target molecule was assumed to be an isolated molecule in the gas phase.

9-hexyl-9 H-carbazole-3-carbaldehyde (3): POCl₃ (1.17 mL, 12.55 mmol) was added dropwise into DMF (1.13 mL, 14.60 mmol) at 0°C under an argon atmosphere. Then, a solution of hexylcarbazole (2; 3.145 g, 12.50 mmol) in dry CHCl₃ (7.5 mL) was added and the reaction mixture was heated at reflux for 16 h and then cooled to RT. The mixture was then poured into ice water and neutralized to pH 8 with sodium bicarbonate. The aqueous solution was extracted several times with CHCl₃. The CHCl₃ solution was washed with water and dried with anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 24:1 v/v) to give the product (2.551 g, 73.0%). ¹H NMR (300 MHz, CDCl₃, 25°C, TMS): δ =10.10 (s, 1H; CHO), 8.62 (d, *J*=1.5 Hz, 1H; Ar-H), 8.16 (d, *J*=7.8 Hz, 1H; Ar-H), 8.01 (dd, *J*=8.6 Hz, 1H; Ar-H), 7.57–7.44 (m, 3H; Ar-H), 7.33 (m, 1H;

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Ar-H), 4.34 (t, J=7.2 Hz, 2H; hexyl-H), 1.90 (m, 2H), 1.38–1.25 (m, 6H; hexyl-H), 0.87 ppm (t, J=7.1 Hz, 3H; hexyl-H); ¹³C NMR (75 MHz, CDCl₃, 25 °C, TMS): δ =191.22, 143.58, 140.68, 128.02, 126.63, 126.18, 123.46, 122.57, 122.51, 120.22, 119.77, 108.87, 108.42, 42.93, 30.99, 28.38, 26.40, 21.99, 13.44 ppm; FTIR (Smart iTR diamond ATR accessory): $\tilde{\nu}$ = 1688 cm⁻¹; elemental analysis calcd (%) for C₁₉H₂₁NO: C 81.68, H 7.58, N 5.01; found: C 81.66, H 7.63, N 4.94.

(E)-1,2-bis(9-hexyl-9H-carbazol-3-yl)ethene (4): To a suspension of Zn powder (5.182 g, 79.2 mmol) in dry THF (200 mL) was added TiCl₄ (4.42 mL, 40.21 mmol) by syringe at 0°C under an argon atmosphere. After addition of pyridine (3.2 mL), the suspension was heated at reflux (80°C) for 2 h. A solution of compound 3 (1.120 g, 4.01 mmol) in dry THF (100 mL) was then added dropwise over 1.5 h to the gently refluxing suspension. The resulting mixture was heated at reflux continuously under stirring for 24 h, and, after cooling to RT, saturated aqueous NaHCO3 (200 mL) was added. The reaction mixture was filtered and the filtrate was extracted several times with $CH_2Cl_2.$ Then, the CH_2Cl_2 solutions of the several times with the transmission of the times of the transmission of transmission of the transmission of the transmission of the transmission of transmission tion was washed with water, dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ CH_2Cl_2 , 1:2 v/v) to give the product (0.655 g, 62.0%). M.p.: 191°C; ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS): $\delta = 8.27$ (d, J = 1.2 Hz, 2H; Ar-H), 8.15 (d, J=7.5 Hz, 2H; Ar-H), 7.72 (dd, J=8.6 Hz, 2H; Ar-H), 7.50-7.44 (m, 2H; Ar-H), 7.39 (t, J=7.8 Hz, 6H; Ar-H), 7.28–7.22 (m, 2H; Ar-H), 4.30 (t, J=7.4 Hz, 4H; hexyl-H), 1.88 (m, 4H; hexyl-H), 1.41-1.29 (m, 12 H; hexyl-H), 0.87 ppm (t, J = 7.1 Hz, 6 H; hexyl-H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ=140.86, 139.97, 129.22, 127.06, 125.66, 124.23, 123.00, 120.41, 118.85, 118.22, 116.93, 108.83, 108.12, 43.22, 31.59, 28.99, 26.98, 22.54, 13.99 ppm; FTIR (Smart iTR diamond ATR accessory): $\tilde{\nu} = 3017$, 1677 cm⁻¹; MS (MALDI-TOF): m/z: calcd for $C_{38}H_{42}N_2$: 526.33; found: 526.1; elemental analysis calcd (%) for C₃₈H₄₂N₂: C 86.65, H 8.04, N 5.32; found: C 86.57, H 8.05, N 5.26.

2,12-dihexyl-2,12-diaza[7]helicene (1): Argon was bubbled through a solution of compound 4 (0.237 g, 0.45 mmol) and I_2 (0.118 g, 0.46 mmol) in benzene (500 mL) for 30 min and then propylene oxide (18 mL) was added. The mixture was irradiated by a Hanovia high-pressure mercury lamp (500 W) through a quartz filter. After about 10 min, the solvent was evaporated in vacuo. The residual product was dissolved in CHCl3 and washed sequentially with 15% Na₂S₂O₃ and H₂O, dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/CH2Cl2, 5:1 v/v) and recrystallized from CH2Cl2/n-hexane (1:10) to give the product (0.19 g, 80.5%).¹H NMR (300 MHz, CDCl₃, 25°C, TMS): $\delta = 9.37$ (s, 1H; Ar-H), 9.05 (d, J = 8.1 Hz, 1H; Ar-H), 8.66 (s, 1H; Ar-H), 8.29 (d, J=7.8 Hz, 1H; Ar-H), 7.92 (t, J=7.1 Hz, 2H; Ar-H), 7.72 (m, 2H; Ar-H), 7.62-7.44 (m, 4H; Ar-H), 7.32-7.18 (m, 2H; Ar-H), 4.49 (t, J=7.4 Hz, 2H; Ar-H), 4.42 (t, J=7.5 Hz, 2H; hexyl-H), 2.05-1.94 (m, 4H; hexyl-H), 1.51–1.21 (m, 12H; hexyl-H), 0.90 (t, J=7.1 Hz, 3H; hexyl-H), 0.81 ppm (t, J = 7.1 Hz, 3H; hexyl-H); ¹³C NMR (75 MHz, CDCl₃, 25°C, TMS): δ=142.10, 139.80, 139.70, 138.70, 127.97, 127.55, 126.62, 126.58, 126.50, 126.17, 124.37, 124.31, 123.76, 123.36, 122.81, 122.35, 120.37, 118.23, 118.15, 117.11, 116.41, 109.00, 108.71, 108.05, 105.49, 43.02, 42.82, 31.12, 31.08, 28.69, 28.61, 26.54, 26.52, 22.14, 22.07, 13.58, 13.49, 13.45 ppm; FTIR Smart iTR diamond ATR accessory): $\tilde{\nu} =$ 3047, 2946 cm⁻¹; HRMS calcd for $C_{38}H_{41}N_2$: 525.3270 [M+H]⁺; found: 525.3272.

Fabrication and characterization of the OLED device: Prior to the fabrication of the OLED, indium-tin-oxide (ITO) glass substrates were cleaned sequentially by ultrasonication in organic solvent and de-ionized water and dried for 2 h. After UV-ozone and plasma treatments, ITO with a sheet resistance of $7 \Omega \text{sq}^{-1}$ on glass was patterned with an active area of $3 \times 3 \text{ mm}^2$. The structure of the blue device was as follows: ITO/ 4,4'-bis(1-naphthyl-*N*-phenylamino)-biphenyl (NPB, 50 nm)/4,4'-*N*,*N*'-dicarbazolebiphenyl (CBP):5% compound 1 (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanhroline (BCP, 20 nm)/Mg:Ag (100 nm)/Ag (50 nm). NPB and BCP were the hole-transport and electron-transport layers, respectively. CBP:5% 1 was used as the emitting layer, ITO as the anode, and Mg:Ag as the cathode, respectively. All of the organic layers were

deposited successively by thermal evaporation at a rate of 1 Ås^{-1} under 5×10^{-4} Pa pressure. The EL spectrum and current-density–voltage– brightness (*J–V–B*) characteristics were measured on a Photo Research PR705 spectrophotometer and a Keithley 4200 semiconductor characterization system, respectively. All of the measurements were performed in air at RT without encapsulation.

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