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PII: S0143-7208(17)31592-9

DOI: 10.1016/j.dyepig.2017.10.013

Reference: DYPI 6311

To appear in: Dyes and Pigments

Received Date: 23 July 2017

Revised Date: 9 October 2017

Accepted Date: 10 October 2017

Please cite this article as: Bezuglyi M, Ivaniuk K, Volyniuk D, Gražulevičius JV, Bagdžiūnas G, An approach to discovering novel exciplex supramolecular complex based on carbazole-containing 1,8-naphthalimide, *Dyes and Pigments* (2017), doi: 10.1016/j.dyepig.2017.10.013.

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Graphical abstract



Highlights

- Semiconductor consisting of the 1,8-naphthalimide and carbazole moieties was synthesized and characterized.
- For this compound, the ambipolar semiconductor properties and recombination of exciton in exciplex complex are indicated.
- The exciplex complex is stabilized by the intermolecular hydrogen bond and electron donor-acceptor interactions.
- OLED from the compound as an emitter exhibited an orange color emission.

An Approach to Discovering Novel Exciplex Supramolecular Complex based on Carbazole-Containing 1,8-Naphthalimide

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Abstract

A new luminescent ambipolar semiconductor consisting of 1,8-naphthalimide as an electronaccepting moiety and carbazole as an electron-donating moiety has been synthesized and characterized. The synthesized compound as ambipolar semiconductor has been investigated by using density functional theory calculations coupled with the charge-hopping model and the time-of-flight experimental method. The time-of-flight hole and electron drift mobilities in the synthesized material's layer approached about 10^{-4} cm² V⁻¹ s⁻¹ at high electric fields. The exciplex complex is stabilized by the intermolecular hydrogen bond and electron donor-acceptor interactions. The energy of interactions between the molecules in the exciplex complex has been

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estimated to be about -100 kJ mol⁻¹ by DFT. Non-doped emissive layer organic light-emitting diode (OLED) using the synthesized compound as an emitter exhibited an orange color emission with the Commission International de L'Eclairage chromaticity coordinates of (0.47, 0.49).

Keywords: carbazole, 1,8-naphthalimide, ambipolar semiconductor, exciplex, hydrogen bonding, OLED.

1. Introduction

The specific intermolecular interactions in the bimolecular electron donor-acceptor systems are broadly investigated and their versatile applications in the optoelectronic devices are extensively studied.^{1 2 3}It is well known that donor-acceptor systems can generate either charge-transfer (CT) complexes in the electronic ground state or excited-state CT complexes (exciplexes) which are formed after the excitation of one of the photoactive moieties.⁴ In particular, an exciplex formation that occurs between the excited singlet state of one molecule or its fragment and the ground state of another one has attracted much attention due to its unique potential in tailoring emission wavelengths without altering the original absorption characteristics of the donoracceptor pair.⁵ Moreover, the exciplexes and their application in the organic light emitting diodes (OLEDs) have attracted significant attention due to the observation of thermally activated delayed fluorescence (TADF).⁶ On the other hand, molecular wires have been intensively studied as electron and/or hole conducting materials.⁷ The molecular wire as a donor-acceptor system has served as a suitable model compound for the elucidation of the electron and/or hole transfer in molecular arrays.⁸ The 1,8-naphthalimide derivatives are known as the photochromic and room-temperature-phosphorescent materials⁹ as well as n-type semiconductors.^{10,11} Moreover, the following derivatives are known to form the various supramolecular assemblies through noncovalent interactions.^{12,13} At the same time, the carbazole derivatives are well known as p-type semiconductors with the interesting luminescent properties^{14,15,16} and ability to form the exciplexes with different acceptors.5 Nowadays, significant progress has been made in the efficient orange-red or orange electroluminescent devices.¹⁷ Several red materials have been developed, such as fluorescent emitter of 4-(dicyanomethylene)-2-*tert*-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4*H*-pyran (DCJTB)¹⁸ and phosphor materials of tris(1-phenylisoquinoline) iridium(III) (Ir(piq)₃)¹⁹ and (bis(2-(3,5-dimethylphenyl)quinoline acetyl-acetonate) bis(2-phenylquinoline iridium(III) (Ir(mphq)2(acac)²⁰ the most common red emission materials. However, the high cost due to the presence of rare heavy metal iridium is a disadvantage to a practical application. Orange-red OLEDs based on the organic materials are still rare.²¹

The aim of this work was the synthesis of the donor-acceptor material based on the carbazole and 1,8-naphtalendicarboxylic acid imide active moieties and investigation of the optical, electrochemical and photophysical properties of the synthesized compound.

2. Experimental Section

2.1. General procedures and instrumentation

Organic solvents were dried according to the standard methods and freshly distilled under argon prior to use. Commercially available hydroxylamine hydrochloride, triethylamine and 1,8-naphthalenedicarboxylic acid anhydride from Sigma-Aldrich were used without further purification. 9-(Oxiran-2-ylmethyl)-9*H*-carbazole from Reahim was twice recrystallized from isopropyl alcohol. Zinc acetate was obtained after reaction of zinc powder with excess of glacial acetic acid, washed with acetone and dried. ¹H and ¹³C NMR spectroscopy was carried out on a

Bruker Avance 400 NMR spectrometer. The chemical shifts are reported in units ppm (parts per million). The residue signals of the solvents were used as internal standards (¹H NMR: standard internal CDCl₃, 7.26 ppm). Attenuated total reflection infrared (ATR IR) spectrum was recorded using a Bruker VERTEX 70 spectrometer. Mass spectrometry (MS) data was recorded on UPLC-MS Acquity Waters SQ Detector 2. The UV/Vis absorption spectra were recorded with Avantes AvaSpec-2048XL spectrometer. The photoluminescence spectra and the fluorescence decay curves were recorded by Edinburgh Instruments FLS980 spectrometer with TMS300 monochromators and a red cooled detector (Hamamatsu R928P). Fluorescence quantum yields were measured using integrated sphere of a 120 mm inside diameter spherical cavity calibrated with two standards: quinine sulfate in 0.1 M H₂SO₄ and rhodamine 6G in ethanol. The cyclic voltammetry (CV) measurements were carried out with a glassy carbon working electrode in a three electrode cell in the dry THF solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte at room temperature under argon atmosphere at 100 mV s⁻¹ potential rate. The electrochemical cell comprised platinum wire with 1 mm diameter of working area as a working electrode, Ag wire calibrated versus ferrocene/ferrocinium redox couple as a quasi-reference electrode and platinum coil as auxiliary electrode. Electron photoemission spectrum were recorded from thin solid films of materials on indium tin oxide (ITO) coated glass substrates under negative voltage of 300 V with illumination by deep UV deuterium light source ASBN-D130-CM and CM110 1/8m monochromator and A 6517B Keithley electrometer connected to the counter-electrode. The charge drift mobility measurements by a time-of-flight (ToF) method were recorded from thin solid film (d=2.0 µm) of material deposited in vacuum on indium tin oxide (ITO) coated glass substrates with delay generator Tektronix AFG3011 used to generate square pulse voltage with a pulsed thirdharmonic Nd:YAG laser EKSPLA PL2140 working at a pulse duration of 25 ps and the wavelength of 355 nm and digital storage oscilloscope Tektronix DPO4032 to record the ToF transients. The charge mobilities were evaluated from the equation $\mu = d^2/(U \times t_{tr})$, where t_{tr} is a transit time. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA851e/LF/1100 apparatus at a heating rate of 20°C min⁻¹ under nitrogen atmosphere. The differential scanning calorimetry (DSC) measurements were done on a DSC Q 100 TA Instrument at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The monocrystal X-ray measurements were made on a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Ka radiation (for further details please see in ESI).

2.2 Theoretical calculations

The geometry of **CbzNI** was optimized from X-ray structure as the starting point by B3LYP functional and 6-31G(d,p) basis set with the Spartan'14 program²², followed by calculations of their harmonic vibrational frequencies to verify their stability. All the calculated vibrational frequencies are real, which indicates the true minimum of the total energy on the potential energy hypersurface. A conformational search was performed applying the Monte–Carlo method and MMFF94 force field. The minimum energy conformers found by molecular mechanics were further optimized at DFT/B3LYP/6-31G(d,p) level using the polarizable continuum model (PCM) in THF (ε = 7.6). This was followed by calculate the conformational free energies. The population percentages were calculated using ΔG° and an applying Boltzmann statistics at T= 298 K. The Tamm-Dancoff approximation (TDA) scheme and the B3LYP/6-31+G(d) method are used for all the calculations of singlet and triplet excitation energies because of its lower computational cost and its avoidance of the triplet instability issue compared to full TD-DFT.²³

The intermolecular interaction energies between the molecules in dimers were estimated using the basis set superposition effect (BSSE) concept²⁴ and at wB97X-D functional with the London dispersion corrections and 6-31G(d,p) basis set. The reorganization energies (λ) for the modelled compounds were calculated by the adiabatic potential energy surface method²⁵ and at the B3LYP/6-31+G(d) level in vacuum. Values of λ were calculated according to the following equation (1):

$$\lambda = [E^{\pm}(g^0) - E^{\pm}(g^{\pm})] + [E^0(g^{\pm}) - E^0(g^0)]$$
(1)

where E corresponds to the energy of neutral molecule (g°) in the geometry of cationic/anionic species (g^{\pm}), respectively. The coupling integrals (V_i) for the pathways (see Figure 1) between molecules *m* and *n* were obtained by the site-energy overlap correction method (2)²⁶ at the long-range corrected hybrid density functional wB97X-D and 6-311G(d) basis set in vacuum as

$$V_i = \frac{H_{mn}^0 - \frac{1}{2}S_{mn}(H_{mm} + H_{nn})}{1 - S_{mn}^2}$$
(2)

where V_{mn}^0 is the electronic coupling (transfer) matrix element, S_{mn} is the overlap integral, and $V_{mm(nn)}$ are the energies of the neutral and charged dimer states.

2.3 Synthesis

2.3.1 2-Hydroxy-1H-benzo[de]isoquinoline-1,3(2H)-dione. Dispersion of 1,8naphthalenedicarboxylic acid anhydride (1.98 g, 10 mmol) in the mixture of hydroxylamine hydrochloride (0.70 g, 10 mmol) and triethylamine (1.01 g,10 mmol) in tetraethylene glycol (20 mL) was heated in microwave oven to 150 °C during 30 min in the presence of zinc acetate (2 mg, 0.01 mmol) as catalyst. After reaction mixture cooling solution was poured into hydrochloric acid (1% water solution of HCl, 300 mL). Formed precipitate was filtered, washed by water (100 mL) and dried. Crude product was purified by recrystallization from methanol. Yield 85 %, m.p. 279-281 °C (lit. mp 280-281 °C). This compound was characterized in literature²⁷.

2-(3-(9H-carbazol-9-yl)-2-hydroxypropoxy)-1H-benzo[de]isoquinoline-1,3(2H)-dione 2.3.2 (*CbzNI*). Solution of 2-Hydroxy-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (0.43 g, 4.0 mmol) in DMSO (20 mL) was heated with equimolar amount of 9-(oxiran-2-ylmethyl)-9H-carbazole (0.89g, 4.0 mmol) in presence of triethylamine (1 mg, 0.01 mmol) to 120 °C during 180 min for target material forming. After reaction finish (control via TLC) solution was poured into hydrochloric acid (2% water solution of HCl, 200 mL). Formed precipitate was filtered, washed by water (100 mL) and dried. The crude material was purified by flash-column chromatography (silica, eluent-hexane:chloroform:ethylacetate 5:1:1, later - dichloromethane:methanol 10:1). Yield 76 %, m.p. 193-195 °C, IR (neat), cm⁻¹ 3462 br., 3057 med. 2950 med. 1712 br., 1656 br., 1625 w., 1581 br., 1512 w., 1485 br., 1455 br., 1402 med., 1375 br., 1356 br., 1326 br., 1260 w., 1233 br., 1193 br., 1151 br., 1118 br., 1085 br., 1036 br., 965 br., 886 br., 841 br., 774 br., 753 br., 724 br., 693 med., 653 med., 614 med; ¹H NMR (400 MHz, CDCl₃) δ 8.62 (dd, J = 7.3, 1.1 Hz, 2H), 8.26 (dd, J = 7.4, 1.1 Hz, 2H), 8.08 (d, J = 7.7 Hz, 2H), 7.82 – 7.74 (m, 2H), 7.56 (d, J = 8.2 Hz, 2H), 7.49 (ddd, J = 8.2, 7.1, 1.2 Hz, 2H), 7.25 (ddd, J = 6.9, 6.9, 1.1 Hz, 2H), 4.56 (d, J = 5.2 Hz, 2H), 4.48 (d, J = 9.0 Hz, 2H), 4.30 (dd, J = 11.6, 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) § 156.3, 149.9, 148.7, 147.6, 144.4, 142.7, 141.2, 139.9, 135.7, 135.2, 120.5, 68.0, 60.5, 58.2; Elemental analyses: found: C, 74.1; H, 4.7; N, 6.65 %; molecular formula C₂₇H₂₀N₂O₄ requires C, 74.3; H, 4.6; N, 6.4 %; MS (ES+) found: m/z [M+23: M+Na]⁺ 459.3; molecular formula $C_{27}H_{20}N_2O_4Na$ requires $[M+Na]^+$ 459.1; UV-Vis (THF, 2×10⁻⁴ M): λ_{max} , 332 nm (23,000 mol⁻¹dm³cm⁻¹), 342 (22,000); fluorescence data (THF, 10^{-5} M), excitation λ_{max} 290 nm, emission λ_{max} 345, 360 nm; quantum yield (QY) 0.45, excited state lifetime 7.2 ns.

2.4 OLED fabrication and characterization

The electroluminescent device was fabricated by vacuum deposition of organic semiconductor layers and metal electrodes onto pre-cleaned ITO coated glass substrate under a vacuum of about 10^{-3} Pa. The devices were fabricated by step-by-step deposition of different layers. MoO₃ was used for the preparation of hole-transporting layer. **CbzNI** and BCP were applied for the fabrication of donor and acceptor layers respectively. The structure of the device was of ITO/MoO₃(5nm)/CbzNI(7nm)/BCP(7nm)/Ca(15nm))/Al(85nm). The active area of the obtained devices was $3x6 \text{ mm}^2$. The density-voltage and luminance-voltage characteristics were measured using a Keithley 6517B meter in air without passivation immediately after the formation of the device. The brightness measurements were done using a calibrated photodiode. The electroluminescence spectrum was accomplished with an Avaspec-2048XL spectrometer.

3. Results and Discussion

3.1 Synthesis and identification

The synthesis of **CbzNI** was done from the commercially available reagents as shown at Scheme 1. Hydroxylimide was synthesized according to a previously published method.²⁸ Cyclic anhydride, hydroxylamine hydrochloride and triethylamine as base in tetraethylene glycol were heated using microwave irradiation. Target compound **CbzNI** was synthesized by a nucleophilic epoxy ring opening with hydroxylimide as nucleofile and triethylamine as base of the target. The molecular structure of target compound **CbzNI** was confirmed employing the nuclear magnetic resonance (NMR) (Fig. S1), infrared (IR) spectroscopy (Fig. S2a) and mass (MS) spectrometry (Fig. S2b) methods.



Scheme 1. Synthesis of target compound CbzNI.

In addition, single crystal X-ray analysis of **CbzNI** was conducted.²⁹ Acetonitrile solvent was employed to grow the **CbzNI** mono-crystals. The cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with a space group of P2₁/c. All data are collected in Table S1. Fig. 1 shows the hydrogen bonded dimer structures of **CbzNI**. Additionally, the intermolecular interaction energies (E_i) were estimated employing BSSE method to be -99.3, -32.5 and -14.5 kJ mol⁻¹, respectively for D1-D3 dimers. In D1 dimer with highest E_i, the carbazole (donor) and 1,8-naphthalimide (acceptor) moieties are regularly arranged one by one with the distance of 3.6 Å between them. The hydrogen bonds between H4…O1 and H15A… π -carbazole system were determined. In D2 and D3 dimers, additional hydrogen bonds between O2…H23 and O4…H5 as well as hidrogens of aliphatic moiety with neighboring π -naphthalene imide and carbazole aromatic systems were found, respectively. Moreover, the X-ray analysis showed that hydrogen bonds are not intramolecular but intermolecular ones. Furthermore, the photoactive moieties planes in the D1 dimer are parallel and interacted *via* strong H-bond and donor-acceptor π … π interactions in the solid state (Fig. 1).



Figure 1. Hydrogen bonded dimer structures of CbzNI and theirs calculated interactions

energies.

3.2 Thermal properties

In optoelectronic devices, the materials are often incorporated as solid amorphous thin films. Therefore, the favorable molecular optoelectronic properties and chemical stability of organic electronic materials need to have desired the morphological and thermophysical properties in the solid state because OLEDs are subject to thermal stress from Joule heating and the external environment. Materials with low glass-transition temperature can be more easily diffused into other layers in OLEDs. Therefore, the interlayer diffusion significant reduces the brightness and efficiency of OLEDs.³⁰ For an investigation of thermal properties, differential scanning calorimetry (DSC) was employed to probe the thermal transition of **CbzNI** compound. From first heating scan, the compound exhibits a melting transition (T_m) at 194 °C, which disappears in the second heating. Moreover, an endothermic baseline shift owing to glass transition (T_g) at 80 °C was observed from second heating cycle. (Fig. 2b) This observation shows that the material can form a stable glassy film. The thermogravimetric analysis (TGA) revealed the thermal stability of **CbzNI** with 5% weight loss (T_{5d}) temperature is above 295 °C (Fig. 2a). Therefore, this data can provide the morphologically stable films for the electroluminescence (EL) applications.



Figure 2. Thermal properties of CbzNI. (a) TGA and (b) DSC curves.

3.3 Photophysical and electrochemical properties

UV/Vis absorption and photoluminescence were investigated in solution, frozen to 77 K solution and in a thin solid film. The dilute solution of CbzNI is transparent in the visible region and characterized by intensive absorption below 300 nm and two maxima at 332 nm and 342 nm (Fig. 3a). For the solid film the low-energy maxima become broader one with absorption up to 400 nm and with a weak absorbance "tail" in the region up to 500 nm. The low-energy absorption bands are due to an intramolecular charge transfer (ICT) between the carbazole and 1,8-naphtalimide moieties. The optical band gaps were estimated to be 3.2 and 2.6 eV in solution and solid state, respectively. Moreover, the absorption spectrum in the solid state is wider than in solution due to an interaction between molecules in bulk. Therefore, an exciton is localized on more than one molecule in the aggregated state. Therefore, a difference between the optical band gaps in the solution and solid state is indicated an intermolecular CT between the associated dyes in the solid state. Small red shift of the absorption maximum of ca. 3 nm of the solid sample as compared to that of the dilute solution indicate that a polarity difference of media (the dielectric permittivities of THF and organic solids are of 7.6 and 3-4, respectively) does not seriously affect because the charge transfer transition between the donor and acceptor moieties is spatially forbidden.



Figure 3. Photopgysical properties of **CbzNI**. (a) Absorbance spectra of **CbzNI** in THF solution and in thin solid film, (b) photoluminescence spectra of the dilute (0.1 mg·ml⁻¹) solution and solid film (λ_{ex} = 290 nm), (c) time-correlated single-photon counting curves of (a) fluorescence (λ_{max} =390 nm) and (b) phosphophorescence (λ_{max} =550 nm).

Photoluminescence (PL) spectrum of dilute **CbzNI** solution in THF characterized by emission in UV region with the intensity maxima at 345 nm and 360 nm corresponded to the carbazole moiety emission and shoulder-type low intensive fluorescence signal near 375-390 nm corresponded to 1,8-naphthalimide fluorescence.³¹ In the PL spectrum of the solution recorded at 77 K and with a delay time of 1 μ s the additional maxima corresponding to the emission from excited triplet state (i.e., phosphorescence) of the carbazole moiety in the region of 400-500 nm were observed (Fig. 3b).³² In addition, the intensive photoluminescence maxima at 539 nm and 584 nm corresponding to emission from the singlet and triplet ICT states of a 1,8-naphthalimide

moiety were recorded, respectively.³³ Due to close distance between the donor and acceptor moieties in the crystal it was expected that the exciplex emission can appear in the solid state. The maxima in a range of 350-400 nm corresponding to the singlet emission of the carbazole and naphthalene imide moieties were observed in the photoluminescence spectrum of the solid sample of **CbzNI**. (Fig. 3b) In addition, the broad band in the region of 500-670 nm (maximum at 560 nm) corresponding to the triplet intermolecular CT emission of exciplex appeared in the spectrum of the **CbzNI** layer. The emission lifetime measurements confirmed that the emission bands appearing in the UV region were due to fluorescence and were characterized with the lifetime of 7.2 ns. (Fig. 3c) The emission band appearing in the visible region of the spectrum was characterized with the lifetime of 0.30 μ s which confirms the phosphophorescence character of emission due to the exciplex formation (Fig.3d). Photoluminescence chromaticity of **CbzNI** was found to be yellow with the CIE 1931 coordinates of (0.41, 0.46), see Fig. S3. The photoluminescence quantum yield of the solution in THF was found to be 45±2 % and that of the solid film was of 6.0±2 %.

The possibility of an intramolecular exciplex formation was estimated from the conformational analysis. However, the energy of the conformer with these properties is higher by 32.5 kJ mol⁻¹ than that of the most energetically favorable conformer *Conf7* (for the details see in ESI, Fig. S4). Taking into account this information, we can conclude that the intramolecular exciplex formation is not possible. On the other hand, for proving stability of exciplex supramolecular complex, the intermolecular interaction energy between the molecules in the complex was estimated to be -99.3 kJ mol⁻¹ using the basis set superposition effect (BSSE) concept³⁴ and at the wB97X-D/6-31G(d,p) method. The structure of the supramolcular complex from X-ray analysis was used. In this case, one of the strongest non-bonding interactions was indicated.³⁵

Moreover, for proving the exciplex formation, the energies of the lowest singlet (S₁) and triplet (T₁) excited states were obtained to be 2.22 and 2.19 eV, respectively, by TD-DFT with Tamm-Dancoff approximation (TDA) using the B3LYP/6-31+G(d) method in vacuum. The following data have a good correlation with the experimental PL spectrum of **CbzNI** in the solid state (Fig. 3b). In addition, the calculations showed that this structure contributes to the small ΔE_{ST} (i.e. 25 meV), enabling efficient exciton-harvesting through TADF.



Figure 4. Cyclic voltamperogram (a) and electron photoemission spectrum of the thin film (b) of **CbzNI**.

For the determination of the energy levels, the electrochemical properties of the resulting chromophores were examined by cyclic voltammetry (CV) under argon. The onset of the

oxidation potential (Eox) and reduction potential (Ered) was estimated by the intersection point of the tangent line. The ferrocene/ferrocenium redox couple (Fc/Fc⁺) was used as the reference. Under the same experimental conditions as those for the resulting chromophores, the redox potential (E_{fer}) of Fc/Fc⁺ was determined to be 0.31 V. The highest occupied molecular orbital energy level HOMO and the lowest unoccupied molecular orbital energy level LUMO were calculated according to the equation HOMO = $-1.40 \times (E_{ox} + 4.60 - E_{fer})^{36}$ (eV) and LUMO = - $1.19 \times (E_{red} + 4.78 - E_{fer})^{37}$, respectively. The HOMO and LUMO energy values were estimated to be -5.83 and -2.95 eV from the cyclic voltammetry data (Fig. 4a). Ionization potential (IP) in the solid state was measured to be 5.81 eV by the electron photoemission spectrometry (Fig. 4b). Moreover, the calculated HOMO and LUMO energies of the most energetically favorable conformer using DFT/B3LYP/6-31G(d,p) and polarizable continuum model (PCM) in tetrahydrofuran (THF) were found to be -5.34 eV and -2.44 eV, respectively. The geometry of the **CbzNI** was optimized by B3LYP functional and 6-31G(d,p) basis set starting from X-ray analysis data. In the HOMO, π -electrons are localized on the carbazole moiety, while in LUMO, the electron orbitals have to be localized on the naphthalimide moiety, creating a donor-acceptor characteristic (Fig. 5).



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Figure 5. Electron density distributions in the HOMO (left) and LUMO (right) states of the most energetically favorable conformer calculated by the B3LYP/6-31G(d,p) level and PCM of THF.

3.4 Charge carrier drift mobilities

Because **CbzNI** includes the n- and p-type moieties, the electron and hole mobilities were estimated at different electric fields so an experimental study of the **CbzNI** layer charge transporting properties was performed by the time of fight (ToF) technique. As indicated by the ToF transients in Fig. 6a, hole and electron transport in the layers of **CbzNI** is dispersive which could be due to the presence of traps. The hole and electron mobilities for **CbzNI** taken from the transit times and the film thickness obeyed the Poole–Frenkel electric field dependence (Fig. 6b).



Figure 6. Charge carrier drift mobilities of **CbzNI** layer. (a) ToF transit times and (b) electric field dependences of charge carrier mobilities.

The electron mobility of the layer of **CbzNI** was found in the range from $2.2 \times 10^{-5} \text{ cm}^2 \text{V}^ ^{1}$ s⁻¹ at the electric field of 2.5×10⁵ V cm⁻¹ to 1.6×10⁻⁴ cm²V⁻¹s⁻¹ at the electric field of 7.0×10^5 V cm⁻¹. The electric field dependence for electrons was found to be weaker than that for holes showing that the electron transport is less dispersive then the hole transport. At the low electric fields, the electron mobility of **CbzNI** is by *ca*. an order of magnitude larger than the hole mobility while at the high electric fields the values of hole and electron mobilities of **CbzNI** which was found to be comparable to *ca*. 10^{-4} cm²V⁻¹s⁻¹. These values are comparable to hole and/or electron mobilities of the conventional *tris*(8-hydroxyquinoline) $(Alq_3),^{38}$ materials aluminium such as 1.8naphtalenedicarboxylicimide derivatives,¹¹ *m*-terphenyl oxadiazole derivatives,³⁹ 1,2,3,5tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)⁴⁰ which were used for preparing very efficient fluorescence, phosphorescence or TADF OLEDs.

The crystal structure of **CbzNI** was used to generate the wide variety of possible charge hopping pathways (dimers) (Fig. S5). The standard Marcus-Hush model was used for the estimation of the probability of charge transfer between the molecules.⁴¹ The reorganization energy (λ) values were calculated using the normal-mode analysis and B3LYP/6-31+G(d) method. The reorganization of **CbzNI** energy was found to be 441 meV for holes (λ_+) and 341 meV for electrons (λ_-). These results show that the reorganization energies for holes and electrons are somewhat similar and indicative of the ambipolar charge-transporting properties. The electronic coupling (transfer) integrals H_i for the pathways (see Table S2) were estimated by the siteenergy overlap correction method⁴² at the long-range corrected hybrid density functional wB97X-D and 6-311G(d) basis set in vacuum.⁴³ However, the lowest electronic coupling integrals which stabilized via the hydrogen bond and electron donor-acceptor intermolecular interactions (exciplex complex) were estimated to be 12.5 and 1.6 meV for holes and electrons, respectively. Presumably, the zone of electron-hole recombination could be localized on this dimer (exciplex complex). On the basis of the theoretical calculations the strong dependency of the charge carrier mobility on electric field can be explained by a comparatively large distance between the mass centre of the donor-donor (*ca.* 10 Å between the carbazole moieties) and acceptor-acceptor moieties (*ca.* 10-15 Å between the naphthalene imide moieties) in the carriers hopping pathways (see Table S2).

3.5 Electroluminescence properties

The undoped orange OLED was fabricated using MoO₃ and tris(4-carbazoyl-9-ylphenyl)amine (TCTA) for the preparation of the hole injection and transporting layers, **CbzNI** for emitting layer and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) for the electron transporting layer. Since Ca is highly reactive and corrodes quickly in the ambient atmosphere, Ca layer was topped with 85 nm aluminum (Al) layer was used as the cathode. The energy levels of the materials used for the layers of device are displayed in Fig 7a.



Figure 7. Electroluminescence properties. (a) Energy-band diagram and (b) electroluminescence spectrum of OLED containing the emitting layer of **CbzNI**, (c) current density/luminance-versus-voltage characteristics and (d) current efficiency/power efficiency-current density (inset: external quantum efficiency-current density) of the device.

The electroluminescence maximum of the device was red-shifted by 30 nm in comparison with photoluminescence intensity maximum of the film of **CbzNI**. The device emitted an orange emission with the CIE 1931 coordinates (0.47, 0.49). (Fig. S3) The switch-on voltage for the device was found to be 3.2 V with maximal brightness near 100 cd m⁻², current efficiency of 2.08 cd A⁻¹, power efficiency of 1.87 lm W⁻¹ and maximum external quantum efficiency (EQE) of 1.02%. All OLED characteristics are show in Fig. 7. The EQE value of OLEDs can be predicted by the equation (3):

 $EQE = \rho \times QY \times \phi \times \eta_{out} \tag{3}$

where ρ is the charge balance of the injected holes and electrons, QY is the quantum yield of the emitting material, ϕ is the efficiency of electrically generated excitons conversion to light or efficiency of radiative exciton production and η_{out} is the light-out-coupling efficiency. Considering the ideal of $\rho = 1$, QY = 6.0 %, and estimating η_{out} as 0.20-0.25 at maximum EQE of the device, the efficiency of electrically generated excitons conversion to light (ϕ) was calculated to be in the range 68 to 85%. This result clearly indicates that the device overcame the theoretical limit of 25% for the singlet exciton production efficiency (ϕ) that is assumed for fluorescence-based OLEDs. In the case of the triplet-triplet annihilation (TTA)⁴⁴ or of thermally activated delayed fluorescence (TADF)⁴⁵ mechanisms that can harvest both singlet and triplet excited states, the theoretical limit are of 62.5% and 100%, respectively.

4. Conclusion

In summary, we have presented a new concept of construction of the hydrogen bonding stabilized exciplex formed donor-acceptor compound. The luminescence lifetimes of 7 ns and 0.3 μ s in the UV region and the visible region have been observed which confirms the fluorescence and phosphophorescence characters of emission bands due to monomolecular and exciplex emission, respectively. This compound showed the ionization potential in the solid state of 5.81 eV and the ambipolar semiconductor properties. The hole and electron drift mobilities have been estimated to be 10⁻⁴ cm² V⁻¹ s⁻¹ at high electric fields. The photophysical and charge mobility features have been supported by using the (TD)-DFT methods. Exciplex of **CbzNI** based organic light-emitting diode emitted an orange emission with the CIE 1931 coordinates (0.47, 0.49). This device exhibits the current efficiency of 2.08 cd A⁻¹, power efficiency of 1.87 lm W⁻¹ and maximum external quantum efficiency of 1.02%. The high efficiency of electrically

generated excitons conversion to light has been calculated to be from 68 to 85 %. We envisage that this concept can be applied to other structures.

Acknowledgment

This research was supported by FP7 REGPOT-2012-2013-1 ICT project CEOSeR under grant agreement No 316010. K. Ivaniuk thanks for the support from "AmbiPOD" project under grant agreement No 612670 (IRSES-GA-2013-612670). We are grateful to D. Gudeika for MS, L. Peciulyte for the TGA, DSC measurements.

Supporting Information

NMR, MS, IR spectra, X-ray crystallographic data, conformation analysis and possible carrier hopping pathways are presented. This material is available free of charge *via* the Internet.

Notes and references

¹ Pander P, Kudelko A, Brzeczek A, Wroblowska M, Walczak K, Data P. Analysis of Exciplex Emitters. Lee K-S editor. In: Display and Imaging, Old City Publishing Inc; 2017, Vol. 2, p. 265–277.

² Goushi K, Yoshida K, Sato K, Adachi C. Organic light-emitting diodes employing efficient reverse intersystem crossing for triplet-to-singlet state conversion. Nat Photon 2012;6:253–8. doi:10.1038/nphoton.2012.31.

³ Data P, Kurowska A, Pluczyk S, Zassowski P, Pander P, Jedrysiak R, et al. Exciplex Enhancement as a Tool to Increase OLED Device Efficiency. J Phys Chem C 2016;120:2070–8. doi:10.1021/acs.jpcc.5b11263.

⁴ Skuodis E, Tomkeviciene A, Reghu R, Peciulyte L, Ivaniuk K, Volyniuk D, et al. OLEDs based on the emission of interface and bulk exciplexes formed by cyano-substituted carbazole derivative. Dyes and Pigments 2017;139:795–807. doi:10.1016/j.dyepig.2017.01.016.

5 Kim JH, An B-K, Yoon S-J, Park SK, Kwon JE, Lim C-K, et al. Highly Fluorescent and Color-Tunable Exciplex Emission from Poly(N-vinylcarbazole) Film Containing Nanostructured Supramolecular Acceptors. Adv Funct Mater 2014;24:2746–53. doi:10.1002/adfm.201302924.

6 dos Santos PL, Dias FB, Monkman AP. Investigation of the Mechanisms Giving Rise to TADF in Exciplex States. J Phys Chem C 2016;120:18259–67. doi:10.1021/acs.jpcc.6b05198.

7 Watanabe M, Goto K, Shibahara M, Shinmyozu T. Synthesis, Structure, and Electronic and Photophysical Properties of Two- and Three-Layered [3.3]Paracyclophane-Based Donor–Acceptor Systems. J Org Chem 2010;75:6104–14. doi:10.1021/jo100688m.

8 Miyazaki T, Shibahara M, Fujishige J, Watanabe M, Goto K, Shinmyozu T. Synthesis and Electronic and Photophysical Properties of [2.2]- and [3.3]Paracyclophane-Based Donor–Donor'–Acceptor Triads. J Org Chem 2014;79:11440–53. doi:10.1021/jo5020273.

9 Chen X, Xu C, Wang T, Zhou C, Du J, Wang Z, et al. Versatile Room-Temperature-Phosphorescent Materials Prepared from N-Substituted Naphthalimides: Emission Enhancement and Chemical Conjugation. Angew Chem Int Ed 2016;55:9872–6. doi:10.1002/anie.201601252.

10 Zhu W, Song L, Yang Y, Tian H. Novel Bisthienylethene Containing Ferrocenyl-Substituted Naphthalimide: A Photo- and Redox Multi-Addressable Molecular Switch. Chem Eur J 2012;18:13388–94. doi:10.1002/chem.201202189.

11 Gudeika D, Michaleviciute A, Grazulevicius JV, Lygaitis R, Grigalevicius S, Jankauskas V, et al. Structure Properties Relationship of Donor–Acceptor Derivatives of Triphenylamine and 1,8-Naphthalimide. J Phys Chem C 2012;116:14811–9. doi:10.1021/jp303172b.

12 Shankar BH, Jayaram DT, Ramaiah D. Naphthalene Imide Conjugates: Formation of Supramolecular Assemblies, and the Encapsulation and Release of Dyes through DNA-Mediated Disassembly. Chem Eur J 2015;21:17657–63. doi:10.1002/chem.201502955.

13 Das A, Ghosh S. H-bonding directed programmed supramolecular assembly of naphthalenediimide (NDI) derivatives. Chem Commun 2016;52:6860–72. doi:10.1039/C6CC01983H.

14 Bagdžiūnas G, Grybauskaitė G, Kostiv N, Ivaniuk K, Volyniuk D, Lazauskas A. Green and red phosphorescent organic light-emitting diodes with ambipolar hosts based on phenothiazine and carbazole moieties: photoelectrical properties, morphology and efficiency. RSC Adv 2016;6:61544–54. doi:10.1039/C6RA12692H.

15 Reig M, Gozálvez C, Bujaldón R, Bagdziunas G, Ivaniuk K, Kostiv N, et al. Easy accessible blue luminescent carbazole-based materials for organic light-emitting diodes. Dyes and Pigments 2017;137:24–35. doi:10.1016/j.dyepig.2016.09.062.

16 Bucinskas A, Bagdziunas G, Tomkeviciene A, Volynyuk D, Kostiv N, Gudeika D, et al. Structure–property relationship of isomeric diphenylethenyl-disubstituted dimethoxycarbazoles. RSC Adv 2015;5:49577–89. doi:10.1039/C5RA09161F.

17Rothberg LJ, Lovinger AJ. Status of and prospects for organic electroluminescence. Journal of Materials Research 1996;11:3174–87. doi:10.1557/JMR.1996.0403.

18 Lee YG, Kang SK, Oh TS, Lee H-N, Lee S, Koh KH. Comparison of two cohost systems for doped red organic light-emitting devices in an effort to improve the efficiency and the lifetime. Organic Electronics 2008;9:339–46. doi:10.1016/j.orgel.2007.12.003.

19 Chou H-H, Cheng C-H. A Highly Efficient Universal Bipolar Host for Blue, Green, and Red Phosphorescent OLEDs. Adv Mater 2010;22:2468–71. doi:10.1002/adma.201000061.

20 Lee S, Limbach D, Kim K-H, Yoo S-J, Park Y-S, Kim J-J. High efficiency and non-colorchanging orange organic light emitting diodes with red and green emitting layers. Organic Electronics 2013;14:1856–60. doi:10.1016/j.orgel.2013.04.020.

21 Zhao B, Zhang T, Chu B, Li W, Su Z, Wu H, et al. Highly efficient red OLEDs using DCJTB as the dopant and delayed fluorescent exciplex as the host. Scientific Reports 2015;5:srep10697. doi:10.1038/srep10697.

22 Spartan'14 for Windows Version 1.1.2. 1840 Von Karman Avenue, Suite 370, Irvine, CA.

23 Sun H, Zhong C, Brédas J-L. Reliable Prediction with Tuned Range-Separated Functionals of the Singlet–Triplet Gap in Organic Emitters for Thermally Activated Delayed Fluorescence. J Chem Theory Comput 2015;11:3851–8. doi:10.1021/acs.jctc.5b00431.

24 Boys SF, Bernardi F. The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. Molecular Physics 1970;19:553–66. doi:10.1080/00268977000101561.

25 Malagoli M, Brédas JL. Density functional theory study of the geometric structure and energetics of triphenylamine-based hole-transporting molecules. Chemical Physics Letters 2000;327:13–7. doi:10.1016/S0009-2614(00)00757-0.

26 Shuai Z, Geng H, Xu W, Liao Y, André J-M. From charge transport parameters to charge mobility in organic semiconductors through multiscale simulation. Chem Soc Rev 2014;43:2662–79. doi:10.1039/C3CS60319A.

27 Ames DE, Grey TF. N-hydroxy-imides. Part II. Derivatives of homophthalic and phthalic acids. J Chem Soc 1955;0:3518–21. doi:10.1039/JR9550003518.

28 Benjamin E, Hijji Y. The Synthesis of Unsubstituted Cyclic Imides Using Hydroxylamine under Microwave Irradiation. Molecules 2008;13:157–69. doi:10.3390/molecules13010157.

29 The crystallographic data for structure reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no CCDC 1476404.

30 McEwan JA, Clulow AJ, Nelson A, Yepuri NR, Burn PL, Gentle IR. Dependence of Organic Interlayer Diffusion on Glass-Transition Temperature in OLEDs. ACS Appl Mater Interfaces 2017;9:14153–61. doi:10.1021/acsami.7b01450.

31 Hrdlovič P, Chmela Š, Danko M. Spectral characteristics and photochemical stability of fluorescence probes based on 1,8-naphthaleneimide in solution and in polymer matrix. Journal of Photochemistry and Photobiology A: Chemistry 1998;112:197–203. doi:10.1016/S1010-6030(97)00277-3.

32 Terenin A, Ermolaev V. Sensitized phosphorescence in organic solutions at low temperature. Energy transfer between triplet states. Trans Faraday Soc 1956;52:1042–52. doi:10.1039/TF9565201042.

33 Tasior M, Gryko DT, Cembor M, Jaworski JS, Ventura B, Flamigni L. Photoinduced energy and electron transfer in 1,8-naphthalimide–corrole dyads. New J Chem 2007;31:247–59. doi:10.1039/B613640K.

34 Ouyang JF, Bettens RPA. Many-Body Basis Set Superposition Effect. J Chem Theory Comput 2015;11:5132–43. doi:10.1021/acs.jctc.5b00343.

35 Biedermann F, Schneider H-J. Experimental Binding Energies in Supramolecular Complexes. Chem Rev 2016;116:5216–300. doi:10.1021/acs.chemrev.5b00583.

36 D'Andrade BW, Datta S, Forrest SR, Djurovich P, Polikarpov E, Thompson ME. Relationship between the ionization and oxidation potentials of molecular organic semiconductors. Organic Electronics 2005;6:11–20. doi:10.1016/j.orgel.2005.01.002.

37 Djurovich PI, Mayo EI, Forrest SR, Thompson ME. Measurement of the lowest unoccupied molecular orbital energies of molecular organic semiconductors. Organic Electronics 2009;10:515–20. doi:10.1016/j.orgel.2008.12.011.

38 Barth S, Müller P, Riel H, Seidler PF, Rieß W, Vestweber H, et al. Electron mobility in tris(8-hydroxy-quinoline)aluminum thin films determined via transient electroluminescence from single- and multilayer organic light-emitting diodes. Journal of Applied Physics 2001;89:3711–9. doi:10.1063/1.1330766.

39 Shih C-H, Rajamalli P, Wu C-A, Hsieh W-T, Cheng C-H. A Universal Electron-Transporting/Exciton-Blocking Material for Blue, Green, and Red Phosphorescent Organic Light-Emitting Diodes (OLEDs). ACS Appl Mater Interfaces 2015;7:10466–74. doi:10.1021/acsami.5b01872.

40 Komino T, Nomura H, Koyanagi T, Adachi C. Suppression of Efficiency Roll-Off Characteristics in Thermally Activated Delayed Fluorescence Based Organic Light-Emitting Diodes Using Randomly Oriented Host Molecules. Chem Mater 2013;25:3038–47. doi:10.1021/cm4011597.

41 Coropceanu V, Cornil J, da Silva Filho DA, Olivier Y, Silbey R, Brédas J-L. Charge Transport in Organic Semiconductors. Chem Rev 2007;107:926–52. doi:10.1021/cr050140x.

42 Z. Shuai, L. Wang, C. Song, *Hopping Mechanism*, in: *Theory of Charge Transport in Carbon Electronic Materials*, Springer Berlin Heidelberg, 2012, pp. 7-41.

43 Reig M, Bagdziunas G, Volyniuk D, Grazulevicius JV, Velasco D. Tuning the ambipolar charge transport properties of tricyanovinyl-substituted carbazole-based materials. Phys Chem Chem Phys 2017;19:6721–30. doi:10.1039/C6CP08078B.

44 Kondakov DY, Pawlik TD, Hatwar TK, Spindler JP. Triplet annihilation exceeding spin statistical limit in highly efficient fluorescent organic light-emitting diodes. Journal of Applied Physics 2009;106:124510. doi:10.1063/1.3273407.

45 Segal M, Singh M, Rivoire K, Difley S, Van Voorhis T, Baldo MA. Extrafluorescent electroluminescence in organic light-emitting devices. Nat Mater 2007;6:374–8. doi:10.1038/nmat1885.

Highlights

- Semiconductor consisting of the 1,8-naphthalimide and carbazole moieties was synthesized and characterized.
- For this compound, the ambipolar semiconductor properties and recombination of exciton in exciplex complex are indicated.
- The exciplex complex is stabilized by the intermolecular hydrogen bond and electron donor-acceptor interactions.
- OLED from the compound as an emitter exhibited an orange color emission.

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