Multifunctional derivatives of pyrimidine-5-carbonitrile and differently substituted carbazoles for doping-free sky-blue OLEDs and luminescent sensors of oxygen

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Highlights
- Pyrimidine-5-carbonitrile-based compounds with efficient TADF exceeding reverse intersystem crossing rates of $10^6 \text{s}^{-1}$
- AIEE properties for the designed compounds allowing to reach PLQYs up to 50% in solid state.
- Bipolar charge-transporting properties showing hole mobility of $1.6 \times 10^{-4} \text{cm}^2/\text{V}\text{s}$ and electron mobility of $1.37 \times 10^{-5} \text{cm}^2/\text{V}\text{s}$.
- Non-doped sky-blue OLED with external quantum efficiency of 12.8%.
- Oxygen probes with fast response, high sensitivity and good stability.

Abstract
Introduction: Evolution of organic light-emitting diodes (OLEDs) reached the point, which allows to obtain maximum internal quantum efficiency of 100% partly using heavy-metal-free emitters exhibiting thermally activated delayed fluorescence (TADF). Such emitters are also predictively perfect candidates for new generation of optical sensors since triplet harvesting can be sensitive to different analytes (at least to oxygen). Although many organic TADF emitters have been reported so far as OLED emitters, the investigation of materials suitable for both OLEDs and optical sensors remains extremely rare.

Objectives: Aiming to achieve high photoluminescence quantum yields in solid-state and triplet harvesting abilities of organic semiconductors with efficient bipolar charge transport required for application in both blue OLEDs and optical sensors, symmetrical donor–acceptor-donor organic emitters containing pyrimidine-5-carbonitrile electron-withdrawing scaffold and carbazole, tert-butylcarbazole and methoxy carbazole donor moieties were designed, synthesized and investigated as the main objectives of this study.

Methods: New compounds were tested by many experimental methods including optical and photoelectron spectroscopy, time of flight technique, electrochemistry and thermal analyses.
Introduction

The technology of organic light emitting diodes (OLED) became one of the most expanding in the markets of displays and lighting devices [1,2]. The pressure-sensitive paint technique for luminescent sensors of oxygen is a widespread tool in various areas such as microelectronics and aerospace engineering [3–6]. Both luminescent sensor and OLED technologies require efficient metal-free emitters as an alternative of transition metals containing phosphorescent emissive species with high photoluminescence quantum yields in solid state exceeding 50%, hole and electron transporting properties with charge mobilities exceeding 10^{-4} cm²/V·s, glass-forming properties with glass transition temperatures reaching 177 °C. Sky-blue OLEDs with non-doped light-emitting layers of the synthesized emitter showed maximum external efficiency of 12.8% while the doped device with the same emitter exhibited maximum external efficiency of 14%. The synthesized emitters were also used as oxygen probes for optical sensors with oxygen sensitivity estimated by the Stern-Volmer constant of 3.24·10^{-5} ppm^{-1}. 

Conclusion: The developed bipolar TADF emitters with pyrimidine-5-carbonitrile and carbazole moieties showed effective applicability in both blue OLEDs and optical sensors.

Results: Demonstrating advantages of the molecular design, the synthesized emitters exhibited sky-blue efficient TADF with reverse intersystem crossing rates exceeding 10^{6} s^{-1}, aggregation-induced emission enhancement with photoluminescence quantum yields in solid state exceeding 50%, hole and electron transporting properties with charge mobilities exceeding 10^{-4} cm²/V·s, glass-forming properties with glass transition temperatures reaching 177 °C. Sky-blue OLEDs with non-doped light-emitting layers of the synthesized emitter showed maximum external efficiency of 12.8% while the doped device with the same emitter exhibited maximum external efficiency of 14%. The synthesized emitters were also used as oxygen probes for optical sensors with oxygen sensitivity estimated by the Stern-Volmer constant of 3.24·10^{-5} ppm^{-1}.

Conclusion: The developed bipolar TADF emitters with pyrimidine-5-carbonitrile and carbazole moieties showed effective applicability in both blue OLEDs and optical sensors.

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Material and methods

General procedure of nucleophilic substitution reactions

Potassium hydroxide (2.5 eq.) was added to a solution of 9H-carbazole (2.5 eq.) or 3,6-di-tert-butyl-9H-carbazole (2.5 eq.) or...
3,6-dimethoxy-9H-carbazole (2.5 eq.) in DMSO (25 ml). The mixture was stirred for 20 min at room temperature and then 4,6-di chloropyrimidine-5-carbonitrile (1 eq.) was added. The reaction mixture was heated to 175 °C and stirred for 1 h. After completion of the reaction, the obtained mixture was cooled down to room temperature, poured into water and filtered. The crude product was purified by column chromatography on silica gel using the eluent mixture of hexane and DCM with the volume ratio of 3:2 and recrystallized from isopropanol/DMF mixture.

4,6-Di[9H-carbazol-9-yl]pyrimidine-5-carbonitrile (CzPCN) was prepared from KOH (2.5 mmol, 0.28 g), 9H-carbazole (5 mmol, 0.84 g) and 4,6-dichloropyrimidine-5-carbonitrile (2 mmol, 0.35 g) using general procedure and yellow needle crystals were isolated in 49% yield (0.41 g). M.P.: 260–262 °C.

1H NMR (400 MHz, CDCl3) δ 9.34 (s, 1H), 8.06 (d, J = 7.7 Hz, 4H), 7.86 (d, J = 8.3 Hz, 4H), 7.58 – 7.48 (m, 4H), 7.39 (t, J = 7.4 Hz, 4H) ppm. 13C NMR (101 MHz, CDCl3) δ 161.86, 161.11, 138.46, 126.74, 125.91, 123.52, 120.71, 112.53, 112.36, 96.79 ppm. Elemental analysis: calculated for C29H16N2O: %: C 82.60; H 4.12; N 15.28. Found, %: C 82.61; H 4.10; N 15.24. ESI-MS (m/z): calculated for C29H16N2O 435.48 [M]+; found 457.99 [M + Na]+.

4,6-bis[3,6-di-tert-butyl-9H-carbazol-9-yl]pyrimidine-5-carbonitrile (MeOCzPCN) was synthesized from KOH (2.5 mmol, 0.28 g), 3,6-dimethoxy-9H-carbazole (5 mmol, 1.14 g) and 4,6-dichloropyrimidine-5-carbonitrile (2 mmol, 0.35 g) and yellow crystals was isolated in 36% yield (0.5 g). M.P.: 258–260 °C.

1H NMR (400 MHz, CDCl3) δ 9.23 (s, 1H), 8.04 (d, J = 1.5 Hz, 4H), 7.80 (d, J = 8.7 Hz, 4H), 7.57 (dd, J = 8.7, 1.8 Hz, 4H), 7.42 (s, 3H) ppm. 13C NMR (101 MHz, CDCl3) δ 161.81, 160.88, 146.63, 136.84, 126.10, 124.31, 116.75, 112.74, 112.33, 95.15, 34.96, 31.86 ppm. Elemental analysis: calculated for C33H25N5O4: %: C 80.75; H 3.78; N 10.6. Found, %: C 82.61; H 3.70; N 10.19. ESI-MS (m/z): calculated for C33H25N5O4 555.58 [M]+; found 582.51 [M + Na]+.

### Results and discussion

#### Synthesis

4,6-Di[9H-carbazol-9-yl]pyrimidine-5-carbonitrile (CzPCN), 4,6-bis[3,6-di-tert-butyl-9H-carbazol-9-yl]pyrimidine-5-carbonitrile (tCzPCN) and 4,6-bis[3,6-dimethoxy-9H-carbazol-9-yl]pyrimidine-5-carbonitrile (MeOCzPCN) were obtained by simple and inexpensive synthesis in a step via nucleophilic substitution reactions between 4,6-dichloropyrimidine-5-carbonitrile and carbazole derivatives. The synthetic route for the target compounds is outlined in Scheme 1. The chemical structures of the compounds were confirmed by 1H and 13C NMR spectroscopies, mass spectrometry and elemental analysis (SI).

Thermal, electrochemical, photoelectrical and charge-transporting properties

Thermal transitions of the synthesized compounds were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of measurements are collected in Table 1 and showed in Fig. 1a,b. S1. All the compounds demonstrated high thermal stability. Their values of 5% weight loss temperatures (Td) significantly exceeded 300 °C (Fig. 1a). In comparison to compound CzPCN with Td of 338 °C, compounds tCzPCN and MeOCzPCN exhibited higher Td values of 396 °C and of 383 °C respectively. Apparently, the presence of heavy tert-butyl and methoxy groups in molecular structures of compounds tCzPCN and MeOCzPCN lead to enhancement of intermolecular interaction in the solid state. Complete weight loss of CzPCN in TGA shows that the compound experienced sublimation.

All the compounds were obtained as crystalline substances after synthesis and showed two melting points in the first DSC scans (Fig. 1b, S1, Table 1). It can be assumed that two crystal forms of the synthesized compounds were obtained [37,38]. In the second heating scan of compound CzPCN (Fig. 1b) glass transition was observed at 112 °C. The further heating revealed crystallization (the temperature of crystallization (Tc) was of 163 °C) and melting of only one type of polymorph at 273 °C. Tg of 177 °C was observed for compound tCzPCN in the repeated heating scan (Fig. S1b) while compound MeOCzPCN (Fig. S1c) did not show any capability of glass formation.

Cyclic voltammetry measurements (CV) were performed for dichloromethane (DCM) solutions of CzPCN, tCzPCN and MeOCzPCN with tetra-n-butylammonium hexafluorophosphate (TBAFx) as supporting electrolyte (Fig. 1c). Potentials of oxidation (Eonset) and reduction (Eonset) half-waves and with respect to ferrocene are collected in Table 1. Using Eonset and Eonset, the values of ionization potential (IPCV) and electron affinity (EACV) were determined for the solutions of CzPCN, tCzPCN and MeOCzPCN (Table 1). The close values of IPCV and EACV were observed for CzPCN and tCzPCN (5.82, 5.87/2.9, 2.8 eV respectively) for CzPCN and tCzPCN due to the similar electron-donating/electron-accepting abilities of the building moieties. Lower IPCV value of MeOCzPCN is attributed to the stronger electron-donating ability of methoxy-substituted carbazole.

Since IPCV and EACV energies can not be referred to HOMO and LUMO of the studied materials [39], UV photoelectron spectrometry was further used for getting ionization potential (IPUPS) and electron affinity (EAUPS) for their solid-state samples (Fig. 1d). The values of EAUPS were calculated by formula EAUPS = IPUPS – Etransport = IPUPS – Eopt + Eeq, assuming that the optical gaps (Eopt) of solid layers is approximately equal to their transport gaps (Etransport). The Eopt values were taken from low-energy set-on of absorption spectra of the films of CzPCN, tCzPCN and MeOCzPCN (Fig. S2). Thus, IPUPS and EAUPS values can be referred to the HOMO and LUMO energies of compounds CzPCN, tCzPCN and MeOCzPCN which are required for the design of appropriate structures of optoelectronic devices, OLEDs in particularly (Table 1). Higher IPUPS values of CzPCN, tCzPCN and MeOCzPCN were realtive to the corresponding IPCV values were observed. However, the trends of IPUPS and IPCV were practically the same mainly referring to the different donor substitutions. The extension on the donating carbazoles resulted in raising HOMO/LUMO energy levels.

Two representative compounds CzPCN and MeOCzPCN were selected for investigation of charge-transporting properties at room temperature. Photocurrent transients for their vacuum deposited films were recorded under positive (for holes) and negative (for electrons) polarities in time of flight (TOF) regime (Fig. 2a, S3). Despite of strong dispersity observed for the film of CzPCN, clear transit times (td) under different electric fields could
be determined for both holes and electrons from the corresponding current transients plotted in log–log scales. Similarly, $t_{tr}$ was detected for electrons for the film of MeOCzPCN, while $t_{tr}$ for holes was not detectable. Charge mobilities were calculated for CzPCN (for holes and electrons) and for MeOCzPCN (for electrons) (Fig. 2b). Hole mobility ($\mu_h$) of $1.6 \times 10^{-4}$ cm$^2$/V·s was observed
for CzPCN at electric field (E) of 7.2 × 105 V/cm, which is close to that of many other typical carbazole-containing emitters [33], (Fig. 2b). Electron mobility (\(\mu_e\)) of 1.37 × 10-3 cm²/Vs at the same electric field. It is by ca. one magnitude lower than hole mobility. The relationship \(\mu_{e^2} = \mu_{e}\) can be attributed to the donor–acceptor-donor molecular structure of compound CzPCN apparently resulting in higher HOMO–HOMO overlapping between neighbouring molecules than LUMO–LUMO overlapping.

Since it was impossible to obtain complete charge-transporting data for the studied compounds by the TOF method, charge extraction by linearly increasing voltage (CELIV) technique was applied using the thinner layers (<300 nm) [40]. The dark-CELIV (grey curves) and photo-CELIV (colour curves) current transients for holes recorded for the film of CzPCN are plotted in Fig. 2c. Taking time \(t_{\text{max}}\) at the maximum of the photo-CELIV, hole mobilities were obtained for CzPCN at different electric fields (Fig. 2b). CELIV hole mobility of CzPCN was in good agreement with the corresponding TOF hole mobility. CELIV hole mobility was also estimated for the layer of MeOcZcPCN (Fig. 2b).

**Photophysical properties**

UV absorption and PL spectra of the dilute solutions and of solid films of the CzPCN, rCzPCN and MeOcZcPCN are presented in Fig. 3a, S2. The major photophysical data are summarized in Table 2. The absorption of neat films and dilute toluene solutions of the compounds in the spectral region below 330 nm corresponds to the great extent to π–π* transition of carbazole [41] (Fig. 3a). The positions of the lowest energy bands (LEB, Fig. S2) of the dilute solutions observed at ca. 360 nm do not fully correlate with the polarity of solvents. Nevertheless, the significant blue shifts observed for the PL spectra of the solutions in polar solvents such as acetonitrile (MeCN) and acetone relative to the spectra of the solutions in less polar dichloromethane (DCM) and tetrahydrofuran (THF) are attributed to the state of intramolecular CT from carbazole-based donors to the acceptor. Attachment of tert-butyl groups to carbazole units in rCzPCN resulted in the redshift of LEB compared to that of CzPCN. Even bigger bathochromic shift was caused by the presence methoxy groups in MeOcZcPCN. These observations can be explained by prolonged \(n–n^*\) conjugation of tert-butyl or methoxy substituted carbazole moieties [36]. Intermolecular interactions enhanced in the solid state caused redshifted and broadened LEB of neat films relative to those of the solutions. The \(E_a\) values were estimated from the plot presented in Fig. 3b. They were found to be of 3.09, 3.08 and 2.9 eV for CzPCN, rCzPCN and MeOcZcPCN, respectively. The Kubelka-Munk plot is used for organic semiconductors in solid amorphous layers of OLEDs as they are commonly characterized by a near flat energy bands and direct allowed transitions [42]. The \(F(R):E_{\text{ph}}\) plot is based on equation \(F(R) = \frac{1.0 \times 10^{-1}}{a \times 10^{-1}}\). A and \(E_{\text{ph}}\) stand for absorbance of neat films in our case and photon energy, respectively. \(F(R)\) is the so-called remission, Kubelka-Munk function.

In order to examine the benefits of tuning emissive properties by electronic excitation energy transfer from host to guest, solid mixtures of the compounds and 1,3-bis(N-carbazolyl)benzene (mCP) with a doping concentration of 10% were investigated. The results are presented in Fig. S2. PL spectra of solutions, doped and non-doped films of the studied compounds contain a single narrow peak in sky-blue/green region with no signs of subvibronic distribution (Fig. 3a, S2). Due to guest:host interactions with the weakly polar mCP [43], the difference in energy levels of ground and first excited states of compounds is changed [44] leading to the pronounced blue shifts by 15–40 nm of PL spectra of the films of 10 wt% solid solutions of the compounds in mCP films in comparison with those neat films.

Photoluminescence quantum yields (\(\Phi\)) of toluene solution of CzPCN is lower that of THF solution highlighting the intrinsic polarity of the compound and the consequent apparent hypsochromic shift of PL spectrum of the film of the molecular mixture CzPCN:mCP compared to that of the film of CzPCN. The \(\Phi\) values of the films are higher than those of the solutions which is a manifestation of AIEE effect. The only exclusion is the \(\Phi\) values observed MeOcZcPCN which were found to be similar (of ca. 2%) for the solid samples and dilute solutions. The bathochromic shift of PL spectral peak with the increase of polarity of solvents (Fig. S2) is a clear evidence of intramolecular CT state of emission. The solvatochromatic effect of absorption and emission of solutions was studied in more detail for examination of polarity of the compounds. Based on the Onsager interpretation of non-specific interactions between particles and solvent [45], the Lippert-Mataga correlation [46,47] of a Stokes shift \(\Delta \nu\) and an orientation polarizability \(\Delta\) \(\nu = \frac{2M}{3\epsilon_0\mu^2}\), \(\mu = \mu_e - \mu_h\) is plotted in Fig. S5 (adjusted \(R^2\) of 0.92–0.97): \(\Delta \nu = \frac{2M}{3\epsilon_0\mu^2}\) (\(\mu_e - \mu_h\)^2 + \(\Delta\nu^2\). The Stokes shift in the condition of absence of solvent is defined as \(\Delta\nu^0\). a is an Onsager cavity radius. The obtained slopes are related to the change of dipole moment of compounds in ground \(\mu_e\) and excited \(\mu_h\) state revealing a significant intrinsic polarity of the compounds owing to the donor–acceptor-donor structure. The slopes of ca. 9.4×10^5 \(\text{cm}^3\) observed for CzPCN and rCzPCN are larger than that for MeOcZcPCN (7.5×10^5 \(\text{cm}^3\)). Based on these data, CzPCN and rCzPCN can be characterized by stronger intramolecular CT than MeOcZcPCN showing that for the designed donor–acceptor-donor structures based on the pyrimidine-5-carbonitile accepting unit attachment of the methoxy groups to carbazoles resulted in suppressing of intramolecular CT and quantum yields.

**Thermally activated delayed fluorescence**

The intensity of PL of toluene solutions and neat films of the compounds was found to be considerably higher in the absence...
of oxygen compared to that of air equilibrated samples (Fig. 3c). For CzPCN the increase was substantially higher reaching the factor of 3–3.85. The increase of emission intensity after deoxygenation is ascribed to delayed fluorescence (DF) [10]. After removal of oxygen, the spectral shape remained the same. This observation shows, that the excitons utilized in DF are recombined radiatively from the same energy levels as for prompt fluorescence (PF) pointing to the triplet up-conversion via RISC. Supressing interactions between molecules of the studied compounds and oxygen quenches non-radiative pathways of deactivation via energy thus stimulating RISC.

Multieponential fitting of PL decay curves (Fig. 3d) of neat films of the compounds revealed PF with the lifetime (τPF) of ca12 ns and DF with the lifetime (τDF) in a µs range (Table 2). Rate constants of RISC and intersystem crossing (ISC), kISC and kRISC respectively, can be estimated using formulas

\[ k_{RISC} = \frac{\Phi_{DF}}{\Phi_{PF} \tau_{DF}} \]

\[ k_{ISC} = \frac{\Phi_{PF}}{\Phi_{DF} \tau_{PF}} \]

where \( \Phi_{PF} \), \( \Phi_{DF} \), and \( \Phi_{RISC} \) stand for yields of PF, DF and RISC respectively [23]. Knowing \( \Phi = \Phi_{PF} + \Phi_{DF} = \frac{\Phi_{PF} \Phi_{DF}}{\Phi_{RISC}} \) and that the maximum value of ISC yield \( \Phi_{ISC} \) is limited by a quantity of electronic excitation energy not utilized in PF, the equation for estimation of \( k_{RISC} \) is simplified to \( k_{RISC} = \frac{\Phi_{PF} \Phi_{DF}}{\Phi_{PF} \Phi_{DF} \tau_{PF} \tau_{DF}} \). The \( \Phi_{DF} \) values are recalculated according to the increase of PL intensity of neat films after degazation (Fig. 3c) [48]. The obtained values of \( k_{RISC} \) of 1.3–1.6 \( 10^6 \) s\(^{-1} \) and \( k_{ISC} \) of ~0.6 \( 10^4 \) s\(^{-1} \) for CzPCN and tCzPCN were found to be competitive with the characteristics of TADF emitters such as 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) [25] or derivatives of pyrimidine-5-carbonitrile and carbazole [36] (Table 2, S1). The fast RISC and ISC are due to satisfactory values of \( \Delta E_{ST} \) which did not exceed 140 meV. The values of \( \Delta E_{ST} \) were obtained from the fluorescence and phosphorescence spectra of the solutions of the compounds recorded at liquid nitrogen temperature (Fig. S6, Table 2). The \( \Phi_{DF} / \Phi_{PF} \) of 10.41 was estimated for the film of MeOCzPCN in air. This observation explains the failure of the measurement of increase of PL intensity in a vacuum condition, since TADF appeared even in presence of oxygen. Taking into account negative effect of methoxy substitution of carbazoles on overall CT performance and corresponding low \( \Phi \) values for MeOCzPCN it can be presumed, that most of excitons are deactivated through non-radiative ways making the proper estimation of rate constants problematic. The obtained value of \( k_{RISC} \) of ~10\(^7\) s\(^{-1} \)

Table 2

| Compounds/Parameters | CzPCN | tCzPCN | MeOCzPCN |
|----------------------|-------|--------|----------|
| \( \Phi_{DF} \) (%)   |       |        |          |
| \( \Phi_{PF} \) (%)   | 39    | 33(53) |          |
| \( \phi_{PL} \) (%)   | 12    | 14     |          |
| \( \phi_{abs} \) (%)  | 1.111 | 1.109  | 1.016    |
| \( \Delta E_{ST, TRF} \) (eV) | 0.08 | 0.07 | 0.03 |
| \( \Delta E_{ST, TRF} \) (eV) | 0.14 | 0.09 | 0.03 |
| \( \Delta E_{ST, TRF} \) (eV) | 1.56 | 1.32 | 10.40 |
| \( \Delta E_{ST, TRF} \) (eV) | 5.73 | 6.06 | 10.40 |
| \( \Delta E_{ST, TRF} \) (eV) | 3.17 | 3.02 | 2.89 |
| \( \Delta E_{ST, TRF} \) (eV) | 3.03 | 2.93 | 2.88 |
| \( \Delta E_{ST, TRF} \) (eV) | 2.99 | 2.93 | 2.74 |
| \( \Delta E_{ST, TRF} \) (eV) | 2.91 | 2.86 | 2.71 |
| \( \Delta E_{ST, TRF} \) (eV) | 0.08 | 0.07 | 0.03 |

Estimated by the measurements; *of neat films; upon removing oxygen: \( \chi \) is a weighted sum of squares of deviations of calculated points of multieponential fitting of a PL decay curve. The empirical formula \( E_{abs} = 1239.84 / \lambda \) was used to estimate energy levels of \( E_{abs} \) and \( E_{em} \), where \( \lambda \) is a wavelengths of onset of fluorescence and phosphorescence spectral bands.

Fig. 3. a) Absorption spectra and normalized PL spectra of dilute 10\(^{-5}\) M toluene, THF and MeCN solutions of CzPCN, tCzPCN and MeOCzPCN; b) Kubelka-Munk plot for neat films; c) PL spectra of air equilibrated and deoxygenated dilute 10\(^{-5}\) M toluene solutions and of neat films recorded in air and in vacuum; d) PL decay curves of neat films.
is an approximated exaggerated to a great extent value. The lowest $\Delta E_{ST}$ of 10 meV observed in the series of investigated emitters is suitable for efficient triplet up-conversion partially explaining the obtained high value of $k_{ISC}$ [23].

The solid molecular mixtures of the studied compounds and mCP were studied. Phosphorescence and PL spectra of the doped films correspond to the respective spectra of neat films with the slight redshifts (Fig. S2) caused by dipolar interactions of guest and host. Doping of CzPCN and tCzPCN into mCP matrix resulted in the reduction of $\Delta E_{ST}$ as it is linked to the spin-vibronic coupling of local excited and CT states which are strongly affected to the polarity and rigidity of the host [23,49]. Experimental results of the measurements at 77 K are collected in (Table 2). Experimental results of the measurements at 77 K are collected in (Table 2). PL spectra and decay curves of the films of the molecular mixtures were recorded at different temperatures. They are presented in Fig. 4, S7-9. PL spectra the films remained steady over heating when the samples were degassed (Fig. 3c). Due to low $\Delta E_{ST}$ (up to 80 meV, Table 2), deactivation of excitons occurred via phosphorescence, PF and DF at different temperatures from excited states having similar energy levels, which is typical for compounds exhibiting TADF. As it is evident from PL decay curves, the intensity of phosphorescent component was quenched over heating due to rapidly enhanced interactions with oxygen. Simultaneously, thermal activation of DF resulted in the essential increase of TADF intensity at the temperatures exceeding 180 K.

To exclude triplet-triplet annihilation utilizing higher triplet excited states $T_2$, $T_3$ etc., investigation of power dependence of DF was performed (Fig. S10). The linear plot (fitting slope of 0.98–1.04) of the DF integrated intensity versus excitation dose in the logarithmic scale in the whole range of intensity maxima at ca.480 nm as the molecules being insoluble in water form aggregates. Consequently, there is a rapid increase of intensity at $f_w > 70\%$ for the dispersions of CzPCN and for tCzPCN in the range of $f_w$ from 40 to 60\% due to AIEE since the rotation motions of moieties of the compounds are restricted in solid state. The following decrease of PL intensity at $f_w$ exceeding 70\% observed for the dispersion of tCzPCN is explained by the formation of precipitates of a significant size. It is important to note that obtained results do not necessarily mean the decrease of $\Phi$ upon aggregation for the dispersions of tCzPCN in THF/water mixtures at high $f_w$.

**Aggregation induced emission enhancement**

The dispersions of CzPCN and tCzPCN in THF/water mixtures were prepared for investigation of AIEE characteristics of the compounds. The dependencies of PL intensities on water fraction are shown in Fig. 4c,d. The PL spectra and the relative correlation of the peak wavelengths and emission intensities are presented in Fig. S11. As it may be seen from the graphs and photos (Fig. 4c, d), at low water fractions ($f_w$) the dispersions of both the compounds are poorly emissive. Decrease of PL intensity in the range $f_w$ below 40\% is ascribed to the emission quenching due to an exhaustion of electronic excitation energy by intramolecular rotations. The bathochromic shift by nearly 50 nm with the increase of water fraction from 0 to 40\% is caused by the increase of concentration of highly polar water influencing strong intramolecular CT processes in the emitters which is an additional reason of PL quenching. At high $f_w$ both compounds emit blue light with the intensity maxima at ca.480 nm as the molecules being insoluble.

**Performance in OLEDs**

Taking into account TADF and AIEE capabilities as well as bipolar charge transport and appropriate HOMO/LUMO levels for charge injections from electrodes, the synthesized compounds can be regarded as promising for doping free devices. The series of OLEDs N1-N3 with the structure of ITO / HAT-CN (10 nm) / TCTA (30 nm) / mCP (7 nm) / EML (25 nm) / TSP10 (3 nm) / TPBi (30 nm) / LiF (0.4 nm) / Al were fabricated in order to test the layers of CzPCN, tCzPCN and MeOcPCN as non-doped light-emitting layers, respectively. Major electroluminescent data are collected in Table 1.
Table 3. Dipyrazino[2,3-f:2’,3’-h]quinoxaline-2,3,6,7, 10,11-hexacarbonitrile (HAT-CN) and LiF were employed for the injection of charge carriers. The layers of tris(4-carbazolyl-9-ylphenyl)amine (TCTA) and 2,2’:7,2’-ter(1,3,5-benzinetrizyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) were utilized as the hole and electron transporting layers, respectively. 1,3-bis[N-carbazolyl]benzene (mCP) and diphenyl[4-(triphenylsilyl)phenyl]phosphine oxide (TSPO1) were employed for the blocking electrons and holes, respectively. The electrodes were indium-tin oxide (ITO) and aluminium.

Unlike OLEDs with neat films of CzPCN and tCzPCN, devices with doped EML of these emitters exhibited practically close to identical efficiencies and EL spectra. High efficiency OLED based on EML of tCzPCN doped in mCP can be additionally explained by suppression of non-radiative ways of relaxation of excited states. Analogous improvement was not achieved for device based on the emitter with methoxy groups since this derivative exhibited low photoluminescence quantim yield (Table 2). Efficiency roll-off evident form the rapid decline of efficiency at 100 cd/m² of I is bigger for device D3 than for N3 despite the exhibition of the same maximum EQE of 1.4%. This observation can apparently be explained by the non-ideal host–guest interaction. The incomplete energy transfer from host to MeOCzPCN is manifested by the presence of EL spectral band of D3 at ca.380 nm, typical for mCP [50]. It also caused a substantial shift of CIE coordinates to those of blue color.

Oxygen sensitivity

Interactions with oxygen are mostly responsible for the non-radiative deactivation of excitations through the energy losses. Taking pronounced AIEE properties into account, and high values of photoluminescence quantum yield in solid-state, CzPCN and tCzPCN were selected for the investigation of the optical oxygen sensitivity. The 10 wt% solid solutions of the compounds in rigid matrix were prepared to detect collisional quenching of a luminesphore. Zeonex® was selected as a matrix because of its well-studied ability of supressing intermolecular interactions [51–53]. The samples were put into an inert atmosphere of nitrogen. Upon increasing of oxygen concentration the PL intensity continuously dropped (Fig. 6a,b, S14). No any significant difference in intensity in the same conditions over time was detected showing a great immediate response to the molecules of oxygen and a great stability of the emission.

PL decay curves of the solid solutions of CzPCN and tCzPCN in Zeonex® were recorded under nitrogen and oxygen conditions to study the impact of collisional quenching on emissive characteristics of the systems (Fig. 6c, S13). The long-lived component of the emission was drastically reduced in the presence of oxygen, espe-

Table 3. Summary of OLED parameters.

| OLED     | EML         | Lmax, 10⁴ cd/m² | ηc, cd/A | ηp, lm/W | λem, nm | EQE, % | CIE 1931 |
|----------|-------------|----------------|----------|----------|---------|--------|----------|
| N1       | CzPCN       | 13.1           | 32.4 (17.5) | 18.8 (9.2) | 494     | 12.8 (6.9) | (0.20, 0.36) |
| D1       | CzPCN:mCP   | 23.1           | 33.3 (17.6) | 20.2 (9.1) | 489     | 14 (7.4)   | (0.18, 0.33) |
| N2       | tCzPCN      | 13.2           | 12.3 (9.9)  | 4.6 (3.6)  | 490     | 5.1 (4.1)  | (0.19, 0.35) |
| D2       | tCzPCN:mCP  | 14.8           | 33.7 (19.4) | 18 (8.7)   | 490     | 13.7 (7.9) | (0.18, 0.35) |
| N3       | MeOCzPCN    | 9.3            | 4.0 (3.4)   | 2.1 (3.6)  | 524     | 1.4 (1.2)  | (0.30, 0.49) |
| D3       | MeOCzPCN:mCP| 13.7           | 3.8 (0.6)   | 1.2 (0.3)  | 500     | 1.4 (0.2)  | (0.21, 0.43) |

Lmax – maximum brightness. ηc and ηp – maximum current and power efficiency, respectively. λem – wavelength of EL spectral peak at 8 V. Efficiency values at I of 100 cd/m² are shown in parentheses.
cially for the solid solutions of CzPCN. In PL decay curve of the solid solution of this compound DF is almost absent. Stern-Volmer relation of $I_0/I_1$ and oxygen flow (Fig. 6d) demonstrated the oxygen sensitivity in the wide range of the oxygen flow corresponding to the oxygen partial pressure [54]. Since the fluorophore quenching by oxygen is a dynamic process, the correlation is linear. However, as expected for dye:matrix systems, downward curvature [48] takes place at the oxygen flow exceeding 20000 ppm. According to the Stern-Volmer equation, the well-known characteristic of optical sensors Stern-Volmer constant $K_{SV} = I_0/I_1$ was estimated from the slope of the linear fit as it is shown in Fig. 6d (adjusted $R^2$ are 0.94 and 0.97 for the samples containing CzPCN and tCzPCN, respectively) [48]. $K_{SV}$ was calculated to be $3.24 \times 10^{-5}$ and $1.49 \times 10^{-5}$ ppm$^{-1}$ for the solid dispersions of CzPCN and tCzPCN in Zeonex®, respectively. These values are comparable with that of TADF oxygen probes [55]. They are slightly lower than $K_{SV}$ values earlier observed for phosphorescent oxygen probes with long-lived emission (>1 ms) [56,57]. Taking into account that the oxygen sensing properties correlate with TADF, thermal motions of molecules activate RISC at elevated temperatures and consequently the oxygen sensitivity is expected to be enhanced [19]. The synthesized compounds have a great potential for the application as optical oxygen sensors reaching necessary requirements: a) fast response to the oxygen postulated from the stability of PL quenching over time; b) sustainable oxygen sensitivity; c) good quality of the films of solid dispersions in Zeonex®; d) appropriate thermal stability and photophysical properties described above [48].

**Conclusions**

Exploiting donor–acceptor-donor molecular structure, simple cost-effective synthesis of new sky-blue luminophores containing pyrimidine-5-carbonitrile electron-withdrawing scaffold and electron-donating carbazole, tert-butylcarbazole or methoxy carbazole moieties were developed. Using the synthesized compounds as blue emitters, maximum external quantum efficiencies of 12.8 and 14% of were achieved for non-doped and doped electro-luminescent devices respectively. Such performances were observed due to bipolar charge transport, thermal stability, and high photoluminescent quantum efficiency in solid state of the newly developed emitters. The different donor substitution of pyrimidine-5-carbonitrile unit affects the thermally activated delayed fluorescence and aggregation-induced emission enhancement properties of the compounds giving a path for oxygen sensor application. The developed oxygen sensor showed good sensitivity characterized by Stern-Volmer constant of $3.24 \times 10^{-5}$ ppm$^{-1}$. They were characterized by high stability and repeatability of the sensitivity.

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

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