THERMALLY ACTIVATED DELAYED FLUORESCENCE OF MULTI-CARBAZOLE DERIVATIVES WITH DIFFERENT ACCPETOR MOIETIES

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mCBP-doped blue OLEDs

Thanks to the high neat film PLQY value of 0.75 and efficient TADF, non-doped device n1 based on CN1 compound shows a sky-blue emission peaking at 481 nm with Commission Internationale de L'Eclairage (CIE) coordinates of (0.16, 0.27), a maximum brightness (B_{max}) of 19735 cd m⁻², a maximum current efficiency (CE_{max}) of 20.5 cd A⁻¹, a maximum power efficiency (PE_{max}) of 12.4 lm W⁻¹, and an EQE_{max} of 8.4%. The optimal doping concentrations of CN1 compound in mCDD baset was determined to be 20 wt%. The mantioned entimized d1a device with an EL pack of 477

Energy levels and thermal properties

The ionization potential (IP_{CV}) and electron affinity (EA_{CV}) values of CN1-5 were estimated by cyclic voltammetry (CV) measurements. Similar single quasi-reversible oxidations were observed for these materials corresponding to the oxidation of the di-*tert*-butyl carbazolyl moiety in the anodic scans. The onset oxidation potentials were found to be of 1.24 V for CN1, 1.31 V for CN2, 1.27 V for CN3, 1.20 V for CN4, and 1.23 V for CN5.



Electron photoemission spectra of the studied compounds (left), CV voltammograms ("Fc" stands for ferrocene) (middle) and TGA curve of compound CN1. During the TGA experiments compounds CN1-5 exhibited complete weight loss indicating sublimation. Their temperatures of the onsets of weight loss ranged from 433 to 462 °C.

compound in mCBP host was determined to be 20 wt%. The mentioned optimized **d1a** device with an EL peak of 477 nm, achieved the remarkable maximum EQE, current efficiency (CE) and brightness of 15.9%, 42.6 cd A^{-1} and 39226 cd/m², respectively



Device	Light emitting layer	V _{on} ,ª V	Max brightness, ^b cd/m ²	CE _{max} c cd/A	EQE _{max,} d %	λ, ^e nm	CIE ^f
OLED structures: ITO/HAT-CN/NPB/TCTA/mCBP/ Light emitting layer /TPBi/LiF:Al							
n1	CN1	5.8	19735	20.5	8.4	481	(0.16, 0.27)
n2	CN2	5.4	10496	10.8	4.9	497	(0.20, 0.40)
n3	CN3	7.9	2387	2.5	0.9	491	(0.21, 0.35)
n4	CN4	5.2	12634	11.5	5.5	476	(0.17, 0.24)
n5	CN5	5.5	15975	14.6	6.3	488	(0.18, 0.31)
d1a	mCBP: CN1(10wt.%)	4.6	34500	37.7	14.6	473	(0.16, 0.24)
d1b	mCBP: CN1(20wt.%)	4.1	39226	42.6	15.9	477	(0.16, 0.25)
d1c	mCBP: CN1(30wt.%)	4.9	30928	33.9	12.8	479	(0.16, 0.26)
d2	mCBP: CN2(10wt.%)	4.9	20154	24	9.4	494	(0.20, 0.40)
d3	mCBP: CN3(10wt.%)	5	4958	4.3	1.9	470	(0.19, 0.23)
d4	mCBP: CN4(10wt.%)	4.5	21963	26.5	9.8	469	(0.16, 0.19)
d5	mCBP: CN5(10wt.%)	4.8	28129	30	11.7	483	(0.17, 0.30)

Photophysical properties

The similar absorption profiles were recorded in the toluene and THF solutions as well as neat films of the compounds. Non-structured photoluminescence spectra of compound neat films with peaks at 482, 508, 482, 490 and 480 nm for **CN1-5**, respectively, were observed. In order to investigate solvatochromic behavior, the photoluminescence spectra of synthesized organic compounds were recorded in 5 different solutions.



To further investigate the photophysical properties of designed compounds, photoluminescence (PL) and phosphorescence spectra of their THF solutions (10^{-5} M) were measured at the liquid nitrogen temperature (77 K). According to the onsets of photoluminescence and phosphorescence spectra of these emitters in THF solution, the ΔE_{ST} of **CN1-5** are estimated to be 0.03, 0.05, 0.04, 0.04 and 0.04 eV, respectively. Additionally, to gain more insight into the delayed fluorescence behaviour, temperature-dependent time-resolved emission measurements were performed for CN1 compound neat film. As we can see, the intensity of delayed fluorescence increases with temperature between 77 to 300

^a Turn-on voltage at a luminance of 10 cd m⁻², ^b Maximum brightness, ^c Maximum current efficiency, ^d Maximum external quantum efficiency, ^e Wavelength of the peak of El spectrum at 6V, ^f Commission Internationale de I'Eclairage (CIE) 1931 color coordinates.

Conclusions

Thanks to the molecular design of thermally activated delayed fluorescence (TADF) compounds, their lowest excited singlet and triplet states lie very close energetically since charge donating and accepting moieties are spatially separated. This features of these compounds can lead to the thermally activated upconversion from the latter to the former state through reverse intersystem crossing which is actually the inverse transition processes of Phosphorescence compounds [1]. In our previous work, we developed various asymmetric multi-carbazole-based emitters by utilizing two different types of *electron*-withdrawing *moieties* which helped to tune their TADF properties and to achieve efficient blue emission. The compounds contained benzonitrile as the general accepting unit and the different additional acceptor moieties. [2] With this fundamental concern, we designed a series of highly efficient blue TADF emitters based on 3,6-di-tert-butylcarbazole as donors and two electron acceptors. Unlike the previous work which compounds consisted of benzonitrile as the general *electron*-withdrawing *moieties*, in this work general electron acceptor for all synthesized compounds was trifluoromethyl (CF_3) which is strong electron-withdrawing group and the difference of the compounds and aim of the work mostly were related to the variety of additional acceptor moiety attached through para substitution. The temperatures of thermal transitions of synthesized materials were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry. During the TGA experiments compounds exhibited complete weight loss indicating sublimation. Their temperatures of the onsets of weight loss ranged from 433 to 462 °C. UV-VIS absorption and photoluminescence spectra of five compounds in both dilute solutions and neat films were recorded and non-structured photoluminescence spectra of compound neat films with peaks at 482, 508, 482, 490 and 480 nm for CN1-5, respectively, were observed. Additionally, Photoelectron emission spectroscopy was used for measuring ionization potentials of the solid-state of compounds in air and showing values in a relatively close range of 5.61-5.72 eV. The best optimized mCBP doped blue OLED exhibited maximum external quantum efficiency of 15.9%, maximum current efficiency of 42.6 cd A⁻¹, maximum power efficiency of 24.1 lm W⁻¹ along with stable electroluminescence spectrum with an emission peak of 477 nm and the CIE1931 colour coordinate of (0.16, 0.25).

K revealed the expected thermal activation of the delayed emission, confirming a TADF mechanism. Following the temperature increase, the ratio of DF showed significant enhancement trend from 14 % at 77 K to 51 % at 300 K, proving the distinct TADF properties of CN1 compound



References and Acknowledgements

Acknowledgments: This work was supported by the project of scientific co-operation program between Lithuania and Ukraine "Development of highly efficient white light-emitting diodes utilizing organic emitters with exciplex and thermally-assisted fluorescence for lighting applications (LUW)" (grant No. S-LU-20-9).

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