

# SYNTHESIS AND TADF PROPERTIES OF 2-SUBSTITUTED 4,6-BIS(3,6-DI-*t*-BUTYL-9-CARBAZOLYL)-5-METHYLPYRIMIDINES

Irina Fiodorova<sup>1</sup>, Rokas Skaigiris<sup>2</sup>, Tomas Serevičius<sup>2</sup>, Saulius Juršėnas<sup>2</sup>, Sigita Tumkevičius<sup>1</sup>

<sup>1</sup> Department of Organic Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko 24, LT-03225 Vilnius, Lithuania

<sup>2</sup> Institute of Photonics and Nanotechnology, Faculty of Physics, Vilnius University, Sauletekio 3, LT-10257 Vilnius, Lithuania.

[irina.fiodorova@chgf.vu.lt](mailto:irina.fiodorova@chgf.vu.lt)

Thermally Activated Delayed Fluorescence (TADF) is an attractive way to achieve 100% internal fluorescence quantum yield without involving any expensive heavy atoms by converting all excitations to singlet ones by thermal activation [1]. Usually, this is achieved by constructing TADF compounds from electron-donating (D) and electron-accepting (A) units, decreasing the spatial overlap of electron density distribution in HOMO and LUMO and narrowing the singlet-triplet energy gap ( $\Delta E_{ST}$ ) up to values, comparable to thermal energy at room temperature [1,2]. It is rather difficult to find suitable D and A units with limited conjugation length and high triplet energy and bound them in a suitable architecture. Among numerous candidates for D and A units, carbazole as D unit and aromatic nitrogen heterocycles as A moieties are considered as being stable-enough and preferable for high stability OLEDs [3]. Recently, compounds containing pyrimidine heterocycle as an A unit have been demonstrated to be promising for TADF applications [4]. Seeing the potential of carbazole-pyrimidine pair for achieving efficient deep-blue TADF, we performed the design, synthesis, photophysical characterization as well as application in OLED devices of some novel single bonded carbazole-pyrimidine conjugates (Scheme 1).

The designed molecules were synthesized starting from an easily accessible pyrimidine derivative **1**. The chlorine groups substitution of **1** with 3,6-di-*t*-butylcarbazole to give compound **2a** was carried out by the palladium-catalyzed Buchwald-Hartwig amination reaction in the presence of  $\text{Pd}_2\text{dba}_3$  and  $\text{P}(\text{t-Bu})_3 \cdot \text{HBF}_4$  as a catalyst system and  $\text{NaOt-Bu}$  as a base. Synthesis of compounds **2b-d** was accomplished by using Liebeskind-Srogl coupling of 2-methylthiopyrimidine derivative **2a** with substituted phenylboronic acids in the presence of  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{CuMeSal}$  as catalysts.

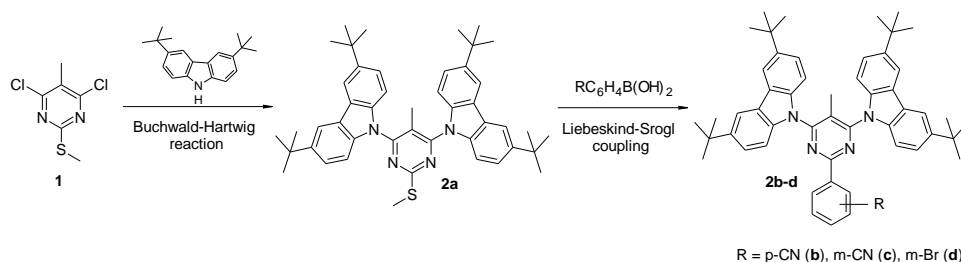


Fig. 1. Synthesis of 2-substituted 4,6-bis(3,6-di-*t*-butyl-9-carbazolyl)-5-methylpyrimidines (**2a-d**).

Optical properties of the synthesized materials **2a-d** were assessed by DFT calculations and investigated by absorption, time integrated and time-resolved fluorescence spectroscopies and fluorescence quantum yield and lifetime measurements. The enhancement of electron-donating properties of carbazole, the increase of twisting angle between D and A units as well as the increase of conjugation length by introduction substituents into the 2nd position of pyrimidine ring was shown to shift the emission towards deep-blue together with lowering the singlet-triplet gap and emergence of TADF. Compound **2a** was shown to be an efficient TADF emitter with peak wavelength of 428 nm, 0.5 solid-state emission yield and average delayed fluorescence lifetime of 143  $\mu\text{s}$ . When used in OLED device, compound **2a** based OLED showed electroluminescence with 8.7% EQE and CIE coordinates of (0.16; 0.12). Thus, simple molecular design steps were shown to be the successful strategy for achieving deep-blue TADF in highly promising carbazole-pyrimidine compounds.

## Acknowledgements

This research was funded by a grant (no. S-MIP-17-73) from the Research Council of Lithuania.

- [1] H. Uoyama, K. Goushi, K. Shizu et al. Highly Efficient Organic Light-emitting Diodes from Delayed Fluorescence, *Nature*, **492**, 234-238 (2012).  
[2] M. K. Etherington, J. Gibson, H. F. Higginbotham et al., Revealing the spin-vibronic coupling mechanism of thermally activated delayed fluorescence. *Nature Communications*, **7**, 13680 (2016).  
[3] Y. Im, M. Kim, Y. J. Cho et al. Molecular Design Strategy of Organic Thermally Activated Delayed Fluorescence Emitters. *Chemistry of Materials*, **29**, 1946–1963 (2017).  
[4] (a) R. Komatsu, H. Sasabe, J. Kido, Recent progress of pyrimidine derivatives for high-performance organic light-emitting devices, *J. Photon. Energy*, **8**, 032108 (2018); (b) T. Serevičius, T. Buciunas, J. Bucevicius et al. Room temperature phosphorescence vs. thermally activated delayed fluorescence in carbazole–pyrimidine cored compounds, *J. Mater. Chem. C*, **6**, 11128-11136 (2018); (c) T. Serevičius, R. Skaigiris, J. Dodonova et al. Emission wavelength dependence on the rISC rate in TADF compounds with large conformational disorder. *Chemical Communications*, **55**, 1975-1978 (2019).