

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRIMIDINE-CARBAZOLE BASED FLUOROPHORES

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OLEDs are considered as one of the most promising green technologies for future displays and lighting resources owing to their low power consumption and their being ultra-thin, lightweight, and flexible. Recently, thermally activated delayed fluorescent (TADF) emitters consisting of pure organic materials have been developed as a new generation of emitters to harvest all the molecular excitons [1]. The main requirement for efficient TADF is thought to be a negligible energy difference between the lowest singlet and triplet states (ΔE_{ST}), which is obtained in the compounds possessing donor–acceptor fragments with strong intermolecular charge transfer (ICT) [2]. One of the promising design strategies for TADF materials is to use a highly twisted structures between the donor and acceptor moieties. The twisted structure has rather small overlap of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and thus results in small singlet–triplet energy gap [3]. Compounds bearing pyrimidine heterocycle as an electron withdrawing unit were demonstrated to be promising for TADF applications [4, 5a]. In this connection and continuing our work aimed to the search of efficient fluorescent materials among the pyrimidine-based heterocycles [5] we present herein results on the synthesis and photophysical properties of a series of novel 4,6-bis(3,6-disubstituted 9-carbazolyl)pyrimidines (**I**) (Fig. 1).

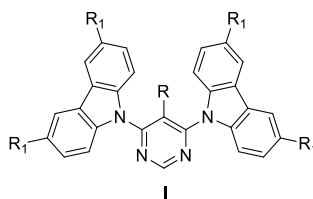


Fig. 1. General structure of pyrimidine-carbazole based fluorophores.

The target compounds **I** were synthesized starting from an easily accessible 4,6-dihydropyrimidine modifying it to appropriate 4,6-dichloro derivatives and performing substitution reactions of chlorine groups with corresponding carbazole derivatives. Aryl groups into the 5th position of pyrimidine ring were introduced by using palladium-catalyzed Suzuki cross-coupling reaction of corresponding 5-bromopyrimidines with selected arylboronic acids.

Optical properties of the synthesized conjugates were assessed by DFT calculations and investigated by absorption, time integrated and time-resolved fluorescence spectroscopies and fluorescence quantum yield measurements. The obtained data revealed that bare pyrimidine – carbazole molecule exhibits near-UV fluorescence (360 nm) with a large ΔE_{ST} gap of about 700 meV, thus only room temperature phosphorescence (RTP) with no TADF was observed. By introducing larger substituents R and/or R₁ we were able to red-shift fluorescence up to blue emission (440 nm) without changing triplet energy much, therefore reducing ΔE_{ST} value to 300 meV, in the process enabling TADF and turning off RTP emissions.

In this work we showed that single-bonded pyrimidine-carbazole molecules are promising as blue TADF emitters and their ΔE_{ST} value can be tuned by different substituents in positions R or R₁.

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