

# Synthesis and photophysical properties of dipyrrolonaphthyridinediones

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The main objective of my PhD project was to gain deep insight into the synthesis, reactivity and photophysical properties of analogs and derivatives of dipyrrolo[1,2-*b*:1',2'-*g*][2,6]naphthyridine-5,11-dione core (DPND). Dipyrrolonaphthyridinedione derivatives bearing alkyl substituents at positions 6 and 12 can be readily synthesized following the two-step protocol from cheap and easily available reagents - succinamide and 2,5-dimethoxytetrahydrofuran. In the first phase, I have synthesized three derivatives bearing ethenyl  $\pi$ -bridges between the core and peripheral, substituted benzene rings, according to the optimized Mizoroki-Heck coupling protocol. These dyes, especially with electron-withdrawing groups at the peripheries, exhibit large two-photon cross-section values ( $\sigma_2$  up to 5180 GM) and beneficial ratio of  $\sigma_2$  and molecular mass which is a crucial factor in the designing of efficient two-photon absorbers. In the next phase, I have developed and optimized direct arylation of DPNDs. I have proved that this reaction exclusively occurs at positions 3 and 9 and allows for the synthesis of dyes with red/NIR emission. Based on the optoelectronic properties and theoretical calculations I have shown that the DPND core has, similarly to other cross-conjugated chromophores, an electron-deficient character. Using the optimized Buchwald-Hartwig amination protocol I was able to obtain a series of electron-rich dipyrrolonaphthyridinediones which all exhibit solvatochromism. Moreover, these dyes absorb in the red and emit in the red/NIR region of the spectrum. I have also obtained a series of bis(nitroaryl)dipyrrolonaphthyridinediones, which differ in the position of the nitro group relative to the DPND core and in the presence/absence of steric hindrance. One of these compounds possesses impressive fluorescence quantum yield value in relatively polar solvent dichloromethane – 0.94. The discovery of direct arylation/condensation sequence not only confirms reactivity of carbonyl moiety within the DPND core, but at the same time leads to novel, nitrogen-doped analogs of polycyclic aromatic hydrocarbons – pyrimidopyrimidoindolizinoindolizine (PPII). These dyes are characterized by blue color of solution and very low values of fluorescence quantum yields which along with theoretical calculations was assigned to deactivation pathway involving vibrational relaxation/internal conversion. Finally, in collaboration with prof. Pi-Tai Chou and dr Irena Deperasińska I have proved that the introduction of a typical AIE-gen - tetraphenylethylene (TPE) moiety into a planar, heterocyclic core does not always lead to efficient solid state emission. Comprehensive studies on the synthesis and optical properties of dipyrrolonaphthyridinediones allowed for better understanding of their nature which may lead to practical applications in the future.