

# Ciano grupėmis modifikuotų rubrenų taikymas NIR fotonų konversijai į regimąją sritį

## Cyano-functionalized rubrene derivatives for NIR-to-visible photon upconversion

Lukas Naimovičius<sup>1</sup>, Edvinas Radiunas<sup>1</sup>, Augustina Jozeliūnaitė<sup>2</sup>, Edvinas Orentas<sup>2</sup>, Karolis Kazlauskas<sup>1</sup>

<sup>1</sup>Institute of Photonics and Nanotechnology, Vilnius University, Saulėtekio al. 3, LT-10257 Vilnius

<sup>2</sup>Department of Organic Chemistry, Vilnius University, Naugarduko g. 24, LT-03225 Vilnius

lukas.naimovicius@ff.vu.lt

NIR-to-visible photon upconversion (UC) via triplet-triplet annihilation (TTA) is a rapidly advancing field of photonics with diverse potential applications. The most promising of them include photocatalysis, bio-imaging, photovoltaics, targeted drug delivery and night vision devices. [1-3] Typically, TTA-UC systems are composed of a sensitizer and an emitter. The sensitizer is responsible for absorption of low energy radiation and generation of triplet excitation via intersystem crossing, whereas the emitter accumulates those triplets and undergoes TTA leading to an upconverted emission of higher energy. The TTA-UC quantum yield ( $\Phi_{UC}$ ) is defined as follows:

$$\Phi_{UC} = \frac{1}{2} f \Phi_{ISC} \Phi_{TET} \Phi_{TTA} \Phi_{FL} \quad (1)$$

where  $f$  – statistical probability to create one singlet from two triplets via TTA,  $\Phi_{ISC}$  – intersystem crossing,  $\Phi_{TET}$  – triplet energy transfer,  $\Phi_{TTA}$  – triplet-triplet annihilation,  $\Phi_{FL}$  – fluorescence quantum yield.

Currently, the most widely used TTA emitter for NIR-to-visible UC is rubrene (9,10,11,12-tetraphenyltetracene). [1] Despite high fluorescence quantum yield (almost unity) in solution and proper energy level alignment suiting the TTA process (two triplets have enough energy to create one singlet), rubrene suffers from strong singlet fission (SF) in the solid-state limiting the  $\Phi_{UC}$  to about 0.07%. [2] This restricts application of rubrene in the solid-state TTA-UC devices. To address this issue SF needs to be suppressed, which can be achieved via the modification of rubrene with cyano functional groups. The cyano side-moieties have been reported to lower the singlet energy level in tetracenes (thereby making SF less probable), thus indicating the similar possible effect on rubrene. [3]

In this work, four different cyano-substituted rubrene compounds (2CN-Rub, 4CN-Rub, 4CNtb-Rub, 6CN-Rub) were investigated as the emitters for NIR-to-visible UC (Fig. 1). Palladium-phthalocyanine (PdPc) served as a sensitizer in this study. DFT calculations performed prior to experiments confirmed the reduction of singlet state energy in cyano-rubrenes. Essentially, the rubrene derivatives exhibited high  $\Phi_{FL}$  (70% - 94%) in the isolated form and a red shift of FL spectrum with increasing number of cyano groups. The latter was found to be in agreement with DFT calculations. Moreover, all the compounds exhibited significantly higher  $\Phi_{FL}$  (6.4% - 19.1%) in the solid state compared to rubrene (1.5%) indicating suppressed SF.

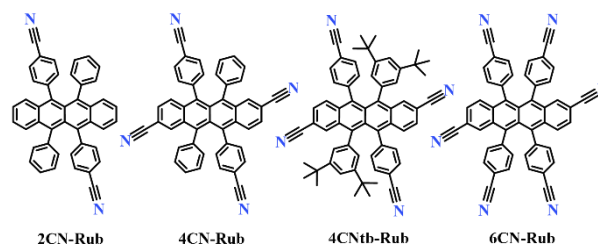


Fig. 1 Chemical structures of cyano-substituted rubrene compounds.

Preliminary data show that all the compounds except 6CN-Rub demonstrate the feasibility for TTA in a solution and solid-state. It was revealed that 6 CN groups reduce not only the singlet energy, but also the triplet energy to an extent unfavorable for TTA. The remaining compounds demonstrated efficient UC with  $\Phi_{UC}$  of 2.6% (4CN-Rub), 2.4% (2CN-Rub) and 1.0% (4CNtb-Rub). (Fig. 2) The obtained efficient UC in solutions demonstrates the potential of these derivatives for TTA-UC application in the solid-state.

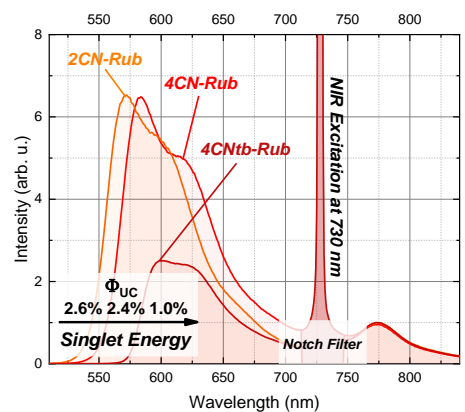


Fig. 2 NIR-to-visible UC spectra and  $\Phi_{UC}$  of cyano-substituted rubrene compounds admixed with PdPc in solution.

**Keywords:** NIR-to-visible, upconversion, singlet fission, triplet fission.

### Literature

- [1] M. Wu et al., Nat. Photonics, vol. 10, no. 1, pp. 31–34, (2016)
- [2] Radiunas, E. et al., J. Mater. Chem. C 8, 5525–5534 (2020).
- [3] Fallon, K. J. et al., J. Am. Chem. Soc. 142, 19917–19925 (2020).