SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRROLO[3,2-B]PYRROLES WITH QUADRUPOLE STRUCTURE

Bartosz Szymański[1,2], Olena Vakuliuk[1], Radosław Kamiński[2], Daniel T. Gryko*[1]

[1] Institute of Organic Chemistry PAS, Team X, Kasprzaka 44/52, 01-224 Warsaw
[2] University of Warsaw, Faculty of Chemistry, Pasteura 1, 02-093 Warsaw
bk.szymanski@student.uw.edu.pl

INTRODUCTION

1,2,4,5-tetraarylpyrrolo[3,2-*b*]pyrroles (TAPPs) are a group of functional dyes, which remained poorly investigated until 2013, when D.T.Gryko's group members serendipitously developed an effective method of their synthesis. After that discovery, TAPPs revealed interesting photophysical properties, which were further investigated by many research groups, and therefore applied in e.g. **OLEDs, excited state-symmetry breaking** studies and **memory chips**. Herein I would like to present synthesis and photophysical properties of pyrrolo[3,2-*b*]pyrroles bearing 2,1,3-benzoxadiazole or 2,1,3-benzothiadiazole moieties. **The main goal of our research was to obtain functional dyes with maximum of emission in biological window (below 650 nm)**, which are suitable for cellular imaging. Such TAPPs have been synthesized never before.

DESIGN AND SYNTHESIS

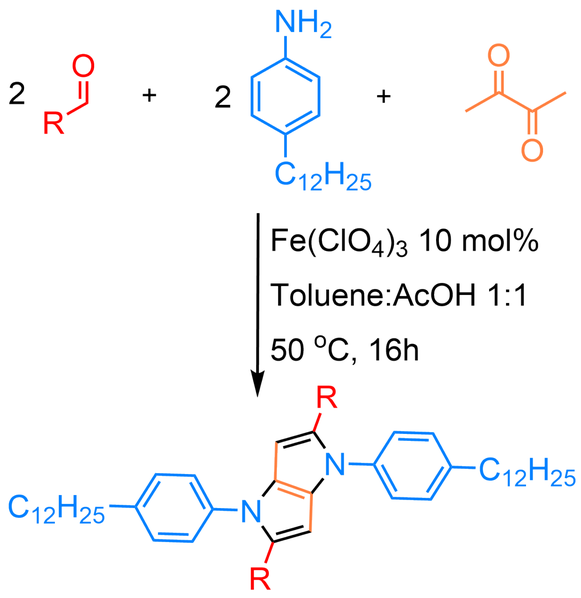

Figure 1: Synthetic approach of TAPPs synthesis developed in 2019 and used in this research metodology. Colour of fragments derived from aldehyde corresponds to colour of dye in solid state. **Yields of synthesis** given.

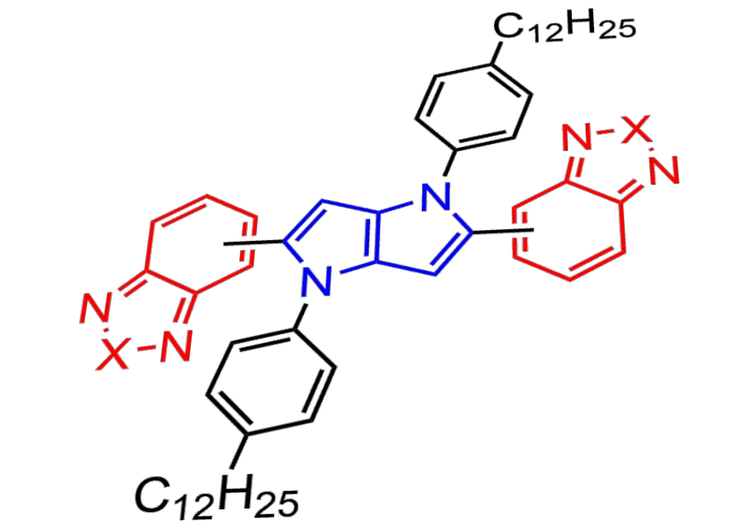

Figure 2: Design of investigated compounds. Acceptor-donor-acceptor structure was provided by electron-withdrawing groups attached to 2 and 5 positions. Pyrrolo[3,2-*b*]pyrrole core is a strong electron donor.

PHOTOPHYSICAL PROPERTIES

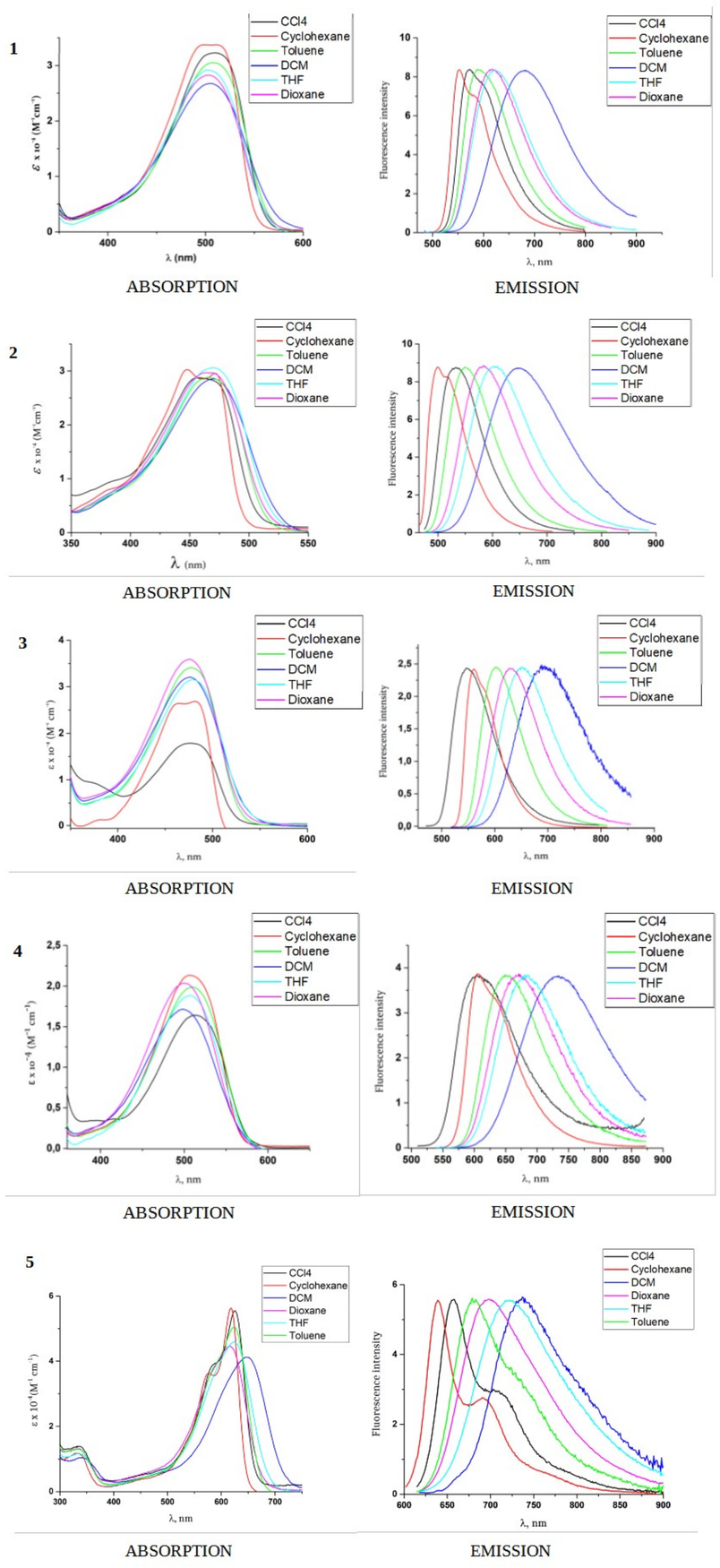

Figure 3: Absorption and emission spectra of compounds **1-5**. Solvatofluorochromism is visible due to large Stokes shift in polar solvents..

Photophysical properties: absorption

Compound	Max of absorption in cyclohexane, nm	Molar absorption coefficient, $mM^{-1}*cm^{-1}*10^{-4}$	Max of absorption is solid state, nm
1	499	2,91	518
2	471	2,80	471
3	482	2,91	489
4	506	1,75	463
5	618	3,57	681

Table 1: Absorption of compounds **1-5** in cyclohexane and in a solid state. Compounds **1, 3** and **5** exhibit batochromic shift in solid state, whereas compound **4** hypsochromic, due to difference as large as 50 nm!

NARODOWE CENTRUM NAUKI

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PHOTOPHYSICAL PROPERTIES

Compound	Solvent	λ^{abs}_{max} [nm]	$\varepsilon \cdot 10^4$ [$M^{-1} \cdot cm^{-1}$]	λ^{em}_{max} [nm]	Stokes' shift [cm^{-1}]	Φ
1	**Cyclohexane**	**499**	**2.91**	**553**	**1957**	**0.77**
1	**THF**	**501**	**2.48**	**623**	**3909**	**0.44**
1	**CH_2Cl_2**	**504**	**2.3**	**673**	**4982**	**0.08**
2	**Cyclohexane**	**471**	**2.80**	**499**	**1191**	**0.88**
2	**THF**	**469**	**2.89**	**609**	**4902**	**0.35**
2	**CH_2Cl_2**	**470**	**2.84**	**646**	**5797**	**0.04**
3	**Cyclohexane**	**482**	**2.91**	**519**	**1 479**	**0.78**
3	**THF**	**479**	**2.96**	**620**	**4 748**	**0.45**
3	**CH_2Cl_2**	**476**	**3.03**	**661**	**5 880**	**0.12**
4	**Cyclohexane**	**506**	**1.75**	**572**	**2 280**	**0.52**
4	**THF**	**507**	**1.44**	**657**	**4 496**	**0.25**
4	**CH_2Cl_2**	**498**	**1.72**	**716**	**6 114**	**0.03**
5	**Cyclohexane**	**618**	**3.57**	**639**	**532**	**0.79**
5	**THF**	**624**	**4.68**	**722**	**2175**	**0.01**
5	**CH_2Cl_2**	**648**	**4.59**	**737**	**1864**	**<0.01**

Table 2: Photophyscial properties of compounds **1-5**. High fluorescence quantum yields in non-polar solvents inform about conservation of quadrupolar symmetry in S_1 state. Decay of the fluorescence in polar solvents is caused by excited state symmetry breaking..

CRYSTAL STRUCTURES

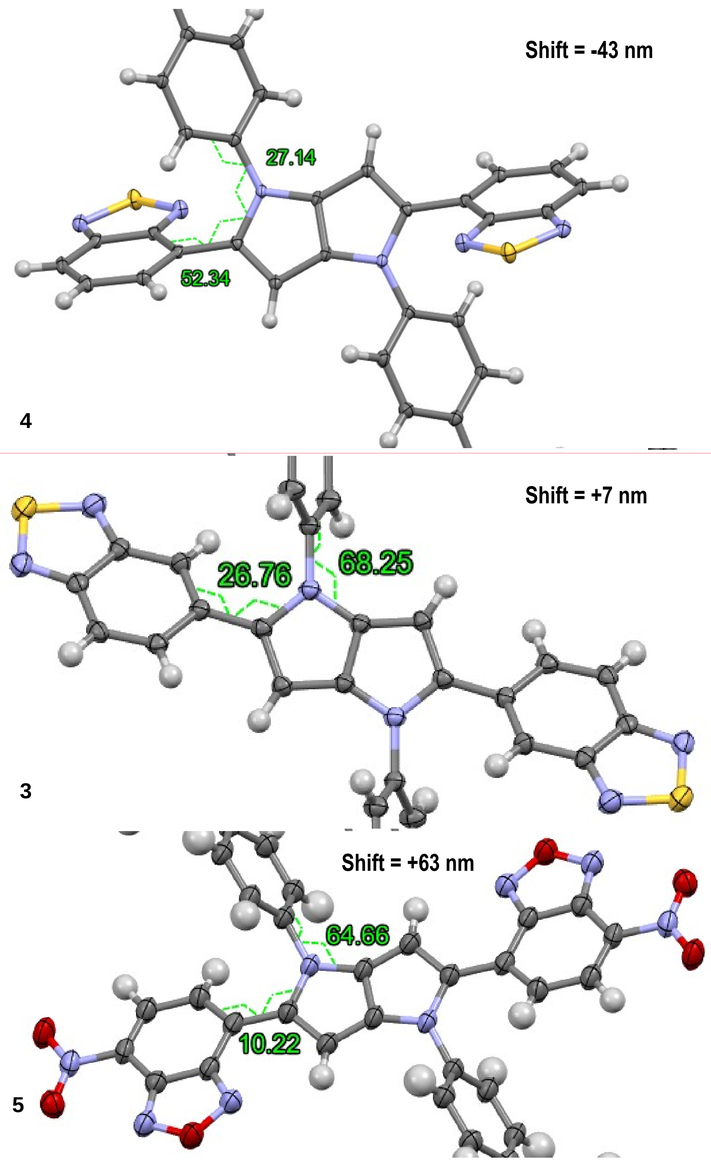

Figure 4 Crystal structure analysis of compounds **3-5**. Torsion angles were measured. We observed a correlation between cosinus of tosion angle A-D and shift of absorption in solid state.

CONCLUSIONS

We synthesized for the first time **red-emitting non-extended TAPP,** bearing strong electron-acceptor groups. Future purposes of our research contain photostability, fluorescence in solid state and two-photon absorption measurement. Obtained compounds:

- Are characterized by maximum of emission above 600 nm with high (up to 0.79 quantum yield)
- Are fluorescent despite possesing nitro groups and similar units
- Exhibit large solvatofluorochromism caused by excited-state symmetry breaking

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