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Introduction

The search for new, more effective dyes that absorb and emit in the red visible / near-infrared (NIR) region of the spectrum is of interest in many different fields of chemistry, ranging from optical sensors and imaging applications to materials chemistry related issues [1]. Particularly advantageous for biological and sensing applications is the spectral region between 650 and 900 nm, known as the "biological window". However, design and synthesis of NIR dyes is demanding, and problems due to aggregation, photobleaching, and low fluorescence quantum yields are often encountered.

Approach

A promising starting point for the construction of highly emissive dyes is the boron-dipyrrromethene (BDP) chromophore. Advantages: high extinction coefficients, high fluorescence quantum yields and good photostability. For example, $\epsilon_{500}=8.80 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $\Phi_f=0.54$ for **1** (Chart 1) in hexane [2a]

Shift into the red/NIR region of the spectra is possible by fusing aromatic rings to the BDP core (**2** and **series 3**), thus extending the cyanine-like chromophoric system of **1**

A series of phenanthrene-BDP derivatives (**series 3**) with different electron donor and acceptor groups **R** is described here

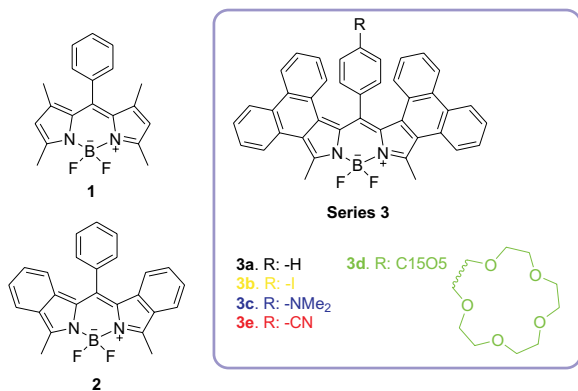


Chart 1. Structures of the BDP derivatives described in this work (**series 3**) and model compounds **1** and **2** included for comparison from refs. 2a and 2b

Conclusions

- A new family of red-NIR emitting BDP dyes has been described
- Introduction of phenanthrene rings shifts absorption and emission bands 130 nm with respect to the simplest BDP core while keeping high emission efficiency
- Compound **3c** can be employed as a NIR-fluorescent pH probe
- The dyes presented here are good candidates for imaging and labeling applications. Suitable for excitation with He-Ne laser (632 nm)

Acknowledgements

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Literature

[1] R. Raghavachari (ed.), In Near-Infrared Applications in Biotechnology, Practical Spectroscopy Series Vol. 25, Marcel Dekker, Inc. 2001. [2] a) M. Kollmannsberger, K. Rurack, U. Resch-Genger, J. Daub, J.Phys. Chem. A 1998, 102, 10211; b) Z. Shen, H. Röhr, K. Rurack, H. Uno, M. Spieles, B.Schulz, G. Reck, N. Ono, Chem. Eur. J. 2004, 4853.

Results

- Absorption and emission bands of **series 3** are centered at $\lambda > 600$ nm. Red shift of > 100 nm with respect to the parent compound **1**
- Quantum yields of fluorescence of ca. 1
- Typical BDP features: narrow and structured absorption and emission bands, high extinction coefficients (for example, $\epsilon_{625}=1.18 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ for **3a** in MeCN) and low dependence of spectroscopic properties on environment polarity

Table 1. Spectroscopic properties of **1**, **2** and **3a-e** in diethyl ether at 298 K

R	$\lambda_{\text{abs}} / \text{nm}$	$\lambda_{\text{em}} / \text{nm}$	Φ_f	τ_f / ns	$k_f / 10^8 \text{ s}^{-1}$	$k_{nr} / 10^8 \text{ s}^{-1}$
1 ^a	498	510	0.59	2.98	2.0	1.4
2 ^a	598	605	0.98	5.83	1.7	0
3a H	627	647	1.00	5.89	1.7	0
3b I	630	652	0.92	5.98	1.5	0.1
3c NMe ₂	618	634	0.94	5.52	1.7	0.1
3d C15O5	623	641	1.00	6.12	1.7	0
3e CN	639	666	0.95	6.08	1.6	0.1

^aValues obtained from references 2a and 2b

Influence of R

- Absorption and emission wavelengths are blue-shifted upon increase on electron donor strength of **R** (Fig.1)
- Negligible influence of **R** on Φ_f and τ in apolar solvents (Table 1)

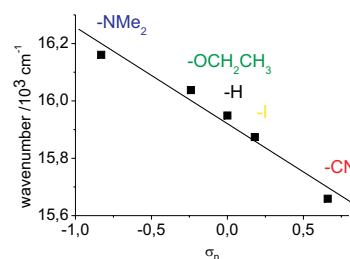


Fig.1. Dependence of absorption maxima in diethyl ether vs. the Hammett constant values for the different phenyl-substituents in **series 3**

- For compound **3c**, a photoinduced charge transfer process (CT) is activated in polar solvents like MeCN, alcohols or aqueous mixtures. This results in a quenching of the fluorescence
- Fluorescence of derivative **3c** can be switched on by protonation (pKa in water is 1.9)

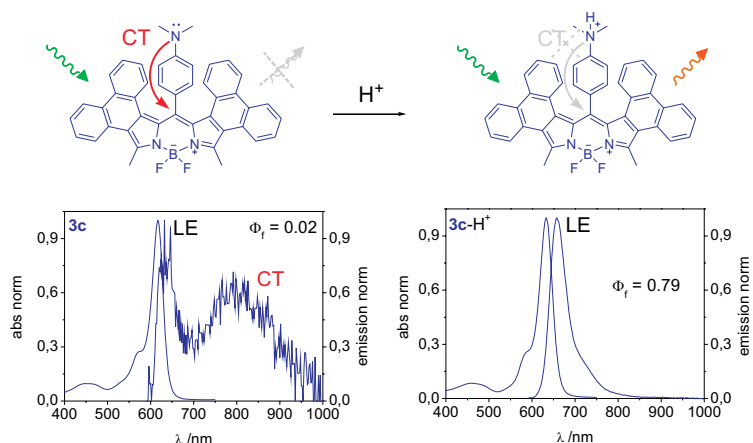


Fig.2. Absorption and emission spectra of compound **3c** in MeCN (left) and after the addition of protons (right)