NIR dyes

Selective NIR chromophores: Bis-Pyrrolopyrrole Cyanines

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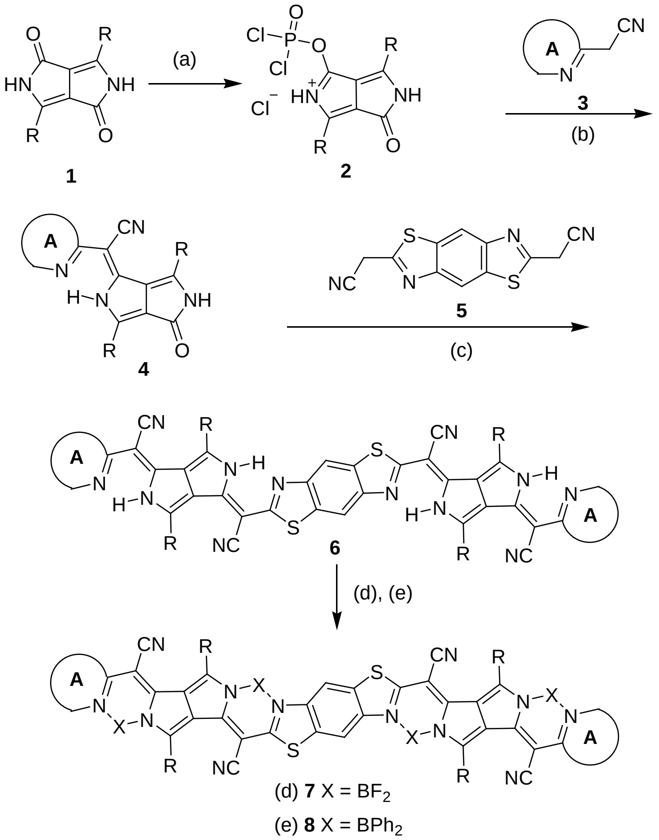
New applications have recently led to an increased interest in near infrared (NIR) dyes. Both, strong NIR absorption and fluorescence emission are important phenomena. While fluorescence is exploited especially for labelling purposes in microscopy,[1] NIR absorption has a broad range of applications mainly in material science.[2] Examples of growing fields of interest are NIR light emitting diodes[3] and the use of NIR-photosensitizers in dye-sensitized solar cells.[4] In the latter cases, the aim is to utilize the NIR part of the solar spectrum in order to generate photocurrents. In many applications, especially selective NIR absorbers which absorb strongly in the NIR while exhibiting negligible absorption in the visible spectral range are required.[2] Dyes with these properties find use as NIR absorbers in paints and windows to block off heat, in laser protecting glasses, as dyes for laser polymer welding of transparent components,[5] or as anti-forgery markers[6]. In all these examples it is required that the dye does not influence the spectral properties of the components in the visible. Thus, photostable dyes with strong, narrowbandwidth NIR absorptions and negligible absorption in the visible spectral range are needed.

Common strategies to achieve bathochromic shifts of the absorption maximum of a dye are the extension of the chromophoric system or the introduction of donor and acceptor groups into the chromophore.[2,7] Cyanine dyes[8] and the rylene dyes[9] are the most popular classes showing significant bathochromic shifts upon extension of their π-system. In cyanine dyes, however, the chemical stability decreases with increasing extension. By contrast, rylene dyes are chemically very stable, but, due to comparably large bondlength changes accompanying the $S_0 \rightarrow S_1$ transition, they show rather intense 01 and 02 vibronic bands (Franck-Condon principle). Thus, their $S_0 \rightarrow S_1$ absorption is extended into the visible range. Other important classes of NIR dyes, showing strong and narrowband NIR absorption are squarine dyes[10], bodipys[11] and some aza[18]annulene derivatives such as porphyrins[12] phthalocyanines[13] and especially naphtolocyanines[7,14].

We recently described pyrrolopyrrole cyanine (PPCy) dyes as a new class of NIR dyes and fluorophores.[15] PPCys are synthesized by a condensation reaction of diketopyrrolopyrrole (DPP) **1** and heteroaromatic acetonitriles (HAA) **3**. Complexation with either BF_2 or BPh_2 yields fluorophores which exhibit narrowband absorption between 650 and 900 nm and fluorescence emission with high quantum yields. By isolation of the monoactivated DPP **2**, selectivly one of the carbonyl groups of the DPP can be reacted with a HAA **3** to the half converted products **4**. Further reaction with another acetonitrile derivative **3** leads to PPCys with an asymmetric substitution pattern. This stepwise reaction scheme allows for the introduction of just one functional group.[16]

Here, we describe the synthesis of a new class of NIR chromophores with unprecedented spectral properties. They have very strong and narrowband NIR absorption while featuring negligible visible absorption. The absorption coefficients of these dyes in the NIR belong to the strongest ever reported for organic fluorophores, being twice as high as those of recently reported rylene dyes.[9] Our previous approaches to shift the absorption of the PPCys bathochromically concerned the modification of the heteroaromatic endgroup (**A**) and/or the complexation agent.[15,16] The selective synthesis of the halfconverted DPPs **4** opens a strategy to enlarge the chromophore of the PPCys by reacting two equivalents of **4** with a bifunctional bridging heteroaromatic acetonitrile such as **5** (Scheme 1.) The resulting condensation products contain two pyrrolopyrrole moieties and can therefore be called bis-pyrrolopyrrole cyanine dyes.



Scheme 1. Reagents and conditions: (a) $POCl_3$ reflux; (b) abs. THF reflux; (c) $POCl_3$, toluene reflux; (d) *N*,*N*-di-*iso*-propylethylamine, $BF_3{\cdot}OEt_2$, methylene chloride, reflux; (e) *N*,*N*-di-*iso*-propylethylamine, chloro-di-phenylborane, toluene, reflux; R = 3,4,5-tris(dodecyloxy)-phenyl; **3**: (6-*tert*-butylbenzothiazol-2-yl)-acetonitrile (**3a**), (6-*tert*-

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butylquinoline-2-yl)-acetonitrile (**3b**), quinoxalin-2-yl-acetonitrile (**3c**). **A**: aromatic ring.

To design an enlarged chromophore with preferably high symmetry, the bifunctional bridging moiety must be symmetric. As a first appropriate example, we synthesized the 2,6-dicyanomethylbenzo[1,2-d:4,5-d']bisthiazole **5** by a condensation of two equivalents of malononitrile with 2,5-diamino-benzen-1,4-dithiol in 86% yield. For most PPCy syntheses described so far, a *para*-octyloxy substituted DPP was used to increase the solubility for both the reaction and purification procedures.[15,16] As bis-PPCys built of this DPP are insoluble in all common solvents, 3,4,5-tridodecyloxy-DPP **1** was synthesized to increase the product solubility. The bis-H-PPCys **6** generated from **1** are soluble in solvents such as chloroform and toluene and could be isolated in yields of 53% (**6a**), 86% (**6b**) and 32% (**6c**) after purification by column chromatography. The H-chelates **6** can be stiffened by exchanging H against BF_2 (**7**) or BPh_2 (**8**).

The optical data of the synthesized bis-PPCys are summarized in Table 1. The longwavelength absorptions ($S_0 \rightarrow S_1$) of **6a**, **7a** and **8a** are depicted in Figure 1 (for the absorption spectra of all derivatives see supporting information).

Table 1. Spectroscopic data of the first electronic transition of the bis-H-PPCys **6**, the bis-BF_2-PPCys **7** and the bis-BPh_2-PPCys **8**.[a]

	λ_{00}^{A} [nm]	ε_{00} [$M^{-1}cm^{-1}$]	$\Delta\tilde{\nu}_{1/2}$ [cm^{-1}]	f	λ_{00}^{F} [nm]	$\Delta\tilde{\nu}_{A-F}$ [cm^{-1}]
6a	829	277000	660	1.63	-	-
6b	827	255000	700	1.61	-	-
6c	834	277000	620	1.60	-	-
7a	815	535000	400	1.67	827	180
7b	823	548000	420	1.73	838	220
7c	849	574000	400	1.72	867	240
8a	894	571000	370	1.58	912	220
8b	905	556000	400	1.61	924	230
8c	941	531000	380	1.57	966	280

[a] In chloroform at room temperature, λ_{00}^{A}: absorption wavelength, ε_{00}: molar decadic absorption coefficient, $\Delta\tilde{\nu}_{1/2}$: halfwidths, f: oscillator strength, λ_{00}^{F}: fluorescence wavelength, $\Delta\tilde{\nu}_{A-F}$: Stokes shift.

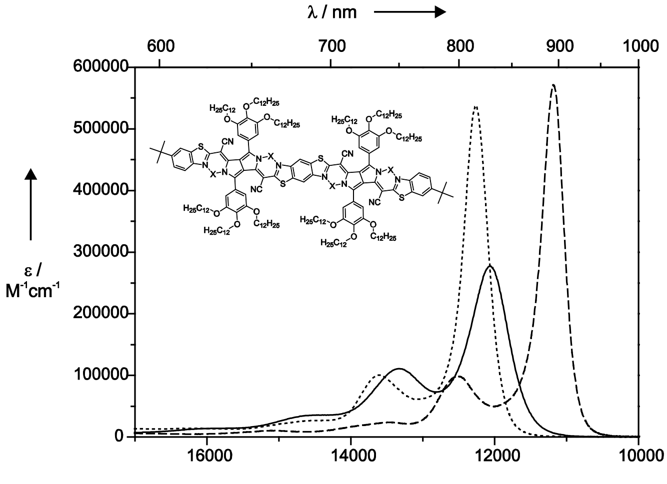

Figure 1. $S_0 \rightarrow S_1$ absorption of the benzothiazole derivatives in chloroform at r.t.: X = H (solid line) **6a**, X = BF_2 (pointed line) **7a**, X = BPh_2 (dashed line) **8a**.

The bis-H-PPCys **6** show intense long wavelength absorption with maxima between 827 and 834 nm. For all derivatives the spectral shape, intensity, and position of the first electronic transition hardly differs. As is the case for PPCys, complexation of **6** to **7** or **8** leads to a sharpening of the vibronic bands, an increase in the absorption coefficients, and a shift of the Franck-Condon-Factors in favour of the 00-transition. Depending on the heterocycle (**A**), the absorption maxima are shifting in the same manner as known for PPCys, while bandshapes and intensities of the $S_0 \rightarrow S_1$ transition within the series of compounds **6**, **7**, or **8** are almost identical. In the case of the series **6**, the intramolecular flexibility of the heteroaromatic endgroups is high compared to the boron-substituted compounds. Therefore the influence of the substituent **A** is increasing in the stiffend π-systems of the complexes **7** and **8**.

We have also characterized the fluorescence properties of the new compounds. As in the case of PPCys, we find that the H-chelates **6** do not exhibit any noticeable fluorescence emission. Also here, we ascribe this to rapid relaxation via torsional vibrational modes[15]. Room temperature fluorescence can be achieved by stiffening the chromophore via the complexation with either BF_2 or BPh_2. All observed Stokes shifts are of the same size and small. The determination of quantum yields in the spectral range beyond 900 nm is difficult due to the lack of well established standards. From the recorded emission spectra, we conservatively estimate the quantum yields to vary between 20 % (**7b**) and 5 % (**8c**). These are extremely high values for these emission wavelengths. Note especially that the latter value refers to fluorescence emission at 966 nm.

As is the case for the PPCys[15,16], the halfwidths of the vibronic bands decrease in the order H>BF_2>BPh_2. Remarkably, for the bis-PPCys the halfwidths $\Delta\tilde{\nu}_{1/2}$ are always more than 100 cm^{-1} smaller than for the corresponding PPCys. An additional increase in the ε_{00}-values of the bis-PPCys arises from the difference in the $\varepsilon_{01}/\varepsilon_{00}$-ratios. These ratios are always smaller for the bis-PPCys than for the corresponding PPCys (see supporting information). Altogether, this leads to ε_{00}-values which are more than twice as high for the bis-PPCys reaching more than 550.000 $M^{-1}cm^{-1}$. These spectroscopic findings and the extremely narrow absorption and emission bands indicate that bis-PPCys have a continuous chromophore. This is striking since the chromophore extends over 11 aromatic rings and 4 BR_2-bridged ringlike structures. The chromophores can be seen as two PPCys which are connected at the terminal benzene ring. The synthetic strategy reported here opens ways for the generation of stiff, linear conjugated systems, e.g. via polycondensation of **1** and **5**. First attempts in this direction yield products with spectral data hinting at the generation of oligomeric species.

Due to the low intensities of the vibronic transitions (small $\varepsilon_{01}/\varepsilon_{00}$-values) of the boron complexes **7** and especially **8**, the first electronic transition lies almost completely in the NIR. The dyes do not show higher transitions of significant intensity in the visible spectral range. Thus, the dyes **7** and **8** come close to the ideal of a selective NIR absorber. To demonstrate the applicability of the dyes, we immersed **8a** in PMMA. For this purpose, a solution of **8a** (1.3 µM) in methylmethacrylate was polymerized in a test-tube. After curing, a cuboid has been milled out. The resulting PMMA block was colorless, while the absorption of **8a** (A_{00} = 1.2) is almost unchanged compared to a solution in chloroform (Figure 2.). The absorption remained almost unchanged after half a year of exposition with daylight. In addition the photostability of **7a** and **8a** in toluene solution was compared to a commercially available naphthalocyanine NIR dye. Both compounds are significantly more photostable (see supporting information).

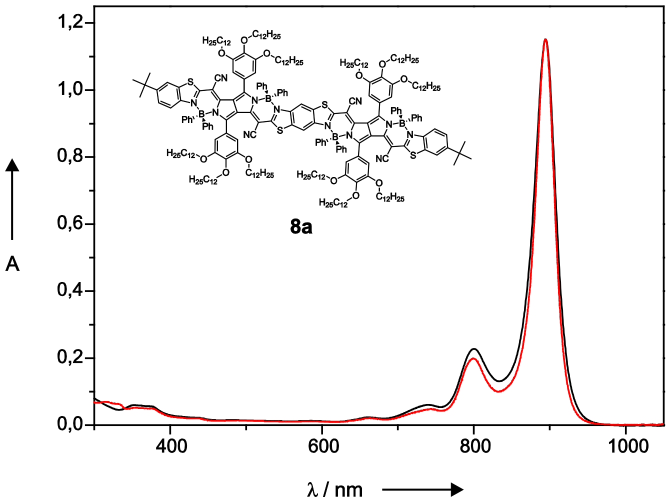

Figure 2. Absorbance of **8a** in chloroform (pointed line) and in PMMA (solid line).

In conclusion, we present a strategy for the synthesis of a new type of chromophores with very large π-electron systems. While the electrons are delocalized over a long quasi-linear system of rings, the molecules absorb as one chomophoric system. This leads to very narrow absorption bands, extremely high absorption coefficients, and high photochemical stability. Due to the lack of any strong absorption in the visible spectral range, the compounds reach the ideal of being selective NIR-absorbers. The BF_2 and BPh_2 derivates in addition exhibit strong fluorescence in the spectral region close to 1 µm. The exquisite spectral properties of the compounds let these appear as interesting candidates in a great variety of technical applications.

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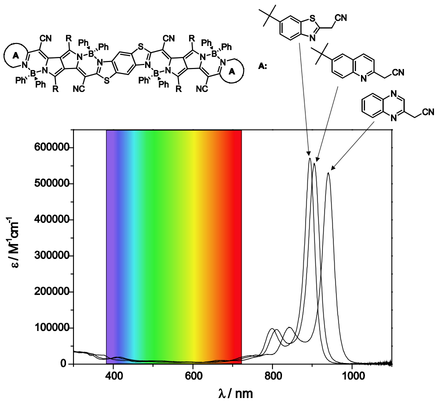
Selective NIR chromophores: Bis-Pyrrolopyrrole Cyanines



Strongly invisible: We present a new type of extended chromophores based on diketopyrrolopyrroles. The compounds are characterized by extremely high extinction coefficients, narrowband absorption in the near infrared, and strong fluorescence around 1 µm. Since absorption in the visible is negligible, they reach the ideal of selective NIR-absorbers.