NIR Dyes

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Selective NIR chromophores: Bis(Pyrrolopyrrole) Cyanines**

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New applications have recently led to increased interest in near-infrared (NIR) dyes. Both strong NIR absorption and fluorescence emission are important phenomena. While fluorescence is exploited especially for labeling 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, the aim is to utilize the NIR part of the solar spectrum to generate photocurrents. Many applications require NIR absorbers that absorb strongly in the NIR while exhibiting negligible absorption in the visible spectral range.[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 welding of transparent polymers,[5] and as antiforgery markers.[6] In all of these examples it is required that the dye does not influence the spectral properties of the components in the visible range. Thus, photostable dyes with strong, narrow-bandwidth 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 and 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, as a result of the relatively large changes in bond length 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 naphthalocyanines.[7,14]

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

Herein we describe the synthesis of a new class of NIR chromophores with unprecedented spectroscopic properties. They have very strong and narrowband NIR absorption while featuring negligible visible absorption. The absorption coefficients of these dyes in the NIR are among the strongest ever reported for organic fluorophores and are twice as high as those of the recently reported rylene dyes.[9] Our previous approaches to shifting 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 half-converted DPPs **4** opens up a strategy to extend 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 considered bis(pyrrolopyrrole) cyanine dyes.

In the design of an extended chromophore with preferably high symmetry, the bifunctional bridging moiety must be symmetric. As a first appropriate example, we synthesized the dicyanomethylbisbenzothiazole **5** by a condensation of two equivalents of malononitrile with 2,5-diaminobenzene-1,4-dithiol in 86 % yield. In most PPCy syntheses described so far, a *para*-octyloxy-substituted DPP served to increase the solubility and facilitate both the reaction and purification procedures.[15,16] As bis(PPCy)s composed 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-PPCy)s **6** generated from **1** are soluble in solvents such as chloroform and toluene and were 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 for BF_2 (**7**) or BPh_2 (**8**). The optical data of the synthesized bis(PPCy)s are summarized in Table 1. The long-wavelength absorptions ($S_0 \rightarrow S_1$) of **6a**, **7a**, and **8a** are depicted in Figure 1 (for the absorption spectra of all derivatives see the Supporting Information).

The bis(H-PPCy)s **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 are very similar. As is the case for

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NIR = near infrared.

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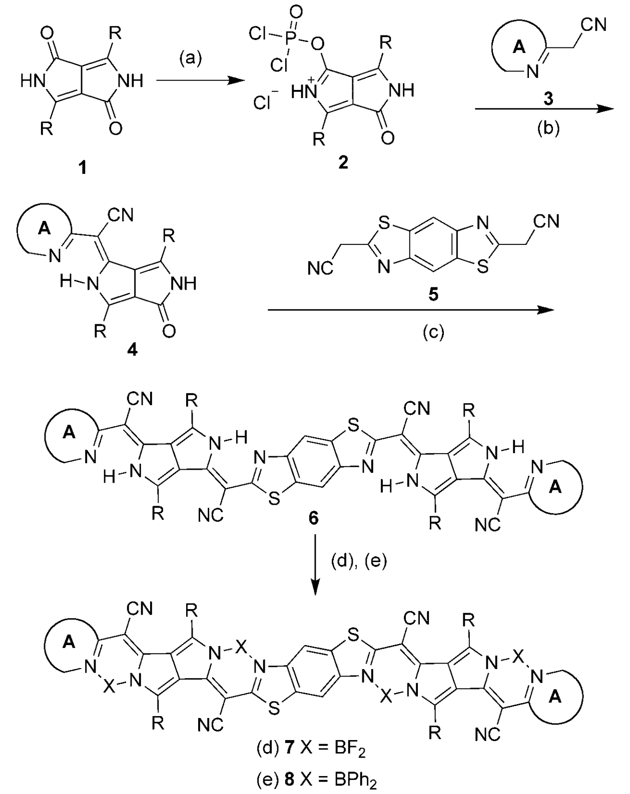


Scheme 1. Reagents and conditions: a) $POCl_3$, reflux; b) abs. THF, reflux; c) $POCl_3$, toluene, reflux; d) *N*,*N*-diisopropylethylamine, $BF_3\cdot OEt_2$, methylene chloride, reflux; e) *N*,*N*-diisopropylethylamine, chlorodiphenylborane, toluene, reflux; R = 3,4,5-tris(dodecyloxy)phenyl; **3**: (6-*tert*-butylbenzothiazol-2-yl)acetonitrile (**3a**), (6-*tert*-butylquinoline-2-yl)acetonitrile (**3b**), (quinoxalin-2-yl)acetonitrile (**3c**). **A**: aromatic ring.

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

Cmpd	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.

PPCys, complexation of **6** to give **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 favor of the 00 transition. Depending on the heterocycle (**A**), the absorption maxima shift in the same manner as known for PPCys, while the bandshapes and intensities of the $S_0{\rightarrow}S_1$ transition within the series of compounds **6**, **7**, and **8** are almost identical. In the case of the series **6**, the intramolecular flexibility of the heteroaromatic endgroups is much higher than that of the boron-substituted compounds. Therefore the influence of the substituent **A** increases in the stiffened π systems of complexes **7** and **8**.

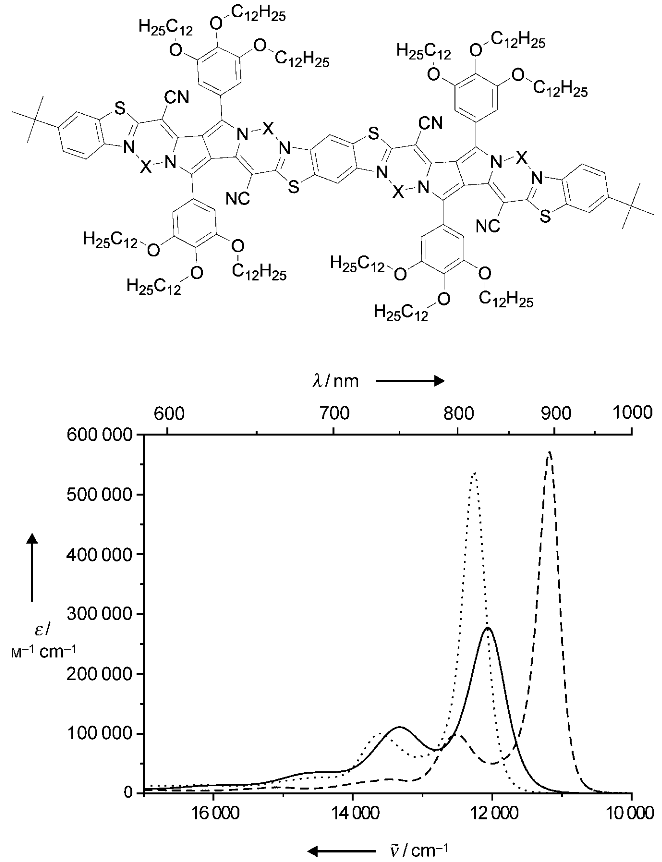


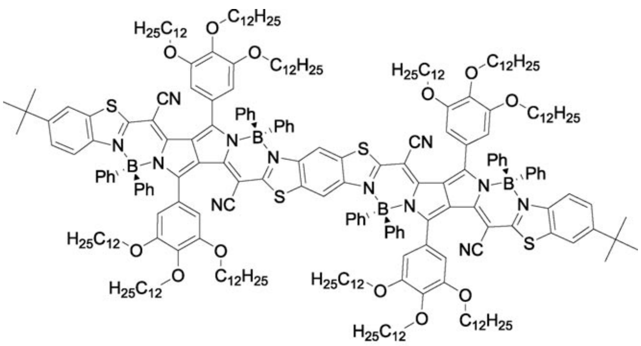
Figure 1. $S_0{\rightarrow}S_1$ absorption of the benzothiazole derivatives in chloroform at room temperature: ——: X = H (**6a**), •••••: X = BF_2 (**7a**), -----: X = BPh_2 (**8a**).

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 through torsional vibrational modes.[15] Room-temperature fluorescence can be achieved by stiffening the chromophore through 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 owing 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(PPCy)s the halfwidths $\Delta\tilde{\nu}_{1/2}$ are always more than 100 cm^{-1} smaller than those of the corresponding PPCys. An additional increase in the ε_{00} values of the bis(PPCy)s arises from the difference in the $\varepsilon_{01}/\varepsilon_{00}$ ratios. These ratios are always smaller for the bis-

(PPCy)s than for the corresponding PPCys (see the Supporting Information). Altogether, this leads to ε_{00} values for the bis(PPCy)s that are more than twice as high reaching more than 550000$\text{M}^{-1}\text{cm}^{-1}$. These spectroscopic findings and the extremely narrow absorption and emission bands indicate that the chromophore in the bis(PPCy)s extends over 11 aromatic rings and four BR_2-bridged ringlike structures. The chromophores can be considered to be two PPCys with a common benzene ring. The synthetic strategy reported here opens up approaches for the generation of stiff, linear conjugated systems, for example, through the polycondensation of **1** and **5**. First attempts in this direction yield products with spectral data hinting at the generation of oligomeric species.

Owing 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 polymerized a solution of **8a** (1.3 μM) in methylmethacrylate in a test tube. After curing, a cuboid was milled out. The resulting PMMA block was colorless, while the absorption of **8a** ($A_{00} = 1.2$) was almost identical to that of a solution in chloroform (Figure 2.). The absorption remained almost unchanged after half a year of exposure to daylight. In addition the photostability of **7a** and **8a** in toluene solution was compared to that of a commercially available naphthalocyanine NIR dye. Both compounds are significantly more photostable (see the Supporting Information).



8a

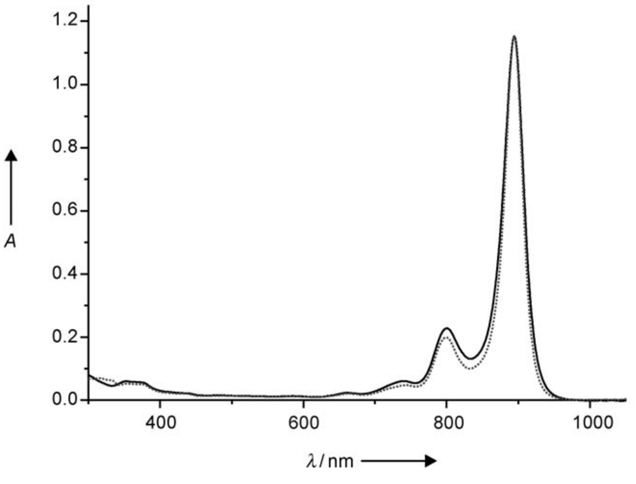


Figure 2. Absorbance of **8a** in chloroform (•••••) and in PMMA (——).

In conclusion, we present a strategy for the synthesis of a new type of chromophore with extended 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. Owing 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 derivatives in addition exhibit strong fluorescence in the spectral region close to 1 μm. The striking spectral properties of the compounds make them promising candidates for a great variety of technical applications.

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