DOI: 10.1002/ejoc.201100108

# Pyrrolopyrrole Cyanines: Effect of Substituents on Optical Properties

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**Keywords:** Chromophores / Dyes/pigments / Fluorescence / Heterocycles / Near-infrared dyes

To tune their optical properties, a large variety of pyrrolopyrrole cyanines (PPCys) were synthesized with substituted heteroaromatics such as quinoline, benzothiazole, and oxazole derivatives as terminal groups. Thus, a broad range of stable, highly fluorescing near-infrared (NIR) dyes with high absorptivities between 690 to 845 nm is accessible. The large number of newly synthesized compounds allows a detailed discussion of the correlation between molecular structure and the optical properties of the first electronic transition.

## Introduction

Much effort has recently been dedicated to the synthesis of new dyes and fluorophores absorbing and emitting in the near-infrared (NIR) spectral region. NIR fluorescence is exploited in imaging methods in biology and medicine. In this context, working in the NIR region offers several advantages over use of the visible spectral range, such as weak absorption and low scattering of tissue, which leads to high penetration depths and sensitive detection because of negligible autofluorescence background.[1] In addition, NIR-absorbing dyes find broad applications in materials science. Growing fields of interest are the use of organic dyes in NIR light-emitting diodes, as sensitizers in dye-sensitized solar cells, as selective NIR absorbers in paints to block heat, or as antiforgery markers.[2] These applications have provided motivation for the recent development of a broad variety of new NIR fluorophores.[3]

In many of the aforementioned applications it is important to match the optical properties of the dyes, such as absorption and fluorescence maxima, bandshape or Stokes shifts, to very specific requirements. To fine-tune the optical molecular properties, a detailed understanding of the relationship between the structures and the properties of the dyes is necessary.

In earlier work, we described the synthesis and spectroscopic characterization of pyrrolopyrrole cyanines (PPCy) as a new class of NIR dyes and fluorophores.[4] PPCys are obtained by condensation reaction of dioxopyrrolopyrrole (DPP) **1** and 2 equiv. of heteroaromatic acetonitrile (HAA) **2** after activation of the carbonyl groups of the DPP with phosphoryl chloride. The resulting H-PPCys **3** can be stiffened by exchanging the protons in the hydrogen bonds by $BF_2$ or $BPh_2$, yielding $BF_2$-PPCys **4** or $BPh_2$-PPCys **5**, respectively (Scheme 1). The spectral properties of PPCys are characterized by strong, narrow-band absorptions in the NIR and very weak bands in the visible spectral range. The stiffened PPCys fluoresce with quantum yields that are extremely high for NIR emission. So far, we have investigated the influence of the heteroaromatic end groups and the bridging $BF_2$ and $BPh_2$ groups on the spectral properties of PPCys. The heterocyclic end groups introduced by HAAs **3** have the same influence on the optical properties as those known for typical cyanine dyes, and show increasing bathochromic shifts in the order: pyrimidine, benzoxazole, pyridine, benzothiaole, quinoline, and quinoxaline.[5] The energy difference between the absorption maxima of a $BF_2$-PPCy and a $BPh_2$-PPCy with the same end group is almost constant (ca. 1000 $cm^{-1}$), irrespective of the nature of the heterocycle.[4b] An alternative possibility to shift the optical properties is the stepwise synthesis of asymmetric PPCys. The photophysical properties, such as absorption and fluorescence, of these compounds lie between those of the corresponding symmetric derivatives.[6] With the exception of bromine- and acetylene-substituted HAA, the acetonitriles used so far have only contained alkyl-substituted groups. In this work, we present an investigation of the influence of the substitution pattern of HAAs **2** on the spectroscopic properties of the PPCys. In particular, substituents on the quinoline and benzothiazole HAAs were altered, and a benzoxazole HAA was enlarged by benzannulation of a benzene ring. We discuss the spectroscopic properties of the resulting PPCy dyes, which give important insights into the photophysical behavior of this class of dyes.

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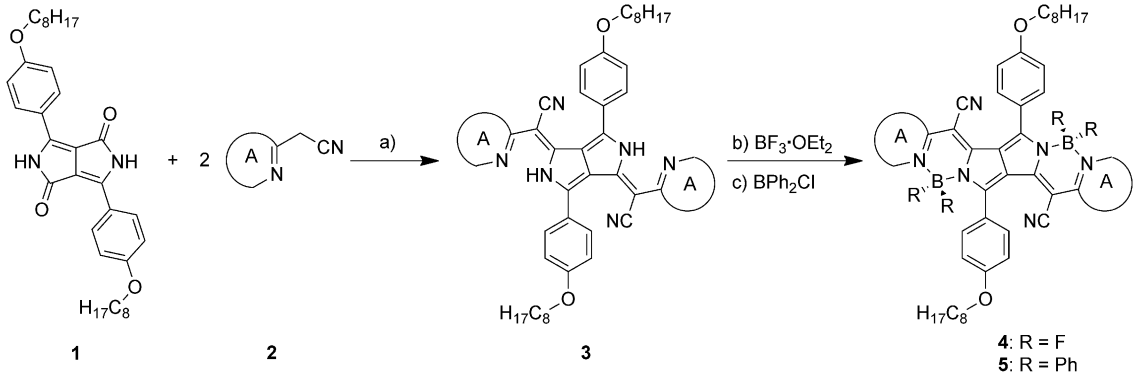
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100108.

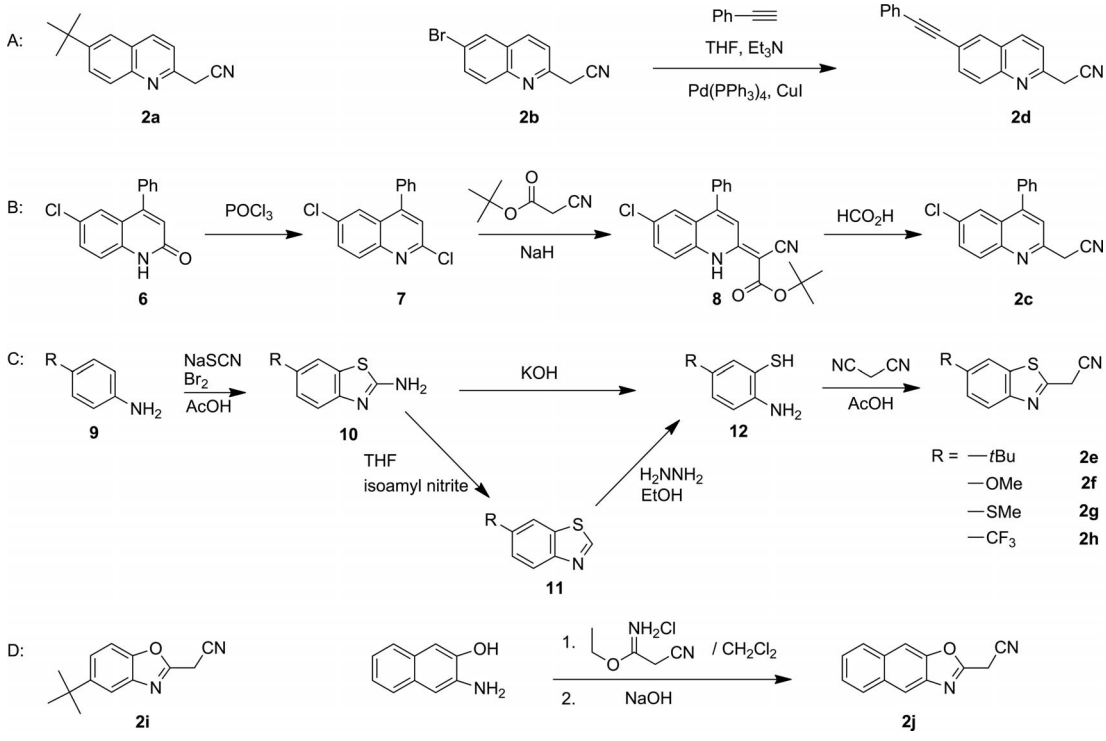



Scheme 1. Reagents and conditions (A = aromatic heterocycle): (a) anhydrous toluene (xylene)/$POCl_3$, reflux; (b) $CH_2Cl_2$/diisopropylethylamine, $BF_3$·$Et_2O$, reflux; (c) toluene/diisopropylethylamine, chlorodiphenylborane, reflux.

## Results and Discussion

### Synthesis

The reaction pathway for PPCy formation is depicted in Scheme 1. As shown in earlier work, *para*-octyloxy-substituted DPP **1** was used to enhance the solubility of both reactants and products.[4,6] The HAAs **2** were synthesized according to different strategies (Scheme 2). The 6-*tert*-butyl- and the 6-bromo-substituted quinoline derivatives **2a** and **2b**, respectively, were synthesized by chlorination of the quinaldine and subsequent Kolbe nitrile reaction (Scheme 2, route A).[4b,6] Derivative **2b** was further modified by introducing phenylacetylene at the 6-position by Sonogashira coupling of **2b** and phenylacetylene, affording **2d** in 88% yield. The (6-chloro-4-phenylquinolinyl)acetonitrile **2c** was synthesized by starting from quinolone **6** (Scheme 2, route B).[7] Compound **6** was chlorinated with $POCl_3$ to give 2-chloroquinoline **7**,[7] which was further treated with the sodium salt of *tert*-butyl cyanoacetate to yield **8** in 88% yield. Saponification of **8** with formic acid and decarboxylation led to **2c** in 84% yield.[8] Alternatively, **2c** could also be obtained in high yields from **8** by thermal elimination of isobutene and decarboxylation in vacuo. The benzothiazole HAAs **2e**–**h** were synthesized by starting from *para*-substituted aniline derivatives **9** (Scheme 2, route C). In the first step, the anilines were converted into the corresponding 2-aminobenzothiazoles **10** by rhodanation. Subsequent opening of the thiazol rings yielded the 2-aminothiophenol derivatives **12**. The *tert*-butyl and the




Scheme 2. Synthetic routes for heteroaromatic acetonitriles **2** (HAA).

methoxy derivatives **10e**[4b] and **10f**[9] were opened by heating in the presence of potassium hydroxide. The thiomethyl and the trifluoromethyl derivatives **12g** and **12h** were synthesized in two steps by a milder method that allowed the inclusion of more functionalities and gave higher yields. For this purpose, the 2-aminobenzothiazoles **10** were deaminated with isoamyl nitrite in tetrahydrofuran (THF), yielding the benzothiazoles **11**, which were subsequently treated with hydrazine monohydrate in ethanol and led to 2-aminothiophenols **12**.[10] Acidic condensation of malononitrile with the 2-aminothiophenols **12e**–**h** yielded the corresponding benzothiazole HAAs **2e**–**h**. The benzoxazole and the naphthoxazole derivatives **2i** and **2j** were synthesized by treating the 2-aminophenols with ethyl 2-cyanoacetimidate hydrochloride[11] in dichloromethane. Subsequent treatment with sodium hydroxide solution afforded the oxazole HAAs (Scheme 2, route D).

The H-PPCys **3** were prepared as previously described by condensation of DPP **1** and HAA **2** in the presence of $POCl_3$.[4] The derivatives **3b**, **3c**, and **3j** are almost insoluble in solvents such as chloroform or toluene and were therefore used for the complexation reactions without further purification. The other H-PPCys were purified by column chromatography. The $BF_2$-PPCys **4** and the $BPh_2$-PPCys **5** were synthesized according to previously described procedures.[4] With the exception of **4d**, the boron derivatives were much more soluble and could therefore be purified by column chromatography more easily than the H-chelates **3**.

Table 1. Spectroscopic data of the first electronic transition ($S_0 \leftrightarrow S_1$) of the H-PPCys **3**, $BF_2$-PPCys **4** and $BPh_2$-PPCys **5**.[a]

| PPCy | $\lambda_{00}^{A}$ [nm] | $\varepsilon_{00}$ [$M^{-1}\,cm^{-1}$] | $f$ | $\lambda_{00}^{F}$ [nm] | $\Delta\tilde{\nu}_{A-F}$ [$cm^{-1}$] | $\Phi_F$ |
|---|---|---|---|---|---|---|
| **3a** | 731 | 118000 | 0.71 | – | – | – |
| **3b** | 734 | _[b] | _[b] | – | – | – |
| **3c** | 737 | _[b] | _[b] | – | – | – |
| **3d** | 752 | 166000 | 0.91 | – | – | – |
| **3e** | 735 | 115000 | 0.74 | – | – | – |
| **3f** | 746 | 106000 | 0.71 | – | – | – |
| **3g** | 751 | 116000 | 0.77 | – | – | – |
| **3h** | 726 | 130000 | 0.73 | – | – | – |
| **3i** | 711 | 98000 | 0.65 | – | – | – |
| **3j** | 721 | _[b] | _[b] | – | – | – |
| **4a** | 754 | 205000 | 0.83 | 772 | 250 | 0.59 |
| **4b** | 761 | 229000 | 0.85 | 775 | 250 | 0.49 |
| **4c** | 767 | 237000 | 0.92 | 781 | 250 | 0.50 |
| **4d** | 778 | 284000 | 1.0 | 791 | 250 | 0.45 |
| **4e** | 732 | 190000 | 0.82 | 749 | 300 | 0.69 |
| **4f** | 745 | 171000 | 0.80 | 763 | 300 | 0.32 |
| **4g** | 753 | 165000 | 0.85 | 773 | 350 | 0.28 |
| **4h** | 719 | 175000 | 0.74 | 738 | 350 | 0.62 |
| **4i** | 690 | 135000 | 0.73 | 712 | 500 | 0.57 |
| **4j** | 699 | 157000 | 0.76 | 720 | 400 | 0.35 |
| **5a** | 819 | 256000 | 0.76 | 831 | 150 | 0.53 |
| **5b** | 827 | 280000 | 0.78 | 837 | 150 | 0.52 |
| **5c** | 832 | 293000 | 0.82 | 843 | 150 | 0.56 |
| **5d** | 843 | 309000 | 0.91 | 855 | 150 | 0.36 |
| **5e** | 790 | 221000 | 0.76 | 803 | 200 | 0.48 |
| **5f** | 803 | 200000 | 0.76 | 817 | 200 | 0.25 |
| **5g** | 808 | 196000 | 0.82 | 827 | 250 | 0.26 |
| **5h** | 776 | 238000 | 0.74 | 785 | 150 | 0.60 |
| **5i** | 747 | 164000 | 0.73 | 762 | 250 | 0.54 |
| **5j** | 759 | 196000 | 0.79 | 771 | 200 | 0.31 |

[a] Conditions: chloroform, room temperature. $\lambda_{00}^{A}$: absorption wavelength; $\varepsilon_{00}$: molar decadic absorption coefficient; $f$: oscillator strength; $\lambda_{00}^{F}$: fluorescence wavelength; $\Delta\tilde{\nu}_{A-F}$: Stokes shift; $\Phi_F$: fluorescence quantum yield. [b] Not determined.

## Spectroscopic Properties

The 4-octyloxy-DPP **1** and ten different HAAs, namely, four quinoline (**2a**–**d**), four benzothiazole (**2e**–**h**), and two oxazole derivatives (**2i** and **2k**), were used as starting materials. From these, ten H-PPCys **3** and their $BF_2$ and $BPh_2$ complexes **4** and **5**, respectively, were synthesized. Their absorption and fluorescence emission were recorded in chloroform solutions at room temperature, and the spectroscopic data of the longest-wavelength electronic transition of **3**, **4**, and **5** are summarized in Table 1.

In general, within the series of **3**, **4** and **5** with the same HAA **2**, the same trends already described were observed upon complexation; sharpening of the vibronic bands, increase of the $S_0 \rightarrow S_1$ transition moment, and a significant shift of the Franck–Condon factors in favor of the 00 transition. The difference between the absorption maxima of $BF_2$-PPCys **4** and $BPh_2$-PPCys **5** remains almost constant ($1050 \pm 100\,cm^{-1}$) even in the case of +M substituents at the heteroaromatic moiety. This demonstrates that the influence of the $BF_2$ and the $BPh_2$ moieties is mainly σ-inductive.[4]

Within the series of $BF_2$-PPCys **4** and $BPh_2$-PPCys **5**, the absorptions of the dyes exhibit similar bandshapes and fluorescence with high quantum yields. The Stokes shifts are generally small, which suggests that, upon $S_0 \rightarrow S_1$ excitation, the molecular geometry changes only slightly. Absorption and fluorescence spectra of all derivatives **4** and **5** are given in the Supporting Information. The trends within the different series are discussed below.

Within the series of quinoline derivatives (Figure 1a), the absorption maximum is shifted bathochromically in the order: 6-*tert*-butyl (**4a/5a**), 6-bromo (**4b/5b**), 6-chloro-4-phenyl (**4c/5c**), and 6-(phenylethynyl) (**4d/5d**). In the same order, the intensity of the first electronic transition ($\varepsilon_{00}$ and $f$) increases, for example, from **4a** ($\varepsilon_{00} = 205000\,M^{-1}\,cm^{-1}$, $f = 0.83$) to **4d** ($\varepsilon_{00} = 284000\,M^{-1}\,cm^{-1}$, $f = 1.00$). The halfwidth of the 00 bands (**4a**–**d**: $500 \pm 20\,cm^{-1}$; **5a**–**d**: $420 \pm 10\,cm^{-1}$) and the ratio of the intensity of the vibronic band $\varepsilon_{01}/\varepsilon_{00}$ (**4a**–**d**: $0.22 \pm 0.01$; **5a**–**d**: $0.13 \pm 0.01$) remains almost constant. By replacing the *tert*-butyl group, which has only an inductive effect, by bromine or chlorine, which have +M effects, the chromophoric system is extended. Therefore, the resulting compounds have a higher transition dipole moment. Compounds **4c/5c** bear a phenyl group in the 4-position as a second conjugating substituent, which can explain the more intense transition compared with those of **4b/5b**. The phenylethynyl moiety in **4d/5d** extends the π-system considerably, leading to a significant increase of $\varepsilon_{00}$ and $f$ values compared with those of **4a/5a**.

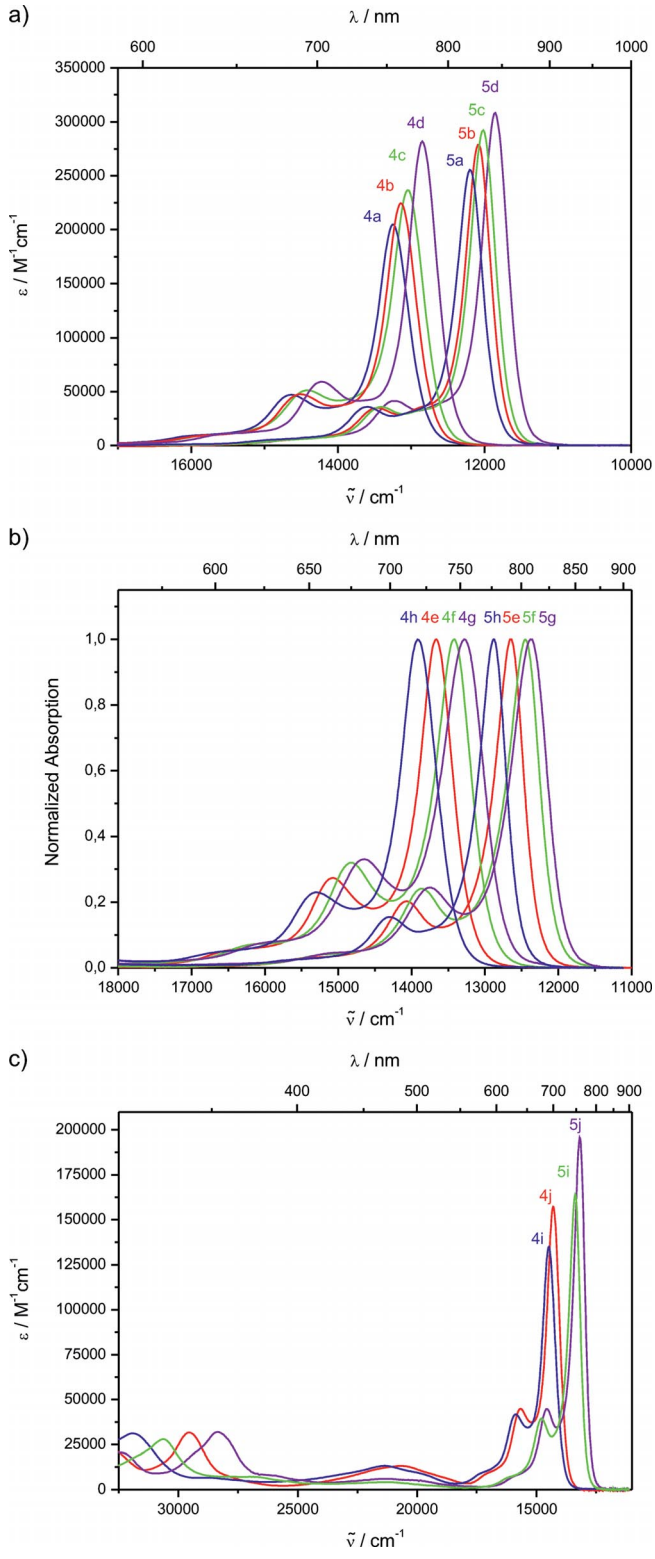



Figure 1. Absorption of the PPCy dyes in chloroform at room temperature: (a) quinoline derivatives, (b) benzothiazole derivatives, (c) benzoxazole and naphthoxazole derivatives.

Within the benzothiazole series (Figure 1b), substitution of the 6-*tert*-butyl group (**4e/5e**) by the +M substituents MeO (**4f/5f**) and MeS (**4g/5g**) leads to a bathochromic shift of the absorption. The shift is accompanied by a decrease in the $\varepsilon_{00}$ value but an increase in the oscillator strength. In contrast, substitution of the *tert*-butyl group by the strongly –I-effective trifluoromethyl group (**4h/5h**) leads to a hypsochromic shift, a slight change in $\varepsilon_{00}$ and a small decrease of *f*. The halfwidths of the 00 bands of **4e/5e** and **4h/5h** are equal, whereas those of **4f/5f** and **4g/5g** are larger. The Franck–Condon factors are shifted in favor of the 00 transition for the $CF_3$ derivatives, whereas for the MeO and MeS derivatives they are strongly shifted in favor of the 01 transition ($\varepsilon_{01}/\varepsilon_{00}$ for **4e**: 0.27; **4f**: 0.32; **4g**: 0.33; **4h**: 0.23; **5e**: 0.20; **5f**: 0.24; **5g**: 0.25; **5h**: 0.15). Compared with the benzothiazole derivatives that have only I substituents, the quantum yields of the MeO and MeS derivatives are approximately halved. These findings can be explained by a steeper potential surface for the $CF_3$ and a smoother one for the MeO and MeS compounds compared with the *tert*-butyl derivatives. The higher oscillator strengths of the MeO and, especially, of the MeS derivatives compared with the other benzothiazole PPCys can be explained by higher transition dipole moments due to an extension of the π-systems onto the substituents.

Expanding the π-system of benzoxazole PPCys (**4i/5i**) by benzannulation to naphthoxazol PPCys **4j/5j** led to a slight bathochromic shift of 200 $cm^{-1}$ and a more intense transition ($BF_2$: *f* +5% and $\varepsilon_{00}$ +16%; $BPh_2$: *f* +8% and $\varepsilon_{00}$ +20%). The absorption spectra are depicted in Figure 1c. Whereas the halfwidths remain constant, the Franck–Condon factors are slightly shifted in favor of the 00 transition, which is readily explained by the extension of the chromophoric system ($\varepsilon_{01}/\varepsilon_{00}$ for **4i**: 0.31; **4j**: 0.28; **5i**: 0.24; **5j**: 0.23). The benzannulation led to a higher transition dipole moment, but also led to a decrease in the quantum yields of about 40%.

It is instructive to compare the linewidths of the purely electronic 00 bands between absorption and emission spectra (Figure 2). The main factor influencing the linewidth of the bands is the potential function of the torsional vibration of the heteroaromatic terminal groups. Vibrations of this type have previously been assumed to represent a major relaxation pathway in PPCys.[4a] This interpretation is supported by the finding that the linewidths of the $BF_2$-PPCys are always broader than those of the respective $BPh_2$-PPCys compounds. Due to the steric hindrance of the $BPh_2$ groups, the potentials are stiffer, which leads to narrower bands and – because the oscillator strengths are almost unaffected – to higher extinction coefficients of the $BPh_2$-PPCys. The linewidths of the 00 bands in absorption are always smaller than in emission. This is particularly true for the $BF_2$-PPCys **4e**, **4h**, **4i**, and **4j**. We ascribe the broader lines in emission to the fact that the torsional potentials are stiffer in the ground than in the excited state.

A variety of influences on the fluorescence quantum yields can be described. No significant difference in quantum yields is observed for the quinoline-, benzothiazole-, and benzoxazole-substituted derivatives. Only naphthoxazole as a terminal group led to a significant decrease. The fluorescence quantum yields of the quinoline-containing compounds **4a/5a**, **4b/5b**, and **4c/5c** are similar, indicat-

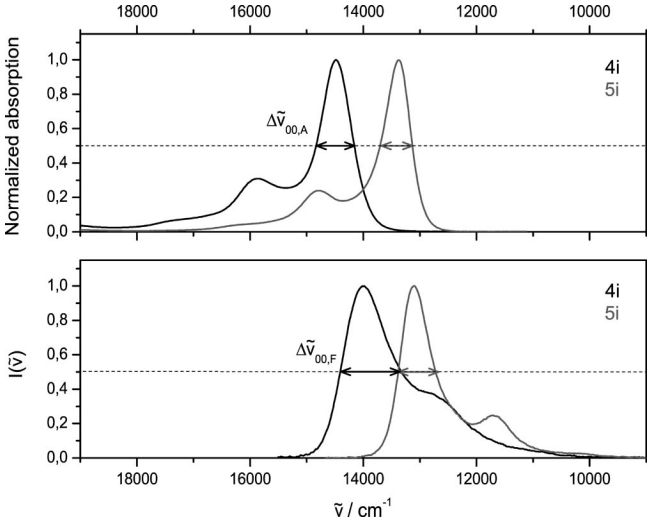



Figure 2. Absorption and fluorescence emission spectra of $BF_2$-PPCy **4i** and $BPh_2$-PPCy **5i**. The respective linewidths for the absorption are $\Delta\tilde{\nu}_{00,A}$(**4i**) = 673 $cm^{-1}$ and $\Delta\tilde{\nu}_{00,A}$(**5i**) = 573 $cm^{-1}$. The corresponding values for the emission are $\Delta\tilde{\nu}_{00,F}$(**4i**) = 1079 $cm^{-1}$ and $\tilde{\nu}_{00,F}$(**5i**) = 663 $cm^{-1}$.

ing that substitution on the quinoline moiety has little influence. However, a pronounced decrease was seen for the phenylethynyl derivatives **4d**/**5d**. For the benzothiazole-containing PPCys, no influence on the quantum yield was observed for compounds with 6-(trifluoromethyl) or 6-*tert*-butyl substitution. In contrast, substitution by π-donors, such as methoxy, thiomethyl, and phenylethynyl groups, led to a significant decrease in the fluorescence quantum yield. No clear trend can be seen when the quantum yields for the $BF_2$-PPCys and their $BPh_2$-PPCys counterparts are compared. We interpret this as a result of two counteracting influences; because torsional vibrations are seen as the main cause of radiationless deactivation, a stiffer torsional potential – as observed for the $BPh_2$-PPCys compared to the $BF_2$-PPCys – will lead to higher fluorescence quantum yield. The bathochromic shift for the $BPh_2$-PPCys with respect to the corresponding $BF_2$-PPCys will, however, lead to lower quantum yields because of better radiationless deactivation, according to the energy gap law. As a result, an increase or a decrease in the quantum yields upon replacing the fluorine atoms by phenyl groups will occur, depending on which of the two effects dominates.

## Conclusions

Many of the applications of NIR chromophores require dyes with very specific spectral properties. For such fine-tuning of the optical properties, we synthesized PPCys with a variety of substituted heteroaromatics as end groups of the chromophoric system. By using this approach, a broad range of stable, highly fluorescing NIR dyes with high absorptivities between 690 and 845 nm is now available. Shorter-wavelength-absorbing PPCys can be obtained with monocyclic aza aromatics (pyridine, pyrimidines, pyrazine, or triazines), longer-wavelength-absorbing PPCys are accessible with aza-aromatics having an extended π-system. Further tuning of the optical properties can be achieved by asymmetric substitution;[6] extension of both absorption and emission up to and even beyond 1000 nm is attainable by variation of the heterocycles used for bis-PPCy syntheses.[12]

## Experimental Section

**General:** Solvents were purified and dried according to standard procedures. All commercially available reagents were used without further purification unless otherwise noted. Column chromatography was performed on Roth silica gel 60 (40–63 μm). All solvents used for UV/Vis/NIR and fluorescence measurements were spectroscopic grade and were purchased from Fluka. NMR spectra were recorded with a Bruker Avance III-400 (400 MHz) or a Bruker Avance III-600 (600 MHz) spectrometer. The residual solvent peak was used as internal reference ($CHCl_3$: $\delta$ = 7.24 ppm; $C_2DHCl_4$: $\delta$ = 5.91 ppm). For $^1$H NMR, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet) and coupling constants are reported whenever possible. Structure and numbering of the atoms for the assignment of the resonances are depicted in the Supporting Information. MALDI-TOF mass spectra were recorded with a Bruker Biflex III instrument in reflection mode or a Bruker microflex; 2,5-dihydroxybenzoic acid (DHB) was used as matrix. Elemental analysis was performed with a CHN analyser Vario EL from Elementar. Absorption and emission spectra were recorded at ambient temperature by using 1 cm quartz cuvettes (3 mL). UV/Vis/NIR absorptions were recorded with a Varian spectrometer, model Cary 50; the spectra were processed with Spekwin to calculate the oscillator strength.[13] Fluorescence spectra were recorded with a self-assembled NIR fluorescence spectrometer with a nitrogen-cooled Ge diode (Northcoast) as detector. Either a diode laser (804 nm, 30 mW, model ACM30/1476 or 690 nm, 19 mW, model ACM19/1203) or an He–Ne laser (632.8 nm, 5 mW, Spectra Physics model 105-1) were used for excitation. $BF_2$-PPCy (**4a**) ($\Phi_F$ = 0.59 in $CHCl_3$) and $BPh_2$-PPCy (**5a**) ($\Phi_F$ = 0.53 in $CHCl_3$) were used as references to determine the quantum yield.[4] Synthesis and physical data of the reactants **1**, **2a**, **2e**, **2i**, $BPh_2Cl$,[4] and **2b**[6] have already been published.

***tert*-Butyl (2*Z*)-2-[6-Chloro-4-phenylquinolin-2(1*H*)-ylidene]-2-cyanoacetate (8):**[8] To a solution of *tert*-butyl 2-cyanoacetate (141.17 g, 150 mmol) and sodium *tert*-butoxide (96.1 g, 150 mmol) in DMF (60 mL), **7**[7] (13.7 g, 50 mmol) was added. After stirring at 105 °C for 3 h, the solution was cooled, DMF was removed under reduced pressure, and a mixture of water (50 mL) and acetic acid (2 mL) was added. The resulting solid was filtered, washed two times with MeOH and filtered to give **8** (16.7 g, 44.0 mmol, 88%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 13.52 (s, 1 H, NH), 8.02 (d, $^3J$ = 9.0 Hz, 1 H, 8-H), 7.84 (d, $^4J$ = 2.3 Hz, 1 H, 5-H), 7.68 (dd, $^3J$ = 9.0, $^4J$ = 2.3 Hz, 1 H, 7-H), 7.50 (m, 5 H, PhH), 7.37 (s, 1 H, 3-H), 1.57 (s, 9 H, *t*Bu) ppm.

**(6-Chloro-4-phenylquinolin-2-yl)acetonitrile (2c):**[8] A solution of **8** (5.00 g, 13.19 mmol) in formic acid (140 mL) was stirred at 45 °C for 1.5 h. The mixture was poured into an ice/ammonia solution, and the resulting yellow solid was filtered and dried. Yield: 3.1 g (11.1 mmol, 84%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.04 (d, $^3J$ = 9.0 Hz, 1 H, 8-H), 7.86 (d, $^4J$ = 2.3 Hz, 1 H, 5-H), 7.67 (dd, $^3J$ = 9.0, $^4J$ = 2.3 Hz, 1 H, 7-H), 7.54 (m, 3 H, PhH), 7.46 (m, 3 H, Ph, 3-H), 4.11 (s, 2 H, $CH_2$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 150.60, 149.90, 147.03, 136.93, 133.42, 131.33, 131.32, 129.57, 129.33, 129.15, 126.80, 124.92, 120.88, 116.94, 27.57 ppm.

**[6-(Phenylethynyl)quinolin-2-yl]acetonitrile (2d):** Compound **2b** (644 mg, 2.6 mmol) and phenylacetylene (850 mg, 8.32 mmol) were dissolved in abs. THF (15 mL) and triethylamine (6 mL). The mixture was degassed, and tetrakis(triphenylphosphane)palladium(0) (150 mg, 0.13 mmol) and CuI (25 mg, 0.13 mmol) were added. The mixture was heated to 60 °C overnight, cooled, added to $CH_2Cl_2$ (200 mL) and washed with $H_2O$ (250 mL), 1 M HCl (250 mL) and again with $H_2O$ (2×). The organic layer was dried with $MgSO_4$, and the solvent was removed. Column chromatography ($CH_2Cl_2$ → $CH_2Cl_2$/ethyl acetate, 20:1) yielded **2d** (615 mg, 2.29 mmol, 88%) as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.23 (d, $^3J$ = 8.5 Hz, 1 H, 4-H), 8.09 (d, $^3J$ = 8.8 Hz, 1 H, 8-H), 8.03 (d, $^4J$ = 1.7 Hz, 1 H, 5-H), 7.86 (dd, $^3J$ = 8.8, $^4J$ = 1.7 Hz, 1 H, 7-H), 7.57 (m, 3 H, 3-H, Ph), 7.37 (m, 3 H, Ph), 4.19 (s, 2 H, $CH_2$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 151.17, 147.12, 137.77, 133.34, 131.91, 130.97, 129.17, 128.91, 128.65, 127.17, 122.95, 122.53, 120.56, 116.83, 91.46, 88.82, 27.44 ppm.

**(6-Methoxybenzothiazol-2-yl)acetonitrile (2f):** 2-Amino-5-methoxythiophenol (**12f**; 5.9 g, 38 mmol),[9] malononitrile (2.5 g, 38 mmol), and glacial acetic acid (5 mL) were heated to reflux in acetonitrile (30 mL) for 10 h. The acetonitrile was removed. Column chromatography (petroleum ether/ethyl acetate, 2:1) yielded **2f** (1.5 g, 7.4 mmol, 20%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.89 (d, $^3J$ = 9.0 Hz, 1 H, 4-H), 7.31 (d, $^4J$ = 2.5 Hz, 1 H, 7-H), 7.09 (dd, $^3J$ = 9.0, $^4J$ = 2.5 Hz, 1 H, 5-H), 4.17 (s, 2 H, $CH_2$), 3.87 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 158.47, 155.49, 147.55, 137.14, 124.10, 116.40, 115.19, 104.29, 56.06, 23.28 ppm.

**[6-(Methylthio)benzothiazol-2-yl]acetonitrile (2g):** 2-Amino-5-(methylthio)benzenethiol (**12g**; 1.78 g, 10.4 mmol)[10] and malononitrile (687 mg, 10.4 mmol) were stirred in a mixture of glacial acetic acid (6 mL) and ethanol (10 mL) at room temperature for 2 d. The mixture was added to water (250 mL) and extracted with $CH_2Cl_2$. The combined organic layers were washed with water, dried with $MgSO_4$, and the solvent was removed. Column chromatography (petroleum ether/ethyl acetate, 4:1) yielded **2g** (1.54 g, 7 mmol, 67%) as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.90 (dd, $^3J$ = 8.9, $^5J$ = 0.6 Hz, 1 H, 4-H), 7.70 (dd, $^4J$ = 1.9, $^5J$ = 0.6 Hz, 1 H, 7-H), 7.40 (dd, $^3J$ = 8.6, $^4J$ = 1.9 Hz, 1 H, 5-H), 4.19 (s, 2 H, $CH_2$), 2.54 (s, 3 H, $CH_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 157.31, 150.91, 137.55, 136.38, 126.36, 123.56, 118.80, 115.00, 23.37, 16.57 ppm.

**6-(Trifluoromethyl)benzothiazole (11h):** Isoamyl nitrite (4.57 g, 39 mmol) was slowly added to a stirred solution of 6-(trifluoromethyl)benzothiazol-2-amine (**10h**; 3.86 g, 17.7 mmol)[14] in abs. THF (30 mL). The mixture was heated to reflux for 30 min, quenched with water, and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried with $MgSO_4$, and the solvent was removed. Column chromatography ($CH_2Cl_2$/petroleum ether, 6:1) yielded **11h** (1.67 g, 8.2 mmol, 46%) as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.13 (s, 1 H, 2-H), 8.25 (m, 1 H, 7-H), 8.21 (m, 1 H, 4-H), 7.74 (m, 1 H, 5-H) ppm.

**2-Amino-5-(trifluoromethyl)benzenethiol (12h):** A solution of **11h** (1.67 g, 8.2 mmol) and hydrazine monohydrate (3.08 g, 62 mmol) in ethanol (20 mL) was heated to reflux for 1.5 h. The mixture was added to a solution of acetic acid (6 mL) in water (200 mL) and extracted with $CH_2Cl_2$. The combined organic layers were washed with water and dried with $MgSO_4$. Removal of the solvent yielded **12h** (1.3 g, 7.18 mmol, 88%) as a yellow oil, which was used without further purification. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.61 (d, $^4J$ = 1.6 Hz, 1 H, 6-H), 7.31 (dd, $^3J$ = 8.5, $^4J$ = 1.6 Hz, 1 H, 4-H), 6.73 (d, $^3J$ = 8.5 Hz, 1 H, 3-H), 4.48 (s, 2 H, $NH_2$), 2.93 (s, 1 H, SH) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 150.47, 132.62 (q, $^3J$ = 4.0 Hz), 126.60 (q, $^3J$ = 3.7 Hz), 124.48 (q, $^1J$ = 271 Hz), 120.6 (q, $^2J$ = 33.4 Hz), 114.42, 111.50 ppm.

**[6-(Trifluoromethyl)benzothiazol-2-yl]acetonitrile (2h):** Compound **12h** (1.36 g, 7.18 mmol) and malononitrile (452 mg, 7.5 mmol) were stirred in a mixture of glacial acetic acid (6 mL) and ethanol (10 mL) at room temperature for 5 d. The mixture was added to water (250 mL) and extracted with $CH_2Cl_2$. The combined organic layers were washed with water, dried with $MgSO_4$, and the solvent was removed. Column chromatography ($CH_2Cl_2$) yielded **2h** (674 mg, 2.8 mmol, 39%) as a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.19 (m, 1 H, 7-H), 8.13 (m, 1 H, 4-H), 7.75 (m, 1 H, 5-H), 4.26 (s, 2 H, $CH_2$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.79, 155.01, 135.82, 128.58 (q, $^2J$ = 32.7 Hz), 124.18, 124.12 (q, $^1J$ = 273 Hz), 124.02 (q, $^3J$ = 3.5 Hz), 119.73 (q, $^3J$ = 4.4 Hz), 114.60, 23.66 ppm.

**2-(Naphtho[2,3-*d*]oxazol-2-yl)acetonitrile (2j):** 2-Aminonaphthol (1 g, 6.3 mmol; Sigma–Aldrich) and ethyl 2-cyanoacetimidate hydrochloride (983 mg, 6.6 mmol)[11] were heated to reflux in anhydrous $CH_2Cl_2$ (25 mL) for 60 h. The reaction mixture was diluted with $CH_2Cl_2$ (25 mL) and washed twice with NaOH solution (10%). The organic layer was dried with $MgSO_4$. Removal of the solvent yielded **2j** (1.06 g, 5.1 mmol, 81%) as a grey solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 8.18 (s, 1 H), 7.98 (m, 2 H), 7.93 (s, 1 H), 7.51 (m, 2 H), 4.15 (s, 2 H, $CH_2$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 157.82, 150.00, 140.52, 132.07, 131.64, 128.91, 128.25, 126.37, 125.43, 118.43, 113.03, 107.14, 19.42 ppm.

**General Procedure for the Synthesis of H–PPCy Dyes 3:** DPP **1** (1 mmol) and heteroarylacetonitrile **3** (2.5 mmol) were heated to reflux in either anhydrous toluene or xylene (30 mL) under nitrogen. Phosphoryl chloride (8 mmol) was then added. The reaction was monitored by UV/Vis/NIR spectroscopic analysis and thin-layer chromatography. As soon as either **1** was used up or the concentration of the short-wavelength-absorbing by-products increased, the reaction was stopped. The solvent and excess phosphoryl chloride were removed under vacuum, the crude product was treated with methanol in an ultrasonic bath, and water was added until a solid precipitated. The solid was collected by filtration and washed with methanol until the filtrate became colorless. If sufficiently soluble, the remaining solid was purified by column chromatography. Synthesis and physical data of **3a**, **3e**, and **3i** have been reported previously.[4]

**Compound 3b:** The solubility of **3b** in common solvents was too low to allow purification by chromatography. The crude product was digested in acetone, collected by filtration and washed with acetone. Drying in air yielded **3b**, which was pure enough to perform further reactions. $^1$H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): $\delta$ = 14.42 (s, 2 H, NH), 7.96 (d, $^3J$ = 8.8 Hz, 2 H, 4-H), 7.90 (s, 2 H, 5-H), 7.77 (m, 8 H, AA′, 7-H, 8-H), 7.66 (d, $^3J$ = 8.8 Hz, 2 H, 3-H), 7.19 (m, 4 H, XX′), 4.16 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.90 (m, 4 H, $OCH_2CH_2$), 1.42 [m, 4 H, $O(CH_2)_2CH_2$], 1.5–1.3 (m, 16 H, alkyl), 0.95 (m, 6 H, $CH_3$) ppm. MALDI-MS: calcd. for $C_{56}H_{54}Br_2N_6O_2$ + 1 $[M + H]^+$ 1003.3; found 1003.9.

**Compound 3c:** The solubility of **3c** in common solvents was too low to allow purification by chromatography. The crude product was digested in acetone, collected by filtration and washed with acetone. Drying in air yielded **3c**, which was pure enough to perform further reactions. MALDI-MS: calcd. for $C_{68}H_{62}Cl_2N_6O_2$ + 1 $[M + H]^+$ 1065.4; found 1065.7.

**Compound 3d:** Column chromatography ($CH_2Cl_2$) afforded **3d** as a dark-green crystalline powder in 54% yield. $^1$H NMR (400 MHz,

$C_2D_2Cl_4$): $\delta$ = 14.45 (s, 2 H, NH), 7.84 (d, $^3J$ = 8.9 Hz, 2 H, 4-H), 7.76 (d, $^4J$ = 1.7 Hz, 2 H, 5-H), 7.67 (m, 4 H, AA′), 7.61 (dd, $^3J$ = 8.8, $^4J$ = 1.7 Hz, 2 H, 7-H), 7.57 (d, $^3J$ = 8.9 Hz, 2 H, 3-H), 7.53 (d, $^3J$ = 8.8 Hz, 2 H, 8-H), 7.41 (m, 4 H, PhH), 7.24 (m, 6 H, PhH), 7.13 (m, 4 H, XX′), 4.07 (t, $^3J$ = 6.4 Hz, 4 H, $OCH_2$), 1.82 (m, 4 H, $OCH_2CH_2$), 1.47 [m, 4 H, $O(CH_2)_2CH_2$], 1.4–1.2 (m, 16 H, alkyl), 0.85 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 752 (166000), 681 (59000 $M^{-1}cm^{-1}$) nm. $C_{72}H_{64}N_6O_2$ (1045.34): calcd. C 82.73, H 6.17, N 8.04; found C 82.41, H 6.08, N 8.01.

**Compound 3f:** Column chromatography ($CH_2Cl_2$ to $CH_2Cl_2$/ethyl acetate, 50:1) afforded **3f** as a green crystalline powder in 19% yield. $^1$H NMR (600 MHz, $C_2D_2Cl_4$, 100 °C): $\delta$ = 7.70 (m, 4 H, AA′), 7.68 (d, $^3J$ = 8.8 Hz, 2 H, 4-H), 7.29 (d, $^4J$ = 2.1 Hz, 2 H, 7-H), 7.12 (m, 4 H, XX′), 7.03 (dd, $^3J$ = 8.8, $^4J$ = 2.1 Hz, 2 H, 5-H), 4.10 (t, $^3J$ = 6.4 Hz, 4 H, $OCH_2$), 3.85 (s, 6 H, $OCH_3$), 1.84 (m, 4 H, $OCH_2CH_2$), 1.51 [m, 4 H, $O(CH_2)_2CH_2$], 1.45–1.25 (m, 16 H, alkyl), 0.91 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 746 (106000), 676 (48000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{54}H_{57}N_6O_4S_2$ [M + H]$^+$ 917.4; found 916.3. $C_{54}H_{56}N_6O_4S_2$ (917.19): calcd. C 70.71, H 6.15, N 9.16, S 6.99; found C 70.57, H 6.18, N 9.00, S 7.09.

**Compound 3g:** Column chromatography ($CH_2Cl_2$ → $CH_2Cl_2$/ethyl acetate, 100:1) afforded **3g** as a green crystalline powder in 16% yield. $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 12.93 (s, 2 H, NH), 7.64 (m, 6 H, 4-H, AA′), 7.55 (d, $^4J$ = 1.7 Hz, 2 H, 7-H), 7.28 (dd, $^3J$ = 8.5, $^4J$ = 1.7 Hz, 2 H, 5-H), 7.08 (m, 4 H, XX′), 4.02 (t, $^3J$ = 6.4 Hz, 4 H, $OCH_2$), 2.48 (s, 6 H, $SCH_3$), 1.78 (m, 4 H, $OCH_2CH_2$), 1.43 [m, 4 H, $O(CH_2)_2CH_2$], 1.37–1.15 (m, 16 H, alkyl), 0.84 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 751 (116000), 681 (52000 $M^{-1}cm^{-1}$) nm. $C_{54}H_{56}N_6O_2S_4$ (949.32): calcd. C 68.32, H 5.95, N 8.85, S 13.51; found C 67.95, H 5.81, N 9.00, S 13.57.

**Compound 3h:** Column chromatography ($CH_2Cl_2$) afforded **3h** as a green crystalline powder in 65% yield. $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 12.91 (s, 2 H, NH), 7.89 (m, 2 H, 7-H), 7.80 (d, $^3J$ = 8.6 Hz, 2 H, 4-H), 7.92 (m, 6 H, 5-H, AA′), 7.06 (m, 4 H, XX′), 4.02 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.79 (m, 4 H, $OCH_2CH_2$), 1.44 [m, 4 H, $O(CH_2)_2CH_2$], 1.40–1.15 (m, 16 H, alkyl), 0.85 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 726 (130000), 659 (47000 $M^{-1}cm^{-1}$) nm. $C_{54}H_{50}B_2F_6N_6O_2S_2$ (1014.76): calcd. C 65.31, H 5.07, N 8.46; found C 66.43, H 5.54, N 8.86.

**Compound 3j:** The solubility of **3j** in common solvents was too low to allow purification by chromatography. The crude product was digested in acetone, collected by filtration, and washed with acetone. Drying in air yielded **3j**, which was pure enough to perform further reactions. MALDI-MS: calcd. for $C_{60}H_{56}N_6O_4$ + 1 [M + H]$^+$ 925.4; found 924.9.

**General Procedure for the Synthesis of $BF_2$–PPCy Dyes 4:** H-PPCy dye **3** (1 mmol) and *N*,*N*-di-isopropylethylamine (20 mmol) were heated to reflux in $CH_2Cl_2$ (100 mL). $BF_3{\cdot}Et_2O$ (40 mmol) was added, and the mixture was heated to reflux for 10 min. The mixture was washed with water and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by column chromatography. Synthesis and physical data of **4a**, **4e**, and **4i** have been previously reported.[4]

**Compound 4b:** The crude product was digested in methanol, collected by filtration, and washed with methanol. Drying in air gave **4b** in 74% yield (relative to the crude product **3b**). $^1$H NMR (400 MHz, $C_2D_2Cl_4$, 100 °C): $\delta$ = 8.42 (d, $^3J$ = 9.5 Hz, 2 H, 8-H), 8.01 (d, $^3J$ = 9.0 Hz, 2 H, 4-H), 7.89 (d, $^4J$ = 2.2 Hz, 2 H, 5-H), 7.77 (dd, $^3J$ = 9.5, $^4J$ = 2.2 Hz, 2 H, 7-H), 7.75 (d, $^3J$ = 9.0 Hz, 2 H, 3-H), 7.72 (m, 4 H, AA′), 7.08 (m, 4 H, XX′), 4.14 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.89 (m, 4 H, $OCH_2CH_2$), 1.56 [m, 4 H, $O(CH_2)_2CH_2$], 1.5–1.3 (m, 16 H, alkyl), 0.96 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 761 (229000), 689 (48000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{56}H_{52}B_2Br_2F_4N_6O_2$ [M + H]$^+$ 1097.3; found 1097.9. $C_{56}H_{52}B_2Br_2F_4N_6O_2$ (1098.49): calcd. C 61.23, H 4.77, N 7.65; found C 61.19, H 4.81, N 7.70.

**Compound 4c:** Column chromatography ($CH_2Cl_2$) afforded **4c** as a green crystalline powder in 34% yield (relative to the crude product **3c**). $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 8.44 (d, $^3J$ = 9.5 Hz, 2 H, 8-H), 7.68 (m, 6 H, 5-H, AA′), 7.56 (m, 2 H, 7-H), 7.55 (s, 2 H, 3-H), 7.50 (m, 6 H, Ph), 7.38 (m, 4 H, Ph), 6.99 (m, 4 H, XX′), 3.99 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.75 (m, 4 H, $OCH_2CH_2$), 1.42 [m, 4 H, $O(CH_2)_2CH_2$], 1.35–1.1 (m, 16 H, alkyl), 0.82 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 767 (237000), 693 (51000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{68}H_{60}B_2Cl_2F_4N_6O_2$ [M + H]$^+$ 1161.4; found 1161.6. $C_{68}H_{60}B_2Cl_2F_4N_6O_2$ (1161.78): calcd. C 70.30, H 5.21, N 7.23; found C 70.36, H 5.37, N 7.28.

**Compound 4d:** The crude product was digested in methanol, collected by filtration, and washed with methanol. Drying in air gave **4d** in 86% yield as a green crystalline powder. $^1$H NMR (600 MHz, $C_2D_2Cl_4$, 100 °C): $\delta$ = 8.47 (d, $^3J$ = 8.9 Hz, 2 H, 8-H), 8.01 (d, $^3J$ = 9.1 Hz, 2 H, 4-H), 7.83 (d, $^4J$ = 1.7 Hz, 2 H, 5-H), 7.74 (dd, $^3J$ = 8.9, $^4J$ = 1.7 Hz, 2 H, 7-H), 7.71 (d, $^3J$ = 9.1 Hz, 2 H, 3-H), 7.68 (m, 4 H, AA′), 7.53 (m, 4 H, Ph), 7.33 (m, 6 H, Ph), 7.05 (m, 4 H, XX′), 4.11 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.86 (m, 4 H, $OCH_2CH_2$), 1.52 [m, 4 H, $O(CH_2)_2CH_2$], 1.45–1.25 (m, 16 H, alkyl), 0.92 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 778 (284000), 703 (59000 $M^{-1}cm^{-1}$) nm. $C_{72}H_{62}B_2F_4N_6O_2$ (1140.93): calcd. C 75.80, H 5.48, N 7.37; found C 75.54, H 5.55, N 7.51.

**Compound 4f:** Column chromatography ($CH_2Cl_2$) afforded **4f** as a green crystalline powder in 63% yield. $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 7.87 (d, $^3J$ = 9.2 Hz, 2 H, 4-H), 7.64 (m, 4 H, AA′), 7.16 (d, $^4J$ = 2.4 Hz, 2 H, 7-H), 7.05 (dd, $^3J$ = 9.2, $^4J$ = 2.4 Hz, 2 H, 5-H), 7.03 (m, 4 H, XX′), 4.08 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 3.83 (s, 6 H, $OCH_3$), 1.84 (m, 4 H, $OCH_2CH_2$), 1.51 [m, 4 H, $O(CH_2)_2CH_2$], 1.45–1.25 (m, 16 H, alkyl), 0.91 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 745 (171000), 674 (54000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{54}H_{54}B_2F_4N_6O_4S_2$ 1013.4 [M + H]$^+$, 1035.4 [M + Na]$^+$; found 1013.2, 1035.2. $C_{54}H_{54}B_2F_4N_6O_4S_2$ (1012.79): calcd. C 64.04, H 5.37, N 8.30; found C 63.98, H 5.35, N 8.21.

**Compound 4g:** Column chromatography ($CH_2Cl_2$) afforded **4g** as a dark-green crystalline powder in 14% yield (relative to the crude product **3g**). $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 7.78 (d, $^3J$ = 8.8 Hz, 2 H, 4-H), 7.62 (m, 4 H, AA′), 7.49 (d, $^4J$ = 1.7 Hz, 2 H, 7-H), 7.28 (dd, $^3J$ = 8.8, $^4J$ = 1.7 Hz, 2 H, 5-H), 7.00 (m, 4 H, XX′), 4.00 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 2.46 (s, 6 H, $SCH_3$), 1.78 (m, 4 H, $OCH_2CH_2$), 1.43 [m, 4 H, $O(CH_2)_2CH_2$], 1.37–1.15 (m, 16 H, alkyl), 0.84 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 753 (165000), 683 (54000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{54}H_{54}B_2F_4N_6O_2S_4$ 1045.3 [M + H]$^+$; found 1044.8. $C_{54}H_{54}B_2F_4N_6O_2S_4$ (1044.91): calcd. C 62.07, H 5.21, N 8.04; found C 61.70, H 5.36, N 8.16.

**Compound 4h:** Column chromatography ($CH_2Cl_2$) afforded **4h** as a green crystalline powder in 79% yield. $^1$H NMR (600 MHz, $C_2D_2Cl_4$, 118 °C): $\delta$ = 8.17 (m, 2 H, 4-H), 7.98 (m, 2 H, 7-H), 7.70 (m, 2 H, 5-H), 7.67 (m, 4 H, AA′), 7.05 (m, 4 H, XX′), 4.10 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.84 (m, 4 H, $OCH_2CH_2$), 1.51 [m, 4 H, $O(CH_2)_2CH_2$], 1.45–1.15 (m, 16 H, alkyl), 0.91 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 719 (175000), 654 (40000 $M^{-1}cm^{-1}$) nm. $C_{54}H_{48}B_2F_{10}N_6O_2S_2$ (1088.73): calcd. C

59.57, H 4.44, N 7.72, S 5.89; found C 60.06, H 4.89, N 7.89, S 5.35.

**Compound 4j:** Column chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/methanol, 50:1) afforded **4j** as a green crystalline powder in 6% yield (relative to the crude product **3j**). $^1$H NMR (600 MHz, $C_2D_2Cl_4$, 100 °C): $\delta$ = 8.06 (s, 2 H, 4-H), 7.91 (m, 6 H, 5-H, 8-H, 9-H), 7.72 (m, 4 H, AA′), 7.53 (m, 4 H, 6-H, 7-H), 7.08 (m, 4 H, XX′), 4.12 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.86 (m, 4 H, $OCH_2CH_2$), 1.53 [m, 4 H, $O(CH_2)_2CH_2$], 1.45–1.3 (m, 16 H, alkyl), 0.92 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 699 (157000), 639 (45000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{60}H_{54}B_2F_4N_6O_4$ 1021.4 [M + H]$^+$, 1043.4 [M + Na]$^+$; found 1020.8, 1042.9. $C_{60}H_{54}B_2F_4N_6O_4$ (1020.74): calcd. C 70.60, H 5.33, N 8.23; found C 69.84, H 5.48, N 8.20.

**General Procedure for the Synthesis of $BPh_2$–PPCy Dyes 5:** H-PPCy **3** (1 mmol) and *N*,*N*-di-isopropylethylamine (3 mmol) were heated to reflux in toluene. Chlorodiphenylborane (4.5 mmol) was added, and the mixture was heated at reflux until the reaction was complete (UV/Vis/NIR). The mixture was washed with water and dried with $MgSO_4$. After removing the solvent, the residue was digested in methanol in an ultrasonic bath. The remaining solid was separated by filtration, washed with methanol, and purified by column chromatography. Synthesis and physical data of **5a**, **5e**, and **5i** have been previously reported.[4]

**Compound 5b:** Column chromatography ($CH_2Cl_2$) afforded **5b** as a brown crystalline powder in 94% yield (relative to the crude product **3b**). $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 7.99 (d, $^3J$ = 9.7 Hz, 2 H, 8-H), 7.65 (d, $^3J$ = 9.3 Hz, 2 H, 4-H), 7.52 (d, $^3J$ = 9.3 Hz, 2 H, 3-H), 7.48 (d, $^4J$ = 2.4 Hz, 2 H, 5-H), 7.20 (m, 8 H, PhH), 7.07 (dd, $^3J$ = 9.7, $^4J$ = 2.4 Hz, 2 H, 7-H), 7.04 (m, 12 H, PhH), 6.49 (m, 4 H, AA′), 6.04 (m, 4 H, XX′), 3.95 (t, $^3J$ = 6.7 Hz, 4 H, $OCH_2$), 1.79 (m, 4 H, $OCH_2CH_2$), 1.45 [m, 4 H, $O(CH_2)_2CH_2$], 1.4–1.1 (m, 16 H, alkyl), 0.85 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 827 (280000), 742 (35000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{80}H_{72}B_2Br_2N_6O_2$ 1329.4 [M + H]$^+$; found 1329.8. $C_{80}H_{72}B_2Br_2N_6O_2$ (1330.92): calcd. C 72.20, H 5.45, N 6.31; found C 72.09, H 5.34, N 6.28.

**Compound 5c:** Column chromatography ($CH_2Cl_2$) afforded **5c** as red-brown crystalline powder in 40% yield (relative to the crude product **3c**). $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 8.20 (d, $^3J$ = 9.7 Hz, 2 H, 8-H), 7.46 (s, 2 H, 3-H), 7.40 (m, 6 H, PhH), 7.37 (d, $^4J$ = 2.5 Hz, 2 H, 5-H), 7.26 (m, 12 H, PhH), 7.06 (m, 12 H, PhH), 6.96 (dd, $^3J$ = 9.7, $^4J$ = 2.5 Hz, 2 H, 7-H), 6.47 (m, 4 H, AA′), 6.04 (m, 4 H, XX′), 3.93 (t, $^3J$ = 6.7 Hz, 4 H, $OCH_2$), 1.78 (m, 4 H, $OCH_2CH_2$), 1.44 [m, 4 H, $O(CH_2)_2CH_2$], 1.4–1.1 (m, 16 H, alkyl), 0.85 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 832 (293000), 746 (36000 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{92}H_{80}B_2Cl_2N_6O_2$ 1394.6 [M + H]$^+$; found 1394.3. $C_{92}H_{80}B_2Cl_2N_6O_2$ (1394.21): calcd. C 79.26, H 5.78, N 6.03; found C 79.05, H 5.92, N 6.11.

**Compound 5d:** Column chromatography ($CH_2Cl_2 \rightarrow CH_2Cl_2$/ethyl acetate, 50:1) afforded **5d** as a brown crystalline powder in 42% yield (relative to the crude product **3d**). $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 8.08 (d, $^3J$ = 9.5 Hz, 2 H, 8-H), 7.71 (d, $^3J$ = 9.5 Hz, 2 H, 4-H), 7.55 (d, $^3J$ = 9.5 Hz, 2 H, 3-H), 7.51 (d, $^4J$ = 1.8 Hz, 2 H, 5-H), 7.37 (m, 4 H, PhH), 7.24 (m, 14 H, PhH), 7.12 (dd, $^3J$ = 9.5, $^4J$ = 1.8 Hz, 2 H, 7-H), 7.04 (m, 12 H, PhH), 6.51 (m, 4 H, AA′), 6.08 (m, 4 H, XX′), 3.97 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.81 (m, 4 H, $OCH_2CH_2$), 1.49 [m, 4 H, $O(CH_2)_2CH_2$], 1.42–1.2 (m, 16 H, alkyl), 0.86 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 843 (309000), 756 (42000 $M^{-1}cm^{-1}$) nm. $C_{96}H_{82}B_2N_6O_2$ (1373.36): calcd. C 83.96, H 6.02, N 6.12; found C 83.75, H 6.19, N 6.09.

**Compound 5f:** Column chromatography ($CH_2Cl_2$) afforded **5f** as a green crystalline powder in 72% yield. $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 7.13 (m, 8 H, PhH), 7.06 (m, 12 H, PhH), 6.92 (d, $^4J$ = 2.6 Hz, 2 H, 7-H), 6.78 (d, $^3J$ = 9.5 Hz, 2 H, 4-H), 6.53 (dd, $^3J$ = 9.5, $^4J$ = 2.6 Hz, 2 H, 5-H), 6.35 (m, 8 H, AA′BB′), 3.85 (t, $^3J$ = 6.7 Hz, 4 H, $OCH_2$), 3.62 (s, 6 H, $OCH_3$), 1.73 (m, 4 H, $OCH_2CH_2$), 1.41 [m, 4 H, $O(CH_2)_2CH_2$], 1.36–1.1 (m, 16 H, alkyl), 0.84 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 803 (200000), 721 (48500 $M^{-1}cm^{-1}$) nm. MALDI-MS: calcd. for $C_{78}H_{74}B_2N_6O_4S_2$ 1244.5 [M + H]$^+$, 1267.5 [M + Na]$^+$; found 1244.1, 1267.1. $C_{78}H_{74}B_2N_6O_4S_2$ (1245.22): calcd. C 75.23, H 5.99, N 6.75; found C 74.93, H 6.12, N 6.65.

**Compound 5g:** Column chromatography ($CH_2Cl_2$/petroleum ether, 3:1) afforded **5g** as an olive-green crystalline powder in 64% yield. $^1$H NMR (600 MHz, $C_2D_2Cl_4$, 118 °C): $\delta$ = 7.32 (m, 2 H, 7-H), 7.22 (m, 8 H, PhH), 7.10 (m, 12 H, PhH), 6.86 (m, 2 H, 5-H), 6.81 (m, 2 H, 4-H), 6.46 (m, 4 H, AA′), 6.42 (m, 4 H, BB′), 3.94 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 2.36 (s, 6 H, $SCH_3$), 1.78 (m, 4 H, $OCH_2CH_2$), 1.48 [m, 4 H, $O(CH_2)_2CH_2$], 145–1.15 (m, 16 H, alkyl), 0.92 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 808 (196000), 727 (48000 $M^{-1}cm^{-1}$) nm. $C_{78}H_{74}B_2N_6O_2S_4$ (1277.34): calcd. C 73.34, H 5.84, N 6.58; found C 73.18, H 5.91, N 6.58.

**Compound 5h:** Column chromatography ($CH_2Cl_2$/petroleum ether, 3:1) afforded **5h** as a dark crystalline powder in 53% yield. $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 7.73 (d, $^4J$ = 1.7 Hz, 2 H, 7-H), 7.20 (dd, $^3J$ = 9.0, $^4J$ = 1.7 Hz, 2 H, 5-H), 7.15 (m, 8 H, PhH), 7.09 (m, 12 H, PhH), 6.98 (d, $^3J$ = 9.0 Hz, 2 H, 4-H), 6.38 (m, 8 H, AA′BB′), 3.86 (t, $^3J$ = 6.7 Hz, 4 H, $OCH_2$), 1.74 (m, 4 H, $OCH_2CH_2$), 1.41 [m, 4 H, $O(CH_2)_2CH_2$], 1.35–1.15 (m, 16 H, alkyl), 0.85 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 776 (238000), 699 (37000 $M^{-1}cm^{-1}$) nm. $C_{78}H_{68}B_2F_6N_6O_2S_2$ (1321.16): calcd. C 70.91, H 5.19, N 6.36, S 4.85; found C 70.29, H 5.60, N 6.27, S 5.23.

**Compound 5j:** Column chromatography ($CH_2Cl_2$) afforded **5j** as a turquoise crystalline powder in 53% yield (relative to the crude product **3j**). $^1$H NMR (400 MHz, $C_2D_2Cl_4$): $\delta$ = 7.73 (m, 2 H, 8-H), 7.68 (s, 2 H, 9-H), 7.48 (m, 2 H, 5-H), 7.36 (m, 2 H, 7-H), 7.31 (m, 2 H, 6-H), 7.21 (m, 8 H, PhH), 7.10 (m, 12 H, PhH), 6.70 (s, 2 H, 4-H), 6.64 (m, 4 H, AA′), 6.37 (m, 4 H, XX′), 3.84 (t, $^3J$ = 6.6 Hz, 4 H, $OCH_2$), 1.72 (m, 4 H, $OCH_2CH_2$), 1.40 [m, 4 H, $O(CH_2)_2CH_2$], 1.35–1.2 (m, 16 H, alkyl), 0.86 (m, 6 H, $CH_3$) ppm. UV/Vis/NIR ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) = 759 (196000), 687 (45000 $M^{-1}cm^{-1}$) nm. $C_{84}H_{74}B_2N_6O_4$ (1253.17): calcd. C 80.51, H 5.95, N 6.71; found C 80.40, H 6.13, N 6.84.

**Supporting Information** (see footnote on the first page of this article): Absorption and fluorescence spectra of all dyes **4** and **5**.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Received: January 25, 2011
Published Online: May 24, 2011

  