

## **Asymmetric PPCs: Strongly fluorescing NIR labels**

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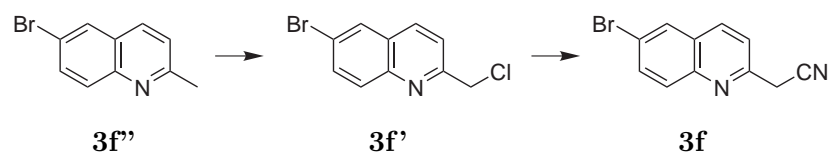
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## Experimental Section

### General

Solvents were purified 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  $\mu\text{m}$ ). All solvents used for UV/Vis/NIR and fluorescence measurements were spectroscopic grade and purchased from Fluka. NMR spectra were recorded on a 400 MHz Bruker Avance III spectrometer equipped with a BBFO probe with a Z gradient. The residual solvent peak was used as internal reference  $^1\text{H}$ : [ $\text{CHCl}_3$   $\delta = 7.24$  ppm;  $\text{C}_2\text{DHCl}_4$   $\delta = 5.91$  ppm;  $\text{DMSO-d}_5$   $\delta = 2.50$  ppm],  $^{13}\text{C}$ : [ $\text{CDCl}_3$   $\delta = 77.23$  ppm]. For  $^1\text{H}$ -NMR, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet and m = multiplet) and coupling constant(s) were reported whenever possible. Spectra were analyzed with MestreNova. MALDI-TOF mass spectra were recorded on a Bruker Biflex III instrument in positive reflection mode. 2,5-Dihydroxybenzoic acid (DHB) or  $\alpha$ -cyano-4-hydroxycinnamic acid (CHCA) were used as matrix. Elemental analyses were performed in the microanalytical lab of University of Konstanz with an CHN-analyzer Vario Micro Cube from Elementar. Absorption and emission were recorded at ambient temperature using quartz 1 cm cuvettes (3 ml). UV/Vis/NIR absorption were recorded using a Varian spectrometer, model Cary 50. The spectra were processed with Spekwin<sup>[13]</sup> to calculate the oscillator strengths. UV/Vis-fluorescence was recorded at a self assembled spectrometer with a Xe flashlight lamp as light source and a nitrogen cooled CCD camera as detector.<sup>[14]</sup> NIR-fluorescence was recorded at a self assembled NIR fluorescence spectrometer with a nitrogen cooled Ge diode (Northcoast) as detector.<sup>[15]</sup> Either a diode laser (804 nm, 30 mW, model ACM30/1476 or 690 nm, 19 mW, model ACM19/1203) or a He-Ne laser (632.8 nm, 5 mW, Spectra Physics model 105-1) were used for excitation. The  $\text{BF}_2$ -PPCy **7e** was used as reference to determine the quantum yields (QY = 0.59 in  $\text{CHCl}_3$ ).<sup>[6a]</sup>

## 2-(6-bromoquinoline-2-yl)acetonitrile (**3f**)



## 6-bromochinaldine (**3f''**)<sup>[16]</sup>

100 g (581 mmol) 4-bromoaniline were refluxed in 300 ml 6 M HCl. 51 g (727 mmol) crotonaldehyde were added over a period of 2 h and the mixture was refluxed for 1 h. For purification **3f''** was precipitated as zinc complex. Therefore, 79.2 g (581 mmol) ZnCl<sub>2</sub> were added to the hot reaction mixture which then was cooled to 0 °C. The precipitate was filtered and dried on air. The crude product was suspended in methylene chloride, filtered and washed with methylene chloride until the filtrate was colourless. The zinc complex was added to 300 ml water and 300 ml concentrated ammonia. The mixture was extracted (3x) with 200 ml methylene chloride. The combined organic layers were dried over MgSO<sub>4</sub>. Removing the solvent yielded 70.21 g (320 mmol, 55 %) **3f''** as a yellow solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 7.98 (d, <sup>3</sup>J = 8.5 Hz, 1 H; H-4), 7.93 (m, 2 H; H-5, H-8), 7.75 (dd, <sup>3</sup>J = 8.9 Hz, <sup>4</sup>J = 2.2 Hz, 1 H; H-7), 7.31 (d, <sup>3</sup>J = 8.5 Hz, 1 H; H-3), 2.75 (s, 3 H; CH<sub>3</sub>).

## 2-chloromethyl-6-bromoquinoline (**3f'**)<sup>[17]</sup>

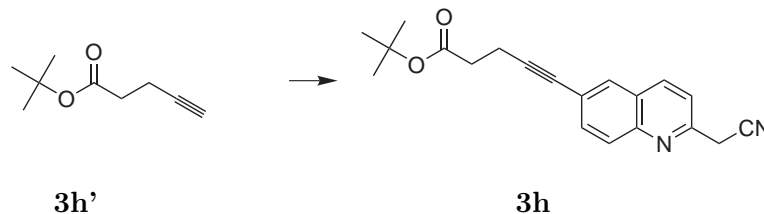
50 g (225 mmol) **3f''** were dissolved in 200 ml chloroform and 19.3 g (83 mmol) trichloroisocyanuric acid were added in portions. The mixture was heated to reflux for 1 h. Then the cyanuric acid was filtered over celite and washed with chloroform. The organic layer was washed with 0.01 M HCl and dried over MgSO<sub>4</sub>. Removing the solvent yielded 49.3 g crude **3f'** as a yellow solid that was used without further purification. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 8.12 (d, <sup>3</sup>J = 8.5 Hz, 1 H; H-4), 7.99 (d, <sup>4</sup>J = 2.2 Hz, 1 H; H-5), 7.94 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-8), 7.80 (dd, <sup>3</sup>J = 8.8 Hz, <sup>4</sup>J = 2.2 Hz, 1 H; H-7), 7.63 (d, <sup>3</sup>J = 8.5 Hz, 1 H; H-3), 4.82 (s, 2 H; CH<sub>2</sub>).

## 2-(6-bromoquinoline-2-yl)acetonitrile (**3f**)

11.03 g (225 mmol) powdered NaCN, a small amount of NaI and 49.3 g **3f'** were stirred in 200 ml DMF at room temperature for 6 h. After removing the solvent the remaining residue was solved in methylene chloride and filtered over celite. The organic layer was washed with water, dried over MgSO<sub>4</sub> and the solvent was removed. Column chromatography (methylene chloride) yielded 17.18 g (70 mmol, 31 % relating to **3f''**) **3f**. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 8.15 (d, <sup>3</sup>J = 8.5 Hz, 1 H; H-4), 8.00 (d, <sup>4</sup>J = 2.2 Hz, 1 H; H-5), 7.96 (d, <sup>3</sup>J = 9.0 Hz, 1 H; H-8), 7.81 (dd, <sup>3</sup>J = 9.0 Hz, <sup>4</sup>J = 2.2 Hz, 1 H; H-7), 7.56 (d, <sup>3</sup>J = 8.5 Hz, 1 H;

H-3), 4.13 (s, 2 H; CH<sub>2</sub>); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ/ppm = 151.00, 146.06, 137.47, 134.37, 130.55, 129.94, 128.51, 121.57, 120.87, 116.65, 27.33; **elemental analysis** calcd (%) for C<sub>11</sub>H<sub>7</sub>BrN<sub>2</sub> [M = 247.09 g/mol]: C 53.47 H 2.86 N 11.34; found: C 53.20 H 2.93 N 11.08.

### ***tert*-butyl 5-(2-(cyanomethyl)quinolin-6-yl)pent-4-ynoate (3g)**



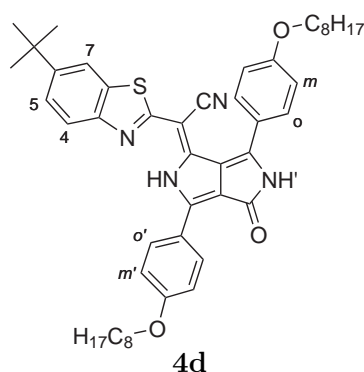
### ***tert*-butyl-4-pentynoate (3h')<sup>[18]</sup>**

2.95 g (30 mmol) 4-pentynoic acid, 4.45 g (60 mmol) *tert*-butanol and 0.147 g (1.2 mmol) 4-(dimethyl-amino) pyridine were stirred in 10 ml methylene chloride at room temperature. A solution of 6.81 g (33 mmol) DCC in 10 ml methylene chloride was added at once. The mixture was stirred over night. The carbamide was filtered and washed with methylene chloride. The filtrate was washed with 0.5 M HCl (2x) and NaHCO<sub>3</sub> solution (2x), dried over MgSO<sub>4</sub> and the solvent was removed. Column chromatography (methylene chloride) yielded 3.98 g (25.8 mmol, 86%) **3h'**. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 2.42 (m, 4 H; CH<sub>2</sub>CH<sub>2</sub>), 1.93 (m, 1 H; CH), 1.42 (s, 9 H; *tert*-butyl); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ/ppm = 171.08, 82.77, 80.83, 68.77, 34.49, 28.08, 14.49.

### ***tert*-butyl 5-(2-(cyanomethyl)quinolin-6-yl)pent-4-ynoate (3h)**

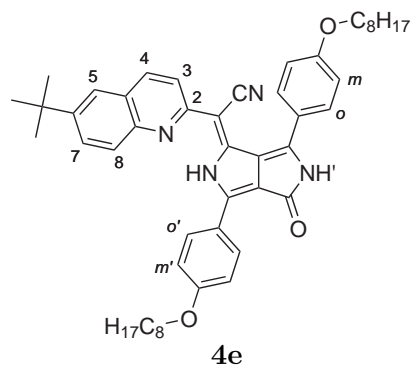
3.0 g (12.1 mmol) **3f** and 3.0 g (19.5 mmol) **3h'** were dissolved in 25 ml abs. THF and 10 ml triethylamine. The mixture was degassed and 69 mg (0.03 mmol) CuI and 419 mg (0.03 mmol) tetrakis(triphenylphosphine)palladium(0) were added. The mixture was heated to 60 °C over night. The mixture was added to 300 ml methylene chloride. The organic phase was washed (3x) with 300 ml water, dried over MgSO<sub>4</sub> and the solvent was removed. Column chromatography (petroleum ether/ethyl acetate 5/2) yielded 3.23 g (10.6 mmol, 83%) **3h**. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ/ppm = 8.15 (d, <sup>3</sup>J = 8.5 Hz, 1 H; H-4), 7.97 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-8), 7.85 (d, <sup>4</sup>J = 1.8 Hz, 1 H; H-5), 7.68 (dd, <sup>3</sup>J = 8.8 Hz, <sup>4</sup>J = 1.8 Hz, 1 H; H-7), 7.52 (d, <sup>3</sup>J = 8.5 Hz, 1 H; H-3), 4.13 (s, 2 H; CH<sub>2</sub>), 2.72 (t, <sup>3</sup>J = 7.3 Hz, 2 H; CCH<sub>2</sub>), 2.55 (t, <sup>3</sup>J = 7.3 Hz, 2 H; COCH<sub>2</sub>), 1.46 (s, 9 H; *tert*-butyl); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ/ppm = 171.32, 150.80, 146.64, 137.99, 133.77, 130.80, 128.77, 127.18, 123.12, 120.48, 116.80, 90.94, 81.10, 80.58, 34.85, 28.32, 27.31, 15.82; **elemental analysis** calcd (%) for C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> [M = 320.38 g/mol]: C 74.98 H 6.29 N 8.74; found: C 74.65 H 6.36 N 8.44.

## 4d



5 g (9.17 mmol) **1** were refluxed in 6 ml POCl<sub>3</sub> for 2 h. The POCl<sub>3</sub> was distilled off and the residue was dried on vacuum. 2.11 g (9.18 mmol) **3d** and 60 ml abs. THF were added and the mixture was heated to reflux for 3 h. The solvent was distilled off, 100 ml methanol and 10 ml water were added and the mixture was stirred over night. The solid was filtered off and washed with methanol, then suspended in methanol again, filtered off and washed. This procedure was repeated until the filtrate was colourless. 2.77 g (3.66 mmol, 40%) of **4d** were obtained as a blue crystalline powder that was pure enough for further reactions. For analytic a small amount was further purified by column chromatography (gradient: methylene chloride to methylene chloride/ethyl acetate 5/1). <sup>1</sup>H-NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ/ppm = 13.33 (s, 1 H; N-H), 8.59 (s, 1 H; N-H'), 8.20 (m, 2 H; o'), 7.75 (m, 1 H; H-4), 7.73 (m, 1 H; H-7), 7.50 (m, 2 H; o), 7.45 (m, 1 H; H-5), 6.98 (m, 4 H; m, m'), 3.98 (m, 4 H; OCH<sub>2</sub>), 1.76 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.15 (m, 20 H; alkyl), 1.31 (s, 9 H; tert-butyl), 0.83 (m, 6 H; CH<sub>3</sub>); UV/Vis/NIR (chloroform): λ<sub>max</sub>(ε) = 618 (33000), 440 nm (18000 M<sup>-1</sup>cm<sup>-1</sup>); MALDI-MS: m/z calcd: 756.4 [M+H]<sup>+</sup>; 778.4 [M+Na]<sup>+</sup> found 756.5; 778.5; elemental analysis calcd (%) for C<sub>47</sub>H<sub>56</sub>N<sub>4</sub>O<sub>3</sub>S [M = 757.04 g/mol]: C 74.57 H 7.46 N 7.40; found: C 74.36 H 7.53 N 7.43.

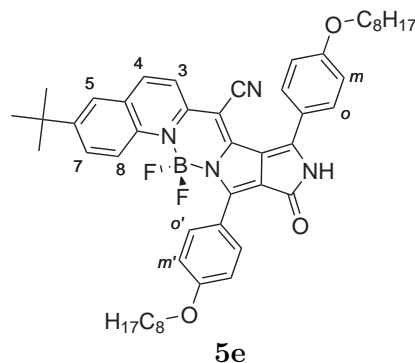
## 4e





430 nm ( $13000 \text{ M}^{-1}\text{cm}^{-1}$ ); **MALDI-MS**:  $m/z$  calcd: 805.4  $[\text{M}+\text{H}]^+$ , found 805.0; **elemental analysis** calcd (%) for  $\text{C}_{47}\text{H}_{55}\text{BF}_2\text{N}_4\text{O}_3\text{S}$  [ $M = 804.84 \text{ g/mol}$ ]: C 70.14 H 6.89 N 6.96; found: C 69.97 H 6.68 N 6.84.

## 5e

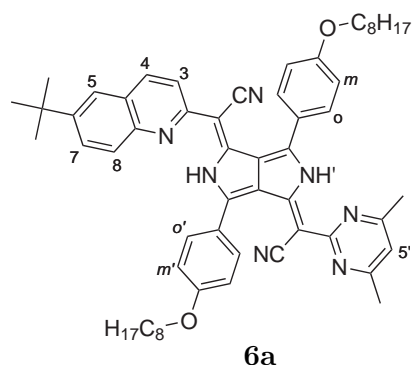


500 mg (0.666 mmol) **4e** and 1.1 ml (6.66 mmol) *N,N*-diisopropylethylamine were refluxed in 50 ml methylene chloride. 1.67 ml (13.3 mmol) boron trifluoride etherate were added and the mixture was refluxed for 30 min. The organic phase was washed (3x) with water, dried over  $\text{MgSO}_4$  and the solvent was removed. Column chromatography (gradient: methylene chloride to methylene chloride/ethyl acetate 20/1) yielded 328 mg (0.478 mmol, 72%) **5e** as a dark green crystalline powder.  **$^1\text{H-NMR}$**  (400 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ):  $\delta/\text{ppm} = 8.48$  (d,  $^3J = 9.3 \text{ Hz}$ , 1 H; H-8), 8.08 (m, 2 H; *o'*), 8.04 (d,  $^3J = 9.0 \text{ Hz}$ , 1 H; H-4), 7.81 (s, 1 H; N-H), 7.73 (dd,  $^3J = 9.3 \text{ Hz}$ ,  $^4J = 2.0 \text{ Hz}$ , 1 H; H-7), 7.63 (d,  $^3J = 9.0 \text{ Hz}$ , 1 H; H-3), 7.59 (d,  $^4J = 2.0 \text{ Hz}$ , 1 H; H-5), 7.53 (m, 2 H; *o*), 7.03 (m, 2 H; *m*), 7.00 (m, 2 H; *m'*), 4.01 (m, 4 H;  $\text{OCH}_2$ ), 1.77 (m, 4 H;  $\text{OCH}_2\text{CH}_2$ ), 1.45-1.15 (m, 20 H; alkyl), 1.32 (s, 9 H; *tert*-butyl), 0.83 (m, 6 H;  $\text{CH}_3$ ); **UV/Vis/NIR** (chloroform):  $\lambda_{\text{max}}(\epsilon) = 630$  (58000), 421 nm ( $15000 \text{ M}^{-1}\text{cm}^{-1}$ ); **MALDI-MS**:  $m/z$  calcd: 799.5  $[\text{M}+\text{H}]^+$ , found 799.5; **elemental analysis** calcd (%) for  $\text{C}_{49}\text{H}_{57}\text{BF}_2\text{N}_4\text{O}_3$  [ $M = 798.81 \text{ g/mol}$ ]: C 73.68 H 7.19 N 7.01; found: C 73.67 H 7.17 N 6.96.

## General procedure for the synthesis of the asymmetric H-PPCy dyes 6:

Under nitrogen atmosphere, 1 mmol half converted PPCy (**4**) and 1.2 mmol heteroarylacetonitril (**3**) are refluxed in absolute toluene and 4 mmol  $\text{POCl}_3$  are added. The reaction is monitored by UV/Vis/NIR spectroscopy and thin-layer chromatography. As soon as **4** is used up the reaction is stopped. Solvent and excess  $\text{POCl}_3$  are removed under vacuum. The crude product is treated with methanol in an ultrasonic bath and water is added until a solid precipitates. The solid is filtered off and washed with methanol until the filtrate is colourless. The remaining solid is purified by column chromatography.

## H-PPCy 6a

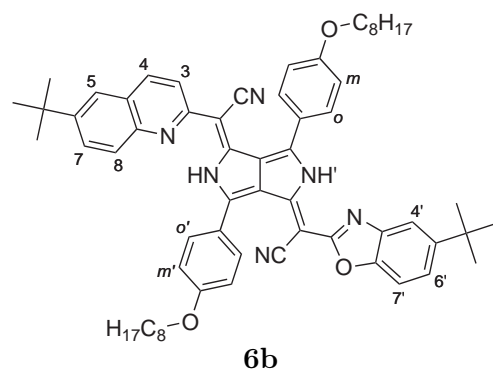


### Batch:

<b>4e</b>	90 mg	0.12 mmol	
<b>3a</b>	23 mg	0.16 mmol	
POCl <sub>3</sub>	74 mg	0.48 mmol	50 $\mu$ l
Toluol			20 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ethylacetate 50/1) yielded 70 mg (79.5  $\mu$ mol, 66%) **6a** as a greenish blue crystalline powder. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 14.1 (br., 1 H; N-H), 13.56 (s, 1 H; N-H'), 7.93 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-4), 7.82 (d, 1 H; H-8), 7.73 (m, 3 H; *o*, H-7), 7.64 (m, 2 H; *o'*), 7.61 (m, 1 H; H-5), 7.58 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-3), 7.11 (m, 2 H; *m*), 6.96 (m, 2 H; *m'*), 6.67 (s, 1 H; H-5'), 4.07 (t, <sup>3</sup>J = 6.6 Hz, 2 H; OCH<sub>2</sub>), 3.98 (t, <sup>3</sup>J = 6.6 Hz, 2 H; OCH<sub>2</sub>'), 2.46 (s, 6 H; CH<sub>3</sub>), 1.83 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.55-1.2 (m, 20 H; alkyl), 1.41 (s, 9 H; *tert*-butyl), 0.90 (m, 6 H; CH<sub>3</sub>); **UV/Vis/NIR** (chloroform):  $\lambda_{\max}(\epsilon)$  = 708 (100000), 645 nm (39000 M<sup>-1</sup>cm<sup>-1</sup>); **MALDI-MS**: *m/z* calcd: 880.5 [M+H]<sup>+</sup>, found 880.2; **elemental analysis** calcd (%) for C<sub>57</sub>H<sub>65</sub>N<sub>7</sub>O<sub>2</sub> [M = 880.17 g/mol]: C 77.78 H 7.44 N 11.14; found: C 77.37 H 7.27 N 11.02.

## H-PPCy 6b



### Batch:

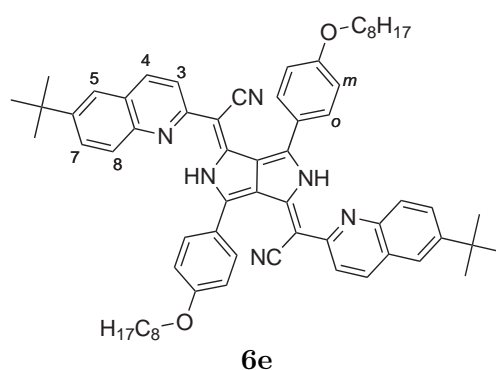
<b>4e</b>	300 mg	0.4 mmol	
<b>3b</b>	103 mg	0.48 mmol	
POCl <sub>3</sub>	245 mg	1.6 mmol	150 $\mu$ l
Toluol			30 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 330 mg (0.35 mmol, 87%) **6b** as a dark-green crystalline powder. **<sup>1</sup>H-NMR** (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$ /ppm = 14.90 (s, 1 H; N-H), 12.24 (s, 1 H; N-H'), 8.02 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-4), 7.75 (m, 4 H; *o*, H-7, H-8), 7.66 (m, 3 H; *o'*, H-3), 7.61 (m, 1 H; H-5), 7.54 (m, 1 H; H-4'), 7.35 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-7'), 7.26 (m, 1 H; H-6'), 7.15 (m, 2 H; *m*), 7.10 (m, 2 H; *m'*), 4.04 (m, 4 H; OCH<sub>2</sub>), 1.79 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.2

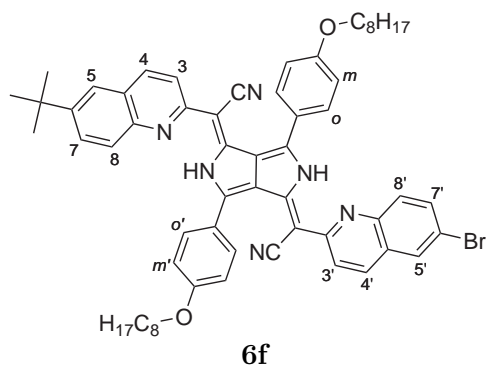


Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 202 mg (0.21 mmol, 79%) **6d** as a green crystalline powder. <sup>1</sup>H-NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ/ppm = 14.85 (s, 1 H; N-H), 13.04 (s, 1 H; N-H'), 8.00 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-4), 7.75 (m, 4 H; *o*, H-7, H-7'), 7.69 (d, 1 H; H-8), 7.68 (d, 1 H; H-4'), 7.64 (m, 3 H; *o'*, H-3), 7.61 (d, <sup>4</sup>J = 2.0 Hz, 1 H; H-5), 7.44 (dd, <sup>3</sup>J = 8.8 Hz, <sup>4</sup>J = 2.0 Hz, 1 H; H-5'), 7.14 (m, 2 H; *m*), 7.09 (m, 2 H; *m'*), 4.04 (m, 4 H; OCH<sub>2</sub>), 1.79 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.15 (m, 20 H; alkyl), 1.36 (s, 9 H; *tert*-butyl), 1.32 (s, 9 H; *tert*-butyl), 0.84 (m, 6 H; CH<sub>3</sub>); UV/Vis/NIR (chloroform): λ<sub>max</sub>(ε) = 734 (116000), 667 nm (47000 M<sup>-1</sup>cm<sup>-1</sup>); MALDI-MS: m/z calcd: 963.5 [M+H]<sup>+</sup>, found 963.2; elemental analysis calcd (%) for C<sub>62</sub>H<sub>70</sub>N<sub>6</sub>O<sub>2</sub>S [M = 963.32 g/mol]: C 77.30 H 7.32 N 8.72; found: C 77.42 H 7.31 N 8.65.

### H-PPCy **6e**<sup>[6]</sup>



### H-PPCy **6f**



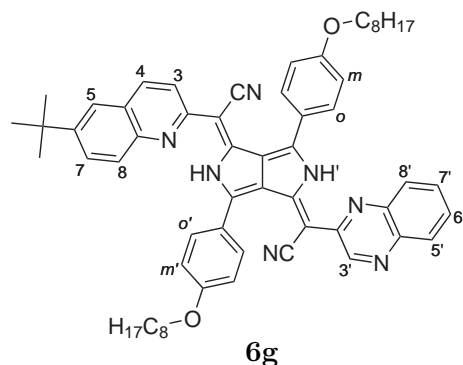
#### Batch:

<b>4e</b>	1 g	1.33 mmol	
<b>3f</b>	412 mg	1.66 mmol	
POCl <sub>3</sub>	612 g	4 mmol	370 μl
Toluol			120 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 1.13 g (1.15 mmol, 87%) **6f** as a green crystalline powder. <sup>1</sup>H-NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ/ppm = 14.79 (s, 1 H; N-H), 14.44 (s, 1 H; N-H), 7.99 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-4), 7.87 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-4'), 7.82 (d, <sup>4</sup>J = 1.9 Hz, 1 H; H-5'), 7.70 (m, 7 H; *o*, *o'*, H-7, H-8, H-7'), 7.62 (m, 4 H; H-3, H-3', H-5, H-8'), 7.12 (m, 4 H; *m*, *m'*), 4.05 (m, 4 H; OCH<sub>2</sub>), 1.79 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.15 (m, 20 H; alkyl),

1.36 (s, 9 H; *tert*-butyl), 0.84 (m, 6 H; CH<sub>3</sub>); **UV/Vis/NIR** (chloroform):  $\lambda_{\max}(\epsilon) = 734$  (122000), 666 nm (45000 M<sup>-1</sup>cm<sup>-1</sup>); **MALDI-MS**: *m/z* calcd: 979.4 [M+H]<sup>+</sup>, found 979.5; **elemental analysis** calcd (%) for C<sub>60</sub>H<sub>63</sub>BrN<sub>6</sub>O<sub>2</sub> [M = 980.09 g/mol]: C 73.53 H 6.48 N 8.57; found: C 73.49 H 6.48 N 8.62.

## H-PPCy 6g



### Batch:

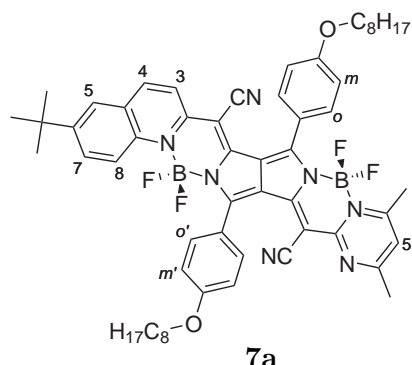
<b>4e</b>	500 mg	0.66 mmol	
<b>3g</b>	135 mg	0.80 mmol	
POCl <sub>3</sub>	405 mg	2.64 mmol	250 $\mu$ l
Toluol			20 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ethylacetate 50/1) yielded 343 mg (0.38 mmol, 58%) **6g** as a green crystalline powder. **<sup>1</sup>H-NMR** (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$ /ppm = 14.80 (s, 1 H; N-H), 13.79 (s, 1 H; N-H'), 8.79 (s, 1 H; H-3'), 7.90 (d, <sup>3</sup>J = 8.3 Hz, 1 H; H-8'), 7.85 (d, <sup>3</sup>J = 8.9 Hz, 1 H; H-4), 7.76 (d, <sup>3</sup>J = 8.3 Hz, 1 H; H-5'), 7.77 (m, 7 H; H-*o,o'*, H-7, H-8, H-6'), 7.57 (m, 1 H; H-5), 7.55 (m, 1 H; H-7'), 7.42 (d, <sup>3</sup>J = 8.9 Hz, 1 H; H-3), 7.09 (m, 4 H; *m, m'*), 4.03 (m, 4 H; OCH<sub>2</sub>), 1.80 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.15 (m, 20 H; alkyl), 1.36 (s, 9 H; *tert*-butyl), 0.83 (m, 6 H; CH<sub>3</sub>); **UV/Vis/NIR** (chloroform):  $\lambda_{\max}(\epsilon) = 739$  (132000), 671 nm (47000 M<sup>-1</sup>cm<sup>-1</sup>); **MALDI-MS**: *m/z* calcd: 902.5 [M+H]<sup>+</sup>; 924.5 [M+Na]<sup>+</sup>; 940.5 [M+K]<sup>+</sup> found 903.0; 925.0; 940.9; **elemental analysis** calcd (%) for C<sub>59</sub>H<sub>63</sub>N<sub>7</sub>O<sub>2</sub> [M = 902.18 g/mol]: C 78.55 H 7.04 N 10.87; found: C 78.19 H 7.05 N 10.92.

### General procedure for the synthesis of the Unsymmetric BF<sub>2</sub>-PPCy dyes 7:

1 mmol H-PPCy dye (**6**) and 20 mmol *N,N*-diisopropylethylamine are refluxed in methylene chloride. 40 mmol boron trifluoride etherate are added and the mixture is refluxed for 10 min. The mixture is washed with water and dried over MgSO<sub>4</sub>. After removing the solvent the crude product is purified by column chromatography.

## BF<sub>2</sub>-PPCy 7a

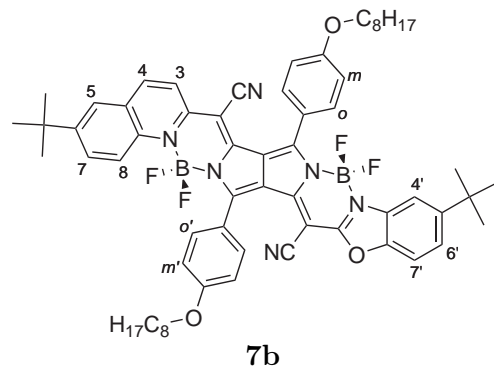


### Batch:

<b>6a</b>	200 mg	0.22 mmol	
BF <sub>3</sub> · Et <sub>2</sub> O	1.25 g	8.8 mmol	1.1 ml
DIPEA	569 mg	4.4 mmol	0.73 ml
CH <sub>2</sub> Cl <sub>2</sub>			20 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 185 mg (0.19 mmol, 86%) **7a** as a green crystalline powder. <sup>1</sup>H-NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ/ppm = 8.33 (d, <sup>3</sup>J = 9.2 Hz, 1 H; H-8), 7.93 (d, <sup>3</sup>J = 9.1 Hz, 1 H; H-4), 7.70 (m, 1 H; H-7), 7.64 (m, 6 H; *o,o'*, H-3, H-5), 6.99 (m, 2 H; *m*), 6.96 (m, 2 H; *m'*), 6.75 (s, 1 H; H-5'), 4.00 (m, 4 H; OCH<sub>2</sub>), 2.58 (s, 3 H; CH<sub>3</sub>), 2.48 (s, 3 H; CH<sub>3</sub>), 1.78 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.55-1.2 (m, 20 H; alkyl), 1.29 (s, 9 H; *tert*-butyl), 0.82 (m, 6 H; CH<sub>3</sub>); UV/Vis/NIR (chloroform): λ<sub>max</sub>(ε) = 719 (178000), 654 nm (43000 M<sup>-1</sup>cm<sup>-1</sup>); MALDI-MS: *m/z* calcd: 976.5 [M+H]<sup>+</sup>; 998.5 [M+Na]<sup>+</sup>; 1014.5 [M+K]<sup>+</sup> found 975.9; 997.9; 1013.9; elemental analysis calcd (%) for C<sub>57</sub>H<sub>63</sub>B<sub>2</sub>F<sub>4</sub>N<sub>7</sub>O<sub>2</sub> [M = 975.77 g/mol]: C 70.16 H 6.51 N 10.05; found: C 70.34 H 6.59 N 10.02.

## BF<sub>2</sub>-PPCy 7b



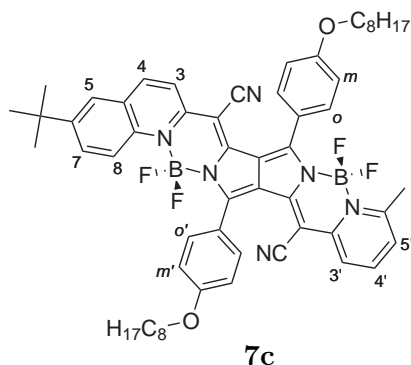
### Batch:

<b>6b</b>	150 mg	0.158 mmol	
BF <sub>3</sub> · Et <sub>2</sub> O	898 mg	3.17 mmol	0.8 ml
DIPEA	410 mg	6.33 mmol	0.52 ml
CH <sub>2</sub> Cl <sub>2</sub>			20 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 128 mg (0.123 mmol, 78%) **7b** as a green crystalline powder. <sup>1</sup>H-NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ/ppm = 8.40 (d, <sup>3</sup>J = 8.9 Hz, 1 H; H-8), 8.17 (d, <sup>3</sup>J = 9.0 Hz, 1 H; H-4), 7.76 (m, 1 H; H-7), 7.68 (m, 6 H; *o,o'*, H-3, H-5), 7.53 (m, 1 H; H-4'), 7.39 (m, 2 H; H-6', H-7'), 7.02 (m, 4 H; *m, m'*), 4.02 (m, 4 H; OCH<sub>2</sub>), 1.79 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.15 (m, 20 H; alkyl), 1.31 (s, 9 H; *tert*-butyl), 1.27 (s, 9 H; *tert*-butyl), 0.85 (m, 6 H; CH<sub>3</sub>); UV/Vis/NIR (chloroform): λ<sub>max</sub>(ε) = 718 (162000), 654 nm

(45000  $M^{-1}cm^{-1}$ ); **MALDI-MS**:  $m/z$  calcd: 1043.6  $[M+H]^+$ ; 1065.6  $[M+Na]^+$  found 1043.0; 1064.9; **elemental analysis** calcd (%) for  $C_{62}H_{68}B_2F_4N_6O_3$  [ $M = 1042.86$  g/mol]: C 71.41 H 6.57 N 8.06; found: C 71.43 H 6.74 N 8.10.

### BF<sub>2</sub>-PPCy 7c

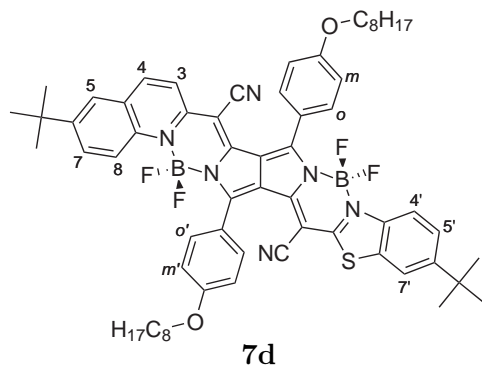


#### Batch:

<b>6c</b>	52 mg	0.06 mmol	
BF <sub>3</sub> · Et <sub>2</sub> O	341 mg	2.4 mmol	0.3 ml
DIPEA	155 mg	1.2 mmol	0.2 ml
CH <sub>2</sub> Cl <sub>2</sub>			20 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 39 mg (41  $\mu$ mol, 68%) **7c** as a green crystalline powder. **<sup>1</sup>H-NMR** (400 MHz, CDCl<sub>3</sub>):  $\delta$ /ppm = 8.40 (d, <sup>3</sup>J = 9.3 Hz, 1 H; H-8), 8.02 (d, <sup>3</sup>J = 9.2 Hz, 1 H; H-4), 7.67 (m, 9 H; *o*, *o'*, H-3, H-5, H-7, H-4', H-3'), 7.03 (m, 5 H; *m*, *m'*, H-5'), 4.05 (m, 4 H; OCH<sub>2</sub>), 2.73 (s, 3 H; CH<sub>3</sub>), 1.81 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.55-1.2 (m, 20 H; alkyl), 1.34 (s, 9 H; *tert*-butyl), 0.89 (m, 6 H; CH<sub>3</sub>); **UV/Vis/NIR** (chloroform):  $\lambda_{max}(\epsilon) = 730$  (179000), 663 nm (46000  $M^{-1}cm^{-1}$ ); **MALDI-MS**:  $m/z$  calcd: 961.5  $[M+H]^+$ ; 983.5  $[M+Na]^+$ ; 999.5  $[M+K]^+$  found 961.1; 983.1; 999.1; **elemental analysis** calcd (%) for  $C_{57}H_{62}B_2F_4N_6O_2$  [ $M = 960.76$  g/mol]: C 71.26 H 6.50 N 8.75; found: C 71.06 H 6.54 N 8.46.

### BF<sub>2</sub>-PPCy 7d



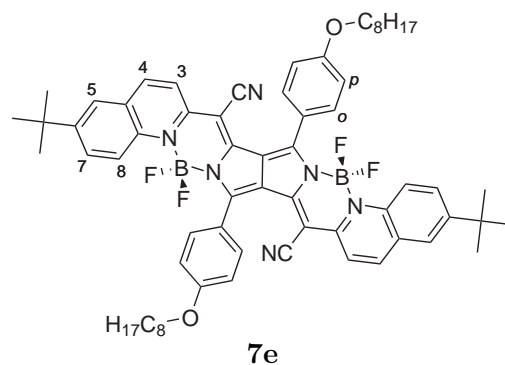
#### Batch:

<b>6d</b>	56 mg	0.058 mmol	
BF <sub>3</sub> · Et <sub>2</sub> O	331 mg	2.33 mmol	0.29 ml
DIPEA	150 mg	1.16 mmol	0.19 ml
CH <sub>2</sub> Cl <sub>2</sub>			20 ml

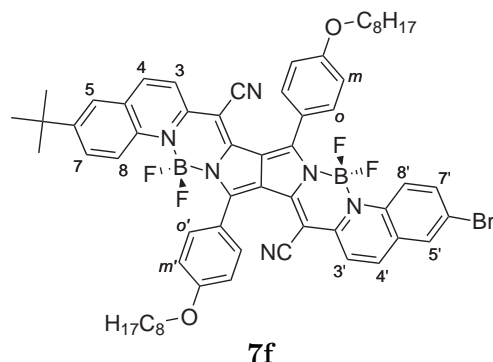
Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 37 mg (35  $\mu$ mol, 60%) **7d** as an olive-green crystalline powder. **<sup>1</sup>H-NMR** (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$ /ppm = 8.37 (d, <sup>3</sup>J = 9.3 Hz, 1 H; H-8), 8.14 (d, <sup>3</sup>J = 9.1 Hz, 1 H; H-4), 7.81 (d, <sup>3</sup>J = 8.8 Hz, 1 H; H-4'), 7.74 (dd, <sup>3</sup>J = 9.3 Hz, <sup>4</sup>J

= 2.0 Hz, 1 H; H-7), 7.65 (m, 7 H; *o*, *o'*, H-3, H-5, H-7'), 7.45 (dd,  $^3J = 8.8$  Hz,  $^4J = 1.8$  Hz, 1 H; H-5'), 7.01 (m, 4 H; *m*, *m'*), 4.02 (m, 4 H; OCH<sub>2</sub>), 1.79 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.15 (m, 20 H; alkyl), 1.30 (s, 9 H; *tert*-butyl), 1.28 (s, 9 H; *tert*-butyl), 0.85 (m, 6 H; CH<sub>3</sub>); **UV/Vis/NIR** (chloroform):  $\lambda_{\max}(\epsilon) = 742$  (191000), 672 nm (48000 M<sup>-1</sup>cm<sup>-1</sup>); **MALDI-MS**: *m/z* calcd: 1059.5 [M+H]<sup>+</sup>; 1081.5 [M+Na]<sup>+</sup> found 1059.0; 1081.1; **elemental analysis** calcd (%) for C<sub>62</sub>H<sub>68</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>2</sub>S [M = 1058.92 g/mol]: C 70.32 H 6.47 N 7.94; found: C 70.27 H 6.45 N 7.89.

### BF<sub>2</sub>-PPCy 7e<sup>[6]</sup>



### BF<sub>2</sub>-PPCy 7f



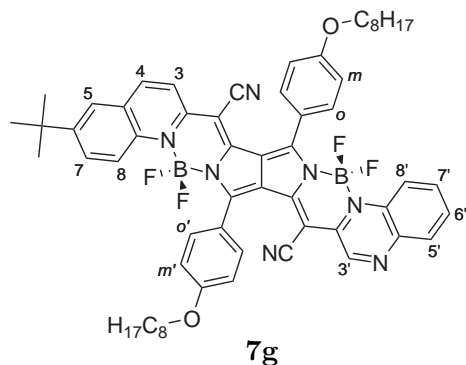
#### Batch:

<b>6f</b>	36 mg	0.037 mmol	
BF <sub>3</sub> · Et <sub>2</sub> O	209 mg	1.47 mmol	0.18 ml
DIPEA	95 mg	0.74 mmol	0.12 ml
CH <sub>2</sub> Cl <sub>2</sub>			20 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 32 mg (30  $\mu$ mol, 80%) **7f** as a green crystalline powder. <sup>1</sup>H-NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>):  $\delta$ /ppm = 8.37 (d,  $^3J = 9.3$  Hz, 1 H; H-8), 8.27 (d,  $^3J = 9.3$  Hz, 1 H; H-8'), 8.13 (d,  $^3J = 9.0$  Hz, 1 H; H-4), 7.91 (d,  $^3J = 9.2$  Hz, 1 H; H-4'), 7.80 (d,  $^4J = 2.0$  Hz, 1 H; H-5'), 7.73 (dd,  $^3J = 9.3$  Hz,  $^4J = 1.9$  Hz, 1 H; H-7), 7.64 (m, 8 H; *o*, *o'*, H-3, H-5, H-3', H-7'), 7.01 (m, 4 H; *m*, *m'*), 4.02 (m, 4 H; OCH<sub>2</sub>), 1.79 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.5-1.15 (m, 20 H; alkyl), 1.30 (s, 9 H; *tert*-butyl), 0.85 (m, 6 H; CH<sub>3</sub>); **UV/Vis/NIR** (chloroform):  $\lambda_{\max}(\epsilon) = 758$  (234000), 686 nm (50000 M<sup>-1</sup>cm<sup>-1</sup>); **MALDI-MS**: *m/z* calcd: 1075.4 [M+H]<sup>+</sup>; 1097.4 [M+Na]<sup>+</sup> found 1076.0; 1098.0; **elemental analysis**

calcd (%) for C<sub>60</sub>H<sub>61</sub>B<sub>2</sub>BrF<sub>4</sub>N<sub>6</sub>O<sub>2</sub> [M = 1075.68 g/mol]: C 66.99 H 5.72 N 7.81; found: C 66.61 H 5.76 N 7.76.

### BF<sub>2</sub>-PPCy 7g

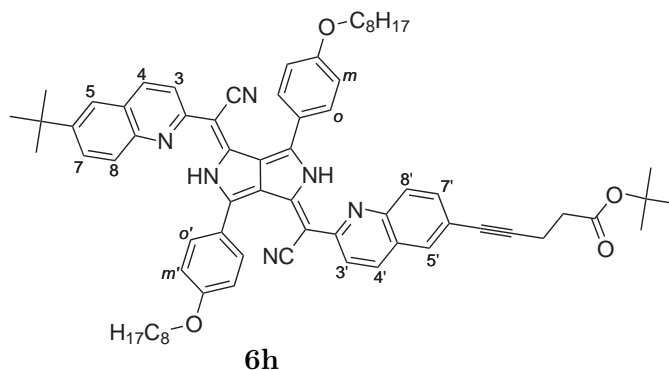


#### Batch:

<b>6g</b>	200 mg	0.22 mmol	
BF <sub>3</sub> ·Et <sub>2</sub> O	1.25 g	8.8 mmol	1.1 ml
DIPEA	573 mg	4.4 mmol	0.73 ml
CH <sub>2</sub> Cl <sub>2</sub>			20 ml

Column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) yielded 182 mg (0.18 mmol, 83%) **7g** as an olive-green crystalline powder. <sup>1</sup>H-NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ/ppm = 8.98 (s, 1 H; H-3'), 8.37 (d, <sup>3</sup>J = 9.1 Hz, 1 H; H-8), 8.18 (m, 2 H; H-4, H-8'), 7.89 (d, <sup>3</sup>J = 7.8 Hz, 1 H; H-5'), 7.75 (m, 1 H; H-7), 7.64 (m, 7 H; *o,o'*, H-3, H-5, H-7'), 7.51 (m, 1 H; H-6'), 6.99 (m, 4 H; *m, m'*), 4.00 (m, 4 H; OCH<sub>2</sub>), 1.76 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.45-1.1 (m, 20 H; alkyl), 1.28 (s, 9 H; *tert*-butyl), 0.81 (m, 6 H; CH<sub>3</sub>); UV/Vis/NIR (chloroform): λ<sub>max</sub>(ε) = 770 (213000), 700 nm (52000 M<sup>-1</sup>cm<sup>-1</sup>); MALDI-MS: m/z calcd: 998.5 [M+H]<sup>+</sup>; 1020.5 [M+Na]<sup>+</sup>; 1036.5 [M+K]<sup>+</sup> found 998.2; 1020.2; 1036.2; **elemental analysis** calcd (%) for C<sub>59</sub>H<sub>61</sub>B<sub>2</sub>F<sub>4</sub>N<sub>7</sub>O<sub>2</sub> [M = 997.78 g/mol]: C 71.02 H 6.16 N 9.83; found: C 71.20 H 6.27 N 9.81.

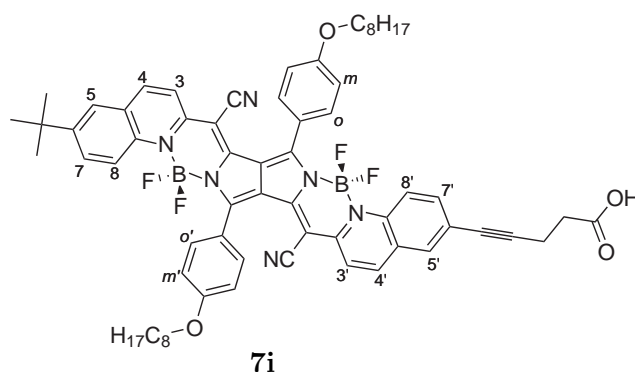
### H-PPCy 6h



Under nitrogen atmosphere 500 mg (0.666 mmol) **4e** were refluxed in 0.6 ml POCl<sub>3</sub> for 1 h. The POCl<sub>3</sub> was distilled off and the remaining solid was dried in vacuo. A solution of 235 mg (0.732 mmol) **3h** in 10 ml abs. THF was added and the mixture was heated to reflux for 30 min. The mixture was quenched in 150 ml CH<sub>2</sub>Cl<sub>2</sub> and 150 ml water. The organic layer

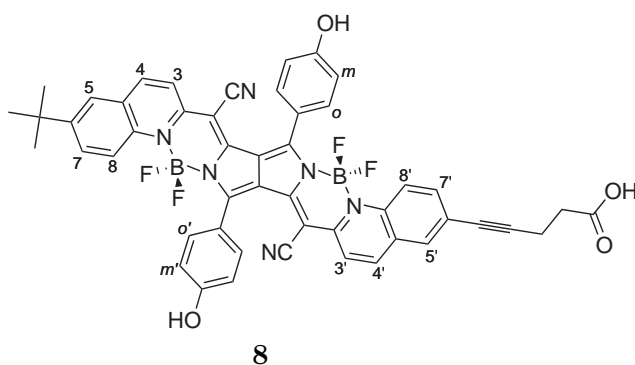


## BF<sub>2</sub>-PPCy 7i



100 mg (0.100 mmol) **6i** and 0.33 ml (2 mmol) *N,N*-di-*iso*-propylethylamine were refluxed in 15 ml CH<sub>2</sub>Cl<sub>2</sub>. 0.5 ml (4 mmol) boron trifluoride etherate were added and the mixture was refluxed for 10 min. The mixture was washed with water, dried over MgSO<sub>4</sub> and the solvent was removed. Column chromatography (gradient: CH<sub>2</sub>Cl<sub>2</sub> to CH<sub>2</sub>Cl<sub>2</sub>/ethylacetate 10/1) yielded 88 mg (0.081 mmol, 81%) **7i** as a green crystalline powder. **<sup>1</sup>H-NMR** (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>): δ/ppm = 8.36 (m, 1 H; H-8), 8.30 (m, 1 H; H-8'), 8.12 (d, <sup>3</sup>J = 9.2 Hz, 1 H; H-4), 7.94 (d, <sup>3</sup>J = 9.3 Hz, 1 H; H-4'), 7.72 (dd, <sup>3</sup>J = 9.5 Hz, <sup>4</sup>J = 1.9 Hz, 1 H; H-7), 7.66 (m, 5 H; *o*, *o'*, H-3), 7.58 (m, 4 H; H-3', H-5, H-5', H7'), 7.00 (m, 4 H; *m*, *m*), 4.01 (m, 4 H; OCH<sub>2</sub>), 2.68 (m, 4 H; (CH<sub>2</sub>)<sub>2</sub>), 1.78 (m, 4 H; OCH<sub>2</sub>CH<sub>2</sub>), 1.44 (m, 4 H; O(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>), 1.29 (s, 9 H; *tert*-butyl), 1.37-1.12 (m, 16 H; alkyl), 0.83 (m, 6 H; CH<sub>3</sub>); **UV/Vis/NIR** (chloroform): λ<sub>max</sub>(ε) = 762 (243000), 690 nm (54000 M<sup>-1</sup>cm<sup>-1</sup>); **MALDI-MS**: *m/z* calcd: 1093.6 [M+H]<sup>+</sup>, found 1092.8; **elemental analysis** calcd (%) for C<sub>65</sub>H<sub>66</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>O<sub>4</sub> [M = 1092.87 g/mol]: C 71.44 H 6.09 N 7.69; found: C 71.39 H 6.17 N 7.64.

## BF<sub>2</sub>-PPCy 8



Under nitrogen atmosphere 50 mg (0.046 mmol) **7i** were dissolved in 10 ml dry CH<sub>2</sub>Cl<sub>2</sub> and 28.7 mg (0.114 mmol) BBr<sub>3</sub> were added. The mixture was stirred at room temperature over night. The mixture was quenched with water and the CH<sub>2</sub>Cl<sub>2</sub> was removed on vacuum. The

green solid was filtered off, washed several times with water and dried in vacuum. 31 mg (0.036 mmol) of a green solid were obtained. Due to its low solubility no further purification could be carried out and the crude product was used for the coupling reaction. **MALDI-MS:** m/z calcd: 869.3 [M+H]<sup>+</sup>, found 870.6.

### Peptide synthesis

H-R<sub>9</sub>-NH<sub>2</sub> was synthesized on an Applied Biosystems ABI 433A peptide synthesizer using Fmoc-Arg(Pbf)-OH, PS-AM-RAM resin and standard Fmoc-SPPS coupling protocols [19]. Cleavage from the resin was achieved using a cleavage solution of 95% TFA, 2.5% TIS and 2.5% H<sub>2</sub>O. The peptide was purified by C18 RP-HPLC (Macherey-Nagel VP 250/10 Nucleosil 100-5 C18) using an Aekta purifier system with a gradient 0 - 10% B in 10 CV (A: 95% H<sub>2</sub>O, 5% MeCN, 0.1% TFA; B: 95% MeCN, 5% H<sub>2</sub>O, 0.1% TFA). The collected fractions were analyzed by MALDI-TOF mass spectrometry, pooled and freeze-dried **MALDI-MS:** m/z calcd: 1423.9 [M+H]<sup>+</sup>, found 1423.2.

### Coupling of 8 to H-R<sub>9</sub>-NH<sub>2</sub><sup>[10b]</sup>

8 (1 eq.), COMU (1-[(1-Cyano-2-ethoxy-2-oxoethylideneaminoxy-dimethylamino-morpholinomethylene)]-methanaminium hexafluorophosphate) (0.95 eq.) and DIPEA (1.9 eq.) were dissolved in NMP and stirred at RT for 15 minutes. H-R<sub>9</sub>-NH<sub>2</sub> was dissolved in NMP and added to the solution. The mixture was stirred at RT over night. The green solution was concentrated to approximately 1 ml and desalted with a Sephadex PD10 column. The obtained fractions were analyzed by MALDI-TOF MS, concentrated and purified by C18 RP-HPLC as described above. The gradient used was 30 - 50% B in 15 CV.

**MALDI-MS:** m/z calcd: 2274.2 [M+H]<sup>+</sup>, found 2270.4.

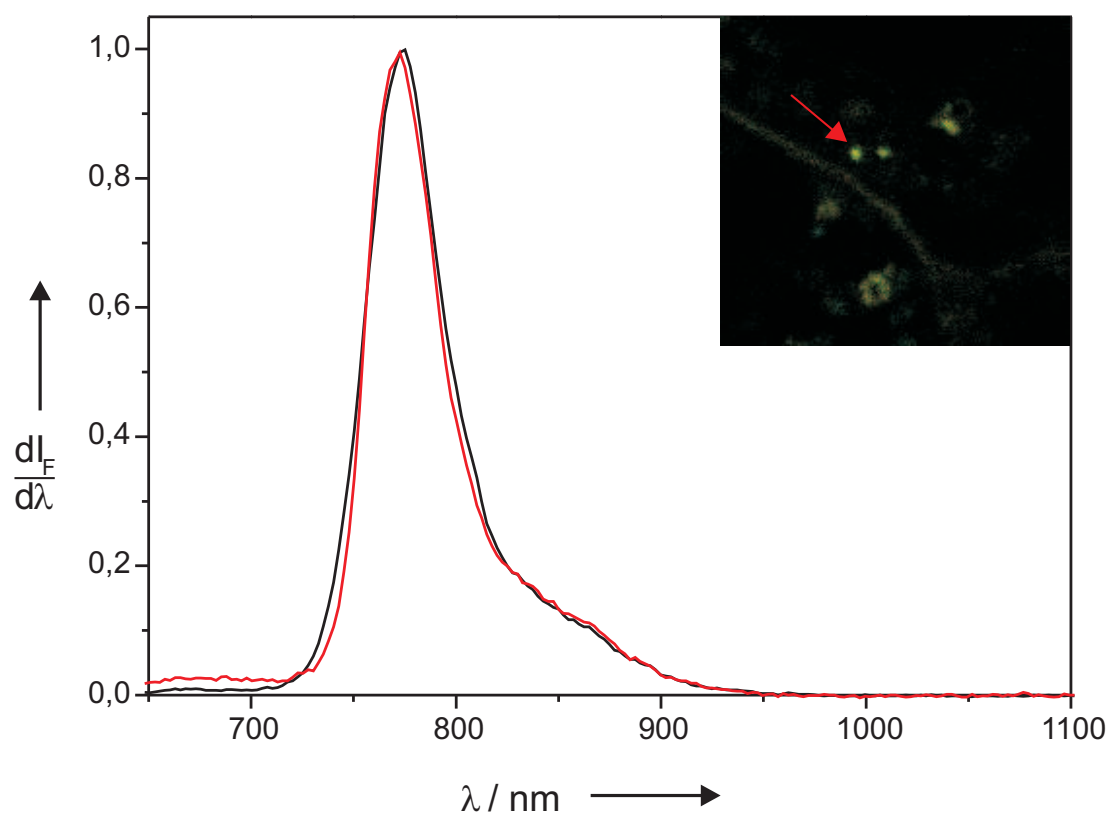
### Live cell imaging<sup>[12]</sup>

Two days before the experiment 100.000 HeLa cells were seeded in a 35 mm  $\mu$ -dish (Ibidi) and the cells were incubated at 37 °C and 5% CO<sub>2</sub>. On the day of the experiment a 2  $\mu$ M solution of the labeled polyarginine in HKR buffer (5 mM HEPES, 137 mM NaCl, 2.68 mM KCl, 2.05 mM MgCl<sub>2</sub> · 6 H<sub>2</sub>O, 1.8 mM CaCl<sub>2</sub> · 2 H<sub>2</sub>O and 1 g/l glucose) was prepared. The cell culture medium was aspirated from the cells and 2 ml of the prepared peptide solution were added. After 30 minutes of incubation the peptide-containing solution was removed and the cells were washed twice with 1 ml HKR buffer. Before live cell imaging a colorless medium including Hoechst 33342 for labeling the nucleus was added and the cells were observed for several hours with a confocal microscope (Zeiss LSM 510 Meta) at 37 °C and 5% CO<sub>2</sub>.

Hoechst 33342 was excited at 405 nm and fluorescence was detected by using a band pass filter 420-480 nm. **Arg<sub>9</sub>-8** was excited at 633 nm and fluorescence was detected by using a long pass

filter 650 nm. At this setup a longer wavelength excitation was not available; due to the low absorption of **8** at 633 nm the fluorescence intensity is relatively low.

To obtain the emission spectrum of **Arg9-8** in the used HKR buffer as well as inside of living cells, 100.000 HeLa cells were seeded in a 35 mm  $\mu$ -dish (Ibidi). Two days later the cells were incubated with **Arg9-8**. 1 h after incubation live cell imaging was performed (Figure 1) using a confocal microscope (Zeiss Axiovert 200) equipped with a pulsed laser (LDH-P-C-690, Picoquant) and a TCSPC module (HydraHarp 400, Picoquant). Spectra were simultaneously recorded by using a PS 857 dispersion prism (Thorlabs) and a CCD-camera (Andor Newton DU970N-BV).



**Figure 1:** Normalized fluorescence spectra of **Arg9-8** in HKR buffer (black line) and inside the endocytotic vesicle (red line) marked in the inset.

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## Optical Spectra

Absorption (and fluorescence for **5d** and **5e**) spectra of the H-Chelates **4** and **6** (black) and the BF<sub>2</sub>-complexes **5** and **7** (red) in chloroform at room temperature.

