Synthesis of a novel building block for the preparation of multi-chromophoric sensitizers for panchromatic dye-sensitized solar cells

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Abstract

A simple 3-step synthesis of a novel pyrazine-containing heteroaromatic building block for use as a scaffold for producing multi-chromophoric sensitizers for use in dye sensitized solar cells has been developed. This moiety features two esterified carboxylic acid groups whose hydrolysis provides moieties for anchoring to nanoparticulate metal oxides and two bromine atoms that facilitate attachment of chromophores via palladium mediated cross-coupling methods. The utility of the building block for the synthesis of complex dye motifs is demonstrated by the preparation of a novel panchromatic dye featuring a BODIPY chromophore and a strongly electron donating porphyrin chromophore using both Suzuki and copper-free Sonogashira cross-coupling methods. The building block could be used either to attach two different or identical dye moieties to the metal oxide, or to attach an electron injection dye plus an auxiliary absorber, photoprotective agent, secondary redox moiety, etc.

1. Introduction

One of the key design features of dye-sensitized solar cells is the linkage that attaches the light-absorbing sensitizer to the nanoparticulate wide gap semiconductor photoanode. This linkage affects the stability of the dye attachment, the arrangement of and interaction between the dye molecules on the surface, the rate of electron donation from the excited sensitizer to the semiconductor, and the rate of charge recombination of the resulting charge-separated state[1-5]. A single linkage can also be used to attached two or more sensitizing dyes to the electrode, and these may be the same or different. We recently published an example of this latter idea: a novel di-porphyrin sensitizer, **P_2-PZ** (Fig. 1).[6] A central feature of this sensitizer is the pyrazine-containing linker, **PZ**, which acts as both an anchor and a scaffold for two porphyrin chromophores. In a comparative DSSC study, **P_2-PZ** dramatically out performed a control dye **P**, which featured the same porphyrin chromophore, anchored by a carboxylic acid moiety. The **P_2-PZ** increased the V_{OC}, J_{SC} and η dramatically. This encouraging result presents a new design strategy for producing multichromophoric dyes. The new linkage was prepared by condensation of *o*-diketones with aromatic *o*-diamines to produce pyrazine-containing quinoxaline substructures. This approach provides a convenient pathway for synthesizing various hetero-aromatic constructs that feature extended domains of aromaticity and specific peripheral functionality.[7-20] This condensation reaction can be used to construct complex motifs in which chromophores and anchoring groups are present on a fused heteroaromatic scaffold suitable for mediating electron transfer.[6,20]

Although the synthesis reported previously for **P_2-PZ** was successful, the final step employed harsh acidic conditions to generate the carboxylic acid functionality from the di-nitrile precursor (Scheme 1), and this in turn required a subsequent Williamson ether synthesis to repair the damaged ether functionalities.[6] This method of hydrolysis is not suitable when more sensitive chromophores are to be employed, limiting the scope of application for the linker **PZ** when produced through the previously reported synthetic strategy.

In order to avoid this problem and make the method amenable to a wide variety of dye choices, the generation of the dicarboxylic acid functionality from the dinitrile compound is required prior to the introduction of sensitive chromophores or peripheral functionalities. Consequently, we have designed a building block **PZ'** (Scheme 2). This moiety bears two bromine atoms that may be functionalized by palladium-mediated cross-coupling methodologies, and two carboxylic acids protected with pentyl esters which are stable to the cross-coupling reactions, may be easily removed under mild conditions, enhance solubility (a problem when working with fused aromatics)[8] and prevent formation of anhydrides. We present here the synthesis of **PZ'** and demonstrate its utility in the synthesis of a novel dichromophoric panchromatic dye featuring both a porphyrin and a BODIPY moiety. Similar strategies could be used with **PZ'** to combine dyes with complementary dyes, photoprotective agents, secondary electron donor moieties, etc.

2. Materials and Methods

2.1. General

Solvents were purchased from BDH Chemicals. Tetrahydrofuran was distilled from sodium/benzophenone under argon prior to use. All starting materials were purchased from Sigma Aldrich except for 3,6-dibromophenathrene-9,10-dione, which was purchased from AstaTech Inc. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectra were determined using an Applied Biosystems Voyager-DE STR workstation and acquired in reflector mode using terthiophene, diphenylbutadiene or dithranol as the matrix. The NMR spectra were acquired using a Varian (Agilent) MR 400 MHz NMR spectrometer operating at an ^{1}H Larmor frequency of 399.87 MHz and equipped with a 5mm broadband Z-gradient probe. The UV-visible spectra were acquired using a Shimadzu UV-2550 UV-visible spectrophotometer. Literature procedures for the synthesis of **3**[21] and **5**[22] were followed.

2.2. Synthesis

Dinitrile 1. A pressure tube containing a magnetic stirrer bar was charged with 3,6-dibromo-9,10-phenanthrenedione (482 mg, 1.32mmol), 4,5-diaminophthaleonitrile (250 mg, 1.58 mmol) and a 1 : 1 : 1 mixture of 1,2-dichlorobenzene : AcOH : EtOH (30 mL). The tube was sealed with a Teflon screw cap and heated at reflux overnight. The solution was then cooled and diluted with methanol (100 mL) , which further promoted precipitation of the product, and then filtered. The yellow product was washed with methanol (300 mL) and dichloromethane (200 mL) and then dried under reduced pressure overnight to yield **1** (629 mg, 1.29 mmol, 98%). ^{1}H NMR (400 MHz, 1,1,2,2-tetrachloroethane-d_2, 110 ^{o}C): δ 9.26 (bs, 2 H), 8.85 (s, 2 H), 8.68 (s, 2 H), 8.01 (bs, 2 H). MS (MALDI-TOF) m/z: calcd for $C_{22}H_8Br_2N_4$ 485.9, obsd 485.9.

Dicarboxylic acid 2. A portion (500 mg, 1.02 mmol) of dinitrile **1** was placed in a 100 mL round-bottomed flask with a magnetic stirrer bar. Ethanol (6 mL) and H_2O (6 mL) were added, followed by KOH (0.862 g, 15.4 mmol). The flask was fitted with a reflux condenser and the solution was heated at reflux for 48 h. After cooling, 4N HCl was used to acidify the solution. The solid precipitate was isolated by filtration and washed with H_2O and methanol, and finally dried under vacuum overnight to yield **2** (0.64 g ,1.22 mmol, 120%) as the product plus included solvent due to incomplete drying. All efforts to characterize the product by NMR failed due to insolubility. The product was used without further purification in the following reactions. MS (MALDI-TOF) m/z: calcd for $C_{22}H_{10}Br_2N_2O_4$ 523.9 obsd 523.9.

PZ’. To a 100 mL round-bottomed flask containing a magnetic stirrer bar was added the crude compound **2** (225 mg), along with toluene (5 mL), 1-pentanol (2 mL) and H_2SO_4 (0.05 mL). The flask was fitted with a Dean-Stark apparatus connected to a dry argon line. The solution was heated at reflux overnight. After cooling, solid $NaHCO_3$ was added to neutralize the solution, followed by methanol (40 mL). The solution was filtered and the solid product obtained was washed with water (3 x 100 mL) and methanol (2 x 100 mL). The resulting beige solid was dried under vacuum overnight, yielding **PZ’** (0.315g, 0.472mmol, 114%). Again a >100% yield revealed the difficulty in drying this class of compounds. ^{1}H NMR (400 MHz, trifluoroacetic acid-d_1, 65 ^{o}C): δ

9.62 (bs, 2 H), 9.51 (bs, 2 H), 9.31 (s, 2 H), 8.58 (s, 2 H), 5.09 (s, 4 H), 2.41 (bs, 4 H), 1.96 (m, 8 H), 1.44 (t *J* = 6.5 Hz, 6 H). MS (MALDI-TOF) m/z: calcd for $C_{32}H_{30}Br_2N_2O_4$ 665.1, obsd 664.9.

BODIPY substituted PZ 4. A pressure tube was charged with **PZ'** (250 mg, 0.375 mmol), the BODIPY boronic ester **3 (**228mg, 0.45 mmol), Cs_2CO_3 (367 mg, 1.13 mmol) and finally deoxygenated tetrahydrofuran (30 mL). Argon was bubbled through the solution while the vessel was placed in ice for 10 min. Following this, $Pd(PPh_3)_4$ (86 mg, 0.075 mmol) was added and the tube was sealed with a Teflon screw cap. The tube was removed from ice, heated to 80 ^{o}C and allowed to stir for 20 h. After cooling, the contents were transferred to a round-bottomed flask and concentrated by evaporation of the solvent at reduced pressure. The residue was taken up in dichloromethane and loaded onto a silica gel column for chromatographic purification using 9:1, dichloromethane:hexanes as the eluting solvent. The appropriate fractions were combined yielding pure **4** (26.2 mg, 0.027 mmol, 7.2%). ^{1}H NMR (400 MHz, $CDCl_3$, 58 ^{o}C): δ 9.18 (d, *J* = 8.8 Hz, 1 H), 9.13 (d, *J* = 8.8 Hz, 1 H), 8.69 (s, 1 H), 8.63 (s, 1 H), 8.61 (s, 1 H), 8.59 (s, 1 H), 8.02 (d, *J* = 8.8 Hz, 1 H), 7.96 (d, *J* = 8.2 Hz, 2 H), 7.81 (d, *J* = 8.8 Hz, 1 H), 7.5 (d, *J* = 8.2 Hz), 4.44 (t, *J* = 6.8 Hz, 4 H), 2.57 (s, 6 H), 2.34 (q, *J* = 7.2 Hz, 4 H), 1.86 (quin, *J* = 7.2 Hz, 4 H), 1.46 (m, 14 H), 1.03 (t, *J* = 7.2 Hz, 6 H), 0.97 (t, *J* = 7.0 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.86, 166.82, 153.98, 143.64, 143.56, 142.97, 142.17, 141.95, 140.59, 139.43, 138.27, 135.98, 133.74, 132.93, 132.80, 132.69, 131.52, 131.49, 131.15, 130.73, 129.28, 129.26, 128.66, 128.42, 127.99, 127.68, 127.46, 126.40, 125.96, 121.46, 66.33, 29.68, 28.33, 28.13, 22.38, 17.11,

14.63, 13.99, 12.54, 12.06. MS (MALDI-TOF) m/z: calcd for $C_{55}H_{56}BBrF_2N_4O_4$ 963.4, obsd 962.9.

BODIPY and porphyrin substituted PZ 6. The synthesis of **6** was analogous to that reported by Yella *et al.* for the synthesis of a molecule with some related structural features[22]. A sample of **5** (175 mg, 0.112 mmol) was taken up in 10 mL of dry tetrahydrofuran. Under an argon atmosphere, 1M TBAF in tetrahydrofuran (0.34 mL, 0.34 mmol) was added dropwise. The solution was allowed to stir for 30 min, the reaction was quenched with water and the mixture was extracted with dichloromethane. The organic phase collected was dried over $MgSO_4$, filtered, concentrated by distillation of the solvent under reduced pressure, and dried under vacuum. The residue was taken up in dry tetrahydrofuran (36 mL) and added to an oven dried glass pressure tube containing **4** (51.7 mg, 0.054 mmol) and $AsPh_3$ (41 mg, 0.134 mmol). Next, Et_3N (6 mL) was added and the tube was placed on ice while argon was bubbled through the solution for 15 min. At this point $Pd_2(dba)_3$ (14.7 mg, 0.0161 mmol) was added and the tube was sealed and heated at reflux for 20 h. After cooling, the contents were concentrated, taken up in dichloromethane and transferred to a silica gel column. Elution with 3:2, dichloromethane:hexanes afforded **6** (32.3 mg, 0.0141mmol, 26%). ^1H NMR (400 MHz, $CDCl_3$ 58^oC) : δ 9.79 (d, *J* = 4.4 Hz, 2 H), 9.6 (d, *J* = 8.4 Hz, 1 H), 9.57 (d, *J* = 8.4 Hz, 1 H), 9.26 (s, 1 H), 9.18 (d, *J* = 4.8 Hz, 1 H), 9.07 (s, 1 H), 8.92 (d, *J* = 4.8 Hz, 2 H), 8.76 (d, *J* = 3.2 Hz, 2 H), 8.68 (d, *J* = 4 Hz, 2 H), 8.40 (d, *J* = 8.4 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 2 H), 7.63 (t, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.4hz, 4 H), 6.95 (d, *J* = 7.6 Hz, 4 H), 6.93 (d, *J* = 7.6 Hz, 4 H), 4.46 (t, *J* = 6.8 Hz, 4 H), 3.81 (t, *J* = 6.8 Hz, 8 H), 2.57 9s, 6 H), 2.47 (t, *J* = 7.8 Hz, 4 H), 2.32 (q, *J* = 7.6 Hz, 4

H), 1.87 (quin, *J* = 6.8 Hz, 4 H), 1.59-1.39 (m, 16 H), 1.35-1.20 (m, 14 H), 1.04-0.92 (m, 16 H), 0.89-0.70 (m, 14 H), 0.67-0.49 (m, 24 H), 0.46 (t, *J* = 7.2 Hz, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$, 58°C) : δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.99, 166.97, 159.80, 159.78, 153.87, 152.10, 151.91, 150.50, 150.44, 150.32, 144.30, 144.15, 142.96, 142.30, 142.21, 140.74, 139.61, 138.38, 135.88, 134.65, 132.86, 132.65, 132.64, 132.55, 132.30, 132.21, 132.15, 131.48, 131.28, 130.77, 130.62, 130.09, 129.84, 129.41, 129.29, 128.66, 128.03, 127.85, 127.63, 127.50, 127.17, 125.84, 123.41, 121.97, 121.94, 121.90, 120.58, 114.69, 105.07, 97.95, 96.84, 95.06, 68.52, 66.32, 35.22, 31.70, 31.50, 31.35, 31.30, 29.09, 28.59, 28.54, 28.44, 28.35, 28.15, 25.11, 22.57, 22.40, 22.23, 17.09, 14.61, 14.05, 14.00, 13.77, 12.53, 12.08. MS (MALDI-TOF) m/z: calcd for $C_{145}H_{172}BF_2N_9O_8Zn$ 2279.3, obsd 2279.2.

Panchromatic dye 7. MALDI-TOF analysis of a crude product mixture obtained in a trial deprotection of the pentyl esters of **6** via KOH hydrolysis revealed that a fluorine atom on a portion of the products had been displaced by OH. It was found that this could be remedied through treatment of the product with Et_3NHF. To a 50 mL round-bottomed flask containing **6** (17.8 mg, 7.8 μmol) were added tetrahydrofuran (30 mL), water (2 mL) and KOH (60 mg), and the mixture was stirred at 40 °C overnight. The solution was cooled to ambient temperature, Et_3NHF (0.25 mL) was added and the mixture was stirred for 10 min. The solution was washed with water and extracted with dichloromethane facilitated by addition of acetic acid. The organic fraction was concentrated by distillation of the solvent under reduced pressure and the residue was purified by column chromatography using dichloromethane with 5 % methanol and 1 %

AcOH as the eluting solvent, yielding **7** (14.3 mg, 6.67 µmol, 86%). MS (MALDI-TOF) m/z calcd for $C_{135}H_{152}BF_2N_9O_8Zn$, 2139.1, 2139.1, obsd 2139.1.

3. Results

The synthesis of **PZ'** was achieved in 3 steps (Scheme 2), beginning with the condensation of 3,6-dibromophenanthrene-9,10-dione with 4,5-diaminophalonitirle to produce dinitrile **1**. This step was conducted in a pressure tube at internal reflux. Reflux of **1** in an ethanolic solution of KOH for 5 days gave **2** in excellent yield. Dicarboxylic acid **2** was insoluble in all common organic solvents and could not be characterized by NMR spectroscopy. The H_2SO_4 catalyzed esterification of **2** with pentanol in toluene was carried out by reflux in a flask fitted with a Dean-Stark apparatus to remove water as it was formed. The final product **PZ'** exhibit limited solubility in chloroform, but could be characterized by NMR spectroscopy using TFA-d_4 as the solvent.

To demonstrate the utility of **PZ'** as a building block for synthesizing functional dyes like that of **P_2-PZ** via palladium mediated cross-coupling reactions, **PZ'** was successively employed via a Suzuki cross-coupling and a copper-free Sonogashira cross-coupling to produce **7** (Scheme 3), in which both a zinc porphyrin and a borondipyrromethene (BODIPY) dye are linked to the same aromatic spacer. Despite the limited solubility of **PZ'** in common organic solvents, the Suzuki cross-coupling of the BODIPY boronic ester **3** with **PZ'** in THF was achieved in good yield. Monobromide **4** was soluble in common chlorinated solvents and could be purified easily by silica-gel chromatography. The copper-free Sonogashira coupling of **4** with the alkyne substituted porphyrin **5** was achieved to yield **6**.

Base hydrolysis of the pentyl esters generated the anchoring groups of the final dye **7**. Mass spectral analysis of the product revealed that despite the comparatively mild hydrolysis of the esters with KOH, some of the fluorine atoms of the BODIPY had been displaced. This was easily remedied by treatment with Et_3NHF which gave **7** in pure form.

4. Discussion

The two chromophores in **7** have complementary absorption spectra, and can thus in principle absorb a larger fraction of the solar spectrum than can either dye operating alone. The zinc porphyrin moiety has absorption maxima at 648, 576 and 442 nm in dichloromethane, whereas the BODIPY portion of the molecule absorbs at 529 and ~485 (sh) nm (Fig. 2). The pyrazine linkage has low-amplitude, broad absorbance in the 432 nm region. Thus, **7** absorbs significantly more light over a broader region of the solar spectrum than either the porphyrin or the BODIPY alone. The porphyrin and pyrazine absorption features of the spectrum of **7** are similar to those for P_2-PZ presented in an earlier report,[6], which also gives fluorescence emission and other spectroscopic data for compounds of this general type. Based on results for P_2-PZ reported earlier,[6] **7** is expected to bind strongly to TiO_2 and to be an efficient sensitizer in a DSSC. The first oxidation potentials of BODIPY dyes with structures similar to the BODIPY moiety of **7** are similar to those of *meso*-tetraphenylporphyrin,[23] and thus direct injection of an electron from the excited BODIPY of **7** into the conduction band of TiO_2 is energetically possible. Porphyrins bearing strong electron donating groups in a *meso*-position have also been found to be excellent sensitizers for DSSC.[22] In addition, as we have demonstrated in other molecules, singlet-singlet energy transfer from BODIPY moieties to *meso*-tetraarylporphyrins is facile.[24] Thus absorption of light by the BODIPY of **7** followed by singlet excitation transfer to the porphyrin and then electron injection into TiO_2 is also likely.

5. Conclusion

The synthesis of a novel pyrazine-containing heteroaromatic building block has been achieved and its utility as a scaffold for creating panchromatic, multi-chromophoric dyes has been demonstrated. The synthesis of this building block now enables preparation of an altogether new series of dyes for use in dye-sensitized solar that may permit significant advances in photovoltaic conversion efficiencies by increasing the amount of light absorbed and converted by the sensitizing dyes.

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Figure Captions – DYPI-D-16-00227

Fig. 1. Diporphyrin dye **P_2-PZ**, containing the heteroaromatic spacer **PZ**.

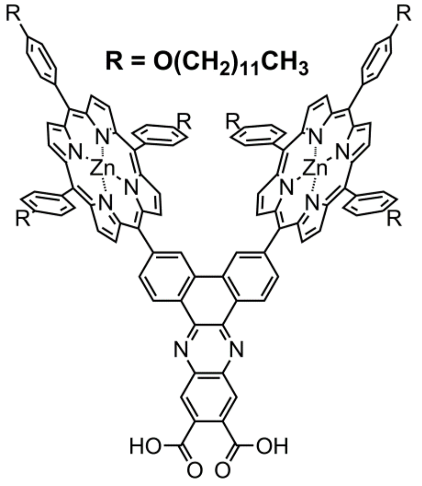
Scheme 1. Method of generation of the carboxylic acid groups in the preparation of **P_2-PZ**. The **R** groups are as in Fig. 1.

Scheme 2. Synthesis of linker scaffold **PZ’**.

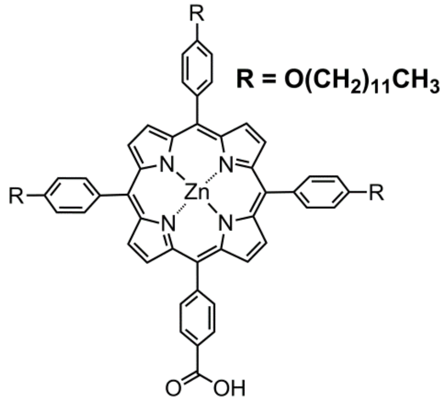
Scheme 3. Preparation of dichromophoric sensitizer **7** using the **PZ’** building block.

Fig. 2. Absorption spectrum of multichromophoric sensitizer **7** in dichloromethane.

Figure 1.

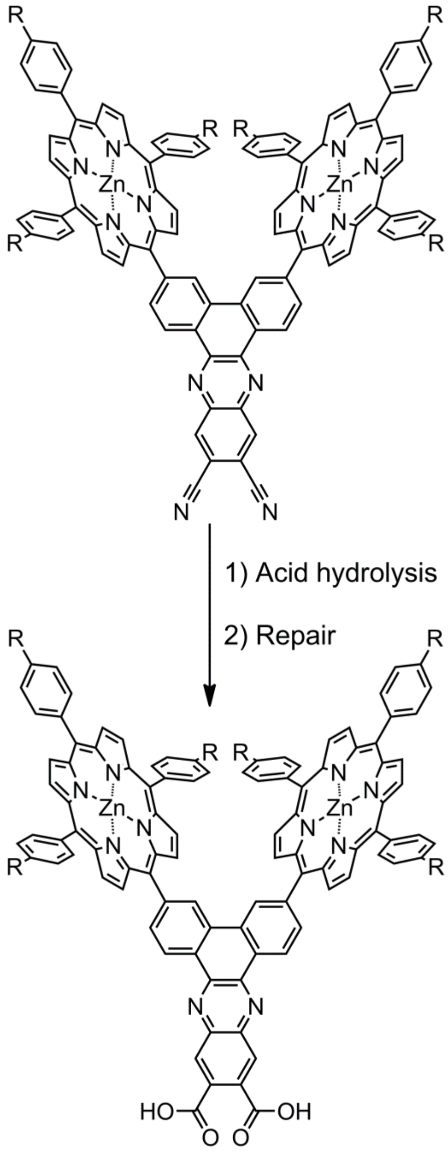


P_2-PZ

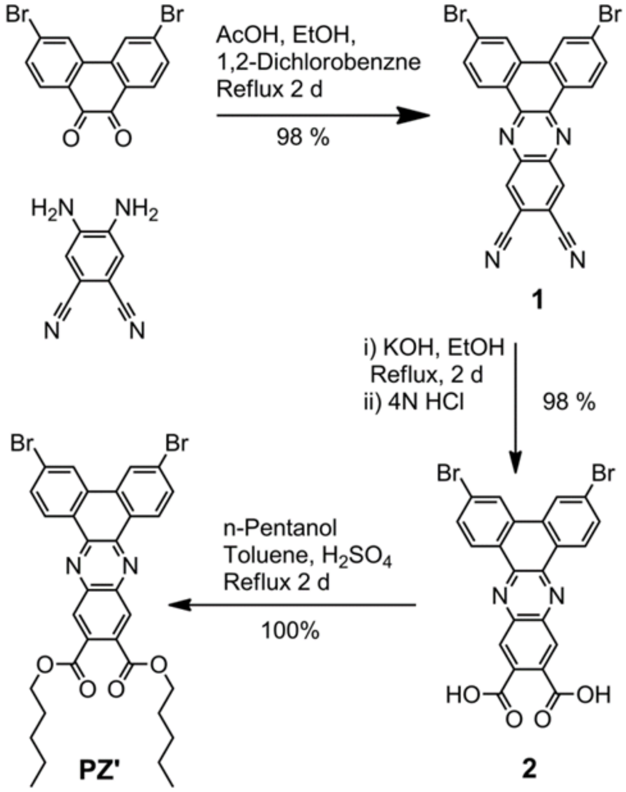


P

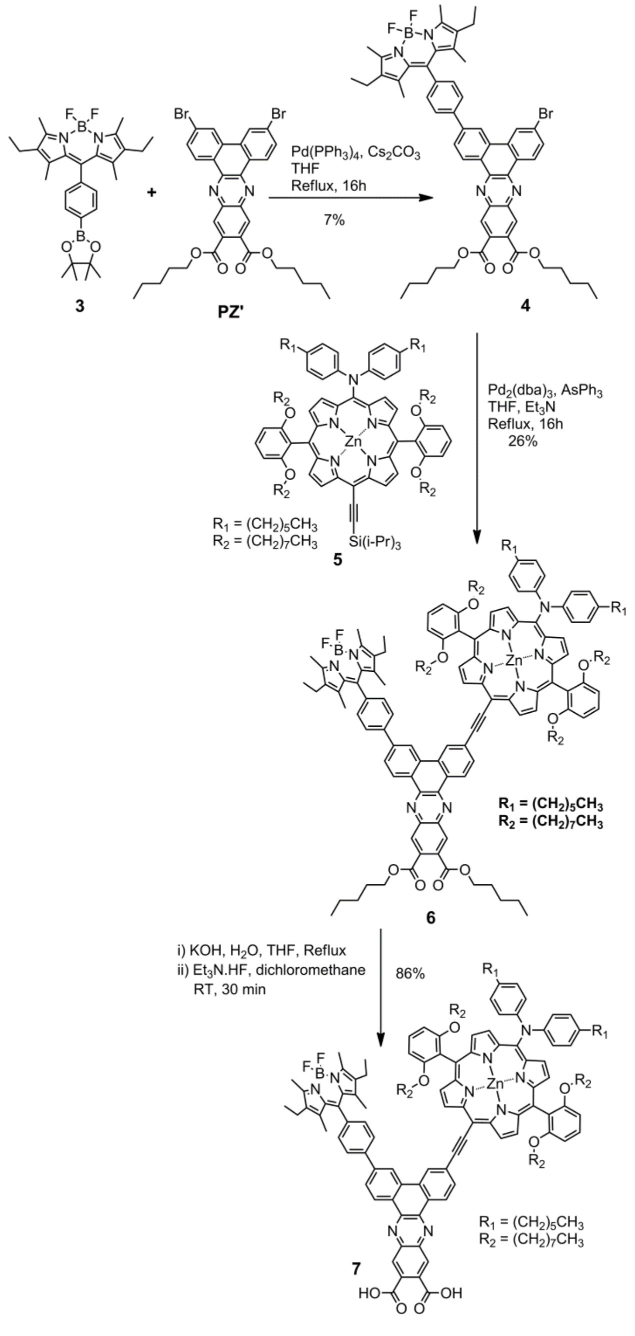
Scheme 1.



Scheme 2.

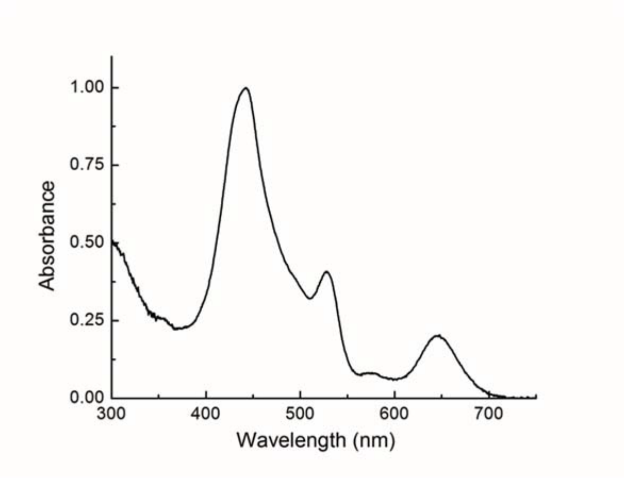

Br
Br
AcOH, EtOH,
1,2-Dichlorobenzne
Reflux 2 d
98 %
H2N
NH2
N
N
1
i) KOH, EtOH
Reflux, 2 d
ii) 4N HCl
98 %
n-Pentanol
Toluene, H2SO4
Reflux 2 d
100%
HO
OH
O
PZ'
2

Scheme 3.



Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$
THF
Reflux, 16h
7%
3
PZ'
4
R$_1$ = (CH$_2$)$_5$CH$_3$
R$_2$ = (CH$_2$)$_7$CH$_3$
Si(i-Pr)$_3$
5
Pd$_2$(dba)$_3$, AsPh$_3$
THF, Et$_3$N
Reflux, 16h
26%
6
i) KOH, H$_2$O, THF, Reflux
ii) Et$_3$N.HF, dichloromethane
RT, 30 min
86%
7

Figure 2.


1.00
0.75
0.50
0.25
0.00
Absorbance
300
400
500
600
700
Wavelength (nm)