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Nucleophilic Substitution on (Pentafluorophenyl)dipyrromethane: A New Route to Building Blocks for Functionalized BODIPYs and Tetrapyrroles

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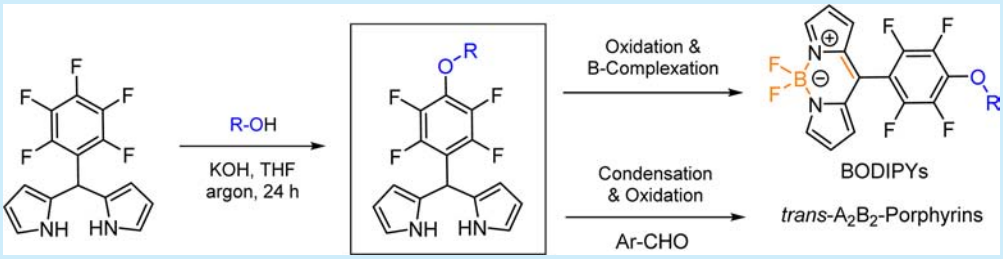
Supporting Information



ABSTRACT: The reaction of alcohols with (pentafluorophenyl)dipyrromethane (PFP-DPM) under basic conditions has been studied, giving access to the corresponding alkoxy-substituted DPMs. This method represents the first high-yielding substitution of PFP-DPM carried out with oxygen nucleophiles. Condensation of these prefunctionalized DPMs with aldehydes led to the respective *trans*-A_2B_2 porphyrins. This pathway allows a simple synthesis of multifunctionalized tetrapyrroles. Oxidation and boron complexation of these DPMs, on the other hand, led to *meso*-functionalized difluoroboraindacenes (BODIPYs). In addition, nucleophilic substitution of PFP-BODIPY with sodium azide led to a 4-azidophenyl derivative, thus further enhancing the scope of reactive sites suitable for subsequent transformations.

The concept of building block chemistry is of essential importance in organic synthesis. Dipyrromethanes (DPMs) are typical building blocks mainly used for the synthesis of porphyrinoids as, e.g., hexaphyrins, dipyrrins, *trans*-porphyrins, corroles, calixphyrins, or calixpyrroles.[1] Porphyrinoids are of wide interest in fields such as medicine, material sciences, and optics due to their photophysical and photochemical properties.[2−4] Furthermore, DPMs are capable of specific metal ion recognition with application in environmental chemistry.[5] Within the past decade, the growth of synthetic approaches toward *meso*-substituted DPMs can be observed. The research with DPMs has also expanded onto the field of boron-centered dipyrromethenes (BODIPYs), which are excellent dyes for imaging probes due to their high fluorescence quantum yields.[6] This type of fluorophore is gaining steadily growing synthetic interest due to their application in fields like organic-based photonics, OLED technology, and fluorescent probes for cell imaging.[7,8] BODIPYs are easily accessible from DPMs in a multistep one-pot reaction.[9]

The synthesis of *meso*-substituted DPMs in particular has improved dramatically within the past decade.[1a,b,i] *meso*-Substituted DPMs can be synthesized via several pathways:[1a] (i) condensation of pyrrole with an aldehyde or ketone under Lewis or Brønsted acid catalysis (e.g., trifluoroacetic acid (TFA),[10a,b] $BF_3{\cdot}OEt_2$,[10c] or $InCl_3$[10d]), where pyrrole is used in excess to minimize the formation of longer chain oligomers; this method allows DPM synthesis typically on a gram scale; (ii) a stepwise approach from α-acylpyrroles which enables the synthesis of unsymmetrical DPMs;[11] (iii) addition of pyrrole to terminal alkynes under $In(OTf)_3$[12] catalysis.

Besides the synthesis of the basic DPM skeleton, subsequent functionalization is an additional option. Modifications have been described for the α- or β-pyrrole position; however, substituents in the *meso*-position are nearly exclusively introduced when the basic DPM structure is formed.[1a,b] DPMs are known to be air-sensitive and acid-labile compounds that may undergo oxidation reactions to dipyrromethenes, "scrambling" (acid-catalyzed recombination of the DPM), or polymerization.[13] As a consequence, adequate reaction conditions and smooth transformations are required. The stability of *meso*-substituted DPMs heavily depends on their substitution: strong electron-withdrawing substituents can stabilize the DPM by decreasing the electron density and thus lower the reactivity toward decomposition or scrambling.[13b] The pentafluorophenyl group (PFP) fulfils this criterion due to the strong electron-withdrawing nature of the PFP group; hence, the corresponding DPM **1**[14] features higher stability compared to simple *meso*-phenyl- or alkyl-substituted derivatives. On the other hand, the susceptibility toward nucleophiles is increased as a result of the electron deficiency of the PFP group. This type of fluorine

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replacement by nucleophilic substitution reaction is known for various compounds such as pentafluorobenzonitrile,[15a] pentafluorobenzaldehyde,[15b] pentafluorobiphenyl[15c] or PFP-substituted porphyrins.[16]

Although five fluorine atoms are present in the PFP group, under suitable reaction conditions the exchange takes place with very high regioselectivity in the *para*-position. This property makes the PFP group interesting as a platform for the subsequent functionalization of *meso*-substituted DPMs. In addition, such prefunctionalized DPMs enable the synthesis of tetrapyrroles with a defined arrangement of substituents, e.g., *trans*-A_2B_2-porphyrins or A_2B-corrols.

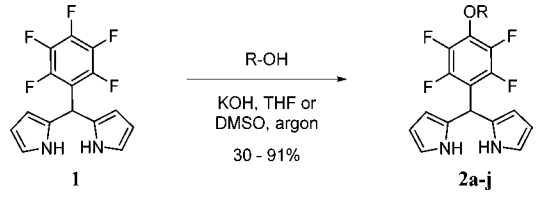
The synthesis and modification of PFP-substituted porphyrinoids and their precursors is one of our main interests. The nucleophilic substitution on such compounds has been investigated with porphyrins, corroles, or other porphyrinoid structures with a focus on amines or thiols.[16] The use of alcohols and alkoxides, respectively, which are relatively weak nucleophiles, on the other hand, has found less attention.[17] Though in most cases strong bases like sodium hydride are used to generate the alkoxide, there have also been occasional reports on milder conditions, employing, for instance, the alcohols together with KOH in THF or DMSO which proved to be the method of choice specifically for functionalized alcohols.[18]

In principle, PFP-DPM **1** should as well be susceptible to a nucleophilic substitution with alcohols. We therefore tested the reaction protocol with this system. For the multigram synthesis of DPM **1**,[14] pentafluorobenzaldehyde (PFBA) was treated with an excess of pyrrole and with TFA (10 mol %) under solvent-free conditions. The *p*-fluorine exchange of **1** was then carried out at room temperature under an inert gas atmosphere to prevent oxidation of the DPM (Table 1). DPM **1** and the alcohol were dissolved in dry THF or DMSO, and fresh finely powdered KOH was added. First attempts were performed in DMSO. However, regardless of whether the reaction was carried out with equimolar amounts of the reactants or with an excess of alcohol, a full conversion was not observed. Side product formation such as replacement of *p*-fluorine by hydroxide or overreaction with the alkoxide (additional *meta*- and *ortho*-substitution) was detected, while starting material was still present. The solubility of KOH in DMSO seems to play an important role during the reaction; therefore, eventually THF was chosen where KOH, in contrast to DMSO, is nearly insoluble. These mild reaction conditions (THF, rt, solid KOH, argon) afforded the *para*-substituted tetrafluorophenyl DPMs **2a**–**j** with good to high yields.

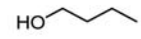
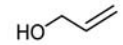
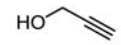
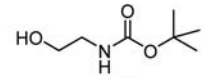
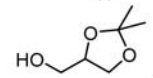
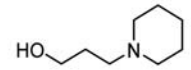
Alcohols carrying an additional alkenyl or alkynyl group were chosen with the intention to obtain products suitable for further transformations, e.g., coupling reactions (Table 1, entries 2–5). To introduce polar substituents, protected glycerol, an *N*-BOC-protected amine, and diols were used (Table 1, entries 4–8). All reactions proceeded smoothly under the chosen reaction conditions. The reaction of **1** with *cis*-butene-1,4-diol to DPM **2d** resulted in the additional formation of the double substitution product **2e** that was isolated in 13% yield. Decreasing the equivalents of alcohol (0.5 equiv) promoted the formation of dimer **2e** (68%). Surprisingly, for 1,4-butynediol the reaction proceeded better in DMSO (Table 1, entry 6). Under these conditions, the yield increased to 78% and no formation of a double substitution product (like **2e**) was observed.

After successful functionalization of DPM **1** with alcohols giving compounds **2a**–**j**, we explored subsequent transformations. First, the oxidation with DDQ followed by reaction with $BF_3{\cdot}OEt_2$ and DIPEA led to the corresponding BODIPYs **3a**–**g** in a two-step, one-pot reaction with yields up to 55% (Table 2). For DPM **2h**, a simultaneous deprotection was observed during BODIPY formation, resulting in the glycerol-substituted BODIPY **3g**. Even the DPM dimer **2e** could successfully be converted to the corresponding BODIPY dimer **3f**. This strategy of functionalizing the DPM followed by conversion into the BODIPY complements already known methods to functionalize BODIPYs via nucleophilic aromatic substitution.[7]

Table 1. Alcohols Investigated in the Nucleophilic Aromatic Substitution of PFP-DPM, 1[a]



1 **2a-j**

entry	ROH	*t* (h)	2	yield (%)[b]
1		24	**2a**	68
2		48	**2b**	70
3		48	**2c**	91
4		48	**2d**	30[c]
5		48	**2f**	5
6[d]		2		78
7		24	**2g**	70
8		24	**2h**[e]	85
9		24	**2i**	85
10	β-cholestanol	24	**2j**	40

[a]All reactions were carried out under an argon atmosphere in a sealed tube. [b]Yield of purified product. [c]Isolation of double substitution product **2e** as side product (13%). [d]Reaction performed in DMSO. [e]Racemic mixture.

In the absorption spectra of **3a**–**e**, and **3g**, as well as the fluorescence maxima there is only little difference (see the Supporting Information), indicating that the *meso*-substituents do not significantly influence the absorbance behavior in contrast to a substitution in the α- or β-position of the BODIPY.[9a]

We then explored the use of *meso*-functionalized DPMs for condensation reactions to *trans*-A_2B_2-porphyrins. Dipyrromethanes **2b**, **2c**, and **2h** were reacted with 3-acetoxybenzaldehyde (Table 3) regioselectively, furnishing the corresponding *trans*-A_2B_2-porphyrins **4a**–**c** with yields up to 27%. All condensation reactions were carried out under standard conditions (TFA catalysis, argon, followed by oxidation with DDQ).[10a,13a]

In addition, DPM **2h** was condensed with PFBA to obtain *trans*-porphyrin **5** carrying two free PFP groups (Scheme 1).

The two free PFP-groups should allow the synthesis of *trans*-A_2B_2-substituted porphyrins carrying four functional groups in a

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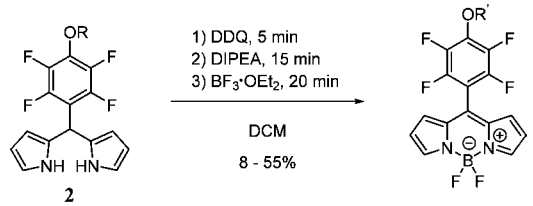
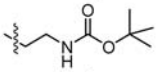
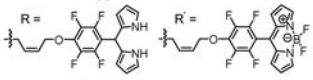
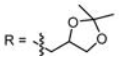
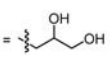
Table 2. Transformation of Functionalized DPMs into BODIPYs[a]

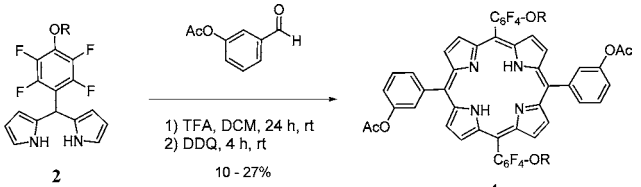


2 → 3a-g

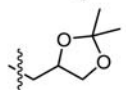
entry	2, R and R′	3	yield (%)[b]
1	R = 	3a	50
2	R = 	3b	55
3	R = 	3c	21
4	R = 	3d	29
5	R = 	3e	8
6	R =  R′ =	3f	19
7	R =  R′ = 	3g[c]	31

[a]All reaction steps were carried out under air and at room temperature. [b]Yield of purified product. [c]Racemic mixture.

Table 3. Condensation of DPMs 2 to *trans*-A_2B_2-porphyrins, 4

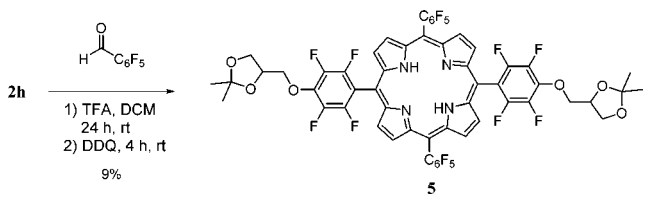


2 → 4a-c

entry	2, R	t (h)	4	yield (%)[a]
1		48	4a	24
2		24	4b	27
3		48	4c[b]	10

[a]Yield of purified product. [b]Racemic mixture.

Scheme 1. Condensation of Functionalized DPM 2e with PFBA to Porphyrin 5

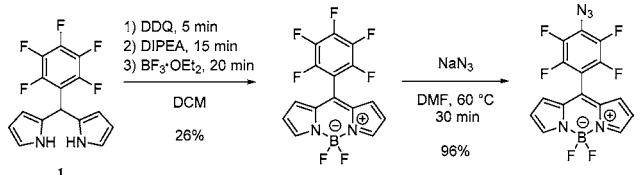


5

defined arrangement employing various nucleophiles such as amines, thiols, alkoxides or azide.[16,17]

In order to increase the variety of substituents, the introduction of an azide group into PFP-dipyrromethane **1** was investigated. While the *p*-fluorine exchange with sodium azide proceeds well with PFP-substituted porphyrins,[16a,18d] no reaction with DPM **1** was observed. However, it was possible to convert PFP-BODIPY **6** into **7** with nearly quantitative yield by direct azidation with NaN_3 in DMF (Scheme 2).

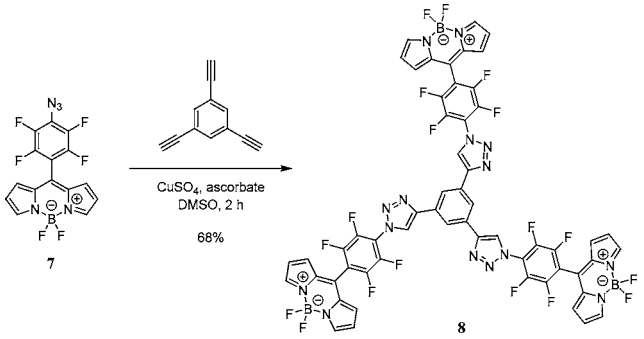
Scheme 2. Synthesis of Azido-Substituted BODIPY 7



1 → 6 → 7

Azido-functionalized BODIPY **7** may serve as a 1,3-dipolar building block for further transformations, e.g., click chemistry.[19] This was exemplified by the reaction of **7** with tris-ethinylbenzene (Scheme 3). Under standard conditions (copper-

Scheme 3. Example for a Triple Azide−Alkyne 1,3-Dipolar Cycloaddition with Azido-Substituted BODIPY 7



7 → 8

(II) sulfate, sodium ascorbate) the corresponding BODIPY-trimer **8** was isolated in 68% yield. This product illustrates that with suitable linker molecules multichromophoric systems can be synthesized. These are not only restricted to BODIPYs; in combination with porphyrins or corroles larger array systems involving different chromophores are accessible.

In conclusion, we have presented the first selective functionalization of (pentafluorophenyl)dipyrromethane **1** with in situ generated alkoxides under basic reaction conditions. With a variety of alcohols that allow the introduction of a broad spectrum of functional groups, a fine-tuning of the DPM for the desired application can be achieved. These *meso*-functionalized DPMs can undergo condensation reactions toward specifically substituted *trans*-A_2B_2-porphyrins without degradation or the need of a postfunctionalization of the macrocycle. The transformation of these substituted DPMs to the corresponding BODIPYs was also achieved. This nucleophilic functionalization of PFP-DPM allows a variety of possibilities toward functionalization of BODIPYs or the coupling of BODIPY fluorophores to other molecular backbones.

Furthermore, it was possible to directly introduce an azido group by the same reaction principle into the PFP-BODIPY **6**. The resulting azido-BODIPY **7** may serve as a platform for further transformations or for simple conjunction to appropriate dipolarophiles by click chemistry.

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■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures; NMR characterization and HRMS analysis data of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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