EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201402816

Synthesis of Highly Fluoroalkyl-Functionalized Oligoporphyrin Systems

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Keywords: Chemical libraries / Porphyrinoids / Fluorine / Aromatic substitution / Mass spectrometry

Four different multiporphyrin systems have been synthesized and characterized. Highly fluoroalkyl-functionalized porphyrins are the most complex objects so far to have exhibited quantum wave nature. We have functionalized larger oligoporphyrin systems with fluoroalkyl chains to increase their mass and minimize their intermolecular interactions. The to-some-extent random substitution of fluorine atoms at the periphery of the oligoporphyrins results in libraries consisting of molecules varying in both the number and spatial distribution of substituents. The mass-selected individual members of these libraries were designed for quantum interference experiments. To investigate the volatilization nature of the molecules within the library, laser desorption and post-ionization studies were performed. These studies demonstrated that molecular beams of suitable velocity and ionization cross-section can be obtained from these libraries. In particular, we present these features for two libraries, based on either a tetrahedrally arranged central porphyrin tetramer or a more planar porphyrin pentamer.

Introduction

The quantum wave nature of massive particles is a fundamental concept of physics and chemistry. It has been seen for electrons,[1] neutrons,[2] atoms,[3] and even complex molecules.[4,5] Quantum delocalization of hot molecules was first observed in 1999 with C_{60}[6] and C_{70}.[7] Full-fledged three-grating molecule interferometers[8] were successfully operated with organic dyes such as tetraphenylporphyrin (TPP).[9] These experiments relied on the availability of stable and lasting effusive thermal beams, a great challenge for complex macromolecules. The use of fluorinated fullerene $C_{60}F_{48}$ was a first step in this direction.[9] Quantum experiments with even larger compounds became possible by attaching fluoroalkyl chains to stable core structures.[10,11] Recently, this strategy was successfully applied to components with a molecular weight even beyond 10000 g/mol, selected from a molecular library consisting of porphyrin structures comprising different numbers of fluoroalkylsulfanyl substituents.[12,13] In the experimental set-up, particles with a small mass range were exclusively observed. Therefore libraries composed of particles of different masses are perfectly suitable as long as the particle with the mass of interest is abundant enough and its mass is sufficiently different to those of its closest members in the library. This concept was successfully demonstrated with a library obtained by random partial substitution of fluorine atoms by fluoroalkylthiolates on *meso*-tetrakis(pentafluorophenyl)porphyrins.[12] To explore the limitations of quantum experiments, high-mass molecules or nanoparticles that can be volatilized with a controlled distribution of mass are required. These molecules or particles should be neutral to avoid perturbation by electric fields. Detection after the interference experiment is facilitated if the particles can be ionized with ultraviolet radiation. To the best of our knowledge, suitable heavy compounds combining the features required for slow beam formation and subsequent photoionization do not yet exist and have therefore to be designed and synthesized. An ideal compound should be stable enough to survive short exposure to temperatures up to 1000 K during laser pulses. In addition, their polarizability/mass ratio should be small to minimize intermolecular binding and facilitate laser evaporation or sublimation. Earlier experiments have already indicated that fluoroalkylsulfanyl side-chains can render large molecules more volatile.[1,3–6] Even for massive molecules, their vapor pressure reached impressive values if they were suitably functionalized at their periphery.[14,15] In a first approach we functionalized the periphery of porphyrin precursors with perfluorinated alkylthiolates with a well-defined substitution pattern[10] as well as randomly to provide a library of potential particles with well-defined molecular weights.[12]

In this work we have extended the library concept to even heavier particles by using oligoporphyrin systems that are not only the core subunits of a larger mass, but that also present an increased number of fluorine atoms that can be

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201402816.

substituted by perfluorinated alkylthiolates. The libraries thereby obtained consist of molecular components of high mass, high volatility, and ionizability under single-photon excitation at 157.6 nm.

Results and Discussion

Molecular Design

We present the synthesis of four different multiporphyrin systems that consist of 2–5 central porphyrin cores and pentafluorophenyl subunits. The synthesis and properties of oligoporphyrin systems are well understood and described in the literature.[16–20] These compounds are appealing starting materials for the assembly of molecular libraries for interference experiments as the molecular weights of their components can be tailored by varying the number and/or length of the perfluoroalkyl side-chains. Also, their desorption and post-ionization properties can be tuned to some extent by the presence or absence of metal ions in their porphyrin systems.

Of particular interest are the precursors **1** and **2**, which consist of four and five porphyrin subunits, respectively. As shown in Figure 1, up to 60 perfluoroalkyl side-chains can be connected by substituting the fluorine atoms of both core units. To the best of our knowledge, there has been only one example of a photoionizable fluorinated porphyrin library reported in the literature[13] so far. By using **1** and **2** as precursors of libraries, the mass of the library components can be increased. In addition, we can investigate the difference between the extended conjugation in **2** and the limited conjugation in **1**. The conjugation in **1** is broken by the tetrahedral sp^3-hybridized carbon center. Pentamer **2** consists of porphyrin centers that are interlinked by ethynyl bridges at their *meso* positions. Acetylene-linked π systems are known for their reduced conjugation due to the mismatch of π–π and π*–π* interactions at the sp^1–sp^2 connection. However, porphyrins interlinked directly by *meso*-ethynyl units are reported to prevent the π systems from twisting out of plane, which extends the conjugation in the case of **2**.[21,22] We hypothesized that the difference in planarity and the extent of conjugation might be reflected in different desorption and photo-ionization behavior of the libraries obtained from both precursors.

To develop the synthetic procedures and investigate the modularity of the strategy, the porphyrin dimer **3** and trimer **4** were also synthesized (Figure 2). These model compounds can be obtained from the same monomeric porphyrin building blocks. As the main focus of our work is on volatile and photo-ionizable molecules with masses well

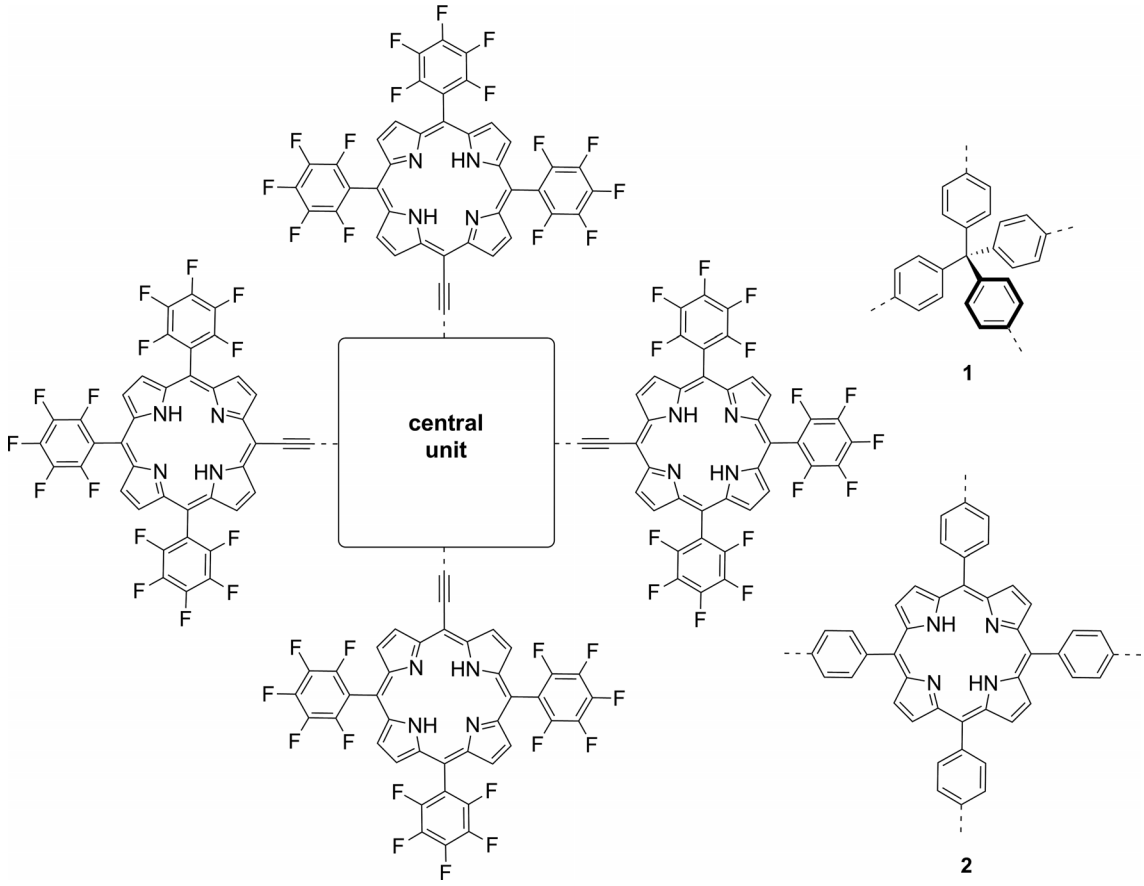
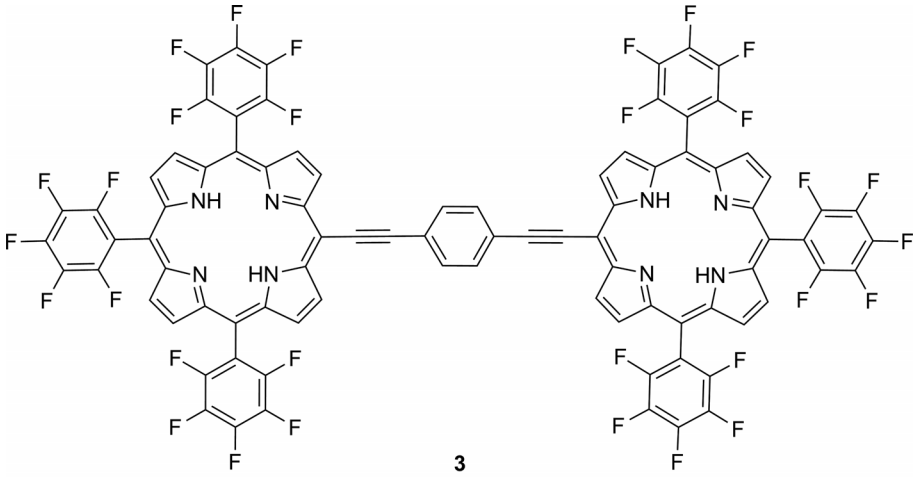


Figure 1. Porphyrin tetramer **1** and pentamer **2** with two different central units, namely a tetraphenylmethane and a porphyrin, respectively. Both compounds have 60 peripheral fluorines that are accessible for S_NAr reactions, which allows their mass to be increased by suitable nucleophiles.



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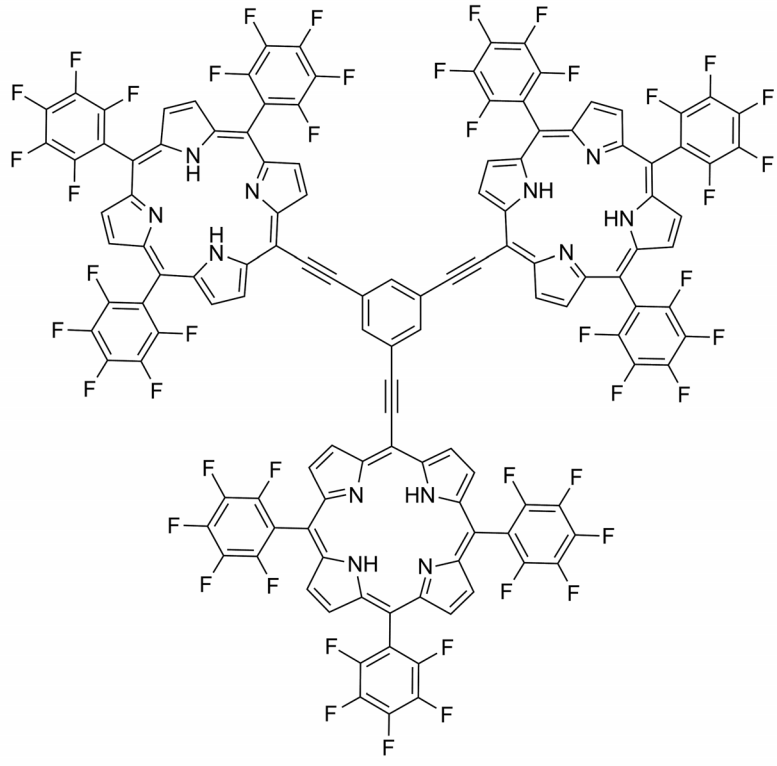

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Figure 2. Porphyrin dimer **3** and trimer **4**. Both are built around a central phenyl unit. Dimer **3** has 30 accessible positions for S_NAr reactions, whereas trimer **4** has 45 accessible positions.

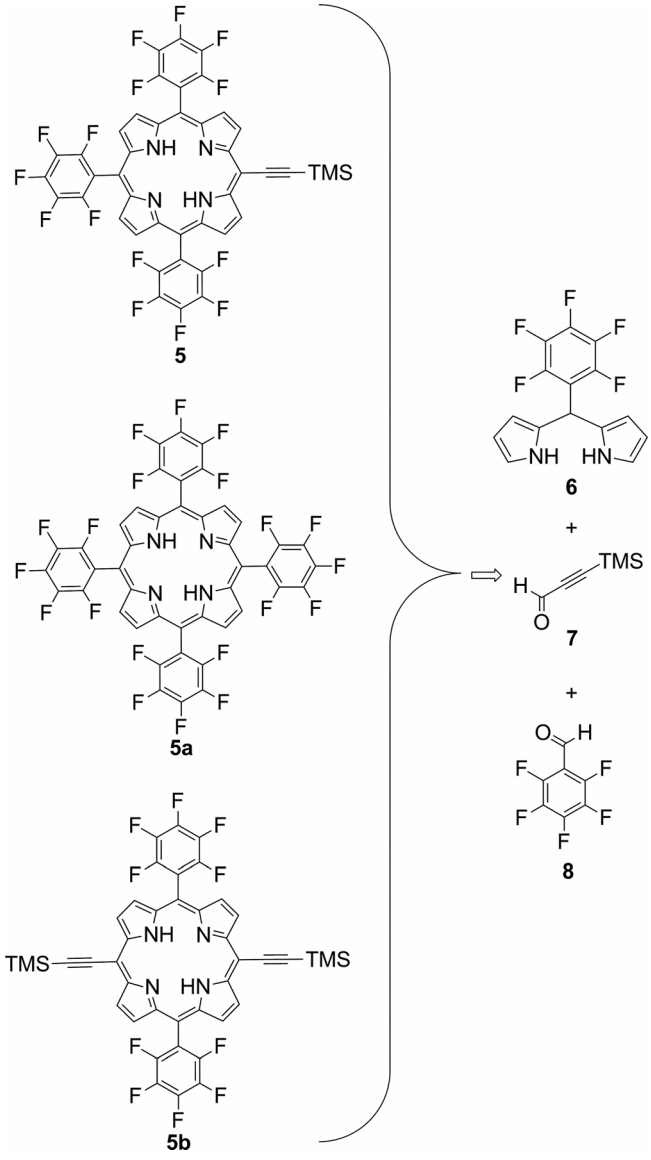
above 20000 g/mol, these two central units (**3** and **4**) were less promising precursors of high-mass libraries than **1** and **2**.[12]

Synthetic Strategy

With these multiporphyrin systems in hand, molecular libraries were obtained by attaching different numbers of perfluoroalkylsulfanyl side-chains to the multiporphyrin cores through a nucleophilic aromatic substitution reaction under basic conditions.

The oligoporphyrin systems can be assembled by using copper-free Sonogashira cross-coupling conditions to avoid coordination of the copper ion to the multidentate porphyrin binding site. Similar copper-free cross-coupling reaction conditions have already been used for the synthesis of porphyrin dimers and trimers by Achelle et al. in 2011 and are reported to be well suited to porphyrin systems.[23–27] All the coupling reactions presented herein used the same monomeric ethynylporphyrin building block **5** (Scheme 1), which can be synthesized from the dipyrromethane compound **6**, TMS-propynal (**7**), and pentafluorobenzaldehyde

(**8**) following the general procedure reported for the synthesis of unsymmetrical porphyrins by Fathalla and Jayawickramarajah.[28] This statistical reaction yields three different porphyrins, namely compound **5**, *meso*-tetrakis(pentafluorophenyl)porphyrin (**5a**), and the diethynyl derivative **5b** (Scheme 1). The statistical nature of the reaction lowers the yield of **5** as the key intermediate. Dipyrromethane **6** can be obtained in one step from pentafluorobenzaldehyde (**8**) and pyrrole.[29,30]



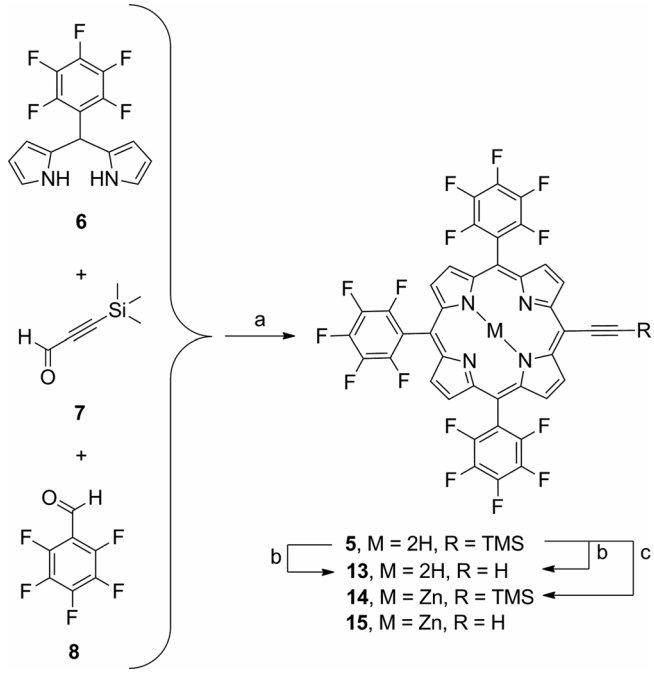
Scheme 1. Synthetic strategy towards the monomeric porphyrin building block **5**. The synthesis using dipyrromethane **6** and the corresponding aldehydes **7** and **8** leads to a statistical mixture of three different porphyrins (**5**, **5a**, and **5b**).

To connect the monomeric porphyrin **5** as efficiently as possible by Sonogashira cross-coupling, iodine precursors are best suited as the connecting units. 1,4-Diiodobenzene (**9**) and 1,3,5-triiodobenzene (**10**) are commercially available and were used as starting materials to synthesize porphyrin dimer **3** and trimer **4**, respectively. The central unit of porphyrin tetramer **1** was derived from tetrakis(4-iodophenyl)-methane (**11**), which can be obtained from tetraphenylmethane,[31] and porphyrin pentamer **2** was synthesized from *meso*-tetrakis(4-iodophenyl)porphyrin (**12**) as the central unit, which can by synthesized as described below following literature procedures.[30,32]

Synthesis

The central units of porphyrin dimer **3** and trimer **4** were synthesized following literature procedures. Tetrakis(4-iodophenyl)methane (**11**) was synthesized from tetraphenylmethane by using the iodination conditions developed by Aujard et al.[31] Tetrakis(4-iodophenyl)methane (**11**) was obtained in 74% yield. By using the conditions developed by Lindsey et al., *meso*-tetrakis(4-iodophenyl)porphyrin (**12**) was obtained in a yield of 14%.[30] In the first step, the key porphyrin building block **5** was synthesized. For this purpose, dipyrromethane **6** was synthesized from pyrrole and pentafluorobenzaldehyde (**8**) in an electrophilic aromatic substitution reaction of pyrrole. The reaction was performed under acidic conditions by using trifluoroacetic acid (TFA) in pyrrole as solvent. These conditions were found to be ideal by Lee and Lindsey.[29,30] Following this procedure, dipyrromethane **6** was obtained in a yield of 91%.

The trimethylsilyl-protected ethynylporphyrin key building block **5** was synthesized from dipyrromethane **6**, trimethylsilylpropynal (**7**), and pentafluorobenzaldehyde (**8**) by using a catalytic amount of boron trifluoride–diethyl



Scheme 2. Synthesis of the unsymmetric porphyrin building block **5** in a statistical reaction, the deprotected porphyrin **13** and their zinc derivatives **14** and **15**. Reagents and conditions: a) 1. $BF_3{\cdot}O(Et)_2$, $CHCl_3$, room temp., 18 h; 2. DDQ, room temp., 2 h, 15%; b) TBAF, CH_2Cl_2, 30 min, quant.; c) $Zn(CH_3COO)_2$, CH_2Cl_2, CH_3OH, 24 h, quant.

ether as Lewis acid (Scheme 2). Subsequent oxidization with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) provided the desired porphyrin derivative. The reaction conditions reported by Fathalla and Jayawickramarajah in 2009 for non-fluorinated porphyrins were systematically varied (Table 1), seeking to optimize the conditions for the fluorinated starting materials.[28,33] Longer reaction times increased the yield, and replacing DDQ by *p*-chloranil reduced the isolated yield of the reaction. The yield was further improved by compensating the lower reactivity of pentafluorobenzaldehyde (**8**) by doubling its concentration.

The crude product was purified by filtration through silica and subsequently divided into its components by multiple column chromatography. Bu using the optimized conditions, the pure porphyrin **5** was obtained in a yield of 15%.

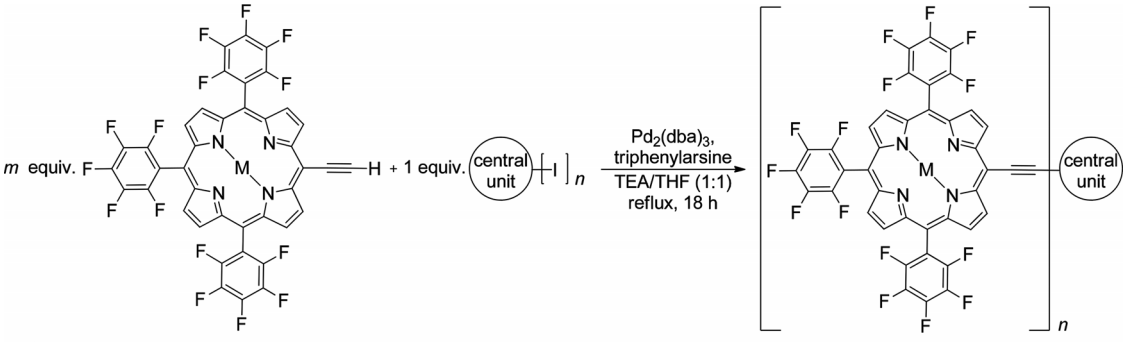
Table 1. Optimization of the reaction conditions for the synthesis of porphyrin monomer **5**.[a]

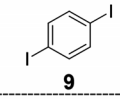
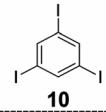
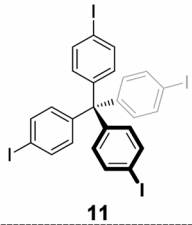
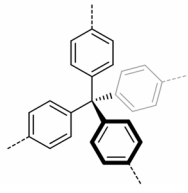
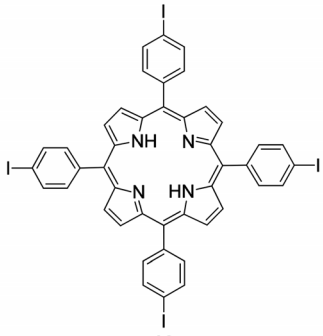
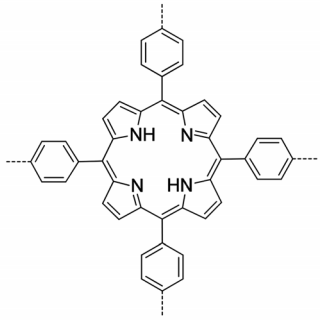
6 [equiv.]	**7** [equiv.]	**8** [equiv.]	Time [h]	Oxidizing agent	Yield[b] [%]
2	1	1	0.75	DDQ	3
2	1	1	0.33	DDQ	0
2	1	1	1	DDQ	8
2	1	1	18	DDQ	10
2	1	1	18	*p*-chloranil	7
2	1.1	2	18	DDQ	15

[a] All reactions were performed at room temp. and with the same concentration and scale. [b] Isolated yields.

The TMS-masked ethynylporphyrin **5** was deprotected by using tetrabutylammonium fluoride (TBAF) in dichloromethane to provide the ethynyl derivative **13** in quantitative

Table 2. Sonogashira cross-coupling reaction using different central units (all yields are isolated yields).



Compound	Central unit	M	*m* (equiv. **5**)	Yield [%]	Product	*n*
 **9**		Zn	2.3	56	**3B**	2
 **10**		Zn	3.5	35	**4B**	3
 **11**		Zn	4.25	51	**1B**	4
 **12**		2H	4.25	60	**2**	4

yield. Initial attempts to substitute the fluorine atoms of the metal-free porphyrins by perfluorinated alkylthiols were not successful in all cases and thus a central Zn atom was inserted prior to the Sonogashira cross-coupling reactions for the synthesis of the porphyrin systems **1**, **3**, and **4** (the zinc porphyrin systems being **1B**, **3B**, and **4B**). Interestingly, the metal-free pentameric porphyrin system **2** turned out to be more stable under basic substitution conditions, which allowed it to be used as starting material for the synthesis of its molecular libraries.

The coordination of a central Zn atom to the porphyrin was achieved by using zinc acetate in a solvent mixture of dichloromethane and methanol. Porphyrin **14** was deprotected under the same conditions as those used for the metal-free derivative **5**. The deprotected zinc ethynylporphyrin **15** was obtained in quantitative yield over two steps from **5**.

With the ethynyl-functionalized porphyrins **13** and **15** in hand, their reactions with different central units comprising various numbers of iodine substituents were investigated for the assembly of porphyrin oligomers by Sonogashira cross-coupling reactions, as shown in Table 2.

The reactions were performed under copper-free cross-coupling reaction conditions following the protocol reported in 2011 by Achelle at al.[23] Preliminary attempts using classical conditions and catalytic amounts of copper iodide resulted in the formation of the diacetylene as the main product. The competing formation of this homo-coupled product not only reduced the yield of the desired porphyrin oligomers, but also the separation of the two structures by column chromatography turned out to be extremely challenging due to their similar polarities. By using the conditions of Achelle et al. without an additional copper co-catalyst, the formation of the diacetylene was no longer observed and thus these reaction conditions were exclusively considered. Subsequent column chromatography provided the porphyrin systems in reasonable yields ranging from 35 to 60% (see Table 2).

These oligoporphyrin systems with various numbers of peripheral pentafluorophenyl groups present a large number of fluorines that can be substituted in S_NAr reactions and are thus ideally suited as precursors of molecular libraries. As the degree of substitution and also the substitution pattern are not uniform in this peripheral functionalization process, these precursors are the last structurally perfectly defined molecular building blocks in the synthesis of the libraries. All four precursors were thus characterized as well as possible by ^1H and ^{19}F NMR spectroscopy and HRMS. Elemental analyses of these compounds were not performed because the highly fluorinated compounds caused severe damage to the GC analyzer column.

Molecule Libraries

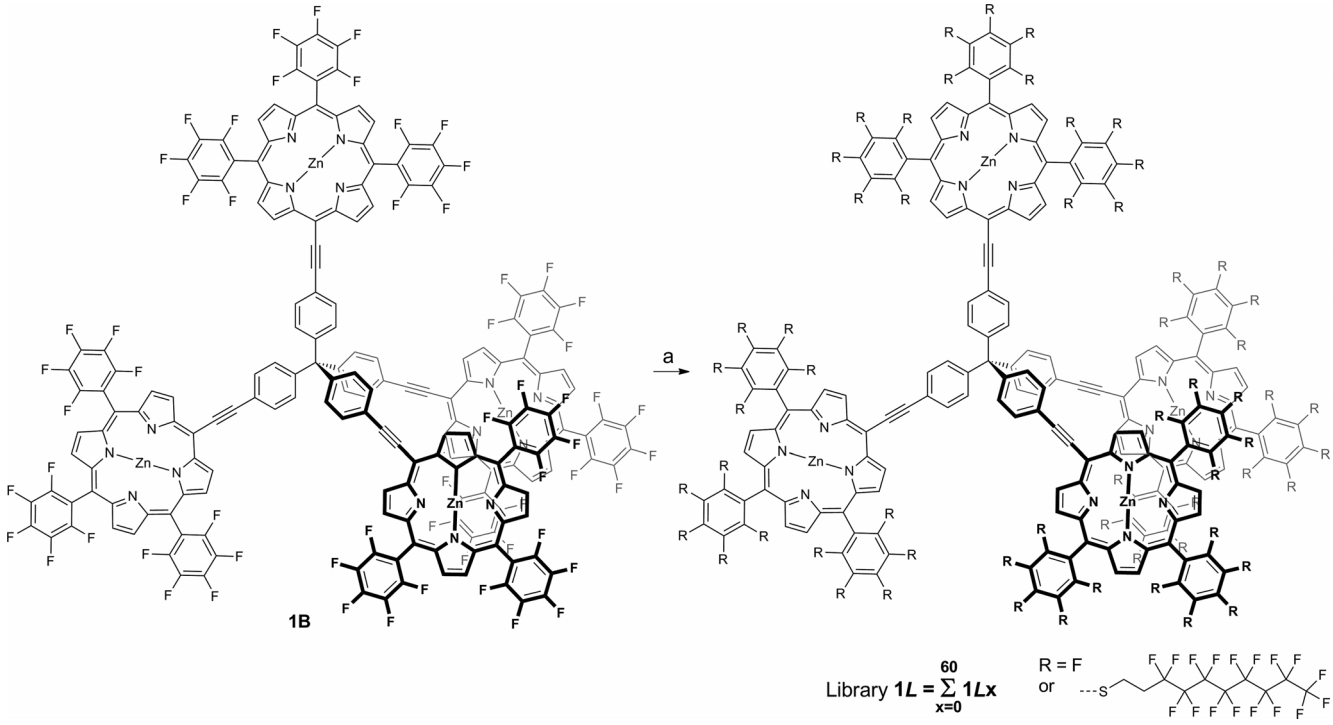
To obtain libraries of high-mass molecules, we focused on the oligoporphyrin systems **1B** and **2**, both presenting 60 fluorine atoms as potential substitution positions for perfluoroalkylthiolates. The peripheral nucleophilic aromatic substitution with fluoroalkylsulfanyl side-chains not only increases the mass of the oligoporphyrin, the reduced polarizability of these chains results in low van der Waals interactions and thus decreases the intermolecular attraction. The peripheral substitution was performed by using the commercially available 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (**16**) under basic conditions. For the tetraporphyrin **1B**, 120 equiv. of the thiol **16** were heated at 90 °C for 18 h in the presence of K_2CO_3 as base. After aqueous work-up and extraction with *tert*-butyl methyl ether (TBME), the combined organic phases were concentrated and purified by filtration through a short plug of silica. The composition of the obtained library **1*L*** was analyzed by MALDI-TOF mass spectrometry. As expected, we observed only library components with masses that differ by $\Delta_m = m(C_{10}H_4F_{17}S) - m(F) = 479 - 19 = 460$. The composition of the library is detailed in Table 3. The most abundant component was **1*L*18** with 18 fluorine atoms substituted by the fluoroalkylsulfanyl side-chain and a mass of 12230 amu. The components of the library include those with between 15 and 22 introduced fluoroalkylsulfanyl side-chains. It is noteworthy that for a given member of the library **1*Lx***, the number *x* of fluoroalkylsulfanyl side-chains is the same in all molecules, but the library is composed of structural isomers. For all molecules of the library member **1*Lx***, exactly *x* of the 60 fluorine atoms have been substituted by fluorinated alkylthiolates, but which of the fluorine atoms has been substituted is to some extent a random process. This results in some structural diversity between the isomers that define the library member **1*Lx***. However, in spite of the statistical reaction, there is some control over the substitution pattern. In earlier studies we observed that the fluorine atoms at the *para* positions are substituted first. Analyzing the ^{19}F NMR spectra of the entire library corroborates this finding. In the library **1*L*** with **1*L*15** as the lowest-molecular-weight member (10895 amu), all 12 fluorine atoms at the *para* positions have been substituted.

For the peripheral functionalization of the porphyrin pentamer **2**, similar conditions were applied, but with an even larger excess of the nucleophile. By exposing **2** to 300 equiv. of both the thiol **16** and K_2CO_3 in DMF at 90 °C for 24 h followed by similar work-up to that described above for the library **1*Lx***, the library **2*Lx*** was obtained. As detailed in Table 4, 35–43 side-chains were introduced into the porphyrin pentamer **2** with the most abundant member being **2*L*40** (22454 amu).

Similarly to the observation made for **1*Lx***, ^{19}F NMR analysis revealed the complete substitution of all the *para*-fluorine substituents for all members of the library **2*Lx***, which points to the increased reactivity of this position.

The considerably higher number of substituted fluorine atoms in the case of **2*Lx*** compared with **1*Lx*** has mainly been attributed to the higher concentration of the nucleophile during its synthesis. However, in the planar and more extended structure of **2**, the fluorine atoms are farther away from each other. Therefore the substitution seems to be easier in **2** than in **1B**.

Table 3. Nucleophilic aromatic substitution reaction of porphyrin tetramer **1B** to give porphyrin library **1*Lx*** with *x* being the number of alkylthiol substituents that have replaced fluorine atoms.



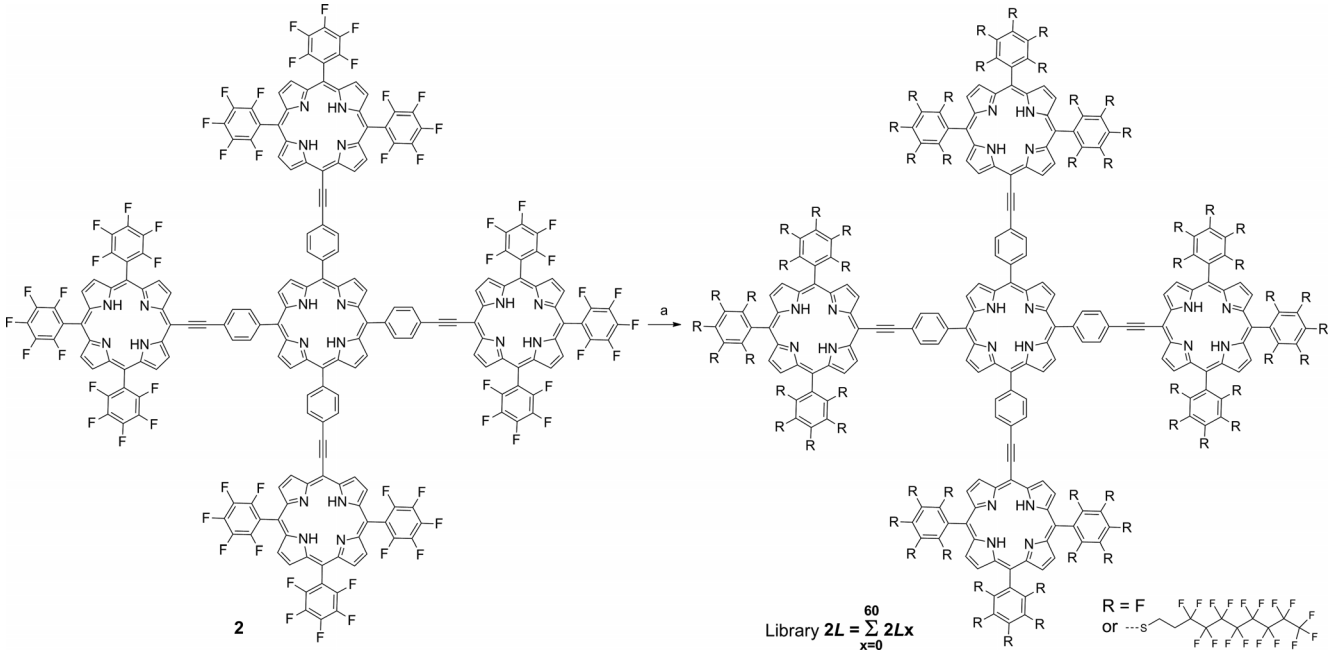
1*Lx*	*x* (number of $C_{10}H_6F_{17}S$ units)	Number of F atoms (= 60 – *x*)	Mass [g/mol]	Calcd. mass [g/mol]	Rel. intensity [%]
1*L*15	15	45	10895	10790	8
1*L*16	16	44	11288	11250	54
1*L*17	17	43	11785	11711	94
1*L*18	18	42	12230	12171	100
1*L*19	19	41	12668	12631	68
1*L*20	20	40	13153	13091	38
1*L*21	21	39	13620	13551	17
1*L*22	22	38	14073	14012	5

[a] The library members have the elemental formula $C_{185}H_{48}F_{20-x}N_{16}Zn_4[S(CH_2)_2C_8F_{17}]_x$ in which x = 15–22 and the most abundant member, **1*L*18**, has x = 18 (12230 g/mol). Reagents and conditions: a) 120 equiv. 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (**16**), 120 equiv. K_2CO_3, DMF, 90 °C, 18 h.

The compositions of both libraries were studied by MALDI-TOF mass spectrometry. Figure 3 shows the mass spectrum of **1*Lx*** with masses between 10000 and 15000 g/mol. Eye-catching is the regular periodic mass difference between adjacent peaks, which corresponds roughly to the mass difference between an additional alkylthiolate substituting a fluorine atom of the porphyrin core (460 ± 10 amu). To label the peaks the strongest signal was selected. Variations from the theoretical values are due to the natural isotopic distribution. Another aspect that leads to broadening of the peaks is the coexistence of signals due to $[M]^+$ and $[M + H]^+$ in the spectra. The specific mass peaks correspond to different numbers of perfluoroalkyl substituents on the fluorinated porphyrin cores. The precise composition of the library determined by MALDI-TOF MS is listed in Table 3 above.

Exposing the porphyrin pentamer **2** to a higher concentration of alkylthiol provided even higher masses. Figure 4 shows the spectrum of library **2*Lx*** in the mass range between 19000 and 24000 g/mol. Interestingly, we observed increased ionization in the MALDI-TOF MS for **2*Lx*** compared with **1*Lx***, as its ion signal is about 10 times higher integrated over the same number of shots. Better ionization properties have previously been observed for metal-free porphyrins in studies on single porphyrins as central cores for libraries. We thus attribute this difference to the difference in the coordination state of the oligoporphyrins. A similar systematic separation of the peaks by the difference in mass between the fluorinated alkylthiol and the substituted fluorine atom is observed. However, the peaks are even broader in the case of **2*Lx***. This broadening of the peaks can be explained by the two-fold higher masses of the components of library **2*Lx*** compared with those of **1*Lx***. The highest signal was obtained for **2*L*40** with x = 40. A complete list of the components of the library is given in Table 4 above.

Table 4. Nucleophilic aromatic substitution reaction of porphyrin pentamer **2** to give porphyrin library **2*Lx*** with *x* being the number of alkylthiol substituents that have replaced a fluorione atom.



2*Lx*	*x* (number of $C_{10}H_6F_{17}S$ units)	Number of F atoms (= 60 – *x*)	Mass [g/mol]	Calcd. mass [g/mol]	Rel. intensity [%]
2*L*35	35	25	20121	20041	6
2*L*36	36	24	20588	20501	26
2*L*37	37	23	21061	20961	50
2*L*38	38	22	21514	21421	78
2*L*39	39	21	21983	21881	89
2*L*40	40	20	22454	22341	100
2*L*41	41	19	22931	22801	62
2*L*42	42	18	23404	23261	24
2*L*43	43	17	23878	23722	5

[a] The members of the library have the elemental formula $C_{204}H_{66}F_{60-x}N_{20}[S(CH_2)_2C_8F_{17}]_x$ in which *x* = 35–43 and with the most abundant member being for *x* = 40 (12230 g/mol). Reagents and conditions: a) 300 equiv. 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (**16**), 300 equiv. K_2CO_3, DMF, 90 °C, 24 h.

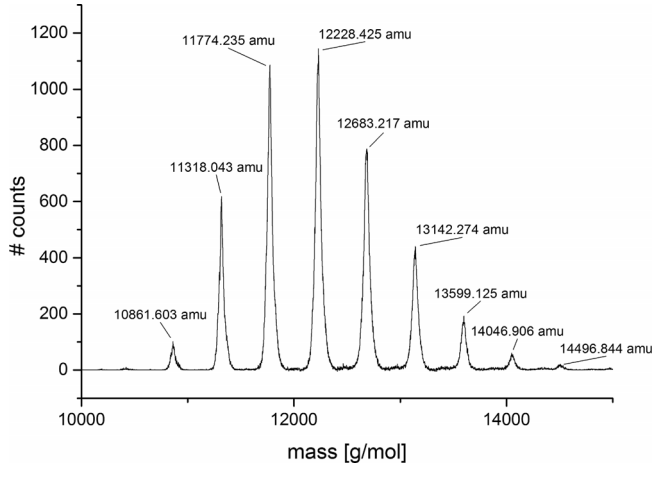


Figure 3. MALDI-TOF analysis of library **1*Lx*** bearing 15–22 perfluoroalkyl side-chains (*x* = 15–22). The masses range between 10000 and 15000 g/mol and a maximum is observed for *x* = 18 (12228 g/mol). The spectrum was calibrated by using CsI_3 clusters.[34] DCTB {*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile} was used as matrix.[35] The spectrum was integrated over 2000 shots.

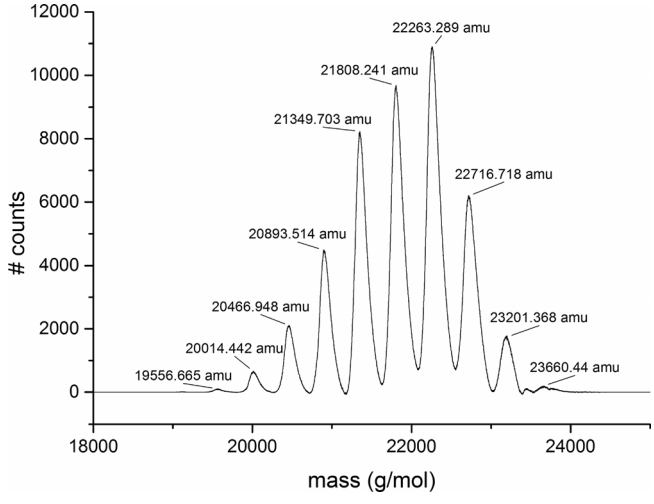


Figure 4. MALDI-TOF analysis library **2*Lx*** bearing 35–43 perfluoroalkyl side-chains (*x* = 35–43). The mass range is between 19000 and 24000 g/mol and a maximum is observed for *x* = 40 (22263 g/mol). The spectrum was calibrated by using CsI_3 clusters.[34] DCTB was used as matrix.[35] The number of counts was obtained by integration over 2000 shots.

Based on the characterization of the libraries **1*Lx*** and **2*Lx***, the ability of their members to provide molecular beams upon excitation was investigated.

Desorption Studies

To test whether the libraries **1*Lx*** and **2*Lx*** fulfil the requirements for future matter-wave experiments, we carried out additional laser desorption and post-ionization studies. We are interested in libraries that can be volatilized at low velocity and post-ionized without major fragmentation. For this purpose, a Nd:YAG laser beam (λ = 355 nm, τ = 4 ns) was focused to a spot diameter of 350 μm and directed onto the target plate at an angle of 30°. The sample was prepared by allowing a droplet of a library solution to dry on the substrate. Either 2.5 mg of **1*Lx*** dissolved in 1.5 mL diethyl ether or 7 mg of **2*Lx*** in 1.5 mL TBME was used. An excimer laser (λ = 157.6 nm, E_{ph} = 7.89 eV) was used for post-ionization of the neutrally desorbed molecules, which were then extracted into a linear TOF-MS.

A comparison of Figure 5 (a) (**1*Lx***) with Figure 5 (b) (**2*Lx***) shows two major differences. The saturation intensity of library **2*Lx*** exceeds that of library **1*Lx*** by almost a factor of two. The faster rise of the **1*Lx*** desorption curve indicates a lower evaporation enthalpy with respect to **2*Lx***.[10,36] This is consistent with a lower polarizability and smaller van der Waals interactions in the components of library **1*Lx*** in comparison with **2*Lx***. **2*Lx*** has on average twice as many fluoroalkylsulfanyl side-chains and a more polarizable core than **1*Lx***.[37,38] Also, the more planar shape of the core structure of **2*Lx*** compared with the rather spherical shape of **1*Lx*** might play a role.

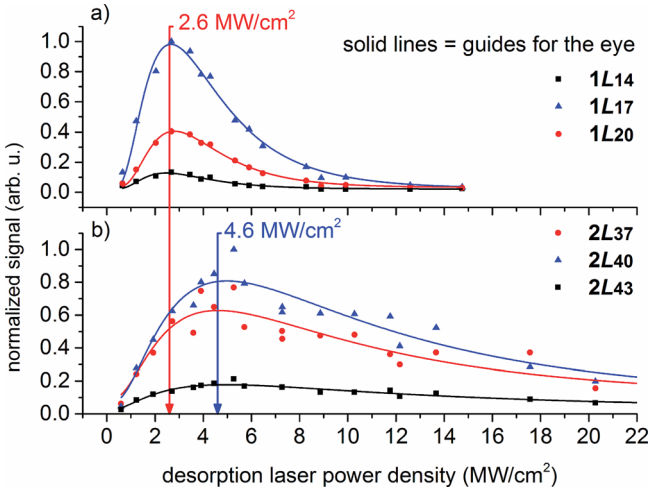


Figure 5. Variation of the desorption laser power at constant post-ionization laser intensity. a) Data for the molecular library **1*Lx***. b) Data for the molecular library **2*Lx***. In comparison with the data for the lower-mass tetramer shown in (a), the pentamer reaches saturation at a higher desorption intensity. This indicates its higher enthalpy of volatilization as well as its higher thermal stability in comparison with the molecular library **1*Lx***. Different symbols (triangles, circles and squares) represent different numbers of perfluoroalkylated chains. The solid lines are guides to the eye. Each data point is a sum of 90 laser shots.

Another difference lies in the fragmentation behavior of the two molecular libraries. Thermal decomposition causes saturation in both cases, but the decay of **1*Lx*** is faster than for **2*Lx***. This is consistent with the observation that relaxation rates are strongly correlated to molecular size.[39] The members of the library **2*Lx*** possess about twice as many energy vibrational relaxation channels as those of **1*Lx***.

Conclusions

We have presented a modular synthetic approach to expanding our concept of molecular libraries to larger molecular masses. Four different porphyrin oligomers have been explored, the two most massive ones as "nuclei" for the synthesis of complex molecular libraries. By varying the synthetic conditions different numbers of fluorine atoms were substituted by fluorinated alkylthiolates leading to a broad mass range.

In the case of **2*Lx***, up to 43 fluorinated alkylsulfanyl side-chains were introduced, corresponding to a mass of about 23.8 kg/mol. Analysis by MALDI-TOF mass spectrometry revealed well-separated individual members of the library with a well-defined mass distribution for both libraries **1*Lx*** and **2*Lx***. Preliminary desorption studies indicate that neutral and intact molecules can be desorbed by using short-pulse UV laser light. Ionization of the desorbed members by 157.6 nm radiation enabled their subsequent detection by mass spectrometry. A most promising intensity window for the desorption laser has been identified that allows us to launch neutral particles without major thermal decomposition. To the best of our knowledge, oligoporphyrins with highly fluorinated alkylsulfanyl chains are the most massive particles reported to date that are sufficiently stable and volatile to be compatible with pulsed laser evaporation and post-ionization.

The concept presented herein is not limited to the mass range of 24 kg/mol. The modularity of the core synthesis and the ease of peripheral functionalization encourage further exploration of the mass limit for volatile particles, either by assembling even larger porphyrin oligomers as core structures or by introducing longer and/or branched fluorinated alkylsulfanyl chains.

Experimental Section

General: All commercially available starting materials were reagent grade and used as received from Sigma–Aldrich, Acros, Apollo Scientific, Alfa Aesar, and Fluorochem, and used as purchased. Dry solvents were purchased from Sigma–Aldrich, stored over molecular sieves (4 Å), and handled under argon. The solvents for column chromatography and extraction were of technical grade. Column chromatography purifications were performed on silica gel 60 (particle size 0.040–0.063 mm) from Silicycle. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded with Bruker DMX 400 (^{1}H: 400 MHz) or DRX 500 or 600 MHz instruments (^{1}H: 500 or 600 MHz) at 298 K. Not all the ^{13}C NMR spectra were recorded because fluorine coupling decreases signal intensity tremendously (see the Supporting Information). Deuteriated solvents were purchased from

Cambridge Isotope Laboratories. UV/Vis spectra were recorded with a Shimadzu UV-1800 spectrophotometer. MALDI-TOF mass spectra were recorded with a Bruker Microflex LRF spectrometer and were calibrated by using CsI_3 clusters.[34] DCTB {*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile} was used as matrix if needed.[35] High-resolution mass spectra were recorded with a Bruker solariX spectrometer (ESI/MALDI-FTICR-MS). Electron impact (EI) mass spectra were recorded with a Finnigan MAT 95Q spectrometer. Elemental analyses were measured with an Elementar Vario Micro Cube instrument.

5,10,15-Tris(pentafluorophenyl)-20-(2-trimethylsilylethynyl)porphyrin (5): A solution of pentafluorobenzaldehyde (**8**, 2.74 mL, 22 mmol, 2.0 equiv.), 3-(trimethylsilyl)-2-propynal (**7**, 1.84 mL, 12 mmol, 1.1 equiv.), and 5-(pentafluorophenyl)dipyrromethane (**6**, 6.9 g, 22 mmol, 2.0 equiv.) in chloroform (2.5 L; high dilution) was degassed under a constant stream of argon for 45 min and then treated with $BF_3{\cdot}O(Et)_2$ (2.5 M in $CHCl_3$, 2.92 mL, 0.66 equiv.). The reaction was stirred at room temperature for 18 h. DDQ (7.68 g, 1.5 mmol) was added and the reaction mixture stirred for another 2 h at room temperature. After filtration through silica the solvent was removed under reduced pressure. The remaining solid was purified three times by column chromatography (silica gel; cyclohexane/dichloromethane, 5:1) to obtain **5** as a dark-purple solid (1.52 g, 11.1 mol, 904.11 g/mol, 15%). UV/Vis ($CHCl_3$): λ = 415, 508, 536, 584 nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.55 (br. s, 2 H, NH), 0.65 (s, 9 H, TMS), 8.85 (s, 4 H, Ar-H), 8.88 (d, $^3J_{HH}$ = 4.8 Hz, 2 H, Ar-H), 9.80 (d, $^3J_{HH}$ = 4.8 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.5 (m, 2 F, Ar-F), –136.6 (m, 4 F, Ar-F), –151.5 (m, 3 F, Ar-F), –161.5 (m, 6 F, Ar-F) ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 0.68 (s, 3 C, TMS), 102.65 (s, 1 C, Cq), 103.36 (s, 1 C, Cq), 103.69 (s, 2 C, Cq), 104.55 (s, 1 C, Cq), 105.56 (s, 1 C, Cq), 115.36 (s, 1 C, Cq), 115.59 (s, 2 C, Cq), 130.25 (m, 2 C, Ct), 130.90 (m, 2 C, Ct), 130.94 (m, 2 C, Ct), 132.40 (m, 2 C, Ct), 137.55 (s, 2 C, Ct), 137.57 (s, 4 C, Ct), 146.47 (m, 4 C, Ct), 146.50 (m, 2 C, Ct) ppm. MS (MALDI-TOF): *m*/*z* (%) = 904.2 (100) $[M]^+$, 905.2 (82), 906.1 (27), 907.1 (10). HRMS (MALDI/ESI): calcd. for $C_{43}H_{19}F_{15}N_4Si$ 904.1134; found 904.1136. $C_{43}H_{19}F_{15}N_4Si$ (904.11): calcd. C 57.09, H 2.12, N 6.19; found C 57.45, H 2.49, N6.62.

5,10,15-Tris(pentafluorophenyl)-20-(ethynyl)porphyrin (13): Porphyrin (**5**, 100 mg, 0.11 mmol, 1.0 equiv.) was dissolved in wet dichloromethane (50 mL) and TBAF (1 M in THF, 220 µL, 0.22 mmol, 2.0 equiv.) was added dropwise. The reaction mixture was stirred for 30 min at room temperature. Then methanol (50 mL) was added and the solvent removed under reduced pressure. The resulting solid was dissolved in dichloromethane (50 mL) and washed with water and brine. The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (silica gel; cyclohexane/acetone, 2:1) to yield the porphyrin **13** as a violet solid in quantitative yield (92 mg, 0.11 mmol, 832.5 g/mol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.65 (br. s, 2 H, NH), 4.17 (s, 1 H, CH), 8.85 (s, 4 H, Ar-H), 8.87 (m, 2 H, Ar-H), 9.80 (m, 2 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.6 (m, 3 F, Ar-F), –151.4 (m, 6 F, Ar-F), –161.4 (m, 6 F, Ar-F) ppm. MS (MALDI-TOF): *m*/*z* (%) = 832.2 (100) $[M]^+$, 833.2 (94), 834.1 (34), 835.1 (17), 836.1 (6). HRMS (MALDI/ESI): calcd. for $C_{40}H_{11}F_{15}N_4$ 832.0739; found 832.0736.

[5,10,15-Tris(pentafluorophenyl)-20-(2-trimethylsilylethynyl)porphyrinato]zinc (14): A solution of zinc acetate (594 mg, 0.13 mmol, 3.2 equiv.) in methanol (25 mL) was added to a solution of porphyrin **5** (507 mg, 0.56 mmol, 1.0 equiv.) in chloroform (110 mL). The reaction mixture was stirred for 24 h at room temperature and then washed with water. The solvent was evaporated under reduced pressure to obtain the zinc complex **14** quantitatively as a purple solid (542 mg, 0.56 mmol, 966.0 g/mol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.64 (s, 9 H, TMS): 8.92 (s, 4 H, Ar-H), 8.96 (d, $^3J_{HH}$ = 4.7 Hz, 2 H, Ar-H), 9.88 (d, $^3J_{HH}$ = 4.7 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.9 (m, 3 F, Ar-F), –152.1 (m, 6 F, Ar-F), –161.7 (m, 6 F, Ar-F) ppm. MS (MALDI-TOF): *m*/*z* (%) = 966.8 (100) $[M]^+$, 967.8 (89), 968.7 (98), 969.6 (80), 970.6 (82), 971.6 (58), 972.6 (20). HRMS (MALDI/ESI): calcd. for $C_{43}H_{17}F_{15}N_4SiZn$ 966.0269; found 966.0269.

[5,10,15-Tris(pentafluorophenyl)-20-(ethynyl)porphyrinato]zinc (15): Zinc complex **14** (250 mg, 0.26 mmol, 1.0 equiv.) was dissolved in wet dichloromethane (100 mL) and TBAF (1 M in THF, 516 mL, 0.52 mmol, 2.0 equiv.) was added dropwise. The reaction mixture was stirred for 30 min at room temperature. Then methanol (100 mL) was added and the solvent removed under reduced pressure. The resulting solid was dissolved in dichloromethane (50 mL) and washed with water. The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (silica gel; cyclohexane/acetone, 2:1) to yield the zinc complex **15** as a violet solid in quantitative yield (229 mg, 0.26 mmol, 895.9 g/mol). UV/Vis ($CHCl_3$): λ = 322, 432, 565, 603 nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 1 H, CH), 8.88 (d, $^3J_{HH}$ = 4.6 Hz, 2 H, Ar-H), 8.94 (s, 4 H, Ar-H), 9.51 (d, $^3J_{HH}$ = 4.7 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.9 (m, 3 F, Ar-F), –152.0 (m, 6 F, Ar-F), –161.8 (m, 6 F, Ar-F) ppm. MS (MALDI-TOF): *m*/*z* (%) = 893.8 (100) $[M]^+$, 894.8 (31), 895.7 (55), 896.7 (22), 897.7 (31), 898.7 (6). HRMS (MALDI/ESI): calcd. for $C_{40}H_9F_{15}N_4Zn$ 893.9874; found 893.9874.

[5,10,15-Tris(pentafluorophenyl)-20-(ethynylphenyl)porphyrinato]zinc Dimer (3B): Zinc complex **15** (30 mg, 33.5 µmol, 1 equiv.) and 1,4-diiodobenzene (**9**, 3.32 mg, 10 µmol, 0.3 equiv.) were dissolved in THF (2 mL) in an oven-dried two-necked flask. The solution was degassed under a constant stream of argon for 20 min. Then tris(dibenzylideneacetone)dipalladium(0) (9.2 mg, 10 µmol, 0.3 equiv.) and triphenylarsine (16 mg, 0.05 mmol, 1.5 equiv.) were added and the reaction started by the addition of triethylamine (2 mL). The reaction mixture was heated at reflux for 18 h, when TLC showed full conversion of the starting materials. After cooling to room temperature *tert*-butyl methyl ether was added and the organic phase was washed with aq. satd. Na_2HCO_3, water, and brine. The combined organic phases were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (silica gel; cyclohexane/acetone, 3:1) to obtain the dimer **3B** as a dark-green solid (35 mg, 18.8 µmol, 1865.87 g/mol, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 4 H, Ar-H), 9.19 (m, 8 H, Ar-H), 9.31 (d, $^3J_{HH}$ = 4.6 Hz, 4 H, Ar-H), 10.10 (d, $^3J_{HH}$ = 4.6 Hz, 4 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –140.0 (m, 6 F, Ar-F), –156.3 (m, 12 F, Ar-F), –165.1 (m, 12 F, Ar-F) ppm. HRMS (MALDI/ESI): calcd. for $C_{86}H_{20}F_{30}N_8Zn_2$ 1861.9909; found 1861.9919.

[5,10,15-Tris(pentafluorophenyl)-20-(ethynylphenyl)porphyrinato]zinc Trimer (4B): The reaction was performed under similar conditions to those used for the synthesis of dimer **3B**. Zinc complex **15** (50 mg, 51.6 µmol, 1 equiv.) and 1,3,5-triiodobenzene (**10**, 4.7 mg, 10 µmol, 0.2 equiv.) were used with 0.45 equiv. catalyst and 3.0 equiv. triphenylarsine in THF/triethylamine (5 mL, 1:1). Purification was performed by column chromatography (silica gel; cyclohexane/ethyl acetate, 4:1) to obtain the trimer **4B** as a dark-green

solid (17 mg, 6 μmol, 2753.96 g/mol, 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.15 (m, 3 H, Ar-H), 9.22 (m, 12 H, Ar-H), 9.38 (m, 6 H, Ar-H), 10.31 (m, 6 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –139.9 (m, 9 F, Ar-F), –156.3 (m, 18 F, Ar-F), –165.0 (m, 18 F, Ar-F) ppm. MS (MALDI-TOF): *m*/*z* (%) = 2753.61 (100) $[M]^+$, 2775.18 (30), 2781.79 (32), 2783.93 (35). HRMS (MALDI/ESI): calcd. for $C_{126}H_{27}F_{45}N_{12}Zn_3$ 2753.9637; found 2754.9710.

[5,10,15-Tris(pentafluorophenyl)-20-(ethynylphenyl)porphyrinato]-zinc Tetramer (1B): The reaction was performed under similar conditions to those used for the synthesis of dimer **3B**. Porphyrin **15** (100 mg, 112 μmol, 1 equiv.) and tetrakis(4-iodophenyl)methane (**11**, 19 mg, 22 μmol, 0.2 equiv.) were used with 0.6 equiv. catalyst and 3.0 equiv. triphenylarsine in THF/triethylamine (12 mL, 1:1). After purification by column chromatography (silica gel; cyclohexane/acetone, 3:1), the tetramer **1B** was obtained as a dark-green solid (56 mg, 14 μmol, 3895.99 g/mol, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.55 (br. s, 2 H, NH), 0.65 (s, 9 H, TMS), 8.85 (s, 4 H, Ar-H), 8.88 (d, $^3J_{HH}$ = 4.8 Hz, 2 H, Ar-H), 9.80 (d, $^3J_{HH}$ = 4.8 Hz, 2 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.6 (m, 12 F, Ar-F), –151.2 (m, 24 F, Ar-F), –161.5 (m, 24 F, Ar-F) ppm. HRMS (MALDI/ESI): calcd. for $C_{185}H_{48}F_{60}N_{16}Zn_4$ 3889.0528; found 3889.0523.

5,10,15-Tris(pentafluorophenyl)-20-(ethynylphenyl)porphyrin Pentamer (2): The reaction was performed under similar conditions to those used for the synthesis of dimer **3B**. Porphyrin **13** (164 mg, 197 μmol, 1 equiv.) and porphyrin **12** (44 mg, 39.3 μmol, 0.2 equiv.) were used with 0.6 equiv. catalyst and 3 equiv. triphenylarsine in THF/triethylamine (20 mL, 1:1). Purification was carried out by column chromatography (silica gel; cyclohexane/acetone, 3:1) to give the pentamer **2** as a dark-green solid (93 mg, 39 μmol, 3936.81 g/mol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.47 (br. s, 2 H, NH), –2.35 (br. s, 8 H, NH), 8.55 (d, $^3J_{HH}$ = 7.8 Hz, 8 H, Ar-H), 8.61 (d, $^3J_{HH}$ = 7.8 Hz, 8 H, Ar-H), 8.85 (m, 16 H, Ar-H), 8.98 (m, 8 H, Ar-H), 9.21 (m, 8 H, Ar-H), 10.08 (m, 8 H, Ar-H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –136.6 (m, 12 F, Ar-F), –151.4 (m, 24 F, Ar-F), –161.4 (m, 24 F, Ar-F) ppm. HRMS (MALDI/ESI): calcd. for $C_{204}H_{66}F_{60}N_{20}$ 3934.4816; found 3934.4847.

Porphyrin Tetramer Library 1*Lx*: The porphyrin tetramer **1B** (25 mg, 6.42 μmol, 1 equiv.) was dissolved in DMF (10 mL) and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (**16**, 220 μL, 770 μmol, 120 equiv.) was added. After the addition of potassium carbonate (106 mg, 770 μmol, 120 equiv.) in two portions the reaction mixture was heated at 90 °C for 18 h in an oil bath. Water was added to the hot reaction mixture and the aqueous phase separated. The aqueous phase was extracted with TBME (3 × 20 mL). The combined organic phases were washed three times with water and brine, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting brown residue was dissolved again in TBME (10 mL) and filtered through silica gel to remove dithiol residues. The solvent was removed under reduced pressure and the resulting library **1*Lx*** (258 mg) analyzed by MALDI-TOF mass spectrometry. MS (MALDI-TOF): *m*/*z* (%) = 14073 (5), 13620 (17), 13153 (38), 12668 (68), 12230 (100), 11785 (94), 11288 (54), 10895 (8).

Porphyrin Pentamer Library 2*Lx*: The porphyrin tetramer **2** (21 mg, 5.33 μmol, 1 equiv.) was dissolved in DMSO (10 mL) and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (**16**, 345 μL, 1.20 mmol, 225 equiv.) was added. After the addition of potassium carbonate (170 mg, 1.20 mmol, 225 equiv.) in two portions the reaction mixture was heated at 90 °C for 18 h in an oil bath. Water was added to the hot reaction mixture and the aqueous phase separated. The aqueous phase was extracted with TBME (3 × 20 mL). The combined organic phases were washed three times with water and brine, and dried with anhydrous sodium sulfate. The solvent was removed under reduced pressure. The resulting brown residue was dissolved again in TBME (10 mL) and filtered through a plug of silica to remove dithiol residues. The solvent was removed under reduced pressure and the resulting library **2*Lx*** (198 mg) analyzed by MALDI-TOF mass spectrometry. MS (MALDI-TOF): *m*/*z* (%) = 23878 (5), 23404 (24), 22931 (62), 22454 (100), 21983 (89), 21514 (78), 21061 (50), 20588 (26), 20121 (6).

Supporting Information (see footnote on the first page of this article): ^{1}H, ^{19}F, and ^{13}C NMR spectra and determination of compounds **1B**, **2**, **3B**, **4B**, **5**, and **13**–**15** (if available), the synthetic procedures for **6**, **11**, and **12**,which are small variations of reported procedures.

Acknowledgments

The authors acknowledge financial support by the Swiss National Science Foundation, NCCR "Nanoscale Science", and the Swiss Nanoscience Institute (SNI). The groups in Basel and Vienna were supported by the FWF programs Wittgenstein (Z149-N16) and the doctoral programm CoQuS (grant W1210-3), and the European Commission through the (NANOQUESTFIT project 304886). The authors thank Michel Rickhaus for the art work for the table of contents.

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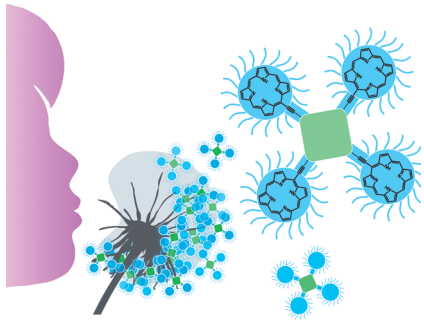
Received: June 26, 2014
Published Online: ■

EurJOC European Journal of Organic Chemistry

Fluorinated Oligoporphyrins

Massive but volatile molecules have been obtained by functionalizing the periphery of oligoporphyrins with highly fluorinated alkyl chains. The statistical nature of the reaction gives libraries consisting of molecules with well-defined masses but small structural diversity. Laser desorption and post-ionization studies demonstrated the potential of these libraries as sources of heavy particles.



Keywords: Chemical libraries / Porphyrinoids / Fluorine / Aromatic substitution / Mass spectrometry

