

Metal–Organic Frameworks

Modular Synthesis of *trans*-A₂B₂-Porphyrins with Terminal Esters: Systematically Extending the Scope of Linear Linkers for Porphyrin-Based MOFsStefan M. Marschner,^[a] Ritesh Haldar,^[b] Olaf Fuhr,^[c] Christof Wöll,^[b] and Stefan Bräse^{*[a, d]}

Abstract: Differently functionalized porphyrin linkers represent the key compounds for the syntheses of new porphyrin-based metal–organic frameworks (MOFs), which have gathered great interest within the last two decades. Herein we report the synthesis of a large range of 5,15-bis(4-ethoxycarbonylphenyl)porphyrin derivatives, through Suzuki and Sonogashira cross-coupling reactions of an easily accessible corresponding *meso*-dibrominated *trans*-A₂B₂-porphyrin with

commercially available boronic acids or terminal alkynes. The resulting porphyrins were fully characterized through NMR, MS, and IR spectroscopy and systematically investigated through UV/Vis absorption. Finally, selected structures were saponified to the corresponding carboxylic acids and subsequently proven to be suitable for the synthesis of surface-anchored MOF thin films.

Introduction

The porphyrin structure with its square-planar geometry, rigidity, thermal stability, and high modifiability was predisposed to be used as a multifunctional linker unit in metal–organic frameworks (MOFs).^[1] Porphyrin-based MOFs (PP-MOFs), like other frameworks, are often explored for applications in gas storage,^[2] separation^[3] and sensing.^[4] However, applications of higher interest are mostly based on the unique properties of the porphyrin core structures. The possibility of the metal complexation inside the porphyrin opens the field for heterogeneous catalysis, for example, for a variety of oxidation reactions,^[5] C–H halogenation^[6] or C–C bond formation.^[7] Another intriguing

feature of porphyrins is the π -electron-rich electronic structure, which results in large light absorption coefficients. These enable applications in photovoltaics,^[8] photocatalytic reactions, for example, CO₂ reduction,^[9] water splitting,^[10] and other optoelectronic applications including nonlinear optics.^[11]

The numerous PP-MOF structures reported within the last two decades contain in particular *meso*-substituted A₄- or *trans*-A₂B₂-porphyrins, bearing carboxylic acids or N-heterocycles (mostly pyridine) as terminal metal-binding sites. Porphyrins with A₄-symmetry are easier to synthesize, but lack in diversity due to saturation of all *meso*-positions with linking moieties. Therefore, they leave no space for further functionalization, except metal insertion or β -substitutions, which are rather limited. Metal complexes of *meso*-tetra(4-carboxyphenyl)porphyrin are probably the most used classes of porphyrins for PP-MOF synthesis.^[1c, 2, 4b, 8, 10, 12] Nevertheless, depending on the desired applications, more complex structures are needed. For example, Zaworotko et al. created a PP-MOF from 5,15-bis(3,5-dicarboxyphenyl)-10,20-bis(2,6-dibromophenyl)porphyrin, which was found to function as an efficient catalyst for the epoxidation of *trans*-stilbene.^[13] Sun et al. introduced up to two pentafluorophenyl moieties in a Mn^{III}-porphyrin linker to enhance the catalytic activity in the selective oxidation of ethylbenzene to acetophenone.^[14] In an investigation by Hupp et al. MOFs based on the linkers [5,15-bis(4-(pyridyl)ethynyl)-10,20-diphenylporphinato] zinc(II) and [5,15-bis(4-pyridyl)-10,20-bis(pentafluorophenyl)porphinato] zinc(II) were studied for efficient energy transport.^[11c] A recent work by Tsotsalas et al. describes the MOF-templated synthesis of a porphyrin polymer thin film based on 5,15-bis(4-carboxyphenyl)-10,20-(4-azidophenyl)porphyrin, using the azide-alkyne click reaction to crosslink porphyrin units.^[15]

These examples illustrate that suitably functionalized porphyrin linkers can improve present applications, for example

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through higher catalytic activities or stronger absorptions in photovoltaic devices, or even allow new applications. Nevertheless, the number of such differently substituted linear porphyrin linkers is marginal compared to other linear linkers used in MOF chemistry. Therefore, extending the scope of linear A_2B_2 -porphyrin linkers is an important step in the development of future MOFs in which combinations of the attached functional groups (and/or inserted metals), the unique optical properties of porphyrins and the ordered spatial arrangement enable improved or entirely new performances.

Herein, a facile and comparably high yielding synthetic route to obtain the linear 5,15-dibromo-10,20-bis(4-ethoxycarbonyl-phenyl)porphyrin (**4**) is described. This structure was then further functionalized with various substituents in its two brominated *meso*-positions (C5 and C15) through cross-coupling reactions, resulting in numerous different new structures for potential uses in catalysis or optoelectronics. Subsequently, few molecules were converted to corresponding carboxylic acids as examples from which PP-MOFs as surface-anchored thin films were fabricated, illustrating the potential of the synthetic design strategy.

Results and Discussion

To create a library with various differently substituted porphyrins, we chose a synthetic route resulting in the common precursor **4**. This includes two ethyl ester termini, attached in two opposite *meso*-positions, therefore already containing the linear arranged motive, as well as two bromides in the remaining *meso*-positions to enable further cross-coupling reactions. The ester moiety was chosen since terminal carboxylic acids do not lead to proper porphyrin formation under the chosen "Lindsey conditions"^[16] for porphyrin syntheses (one-pot, two-step procedure through condensation of aldehyde and dipyrromethane catalyzed by Lewis-acid and subsequent oxidation with a benzoquinone). Furthermore, the ester groups improve the solubility in solvents like dichloromethane, chloroform, toluene, and THF, compared to the corresponding carboxylic acid terminated porphyrins. This simplifies the handling and analysis of the resulting compounds. The ethyl esters can easily be hydrolyzed in a final step to get the carboxylic acid linkers.

Though this last step was only performed for structures selected for subsequent MOF building. For the synthesis of **4**, literature known partly modified procedures were used,^[17] achieving an overall yield of 25% over 3 steps (Scheme 1, Table 1, synthesis of dipyrromethane **1** not shown (yield: 65%)). Single crystals of **4**, suitable for XRD analysis, were obtained by slow evaporation of a corresponding chloroform solution (Figure 1, details on structure determination and structure are given in Supporting Information).

The chosen synthetic route has several advantages over the syntheses of the porphyrins for example from 5-(4-ethoxycarbonylphenyl)dipyrromethane and the respective aldehydes:

- 1) No scrambling^[18] (the acid-catalyzed formation of porphyrins with different symmetry) was observed in this approach, which is crucial for the formation of MOFs, since especially the separation of *cis*- from *trans*- A_2B_2 -porphyrins often tends to be a difficult procedure. Impurities like the *cis*-product or AB_3 -porphyrins not only decrease the yield of the *trans*-product but lead to unsuccessful MOF growth, due to their non-linearity. Even though electron-withdrawing substituents like esters on the phenylene generally are reported to promote scrambling in porphyrin synthesis,^[19] in this reaction no other porphyrin products were detected. The importance of an absence of scrambling was also confirmed by the synthesis of diethyl 4,4'-(10,20-diphenylporphyrin-5,15-diyl)dibenzoate (**5a**) from ethyl 5-(4-ethoxycarbonylphenyl)-dipyrromethane under Lindsey conditions. Although the scrambled products resulting from this approach seemed to be separable, subsequent SURMOF growth with the later obtained respective dicarboxylate failed, most likely due to residual *cis*-product.

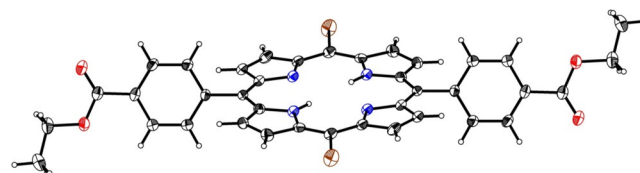
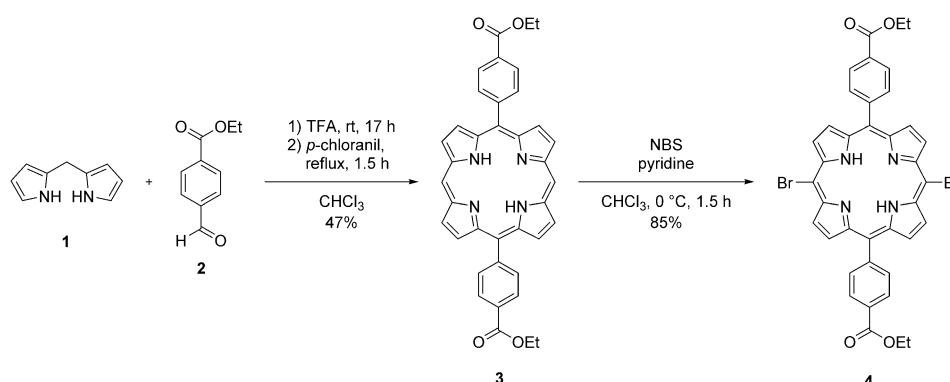
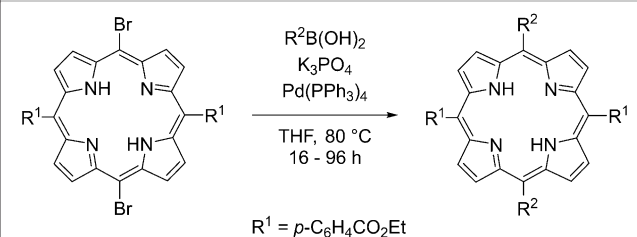


Figure 1. Molecular structure of **4** as ORTEP plot at 50% probability level, Br: brown, O: red, N: blue, C: black, H: white.



Scheme 1. Synthetic route towards the precursor porphyrin **4** for further functionalization through cross-coupling reactions.

Table 1. Suzuki cross-coupling reactions of **4** with different boronic acids, resulting in 24 successfully synthesized porphyrins **5a–x**. Isolated yields for the cross-coupling reaction given first, overall yield (starting from **1** and **2**) in brackets.






















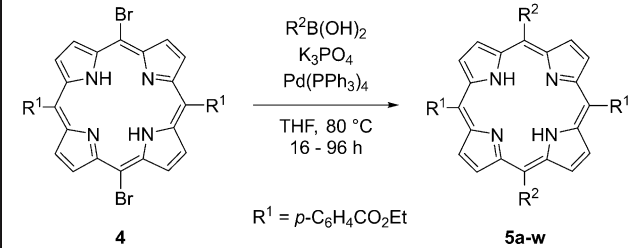
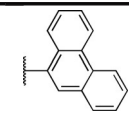
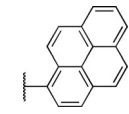
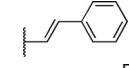
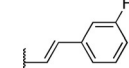
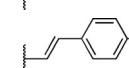
Entry	R =	Product	5a-w Yield [%]
1		5a	89 (36)
2		5b	97 (39)
3		5c	78 (31)
4		5d	89 (36)
5		5e	93 (37)
6		5f	91 (36)
7		5g	85 (34)
8		5h	95 (38)
9		5i	85 (34)
10		5j	79 (32)
11		5k	83 (33)
12		5l	61 (24)
13		5m	32 (13)
14		5n	62 (25)
15		5o	28 (11)
16		5p	72 (29)
17		5q	61 (24)
18		5r	91 (36)
19		5s	99 (40)

Table 1. (Continued)



Entry	R =	Product	Yield [%]
20		5t	68 (27)
21		5u	47 (19)
22		5v	71 (28)
23		5w	76 (30)
24		5x	52 (21)

- 2) Compared to other porphyrin syntheses^[20] the porphyrin building step of this route using Lindsey conditions has a high yield of 47%, which among other aspects, like a high degree of ring closure instead of chain elongation, also results from the absence of scrambling (as mentioned before).
- 3) Porphyrin syntheses often require different reaction conditions in terms of Lewis acid, oxidant, condensation time, or reagent concentrations when employing different aldehydes.^[16] The optimal conditions usually have to be determined empirically, hampering the synthesis of a library of structures.
- 4) The cross-coupling reactions can easily be performed on a small scale of 10–20 mg, allowing the quick generation of multiple compounds, but are also scalable to larger amounts of several hundred milligrams without optimization needed.

A variety of boronic acids, containing derivatives of phenylboronic acids, boronic acids of heteroaromatics and fused benzenes, as well as ethylene bridged boronic acids, were coupled to the dibromo porphyrin **4** via Suzuki cross-coupling reactions.^[21] Using conditions established by Senge et al.,^[22] these reactions resulted in 24 successfully synthesized structures (Table 1). Some of these and similar other saponified aryl porphyrins have been successfully assembled in metal–organic frameworks.^[23]

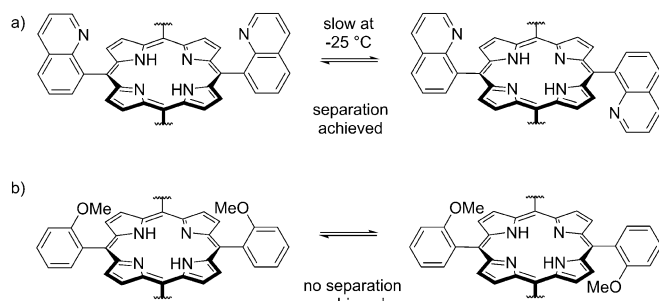
The reactions with differently substituted phenylboronic acids, including those with electron-withdrawing and electron-donating substituents, as well as with different positioning of

these substituents, proceed with good to excellent yields of target porphyrins, ranging from 78 to 97% (Table 1, entries 1–11). Also, the two heteroaromatic compounds 5-indolylboronic acid and 3-thienylboronic acid (Table 1, entries 18 and 19) gave excellent yields of 91% and 99% respectively. Generally, yields dropped in reactions with pyridyl and pyrimidyl boronic acids (Table 1, entries 14–16). Even by prolonging the reaction times to up to 96 h, a full conversion of the starting material (as indicated by TLC) could not be achieved in the shown cases. Though, the starting materials and mono-coupled byproducts could still be separated from the products in all three cases through column chromatography. For entry 15 for example the recovery of over 40% of the starting material and a yield of $\approx 15\%$ for the mono-coupled byproduct was achieved even after a reaction time of four days.

The reaction towards the novel quinolinyl-substituted porphyrin^[24] **5q** (Table 1, entry 17) showed a remarkable behavior: Although separation of the two formed products through column chromatography was easily achieved, subsequent removal of the solvents at 40 °C already resulted in what seemed to be two mixtures of both products in a 1:1 ratio as indicated by TLC. We, therefore, assume that the two possible atropisomers (Scheme 2) are separable, but the change of orientation is facile^[25] (related systems showed a barrier of 80–140 kJ mol⁻¹^[25v, 26]).

Repetition of chromatography and the removal of solvents by a compressed air stream resulted in two separate single products. Unfortunately, even the isolated solids, when stored at -25 °C, showed slow conversion to the other atropisomer, which complicated the full analysis of a single compound.

Nevertheless, ¹H NMR spectra of both products were recorded showing slight differences in their low field signals (see experimental section). Moreover, similar effects can be observed for the structures **5g** and **5h**, caused by the two opposite 2-methoxy substituents facing either the same or different sites of the porphyrin. As a result, the ¹H NMR spectra show two slightly shifted peaks for the methoxy groups and further signal splitting in the aromatic region. In contrast to **5q**, those isomers were not separated due to their similar *R_f* values of $\Delta R_f = 0.04$ (**5g**) and 0.07 (**5h**).



Scheme 2. a) The two separable atropisomers of **5q**. The rotation barrier between β -hydrogen atoms and the quinoline can be surpassed already at -25 °C in solid state. b) For the two possible structures of **5g** (and **5h** analogue) a separation could not be achieved, but the structures can be distinguished in their respective ¹H NMR spectra.

The novel thiophene-substituted porphyrin **5s** was obtained with an excellent yield of 99% (Table 1, entry 19). This material might serve also as a platform for electrochemical polymerization.^[27]

In reactions with boronic acids of annulated arenes (Table 1, entries 20 and 21, for annulated aryl-substituted porphyrins, compare^[22, 28]) the conformational isomerism as for **5g**, **5h** and **5q** were not observed, probably since it does not significantly change the polarity of the product. The isolated yields dropped with increasing size of the attached π -system. We explain this with the decrease of solubility and a resulting higher loss of product in the purification through column chromatography since both reactions showed full conversion of starting material **4** and no indication of the mono coupled side products. The same results are observed for reactions with 4-(*N,N*-diphenylamino)-1-phenylboronic acid and 4-(*N*-carbazolyl)phenylboronic acid (Table 1, entries 12 and 13), which also show decreasing isolated yields with an attachment of larger and planar structures. Lastly, the vinylic boronic acids (entry 22–24), which enlarge the π -conjugation of the porphyrin core, also suffer from decrease of the isolated product yield, probably for similar reasons as mentioned before, since the vinyl bridge lowers the torsion angle between the porphyrin core and its substituent. In the case of porphyrin **5x** with two diphenyl substituents, the solubility is reduced to such an extent that recording of evaluable NMR spectra could only be achieved by the addition of TFA to protonate the porphyrin, resulting in the repulsion of the respective positively charged molecules.

Furthermore, a series of Sonogashira cross-coupling reactions^[29] were performed similarly to established conditions^[22] using dibromo porphyrin **4** as starting material, successfully yielding nine different structures (Table 2).^[17d, 23, 30] The reactions of **4** with phenylacetylene, as well as with 4-cyano-, 2-methoxy- and 4-methoxyphenyl acetylenes succeeded with good yields of 64–77% (Table 2, entries 1–4). The influence of electron-withdrawing or donating substituents on the isolated yield was not observed. Yields dropped with the use of methyl 4-ethynylbenzoate (Table 2, entry 6) as well as with pyridyl acetylenes (Table 2, entries 7 and 8). As in the Suzuki cross-coupling reactions, a correlation between the product solubility and the isolated product yield was observed.

The isolated product in the reaction with 1-(4-ethynylphenyl)ethan-1-one (Table 2, entry 5) however could not be confirmed by NMR spectroscopy since the received spectrum of the compound showed almost no clear or sharp signals. This led to the suspect of impurities in the form of critical amounts of paramagnetic copper(II) coordinated by the porphyrin molecules, thus interrupting the magnetic field.

We, therefore, attempted to remove the metal through stirring with perchloric acid, which after workup indeed gave the pure product, but only in a moderate yield of 30%.

In all other reactions the respective Cu^{II} porphyrin was either not observed or removed through column chromatography as small fractions, which were evaluated to account for less than 5% of the product.

Furthermore, the coupling of larger aromatic systems to the porphyrin core was attempted by the use of 9-ethynylphenan-

Table 2. Sonogashira cross-couplings of **4** with different alkynes, resulting in nine porphyrins **6a–i**. Isolated yields for the cross-coupling reaction given first, overall yield (starting from **1** and **2**) in brackets.

Entry	R =	Product	Yield [%]
1		6a	76 (30)
2		6b	75 (30)
3		6c	77 (31)
4		6d	64 (26)
5		6e	30 (12)
6		6f	43 (17)
7		6g	36 (14)
8		6h	51 (20)
9		6i	15 (6)
10		6j	–

threne and 1-ethynylpyrene (Table 2, entries 9 and 10). Compared to **5t** and **5u** in the resulting molecules, the attached moieties probably will be less twisted out of the porphyrin plane due to the alkyne bridges. Thus large flat aromatic systems are created enabling strong π - π -stacking, probably heavily reducing their solubility.

In both cases, a complete conversion of the starting material was observed as indicated by TLC. The phenanthrene porphyrin could be isolated in 15% yield, but (as for **5u**) to get evaluable NMR spectra, protonation of an NH-group was crucial to a lower stacking of the molecules.

The desired product of the reaction with 1-ethynylpyrene could not be isolated though. In ^1H NMR spectra, the fractions obtained through column chromatography showed neither signals of the central nitrogen bound protons nor of the characteristic ethyl ester groups. Based on the already really bad solubility of **6i**, we assume that a twofold alkyne bridged pyrene porphyrin simply exceeds the size of soluble, planar systems, caused by the resulting enormous π - π -stacking.

UV/Vis results

Especially applications in photoredox catalysis or photovoltaics require the porphyrins to possess significant light absorption properties. Therefore, the quantitative absorption spectra of the porphyrins were measured. An overview of the results is illustrated in Figure 2, where the decimal logarithms of the maximal extinction coefficients ϵ of each porphyrins Soret- and Q-bands are plotted against the corresponding wavelengths (data for **5x** are not depicted due to an insufficient solubility for quantitative measurement). The data clearly show the influence of *meso*-substituents on the light absorption behavior of the porphyrins. Each porphyrin with aryl derivatives directly coupled to the porphyrin core shows a similar result. Due to the substituents being twisted out of the planar aromatic system, the conjugation of the porphyrin core is not extended.

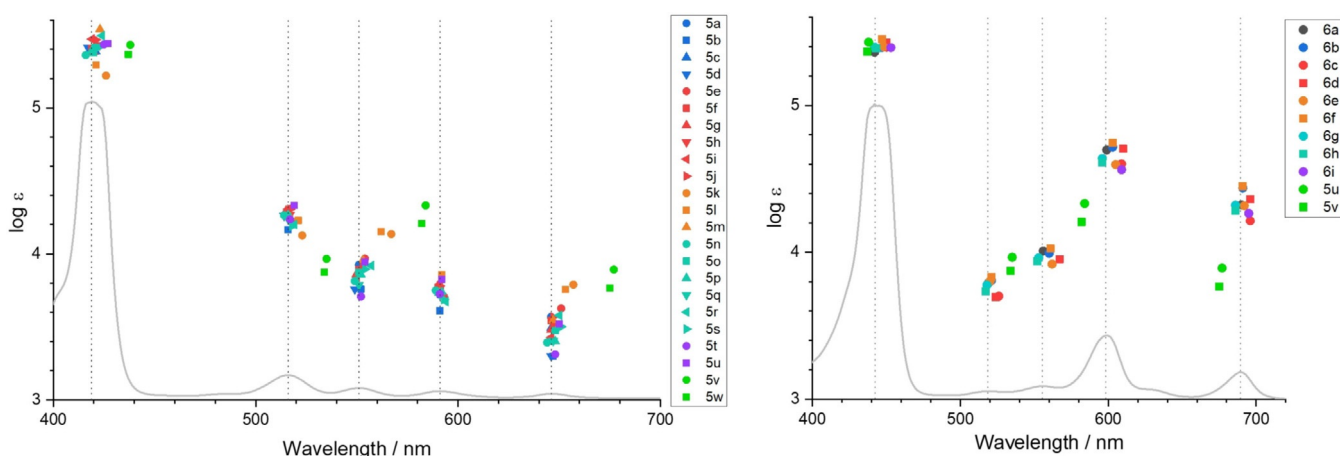


Figure 2. Analysis of the synthesized porphyrins' UV/Vis absorption in chloroform. The decimal logarithms of the maximal molar extinction coefficients ($\log \epsilon$) are plotted against the corresponding wavelengths. Products of the Suzuki cross-coupling reactions (**5a–w**) are shown left and of the Sonogashira cross-coupling reactions (**6a–i**) on the right (porphyrins **5u** and **5v** added for comparison). For further clarity, the spectra of **5a** (left) and **6a** (right) are depicted in light grey (y-axis not related).

A remarkably increased absorption of the $Q_x(0,0)$ and $Q_y(0,0)$ transitions as well as slight bathochromic shifts was observed in the case of the porphyrins **5k** and **5l**. As an explanation, we suggest the mesomeric effect of the amine derivatives to increase electron density to a decisive extent, especially on the porphyrin's *meso*-carbon atoms. The comparison with **5m**, having two 4-carbazolylphenyl substituents attached, supports this assumption. **5m** shows no increase in absorbance since the nitrogen's lone electron pair is delocalized over the carbazole unit, thus causing a less pronounced mesomeric effect.

The alkene substituted porphyrins **5v** and **5w** give even higher values for ϵ , due to less steric hindrance and therefore a better π -orbital overlap. As a result, strong bathochromic shifts of up to 39 nm compared to **5a** are observed. Also, the Q-band intensities raise further in the case of $Q_x(0,0)$ and $Q_y(0,0)$, reaching $\log \epsilon$ values of up to 4.33 and 3.89 for **5v**.

The Sonogashira cross-coupling products exhibit optimal π -orbital overlap since no steric hindrance is given by the alkyne bridges and therefore an optimal conjugation through the connected substituents occurs. These porphyrins (**6a–i**) therefore show further bathochromic shifts and stronger absorbance, also compared to the alkene substituents. Noteworthy, the rise of the $Q_x(0,0)$ and $Q_y(0,0)$ transitions is simultaneously accompanied by decreasing intensities of $Q_x(0,1)$ and $Q_y(0,1)$. For porphyrins **6a–i** the absorbance of the weakened Q-bands sometimes became unrecognizably low, for which reason these values are partly not stated.

Hydrolysis to dicarboxylic acids and resulting MOFs

The synthesized porphyrins can easily be transformed to the corresponding dicarboxylic acid linkers by hydrolysis with LiOH, NaOH or KOH. This reaction was performed for the porphyrins **3**, **5a–d**, **5j**, **5p**, **5t**, and **6a** as examples, giving the structures summarized in Figure 3. Unfortunately, these products could not be analyzed through NMR spectroscopy due to low solubility, but the success of the reaction was proven by mass spectrometry, also proving full conversion to the dicarboxylates without remaining ester groups. The suitability of the synthesized linkers for applications in MOFs was already

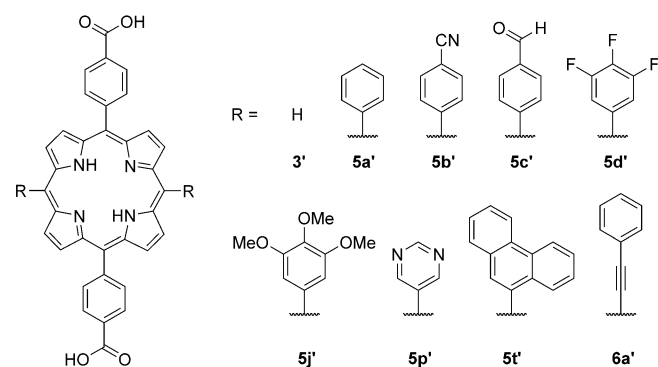


Figure 3. Depiction of synthesized dicarboxylic acid linkers. Structures **3'**, **5a'**, **5c'**, **5d'**, **5j'**, **5t'** and **6a'** were proven to be suitable for the preparation of MOFs of the type SURMOF-2.

demonstrated in previously published works by Wöll and Heinke et al.^[31] In those works, using layer-by-layer (lbl) liquid-phase epitaxy method, MOFs were grown on functionalized surfaces, as a surface-anchored MOF (SURMOF). Compared to powder MOFs, SURMOFs are advantageous regarding optoelectronic applications, as demonstrated previously for PP-MOFs and other related SURMOFs.^[32] Using an lbl spin-coating method^[33] (see Experimental Section), Zn-PP-1, -2, and -3 SURMOF-2 structures were fabricated from the linkers **3'**, **5t'** and **5c'**, respectively. The out-of-plane X-ray diffraction measurements, shown in Figure 4b, exhibited diffraction peaks related to the (001), (002) and (003) planes, indicating isorecticular SURMOF-2 type structures as obtained by using porphyrins **5a'**, **5d'**, **5j'** and **6a'** (Figure 4a, b).^[31,34] In the SURMOF-2 structure, porphyrin linkers are linked by Zn-based paddle-wheel type secondary building units (SBUs) to form a 2D square grid-type-lattice. These 2D sheets are stacked by van der Waals interactions along [010] direction, as shown in Figure 4a. The XRD results indicated unit cell dimensions of $a=b=2.3$ nm. Attempts for SURMOF fabrication from linkers **5b'** and **5p'** were not successful though, in which cases we assume the easily accessible nitrogen atoms to compete for coordination to the Zn_2 -SBU. The resulting materials thus did not show crystallinity as recognized by their respective XRD measurements.

Concerning absorptions the electron-donating phenanthrene substitution of **5t'** results in a redshift (≈ 18 nm) of the Soret-band, compared to **3'**, measured in its solvated state, as illustrated in Figure 4c. The strong Soret-band and four Q-band absorptions observed for the solvated linkers, are also distinct in the absorption spectra of the corresponding SURMOFs, indicating a non-metallated state of the porphyrins.^[35] A distinct effect of 10,20-position substitution on the PP-assem-

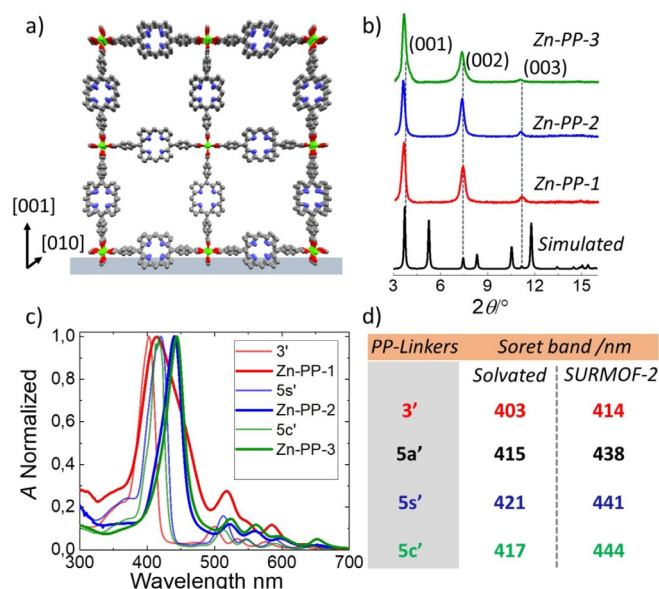


Figure 4. a) A drawing of SURMOF-2 structure of Zn-PP-1. b) Simulated X-ray diffraction pattern of Zn-PP-1 structure and the experimental out-of-plane diffraction patterns of Zn-PP-1, -2 and -3. c) UV/Vis absorption spectra of solvated linkers in ethanol and the corresponding SURMOFs. d) Comparison of Soret-band maxima in different state of PP linkers (**5a'**^[32]).

ably in the SURMOF-2 structure is evident when the Soret-band position of the solvated state and SURMOF state is compared (Figure 4d). For **3'**, the Zn-PP-1 structure Soret-band is redshifted by ≈ 11 nm compared to its solvated state. With a substituent, like a phenyl, phenanthrene, or formylphenyl, corresponding redshifts amounted to be > 20 nm. This suggests different porphyrin packings along [010] direction resulting in a different extent of inter-porphyrin electronic coupling. The evident steric effect on SURMOF absorption spectra can be a potentially attractive strategy to tune PP-SURMOF photophysics (band gap) and a combined effort of computational method and experiment would be beneficial for further development.^[36] Also, the functionalization with aldehyde groups for example should allow easy post-synthetic modifications of the resulting SURMOF-2 structure,^[37] which will be further investigated amongst others through rearranging porphyrin orientation and resulting changes in absorption.

Conclusions

A large variety of differently substituted porphyrin precursors was synthesized and characterized, which using examples have been proven to be suitable for a conversion to linear dicarboxylic acid linkers to build SURMOF-2 type frameworks. In this regard, the synthesis of the easily accessible 5,15-dibromo-10,20-bis(4-ethoxy-carbonylphenyl)porphyrin (**4**), which allows further *meso*-functionalization, is described. The importance of the absence of scrambling in the porphyrin synthesis for (SUR)MOF-applications was highlighted, ensuring the intended linear symmetry of the desired linkers. Suzuki and Sonogashira cross-coupling reactions were further used to attach numerous aromatic substituents to the porphyrin core in mostly good up to excellent isolated yields. In UV/Vis absorption analysis of the resulting products, influences of the substituents, particularly through the change of electron density on the porphyrin core, as well as enlargement of the conjugated π -electron systems were demonstrated. Lastly, the final hydrolysis of the ester terminal porphyrins was depicted as a facile conversion to the respective dicarboxylic acids, allowing their use as linear linkers in MOF preparation. This molecular design allows a much broader functionalization of PP-MOFs thus enabling new and improving present properties of MOF structures, for example, by extending the absorption range in photovoltaic devices.

Experimental Section

General methods

All NMR spectra were recorded on a Bruker Avance 300 (^1H NMR: 300 MHz, ^{13}C NMR: 75 MHz), Bruker Avance 400 (^1H NMR: 400 MHz, ^{13}C NMR: 101 MHz, ^{19}F NMR: 377 MHz), Bruker Ascend 400 (^1H NMR: 400 MHz, ^{13}C NMR: 101 MHz, ^{19}F NMR: 377 MHz) or Bruker Avance DRX 500 (^1H NMR: 500 MHz, ^{13}C NMR: 126 MHz) at room temperature using deuterated solvents purchased from Eurisotop. Chemical shift δ were given in ppm, with the residual solvent peak as reference (7.26 ppm for ^1H and 77.16 ppm for ^{13}C NMR). Coupling constants J were given in Hertz (Hz) as absolute values. For examination of spectra the following abbreviations are used: s =

singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. The spectra were analyzed according to the first order. For multiplicities in ^{13}C spectra, the following abbreviations were used: $+$ = primary or tertiary C, $-$ = secondary C, C_q = quaternary C. For the assignment of signals the following indices were used: Ar = aromatic, $meso$ = *meso*-position of porphyrin, β = β -positions of porphyrin, ph = phenyl; also names of other aromatic moieties. UV/Vis spectra were recorded quantitative on a Specord 50 Plus from Analytic Jena using CHCl_3 as solvent and cuvettes with a thickness of 0.1 cm. IR spectra were recorded on a Bruker Alpha-T instrument by diamond ATR technique (attenuated total reflection). The absorption is given in wavenumbers $\tilde{\nu}$. (High resolution) Mass spectra were recorded on a Finnigan MAT 95 instrument using either FAB (fast atom bombardment), with 3-nitrobenzyl alcohol used as a matrix or EI (electron impact) with 70 eV as ionization method or were measured with ESI-MS ionization on a Q Exactive machine from Thermo Fisher Scientific. Mass spectra were interpreted by listing the mass/charge ratios (m/z) of molecule fragments together with their intensities relative to the base peak (100%). For high-resolution MS the calculated (calc.) values are listed together with the measured (found) ones. Exact amounts and analytical data of products which were lastly not converted to carboxylic acid linkers can be found in Supporting Information.

The obtained data were deposited in the repository Chemotion (reaction details and compound characterization). The related DOIs (provided below) can be used to identify the submissions (web access: <https://www.chemotion-repository.net/home/publications>).

Deposition number 1883129 (for **4**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Synthesis and characterization

Di(1*H*-pyrrol-2-yl)methane (1):^[17a] To 340 mL of freshly distilled pyrrole (330 g, 4.92 mol, 92.7 equiv) were added 1.59 g of paraformaldehyde (53.1 mmol, 1.00 equiv) and the resulting suspension was stirred for 10 min at 55 °C. Then 1.16 g InCl_3 (5.25 mmol, 0.10 equiv) was added and the resulting mixture was stirred for an additional 3 h at 55 °C. After cooling to rt, 7.02 g powdered NaOH (176 mmol, 3.31 equiv) were added and the mixture was stirred for another hour, followed by filtration. The filtrate was evaporated under reduced pressure and the remaining crude product was purified by column chromatography (cyclohexane/EtOAc 10:1 with a gradient to 2:1) to yield 5.05 g of **1** (34.5 mmol, 65%) as a white solid. R_f (cyclohexane/EtOAc, 2:1) = 0.57. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = 3.94 (s, 2H, CH_2), 6.03–6.09 (m, 2H, $2 \times \text{CH}_{\text{pyr}}$), 6.18 (q, $^3J = 2.9$ Hz, 2H, $2 \times \text{CH}_{\text{pyr}}$), 6.62 (td, $^3J = 2.7$, $^4J = 1.6$ Hz, 2H, $2 \times \text{CH}_{\text{pyr}}$), 7.67 (bs, 2H, $2 \times \text{NH}$). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 26.4 (–, CH_2), 106.6 (+, $2 \times \text{CH}$), 108.4 (+, $2 \times \text{CH}$), 117.5 (+, $2 \times \text{CH}$), 129.2 (C_{qr} , $2 \times C_{\text{pyr}}$). IR (ATR): $\tilde{\nu} = 3325, 1561, 1468, 1439, 1327, 1244, 1181, 1119, 1108, 1095, 1024, 961, 884, 857, 797, 720, 667, 600, 586$ cm^{-1} . MS (EI, 70 eV, 20 °C): m/z (%) = 146 (100) [M] $^+$, 145 (70) [$M - \text{H}$] $^+$, 80 (30) [$\text{C}_5\text{H}_6\text{N}$] $^+$. HRMS ($\text{C}_9\text{H}_{10}\text{N}_2$): calc.: 146.0844, found: 146.0845.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-PBTPREHATA-UHFFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ.4>.

Ethyl 4-formylbenzoate (2):^[17b] To a solution of 4.87 g 4-formylbenzoic acid (32.4 mmol, 1.00 equiv) in 125 mL of DMF were added 8.68 g K_2CO_3 (62.8 mmol, 1.94 equiv) and 6.60 mL of iodo-

ethane (12.8 g, 82.1 mmol, 2.54 equiv). After stirring the reaction for 3 h at rt, water was added, the phases got separated and the aqueous phase was extracted with diethyl ether two times. The combined organic phases were washed with brine, dried over MgSO_4 , and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (cyclohexane/EtOAc 6:1) to yield 4.90 g of **2** (27.5 mmol, 85%) as a light yellowish liquid. R_f (cyclohexane/EtOAc, 6:1)=0.83. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm)=1.38 (t, $^3J=7.1$ Hz, 3H, CH_3), 4.38 (q, $^3J=7.1$ Hz, 2H, CH_2), 7.91 (d, $^3J=8.5$ Hz, 2H, $2 \times \text{CH}_A$), 8.16 (d, $^3J=8.5$ Hz, 2H, $2 \times \text{CH}_B$), 10.06 (s, 1H, OCH). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm)=14.3 (+, CH_3), 61.6 (–, CH_2), 129.5 (+, $2 \times \text{C}_{ArH}$), 130.2 (+, $2 \times \text{C}_{ArH}$), 135.5 (C_q , C_{Ar}), 139.2 (C_q , C_{Ar}), 165.6 (C_q , COO), 191.7 (+, OCH). IR (ATR): $\tilde{\nu}=2924, 2854, 1701, 1577, 1503, 1448, 1367, 1272, 1200, 1172, 1103, 1017, 854, 818, 758, 733, 690, 630, 461$ cm^{-1} . MS (EI, 70 eV, 20 °C): m/z (%)=178 (44) [$\text{M}]^+$, 149 (24) [$\text{M}-\text{CO}]^+$, 133 (100) [$\text{M}-\text{C}_2\text{H}_5\text{O}]^+$, 105 (18) [$\text{M}-\text{CO}_2\text{C}_2\text{H}_5\text{O}]^+$. HRMS ($\text{C}_{10}\text{H}_{10}\text{O}_3$): calc.: 178.0630, found: 178.0630.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFADPSC-BHYVHYPRY-UHFFADPSC-NUHFF-NUHFF-NUHFF-ZZZ>.

5,15-Bis(4-ethoxycarbonylphenyl)porphyrin (3):^[17c] Through a solution of 1.10 g of dipyrromethane **1** (7.53 mmol, 2.00 equiv) and 1.36 g of aldehyde **2** (7.62 mmol, 2.02 equiv) in 800 mL of CHCl_3 was passed Ar gas for 30 min, followed by the dropwise addition of 580 μL of TFA (858 mg, 7.53 mmol, 2.00 equiv). The reaction was stirred for 17 h in the dark, after which time 3.21 mL NEt_3 (2.35 g, 23.2 mmol, 6.16 equiv) and 5.52 g *p*-chloranil (22.4 mmol, 5.96 equiv) were added in this order. The mixture was then refluxed for 90 min and the solvent was removed under reduced pressure. After filtration through silica gel (CH_2Cl_2) to remove most of the oligomeric side products, the crude product was purified by column chromatography ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 1:0 with a gradient to 50:1). The obtained solid was thoroughly washed with MeOH, leaving 1.07 g of **3** (1.76 mmol, 47%) as a purple solid. R_f (CH_2Cl_2)=0.42. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm)=–3.10 (bs, 2H, $2 \times \text{NH}$), 1.58 (t, $^3J=7.1$ Hz, 6H, $2 \times \text{CH}_3$), 4.61 (q, $^3J=7.1$ Hz, 4H, $2 \times \text{CH}_2$), 8.36 (d, $^3J=8.2$ Hz, 4H, $4 \times \text{CH}_A$), 8.51 (d, $^3J=8.2$ Hz, 4H, $2 \times \text{CH}_B$), 9.04 (d, $^3J=4.6$ Hz, 4H, $4 \times \text{H}_\beta$), 9.42 (d, $^3J=4.6$ Hz, 4H, $4 \times \text{CH}_\beta$), 10.34 (s, 2H, $2 \times \text{H}_{\text{meso}}$). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm)=14.7 (+, $2 \times \text{CH}_3$), 61.5 (–, $2 \times \text{CH}_2$), 105.8 (+, CH), 118.3 (C_q), 128.3 (+, CH), 130.1 (C_q), 130.9 (+, CH), 132.2 (+, CH), 135.0 (+, CH), 145.5 (C_q), 146.2 (C_q), 146.8 (C_q), 167.0 (C_q , $2 \times \text{COO}$). UV/Vis (CHCl_3): λ_{max} (log ϵ)=405 (5.27), 504 (4.22), 539 (3.85), 576 (3.74), 631 (3.33) nm. IR (ATR): $\tilde{\nu}=3484, 3276, 2976, 1703, 1602, 1437, 1398, 1363, 1305, 1268, 1239, 1194, 1173, 1096, 1051, 1017, 986, 971, 952, 900, 868, 843, 812, 792, 752, 736, 723, 691, 520, 489, 435, 411$ cm^{-1} . MS (FAB, 3-NBA): m/z (%)=607 (100) [$\text{M}+\text{H}]^+$. HRMS ($\text{C}_{38}\text{H}_{31}\text{O}_4\text{N}_4$): calc.: 607.2340, found: 607.2340.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFADPSC-QKHPYPU-CYC-UHFFADPSC-NUHFF-NHYOA-NUHFF-ZZZ>.

5,15-Dibromo-10,20-bis(4-ethoxycarbonylphenyl)porphyrin

(4):^[17d,e] To a solution of 933 mg of porphyrin **3** (1.54 mmol, 1.00 equiv) in 385 mL of CHCl_3 was added 0.38 mL pyridine (377 mg, 4.77 mmol, 3.10 equiv). The mixture was cooled to 0 °C and 646 mg NBS was added, as well as 50 mg in intervals of 30 min, respectively, until complete conversion was observed by TLC (Σ 746 mg, 4.19 mmol, 2.72 equiv). After the addition of the last portion, the reaction was stirred for 30 min and the mixture was directly filtered through silica gel eluting with CH_2Cl_2 . The sol-

vent of the filtrate was removed under reduced pressure and the crude product was purified by column chromatography (CH_2Cl_2). The obtained solid was recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ yielding 1.00 g of **4** (1.31 mmol, 85%) as a purple solid. R_f (CH_2Cl_2)=0.60. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm)=–2.77 (bs, 2H, $2 \times \text{NH}$), 1.57 (t, $^3J=7.1$ Hz, 6H, $2 \times \text{CH}_3$), 4.60 (q, $^3J=7.1$ Hz, 4H, $2 \times \text{CH}_2$), 8.23 (d, $^3J=8.1$ Hz, 4H, $4 \times \text{o-CH}_{Ar}$), 8.47 (d, $^3J=8.1$ Hz, 4H, $4 \times \text{m-CH}_{Ar}$), 8.78 (d, $^3J=4.8$ Hz, 4H, $4 \times \text{CH}_\beta$), 9.62 (d, $^3J=4.9$ Hz, 4H, $4 \times \text{CH}_\beta$). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm)=14.7 (+, $2 \times \text{CH}_3$), 61.6 (–, $2 \times \text{CH}_2$), 104.3 (C_q), 120.4 (C_q), 128.2 (+, CH), 130.5 (C_q), 134.6 (+, CH), 146.1 (C_q), 166.8 (C_q , $2 \times \text{COO}$). UV/Vis (CHCl_3): λ_{max} (log ϵ)=423 (5.42), 522 (4.21), 557 (4.01), 601 (3.66), 659 (3.62) nm. IR (ATR): $\tilde{\nu}=3314, 2921, 1709, 1605, 1557, 1465, 1397, 1366, 1336, 1302, 1272, 1193, 1175, 1122, 1106, 1018, 997, 979, 961, 869, 848, 795, 785, 755, 729, 706, 630, 555, 523, 500, 458, 394$ cm^{-1} . MS (FAB, 3-NBA): m/z (%)=762/763/764/765/766/767/768 (34/51/87/100/72/56/31) [$\text{M}]^+$ / [$\text{M}+\text{H}]^+$. HRMS (FAB, $\text{C}_{38}\text{H}_{29}\text{O}_4\text{N}_4^{79}\text{Br}^{81}\text{Br}$): calc.: 765.0530, found: 765.0528.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFADPSC-DJGWMTKMO-UHFFADPSC-NUHFF-NNYHH-NUHFF-ZZZ>.

General procedure A for Suzuki cross-coupling reactions:^[22] In a vial (or divided into several vials) the porphyrin (1.00 equiv), the boronic acid (12.4 equiv), K_3PO_4 (25.0 equiv) and $\text{Pd}(\text{PPh}_3)_4$ (0.12 equiv) were put under Ar atmosphere and dissolved in dry THF. The reaction was stirred at 80 °C until TLC control showed no further conversion of starting material (at least 15 h). After letting the solution cool down to rt the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 . After washing with saturated aqueous NaHCO_3 solution and H_2O the organic phase was dried over Na_2SO_4 , filtered and the solvent removed under reduced pressure. The crude product was isolated by flash column chromatography (silica) and, if necessary, finally washed with MeOH.

General procedure B for Sonogashira cross-coupling reactions:^[22] The porphyrin (1.00 equiv), the alkyne (4.00 equiv), CuI (0.12 equiv) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.10 equiv) were put under Ar atmosphere, dissolved in dry THF and dry NEt_3 and degassed with an Ar stream for 10 min (liquid alkynes were added after degassing the solution). The solution was stirred until TLC control showed no further conversion of starting material (at least 16 h). The solvents were removed under reduced pressure, the residue was dissolved in CH_2Cl_2 , washed with saturated aqueous NaHCO_3 solution and H_2O and the organic phase was dried over Na_2SO_4 . After filtration, the solvent was removed under reduced pressure. The crude product was isolated by flash column chromatography (silica). If necessary, the product was finally dissolved in a minimal amount of CH_2Cl_2 and three times the amount of MeOH was added. The CH_2Cl_2 was removed under reduced pressure and the resulting solid was isolated by filtration.

General procedure C for the hydrolysis of ester terminated porphyrins:^[38] In a vial, the porphyrin was dissolved in THF and MeOH or EtOH, as well as an aqueous solution of LiOH, NaOH or KOH, was added. The reaction mixture was heated for at least 16 h and the organic solvents were subsequently removed under reduced pressure. Precipitating porphyrins were filtered off and washed with CH_2Cl_2 and H_2O . The aqueous filtrate was combined with the washing water and washed with CH_2Cl_2 . By the addition of diluted hydrochloric acid, a pH value of 4–5 was adjusted, leading to precipitation of the porphyrin. The solid was filtered off and washed with diluted hydrochloric acid (pH 4–5). The obtained solids were combined, dissolved in MeOH/EtOH/DMF/ NEt_3 and filtered. Remov-

al of the solvents under reduced pressure gave the products. As contaminations in form of remaining salts, as well as the formation of Li-/Na-/K-salts of the carboxylic acids, could not be excluded, yields for the carboxylic acids were not determined (calculated yields exceeded 100% in all cases). A complete conversion to the corresponding dicarboxylic acids is assumed.

Diethyl 4,4'-(10,20-diphenylporphyrin-5,15-diyl)dibenzoate (5a): The compound was synthesized according to general procedure A using 152 mg of porphyrin **4** (198 μmol), 287 mg phenylboronic acid (2.36 mmol), 1.04 g K_3PO_4 (4.91 mmol) and 27 mg $\text{Pd}(\text{PPh}_3)_4$ (24 μmol) in 45 mL of THF equally divided on three vials and a reaction time of 15 h. Column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ (1:1 to 1:0) yielded 134 mg of the desired porphyrin **5a** (176 μmol , 89%) as a violet solid. R_f (CH_2Cl_2)=0.50. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm)=−2.78 (bs, 2H, 2 \times NH), 1.57 (t, $^3J=7.1$ Hz, 6H, 2 \times CH_3), 4.59 (q, $^3J=7.2$ Hz, 4H, 2 \times CH_2), 7.72–7.85 (m, 6H, 6 \times CH_{Ph}), 8.23 (dd, $J=7.6$, 1.7 Hz, 4H, 4 \times CH_{Ph}), 8.32 (d, $^3J=8.2$ Hz, 4H, 4 \times $o\text{-CH}_{\text{Ar}}$), 8.47 (d, $^3J=8.2$ Hz, 4H, 4 \times $m\text{-CH}_{\text{Ar}}$), 8.82 (d, $^3J=4.9$ Hz, 4H, 4 \times CH_{P}), 8.89 (d, $^3J=4.9$ Hz, 4H, 4 \times CH_{P}). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm)=14.7 (+, 2 \times CH_3), 61.5 −, 2 \times CH_2), 119.1 (C_q), 120.7 (C_q), 126.9 (+, CH), 128.0 (+, CH), 128.0 (+, CH), 130.1 (C_q), 142.0 (C_q), 147.0 (C_q), 167.0 (C_q , 2 \times COO). UV/Vis (CHCl_3): λ_{max} (log ϵ)=419 (5.39), 516 (4.28), 551 (3.92), 591 (3.76), 646 (3.57) nm. IR (ATR): $\tilde{\nu}$ =3297, 3048, 3103, 2906, 2978, 1713, 1604, 1473, 1438, 1401, 1364, 1309, 1269, 1177, 1099, 1023, 980, 964, 863, 799, 754, 730, 704, 656, 635, 564, 455 cm^{-1} . MS (FAB, 3-NBA): m/z (%)=759 (100) $[\text{M}+\text{H}]^+$, 758 (80) $[\text{M}]^+$. HRMS (FAB, $\text{C}_{50}\text{H}_{39}\text{N}_4\text{O}_4$): calc.: 759.2971, found: 759.2969.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-CQICNQVIXS-UHFFFADPSC-NUHFF-NKDHF-NUHFF-ZZZ>.

Diethyl 4,4'-(10,20-bis(4-cyanophenyl)porphyrin-5,15-diyl)dibenzoate (5b): The compound was synthesized according to general procedure A using 81 mg of porphyrin **4** (106 μmol), 190 mg (4-cyanophenyl)boronic acid (1.29 mmol), 560 mg K_3PO_4 (2.64 mmol) and 15 mg $\text{Pd}(\text{PPh}_3)_4$ (13 μmol) in 70 mL of THF and a reaction time of 18 h. Column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (100:1) yielded 83 mg of the desired porphyrin **5b** (103 μmol , 97%) as a violet solid. R_f (CH_2Cl_2)=0.52. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm)=−2.84 (bs, 2H, 2 \times NH), 1.57 (t, $^3J=7.2$ Hz, 6H, 2 \times CH_3), 4.59 (q, $^3J=7.1$ Hz, 4H, 2 \times CH_2), 8.09 (d, $^3J=8.3$ Hz, 4H, 4 \times CH_{ArCN}), 8.29 (d, $^3J=8.2$ Hz, 4H, 4 \times $o\text{-CH}_{\text{Ar}}$), 8.34 (d, $^3J=8.4$ Hz, 4H, 4 \times CH_{ArCN}), 8.47 (d, $^3J=8.3$ Hz, 4H, 4 \times $m\text{-CH}_{\text{Ar}}$), 8.77 (d, $^3J=4.8$ Hz, 4H, 4 \times CH_{P}), 8.85 (d, $^3J=4.9$ Hz, 4H, 4 \times CH_{P}). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm)=14.7 (+, 2 \times CH_3), 61.6 −, 2 \times CH_2), 112.4 (C_q), 112.6 (C_q), 118.5 (C_q), 118.6 (C_q), 119.0 (C_q), 120.0 (C_q), 128.1 (+, CH), 128.2 (+, CH), 130.4 (C_q), 130.8 (+, CH), 133.0 (+, CH), 134.6 (+, CH), 135.1 (+, CH), 143.7 (C_q), 146.4 (C_q), 146.8 (C_q), 166.8 (C_q , COO). UV/Vis (CHCl_3): λ_{max} (log ϵ)=420 (5.40), 516 (4.16), 552 (3.76), 591 (3.61), 647 (3.30) nm. IR (ATR): $\tilde{\nu}$ =2922, 2224, 1710, 1601, 1557, 1472, 1396, 1363, 1306, 1266, 1175, 1067, 1020, 980, 964, 860, 798, 753, 731, 634, 568, 543 cm^{-1} . MS (FAB, 3-NBA): m/z (%)=809 (40) $[\text{M}+\text{H}]^+$, 663 (100) $[\text{M}-2\times\text{CO}_2\text{Et}]^+$, 647 (50). HRMS (FAB, $\text{C}_{52}\text{H}_{37}\text{O}_4\text{N}_6$): calc.: 809.2871, found: 809.2873.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-UYKMRQ-XETK-UHFFFADPSC-NUHFF-NWLSV-NUHFF-ZZZ>.

Diethyl 4,4'-(10,20-bis(4-formylphenyl)porphyrin-5,15-diyl)dibenzoate (5c): The compound was synthesized according to general procedure A using 103 mg of porphyrin **4** (134 μmol), 235 mg (4-formylphenyl)boronic acid (1.57 mmol), 739 mg K_3PO_4

(3.48 mmol) and 22.8 mg $\text{Pd}(\text{PPh}_3)_4$ (19.7 μmol) in 48 mL of THF and a reaction time of 18 h. Column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (100:1 to 20:1) yielded 84.8 mg of the desired porphyrin **5c** (104 μmol , 78%) as a violet solid. R_f ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 9:1)=0.79. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm)=−2.79 (bs, 2H, 2 \times NH), 1.56 (t, $^3J=7.1$ Hz, 6H, 2 \times CH_2CH_3), 4.57 (q, $^3J=7.1$ Hz, 4H, 2 \times CH_2), 8.30 (d, $^3J=8.1$ Hz, 8H, 8 \times CH_{Ar}), 8.40 (d, $^3J=7.9$ Hz, 4H, 4 \times CH_{Ar}), 8.46 (d, $^3J=8.2$ Hz, 4H, 4 \times CH_{Ar}), 8.82 (d, $^3J=4.8$ Hz, 4H, 4 \times CH_{P}), 8.84 (d, $^3J=4.9$ Hz, 4H, 4 \times CH_{P}), 10.40 (s, 2H, 2 \times CHO). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm)=14.7 (+, 2 \times CH_2CH_3), 61.5 −, 2 \times CH_2), 119.2 (C_q), 119.8 (C_q), 128.1 (+, CH), 128.2 (+, CH), 130.4 (C_q), 134.6 (+, CH), 135.3 (+, CH), 136.0 (C_q), 146.5 (C_q), 148.4 (C_q), 166.9 (C_q , 2 \times COO), 192.4 (+, 2 \times CHO). UV/Vis (CHCl_3): λ_{max} (log ϵ)=421 (5.39), 516 (4.26), 552 (3.91), 591 (3.74), 646 (3.49) nm. IR (ATR): $\tilde{\nu}$ =3306, 3109, 2979, 2922, 2902, 2820, 2724, 2707, 1698, 1599, 1564, 1473, 1400, 1384, 1364, 1305, 1266, 1204, 1176, 1167, 1098, 1020, 990, 980, 965, 851, 796, 756, 731, 704, 671, 632, 490 cm^{-1} . MS (ESI): m/z (%)=815 (100) $[\text{M}+\text{H}]^+$, 681 (21), 563 (30). HRMS (ESI, $\text{C}_{52}\text{H}_{37}\text{O}_4\text{N}_6$): calc.: 815.2864 found: 815.2853.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-DVNRJFZLK-UHFFFADPSC-NUHFF-NWLSV-NUHFF-ZZZ>.

Diethyl 4,4'-(10,20-bis(3,4,5-trifluorophenyl)porphyrin-5,15-diyl)dibenzoate (5d): The compound was synthesized according to general procedure A using 95 mg of porphyrin **4** (124 μmol), 265 mg (3,4,5-trifluorophenyl)boronic acid (1.51 mmol), 650 mg K_3PO_4 (3.06 mmol) and 15 mg $\text{Pd}(\text{PPh}_3)_4$ (13 μmol) in 85 mL of THF and a reaction time of 16 h. Column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (1:0 to 100:1) yielded 96 mg of the desired porphyrin **5d** (110 μmol , 89%) as a violet solid. R_f (CH_2Cl_2)=0.74. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ (ppm)=−2.91 (bs, 2H, 2 \times NH), 1.57 (t, $^3J=7.1$ Hz, 6H, 2 \times CH_3), 4.60 (q, $^3J=7.1$ Hz, 4H, 2 \times CH_2), 7.80–7.91 (m, 4H, 4 \times CH_{ArF}), 8.30 (d, $^3J=8.2$ Hz, 4H, 4 \times $o\text{-CH}_{\text{Ar}}$), 8.48 (d, $^3J=8.3$ Hz, 4H, 4 \times $m\text{-CH}_{\text{Ar}}$), 8.79–8.93 (m, 8H, 8 \times CH_{P}). $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ (ppm)=14.7 (+, 2 \times CH_3), 61.6 −, 2 \times CH_2), 117.1 (C_q), 118.8 (m, 4 \times CHCF), 120.0 (C_q), 128.2 (+, CH), 130.5 (C_q), 134.6 (+, CH), 137.8 (m, 2 \times CCHCF), 140.3 (dt, $^1J=254.0$, $^2J=15.3$ Hz, 2 \times $p\text{-CF}$), 146.3 (C_q), 149.8 (ddd, $^1J=252.8$, $^2J=9.8$, $^3J=4.1$ Hz, 4 \times $m\text{-CF}$), 166.8 (C_q , COO). $^{19}\text{F-NMR}$ (377 MHz, CDCl_3): δ (ppm)=−140.0 (d, $^3J=20.6$ Hz, 4F, 4 \times $m\text{-CF}$), −165.4 (t, $^3J=20.6$ Hz, 2F, 2 \times $p\text{-CF}$). UV/Vis (CHCl_3): λ_{max} (log ϵ)=417 (5.41), 514 (4.26), 549 (3.76), 590 (3.73), 646 (3.30) nm. IR (ATR): $\tilde{\nu}$ =3302, 3070, 1707, 1607, 1525, 1475, 1423, 1401, 1365, 1307, 1271, 1237, 1176, 1108, 1040, 1022, 973, 928, 869, 849, 805, 762, 732, 717, 636, 561, 541, 408 cm^{-1} . MS (FAB, 3-NBA): m/z (%)=867 (100) $[\text{M}+\text{H}]^+$, 866 (78) $[\text{M}]^+$. HRMS (FAB, $\text{C}_{50}\text{H}_{33}\text{O}_4\text{N}_4\text{F}_6$): calc.: 867.2401, found: 867.2403.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-LVGO-HACWPD-UHFFFADPSC-NUHFF-NUVBP-NUHFF-ZZZ>.

Diethyl 4,4'-(10,20-bis(3,4,5-trimethoxyphenyl)porphyrin-5,15-diyl)dibenzoate (5j): The compound was synthesized according to general procedure A using 153 mg of porphyrin **4** (200 μmol), 509 mg (3,4,5-trimethoxyphenyl)boronic acid (2.40 mmol), 1.06 g K_3PO_4 (5.00 mmol) and 27.7 mg $\text{Pd}(\text{PPh}_3)_4$ (24.0 μmol) in 80 mL of THF and a reaction time of 19 h. Column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (100:1 to 10:1) yielded 148 mg of the desired porphyrin **5j** (158 μmol , 79%) as a violet solid. R_f ($\text{CH}_2\text{Cl}_2/\text{EtOAc}$, 20:1)=0.52. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ (ppm)=−2.08 (s, 2 \times NH), 1.57 (t, $^3J=7.2$ Hz, 6H, 2 \times CH_2CH_3), 3.98 (s, 12H, 4 \times OCH_3), 4.19 (s, 6H, 2 \times OCH_3), 4.60 (q, $^3J=7.1$ Hz, 4H, 2 \times CH_2CH_3), 7.48 (s,

4H, 4 × CH_{AROMe} , 8.31 (d, $^3J=8.2$ Hz, 4H, 4 × $o\text{-CH}_{\text{Ar}}$), 8.47 (d, $^3J=8.2$ Hz, 4H, 4 × $m\text{-CH}_{\text{Ar}}$), 8.82 (d, $^3J=4.8$ Hz, 4H, 4 × CH_{β}), 8.99 (d, $^3J=4.8$ Hz, 4H, 4 × CH_{β}). ^{13}C NMR (126 MHz, CDCl_3): δ (ppm) = 14.7 (2 × CH_2CH_3), 56.5, 61.5, 61.5, 113.0, 119.3, 120.5, 128.1, 130.2, 134.6, 137.5, 138.0, 146.8, 151.6, 166.9 (2 × COO). UV/Vis (CHCl_3): λ_{max} (log ϵ) = 421 (5.47), 517 (4.30), 553 (3.93), 591 (3.78), 647 (3.57) nm. IR (ATR): $\tilde{\nu}=2929, 1713, 1605, 1577, 1494, 1462, 1448, 1431, 1402, 1354, 1324, 1268, 1232, 1177, 1123, 1096, 1058, 1020, 1003, 984, 972, 925, 868, 850, 796, 767, 730, 722, 701, 663, 633$ cm^{-1} . MS (FAB, 3-NBA): m/z (%) = 939 (100) $[\text{M}+\text{H}]^+$, 938 (88) $[\text{M}]^+$, 940 (54), 941 (20). HRMS (FAB, $\text{C}_{56}\text{H}_{51}\text{O}_{10}\text{N}_4$): calc.: 939.3605, found: 939.3607.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-JQMQMHNZHWI-UHFFFADPSC-NUHFF-NNSBK-NUHFF-ZZZ>.

Diethyl 4,4'-(10,20-bis(pyrimidin-5-yl)porphyrin-5,15-diyl)dibenzoate (5p): The compound was synthesized according to general procedure A using 90 mg of porphyrin **4** (118 μmol), 185 mg pyridin-3-ylboronic acid (1.49 mmol), 640 mg K_3PO_4 (3.02 mmol) and 15.3 mg $\text{Pd}(\text{PPh}_3)_4$ (13.2 μmol) divided into five vials with 16.5 mL of THF respectively and a reaction time of 96 h. Column chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{acetone}$ (50:3 to 1:1) yielded 64.6 mg of the desired porphyrin **5p** (84.7 μmol , 72%) as a violet solid. R_f ($\text{CH}_2\text{Cl}_2/\text{acetone}$, 10:1) = 0.70. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = -2.84 (bs, 2H, 2 × NH), 1.57 (t, $^3J=7.1$ Hz, 6H, 2 × CH_3), 4.60 (q, $^3J=7.1$ Hz, 4H, 2 × CH_2), 8.32 (d, $^3J=8.2$ Hz, 4H, 4 × $o\text{-CH}_{\text{Ar}}$), 8.49 (d, $^3J=8.2$ Hz, 4H, 4 × $m\text{-CH}_{\text{Ar}}$), 8.82 (d, $^3J=4.9$ Hz, 4H, 4 × CH_{β}), 8.94 (d, $^3J=4.9$ Hz, 4H, 4 × CH_{β}), 9.58 (s, 4H, 4 × $\text{CH}_{\text{pyrimidin-4,6}}$), 9.68 (s, 2H, 2 × $\text{CH}_{\text{pyrimidin-2}}$). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 14.7 (+, 2 × CH_3), 61.6 (-, 2 × CH_2), 112.7 (C_q), 120.5 (C_q), 128.2 (+, CH), 130.6 (C_q), 134.7 (+, CH), 136.1 (C_q), 146.1 (C_q), 158.3 (+, CH), 159.7 (+, CH), 166.8 (C_q , 2 × COO). UV/Vis (CHCl_3): λ_{max} (log ϵ) = 419 (5.39), 516 (4.27), 552 (3.86), 592 (3.74), 648 (3.40) nm. IR (ATR): $\tilde{\nu}=3312, 2919, 1708, 1606, 1549, 1475, 1405, 1367, 1307, 1270, 1221, 1179, 1124, 1110, 1075, 1023, 979, 964, 864, 847, 803, 762, 715, 631, 515, 453, 414$ cm^{-1} . MS (FAB, 3-NBA): m/z (%) = 763 (100) $[\text{M}+\text{H}]^+$, 762 (58) $[\text{M}]^+$, 663 (63). HRMS (FAB, $\text{C}_{46}\text{H}_{35}\text{O}_4\text{N}_8$): calc.: 763.2781, found: 763.2782.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-DJCDFXZBRU-UHFFFADPSC-NUHFF-NOCLW-NUHFF-ZZZ>.

Diethyl 4,4'-(10,20-bis(phenanthren-9-yl)porphyrin-5,15-diyl)dibenzoate (5t): The compound was synthesized according to general procedure A using 54.5 mg of porphyrin **4** (71.3 μmol), 190 mg phenanthren-9-ylboronic acid (856 μmol), 378 mg K_3PO_4 (1.78 mmol) and 15.8 mg $\text{Pd}(\text{PPh}_3)_4$ (13.7 μmol) in 48 mL of THF and a reaction time of 18 h. Column chromatography eluting with CH_2Cl_2 yielded 46.2 mg of the desired porphyrin **5t** (48.2 μmol , 68%) as a violet solid. R_f (CH_2Cl_2) = 0.77. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = -2.44 (bs, 2H, 2 × NH), 1.51 (t, $^3J=7.1$ Hz, 6H, 2 × CH_3), 4.54 (q, $^3J=7.1$ Hz, 4H, 2 × CH_2), 7.16–7.22 (m, 4H, 4 × CH_{phen}), 7.64–7.70 (m, 2H, 2 × CH_{phen}), 7.81 (t, $^3J=7.4$ Hz, 2H, 2 × CH_{phen}), 7.91 (t, $^3J=7.7$ Hz, 2H, 2 × CH_{phen}), 8.09 (d, $^3J=7.7$ Hz, 2H, 2 × CH_{phen}), 8.24–8.32 (m, 4H, 4 × $o\text{-CH}_{\text{Ar}}$), 8.37–8.45 (m, 4H, 4 × $m\text{-CH}_{\text{Ar}}$), 8.57 (d, $^3J=7.8$ Hz, 2H, 2 × CH_{β}), 8.71 (d, $^3J=4.7$ Hz, 4H, 4 × CH_{β}), 8.75 (d, $^3J=4.4$ Hz, 4H, 4 × CH_{β}), 9.02 (t, $^3J=8.2$ Hz, 4H, 4 × CH_{phen}). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 14.6 (+, 2 × CH_3), 61.4 (2 × CH_2), 118.2 (C_q), 119.2 (C_q), 122.7 (+, CH), 123.0 (+, CH), 126.5 (+, CH), 126.9 (+, CH), 127.5 (+, CH), 127.6 (+, CH), 128.0 (+, CH), 129.3 (+, CH), 129.8 (C_q), 130.1 (+, CH), 130.9 (C_q), 131.0 (C_q), 133.8 (+, CH), 133.9 (+, CH), 134.6 (+, CH), 136.4 (C_q), 137.8 (C_q), 146.7

(C_q), 166.9 (C_q , 2 × COO). UV/Vis (CHCl_3): λ_{max} (log ϵ) = 255 (4.95), 425 (5.43), 517 (4.24), 552 (3.71), 591 (3.73), 648 (3.31) nm. IR (ATR): $\tilde{\nu}=3310, 2920, 1713, 1605, 1448, 1400, 1365, 1267, 1175, 1097, 1021, 974, 942, 819, 798, 722, 616, 481, 427, 403, 387$ cm^{-1} . MS (FAB, 3-NBA): m/z (%) = 959 (100) $[\text{M}+\text{H}]^+$, 958 (79) $[\text{M}]^+$. HRMS (FAB, $\text{C}_{66}\text{H}_{47}\text{O}_4\text{N}_4$): calc.: 959.3592, found: 959.3589.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-LLIFZWKYAN-UHFFFADPSC-NUHFF-NHDGP-NUHFF-ZZZ>.

Diethyl 4,4'-(10,20-bis(phenylethynyl)porphyrin-5,15-diyl)dibenzoate (6a): The compound was synthesized according to general procedure B using 77.2 mg of porphyrin **4** (101 μmol), 3.9 mg CuI (20 μmol), 7.0 mg $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (10 μmol), 44 μL phenylacetylene (41 mg, 0.40 mmol), 10 mL dry THF and 21 mL dry NEt_3 with a reaction time of 18 h. Column chromatography eluting with CHCl_3 yielded 62.1 mg of porphyrin **6a** (77.0 μmol , 76%) as a greenish-violet solid. R_f (CH_2Cl_2) = 0.69. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = -2.06 (bs, 2H, 2 × NH), 1.58 (t, $^3J=7.2$ Hz, 6H, 2 × CH_3), 4.61 (q, $^3J=7.1$ Hz, 4H, 2 × CH_2), 7.47–7.55 (m, 2H, 2 × $p\text{-CH}_{\text{Ph}}$), 7.55–7.63 (m, 4H, 4 × $m\text{-CH}_{\text{Ph}}$), 7.98–8.07 (m, 4H, 4 × $o\text{-CH}_{\text{Ph}}$), 8.27 (d, $^3J=8.2$ Hz, 4H, 4 × $o\text{-CH}_{\text{Ar}}$), 8.48 (d, $^3J=8.2$ Hz, 4H, 4 × $m\text{-CH}_{\text{Ar}}$), 8.77 (d, $^3J=4.7$ Hz, 4H, 4 × CH_{β}), 9.68 (d, $^3J=4.7$ Hz, 4H, 4 × CH_{β}). ^{13}C NMR (101 MHz, CDCl_3): δ (ppm) = 14.7 (+, 2 × CH_3), 61.5 (-, 2 × CH_2), 91.8 (C_q), 97.8 (C_q), 101.8 (C_q), 120.8 (C_q), 123.8 (C_q), 128.2 (+, CH), 128.9 (+, CH), 129.0 (+, CH), 130.4 (C_q), 131.9 (+, CH), 134.6 (+, CH), 146.1 (C_q), 166.9 (C_q , 2 × COO). UV/Vis (CHCl_3): λ_{max} (log ϵ) = 307 (4.45), 442 (5.36), 519 (3.79), 556 (4.01), 599 (4.70), 690 (4.32) nm. IR (ATR): $\tilde{\nu}=2972, 1709, 1604, 1553, 1487, 1470, 1399, 1362, 1264, 1176, 1159, 1099, 1065, 1019, 973, 923, 866, 807, 788, 761, 749, 716, 683, 633, 581, 565, 540, 514, 441$ cm^{-1} . MS (FAB, 3-NBA): m/z (%) = 807 (100) $[\text{M}+\text{H}]^+$, 806 (76) $[\text{M}]^+$. HRMS (FAB, $\text{C}_{54}\text{H}_{39}\text{O}_4\text{N}_4$): calc.: 807.2966, found: 807.2964.

Additional reaction details and data obtained from the characterization of the target compound can be accessed at: <https://dx.doi.org/10.14272/reaction/SA-FUHFF-UHFFFADPSC-LHQKMBXIU-UHFFFADPSC-NUHFF-NLTS-NUHFF-ZZZ>.

4,4'-(Porphyrin-5,15-diyl)bisbenzoic acid (3'): The compound was synthesized according to general procedure C using 60 mg of porphyrin **3** (98.9 μmol), 11.6 mL THF, 4.4 mL MeOH and a solution of 1.18 g LiOH (49.5 mmol) in 10.7 mL of H_2O . The reaction ran for 20 h at 50 °C. UV/Vis (MeOH): λ_{max} (rel. Abs.) = 403 (2.91), 500 (0.17), 533 (0.08), 574 (0.06), 629 (0.03) nm. IR (ATR): $\tilde{\nu}=3357, 3274, 2978, 2944, 2928, 2621, 2602, 2496, 1585, 1541, 1475, 1397, 1269, 1238, 1197, 1171, 1147, 1035, 989, 975, 955, 905, 875, 853, 781, 772, 732, 691, 635, 487, 424, 414, 404, 391$ cm^{-1} . MS (ESI): m/z (%) = 549 (46) $[\text{M}-\text{H}]^-$, 274 (100) $[\text{M}-2\text{H}]^{2-}$. HRMS (ESI, $\text{C}_{34}\text{H}_{21}\text{O}_4\text{N}_4$): calc.: 549.1568, found: 549.1573.

4,4'-(10,20-Diphenylporphyrin-5,15-diyl)bisbenzoic acid (5a'): The compound was synthesized according to general procedure C using 75.5 mg of porphyrin **5a** (99.5 μmol), 8.0 mL THF, 2.0 mL MeOH, and 6.0 mL aqueous NaOH solution (40w%). The reaction ran for 16 h at 90 °C. UV/Vis (MeOH): λ_{max} (rel. Abs.) = 294 (0.13), 414 (2.59), 512 (0.13), 547 (0.07), 589 (0.05), 645 (0.04) nm. IR (ATR): $\tilde{\nu}=2324, 1683, 1604, 1555, 1471, 1419, 1399, 1349, 1314, 1286, 1179, 1152, 1127, 1074, 1020, 979, 963, 878, 868, 847, 798, 771, 753, 720, 701, 685, 656, 634, 570, 537, 508, 471, 407$ cm^{-1} . MS (ESI): m/z (%) = 703 (100) $[\text{M}+\text{H}]^+$. HRMS (ESI, $\text{C}_{46}\text{H}_{31}\text{O}_4\text{N}_4$): calc.: 703.2340, found: 703.2332.

4,4'-(10,20-Bis(4-cyanophenyl)porphyrin-5,15-diyl)bisbenzoic acid (5b'): The compound was synthesized according to general procedure C using 43 mg of porphyrin **5b** (53 μmol), 5.0 mL THF,

1.3 mL EtOH and 5.1 mL aqueous KOH solution (40w%). UV/Vis (MeOH): λ_{max} (rel. Abs.)=225 (0.39), 294 (0.14), 415 (2.84), 513 (0.14), 547 (0.06), 589 (0.04), 645 (0.03) nm. IR (ATR): $\tilde{\nu}$ =3315, 2868, 1686, 1604, 1547, 1380, 1309, 1244, 1166, 1040, 1018, 980, 963, 897, 866, 793, 766, 710, 649, 630, 562, 555, 518, 504, 494, 462, 448, 424, 384 cm^{-1} . MS (ESI): m/z (%)=751 (100) $[M-H]^-$. HRMS (ESI, $\text{C}_{48}\text{H}_{27}\text{O}_4\text{N}_6$): calc.: 751.2099, found: 751.2112.

4,4'-(10,20-Bis(4-formylphenyl)porphyrin-5,15-diyl)bisbenzoic acid (5c'): The compound was synthesized according to general procedure C using 31.0 mg of porphyrin **5c** (38.0 μmol), 4.5 mL THF, 1.7 mL MeOH and a solution of 456 mg LiOH (19.0 mmol) in 4.1 mL of H_2O . MS (ESI): m/z (%)=757 (100) $[M-H]^-$. HRMS (ESI, $\text{C}_{50}\text{H}_{31}\text{O}_4\text{N}_4$): calc.: 757.2093, found: 757.2109.

4,4'-(10,20-Bis(3,4,5-trifluorophenyl)porphyrin-5,15-diyl)bisbenzoic acid (5d'): The compound was synthesized according to general procedure C using 35 mg of porphyrin **5c** (39 μmol), 3.8 mL THF, 0.9 mL EtOH, and 3.8 mL aqueous KOH solution (40w%). UV/Vis (MeOH): λ_{max} (rel. Abs.)=301 (0.06), 413 (1.63), 511 (0.8), 545 (0.03), 587 (0.02), 643 (0.01) nm. IR (ATR): $\tilde{\nu}$ =2367, 1617, 1589, 1537, 1384, 1044, 973, 829, 797, 719, 703, 660, 440 cm^{-1} . MS (ESI): m/z (%)=809 (100) $[M-H]^-$. HRMS (ESI, $\text{C}_{46}\text{H}_{23}\text{O}_4\text{N}_4\text{F}_6$): calc.: 809.1629, found: 809.1655.

4,4'-(10,20-Bis(3,4,5-trimethoxyphenyl)porphyrin-5,15-diyl)bisbenzoic acid (5j'): The compound was synthesized according to general procedure C using 55.5 mg of porphyrin **5i** (59.1 μmol), 8.5 mL THF, 1.8 mL MeOH, and 8.5 mL aqueous NaOH solution (40w%). UV/Vis (MeOH): λ_{max} (rel. Abs.)=417 (2.20), 514 (0.10), 548 (0.04), 589 (0.03), 645 (0.02) nm. IR (ATR): $\tilde{\nu}$ =2928, 2833, 1683, 1604, 1579, 1499, 1462, 1408, 1354, 1313, 1283, 1231, 1179, 1122, 1006, 986, 972, 924, 867, 796, 764, 721, 686, 633, 540, 526, 500, 483 cm^{-1} . MS (ESI): m/z (%)=883 (100) $[M+H]^+$. HRMS (ESI, $\text{C}_{52}\text{H}_{43}\text{O}_{10}\text{N}_4$): calc.: 883.2974, found: 883.2961.

4,4'-(10,20-Di(pyrimidin-5-yl)porphyrin-5,15-diyl)bisbenzoic acid (5p'): The compound was synthesized according to general procedure C using 34 mg of porphyrin **5o** (45 μmol), 4.3 mL THF, 1.1 mL EtOH, and 4.3 mL aqueous NaOH solution (40w%). UV/Vis (MeOH): λ_{max} (rel. Abs.)=304 (0.14), 415 (3.00), 513 (0.16), 547 (0.07), 589 (0.05), 645 (0.03) nm. IR (ATR): $\tilde{\nu}$ =2339, 1586, 1539, 1417, 1386, 1230, 1187, 1158, 1100, 983, 965, 833, 796, 784, 734, 718, 699, 634, 597, 553, 492, 461, 426, 418 cm^{-1} . MS (ESI): m/z (%)=705 (100) $[M-H]^-$. HRMS (ESI, $\text{C}_{42}\text{H}_{25}\text{O}_4\text{N}_8$): calc.: 705.2004, found: 705.2020.

4,4'-(10,20-Di(phenanthren-9-yl)porphyrin-5,15-diyl)bisbenzoic acid (5t'): The compound was synthesized according to general procedure C using 46.2 mg of porphyrin **5s** (48.2 μmol), 5.7 mL THF, 2.1 mL MeOH and a solution of 577 mg LiOH (24.1 mmol) in 5.3 mL of H_2O . UV/Vis (MeOH): λ_{max} (rel. Abs.)=252 (0.42), 419 (1.51), 514 (0.08), 548 (0.03), 589 (0.02), 645 (0.01) nm. IR (ATR): $\tilde{\nu}$ =3366, 3310, 2978, 2927, 2606, 2495, 1591, 1544, 1472, 1448, 1381, 1346, 1249, 1218, 1159, 1037, 1017, 975, 943, 875, 798, 772, 748, 721, 666, 630, 616, 585, 509, 483, 465, 449, 425, 407, 398 cm^{-1} . MS (ESI): m/z (%)=901 (56) $[M-H]^-$, 450 (100) $[M-2H]^{2-}$. HRMS (ESI, $\text{C}_{50}\text{H}_{31}\text{O}_4\text{N}_4$): calc.: 901.2820, found: 901.2825.

4,4'-(10,20-Bis(phenylethynyl)porphyrin-5,15-diyl)bisbenzoic acid (6a'): The compound was synthesized according to general procedure C using 40.0 mg of porphyrin **6a** (49.6 μmol), 7.1 mL THF, 1.5 mL MeOH, and 7.1 mL aqueous NaOH solution (40w%). UV/Vis (MeOH): λ_{max} (rel. Abs.)=306 (0.16), 434 (0.72), 595 (0.14), 686 (0.10) nm. IR (ATR): $\tilde{\nu}$ =3379, 2987, 2775, 2450, 1687, 1633, 1606, 1467, 1423, 1022, 887, 792, 751, 716, 685, 582, 557, 537 cm^{-1} . MS (ESI): m/z (%)=751 (100) $[M+H]^+$. HRMS (ESI, $\text{C}_{50}\text{H}_{31}\text{O}_4\text{N}_4$): calc.: 751.2340, found: 751.2346.

SURMOF fabrication: According to the previous method,^[33] ethanolic solutions of 1 mM zinc acetate and 20 μM PP linker solutions (in ethanol) were sequentially deposited onto the pre-cleaned quartz glass substrates using a spin-coating method in an lbl fashion. After the metal or linker deposition, the substrates were washed with ethanol to remove unreacted metal or linker or any byproducts from the sample surface.

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Conflict of interest

The authors declare no conflict of interest.

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