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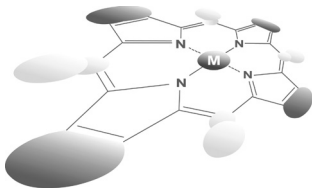

Soluble *meso*-tetrakis(arylethynyl)porphyrins — synthesis and optical properties

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Dedicated to Professor Nagao Kobayashi on the occasion of his 65th birthday

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ABSTRACT: *Trans*-A_2B_2-tetrakis(arylethynyl)porphyrins with suitable solubility in CH_2Cl_2, $CHCl_3$, EtOAc, acetone and toluene have been obtained for the first time. Among two possible strategies the one comprising the synthesis of 5,15-dibromo-10,20-bis[(isopropylsilyl)ethynyl]porphyrin proved to be more efficient. The pathway towards densely substituted arylacetylenes has been optimized. The use of previously identified 3,4,5-trialkoxyaryl substituent was crucial for achieving the reasonable solubility. The optical properties of *meso*-substituted tetrakis(arylethynyl)porphyrins were studied showing that strong polarization imparted by direct conjugation of all four substituents with porphyrin core resulted not only in strong absorption of red light but also in a relatively long triplet lifetime. *Meso*-tetrakis(arylethynyl)porphyrins have a significantly longer lifetime of T_1 state than bis(arylethynyl) porphyrins and in their case all the states are mixtures of transitions between the HOMO-1, HOMO and LUMO, LUMO+1 MOs. We show that the presence of two additional arylethynyl substituents at *meso*-positions enhance the maximum two-photon absorption cross-section of *trans*-A_2B_2-tetrakis(arylethynyl) porphyrins by more than one order of magnitude. Maximum values as high as σ_2 = 500 GM at 950 nm result from realization of suitable conditions for effective resonance enhancement along with a lowering of the energy and intensification of the two-photon allowed transitions in the Soret region.

KEYWORDS: porphyrins, alkynes, absorption, Sonogashira, triplet.

INTRODUCTION

Since the mean angle between *meso*-aryl substituents and porphyrin core is ~50°, alteration of these substituents has rather limited impact on porphyrin's physicochemical properties [1]. These properties, however, may be effectively and widely tuned *via* extension of the porphyrin core. Such π-extension of the porphyrin chromophore attracts non-stopping attention of scientific community [2]. Conceptually, there are several approaches to reach this goal without interfering in a construction of a porphyrin core, *i.e*. without changing the number of pyrrole subunits and methine bridges. The first approach is based on placement of one or more fused aromatic or heteroaromatic rings at adjacent β-positions of the tetrapyrrolic macrocycle [3]. Another route to gain extended π-system arises from the fact that porphyrins are electron-rich and as such may undergo inter- and intramolecular oxidative aromatic coupling [4]. A complementary idea combines both aforementioned strategies *i.e*. elongation

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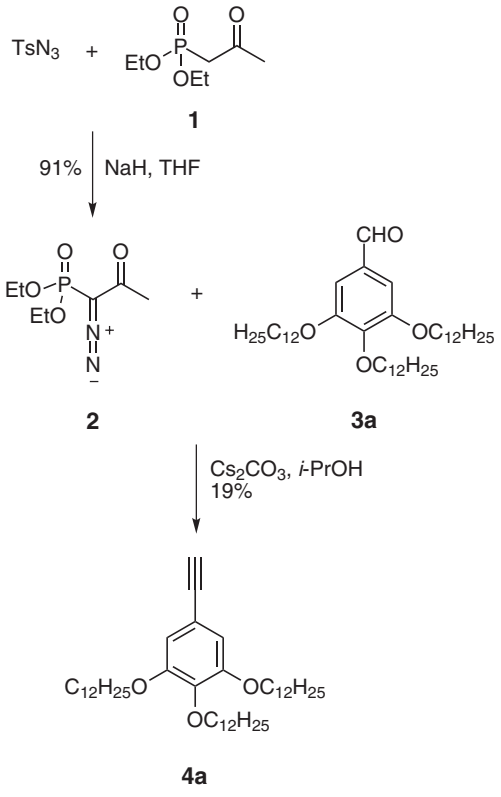
of the porphyrin π-electron system is achieved by fusing adjacent β substituents [5]. Still, among many options which were explored in the last 30 years the extension *via* triple bonds is conceptually perhaps the simplest. This approach has been intensively explored over last decades both theoretically and practically [6–8]. The studies of bis(arylethynyl)porphyrins are widespread but the synthesis and photophysical studies of compounds possessing four arylethynyl groups at all *meso*-positions are rare cases and only dozen papers have appeared up-to-date on this topic [9]. Among them only five deal with *trans*-A_2B_2-porphyrins of that type [10]. Very poor solubility of these compounds and not the lack of suitable synthetic methodologies is the crucial reason for that situation. In this context, we wondered if using the motive, which we identified in recent years to improve solubility of porphyrins (and to reach liquidity at room temperature) [11] would finally allow to obtain *meso*-tetrakis(arylethynyl)porphyrins with sufficient solubility.

RESULTS AND DISCUSSION

Initially we planned to obtain targeted porphyrins *via* [2+2] condensation of 5-[3,4,5-tris(decyloxy)phenyl] dipyrrane (**7**) with corresponding [tris(alkoxy)phenyl] propynals. While the synthesis of dipyrrane **7** was straightforward [13, 14], the preparation of arylpropargyl aldehydes required an investigation of a few options.

Among various general strategies we decided to apply the synthesis of arylalkynes from aromatic aldehydes. One of the most efficient general methods to achieve this transformation is reaction of aldehydes with dialkyl diazomethylphosphonates. In the presence of base, these esters undergo deprotonation leading to unstable diazoalkene followed by Horner–Wadsworth–Emmons reaction with aldehydes. As originally observed by groups of Seyferth [15], Gilbert [16] and Colvin [17] the first intermediate after thermal extrusion of N_2 gives carbene which finally undergoes rearrangement into alkyne. We generated stable diethyl 1-diazo-2-oxopropylphosphonate (**2**), in reaction of diethyl 2-oxopropylphosphonate (**1**) [18] with tosyl azide [18] (Scheme 1).

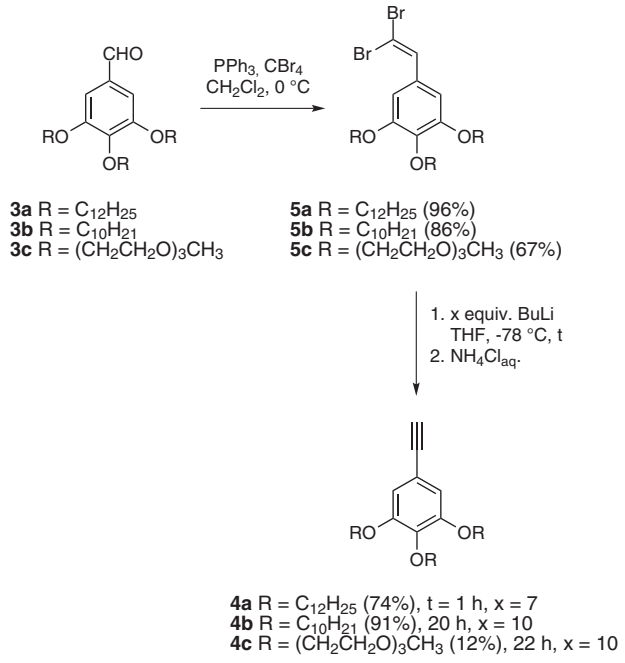
Only traces of alkyne **4a** were observed in the subsequent reaction with aldehyde **3a** [11] following conditions developed by Bestmann and co-workers (MeOH, K_2CO_3) [19]. Both bad solubility of lypophilic aldehyde **3a** and its electron-rich (hence less reactive) character plausibly contributed to this failure [20]. The yield of **4a** increased to 19% when MeOH was replaced by *i*-PrOH, following the conditions published by Ghosh (Scheme 1) [18]. Still, the reaction was very slow and in order to increase conversion the large excess of both base and phosphonate have been used. Not satisfied with overall efficiency of this transformation we focused our investigation on Corey–Fuchs method.



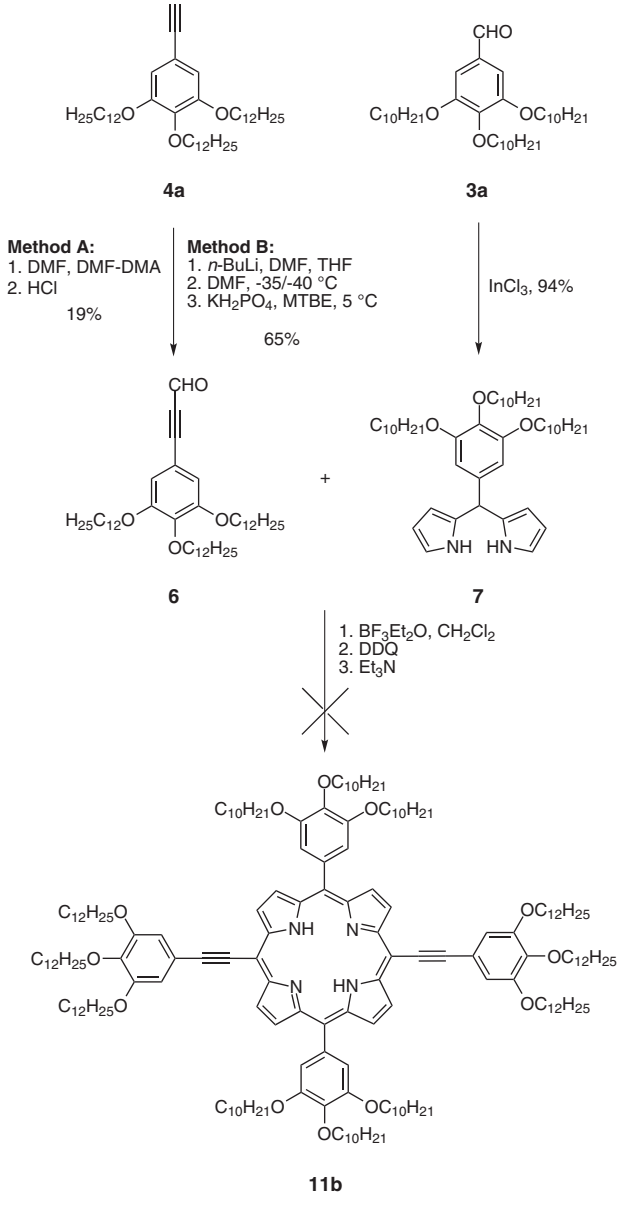
Scheme 1.

In the first step, we transformed aldehyde **3a** into compound **5a** *via* the reaction with triphenylphosphine and tetrabromomethane (Scheme 2) [21]. Subsequent elimination led directly to alkyne **4a**. Although TLC monitoring of the reaction mixture showed that conversion was full after 1 h, substrate was still present and its removal from product required careful chromatography. Replacing of *n*-buthyllithium with *t*-BuOLi did not improve the yield of alkyne **4a**. Finally, a change of substrate **3b** combined with bigger excess of *n*-BuLi and a longer reaction time allowed us to obtain alkyne **4b** in satisfactory yield (Scheme 2). Unfortunately, when aldehyde **3a** was replaced with aldehyde **3c**, possessing tetraethyleneglycol chains, the yield of the corresponding alkyne dropped to 12% (Scheme 2).

The next step towards targeted arylpropargylaldehydes required formylation of alkyne. Among many possible reagents, DMF-DMA (DMA- *N,N*-dimethylacetamide) has been chosen. Applying gentle reactions conditions proposed by Kim and co-workers [22] afforded aldehyde **6** in 11% yield. Adding higher amount of DMF led to improvement of yield of compound **6** to 19%. Subsequently, different procedure was used with alkyl-lithium compounds as generators of acetylenic anions, and DMF as formylating agent. The use of non-typical hydrolysis consisting of addition of reaction mixture into biphasic emulsion of MTBE (*t*-butyl-methyl ether) and phosphorane buffer at 5 °C (*reverse quenching method*)



Scheme 2.



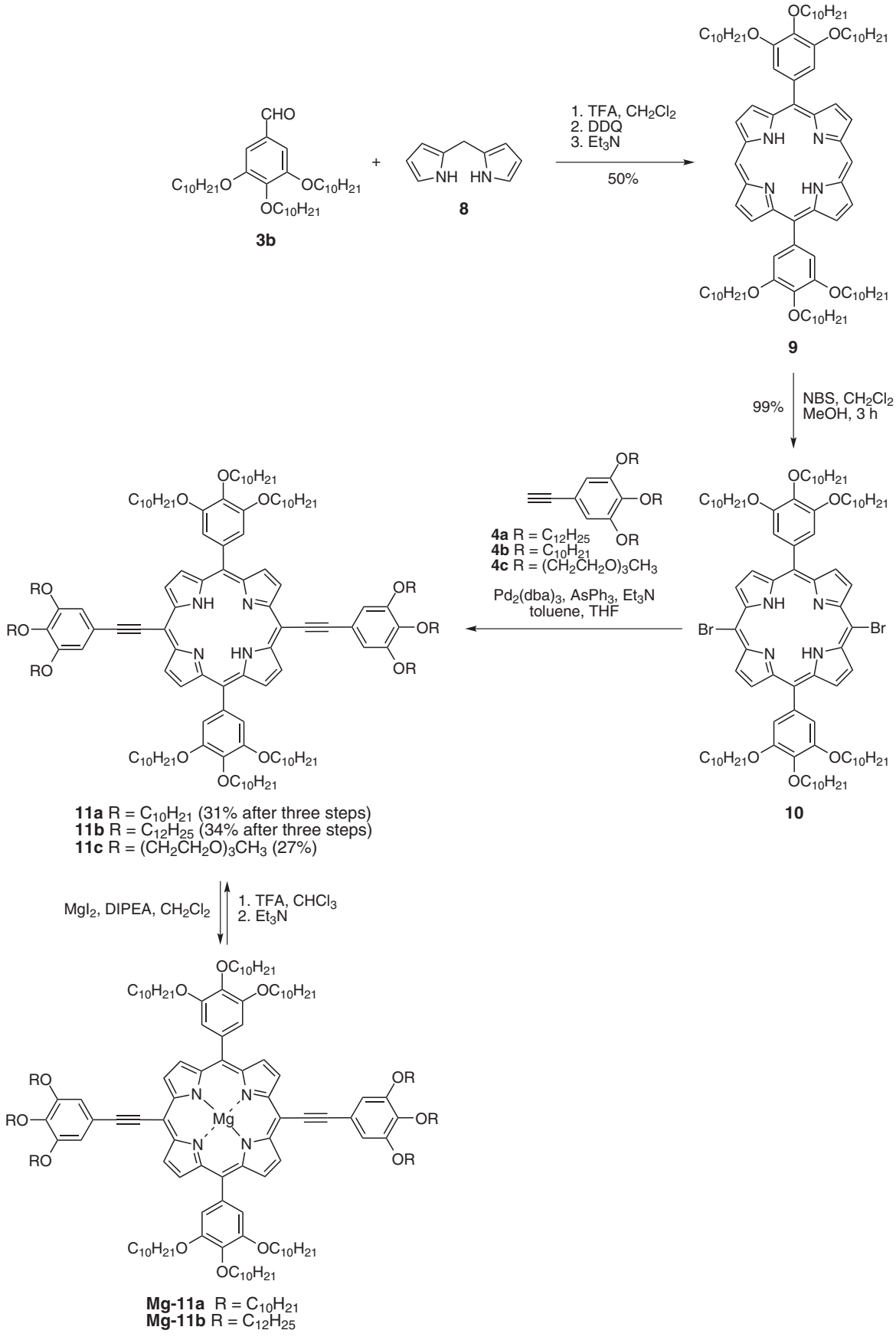
Scheme 3.

[23] allowed us to transform alkyne **4a** into aldehyde **6** in 65% (Scheme 3). In order to increase conversion and improve the yield of **6**, various modifications have been subsequently attempted (such as replacement of *n*-BuLi with *t*-BuLi, varying reaction time, temperature as well as substrate ratio) but all in vain.

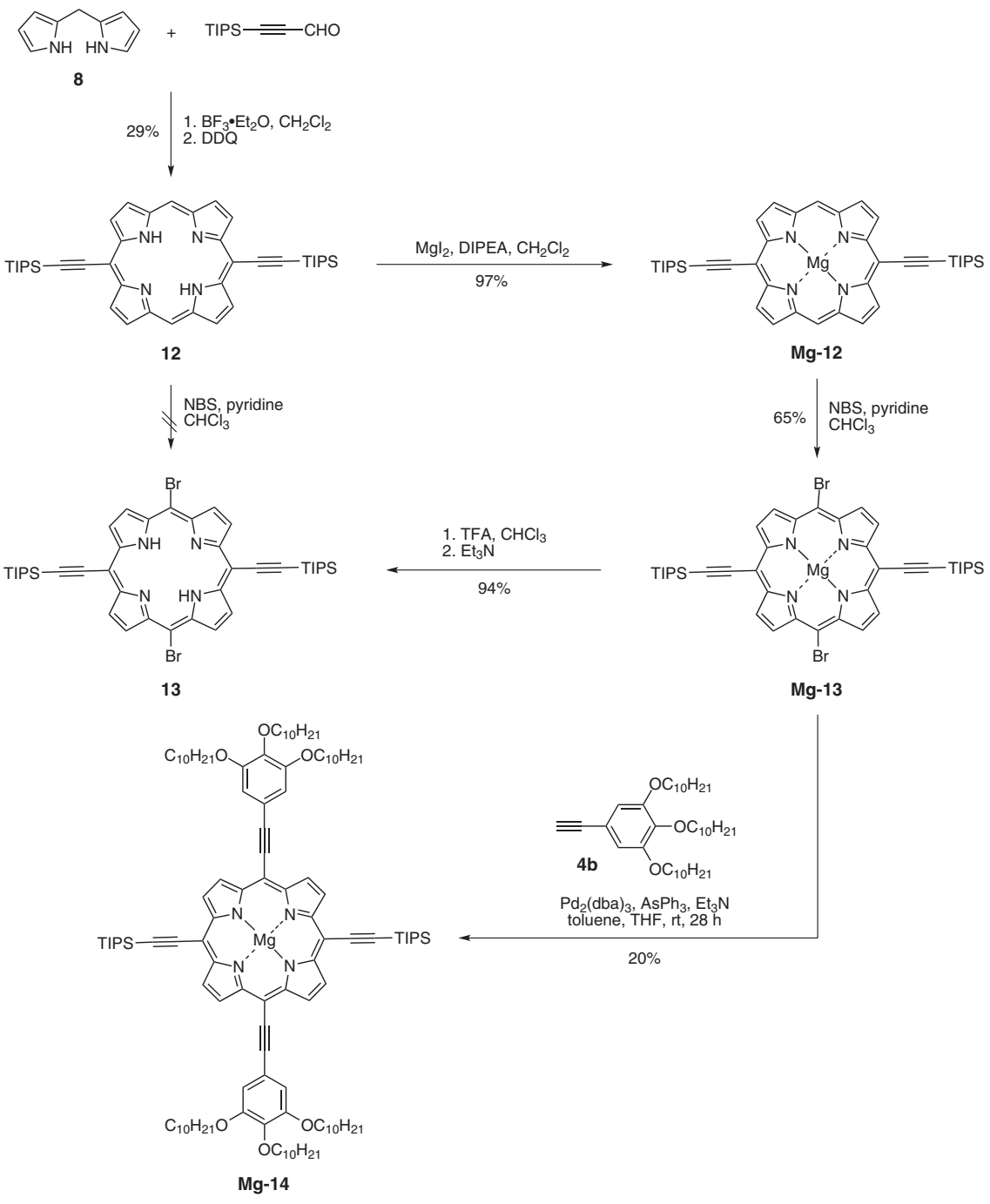
Having both substrates in hand, we carried out the reaction of aldehyde **6** with dipyrrane **7** in toluene with $BF_3{\cdot}Et_2O$ [13a] as catalyst (Scheme 3). Unfortunately, only traces of the expected product were detected by (ESI-MS), which could not be isolated. Reaction of **6** with **7** under other reaction conditions such as TFA/CH_2Cl_2 [24] and $BF_3{\cdot}Et_2O/MeCN/NH_4Cl$ [24] also failed. Consequently, we have changed the strategy. Unsubstituted dipyrrane **8** [25] was reacted with aldehyde **3b** into *trans*-A_2-porphyrin **9** (Scheme 4). In the next step smooth bromination afforded dibromoporphyrin **10** [8c].

Compounds **11a** and **11b** were prepared *via* Sonogashira coupling of porphyrin **10** with alkynes **4b** and **4a** (Scheme 4). One has to emphasize that purification of these porphyrins was more troublesome than typically, since non-porphyrin impurities possessed almost the same R_f. Since SEC column also did not helped to purify these products, we finally decided to utilize magnesium insertion (which is known to drastically change the polarity of porphyrin). Insertion of magnesium [26] followed by straightforward purification and removal of magnesium (TFA, $CHCl_3$, RT), led to compounds **11a** and **11b** in 31% and 34% respectively after three steps. Dibromoporphyrin **10** was also subjected to Sonogashira reaction with alkyne **4c** possessing tetraethylene glycol chains. In this case porphyrin **11c** was isolated in 27% yield after straightforward purification. This was possible due to different character of tetraethylene glycol chains *vs*. decyl and dodecyl substituents. Higher polarity of porphyrin **11c** imparted by the presence of multiple CH_2CH_2O groups resulted in differentiating of its R_f *vs*. non-porphyrin impurities.

The strategy towards *trans*-A_2B_2-tetrakis(arylethynyl) porphyrins, implied the synthesis of compound **13**, which is a perfect substrate for the Sonogashira reaction leading to required products (Schemes 5 and 6). Direct bromination of porphyrin **12** [10e] at two free *meso*-positions with NBS was unsuccessful due to the formation of more than five products which could not be separated.



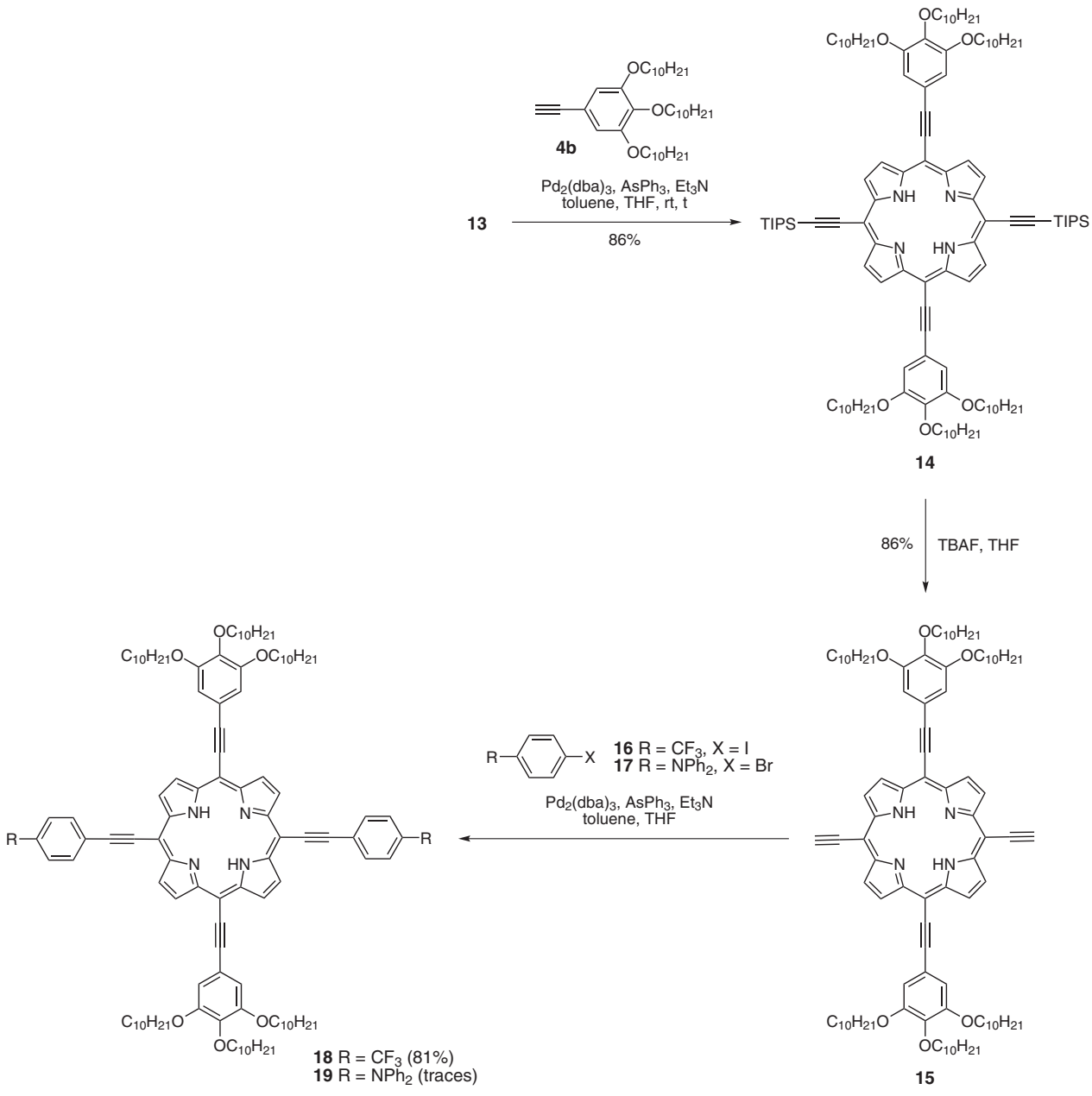
Scheme 4.



Scheme 5.

Consequently, we performed bromination on magnesium complex **Mg-12**, leading to Mg-complex 5,15-dibromo-10,20-bis[(triisopropylsilyl)ethynyl]porphyrin (**Mg-13**) [10b]. Removal of Mg^{2+} led smoothly to free base **13**. This porphyrin was subsequently transformed *via* Sonogashira reaction with acetylene **4b** into porphyrin **14** in 32% yield (Scheme 6). Prolongation of the reaction time led to increase in the yield of *trans*-A_2B_2-porphyrin **14** to 86%. Analogous reaction with complex **Mg-13**, afforded **Mg-14** in 20% yield only (Scheme 5).

In the next step, silyl groups have been removed using TBAF [27], and porphyrin **15** was subjected to Sonogashira reaction with selected bromoarenes **16–17**. *Meso*-tetrakis(arylethynyl)porphyrin **18** was formed in 81% yields, however bromoarene **17** failed to react with porphyrin **15**.



Scheme 6.

Needless to say, the presence of four arylethynyl substituents at the periphery of porphyrin led to drop in solubility of porphyrin **18** *vs*. porphyrins **11a** and **15**. While porphyrins **11a** and **15** (possessing two arylethynyl substituents) were soluble in CH_2Cl_2, $CHCl_3$, toluene, EtOAc and acetone on the level >50 mg/1 mL, the solubility of compound **18** was ~5 mg/1 mL (in CH_2Cl_2, $CHCl_3$, and toluene) and ~1 mg/mL in EtOAc and acetone.

Optical studies were performed in CH_2Cl_2 and in CCl_4 (for porphyrin **18** due to the planned two-photon absorption studies). Both Soret band and Q-bands undergo significant red-shift while moving from 5,15-diarylporphyrin **9** through bis(arylethynyl)porphyrins **11a**–**11b** to *meso*-tetrakis(arylethynyl)porphyrins **14** and **18** (Fig. 1). Most of free-base *trans*-A_2B_2-bis(arylethynyl)porphyrins described so far possess absorption maxima around 445–460 nm for Soret band and 700 nm for Q-band [8b,c, 13a, 28–30]. The exact λ_{max} is rather insensitive to the electronic nature of substituents at arylethynyl moieties. Both electron-withdrawing substituents and electron-donating substituents have negligible effect on linear absoprtion properties [8b, 28, 29]. The red shift of absorption between *trans*-A_2B_2-bis(arylethynyl) porphyrins and *meso*-tetrakis(arylethynyl)porphyrins is ~20 nm on the Soret band and ~40 nm on the lowest

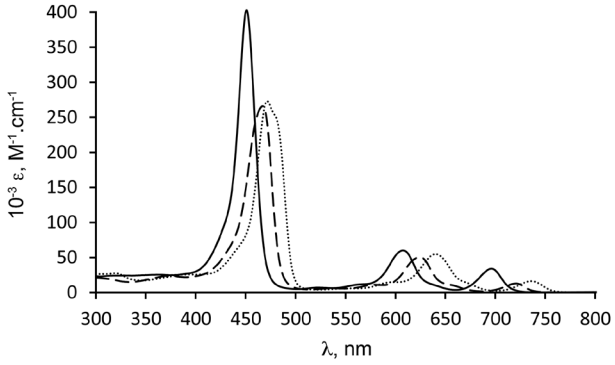


Fig. 1. Absorption spectra of porphyrins **11a** (solid line), **15** (dashed line), **18** (dotted line) in CH_2Cl_2

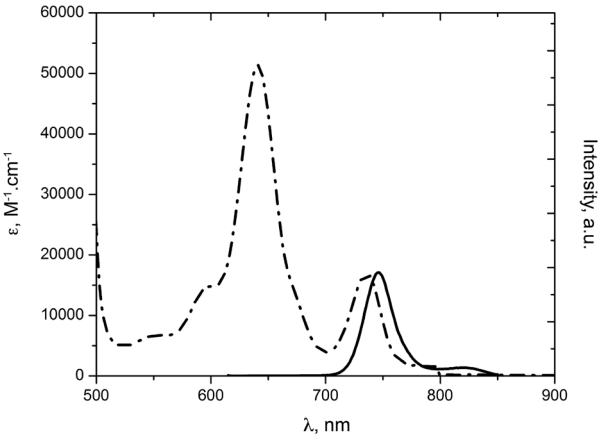


Fig. 2. Absorption (dotted line) and emission (solid line) spectra of porphyrin **18** in air saturated toluene. Porphyrin was excited at 630 nm

Table 1. Linear optical properties of porphyrins **9**, **11a**, **11b**, **Mg-14, 14** and **18**

Porphyrin	λ_{Soret}, nm	ε, 10^3 $cm^{-1}.M^{-1}$	λ_Q, nm
9[a]	412	286	635
11a[b]	451	403	696
11b[b]	452	280	705
Mg-14[b]	480	562	692
14[b]	468	317	730
18[a]	472	273	640, 736

[a] in CCl_4; [b] in CH_2Cl_2.

Table 2. Selected singlet and triplet data of porphyrin **18** in toluene

Porphyrin	λ_{fl}, nm	T_s, ns	T, $T_{n\,max}$	τ_T, μs
18	746	7.1	505	445 ± 5

energy Q-band (Table 1). At the same time the Soret band undergoes significant broadening. Only slightly smaller effect is visible if only two unsubstituted C–C triple bonds are present at positions 10 and 20 (**15**, Fig. 1).

Porphyrin **18** displays Q-band absorption centered at 736 nm, which is more bathochromically shifted than in the case of 5,15-bis[(4′-nitrophenyl)ethynyl]-10,20-bis[(triisopropylsilyl)ethynyl]porphyrin described by Matsuo and co-workers (710 nm) [10b]. The Q-band pattern of **18** is markedly different than that of H_2TPP. The bands are broadened, red-shifted and the peak extinction is enhanced by nearly one order of magnitude. Bathochromic shift of absorptio n is also reflected in red-shift of emission (Fig. 2). The fluorescence of porphyrin **18** has its maximum at 746 nm, while *trans*-A_2B_2-bis(arylethynyl)porphyrins have emission typically around 700 nm [28].

Detailed triplet studies were performed for porphyrin **18** (Table 2, Fig. 3) using nanosecond laser flash photolysis. Deoxygenated samples in toluene were excited at 355 nm

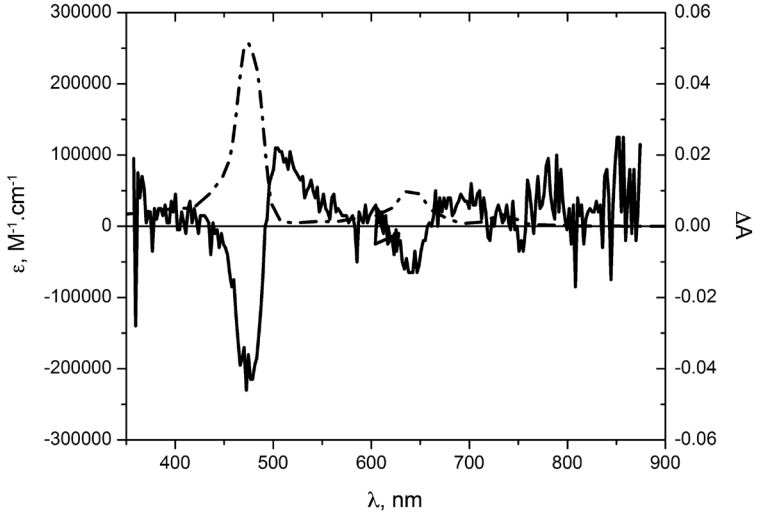
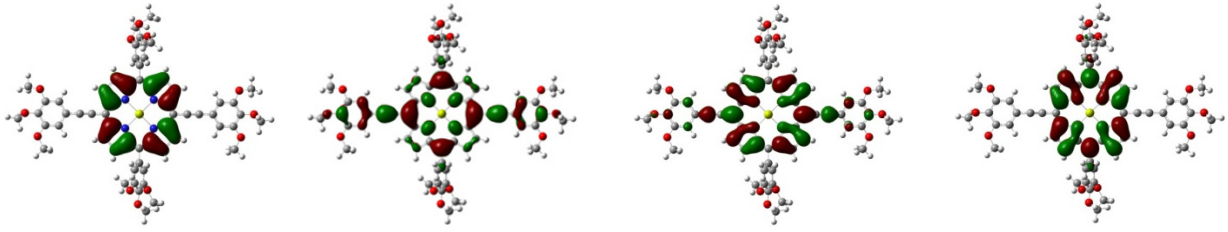


Fig. 3. Triplet absorption of porphyrin **18** in deoxygenated toluene. Porphyrin was excited at 355 nm

Table 3. Calculated energy levels and molecular orbitals for transitions for porphyrin **Mg-11a**

State	Energy, eV	f[a]	μ_x[b]	μ_y[b]	H → L[d]	H → L + 1	H-1 → L	H-1 → L + 1
1	1.96	0.65	-9.34	0.04	0.890049	0	0	0.430939
2	2.1	0.0009	0.01	0.34	0	-0.69304	0.706272	0
3	3.0	2.42	14.6	-0.14	-0.43561	0	0	0.876515
4	3.01	1.68	0.22	12.1	0	0.718717	0.699442	0

HOMO-1 HOMO LUMO LUMO + 1



[a]Calculated oscillator strength. [b]Transition dipole x component(D). [c]Transition dipole y component(D). [d]HOMO and LUMO CI mixing coefficient.

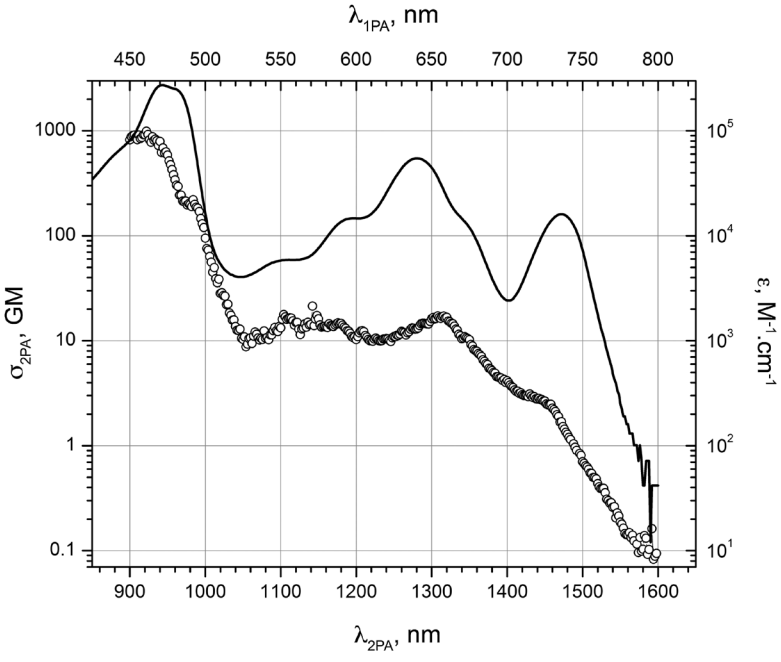
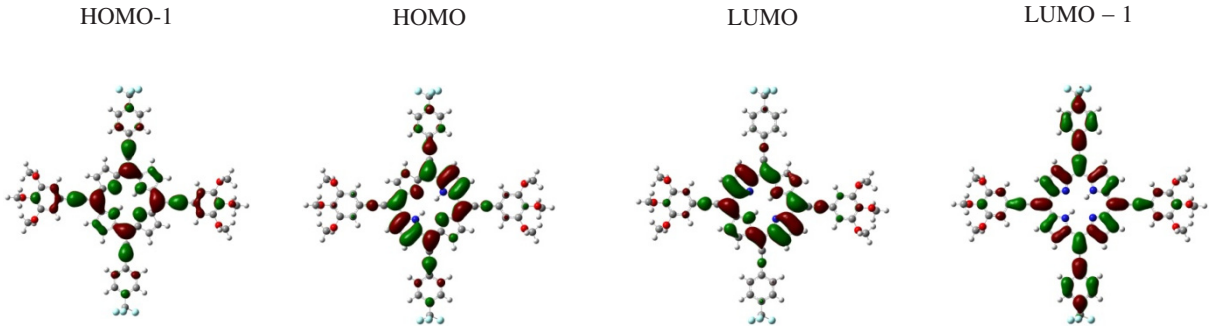


Fig. 4. Dependence of the 2PA cross-section of porphyrin **18** on laser wavelength in CCl_4 solution

and the T_1-T_n absorption was probed using a xenon white light source. Lifetimes were obtained by fitting to a single exponential decay. The results show that $\lambda_{max}(T_1\text{-}T_n)$ absorption occurs at 505 nm and that τ_T ~ 450 μs, which is ~4 times longer than that for two previously studied *trans*-A_2B_2-bis(arylethynyl)porphyrins [8b]. One has to note that corresponding values for H_2TPP are in the range 220–1500 μs depending on the solvent [31] while tetrakis(diphenylaminophenyl)porphyrin in toluene decay with τ_T ~ 200 μs [31]. Previously we found that the presence of two 4-cyanophenylethynyl substituents at *meso*-positions of porphyrins enhances two-photon absorption cross-section (σ_2) from ~10 GM to 100 GM at 840 nm excitation wavelength [29]. In this context it seemed valuable to perform the study of two-photon absorption for porphyrin **18**, possessing analogous electron-withdrawing groups (CF_3) but different architecture. Due to the larger bathocromic shift of the

Table 4. Calculated energy levels and molecular orbitals for transitions for porphyrin **18**

State	Energy, eV	f[a]	μ_x[b]	μ_y[c]	H → L[d]	H → L + 1	H-1 → L	H-1 → L + 1
1	1.83	0.23	1.54	5.50	0.369958	0.750438	-0.49076	0.184583
2	1.91	0.65	-7.94	5.24	0.823864	-0.34894	0.220575	-0.34894
3	2.76	2.49	11.4	10.4	0	0.531094	0.827315	0
4	2.92	1.95	9.14	-9.63	-0.41469	0	0	0.895819



[a]Calculated oscillator strength. [b]Transition dipole x component(D). [c]Transition dipole y component(D). [d]HOMO and LUMO CI mixing coefficient.

lowest energy Q-band the quadratic power dependence of fluorescence intensity was observed above 950 nm where maximum 2PA cross-section is, σ_2 ~500 GM (Fig. 4).

Comparison of the 2PA spectra with previously reported data shows that end-capping with the CF_3 group combined with the presence of two electron-donating 3,4,5-trialkoxyphenylethynyl substituents amplify the maximum 2PA cross-section with respect to both neutral bis(arylethynyl)porphyrins and bis(4′-cyanophenylethynyl)porphyrins [29]. Finally DFT calculations were performed to elucidate the origin of transitions for two the most representative compounds i.e. **Mg-11a** and **18**. The calculation results, show that both Q and Soret bands originate from the combination of transitions from HOMO-1, HOMO to LUMO and LUMO+1 levels (Tables 3 and 4). Although the overall molecule has low symmetry, **Mg-11a** has a porphyrin core with D_{4h} symmetry and the optical transitions can be analyzed assuming the entire molecule approximates this symmetry. States 1 and 3 are polarized along the phenylethynyl-porphyrin-phenylethynyl(x) axis while states 2 and 4 are nearly degenerate with states 1 and 3 and are polarized along the phenyl-porphyrin-phenyl(y) axis. The HOMO has significant contribution from the phenylethynyl ligand π orbitals and as a result states 1 and 3 have x polarization due to the HOMO→LUMO contribution. Compound **18** is a free base porphyrin having a core with D_{2h} symmetry. All the states are mixtures of transitions between the HOMO-1, HOMO and LUMO, LUMO+1 MOs. State 1 is predominately y polarized, while states 2-4 have almost equal x and y polarization.

EXPERIMENTAL

General

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. All reported ^{1}H NMR spectra were collected using a 200 MHz, 400 MHz, 500 MHz or 600 MHz spectrometer. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values were given in Hz. Due to the presence of long alkyl chains, in ^{13}C NMR spectra of many compounds the signals of carbon atoms overlap very strongly and it is impossible to assign the number of signals corresponding to actual number of magnetically non-identical protons. The UV-vis absorption spectra were recorded in CH_2Cl_2 and CCl_4. The absorption wavelengths were reported in nm with the extinction coefficient in $M^{-1}cm^{-1}$ in brackets. The purge gas was high purity argon. Chromatography was performed on silica (200–400 mesh) or alumina. Preparative scale size exclusion chromatography (SEC) was carried out using BioRad Bio-Beads S-X1 with toluene or THF as an eluent. Dry column vacuum chromatography (DCVC) was performed on Silicagel type D 5F. The mass spectra were obtained by field desorption MS (FD-MS) or by electrospray MS (ESI-MS). Diethyl (1-diazo-2-oxopropyl)phosphonate

(**2**) was obtained according to literature procedure [12]. 5-[3,4,5-tris(decyloxy)phenyl]dipyrrane (**7**) was obtained according to literature procedure [13].

Synthesis

5-(2,2-Dibromovinyl)-1,2,3-tris(dodecyloxy)benzene (5a). CBr_4 (755 mg, 2.3 mmol) was placed in a round-bottomed flask purged with argon and then dissolved in anhydrous CH_2Cl_2 (6 mL). The reaction mixture was cooled to 0 °C and PPh_3 (1.185 g, 4.5 mmol) was added. The mixture turned orange. In another round-bottomed flask purged with argon, aldehyde **3a** (1.0 g, 1.5 mmol) was dissolved in anhydrous CH_2Cl_2 (3 mL). After 15 min (after PPh_3 was added to CBr_4 solution) the solution of aldehyde **3a** was added dropwise to the flask containing the generated ylide. After 5 min the solvent was evaporated and the crude product was purified by column chromatography (silica, hexanes/CH_2Cl_2 3:2) to obtain pure olefin **5a** (1.192 g, 96%) as a colorless solid, which was crystallized (hexanes/EtOH) for analyses; mp 35.3–36.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 7.0 Hz, 9H, CH_3), 1.24–1.37 (m, 48H, CH_2), 1.41–1.51 (m, 6H, $OCH_2CH_2CH_2$), 1.69–1.83 (m, 6H, OCH_2CH_2), 3.93–3.99 (m, 6H, OCH_2), 6.76 (s, 2H, ArH), 7.37 (s, 1H, CH_{vinyl}). ^{13}C NMR (125 MHz, $CDCl_3$): δ, ppm 14.1, 22.7, 26.1, 29.36, 29.39, 29.41, 29.59, 29.63, 29.66, 29.69, 29.72, 29.74, 29.75, 30.3, 31.93, 31.94, 69.3, 73.4, 88.0, 107.3, 130.0, 136.8, 138.8, 152.9. HR MS (FD): *m/z* calcd. for $C_{44}H_{78}Br_2O_3$ 812.4318, found 812.4331, isotope profiles match. Anal. calcd. (%) $C_{44}H_{78}Br_2O_3$: C, 64.85; H, 9.65; Br, 19.61, found C, 64.67; H, 9.54; Br, 19.58.

1,2,3-Tris(dodecyloxy)-5-ethynylbenzene (4a). Method A. Diethyl 1-diazo-2-oxopropylphosphonate (198 mg, 0.9 mmol) was added to a solution of aldehyde **3a** (500 mg, 0.75 mmol) and Cs_2CO_3 (489 mg, 1.5 mmol) in *i*-PrOH (10 mL) and stirring was continued for 8 h. The reaction mixture was diluted with Et_2O (20 mL), washed with $NaHCO_3$ (aq., 5%, 10 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by two column chromatographies (silica, hexanes/CH_2Cl_2 4:1) to yield pure product **4a** (96 mg, 19%), which was crystallized from hexanes. **Method B.** Alkene **5a** (209 mg, 0.26 mmol) was placed in a round-bottomed flask purged with argon and anhydrous THF (3.5 mL) was added. The substrate was dissolved and the solution was cooled to -78 °C. Then, BuLi (2.5 M in hexane, 0.73 mL, 1.83 mmol) was added and the mixture turned orange. The reaction mixture was stirred at -78 °C for 1 h. Afterwards, saturated NH_4Cl (6 mL) was added. The layers were separated and the organic layer was washed with water, dried (Na_2SO_4), filtered and the solvent was evaporated to obtain an orange oil. The initial purification by column chromatography (silica, hexanes/CH_2Cl_2 4:1) afforded a mixture of the substrate and product **4a**. The consecutive chromatography (silica, hexanes/CH_2Cl_2 3:1) was performed to yield pure product **4a** (125 mg, 74%), which was crystallized from hexanes; mp 44.5–45.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 6.8 Hz, 9H, CH_3), 1.18–1.38 (m, 48H, CH_2), 1.40–1.51 (m, 6H, $OCH_2CH_2CH_2$), 1.66–1.86 (m, 6H, OCH_2CH_2), 2.99 (s, 1H, CH_{alkyne}), 3.91–3.99 (m, 6H, OCH_2), 6.69 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ, ppm 14.1, 22.7, 26.0, 26.1, 29.3, 29.36, 29.38, 29.57, 29.62, 29.65, 29.68, 29.73, 30.3, 31.91, 31.93, 69.1, 73.5, 75.7, 84.0, 110.6, 116.3, 139.4, 152.9. HR MS (ESI): *m/z* calcd. for $C_{44}H_{78}O_3Na$ $[M + Na]^+$ 677.5849, found 677.5848.

5-(2,2-Dibromovinyl)-1,2,3-tris(decyloxy)benzene (5b). CBr_4 (1.133 g, 3.4 mmol) was placed in a round-bottomed flask purged with argon. Then, it was dissolved in anhydrous CH_2Cl_2 (9 mL). The reaction mixture was cooled to 0 °C and PPh_3 (1.778 g, 6.8 mmol) was added. The mixture turned orange. In the second round-bottomed flask purged with argon aldehyde **3b** (1.293 g, 2.25 mmol) was dissolved in anhydrous CH_2Cl_2 (9 mL). After 15 min (after PPh_3 was added to CBr_4 solution), the solution of aldehyde **3b** was added dropwise to the flask containing the generated ylide. After 20 min the solvent was evaporated and the crude product was purified by column chromatography (silica, hexanes to hexanes/CH_2Cl_2 7:3) to obtain pure olefin **5b** (1.408 g, 86%) as an colorless product. ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 6.9 Hz, 9H, CH_3), 1.20–1.39 (m, 36H, CH_2), 1.41–1.50 (m, 6H, $OCH_2CH_2CH_2$), 1.70–1.84 (m, 6H, OCH_2CH_2), 3.94–3.99 (m, 6H, OCH_2), 6.76 (s, 2H, ArH), 7.37 (s, 1H, CH_{vinyl}). ^{13}C NMR (125 MHz, $CDCl_3$): δ, ppm 14.1, 22.67, 22.69, 26.1, 29.33, 29.38, 29.39, 29.57, 29.62, 29.66, 29.72, 30.3, 31.90, 31.93, 69.2, 73.4, 88.0, 107.2, 130.0, 136.8, 138.7, 152.8. HR MS (ESI): *m/z* calcd. for $C_{38}H_{67}Br_2O_3$ $[M + H]^+$ 729.3452, found 729.3430. Elemental analysis calcd. (%) $C_{38}H_{66}Br_2O_3$: C, 62.46; H, 9.10; Br, 21.87, found C, 62.52; H, 9.18; Br, 21.84.

1,2,3-Tris(decyloxy)-5-ethynylbenzene (4b). Alkene **5b** (1.376 g, 1.88 mmol) was placed in a round-bottomed flask purged with argon and anhydrous THF (25 mL) was added. The substrate was dissolved and the solution was cooled to -78 °C. Then, BuLi (2.5 M in hexane, 7.5 mL, 18.8 mmol) was added, the reaction mixture was stirred at -78 °C for 20 h and saturated NH_4Cl (60 mL) was added. The layers were separated and the water layer was extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4), filtered and the solvent was evaporated to obtain an oil which slowly solidified. The crude product was purified by column chromatography (silica, hexanes/CH_2Cl_2 7:3) to obtain pure alkyne **4b** (973 mg, 91%) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 6.8 Hz, 9H, CH_3), 1.22–1.40 (m, 36H, CH_2), 1.40–1.50 (m, 6H, $OCH_2CH_2CH_2$), 1.67–1.75 (m, 2H, OCH_2CH_2), 1.76–1.83 (m, 4H, OCH_2CH_2), 2.99 (s, 1H, CH_{alkyne}), 3.94 (t, J = 6.4 Hz, 6H, OCH_2), 6.69 (s, 2H, ArH). HR MS (ESI): *m/z* calcd. for $C_{38}H_{67}O_3$ $[M + H]^+$ 571.5090, found 571.5096.

5-(2,2-Dibromovinyl)-1,2,3-tris(2-(2-(2-methoksyethoxy)ethoxy)ethoxy)benzene (5c). CBr_4 (0.910 g, 2.74 mmol) was placed in a round-bottomed flask purged with argon. Then, it was dissolved in anhydrous CH_2Cl_2 (7.5 mL). The reaction mixture was cooled to 0°C, PPh_3 (1.430 g, 5.45 mmol) was added and the mixture turned orange. In another round-bottomed flask purged with argon aldehyde **3c** (1.071 g, 1.81 mmol) was dissolved in anhydrous CH_2Cl_2 (7.5 mL). After 15 min (after PPh_3 was added to CBr_4 solution), the solution of aldehyde **3c** was added dropwise to the flask containing the generated ylide. After 20 min the solvent was evaporated and the crude product was purified by column chromatography (silica, EtOAc then EtOAc/5% MeOH). The consecutive chromatography (silica, EtOAc then EtOAc/MeOH 9:1) afforded to obtain pure olefin **5c** (912 mg, 67%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 3.37 (s, 9H, CH_3), 3.48–3.57 (m, 6H, OCH_2), 3.59–3.68 (m, 6H, OCH_2), 3.69-3.74 (m, 6H, OCH_2), 3.78–3.81 (m, 6H, OCH_2), 3.82–3.88, (m, 6H, OCH_2), 4.11–4.21 (m, 6H, OCH_2), 6.80 (s, 2H, ArH), 7.35 (s, 1H, H_{vinyl}). ^{13}C NMR (100 MHz, $CDCl_3$): δ, ppm 29.7, 59.0, 68.9, 69.6, 70.48, 70.53, 70.64, 70.77, 71.9, 72.3, 84.7, 88.7, 108.3, 130.3, 136.4, 152.3. HR MS (ESI): *m/z* calcd. for $C_{29}H_{48}Br_2O_{12}Na$ $[M + Na]^+$ 769.1405, found 769.1428.

5-Ethynyl-1,2,3-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene (4c). Olefin **5c** (724 mg, 0.97 mmol) was placed in a round-bottomed flask purged with argon and anhydrous THF (13 mL) was added. The substrate was dissolved and the solution was cooled to -78 °C. Then, BuLi (2.5 M in hexane, 3.9 mL, 9.8 mmol) was added and the reaction mixture was stirred at -78 °C for 22 h. Afterwards, saturated NH_4Cl (30 mL) was added. The layers were separated and the water layer was extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4), filtered and the solvent was evaporated. The crude product was purified by column chromatography (silica, EtOAc, then EtOAc/MeOH 19:1 to 9:1) to obtain pure alkyne **4c** (68 mg, 12%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 3.36 (s, 9H, CH_3), 3.50–3.55 (m, 6H, OCH_2), 3.60–3.66 (m, 7H, H_{alkyne}, OCH_2), 3.69–3.75 (m, 6H, OCH_2), 3.77 (t, J = 4.8 Hz, 6H, OCH_2), 3.83 (t, J = 5.2 Hz, 6H, OCH_2), 4.11–4.16 (m, 6H, OCH_2), 6.72 (s, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ, ppm 59.0, 68.8, 69.6, 70.47, 70.51, 70.61, 70.64, 70.78, 71.9, 72.3, 76.2, 83.5, 111.7, 116.8, 139.7, 152.4. HR MS (ESI): *m/z* calcd. for $C_{29}H_{48}O_{12}Na$ $[M + Na]^+$ 611.3038, found 611.3055.

[3,4,5-Tris(dodecyloxy)phenyl]propynal (6). Method A. To alkyne **4a** (60 mg, 0.092 mmol), placed in a sealed tube, DMF (135 µl) and DMF-DMA (25 µl, 0.188 mmol) were added. The solution was stirred at 80 °C for 23 h. Later, the reaction mixture was poured into HCl_{aq} (pH = 4; 20 mL) and extracted three times with Et_2O. The organic extracts were dried (Na_2SO_4), filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica, hexanes/CH_2Cl_2 4:1 to 1:1) to collect the substrates and pure product **6** (12 mg, 19%). ^{1}H NMR (400 MHz, $CDCl_3$): δ, ppm 0.88 (t, J = 6.8 Hz, 9H, CH_3), 1.21–1.40 (m, 48H, CH_2), 1.41–1.52 (m, 6H $OCH_2CH_2CH_2$), 1.68–1.77 (m, 2H, OCH_2CH_2), 1.78–1.86 (m, 4H, OCH_2CH_2), 3.96 (t, J = 6.8 Hz, OCH_2), 4.01 (t, J = 6.4 Hz, OCH_2), 6.81 (s, 2H, ArH), 9.39 (s, 1H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ, ppm 14.1, 22.7, 26.0, 29.20, 29.36, 29.38, 29.54, 29.61, 29.65, 29.68, 29.71, 30.3, 31.9, 69.2, 73.7, 88.0, 96.5, 111.8, 113.3, 141.8, 153.1, 176.6. HR MS (ESI): *m/z* calcd. for $C_{45}H_{79}O_4$ $[M + H]^+$ 683.5978, found 683.5984. **Method B.** Alkyne **4a** (60 mg, 0.09 mmol) was placed in a round-bottomed flask and dried under vacuum for 1 h. Then, anhydrous THF (2.25 mL) was added. The solution was cooled to -35 °C and BuLi (2.5 M in hexane, 0.36 mL, 0.9 mmol) was added dropwise. Subsequently, DMF (0.14 mL, 1.8 mmol) was added to the reaction mixture at -35–(-40) °C and the solution was stirred for 45 min. Afterwards, the reaction mixture was poured into the vigorously stirred bilayer mixture of aqueous solution of KH_2PO_4 (490 mg, 3.6 mmol) and MTBE (2.7 mL). The layers were separated and the organic layer was washed with water. The organic extracts were dried ($MgSO_4$), filtered and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica, hexanes, then hexanes/CH_2Cl_2 4:1) to obtain pure aldehyde **6** (41 mg, 65%).

5,15-Bis[3,4,5-tris(decyloxy)phenyl]porphyrin (9). Dipyrrane **8** (1.14 g, 7.8 mmol) and aldehyde **3b** (4.46 g, 7.8 mmol) were dissolved in CH_2Cl_2 (1 l). For 0.5 h the solution was purged with argon and simultaneous sonication was applied. Then, TFA (0.38 mL, 5.0 mmol) was added and the reaction was stirred for 75 min. In the second step, DDQ (2.25 g, 9.9 mmol) was added and the mixture was stirred for 1 h. Afterwards, the reaction mixture was filtered through a plug of Al_2O_3 (Al_2O_3, CH_2Cl_2) and evaporated to dryness. The crude product was chromatographed (silica, hexane/CH_2Cl_2 4:1 to 1:1), to obtain pure product **9** (2.69 g, 50%). Spectral and physical properties concur with published data [8c].

5,15-Dibromo-10,20-bis[3,4,5-tris(decyloxy)phenyl]porphyrin (10). To the solution of porphyrin **9** (100 mg, 0.071 mmol) in CH_2Cl_2 (3.5 mL), MeOH (0.5 mL) and NBS (38 mg, 0.21 mmol) were added and the reaction was stirred at rt for 3 h. Then, the crude product was evaporated and purified by column chromatography (silica, hexanes/0.9% EtOAc) to obtain pure product **10** (110 mg, 99%). Spectral and physical properties concur with published data [8c].

5,15-Bis[3,4,5-tris(decyloxy)phenyl]-10,20-bis[(3,4,5-tris(decyloxy)phenyl)ethynylporphyrin (11a). A dried Schlenk tube, purged with argon, was charged with porphyrin **10** (100 mg, 0.064 mmol) and alkyne **4b** (220 mg, 0.39 mmol). The substrates were dissolved in anhydrous toluene (10 mL) and anhydrous THF (3 mL). Then, Et_2NH (3 mL, 21 mmol) was added, followed by $AsPh_3$ (64 mg, 0.21 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (36 mg,

0.035 mmol). The reaction mixture was stirred at rt for 40 h. Next, the second portion of alkyne **4b** (110 mg, 0.19 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (36 mg, 0.035 mmol), $AsPh_3$ (64 mg, 0.21 mmol) as well as Et_3N (2 mL, 14 mmol) were added. The reaction mixture was stirred additionally at rt for 30 h. Afterwards, the reaction mixture was filtered through a short plug of celite and evaporated. The crude product was chromatographed (silica, hexanes/CH_2Cl_2 7:3 to 7:13). The consecutive SEC (THF) did not allow to remove a non-porphyrinogen fluorescent compound. Therefore, compound **11a** was transformed into magnesium complex. Porphyrin **11a** was dissolved in CH_2Cl_2 (2.5 mL) and DIPEA (*N,N*-diisopropylethylamine) (0.21 mL, 1.2 mmol) was added, followed by MgI_2 (905 mg, 3.3 mmol). After 2.5 h the solvent was removed *in vacuo* and the crude product was purified by column chromatography (silica, hexanes then hexanes/CH_2Cl_2 1:1, then CH_2Cl_2) to obtain pure complex **Mg-11a**. Then, the complex was dissolved in $CHCl_3$ (2.1 mL) and TFA (11 µl, 0.14 mmol) was added. The color of the mixture changed from green to brown. After 8 min Et_3N (34 µl, 0.24 mmol) was added. Then, the crude product was evaporated and purified by column chromatography (silica, hexanes, then hexanes/CH_2Cl_2 7:3 to 1:1) to obtain pure product **11a** (50 mg, 31% after three steps). UV-vis (CH_2Cl_2): λ, nm (ε) 451 (403 000), 523 (7 200), 608 (60 100), 696 (34 100), 805 (1 000). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -1.93 (br s, 2H; NH), 0.78–0.96 (m, 36H, CH_3), 1.15–1.61 (m, 164H, CH_2), 1.64–1.73 (m, 4H, $OCH_2CH_2C\mathbf{H}_2$), 1.79–2.03 (m, 24H, $OCH_2C\mathbf{H}_2$), 4.07–4.14 (m, 12H, OCH_2), 4.17 (t, *J* = 6.5 Hz, 8H, OCH_2), 4.31 (t, *J* = 6.5 Hz, 4H; OCH_2), 7.21 (s, 4H, ArH), 7.40 (s, 4H, ArH), 8.93 (d, *J* = 4.6 Hz, 4H, β-H), 9.65 (d, *J* = 4.6 Hz, 4H, β-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ, ppm 14.05, 14.09, 14.12, 14.14, 22.63, 22.67, 22.71, 22.74, 26.15, 26.16, 26.3, 29.31, 29.36, 29.42, 29.44, 29.45, 29.47, 29.51, 29.54, 29.61, 29.61, 29.64, 29.67, 29.70, 29.75, 29.77, 29.9, 30.4, 30.6, 31.86, 31.91, 31.96, 31.99, 69.4, 73.7, 73.8, 90.6, 97.8, 101.3, 110.3, 114.3, 118.2, 122.0, 136.3, 138.1, 139.7, 151.4, 153.4. HR MS (FD): *m/z* calcd. for $C_{168}H_{270}N_4O_{12}$ 2536.0640, found 2536.0601, isotope profiles match.

5,15-Bis[3,4,5-tris(decyloxy)phenyl]-10,20-bis[(3,4,5-tris(dodecyloxy)phenyl)ethynyl]porphyrin (11b). A dried Schlenk tube, purged with argon, was charged with porphyrin **10** (50 mg, 0.032 mmol) and alkyne **4a** (65 mg, 0.099 mmol). The substrates were dissolved in anhydrous toluene (10 mL) and anhydrous THF (10 mL). Then, $AsPh_3$ (20 mg, 0.065 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (18 mg, 0.017 mmol) were added. The reaction mixture was stirred at rt for 18 h. Afterwards, the reaction mixture was filtered through a short plug of celite and evaporated. The crude product was chromatographed (SEC, toluene, then SEC, THF). The consecutive DCVC was performed (silica, hexanes/CH_2Cl_2 3:2). Subsequently, porphyrin **11b**, contaminated with a fluorescent compound, was dissolved in CH_2Cl_2 (1 mL) and DIPEA (0.9 mL, 1.2 mmol) was added, followed by MgI_2 (100 mg, 0.36 mmol). After 3.5 h the solvents were removed *in vacuo* and the crude product was purified by column chromatography (silica, hexanes/CH_2Cl_2 3:1 to 7:3) to obtain pure complex **Mg-11b**. Then, the complex was dissolved in $CHCl_3$ (0.9 mL) and TFA (5 µl, 0.065 mmol) was added. After 10 min the reaction was quenched with Et_3N (34 µl, 0.24 mmol). The solvents were evaporated and the crude product was purified by column chromatography (silica, hexanes/CH_2Cl_2 7:3 to 1:1) to obtain pure product **11b** (30 mg, 34% after three steps). UV-vis (CH_2Cl_2): λ, nm (ε) 452 (280 000), 613 (42 300), 705 (22 900). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -1.93 (br s, 2H; NH), 0.81–0.94 (m, 36H, CH_3), 1.02–1.47 (m, 168H, CH_2), 1.47–1.62 (m, 20H, $OCH_2CH_2C\mathbf{H}_2$), 1.64–1.74 (m, 4H, $OCH_2CH_2C\mathbf{H}_2$), 1.76–2.08 (m, 24H, $OCH_2C\mathbf{H}_2$), 4.08–4.15 (m, 12H, OCH_2), 4.18 (t, *J* = 6.5 Hz, 8H, OCH_2), 4.31 (t, *J* = 6.5 Hz, 4H; OCH_2), 7.21 (s, 4H, ArH), 7.41 (s, 4H, ArH), 8.94 (d, *J* = 4.6 Hz, 4H, β-H), 9.66 (d, *J* = 4.6 Hz, 4H, β-H). HR MS (FD): *m/z* calcd. for $C_{180}H_{294}N_4O_{12}$ 2704.2518, found 2704.2473, isotope profiles match.

5,15-Bis[3,4,5-tris(decyloxy)phenyl]-10,20-bis[(3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)phenyl)-ethynyl]porphyrin (11c). A dried Schlenk tube, purged with argon, was charged with porphyrin **10** (31 mg, 0.020 mmol) and alkyne **4c** (47 mg, 0.080 mmol). The substrates were dissolved in anhydrous toluene (3.1mL) and anhydrous THF (0.85 mL). Next, $AsPh_3$ (32 mg, 0.10 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (18 mg, 0.017 mmol) and Et_3N (1.1 mL, 7.9 mmol) were added. The reaction mixture was stirred at rt for 21.5 h. Then, the second portion of $Pd_2(dba)_3{\cdot}CHCl_3$ (18 mg, 0.017 mmol) was added. The reaction mixture was stirred at rt for 2 d. Later, the reaction mixture was filtered through a short plug of celite and evaporated. The crude product was chromatographed (silica, hexanes, then hexanes/EtOAc 4:1 to 1:4, then EtOAc, then EtOAc/2% MeOH to EtOAc/5% MeOH). The consecutive chromatography (silica, toluene/acetone 7:3) was performed to obtain pure product **11c** (14 mg, 27%) as a green solid. UV-vis (CCl_4): λ, nm (ε) 450 (154 000), 521 (5 000), 606 (20 600), 697 (10 500). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -1.95 (br s, 2H, NH); 0.78–0.96 (m, 18H, CH_3), 1.04–1.73 (m, 84H, CH_2), 1.85–1.92 (m, 8H, $OCH_2C\mathbf{H}_2$), 1.94–2.03 (m, 4H, $OCH_2C\mathbf{H}_2$), 3.35 (s, 12H, OCH_3), 3.39 (s, 6H, OCH_3), 3.51–3.57 (m, 8H, OCH_2), 3.57–3.61 (m, 4H, OCH_2), 3.64–3.70 (m, 12H, OCH_2), 3.64–3.76 (m, 12H, OCH_2), 3.76–3.85 (m, 12H, OCH_2), 3.87–3.93 (m, 4H, OCH_2), 3.95–4.02 (m, 8H, OCH_2), 4.12 (t, *J* = 6.5 Hz, 8H, OCH_2), 4.24–4.34 (m, 8H, OCH_2), 4.34–4.40 (m, 8H, OCH_2), 7.26 (overlapping with the signal of $CHCl_3$ s, 4H, ArH), 7.40 (s, 4H, ArH), 8.94 (d, *J* = 4.4 Hz, 4H, β-H), 9.63 (d, *J* = 4.4 Hz, 4H, β-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ, ppm 14.06, 14.10, 14.14, 22.63, 22.68, 22.74, 26.2, 26.3, 29.3, 29.46, 29.47, 29.54, 29.6, 29.7, 29.8, 29.9, 30.6, 31.9, 32.0, 59.0, 69.2, 69.4, 69.8, 70.6, 70.8,

70.9, 72.0, 72.6, 73.8, 91.0, 97.3, 101.0, 111.5, 114.2, 118.6, 122.0, 127.8, 136.2, 138.1, 151.4, 152.9. HR MS (ESI): *m/z* calcd. for $C_{150}H_{234}N_4O_{30}Na_2$ $[M + 2Na]^{2+}$ 1308.8346, found 1308.8376, isotope profiles match.

[5,15-Bis[[3,4,5-tris(decyloxy)phenyl]ethynyl]-10,20-bis[(triizoprophylosilyl)ethynyl]-porphyrinato] magnesium (Mg-14). A dried Schlenk tube, purged with argon, was charged with porphyrin **Mg-13** (100 mg, 0.12 mmol) and alkyne **4b** (272 mg, 0.48 mmol). The substrates were dissolved in anhydrous toluene (18 mL), anhydrous THF (5 mL) and Et_3N (6.8 mL, 0.049 mol). The vessel was evacuated and backfilled with argon (this process was repeated three times). Then, $AsPh_3$ (90 mg, 0.29 mmol) and $Pd_2(dba)_3$ (54 mg, 0.052 mmol) were added. The reaction mixture was stirred at rt for 28 h. Afterwards, the reaction mixture was filtered through a short plug of celite and evaporated. The crude product was chromatographed (Al_2O_3, hexanes/EtOAc/Et_3N 98:1:1 to 97:2:1). The consecutive chromatography (Al_2O_3, hexanes/CH_2Cl_2 1:1 to 9:16) afforded pure product **Mg-14** (43 mg, 20%) as a green solid. UV-vis (CH_2Cl_2): λ, nm (ε) 480 (562 000), 634 (20 100), 692 (80 800). ^{1}H NMR (400 MHz, CD_2Cl_2): δ, ppm 0.78–0.83 (m, 24H, CH_3, CH), 1.00–1.40 (m, 72H, CH_2), 1.40–1.60 (m, 36H, CH_3), 1.48–1.55 (m, 12H, $OCH_2CH_2CH_2$), 2.50–2.95 (m, 12H, OCH_2CH_2), 3.65–3.95 (m, 6H, OCH_2), 6.83 (s, 4H, ArH), 9.56 (d, J = 4.0 Hz, 4H, β-H), 9.62 (d, J = 4.0 Hz, 4H, β-H).

5,15-Bis[[3,4,5-tris(decyloxy)phenyl]ethynyl]-10, 20-bis[(triizoprophylosilyl)ethynyl]porphyrin (14). A dried Schlenk tube, purged with argon, was charged with porphyrin **13** (204 mg, 0.25 mmol) and alkyne **4b** (551 mg, 0.97 mmol). The substrates were dissolved in anhydrous toluene (37 mL), anhydrous THF (10 mL) and Et_3N (14 mL, 0.1 mol). The vessel was evacuated and backfilled with argon (this process was repeated three times). Then, $AsPh_3$ (150 mg, 0.49 mmol) and $Pd_2(dba)_3$ (100 mg, 0.097 mmol) were added. The reaction mixture was stirred at rt for 14.5 h. Later, the mixture was filtered through a short plug of celite and evaporated. The crude product was purified twice by SEC (toluene). The consecutive chromatography (silica, hexanes/CH_2Cl_2 4:1 to 7:3) afforded pure product **14** (384 mg, 86%). UV-vis (CH_2Cl_2): λ, nm (ε) 468 (317 000), 588 (14 700), 635 (63 700), 730 (20 300). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -1.52 (s, 2H, NH), 0.87–0.92 (2 overlapping t, 18H, CH_3), 1.29–1.54 (m, 114H, $SiCHCH_3$, CH_2, SiCH), 1.56–1.62 (m, 12H, $OCH_2CH_2CH_2$), 1.81–1.88 (m, 4H, OCH_2CH_2), 1.90–1.98 (m, 8H, OCH_2CH_2), 4.12 (t, J = 6.6 Hz, 4H, OCH_2), 4.18–4.22 (m, 8H, OCH_2), 7.22 (s, 4H, ArH), 9.57–9.61 (m, 8H, β-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ, ppm 11.9, 14.11, 14.14, 19.1, 22.70, 22.73, 26.18, 26.20, 29.39, 29.44, 29.49, 29.51, 29.64, 29.66, 29.71, 29.73, 29.80, 30.4, 31.9, 32.0, 69.5, 73.7, 89.8, 98.3, 100.3, 102.7, 102.9, 107.8, 110.4, 118.0, 139.9, 153.4. HR MS (FD): *m/z* calcd. for $C_{118}H_{182}N_4O_6Si_2$ 1807.3598, found 1807.3528, isotope profiles match. Anal. calcd. (%) for $C_{118}H_{182}N_4O_6Si_2$: C, 78.35; H, 10.14; N, 3.10, found C, 78.38; H, 10.07; N, 3.28.

5,15-Bis[[3,4,5-tris(decyloxy)phenyl]ethynyl]-10,20-diethynylporphyrin (15). A dried Schlenk tube, purged with argon, was charged with porphyrin **14** (190 mg, 0.105 mmol). The porphyrin was dissolved in anhydrous THF (20 mL). Then, TBAF (1.0 M, 0.45 mL, 0.45 mmol) was added. The reaction was stirred at rt in argon atmosphere for 40 min. The solution was concentrated and the crude product was chromatographed (silica, hexanes/CH_2Cl_2 3:2) to obtain pure product **15** which was suspended in hexanes and centrifuged (135 mg, 86%) affording porphyrin **15** as a green solid. UV-vis (CH_2Cl_2): λ, nm (ε) 467 (266 000), 537 (6 100), 578 (11 200), 625 (50 500), 721 (12 900). ^{1}H NMR (600 MHz, $CDCl_3$): δ, ppm -2.57 (s, 2H, NH), 0.87–0.92 (2 overlapping t, 18H, CH_3), 1.29–1.48 (m, 72H, CH_2), 1.56–1.63 (m, 12H, $OCH_2CH_2CH_2$), 1.82–1.89 (m, 4H, OCH_2CH_2), 1.92–1.99 (m, 8H, OCH_2CH_2), 4.10–4.14 (m, 4H, OCH_2), 4.15 (s, 2H, CH_{alkyne}), 4.20–4.24 (m, 8H, OCH_2), 7.21 (s, 4H, ArH), 9.32–9.37 (m, 8H, β-H). ^{13}C NMR (150 MHz, $CDCl_3$): δ, ppm 14.11, 14.13, 22.70, 22.73, 26.20, 26.22, 29.40, 29.44, 29.52, 29.65, 29.68, 29.73, 29.80, 30.5, 31.9, 32.0, 69.5, 73.8, 84.6, 84.8, 89.7, 98.2, 100.6, 102.5, 110.5, 118.0, 139.9, 153.4. Anal. calcd. (%) for $C_{100}H_{142}N_4O_6$: C, 80.27; H, 9.57; N, 3.74, found C, 80.07; H, 9.61; N, 3.67.

5,15-bis[[3,4,5-tris(decyloxy)phenyl]ethynyl]-10,20-bis[[4-(trifluoromethyl)phenyl]ethynyl]porphyrin (18). A dried Schlenk tube, purged with argon, was charged with porphyrin **15** (40 mg, 0.027 mmol). The porphyrin was dissolved in anhydrous THF (6 mL) and 1-iodo-4-(trifluoromethyl)benzene (**16**; 31 µl, 0.21 mmol), followed by Et_3N (1.5 mL, 11 mmol), Pd_2dba_3 (18 mg, 0.017 mmol) and $AsPh_3$ (30 mg, 0.098 mmol) were added. The reaction mixture was stirred at rt for 26.5 h. Afterwards, the reaction mixture was filtered through a short plug of celite and evaporated. The crude product was purified by SEC (THF). The consecutive chromatography (silica, hexanes/CH_2Cl_2 3:1) was performed to obtain pure product **26** (39 mg, 81%) as a green solid. UV-vis (CCl_4): λ, nm (ε) 472 (273 000), 640 (54 900), 736 (16 200). ^{1}H NMR (500 MHz, $CDCl_3$): δ, ppm -2.91 (s, 2H, NH), 0.82–0.96 (m, 18H, CH_3), 1.28–1.50 (m, 72H, CH_2), 1.51–1.58 (m, 8H, $OCH_2CH_2CH_2$), 1.59–1.68 (m, 4H, $OCH_2CH_2CH_2$), 1.83–1.91 (m, 4H, OCH_2CH_2), 1.92–2.01 (m, 8H, OCH_2CH_2), 4.09–4.15 (m, 4H, OCH_2), 4.16–4.24 (m, 8H, OCH_2), 7.12 (s, 4H, ArH), 7.81 (br s, 4H, ArH), 8.02 (AA'BB', J = 5.4 Hz, 2x2H,), 9.00–9.13 (m, 8H, β-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ, ppm 14.1, 22.7, 26.26, 26.30, 29.44, 29.48, 29.60, 29.70, 29.77, 29.85, 30.5, 32.0, 69.5, 73.8, 89.6, 93.5, 95.8, 98.4, 101.0, 102.6, 110.4, 117.9, 118.7, 122 (q, J = 251.4 Hz), 125.1, 125.6, 127.4, 130.2, 131.83, 140.0, 153.4. LR MS (FD): *m/z* calcd. for $C_{114}H_{148}F_6N_4O_6$ 1783.1, found 1783.1; isotope profiles match.

Two-photon absorption measurements were carried out using a wavelength-tunable femtosecond laser system that comprises a Ti:Sapphire femtosecond oscillator

(Mira 900, Coherent Inc.) pumped by a CW frequency-doubled Nd:YAG laser (Verdi, Coherent Inc.) and a 1-kHz repetition rate Ti:Sapphire femtosecond regenerative amplifier (Legend H, Coherent Inc.). The pulses from the Ti:sapphire amplifier are down converted with an optical parametric amplifier, OPA (TOPAS-C, Quantronix), whose output signal (idler) is continuously tunable from 1100 to 1600 (1600 to 2200) nm. The second harmonic of idler was used for two-photon excitation in the λ_{ex} = 800–1100 nm region and the fundamental of signal in the 1100–1400 nm region. The OPA output signal pulse energy was 100–250 μJ (5–10 μJ after frequency doubling), and the pulse duration was 70–120 fs. Briefly, the linearly polarized excitation laser beam was slightly focused with an f = 25-cm lens onto the sample solution contained in a 1×1 cm^2 spectroscopic cell and placed 15 cm behind the lens. A small fraction of the beam was split off by a thin glass plate placed just before the sample and directed to the reference detector (Molectron). The sample fluorescence was collected with a spherical mirror (f = 50 cm, diameter d = 10 cm) and focused with magnification ratio ~1 on the entrance slit of an imaging grating spectrometer (Jobin Yvon Triax 550). The 2PA spectrum (in relative units) was obtained by tuning the wavelength of OPA, and measuring the corresponding intensity of two-photon excited fluorescence. The wavelength tuning of OPA and data collection were computer-controlled with a LabView routine. At each wavelength, the fluorescence intensity was normalized to the square of the excitation photon flux, measured in the reference channel. The correction to the spectral variations of the OPA output (pulse duration and beam spatial profile) was done by using Rhodamine B in methanol as a standard, whose 2PA spectrum is well-characterized. To exclude possible artifacts, *e.g.* due to absorption at wavelengths close to the linear absorption, we checked that at each wavelength the fluorescence signal increased as a square of the excitation intensity. Absolute 2PA cross-sections were measured using relative fluorescence technique as described with Rhodamine B as a standard. To obtain absolute 2PA spectra in GM units, all relative 2PA spectra were calibrated to the known (at one wavelength in each spectral region) absolute cross-section value. Styryl 9M in $CHCl_3$ was used as reference standard [32]. The 2PA properties were measured in CCl_4 solutions.

Calculations performed with Gaussian 09, Revision C.01. Following ground state optimization(b3lyp/6-31g(d)/PCM(CCl_4), TDDFT(cam-b3lyp/6-31g(d))/PCM(CCl_4) calculations were carried out. The calculated state energies, oscillator strengths, transition dipoles, CI mixing coefficients and molecular orbital images for compounds **Mg-11a** and **18** are shown in Table 3 and 4.

CONCLUSION

The optimal methodology towards *trans*-A_2B_2-tetrakis(arylethynyl)porphyrins comprised of synthesis of *meso*-substituted A_2-porphyrins followed by bromination and two consecutive Sonogashira couplings. We proved that the presence of polyalkoxyphenyl substituents ensures desirable physical parameters of such π-extended porphyrins. Combining this property with very good secondary properties (strong absorption of red light — ε ~50000 and a long triplet state lifetime) makes them good candidates for nonlinear optical materials. Porphyrin possessing two aromatic electron-withdrawing substituents and two aromatic electron-donating substituents at *trans*-arrangement is more polarized than in majority of other porphyrins, which is probably the reason for a significant increase of triplet state lifetime and in two-photon absorption cross-section.

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