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Selective Cycloaddition of Tetracyanoethene (TCNE) and 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) to Afford *meso*-Substituted Phenylethynyl Porphyrins

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Abstract: π-Extended TCBD-porphyrins that contained a 1,1,4,4-tetracyanobuta-1,3-diene unit were prepared by a highly efficient [2+2] cycloaddition of tetracyanoethene (TCNE) or 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) with *meso*-substituted *trans*-A_2B_2-porphyrins that contained two phenylethynyl groups, followed by a retro-electrocyclization reaction. Depending on the electronic properties of the arylethynyl groups, the cycloaddition reaction took place exclusively on either one or two ethynyl moieties with high yield. The addition of TCNQ proceeded with complete regioselectivity. The resulting π-expanded TCBD-porphyrins had a hypsochromically shifted Soret band and showed unique, broad absorption in the visible region.

Keywords: chromophores · cycloaddition · porphyrins · tetracyanoethene · UV/Vis spectroscopy

Introduction

Donor–acceptor (D-A)-substituted conjugated organic chromophores have received increasing interest because of their desirable properties, such as high electrical conductivity and large nonlinear optical (NLO) responses.[1] TCNE is one of the strongest organic electron acceptors, and has found widespread application in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells.[2,3] In 1981, Bruce et al. reported that the reaction of electron-rich alkynes with TCNE afforded [2+2] cycloaddition products, namely, cyclobutane derivatives, which underwent ring-opening reactions to give their corresponding 1,1,4,4-tetracyano-1,3-butadienes (TCBDs).[4] Subsequently, Diederich and co-workers reported that a variety of *N*,*N*-dialkylaniline-substituted alkynes reacted with TCNE to give their corresponding TCBDs in high yields. The same group also discovered that this new class of chromophores was characterized by intense intramolecular charge-transfer (CT) interactions with absorption maxima in the visible region, as well as promising third-order optical nonlinearities.[5] Recently, other groups have reported the addition of TCNE to heterocyclic alkynes.[6]

Over the last two decades, *meso*-arylethynylporphyrins have received considerable attention in the field of materials chemistry owing to their unique optical properties.[7] These structures have also emerged as promising candidates for a wide range of applications, including artificial photosynthetic systems,[8] optical limiters,[9] reverse saturable absorbers (RSA),[10] biological imaging,[11] and dye-sensitized solar cells (DSSCs).[12]

Arylethynylporphyrins have a significantly altered electronic structure compared to their parent macrocycle. The incorporation of two arylethynyl moieties elongates their π-conjugation pathway and improves the electronic interactions between the phenyl substituents.[13] As part of our systematic investigation on the synthesis and reactivity of π-extended porphyrins,[14,15] herein, we report the first studies of the reaction between *meso*-arylethynylporphyrins and TCNE.

Results and Discussion

We have designed a small library of *trans*-A_2B_2-porphyrins that contained carbon–carbon triple bonds with substituted phenyl units at their two *meso*-positions. These substituents were carefully chosen to afford porphyrins with various electronic properties.

We envisioned that these prospective addition products would possess rather poor solubility unless suitable substituents were placed at the remaining two *meso*-positions. Indeed, in most cases we used tris(alkyloxyphenyl)substituents, which afforded products with high solubility in nonpolar organic solvents.

Readily available 3,4,5-trihydroxybenzaldehyde[16] was alkylated under classical Williamson conditions with alkyl bromides or iodides to give 3,4,5-trialkoxybenzaldehydes **1** and **2**.[7] These aldehydes were reacted with dipyrrane[18] and trifluoroacetic acid to give A_2-porphyrins in 48–52% yield, fol-

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lowed by bromination with *N*-bromosuccinimide (NBS), thereby leading to porphyrins **3** and **4** in 98% and 95% yield, respectively (Scheme 1). Finally, the target *meso*-arylethynyl *trans*-A_2B_2-porphyrins, which contained 3,4,5-$(OC_{10}H_{21})_3C_6H_2$ (**11**, **12**, **14**–**16**) and 3,4,5-$(OC_{11}H_{23})_3C_6H_2$ groups (**10**, **13**), were synthesized in 63–85% yield through Sonogashira coupling, which allowed the direct cross-coupling of terminal alkynes **5**–**9** with porphyrin halides under mild conditions in the presence of catalytic $[Pd_2(dba)_3]$, $AsPh_3$ as the co-catalyst, and an aliphatic amine.[19] The remaining porphyrins, which contained 3,4,5-tri(*tert*-butoxycarbonylmethyloxy)phenyl- (**18**, **19**) and mesityl (**17**) substituents, were obtained according to our recently reported procedure, starting from phenylpropargyl aldehydes and dipyrranes, by using a [2+2] condensation approach (Scheme 2).[14] Subsequently, these porphyrins (**10**–**19**) were treated with TCNE or TCNQ in CH_2Cl_2 at room temperature (Scheme 2, Scheme 3, Table 1).

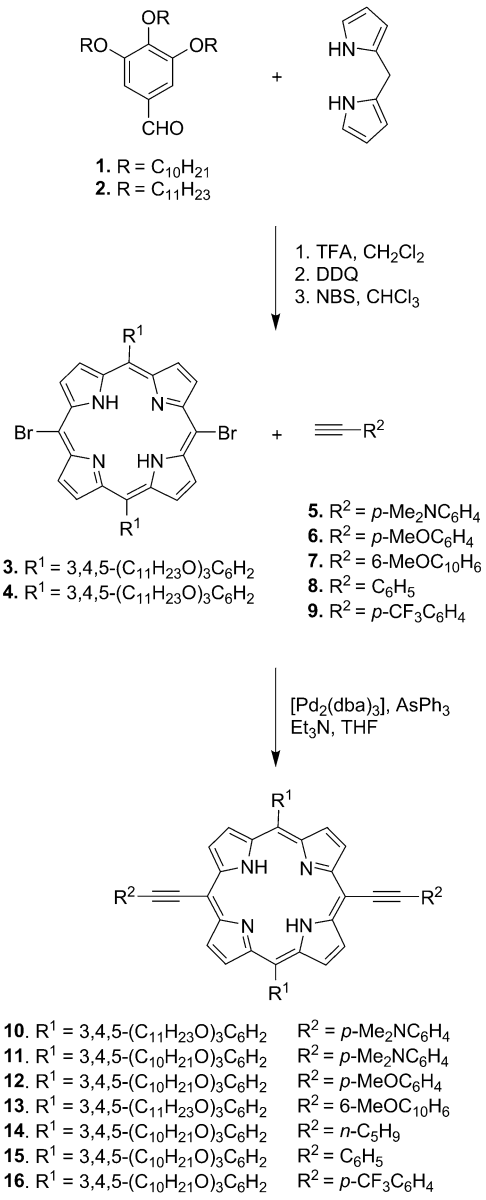
Table 1. Reactions of *meso*-arylethynyl-substituted porphyrins with TCNE and TCNQ.[a]

Entry	Substrate	R^2	Product	t [h]	Yield [%][b]
1	**10**	*p*-$(CH_3)_2NC_6H_4$	**20**	1.5	95[c]
2	**11**	*p*-$(CH_3)_2NC_6H_4$	**26**	24	36
3	**12**	*p*-$MeOC_6H_4$	**21**	2	81
4	**12**	*p*-$MeOC_6H_4$	**27**	48	86
5	**17**	*p*-$MeOC_6H_4$	**22**	8	80
6	**13**	6-$MeOC_{10}H_6$	**23**	3	86
7	**14**	*n*-C_4H_9	–	4	n.d.[d]
8	**15**	Ph	**24**	4	83
9	**15**	Ph	**28**	48	80
10	**16**	*p*-$CF_3C_6H_4$	**25**	15	98
11	**18**	*p*-CNC_6H_4	–	26	0[e]
12	**19**	*p*-$NO_2C_6H_4$	–	24[f]	0[e]
13	**19**	*p*-$NO_2C_6H_4$	–	48[g]	0[e]

[a] All reactions were performed on a 0.02 mmol scale in CH_2Cl_2 at ambient temperature with 2 equiv of TCNE or TCNQ; [b] yields of isolated product; [c] calculated for the mixture of isomers; [d] product decomposed during purification; [e] substrate was recovered; [f] reaction with TCNE; [g] reaction with TCNQ.

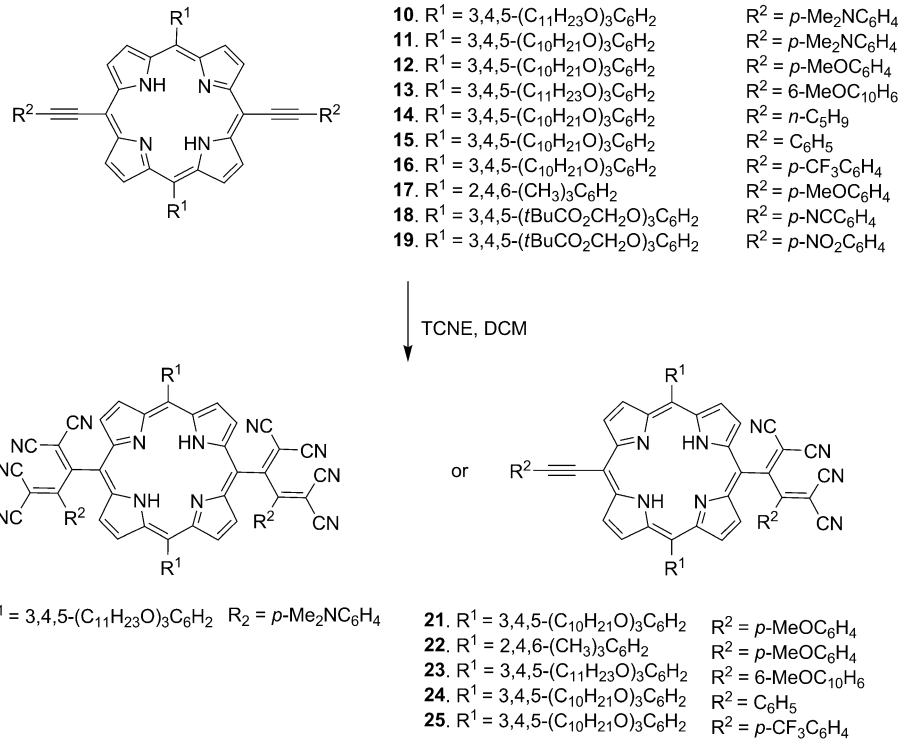
The addition of TCNE or TCNQ to a triple bond afforded the corresponding products (**20**–**28**) in very high yields (in most cases), even in the presence of some strongly electron-withdrawing groups at the *para* position of the phenylethynyl moiety (Table 1). This result was in contrast with earlier reports, which showed that the addition of TCNE could only take place if at least one aromatic unit contained a strongly electron-donating substituent (NMe_2, OMe, or thiophene).[5,6] Apparently, in our case, the porphyrin acted as an electron-donating "substituent", which, given its propensity for electrophilic aromatic substitution, was not totally unexpected. Moreover, mono-cycloaddition occurred in most cases, thus suggesting that strong conjugation between the newly formed electron-withdrawing group at the *meso* position of the porphyrin deactivated the remaining triple bond.

In view of the excellent yield of TCBD-porphyrin **25**, it was rather unexpected that *trans*-A_2B_2-porphyrins **18** and

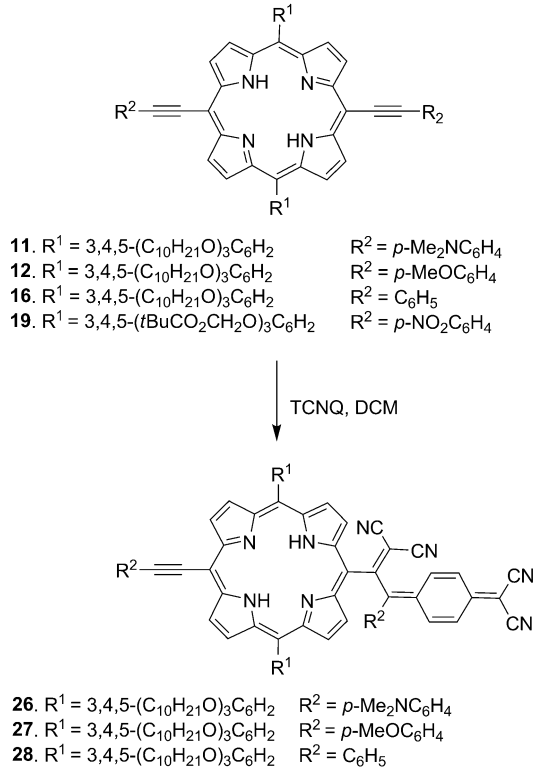


Scheme 1. Synthesis of *meso*-phenylethynyl-substituted *trans*-A_2B_2-porphyrins. TFA = trifluoroacetic acid.

Abstract in Polish: W wyniku reakcji cykloaddycji tetracyjanoetylenu (TCNE) oraz pochodnej TCNQ do wiązania potrójnego trans podstawionych porfiryn i następczej reakcji retro-elektrocyklizacji otrzymano serię nowych TCBD-porfiryn zawierających jednostkę 1,1,4,4-tetracyjano-1,3-dienu. W zależności od charakteru elektronowego podstawnika grupy etynylofenylowej otrzymano z wysoką selektywnością jak i wydajnością produkty mono bądź di-podstawione. Tak otrzymane związki charakteryzują się hipsochromowym przesunięciem pasma Soreta oraz szerszym pasmem absorpcji w zakresie widzialnym.



Scheme 2. Reaction between TCNE and *meso*-phenylethynyl-substituted *trans*-A_2B_2-porphyrins **10**–**19**.



Scheme 3. Reaction between TCNQ and *meso*-phenylethynyl-substituted *trans*-A_2B_2-porphyrins **11**, **12**, **16**, and **19**.

19, which contained strongly electron-withdrawing cyano- and nitro substituents, respectively, as well as 3,4,5-tris(*tert*-butoxycarbonylmethyloxy)-phenyl groups, were unreactive (Table 1, entries 11–13). We presumed that the difference in the electronic influence between the 3,4,5-trialkoxyphenyl substituent and its analogue that contained three OCH_2CO_2tBu groups was miniscule and could not explain the difference in reactivity between porphyrins **16** and **18**–**19**. Consequently, the only probable explanation lay in a difference between the nature of these two electron-withdrawing groups (CF_3: inductive effect, CN: resonance effect). Heating from ambient temperature up to 100 °C did not improve the yield of this reaction. The electronic nature of the substituent strongly affected the reaction time, which was in the range from 1.5 hours for amino-substituted porphyrin **10** to 15 hours for trifluoromethyl-porphyrin **16** (Table 1, entries 1 and 10). Performing these reactions with either a larger excess of TCNE or in boiling toluene led to the partial decomposition of the starting material. With TCNQ, a longer reaction time of up to 48 hours was required. All newly prepared TCBD-porphyrins (**21**–**28**) were brownish semi-solids that were stable at ambient temperature under air and well-soluble in common organic solvents, such as CH_2Cl_2, THF, toluene, and *n*-hexane. The use of porphyrin **14**, which contained two *n*-hexynyl substituents, unexpectedly led to complete decomposition during the attempted work-up to afford a dark, insoluble, polymeric material (Table 1, entry 7).

Me_2N-substituted porphyrin **10** reacted with TCNE to form a bis-adduct, TCBD-porphyrin **20**. Although the reaction time was very short (1.5 hours), the bis-adduct was formed in 95 % yield (Table 1, entry 1). Directly after the reaction had been completed, the product was observed as a single spot by TLC; however, after a couple of hours, TLC analysis showed two spots that were the same color and only slightly different in their retention factor (R_f). ^1H NMR spectroscopy, as well as MS, indicated that spontaneous isomerization had occurred. Performing an analogous reaction with TCNQ afforded mono-adduct **26** in moderate yield (36 %) after 24 hours (Table 1, entry 2). Owing to the fact that the dimethylanilino moiety was the superior electron donor and -activator (Hammett constant $\sigma_P(NMe_2) = -0.83$), only one regioisomer was isolated and verified by 2D NOESY NMR spectroscopy (see the Supporting Infor-

mation). No side-products were formed in the solution-phase reactions, as determined by ^{1}H NMR spectroscopy.

Significant influence on the reaction time was observed for *trans*-A_2B_2-porphyrins that contained two mesityl substituents at the *meso* positions. The corresponding TCBD-porphyrin (**22**) was obtained in 80% yield after 8 hours, versus 2 and 3 hours for TCBD-porphyrins **21** and **23**, respectively (Table 1, entries 3, 5, and 6). Substantially longer reaction times, up to 48 hours, were also required in the reaction between TCNQ and porphyrins **12** and **15**, thereby leading to their corresponding mono-adducts (**27** and **28**, respectively) with high yields (86 and 80%, respectively; Table 1, entries 4 and 9). These results clearly demonstrated the influence of substituents on the course of the reaction with porphyrins that exhibited strong electronic interactions between the phenyl substituents.

A comparison of the UV/Vis spectra of TCBD-porphyrin **24** and porphyrin **15** showed a distinct hypsochromic shift of the Soret band (about 15 nm). Slight broadening of the Soret band was accompanied by a decrease in the molar extinction coefficient ($\varepsilon = 334000\ dm^3 mol^{-1} cm^{-1}$ for porphyrin **15** versus $\varepsilon = 221000\ dm^3 mol^{-1} cm^{-1}$ for TCBD-porphyrin **24**; Figure 1). The analogous phenomenon was observed in

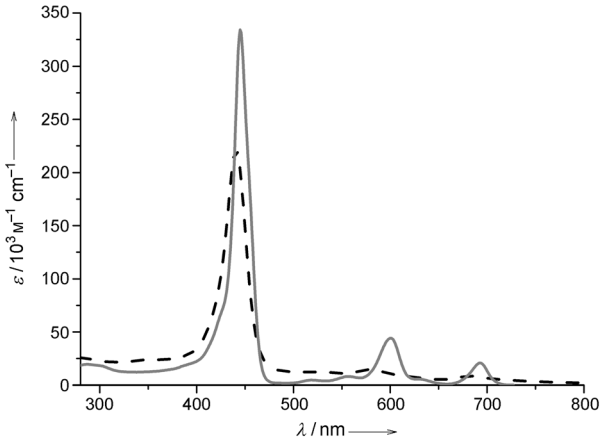


Figure 1. Electronic absorption spectra of *trans*-A_2B_2-porphyrin **15** (solid line) and TCBD-porphyrin **24** (dashed line) in CCl_4 at 298 K.

all other cases. The two Q bands near 600 and 690 nm in the spectra of *trans*-A_2B_2-porphyrins (2.06 and 1.79 eV, respectively) were replaced by a very broad intramolecular charge-transfer (CT) band with end-absorptions into the near infrared (NIR) region (see the Supporting Information, Figure S1). This result was in strong contrast to the structurally smaller TCBDs reported by Diederich and co-workers, which displayed only CT bands.

Compared to substrate **10**, TCBD-porphyrin **20** exhibited an even more pronounced hypsochromic shift (32 nm, 0.19 eV) of the Soret band, which was accompanied by a strong decrease in the molar extinction coefficient ($\varepsilon = 157000\ dm^3 mol^{-1} cm^{-1}$ at 433 nm; Figure 2). This shift was not observed in the case of TCBD-porphyrin **26**. The tail

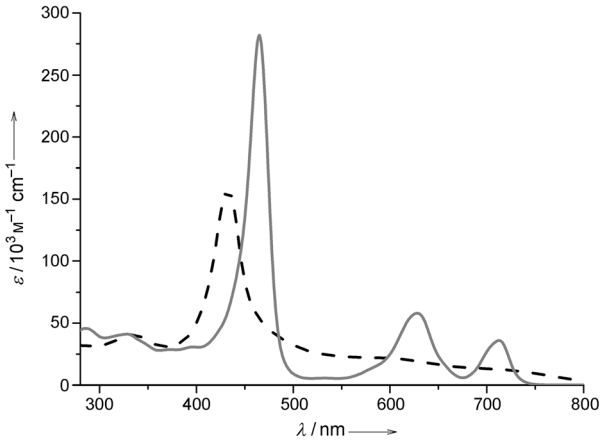


Figure 2. Electronic absorption spectra of *trans*-A_2B_2-porphyrin **10** (solid line) and TCBD-porphyrin **20** (dashed line) in CCl_4 at 298 K.

that was present in the UV/Vis spectra from 500 nm to the NIR region probably involved charge transfer from the aniline to the cross-conjugated tetracyanobutadiene moiety.

Comparison of the spectrum of TCBD-porphyrin **20** with that of an analogous dye that was prepared by Diederich and co-workers from TCNE and 1,4-bis(4-aminophenylethynyl)benzene showed the same features, that is, strong peak-broadening between 500–800 nm. A hypsochromic shift of the Soret band for TCBD-porphyrins **20**–**25** reflected the lower level of conjugation of the porphyrin core with TCBDs compared to porphyrins **10**–**13** and **15**–**17**, which contained two arylethynyl units. Presumably, the presence of two hydrogen atoms at the β position of the porphyrin core forced the TCBD unit to be almost perpendicular to the porphyrin plane. On the other hand, the electronic communication was strong enough to alter the electron density of the porphyrin unit and prevent a second cycloaddition.

It is known that porphyrins that are substituted at the *meso* positions with only one phenylethynyl unit still show characteristic sharp Q bands. The lack of these bands in the electronic spectra of compounds **20**–**28** suggested that their electronic structure was strongly affected by the adjacent TCBD unit. Owing to significant peak-broadening and to the complexity of the system, we were unable to determine whether phenylethynylporphyrin-to-TCBD, substituted aryl-to-TCBD, or a combination of both CT transitions were active. Porphyrins **20**–**28** did not display any fluorescence, in analogy to the TCNE adducts of BODIPY.[6a] This result was most-probably caused by electron transfer from the electron-rich π-extended porphyrin to the 1,1,4,4-tetracyano-1,3-butadiene moiety, followed by deactivation by vibrational relaxation.

Conclusions

A new family of chromophores was synthetized by the mono- or double [2+2] cycloaddition of TCNE or TCNQ to *meso*-substituted phenylethynylporphyrins, followed by

retro-electrocyclization.[20] The scope and efficiency of this atom-economic transformation was demonstrated by performing the reaction with a series of acetylenic porphyrins. The reaction of TCNE with these substrates added a new dimension to this chemistry owing to the exceptional steric hindrance that was imparted by the porphyrin ring, which forced a unique geometry (and hence UV/Vis absorption) of the final products. Despite the non-planarity of these systems, strong intramolecular charge-transfer (CT) interactions were apparent. Depending on the electronic character of the substituents, the reaction exclusively afforded mono- or di-substituted TCBD derivatives in very high yields. The full scope of the reaction between tetracyanoethene or 7,7,8,8-tetracyanoquinodimethane and various *meso*-substituted ethynylporphyrins is currently under investigation within the group. The applications of this readily available new class of D–A compounds in NLO and other optoelectronic devices represent a worthwhile objective for future work.

Experimental Section

General

All chemicals were used as received unless otherwise stated. Reagent-grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. All ^{1}H NMR spectra were collected on a 500 or 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm with TMS as an internal reference; J values are given in Hz. UV/Vis absorption spectra were recorded in CCl_4; purge gas was high-purity argon. Column chromatography was performed on silica gel (200–400 mesh) or alumina. Preparative scale size-exclusion chromatography (SEC) was carried out by using BioRad Bio-Beads SX-1 with toluene as an eluent. Mass spectra were obtained by using field-desorption mass spectrometry (FD-MS). 3,4,5-Trinonyloxybenzaldehyde (**1**), 3,4,5-tridecyloxybenzaldehyde (**2**), as well as *trans*-A_2B_2-porphyrins **17--19**, were prepared according to literature procedures.[14,17]

General Procedure for the Synthesis of A_2-Porphyrins

A mixture of dipyrrane (15.5 mmol) and an aldehyde (15.5 mmol) in CH_2Cl_2 (2 L) was purged with argon. CF_3COOH (0.75 mL, 9.8 mmol) was added dropwise and the flask was kept in the dark with aluminum foil. The solution was stirred under an argon atmosphere at RT for 3 h. The reaction was quenched by the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 4.5 g, 20 mmol) and the solution was stirred for an additional 30 min. The mixture was neutralized with triethylamine (15 mL) and then directly poured on top of a silica gel column that was packed with CH_2Cl_2. The column was eluted with CH_2Cl_2 and the fractions that contained product were collected, concentrated under reduced pressure, and purified by column chromatography on silica gel (hexanes/EtOAc). The resulting viscous violet residue was purified by size-exclusion chromatography (toluene).

5,15-Bis-(3,4,5-tridecyloxyphenyl)-porphyrin

The product was obtained in 48% yield (0.52 g, 0.37 mmol). $R_f = 0.40$ (hexanes/EtOAc 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -3.11$ (br s, 2H; NH), 0.83 (m, 12H; CH_3), 0.92 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 4.13 (t, $J = 6.4$ Hz, 8H; OCH_2), 4.33 (t, $J = 6.4$ Hz, 4H; OCH_2), 7.52 (s, 4H; ArH), 9.18 (d, $J = 5.0$ Hz, 4H; β-H), 9.37 (d, $J = 5.0$ Hz, 4H; β-H), 10.32 ppm (s, 2H; *meso*-H); UV/Vis (CCl_4): λ_{max} (ε) = 412 (286000), 504 (17500), 299 (16600), 539 (8000), 578 (6700), 635 nm (2900 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): calcd for $C_{92}H_{142}N_4O_6$: 1400.14; found: 1400.9 (the isotope profiles matched); elemental analysis calcd (%) for $C_{92}H_{142}N_4O_6$: C 78.92, H 10.22 N 4.00; found: C 78.71 H 10.18, N 3.96.

5,15-Bis-(3,4,5-triundecyloxyphenyl)-porphyrin

The product was obtained in 52% yield (0.59 g, 0.40 mmol). $R_f = 0.39$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -3.11$ (br s, 2H; NH), 0.83–0.86 (m, 12H; CH_3), 0.88–0.91 (m, 6H; CH_3), 1.23–1.26 (m, 80H; CH_3), 1.34–1.40 (m, 12H; CH_2), 1.64–1.68 (m, 4H; CH_2), 1.89–1.91 (m, 8H; CH_2), 1.96–1.99 (m, 4H; CH_2), 4.13 (t, $J = 6.5$ Hz, 8H; OCH_2), 4.32 (t, $J = 6.5$ Hz, 4H; OCH_2), 7.47 (s, 4H; ArH), 9.18 (d, $J = 5.0$ Hz, 4H; β-H), 9.38 (d, $J = 5.0$ Hz, 4H; β-H), 10.32 ppm (s, 2H; *meso*-H); UV/Vis (CCl_4): λ_{max} (ε) = 413 (319600), 505 (16100), 230 (14700), 540 (6200), 578 (5000), 636 nm (1200 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{98}H_{154}N_4O_6$: 1484.30; found: 1484.2 (the isotope profiles matched); elemental analysis calcd (%) for $C_{98}H_{154}N_4O_6$ C 79.30, H 10.46, N 3.77; found: C 79.50, H 10.73, N 3.50.

General Procedure for the Synthesis of 5,15-Dibromo-porphyrins

N-bromosuccinimide (NBS, 125 mg, 0.70 mmol) was added to a solution of A_2-porphyrin (0.35 mmol) in $CHCl_3$ (40 mL) at ambient temperature and the mixture was stirred for 1 h. The bromination reaction was quenched by the addition of acetone (5 mL) and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel (hexanes/EtOAc) and by size-exclusion chromatography (toluene).

*5,15-Dibromo-10,20-bis-(3,4,5-tridecyloxyphenyl)-porphyrin (**3**)*

The product was obtained in 98% yield (0.53 g, 0.34 mmol). $R_f = 0.42$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.72$ (br s, 2H; NH), 0.83 (m, 12H; CH_3), 0.92 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 4.10 (t, $J = 6.4$ Hz, 8H; OCH_2), 4.31 (t, $J = 6.4$ Hz, 4H; OCH_2), 7.37 (s, 4H; ArH), 8.94 (d, $J = 5.0$ Hz, 4H; β-H), 9.59 ppm (d, $J = 5.0$ Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 428 (296100), 523 (15800), 306 (13700), 558 (10500), 603 (4600), 662 (4400), 490 nm (4300 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{92}H_{140}Br_2N_4O_6$: 1557.93; found: 1557.9 (the isotope profiles matched); elemental analysis calcd (%) for $C_{92}H_{140}Br_2N_4O_6$: C 70.93, H 9.06, N 3.60; found: C 70.99, H 9.31, N 3.43.

*5,15-Dibromo-10,20-bis-(3,4,5-triundecyloxyphenyl)-porphyrin (**4**)*

The product was obtained in 95% yield (0.55 g, 0.33 mmol). $R_f = 0.41$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.72$ (br s, 2H; NH), 0.84–0.86 (m, 12H; CH_3), 0.87–0.91 (m, 6H; CH_3), 1.28–1.31 (m, 80H; CH_2), 1.35–1.40 (m, 12H; CH_2), 1.62–1.68 (m, 4H; CH_2), 1.85–1.91 (m, 8H; CH_2), 1.98–2.03 (m, 4H; CH_2), 4.10 (t, $J = 6.5$ Hz, 8H; OCH_2), 4.32 (t, $J = 6.5$ Hz, 4H; OCH_2), 7.37 (s, 4H; ArH), 8.95 (d, $J = 5.0$ Hz, 4H; β-H), 9.59 ppm (d, $J = 5.0$ Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 428 (307800), 523 (16600), 558 (11000), 603 (4900), 662 (4600), 489 nm (4500 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{98}H_{152}Br_2N_4O_6$: 1642.09; found: 1642.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{98}H_{152}Br_2N_4O_6$: C 71.68, H 9.33, N 3.41; found: C 71.64, H 9.60, N 3.16.

General Procedure for the Synthesis of trans-A_2B_2-Porphyrins

The mixture of 5,15-dibromo-porphyrin (0.04 mmol) and corresponding arylacetylene (0.1 mmol) in THF (5 mL) with toluene (0.5 mL) and triethylamine (1 mL) was deoxygenated by freeze–pump–thaw cycles and purged with argon gas in a Schlenk flask. Triphenylarsine (6.5 mg, 0.02 mmol) and [$Pd_2(dba)_3$] (25 mg, 30 μmol) were added and the mixture was stirred at 30°C in the dark for 24 h. The crude mixture was filtered through celite. The organic layer was separated, dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude green product was purified by column chromatography on silica gel (hexanes/EtOAc) and size-exclusion chromatography (toluene).

*5,15-Bis-(3,4,5-trisundecyloxyphenyl)-10,20-bis-(4-ethynyl-N,N-dimethylaniline)-porphyrin (**10**)*

The product was obtained in 85% yield (60 mg, 0.03 mmol). R_f=0.45 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −1.73 (br s, 2H; NH), 0.84–0.86 (m, 12H; CH_3), 0.87–0.91 (m, 6H; CH_3), 1.28–1.31 (m, 80H; CH_2), 1.35–1.40 (m, 12H; CH_2), 1.62–1.68 (m, 4H; CH_2), 1.85–1.91 (m, 8H; CH_2), 1.98–2.03 (m, 4H; CH_2), 3.11 (s, 12H; NCH_3), 4.12 (t, J=6.5 Hz, 8H; OCH_2), 4.30 (t, J=6.5 Hz, 4H; OCH_2), 6.88 (d, J=9.0 Hz, 4H; ArH), 7.40 (s, 4H; ArH), 7.88 (d, J=9.0 Hz, 4H; ArH), 8.88 (d, J=5.0 Hz, 4H; β-H), 9.63 ppm (d, J=5.0 Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=465 (279600), 628 (57500), 287 (46600), 328 (44900), 712 nm (3600 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{118}H_{172}N_6O_6$: 1770.67; found: 1770.2 (the isotope profiles matched); elemental analysis calcd (%) for $C_{118}H_{172}N_6O_6$: C 80.04, H 9.79, N 4.75; found: C 80.29, H 9.75, N 4.45.

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10,20-bis-(4-ethynyl-N,N-dimethylaniline)-porphyrin (**11**)*

The product was obtained in 78% yield (53 mg, 0.03 mmol). R_f=0.40 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −1.90 (br s, 2H; NH), 0.82–0.90 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 3.11 (s, 12H; NCH_3), 4.12 (t, J=6.4 Hz, 8H; OCH_2), 4.31 (t, J=6.4 Hz, 4H; OCH_2), 6.87 (d, J=8.5 Hz, 4H; ArH), 7.40 (s, 4H; ArH), 7.88 (d, J=8.5 Hz, 4H; ArH), 8.87 (d, J=5.0 Hz, 4H; β-H), 9.63 ppm (d, J=5.0 Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=464 (285000), 628 (58000), 712 nm (36000 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{110}H_{160}N_6O_6$: 1686.56; found: 1686.2 (the isotope profiles matched); elemental analysis calcd (%) for $C_{110}H_{160}N_6O_6$: C 79.76, H 9.56, N 4.98; found: C 79.37, H 10.23, N 4.49.

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10,20-bis-(4-methoxyphenylethynyl)-porphyrin (**12**)*

The product was obtained in 78% yield (52 mg, 0.03 mmol). R_f=0.42 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −1.90 (br s, 2H; NH), 0.82–0.90 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 3.94 (s, 6H; OCH_3), 4.13 (t, J=6.4 Hz, 8H; OCH_2), 4.32 (t, J=6.4 Hz, 4H; OCH_2), 7.10 (d, J=8.5 Hz, 4H; ArH), 7.41 (s, 4H; ArH), 7.95 (d, J=8.5 Hz, 4H; ArH), 8.92 (d, J=5.0 Hz, 4H; β-H), 9.65 ppm (d, J=5.0 Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=449 (402600), 607 (52600), 698 (26000), 523 nm (6400 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{110}H_{154}N_4O_8$: 1660.43; found: 1660.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{110}H_{154}N_4O_8$ C 79.57, H 9.35, N 3.37; found: C 79.30, H 9.54, N 3.59.

*5,15-Bis-(3,4,5-trisundecyloxyphenyl)-10,20-bis-(2-ethynyl-6-methoxynaphthalene)-porphyrin (**13**)*

The product was obtained in 85% yield (63 mg, 0.03 mmol). R_f=0.42 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −1.87 (br s, 2H; NH), 0.84–0.86 (m, 12H; CH_3), 0.87–0.91 (m, 6H; CH_3), 1.28–1.31 (m, 80H; CH_2), 1.35–1.40 (m, 12H; CH_2), 1.62–1.68 (m, 4H; CH_2), 1.85–1.91 (m, 8H; CH_2), 1.98–2.03 (m, 4H; CH_2), 3.99 (s, 6H; OCH_3), 4.14 (t, J=6.5 Hz, 8H; OCH_2), 4.33 (t, J=6.5 Hz, 4H; OCH_2), 7.20–7.21 (m, 2H; ArH), 7.23–7.24 (m, 1H; ArH), 7.25–7.26 (m, 1H; ArH), 7.44 (s, 4H; ArH), 7.86–7.87 (m, 4H; ArH), 7.99–8.00 (m, 2H; ArH), 8.42–8.43 (m, 2H; ArH), 8.96 (d, J=5.0 Hz, 4H; β-H), 9.73 ppm (d, J=5.0 Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=454 (410400), 612 (57800), 333 (27800), 525 nm (7600 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{124}H_{170}N_4O_8$: 1844.71; found: 1844.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{124}H_{170}N_4O_8$: C 80.74, H 9.29, N 3.04; found: C 80.39, H 9.26, N 2.69.

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10,20-bis-(hexyne)-porphyrin (**14**)*

The product was obtained in 63% yield (39 mg, 0.03 mmol). R_f=0.48 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −2.17 (br s, 2H; NH), 0.82–0.90 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 94H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 3.01 (t, J=7.4 Hz, 4H; CH_2), 4.11 (t, J=6.4 Hz, 8H; CH_2), 4.31 (t, J=6.4 Hz, 4H; CH_2), 7.39 (s, 4H; ArH), 8.89 (d, J=5.0 Hz, 4H; β-H), 9.56 ppm (d, J=5.0 Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=434 (399800), 580 (36600), 539 (16700), 680 (12200), 618 nm (7200 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{104}H_{158}N_4O_6$: 1560.40; found: 1560.2 (the isotope profiles matched).

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10,20-bis-(phenylethynyl)-porphyrin (**15**)*

The product was obtained in 85% yield (55 mg, 0.03 mmol). R_f=0.45 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −1.97 (br s, 2H; NH), 0.83–0.89 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90–1.92 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 4.13 (t, J=6.4 Hz, 8H; OCH_3), 4.32 (t, J=6.4 Hz, 4H; OCH_3), 7.41 (s, 4H; ArH), 7.48–7.54 (m, 2H; ArH), 7.56–7.60 (m, 4H; ArH), 8.00–8.06 (m, 4H; ArH), 8.95 (d, J=5.0 Hz, 4H; β-H), 9.68 ppm (d, J=5.0 Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=445 (334200), 600 (44300), 693 (20800), 287 (19500), 558 (8100), 518 nm (4631 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{108}H_{150}N_4O_6$: 1600.37; found: 1600.2 (the isotope profiles matched); elemental analysis calcd (%) for $C_{108}H_{150}N_4O_6$: C 81.05, H 9.45, N 3.50; found: C 81.33, H 9.49, N 3.38.

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10,20-bis-(4-trifluoromethylphenylethynyl)-porphyrin (**16**)*

The product was obtained in 72% yield (50 mg, 0.03 mmol). R_f=0.43 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −2.02 (br s, 2H; NH), 0.82–0.90 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 4.13 (t, J=6.4 Hz, 8H; OCH_2), 4.31 (t, J=6.4 Hz, 4H; OCH_2), 7.41 (s, 4H; ArH), 7.83 (d, J=8.5 Hz, 4H; ArH), 8.12 (d, J=8.5 Hz, 4H; ArH), 8.98 (d, J=5.0 Hz, 4H; β-H), 9.65 ppm (d, J=5.0 Hz, 4H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=454 (410400), 612 (57800), 701 (32600), 333 (27800), 525 nm (7600 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{110}H_{148}F_6N_4O_6$: 1736.37; found: 1736.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{110}H_{148}F_6N_4O_6$: C 76.09, H 8.59, N 3.23; found: C 75.81, H 8.56, N 3.04.

General Procedure for the Synthesis of TCBD-Porphyrins

TCNE (8.0 mg, 0.06 mmol) or TCNQ (13.0 mg, 0.06 mmol) were added to a solution of *trans*-A_2B_2-porphyrin (**1**–**10**, 0.03 mmol) in CH_2Cl_2 (3 mL) and the mixture was stirred at ambient temperature. Evaporation of solvent under reduced pressure followed by column chromatography on silica gel (hexanes/EtOAc, 95:5) and size-exclusion chromatography (toluene) afforded the product as a brownish solid.

*5,15-Bis-(3,4,5-trisundecyloxyphenyl)-10,20-bis-{(4-ethynyl-N,N-dimethylaniline)-1,3-diene-1,1,4,4-tetracarbonitrile)}-porphyrin (**20**)*

The product was obtained in 95% yield (58 mg, 0.03 mmol). R_f=0.32 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −2.10 (br s, 2H; NH), −2.01 ppm (br s, 2H; NH); UV/Vis (CCl_4): λ_{max} (ε)=433 nm (157300 $mol^{-1}dm^3cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{130}H_{172}N_{14}O_6$: 2026.91; found: 2027.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{130}H_{172}N_{14}O_6$: C 77.04, H 8.53, N 9.67; found: C 77.16, H 8.44, N 9.30.

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10-(4-methoxyphenylethynyl)-20-{(4-methoxyphenylethynyl)-1,3-diene-1,1,4,4-tetracarbonitrile)}-porphyrin (**21**)*

The product was obtained in 81% yield (43 mg, 0.02 mmol). R_f=0.39 (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): δ= −1.76 (br s, 2H; NH), 0.83–0.89 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 3.81 (s, 3H; OCH_3), 3.95 (s, 3H; OCH_3), 4.11 (t, J=6.4 Hz, 8H; OCH_2), 4.31 (t, J=6.4 Hz, 4H; OCH_2), 6.95 (d, J=8.5 Hz, 2H; ArH), 7.12 (d, J=8.5 Hz, 2H; ArH), 7.33 (s, 2H; ArH), 7.34 (s, 2H; ArH), 7.75 (d, J=8.5 Hz, 2H; ArH), 7.96 (d, J=8.5 Hz, 2H; ArH), 8.85 (d, J=5.0 Hz, 2H; β-H), 8.99 (d, J=4.5 Hz, 4H; β-H), 9.64 ppm (d, J=5.0 Hz, 2H; β-H); UV/Vis (CCl_4): λ_{max} (ε)=446 (249100), 347 (29900),

581 (17100), 688 nm (12100 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{116}H_{154}N_8O_8$: 1788.52; found: 1788.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{116}H_{154}N_8O_8$: C 77.90, H 8.68, N 6.26; found: C 77.86, H 8.57, N 6.17.

*5,15-Dimesityl-10-(4-methoxyphenylethynyl)-20-{(4-methoxyphenylethynyl)-1,3-diene-1,1,4,4-tetracarbonitrile)}-porphyrin (**22**)*

The product was obtained in 80% yield (22 mg, 0.02 mmol). $R_f = 0.40$ (hexanes/CH_2Cl_2, 2:3); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -1.64$ (br s, 2H; NH), 1.80 (s, 6H; CH_3), 1.90 (s, 6H; CH_3), 2.64 (s, 6H; CH_3), 3.67 (s, 3H; OCH_3), 3.94 (s, 3H; OCH_3), 6.73 (d, $J = 8.5$ Hz, 2H; ArH), 6.09 (d, $J = 8.5$ Hz, 2H; ArH), 7.28 (s, 2H; ArH), 7.31 (s, 2H; ArH), 7.50 (d, $J = 8.5$ Hz, 2H; ArH), 7.94 (d, $J = 8.5$ Hz, 2H; ArH), 8.65 (d, $J = 5.0$ Hz, 2H; β-H), 8.71 (d, $J = 4.5$ Hz, 2H; β-H), 8.93 (d, $J = 4.5$ Hz, 2H; β-H), 9.59 ppm (d, $J = 5.0$ Hz, 2H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 442 (165500), 580 (12600), 685 nm (9900 $mol^{-1} dm^3 cm^{-1}$); HRMS (FD): *m/z* calcd for $C_{62}H_{46}N_8O_2$: 934.3744; found: 934.3730 (the isotope profiles matched).

*5,15-Bis-(3,4,5-trisundecyloxyphenyl)-10-(2-ethynyl-6-methoxynaphthalene)-20-{(2-ethynyl-6-methoxynaphthalene)-1,3-diene-1,1,4,4-tetracarbonitrile)}-porphyrin (**23**)*

The product was obtained in 86% yield (51 mg, 0.03 mmol). $R_f = 0.41$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -1.81$ (br s, 2H; NH), 0.84–0.86 (m, 12H; CH_3), 0.87–0.91 (m, 6H; CH_3), 1.28–1.31 (m, 80H; CH_2), 1.35–1.40 (m, 12H; CH_2), 1.62–1.68 (m, 4H; CH_2), 1.85–1.91 (m, 8H; CH_2), 1.98–2.03 (m, 4H; CH_2), 3.86 (s, 3H; OCH_3), 3.97 (s, 3H; OCH_3), 4.13 (t, $J = 6.5$ Hz, 8H; CH_2), 4.32 (t, $J = 6.5$ Hz, 4H; CH_2), 7.01 (s, 1H; ArH), 7.13 (d, $J = 9.5$ Hz, 1H; ArH), 7.20 (d, $J = 9.5$ Hz, 1H; ArH), 7.25 (d, $J = 9.5$ Hz, 1H; ArH), 7.44 (s, 2H; ArH), 7.45 (s, 2H; ArH), 7.59 (d, $J = 9.0$ Hz, 2H; ArH), 7.65 (m, 2H; ArH), 7.89 (d, $J = 9.5$ Hz, 1H; ArH), 8.01 (d, $J = 9.5$ Hz, 1H; ArH), 8.18 (s, 1H; ArH), 8.45 (s, 1H; ArH), 8.92 (d, $J = 5.0$ Hz, 2H; β-H), 9.01 (d, $J = 5.0$ Hz, 2H; β-H), 9.04 (d, $J = 5.0$ Hz, 2H; β-H), 9.73 ppm (d, $J = 5.0$ Hz, 2H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 449 (189300), 585 (18000), 689 nm (11200 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{130}H_{170}N_8O_8$: 1972.80; found: 1972.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{130}H_{170}N_8O_8$: C 79.15, H 8.69, N 5.68; found: C 78.93, H 8.51, N 5.62.

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10-(phenylethynyl)-20-{(phenylethynyl)-1,3-diene-1,1,4,4-tetracarbonitrile)}-porphyrin (**24**)*

The product was obtained in 83% yield (43 mg, 0.02 mmol). $R_f = 0.39$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.05$ (br s, 2H; NH), 0.83–0.89 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 4.12 (t, $J = 6.4$ Hz, 8H; OCH_2), 4.32 (t, $J = 6.4$ Hz, 4H; OCH_2), 7.19–7.21 (m, 4H; ArH), 7.32–7.40 (m, 6H; ArH), 7.59–7.60 (m, 2H; ArH), 8.02–8.05 (m, 2H; ArH), 8.94 (d, $J = 5.0$ Hz, 2H; β-H), 9.01 (d, $J = 4.5$ Hz, 4H; β-H), 9.69 ppm (d, $J = 5.0$ Hz, 2H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 441 (221400), 579 (14400), 682 nm (8600 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{114}H_{150}N_8O_6$: 1728.52; found: 1728.0 (the isotope profiles matched); elemental analysis calcd (%) for $C_{114}H_{150}N_8O_6$: C 79.22, H 8.75, N 6.48; found: C 79.03, H 8.83, N 6.32.

*15-Bis-(3,4,5-trisdecyloxyphenyl)-10-(4-trifluoromethylphenylethynyl)-20-{(4-trifluoromethylphenylethynyl)-1,3-diene-1,1,4,4-tetracarbonitrile)}-porphyrin (**25**)*

The product was obtained in 98% yield (55 mg, 0.03 mmol). $R_f = 0.37$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.22$ (br s, 2H; NH), 0.83–0.89 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 4.12 (t, $J = 6.4$ Hz, 8H; OCH_2), 4.32 (t, $J = 6.4$ Hz, 4H; OCH_2), 7.11 (d, $J = 7.2$ Hz, 2H; ArH), 7.23 (d, $J = 7.2$ Hz, 2H; ArH), 7.35 (s, 2H; ArH), 7.37 (s, 2H; ArH), 7.85 (d, $J = 7.5$ Hz, 2H; ArH), 8.14 (d, $J = 8.5$ Hz, 2H; ArH), 8.89 (d, $J = 5.0$ Hz, 2H; β-H), 9.02 (d, $J = 4.5$ Hz, 4H; β-H), 9.68 ppm (d, $J = 5.0$ Hz, 2H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 440 (153700), 576 (12200), 527 (10400), 683 nm (6700 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{116}H_{148}F_6N_8O_6$: 1864.51; found: 1864.8 (the isotope profiles matched); elemental analysis calcd (%) for $C_{116}H_{148}F_6N_8O_6$: C 74.73, H 8.00, N 6.01; found: C 74.36, H 8.15, N 5.88.

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10-(4-ethynyl-N,N-dimethylaniline)-20-{(4-ethynyl-N,N-dimethylaniline)- 1,1-dicyano-3-[4-(dicyanomethylene)cyclohexa-2,5-dienylidene)}-porphyrin (**26**)*

The product was obtained in 36% yield (20 mg, 0.01 mmol). $R_f = 0.37$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -1.48$ (br s, 2H; NH), 0.83–0.89 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 2.94 (s, 3H; NCH_3), 3.13 (s, 3H; NCH_3), 4.10–4.12 (m, 8H; OCH_2), 4.30 (t, $J = 6.4$ Hz, 4H; OCH_2), 6.33 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 6.47 (d, $J = 9.0$ Hz, 2H; ArH), 6.84 (d, $J = 9.0$ Hz, 2H; ArH), 6.88 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.34 (s, 2H; ArH), 7.39 (s, 2H; ArH), 7.41 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.65 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.66 (d, $J = 9.0$ Hz, 2H; ArH), 7.88 (d, $J = 9.0$ Hz, 2H; ArH), 8.81–8.86 (m, 4H; ArH), 9.62 ppm (d, $J = 5.0$ Hz, 2H; ArH); UV/Vis (CCl_4): λ_{max} (ε) = 463 (127900), 603 (30800), 843 nm (1900 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{124}H_{164}N_{10}O_6$: 1890.69; found: 1890.4 (the isotope profiles matched).

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10-(4-methoxyphenylethynyl)-20-{(4-methoxyphenylethynyl)-1,1-dicyano-3-[4-(dicyanomethylene)cyclohexa-2,5-dienylidene)}-porphyrin (**27**)*

The product was obtained in 86% yield (48 mg, 0.03 mmol). $R_f = 0.39$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -1.98$ (br s, 2H; NH), 0.83–0.89 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 3.48 (s, 3H; OCH_3), 3.96 (s, 3H; OCH_3), 4.08 (t, $J = 6.4$ Hz, 4H; OCH_2), 4.14 (t, $J = 6.4$ Hz, 4H; OCH_2), 4.29 (t, $J = 6.4$ Hz, 4H; OCH_2), 6.48 (d, $J = 8.5$ Hz, 2H; ArH), 6.50 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 6.93 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.11 (d, $J = 8.5$ Hz, 2H; ArH), 7.31 (s, 2H; ArH), 7.39 (s, 2H; ArH), 7.49 (d, $J = 8.5$ Hz, 2H; ArH), 7.60 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.82 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.96 (d, $J = 8.5$ Hz, 2H; ArH), 8.81–8.84 (m, 2H; β-H), 8.87 (d, $J = 4.8$ Hz, 2H; β-H), 8.90 (d, $J = 4.8$ Hz, 2H; β-H), 9.63 ppm (d, $J = 5.0$ Hz, 2H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 451 (248000), 584 (30000), 822 nm (1600 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{122}H_{158}N_8O_8$: 1864.60; found: 1864.1 (the isotope profiles matched).

*5,15-Bis-(3,4,5-trisdecyloxyphenyl)-10-(phenylethynyl)-20-{(phenylethynyl)-1,1-dicyano-3-[4-(dicyanomethylene)cyclohexa-2,5-dienylidene)}-porphyrin (**28**)*

The product was obtained in 80% yield (43 mg, 0.02 mmol). $R_f = 0.40$ (hexanes/EtOAc, 95:5); ^{1}H NMR (500 MHz, $CDCl_3$, 25°C, TMS): $\delta = -2.18$ (br s, 2H; NH), 0.83–0.89 (m, 12H; CH_3), 0.92–0.98 (m, 6H; CH_3), 1.22–1.54 (m, 80H; CH_2), 1.69 (m, 4H; CH_2), 1.90 (m, 8H; CH_2), 2.00 (m, 4H; CH_2), 4.08 (t, $J = 6.4$ Hz, 4H; OCH_2), 4.15 (t, $J = 6.4$ Hz, 4H; OCH_2), 4.30 (t, $J = 6.4$ Hz, 4H; OCH_2), 6.55 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 6.94 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.31 (s, 2H; ArH), 7.32–7.40 (m, 6H; ArH), 7.41 (s, 2H; ArH), 7.59–7.60 (m, 2H; ArH), 7.66 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 7.93 (dd, $J = 1.8$, 7.8 Hz, 1H; CH), 8.02–8.05 (m, 2H; ArH), 8.70–8.88 (m, $J = 4.8$ Hz, 2H; β-H), 8.89–8.98 (m, 4H; β-H), 9.67 ppm (d, $J = 5.0$ Hz, 2H; β-H); UV/Vis (CCl_4): λ_{max} (ε) = 447 (226000), 578 (26000), 780 nm (1000 $mol^{-1} dm^3 cm^{-1}$); LRMS (FD): *m/z* calcd for $C_{120}H_{154}N_8O_6$: 1804.55; found: 1804.0 (the isotope profiles matched).

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