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An efficient route to biscardanol derivatives and cardanol-based porphyrins via olefin metathesis

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Abstract

Ru-catalyzed olefin metathesis has been successfully applied to the synthesis of biscardanol derivatives and cardanol-based porphyrins. Using Hoveyda–Grubbs catalyst (**C627**), the reactions were performed with various cardanol derivatives (**2**, **5**, **7**, and **9**) to make novel biscardanol derivatives. With the use of the second-generation Grubbs catalyst (**C848**) and $Ti(O^iPr)_4$, the ring-closing metathesis of cardanol-based porphyrin **11** was carried out to afford cyclic cardanol-based porphyrin derivative **12**.

Keywords: Cardanol; Olefin metathesis; Porphyrins

1. Introduction

Olefin metathesis reactions have become powerful tools to achieve molecular complexity in an elegant way [1]. Since the development of well-defined single component molybdenum and ruthenium carbene catalysts, the olefin metathesis has already commercially utilized in the processing of fine chemicals. For instance, with the use of Grubbs ruthenium-based catalyst olefin metathesis enables vegetable oils to be efficiently processed into compounds that can serve as renewable sources of petroleum product alternatives [2]. The solvent-free cross-metathesis of 1-hexene with hexenyl acetate represents another example of the use of metathesis to generate the precursor of a pheromone of the peach twig borer moth [3]. Encouraged by these studies and as a part of our research program aimed at boarding the scope of olefin metathesis [4], we became interested in devising a practical and concise route to novel compounds that possessed interesting structures or physical properties or potential applications, from inexpensive starting materials and/or renewable resources.

Cardanol is a unique natural source for unsaturated long-chain phenols. It is a cheap and renewable material, obtained by vacuum distillation of cashew nut shell liquid (CNSL) [5]. Interest in cardanol derivatives has grown over the last few years due to their potential use in resins, friction lining materials, surface coatings, and organic synthesis [6]. More recent work has focused on molecular hybrid systems, in which cardanol is involved [7]. Furthermore, other molecular hybrid systems such as porphyrin-containing rotaxanes [8], "magic" ring rotaxanes and catenanes [9], and align conjugated polymers [10] have received much attention because of their unique molecular structures. Accordingly, we design biscardanol derivatives and cardanol-based porphyrins for their large size, extended π-system and possible metal ion binding ability. Herein we report the

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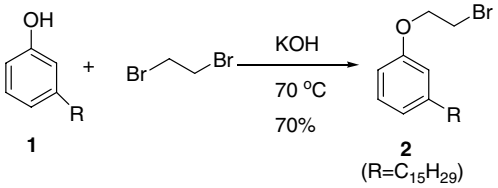
synthesis of these compounds by using olefin metathesis protocols.

2. Results and discussion

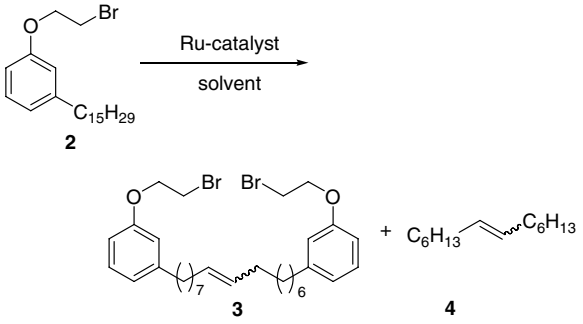
Cardanol, the main component of CNSL, is a mixture of 3-*n*-pentadecyl phenol, 3-(pentadeca-8-enyl) phenol (85%), 3-(pentadeca-8,11-dienyl) phenol, and 3-(pentadeca-8,11,14-trienyl) phenol (Fig. 1). In this work cardanol is referred to the monoolefinic component.

Actually, cardanol is rather difficult to purify, and it has to be run on a few columns to get the monoolefinic component. Thus, we converted it to compound **2** via the reaction with 1,2-dibromoethane in the presence of KOH at 70 °C (Eq. (1)), which is much easier to separate from others, for further study.



1 **2** ($R=C_{15}H_{29}$) (1)

Metathesis catalysts (Scheme 1) were initially screened in the homo-cross-metathesis (HCM) reaction of cardanol derivative **2** (Eq. (2)). For convenience, these catalysts are identified by their molecular weights.



2 (2)

3 **4**

The catalyst screening indicated that the HCM reaction of **2** did work in the presence of Ru-based catalysts at 40 °C in dichloromethane (Table 1); however, small variations in Ru carbene catalysts (**C627**, **C823**, **C801**, **C848**) resulted in varying yields of the product. Among the catalysts examined, Hoveyda–Grubbs second generation catalyst (**C627**) and Grubbs second generation catalyst (**C848**) exhibited good catalytic activities to afford the HCM product **3** (entries 1 and 4 in Table 1). In particular, the use of 2 mol% **C627** was the most effective catalyst for the formation of **3** in 60% isolated yield (entry 1 in Table 1). Other Grubbs catalysts, such as **C823** (entry 2 in Table 1) and **C801** (entry 3 in Table 1), were less effective for this transformation. Thus, **C627** was chosen as the catalyst for other optimizations. Increasing the catalyst loading from 2 to 5 mol% did not change the reaction efficiency (entry 6 in Table 1), while decreasing the catalyst loading from 2 to 1 mol% reduced the yield of the product **3** (entry 5 in Table 1). We ran the reaction in different solvents (1,2-dichloroethane, chloroform, and chlorobenzene) at higher temperature; however, the efficiency of the reaction did not improve (entries 7–9 in Table 1). The conversion of the substrate **2** could not reach 100% in all cases, which should attribute to the reaction's reversibility [11]. In order to improve the conversion, we tried to remove the second product **4** by bubbling N_2 inside the reaction mixture at 132 °C in chlorobenzene; however, the starting material **2** was recovered in 90–95% yield after 64 h and the catalyst decomposition was observed (entry 8 in Table 1). We did not rigorously examine the effect of the concentration of the substrate on the reaction; however, we found that the reaction gave poor yields when the concentration reduced to 0.1 and 0.5 mol/L.

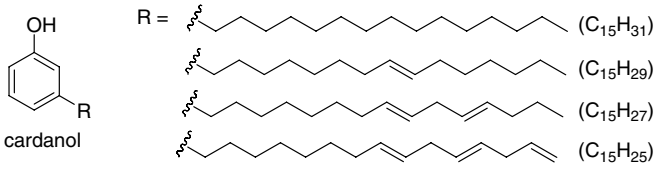
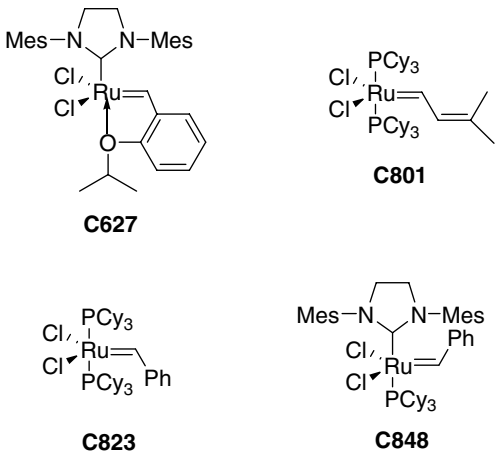


Fig. 1. The structure and composition of cardanol.



Scheme 1. Ruthenium catalysts investigated.

The optimized conditions were then successfully employed in the synthesis of novel biscardanol derivatives. The HCM reactions of cardanol and its derivatives were performed using 2 mol% **C627** in dichloromethane at 40 °C for 45–87 h, and the results are summarized in Table 2.

As can be seen from Table 2, the HCM reaction reactions of cardanol and three of its derivatives worked very well under the optimized conditions. The reaction afforded the corresponding biscardanol derivatives in moderate isolated yields. All products were formed as a mixture of *E*- and *Z*-isomers, in which *E*-isomers were dominant.

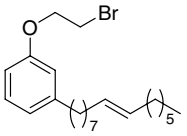
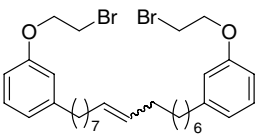
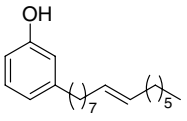
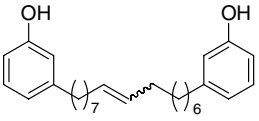
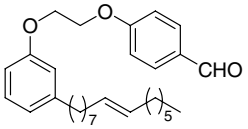
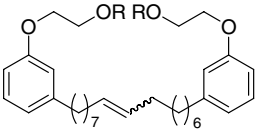
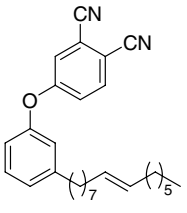
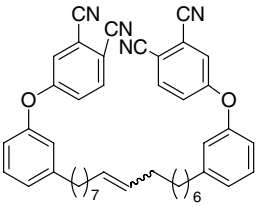
Porphyrins and metalloporphyrins are important materials which can be used as gas sensors, photocatalysts, and so on [12]. However, porphyrin and its derivative do not have good solubility in organic solvents. We believe

Table 1
Ru-catalyzed HCM reaction of **2**[a]

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion[b] (%)	Yield[c] (%)
1	**C627** (2 mol%)	CH_2Cl_2	40	64	86	60
2	**C823** (2 mol%)	CH_2Cl_2	40	64	47	32
3	**C801** (2 mol%)	CH_2Cl_2	40	64	30	16
4	**C848** (2 mol%)	CH_2Cl_2	40	64	54	44
5	**C627** (1 mol%)	CH_2Cl_2	40	64	74	41
6	**C627** (5 mol%)	CH_2Cl_2	40	48	84	60
7	**C627** (2 mol%)	$CHCL_3$	60	64	57	44
8	**C627** (2 mol%)	PhCl	132	64	5	0
9	**C627** (2 mol%)	DCE[d]	80	64	50	40

[a] Reaction conditions: substrate **2** (1.67 mol/L), catalyst (1–5 mol% to **2**), Ch_2Cl_2 (1.2 mL), N_2 atmosphere.
[b] Calculated on the base of the amount of recovered substrate.
[c] Isolated yields.
[d] 1,2-Dichloroethane.

Table 2
The synthesis of biscardanol derivatives via olefine methathesis[a]

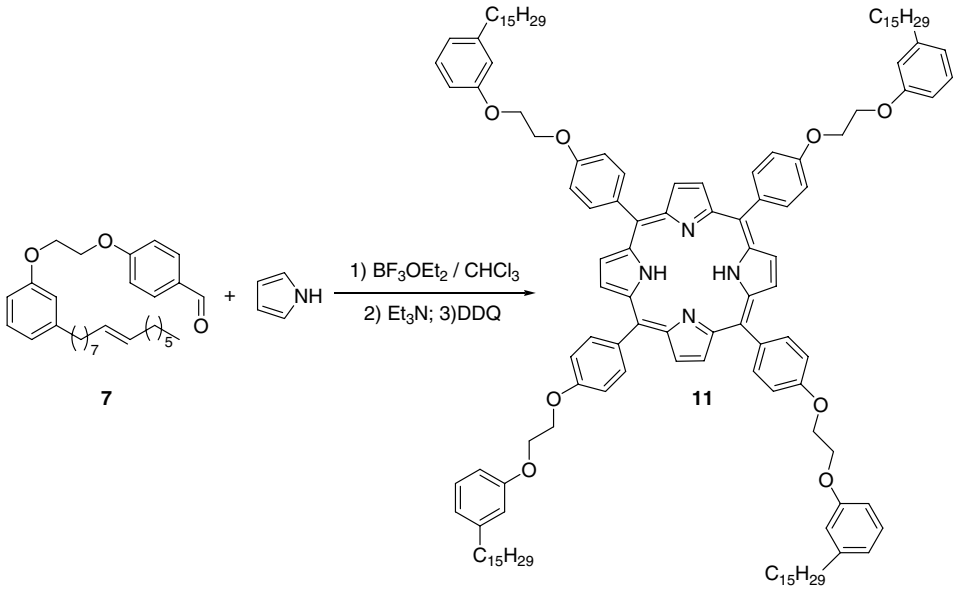
Entry	Substrate	Product	Time (h)	Yield[b] (%)
1	 **2**	 **3**	64	60
2	 **5**	 **6**	72	56
3	 **7**	 **8** R = 4-formylphenyl	45	42
4	 **9**	 **10**	87	65

[a] Reaction conditions: substrate (2.0 mmol), catalyst **C627** (2 mol% based on the substrate), dichloromethane (1.2 mL), 40 °C.
[b] Isolated yields.

that the long chain of the cardanol should improve the solubility of porphyrins and metalloporphyrins. Thus, the cardanol-based porphyrin was designed and obtained successfully by reaction of cardanol derivative **7** with pyrrole, as shown in Scheme 2.

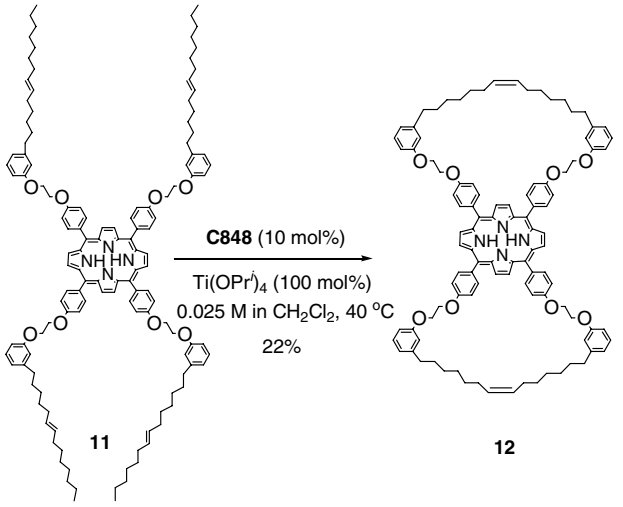
Cardanol derivative **7** reacted with pyrrole in the presence of catalytic amounts of $BF_3 \cdot OEt_2$ at room temperature for 30 h using chloroform as the solvent. The subsequent oxidation in situ with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at room temperature for 64 h afforded cardanol-based porphyrin **11** in 14% overall yield.

Subsequently, ring-closing metathesis (RCM) of **11** was tested in order to get more complex porphyrins. Treatment of **11** with **C848** under dilute conditions did not give the corresponding RCM product. We believe that the strong coordination function of porphyrins plays a crucial role in this RCM reaction and the coordination between the porphyrins and a ruthenium species may turn down the



Scheme 2. The synthesis of cardanol-based porphyin **11**.

expected RCM reaction of **11** [13]. According to our previous finding [4], we may be able to resolve this problem by adding certain amount of $Ti(OPr^i)_4$ to the reaction system [14]. Thus, in the solution of porphyrin **11** in dichloromethane, $Ti(OPr^i)_4$ and the Grubbs' catalyst **C848** were added and the solution then refluxed for 64 h. As expected, the reaction occurred and the RCM product were formed in 22% isolated yield (Eq. (3)).



(3)

NMR and MS spectra of **12** was consistent with the proposed structure. Indeed, ^1H NMR spectrum of **13** shows the disappearing of the signal corresponding to methyl group at 0.9 ppm. LC–MS data also confirmed the proposed structures. The mass spectrum of **12** exhibits a signal at m/z 1602 $[M + H]^+$ and 801 (Fig. 2).

3. Conclusion

We have presented a novel procedure to synthesize biscardanol derivatives and cardanol-based porphyrins starting from a cheap and renewable starting material through a home-cross-metathesis and ring-closing metathesis reactions using Grubbs' catalysts. This methodology provides a versatile approach for the efficient synthesis of various molecular hybrid systems. Further studies will be focused on the synthesis of structurally more complex porphyrin derivatives and examine their physical and chemical properties.

4. Experimental

4.1. General

All the starting materials were purchased from Aldrich Chemical Co and used as received. Stabilcardo, a distilled technical grade cardanol provided by Oltremare S.P.A. (Bologna, Italy), has been used as a base compound in this study. Silica gel (Merck) was used in the chromatographic separations. Solvents were dried and distilled under an atmosphere of dry nitrogen. Melting points were taken on an electro thermal apparatus. FT-IR spectra were recorded on a JASCO FT-IR 660 *Plus* spectrometer. UV–Vis spectra were recorded on a Cary 100 scan UV–Vis spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 at room temperature and chemical shifts are reported relative to tetramethylsilane.

Mass spectrum was recorded by using a LC mass spectrometer 1100 Series (Agilent) equipped with an Electrospray (ESI) interface. Ions were extracted via a heated capillary to a skimmer lens arrangement at reduced pressure and transferred by an octapole to the main analytical quadrupole assembly. The instrumental conditions were as follow: drying gas (nitrogen) 7 L/min, nebulizer pressure 60 psi, drying gas temperature 300 °C, capillary voltage 4000 V, mass range 500–3000 amu.

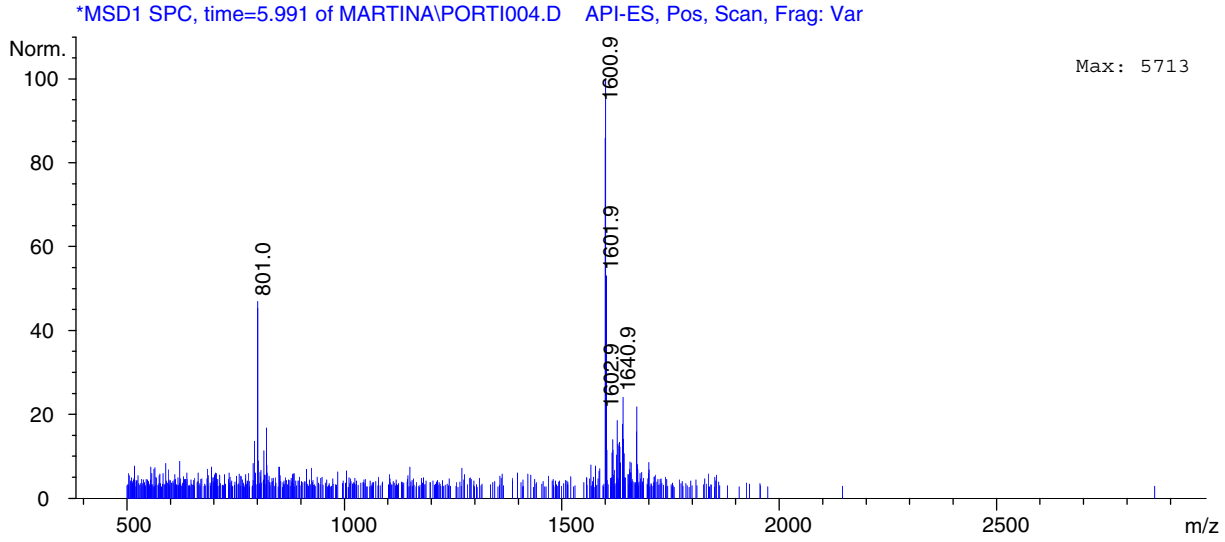


Fig. 2. Mass spectrum of **12**.

*4.2. 1-(2-Bromo-ethoxy)-3-(pentadeca-8-enyl)-benzene (**2**)*

To the solution of 3-(pentadeca-8-enyl)-phenol **1** (4.00 g, 13.25 mmol) in 1,2-dibromoethane (15 mL), potassium hydroxide (1.15 g, 20.49 mmol) were added. The mixture was stirred at 70 °C for 6 h. The mixture was then cooled to room temperature and filtered to remove the by product, NaBr. The filtration was concentrated at a reduced pressure, and then purified by silica gel chromatography (petroleum ether (40–60 °C) first, then diethyl ether/petroleum ether: 3/7) affording compound **2** as colourless liquid (3.77 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.89 (t, 3H, $J = 6.8$ Hz), 1.25–1.39 (m, 16H), 1.58 (q, 2H, $J = 7.6$ Hz), 2.00 (q, 4H, $J = 7.0$ Hz), 2.57 (t, 2H, $J = 7.6$ Hz), 3.62 (t, 2H, $J = 6.3$ Hz), 4.27 (t, 2H, $J = 6.3$ Hz), 5.33–5.39 (m, 2H), 6.70 (s, 1H), 6.73 (d, 1H, $J = 5.2$ Hz), 6.80 (d, 1H, $J = 7.6$ Hz), 7.18 (t, 1H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.1, 22.7, 22.8, 25.6, 27.20 (CH_2), 29.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.33 (CH_2), 31.8, 36.0, 67.7, 111.6, 115.0, 121.6, 129.2, 129.8, 129.9, 144.8, 158.1. FTIR (neat, υ/cm^{-1}): 2925, 2854,1662, 1599, 1588, 1484, 1456,1386, 1258, 1154, 1063, 947, 913, 873. MS (EI, 70 eV): m/z (%) 408 [M$^+$]. Anal. Calc. for $C_{23}H_{37}BrO$: C, 67.48; H, 9.05. Found: C, 67.49; H, 9.06%.

*4.3. 1,16-Bis(3-(2-bromoethoxy)phenyl)-hexadec-8-ene (**3**)*

C627 (25.10 mg, 0.04 mmol) was added under N_2 atmosphere to a stirred solution of **2** (818.0 mg, 2 mmol) in 1.2 mL of dichloromethane. The light green solution which were stirred at reflux for 64 h. The mixture was then concentrated in vacuo to a dark brown oil. The crude material was purified by silica gel chromatography (ethyl acetate/petroleum ether: 1/100) to afford compound **3** as a white solid (342.5 mg, 60%). Mp 48–49 °C. FTIR (neat), ν/cm^{-1}: 3010, 2922, 2851, 1602, 1584, 1485, 1463, 1377, 1257, 1218, 1078, 1040, 967,911 cm^{-1}; ^{1}H NMR (400 MHz,$CDCl_3$, ppm): δ 1.26–1.30 (m, 16H), 1.63–1.66 (m, 4H),1.95–1.96 (m, 4H), 2.57 (t, 4H, $J = 8.0$ Hz), 3.63 (t, 4H, $J = 6.0$ Hz), 4.28 (t, 4H, $J = 6.0$ Hz), 5.38 (t, $J = 2.8$ Hz), 6.72 (d, 2H, $J = 8.0$ Hz), 6.74 (s, 2H), 6.80 (d, 2H, $J = 7.6$ Hz), 7.19 (t, 2H, $J = 7.6$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$,ppm): δ: 29.0, 29.2, 29.3, 29.3, 29.6, 31.3, 32.6, 35.9, 67.7, 111.5, 115.0, 121.6, 129.2, 130.3, 144.7, 158.1. MS (EI, 70 eV): m/z (%): 623 [M + 1]$^+$. Anal. Calc. for $C_{32}H_{46}O_2Br_2$: C, 61.76; H, 7.40. Found: C, 61.88; H, 7.52%.

*4.4. 3,3′-(Hexadec-8-ene-1,16-diyl)diphenol (**6**)*

C627 (25.10 mg, 0.04 mmol) was added under N_2 atmosphere to a solution of **1** (605.0, 2 mmol) in 1.2 mL of dichloromethane with stirring, producing a light green solution which were stirred at reflux for 72 h. The mixture was then concentrated in vacuo to a dark brown oil. The crude material was purified by silica gel chromatography (ethyl acetate/petroleum ether: 1/100) affords compound **6** as a brown oil (264.6 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.26–1.30 (m, 16H), 1.57–1.60 (m, 4H), 1.95–1.96 (m, 4H), 2.54 (t, 4H, $J = 7.8$ Hz), 4.80 (s, 2H), 5.36–5.40 (m, 2H), 6.63 (d, 2H, $J = 7.8$ Hz), 6.65 (s, 2H), 6.75 (d, 2H, $J = 7.8$ Hz), 7.13 (t, 2H, $J = 7.6$ Hz). ^{13}CNMR (100 MHz, $CDCl_3$, ppm): δ 29.0, 29.2, 29.3, 29.6, 31.2, 32.5, 35.8, 112.5, 115.3, 120.9, 129.3, 130.3, 144.9, 155.3. FTIR (neat), ν/cm^{-1}: 3336, 3020, 2924, 2852, 1714, 1611, 1588, 1487, 1455, 1262, 1220, 1154, 1073, 1000, 944, 874 cm^{-1}. MS (EI, 70 eV): m/z (%) = 407 [M$^+$ − 1]. Anal. Calc. for $C_{28}H_{40}O_2$: C, 82.35; H, 9.80. Found: C, 82.28; H, 9.72%.

4.5. 4-[2-(3-(Pentadeca-8-enyl)phenoxy)-ethoxy]-benzaldehyde (7)

To the solution of **2** (3.00 g, 7.33 mmol) in acetone (15 mL), 4-hydroxy benzaldehyde (1.33 g, 10.90 mmol) and anhydrous potassium carbonate (3.04 g, 22.03 mmol) were added. The mixture was refluxing with stirring for 30 h and then cooled to room temperature. The mixture was then concentrated in vacuo to a dark brown oil. The crude material was purified by silica gel chromatography (diethyl ether/petroleum ether: 3/7) to give compound **7** as a white solid (1.32 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.89 (t, 3H, $J = 6.8$ Hz), 1.26–1.39 (m, 16H), 1.57–1.60 (m, 2H), 2.00–2.02 (m, 4H), 2.58 (t, 2H, $J = 7.6$ Hz), 4.36 (t, 2H, $J = 7.6$ Hz), 4.41 (t, 2H, $J = 7.6$ Hz), 5.34–5.36 (m, 2H), 6.76–6.82 (m, 3H), 7.06 (d, 1H, $J = 8.8$ Hz), 7.21 (t, 1H, $J = 8.0$ Hz), 7.85 (d, 2H, $J = 8.8$ Hz), 9.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 14.5, 23.1, 27.6, 28.9, 29.4, 30.0, 30.1, 31.9, 32.2, 36.4, 66.5, 67.3, 111.9, 115.1, 121.9, 129.7, 130.2, 130.38 (C=), 130.6, 132.4, 145.2, 158.9, 164.1, 191.2. FTIR (neat), ν/cm^{-1}: 2925, 2853, 2737, 1696, 1601, 1579, 1486, 1449, 1376, 1312, 1251, 1158, 1110, 1066, 946, 913, 832. MS (EI, 70 eV): m/z (%) = 448 [M$^+$]. Anal. Calc. for $C_{30}H_{42}O_3$: C, 80.18; H, 9.35. Found: C, 80.19; H, 9.36%.

4.6. 4,4′-(2,2′-(3,3′-(Hexadec-8-ene-1,16-diyl)bis(3,1-phenylene))bis(oxy)bis(ethane-2,1-diyl))bis(oxy)dibenzaldehyde (8)

C627 (15.60 mg, 0.025 mmol) was added under N_2 atmosphere to a solution of **7** (559.7 mg, 1.2 mmol) in 6 mL of dichloromethane, producing a light green solution which were stirred at reflux for 45 h. The mixture was then concentrated in vacuo to a dark brown oil. The crude material was purified by silica gel chromatography (dichloromethane) affords compound **8** as a white solid (183.9 mg, 42%). Mp 69–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29–1.31 (m, 16H), 1.58–1.61 (m, 4H), 1.96–2.01 (m, 4H), 2.57 (t, 4H, $J = 8.0$ Hz), 4.34 (t, 4H, $J = 4.8$ Hz), 4.41 (t, 4H, $J = 4.8$ Hz), 5.38 (t, 2H, $J = 3.2$ Hz), 6.76 (d, 2H, $J = 8.0$ Hz), 6.78 (s, 2H), 6.81 (d, 2H), 7.04 (d, 2H, $J = 8.0$ Hz), 7.19 (t, 2H, $J = 8.4$ Hz), 7.83 (d, 2H, $J = 8.4$ Hz), 9.88 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.1, 29.2, 29.3, 29.6, 31.3, 32.5, 35.9, 66.0, 66.8, 111.4, 114.8, 121.4, 129.2, 129.8, 130.1, 130.3, 131.9, 144.7, 158.4, 163.6, 190.7. FTIR (neat), ν/cm^{-1}: 2992, 2919, 2848, 1770, 1759, 1680, 1605, 1509, 1454, 1376, 1307, 1275, 1246, 1167, 1065, 962, 929, 858, 837 cm^{-1}. MS (EI, 70 eV): m/z (%) = 705 [M+1]$^+$. Anal. Calc. for $C_{46}H_{56}O_6$: C, 78.41; H, 7.95. Found: C, 78.18; H, 7.72%.

4.7. 4-[3-(Pentadeca-8-enyl)-phenoxy]-phthalonitrile (9)

Finely ground anhydrous K_2CO_3 (5.5 g, 0.04 mol) were added gradually (1.1 g at intervals of 0.5–1 h) under N_2 atmosphere to a stirred solution of **1** (9.06 g, 0.03 mol) and 4-nitrophthalonitrile (5.2 g, 0.03 mol) in dry DMSO (170 mL). The reaction mixture was stirred and after 1 day it was filtered, added to 100 mL of water, extracted with CH_2Cl_2 and dried on anhydrous sodium sulfate. The crude product of the reaction, obtained after evaporation of the solvent, was further purified by silica gel chromatography (ethyl acetate/petroleum ether: 1/5) to give compound **9** as a yellow liquid (4.42 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, $J = 7.5$ Hz, 3H), 1.37–1.27 (m, 22H), 1.64 (q, $J = 7.2$ Hz, 2H), 2.04 (q, $J = 7.2$ Hz, 4H), 2.65 (t, 2H, $J = 7.6$ Hz), 5.38–5.35 (m, 2H), 6.90 (s, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.24 (d, $J = 6.5$ Hz, 1H), 7.26 (d, 1H), 7.28 (s, 1H), 7.38 (t, 1H), 7.73 (d, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 23.1, 27.6, 27.6, 29.4, 29.6, 29.7, 30.1, 31.6, 32.2, 109.0, 115.4, 115.9, 118.1, 120.9, 121.8, 125.7, 130.2, 130.4, 130.8, 135.8, 146.7, 153.9, 162.4. FTIR (neat), ν/cm^{-1}: 2925, 2854, 1599, 1580, 1564, 1483, 1444, 1310, 1280, 1248, 1166, 1138, 1087, 963, 879 cm^{-1}. MS (EI, 70 eV): m/z (%) = 429 [M + 1]$^+$. Anal. Calc. for $C_{29}H_{36}N_2O$: C, 81.31; H, 8.41. Found: C, 81.32; H, 8.42%.

4.8. 4,4′-(3,3′-(Hexadec-8-ene-1,16-diyl)bis(3,1-phenylene))bis(oxy)diphthalonitrile (10)

C627 (22.80 mg, 0.036 mmol) was added under N_2 atmosphere to a stirred solution of **9** (779.0 mg, 1.8 mmol) in dichloromethane (4 mL), producing a light green solution which were stirred at reflux for 87 h. The mixture was then concentrated in vacuo to a dark brown oil. The crude material was purified by silica gel chromatography (methylene chloride) to afford compound **10** as a brown oil (390.4 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26–1.31 (m, 16H), 1.60–1.62 (m, 4H), 1.95–1.96 (m, 4H), 2.63 (t, 4H, $J = 7.6$ Hz), 5.38 (t, $J = 3.8$ Hz, 2H), 6.88 (s, 2H), 7.12 (d, 2H, $J = 7.6$ Hz), 7.25 (d, 2H, $J = 8.0$ Hz), 7.36 (d, 2H, $J = 8.0$ Hz), 7.38 (s, 2H), 7.40 (t, 2H, $J =$ 8.4 Hz), 7.73 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 29.0, 29.0, 29.3, 30.9, 32.3, 35.5, 108.3, 114.8, 115.3, 117.2, 117.5, 120.2, 121.2, 126.1, 130.1, 130.1, 135.2, 145.97 (2C, Ar), 153.3, 161.7. FTIR (neat), ν/cm^{-1}: 3019, 2923, 2851, 1599, 1580, 1563, 1483, 1444, 1421, 1310, 1289, 1249, 1219, 1087, 964, 878, 836 cm^{-1}. MS (EI, 70 eV): m/z (%) = 661 [M + 1]$^+$. Anal. Calc. for $C_{44}H_{44}N_4O_2$: C, 80.00; H, 6.67. Found: C, 80.28; H, 6.72%.

4.9. 5,10,15,20-Tetra-[4-(2-(3-pentadec-8-enyl)phenoxy)ethoxy]phenylporphyrin (11)

Aldehyde **7** (220.0 mg, 0.486 mmol) and pyrrole (32.6 mg, 0.486 mmol) in chloroform (60 mL) were stirred at room temperature for 10 min and then $BF_3 \cdot OEt_2$ (23.0 mg, 0.162 mmol) solution was added. The reaction mixture was stirred at room temperature for 30 h, then triethylamine (21 mg, 0.208 mmol) were added. After 30 min DDQ was added and the reaction mixture was stirred for

64 h. The solvent was removed under vacuum and the crude was purified by silica gel chromatography (methylene chloride) affording compound **11** as a brownish solid (135.5 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.76 (br s, 2H), 0.86 (t, 12H, $J = 7.0$ Hz), 1.26–1.34 (m, 88H), 1.65–1.67 (m, 8H), 2.02–2.04 (m, 16H), 2.64 (t, 8H, $J = 7.6$ Hz), 4.53 (t, 8H, $J = 4.6$ Hz), 4.63 (t, 8H, $J = 4.6$ Hz) 5.34–5.37 (m, 8H), 6.85–6.92 (m, 12H), 7.28 (t, 4H, $J = 7.8$ Hz), 7.34 (d, 8H, $J = 8.8$ Hz), 8.13 (d, 8H, $J = 8.2$ Hz), 8.87 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 23.1, 27.6, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 30.2, 31.8, 32.2, 36.5, 66.9, 67.3, 112.1, 113.3, 115.5, 119.6, 121.8, 129.7, 130.3, 130.4, 130.4, 130.6, 135.4, 135.6, 136.0, 145.2, 158.9, 159.2. FTIR (neat), ν/cm^{-1}: 3318, 3006, 2925, 2853, 1606, 1582, 1508, 1448, 1351, 1262, 1175, 1108, 1067, 1015, 931, 895. UV–Vis (CH_2Cl_2), nm, ($\log\varepsilon$/M^{-1} cm^{-1}): 409, 518, 556, 593, 649. MS (ESI) m/z: 1990 $(M + H)^+$, 995 $(M + H)^{2+}$ amu. Anal. Calc. for $C_{136}H_{174}N_4O_8$: C, 82.01; H, 8.74; N, 2.81. Found: C, 82.32; H, 8.76; N, 2.93%.

4.10. Synthesis of compound *12*

Compound **11** (64 mg, 0.032 mmol) was dissolved in dichloromethane (20 mL). Then, 10 μL of $Ti(O^iPr)_4$ (1 equiv, 0.032 mmol) was added and the solution was refluxing. After 1 h a solution of **C848** (0.6 mg in 1.5 mL of CH_2Cl_2, 0.02 equiv) was added and the resulting mixture was stirred for 44 h. The progress of the reaction was monitored by TLC analysis until the complete disappearance of **11**. The mixture was cooled to room temperature and concentrated in vacuum. The crude product was purified by silica gel chromatography (methylene chloride) to give product **12** as a brownish solid (15.4 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.73 (br s, 2H), 1.36–1.28 (m, 32H), 1.65 (m, 8H), 2.07–1.99 (m, 8H), 2.66 (t, 8H), 4.36–4.42 (m, 8H), 4.65–4.73 (m, 8H), 5.42–5.38 (m, 4H), 6.97–6.84 (m, 12H), 7.30–7.33 (m, 4H), 7.36–7.42 (m, 8H), 8.15–8.30 (m, 8H), 8.89 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 145.3, 135.6, 135.4, 131.3, 130.6, 130.4, 130.3, 129.7, 121.9, 119.0, 114.8, 112.3, 112.7, 111.7, 67.1, 36.5, 33.6, 32.2, 30.1, 29.8, 29.5, 22.8. FTIR (neat), ν/cm^{-1}: 3461, 3006, 2984, 2909, 1740, 1465, 1447, 1372, 1233, 1097, 1047, 938, 918, 847. UV–Vis (CH_2Cl_2) λ_{max}, nm, ($\log\varepsilon$/M^{-1} cm^{-1}): 420, 516, 552, 593, 650. MS (ESI) m/z: 1601 $(M + H)^+$, 801 $(M + H)^{2+}$ amu. Anal. Calc. for $C_{108}H_{146}N_4O_8$: C, 81.00; H, 9.12; N, 3.50. Found: C, 81.22; H, 9.21; N, 3.48%.

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