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Synthesis of new crosslinkable co-polymers containing a push–pull zinc porphyrin for non-linear optical applications

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Abstract—In this paper, the synthesis of a crosslinkable co-polymer containing new push–pull arylethynyl zinc porphyrins is described. The synthesis of porphyrin chromophores, analogous to Therien's porphyrin (*J. Am. Chem. Soc.* **1996**, *118*, 1497–1503) functionalized with a methacrylic polymerizable group and a carboxylic acid crosslinking group was achieved with a new synthetic procedure leading to a higher overall yield compared to what was previously reported in the literature for similar and simpler structures. Radical copolymerization of the porphyrin chromophore with glycidyl methacrylate has then been carried out with success. This work opens a perspective on the possibility to integrate porphyrinic chromophore with high first-order molecular quadratic hyperpolarizability coefficient in opto-electronic devices.

1. Introduction

The increasing need of optoelectronic devices for telecommunications, optical switching and information storage has led to a tremendous research activity in the area of non-linear optic (NLO) materials.[1,2] Amongst the wide range of NLO chromophores investigated in the last 15 years, organometallic and coordination compounds probably appear as the most promising.[3–6] Therien and co-workers have reported a push–pull arylethynyl porphyrin chromophore with exceptional first-order molecular quadratic hyperpolarizability coefficient (β).[7–9] The presence of zinc inside the porphyrin core appears to be essential to guarantee high β value, as demonstrated by other studies on push–pull nickel or copper porphyrins.[10–12] However, to consider practical applications, the active NLO chromophores must be inserted in a matrix to be subsequently cast into films. Polymeric materials are, by far, the most convenient matrix used to host NLO chromophores for the development of materials exhibiting macroscopic electro-optic properties.[1,2] Besides this, long-term stability of the macroscopic electro-optic activity of the material is of a high importance for its future commercial development.[13,14] Increasing stability of the nonlinear response consists in limiting the relaxation of the field-induced orientation of the chromophores in the matrix. This is generally achieved by two strategies. The first one consists in grafting the chromophore into a polymeric matrix of high glass-transition temperature. Many examples using polyimide matrices have proved the efficiency of such approach.[1,2,15] Its main drawback stems from the need to perform the poling process at high temperature, which can cause partial thermal decomposition of the chromophores. A less severe approach consists in locking the chromophore orientation after the poling process by a crosslinking reaction. Some recent examples using different crosslinkable strategies have been reported and have fully demonstrated the validity of such an approach.[1,2,16–20] More particularly, a cross-linking reaction based on the opening of an epoxy group by a carboxylic acid carried by the chromophore proved to be quite efficient to lock the chromophores orientation after poling.[21–23]

In spite of its numerous qualities (large β value and high thermal stability), Therien's chromophore has never been, up to now, covalently integrated into a polymeric material. Herein, we report on a new synthetic strategy to prepare gram-scale of new push–pull porphyrins and their successful copolymerization with glycidyl methacrylate (GMA). The introduction of a methacrylate group and a carboxylic

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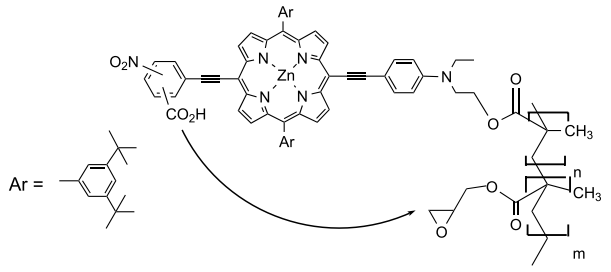


Figure 1. Structures of the electro-optic materials described in this study.

acid group on the porphyrins makes it possible to copolymerize them with GMA and to produce a material that could be subsequently thermally crosslinked after poling (Fig. 1).

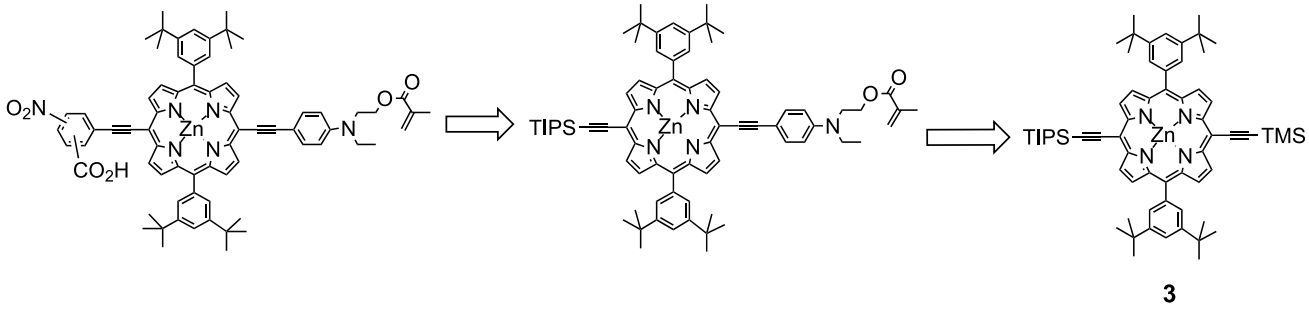
2. Results and discussion

The synthesis of the donor–acceptor porphyrins was performed using a new converging approach, which differs from the procedures originally described by Therien[7] and later used by Plater[24] for the preparation of other arylethynyl porphyrins.

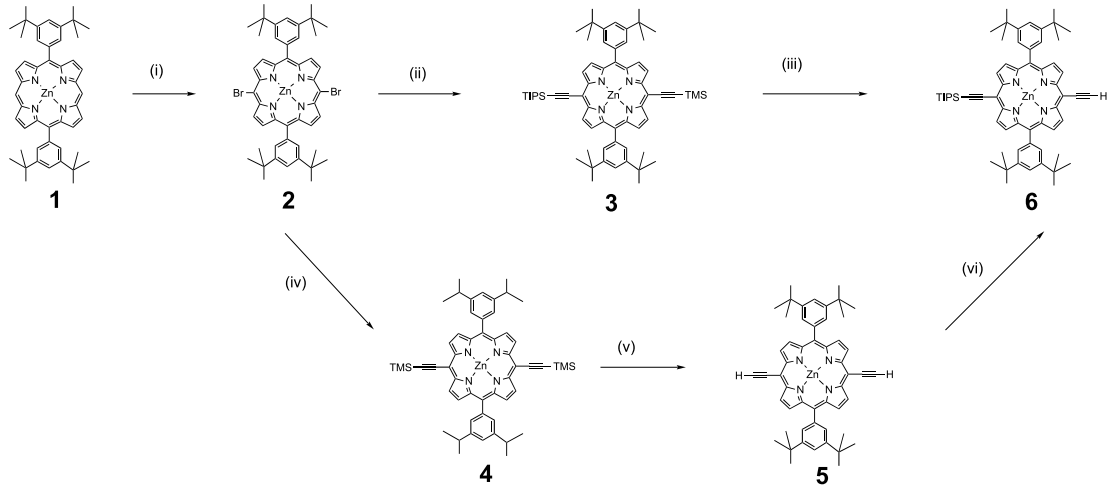
The synthetic approach relies on a key synthon: the bisethynyl porphyrin **3** in which the ethynyl groups are protected with silyl groups of different labilities (trimethylsilyl: TMS and trisisopropylsilyl: TIPS). The selective cleavage of the ethynyl protective groups allows for successive Sonogashira cross-coupling reactions of the porphyrin with the electron donor moiety and then with the electron acceptor unit (Scheme 1). The preparation of the starting porphyrin **6** is depicted in Scheme 2.

The bisbrominated porphyrin **2** is readily synthesized in gram-scale following literature methodology. The conditions used here were mostly inspired by those reported by Plater,[24] with a slight modification on the bis bromination step. This reaction offers a higher yield when the *N*-bromosuccinimide (NBS) was added dropwise and at low temperature (90% yield) instead of in one fraction at room temperature (70% yield).

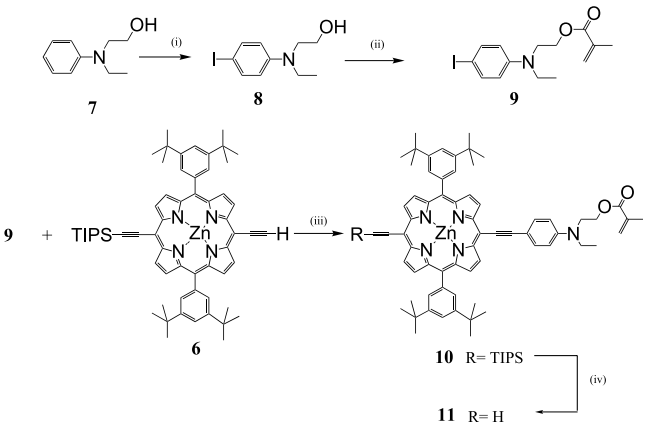
We tested two different routes to prepare porphyrin **6** (Scheme 2). A straightforward approach consists in a statistical Sonogashira cross-coupling reaction of porphyrin **2** with a mixture of trisisopropylsilyl acetylene and trimethylsilyl acetylene, followed by a selective deprotection of the trimethylsilyl group under basic conditions, as described by Therien.[25] The second route requires the preparation of the symmetrical bis trimethylsylilacetylene porphyrin **4**, followed by the cleavage of both trimethylsilyl groups by fluoride. Then, the deprotonation of one ethynyl group of **5** with lithium bis(trimethylsilyl)amide (LiHMDS) and the quenching of the resulting anion with trisisopropylsilyl chloride also afforded porphyrin **6**[24] as analogous to



Scheme 1. Retrosynthetic scheme for the synthesis of the push–pull porphyrin.



Scheme 2. Synthesis of the porphyrin **6**. Reagents and conditions: (i) NBS (2 equiv), CH_2Cl_2, 0 °C, 90%; (ii) trisisopropylsilyl acetylene (6 equiv)/trimethylsilyl acetylene (2 equiv), $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, 20 h, 40 °C, 40%; (iii) NaOH (1 M aq), THF/MeOH, rt, 88%; (iv) trimethylsilylacetylene (5 equiv), $Pd(PPh)_3Cl_2$, THF, Et_3N, 20H, 45 °C, 95%; (v) BuN_4F, THF, rt, 92%; (vi) LiHMDS (1.4 equiv), THF, 10 min, then *iso*Pr_3SiCl (1.4 equiv), 38%.

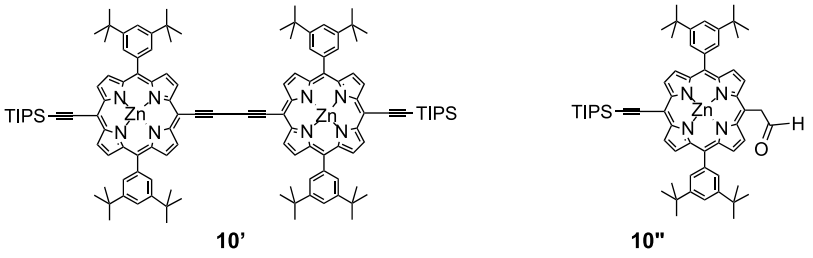


Scheme 3. Synthesis of the donor moiety **9** and its coupling with porphyrin **6**. Reagents and conditions: (i) iodine (3 equiv), pyridine, dioxane, 1 h, 0 °C, 96%; (ii) methacryloyl chloride, $CHCl_3$, Et_3N, 0 °C, 70%; (iii) $Pd_2(dba)_3 \cdot CHCl_3$, $AsPh_3$, THF/toluene/Et_3N, 40 °C, 20 h, 85%; (iv) Bu_4NF, THF, rt, 99%.

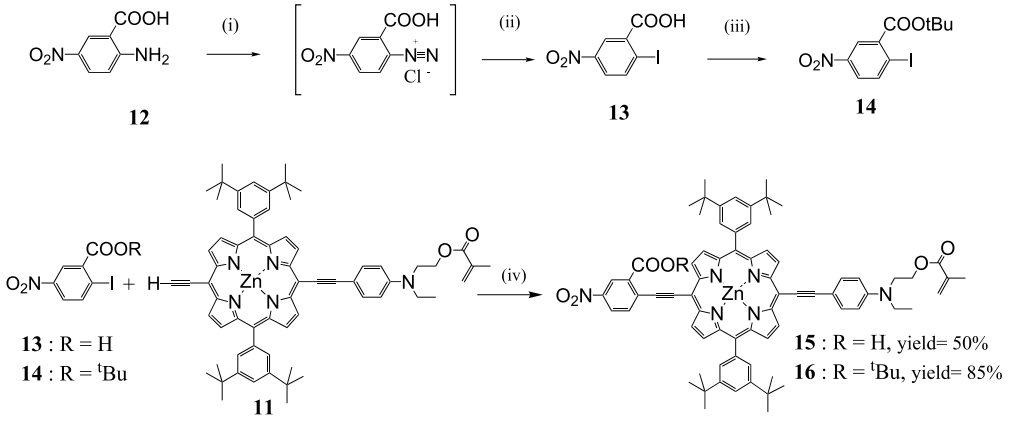
Anderson's similar species with trihexylsilylethynyl and unsubsituted ethynyl groups.[26] The two routes gave a similar overall yield (38%), but the second route avoids the utilization of the costly trisisopropylsylil acetylene reagent, on the other hand the first route is one step shorter.

Various attempts to couple the easily available 4-bromo-*N*-ethyl-*N*-hydroxyaniline with the porphyrin **6** failed. This can be explained by the inefficient oxidative addition of electron rich amino phenyl bromide on the Pd^0 center of the catalyst. This failure prompted us to replace the bromo group by the more reactive iodo halogen. Numerous approaches for the iodination in the *para* position of aniline derivatives already exist in literature[27,28], but few of them operate in mild and neutral conditions compatible with the free alcoholic group of **7**. The iodination reaction used in the synthesis of **8** was inspired by a method originally described by Irie for the iodination of indole derivatives.[29] It consists in reacting an excess of iodine on the *N*-ethyl-*N*-hydroxyethyl-aniline **7**, in a mixture of pyridine–dioxane (1/1). It appeared that these simple and mild conditions were perfectly suitable for the selective iodination of compound **7** with an excellent 96% yield (Scheme 3). Compound **8** was then reacted with methacryloyl chloride in the presence of Et_3N, affording **9** with a 70% yield. The Sonogashira cross-coupling reaction of **9** with the porphyrin **6** was carried out using Lindsey's conditions[30] because they gave higher yield and higher reproducibility than those used by Plater.[24] We attribute this to the formation of two undesired by-products, namely the compound **10′** resulting from the Glaser's homocoupling and the compound **10″** in which the acetylenic was transformed into vinyl alcohol group following an anti-Markovnikov hydration type reaction[31,32] (Scheme 4). Purification of the porphyrin **10** was not possible by column chromatography on silica gel or alumina due to the degradation of the zinc porphyrin. A size exclusion chromatography on Sephadex LH20 stationary phase was instead performed after a flash filtration on silica gel initially neutralized by triethylamine. The trisisopropylsilyl group of **10** was finally cleaved by tetrabutylammonium fluoride in a quantitative yield.

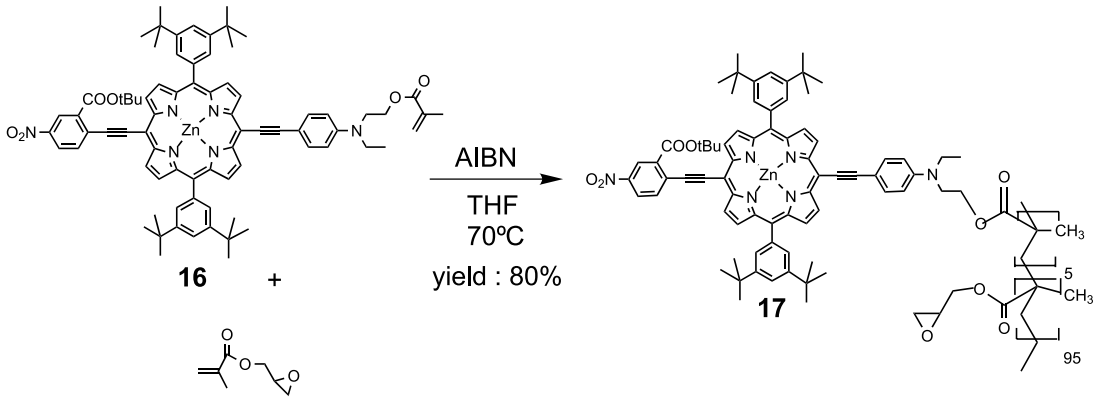
The iodinated acceptor moiety **13** was prepared from the commercially available 2-amino-5-nitro-benzoic acid **12** according to a Sandmeyer reaction from the diazonium salt of **12** and potassium iodide (Scheme 5). The Sonogashira



Scheme 4. Structure of the by-products **10′** and **10″** formed during the reaction of **6** and **9** using the catalyst $Pd(PPh_3)_4$.



Scheme 5. Synthesis of the acceptor moieties **13** and **14** and coupling with porphyrin **11**. Reagents and conditions: (i) NaOH (O, 5 N aq), 70 °C, then HCl (12 N), then $NaNO_2$, 0 °C; (ii) KI (satd aq), H_2O, 0 °C, 65% for the two steps; (iii) *tert*-BuOH, DCC/DMAP, THF, 70 °C, 51%; (iv) $Pd_2(dba)_3 \cdot CHCl_3$, $AsPh_3$, THF/toluene/Et_3N, 40 °C, 20 h.



Scheme 6. Polymerization reaction of the esterified push–pull porphyrin **17**.

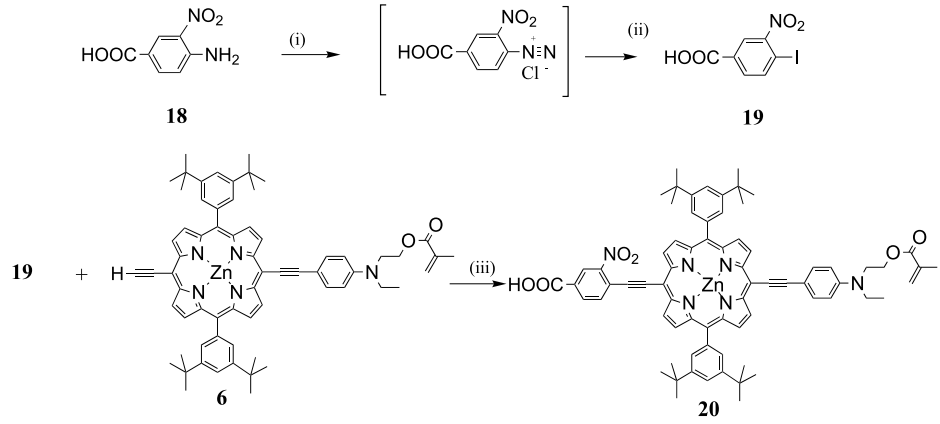
cross-coupling reaction of porphyrin **6** with **13** afforded the expected product **15** with a 50% yield, but unfortunately the lack of reproducibility of this reaction prevented us from preparing the expected push–pull porphyrin **15** in large quantity. This problem was not surprising, since Mioskowsky and co-workers[33] have shown that a carboxylic acid in *ortho* position of an iodo group prevents Sonogashira cross-coupling, most probably by the irreversible chelation of the Pd catalyst by COOH after oxidative addition of aryl iodide. We decided therefore, to protect the acid group by a *tert*-butyl ester group. The esterification was carried out by reacting **13** and *tert*-butanol in THF in the presence of dicyclohexylcarbodiimide and a catalytic amount of dimethylaminopyridine and afforded **14** in a quite satisfying yield of 65%. Compound **14** was then successfully coupled with porphyrin **11** in a Sonogashira cross-coupling reaction, to give **16** in 85% yield (Scheme 5). Unfortunately, all our attempts to deprotect selectively the *tert*-butyl group without affecting the methacrylate function (including the use of mild basic condition, trifluoroacetic acid, or cerium chloride) failed. The best results were obtained using cerium chloride chloroform but with only 15% yield.

Still, we decided to copolymerize the protected esterified porphyrin **16** with glycidyl methacrylate. The copolymerization was performed in THF with a molar ratio GMA/chromophore of 95:5, using 10% mol AIBN as an initiator, and leads to a total conversion of the monomer **16** (Scheme 6). A size exclusion chromatography (polystyrene standards) was performed on **17** and it showed a $\overline{M_w}$ of only 2400 D with a polydispersity index (PDI) = 1.2, indicating an oligomeric structure rather than polymeric.

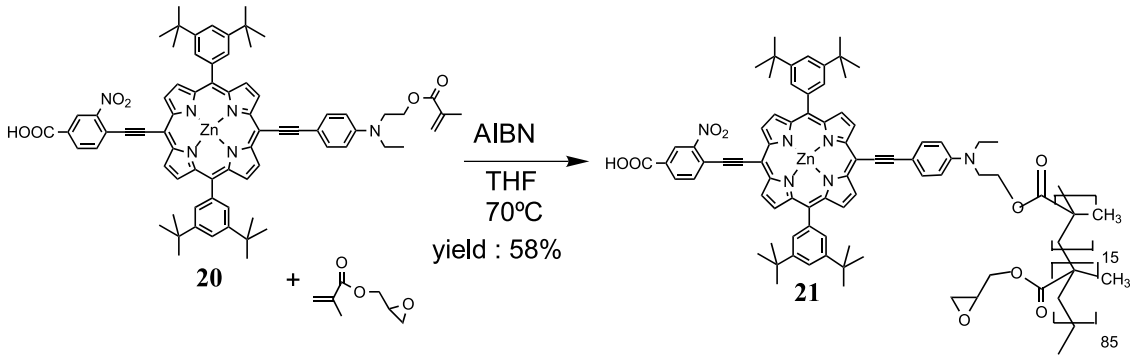
These unsatisfying results prompted us to direct our efforts to a new porphyrin chromophore in which the position of the respective nitro and carboxylic acid groups on the electron acceptor moiety were inverted (compound **20**). Previous works on azo push–pull chromophores have indeed shown that such a change did not affect significantly the value of the electro-optic coefficient.[34–36] In compound **19**, the new position of the carboxylic acid group with respect to the iodo group should avoid the problem encountered in the final Sonogashira cross-coupling step. In addition, the more accessible carboxylic acid group, compared to that in the original target **15**, could facilitate the crosslinking reaction with epoxy functions of the polymer.

The new acceptor moiety **19** was synthesized according to a similar Sandmeyer reaction to that previously used for **13**, but using the commercially available 4-amino-3-nitrobenzoic acid **18** as a starting material (Scheme 7). The iodinated acceptor **19** was finally coupled with porphyrin **6** leading to **20** with an excellent 85% yield with high reproducibility.

Copolymerization of **20** with GMA was performed in THF with 10% mol. AIBN as an initiator and with an increased amount of porphyrin **16** (15% mol) compared to that used in



Scheme 7. Synthesis of the acceptor moietie **19** and its coupling with porphyrin **11**. Reagents and conditions: (i) NaOH (O, 5 N aq), 70 °C, then HCl (12 N), then $NaNO_2$, 0 °C; (ii) KI (satd aq), H_2O, 0 °C, 65% for the two steps; (iii) $Pd_2(dba)_3 \cdot CHCl$, $AsPh_3$, THF/toluene/Et_3N, 40 °C, 20 h, 85%.



Scheme 8. Polymerization reaction of the chromophore **20** with glycidyl methacrylate.

the case of **17**. Precipitation of the crude reaction mixture with methanol followed by a vacuum filtration afforded polymer **21** with a 60% yield (Scheme 8). A size exclusion chromatography was performed and indicated a satisfying molecular weight $\overline{M}_w = 8600$ D with a polydispersity index = 1.6.

ATG measurements performed on the push–pull chromophore **20** and on the corresponding polymer **21** indicated no degradation of both materials until 220 °C confirming the high thermal stability of these substances.

3. Conclusion

This work is the first example of incorporation of a porphyrin displaying NLO properties into a crosslinkable polymeric matrix. Notably, the satisfying overall yield of 22% from the free base bis-aryl porphyrin **1** to the push–pull chromophore **20**, has been increased compared to that reported in previous papers for simpler push–pull porphyrin chromophores. The push–pull porphyrin **20** has been successfully copolymerized with glycidyl methacrylate leading to a soluble material. It is noteworthy that the synthetic strategy described herein, allows for the preparation of significant quantity of both monomeric porphyrin **20** and polymer **17** permitting thus, a complete study of the electro-optical properties of these new materials. The investigation of the magnitude and the stability of the electro-optical properties of these new materials is under way and will be reported in due course.

4. Experimental

4.1. General methods

^{1}H NMR spectra were recorded on a ARX 400 MHz Bruker spectrometer. Chemical shifts for ^{1}H NMR spectra are referenced relative to residual protium in the deuterated solvent ($CDCl_3$, $\delta = 7.26$ ppm; *d*-THF $\delta_1 = 3.57$ ppm–$\delta =$ 1.72 ppm). UV–vis absorption spectra were recorded on a Cary 5G Varian spectrophotometer. Mass spectra were recorded on a EI-MS HP 5989A spectrometer or on a JMS-700 (JEOL LTD, Akishima, Tokyo, Japan) double focusing mass spectrometer of reversed geometry equipped with electrospray ionization (ESI) source. Thin-layer chromatography (TLC) was performed on aluminum sheets precoated with Merck 5735 Kieselgel 60F_{254}. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040–0.063 mm mesh). Air sensitive reactions were carried out under argon in dry solvents and glassware. Chemicals were purchased from Aldrich and used as received. 5,15-Bis-(3,5-di-*tert*-butylphenyl)porphyrin was prepared according to literature method.[37]

UV–vis absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fourier transform infrared spectra were recorded in pressed KBr pellets on a Bruker Vector 22 spectrometer.

Molecular masses and molecular mass distributions were measured using size exclusion chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 m Guard, 50×7.5 mm) followed by two columns (Polymer Laboratories, 2 PL gel 5 m MIXED-D columns, 2×300×7.5 mm), with a SpectraSYSTEM RI-150 detector and a SpectraSYSTEM UV2000 detector. The eluent used was THF at a flow rate of 1 mL min^{-1} at 35 °C. Polystyrene standards [(580–483)×10^3 g mol^{-1}] were used to calibrate the SEC. The purity of the compounds was better than 95% as judged by ^{1}H NMR spectroscopy.

4.1.1. [5,15-Dibromo-10,20-bis-(3,5-di-*tert*-butylphenyl) porphyrinato] zinc (II): 2. Porphyrin **1** (1.21 g, 1.62 mmol) was dissolved in 60 mL of dichloromethane. The mixture was cooled to 0 °C and NBS (560 mg, 3.16 mmol in 10 mL of dichloromethane) was added dropwise with an addition funnel. The ice bath was removed and methanol (200 mL) was added and the volume of the resulting solution was reduced (roughly 20 mL). The precipitate was filtered and intensively washed with methanol to give a violet powder (1.31 g, 90%). The analytical data of this compound agreed completely with those reported by Plater.[24]

^{1}H NMR (300 MHz, DMSO), δ (ppm): 9.60 (d, 4H, $^3J =$ 4.2 Hz); 8.77 (d, 4H, $^3J = 4.2$ Hz); 7.97 (d, 4H, $^4J = 1.5$ Hz); 7.83 (t, 2H, $^4J = 1.5$ Hz); 1.57 (s, 36H).

4.1.2. [5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-(trisisopropylsilyl)ethynyl-20-(trimethylsilyl)ethynyl-porphyrinato] zinc (II): 3. Porphyrin **2** (300 mg, 0.33 mmol), $Pd(PPh_3)_2Cl_2$ (24 mg), CuI (7 mg), trimethylsilylacetylene (100 μL, 0.7 mmol), trisisopropylsilyl acetylene (0.4 mL,

1.78 mmol) were loaded in a sealed tube. THF (10 mL) and Et_3N (3 mL) were added and the mixture was stirred for 20 h at 40 °C. After evaporation of the solvents, the residue was purified by flash column chromatography on silica gel eluted with a gradient of petroleum ether/dichloromethane: from 90:10 to 70:30. The middle green fraction was isolated giving, after evaporation, the pure asymmetric disilylated porphyrin **3** (135 mg, 40%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.74 (d, 2H, ^3J= 4.8 Hz); 9.69 (d, 2H, ^3J=4.8 Hz); 8.98 (d, 2H, ^3J=4.8 Hz); 8.95 (d, 2H, ^3J=4.8 Hz); 8.03 (d, 4H, ^4J=1.8 Hz); 7.81 (t, 2H, ^4J=1.8 Hz); 1.54 (s, 36H); 1.51–1.42 (m, 21H); 0.59 (s, 9H). UV–vis (CH_2Cl_2): λ_{max}, nm (ε, mol^{-1} L cm^{-1}) 434 (210,000); 576 (9500); 629 (17,000). FT-IR (cm^{-1}): 2960 (s, *tert*-Bu); 2141 (m, C≡C); 1592 (m, Ar); 1213 (m); 852 (s). HR-ESMS, *m/z*: calcd for $C_{64}H_{80}N_4Si_2Zn$: 1024.521 ($M^+\cdot$), found: 1024.520 ($M^+\cdot$).

4.1.3. [5,15-Bis-(3,5-di-*tert*-butylphenyl)-10,20-bis-ethynyl-porphyrinato] zinc (II): 5. Porphyrin **2** (1.01 g, 1.11 mmol), trimethylsilylacetylene (560 μL, 4.44 mmol), CuI (21 mg), $Pd(PPh_3)_2Cl_2$ (84 mg) were dissolved in THF (40 mL) and Et_3N (10 mL) in a Schlenk tube set under argon atmosphere. The mixture was heated at 45 °C for 20 h. The solvents were evaporated and the residue was filtered through silica gel, eluted with dichloromethane/petroleum ether: 50:50. The green solid was dissolved in THF (100 mL) and Bu_4NF 1 M in THF (2.5 mL, 2.5 mmol) was added. The solvents were evaporated to 1/4 of the initial volume and MeOH was added to precipitate the porphyrin. After filtration and washing with methanol, porphyrin **5** was obtained as a green-blue powder (790 mg, 90%).

^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 9.68 (d, 4H, ^3J= 4.8 Hz); 8.90 (d, 4H, ^3J=4.8 Hz); 8.10 (d, 4H, ^4J=1.5 Hz); 7.92 (t, 2H, ^4J=1.5 Hz); 4.63 (s, 2H); 1.59 (s, 36H). HR-ESMS, *m/z*: calcd for $C_{52}H_{52}N_4Zn$: 796.351 ($M^+\cdot$), found: 796.353 ($M^+\cdot$).

4.1.4. [5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-(trisisopropylsilyl)ethynyl-porphyrinato] zinc (II): 6. *Route 1*. Porphyrin **3** was dissolved in a mixture of THF/MeOH (15 mL/15 mL). 1 M aq NaOH (2 mL) was added and the mixture was stirred at room temperature for 15 min. Dichloromethane and water were then added and the organic layer was extracted, dried and rotary-evaporated. The residue was dissolved in a minimum amount of dichloromethane, precipitated with methanol and filtered. Porphyrin **6** was obtained as a green solid (110 mg, 88%).

Route 2. Porphyrin **5** (500 mg, 0.63 mmol) was dissolved in distilled THF (60 mL). Bistrimethylsilyl-lithium bis(trimethylsilyl)amide (LiHMDS) 1 M in THF (0.9 mL, 0.9 mmol) was rapidly added (in one portion) to the stirred mixture. After 10 min at room temperature, trisisopropylsilyl chloride (0.25 mL) was added and the mixture was further stirred for 10 min. 30 mL of 1 M aq KOH were added and the mixture was extracted with dichloromethane. After removal of the solvent, the residue was purified by flash chromatography on silica gel eluted with the mixture petroleum ether/dichloromethane: 80:20 leading to the awaited porphyrin **6** (230 mg, 38%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.78 (d, 2H, ^3J= 4.8 Hz); 9.69 (d, 2H, ^3J=4.8 Hz); 8.99 (d, 2H, ^3J=4.8 Hz); 8.98 (d, 2H, ^3J=4.8 Hz); 8.03 (d, 4H, ^4J=1.8 Hz); 7.81 (t, 2H, ^4J=1.8 Hz); 4.19 (s, 1H); 1.55 (s, 36H); 1.51–1.42 (m, 21H). UV–vis (CH_2Cl_2): λ_{max}, nm (ε, mol^{-1} L cm^{-1}): 435 (205,000); 576 (9000); 630 (15,000). HR-ESMS, *m/z*: calcd for $C_{61}H_{72}N_4SiZn$: 952.484 ($M^+\cdot$), found: 952.485 ($M^+\cdot$).

4.1.5. 1-Iodo-4-[*N*-ethyl,*N*-(2-hydroxyethyl)amino]benzene: 8. To a solution of *N*-ethyl,*N*-hydroxyethylaniline (4 g, 24.2 mmol) in dioxane (180 mL) and pyridine (180 mL) cooled in an ice bath, iodine (9.22 g, 36.2 mmol) was added. After 1 h of stirring the mixture was warmed to room temperature for one further hour. Then iodine (3 g, 13 mmol) was added and the mixture was stirred for one supplementary hour. The crude reaction mixture was washed with 10% aq $Na_2S_2O_3$ until the brown color disappeared. After addition of water, the mixture was extracted with dichloromethane. The solvent was rotary-evaporated and the residue was purified by flash column chromatography on silica gel eluted with dichloromethane. White crystals were obtained (6.52 g, 96%).[38]

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.44 (d, 2H, ^3J= 8.7 Hz); 6.52 (d, 2H, ^3J=8.7 Hz); 3.77 (t, 2H, ^3J=5.7 Hz); 3.37–3.45 (m, 4H); 1.7 (s(broad), 1H); 1.14 (t, 3H, ^3J= 6.9 Hz). ^{13}C NMR (300 MHz, $CDCl_3$), δ (ppm): 147.72; 137.81; 123.94; 114.92; 59.97; 52.44; 45.58; 11.72. EI-MS: $M^+\cdot$ (%): 293 (100); 263 (22); 247 (18); 136 (28); 92 (37). Mp=33 °C.

4.1.6. 2-[Ethyl(4-iodophenyl)amino]ethyl methacrylate: 9. A two necked flask equipped with a reflux condenser and an argon outlet was charged with **8** (5 g, 17.2 mmol) and THF (75 mL). Et_3N (3.62 mL) was added and the mixture was cooled at 0 °C. Methacryloyl chloride (1.95 mL, 17.2 mmol) was added dropwise with a syringe over a period of 1 h and the solution was then heated for 20 h at 40 °C. The solution was filtered, evaporated and the residue was chromatographed on silica gel eluted with the mixture dichloromethane/petroleum ether: 50:50. The pure desired product was isolated as a colorless oil (4.25 g, 75%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.47 (d, 2H, ^3J= 9.0 Hz); 6.54 (d, 2H, ^3J=9.0 Hz); 6.08 (s, 1H); 5.58 (s, 1H); 4.28 (t, 2H, ^3J=6.3 Hz); 3.58 (t, 2H, ^3J=6.3 Hz); 3.45 (q, 2H, ^3J=7.2 Hz); 1.91 (s, 3H); 1.14 (t, 3H, ^3J=7.2 Hz). ^{13}C NMR (300 MHz, $CDCl_3$), δ (ppm): 166.25; 146.13; 136.76; 134.96; 127.99; 124.92; 113.25; 60.78; 47.46; 44.11; 17.30; 11.01. FT-IR (cm^{-1}): 2895–2970 (w, alk); 1717 (s, C=O); 1637 (w, CH_2=C); 1587 (m, Ar); 1163 (s). EI-MS: $M^+\cdot$ (%): 359 (24); 260 (100).

4.1.7. {5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-[ethyl-(methacryloyloxyethyl)aminophenylethynyl]-20-(trisisopropylsilyl)ethynyl-porphyrinato} zinc (II): 10. Porphyrin **6** (300 mg, 0.315 mol) and compound **9** (224 mg, 0.630 mol) were placed in a schlenk tube and toluene (30 mL), THF (10 mL) and Et_3N (10 mL) were added. The solution was deaerated by three freeze–pump–thaw cycles and $Pd_2(dba)_3\cdot CHCl_3$ (30 mg) and triphenylarsine (30 mg) were added. The solution was stirred 30 min at room temperature. After solvents removal, the residue was

dissolved in THF and chromatographied on LH 20 Sephadex stationary phase and the major green band was collected. Finally, the green powder was dissolved in a minimum volume of dichloromethane and precipitated with methanol. After filtration, a green powder was obtained (320 mg, 85%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.77 (d, 2H, ^3J= 4.8 Hz); 9.72 (d, 2H, ^3J=4.5 Hz); 8.94 (m, 4H); 8.05 (d, 4H, ^4J=1.8 Hz); 7.87 (d, 2H, ^3J=9.0 Hz); 7.81 (t, 2H, ^4J= 1.8 Hz); 6.88 (d, 2H, ^3J=9.0 Hz); 6.14 (s, 1H); 5.62 (s, 1H); 4.38 (t, 2H, ^3J=6.3 Hz); 3.72 (t, 2H, ^3J=6.3 Hz); 3.55 (q, 2H, ^3J=7.2 Hz); 1.97 (s, 3H); 1.4–1.6 (m, 57H); 1.25 (t, 3H, ^3J=7.2 Hz). FT-IR (cm^{-1}): 2960 (s, *t*-Bu); 2930 (s, *i*-Pr); 2863 (m, –CH_2–); 2183 (m, C≡C); 2136 (m, C≡C); 1718 (m, C=O); 1212 (s). HR-ESMS, *m/z*: calcd for $C_{75}H_{89}N_5O_2SiZn$: 1183.608 ($M^+\cdot$), found: 1183.609 ($M^+\cdot$).

When Plater's conditions were used (mixture of tetrahydrofurane (6 mL) and pyrrolidine (20mL) as solvents) and the above catalyst ($Pd_2(dba)_3\cdot CHCl_3$ and triphenylarsine) was replaced by $Pd(PPh_3)_4$ (6 mg) and CuI (3 mg)) the two major products were formed. These two products were the porphyrins **10′** and **10″** that were isolated in variable yields from one run to the other **10′** (70–50%) and **10″** (10–30%).

Porphyrin dimer **10′**. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.73 (m, 8H); 8.91 (m, 8H); 8.02 (d, 8H, ^4J=1.8 Hz); 7.80 (t, 4H, ^4J=1.8 Hz); 1.4–1.6 (m, 114H).

Porphyrin **10″**. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 10.44 (s, 1H, CHO); 9.78 (d, 2H, ^3J=4.5 Hz); 9.42 (d, 2H, ^3J= 4.5 Hz); 9.05 (d, 2H, ^3J=4.5 Hz); 9.01 (d, 2H, ^3J=4.5 Hz); 8.04 (d, 4H, ^4J=1.8 Hz); 7.80 (t, 2H, ^4J=1.8 Hz); 5.98 (s, 2H); 1.4–1.6 (m, 57H). FT-IR (cm^{-1}): 2956–2900 (vs, *t*-Bu, *i*-Pr); 2864 (m, –CH_2–); 2810 and 2710 (w, CO–H); 2138 (m, C≡C); 1724 (m, C=O). MS(MALDI-TOF), *m/z*: calcd for $C_{61}H_{72}N_4OSiZn$: 970.492 ($M^+\cdot$), found: 970 (77%), 971 (48%), 972 (100%), 973 (72%), 974 (74%), 975 (35%).

4.1.8. {5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-ethynyl-20-[ethyl(methacryloyloxyethyl) aminophenylethynyl]-porphyrinato} zinc (II): 11. One hundred and fifty microlitres of 1 M Bu_4NF in THF (0.15 mmol) was added to a solution of porphyrin **10** (150 mg, 0.126 mmol in 150 mL of THF). The mixture was stirred for 30 min at room temperature. The solvent was partly removed, water was added and the mixture was extracted with dichloromethane. After evaporation of the solvents, the residue was redissolved in a minimum amount of dichloromethane, petroleum ether was added to precipitate the porphyrin (130 mg, 100%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.74 (d, 2H, ^3J= 4.8 Hz); 9.64 (d, 2H, ^3J=4.5 Hz); 8.96 (m, 4H); 8.06 (d, 4H, ^4J=1.8 Hz); 7.82 (d, 2H, ^3J=9.0 Hz); 7.80 (t, 2H, ^4J= 1.8 Hz); 6.85 (d, 2H, ^3J=9.0 Hz); 6.13 (s, 1H); 5.61 (s, 1H); 4.38 (t, 2H, ^3J=6.3 Hz); 4.06 (s, 1H); 3.71 (t, 2H, ^3J= 6.3 Hz); 3.54 (q, 2H, ^3J=7.2 Hz); 1.97 (s, 3H); 1.4–1.6 (m, 57H); 1.28 (t, 3H, ^3J=7.2 Hz). FT-IR (cm^{-1}): 2960 (s, *tert*-Bu); 2863 (m, –CH_2–); 2138 (m, C≡C); 1718 (m, C=O); 1212 (s). UV–vis (CH_2Cl_2): λ_{max}, nm (ε, mol^{-1} L cm^{-1}): 432 (205,000); 568 (11,000); 616 (10,000).

4.2. General procedure for iodination of amino nitrobenzoic acid (compound 13 or 19)

A solution of the amino nitrobenzoic acid **12** or **18** (4.5 g, 24.7 mmol) in 45 mL of 0.5 M aq NaOH was heated at 70 °C until complete dissolution. Then, 10 mL of 12 N HCl were added dropwise, giving rise to a fine precipitate. The mixture was then cooled at 0 °C with an ice bath and $NaNO_2$ (1.7 g, 21.7 mmol) in 5 mL of water was added. The precipitate partly dissolved and the mixture was stirred for 1 h at 0 °C. The mixture was filtered while the filtrate was carefully kept at 0 °C. Then, a saturated solution of KI (8.4 g, 50 mmol) was added dropwise on the precipitate causing a strong release of N_2. The mixture turned to red and a precipitate appeared. The ice bath was removed and the mixture was stirred for two additional hours. After filtration and washing with water, the iodo nitrobenzoic acid was obtained as an orange solid (4.7 g, 65%).

4.2.1. 2-Iodo-5-nitrobenzoic acid 13.[39,40] ^{1}H NMR **13** (300 MHz, $CDCl_3$), δ (ppm): 8.83 (d, 1H, ^4J=2.7 Hz); 8.30 (d, 1H, ^3J=8.7 Hz); 8.02 (dd, 1H, ^3J=8.7 Hz, ^4J=2.7 Hz); 6.3 (s broad, 1H). FT-IR (cm^{-1}): 1710 (s, C=O); 1526 (s, ν_{asym} NO_2); 1347 (s, ν_{sym} NO_2). EI-MS: $M^+\cdot$ (%): 293 (100); 263 (36); 92 (35). Mp=197 °C.

4.2.2. 4-Iodo-3-nitrobenzoic acid 19.[41,42] ^{1}H NMR **18** (300 MHz, $CDCl_3$), δ (ppm): 8.52 (d, 1H, ^4J=1.5 Hz); 8.21 (d, 1H, ^3J=6.0 Hz); 7.94 (dd, 1H, ^3J=6.0 Hz, ^4J=1.5 Hz); 4.8 (s broad, 1H). FT-IR (cm^{-1}): 1700 (s, C=O); 1535 (s, ν_{asym} NO_2); 1351 (s, ν_{sym} NO_2). EI-MS: $M^+\cdot$ (%): 293 (100); 263 (25); 136 (32); 92 (40). Mp=201 °C.

4.2.3. *tert*-Butyl 2-iodo-5-nitrobenzoate: 14. Compound **13** (1.75 g, 6 mmol) was dissolved in THF (36 mL). Dicyclohexylcarbodiimide (DCC, 1.85 g, 6.9 mmol) and *tert*-BuOH (2.83 mL, 30 mmol) were added. DMAP (20 mg) were added and the mixture was heated for 20 h at 70 °C. The solvents were removed and the residue was purified by a column chromatography on silica gel eluted with the mixture dichloromethane/petroleum ether: 30:70. The pure product **14** was isolated as white crystals (1.35 g, 65%).

^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.47 (d, 1H, ^4J= 3.1 Hz); 8.16 (d, 1H, ^3J=8.7 Hz); 7.93 (dd, 1H, ^3J=8.7 Hz, ^4J=3.1 Hz); 1.65 (s, 9H). ^{13}C NMR (300 MHz, $CDCl_3$), δ (ppm): 164.22; 147.69; 142.30; 138.71; 125.69; 124.89; 101.83; 84.20; 28.07. FT-IR (cm^{-1}): 2980 (m, *tert*-Bu); 1713 (s, C=O); 1526 (s, ν_{asym} NO_2); 1341 (s, ν_{sym} NO_2). EI-MS: $M^+\cdot$ (%): 349 (16); 293 (97); 276 (38); 75 (36); 57 (89); 56 (100). Mp=107 °C.

4.2.4. {5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-(4-nitro-2-carboxyphenyl)ethynyl-20-[ethyl (methacryloyloxyethyl)aminophenylethynyl]-porphyrinato} zinc (II): 15. Porphyrin **11** (75 mg, 0.073 mmol) and compound **13** (25 mg, 0.085 mmol) were dissolved in THF (2 mL), Et_3N (2 mL) and toluene (6 mL). The mixture was intensively degassed with three freeze–pump–thaw cycles. $Pd_2(dba)_3\cdot CHCl_3$ (7 mg) and $AsPh_3$ (7 mg) were added and the mixture was heated for 2 h at 50 °C. The crude reaction mixture was filtered through a short plug of celite and the

solvents were removed. The crude porphyrin was dissolved in a minimum amount of dichloromethane and was precipitated with petroleum ether. Porphyrin **15** was obtained as a green-brown powder upon vacuum filtration. (43 mg, 51%).

^{1}H NMR (300 MHz, THF), δ (ppm): 10.03 (d, 2H, ^3J= 4.2 Hz); 9.68 (d, 2H, ^3J=4.2 Hz); 8.98 (d, 1H, ^3J=1.8 Hz); 8.85 (d, 2H, ^3J=4.2 Hz); 8.82 (d, 2H, ^3J=4.2 Hz); 8.48 (dd, 1H, ^3J=4.8 Hz, ^4J=1.8 Hz); 8.45 (d, 1H, ^3J=4.8 Hz); 8.08 (d, 4H, ^4J=1.2 Hz); 7.85–7.92 (m, 4H); 6.98 (d, 2H, ^3J= 8.7 Hz); 6.08 (s, 1H); 5.61 (s, 1H); 4.42 (t, 2H, ^3J=5.2 Hz); 3.75 (t, 2H, ^3J=5.2 Hz); 3.57 (m, 2H); 1.94 (s, 3H); 1.58 (s, 36H); 1.35 (t, 3H, ^3J=5.7 Hz). UV–vis (CH_2Cl_2): λ_{max}, nm (ε, mol^{-1} L cm^{-1}) 458 (123,000); 686 (48,000). FT-IR (cm^{-1}): 2961 (s, *tert*-Bu); 2867 (m, –CH_2–); 2181 (s, C≡C); 1750 (s, C=O acid); 1718 (m, C=O ester) ; 1525 (s, ν_{asym} NO_2); 1348 (s, ν_{sym} NO_2); 1191 (s, ν_s, C–O). HR-ESMS, *m/z*: calcd for $C_{73}H_{72}N_6O_6Zn$: 1193.488 ([M+H]$^+$·), found: 1193.486 ([M+H]$^+$·).

4.2.5. {5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-(4-nitro-2-*tert*-butylcarboxyphenyl)ethynyl-20-[ethyl (methacryloyloxyethyl)aminophenylethynyl]-porphyrinato} zinc (II): 16. Porphyrin **11** (225 mg, 0.22 mmol) and **14** (114 mg, 0.33 mmol) were dissolved in THF (6 mL), Et_3N (6 mL) and toluene (20 mL). The mixture was intensively degassed with three freeze–pump–thaw cycles. $Pd_2(dba)_3\cdot CHCl_3$ (20 mg) and $AsPh_3$ (20 mg) were added and the mixture was heated for 12 h at 50 °C. The crude reaction mixture was evaporated and the residue was purified by flash chromatography on silica gel using the mixture petroleum ether/dichloromethane: 30:70. The porphyrin was dissolved in a minimum amount of dichloromethane and was precipitated with methanol affording a green-brown powder (235 mg, 85%).

^{1}H NMR (300 MHz, THF), δ (ppm): 9.94 (d, 2H, ^3J= 4.5 Hz); 9.66 (d, 2H, ^3J=4.5 Hz); 8.85 (m, 3H); 8.77 (d, 2H, ^3J=4.5 Hz); 8.50 (dd, 1H, ^3J=4.8 Hz, ^4J=1.8 Hz); 8.40 (d, 1H, ^3J=4.8 Hz); 8.05 (d, 2H, ^4J=1.2 Hz); 7.8 (m, 4H); 6.92 (d, 2H, ^3J=8.7 Hz); 6.04 (s, 1H); 5.54 (s, 1H); 4.32 (t, 2H, ^3J=5.2 Hz); 3.72 (t, 2H, ^3J=5.2 Hz); 3.57 (q, 2H, ^3J=5.2 Hz); 1.88 (s, 3H); 1.75 (s, 9H); 1.52 (s, 36H); 1.22 (t, 3H, ^3J=5.2 Hz). UV–vis (CH_2Cl_2): λ_{max}, nm (ε, mol^{-1} L cm^{-1}) 465 (110,000); 689 (56,000). FT-IR (cm^{-1}): 2960 (vs, *t*-Bu); 2867 (m, –CH_2–); 2183 (s, C≡C); 1724 (s, COO*t*Bu); 1718 (m, C=O); 1524 (s, ν_{asym} NO_2); 1348 (s, ν_{sym} NO_2); 1200 (s, ν_s, C–O). HR-ESMS, *m/z*: calcd for $C_{77}H_{81}N_6O_6Zn$: 1249.551 ([M+H]$^+$·), found: 1249.552 ([M+H]$^+$·).

4.2.6. {5,15-Bis-(3,5-di-*tert*-butylphenyl)-10-(2-nitro-4-carboxyphenyl)ethynyl-20-[ethyl (methacryloyloxyethyl)aminophenylethynyl]-porphyrinato} zinc (II): 20. The same protocol as used for **15** was applied, with 200 mg of porphyrin **11**, 65 mg of **19**, 20 mL of toluene, 6 mL of Et_3N and 6 mL of THF. Porphyrin **20** was obtained as a brown solid (208 mg, 87%).

^{1}H NMR (300 MHz, THF), δ (ppm): 9.86 (d, 2H, ^3J= 4.5 Hz); 9.70 (d, 2H, ^3J=4.5 Hz); 8.90 (m, 3H); 8.82 (d, 2H, ^3J=4.5 Hz); 8.46 (m, 2H); 8.10 (s, 4H); 7.90 (s, 2H); 7.87 (d, 2H, ^3J=9 Hz); 6.97 (d, 2H, ^3J=9 Hz); 6.11 (s, 1H); 5.60 (s, 1H); 4.40 (t, 2H, ^3J=6 Hz); 3.78 (t, 2H, ^3J=6 Hz); 3.58 (q, 2H, ^3J=5 Hz); 1.95 (s, 3H); 1.58 (s, 36H); 1.28 (t, 3H, ^3J=5 Hz). UV–vis (CH_2Cl_2): λ_{max}, nm (ε, mol^{-1} L cm^{-1}): 463 (125,000); 691 (52,000). FT-IR (cm^{-1}): 2961 (s, *t*-Bu); 2867 (m, –CH_2–); 2168 (m, C≡C); 1742 (s, C=O acid); 1718 (m, C=O); 1518 (s, ν_{asym} NO_2); 1342 (s, ν_{sym} NO_2); 1212 (s, ν_s, C–O). HR-ESMS, *m/z*: calcd for $C_{73}H_{72}N_6O_6Zn$: 1193.488 ([M+H]$^+$·), found: 1193.487 ([M+H]$^+$·)

4.3. General procedure for porphyrin polymerization with glycidyl methacrylate (polymers 17 and 21)

A mixture of porphyrin (**16** or **20**) and glycidyl methacrylate (with a molar ratio porphyrin/GMA of 1:19 and 1:6, for respectively **17** and **21**) was dissolved in THF (25 mL/ 1 mmol porphyrin) in a sealed tube. AIBN was added (10% weight of the monomers) and the mixture was degassed by three freeze–pump–thaw cycles. The mixture was heated at 70 °C for 20 h. The mixture was added dropwise in 10 volumes of methanol to precipitate the polymer. The precipitate was filtered and intensively washed with methanol affording the polymer as a green powder.

4.3.1. Polymer 17. Yield: 80%, 280 mg. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.7–9.9 (m, 4H); 8.7–8.9 (m, 4H); 7.95–8.05 (m, 4H); 7.7–7.8 (m, 4H); 6.8–6.9 (m, 2H); 4.4–4.2 (m, 19H); 3.8–3.6 (m, 21H); 3.05–3.2 (m, 19H); 2.7–2.9 (m, 19H); 2.5–2.6 (m, 19H); 1.8–2.0 (m, 20H); 0.8–1.6 (m, 140H). FT-IR (cm^{-1}): 2961 (m); 2181 (w, C≡C); 1731 (s); 1148 (s); 907 (m, n_{as}, epoxy). GPC averages: ($\overline{M_n}$)=1900; ($\overline{M_w}$)=2400; PDI=1.2.

4.3.2. Polymer 21. Yield: 58%, 250 mg. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 9.7–9.9 (m, 4H); 8.8–9.0 (m, 4H); 7.6–8.2 (m, 8H); 6.8–7.0 (m, 2H); 4.4–4.2 (m, 11H); 3.8–3.6 (m, 13H); 3.05–3.2 (m, 11H); 2.5–2.9 (m, 22H); 0.8–2 (m, 80H). FT-IR (cm^{-1}): 2956 (m); 2178 (w, C≡C); 1730 (s); 1150 (s); 908 (m, n_{as}, epoxy). GPC averages: ($\overline{M_n}$)=5100; ($\overline{M_w}$)=8618; PDI=1.6.

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