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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.

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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 crosslinking 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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Keywords: Porphyrin; Push–pull; Polymer; Non-linear optic; Crosslinking.

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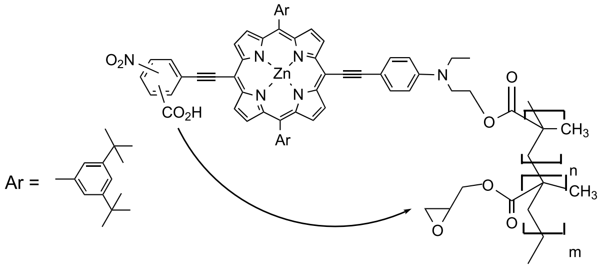


Figure 1. Structures of the electro-optic materials described in this study.

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).

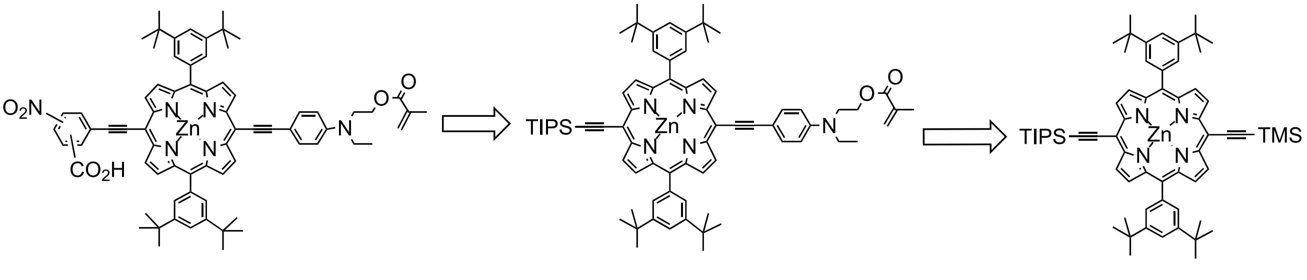
2. Results and discussion

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 (trimethyl silyl: 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



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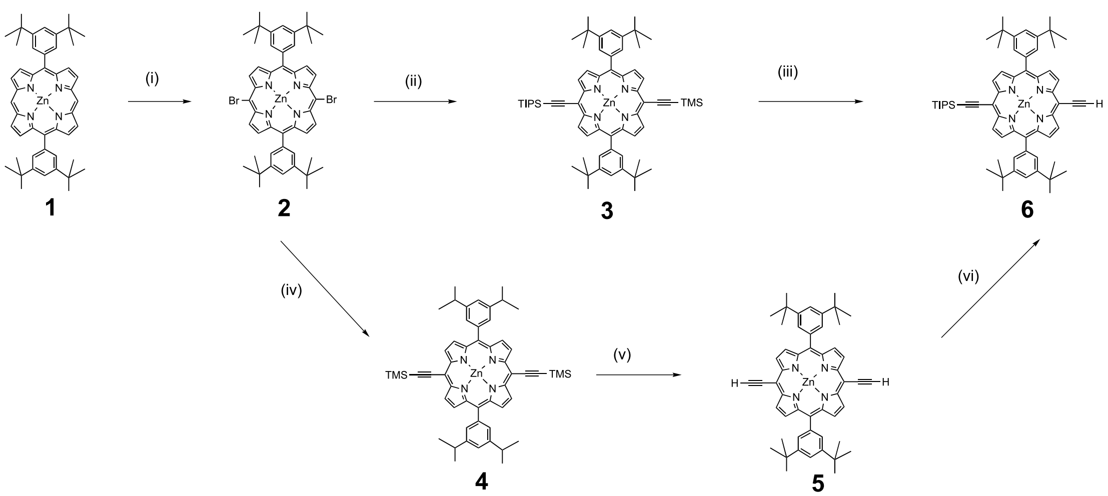
Scheme 1. Retrosynthetic scheme for the synthesis of the push–pull porphyrin.



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%.