

Communication

Bis(2,2,6,6-tetramethyl-1-(λ^1 -oxidaneyl)piperidin-4-yl) 3,3'-((2-hydroxyethyl)azanediyl)dipropionate

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Abstract: TEMPO-containing conductive polymers are used in organic electronics due to their electrochemical properties. One of significant limitations in developing such materials is the structural modification by several TEMPO moieties. Here, we report a synthesis of the first-generation dendrimer containing two TEMPO fragments, bis(2,2,6,6-tetramethyl-1-(λ^1 -oxidaneyl)piperidin-4-yl) 3,3'-((2-hydroxyethyl)azanediyl)dipropionate, that can be implemented into a conductive polymer structure. The resulting product was characterized using ^1H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) and high-resolution mass spectroscopy (HRMS).

Keywords: TEMPO; dendrimer; electrochemistry

1. Introduction

2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is a stable organic radical well known as a building block for the construction of redox polymers for organic radical batteries [1–7]. The advantages of such polymers in batteries and supercapacitors are their high redox potential and theoretical specific capacity [8]. The incorporation of TEMPO moieties in the polymer structure is a key challenge in the design of such conductive polymers due to their low thermal stability and chemical lability. For instance, an actual problem to be solved is to attach several TEMPO fragments to the monomeric unit of the conductive polymer. A possible solution of this problem may be to use the dendrimer-like scaffold [9] with a reactive focal fragment as a side chain of the conducting polymer, which can enhance the range of tools for developing such materials.

Here, we report the synthesis of a dendron-like compound bearing two TEMPO fragments on the basis of the amine-acrylate Michael dendron constructive approach. The obtained product was characterized using nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared spectroscopy (FTIR), and high-resolution mass spectrometry (HRMS).

2. Results and Discussion

The starting TEMPO-acrylate **1** was prepared using a modified procedure and its NMR spectra (Figures S1 and S2 in Supplementary Materials) are consistent with the literature [10].

The attempted Michael addition of 2-aminoethanol to acrylate **1** in primary alcohols (methanol or ethanol) suffered from the simultaneous alcoholysis of the product, which led to the formation of re-esterification products. The replacement of the primary alcohols by 2-propanol allowed us to avoid the undesired re-esterification. The treatment of 2-aminoethanol with 2 equivalents of **1** at room temperature in 2-propanol media (Scheme 1) resulted in the formation of the desired compound **2** with a 59% yield after purification via column chromatography.



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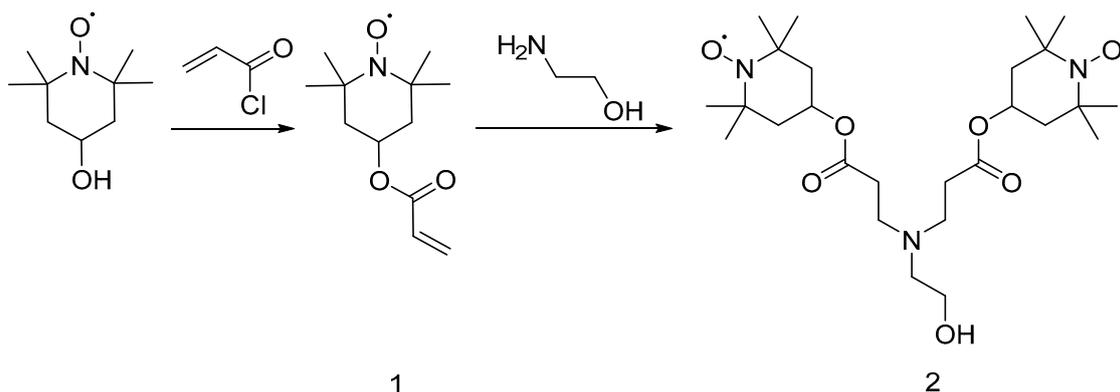
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Scheme 1. Synthesis of the title compound.

Since TEMPO fragments are paramagnetic, radical centers should be quenched to acquire the NMR spectra. The reductive quenching of the radical centers in **1** and **2** was performed in situ with the addition of the *N*-deuterated 2,3,4,5,6-pentafluorophenylhydrazine. To establish the purity of the product, quantitative ^1H NMR with *p*-xylene as internal standard was acquired (Figure S7). Accordingly, the sample was found to contain 98% of the title compound based on the integral intensity ratio.

As a result, a first-generation dendron with TEMPO periphery and a reactive -OH focal group was obtained. This compound can further be used to implement two TEMPO fragments at once to enhance the electrochemical and electrical properties of organic conductive polymers for organic electronics.

3. Materials and Methods

3.1. General Consideration

Reagents of “reagent grade” purity were purchased from Sigma–Aldrich (Hamburg, Germany). The starting TEMPO-acrylate **1** was prepared following the modified procedure in the literature [10]. ^1H and ^{13}C -NMR spectra were acquired on a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in CDCl_3 with the presence of *N*-deuterated 2,3,4,5,6-pentafluorophenylhydrazine. The Fourier-transform infrared spectra were recorded on the Shimadzu IRAffinity-1 FTIR spectrophotometer (Shimadzu Europa GmbH, Kyoto, Japan) in KBr pellets. The HRMS spectrum was recorded using electrospray ionization on a Bruker microTOF apparatus (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) in positive mode.

3.2. Synthesis of TEMPO-Acrylate **1**

To a solution of 4-hydroxyTEMPO (5.21 g, 30 mmol) with Et_3N (3.361 g, 33 mmol), 15 mL of dry dichloromethane acryloylchloride (3.011 g, 33 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. Then, the reaction solution was poured into cold water (100 mL), and organic layer was washed with brine, separated, and dried over Na_2SO_4 . The solvent was partly evaporated under reduced pressure and the residue was subjected to silica gel column chromatography (EtOAc/hexane 1:1) to obtain acrylate **1** (5.42 g, 80%) as orange crystals.

^1H NMR (400 MHz, CDCl_3) δ , ppm: 1.24 (s, 12H), 1.64 (t, $J = 12$ Hz, 2H), 1.97 (dd, $J = 4$ Hz, 12 Hz, 2H), 2.45 (t, $J = 7$ Hz, 4H), 5.14 (tt, $J = 4$ Hz, 11 Hz, 1H), 5.82 (dd, $J = 1.5$ Hz, 10 Hz 1H), 6.09 (dd, $J = 10$ Hz, 17 Hz, 1H), 6.39 (dd, $J = 1.5$ Hz, 17 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 20.58, 31.65, 43.72, 66.81, 128.75, 130.54, 165.74.

3.3. Synthesis of Bis(2,2,6,6-tetramethyl-1-(λ^1 -oxidaneyl)piperidin-4-yl 3,3'-((2-hydroxyethyl)azanediyl)dipropionate **2**

To a solution of **1** (1.12 g, 4.96 mmol) in dry isopropanol (10 mL), 2-aminoethanol (0.145 g, 2.4 mmol) was added. The reaction mixture was stirred at room temperature for 72 h. The resulting solution was then poured into water and extracted with dichloromethane (3 \times 40 mL). The organic phase was dried over sodium sulphate, the solvent was partly evaporated in vacuo, and the residue was purified using silica gel column chromatography (EtOAc/hexane 1:2), giving **2** as an orange oil (59%).

^1H NMR (400 MHz, CDCl_3) δ , ppm: 1.21 (s, 12H), 1.23 (s, 12H), 1.60 (t, J = 12 Hz, 4H), 1.92 (dd, J = 4 Hz, 12Hz, 4H), 2.45 (t, J = 7 Hz, 4H), 2.81 (t, J = 7 Hz, 4H), 3.59 (t, J = 5 Hz, 2H), 5.07 (m, 2H). 5.24 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ , ppm: 20.47, 31.72, 32.74, 43.71, 49.03, 55.75, 58.89, 59.52, 66.92, 172.09. FTIR (KBr) $\tilde{\nu}$, cm^{-1} : 2976 (br, C-H), 1730 (C=O ester). HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{48}\text{N}_3\text{O}_7^+$ 514.3487, found 514.3483.

The sample for the quantitative NMR analysis was prepared as follows: 21.0 mg of product **2** and 6.24 mg of *p*-xylene were precisely weighed in the NMR tube, dissolved in CDCl_3 , and quenched with *N*-deuterated 2,3,4,5,6-pentafluorophenylhydrazine. The quantity of the dendron was calculated from the ratio of the integral intensities of the aromatic singlet of the *p*-xylene on 7.09 ppm and the signal of the TEMPO protons at 1.92 ppm.

Supplementary Materials: Figures S1–S7: ^1H and ^{13}C NMR spectra for compounds **1** and **2**, FTIR and HRMS spectrum for compound **2**.

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