Pyridinium complexes supported on a polymeric biomaterial: Synthesis of NLO-phores at molecular level

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Abstract

It is known that pyridinium compounds such as betaines have interesting electronic characteristics including NLO properties. The main strands of this work include electronic modifications on pyridinium cation. We carried out a novel easy synthesis and characterization of new anchored pyridinium moieties into a polymeric backbone. Moreover, DFT calculations have been performed on suitable model to explore molecular parameters involved in lineal and non-lineal optical properties.

Keywords

Pyridinium salts, carbohydrates, NLO properties, DFT calculations

Introduction

Pyridinium salts are very useful synthetic building blocks to obtain substituted pyridines, dihydropyridines or piperidines. Furthermore, pyridinium dyes present multiple application fields including biological[1] and optical responses due to their photophysical features, in particular, high fluorescence, charge transfer character and solvatochromic properties.[2] Different methods are available for the synthesis of pyridinium salts depending on the symmetry around the cation. One of them involves the use of pyrylium salts as precursor.[3] These salts are cationic organic molecules with trivalent oxygen in a six member aromatic rings.[4] The factors that govern the reactivity of these cations have been previously reported.[5]

An increased number of compounds with NLO properties have been reported based on inorganic salts, organic zwitterions or *push-pull* molecules.[6] Linear and non-linear optical behaviours are controlled by different parameters at both macro- and microscopically level. At molecular level is necessary to know parameters such as dipole moment, polarizatility, first-order hyperpolarizability, among others.

On the other hand, chitosan as polymeric support has a wide working window in numerous areas of everyday life. This polymer was obtained from agroalimentary wastes of chitin crab shells and its transformation leave high added value products.

In this communication, we have focused on synthesis and characterization of a new anchored pyridinium moiety into a polymeric backbone. Moreover, DFT calculations have been performed on suitable model to explore molecular parameters involved in lineal and non-lineal optical properties.

Experimental Methods

All chemicals were purchased and used without further purification. Evaporations were conducted under reduced pressure. TLC was performed on silica gel plates (DC-Alufolien F254, E. Merck). The synthesis of pyrylium tetrafluorobate from aldehydes and ketones was previously carried out[3] and detection of compounds was accomplished with UV light (254 nm) and by charring with H_2SO_4 and characterization with NMR spectroscopy and Mass spectrometry.

For the synthesis of pyridinium salts, reaction between different pyrylium salts and amines were carried out by using acetic acid as catalyst.

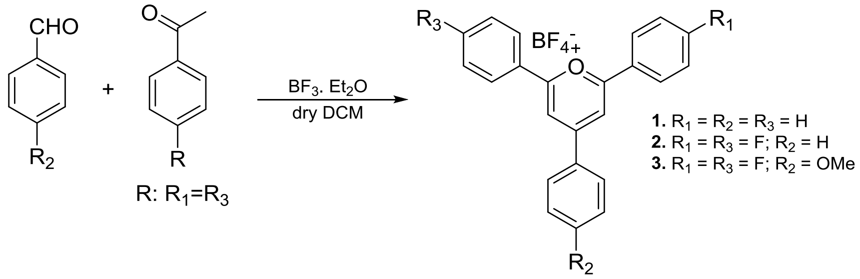
E.g.: *N*-[(1→4)-2-deoxy-*β*-D-glucanyl]-2,4,6-triphenylpyridinium tetrafluoroborate (**4**)

To a solution of chitosan (100 mg, 0.60 mmol) in AcOH aq. (25 mL) a solution of compound **1** (118.9 mg, 0.30 mmol) in MeOH (100 mL) was added. The resulting solution was heated to 65 ºC for 144 h. After that, monitoring of the reaction (TLC, MeOH) indicates an incorporation of salts. The reaction mixture was left to reach the room temperature and then was precipitated with 4 M NaOH (pH 12.3). The resulting solid was filtered off and successively washed with H_2O (2 × 2 mL), EtOH (2 × 4 mL), CH_2Cl_2 (2 × 2 mL) and acetone (2 × 2 mL) to leave compound **4** (84.1 mg, 97 %) as a yellow-pale solid. ^1H NMR (700 MHz, CD_3COOD/D_2O): δ 7.64-7.07 (17H, m), 4.93 (1H, s), 4.63 (1H, s), 3.95 – 3.75 (6H, m), 3.24 (1H, s) and 2.05 (3H, m).

Results and discussion

For generating the NLO-phore units on the polymer backbone is previously necessary to obtain the corresponding pyrylium complexes. These pyrylium salts are employed for reacting with the biopolymer. The substituents were chosen for modifying the electronic properties of the Chitosan derived system.

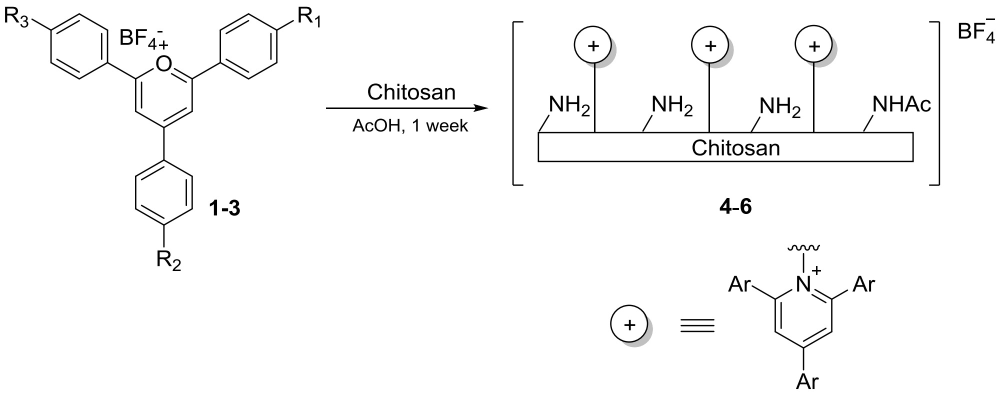
The synthesis of compounds **1-3** was carried out directly from aromatic aldehydes and ketones mediated with $BF_3.Et_2O$ (Scheme 1). After 24 h, fluorescent pyrylium salts were obtained with moderate yields.



Scheme 1. Synthesis of pyrylium salts from aldehydes and ketones

As previously described,[7] subsequent nucleophilic attack of the Chitosan amino groups to these pyrylium compounds gave the pyridinium complexes (**4-6**) supported on Chitosan as polycationic biomaterial (Scheme 2). Chitosan used for the synthesis presents a degree of deacetylation (DD) of 84 % and a molecular weight (M_w) of 87875 $gmol^{-1}$ determined by HPLC-SEC. In the case of compound **6**, the counter-anion acetate was confirmed by ^1H NMR.

The obtained compounds were characterized by both ^1H and ^{13}C NMR. ^1H NMR spectra show new protons in the range 7.89-6.84 ppm corresponding to the aromatic moiety introduced into Chitosan backbone. On the other hand, characteristic protons at 4.93 and 3.24 ppm are assigned to H-1 and H-2 of the carbohydrate moiety, respectively, were also observed.



Scheme 2. Synthesis of NLO-phore (**4-6**) from pyrylium salts and chitosan

For studying the NLO properties at molecular level, we performed DFT calculations at B3LYP level of theory (Table 1). Ideally, a good NLO-phore must have moderate dipole moment (μ) and highly first-order hyperpolarizability (β). All results obtained were compared with *p*-nitroaniline (PNA) as a simple model with non lineal optical properties.

Table 1. Molecular parameters (dipole moment, polarizability, first-order hyperpolarizability and HOMO-LUMO gap) for NLO features studied for compounds **4**-**6**.

Compound	μ_g (D)	α (a.u.)	β (10^{-30} esu)	$E_{HOMO-LUMO}$ (eV)
4	14.2	367	9.03	3.88
5	14.7	370	7.08	3.79
6	8.5	414	19.64	2.49
PNA	7.2	86	7.98	4.29

The results shed light that compound **6** have the best hyperpolarizabilty value (19.64×10^{-30} esu) compared with PNA (7.98×10^{-30} esu) and similar dipole moment. Furthermore, a decrease of β value (7.08×10^{-30} esu) with fluorine atoms at 2,6 positions is observed in compound **5**.

Conclusions

Synthesis of Chitosan pyridinium complexes (**4**-**6**) were easily carried out from pyrylium salts previously synthesized. Chitosan provides an environment non-centrosymmetric and thermal and chemical stability. By means of quantum calculation NLO parameters for model compounds have been explored. Taking into account the results obtained, compounds **4** and **6** proved to have better NLO properties than *p*-nitroanilene. The best NLO-phore studied turned to be compound **6** ($R_1 = R_3 = F$; $R_2 = OMe$) with a high polarizability and hyperpolarizability values.

Acknowledgements

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