

Amphiphilic polyenic push–pull chromophores for nonlinear optical applications

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Amphiphilic cationic polyenic push–pull chromophores which offer interesting supramolecular possibilities for second harmonic generation have been synthesised and their optical non-linearities studied for the first time by electric field induced second harmonic (EFISH) generation in solution.

Molecular nonlinear optics (NLO) has attracted increasing interest over the past ten years.¹ NLO materials are highly promising for applications in various fields including telecommunications, optical data storage and processing, optical power limitation *etc.* NLO phenomena also present interesting opportunities for probing and imaging purposes. For instance, second harmonic generation (SHG) has been successfully used for probing asymmetrical systems (such as interfaces)² or high resolution imaging of biological cells.³

Within this context, we have investigated a strategy based on the design of amphiphilic push–pull chromophores [*i.e.* molecules combining an electron-donating group (D) and an electron-withdrawing group (A) connected by a conjugated system] with enhanced quadratic molecular response (*i.e.* hyperpolarizability β) and prone to interact in an asymmetrical way with a lipid membrane. Such characteristics provide an interesting way to induce the asymmetry required for quadratic NLO phenomena both at the molecular and macroscopic levels, by taking advantage of specific interactions with hydrophilic–hydrophobic interfaces. Hereafter, we present the design and synthesis of amphiphilic cationic polyenic chromophores showing large nonlinearities. Their quadratic nonlinearities have been studied for the first time by electric field induced second harmonic (EFISH) generation in solution, a technique usually precluded for ionic species.

Stilbazolium dyes have been the topic of many studies in the field of NLO. They have led to highly SHG efficient crystals.⁴ In addition, they are interesting candidates for designing NLO micro- and nanostructures. For examples, derivatives bearing an elongated alkyl chain have been deposited into Langmuir–Blodgett films showing SHG activity⁵ and amphiphilic derivatives have been shown to be of interest for the design of optical probes for membrane potentials.⁶ Our choice has been to investigate amphiphilic vinylogous derivatives of stilbazolium dyes (Fig. 1). The presence of two butyl hydrophobic tails grafted on the donor end group and of the positively-charged hydrophilic acceptor moiety confers an amphiphilic character to these push–pull chromophores and should facilitate their interaction with a lipidic membrane while avoiding deleterious detergent effects. Increasing the polyenic chain length is expected to lead to a marked increase of β as already known for other push–pull polyenic systems.^{7–9} Similarly, by substituting

the pyridinium acceptor end group by a quinolinium end group, larger nonlinearities are expected.

Stilbazolium dyes and analogous chromophores are usually prepared using Konevenagel condensation (Scheme 1).⁶ However, this simple strategy proved ineffective in the case of polyenic analogues ($n > 1$) bearing long alkyl chains. It leads to both poor yields and purification problems due to the side formation of shorter homologues. To ensure satisfactory preparation yields, we have implemented an alternative synthetic scheme based on the Wittig–Horner condensation of a pyridine moiety¹⁰ on a polyenal bearing the donating end group (Scheme 1). This allows for the preparation in medium to good yield of compounds of series **4** from polyenals of series **1** using solid–liquid phase transfer conditions. Polyenals of series **1** can be obtained in high yields from the generic molecule **1**[0] using a sequential vinylic homologation.⁹ Molecules of series **4** were obtained as pure all-*E* isomers (as shown by NMR spectra and elemental analyses) after catalytic isomerisation and column chromatography ($n = 1, 2$) or recrystallisation ($n > 2$). Alkylation of molecules of series **4** in neat MeI readily afforded pure amphiphilic push–pull polyenic chromophores of series **2**.

The electric field induced second harmonic (EFISH) generation technique¹¹ is a useful method to derive the quadratic nonlinearity (and more precisely the projection of the dipolar part of the β tensor on the dipole moment μ) of dipolar chromophores. It is in principle precluded in the case of ionic species. Yet, we have been able to implement the EFISH technique for the determination of the $\mu\beta$ values of ionic amphiphilic chromophores **2** and **3** by operating in a solvent of low polarity thanks to the formation of close ion pairs. The EFISH experiments were carried out in chloroform ($\epsilon_r = 4.7$) and at 1.907 μm in order to avoid absorption of the second harmonic. The $\mu\beta$ values and the wavelength of the maximum absorption (λ_{max}) are collected in Table 1. The static $\mu\beta(0)$ values extrapolated at zero frequency by using the two-level dispersion model for β ¹¹ (valid in the case of 1-D intramolecular charge transfer only) are also included.

As clearly observed from Table 1, amphiphilic salts of series **2**[*n*] and **3**[1] show large $\mu\beta$ values. Lengthening the polyenic chain induces both a bathochromic shift and a significant increase of the quadratic nonlinearity, although the effect seems to slow down for the longest derivatives. This leads to a $\mu\beta(0)$

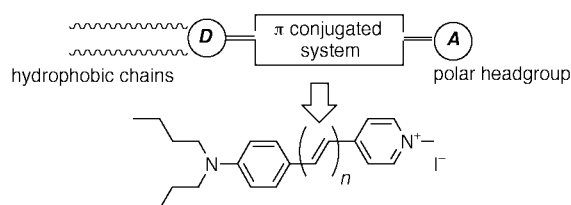
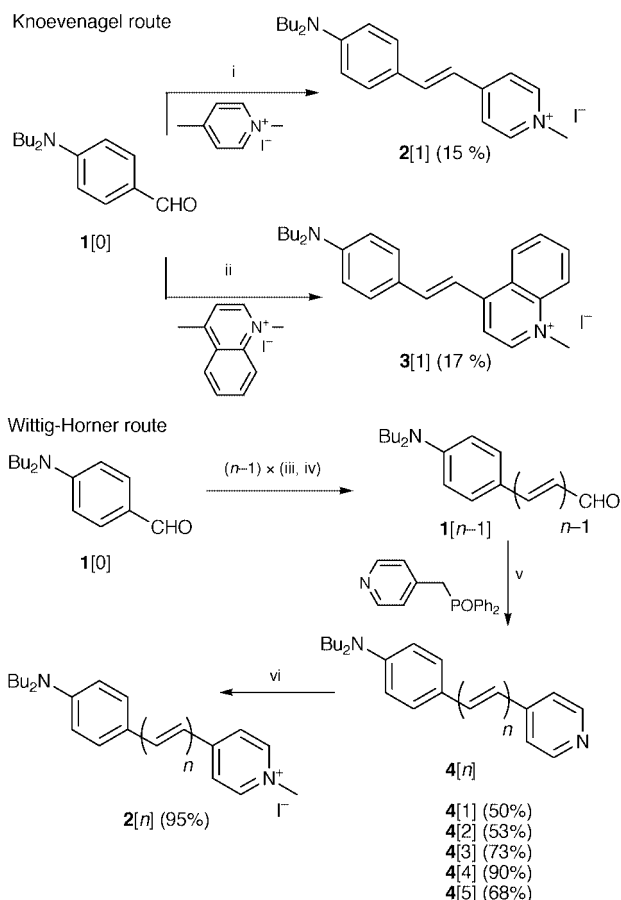


Fig. 1 Molecular engineering of amphiphilic push–pull chromophores.

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Scheme 1 Reagents and conditions: i, *N*-methyl-4-picolinium iodide (0.9 equiv.), cat. piperidine, EtOH, reflux, 16 h; ii, *N*-methyllepidinium iodide (0.9 equiv.), cat. piperidine, EtOH, reflux, 16 h; iii, (1,3-dioxolan-2-ylmethyl)tributylphosphonium bromide (1.1 equiv.), NaH (1.5 equiv.), cat. 18-C-6, THF, room temp., 20 h; iv, HCl (10%), THF, room temp., 1 h; v, diphenyl(4-pyridyl)methylphosphine oxide (1.1 equiv.), THF, NaH (1.5 equiv.), cat. 18-C-6, room temp. 15 h; vi, MeI, room temp., 1 h.

Table 1 Linear and nonlinear optical properties of amphiphilic push-pull chromophores **2**[1–5] and **3**[1] in chloroform; $\mu\beta$ values were derived from EFISH measurements at 1.907 μm

Compound	$\mu\beta(2\omega)^a/10^{-48}$ esu	$\lambda_{\text{max}}/\text{nm}$	$\mu\beta(0)/10^{-48}$ esu
2 [1]	840	517	550
2 [2]	2230	558	1340
2 [3]	2700	581	1540
2 [4]	3380	589	1890
2 [5]	3690	598	2020
3 [1]	1380	603	745

^a The β values are defined using the X convention (ref. 15).

value as high as 2000×10^{-48} esu for the **2**[5] ion pair, which is more than four times larger than the corresponding experimental value (450×10^{-48} esu) determined in similar conditions for the benchmark *dipolar* chromophore Disperse Red 1. Compound **3**[1], which bears the stronger heterocyclic acceptor, shows a $\mu\beta(0)$ value about 50% larger than that of compound **2**[1], but at the expense of a much reduced

transparency. Compound **2**[3] exhibits a $\mu\beta(0)$ value twice as large as that for compound **3**[1] for a similar molecular weight while remaining significantly blue-shifted. Elongation of the polyenic chain of derivatives of series **2** is thus preferable—in terms of nonlinearity–transparency trade-off—to turning to a stronger acceptor moiety.

Finally, cationic polyenic push–pull chromophores have been synthesised and their optical non-linearities studied for the first time by electric field induced second harmonic generation in solution, owing to the formation of ion pairs in a solvent of low relative permittivity. Their quadratic nonlinearities can be enhanced by increasing the polyenic chain length and/or adjusting the charged heterocyclic acceptor. Recent second harmonic generation and two-photon excited fluorescence experiments reported in ref. 12 provide evidence that chromophores of type **2** are incorporated in the outer leaflet of model bilayer lipid membranes and orientated perpendicular to the membrane surface. These amphiphilic chromophores hold promise as sensitive probes for SHG imaging of membrane potentials.^{3,13} In addition, incorporation of the chromophores in the lipid bilayer is expected to significantly influence the molecular nonlinear responses, as shown recently for the inclusion of a stilbazolium dye in a supramolecular complex.¹⁴

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