



Unprecedented intramolecular cyclization in strongly dipolar extended merocyanine dyes: A route to novel dyes with improved transparency, nonlinear optical properties and thermal stability



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ARTICLE INFO

Article history:

Received 25 January 2016

Received in revised form

6 March 2016

Accepted 7 March 2016

Available online 9 March 2016

Keywords:

Merocyanine dyes

Hyperpolarizability

Hyper-Rayleigh scattering

Nonlinear optics

Intramolecular charge transfer

ABSTRACT

Novel magenta dyes were obtained via an unprecedented base-promoted intramolecular cyclization of strongly dipolar elongated merocyanine dyes bearing a phthalimide substituted tricyanopropylidene terminal segment. These shorter diarylpolyene derivatives retain a dipolar character and show a typical intramolecular charge transfer (ICT) transition. The cyclization noticeably modifies the electronic structure inducing both onset of bond length alternation and reduction of dipole moment as well as a marked hypsochromic and hypochromic shift of the ICT absorption band compared to their merocyanine precursors. Yet the new dyes show improved quadratic hyperpolarizability and thermal stability as compared to the merocyanine dyes having the same number of conjugated double bonds in the polyenic linker. As such these derivatives hold promise as new class of dyes for NLO materials and SHG probes.

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1. Introduction

Push-pull chromophores have gained tremendous interest in recent decades due to their many applications in various fields including nonlinear optics (NLO), NLO bioimaging, biochemical sensing, solar cells, etc. [1]. Push-pull systems are generally composed of an electron-releasing group (or donor D) connected to an electron-withdrawing group (or acceptor A) via a π -conjugated linker. Among them push-pull polyenes have attracted a lot of

attention due to their large electronic polarizability. A number of reports on different series of push-pull polyenes have shown that the structure of the chromophore, i.e., length of the π -conjugated chain, and nature of the D and A groups play a vital role in achieving huge optical nonlinearities (i.e., quadratic and cubic hyperpolarizabilities) [2]. From a synthetic point of view, in many occurrences, D- π -A based polyenic chromophores were prepared starting from the donor end followed by stepwise vinylic elongation [2,3]. Elongation of the polyenic structures with terminal carbonyl functionalities was usually achieved by a Wittig oxypropenylation method [2b,4] or via an iminium salt (activated equivalent of aldehyde) formation [5]. Finally, the end carbonyl functionalities were subjected to Knoevenagel condensation with the acceptors bearing an active methylene group or Wittig/Horner-Wadsworth-Emmons reactions with corresponding electron deficient phosphonium salts/phosphonates to achieve variety of D-A polyenic chromophores [2,3]. These D- π -A molecules exhibit an intense absorption band in the visible region due to an intramolecular charge transfer (ICT) phenomenon.

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In terms of acceptor group, the popularity of polycyano acceptors is well documented in the literature [6]. Among them, 2-amino-1,1,3-tricyano-1-propene has caught our attention as it has been explored not only in the preparation of several dyes for application in NLO but also as a crucial building block for heterocyclic synthesis [7]. In continuation to our efforts on push–pull chromophores for NLO, we recently reported the synthesis of a new set of chromophores incorporating *N,N*-dihexylamino-substituted thiophene as strong donor and phthalimide substituted tricyanopropylidene as strong acceptor while varying the π -conjugation length (n) from $0 \rightarrow 3$ (Chart 1). For this, we followed a synthetic strategy as sketched in Scheme 1. The synthetic protocols as well as the linear and nonlinear optical properties and large dipole moments of derivatives **2** have been described in detail in our recent publication [8]. Although the optical properties of such various yellow/orange or magenta dyes derived from the condensation reactions of malononitrile dimer have been measured [2,3], the fate of such in reaction media in relation to the extension of conjugation has been scarcely registered. In this report, we present an unprecedented observation that we came across during the final step of base-mediated dehydrative cyclocondensation of the π -extended amines **3** (when $n > 1$) with phthalic anhydride (Scheme 1). Interestingly, besides formation of the desired product **2**, we noted a product **1** that is shorter in conjugation length ($n-1$) formed as a result of consecutive intramolecular cyclization (Chart 1). The resultant novel cyclized products **1**, viz., phenylthienylethene derivatives, obtained along with **2** during the final step via an intramolecular cyclization are thoroughly characterized and the mechanism for the intramolecular cyclization reaction has been investigated. Herein, we focus our attention mainly on the linear and nonlinear optical as well as on the thermal properties of these newly derived products **1** and on their comparison with the analogous linear π -extended molecules **2**. The experimental studies are further supported by theoretical calculations to identify the alteration of electronic structure induced by cyclization and responsible for the modification in optical properties.

2. Results and discussion

2.1. Synthesis

The general synthetic approach for the preparation of extended push–pull chromophores is described below (Scheme 1). As shown in Scheme 1, the push–pull polyenals upon Knoevenagel condensation with malononitrile dimer (2-amino-1,1,3-tricyanopropene) yielded the required amino compounds **3** which upon further

condensation with phthalic anhydride in the presence of triethylamine afforded the corresponding polyenic push–pull chromophores **2** [8]. The resultant polyenic push–pull chromophores (both amines **3** and imides **2**) were strongly colored. The synthesis of the imides **2** has been published earlier [8] and will thus not be discussed here in detail. Imides **2** were shown to exhibit an intriguing typical cyanine-like behavior and specific features associated with non-alternated conjugated π -system, i.e., narrow absorption band that steadily shifts from the visible to the NIR region upon increasing length (vinylene shift of about 110 nm). This cyanine-like behavior implies a significant and steady ($\rho = 0.5$) intramolecular charge transfer from the electron-donating end moiety to the electron-withdrawing opposite end in the ground state, resulting in steadily increasing dipole moment values with increasing polyenic chain length. As a result compounds **2c** and **2d** exhibit unusually large dipole moments (i.e. over 20D) while showing exponentially increasing quadratic polarizability (β), thus breaking the well-known Bond Length Alternation (BLA)- β paradigm. We propose that these unusually large dipole moment values may facilitate intramolecular cyclization in solution (see below).

Indeed during the synthesis of **2c,d** from amines **3c,d**, we observed the formation of side products **1c,d**, respectively, in reasonable amounts; under the same reaction conditions, **3c** afforded the by-product **1c** in 16% yield while **3d** yielded **1d** in 32%. The isolated by-products **1c,d** were soluble in common organic solvents, such as, toluene, chloroform, dichloromethane, tetrahydrofuran, ethyl acetate, etc. and they were different in color when compared to their polyenic counterparts **2** and **3**. All these compounds were thoroughly characterized and identified by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

2.2. ^1H NMR and theoretical studies: identification of the structure of compounds **1c-d**

As mentioned earlier, the reaction from **3** to **2** afforded the side product **1** for compounds with $n > 1$ (Scheme 1), which was isolated carefully and analyzed by ^1H NMR spectroscopy. ^1H NMR spectrum of **1-3** in deuterated chloroform revealed all-*trans* geometry for the protons at the poly[n]enic backbone. The polyenic protons were assigned based on ^1H - ^1H COSY experiments. Notably, other than the two doublets ($J = 4.0$ Hz) for the thiophene protons, ^1H NMR spectrum of the side product **1c** in chloroform-*d* revealed two doublets centered at 7.73 and 7.77 ppm with a characteristic *ortho* coupling value of $J = 8.5$ Hz, each integrating for one proton, respectively. In addition, ^1H NMR spectrum of **1c** revealed *trans*-olefinic protons at 6.61 and 7.47 ppm with a characteristic J value of

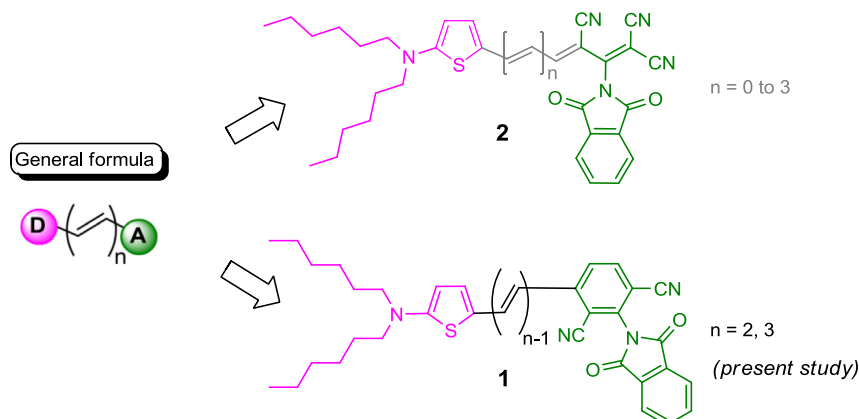


Chart 1. General formula for the chemical structures of push–pull systems **1** and **2**.

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