N-Methylquinolinium derivatives for photonic applications: Enhancement of electron-withdrawing character beyond that of the widely-used N-methylpyridinium

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ARTICLE INFO

ABSTRACT

A series of π-conjugated styryl quinolinium push–pull chromophores have been designed and synthesized in order to examine the electron-withdrawing strength of various quinolinium electron acceptor groups, and their influence on the photophysical properties and in particular on the second-order nonlinear optical response. The static molecular first hyperpolarizabilities measured by long-wavelength hyper-Rayleigh scattering are found to follow the order of the electron withdrawing strength of their acceptor groups as determined by NMR analysis. The quinolinium chromophores based on the strongest electron acceptor groups (1,2- and 1,4-dimethylquinolinium) exhibit remarkably large first hyperpolarizability values of 233 and 256×10^{-30} esu respectively, which is higher than that of the well-known and widely-used pyridinium analogue 4-(4-(dimethylamino)styryl)-1-methylpyridinium 4-methylbenzenesulfonate with first hyperpolarizability $= 183 \times 10^{-30}$ esu. The dimethylquinolinium electron acceptor groups exhibit increased electron-withdrawing strength compared to the dimethylpyridinium group used in 4-(4-(dimethylamino)styryl)-1-methylpyridinium 4-methylbenzenesulfonate, and therefore have a high potential for photonic applications.

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1. Introduction

Organic π-conjugated molecules with electron donor and acceptor groups are very attractive for numerous photonic applications including nonlinear optics (NLO) [1–9], electroluminescence [10–13], photovoltaics [14], and molecular electronics [15]. Typically (e.g. for the case of stilbene derivatives), the molecular second-order NLO response (expressed by the first hyperpolarizability β) increases with increasing electron-withdrawing strength of the electron acceptor group [16], which generally also results in an increase of the wavelength of maximum absorption λ_{abs} [1] and of the wavelength of maximum emission λ_{em} [12]. Therefore, the electron-withdrawing strength of electron acceptor groups is obviously very important to obtain the desired optical and photophysical properties for many applications.

Up to now, a wide range of electron acceptor groups have been investigated [1–4,16–31]. Among them, heteroaromatic salt-type electron acceptors exhibit large electron-withdrawing strength and lead to a large molecular NLO response [25–31]. For example, the well-known and widely applied styryl pyridinium analogue DAST (4-(4-(dimethylamino)styryl)-1-methylpyridinium 4-methylbenzenesulfonate) [25,26] – having a pyridinium electron acceptor (see Fig. 1a) – exhibits a large molecular optical nonlinearity with a high static first hyperpolarizability β_0 of 150-194 $\times 10^{-30}$ esu [31,32] and derivatives which are soluble in water as well as organic solvents have been developed [24]. Recently, a quinolinium electron acceptor group has been introduced [33–38]. The HMQ cation (2-(4-hydroxy-3-methoxystyryl)-1-methylquinolinium) based on a quinolinium electron acceptor (see Fig. 1b), exhibits a large molecular nonlinearity and has moreover led to several bulk materials with a large macroscopic
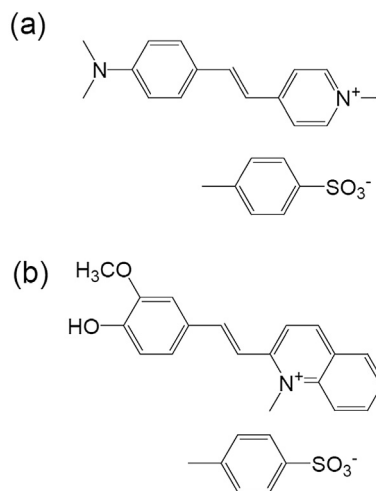
Fig. 1. The chemical structure of (a) the styryl pyridinium chromophore DAST and (b) the previously studied styryl quinolinium chromophore.

nonlinear optical response [33–35,38]. However, for quinolinium derivatives the electron-withdrawing strength and its influence on the photophysical properties have not been fully characterized yet.

Here we designed and synthesized a series of π-conjugated styryl quinolinium chromophores based on various quinolinium electron acceptors (see Fig. 2). We analyzed the electron-withdrawing strength of the styryl quinolinium chromophores in relation to their optical nonlinearity and photophysical properties. Compared to the structurally similar pyridinium-based DAST chromophore, the quinolinium-based derivatives exhibit large differences in electron-withdrawing strength, and consequently in absorption and fluorescence behavior, as well as in NLO response.

2. Experimental

2.1. Synthesis of the quinolinium intermediates

To synthesize the chromophores based on quinolinium electron acceptors, various dimethylquinolinium (DMQ) 4-methylbenzenesulfonate (DMQ-T) intermediates (see Fig. 3) were synthesized in a similar manner as reported previously [33–35]. Methanol was used as solvent for DMQ1,6-T and DMQ1,3-T, and 1,2-dimethoxyethane was used for DMQ1,2-T, DMQ1,7-T, DMQ2,3-T and DMQ1,4-T.

#### 2.1.1. 1,2-dimethylquinolinium 4-methylbenzenesulfonate (DMQ1,2-T)

A mixture of 2-methylquinoline (50 mL, 0.351 mol) and methyl 4-methylbenzenesulfonate (54 mL, 0.351 mol) in 1,2-dimethoxyethane (300 mL) was stirred at 50 °C. After stirring for 6 days, the precipitated powder was filtered and then dried in vacuum oven at 100 °C for overnight [33]. Yield = 35%. M.p. 164 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.07 (d, 1H, J = 8.4 Hz, C_5H_2N), 8.57 (d, 1H, J = 8.8 Hz, C_6H_4), 8.38 (d, 1H, J = 8.4 Hz, C_5H_2N), 8.21 (m, 1H, C_6H_4), 8.09 (d, 1H, J = 8.4 Hz, C_6H_4), 7.97 (t, 1H, J = 7.6 Hz, C_6H_4), 7.44 (d, 2H, J = 8.4 Hz, $C_6H_4SO_3^-$), 7.08 (d, 2H, J = 8.4 Hz, $C_6H_4SO_3^-$), 4.42 (s, 3H, NCH_3), 3.05 (s, 3H, CH_3), 2.26 (s, 3H, CH_3). Elemental analysis for $C_{18}H_{19}NO_3S$: Calcd. C 65.63, H 5.81, N 4.25, S 9.73; Found: C 65.63, H 5.84, N 4.27, S 9.76.

2.1.2. 1,7-dimethylquinolinium 4-methylbenzenesulfonate (DMQ1,7-T)

A mixture of 7-methylquinoline (0.70 g, 4.89 mmol) and methyl 4-methylbenzenesulfonate (0.74 mL, 4.89 mmol) in 1,2-dimethoxyethane (30 mL) was stirred at 50 °C. After stirring for 4 days, the precipitated powder was filtered and then dried in vacuum oven at 65 °C for overnight. Yield = 42%. M.p. 182 °C. ^{1}H NMR
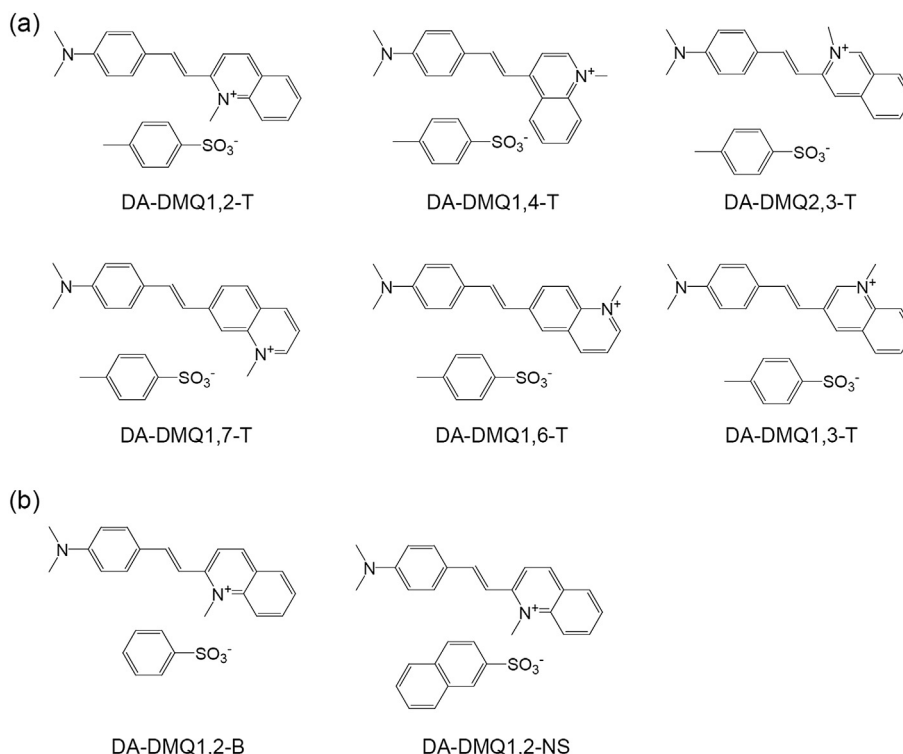
Fig. 2. Chemical structures of the investigated styryl quinolinium chromophores.
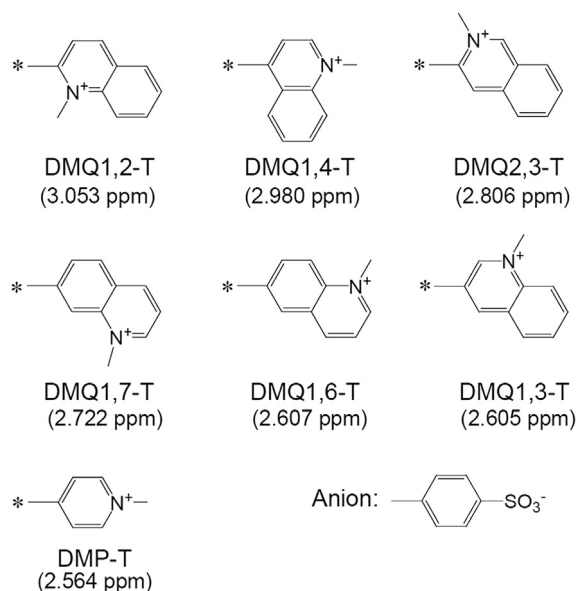
Fig. 3. Chemical structures of the dimethylquinolinium (DMQ) derivatives, as well as dimethylpyridinium (DMP) as in the DAST reference compound. The asterisk presents the activated methyl group which forms a double bond with the aldehyde in the condensation reaction. ^{1}H NMR chemical shifts of the activated methyl group are indicated as a measure of acceptor strength (see Fig. 4).

(400 MHz, DMSO-d_6, δ): 9.43 (d, 1H, J = 5.6 Hz, C$_5$H$_2$N), 9.22 (d, 1H, J = 8.0 Hz, C$_6$H$_4$), 8.38 (d, 1H, J = 8.4 Hz, C$_5$H$_2$N), 8.34 (m, 1H, C$_6$H$_4$), 8.10 (t, 1H, J = 8.4 Hz, C$_6$H$_4$), 7.93 (d, 1H, J = 9.6 Hz, C$_6$H$_4$), 7.48 (d, 2H, J = 8.4 Hz, C$_6$H$_4$SO$_3^-$), 7.12 (d, 2H, J = 8.4 Hz, C$_6$H$_4$SO$_3^-$), 4.60 (s, 3H, NCH$_3$), 2.72 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$). Elemental analysis for C$_{18}$H$_{19}$NO$_3$S: Calcd. C 65.63, H 5.81, N 4.25, S 9.73; Found: C 65.60, H 5.79, N 4.28, S 9.76.

2.1.3. 1,6-dimethylquinolinium 4-methylbenzenesulfonate (DMQ1,6-T)

A mixture of 6-methylquinoline (5.00 mL, 36.50 mmol) and methyl 4-methylbenzenesulfonate (5.51 mL, 36.50 mmol) in methanol (50 mL) was stirred at 50 °C. After stirring for 1 day, a product was precipitated by evaporating methanol and added 1,2-dimethoxyethane. The precipitated powder was filtered and then dried in vacuum oven at 100 °C for overnight. Yield = 81%. M.p. 152 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.39 (d, 1H, J = 5.2 Hz, C$_5$H$_3$N), 9.12 (d, 1H, J = 8.0 Hz, C$_5$H$_3$N), 8.39 (d, 1H, J = 8.8 Hz, C$_6$H$_3$), 8.21 (s, 1H, C$_6$H$_3$), 8.11 (d, 1H, J = 9.2 Hz, C$_6$H$_3$), 8.09 (t, 1H, J = 7.0 Hz, C$_5$H$_3$N), 7.44 (d, 2H, J = 8.0 Hz, C$_6$H$_4$SO$_3^-$), 7.07 (d, 2H, J = 7.6 Hz, C$_6$H$_4$SO$_3^-$), 4.58 (s, 3H, NCH$_3$), 2.60 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$). Elemental analysis for C$_{18}$H$_{19}$NO$_3$S: Calcd. C 65.63, H 5.81, N 4.25, S 9.73; Found: C 65.66, H 5.83, N 4.26, S 9.80.

2.1.4. 1,3-dimethylquinolinium 4-methylbenzenesulfonate (DMQ1,3-T)

A mixture of 3-methylquinoline (2.00 mL, 14.78 mmol) and methyl 4-methylbenzenesulfonate (2.27 mL, 14.78 mmol) in methanol (50 mL) was stirred at 50 °C. After stirring for 2 days, a product was precipitated by evaporating methanol and added 1,2-dimethoxyethane. The precipitated powder was filtered and then dried in vacuum oven at 100 °C for overnight. Yield = 79%. M.p. 174 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.46 (s, 1H, C$_5$H$_2$N), 9.05 (s, 1H, C$_5$H$_2$N), 8.43 (d, 1H, J = 9.2 Hz, C$_6$H$_4$), 8.33 (d, 1H, J = 8.0 Hz, C$_6$H$_4$), 8.18 (m, 1H, C$_6$H$_4$), 7.99 (t, 1H, J = 8.0 Hz, C$_6$H$_4$), 7.44 (d, 2H, J = 8.4 Hz, C$_6$H$_4$SO$_3^-$), 7.07 (d, 2H, J = 7.6 Hz, C$_6$H$_4$SO$_3^-$), 4.58 (s, 3H, NCH$_3$), 2.61 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$). Elemental analysis for C$_{18}$H$_{19}$NO$_3$S: Calcd. C 65.63, H 5.81, N 4.25, S 9.73; Found: C 65.66, H 5.83, N 4.24, S 9.69.

2.1.5. 2,3-dimethylisoquinolinium 4-methylbenzenesulfonate (DMQ2,3-T)

A mixture of 3-methylisoquinoline (1.45 g, 9.92 mmol) and methyl 4-methylbenzenesulfonate (1.53 mL, 9.92 mmol) in 1,2-dimethoxyethane (40 mL) stirred at 50 °C. After stirring for 5 days, the precipitated powder was filtered and then dried in vacuum oven at 50 °C for overnight. Yield = 65%. M.p. 174 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 10.00 (s, 1H, C$_5$H$_2$N), 8.41 (s, 1H, C$_5$H$_2$N), 8.37 (d, 1H, J = 8.4 Hz, C$_6$H$_4$), 8.17 (d, 1H, J = 4.8 Hz, C$_6$H$_4$), 8.16 (t, 1H, J = 6.6 Hz, C$_6$H$_4$), 7.96 (m, 1H, C$_6$H$_4$), 7.44 (d, 2H, J = 8.0 Hz, C$_6$H$_4$SO$_3^-$), 7.07 (d, 2H, J = 7.6 Hz, C$_6$H$_4$SO$_3^-$), 4.36 (s, 3H, NCH$_3$), 2.81 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$). Elemental analysis for C$_{18}$H$_{19}$NO$_3$S: Calcd. C 65.63, H 5.81, N 4.25, S 9.73; Found: C 65.62, H 5.81, N 4.24, S 9.76.

2.1.6. 1,4-dimethylisoquinolinium 4-methylbenzenesulfonate (DMQ1,4-T)

A mixture of 4-methylquinoline (2.00 g, 33.00 mmol) and methyl 4-methylbenzenesulfonate (2.62 g, 33.00 mmol) in 1,2-dimethoxyethane (20 mL) was stirred at 50 °C. After stirring for 5 days, the precipitated powder was filtered and then dried in vacuum oven at 70 °C for overnight. Yield = 87%. M.p. 156 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.33 (d, 1H, J = 6.0 Hz Hz, C$_5$H$_2$N), 8.52 (d, 1H, J = 7.6 Hz, C$_6$H$_4$), 8.47 (d, 1H, J = 9.2 Hz, C$_6$H$_4$), 8.27 (t, 1H, J = 15.6 Hz, C$_6$H$_4$), 8.06 (t, 1H, J = 15.2 Hz, C$_6$H$_4$), 8.03 (d, 1H, J = 4.8 Hz, C$_5$H$_2$N), 7.45 (d, 2H, J = 6.8 Hz, C$_6$H$_4$SO$_3^-$), 7.09 (d, 2H, J = 7.6 Hz, C$_6$H$_4$SO$_3^-$), 4.55 (s, 3H, NCH$_3$), 2.98 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$). Elemental analysis for C$_{18}$H$_{19}$NO$_3$S: Calcd. C 65.63, H 5.81, N 4.25, S 9.73; Found: C 65.64, H 5.82, N 4.27, S 9.77.

2.2. Synthesis of the quinolinium-based chromophores (I)

The quinolinium-based chromophores with 4-methylbenzenesulfonate (see Fig. 2a) were synthesized by a condensation of 4-(dimethylamino)benzaldehyde with the corresponding dimethylquinolinium 4-methylbenzenesulfonate (DMQ-T) intermediates in a similar manner as reported previously [33]. For comparison, the pyridinium-based DAST chromophore was synthesized by a condensation of 4-(dimethylamino)benzaldehyde with 1,4-dimethylpyridinium 4-methylbenzenesulfonate (DMP-T) in a similar manner as reported previously [27].

2.2.1. 2-(4-(dimethylamino)styryl)-1-methylquinolinium 4-methylbenzenesulfonate (DA-DMQ1,2-T)

The intermediate DMQ1,2-T (5.00 g, 15.18 mmol) and 4-(dimethylamino)benzaldehyde (2.26 g, 15.18 mmol) were dissolved in methanol (100 mL) and the catalyst piperidine (0.5 mL, 5.00 mmol) was added in the solution. After stirring for 2 days at 70 °C, the solution was cooled to room temperature and filtered. The final product was obtained by recrystallization in methanol and dried in vacuum oven at 100 °C for overnight. Yield = 28%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.79 (d, 1H, J = 8.8 Hz, C$_5$H$_2$N), 8.49 (d, 1H, J = 9.2 Hz, C$_6$H$_4$), 8.41 (d, 1H, J = 8.4 Hz, C$_5$H$_2$N), 8.25 (d, 1H, J = 14.8 Hz, CH), 8.22 (d, 1H, J = 6.4 Hz Hz, C$_6$H$_4$), 8.07 (m, 1H, C$_6$H$_4$), 7.84 (d, 2H, J = 8.8 Hz, C$_6$H$_4$), 7.83 (t, 1H, J = 7.6 Hz, C$_6$H$_4$), 7.55 (d, 1H, J = 15.6 Hz, CH), 7.44 (d, 2H, J = 8.4 Hz, C$_6$H$_4$SO$_3^-$), 7.09 (d, 2H, J = 7.6 Hz, C$_6$H$_4$SO$_3^-$), 6.82 (d, 2H, J = 9.2 Hz, C$_6$H$_4$), 4.43 (s, 3H, NCH$_3$), 3.07 (s, 6H, NCH$_3$), 2.27 (s, 3H, CH$_3$). Elemental analysis for C$_{27}$H$_{28}$N$_2$O$_3$S: Calcd. C 70.41, H 6.13, N 6.08, S 6.96; Found: C 70.46, H 6.15, N 6.07, S 6.78.

2.2.2. 3-(4-(dimethylamino)styryl)-2-methylisoquinolinium 4-methylbenzenesulfonate (DA-DMQ2,3-T)

The intermediate DMQ2,3-T (2.17 g, 6.48 mmol) and 4-(dimethylamino)benzaldehyde (1.49 g, 9.72 mmol) were dissolved in methanol (50 mL). After adding the catalyst piperidine (0.26 mL, 2.6 mmol), the solution was stirred for 12 days at 70 °C. After the reaction, the solution was cooled to room temperature and a product was precipitated by evaporating methanol and added 1,2-dimethoxyethane. The solution was filtered and filtrate was dried in vacuum oven. The final product was obtained by recrystallization in methanol and diethyl ether and dried in vacuum oven at 100 °C for overnight. Yield = 27%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.89 (s, 1H, C_5H_2N), 8.84 (s, 1H, C_5H_2N), 8.30 (d, 1H, J = 8.4 Hz, C_6H_4), 8.18 (d, 1H, J = 8.0 Hz, C_6H_4), 8.11 (t, 1H, J = 8.0 Hz, C_6H_4), 8.11 (t, 1H, J = 8.2 Hz, C_6H_4), 7.67 (d, 1H, J = 15.6 Hz, CH), 7.65 (d, 2H, J = 8.8 Hz, C_6H_4), 7.45 (d, 2H, J = 8.4 Hz, $C_6H_4SO_3^-$), 7.33 (d, 1H, J = 15.6 Hz, CH), 7.08 (d, 2H, J = 8.0 Hz, $C_6H_4SO_3^-$), 6.77 (d, 2H, J = 8.8 Hz, C_6H_4), 4.45 (s, 3H, NCH₃), 3.00 (s, 3H, CH₃), 2.26 (s, 3H, CH₃). Elemental analysis for $C_{27}H_{28}N_2O_3S$: Calcd. C 70.41, H 6.13, N 6.08, S 6.96; Found: C 70.44, H 6.10, N 6.09, S 6.96.

2.2.3. 4-(4-(dimethylamino)styryl)-1-methylquinolinium 4-methylbenzenesulfonate (DA-DMQ1,4-T)

The intermediate DMQ1,4-T (1.00 g, 3.04 mmol) and 4-(dimethylamino)benzaldehyde (0.46 g, 3.04 mmol) were dissolved in methanol (20 mL). After adding the catalyst piperidine (0.06 mL, 0.61 mmol), the solution was stirred for 2 days at 70 °C. After the reaction, the solution was cooled to room temperature and filtered. The final product was obtained by recrystallization in methanol and dried in vacuum oven overnight. Yield = 14%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.09 (d, 1H, J = 6.8 Hz, C_5H_2N), 9.01 (d, 1H, J = 8.4 Hz, C_5H_2N), 8.32 (d, 1H, J = 6.8 Hz, C_6H_4), 8.32 (d, 1H, J = 6.8 Hz, C_6H_4), 8.19 (t, 1H, J = 7.8 Hz, C_6H_4), 8.16 (d, 1H, J = 15.6 Hz, CH), 8.00 (d, 1H, J = 15.6 Hz, CH), 7.83 (t, 1H, J = 8.6 Hz, C_6H_4), 7.85 (d, 2H, J = 8.8 Hz, C_6H_4), 7.45 (d, 2H, J = 8 Hz, $C_6H_4SO_3^-$), 7.08 (d, 2H, J = 7.6 Hz, $C_6H_4SO_3^-$), 6.81 (d, 2H, J = 9.2 Hz, C_6H_4), 4.42 (s, 3H, NCH₃), 3.05 (s, 6H, NCH₃), 2.27 (s, 3H, CH₃). Elemental analysis for $C_{27}H_{28}N_2O_3S \cdot H_2O$: Calcd. C 67.76, H 6.32, N 5.85, S 6.70; Found: C 67.97, H 6.26, N 5.78, S 6.85.

The condensation reaction of 4-(dimethylamino)benzaldehyde with the corresponding DMQ-T intermediates for DA-DMQ1,7-T (7-(4-(dimethylamino)styryl)-1-methylquinolinium 4-methylbenzenesulfonate), DA-DMQ1,6-T (6-(4-(dimethylamino)styryl)-1-methylquinolinium 4-methylbenzenesulfonate) and DA-DMQ1,3-T (3-(4-(dimethylamino)styryl)-1-methylquinolinium 4-methylbenzenesulfonate) were not successful, as will be discussed later.

2.3. Synthesis of the quinolinium-based chromophores (II)

The quinolinium-based chromophores DA-DMQ1,2-B with benzenesulfonate and DA-DMQ1,2-NS with naphthalene-2-sulfonate (see Fig. 2b) were synthesized in a similar manner as the metathesization of styrylquinolinium iodide with silver precursor [33−37].

2.3.1. 2-(4-(dimethylamino)styryl)-1-methylquinolinium benzenesulfonate (DA-DMQ1,2-B)

2-(4-(Dimethylamino)styryl)-1-methylquinolinium iodide (MQ1-DA-I, 1.00 g, 2.40 mmol) and silver(I) benzenesulfonate (Ag−B, 0.64 g, 2.40 mmol) were dissolved in methanol (280 mL and 60 mL, respectively). After completely dissolve each solutions, Ag−B solution dropwised into MQ1-DA-I solution and the solution was shaked. A few hours later, white AgI powder was precipitated and removed by filtration. The solution was evaporated and added 1,2-dimethoxyethane. For obtaining product, the solution kept in −24 °C. The precipitate was filtered and dried in vacuum oven at 105 °C for overnight. The final product was obtained by recrystallization in methanol and dried in vacuum oven at 100 °C for overnight. Yield = 30%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.79 (d, 1H, J = 9.2 Hz, C_5H_2N), 8.49 (d, 1H, J = 8.0 Hz, C_6H_4), 8.41 (d, 1H, J = 8.4 Hz, C_5H_2N), 8.24 (d, 1H, J = 15.2 Hz, CH), 8.22 (d, 1H, J = 6.8 Hz, C_6H_4), 8.06 (m, 1H, C_6H_4), 7.84 (d, 2H, J = 8.8 Hz, C_6H_4), 7.83 (t, 1H, J = 7.2 Hz, C_6H_4), 7.57 (m, 2H, $C_6H_5SO_3^-$), 7.54 (d, 1H, J = 14.0 Hz, CH), 7.29 (m, 1H, $C_6H_5SO_3^-$), 7.28 (d, 2H, J = 5.6 Hz, $C_6H_5SO_3^-$), 6.83 (d, 2H, J = 8.0 Hz, C_6H_4), 4.43 (s, 3H, NCH₃), 3.07 (s, 6H, NCH₃). Elemental analysis for $C_{26}H_{26}N_2O_3S$: Calcd. C 69.93, H 5.87, N 6.27, S 7.17; Found: C 69.61, H 6.08, N 6.27, S 6.93.

2.3.2. 2-(4-(dimethylamino)styryl)-1-methylquinolinium naphthalene-2-sulfonate (DA-DMQ1,2-NS)

MQ1-DA-I (1.32 g, 3.17 mmol) and silver(I) naphthalene-2-sulfonate (Ag-NS, 1.00 g, 3.17 mmol,) were dissolved in methanol (350 mL and 500 mL, respectively). After completely dissolve each solutions, Ag-NS solution dropwised into MQ1-DA-I solution and the solution was stirred. A few hours later, white AgI powder was precipitated and removed by filtration. The solution was kept in −24 °C for 4days for precipitation of product. After precipitation, the solution was filtered and dried in vacuum oven at 105 °C. The final product was obtained by recrystallization in methanol and dried in vacuum oven at 100 °C for overnight. Yield = 47%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 8.78 (d, 1H, J = 9.2 Hz, C_5H_2N), 8.48 (d, 1H, J = 9.2 Hz, C_6H_4), 8.41 (d, 1H, J = 8.4 Hz, C_5H_2N), 8.24 (d, 1H, J = 15.2 Hz, CH), 8.21 (d, 1H, J = 6.0 Hz, C_6H_4), 8.11 (s, 1H, $C_{10}H_7SO_3^-$), 8.06 (m, 1H, C_6H_4), 7.94 (m, 1H, $C_{10}H_7SO_3^-$), 7.87 (m, 1H, $C_{10}H_7SO_3^-$), 7.84 (d, 1H, J = 8.8 Hz, $C_{10}H_7SO_3^-$), 7.83 (d, 2H, J = 8.0 Hz, C_6H_4), 7.82 (t, 1H, J = 7.6 Hz, C_6H_4), 7.68 (m, 1H, $C_{10}H_7SO_3^-$), 7.54 (d, 1H, J = 15.6 Hz, CH), 7.50 (m, 1H, $C_{10}H_7SO_3^-$), 7.49 (m, 1H, $C_{10}H_7SO_3^-$), 6.82 (d, 2H, J = 8.8 Hz, C_6H_4), 4.42 (s, 3H, NCH₃), 3.07 (s, 6H, NCH₃). The DA-DMQ1,2-NS is also synthesized by a condensation reaction of 4-(dimethylamino)benzaldehyde with 1,2-dimethylquinolinium naphthalene-2-sulfonate. The NMR spectrum of condensation is practically identical with metathesization. Yield = 43%. Elemental analysis for $C_{30}H_{28}N_2O_3S$: Calcd. C 72.55, H 5.68, N 5.64, S 6.46; Found: C 72.55, H 5.72, N 5.67, S 6.43.

2.4. Crystal structures analysis

DA-DMQ1,2-B: slow evaporation method in methanol, $C_{26}H_{26}N_2O_3S \cdot H_2O$, M_r = 464.57, monoclinic, space group $P2_1/n$, a = 12.5055(12) Å, b = 10.3774(8) Å, c = 18.5700(14) Å, $β$ = 103.721(3)°, V = 2341.2(3) Å³, Z = 4, T = 290(1) K, μ(MoKα) = 0.168 mm^{-1}. Of 17898 reflections collected in the $θ$ range 2.99°−25.00° using an ω scan on a Rigaku R-axis Rapid S diffractometer, 4116 were unique reflections (R_{int} = 0.0324, completeness = 99.8%). The structure was solved and refined against F² using SHELX97 [39] 410 variables, wR_2 = 0.2228, R_1 = 0.0624 (Fo² > 2σ(Fo²)), GOF = 1.095, and max/min residual electron density 0.706/-0.427 eÅ^{-3}. CCDC-948586.

DA-DMQ1,2-NS (I): rapid cooling method in methanol, $C_{30}H_{28}N_2O_3S$, M_r = 496.60, triclinic, space group P-1, a = 11.4237(6) Å, b = 11.6934(6) Å, c = 12.0951(6) Å, $α$ = 68.2997(15)°, $β$ = 65.327(2)°, $γ$ = 61.930(2)°, V = 1264.85(10) Å³, Z = 2, T = 290(1) K, μ(MoKα) = 0.163 mm^{-1}. Of 9073 reflections collected in the $θ$ range 3.06°−24.00° using an ω scans on a Rigaku R-axis Rapid S diffractometer, 3966 were unique reflections (R_{int} = 0.0171, completeness = 99.8%). The structure was solved and refined against F² using SHELX97 [39], 325 variables, wR_2 = 0.1142, R_1 = 0.0373 (Fo² > 2σ(Fo²)), GOF = 1.081, and max/min residual electron density 0.211/-0.274 eÅ^{-3}. CCDC-948584.

DA-DMQ1,2-NS (II): slow cooling method in methanol, $C_{30}H_{28}N_2O_3S$, M_r = 496.60, *monoclinic*, space group $P2_1/n$, a = 11.4414(9)Å, b = 19.6315(16)Å, c = 12.0851(11)Å, β = 113.450(2)°, V = 2490.3(4)Å³, Z = 4, T = 290(1) K, μ(MoKα) = 0.17 mm⁻¹. Of 24027 reflections collected in the θ range 3.20°−27.50° using an ω scans on a Rigaku R-axis Rapid S diffractometer, 5706 were unique reflections (R_{int} = 0.122, completeness = 99.7%). The structure was solved and refined against F² using SHELX97 [39], 437 variables, wR_2 = 0.1866, R_1 = 0.0749 (Fo² > 2σ(Fo²)), GOF = 1.02, and max/min residual electron density 0.43/-0.26 eÅ⁻³. CCDC-948585.

2.5. Hyper-Rayleigh scattering measurement

The molecular first hyperpolarizabilities β of the synthesized compounds DA-DMQ1,2-T, DA-DMQ2,3-T, and DA-DMQ1,4-T, as well as for DAST were determined in acetonitrile solution at the long fundamental wavelength of 1550 nm, far from two-photon resonance, by means of the hyper-Rayleigh scattering (HRS) technique. The highly sensitive and broadly wavelength-tunable HRS setup (described in detail in Ref. [40]) consists of a Ti:Sapphire regenerative amplifier (Spectra-Physics Spitfire) which is pumping an optical parametric amplifier (Spectra-Physics OPA-800CP, pulse duration ~2 ps, repetition rate = 1 kHz, pulse energy at the sample at 1550 nm ~20 μJ). Parallel detection of a narrow wavelength range around the second harmonic is achieved by use of a nitrogen cooled CCD coupled to a spectrograph, enabling fast and complete correction for broadband multi-photon fluorescence. Such a background was observed for all four compounds, varying in strength from (integrated over the central 11 nm wide region) about 20 times the actual HRS signal for DA-DMQ1,4-T, about 4 times for DAST, about 2.2 times for DA-DMQ1,2-T and down to less than 0.1 times for DA-DMQ2,3-T.

A single significant β tensor component along the *z*-axis (*i.e.* the conjugated chain) was assumed for all measured molecules. Acetonitrile itself was used as secondary internal reference standard. We previously calibrated this solvent extensively against chloroform [40], adopting the effective $|\beta_{zzz}|$ value of 0.49×10^{-30} esu as determined in Ref. [41]. Specifically, we used a β value of 0.599×10^{-30} esu at 1550 nm for acetonitrile [40]. The reported results for β are expressed in the B* convention [42].

All compounds were found to be very stable in solution, and to limit effects of local photodecomposition in the laser focus, the solutions were stirred during the measurement to continuously refresh the exposed molecules. In these conditions, no decomposition was observed in the linear absorption spectra. As the laser wavelength was chosen to be far from (one- and) two-photon resonance, no correction for reabsorption of the HRS light (at 775 nm) was necessary. The experimental error on β, disregarding the systematic error on the reference value, is estimated to be ±5%, based on the excellent reproducibility of independent measurements.

3. Results and discussion

3.1. Design and synthesis

In order to examine the electron-withdrawing strength of different quinolinium electron acceptors and its influence on physical properties, we designed a rational series of quinolinium-based chromophores. The chemical structures of the investigated chromophores are shown in Fig. 2a. They consist of a dimethylamino electron donor group and a methylquinolinium-based electron acceptor group. All these cationic chromophores are combined with a 4-methylbenzenesulfonate counter anion. For comparison, we also included a methylpyridinium-based

analogue, the well-known DAST compound (see Fig. 1a) [25−27], in which an identical dimethylamino electron donor group as well as the same 4-methylbenzenesulfonate counter anion is used.

To synthesize the quinolinium-based chromophores with 4-methylbenzenesulfonate, six intermediates of dimethylquinolinium (DMQ) with 4-methylbenzenesulfonate, having a different position of the nitrogen atom at the acceptor side, were synthesized first (see Fig. 3). The quinolinium-based chromophores with 4-methylbenzenesulfonate were synthesized by Knoevenagel condensation of dimethylamino benzaldehyde with the corresponding DMQ-T intermediates with the weak base, piperidine, as the catalyst [33−35]. The condensation reactions for DA-DMQ1,2-T, DA-DMQ2,3-T and DA-DMQ1,4-T were successful, unlike for DA-DMQ1,7-T, DA-DMQ1,6-T and DA-DMQ1,3-T. The different reactivity in the condensation reactions with different electron-acceptor groups is related to the electron-withdrawing strength of the methylquinolinium group in the DMQ-T intermediates, as discussed in the following Section 3.2.

3.2. Electron-withdrawing strengths

Fig. 3 shows the chemical structures of the quinolinium-based DMQ-T and pyridinium-based DMP-T intermediates. In order to investigate the electron-withdrawing strength of the various quinolinium electron acceptors, ¹H NMR spectra of the DMQ-T and DMP-T intermediates were measured. Fig. 4 shows the ¹H NMR spectra of the DMQ and DMP derivatives in dimethylsulfoxide (DMSO)-d_6 solution. The asterisks in Fig. 4 present the corresponding proton peaks on the active methyl groups of the DMQ and DMP intermediates, denoted by the asterisks in Fig. 3. In DMQ derivatives, the chemical shift of the protons on the active methyl group is 3.053 ppm for DMQ1,2-T, 2.980 ppm for DMQ1,4-T, 2.806 ppm for DMQ2,3-T, 2.722 ppm for DMQ1,7-T, 2.607 ppm for DMQ1,6-T and 2.605 ppm for DMQ1,3-T. Therefore, the electron-withdrawing strength of the derivatives as determined by comparison of their chemical shifts follows the order of DMQ1,2 > DMQ1,4 > DMQ2,3 > DMQ1,7 > DMQ1,6 ≈ DMQ1,3.

The observed relative electron-withdrawing strength of the quinolinium derivatives agrees very well with the results of the condensation reactions. In the condensation reaction to synthesize the styryl quinolinium chromophores, an aldehyde group and an active methyl group on the DMQ cation form a double bond. First the proton of the active methyl group of the DMQ cation, denoted by an asterisk in Fig. 3, is eliminated by a weak base catalyst and thus a resonance-stabilized anion is formed. Second, the activated methyl anion attacks the carbon atom on the aldehyde as a nucleophile. [18,27] Therefore, the reactivity of the activated methyl group with the aldehyde increases with increasing electron-withdrawing strength of *N*-methylquinolinium. As described in the Experimental section, the DA-DMQ1,2-T, DA-DMQ1,4-T, and DA-DMQ2,3-T chromophores, which are based on DMQ electron acceptors having a relatively large electron-withdrawing strength, were successfully synthesized by a condensation reaction, while for DA-DMQ1,7-T, DA-DMQ1,6-T, and DA-DMQ1,3-T the condensation reaction was unsuccessful. Compared to quinolinium-based DMQ1,7, DMQ1,6 and DMQ1,3, pyridinium-based DMP having lower chemical shift was reacted with the aldehyde. Since DMQ and DMP cations are based on different heteroaromatic characteristics, a fused benzene ring and a benzene ring, respectively, the reactivity might be related with not only electron-withdrawing strength, but also steric hindrance and other effects. Therefore, comparison between DMP and DMQ is discussed in the following section on hyper-Rayleigh scattering (HRS) measurements.
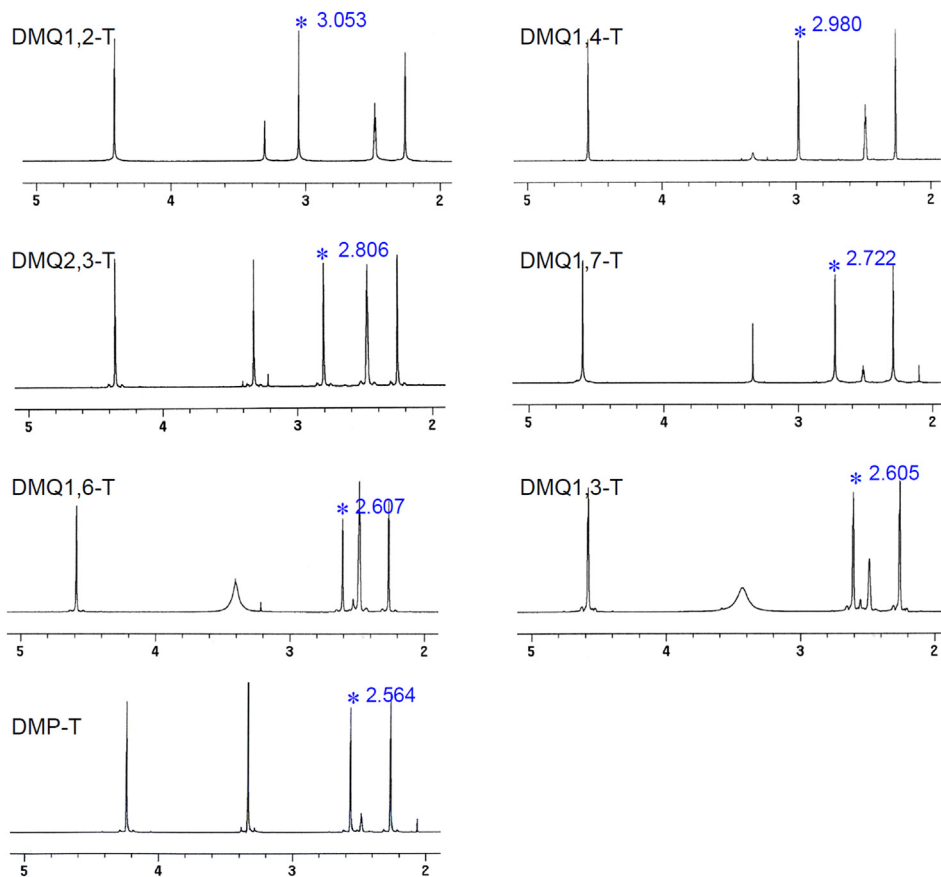
Fig. 4. ^{1}H NMR spectra of the DMQ and DMP acceptor groups in DMSO-d_6. The asterisk denotes the proton peak of the methyl groups which are active in the condensation reaction (denoted by the asterisk in Fig. 3).

In order to further investigate our hypothesis, the molecular first hyperpolarizabilities β of the successfully synthesized quinolinium dyes (DA-DMQ1,2-T, DA-DMQ1,4-T and DA-DMQ2,3-T), having different acceptor strengths and different conjugation lengths counting between the donor and acceptor nitrogens (but identical overall size), were directly determined by the hyper-Rayleigh scattering (HRS) technique (see Table 1) [40]. The HRS measurements were performed at the long laser wavelength of 1550 nm, well beyond (one- and) two-photon resonance for all three compounds, so that the simple undamped two-level model (TLM) of Oudar and Chemla [43] can be used to reliably extrapolate the experimental β values to the static ('resonance free') limit β_0 [44], needed for correct comparison between different molecules.

Remarkably high β_0 values of 256 and 233 $\times$ 10^{-30} esu are obtained for DA-DMQ1,4-T and DA-DMQ1,2-T respectively, essentially two times considerably higher than the β_0 of DA-DMQ2,3-T (122 $\times$ 10^{-30} esu). To qualitatively interpret these values we can

again make use of the TLM [43], which predicts β_0 to be inversely proportional to the (cube of) the transition frequency ω_{eg}, and directly proportional to the difference in dipole moment between the ground- and electronic excited state $\Delta\mu$ and to the oscillator strength of the transition f_{osc}. The increase of β_0 for DA-DMQ1,2-T compared to DA-DMQ2,3-T having identical conjugation length can be explained by the strongly red-shifted λ_{abs} of the former (see Table 1), caused by its stronger acceptor (1,2-dimethylquinolinium vs. 2,3-dimethylquinolinium as also determined above by ^{1}H NMR analysis). Clearly, it is favorable for the fused benzene ring to be close to the nitrogen to increase the electron accepting abilities of the quinolinium end group. Note that this increase in λ_{abs} is overcompensating for the slight decrease in oscillator strength (see Table 1).

The further improvement of DA-DMQ1,4-T over DA-DMQ1,2-T can be attributed to the larger distance between the nitrogen atoms of the former, resulting in an increase in λ_{abs} (and $\Delta\mu$), again

Table 1
Measured physical data for the investigated chromophores: the first hyperpolarizability β measured by HRS and the corresponding β_0 values determined by means of the undamped two-level model; the oscillator strength f_{osc} of the lowest-energy absorption band; the wavelength of maximum absorption λ_{abs}; the wavelength of maximum emission λ_{em}.

	HRS (10^{-30} esu)		f_{osc}	λ_{abs} (nm)						λ_{em} (nm)		
	β_{1550nm}	β_0	AcCN	DCM	Acetone	MeOH	AcCN	H$_2$O	DCM	AcCN	H$_2$O
DA-DMQ1,2-T	475	233	0.65	556	522	523	519	500	645	618	622
DA-DMQ1,4-T	560	256	0.61	581	540	543	536	510	680	703	698
DA-DMQ2,3-T	188	122	0.69	441	425	425	422	394	539	530	625[a]
DAST	320	183	0.66	522	468	474	470	450	608	625	624

[a] This value has a higher uncertainty due to low solubility and low fluorescence quantum yield (<0.05%).

despite a further reduction in oscillator strength. In terms of conjugation length, DA-DMQ1,4-T can be directly compared to the pyridinium analogue DAST based on DMP intermediate. Therefore, we also carried out HRS measurements on DAST, under the exact same conditions (same non-resonant wavelength, same solvent). Our β value of 320×10^{-30} esu obtained for DAST at 1550 nm in acetonitrile (see Table 1) is in reasonable agreement with the value of 367×10^{-30} esu reported at 1542 nm in dimethyl sulfoxide (DMSO) solution by Bosshard and co-workers [45]. Furthermore, the β_0 value of 183×10^{-30} esu obtained for DAST is in excellent agreement with the values obtained from quantum chemical calculations in the gas and solid phases (150-194 $\times 10^{-30}$ esu) as reported in Refs. [31,32]. The β_0 value for DA-DMQ1,4-T is ~40% higher than for DAST, which can again be explained by the increase in λ_{abs} due to the stronger acceptor of the former (again in agreement with the ^{1}H NMR analysis), despite the slightly smaller oscillator strength. Note that the molecular nonlinearity of the DA-DMQ1,4 cation has also been previously estimated by Stark electroabsorption spectroscopy in Ref. [46], where a 1.1 times higher β_0 was reported for the DA-DMQ1,4 cation than for the DAST cation.

Even the DA-DMQ1,2-T compound with a shorter N—N$^+$ distance exhibits a 25% higher β_0 value than DAST, showing that 1,2-dimethylquinolinium is a much better electron acceptor than 1,4 dimethylpyridinium (in agreement with the NMR results), so much that it can even overcompensate for a decrease in conjugation length of two bonds. DA-DMQ2,3-T however exhibits weaker performance, as the lower acceptor strength of the 2,3-dimethylquinolinium group combined with the decreased conjugation length results in a 35% lower β_0 than DAST.

Hence, the molecular optical nonlinearity follows the order of DA-DMQ1,4-T > DA-DMQ1,2-T > DAST > DA-DMQ2,3-T, and thus, comparing compounds with the same N—N$^+$ distance, the electron-withdrawing strength of quinolinium follows the order of DMQ1,2 > DMQ2,3 and DMQ1,4 > DMP (used in DAST), in perfect agreement with the results of the ^{1}H NMR measurements. The further increase in β_0 for DA-DMQ1,4-T compared to DA-DMQ1,2-T is significant (~10%), but less than might be expected considering the sizeable increase in N—N$^+$ distance alone, which can be attributed to the larger acceptor strength of DMQ1,2.

3.3. Molecular conformation

The molecular optical nonlinearity of chromophores is strongly affected by the molecular conformation [47—51]. In general, a planar conformation of the π-conjugated bridge yields efficient delocalization of the π-electrons which is beneficial for the optical nonlinearity [1—4]. Yet, twisting of the π-conjugated bridge can either lead to a decrease of the optical nonlinearity, through a breaking of the conjugation [50], or to an increase of it, through enhanced charge-separation [51].

In order to investigate the molecular conformation of the quinolinium-based chromophores, the crystal structure of the quinolinium crystals based on the electron acceptor DMQ1,2 having the largest electron-withdrawing strength in this work, was analyzed. Unfortunately, the grown DA-DMQ1,2-T crystals with 4-methylbenzenesulfonate counter anion did not exhibit sufficient crystal quality to determine their crystal structure by X-ray analysis. Instead, two DA-DMQ1,2 analogues with different anions, benzenesulfonate and naphthalene-2-sulfonate (see Fig. 2b) were newly synthesized. DA-DMQ1,2-B (2-(4-(dimethylamino)styryl)-1-methylquinolinium benzenesulfonate) was synthesized by meta-thesization, while DA-DMQ1,2-NS (2-(4-(dimethylamino)styryl)-1-methylquinolinium naphthalene-2-sulfonate) was synthesized by either metathesization or condensation (see Experimental section). The DA-DMQ1,2-B single crystals grown by the slow evaporation

method in methanol solution were found to exhibit monoclinic space group symmetry P2$_1$/n. For the DA-DMQ1,2-NS crystals we found two polymorphs: the DA-DMQ1,2-NS(I) phase grown by the rapid cooling method in methanol solution exhibits monoclinic space group symmetry P-1, while the DA-DMQ1,2-NS(II) phase grown by slow cooling method in methanol solution from the saturation temperature of 40 °C exhibits monoclinic space group symmetry P2$_1$/n. In this way we have three examples of molecular conformation of the DA-DMQ1,2 chromophore in the crystalline state. Unfortunately, the DA-DMQ1,2 compound crystallizes centrosymmetrically, but many structural variations (side groups, other counter ions) could be considered to change the crystal structure without significantly changing the molecular nonlinearity, as have been used successfully for other related compounds such as DAST [25] and the HMQ cation from Fig. 1b [33—38].
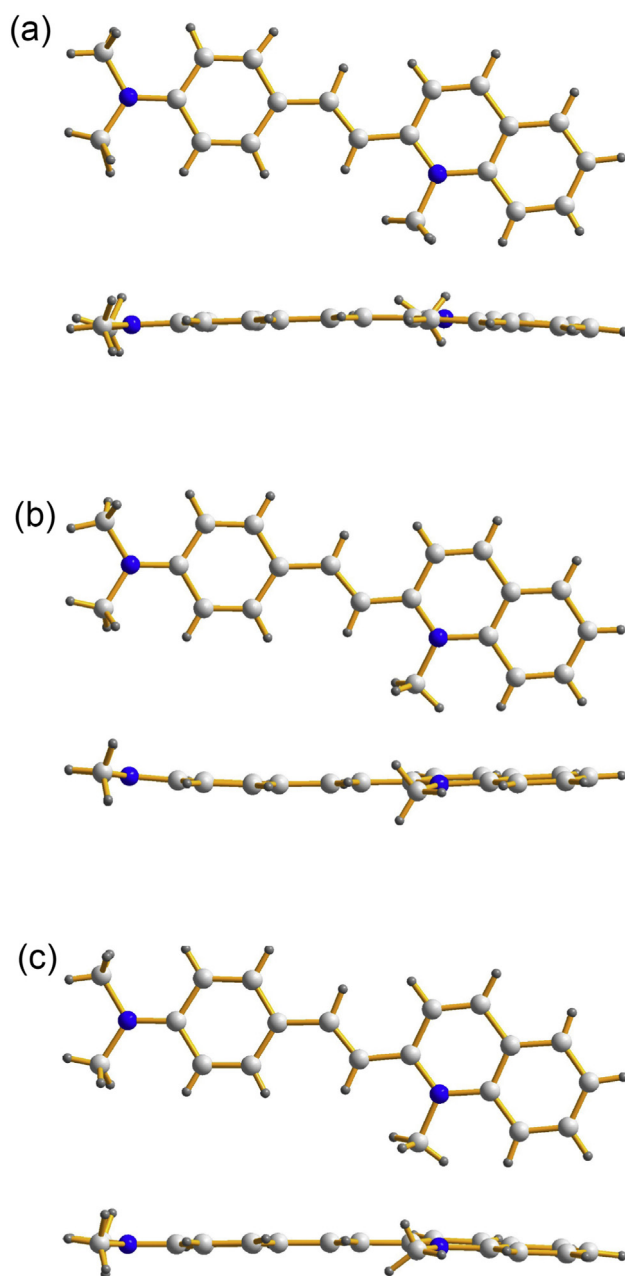

Fig. 5. Molecular conformation of the DA-DMQ1,2 cation in the crystalline state of (a) DA-DMQ1,2-B, (b) DA-DMQ1,2-NS (I) and (c) DA-DMQ1,2-NS (II).

Fig. 5 shows the molecular conformation of the DA-DMQ1,2 cation in the crystalline state of DA-DMQ1,2-B, DA-DMQ1,2-NS (I) and DA-DMQ1,2-NS (II) compounds. The molecular conformation of the DA-DMQ1,2 cation in these three phases is similar: the plane of the 4-(dimethylamino)styryl groups is practically planar with the plane of the quinolinium ring within 8° (see Fig. 5), ensuring good delocalization of the π-electrons.

The molecular conformation can be strongly affected by environmental conditions. In previously reported DMQ1,2-based chromophores, tilting angles between the planes of the phenyl ring and quinolinium ring were up to 27° [33–38], but according to FF-DFT (finite field-density functional theory) calculations in gas and solid phase the accompanying change of the molecular nonlinearity with respect to non-tilted chromophores is relatively small, less than 15% [33–35,38], suggesting that the effects of conjugation and charge-separation compensate in these DMQ1,2 derivatives. Such insensitivity of the molecular nonlinearity to variations of the molecular conformation in the quinolinium based DMQ1,2 electron acceptor is an important practical advantage towards implementation in various applications, compared to other electron acceptors, whose optical nonlinearity may be very sensitive to a change of molecular conformation.

3.4. Photophysical properties

While the photophysical properties of pyridinium-based chromophores have been widely investigated [24], those of DMQ1,2- and DMQ2,3-based chromophores are scarcely known. We investigated the absorption and fluorescence behavior of the DA-DMQ1,2-T, DA-DMQ1,4-T and DA-DMQ2,3-T chromophores. For comparison, the pyridinium-based DAST chromophore was also investigated under the same experimental conditions.

Fig. 6 shows absorption spectra of the chromophores in various solvents (methanol (MeOH), dichloromethane (DCM), acetonitrile (AcCN), acetone and water). The results are summarized in Table 1. In addition to the large variation of the wavelength of maximum absorption λ_{abs} among the different chromophores in line with the respective acceptor strengths and NLO results as discussed before, all of the chromophores (DMQ based as well as DAST), show a negative solvatochromism (i.e. λ_{abs} decreasing with increasing solvent polarity).

Fig. 7 shows the fluorescence spectra of the DA-DMQ1,2-T, DA-DMQ2,3-T, and DAST chromophores in acetonitrile, excited at 405 nm. All chromophores show weak fluorescence in water (quantum yield less than 1%). In acetonitrile solution however, the DA-DMQ1,2-T and DAST chromophores exhibit a significant fluorescence intensity, while it is extremely weak for DA-DMQ2,3-T (see Fig. 7). For quantitative comparison, quantum yields Φ of chromophores in acetonitrile, excited at 405 nm are measured using coumarin 153 ($\Phi = 56\%$) as a reference standard [52]. The DA-DMQ1,2-T chromophore exhibits 6 times higher quantum yield ($\Phi = 1.9\%$) than DAST ($\Phi = 0.32\%$). Unlike the absorption wavelength λ_{abs}, the emission wavelength λ_{em} does not show a clear solvatochromic trend (which may be due to the more complex behavior typically associated with relaxations in the excited state), but does correlate well with the NLO results and acceptor strengths among the different compounds.

4. Conclusion

We have investigated a series of π-conjugated styryl quinolinium chromophores based on various quinolinium electron acceptor groups. The order of the strength of the different electron acceptors was determined from ^{1}H NMR analysis to be
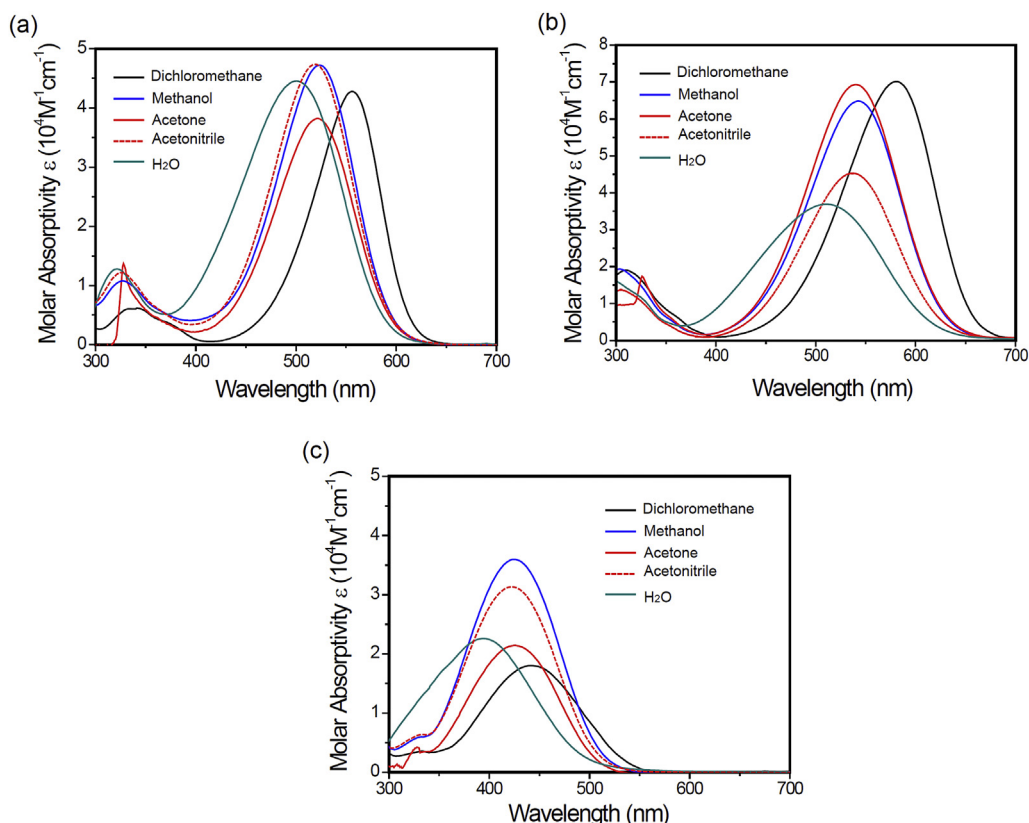

Fig. 6. Absorption spectra of the (a) DA-DMQ1,2-T, (b) DA-DMQ1,4-T and (c) DA-DMQ2,3-T chromophores in various solvents.
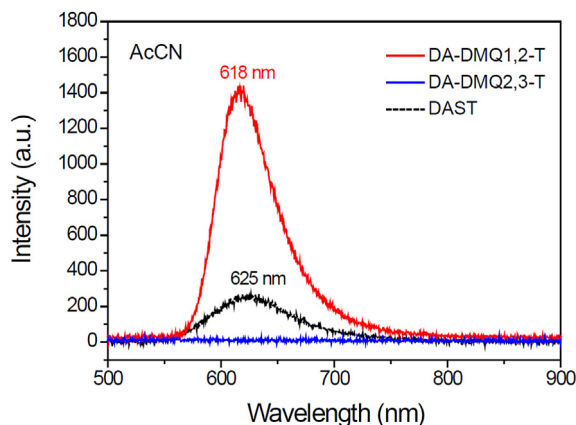
Fig. 7. Fluorescence spectra of the DA-DMQ1,2-T, DA-DMQ2,3-T, and DAST chromophores in acetonitrile excited at 405 nm.

DMQ1,2 > DMQ1,4 > DMQ2,3 > DMQ1,7 > DMQ1,6 ≈ DMQ1,3, and the wavelength of maximum absorption λ_{abs} of the different compounds was indeed found to follow the same order. The static first hyperpolarizability β_0 of the quinolinium compounds, having different acceptor strengths and different conjugation lengths was determined by long-wavelength hyper-Rayleigh scattering (HRS) experiments and, as expected, also the β_0 value follows the order of the electron withdrawing strength among equally long compounds. The compounds with the strongest acceptor groups (DA-DMQ1,2-T and DA-DMQ1,4-T) are found to exhibit remarkably large β_0 values of 233 and 256 × 10^{-30} esu respectively, which is higher than the β_0 of the widely applied pyridinium-based analogue DAST. This is attributed to a higher electron-withdrawing capability of the dimethylquinolinium groups (DMQ1,2 and DMQ1,4) in comparison to the dimethylpyridinium group (DMP) of DAST. DMQ1,2 is found to form the strongest electron acceptor group, as it even succeeds in compensating for the smaller N−N$^+$ separation of the DA-DMQ1,2-T compound. Therefore, the dimethylquinolinium electron acceptor groups DMQ1,2 and DMQ1,4 form an interesting potential alternative for the widely used pyridinium electron acceptor for various photonic applications.

Acknowledgement

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