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► **To cite this version:**

Sylvain Achelle, Egor V Verbitskiy, Michaela Fecková, Filip Bureš, Alberto Barsella, et al.. V-Shaped Methylpyrimidinium Chromophores for Nonlinear Optics. *ChemPlusChem*, 2021, 86 (5), pp.758-762. 10.1002/cplu.202100081 . hal-03247404

HAL Id: hal-03247404

<https://hal.science/hal-03247404>

Submitted on 14 Jun 2021

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V-Shaped Methylpyrimidinium Chromophores for Nonlinear Optics

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Accepted Manuscript

Abstract

In this communication, a series of four V-shaped methylpyrimidinium salts bearing diphenylamino-electron-donating groups appended at various pyrimidine positions were designed. The titled chromophores were obtained by regioselective N(1) monomethylation by methyl methanesulfonate of the pyrimidine core. Linear optical properties were studied experimentally and electronic properties were further completed by (TD)-DFT calculations. The second order nonlinear optical (NLO) properties were also studied using electric field induced second harmonic generation (EFISH) method in chloroform and all pyrimidinium salts exhibited $\mu\beta_0 > 1\,000 \times 10^{-48}$ esu. It has been revealed that 2,4-disubstituted pyrimidinium core is preferred over 4,6-disubstitution as it enhances the NLO response and increases the dipole moment. (E,E)-2,4-Bis[4-(diphenylamino)styryl]-1-methylpyrimidin-1-ium methanesulfonate appears as the best NLOphore in chloroform of the series ($\mu\beta_0 = 2\,500 \times 10^{-48}$ esu) with a figure of merit $\mu\beta_0/MW = 3.4 \times 10^{-48}$ esu.mol.g⁻¹.

Introduction

The development of second order nonlinear (NLO) material is still subject to intensive research.^[1] These materials can be used for sum frequency generation such as second harmonic generation,^[2] Pockels effect as well as optical rectification^[3] and can found applications in optical signal processing and integrated optics.^[4] Organic materials are easily tunable and present higher and fast NLO response than well-established inorganic materials such as lithium niobate.^[5]

The push-pull structure consisting of an electron-donating group linked to an electron-withdrawing one via a π -conjugated linker (D- π -A), leading to intramolecular charge transfer (ICT), is the typical design of second order NLO chromophores.^[6] In this context, a large library of pyrimidine second order NLO chromophores has been developed.^[7] The pyrimidine

ring possesses a strong electron-deficient character^[8] that can be advantageously used for fluorescent sensors,^[9] OLED emitters^[10] or two-photon chromophores.^[7] Whereas 4-styrylpyrimidines bearing an electron-donating substituent exhibit relatively weak NLO response,^[11] the optimization of the π -conjugated core between the pyrimidine and the donor group^[12] and more importantly the methylation of pyrimidine^[12,13] significantly enhance the NLO response. It has been also demonstrated that V-shaped 4,6-disubstituted pyrimidines exhibit more than 2-times higher NLO response than their monosubstituted pyrimidine analogues.^[11b]

In this contribution we designed a series of V-shaped chromophores based on a methylpyrimidinium central core substituted in positions C4 and C6 (compounds **1** and **2**) or in positions C2 and C4 (compounds **3** and **4**) (Chart 1).

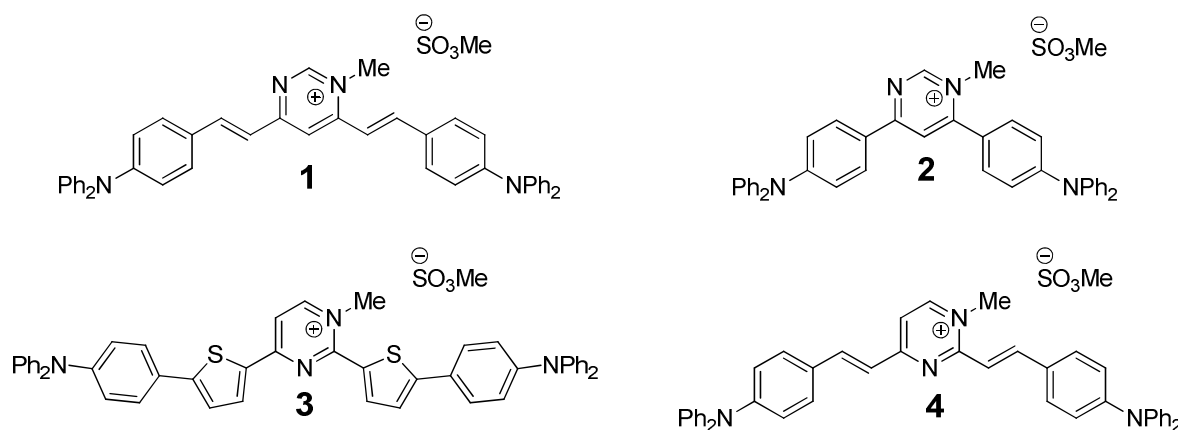


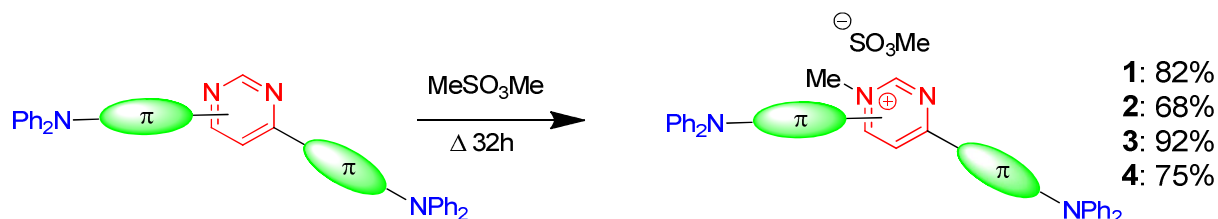
Chart 1: Structure of studied methanesulfonate methylpyrimidinium salts **1-4**.

Results and Discussion

Synthesis

Pyrimidine starting materials were synthesized according to reported procedure.^[14] Whereas the methylation of 4-substituted pyrimidine derivatives can be performed by methyl iodide used as solvent,^[13] disubstituted pyrimidines require a stronger methylating agent: methylmethane sulfonate.^[15] Methanesulfonate methylpyrimidinium salts **1-4** have

been obtained in good yields (Scheme 1). In all cases, only one nitrogen atom was methylated and for 2,4-disubstituted pyrimidine, the methylation occurs regioselectively on the N1 atom.



Scheme 1: Synthesis of methanesulfonate methylpyrimidinium salts **1-4**

UV-visible absorption

The absorption properties of compounds **1-4** were measured in various solvents and the results are summarized in Table 1. The absorption spectra in chloroform are shown in Figure 1, and the picture of the related solutions is provided in Figure 2. Compound **1** exhibited the strongest absorbance and the most red-shifted absorption band. The bathochromic shifts observed for **1** vs **4** indicates a stronger ICT for 4,6-disubstituted pyrimidine. Similarly, when compared to diaryl analogue **2**, the absorbance of distyrylpyrimidine **1** is red-shifted by ~ 100 nm indicating a significant enhancement of the ICT by addition of ethenylene linkers. Absorption maxima are almost the same for compounds **3** and **4**, which points to similar transparency of 2,5-thienylene and ethenylene bridges.

Compounds **1-4** exhibited a significant solvatochromism (Table 1, Figure 3). As observed for 4-styrylpyrimidinium iodide,^[13a] the absorption maxima are not related to the polarity of the solvent but the most red-shifted absorptions are clearly observed in chlorinated solvents (CHCl₃ and DCM). This bathochromic shift is attributed to the formation of halogen bound between the chlorinated solvent and the counter anion.^[16]

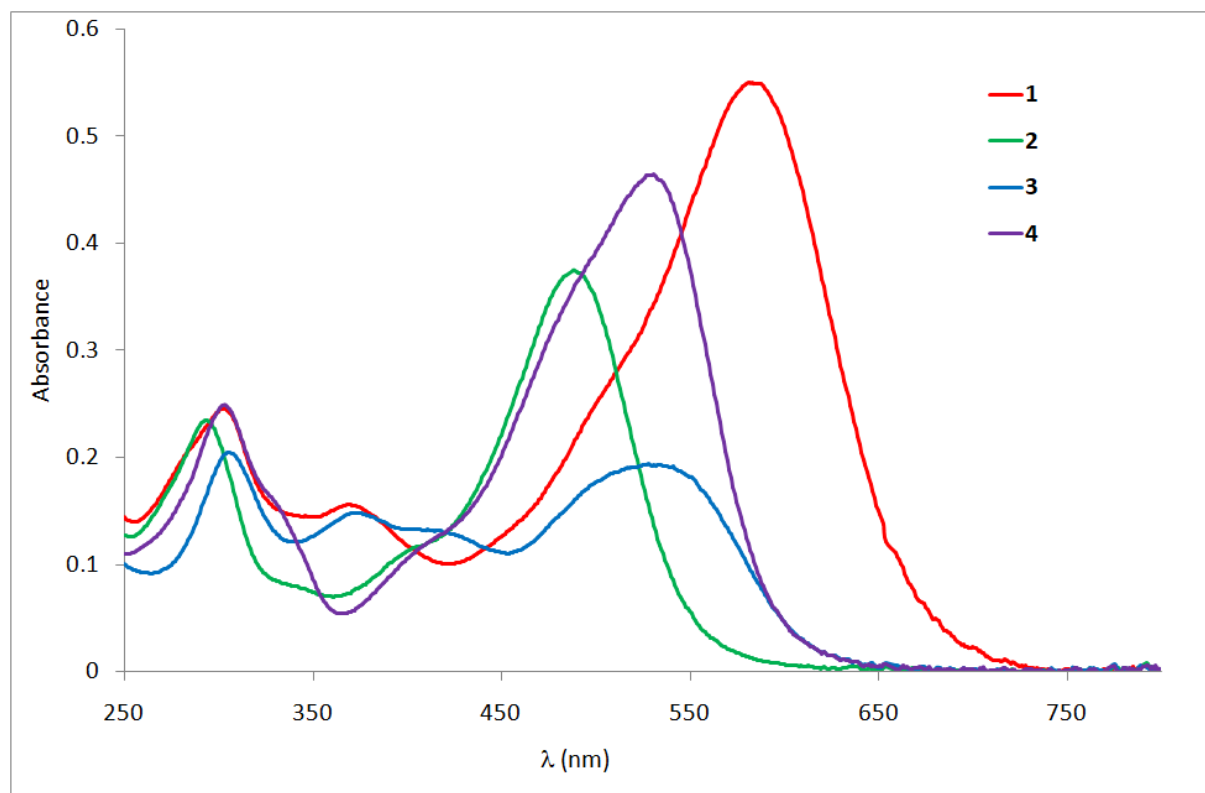


Figure 1: Absorption spectra of compounds **1-4** in CHCl_3 ($c = 1 \times 10^{-5}$ M)



Figure 2: Photograph of solution of **1-4** (from left to right) in CHCl_3 ($c = 1 \times 10^{-5}$ M).

Table 1. Absorption maxima of compounds **1-4** in various solvents.

	<i>n</i> -heptane	Toluene	λ_{abs} [nm] (ϵ [$\text{mM}^{-1} \text{cm}^{-1}$])				
			CHCl_3	CH_2Cl_2	MeCN	DMSO	MeOH

1	534 (34.6)	550 (50.4)	586 (55.0)	619 (52.0)	555 (55.5)	549 (51.0)	557 (60.4)
2	476 (31.4)	471 (38.2)	488 (37.4)	511 (42.3)	475 (34.5)	469 (27.5)	479 (46.7)
3	489 (14.3)	502 (21.6)	528 (19.4)	538 (21.4)	503 (18.9)	493 (14.5)	506 (21.5)
4	492 (30.4)	506 (44.1)	531 (46.4)	556 (35.4)	501 (40.1)	493 (33.2)	509 (34.6)



Figure 3: Picture of solution of **1** in various solvents (from left to right: *n*-heptane, toluene, CHCl₃, CH₂Cl₂, MeCN, DMSO, MeOH) ($c = 1 \times 10^{-5}$ M)

DFT Calculations

Spatial and electronic properties of pyrimidiniums **1-4** were investigated using Gaussian[®]16W software package^[17] at the DFT level. The initial geometries were optimized by DFT B3LYP/6-311+G(2d,f,p) method. Energies of the frontier molecular orbitals, their differences ΔE , and ground state dipole moments μ were calculated in CHCl₃ by using DFT B3LYP/6-311+G(2d,f,p) method. Linear and nonlinear optical properties were calculated at (TD-)DFT CAM-B3LYP/6-311+G(2d,f,p) level in CHCl₃. The calculated data are summarized in Table 2.

Table 2: DFT-calculated parameters of compounds **1-4**.

	1	2	3	4
E_{HOMO} [eV] ^[a]	-5.81	-6.07	-5.75	-5.89
E_{LUMO} [eV] ^[a]	-3.62	-3.43	-3.57	-3.44
ΔE_{HOMO} [eV] ^[a]	2.19	2.64	2.18	2.45

μ [D] ^[a]	9.7	7.1	19.4	13.4
λ_{\max} [nm/eV] ^[b]	502/2.47	423/2.93	466/2.66	458/2.71
$\beta(-2\omega, \omega, \omega)$ [10^{-30} esu] ^[c]	346	139	401	332

[a] Calculated by DFT B3LYP/6-311+G(2df,p) in CHCl₃. [b] Calculated by TD-DFT CAM-B3LYP/6-311+G(2df,p) in CHCl₃ [c] Calculated by DFT CAM-B3LYP/6-311+G(2df,p) at 1907 nm in CHCl₃.

Several possible conformers of **1-4** were considered for initial calculations; Figure 4 shows those with optimized geometry and the lowest energy. As expected, V-shaped chromophores **1-4** are unsymmetrical with none group of symmetry. Whereas in **1**, **3**, and **4** is the central pyrimidinium ring coplanar with the remaining π -systems appended at C2/C4 and C4/C6, a direct interconnection of the peripheral amino donors via 1,4-phenylene moiety as in **2** caused significant twist with the torsion angle around 30°. A typical out-of-plane arrangement of both phenyl substituents of the peripheral *N,N*-diphenylamino groups is seen in all molecules. Both sulfur atoms of 2,5-thienylene moieties in **3** are oriented inwards. Unsymmetrical arrangement is also reflected by the calculated ground state dipole moments μ that range from 7.1 to 19.4 D. In general, largest values were calculated for unsymmetrically C2/C4-substituted chromophores **3** and **4**.

Chromophores **1** and **3** showed the highest HOMO and the lowest LUMO, which resulted in the narrowest HOMO-LUMO gap of 2.19/2.18 eV. As compared to parent diaryl derivative **2**, both **1** and **3** possess extended, planarized, and polarizable π -system made of styryl or phenylene-thienylene linkers. Chromophore **4**, bearing identical branches as derivative **1** connected at C2/C4, possesses an increased HOMO-LUMO gap of 2.45 eV. This implies suppressed ICT from the peripheral amino donors to central methylpyrimidinium acceptor than in **1** with C4/C6 substitution. Figure 4 shows HOMO/LUMO localization in

particular chromophores; for complete localizations of frontier molecular orbitals see the Supporting information. As expected, the HOMO occupies the amino donor, predominantly on one branch, whereas the LUMO is spread over the central pyrimidinium acceptor. In contrast to chromophores **1**, **3**, and **4** with the HOMO localized over C4-branch, nonplanar chromophore **2** possesses the HOMO on C6-branch. The HOMO-1 always occupies the opposite branch to that occupied by the HOMO. The LUMO+1 is centrally localized involving the π -system adjacent to the pyrimidinium acceptor.

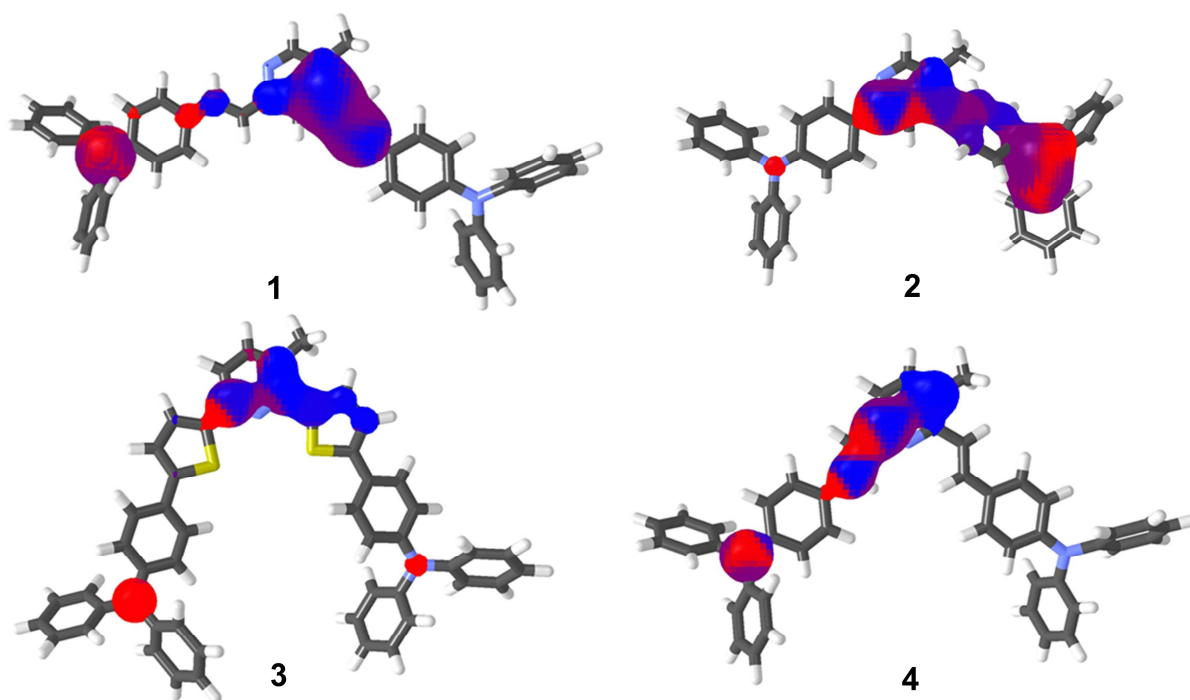


Figure 4: HOMO (red) and LUMO (blue) localizations in chromophores **1-4** (counter ions are omitted for clarity).

Electronic absorption spectra were investigated using TD-DFT as shown in Figure S13 of the supporting information. As compared to the experimental spectra in CHCl_3 , the calculated spectra are hypsochromically shifted but feature the same bands and both calculated and experimental longest-wavelength absorption maxima λ_{max} correlate tightly (Figure S14). Similarly to the experimental data (Table 1), the most bathochromically shifted bands were identified for chromophore **1**, while bands of **2** are the most blue-shifted. An

analysis of the transitions revealed differences forming the particular bands. Whereas the longest-wavelength bands of C4/C6-substituted chromophores **1** and **2** are predominantly generated by the HOMO→LUMO transition, the HOMO-1→LUMO transitions are also significantly involved in the CT-bands of chromophores **3** and **4**. Considering the aforementioned localization of the frontier molecular orbitals, it would imply that the amino donors appended at both C2 and C4 of the pyrimidinium are similarly involved in formation of the CT-band. However, the HOMO-1→LUMO transitions in all chromophores are localized around 400 nm but in **1** and **2** are these less dominant and well-separated from the HOMO→LUMO transitions.

The calculated second-order polarizabilities β range from 139 to 401×10^{-30} esu. Similarly to the EFISH experiment (see below), the lowest NLO response has been identified for diaryl derivative **2** with a truncated π -system. The largest β coefficient of 401×10^{-30} esu has been calculated for C2/C4-substituted chromophore **3** with 2,5-thienylene units but this value is not far from those of **4** and **1** bearing also extended π -systems. When calculating $\mu\beta$ products, C2/C4-substituted chromophore **3** and **4** possess enhanced NLO response over **1**, mostly due to their large dipole moments (refer also to Table 3 with the experimental data below).

NLO measurement

The second order NLO properties have been studied in chloroform solution by the electric-field induced second harmonic generation (EFISH) method at a non-resonant incident wavelength of 1907 nm. The second harmonic at $\lambda = 953$ nm is therefore well clear of the absorption bands of the chromophores.

The EFISH method provides an estimation of the NLO response as the scalar product between the permanent dipolar moment of the molecule $\vec{\mu}$ in the fundamental state and the

vector component of β described as β_{\parallel} .^[18] The two level corrected $\mu\beta$ values ($\mu\beta_0$) have been also calculated.^[19] In principle, electrostatic interaction of ions weakens with the square of their distance. As demonstrated by Tessore et al., EFISH-measured NLO response of methylpyridinium chromophores is dependent on the type of used anion, environment, and concentration.^[20] In aprotic and weakly acidic chloroform, we can reasonably assume a significant solvation of the methanesulfonate anion and diminished interaction with the pyrimidinium cation. According to the conclusion made by Tessore et al., significant dissociation of sulfonate ions affecting NLO response has been observed only in diluted solutions with concentrations below $10^{-3}/10^{-4}$ M. At higher concentrations, the ion pair is tightly bound and even forms aggregates with almost constant NLO response. Our recent investigation on pyridium iodides and phosphate intercalates revealed that the NLO response is mainly affected by the chromophore (supramolecular) arrangement and much less by the used anion.^[21] Bearing in mind the aforementioned conclusions, we consider the use of EFISH in CHCl_3 solvent at the concentration range of 10^{-3} to 10^{-2} M as a reasonable method with sufficient precautions towards obtaining unified NLO results comparable across the series of studied molecules **1-4**. The results are presented in Table 3. It should be noted that positive $\mu\beta$ values are obtained indicating that both ground and excited states are polarized in the same direction and that the excited state is more polar than the ground state. All compounds exhibit $\mu\beta_0$ values higher than $1000 \cdot 10^{-48}$ esu. Compared with already published (*E*)-4-(4-diphenylaminostyryl)-1-methyl-pyrimidin-1-ium iodine ($\mu\beta_0 = 1400 \cdot 10^{-48}$ esu, $\mu\beta_0/\text{MW} = 2.8 \cdot 10^{-48}$ esu mol g^{-1}) used as reference,^[13a] the 4,6-disubstituted pyrimidinium **1** exhibits a slightly higher NLO response, but the figure of merit is lower. On the other hand, pyrimidinium salt **4** exhibits a significantly higher $\mu\beta_0$ value and figure of merit than the reference and salt **1**. The 2,4-disubstitution of the pyrimidinium core appears therefore as the best strategy. It should be noted that the replacement of ethenylene linkers by 2,5-thienylene

ones (**3** vs **4**) significantly reduces the NLO response similarly to shortening the π -linkers (**2** vs **1**). The NLO response observed for these chromophores remains nevertheless significantly lower than the record value observed for values observed for twisted push-pull pyridinium derivatives described by Marks *et al.*^[22]

Table 3: Results for EFISH measurements for compounds **1-4**.

	1	2	3	4
$\mu\beta$ [10^{-48} esu] ^[a]	2600	1700	2400	3900
$\mu\beta_0$ [10^{-48} esu] ^[b]	1500	1200	1500	2500
$\mu\beta_0/MW$ ^[c]	2.1	1.8	1.8	3.4

[a] $\mu\beta(2\omega)$ at 1907 nm in CHCl_3 . Molecular concentrations used for the measurements were in the range of 10^{-3} to 10^{-2} M, $\mu\beta \pm 10\%$. [b] Two level corrected $\mu\beta$ values ($\mu\beta_0$).^[14] [c] Figure of merit 10^{-48} esu mol g^{-1}

Conclusion

In summary, four V-shaped pyrimidinium salts bearing diphenylamine as electron-donating group were designed. UV-visible spectrometry and (TD)-DFT theoretical calculation clearly revealed strong ICT in these chromophores. All chromophores exhibited strong 2nd order NLO response with $\mu\beta_0 > 1000 \times 10^{-48}$ esu. The best NLO chromophore is the 2-4-disubstituted methylpyrimidium salt **4** which exhibited significantly higher $\mu\beta_0$ value and figure of merit than 4-monosubstituted and 4,6-disubstituted analogues. These NLO chromophores with easy synthesis and high NLO figure of merit, appear as particularly promising for incorporation in polymer matrix to obtain material with high electro-optic coefficients for integrated optics.

Experimental part

General Conditions. Pyrimidine starting materials were synthesized according to reported procedure.^[14] Reagents and solvents were reagent-grade and were purchased from Sigma Aldrich or TCI Europe and used as received. NMR spectra were acquired at room temperature at 300/75 MHz or 500/126 MHz with a Bruker AVANCE spectrometers. Chemical shifts are given in parts per million relative to TMS (¹H, 0.0 ppm) and CDCl₃ (¹³C, 77.0 ppm). Acidic impurities in CDCl₃ were removed by treatment with anhydrous K₂CO₃. High-resolution mass analyses using a Bruker MicroTOFQ II apparatus were performed at the “Centre régional de Mesures Physiques de l’Ouest” (CRMPO, University of Rennes 1). High-resolution mass spectrometry for **3** was performed using a Bruker maXis Impact HD spectrometer (Center for Joint Use «Spectroscopy and Analysis of Organic Compounds» at the Postovsky Institute of Organic Synthesis of the Ural Branch of the Russian Academy of Sciences.). The absorption spectra were recorded with a Jasco V-650 spectrometer. Experimental details on EFISH measurements are described elsewhere.^[23]

General procedure for the synthesis of methylpyrimidinium methanesulfonate: A mixture 0.1 mmol of V-shaped pyrimidine **1-4** and 1 mL (11 mmol) of methyl methanesulfonate was heated at 120 °C and stirred for 32 h. After cooling, diethyl ether was added, the insoluble solid was filtered off, washed several times with diethyl ether to remove the excess of reagent, and dried under vacuum.

(*E,E*)-4,6-Bis[4-(diphenylamino)styryl]-1-methylpyrimidin-1-ium methanesulfonate (1**):** Dark blue solid. Yield: 60 mg (82%). ¹H NMR (300 MHz, DMSO-d₆) δ 9.21 (s, 1H), 8.43 (s, 1H), 8.19 (d, ³J_{H,H} = 16.2 Hz, 1H), 8.14 (d, ³J_{H,H} = 17.1 Hz, 1H), 7.79 (d, ³J_{H,H} = 8.7 Hz, 2H), 7.69 (d, ³J_{H,H} = 8.4 Hz, 2H), 7.44-7.33 (m, 8H), 7.28-7.08 (m, 16H), 6.93 (d, ³J_{H,H} = 7.5 Hz, 2H), 4.09 (s, 3H), 2.31 (s, 3H) ppm. ¹³C NMR (126 MHz, DMSO-d₆) δ 164.4, 156.9, 150.8, 150.0, 146.2, 145.9, 145.7, 142.6, 131.1, 130.3, 129.94, 129.89, 129.7, 127.2, 126.9, 125.9,

125.7, 125.1, 125.0, 124.8, 120.1, 119.5, 113.7, 112.4 ppm HRMS (ESI): m/z calcd for $C_{45}H_{37}N_4^+$: 633.3013 $[M-CH_3SO_3]^+$; found: 633.3011.

4,6-Bis[4-(diphenylamino)phenyl]-1-methylpyrimidin-1-ium methanesulfonate (2): Red solid. Yield: 46 mg (68%). 1H NMR (300 MHz, DMSO- d_6) δ 9.21 (s, 1H), 8.43 (s, 1H), 8.19 (d, $^3J_{H,H}$ = 16.2 Hz, 1H), 8.14 (d, $^3J_{H,H}$ = 17.1 Hz, 1H), 7.79 (d, $^3J_{H,H}$ = 8.7 Hz, 2H), 7.69 (d, $^3J_{H,H}$ = 8.4 Hz, 2H), 7.44-7.33 (m, 8H), 7.28-7.08 (m, 16H), 6.93 (d, $^3J_{H,H}$ = 7.5 Hz, 2H), 4.09 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, DMSO- d_6) δ 165.3, 159.8, 152.7, 150.5, 150.0, 146.3, 145.5, 145.0, 131.1, 130.8, 130.0, 129.9, 129.6, 126.5, 126.0, 125.8, 125.2, 125.1, 123.8, 123.1, 118.7, 118.1 ppm HRMS (ESI): m/z calcd for $C_{41}H_{33}N_4^+$: 581.2700 $[M-CH_3SO_3]^+$; found: 581.2699.

2,4-Bis{5-[4-(diphenylamino)phenyl]thiophen-2-yl}-1-methylpyrimidin-1-ium

methanesulfonate (3): Deep brown solid. Yield 77 mg (92%), mp 223-225 °C. 1H NMR (500 MHz, DMSO- d_6) δ 8.97 (d, $^3J_{H,H}$ = 7.0 Hz, 1H), 8.44 (d, $^3J_{H,H}$ = 4.2 Hz, 1H), 8.27-8.25 (m, 2H), 7.79-7.72 (m, 6H), 7.39-7.35 (m, 8H), 7.17-7.14 (m, 4H), 7.12-7.09 (m, 8H), 7.00-6.95 (m, 4H), 4.31 (s, 3H), 2.33 (s, 3H) ppm. ^{13}C NMR (126 MHz, DMSO- d_6) δ 160.9, 155.1, 153.9, 153.8, 152.5, 148.81, 148.78, 146.22, 146.18, 137.4, 136.8, 136.0, 132.0, 129.7, 127.4, 125.7, 125.3, 125.2, 125.1, 125.0, 124.8, 124.3, 124.2, 121.4, 121.2, 112.0, 46.1, 34.3 ppm. HRMS (ESI): m/z calcd for $C_{49}H_{37}N_4S_2^+$: 745.2454 $[M-CH_3SO_3]^+$; found: 745.2450.

(E,E)-2,4-Bis[4-(diphenylamino)styryl]-1-methylpyrimidin-1-ium methanesulfonate (4):

red. Solid. Yield 55 mg (75%). 1H NMR (300 MHz, $CDCl_3$) δ = 9.20 (br s, 1H), 8.36 (d, $^3J_{H,H}$ = 15 Hz, 1H), 8.04 (d, $^3J_{H,H}$ = 16 Hz, 1H), 7.57-7.50 (m, 5H), 7.36-7.30 (m, 7H), 7.18-6.96 (m, 19H), 4.28 (s, 3H), 2.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.4, 158.0, 152.5, 151.8, 151.3, 148.9, 146.5, 146.3, 145.5, 131.0, 130.6, 129.8, 129.8, 127.1, 126.5, 126.2, 126.1, 125.1, 124.9, 120.8, 120.6, 115.5, 110.8, 44.0, 39.6 ppm. HRMS (ESI): m/z calcd for $C_{45}H_{37}N_4^+$: 633.3013 $[M-CH_3SO_3]^+$; found: 633.3011.

Acknowledgments

VEV is grateful for the financial support for the synthetic part related to compound **3** from the Russian Foundation for Basic Research (Research Project No. 18-29-23045 mk). MF acknowledges the Région Bretagne, France for her Ph.D. funding (HOLED project).

Keywords

chromophores • donor-acceptor systems • photophysics • pyrimidines • second-order nonlinear optics

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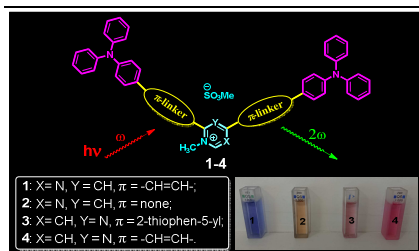
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A series of four diphenylamino substituted V-shaped pyrimidinium methanesulfonate salt were designed and their second order nonlinear optical (NLO) properties were thoroughly studied thanks to electric field induced second harmonic generation (EFISH) method. All pyrimidinium salts exhibited $\mu\beta_0 > 1\,000 \times 10^{-48}$ esu in chloroform. It has been shown that the 2,4-disubstituted pyrimidinium core enhances the NLO response over 4,6-disubstituted analogues.

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