

Short communication

Synthesis, characterization and nonlinear optical properties of 2-[(E)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-substitutedbenzenesulfonate compounds

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ABSTRACT

In the present investigation, 2-[(E)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-substituted benzenesulfonate ($X = \text{CH}_3$ (**1**), $X = \text{OCH}_3$ (**2**), $X = \text{Cl}$ (**3**), $X = \text{Br}$ (**4**)) have been synthesized and characterized by ¹H NMR, UV–Vis and FT-IR spectroscopy methods. In addition compound **3** was also characterized by single crystal X-ray diffraction (XRD) and found that it crystallized out in the monoclinic space group $P2_1$ with cell parameters, $a = 9.8072(9) \text{ \AA}$, $b = 6.4848(5) \text{ \AA}$, $c = 19.4405(16) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 103.421(5)^\circ$, $\gamma = 90^\circ$, $z = 2$ and $V = 1202.61(17) \text{ \AA}^3$. The nonlinear optical absorption of the samples has been studied at 532 nm using 5 ns laser pulses, employing the open-aperture z-scan technique. It is found that some of the samples are potential candidates for optical limiting applications.

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1. Introduction

The beginning of nonlinear optics is often taken to be the discovery of second-harmonic generation in a quartz crystal by Franken et al. [1] in 1961, shortly after the invention of the laser by Maiman in the previous year [2]. Interest in this field has grown continuously since it has significant impact on optical storage technology and integrated optics technology [3,4].

Much attention has been given to nonlinear optical (NLO) materials because of their promising applications including telecommunication, optical data storage, switching and limiting, and optical frequency conversion. Organic compounds with non-centrosymmetric structures have shown second-order nonlinear optical properties resulting from highly delocalized π -electrons with electron donor and electron acceptor groups on opposite sides of the molecules. For instance, many organic ionic salt crystals have shown a large second-order nonlinear susceptibility ($\chi^{(2)}$) [5–9]. Organic ionic crystals are interesting because they exhibit large

first hyperpolarizabilities, possess an easy tunability by changing the counter anion to crystallize into non-centrosymmetric structures, and have high melting points and hardness. The magnitude of optical nonlinearities depends on the strength of donor–acceptor groups and also their combinations: the best combination of donor–acceptor groups provides a better enhancement.

From literature it was found that styryl-quinolinium derivatives are good conjugated π -systems, and therefore, in our previous works, we synthesized and investigated the second-order NLO properties of a number of pyridinium and quinolinium salts. These were based on molecular units containing delocalized π -electrons with electron donor and electron acceptor groups on opposite sides of the molecules, and we found that the substituted quinolinium cationic parts have unique NLO features owing to their charge transfer resonant structures contributing to the ground state [10–14].

In view of the second-order effects observed, we were encouraged to investigate the third order nonlinearity of these materials as well. Therefore, by the salt methodology approach, we synthesized the donor–acceptor substituted quinolinium derivatives 2-[(E)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-substitutedbenzenesulfonate ($X = \text{CH}_3$ (**1**), $X = \text{OCH}_3$ (**2**), $X = \text{Cl}$ (**3**), $X = \text{Br}$ (**4**)). In order to induce non-centrosymmetric crystal structures the counter ions of the quinolinium salts were varied.

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The third order nonlinear optical property was measured by the open-aperture *z*-scan technique, which revealed the occurrence of induced absorption in these samples, making them potential candidates for the optical limiting application. The strength of the nonlinearity has been compared with those obtained in other organic systems under identical experimental conditions.

2. Experimental

2.1. Materials and methods

All the chemical reagents and solvents were of analytical grade and were purchased commercially and used without further purification.

Melting point was recorded in °C and was measured using an Electrothermal melting point apparatus. Infrared spectra were recorded by using FTS 165 FT-IR spectrophotometer. Ultraviolet–Visible (UV–Vis) absorption spectra were recorded using a SPECORD S 100 (Analytikjena). The ¹H NMR spectra were recorded on 300 MHz Bruker FTNMR Ultra Shield™ spectrometer in CDCl₃+DMSO-*d*₆ with TMS as the internal standard. Chemical shifts are reported in (ppm) and coupling constants (J) are expressed in hertz. Single crystal X-ray diffraction measurements were collected using a Bruker Apex2 CCD diffractometer with a graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$).

2.2. Synthesis

2.2.1. Synthesis of

2-[(*E*)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium iodide

2-[(*E*)-2-(4-Ethoxyphenyl)ethenyl]-1-methylquinolinium iodide was prepared to be employed as cationic part by refluxing a stirred solution of 1,2-dimethylquinolinium iodide (2.98 g, 10.05 mmol), 4-ethoxybenzaldehyde (1.46 ml, 10.05 mmol) and piperidine (1.00 ml, 10.00 mmol) in methanol (25 ml) for 3 h under nitrogen atmosphere. The solid was filtered, washed with diethyl ether to give brown-red solid of 2-[(*E*)-2-(4-Ethoxyphenyl)ethenyl]-1-methylquinolinium (3.86 g, 92%), mp. 219–221 °C, UV (CH₃OH) λ_{max} (nm) (log ϵ): 217.5 (3.59), 252.8 (3.02), 314.1 (3.54) and 416.2 (3.19) nm, IR (KBr) ν (cm⁻¹): C=C (1605 cm⁻¹) and C–O (1233 cm⁻¹), ¹H NMR (300 MHz, DMSO-*d*₆+CDCl₃): δ 8.09 (1H, *d*, *J*=15.6 Hz), δ 7.74 (1H, *d*, *J*=15.6 Hz), δ 4.62 (3H, *s*), δ 1.42 (3H, *t*, *J*=6.9 Hz), δ 4.15 (2H, *q*, *J*=6.9 Hz), δ 7.89 (2H, *d*, *J*=8.7 Hz), δ 7.02 (2H, *d*, *J*=8.7 Hz), δ 8.93 (1H, *d*, *J*=9.0 Hz), δ 8.50 (1H, *d*, *J*=9.0 Hz), δ 8.27 (1H, *d*, *J*=8.7 Hz), δ 7.90 (1H, *t*, *J*=8.7 Hz), δ 8.15 (1H, *t*, *J*=8.7 Hz) and δ 8.45 (1H, *d*, *J*=8.7 Hz).

2.2.2. Synthesis of

2-[(*E*)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-methylbenzenesulfonate (**1**)

2-[(*E*)-2-(4-Ethoxyphenyl)ethenyl]-1-methylquinolinium 4-methylbenzenesulfonate (**1**), was synthesized by addition of a solution of silver (I) 4-methylbenzenesulfonate [10] (0.067 g, 0.24 mmol) in hot methanol (10 ml) to a solution of **1** (0.10 g, 0.24 mmol) in hot methanol (70 ml). Upon addition, a yellow solid of silver iodide was immediately formed which was removed by filtration and the yellow filtrate was evaporated under reduced pressure to yield a yellow solid of **1** (0.06 g, 54%), mp. 250–252 °C, UV (CH₃OH) λ_{max} (nm) (log ϵ): 202.7 (4.68), 217.6 (4.88), 256.2 (3.45) and 413.9 (3.75) nm, IR (KBr) ν (cm⁻¹): C=C (1592 cm⁻¹), C–O (1220 cm⁻¹) and S=O in sulfonates (1175 cm⁻¹), ¹H NMR (300 MHz, DMSO-*d*₆+CDCl₃): δ 7.69 (1H, *d*, *J*=15.9 Hz), δ 8.09 (1H, *d*, *J*=15.9 Hz), δ 1.49 (3H, *t*, *J*=6.9 Hz), δ 4.08 (2H, *q*, *J*=6.9 Hz), δ 7.83 (2H, *d*, *J*=8.7 Hz), δ 6.96 (2H, *d*, *J*=8.7 Hz), δ 8.43 (1H, *d*, *J*=9.0 Hz), δ 8.85 (1H, *d*, *J*=9.0 Hz), δ 8.22 (1H, *d*, *J*=7.5 Hz), δ 7.84 (1H, *t*,

δ 7.5 Hz), δ 8.09 (1H, *t*, *J*=7.5 Hz), δ 8.39 (1H, *d*, *J*=7.5 Hz), δ 7.57 (2H, *J*=8.1 Hz, H-2''', H-6'''), δ 7.03 (2H, *J*=8.1 Hz) and δ 2.27 (3H).

2.2.3. Synthesis of

2-[(*E*)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (**2**)

2-[(*E*)-2-(4-Ethoxyphenyl)ethenyl]-1-methylquinolinium 4-methoxybenzenesulfonate (**2**), was synthesized by addition of a solution of silver (I) 4-methoxybenzenesulfonate [13] (0.071 g, 0.24 mmol) in hot methanol (20 ml) to a solution of **2** (0.10 g, 0.24 mmol) in hot methanol (70 ml). Upon addition a yellow solid of silver iodide was immediately formed which was removed by filtration and the yellow filtrate was evaporated under reduced pressure to yield a yellow solid of **2** (0.07 g, 61%), mp. 256–257 °C, UV (CH₃OH) λ_{max} (nm) (log ϵ): 330.3 (3.21) and 413.1 (4.46) nm, IR (KBr) ν (cm⁻¹): C=C (1572 cm⁻¹), C–O (1220 cm⁻¹) and S=O in sulfonates (1164 cm⁻¹), ¹H NMR (300 MHz, DMSO-*d*₆+CDCl₃): 4.60 (3H, *s*), 1.45 (3H, *t*, *J*=6.9 Hz), 4.13 (2H, *q*, *J*=6.9 Hz), 8.47 (1H, *d*, *J*=9.0 Hz), 8.89 (1H, *d*, *J*=9.0 Hz), 8.25 (1H, *d*, *J*=7.5 Hz), 7.89 (1H, *t*, *J*=7.5 Hz), 8.18 (1H, *t*, *J*=7.5 Hz), 8.40 (1H, *d*, *J*=7.5 Hz), 7.70 (1H, *d*, *J*=15.8), 8.09 (1H, *d*, *J*=15.8), 7.85 (2H, *d*, *J*=8.7), 6.80 (2H, *d*, *J*=8.7), 7.60 (2H, *d*, *J*=8.1) and 7.01 (2H, *d*, *J*=8.1), 3.78 (3H, *s*).

2.2.4. Synthesis of 2-[(*E*)-2-(4-

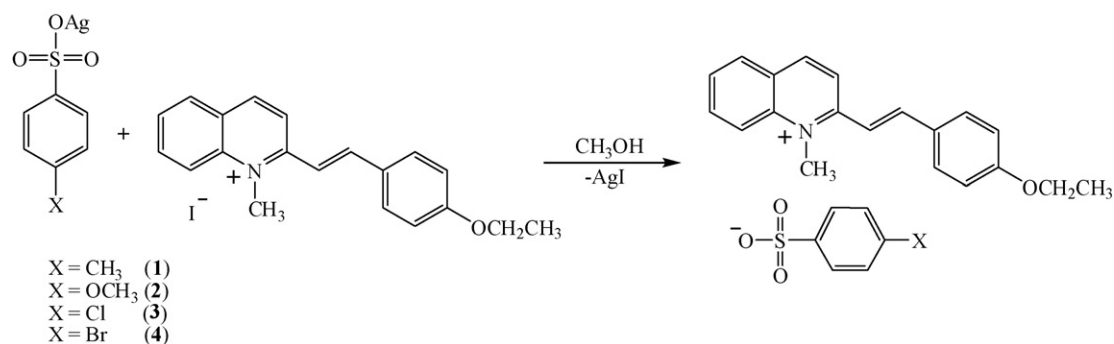
ethoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (**3**)

2-[(*E*)-2-(4-Ethoxyphenyl)ethenyl]-1-methylquinolinium 4-chlorobenzenesulfonate (**3**), was synthesized by addition of a solution of silver (I) 4-chlorobenzenesulfonate [14] (0.072 g, 0.24 mmol) in hot methanol (20 ml) to a solution of 2-[(*E*)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium iodide (0.10 g, 0.24 mmol) in hot methanol (70 ml). Upon addition a yellow solid of silver iodide was immediately formed which was removed by filtration and the yellow filtrate was evaporated under reduced pressure to yield a yellow-orange solid, The brown solid was re-crystallized from methanol to give yellow crystals of **3** (0.07 g, 62%) (mp. 254–256 °C), UV (CH₃OH) λ_{max} (nm) (log ϵ): 228.7 (3.86), 268.4 (3.12) and 410.2 (4.37) nm, IR (KBr) ν (cm⁻¹): C=C (1592 cm⁻¹), C–O (1225 cm⁻¹) and S=O in sulfonates (1153 cm⁻¹), ¹H NMR (300 MHz, DMSO-*d*₆+CDCl₃): 4.60 (3H, *s*), 1.46 (3H, *t*, *J*=6.9 Hz), 4.18 (2H, *q*, *J*=6.9 Hz), 8.45 (1H, *d*, *J*=9.0 Hz), 8.90 (1H, *d*, *J*=9.0 Hz), 8.35 (1H, *d*, *J*=7.5 Hz), 7.91 (1H, *t*, *J*=7.5 Hz), 8.12 (1H, *t*, *J*=7.5 Hz), 8.41 (1H, *d*, *J*=7.5 Hz), 7.72 (1H, *d*, *J*=15.9), 8.09 (1H, *d*, *J*=15.9), 7.78 (2H, *d*, *J*=8.7), 7.05 (2H, *d*, *J*=8.7), 7.74 (2H, *d*, *J*=8.1) and 7.30 (2H, *d*, *J*=8.1).

2.2.5. Synthesis of

2-[(*E*)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-bromobenzenesulfonate (**4**)

2-[(*E*)-2-(4-Ethoxyphenyl)ethenyl]-1-methylquinolinium 4-bromobenzenesulfonate (**4**), was synthesized by addition of a solution of silver (I) 4-bromobenzenesulfonate [12] (0.083 g, 0.24 mmol) in hot methanol (20 ml) to a solution of 2-[(*E*)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium iodide (0.10 g, 0.24 mmol) in hot methanol (70 ml). Upon addition a yellow solid of silver iodide was immediately formed which was removed by filtration and the yellow filtrate was evaporated under reduced pressure to yield a yellow-orange solid, The brown solid was re-crystallized from methanol to give yellow crystals of compound **4** (0.07 g, 62%) (mp. 254–256 °C), UV (CH₃OH) λ_{max} (nm) (log ϵ): 221.0 (4.20), 255.5 (3.69) and 413.9 (2.68) nm, IR (KBr) ν (cm⁻¹): C=C (1592 cm⁻¹), C–O (1224 cm⁻¹) and S=O in sulfonates (1169 cm⁻¹), ¹H NMR (300 MHz, DMSO-*d*₆+CDCl₃): 4.55 (3H, *s*), 1.40 (3H, *t*, 6.9 Hz), 4.10 (2H, *q*, 6.9 Hz), 8.48 (1H, *d*, 9.0 Hz), 8.89 (1H, *d*, 9.0 Hz), 8.25 (1H, *d*, 7.5 Hz), 7.87 (1H, *t*, 7.5 Hz), 8.09 (1H, *t*, 7.5 Hz), 8.44 (1H, *d*, 7.5 Hz), 7.72 (1H, *d*, 15.9), 8.00 (1H, *d*, 15.9),



Scheme 1. Synthesis of 2-[(E)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-substitutedbenzenesulfonate (1–4).

7.84 (2H, *d*, 8.7), 6.98 (2H, *d*, 8.7), 7.60 (2H, *d*, 8.1) and 7.41 (2H, *d*, 8.1) (Scheme 1).

3. Results and discussion

3.1. UV–Vis spectroscopy

The UV–Vis absorption spectra were made using methanol in the wavelength range of 200–800 nm. The UV–Vis spectra of compounds 1–4 in methanol showed absorption bands between 200 and 415 nm. All compounds 1–4 showed the absorption maximum in the same ranges at the position ca. 415–420 nm which is ascribed to the π -extended system from donor (ethoxy) to acceptor (quinolinium). The UV–Vis absorption spectra of compounds 1–4 are shown in Fig. 1a–d.

3.2. FT-IR spectroscopy

As FT-IR spectroscopy is one of the major physical methods of investigation of the molecular structure, FT-IR spectra of compounds 1–4 have been investigated in the frequency range 400–4000 cm^{-1} . From the FT-IR analysis seen in Fig. 2a–d it was found that the peaks observed at 1570–1600, 1220–1225 and 1150–1180 cm^{-1} were numbers pertain to the C=C bonds in aromatic rings, the C–O bonds and S=O bonds in sulfonates, respectively.

3.3. X-ray structure

The single crystal X-ray diffraction data for compound 3 was collected using a Bruker Apex2 CCD diffractometer with a graphite monochromated MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) at a detector distance of 5 cm and with APEX2 software. The collected data were reduced using the S_{AINT} [15] program and the empirical absorption corrections were performed using the S_{ADABS} program. The structure was solved by direct methods and refined by least-squares using the S_{HELXTL} [16] software package. The crystallographic data and selected bond lengths (Å) and bond angles (°) for compound 3 are listed in Tables 1 and 2, respectively. X-ray ORTEP diagram and packing diagram of compound 3 are shown in Figs. 3 and 4, respectively.

The crystallographic-information files for compound 3 have been deposited in the Cambridge Crystallographic Data Centre as CCDC742146. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 1
Crystal data of compound 3.

Empirical formula	C ₂₆ H ₂₈ ClNO ₆ S
Formula weight	518.00
Temperature	100.0(1) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁
Unit cell dimensions	<i>a</i> = 9.8072(9) Å, α = 90° <i>b</i> = 6.4848(5) Å, β = 103.421(5)° <i>c</i> = 19.4405(16) Å, γ = 90°
Volume	1202.61(17) Å ³
Z, Calculated density	2, 1.431 Mg/m ³
Absorption coefficient	0.290 mm ⁻¹
<i>F</i> (000)	544
Crystal size	0.58 mm × 0.26 mm × 0.06 mm
Theta range for data collection	2.13–30.00°
Limiting indices	−13 ≤ <i>h</i> ≤ 13, −9 ≤ <i>k</i> ≤ 9, −27 ≤ <i>l</i> ≤ 27
Reflections collected/unique	12272/6192 [<i>R</i> (int) = 0.0603]
Completeness to theta = 30.00	99.7%
Max. and min. transmission	0.9820 and 0.8505
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6192/1/316
Goodness-of-fit on <i>F</i> ²	1.035
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0705, <i>wR</i> 2 = 0.1494
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0907, <i>wR</i> 2 = 0.1585
Largest diff. peak and hole	0.747 and −0.589 e Å ³

Table 2
Selected bond lengths (Å) and angles (°) of compound 3.

Bond	Length (Å)	Bond angle	Angle (°)
S1–O2	1.445(5)	O2–S1–O4	113.1(3)
S1–O4	1.454(5)	O2–S1–O3	113.1(3)
S1–O3	1.455(4)	O4–S1–O3	112.7(3)
C11–C21	1.744(6)	O2–S1–C24	105.9(3)
O1–C15	1.364(7)	O4–S1–C24	105.4(3)
O1–C18	1.444(7)	O3–S1–C24	105.8(3)
C1–N1	1.413(8)	C15–O1–C18	118.8(4)
C15–C16	1.406(8)	C6–C1–C2	119.5(6)
C16–C17	1.386(9)	C6–C1–N1	119.2(5)
C20–N1	1.470(8)	C2–C1–N1	121.3(5)
C21–C26	1.365(9)	C3–C2–C1	119.5(6)
C21–C22	1.397(10)	C2–C3–C4	121.1(6)
C22–C23	1.381(9)	N1–C9–C8	118.2(5)
C23–C24	1.389(8)	N1–C9–C10	121.1(5)
C24–C25	1.398(9)	O1–C18–C19	106.2(5)
C25–C26	1.381(9)	C9–N1–C1	121.9(5)
		C9–N1–C20	121.7(5)
		C1–N1–C20	116.4(5)
Torsion angle		Angle (°)	
C9–C10–C11–C12		−179.1(6)	
C8–C9–C10–C11		0.0(9)	
C10–C11–C12–C17		8.4(10)	

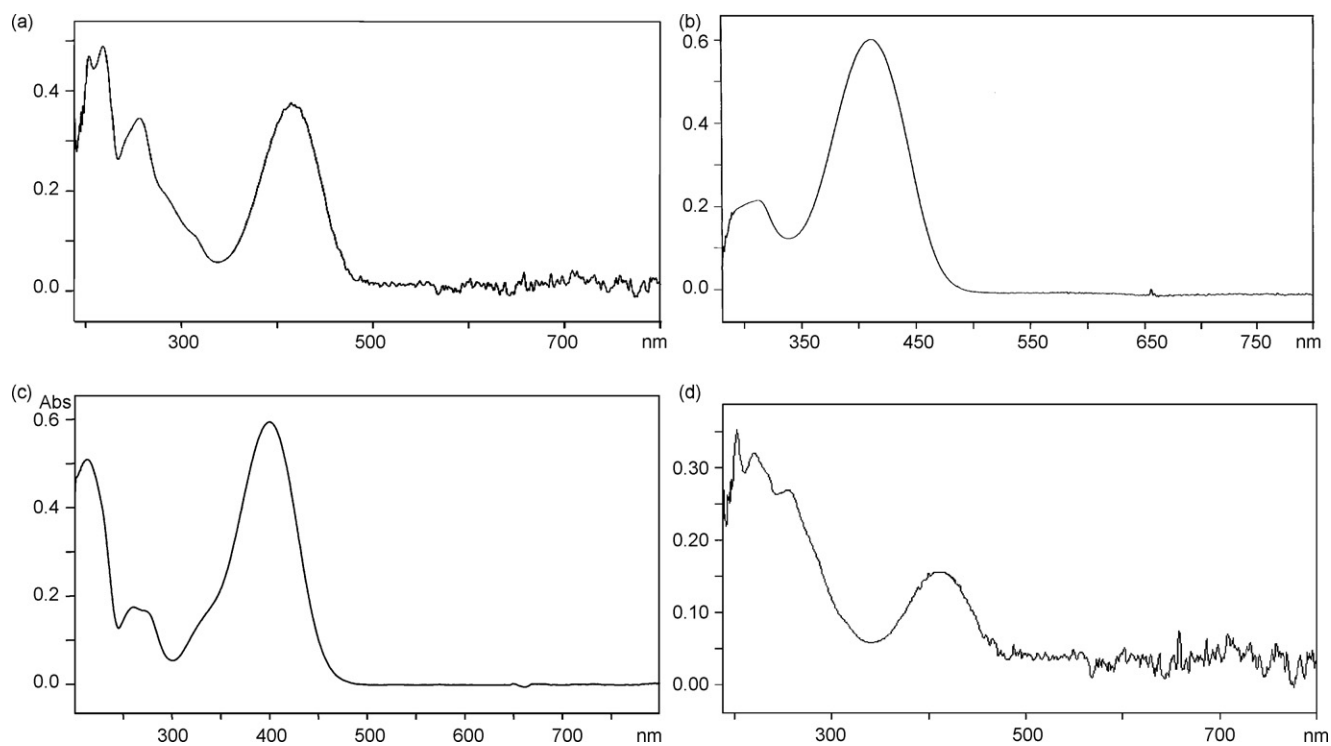


Fig. 1. UV-Vis (CH₃OH) spectrum of compounds 1 (a), 2 (b), 3 (c) and 4 (d).

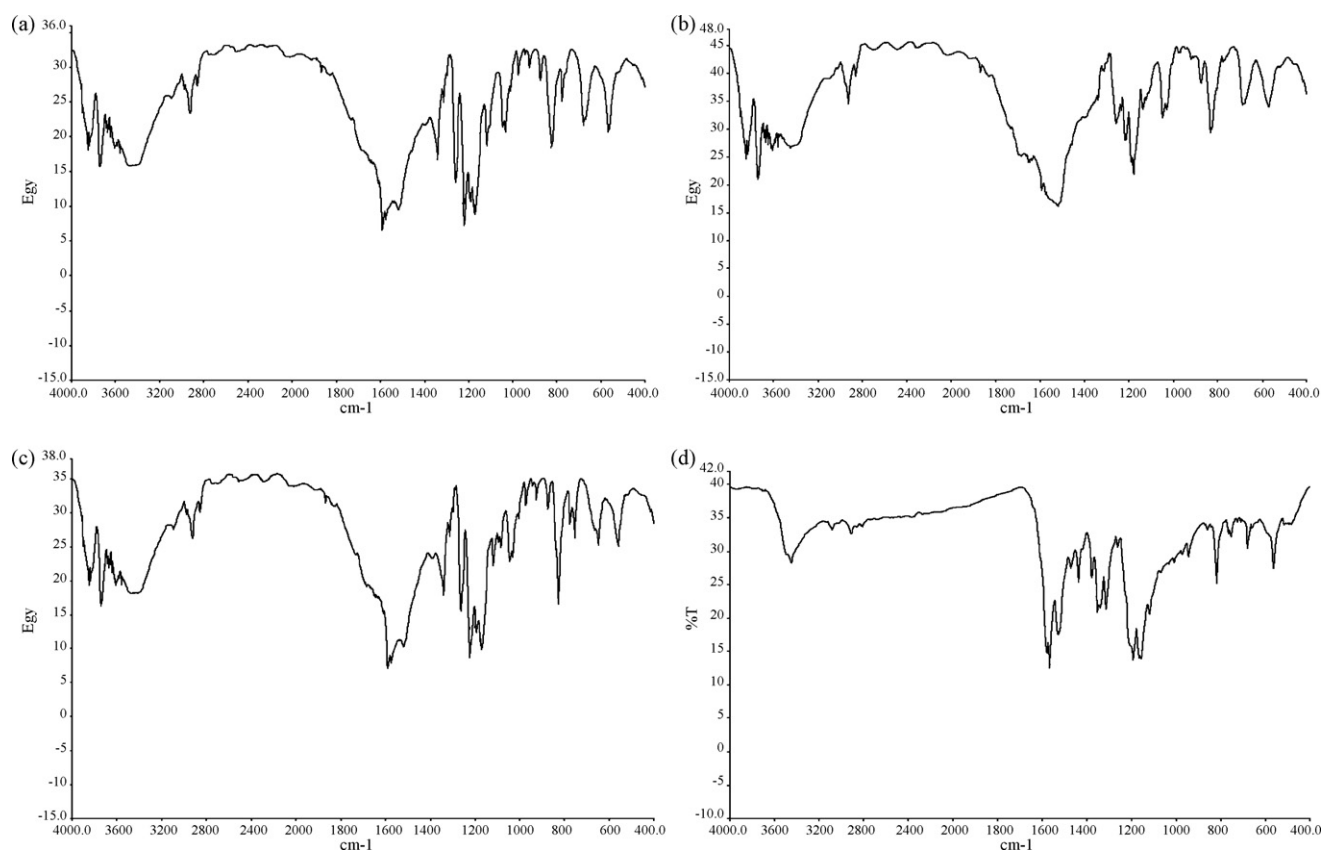


Fig. 2. FT-IR (KBr) spectrum of compounds 1 (a), 2 (b), 3 (c) and 4 (d).

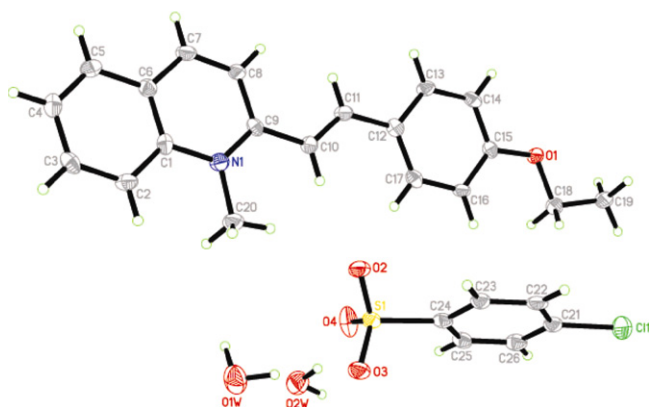


Fig. 3. X-ray ORTEP diagram of compound **3**.

4. Nonlinear optical properties

The samples used in the present nonlinear optical measurements were so prepared that each of them gave a linear transmission of 70% at the excitation wavelength of 532 nm, when taken in a 1 mm pathlength cuvette. To measure the nonlinear absorption, we used the *z*-scan technique, which is a popular method developed by Sheik Bahae et al. [17]. The “open-aperture” *z*-scan is used for nonlinear absorption coefficient measurements. Here a laser beam is used for sample excitation, and its propagation direction is taken as the *z*-axis. The beam is focused using a convex lens, and the focal point is taken as *z* = 0. The experiment is done by placing the sample in the beam at different positions with respect to the focus (different values of *z*), and measuring the corresponding transmission. The beam will have maximum energy density at the focus, which will symmetrically reduce towards either side of it, for the positive and negative values of *z*. Thus the sample sees different laser intensity at each *z* position. From a set of transmission values corresponding to the *z* values, the open-aperture *z*-scan curve can be drawn. The nonlinear absorption coefficient of the sample can be calculated by fitting the experimental data to theory.

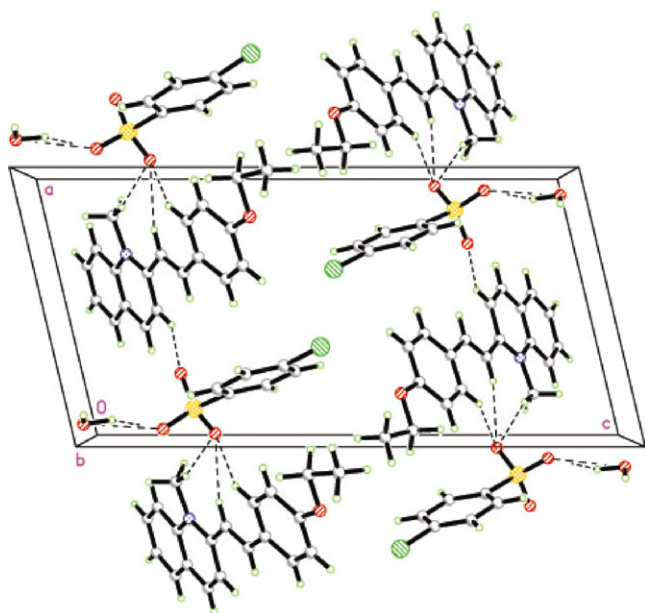


Fig. 4. Packing diagram of compound **3** viewed down the *b* axis with H-bonds shown as dashed lines.

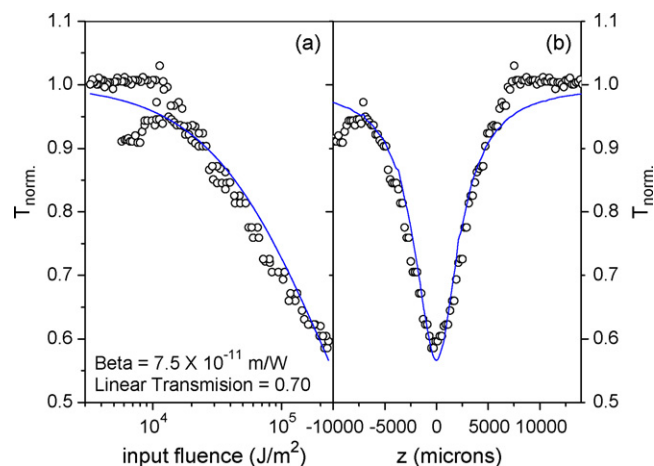


Fig. 5. Nonlinear absorption in compound **1**, when excited at 532 nm using 5 ns laser pulses. (a) Normalized transmission of the sample as a function of the input laser fluence and (b) the open-aperture *z*-scan curve. Circles are experimental data points while the solid curves are numerical fits using Eq. (1).

We used the second-harmonic output from a Q-switched Nd:YAG nanosecond laser (Quanta Ray, Spectra Physics), at 532 nm, for the measurements. The linear absorption spectra of the compounds show that this wavelength is in the off-resonant region. The laser pulses had a width (FWHM) of 7 ns. The output of the laser had a nearly Gaussian spatial intensity profile. The sample was taken in a 1 mm cuvette. The transmission of the sample at each point was measured by means of two pyroelectric energy probes (Rj7620, Laser Probe Inc.). One energy probe monitored the input energy, while the other monitored the transmitted energy through the sample. The pulses were fired in the “single shot” mode, allowing sufficient time between successive pulses to avoid accumulative thermal effects in the sample.

Compounds **1** and **2** exhibited the nonlinear optical absorption property, and the data obtained for compound **1** is shown in Fig. 5. In an optical limiter, the sample transmittance decreases when the input light intensity is increased. Optical limiting is an application useful for the protection of human eyes and sensitive optical detectors from accidental exposure to intense light beams. Another interesting application of optical limiting is in laser stabilization [18].

It is seen that a two-photon absorption (2PA) type process gives the best fit to the obtained experimental data. The *z*-scan curves obtained are therefore numerically fitted to the nonlinear transmission equation for a two-photon absorption process, given by the equation [19]:

$$T = \left((1 - R)^2 \frac{\exp(-\alpha_0 L)}{\sqrt{\pi} q_0} \right) \int_{-\infty}^{+\infty} \ln [1 + q_0 \exp(-t^2)] dt \quad (1)$$

where *T* is the net transmission of the sample, *L* and *R* are the sample length and surface reflectivity respectively, and α_0 is the linear absorption coefficient. The parameter q_0 in Eq. (1) is given by $\beta(1 - R)I_0 L_{eff}$, where I_0 is the on-axis peak laser intensity, L_{eff} is given by $[1 - \exp(-\alpha_0 L)]/\alpha_0$, and β is the two-photon absorption coefficient. The observed two-photon type nonlinearity originates from genuine two-photon as well as two-step (excited state) absorptions, and hence the nonlinearity can be considered as an “effective” two-photon absorption process. Absorptive nonlinearities involving real excited states have been reported earlier in C₆₀ (fullerenes), metal-nanoclusters, semiconductors, porphyrins, etc. [20–25]. The effective 2PA coefficient for compound **1** obtained from the best numerical fit to the data is 7.5×10^{-11} m/W. In comparison, earlier

we have obtained values of 9 and 23×10^{-11} m/W in polyaniline and a polyaniline-porphyrin nanocomposite, respectively [26], and 30×10^{-11} m/W in a copolymer containing oxadiazole and substituted thiophenes [27] under similar experimental conditions.

5. Conclusions

In conclusion, we have successfully prepared 2-[(E)-2-(4-ethoxyphenyl)ethenyl]-1-methylquinolinium 4-substitutedbenzenesulfonate (X=CH₃ (**1**), X=OCH₃ (**2**), X=Cl (**3**), X=Br (**4**)), characterized them, and studied their third order optical nonlinearity by the open-aperture z-scan technique. Compounds **1** and **2** exhibited nonlinear absorption which fits well to an effective two-photon absorption (**2PA**) behavior. The value of the effective two-photon absorption coefficient (β) has been numerically calculated for compound **1**, and compared with our earlier measurements in other organic systems. The absorptive nonlinearity observed is of the optical limiting type, which can have potential applications in the design and fabrication of optical power limiting devices.

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References

[1] P.A. Franken, A.E. Hill, C.W. Peters, G. Weinreich, Phys. Rev. Lett. 7 (1961) 118.

- [2] T.H. Maiman, Nature 187 (1960) 493.
 [3] M. Bass, P.A. Franken, J.F. Ward, G. Weinreich, Phys. Rev. Lett. 9 (1962) 446.
 [4] D.J. Williams, Angew. Chem. Int. Ed. Engl. 23 (1984) 690.
 [5] H. Unver, A. Karakas, A. Elmali, T.N. Durlu, J. Mol. Struct. 737 (2005) 131.
 [6] A. Usman, K. Hiroaki, O. Shuji, O. Hidetoshi, N. Hachiro, J. Appl. Phys. 40 (2001) 4213.
 [7] S. Dhanuskodi, S. Manivannan, J. Cryst. Growth 262 (2004) 395.
 [8] S.K. Lakshmana Perumal, A.A. Chakkaravarthi, N.P. Rajesh, P. Santhana Raghavan, Y.C. Huang, M. Ichimura, P. Ramasamy, J. Cryst. Growth 240 (2002) 212.
 [9] V. Crasta, V. Ravindrachary, S. Lakshmi, S.N. Pramod, M.A. Shridar, J. Shashidhara Prasad, J. Cryst. Growth 275 (2005) e329.
 [10] S. Chantrapromma, B. Jindawong, H.-K. Fun, P.S. Patil, C. Karalai, Anal. Sci. 23 (2007), x27.
 [11] S. Chantrapromma, B. Jindawong, H.-K. Fun, P.S. Patil, C. Karalai, Acta Cryst. E 62 (2006), o1802.
 [12] S. Chantrapromma, P. Ruanwas, H.-K. Fun, P.S. Patil, Acta Cryst. E 62 (2006) o5494.
 [13] S. Chantrapromma, B. Jindawong, H.-K. Fun, P.S. Patil, Anal. Sci. 23 (2007), x81.
 [14] S. Chantrapromma, T. Suwanwong, H.-K. Fun, Acta Cryst. E 63 (2007) o821.
 [15] Bruker, APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2005).
 [16] G.M. Sheldrick, Acta Cryst. A 64 (2008) 112.
 [17] M. Sheik Bahae, A.A. Said, T.M. Wei, D.J. Hagan, E.W. Vanstryland, IEEE J. Quant. Electron 26 (1990) 760.
 [18] F.J. Aranda, M.T. Harris, M.J. Callahan, J.S. Bailey, M.J. Suscavage, D.F. Bliss, B.R. Kimball, M. Nakashima, B.S. Decristofano, D.V.G.L.N. Rao, Proc. SPIE 3798 (1999) 22.
 [19] R.L. Sutherland, Handbook of Nonlinear Optics, Dekker, New York, 1996.
 [20] S. Couris, E. Koudoumas, A.A. Ruth, S. Leach, J. Phys. B: Atom. Mol. Opt. Phys. 28 (1995) 4537.
 [21] R. Philip, G. Ravindra Kumar, N. Sandhyarani, T. Pradeep, Phys. Rev. B 62 (2000) 13160.
 [22] E.M. Ni Mhuircheartaigh, S. Giordan, W.J. Blau, J. Phys. Chem. B 110 (2006) 23136.
 [23] L. Irimpan, V.P.N. Nampoore, P. Radhakrishnan, B. Krishnan, A. Deepthy, J. Appl. Phys. 103 (2008) 033105.
 [24] I. Cohanoschi, M. Garci, C. Toro, F.K.D. Belfield, F.E. Hernandez, Chem. Phys. Lett. 430 (2006) 133.
 [25] P. Wang, H. Ming, J. Xie, W. Zhang, X. Gao, Z. Xu, X. Wei, Opt. Commun. 192 (2001) 387.
 [26] R.K. Pandey, C.S. Suchand Sandeep, R. Philip, V. Lakshminarayanan, J. Phys. Chem. C 113 (2009) 8630.
 [27] A.J. Kiran, D. Udayakumar, K. Chandrasekharan, A.V. Adhikari, H.D. Shashikala, R. Philip, Opt. Commun. 271 (2007) 236.