Supplementary Informations

Table S1 Short contacts in [**1**](ClO$_4$)$_3$.H$_2$O

Table S2 C$-$H….O interactions in [**4**]ClO$_4$.C$_6$H$_6$

Fig. S1 Packing diagram of [**1**](ClO$_4$)$_3$.H$_2$O (down *b*$-$axis).

Fig. S2 Electrospray mass spectrum of [**1**](ClO$_4$)$_3$ in CH$_3$CN.

Fig. S3 Electrospray mass spectrum of [**4**](ClO$_4$)$_3$ in CH$_3$CN.

Fig. S4 Experimental layout for nonlinear absorption and z$-$scan measurements.

Description of the Z$-$scan technique used.

Table S1 Short contacts in [**1**](ClO$_4$)$_3$.H$_2$O

Donor --- H....Acceptor	H...A (Å)	D...A (Å)	D – H...A (º)
C(13) -- H(13) .. O(1) ii	2.4902	3.3946	164.21
C(18) -- H(18) .. N(1) [Intra]	2.4957	3.1527	127.82
C(21) -- H(21) .. O(3) ii	2.5625	3.3301	140.13
C(23) -- H(23) .. O(1) [Intra]	2.5740	3.2642	131.37
C(30) -- H(30) .. O(12) iii	2.5011	3.4274	174.02
C(34) -- H(34) .. S(2) [Intra]	2.8173	3.4213	123.64
C(35) -- H(35) ..*O(14) iii	2.4216	3.2820	153.83
C(43) -- H(43) .. O(11) iv	2.5046	3.1935	131.07
C(55) -- H(55) .. S(3) [Intra]	2.7701	3.3432	120.80
C(61) -- H(61) ..*O(13) iii	2.5971	3.4591	154.37
C(63) -- H(63) .. N(11) i	2.5665	3.4890	171.51
C(64) -- H(64) .. O(5) v	2.4719	3.3099	149.96
C(65) -- H(65) .. N(13) [Intra]	2.5704	3.1193	118.19

Equivalent Position Code

i = 1/2–x,1/2+y,1/2–z

ii   = 1–x, –y,1–z

iii = –1/2+x,1/2–y, –1/2+z

iv = 3/2–x, –1/2+y,1/2–z

v = –1/2+x,1/2–y,1/2+z

Table S2 C‑H….O interactions in [**4**]$ClO_4.C_6H_6$

	Donor --- H….Acceptor	H...A (Å)	D...A (Å)	D – H...A(º)
1	C(3) -- H(3) .. O(1)^{i}	2.5677	3.3209	138.39
2	C(4) -- H(4) .. O(3)^{i}	2.5960	3.4792	158.78
3	C(7) -- H(7) .. O(4)^{ii}	2.4626	3.1795	133.96
4	C(30) -- H(30) .. O(4)^{iii}	2.5808	3.4856	164.42

Equivalent Position Code

i = 1–x, –y, 1–z
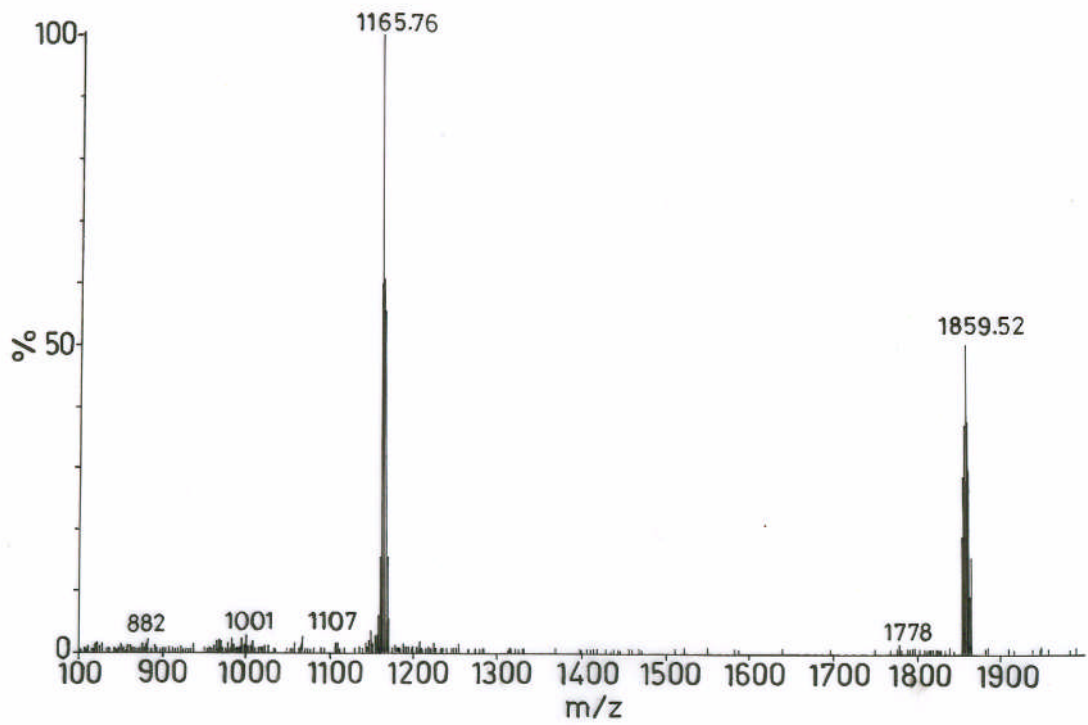
ii = 1+x, y, –1+z

iii = x, y, –1+z

Fig. S1

Fig. S2

Fig. S3

Nd:YAG Laser
(λ = 532 nm)

B.S

Lens

S

B.S

A

P.D 3

-z   +z

P.D 1

P.D 2

CRO

DAQ
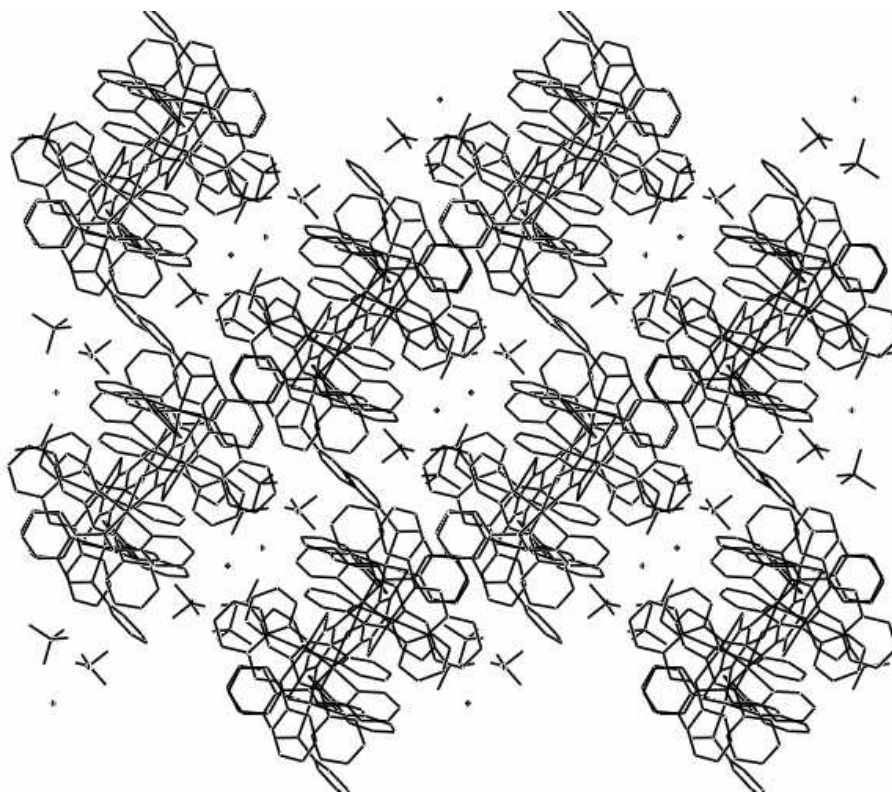
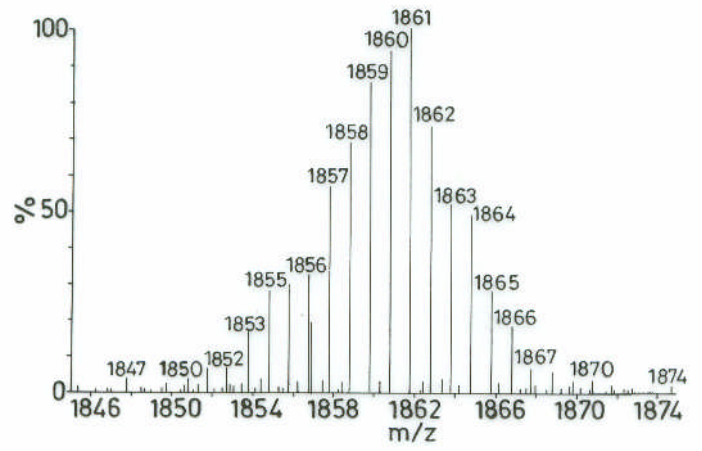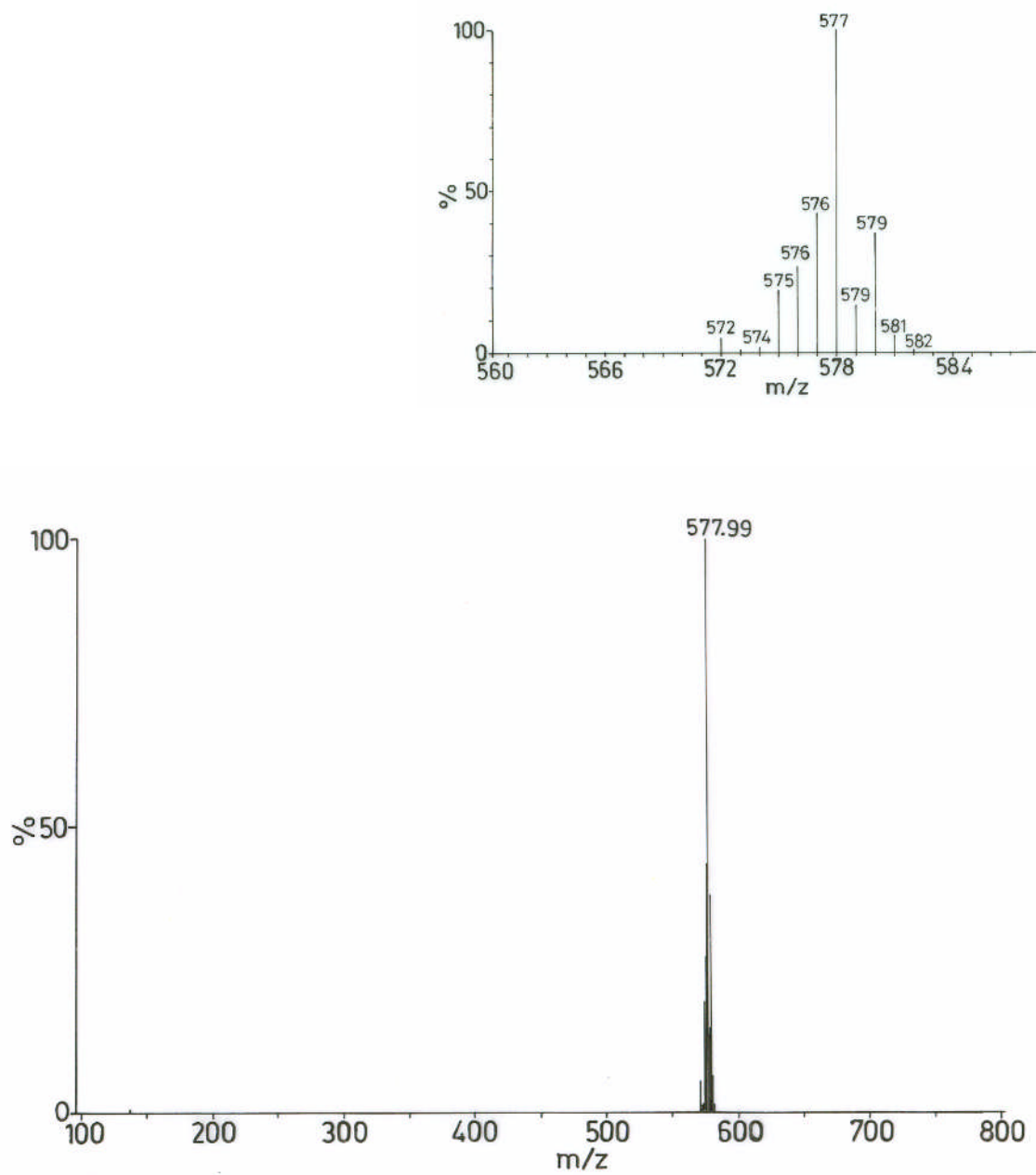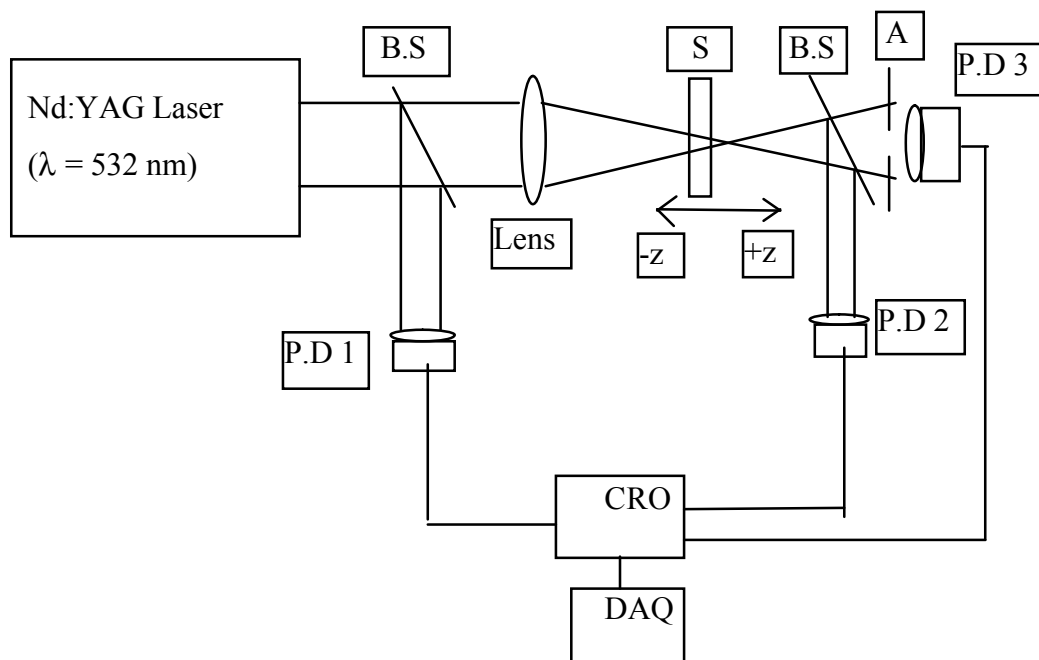**Fig. S4**

Description of the Z–scan technique used

This single beam technique is based on the transformation of the phase distortion due to nonlinear refractive index to amplitude distortion in the far field. In this technique the sample is scanned across the focused Gaussian beam along its propagation direction z. The nonlinear optical parameters are estimated from the far field transmittance variation of the laser beam through the sample with the scan position. The open aperture scan gives the information about the nonlinear absorption coefficient (β). The variation of normalised transmittance with the nonlinear absorption coefficient is given by the eqn. 3,[27]

$$T_{norm}(z) = \frac{1}{q_0\sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2})dt \qquad (3)$$

here q_0 is given by eqn. 4,

$$q_0 = \frac{\beta I_0(1 - e^{-\alpha_0 l})}{(1 + z^2/z_0^2)\alpha_0} \qquad (4)$$

where I_0 is the on axis intensity of the beam at the focus, l is the path length of the sample, z_0 is the Rayleigh range of the beam and α_0 is the linear absorption coefficient of the sample at the excitation wavelength. The closed aperture scan, on the other hand contains the information of both the nonlinear refraction as well as the nonlinear absorption. The refractive part of nonlinearity is then easily separated out by taking the ratio of close aperture data and open aperture data. The nature of the curve of pure refractive part directly provides the information related to the sign of nonlinearity. A pre-focal maxima and post-focal minima represents the negative nonlinearity, the self-defocusing effect, while a reverse signature represents the positive nonlinearity, the self-focusing effect. The peak to valley transmittance difference ΔT_{pv} is a measure of

nonlinear refractive index as it is linearly related to the spatial phase distortion $\Delta\phi$ of the beam, which is due to the nonlinear refractive index. The relation is given by the eqn. 5.

$$\Delta T_{pv} = 0.406\,(1-S)^{0.25}\,|\Delta\phi| \tag{5}$$

Here S is the linear transmittance of the aperture defined by,

$$S = 1 - \exp(-2r_a^2/w_a^2)$$

where r_a is the radius of the aperture and w_a is the beam spot radius on the aperture. This linear relation between ΔT_{pv} and $\Delta\phi$ holds as long as the sample length $\ll z_0$ and $\Delta\phi \leq 1$.[27] Thus this ΔT_{pv} parameter directly gives the information regarding the nonlinear refractive index n_2. The concerned expression is given by eqn. 6,

$$n_2 = \frac{\lambda}{0.699\pi I_0 L_{eff}}\Delta T_{pv} \tag{6}$$

where L_{eff} is the effective length of the sample defined as,

$$L_{eff} = \frac{(1 - e^{-\alpha_0 l})}{\alpha_0}$$

From the known values of n_2 and β, the magnitude of third order susceptibility can be calculated by using the eqn. 7.

$$\left|\chi^{(3)}\right| = \sqrt{\left(\left|\frac{c\lambda n_0^2\beta}{64\pi^3}\right|^2 + \left|\frac{cn_0^2 n_2}{16\pi^2}\right|^2\right)} \tag{7}$$

Here n_0 is the linear refractive index, c is the speed of light and λ is the excitation wavelength. This value of third order nonlinear susceptibility in turn gives the numerical value of the second order hyperpolarizability of the molecule by eqn. 8,

$$|\gamma| = \frac{|\chi^{(3)}|}{N\left(\dfrac{n_0^2 + 2}{3}\right)^4} \qquad (8)$$

where N is the number density of molecules in /cm^3.