Supplementary Informations

Table S1  Short contacts in [1](ClO_4)_3.H_2O


Fig. S1  Packing diagram of [1](ClO_4)_3.H_2O (down b–axis).

Fig. S2  Electrospray mass spectrum of [1](ClO_4)_3 in CH_3CN.

Fig. S3  Electrospray mass spectrum of [4](ClO_4)_3 in CH_3CN.

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

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

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>
<thead>
<tr>
<th></th>
<th>Donor --- H...Acceptor</th>
<th>H...A (Å)</th>
<th>D...A (Å)</th>
<th>D – H...A(º)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C(3) -- H(3) .. O(1) ̄</td>
<td>2.5677</td>
<td>3.3209</td>
<td>138.39</td>
</tr>
<tr>
<td>2</td>
<td>C(4) -- H(4) .. O(3) ̄</td>
<td>2.5960</td>
<td>3.4792</td>
<td>158.78</td>
</tr>
<tr>
<td>3</td>
<td>C(7) -- H(7) .. O(4) ̄</td>
<td>2.4626</td>
<td>3.1795</td>
<td>133.96</td>
</tr>
<tr>
<td>4</td>
<td>C(30) -- H(30) .. O(4) ̄</td>
<td>2.5808</td>
<td>3.4856</td>
<td>164.42</td>
</tr>
</tbody>
</table>

Equivalent Position Code

i = 1−x, −y, 1−z

ii = 1+x, y, −1+z

iii = x, y, −1+z
Nd:YAG Laser
($\lambda = 532$ nm)

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 ($\beta$). The variation of normalised transmittance with the nonlinear absorption coefficient is given by the eqn. 3, \[ T_{\text{norm}}(z) = \frac{1}{q_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2}) dt \] (3)

where $q_0$ is given by eqn. 4, \[ q_0 = \frac{\beta I_0 (1 - e^{-\alpha_0^2})}{(1 + z^2 / z_0^2) \alpha_0} \] (4)

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 $\Delta T_{pv}$ 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.

\[
\Delta T_{pv} = 0.406 \left(1 - S\right)^{0.25} |\Delta \phi|
\]  

(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 \(\Delta T_{pv}\) and \(\Delta \phi\) holds as long as the sample length \(<<z_0\) and \(\Delta \phi \leq 1\). Thus this \(\Delta T_{pv}\) parameter directly gives the information regarding the nonlinear refractive index \(n_2\). The concerned expression is given by eqn. 6,

\[
n_2 = \frac{\lambda}{0.699\pi L_{\text{eff}}} \Delta T_{pv}
\]  

(6)

where \(L_{\text{eff}}\) is the effective length of the sample defined as,

\[
L_{\text{eff}} = \frac{(1 - e^{-\alpha_0})}{\alpha_0}
\]

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

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

(7)

Here \(n_0\) is the linear refractive index, \(c\) is the speed of light and \(\lambda\) 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,
where $N$ is the number density of molecules in $\text{cm}^3$. 

$$|n| = \sqrt{\frac{\kappa^{(3)}}{N \left( \frac{n_0^2 + 2}{3} \right)}}$$