Supporting Information

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Donor-substituted Triaryl-1,3,5-Triazinanes-2,4,6-Triones: Octupolar NLO-phores with a Remarkable Transparency–Nonlinearity Trade-off

Including:

1. NLO Measurements p. S2
2. Crystal data and structure refinement for 4 p. S3
1. NLO Measurements

The first hyperpolarizabilities were determined by performing hyper-Raleigh scattering (HRS) experiments in CH₂Cl₂ solutions. This technique is based on the analysis of the incoherent light scattered second-harmonic signal from an isotropic medium. The scattered nonlinear intensity $I^{2\omega}$ can be expressed as $I^{2\omega} = C(N_S\langle\beta_S^2\rangle + N\langle\beta^2\rangle)(I^{\omega})^2$ for a solution containing $N$ chromophores dissolved in $N_S$ solvent molecules (concentrations expressed per milliliter of solution), where the $C$ coefficient represents geometrical factors and experimental terms. The brackets refer to orientationally averaged $\beta$ values. The $C$ scaling factor is empirically deduced by a calibration experiment using a reference.

HRS measurements were conducted with a single-mode Nd:YAG laser emitting pulses of 10-MW peak power and 10-ns duration at 10-Hz repetition rate. The incident intensity $I^{\omega}$ is monitored by a half-wave plate and a Glan polarizer. A fraction of the incident beam is extracted from the main beam by a glass plate and sent onto a reference NPP frequency doubling calibrated powder. The fundamental beam is focused in a cell which contains the solution. The scattered harmonic signal is then collected at a right angle on a second photomultiplier after spectral selection through an interferential filter with 3-nm spectral resolution. For measurements performed in chloroform, the solvent was taken as reference, with a $\langle\beta_S^2\rangle^{1/2}$ value of 0.19 $10^{-30}$ esu at 1.064 µm. For measurements effected in dichloromethane, ethyl violet was taken as an external reference standard with a $\langle\beta^2\rangle^{1/2}$ value of 170 $10^{-30}$ esu at 1.907 µm. In both cases, ca. $10^{-3}$ M solutions were used. Note that the excitation wavelength was chosen so as not to allow two-photon excitation of any of the chromophores examined, i.e. at a much longer wavelength than twice the their absorption wavelength. The experimental accuracy is estimated to be ± 15%.
2. Crystal data and structure refinement for 4

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<th>Value</th>
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<td>Empirical formula</td>
<td>C&lt;sub&gt;27&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Formula weight</td>
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<tr>
<td>Temperature</td>
<td>100(2) K</td>
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<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
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<tr>
<td>Crystal system, space group</td>
<td>Trigonal, R 3 c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 13.5264(13) Å, alpha = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>b = 13.526 Å, beta = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>c = 24.608(2) Å, gamma = 120 deg.</td>
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<tr>
<td>Volume</td>
<td>3899.2(5) Å&lt;sup&gt;3&lt;/sup&gt;</td>
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<tr>
<td>Z, Calculated density</td>
<td>6, 1.097 Mg/m&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.073 mm&lt;sup&gt;-1&lt;/sup&gt;</td>
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<tr>
<td>F(000)</td>
<td>1332</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.25 × 0.23 × 0.15 mm</td>
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<tr>
<td>Theta range for data collection</td>
<td>3.01 to 27.48 deg.</td>
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<tr>
<td>Limiting indices</td>
<td>-16&lt;=h&lt;=17, -17&lt;=k&lt;=16, -25&lt;=l&lt;=31</td>
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<tr>
<td>Reflections collected / unique</td>
<td>7587 / 1002 [R(int) = 0.0576]</td>
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<tr>
<td>Completeness to theta</td>
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<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.989 and 0.975</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1002 / 1 / 100</td>
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<td>Goodness-of-fit on F&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0693, wR2 = 0.1716</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0720, wR2 = 0.1732</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>-10(10)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.326 and -0.320 e.Å&lt;sup&gt;-3&lt;/sup&gt;</td>
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Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for 4. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<th>x</th>
<th>y</th>
<th>z</th>
<th>$U(\text{eq})$</th>
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<td>1777(2)</td>
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Bond lengths [Å] and angles [deg] for 4.

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<tr>
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<tr>
<td>C(4)-C(5)</td>
<td>1.415(6)</td>
</tr>
<tr>
<td>C(4)-H(4)</td>
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<td>C(5)-C(8)</td>
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<td>C(4)-C(5)-H(5)</td>
<td>122.2</td>
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C(7)-C(6)-C(3)  120.5(4)
C(7)-C(6)-H(6)  119.8
C(3)-C(6)-H(6)  119.8
C(8)-C(7)-C(6)  118.1(4)
C(8)-C(7)-H(7)  120.9
C(6)-C(7)-H(7)  120.9
C(7)-C(8)-C(5)  123.3(4)
C(7)-C(8)-N(9)  119.0(4)
C(5)-C(8)-N(9)  117.6(4)
C(10)#1-N(9)-C(10)  123.8(4)
C(10)#1-N(9)-C(8)  118.0(3)
C(10)-N(9)-C(8)  116.8(3)
O(10)-C(10)-N(9)#2  121.7(3)
O(10)-C(10)-N(9)  122.3(4)
N(9)#2-C(10)-N(9)  115.9(4)

Symmetry transformations used to generate equivalent atoms:
#1  -x+y,-x,z   #2  -y,x-y,z
**Anisotropic displacement parameters (Å² x 10³) for 4.**
The anisotropic displacement factor exponent takes the form: -2π² [ h² a*² U11 + ... + 2 h k a* b* U_{12} ]

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<th>U22</th>
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<td>31(2)</td>
<td>4(1)</td>
<td>3(1)</td>
<td>6(1)</td>
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Torsion angles [deg] for 4.

C(1)-C(2)-C(3)-C(4)        -26(16)
C(1)-C(2)-C(3)-C(6)         153(16)
C(6)-C(3)-C(4)-C(5)         0.4(6)
C(2)-C(3)-C(4)-C(5)        -180.0(4)
C(3)-C(4)-C(5)-C(8)         1.0(6)
C(4)-C(3)-C(6)-C(7)         -1.0(6)
C(2)-C(3)-C(6)-C(7)        179.3(4)
C(3)-C(6)-C(7)-C(8)        0.2(6)
C(6)-C(7)-C(8)-C(5)         1.4(6)
C(6)-C(7)-C(8)-N(9)        -178.3(4)
C(4)-C(5)-C(8)-C(7)        -1.9(6)
C(4)-C(5)-C(8)-N(9)        177.7(3)
C(7)-C(8)-N(9)-C(10)#1    -70.8(5)
C(5)-C(8)-N(9)-C(10)#1     109.6(4)
C(7)-C(8)-N(9)-C(10)       96.3(4)
C(5)-C(8)-N(9)-C(10)      -83.4(4)
C(10)#1-N(9)-C(10)-O(10)   171.7(3)
C(8)-N(9)-C(10)-O(10)      5.4(6)
C(10)#1-N(9)-C(10)-N(9)#2 -7.2(8)
C(8)-N(9)-C(10)-N(9)#2    -173.4(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y,-x,z   #2 -y,x-y,z