Supporting Information

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A Hybrid Ruthenium Alkynyl/Zinc Porphyrin "Cross Fourchée" with Large Cubic Nonlinear Optical Properties

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Including:

1. Synthesis of the Organometallic Dendrimer 2

General. The reaction was performed under argon and was magnetically stirred. CH_2Cl_2 was distilled from CaH_2 prior to use; all other solvents were HPLC grade. Commercially available reagents were used without further purification unless otherwise stated. The reaction was monitored by thin-layer chromatography (TLC) with Merck pre-coated aluminium foil sheets (silica gel 60 with fluorescent indicator UV_{254}). Compounds were visualized with ultra-violet light at 254 and 365 nm. Column chromatography was carried out using silica gel from Merck (0.063-0.200 mm). ^1H NMR, ^{31}P NMR and ^{13}C NMR spectra in $CDCl_3$ were recorded using Bruker 200 DPX, 300 DPX and 500 DPX spectrometers. The chemical shifts are referenced to internal tetramethylsilane. IR spectra were recorded on a Bruker IFS 28 spectrometer, using KBr pellets or in dichloromethane solution. UV spectra were recorded on UVIKON XL spectrometer from Biotek instruments. The cyclic voltammetry study of **2** was performed in CH_2Cl_2 at 0.1 $V.s^{-1}$, with 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte. Potentials reported were measured and are expressed relative to the saturated calomel electrode (SCE) using ferrocene as an internal calibrant.

The tetraruthenium porphyrin precursor complexes **1-X** (X = NO_2, H) were obtained from the known zinc(II)-5,10,15,20-tetra((4-ethynyl)phenyl)porphyrin **(ZnTEP)**[1] and *cis*-$[RuCl_2(dppe)_2]$[2] as previously described, while the syntheses of the known organometallic wedges **3-R** (R = TMS, H) were carried out following published syntheses.[3]

Synthesis of the dodecaruthenium(II) porphyrin dendrimer 2. $NaPF_6$ (95 mg, 0.57 mmol) was added to a solution of zinc(II)-5,10,15,20-tetra(4-ethynylphenyl)porphyrin (**ZnTEP**; 100 mg, 0.13 mmol) and *cis*-$[RuCl_2(\kappa^2\text{-dppe})_2]$ (551 mg, 0.57 mmol) in CH_2Cl_2 (100 mL). This mixture was stirred at room temperature for 12 h and the solution was filtered. The product was then precipitated as a dark green solid by addition of Et_2O. This crude precipitate (478 mg, 0.094 mmol) was used without further purification as described below. Yield: 73%. $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$, δ in ppm): 38.8 ppm. To

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[1] (a) K. Onitsuka, H. Kitajima, M. Fujimoto, A. Iuchi, F. Takei and S. Takahashi *Chem. Commun.* **2002**, 2576-2577; (b) S. Drouet, A. Merhi, D. Yao, M. P. Cifuentes, M. G. Humphrey, M. Wieglus, J. Olesiak-Banska, K. Matczyszyn, M. Samoc, F. Paul and C. O. Paul-Roth *Tetrahedron* **2012**, *68*, 10351-10359.
[2] K. A. Green, M. P. Cifuentes, T. C. Corkery, M. Samoc and M. G. Humphrey, *Angew. Chem., Int. Ed. Engl.* **2009**, *48*, 7867-70.
[3] (a) R. L. Roberts, T. Schwich, T. C. Corkery, M. P. Cifuentes, K. A. Green, J. D. Farmer, P. J. Low, T. B. Marder, M. Samoc and M. G. Humphrey *Adv. Mat.* **2009**, *21*, 2318-2322; (b) K. A. Green, Hons Thesis, Australian National University, 2005.

a solution of this precipitate (57 mg, 0.011 mmol) was added the dendron **3-H** (110 mg, 0.047 mmol), $NaPF_6$ (30 mg, 0.18 mmol) and triethylamine (0.05 mL) in distilled CH_2Cl_2 (12 mL) under nitrogen. The reaction was followed by ^{31}P NMR, and it was complete after 48 h at room temperature. The reaction mixture was filtered, concentrated under reduced pressure, and the desired product was precipitated from hexane as a green solid (90 mg). Yield: 60%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 9.20 (s, 8H, $H_{\beta\text{-pyrrolic}}$), 8.05 (d, 8H, $^{3}J_{H,H}$ = 8.2 Hz, H_{Ar}), 7.70–6.50 (m, 572H, $H_{Ar/dppe}$), 2.70 (s, 96H, $CH_{2/dppe}$). $^{31}P\{^{1}H\}$ NMR (121MHz, $CDCl_3$, ppm): δ = 54.57 (broad s), 54.35 (s). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$, ppm): δ = 151.1 (s, $C_{\alpha\text{-pyrrolic}}$), 138.2-137.2 (m, $C_{ipso/dppe}$ & C_{Ar}), 135.03 (broad s, $C_{ortho/dppe}$), 132.1 (s, $C_{\beta\text{-pyrrolic}}$), 131.6 (broad s, C_{Ar}), 131.4 (s,), 130.7 (s, CH_{Ar}), 129.4-129.2(m, $C_{para/dppe}$), 129.1 (s, CH_{Ar}), 128.2 (s, CH_{Ar}), 127.8 (broad s, $C_{meta/dppe}$), 126.9 (broad s, overlapped C_{Ph}), 124.2-123.9, 123.4, 117.6-116.8 (m, (s, C_{Ph}, C_{meso}, $C_{RuC\equiv C}$), 93.7 (s, $C_{C\equiv C}$), 93.2 (s, $C_{C\equiv C}$), 90.1 (s, $C_{C\equiv C}$), 88.3 (s, $C_{C\equiv C}$), 32.4 (m, $CH_{2/dppe}$); not all aromatic signals detected and Ru*C*≡C not observed (weak quintuplets), possibly overlapped. Anal. calc. For $C_{852}H_{684}N_4P_{48}Ru_{12}Zn$: C, 74.46; H: 5.02; N: 0.41; found C: 74.35; H: 5.18; N: 0.42. FT-IR (KBr, cm^{-1}): ν = 2202 (w, C≡C), 2051 (s, RuC≡C). C.V. (CH_2Cl_2, 0.1 M $[Bu_4N][PF_6]$, 20 °C, V) $E°$ = 0.45, 0.53.

2. ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra of 2

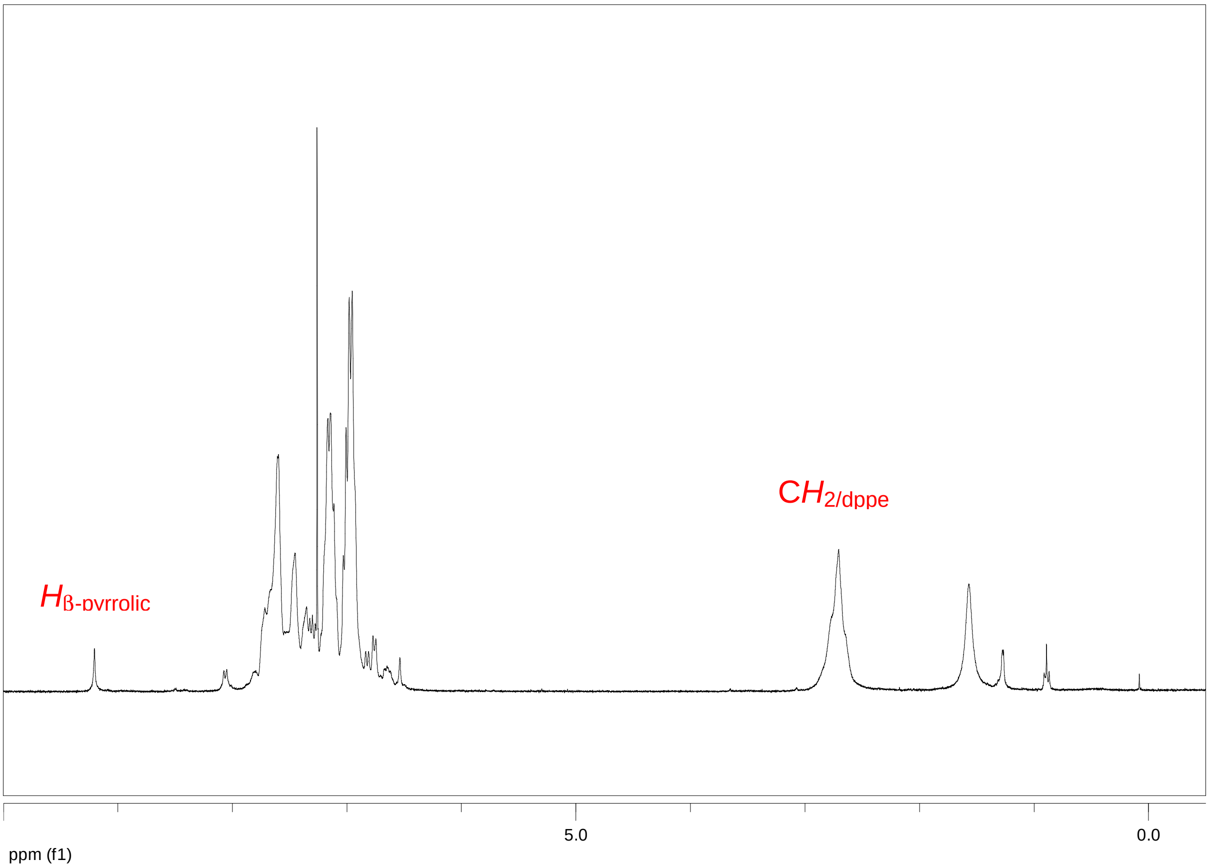

Fig. S1. ^{1}H NMR spectrum of **2** in $CDCl_3$.

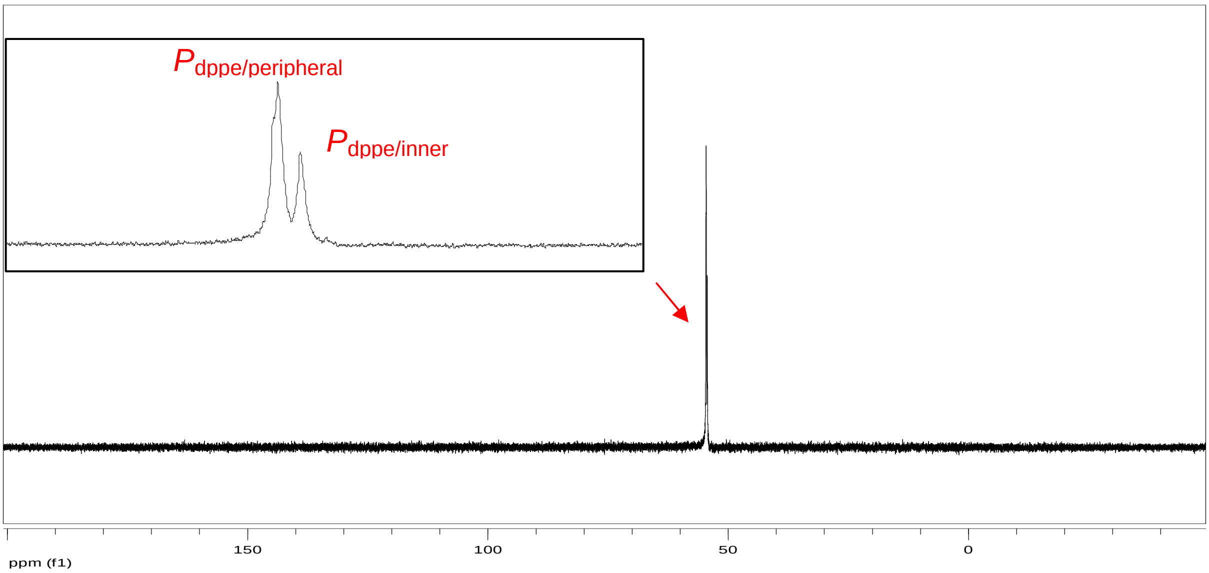

Fig. S2. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in $CDCl_3$ showing the expanded ^{31}P signal detected in inset.

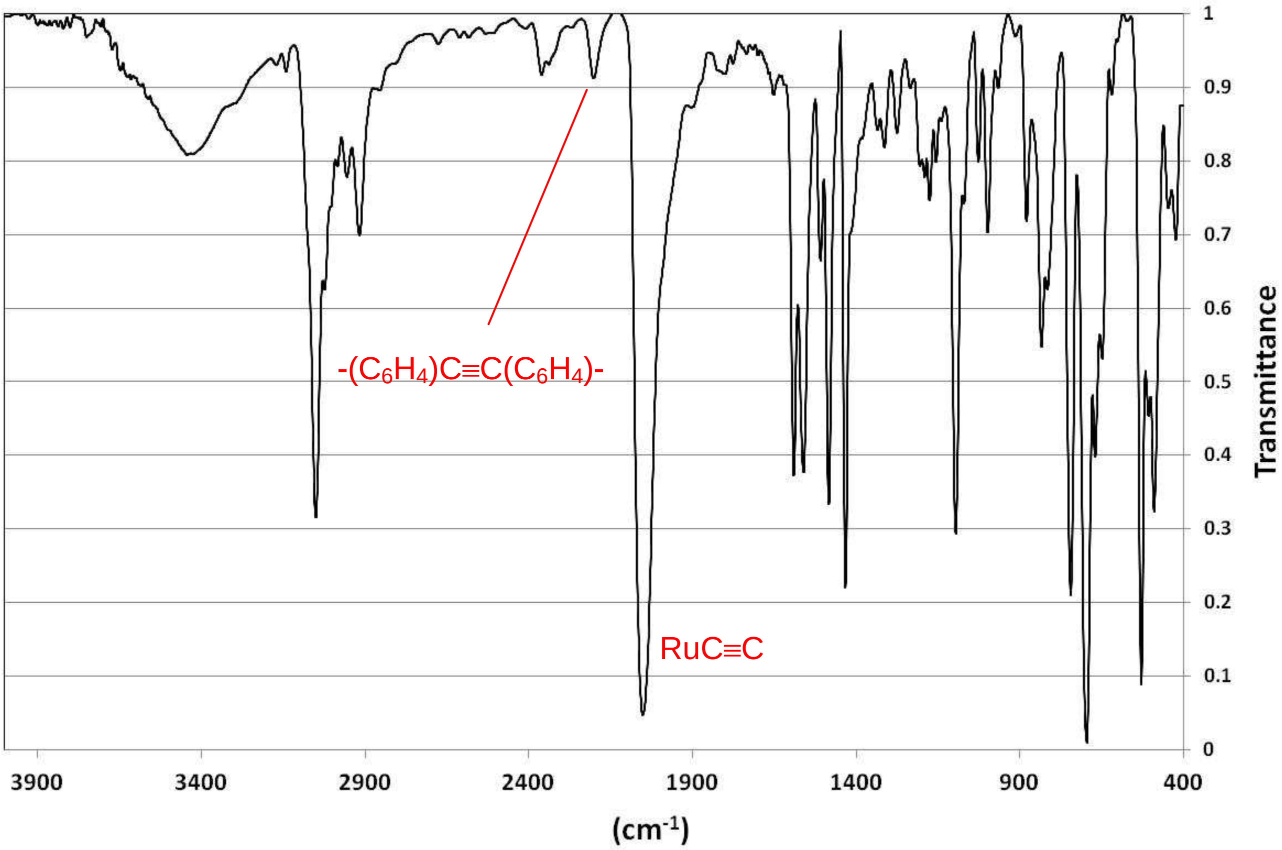

Fig. S3. FTIR spectrum of **2** in KBr with $\nu_{C\equiv C}$ modes indicated.

3. Cyclic Voltammogram of 2

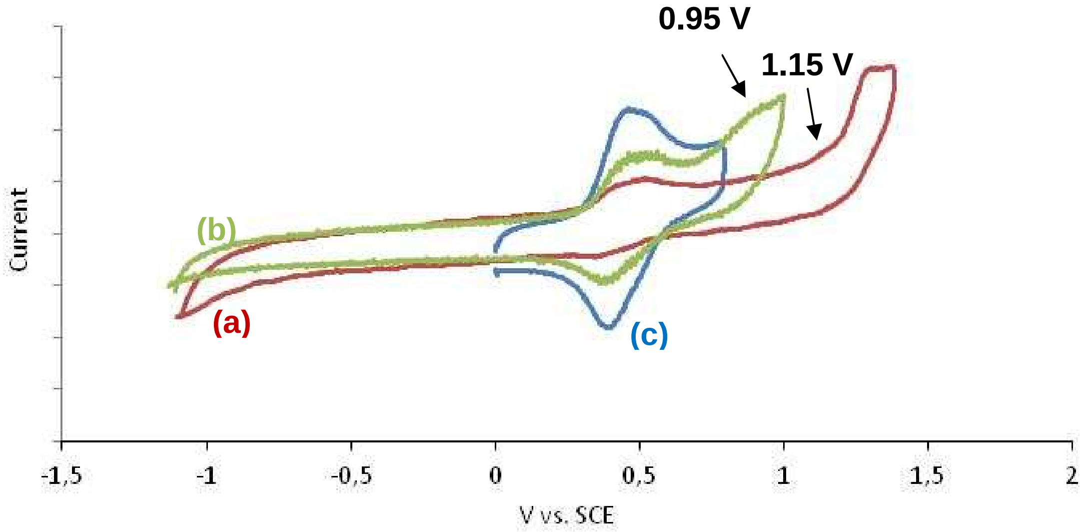

Fig. S4. Cyclic voltammogram of the zinc porphyrin **2** in CH_2Cl_2/[NBu_4][PF_6] (0.1 M) at 25 °C at 0.1 V/s between -1.0 and 1.2 V *vs.* SCE (b: current x 2; c: current x 3). Arrows indicate possible porphyrin-based oxidations.

4. THG Measurements

Third-harmonic generation (THG) experiments have been performed at 1.907 µm, using a commercial (SAGA from Thales Laser) Q-switched Nd^{3+}:YAG nanosecond laser operating at λ = 1064 nm, 10 Hz repetition rate and 9 ns pulsed duration. The 1064 nm laser beam was focused into a 50 cm long, high pressure (50 bar) hydrogen Raman cell which shifts the fundamental beam to λ = 1.907 µm by stimulated Raman scattering (only the back-scattered 1910 nm Raman emission was collected at a 45^{o} incidence angle by use of a dichroic mirror, in order to eliminate most of the residual 1064 nm pump photons). A Schott RG 1000 filter was used to filter out any remaining visible light from the laser flash lamp and from anti-Stokes emission from H_2. Suitable attenuators were used to control the power of the incident beam which was focused into the THG cell with a 20 cm focal length lens.

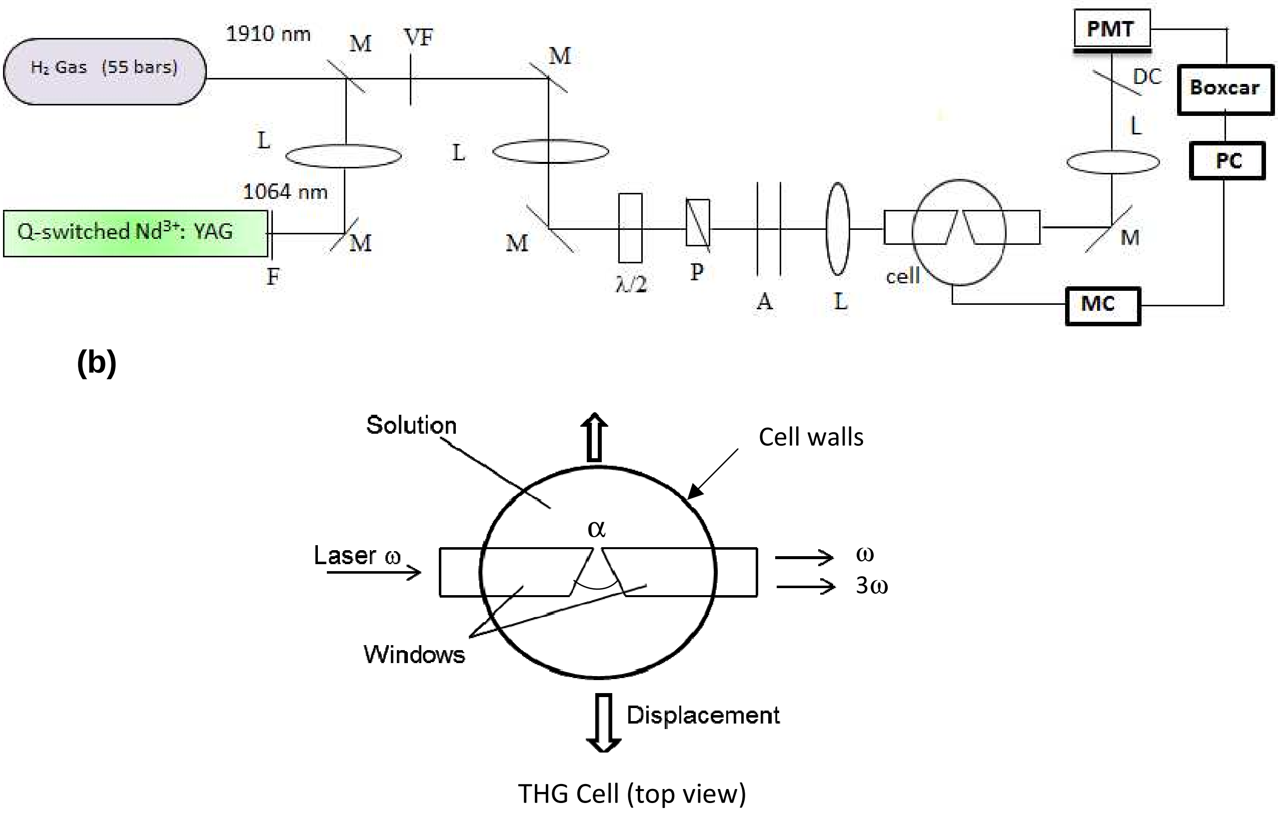

Fig. S5. (a) THG experimental set-up at 1.907 µm. [F: Filter; M: Mirrors; L: Lens; λ/2: Half wave plate; P: Polarizer; A: Attenuator; PMT: Photomultiplier tube: DC: dichroic mirror; MC: Micro controller; PC: personal computer]. (b) THG measurement cell.

The measurements were carried out using a wedge-shaped cell, consisting of two fused silica windows assembled on a stainless steel support, their inner interfaces with the liquid forming a small angle α. This cell follows the classic design implemented by Levine and Bethea for electric-field induced second-harmonic generation[4]. The wedge shapes are to measure the intensity of the harmonic radiation 3ω as a function of the cell displacement, i.e. without changing the incidence angle, resulting in fringes with constant amplitudes, and thereby making data processing much easier than is the case for a rotating cell with parallel windows. The whole cell was translated horizontally relative to the incident beam, producing a periodic third-harmonic generation signal (Maker fringes). The schematic diagram of the THG experimental set-up is shown in Fig. S5, together with the sketch of the THG measurement cell.

After passing through the cell, the fundamental radiation was removed by filters, and only the third-harmonic radiation was detected by a photomultiplier and processed by a home-made computer program to calculate the inter-fringe distance and the fringe amplitude. These data were then used to calculate the γ value of the sample.

In our THG experiments, the fundamental field E^{ω} was polarized along the vertical direction. The generated third-harmonic was therefore also polarized along this direction, because of the symmetry properties of an isotropic medium.

The resulting cubic susceptibility $\Gamma(x)$ of a solution was deduced from the fringe amplitude $I^{3\omega}$ and period δ. From δ, the value of the coherence length $l_c = \pi/\Delta k$, Δk being the wavevector mismatch between the fundamental and third-harmonic waves in the nonlinear medium, can be inferred using the relation $l_c = 2\delta \mathrm{tg}(\alpha/2)$. If x is the concentration of the molecule of interest in a solvent taken as reference material:

$$\Gamma(x) = \frac{1}{l_c(x)}\left[A\frac{\sqrt{I^{3\omega}(x)}}{\sqrt{I^{3\omega}(0)}} + B\right] \text{ (in } 10^{-12} \text{ esu)}$$

Then, the cubic hyperpolarizability γ of the molecule can be inferred using:

$$\gamma = \frac{M}{\rho N_A f^{3\omega}(f^{\omega})^3 x}\left[(1+x)\Gamma(x) - \Gamma(0)\right]$$

where N_A is the Avogadro‘s number (6.02×10^{23}), M the molecular weight of the compound, ρ the density of the solvent, x the molar fraction of the compound, $\Gamma(0)$ the susceptibility of the pure solvent and $f^{\omega,3\omega}$ are local field corrections factors for the E^{ω} and $E^{3\omega}$ electric fields, respectively.

[4] Levine, B. F., and Bethea, C. G., J. Chem. Phys., 1975, 63 (6), 2666-2682.

5. Z-scan Measurement at 780 nm

Third-order nonlinear optical properties of **2** were investigated by Z-scan as previously described,[5] but with some modifications. The laser system consisted of a Quantronix Integra-C3.5F pumping a Quantronix Palitra-FS optical parametric amplifier at a wavelength of 780 nm. The output delivered 130 fs pulses with a 1 kHz repetition rate. Coloured glass filters and a Thorlabs polarizing filter were used to remove unwanted wavelengths and the power adjusted by use of neutral density filters to obtain nonlinear phase shifts between 0.1 to 1.3 rad. The focal length of the beam at the experiment was 75 mm, which gave 25-40 mm beam waists resulting in Rayleigh lengths longer than that of the sample thickness. Solutions of compounds in deoxygenated and distilled CH_2Cl_2 of 0.1 w/w% concentration in 1 mm glass cells were analyzed. Samples travelled down the Z axis on a Thorlabs motorised stage between 5-45 mm. Data was collected by three Thorlabs photodiodes, 500-900 nm with Si based detectors, 900-1300 nm with InGaAs detectors and 1300-2000 nm with amplified InGaAs detectors. Data from the detectors were collected by a Tektronix oscilloscope feeding a custom LabVIEW program (written by Prof. Marek Samoc, Wroclaw University of Technology) permitting fitting of a theoretical trace. A sample of CH_2Cl_2 was run at each wavelength as an aid in referencing to a 3 mm fused silica plate. The open- and closed-aperture traces obtained after dividing the corresponding signals by the laser input reference were analyzed with the help of a custom fitting program that used equations derived by Sheik-Bahae *et al*.[6]; the real and imaginary parts of the second hyperpolarizability, γ, of the solutes were then calculated assuming additivity of the nonlinear contributions of the solvent and the solute and the applicability of the Lorentz local field approximation.[7].

[5] S. Drouet, A. Merhi, D. Yao, M. P. Cifuentes, M. G. Humphrey, M. Wieglus, J. Olesiak-Banska, K. Matczyszyn, M. Samoc, F. Paul and C. O. Paul-Roth *Tetrahedron* 2012, *68*, 10351-10359.
[6] M. Sheikh-Bahae, A. A. Said, T. Wei, D. J. Hagan and E. W. V. Stryland *IEEE J. Quant. Electr.* 1990, *26*, 760-769.
[7] M. Samoc, A. Samoc, B. Luther-Davies, M. G. Humphrey and M. S. Wong *Opt. Mater.* 2003, *21*, 485-488.