Supplementary Information for:

Synthesis and Linear and Nonlinear Optical Properties of Metal-Terminated Bisdioxaborine Polymethines

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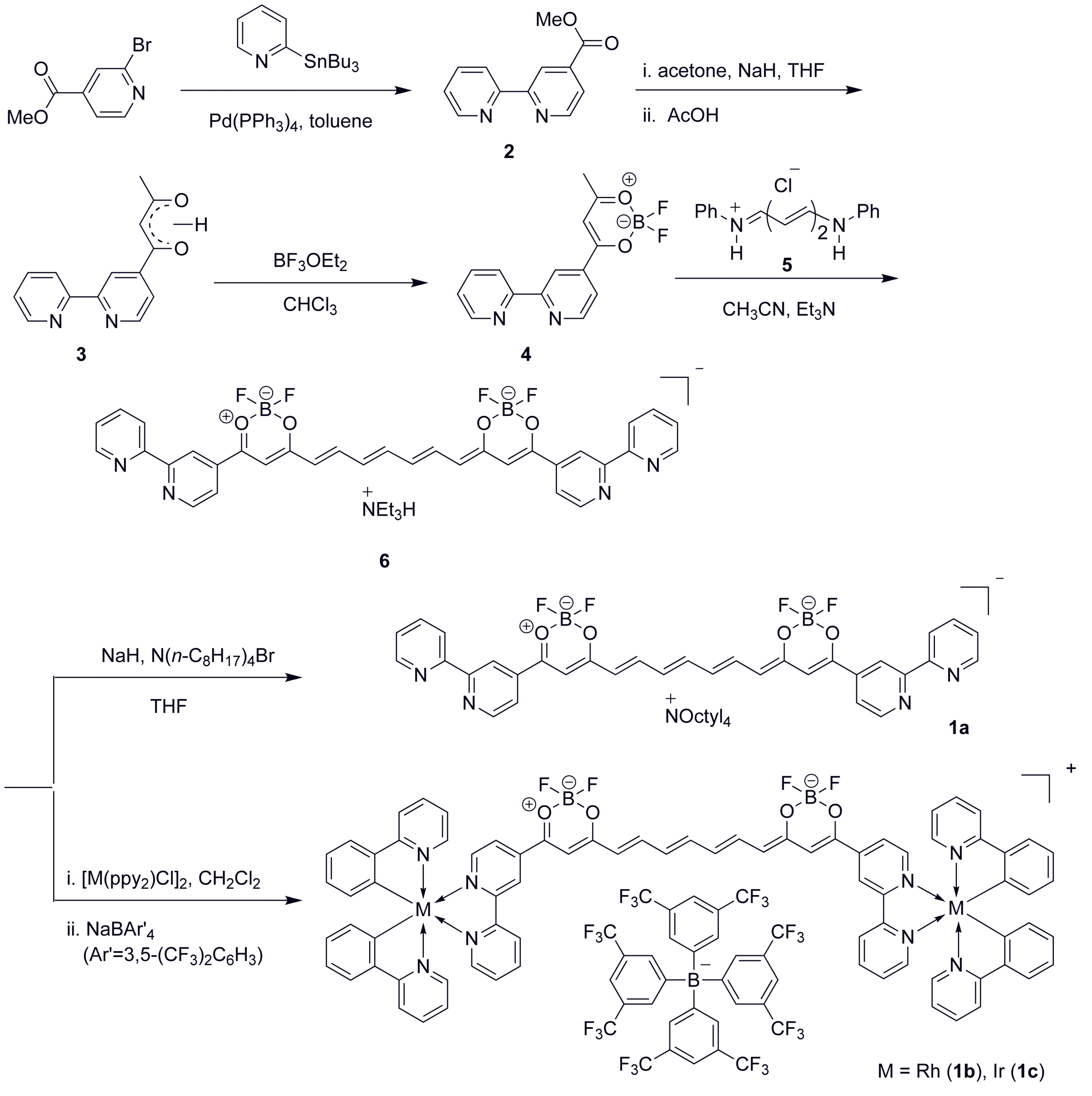
1. Synthetic Details and Characterising Data pS2-S7
2. Electrochemical Characterisation pS7
3. Materials Preparation and Linear Optical Characterisation pS7-8
4. Nonlinear Optical Characterisation Techniques pS8-S9
5. References for Supplementary Information pS10

1. Synthetic Details and Characterising Data

Compounds **1a-c** were synthesised as shown in Scheme S1.

Scheme S1



Methyl 2,2'-bipyridine-4-carboxylate, 2.[S1] 2-(Tri-*n*-butylstannyl)pyridine (55 g, 119 mmol, 80%) and methyl 2-bromo-pyridine-4-carboxylate (25 g, 116 mol) were dissolved in toluene (400 mL). The solution was deoxygenated for 10 min, then tetrakis(triphenylphosphine)palladium (3.4 g, 2.5 mol%) was added. The mixture was heated to reflux for 3 d. Aqueous potassium fluoride (8 g in 200 mL) was added to the solution and undesired salts were filtered off after 30 min. The toluene solution was separated and the aqueous solution was extracted with toluene (3 × 150 mL). Combined the organic solutions and the solvent was removed by rotary evaporation. The crude product was run through a short pad of silica gel, eluting with ethyl acetate. The eluate was evaporated and the crude product was recrystallized from dichloromethane / hexane (22.3 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.91 (s, 1H), 8.80 (d, *J* = 4.9 Hz, 1H), 8.69 (m, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 7.85-7.79 (m, 2H), 7.35 (m, 1H), 3.97 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 165.7, 157.3, 155.3, 149.9, 149.4, 138.5, 137.0, 124.1, 122.8, 121.2, 120.4, 52.7. MS(FAB): *m/z* 215 (MH^+). Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71; N, 13.08. Found: C, 66.92; H, 5.06; N, 13.30.

3. A solution of **2** (2.0 g, 9.34 mmol) and anhydrous acetone (3.2 mL, 43.7 mmol) in anhydrous THF (15 mL) was warmed under nitrogen to 38 °C; sodium hydride (540 mg, 22.4 mmol) was then added in several portion over a period of 15 min. The reaction was stirred at ambient temperature for 10 min and then heated at reflux for 2.5 h. After cooling into room temperature, water (50 mL) was added into the solution and the organic solvent was evaporated. The residue was extracted with dichloromethane (5 × 40 mL) to remove impurities. The aqueous layer was poured into dichloromethane (40 mL) in a beaker and the pH adjusted to 7.0 ± 0.1 with acetic acid and sodium hydroxide (1 M). The organic layer was separated and the aqueous layer was extracted with dichloromethane (2 × 40 mL). The combined organic extracts were evaporated by rotary evaporation (1.06 g, 47%). The NMR evidence suggests that, at least in $CDCl_3$, this compound exists as one of the two possible enol forms. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 15.75 (s, 1H), 8.78 (d, *J* = 5.0 Hz, 1H), 8.73 (s, 1H), 8.69 (d, *J* = 4.4 Hz, 1H), 8.41 (d, *J*= 8.0 Hz, 1H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.72 (m, 1H), 7.32 (m, 1H), 6.37 (s, 1H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 197.0, 178.7, 157.0, 155.4, 150.1, 149.2, 142.8, 137.0, 124.1, 121.3, 120.3, 117.6, 98.1, 26.7. MS(FAB): *m/z* 241 (MH^+). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.73; H, 5.21; N, 11.54.

6-(2,2'-Bipyridin-4-yl)-2,2-difluoro-4-methyl-1,3,2(2*H*)-dioxaborine, 4. Compound **3** (720 mg, 3.0 mmol) in chloroform (3 mL) was added dropwise to a stirred solution of the $BF_3 \cdot OEt_2$ (4.3 mL, 33.1 mmol) in chloroform (40 mL) at ambient temperature. Upon completion of the addition, the reaction mixture was stirred for 10 min. Water (50 mL) was added into the reaction mixture and the pH adjusted to 7.0 with acetic acid and sodium hydroxide (1 M). The organic layer was separated, and the aqueous layer was extracted with chloroform (2 × 40 mL), dried over anhydrous magnesium sulfate and the solvent was removed by rotary evaporation. The product was purified by reprecipitation from dichloromethane / hexane to afford an off-white powder. The residue was concentrated by rotary evaporation and the same reaction was repeated once using the recovered compound, the total yield was 68% (584 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, J= 5.2 Hz, 1H), 8.89 (s, 1H), 8.71-8.69 (m, 1H), 8.46 (d, J= 7.6 Hz, 1H), 7.90-7.83 (m, 2H), 7.39-7.36 (m, 1H), 6.81 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 181.0 157.7, 154.6, 150.7, 149.3, 139.4, 137.3, 124.6, 121.4, 121.1, 118.6, 98.8, 25.2. MS (FAB): *m/z* 289 (MH^+). Anal. Calcd for $C_{14}H_{11}BF_2N_2O_2$: C, 58.37; H, 3.85; N, 9.72. Found: C, 58.30; H, 3.88; N, 9.68.

6. To a solution of **4** (144 mg, 0.50 mmol), triethylamine (0.25 mL), and the pentamethine cyanine **5** (50 mg, 0.20 mmol)[S2] in dichloromethane (5 mL) was heated at reflux for 20 min. After cooling to room temperature, the reaction mixture was concentrated by rotary evaporation and reprecipitation from acetonitrile (5 mL) using diethyl ether (30 mL) afforded the crude product as a shiny red solid (140 mg), which was used without further characterization or purification in the following reactions.

1a. Under nitrogen, a solution of sodium hydride (50 mg, 2.08 mmol) in THF (5 mL) was added dropwise to a stirred solution of crude **6** (140 mg) and tetra-*n*-octylammonium bromide (218 mg, 0.40 mmol) in THF (15 mL). The reaction mixture was stirred for 10 min, filtered off, the filtrate was collected and the solvent was concentrated by rotary evaporation. The crude product was dissolved in acetonitrile (5 mL) and the solution was poured into diethyl ether (50 mL) / hexane (50 mL) to obtain **1a** (118 mg, 53% from **5**). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.75 (s, 2H), 8.72 (d, *J*= 5.2 Hz, 2H), 8.68 (d, *J* = 4.0 Hz, 2H), 8.41 (d, *J* = 7.6 Hz, 2H), 7.85-7.70 (m, 6H), 7.35-7.30 (m, 2H), 7.07 (t, *J* = 12.6 Hz, 1H), 6.42 (s, 2H), 6.31 (t, *J* = 12.6 Hz, 2H), 5.77 (d, *J* = 12.8 Hz, 2H), 3.16 (t, *J* = 8.2 Hz, 8H), 1.70-1.60 (m, 4H), 1.45-1.15 (m, 44H), 0.83 (t, *J*= 7.0 Hz, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): *δ* 165.0, 156.6, 155.7, 149.9, 149.4, 149.1, 145.7, 142.8, 137.0, 124.0, 121.3, 120.3, 117.4, 111.7, 59.0, 31.6, 29.01, 28.99, 26.3, 22.6, 22.0, 14.0 (3 missing peaks presumably obscured by overlap). MS(ESI) (–) *m/z* 637.1 (anion). MS(ESI) (+) *m/z* 466.6 (cation). Anal. Calcd for $C_{65}H_{91}B_2F_4N_5O_4$: C, 70.71; H, 8.31; N, 6.34. Found: C, 70.97; H, 8.28; N, 6.33.

1b. A mixture of **6** (280 mg) and $[Rh(ppy)_2Cl]_2$[S3] (375 mg, 0.40 mmol) in dichloromethane (40 mL) was heated at reflux for 20 min. The reaction mixture was cooled to room temperature and NaBAr'$_4$ {Ar' = 3,5-$(CF_3)_2C_6H_3$}[S4] (505 mg, 0.57 mmol) was added. The solution was heated under reflux for another 10 min and then stirred at room temperature for 30 min. The solvent was concentrated by rotary evaporation, giving crude product (1.2 g). The crude product was run through a column of silica gel, eluting with dichloromethane, then methanol (4%) / dichloromethane. After concentration by rotary evaporation, the product was run through a size exclusion column (SX1, Biobeads, and dichloromethane eluent), loading and eluting with dichloromethane. Concentration by rotary evaporation, yielded **1b** (385 mg, 42% (from **5**)). ^{1}H NMR (400 MHz, CD_2Cl_2): *δ* 8.80 (s, 2H), 8.50-8.60 (br, 2H), 8.15-7.90 (m, 12H), 7.85-7.65 (m, 20H), 7.60-7.40 (m, 10H), 7.23 (bt, *J* = 12.6 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 4H), 7.01 (t, *J* = 6.4 Hz, 8H), 6.48-6.30 (m, 8H), 5.90-5.80 (bd, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): *δ* 167.3, 167.2, 167.0, 166.8, 165.3, 162.1 (1:1:1:1 q, J_{CB} = 49 Hz), 155.3, 154.5, 150.8, 150.6, 148.9, 148.8, 145.4, 143.93, 143.90, 139.9, 138.7, 138.6, 135.2, 133.1, 130.9, 128.9 (qq, J_{CF} = 29, 3 Hz), 128.2, 125.1, 124.9 (q, J_{CF} = 271 Hz), 124.3, 124.1, 123.8, 123.7, 120.5, 120.2, 117.9 (septet, J = ca. 4 Hz) (Extensive overlap means that the number of observed peaks falls considerably short of that expected for even a single isomer of the desired compound and precludes assignment of any coupling to ^{103}Rh and some of that to ^{19}F). HRMS(MALDI) calcd for cation $C_{77}H_{55}B_2N_8O_4F_4Rh_2$: 1459.2579. Found: 1459.2314. Anal. Calcd for $C_{109}H_{67}B_3N_8O_4F_{28}Rh_2$: C, 56.36; H, 2.91; N, 4.82. Found: C, 55.17; H, 2.83; N, 4.42. Despite multiple attempts at purification, analytical data were not obtained within acceptable limits. However, ^{1}H NMR data suggest that the major impurity is $Et_3NH^+BAr'_4{}^-$ and that **1b** is ca. 96 wt % pure. $Et_3NH^+BAr'_4{}^-$ does absorb in the visible and so does not interfere with the reported solution spectra or absorption maxima, although the magnitudes of reported values of $\varepsilon_{\max}$, Re(γ), and Im(γ) are likely to be slightly underestimated and small dilution effect on the solid-state absorption data is possible.

1c. To a mixture of **6** (280 mg) and $[Ir(ppy)_2Cl]_2$[S3] (429 mg, 0.40 mmol) in dichloromethane (40 mL) was heated at reflux for 20 min under nitrogen. The reaction mixture was cooled to room temperature and $NaBAr'_4$ (505 mg, 0.57 mmol) was added. The solution was heated under reflux for another 10 min and then stirred at rt for 10 min. The solvent was concentrated by rotary evaporation, giving crude product (1.3 g). The crude product was run through a column of silica gel, eluting with dichloromethane, then methanol (4%) / dichloromethane. After concentration by rotary evaporation, the product was run through a size exclusion column (SX1, Biobeads, and dichloromethane eluent), loading and eluting with dichloromethane. Concentration by rotary evaporation yielded **1c** (553 mg, 55% (from **5**)). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.80 (s, 2H), 8.60-8.50 (br, 2H), 8.12-7.95 (m, 12H), 7.86-7.65 (m, 20H), 7.55-7.35 (m, 10H), 7.23 (bt, J = 12.6 Hz, 1H), 7.09 (t, J = 8.0 Hz, 4H), 6.97 (t, J = 6.6 Hz, 8H), 6.48-6.25 (m, 8H), 5.85 (d, J = 11.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 168.1, 162.1, (1:1:1:1 q, J_{CB} = 50 Hz), 156.7, 155.8, 151.4, 151.2, 150.1, 149.7, 148.7, 144.8, 143.94, 143.90, 139.5, 138.7, 135.2, 132.0, 131.2, 129.21 (qq, J_{CF} = 29, 3 Hz), 128.9, 126.8, 125.4, 124.94 (q, J_{CF} = 271 Hz), 124.88, 124.5, 123.6, 123.3, 120.9, 120.8, 120.4, 117.9 (sept) (Extensive overlap means that the number of observed peaks falls considerably short of that expected for even a single isomer of the desired compound and complicates assignment of some of the coupling to ^{19}F). HRMS (MALDI) calcd for cation $C_{77}H_{55}B_2N_8O_4F_4Ir_2$: 1639.3727. Found: 1639.3577. Anal. Calcd for $C_{109}H_{67}B_3N_8O_4F_{28}Ir_2$: C, 52.33; H, 2.70; N, 4.48. Found: C, 52.39; H, 2.81; N, 4.10.

2. Electrochemical Characterisation

Electrochemical measurements were carried out under nitrogen on dry deoxygenated dichloromethane solutions ca. 10^{-4} M in analyte and 0.1 M in tetra-*n*-butylammonium hexafluorophosphate using a BAS Potentiostat, a glassy carbon working electrode, a platinum auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodised in 1 M aqueous potassium chloride. Potentials were referenced to ferrocenium / ferrocene by using decamethylferrocene (measured at –0.55 V vs. ferrocenium / ferrocene) as an internal reference. Cyclic voltammograms were recorded at a scan rate of 150 mVs^{-1}.

3. Materials Preparation and Linear Optical Characterisation

Absorption spectra were recorded using a dual-beam Cary-5E UV-Vis-NIR spectrophotometer. For all spectroscopic measurements on solutions, both linear and nonlinear, spectrophotometric grade solvents purchased from Sigma-Aldrich were used. Linear absorption measurements were performed in 1 cm pathlength quartz cuvettes. Dichloromethane was used for preparing solutions of compounds **1a-c** (concentrations ranging between 1×10^{-6} and 1×10^{-5} M). The absorption spectra of the films were taken using microscope coverslides as references.

The solutions used for the Z-scans were contained in 1 mm glass cuvettes (concentrations ranging between 3.5×10^{-3} and 4.3×10^{-3} M), and those for transient absorption experiments were in 2 mm glass cuvettes (concentrations between 8.1 ×

10^{-6} and 10.0×10^{-6} M). Linear absorption spectra taken of these highly concentrated solutions in short pathlength quartz cuvettes (50 μm) revealed no evidence of aggregation at these concentrations.

The neat films were fabricated by first filtering a ~50 mM solution of molecule **1a-c** in cyclopentanone through a 0.2 μm PTFE filter to remove dust particulates. The films were subsequently spin-coated on microscope coverslides using a spin rate of 300 rpm for 7 s, followed by a spin rate of 750 rpm for 2 min.

4. Nonlinear Characterisation Techniques

The light source used for all nonlinear optical measurements was a regeneratively amplified Ti:Sapphire system (Spitfire, Spectra-Physics) that produces ~100 fs pulses at 800 nm with a repetition rate of 1 kHz. This, in turn, pumps a non-collinear optical parametric amplifier of white-light continuum (TOPAS-White, Spectra-Physics) that provides output pulses of <100 fs in the appropriate spectral bands.

Z-scans[S5] were performed to determine the real and imaginary components of the nonlinearity of the samples. The open-aperture scan, which monitors the entire transmitted beam collected, and thus is only sensitive to nonlinear absorption, was used to obtain the nonlinear absorption coefficient β, from which the imaginary part of γ was extracted.[S6,S7] With β known, the closed-aperture scan, sensitive to both nonlinear refraction and nonlinear absorption, allows for extraction of n_2 and thus the real part of γ.[S6] Since Z-scan is an absolute method, the spatial and temporal properties of the beam/pulse had to be carefully measured. The half-width $1/e^2$ of the beam used for the experiment was ~60 μm, its Rayleigh range was ~6.7 mm, the pulse width was 120 fs, and the beam shape was found to be Gaussian with an M value of ~1.10. The experimental setup was first calibrated using well-established nonlinearities for samples of fused silica,[S8] ZnSe,[S9] and GaAs[S10] using the pulse energies of 1.92, 0.068, and 0.017 μJ, respectively. It should be noted that for the samples in solution, the 1 kHz pulse repetition rate has been found to obscure the closed-aperture results due to thermal nonlinearities.[S11] In order to eliminate these effects, the repetition rate of the system was reduced to 50 Hz. This lower repetition rate minimized the thermal contributions to the resulting closed aperture signals. To ensure that the extracted values of Re(γ) and Im(γ) are third-order in nature, the Z-scans on each sample were performed at varying excitation energies ranging from 0.30 μJ to 0.90 μJ. The Im(γ) values for the heptamethines showed a negligible level of irradiance dependence, as expected for a purely third-order nonlinearity. Re(γ), on the other hand, showed an appreciable irradiance dependence, indicating the presence of a higher-order nonlinear process. Therefore, the Re(γ) value reported in the paper was extrapolated from the linear regression of irradiance dependent Re(γ) to zero intensity. Femtosecond transient absorption spectra (excited at the peak linear absorption maxima of the compounds in solution with excitation pulse energies of ~4.1 μJ; experimental details are given in Ref. S12) of the heptamethines [Fig. S1] also corroborate the lack of irradiance dependence of the Im(γ). The Z-scan probe wavelength of 1550 nm is significantly detuned from the peak of the transient absorption band at ~1430 nm; thus the value of Im(γ) is likely entirely attributable to the two-photon absorption process.

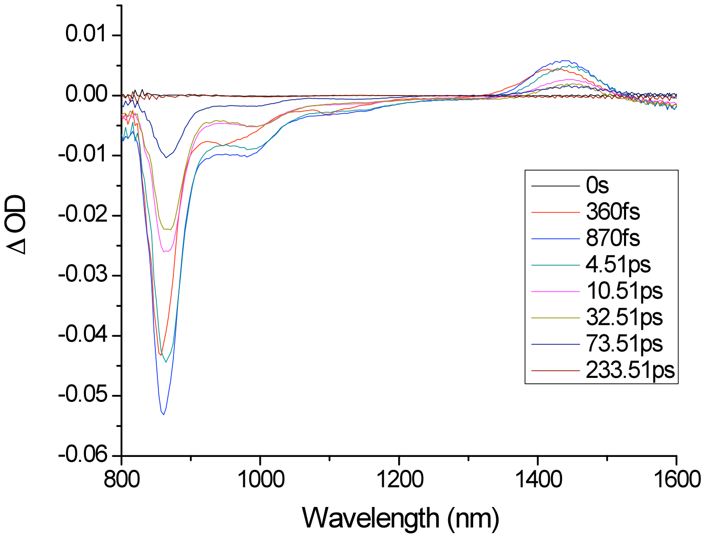


Fig. S1. Transient absorption spectrum of **1a** in CH_2Cl_2; the sample concentration, 9.3 μM; the pump wavelength, 830 nm; pump energy, 4.1 μJ. The negative signal at ca. 1000 nm is assumed to be due to stimulated emission.

5. References for Supplementary Information

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S6. The nonlinear refractive index and the two-photon absorption coefficient can be related to the third-order susceptibility, $\chi^{(3)}$, according to the following reference: Sutherland, R. L.; *Handbook of Nonlinear Optics* (Marcel Dekker, New York, ed. 2, 2003), pp. 341,583. The relationship between $\chi^{(3)}$ and γ, the microscopic third-order polarizability, is given by $\chi^{(3)} = N L^4 \gamma$, where N is the number density and L is the local field factor.

S7. The relationship between the two-photon absorption coefficient and the two-photon absorption cross-section, δ, can be found in Reference S6.

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