

Supplementary material to:

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Synthesis, Spectroscopic and DFT Characterization of 4 β -(4-*tert*-Butylphenoxy)phthalocyanine
Positional Isomers for Non-linear Optical Absorption,

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**Synthesis, spectroscopic and DFT characterisation of
4β-(4-*tert*- butylphenoxy)phthalocyanine positional isomers for non-linear optical
absorption**

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1. Equations used for Z-Scan measurements

The normalized open aperture Z-scan transmittance was measured in order to experimentally determine the second order NLO parameter. This normalized transmittance can be calculated by Equation (S1) ^{1,2}:

$$T_n(z_s) = \frac{1}{Aq_0(z_s)} \int_{-\infty}^{+\infty} \ln[1 + q_0(z_s)f(\tau)]d\tau \quad (S1)$$

Where $f(\tau)$ is a function of time detailing the temporal profile of the Gaussian pulses in the form of $f(\tau) = e^{-(\tau^2)}$. A is the normalization constant equal to $\int_{-\infty}^{+\infty} f(\tau)d\tau$, whilst the $q_0(z_s)$ parameter characterizes the strength of the nonlinearity. In the event of a circular Gaussian beam, it is represented by Equation (S2) ³:

$$q_0(z_s) = \frac{2\beta P_0 L_{eff}}{\pi w^2(z_s)} \quad (S2)$$

Where β is the nonlinear absorption coefficient of the material, P_0 is the peak power of the pulses and L_{eff} is the effective propagation length in the material, given by the following Equation (S3):

$$L_{eff} = \frac{1 - e^{-(\alpha L)}}{\alpha} \quad (S3)$$

Where L is the sample length and α is the linear absorption coefficient which is calculated by Equation (S4):

$$\alpha = \frac{h\nu}{N} \beta \quad (S4)$$

Where h is Planck's constant, ν is the frequency of the laser excitation and N corresponds to the number of active species per unit volume. The $w(z_s)$ parameter (Equation (S2)) is the beam width at the sample plane defined as the distance from the beam centre to the point where the intensity reduces to $1/e^2$ of its axis value. The $w(z_s)$ parameter is defined by Equation (S5) ¹:

$$w(z_s) = w_0 \sqrt{\left(\frac{z_s - z_0}{z_R}\right)^2} \quad (S5)$$

Where w_0 is the beam width at the focal point and z_0 is the location of the beam focus. The z_R parameter is the Rayleigh length and is given by the relation in Equation (S6):

$$z_R = \frac{\pi w_0^2}{\lambda} \quad (S6)$$

Where λ is the wavelength. Equations (S1-S6) are adequate for determining the nonlinear absorption coefficient (β) from the experimentally measured transmittance. G. Tsigaridas et. al derived an analytical formula Equation (S7) that provides values for $q_0(z_s)$ directly from the normalized transmittance $T_n(z_s)$ ¹.

$$q_0 = \begin{cases} a_0 + a_1 T_n(z_s) + a_2 T_n^2(z_s) + a_3 T_n^3(z_s) & \text{for } T_n(z_s) \leq 0.75 \\ c_0 + c_1 [T_n(z_s)]^2 & \text{for } T_n(z_s) \geq 0.75 \end{cases} \quad (S7)$$

Where the coefficients $a_0, a_1, a_2, a_3, c_0, c_1, c_2$ for Gaussian pulses are reported as 15.66, -37.45, 30.76, -8.97, -2.301, 2.156, -1.563 respectively ¹. Their work demonstrates that this technique allows for the simple determination of β , and is robust in the presence of signal noise ¹. Absorption coefficient (β) value and the beam parameters z_0 and z_s can be determine from the $q_0(z_s)$ values obtained from Equation (S7). Substituting Equation (S5) into Equation (S2), $q_0(z_s)$ is then defined by Equation (S8):

$$q_0(z_s) = \frac{Q_0}{1 + (z_s + z_0)^2 / z_R^2} \quad (S8)$$

Where:

$$Q_0 = \frac{2\beta P_0 L_{\text{eff}}}{\pi w_0^2} = \frac{2\beta P_0 L_{\text{eff}}}{\lambda(z_R)} \quad (S9)$$

Equation (S7) describes a Gaussian plot with Q_0 as the maximum value at the beam waist ($z_s = z_0$). The full width at half maximum (FWHM) of the $q_0(z_s)$ is equal to $2z_R$. The peak value and the FWHM of the plot provides the values for Q_0 and z_R . Equation (S10) can be used to calculate the nonlinear absorption coefficient (β).

$$\beta = \frac{\lambda z_R Q_0}{2 P_0 L_{eff}} \quad (S10)$$

2. Input file for the four positional isomers and optimised Cartesian coordinates of the structures.

All calculations were done on Gaussian 09, Revision D.01. Geometric optimizations were done using the Becke, three-parameter, Lee-Yang-Parr (B3LYP) functional at the 6-31G basis set. These Optimised structures were used to calculate the electronic absorption properties using the TD-DFT method. These calculations were done on the Coulomb-attenuated B3LYP functional and were also done with the 6-31G basis set. The Cartesian coordinates for each optimised structure follows.

DI1:

C	-3.63280300	-2.16700900	-0.41138300
C	-4.14680700	-0.86277700	-0.32497200
C	-5.52130300	-0.64083300	-0.27427800
C	-6.37156400	-1.74550400	-0.30950600
C	-5.84403800	-3.04958000	-0.38588500
C	-4.46543300	-3.27928600	-0.43991100
C	-2.17277800	-2.01351500	-0.44933600
C	-2.98191400	0.02264100	-0.31450500
H	-7.44733300	-1.60986100	-0.28395600
H	-4.08054800	-4.29104100	-0.50503900
N	-1.82248200	-0.69601100	-0.39051900
N	-1.36513100	-3.07395700	-0.53159500
N	-3.11506800	1.35058600	-0.23851200
C	-2.09959000	2.18953300	-0.22948100
C	-2.20067500	3.63797800	-0.14945900
C	-0.88745800	4.15685800	-0.17074900
C	-3.31993600	4.46818400	-0.05963400
C	0.02878100	3.03834500	-0.26357200
C	-0.67090400	5.53811400	-0.10285900
C	-3.08742400	5.84132800	0.00139300
H	-4.32071400	4.05454600	-0.03557700
C	-1.77521900	6.37077000	-0.01904600
H	-1.66419600	7.44898000	0.03427500
N	-0.75313400	1.90280200	-0.29373600
H	-0.37866400	0.96280900	-0.35585000
C	-0.04974800	-2.99148300	-0.57359700
C	0.86644200	-4.11007500	-0.66564300
C	2.17967800	-3.59128200	-0.68713300

C	0.64971600	-5.49129600	-0.73391900
C	2.07859700	-2.14278500	-0.60808100
C	3.29886700	-4.42158300	-0.77740600
C	1.75391400	-6.32402800	-0.81803600
C	3.06617000	-5.79467000	-0.83868200
H	4.29966100	-4.00802400	-0.80216500
N	0.73214100	-1.85601600	-0.54320000
H	0.35772400	-0.91595500	-0.48177900
N	1.34406600	3.12095400	-0.30778700
N	3.09384500	-1.30360700	-0.60202800
C	2.96046300	0.02445300	-0.52818500
C	4.12505400	0.91026600	-0.52814900
C	3.61134400	2.21455500	-0.44172000
C	5.49890000	0.68837300	-0.59636700
C	2.15169100	2.06065500	-0.39261600
C	4.44461500	3.32664400	-0.41136200
C	6.34883900	1.79339400	-0.57421000
C	5.82239800	3.09662000	-0.47699900
H	7.42345500	1.66000400	-0.63689700
N	1.80137100	0.74288600	-0.44622400
H	4.06021100	4.33838100	-0.34306900
H	-0.35810400	-5.89346100	-0.71866700
H	-5.92051700	0.36724300	-0.21809700
H	0.33684700	5.94043000	-0.11865200
H	5.89675600	-0.31882600	-0.67378000
C	-5.40737700	6.43817900	-0.11033300
C	-6.31644600	6.55875000	0.93392100
C	-5.84477100	6.07053200	-1.38418400
C	-7.67167900	6.30788200	0.70300300
H	-5.96126300	6.85403700	1.91634100
C	-7.19732100	5.81729600	-1.59319200
H	-5.13143600	5.98960800	-2.19870400
C	-8.14549300	5.92832700	-0.55981300
H	-8.35802500	6.41245600	1.53565800
H	-7.51741800	5.53299400	-2.59150600
O	-4.08130800	6.78094000	0.12414200
C	-7.88089400	-4.22050500	0.13228500
C	-8.07976800	-3.81262200	1.45031900
C	-8.93086500	-4.79673800	-0.58358700
C	-9.33619900	-3.97331500	2.03892800
H	-7.26134600	-3.37701300	2.01471900
C	-10.17271700	-4.95623000	0.02413900
H	-8.75882700	-5.11674000	-1.60658500
C	-10.41234400	-4.54653300	1.34736900
H	-9.45964500	-3.64645200	3.06546400
H	-10.97306200	-5.40835500	-0.55494700
O	-6.64751100	-4.16491900	-0.49252700
C	7.88630100	4.21056700	0.04675600
C	8.14013100	3.68410200	1.31229100
C	8.90932500	4.84054300	-0.66264400

C	9.42348500	3.78212600	1.85438600
H	7.34317800	3.20493300	1.87209700
C	10.17956500	4.93488000	-0.10141400
H	8.69502300	5.25211300	-1.64408900
C	10.47402600	4.40640600	1.16765600
H	9.58917300	3.36399500	2.84111400
H	10.95810100	5.42999600	-0.67522600
O	6.62458000	4.21755700	-0.52171200
C	-11.80689900	-4.73565900	1.97093300
C	-12.18048300	-6.23707600	1.95830400
H	-13.17660500	-6.38691400	2.39261500
H	-12.19678400	-6.64559800	0.94232700
H	-11.46284300	-6.82420300	2.54255300
C	-12.85051300	-3.94227800	1.14881600
H	-13.85273900	-4.07197900	1.57559900
H	-12.61698900	-2.87139200	1.14884900
H	-12.88680400	-4.27572100	0.10632700
C	-11.86850100	-4.24028900	3.42848100
H	-11.16834900	-4.78284400	4.07397600
H	-11.64693300	-3.16965100	3.50651500
H	-12.87611800	-4.39775400	3.82920200
C	-9.63047200	5.64013900	-0.84603200
C	-9.78557900	4.18515600	-1.34919900
H	-10.83859700	3.96670500	-1.56463600
H	-9.21475600	4.00666800	-2.26664100
H	-9.43737700	3.47018400	-0.59502000
C	-10.14515100	6.61506300	-1.93182500
H	-11.20281600	6.42091200	-2.14795600
H	-10.05099600	7.65547900	-1.60058100
H	-9.58991100	6.51167400	-2.86995600
C	-10.51060200	5.81059000	0.40674800
H	-10.21452500	5.12618400	1.20996000
H	-10.47212400	6.83408700	0.79685500
H	-11.55481700	5.59271900	0.15621700
C	11.89741100	4.52752000	1.74133000
C	12.28814300	6.02113300	1.84556900
H	13.30431100	6.12371100	2.24581100
H	12.26387700	6.51852200	0.87026800
H	11.60398600	6.55926100	2.51149100
C	12.89315900	3.80296900	0.80452100
H	13.91555300	3.88873400	1.19277200
H	12.64882600	2.73769500	0.72180500
H	12.88406800	4.22647000	-0.20537200
C	12.01807500	3.90263600	3.14417900
H	11.35727800	4.39339700	3.86787400
H	11.78266700	2.83222900	3.13585500
H	13.04557000	4.01103700	3.50915400
O	4.05984600	-6.73446700	-0.96160600
C	5.38642800	-6.39076700	-0.73139500
C	5.82797500	-6.02712700	0.54214900

C	6.29177200	-6.50630500	-1.77944400
C	7.18098900	-5.77308500	0.74719400
H	5.11739000	-5.95014700	1.35946000
C	7.64753100	-6.25462300	-1.55255200
H	5.93339100	-6.79835600	-2.76166200
C	8.12548700	-5.87928600	-0.29003800
H	7.50450100	-5.49215000	1.74537200
H	8.33094100	-6.35516000	-2.38809000
C	9.61122200	-5.59072200	-0.00809600
C	9.76682000	-4.13718900	0.49908600
H	9.41530400	-3.42013400	-0.25154900
H	9.19906400	-3.96225500	1.41915100
H	10.82043400	-3.91849500	0.71141800
C	10.13044600	-6.56857700	1.07288300
H	10.03573000	-7.60803600	0.73883000
H	11.18879000	-6.37443800	1.28571400
H	9.57854400	-6.46838200	2.01334600
C	10.48719400	-5.75650700	-1.26442000
H	10.44810900	-6.77877500	-1.65766600
H	10.18796300	-5.06976300	-2.06443800
H	11.53211800	-5.53870000	-1.01678800
H	1.64280300	-7.40220100	-0.87192800

DI2:

C	-4.10672300	1.05386200	-0.38637600
C	-3.53057300	2.32991000	-0.49572600
C	-4.32967300	3.47028700	-0.54678700
C	-5.71332900	3.31148900	-0.48145000
C	-6.27904400	2.02723300	-0.35654600
C	-5.48364000	0.87830700	-0.31081200
C	-2.97975000	0.11317000	-0.36735700
C	-2.08398500	2.11032100	-0.53422300
H	-6.36736600	4.17546200	-0.53003800
H	-5.93948800	-0.10170600	-0.22188400
N	-1.79183100	0.77720800	-0.45633100
N	-3.17705500	-1.20514700	-0.27490400
N	-1.22582200	3.12989100	-0.62982800
C	0.08424800	2.98562900	-0.66521300
C	1.05234300	4.05952500	-0.76247000
C	2.34017900	3.48009900	-0.76911300
C	0.90178500	5.44869200	-0.84428600
C	2.17121800	2.03911600	-0.67641600
C	3.49799300	4.25581000	-0.85665700
C	2.04466800	6.22795100	-0.92560000
H	-0.08592300	5.89825200	-0.84070600
C	3.33102100	5.63789300	-0.93015500
N	0.81264400	1.81540600	-0.61855900
H	0.39447600	0.89448800	-0.54971900
C	-2.20215300	-2.09090200	-0.25592300
C	-2.37118800	-3.53197100	-0.16482400

C	-1.08353200	-4.11172900	-0.17649300
C	-3.52890900	-4.30753200	-0.07518400
C	-0.11547100	-3.03787700	-0.27475200
C	-0.93308500	-5.50107000	-0.09763000
C	-3.36209300	-5.68980000	-0.00469600
C	-2.07593600	-6.28018400	-0.01418900
H	0.05447500	-5.95090000	-0.10552600
N	-0.84369800	-1.86745200	-0.31778800
H	-0.42548500	-0.94658700	-0.38710800
N	3.14633200	1.15363400	-0.65287500
N	1.19451900	-3.18225500	-0.31231100
C	2.05275500	-2.16251500	-0.40538200
C	3.49933000	-2.38211200	-0.44214000
C	4.07598400	-1.10561800	-0.54361100
C	4.29775400	-3.52328200	-0.40001600
C	2.94897500	-0.16482900	-0.56292700
C	5.45377200	-0.92874300	-0.59694000
C	5.68161200	-3.36432800	-0.45911800
C	6.24880100	-2.07799400	-0.55103600
H	6.33472200	-4.23014300	-0.43967300
N	1.76079800	-0.82910700	-0.47884100
H	5.91026500	0.05198100	-0.67391300
H	-4.50899500	-3.84649600	-0.05949100
H	-3.88676200	4.45673800	-0.64373900
H	4.47820800	3.79495500	-0.86904700
H	3.85356200	-4.51154300	-0.33161400
C	-8.49925200	2.71526500	0.26473500
C	-8.22186400	3.30523700	1.49693600
C	-9.72740400	2.94821900	-0.35602500
C	-9.17321700	4.13693600	2.09206000
H	-7.27420100	3.11653000	1.99097500
C	-10.66554600	3.77203000	0.25864700
H	-9.93291900	2.47618100	-1.31182000
C	-10.41501000	4.39329300	1.49481100
H	-8.92649100	4.58137600	3.04994100
H	-11.61376300	3.93389800	-0.24665500
O	-7.64326100	1.82331800	-0.35592000
C	8.50903900	-2.70136300	-0.02146100
C	8.34849100	-3.08405600	1.30933600
C	9.66041500	-3.07166900	-0.71738800
C	9.33974800	-3.84653000	1.93120500
H	7.45996600	-2.78747500	1.85759800
C	10.64035000	-3.82422200	-0.07674800
H	9.77445500	-2.76150400	-1.75148400
C	10.50756000	-4.23583200	1.26088500
H	9.18588400	-4.12878300	2.96673900
H	11.52662000	-4.09936600	-0.64170000
O	7.60830000	-1.88429000	-0.68165800
C	-11.48156600	5.30101500	2.13375100
C	-12.76963400	4.48237600	2.38849800

H	-13.54321500	5.11599900	2.83966100
H	-13.17846200	4.06709700	1.46131000
H	-12.57435800	3.64668400	3.07018900
C	-11.80222700	6.47475800	1.17817300
H	-12.56515400	7.12882700	1.61804500
H	-10.90780400	7.07800200	0.98517100
H	-12.18239000	6.12295800	0.21338700
C	-11.01595200	5.89264400	3.47782600
H	-10.80170200	5.11167800	4.21627000
H	-10.11770700	6.51000400	3.36215200
H	-11.80410200	6.53094000	3.89283100
C	11.61658600	-5.07324700	1.92379300
C	12.94396400	-4.27836100	1.90504100
H	13.74765700	-4.86439400	2.36753300
H	13.25711800	-4.03146800	0.88511900
H	12.84539000	-3.33860900	2.46028200
C	11.80177900	-6.39580600	1.14240200
H	12.59444200	-7.00168000	1.59839800
H	10.87824600	-6.98592200	1.14588400
H	12.07905700	-6.21676600	0.09821900
C	11.28892500	-5.42382600	3.38772900
H	11.17517400	-4.52682200	4.00717600
H	10.36998700	-6.01551800	3.47027000
H	12.10352400	-6.01869500	3.81600100
C	-5.70596400	-6.18038800	-0.13727300
C	-6.63617000	-6.26875800	0.89137400
C	-6.10662300	-5.78668300	-1.41541300
C	-7.97557900	-5.95909500	0.64052800
H	-6.30984200	-6.58451000	1.87743400
C	-7.44349400	-5.47404700	-1.64391700
H	-5.37767900	-5.73062300	-2.21810500
C	-8.41234700	-5.55124200	-0.62673400
H	-8.67886400	-6.03950800	1.46155400
H	-7.73463200	-5.16854500	-2.64482300
C	-9.87854000	-5.19686300	-0.93469100
C	-10.41655600	-6.14155200	-2.03590700
H	-11.46096700	-5.90004700	-2.26816700
H	-9.84163700	-6.05617000	-2.96393900
H	-10.37338900	-7.18732400	-1.71087000
C	-10.78600300	-5.33742300	0.30220200
H	-10.47441300	-4.67168900	1.11515100
H	-11.81526600	-5.07233200	0.03573200
H	-10.79845400	-6.36431900	0.68506500
C	-9.96180700	-3.73325600	-1.42990600
H	-9.59685900	-3.03812900	-0.66537500
H	-9.36734900	-3.57442100	-2.33578400
H	-11.00045300	-3.46845700	-1.66251600
O	-4.39955900	-6.58041500	0.11795100
H	-2.01605100	-7.36206600	0.04653700
O	4.36848600	6.52874100	-1.05103500

C	5.67480500	6.12843400	-0.79581200
C	6.60440800	6.21314400	-1.82530300
C	6.07596900	5.73801500	0.48316500
C	7.94372100	5.90311500	-1.57443200
H	6.27771100	6.52630600	-2.81206100
C	7.41274700	5.42495600	0.71172700
H	5.34741000	5.68492200	1.28642200
C	8.38100100	5.49852000	-0.30629900
H	8.64650800	5.98061200	-2.39615200
H	7.70437500	5.12206100	1.71329500
C	9.84708200	5.14365800	0.00166200
C	10.75393400	5.28043500	-1.23610600
H	10.76714100	6.30640500	-1.62141800
H	11.78308500	5.01495200	-0.96960600
H	10.44120200	4.61310100	-2.04730500
C	9.92933500	3.68121000	0.50042400
H	9.33542300	3.52525800	1.40716600
H	9.56308000	2.98450600	-0.26203600
H	10.96780500	3.41575600	0.73295500
C	10.38659200	6.09058000	1.10022400
H	11.43092200	5.84869800	1.33243800
H	10.34414400	7.13559600	0.77266600
H	9.81217700	6.00794200	2.02882400
H	1.98468200	7.30968500	-0.98881100

DI3:

C	5.67314700	-0.11555500	0.07961000
C	5.50073600	-1.52388600	0.09995100
C	6.56463800	-2.38364600	0.17669300
C	7.91477900	-1.82345500	0.23969500
C	8.04971100	-0.36488200	0.22001800
C	6.96056200	0.46597300	0.14114000
C	4.34886500	0.43910200	-0.00839600
C	4.04320400	-1.73902300	0.02287200
H	7.06775700	1.54663300	0.12640400
N	3.38906400	-0.55812400	-0.04022700
N	4.13932600	1.76335000	-0.05165000
N	3.52698700	-2.97615600	0.02328100
C	2.23725400	-3.22489900	-0.03964300
C	1.62583600	-4.54119800	-0.03938400
C	0.22800400	-4.36751300	-0.11536100
C	2.17704300	-5.82543500	0.01934200
C	-0.03236500	-2.93584900	-0.16518000
C	-0.65172800	-5.45016600	-0.13358600
C	1.31333400	-6.90961900	0.00126700
H	3.25170600	-5.96409100	0.07742200
C	-0.08732200	-6.72542700	-0.07365700
N	1.19927500	-2.31869100	-0.11609700
H	1.32652100	-1.31331700	-0.13384100

C	2.95247100	2.31781500	-0.13424800
C	2.68524500	3.74382800	-0.18664400
C	1.28853600	3.91864800	-0.27215200
C	3.53664300	4.85353900	-0.16767100
C	0.68072100	2.59497300	-0.27337000
C	0.70416500	5.18391800	-0.34087300
C	2.96808000	6.11615600	-0.23301100
C	1.56568000	6.28125400	-0.31833700
H	-0.37055700	5.29882200	-0.41001400
H	3.58264100	7.01049100	-0.22095100
N	1.71793600	1.69518600	-0.18955300
H	1.59360600	0.68957200	-0.17117000
N	-1.22119400	-2.37685400	-0.24313100
N	-0.61188800	2.35168000	-0.34118200
C	-1.13735600	1.12172300	-0.33744500
C	-2.58288700	0.90881300	-0.41356300
C	-2.76462500	-0.48335200	-0.38360700
C	-3.67541700	1.76791600	-0.50420400
C	-1.41471100	-1.05425200	-0.29094100
C	-4.02894700	-1.05617800	-0.43219700
C	-4.95262000	1.21003200	-0.56067500
C	-5.12329100	-0.18749700	-0.51861300
H	-5.82602800	1.84770000	-0.64284900
N	-0.47127500	-0.06968800	-0.26615000
H	-4.18173900	-2.12951100	-0.40784600
H	4.61209900	4.72457800	-0.10209900
H	6.45192400	-3.46273600	0.19236700
H	-1.72267400	-5.29907300	-0.19143900
H	-3.53604300	2.84400700	-0.53897300
C	-0.21239800	7.88197700	-0.34899300
C	-0.89217400	7.89515300	0.86478200
C	-0.86366500	8.24742300	-1.52514500
C	-2.23693400	8.27163400	0.89568800
H	-0.37104100	7.61963100	1.77665700
C	-2.20375500	8.62412300	-1.47434700
H	-0.31644800	8.24078800	-2.46272800
C	-2.92519400	8.64404700	-0.26794900
H	-2.74251300	8.27506200	1.85458200
H	-2.69418800	8.90794200	-2.40094700
O	1.14690100	7.58485300	-0.39511300
C	-7.49818200	-0.18266200	-0.13110200
C	-7.54852000	0.39170900	1.13785000
C	-8.65276200	-0.25133600	-0.91120000
C	-8.75699900	0.90659300	1.61254000
H	-6.65537000	0.43326000	1.75320800
C	-9.84901000	0.25939500	-0.41596200
H	-8.59933400	-0.70850500	-1.89437100
C	-9.93495600	0.85551600	0.85437300
H	-8.76474000	1.34713200	2.60318700
H	-10.73381000	0.19250600	-1.04268800

O	-6.35841600	-0.78445800	-0.63801400
C	-11.28007900	1.41274600	1.35492000
C	-12.32503500	0.27262700	1.40478100
H	-13.29158400	0.65565000	1.75459100
H	-12.48352300	-0.17918700	0.41991700
H	-12.00626400	-0.52198300	2.08894600
C	-11.77399900	2.51593000	0.38876300
H	-12.73604900	2.91824600	0.72897600
H	-11.05751900	3.34384800	0.33975900
H	-11.91434700	2.13486100	-0.62826800
C	-11.17139900	2.02488200	2.76435700
H	-10.85420600	1.28510500	3.50818300
H	-10.46561800	2.86301400	2.79213000
H	-12.14963100	2.40714000	3.07667800
C	-4.40632100	9.06501600	-0.26592300
C	-5.21315000	8.11091300	-1.17871900
H	-6.27210700	8.39630700	-1.18717900
H	-4.85448600	8.13427700	-2.21315200
H	-5.14276800	7.07632200	-0.82389700
C	-4.53264000	10.51222100	-0.79846800
H	-5.58408600	10.82412500	-0.80715300
H	-3.97561500	11.21298900	-0.16630900
H	-4.14962700	10.60713100	-1.82003100
C	-5.02555100	9.01784500	1.14400200
H	-4.99384900	8.00920000	1.57164400
H	-4.51807300	9.69985200	1.83569600
H	-6.07708200	9.32168000	1.09489400
C	-2.20701300	-7.82714300	-0.14712900
C	-2.95399100	-7.80141900	1.02508000
C	-2.84138400	-7.87559300	-1.38727000
C	-4.34920500	-7.81837100	0.95212100
H	-2.44622400	-7.77592400	1.98446600
C	-4.23284500	-7.89322200	-1.44052400
H	-2.24482200	-7.90685600	-2.29390400
C	-5.02197000	-7.86236000	-0.27687900
H	-4.90844100	-7.79889800	1.88042100
H	-4.70962700	-7.93499800	-2.41554400
C	-6.55757100	-7.88454200	-0.38957000
C	-7.00185100	-9.18935300	-1.09293400
H	-8.09425300	-9.21807900	-1.18701900
H	-6.57888800	-9.27512900	-2.09935600
H	-6.68685500	-10.06997200	-0.52164900
C	-7.24694300	-7.82237800	0.98652200
H	-6.99098600	-6.90557300	1.52966800
H	-8.33444600	-7.83438400	0.85379700
H	-6.98304500	-8.67999500	1.61585800
C	-7.03140100	-6.66784000	-1.22010200
H	-6.73699300	-5.72656000	-0.74229000
H	-6.61254100	-6.67410600	-2.23193700
H	-8.12416300	-6.67400600	-1.31299400

O	-0.81686100	-7.88517700	-0.08135800
H	1.68782700	-7.92720000	0.04464700
H	9.06141900	0.02552000	0.27170500
O	9.06382900	-2.67108500	0.31783800
C	10.24793100	-1.86954100	0.33603400
C	10.77941100	-1.43774300	1.55120000
C	10.87187700	-1.51988700	-0.86181500
C	11.93480000	-0.65592400	1.56873300
H	10.28787800	-1.71356700	2.49537100
C	12.02672300	-0.73786200	-0.84438800
H	10.45283300	-1.86082900	-1.81974800
C	12.55812000	-0.30546600	0.37128800
H	12.35312400	-0.31501900	2.52687200
H	12.51839600	-0.46146200	-1.78839900
C	13.83296400	0.55824900	0.39048600
C	13.89840500	1.40547700	-0.89385200
H	14.70115000	2.10871900	-0.81671300
H	14.06443700	0.76556100	-1.73518500
H	12.97509600	1.93080800	-1.02202200
C	13.80469800	1.48795900	1.61785700
H	12.88595900	2.03631900	1.62884200
H	13.88150400	0.90280800	2.51038100
H	14.62699200	2.17071800	1.56713200
C	15.07063200	-0.35497300	0.46665000
H	15.08999900	-1.00128700	-0.38587800
H	15.95642000	0.24512400	0.47948000
H	15.02541600	-0.94326800	1.35926600

DI4:

C	-2.82216130	-0.56439168	-0.10012465
C	-2.75391712	0.83847948	-0.07106540
C	-3.91558499	1.60722034	-0.02283526
C	-5.14400579	0.94836079	-0.00255336
C	-5.19907756	-0.45952717	-0.02193251
C	-4.03877664	-1.23703668	-0.07266452
C	-1.43042168	-1.02545361	-0.15339966
C	-1.32871785	1.16631695	-0.10821506
H	-6.06957065	1.51349697	0.02340721
H	-4.10366430	-2.31940237	-0.09314070
N	-0.56877154	0.03182174	-0.15667116
N	-1.12979289	-2.32748212	-0.19319095
N	-0.90138154	2.43340407	-0.09585057
C	0.36824725	2.77937536	-0.13136334
C	0.87450618	4.14239463	-0.12716727
C	2.28434715	4.07201205	-0.17746623
C	0.19930793	5.36356015	-0.08299440
C	2.65613883	2.67214593	-0.21458650
C	3.05196120	5.24231529	-0.18378091
C	0.97780088	6.52006549	-0.10048196

H	-0.88234806	5.40120783	-0.03665292
C	2.39045934	6.45964874	-0.14743180
H	2.93688159	7.39720408	-0.15416209
N	1.47681576	1.96024521	-0.18394015
H	1.42893399	0.94772416	-0.19985474
C	0.10009922	-2.79335300	-0.24654210
C	0.47178841	-4.19801381	-0.29526861
C	1.88149888	-4.26224340	-0.34671200
C	-0.31962901	-5.34824401	-0.29448655
C	2.38742327	-2.90430051	-0.33121798
C	2.53134011	-5.50093276	-0.39895431
C	0.34257553	-6.57369945	-0.35383479
C	1.75491342	-6.64864117	-0.40378824
H	3.61451296	-5.55511014	-0.43797523
N	1.28233549	-2.08332240	-0.27107689
H	1.33228219	-1.07106379	-0.24907603
N	3.88875994	2.20395669	-0.26784496
N	3.65943892	-2.55608891	-0.36819520
C	4.08328341	-1.28961564	-0.35284104
C	5.50947680	-0.96167427	-0.39780305
C	5.57929216	0.44031697	-0.36787907
C	6.66866402	-1.73129642	-0.46136846
C	4.18593288	0.90314749	-0.30582793
C	6.79552685	1.11159889	-0.39040998
C	7.89831393	-1.07399709	-0.49158755
C	7.95627831	0.33274464	-0.45043410
H	8.82108099	-1.64064689	-0.55188693
N	3.32404124	-0.15443677	-0.29798304
H	6.86202237	2.19373282	-0.36546308
H	-1.39979363	-5.28130365	-0.24824837
H	-3.86538058	2.69167776	-0.01066188
H	4.13534510	5.19202116	-0.22118229
H	6.61631680	-2.81516244	-0.49482316
C	-0.86545350	8.04024879	-0.35230775
C	-1.64388472	8.73230934	0.56848507
C	-1.39083605	7.70330984	-1.60178911
C	-2.95479052	9.08630124	0.23930110
H	-1.21807479	8.99464637	1.53196260
C	-2.70228989	8.05530733	-1.90684332
H	-0.77716482	7.17493667	-2.32474341
C	-3.51861584	8.75490727	-0.99968718
H	-3.53622605	9.62824817	0.97660290
H	-3.09137229	7.78167818	-2.88350016
O	0.45977828	7.78985037	-0.02375562
C	-7.50777604	-0.69632820	0.61064081
C	-7.44773273	-0.19880549	1.91156567
C	-8.74352742	-0.84156088	-0.02163604
C	-8.62784060	0.16101075	2.56649792
H	-6.49020603	-0.09633829	2.41209881
C	-9.90816971	-0.48567279	0.65163691

H	-8.77518148	-1.23619507	-1.03250350
C	-9.88449824	0.02861521	1.95994660
H	-8.54811512	0.54457394	3.57757570
H	-10.85673131	-0.60934227	0.13660709
O	-6.39494417	-1.14539506	-0.07717612
C	10.31303746	0.50536596	-0.01137767
C	10.37821738	-0.03920384	1.27000129
C	11.47344156	0.62563780	-0.77633311
C	11.60713968	-0.47200549	1.77261030
H	9.47899691	-0.12172049	1.87232653
C	12.69006546	0.19610820	-0.25378161
H	11.40836927	1.05793280	-1.77002760
C	12.79165098	-0.36732390	1.03017807
H	11.62547228	-0.89012866	2.77290597
H	13.57838621	0.30092325	-0.87053350
O	9.14510263	1.02400014	-0.54409472
C	-11.20012538	0.41537857	2.65992399
C	-12.11542411	-0.82792893	2.76221576
H	-13.06208252	-0.56742829	3.25158071
H	-12.35353514	-1.24051994	1.77612518
H	-11.63606297	-1.62013857	3.34844837
C	-11.91881941	1.51249495	1.83897375
H	-12.86216756	1.79523852	2.32217283
H	-11.29626095	2.41072931	1.75644811
H	-12.15341565	1.17487907	0.82390271
C	-10.96830865	0.95732512	4.08306690
H	-10.48759784	0.21438201	4.72971388
H	-10.34856335	1.86131579	4.08030729
H	-11.92986080	1.21824692	4.53938184
C	-4.96248995	9.12040836	-1.38940452
C	-5.76260525	7.82499928	-1.66579428
H	-6.79280831	8.06629056	-1.95503447
H	-5.31797931	7.23750162	-2.47593472
H	-5.80021567	7.18928950	-0.77377685
C	-4.94913762	9.99518365	-2.66554648
H	-5.97314604	10.25802943	-2.95760653
H	-4.39367622	10.92484896	-2.49766848
H	-4.48555614	9.47724977	-3.51167413
C	-5.68715362	9.90516965	-0.27929555
H	-5.76189065	9.32677907	0.64866791
H	-5.18345330	10.85206788	-0.05363866
H	-6.70709700	10.14279235	-0.60167554
C	14.15930800	-0.83215138	1.56257035
C	15.13272912	0.36997317	1.60221870
H	16.11513171	0.05520955	1.97528829
H	15.27933218	0.80889071	0.60964176
H	14.75436374	1.15827887	2.26288659
C	14.73309663	-1.92426855	0.62874666
H	15.71546826	-2.25591523	0.98687647
H	14.07140896	-2.79737021	0.59392374

H	14.85847322	-1.55963091	-0.39620216
C	14.06501422	-1.41912029	2.98382687
H	13.69608227	-0.68223760	3.70637239
H	13.40742735	-2.29520676	3.02158470
H	15.05863161	-1.73867203	3.31743270
C	-1.66642864	-7.86331965	-0.55275435
C	-2.47944262	-8.33280597	0.47176736
C	-2.21256786	-7.55946237	-1.80100666
C	-3.84931502	-8.49503325	0.24715198
H	-2.03772965	-8.57282490	1.43395689
C	-3.58001389	-7.72036152	-2.00356917
H	-1.56950389	-7.20464125	-2.60066712
C	-4.43407555	-8.18962331	-0.98887340
H	-4.45944116	-8.86380327	1.06380114
H	-3.98577460	-7.47792965	-2.98152766
C	-5.94030688	-8.34714027	-1.26596636
C	-6.14939492	-9.34810391	-2.42719320
H	-7.21870297	-9.46534816	-2.64130573
H	-5.66077985	-9.01360838	-3.34833509
H	-5.74372632	-10.33395366	-2.17273187
C	-6.70933711	-8.87107856	-0.03825656
H	-6.62934847	-8.18890405	0.81578608
H	-7.77278869	-8.96754657	-0.28403404
H	-6.35339603	-9.85876990	0.27658927
C	-6.53745277	-6.97443814	-1.65760510
H	-6.40708323	-6.24479045	-0.85045592
H	-6.06581598	-6.56428534	-2.55691684
H	-7.61139937	-7.06975735	-1.85931929
O	-0.29552043	-7.78903232	-0.33295044
H	2.20770047	-7.63399773	-0.44606603

Figure S1. MALDI-TOF spectra of tBuH₂Pc positional isomers.

The phthalocyanine structure is highly conjugated and as a result Pc molecules are susceptible to aggregation in highly concentrated solutions. The aggregations causes broadening and overlap of proton NMR peaks making peak assignment difficult. In this work MALD-TOF (and other characterisation techniques) was used to verify the structure and purity of the isomers. The results obtained correlated with previously reported data for a pure tBuH₂Pc compound (i.e. a mixture of the four isomers).

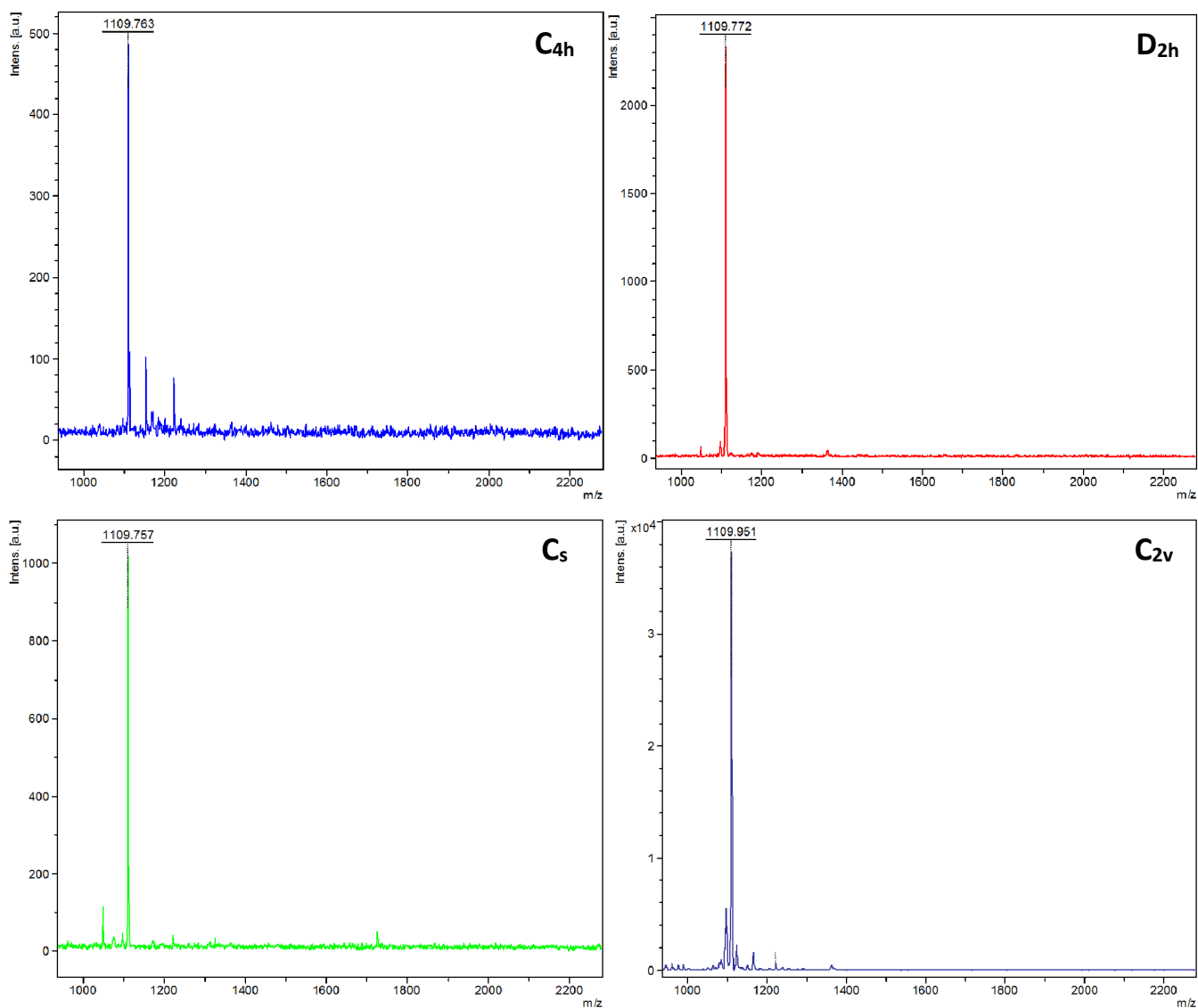
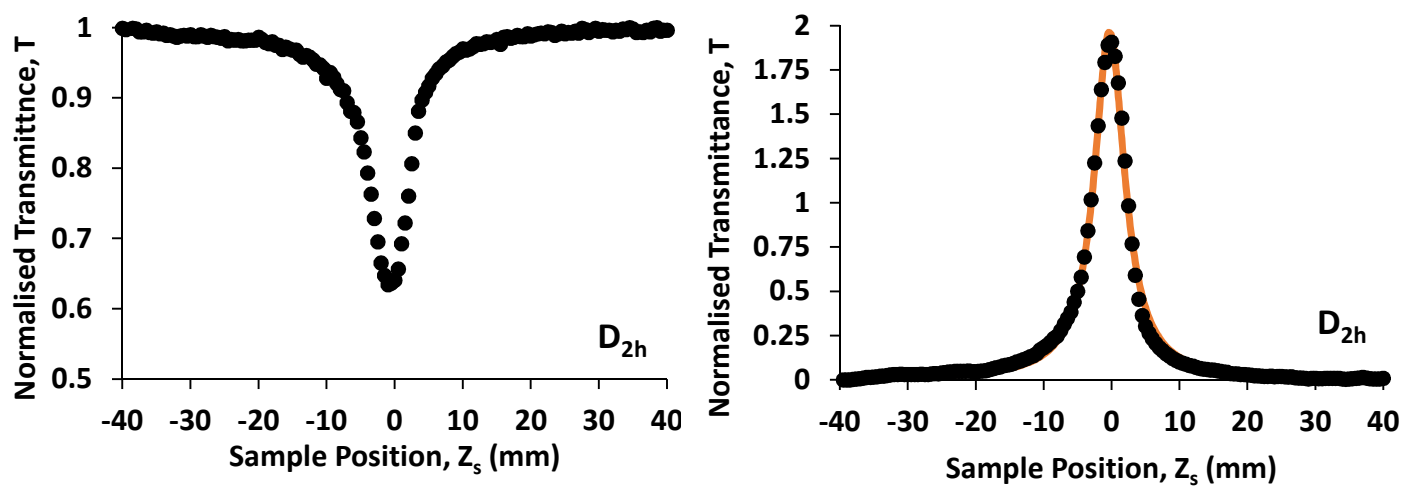


Figure S2. Z-scan (left) and NLO fit (right) for isomers D_{2h} , C_s and C_{2v} .



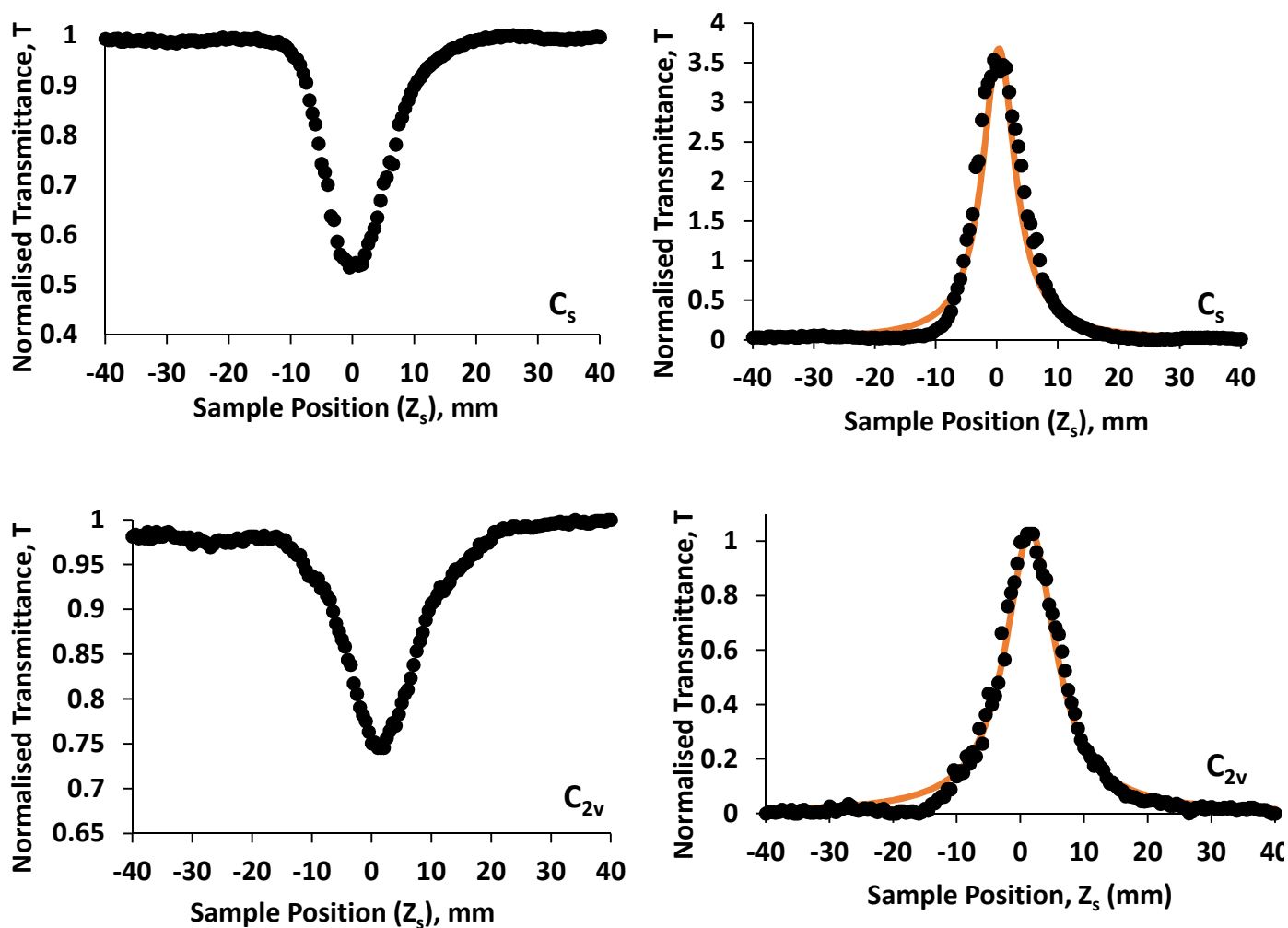
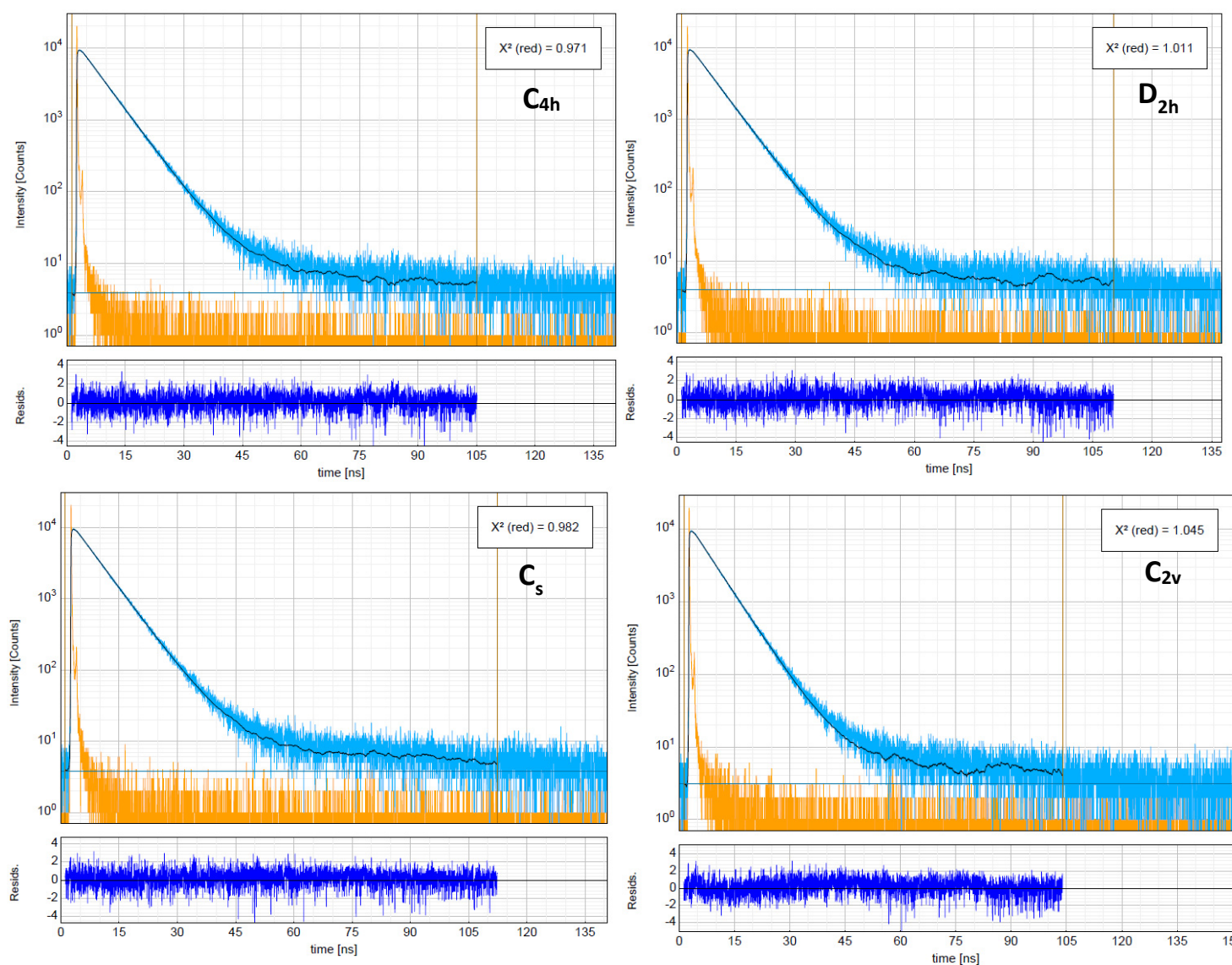


Figure S3. TCSPC trace of the four positional isomers.



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