Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supporting Information

Two- and Three-photon Absorption Properties of Fan-shaped Dendrons Derived from 2,3,8-Trifunctionalized Indenoquinoxaline Units: Synthesis and Characterization

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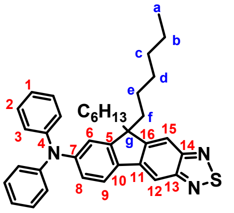
◆ Numbering of C and H of the precursors and final chromophores for NMR assignment



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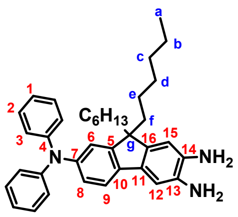

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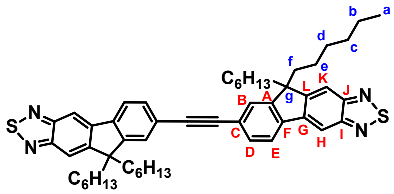

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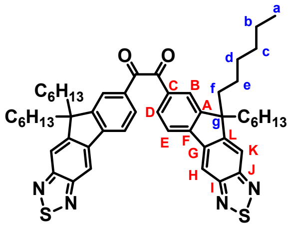

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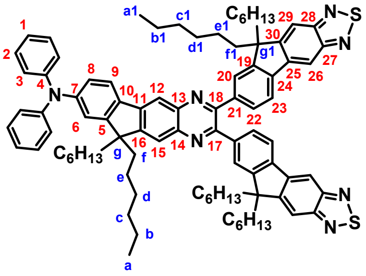

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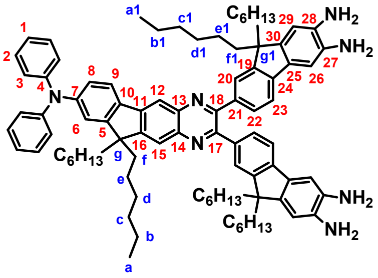

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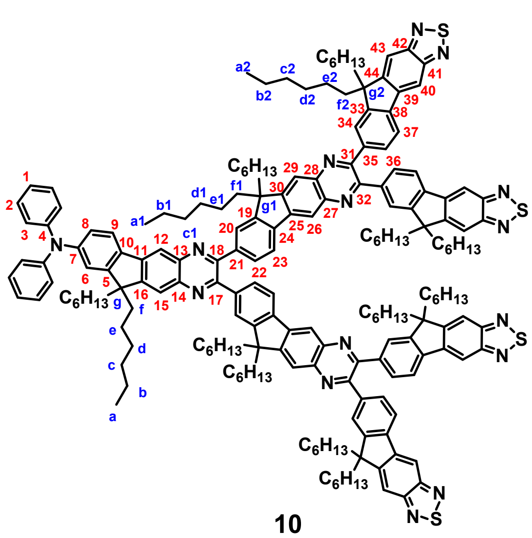

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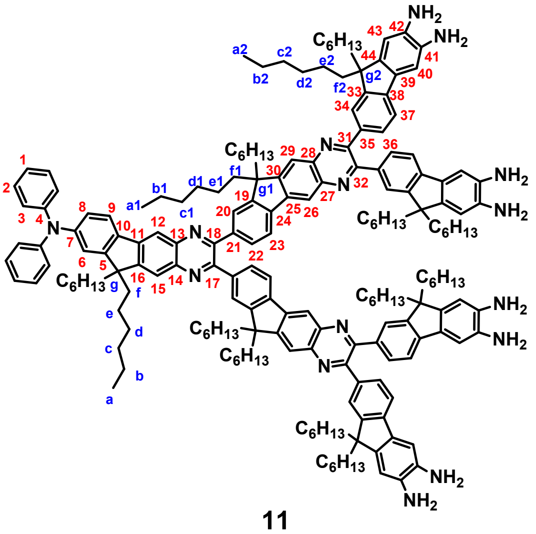

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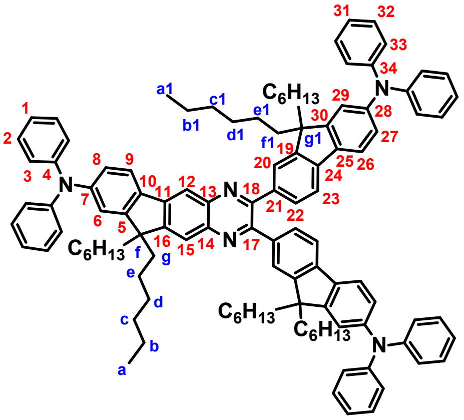
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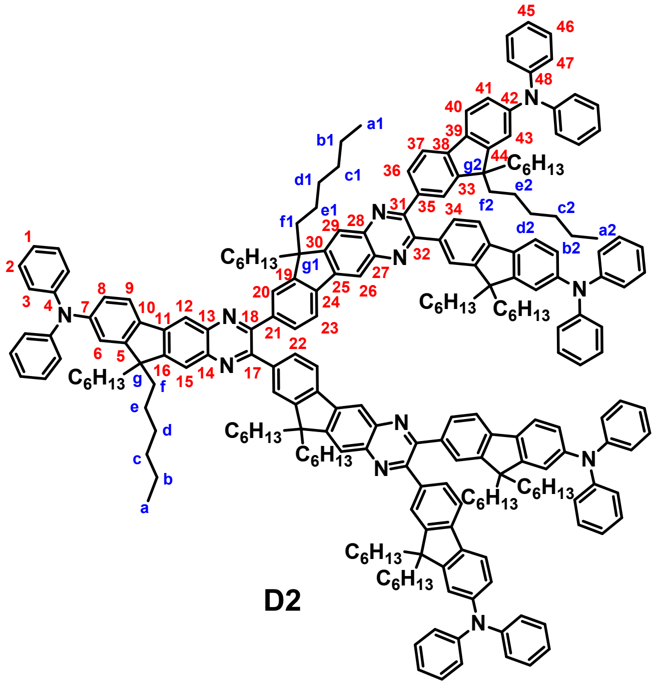
D1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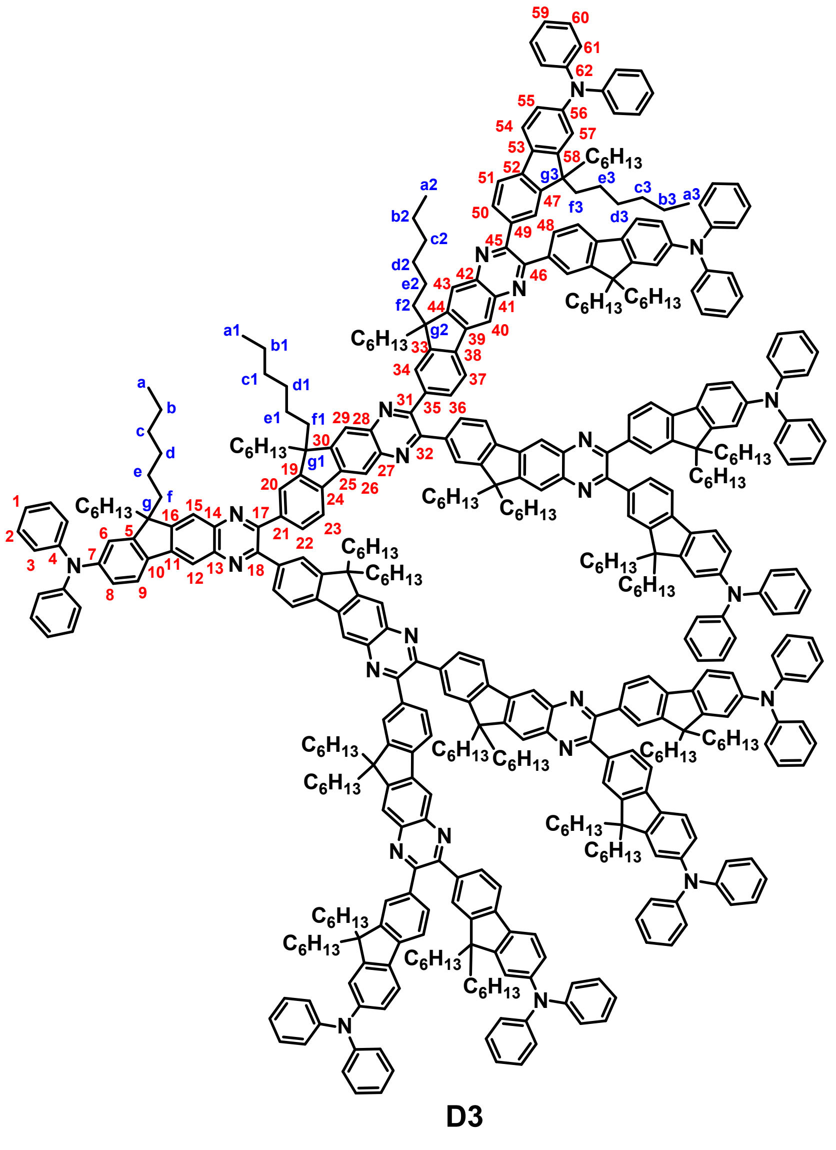
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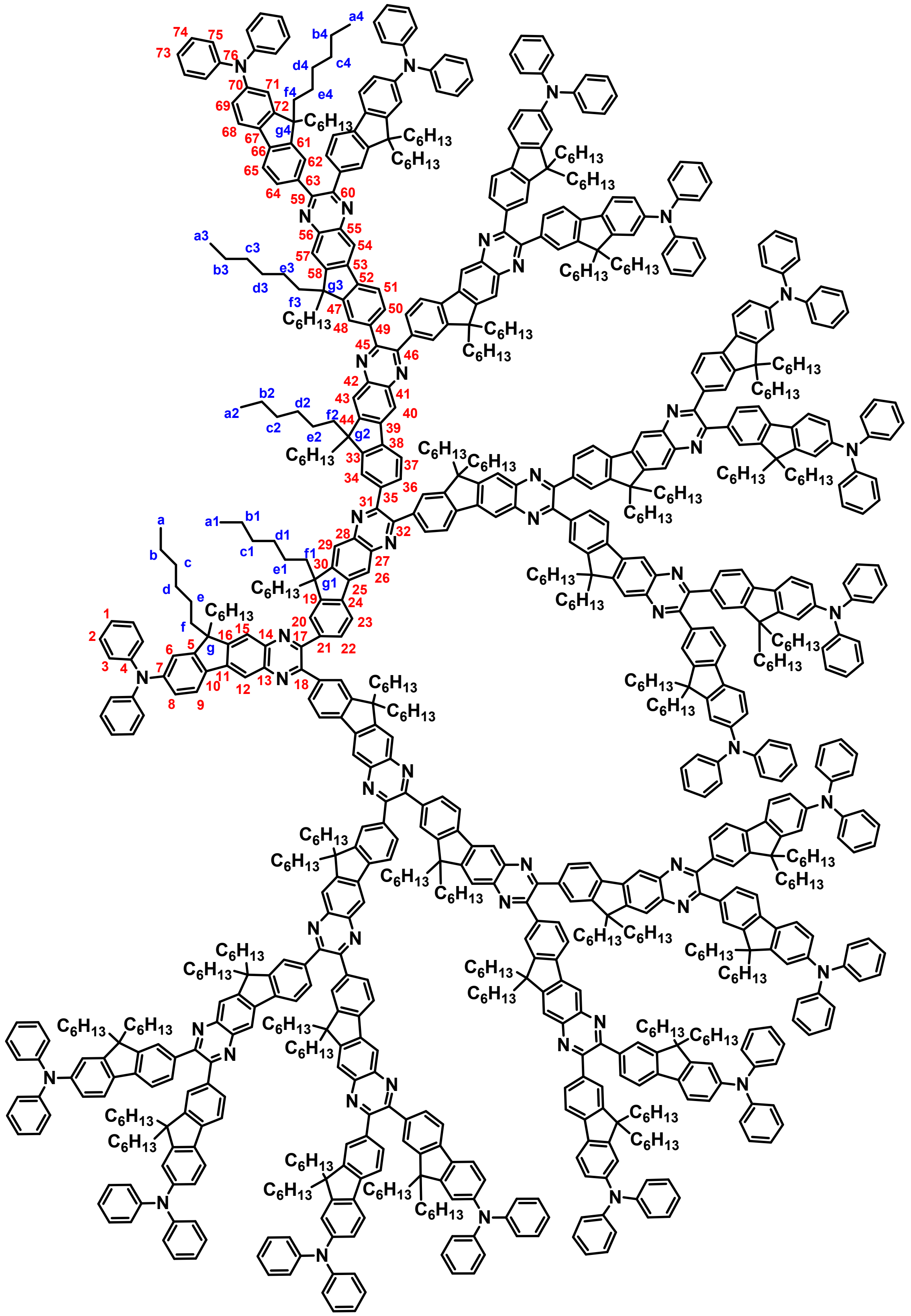
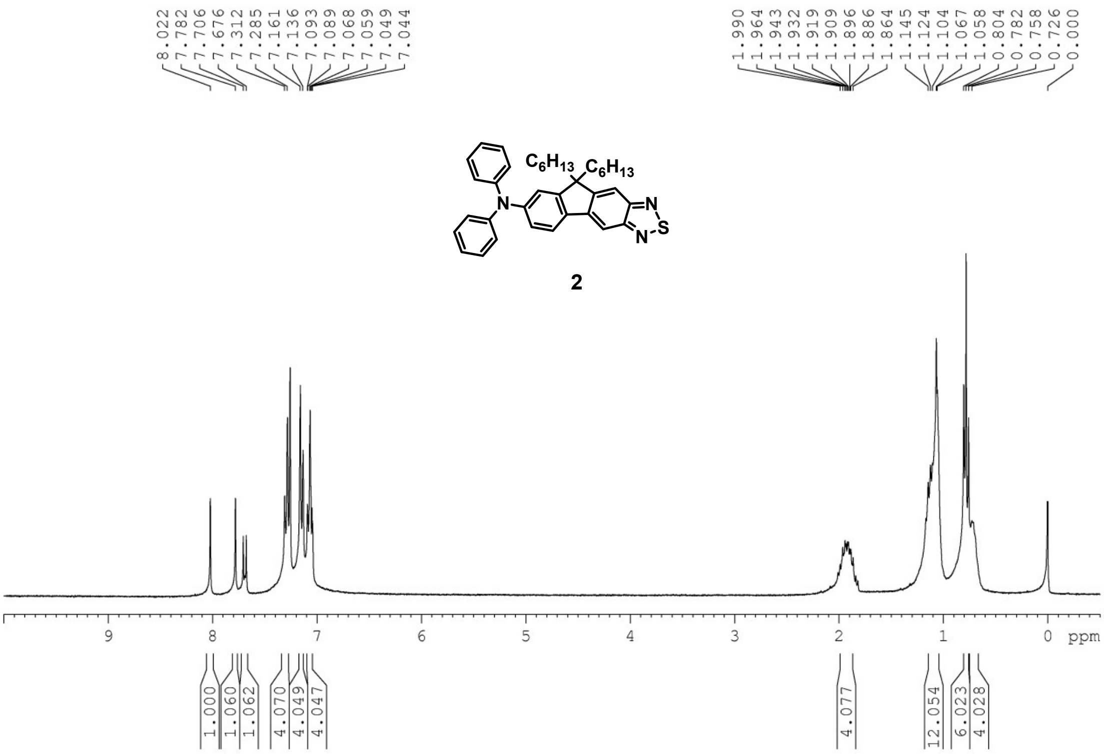


D4

^{1}H-NMR/^{13}C-NMR spectra of compounds 2-7, 10-11, D1-D4



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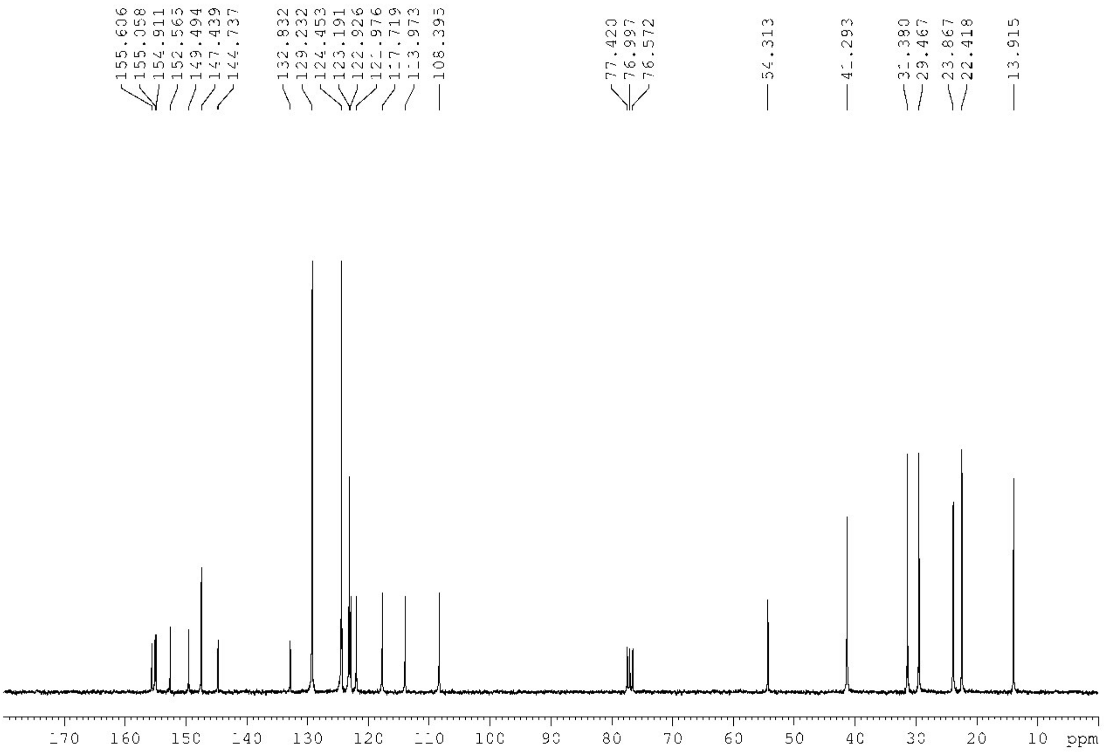

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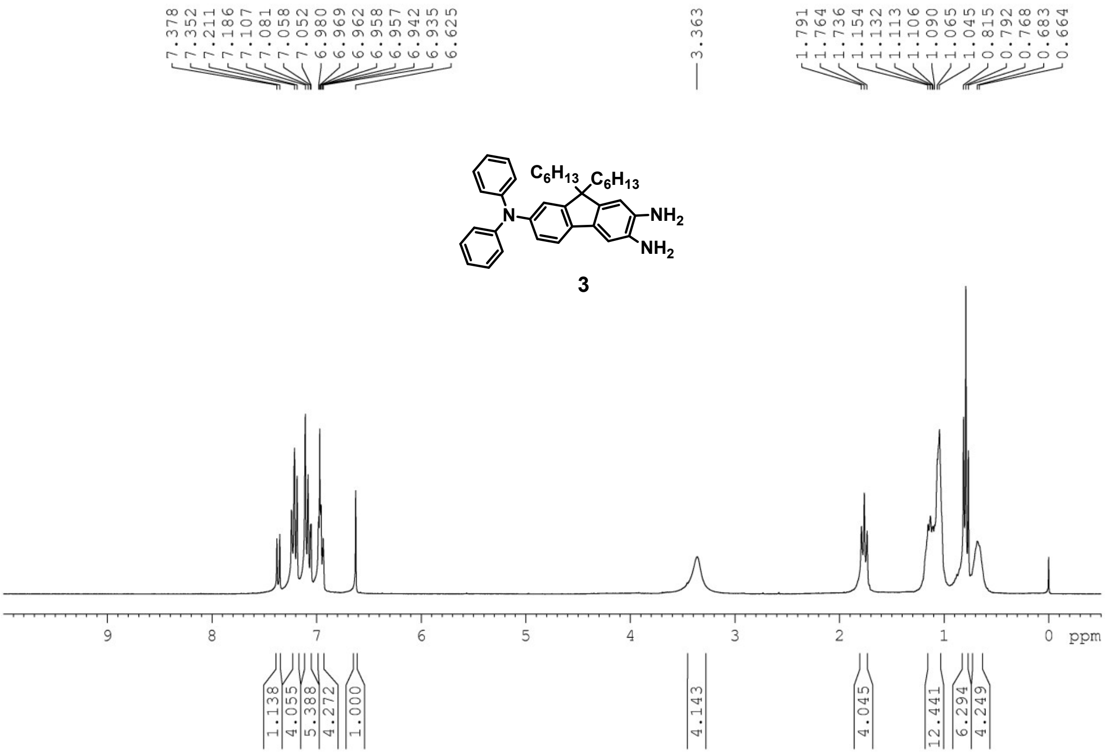

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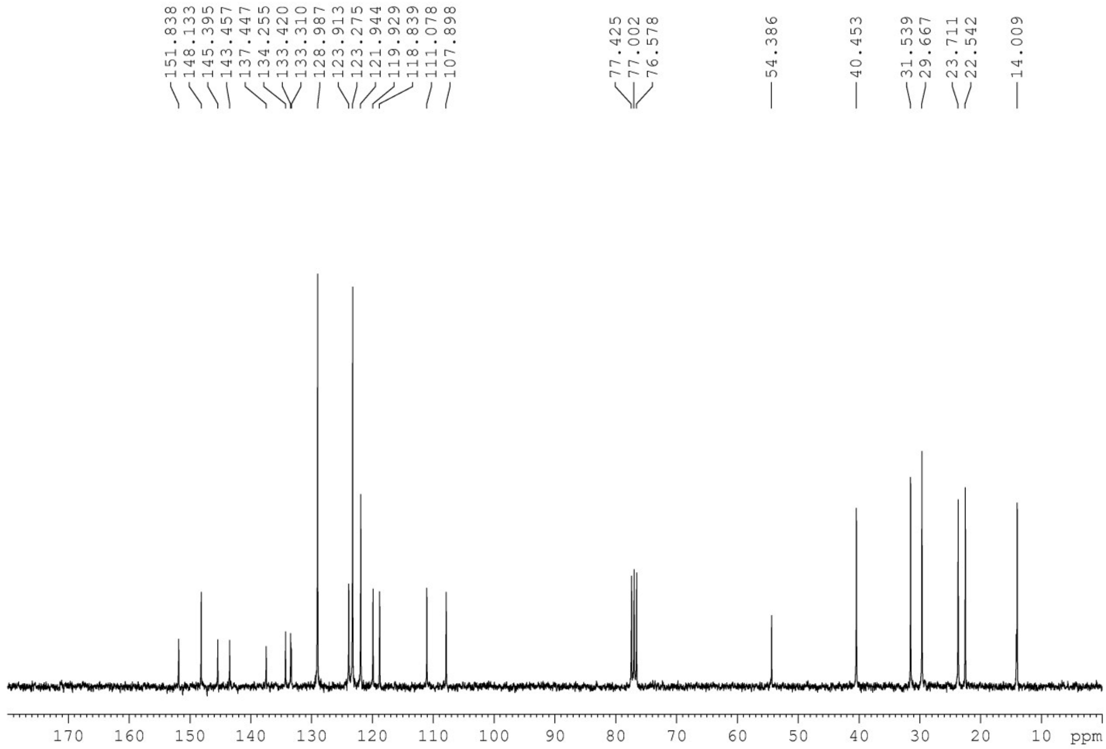

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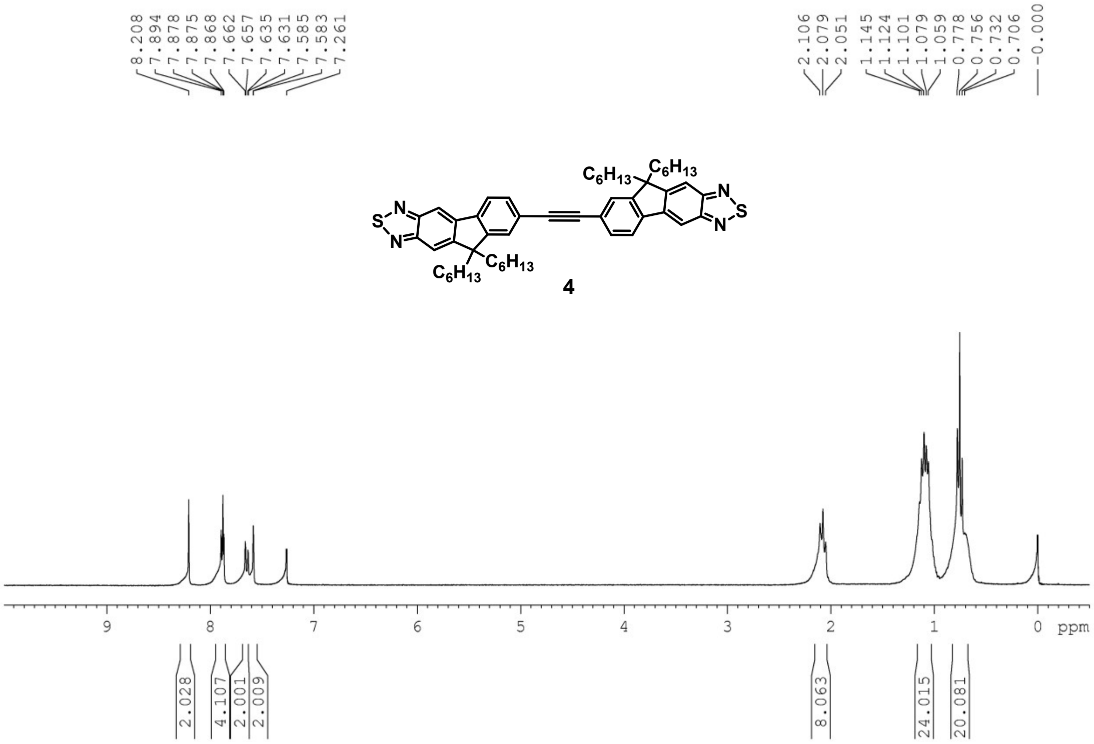

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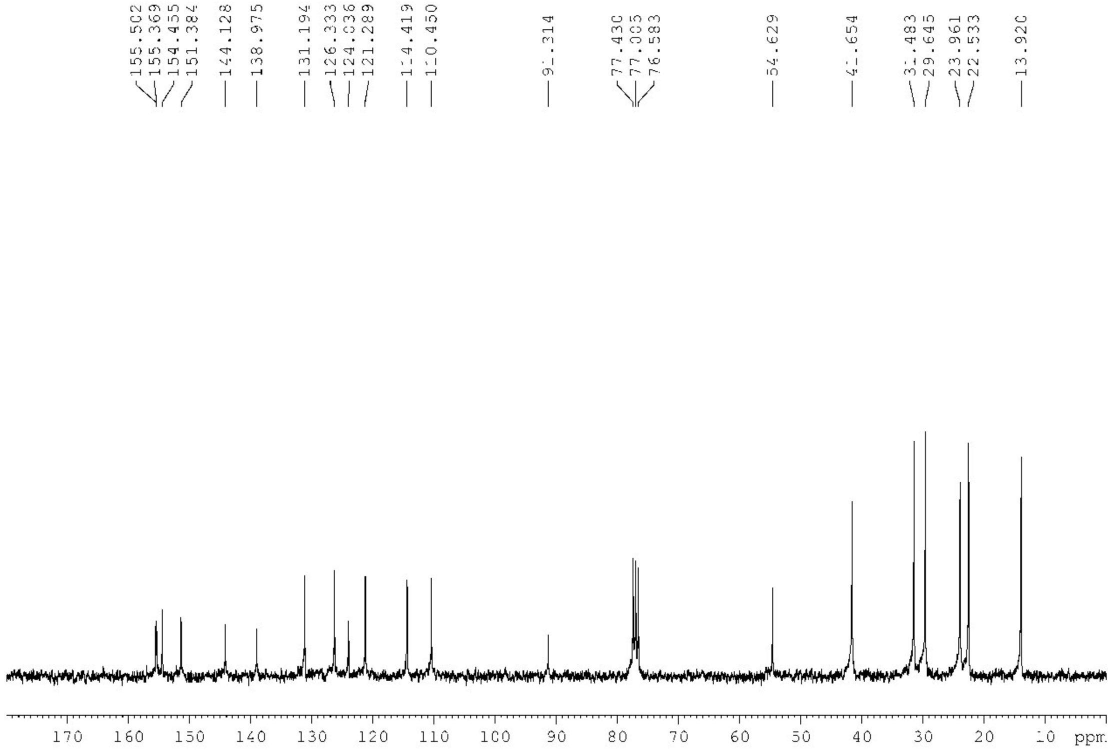
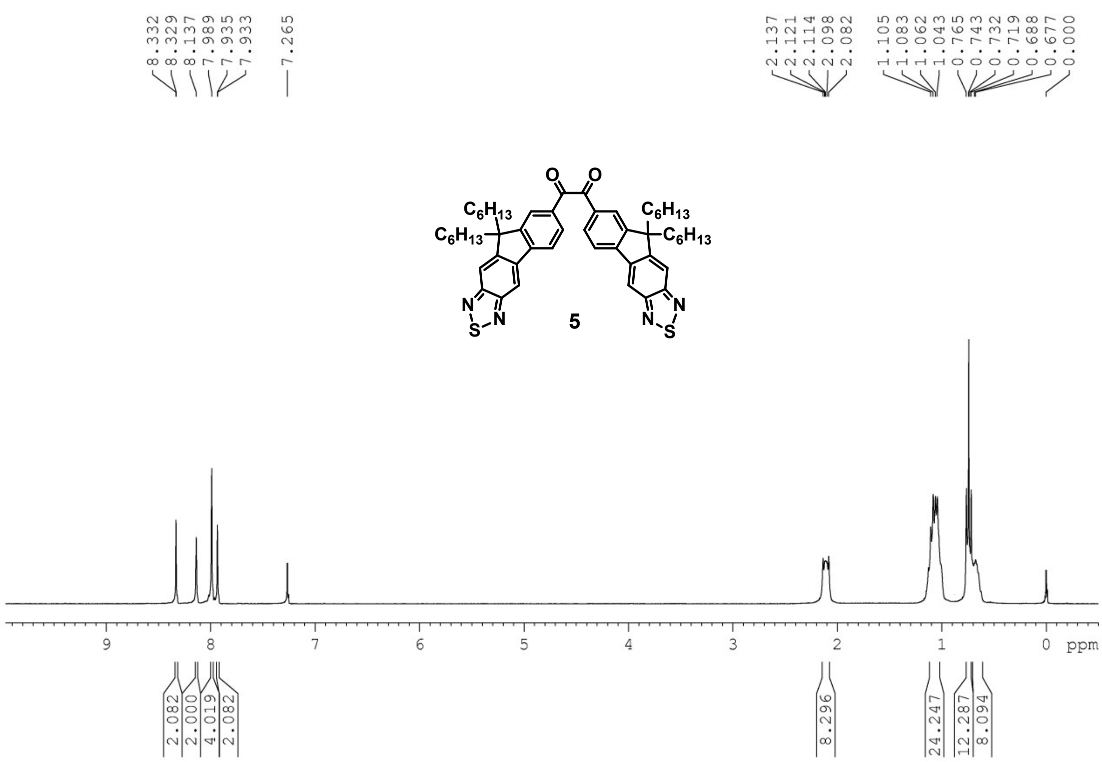


^{13}C-NMR spectrum of compound **4** (solvent: $CDCl_3$)



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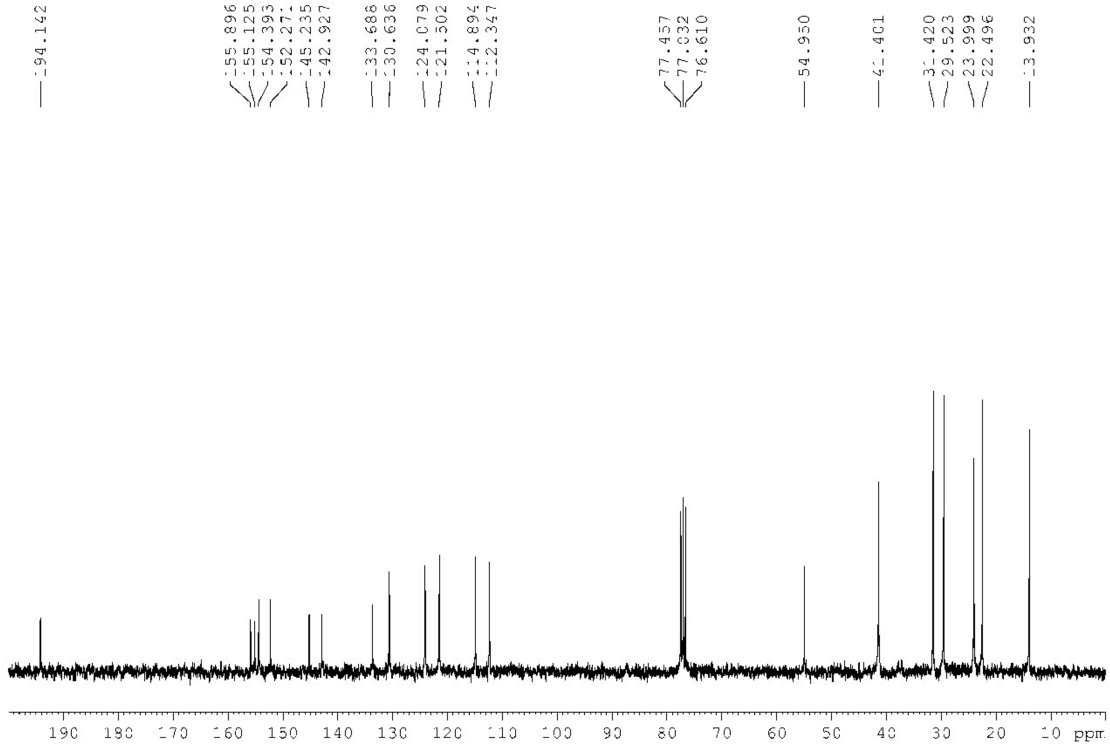

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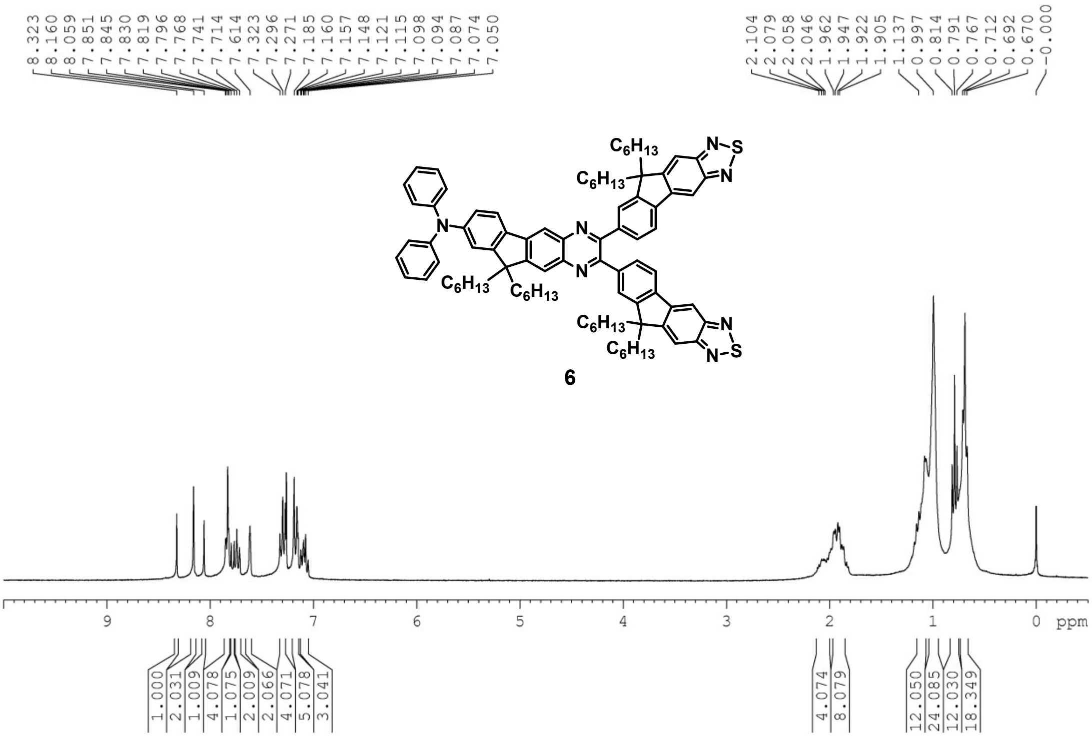

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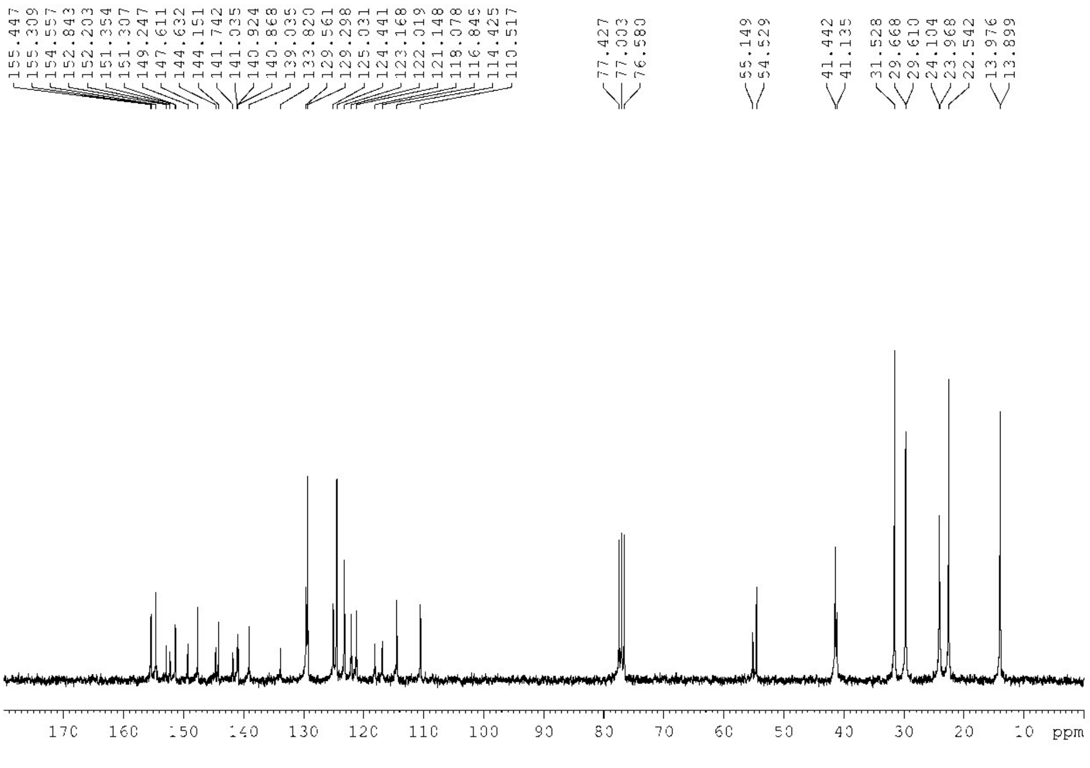

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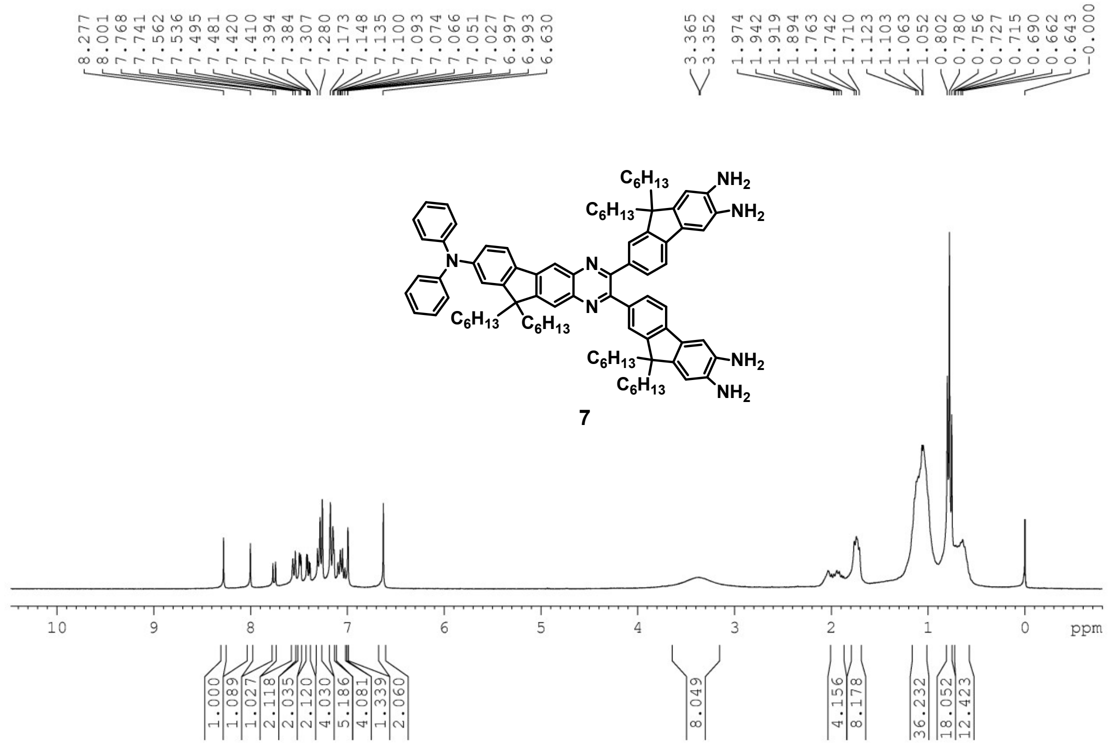

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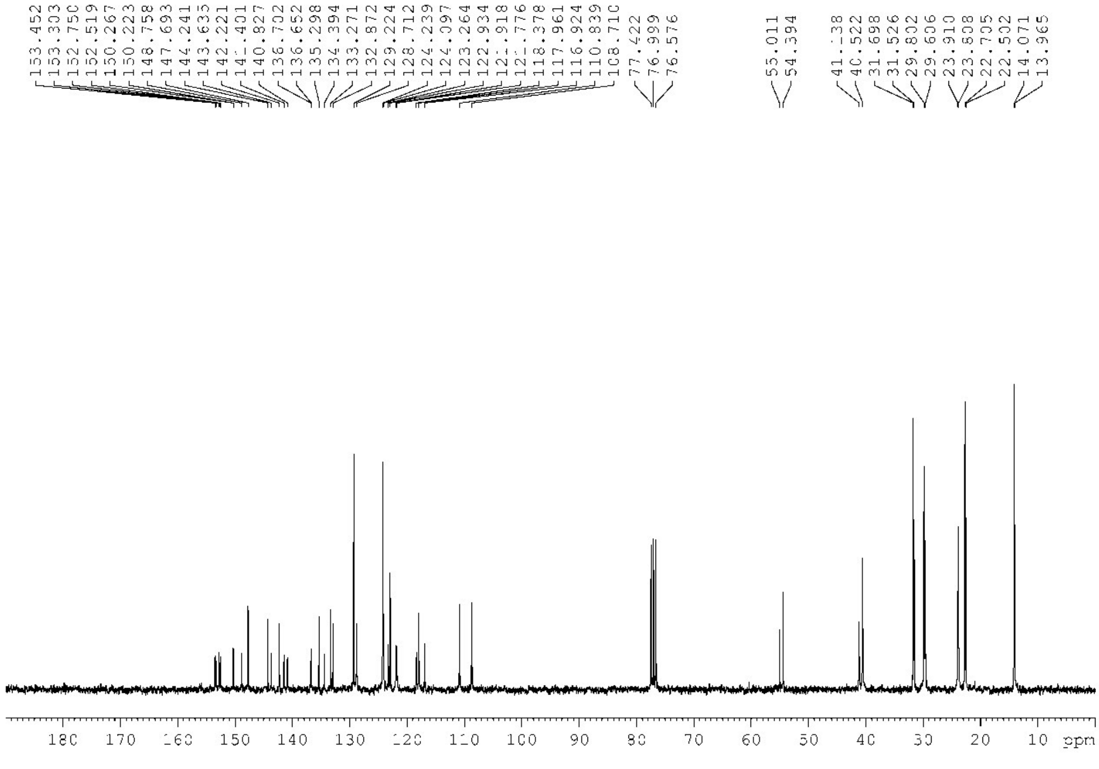

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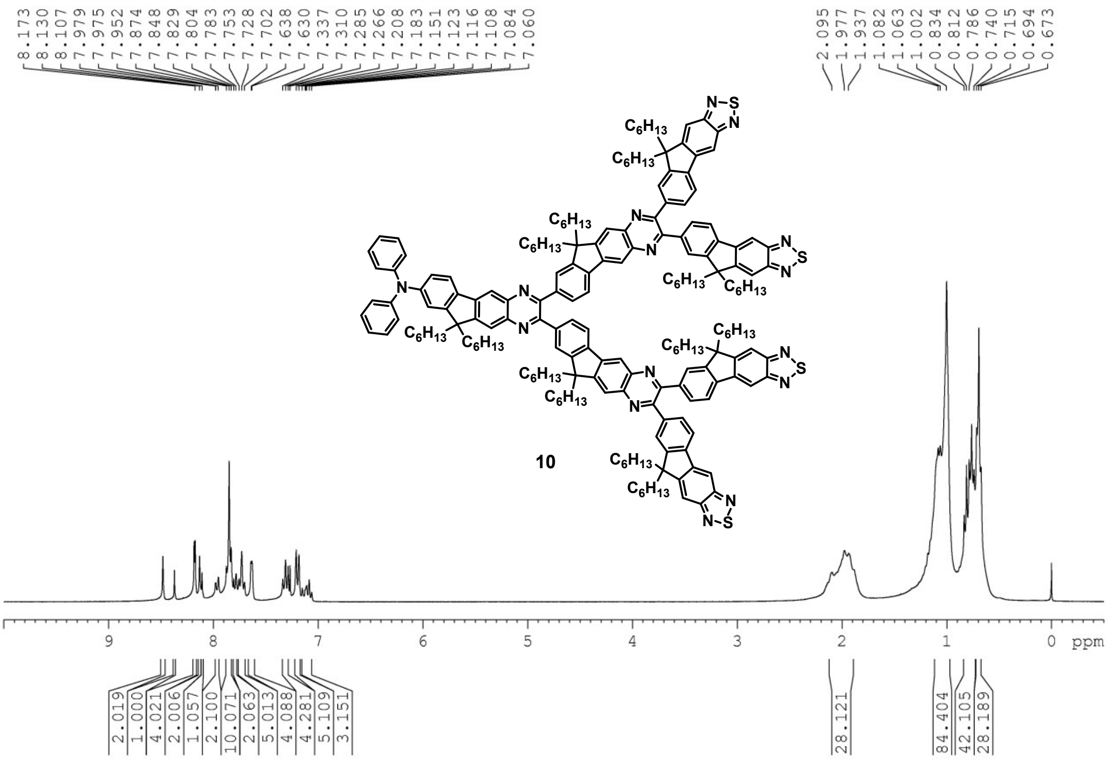

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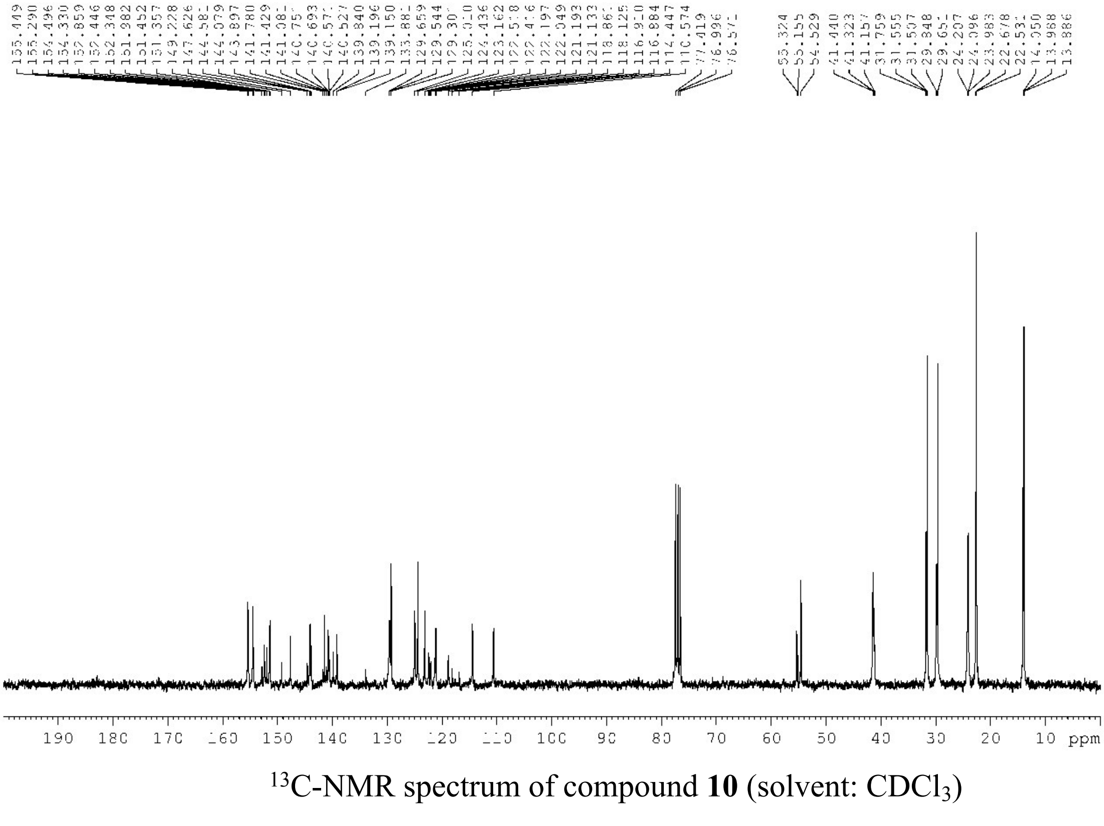

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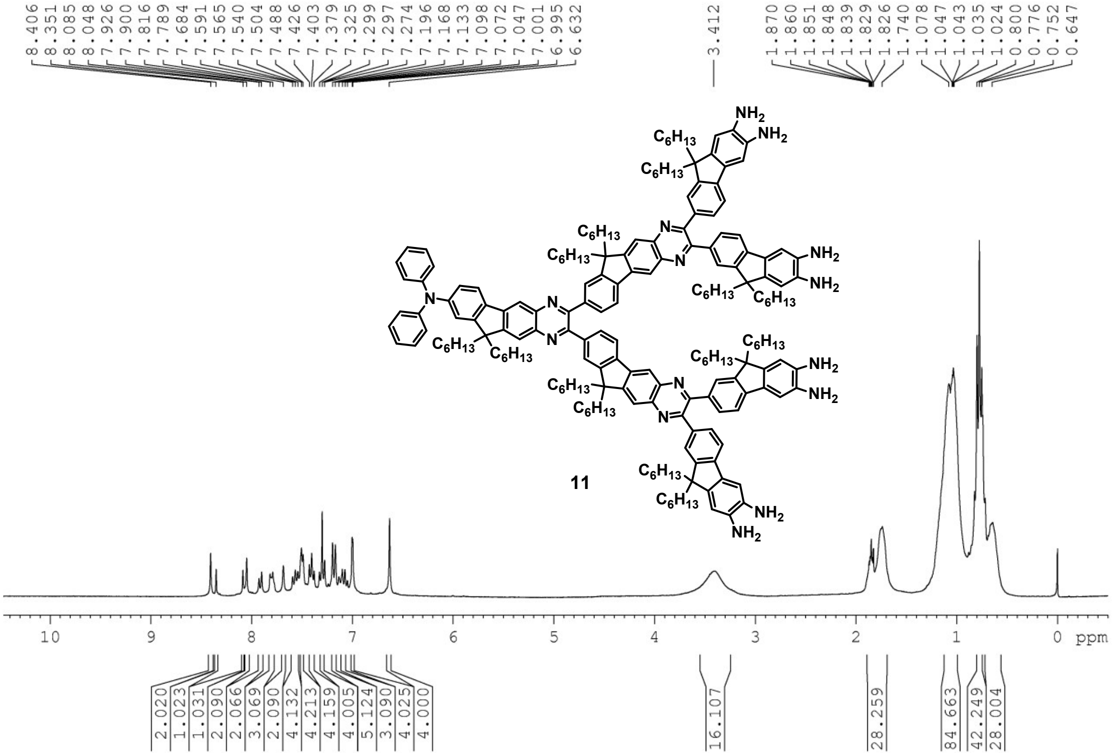

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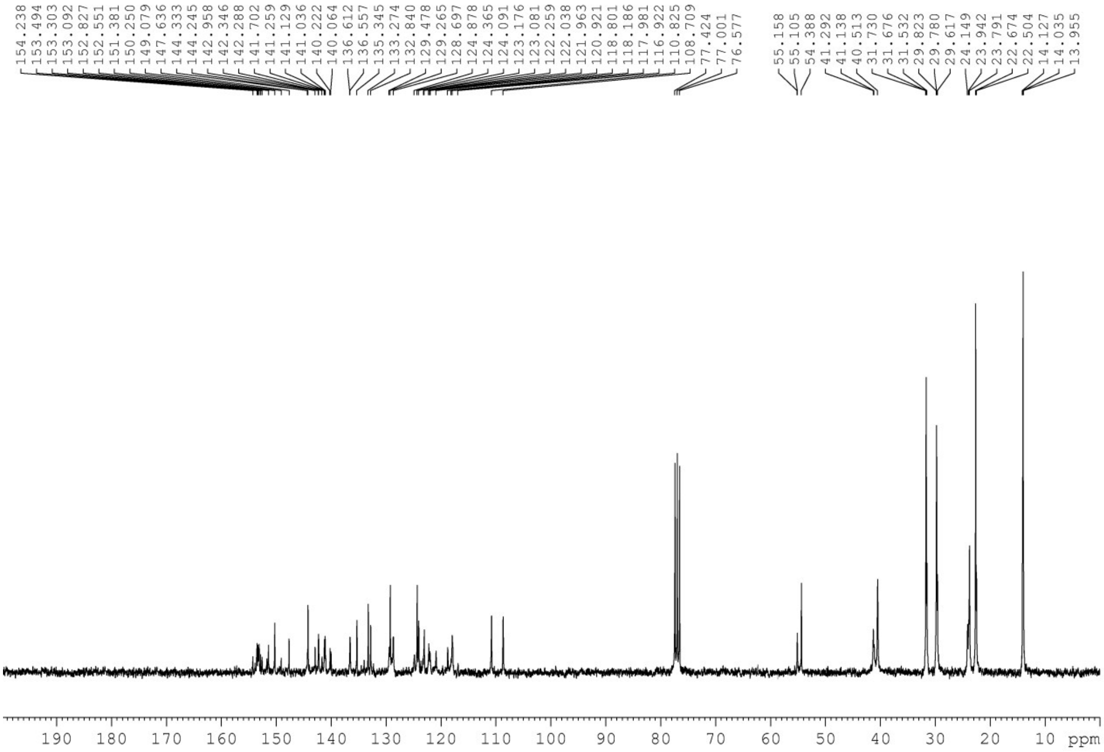

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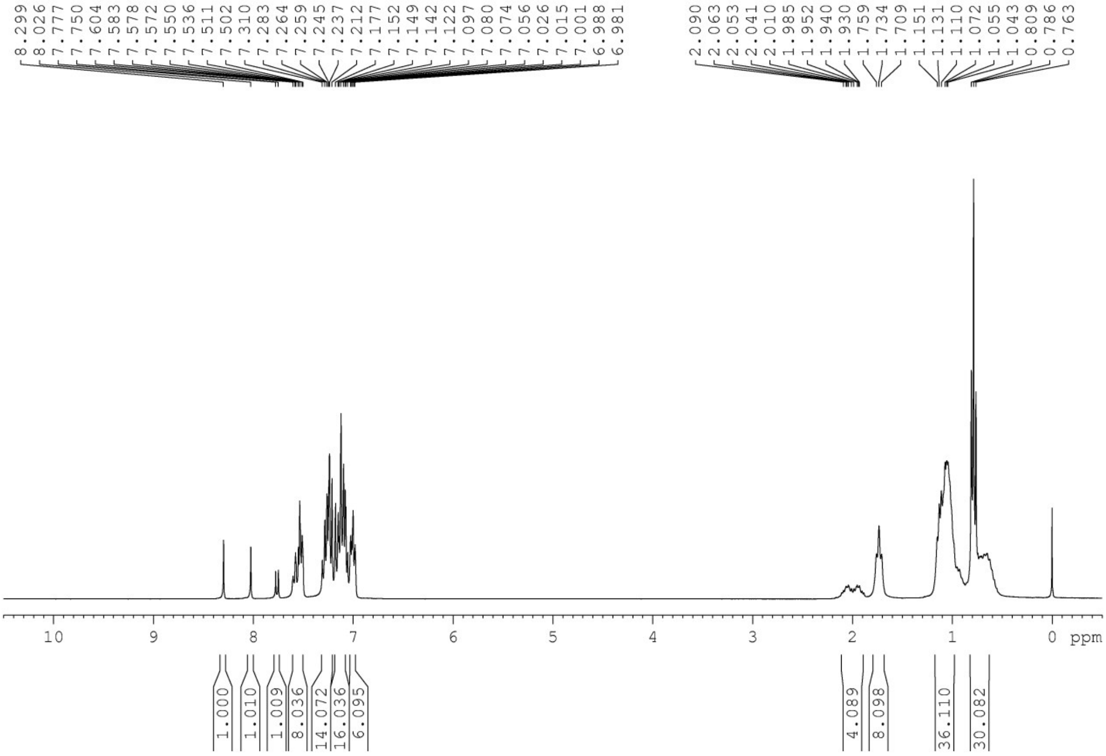

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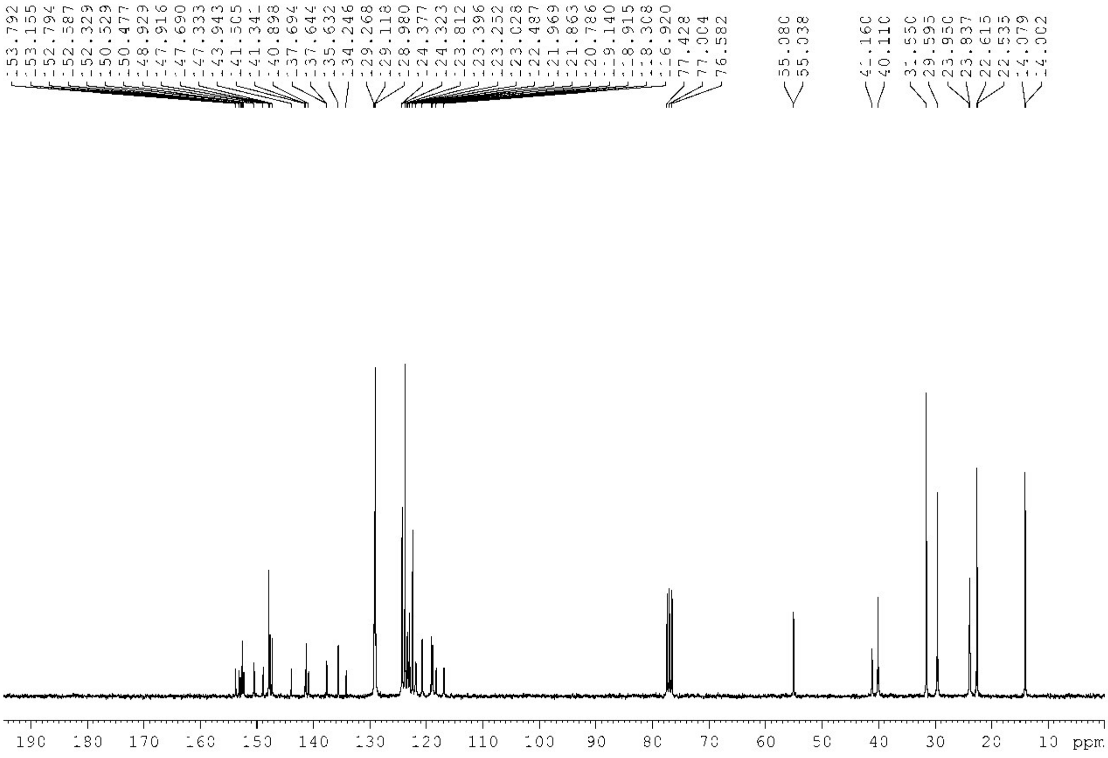

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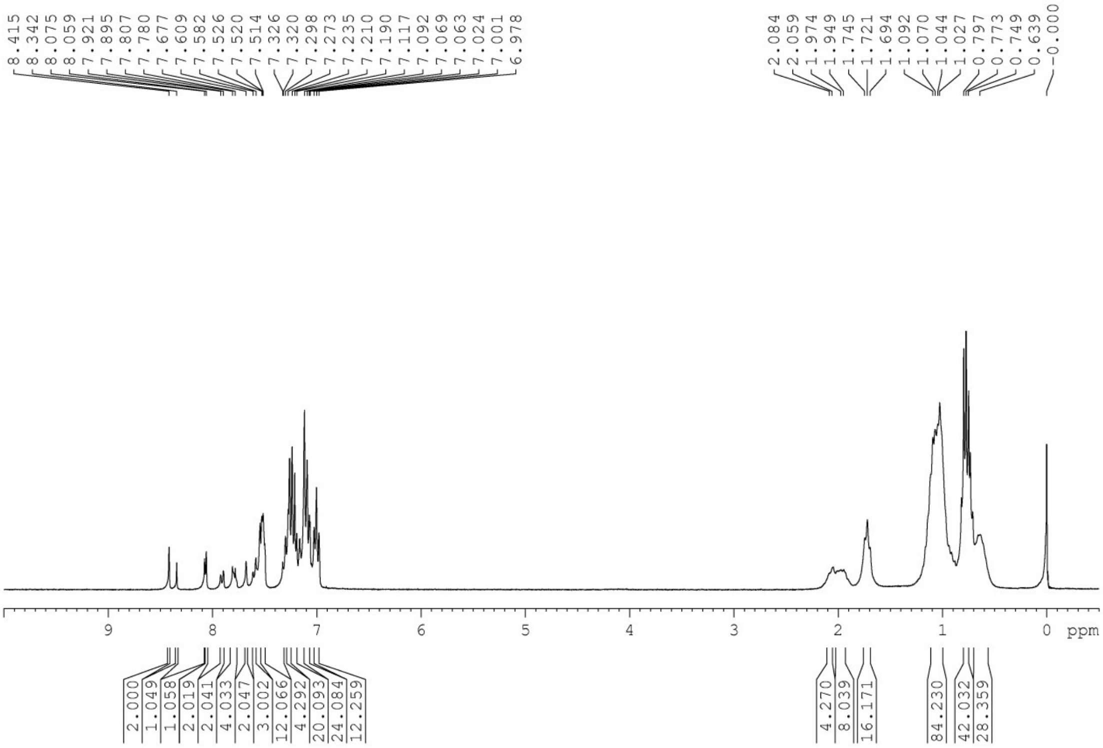

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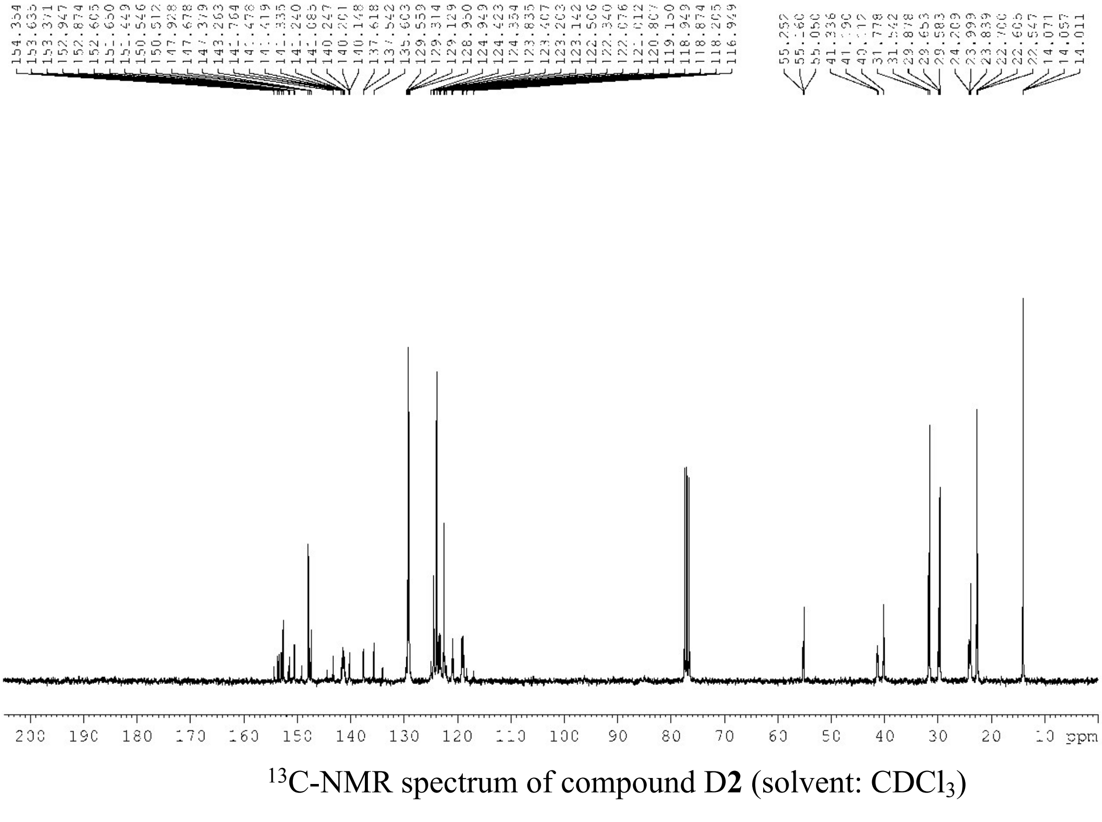
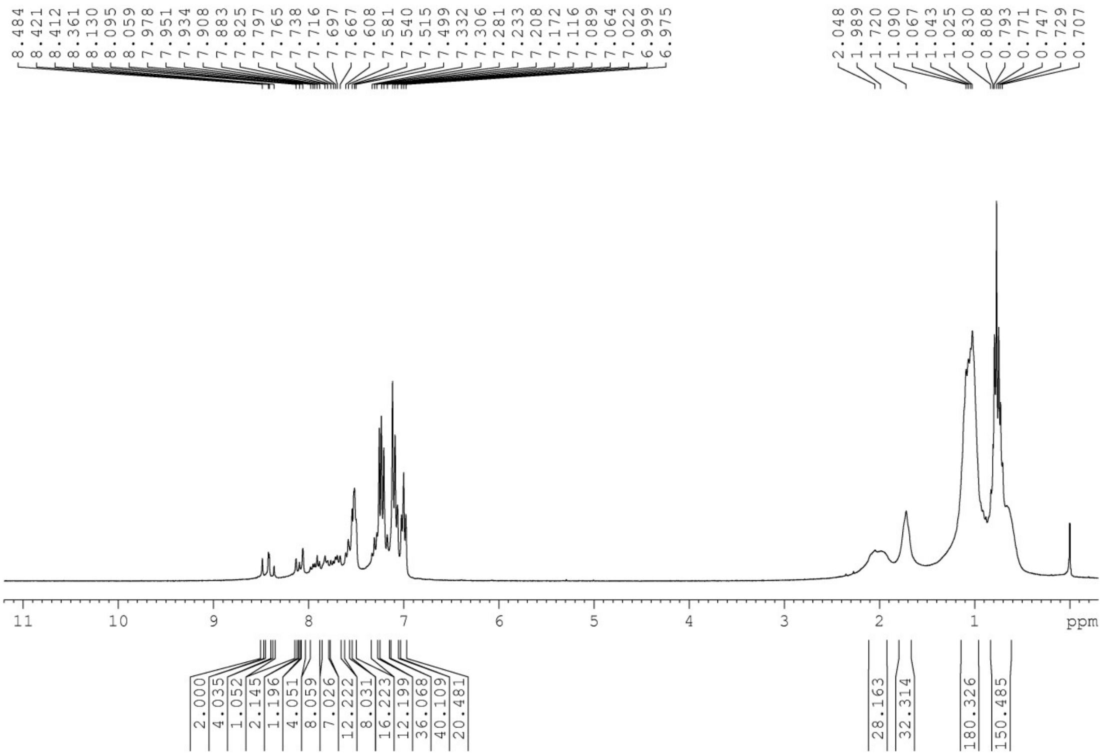


^{13}C-NMR spectrum of compound D**2** (solvent: $CDCl_3$)



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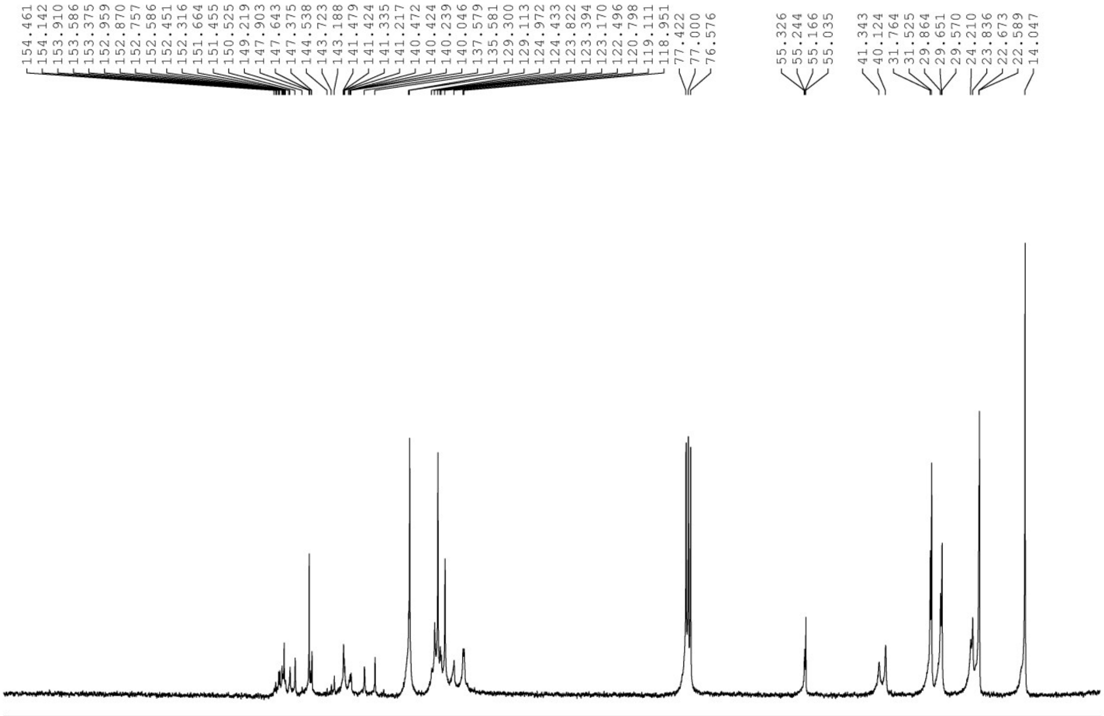

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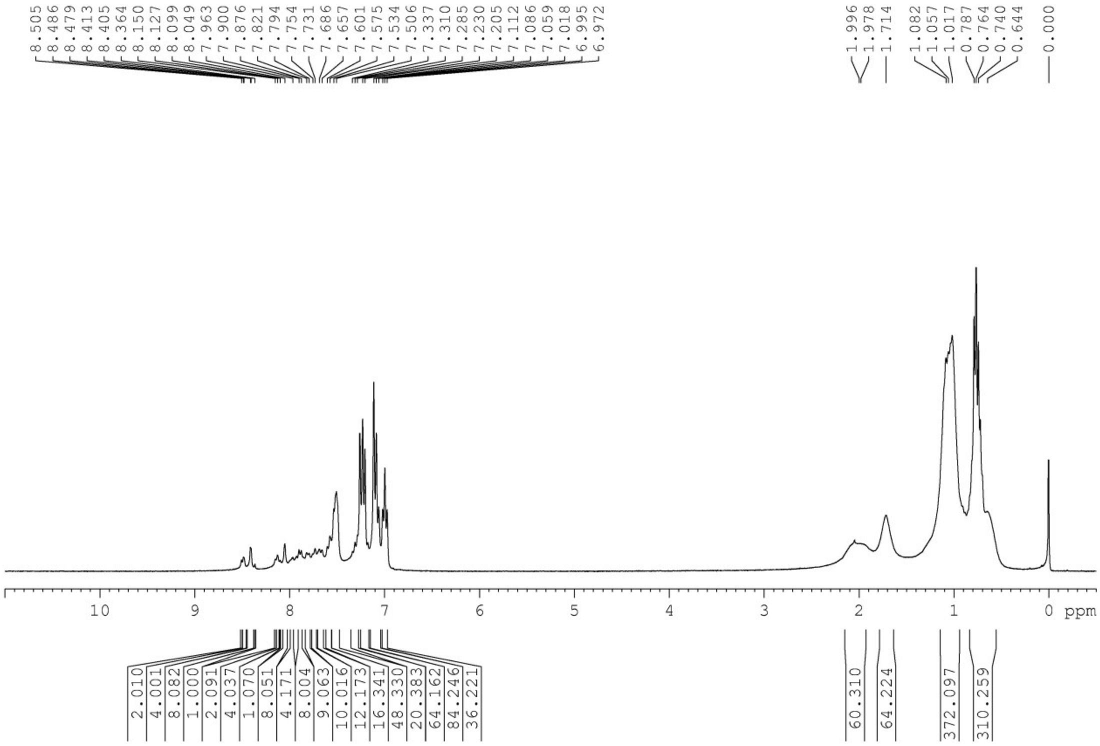
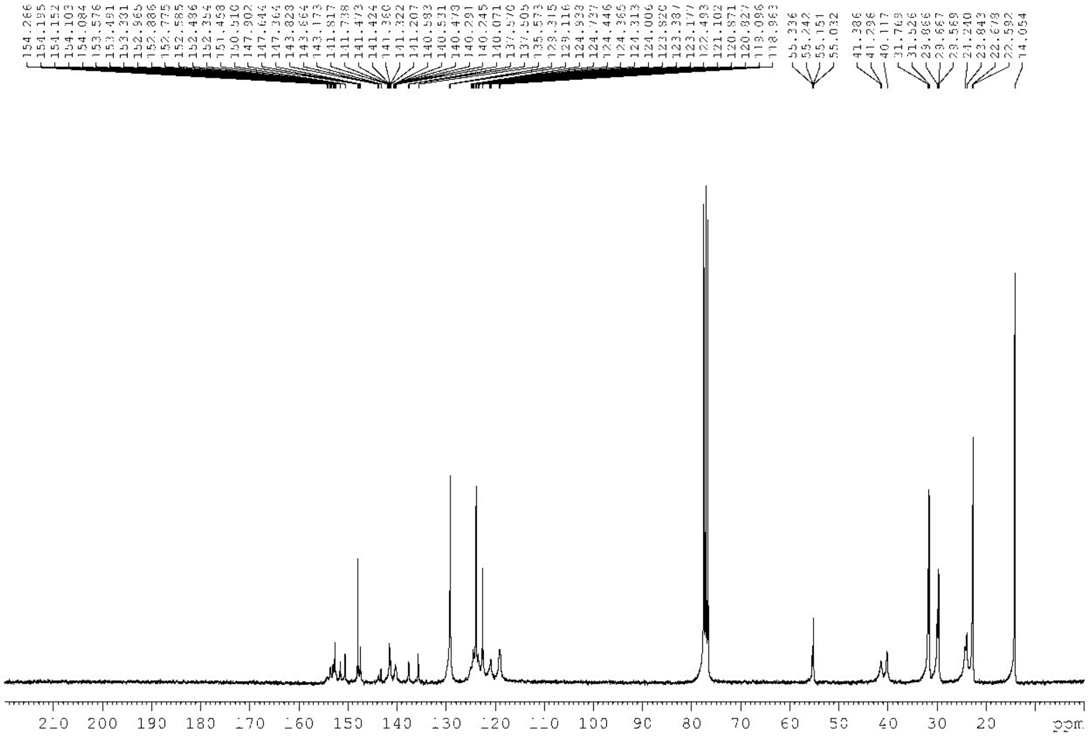


^{1}H-NMR spectrum of compound D**4** (solvent: CDCl$_3$)



^{1}C-NMR spectrum of compound D**4** (solvent: CDCl$_3$)

◆ Photophysical Methods

Linear absorption and emission spectra measurements

Linear absorption spectra were recorded on a Shimadzu 3150 PC spectrophotometer with freshly prepared sample solutions in various solvents. The same sample solutions were also used for the measurement of one-photon-induced fluorescence emission spectra and life-time by utilizing a Jobin-Yvon FluoroMax-4 spectrometer equipped with TCSPC accessories (FluoroHub-B + NanoLED from Jobin-Yvon). The aforementioned fluorospectrometer equipped with an integrating sphere (Labsphere from Jobin-Yvon; diameter = 100 mm) was also employed to measure the absolute fluorescence quantum yield of each model compound in solution phase at room temperature;[1] Coumarin 153 ($\Phi_F = 0.38 \pm 5\%$ at $\lambda_{exc} = 423$ nm) was used as the standard for the calibration of the integrating sphere and the instrument.[2]

Two-photon-excited fluorescence (2PEF) measurements

Two-photon-excited fluorescence spectra of the studied model fluorophore in solution phase (concentration: 1×10^{-4} M) were measured according to the protocol established by Xu and Webb using Fluorescein (0.1 N NaOH solution) as the standard.[3] The experimental setup is illustrated in Figure S1. In brief, the excitation light source was a mode-locked Ti:Sapphire laser (Chameleon Ultra II, Coherent Inc.) which delivers ~140 fs pulses with the repetition rate of 80 MHz and the beam diameter of 2 mm. The intensity level of the excitation beam was carefully controlled by the combination of a λ/2 wave plate and a polarizer in order to avoid the saturation of absorption and photodegradation. To minimize the effects of re-absorption, the excitation beam was focused as close as possible to the wall of the quartz cell (10 mm×10 mm cuvette) and the 2PEF emissions were collected and induced by a fiber bundle into a CCD imaging spectrometer (USB-4000, Ocean Optics) for the spectra recording. This optical system was also utilized for the characterization of the quadratic dependence of the 2PA-induced up-conversion emission intensity on the pumping intensity for every data point.

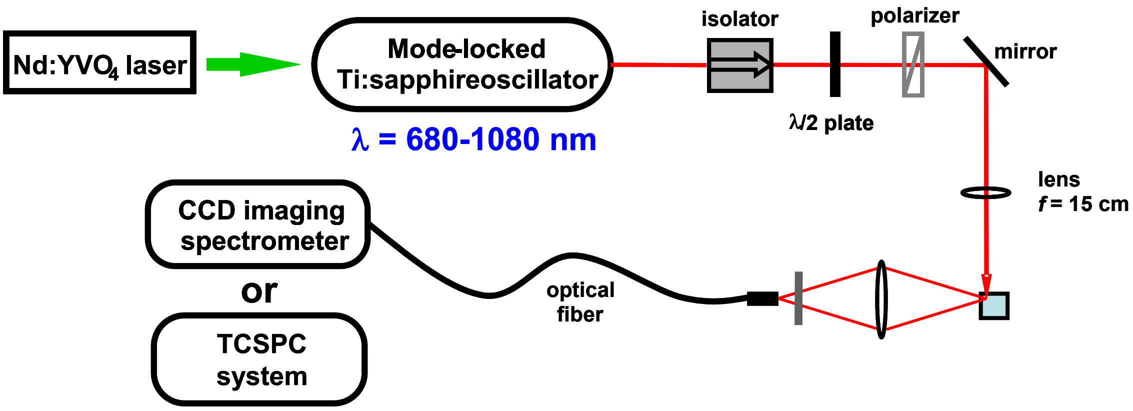


Figure S1. Optical setup for 2PEF-related experiments.

Optical-power limiting property study

The optical-power limiting performance of the compound **D4** in solution phase (0.02M in toluene, light path-length = 1 cm) was probed at ~790 nm using femtosecond laser pulses as the working tool. As shown in Figure S2, a regenerative amplifier system (Legend, Coherent) was employed as the excitation source to provide ~30 fs laser pulses with repetition rate of 5 KHz for this study. The laser beam was slightly focused onto the center of the sample solution in order to obtain a nearly uniform laser beam radius within the whole cell path-length. The local intensity within the sample solution was tuned by adjusting the incident laser power level with the aid of the combination of a half-wave plate and a polarizing beam splitter. In all cases, the incident and transmitted laser power were simultaneously acquired and recorded by a data acquisition card (myDAQ, National Instruments) and a computer.

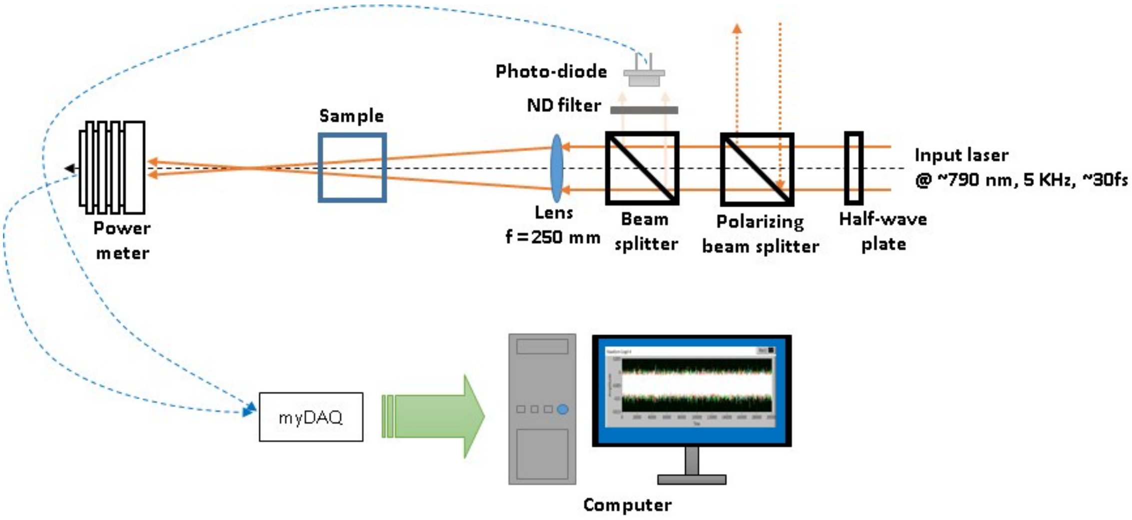


Figure S2. Experimental setup for the optical power limiting behavior study.

Three-photon absorption spectra measurement based on Z-scan technique

The compounds were dissolved in toluene at concentration 2.0% (w/w) and the solutions were placed in 1 mm path length optical glass cells. The measurements were carried out in a relative manner, calibrating all the data against Z-scans carried out on a fused silica plate and taking into account the nonlinear signals obtained on a cell containing pure solvent. The tunable excitation was achieved by directing the beam from a Quantronix Integra Ti:Sapphire regenerative amplifier (output wavelength 800 nm, pulse duration 130 fs, repetition rate 1 kHz) into an optical parametric amplifier (OPA, a Quantronix Palitra). The nonlinear absorption of the dendrimers was investigated in the 1000-1500 nm wavelength range. A scheme of the setup may be found in our previously reported work [4].

The theoretical formalism of Z-scan studies was introduced by Sheik-Bahae and the derivations were already described in the literature [5]. Here, we describe how to discriminate between two- and three-photon absorption in the Open Aperture Z-scan curves. In order to do that, a set of measurements at a single wavelength is necessary:

First, when the optical setup is properly aligned, a Z-scan experiment is done for a silica plate with known n_2 coefficient. From the Closed Aperture scan, $\Delta\varphi_0$ can be determined:

$$\Delta\varphi_0 = \frac{2\pi}{\lambda}\boldsymbol{n}_2\boldsymbol{I}_0\boldsymbol{L}_{\boldsymbol{eff}} \qquad (1)$$

where n_2 is the third-order nonlinear refractive index, $\Delta\varphi_0$ and $\boldsymbol{I}_0$ are the on-axis (r = 0), peak (t = 0) nonlinear phase shift and the irradiance with the sample at focus (Z = 0), respectively. $\boldsymbol{L}_{\boldsymbol{eff}} = (1-\mathrm{e}^{-\alpha l})/\alpha$ is the effective sample length, where α is the absorption coefficient and l is a factor that depends on the actual sample length and the Rayleigh range.

The irradiance can be calculated by transforming (1):

$$\boldsymbol{I}_0 = \frac{\Delta\varphi_0\lambda}{2\pi\boldsymbol{n}_2\boldsymbol{L}_{\boldsymbol{eff}}} \qquad (2)$$

Usually for the Z-scan studies reported here the peak irradiance at the focus was around 100 GW/cm^2.

From this scan, we can also approximate $\boldsymbol{w}_0$, which is the Gaussian beam spot radius at the focus, taken at I_0/e^2. Furthermore, the Rayleigh range, Z_0, can be calculated:

$$\boldsymbol{Z}_0 = \frac{\boldsymbol{k}\cdot\boldsymbol{w}_0^2}{2} \qquad (3)$$

where $\boldsymbol{k}$ is the wave vector.

Then, the experiment is done for cuvette with solvent, in order to take into account the nonlinearities coming from the glass walls and the solvent itself. Finally, the Closed and Open Aperture scans are recorded for the cuvette with the sample.

The general expression for normalized transmittance of the Open Aperture scans is as follows:

$$\boldsymbol{T}(\boldsymbol{z}) = 1 - \frac{(\boldsymbol{q}_0)^{\boldsymbol{m}}}{(\boldsymbol{m}+1)^{3/2}(1+\frac{\boldsymbol{z}^2}{\boldsymbol{z}_0^2})^{\boldsymbol{m}}} \qquad (4\text{-}1)$$

Where $\boldsymbol{q}_0 = \beta\boldsymbol{I}_0\boldsymbol{L}_{\boldsymbol{eff}}$ and (m+1) is the number of photons absorbed.

In the case of two-photon absorption, Eq. 4 develops into:

$$\boldsymbol{T}(\boldsymbol{z}) = 1 - \frac{\beta_2\boldsymbol{I}_0\boldsymbol{L}_{\boldsymbol{eff}}}{2\sqrt{2}\left(1+\frac{\boldsymbol{z}^2}{\boldsymbol{z}_0^2}\right)} \qquad (4\text{-}2)$$

where β_2 is the two-photon absorption coefficient. From this parameter, the two-photon absorption cross-section, σ_2, can be determined by using the following relationship:

$$\beta_2 = \frac{\sigma_2 \cdot N_A \cdot c \cdot 10^{-3}}{h \cdot \nu} \qquad (5)$$

where N_A is the Avogadro constant, c is the concentration of the compound in solution, h is the Planck constant, and ν is the frequency of the incident laser beam.

A similar approach can be taken to determine the Open Aperture transmittance for a three-photon process [6]. Analogically to (4-2), the transmittance for three-photon absorption can be calculated as follows:

$$T(z) = 1 - \frac{\beta_3 I_0^2 L'_{eff}}{2\left(1 + \frac{z^2}{z_0^2}\right)^2} \qquad (6)$$

where β_3 is the three-photon absorption coefficient and $L'_{eff} = (1 - e^{-2\alpha l}) / 2\alpha$. The three-photon absorption cross-section, σ_3 can be calculated from Eq. 7:

$$\beta_3 = \frac{\sigma_3 \cdot N_A \cdot c \cdot 10^{-3}}{h \cdot \nu} \qquad (7)$$

The difference between fitting an experimental Open Aperture Z-scan with theoretical functions corresponding to two- and three-photon absorption is illustrated below. The data points were measured at 1050 nm for compound **D-4**. Clearly, the experimental points are much better fitted with expressions for a three-photon process.

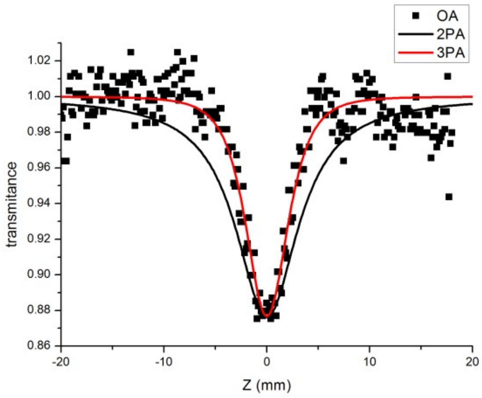


Figure S3. Normalized transmittance of the Open Aperture scan measured at 1050 nm for compound **D-4**.

Three-photon-induced fluorescence measurements

The solutions of dendrimers in toluene were prepared with 2.5×10^{-6} mol/L concentration. The samples were excited at 1050 nm by the Quantronix Palitra OPA laser beam with the intensities set to be below the degradation threshold, as determined from power-dependent measurements. The fluorescence spectra were recorded by an Ocean Optics 2000 fiber spectrometer as a function of the incident power of the laser. Then, the integrated intensities were plotted in double logarithmic (log-log) scale. Fitting of these data with linear functions allowed determining the order of the nonlinear absorption process.

♦ Tentative analysis of the relationship between some molecular parameters and 2PA

We tentatively analyzed the relationship between the measured maximal 2PA and several molecular parameters including molecular weight, total π-electron numbers, and subunits numbers. For the subunits, the peripheral diphenylaminofluorene and indenoquinoxaline were selected for this analysis. As shown in Fig. S4, it is found that the measured maximal 2PA values of the studied model chromophores scale linearly with the aforementioned molecular parameters. This feature may imply that the currently adopted strategy to systematically expand the molecular structure in this dendron system possesses neither cooperative nor deleterious effect on the molecular 2PA. It is also revealed that both 2,3,8-trisubstituted indenoquinoxaline and diphenylaminofluorene are useful building units to construct highly two-photon active materials when they are appropriately incorporated into the molecular structures.

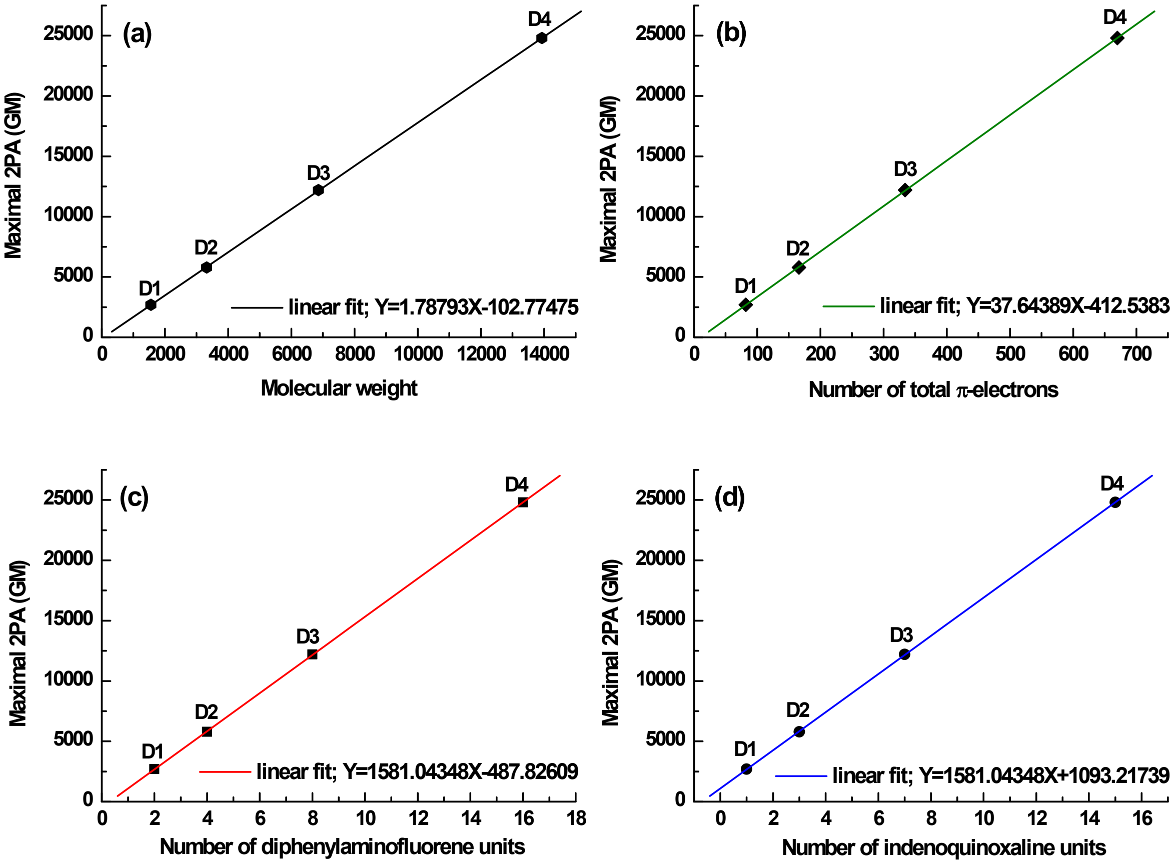


Figure S4. Dependence of various structural parameters versus measured maximal 2PA of the studied model chromophores.

References

[1] L. Porres, A. Holland, L.-O. Palsson, A. P. Monkman, C. Kemp and A. Beeby, *J. Fluoresc.* **2006**, *16*, 267-273.

[2] a) J. A. Gardecki and M. Maroncelli, *Applied Spectroscopy* **1998**, *52*, 1179-1189; b) G. A.

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