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

Supporting Information

Synthesis and Characterization of A Highly Two-photon Active Dendrimer Derived from 2,3,8-Trifunctionalized Indenoquinoxaline Units

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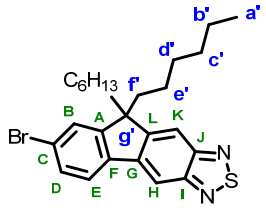
♦ Numbering of C and H of the precursors and final chromophore



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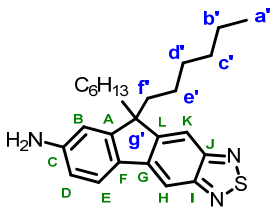

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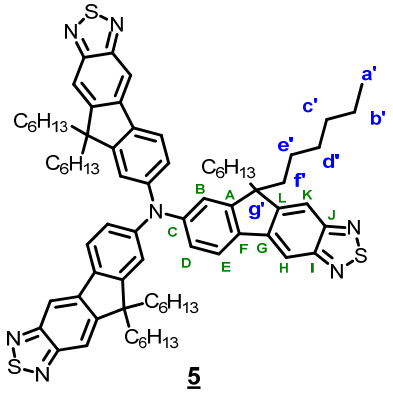

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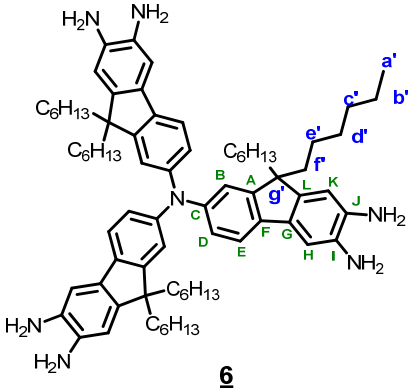

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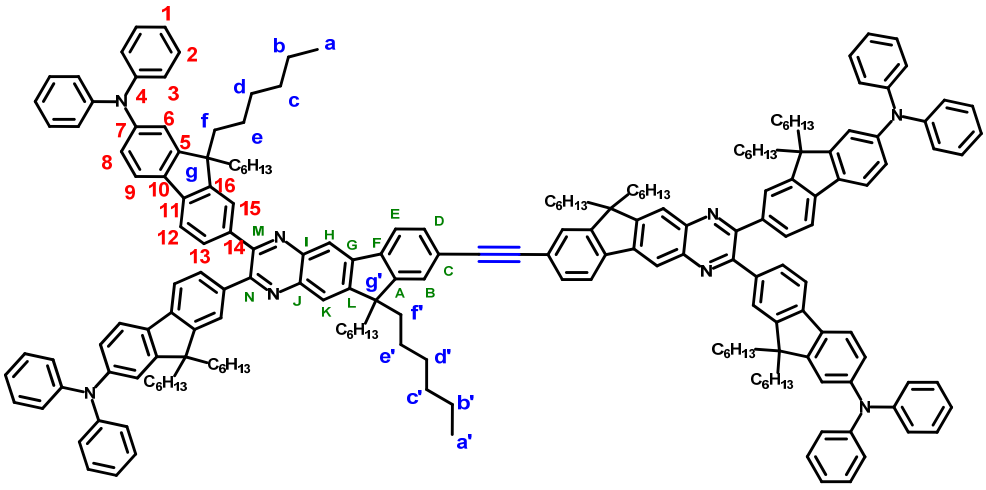

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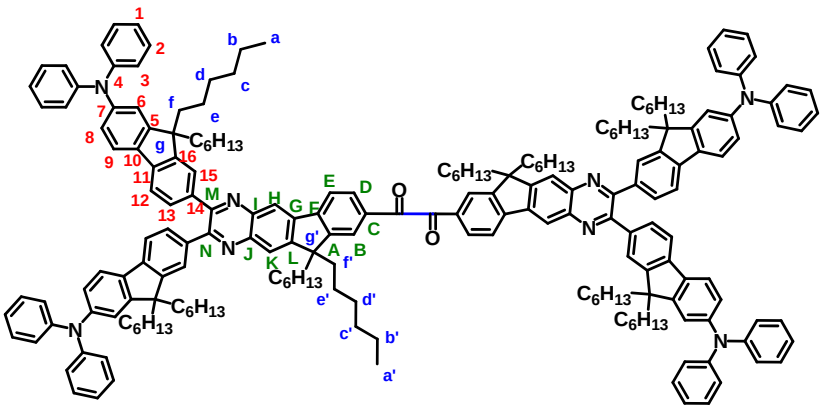

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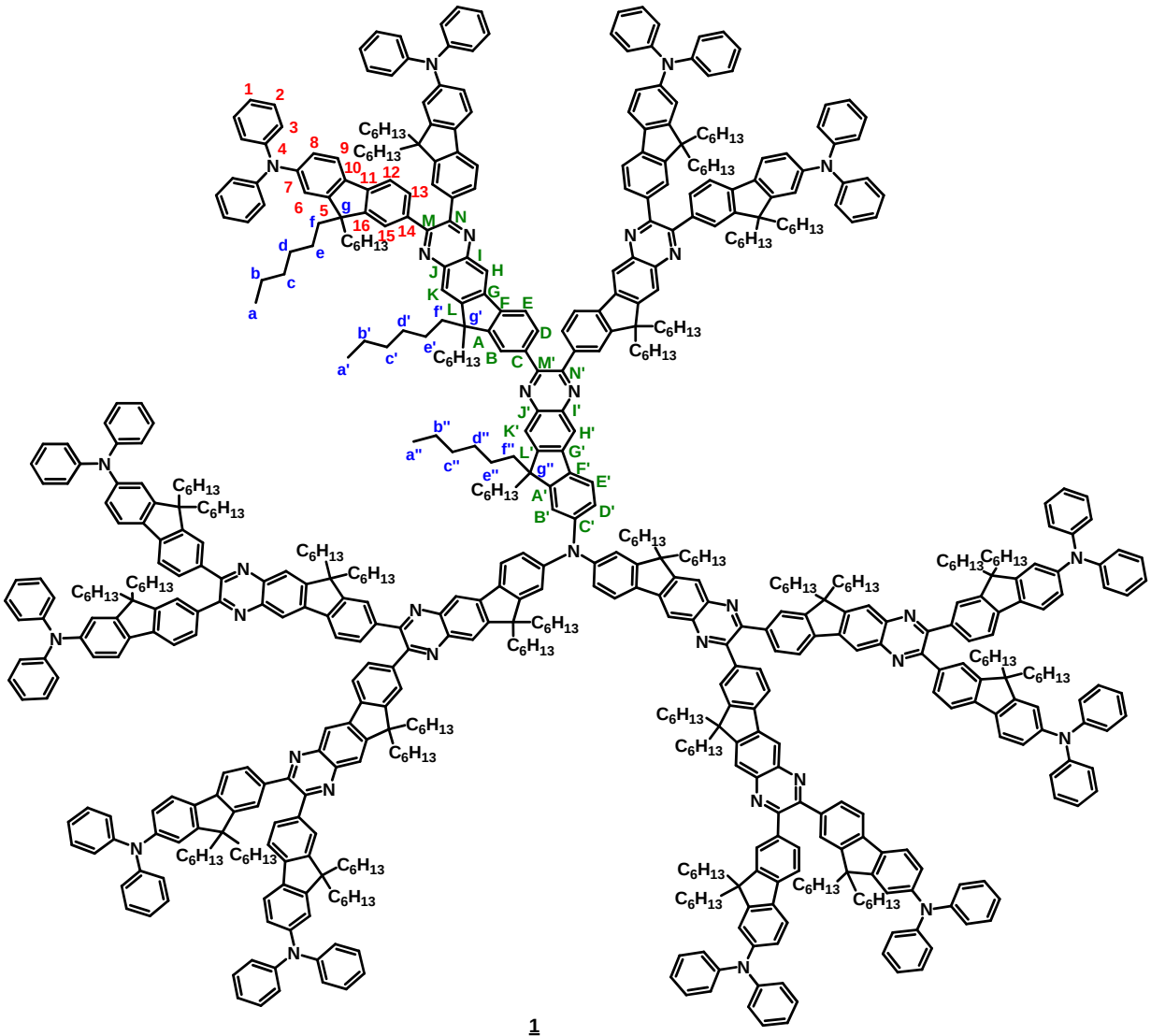

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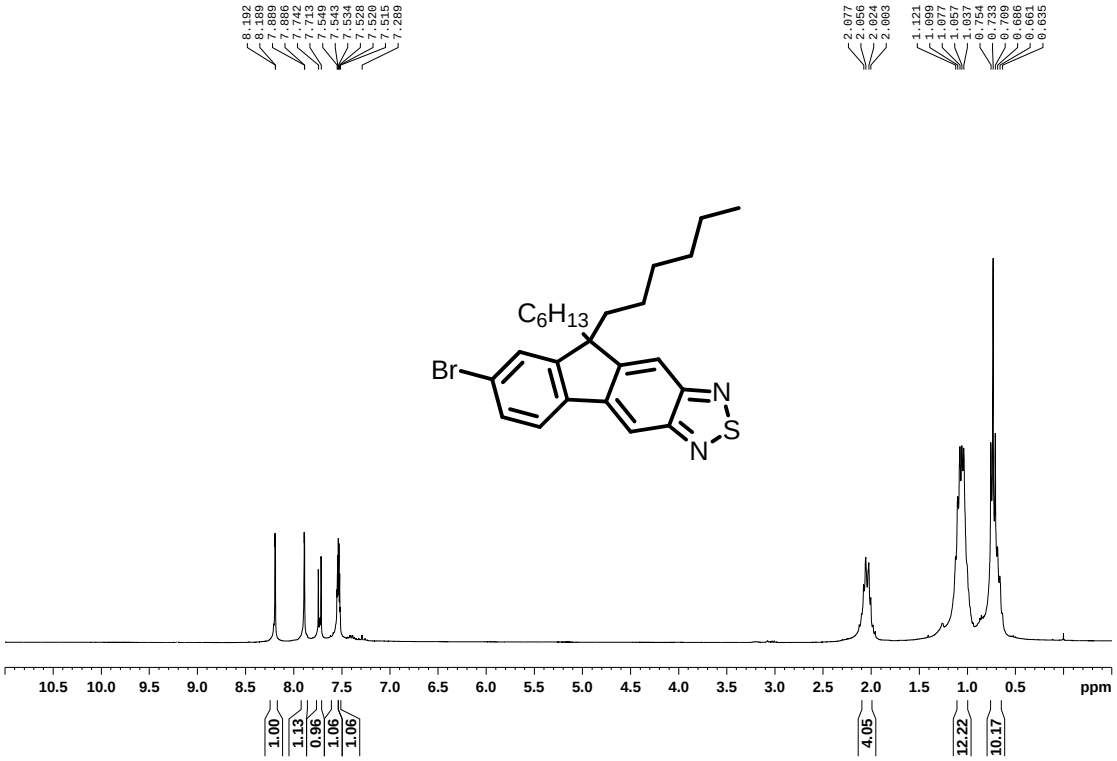
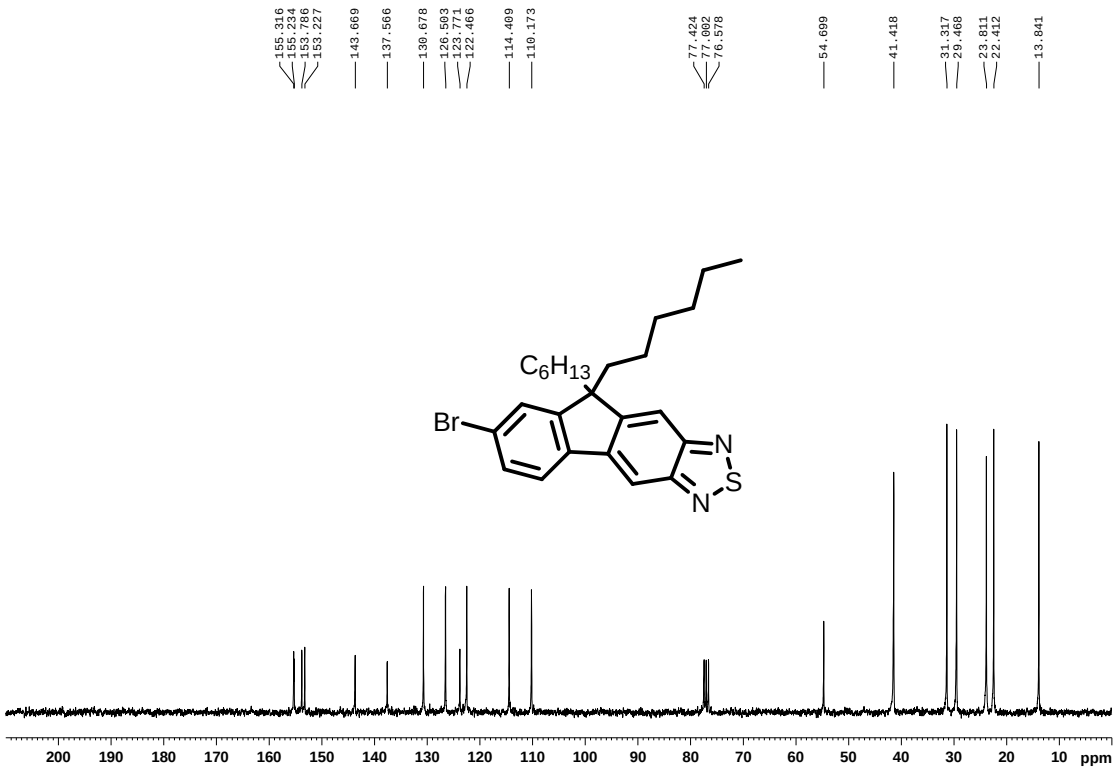


^{1}H-NMR spectrum of compound **3**



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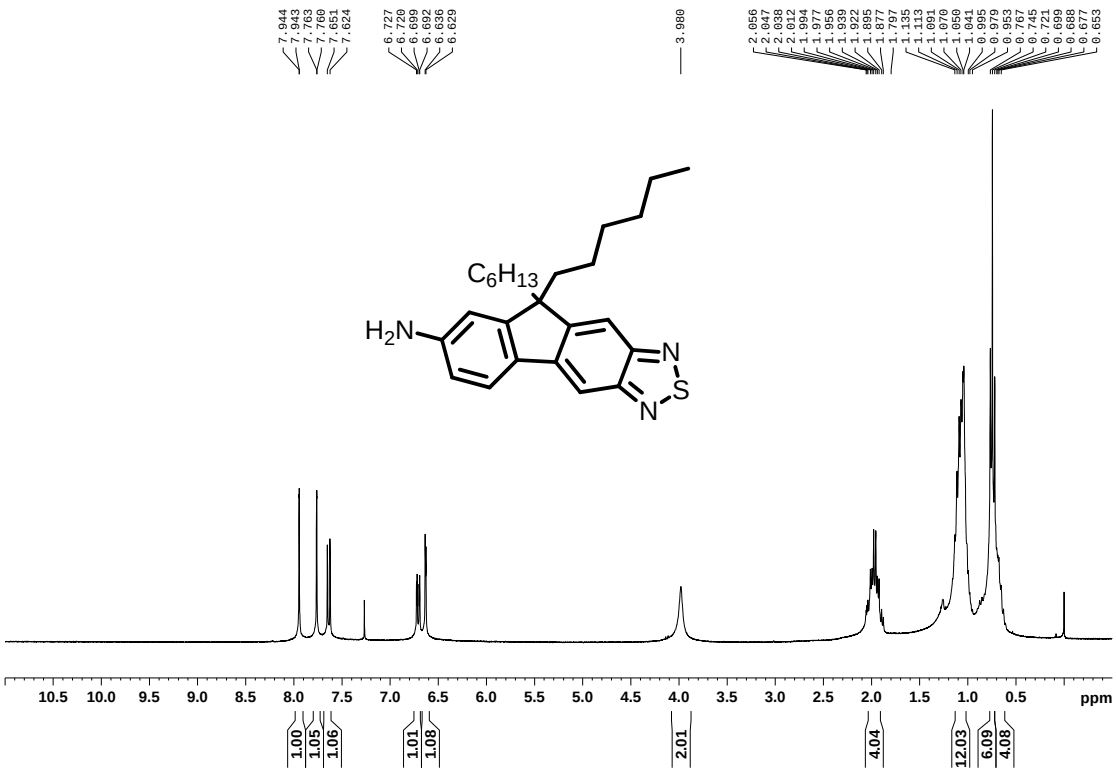

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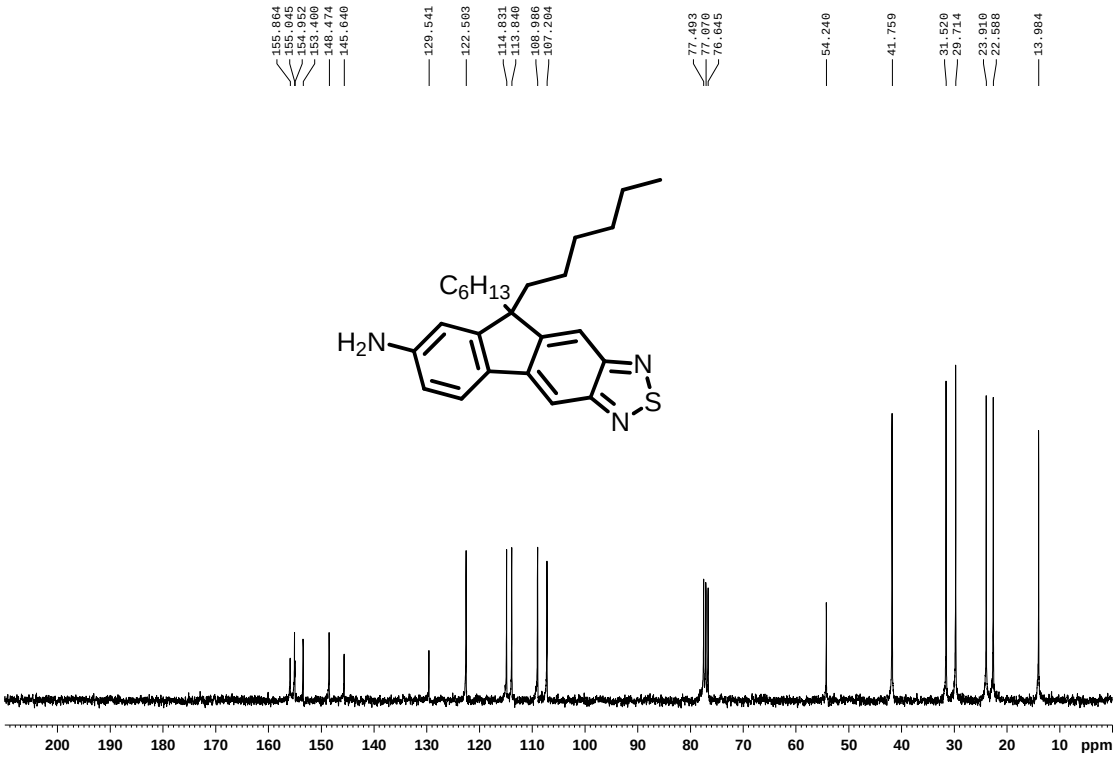

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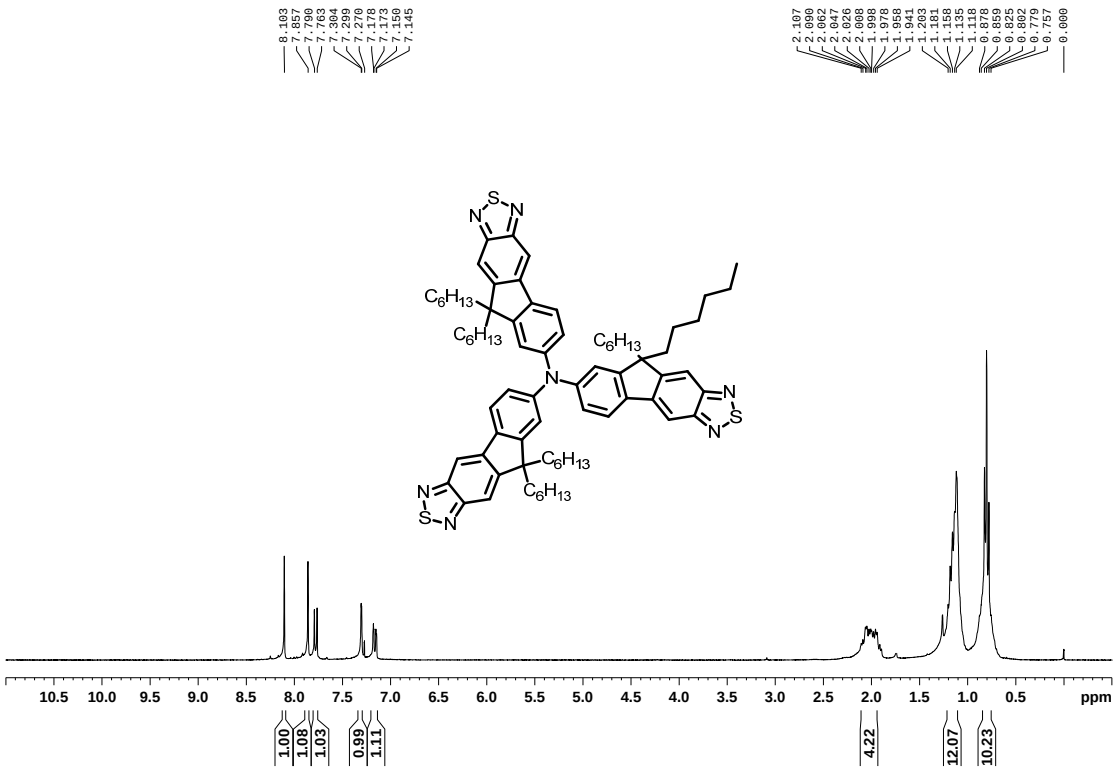

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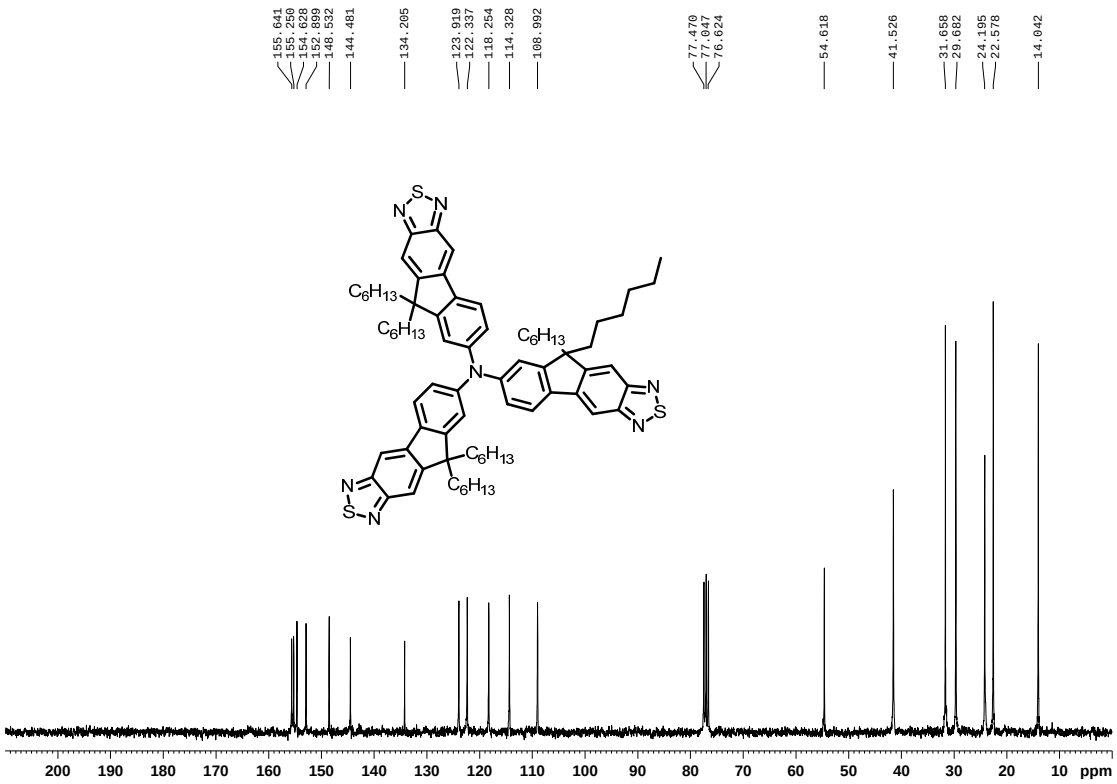

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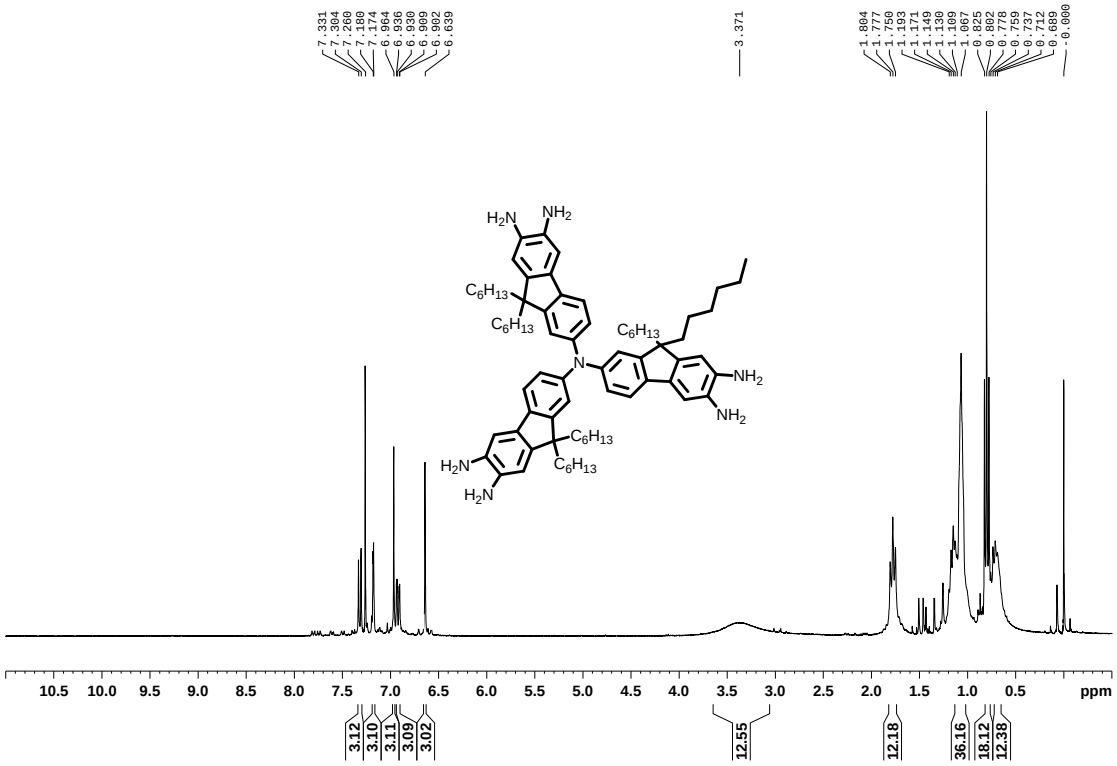

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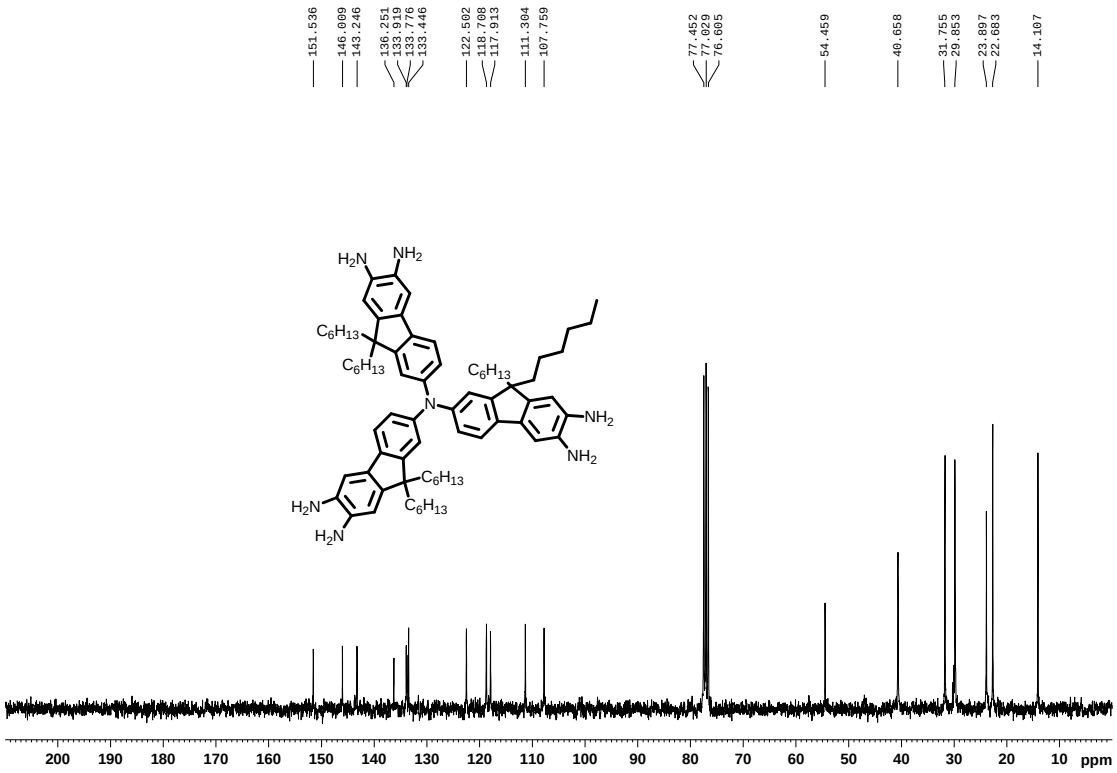

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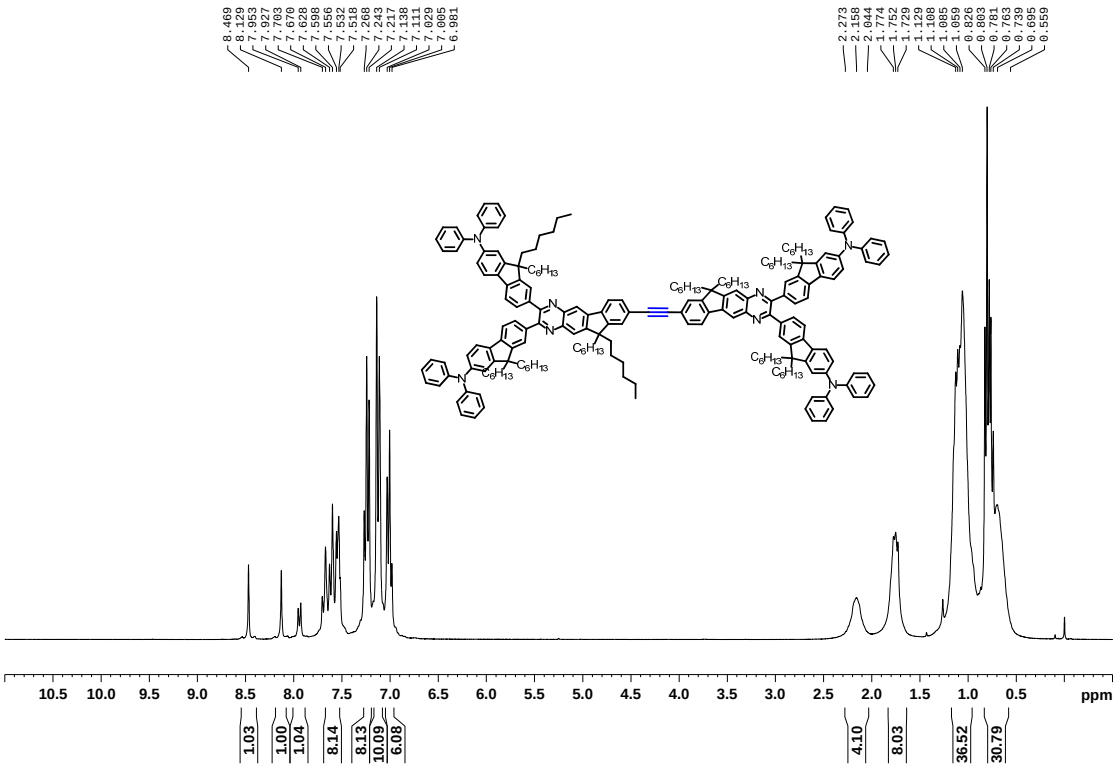

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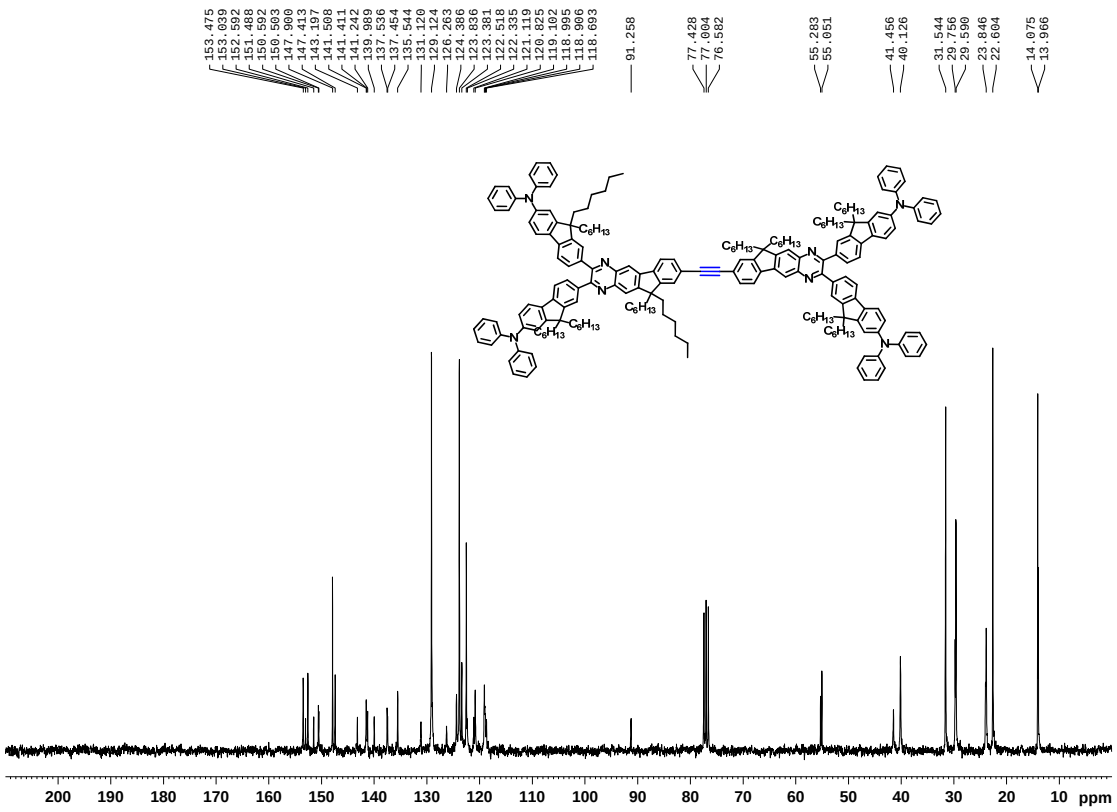

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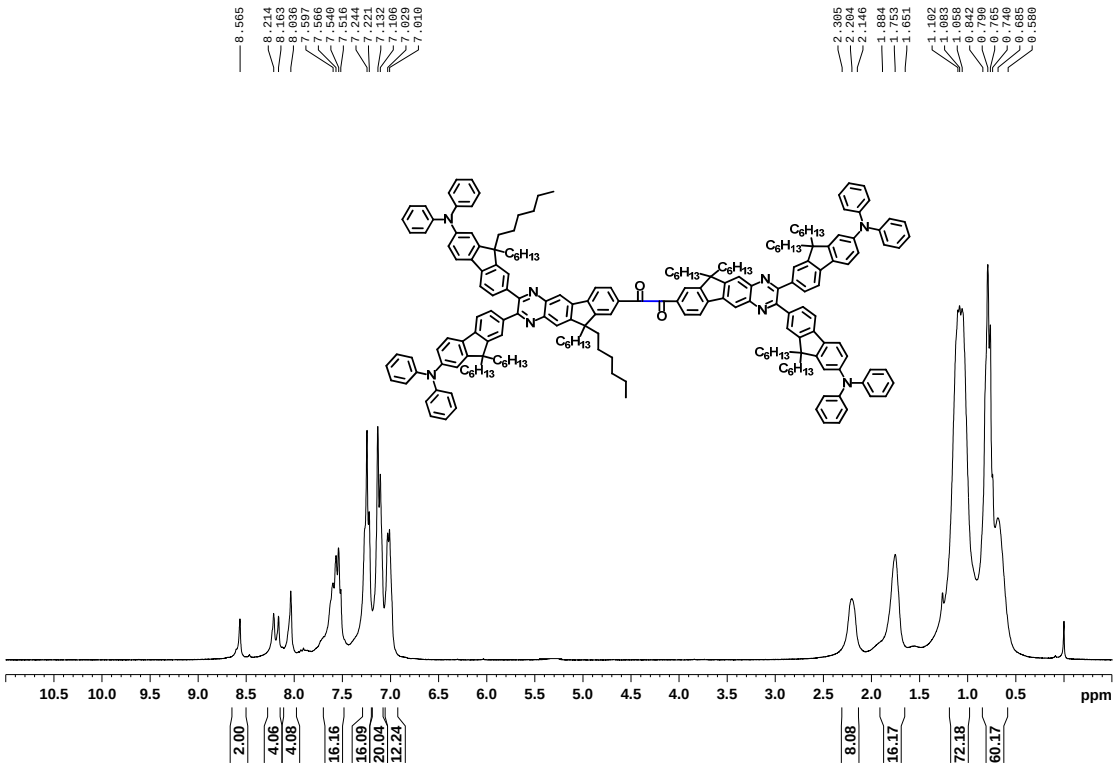

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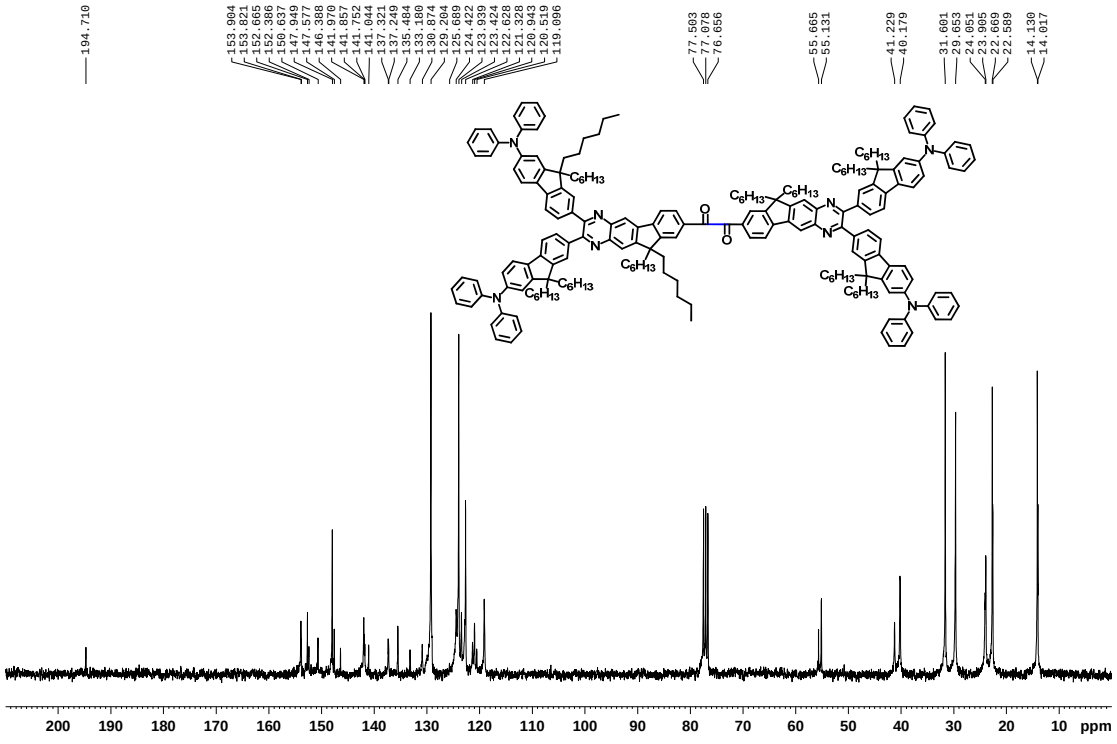

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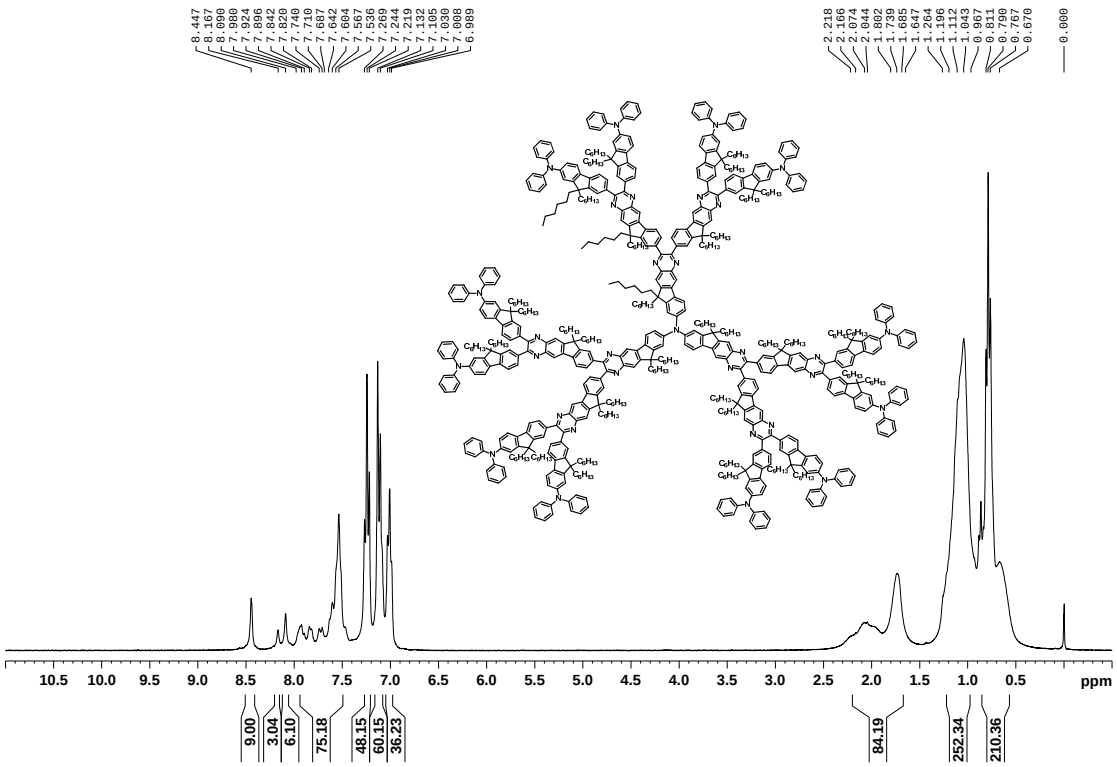
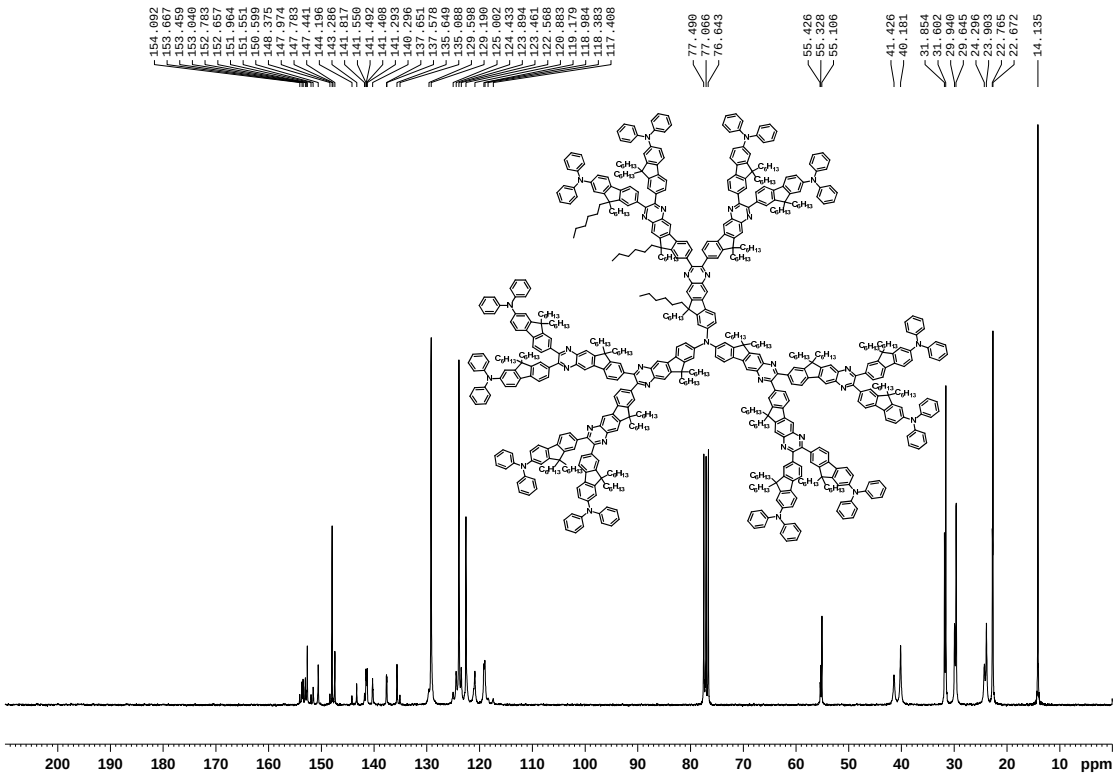


^{1}H-NMR spectrum of compound **1**



^{13}C-NMR spectrum of compound **1**

♦ 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 integrated sphere (Labsphere from Jobin-Yvon; diameter = 100mm) was also employed to measure the absolute fluorescence quantum yield of each model compound in solution phase at room temperature;[1] Coumarin 153 (Φ_F = 0.38±5% at λ_{exc} = 423 nm) was used as the standard for the calibration of the integrated sphere and the instrument.[2, 3]

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 (0.1N NaOH solution) as the standard.[4,5] 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 ~80fs pulses with the repetition rate of 80MHz and the beam diameter of 2mm. The intensity level of the excitation beam was carefully controlled by a λ/2 wave plate 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 (10mm×10mm 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.

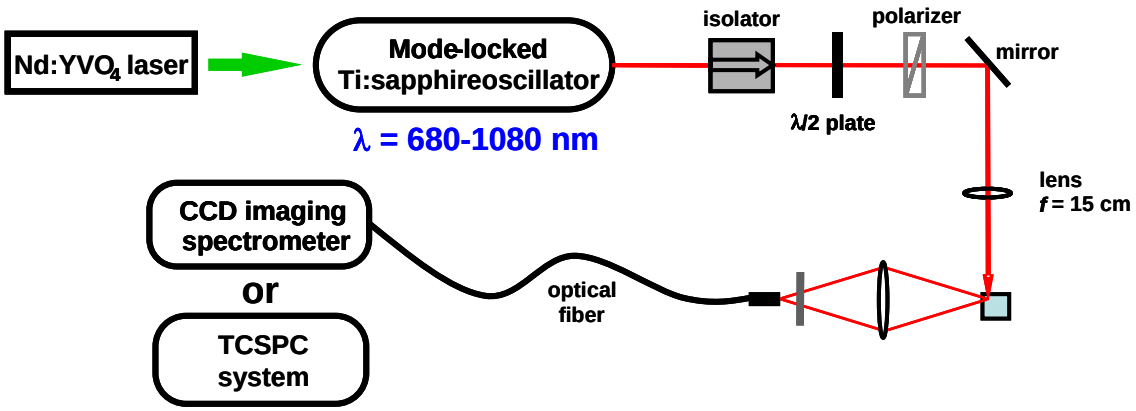


Figure S1. Optical setup for 2PEF-related experiments.

The 1PA- and 2PA-induced fluorescence lifetime of the same sample solutions were measured based on TCSPC technique by highly sensitive photomultiplier equipped with accumulating real-time processor as the detection system (PMA-182 and TimeHarp 200, PicoQuant). The optical setup for this experiment was very similar with the one shown in Figure S1, only differs in the detection system. The excitation light source for this measurement was the above-mentioned Ti: sapphire laser system to provide laser pulses at desired wavelength for the 2PA-induced fluorescence lifetime measurements and it can be used to pump a BBO crystal in order to generate frequency-doubled laser pulses for 1PA-induced fluorescence lifetime studies of the investigated samples.

Optical-power limiting property study

The optical-power limiting performance of the studied dendrimer (**1**) in solution phase (0.01M in toluene, light path-length = 1 cm) was probed at ~800nm 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 recoded by a data acquisition card (myDAQ, National Instruments) and a computer.

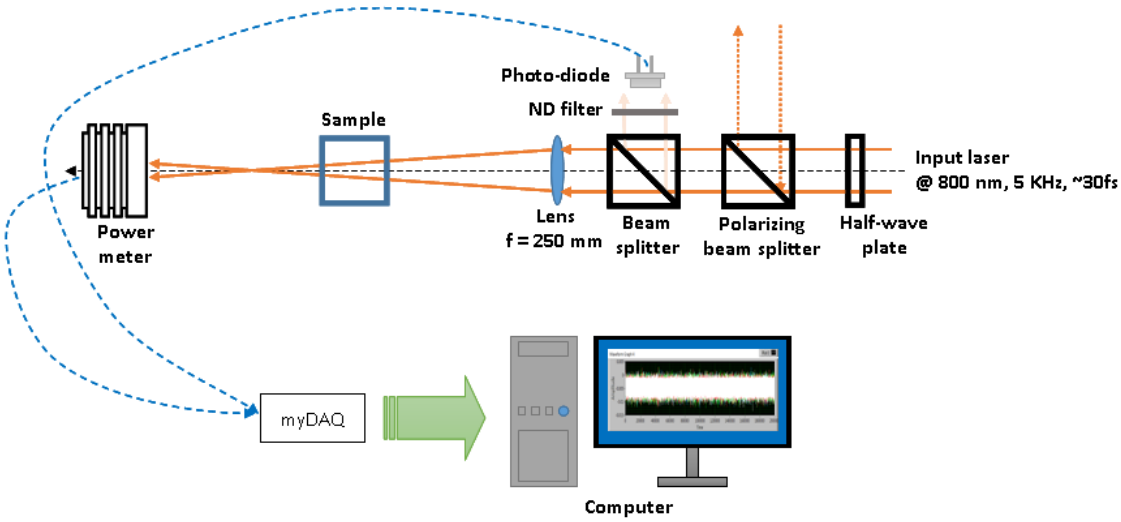


Figure S2. Experimental setup for the optical power limiting behavior study.

References

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[2] J. A. Gardecki, M. Maroncelli, *Appl. Spectrosc.* **1998**, **52**, 1179.

[3] G. A. Reynolds, K. H. Drexhage, *Opt. Commun.* 1975, **13**, 222.

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[5] N. S. Makarov, M. Drobizhev and A. Rebane, *Opt. Express*, 2008, **16**, 4029-4047.