Supporting Information

Two-Photon Triggered NO-Release Via a Ruthenium-Nitrosyl Complex With a Star-Shaped Architecture

Margarita Romero Ávila,[1, 2] Andrés Felipe León Rojas,[2] Pascal G. Lacroix,*[1] Isabelle Malfant,[1] Norberto Farfán,*[2] Rana Mhanna,[3] Rosa Santillan,[4] Gabriel Ramos-Ortiz,[5] Jean-Pierre Malval.*[3]

[1] Laboratoire de Chimie de Coordination (LCC), CNRS, 205 route de Narbonne, BP44099, Toulouse Cedex 4, 31077 France
[2] Facultad de Química, Departamento de Química Orgánica, Universidad Nacional Autónoma de México,04510 México D.F., México
[3] Institut de Science des Matériaux de Mulhouse CNRS-UMR 7361, Université de Haute Alsace, 15 rue Jean Starcky, 68057, Mulhouse, France.
[4] Departamento de Química, Centro de Investigación y de Estudios del IPN, CINVESTAV, Apdo., Postal 14-740, México, D.F., 07000, México.
[5] Centro de Investigaciones en Óptica, A.P. 1-948, 37000 León, Mexico
E-Mails: pascal.lacroix@lcc-toulouse.fr, norberto.farfan@gmail.com, and jean-pierre.malval@uha.fr

CONTENTS

1. Figures and Tables.

	λ_{abs} / nm	ε_{abs} / 10^3 M^{-1} cm^{-1}	λ_{fluo} / nm	Φ_{fluo} / nm	E_{00} / eV	λ_{2PA} / nm	δ_{2PA} / GM
TX [a]	340	133.2	394	0.39	3.38	690	400
RTX[b]	504	131.7	-	-	-	806	1602

[a] in DCM, [b] in ACN

Table S1. Photophysical properties of truxene-based derivatives.

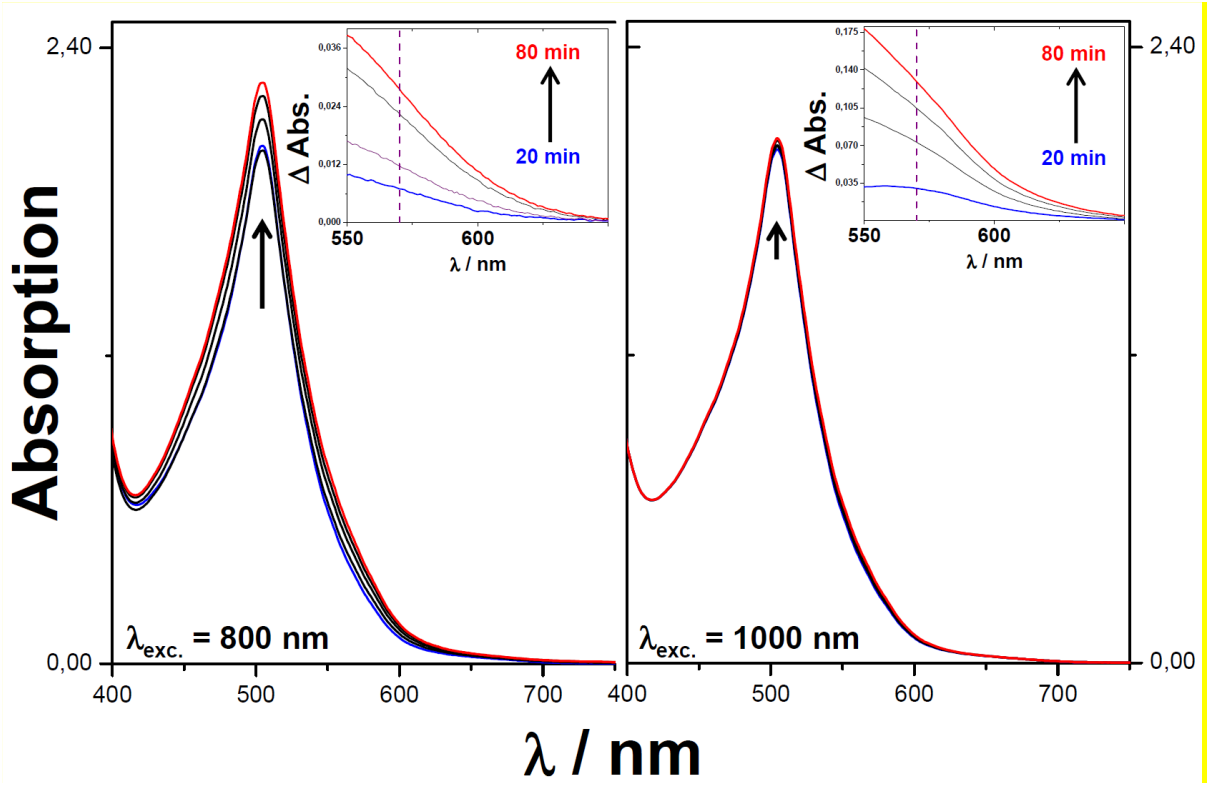


Figure S1. Evolution of the absorption spectrum of **RuTX** upon two-photon irradiation at two distinctive wavelengths (800 nm and 1000 nm) and in presence of Griess reagent. (Solvent: isovolume mixture of ACN / Water, [**RuTX**] = 0.15 mM, µ-volume cuvette with 1 mm optical path, P_{800nm} = P_{1000nm} = 1.2 W). Inserts: Differential absorption spectra in the 550-650 nm range after each 20 min irradiation increment.

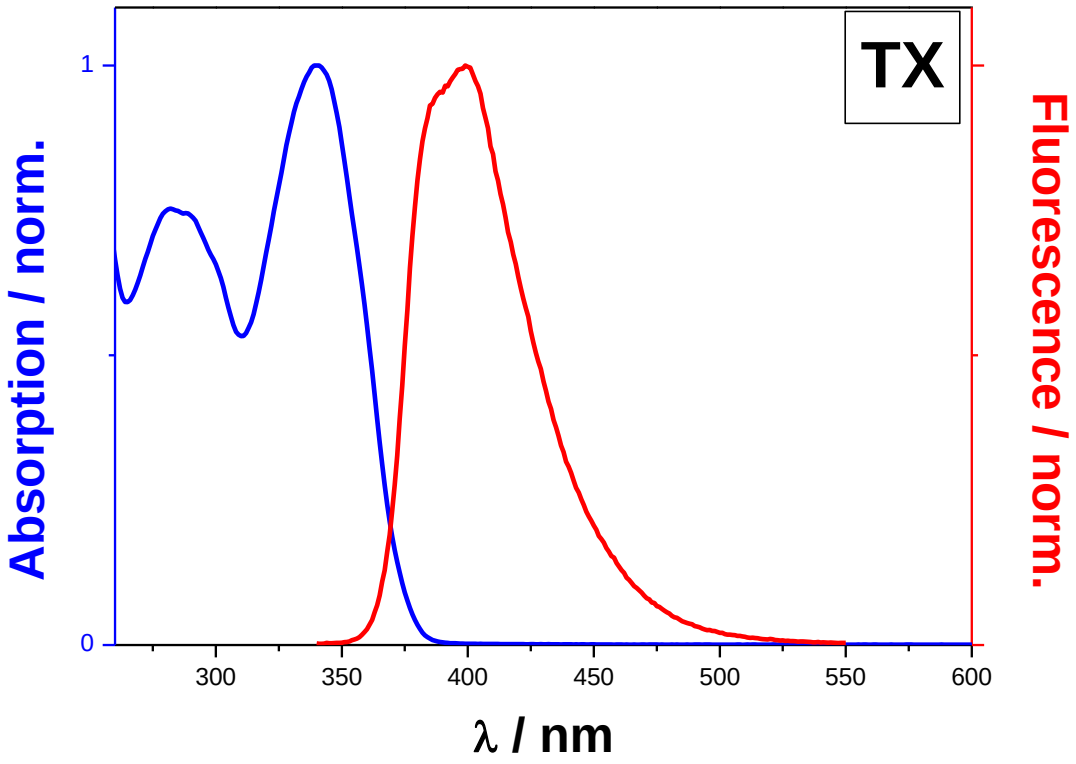


Figure S2. Normalized absorption and fluorescence spectra of **TX** in DCM.

2. Materials and General Characterization Methods.

Materials and general methods.

Materials. All the solvents employed were Aldrich spectroscopic grade. The absorption and fluorescence of all solvents were checked for impurities and have been subtracted from the sample spectra. The Griess reagent kit was purchased from Sigma-Aldrich (Catalog Number G4410).

Steady-state absorption and luminescence spectra. The absorption measurements were carried out with a Perkin Elmer Lambda 2 spectrometer. Steady-state fluorescence spectra in solution were collected from a FluoroMax-4 spectrofluorometer. Emission spectra are spectrally corrected, and fluorescence quantum yields include the correction due to solvent refractive index and were determined relative to quinine bisulfate in 0.05 molar sulfuric acid ($\Phi = 0.52$)[1].

Photolysis reactions.

1PA Photolysis. The photolysis of **RuTX** was carried out in ACN under continuous irradiation at 532 nm using a compact Q-switch diode-pumped CW laser from CrystaLaser (irradiation power: 150 mW). The photolysis was performed at 25°C in air-saturated ACN solution ([**RuTX**]: 5µM) which was continuously stirred. The progress of the reaction was monitored via the absorbance change using a Perkin Elmer Lambda 2 spectrometer.

2PA Photolysis. The two-photon irradiation of **RuTX** in presence of Griess reagent was performed in an isovolume mixture of water/ACN. The Griess reagent was prepared in ultra pure water (i.e., nitrite free) based on a method which was previously described[2]. As a typical experiment, 150 µl of a concentrated **RuTX** solution (0.3 mM in ACN) is mixed with 150 µl of Griess reagent. The mixture is then transferred into a µ-volume quartz cuvette (V_{tot} : 350 µl, optical path = 1 mm) which is positioned at the focal point of the NIR *fs*-pulse laser. The optical set-up is detailed in the Z-scan and TPEF experimental parts. Due to the very small irradiation volume (~ 1 pL), increments of 20 min of irradiation were chosen. The average irradiation power was maintained at 1.2 W for both $\lambda_{irr.}$. Here also, the progress of the reaction was monitored via the absorbance change using a Perkin Elmer Lambda 2.

Since **RuTX** and the 'azo' dye by-product are both absorbing in the same spectral range, two additional photolysis experiments at λ_{irr} = 800 nm and 1000 nm were conducted using **RuTX** in ACN/water (1v/1v) without Griess reagent in order to that confirm that the gradual increase of the absorbance at 570 nm (A_{570nm}) mainly stems from the two-photon generation of the 'azo' dye product. **Figure S3** displays the time-dependent changes of A_{570nm} from **RuTX** solutions with and without Griess reagent for both λ_{irr}.

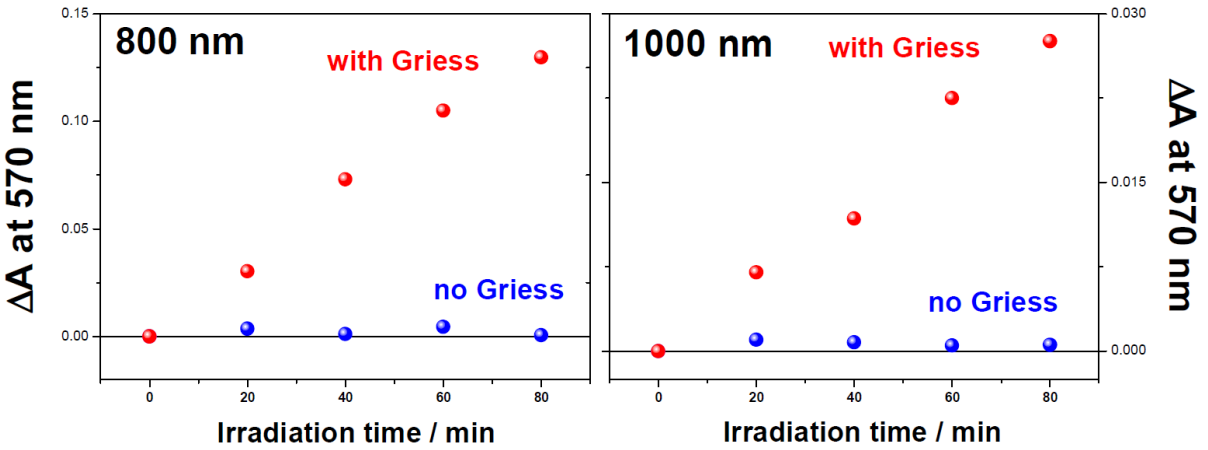


Figure S3 Time-dependent changes of the absorbance at 570 nm relative to aqueous solutions of **RuTX** (0.15 mM in water/ACN 1v/1v) with and without Griess reagent upon two-photon irradiation at 800 nm and 1000 nm respectively.

Electron spin resonance experiments (ESR) were carried out using a Brucker ESP 500E spectrometer. The following setting was employed for the measurements: microwave power, 20 mW, field modulation amplitude, 0.1 mT; field modulation frequency, 100 kHz; microwave frequency, 9.856608 GHz. N–methyl-D-glucamine dithiocarbamate previously synthetized reacted with Mohr salts to get $[Fe(MGD)_2]$.[3] 90 µL of 1 mM of **RuTX** were mixed with 10 µL of a 20mM aqueous solution of $[Fe(MGD)_2]$ with 24µl of 0.12 M HCl solution and injected into quartz capillaries. An initial set of ESR spectra was recorded after keeping the tube in the dark. A second set of acquisitions were performed just after 20 min *in situ* irradiation. The irradiation in the ESR apparatus was performed using a 530 nm LED-light source from Mightex (WheeLED wavelength-switchable LED sources).

Open-aperture Z-scan method. The two-photon absorption spectra were measured using open-aperture Z-scan method[4,6] with a femtosecond mode-locked Ti: Sapphire laser (Coherent, Chameleon Ultra II : pulse duration: 140 ± 20 fs; repetition rate: 80 MHz; wavelength range: 680-1080 nm). After passing through a beam expander (x 4), the laser beam is focused using an f = 15 cm lens and passed through a quartz cell (1 mm optical path length). The position of the sample cell is varied along the laser-beam direction (z-axis) using a Z-step motorized stage controlled by a computer. At constant incident excitation, the local power density within the sample is changed and the corresponding transmitted laser beam, *T(z)*, recorded with a silicon photodetector (Ophir PD300) is monitored in connection with the z-position of the cell. The on-axis peak intensity of the incident pulses at the focal point, I_0, ranged from 0.5 to 3 GW cm^{-2}. If we assume that the linear absorption of the sample is negligible at working wavelength and that the laser exhibits a Gaussian beam profile in space and time, the nonlinear absorption coefficient β can be calculated from the curve fitting to the experimental transmittance with the following equation:

$$T(z) = 1 - \frac{\beta l I_0}{2\sqrt{2}(1+(\frac{z}{z_0})^2)} \qquad (1)$$

Where z_0 is the coordinate along the propagation direction of the focal point of the beam, l the optical path length. The 2PA cross-section, δ, (in units of 1 GM : 10^{-50} cm^4 s photon^{-1} molecule^{-1}) is then determined by using the relationship:

$$\beta = \frac{\delta . N_A d}{h\nu} 10^{-3} \qquad (2)$$

Where h is the Planck constant, ν the frequency of the incident laser beam, N_A the Avogadro constant and d is the concentration of the chromophore (mol. L^{-1}). The rhodamine 6G in methanol[7] (16.2 ± 2.4 GM at 806 nm) was used for the calibration of our measurement technique. As a typical example, **Figure S4** depicts z-scan traces of **RuTX** (0.7 mM in ACN) at 800 nm for distinctive incident powers. The linear correlation between the variation of transmission (ΔT) and the incident power (inset **Figure S4**) confirms the two-photon absorption regime.[6] The resulting 2PA cross-sections were then measured with an uncertainty of 15 %. A strong deviation from linearity was observed for laser wavelengths below 790 nm presumably because of additional absorption of long lived excited species such as triplet states or charge separated species for instance. As a consequence, the spectral range for the measurement of **RuTX** 2PA spectrum has been limited to the 800-1060 nm window.

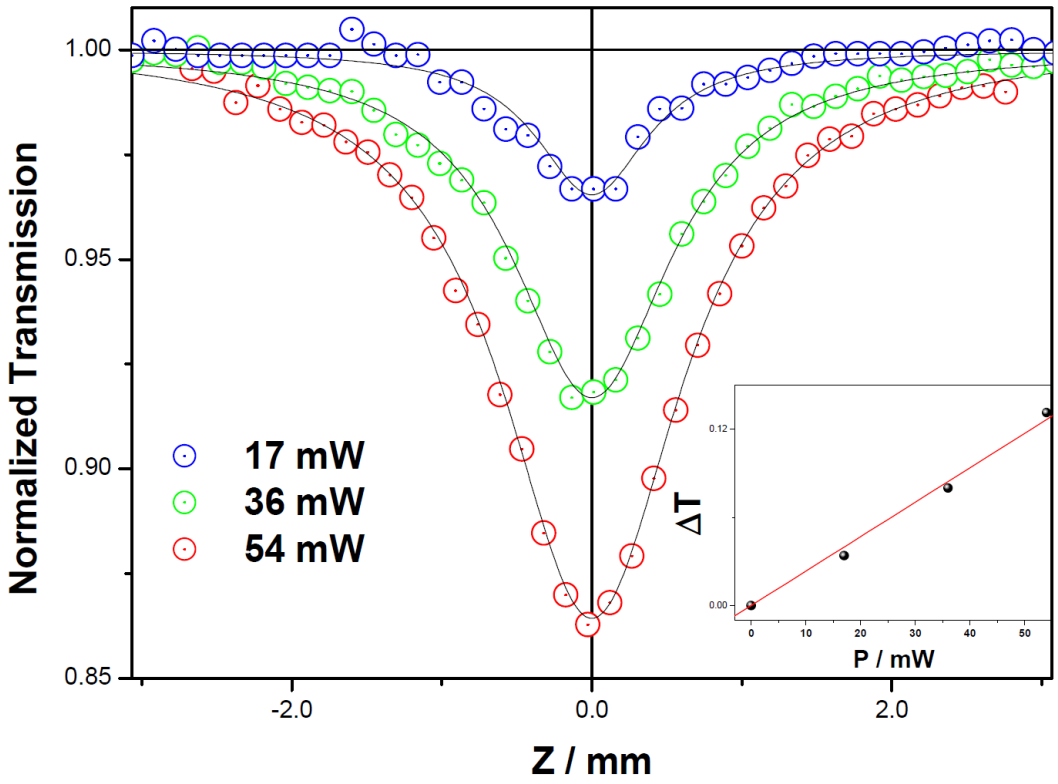


Figure S4 Z-scan traces of **RuTX** in ACN (0.7 mM) at 800 nm for various excitation powers. On the basis of equation 1, the least squares fitted curves for each Z-scan trajectory are also reported. Inset: Transmittance variation *vs.* excitation power.

Two-photon excited fluorescence method. A relative two-photon excited fluorescence (2PEF) method[8] was employed to measure the two-photon absorption cross-sections of **TX** which is emissive (see **Table S1**). The same *fs*-pulse laser used for z-scan measurement was employed for 2PEF. The measurements of 2PA cross-sections were performed relative to reference molecules (*r*) such as fluorescein[8,9] in water at pH = 11. The value of δ for a sample (*s*) is given by:

$$\delta_S = \frac{S_S \Phi_r \eta_r c_r}{S_r \Phi_S \eta_S c_S} . \delta_r$$

Where S is the detected two-photon excited fluorescence integral area, c the concentration of the chromophores, and Φ is the fluorescence quantum yield of the chromophores. η is the collection efficiency of the experimental set-up and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved. The measurements were

conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon induced emission. As a representative example, **Figure S5** shows various two-photon induced fluorescence spectra of **TX** in dichloromethane recorded at various excitation powers ($\lambda_{exc.}$ = 720 nm). The inset in **Figure S5** shows the quadratic dependence correlation between the fluorescence intensity at λ_{MAX} and the incident excitation power.For the calibration of the two-photon absorption spectra, the two-photon excited fluorescence signal of each compound was recorded at the same excitation wavelength as that used for standards (i.e. λ_{exc} = 782 nm for fluorescein). The laser intensity was in the range of 0.2-2 x GW/cm^2. The experimental error on the reported cross section is 15 %.

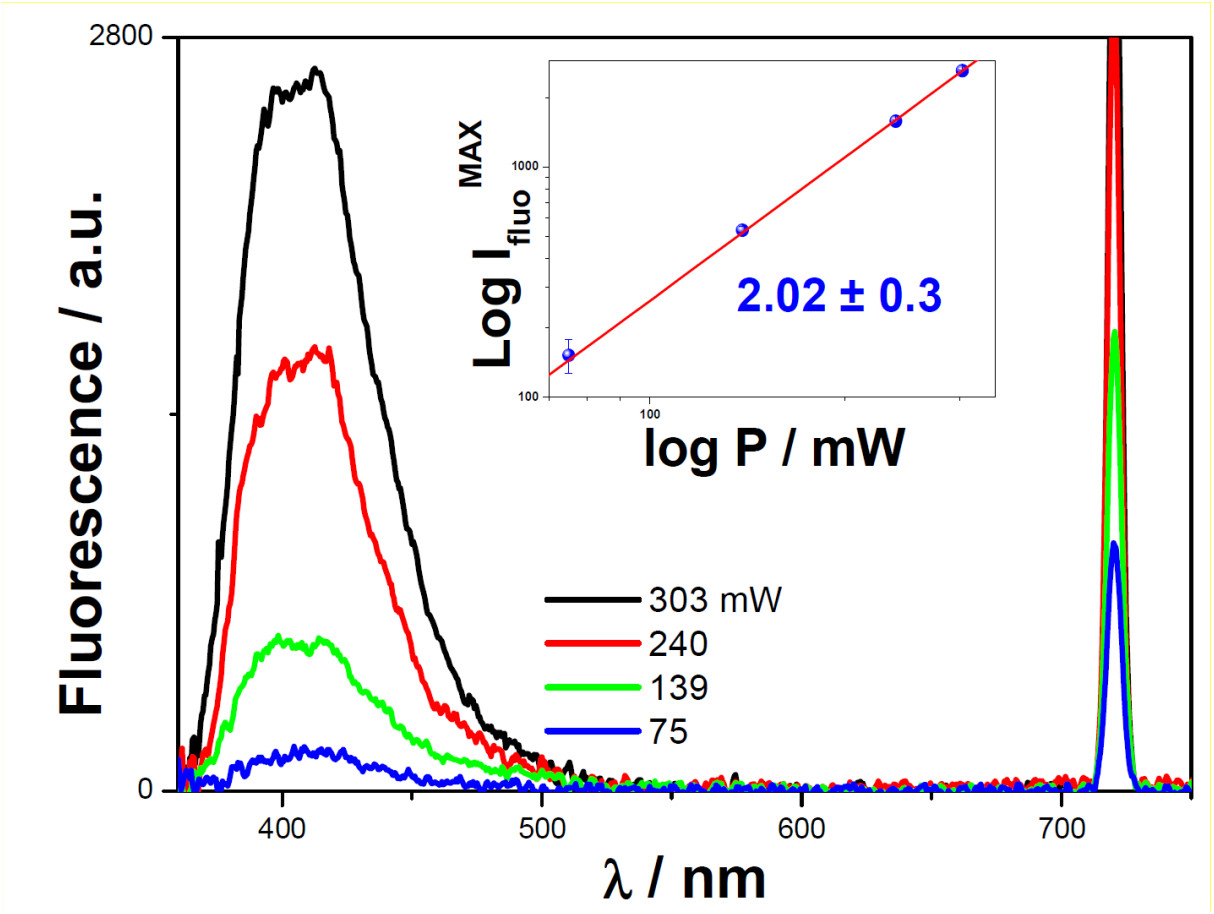
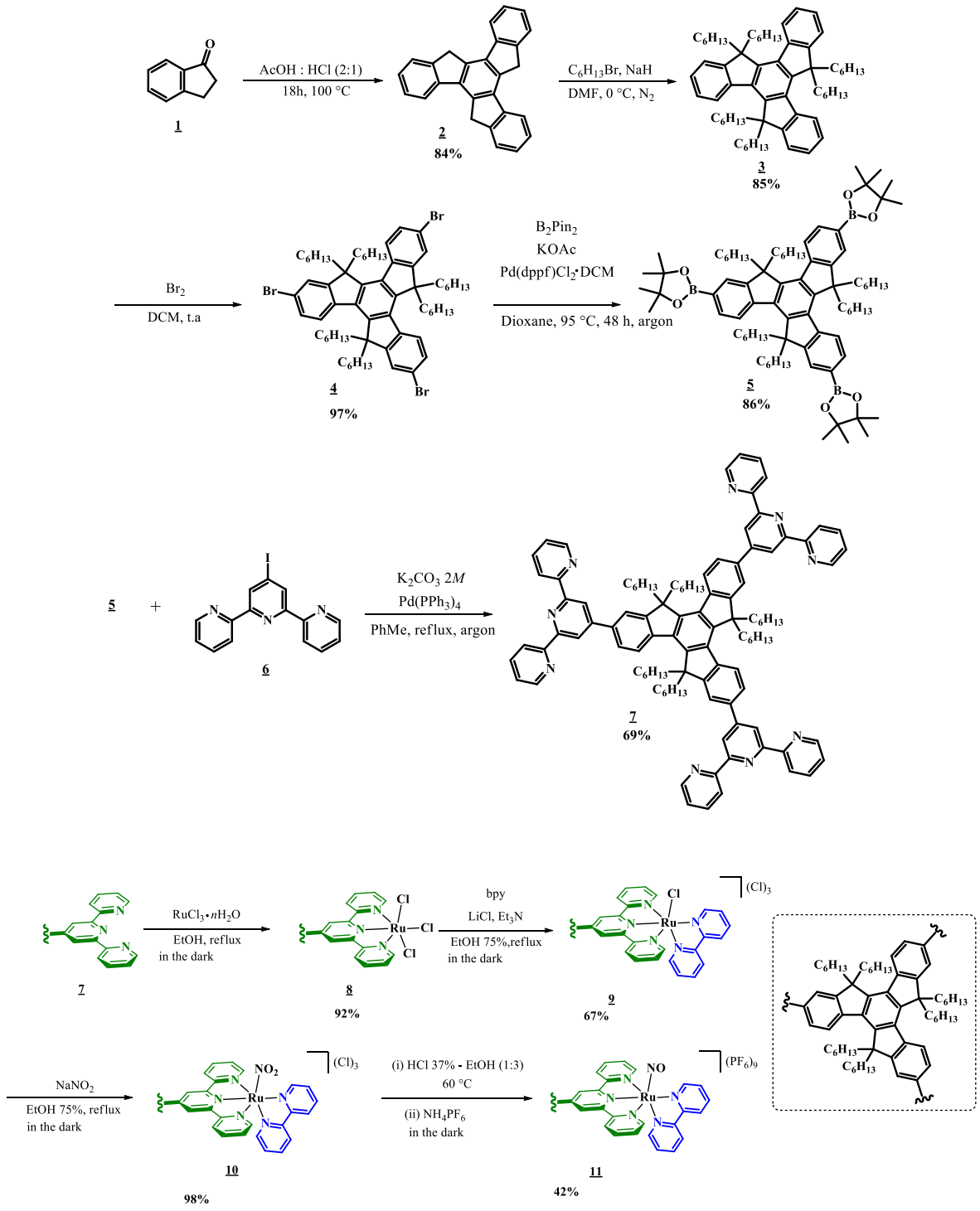


Figure S5. Two-photon induced fluorescence spectra of **TX** (2.10^{-4} M) in DCM as function of the incident laser excitation power at 720 nm. Inset: Plots of log $I_{fluo.}^{MAX}$ *vs.* log [excitation power].

3. Synthesis of chromophores

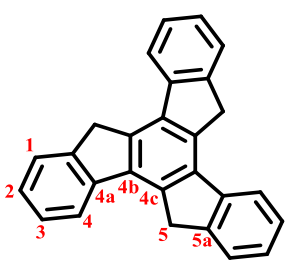


General specifications. Materials and equipment

All the experiments were carried out under a nitrogen or argon atmosphere, unless otherwise noted. All the experiments were performed at least in triplicate. Dry solvents were obtained

through conventional techniques[10] or were purchased from Sigma-Aldrich. All available reagents were purchased at the highest commercial quality from Sigma-Aldrich, Merck or Acros, and were used as received, unless otherwise stated. The reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60 F254) or 0.17 – 0.22 mm Aldrich neutral aluminium oxide plates (60 F254) using UV light or iodine as visualizing agent. Merck silica gel (60, particle size 0.0040 – 0.063 mm) or Merck neutral aluminium oxide (Brockmann Grade I, particle size 150 mesh) were used for flash column chromatography.

1D and 2D NMR spectra were recorded at 298 K on Bruker Fourier 300 MHz or Bruker Avance III 400 MHz, Varian 400 MHz instruments and calibrated using residual nondeuterated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_3CN: δ_H = 1.94 ppm, δ_C = 1.32 ppm) as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet, br = broad, dd = doublet of doublets, dt = doublet of triplets, etc. The chemical shift is quoted in ppm. Coupling constants (*J*) are quoted in Hz. Infrared (IR) spectra were recorded on a Corey Agilent and Perkin–Elmer ATR FTIR/FIR 100 spectrometer. The frequency of the absorption bands is quoted in cm^{-1}. The quantitative UV–Vis experiments were carried out at room temperature on a Thermo Scientific Evolution 220 spectrophotometers, using a quartz glass cell with a path length of 10 mm. The samples were prepared in a concentration of ~10^{-6} M in acetonitrile (HPLC grade), the solutions were protected from light and the absorbance was then measured immediately. All UV–Vis experiments were performed in triplicate. High–resolution mass spectra (HRMS) were collected on and Bruker Daltonics FlexAnalysis MALDI-TOF mass spectrometer, and The ESI mass spectra were performed on an LC/MS Thermo Scientific LCQ Fleet with reverse phase column equipped with an ESI source. Melting points are uncorrected and were determined on a Fisher – Johns (±1 °C) or a Stuat SMP10 (±1 °C) melting point apparatus.

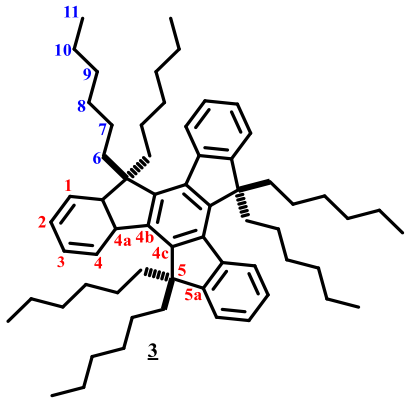


2

10,15-Dihydro-5*H*-tribenzo[*a,f,k*]trindene (*2*, truxene)[11]

To a stirrined solution of glacial acetic acid (22 mL) and concentrated hydrochloric acid (11 mL) at 100 °C was added the indan-1-one ***1*** (5g, 37.8 mmol). The yellow solution was then heated at 100 °C for 18 h before removing the bath, allowing the reaction

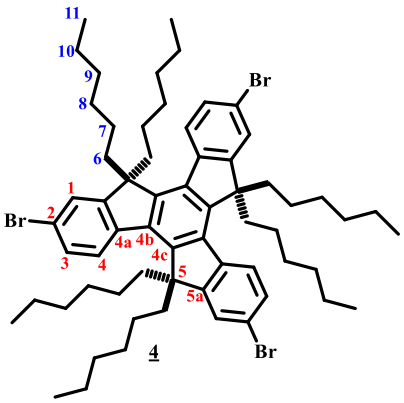
mixture to cool to room temperature. Then the reaction mixture was quenched by the addition of 50 mL of water and stirred for 15 minutes, after which, the heterogeneous mixture was poured onto a water-ice mixture. The solid precipitate was collected by vacuum filtration and washed sequentially with water (4 x 10 mL), DCM (4 x 5 mL) and Et_2O (4 x 5 mL). Truxene ***2*** was obtained as a white powder (3.683 g, 10.76 mmol, 84 %). $\mathbf{R_f}$ = 0.46 (silica gel, hexane – EtOAc 9:1); **m.p. =** the compound decomposes at temperatures higher than 290 °C. The NMR data of ***2*** was not collected due to its poor solubility.



3

10,15-Dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a,f,k*]trindene (*3*)[12]

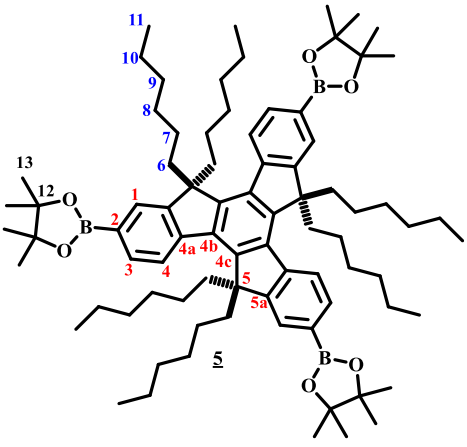
To a mixture of NaH (1.44 g, 50% dispersion in mineral oil, 30 mmol) and truxene ***2*** (1.03 g, 3 mmol) placed in an ice-water bath and under nitrogen atmosphere, was added anhydrous DMF (75 mL). The mixture was stirred vigorously over 15 minutes followed by addition of 1-bromo-*n*-hexane (3.16 mL, 22.5 mmol) in four portions (adding each one of them every 30 minutes). The reaction mixture was stirred for 3 h at room temperature and then poured into water and extracted with EtOAc (5 x 20 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography over silica gel using hexane as an eluent to yield the hexaalkylated macrocycle ***3*** as a light yellow solid (2.17g, 2.563 mmol, 85%). $\mathbf{R_f}$ = 0.60 (silica gel, hexane); **m.p.** = 78 – 80 °C (hexane); **^{1}H NMR(400 MHz, $CDCl_3$), δ (ppm):** 8.39 (d, ^3J = 7.5 Hz, 3H, H-4), 7.48 (d, ^3J = 7.1 Hz, 3H, H-1), 7.40 (dd, ^3J = 7.6 Hz, ^3J = 7.5 Hz, 3H, H-3), 7.37 (dd, ^3J = 7.6 Hz, ^3J = 7.1 Hz, 3H, H-2), 3.06 – 2.91 (m, 6H, H-6x), 2.15 – 2.02 (m, 6H, H-6y), 1.01 – 0.78 (m, 36H, H-8, H-9, H-10), 0.61 (t, ^3J = 7.0 Hz, 18H, H-11), 0.57 – 0.46 (m, 12H, H-7); **^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):** 153.78 (C-5a), 144.96 (C-4c), 140.49 (C-4a), 138.52 (C-4b), 126.46 (C-2), 126.09 (C-3), 124.78 (C-4), 122.31 (C-1), 55.76 (C-5), 37.12 (C-6), 31.65 (C-9), 29.66 (C-8), 24.05 (C-7), 22.44 (C-10), 14.04 (C-11).



2,7,12-Tribromo-10,15-dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene (*4*)[13]

To a solution of hexahexyltruxene ***3*** (850 mg, 1 mmol) in DCM (15 mL), placed in an ice-water bath and light protected, was added dropwise a solution of bromine (0.26 mL, 5 mmol) in DCM (5 mL). After 15 minutes, the bath was removed, and the mixture was left under vigorous stirring for 20 h at room temperature. The reaction was quenched by adding $Na_2S_2O_4$ in order to remove the excess of bromine. The organic components were extracted with DCM (4 x 10 mL), and the combined organic layers were washed with a saturated solution of $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography over silica gel using hexane as an eluent to yield the tribromo-functionalized macrocycle ***4*** as a light brown solid (1.05 g, 0.969 mmol, 97%). $\mathbf{R_f}$ = 0.66 (silica gel, hexane); **m.p.** = 221 – 222 °C (hexane); **^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):** 8.17 (d, ^3J = 8.4 Hz, 3H, H-4), 7.57 (d, ^3J = 1.9 Hz, 3H, H-1), 7.51 (dd, ^3J = 8.4 Hz, ^4J = 1.9 Hz, 3H, H-3), 2.90 -2.76 (m, 6H, H-6x), 2.08 -1.93 (m, 6H, H-6y), 1.00 – 0.75 (m, 36H, H-8, H-9, H-10), 0.62 (t, ^3J = 7.1 Hz, 18H, H-11), 0.55- 0.35 (m, 12H, H-7); **^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):** 156.01 (C-5a), 145.03 (C-4c), 139.00 (C-4a), 137.77 (C-4b), 129.51 (C-3), 126.04 (C-4), 125.66 (C-1), 121.18 (C-2), 56.13 (C-5), 36.96 (C-6), 31.60 (C-9), 29.52 (C-8), 24.03 (C-7), 22.41 (C-10), 14.02 (C-11).

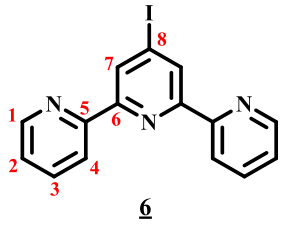
2,7,12-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,15-dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene (*5*)[14]



A round flask charged with 2,7,12-tribromohexahexyltruxene ***4*** (0.5g, 0.4612 mmol), bis(pinacolato)diboron (570 mg, 2.24 mmol), potassium acetate (509 mg, 5.18 mmol), $Pd(dppf)_2Cl_2 \cdot CH_2Cl_2$ (120 mg, 0.15 mmol), and 5 mL of anhydrous dioxane was degassed with argon for 1 h. Then the mixture was stirred at 95°C for 48 h, cooled to room temperature and then poured into water (5 mL). The mixture was then extracted with CH_2Cl_2 (5 x 20 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. After in vacuo concentration, the residue was purified by flash column chromatography over silica gel using a mixture hexane-CH_2Cl_2 (3:2) to afford compound ***5*** (485 mg, 0.342 mmol, 86%)

as a white solid. **^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):** 8.38 (d, ^3J = 8.0 Hz, 3H, H-4), 7.87 (dd, ^3J = 8.0 Hz, ^4J = 0.9 Hz, 3H, H-3), 7.85 (d, ^4J = 0.9 Hz, 3H, H-1), 2.99 – 2.87 (m, 6H, H-6x), 2.21 – 2.08 (m, 6H, H-6y), 1.42 (s, 36H, H-13), 0.94 – 0.73 (m, 36H, H-8, H-9, H-10), 0.58 (t, ^3J = 7.2 Hz, 18H, H-11), 0.50 – 0.40 (m, 12H, H-7); **^{13}C NMR (100 MHz, $CDCl_3$):** 152.90 (C-5a), 146.58 (C-4c), 143.38 (C-4a), 138.47 (C-4b), 133.01 (C-3), 128.35 (C-4), 124.09 (C-1), 83.87 (C-12), 55.92 (C-5), 37.00 (C-6), 31.68 (C-9), 29.67 (C-8), 25.15 (C-13), 24.12 (C-7), 22.45 (C-10), 14.03 (C-11).

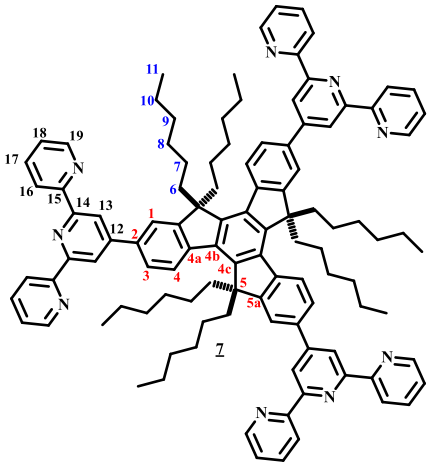
4'-Iodo-2,2':6',2''-terpyridine (*6*)[15]



6

2,2':6',6''-Terpyridin-4´-yl trifluoromethanesulfonate ***6*a** (500 mg, 1.31 mmol) and KI (650 mg, 3.91 mmol) were mixed in a round-bottom flask, containing a magnetic stirrer bar. The vessel was evacuated and refilled with argon for three cycles. Anhydrous NMP (4 mL) was then added by syringe. The mixture was heated at 150 °C for 21 h with vigorous stirring. After cooling to room temperature, the reaction was quenched by adding water (50 mL). The organic components were extracted with EtOAc (4 x 50 mL), and the combined organic layer were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography over silica gel using a mixture of petroleum ether –ethyl acetate (95/5) as an eluent to yield the pure terpyridine derivative ***6*** as a white solid (0.375 g, 1.045 mmol, 78%). **R_f** = 0.66 (silica gel, hexane); **^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):** 8.86 (s, 2H, H-7), 8.70 (d, *J* = 4.8 Hz, 2H), 8.57 (d, *J* = 8.0 Hz, 2H), 7.86 (ddd, *J* = 7.9 Hz, *J* = 7.5 Hz, *J* = 1.8 Hz, 2H), 7.35 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, *J* = 1.2 Hz, 2H, H-2).

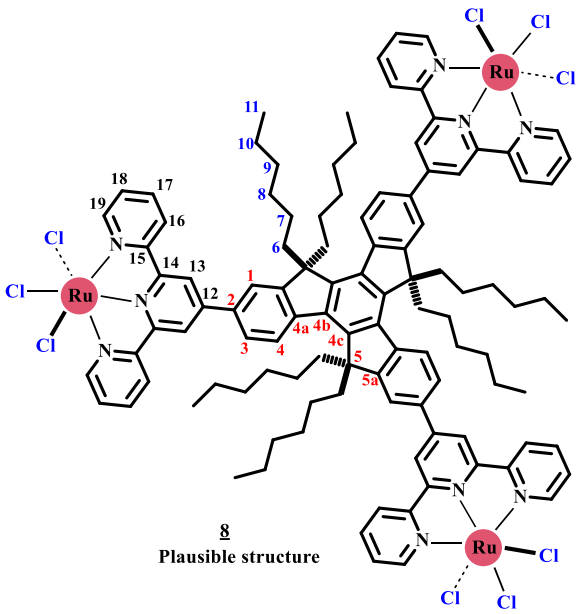
2,7,12-Tris([2,2':6',2''-terpyridin]-4'-yl)-10,15-dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene (*7*) {Abbreviation: TTPYTRUX = ligand *7*}



2,7,12-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,15-dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene ***5*** (183 mg, 0.149 mmol), 4'-iodo-2,2':6',2''-terpyridine ***6*** (242 mg, 0.673 mmol), K_2CO_3 (828 mg, 5.99 mmol) and $Pd(PPh_3)_4$ (120 mg, 0.103 mmol) were mixed in a round-bottom flask, containing a

magnetic stirrer bar. The vessel was evacuated and refilled with argon for three cycles. A degassed mixture of toluene – H_2O (9 mL, 2/1) was then added with syringe. The mixture was heated at 120 °C for 48 h. After cooling to room temperature, the reaction was quenched by adding water (10 mL). The organic components were extracted with DCM (5 x 20 mL), and the combined organic layer were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography over neutral alumina using a mixture of DCM – methanol (98:2) as an eluent to yield the pure tris(terpyridine) ***7*** as a white solid (158 mg, 1.025 mmol, 69%). $\mathbf{R_f}$ = 0.66 (alumina , CH_2Cl_2 – MeOH 98/2); **UV-Vis (in MeCN):** λ_{max}/nm [ε/$M^{-1}cm^{-1}$] = 322 [66009], 422 [27956]; **^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):** 8.91 (s, 6H, H-13), 8.81 (d ^3J = 4.8 Hz, 6H, H-19), 8.73 (d, ^3J = 7.8 Hz, 6H, H-16), 8.57 (d, ^3J = 8.2 Hz, 3H, H-4), 8.03 (d, ^3J = 8.2 Hz, 3H, H-3), 8.02 (d, ^4J = 1.8 Hz, 3H, H-1), 7.92 (ddd, ^3J = 7.8 Hz, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 6H, H-17), 7.40 (ddd, ^3J = 7.5 Hz, ^3J = 4.8 Hz, ^4J =1.2 Hz, 6H, H-18), 3.13 – 3.01 (m, 6H, H-6x), 2.35 – 2.25 (m, 6H, H-6y), 1.10 – 0.84 (m, 36H, H-8, H-9, H-10), 0.70 – 0.53 (m, 30H, H-7, H-11); **^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm):** 156.64 (C-15), 156.16 (C-14), 154.64 (C-5a), 150.78 (C-12), 149.32 (C-19), 146.32 (C-4c), 141.40 (C-4a), 138.19 (C-4b), 137.09 (C-17), 136.76 (C-2), 125.93 (C-3), 125.25 (C-4), 123.98 (C-18), 121.63 (C-16), 120.85 (C-1), 119.14 (C-13), 56.33 (C-5), 37.27 (C-6) , 31.72 (C-9), 29.67 (C-8), 24.26 (C-7), 22.46 (C-10), 14.05 (C-11). **MS (ESI-Quadrupole ion trap, positive mode):** calcd. for $C_{108}H_{118}N_9$ $[M+H]^+$ 1541.95, found 1542.00, error 32.42 ppm.

[Ru_3(TTPYTRUX)Cl_9] {Abbreviation: TTPYTRUX = ligand *7*} (*8*)



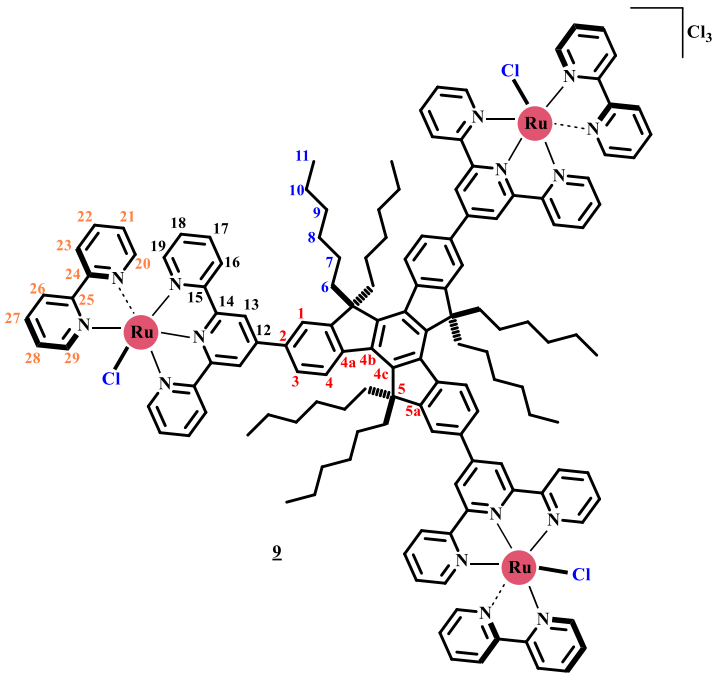
8
Plausible structure

To a light protected solution of the tris(terpyridine) ligand ***7*** (52 mg, 33.74 µmol) in EtOH 96% (100 mL) was added $RuCl_3$•$3H_2O$ (66.22 mg of 40% of ruthenium; 101.3 µmol). The solution was heated at 100 °C for 4 h. Then it was allowed to cool down, and the solvent was removed under vacuum. Subsequently, EtOH (10 mL) was added and the mixture was refrigerated at -78 °C for 2 h and filtered under vacuum to isolate the solid formed. The solid was washed

with EtOH 96% (2 x 10 mL) and diethyl ether (2 x 10 mL) respectively, and then it was dried in a vacuum desiccator to yield the complex ***8*** as a black solid (66.9 mg, 30.92 µmol, 92%).

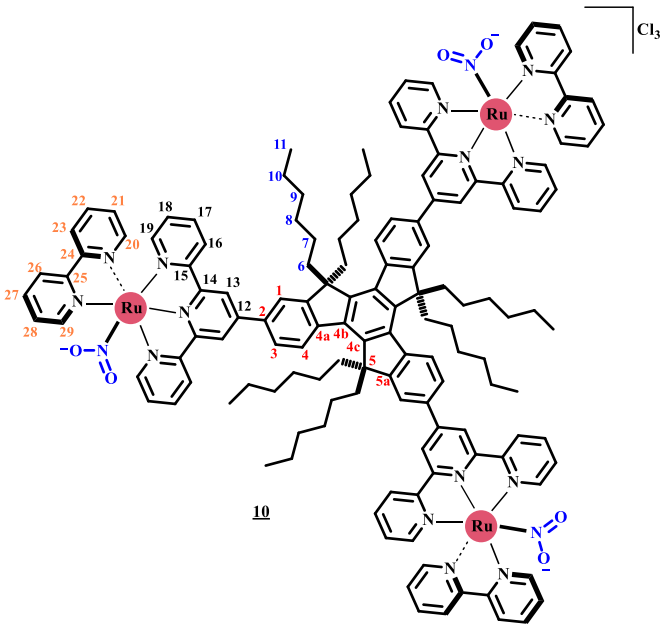
$[Ru_3(TTPYTRUX)(Cl)_3(bpy)_3]Cl_3$ {Abbreviation: TTPYTRUX = ligand *7*} (*9*)

To a light protected mixture of the complex $[Ru_3(TTPYTRUX)Cl_9]$ ***8*** (66.9 mg, 30.92 µmol) in a solution 3:1 EtOH/water (100 mL) was added 2,2'-bipyridine (16 mg, 102.6 µmol), anhydrous lithium chloride (24 mg, 571.4 µmol) and Et_3N (50 µL, 359 µmol). The solution was heated at 100 °C for 4 h. Then it was allowed to cool down, and the solvent was removed under vacuum. Subsequently, diethyl ether (10 mL) was added and the mixture was refrigerated at -78 °C for 2 h, and filtered under vacuum to isolate the solid formed. The solid was washed with acetone 96% (2 x 2 mL), 3*M* HCl (1 x 5 mL), acetone (1 x 2 mL) and diethyl ether (5 mL), respectively. After washing the solid, it was dried in a vacuum desiccator to yield the complex ***9*** as a red solid (52 mg, 20.58 µmol, 67%). **FTIR-ATR (ν, cm^{-1}):** 3065*vw*, 2950*w*, 2963*m*, 2850*w*, 1602*m*, 1465*m*, 1416*m*, 1398*m*, 1375*m*, 1244*w*, 1023*m*,786*s*, 752*s*, 726*s*.; **^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm):** 10.15 (d, *J* = 4.6 Hz, 2H), 9.41 (d, *J* = 7 Hz, 4H), 9.10 (dd, *J* = 8Hz, *J* = 7.5Hz, 2H), 8.91-8.58 (m, 4H), 8.39 (t, *J* = 6.5Hz, 1H), 8.29-8.04 (m, 3H), 7.70 (s, 2H), 7.56-7.27 (m, 2H), 7.11-7.05 (m, 1H), 1.20-1.05 (m, 36H), 0.80-0.66 (m, 30H).



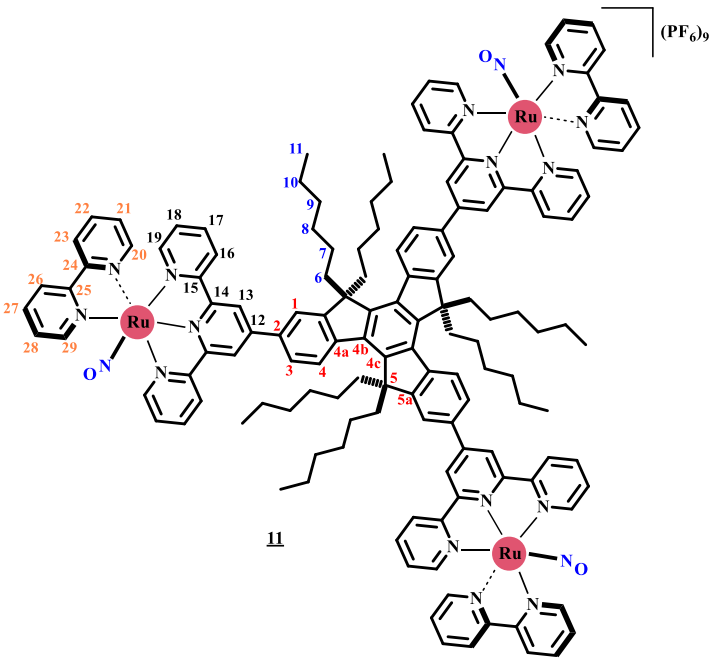
[Ru_3(TTPYTRUX)$(NO_2)_3$(bpy)$_3$]Cl_3 {Abbreviation: TTPYTRUX = ligand *7*} (*10*)

To a light protected mixture of the complex [Ru_3(TTPYTRUX)$(Cl)_3$(bpy)$_3$]Cl_3 ***9*** (37.1 mg, 14.69 µmol) in 3:1 EtOH/water (20 mL) was added sodium nitrite (42.4 mg, 614.5 µmol). The solution was then heated at 100 °C for 4 h. The solution was allowed to cool down, and the solvent was removed under vacuum. Subsequently, water (2 mL) was added to the mixture, which was stirred vigorously, and then it was filtered under vacuum to isolate the solid formed. The solid was washed with diethyl ether (2 x 5 mL), and then dried in a vacuum desiccator to yield the complex ***10*** as a red solid (36.7 mg, 14.35 µmol, 98%). **FTIR-ATR (ν, cm^{-1}):** 3069*vw*, 2926*w*, 2861*w*, 1836*w*, 1596*m*, 1464*m*, 1406*m* (ν_{assym} NO_2), 1299*m* (ν_{sym} NO_2), 1216*m*, 1026*m*, 786*vs*, 754*vs*, 731*vs*; **^{1}H NMR (400 MHz, CD_3CN), δ (ppm):** 9.93 (d, *J* = 5.5 Hz, 3H), 8.95 (d, *J* = 7.6 Hz, 6H), 8.72-8.61 (m, 9H), 8.42-8.26 (m, 9H), 8.09-8.02 (m, 9H), 7.99 (t, *J* = 6.6 Hz, 3H), 7.82 (m, 6H), 7.61-7.49 (m, 6H), 7.38 (m, 6H), 7.32-7.23 (m, 3H), 7.16-7.08 (m, 3H), 3.39-3.20 (m, 6H), 2.75-2.47 (m, 6H), 1.17-0.94 (m, 36H), 0.81-052 (m, 30H).



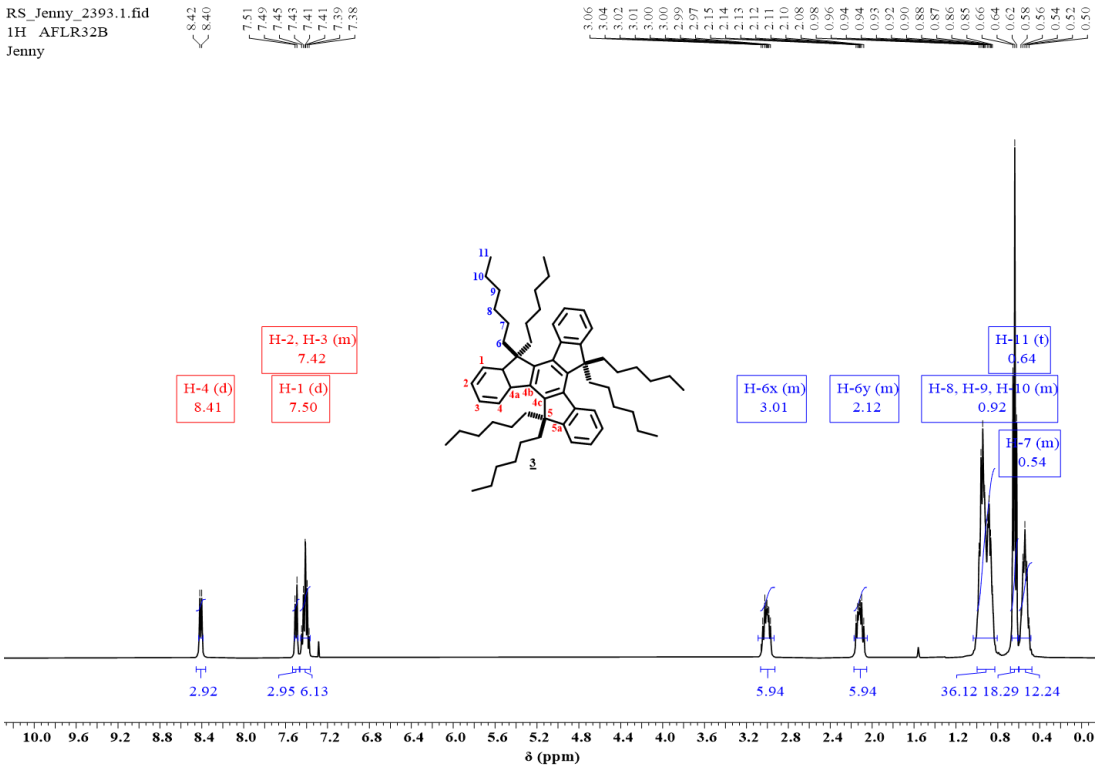
$[Ru_3(TTPYTRUX)(NO)_3(bpy)_3][PF_6]_9$ {Abbreviation: TTPYTRUX = ligand *7*} (*11*)

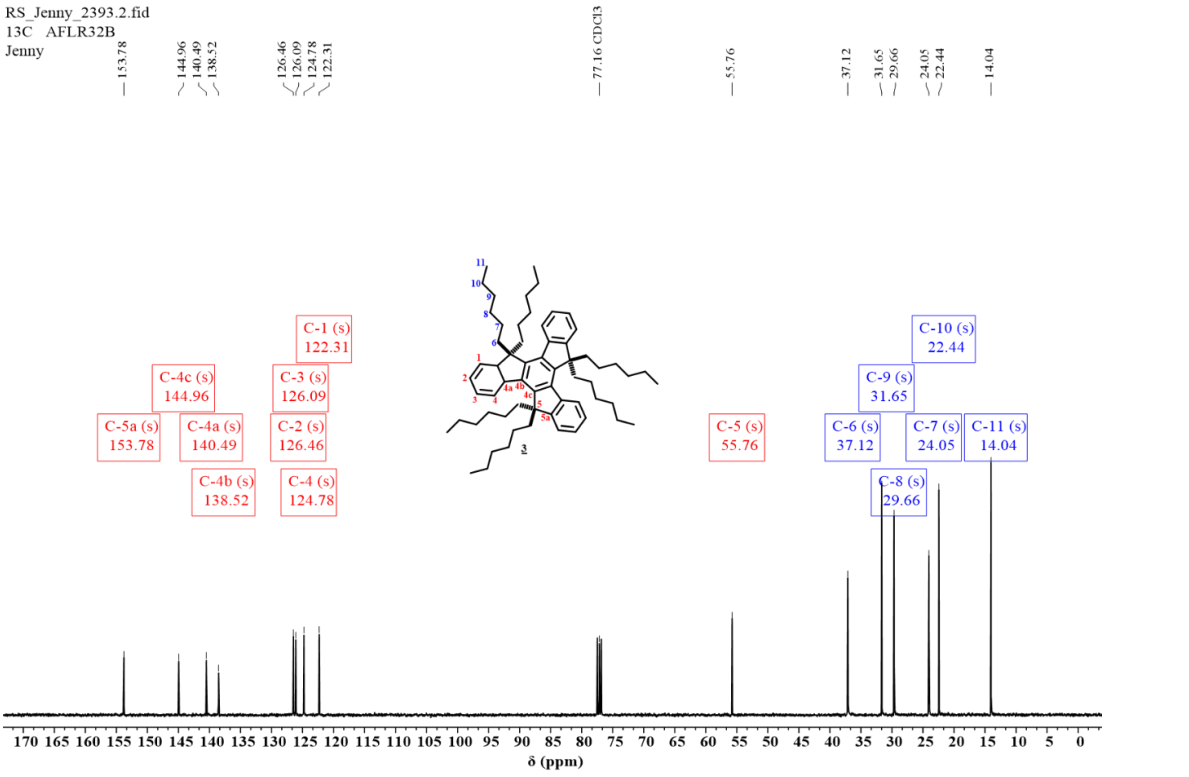
Complex $[Ru_3(TTPYTRUX)(NO_2)_3(bpy)_3]Cl_3$ ***10*** (36.7 mg, 14.35 µmol) was placed in a round-bottom flask containing a magnetic stirrer. Then a 1:3 solution of EtOH – concentrated HCl (5 mL) was added. The reaction mixture was protected from the light and heated at 60 °C for 90 minutes. The solution was allowed to cool down, and subsequently an aqueous solution of NH_4PF_6 (210 mg, 1.3 mmol) was added (11 mL). The mixture was stirred vigorously for 1 h at room temperature, and then filtered under vacuum to isolate the solid formed. The solid was washed with cold diethyl ether (2 mL), water (2 mL) and EtOH (2 mL), respectively. The solid was dried in a vacuum desiccator to yield the trinuclear complex ***11*** as a red solid (22 mg, 5.93 µmol, 42%). **FTIR-ATR (ν, cm^{-1}):** 2955*vw*, 2926*vw*, 2852*vw*, 1934*vw* (NO), 1601*w*, 1467*vw*, 1396*vw*, 1362*vw*, 1246*vw*, 1029*vw*, 831*vs* (PF_6), 778*s*, 559*m* (PF_6); **UV-Vis (in MeCN):** λ_{max}/nm [$\varepsilon/M^{-1}cm^{-1}$] = 288 [201298], 311 [210037], 355 [149906], 503 [132387]; **^{1}H NMR (400 MHz, CD_3CN), δ (ppm)**: 9.58 (sbr, 3H), 9.47-9.26 (m, 9H), 8.99-8.84 (m, 12H), 8.79-8.46 (m, 12H), 8.40-8.27 (m, 4H), 8.10-8.03 (m, 7H), 7.77 (s, 3H), 7.65-7.45 (m, 9H), 7.37-7.26 (m, 6H), 3.52-3.17 (m, 6H), 2.89-2.57 (m, 6H), 1.26-0.97 (m, 36H), 0.83-0.57 (m, 30H)**;** MALDI-TOF HRMS $C_{138}H_{141}F_{54}N_{18}O_3P_9Ru_3$, calculated $[M-(PF_6)_9+H]^+$ 2404.864 m/z, found: 2404.867 m/z (error 1.247 ppm).

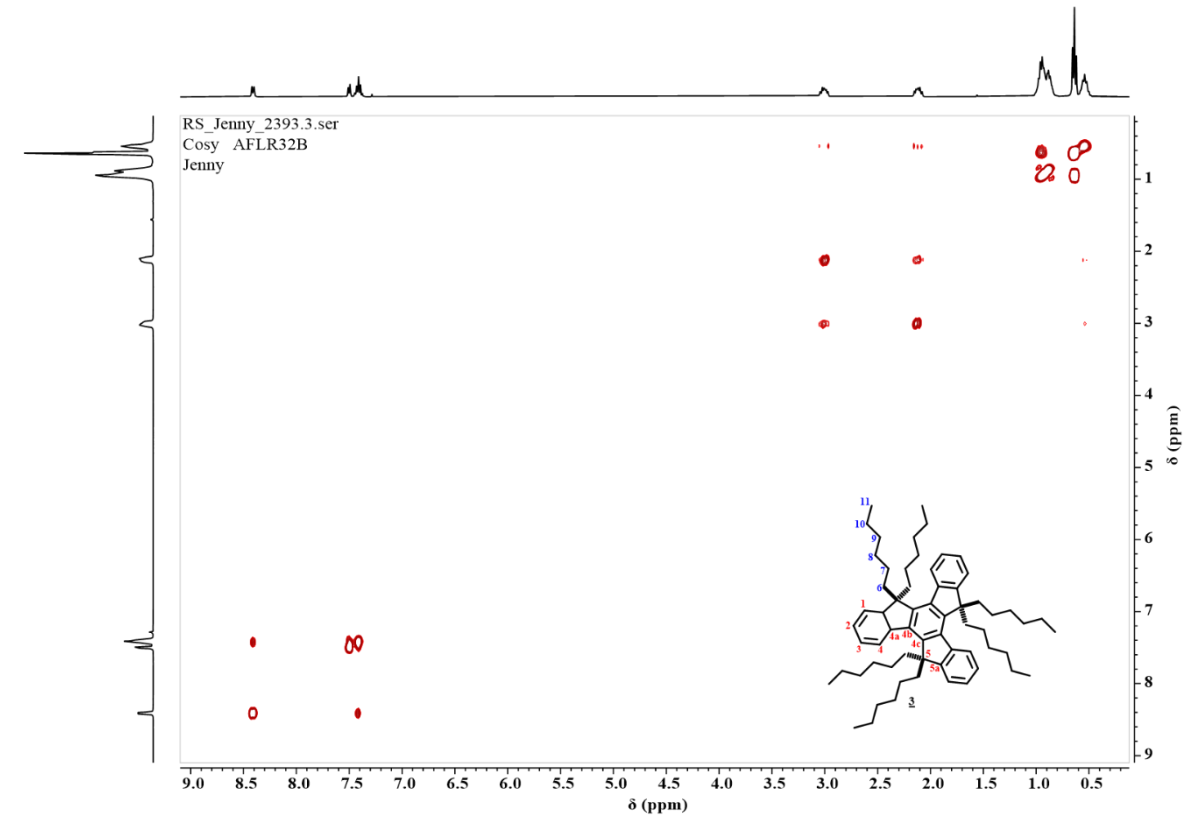


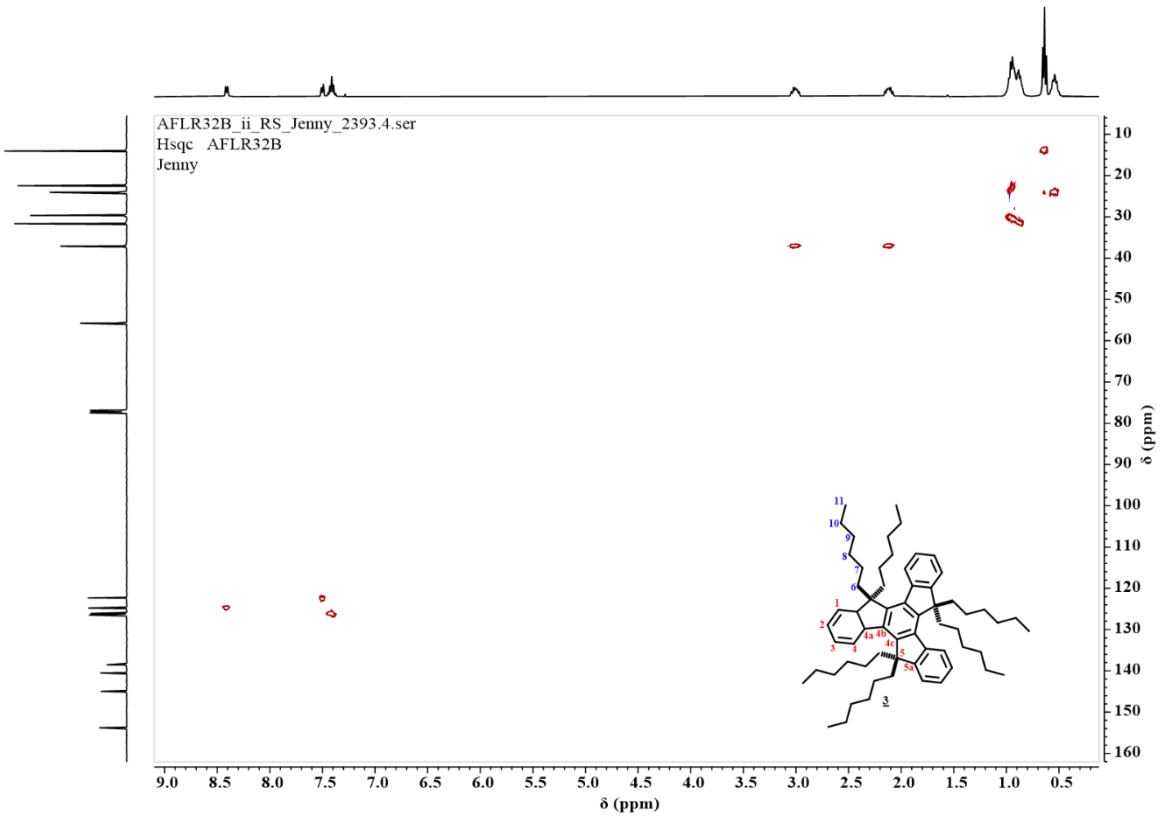
NMR Spectra

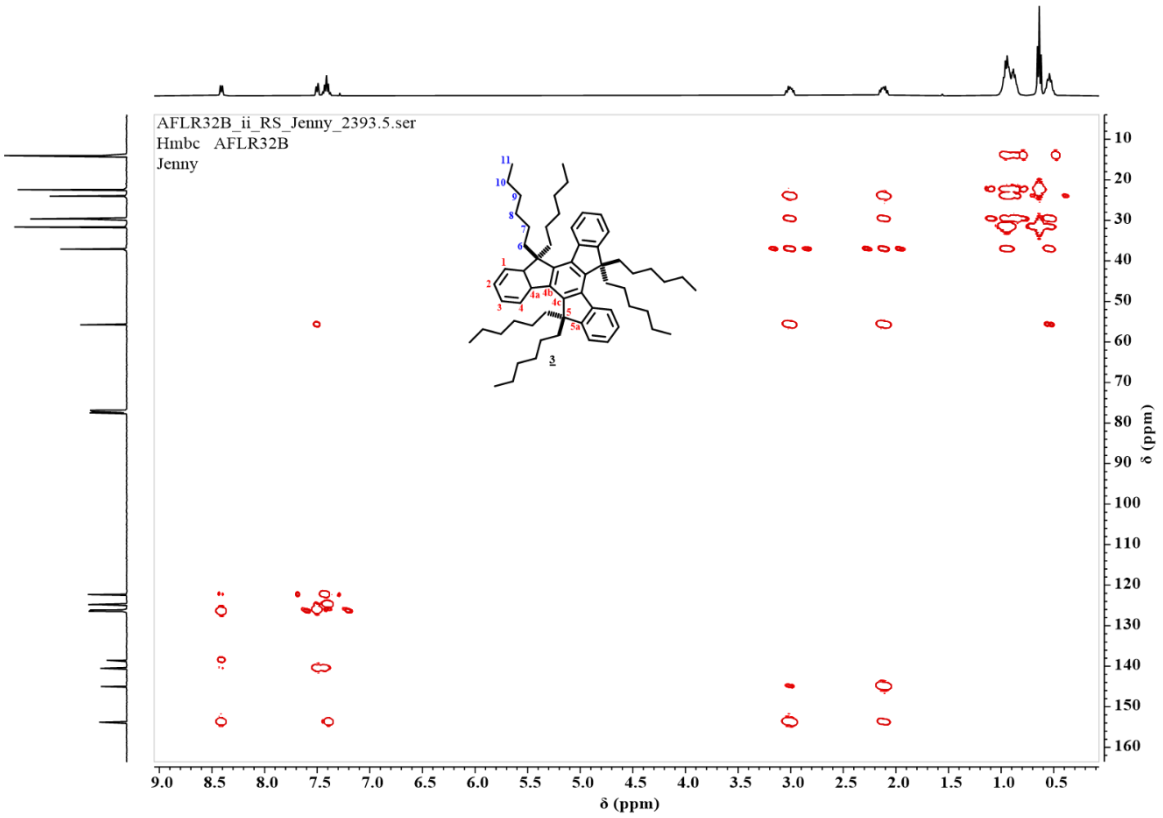
10,15-Dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene (**3**)



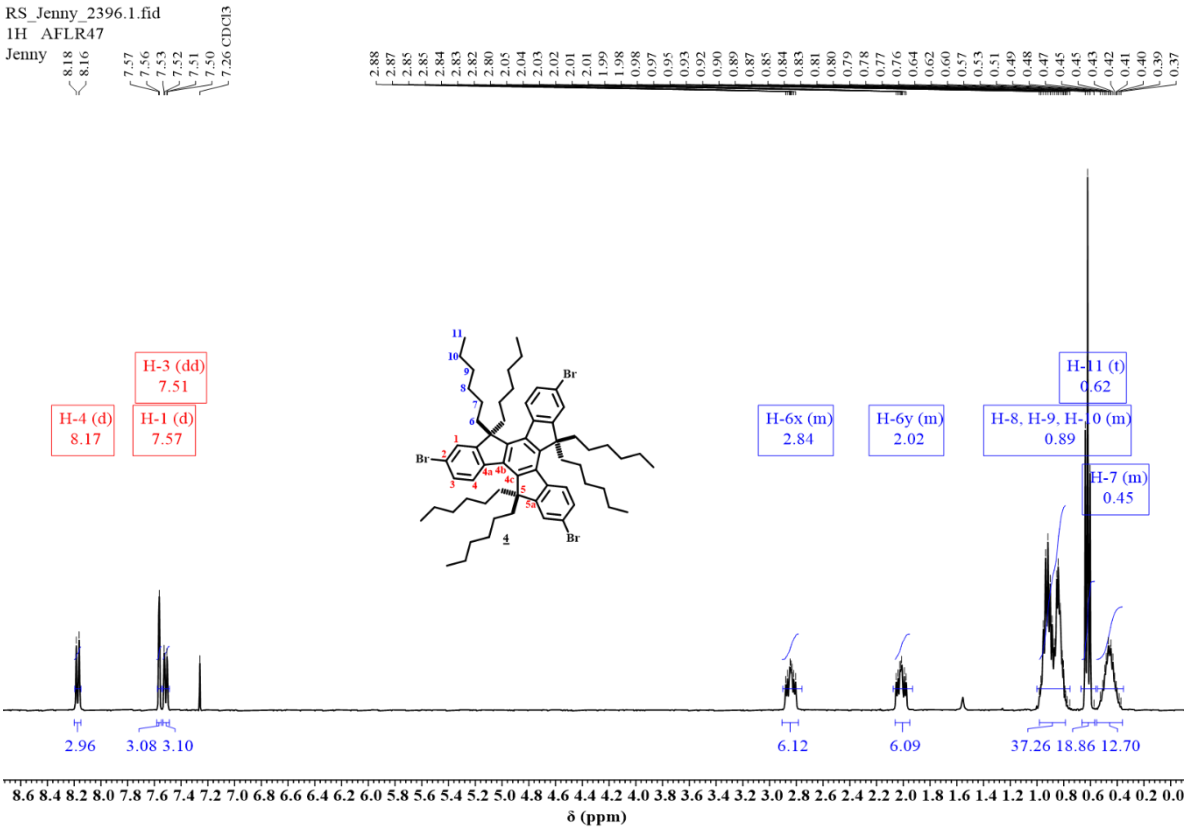

RS_Jenny_2393.2.fid
13C AFLR32B
Jenny
153.78
144.96
140.49
138.52
126.46
126.09
124.78
122.31
77.16 CDCl3
55.76
37.12
31.65
29.66
24.05
22.44
14.04
C-1 (s) 122.31
C-3 (s) 126.09
C-2 (s) 126.46
C-4 (s) 124.78
C-4c (s) 144.96
C-5a (s) 153.78
C-4a (s) 140.49
C-4b (s) 138.52
C-5 (s) 55.76
C-10 (s) 22.44
C-9 (s) 31.65
C-6 (s) 37.12
C-7 (s) 24.05
C-11 (s) 14.04
C-8 (s) 29.66
δ (ppm)

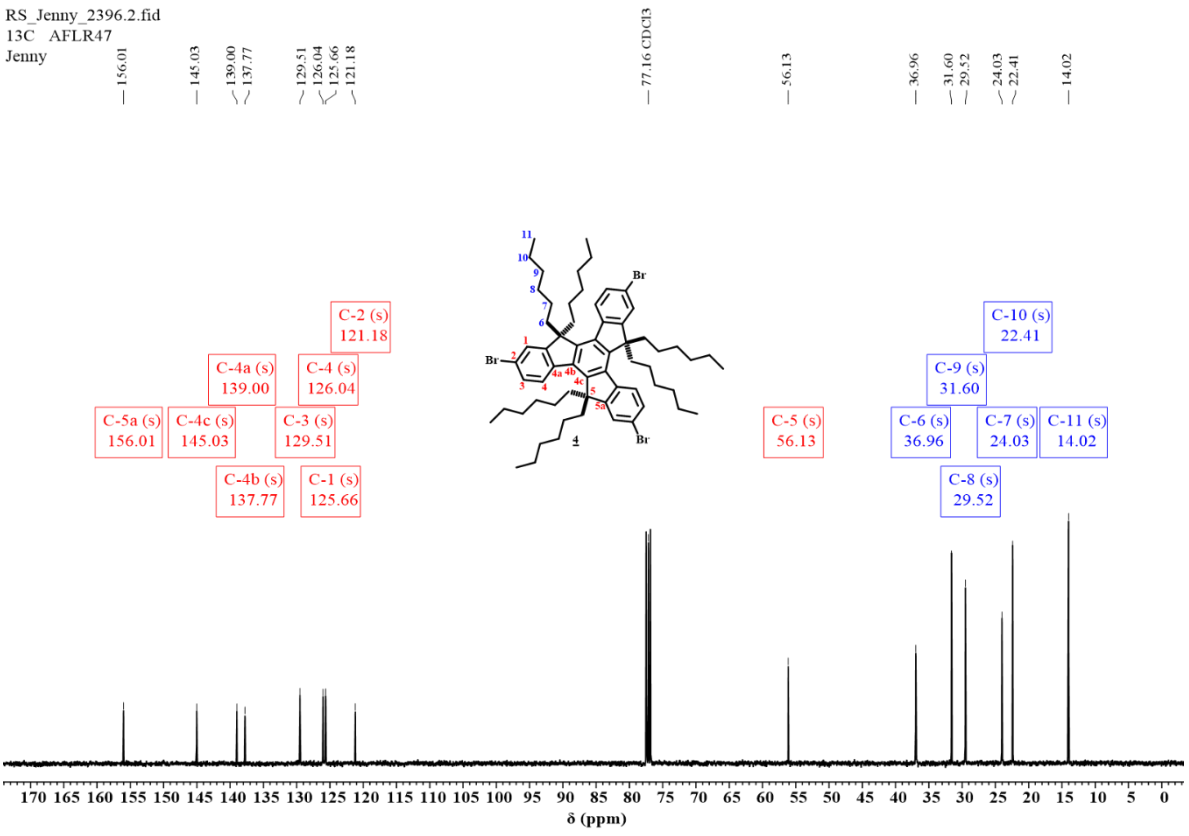

RS_Jenny_2393.3.ser
Cosy AFLR32B
Jenny
δ (ppm)
δ (ppm)

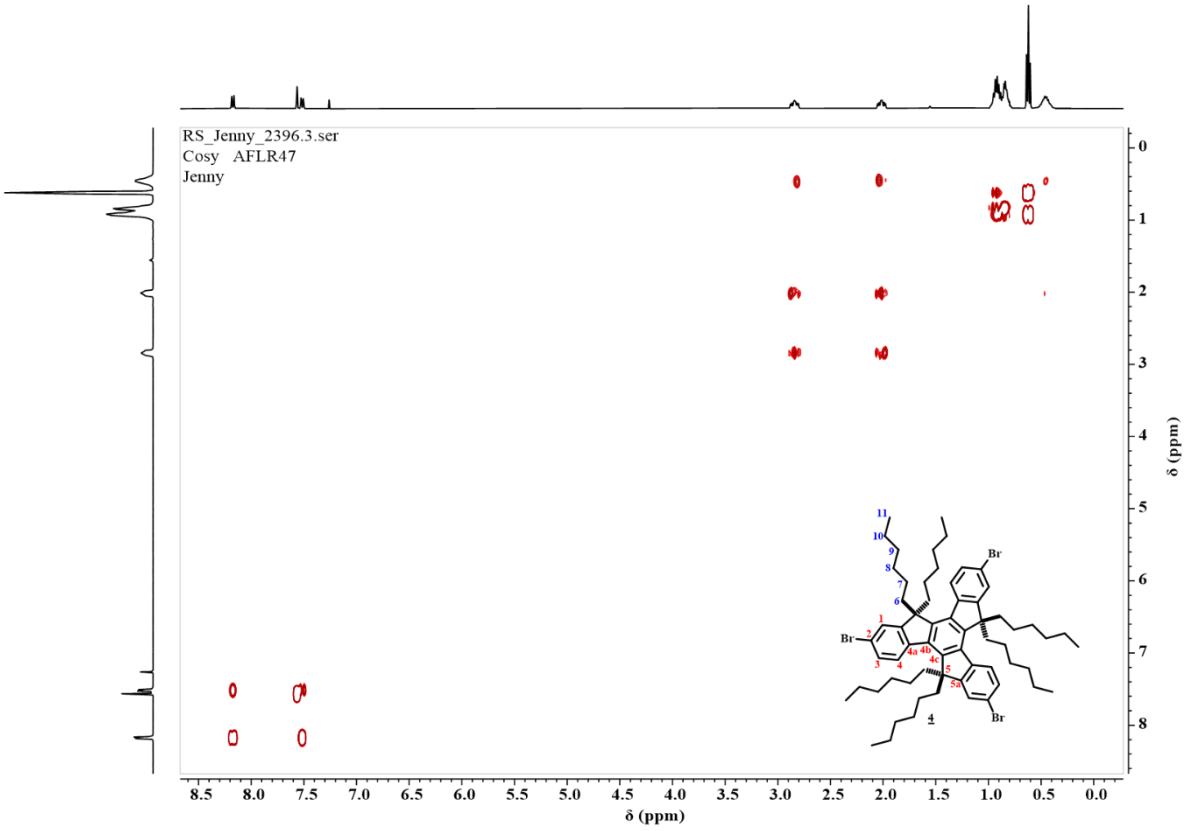

AFLR32B_ii_RS_Jenny_2393.4.ser
Hsqc AFLR32B
Jenny
δ (ppm)
δ (ppm)

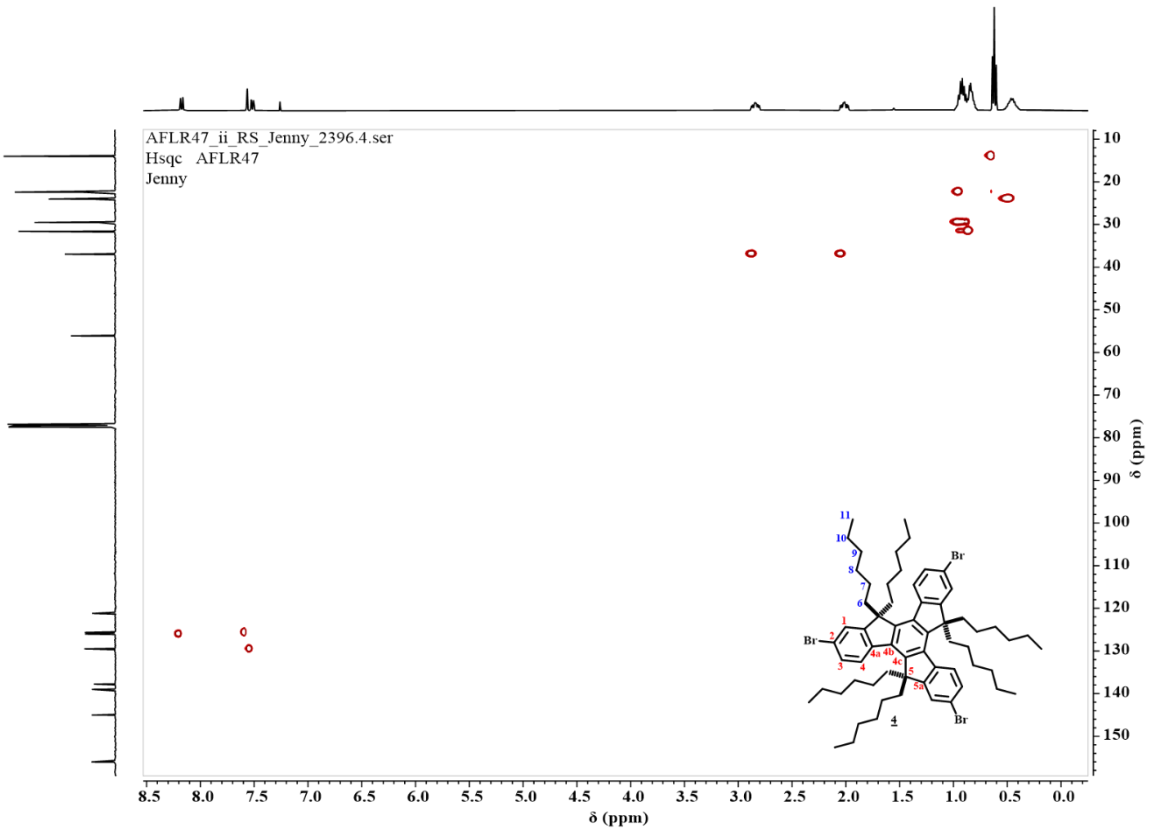

AFLR32B_ii_RS_Jenny_2393.5.ser
Hmbc AFLR32B
Jenny
δ (ppm)
δ (ppm)

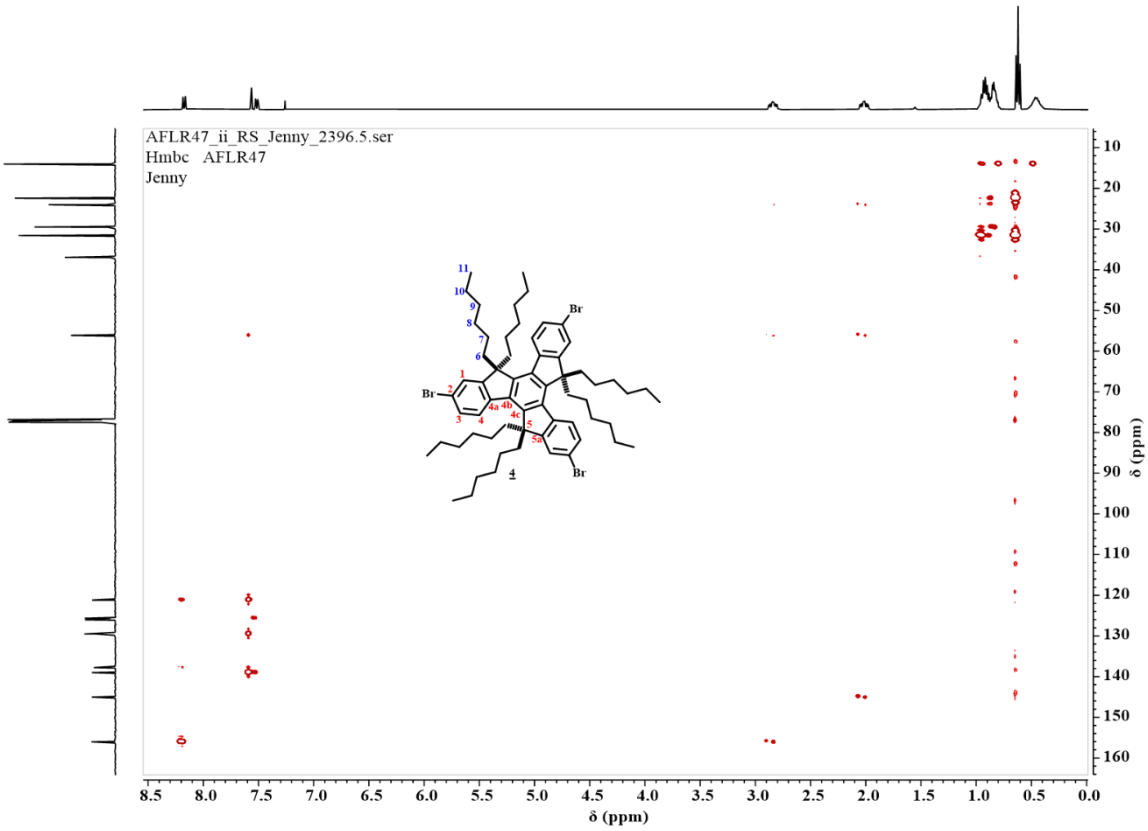
2,7,12-Tribromo-10,15-dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene (***4***)



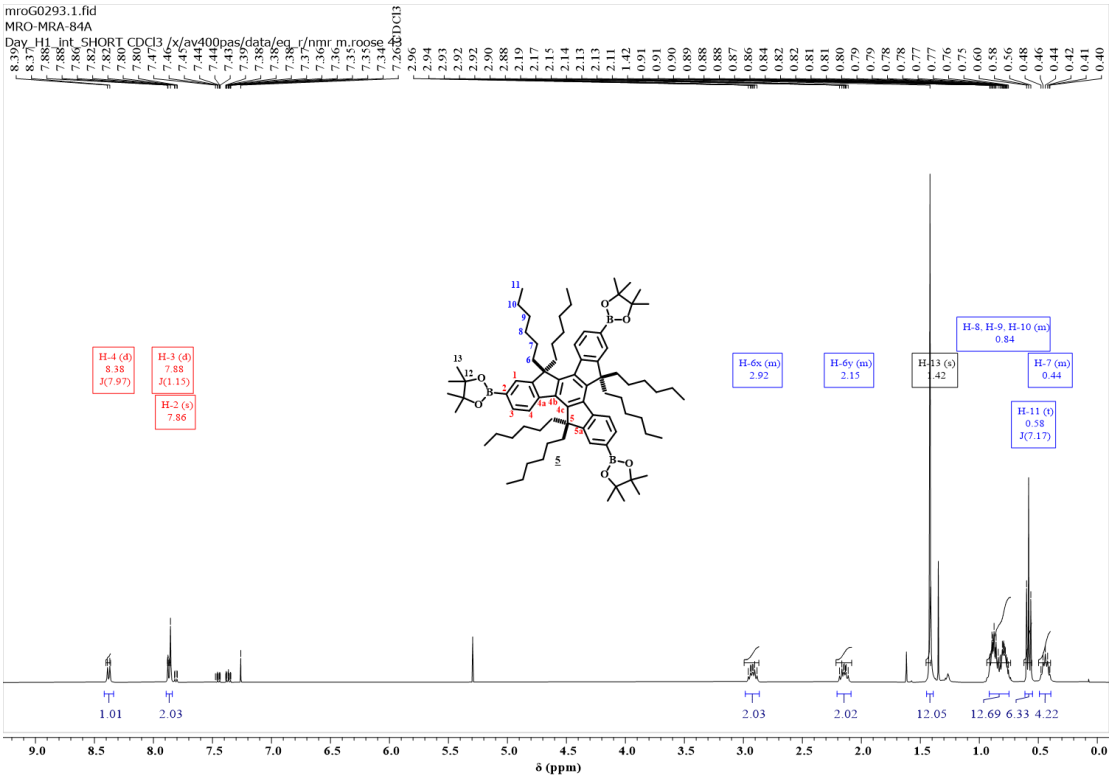


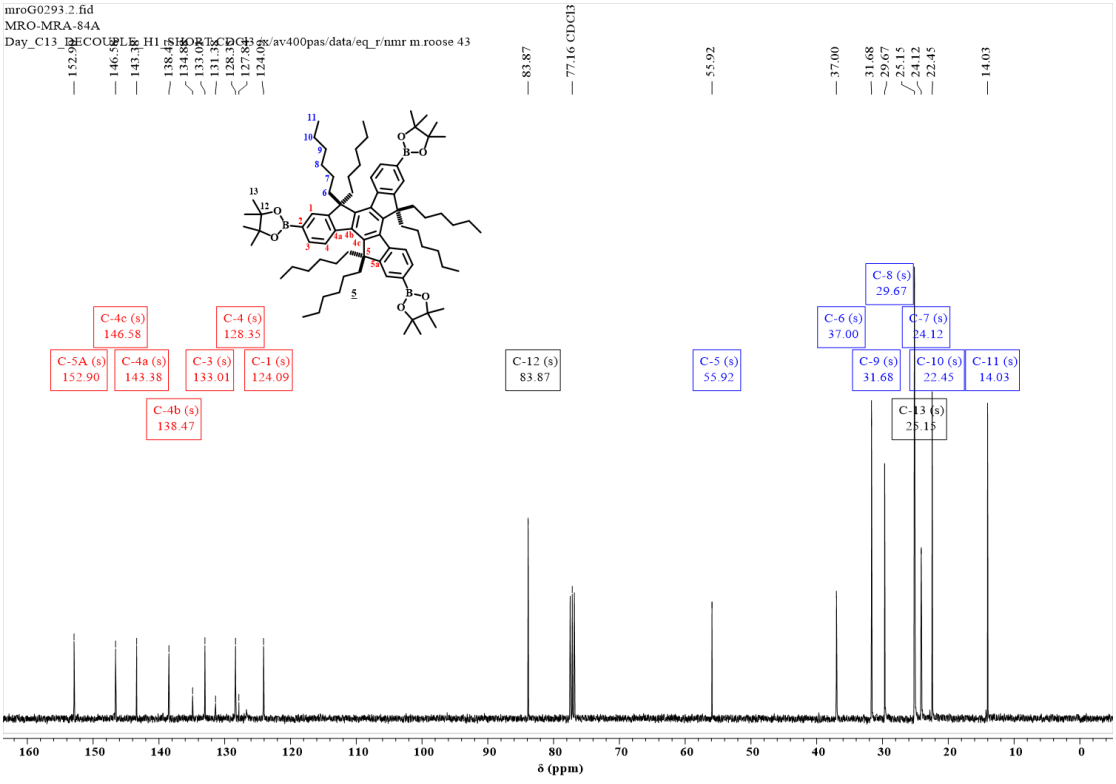

RS_Jenny_2396.3.ser
Cosy AFLR47
Jenny
δ (ppm)
δ (ppm)


AFLR47_ii_RS_Jenny_2396.4.ser
Hsqc AFLR47
Jenny
δ (ppm)
δ (ppm)

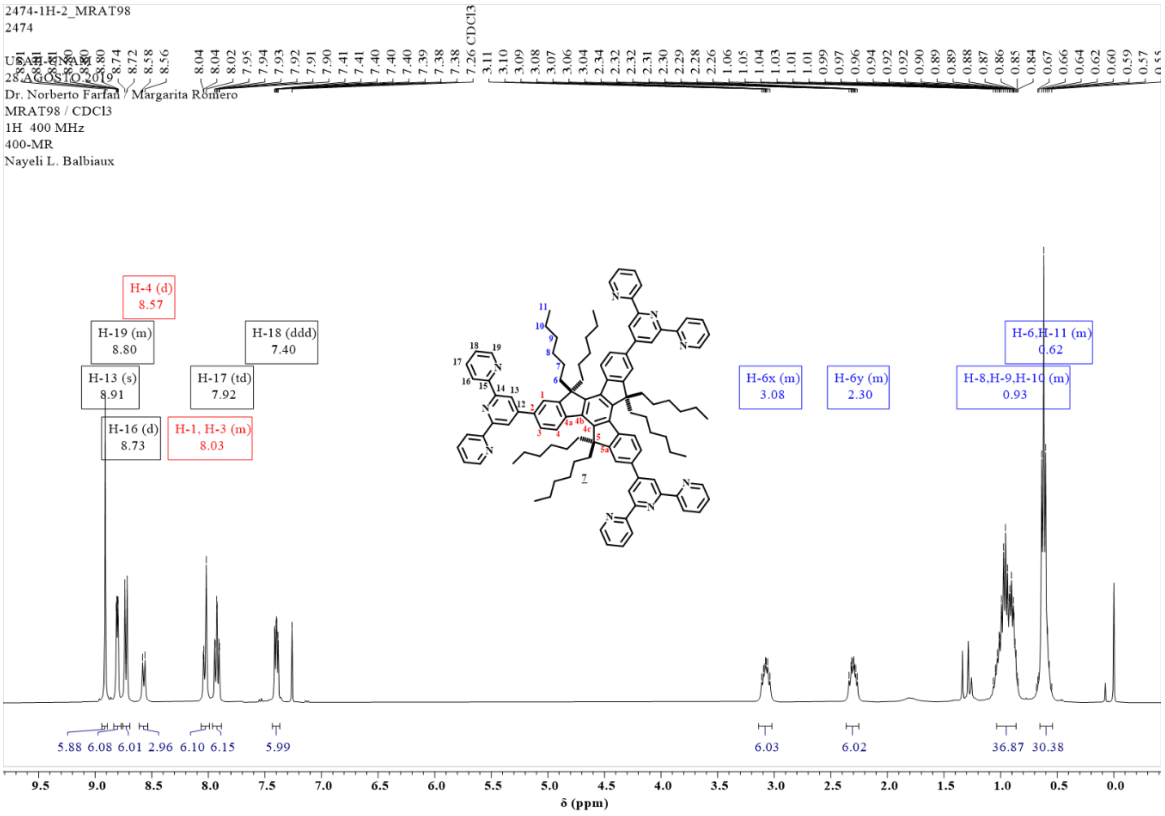

AFLR47_ii_RS_Jenny_2396.5.ser
Hmbc AFLR47
Jenny
Br
Br
Br
δ (ppm)
δ (ppm)

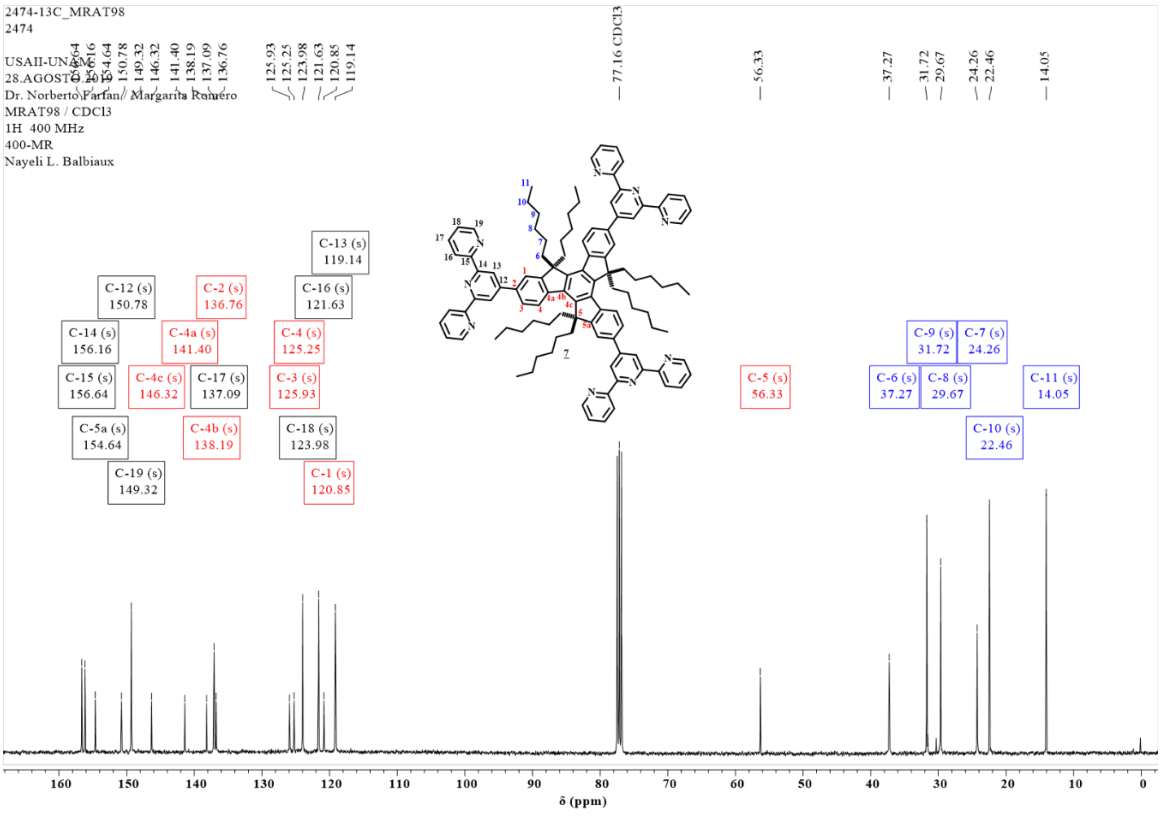
2,7,12-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,15-dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene (***5***)

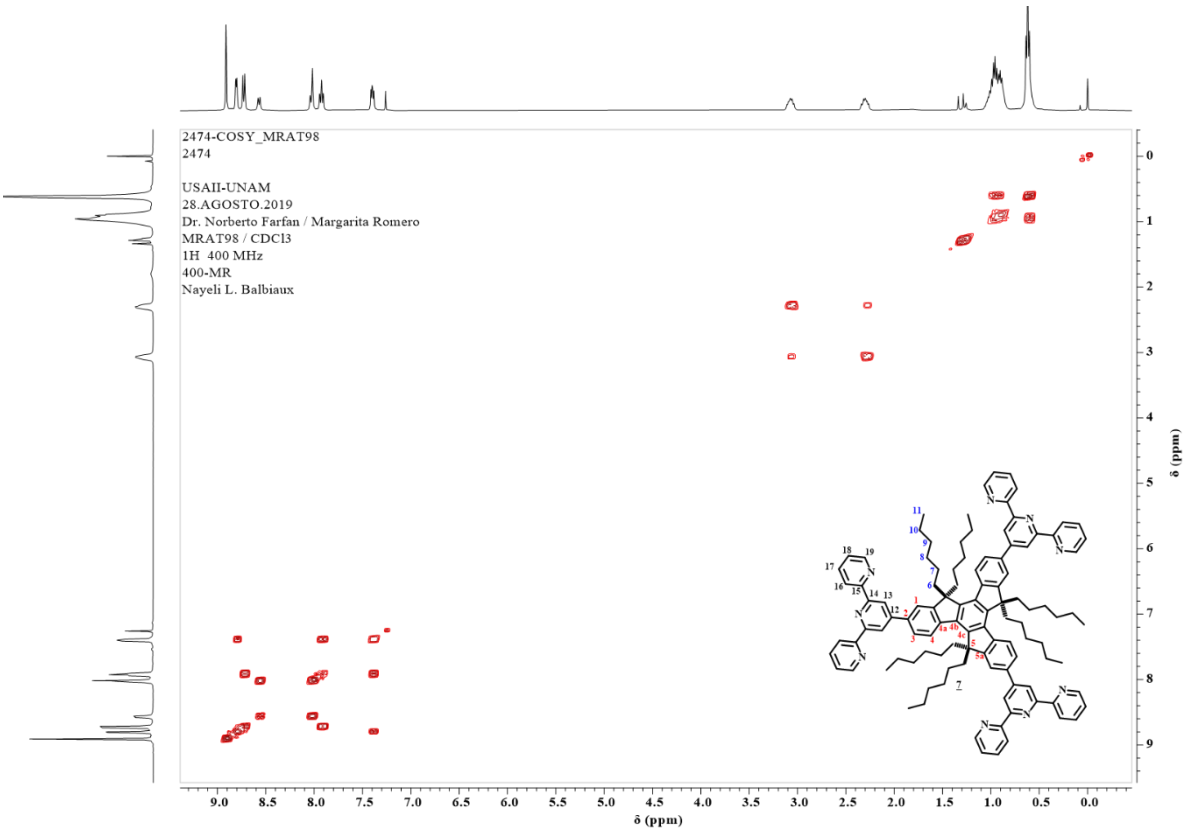


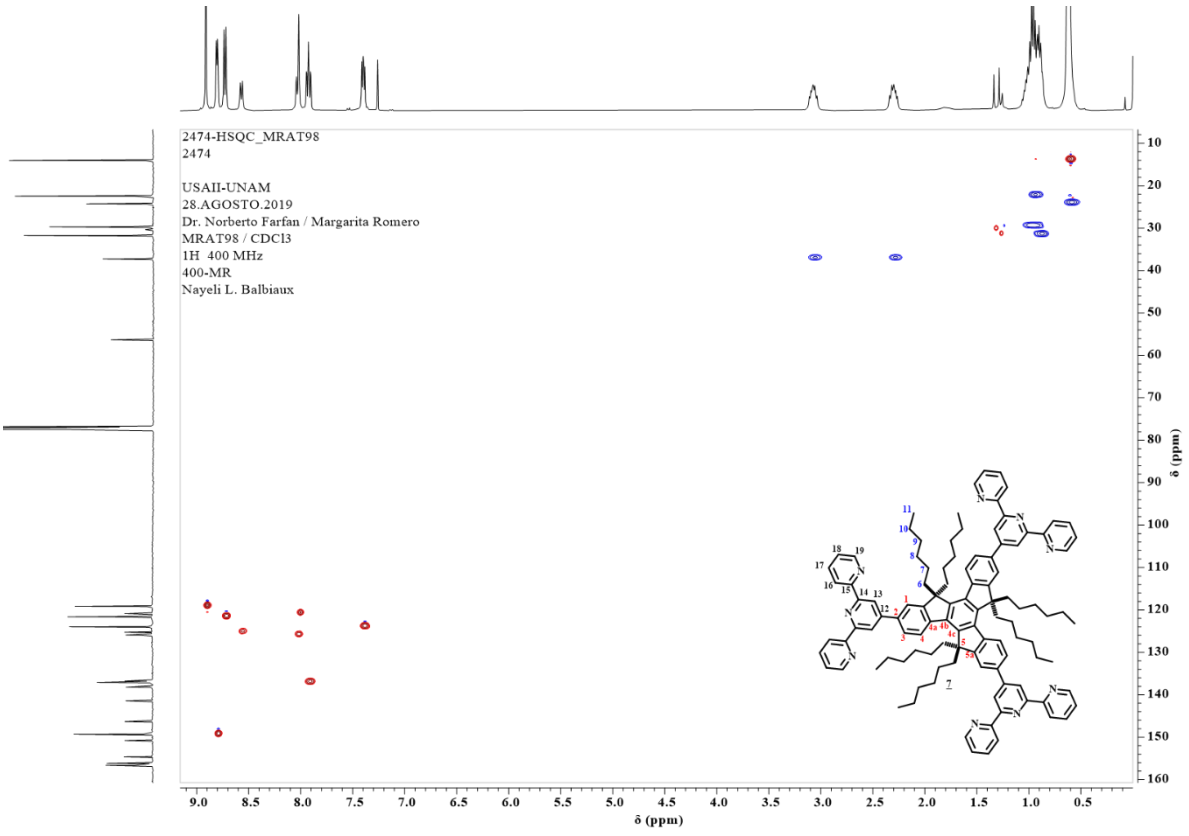


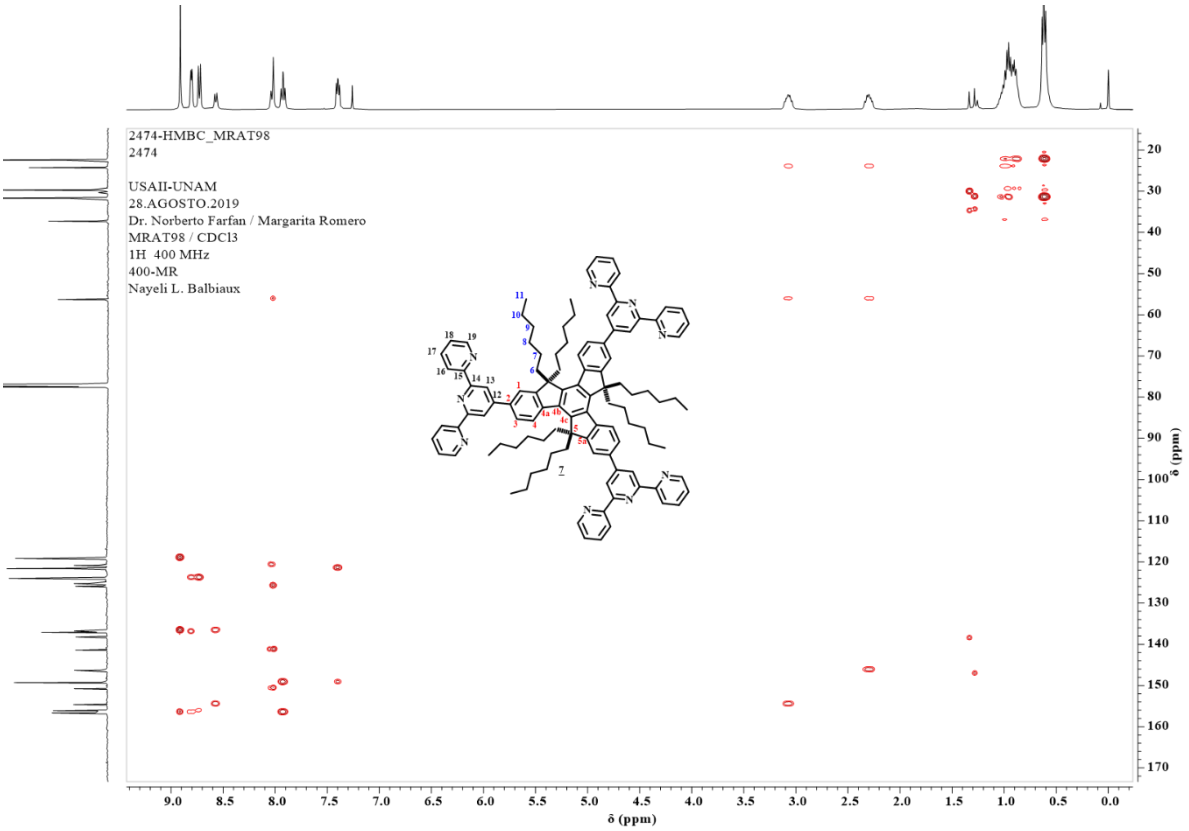
2,7,12-Tris([2,2':6',2''-terpyridin]-4'-yl)-10,15-dihydro-5,5,10,10,15,15-hexahexyl-5*H*-tribenzo[*a*,*f*,*k*]trindene (*Z*)



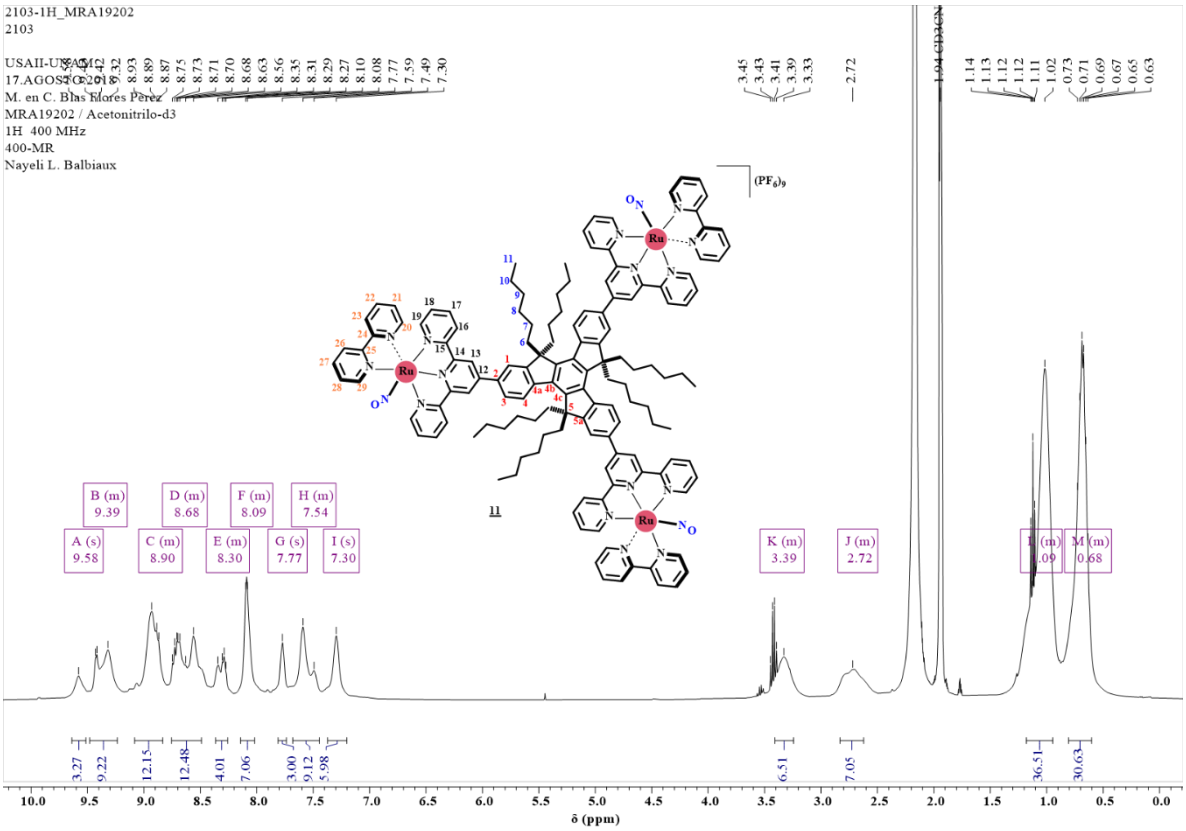


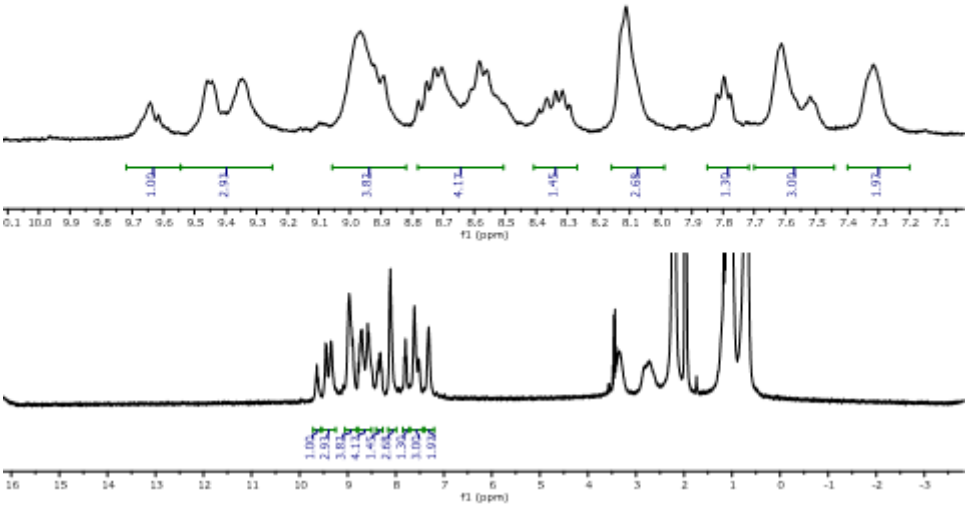

2474-COSY_MRAT98
2474
USAII-UNAM
28.AGOSTO.2019
Dr. Norberto Farfan / Margarita Romero
MRAT98 / CDCl3
1H 400 MHz
400-MR
Nayeli L. Balbiaux
δ (ppm)
δ (ppm)


2474-HSQC_MRAT98
2474
USAII-UNAM
28.AGOSTO.2019
Dr. Norberto Farfan / Margarita Romero
MRAT98 / CDCl3
1H 400 MHz
400-MR
Nayeli L. Balbiaux
δ (ppm)
δ (ppm)


2474-HMBC_MRAT98
2474
USAII-UNAM
28.AGOSTO.2019
Dr. Norberto Farfan / Margarita Romero
MRAT98 / CDCl3
1H 400 MHz
400-MR
Nayeli L. Balbiaux
7
δ (ppm)
δ (ppm)

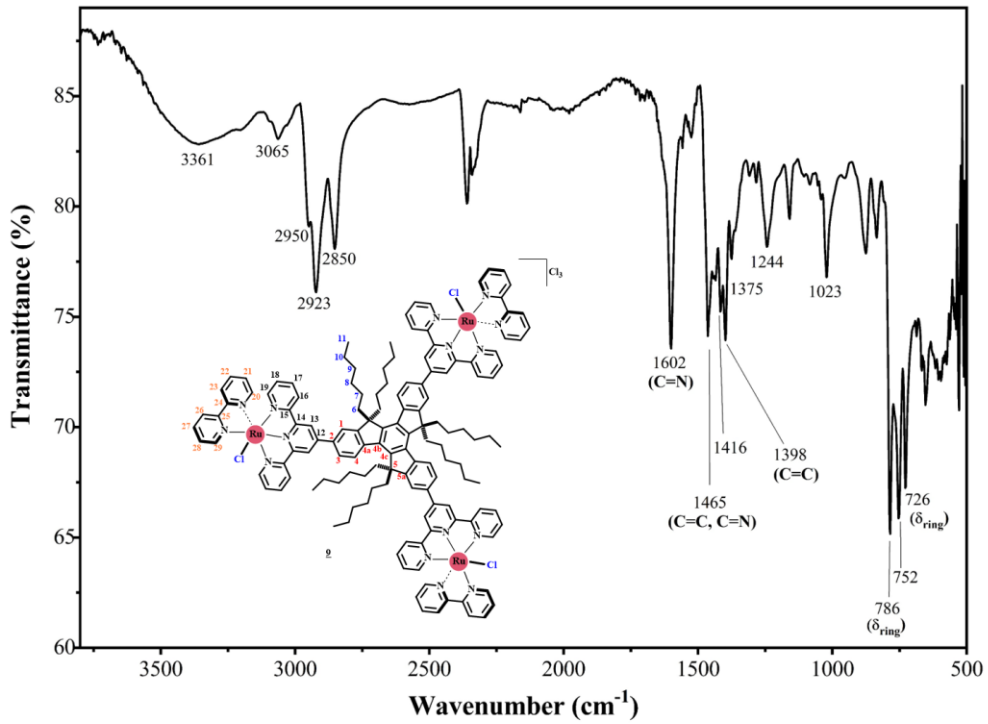
$[Ru_3(TTPYTRUX)(NO)_3(bpy)_3][PF_6]_9$ (***11***)



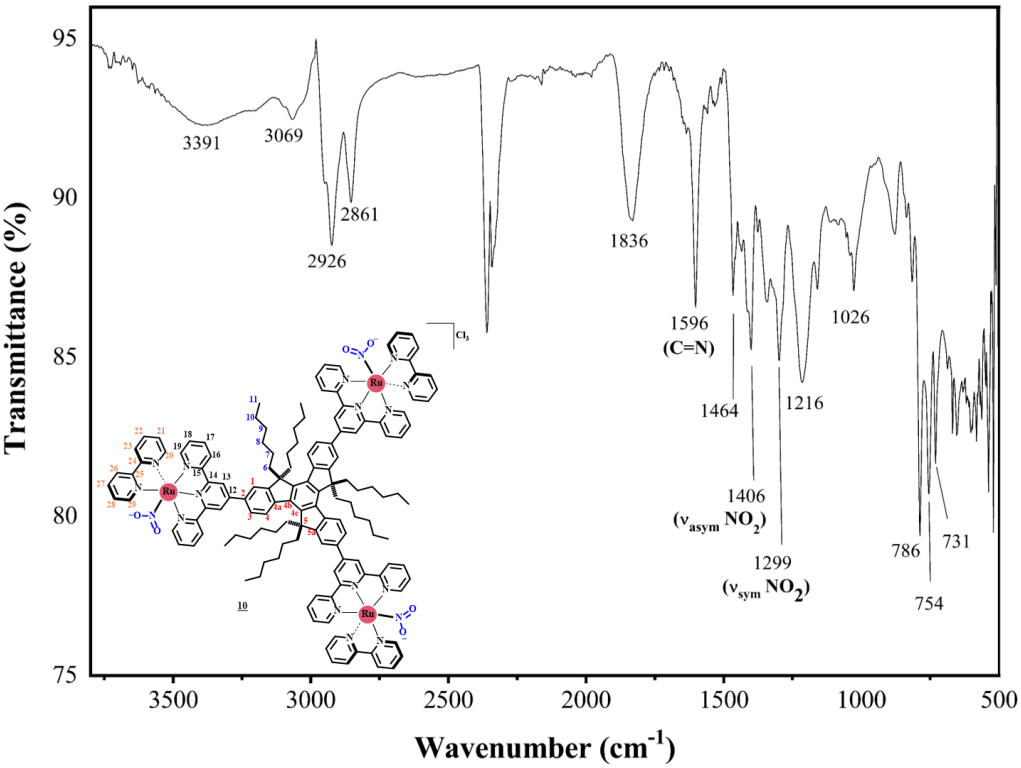


Infra-red spectra

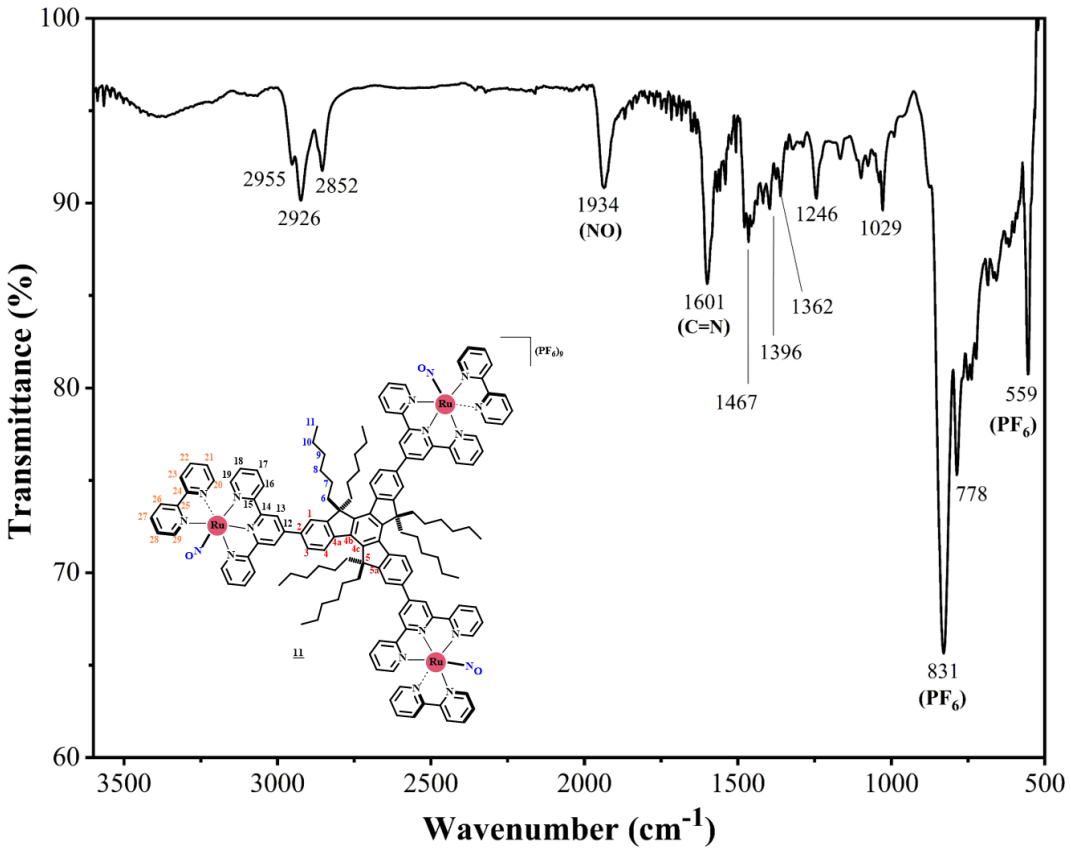
$[Ru_3(TTPYTRUX)(Cl)_3(bpy)_3]Cl_3$ {Abreviación: TTPYTRUX = ligand ***7***} (***9***)



$[Ru_3(TTPYTRUX)(NO_2)_3(bpy)_3]Cl_3$ {Abreviation: TTPYTRUX = ligand ***7***} (***10***)



$[Ru_3(TTPYTRUX)(NO)_3(bpy)_3][PF_6]_9$ {Abreviación: TTPYTRUX = ligand ***7***} (***11***)



4. References

(1) R. Meech, D. Phillips. *J. Photochem.*, 1983, **23**, 193–217.

(2) J. Akl, I. Sasaki, P. G. Lacroix, V. Hugues, P. Vicendo, M. Bocé, S. Mallet-Ladeira, M. Blanchard-Desce, I. Malfant. *Photochem. Photobiol. Sci.*, 2016, **15**, 1484-1491.

(3) A. F. Vanin, A. P. Poltorakov, V. D. Mikoyan, L. N. Kubrina, E. van Faassen. *Nitric oxide : biology and chemistry* 2006, **15**, 295-311.

(4) M.Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. V. Stryland. *IEEE J. Quant. Electron.* , 1990, **26**, 760.

(5) M.Sheik-Bahae, A. A. Said, E. W. V. Stryland. *Opt. Lett.*, 1989, **14**, 955-957.

(6) E. W. V. Stryland, M. Sheik-Bahae. in *Characterization Techniques and Tabulations for Organic Nonlinear Materials*, ed. M. G. Kuzyk and C. W. Dirk, Marcel Dekker, Inc., 1998, pp. 655-692.

(7) P. Sengupta, J. Balaji, S. Banerjee, R. Philip, G. R. Kumar, S. Maiti. *J. Chem. Phys.*, 2000, **112**, 9201-9205.

(8) C. Xu, W. W. Webb. *J. Opt. Soc. Am. B*, 1996, **13**, 481-491.

(9) M. A. Albota, C. Xu, W. W. Webb. *Appl. Opt.*, 1998, **37**, 7352-7356.

(10) G. D. Bradley, W. M. Lawton. *J. Org. Chem.,* 2010, **75**, 8351–8354.

(11) E. V. Dehmolow, T. Kelle. *Synth. Commun.*, 1997, **27**, 2021–2031.

(12) P. Sam-Ang, D. Raksasorn, M. Sukwattanasinitt, P. Rashatasakhon. *RSC Adv.*, 2014, **4**, 58077–58082.

(13) A. L. Kanibolotsky, R. Berridge, P. J. Skabara, I. F. Perepichka, D. D. C. Bradley, M. Koeberg. *J. Am. Chem. Soc.*, 2004, **126**, 13695–13702.

(14) W. D. Xu, W. Y. Lai, Q. Hu, X. Y. Teng, X. W. Zhang, W. Huang. *Polym. Chem.*, 2014, **5**, 2942–2950.

(15) C. P. Lin, P. Florio, E. M. Campi, C. Zhang, D. P. Fredericks, K. Saito, W. Roy Jackson, M. T. W. Hearn. *Tetrahedron*, 2014, **70**, 8520–8531. To consult the ^{1}H NMR data see: Jürgen, S. *Eur. J. Org. Chem.*, 1999, **1999,** 313-321.