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Star-Shaped Triazine-Cored Ladder-Type Ter(*p*-phenylene)s for High-Performance Multiphoton Absorption and Amplified Spontaneous Blue Emission

Lei Guo, Xiao Liu, Tongxin Zhang, Hai-Bin Luo, Hai Hua Fan, and Man Shing Wong**

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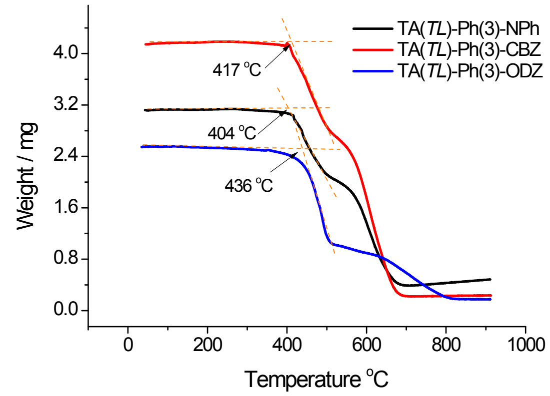


Fig. S1 Thermogravimetric traces of the star-shaped triazine-cored ladder-type oligo(*p*-phenylene)s.

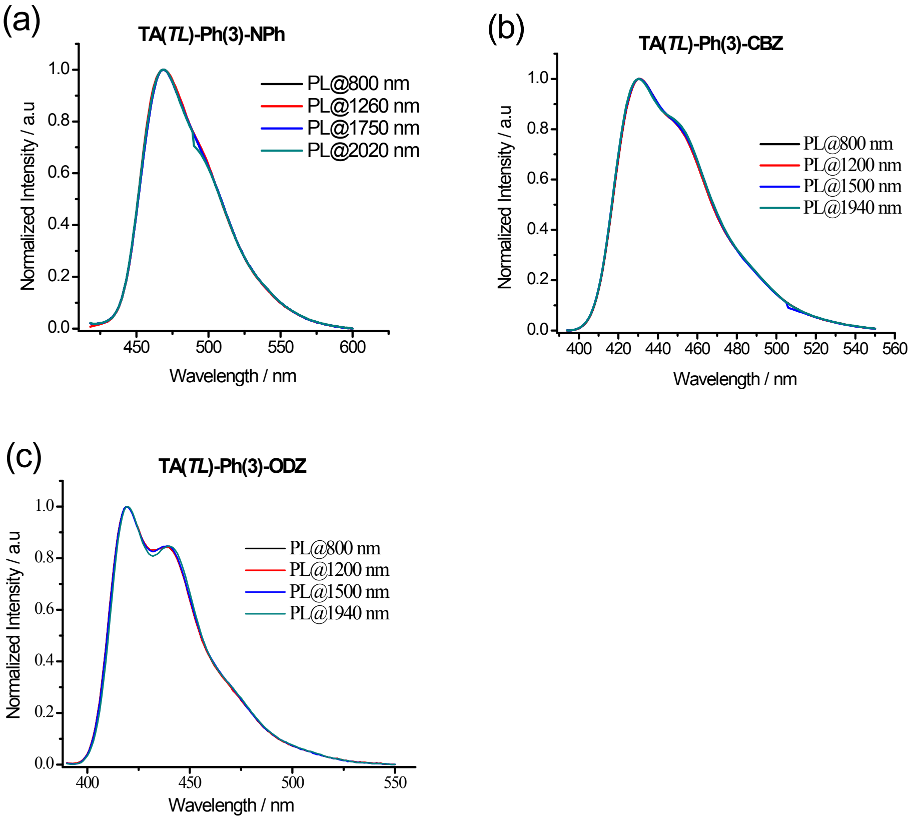


Fig. S2 Multiphoton absorption induced fluorescence spectra of (a) TA(*TL*)-Ph(3)-NPh, (b) TA(*TL*)-Ph(3)-CBZ and (c) TA(*TL*)-Ph(3)-ODZ, respectively, excited at 800 nm in toluene (1×10^{-4} mol/L) and other wavelengths in toluene (1×10^{-2} mol/L), respectively.

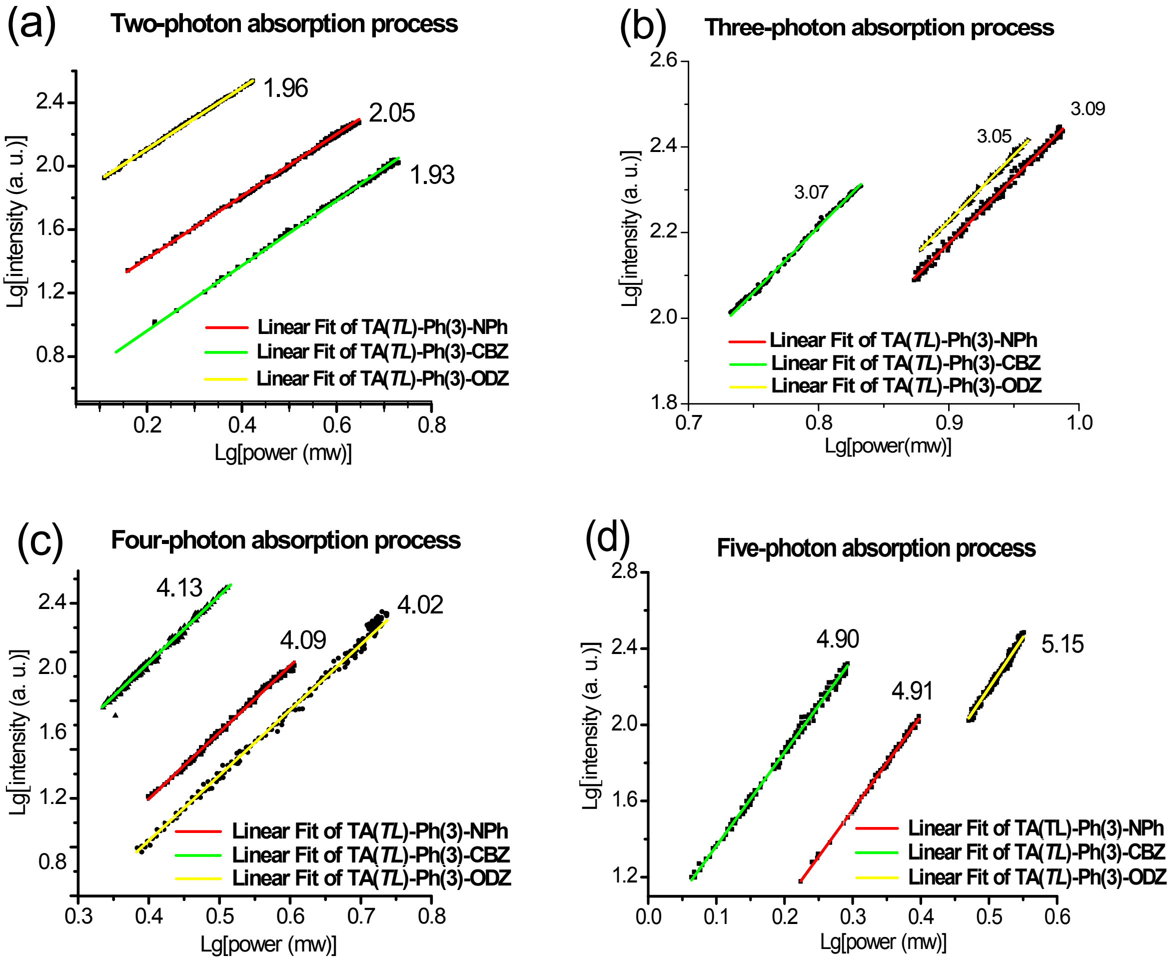


Fig. S3 Logarithmic plots of the power dependence of relative multiphoton-induced fluorescence intensity versus input pulse intensity by femtosecond laser pulses excited at 800, 1200, 1500 and 1900 nm, respectively, for TA(*TL*)-Ph(3)-CBZ and TA(*TL*)-Ph(3)-ODZ, and at 800, 1260, 1750 and 2020 nm for TA(*TL*)-Ph(3)-NPh. The color solid lines are the best-fit straight lines for (a) two-photon absorption process; (b) three-photon absorption process; (c) four-photon absorption process; and (d) five-photon absorption process, respectively.

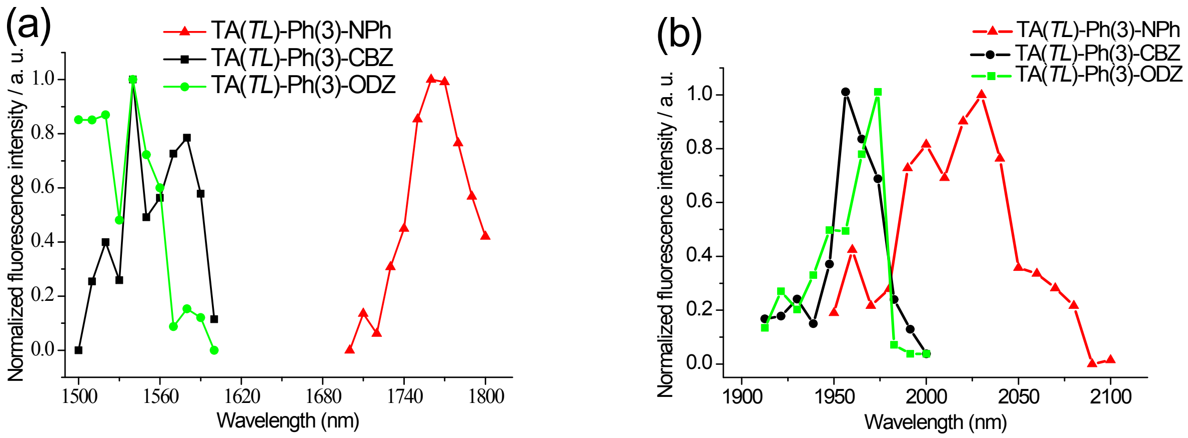


Fig. S4 (a) Four-photon and (b) five-photon excited spectra of the star-shaped triazine-cored ladder-type *ter*(*p*-phenylene)s measured in toluene (1 × 10^{-2} mol/L) by femtosecond laser pulses.

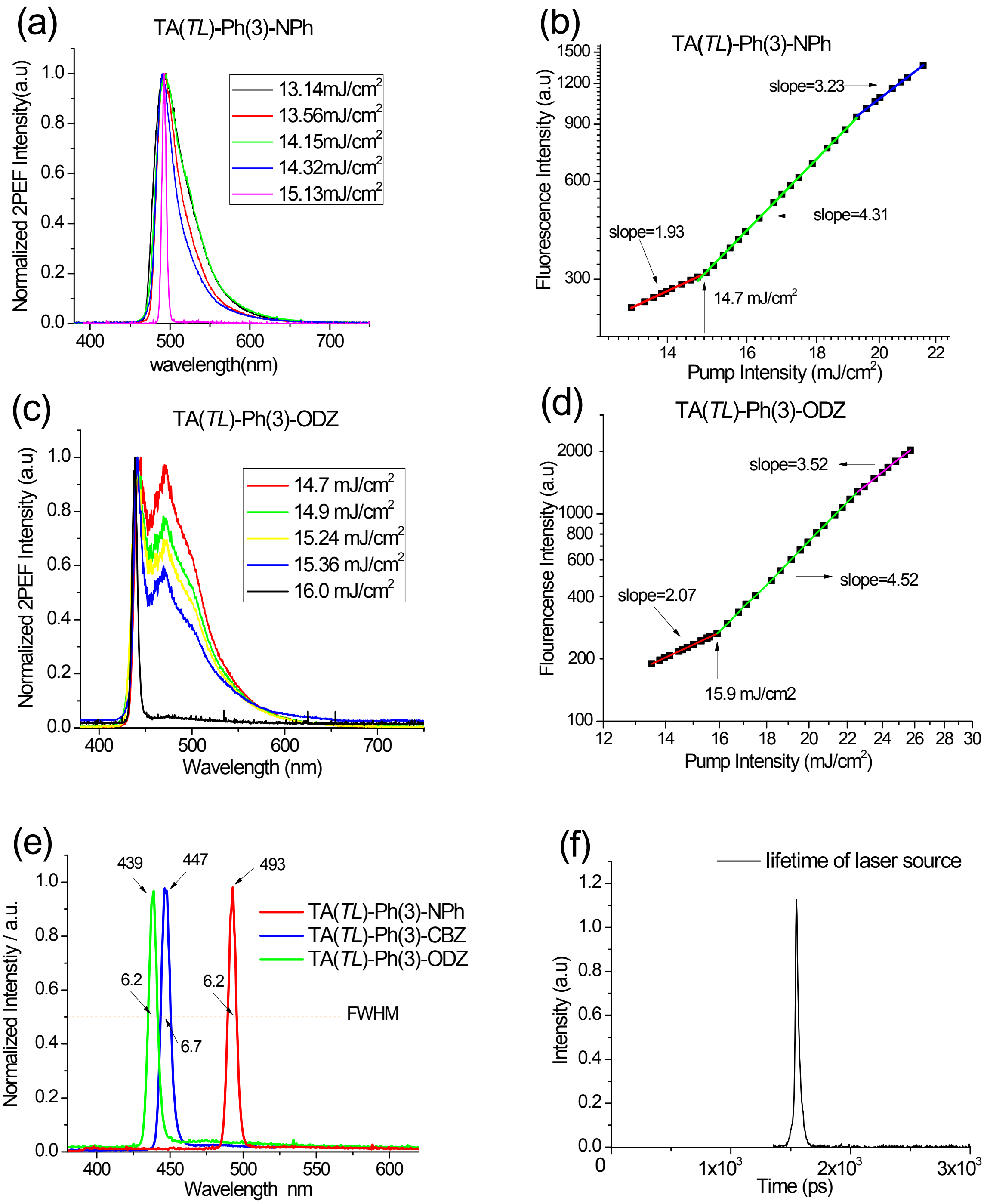


Fig. S5 (a) Normalized PL emission spectra of TA(*TL*)-Ph(3)-NPh in toluene under different incident laser fluences pumped at 800 nm; (b) Plots of input pumped energy vs. integrated emission intensity for TA(*TL*)-Ph(3)-NPh in toluene (1×10^{-2} mol/L); (c) Normalized PL emission spectra of TA(*TL*)-Ph(3)-ODZ in toluene under different incident laser fluences pumped at 800 nm; (d) Plots of input pumped energy vs. integrated emission intensity for TA(*TL*)-Ph(3)-ODZ in toluene (1×10^{-2} mol/L; (e) 2PP ASE spectra of TA(*TL*)-Ph(3)-NPh, TA(*TL*)-Ph(3)-CBZ and TA(*TL*)-Ph(3)-ODZ in toluene (1×10^{-2} mol/L); (f) The temporal behavior of laser source with the 120 femtosecond pulse width resulted in the single exponential fitting result of life time with $\tau = 26.3$ ps on account of the accuracy limitation of the lifetime measurement in the picosecond range.

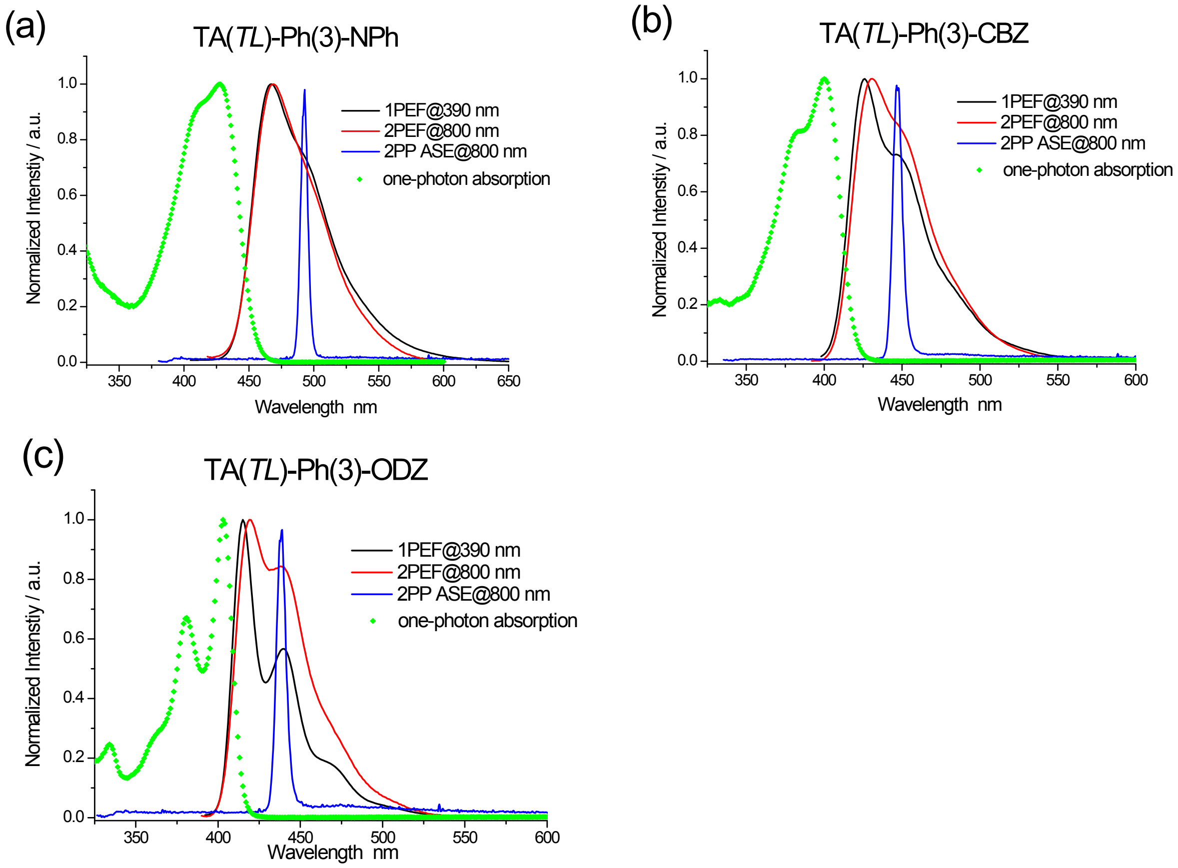


Fig. S6 One-photon absorption (1×10^{-6} mol/L), One-photon excited fluorescence (1×10^{-6} mol/L), two-photon excited fluorescence (1×10^{-4} mol/L) and two-photon pumped ASE (1×10^{-2} mol/L) spectra in toluene of (a) TA(*TL*)-Ph(3)-NPh, (b) TA(*TL*)-Ph(3)-CBZ and (c) TA(*TL*)-Ph(3)-ODZ, respectively.

Experimental Procedures

General Procedures and Requirements

All the solvents were dried by the standard methods wherever needed. The palladium catalysts including $Pd(dppf)_2Cl_2$, $Pd(PPh_3)_4$ and $Pd(OAc)_2$ were purchased from Aldrich. Other chemicals were purchased from Dieckmann (Hong Kong) Chemical Industry Co. Ltd. including diethyl 2,5-dibromoterephthalate, bis(pinacolato)diboron, *n*-BuLi (2.5 mol/L / 1.6 mol/L) and 1-bromo-4-decylbenzene. ^{1}H NMR spectra were recorded by using a Bruker advanced-III 400 NMR spectrometer at 400 MHz with a reference of the residual $CHCl_3$ 7.26 ppm. ^{13}C NMR spectra were recorded by using a Bruker advanced-III 400 NMR spectrometer at 100 MHz with a reference of the residual $CHCl_3$ 77.16 ppm. Mass spectrometric (MS) measurements were carried out via matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) technique by using Bruker autoflex MALDI TOF MS. The experimental conditions were followed: After the sample was dissolved in CH_2Cl_2 with DCTB (CAS No.: 300364-84-5) as matrix, 1ul of the sample solution was dropped on that 1ul dried matrix spot and dried. After that, the sample went to MS for analysis. Elemental analysis (C, N, H) test was performed by using Vario EL cube elemental analyzer. Thermal stability was determined by thermal gravimetric analyzer (PE-TGA6) with a heating rate of 10 ˚C/min under N_2. All the physical measurements were performed in toluene including electronic absorption (UV-Vis) recorded by a Varian Cary 100 Scan Spectrophotometer and fluorescence spectra determined by a PTI Luminescence Spectrophotometer. The fluorescence quantum yields were determined by dilution method in toluene using norharman ($\Phi_{330\sim390\text{nm}} = 0.58$) as a standard.

Multiphoton Absorption Measurements

The two-photon absorption (2PA) cross-section was measured by the 2PA induced fluorescence method. The 2PA cross-section, σ_2 was determined by comparing their 2PA induced up-converted fluorescence to that of Rhodamine 6G (both at the concentration of 1×10^{-4} mol/L).

$$\sigma_2 = \sigma_{2r}\frac{\phi_r c_r n_r S}{\phi c n S_r}$$

Equation S1

Where Φ is the fluorescence quantum yield assuming equal one- and two-photon fluorescence quantum yields, c is the concentration of solution, n is the refractive index, and S is the integrated intensity of up-conversed fluorescence. σ_2 is the two-photon excitation cross-section. The r subscript refers to the standard reference solution.

For the femtosecond pulse experiment, the excitation source is an optical parametric amplifier (OPA) (Light Conversion Topas-C) pumped by a mode-locked Ti: sapphire laser oscillator (Coherent Mira)–amplifier system (Coherent Legend). The pulse width of the laser is 130 fs, and its repetition rate is 1 kHz. The fluorescence is collected by a telescope system which consists of a lens f = 7.5 cm and a lens f = 30 cm. A monochromator connected with a PMT is used as the recorder for the MPA induced up-converted fluorescence. In the 3-photon absorption cross-section measurements, since self-focusing is a 3-order nonlinear process while 3- and 4-photon absorption are 5- and 7-order nonlinear process, self-focusing generally occurs before 3- and 4-photon absorption becomes significant if the medium is sufficiently long. For the experiment of the measurements of up-conversion fluorescence and the 3-photon absorption cross-section, self-focusing must be avoided. The method is to fill the solutions in a 1 mm quartz cell. The excitation fs laser beam is focused by a lens with f = 15 cm, and the cell is placed 2 cm behind the focused plane. The lifetime of the sample is measured by the spectrograph (Spectra Pro HRS-300) connected with a Streak-Camera (OPTOSCOPE SC 10 with SRU-BA). The Temporal resolution is 25 ps for this system.

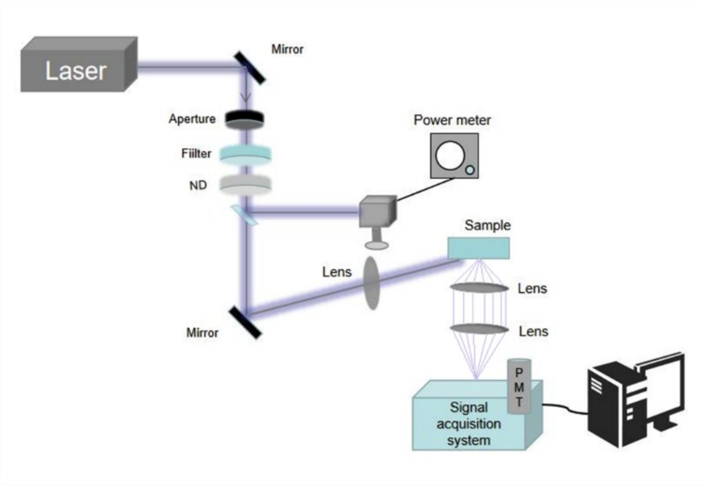


Fig. S7 The experiment setup of up-converted fluorescence measurement.

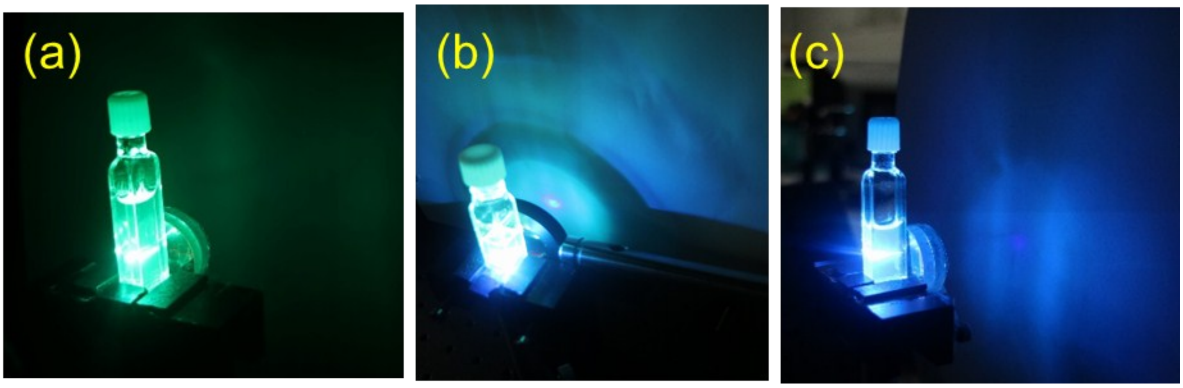
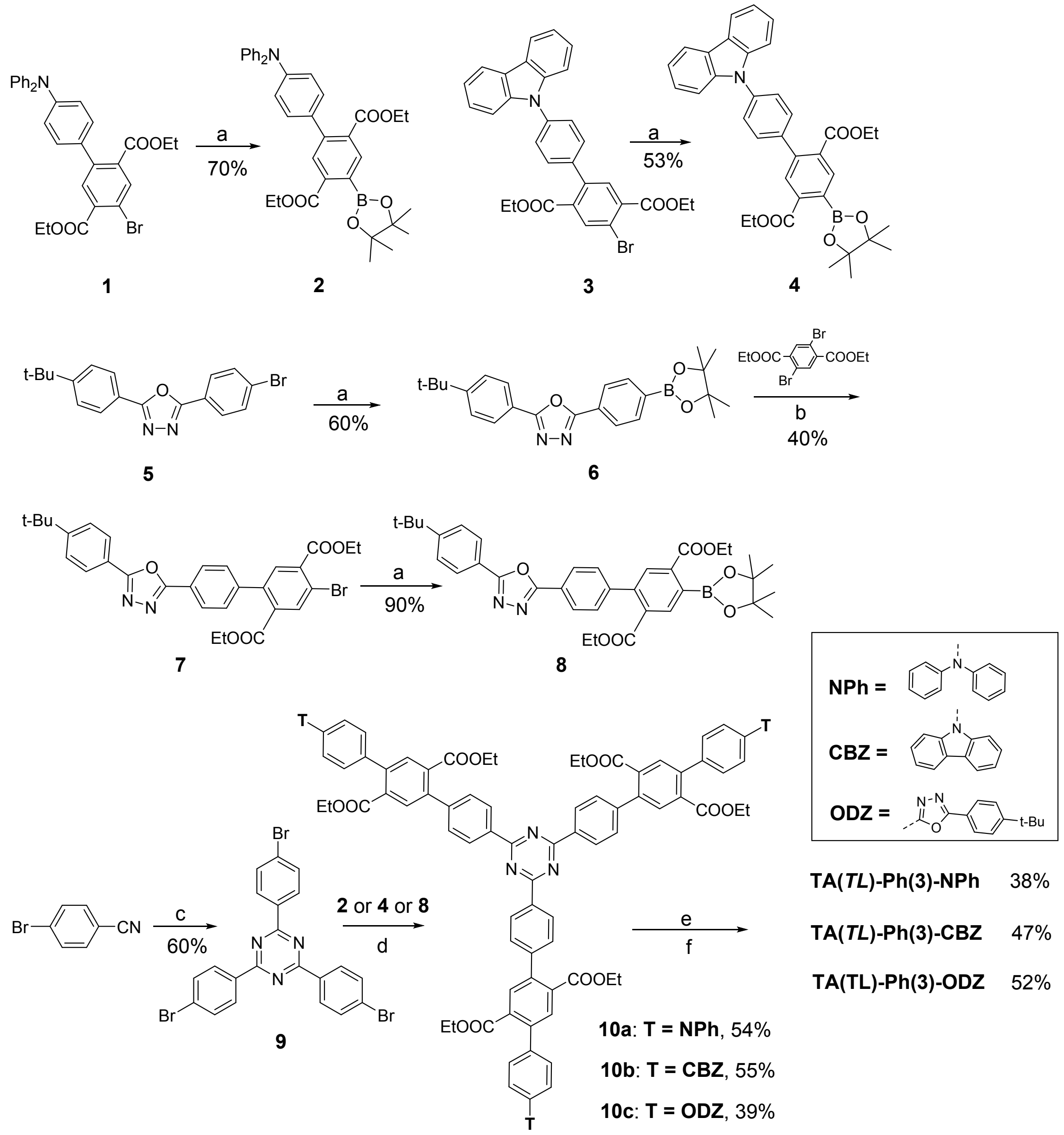


Fig. S8 Photographs of highly directional, frequency-upconverted stimulated (blue) emission of TA(*TL*)-Ph(3)-NPh (a), TA(*TL*)-Ph(3)-CBZ (b) and TA(*TL*)-Ph(3)-ODZ (c), respectively.



Reagents and Conditions: (a) $PdCl_2$(dppf), bis(pinacolato)diboron, KOAc, 1,4-dioxane, 80 °C; (b) $Pd(OAc)_2$, PPh_3, 4 mol/L K_2CO_3, H_2O/EtOH/toluene, 75 ~ 80 °C; (c) F_3CSO_3H, $CHCl_3$, 0 °C to r.t.; (d) $Pd(OAc)_2$, PPh_3, K_2CO_3, H_2O/EtOH/toluene, reflux; (e) 1-bromo-4-decylbenzene, *n*-BuLi, THF, -70 °C, 1.5 h, then r.t. overnight; (f) BF_3OEt_2, CH_2Cl_2, 24 h.

Scheme S1. The synthetic route of the star-shaped triazine-cored ladder type *ter*(*p*-phenylene)s.

Synthetic Procedures:

The starting intermediates depicted in Scheme S1 were synthesized according to the literature protocols including compound **1**,[1] **3**,[1] and **5**[2].

Synthesis of compound **2**. A mixture of compound **1** (1.41 g, 2.58 mmol), bis(pinacolato)diboron (1.31 g, 5.16 mmol), potassium acetate (1.27 g, 12.9 mmol), 1,4-dioxane (45 mL) and $PdCl_2$(dppf) (50 mg) was heated at 80 °C for 24 h under nitrogen atmosphere. After solvent removal under vacuum, the residue was diluted with water and extracted with ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous sodium sulfate and evaporated to dryness to afford a black grey solid. The crude product was purified through a short silica gel column chromatography to afford a white solid product of 1.07 g (70% yield) which was directly used in the next step.

Synthesis of compound **4**. To a 250 mL two-necked round bottom flask containing compound **3** (5.1 g, 9.41 mmol), bis(pinacolato)diboron (4.78 g, 18.8 mmol), anhydrous KOAc (3.7 g, 37.7 mmol) and $PdCl_2$(dppf) (0.15 g, 0.184 mmol) was added anhydrous 1,4-dioxane (120 mL). The reaction mixture was heated at 80 °C and stirred under argon protection for 24 hours. Solvent was evaporated in *vacuo* and the residue was diluted with water. The aqueous solution was extracted with dichloromethane twice. The organic layer was combined and dried over anhydrous Na_2SO_4. The crude product was purified via column chromatography to afford the yellow powder of 2.94 g with 53 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.13 (d, *J* = 7.7 Hz, 2H), 8.04 (d, 16 Hz, 2H), 7.57 (m, 4H), 7.43 (m, 4H), 7.28 (m, 2H), 4.44 (q, *J* = 7.2 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.55 (m, 12H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 168.3, 167.3, 142.1, 140.8, 139.8, 137.2, 136.6, 137.2, 136.6, 134.1, 134.0, 130.6, 130.0, 126.7, 126.1, 123.5, 120.5, 120.2, 109.8, 84.5, 75.0, 67.1, 61.7 (d), 25.0, 24.9, 24.6. MS (MALDI-TOF, m/z) [M^+] found 589.2680

Synthesis of compound **6**. To a 500 mL round bottom flask conatining compound **5** (7.48 g, 20.93 mmol), bis(pinacolato)diboron (10.63 g, 41.86 mmol), KOAc (8.22 g, 83.74 mmol) and $PdCl_2$(dppf) (0.34 g, 0.42 mmol) was added 1,4-dioxane (360 mL) with stirring under N_2 protection. The reaction mixture was heated at 80°C for 24 hours. Solvent was evaporated under vacuum and then diluted with water. The aqueous solution was extracted with DCM twice. The organic layer was combined and dried over anhydrous Na_2SO_4. The crude product was purified via column chromatography to afford a yellow oil of 7.46 g with 60 % yield, which was directly used in the next step.

Synthesis of compound **7.** To a 250 mL two-necked round bottom flask containing compound **6** (7.46 g, 18.46 mmol), diethyl 2,5-dibromoterephthalate (14.02 g, 36.89 mmol), palladium (II) acetate (471 mg), triphenylphosphine (96 mg), 4 mol/L potassium carbonate (10 mL) were added ethanol (30 mL) and toluene (150 mL) with stirring. The reaction mixture was heated at 55 °C with nitrogen protection for 24 hours. After cooling down to room temperature, the mixture was quenched with water and acidified with 6 mol/L hydrochloric acid (15 mL). Thereafter, the aqueous layer was extracted with ethyl acetate twice and the combined organic phase was dried over anhydrous sodium sulphate. The crude product was purified via column chromatography to afford a white solid of 4.31 g in 40 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.21-8.15 (m, 3H), 8.08 (d, J = 8.6 Hz, 2H), 7.77 (s, 1H), 7.57 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.36 (s, 9H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 166.0, 165.4, 164.9, 164.0, 155.5, 142.9, 140.3, 135.7, 135.1, 134.2, 132.9, 129.1, 126.8(d), 126.1, 123.5, 121.0, 120.8, 62.0 (d), 35.1, 31.1, 14.0 (d). MS (MALDI-TOF, m/z) $[M+H]^+$ found 579.1328.

Synthesis of compound **8**. To a 250 mL two-necked round bottom flask containing compound **7** (4.31 g, 7.46 mmol), bis(pinacolato)diboron (3.81 g, 15.0 mmol), KOAc (2.92 g, 29.75 mmol) and $PdCl_2$(dppf) (1.22 g, 1.49 mmol) was added 1,4-dioxane (120 mL) with stirring under N_2 protection. The reaction mixture was heated 80 °C for 24 hours. Solvent was removed by rotary evaporator and then the residue was diluted with water. The aqueous solution was extracted with ethyl acetate twice. The combined organic layer was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude product was purified with silica gel column chromatography to afford a white solid of 4.26 g with 90 % yield, which was directly used in the next step.

Synthesis of compound **9** was according to the literature procedure.[3] To a vigorously stirred solution of trifluoromethanesulfonic acid (2 mL, 22 mmol) in dry chloroform (5 mL) at 0 °C was added 4-bromobenzonitrile (2.0 g, 11 mmol) in dry chloroform (30 mL) dropwise. The reaction was slightly exothermic upon addition of the latter solution. Stirring was continued for 2 h at 0 °C. The mixture was further stirred for 24 h at ambient temperature. It was then poured into water containing a small amount of ammonium hydroxide. The organic layer was washed four times with water and then dried over anhydrous sodium sulphate. The solvent was evaporated *in vacuo*. The residue was recrystallized from chloroform to afford a white solid of 1.2 g in 60 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.56 (d, *J* = 8.5 Hz, 6H), 7.68 (d, *J* = 8.5 Hz, 6H).

Synthesis of compound **10a**. A mixture of compound **2** (1.86 g, 3.14 mmol), compound **9** (0.429 g, 0.786 mmol), palladium(II) acetate (70 mg, 0.31 mmol), triphenylphosphine (99 mg, 0.63 mmol), 4 mol/L potassium carbonate (3 mL), ethanol (10 mL) and toluene (40 mL) in a 100 mL round-bottom flask was refluxed for 30 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, acidified by 3 mL of 6 mol/L HCl and extracted with CH_2Cl_2 twice. The combined organic layer was dried over anhydrous Na_2SO_4, evaporated to dryness and the residue was purified by silica gel column chromatography to afford a yellow solid of 0.74 g (54 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.88 (d, *J* = 8.0 Hz, 6H), 7.92 (s, 3H), 7.86 (s, 3H), 7.60 (d, *J* = 8.0 Hz, 6H), 7.31-7.26 (m, 19H), 7.16-7.12 (m, 17H), 7.08-7.04 (m, 6H), 4.24-4.16 (m, 12H), 1.16 (t, *J* = 6.8 Hz, 9H), 1.08 (t, *J* = 6.8 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.5, 168.4, 167.9, 147.7(d), 144.7, 141.1, 140.2, 135.5, 133.8, 133.7, 133.4, 132.1, 131.8, 129.4, 129.0, 124.7, 123.3, 123.1, 61.6 (d), 14.0. HRMS (MALDI-TOF, m/z) [M$^+$] Calcd. For $C_{111}H_{90}N_6O_{12}$, 1699.6643, Found 1699.6647.

Synthesis of compound **TA(*TL*)-Ph(3)-NPh**. To a flame-dried 100 mL two necked round-bottom flask under nitrogen protection was added 1-bromo-4-decylbenzene (1.77 g, 5.96 mmol) and anhydrous THF (15 mL). The solution was cooled to –78 °C and 2.5 mol/L *n*-BuLi (1.8 mL, 4.5 mmol) was added dropwise over 15 min. The reaction mixture was stirred at –70 °C for another 1.5 h before compound **10a** (312 mg, 0.184 mmol) in 5 mL THF was added. The reaction was allowed to warm up to r.t. and stirred overnight before being quenched with 1 mol/L HCl (20 mL) at 0 °C. The reaction mixture was diluted with ethyl acetate and extracted with ethyl acetate twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated in *vacuo*, affording yellow oil which was used directly in the next step. To a solution of the above mixture dissolved in 40 mL CH_2Cl_2 was added boron trifluoride etherate (0.05 mL). The solution mixture was stirred for 24 hours at room temperature before being quenched with water. The reaction mixture was extracted with CH_2Cl_2 twice. The combined organic layer was washed with water, dried over anhydrous sodium sulfate, filtered and concentrated in *vacuo*. The crude product was purified by silica gel column chromatography affording a yellow solid of 276 mg in 38 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.66 (s, 3H), 8.59 (d, *J* = 8.0 Hz, 3H), 7.78-7.76 (m, 6H), 7.71 (s, 3H), 7.53 (d, *J* = 8.0 Hz, 3H), 7.22-7.12 (m, 37H), 7.08-6.88 (m, 47H), 2.59-2.49 (m, 24H), 1.60-1.52 (m, 24H), 1.31-1.23 (m, 168H), 0.89-0.82 (m, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.5, 153.7, 152.6, 152.1, 151.1, 147.7, 147.5, 144.6, 143.3, 143.2, 141.4(d), 141.0, 138.6, 135.5, 134.7, 128.6(d), 128.4, 128.3, 127.9, 126.9, 124.2, 123.3, 122.8, 121.9, 120.9, 120.0, 118.7, 117.6, 64.8, 64.7, 35.8, 35.7, 32.1, 31.6, 29.9, 29.8, 29.7(t), 29.5, 22.9, 22.8, 14.3(d). HRMS (MALDI-TOF, m/z) $[M+H]^+$ For $C_{291}H_{354}N_6$, 3936.8058, Found 3936.8021. Anal. Calcd. for $C_{291}H_{354}N_6$: C 88.80; H 9.07; N 2.14; Found: C 88.95, H 9.26, N 1.82.

Synthesis of compound **10b**. To a 100 mL two-necked round bottom flask, compound **4** (1.47 g, 2.49 mmol), compound **9** (0.344 g, 0.63 mmol), palladium (II) acetate (56 mg), triphenylphosphine (0.262 g, 1.0 mmol), 4 mol/L potassium carbonate (2 mL), ethanol (10 mL) and toluene (30 mL) were added with stirring. The reaction mixture was refluxed at 80 °C with nitrogen protection for 36 hours. After cooling down to room temperature, the reaction mixture was quenched with water and acidified by 6 mol/L HCl (3 mL). Thereafter, the aqueous layer was extracted with 3 portions of ethyl acetate and then dried over anhydrous sodium sulphate. The crude product was purified via column chromatography to afford light yellow solid of 587 mg in 55 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.00 (d, *J* = 8.2Hz, 6H), 8.16 (m, 12H), 7.74 (m, 18H), 7.53 (m, 12H), 7.37 (t, *J* = 7.2 Hz, 6H), 4.30 (m, 12H), 1.20 (m, 18H).^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.5, 167.8 (d), 144.6, 141.0, 140.8, 139.3, 137.4, 135.7, 133.7 (d), 132.2 (d), 130.1, 129.0 (d), 126.8, 126.1, 123.6, 109.8, 61.7 (d), 14.0. MS (MALDI-TOF, m/z) $[M]^+$ found 1693.6163

Synthesis of **TA(*TL*)-Ph(3)-CBZ**. To a dried 100 mL two necked round-bottom flask under nitrogen protection was added 1-bromo-4-decylbenzene (0.70 g, 2.36 mmol) and anhydrous THF (5 mL). The solution was cooled to –70 °C and 1.6 mol/L *n*-BuLi (1.3 mL, 2.12 mmol) was added dropwise. The reaction mixture was stirred at –70 °C for another 1 hour, and then compound **10b** (100 mg, 0.059 mmol) in 3 mL anhydrous THF was added. The reaction was allowed to warm up to room temperature and stirred overnight before being quenched with ice water. The reaction mixture was acidified to pH = 2 and the aqueous layer was extracted by ethyl acetate twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated in *vacuo*, affording a sticky yellow oil which was used directly in the next step. To solution of the above yellow oil diluted in 25 mL dichloromethane, boron trifluoride etherate (0.05 mL) was added. The reaction mixture was continued to stir overnight at room temperature. The reaction was quenched with ice water and the aqueous layer was extracted by dichloromethane. The organic layers were combined, washed with H_2O and dried over anhydrous Na_2SO_4. Purification of crude product was carried out via column chromatography to afford the yellow solid 95 mg with a total yield of 47 % in 2 steps. ^{1}H NMR (400 MHz, $CDCl_3$, δ) : 8.74 (s, 3H), 8.68 (d, *J* = 8.0, 3H), 8.15 (d, *J* = 7.7, 6H), 7.96-7.90 (m, 9H), 7.87 (d, *J* = 8.0, 3H), 7.66 (s, 3H), 7.57 (d, *J* = 8.0, 3H), 7.41-7.36 (m, 12H), 7.31-7.28 (m, 30H), 7.13 (d, *J* = 8.2, 12H), 7.04 (d, *J* = 8.0, 12H), 2.59 (dd, *J* = 17.3, 9.7, 24H), 1.63-1.61 (m, 24H), 1.40-1.27 (m, 168H), 0.88 (q, *J* = 6.6, 36H). ^{13}C NMR (100 MHz, $CDCl_3$, δ) 171.5, 154.2, 152.7, 152.3, 151.7, 144.4, 143.2, 142.9, 141.8, 141.6, 140.7, 140.3, 139.8, 139.0, 136.9, 135.9, 128.5(d), 128.3, 127.0, 126.0, 125.8, 124.8, 123.5, 121.5, 120.4, 120.1, 118.9, 118.4, 110.1, 65.0, 64.9, 35.8, 35.7, 32.1, 31.6, 29.8(t), 29.7, 29.6, 29.5(d), 22.8, 14.3. HRMS (MALDI-TOF, m/z) $[M]^+$ For $C_{291}H_{348}N_6$, 3929.7510, Found 3929.7586. Anal. Calcd for $C_{291}H_{348}N_6$: C 88.94; H 8.93; N 2.14; Found: C 88.76, H 9.10, N 1.86.

Synthesis of compound **10c**. To a 250 mL two-necked round bottom flask were added compound **8** (4.25 g, 6.8 mmol), compound **9** (0.93 g, 1.70 mmol), palladium (II) acetate (77 mg, 0.35 mmol), triphenylphosphine (0.89 g, 3.41 mmol), 4 mol/L potassium carbonate (6 mL), ethanol (30 mL) and toluene (80 mL). The reaction mixture was stirred at 80 °C with nitrogen protection for 36 hours. After cooling down to room temperature, the reaction mixture was quenched with water and acidified by 6 mol/L HCl (8.5 mL). Thereafter, the mixture was extracted with ethyl acetate and then dried over anhydrous sodium sulphate. The crude product was purified with silica gel column chromatography to afford a white solid of 1.19 g in 39 % yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.92 (d, *J* = 8.4, 2H), 8.24 (d, *J* = 8.4, 2H), 8.10 (d, *J* = 8.4 2H), 8.01 (s, 2H), 7.94 (s, 2H), 7.64 (d, *J* = 8.4, 2H), 7.59-7.56 (m, 4H), 4.20 (p, *J* = 7.2, 2H), 1.38 (s, 9H), 1.09 (q, *J* = 7.1, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.5, 167.6, 167.5, 165.0, 164.3, 155.6, 144.5, 143.7, 141.4, 140.7, 135.8, 133.5, 132.3, 132.1, 129.4, 129.1, 129.0, 127.0, 126.9, 126.3, 123.5, 121.2, 61.8(d), 35.3, 31.3, 14.0, 13.9. MS (MALDI-TOF, m/z) $[M^+]$ found 1798.8251.

Synthesis of compound **TA(*TL*)-Ph(3)-ODZ**. To a solution of 1-bromo-4-decylbenzene (534 mg, 1.8 mmol) in dry THF (15 mL) at -70 °C was added *n*-BuLi (0.625 mL, 2.4 mol/L in hexane) under N_2 protection. After stirring below -70 °C for 1 hour, the solution of compound **10c** (90 mg, 0.05

mmol) in dry THF (5 mL) was added. The reaction was then allowed to warm up to room temperature and stirred overnight. The reaction mixture was then quenched with water and extracted with ethyl acetate twice. The combined organic phase was dried over anhydrous sodium sulfate and then the solvent was evaporated in vacuum. The crude product was purified through silica gel column chromatography to afford an intermediate of 170 mg in a yield of 82 %. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.40 (d, J = 8.4 Hz, 6H), 8.06 (d, J = 8.4 Hz, 6H), 7.83 (d, J = 8.4 Hz, 6H), 7.57 (d, J = 8.8 Hz, 6H), 7.10 (d, J = 2.8 Hz, 48H), 7.00 (d, J = 8.4 Hz, 6H), 6.96 (d, J = 8.4 Hz, 6H), 6.81 (s, 3H), 6.72 (s, 3H), 2.78 (s, 3H), 2.70 (s, 3H), 2.59-2.64 (m, 24H), 1.62-1.66 (m, 24H), 1.40 (s, 27H), 1.23-1.32 (m, 168H), 0.83-0.86 (m, 36H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 171.4, 164.8, 164.3, 155.5, 147.0, 146.2, 144.7, 144.5, 144.2, 144.0, 142.2, 142.1, 139.0, 138.6, 134.8, 134.3, 134.0, 130.4, 129.9, 128.4, 128.07, 128.05, 128.0, 127.9, 126.9, 126.2, 126.1, 122.5, 121.2, 83.1, 83.0, 35.6, 35.2, 32.0, 31.5(d), 31.3, 29.8, 29.6(d), 29.5(d), 29.4(d), 22.8, 14,2. MS HRMS (MALDI-TOF, m/z) [M-H]$^+$ For $C_{291}H_{375}N_9O_9$, 4142.9257, Found 4142.8726. To a solution of the above intermediate (100 mg, 0.024 mmol) in dichloromethane (35 mL) boron trifluoride etherate (0.05 mL) was added. The reaction mixture stirred overnight at room temperature and then the mixture was diluted by water, extracted with dichloromethane twice. The organic phase was combined and dried over anhydrous sodium sulfate. The crude product was purified through silica gel column chromatography to afford a yellow solid of 61 mg with 63 % yield. ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.68 (s, 3H), 8.63 (d, J = 8.0 Hz, 3H), 8.16 (s, 3H), 8.12 (d, J = 8.0 Hz, 3H), 8.05 (d, J = 8.8 Hz, 6H), 7.88 (d, J = 2.0 Hz, 6H), 7.82-7.85 (m, 6H), 7.55 (d, J = 8.4 Hz, 6H), 7.22-7.25 (m, 24H), 7.11 (d, J = 8.4 Hz, 12H), 7.00 (d, J = 8.0 Hz, 12H), 2.51-2.59 (m, 24H), 1.58-1.68 (m, 24H), 1.38 (s, 27H), 1.23-1.28 (m, 168H), 0.82-0.88 (m, 36H). ^{13}C NMR (100 MHz, CDCl$_3$, δ): 175.5, 164.8, 164.6, 155.4, 153.2, 152.7, 152.5, 152.4, 144.1, 143.6, 143.0, 142.5, 141.9, 141.6, 140.7, 139.8, 136.0, 128.6, 128.5, 128.3, 128.2, 126.9, 126.5, 126.2, 124.8, 123.0, 121.2, 121.0, 120.5, 118.8, 65.0, 64.9, 35.8, 35.7, 35.2, 32.1, 32.0, 31.6, 31.5, 31.3, 29.9, 29.8, 29.8, 29.7(t), 29.5, 22.8, 14.3. HRMS (MALDI-TOF, m/z) [M+H]$^+$ For $C_{291}H_{363}N_9O_3$, 4034.8623, Found 4034.8664. Anal. Calcd for $C_{291}H_{363}N_9O_3$: C 86.62; H 9.07; N 3.12; Found: C 86.30; H 9.26; N 2.62.

References

[1] L. Guo, K. F. Li, M. S. Wong, K. W. Cheah, *Chem. Commun.* **2013**, *49*, 3597.

[2] C. Wang, L.-O. Pålsson, A. S. Batsanov, M. R. Bryce, *J. Am. Chem. Soc.* **2006** *128*, 3789.

[3] A. Ranganathan, B. C. Heisen, I. Dix, F. Meyer, *Chem. Commun.* **2007**, 3637.

Appendix of ^{1}H NMR, ^{13}C NMR and HRMS Spectra

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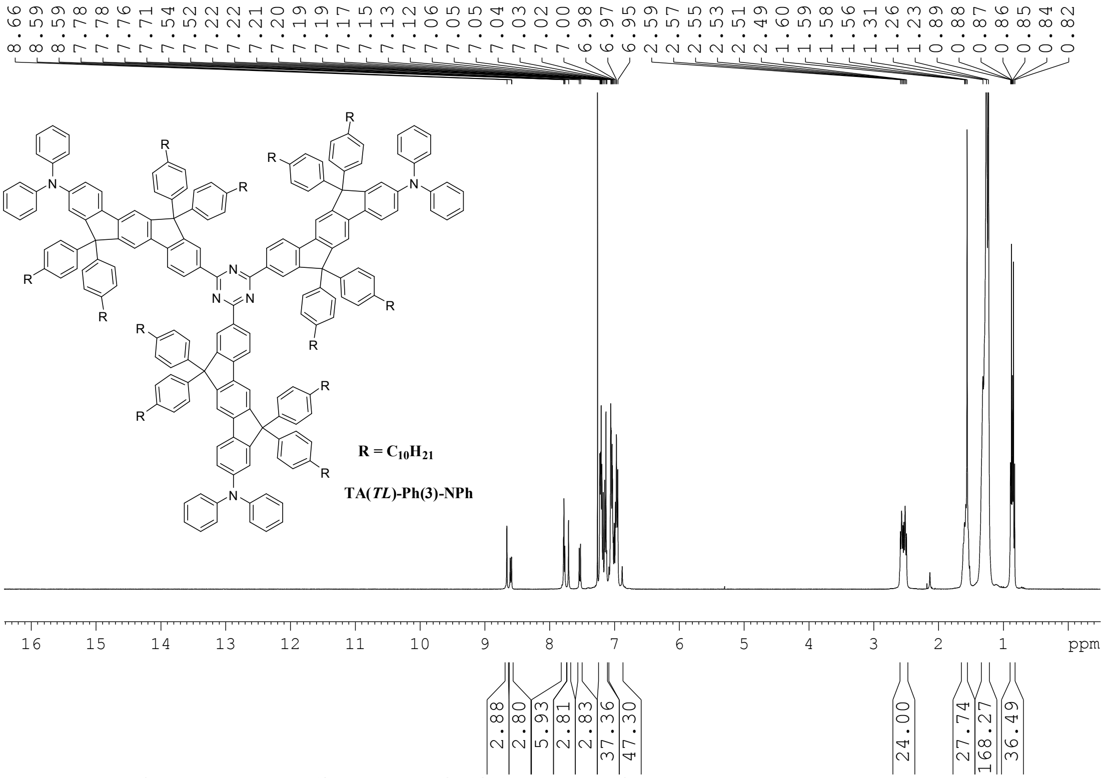

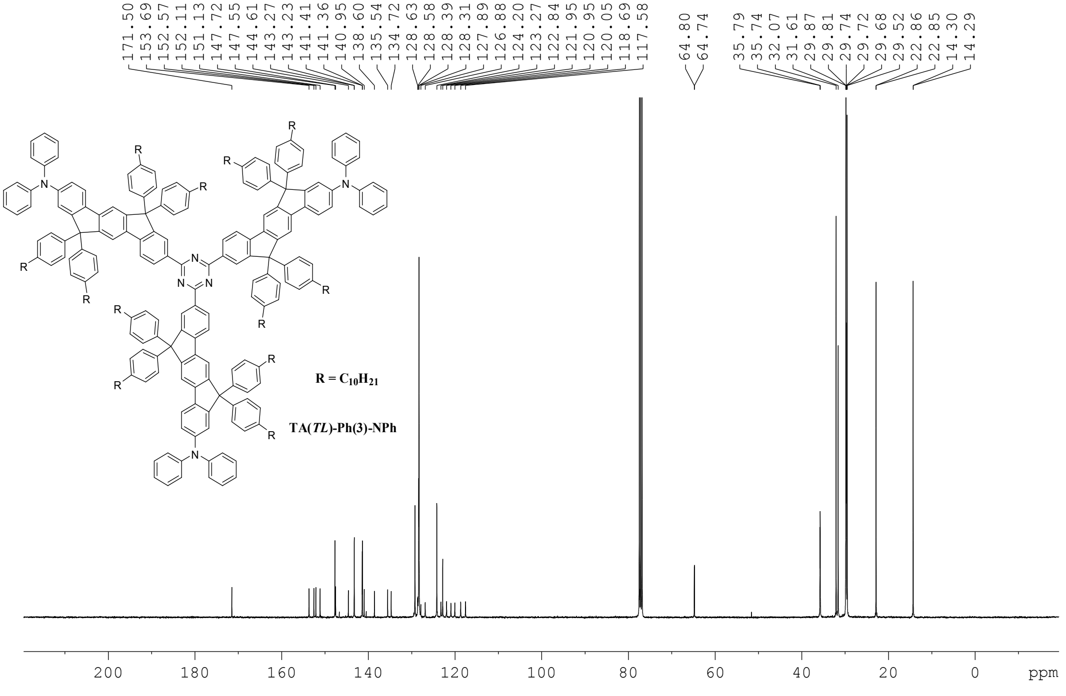

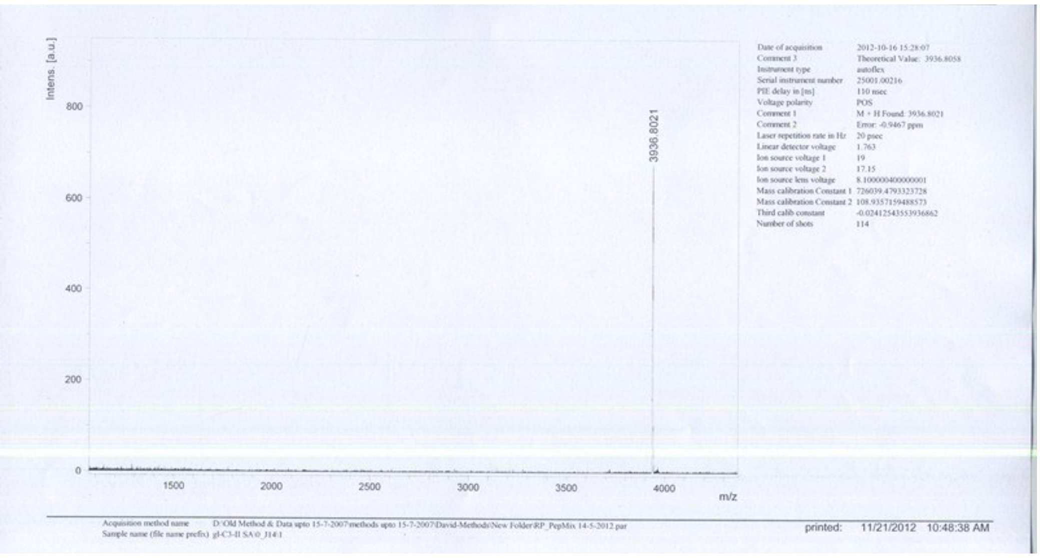

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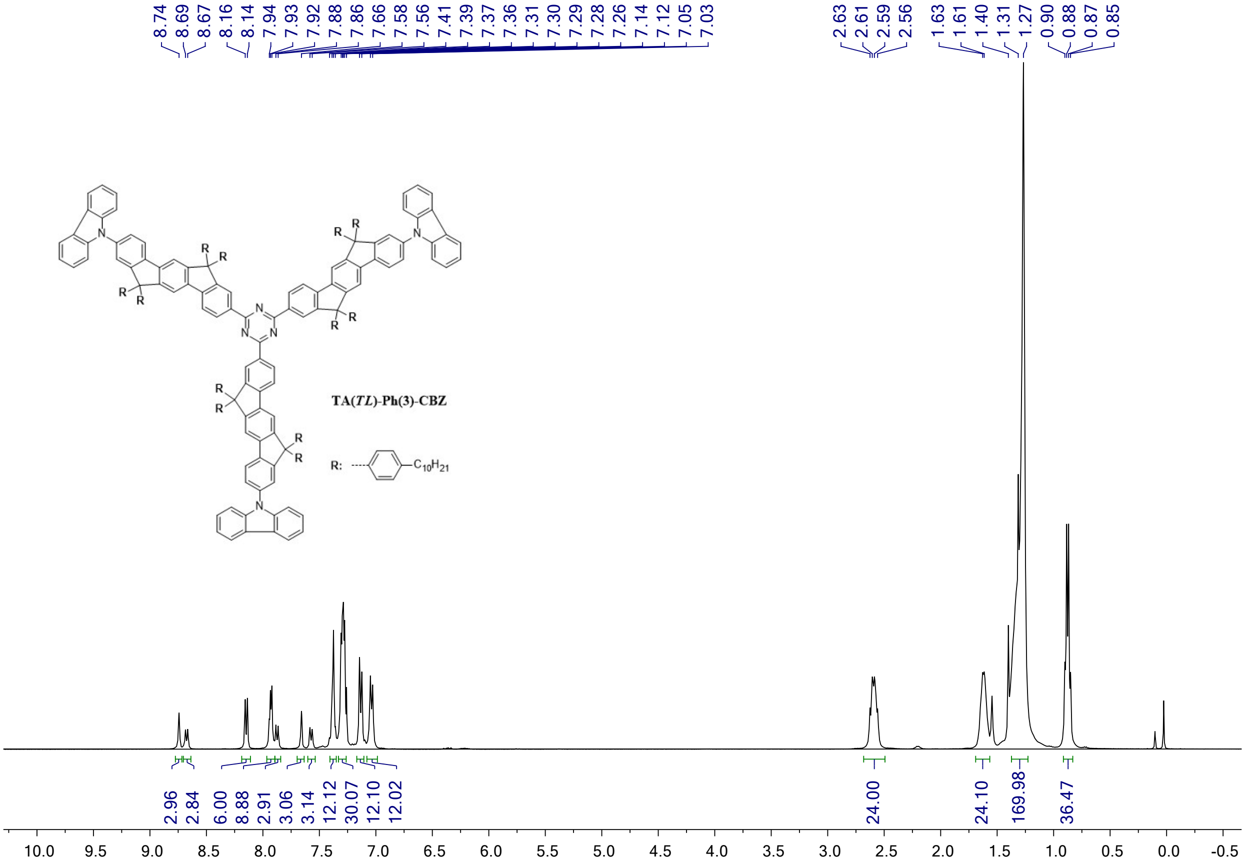

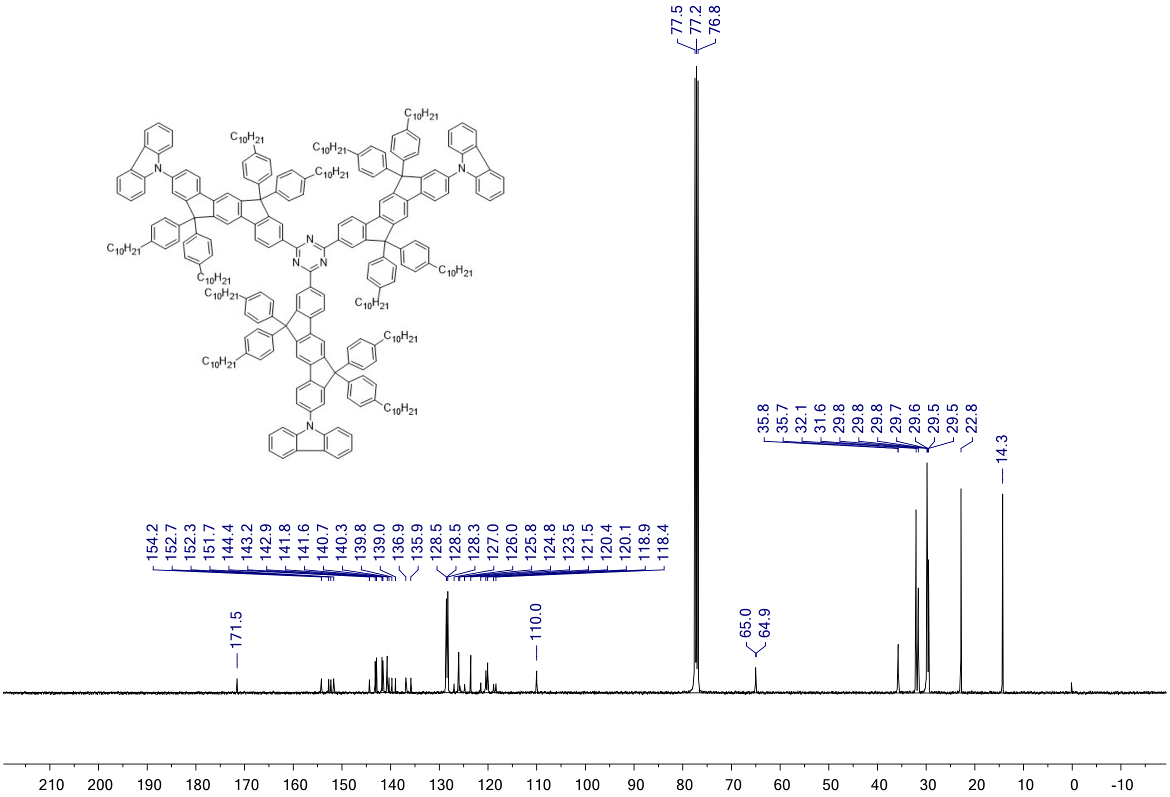

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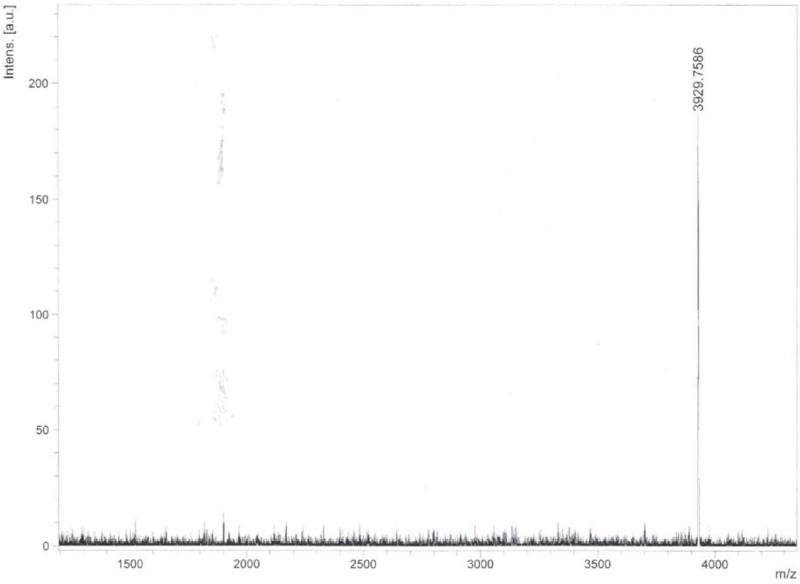

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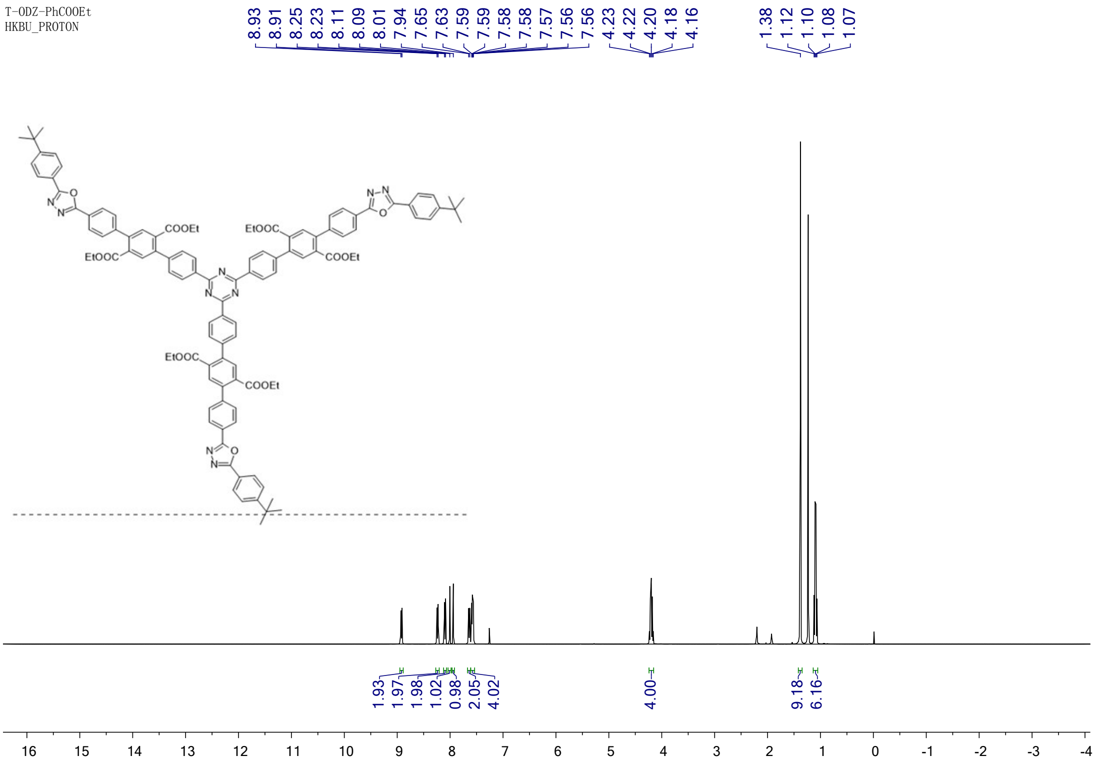
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16
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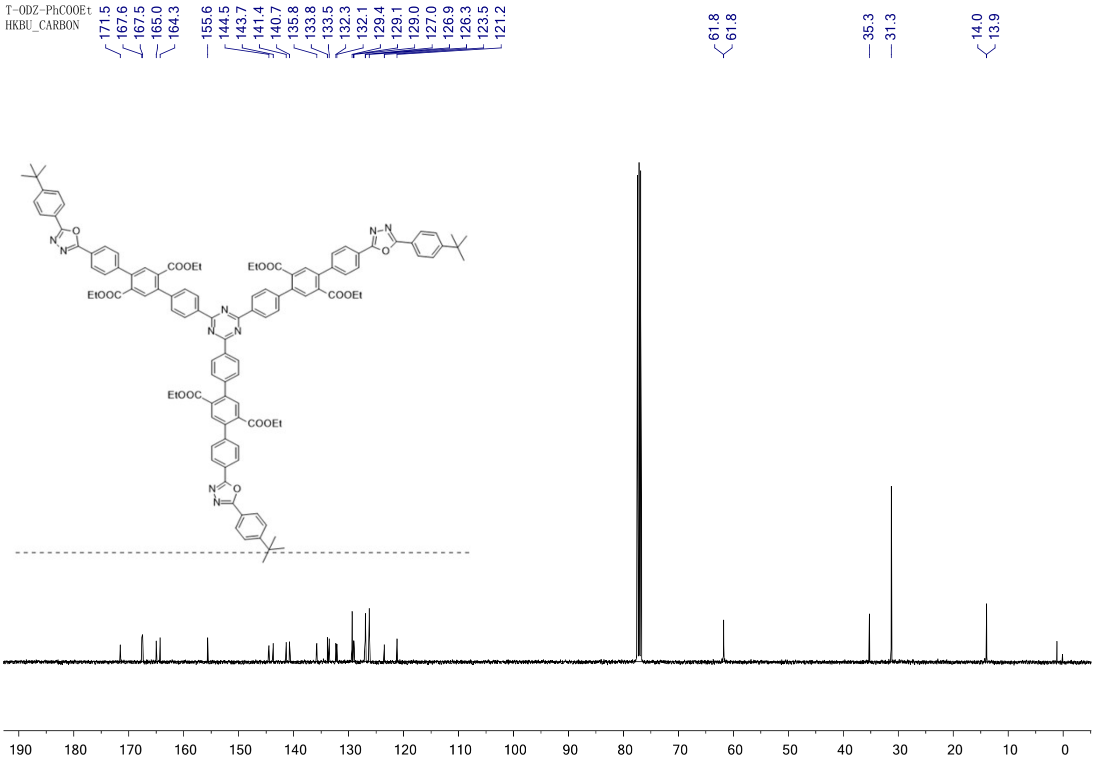
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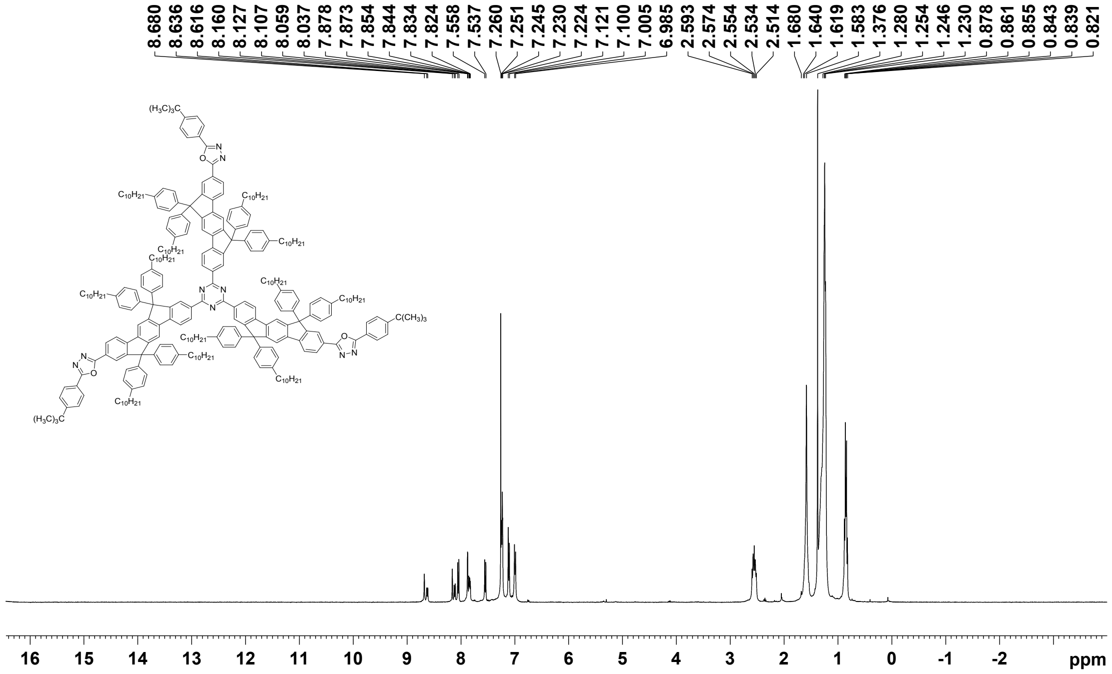
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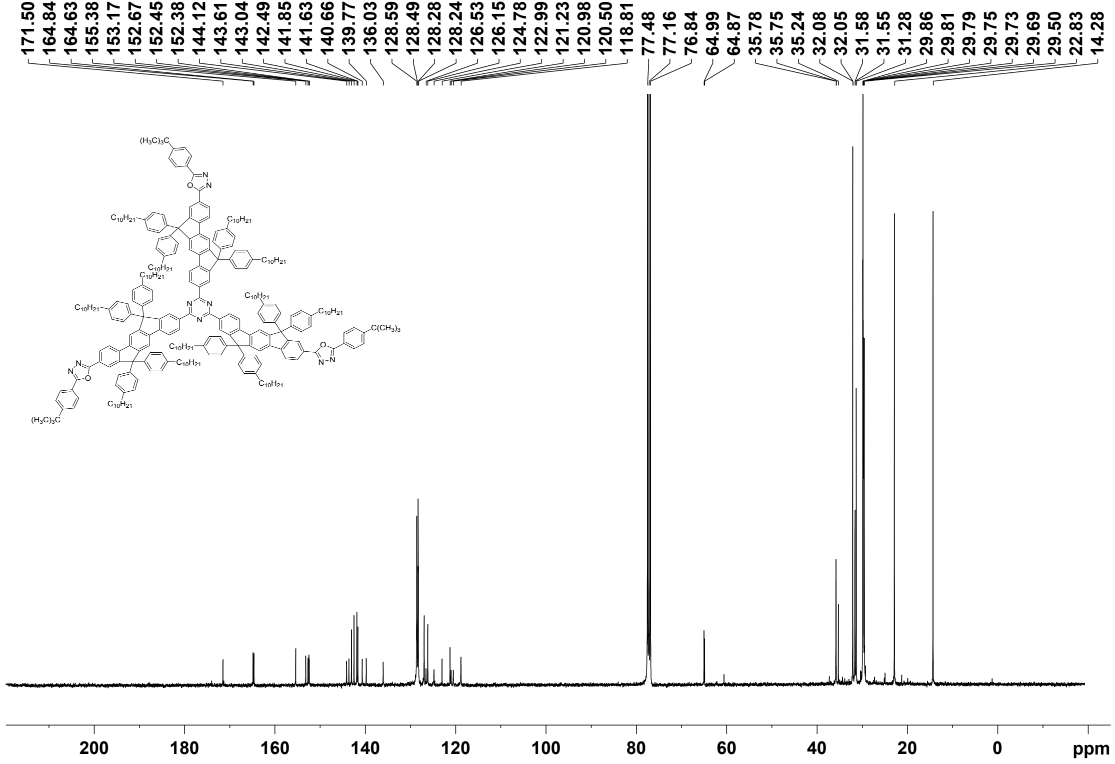
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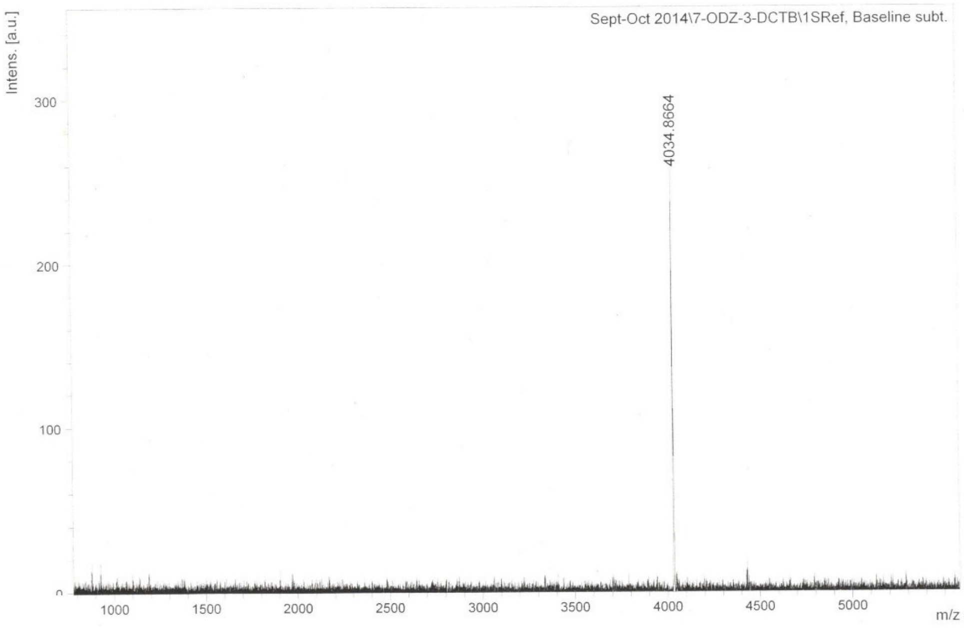

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