Tris(triazolo)triazine-based Emitters for Solution-processed Blue Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes

Fabian Hundemer[a], Ettore Crovini[b], Yoshimasa Wada[c], Hironori Kaji*[c], Stefan Bräse*[a] and Eli Zysman-Colman*[b]

[a] Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131 Karlsruhe, Germany. E-mail: braese@kit.edu;Fax: (+49)-721-6084-8581; Tel: (+49)-721-6084-2903

[b] Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK. E-mail: eli.zysman-colman@st-andrews.ac.uk; Web: http://www.zysman-colman.com; Tel: +44 (0)1334 463826

[c] Institute for Chemical Research Kyoto University Uji, Kyoto 611-0011, Japan E-mail: kaji@scl.kyoto-u.ac.jp

SUPPORTING INFORMATION

Table of Contents

General Methods

General information: NMR spectra of the compounds described herein were recorded on a Bruker Avance 300 NMR instrument at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR, and a Bruker Avance 400 NMR instrument at 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR. The NMR spectra were recorded at room temperature in deuterated solvents acquired from Eurisotop. The chemical shift δ is displayed in parts per million [ppm] and the references used were the ^{1}H and ^{13}C peaks of the solvents themselves: d_1-chloroform ($CDCl_3$): 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C, d_6-dimethyl sulfoxide (DMSO-d_6): 2.50 ppm for ^{1}H and 39.4 ppm for ^{13}C, d_6-acetone (acetone-d_6): 2.05 ppm for ^{1}H and 206.26 ppm for ^{13}C, methylene chloride-d_2 (CD_2Cl_2): 5.32 ppm for ^{1}H and 54.00 ppm for ^{13}C. For the characterization of centrosymmetric signals, the signal's median point was chosen, for multiplets the signal range. The following abbreviations were used to describe the proton splitting pattern: d=doublet, t=triplet, m=multiplet, dd=doublet of doublet, ddd=doublet of doublet of doublet, dt=doublet of triplet. Absolute values of the coupling constants "*J*" are given in Hertz [Hz] in absolute value and decreasing order.

The infrared spectra were recorded with a Bruker, IFS 88 instrument. Solids were measured by attenuated total reflection (ATR) method. The positions of the respective transmittance bands are given in wavenumbers $\bar{\upsilon}$ [cm^{-1}] and were measured in the range from 3600 cm^{-1} to 500 cm^{-1}. Characterization of the transmittance bands was done in a sequence of transmission strength T with following abbreviations: vs (very strong, 0–9% T), s (strong, 10–39% T), m (medium, 40–69% T), w (weak, 70–89% T), vw (very weak, 90–100% T) and br (broad).

Fast atom bombardment (FAB) experiments were conducted using a Finnigan, MAT 90 (70 eV) instrument, with 3-nitrobenzyl alcohol (3-NBA) as matrix and reference for high resolution. For the interpretation of the spectra, molecular peaks [M]+, peaks of protonated molecules $[M+H]^+$ and characteristic fragment peaks are indicated with their mass-to-charge ratio (*m/z*) and in case of EI their intensity in percent, relative to the base peak (100%) is given. In the case of high-resolution measurements, the tolerated error is 0.0005 m/z. APCI and ESI experiments were recorded on a Q-Exactive (Orbitrap) mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with a HESI II probe to record high resolution. The tolerated error is 5 ppm of the molecular mass. Again, the

spectra were interpreted by molecular peaks $[M]^+$, peaks of protonated molecules $[M+H]^+$ and characteristic fragment peaks and indicated with their mass-to-charge ratio (*m/z*).

Elemental analysis was done on an Elementar vario MICRO instrument. The weight scale used was a Sartorius M2P. Calculated (calc.) and found percentage by mass values for carbon, hydrogen, nitrogen and sulfur are indicated in fractions of 100%.

For the analytical thin layer chromatography, TLC silica plates coated with fluorescence indicator, from Merck (silica gel 60 F254, thickness 0.2 mm) were used. UV-active compounds were detected at 254 nm and 366 nm excitation wavelength with a Heraeus UV-lamp, model Fluotest.

Solvents of p.a. quality (per analysis) were commercially acquired from Sigma Aldrich, Carl Roth or Acros Fisher Scientific and, unless otherwise stated, used without further purification. Dry solvents were commercially available (< 50 ppm H_2O over molecular sieves). All reagents were commercially available. Unless otherwise stated, all chemicals were used without further purification.

Air- and moisture-sensitive reactions were carried out under argon atmosphere in previously baked out glassware using standard Schlenk techniques. Solid compounds were ground using a mortar and pestle before use, liquid reagents and solvents were injected with plastic syringes and stainless-steel cannula of different sizes unless otherwise specified. Reactions at low temperature were cooled using shallow vacuum flasks produced by Isotherm, Karlsruhe, filled with a water/ice mixture for 0°C, water/ice/sodium chloride for –20°C or isopropanol/dry ice mixture for –78°C. For reactions at high temperature, the reaction flask was equipped with a reflux condenser and connected to the argon line. Solvents were evaporated under reduced pressure at 40°C using a rotary evaporator. Unless otherwise stated, solutions of inorganic salts are saturated aqueous solutions.

The progress of the reaction in the liquid phase was monitored by TLC. UV active compounds were detected with a UV-lamp at 254 nm and 366 nm excitation wavelength. When required, vanillin solution, potassium permanganate solution or methanolic bromocresol green solution was used as TLC-stain, followed by heating. Additionally,

APCI-MS (atmospheric pressure chemical ionization mass spectrometry) was recorded on an Advion expression CMS in positive ion mode with a single quadrupole mass analyzer. The observed molecule ion is interpreted as $[M+H]^+$.

Unless otherwise stated, the crude compounds were purified by column chromatography. For the stationary phase of the column, silica gel, produced by Merck (silica gel 60, 0.040 × 0.063 mm, 260 – 400 mesh ASTM), and sea sand by Riedel de-Haën (baked out and washed with hydrochloric acid) were used. Solvents used were commercially acquired in HPLC-grade and individually measured volumetrically before mixing.

Electrochemistry measurements. Cyclic Voltammetry (CV) and Differential Pulse Voltammetry analyses were performed on an Electrochemical Analyzer potentiostat model 620D from CH Instruments. Samples of **3,4,5-3TCz-TTT** and **3DMAC-TTT** were prepared in MeCN and DCM respectively that was degassed by sparging with MeCN/DCM-saturated nitrogen gas for 10 minutes before measurements. All measurements were performed in 0.1 M MeCN or DCM solution of tetrabutylammonium hexafluorophosphate, which was used as the supporting electrolyte. An Ag/Ag^+ electrode was used as the reference electrode while a glassy carbon electrode and a platinum wire were used as the working electrode and counter electrode, respectively. The redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocene/ferrocenium (Fc/Fc^+) redox couple as the internal standard (0.38 V vs SCE for MeCN[1] and 0.46 V vs SCE for DCM[2]).

Photophysical measurements. Optically dilute solutions of concentrations on the order of 10^{-5} M were prepared in HPLC grade methyl-cyclohexane, toluene, DCM, THF, and MeCN for absorption and emission analysis. Absorption spectra were recorded at room temperature on a Shimadzu UV-1800 double beam spectrophotometer with a 1 cm quartz cuvette. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least five independent solutions at varying concentrations with absorbance ranging from 1.67×10^{-5} to 3.23×10^{-6} M.

For emission studies, aerated solutions were bubbled with compressed air for 5 minutes and spectra were taken using the same cuvette as for the absorption analysis. Degassed solutions were prepared via three freeze-pump-thaw cycles and spectra were taken using

a home-made Schlenk quartz cuvette. Steady-state emission, excitation spectra and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980. Samples were excited at 340 nm for steady-state measurements and at 378 nm for time-resolved measurements. Photoluminescence quantum yields for solutions were determined using the optically dilute method[3] in which four sample solutions with absorbances of ca. 0.079, 0.059, 0.040 and 0.023 for **3,4,5-3TCz-TTT** and c.a. 0.088, 0.066, 0.049, and 0.036 for **3DMAC-TTT**, at 360 nm were used. The Beer-Lambert law was found to remain linear at the concentrations of the solutions. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis with the Pearson regression factor (R^2) for the linear fit of the data set surpassing 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope obtained from the linear fit of these results. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$ was used to calculate the relative quantum yield of the sample, where (Φ_r) is the absolute quantum yield of the external reference quinine sulfate (Φ_r = 54.6% in 1 *N* H_2SO_4[4]), A stands for the absorbance at the excitation wavelength, I is the integrated area under the corrected emission curve and n is the refractive index of the solvent. The subscripts "s" and "r" representing sample and reference, respectively. The experimental uncertainty in the emission quantum yields is conservatively estimated to be 10%, though we have found that statistically, we can reproduce Φ_{PL}s to 3% relative error. Thin-film Φ_{PL} measurements were performed using an integrating sphere in a Hamamatsu C9920-02 system. A xenon lamp coupled to a monochromator enabled excitation selectivity, chosen here to be 340 nm. The output was then fed into the integrating sphere via a fibre, exciting the sample. PL spectra were collected with a multimode fibre and detected with a back-thinned CCD. Doped thin films were prepared by mixing sample (15 wt%) and host material in DCM solution, followed by spin-casting on a quartz substrate. The Φ_{PL} of the films were then measured in air and by purging the integrating sphere with flowing N_2 gas. Time-resolved PL measurements of the thin films were carried out using the time-correlated single-photon counting technique. The samples were excited at 378 nm by a pulsed laser diode (Picoquant, model PLS 370) and were kept in a vacuum of $< 8 \times 10^{-4}$ mbar.

The singlet-triplet splitting energy ΔE_{ST} was estimated by recording the prompt fluorescence spectra and phosphorescence emission at 77 K. The films were excited either by a Q-switched Nd:YAG laser emitting at 343 nm (Laser-export) or by a femtosecond

optical parametric amplifier emitting at 320 nm (Orpheus-N, Light Conversion). Emission from the samples was focused onto a spectrograph (Chromex imaging, 250is spectrograph) and detected on a sensitive gated iCCD camera (Stanford Computer Optics, 4Picos) having a subnanosecond resolution. Phosphorescence spectra were measured 1ms ms after the excitation of the Nd:YAG laser with iCCD exposure time of 8.5 ms. Prompt fluorescence spectra were measured 1 ns after the excitation of the femtosecond laser with iCCD exposure time of 100 ns.

Fitting time-resolved luminescence measurements: Time-resolved PL measurements were fitted to a sum of exponentials decay model with chi-squared (χ^2) values between 1 and 2, using the EI FLS980 software. Each component of the decay is assigned a weight, (w_i), which is the contribution of the emission from each component to the total emission.

The average lifetime was then calculated using the following:

- Two exponential decay model:

$$\tau_{AVG} = \tau_1 w_1 + \tau_2 w_2$$

with weight defined as $w_1 = \frac{A1\tau_1}{A1\tau_1 + A2\tau_2}$ and $w_2 = \frac{A2\tau_2}{A1\tau_1 + A2\tau_2}$ where A1 and A2 are the preexponential-factors of each component.

- Three exponential decay model:

$$\tau_{AVG} = \tau_1 w_1 + \tau_2 w_2 + \tau_3 w_3$$

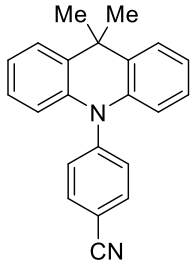
with weight defined as $w_1 = \frac{A1\tau_1}{A1\tau_1 + A2\tau_2 + A3\tau_3}$, $w_2 = \frac{A2\tau_2}{A1\tau_1 + A2\tau_2 + A3\tau_3}$ and $w_3 = \frac{A3\tau_3}{A1\tau_1 + A2\tau_2 + A3\tau_3}$ where A1, A2 and A3 are the preexponential-factors of each component.

Theoretical calculations: All ground state optimizations have been carried out at the Density Functional Theory (DFT) level with Gaussian09[5] using the PBE0[6] functional and the 6-31G(d,p) basis set.[7] Excited state calculations have been performed at Time-Dependent DFT (TD-DFT) within the Tamm-Dancoff approximation (TDA[8,9]) using the same functional and basis set as for ground state geometry optimization. This methodology has been demonstrated to show a quantitative estimate of ΔE_{ST} in comparison to experiment.[10]

Device fabrication: PEDOT:PSS was prepared by diluting CLEVIOS™ P VP CH 8000 (Hereus) in ultrapure H_2O at the ratio of 1:1 wt% and was spin-coated onto pre-cleaned ITO substrate at 4000 rpm. After 10 mins of annealing at 150 ºC, a 10 mg mL^{-1} solution of PVK in orthodichlorobenzene was spin-coated onto the PEDOT:PSS layer at 2000 rpm. After 10 mins of baking at 120 ºC, a 10 mg mL^{-1} emitter solution in toluene was spin-coated and the device was baked at 100 ºC for 10 mins and then transferred into the vacuum chamber. The PPF (5 nm), TPBi (50 nm), Liq (1 nm), and Al (80 nm) layers were vacuum deposited at ~10^{-4} Pa using a deposition apparatus (SE-4260, ALS Technology, Japan), resulting in active areas of 4 mm^2 for each pixcel. Performance of OLEDs were characterized using an integrating sphere integrated with an absolute EQE measurement system (C9920-12, Hamamatsu Photonics, Japan) equipped with a source meter (2400, Keithley, Japan). The device performances were measured in the forward direction in 200-meV steps.

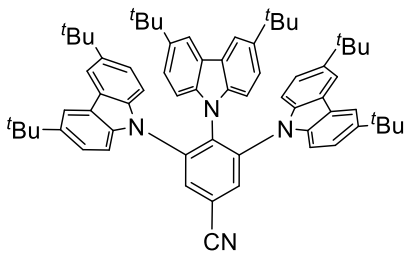
Experimental Section

4-(9,9-Dimethylacridin-10(9)-yl)benzonitrile



In a sealable vial, 4-fluorobenzonitrile (303 mg, 2.50 mmol, 1.00 equiv.), 9,9-dimethyl-9,10-dihydroacridine (524 mg, 2.50 mmol, 1.00 equiv.) and tripotassium phosphate (1.06 g, 5.00 mmol, 2.00 equiv.) were evacuated and backfilled with argon. Dry DMSO (10 ml) was added and the resulting mixture heated at 110 C for 16 h. After cooling to room temperature, the reaction mixture was poured into an excess of water and extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over sodium sulfate, reduced in vacuum. The crude product was purified by column chromatography over SiO_2 (dichloromethane/pentane 1:1) to yield 520 mg of the title compound (1.68 mmol) as a colorless solid. **Yield** = 67%. $\mathbf{R}_f$ (dichloromethane/pentane 1:1) = 0.49. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.17 – 8.09 (m, 2H), 7.66 – 7.56 (m, 2H), 7.52 (dd, J = 7.6, 1.7 Hz, 2H), 7.05 – 6.92 (m, 4H), 6.21 (dd, J = 8.0, 1.4 Hz, 2H), 1.61 (s, 6H). **^{13}C NMR** (101 MHz, DMSO) δ 145.4, 139.7, 135.3, 131.2, 130.8, 126.6, 125.6, 121.4, 118.5, 114.5, 110.6, 35.7, 31.0. **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3973 (w), 3878 (w), 3765 (w), 3699 (w), 3620 (w), 3503 (w), 3410 (w), 3053 (w), 2973 (w), 2595 (w), 2387 (w), 2324 (w), 2229 (w), 2112 (w), 1924 (w), 1815 (w), 1700 (w), 1586 (m), 1445 (m), 1321 (m), 1045 (w), 924 (w), 837 (w), 744 (m), 622 (m), 558 (m), 433 (m). **HRMS** (APCI, $C_{22}H_{18}N_2$) calc. 311.1543 $[M+H]^+$, found 311.1532 $[M+H]^+$.

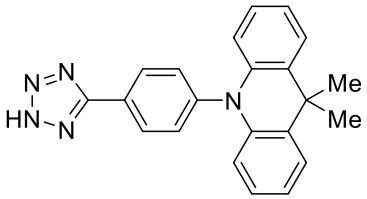
3,4,5-Tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzonitrile



In a sealable vial, 3,4,5-trifluorobenzonitrile (393 mg, 2.50 mmol, 1.00 equiv.), 3,6-di-*tert*-butyl-9*H*-carbazole (2.20 g, 7.88 mmol, 3.15 equiv.) and tripotassium phosphate (3.19 g,

15.0 mmol, 6.00 equiv.) were evacuated and backfilled with argon. Dry DMSO (32 ml) was added and the resulting mixture heated at 110 C for 16 h. After cooling to room temperature, the reaction mixture was poured into an excess of water and extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over sodium sulfate, reduced in vacuum. The crude product was purified by column chromatography over SiO_2 (dichloromethane/pentane 1:2 to 1:1) to yield 1.17 g of the title compound (1.25 mmol) as a colorless solid. **Yield** = 50%. $\mathbf{R_f}$ (dichloromethane/pentane 1:1) = 0.61. **^{1}H NMR** (400 MHz,$CDCl_3$) δ 8.07 (s, 2H), 7.79 – 7.70 (m, 4H), 7.30 – 7.27 (m, 2H), 7.06 (dd, *J* = 8.6, 1.9 Hz, 4H), 6.98 (d, *J* = 8.6 Hz, 4H), 6.69 (d, *J* = 8.6 Hz, 2H), 6.60 (ddd, *J* = 8.6, 2.0, 0.9 Hz, 2H), 1.36 (s, 36H), 1.23 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.7, 143.2, 139.2, 138.3, 137.1, 136.8, 132.4, 124.6, 124.3, 123.4, 122.7, 117.3, 116.1, 115.2, 112.5, 109.7, 109.2, 34.7, 34.4, 32.0, 31.9. **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3986 (vw), 3883 (vw), 3693 (vw), 3621 (vw), 3506 (vw), 3442 (vw), 2954 (w), 2361 (vw), 2232 (w), 1747 (vw), 1485 (m), 1362 (w), 1262 (w), 1135 (w), 1034 (w), 876 (w), 809 (m), 731 (w), 612 (w), 428 (w). **HRMS** (APCI, $C_{67}H_{74}N_4$) calc. 935.5986 $[M+H]^+$, found 935.5972 $[M+H]^+$.

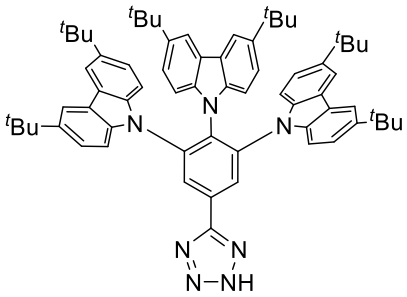
10-(4-(2*H*-Tetrazol-5-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine



In a sealable vial, 4-(9,9-dimethylacridin-10(9)-yl)benzonitrile (776 mg, 2.50 mmol, 1.00 equiv.), sodium azide (487 mg, 7.50 mmol, 3.00 equiv.) and ammonium chloride (401 mg, 7.50 mmol, 3.00 equiv.) were evacuated and backfilled with argon. Dry DMF (16 ml) was added and the resulting mixture heated at 130 C for 16 h. After cooling to room temperature, the reaction mixture was poured into an excess of 1M HCl and mixed thoroughly. The white solid was filtered off, washed several times with water and thoroughly dried to yield 867 mg of the title compound (2.45 mmol) as a white solid. **Yield** = 98%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.37 – 8.31 (m, 2H), 7.66 – 7.59 (m, 2H), 7.51 (dd, *J* = 7.7, 1.6 Hz, 2H), 6.99 (ddd, *J* = 8.3, 7.3, 1.6 Hz, 2H), 6.93 (td, *J* = 7.4, 1.4 Hz, 2H), 6.21 (dd, *J* = 8.2, 1.3 Hz, 2H), 1.63 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 143.3, 140.0, 132.2, 129.9, 129.8, 126.6, 125.5, 120.9, 113.7, 35.6, 31.2. **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3980 (w), 3842 (vw), 3678 (vw), 2967 (w), 2858 (w), 2726 (w), 2603 (w), 1594 (m), 1484 (m), 1334 (m), 1268 (m),

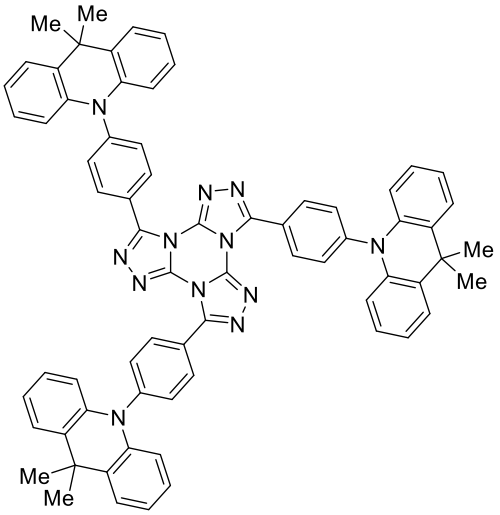
1155 (w), 992 (w), 928 (w), 853 (w), 745 (m), 623 (m), 522 (w), 382 (w). **HRMS** (APCI, $C_{22}H_{19}N_5$) calc. 354.1713 $[M+H]^+$, found 354.1707 $[M+H]^+$.

9,9',9''-(5-(2*H*-Tetrazol-5-yl)benzene-1,2,3-triyl)tris(3,6-di-*tert*-butyl-9*H*-carbazole)



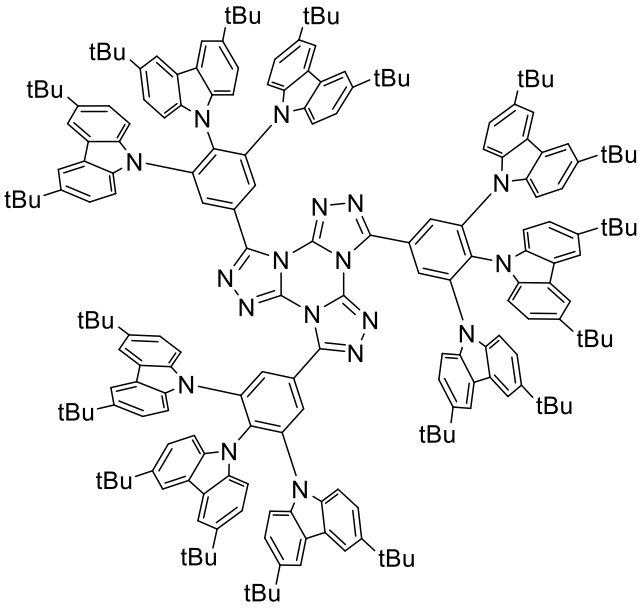
In a sealable vial, 3,4,5-tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)benzonitrile (935 mg, 1.00 mmol, 1.00 equiv.), sodium azide (195 mg, 3.00 mmol, 3.00 equiv.) and ammonium chloride (160 mg, 3.00 mmol, 3.00 equiv.) were evacuated and backfilled with argon. Dry DMF (10 ml) was added and the resulting mixture heated at 130 C for 16 h. After cooling to room temperature, the reaction mixture was poured into an excess of 1M HCl and mixed thoroughly. The white solid was filtered off, washed several times with water and thoroughly dried. The crude product was purified by column chromatography over SiO_2 (dichloromethane/ethyl acetate 20:1 to 1:1) to yield 850 mg of the title compound (0.871 mmol) as a white solid. **Yield** = 87%. $\mathbf{R_f}$ (dichloromethane/ethyl acetate 1:1) = 0.82. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 14.09 (s, 1H), 8.56 (s, 2H), 7.75 (d, *J* = 1.6 Hz, 4H), 7.28 (d, *J* = 1.9 Hz, 2H), 7.08 – 6.97 (m, 8H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.60 (dd, *J* = 8.6, 1.9 Hz, 2H), 1.35 (s, 36H), 1.23 (s, 18H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 142.7, 138.9, 138.6, 137.3, 127.7, 124.4, 124.1, 123.3, 122.5, 115.9, 115.1, 109.8, 109.5, 34.7, 34.4, 32.0, 31.9. **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3991 (vw), 3820 (vw), 3733 (vw), 3605 (vw), 3270 (vw), 3190 (vw), 3043 (vw), 2952 (w), 2324 (vw), 2162 (vw), 2027 (vw), 1862 (vw), 1747 (vw), 1560 (w), 1472 (m), 1362 (w), 1262 (w), 1034 (w), 875 (w), 806 (m), 608 (w), 423 (w). **HRMS** (APCI, $C_{67}H_{75}N_7$) calc. 978.6157 $[M+H]^+$, found 978.6150 $[M+H]^+$.

3,7,11-Tris(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine – 3DMAC-TTT



In a sealable vial, 10-(4-(2*H*-tetrazol-5-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine (566 mg, 1.60 mmol, 1.00 equiv.) and cyanuric chloride (88.6 mg, 0.480 mmol, 0.30 equiv.) were evacuated and backfilled with argon. Dry toluene (32 mL) and lutidine (85.8 mg, 3.20 mmol, 2.00 equiv.) were added and the resulting mixture heated at 80°C for 4 hours. After cooling to room temperature, the reaction mixture was poured into an excess of water, acidified with 1M HCl and extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over sodium sulfate, reduced in vacuum and purified by silica column chromatography (dichloromethane/ethyl acetate 98:2 to 90:10) to yield 449 mg of the title compound (0.427 mmol, 89%) as an off-white solid. **Yield** = 89%. $\mathbf{R}_f$ (dichloromethane/ethyl acetate 98:2) = 0.23. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.41 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.55 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.08 (td, *J* = 7.7, 1.6 Hz, 2H), 6.98 (td, *J* = 7.5, 1.3 Hz, 2H), 6.34 (dd, *J* = 8.1, 1.3 Hz, 2H), 1.67 (s, 6H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 148.8, 143.6, 142.2, 140.0, 132.8, 131.2, 130.1, 126.6, 125.6, 124.4, 121.0, 113.9, 35.7, 31.2. **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3974 (vw), 3857 (vw), 3630 (vw), 3420 (vw), 3304 (vw), 2968 (w), 2621 (vw), 2376 (vw), 2217 (vw), 2103 (vw), 1911 (vw), 1591 (w), 1477 (w), 1324 (w), 1046 (w), 923 (w), 844 (w), 742 (m), 623 (w), 532 (w), 421 (vw). **HRMS** (ESI, $C_{69}H_{54}N_{12}$) calc. 1051.4667 [M+H]$^+$, found 1051.4610 [M+H]$^+$. **EA** ($C_{69}H_{54}N_{12}$) calc. C: 78.83, H: 5.18, N: 15.99; found C: 78.75 H: 5.46, N: 15.17.

3,7,11-Tris(3,4,5-tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine – 3,4,5-3TCz-TTT



In a sealable vial, 9,9',9''-(5-(2*H*-tetrazol-5-yl)benzene-1,2,3-triyl)tris(3,6-di-*tert*-butyl-9*H*-carbazole) (649 mg, 0.663 mmol, 1.00 equiv.) and cyanuric chloride (36.7 mg, 0.199 mmol, 0.30 equiv.) were evacuated and backfilled with argon. Dry toluene (14 mL) and lutidine (140 mg, 1.33 mmol, 2.00 equiv.) were added and the resulting mixture heated at 80°C for 4 hours. After cooling to room temperature, the reaction mixture was poured into an excess of water, acidified with 1M HCl and extracted with dichloromethane three times. The combined organic layers were washed with brine, dried over sodium sulfate, reduced in vacuum and purified by silica column chromatography (dichloromethane/pentane 1:2 to 1:1) to yield 390 mg of the title compound (0.133 mmol) as a yellow solid. **Yield** = 67%. $\mathbf{R_f}$ (dichloromethane/pentane 1:1) = 0.45. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (s, 6H), 7.78 – 7.69 (m, 12H), 7.35 (d, *J* = 8.6 Hz, 12H), 7.33 – 7.28 (m, 6H), 7.14 (d, *J* = 8.7 Hz, 12H), 6.86 (d, *J* = 8.5 Hz, 6H), 6.66 (d, *J* = 8.6 Hz, 6H), 1.36 (s, 108H), 1.27 (s, 54H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.5, 143.2, 142.8, 140.8, 138.6, 138.3, 137.2, 135.6, 130.6, 124.5, 124.2, 124.1, 123.4, 122.6, 115.8, 115.0, 110.0, 109.9, 34.7, 34.5, 32.1, 31.9. **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 3928 (vw), 3856 (vw), 3546 (vw), 3414 (vw), 3050 (vw), 2953 (w), 2659 (vw), 2382 (vw), 2281 (vw), 2165 (vw), 2107 (vw), 1862 (vw), 1747 (vw), 1591 (w), 1472 (m), 1362 (w), 1262 (m), 1137 (w), 1034 (w), 875 (w), 806 (m), 609 (w), 422 (w). **HRMS** (ESI, $C_{204}H_{222}N_{18}$) calc. 2924.7998 $[M+H]^+$, found 2924.7997 $[M+H]^+$. **EA** ($C_{204}H_{222}N_{18}$) calc. C: 83.74, H: 7.65, N: 8.62; found C: 83.37 H: 7.92, N: 8.15.

^{1}H and ^{13}C NMR spectra

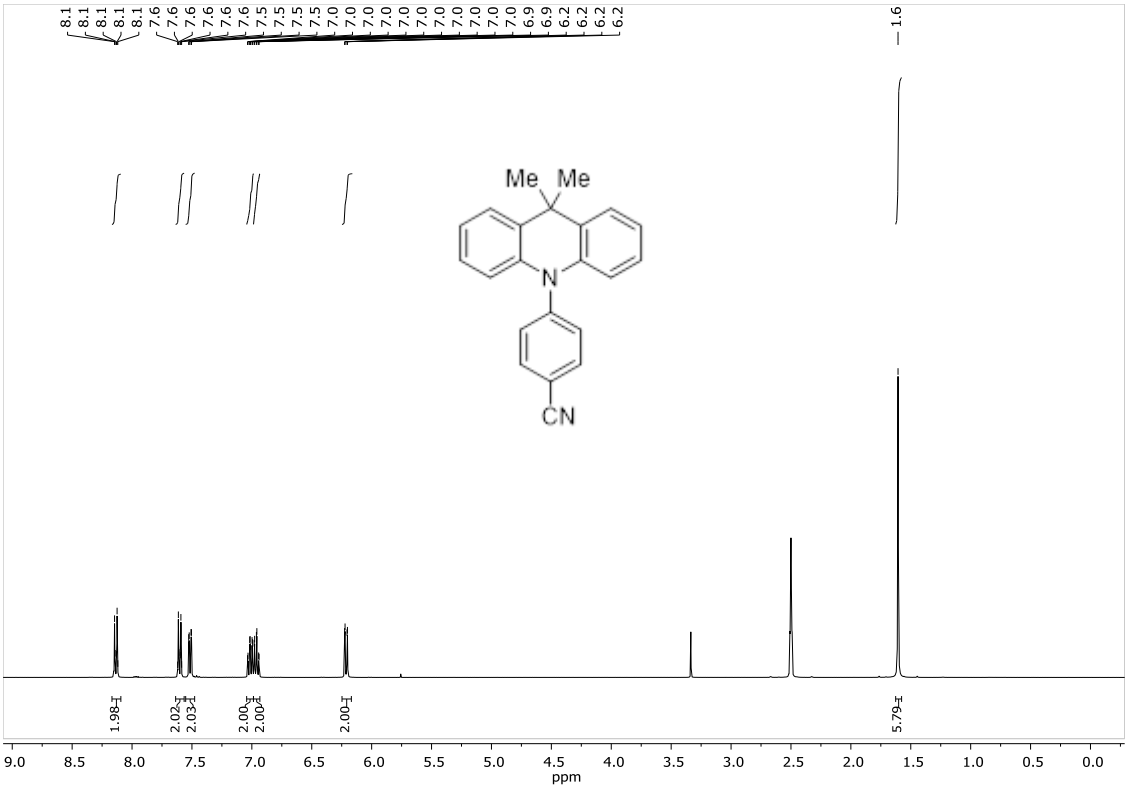


Figure **S1**. ^{1}H NMR of 4-(9,9-Dimethylacridin-10(9)-yl)benzonitrile in DMSO-d_6.

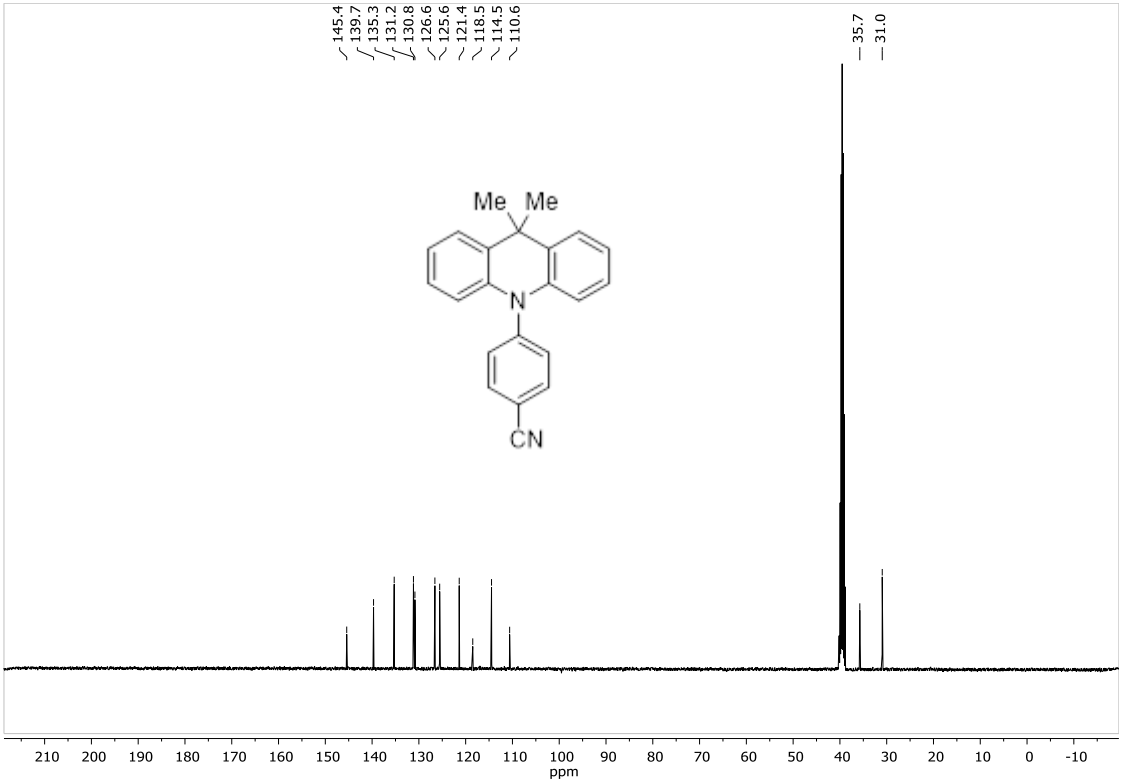


Figure **S2**. ^{13}C NMR of 4-(9,9-Dimethylacridin-10(9)-yl)benzonitrile in DMSO-d_6.

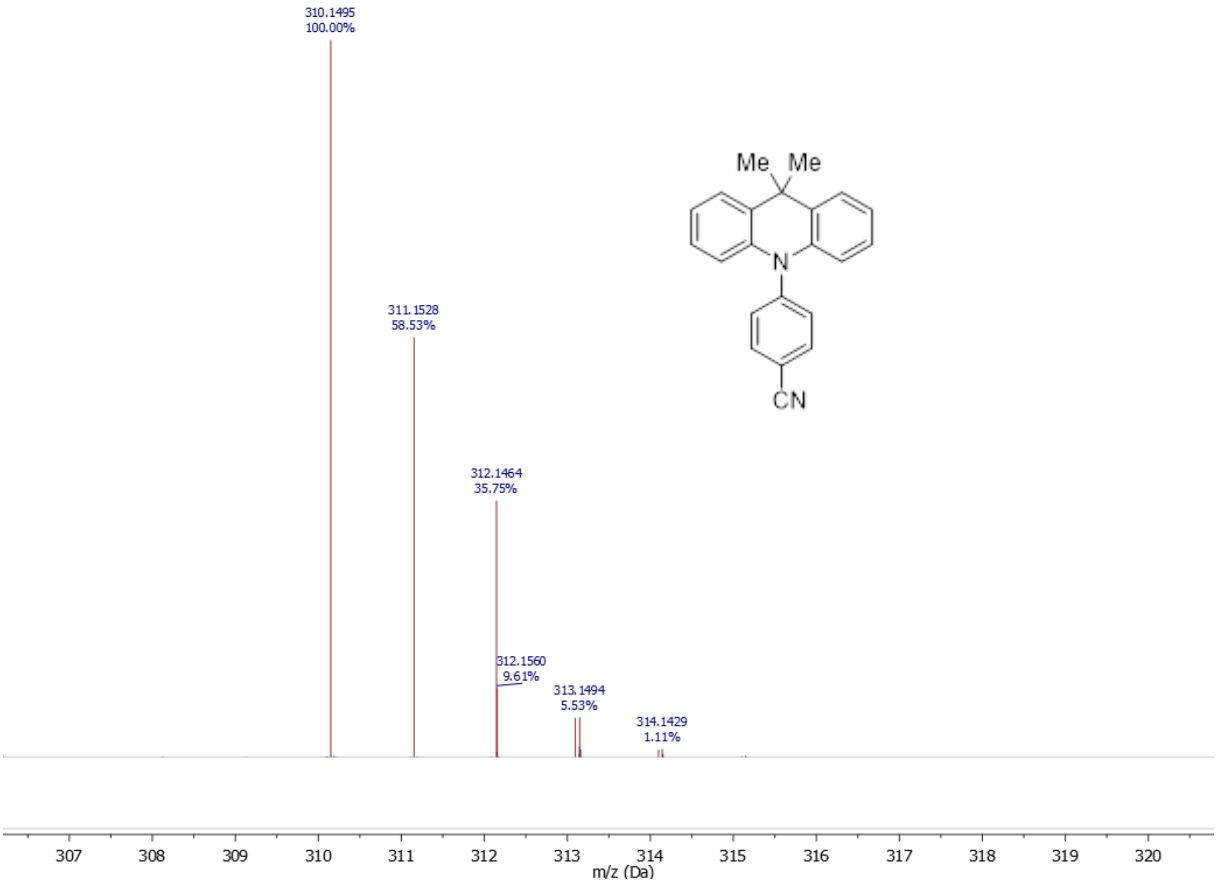


Figure **S3**. HRMS spectra of 4-(9,9-Dimethylacridin-10(9)-yl)benzonitrile.

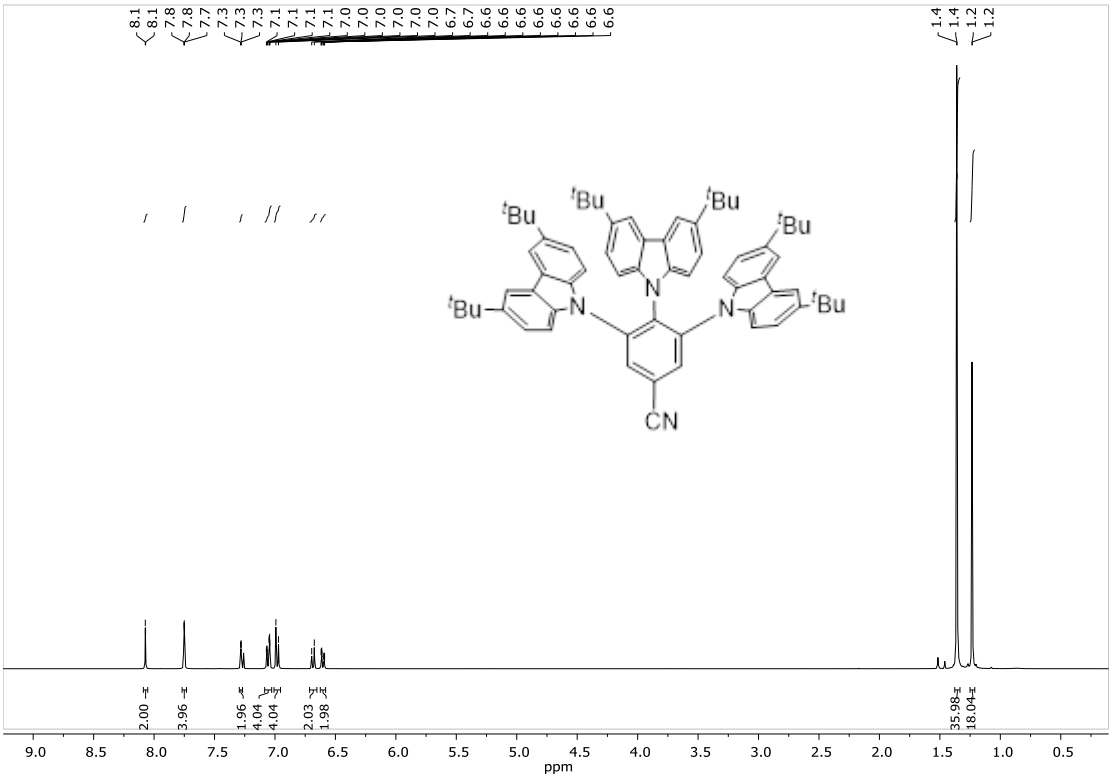


Figure **S4**. ^{1}H NMR of 3,4,5-Tris(3,6-di-*tert*-butyl-9H-carbazol-9-yl)benzonitrile in $CDCl_3$.

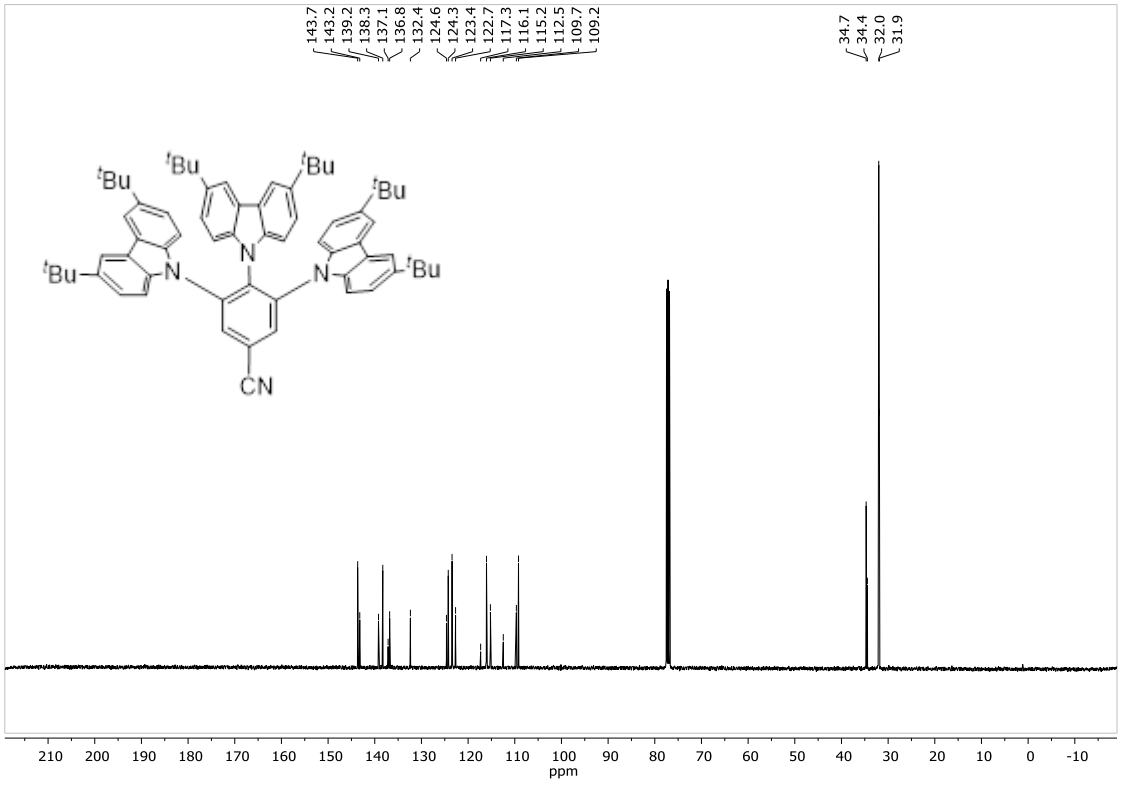


Figure **S5**. ^{13}C NMR of 3,4,5-Tris(3,6-di-*tert*-butyl-9H-carbazol-9-yl)benzonitrile in $CDCl_3$.

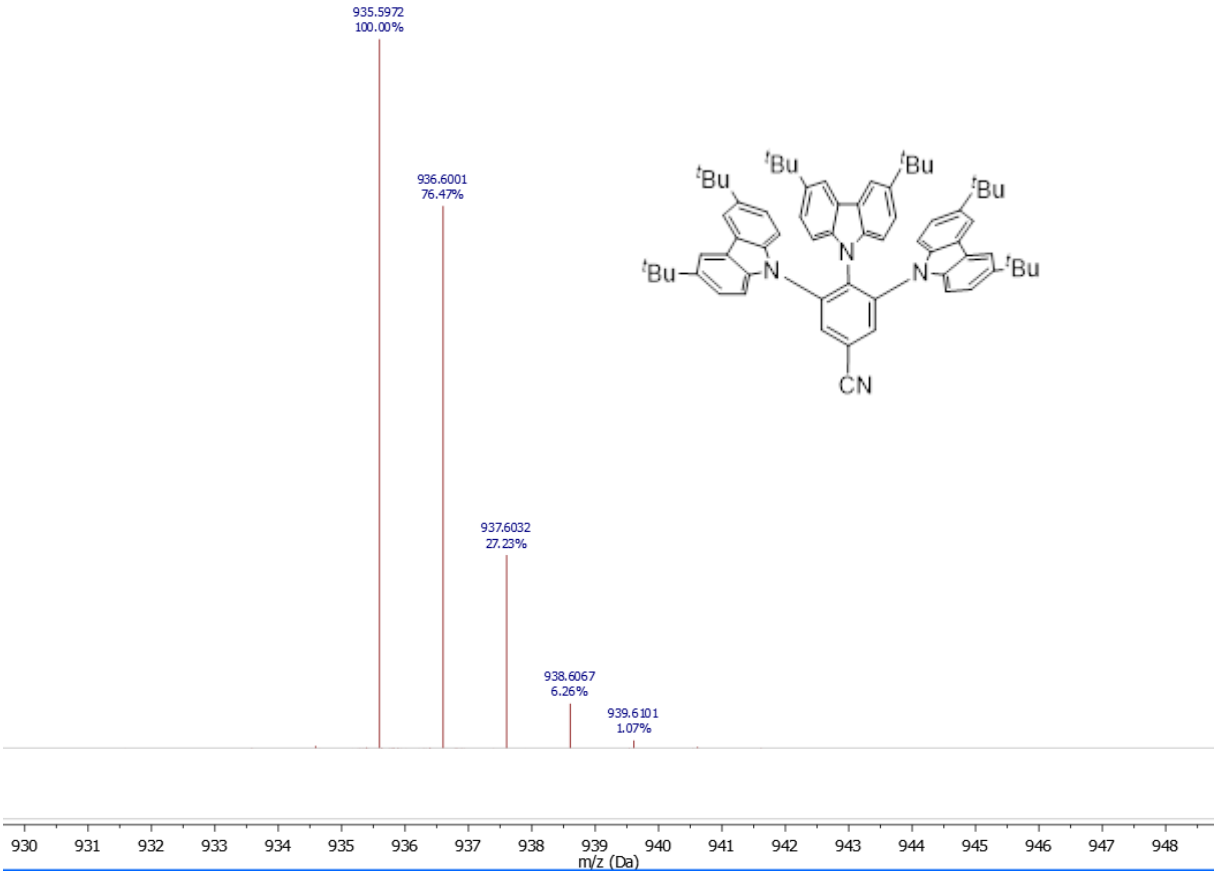


Figure **S6**. HRMS 3,4,5-Tris(3,6-di-*tert*-butyl-9H-carbazol-9-yl)benzonitrile.

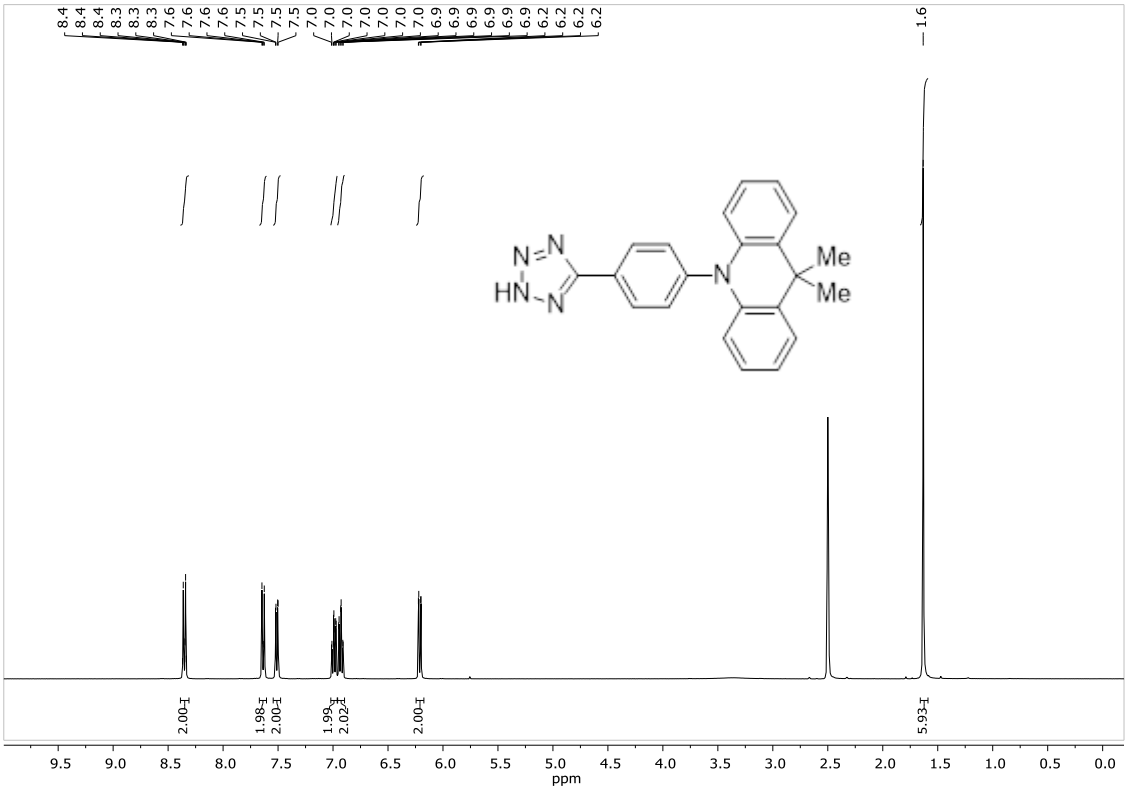


Figure **S7**. ^{1}H NMR of 10-(4-(2*H*-Tetrazol-5-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine in DMSO-d_6.

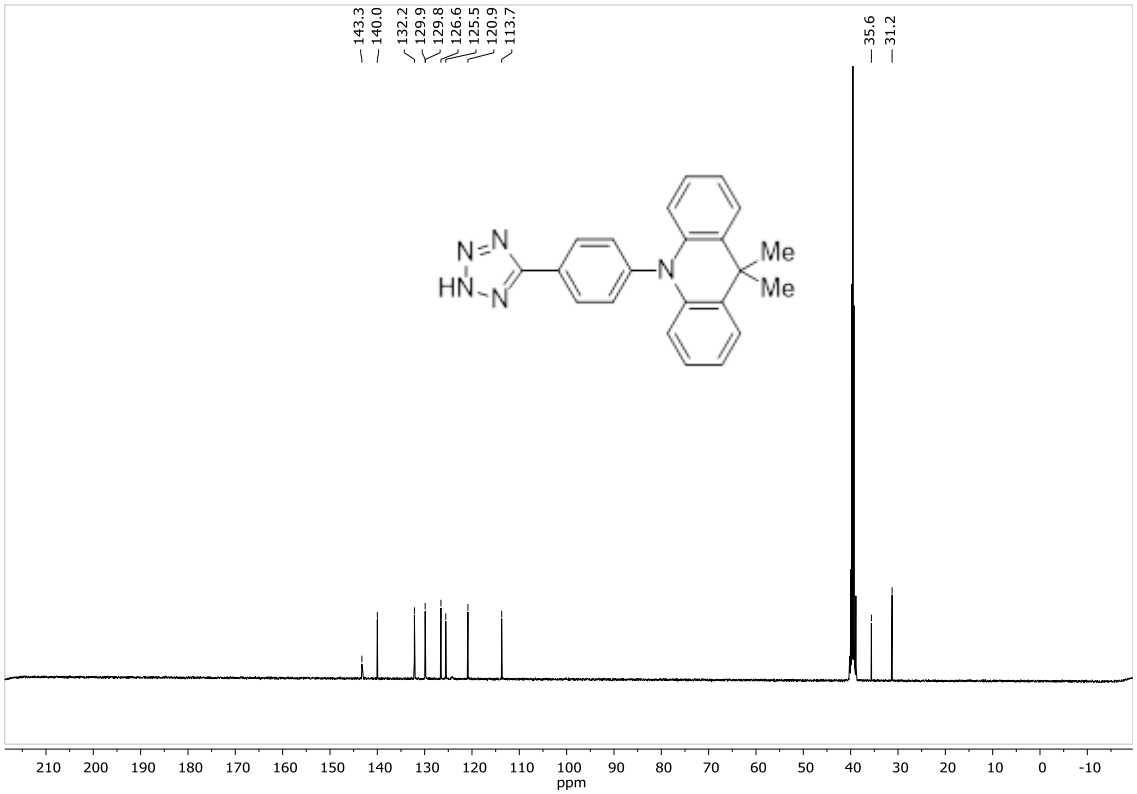


Figure **S8**. ^{13}C NMR of 10-(4-(2*H*-Tetrazol-5-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine in DMSO-d_6.

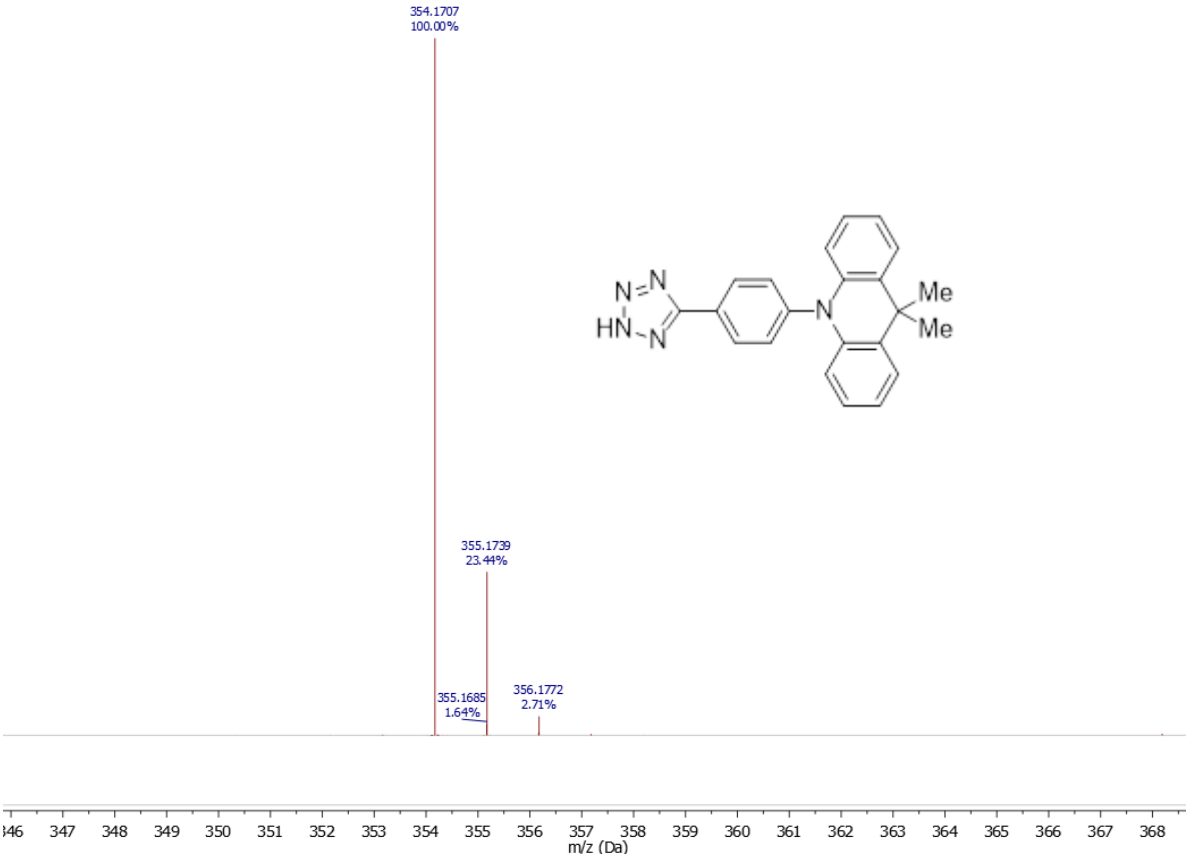


Figure **S9**. HRMS of 10-(4-(2*H*-Tetrazol-5-yl)phenyl)-9,9-dimethyl-9,10-dihydroacridine

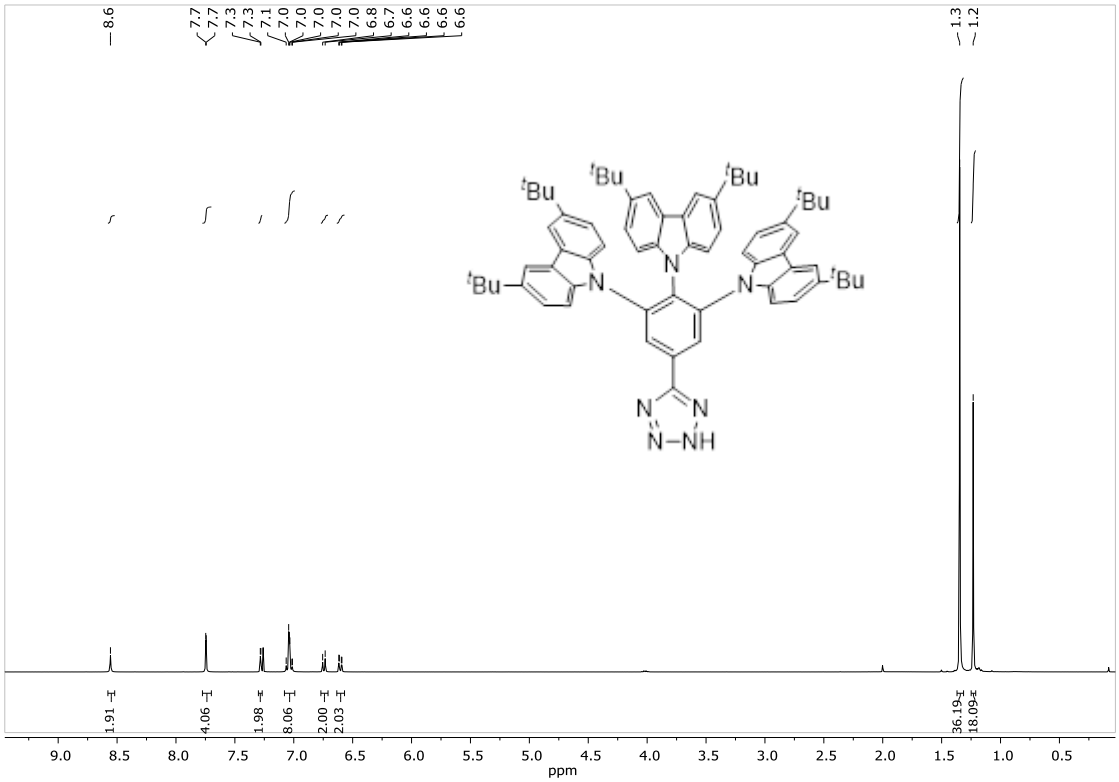


Figure **S10**. ^{1}H NMR of 9,9',9''-(5-(2*H*-Tetrazol-5-yl)benzene-1,2,3-triyl)tris(3,6-di-*tert*-butyl-9*H*-carbazole) in $CDCl_3$.

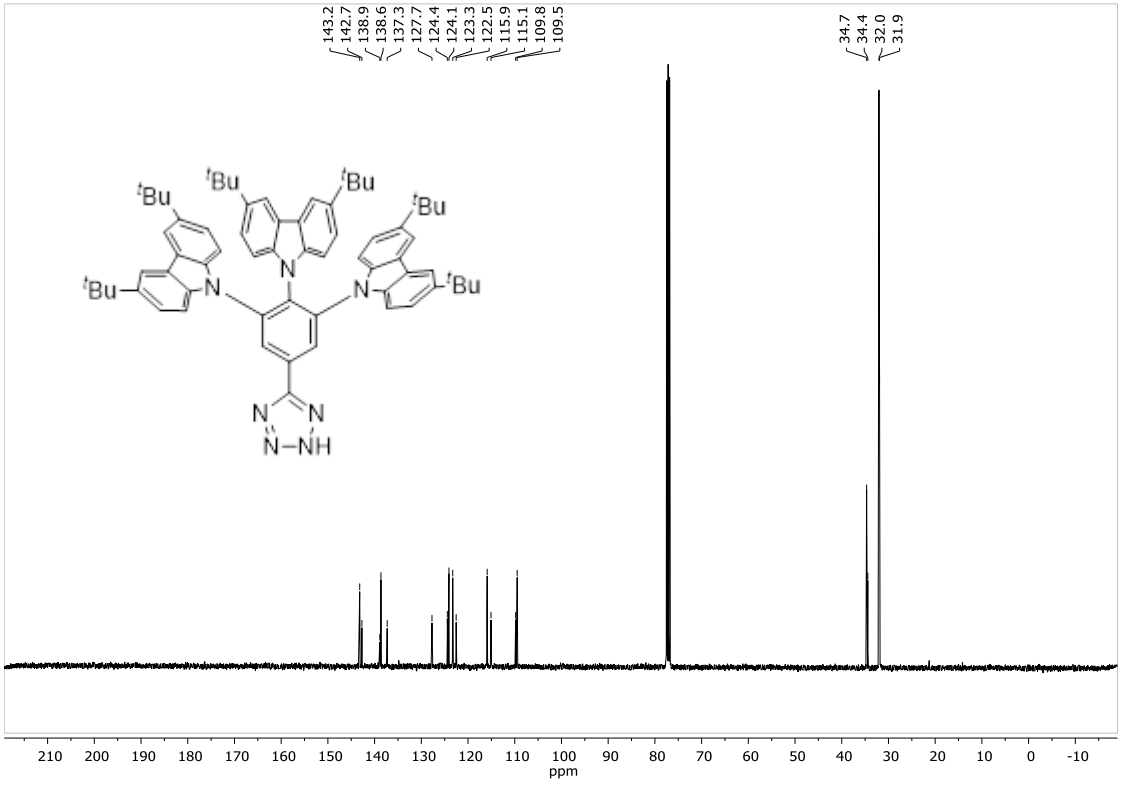


Figure **S11**. ^{13}C NMR of 9,9',9''-(5-(2H-Tetrazol-5-yl)benzene-1,2,3-triyl)tris(3,6-di-*tert*-butyl-9*H*-carbazole) in $CDCl_3$.

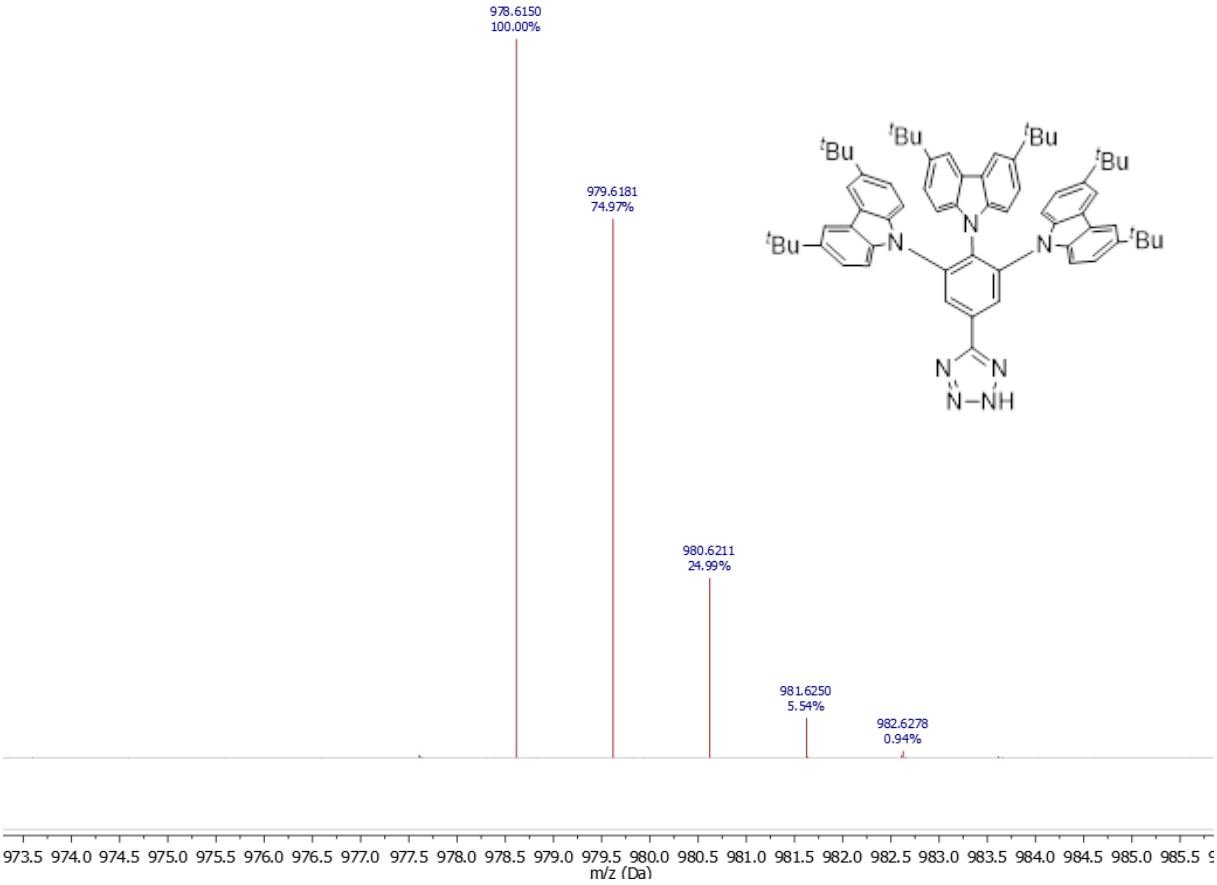


Figure **S12**. HRMS of 9,9',9''-(5-(2H-Tetrazol-5-yl)benzene-1,2,3-triyl)tris(3,6-di-*tert*-butyl-9*H*-carbazole).

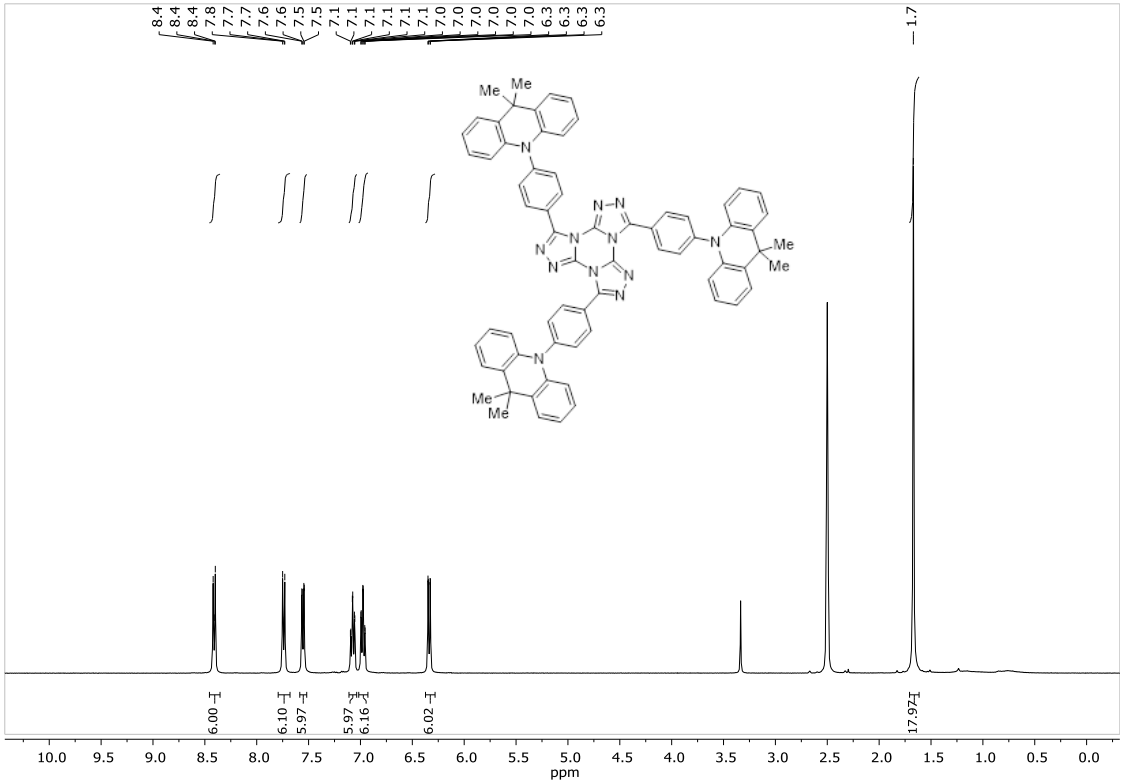


Figure **S13**. ^{1}H NMR of 3,7,11-Tris(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine, **3DMAC-TTT** in DMSO-d_6.

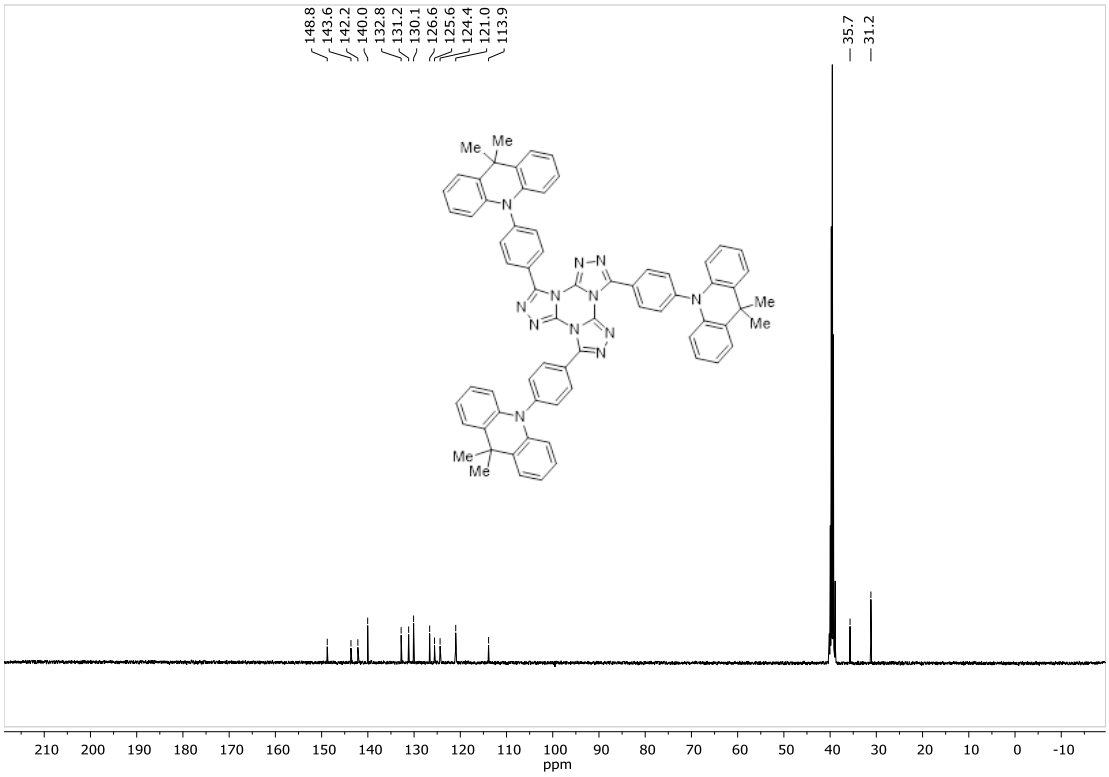


Figure **S14**. ^{13}C NMR of 3,7,11-Tris(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine **– 3DMAC-TTT** in DMSO-d_6.

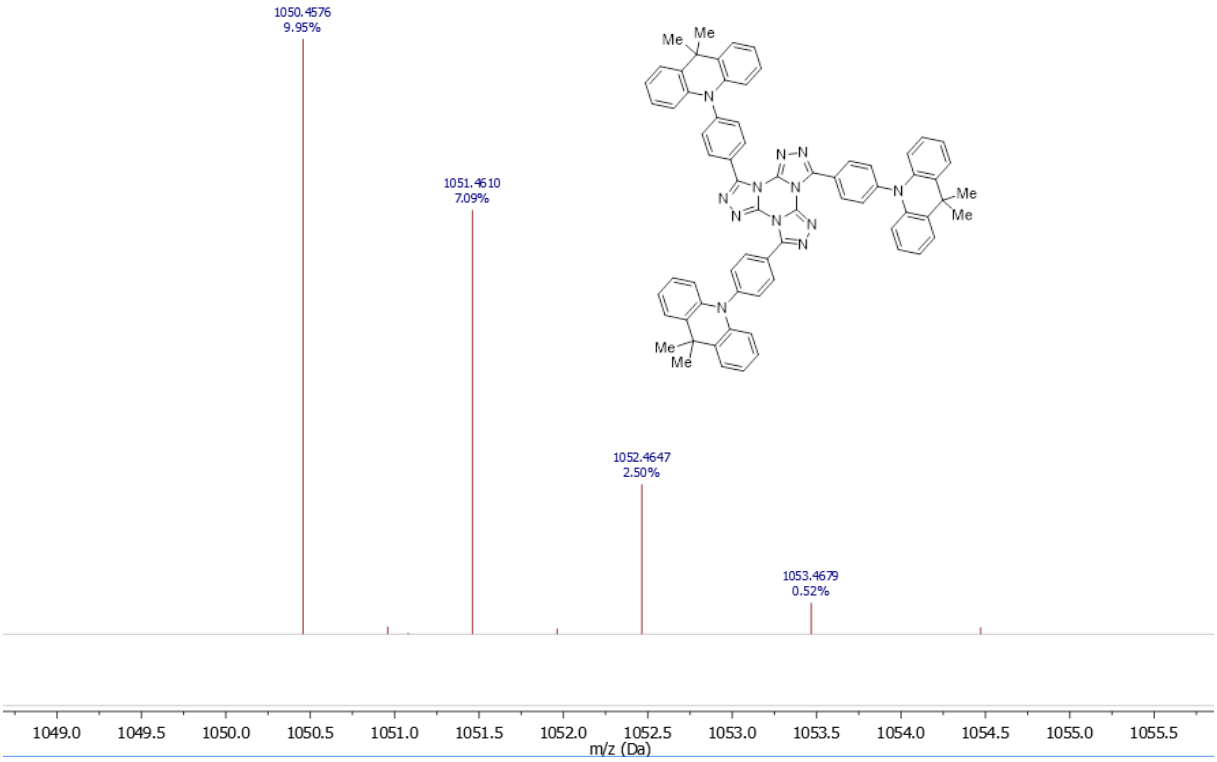


Figure **S15**. HRMS of 3,7,11-Tris(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine **– 3DMAC-TTT**.

Elementaranalyse

Auftraggeber: Fabian Hundemer **Campus Nord** ☐

Datum: 17.9.19 **Tel.:** +49721 608 46794

Substanzbezeichnung: FHUtt036

Summenformel: $C_{69}H_{54}N_{12}$

Berechnet:	**N:**	15.99	**C:**	78.83	**H:**	5.18	**S:** /
Gefunden:	**N:**	15,21	**C:**	78,64	**H:**	5,51	**S:** /
Gefunden:	**N:**	15,17	**C:**	78,75	**H:**	5,46	**S:** /

EI ☐ **FAB** ☐ **ESI** ☐ **ASAP** ☐ **IR** ☐ **UV** ☐

Figure **S16**. Elemental analysis of 3,7,11-Tris(4-(9,9-dimethylacridin-10(9*H*)-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine **– 3DMAC-TTT.**

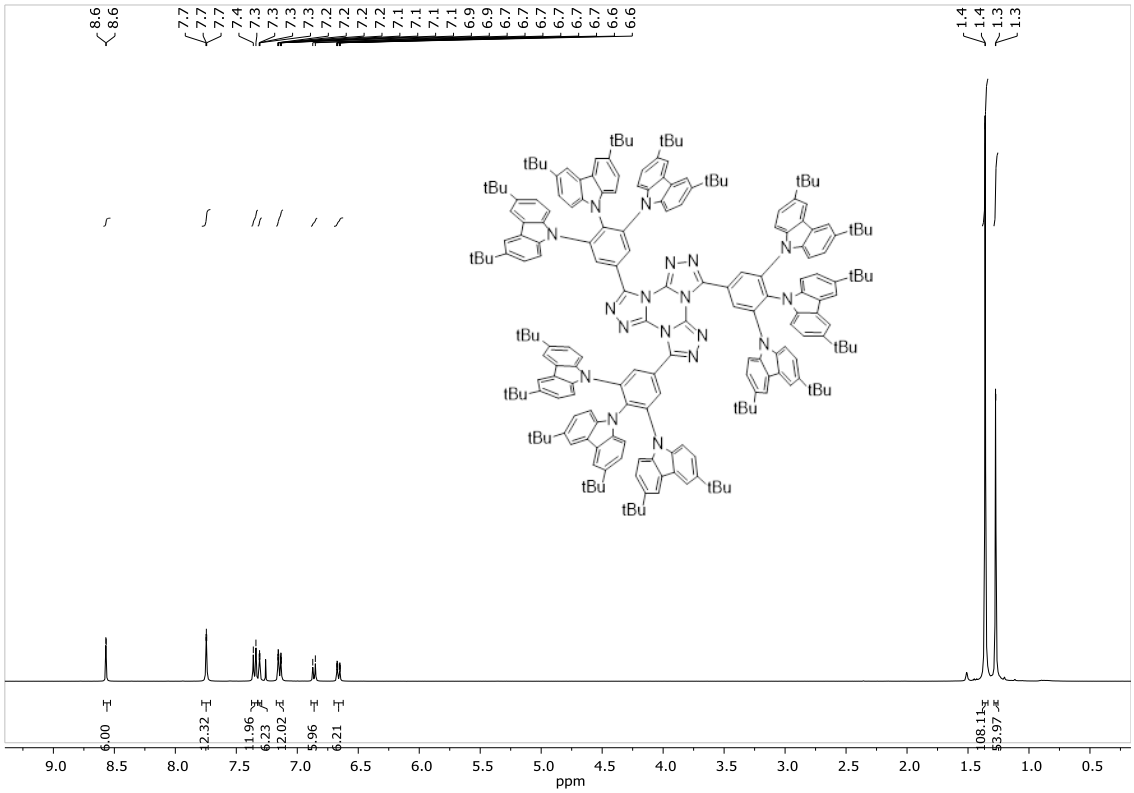


Figure **S17**. ^{1}H NMR of 3,7,11-Tris(3,4,5-tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine **– 3,4,5-3TCz-TTT** in $CDCl_3$.

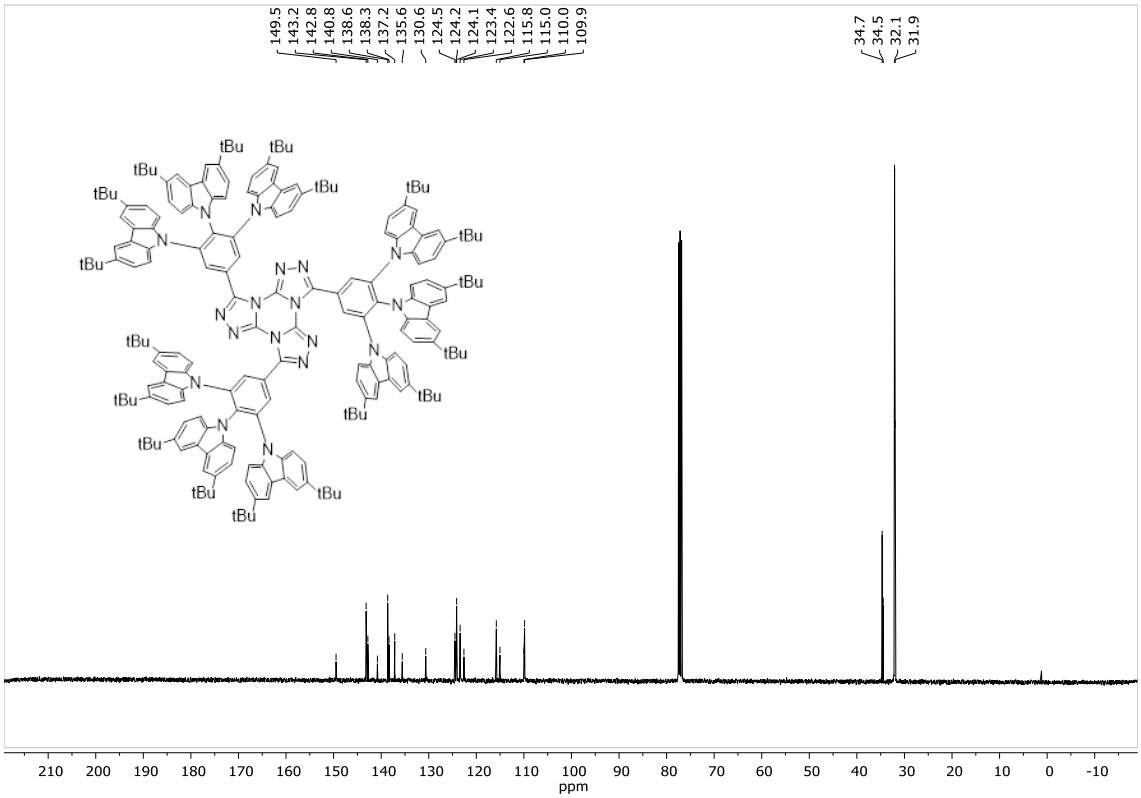


Figure **S18**. ^{13}C NMR of 3,7,11-Tris(3,4,5-tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine **– 3,4,5-3TCz-TTT** in $CDCl_3$.

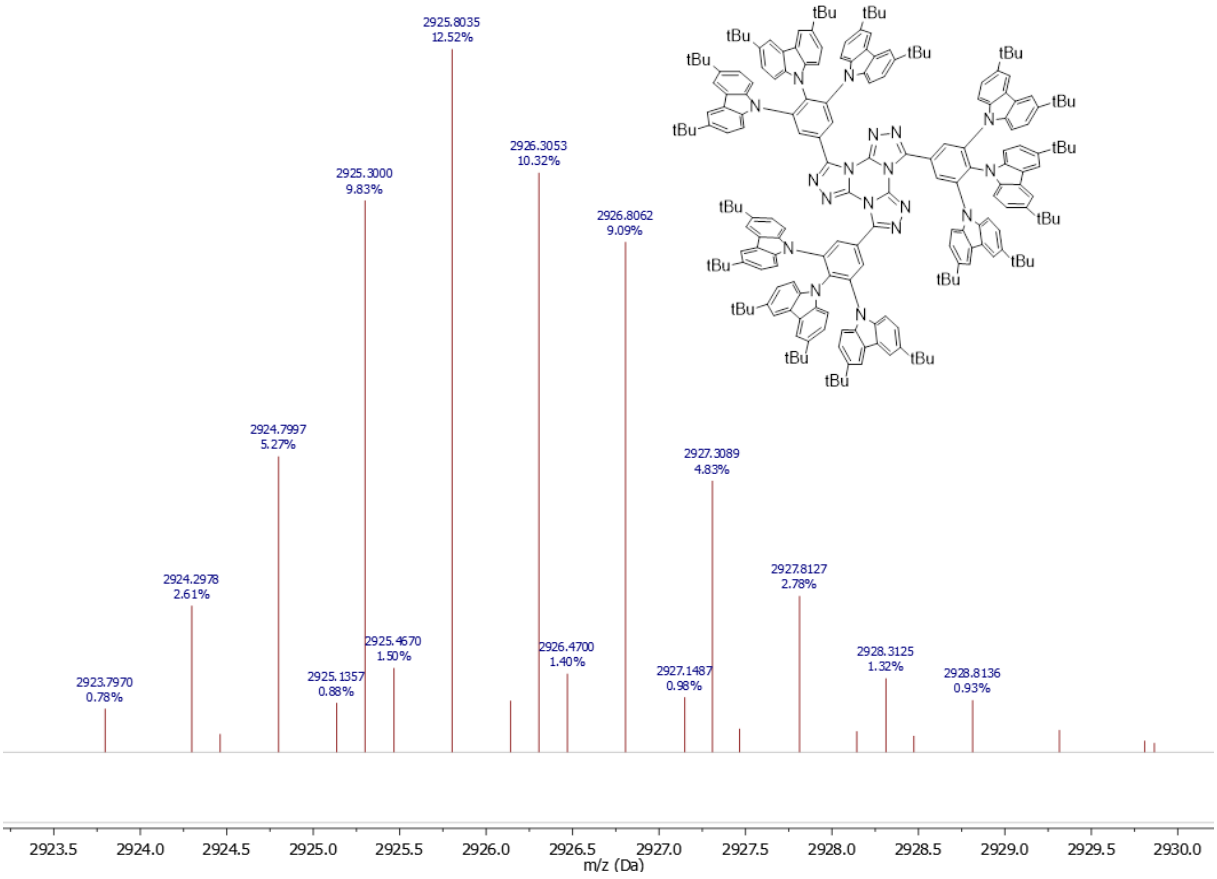
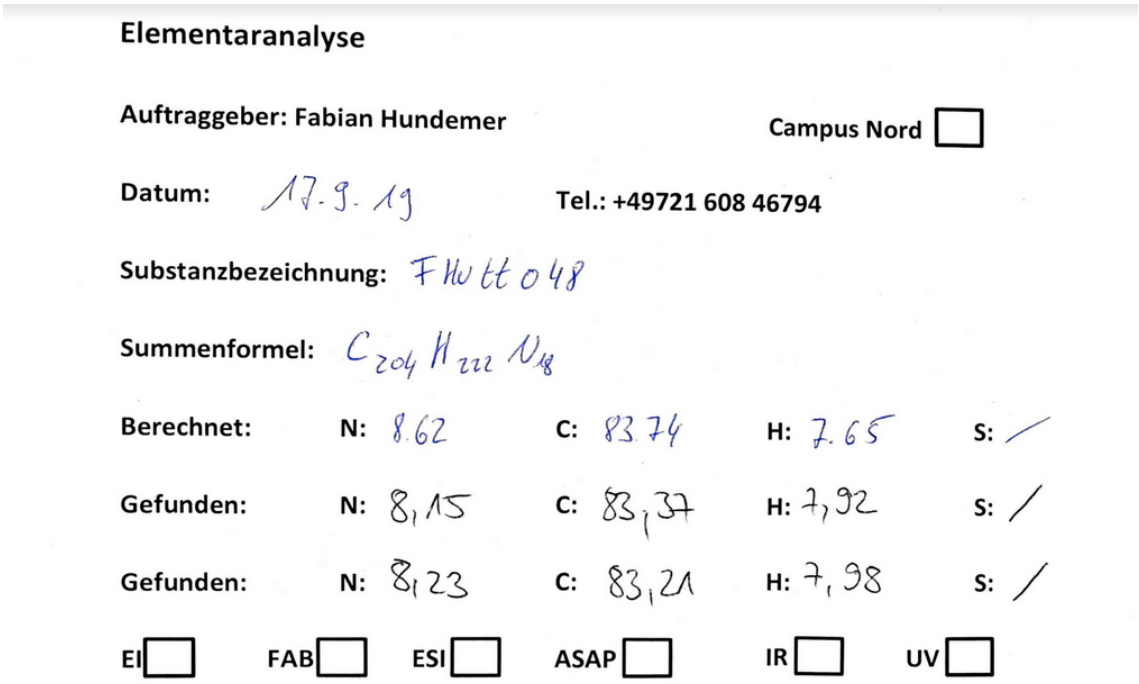


Figure **S19**: HRMS of 3,7,11-Tris(3,4,5-tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine **– 3,4,5-3TCz-TTT.**



Elementaranalyse

Auftraggeber: Fabian Hundemer — **Campus Nord** ☐

Datum: 17.9.19 — **Tel.:** +49721 608 46794

Substanzbezeichnung: FHutt048

Summenformel: $C_{204}H_{222}N_{18}$

Berechnet:	**N:**	8.62	**C:**	83.74	**H:**	7.65	**S:**	/
Gefunden:	**N:**	8,15	**C:**	83,37	**H:**	7,92	**S:**	/
Gefunden:	**N:**	8,23	**C:**	83,21	**H:**	7,98	**S:**	/

EI ☐ **FAB** ☐ **ESI** ☐ **ASAP** ☐ **IR** ☐ **UV** ☐

Figure **S20**: Elemental analysis of 3,7,11-Tris(3,4,5-tris(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)tris([1,2,4]triazolo)[4,3-a:4',3'-c:4'',3''-e][1,3,5]triazine **– 3,4,5-3TCz-TTT.**

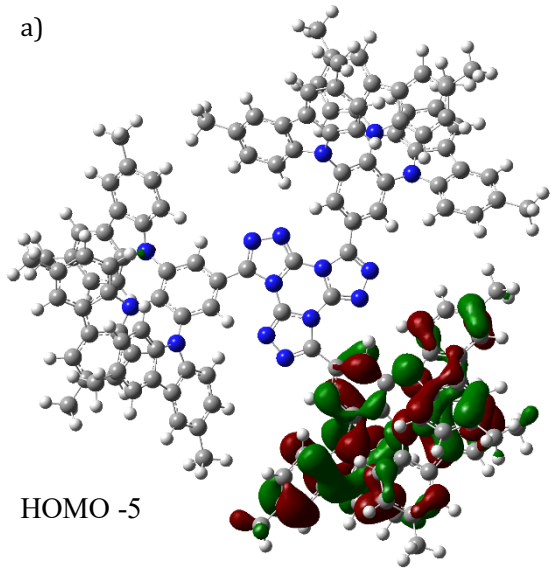
DFT Calculations

Table **S1** Exited states properties of **3,4,5-3MCz-TTT** (PBE0/6-31G(d,p))

Excited State	**Energy / eV ; nm**	**Nature**	**Character of the transition**
T1	2.54 ; 488	(H-2)→L (42%) (H-2)→(L+1) (7%) (H-2)→(L+2) (8%) (H-1)→L (19%) H→L (7%) H→(L+1) (6%)	CT
T2	2.54 ; 488	(H-2)→L (2%) (H-2)→(L+1) (5%) (H-1)→L (20%) (H-1)→(L+1) (4%) (H-1)→(L+2) (5%) H→(L+1) (50%) H→(L+2) (3%)	CT
T3	2.54 ; 488	(H-2)→L (25%) (H-1)→L (5%) (H-1)→(L+1) (31%) (H-1)→(L+2) (3%) H→L (3%) H→(L+1) (17%) H→(L+2) (7%)	CT
T4	2.66 ; 466	(H-4)→L (5%) (H-3)→L (73%) (H-3)→(L+1) (7%) (H-3)→(L+2) (8%)	CT
T5	2.66 ; 466	(H-4)→L (43%) (H-4)→(L+1) (35%) (H-4)→(L+2) (8%) (H-3)→L (3%)	CT
T6	2.67 ; 464	(H-5)→L (4%) (H-5)→(L+1) (77%) (H-5)→(L+2) (9%) (H-5)→(L+1) (2%)	CT
S1 (f=0.10)	2.70 ; 459	(H-2)→L (16%)	CT

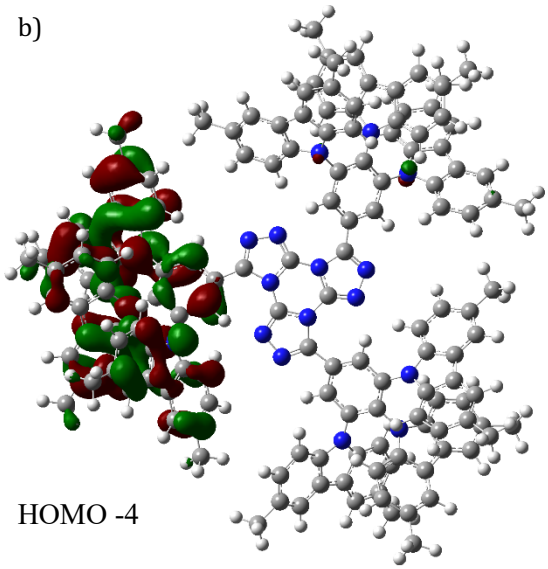
		H→L (7%) H→(L+1) (68%)	

a)



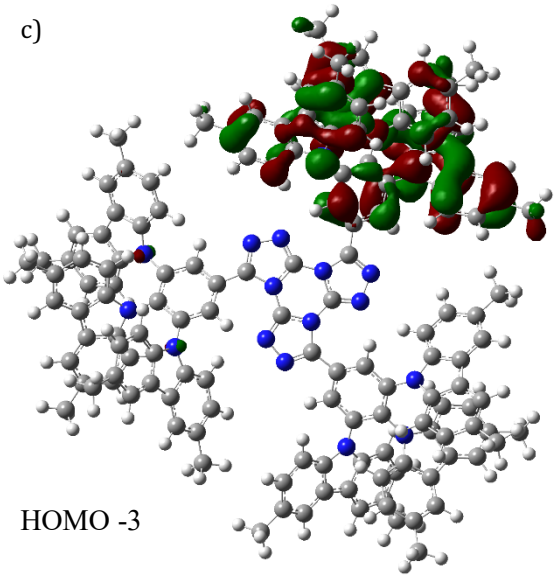
HOMO -5

b)



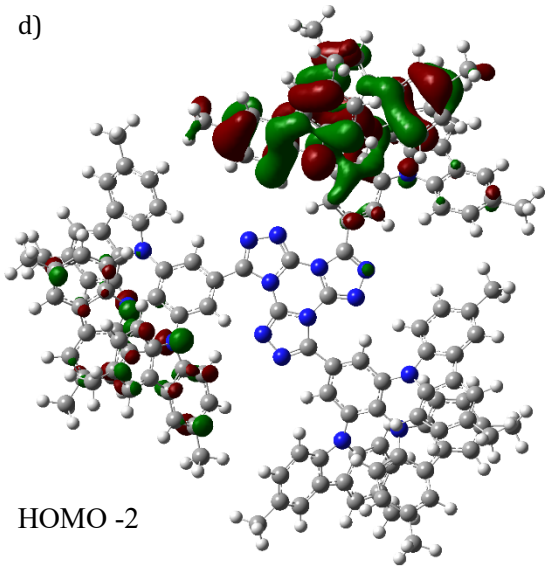
HOMO -4

c)



HOMO -3

d)



HOMO -2

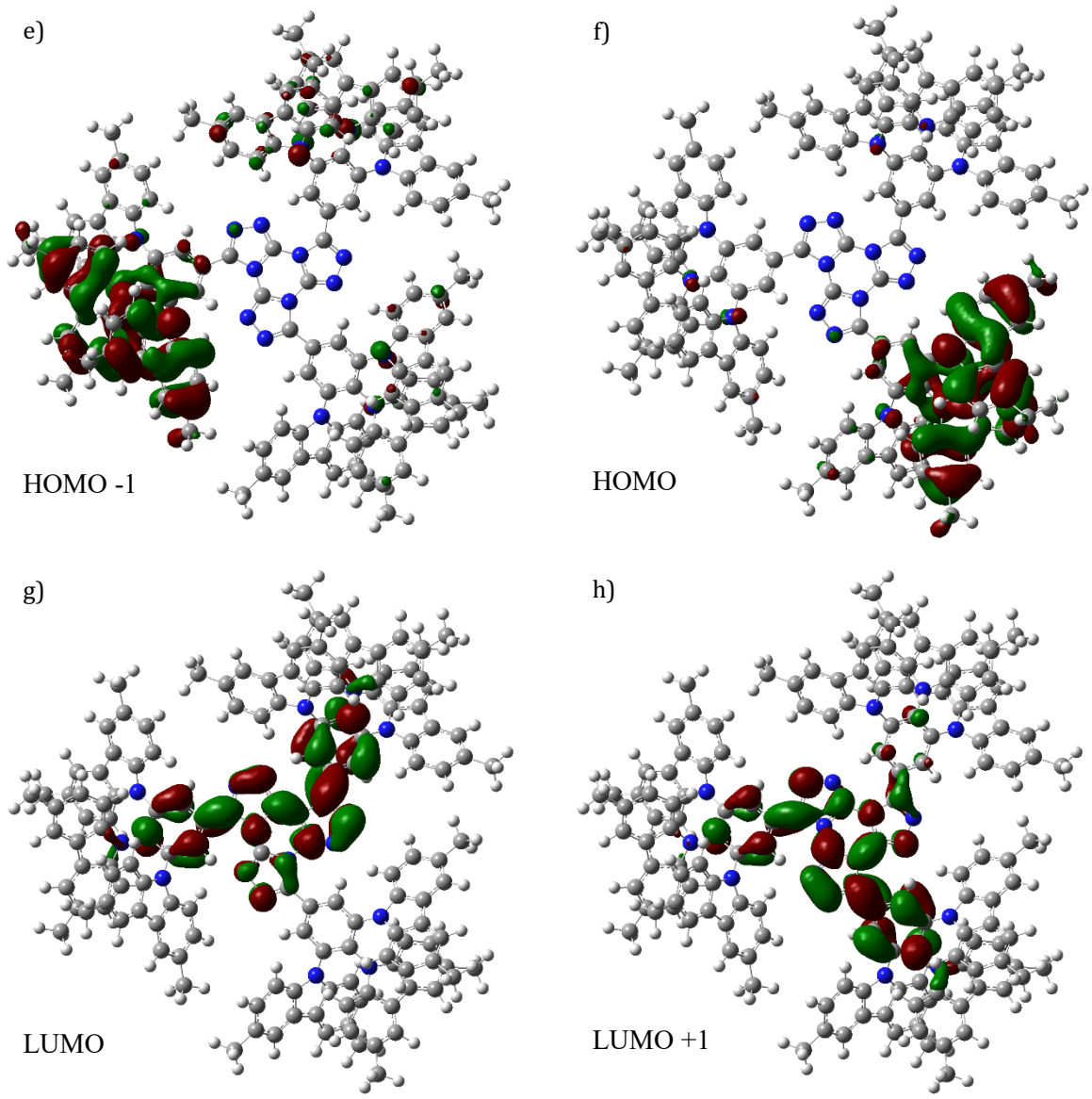


Figure **S21**. Electronic density surfaces of **3,4,5-3MCz-TTT** of a) HOMO-5 b) HOMO-4 c) HOMO-3 d) HOMO-2 e) HOMO-1 f) HOMO g) LUMO h) LUMO +1 (Isovalue for new surfaces: MO=0.02, Density=0.0004).

Table **S2**. Computational ground state geometry of **3,4,5-3MeCz-TTT**

C	1.65823300	-3.56244500	-0.07218600
C	2.87149700	-3.25455900	0.54111700
C	1.48360500	-4.81924900	-0.65504400
C	3.91232100	-4.18053900	0.55315800
H	3.03198400	-2.30475500	1.03276100
C	2.50032200	-5.76373500	-0.63308900
H	0.54555400	-5.06216800	-1.13996000

C	3.74505700	-5.45556000	-0.03851000
C	6.07057200	-6.16748300	-0.53667600
C	4.74003600	-7.67023900	0.51829500
C	6.57247900	-5.07372400	-1.23282800
C	6.85658800	-7.31011600	-0.29179800
C	3.70438100	-8.31124200	1.18930800
C	6.00727000	-8.26951400	0.37694900
C	7.90296800	-5.11724600	-1.62415600
H	5.96117900	-4.20600600	-1.45343400
C	8.18764500	-7.32893100	-0.70688600
C	3.94682300	-9.58725200	1.67771100
H	2.73633700	-7.84401900	1.32938700
C	6.22239300	-9.55023700	0.88444800
C	8.72721700	-6.22593200	-1.36217200
H	8.32092700	-4.26017000	-2.14554800
H	8.80503000	-8.20381300	-0.51913800
C	5.19098400	-10.22571100	1.52959100
H	3.14370800	-10.11029300	2.19041700
H	7.19731600	-10.02008800	0.78138600
N	4.78383600	-6.38871100	-0.03855600
N	5.11757800	-3.81709800	1.17435100
C	5.92352100	-2.74364100	0.77149400
C	5.83783100	-4.58358600	2.09308500
C	5.65369600	-1.72143900	-0.13190700
C	7.17372400	-2.84632600	1.41695000
C	5.43687200	-5.69845800	2.82080300
C	7.11844000	-4.02026100	2.25838500
C	6.66136600	-0.79517400	-0.37340200
H	4.68624600	-1.62144300	-0.61013800
C	8.16587800	-1.90457200	1.14800500
C	6.36671500	-6.28464600	3.66562000
H	4.43910600	-6.11101300	2.72735800
C	8.02935400	-4.62443600	3.12557200
C	7.92096300	-0.87235500	0.24506700
H	6.46085600	0.02538700	-1.05727100
H	9.13408300	-1.98028700	1.63707500
C	7.66757800	-5.77213700	3.82301900

H	6.07912900	-7.17421500	4.21992400
H	9.02270700	-4.20179000	3.25379500
N	2.24022300	-7.02040200	-1.19949300
C	1.18586600	-7.84456700	-0.79842100
C	3.01388700	-7.71308000	-2.13084400
C	0.18245200	-7.61052000	0.13882600
C	1.29600500	-9.08215500	-1.46578900
C	4.12542900	-7.29097000	-2.85331900
C	2.46303800	-8.99786300	-2.31378300
C	-0.72189100	-8.63581000	0.38208600
H	0.10072000	-6.66539100	0.66545400
C	0.36497700	-10.08847300	-1.20569300
C	4.71027400	-8.20028700	-3.72075700
H	4.53453100	-6.29376600	-2.74175500
C	3.06824700	-9.88720400	-3.20298100
C	-0.65510300	-9.87373200	-0.28349300
H	-1.50851500	-8.47403100	1.11446200
H	0.44051000	-11.04474300	-1.71724100
C	4.20533000	-9.50139800	-3.90366200
H	5.59276700	-7.89531100	-4.27713900
H	2.65303600	-10.88155200	-3.34672500
C	0.48403600	-2.69553600	-0.07492900
N	0.41371600	-1.30562500	-0.00598900
N	-0.73993000	-3.16632100	-0.14564000
C	1.34987100	-0.28709700	-0.04574400
C	-0.93894000	-1.04355700	-0.04730400
N	-1.63085900	-2.13546400	-0.13692300
N	0.90174200	1.01625400	-0.01049500
N	2.64155100	-0.34271800	-0.13012000
N	-1.35312900	0.27652800	-0.00845000
C	-0.44908100	1.31680700	-0.05013400
C	2.07217100	1.77036300	-0.07675300
N	3.09047900	0.94317600	-0.14079100
C	-2.59172300	0.91133000	-0.07589000
N	-1.04868300	2.46203600	-0.13903000
N	-2.38657700	2.20667400	-0.14670400
C	-3.93105700	0.33136700	-0.06701800

C	-4.93557200	1.12231800	-0.62877400
C	-4.26976600	-0.87946200	0.53441100
C	-6.26360800	0.72117400	-0.59491800
H	-4.67779200	2.06011700	-1.10636000
C	-5.59450000	-1.31071400	0.55821100
H	-3.52456700	-1.50446500	1.00742500
C	-6.61880000	-0.51549400	-0.00815800
N	-7.22284500	1.58653000	-1.14172700
N	-5.88004200	-2.54261000	1.16725100
N	-7.94919200	-0.93982900	0.00844900
C	-7.39858500	2.90817200	-0.72398400
C	-8.22520000	1.27620300	-2.06063700
C	-5.35231000	-3.77242800	0.75253700
C	-6.88643500	-2.79134600	2.10265200
C	-9.02640200	-0.24573000	0.56687000
C	-8.42361900	-2.14814000	-0.50975100
C	-6.67549400	3.64888700	0.20792400
C	-8.53562200	3.44125600	-1.36583000
C	-8.42881800	0.11184300	-2.79432600
C	-9.06262400	2.39945400	-2.21727800
C	-4.34603500	-4.04109500	-0.16894600
C	-6.04924400	-4.81008700	1.40693800
C	-7.64552200	-1.89291000	2.84433400
C	-7.02658800	-4.18346300	2.26813500
C	-9.04324900	0.96367800	1.25308400
C	-10.19551000	-1.01442900	0.40344600
C	-7.74481100	-3.13510800	-1.21554300
C	-9.81052700	-2.22950300	-0.27776900
C	-7.10381300	4.94293100	0.47307600
H	-5.80725100	3.24012000	0.71421300
C	-8.93504600	4.74801000	-1.08289100
C	-9.52275500	0.07202900	-3.64462800
H	-7.76857000	-0.74270500	-2.70510900
C	-10.15008500	2.33221900	-3.08941200
C	-4.04431000	-5.37442000	-0.42019900
H	-3.78734200	-3.24872400	-0.65337900
C	-5.72671100	-6.13744200	1.12782400

C	-8.59859700	-2.41298400	3.70641800
H	-7.51311400	-0.82142500	2.75027300
C	-7.98619600	-4.67792100	3.15234700
C	-10.26558600	1.41754600	1.72749300
H	-8.14232400	1.54488700	1.41307200
C	-11.40800800	-0.53581700	0.89857400
C	-8.47167300	-4.24023900	-1.63471100
H	-6.68392900	-3.06199800	-1.42567000
C	-10.51589200	-3.34853800	-0.71906000
C	-8.22117300	5.51267700	-0.16495100
H	-6.55388400	5.53529100	1.19981700
H	-9.80930100	5.16776200	-1.57408400
C	-10.39835700	1.16310500	-3.79971100
H	-9.71003100	-0.83711500	-4.21006400
H	-10.80416000	3.19178100	-3.21231500
C	-4.72413000	-6.43249000	0.20661100
H	-3.24408300	-5.60441200	-1.11865600
H	-6.26322000	-6.94319800	1.62311600
C	-8.79230400	-3.79742600	3.86598600
H	-9.21885600	-1.72464200	4.27451600
H	-8.10692300	-5.75051000	3.28197700
C	-11.45686400	0.69073600	1.55389400
H	-10.30049000	2.37058000	2.24891200
H	-12.31543200	-1.12173900	0.77571600
C	-9.84998000	-4.37090200	-1.38850700
H	-7.95299100	-5.03329800	-2.16692600
H	-11.58587000	-3.42298000	-0.54195900
C	2.24374500	3.22005600	-0.07416000
C	3.44243000	3.68649700	-0.61877400
C	1.35633900	4.12690900	0.50216600
C	3.76266800	5.03626900	-0.59005800
H	4.13203600	2.98860200	-1.07852300
C	1.64863000	5.48934500	0.51851600
H	0.43170000	3.80127300	0.95871200
C	2.86144200	5.97019800	-0.02770800
N	5.00210400	5.42646500	-1.11842400
N	0.71295900	6.36025800	1.09785300

N	3.16424000	7.33334000	-0.01437600
C	6.22716000	4.92238800	-0.67406700
C	5.25097600	6.44454600	-2.03883100
C	-0.60969000	6.50553600	0.66007600
C	0.97583700	7.35902400	2.03723900
C	4.29827900	7.91557100	0.55867300
C	2.37765900	8.34813600	-0.56642200
C	6.49111900	3.93116500	0.26809100
C	7.26832300	5.63906200	-1.30016600
C	4.35646700	7.19607600	-2.79380200
C	6.64458700	6.61099200	-2.16886800
C	-1.32255500	5.76189700	-0.27466700
C	-1.18216500	7.62185600	1.30483700
C	2.11759200	7.57901600	2.80033700
C	-0.17112100	8.16448400	2.18351800
C	5.33049100	7.32439700	1.27887200
C	4.23757200	9.31017700	0.36952400
C	1.19726900	8.25597400	-1.29539600
C	3.01154200	9.58622900	-0.34438600
C	7.82133900	3.65875900	0.55965500
H	5.69462300	3.38478600	0.76245000
C	8.59458200	5.33510300	-0.99097800
C	4.88181100	8.16278500	-3.63686700
H	3.28525700	7.04799500	-2.72439400
C	7.14360700	7.58494400	-3.03527500
C	-2.62770100	6.15298300	-0.54692900
H	-0.89822600	4.88685100	-0.75285200
C	-2.49257500	7.99247100	1.00413500
C	2.11486500	8.66183800	3.66603500
H	2.98870300	6.93935800	2.72024900
C	-0.14818400	9.24091500	3.07106800
C	6.33249800	8.15253000	1.76434100
H	5.36586700	6.25559100	1.45684300
C	5.25563400	10.11732900	0.87561200
C	0.63048700	9.43721700	-1.75257900
H	0.72110000	7.30331000	-1.49728600
C	2.42256300	10.75544500	-0.82437900

C	8.88398700	4.33941200	-0.06259000
H	8.04745300	2.89164600	1.29574400
H	9.40364500	5.88136000	-1.46939300
C	6.26661600	8.37967900	-3.76486400
H	4.19709600	8.77554200	-4.21736400
H	8.21671600	7.72476100	-3.13864800
C	-3.22669900	7.26425900	0.07117000
H	-3.20903300	5.56904600	-1.25564800
H	-2.93912500	8.85501100	1.49297200
C	1.00040800	9.50895300	3.80803200
H	3.00784800	8.86292000	4.25211300
H	-1.02615400	9.87173100	3.18549800
C	6.31915200	9.54470900	1.56664400
H	7.15715700	7.70603600	2.31379200
H	5.21750900	11.19454700	0.73438700
C	1.21937300	10.69297000	-1.52091900
H	-0.30408800	9.38642900	-2.30503200
H	2.90337100	11.71600300	-0.65718500
C	-4.62649700	7.66985400	-0.29970300
H	-5.25118600	6.79834600	-0.51731900
H	-5.10398700	8.23715400	0.50497500
H	-4.63173400	8.30503700	-1.19387800
C	1.06559400	10.68333800	4.74366600
H	1.77968500	11.43461400	4.38736800
H	0.09162700	11.17060000	4.83865300
H	1.38867100	10.38111400	5.74557500
C	0.54623700	11.94159200	-2.01777200
H	0.26806000	11.85474200	-3.07334500
H	-0.37347400	12.14652300	-1.45769100
H	1.19783600	12.81311900	-1.91318200
C	7.44641000	10.38934600	2.09100300
H	7.67255500	10.15300200	3.13597700
H	8.36569900	10.22545700	1.51677700
H	7.20600900	11.45418700	2.03222500
C	6.77484500	9.45920900	-4.67878700
H	7.86501200	9.43459100	-4.75573100
H	6.36486600	9.35559200	-5.68910700

H	6.48974700	10.45302900	-4.31523200
C	10.30396800	3.97679100	0.27160900
H	10.46730600	3.95557800	1.35415500
H	10.56162400	2.98271400	-0.11238400
H	11.00937100	4.69134600	-0.16045600
C	8.99145300	0.12847100	-0.09290400
H	8.56187900	1.10037300	-0.35260300
H	9.68077600	0.27495000	0.74433200
H	9.58834600	-0.20361400	-0.95117300
C	8.64107200	-6.46604500	4.73381600
H	8.89573600	-7.46260300	4.35542600
H	9.57101500	-5.89918300	4.82798900
H	8.22617500	-6.59915100	5.73874200
C	10.17072100	-6.20398800	-1.78027000
H	10.28284800	-5.88632100	-2.82216100
H	10.75021300	-5.50527500	-1.16573400
H	10.62937000	-7.19120100	-1.67924500
C	5.38853200	-11.61941200	2.05657500
H	5.04338900	-11.70990400	3.09186600
H	4.82737300	-12.35149600	1.46434100
H	6.44214300	-11.90955000	2.02770300
C	4.89641800	-10.44830600	-4.84411200
H	5.90020500	-10.70198000	-4.48487800
H	4.33678900	-11.38116900	-4.95127700
H	5.01195400	-10.01014800	-5.84129300
C	-1.68237100	-10.93365500	0.00077200
H	-1.78225500	-11.11619200	1.07589500
H	-2.67164100	-10.63908700	-0.36878400
H	-1.41915900	-11.88083600	-0.47714500
C	-11.58066500	1.05065700	-4.72069900
H	-12.30515900	0.31751200	-4.34820400
H	-12.09916700	2.00779800	-4.82082500
H	-11.27948300	0.72606000	-5.72244000
C	-8.61841100	6.92929200	0.14294300
H	-8.72128500	7.09090000	1.22118000
H	-7.86709000	7.64101600	-0.21881900
H	-9.57135500	7.18609600	-0.32693500

C	-12.75653900	1.24325600	2.06830300
H	-12.67896400	1.53915300	3.11988300
H	-13.06103500	2.13260500	1.50465000
H	-13.56120700	0.50790500	1.98563700
C	-10.57998600	-5.60456200	-1.84040100
H	-10.37548500	-5.82961000	-2.89241900
H	-10.27495300	-6.48151400	-1.25779900
H	-11.66122800	-5.49136400	-1.72555300
C	-9.86064100	-4.30276800	4.79457500
H	-9.80554000	-5.38833100	4.91113500
H	-9.77352700	-3.85346700	5.78956900
H	-10.86054900	-4.05962700	4.41716400
C	-4.39096000	-7.85709200	-0.14189900
H	-3.34321900	-7.96090600	-0.43844600
H	-4.57295800	-8.52884700	0.70270900
H	-5.00335500	-8.21441000	-0.97884900

Table **S3.** Exited states properties of **3DMAC-TTT** (PBE0/6-31G(d,p))

Excited State	**Energy / eV ; nm**	**Nature**	**Character of the transition**
T1	2.83 ; 438	(H-2)→L (84%) (H-2)→(L+2) (8%) (H-1)→(L+1) (3%)	CT
T2	2.83 ; 438	(H-2)→L (4%) (H-1)→L (27%) (H-1)→(L+1) (58%) (H-1)→(L+2) (8%)	CT
T3	2.83 ; 438	H→L (19%) H→(L+1) (70%) H→(L+2) (9%)	CT
S1 (f=0.0014)	2.84 ; 437	(H-2)→L (22%) (H-2)→(L+2) (2%) (H-1)→L (22%) (H-1)→L+1 (45%) (H-1)→(L+2) (6%)	CT

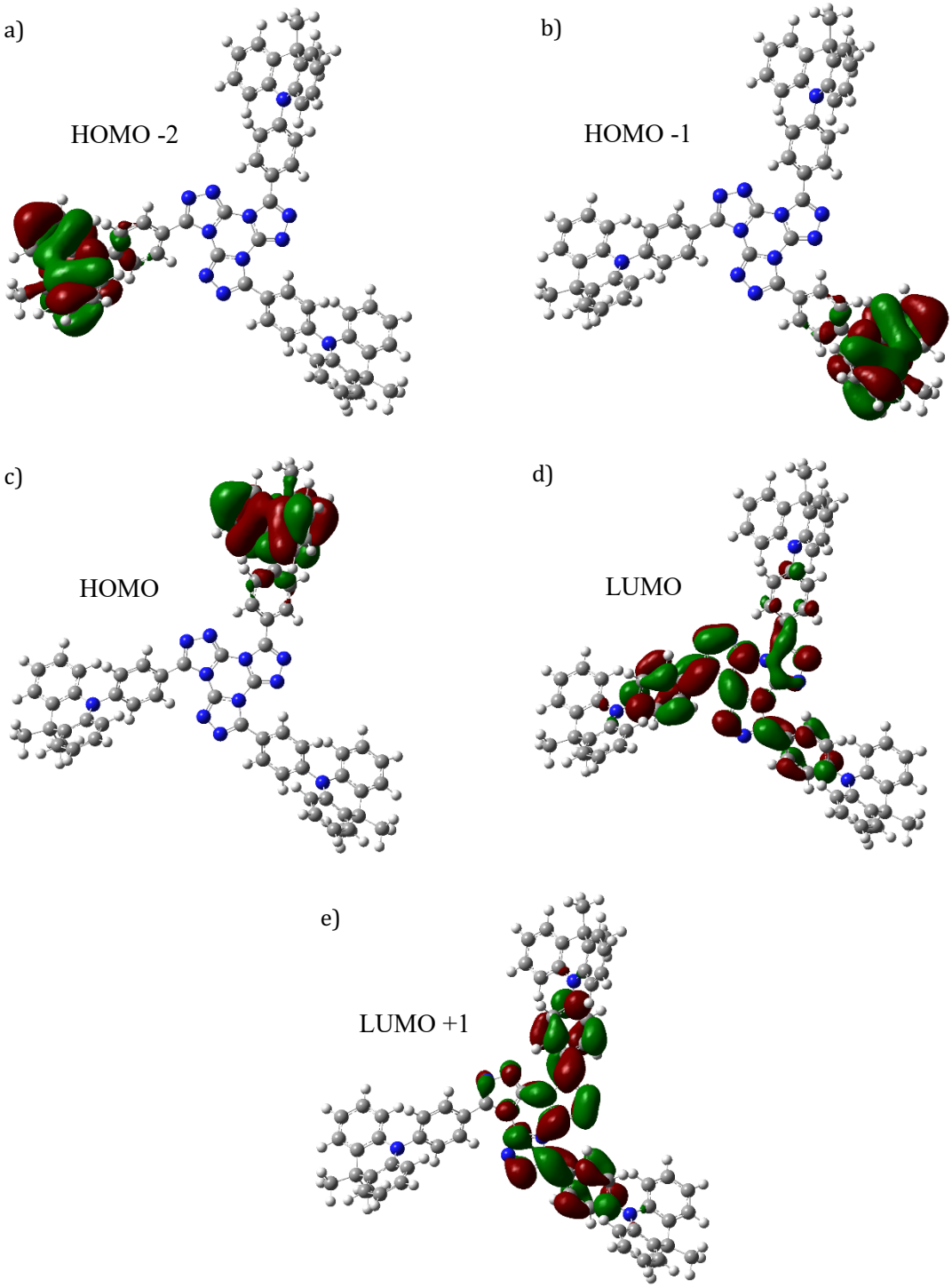


Figure **S22**. Electronic density distributions of **3DMAC-TTT** of a) HOMO -2 b) HOMO -1 c) HOMO d) LUMO e) LUMO +1 (Isovalue for new surfaces: MO=0.02, Density=0.0004).

Table **S4.** Computational ground state geometry of **3DMAC-TTT**

C	-0.48124600	1.25075200	0.09462600
C	1.33090800	-0.32983200	-0.09175800

C	-0.95432900	-1.10409100	-0.15822900
C	0.48553800	-2.73906600	-0.21724800
C	-2.62155400	0.82785100	0.06829700
N	0.87408500	0.96536800	0.03195100
N	0.39916200	-1.35514000	-0.09189800
N	-1.37735800	0.21198000	-0.05783000
N	2.61933200	-0.37457100	-0.22660400
N	3.05725100	0.91706300	-0.18966700
N	-1.09160400	2.37745600	0.29276900
N	-2.42873800	2.11005100	0.26927900
N	-1.63405900	-2.19846800	-0.30789400
N	-0.72871800	-3.22019800	-0.33943800
C	2.03828500	1.73159500	-0.04439300
C	2.19167600	3.18582900	-0.00520700
C	1.36815800	4.04145800	0.73450600
C	3.28986700	3.71267300	-0.69957300
C	1.63447000	5.40334400	0.76120300
H	0.51114900	3.65443300	1.26968000
C	3.54994000	5.07412400	-0.66698900
H	3.93156200	3.03878800	-1.25631100
C	2.72158600	5.92497900	0.06028400
H	1.00031000	6.07525800	1.33063800
H	4.39254800	5.49355500	-1.20662300
C	-3.95159200	0.22168300	0.02546600
C	-4.28223300	-0.87163800	-0.77913300
C	-4.94807500	0.84524400	0.79175700
C	-5.58819600	-1.34537500	-0.79912500
H	-3.52577100	-1.36742100	-1.37279500
C	-6.24745900	0.36679800	0.76782800
H	-4.68348300	1.70340100	1.39979800
C	-6.57098400	-0.73505800	-0.02777900
H	-5.85712600	-2.19730100	-1.41447000
H	-7.02240800	0.83336700	1.36762700
C	1.68701000	-3.57067000	-0.21930800
C	2.82320000	-3.27732900	0.54207700
C	1.64142000	-4.75117700	-0.97102800
C	3.90489300	-4.14524000	0.53111400

H	2.87297300	-2.37121100	1.13202000
C	2.72792900	-5.61329100	-0.98054300
H	0.74765700	-4.97698700	-1.54230000
C	3.86482100	-5.31034100	-0.23596800
H	4.79319600	-3.92660700	1.11484500
H	2.71158100	-6.52490300	-1.56854200
N	-7.89534800	-1.25635000	-0.04634200
C	-8.88650300	-0.56677600	-0.76642600
C	-8.28166500	-2.12345800	0.99134700
C	-10.17664800	-1.12390400	-0.84203200
C	-8.61044400	0.64959400	-1.40001000
C	-9.56063800	-2.70722900	0.94436800
C	-7.42192800	-2.40142600	2.05935700
C	-11.17326700	-0.39547000	-1.48656800
C	-10.37880800	-2.54073800	-0.32698000
C	-9.61876400	1.33780000	-2.06235700
H	-7.60917300	1.06290600	-1.36772600
C	-9.96506300	-3.49659900	2.01814600
C	-7.84219100	-3.21915400	3.10019500
H	-6.42771100	-1.97089700	2.08009200
C	-10.91117100	0.82986700	-2.09185800
H	-12.17797500	-0.80058100	-1.53595100
H	-9.38714400	2.28238400	-2.54541100
H	-10.95551700	-3.93807700	2.00883900
C	-9.12346300	-3.75542400	3.09576900
H	-7.16261100	-3.42342500	3.92215800
H	-11.70697300	1.36998900	-2.59469300
H	-9.46360200	-4.38306700	3.91323700
N	3.00187800	7.32045100	0.08228000
C	3.67497900	7.84938300	1.19762000
C	2.22351800	8.17737400	-0.71616900
C	4.02385500	9.21229400	1.19310700
C	3.99173400	7.04762700	2.29949600
C	2.54882400	9.54583800	-0.75380400
C	1.14273400	7.69249200	-1.46033600
C	4.61469700	9.74554500	2.33597200
C	3.84682000	9.99428300	-0.09925600

C	4.61065800	7.60187600	3.41238300
H	3.74458100	5.99255200	2.29001400
C	1.72414200	10.40015500	-1.48165900
C	0.35714400	8.56535300	-2.20179300
H	0.90833200	6.63455400	-1.45006700
C	4.90761100	8.95832500	3.44552500
H	4.87160300	10.79890800	2.35836500
H	4.84717600	6.96561700	4.26002300
H	1.94771000	11.46107100	-1.50511800
C	0.63098100	9.92706100	-2.20110700
H	-0.48068000	8.17234800	-2.76992300
H	5.37743000	9.40098000	4.31800300
H	0.01182700	10.61639400	-2.76623200
N	4.97536700	-6.19931100	-0.26893600
C	5.12819200	-7.12330200	0.77933600
C	6.09652700	-5.85128700	-1.04381600
C	6.16910900	-8.06658700	0.70169400
C	4.27316400	-7.11076100	1.88646100
C	7.15441700	-6.77292300	-1.15025600
C	6.17275400	-4.61753000	-1.69897300
C	6.36403300	-8.92386300	1.78173900
C	6.94225000	-8.17618100	-0.60302000
C	4.47334300	-8.00053400	2.93397600
H	3.45779700	-6.39825800	1.93235600
C	8.29617800	-6.38941300	-1.84943700
C	7.31253200	-4.27646600	-2.41569800
H	5.34670200	-3.91851200	-1.64024700
C	5.53186000	-8.89922900	2.89682100
H	7.17392700	-9.64437200	1.74823700
H	3.80156000	-7.97612000	3.78683700
H	9.12973500	-7.07921500	-1.92354600
C	8.38938500	-5.15151300	-2.47816400
H	7.35615800	-3.31266800	-2.91401700
H	5.70282000	-9.58708200	3.71871900
H	9.28895600	-4.88429700	-3.02337900
C	5.00628600	9.60506300	-1.04420000
H	4.90007200	10.12104800	-2.00399500

H	5.96660100	9.88015500	-0.59597200
H	5.01210000	8.52823900	-1.23307200
C	3.89472900	11.50346600	0.12281200
H	3.09285600	11.84255700	0.78543700
H	4.85395200	11.79827100	0.55583100
H	3.81019000	12.03471600	-0.82850700
C	8.25227100	-8.94202900	-0.43959000
H	8.76311100	-9.04125400	-1.40069300
H	8.92680000	-8.44705800	0.26545000
H	8.06145100	-9.95828000	-0.08553400
C	6.05429000	-8.94149800	-1.61039300
H	5.10062400	-8.42828400	-1.76031000
H	6.56005800	-9.01485600	-2.57862200
H	5.84646300	-9.95029700	-1.23916400
C	-9.80202900	-3.50849200	-1.38522900
H	-9.89697100	-4.54361400	-1.04149200
H	-10.34077900	-3.39616200	-2.33171200
H	-8.74361600	-3.30365100	-1.56716400
C	-11.85220400	-2.87996300	-0.11851200
H	-12.31933300	-2.22417200	0.62231700
H	-12.40391000	-2.79457600	-1.05811400
H	-11.96507900	-3.91574100	0.21137100

Optoelectronic Characterization

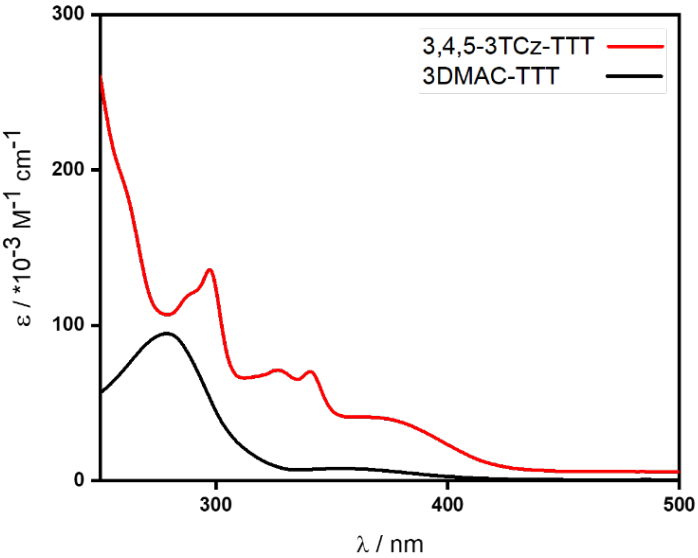


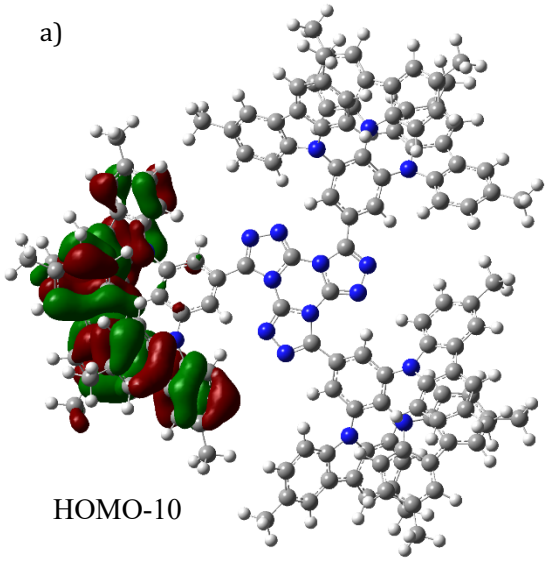
Figure S23: UV-vis absorption spectrum of **3,4,5-3TCz-TTT** (red) and **3DMAC-TTT** (black) in DCM.

Table **S5.** Exited states involved in the main UV-vis transitions of **3,4,5-3TCz-TTT.**

Excited State	**Energy / eV ; nm**	**Nature**	**Character of the transition**
S47 (f=0.0049)	3.68 ; 337	(H-9)→(L+1) (5%) (H-9)→(L+2) (91%)	CT
S51 (f=0.1657)	3.78 ; 328	(H-2)→(L+3) (30%) (H-2)→(L+5) (27%) (H-1)→(L+3) (10%) (H-1)→(L+4) (14%) (H-1)→(L+7) (2%) (H)→(L+3) (4%)	CT
S80 (f= 0.0445)	4.17 ; 297	(H-10)→(L+3) (2%) (H-10)→(L+4) (24%) (H-10)→(L+5) (11%) (H-4)→(L+6) (5%) (H-4)→(L+11) 30%) (H-1)→(L+9) (2%) (H-1)→(L+11) (5%) (H-1)→(L+12) (10%) (H-1)→(L+13) (5%)	CT
S100 (f=0.0052)	4.29 ; 289	(H-6)→(L+7) (3%) (H-5)→(L+3) (4%)	CT

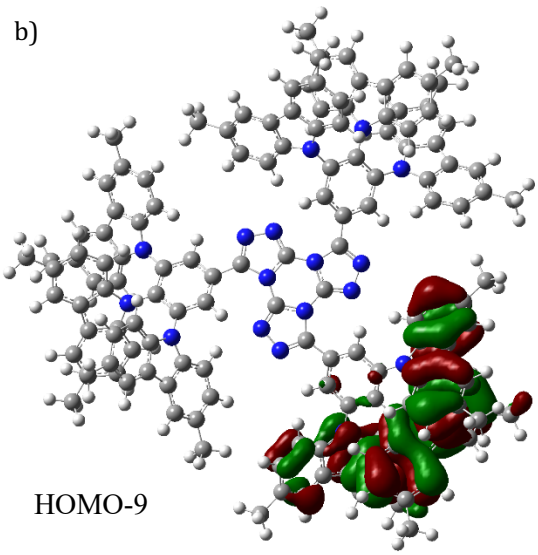
		(H-1)→(L+4) (2%) H→(L+3) (3%) H→(L+4) (22%) H→(L+5) (3%) H→(L+6) (8%) H→(L+7) (9%) H→(L+8) (3%) H→(L+9) (3%) H→(L+13) (8%) H→(L+16) (8%)	

a)



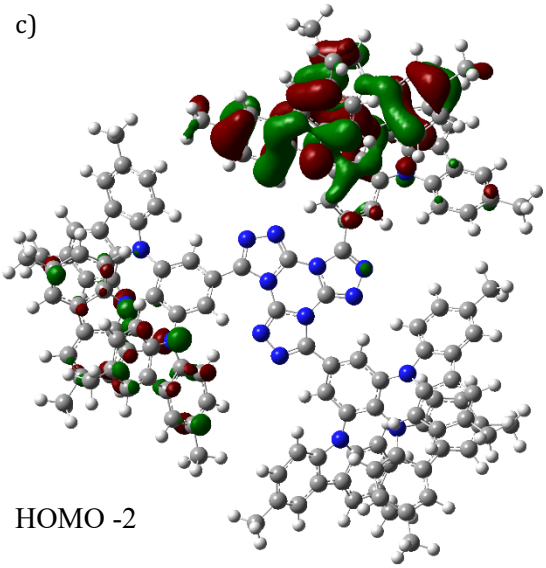
HOMO-10

b)



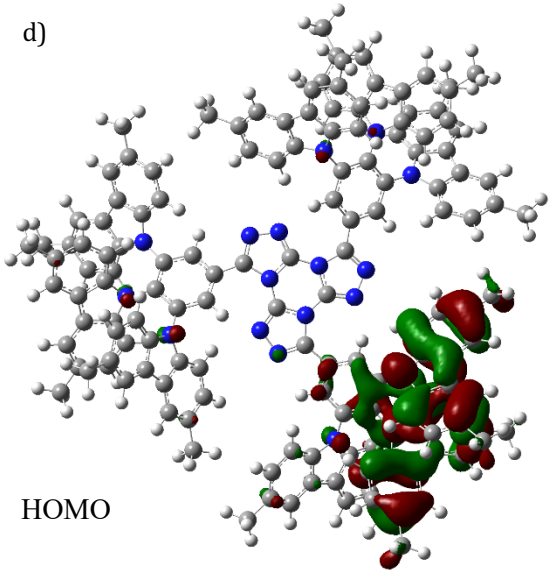
HOMO-9

c)



HOMO -2

d)



HOMO

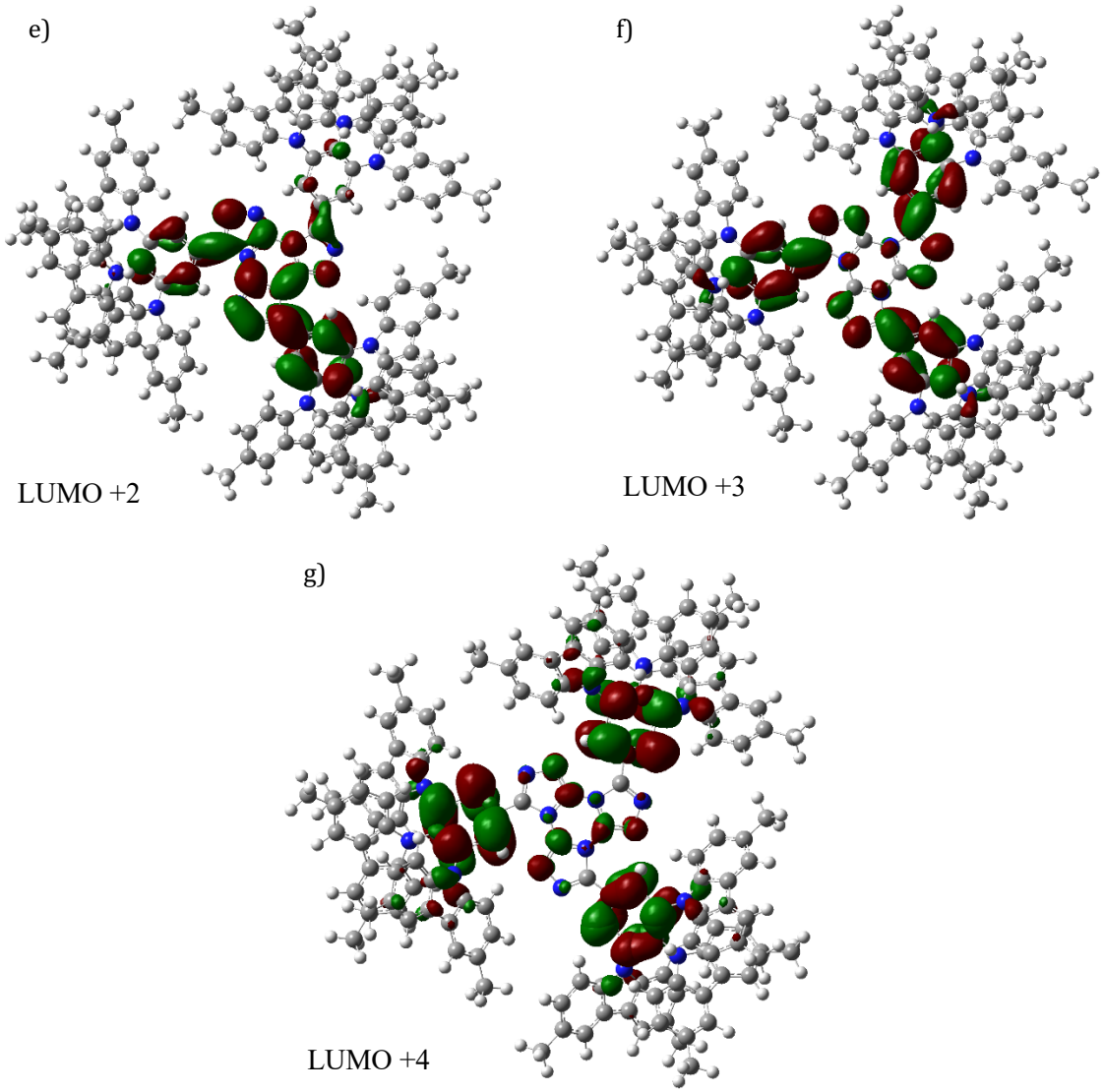


Figure **S24**. Electronic density distributions of **3DMAC-TTT** of a) HOMO -10 b) HOMO -9 c) HOMO-2 d) HOMO e) LUMO +2 f) LUMO +3 g) LUMO +4 (Isovalue for new surfaces: MO=0.02, Density=0.0004).

Table **S6.** Host optimization of spin-coated films of **3,4,5-3TCz-TTT**.

Host	**Doping concentration / wt%**	**PLQY air; N_2[a] / %**
DPEPO	3	5; 7
	5	8; 10
	10	20; 27
	15	19; 24
	20	16; 21
PPT	3	7; 8
	5	10; 14
	10	14; 17
	15	13; 16
	20	20; 25
mCP	3	31; 34
	5	41; 44
	10	40; 43
	15	51; 56
	20	43; 50
CzSi	3	43; 73
	5	47; 79
	10	48; 80
	15	47, 80
	20	46; 77

[a] λ_{exc} = 340nm.

Table **S7**. Doping concentration optimization of spin-coated films of **3DMAC-TTT** in CzSi host.

Host	**Doping concentration / wt%**	**PLQY air; N_2[a] / %**
CzSi	3	25; 72
	5	25; 74
	10	27; 76
	15	28; 79
	20	28; 78

[a] λ_{exc} = 340nm.

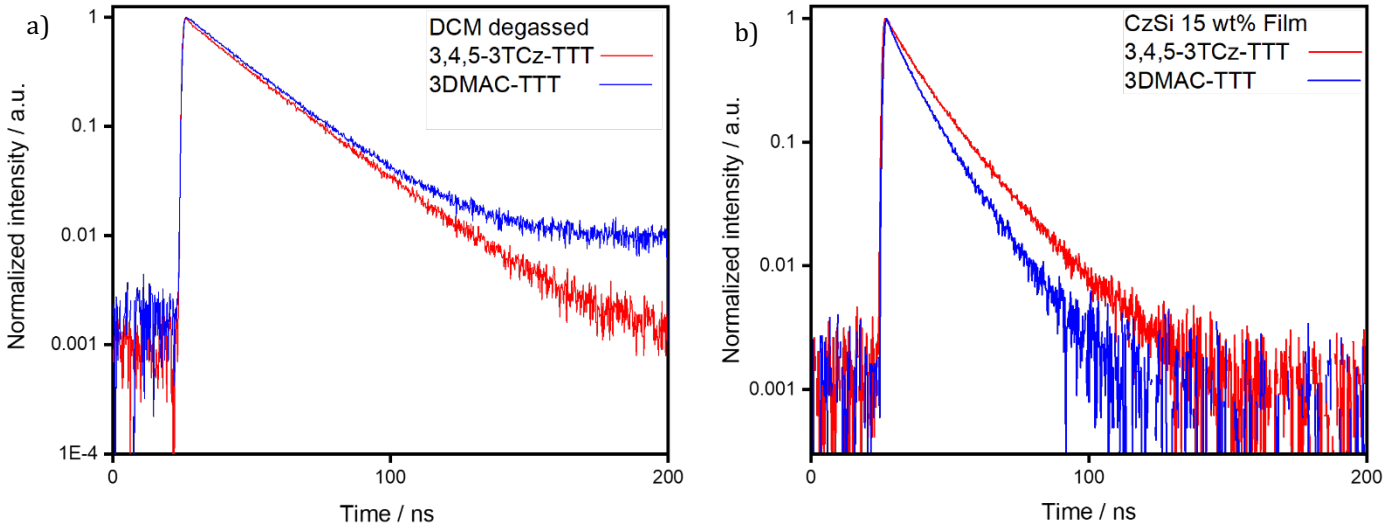


Figure **S25**: Time-resolved PL decay of **3,4,5-3TCz-TTT** and **3DMAC-TTT** in a) degassed DCM solution; b) spin-coated CzSi film (15 wt%),λ_{exc} = 378 nm.

Devices

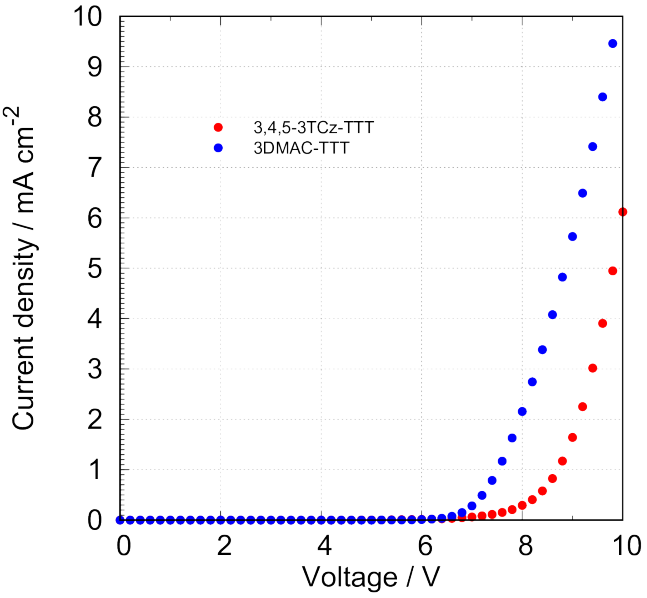


Figure **S26**. Current density-voltage characteristics for the 3,4,5-3TCz-TTT and 3DMAC-TTT OLEDs.

References

1 A. W. Pavlishchuk, V. V.; Addison, *Inorg. Chim. Acta*, 2000, **298**, 97.

2 W. E. Connelly, N. G., and Geiger, *Chem. Rev.*, 1996, **96**, 877–910.

3 G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991–1024.

4 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229–235.

5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. a. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. a. Petersson, H. Nakatsuji, X. Li, M. Caricato, a. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, a. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. a. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. a. Keith, R. Kobayashi, J. Normand, K. Raghavachari, a. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, 2016, Gaussian 16, Revision C.01, Gaussian, Inc., Wallin.

6 V. Adamo, C.; Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

7 T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007–1023.

8 S. Grimme, *Chem. Phys. Lett.*, 1996, **259**, 128–137.

9 S. Hirata and M. Head-Gordon, *Chem. Phys. Lett.*, 1999, **314**, 291–299.

10 M. Moral, L. Muccioli, W. J. Son, Y. Olivier and J. C. Sancho-Garcia, *J. Chem. Theory Comput.*, 2015, **11**, 168–177.