Supporting Information

Electron-withdrawing Group Modified Carbazolophane Donors for Deep Blue Thermally Activated Delayed Fluorescence OLEDs

Abhishek Kumar Gupta,‡[a,b] Zhen Zhang,‡[c] Eduard Spuling,[a,c] Maria Kaczmarek,[c] Yichuan Wang,[c] Zahid Hassan,[c] Ifor D. W. Samuel,*[b] Stefan Bräse,*[c,d] and Eli Zysman-Colman*[a]

[a] 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

[b] Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews, KY16 9SS, UK. E-mail: idws@st-andrews.ac.uk

[c] Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 6, 76131, Karlsruhe, Germany. E-mail: braese@kit.edu

[d] Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS-FMS), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafen, Germany.

‡ Abhishek Kumar Gupta and Zhen Zhang contributed equally to this work.

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Materials and Experimental procedures

General information

NMR spectra were recorded using the following devices: ^{1}H NMR: *Bruker* Avance 400 (400 MHz), ^{13}C NMR: *Bruker* AM 400 (100 MHz). Chloroform-*d*$_1$ from *Eurisotop* was used. Chemical shifts δ were expressed in parts per million (ppm) and referenced to chloroform (^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.16 ppm). The signal structure is described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, b = broad singlet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet. The spectra were analyzed according to the first order. All coupling constants are absolute values and expressed in Hertz (Hz). The multiplicities of the signals of ^{13}C NMR spectra were determined using DEPT (Distortionless Enhancement by Polarization Transfer) and are described as follows: + = primary or tertiary (positive DEPT signal), – = secondary (negative DEPT signal), Cq = quarternary carbon atoms (no DEPT signal). The electron ionization (EI) and fast atom bombardment (FAB) methods were conducted using an instrument by Finnigan, model MAT 90 (70 eV), and 3-nitrobenzyl alcohol (3-NBA) was used as matrix and reference for high-resolution mass spectrometry. For the interpretation of the spectra, molecular peaks $[M]^{+}$, peaks of pseudomolecules $[M+H]^{+}$ and characteristic fragment peaks are indicated with their mass to charge ratio (m/z), and in the case of EI, their intensity in per cent, relative to the base peak (100%) is given. In the case of high-resolution measurements, the tolerated error is 0.0005 m/z. The infrared spectra of solid samples were recorded on Bruker IFS 88 and measured by attenuated total reflection (ATR method). Absorption is given in wavenumbers ῡ [cm^{-1}]. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel coated aluminium plates (silica gel 60, F254), detected under UV-light at 254 nm or stained with "Seebach staining solution" (mixture of molybdatophosphoric acid, cerium(IV)-sulphate tetrahydrate, sulfuric acid and water) or basic potassium permanganate solution. Solvent mixtures are understood as volume/volume. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, Chempure, ABCR and Acros Organics. All solvents, reagents and chemicals were used as purchased unless stated otherwise.

DFT Calculations

The DFT calculations, including geometry optimization of the emitters, were performed by the Gaussian 09 Revision D.01 software[1] in the gas phase at the Density Functional Theory (DFT) level using the PBE0 functional[2] and the 6-31G(d,p) basis set starting with the molecular geometry.[3] Excited singlet and triplet states were calculated by performing time-dependent DFT (TD-DFT) calculations within the Tamm-Dancoff approximation using the same functional and basis set.[4]

Electrochemistry

Cyclic Voltammetry (CV) and Differential pulse voltammetry (DPV) analysis were performed on an Electrochemical Analyzer potentiostat model 620D from CH Instruments. Samples were prepared in dichloromethane (DCM) solutions, degassed by sparging with DCM-saturated nitrogen gas for 5 minutes before measurements. All measurements were performed using 0.1M tetra-*n*-butylammonium hexafluorophosphate, [*n*Bu_4N]PF_6], in DCM at scan rate of 100 mV s^{-1}. An Ag/Ag^+ electrode was used as the reference electrode, a glassy carbon electrode was used as the working electrode, and a platinum wire was used as the counter electrode. The redox potentials are reported relative to a saturated calomel electrode (SCE) with a ferrocene/ferrocenium/ ($\mathrm{F_c/F_c^+}$) redox couple as the internal standard (0.46 V vs SCE).[5] The HOMO and LUMO energies were determined using $E_{HOMO/LUMO} = -(E^{ox}/E^{red} + 4.8)eV$,[6] where E^{ox} is anodic peak potential and $E^{red}$is cathodic peak potential calculated from DPV relative to $\mathrm{F_c/F_c^+}$.

Thermal Stability

Differential scanning calorimetry (DSC) was measured on a TA DSC 2500 with a heat rate of 10 °C min^{-1} between 40 °C and 300 °C. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA 5500 with a heating rate of 10 °C min^{-1} in a temperature range from ambient temperature to 1000 °C.

Photophysics

Photophysics in the solution

Solution samples were prepared using HPLC-grade solvents with varying concentrations on the order of 10^{-5} M for absorption and emission studies, respectively. Solutions were put into quartz cuvettes for all the photophysics measurements. Aerated solutions were prepared by bubbling with compressed air for 5 minutes, whereas degassed solutions were prepared via three freeze-pump-thaw cycles before emission and lifetime analysis using an in-house adapted fluorescence cuvette purchased from Starna. Absorption spectra were recorded at RT using a Shimadzu UV-2600 double beam spectrophotometer Molar absorptivity values were determined from at least four solutions followed by linear regression analysis having concentration 3.65×10^{-5} M, 2.43×10^{-5} M, 1.83×10^{-5} M and 1.46×10^{-5} M with corresponding absorbance intensity 0.513, 0.341, 0.256 and 0.214, respectively at absorbance wavelength 365 nm for **CNCzpPhTRZ** and 2.73×10^{-5} M, 1.82×10^{-5} M, 1.36×10^{-5} M and 1.09×10^{-5} M corresponding absorbance intensity 0.427, 0.287, 0.216 and 0.170, respectively at absorbance wavelength 363 nm for **CF_3CzpPhTRZ**.

Photophysics in the solid-state

Samples for PL decay measurements were prepared by spin-coating a thin film from chloroform (Sigma Aldrich, HPLC grade) at 2000 RPM in an ambient environment on quartz substrates and annealed at 65 °C for 10 min. The films for ΔE_{ST} measurements were prepared by drop-casting a chloroform solution on cleaned sapphire substrates and annealed at 65 °C for 1 min under N_2 atmosphere to obtain a sufficiently homogeneous thick film to acquire sufficient signal for the phosphorescence. Film samples for PLQY measurement were spin-coated.

Steady-state emission and time-resolved PL decay

Steady-state and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments F980 fluorimeter in an oxygen-free atmosphere. All the samples for the steady-state measurements were excited at 360 nm using a Xenon lamp, while the samples for the time-resolved measurements were excited at 378 nm using a pico-second laser (PicoQuant, LDH-D-C-375) driven by a laser driver (PDL 800-D). PL decays were measured using time-correlated single-photon counting (TCSPC) mode and MCS.

Photoluminescence quantum yields (PLQY) in solution

Photoluminescence quantum yields for solutions were determined using the optically dilute method[7], in which four sample solutions with an absorbance of ca. 0.577, 0.288, 0.115 and 0.044 at 365 nm were used. Their emission intensities were compared with those of a reference, quinine sulphate, whose quantum yield (Φ_{PL}) in 0.5M H_2SO_4 was determined to be 54.6% using the absolute method.[7] The quantum yield of the sample, Φ_{PL}, can be determined by the equation $\Phi_{PL} = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$, where A stands for the absorbance at the excitation wavelength ($\lambda_{exc} = 365$ nm), I is the integrated area under the corrected emission curve and n is the refractive index of the solvent with the subscripts “s” and “r” representing sample and reference respectively.

Photoluminescence quantum yields (PLQY) in solid thin film

A Hamamatsu C9920-02 integrating sphere was employed for PLQY measurements for thin-film samples.[8] A xenon lamp coupled to a monochromator enabled selective excitation chosen here to be 300 nm and 360 nm for PPT, DPEPO and PMMA thin films. The output was then fed into the integrating sphere via a fibre, exciting the sample. PL spectra were collected with multimode fibre and detected with a back-thinned CCD under a nitrogen or oxygen atmosphere as required.

ΔE_{ST} measurement

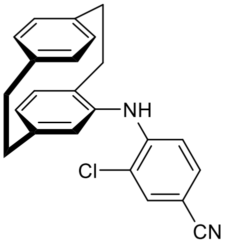
The singlet-triplet splitting energy, ΔE_{ST}, was estimated by recording the prompt fluorescence and the delayed phosphorescence spectra at 77 K., The film for ΔEST measurement, was prepared through drop-casting of a 10 wt% emitters in 2,8-bis(diphenyl-phosphoryl)-dibenzo[b,d]thiophene (PPT), bis[2-(diphenylphosphine)phenyl]ether oxide (DPEPO) and poly(methyl methacrylate) (PMMA) host chloroform solution on cleaned sapphire substrates. All samples were loaded inside a cold finger cryostat (Oxford Instruments) for vacuum condition and 300 K – 77 K temperature control. All samples were photoexcited using the third harmonic emission (343 nm) from a femtosecond laser which originally emits at 1030 nm (Orpheus-N, model: PN13F1). Emission from the samples was focused onto a spectrograph

(Chromex imaging, 250 is spectrograph) and detected with a sensitive gated iCCD camera (Stanford Computer Optics, 4Picos) having sub-nanosecond resolution. Prompt fluorescence spectra were integrated by iCCD between 1 ns – 100 ns after the laser excitation. Phosphorescence spectra were integrated by iCCD between 1– 10 ms after the laser excitation. The energy values of the lowest singlet and triplet states were determined from the onset of the fluorescence spectrum at 77 K and phosphorescence spectrum at 77 K.

Experimental part

Synthetic procedures and analytical data

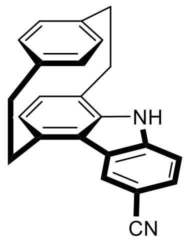
(rac)-4-N-(2-Chloro-4-(cyano)phenyl)amino[2.2]paracyclophane (1a)



Under argon atmosphere, a mixture of (*rac*)-4-bromo[2.2]paracyclophane (3.42 g, 11.9 mmol, 1.00 equiv), 4-amino-3-chlorobenzonitrile (2.18 g, 14.3 mmol, 1.20 equiv.), $Pd_2(dba)_3$ (550 mg, 601 µmol, 5 mol%), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 570 mg, 1.20 mmol, 10 mol%) and sodium *tert*-butoxide sodium (1.73 g, 18.0 mmol, 1.51 equiv.) in toluene (60 mL) was stirred at 100 °C for 12 h. The mixture was cooled to room temperature and diluted with dichloromethane (100 mL). Then it was washed with brine (3 × 100 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The obtained crude product was purified *via* column chromatography on silica gel (cyclohexane/dichloromethane = 5:1 to 2:1) to yield the product as a white solid (2.68 g, 7.47 mmol, 63%).

R_f = 0.30 (cyclohexane/dichloromethane = 2:1). – **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ = 7.64 (s, 1H), 7.32–7.26 (m, 1H), 7.00–6.97 (m, 1H), 6.80 (d, J = 8.6 Hz, 1H), 6.61–6.41 (m, 4H), 6.34 (s, 1H), 5.99 (s, 1H), 3.17–2.68 (m, 8H). – **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ = 144.4 (C_q, C_{Ar}), 142.1 (C_q, C_{Ar}), 139.5 (C_q, C_{Ar}), 139.3 (C_q, C_{Ar}), 137.1 (C_q, C_{Ar}), 135.9 (+, $C_{Ar}H$), 135.0 (C_q, C_{Ar}), 134.0 (+, $C_{Ar}H$), 133.3 (+, $C_{Ar}H$), 133.0 (+, $C_{Ar}H$), 132.1 (+, $C_{Ar}H$), 131.4 (+, $C_{Ar}H$), 130.4 (+, $C_{Ar}H$), 129.8 (+, $C_{Ar}H$), 126.4 (+, $C_{Ar}H$), 119.3 (+, $C_{Ar}H$), 118.4 (+, $C_{Ar}H$), 113.6 (+, $C_{Ar}H$), 100.7 (C_q, CN), 35.2 (–, CH_2), 34.8 (–, CH_2), 34.0 (–, CH_2), 33.8 (–, CH_2). – **IR** (ATR, ṽ) = 3401 (w), 2953 (w), 2925 (m), 2890 (w), 2851 (w), 2221 (s), 1602 (vs), 1561 (w), 1517 (vs), 1493 (vs), 1451 (m), 1409 (s), 1336 (vs), 1286 (w), 1244 (w), 1193 (m), 1091 (w), 1048 (m), 897 (w), 887 (s), 867 (s), 827 (vs), 798 (m), 788 (m), 713 (s), 654 (w), 640 (w), 586 (m), 520 (m), 489 (vs), 473 (m), 446 (vs), 429 (vs), 395 (m), 378 (s) cm^{-1}. – **MS** (EI, 70 eV, 120 °C), *m/z* (%): 358 $[M]^+$. – **HRMS** (FAB, 3-NBA) calc. for $C_{23}H_{19}N_2{}^{35}Cl_1$ $[M]^+$ 358.1231; found 358.1232.

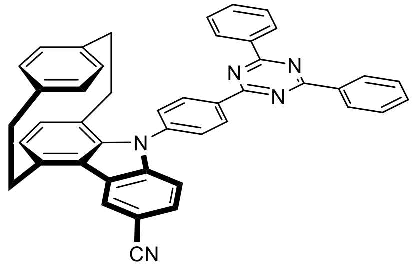
(rac)-[2]Paracyclo[2]6-(cyano)(1,4)carbazolophane (2a)



Under argon atmosphere, a mixture of (rac)-4-N-(2-Chloro-4-(cyano)phenyl)amino[2.2]paracyclophane (320 mg, 892 µmol, 1.00 equiv.), $Pd_2(dba)_3$ (81.6 mg, 89.1 µmol, 10 mol%), 2-dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl (XPhos, 128 mg, 267 µmol, 30 mol%), pivalic acid (54.6 mg, 535 µmol, 60 mol%) and potassium carbonate (616 mg, 4.46 mmol, 5.00 equiv.) in anhydrous *N*,*N*-dimethylacetamide (8 mL) was stirred at 110 °C for 12 h. Then the mixture was cooled to room temperature and diluted with dichloromethane (50 mL). Then it was washed with brine (3 × 50 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The obtained crude product was purified *via* column chromatography on silica gel (cyclohexane/dichloromethane = 5:1 to 3:1) to yield the product as a yellow solid (125 mg, 388 µmol, 43%).

R*f* = 0.50 (cyclohexane/dichloromethane = 5:1). – **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ = 8.37 (s, 1H), 8.21 (bs, NH, 1H), 7.67 (dd, *J* = 8.4 Hz, *J* = 1.5 Hz, 1H), 7.53 (dd, *J* = 8.4 Hz, *J* = 0.6 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.52 (dd, *J* = 7.9, *J* = 1.9 Hz, 1H), 6.38 (dd, *J* = 7.8 Hz, *J* = 2.0 Hz, 1H), 5.91 (dd, *J* = 7.8 Hz, *J* = 2.0 Hz, 1H), 5.22 (dd, *J* = 7.8 Hz, *J* = 1.9 Hz, 1H), 4.05–3.84 (m, 1H), 3.44–3.26 (m, 1H), 3.25–2.78 (m, 6H). – **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ = 140.8 (C_q, C_{Ar}), 138.1 (C_q, C_{Ar}), 137.6 (C_q, C_{Ar}), 136.4 (C_q, C_{Ar}), 132.7 (+, $C_{Ar}H$), 132.6 (+, $C_{Ar}H$), 132.2 (+, $C_{Ar}H$), 128.5 (+, $C_{Ar}H$), 128.1 (+, $C_{Ar}H$), 127.5 (+, $C_{Ar}H$), 126.5 (+, $C_{Ar}H$), 125.4 (C_q, C_{Ar}), 124.9 (+, $C_{Ar}H$), 124.6 (C_q, C_{Ar}), 122.9 (C_q, C_{Ar}), 121.0 (C_q, C_{Ar}), 111.6 (+, $C_{Ar}H$), 102.7 (C_q, C_{Ar}), 34.1 (–, CH_2), 33.8 (–, CH_2), 33.3 (–, CH_2), 31.2 (–, CH_2). – **IR** (ATR, ṽ) = 3301 (m), 2934 (m), 2919 (m), 2220 (vs), 1595 (m), 1572 (m), 1468 (m), 1407 (w), 1307 (vs), 1261 (m), 1244 (w), 1215 (w), 1174 (m), 1130 (m), 892 (w), 875 (m), 809 (vs), 795 (s), 773 (m), 768 (m), 739 (w), 717 (m), 637 (s), 629 (m), 618 (vs), 569 (m), 520 (s), 514 (s), 499 (s) cm^{-1}. – **MS** (EI, 160°C), *m/z* (%): 322 $[M]^+$. – **HRMS** (EI, 160°C) calc. for $C_{23}H_{18}N_2$ $[M]^+$ 322.1470, found 322.1471.

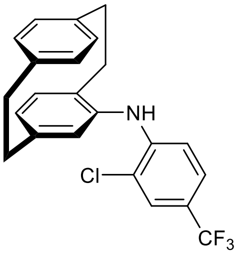
*(rac)-1-(N-[2]Paracyclo[2]-6-(cyano)(1,4)carbazolophanyl)-4-(4,6-diphenyl-1,3,5-triazin-2-yl)-benzene (**CNCzpPhTRZ**)*



A 20 mL sealable vial was charged with (*rac*)-[2]paracyclo[2]6-(cyano)(1,4)carbazolophane (120 mg, 372 µmol, 1.00 equiv.), 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (146 mg, 447 µmol, 1.20 equiv.) and potassium phosphate tribasic (395 mg, 1.86 mmol, 5.00 equiv.). It was evacuated and flushed with argon three times. Through the septum, 8 mL of anhydrous DMSO were added, then it was heated to 150 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was diluted with 50 mL of dichloromethane and washed with brine (3 × 50 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The obtained crude product was purified *via* column chromatography on silica gel (cyclohexane/dichloromethane = 2:1 to 1:1) to yield the title compound as a white solid (91.0 mg, 145 µmol, 39%). The product was further purified by temperature gradient sublimation. HPLC purity > 99.5%.

Melting point = 273-278 °C, **R$_f$** = 0.60 (cyclohexane/dichloromethane = 1:2). – **^{1}H NMR** (400 MHz, CDCl$_3$, ppm) δ = 9.05 (bs, 2H), 8.90–8.75 (m, 4H), 8.47 (d, *J* = 1.5 Hz, 1H), 8.08 (s, 1H), 7.75–7.37 (m, 9H), 6.82–6.70 (m, 2H), 6.53 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.36 (dd, *J* = 7.9 Hz, *J* = 1.8 Hz, 1H), 5.95 (dd, *J* = 7.8 Hz, *J* = 1.9 Hz, 1H), 5.52 (dd, *J* = 7.8 Hz, *J* = 1.9 Hz, 1H), 4.1–3.92 (m, 1H), 3.32–3.15 (m, 2H), 3.13–3.03 (m, 1H), 2.99–2.83 (m, 1H), 2.78–2.70 (m, 2H), 2.36–2.23 (m, 1H). – **^{13}C NMR** (101 MHz, CDCl$_3$, ppm) δ = 172.0 (C$_q$, C$_{Ar}$), 170.7 (C$_q$, C$_{Ar}$), 142.2 (C$_q$, C$_{Ar}$), 141.6 (C$_q$, C$_{Ar}$), 137.5 (C$_q$, C$_{Ar}$), 136.3 (C$_q$, C$_{Ar}$), 136.1 (C$_q$, C$_{Ar}$), 136.1 (C$_q$, C$_{Ar}$), 135.1 (+, C$_{Ar}$H), 132.9 (+, C$_{Ar}$H), 132.2 (+, C$_{Ar}$H), 131.8 (+, C$_{Ar}$H), 130.6 (+, C$_{Ar}$H), 129.2 (+, C$_{Ar}$H), 128.9 (+, C$_{Ar}$H), 128.6 (+, C$_{Ar}$H), 127.4 (+, C$_{Ar}$H), 126.6 (+, C$_{Ar}$H), 125.8 (C$_q$, C$_{Ar}$), 125.8 (C$_q$, C$_{Ar}$), 125.7 (+, C$_{Ar}$H), 124.9 (C$_q$, C$_{Ar}$), 120.7 (C$_q$, C$_{Ar}$), 110.8 (+, C$_{Ar}$H), 103.7 (C$_q$, C$_{Ar}$), 35.1 (–, CH$_2$), 33.6 (–, CH$_2$), 33.4 (–, CH$_2$), 33.2 (–, CH$_2$). – **IR** (ATR, ṽ) = 2925 (w), 2854 (w), 2220 (w), 1596 (w), 1588 (w), 1509 (vs), 1462 (s), 1442 (s), 1411 (m), 1392 (m), 1361 (vs), 1299 (s), 1262 (s), 1244 (m), 1174 (m), 1146 (m), 1014 (m), 837 (m), 833 (m), 802 (s), 772 (s), 762 (vs), 735 (vs), 687 (vs), 667 (s), 660 (s), 645 (s), 640 (s), 615 (s), 592 (s), 584 (m), 562 (m), 517 (vs), 496 (s), 487 (m), 467 (m), 456 (m), 401 (m) cm^{-1}. – **MS** (FAB, 3-NBA), *m/z* (%): 630 [M+H]$^+$, 629 [M]$^+$. – **HRMS** (FAB, 3-NBA) calc. for $C_{44}H_{32}N_5$ [M+H]$^+$ 630.2658, found 630.2660.

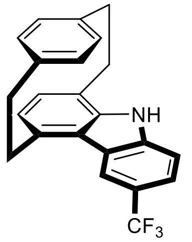
(rac)-4-N-(2-Chloro-4-(trifluoromethyl)phenyl)amino[2.2]paracyclophane (1b)



Under argon atmosphere, a mixture of (*rac*)-4-bromo[2.2]paracyclophane (287 mg, 1.00 mmol, 1.00 equiv.), 2-chloro-4-(trifluoromethyl)aniline (235 mg, 1.20 mmol, 1.20 equiv.), Pd$_2$(dba)$_3$ (45.8 mg, 50.0 µmol, 5 mol%), 2-dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl (XPhos, 47.6 mg, 99.8 µmol, 10 mol%) and sodium *tert*-butoxide (144 mg, 1.50 mmol, 1.50 equiv.) in toluene (5 mL) was stirred at 100 °C for 12 h. The mixture was cooled to room temperature and diluted with dichloromethane (20 mL). Then it was washed with brine (3 × 20 mL). The organic layer was dried over MgSO$_4$, and the solvent was removed under reduced pressure. The obtained crude product was purified *via* column chromatography on silica gel (cyclohexane/dichloromethane = 10:1 to 7.5:1) to yield the title compound as a white solid (220 mg, 547 µmol, 55%).

R$_f$ = 0.50 (cyclohexane/dichloromethane = 5:1). – **^{1}H NMR** (400 MHz, CDCl$_3$, ppm) δ = 7.64 (d, *J* = 2.1 Hz, 1H), 7.33–7.22 (m, 1H), 7.05 (dd, *J* = 7.9 Hz, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.62–6.45 (m, 5H), 6.19 (s, 1H), 5.98 (s, 1H), 3.15–2.88 (m, 7H), 2.78–2.66 (m, 1H). – **^{13}C NMR** (101 MHz, CDCl$_3$, ppm) δ = 143.3 (C$_q$, C$_{Ar}$), 141.9 (C$_q$, C$_{Ar}$), 139.7 (C$_q$, C$_{Ar}$), 139.5 (C$_q$, C$_{Ar}$), 139.2 (C$_q$, C$_{Ar}$), 137.5 (C$_q$, C$_{Ar}$), 136.2, 134.2 (C_q, C_{Ar}), 133.9 (+, $C_{Ar}H$), 133.2 (+, $C_{Ar}H$), 133.1 (+, $C_{Ar}H$), 131.4 (+, $C_{Ar}H$), 129.6 (+, $C_{Ar}H$), 129.3 (+, $C_{Ar}H$), 127.2 (+, $C_{Ar}H$), 126.8 (+, q, J = 3.9 Hz, $C_{Ar}H$), 124.9 (+, q, J = 3.7 Hz, $C_{Ar}H$), 124.1 (C_q, q, J = 270.9 Hz, CF_3), 121.0 (C_q, q, J = 33.4 Hz, C_{Ar}), 119.4 (C_q, C_{Ar}), 113.1 (+, $C_{Ar}H$), 35.8 (–, CH_2), 35.3 (–, CH_2), 34.9 (–, CH_2), 33.9 (–, CH_2). – **^{19}F NMR** (101 MHz, $CDCl_3$, ppm) δ = –65.71. – **IR** (ATR, ṽ) = 3119 (vw), 2975 (w), 2104 (vs), 1686 (vs), 1456 (w), 1366 (vs), 1341 (vs), 1251 (s), 1214 (s), 1166 (vs), 1142 (vs), 977 (s), 846 (m), 747 (vs), 741 (vs), 660 (s), 595 (vs), 452 (vs), 443 (s) cm^{-1}. – **MS** (FAB, 3-NBA), *m/z* (%): 401 $[M]^+$. –**HRMS** (FAB, 3-NBA) calc. for $C_{23}H_{19}{}^{35}Cl_1F_3$ $[M]^+$ 401.1158, found 401.1158.

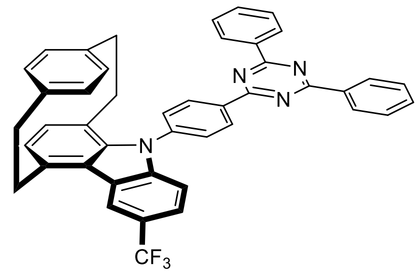
(rac)-[2]Paracyclo[2]6-(trifluoromethyl)(1,4)carbazolophane (2b)



Under argon atmosphere, a mixture of (*rac*)-4-*N*-(2-chloro-4-(trifluoromethyl)phenyl)amino[2.2]paracyclophane (1.10 g, 2.70 mmol, 1.00 equiv.), $Pd_2(dba)_3$ (0.248 g, 0.271 mmol, 10 mol%), 2-dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl (XPhos, 0.388 g, 0.813 mmol, 30 mol%), pivalic acid (0.166 g, 1.60 mmol, 60 mol%) and potassium carbonate (1.87 g, 14.0 mmol, 5.00 equiv.) in anhydrous *N*,*N*-dimethylacetamide (25 mL) was stirred at 110 °C for 12 h. Then the mixture was cooled to room temperature and diluted with dichloromethane (50 mL). Then it was washed with brine (3 × 50 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The obtained crude product was purified *via* column chromatography on silica gel (cyclohexane/dichloromethane = 5:1 to 3:1) to yield the title compound as a white solid (0.618 g, 1.70 mmol, 62%).

R_f = 0.20 (cyclohexane/dichloromethane = 2:1). – **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ = 8.31 (s, 1H), 8.14 (bs, NH, 1H), 7.65 (dd, J = 8.5 Hz, J = 1.7 Hz, 1H), 7.54 (d, J = 8.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 1H), 6.63 (d, J = 7.5 Hz, 1H), 6.52 (dd, J = 7.8 Hz, J = 1.9 Hz, 1H), 6.38 (dd, J = 7.8 Hz, J = 2.0 Hz, 1H), 5.92 (dd, J = 7.8 Hz, J = 2.0 Hz, 1H), 5.21 (dd, J = 7.8 Hz, J = 2.0 Hz, 1H), 4.00 (dd, J = 12.5 Hz, J = 9.8 Hz, 1H), 3.43–3.29 (m, 1H), 3.23–2.98 (m, 5H), 2.97–2.88 (m, 1H). – **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ = 140.8 (C_q, C_{Ar}), 140.4 (C_q, C_{Ar}), 138.0 (C_q, C_{Ar}), 137.5 (C_q, C_{Ar}), 136.2 (C_q, C_{Ar}), 132.4 (+, $C_{Ar}H$), 132.1 (+, $C_{Ar}H$), 131.9 (+, $C_{Ar}H$), 127.4 (+, $C_{Ar}H$), 126.4 (+, $C_{Ar}H$), 125.5 (C_q, q, J = 271.3 Hz, CF_3), 125.1 (C_q, C_{Ar}), 124.8 (C_q, C_{Ar}), 124.7 (+, $C_{Ar}H$), 122.7 (C_q, C_{Ar}), 122.02 (C_q, q, J = 31.9 Hz, C_{Ar}), 121.95 (+, q, J = 3.6 Hz, $C_{Ar}H$), 119.81 (+, q, J = 4.1 Hz, $C_{Ar}H$), 110.9 (+, $C_{Ar}H$), 34.0 (–, CH_2), 33.8 (–, CH_2), 33.3 (–, CH_2), 31.2 (–, CH_2). – **^{19}F NMR** (101 MHz, $CDCl_3$, ppm) δ = –64.26. – **IR** (ATR, ṽ) = 3393 (m), 2927 (w), 1596 (w), 1387 (w), 1324 (vs), 1266 (vs), 1249 (m), 1211 (w), 1166 (s), 1109 (vs), 1075 (s), 1060 (s), 1018 (w), 984 (w), 933 (w), 892 (m), 877 (m), 812 (s), 798 (m), 775 (w), 744 (w), 720 (m), 705 (w), 645 (s), 608 (m), 581 (w), 523 (s), 490 (m), 436 (m), 422 (w), 411 (m) cm^{-1}. – **MS** (FAB, 3-NBA), *m/z* (%): 365 $[M]^+$. – **HRMS** (FAB, 3-NBA) calc. for $C_{23}H_{18}N_1F_3$ $[M]^+$ 365.1391, found 365.1391.

*(rac)-1-(N-[2]Paracyclo[2]-6-(rifluoromethyl)(1,4)carbazolophanyl)-4-(4,6-diphenyl-1,3,5-triazin-2-yl)-benzene (**CF_3CzpPhTRZ**)*



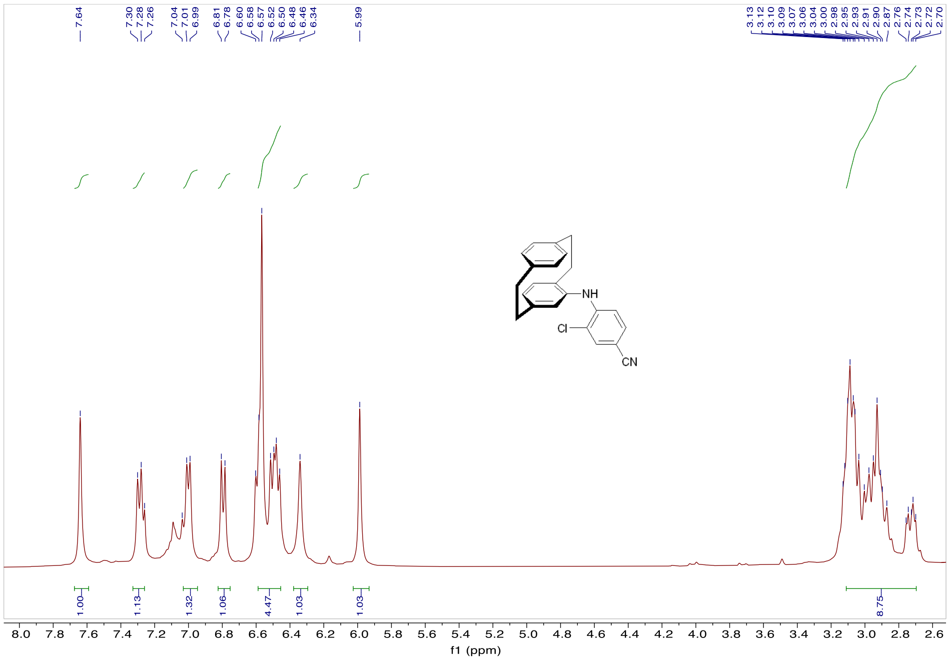
A 100 mL round bottom flask was charged with (*rac*)-[2]paracyclo[2]6-(trifluoromethyl)(1,4)carbazolophane (457 mg, 1.30 mmol, 1.00 equiv.), 2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (512 mg, 1.60 mmol, 1.25 equiv.) and potassium phosphate tribasic (1.33 g, 6.30 mmol, 5.00 equiv.). It was evacuated and flushed with argon three times. Through the septum, 42 mL of anhydrous DMSO were added, then it was heated to 150 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was diluted with 50 mL of dichloromethane and washed with brine (3 × 50 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The obtained crude product was purified *via* column chromatography on silica gel (cyclohexane/dichloromethane = 2.5:1) to yield the title compound as a white luminescent solid (460 mg, 0.684 mmol, 55%). The final product was further purified by temperature gradient sublimation. HPLC purity > 99.9%.

Melting point = 295-300 °C, **R_f** = 0.60 (cyclohexane/dichloromethane = 2.5:1). – **^{1}H NMR** (400 MHz, $CDCl_3$, ppm) δ = 9.05 (bs, 2H), 8.91 – 8.80 (m, 4H), 8.41 (s, 1H), 8.07 (bs, 1H), 7.71–7.54 (m, 9H), 6.79–6.67 (m, 2H), 6.53 (dd, *J* = 7.9, 1.9 Hz, 1H), 6.37 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.97 (dd, *J* = 7.8, 1.9 Hz, 1H), 5.52 (dd, *J* = 7.7, 1.9 Hz, 1H), 4.16–4.00 (m, 1H), 3.31–3.13 (m, 2H), 3.14–3.03 (m, 1H), 2.92 (ddd, *J* = 12.6, 8.3, 3.2 Hz, 1H), 2.82–2.70 (m, 2H), 2.38–2.23 (m, 1H). – **^{13}C NMR** (101 MHz, $CDCl_3$, ppm) δ = 172.0 (C_q, C_{Ar}), 170.8 (C_q, C_{Ar}), 142.1 (C_q, C_{Ar}), 142.0 (C_q, C_{Ar}), 141.5 (C_q, C_{Ar}), 138.1 (C_q, C_{Ar}), 137.5 (C_q, C_{Ar}), 136.2 (C_q, C_{Ar}), 136.2 (C_q, C_{Ar}), 135.7 (C_q, C_{Ar}), 134.6 (+, $C_{Ar}H$), 132.9 (+, $C_{Ar}H$), 132.0 (+, $C_{Ar}H$), 131.6 (+, $C_{Ar}H$), 130.5 (+, $C_{Ar}H$), 129.2 (+, $C_{Ar}H$), 128.9 (+, $C_{Ar}H$), 128.5 (+, $C_{Ar}H$), 126.7 (+, $C_{Ar}H$), 126.5 (C_q, C_{Ar}), 125.7 (+, $C_{Ar}H$), 125.4 (C_q, C_{Ar}), 124.8 (C_q, C_{Ar}), 124.0 (C_q, C_{Ar}), 123.1 (C_q, q, *J* = 31.9 Hz, C_{Ar}). 122.3 (+, q, *J* = 3.6 Hz, $C_{Ar}H$), 119.9 (+, q, *J* = 4.1 Hz, $C_{Ar}H$), 110.1 (+, $C_{Ar}H$) 35.1 (–, CH_2), 33.8 (–, CH_2), 33.5 (–, CH_2), 33.2 (–, CH_2). – **^{19}F NMR** (101 MHz, $CDCl_3$, ppm) δ = –64.41. – **IR** (ATR, ṽ) = 2929 (w), 1601 (w), 1588 (w), 1510 (vs), 1445 (m), 1392 (m), 1363 (vs), 1332 (vs), 1303 (s), 1268 (s), 1237 (m), 1157 (m), 1147 (m), 1129 (m), 1111 (vs), 1082 (s), 1064 (s), 1026 (m), 1014 (m), 989 (w), 887 (w), 833 (m), 800 (m), 772 (s), 764 (s), 744 (s), 737 (s), 687 (vs), 646 (s), 639 (s), 596 (m), 545 (w), 514 (s), 493 (m), 467 (w) cm^{-1}. – **MS** (FAB, 3-NBA), *m/z* (%): 673 $[M+H]^+$, 672 $[M]^+$. – **HRMS** (FAB, 3-NBA) calc. for $C_{44}H_{32}N_4F_3$ $[M+H]^+$ 673.2579, found 673.2580. – **EA** ($C_{44}H_{31}F_3N_4$) calc. C: 78.56, H: 4.64, N: 8.33; found C: 78.54, H: 4.71, N: 8.36.

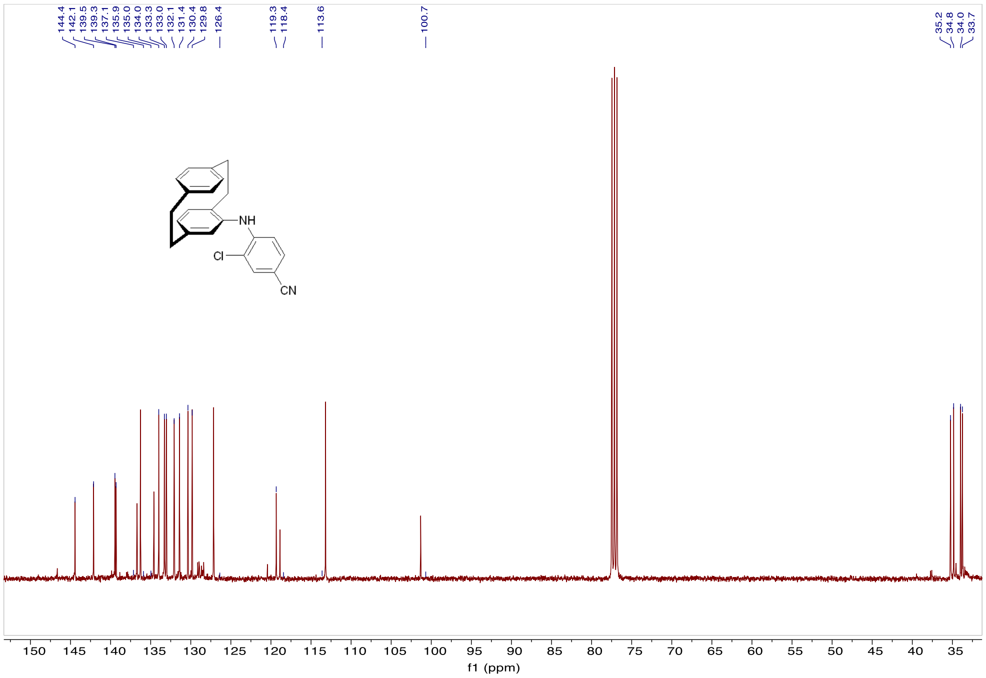
NMR characterizations

(rac)-4-N-(2-Chloro-4-(cyano)phenyl)amino[2.2]paracyclophane (1a)

^{1}H NMR in CDCl$_3$-d_1

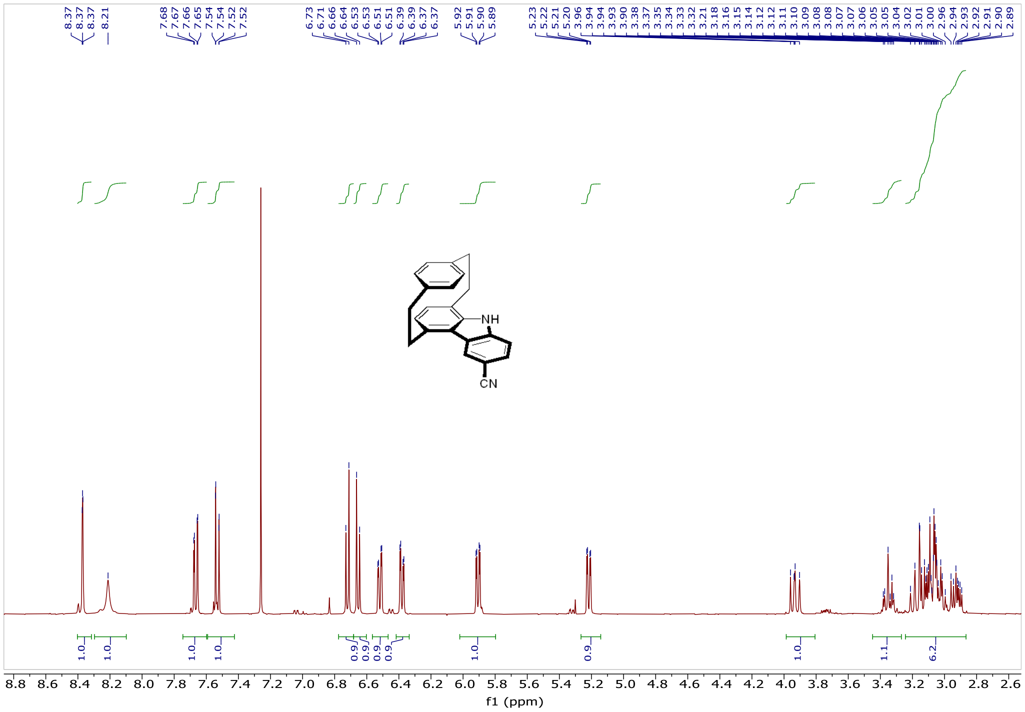


^{13}C NMR in CDCl$_3$-d_1

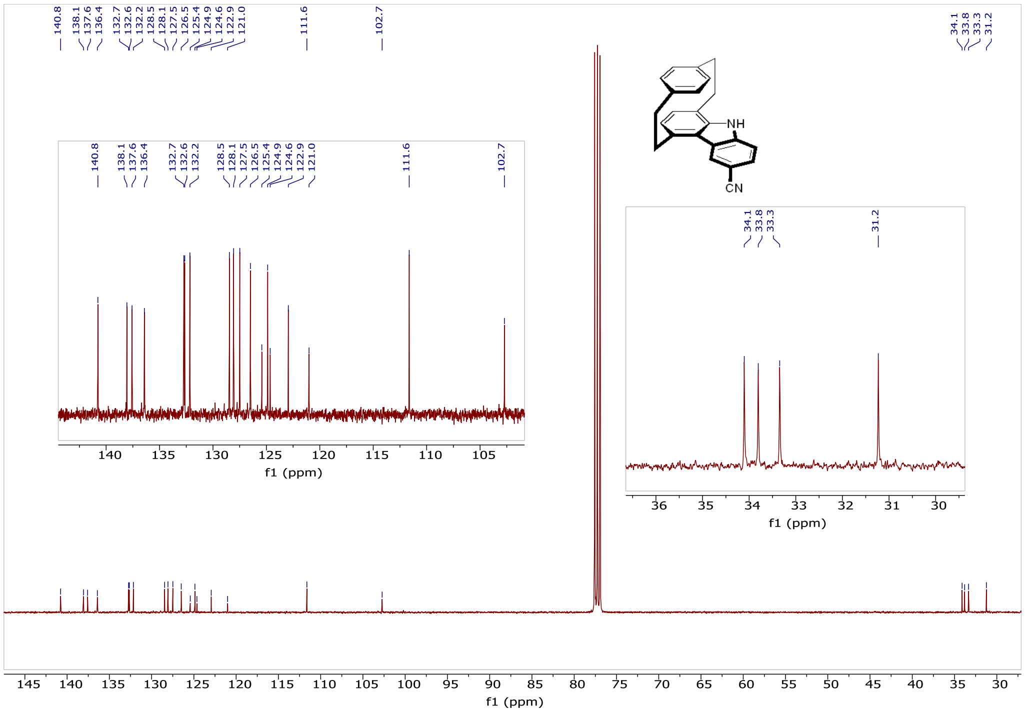


(rac)-[2]Paracyclo[2]6-(cyano)(1,4)carbazolophane (2a)

^{1}H NMR in CDCl$_3$-*d*$_1$

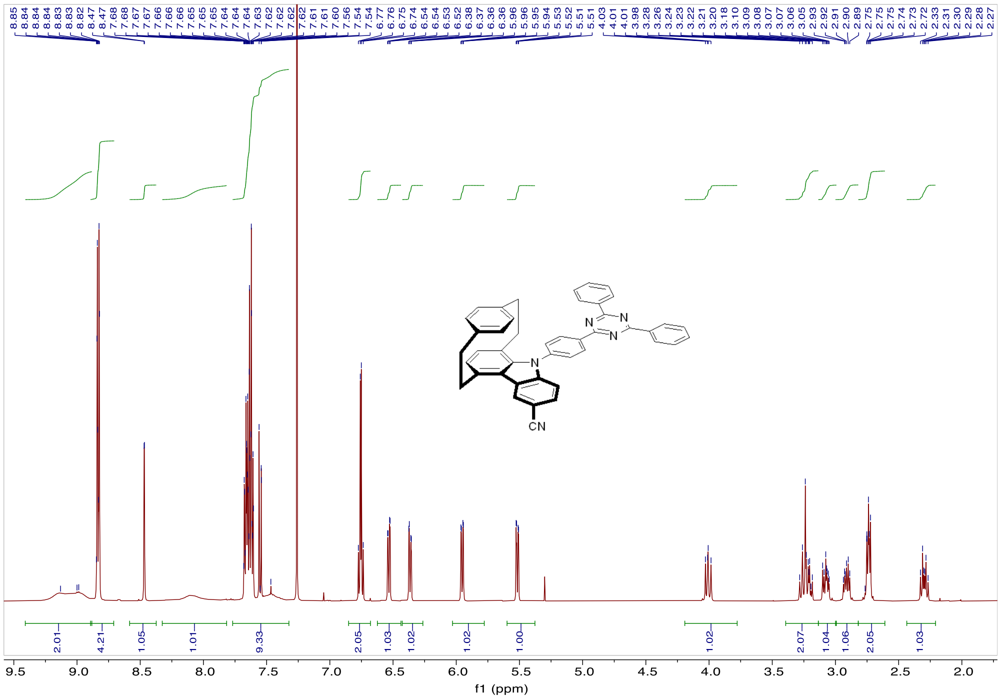


^{13}C NMR in CDCl$_3$-*d*$_1$

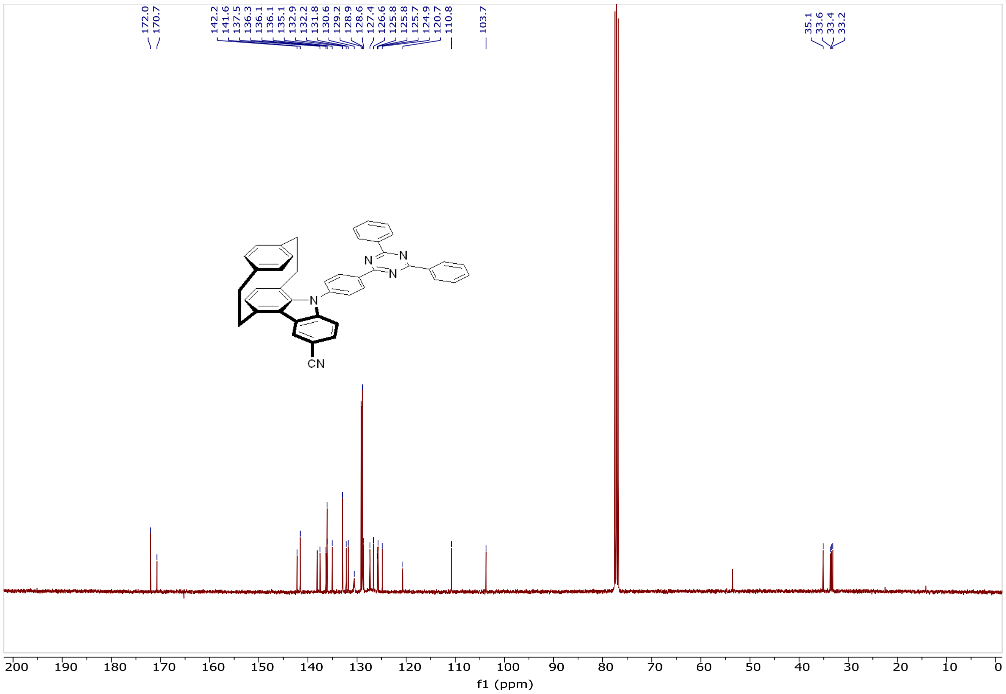


(rac)-1-(N-[2]Paracyclo[2]-6-(cyano)(1,4)carbazolophanyl)-4-(4,6-diphenyl-1,3,5-triazin-2-yl)-benzene (CNCzpPhTRZ)

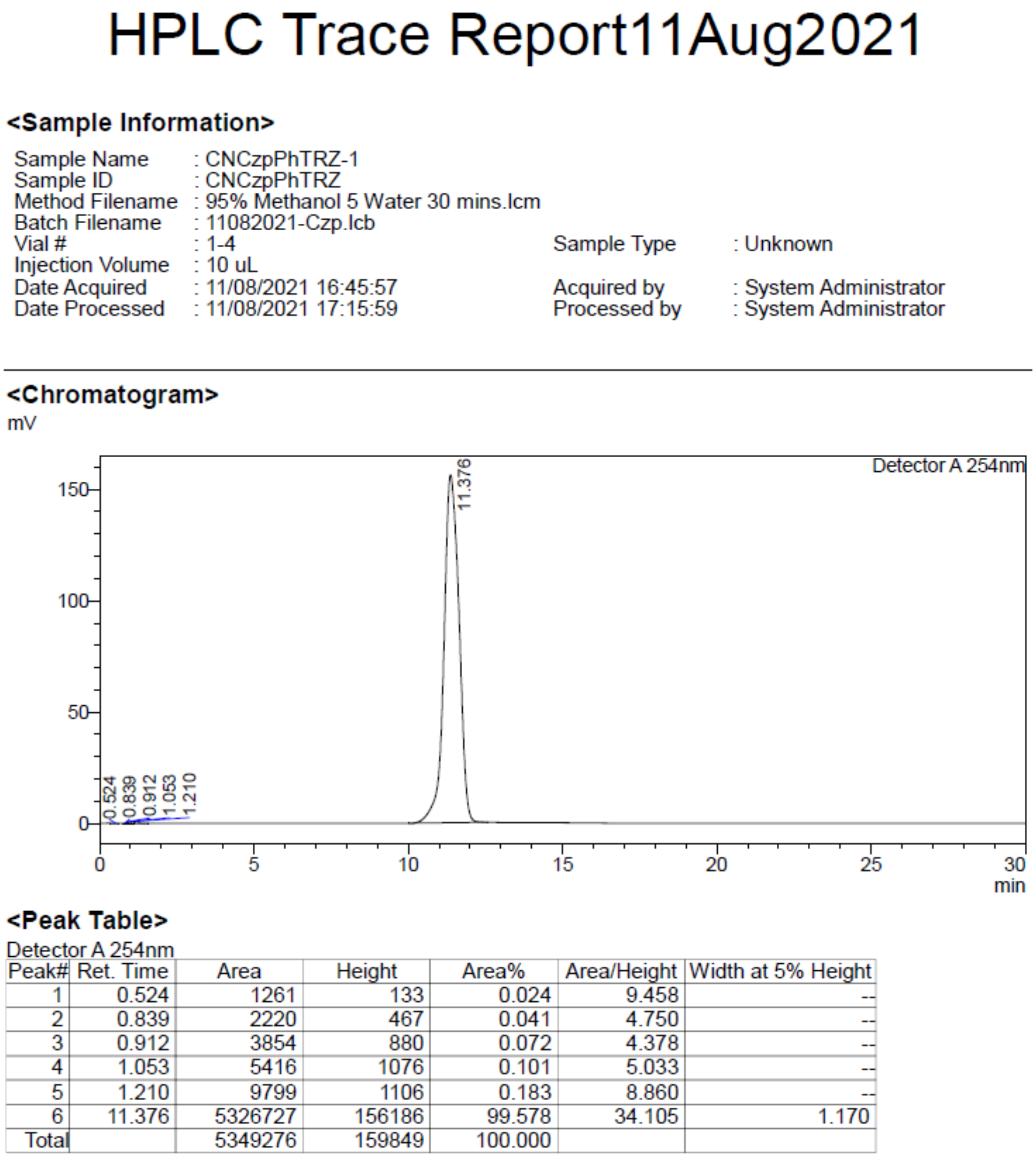
^{1}H NMR in CDCl$_3$-*d_1*



^{13}C NMR in CDCl$_3$-*d_1*



HPLC data of **CNCzpPhTRZ**



HPLC Trace Report11Aug2021

<Sample Information>

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Sample ID	: CNCzpPhTRZ		
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Batch Filename	: 11082021-Czp.lcb		
Vial #	: 1-4	Sample Type	: Unknown
Injection Volume	: 10 uL		
Date Acquired	: 11/08/2021 16:45:57	Acquired by	: System Administrator
Date Processed	: 11/08/2021 17:15:59	Processed by	: System Administrator

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Detector A 254nm

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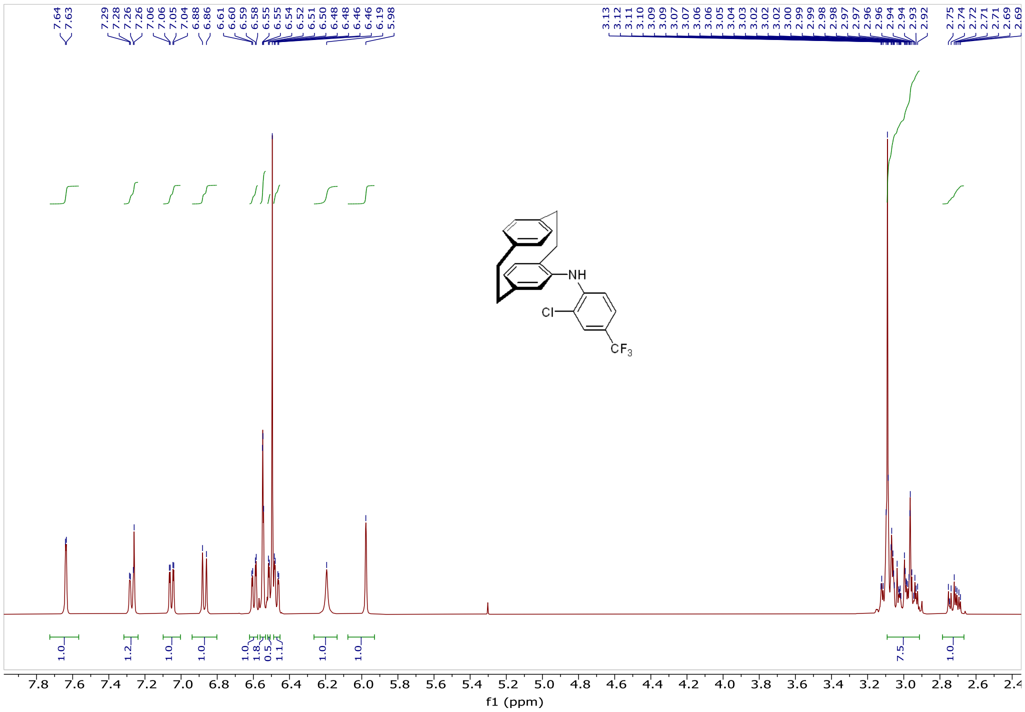
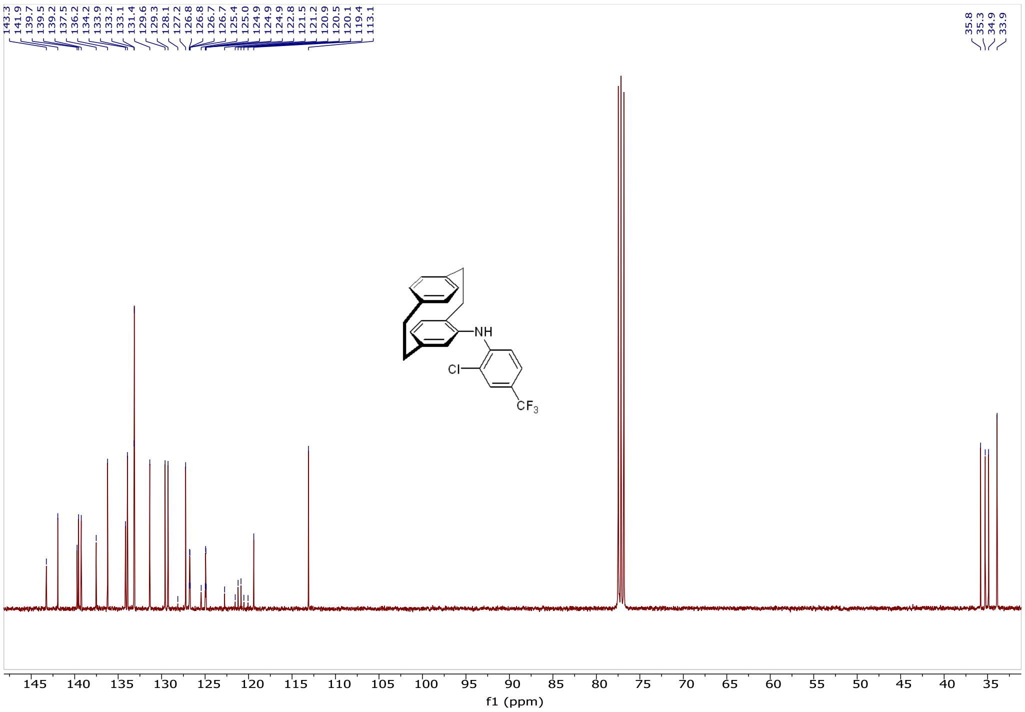
2	0.839	2220	467	0.041	4.750	--
3	0.912	3854	880	0.072	4.378	--
4	1.053	5416	1076	0.101	5.033	--
5	1.210	9799	1106	0.183	8.860	--
6	11.376	5326727	156186	99.578	34.105	1.170
Total		5349276	159849	100.000		

(rac)-4-N-(2-Chloro-4-(trifluoromethyl)phenyl)amino[2.2]paracyclophane (1b)

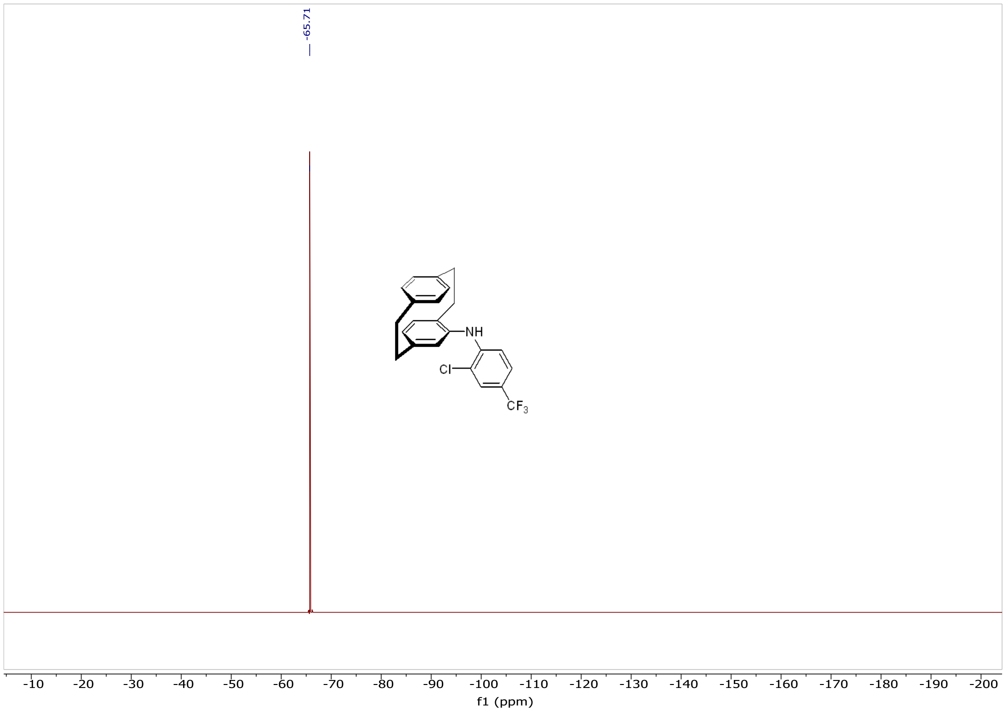
^{1}H NMR in CDCl$_3$-*d$_1$*



^{13}C NMR CDCl$_3$-*d$_1$*

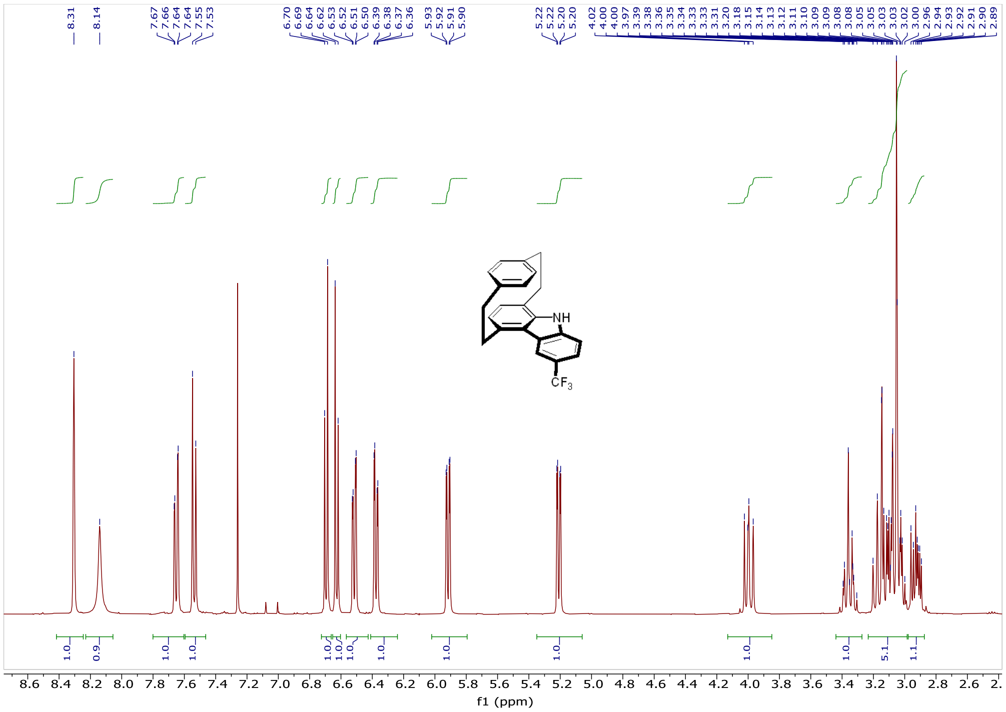


^{19}F NMR in $CDCl_3$-d_1

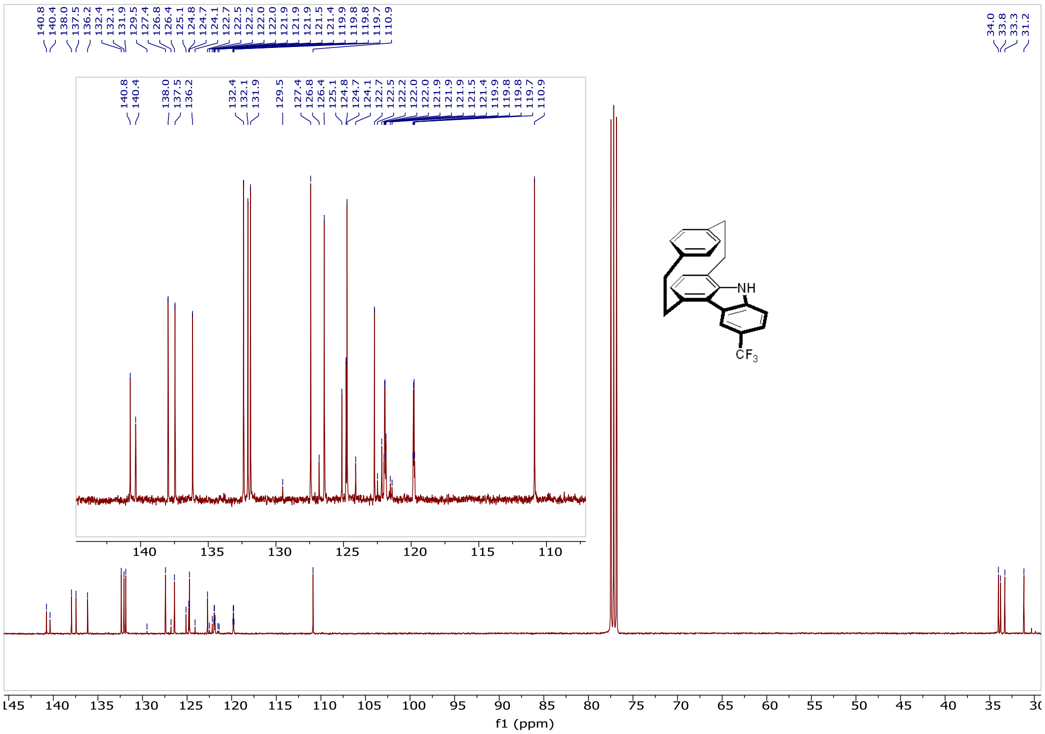


(rac)-[2]Paracyclo[2]6-(trifluoromethyl)(1,4)carbazolophane (2b)

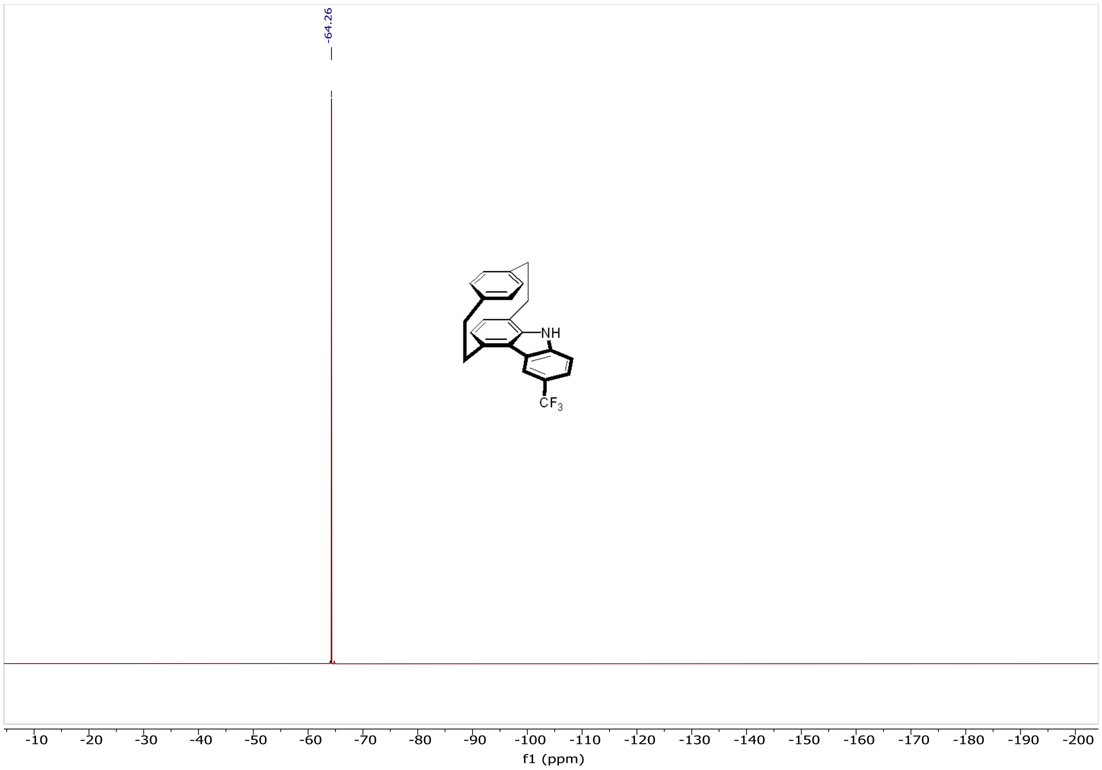
^{1}H NMR in $CDCl_3$-d_1



^{13}C NMR in $CDCl_3$-*d₁*

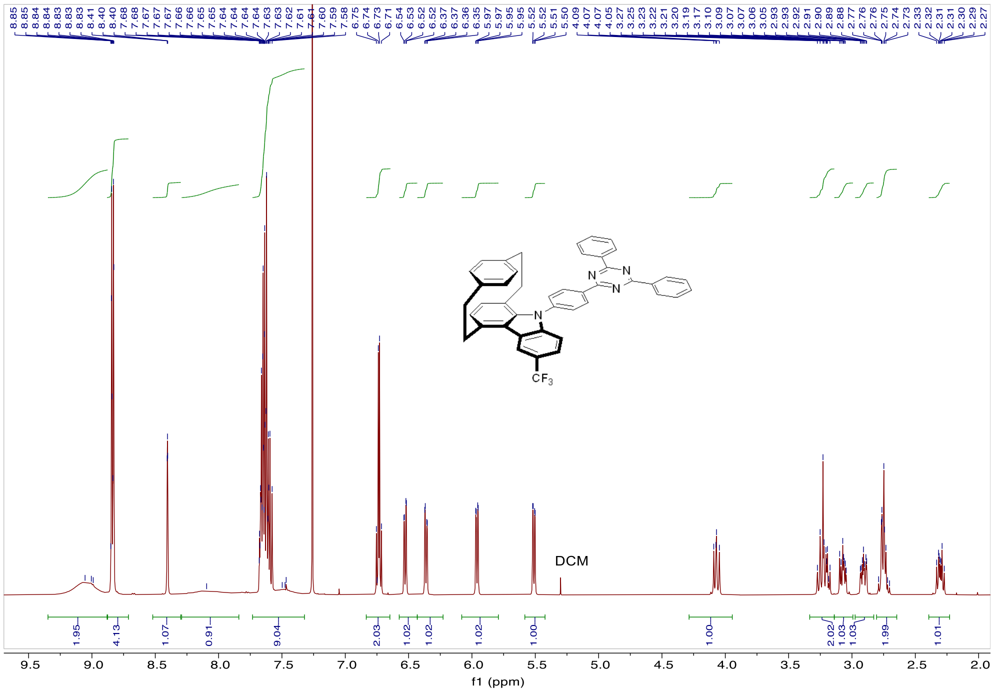


^{19}F NMR in $CDCl_3$-*d₁*

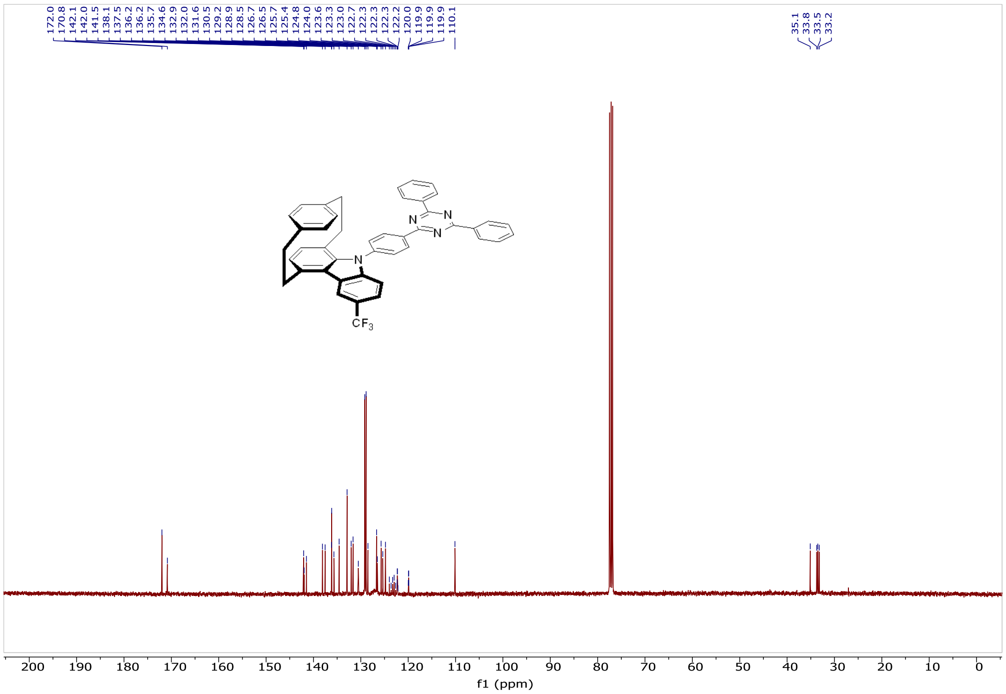


(rac)-1-(N-[2]Paracyclo[2]-6-(rifluoromethyl)(1,4)carbazolophanyl)-4-(4,6-diphenyl-1,3,5-triazin-2-yl)-benzene (CF_3CzpPhTRZ)

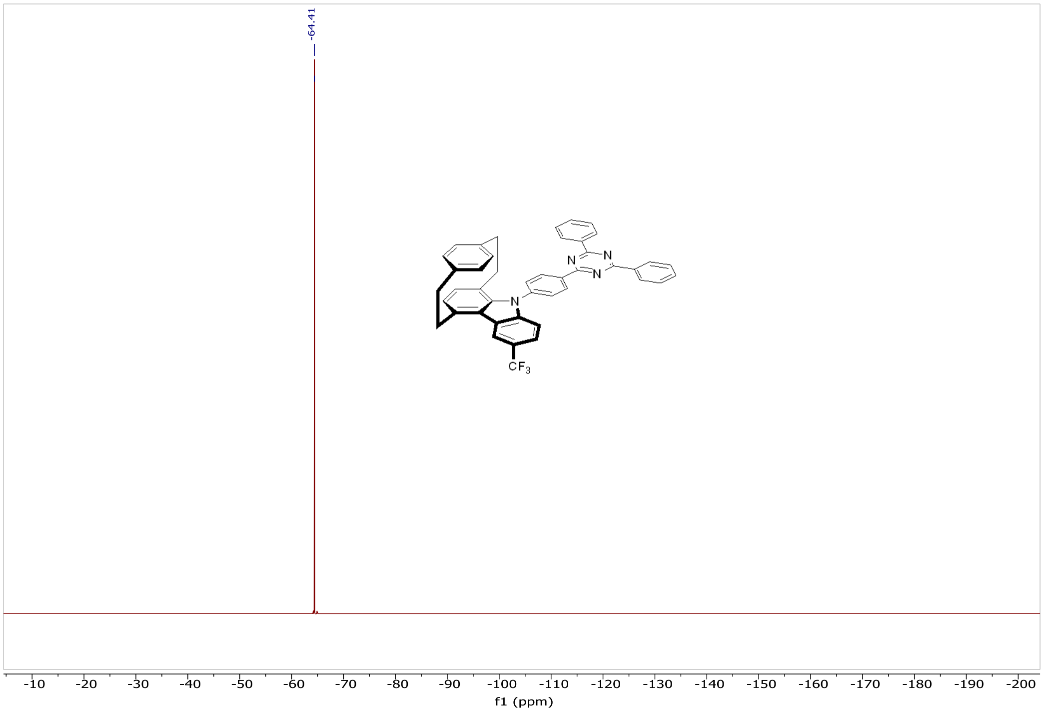
^{1}H NMR in $CDCl_3$-*d_1*



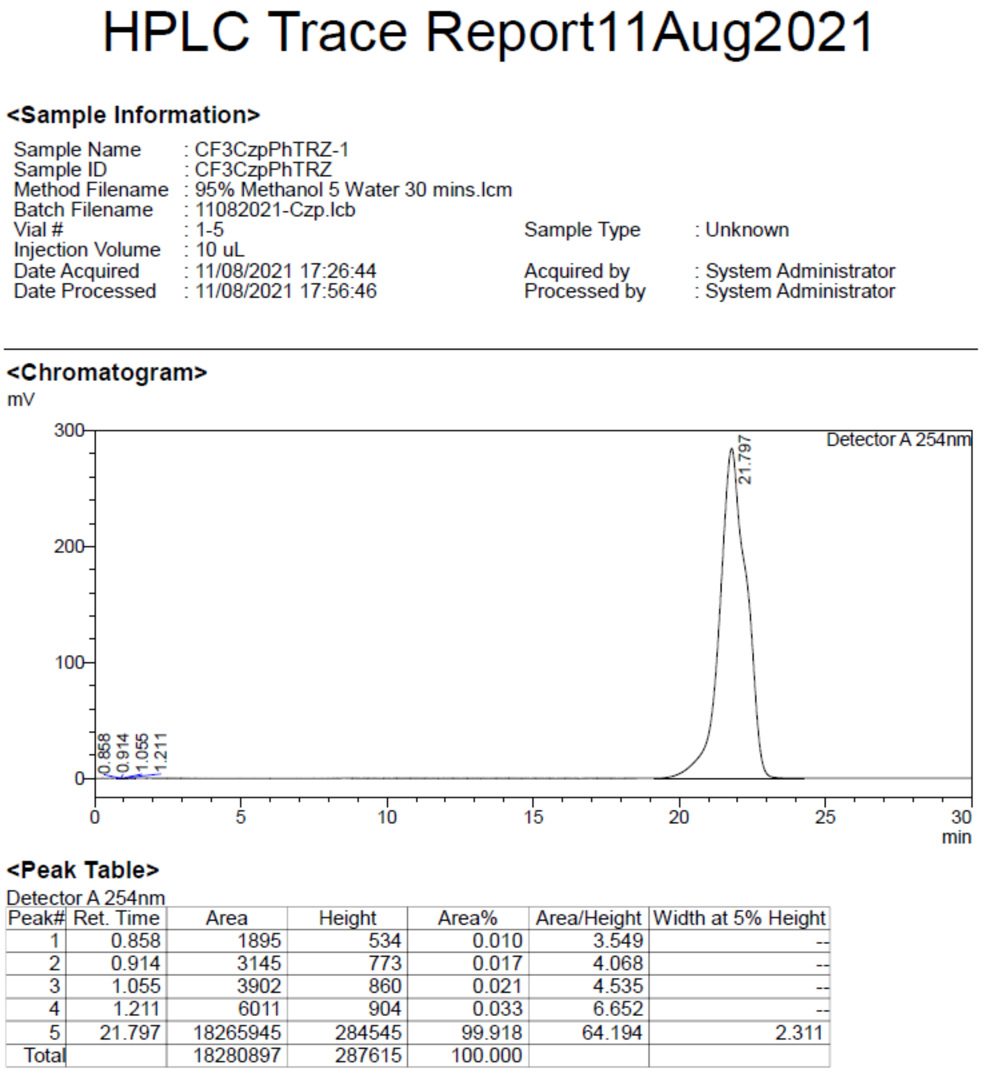
^{13}C NMR in $CDCl_3$-*d_1*



^{19}F NMR in CDCl$_3$-d_1



HPLC data of **CF_3CzpPhTRZ**



HPLC Trace Report11Aug2021

<Sample Information>

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Sample ID : CF3CzpPhTRZ
Method Filename : 95% Methanol 5 Water 30 mins.lcm
Batch Filename : 11082021-Czp.lcb
Vial # : 1-5
Sample Type : Unknown
Injection Volume : 10 uL
Date Acquired : 11/08/2021 17:26:44
Acquired by : System Administrator
Date Processed : 11/08/2021 17:56:46
Processed by : System Administrator

<Chromatogram>

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	0.858	1895	534	0.010	3.549	--
2	0.914	3145	773	0.017	4.068	--
3	1.055	3902	860	0.021	4.535	--
4	1.211	6011	904	0.033	6.652	--
5	21.797	18265945	284545	99.918	64.194	2.311
Total		18280897	287615	100.000		

Table S1. DFT Calculations of **Czp**-based emitters.

Compounds	HOMO/LUMO [eV]	*ΔE* [eV]	*f*	S_1 [eV]	T_1 [eV]	ΔE_{ST} [eV]
CNCzpPhTRZ	–5.91/–2.08	3.83	0.3185	3.27	2.96	0.31
CF_3CzpPhTRZ	–5.78/–2.00	3.78	0.3250	3.23	2.92	0.31
CzpPhTRZ[a]	–5.54/–1.88	3.65	0.3420	3.12	2.81	0.30

[a] Value obtained for **CzpPhTRZ** from Ref. [9]

Electrochemical results

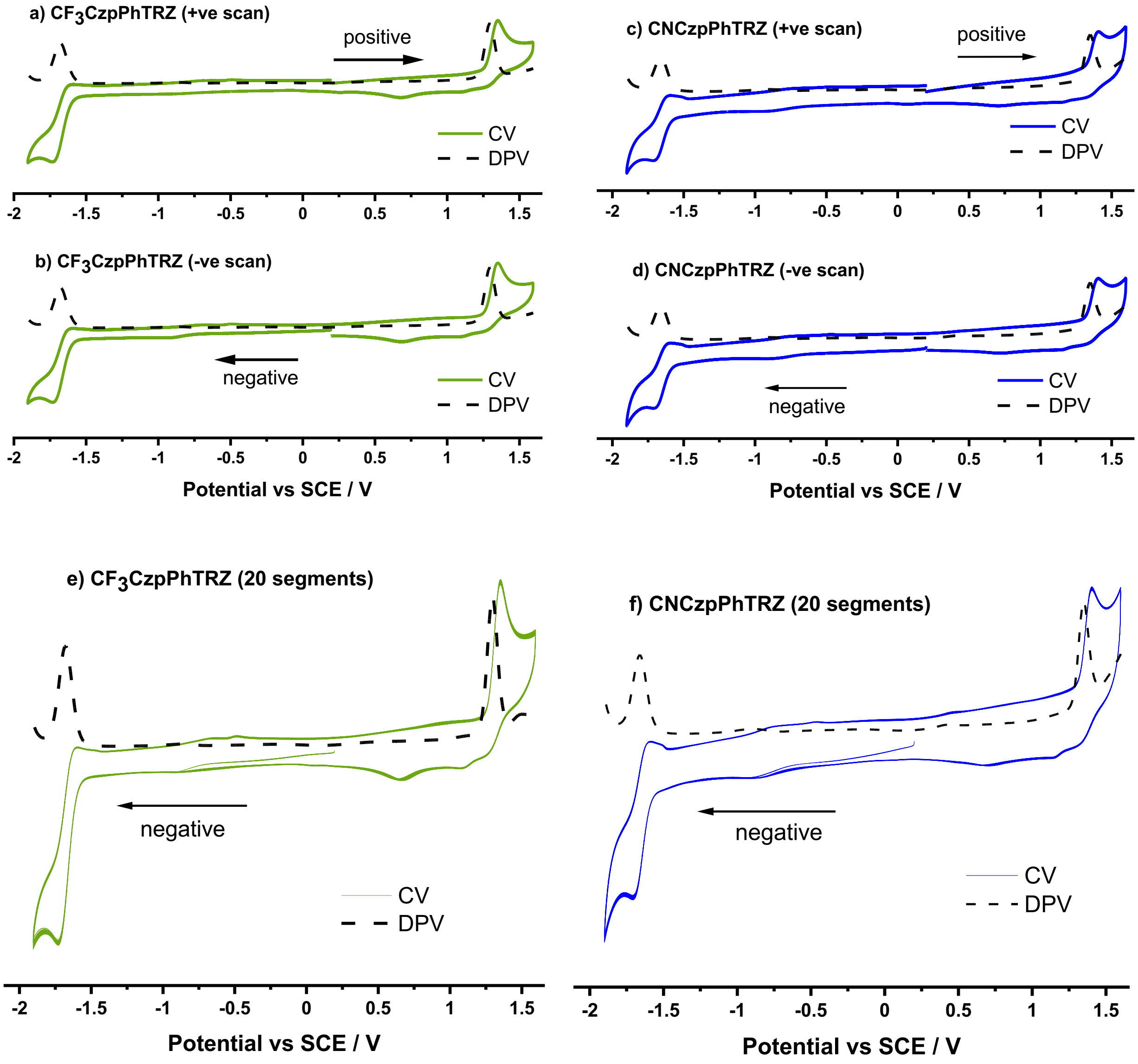

Figure S1. Cyclic and Differential Pulse Voltammograms of a) **CF_3CzpPhTRZ** with positive scan; b) **CF_3CzpPhTRZ** with negative scan; c) **CNCzpPhTRZ** with positive scan; d) **CNCzpPhTRZ** with negative scan; e) **CF_3CzpPhTRZ** 20 segments with negative scan and f) **CNCzpPhTRZ** 20 segments with negative scan in degassed DCM (scan rate = 100 mV s^{-1}).

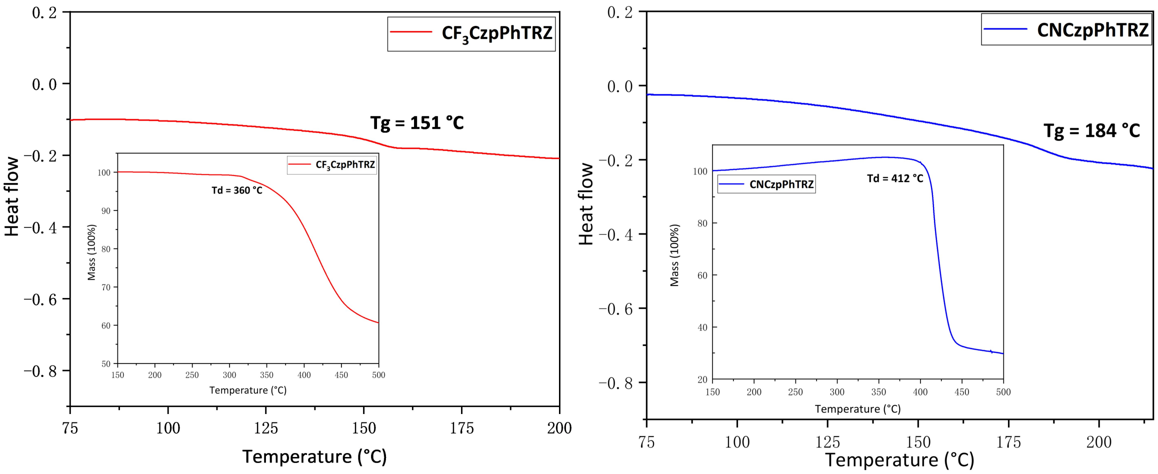

Figure S2. DSC and TGA curves of **CNCzpPhTRZ** and **CF$_3$CzpPhTRZ**.

Photophysical studies

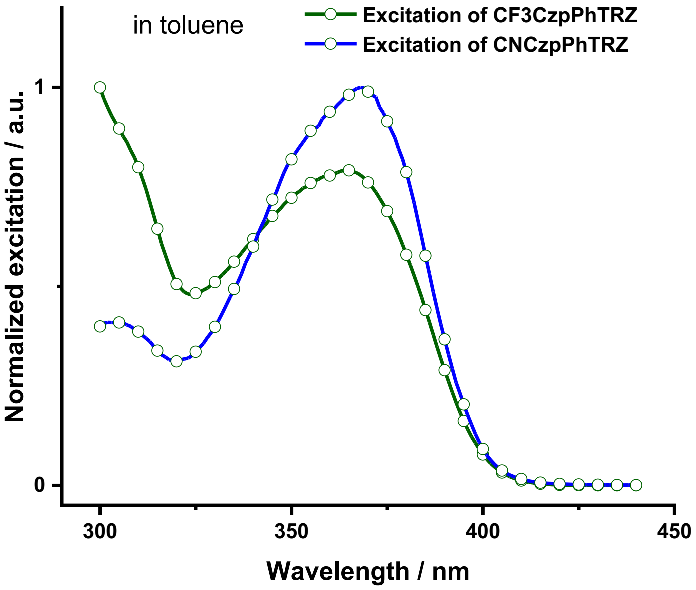

Figure S3. Photoexcitation spectra of **CF$_3$CzpPhTRZ** and **CNCzpPhTRZ** in toluene at 298 K (λ_{em} = 432 nm and 426 nm, respectively).

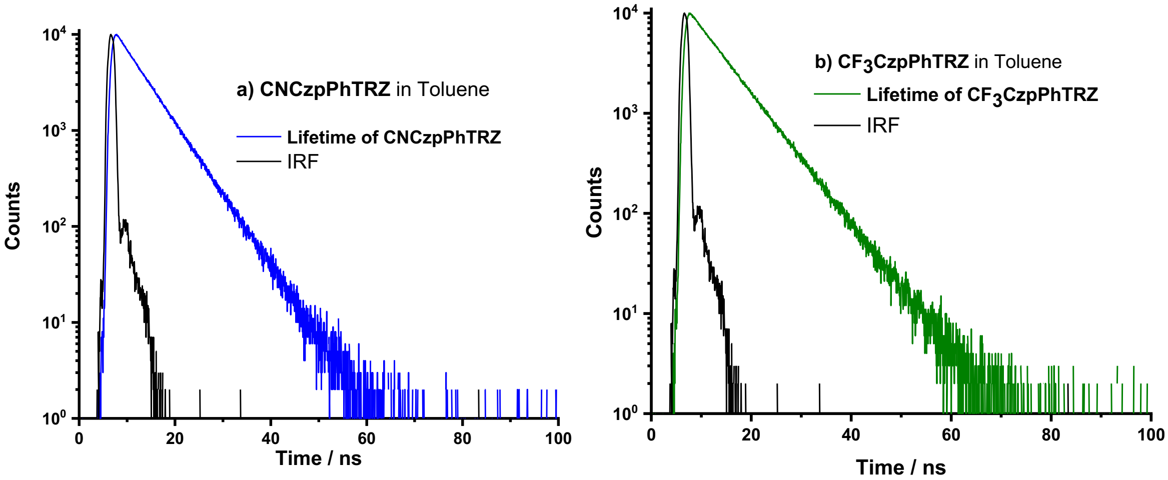

Figure S4. Lifetime spectra of 10^{-5} M **a) CNCzpPhTRZ and b) CF$_3$CzpPhTRZ** in toluene under degassed conditions (λ_{exc} = 379 nm and λ_{em} = 426 nm and 432 nm, respectively).

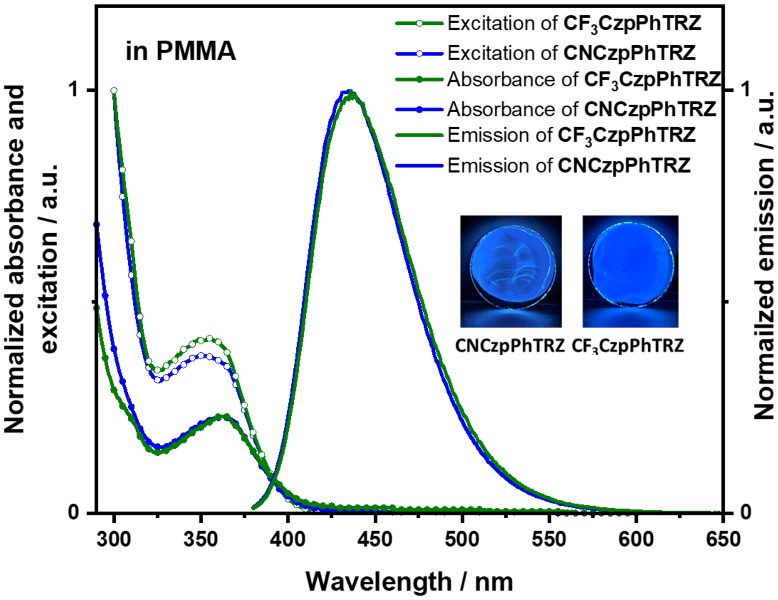

Figure S5. Absorbance, photoexcitation, and photoemission spectra of 10 wt% **CF$_3$CzpPhTRZ** and **CNCzpPhTRZ** doped in PMMA at 298 K (λ_{exc} = 360 nm).

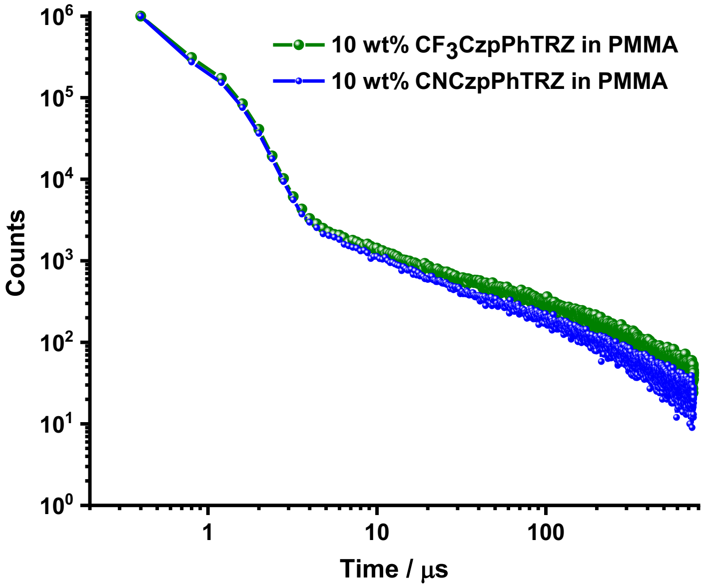

Figure S6. Time-resolved photoluminescence lifetime of 10 wt% doped films of **CF_3CzpPhTRZ** and **CNCzpPhTRZ** in PMMA (λ_{exc} = 379 nm).

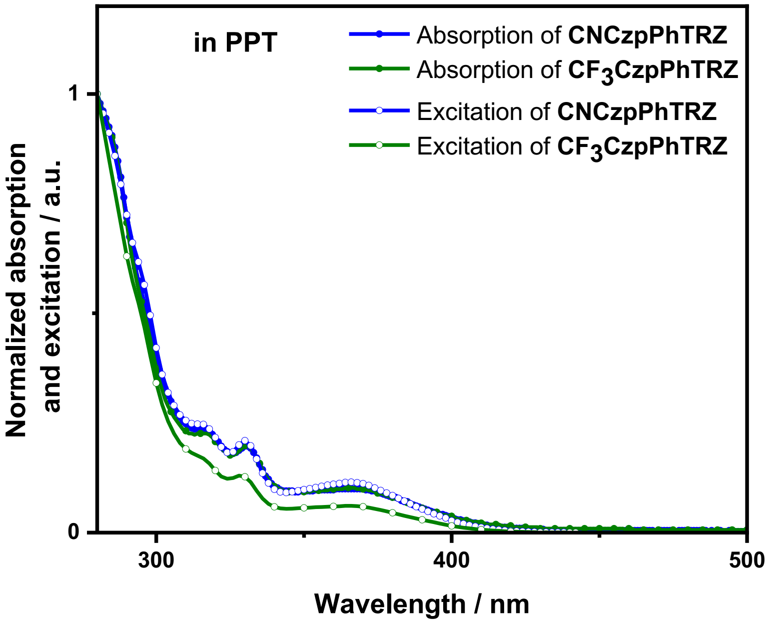

Figure S7. Absorbance and photoexcitation spectra of **CF_3CzpPhTRZ** and **CNCzpPhTRZ** in PPT at 298 K and λ_{em} = 460 nm.

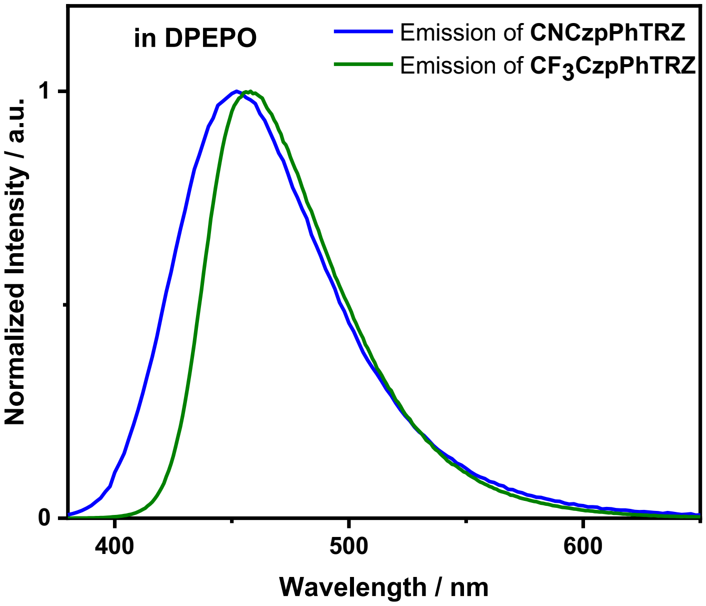

Figure S8. Photoemission spectra of 10 wt% **CF_3CzpPhTRZ** and **CNCzpPhTRZ** doped in DPEPO at 298 K (λ_{exc} = 360 nm).

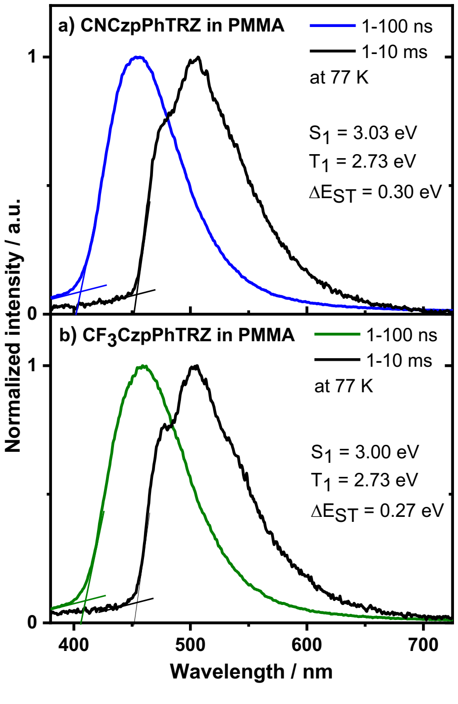

Figure S9. 77 K prompt PL and phosphorescence spectra measurement of a) 10 wt% **CNCzpPhTRZ** and b) 10 wt% **CF_3CzpPhTRZ** doped in PMMA (λ_{exc} = 343 nm), the ΔE_{ST} value is taken from the onset value difference between the 77 K prompt fluorescence and phosphorescence spectra.

Table S2. Absolute Φ_{PL} measurements of doped films of **CF$_3$CzpPhTRZ** and **CNCzpPhTRZ** in different host materials as a function of doping concentrations.

	Doping conc.^{a} / wt%	**Φ_{PL}^{b}/ %**				
		mCBP	**PVK**	**DPEPO**	**PPT**	**PMMA**
CF3CzpPhTRZ	5	54	-	41	53	-
	7	-	-	-	62	-
	10	56	17	53	70^c	63
	15	-	-	50	-	-
	20	-	-	-	67	
CNCzpPhTRZ	5	49	-	38	-	-
	10	44	19	52	65^c	62
	15	-	-	54	-	-
	20	-	-	-	63	

[a]Thin films were prepared by spin-coating, and values were determined using an integrating sphere (λ_{exc} = 300 nm or 360 nm); degassing was done by N_2 purge. [b]Within error limit of ± 2%. [c] 10 wt% doped films in PPT of both emitters were made by vacuum deposition and spin coating methods and in both procedures, obtained Φ_{PL} were very similar. Average Φ_{PL} value of 3 different measurements.

OLED fabrication and characterization

The OLED devices were fabricated in bottom emitting architecture via vacuum sublimation in a high vacuum at a base pressure of $<1\times10^{-6}$ mbar. A pre-patterned glass substrate coated with indium doped tin oxide (ITO) was washed sequentially by ultrasonication in chloroform, acetone, and isopropanol for 15 min and then exposed to oxygen plasma for 3 min to remove all the dust and organics on the ITO surface. The organic layer sequence and the metal cathode were deposited onto pre-cleaned glass substrates coated with indium tin oxide (ITO), which has a sheet resistance of around 30 Ω/sq. Organic layers were deposited at a rate of 0.3-0.6 Å/s, controlled in situ using the quartz crystal monitors. Doping of the emission layers was achieved through co-evaporation of the emitter and host materials. The electron injection layer LiF was deposited at a rate of 0.05 Å/s, while the Al cathode was deposited at a rate of 0.5 Å/s through the shadow mask defining the top electrode. The spatial overlap of the anode and cathode electrodes determined the active area of the OLED, which was estimated to be 2 mm^2. All the devices were encapsulated with glass lids and UV epoxy resin inside the inert atmosphere. The luminance-current-voltage characteristics were measured in an ambient environment using a Keithley 2400 source meter combined with a homemade photodiode connected to a multimeter (Keithley 2000) for the voltage reading. The external quantum efficiency was calculated assuming Lambertian emission distribution. The electroluminescence spectra were recorded by an Andor DV420-BV CCD spectrometer.

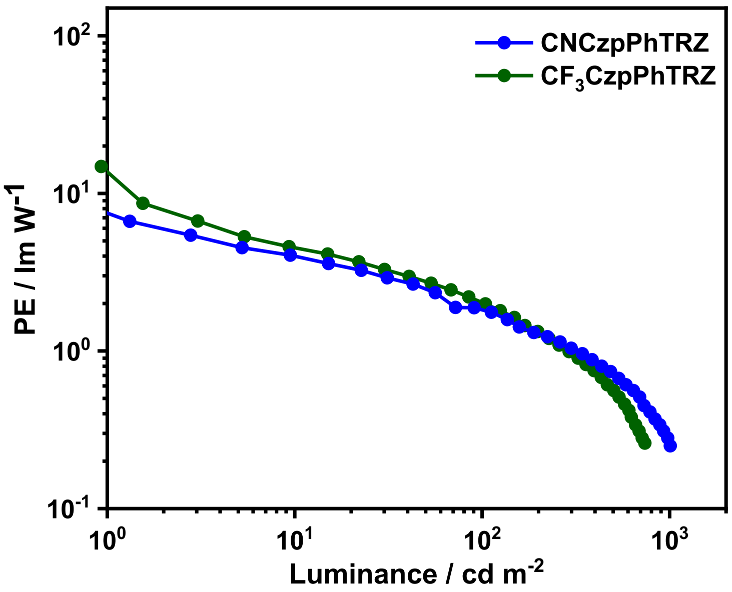

Figure S10. Power efficiency versus luminance curves for devices of **CF$_3$CzpPhTRZ** (10 wt%) and **CNCzpPhTRZ** (10 wt%) emitters in PPT host fabricated by thermal evaporation.

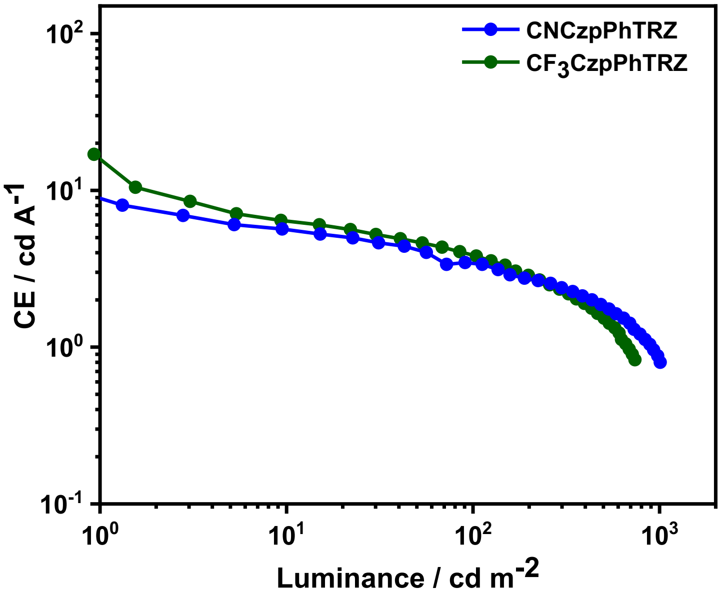

Figure S11. Current efficiency versus luminance curves for devices of **CF$_3$CzpPhTRZ** (10 wt%) and **CNCzpPhTRZ** (10 wt%) emitters in PPT host fabricated by thermal evaporation.

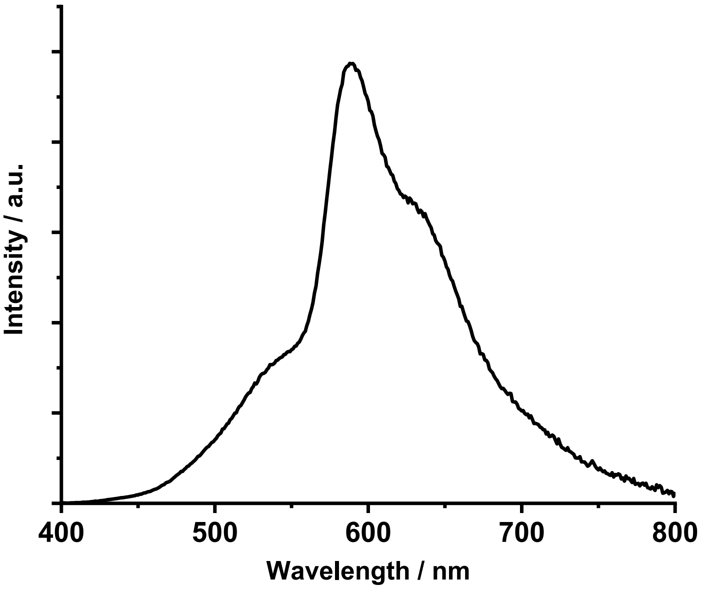

Figure **S12**. PL emission spectrum of the decomposed by-product of **CF$_3$CzpPhTRZ** during train sublimation (λ_{exc} = 360 nm).

Optimized atomic coordinates.

Table S3. Optimized atomic coordinates of compound **CF$_3$CzpPhTRZ** obtained from DFT calculations.

Centre	**Atomic**	**Atomic**	**Coordinates**	**(Å)**	
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	-1.42378	1.09706	0.140235
2	6	0	-0.08505	1.014548	0.067401
3	6	0	0.570403	-0.07085	-0.38946
4	6	0	-0.25058	-1.05328	-0.81118
5	6	0	-1.59029	-0.98325	-0.75444
6	6	0	-2.22808	0.097153	-0.26697
7	6	0	3.674644	-2.8597	2.594724
8	6	0	4.960163	-2.64103	2.273278
9	6	0	5.357274	-1.41295	1.895828
10	6	0	4.534392	-0.37225	2.116654
11	6	0	3.247055	-0.59292	2.424824
12	6	0	2.786337	-1.85207	2.530673
13	6	0	3.08646	-3.524	-0.21717
14	6	0	4.360013	-3.26817	-0.54007
15	6	0	4.791432	-1.99699	-0.61541
16	6	0	3.835953	-1.04591	-0.66777
17	6	0	2.520998	-1.28904	-0.45338

18	6	0	2.196207	-2.53287	-0.01546
19	6	0	6.599109	-1.23924	1.034919
20	6	0	6.290437	-1.76253	-0.41169
21	6	0	1.303907	-2.14417	2.360476
22	6	0	1.07442	-2.87115	0.993599
23	7	0	1.846271	-0.19099	-0.49278
24	6	0	2.679354	0.766912	-0.69326
25	6	0	-3.57865	0.174021	-0.19706
26	7	0	-4.14317	1.212081	0.260817
27	6	0	-5.40588	1.296612	0.330888
28	7	0	-6.10403	0.315958	-0.06612
29	6	0	-5.56469	-0.73446	-0.52696
30	7	0	-4.3	-0.79185	-0.5878
31	6	0	3.928313	0.284045	-0.80162
32	6	0	4.98177	1.086104	-1.01554
33	6	0	4.825095	2.410394	-1.17849
34	6	0	3.575412	2.895587	-1.10747
35	6	0	2.522895	2.087734	-0.90279
36	6	0	-6.32458	-1.77592	-0.94614
37	6	0	-5.77285	-2.90524	-1.43994
38	6	0	-6.52025	-3.94016	-1.85592
39	6	0	-7.85695	-3.87664	-1.79016
40	6	0	-8.43115	-2.76781	-1.30447
41	6	0	-7.67327	-1.73921	-0.89139
42	6	0	-5.99764	2.413848	0.820273
43	6	0	-7.34049	2.52832	0.904655
44	6	0	-7.93232	3.632626	1.387563
45	6	0	-7.19096	4.66744	1.805604
46	6	0	-5.85592	4.580857	1.733613
47	6	0	-5.27542	3.471437	1.248753
48	6	0	6.01755	3.320417	-1.36125
49	9	0	7.082867	2.888272	-0.70362
50	9	0	5.782386	4.56291	-0.96988
51	9	0	6.343528	3.366564	-2.64404
52	1	0	-1.83847	2.022128	0.576457
53	1	0	0.453395	1.866654	0.507125
54	1	0	0.159135	-1.94657	-1.31422
55	1	0	-2.14715	-1.84753	-1.15498
56	1	0	3.321017	-3.8994	2.694933
57	1	0	5.623541	-3.50752	2.113496
58	1	0	4.838169	0.649539	1.835021
59	1	0	2.545611	0.257107	2.380627
60	1	0	2.864295	-4.55854	0.096679
61	1	0	5.076746	-4.10565	-0.49072

62	1	0	6.88726	-0.16384	0.987986
63	1	0	7.467022	-1.77236	1.487157
64	1	0	6.825398	-2.7373	-0.51157
65	1	0	6.754583	-1.16268	-1.22064
66	1	0	0.915525	-2.73905	3.218947
67	1	0	0.726107	-1.19031	2.347355
68	1	0	0.023599	-2.79301	0.662203
69	1	0	1.129783	-3.95979	1.235359
70	1	0	6.000041	0.693445	-1.08868
71	1	0	3.399384	3.974123	-1.25703
72	1	0	1.546051	2.58483	-0.95923
73	1	0	-4.68033	-3.03112	-1.52455
74	1	0	-6.03649	-4.84848	-2.25389
75	1	0	-8.47496	-4.72398	-2.13044
76	1	0	-9.53102	-2.70439	-1.24553
77	1	0	-8.2168	-0.86116	-0.50389
78	1	0	-8.0157	1.718806	0.579852
79	1	0	-9.03262	3.692789	1.442101
80	1	0	-7.67233	5.576379	2.202738
81	1	0	-5.23536	5.426965	2.074952
82	1	0	-4.17283	3.473886	1.220226

Table S4. Optimized atomic coordinates of compound **CNCzpPhTRZ** obtained from DFT calculations.

Centre	**Atomic**	**Atomic**	**Coordinates**	**(Å)**	
Number	**Number**	**Type**	**X**	**Y**	**Z**
1	6	0	-1.07569	1.092432	0.106276
2	6	0	0.30838	1.049667	0.032764
3	6	0	0.944872	-0.09664	-0.44901
4	6	0	0.187908	-1.20021	-0.84951
5	6	0	-1.19401	-1.15686	-0.76064
6	6	0	-1.83982	-0.00998	-0.28642
7	6	0	4.454232	-1.0953	3.259433
8	6	0	5.73985	-0.89026	2.775941
9	6	0	5.998949	0.116568	1.84128
10	6	0	5.003192	1.075503	1.641609
11	6	0	3.714036	0.866972	2.123888
12	6	0	3.39201	-0.30103	2.818174
13	6	0	3.919733	-3.11565	0.981692
14	6	0	5.214285	-2.90994	0.493942
15	6	0	5.55807	-1.73798	-0.17254

16	6	0	4.487375	-0.94117	-0.60584
17	6	0	3.177606	-1.17978	-0.12352
18	6	0	2.899372	-2.17842	0.823001
19	6	0	7.152247	-0.00686	0.878101
20	6	0	6.973969	-1.22348	-0.12114
21	6	0	1.981339	-0.83118	2.817577
22	6	0	1.81001	-2.07921	1.864251
23	7	0	2.35097	-0.1343	-0.54461
24	6	0	3.098046	0.758537	-1.29305
25	6	0	-3.31232	0.035237	-0.20033
26	7	0	-3.87223	1.163667	0.242486
27	6	0	-5.20845	1.157495	0.30288
28	7	0	-5.97266	0.118109	-0.04547
29	6	0	-5.31987	-0.96529	-0.47644
30	7	0	-3.98853	-1.05476	-0.57102
31	6	0	4.437209	0.300235	-1.34204
32	6	0	5.382351	1.042494	-2.04371
33	6	0	4.981946	2.216535	-2.68687
34	6	0	3.637446	2.638172	-2.6509
35	6	0	2.683453	1.90987	-1.96292
36	6	0	-6.11932	-2.13931	-0.87388
37	6	0	-5.4871	-3.29904	-1.33399
38	6	0	-6.242	-4.40254	-1.70802
39	6	0	-7.6321	-4.3579	-1.62595
40	6	0	-8.26644	-3.20497	-1.16814
41	6	0	-7.51511	-2.09937	-0.79326
42	6	0	-5.88221	2.37794	0.784419
43	6	0	-7.27752	2.423686	0.870047
44	6	0	-7.91034	3.573589	1.322509
45	6	0	-7.15718	4.685752	1.692699
46	6	0	-5.76703	4.644985	1.60923
47	6	0	-5.13051	3.496933	1.157331
48	6	0	5.946125	2.99557	-3.39631
49	7	0	6.73232	3.630198	-3.97069
50	1	0	-1.58546	1.972529	0.481683
51	1	0	0.905701	1.894078	0.361309
52	1	0	0.696488	-2.08142	-1.2272
53	1	0	-1.79716	-2.0038	-1.06783
54	1	0	4.250092	-1.97273	3.868651
55	1	0	6.517936	-1.61057	3.017776
56	1	0	5.194524	1.917246	0.981199
57	1	0	2.921747	1.554041	1.837062
58	1	0	3.751424	-3.94672	1.662353
59	1	0	6.001572	-3.59147	0.805275

60	1	0	7.237323	0.921498	0.305014
61	1	0	8.105751	-0.14425	1.399501
62	1	0	7.617508	-2.04508	0.207413
63	1	0	7.346776	-0.92373	-1.1065
64	1	0	1.654463	-1.13406	3.818673
65	1	0	1.301565	-0.03916	2.48813
66	1	0	0.80233	-2.04505	1.440099
67	1	0	1.861686	-2.9902	2.468694
68	1	0	6.416506	0.725834	-2.10662
69	1	0	3.355333	3.545105	-3.1743
70	1	0	1.647132	2.227306	-1.95011
71	1	0	-4.40444	-3.31443	-1.39093
72	1	0	-5.7467	-5.30046	-2.06491
73	1	0	-8.22133	-5.22197	-1.91906
74	1	0	-9.34974	-3.16915	-1.10396
75	1	0	-7.98996	-1.19294	-0.43477
76	1	0	-7.84576	1.5479	0.577161
77	1	0	-8.99377	3.604357	1.387106
78	1	0	-7.65376	5.584709	2.046162
79	1	0	-5.17918	5.511271	1.897253
80	1	0	-4.04986	3.446206	1.084984

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