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

Enhanced Thermally Activated Delayed Fluorescence Through Bridge Modification in Sulfone-Based Emitters Employed in Deep Blue Organic Light-Emitting Diodes

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Supporting Information

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Methods

Theoretical calculation.

The calculations were performed on Gaussian 09[1] revision D.018 suite. Initially the geometries of all the derivatives were fully optimized using a DFT methodology employing the PBE0[2] functional with the standard Pople[3] 6-31G(d,p) basis set and Tamm–Dancoff approximation (TDA) was treated as a variant of Time-dependent density functional theory (TD-DFT).

Photophysical measurements. The sample solutions for the emission spectra were prepared in spectroscopy grade solvents. Absorption spectra were recorded at room temperature using a Shimadzu UV-1800 double beam spectrophotometer. The sample solutions for the emission spectra were prepared in toluene and degassed via three freeze–pump–thaw cycles using a quartz cuvette designed in-house. Steady-state emission and excitation spectra and time-resolved emission spectra were recorded at 298 K using an Edinburgh Instruments FLS980 fluorimeter. All samples for steady-state measurements were excited at 360 nm using a xenon lamp, while samples for time-resolved measurements were excited at 378 nm using a PicoQuant, LDH-D-C-375 pulsed diode laser. 2,8-Bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT)-doped (7 wt%) thin films were prepared by spin-coating the samples from a solution of chlorobenzene of the desired sample on a quartz substrate. Solid-state Φ_{PL} measurements of thin films were performed in an integrating sphere[4] under a nitrogen atmosphere or air in a Hamamatsu C9920-02 luminescence measurement system. For temperature-dependent measurements samples were prepared on sapphire substrates and cooled down to 77 K in a cryostat (Oxford Instruments). The same fluorimeter was used to measure phosphorescence spectra using a Multi-Channel Scaling (MCS) mode. The time window for the MCS measurement was 10 ms. The acquisition time for each MCS measurement was 150 s and the wavelength step for the TRES measurement was 3 nm. The excitation source was a picosecond laser emitting at 378 nm (PicoQuant, LDH-D-C-375) triggered by a delay generator (Stanford Research Systems, DG645) in burst mode. The burst mode was used to increase the excitation power so as to get more emitted photons from the samples and speed up the measurement. Phosphorescence spectra were integrated in the TRES mode between 1 ms – 2 ms after the laser excitation.

Electrochemistry measurements. An electrochemical Analyzer potentiostat model 600E from CH Instruments was used for Cyclic Voltammetry (CV) analysis. All samples were prepared as dichloromethane (DCM) solutions, and bubbled with DCM saturated nitrogen gas for 15 minutes before measurements. 0.1 M DCM solution of tetra-*n*-butylammonium hexafluorophosphate [$n\mathrm{Bu}_4\mathrm{N}]\mathrm{PF}_6$] was used as electrolyte solution and Ag/Ag$^+$ electrode was used as the reference electrode while a platinum 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 (0.34 V vs SCE in DCM).[5]

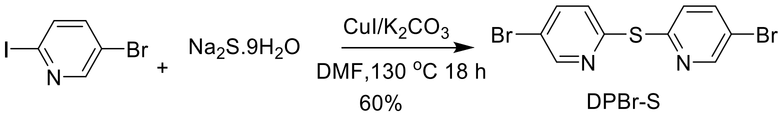
OLED fabrication and characterization. All the OLED devices were fabricated under high vacuum at a base pressure of 2-5 × 10^{-7} mbar in a bottom-emitting architecture via vacuum sublimation. The organic layers and the cathode were deposited on pre-cleaned glass substrates coated with indium tin oxide (ITO) with a substrate sheet resistance of 30 Ω/sq. A pre-patterned ITO glass substrate was treated by ultrasonic cleaning in acetone (15 min) and isopropanol (15 min) sequentially and then treated with oxygen plasma before the transfer to the vacuum chamber. The following device structure is used to fabricate all the device: ITO (90 nm)/NPB (30)/TAPC (20)/mCP (10 nm)/DPEPO or PPT: emitter (7 wt%) (30 nm)/DPEPO (5 nm)/TmPyPb (30 nm)/LiF (1 nm)/Al (100 nm). Here, TmPyPb stands for 1,3,5-Tri(m-pyridin-3-ylphenyl)benzene and is used as an electron transporting layer. Hole injection layer (HIL) consists of 30 nm of N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) and hole transporting layer (HTL) contains 20 nm of 4,4′-Cyclohexylidene-bis[N,N-bis(4- methylphenyl)benzenamine] (TAPC). mCP stands for (1,3-Bis(*N*-carbazolyl)benzene) and used as an electron blocking layer (EBL). Bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO) is used as both host and hole blocking layer (HBL). Organic layers were deposited at a rate of 0.3-0.6 Å/s and deposition rate was controlled in situ using a quartz crystal monitor. Emission layers was deposited through co-evaporation of the emitter and host material. Electron injection layer (EIL) LiF was deposited at a rate of 0.05 Å/s and the Al cathode was deposited at a rate of 0.5 Å/s up to 10 nm then increased to 2 Å/s using the shadow mask defining the top electrode. The spatial overlap of the anode and cathode electrodes determined the active area of the OLED and this is estimated to be 2 mm^2. All the devices were encapsulated with UV epoxy resin under the inert atmosphere. The luminance-current-voltage characteristics were measured in an ambient environment using a Keithley 2400 source meter and Keithley 2000 multimeter connected to a calibrated Si photodiode. The external quantum efficiency (EQE) was calculated assuming Lambertian emission distribution. The electroluminescence spectra were recorded by an Andor DV420-BV CCD spectrometer.

Synthesis

General Synthetic Procedures

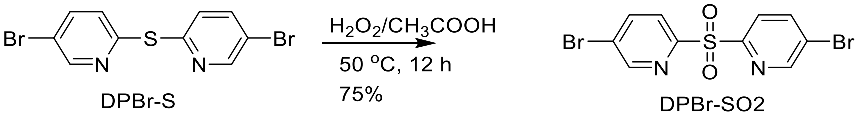
Commercial chemicals were used without further purification. All reactions were performed using standard Schlenk techniques with dry solvents. Column chromatography was performed using silica gel (Silia-P from Silicycle, 60 Å, 40 to 63 µm). Analytical thin layer chromatography was performed with silica plates with polymer (250 µm with indicator F-254), and compounds were visualized under UV light. ^{1}H and ^{13}C solution-phase NMR spectra were recorded on a Bruker Avance spectrometer operating at 11.7 T (Larmor frequencies of 400 and 100, respectively) in chloroform-d ($CDCl_3$) solvent. The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet, and “br” for broad. Melting points (Mps) were recorded using open-ended capillaries on an electrothermal Mp apparatus and are uncorrected. High-resolution mass spectra of all compounds were recorded at the Engineering and Physical Sciences Research Council UK National Mass Spectrometry Facility at Swansea University on a LTQ Orbitrap XL Fourier transform mass spectrometer (FTMS), in positive electrospray or nanospray ionization mode. Elemental analysis was done by Mr. Stephen Boyer, London Metropolitan University. High-performance liquid chromatography (HPLC) analysis was conducted on a Shimadzu Prominence Modular HPLC system. HPLC traces were measured using an ACE Excel 2 C18 analytical column.

bis(5-bromopyridin-2-yl)sulfone (DPBr-S)



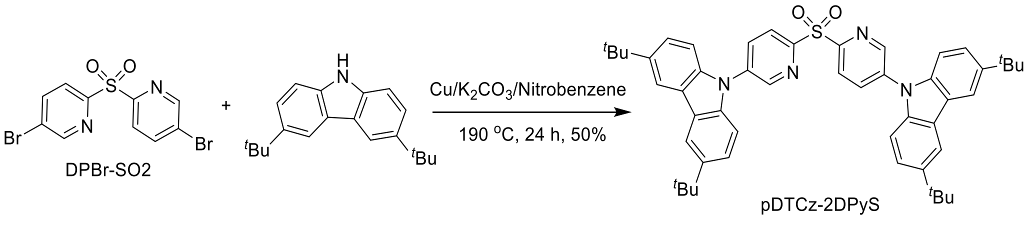
To a 150 mL three neck flask were added 2-iodo-5-bromopyridine (280 mg, 1 mmol, 1 equiv.), sodium sulfide (140 mg, 0.6 mmol, 0.6 equiv.), copper (I) iodide (30 mg, 0.1 mmol, 0.1 equiv.) and potassium carbonate (140 mg, 1 mmol, 1 equiv.). The flask was degassed by three cycles of vacuum-nitrogen purging and 10 mL of DMF was injected. The mixture was stirred at 130 °C for 18 h under nitrogen atmosphere. The mixture was washed with water and extracted with ethyl acetate (3×50 mL). The combined organic layers were dried with anhydrous magnesium sulfate and organic solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography. DCM/Hexane=1/1 was used as eluent to obtain **DPBr-S** as a white solid. **DPBr-S: R$_f$** = 0.5 (50% DCM/Hexane). **Yield:** 80%. **Mp:** 75-77˚C. **^{1}H NMR δ (ppm):** 8.61 (s, 2H), 7.77 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H). **^{13}C NMR δ (ppm):** 154.69, 151.19, 139.68, 127.06, 125.27. **HR ESI-MS: [M+H]$^+$:** calcd for $[C_{10}H_7Br_2N_2S]^+$: 346.8670; found: 346.8673.

6,6'-sulfonylbis(3-bromopyridine) (DPBr-SO$_2$)



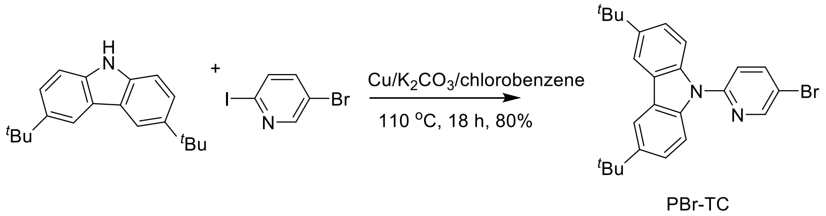
In a 50 mL flask DPBr-S (60 mg, 0.2 mmol, 1 equiv.) was dissolved in 2 mL of glacial acetic acid. 2 mL of hydrogen peroxide solution (30 wt%, 100 equiv.) was added and the mixture was stirred at 50 °C for 12 h. The mixture was poured into 20 mL of ice water and extracted with DCM (3×20 mL). The combined organic layers were dried with anhydrous magnesium sulfate and organic solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography. DCM/Hexane=1/1 was used as eluent to obtain DPBr-SO$_2$ as a white solid. **DPBr-SO$_2$: R$_f$** = 0.3 (50% DCM/Hexane). **Yield:** 75%. **Mp:** 98-100˚C. **^{1}H NMR δ (ppm):** 8.72 - 8.65 (m, 2H), 8.02 (dd, *J* = 8.4 Hz, 2.3 Hz, 2H), 7.93 (dd, *J* = 8.4 Hz, 0.7 Hz, 2H). **^{13}C NMR δ (ppm):** 162.02, 151.29, 140.74, 122.97, 120.92. **HR ESI-MS: [M+H]$^+$:** calcd for $[C_{10}H_7Br_2N_2O_2S]^+$: 378.8569; found: 378.8567.

9,9'-(sulfonylbis(pyridine-6,3-diyl))bis(3,6-di-*tert*-butyl-9H-carbazole) (pDTCz-2DPyS)



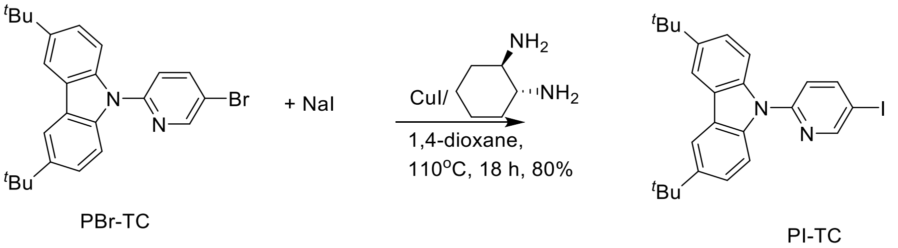
To a 50 mL flask were added DPBr-SO$_2$ (50 mg, 0.13 mmol, 1 equiv.), di-*tert*-butyl-9H-carbazole (100 mg, 0.3 mmol, 2.3 equiv.), copper powder (10 mg, 0.14 mmol, 1.1 equiv.) and potassium carbonate (50 mg, 0.4 mmol, 3 equiv.). The flask was degassed by three cycles of vacuum-nitrogen purging and 5 mL of nitrobenzene was added. The mixture was stirred at 190 °C for 24 h under a nitrogen atmosphere. After completion of reaction, water was added to the reaction mixture and extracted with DCM (3×50 mL). The combined organic layers were dried with anhydrous magnesium sulfate and organic solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography. DCM/Hexane=1/2 was used as eluent to afford **pDTCz-2DPyS** as a white solid. **pDTCz-2DPyS: R$_f$** = 0.7 (90% DCM/Hexane). **Yield:** 50%. **Mp:** 220-225˚C. **^{1}H NMR δ (ppm):** 9.08 (dd, *J* = 2.5, 0.7 Hz, 2H), 8.67 (dd, J = 8.4, 0.7 Hz, 2H), 8.29 (dd, J = 8.4, 2.5 Hz, 2H), 8.16 (dd, *J* = 1.9, 0.7 Hz, 4H), 7.53 (dd, *J* = 8.7, 1.9 Hz, 4H), 7.48 (dd, *J* = 8.6, 0.7 Hz, 4H), 1.49 (s, 36H). **^{13}C NMR δ (ppm):** 153.28, 147.70, 144.85, 138.88, 137.91, 134.80, 125.39, 124.47, 124.23, 116.76, 108.79, 34.86, 31.91. **HR ESI-MS: [M+H]$^+$:** calcd for $[C_{50}H_{54}N_4O_2SH]^+$: 775.4040, found 775.4033. **Elemental analysis:** Calcd for $C_{50}H_{54}N_4O_2S$: C, 77.48; H, 7.02; N, 7.23. Found: C, 77.37; H, 6.91; N, 7.29. **HPLC:** H_2O (5%) /MeCN, 1.0 mL min^{-1}, 300 nm; tr (99.4 %) = 1.6 min.

9-(5-bromopyridin-2-yl)-3,6-di-*tert*-butyl-9H-carbazole (PBr-TC)



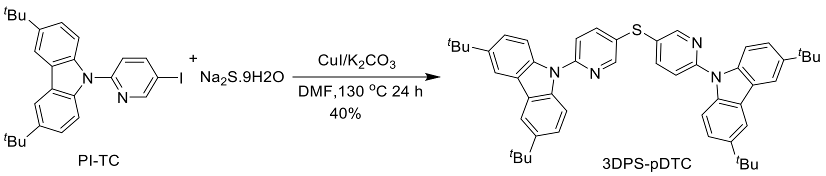
To a 250 mL flask were added 2-iodo-5-bromopyridine (1.4 g, 5 mmol, 1 equiv.), di-*tert*-butyl-9H-carbazole (1.4 g, 5 mmol, 1 equiv.), copper powder (320 mg, 5 mmol, 1 equiv.) and potassium carbonate (2.2 g, 15 mmol, 3 equiv.) were added. The flask was degassed by three cycles of vacuum-nitrogen purging and 20 mL of chlorobenzene was injected. The mixture was stirred at 110 ºC for 18 h under nitrogen atmosphere. After completion of reaction, water was added to the reaction mixture and extracted with DCM (3 x 50 mL). The combined organic layers were dried with anhydrous magnesium sulfate. The organic solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography. DCM/Hexane=1/3 was used as eluent to afford **PBr-TC** as a white solid. **PBr-TC: R$_f$** = 0.4 (20% DCM/Hexane). **Yield: 80%**. **Mp:** 185-188˚C. **^{1}H NMR δ (ppm):** 8.75 (dd, *J* = 2.6 Hz, 0.7 Hz, 1H), 8.12 (d, *J* = 1.9 Hz, 2H), 8.01 (dd, *J* = 8.6 Hz, 2.5 Hz, 1H), 7.80 (dd, *J* = 8.7 Hz, 0.6 Hz, 2H), 7.58 (dd, *J* = 8.6 Hz, 0.7 Hz, 1H), 7.52 (dd, *J* = 8.7 Hz, 2.0 Hz, 2H), 1.49 (s, 18H). **^{13}C NMR δ (ppm):** 150.88, 150.37, 144.30, 140.84, 137.54, 124.55, 124.06, 119.23, 116.21, 110.73, 34.79, 31.93. **HR TOF-MS: [M+H]$^+$:** calcd for [$C_{25}H_{28}BrN_2$]$^+$: 435.1436; found: 435.1433.

9-(5-iodopyridin-2-yl)-3,6-di-*tert*-butyl-9H-carbazole (PI-TC)



To a 100 mL flask were added **PBr-TC** (250 mg, 0.6 mmol, 0.6 equiv.), sodium iodide (150 mg, 1 mmol, 1 equiv.), *trans*-1,2-diaminocyclohexaneand (23 mg, 0.2 mmol, 0.2 equiv.), copper(I) iodide (20 mg, 0.1 mmol, 0.1 equiv.). The flask was degassed by three cycles of vacuum-nitrogen purging and 20 mL of 1,4-dioxane was injected. The reaction mixture was stirred at 110 °C for 18 h under a nitrogen atmosphere. After completion of reaction, water was slowly added to the reaction mixture and extracted with DCM (3 x 50 mL). The combined organic layers were dried with anhydrous magnesium sulfate and organic solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography. DCM/Hexane=1/3 was used as eluent to obtain **PI-TC** as a white solid. **PI-TC: R_f** = 0.5 (25% DCM/Hexane). **Yield: 80%**. **Mp:** 200-203˚C. **^{1}H NMR δ (ppm):** 8.89 (dd, *J* = 2.3 Hz, 0.7 Hz, 1H), 8.18 (dd, *J* = 8.5 Hz, 2.4 Hz, 1H), 8.12 (dd, *J* = 2.0 Hz, 0.6 Hz, 2H), 7.81 (dd, *J* = 8.7 Hz, 0.6 Hz, 2H), 7.55 - 7.47 (m, 3H), 1.48 (s, 18H). **^{13}C NMR δ (ppm):** 155.36, 150.37, 146.31, 144.33, 140.84, 137.54, 124.55, 124.06, 119.22, 116.21, 110.74, 34.79, 31.93. **HR ESI-MS: [M+H]$^+$:** calcd for [$C_{25}H_{28}IN_2$]$^+$: 483.1285; found: 483.1292.

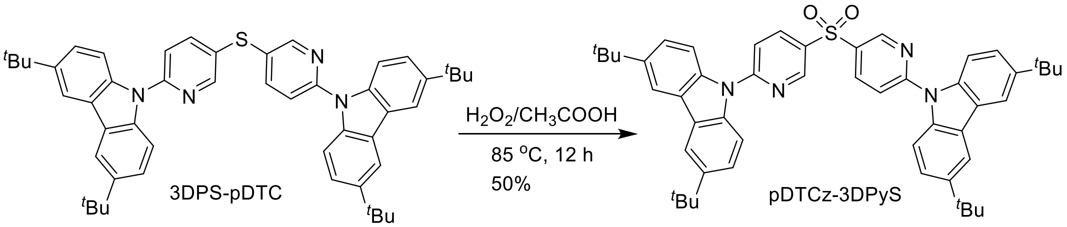
bis(6-(3,6-di-*tert*-butyl-9H-carbazol-9-yl)pyridin-3-yl)sulfone (3DPS-pDTC)



To a 100 mL three neck flask were added PI-TC (300 mg, 0.6 mmol, 2 equiv.), sodium sulfide (70 mg, 0.3 mmol, 1 equiv.), copper(I) iodide (15 mg, 0.05 mmol, 0.3 equiv.) and potassium carbonate

(80 mg, 0.7 mmol, 2.3 equiv.). The flask was degassed by three cycles of vacuum-nitrogen purging and 10 mL of DMF was injected. The mixture was stirred at 130 °C for 24 h under a nitrogen atmosphere. The reaction mixture poured into water and extracted with ethyl acetate (3×20 mL). The combined organic layers were dried with magnesium sulfate and organic solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography. DCM/Hexane=1/1 was used as eluent to afford **3DPS-pDTC** as white solid. 3DPS-pDTC**: R$_f$** = 0.6 (60% DCM/Hexane). **Yield: 40%**. **Mp:** 165-168˚C. **^{1}H NMR δ (ppm):** 8.78 (dd, *J* = 2.5 Hz, 0.7 Hz, 2H), 8.12 (dd, *J* = 2.0 Hz, 0.6 Hz, 4H), 7.96 (dd, *J* = 8.5 Hz, 2.5 Hz, 2H), 7.87 (dd, *J* = 8.7 Hz, 0.6 Hz, 4H), 7.69 (dd, *J* = 8.5 Hz, 0.8 Hz, 2H), 7.55 - 7.49 (m, 4H), 1.49 (s, 36H). **^{13}C NMR δ (ppm):** 151.71, 151.41, 144.41, 141.24, 137.59, 127.61, 124.68, 124.04, 118.34, 116.19, 111.05, 34.78, 31.91. **HR ESI-MS: [M+H]$^+$:** calcd for [$C_{50}H_{55}N_2S$]$^+$: 742.4040, found 742.4034.

9,9'-(sulfonylbis(pyridine-5,2-diyl))bis(3,6-di-tert-butyl-9H-carbazole) (pDTCz-3DPyS)



To **3DPS-pDTC** (70 mg, 0.1 mmol, 1 equiv.) in 2 mL of glacial acetic acid was added 2 mL of hydrogen peroxide solution (30 wt%, 200 equiv.). The reaction mixture was stirred at 50 °C for 12 h. The mixture was poured into 20 mL of ice water and extracted with dichloromethane (3×20 mL). The combined organic layer was dried with magnesium sulfate and dried with anhydrous magnesium sulfate and organic solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography. DCM/Hexane=1/1 was used as eluent to obtain **pDTCz-3DPyS** as a white solid.

pDTCz-3DPyS: R$_f$ = 0.3 (50% DCM/Hexane). **Yield: 50%**. **Mp:** 268-270 ˚C. **^{1}H NMR δ (ppm):** 9.30 (d, *J* = 2.5 Hz, 2H), 8.43 (dd, *J* = 8.7, 2.6 Hz, 2H), 8.10 (d, *J* = 2.0 Hz, 4H), 7.99 (d, *J* = 8.8 Hz, 4H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 4H), 1.48 (s, 36H). **^{13}C NMR δ (ppm):** 55.96, 149.10, 137.17, 131.11, 132.75, 125.47, 124.35, 116.75, 116.35, 111.85, 34.83, 31.84. **HR ESI-MS: [M+H]$^+$:** calcd for [$C_{50}H_{55}N_2O_2S$]$^+$: 775.4040, found 775.4034. **Elemental analysis:**

Calcd for $C_{50}H_{54}N_4O_2S$: C, 77.48; H, 7.02; N, 7.23. Found: C, 77.31; H, 7.05; N, 7.30. **HPLC:** 5% H_2O/MeCN, 1.0 mL min^{-1}, 300 nm; tr (98.2 %) = 6.1 min.

X-Ray Crystallography

X-ray quality crystals of **pDTCz-2DPyS** were grown by the slow diffusion of methanol into a solution of **pDTCz-2DPyS** in chlorobenzene. Diffraction data were collected at 173 K using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics with XtaLAB P200 diffractometer [Mo Kα radiation (λ = 0.71075 Å)]. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. Data were collected using CrystalClear,[6] and processed (including correction for Lorentz, polarization and absorption) using CrysAlisPro.[7] Structures were solved by direct methods (SIR2011)[8] and refined by full-matrix least-squares against F^2 (SHELXL-2018/3)[9]. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the CrystalStructure[10] interface. One of the chlorobenzene solvent molecules and one of the *t*-butyl groups were modelled as disordered over two sites. Crystal data: $C_{62}H_{64}Cl_2N_4O_2S$, $M = 1000.18$, monoclinic, $a = 14.8846(5)$, $b = 31.8944(10)$, $c = 11.5391(4)$ Å, $\beta = 97.384(3)$ °, $U = 5432.6(3)$ Å^3, $T = 173$ K, space group $P2_1/c$ (no. 14), $Z = 4$, 70537 reflections measured, 12471 unique ($R_{\text{int}} = 0.0685$), which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0623 and wR_2 (all data) was 0.1757. CCDC 1908262 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

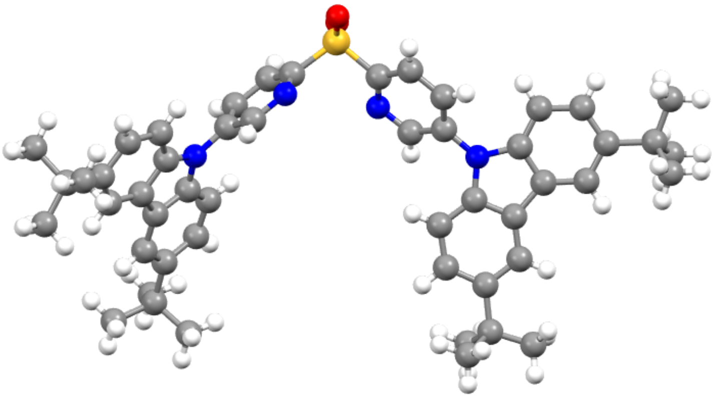


Fig. S1 Single crystal structure of pDTCz-2DPyS.

Photophysical Properties

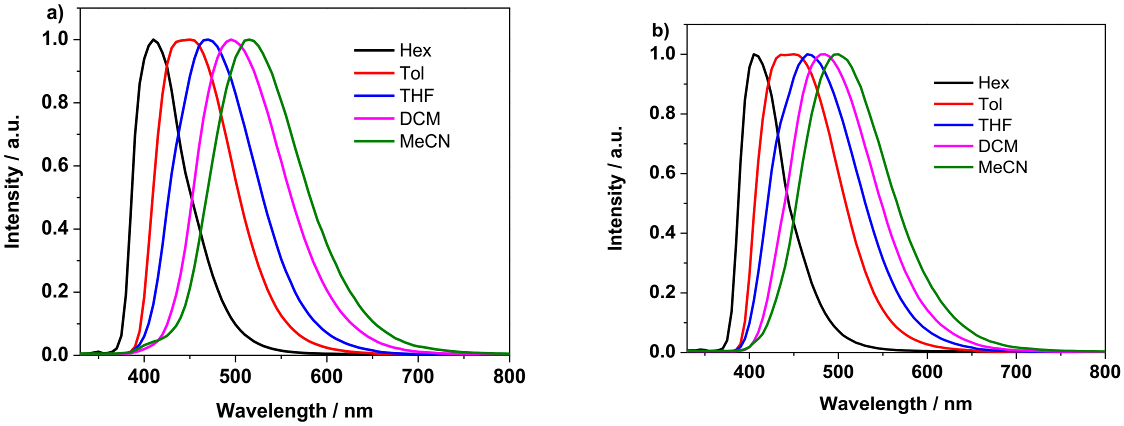


Fig. S2 Photoluminescence solvatochromic study for a) **pDTCz-2DPyS**, and b) **pDTCz-3DPyS**. λ_{exc} = 360 nm.

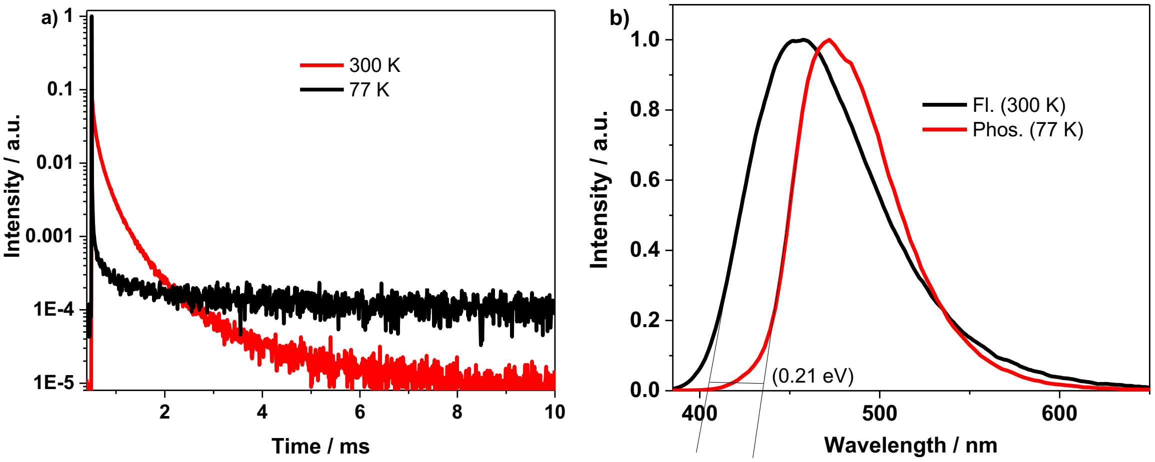


Fig. S3 a) Variable temperature time-resolved PL of 7 wt% doped thin films in DPEPO of **pDTCz-2DPyS**. λ_{exc} = 378 nm, b) Fluorescence (Fl.) phosphorescence (Phos.) spectra and of **pDTCz-2DPyS** in 7 wt% doped DPEPO film. λ_{exc} = 360 nm.

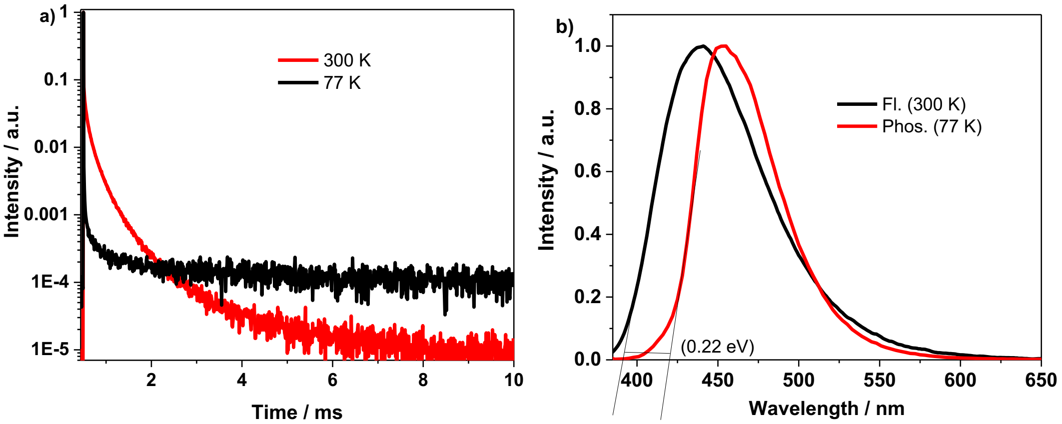


Fig. S4 a) Variable temperature time-resolved PL of 7 wt% doped thin films in DPEPO of **pDTCz-3DPyS**. λ_{exc} = 378 nm, b) Fluorescence (Fl.) phosphorescence (Phos.) spectra and of **pDTCz-3DPyS** in 7 wt% doped DPEPO film. λ_{exc} = 360 nm.

Device performance

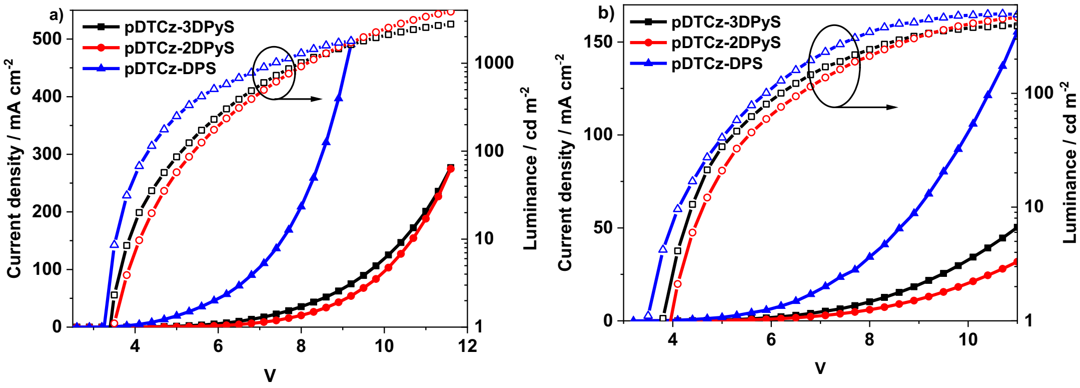


Fig. S5 Current density-voltage-brightness **pDTCz-2DPyS**, **pDTCz-3DPyS** and **pDTCz-DPS** a) in PPT host, b) in DPEPO host (arrow indicate the device luminance).

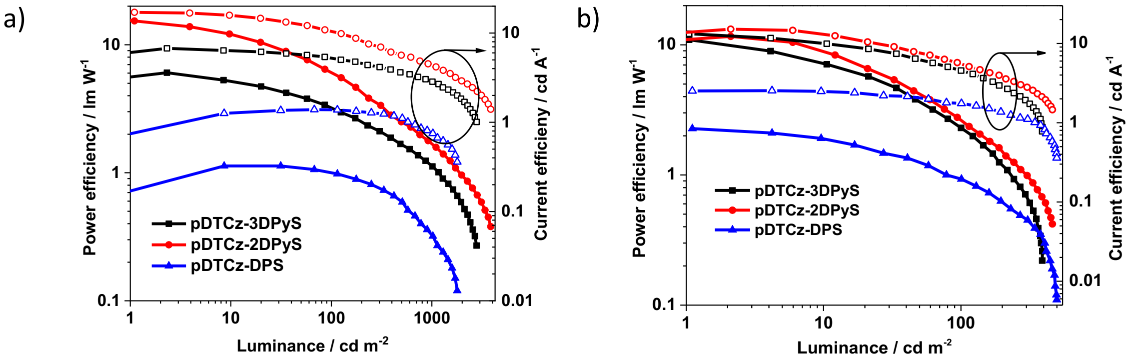


Fig. S6 Luminance vs current efficiency and power efficiency **pDTCz-2DPyS**, **pDTCz-3DPyS** and **pDTCz-DPS** a) in PPT host, b) DPEPO host (arrow indicate the device current efficiency).

^{1}H and ^{13}C NMR spectra for all compound

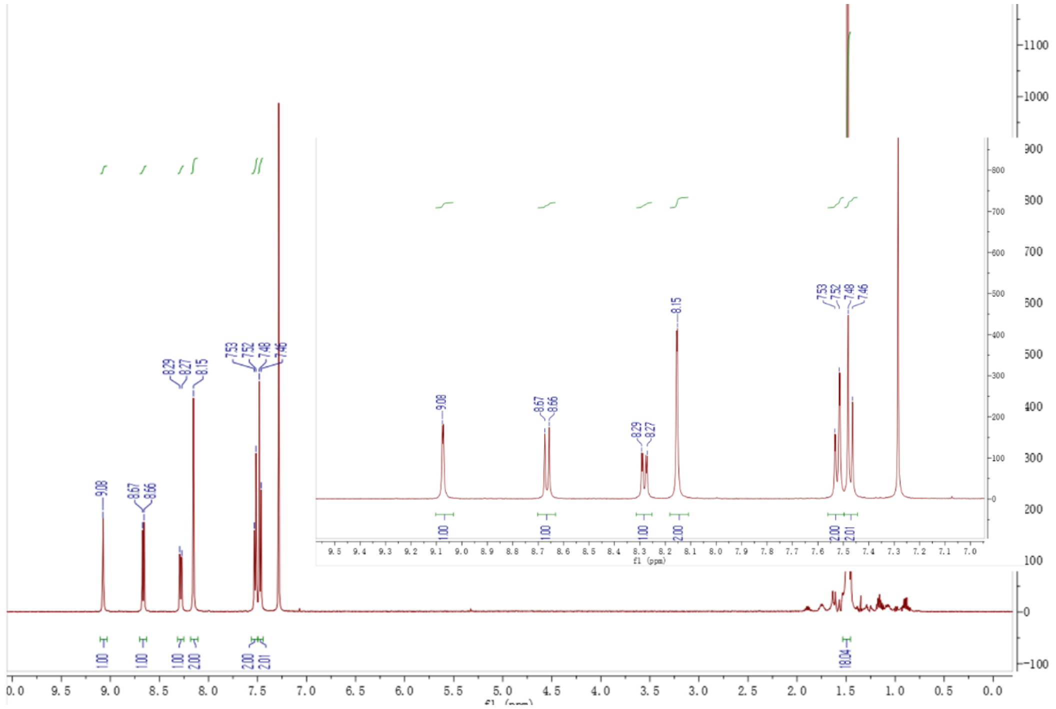


Fig. S7 ^{1}H NMR of **pDTCz-2DPyS**

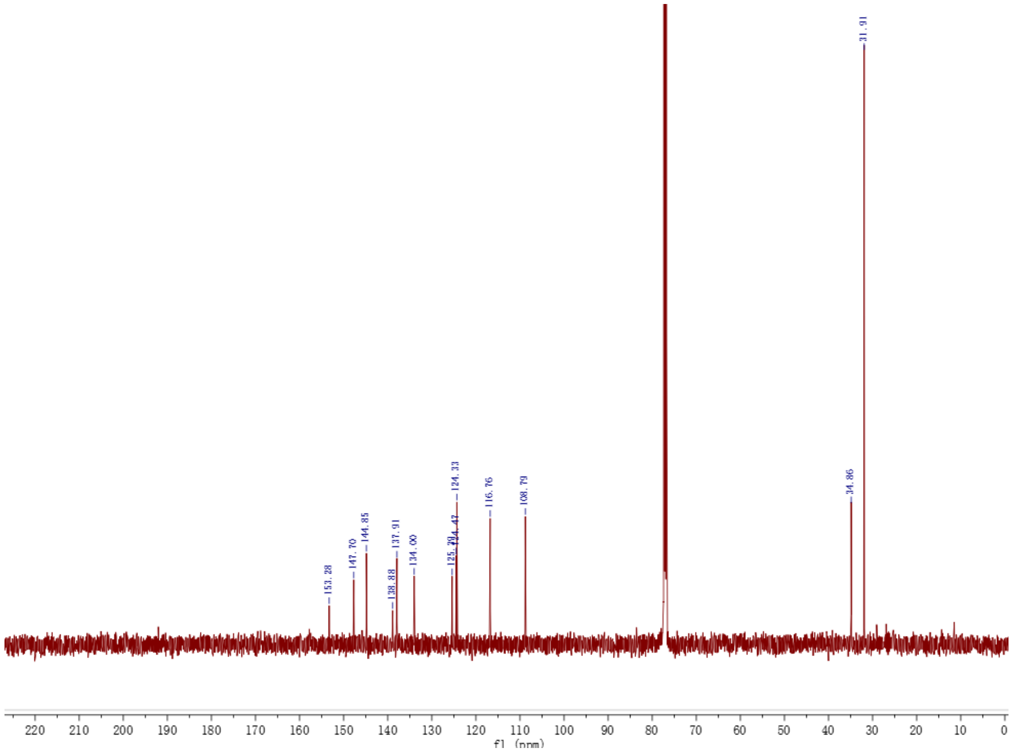


Fig. S8 ^{13}C NMR of **pDTCz-2DPyS**

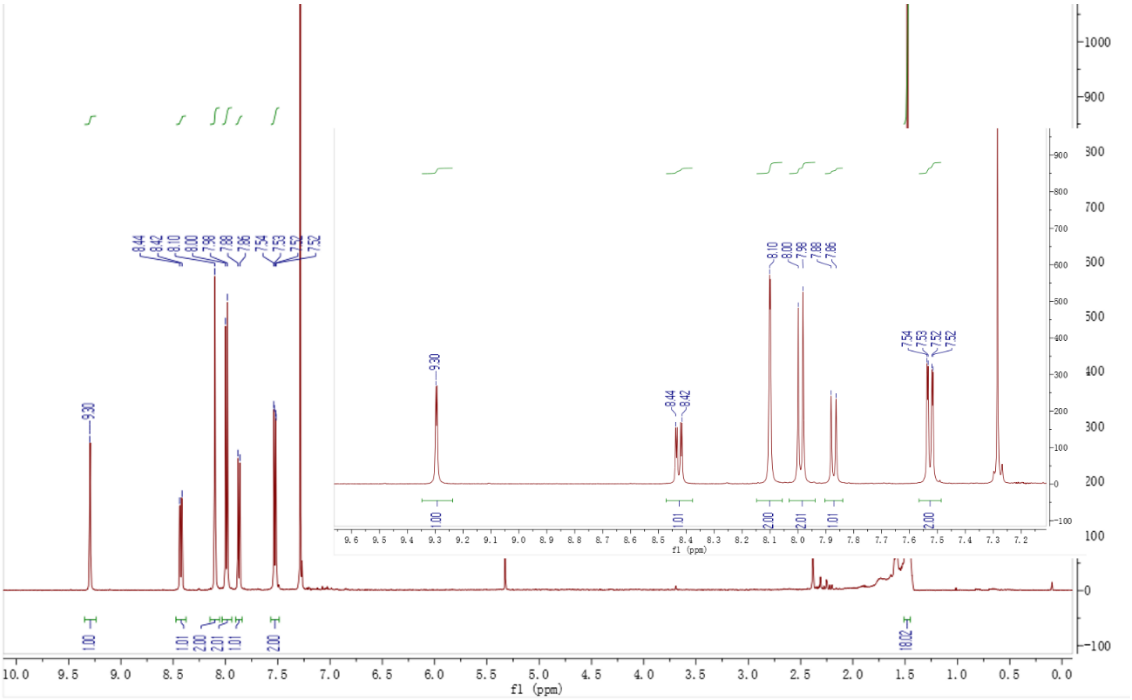


Fig. S9 ^{1}H NMR of **pDTCz-3DPyS**

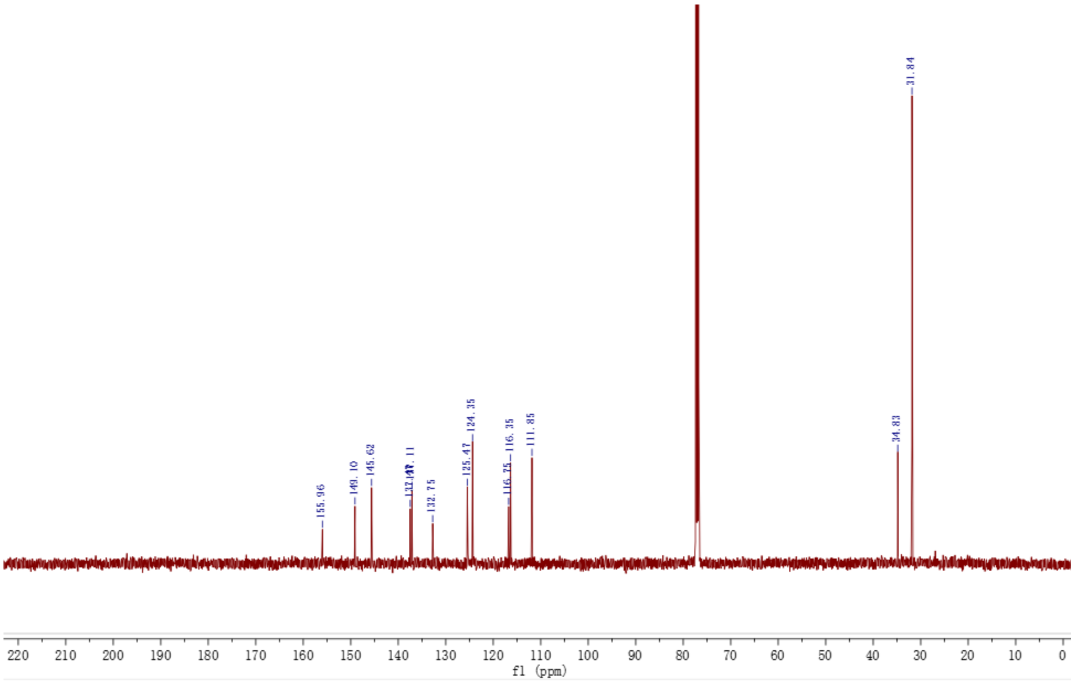


Fig. S10 ^{13}C NMR of **pDTCz-3DPyS**

HPLC Trace Report30May2018

<Sample Information>

Sample Name : 2PyS
Sample ID :
Method Filename : AcN (95).lcm
Batch Filename : ACN-95-350.lcb
Vial # : 1-73
Injection Volume : 5 uL
Date Acquired : 23/05/2018 20:57:40
Date Processed : 23/05/2018 21:27:43
Sample Type : Unknown
Acquired by : ezc-7
Processed by : ezc-7

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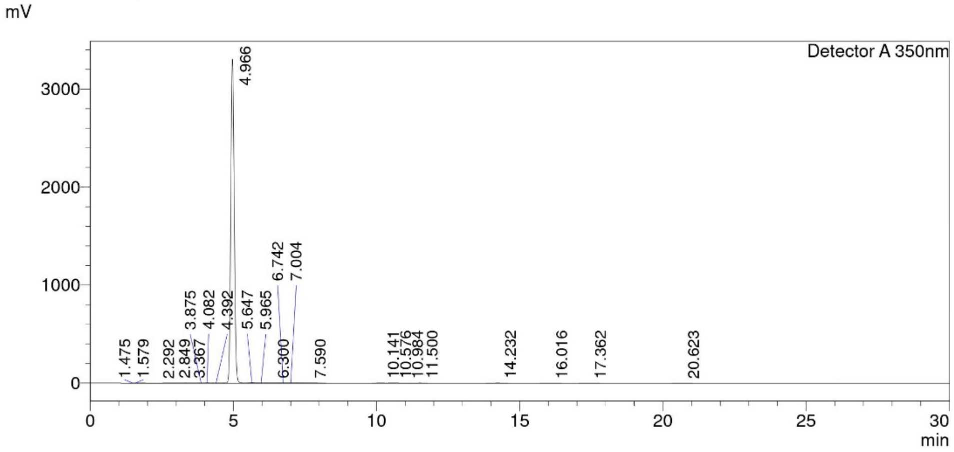


<Peak Table>

Detector A 350nm

Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	1.475	1771	658	0.006	2.693	0.132
2	1.579	17481	1370	0.063	12.761	--
3	2.292	1633	110	0.006	14.886	--
4	2.849	27078	771	0.098	35.107	--
5	3.367	10741	470	0.039	22.850	--
6	3.875	1638	300	0.006	5.470	--
7	4.082	41109	4902	0.148	8.387	--
8	4.392	11258	958	0.041	11.756	--
9	4.966	27478535	3301817	99.022	8.322	0.271
10	5.647	48734	5154	0.176	9.455	--
11	5.965	17151	1931	0.062	8.882	--
12	6.300	7738	846	0.028	9.142	0.290
13	6.742	2749	330	0.010	8.326	--
14	7.004	22471	2199	0.081	10.217	--
15	7.590	25297	1167	0.091	21.669	0.740
16	10.141	4248	251	0.015	16.918	--
17	10.576	13087	912	0.047	14.349	--
18	10.984	1417	97	0.005	14.572	--
19	11.500	3161	186	0.011	16.984	--
20	14.232	5646	295	0.020	19.147	0.717
21	16.016	1529	70	0.006	21.838	0.640
22	17.362	3054	163	0.011	18.692	0.612

Fig. S11 HPLC trace report of **pDTCz-2DPyS**

HPLC Trace Report30May2018

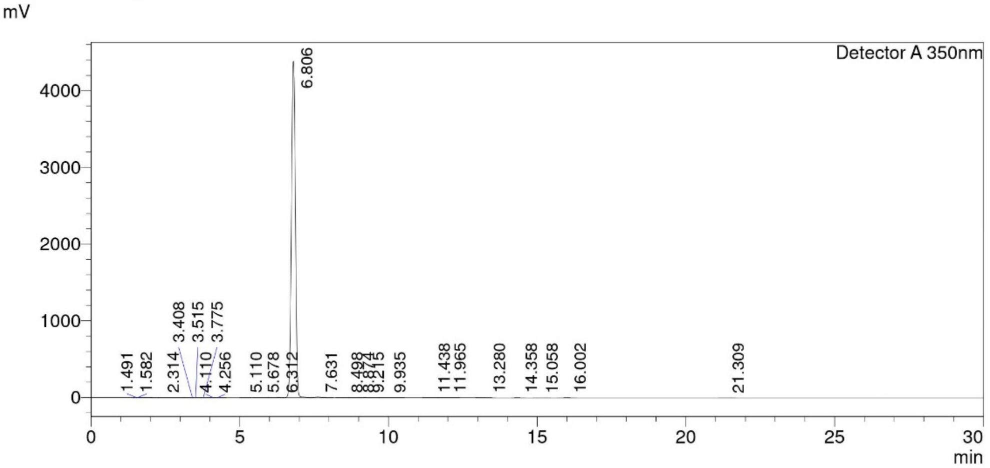
<Sample Information>

Sample Name : 3PyS
Sample ID :
Method Filename : AcN (95).lcm
Batch Filename : ACN-95-350.lcb
Vial # : 1-72
Injection Volume : 10 uL
Date Acquired : 23/05/2018 20:06:43
Date Processed : 23/05/2018 20:36:47

Sample Type : Unknown

Acquired by : ezc-7
Processed by : ezc-7

<Chromatogram>

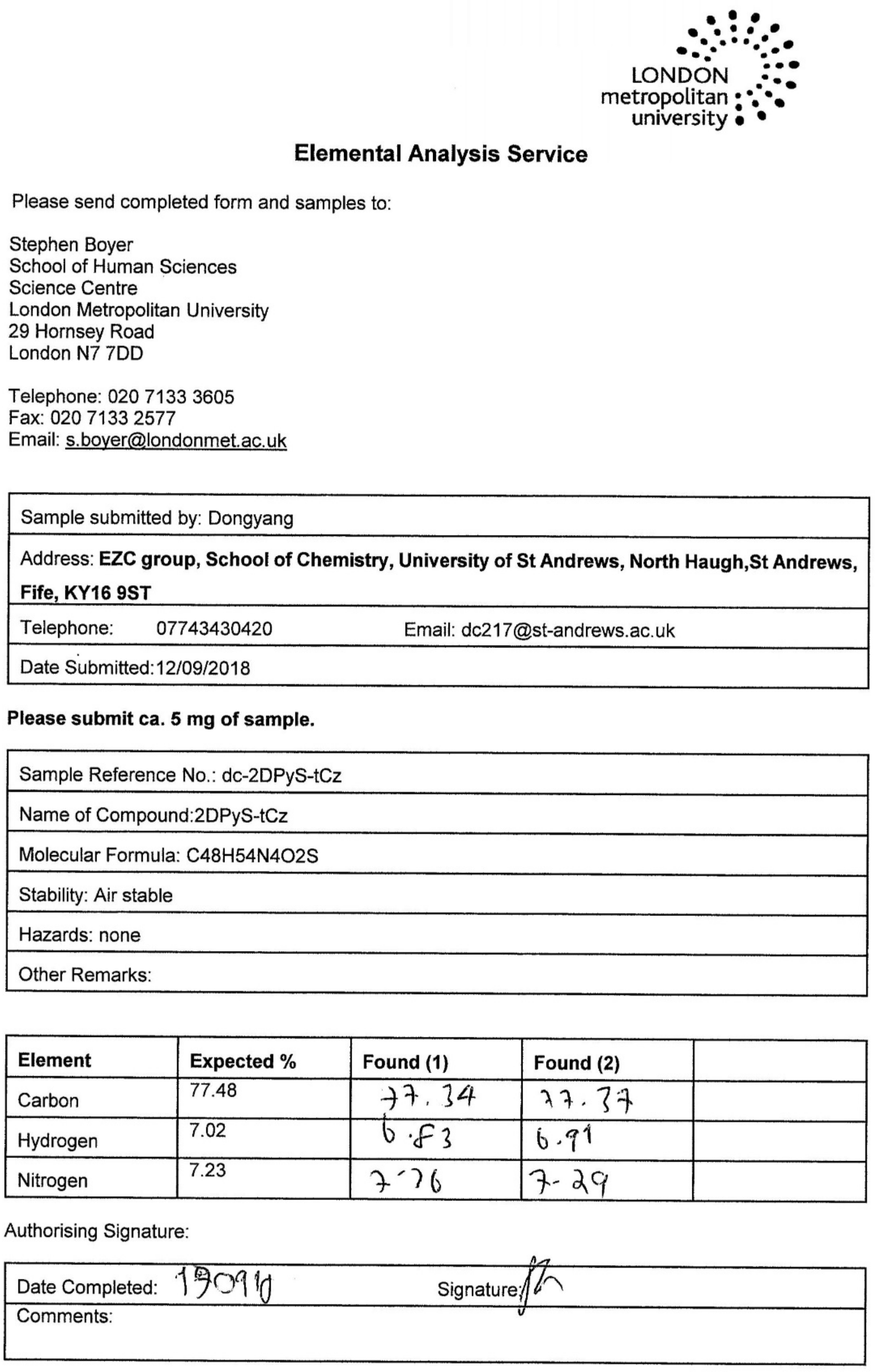


<Peak Table>

Detector A 350nm

Peak#	Ret. Time	Area	Height	Area%	Area/Height	Width at 5% Height
1	1.491	11408	5579	0.029	2.045	0.074
2	1.582	65401	3956	0.166	16.530	--
3	2.314	26912	761	0.068	35.377	--
4	3.408	2239	201	0.006	11.116	--
5	3.515	3528	250	0.009	14.093	--
6	3.775	3502	220	0.009	15.917	--
7	4.110	1570	194	0.004	8.101	--
8	4.256	4244	347	0.011	12.218	--
9	5.110	3777	514	0.010	7.346	0.311
10	5.678	14387	1512	0.036	9.513	0.391
11	6.312	31922	2883	0.081	11.072	--
12	6.806	38946211	4384056	98.806	8.884	0.286
13	7.631	162559	9513	0.412	17.088	--
14	8.498	12420	1108	0.032	11.208	--
15	8.874	13087	860	0.033	15.224	--
16	9.215	51141	3124	0.130	16.372	--
17	9.935	18667	922	0.047	20.253	0.716
18	11.438	6550	488	0.017	13.430	0.418
19	11.965	24207	1645	0.061	14.718	0.498
20	13.280	3803	221	0.010	17.171	0.562
21	14.358	1472	104	0.004	14.164	0.450
22	15.058	1197	57	0.003	21.154	0.569

Fig. S12 HPLC trace report of **pDTCz-3DPyS**



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Elemental Analysis Service

Please send completed form and samples to:

Stephen Boyer
School of Human Sciences
Science Centre
London Metropolitan University
29 Hornsey Road
London N7 7DD

Telephone: 020 7133 3605
Fax: 020 7133 2577
Email: s.boyer@londonmet.ac.uk

Sample submitted by: Dongyang
Address: **EZC group, School of Chemistry, University of St Andrews, North Haugh,St Andrews, Fife, KY16 9ST**
Telephone: 07743430420 Email: dc217@st-andrews.ac.uk
Date Submitted:12/09/2018

Please submit ca. 5 mg of sample.

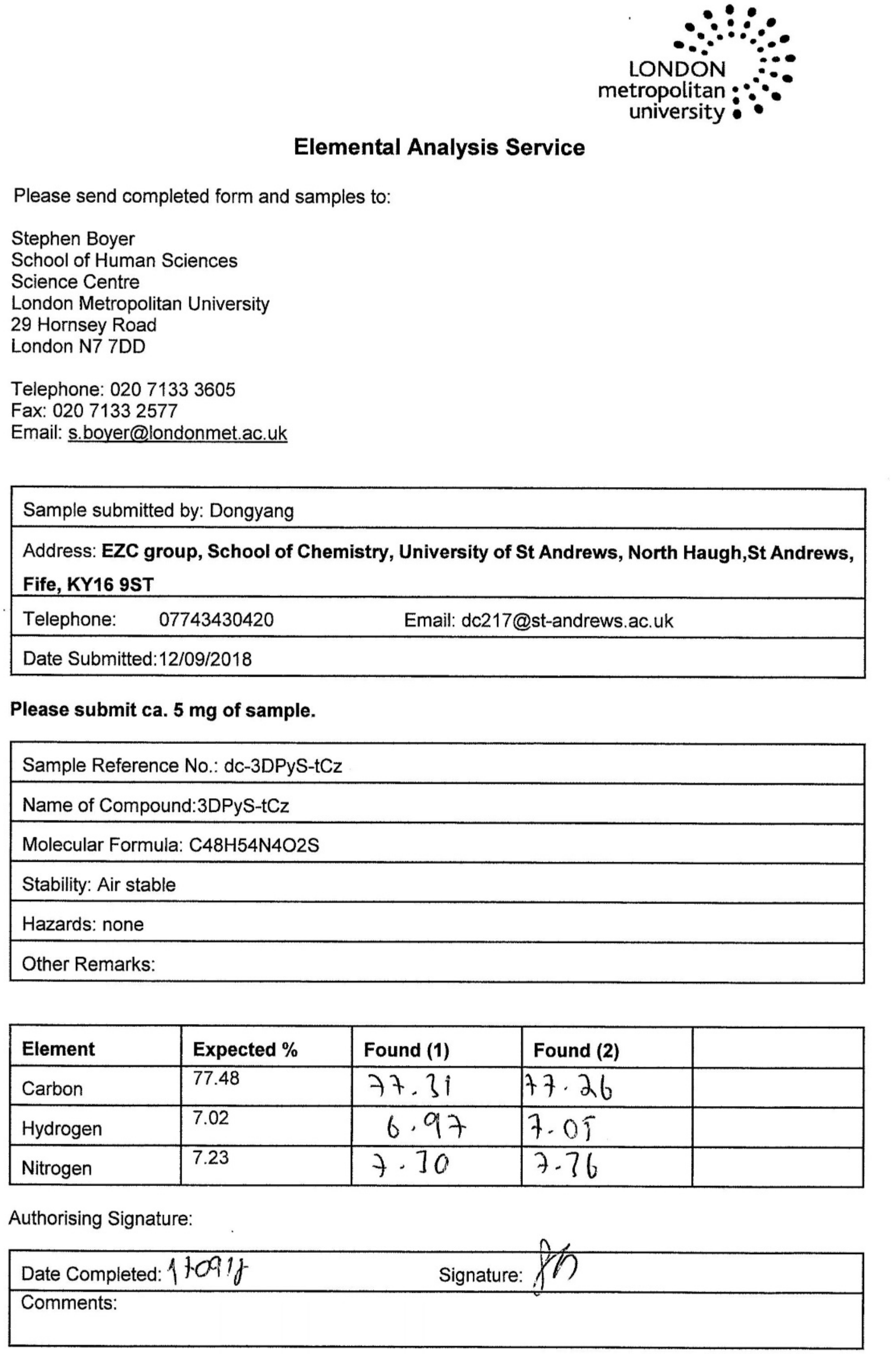
Sample Reference No.: dc-2DPyS-tCz
Name of Compound:2DPyS-tCz
Molecular Formula: C48H54N4O2S
Stability: Air stable
Hazards: none
Other Remarks:

Element	Expected %	Found (1)	Found (2)	
Carbon	77.48	77.34	77.77	
Hydrogen	7.02	6.83	6.91	
Nitrogen	7.23	7.76	7.29	

Authorising Signature:

Date Completed: 190918	Signature:
Comments:	

Fig. S13 Elemental analysis report of **pDTCz-2DPyS**



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Please send completed form and samples to:

Stephen Boyer
School of Human Sciences
Science Centre
London Metropolitan University
29 Hornsey Road
London N7 7DD

Telephone: 020 7133 3605
Fax: 020 7133 2577
Email: s.boyer@londonmet.ac.uk

Sample submitted by: Dongyang

Address: **EZC group, School of Chemistry, University of St Andrews, North Haugh,St Andrews, Fife, KY16 9ST**

Telephone: 07743430420 Email: dc217@st-andrews.ac.uk

Date Submitted:12/09/2018

Please submit ca. 5 mg of sample.

Sample Reference No.: dc-3DPyS-tCz

Name of Compound:3DPyS-tCz

Molecular Formula: C48H54N4O2S

Stability: Air stable

Hazards: none

Other Remarks:

Element	Expected %	Found (1)	Found (2)	
Carbon	77.48	77.31	77.26	
Hydrogen	7.02	6.97	7.05	
Nitrogen	7.23	7.70	7.76	

Authorising Signature:

Date Completed: 170918 Signature:

Comments:

Fig. S14 Elemental analysis report of **pDTCz-3DPyS**

Coordinates of the ground state optimized geometry of pDTCz-2DPyS

Atomic Type	X	Y	Z
C	1.38702100	0.13436000	-3.38742500
S	0.00001300	0.00044300	-4.52075600
C	-1.38679800	-0.13362000	-3.38718000
N	1.49857200	-0.84831000	-2.50560000
C	2.50774400	-0.78174400	-1.64788400
C	3.45380400	0.25439100	-1.66062600
C	3.31478300	1.26949400	-2.60925100
C	2.24329800	1.22091000	-3.49013100
N	-1.49809400	0.84880800	-2.50506400
C	-2.50713600	0.78208600	-1.64719700
C	-3.45331400	-0.25393100	-1.66009900
C	-3.31454500	-1.26879300	-2.60902200
C	-2.24320000	-1.22006500	-3.49005800
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O	0.07457900	-1.26828500	-5.24378400
N	4.49691400	0.26749900	-0.73152900
N	-4.49627800	-0.26714100	-0.73084800
C	5.31637500	-0.81664400	-0.40479500
C	6.23426700	-0.41123000	0.58727900
C	5.95610000	0.97853500	0.87594000
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C	-4.88240100	-1.36357800	0.04492700
C	-5.95616600	-0.97873300	0.87573800
C	-6.23425400	0.41111500	0.58738300
C	-5.31597000	0.81686000	-0.40419000
C	5.35898900	-2.09992900	-0.93504600
C	6.31352000	-2.97929100	-0.43331200
C	7.22822800	-2.61755900	0.56944900

C	7.17738400	-1.31408700	1.06727000
C	6.50652000	1.89650300	1.76435100
C	6.00191200	3.19602800	1.84468200
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C	4.34541400	2.64244000	0.11998100
C	-4.34502900	-2.64231300	0.12000900
C	-4.91939900	-3.53784800	1.01690000
C	-6.00207500	-3.19643000	1.84401500
C	-6.50677700	-1.89693300	1.76378900
C	-7.17763700	1.31377800	1.06721700
C	-7.22833900	2.61738900	0.56974500
C	-6.31322300	2.97945800	-0.43252200
C	-5.35842000	2.10029500	-0.93408900
C	8.27029400	-3.59265100	1.12037500
C	8.18373300	-4.97064100	0.46152500
C	9.67712400	-3.02942800	0.86953500
C	8.05252000	-3.76759700	2.63078400
C	6.62736800	4.18683200	2.82826900
C	5.96804400	5.56571000	2.76212800
C	6.47151000	3.64792900	4.25816300
C	8.11973700	4.35281600	2.50506100
C	-6.62768800	-4.18744900	2.82729200
C	-5.96838600	-5.56633400	2.76098600
C	-6.47200700	-3.64881200	4.25730900
C	-8.12001200	-4.35335700	2.50388100
C	-8.27065600	3.59228000	1.12054800
C	-8.18411000	4.97036500	0.46189800
C	-9.67736700	3.02894000	0.86932300
C	-8.05323100	3.76704700	2.63103100
H	2.57919600	-1.57112000	-0.90403700
H	4.04178300	2.07357100	-2.65229200

H	2.06377500	1.98349100	-4.23920600
H	-2.57836700	1.57122900	-0.90307900
H	-4.04162000	-2.07280100	-2.65214100
H	-2.06384600	-1.98245800	-4.23936500
H	4.68329900	-2.41599700	-1.72262500
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H	7.33118400	1.58893600	2.40146000
H	4.49999200	4.53566200	1.07058400
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H	-4.49981300	-4.53578000	1.07008500
H	-7.33170500	-1.58959200	2.40066600
H	-7.88023000	0.99144200	1.83083600
H	-6.34164900	3.98108100	-0.84547700
H	-4.68239200	2.41663000	-1.72127100
H	8.94366100	-5.63041300	0.89175400
H	7.20785700	-5.43938300	0.62525600
H	8.36497100	-4.91738500	-0.61689700
H	10.43748800	-3.71319400	1.26285100
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H	9.85722000	-2.89599300	-0.20169300
H	7.05632100	-4.17177000	2.83625200
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H	6.92080400	4.34053000	4.97849400
H	6.95928200	2.67623300	4.37943200
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H	8.58483000	5.05816500	3.20260600
H	8.65878000	3.40395600	2.58155400
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H	-6.06311700	-6.01411200	1.76625200
H	-4.90559800	-5.52174600	3.02019300
H	-6.92142900	-4.34152500	4.97745300
H	-6.95976100	-2.67711700	4.37866500
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H	-10.43788500	3.71256300	1.26258800
H	-9.81820000	2.05860400	1.35454600
H	-9.85723000	2.89565000	-0.20196200
H	-7.05713400	4.17134000	2.83676000
H	-8.79618300	4.45692900	3.04637900
H	-8.14407600	2.81664100	3.16519400

Coordinates of the ground state optimized geometry of pDTCz-3DPyS

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	2.87525600	2.09153500	1.31274200
C	3.46264800	1.53889100	0.15963300
N	3.07685300	1.86788200	-1.07691300
C	2.05982200	2.71058600	-1.21437400
C	1.37026900	3.24603700	-0.13183000
C	1.80346800	2.94787300	1.15949600
S	-0.01852200	4.31495200	-0.39177600
C	-1.40021600	3.20704000	-0.44279300
C	-1.83147900	2.67157000	-1.65575800
C	-2.89731600	1.79461200	-1.64572700
C	-3.48072000	1.46201800	-0.40926500
N	-3.09753700	2.01737600	0.74432700
C	-2.08632300	2.87801600	0.72130100
O	-0.16231500	5.13812800	0.80816800
O	0.12044800	4.89285600	-1.72782400
N	4.51566000	0.64064100	0.26239100
N	-4.52851300	0.55373900	-0.34386700
C	5.60250500	0.54682300	-0.62875700
C	6.53346400	-0.37260000	-0.10646400
C	5.98181900	-0.88849000	1.12674600
C	4.73756600	-0.25469100	1.32159100
C	-5.62311700	0.62682900	0.53847300
C	-6.55283400	-0.37111300	0.18297700
C	-5.99006600	-1.10534300	-0.92793400
C	-4.74504700	-0.51996300	-1.22184700
C	6.43031900	-1.84514000	2.02904600
C	5.64914200	-2.20381700	3.12988200
C	4.39728700	-1.58764200	3.27371600

C	3.92329000	-0.62498200	2.38604300
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C	8.01040400	0.03417900	-1.97579000
C	7.72349400	-0.62475500	-0.77919600
C	-5.89019400	1.50475800	1.58132500
C	-7.09918400	1.36236800	2.25566600
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C	-7.75178300	-0.49022500	0.87732100
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C	-4.38345800	-2.18713500	-2.88744600
C	-3.91630000	-1.08082600	-2.19187700
C	6.17000300	-3.24889600	4.11684100
C	5.18017800	-3.52017800	5.25106800
C	6.42496400	-4.56959000	3.37506400
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C	-6.12702800	-3.58634700	-4.95713100
C	-5.07900400	-5.12424200	-3.27596100
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C	-9.36943300	0.22865300	2.68224100
C	-9.51641400	1.25236200	3.80925800
C	-10.53476400	0.42329100	1.70081400
C	-9.44918100	-1.17634200	3.29776100
H	3.28718000	1.88429400	2.29202900
H	1.77874600	2.98367000	-2.22870400

H	1.32728200	3.41887900	2.01373600
H	-1.35818400	2.97946100	-2.58281500
H	-3.30831800	1.40640800	-2.56881300
H	-1.80740300	3.33711700	1.66677200
H	7.39363600	-2.31884600	1.86118400
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H	-2.92255600	-0.69800300	-2.39205300
H	5.59945400	-4.26634000	5.93319000
H	4.97497900	-2.61697400	5.83481600
H	4.22969500	-3.91318700	4.87566400
H	6.79954300	-5.32953800	4.06970000
H	7.16599900	-4.45130400	2.57907400
H	5.50302100	-4.94493100	2.92018100
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H	7.88179900	-3.48959800	5.43734500
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H	10.42383800	0.30625200	-4.47021200
H	8.67307000	0.32929500	-4.70473300
H	9.46833800	1.62782300	-3.79072000
H	11.45303200	-0.13493500	-2.28359800
H	10.47724300	-0.50600000	-0.85597100
H	10.48994200	1.13764600	-1.50722400

H	8.54288100	-2.02095300	-3.72784000
H	10.31163200	-1.98828600	-3.58406000
H	9.31292800	-2.38978800	-2.17989000
H	-6.43849100	-4.44152900	-5.56698400
H	-6.83727800	-2.77023200	-5.12276800
H	-5.14856300	-3.25691800	-5.31898800
H	-5.38166500	-5.99822600	-3.86308600
H	-5.02707000	-5.41940600	-2.22338500
H	-4.07126200	-4.84237900	-3.59466300
H	-8.23519600	-3.71027100	-3.20661700
H	-7.74392300	-5.33884400	-3.68443800
H	-7.49135600	-4.80321300	-2.02031900
H	-10.47515900	1.10433000	4.31611500
H	-8.72570600	1.14665000	4.55917800
H	-9.49769900	2.27931700	3.43022000
H	-11.49344700	0.31610400	2.22033900
H	-10.50848400	-0.31252000	0.89169000
H	-10.49936100	1.41922400	1.24838100
H	-8.62450500	-1.34141100	3.99810900
H	-10.39197700	-1.30133400	3.84187700
H	-9.39938000	-1.95689900	2.53293600

References

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