Supporting Information

1,4-Bis(trifluoromethyl)benzene as a New Acceptor for the Design and Synthesis of Emitters Exhibiting Blue Thermally Activated Delayed Fluorescence

Levani Skhirtladze[1], Karolis Lietonas[1], Audrius Bucinskas[1], Dmytro Volyniuk[1], Malek Mahmoudi[1], Omar Mukbaniani[2], Kai Lin Woon***[3], Azhar Ariffin**[1,4], Juozas V. Grazulevicius[1]*

[1]Department of Polymer Chemistry and Technology, Faculty of Chemical Technology Kaunas University of Technology, Lithuania
[2]Department of Chemistry, Faculty of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia.
[3]Low Dimensional Material Research Centre, Department of Physics, University Malaya, Kuala Lumpur, Malaysia
[4]Department of Chemistry, Faculty of Science, University Malaya, Kuala Lumpur, Malaysia

***Corresponding author**

Juozas V. Grazulevivius: Department of Polymer Chemistry and Technology, Faculty of Chemical Technology Kaunas University of Technology, Lithuania, Email: juozas.grazulevicius@ktu.lt

Kai Lin Woon: Low Dimensional Material Research Centre, Department of Physics, University Malaya, Kuala Lumpur, Malaysia, Email: ph7klw76@um.edu.my

Azhar Ariffin: Department of Chemistry, Faculty of Science, University Malaya, Kuala Lumpur, Malaysia, Email: azhar70@um.edu.my

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1. Instrumentations

^{1}H NMR and ^{13}C NMR spectra were obtained of the solutions in deuterated chloroform ($CDCl_3$-d6) with a 400 MHz Bruker Avance III spectrometer. The data are given as chemical shifts in δ (ppm) and tetramethylsilane was used as internal standard. Mass spectra were obtained on a Waters ZQ 2000 mass spectrometer using ES+ ionization method. Cyclic voltammetry (CV) measurements were carried out using Autolab Potentiate PGSTAT20 in a three-electrode cell using the platinum rod as a counter electrode, glassy carbon as the working electrode and $Ag/AgNO_3$ as the reference electrode. The experiments were carried out in dry dichloromethane solution containing 0.1 M tetrabutylammonium perchlorate as an electrolyte at room temperature under argon atmosphere at a scan rate of 50 mV/s. The measurements were calibrated using the internal standard ferrocene/ferrocenium (Fc/Fc+). Steady-state photophysical characterization was performed by using the samples prepared by spin-coating from 1 mg/ml toluene solution on quartz substrates. Ultraviolet-visible (UV-vis) spectra were measured by a Perkin Elmer Lambda 35 while photoluminescence spectra were recorded by Edinburgh Instruments FLS980 spectrometer. The samples were excited by the Xenon lamp at 330 nm. Time-resolved luminescence spectroscopy measurements were

performed by utilizing a PicoQuant LDH-D-C-375 laser (wavelength 374 nm) as the excitation source. Phosphorescence spectra were taken at 77 K using Edinburgh Instruments μF2 microsecond lamp as an excitation source with a set delay of 1 ms.

The single crystals for X-ray diffraction analysis of target compounds **2AC-2CF3Ph, 2PO-2CF3Ph** and **2PS-2CF3Ph** were obtained by slow evaporation technique using THF solutions. The yellow crystal was mounted on the glass stick using glue. The crystallographic analysis was performed employing XtaLAB mini diffractometer (Rigaku) with graphite monochromated Mo Kα (λ = 0.71075 Å) X-ray source. The measurements were performed at room temperature.

The experimental procedures and instrumentations are presented in the supporting information.

The crystallographic data for 2AC-2CF3Ph, 2PO-2CF3Ph and 2PS-2CF3Ph structures reported in this paper have been deposited in Cambridge Crystallographic Data Centre with respective CCDC no (2108557, 2101143 and 2108558). The copies of data can be obtained free of charge on application to CCDC. (The Cambridge Structural Database (CSD)- The Cambridge Crystallographic Data Centre (CCDC), (http://www.ccdc. cam.ac.uk/solutions/csd-system/components/csd/). Calculations and visualization of the structures (Fig. 1) were performed using the OLEX2 [1], crystallographic software package except for refinement, which was performed using SHELXL [2]. For 2PS-2CF3Ph molecule solvent mask procedure was used. Anisotropic thermal parameters were assigned to all nonhydrogen atoms. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically.

The ionization potentials of solid samples were estimated by using electron photoemission spectrometry in air. To get samples for the measurements of ionization potential the spin-

coating onto fluorine doped tin oxide coated glass slides as substrates was used. ASBN-D130-CM deep UV deuterium light source, CM110 1/ 8m monochromator and 6517B Keithley electrometer were used for recording photoelectron emission spectra.

The studied OLEDs were fabricated by step-by-step vacuum deposition of organic and metal layers onto pre-cleaned ITO coated glass substrates under vacuum higher than 2×10^{-6} mBar (Figure S1). ITO-coated glass substrates with a sheet resistance of 15 Ω/sq were pre-patterned getting seven independent devices with area 6 mm^2. Substrate surface were cleaned by sonicating 10 minutes in pure acetone following by 10 minutes in isopropyl alcohol (IPA) and dried by nitrogen gun. Afterwards substrates had 15 minutes UV Ozone treatment. Density-voltage and luminance-voltage characteristics were recorded utilizing certificated photodiode PH100-Si-HA-D0 together with the PC-Based Power and Energy Monitor 11S-LINK (from STANDA) and Keithley 2400C source meter. Electroluminescence (EL) spectra were taken by the Avantes AvaSpec-2048XL spectrometer. Device efficiencies were calculated using the luminance, current density, and EL spectra.

Computation

Density functional theory (DFT) using range-separated hybrid functional LC-ωPBEh was used to obtain the ground state molecular geometry. ω was tuned using the golden ratio algorithm under polarizable continuum model (PCM) with a dielectric constant of 2.38 corresponding to toluene and solvent radius of 3.48Å. The calculation was performed using Terachem 1.93 software [3] and a Graphic Processing Unit server that had 64 GB RAM installed to support eight Tesla K10 graphic cards. Vertical excited states were obtained using Time dependent-DFT/ LC-ωPBEh//cc-pVDZ at optimal ω under the same PCM model. For excited quantum molecular dynamics simulations, the initial temperature was set at 550 K with equilibrium temperature of 300 K using Langevin as a thermostat. Langevin was chosen to simulate the

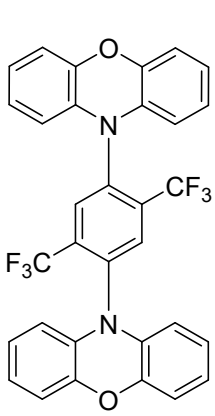
effect of jostling of solvents. The QMDs were carried out with 1 femtosecond (fs) time step with 10000 steps. The solvent radius was set to be 3.48 Å and dielectric constant of 2.38, the typical values for a toluene. Time-reversible integrator with dissipation was also implemented. The results were visualized using VMD software.

Chemicals

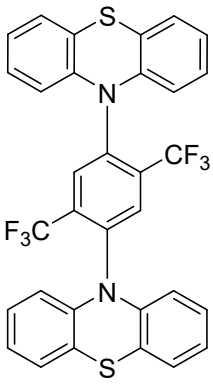
Unless specifically stated otherwise, all the reactions were performed under an argon atmosphere. Starting reagents necessary for the synthesis were purchased from Fluorochem or Sigma-Aldrich and used as received. Organic solvents were dried either by refluxing with calcium hydride or sodium benzophenone ketyl and distilled under inert atmosphere. 1,4-dibromo-2,5-bis(trifluoromethyl) (**2**) was synthesized according to the reported procedure [4].

2. General procedure for the synthesis of target derivatives

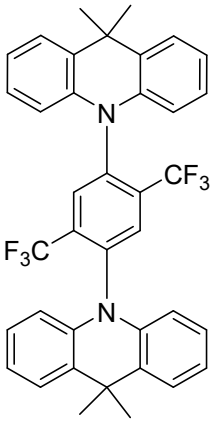
A mixture of **2** (1.0 equiv.), secondary aromatic amine, **3** (2.2 equiv.), tris(dibenzylideneacetone)dipalladium(0) ($(Pd_2(dba)_3$, 0.05 equiv.), X-Phos (0.07 equiv.), sodium-*tert*-butoxide (*t*-BuONa, 2.2 equiv.) and dry toluene (5 ml) were added into a two-neck round bottom flask under argon atmosphere. The reaction mixture was refluxed for 24 hours. After cooling, the reaction mixture was diluted with DCM and the organic phase was washed with water and brine. After being dried over anhydrous Na_2SO_4 and filtered, the solvent was removed, and the crude product was purified by column chromatography using hexane/DCM as eluent.



2PO-2CF$_3$Ph



2PS-2CF$_3$Ph



2AC-2CF$_3$Ph

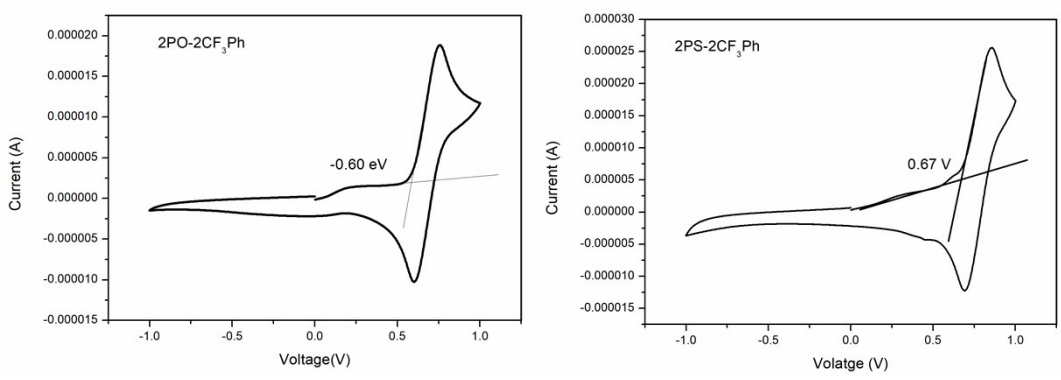
10,10'-(2,5-bis(trifluoromethyl)-1,4-phenylene)bis(10H-phenoxazine), (**2PO-2CF$_3$Ph**) was prepared by the general procedure using 1,4-dibromo-2,5-bis(trifluoromethyl) (**2**, 0.50 g, 1.34 mmol), 10*H*-phenoxazine (0.54 g, 2.95 mmol), $Pd_2(dba)_3$ (0.06 g, 0.07 mmol), X-Phos (0.04 g, 0.09 mmol), *t*-BuONa (0.28 g, 2.96 mmol) and 5 ml of dry toluene. The crude product was washed with ethyl acetate. The target compound was obtained as yellow powder and was further purified by recrystallisation using slow evaporation technique using a mixture of different solvents. Yield: 56 % (0.43 g). Mp = 385.53 ºC. Single crystal x-ray crystallography was obtained to confirm the structure. (Figure 1). $C_{32}H_{18}F_6N_2O_2$, calculated m/z: 576.13, observed 576.01.

10,10'-(2,5-bis(trifluoromethyl)-1,4-phenylene)bis(10H-phenothiazine) (**2PS-2CF$_3$Ph**) was prepared by the general procedure using compound **2** (0.50 g, 1.34 mmol), 10*H*-phenothiazine (0.59 g, 2.96 mmol), $Pd_2(dba)_3$ (0.06 g, 0.07 mmol), X-Phos (0.04 g, 0.09 mmol), *t*-BuONa (0.28 g, 2.96 mmol) and 5 ml of dry toluene. The crude product was purified by column chromatography using hexane/DCM (3/2) as an eluent. The target compound was obtained as yellow powder. Yield: 45 % (0.40 g). Mp = 321.09 ºC; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.15 (s, 2H), 7.07 (dd, *J* = 7.5, 1.3 Hz, 4H), 6.97 – 6.79 (m, 8H), 6.02 (d, *J* = 7.9 Hz,

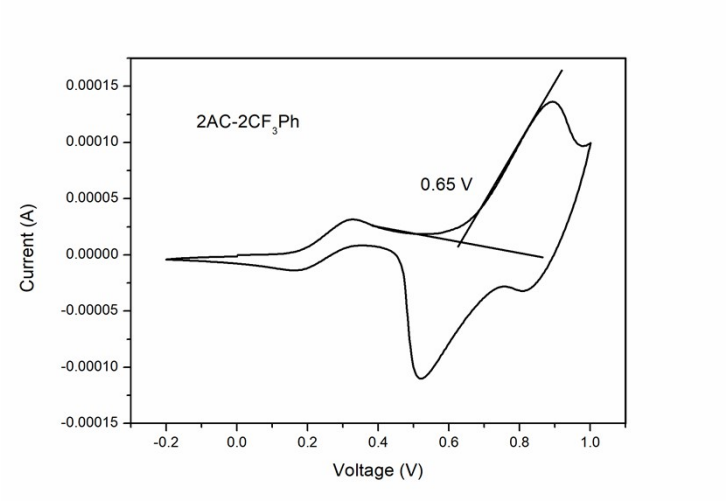
4H). ^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): 154.8, 151.8, 143.4, 139.6, 136.7, 127.4, 127.1, 123.6, 121.0, 115.1. $C_{32}H_{18}F_6N_2S_2$, calculated *m/z*: 608.08, observed: 608.60.

10,10'-(2,5-bis(trifluoromethyl)-1,4-phenylene)bis(9,9-dimethyl-9,10-dihydroacridine) (**2AC-2CF3Ph**) was prepared by general procedure using compound **2** (0.50 g, 1.34 mmol), 9,10-dihydro-9,9-dimethylacridine (0.62 g, 2.96 mmol), $Pd_2(dba)_3$ (0.06 g, 0.07 mmol), X-Phos (0.04 g, 0.09 mmol), *t*-BuONa (0.28 g, 2.96 mmol) and 5 ml of dry toluene. The crude product was purified by column chromatography using hexane/DCM (3/2) as an eluent. The target compound was obtained as yellow powder. Yield: 45 % (0.4 g). Mp = 311.01 ºC; ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.99 (s, 2H), 7.49 (d, *J* = 7.6 Hz, 4H), 7.06 (t, *J* = 7.6 Hz, 4H), 6.99 (t, *J* = 7.4 Hz, 4H), 6.06 (d, *J* = 8.0 Hz, 4H), 1.90 (s, 6H, CH_3), 1.41 (s, 6H, CH_3).^{13}C NMR (101 MHz, $CDCl_3$), δ (ppm): 140.6, 135.7, 130.5, 126.7, 125.5, 121.9, 113.6, 36.1, 34.5, 27.4. $C38H_{30}F6N_2$, calculated *m/z*: 628.23, observed: 628.38.

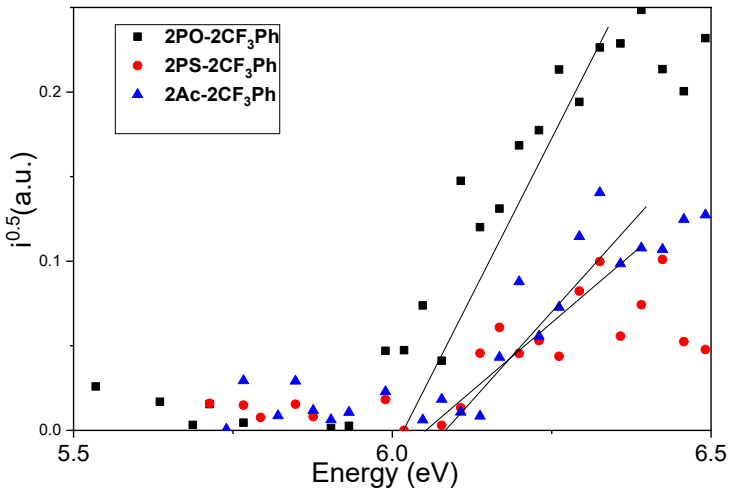
3. Cyclic voltammograms and photoelectron emission spectra of 2PO-2CF3Ph, 2PS-2CF3Ph and 2AC-2CF3Ph



a) b)



c)



d)

Figure S1: CV curves (a-c) and photoelectron emission spectra (d) of 2PO-2CF_3Ph, 2PS-2CF_3 Ph, and 2AC-2CF_3Ph

4. Computational simulation data

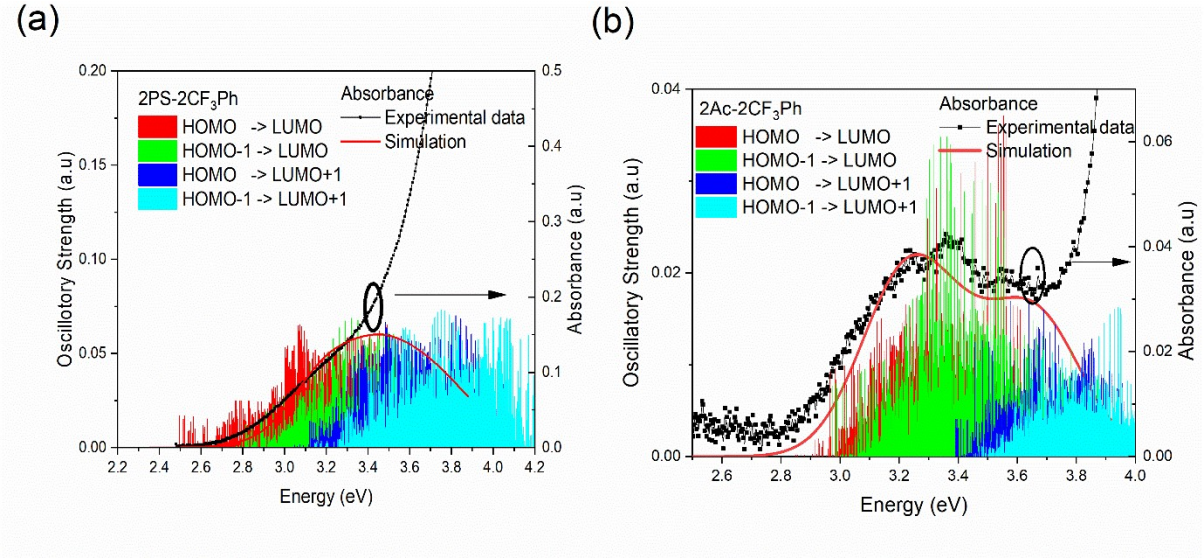


Figure S2: the quantum molecular dynamics simulations of vertical excitation of the 4 lowest excited states for (a) 2PS-2CF$_3$Ph and (b) 2Ac-2CF$_3$Ph along with their oscillatory strengths and simulated absorption curve by applying gaussian broadening

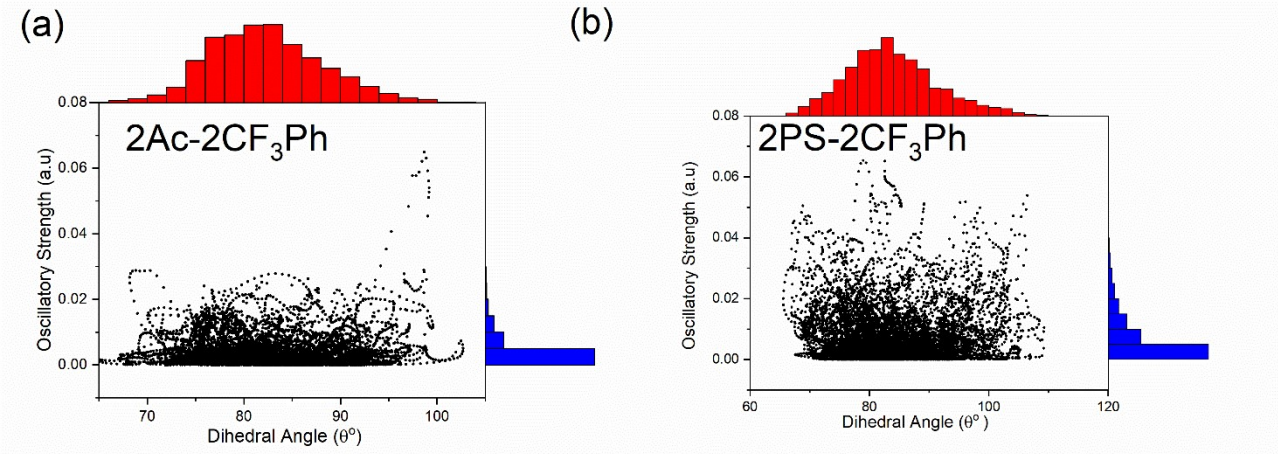
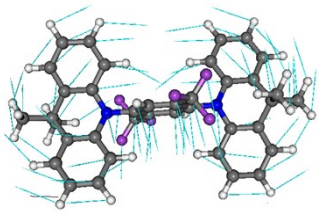
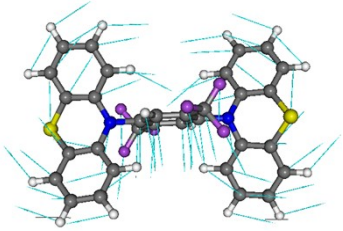
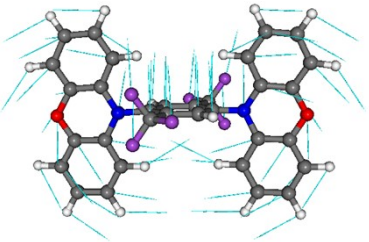


Figure S3: Dihedral angle between donor and acceptor and their respective oscillatory strengths with the top histogram corresponding to the distribution of dihedral angle and the right axis histogram correspond to the distribution of oscillatory strength for (a) 2Ac-2CF$_3$Ph (b) 2PS-2CF¬3¬Ph

	2Ac-2CF$_3$Ph	**2PS-2CF3Ph**	**2PO-2CF$_3$Ph**
	 **18.6 cm^{-1}**	 **15.2 cm^{-1}**	 7.2 **cm^{-1}**

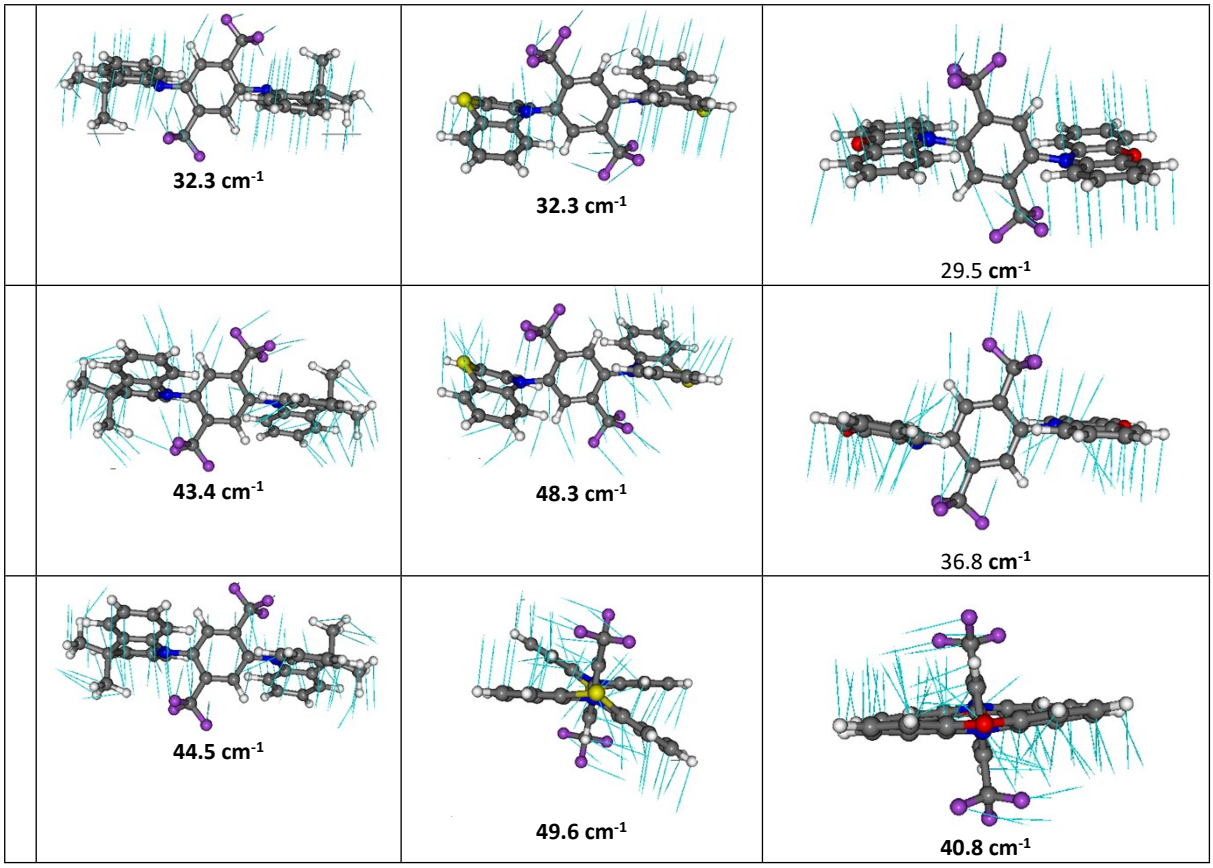
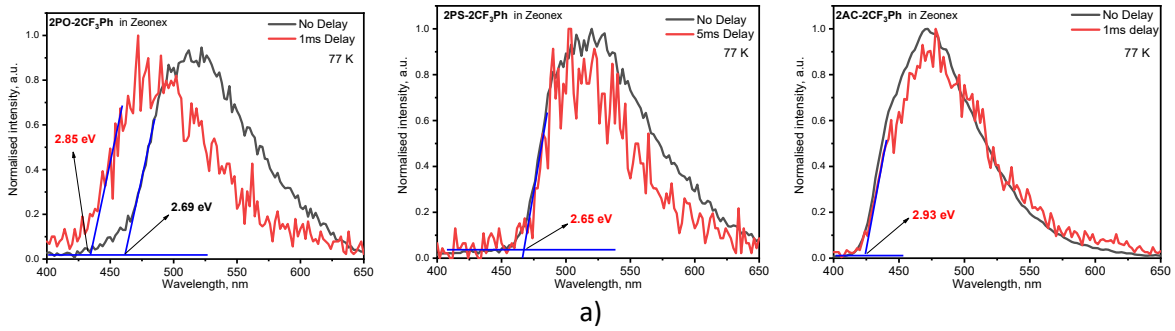


Figure S4: The 4th lowest vibrational frequency of the three molecules

5. Prompt and delay decay curve analyses



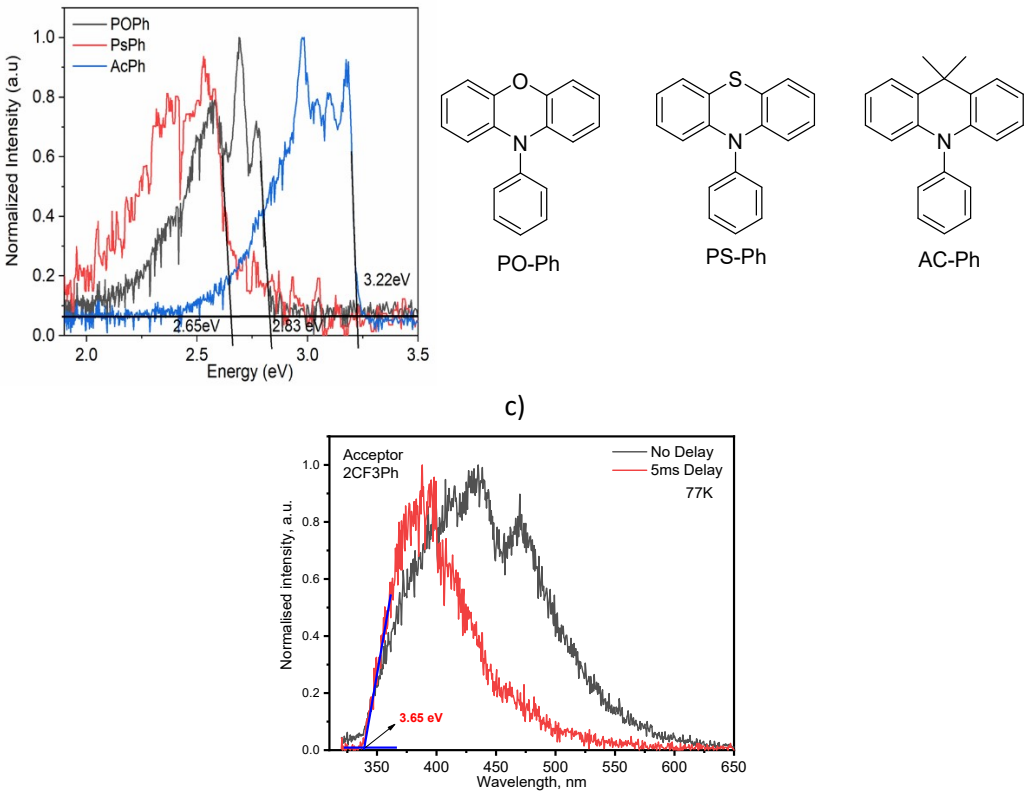


Figure S5: The low-temperature PL and phosphorescence spectra of the matrix of **2PO-2CF$_3$Ph[1 wt.%], 2PS-2CF$_3$Ph[1 wt.%], 2AC-2CF$_3$Ph[1 wt.%]** in Zeonex (a). The low-temperature PL and phosphorescence spectra of MeTHF solutions (10^{-5} M) of **2PO-2CF$_3$Ph, 2PS-2CF$_3$Ph, 2AC-2CF$_3$Ph** (b). The phosphorescence spectra of the solid solutions (10^{-5} M) of PO-Ph, PS-Ph, AC-Ph (together with their molecular structures) in THF at 77K (c). The phosphorescence spectra of **2CF$_3$Ph** (d). The corresponding onsets of emission at 77K are given in eV. The onset wavelengths (λ) were taken from the corresponding spectra (as it schematically shown by the blue lines). The energies were calculated using the empiric formula E=1240/λ [eV].

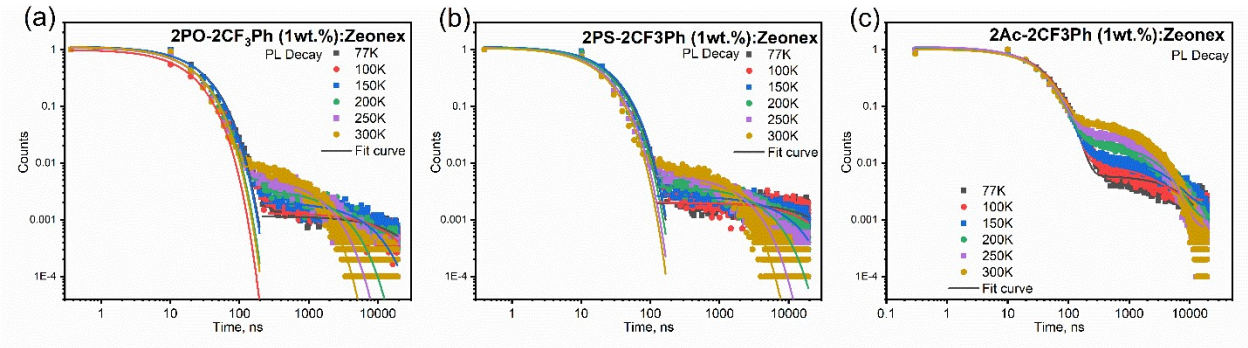


Figure S6: PL decay of the matrix of (a) **2PO-2CF$_3$Ph[1 wt.%]** (b) **2PS-2CF$_3$Ph[1 wt.%]** (c) **2AC-2CF$_3$Ph[1 wt.%]** in Zeonex at different temperatures and the corresponding exponential fit curves at each temperature.

Table S1: Data of PL decay exponential fit curves of **2PO-2CF$_3$Ph[1 wt.%]** in Zeonex at different temperatures and calculated values of fluorescence kinetics.

T, K	300	250	200	150	100	77
A_1	1.12	1.10	1.09	1.13	0.99	1.12
τ_1, ns	21.46	21.53	22.37	25.83	19.04	26.76
A_2	0.01	0.01	0.00	0.00	0.00	0.00
τ_2, ns	925.83	1568.44	2794.29	7500.69	16627.27	24179.45
I_{PL}	597893	792245	892771	600526	470799	372905
$I_{300K}/I_{\#K}$	1.00	0.75	0.67	1.00	1.27	1.60
PLQY adjusted %	4.64	6.15	6.93	4.66	3.66	2.90
Area	33.3	32.5	34	44.5	40.9	57.8
Area PF	24.06	23.67	24.35	29.22	18.94	29.99
Area DF	9.22	8.83	9.64	15.30	21.95	27.81
PF %	72.29	72.83	71.64	65.63	46.33	51.89
DF %	27.71	27.17	28.36	34.37	53.67	48.11
DF/PF ratio	0.38	0.37	0.40	0.52	1.16	0.93
ΦPF, %	3.36	4.48	4.97	3.06	1.69	1.50
ΦDF, %	1.29	1.67	1.97	1.60	1.96	1.39
kPF, s^{-1}	1.56E+06	2.08E+06	2.22E+06	1.19E+06	8.90E+05	5.62E+05
kDF, s^{-1}	1.39E+04	1.07E+04	7.04E+03	2.14E+03	1.18E+03	5.76E+02
kISC, s^{-1}	4.33E+05	5.66E+05	6.30E+05	4.07E+05	4.78E+05	2.70E+05
kRISC, s^{-1}	1.92E+04	1.46E+04	9.82E+03	3.26E+03	2.55E+03	1.11E+03
ΦISC	0.97	0.96	0.95	0.97	0.98	0.98
ΦRISC	0.29	0.28	0.30	0.35	0.55	0.49
τPFrad, ns	639.10	480.30	450.30	843.70	1124.00	1780.40
τPFnrad, ns	22.20	22.50	23.50	26.60	19.40	27.20
kPFrad, s^{-1}	1.56E+06	2.08E+06	2.22E+06	1.19E+06	8.90E+05	5.62E+05
kPFnrad, s^{-1}	4.50E+07	4.44E+07	4.25E+07	3.75E+07	5.16E+07	3.68E+07
kTnrad, s^{-1}	4.78E+04	3.68E+04	2.31E+04	5.93E+03	2.12E+03	1.16E+03

Table S2: Data of PL decay exponential fit curves of **2PS-2CF$_3$Ph[1 wt.%]** in Zeonex at different temperatures and calculated values of fluorescence kinetics.

T, K	300	250	200	150	100	77
A_1	1.08	1.08	1.11	1.12	1.12	1.09
τ_1, ns	18.16	19.67	21.94	24.23	24.30	23.79
A_2	0.01	0.01	0.00	0.00	0.00	0.00
τ_2, ns	1406.37	2302.01	4654.99	10693.29	23822.02	33204.94
I_{PL}	671900	719387	705600	544949	522738	425275
$I_{300K}/I_{\#K}$	1.00	0.93	0.95	1.23	1.29	1.58

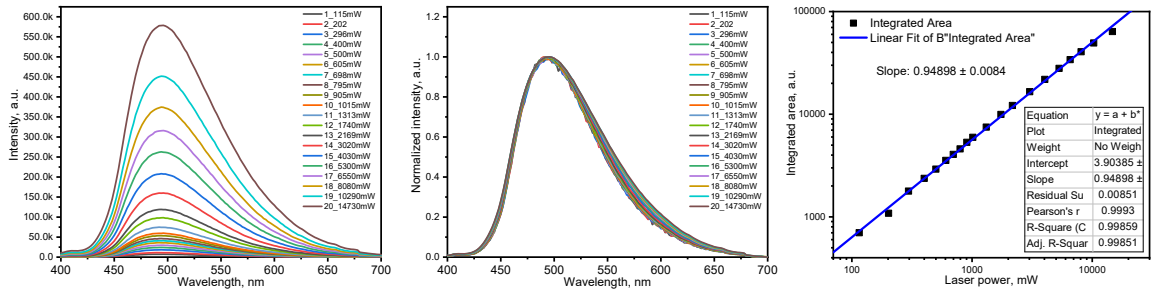
PLQY adjusted	5.24	5.61	5.50	4.25	4.07	3.32
Area	91.7	75	55.4	42.4	35.5	32.4
Area PF	25.87	27.10	27.19	24.26	21.24	19.54
Area DF	65.87	47.92	28.18	18.12	14.24	12.90
PF %	28.20	36.13	49.11	57.24	59.87	60.23
DF %	71.80	63.87	50.89	42.76	40.13	39.77
DF/PF ratio	2.55	1.77	1.04	0.75	0.67	0.66
ΦPF, %	3.15	3.36	3.15	2.09	1.47	0.93
ΦDF, %	2.08	2.25	2.35	2.16	2.60	2.38
kPF, s^{-1}	1.74E+06	1.71E+06	1.43E+06	8.61E+05	6.06E+05	3.93E+05
kDF, s^{-1}	1.48E+04	9.78E+03	5.05E+03	2.02E+03	1.09E+03	7.17E+02
kISC, s^{-1}	6.91E+05	6.85E+05	6.14E+05	4.38E+05	3.87E+05	2.82E+05
kRISC, s^{-1}	2.46E+04	1.63E+04	8.83E+03	4.12E+03	3.02E+03	2.54E+03
ΦISC	0.97	0.97	0.97	0.98	0.99	0.99
ΦRISC	0.41	0.42	0.44	0.52	0.65	0.72
τPFrad, ns	575.50	585.80	696.90	1161.20	1650.50	2545.20
τPFnrad, ns	18.70	20.30	22.70	24.70	24.70	24.00
kPFrad, s^{-1}	1.74E+06	1.71E+06	1.43E+06	8.61E+05	6.06E+05	3.93E+05
kPFnrad, s^{-1}	5.33E+07	4.91E+07	4.41E+07	4.04E+07	4.06E+07	4.16E+07
kTnrad, s^{-1}	3.53E+04	2.30E+04	1.12E+04	3.80E+03	1.64E+03	9.65E+02

Table S3: Data of PL decay exponential fit curves of **2Ac-2CF$_3$Ph[1 wt.%]** in Zeonex at different temperatures and calculated values of fluorescence kinetics.

T, K	**300**	**250**	**200**	**150**	**100**	**77**
A_1	0.97	1.08	1.08	1.06	1.07	1.07
τ_1, ns	35.40	33.31	34.38	36.47	38.53	39.81
A_2	0.05	0.03	0.02	0.01	0.01	0.01
τ_2, ns	2560.14	2782.56	3864.05	6747.25	9510.85	9477.75
I_{PL}	607348	515701	482359	451700	461080	451700
$I_{300K}/I_{\#K}$	1.00	1.18	1.26	1.34	1.32	1.34
PLQY adjusted	38.49	32.68	30.57	28.63	29.22	28.63
Area	158	128	120	117	109	99.6
Area PF	34.20	35.98	37.07	38.66	41.17	42.48
Area DF	124.05	92.07	82.62	77.92	67.71	57.15
PF %	21.61	28.10	30.97	33.16	37.81	42.64
DF %	78.39	71.90	69.03	66.84	62.19	57.36
DF/PF ratio	3.63	2.56	2.23	2.02	1.64	1.35
ΦPF, %	8.32	9.18	9.47	9.49	11.05	12.20
ΦDF, %	30.17	23.50	21.10	19.13	18.17	16.42

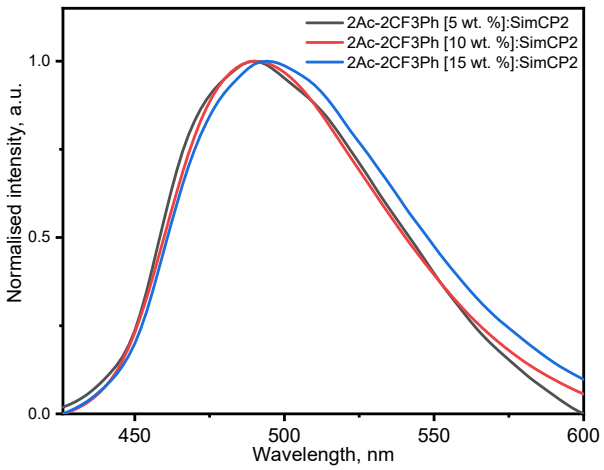
kPF, s^{-1}	2.35E+06	2.76E+06	2.75E+06	2.60E+06	2.87E+06	3.07E+06
kDF, s^{-1}	1.18E+05	8.44E+04	5.46E+04	2.84E+04	1.91E+04	1.73E+04
kISC, s^{-1}	1.84E+06	1.98E+06	1.90E+06	1.74E+06	1.78E+06	1.76E+06
kRISC, s^{-1}	5.45E+05	3.01E+05	1.76E+05	8.55E+04	5.05E+04	4.06E+04
ΦISC	0.92	0.91	0.91	0.91	0.89	0.88
ΦRISC	0.86	0.79	0.76	0.74	0.70	0.65
τPFrad, ns	425.60	362.70	363.10	384.20	348.70	326.20
τPFnrad, ns	38.60	36.70	38.00	40.30	43.30	45.30
kPFrad, s^{-1}	2.35E+06	2.76E+06	2.75E+06	2.60E+06	2.87E+06	3.07E+06
kPFnrad, s^{-1}	2.59E+07	2.73E+07	2.63E+07	2.48E+07	2.31E+07	2.21E+07
kTnrad, s^{-1}	9.25E+04	7.91E+04	5.49E+04	3.03E+04	2.17E+04	2.16E+04

6. The laser energy dependence of the delayed emission for 2Ac-2CF_3Ph in SimCP2.



a) b) c)

Figure S7: Non-normalized (a) and normalized (b) PL spectra recorded with the delay of 1 μs after excitation under vacuum and at the different optical excitation powers and the corresponding the laser energy dependence of the integrated area the delayed emission band (c) for **2Ac-2CF_3Ph[10 wt.%]** in **SimCP2**.



a)

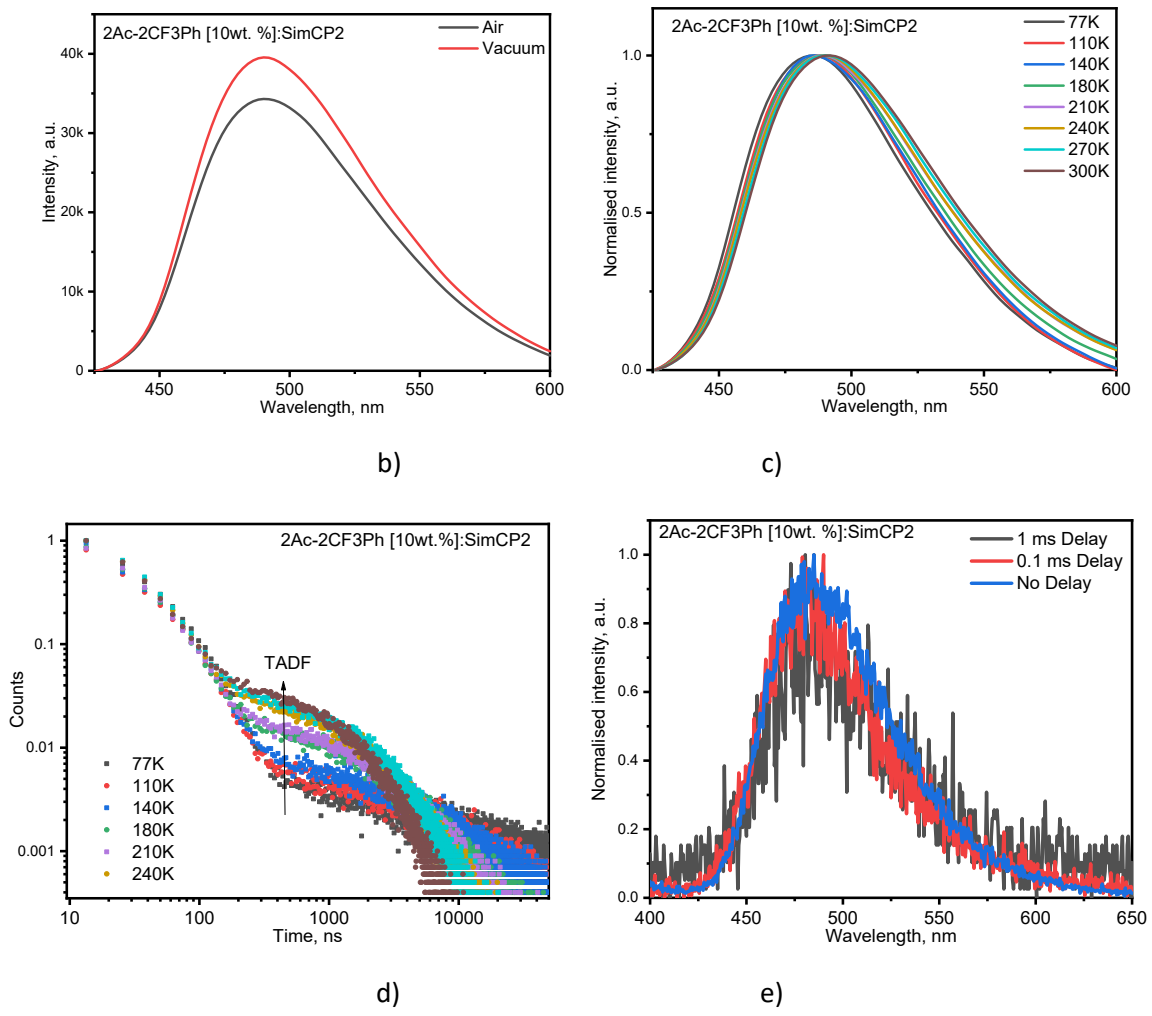


Figure S8. PL spectra of the films of the molecular mixtures of **2AC-2CF$_3$Ph** and **SimCP2** containing 5**,** 10 and 15 wt. % of **2AC-2CF$_3$Ph.** (a)**;** PL spectra of the film of 10 wt. % molecular dispersion of **2AC-2CF$_3$Ph** in **SimCP2** recorded in air and in vacuum (b); the low-temperature and room-temperature PL spectra (c) and PL decay curves (d) of the films of 10 wt. % molecular dispersion of **2AC-2CF$_3$Ph** in **SimCP2** recorded at 77K. PL spectra of th**e** film 10 wt. % molecular dispersion of **2AC-2CF$_3$Ph** in **SimCP2** recorded at the different delay time after excitation (e).

7. Optimized Molecular structure data for 2PO-2CF$_3$Ph using wPBEh

Optimized Molecular structure for **2PO-2CF$_3$Ph** using wPBEh functional at cc-pvdz with w of 0.04938

C	3.6611552450	0.7162790913	0.1460287947
C	3.6601822868	-0.6692938859	0.2658194205
C	2.4569041004	-1.3673732893	0.1433820900
C	1.2719666011	-0.6859533822	-0.0978742988
C	1.2586672760	0.7139779912	-0.2186275250
C	2.4681423187	1.4021656395	-0.0935750681
O	0.1337888160	-1.4447413484	-0.2251519308
C	-1.0689983821	-0.7864372030	-0.3103643068
C	-1.1530663502	0.6103673997	-0.4385115422
N	0.0359829548	1.3679142150	-0.4770678980
C	-2.2157853109	-1.5678566052	-0.2807920333

C	-3.4761935608	-0.9755682948	-0.3843502046
C	-3.5731638273	0.4056090951	-0.5153452332
C	-2.4191351796	1.1921524910	-0.5415942944
C	-0.0418374250	2.7765980740	-0.2889109108
C	-0.1859105289	3.2953957609	0.9990672899
C	-0.2656062201	4.6704909554	1.2132124078
C	-0.1997770885	5.5496154456	0.1226056104
C	-0.0549317181	5.0309067389	-1.1653235767
C	0.0245739299	3.6557692002	-1.3794483475
C	0.1783964401	3.1235481417	-2.7854092911
C	-0.4184519397	5.2026724615	2.6193010787
N	-0.2769562941	6.9582529664	0.3111929841
C	-1.4993245009	7.6126610828	0.0523188113
C	-1.5124915969	9.0127767773	-0.0660364644
O	-0.3743134212	9.7711152657	0.0638792996
C	0.8285016049	9.1123174734	0.1454489602
C	0.9123779114	7.7153273318	0.2715657439
C	-2.7088128388	6.9247938721	-0.0742759415
C	-3.9015783827	7.6111099871	-0.3137428112
C	-3.9004218280	8.9968365977	-0.4315683682
C	-2.6971525391	9.6946519531	-0.3075039594
C	1.9755544768	9.8933289476	0.1150318294
C	3.2359276862	9.3004386855	0.2160223001
C	3.3326072038	7.9190953935	0.3453557009
C	2.1783522182	7.1329458898	0.3722475511
F	0.6061771037	6.0012616631	2.9601088692
F	-1.5508794342	5.9105571145	2.7607598485
F	-0.4594182110	4.2017077101	3.5183042769
F	0.2203995044	4.1244815652	-3.6843812682
F	1.3106749264	2.4152986627	-2.9260055261
F	-0.8462250500	2.3252550770	-3.1270227083
H	4.5922608330	1.2801470188	0.2349559007
H	4.5877909088	-1.2141146503	0.4529068251
H	2.4109757651	-2.4548253522	0.2317920105
H	2.4783749198	2.4882273773	-0.1993776206
H	-2.0944254496	-2.6480263715	-0.1759636707
H	-4.3726629250	-1.5986011051	-0.3627901757
H	-4.5493995735	0.8874634340	-0.6024202707
H	-2.5021184263	2.2739978981	-0.6582087226
H	-0.2358633039	2.6077259725	1.8442868341
H	-0.0054069654	5.7186423528	-2.0105338125
H	-2.7192265952	5.8385474886	0.0296863157
H	-4.8326792941	7.0474740008	-0.4041074730
H	-4.8278925747	9.5419308208	-0.6185632015
H	-2.6511490746	10.7822305722	-0.3942845348
H	1.8544528648	10.9736885769	0.0118496595
H	4.1326053356	9.9231495144	0.1939327596
H	4.3088056853	7.4368308127	0.4305793787
H	2.2611351207	6.0509513380	0.4875601715

8. Optimized Molecular structure data for 2PS-2CF_3Ph using wPBEh

Optimized Molecular structure for **2PS-2CF_3Ph** using wPBEh functional at cc-pvdz with w of 0.04938

C	3.1174367531	0.8934415274	2.1120577267
C	3.3155418549	-0.4795246773	1.9989562157
C	2.4028115471	-1.2399323812	1.2687185697
C	1.3164114145	-0.6328795686	0.6379866693
C	1.0914245157	0.7490634427	0.7746919826
C	2.0089962452	1.5006736428	1.5205460890
S	0.2897285829	-1.5965605791	-0.4394690880
C	-1.2476230213	-0.7537019361	-0.1793368837
C	-1.2605301660	0.6375154440	0.0277069423
N	-0.0358554636	1.3424165811	0.1507312615
C	-2.4421019524	-1.4676265054	-0.2770290994
C	-3.6695563723	-0.8079256801	-0.2248921553
C	-3.6904620684	0.5727610301	-0.0505365964
C	-2.5004017824	1.2874744420	0.0893814534
C	-0.0724060801	2.7625346811	0.0370565095
C	-0.4560228144	3.5573626536	1.1200935001
C	-0.5017482988	4.9468566536	1.0143856097
C	-0.1577223551	5.5649552179	-0.1966381619
C	0.2256998618	4.7701987132	-1.2798689770
C	0.2693704892	3.3804672733	-1.1747719936
C	0.6980628789	2.5571148204	-2.3677563349
C	-0.9363220013	5.7692659987	2.2061290885
N	-0.1925199651	6.9852841195	-0.3088470433
C	-1.3167176446	7.5803537890	-0.9368893275
C	-1.5432469363	8.9616658429	-0.7963164074
S	-0.5185230024	9.9230454315	0.2849694683
C	1.0191943903	9.0805749950	0.0253396184
C	1.0321712057	7.6892153815	-0.1813152801
C	-2.2295529692	6.8310173726	-1.6907617936
C	-3.3359797449	7.4392886337	-2.2846808807
C	-3.5373603771	8.8112912002	-2.1648411600
C	-2.6286257767	9.5699016737	-1.4276948340
C	2.2136811155	9.7945840407	0.1235282135
C	3.4410383381	9.1343943235	0.0740332662
C	3.4619228115	7.7532454706	-0.0972406672
C	2.2718769915	7.0385705134	-0.2382720898
F	0.0001434827	6.6581939244	2.5759591299
F	-2.0682562406	6.4491133776	1.9535297519
F	-1.1773000038	4.9865631113	3.2781525760
F	0.9385107911	3.3390478109	-3.4404784254
F	1.8284527679	1.8734614870	-2.1184012894
F	-0.2425019475	1.6714101768	-2.7347928317
H	3.8228216402	1.5093141964	2.6748462960
H	4.1753358681	-0.9602372620	2.4706521372
H	2.5380420977	-2.3189636552	1.1608200509
H	1.8715727934	2.5770483501	1.6298572010
H	-2.3972304974	-2.5502896546	-0.4188632211
H	-4.5991661678	-1.3725048484	-0.3235888808

H	-4.6404720917	1.1106852793	-0.0111581285
H	-2.5429826617	2.3677566337	0.2319514152
H	-0.7257159190	3.0767339704	2.0615347399
H	0.4959441869	5.2511793857	-2.2210706046
H	-2.0899189617	5.7554437388	-1.8044684709
H	-4.0371079909	6.8251049873	-2.8546744705
H	-4.3960902211	9.2927549008	-2.6374502525
H	-2.7661295977	10.6482159770	-1.3151403795
H	2.1687625205	10.8775075104	0.2636765162
H	4.3706312336	9.6990575238	0.1718541294
H	4.4119450606	7.2149234594	-0.1334465764
H	2.3142500169	5.9579538446	-0.3782276975

9. Optimized Molecular structure data for 2AC-2CF_3Ph using wPBEh

Optimized Molecular structure for **2Ac-2CF_3Ph** using wPBEh functional at cc-pvdz with w of 0.04250

C	3.3338907624	1.0974073107	2.0405674255
C	3.4589256692	-0.2811577367	2.1842053277
C	2.5008647189	-1.1144452243	1.6074710122
C	1.4096524850	-0.6104645784	0.8940642250
C	1.2681140687	0.7900957620	0.8043435735
C	2.2436145723	1.6316667551	1.3595020599
C	0.4486913061	-1.5044029476	0.1159073239
C	-0.9352795942	-0.8608148745	0.1342684137
C	-1.0391047197	0.5436496275	0.0550430732
N	0.1351502576	1.3222819086	0.1502705434
C	-2.1169366507	-1.6069780124	0.1120450586
C	-3.3690964309	-1.0095544980	-0.0307511508
C	-3.4498407304	0.3733069884	-0.1648508984
C	-2.2937697436	1.1471387376	-0.1176429334
C	0.0156550579	2.7386576469	0.0469981152
C	-0.4125247254	3.4890130648	1.1444262811
C	-0.5410165041	4.8750973787	1.0615123001
C	-0.2380292722	5.5329808814	-0.1387752097
C	0.1931525645	4.7831710551	-1.2352924960
C	0.3213192947	3.3977702856	-1.1525799231
C	0.7754960585	2.6172815154	-2.3630454265
C	-0.9944424116	5.6581615358	2.2703255458
N	-0.3679080064	6.9484132077	-0.2515310415
C	-1.4984059181	7.4570895365	-0.9291088261
C	-1.6308264788	8.8517696865	-1.0918420371
C	-0.6713911031	9.7784797525	-0.3521125667
C	0.7090949509	9.1295722281	-0.3231899635
C	0.8057890294	7.7303818647	-0.1739434230
C	-2.4830106773	6.5953153003	-1.4362109093
C	-3.5684498219	7.1007986170	-2.1460326798
C	-3.6797349669	8.4700672734	-2.3681686956
C	-2.7158042834	9.3252581832	-1.8350703101
C	1.8930957784	9.8724057981	-0.3183690797
C	3.1404295505	9.2793906692	-0.1252579560
C	3.2134064990	7.9047089925	0.0796427936
C	2.0555478270	7.1329775859	0.0500247249

F	-0.0652423415	6.5520663846	2.6599851400
F	-2.1312780615	6.3392462061	2.0302994793
F	-1.2309586530	4.8539228019	3.3235843208
F	1.0089851557	3.4232509162	-3.4155129356
F	1.9144870993	1.9390348144	-2.1252051816
F	-0.1517246029	1.7214905900	-2.7533143764
C	-0.6382514789	11.1802028942	-0.9647717815
C	-1.1662636511	9.8975734161	1.1104575088
C	0.9316885369	-1.5546955060	-1.3545359729
C	0.4258370339	-2.9343410595	0.6608963353
H	4.0806435232	1.7716133486	2.4674000594
H	4.3031823257	-0.7115690070	2.7275402647
H	2.6211250324	-2.1948304398	1.7018531453
H	2.1516058723	2.7141055111	1.2631158335
H	-2.0612654065	-2.6940845494	0.1881018244
H	-4.2705451161	-1.6260741590	-0.0527898663
H	-4.4174126670	0.8640231598	-0.2968507596
H	-2.3709921533	2.2310160905	-0.2113499250
H	-0.6464506884	2.9739130343	2.0770837374
H	0.4258024892	5.2984577868	-2.1681546963
H	-2.4026417694	5.5192909833	-1.2779496557
H	-4.3225858949	6.4107434301	-2.5326822263
H	-4.5185573991	8.8771953882	-2.9371916160
H	-2.8260028718	10.3998121188	-1.9892712912
H	1.8425496460	10.9544133917	-0.4504242444
H	4.0437427732	9.8935071264	-0.1187007066
H	4.1763310542	7.4184999898	0.2550413225
H	2.1267106815	6.0551205409	0.2007588565
H	-0.2960222076	11.1647720876	-2.0116809999
H	0.0261047156	11.8416942070	-0.3892779933
H	-1.6352333309	11.6434669230	-0.9278772399
H	-1.2171560573	8.9136320593	1.5987215066
H	-2.1743271268	10.3444786365	1.1351810239
H	-0.4811387269	10.5360214669	1.6930758260
H	0.9737347982	-0.5517296452	-1.8024174095
H	0.2452566033	-2.1715220162	-1.9585895739
H	1.9413693613	-1.9954842076	-1.4054400942
H	0.0935132498	-2.9706664308	1.7103327873
H	1.4235265639	-3.3926323453	0.5919375628
H	-0.2418542017	-3.5693000034	0.0598569277

10. Optimized Molecular structure data for 2PO-2CF_3Ph using wPBEh with functional at cc-pydz

Molecular structure for 2PO-2CF3Ph using wPBEh functional at cc-pvdz with w of 0.04938 that display high oscillatory strength

C	2.4397960191	-0.2313568021	0.6707539429
C	2.6272443004	-1.5778809150	0.3571516742
C	2.9372361126	-2.5458946083	1.3426044084
C	3.0428687654	-2.1303281118	2.6685736344
C	2.8942160583	-0.7460355930	2.9863279713
C	2.5417845936	0.1938023100	1.9886490789
O	3.1882432534	-3.0855622573	3.6306324976
C	3.1031288528	-2.7478155007	4.9064127348
C	3.0942982942	-1.3217780129	5.2844010649
N	3.1748532496	-0.3092241037	4.3334406873
C	3.1937303540	-3.7224235880	5.8983164476
C	3.1779747638	-3.3386876055	7.2296402500
C	3.2134031322	-2.0329312039	7.6172280626
C	3.1700273092	-1.0868761241	6.6236007744
C	3.3000254186	1.0344513400	4.8231586821
C	4.6194260724	1.4822227700	5.2932621410
C	4.8832869445	2.7783838916	5.6597449401
C	3.8110232484	3.7442314171	5.5194672386
C	2.5372028763	3.3357332508	5.1049051443
C	2.2998666819	2.0108634891	4.7023096290
C	0.8513284593	1.5976065107	4.4468033087
C	6.3278545008	3.2321191979	5.9204586155
N	3.9832937109	5.1110829416	5.7810606597
C	4.0656826563	5.5499926543	7.0968987659
C	4.5782918252	6.8362629413	7.2647689024
O	4.9283121514	7.6591320462	6.2304223619
C	4.9320152576	7.1508556340	5.0145237028
C	4.5079110306	5.8762874618	4.7171891487
C	3.6783703834	4.8773583923	8.2799506927
C	3.7193152851	5.4150980075	9.5431887438
C	4.1054628079	6.7007842038	9.6468758173
C	4.5662900958	7.4333618178	8.5291465397
C	5.4679928364	7.9475390024	3.9621868343
C	5.5282116524	7.5453999860	2.5928715468
C	5.2029344755	6.2228549482	2.3421632060
C	4.7088514831	5.4580277014	3.3931884435
F	6.7135473292	3.9616175442	4.8090958559
F	6.4175667743	4.0294026211	6.9981824870
F	7.1000189391	2.1345156062	6.1090173528
F	0.0999115930	2.2851093738	5.3003185813
F	0.3941353353	1.8858639917	3.2543568623
F	0.7166376397	0.2341797867	4.6557398465
H	2.1928085038	0.4950534008	-0.2194205567
H	2.5346579179	-1.9391704716	-0.6417510730
H	2.9185278390	-3.6501975462	1.1866876442
H	2.3245793601	1.2348783206	2.3337298308
H	3.1866163858	-4.7257065851	5.6010575429
H	3.3056563663	-4.1272385071	7.9677733965
H	3.1435957593	-1.6393943956	8.6373989086

H	3.2171625519	-0.0421269812	6.9655122972
H	5.4729392213	0.7060196302	5.2732666058
H	1.7141858621	4.0845878302	5.1207293825
H	3.1568081254	3.8694298935	8.1504493312
H	3.2393304085	4.9551348899	10.3812396098
H	3.9429063625	7.2891457263	10.4862532879
H	4.9234590389	8.4458777858	8.8312385066
H	5.7509640012	8.9883273714	4.1901187709
H	6.1202596668	8.0886603780	1.8585798014
H	5.3910494918	5.7114144689	1.3999095502
H	4.4811063823	4.3829867646	3.2846914845

11. Characterisations of **2PS-2CF$_3$Ph** by 1H, 13C-NMR spectroscopy

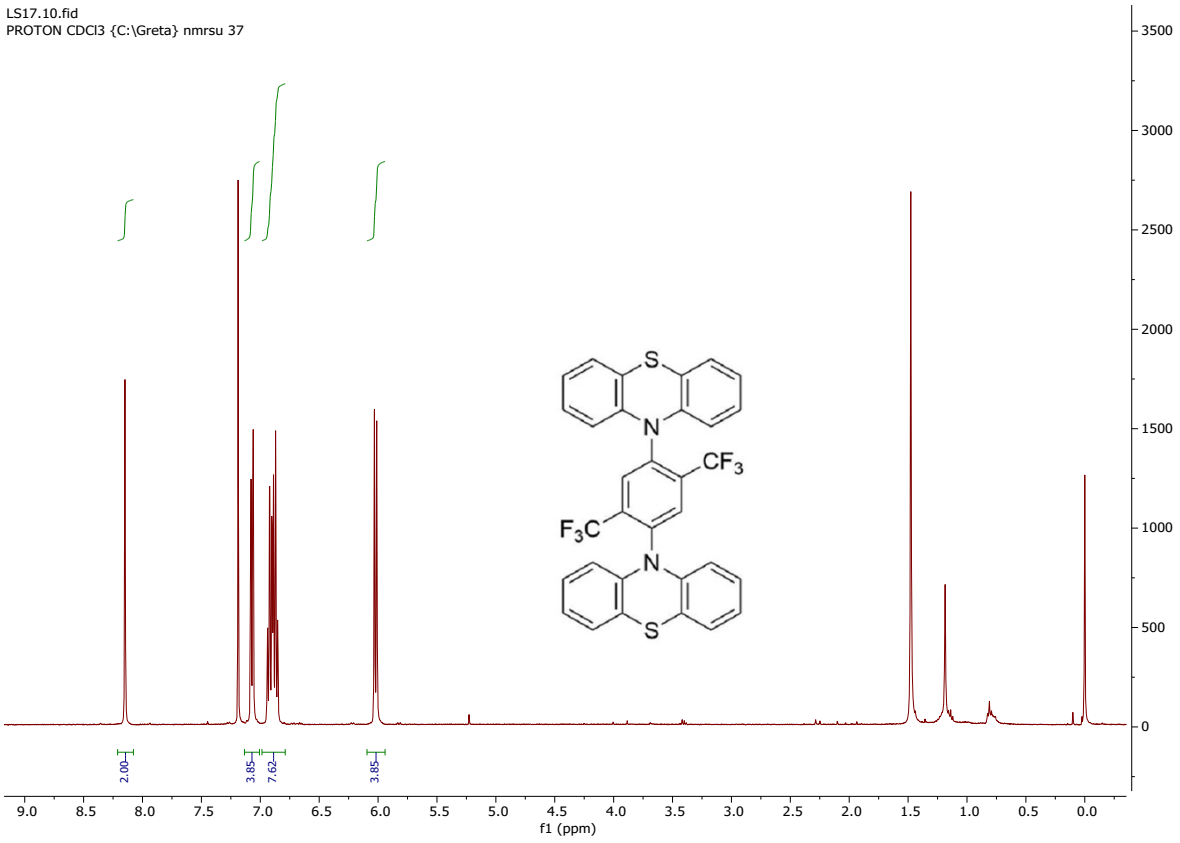


Figure S9: 1H-NMR for **2PS-2CF$_3$-Ph**

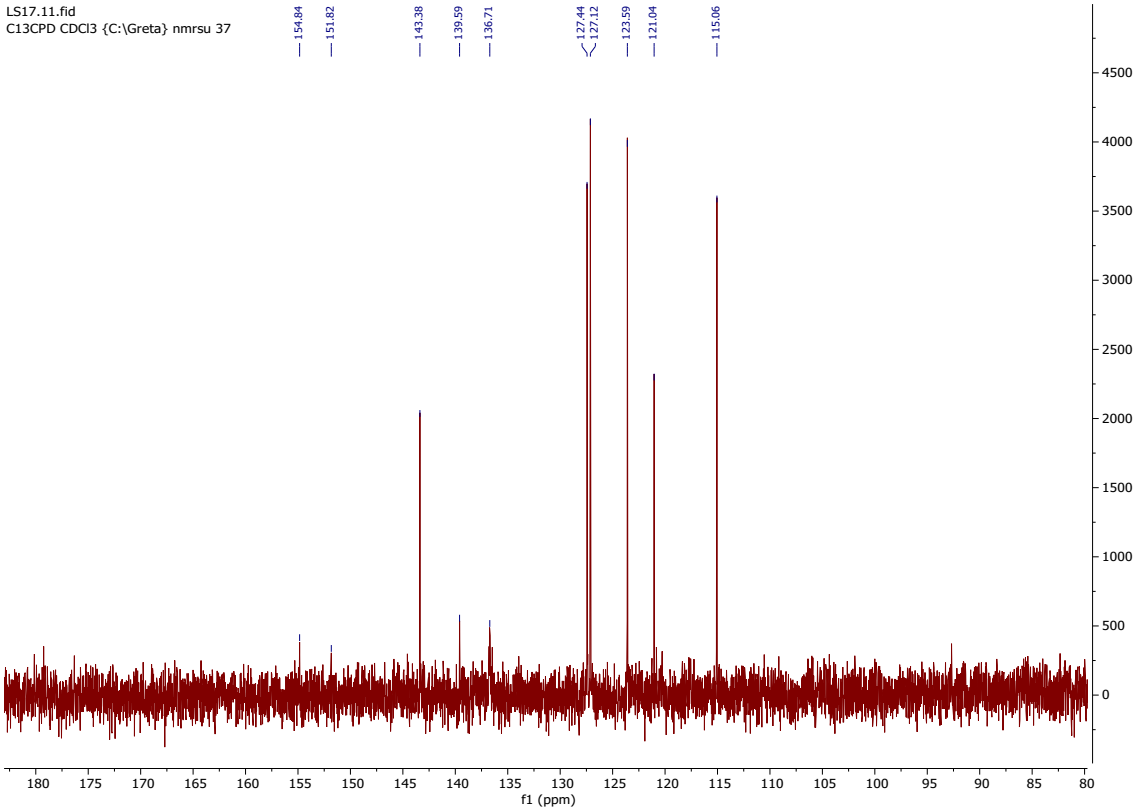


Figure S10: 13C-NMR for **2PS-2CF$_3$-Ph**

12. Characterisations of 2AC-2CF$_3$Ph by 1H, 13C-NMR spectroscopy

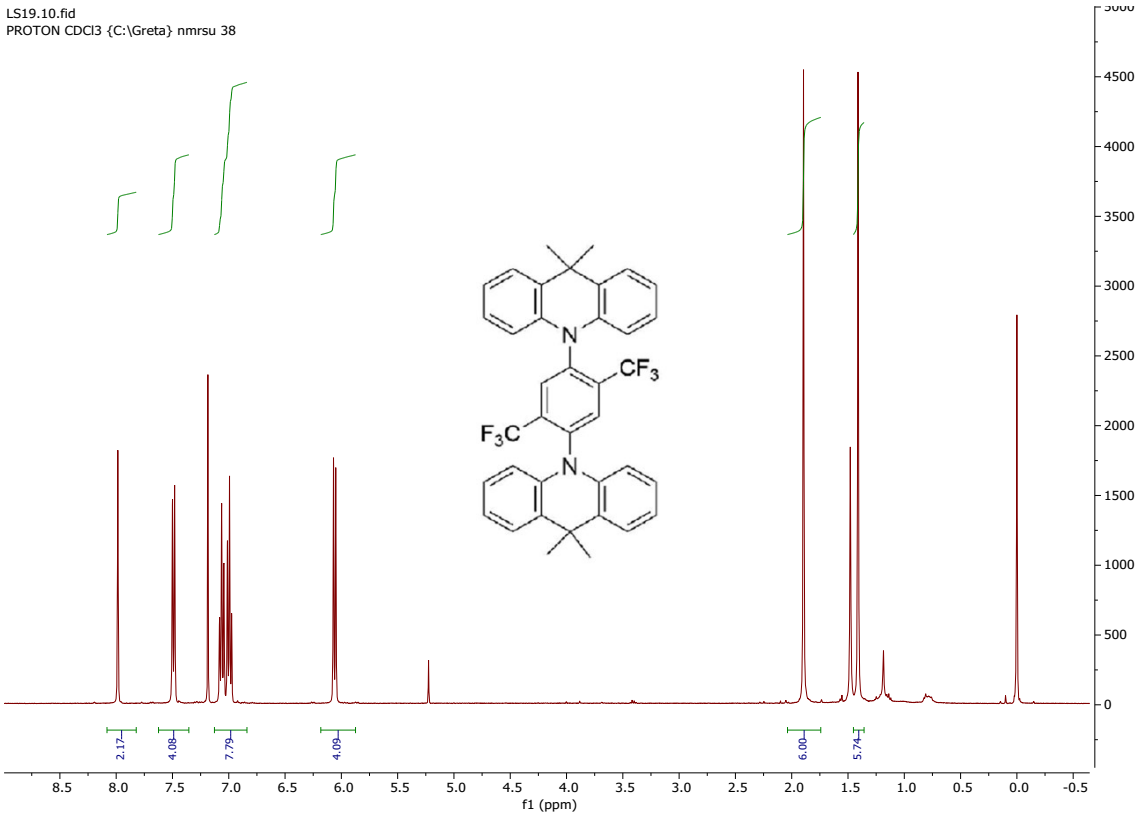


Figure S11: 1H-NMR **2AC-2CF$_3$Ph**

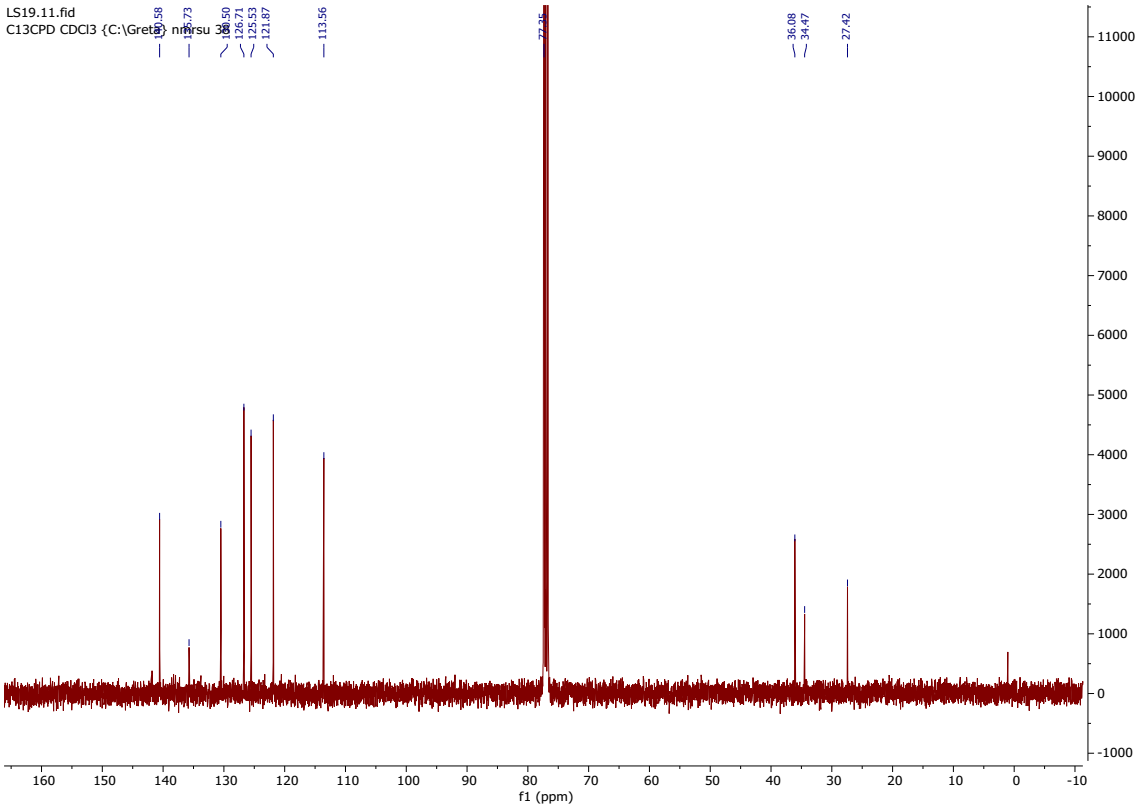


Figure S12: 13C-NMR **2AC-2CF$_3$Ph**

13. Characterisations of 2PO-2CF$_3$Ph, 2PS-2CF$_3$Ph, 2AC-2CF$_3$Ph by mass spectroscopy

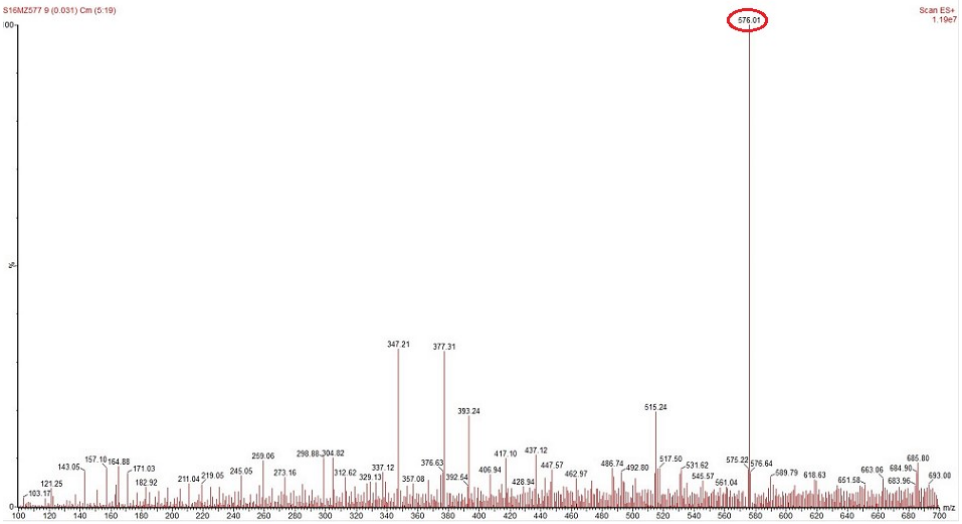


Figure S13: Mass spectrum for 2PO-2CF$_3$Ph

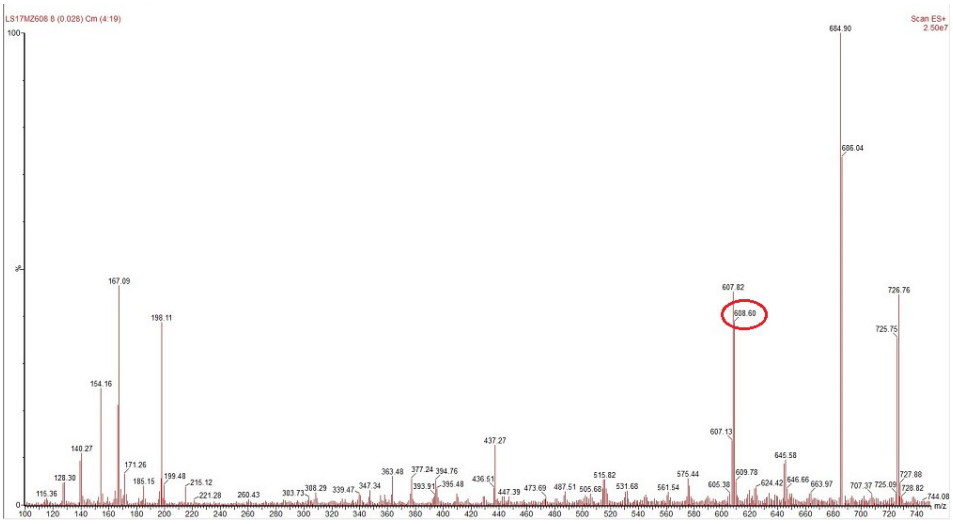


Figure S14: Mass spectrum for 2PS-2CF$_3$Ph

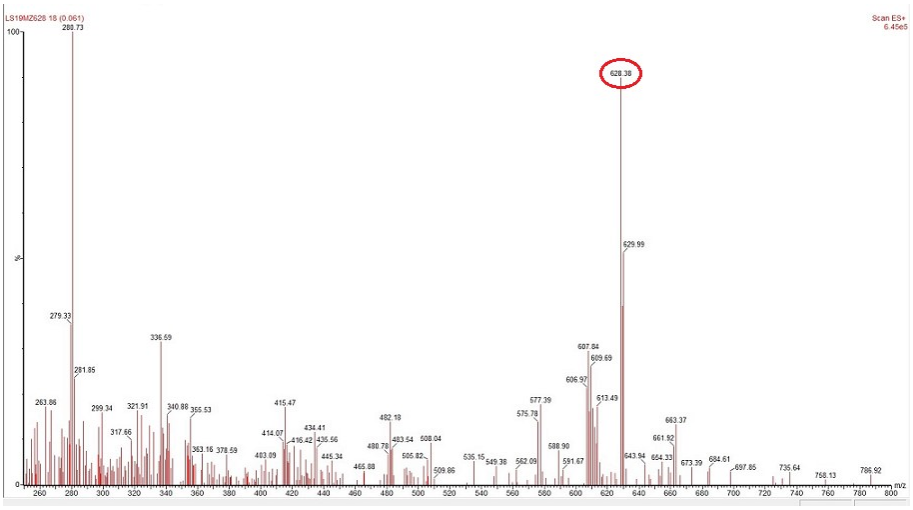


Figure S15: Mass spectrum for 2AC-2CF3Ph

14. Characterisations of 2PO-2CF_3Ph, 2PS-2CF_3Ph, 2AC-2CF_3Ph by DSC

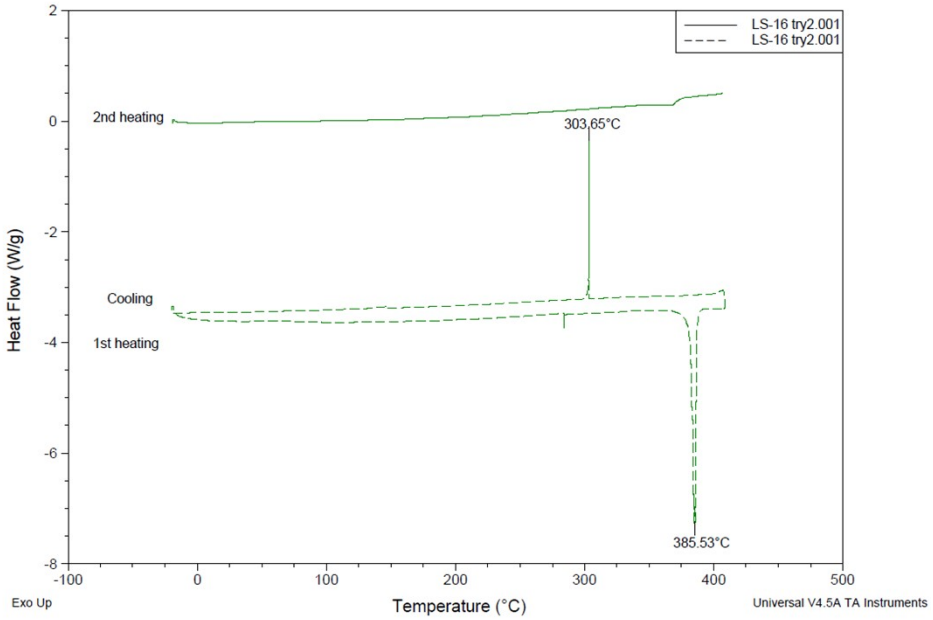


Figure S16: DSC curve for compound 2PO-2CF_3Ph

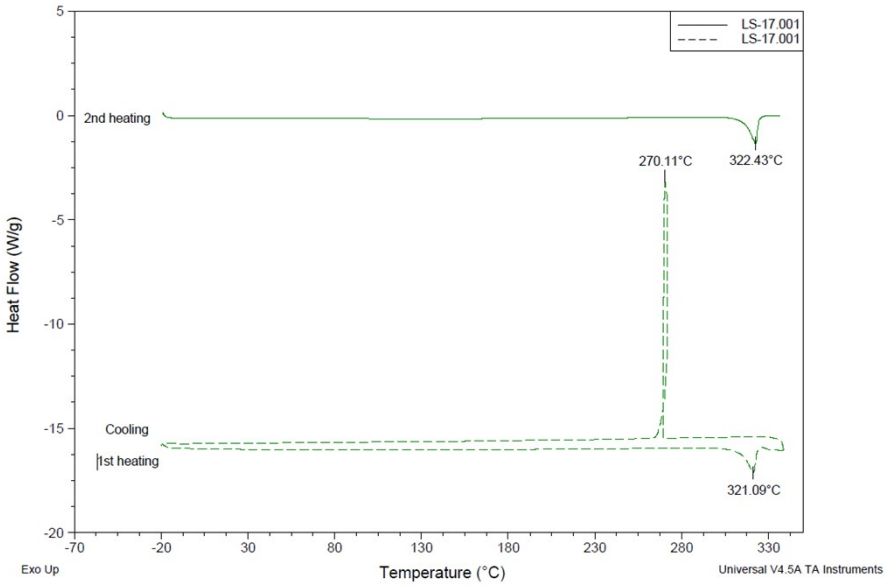


Figure S17: DSC curve for compound 2PS-2CF_3Ph

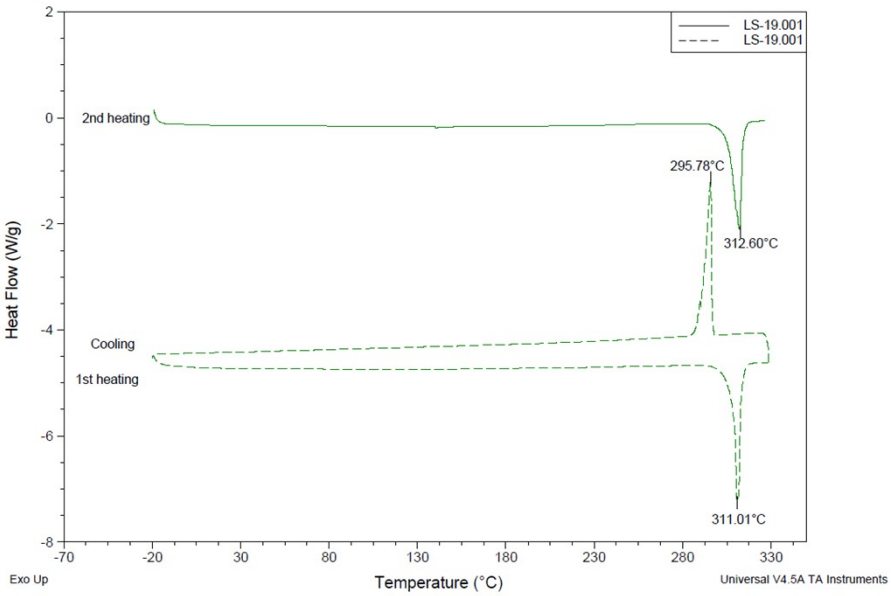


Figure S18: DSC curve for compound 2AC-2CF$_3$Ph

15. Characterisations of 2PO-2CF3Ph, 2PS-2CF3Ph, 2AC-2CF3Ph by TGA

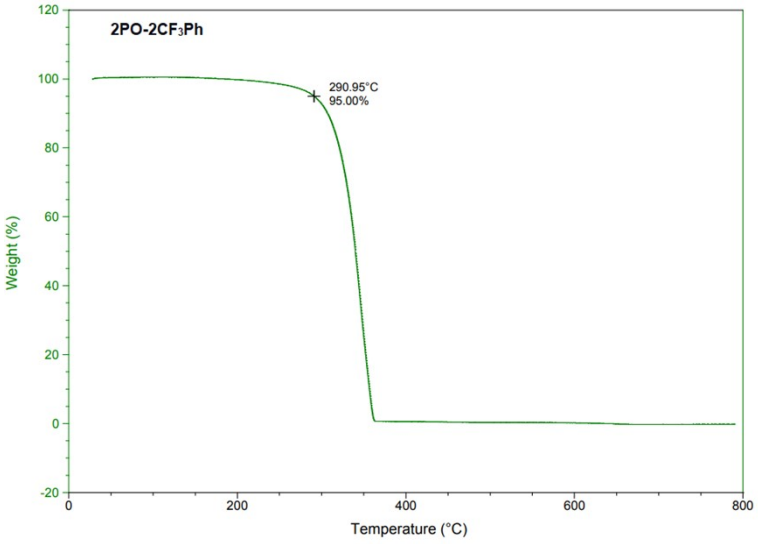


Figure S19: TGA curve for compound 2PO-2CF3Ph

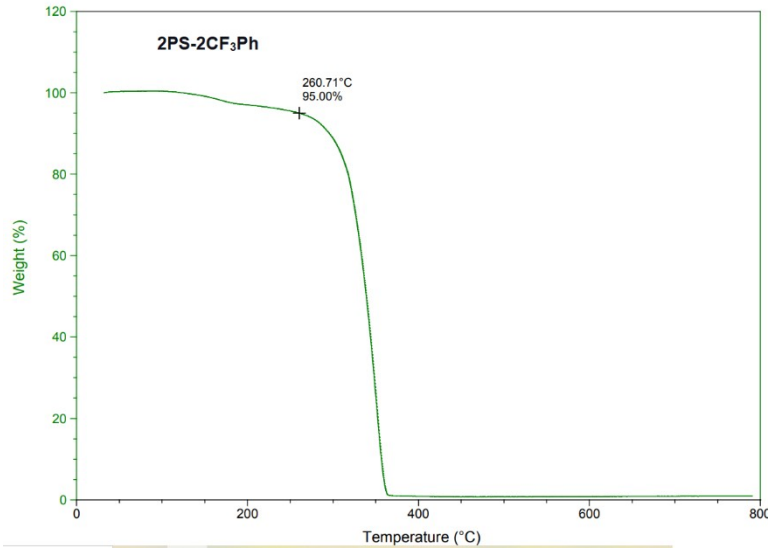


Figure S20: TGA curve for compound 2PS-2CF$_3$Ph

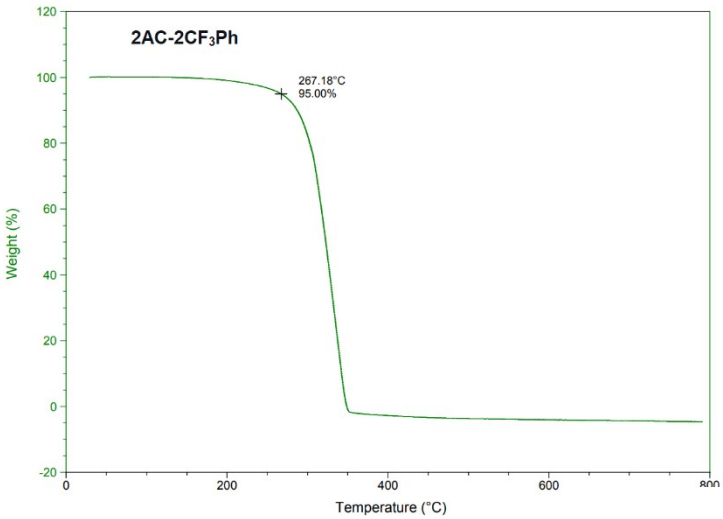


Figure S21: TGA curve for compound 2AC-2CF$_3$Ph

17. References

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