Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Photophysical studies of pyrenyl cyanostyrenes: Effect of trifluoromethyl substitution on gelation

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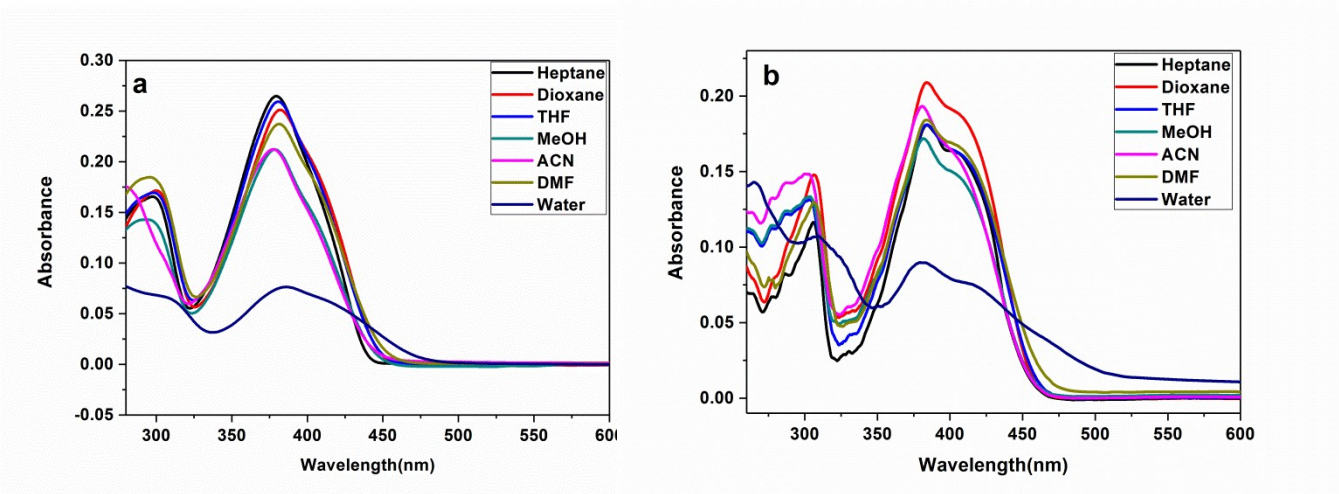


Fig. S1 a) Absorption spectra of a) (**1**) & b) (**3**) in organic solvents

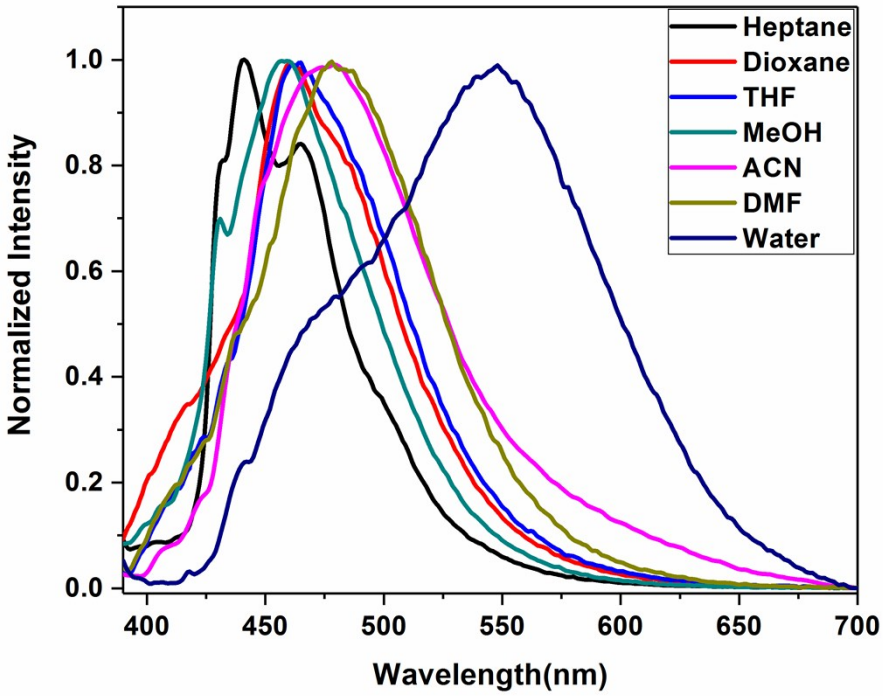


Fig. S2 Emission spectra of (**1**) in different organic solvents

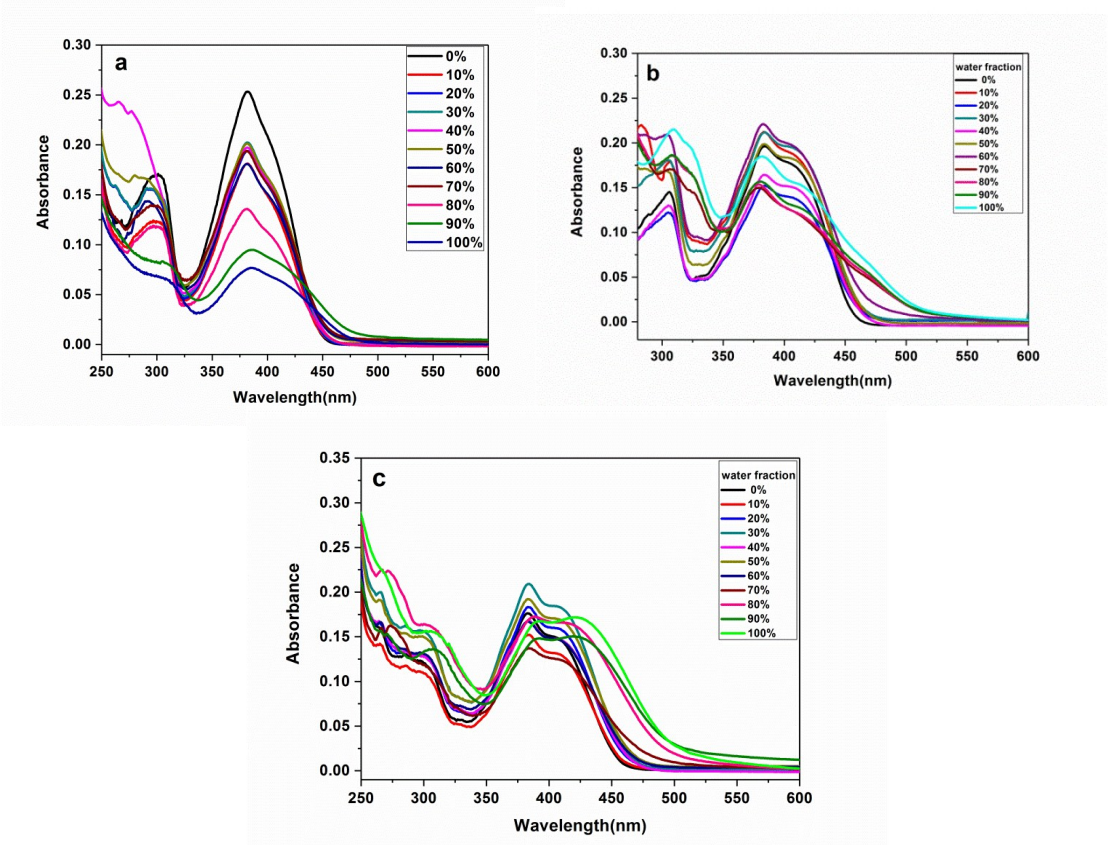


Fig. S3 a) Absorption spectra of a) (**1**), b) (**2**) & c) (**3**) in dioxane-water mixtures

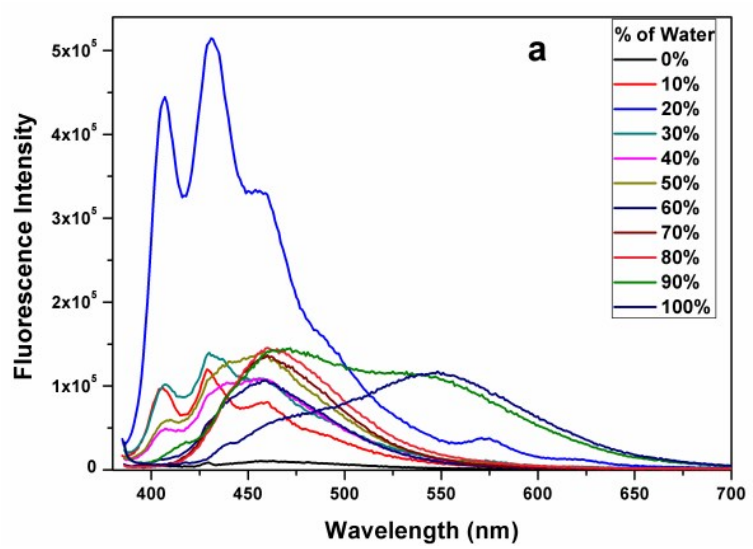


Fig. S4 Fluorescence spectra of (**1**) in 1, 4-dioxane/water system.

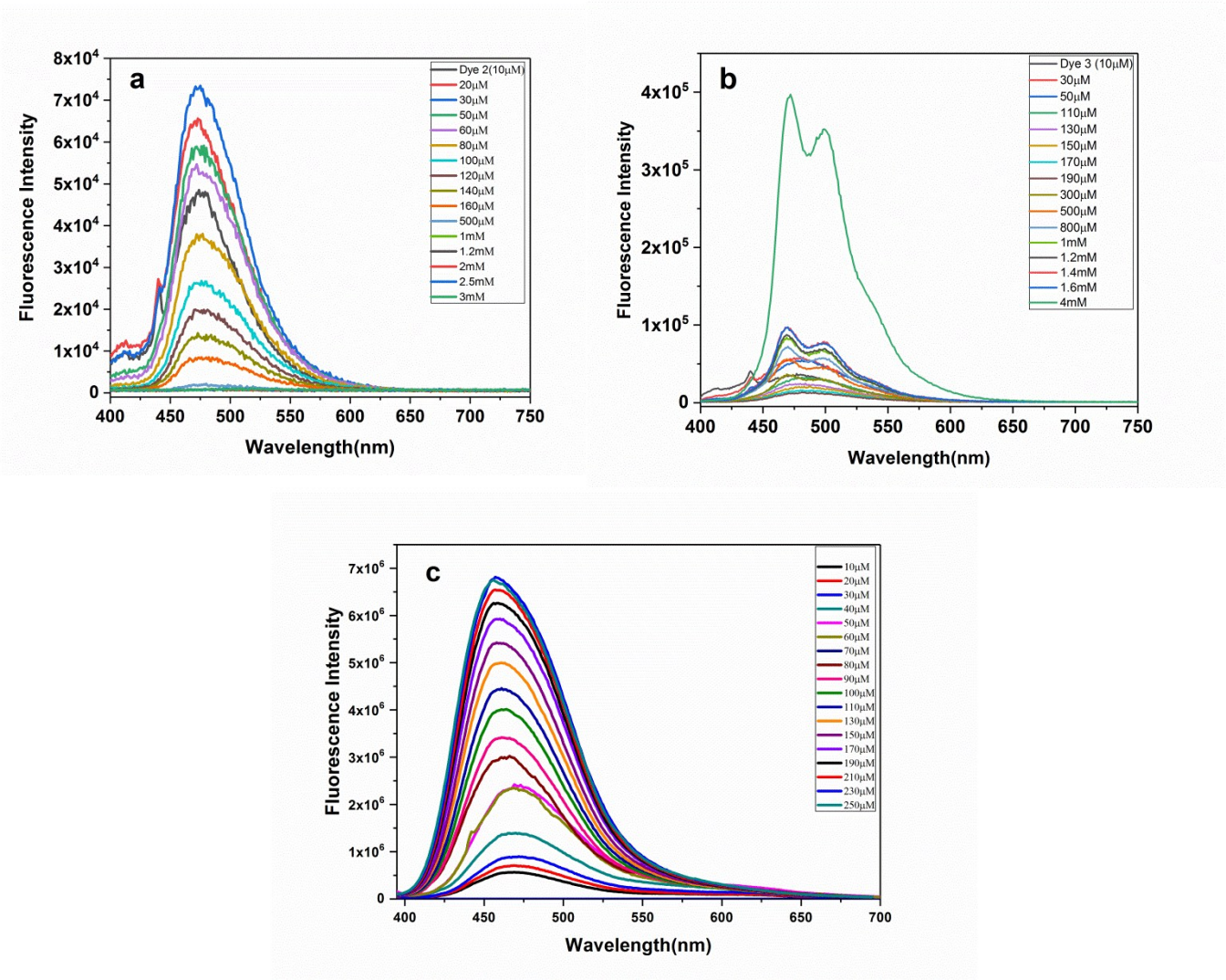


Fig. S5 Concentration dependence studies of a) (2) and b) (3) in dioxane and in water. No excimer formation is detected with increase in concentration. The experiment was also done for (2) in water- Figure c but the data for (3) is very irregular in water and is not included. The compounds have poor solubility in water and therefore difficult to perform experiments with increased concentration.

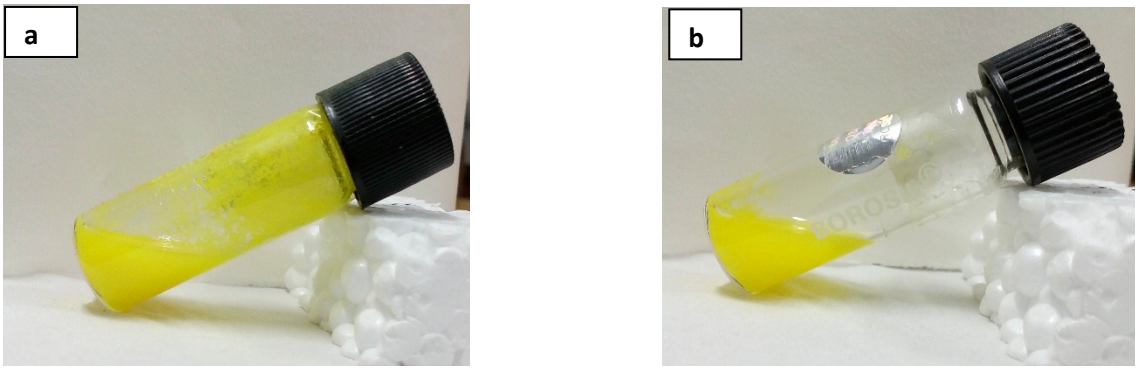


Fig. S6 No formation of gel is observed after heating the solutions of a) (**1**) & b) (**3**) in t-BuOH.

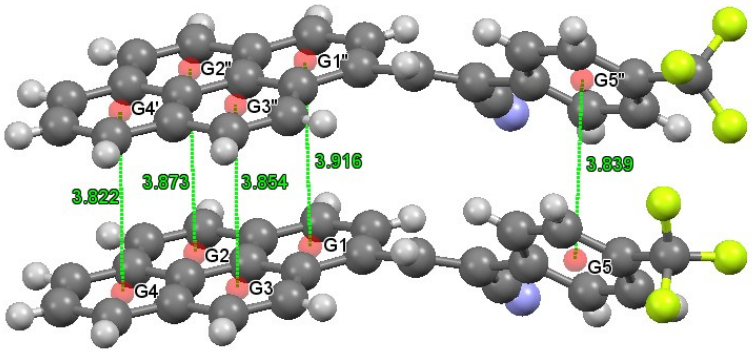


Fig. S7 Molecular packing arrangement and depiction the intermolecular π-π interactions between the two mono substituted styrylpyrenes compound (**2**).

Table S1: Non-covalent bond interaction lengths

Number	Atom1	Atom2	Length	Length-VdW	Symm. op. 1	Symm. op. 2
1	N1'	H21'	2.554	-0.196	1+x,y,z	1+x,1.5-y,-1/2+z
2	N1	H21	2.576	-0.174	x,y,z	x,1.5-y,-1/2+z
3	N1'	H17'	2.588	-0.162	1+x,y,z	1+x,1.5-y,-1/2+z
4	N1	H17	2.604	-0.146	x,y,z	x,1.5-y,-1/2+z
5	F3	F2'	2.824	-0.116	x,y,z	1+x,y,z
6	F2	F3'	2.841	-0.099	x,y,z	x,y,z
7	F3	F1'	2.864	-0.076	x,y,z	1+x,y,z
8	F1	F3'	2.875	-0.065	x,y,z	x,y,z
9	F1	F1'	2.915	-0.025	x,y,z	x,y,z
10	H11	F1	2.582	-0.088	x,y,z	-x,-1/2+y,1.5-z
11	H12	F3'	2.661	-0.009	x,y,z	-x,-1/2+y,1.5-z

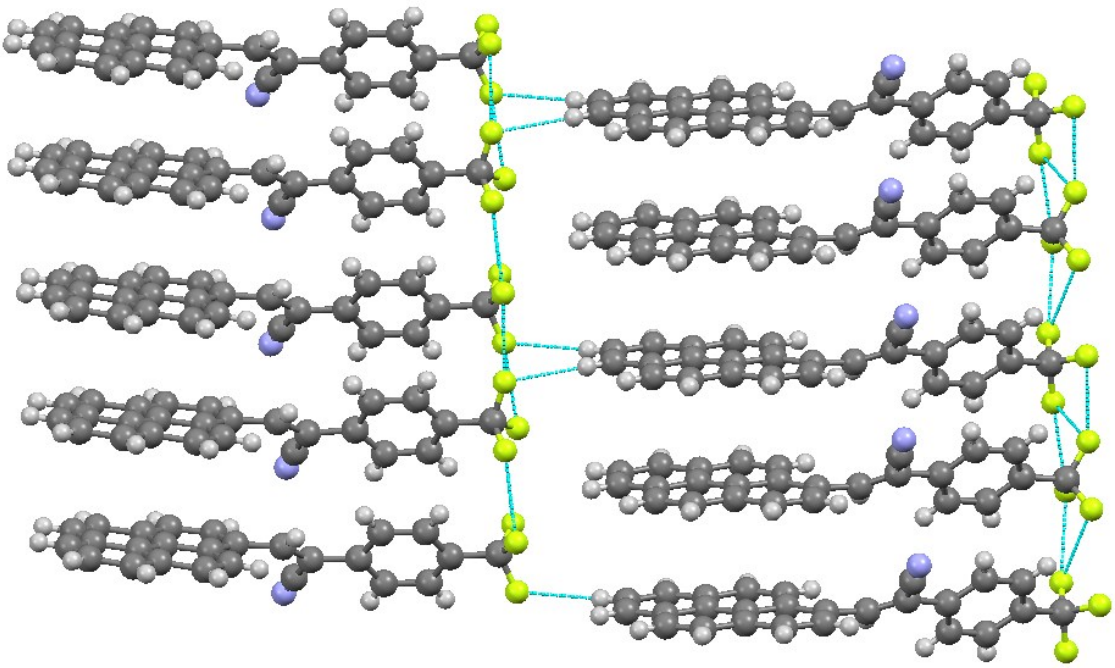


Fig. S8 The molecular packing arrangement of monosubstituted pyrene (**1**) and the depiction of intermolecular interactions involving the terminal CF_3 moiety.

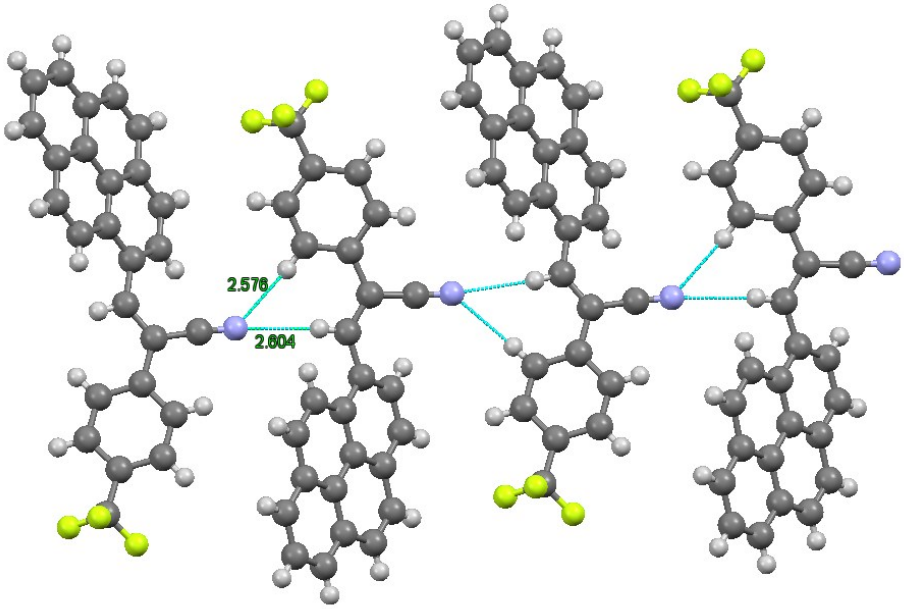


Fig. S9 The molecular packing arrangement of the mono-substituted pyrene (**2**) and the depiction of interactions involving the vinyl cyano group.

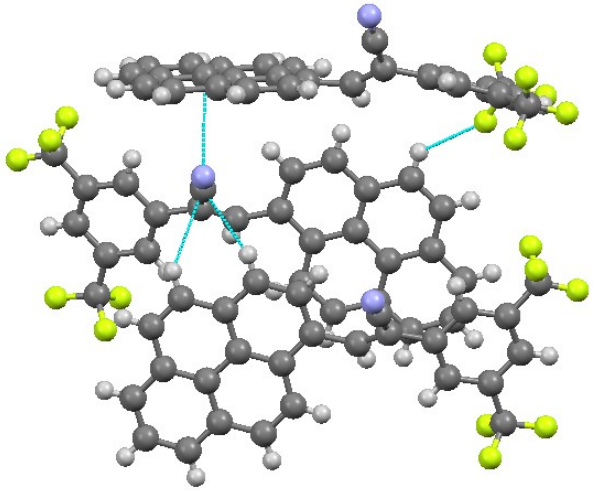


Fig. S10 Molecular packing arrangement and intermolecular interaction of compound (**3**)

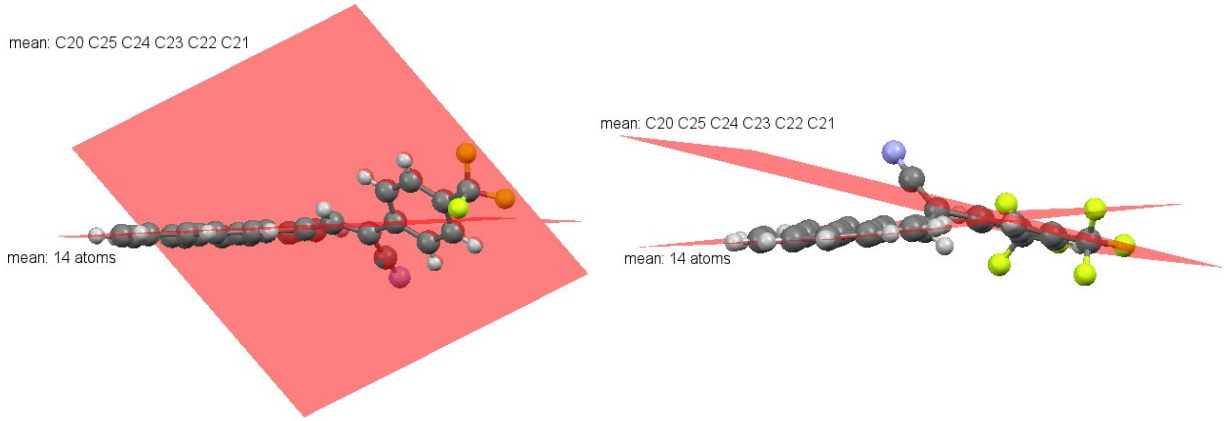


Fig. S11 The orientations of pyrene ring and phenyl rings planes in compound (**2**) and (**3**).

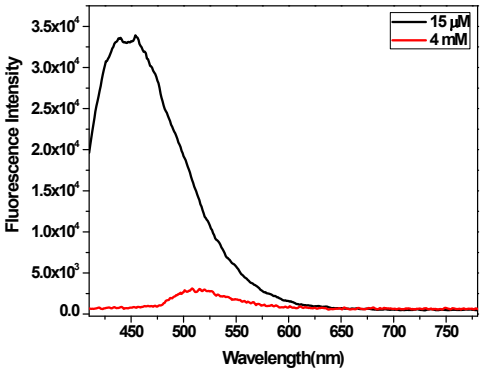


Fig.S12 Emission spectra of (**3**) with concentrations of 15 μM and 4 mM.

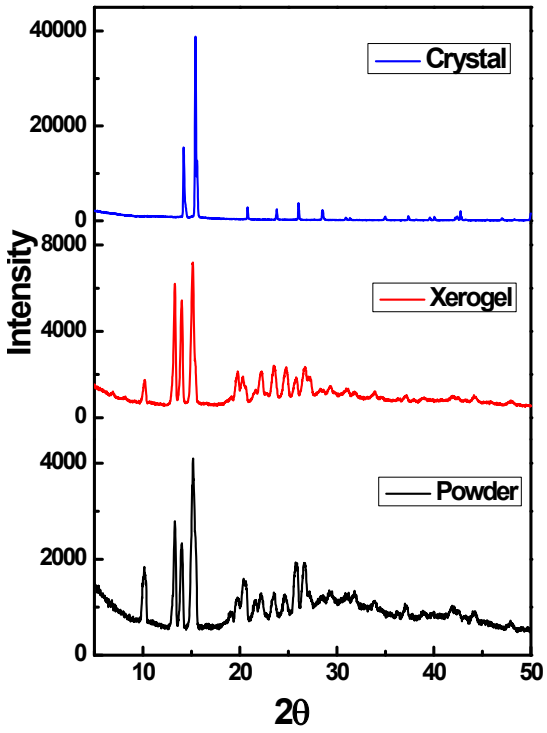
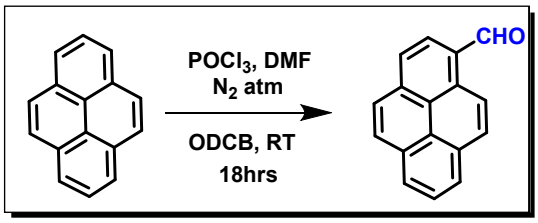


Fig. S13 Powder XRD patterns of compound (**2**) crystal along with powder and xerogel formed in *t*-BuOH.

Synthetic Procedures

Pyrene-1-carbaldehyde is obtained using Vilsmeyer-Haack formylation reaction of Pyrene with DMF in the presence of phosphorus oxychloride. In a three-necked round bottomed flask equipped with a reflux condenser, nitrogen inlet and outlet adapter, dried DMF (3.2 mL 41.3 mmol) was added in anhydrous 1, 2-dichlorobenzene (30 mL). Phosphorous oxychloride (2.3mL, 24.7 mmol) was added with vigorous stirring at 0°C. The contents were stirred for 45 min at 0°C and later at room temperature for 1h. A solution of Pyrene (5g, 20.4 mmol) in anhydrous 1, 2-dichlorobenzene (20 mL) was added to the above reaction mixture using a dropping funnel at room temperature. The reaction was allowed to stir overnight and refluxed for 2h. Upon confirmation of the product formation by TLC, the reaction mixture was cooled and poured into a mixture of ice-cooled water and toluene (100 mL). The solution was neutralized with sodium carbonate to a final pH 7. After neutralization, the mixture is stirred for 1h at 90°C and then subjected to liquid separation. The organic phase was washed with water and dried with anhydrous sodium sulfate and concentrated under reduced pressure to

obtain the desired product. The final product was re-crystallized from isopropyl alcohol. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm) 10.81 (s, 1H), 9.45 (d, J = 9.3 Hz, 2H), 8.47 (d, J = 7.9 Hz, 1H), 8.30 (ddd, J = 31.6, 16.8, 8.9 Hz, 5H), 8.16 – 8.08 (m, 2H).



Scheme 1. Synthesis of pyrene-1-carbaldehyde

(E)-3-(pyren-1-yl)-2-(4-(trifluoromethyl)phenyl)acrylonitrile (**2**)*:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, J = 8 Hz, 1H), 8.67(s, 1H), 8.27 (m, 4H), 8.17 – 8.22 (m, 2H), 8.06 – 8.12 (m, 2H), 7.96 (d, J = 8 Hz, 2H), 7.79 (d, J = 8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.23, 138.03, 133.29, 131.27, 130.64, 130.07, 129.13, 129.08, 127.41, 127.23, 126.52, 126.48, 126.26, 126.22, 126.19, 126.09, 125.01, 124.74, 124.50, 122.77, 122.26, 117.71, 113.22, 96.15; HRMS (ESI-MS) *m/z*: calcd for $[M]^+$ 397.1078, found 397.1073

(Z)-2-(3,5-bis(trifluoromethyl)phenyl)-3-(pyren-1-yl)acrylonitrile (**3**)*:* ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 8 Hz, 1H), 8.65(s, 1H), 8.23 – 8.27 (m, 5H), 8.16 – 8.19 (m, 3H), 8.05 - 8.095 (m, 2H), 7.97 (d, J = 8.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.53, 136.90, 133.62, 133.00, 132.73, 131.20, 130.57, 130.18, 129.40, 129.33, 127.37, 126.70, 126.57, 126.46, 126.17, 126.04, 125.00, 124.67, 124.38, 124.11, 122.81, 122.08, 117.28, 111.63; HRMS (ESI-MS) *m/z*: calcd for $[M]^+$ 465.0952, found 465.0936.

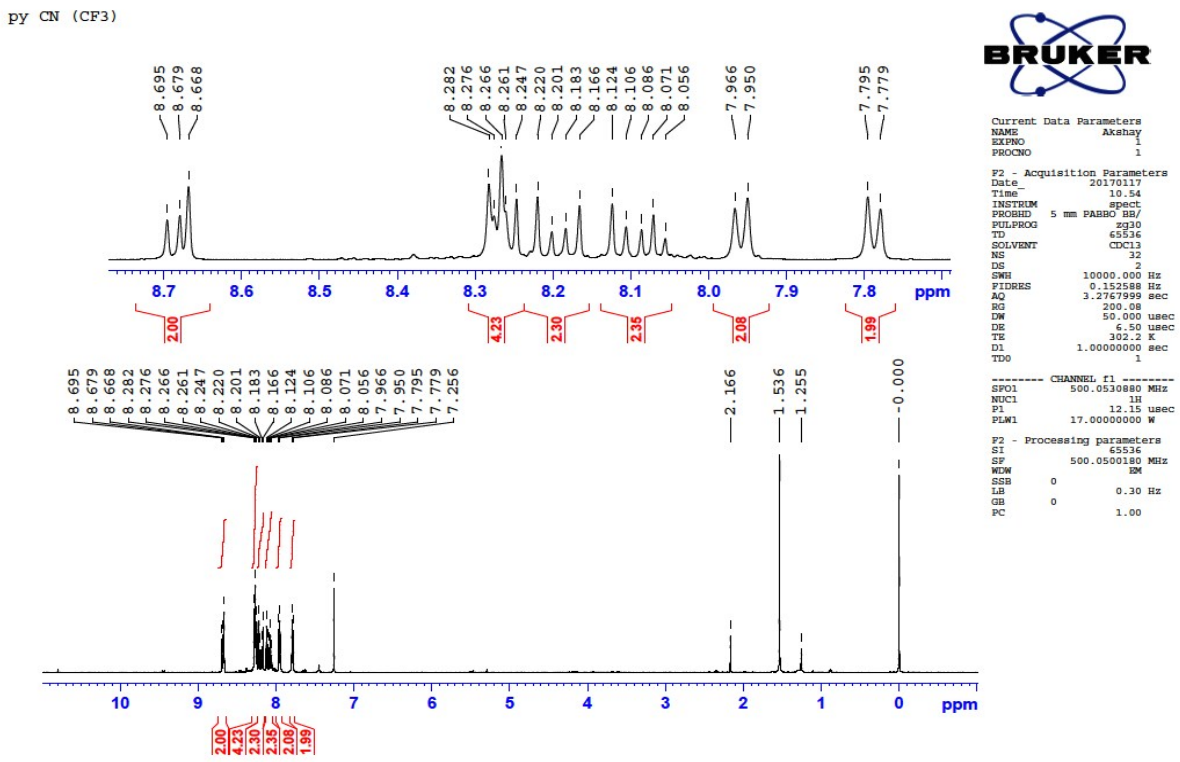


Fig.S14 ^{1}H NMR of compound (**2**)

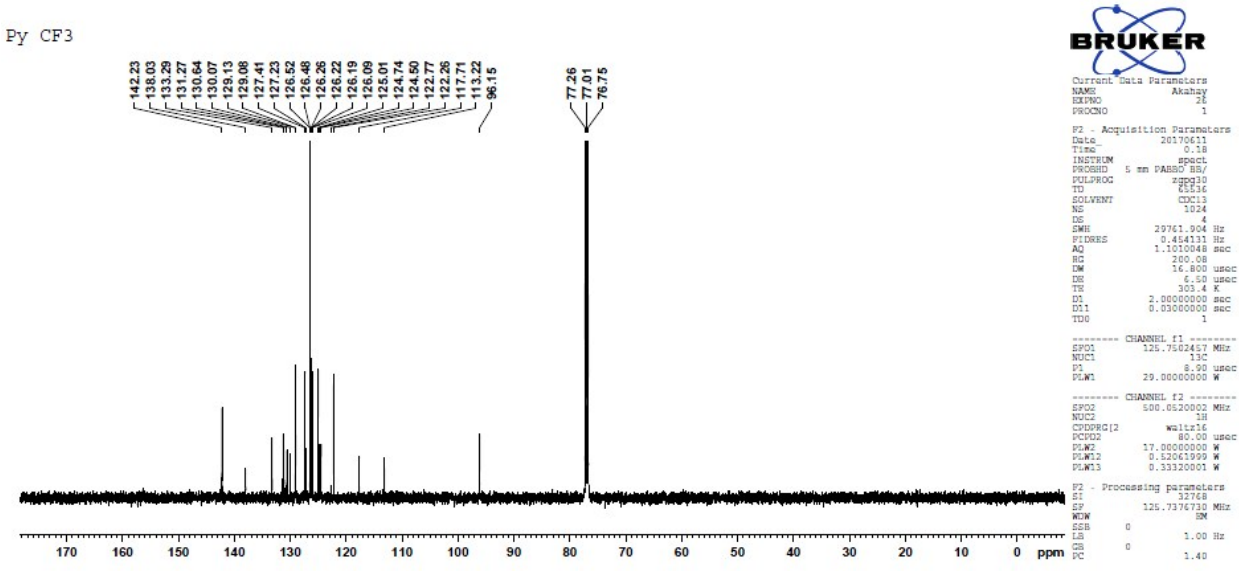


Fig. S15 ^{13}C NMR of compound (**2**)

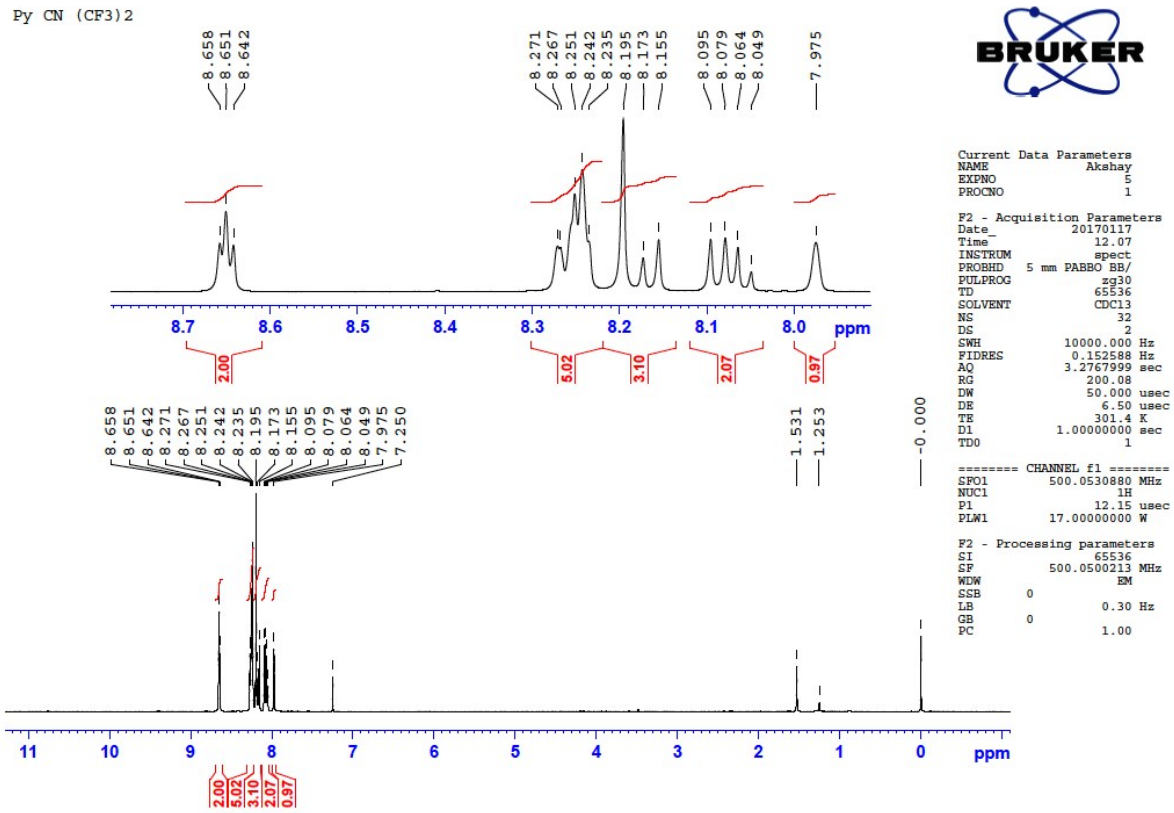


Fig. S16 ^{1}H NMR of compound (**3**)

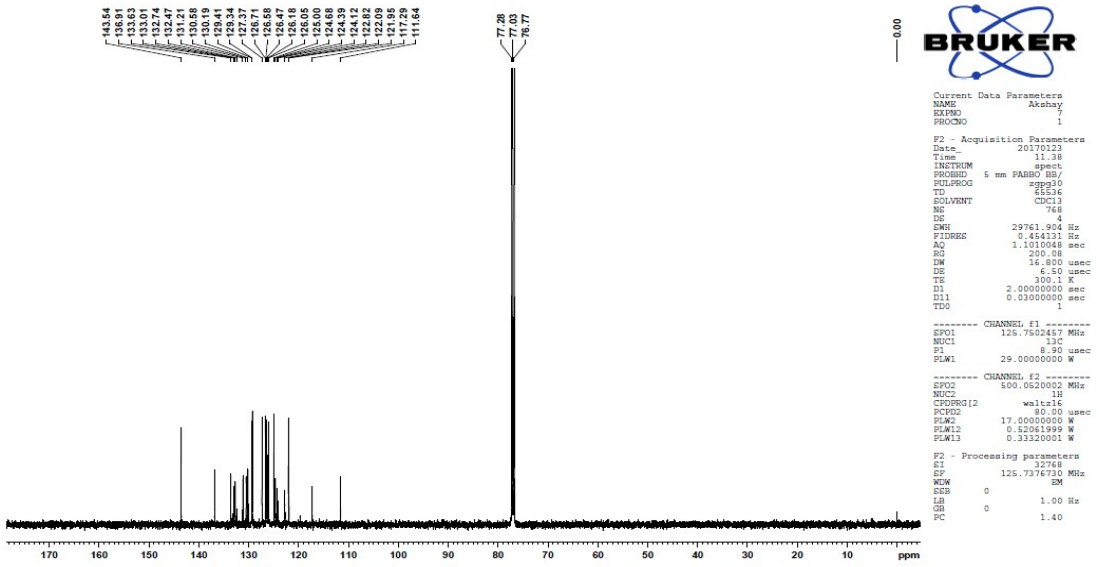


Fig.S17 ^{13}C NMR of compound (**3**)

Single Crystal Structures of Compounds (2) & (3):

The crystal data collection and data reduction were performed using CrysAlis PRO on a single crystal Rigaku Oxford XtaLab Pro diffractometer. The crystals were kept at 93(2) K during data collection using CuKα (λ = 1.54184) radiation. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

1. Single Crystal structure, Cell parameters and structure data of Compound-2 (Exp 273)

The single crystals of the compound-2 were obtained as yellow blocks from pentane-dichloromethane mixed solvent. The crystal structure of this is given below.

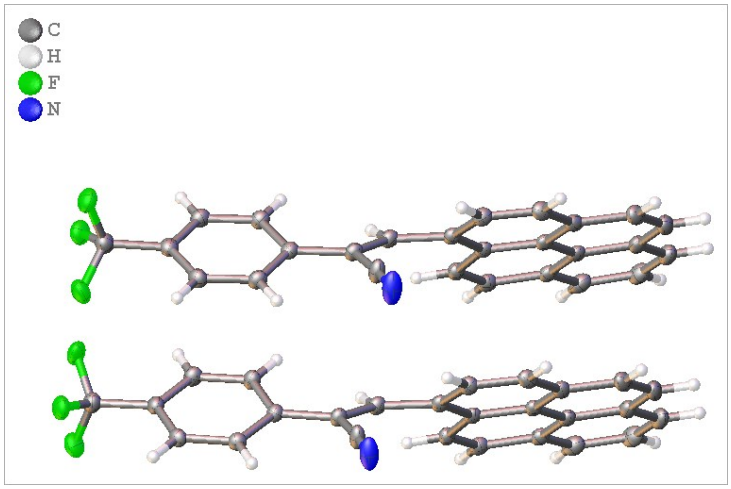


Table 1S-(2): Crystal data and structure refinement for exp_273-PYCF3.

Identification code	exp_273-PYCF3
Empirical formula	$C_{26}H_{14}F_3N$
Formula weight	397.38
Temperature/K	93(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.87500(10)
b/Å	34.3134(5)
c/Å	13.7389(2)
α/°	90
β/°	101.2370(10)
γ/°	90
Volume/Å^3	3641.33(9)

Z	8
ρ_{calc}g/cm^3	1.450
μ/mm^{-1}	0.882
F(000)	1632.0
Crystal size/mm^3	0.2 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.048 to 148.68
Index ranges	-8 ≤ h ≤ 9, -41 ≤ k ≤ 22, -16 ≤ l ≤ 17
Reflections collected	20408
Independent reflections	7225 [R_{int} = 0.0165, R_{sigma} = 0.0147]
Data/restraints/parameters	7225/0/541
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.1037
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.1048
Largest diff. peak/hole / e Å^{-3}	0.23/-0.24

Table 2S-(2): Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_273-PYCF3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F2	413.3(10)	9469.6(2)	6138.5(6)	29.05(17)
F3	2265.1(10)	9237.0(2)	7367.3(5)	30.17(18)
F2'	-5988.4(10)	9411.2(2)	5809.4(6)	30.66(18)
F1'	-4187.4(10)	9309.8(2)	7185.3(5)	30.48(18)
F1	-430.7(10)	9256.7(2)	7449.0(6)	33.19(19)
F3'	-3253.1(10)	9415.0(2)	5828.1(6)	34.14(19)
N1	-172.0(19)	7587.0(3)	3324.3(8)	37.7(3)
C6	340.0(14)	6601.7(3)	6156.1(8)	17.0(2)
N1'	-5150(2)	7505.4(3)	3289.2(8)	40.1(3)
C18	-81.3(15)	7627.6(3)	5213.6(8)	18.5(2)
C1	-398.4(14)	6901.0(3)	5490.2(8)	17.8(2)
C5	-83.2(14)	6206.5(3)	5907.9(8)	17.7(2)
C20	86.5(14)	8030.5(3)	5614.2(8)	17.5(2)
C2	-1500.4(15)	6798.5(3)	4597.1(8)	19.9(2)
C24	796.0(14)	8711.2(3)	5451.4(8)	19.3(2)
C16	1532.9(15)	6680.1(3)	7069.7(8)	19.2(2)
C16'	-3359.3(15)	6684.7(3)	7110.5(8)	19.1(2)
C1'	-5370.9(14)	6885.6(3)	5540.7(8)	18.6(2)
C21	-317.2(15)	8113.9(3)	6542.5(8)	20.2(2)
C18'	-5051.0(15)	7600.7(3)	5168.5(8)	19.1(2)
C20'	-4860.0(14)	8016.0(3)	5474.4(8)	18.0(2)
C25	635.0(14)	8335.3(3)	5075.7(8)	18.7(2)
C21'	-5195.7(15)	8145.0(3)	6387.8(8)	19.8(2)
C15'	-2654.7(15)	6401.1(3)	7750.6(8)	20.5(2)
C10'	-4246.2(15)	5898.4(3)	6682.2(8)	19.3(2)

C23	413.1(14)	8787.9(3)	6380.7(8)	19.4(2)
C4	-1205.1(15)	6111.2(3)	4996.7(8)	19.9(2)
C15	2182.1(15)	6389.2(3)	7699.8(8)	20.6(2)
C25'	-4348.6(15)	8289.6(3)	4835.7(8)	20.6(2)
C17	-106.9(14)	7307.5(3)	5790.0(8)	18.5(2)
C6'	-4580.2(14)	6594.6(3)	6216.1(8)	17.7(2)
C14'	-3087.6(15)	5999.0(3)	7573.2(8)	20.3(2)
C3	-1891.0(15)	6414.1(4)	4352.3(8)	21.3(2)
C23'	-4550.4(14)	8805.1(3)	5987.5(9)	20.6(2)
C22'	-5040.4(15)	8535.1(3)	6640.5(8)	21.2(2)
C5'	-4974.6(14)	6196.0(3)	5997.7(8)	18.4(2)
C17'	-5086.1(14)	7297.3(3)	5796.5(8)	19.0(2)
C14	1729.9(15)	5989.6(3)	7487.9(9)	20.5(2)
C22	-142.5(15)	8486.4(3)	6922.9(8)	20.8(2)
C10	600.2(15)	5901.1(3)	6577.8(8)	19.3(2)
C2'	-6500.7(15)	6771.2(3)	4666.9(8)	21.0(2)
C3'	-6854.1(15)	6383.7(4)	4449.5(9)	22.8(2)
C24'	-4194.9(15)	8680.2(3)	5087.3(9)	21.4(2)
C4'	-6119.0(15)	6088.8(3)	5104.7(8)	20.5(2)
C9'	-4685.8(16)	5501.2(3)	6479.2(9)	22.9(2)
C9	143.2(16)	5507.3(3)	6339.7(9)	22.8(2)
C19'	-5132.2(17)	7535.0(3)	4122.7(9)	25.1(3)
C7	-1628.8(16)	5709.2(4)	4773.3(9)	24.5(3)
C19	-151.4(17)	7594.7(3)	4160.4(9)	24.2(3)
C26'	-4486.3(16)	9231.6(4)	6210.4(9)	25.0(3)
C13	2369.1(16)	5686.2(4)	8141.8(10)	25.9(3)
C26	651.7(16)	9186.5(3)	6821.0(9)	23.8(2)
C7'	-6520.3(16)	5683.3(4)	4914.0(9)	24.5(3)
C8'	-5844.9(16)	5406.0(4)	5573.6(10)	26.0(3)
C13'	-2408.8(16)	5703.1(4)	8243.9(9)	24.9(3)
C8	-992.4(16)	5424.2(4)	5415.7(10)	26.1(3)
C11'	-3981.7(17)	5216.2(4)	7173.4(10)	27.7(3)
C11	812.9(17)	5213.4(4)	7013.1(10)	28.7(3)
C12	1909.5(17)	5302.7(4)	7904.2(10)	29.5(3)
C12'	-2865.2(17)	5316.9(4)	8044.5(10)	28.2(3)

Table 3S-(2): Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_273-PYCF3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F2	36.0(4)	16.2(3)	35.3(4)	2.3(3)	8.0(3)	0.0(3)
F3	32.9(4)	27.6(4)	28.2(4)	-6.1(3)	1.3(3)	-6.9(3)
F2'	34.8(4)	21.1(4)	35.3(4)	-0.9(3)	5.0(3)	4.7(3)
F1'	35.4(4)	29.0(4)	26.7(4)	-10.5(3)	5.2(3)	-4.2(3)

F1	43.3(4)	22.5(4)	39.7(4)	-8.5(3)	22.6(4)	-0.5(3)
F3'	38.8(4)	26.3(4)	40.4(4)	-6.5(3)	15.7(3)	-12.8(3)
N1	73.3(9)	21.9(6)	21.2(6)	-1.3(4)	17.1(5)	-8.7(6)
C6	19.6(5)	18.0(5)	15.3(5)	-0.2(4)	8.0(4)	0.4(4)
N1'	78.0(10)	23.8(6)	22.3(6)	-1.1(4)	19.0(6)	-5.2(6)
C18	22.6(5)	18.1(5)	15.7(5)	-0.4(4)	6.2(4)	0.5(4)
C1	21.1(5)	18.0(5)	15.9(5)	0.3(4)	7.7(4)	-0.1(4)
C5	19.9(5)	17.8(6)	17.3(5)	-0.4(4)	8.7(4)	0.0(4)
C20	19.1(5)	17.5(5)	15.7(5)	0.7(4)	2.6(4)	1.4(4)
C2	22.6(6)	21.1(6)	16.6(5)	2.1(4)	5.3(4)	0.6(4)
C24	19.8(5)	18.4(5)	19.6(5)	3.2(4)	3.4(4)	-0.7(4)
C16	21.7(5)	17.7(5)	19.1(5)	-2.0(4)	6.5(4)	-0.9(4)
C16'	22.0(5)	18.5(5)	18.2(5)	-2.2(4)	7.1(4)	-1.1(4)
C1'	21.1(5)	19.6(6)	16.8(5)	0.4(4)	8.0(4)	0.6(4)
C21	26.1(6)	17.6(5)	17.8(5)	2.2(4)	7.0(4)	0.8(4)
C18'	22.2(5)	20.1(6)	16.1(5)	0.0(4)	6.6(4)	1.6(4)
C20'	18.5(5)	19.1(5)	16.3(5)	0.7(4)	2.9(4)	2.4(4)
C25	19.8(5)	20.8(6)	15.9(5)	1.6(4)	4.2(4)	0.7(4)
C21'	22.5(5)	21.2(6)	16.3(5)	2.5(4)	5.1(4)	2.1(4)
C15'	21.8(5)	24.2(6)	16.2(5)	-1.9(4)	5.8(4)	0.7(4)
C10'	20.8(5)	19.5(6)	20.4(5)	-0.3(4)	10.5(4)	1.4(4)
C23	19.4(5)	17.0(5)	21.8(6)	-0.7(4)	3.6(4)	1.0(4)
C4	22.5(5)	19.4(6)	19.8(5)	-2.7(4)	9.5(4)	-2.2(4)
C15	21.9(5)	23.4(6)	17.2(5)	-1.0(4)	5.3(4)	1.0(4)
C25'	23.7(6)	22.7(6)	16.5(5)	0.8(4)	6.6(4)	1.8(4)
C17	22.1(5)	19.4(6)	14.6(5)	0.0(4)	4.8(4)	1.7(4)
C6'	19.4(5)	19.8(6)	15.7(5)	-0.4(4)	7.9(4)	0.7(4)
C14'	21.8(5)	21.0(6)	20.2(5)	1.3(4)	9.6(4)	3.4(4)
C3	22.6(6)	25.7(6)	16.3(5)	-2.4(4)	5.1(4)	-3.1(5)
C23'	18.9(5)	21.2(6)	20.9(6)	-0.6(4)	1.8(4)	0.2(4)
C22'	22.8(5)	23.9(6)	17.1(5)	-1.8(4)	4.5(4)	1.2(4)
C5'	19.5(5)	19.3(6)	18.4(5)	-1.4(4)	8.8(4)	0.4(4)
C17'	21.3(5)	21.0(6)	15.5(5)	0.0(4)	5.1(4)	2.0(4)
C14	21.4(5)	21.3(6)	20.5(5)	3.0(4)	8.5(4)	3.2(4)
C22	25.1(6)	21.5(6)	16.4(5)	-0.5(4)	5.8(4)	1.0(4)
C10	21.5(5)	17.5(6)	21.5(6)	1.1(4)	10.4(4)	1.2(4)
C2'	22.4(6)	23.1(6)	17.9(5)	1.9(4)	5.0(4)	1.7(4)
C3'	22.7(6)	27.1(6)	18.5(5)	-2.9(5)	3.9(4)	-1.9(5)
C24'	23.5(6)	21.0(6)	20.5(6)	2.7(4)	6.0(4)	-1.1(4)
C4'	20.8(5)	22.0(6)	20.1(6)	-3.3(4)	7.7(4)	-1.7(4)
C9'	24.7(6)	18.8(6)	28.3(6)	-0.9(5)	12.9(5)	0.9(4)
C9	25.6(6)	17.6(6)	28.6(6)	0.5(5)	13.5(5)	-0.1(4)
C19'	40.3(7)	15.9(5)	21.0(6)	0.3(4)	10.7(5)	0.1(5)
C7	26.2(6)	23.9(6)	24.9(6)	-7.6(5)	8.7(5)	-6.1(5)
C19	38.4(7)	14.8(5)	21.0(6)	-0.3(4)	9.6(5)	-2.3(5)

C26'	26.6(6)	23.9(6)	25.0(6)	-3.1(5)	6.4(5)	-2.7(5)
C13	26.9(6)	26.7(6)	25.4(6)	6.6(5)	8.7(5)	5.8(5)
C26	26.9(6)	20.4(6)	25.1(6)	-1.3(5)	7.4(5)	-1.0(5)
C7'	24.9(6)	25.1(6)	24.3(6)	-6.7(5)	6.6(5)	-4.7(5)
C8'	27.6(6)	19.9(6)	32.8(7)	-6.2(5)	11.4(5)	-3.7(5)
C13'	26.3(6)	27.0(6)	22.6(6)	3.0(5)	8.0(5)	7.1(5)
C8	29.2(6)	17.6(6)	34.6(7)	-6.0(5)	14.0(5)	-4.8(5)
C11'	31.7(6)	17.9(6)	36.9(7)	2.1(5)	14.7(5)	2.5(5)
C11	34.2(7)	16.0(6)	40.0(7)	4.4(5)	17.1(6)	1.9(5)
C12	32.5(7)	23.2(6)	35.5(7)	11.7(5)	12.9(5)	7.8(5)
C12'	32.4(7)	22.8(6)	31.9(7)	7.9(5)	12.5(5)	8.8(5)

Table 4S-(2): Bond Lengths for exp_273-PYCF3.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F2	C26	1.3377(14)	C20'	C25'	1.3969(16)
F3	C26	1.3550(14)	C21'	C22'	1.3822(16)
F2'	C26'	1.3522(15)	C15'	C14'	1.4308(17)
F1'	C26'	1.3410(14)	C10'	C14'	1.4195(16)
F1	C26	1.3475(14)	C10'	C5'	1.4304(16)
F3'	C26'	1.3467(14)	C10'	C9'	1.4202(16)
N1	C19	1.1460(16)	C23	C22	1.3944(16)
C6	C1	1.4220(15)	C23	C26	1.4925(16)
C6	C5	1.4220(15)	C4	C3	1.4034(17)
C6	C16	1.4390(15)	C4	C7	1.4380(16)
N1'	C19'	1.1469(17)	C15	C14	1.4320(17)
C18	C20	1.4845(15)	C25'	C24'	1.3835(16)
C18	C17	1.3566(16)	C6'	C5'	1.4216(16)
C18	C19	1.4416(15)	C14'	C13'	1.4048(16)
C1	C2	1.4026(16)	C23'	C22'	1.3953(16)
C1	C17	1.4598(15)	C23'	C24'	1.3879(16)
C5	C4	1.4226(16)	C23'	C26'	1.4942(17)
C5	C10	1.4291(16)	C5'	C4'	1.4219(16)
C20	C21	1.4027(15)	C14	C10	1.4191(16)
C20	C25	1.3972(16)	C14	C13	1.4031(16)
C2	C3	1.3811(16)	C10	C9	1.4199(16)
C24	C25	1.3858(16)	C2'	C3'	1.3792(17)
C24	C23	1.3929(16)	C3'	C4'	1.4021(17)
C16	C15	1.3544(16)	C4'	C7'	1.4395(16)
C16'	C15'	1.3555(16)	C9'	C8'	1.4301(18)
C16'	C6'	1.4386(15)	C9'	C11'	1.4027(17)
C1'	C6'	1.4215(16)	C9	C8	1.4318(18)
C1'	C17'	1.4624(16)	C9	C11	1.4004(17)
C1'	C2'	1.4038(16)	C7	C8	1.3470(18)

C21	C22	1.3775(16)	C13	C12	1.3867(19)
C18'	C20'	1.4851(15)	C7'	C8'	1.3498(18)
C18'	C17'	1.3558(16)	C13'	C12'	1.3865(18)
C18'	C19'	1.4434(16)	C11'	C12'	1.3836(19)
C20'	C21'	1.4036(15)	C11	C12	1.388(2)

Table 5S-(2): Bond Angles for exp_273-PYCF3.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	C6	C16	122.81(10)	C22'	C23'	C26'	121.41(11)
C5	C6	C1	119.14(10)	C24'	C23'	C22'	119.80(11)
C5	C6	C16	118.03(10)	C24'	C23'	C26'	118.72(11)
C17	C18	C20	123.24(10)	C21'	C22'	C23'	120.23(11)
C17	C18	C19	121.37(10)	C6'	C5'	C10'	120.33(10)
C19	C18	C20	115.36(10)	C6'	C5'	C4'	120.43(10)
C6	C1	C17	119.10(10)	C4'	C5'	C10'	119.23(10)
C2	C1	C6	119.18(10)	C18'	C17'	C1'	127.59(10)
C2	C1	C17	121.52(10)	C10	C14	C15	118.20(10)
C6	C5	C4	120.45(10)	C13	C14	C15	122.44(11)
C6	C5	C10	120.25(10)	C13	C14	C10	119.36(11)
C4	C5	C10	119.30(10)	C21	C22	C23	120.30(10)
C21	C20	C18	120.49(10)	C14	C10	C5	120.21(11)
C25	C20	C18	121.01(10)	C14	C10	C9	119.61(11)
C25	C20	C21	118.50(10)	C9	C10	C5	120.19(11)
C3	C2	C1	121.53(11)	C3'	C2'	C1'	121.49(11)
C25	C24	C23	119.80(10)	C2'	C3'	C4'	121.06(11)
C15	C16	C6	121.38(11)	C25'	C24'	C23'	119.92(11)
C15'	C16'	C6'	121.39(11)	C5'	C4'	C7'	119.12(11)
C6'	C1'	C17'	119.64(10)	C3'	C4'	C5'	118.71(11)
C2'	C1'	C6'	119.07(10)	C3'	C4'	C7'	122.15(11)
C2'	C1'	C17'	121.17(10)	C10'	C9'	C8'	118.68(11)
C22	C21	C20	120.70(11)	C11'	C9'	C10'	119.11(12)
C17'	C18'	C20'	124.77(10)	C11'	C9'	C8'	122.21(12)
C17'	C18'	C19'	120.74(11)	C10	C9	C8	118.71(11)
C19'	C18'	C20'	114.45(10)	C11	C9	C10	119.15(12)
C21'	C20'	C18'	121.97(10)	C11	C9	C8	122.14(12)
C25'	C20'	C18'	119.53(10)	N1'	C19'	C18'	175.71(13)
C25'	C20'	C21'	118.50(10)	C8	C7	C4	121.03(11)
C24	C25	C20	120.97(10)	N1	C19	C18	176.55(13)
C22'	C21'	C20'	120.48(10)	F2'	C26'	C23'	111.78(10)
C16'	C15'	C14'	121.86(11)	F1'	C26'	F2'	106.57(10)
C14'	C10'	C5'	120.09(11)	F1'	C26'	F3'	107.25(10)
C14'	C10'	C9'	119.60(11)	F1'	C26'	C23'	113.14(10)
C9'	C10'	C5'	120.31(11)	F3'	C26'	F2'	105.56(10)

C24	C23	C22	119.72(10)	F3'	C26'	C23'	112.07(10)
C24	C23	C26	120.81(10)	C12	C13	C14	120.59(12)
C22	C23	C26	119.43(10)	F2	C26	F3	106.49(9)
C5	C4	C7	119.14(11)	F2	C26	F1	107.41(10)
C3	C4	C5	118.78(10)	F2	C26	C23	113.07(10)
C3	C4	C7	122.07(11)	F3	C26	C23	111.84(10)
C16	C15	C14	121.85(11)	F1	C26	F3	105.33(10)
C24'	C25'	C20'	121.07(10)	F1	C26	C23	112.21(10)
C18	C17	C1	128.93(10)	C8'	C7'	C4'	121.03(11)
C1'	C6'	C16'	122.79(10)	C7'	C8'	C9'	121.61(11)
C1'	C6'	C5'	119.22(10)	C12'	C13'	C14'	120.68(12)
C5'	C6'	C16'	117.98(10)	C7	C8	C9	121.64(11)
C10'	C14'	C15'	118.25(10)	C12'	C11'	C9'	120.96(12)
C13'	C14'	C15'	122.52(11)	C12	C11	C9	120.87(12)
C13'	C14'	C10'	119.23(11)	C13	C12	C11	120.42(12)
C2	C3	C4	120.91(11)	C11'	C12'	C13'	120.41(12)

Table 6S-(2): Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_273-PYCF3.

Atom	*x*	*y*	*z*	U(eq)
H2	-1978.99	6993.95	4159.53	24
H24	1158.51	8911.53	5084.21	23
H16	1865.16	6935.8	7230.86	23
H16'	-3046.78	6942.86	7252.65	23
H21	-706.97	7915.56	6905.04	24
H25	895.82	8285.16	4455.92	22
H21'	-5525	7966.8	6826.18	24
H15'	-1867.68	6469.92	8321.11	25
H15	2942.8	6450.66	8286.47	25
H25'	-4107.39	8207.87	4231.67	25
H17	88.28	7353.29	6469.87	22
H3	-2618.73	6355.12	3752.2	26
H22'	-5263.25	8617.91	7247.82	25
H17'	-4908.25	7358.09	6468.37	23
H22	-396.36	8536.92	7544.05	25
H2'	-7022.71	6960.97	4224.66	25
H3'	-7591.92	6316.9	3858.82	27
H24'	-3853.91	8858.83	4653.86	26
H7	-2353.36	5645.06	4176.06	29
H13	3107.5	5742.7	8740.01	31
H7'	-7256.41	5611.34	4327.23	29
H8'	-6140.49	5146.62	5435.77	31
H13'	-1645.48	5767.03	8827.76	30

H8	-1298.31	5166.94	5255.14	31
H11'	-4269.37	4955.79	7046.42	33
H11	519.02	4954.9	6861.18	34
H12	2338.64	5104.15	8344.59	35
H12'	-2418.17	5124.31	8499.02	34

Crystal structure determination of compound-2[exp_273-PYCF3]

Crystal Data for $C_{26}H_{14}F_3N$ (M=397.38 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 7.87500(10) Å, b = 34.3134(5) Å, c = 13.7389(2) Å, β = 101.2370(10)°, V = 3641.33(9) Å^3, Z = 8, T = 93(2) K, μ(CuKα) = 0.882 mm^{-1}, *Dcalc* = 1.450 g/cm^3, 20408 reflections measured (7.048° ≤ 2Θ ≤ 148.68°), 7225 unique (R_{int} = 0.0165, R_{sigma} = 0.0147) which were used in all calculations. The final R_1 was 0.0362 (I > 2σ(I)) and wR_2 was 0.1048 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C2(H2), C24(H24), C16(H16), C16'(H16'), C21(H21), C25(H25), C21'(H21'),
 C15'(H15'), C15(H15), C25'(H25'), C17(H17), C3(H3), C22'(H22'), C17'(H17'),
 C22(H22), C2'(H2'), C3'(H3'), C24'(H24'), C7(H7), C13(H13), C7'(H7'), C8'(H8'),
  C13'(H13'), C8(H8), C11'(H11'), C11(H11), C12(H12), C12'(H12')
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This report has been created with Olex2, compiled on 2018.04.26 svn.r3504 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

2. Single Crystal structure, Cell parameters and structure data of compound-3 (Exp283):

The single crystals of the compound 3ha were obtained as yellow blocks from pentane-dichloromethane mixed solvent. The crystal structure of this is given below.

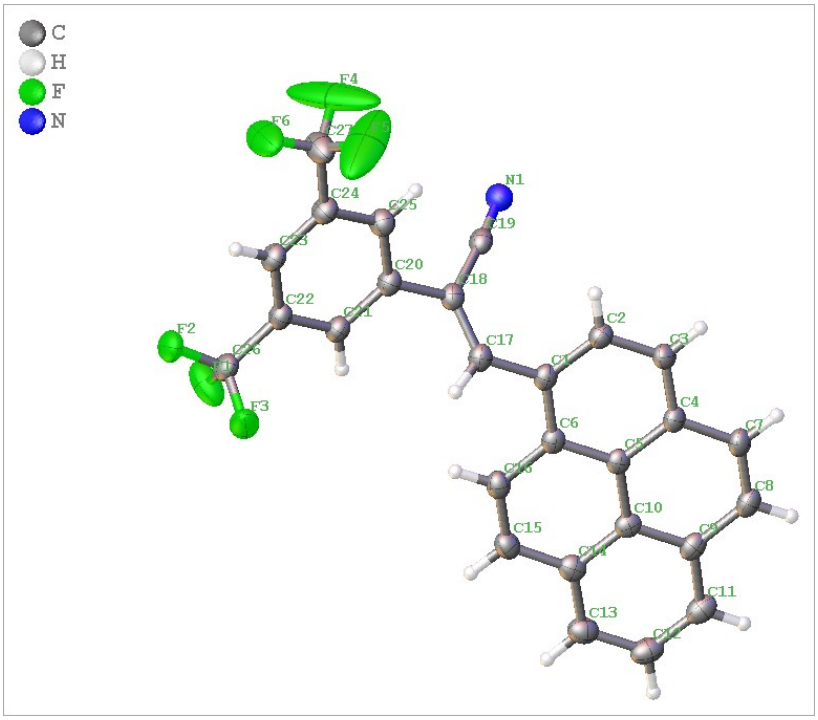

Table 7S-(3): Crystal data and structure refinement for exp_283_Py(CF3)2.

Identification code	exp_283_Py(CF3)
Empirical formula	$C_{27}H_{13}F_6N$
Formula weight	465.38
Temperature/K	93(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	8.9151(2)
b/Å	13.3283(3)
c/Å	33.8692(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4024.44(15)
Z	8
ρ_{calc}g/cm^3	1.536
μ/mm^{-1}	1.113
F(000)	1888.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	10.448 to 149.096
Index ranges	-10 ≤ h ≤ 5, -15 ≤ k ≤ 16, -39 ≤ l ≤ 42
Reflections collected	13860
Independent reflections	4002 [R_{int} = 0.0347, R_{sigma} = 0.0309]
Data/restraints/parameters	4002/15/307
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0776, wR_2 = 0.2186
Final R indexes [all data]	R_1 = 0.0849, wR_2 = 0.2251
Largest diff. peak/hole / e Å^{-3}	0.24/-0.26

Table 8S-(3): Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_283_Py(CF3). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F2	2949(2)	4735.0(15)	4816.9(5)	42.1(5)
F1	1466(3)	4952.2(19)	4330.3(7)	60.9(7)
F3	3500(3)	4139.1(16)	4249.2(7)	63.7(7)
F6	6089(4)	7532(2)	5143.2(6)	79.3(10)
N1	3869(3)	9380.7(19)	3327.6(7)	32.8(6)
C5	4177(3)	6655(2)	1993.0(8)	24.2(6)
C6	3880(3)	6468(2)	2398.0(8)	25.1(6)
C1	4568(3)	7082(2)	2686.6(8)	26.1(6)
C20	4324(3)	7119(2)	3830.1(8)	27.2(6)
C18	4308(3)	7471(2)	3412.6(8)	27.2(6)
C19	4127(3)	8538(2)	3358.6(8)	27.6(6)

C10	3494(3)	6050(2)	1694.1(8)	26.4(6)
C21	3609(3)	6230(2)	3936.7(8)	28.3(6)
C4	5166(3)	7441(2)	1879.4(8)	25.2(6)
C2	5507(3)	7866(2)	2569.7(8)	27.3(6)
C22	3704(3)	5882(2)	4324.6(8)	27.5(6)
C17	4411(3)	6837(2)	3106.8(8)	28.3(6)
C16	2861(3)	5671(2)	2497.5(9)	29.2(6)
C9	3803(3)	6231(2)	1288.3(8)	29.0(6)
C14	2513(3)	5257(2)	1803.8(9)	29.9(6)
C23	4507(3)	6414(2)	4606.5(8)	30.0(6)
C3	5806(3)	8044(2)	2174.5(8)	27.7(6)
C7	5470(3)	7596(2)	1467.1(8)	29.6(6)
C8	4815(3)	7025(2)	1186.1(9)	30.8(6)
C25	5091(3)	7667(2)	4113.9(9)	30.5(6)
C24	5188(3)	7308(2)	4499.1(9)	31.4(6)
C26	2914(4)	4933(2)	4430.4(9)	32.7(7)
C15	2216(3)	5096(2)	2214.5(9)	31.2(7)
C11	3125(3)	5621(3)	1001.7(9)	35.0(7)
C13	1868(4)	4669(2)	1506.6(10)	36.1(7)
C12	2177(4)	4855(3)	1110.4(10)	38.1(7)
F4	5783(8)	8799(2)	4801.1(14)	187(3)
C27	6080(4)	7880(3)	4790.8(10)	44.9(9)
F5	7500(5)	7910(6)	4696.9(11)	182(3)

Table 9S-(3): Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_283_Py(CF3). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F2	57.2(12)	42.4(11)	26.7(9)	7.2(8)	2.1(8)	-4.9(9)
F1	45.9(12)	67.1(15)	69.9(15)	31.0(12)	-18.2(11)	-21.3(11)
F3	98.3(19)	32.7(11)	60.0(14)	-6.4(10)	38.9(13)	-3.3(11)
F6	130(3)	77.5(17)	30.2(11)	6.2(11)	-24.2(13)	-43.5(17)
N1	35.4(14)	33.2(14)	29.9(12)	1.3(10)	-3.3(10)	-2.4(11)
C5	20.9(12)	25.8(13)	25.9(13)	1.4(10)	0.3(10)	4.7(10)
C6	21.9(12)	26.9(13)	26.6(13)	1.8(11)	1.0(10)	5.1(10)
C1	24.0(13)	28.8(14)	25.4(13)	2.0(11)	1.2(10)	4.5(11)
C20	25.6(13)	32.1(14)	24.0(13)	2.7(11)	-0.5(10)	4.6(11)
C18	23.3(13)	32.3(14)	26.0(13)	3.2(11)	-1.7(10)	-0.5(11)
C19	25.9(13)	35.2(16)	21.7(12)	1.0(11)	-1.9(10)	-2.7(11)
C10	22.2(12)	28.2(14)	28.8(14)	-2.4(11)	-2.0(10)	5.2(11)
C21	29.1(14)	31.9(14)	23.9(13)	0.1(11)	0.1(11)	2.6(12)
C4	22.4(13)	29.2(14)	24.0(13)	1.3(11)	2.8(10)	2.3(11)
C2	25.7(13)	31.3(14)	24.9(13)	-1.4(11)	0.5(10)	0.6(11)
C22	28.7(14)	29.7(14)	24.2(13)	2.0(11)	0.6(10)	4.3(11)
C17	25.7(13)	32.4(15)	26.8(13)	3.4(11)	0.9(11)	2.8(11)

C16	26.8(13)	30.2(14)	30.8(14)	4.8(12)	2.8(11)	2.5(11)
C9	25.9(13)	35.4(15)	25.7(13)	-1.3(11)	-0.6(11)	7.3(12)
C14	24.3(13)	29.9(15)	35.6(16)	-0.4(12)	-1.7(11)	3.5(11)
C23	31.8(14)	35.5(15)	22.6(13)	2.8(11)	-1.8(11)	3.7(12)
C3	25.9(13)	29.2(14)	27.9(14)	0.5(11)	3.1(11)	-1.8(11)
C7	27.6(14)	33.9(15)	27.1(14)	3.3(11)	4.9(11)	1.3(12)
C8	29.9(14)	37.9(16)	24.5(13)	0.7(12)	2.9(11)	5.9(12)
C25	30.3(14)	32.4(15)	28.8(14)	4.0(12)	-2.9(11)	1.1(12)
C24	33.2(15)	35.4(16)	25.6(14)	0.8(12)	-3.5(11)	2.2(12)
C26	39.6(17)	35.7(16)	22.7(13)	1.6(12)	-0.8(12)	0.3(13)
C15	26.6(14)	30.2(15)	36.9(16)	2.2(12)	2.1(11)	-1.6(11)
C11	32.0(15)	43.5(17)	29.5(14)	-5.4(13)	-4.7(12)	9.0(13)
C13	31.4(15)	35.2(16)	41.7(17)	-5.5(14)	-3.5(13)	-1.6(13)
C12	33.2(16)	43.2(18)	38.0(17)	-11.8(14)	-6.5(13)	3.5(13)
F4	345(8)	45.6(17)	170(4)	-21(2)	-203(5)	8(3)
C27	54(2)	47(2)	33.7(17)	8.6(15)	-13.0(15)	-14.8(17)
F5	90(3)	384(9)	70(2)	-75(4)	2(2)	-115(4)

Table 10S-(3): Bond Lengths for exp_283_Py(CF3).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F2	C26	1.336(3)	C21	C22	1.396(4)
F1	C26	1.335(4)	C4	C3	1.403(4)
F3	C26	1.330(4)	C4	C7	1.437(4)
F6	C27	1.281(4)	C2	C3	1.385(4)
N1	C19	1.152(4)	C22	C23	1.387(4)
C5	C6	1.419(4)	C22	C26	1.492(4)
C5	C10	1.430(4)	C16	C15	1.356(4)
C5	C4	1.423(4)	C9	C8	1.433(4)
C6	C1	1.415(4)	C9	C11	1.402(4)
C6	C16	1.437(4)	C14	C15	1.432(4)
C1	C2	1.396(4)	C14	C13	1.399(4)
C1	C17	1.467(4)	C23	C24	1.387(4)
C20	C18	1.490(4)	C7	C8	1.352(4)
C20	C21	1.393(4)	C25	C24	1.392(4)
C20	C25	1.387(4)	C24	C27	1.480(4)
C18	C19	1.443(4)	C11	C12	1.376(5)
C18	C17	1.340(4)	C13	C12	1.392(5)
C10	C9	1.422(4)	F4	C27	1.253(5)
C10	C14	1.421(4)	C27	F5	1.305(5)

Table 11S-(3): Bond Angles for exp_283_Py(CF3).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C5	C10	120.4(3)	C11	C9	C10	119.2(3)
C6	C5	C4	120.4(3)	C11	C9	C8	122.1(3)
C4	C5	C10	119.2(2)	C10	C14	C15	118.7(3)
C5	C6	C16	118.3(3)	C13	C14	C10	118.8(3)
C1	C6	C5	119.0(3)	C13	C14	C15	122.6(3)

C1	C6	C16	122.7(3)	C24	C23	C22	119.0(3)
C6	C1	C17	120.0(3)	C2	C3	C4	120.8(3)
C2	C1	C6	119.8(3)	C8	C7	C4	121.5(3)
C2	C1	C17	120.0(3)	C7	C8	C9	121.2(3)
C21	C20	C18	120.6(3)	C20	C25	C24	119.9(3)
C25	C20	C18	119.8(3)	C23	C24	C25	120.9(3)
C25	C20	C21	119.6(3)	C23	C24	C27	120.2(3)
C19	C18	C20	115.6(3)	C25	C24	C27	118.8(3)
C17	C18	C20	122.3(3)	F2	C26	C22	113.1(2)
C17	C18	C19	122.1(3)	F1	C26	F2	106.0(3)
N1	C19	C18	174.5(3)	F1	C26	C22	112.3(3)
C9	C10	C5	120.4(3)	F3	C26	F2	106.6(3)
C14	C10	C5	119.7(3)	F3	C26	F1	106.1(3)
C14	C10	C9	119.8(3)	F3	C26	C22	112.2(3)
C20	C21	C22	119.9(3)	C16	C15	C14	121.5(3)
C5	C4	C7	119.0(3)	C12	C11	C9	120.6(3)
C3	C4	C5	118.8(2)	C12	C13	C14	120.8(3)
C3	C4	C7	122.2(3)	C11	C12	C13	120.7(3)
C3	C2	C1	121.2(3)	F6	C27	C24	116.0(3)
C21	C22	C26	118.6(3)	F6	C27	F5	103.4(4)
C23	C22	C21	120.6(3)	F4	C27	F6	109.3(4)
C23	C22	C26	120.8(3)	F4	C27	C24	114.1(3)
C18	C17	C1	128.0(3)	F4	C27	F5	100.5(5)
C15	C16	C6	121.3(3)	F5	C27	C24	111.9(3)
C10	C9	C8	118.7(3)				

Table 12S-(3): Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_283_Py(CF3).

Atom	*x*	*y*	*z*	U(eq)
H21	3070.02	5868.08	3749.62	34
H2	5939.49	8275.66	2760.56	33
H17	4378.26	6157.22	3168.51	34
H16	2640.14	5548.02	2761.46	35
H23	4586.2	6173.78	4863.48	36
H3	6439.03	8568.8	2103.89	33
H7	6130.79	8101.06	1392.02	35
H8	5025.16	7148.99	921.62	37
H25	5539.48	8273.49	4046.85	37
H15	1565.86	4583.68	2288.83	37
H11	3317.17	5736.88	735.72	42
H13	1225.78	4147.23	1574.71	43
H12	1737.54	4456.09	916.93	46

Crystal structure determination of compound-3[exp_283_Py(CF3)]

Crystal Data for $C_{27}H_{13}F_6N$ (M =465.38 g/mol): orthorhombic, space group Pbca (no. 61), a = 8.9151(2) Å, b = 13.3283(3) Å, c = 33.8692(7) Å, V = 4024.44(15) Å^3, Z = 8, T = 93(2) K, μ(CuKα) = 1.113 mm^{-1}, $Dcalc$ = 1.536 g/cm^3, 13860 reflections measured (10.448° ≤ 2Θ ≤ 149.096°), 4002 unique (R_{int} = 0.0347, R_{sigma} = 0.0309) which were used in all calculations. The final R_1 was 0.0776 (I > 2σ(I)) and wR_2 was 0.2251 (all data).

Refinement model description

Number of restraints - 15, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2. Restrained distances
 F6-C27 = F4-C27 = F5-C27
 1.31 with sigma of 0.02
 F4-C27
 1.31 with sigma of 0.02
 F5-C27
 1.31 with sigma of 0.02
 F6-C27
 1.31 with sigma of 0.02
 F4-C27 = C27-F5
 1.31 with sigma of 0.02
 F5-C27 = C27-F6
 1.31 with sigma of 0.02
 F4-C27 = C27-F6
 1.31 with sigma of 0.02
 F4-F5
 2.133 with sigma of 0.04
 F5-F6
 2.133 with sigma of 0.04
 F4-F6
 2.133 with sigma of 0.04
3.a Aromatic/amide H refined with riding coordinates:
 C21(H21), C2(H2), C17(H17), C16(H16), C23(H23), C3(H3), C7(H7), C8(H8),
 C25(H25), C15(H15), C11(H11), C13(H13), C12(H12)
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