Supplementary Information

Aggregation Induced Emission (AIE) based Donor-π-acceptor Fluorophores: An approach to fabricate acidochromic sensors and white light emitting diodes

Snigdhamayee Rana[a], Sivakumar Vaidyanathan[b*], Sabita Patel[a*]

[a]Department of Chemistry, National Institute of Technology Rourkela, Rourkela-769 008, Odisha, India. E-mail: sabitap@nitrkl.ac.in

[b]Department of Chemistry, Indian Institute of Technology, Hyderabad, Kandi, Sangareddy-502285, Telangana, India. E-mail: vsiva@chy.iith.ac.in

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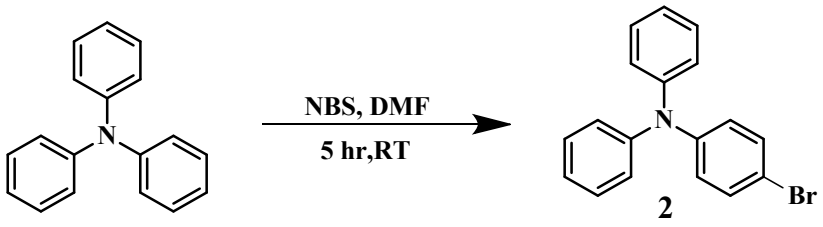
1. Synthesis

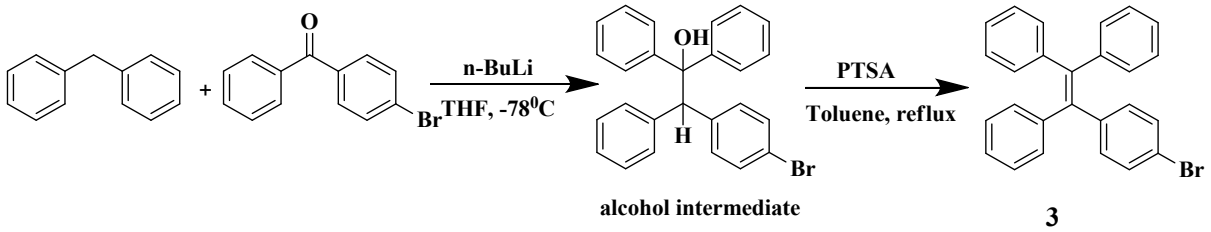
1.1. Synthesis procedure of 4-Bromotriphenylamine:



Scheme S1: Synthesis procedure for 4-Bromotriphenylamine.

To a solution of triphenylamine (1g, 4.08 mmol) was added n-Bromosuccinimide (577 mg, 4.89 mmol) was stirred with THF (20 mL) under nitrogen atmosphere at room temperature for 20 hr. Then the reaction was quenched by adding water and extracted with dichloromethane three times. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. Finally, the crude product was purified by silica column chromatography to afford 4-Bromotriphenylamine as a white amorphous solid (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.31 – 7.25 (m, 4H), 7.12 – 7.03 (m, 6H), 7.00 – 6.95 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.38, 147.03, 132.16, 129.39, 125.14, 124.42, 123.23, 114.76. (Fig. S1 and S2)

1.2. Synthesis procedure of 1-(4-Bromophenyl)-1,2,2-triphenylethylene**:**



Scheme S2: Synthesis procedure for 1-(4-Bromophenyl)-1,2,2-triphenylethylene.

Diphenylmethane, n-butyllithium, and 4-bromobenzophenone were used as starting materials in a low-temperature reaction setup to synthesize 1-(4-Bromophenyl)-1,2,2-triphenylethylene.

Under nitrogen atmosphere, n-Butyllithium (2 M in hexane, 0.59 mmol) was added dropwise at -78°C to the colorless stirred mixture of dry THF (10mL) and diphenylmethane (0.59 mmol) and was allowed to stir for 20 min at -78°C. The colourless reaction mixture turned yellowish-orange after the addition of n-butyllithium. The yellowish-orange mixture was then mixed with a solution of 4-bromobenzophenone (0.49 mmol) in dry THF (10 mL), which was then stirred for 30 minutes at -78^{0}C. After that, the reaction mixture was stirred at room temperature for 12 hours. Following the end of the reaction, the mixture was quenched with an aqueous solution of ammonium chloride before being extracted with dichloromethane (3 x 50 mL). The solvent evaporation process was then carried out to produce the alcohol intermediate by collecting and drying the dichloromethane layers over anhydrous sodium sulphate. The alcohol intermediate was then dissolved in toluene (60 mL), to which p-toluene sulfonic acid (PTSA) (30 mg) was added, and the mixture was refluxed for 16 hours. As soon as the reaction was finished, the mixture was cooled to room temperature and evaporated on a rotary evaporator. The resulting crude residue was then purified using column chromatography and hexane to get 1-(4-Bromophenyl)-1,2,2-triphenylethylene as a white solid (yield 20%).

Alcohol intermediate ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.50 – 7.43 (m, 6H), 7.37 (d, J = 4.3 Hz, 6H), 7.34 – 7.25 (m, 8H), 7.21 – 7.16 (m, 3H), 5.80 (s, 1H). (Fig. S3)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.24 (d, J = 7.7 Hz, 3H), 7.14 (d, J = 10.2 Hz, 11H), 7.04 (s, 3H), 6.92 (d, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.41, 143.33, 143.22, 142.71, 141.61, 139.66, 132.98, 131.29, 131.24, 131.22, 130.85, 127.88, 127.78, 127.68, 126.70, 126.64, 126.59, 120.44. (Fig. S4 and S5)

2. NMR Spectra

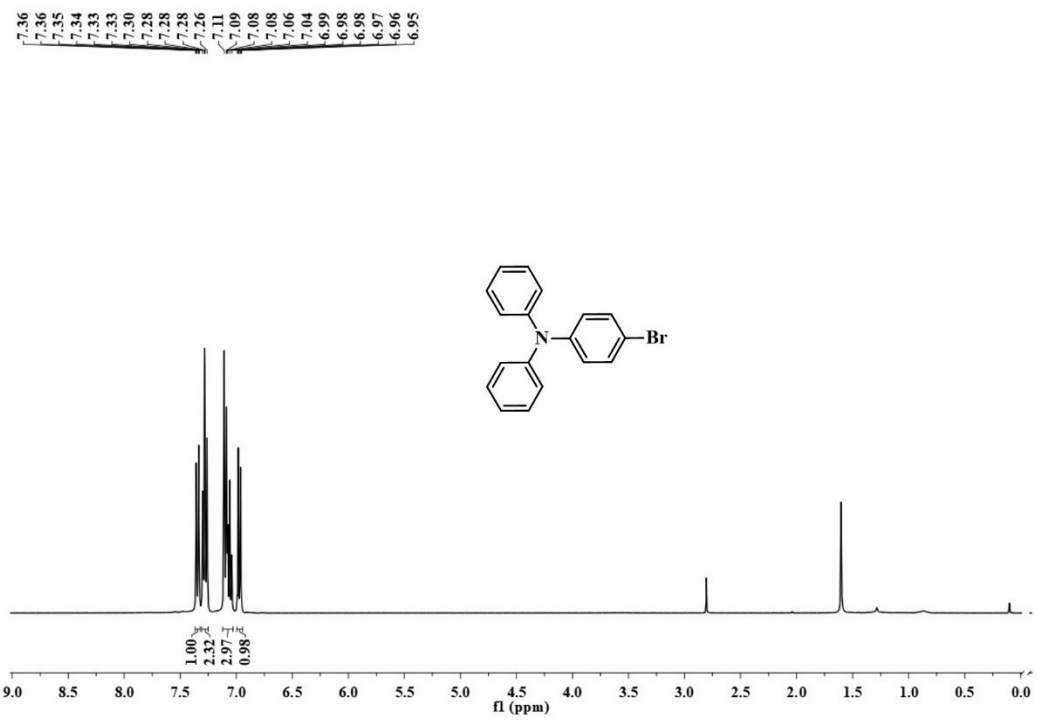


Fig. S1 ^{1}H NMR spectrum of 4-Bromotriphenylamine in $CDCl_3$.

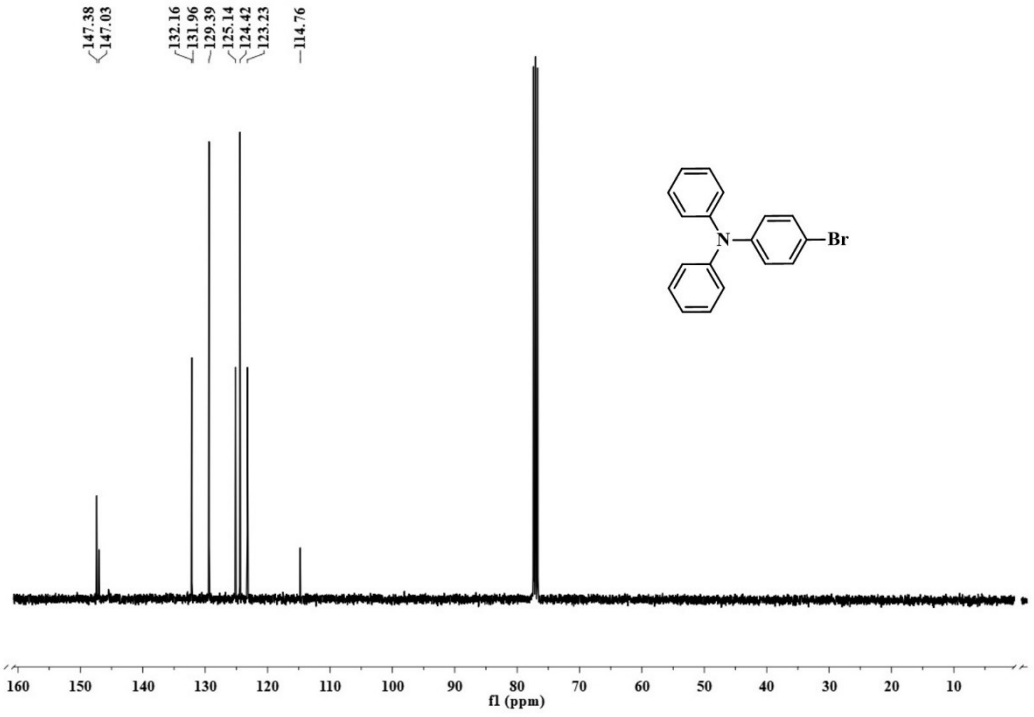


Fig. S2 ^{13}C NMR spectrum of 4-Bromotriphenylamine in $CDCl_3$.

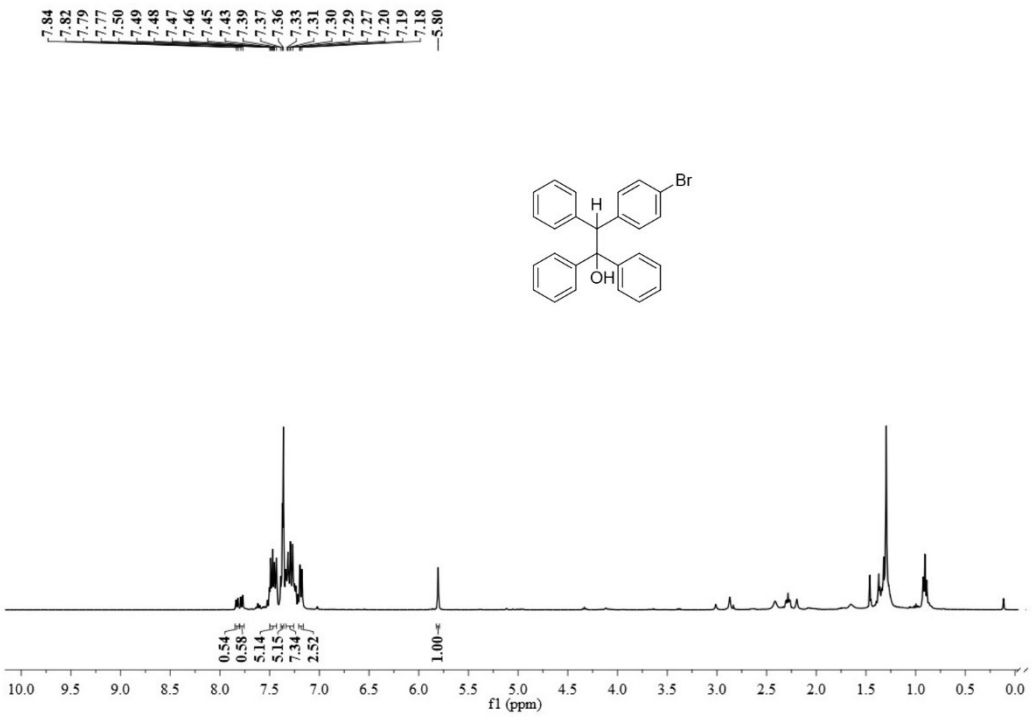


Fig. S3 ^{1}H NMR spectrum of alcohol intermediate in $CDCl_3$.

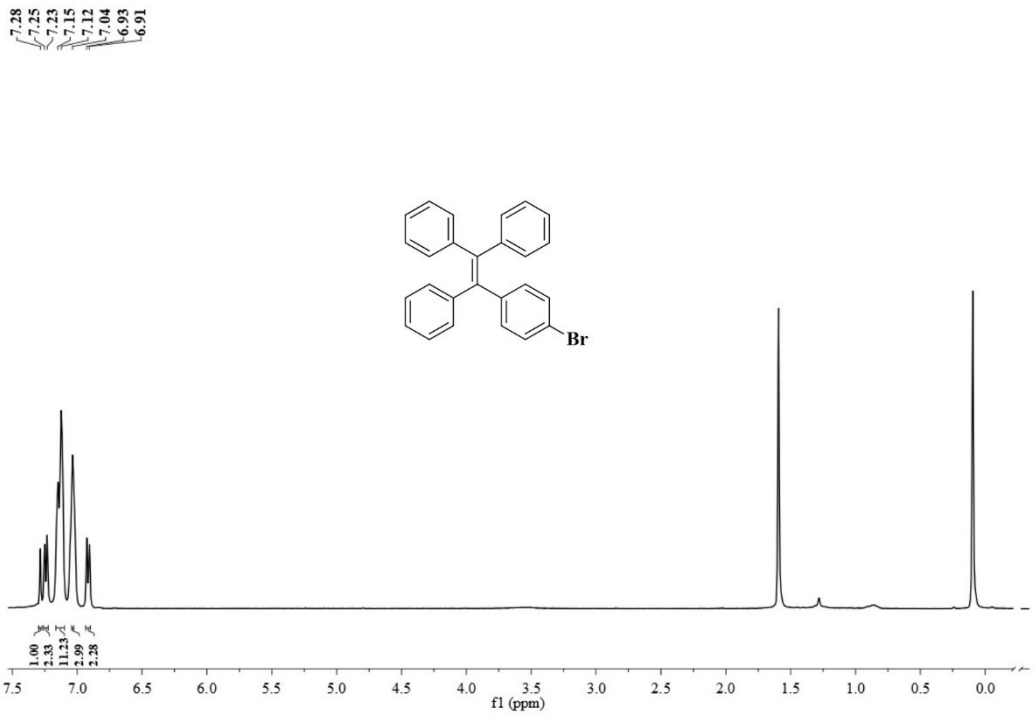


Fig. S4 ^{1}H NMR spectrum of 1-(4-Bromophenyl)-1,2,2-triphenylethylene in $CDCl_3$.

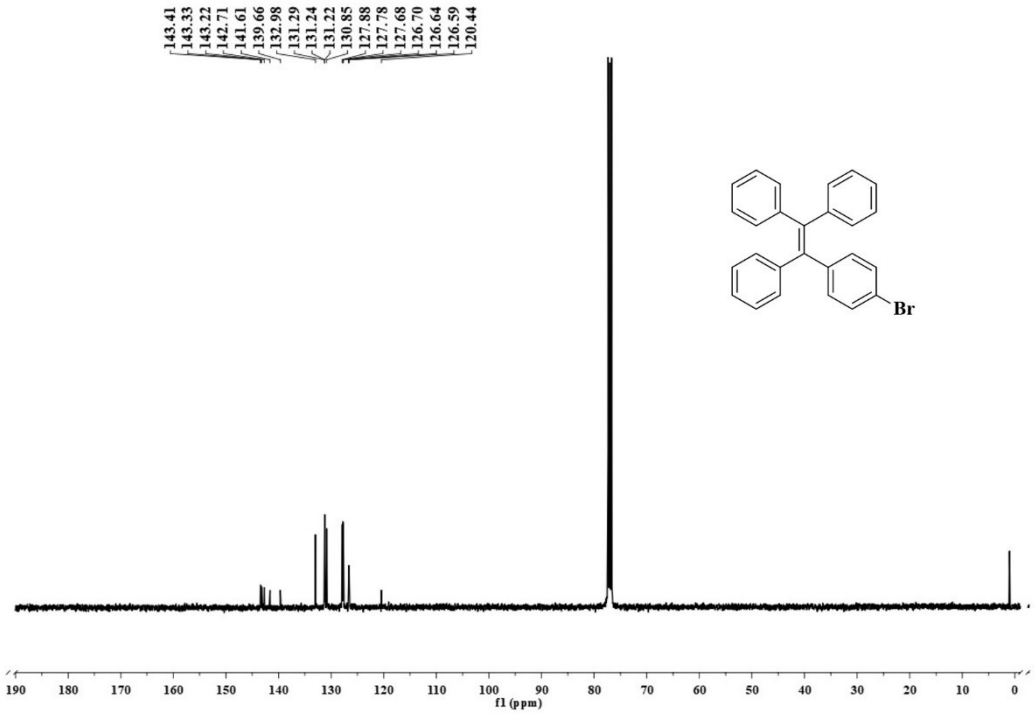


Fig. S5 ^{13}C NMR spectrum of 1-(4-Bromophenyl)-1,2,2-triphenylethylene in $CDCl_3$.

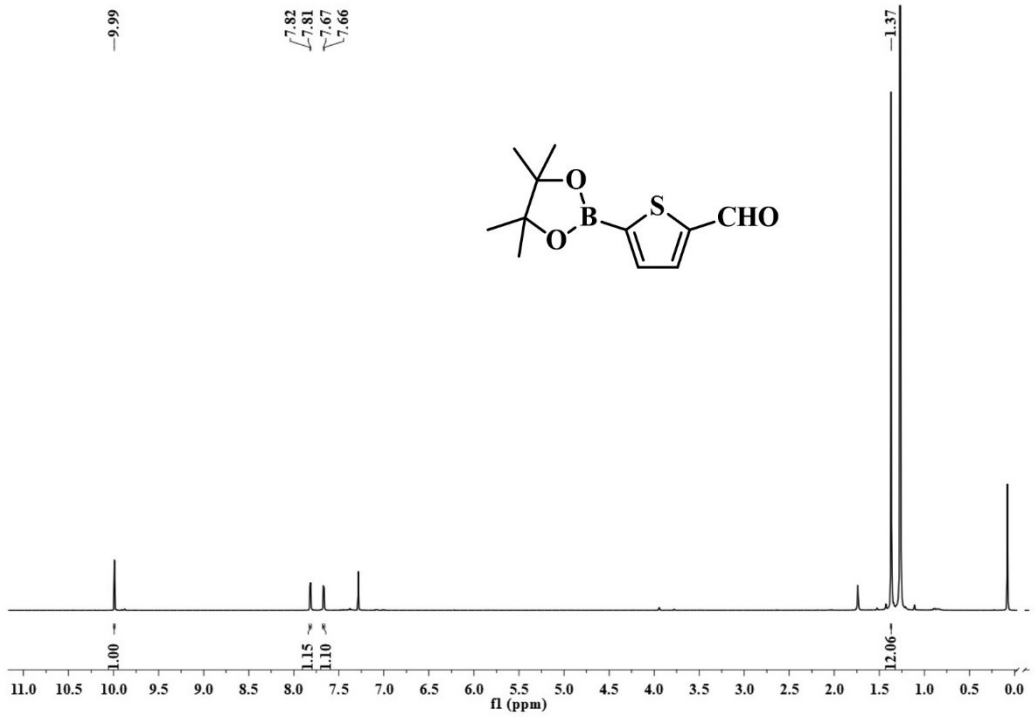


Fig. S6 ^{1}H NMR spectrum of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene-2-carbaldehyde (**1**) in $CDCl_3$.

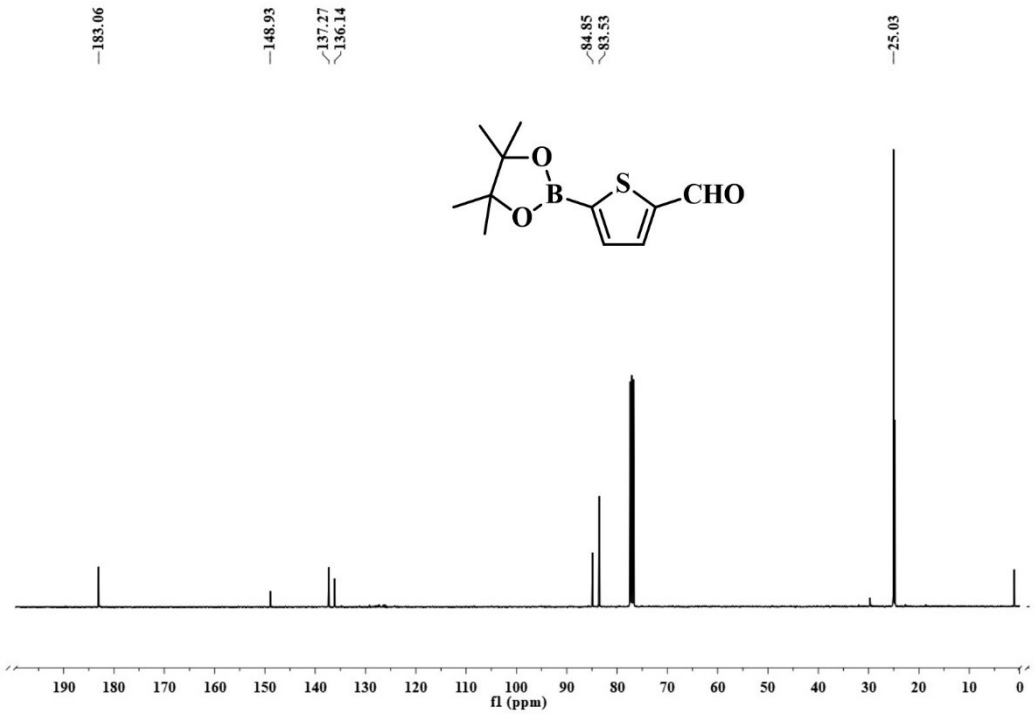


Fig. S7 ^{13}C NMR spectrum of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiophene-2-carbaldehyde (**1**) in $CDCl_3$.

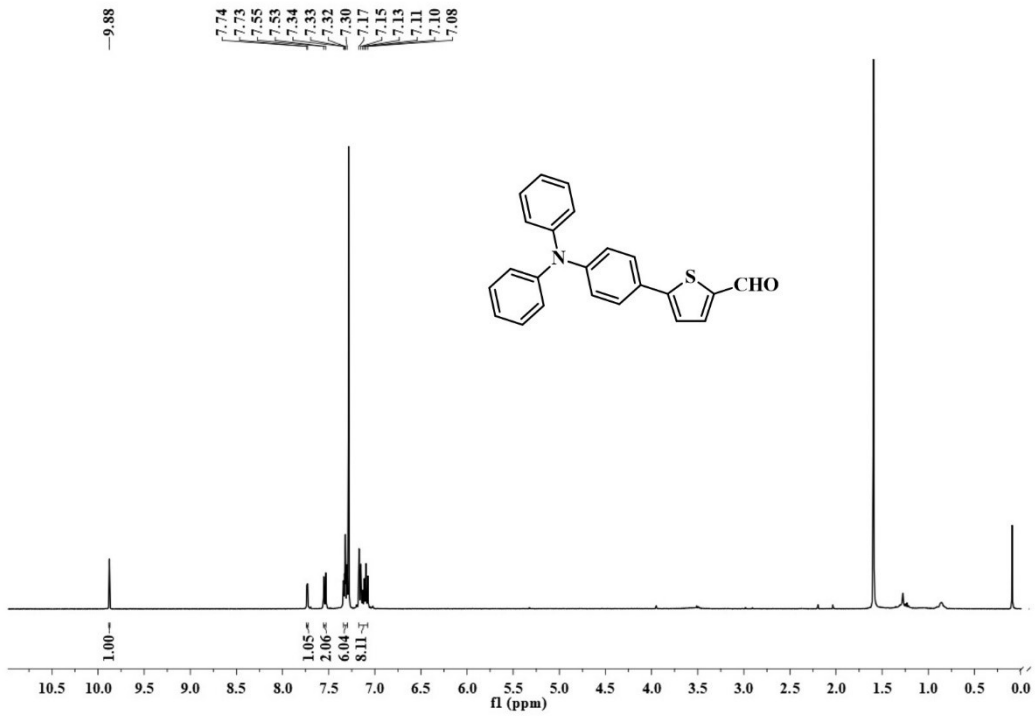


Fig. S8 ^{1}H NMR spectrum of 5-(4-(diphenylamino) phenyl) thiophene-2-carbaldehyde (**2**) in $CDCl_3$.

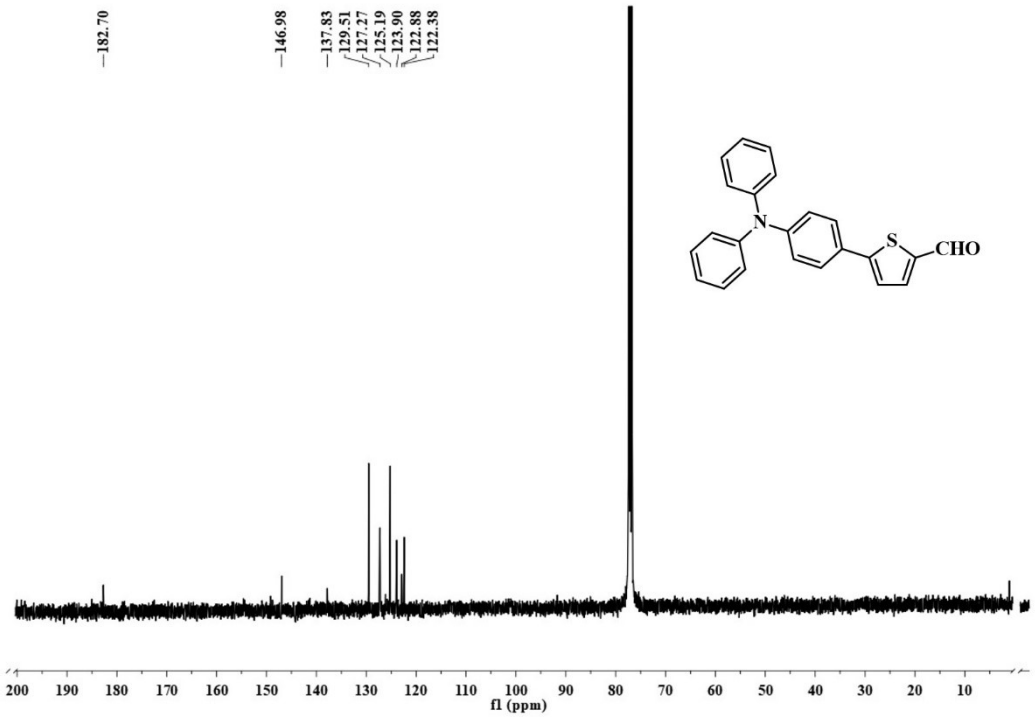


Fig. S9 ^{13}C NMR spectrum of 5-(4-(diphenylamino) phenyl) thiophene-2-carbaldehyde (**2**) in $CDCl_3$.

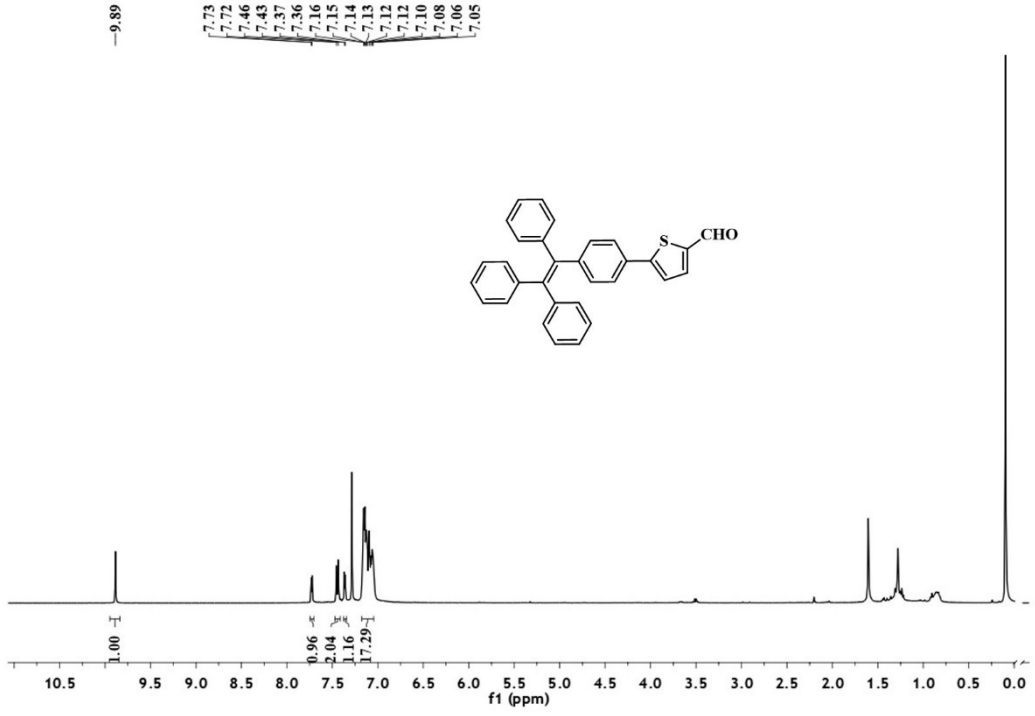


Fig. S10 ^{1}H NMR spectrum of 5-(4-(1,2,2-triphenylvinyl) phenyl) thiophene-2-carbaldehyde (**3**) in $CDCl_3$.

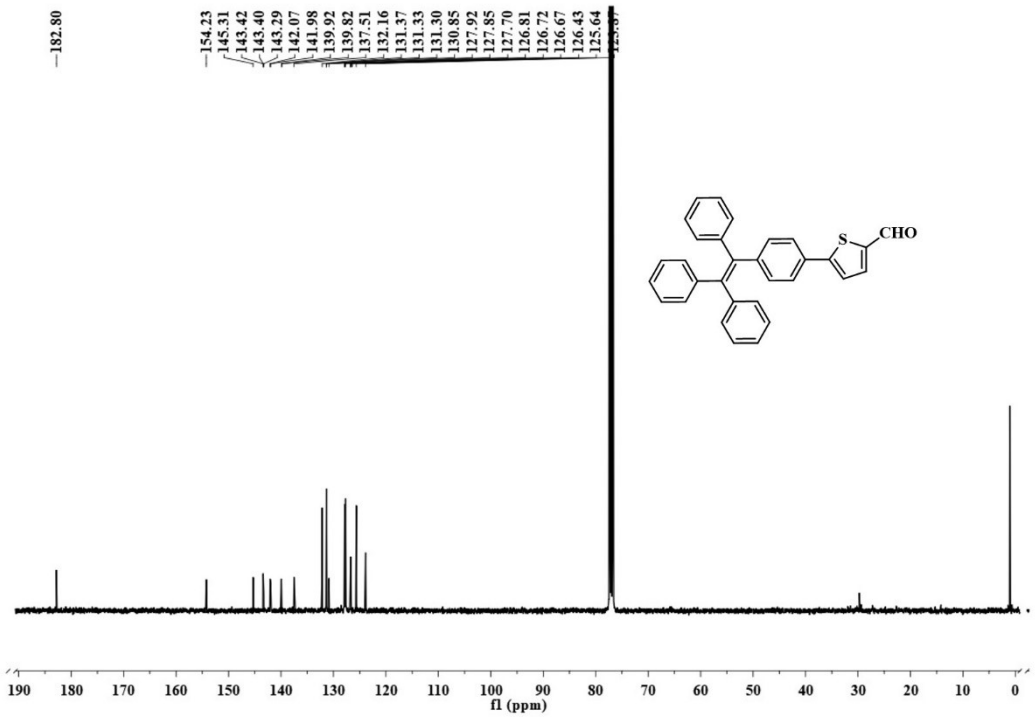


Fig. S11 ^{13}C NMR spectrum of 5-(4-(1,2,2-triphenylvinyl) phenyl) thiophene-2-carbaldehyde (**3**) in $CDCl_3$.

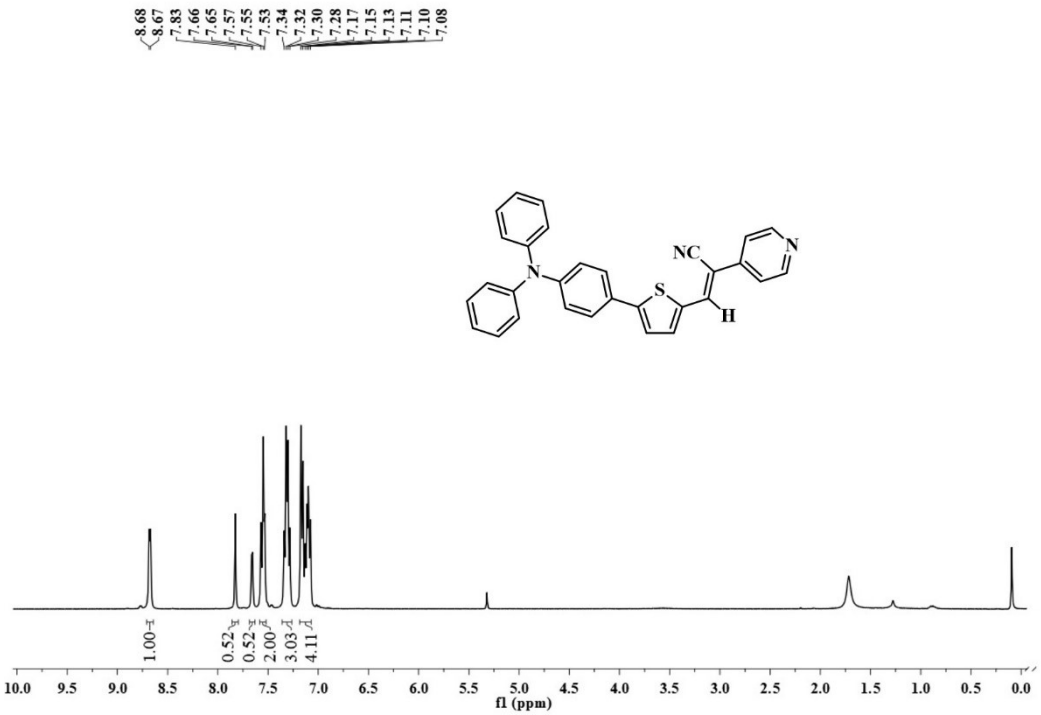


Fig. S12 ^{1}H NMR spectrum of 3-(5-(4-(diphenylamino) phenyl) thiophen-2-yl)-2-(pyridin-4-yl) acrylonitrile (**TPASCNPy)** in $CDCl_3$.

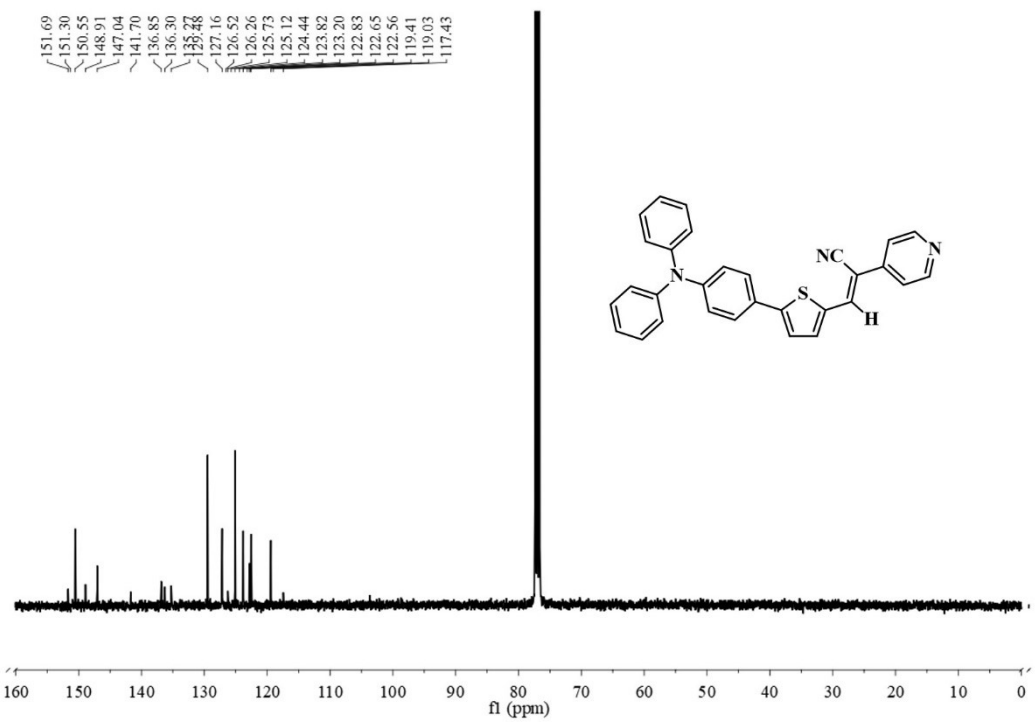


Fig. S13 ^{13}C NMR spectrum of 3-(5-(4-(diphenylamino) phenyl) thiophen-2-yl)-2-(pyridin-4-yl) acrylonitrile (**TPASCNPy)** in $CDCl_3$.

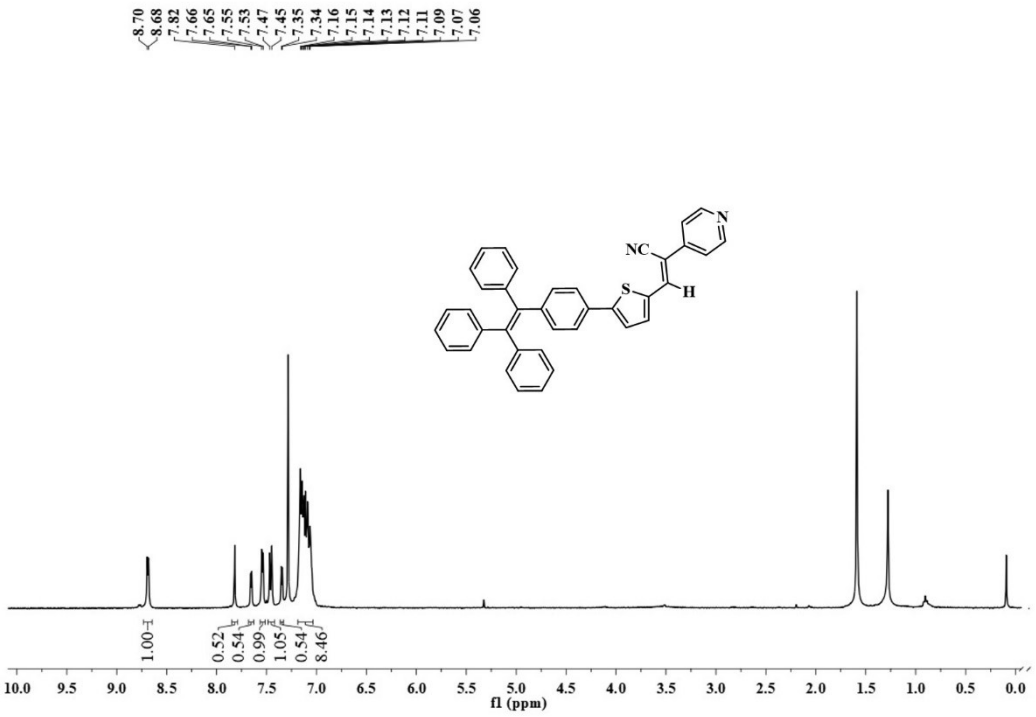


Fig. S14 ^{1}H NMR spectrum of 2-(pyridin-4-yl)-3-(5-(4-(1,2,2-triphenylvinyl) phenyl) thiophen-2-yl) acrylonitrile (**TPESCNPy)** in $CDCl_3$.

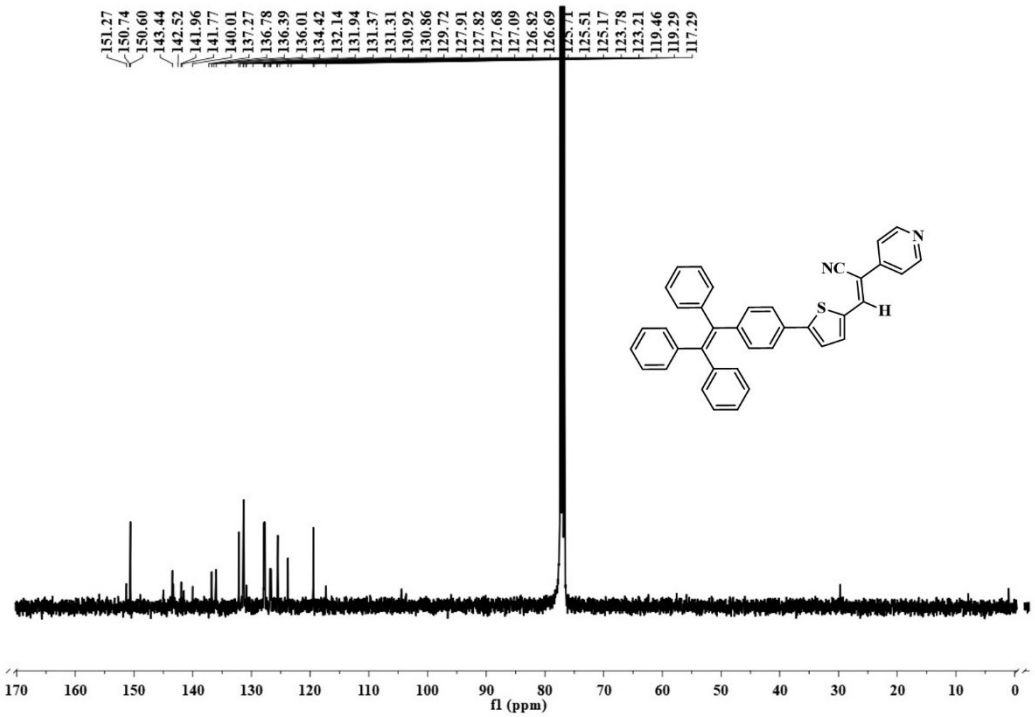


Fig. S15 ^{13}C NMR spectrum of 2-(pyridine-4-yl)-3-(5-(4-(1,2,2-triphenylvinyl) phenyl) thiophen-2-yl) acrylonitrile (**TPESCNPy)** in $CDCl_3$.

3. HRMS data

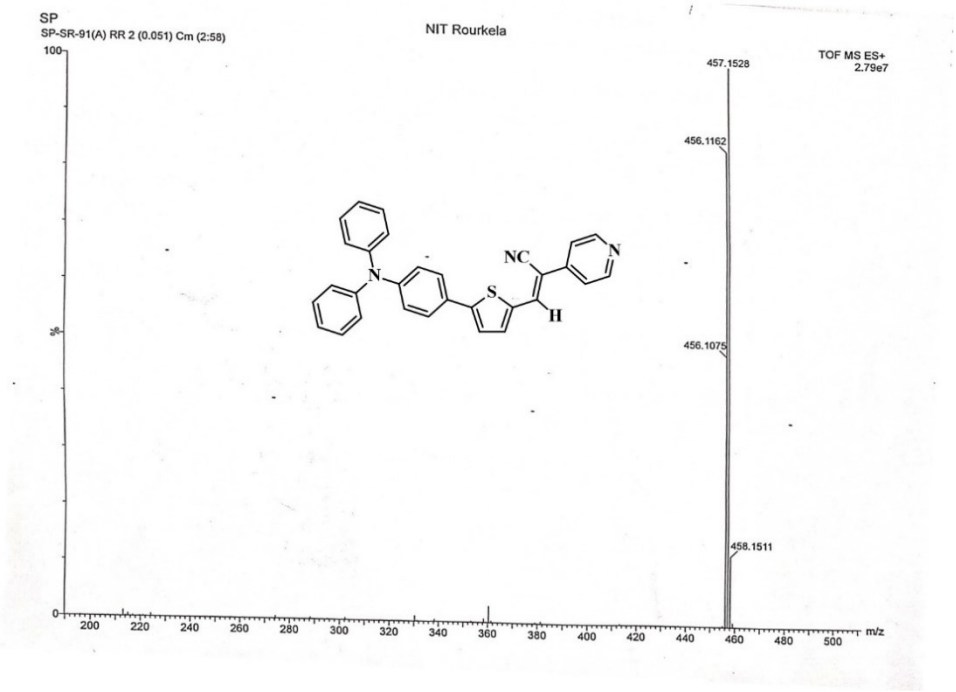


Fig. S16 HRMS spectrum of 3-(5-(4-(diphenylamino) phenyl) thiophen-2-yl)-2-(pyridin-4-yl) acrylonitrile (**TPASCNPy).**

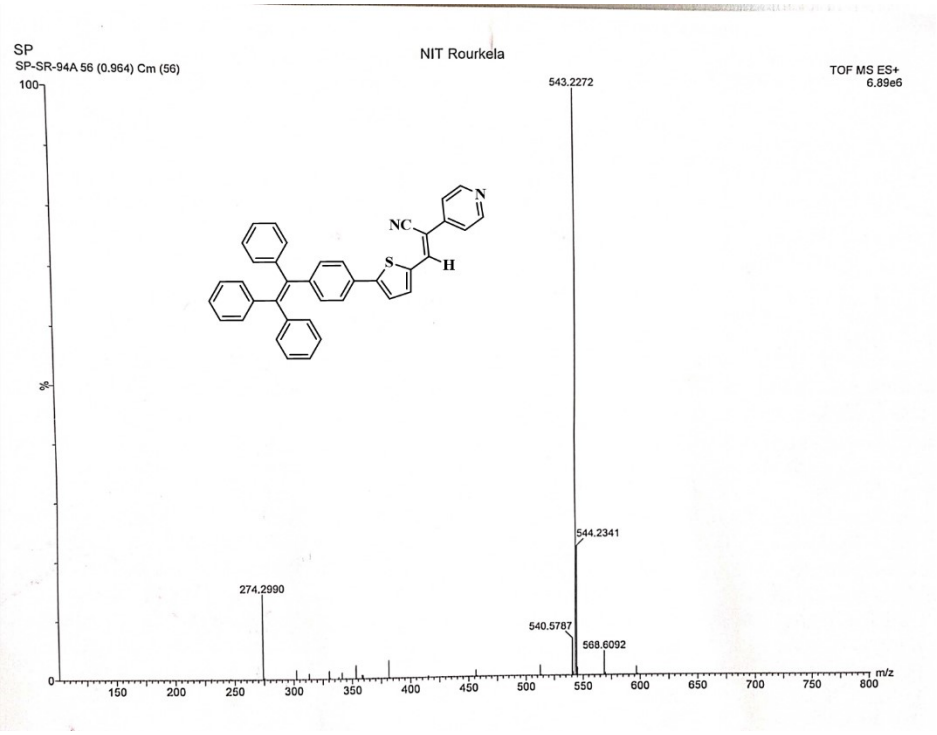


Fig. S17 HRMS spectrum of 2-(pyridine-4-yl)-3-(5-(4-(1,2,2-triphenylvinyl) phenyl) thiophen-2-yl) acrylonitrile (**TPESCNPy).**

4. FT-IR study of TPASCNPy and TPESCNPy

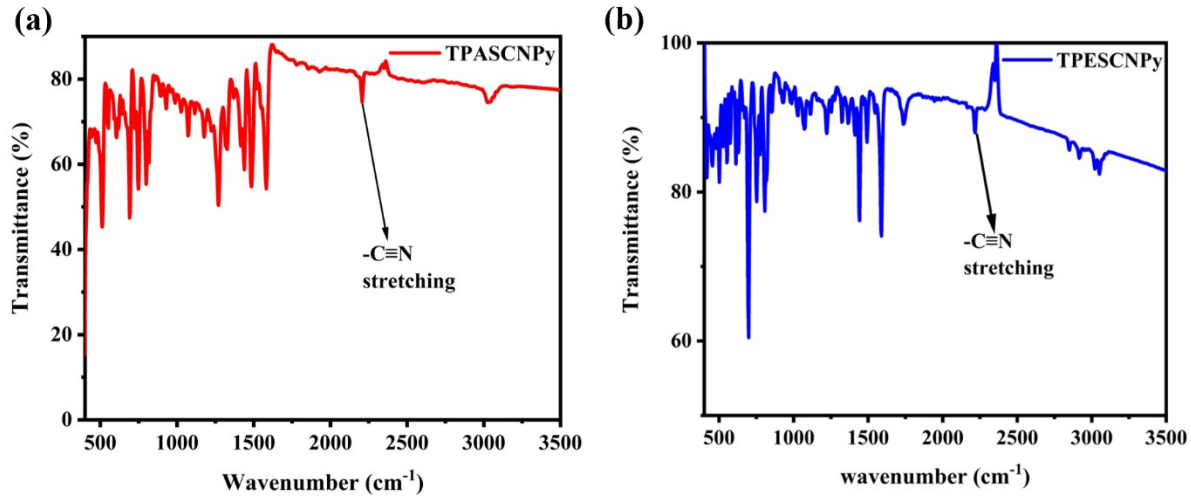


Fig. S18 FT-IR analysis of (a) **TPASCNPy** (b) **TPESCNPy**.

5. Crystal data of TPASCNPy

Table S1. Bond Lengths for TPASCNPy.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C22	1.729(2)	C21	C22	1.367(3)
S1	C19	1.723(2)	C21	C20	1.394(3)
N1	C12	1.414(2)	C13	C14	1.379(3)
N1	C5	1.417(2)	C26	C27	1.384(3)
N1	C13	1.426(2)	C26	C30	1.382(3)
C23	C24	1.345(3)	C19	C20	1.368(3)
C23	C22	1.432(3)	C6	C1	1.378(3)
N2	C25	1.142(2)	C15	C14	1.375(3)
C24	C25	1.439(3)	N3	C28	1.315(3)
C24	C26	1.481(3)	N3	C29	1.319(3)
C16	C17	1.386(3)	C7	C8	1.359(3)
C16	C19	1.466(2)	C27	C28	1.384(3)
C16	C15	1.386(3)	C4	C3	1.381(3)
C12	C7	1.386(3)	C11	C10	1.397(3)
C12	C11	1.372(3)	C30	C29	1.374(3)
C18	C13	1.377(3)	C1	C2	1.362(3)
C18	C17	1.383(2)	C8	C9	1.343(4)
C5	C6	1.387(3)	C3	C2	1.370(4)
C5	C4	1.388(3)	C9	C10	1.376(4)

Table S2. Bond Angles for TPASCNPy.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C19	S1	C22	92.26(10)	C27	C26	C24	121.8(2)
C12	N1	C5	119.95(15)	C30	C26	C24	121.9(2)
C12	N1	C13	118.97(15)	C30	C26	C27	116.3(2)
C5	N1	C13	119.29(16)	C18	C17	C16	121.5(2)
C24	C23	C22	132.2(2)	C16	C19	S1	122.02(16)
C23	C24	C25	121.06(18)	C20	C19	S1	110.63(14)
C23	C24	C26	122.7(2)	C20	C19	C16	127.35(19)
C25	C24	C26	116.19(19)	C19	C20	C21	113.10(19)
C17	C16	C19	122.46(19)	C1	C6	C5	120.3(2)
C15	C16	C17	117.19(18)	C14	C15	C16	121.4(2)
C15	C16	C19	120.3(2)	C28	N3	C29	114.7(2)
N2	C25	C24	178.2(2)	C8	C7	C12	120.8(2)
C7	C12	N1	119.46(19)	C15	C14	C13	120.8(2)
C11	C12	N1	121.27(19)	C28	C27	C26	119.4(2)
C11	C12	C7	119.2(2)	C3	C4	C5	120.8(2)
C13	C18	C17	120.5(2)	C12	C11	C10	119.3(2)
C6	C5	N1	121.79(19)	C29	C30	C26	118.8(2)
C6	C5	C4	118.2(2)	C2	C1	C6	120.8(2)
C4	C5	N1	119.98(19)	N3	C28	C27	124.8(3)

C22	C21	C20	114.09(19)	C9	C8	C7	120.2(3)
C23	C22	S1	127.10(17)	C2	C3	C4	119.9(2)
C21	C22	S1	109.92(15)	C1	C2	C3	120.0(2)
C21	C22	C23	122.98(19)	C8	C9	C10	120.9(3)
C18	C13	N1	120.3(2)	C9	C10	C11	119.4(3)
C18	C13	C14	118.52(18)	N3	C29	C30	126.0(3)
C14	C13	N1	121.18(19)				

6. Lippert–Mataga equation:

The Lippert–Mataga (L–M) theory describes the solvent dependency of spectral shifts as given in Equation S1.

$$\Delta v = va - vf = \frac{2}{hc}\left(\frac{\varepsilon - 1}{2\varepsilon - 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\frac{(\mu_E - \mu_G)2}{a^3} + \text{Constant} \quad \text{.....(S1)}$$

$$va = \frac{1}{\lambda_{abs}},\ vf = \frac{1}{\lambda_{em}} \text{ and } \Delta f = \left(\frac{\varepsilon - 1}{2\varepsilon - 1} - \frac{n^2 - 1}{2n^2 + 1}\right) \quad \text{..... (S2)}$$

Equation 1 shows that the Stokes shift ($\Delta\bar{v}$) depends on the dipole moments of the fluorophore in the ground (μG) and the excited (μE) state, respectively. It also depends on the dielectric constant (ε) and the refractive index (η) of the corresponding solvent. va and vf represent the wavenumbers of the absorption and the fluorescence emission, respectively, h is the Planck's constant, c is the speed of light in vacuum, and a is the Onsager radius of the cavity in which the fluorophore resides. Δf is the orientation polarizability of the solvent (Equation S2). Plotting the Stokes shift as a function of the orientation polarizability of the solvents gives the Lippert–Mataga plot (Fig. S19).

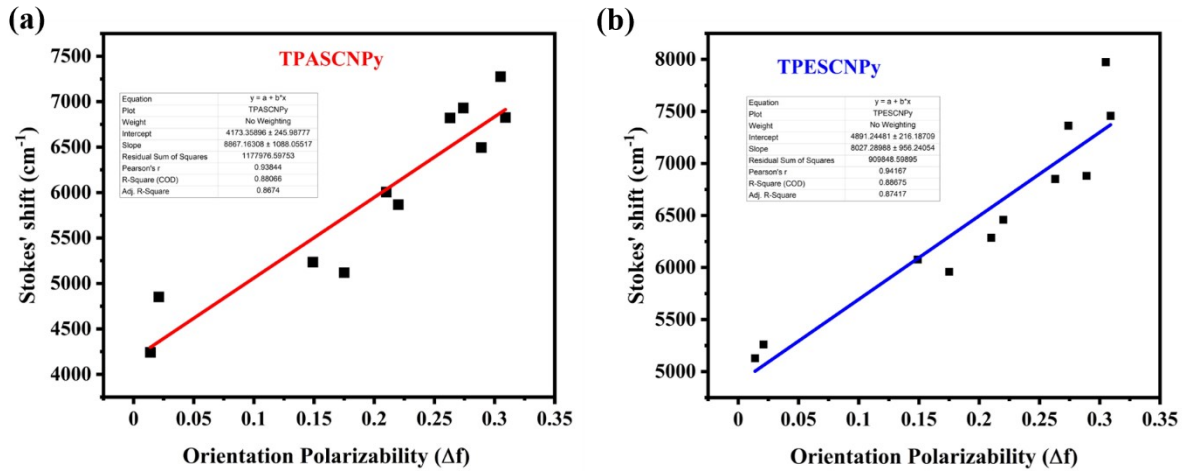


Fig. S19 Lippert–Mataga plot depicting Stokes shift ($\Delta\nu$) versus the solvent orientation polarizability (Δf) of (a) **TPASCNPy** and (b) **TPESCNPy**.

The change of the dipole moment (Δμ) can be estimated using the equation (1) from the slope obtained from the L–M plot as following

$$(\mu_E - \mu_G)_2 = \frac{Slpope * (hca^3)}{2} \quad \ldots\ldots (S3)$$

$\Delta\mu = (\mu_E - \mu_G)$ is the change of dipole moment from the ground to an excited state.

Table S3: Fitting parameters of Lippert–Mataga plots and calculated Onsager radius (a), $(\mu_E - \mu_G)$ refers to the change in dipole moment. (R^2: regression coefficient).

Compound	Slope (cm^{-1})	R^2	a (A°)	(μE − μG) D
TPASCNPy	8867	0.880	7.04	17.5
TPESCNPy	8027	0.886	8.41	21.86

7. Fluorescence Spectra of TPASCNPy and TPESCNPy in THF: water fraction and in thin film.

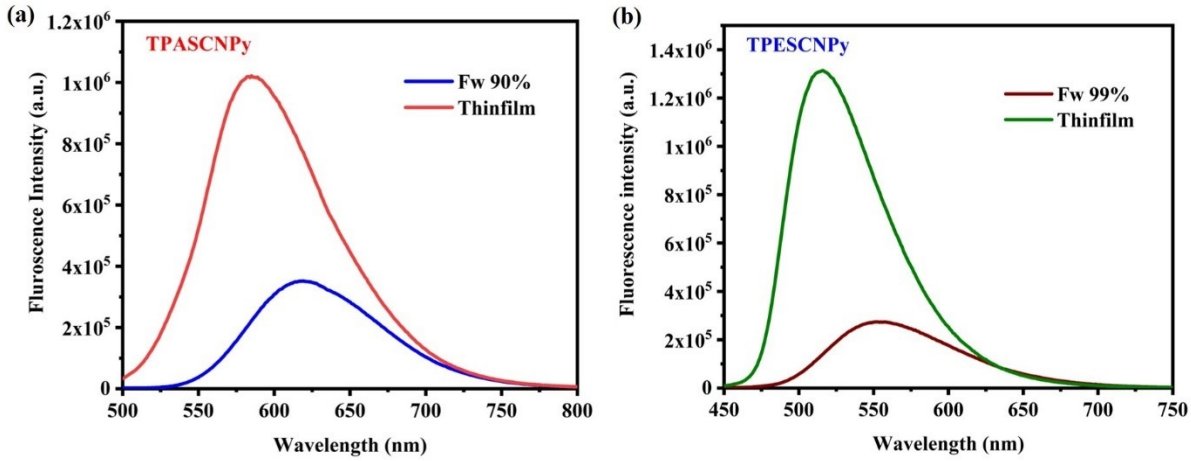


Fig. S20 Fluorescence Spectra of (a) TPASCNPy and (b)TPESCNPy in THF: water fraction and in a thin film.

8. Application on paper strips

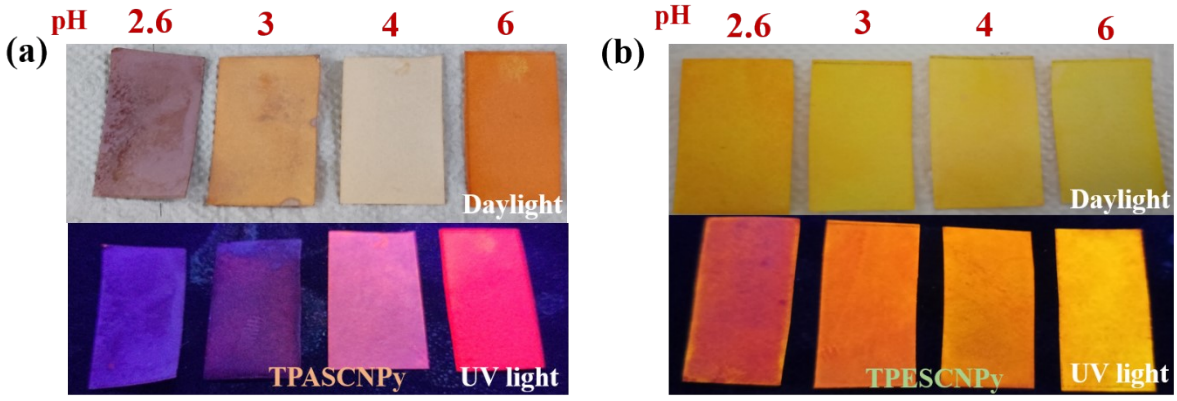


Fig. S21 Photographs of test strips with (a) **TPASCNPy** ($0.5x10^{-3}$ M); and (b) **TPESCNPy** ($0.5x10^{-3}$ M) upon dipping in different pH solutions in daylight and UV light.

Table S4. The optimized geometry coordinates for **TPASCNPy**

C	5.196071000	3.634553000	-1.124497000
C	4.662449000	2.352249000	-1.044649000
C	5.144854000	1.446029000	-0.091790000
C	6.175724000	1.844058000	0.768161000
C	6.714964000	3.122893000	0.670374000
C	6.226639000	4.026416000	-0.271655000
H	4.813497000	4.324970000	-1.867884000
H	3.871843000	2.046599000	-1.719351000
H	7.513194000	3.416877000	1.342669000
H	6.645099000	5.023568000	-0.341674000
N	4.605355000	0.129266000	-0.005143000
C	0.401818000	-0.484554000	-0.035044000
C	1.280888000	-1.411596000	-0.623222000
C	2.651092000	-1.213856000	-0.617267000
C	3.211586000	-0.074146000	-0.014716000
C	2.340516000	0.857173000	0.575633000
C	0.970686000	0.654242000	0.560324000
H	0.881438000	-2.283571000	-1.127499000
H	3.298995000	-1.937254000	-1.095708000
H	2.746707000	1.736170000	1.059477000
H	0.331413000	1.379009000	1.052284000
C	5.498577000	-0.976926000	0.097970000
C	5.276811000	-1.986951000	1.042844000
C	6.156257000	-3.060630000	1.139382000
C	7.275211000	-3.135258000	0.311687000
C	7.503348000	-2.126051000	-0.621960000
C	6.620154000	-1.057211000	-0.736617000
H	4.416266000	-1.924968000	1.697944000
H	5.972422000	-3.834779000	1.875971000

H	7.961954000	-3.969433000	0.394543000
H	8.367829000	-2.174800000	-1.274553000
C	-3.560392000	-0.489843000	-0.009219000
C	-3.116505000	-1.797205000	-0.139697000
C	-1.716435000	-1.916506000	-0.159860000
C	-1.039413000	-0.714018000	-0.047830000
S	-2.178213000	0.598396000	0.072595000
H	-3.784160000	-2.643482000	-0.204004000
H	-1.206212000	-2.868089000	-0.222752000
C	-4.868381000	0.088372000	0.061656000
C	-6.097762000	-0.498892000	-0.042493000
H	-4.878247000	1.164330000	0.202179000
C	-9.724428000	0.507383000	-0.356556000
C	-8.558423000	-0.243820000	-0.460773000
C	-7.362854000	0.263179000	0.066761000
C	-7.437614000	1.514163000	0.697431000
C	-8.654888000	2.182047000	0.744882000
N	-9.793388000	1.705828000	0.229629000
H	-10.653149000	0.122230000	-0.768310000
H	-8.581446000	-1.209454000	-0.951157000
H	-6.573444000	1.960094000	1.173957000
H	-8.720417000	3.150308000	1.233699000
C	-6.219395000	-1.897305000	-0.294683000
N	-6.329983000	-3.030646000	-0.499793000
H	6.795794000	-0.278542000	-1.468894000
H	6.551221000	1.146806000	1.507220000

Table S5. The optimized geometry coordinates for **TPESCNPy**

C	0.645748000	0.105078000	0.511547000
C	-0.247759000	-0.684361000	1.255636000
C	-1.618498000	-0.565795000	1.085536000
C	-2.163601000	0.341540000	0.163599000
C	-1.270028000	1.141452000	-0.565862000
C	0.101986000	1.020535000	-0.404580000
H	0.136589000	-1.411768000	1.960631000
H	-2.281627000	-1.188862000	1.672320000
H	-1.659670000	1.870518000	-1.266461000
H	0.760234000	1.663510000	-0.978147000
C	4.606648000	-0.005531000	0.470487000
C	4.165137000	-0.472104000	1.699042000
C	2.764870000	-0.478909000	1.826198000
C	2.089328000	-0.021702000	0.708950000
S	3.225870000	0.416536000	-0.534876000
H	4.833361000	-0.786805000	2.486642000
H	2.255702000	-0.784312000	2.730167000
C	5.914906000	0.177295000	-0.085781000
C	7.141707000	-0.118061000	0.435894000
H	5.924651000	0.601883000	-1.084414000
C	10.746601000	-0.269127000	-0.679968000
C	9.581832000	-0.538644000	0.031154000
C	8.406506000	0.156051000	-0.285113000
C	8.498755000	1.113513000	-1.306017000
C	9.713036000	1.303068000	-1.954163000
N	10.831876000	0.630829000	-1.663408000
H	11.660078000	-0.807871000	-0.444109000
H	9.590354000	-1.283655000	0.817534000

H	7.651821000	1.729486000	-1.581803000
H	9.793208000	2.044393000	-2.744527000
C	7.262098000	-0.742430000	1.712763000
N	7.371774000	-1.249918000	2.746631000
C	-3.637059000	0.503461000	-0.001444000
C	-3.095240000	-2.223063000	-1.428932000
C	-2.672118000	-3.525604000	-1.676363000
C	-3.143464000	-4.577212000	-0.893311000
C	-4.054229000	-4.317485000	0.129628000
C	-4.488575000	-3.017197000	0.366919000
C	-4.002019000	-1.944917000	-0.396285000
H	-2.725574000	-1.410643000	-2.042898000
H	-1.974764000	-3.719131000	-2.483869000
H	-2.810929000	-5.591392000	-1.083653000
H	-4.431730000	-5.130163000	0.740350000
H	-5.208408000	-2.825168000	1.154516000
C	-6.587291000	0.267286000	0.990305000
C	-5.970211000	-0.411946000	-0.070116000
C	-6.788783000	-1.005420000	-1.043193000
C	-8.173987000	-0.893265000	-0.977237000
C	-8.772486000	-0.206284000	0.077491000
C	-7.973135000	0.367119000	1.064285000
H	-5.974036000	0.716297000	1.761961000
H	-6.332097000	-1.553308000	-1.859572000
H	-8.787091000	-1.347802000	-1.747606000
H	-9.852181000	-0.125488000	0.133853000
H	-8.429078000	0.892082000	1.896368000
C	-4.485029000	-0.553602000	-0.143713000
C	-4.125873000	4.135851000	1.000297000
C	-3.705796000	2.809364000	1.004550000

C	-4.109996000	1.922071000	-0.004371000
C	-4.922523000	2.415045000	-1.034872000
C	-5.332110000	3.745061000	-1.046678000
C	-4.941111000	4.609455000	-0.026195000
H	-3.813117000	4.801455000	1.797240000
H	-3.062927000	2.452182000	1.801298000
H	-5.231344000	1.748856000	-1.831251000
H	-5.956923000	4.106644000	-1.855808000
H	-5.263389000	5.644590000	-0.033839000