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Synthesis and Photophysical Properties of Pyridyl Conjugated Triazole Appended Naphthalenediimide Derivatives

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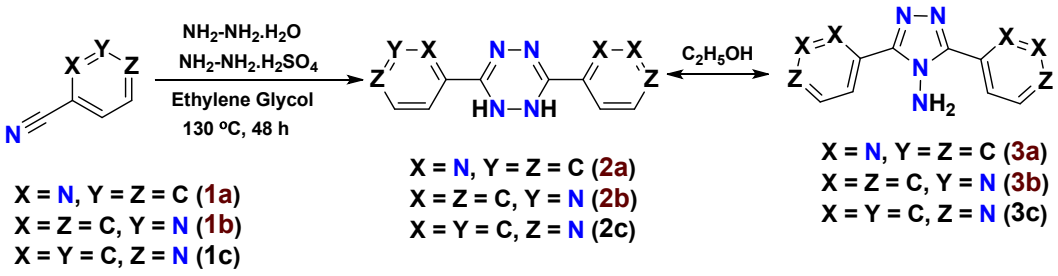
Synthesis of Pyridyl Substituted Triazole Units 3a – 3c.

3,5-di(pyridin-2-yl)-4H-1,2,4-triazol-4-amine (3a). Initially compound **2a** was synthesized by the slight modification of Geldard and Lions two steps method[S1]. Wherein, 2-cyanopyridine (**1a**) (10.4 g, 10 mmol) was condensed with $NH_2–NH_2•H_2O$ (14.56 mL, 30 mmol) and $NH_2–NH_2•H_2SO_4$ (13 g, 10 mmol) in molar ratio of 1:3:1 at 130 ^oC in ethylene glycol for 48 h (Scheme S1). The progress of the reaction was monitored by the thin layer chromatography (TLC). After completion of reaction the reaction mixture was cooled to 0 ^oC and orange color crystalline solid of **2a** (up to 85%) was filtered off and dried. Further, compound **2a** afforded white color solid of 3a after soaking the former in ethanol for one weak. For **2a**, Yield: 85%. ^1H NMR (400 MHz, DMSO-d_6): δ 8.77 (2H, d, J = 4.4 Hz, H_a),8.23 (2H, d, J = 7.6 Hz, H_e), 8.03 (2H, t, J = 7.6 Hz, H_b), 7.84 (2H, s, H_d), 7.58 (2H, d, J = 5.2 Hz, H_c). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.41 (C_2+C_6), 147.51 (C_1), 138.26 (C_5), 125.04 (C_4), 123.28 (C_3). For **3a**, Yield: 72%. ^1H NMR (400 MHz, DMSO-d_6): δ 9.32 (2H, s, H_e), 8.83 (2H, s, H_d), 8.52 (2H, d, H_b), 7.71 (2H, s, H_c), 6.60 (2H, s, H_a). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.25 (C_1),149.55 (C_2), 145.95 (C_6), 137.41 (C_5), 125.21 (C_3), 123.77 (C_4). Similar procedure was adopted for thepreparation of **2b**, **2c**, **3b** and **3c**. However, using 3-cyanopyridine (**1b**) and 4-cyanopyridine (**1c**), respectively as starting material.

3,5-di(pyridin-3-yl)-4H-1,2,4-triazol-4-amine (3b). White color solid. Yield: 64%. ^1H NMR (400 MHz, DMSO-d_6): δ 9.24 (2H, s, H_e), 8.75 (2H, s, H_d), 8.45 (2H, d, J = 7.6 Hz, H_c), 7.62 (2H, s, H_b), 6.52 (2H, s, H_a). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.21 (C_1), 150.97 (C_2), 149.17 (C_6), 136.17 (C_5), 124.12 (C_3), 123.70 (C_4).

3,5-di(pyridin-4-yl)-4H-1,2,4-triazol-4-amine (3c). White color solid. Yield: 70%. ^{1}HNMR (400 MHz, DMSO-d_6): δ 8.80 (4H, d, J = 5.92 Hz, Hc), 8.08 (4H, d, J = 6.00 Hz, H_b), 6.55 (2H, s, H_a). ^{13}C NMR (100 MHz, DMSO-d_6): δ 153.57 (C_1), 150.59 (C_4), 134.47 (C_2), 122.60 (C_3).



Scheme S1. Synthetic route for the pyridyl substituted trizole units **3a** – **3c**.

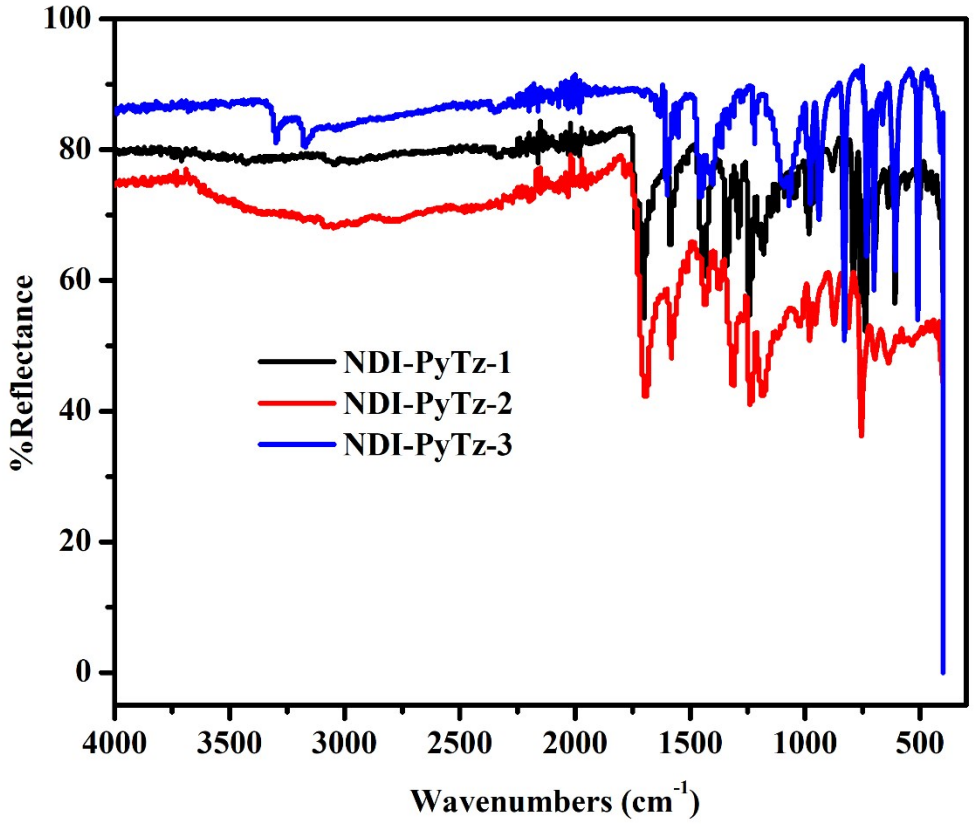


Fig. S1. FTIR spectra of compounds **NDI-PyTz-1, NDI-PyTz-2** and **NDI-PyTz-3**.

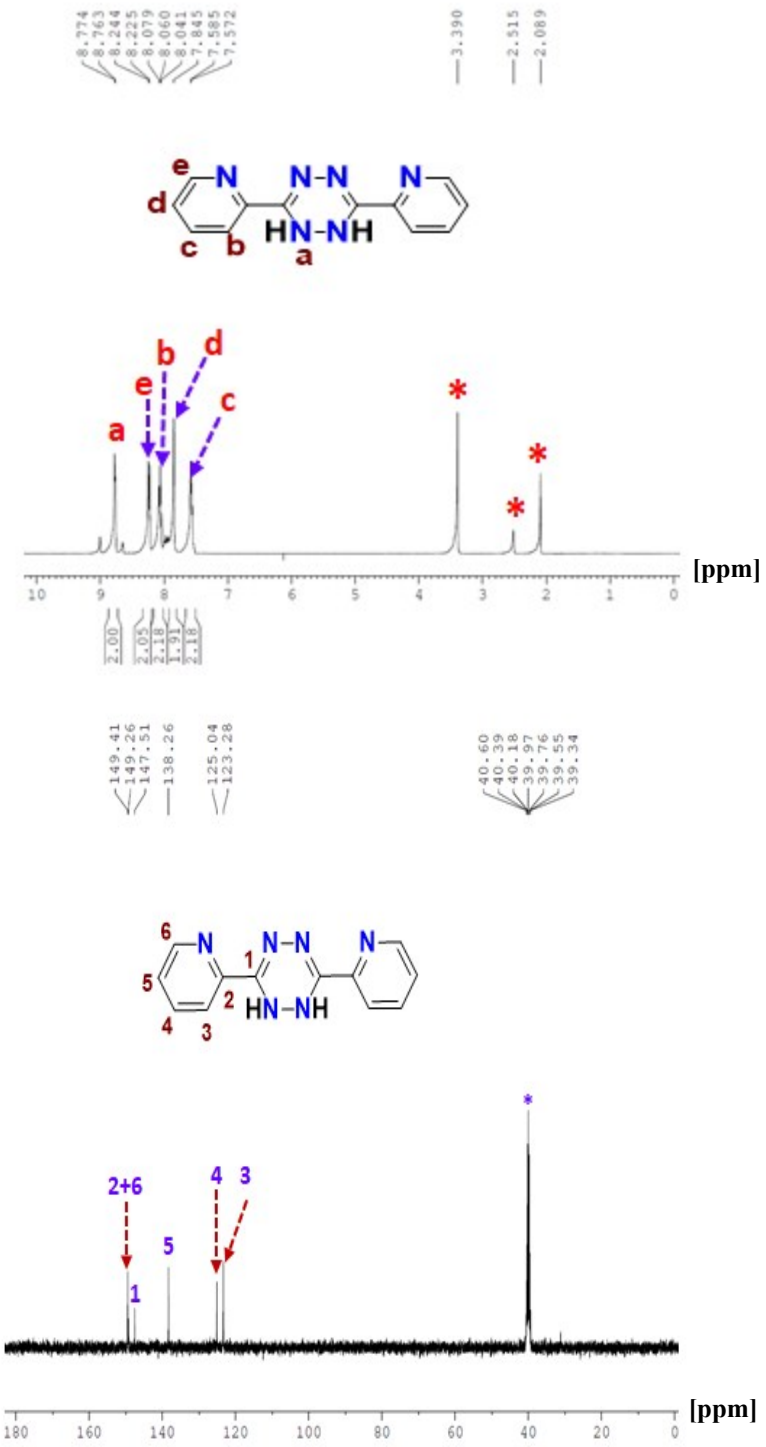


Fig. S2. ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) of compound **2a** in DMSO-d_6. *Represents the residual solvent peak.

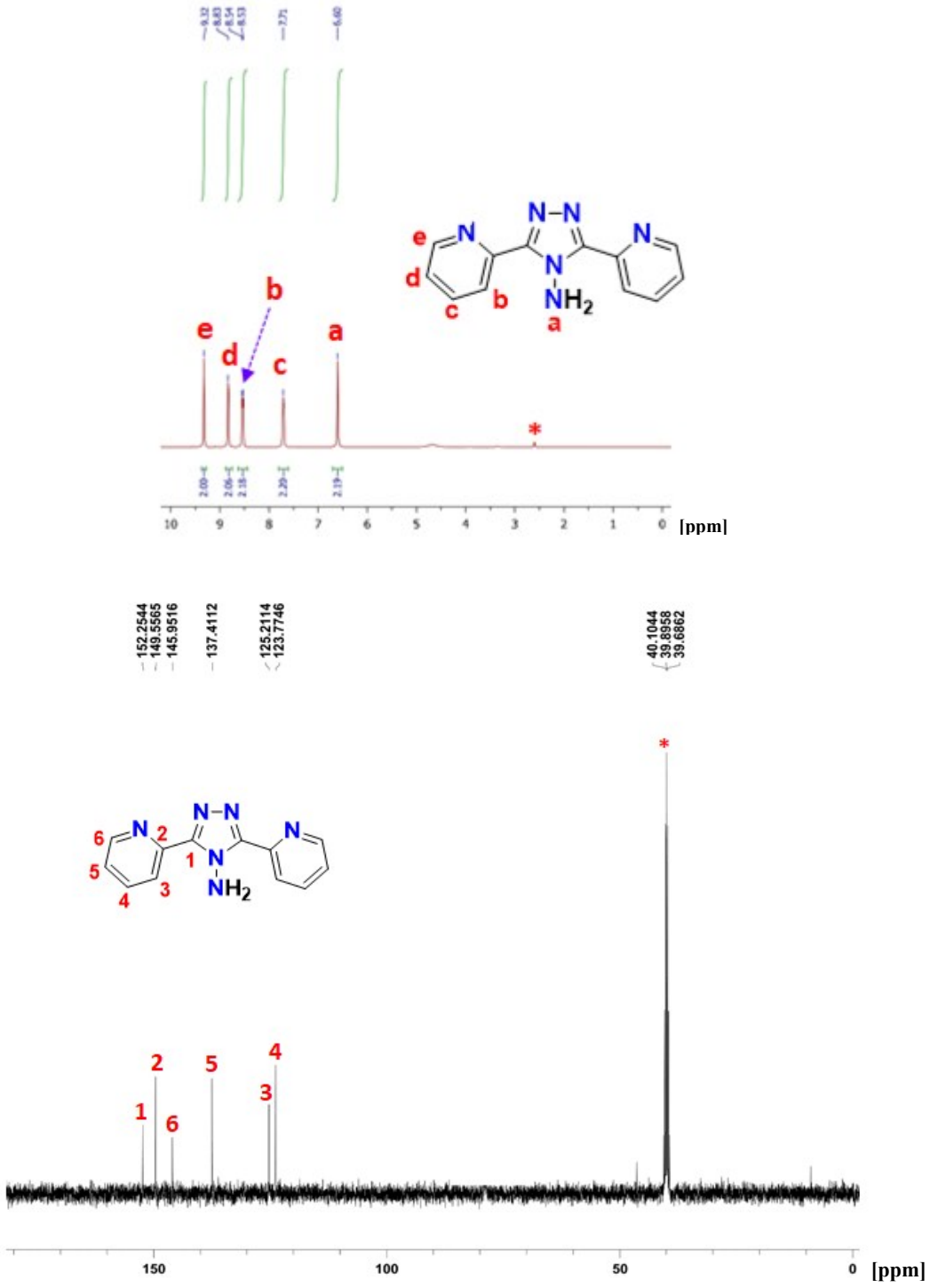


Fig. S3. ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) of compound **3a** in DMSO-d_6. *Represents the residual solvent peaks.

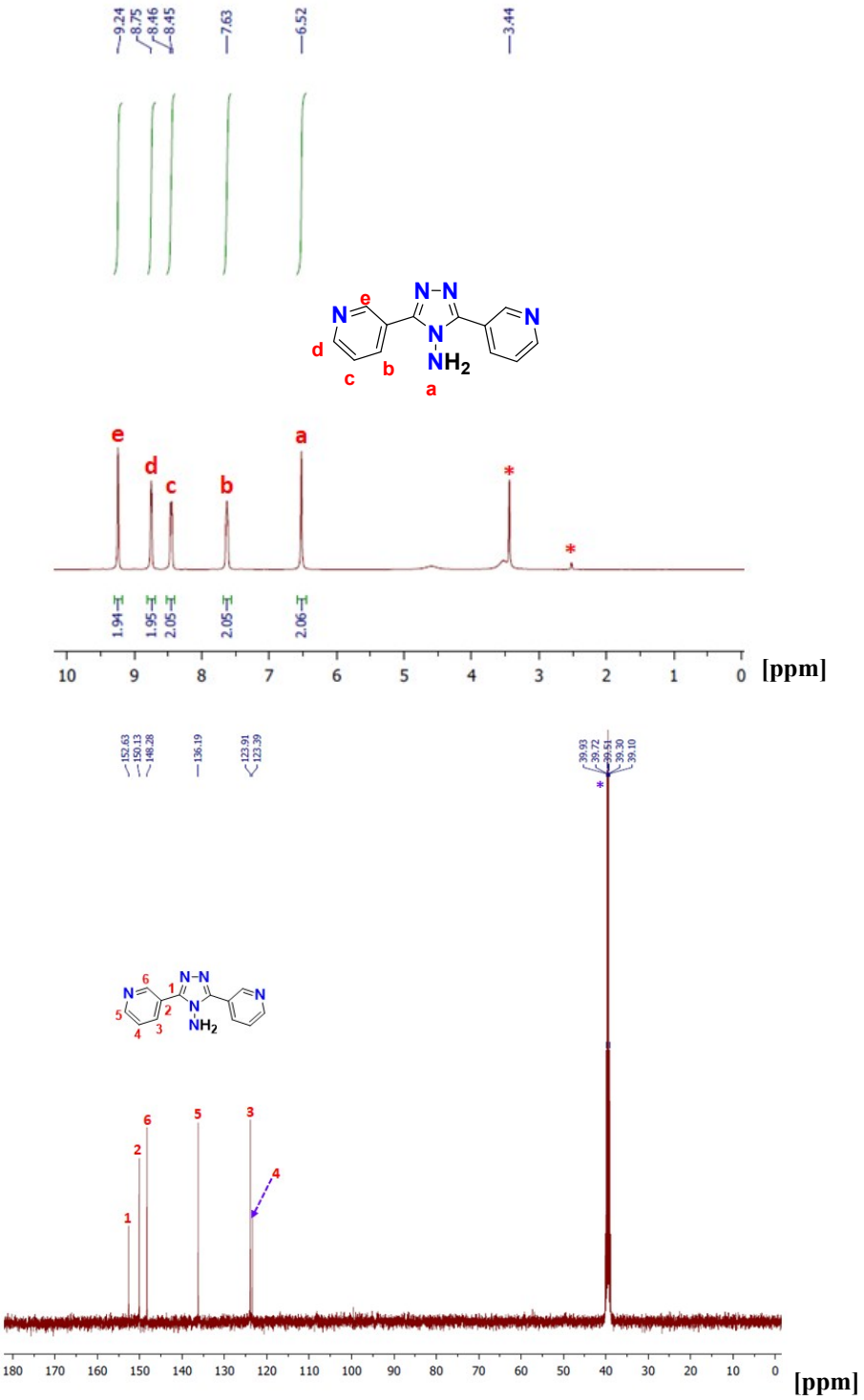


Fig. S4. ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) of compound **3b** in DMSO-d_6. *Represents the solvent residual peaks.

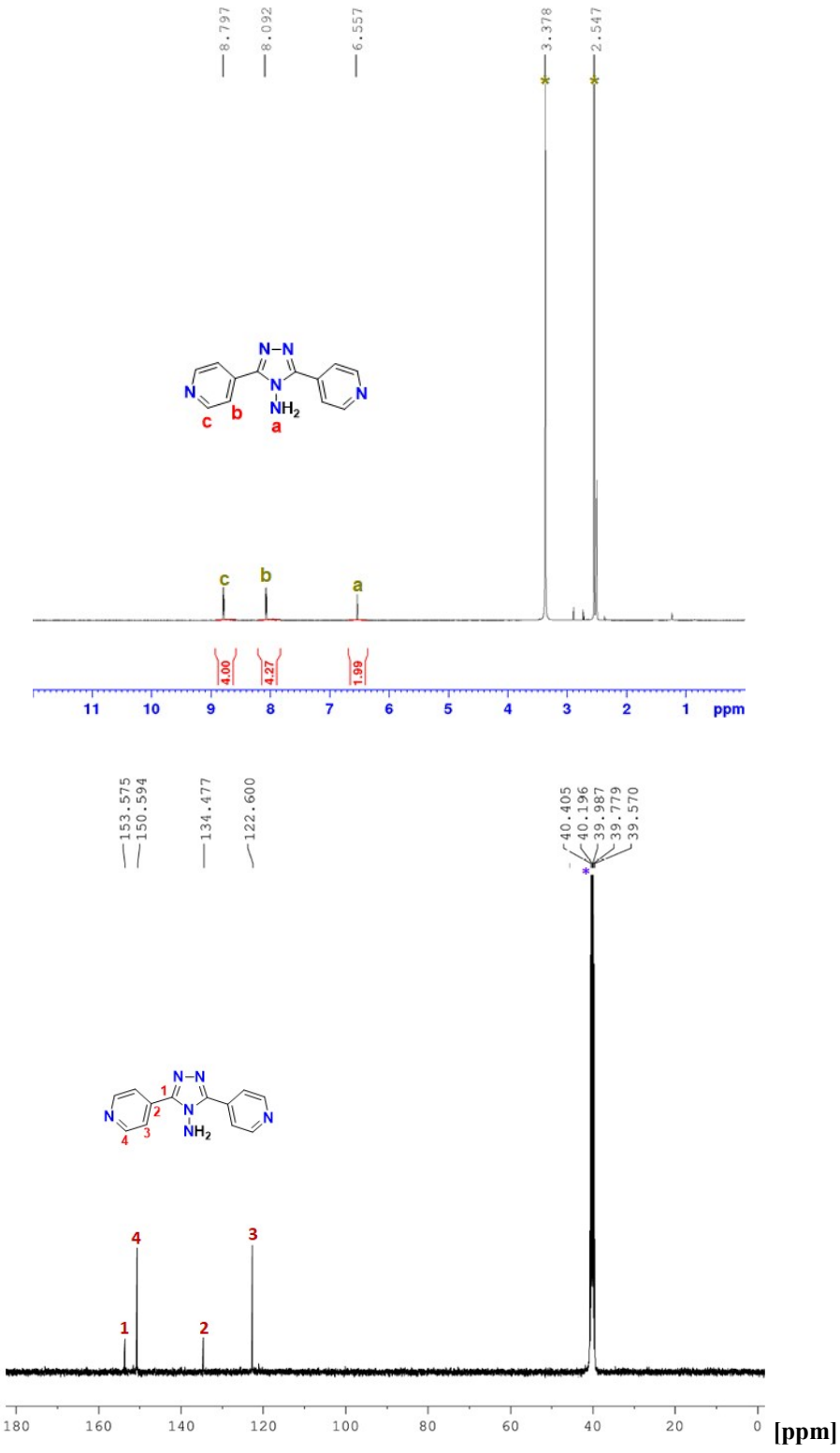


Fig. S5. ^{1}H NMR (top) and ^{13}C NMR spectra (bottom) of compound **3c** in DMSO-d_6. *Represents the solvent residual peaks.

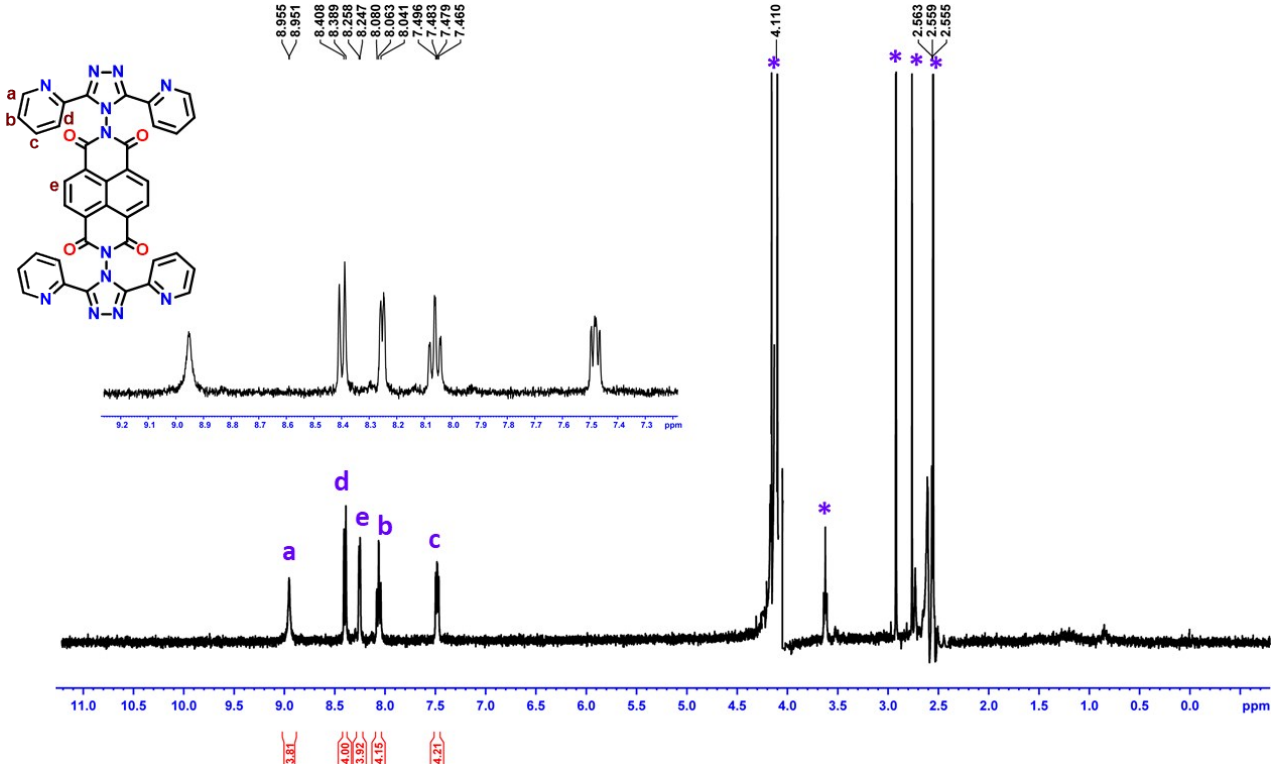


Fig. S6. ^{1}H NMR spectrum of compound **NDI-PyTz-1** in DMSO-d_6 and D_2O mixture.*Represents the solvent residual peaks.

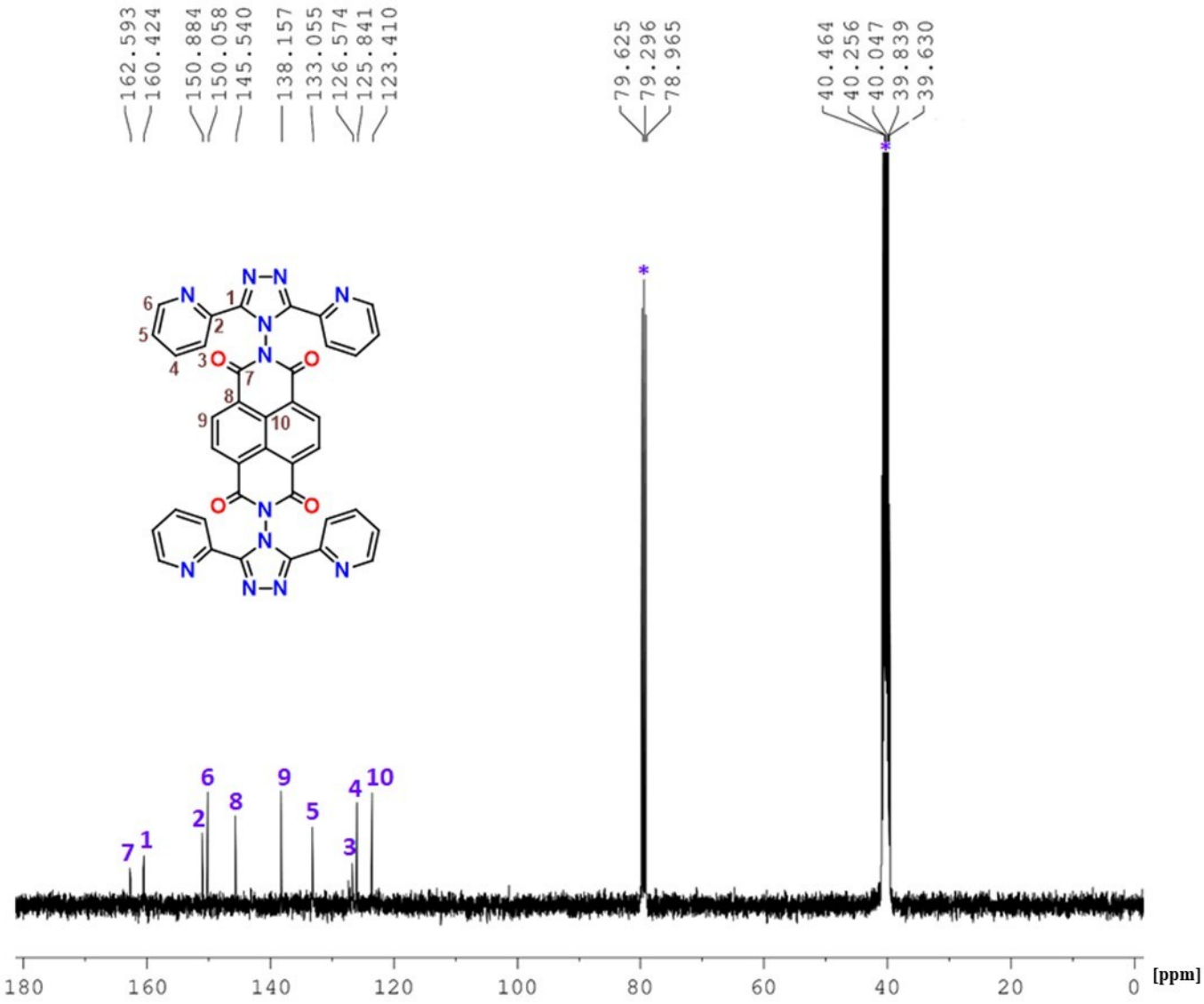


Fig. S7. ^{13}C NMR spectrum of compound **NDI-PyTz-1** in DMSO-d_6.*Represents the solvent residual peaks.

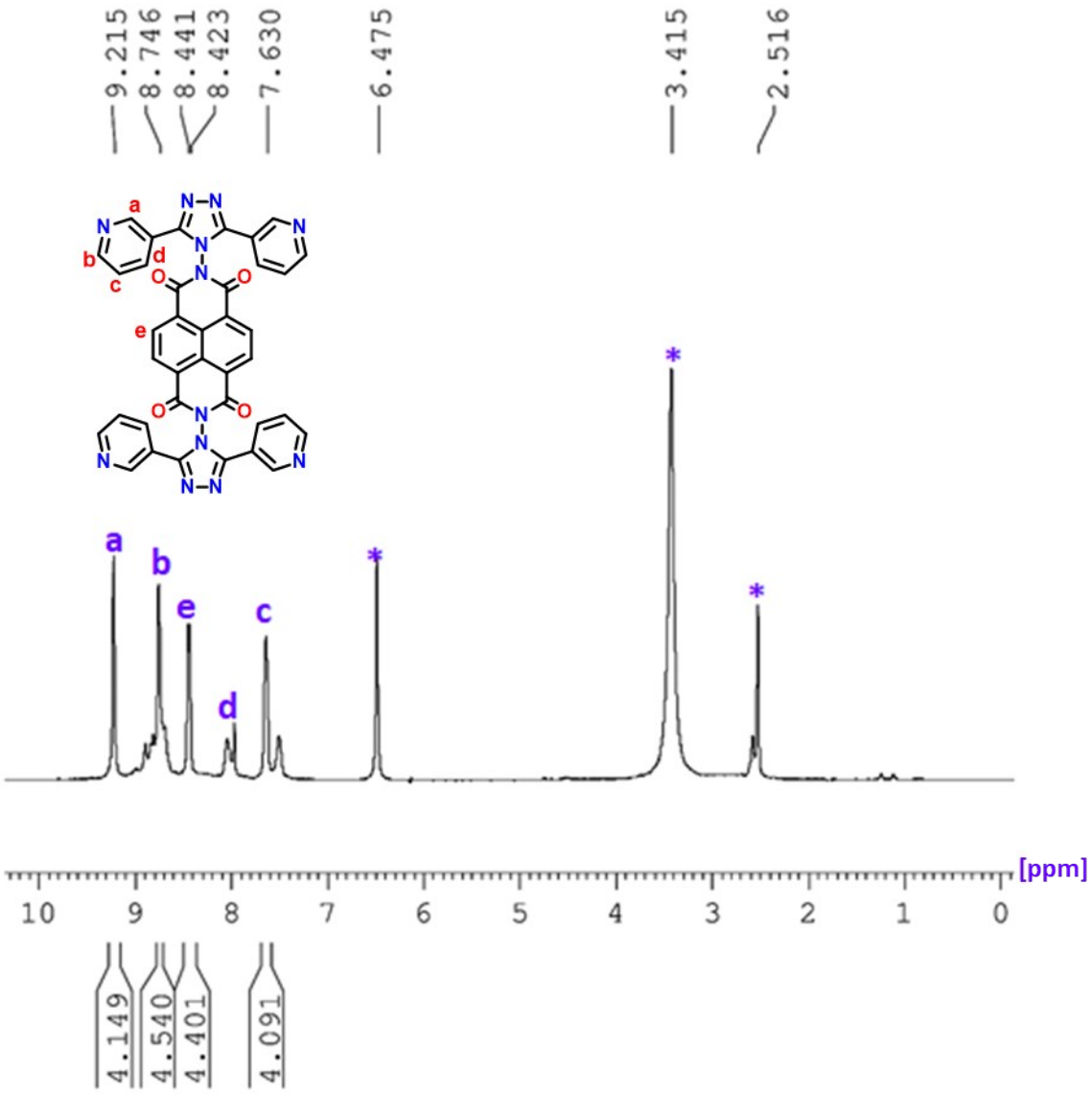


Fig. S8. ^{1}H NMR spectrum of compound **NDI-PyTz-2** in DMSO-d_6. *Represents the solvent residual peaks.

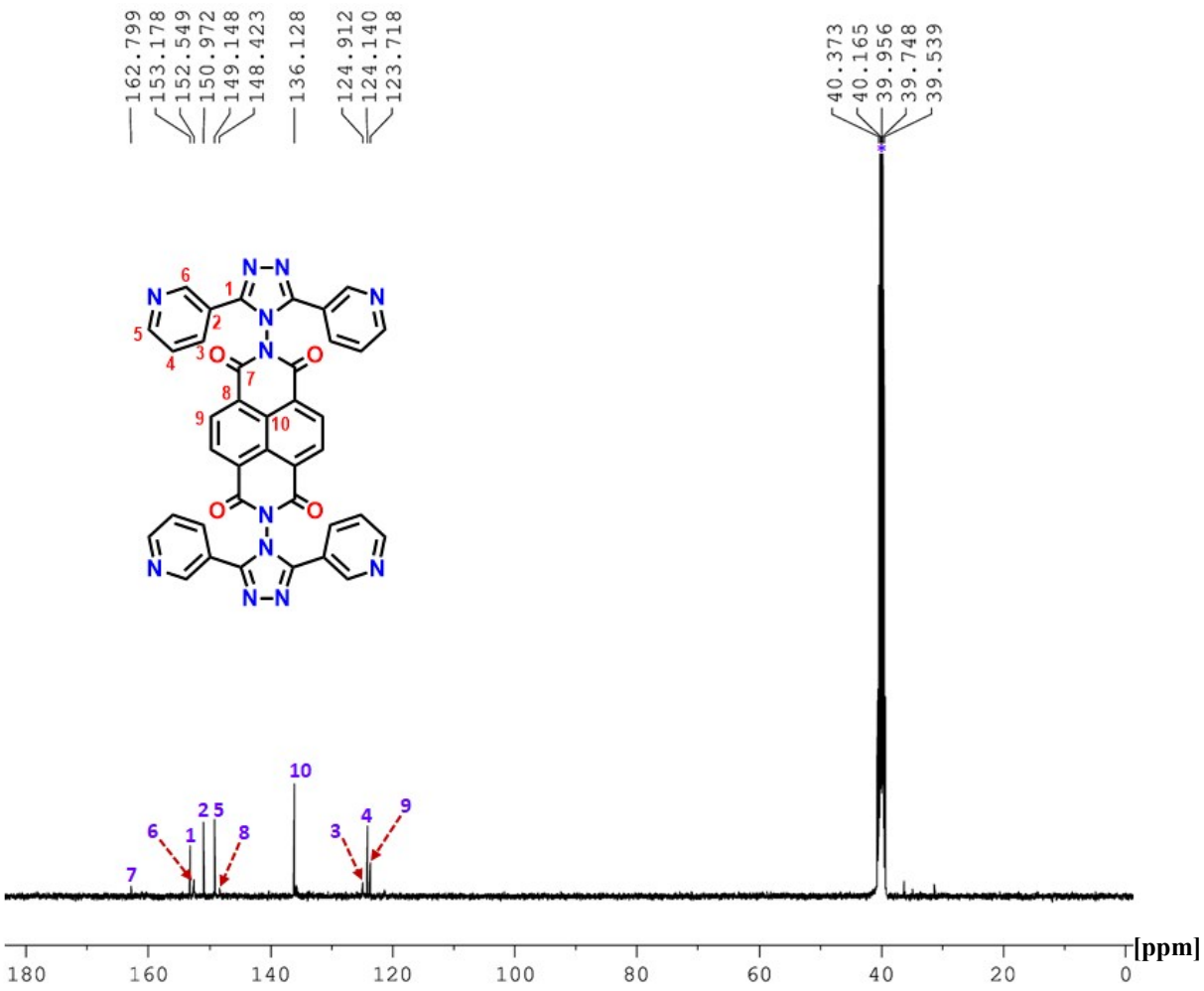


Fig. S9. ^{13}C NMR spectrum of compound **NDI-PyTz-2** in DMSO-d_6. *Represents the solvent residual peaks.

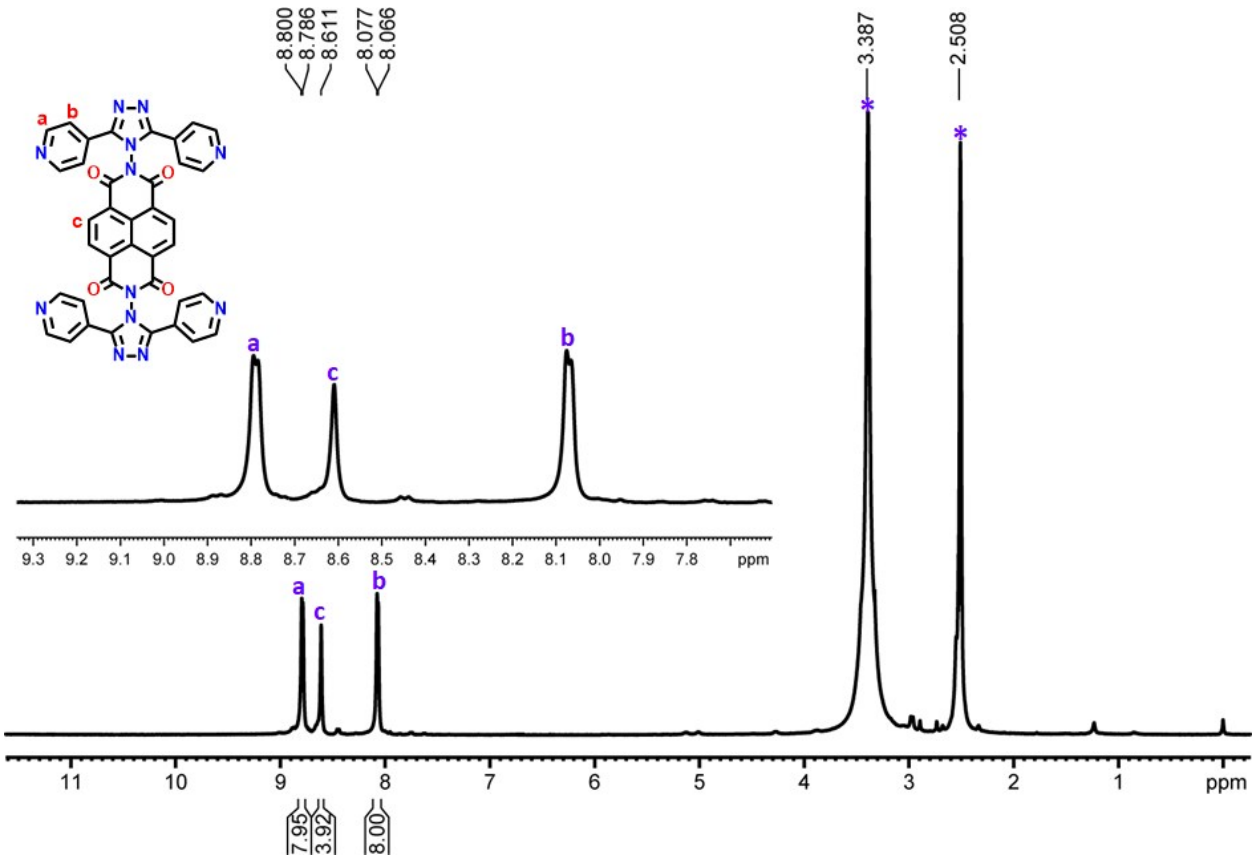


Fig. S10. ^{1}H NMR spectrum of compound **NDI-PyTz-3** in DMSO-d_6.*Represents the solvent residual peaks.

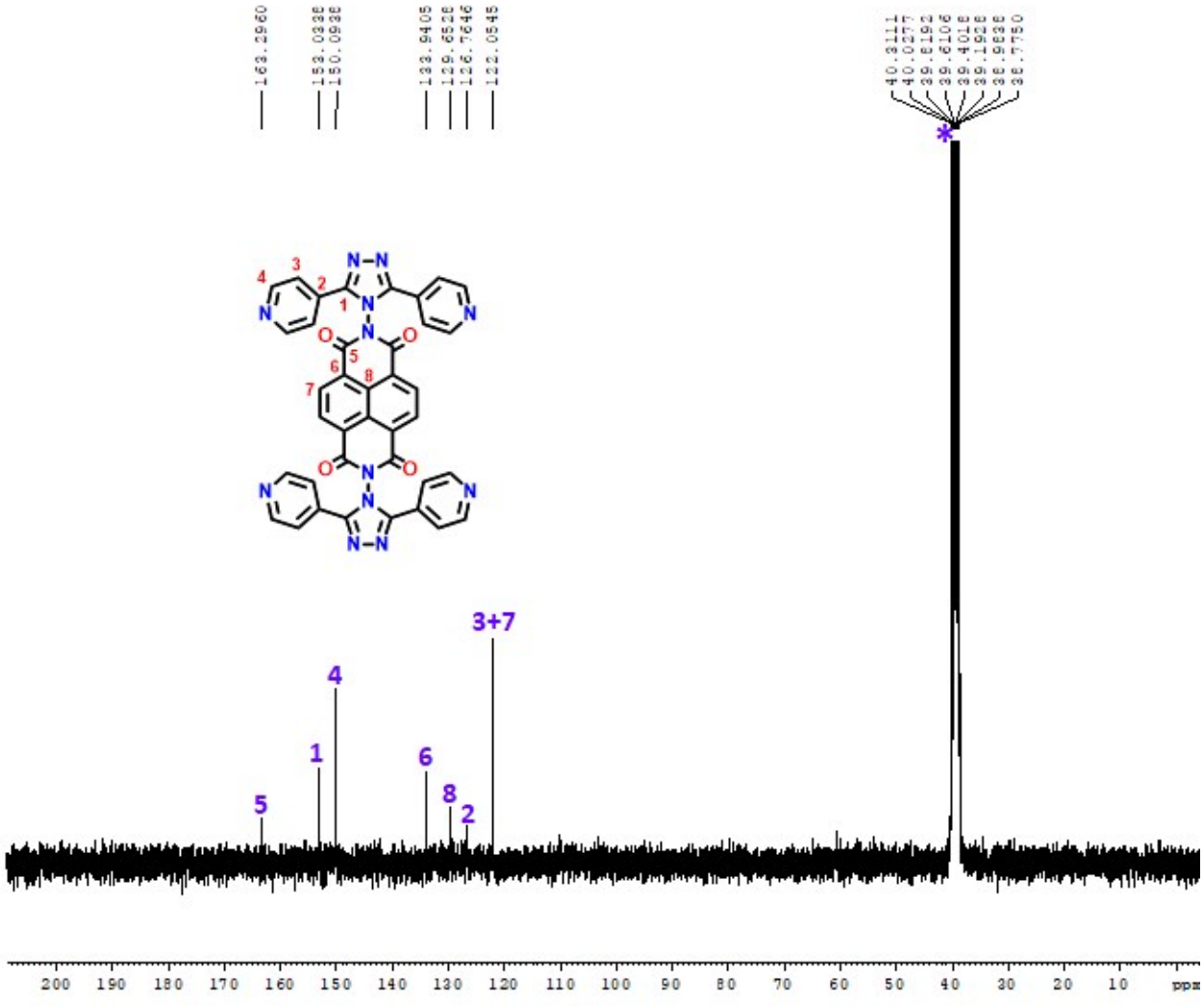


Fig. S11. ^{13}C NMR spectrum of compound **NDI-PyTz-3** in DMSO-d_6.*Represents the solvent residual peaks.

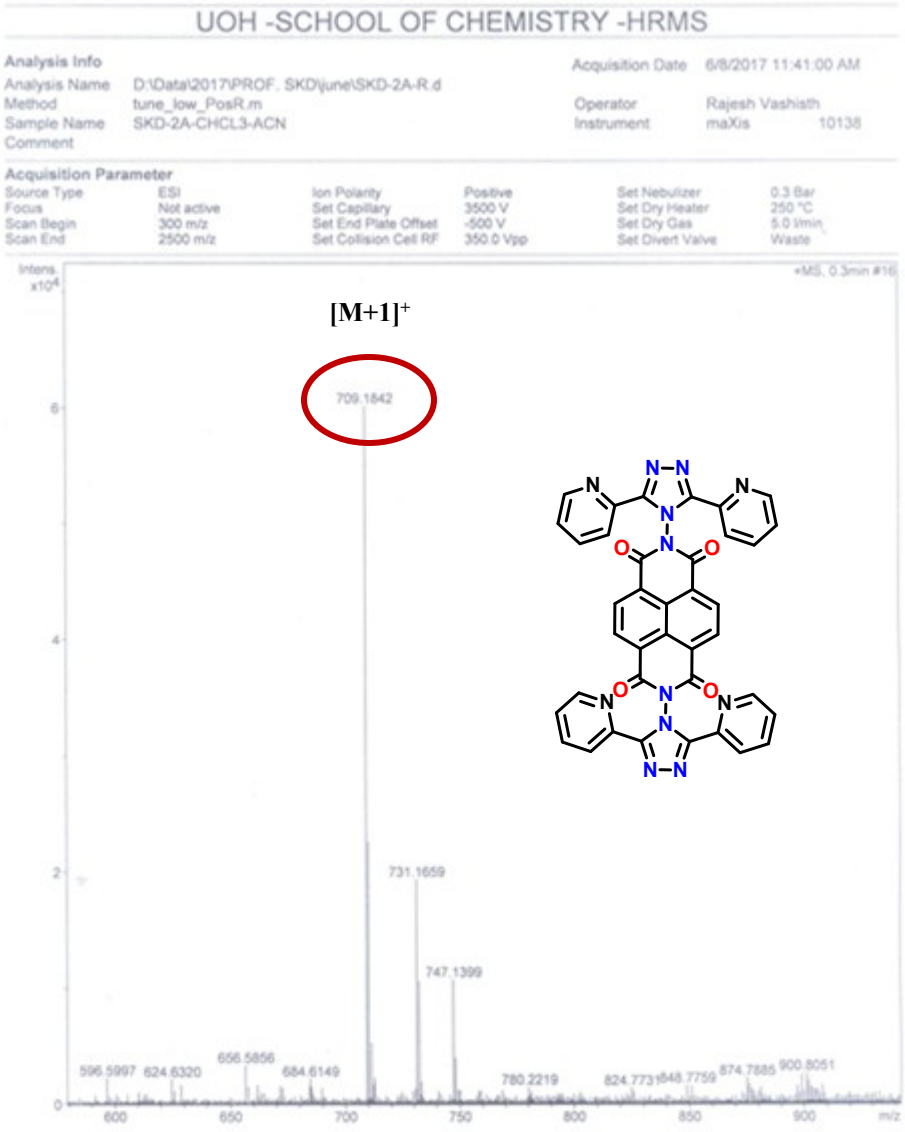


Fig. S12. HRMS spectrum of compound **NDI-PyTz-1**.

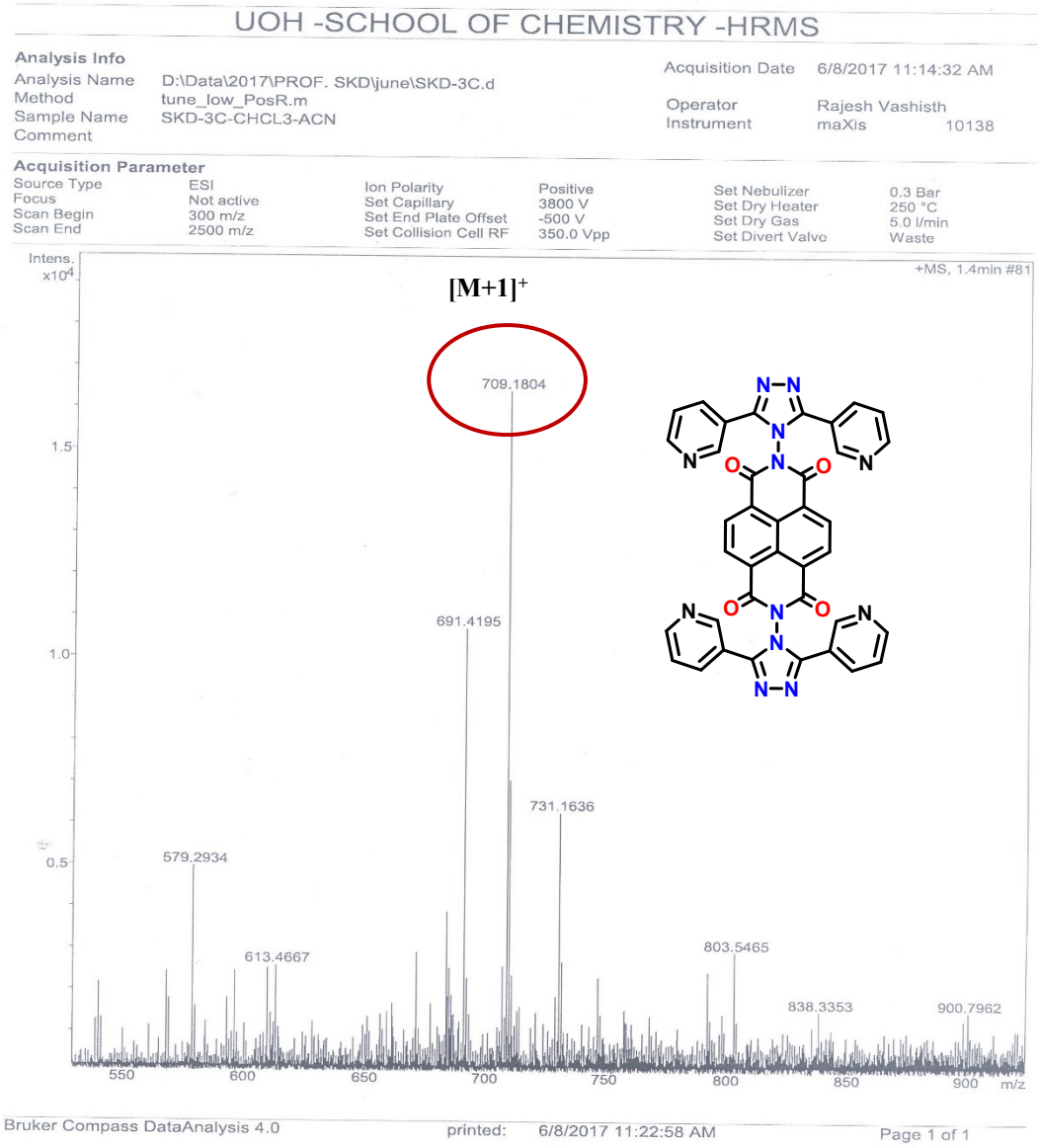


Fig. S13. HRMS spectrum of compound **NDI-PyTz-2**.

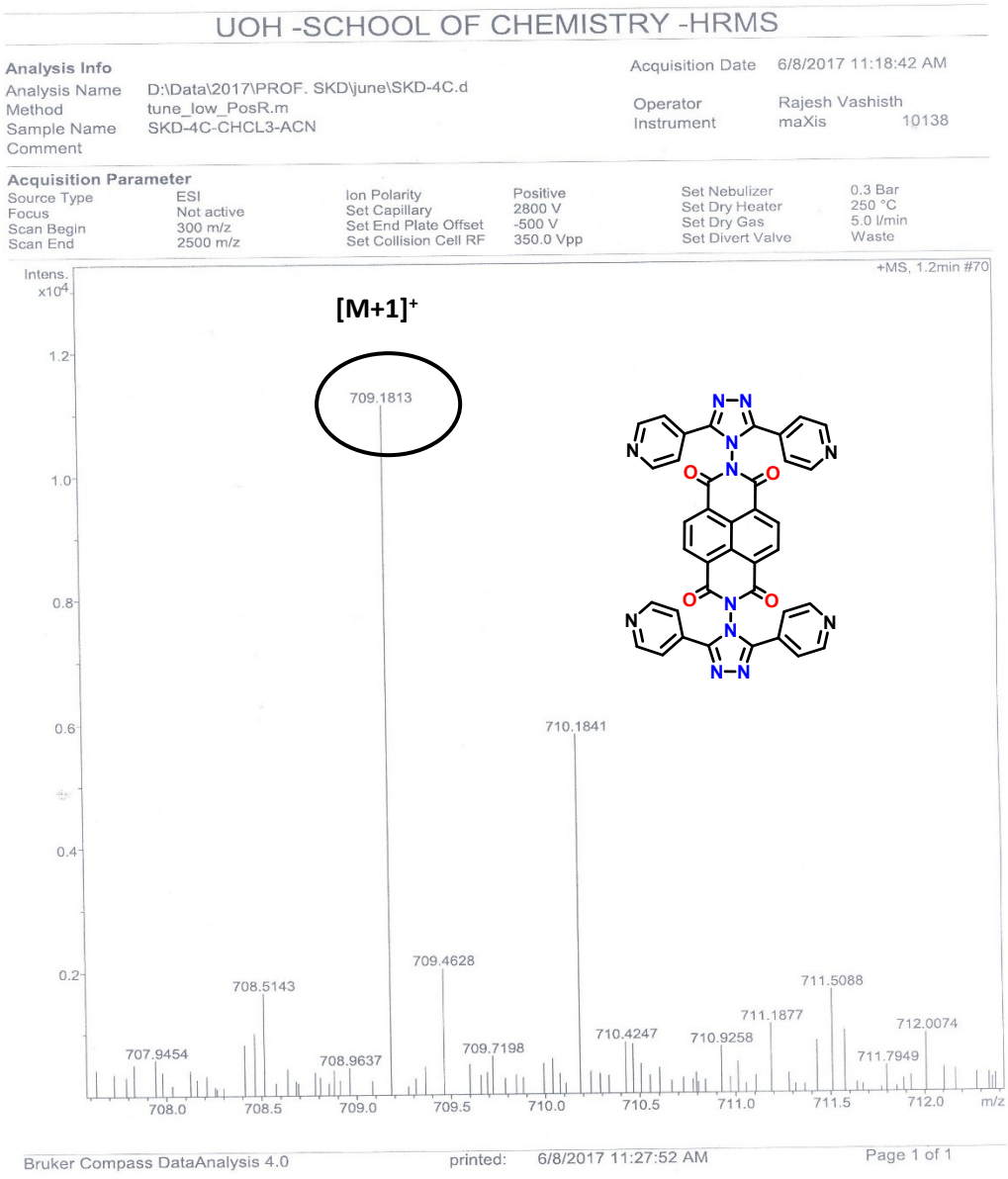


Fig. S14. HRMS spectrum of compound **NDI-PyTz-3**.

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THERMO FINNIGAN

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Analysis type:	UnkNown
Chromatogram filename:	UNK-08062017-3.dat
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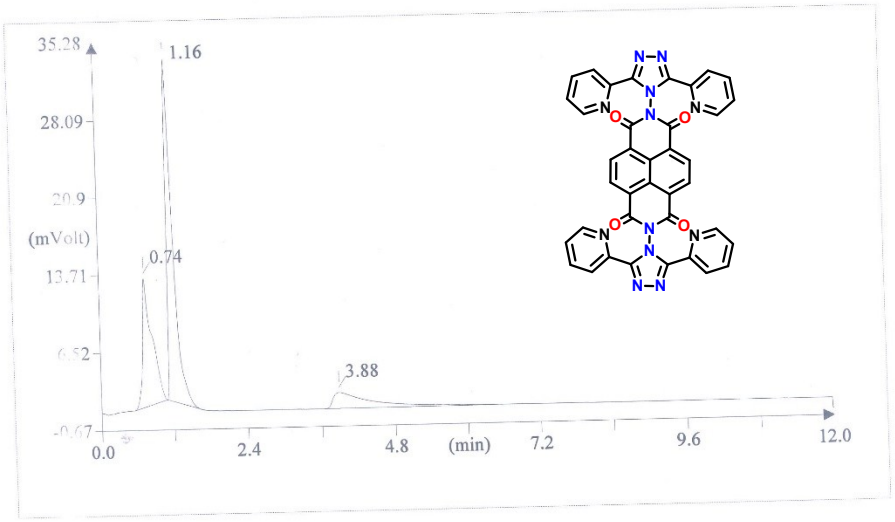

Element Name	Element %	Ret. Time
Nitrogen	23. 15	0. 74
Carbon	62. 85	1. 16
Hydrogen	3. 56	3. 88

Fig. S15. Element analysis for compound **NDI-PyTz-1**.

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THERMO FINNIGAN

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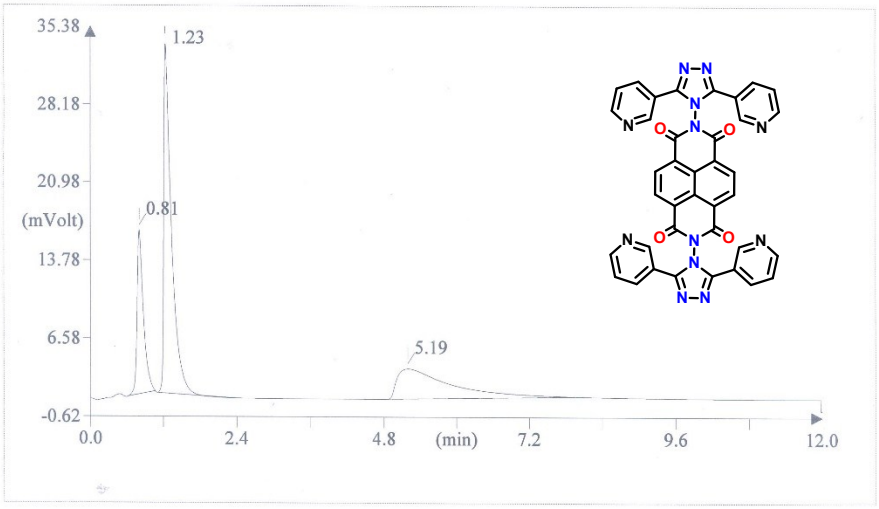

Element Name	Element %	Ret. Time
Nitrogen	23. 61	0. 81
Carbon	64. 32	1. 23
Hydrogen	2. 92	5. 19

Fig. S16. Element analysis for compound **NDI-PyTz-2**.

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THERMO FINNIGAN

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Analysis type:	UnkNown
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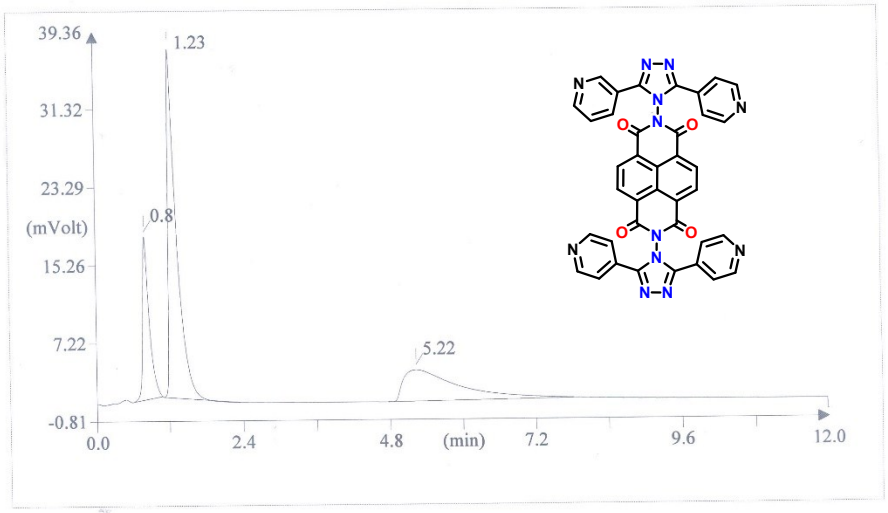
Sample weight:	1.283



Element Name	Element %	Ret. Time
Nitrogen	23. 78	0. 80
Carbon	64. 52	1. 23
Hydrogen	2. 81	5. 22

Fig. S17. Element analysis for compound **NDI-PyTz-3**.

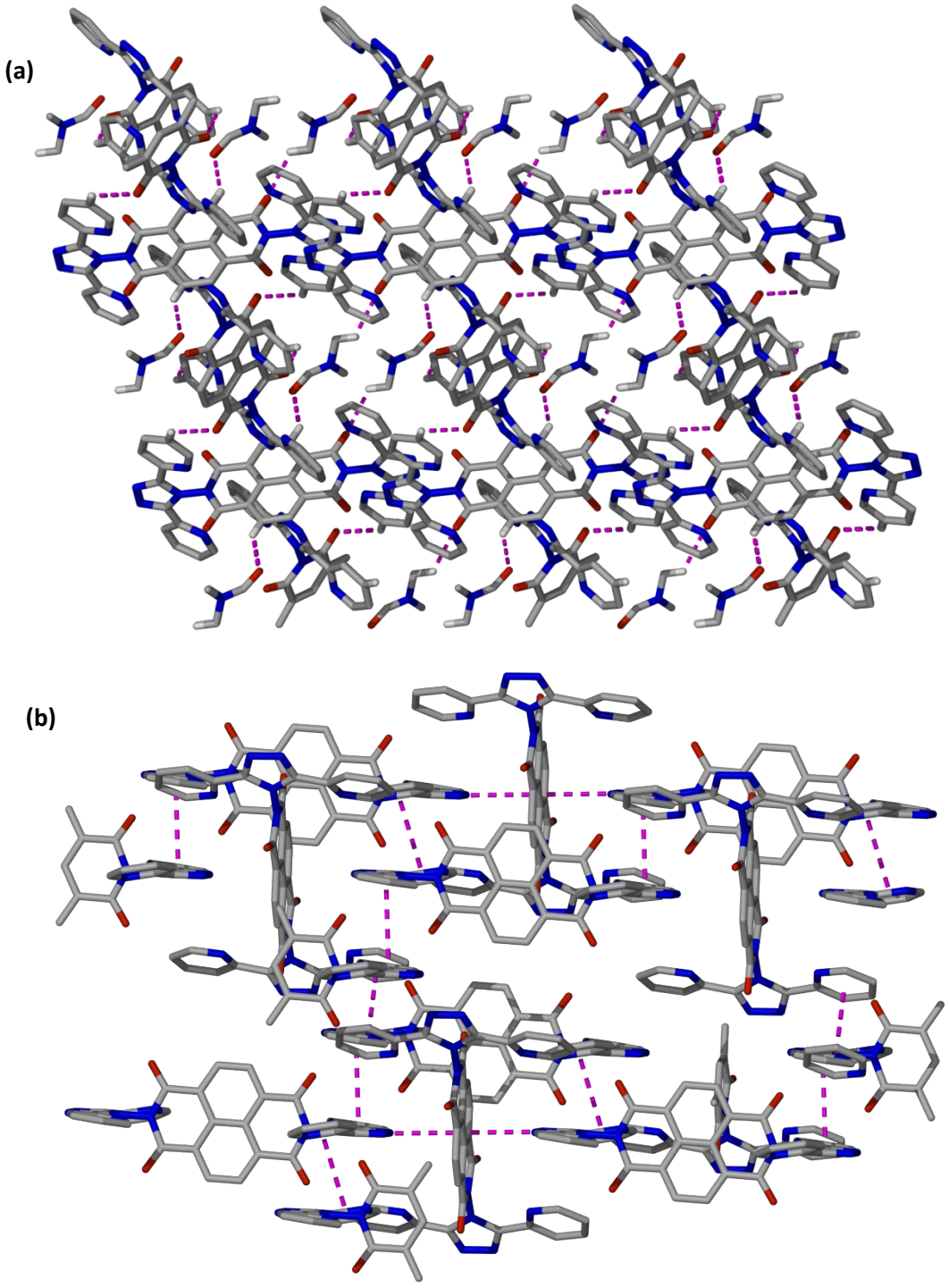


Fig. S18. (a) Packing view of **NDI-PyTz-1** showing C-H···O interactions. (b) Packing view of NDI-PyTz-1 displaying π---π interactions among the pyridyl rings.

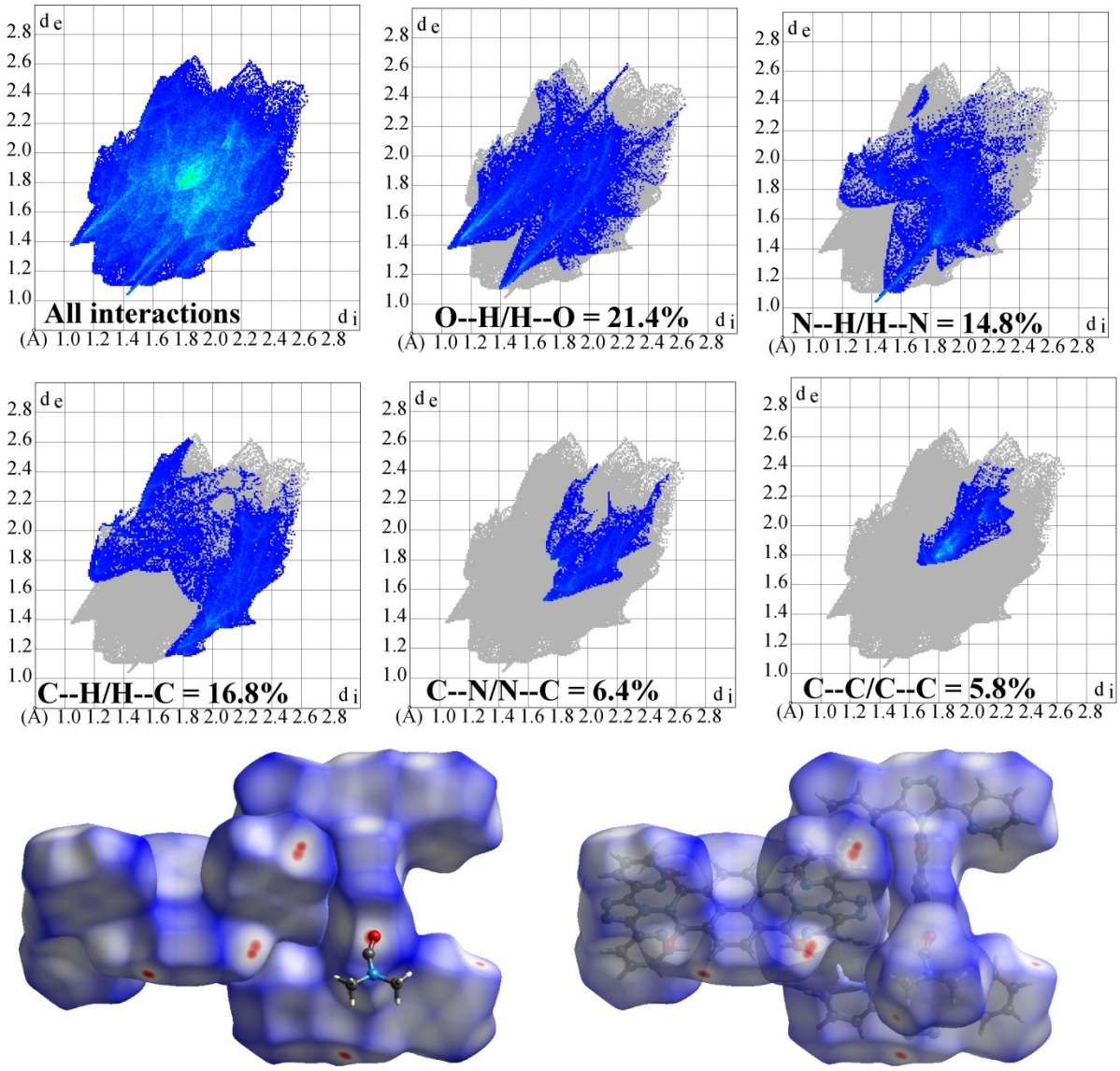


Fig.S19. Hirshfeld calculation**NDI-PyTz-1** showing the % of hydrogen bonding.

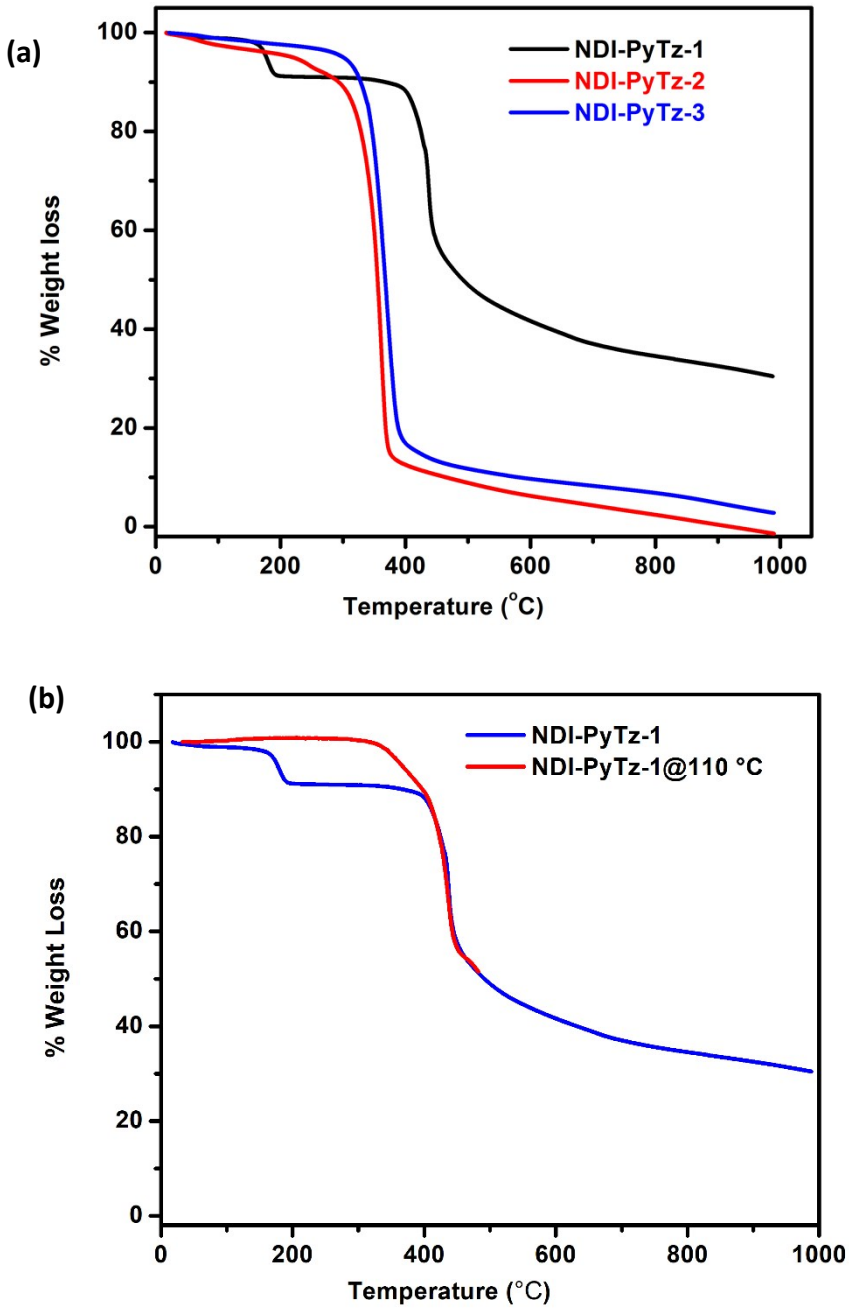


Fig. S20. (a) Thermal plots for compounds **NDI-PyTz-1, NDI-PyTz-2** and **NDI-PyTz-3. (b)** Comparison of thermal plots for **NDI-PyTz-1**; as-synthesiszed (blue trace) and after evaculation of DMF molecule (Red trace-recorded upto 500°C).

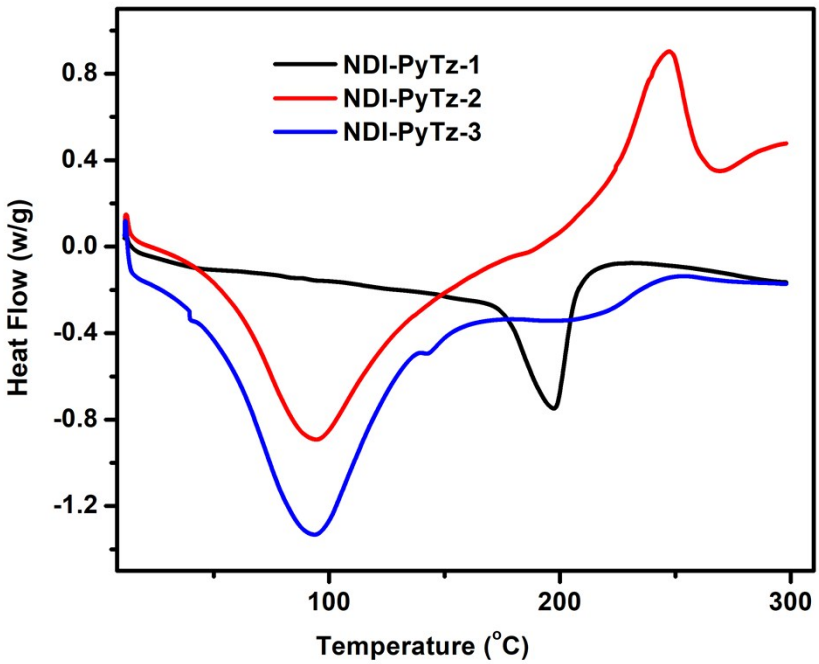


Fig. S21. DSC plots for compounds **NDI-PyTz-1**, **NDI-PyTz-2** and **NDI-PyTz-3**.

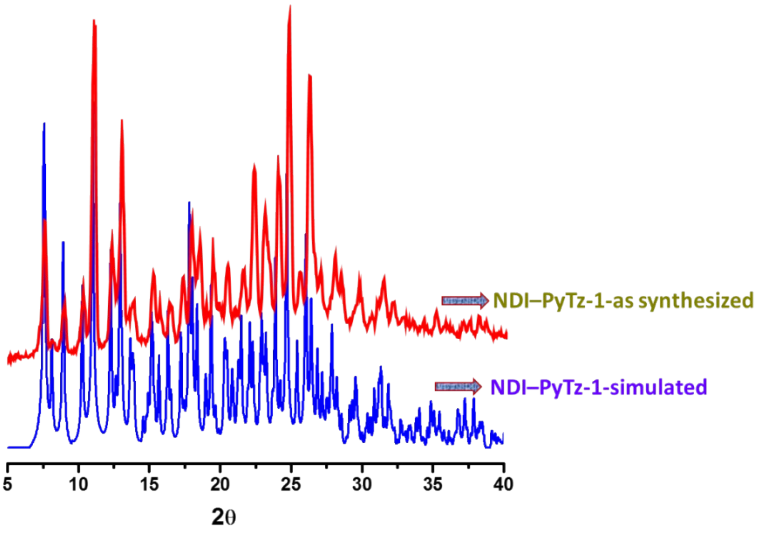


Fig. S22. The powder X-ray pattern of the **NDI-PyTz-1**, simulated from the single crystal X-ray structure using the Mercury 3.7 software (lower, blue trace) and the as synthesized sample of **NDI-PyTz-1** (upper, red trace).

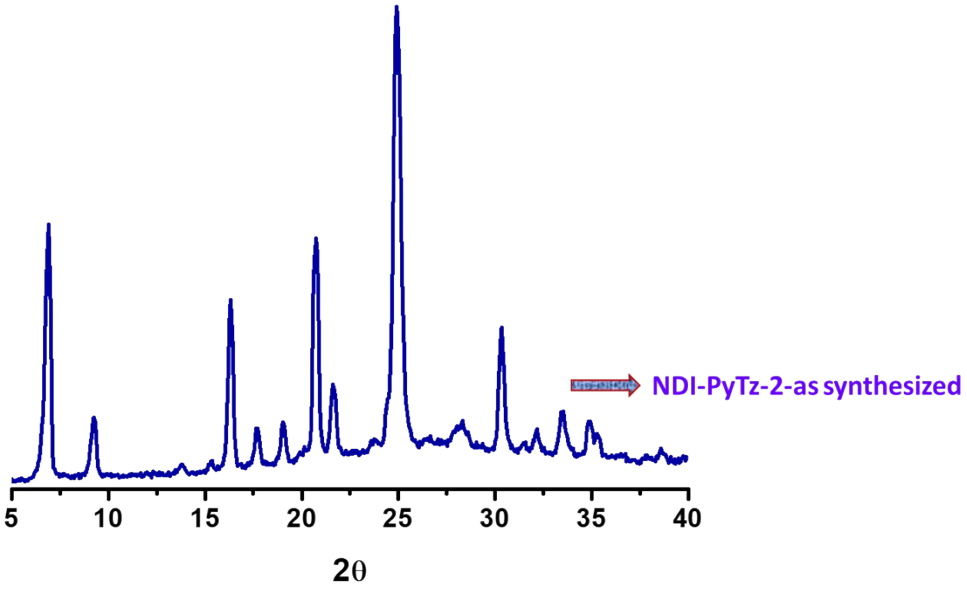


Fig. S23. The powder X-ray pattern of the as synthesized sample of **NDI-PyTz-2.**

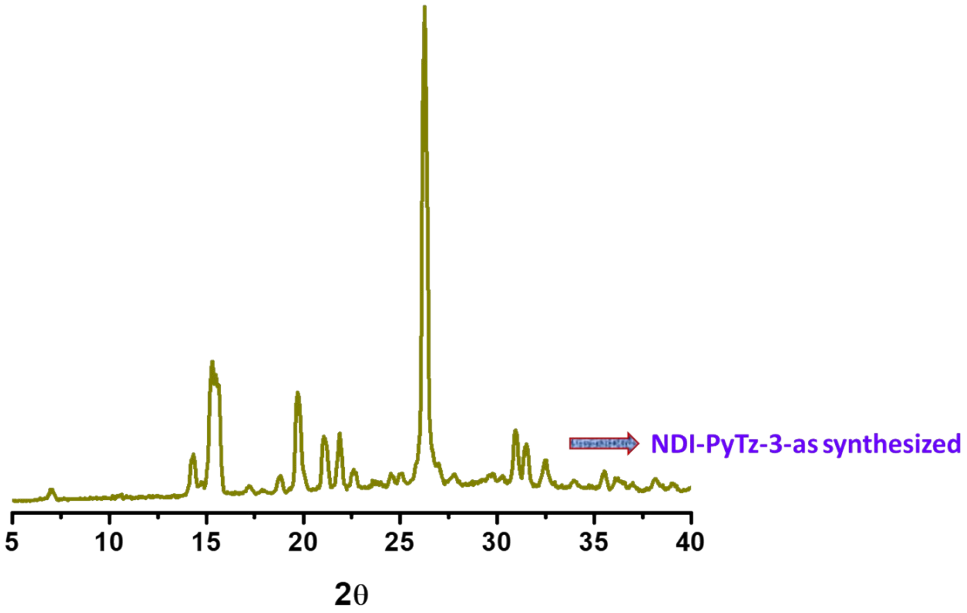


Fig. S24. The powder X-ray pattern of the as synthesized sample of **NDI-PyTz-3.**

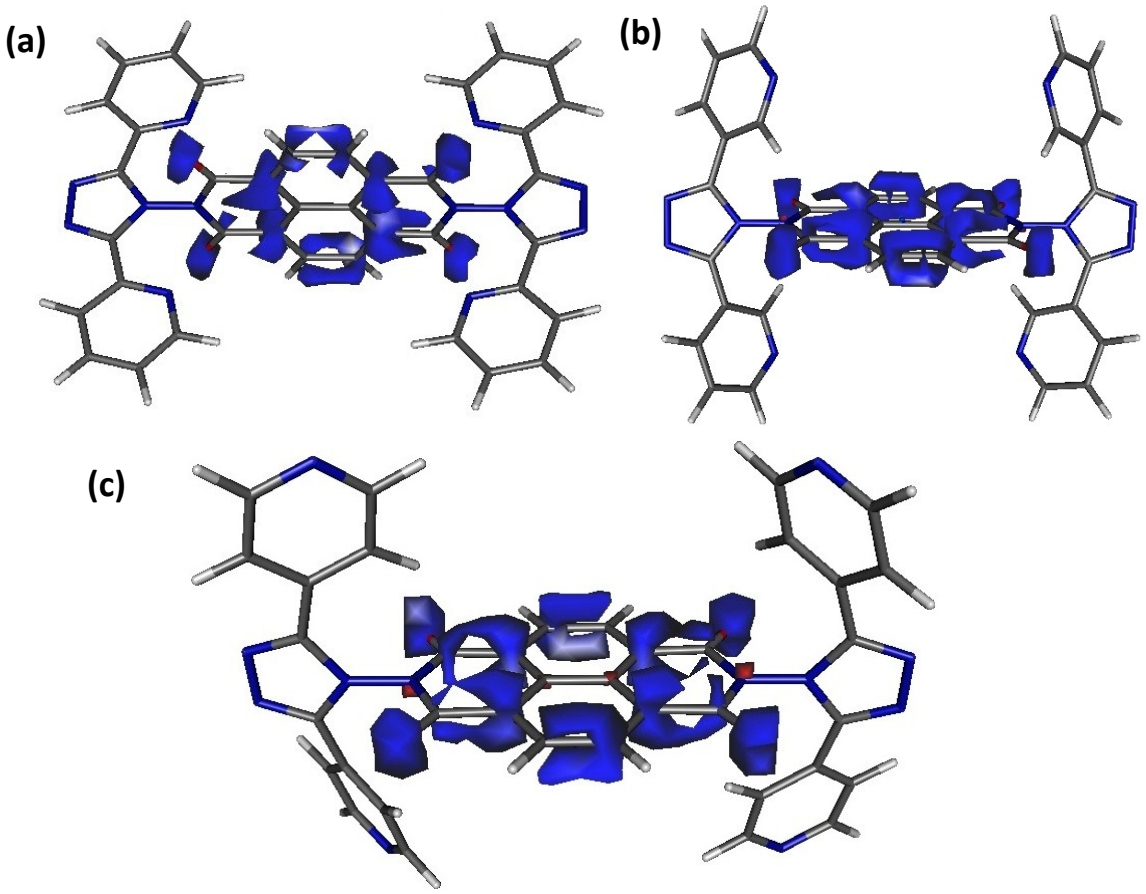


Fig. S25. Spin density maps (isovalue = 0.003, blue and grey color stand for negative and positive density, respectively for (a) **NDI-PyTz-1**; (b) **NDI-PyTz-2**; (c) **NDI-PyTz-3** upon one electron reduction.

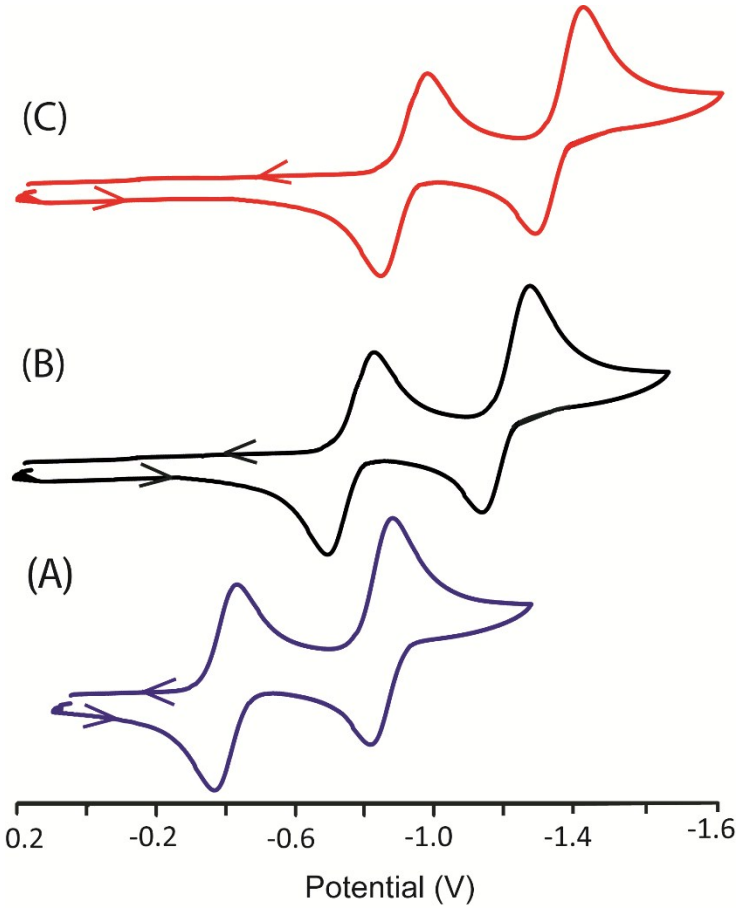


Fig. S26. Cyclic voltammograms for compounds (A) **NDI-PyTz-1** (B) **NDI-PyTz-2** and (C) **NDI-PyTz-3** in DMF in presence of 0.1 M $\{[^{t}Bu_4N]^{+}\cdot ClO_4\}$ as an electrolyte and using Ag/AgCl as reference electrode.

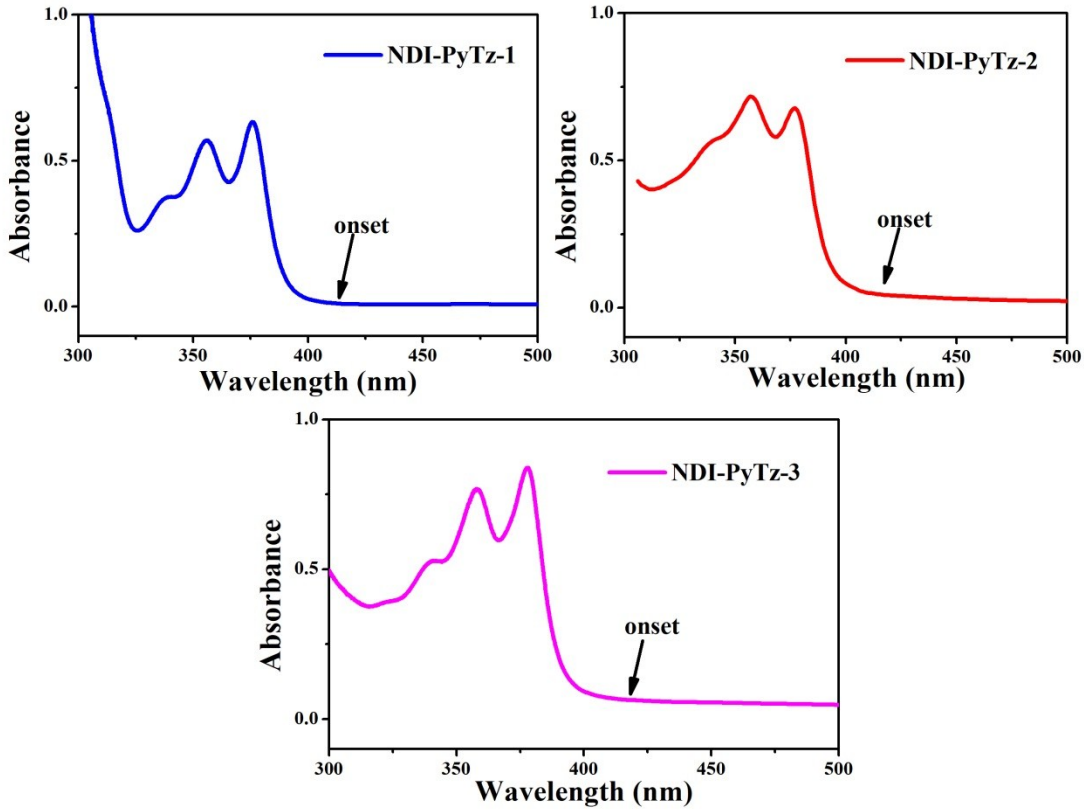


Fig. S27. Absorption spectrum of compounds (a) **NDI-PyTz-1**; (b) **NDI-PyTz-2**; (c) **NDI-PyTz-3** in DMF.

Method followed for the calculation of k_r, and k_{nr}

From the observed $\boldsymbol{\phi}_f$ and $\boldsymbol{\tau}_f$, we can calculate the radiative ($\boldsymbol{k}_r$) and nonradiative ($\boldsymbol{k}_{nr}$) rate constants for the ICT processes using the following relations (i) and (ii), which is more important in supporting and for explaining the observation.

$$k_r = \frac{\varphi_f}{\tau_f} \quad \text{..... (i)}$$

$$\frac{1}{\tau_f} = k_r + k_{nr} \quad \text{..... (ii)}$$

Where, φ_f, τ_f, k_r, and k_{nr} are the fluorescence quantum yield, mean fluorescence lifetime, radiative rate constant, and nonradiative rate constants, respectively.[S2] All the photophysical parameters are tabulated in Table S5 of this supporting information.

Coordinates of optimization of geometry of **NDI-PyTz-1**,**NDI-PyTz-2**and **NDI-PyTz-3**.

NDI-PyTz-1

Opt TightSCF B3LYP
! PrintBasis 6-31G*
%output
print[p_mos] 1
end #output
* xyz 0 1
O 5.814000 4.350000 3.855000
O 4.508000 5.701000 7.945000
N 5.061000 5.051000 5.860000
C 3.073000 3.135000 5.850000
N 6.106000 5.976000 5.875000
C 3.146000 4.048000 6.928000
C 3.993000 3.159000 4.792000
C 5.040000 4.205000 4.750000
C 4.266000 5.012000 6.986000
C 3.921000 2.249000 3.779000
H 4.551000 2.262000 3.095000
N 8.050000 6.874000 6.165000
C 2.213000 4.016000 7.917000
H 2.256000 4.636000 8.609000
N 7.080000 3.485000 6.918000
N 7.230000 7.813000 5.552000
C 6.065000 7.274000 5.375000
C 7.363000 5.781000 6.342000
N 3.797000 7.323000 4.802000
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C 7.855000 4.578000 6.932000
C 8.841000 2.304000 8.045000
H 9.150000 1.517000 8.435000
C 9.587000 3.411000 8.026000
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C 9.142000 4.537000 7.484000
H 9.680000 5.296000 7.473000
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H 7.027000 1.613000 7.426000
C 5.198000 9.076000 3.991000

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C 2.876000 9.019000 3.412000
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O 0.607000 -0.388000 3.740000
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N 1.317000 -2.010000 6.884000
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C -3.727000 3.009000 3.640000
H -4.036000 3.796000 3.251000
C -4.473000 1.902000 3.660000
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C -4.027000 0.776000 4.201000
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H -1.912000 3.699000 4.259000
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H -0.920000 -4.170000 7.712000
C 2.238000 -3.706000 8.273000
H 2.982000 -4.068000 8.696000
C 2.339000 -2.590000 7.543000
H 3.175000 -2.187000 7.484000

NDI-PyTz-2

```
 Opt   TightSCF  B3LYP
PrintBasis 6-31G*
 %output
print[p_mos] 1
end #output
 * xyz 0   1
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N  2.504000 2.394000 0.017000
C  0.516000 0.478000 0.007000
N  3.549000 3.320000 0.032000
C  0.589000 1.392000 1.085000
C  1.436000 0.502000 -1.051000
C  2.483000 1.549000 -1.093000
C  1.709000 2.356000 1.143000
C  1.364000 -0.407000 -2.064000
H  1.994000 -0.395000 -2.748000
N  5.493000 4.218000 0.322000
C  -0.344000 1.359000 2.074000
H  -0.301000 1.980000 2.766000
N  4.673000 5.157000 -0.291000
C  3.508000 4.617000 -0.468000
C  4.806000 3.124000 0.499000
C  2.381000 5.245000 -1.152000
C  5.298000 1.922000 1.089000
C  6.284000 -0.352000 2.202000
H  6.593000 -1.140000 2.592000
C  7.030000 0.754000 2.183000
H  7.882000 0.737000 2.556000
C  6.585000 1.881000 1.641000
H  7.123000 2.640000 1.630000
C  1.509000 6.938000 -2.536000
H  1.604000 7.694000 -3.068000
C  2.641000 6.420000 -1.852000
H  3.478000 6.827000 -1.870000
C  0.319000 6.362000 -2.431000
H  -0.425000 6.724000 -2.854000
O  -3.256000 -1.694000 1.987000
O  -1.950000 -3.045000 -2.103000
N  -2.504000 -2.394000 -0.018000
C  -0.515000 -0.478000 -0.007000
```

N -3.549000 -3.320000 -0.033000
C -0.589000 -1.392000 -1.086000
C -1.436000 -0.502000 1.050000
C -2.483000 -1.549000 1.092000
C -1.708000 -2.356000 -1.143000
C -1.363000 0.407000 2.063000
H -1.994000 0.395000 2.747000
N -5.492000 -4.218000 -0.323000
C 0.344000 -1.361000 -2.074000
H 0.301000 -1.980000 -2.766000
N -4.673000 -5.157000 0.291000
C -3.508000 -4.617000 0.467000
C -4.805000 -3.124000 -0.499000
C -2.381000 -5.245000 1.152000
C -5.298000 -1.922000 -1.089000
C -6.284000 0.352000 -2.203000
H -6.593000 1.140000 -2.592000
C -7.030000 -0.754000 -2.183000
H -7.882000 -0.737000 -2.557000
C -6.584000 -1.881000 -1.642000
H -7.122000 -2.640000 -1.630000
C -1.509000 -6.938000 2.535000
H -1.604000 -7.694000 3.067000
C -2.641000 -6.420000 1.852000
H -3.477000 -6.827000 1.869000
C -0.319000 -6.362000 2.430000
H 0.425000 -6.724000 2.853000
N 4.998000 -0.277000 1.603000
N -0.218000 -5.247000 1.700000
N -4.998000 0.277000 -1.604000
N 0.219000 5.247000 -1.701000
C -4.522000 -0.829000 -1.075000
H -3.541000 -0.838000 -0.649000
C -1.240000 -4.667000 1.041000
H -1.149000 -3.779000 0.451000
H 3.541000 0.838000 0.650000
C 1.240000 4.667000 -1.041000
C 4.523000 0.829000 1.075000
H 1.148000 3.779000 -0.450000

NDI-PyTz-3

```
Opt   TightSCF  B3LYP
PrintBasis 6-31G*
%output
print[p_mos] 1
end #output
xyz 0   1
O  3.257000 1.694000 -1.988000
O  1.951000 3.045000 2.102000
N  2.504000 2.394000 0.017000
C  0.516000 0.478000 0.007000
N  3.549000 3.320000 0.032000
C  0.589000 1.392000 1.085000
C  1.436000 0.502000 -1.051000
C  2.483000 1.549000 -1.093000
C  1.709000 2.356000 1.143000
C  1.364000 -0.407000 -2.064000
H  1.994000 -0.395000 -2.748000
N  5.493000 4.218000 0.322000
C  -0.344000 1.359000 2.074000
H  -0.301000 1.980000 2.766000
N  4.673000 5.157000 -0.291000
C  3.508000 4.617000 -0.468000
C  4.806000 3.124000 0.499000
C  2.381000 5.245000 -1.152000
C  5.298000 1.922000 1.089000
C  6.284000 -0.352000 2.202000
H  6.593000 -1.140000 2.592000
C  7.030000 0.754000 2.183000
H  7.882000 0.737000 2.556000
C  6.585000 1.881000 1.641000
H  7.123000 2.640000 1.630000
C  1.509000 6.938000 -2.536000
H  1.604000 7.694000 -3.068000
C  2.641000 6.420000 -1.852000
H  3.478000 6.827000 -1.870000
C  0.319000 6.362000 -2.431000
H  -0.425000 6.724000 -2.854000
O  -3.256000 -1.694000 1.987000
O  -1.950000 -3.045000 -2.103000
N  -2.504000 -2.394000 -0.018000
C  -0.515000 -0.478000 -0.007000
```

N -3.549000 -3.320000 -0.033000
C -0.589000 -1.392000 -1.086000
C -1.436000 -0.502000 1.050000
C -2.483000 -1.549000 1.092000
C -1.708000 -2.356000 -1.143000
C -1.363000 0.407000 2.063000
H -1.994000 0.395000 2.747000
N -5.492000 -4.218000 -0.323000
C 0.344000 -1.361000 -2.074000
H 0.301000 -1.980000 -2.766000
N -4.673000 -5.157000 0.291000
C -3.508000 -4.617000 0.467000
C -4.805000 -3.124000 -0.499000
C -2.381000 -5.245000 1.152000
C -5.298000 -1.922000 -1.089000
C -6.284000 0.352000 -2.203000
H -6.593000 1.140000 -2.592000
C -7.030000 -0.754000 -2.183000
H -7.882000 -0.737000 -2.557000
C -6.584000 -1.881000 -1.642000
H -7.122000 -2.640000 -1.630000
C -1.509000 -6.938000 2.535000
H -1.604000 -7.694000 3.067000
C -2.641000 -6.420000 1.852000
H -3.477000 -6.827000 1.869000
C -0.319000 -6.362000 2.430000
H 0.425000 -6.724000 2.853000
N 4.998000 -0.277000 1.603000
N -0.218000 -5.247000 1.700000
N -4.998000 0.277000 -1.604000
N 0.219000 5.247000 -1.701000
C -4.522000 -0.829000 -1.075000
H -3.541000 -0.838000 -0.649000
C -1.240000 -4.667000 1.041000
H -1.149000 -3.779000 0.451000
C 4.523000 0.829000 1.075000
H 3.541000 0.838000 0.650000
C 1.240000 4.667000 -1.041000
H 1.148000 3.779000 -0.450000

Frequency with intensity of the optimized geometry of **NDI-PyTz-1**, **NDI-PyTz-2** and **NDI-PyTz-3**.

NDI-PyTz-1		**NDI-PyTz-2**		**NDI-PyTz-3**	
Frequency (cm^{-1})	Intensity	Frequency(cm^{-1})	Intensity	Frequency(cm^{-1})	Intensity
7.7211	0	3.6073	0.1701	8.026	0.0171
11.6678	0.0002	10.6846	0.177	9.8568	0.3106
11.7745	4.3528	15.8386	0	15.0727	0
11.8175	0.1882	22.1617	0.696	29.1699	0
18.5856	0	23.3691	0.0025	30.1821	0.19
18.7975	0	29.2658	0.0018	30.6833	0
18.9404	0	32.7287	6.877	33.078	0
27.0162	0	33.5549	0.0027	36.1042	1.7401
37.6105	7.2091	35.8042	1.5864	36.2533	0.0152
38.7807	0	42.9349	0	46.7763	0
56.8842	1.0354	53.9878	11.9207	56.4657	7.8693
58.1791	16.8608	55.2419	0.0002	57.4297	0.7076
60.6892	0	55.9446	0.346	59.6953	0
61.8081	0.0003	71.6698	0.0212	71.557	0.2584
77.7531	4.1849	72.8489	8.0601	74.6889	1.4937
79.9284	0	73.5475	0.0006	75.6676	0
80.2268	0	90.764	0	89.7699	0
100.457	0	97.7841	0	96.7863	0
108.7745	16.4384	106.8787	19.0751	105.3218	21.3985
123.6665	0	133.7609	0	133.2642	0
123.7081	0	134.5043	0.0007	134.7652	0.1429
159.991	0	143.6222	0.4202	146.8522	0.0372
180.0177	3.5974	143.6774	11.0787	146.8863	8.7944
185.1263	4.5497	149.3345	0	152.5152	0
190.9133	0	190.1112	4.1486	190.4014	4.2829
194.3903	0	195.1878	2.6335	196.4948	0.4838
196.3998	23.6853	209.6638	10.5306	213.5092	21.9749
223.6146	9.535	227.5494	0	227.0419	0
225.4201	7.7453	237.3535	0	238.0488	0
236.9744	0	243.7846	0.0002	239.1771	0
253.8367	0	244.1028	2.643	240.0819	14.4883
257.0638	0.6562	249.6426	24.135	249.4573	38.932
301.236	0	297.5419	0.1259	297.3197	0.0882
324.4368	0	307.9241	0	312.5586	0
324.519	0.0001	316.0199	7.534	318.1892	2.1523
336.5656	0	326.9231	0	329.294	0
337.4792	0	334.8888	32.8478	339.0094	12.0766
365.8488	4.9372	343.6387	0	344.6533	0
385.4532	0	352.3868	0	353.888	0

393.5845	4.8625	387.0449	5.0195	391.0798	0.0009
395.9275	0	389.5101	0.0001	391.0845	0.0529
403.36	112.8256	402.1557	0	391.1593	0.005
405.3804	0	409.1979	30.6396	391.2078	0
412.2359	0	410.104	0.0038	392.1079	0.1616
412.2721	0	411.2435	10.7474	393.2768	0
413.749	31.349	411.3106	0.1816	402.3685	0
415.1464	0	417.2871	5.4505	416.6603	3.5148
421.1864	0	419.1802	36.4419	419.4716	75.8701
437.8284	0.4431	431.911	0	431.7027	0
437.9771	4.5706	434.2257	0	437.738	0
439.554	0	441.7994	2.8483	442.4395	7.8503
451.4328	0	451.9531	0	451.7887	0
471.2229	0	463.6639	43.9658	466.0725	43.5739
474.84	27.8657	468.3	0	468.3075	0
483.7437	0.0612	472.9194	0.951	474.492	0.6206
515.4462	9.73	494.3056	0.2253	509.0466	16.6122
515.7586	0	497.6446	0	513.87	0
530.5959	0	522.7289	0	539.6464	0
530.612	0	533.6654	0.5172	542.808	0
548.4552	0	541.3146	0	552.8064	27.084
564.0618	2.8655	571.2494	14.9244	572.8162	14.7697
576.9619	0	574.9201	0	577.3584	0
608.6103	0	609.1929	0.0883	609.0601	0.0001
614.9614	0	613.8316	0	613.7978	0
615.0271	0	629.6325	0	628.6168	0
621.6341	96.1101	630.1486	8.0938	635.5952	142.7279
634.1165	14.761	630.5157	26.5532	677.8417	8.6569
634.2172	0	630.951	0	677.9743	0.0001
649.3362	0	637.6431	0	678.2334	0.093
656.3323	21.4571	645.7367	52.8877	678.2569	0.0001
710.1203	0	714.3313	18.5943	683.4177	9.8864
711.6088	0	714.7828	0	685.134	0
711.7615	0	715.5511	0	711.294	0
712.6481	24.2274	722.7395	0	719.9927	0
713.9812	46.845	725.1078	57.2737	722.4484	10.419
714.5814	0	725.2614	81.0541	723.3302	19.1366
718.8146	0	725.9017	0.0064	727.68	0
732.5495	0	726.6872	0.0001	737.4414	0.0001
743.2658	177.6333	727.0485	12.7733	738.7367	179.8314
751.1451	1.8804	728.5859	30.2685	746.4632	0
758.0684	10.924	732.3612	0	748.8845	3.5241
758.2842	0.0001	739.3443	0	753.2172	28.8883

758.3872	0	747.2219	130.6807	757.4207	70.4845
758.6694	0	749.3776	0.3398	759.1756	0
760.3501	0	759.2497	100.7501	759.5354	1.5826
762.6866	0.3211	760.9976	0	763.4602	0
763.8926	169.5873	762.3604	11.6751	765.1646	41.6582
766.2982	0	769.4363	0.0732	768.8507	0.5958
790.6521	0	792.734	0	792.7122	0
799.1886	73.1956	795.3695	49.5874	795.8628	67.3188
808.4739	0	803.74	0	804.9209	0
808.524	0	829.5297	17.7618	842.4766	1.2171
810.5141	0	832.1012	0	847.4497	0
812.1609	0	834.0684	0.0014	851.8273	0.0004
812.6643	85.0364	834.1964	23.8591	851.9686	49.092
851.2038	185.6696	849.6105	208.8453	852.9343	290.5764
893.7946	28.1448	889.5096	0	889.7541	0
896.7308	0	896.3165	28.6243	896.0582	15.713
898.1801	0	900.4076	0	896.6756	0.0007
926.1673	0	958.4327	3.3388	896.7987	1.0856
926.1779	0	958.4831	1.5617	896.9348	0.0008
926.3859	0.0008	958.637	1.7059	897.3936	13.7046
926.3951	3.6583	958.6842	2.1552	900.8893	0
981.1743	0.1606	970.7821	58.8942	977.2673	8.8849
981.1792	41.2379	971.0014	0	977.5843	0
991.6597	0.0001	984.3613	1.8863	989.8123	4.8166
991.6716	0.0002	984.3818	6.2622	989.8227	0.0093
991.6765	0.0003	985.4007	2.6494	990.5229	3.9636
991.6894	1.4439	985.423	0.6738	990.5271	0.0417
1005.5282	0	1005.6284	124.5379	1003.5747	2.5148
1007.3463	126.071	1008.9955	0.0142	1003.599	0.0001
1009.2881	0	1012.1496	0.0711	1003.6268	0.2479
1011.7076	0	1012.1545	0.0628	1003.629	0.0005
1011.8388	49.203	1012.1608	0.2193	1005.9002	120.0881
1013.3314	0	1012.1695	3.0325	1009.4891	0.0156
1013.3365	21.5622	1012.4877	0	1012.8157	0
1025.9231	0	1021.0509	0	1013.1697	0.0033
1025.9245	0.0001	1024.463	25.5767	1013.186	28.61
1025.9408	0.0066	1038.9163	0.0016	1013.195	0.3082
1025.9428	0.0388	1038.9283	41.1461	1013.2795	0.0001
1043.2882	0	1043.3425	0	1038.8457	0
1057.1652	5.9012	1044.847	6.7626	1049.4471	0.0381
1063.2596	0	1050.7602	0	1056.758	0
1070.7889	0	1068.1188	0.0235	1093.9962	1.6299
1070.8175	11.5095	1068.1386	2.9855	1094.1154	0.4678

1084.8098	13.9884	1075.3571	0.0031	1094.1208	31.6964
1086.3127	0	1075.418	0	1094.2056	0.0002
1122.0224	0.0079	1114.9018	0.5794	1113.4385	1.8019
1122.0325	19.8141	1118.7865	0	1115.9139	0
1123.0605	23.7589	1143.9602	35.4197	1120.6178	1.9947
1123.154	0.0001	1143.9747	0.9207	1120.6226	0.0859
1130.8996	0	1144.0003	0.0244	1123.4933	0.736
1138.811	0.1325	1144.1155	28.8931	1124.3219	0
1155.1174	44.4384	1146.8678	143.0155	1146.9386	155.4188
1159.443	0	1151.1559	0	1152.0724	0
1167.9285	0	1162.1267	0	1162.1429	0
1177.2877	0.3147	1177.0356	0	1176.5917	0
1177.2902	9.5402	1191.5856	42.1626	1192.2855	43.4117
1177.3303	6.928	1191.6113	113.508	1192.332	138.1439
1177.5799	0	1194.197	0.0001	1195.1932	0
1201.9793	107.7393	1204.2043	416.3733	1204.4003	402.1803
1205.1976	0	1228.3511	0	1237.8262	0
1208.974	0.573	1228.829	14.8042	1248.0112	13.9364
1208.9779	10.4514	1232.1849	0.0007	1248.0767	0.0003
1221.3056	412.942	1232.2987	21.2952	1248.4299	0.0008
1243.9012	0	1237.8266	0	1248.4597	8.7634
1272.3717	575.5914	1267.4913	389.2981	1267.3568	385.7659
1298.6404	0	1290.528	0	1287.9494	29.0274
1311.7367	134.574	1299.5645	18.9863	1287.986	0
1312.7997	0	1299.7752	0.0006	1289.853	0.0116
1314.1584	0.0129	1301.2774	0.0276	1289.8565	3.792
1314.18	17.4185	1301.2817	0.2779	1289.9171	0.0003
1318.8563	71.4365	1314.4759	469.9787	1314.1148	430.1311
1319.5916	0.0001	1351.322	874.1285	1343.8889	634.082
1320.8053	383.9204	1354.3581	0	1346.5036	0
1322.0905	0.2253	1361.3182	0.0009	1350.8533	0.0069
1322.0968	45.7803	1361.3258	10.9301	1350.8583	6.2938
1370.4297	0	1369.1017	0	1363.6512	0
1373.9607	712.3	1370.2108	81.5772	1364.3608	325.7922
1385.653	0.0062	1378.1026	2.4759	1378.5533	7.2955
1385.6544	31.1106	1378.1113	22.6068	1378.5553	3.9003
1404.3893	1.3501	1398.2389	0	1398.5633	0
1406.13	0	1402.7009	1.3157	1402.6549	1.2297
1443.0647	0	1430.5872	15.3547	1434.3004	1.6903
1446.5009	6.5043	1432.4763	0	1436.4232	0
1451.8449	0	1440.6197	0	1440.3379	0
1468.0019	180.6105	1451.2885	0.6637	1450.7558	0.0037
1474.7247	0.0071	1451.3001	272.9148	1450.7765	91.7793

1474.7575	202.2672	1455.7871	127.7337	1458.8834	320.9882
1481.3049	0.0021	1460.0947	0	1462.8984	0
1481.5545	184.0123	1466.1072	51.277	1466.054	0.0114
1494.6889	0.0011	1504.6104	0	1504.5133	0
1494.6996	271.9225	1514.496	95.19	1508.6883	0.281
1500.6069	153.4206	1514.5072	0.3765	1508.7302	81.9436
1500.6129	0.0327	1516.2923	0.8233	1523.6205	0.4952
1505.6343	0	1516.3036	98.5943	1523.6317	98.2202
1548.9715	0	1557.6754	0.4486	1558.882	37.0141
1548.9793	6.696	1557.6814	1.9196	1561.0627	2.8264
1558.9478	27.0172	1558.9542	36.6916	1561.0667	4.6235
1576.1991	0.0571	1579.2977	2.9115	1575.4162	2.8122
1576.2004	0.0143	1579.3051	25.1594	1575.433	94.2946
1621.7692	0	1618.9561	0.0392	1607.8745	0.1413
1621.804	3.215	1618.9633	26.5284	1607.8834	94.9946
1624.6875	37.3806	1619.9168	138.1884	1607.9737	4.4821
1624.731	0.0007	1620.0426	0	1608.0253	0.0009
1626.8301	301.5332	1624.3329	251.0933	1624.1717	303.2303
1639.0895	0.2084	1644.462	0	1644.405	0
1639.0993	258.3693	1648.1583	33.3621	1653.5192	0.0974
1640.3285	0.0036	1648.168	0.0164	1653.5418	291.2715
1640.3525	12.3362	1648.687	0.0004	1655.3366	11.5137
1645.665	0	1648.6966	106.3481	1655.3454	0.017
1662.8897	0	1660.7348	0	1660.5268	0
1761.2327	1374.1636	1766.0833	1228.6262	1767.6093	1214.9442
1762.4666	0.0022	1766.4644	0.3658	1767.9297	0.0085
1791.4429	792.6085	1791.7208	925.0134	1792.8888	931.7303
1800.2986	0	1801.8608	0.0003	1803.0189	0
3179.078	0.0157	3179.7542	31.2179	3178.3982	34.1015
3179.1343	36.0476	3179.7606	75.0117	3178.4029	58.6325
3179.1962	90.1582	3179.7658	3.8588	3178.406	49.3598
3179.252	0.0318	3179.7824	18.5562	3178.4105	41.4731
3207.5458	3.48	3192.8052	11.845	3182.0713	0.2155
3207.5521	5.4069	3192.8212	27.2909	3182.076	93.9253
3207.5711	24.3962	3192.8875	10.5639	3182.2136	2.193
3207.5754	8.0706	3192.8969	3.0903	3182.2189	0.0175
3223.7831	0.8708	3214.8078	13.54	3230.3392	4.6502
3223.7866	70.6009	3214.8134	18.384	3230.3413	7.3365
3223.826	4.1531	3214.8216	0.3045	3230.3666	5.0317
3223.8308	0.5493	3214.8272	0.2769	3230.3718	2.882
3229.9239	0.039	3227.615	13.0951	3232.8344	0.5312
3230.1551	0	3227.62	23.7016	3233.064	0
3237.7797	3.0987	3227.6578	5.0555	3237.4155	4.1143

3237.7817	3.4714	3227.6636	1.6606	3237.4268	7.8814
3237.8078	2.3458	3232.6722	0.4287	3237.4932	4.6938
3237.8104	0.6361	3232.9011	0	3237.5058	1.7247
3239.807	0.0765	3242.2459	0.5702	3242.3831	0.7511
3239.867	0	3242.29	0.0003	3242.4257	0.0012

Energies of the optimized structures of **NDI-PyTz-1**,**NDI-PyTz-2**and **NDI-PyTz-3**.

NDI-PyTz-1 (a.u.)	**NDI-PyTz-2 (a.u.)**	**NDI-PyTz-3 (a.u.)**
-2418.05868	-2418.03574	-2418.032736

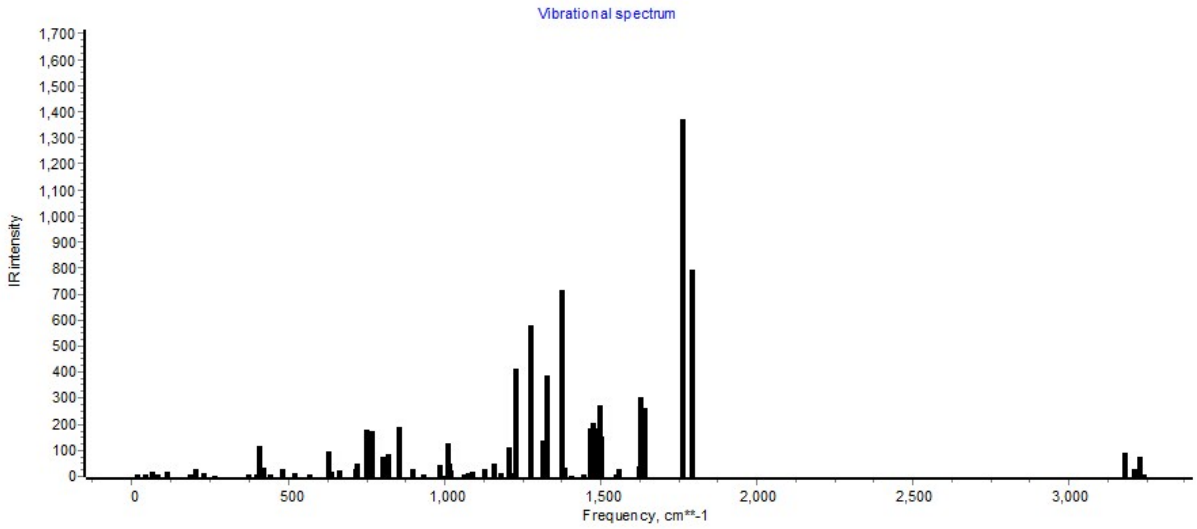

Fig. S28. Vibrational spectrum of compound **NDI-PyTz-1**.

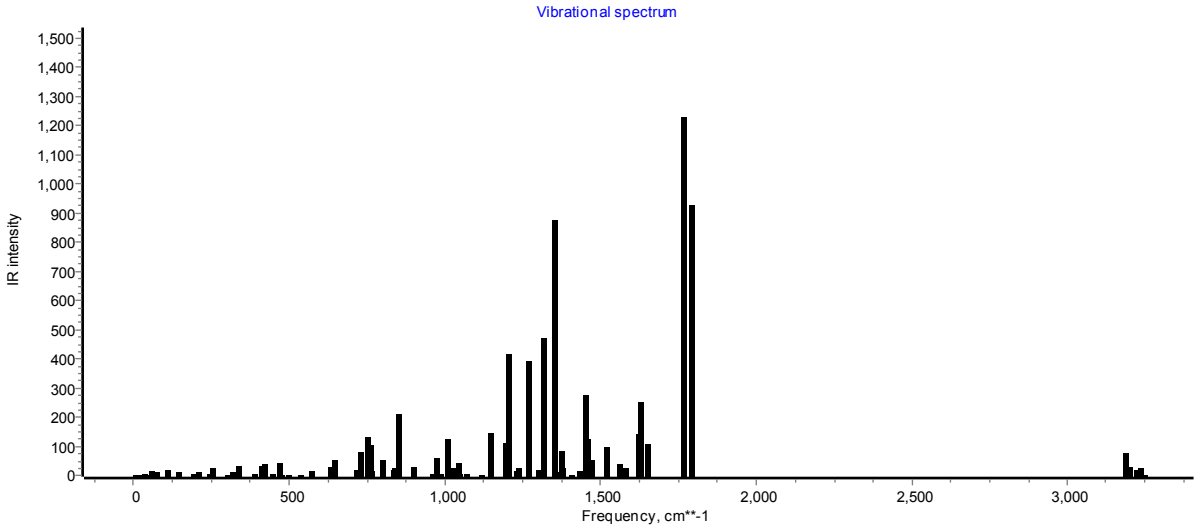

Fig. S29. Vibrational spectrum of compound **NDI-PyTz-2**.

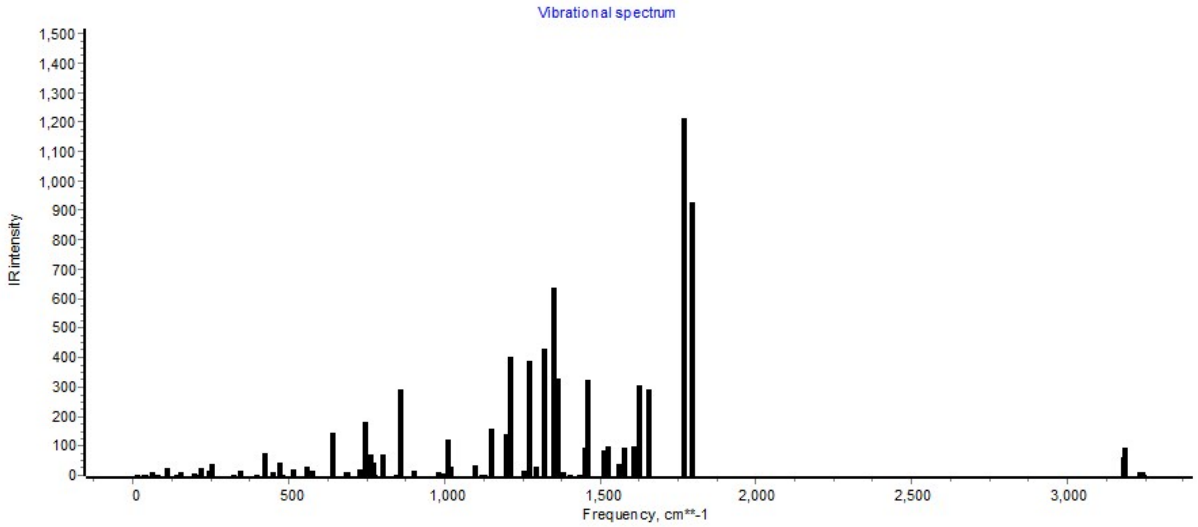

Fig. S30. Vibrational spectrum of compound **NDI-PyTz-3**.

Table S1. Crystal data and structure refinement for **NDI-PyTZ-1**.

Compound	**NDI-PyTZ-1**
Empirical formula	$C_{41}H_{27}N_{13}O_5$
Formula weight	781.75
Temperature/K	300(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.5300(7)
b/Å	13.3747(7)
c/Å	13.8179(8)
α/°	62.734(2)
β/°	68.276(2)
γ/°	76.955(2)
V/Å^3	1907.76(19)
Z	2
ρ_{calc}g/cm^3	1.359
μ/mm^{-1}	0.095
F(000)	806
Crystal size/mm^3	0.30 × 0.12 × 0.06
2ϑ range for data collection/°	2.37-26.371
Completeness to theta	99.6 %
Index ranges	-15≤*h*≤15, -16≤*k*≤16, -16≤*l*≤17
Reflections collected	32354
Independent reflections	7468 [R_{int} = 0.0696]
Data/restraints/parameters	7468 / 160 / 534
Goodness-of-fit on F^2	1.031
Final *R* indexes [$I>2\sigma(I)$]	R_1 = 0.0841, wR_2 = 0.2378
Final *R* indexes [all data]	R_1 = 0.1591, wR_2 = 0.2701
Largest diff. peak/hole / e Å^{-3}	0.42 and -0.33

[a]$R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR_2 = \{\Sigma[w(|Fo|^2 - |Fc|^2)_2]/\Sigma[wFo_4]\}^{1/2}$.

Table S2. Selected bond lengths [Å] and angles [°] for **NDI-PyTz-1**.

Bond	**Lengths**
O(4)-C(36)	1.194(3)
O(2)-C(13)	1.202(4)
O(3)-C(32)	1.207(3)
O(1)-C(17)	1.206(4)
N(11)-C(32)	1.381(4)
N(11)-N(10)	1.394(3)
N(1)-C(2)	1.334(5)
N(1)-C(5)	1.340(4)
N(8)-N(9)	1.393(6)
Bond	**Angles**
N(2)-C(6)-N(4)	108.4(3)
C(41)-N(13)-C(40)	110.5(11)
C(41)-N(13)-C(39)	125.0(12)
C(40)-N(13)-C(39)	121.6(12)

Table S3. Hydrogen bonds for **NDI-PyTz-1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11)...O(4)	0.93	2.59	3.229(6)	126.2
C(40)-H(40B)...O(2)$^{\#3}$	0.96	2.60	3.242(11)	124.6

Symmetry transformations used to generate equivalent atoms: #3 x-1,y,z+1.

Table S4. Stokes shift of **NDI-PyTz-1**, **NDI-PyTz-2** and **NDI- PyTz-3** calculated with λ_{em} and λ_{ex}.

	λ_{em} (nm)	λ_{ex} (nm)	Stokes shifts (nm)
NDI-PyTz-1	432	374	58
NDI-PyTz-2	432	374	58
NDI-PyTz-3	428	374	54

Table S5. De-convoluted data for the time resolved fluorescence decays of the **NDI-PyTz-1**, **NDI-PyTz-2** and **NDI- PyTz-3**.

Probe	a_1	τ_1 (ns)	a_2	τ_2 (ns)	τ_{avg} (ns)	χ^2
NDI-PyTz-1	0.15	1.20	0.84	0.18	0.33	1.07
NDI-PyTz-2	0.17	1.34	0.80	0.24	0.42	1.08
NDI-PyTz-3	0.092	1.63	0.038	6.36	0.40	1.04

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