Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

Synthesis, optical properties and cation mediated tuning of reduction potentials of core-annulated naphthalene diimide derivatives

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1. Materials and Methods

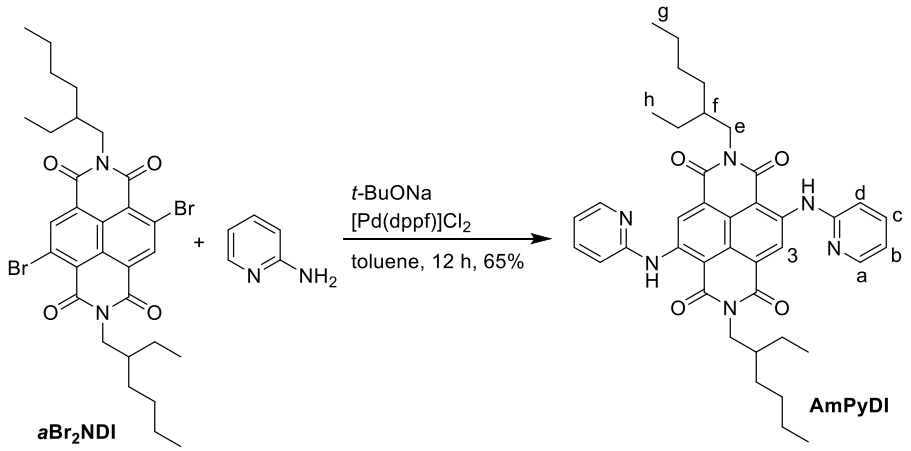
Naphthalene-1,4,5,8-tetracarboxylic dianhydride, zinc trifluoromethanesulfonate salt, and [Pd(dppf)]Cl_2 were purchased from Alfa-Aesar. Deuterated solvents ($CDCl_3$: 99.8 atom % D; CD_3CN: 99.8 atom % D), and 2-ethyl-1-hexylamine were procured from Sigma Aldrich. Triflic acid, 2-aminopyridine and *t*-BuONa were purchased from Spectrochem. Trifluoroacetic acid, HCl and triethylamine were purchased from Merck. DBH was procured from Avra. UV and HPLC grade solvents were purchased from either Merck or Spectrochem. Tetrabutylammonium hexafluorophosphate was purchased from TCI. All of the above mentioned reagents were used without further purification. Neutral alumina (activity-II) for column chromatography was procured from Merck. Silica gel for column chromatography (60-120 mesh) was obtained from Spectrochem. Analytical thin layer chromatography (TLC) plate (silica gel 60 F254) was purchased from Merck.

Reactions were monitored by TLC and visualised under 254 nm and 365 nm UV-light. ^1H and ^{13}C NMR measurements were done at 293K either on a Bruker Avance 500 MHz NMR spectrometer or on a Bruker Avance III 600 MHz NMR spectrometer using deuterated solvent as the lock and residual solvent as the internal reference. Chemical shifts are reported in δ (ppm) relative to the residual solvent peak ($CDCl_3$: 7.26 for ^1H, 77.0 for ^{13}C; CD_3CN: 1.94 for ^1H). The following abbreviations were utilized to describe peak patterns: s = singlet, d = doublet, t= triplet, br = broad, and m = multiplet. The numbering of the carbon atoms of the molecular formulae shown in the experimental section is only used for the assignments of the NMR signal and is not in accordance with the IUPAC nomenclature rules. High resolution mass spectrometry (HRMS) measurements were done with Agilent QTOF 6520 mass spectrometer using electrospray ionization (ESI) mode. Infra-red (IR) spectra were collected on a diamond tipped Perkin-Elmer Spectrum Two FT-IR spectrometer and frequencies are presented in reciprocal centimeter (cm^{-1}). UV-vis absorption measurements were carried out on a Cary-100 UV-Vis spectrophotometer at 293K. Photoluminescence properties were studied on a Horiba Fluoromax fluorimeter. Corrections of the spectra were done by the correction factor implemented in the software. For photophysical measurements, quartz UV-cuvettes of 10 mm path length were used. Cyclic voltammetry measurements were done in dry and deoxygenated chloroform and acetonitrile using PGSTAT101 potentiostat from Metrohm© and the corresponding software NOVA 1.11.

Compound ***a*Br$_2$NDI** and ***b*BrNDI** were prepared following literature procedure.[1] All of the coupling reactions were carried out under Argon atmosphere. The highest occupied molecular orbital (HOMO) and LUMO energy levels of the doubly-annulated imide was calculated by the DFT/B3LYP method with 6-31+G(d,p) basis set in chloroform.[2]

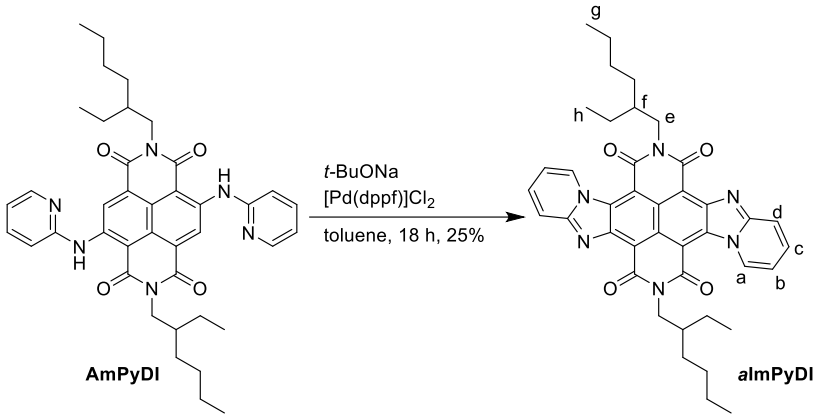
2. Synthesis

Synthesis of AmPyDI



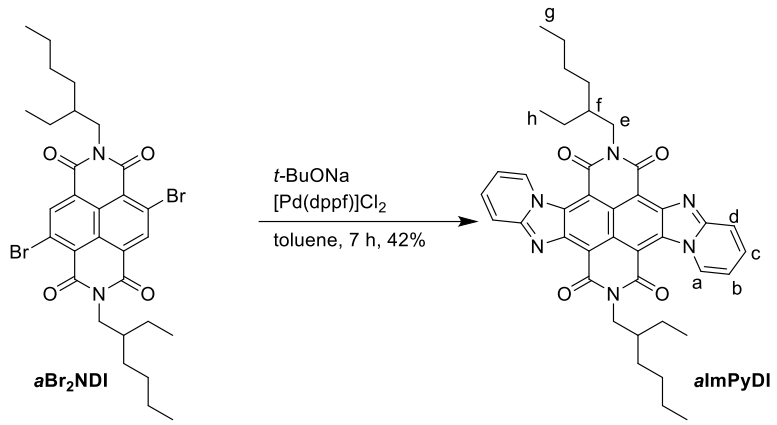
2-Aminopyridine (44.0 mg, 461 µmol) was loaded in to a 100 mL two-neck round bottomed flask under inert condition. After addition of 4 mL of toluene, *t*-BuONa (44.0 mg, 461 µmol) and [Pd(dppf)]Cl_2 (6.00 mg, 7.60 µmol) were added. Finally, ***a*Br$_2$NDI** (100 mg, 153 µmol) was added to the reaction mixture, and subsequently refluxed for 12 h. The reaction mixture was then cooled down to room temperature, and 20 mL of hexane was added to precipitate out the product, which was separated by filtration. After washing with hexane (3 x 40 mL), the precipitate was dissolved in 1 mL of chloroform. The crude mixture was further precipitated out by adding 20 mL of methanol. The purple residue was separated by filtration and washed with hexane (3 x 40 mL). After drying in vacuum, **AmPyDI** was received as purple solid. Yield: 67.0 mg (65%) ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.13 (s, 2H, N-H), 10.14 (s, 2H, 3-H), 8.48 (dd, ^3J = 5.5 Hz, ^4J = 2.0 Hz 2H, a-H), 7.70 (ddd, ^3J = 7.0 Hz, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2H, c-H), 7.09 (d, ^3J = 8.0 Hz, 2H, d-H), 7.02 (dd, ^3J = 7.0 Hz, ^3J = 5.5 Hz, 2H, b-H), 4.22-4.14 (m, 4H, e-H), 2.02-1.96 (m, 2H, f-h), 1.43-1.37 (m, 8H), 1.35-1.29 (m, 8H), 0.94 (t, ^3J = 7.5 Hz, 6H, [g/h]-H), 0.89 (t, ^3J = 7.0 Hz, 6H, [g/h]-H) ppm.; ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 163.1, 153.6, 148.2, 144.7, 138.1, 125.7, 124.3, 122.5, 118.2, 114.5, 104.8, 44.5, 37.7, 30.7, 28.7, 24.0, 23.1, 14.1, 10.7 ppm.; HRMS (ESI) m/z calculated for $[C_{40}H_{46}N_6O_4+H]^+$ 675.3653, found: 675.3651; IR 2958, 1690, 1663, 1590, 1466, 1292, 1198, 1153, 773 cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm (ε/$M^{-1}cm^{-1}$) 587 (90 400); mp > 200 °C.

Synthesis of *a*ImPyDI from AmPyDI



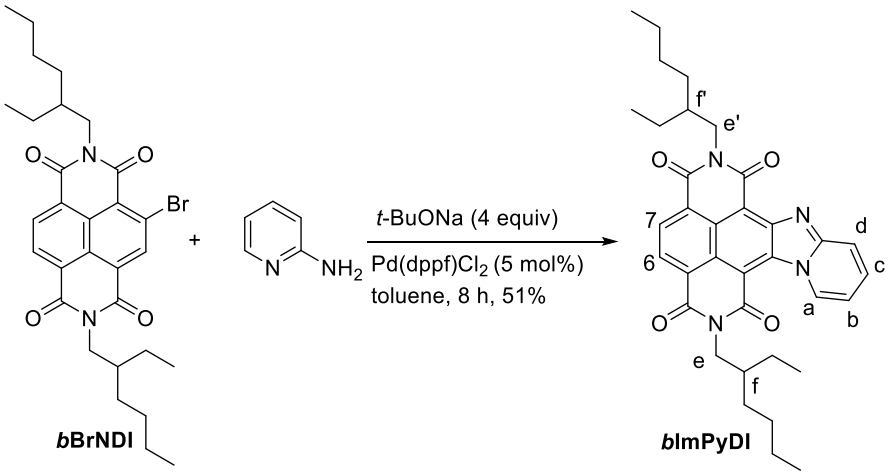
Under an inert condition **AmPyDI** (40.0 mg, 59.0 µmol), [Pd(dppf)]Cl_2 (5.00 mg, 6.00 µmol) and *t*-BuONa (23.0 mg, 240 µmol) were refluxed in argon-purged toluene (10 mL) in an oven-dried 100-mL two-neck round-bottom flask for 18 h. After cooling down the reaction mixture to room temperature, the dark precipitate was separated. The residue was then washed successively with hexane (3 x 50 mL) and DCM (2 x 20 mL). Finally, the crude product was purified by column chromatography in neutral alumina using DCM as eluent. The analytically pure product ***a*ImPyDI** was obtained as green solid. Yield 9.00 mg (25%).^{1}H NMR (600 MHz, $CDCl_3$) δ 10.32 (d, ^{3}J =7.2 Hz, 2H, a-H), 8.08 (d, ^{3}J = 8.4 Hz, 2H, d-H), 7.77 (dd, ^{3}J = 7.8 Hz, ^{3}J = 8.4 Hz, 2H, c-H), 7.04 (dd, ^{3}J = 7.2 Hz, ^{3}J = 7.8 Hz, 2H, b-H), 4.44-4.36 (m, 4H, e-H), 2.24-2.19 (m, 2H, f-H), 1.53-1.47 (m, 8H), 1.44-1.29 (m, 8H), 1.00 (t, ^{3}J = 7.2 Hz, 6H, [g/h]-H), 0.09 (t, ^{3}J = 7.2 Hz, 6H, [g/h]-H), ppm.; ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 162.0, 156.7, 135.4, 134.6, 133.6, 121.9, 118.7, 113.3, 112.9, 111.4, 45.1, 38.0, 31.0, 28.7, 24.3, 23.2, 14.1, 10.7 ppm.; HRMS (ESI) m/z calculated for $[C_{40}H_{42}N_6O_4+H]^+$ 671.3340, found: 671.3315; IR 3035, 2954, 2849, 2870, 1699, 1644, 1579, 1515, 1467, 1441, 1389, 1378, 1364, 1321, 1303, 1273, 1252, 1226, 1205, 1179, 1145, 1119, 1077, 879, 858, 788, 753 cm^{-1}; UV-vis ($CHCl_3$) λ_{max}/nm ($\varepsilon/M^{-1}cm^{-1}$) 667 (35 140); mp 186 °C.

Synthesis of *a*ImPyDI from *a*Br$_2$NDI



Into a 100 mL two-neck round-bottom flask was added compound ***a*Br$_2$NDI** (120 mg, 185 µmol) 2-aminopyridine (43.0 mg, 462 µmol), *t*-BuONa (106 mg, 1.11 mmol.) and [Pd(dppf)]Cl_2 (14.0 mg, 18.5 µmol) under inert atmosphere. After addition of argon-purged toluene (15mL), the reaction mixture was refluxed for 7 h. It was then cooled down to room temperature. The dark precipitate was separated by filtration, washed successively with hexane (3 x 50 mL) and DCM (2 x 40 mL). The crude product was purified using column chromatography (neutral alumina) with DCM/hexane (4:1) mixture as eluent. The desired product was obtained as green solid in 42% yield (50.0 mg).

Synthesis of *b*ImPyDI



Under an inert condition ***b*BrNDI** (75.0 mg, 130 µmol), 2-aminopyridine (25.0 mg, 260 µmol), *t*-BuONa (56.0 mg, 520 µmol) and [Pd(dppf)]Cl_2 (10.0 mg, 13.0 µmol) were refluxed in argon-purged toluene (15 mL) in an oven-dried 100-mL two-neck round-bottom flask for 7 h. After

cooling down the reaction mixture to room temperature, the precipitate separated, and washed with hexane (3 x 50 mL). The crude product was purified to further purification by column chromatography in silica gel with DCM as eluent. Compound ***b*ImPyDI** was received as magenta coloured solid. Yield 41.0 mg (51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.54 (d, ^{3}J = 6.5 Hz, 1H, a-H), 8.93 (d, ^{3}J = 7.5 Hz, 1H, [6/7]-H), 8.87 (d, ^{3}J = 7.5 Hz, 1H, [6/7]-H), 8.08 (d, ^{3}J = 7.5 Hz, 1H, d-H), 7.79 (dd, ^{3}J = 7.5 Hz, ^{3}J = 7.5 Hz, 1H c-H), 7.06 (dd, ^{3}J = 7.5 Hz, ^{3}J = 6.5 Hz, 1H, b-H), 4.33-4.22 (m, 4H, [e.e']-H), 2.14-2.09 (m, 1H, [f/f']-H), 2.07-2.02 (m, 1H, [f/f']-H), 1.46-1.27 (m, 16H), 1.00-0.94 (m, 6H), 0.91-0.86 (m, 6H) ppm.; ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5, 163.4, 163.2, 162.2, 156.9, 147.8, 135.5, 134.8, 133.6, 130.7, 129.6, 126.4, 126.2, 125.5, 122.2, 118.8, 113.9, 113.1, 111.7, 45.0, 44.6, 37.8 (2C), 30.8, 30.6, 28.8, 28.5, 24.1, 23.9, 23.1, 14.2, 14.1, 10.7, 10.6 ppm.; HRMS (ESI) m/z calculated for $[C_{35}H_{40}N_4O_4+H]^+$ 581.3182, found: 581.3151; IR 2957, 2919, 2870, 1700, 1651, 1580, 1510, 1459, 1378, 1332, 1273, 1244, 1205, 1084, 975, 773, 749 cm^{-1}. UV-vis ($CHCl_3$) λ_{max} /nm (ε /$M^{-1}cm^{-1}$) 537 (7830), 412 (12730) cm^{-1}; mp > 200 °C.

Optimisation of condition for the synthesis of *a*ImPyDI in two-step procedure

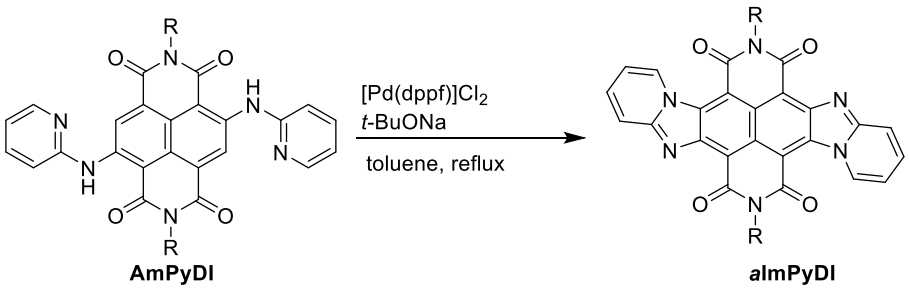


Table S1.

Sl no	[Pd(dppf)]Cl_2	*t*-BuONa (equiv)	solvent	yield (%) (for final step)	over all yield (%)
1.	10 mol%	2.5	toluene	20	13
2.	10 mol%	4.0	toluene	25	16
3.	10 mol%	6.0	toluene	25	16

Optimisation of condition for single-step synthesis of *a*ImPyDI

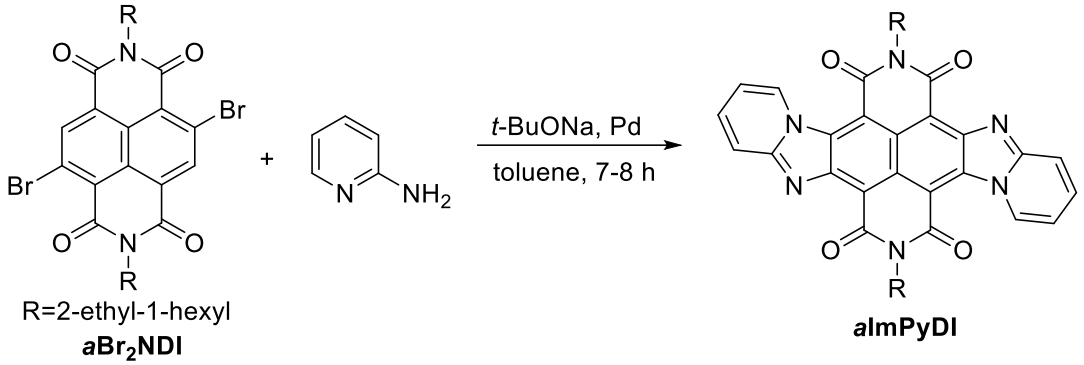
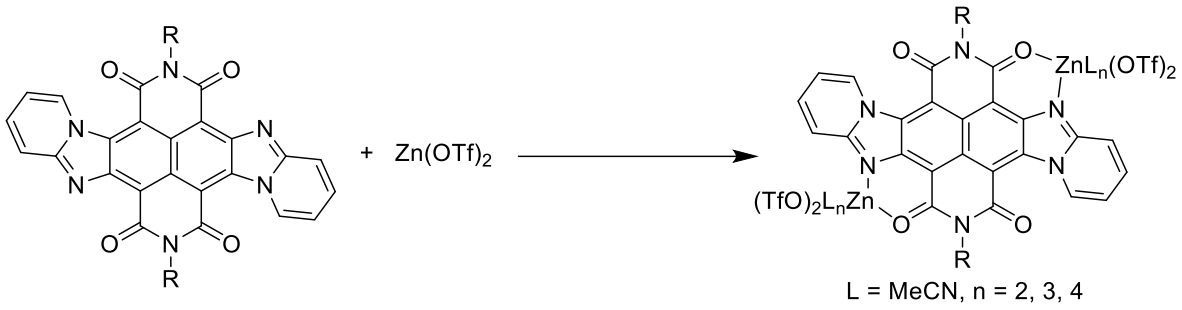


Table S2. Optimization of reaction conditions

Sl.No.	Catalyst (10 mol%)	*t*-BuONa (equiv)	Solvent	Yield (%)
1	$[Pd(dppf)]Cl_2$	2.5	Toluene	Trace
2	$[Pd(dppf)]Cl_2$	4	Toluene	15
3	**$[Pd(dppf)]Cl_2$**	**6**	**Toluene**	**42**
4	$[Pd(dppf)]Cl_2$	6	DMF	10
5	$[Pd(dppf)]Cl_2$	6	1,4-Dioxane	Trace
6	$Pd(OAc)_2$	6	Toluene	22
7	$Pd(PPh_3)_4$	6	Toluene	15

Synthesis of zinc complex of *a*ImPyDI

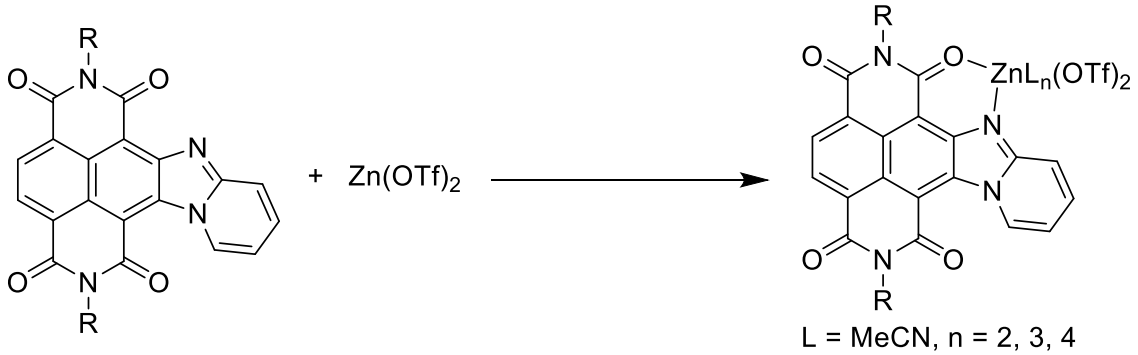


Method A: A mixture of the ligand ***a*ImPyDI** (3.00 mg, 4.46 µmol) and excess of zinc trifluoromethanesulfonate (6.68 mg, 18.4 µmol) were loaded into a 10 mL sealed tube. After addition of 1.5 mL of acetonitrile, the suspension was sonicated at 45 ^{o}C for 1.5 h until a clear green solution appeared. The resulting solution was subjected to analytical characterization and investigations without doing further purification.

Method B: To a clear solution of the dye in chloroform, was added excess of zinc trifluoromethanesulfonate (4 eq.) in acetonitrile. The mixture was sonicated for 30 minutes at 45 ^{o}C before it was used for further investigation.

Yield: quantitative. ^{1}H NMR (500 MHz, CD_3CN) δ 10.23 (br, 2H, a-H), 8.38 (d, ^{3}J = 7.5 Hz, 2H, d-H), 8.26 (dd, ^{3}J = 7.5 Hz, ^{3}J = 6.0 Hz, 2H, c-H), 7.49 (br, 2H, b-H), 4.41 (br, 4H, e-H), 2.16 (br, 2H, f-H), 1.52-1.49 (m, 8H), 1.39-1.30 (m, 8H), 1.01 (br, 6H, [g/h]-H), 0.91 (br, 6H, [g/h]-H), ppm. λ_{max} /nm (ε /$M^{-1}cm^{-1}$) 637 (29820) 452 (26720) ($CHCl_3$/MeCN 30:1 v/v).

Synthesis of zinc complex of *b*ImPyDI



Method A: A 1:1 mixture of the ligand ***b*ImPyDI** (3.00 mg, 5.10 µmol) and zinc trifluoromethanesulfonate (1.85 mg, 5.10 µmol) were loaded into a 10 mL sealed tube. After addition of 1.0 mL of acetonitrile, the suspension was sonicated at 45 °C for 1 h until a clear peach colour solution appeared. The resulting complex was subjected to analytical characterization and investigations without doing further purification.

Method B: To a clear solution of the dye in chloroform, was added one equivalent of zinc trifluoromethanesulfonate in acetonitrile. The mixture was sonicated for 30 minutes at 45 °C before it was used for further investigation.

Yield: quantitative. ^{1}H NMR (500 MHz, $CDCl_3$/CD_3CN 40:1) δ 10.67 (d, ^{3}J = 4.5 Hz, 1H, a-H), 8.90 (d, ^{3}J = 6.5 Hz, 1H, [6/7]-H), 8.84 (d, ^{3}J = 6.5 Hz, 1H, [6/7]-H), 8.62 (br, 1H, d-H), 8.11 (br, 1H, c-H), 7.39 (br, 1H, b-H), 4.24-4.17 (m, 2H, [e/e']-H), 3.88 (br, 2H, [e/e']-H), 1.38-1.17 (m, 12H), 0.96-0.75 (m,12H), 0.44-0.35 (m, 6H) ppm. λ_{max} /nm (ε /$M^{-1}cm^{-1}$) 536 (7830) ($CHCl_3$/MeCN 300/1 v/v).

General procedure for Halochromism

Halochromism was studied by acidification of the compounds. As dissociation of acid in organic solvents is not quantitative, more than stoichiometric amount of acids were needed. In a typical experiment 3 mL of the compound was taken in cuvette. Acid were added gradually until protonation was complete. The deprotonation of the acidified compounds in chloroform was achieved by treatment with triethylamine. After treatment with base, the respective solutions were checked by UV-vis spectroscopy. The initial spectra of the compunds and deprotonated (xImPyDIH^{+}) X^{-} [x = a or b, X = $CF_3CO_2^{-}$, SO_4^{2-}, $CF_3SO_3^{-}$,] were found to be same. This experiment confirmed reversibility of the process.

3. ^{1}H and ^{13}C NMR Spectra

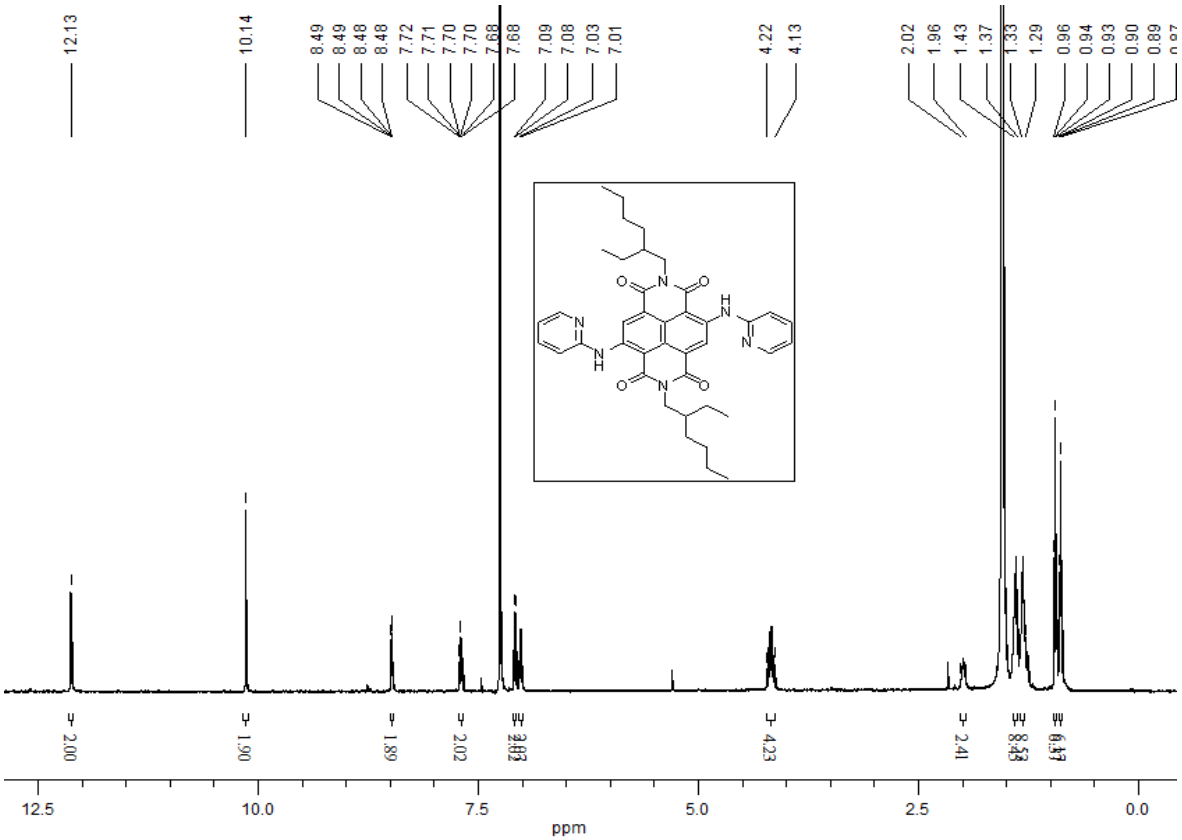


Fig. S1 ^{1}H NMR spectra of **AmPyDI** (500 MHz, $CDCl_3$, 293K).

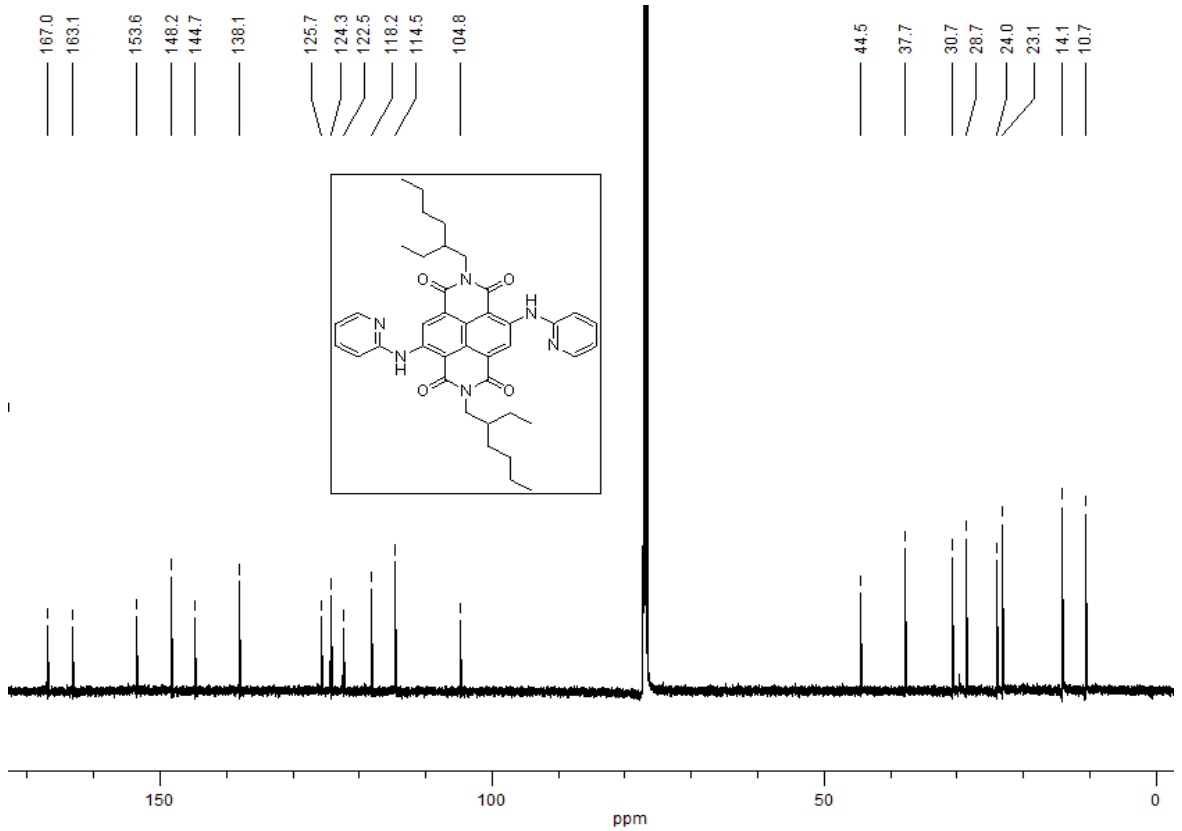


Fig. S2 ^{13}C NMR spectra of **AmPyDI** (150 MHz, $CDCl_3$, 293K).

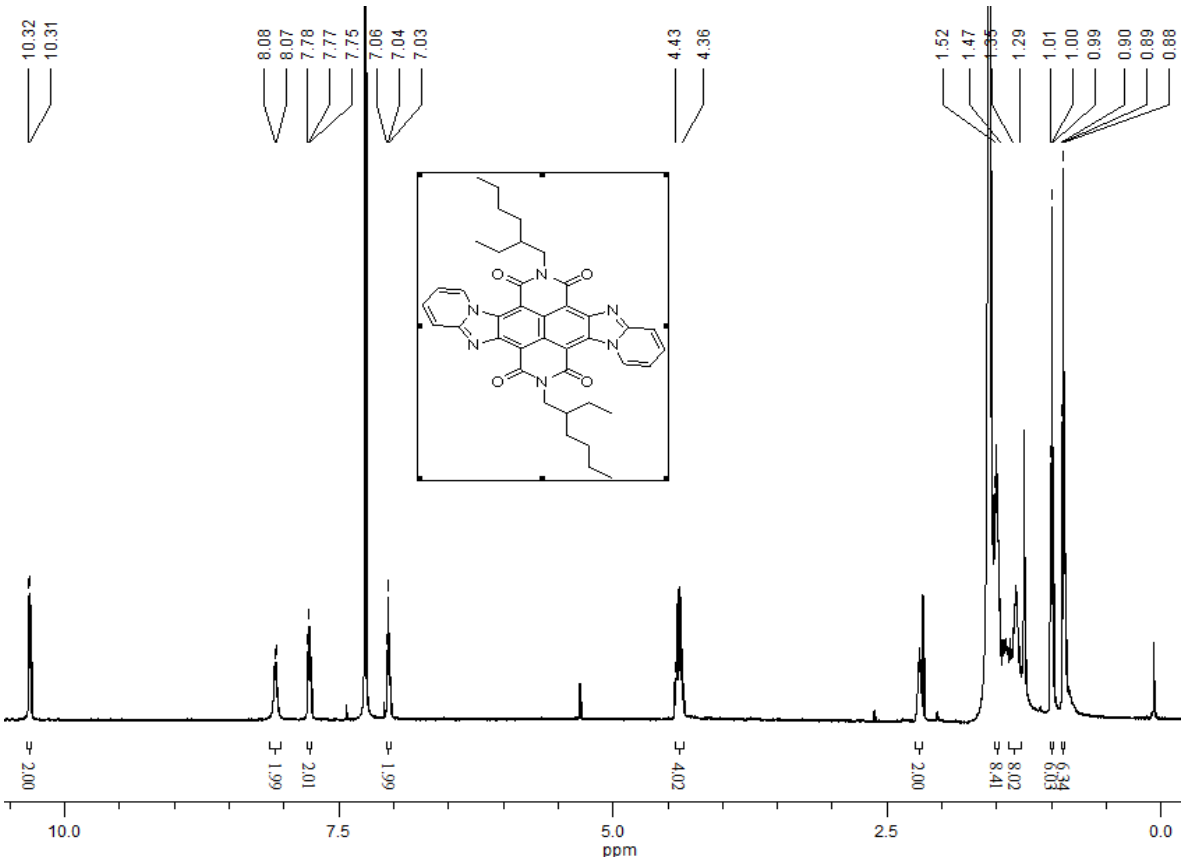


Fig. S3 ^{1}H NMR spectra of ***a*ImPyDI** (600 MHz, $CDCl_3$, 293K).

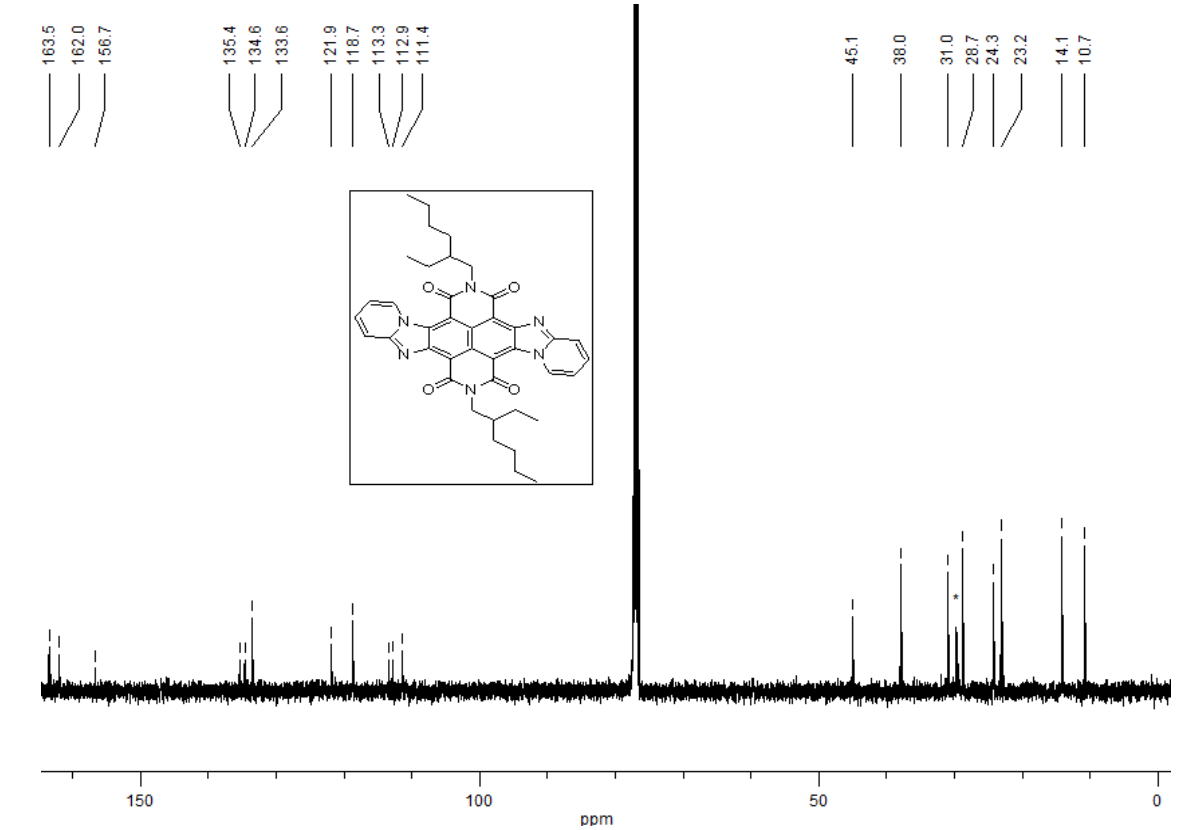


Fig. S4 ^{13}C NMR spectra of ***a*ImPyDI** (150 MHz, $CDCl_3$, 293K).

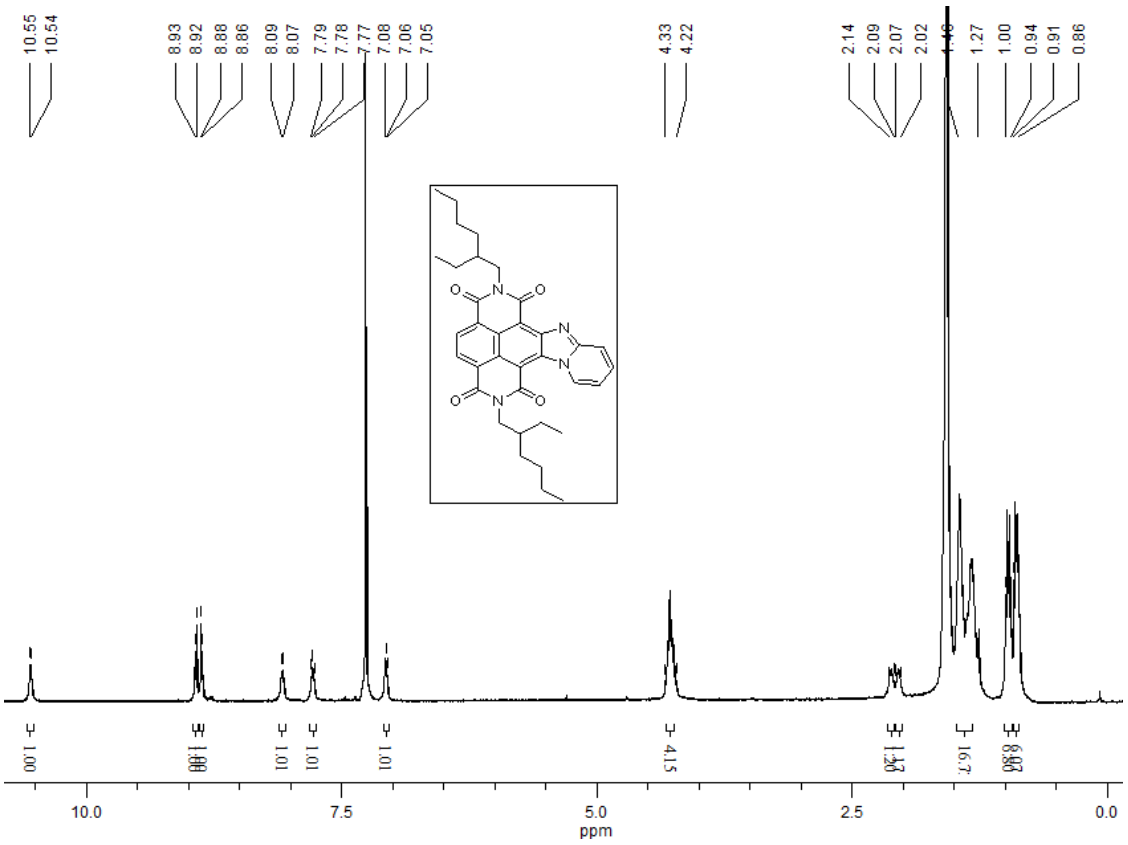


Fig. S5 ^{1}H NMR spectra of ***b*ImPyDI** (500 MHz, $CDCl_3$, 293K).

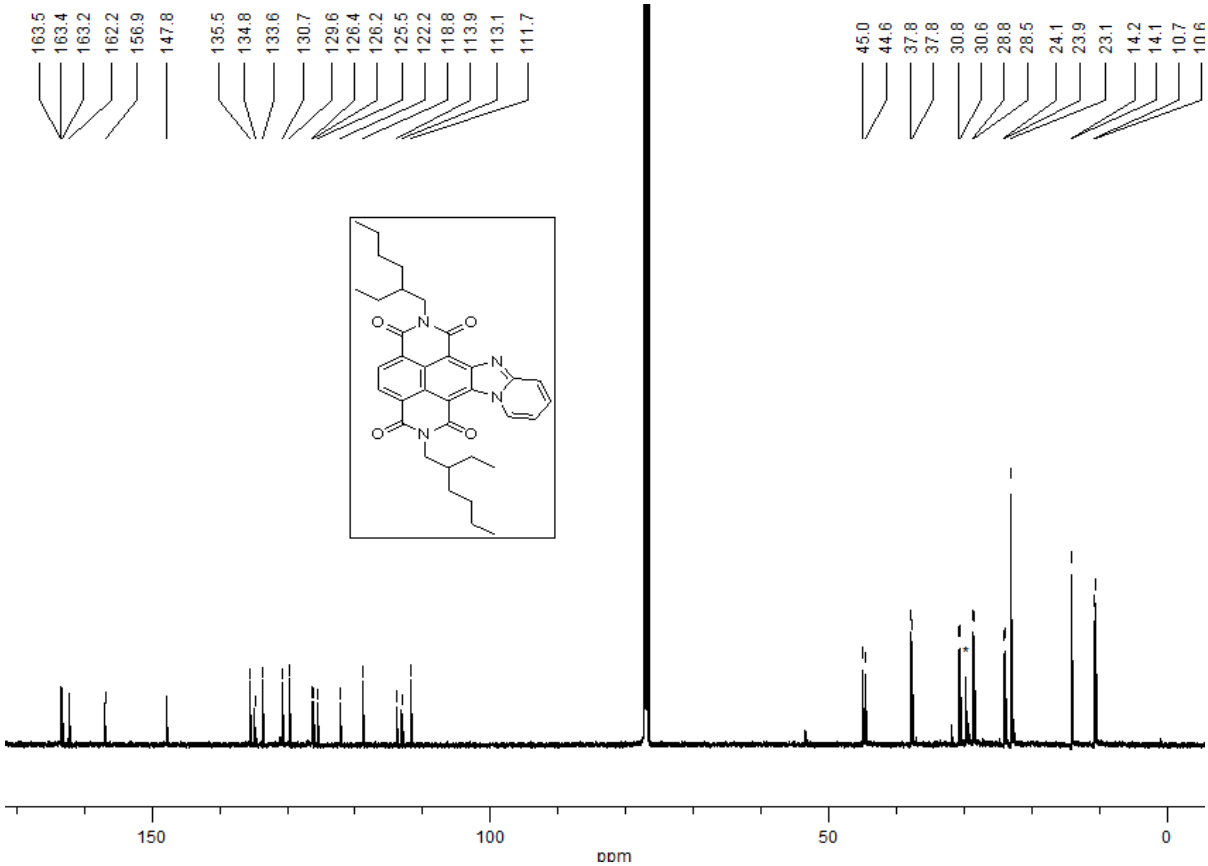


Fig. S6 ^{13}C NMR spectra of ***b*ImPyDI** (150 MHz, $CDCl_3$, 293K).

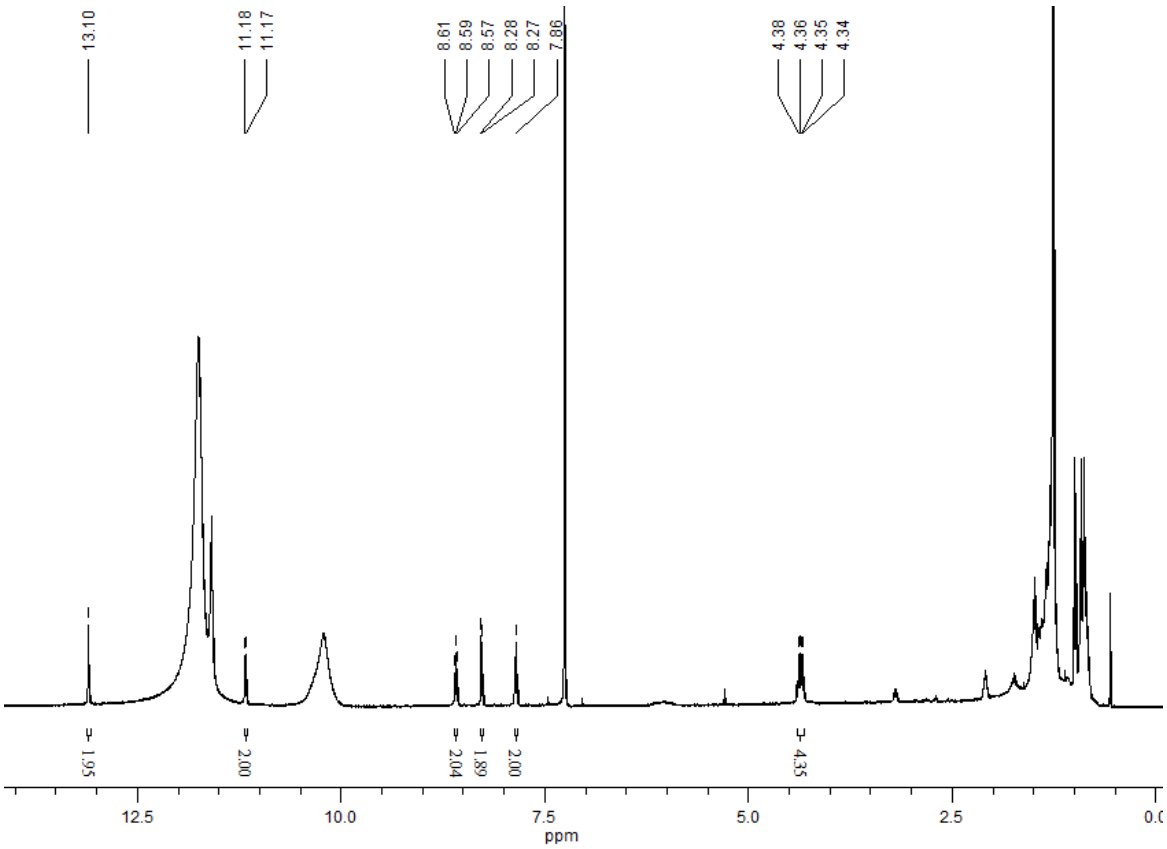


Fig. S7 ^{1}H NMR (500 MHz, $CDCl_3$, 293K) spectra of ***a*ImPyDI** in presence of triflic acid.

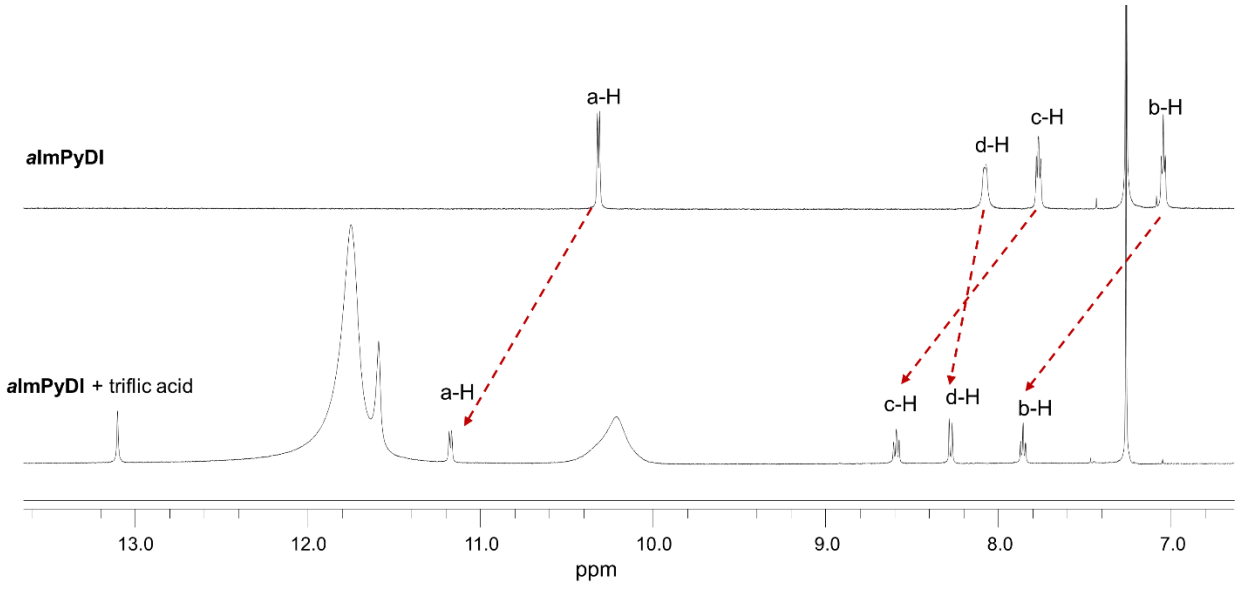


Fig. S8 Partial ^{1}H NMR (500 MHz, $CDCl_3$, 293K) spectra of ***a*ImPyDI** (top) and its protonated form (bottom).

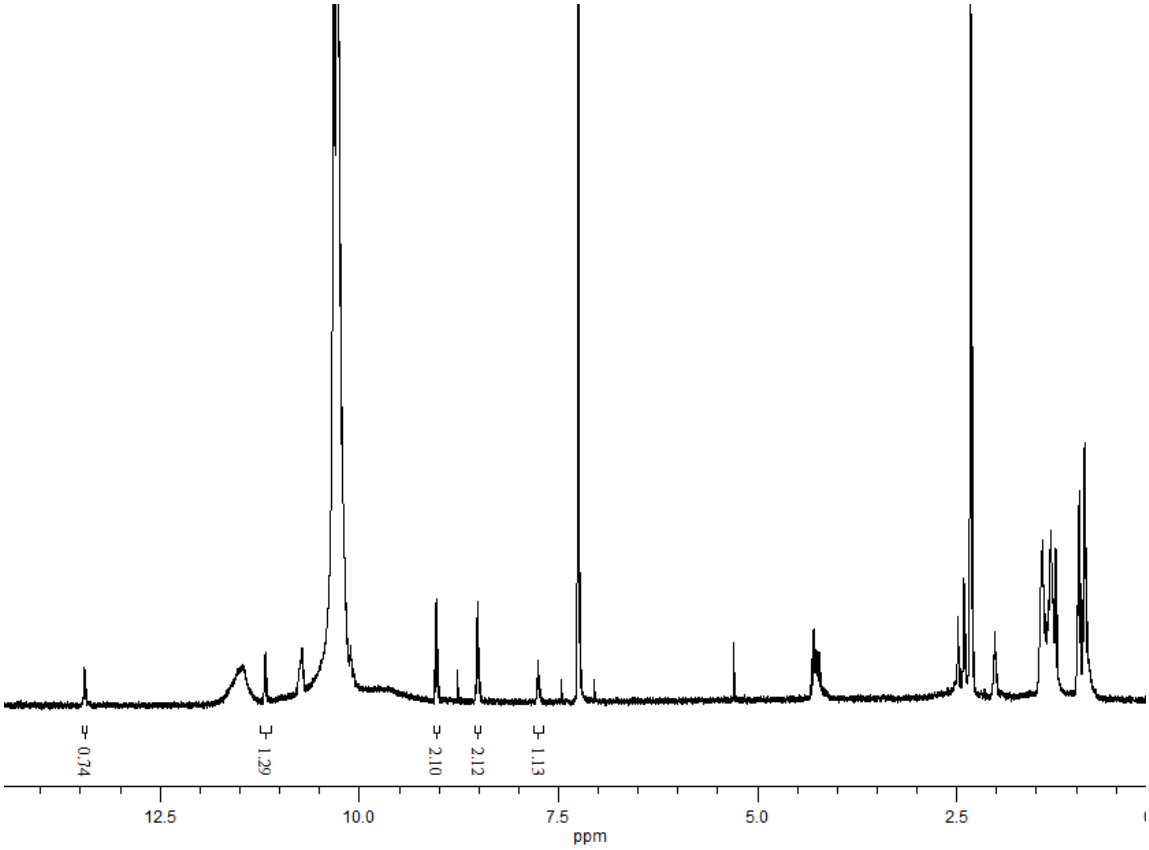


Fig. S9 ^{1}H NMR (500 MHz, $CDCl_3$, 293K) spectra of ***b*ImPyDI** in presence of triflic acid.

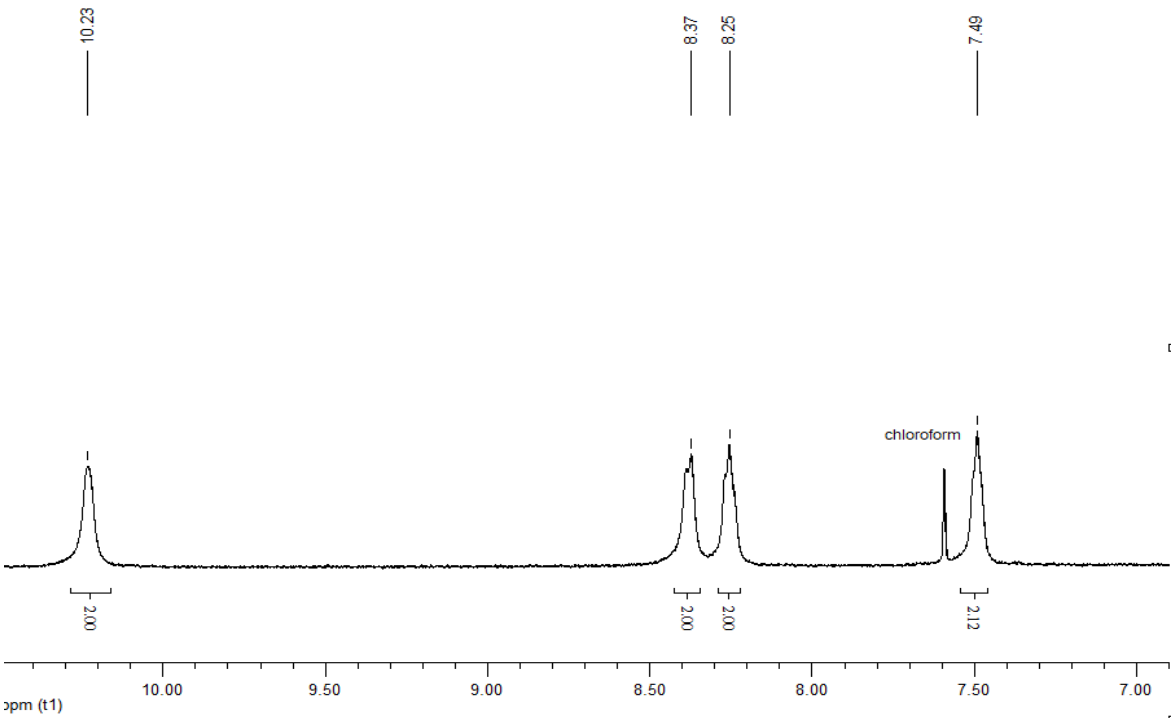


Fig. S10 Partial ^{1}H NMR (500 MHz, 293K) spectra of [(***a*ImPyDI**)Zn_2](OTf)$_4$ in CD_3CN. Single set of protons for imidazo[1,2-a]pyridine moiety confirms the formation of single product.

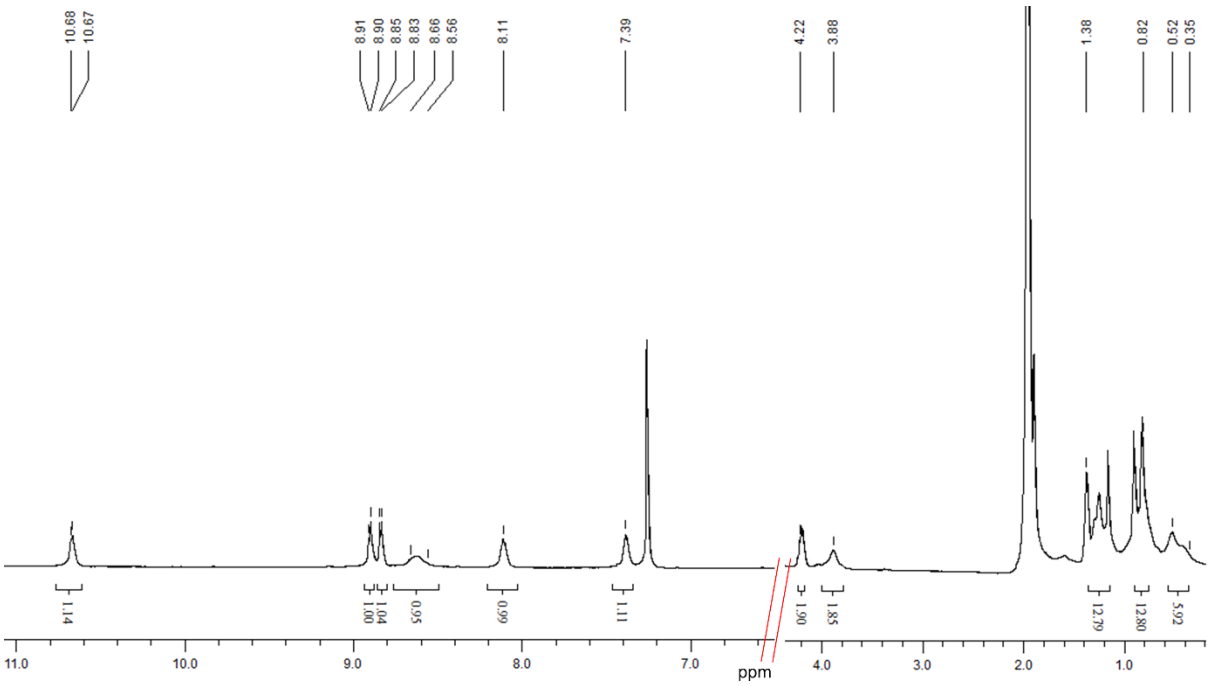


Fig. S11 ^{1}H NMR (500 MHz, 293K) spectra of [(***b*ImPyDI**)Zn](OTf)$_2$ in $CD_3CN/CDCl_3$ 40:1 (v/v).

4. Mass Spectra

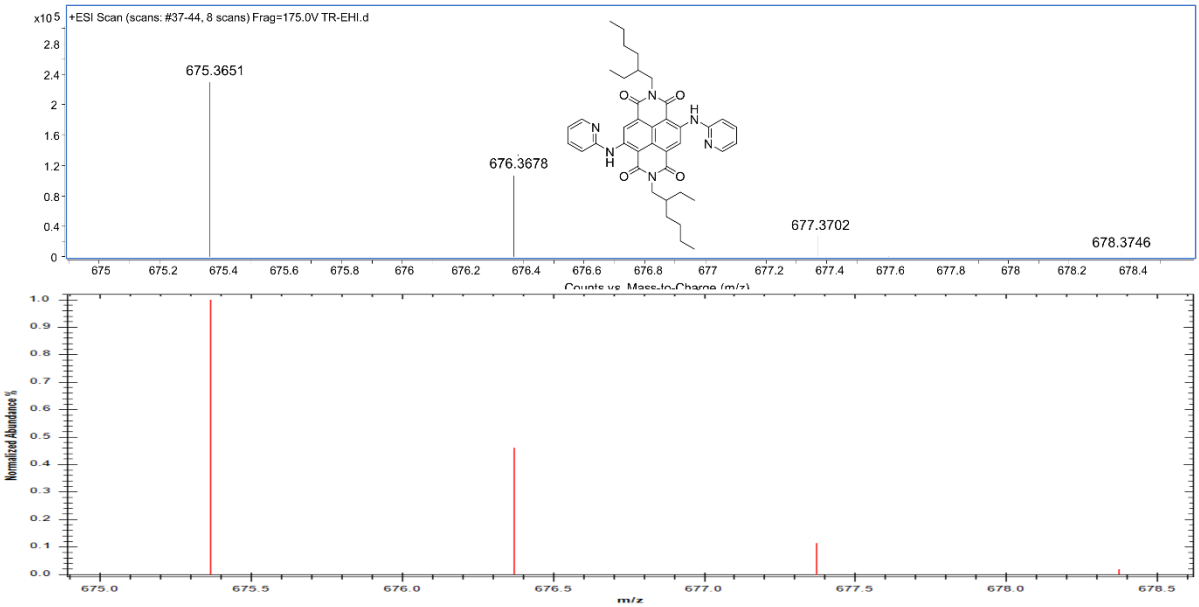


Fig. S12 HRMS (ESI) spectrum (acetonitrile) of [**AmPyDI** + H]$^+$ along with calculated isotopic distribution (below, red).

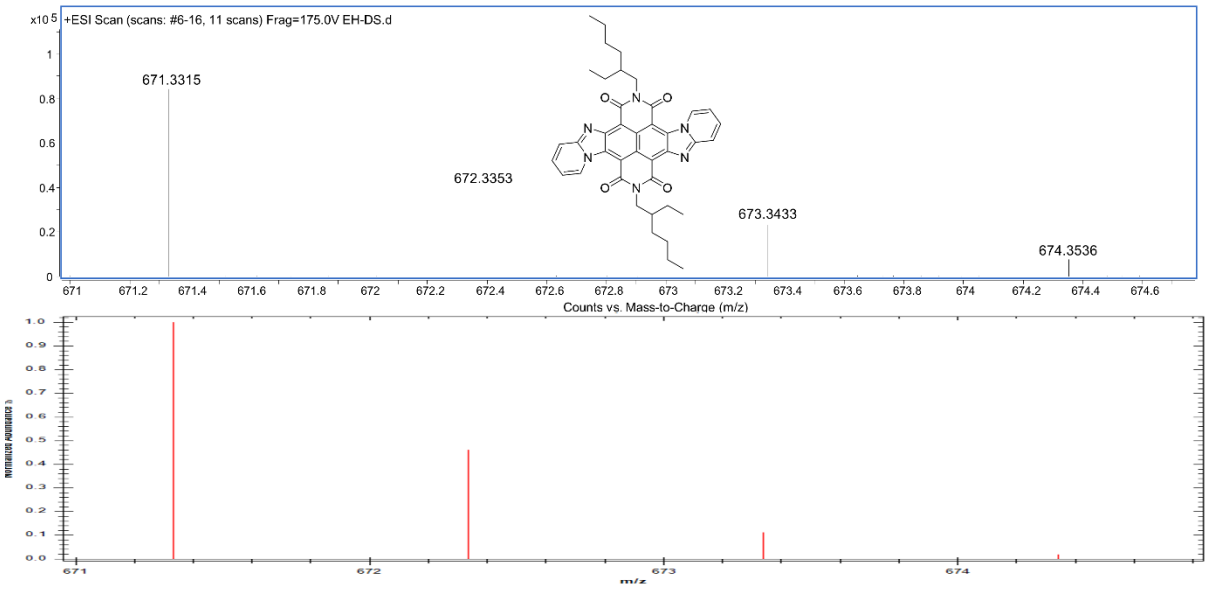


Fig. S13 HRMS (ESI) spectrum (acetonitrile) of [***a*ImPyDI** + H]$^+$ along with calculated isotopic distribution (below, red).

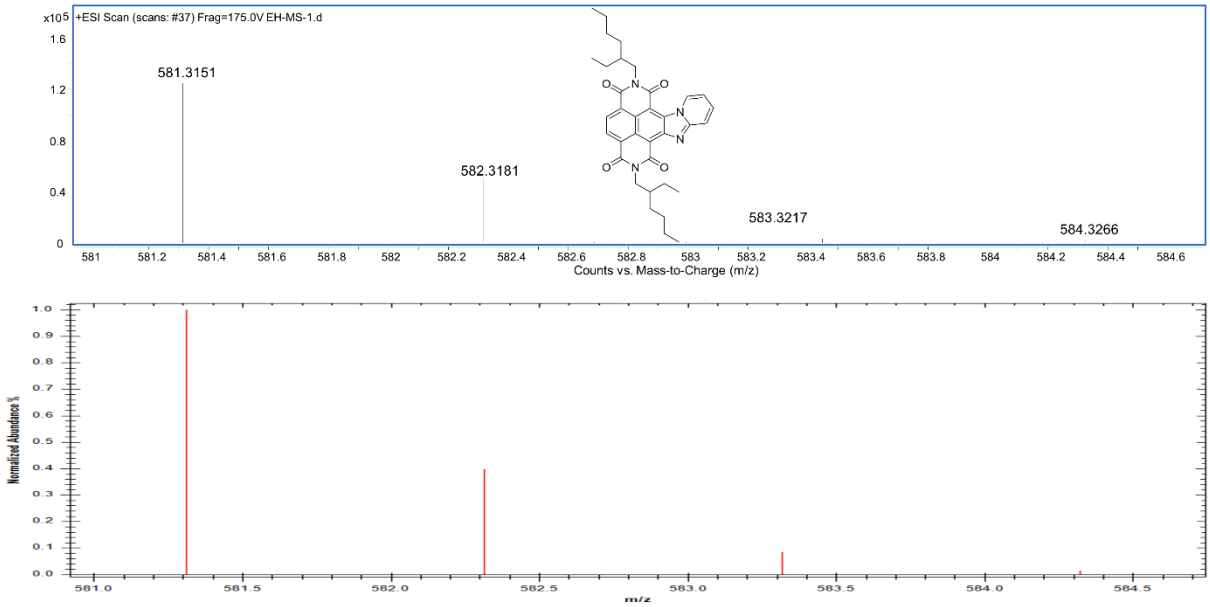


Fig. S14 HRMS (ESI) spectrum (acetonitrile) of [***b*ImPyDI** + H]$^+$ along with calculated isotopic distribution (below, red).

5. IR Spectra

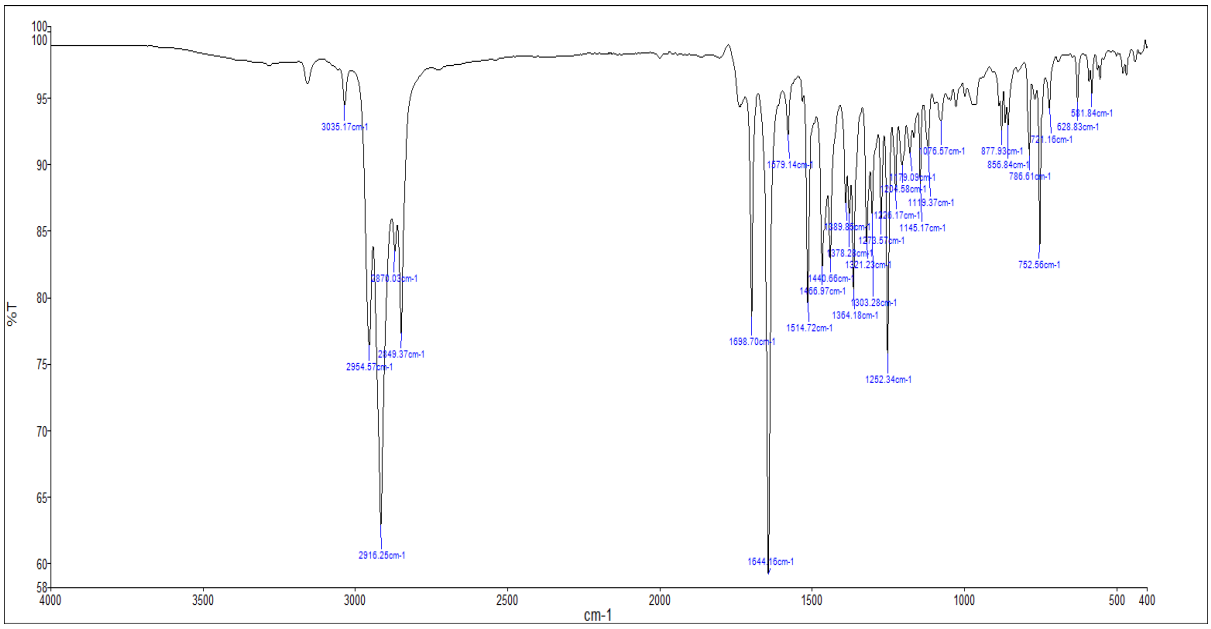


Fig. S15 IR spectrum of ***a*ImPyDI**. The measurement was done by drop casting a solution (chloroform) of the dye on the IR plate.

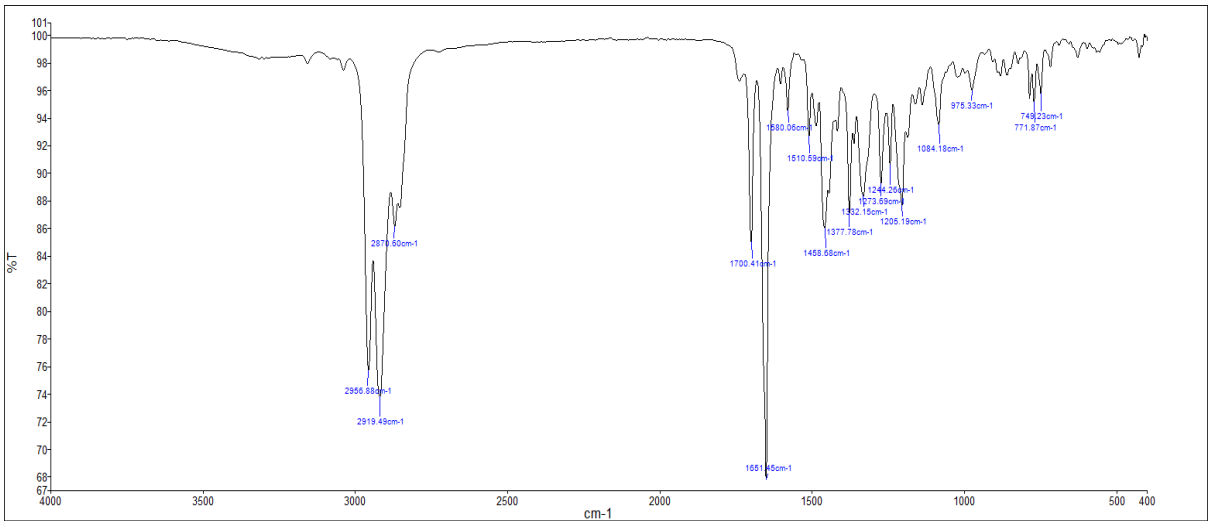


Fig. S16 IR spectrum of ***b*ImPyDI**. The measurement was done by drop casting a solution (chloroform) of the dye on the IR plate.

6. Absorption and photoluminescence spectroscopy

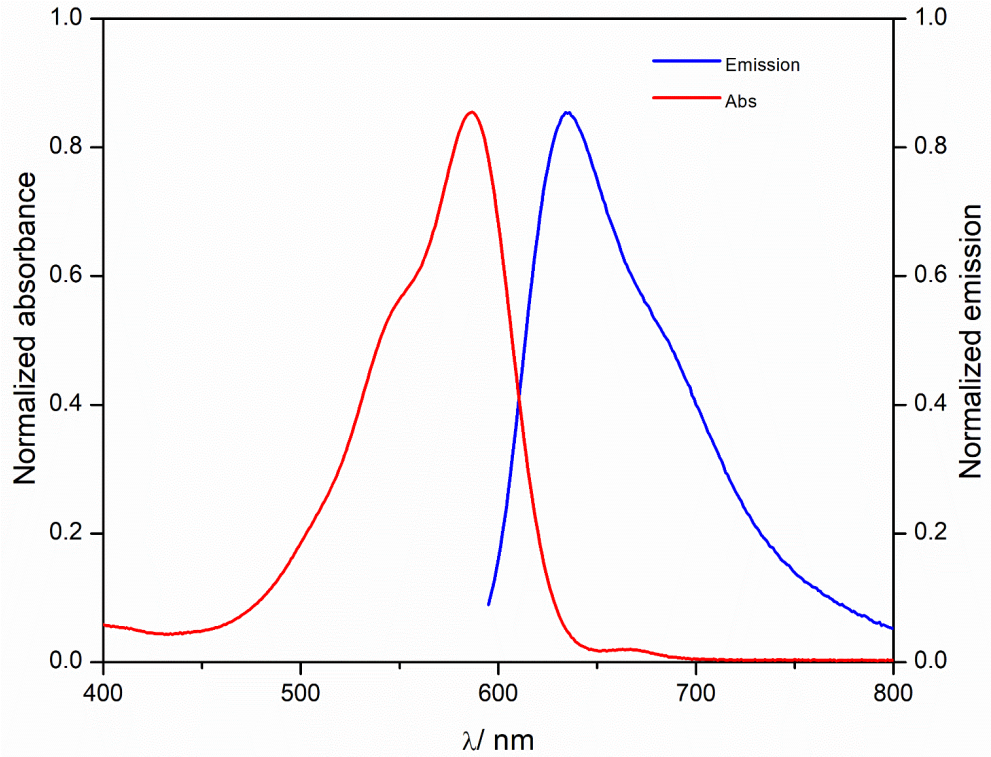


Fig. S17 Absorption (red) and emission (blue) spectra of **AmPyDI** in chloroform (c~1 x 10^{-5} M).

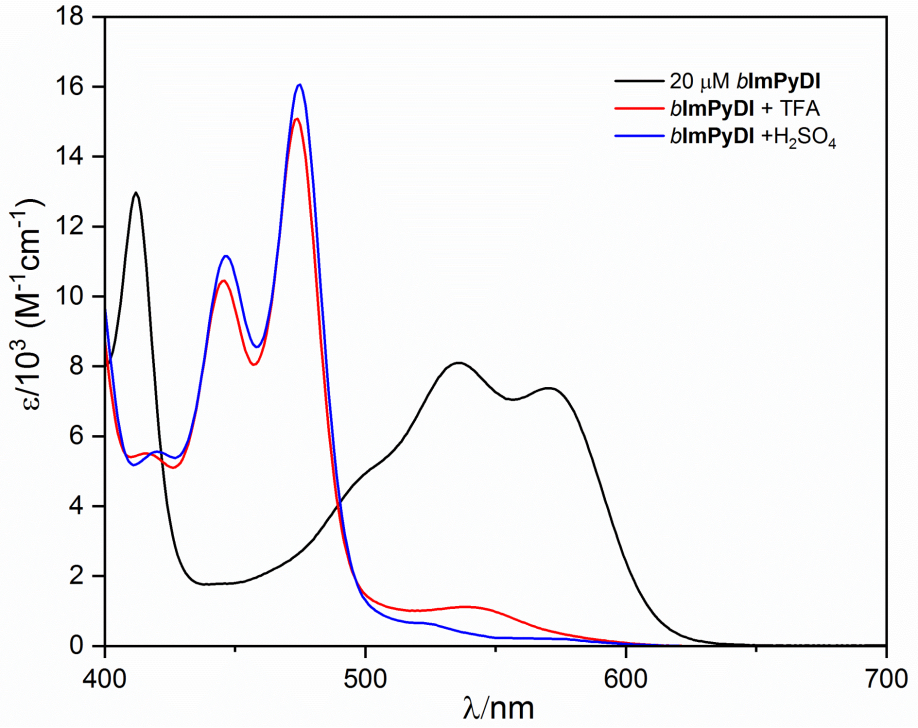


Fig. S 18 Absorption spectra of ***b*ImPyDI** in presence of various acids in chloroform.

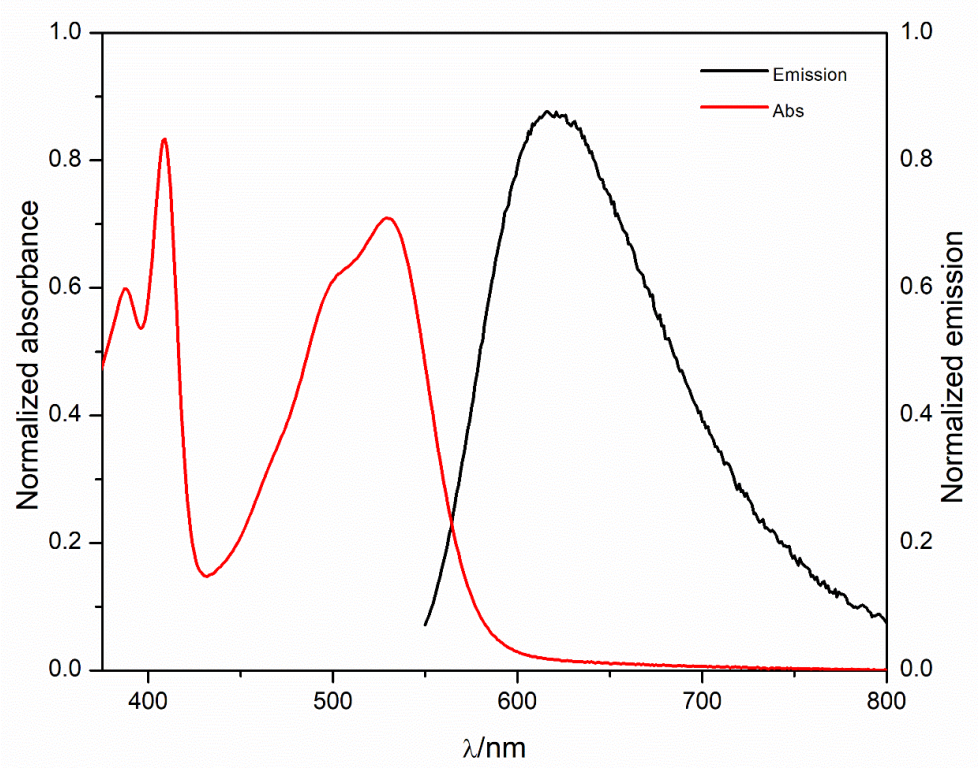


Fig. S19 Absorption (red) and emission (black) spectra of [(***b*ImPyDI)**Zn](OTf)$_2$ in acetonitrile (c ~ 5 x 10^{-5} M).

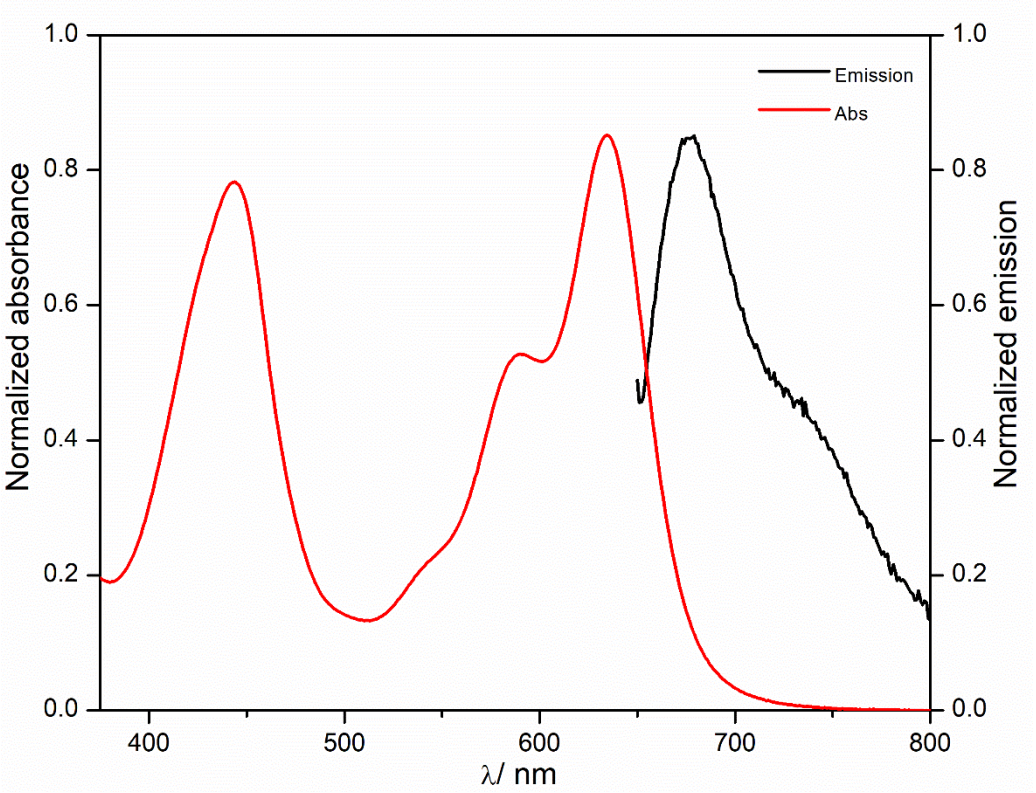


Fig. S20 Absorption (red) and emission (black) spectra [(***a*ImPyDI**)Zn$_2$**]**(OTf)$_4$ in acetonitrile (c ~ 5 x 10^{-4} M).

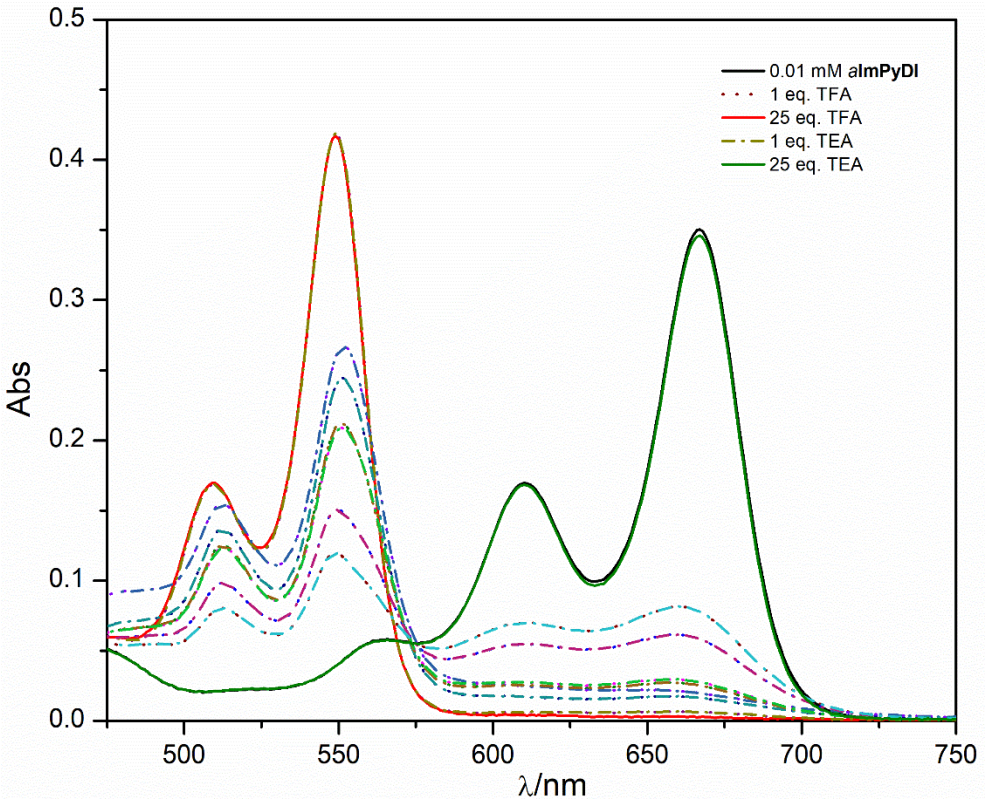


Fig. S21 Halochromism and its reversibility of ***a*ImPyDI** (0.01 mM) in chloroform (TFA: trifluoroacetic acid, TEA : tritethylamine)

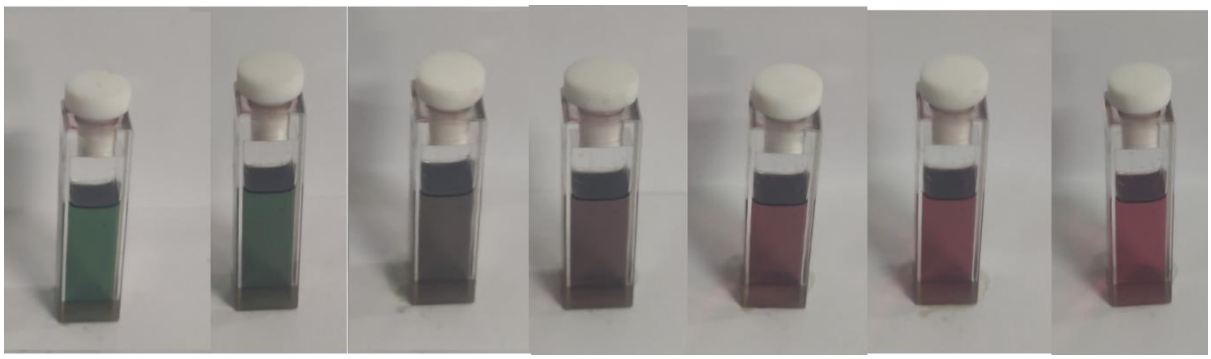


Fig. S22 Visual change in colour of ***a*ImPyDI** (0.01 mM) in chloroform with gradual addition of TFA (left to right).

Measurement of emission quantum yield

Relative quantum yield was measured in deoxygenated and dry chloroform using the following equation.

$$\Phi^{i} = \frac{F^{i} f_{s} n_{i}^{2}}{F^{s} f_{i} n_{s}^{2}} \Phi^{s}$$

where Φ^{i} and Φ^{s} are the photoluminescence quantum yields of the sample and that of the standard, respectively; F^{i} and F^{s} are the integrated intensities (areas) of sample and standard spectra, respectively; f_x is the absorption factor ($f_x = 1 - 10^{-Ax}$, where A = absorbance); the refractive indices of the sample and reference solution are n_i and n_s, respectively. Rhodamine 6G was used as reference ($\Phi^{s} = 0.95$ in ethanol).

Relative quantum yield of ***a*ImPyDI** and ***b*ImPyDI** were found to be 0.45 and 0.52 respectively.

Table S3 Quantum yield calculation data

Compound	Excitation Wavelength (nm)	F^x	Absorbance	f_x	Solvent / n_x	Quantum Yield
Rhodamine 6G	480	5.638×10^8	0.0995	0.2048	Ethanol /1.3614	0.95
***a*ImPyDI** (1st Reading)	480	2.186×10^8	0.0914	0.1897	Chloroform / 1.4458	0.448
***a*ImPyDI** (2nd Reading)	480	1.684×10^8	0.068	0.1451	Chloroform / 1.4458	0.452
***a*ImPyDI** (3rd Reading)	480	2.083×10^8	0.0861	0.1798	Chloroform / 1.4458	0.451
***b*ImPyDI** (1st Reading)	480	2.363×10^8	0.0845	0.1768	Chloroform / 1.4458	0.528
***b*ImPyDI** (2nd Reading)	480	2.323×10^8	0.0813	0.1707	Chloroform / 1.4458	0.529
***b*ImPyDI** (3rd Reading)	480	1.674×10^8	0.0651	0.1392	Chloroform / 1.4458	0.528

7. Electrochemistry

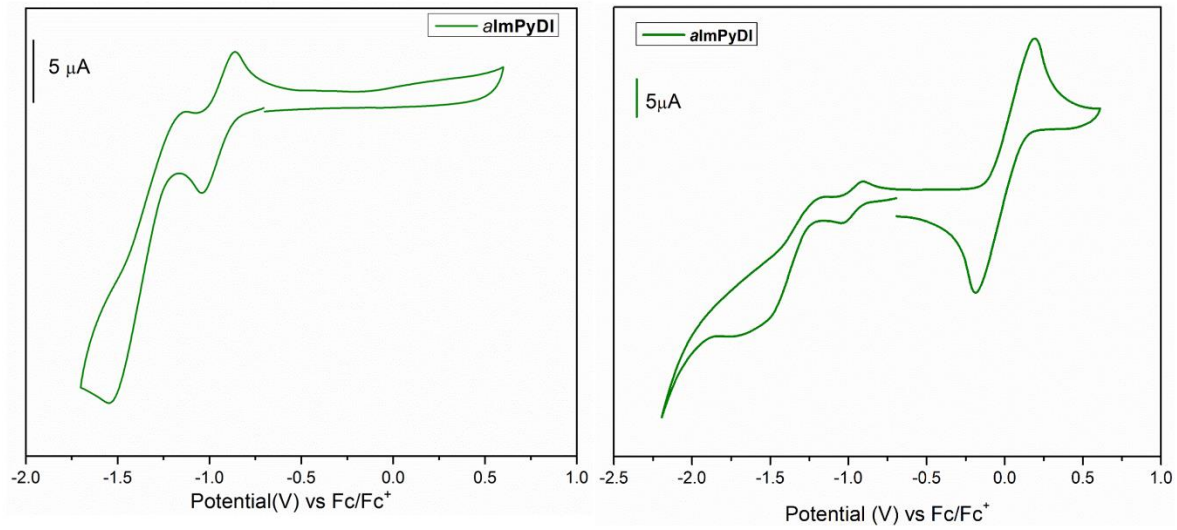


Fig. S23 Cyclic voltammogram of ***a*ImPyDI** in dry and deoxygenated chloroform in absence (left), and in presence (right) of internal standard ferrocene. The experiments were carried out using a 0.75 mM solution of the dye with nBu$_4$NPF$_6$ (0.1 M) as electrolyte against a Ag/AgCl reference electrode. Pt wire was used as auxiliary electrode and 3 mm glassy carbon disk as working electrode (scan rate 100 mVs^{-1}).

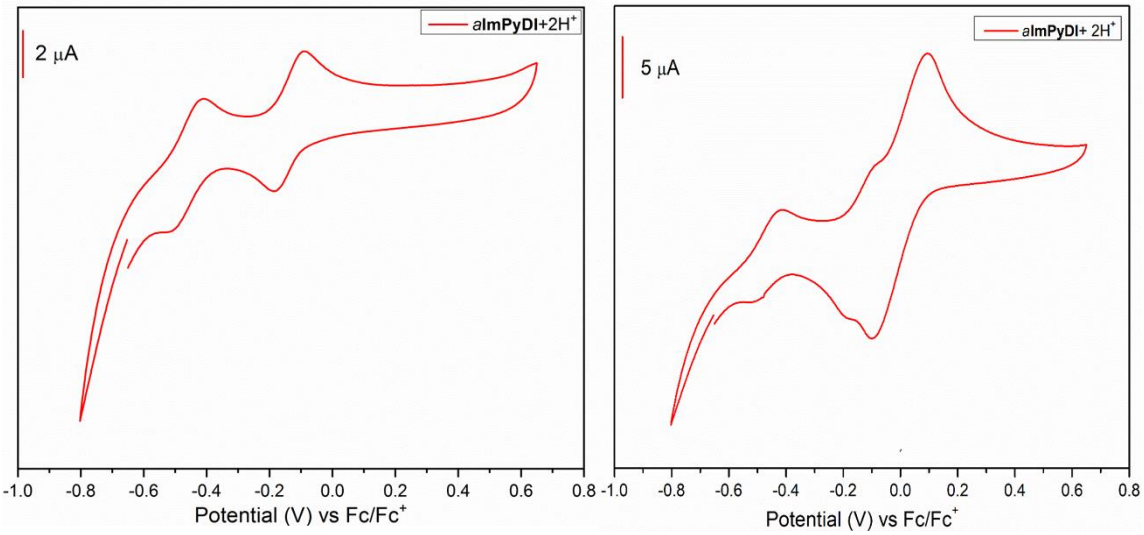


Fig. S24. Cyclic voltammogram of protonated ***a*ImPyDI** in deoxygenated chloroform in absence (left), and in presence (right) of internal standard ferrocene. The experiments were carried out using a 0.75 mM solution of the dye with nBu$_4$NPF$_6$ (0.1 M) as electrolyte against a Ag/AgCl reference electrode. Pt wire was used as auxiliary electrode and 3 mm glassy carbon disk as working electrode (scan rate 100 mVs^{-1}).

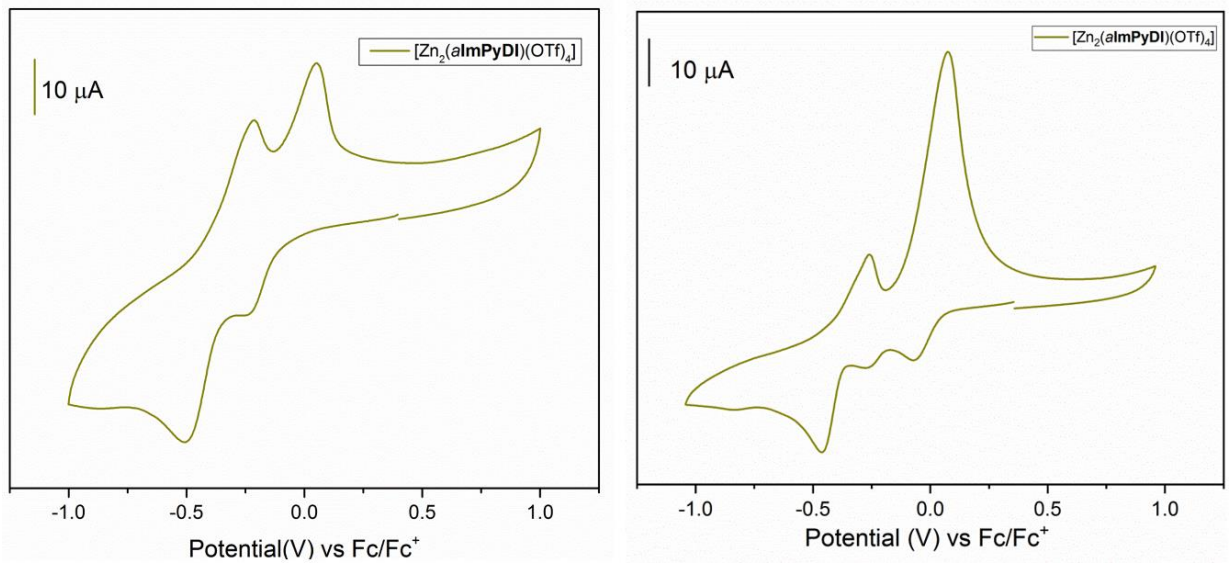


Fig. S25 Cyclic voltammogram of Zn^{2+}-coordinated ***a*ImPyDI** in dry and deoxygenated acetonitrile in absence (left), and in presence (right) of internal standard ferrocene. The experiments were carried out using a 0.75 mM solution of the dye with nBu$_4$NPF$_6$ (0.1 M) as electrolyte against a Ag/AgCl reference electrode. Pt wire was used as auxiliary electrode and 3 mm glassy carbon disk as working electrode (scan rate 100 mVs^{-1}).

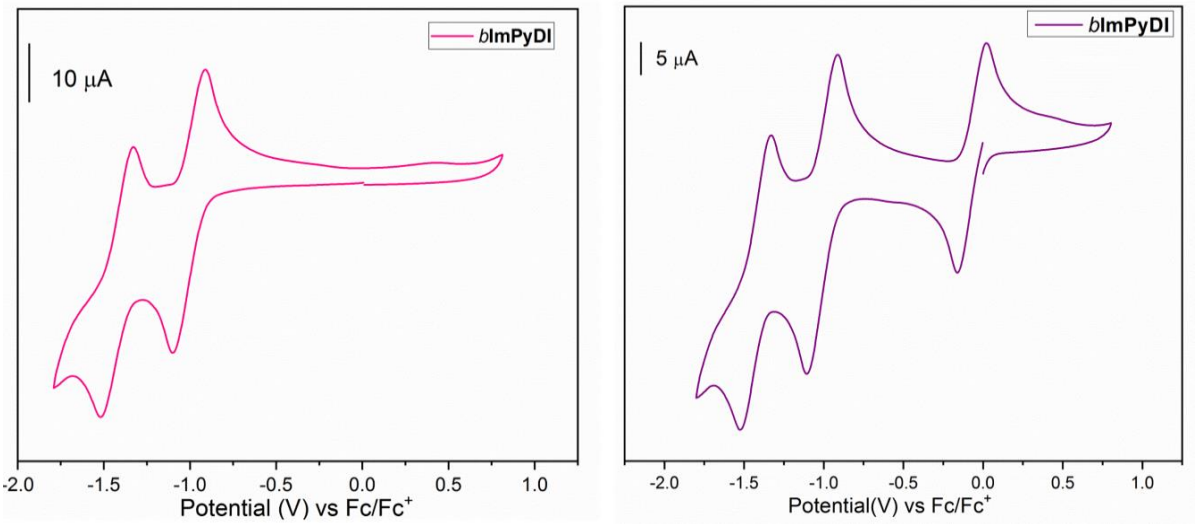


Fig. S26 Cyclic voltammogram of ***b*ImPyDI** in dry and deoxygenated chloroform in absence (left), and in presence (right) of internal standard ferrocene. The experiments were carried out using a 0.75 mM solution of the dye with nBu$_4$NPF$_6$ (0.1 M) as electrolyte against a Ag/AgCl reference electrode. Pt wire as used as auxiliary electrode and 3 mm glassy carbon disk as working electrode (scan rate 100 mVs^{-1}).

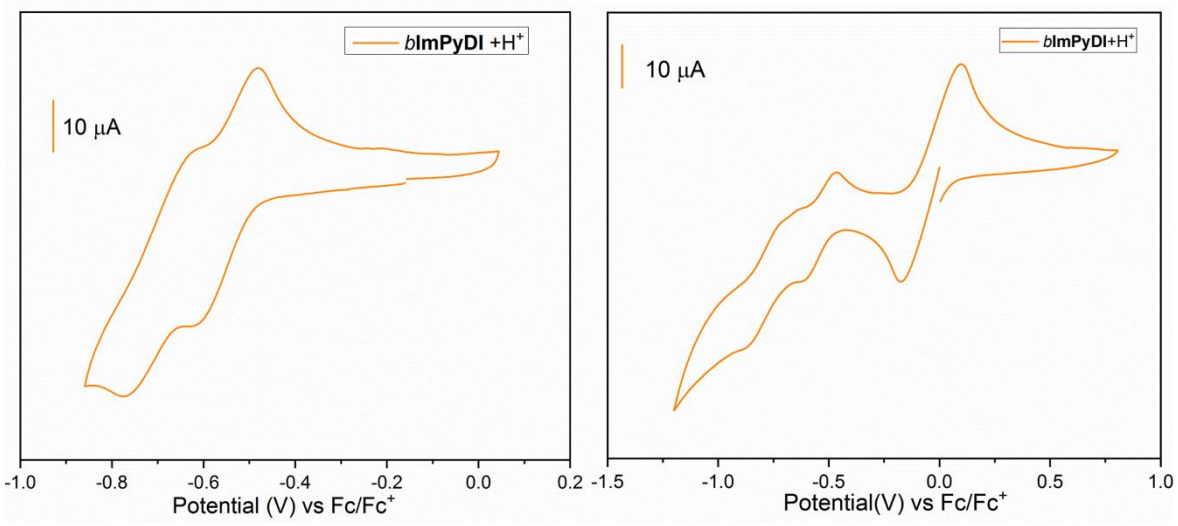


Fig. S27 Cyclic voltammogram of protonated ***b*ImPyDI** in deoxygenated chloroform in absence (left), and in presence (right) of internal standard ferrocene. The experiments were carried out using a 0.75 mM solution of the dye with nBu$_4$NPF$_6$ (0.1 M) as electrolyte against a Ag/AgCl reference electrode. Pt wire was used as auxiliary electrode and 3 mm glassy carbon disk as working electrode (scan rate 100 mVs^{-1}).

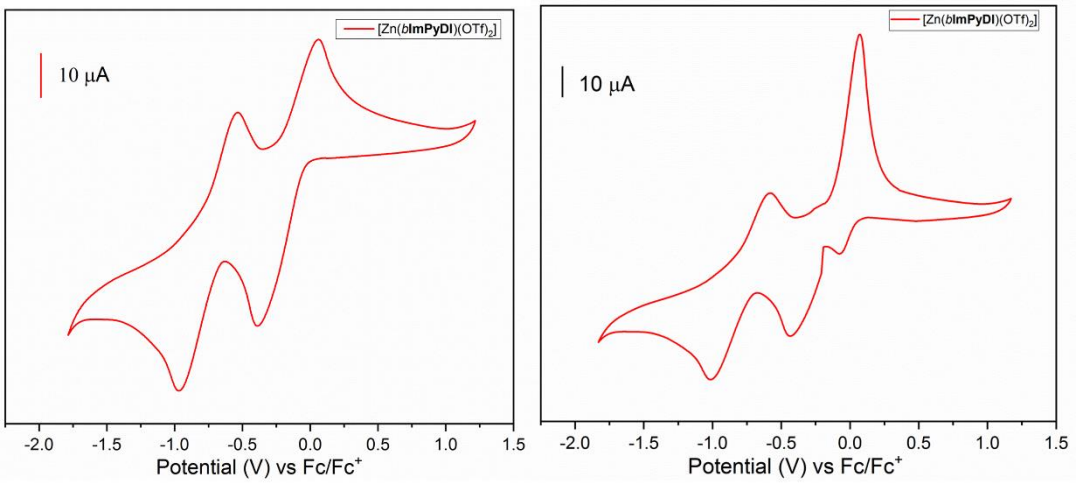


Fig. S28 Cyclic voltammogram of Zn^{2+}-coordinated ***b*ImPyDI** in dry and deoxygenated chloroform/acetonitrile (80/1 v/v) mixture in absence (left), and in presence (right) of internal standard ferrocene. The experiments were carried out using a 0.75 mM solution of the dye with nBu$_4$NPF$_6$ (0.1 M) as electrolyte against a Ag/AgCl reference electrode. Pt wire was used as auxiliary electrode and 3 mm glassy carbon disk as working electrode (scan rate 100 mVs^{-1}).

8. References

1 (a) S. Kuila, A. Ghorai, P. K. Samanta, R. B. K. Siram, S. K. Pati, K. S. Narayan and S. J. George, *Chem. Eur. J.*, **2019,** 25, 16007-16011; (b) S. Debnath, C. J. Boyle, D. Zhou, B. M. Wong, K. R. Kittilstved and D. Venkataraman, *RSC Adv.*, **2018**, 8, 14760-14764; (c) M. Sasikumar, Y. V. Suseela and T. Govindaraju, *Asian J. Org. Chem.*, **2013**, 2, 779-785.

2 (a) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett*. **1989**, 157, 200–206; (b) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, 28, 213–222.