HLCT-AIE active Deep Blue Fluorophores and their versatile applications: A Multifunctional Approach for Advanced White LED Materials, Picric Acid Sensing and Fingerprint Visualization

Bhabana Priyadarshini Debata[a], Jagannath Dash[a], Sabita Patel*[a] and Sivakumar Vaidyanathan*[b]

[a] Department of Chemistry, National Institute of Technology Rourkela, Rourkela-769008, Odisha, India.

[b]Department of Chemistry, Indian Institute of Technology, Hyderabad, Kandi, Sangareddy-502285, Telangana, India.

* To whom correspondence should be addressed. Email: sabitap@nitrkl.ac.in (Sabita Patel), vsiva@chy.iith.ac.in (V. Sivakumar),

Contents:

SI1. Experimental section

SI1.1 General information and measurements

Thermogravimetric analysis (TGA) was performed using the TA Instrument TGAQ50 thermal analysis system. UV-vis absorption was measured using a UV-vis spectrophotometer (Shimadzu Corporation, japan/UV-2450 Pekin Elmer, USA/Lamda 25), and photoluminescence (PL) spectra were recorded using an Edinburgh instrument FLS980 spectrofluorometer. The absolute PL Quantum yields (PLQY) were measured using an Edinburgh instrument spectrofluorometer, integrating the sphere SC-30 model. The photoluminescence lifetime of the dyes was measured at 298 K with an Edinburgh Instrument FLS 980 luminescence spectrometer based on the time-correlated single photon counting technology for all the dyes. Cyclic voltammetry (CV) of the fluorophores were carried out by using AUTOLAB 302 Modular Potentiostat electrochemical analyzer at 298 ± 1 K. The tests were carried out in dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) as a supporting electrolyte, and the scan rate were maintained at 100 mVs^{-1} with three conventional electrode configurations viz, a glassy carbon working electrode, a platinum plate auxiliary electrode, and an Ag/AgCl reference electrode.

SI1.2 Synthesis procedure

Synthesis of 2-(4-bromophenyl)-4,5-diphenyl-1-(3-(trifluoromethyl)phenyl)-1H-imidazole: 3-(trifluoromethyl)aniline (0.43g, 1eq) was added to a stirred solution of 4-bromobenzaldehyde (0.38g, 1eq) in glacial acetic acid (25mL) at room temperature (RT). Subsequently, ammonium acetate (1.75g, 10eq) and benzil (0.5g, 1eq) were added to this reaction mixture. The reaction mixture was stirred at 110 °C for 12 hrs. After cooling, the reaction mixture was poured into ice-cold water and extracted with DCM three times. The extracted organic phase was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to get a crude compound. The resultant compound was purified with column chromatography using silica gel (100- 200 mesh) and ethyl acetate/petroleum ether as the eluent. Yield: 75%

4,5-diphenyl-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1-(3-(trifluoromethyl)phenyl)-1H-imidazole: 2-(4-bromophenyl)-4,5-diphenyl-1-(3-(trifluoromethyl)phenyl)-1H-imidazole (0.92g, 1 eq), bis(pinacolato)diboron (0.54g, 1.2 eq), anhydrous potassium acetate (KOAc) (0.52 g, 3 eq), were taken with (30 ml) of dioxane then, 1,1' Bis [(diphenylphosphino) ferrocene] palladium (II) dichloride ($Pd(dppf)_2Cl_2$) (0.065 g, 0.05 eq) was added to it. Then, it was degassed with the help of nitrogen and was heated for 18-20 hours at 80ºC. The organic phase was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to get the crude. Then, the resultant product was purified with the help of column chromatography to obtain a white crystalline solid, yielding 78%.

SI1.3 Detection Measurement of Nitroaromatic Compound:

For quantitative measurement, the emission measurements were performed by increasing the different concentrations of PA in THF(1 x10^{-3} M). Subsequent addition of 0µL to 400µL in the respective fluorophores (1 x10^{-6} M) of the solution. By subsequent addition of picric acid, an absolute decrease in intensity was observed compared to other nitroaromatic compounds. We also check the response time within 10 sec, adding the concentration of PA, and the quenching of emission happens, which results in the fluorophores occurring perfectly even with the low concentration of PA. The fluorescence quenching efficiency (η) for each analyte was calculated by the following equation:

$$\eta = \frac{I_0 - I}{I_0} \times 100$$

in which I_0 and I were the fluorescence intensities in the absence and presence of analyte, respectively.

SI2. NMR (^{1}H and ^{13}C) spectra and HRMS spectra.

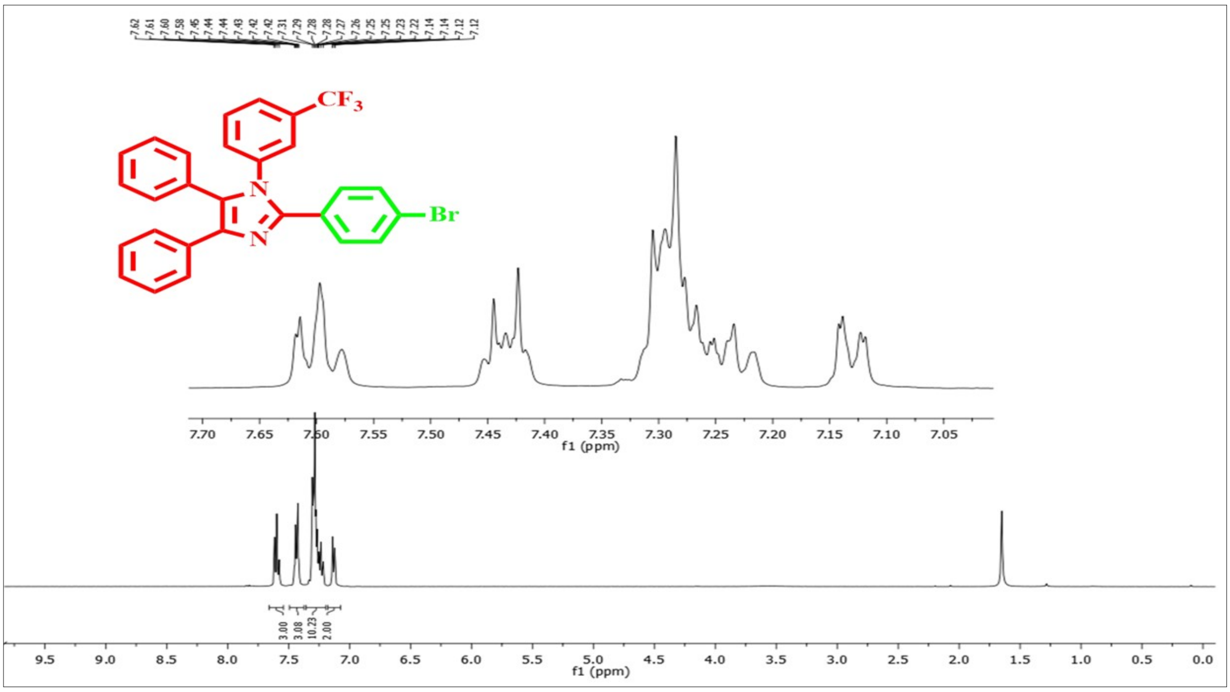

Fig. S1. The ^{1}H NMR spectra of Intermediate I.

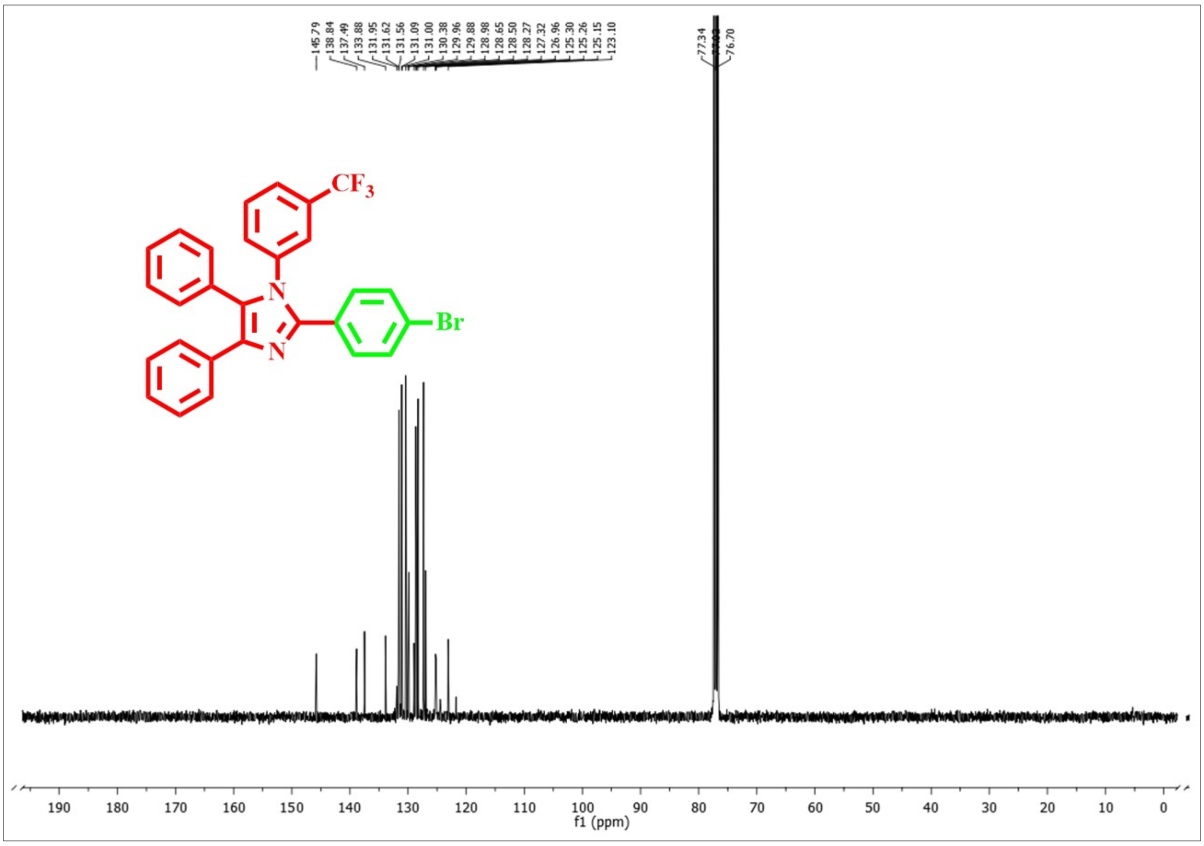

Fig. S2. The ^{13}C NMR spectra of Intermediate I.

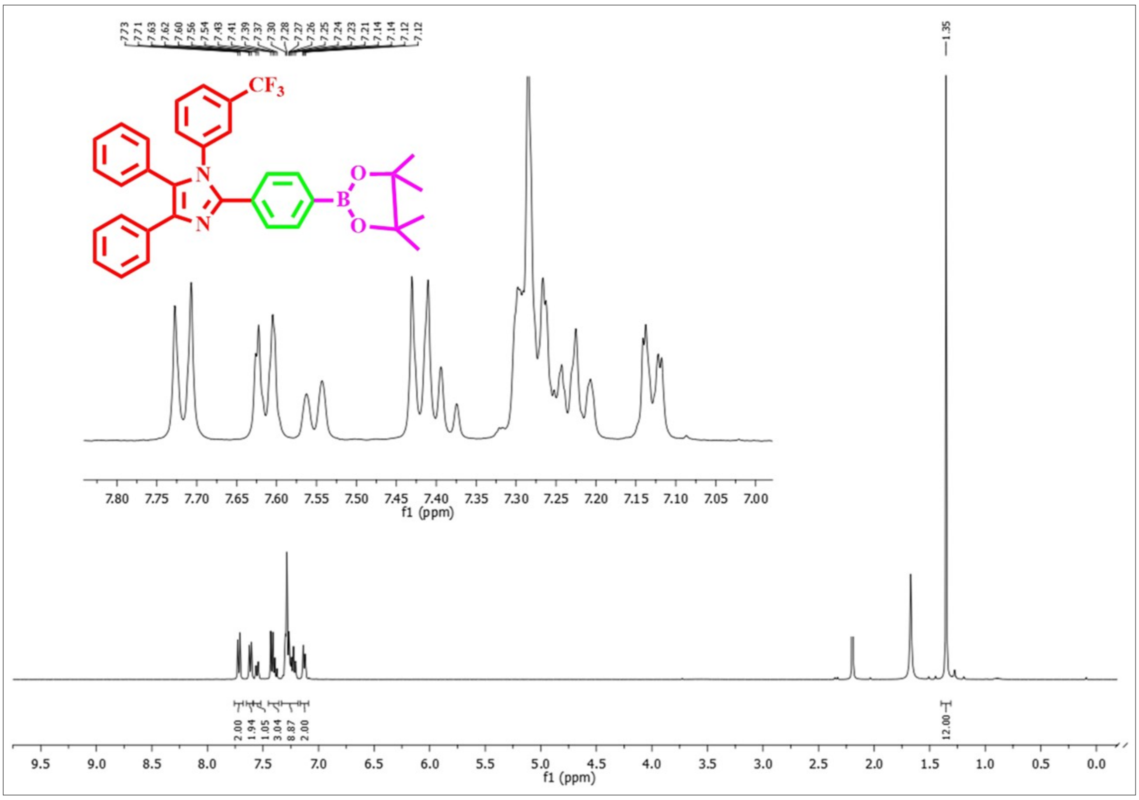

Fig. S3. The ^{1}H NMR spectra of Intermediate II.

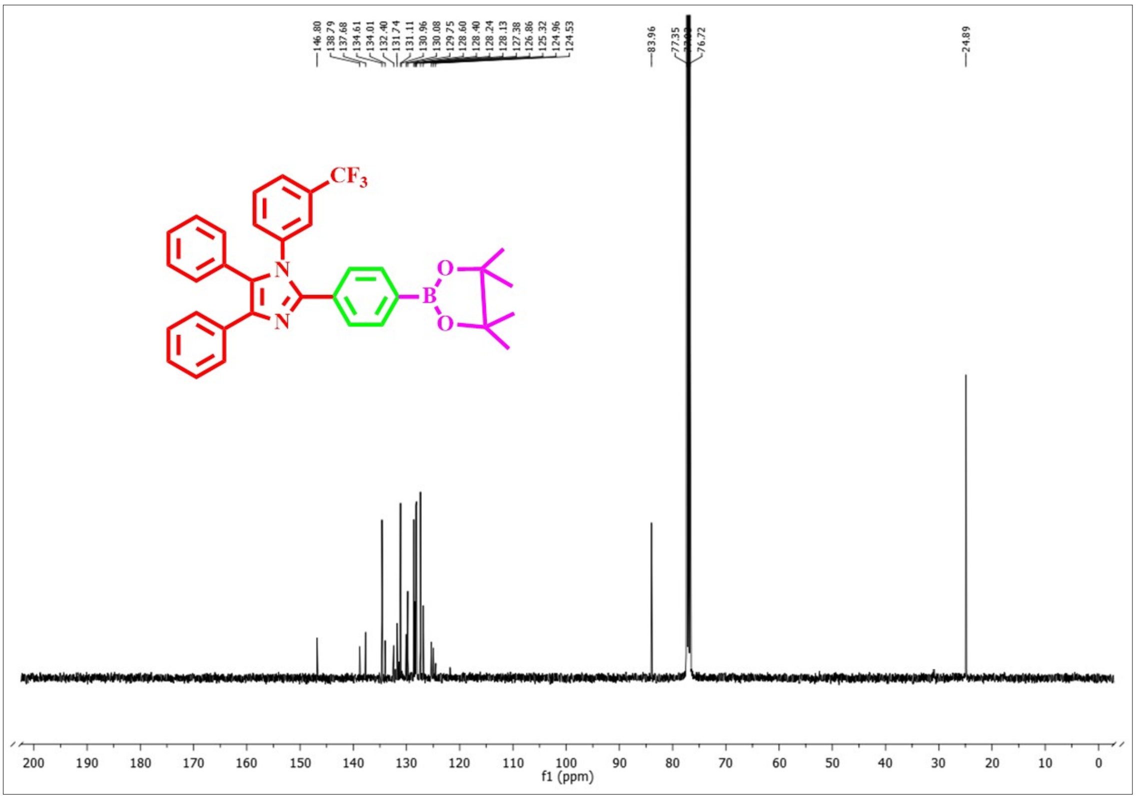

Fig. S4. The ^{13}C NMR spectra of Intermediate II.

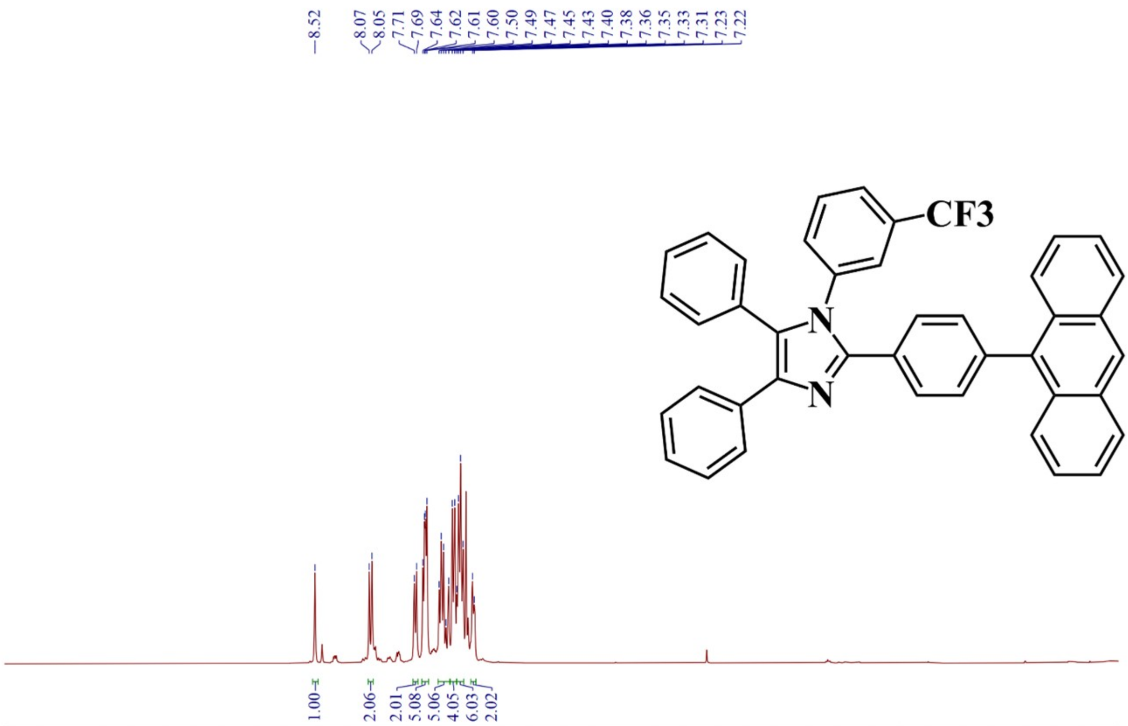

Fig. S5. ^{1}H NMR spectra of BI-Ac

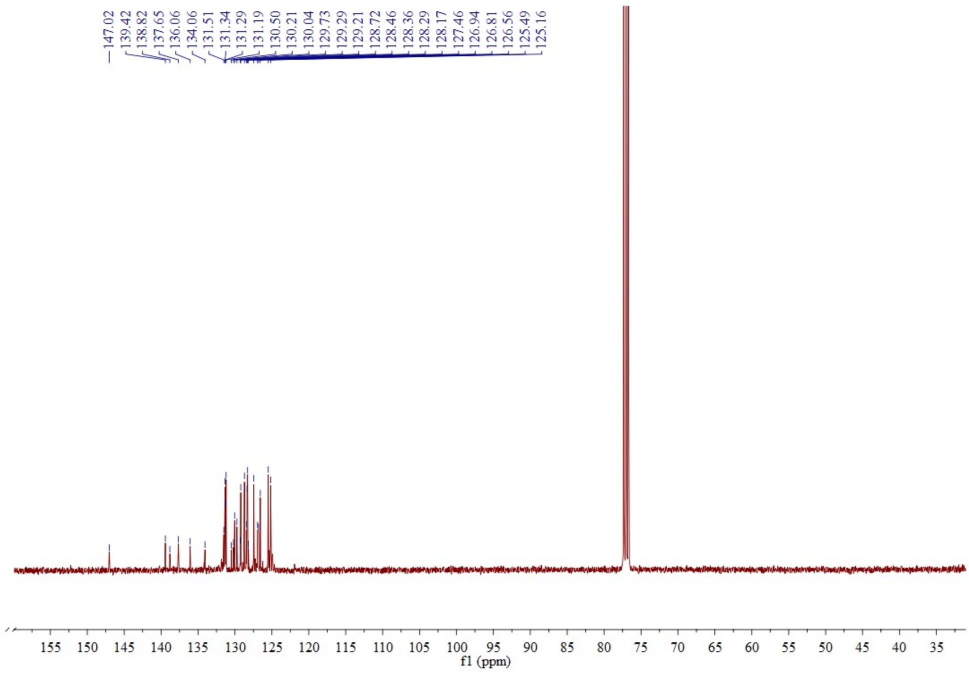

Fig. S6.[13]C NMR spectra of BI-Ac

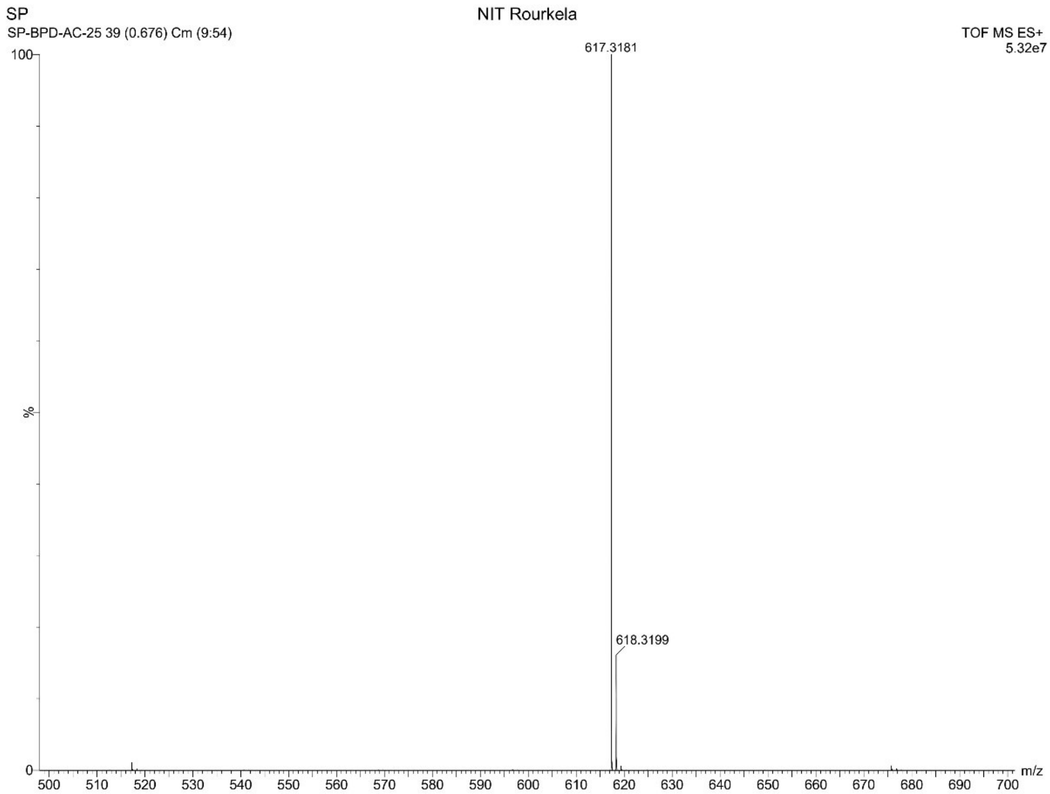

Fig. S7. HRMS spectra of the BI-Ac

SI3. Theoretical study of BI-Ac

SI3.1: Optimized Cartesian coordinates.

6	4.810882000	5.115243000	1.379926000
6	3.926854000	4.129198000	0.948898000
6	4.322250000	2.781143000	0.900146000
6	6.505247000	3.439186000	1.744659000
6	6.106439000	4.776426000	1.775639000
6	3.347734000	1.769719000	0.450293000
6	3.550272000	0.510347000	-0.097948000
1	4.487211000	6.152012000	1.406859000
1	2.916556000	4.384080000	0.648409000
1	7.505339000	3.161748000	2.065803000
1	6.795911000	5.545601000	2.111517000
6	-0.104532000	0.861239000	0.066189000
6	-0.804148000	0.176540000	-0.940612000
6	-0.843818000	1.547705000	1.044808000
6	-2.197417000	0.164699000	-0.952960000
6	-2.234539000	1.532143000	1.026844000
1	-0.307235000	2.096536000	1.810811000
6	-2.937345000	0.836040000	0.030621000
1	-2.721883000	-0.367525000	-1.740899000
1	-2.788817000	2.064809000	1.793884000
6	1.364279000	0.955676000	0.120544000
7	2.265402000	-0.013815000	-0.296158000
7	1.999690000	2.019694000	0.567588000
6	5.622667000	2.449107000	1.315777000
6	-5.187288000	3.419803000	-2.572964000
6	-4.477044000	2.598498000	-1.737185000
6	-5.138555000	1.677829000	-0.861152000
6	-6.583859000	1.652163000	-0.877191000

6	-7.285084000	2.525043000	-1.766861000
6	-6.610893000	3.382934000	-2.592922000
6	-4.433848000	0.817181000	0.012874000
6	-7.265122000	0.780844000	-0.022512000
6	-6.583263000	-0.072778000	0.849391000
6	-5.137863000	-0.061022000	0.869714000
6	-4.475088000	-0.964460000	1.762399000
1	-3.391387000	-0.978306000	1.781419000
6	-5.184414000	-1.804395000	2.580148000
6	-6.608527000	-1.804596000	2.563997000
6	-7.283802000	-0.964034000	1.721188000
1	-4.661963000	4.110228000	-3.226418000
1	-3.393873000	2.640712000	-1.728370000
1	-8.371467000	2.491937000	-1.769757000
1	-7.156088000	4.041019000	-3.263088000
1	-4.657912000	-2.481120000	3.246756000
1	-7.153070000	-2.476944000	3.220369000
1	-8.370405000	-0.958968000	1.696900000
1	5.940392000	1.412721000	1.319481000
1	-8.352545000	0.766774000	-0.036180000
6	2.345251000	-1.716562000	-2.057559000
6	1.967535000	-1.329281000	-0.768247000
6	1.303958000	-2.227430000	0.070167000
6	1.006409000	-3.509417000	-0.392804000
6	1.381632000	-3.903456000	-1.679558000
6	2.054605000	-3.004494000	-2.505515000
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1	1.156016000	-4.906382000	-2.024160000
1	2.353462000	-3.306625000	-3.504006000
6	6.256093000	-2.142034000	-0.275674000

6	5.087084000	-1.473221000	0.085176000
6	4.779648000	-0.218563000	-0.468098000
6	5.678128000	0.348717000	-1.388205000
6	6.849482000	-0.318750000	-1.742143000
6	7.140928000	-1.567470000	-1.189642000
1	6.478699000	-3.109950000	0.163772000
1	4.410866000	-1.920403000	0.806932000
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1	7.532897000	0.135539000	-2.453582000
1	8.052550000	-2.088079000	-1.467600000
6	0.231179000	-4.456097000	0.486116000
9	-1.100282000	-4.347056000	0.278688000
9	0.563009000	-5.744134000	0.247822000
9	0.447539000	-4.214808000	1.797672000
1	-0.266128000	-0.334964000	-1.730306000
1	1.025734000	-1.926088000	1.072927000

SI3.2: The computed vertical transition and their oscillator strengths (*f*) and configuration of the BI-Ac.

singlet

```
Excited State   1:      Singlet-A      3.1860 eV  389.15 nm  f=0.2156  <S**2>=0.000
     160 ->161         0.69711

 Excited State   2:      Singlet-A      3.4084 eV  363.76 nm  f=0.0003  <S**2>=0.000
     159 ->161         0.70038

 Excited State   3:      Singlet-A      3.5204 eV  352.19 nm  f=0.0102  <S**2>=0.000
     159 ->162        -0.33325
     160 ->162         0.60472

 Excited State   4:      Singlet-A      3.6052 eV  343.90 nm  f=0.0002  <S**2>=0.000
     159 ->162         0.53464
     159 ->163        -0.11914
     160 ->162         0.23635
     160 ->163         0.34409
     160 ->164         0.11357
```

Excited State 5: Singlet-A 3.6591 eV 338.84 nm f=0.0385 <S**2>=0.000
159 ->162 -0.29534
159 ->163 -0.24181
160 ->162 -0.23735
160 ->163 0.52725

Excited State 6: Singlet-A 3.7465 eV 330.94 nm f=0.0367 <S**2>=0.000
159 ->163 0.61900
159 ->164 -0.11156
160 ->163 0.23633
160 ->164 0.14964

Excited State 7: Singlet-A 3.8638 eV 320.89 nm f=0.0003 <S**2>=0.000
158 ->161 0.48565
160 ->166 0.46591
160 ->168 0.14893

Excited State 8: Singlet-A 3.9407 eV 314.62 nm f=0.0612 <S**2>=0.000
159 ->163 -0.14788
160 ->163 -0.15785
160 ->164 0.61873
160 ->165 0.22031

Excited State 9: Singlet-A 4.0572 eV 305.59 nm f=0.1978 <S**2>=0.000
159 ->163 0.10445
159 ->164 0.63610
159 ->165 -0.13493
160 ->165 0.19910

Excited State 10: Singlet-A 4.2090 eV 294.57 nm f=0.1788 <S**2>=0.000
159 ->164 -0.22814
159 ->165 -0.40540
160 ->164 -0.19358
160 ->165 0.48008

Triplet

Excited State 1: Triplet-A 1.7671 eV 701.63 nm f=0.0000 <S**2>=2.000

159 ->161 0.12423

160 ->161 0.68619

160 <-161 0.13372

Excited State 2: Triplet-A 2.8793 eV 430.60 nm f=0.0000 <S**2>=2.000

157 ->165 0.10453

159 ->161 0.11018

159 ->162 0.25019

159 ->163 0.45114

159 ->164 0.28161

159 ->169 0.14236

160 ->163 -0.13936

Excited State 3: Triplet-A 3.2588 eV 380.45 nm f=0.0000 <S**2>=2.000

156 ->170 -0.10842

157 ->169 0.10771

159 ->161 0.21547

159 ->162 0.19047

159 ->163 -0.11522

159 ->165 0.44465

159 ->169 -0.13689

160 ->162 -0.12338

160 ->165 -0.14826

Excited State 4: Triplet-A 3.2799 eV 378.02 nm f=0.0000 <S**2>=2.000

153 ->161 -0.25060

154 ->161 0.19354

155 ->161 0.41260

160 ->168 0.17963

160 ->171 -0.37109

Excited State 5: Triplet-A 3.4066 eV 363.95 nm f=0.0000 <S**2>=2.000

159 ->161 0.63649

159 ->162 -0.16704

159 ->165 -0.11248

160 ->161 -0.11526

160 ->162 0.11544

Excited State 6: Triplet-A 3.4878 eV 355.48 nm f=0.0000 <S**2>=2.000

157 ->161 0.10613

158 ->161 0.54100

160 ->162 0.13038

160 ->166 -0.34550

160 ->168 -0.15927

Excited State 7: Triplet-A 3.5114 eV 353.09 nm f=0.0000 <S**2>=2.000

152 ->167 0.11381

154 ->165 -0.11142

158 ->161 0.13978

159 ->162 0.38638

159 ->163 -0.13298

159 ->164 -0.20826

159 ->165 -0.12835

159 ->169 0.15902

160 ->162 -0.25824

Excited State 8: Triplet-A 3.5545 eV 348.81 nm f=0.0000 <S**2>=2.000

159 ->162 0.25512

159 ->163 0.11109

160 ->162 0.53001

160 ->163 0.16161

160 ->164 0.14195

Excited State 9: Triplet-A 3.5951 eV 344.87 nm f=0.0000 <S**2>=2.000

148 ->162 0.12753

149 ->163 0.17047

150 ->162 -0.15080

151 ->162 -0.11366

151 ->167 0.10632

152 ->167 0.16000

154 ->162 -0.10254

154 ->164 0.18870

156 ->170 0.11746

157 ->165 0.15193

159 ->163 -0.12483

159 ->164 0.11301

159 ->169 0.24589

160 ->162 0.19997

160 ->163 0.11584

Excited State 10: Triplet-A 3.6364 eV 340.95 nm f=0.0000 <S**2>=2.000

152 ->167 -0.15309

154 ->163 -0.12847

158 ->161 0.12792

159 ->162 0.19265

159 ->164 0.16779

159 ->169 -0.13703

160 ->162 -0.10318

160 ->163 0.42324

160 ->165 0.11721

160 ->166 0.11306

SI4. Chemosesning Applications

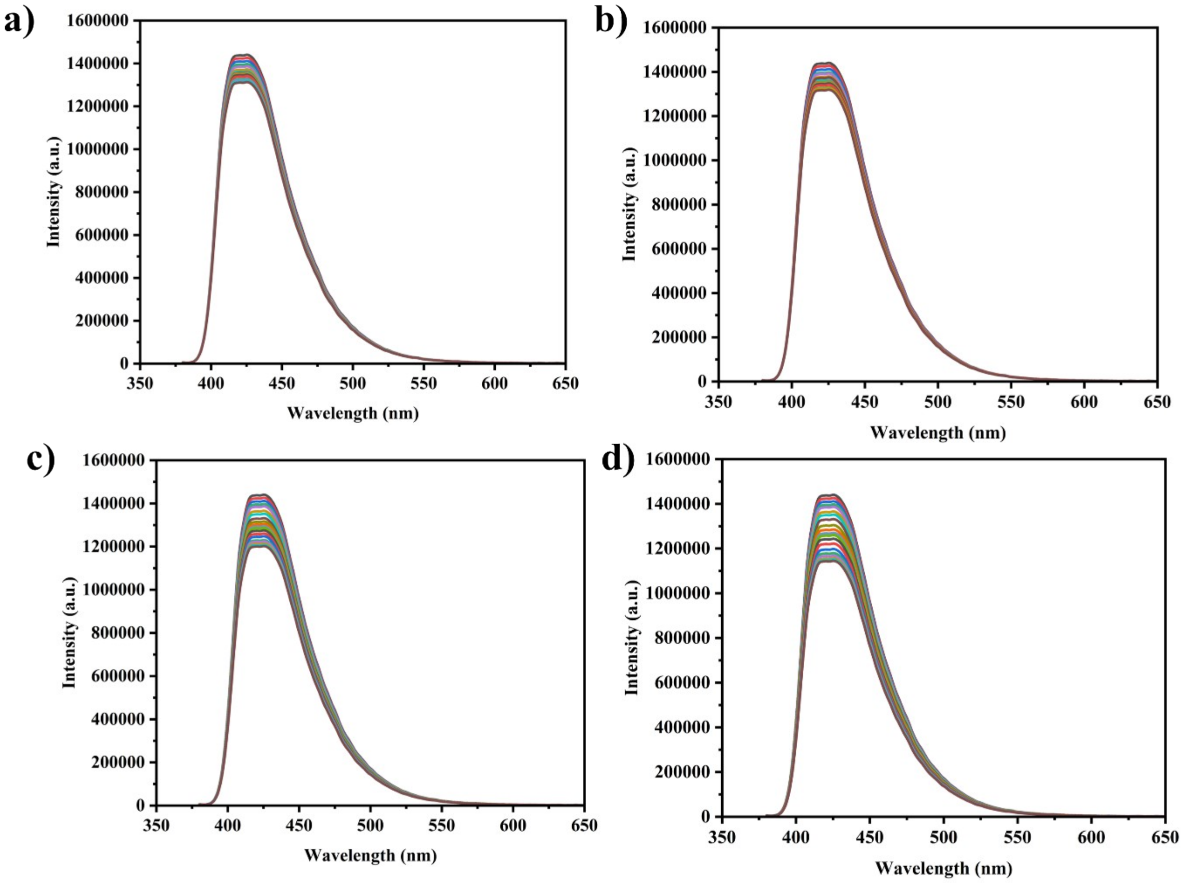

Fig. S8: Change in the fluorescence of BI-Ac upon the addition of (a) (b) (c) and (d)

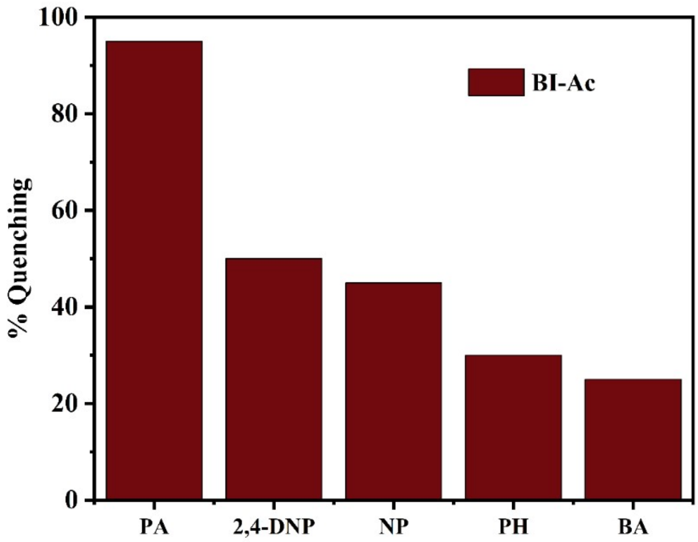

Fig. S9: Fluorescence quenching efficiency of the different nitroaromatic quenchers towards the BI-Ac. (% Quenching at quencher concentration of xxxxxx)

SI5. Single crystal analysis of BI-Ac

Table S1. Bond lengths for BI-Ac.

Atoms 1,2	d 1,2 [Å]	Atoms 1,2	d 1,2 [Å]
N2—C21	1.378(2)	C35—H35	0.9300
N2—C36	1.432(2)	C35—C34	1.379(3)
N2—C22	1.394(2)	C40B—C39	1.383(9)
N1—C21	1.315(2)	C40B—C42	1.506(9)
N1—C23	1.385(2)	C25—H25	0.9300
C21—C18	1.469(2)	C25—C26	1.379(3)
C23—C22	1.371(2)	C14—H14	0.9300
C23—C24	1.473(2)	C14—C13	1.352(3)
C30—C22	1.481(2)	C37—H37	0.9300
C30—C35	1.377(2)	C37—C38	1.374(3)
C30—C31	1.377(2)	C28—H28	0.9300
C15—C7	1.495(2)	C28—C27	1.365(3)
C15—C16	1.382(2)	C31—H31	0.9300
C15—C20	1.389(2)	C31—C32	1.380(3)
C7—C6	1.400(2)	C11—H11	0.9300
C7—C8	1.408(2)	C11—C12	1.341(3)
C36—C41	1.381(2)	C4—H4	0.9300
C36—C37	1.376(2)	C4—C3	1.352(3)
C6—C5	1.433(2)	C27—H27	0.9300
C6—C1	1.433(2)	C27—C26	1.372(3)
C8—C9	1.433(2)	C39—H39	0.9300
C8—C14	1.424(3)	C39—H39A	0.9300
C18—C19	1.389(2)	C39—C38	1.371(3)
C18—C17	1.387(2)	C39—C40A	1.391(9)
C24—C29	1.381(2)	C2—H2	0.9300
C24—C25	1.382(2)	C2—C3	1.406(3)
C9—C10	1.381(3)	C3—H3	0.9300
C9—C11	1.422(3)	C12—H12	0.9300
C5—C10	1.389(3)	C12—C13	1.408(3)
C5—C4	1.420(3)	C38—H38	0.9300
C16—H16	0.9300	C13—H13	0.9300
C16—C17	1.377(2)	C26—H26	0.9300
C20—H20	0.9300	C34—H34	0.9300
C20—C19	1.378(2)	C34—C33	1.363(3)
C19—H19	0.9300	C33—H33	0.9300
C1—H1	0.9300	C33—C32	1.359(3)
C1—C2	1.352(3)	C32—H32	0.9300
C41—H41	0.9300	C42—F3A	1.315(8)
C41—H41A	0.9300	C42—F1A	1.383(8)
C41—C40B	1.391(9)	C42—F2A	1.279(7)
C41—C40A	1.395(9)	C42—F1B	1.208(6)
C17—H17	0.9300	C42—F2B	1.253(8)
C10—H10	0.9300	C42—F3B	1.377(7)
C29—H29	0.9300	C42—C40A	1.490(9)
C29—C28	1.381(2)		

Table S2. Bond angles for BI-Ac.

Atoms 1,2,3	Angle 1,2,3 [°]	Atoms 1,2,3	Angle 1,2,3 [°]
C21—N2—C36	126.21(14)	C39—C40B—C41	119.5(7)
C21—N2—C22	107.24(14)	C39—C40B—C42	118.4(7)
C22—N2—C36	126.51(14)	C24—C25—H25	119.400
C21—N1—C23	106.49(14)	C26—C25—C24	121.3(2)
N2—C21—C18	124.14(16)	C26—C25—H25	119.400
N1—C21—N2	110.79(15)	C8—C14—H14	119.300
N1—C21—C18	125.03(16)	C13—C14—C8	121.4(2)
N1—C23—C24	119.39(16)	C13—C14—H14	119.300
C22—C23—N1	110.21(15)	C36—C37—H37	120.300
C22—C23—C24	130.40(16)	C38—C37—C36	119.5(2)
C35—C30—C22	121.02(17)	C38—C37—H37	120.300
C31—C30—C22	120.36(18)	C29—C28—H28	119.700
C31—C30—C35	118.52(18)	C27—C28—C29	120.5(2)
C16—C15—C7	120.46(16)	C27—C28—H28	119.700
C16—C15—C20	117.70(16)	C30—C31—H31	119.900
C20—C15—C7	121.84(16)	C30—C31—C32	120.3(2)
C6—C7—C15	120.13(17)	C32—C31—H31	119.900
C6—C7—C8	120.34(17)	C9—C11—H11	119.200
C8—C7—C15	119.51(17)	C12—C11—C9	121.6(2)
C41—C36—N2	119.20(16)	C12—C11—H11	119.200
C37—C36—N2	119.81(17)	C5—C4—H4	119.300
C37—C36—C41	120.93(18)	C3—C4—C5	121.3(2)
N2—C22—C30	119.93(15)	C3—C4—H4	119.300
C23—C22—N2	105.26(15)	C28—C27—H27	120.500
C23—C22—C30	134.79(16)	C28—C27—C26	119.1(2)
C7—C6—C5	120.02(18)	C26—C27—H27	120.500
C7—C6—C1	122.92(18)	C40B—C39—H39	120.300
C5—C6—C1	117.06(19)	C38—C39—C40B	119.4(4)
C7—C8—C9	119.22(19)	C38—C39—H39	120.300
C7—C8—C14	123.14(18)	C38—C39—H39A	120.100
C14—C8—C9	117.64(19)	C38—C39—C40A	119.8(4)
C19—C18—C21	119.71(16)	C40A—C39—H39A	120.100
C17—C18—C21	122.21(16)	C1—C2—H2	119.700
C17—C18—C19	118.01(17)	C1—C2—C3	120.6(2)
C29—C24—C23	123.21(17)	C3—C2—H2	119.700
C29—C24—C25	117.37(18)	C4—C3—C2	120.2(2)
C25—C24—C23	119.42(17)	C4—C3—H3	119.900
C10—C9—C8	119.44(19)	C2—C3—H3	119.900
C10—C9—C11	122.0(2)	C11—C12—H12	119.900
C11—C9—C8	118.5(2)	C11—C12—C13	120.2(2)
C10—C5—C6	118.6(2)	C13—C12—H12	119.900
C10—C5—C4	122.3(2)	C37—C38—H38	119.800
C4—C5—C6	119.1(2)	C39—C38—C37	120.4(2)
C15—C16—H16	119.300	C39—C38—H38	119.800
C17—C16—C15	121.35(17)	C14—C13—C12	120.6(2)
C17—C16—H16	119.300	C14—C13—H13	119.700
C15—C20—H20	119.400	C12—C13—H13	119.700

C19—C20—C15	121.28(17)	C25—C26—H26	119.800
C19—C20—H20	119.400	C27—C26—C25	120.4(2)
C18—C19—H19	119.600	C27—C26—H26	119.800
C20—C19—C18	120.71(17)	C35—C34—H34	119.900
C20—C19—H19	119.600	C33—C34—C35	120.1(2)
C6—C1—H1	119.100	C33—C34—H34	119.900
C2—C1—C6	121.7(2)	C34—C33—H33	120.100
C2—C1—H1	119.100	C32—C33—C34	119.8(2)
C36—C41—H41	120.800	C32—C33—H33	120.100
C36—C41—H41A	120.800	C31—C32—H32	119.700
C36—C41—C40B	118.4(4)	C33—C32—C31	120.6(2)
C36—C41—C40A	118.4(4)	C33—C32—H32	119.700
C40B—C41—H41	120.800	F3A—C42—C40B	109.0(8)
C40A—C41—H41A	120.800	F3A—C42—F1A	99.1(6)
C18—C17—H17	119.500	F1A—C42—C40B	116.8(6)
C16—C17—C18	120.93(17)	F2A—C42—C40B	118.9(5)
C16—C17—H17	119.500	F2A—C42—F3A	109.9(6)
C9—C10—C5	122.31(19)	F2A—C42—F1A	101.3(7)
C9—C10—H10	118.800	F1B—C42—F2B	110.3(8)
C5—C10—H10	118.800	F1B—C42—F3B	105.8(7)
C24—C29—H29	119.400	F1B—C42—C40A	117.2(5)
C24—C29—C28	121.30(19)	F2B—C42—F3B	106.1(6)
C28—C29—H29	119.400	F2B—C42—C40A	105.6(9)
C30—C35—H35	119.700	F3B—C42—C40A	111.4(7)
C30—C35—C34	120.7(2)	C41—C40A—C42	118.2(7)
C34—C35—H35	119.700	C39—C40A—C41	118.6(7)
C41—C40B—C42	117.4(6)	C39—C40A—C42	119.0(7)