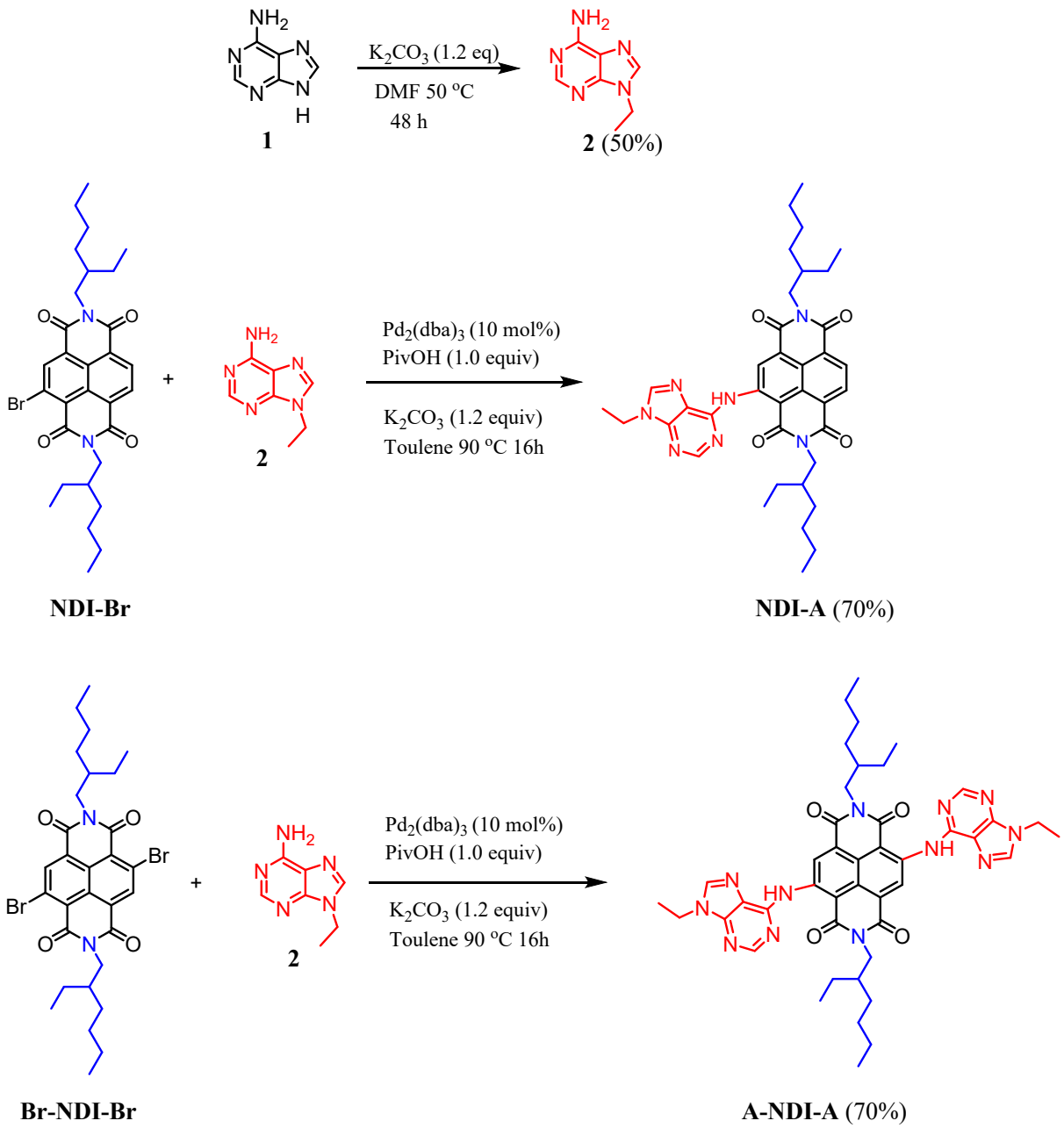
Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information



Scheme S1. Synthesis of **NDI-A** and **A-NDI-A**.

Synthesis of NDI-A[1]

A clean dried 50 mL reaction RB charged with *mono*-bromo naphthalene diimide derivative (NDI-Br)[2] (150 mg, 0.263 mmol), alkylated adenine (1) (66.59 mg, 0.395 mmol) and K_2CO_3(weak base) (164 mg, 1.187 mmol) in dry toluene (10 mL). Then $Pd_2(dba)_3$ (10 mmol %) catalyst and pivallic acid (121.33 mg, 1.187 mmol) were added to the mixture at r.t. under N_2 atmosphere. The reaction was stirred at 90 ^oC for 16 h. The color of reaction mixture was changed from yellow to dark orange. After consumption of starting material cool reaction mixture at rt. evaporated the solvent on rota evaporation and purified the orange color compound on column chromatography over silica gel in DCM system and washed with pentane to yield (70%) dark orange solid **NDI-A**. ^1H NMR (400 MHz, CDCl3) δ 13.44 (s, 1H), 10.79 (s, 1H), 8.81 (s, 1H), 8.73 (d, J = 7.7 Hz, 1H), 8.55 (d, J = 7.7 Hz, 1H), 8.08 (s, 1H), 4.43 – 4.09 (m, 6H), 2.10 – 1.91 (m, 2H), 1.66 – 1.60 (m, 6H), 1.47 – 1.24 (m, 16H), 0.98 – 0.84 (m, 12H);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.83, 163.46, 162.91, 152.21, 151.12, 150.88, 146.34, 142.35, 131.49, 128.13, 127.85, 127.57, 127.51, 127.23, 126.33, 125.97, 124.77, 122.63, 121.80, 105.62, 44.72, 44.52, 39.18, 37.88, 37.52, 30.70, 30.54, 28.67, 24.22, 24.01, 23.07, 15.58, 14.09, 10.70, 10.61. MALDI-TOF m/z: calcd. for $C_{37}H_{45}N_7O_4$: 651.35; found: 652.18 $(M + H)^+$.

Synthesis of A-NDI-A[1]

In a clean dried 50 mL reaction RB charged with dibromo Naphthalene diimide derivative (Br-NDI-Br)[2] (150 mg, 0.263 mmol), alkylated adenine (1) (66.59 mg, 0.395 mmol) and weak base K_2CO_3 (164 mg, 1.187 mmol) in dry toluene (10 mL) solvent. Addition of catalyst$Pd_2(dba)_3$ (10 mmol %) and pivallic acid (121.33 mg, 1.187 mmol) respectively at room temperature under N_2 atmosphere. Kept reaction at 90 ^oC for 16 h to change colour yellow to dark Blue, after completion of starting material cool reaction mixture at rt. evaporated the solvent on rota evaporation and purified the dark blue color compound on column chromatography over silica

gel in DCM system and washed with pentane to yield (70%) dark blue solid **A-NDI-A**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.14 (s, 2H), 10.76 (s, 2H), 8.76 (s, 2H), 8.01 (s, 2H), 4.33 – 4.22 (m, 6H), 2.09 – 1.97 (m, 1H), 1.55 (s, 6H), 1.40 – 1.23 (m, 16H), 0.88 (t, J = 7.4 Hz, 3H), 0.82 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CDCl3) δ 166.90, 162.88, 152.78, 152.37, 151.07, 150.62, 143.54, 142.00, 126.16, 126.08, 123.06, 122.44, 106.89, 44.75, 39.13, 37.52, 33.19, 31.92, 30.61, 30.26, 29.70, 29.36, 28.64, 26.72, 23.94, 23.15, 15.60, 14.12, 10.75. MALDI-TOF m/z: calcd. for $C_{44}H_{52}N_{12}O_4$: 812.42; found: 813.40 $(M + H)^+$.

Synthesis of Alkylated Adenine (2)[3]

In a 100 mL oven dried reaction RB added the compound of adenine (1 g, 0.00305 mole) and Cs_2CO_3 (4.82 g, 0.0148 mole) in dried DMF (30 mL). After stirring at rt for 15 min addition of bromo ethane (1 mL) by syringe in a reaction mixture. Heat the reaction mixture at 50 ^{o}C for 36 h, after completion of reaction the solvent evaporated on rota evaporation to give white solid residue. Separate the compound in column chromatography over silica gel in 1% (DCM - MeOH) system to give white crystalline compound 62% yield. ^{1}H NMR (400 MHz, DMSO-d6): δ 8.15 (s, 1 H), 8.13 (s, 1 H), 7.16 (br s, 2 H), 4.19-4.13 (q, J = 7.3 Hz, 2 H), 1.39 (t, J = 7.3 Hz, 3 H); ^{13}C NMR (100 MHz, DMSO-d6): δ 155.9, 152.3, 149.3, 140.4, 118.8, 38.0, 15.3; ESI-MS (m/z): $[M + H]^+$ calcd. for C7H9N5, 164.1; found, 164.9.

Preparation of Stock Solution:

1] NDI-A = 3.9 mg in 3 mL DCM.

2] A-NDI-A = 4.8 mg in 3 mL DCM

3] TBAF (Tetrabutyl ammonium fluoride) = 9.45 mg in 3 mL DCM.

Solution Preparation for Measurements:

1] 15 µL (micro litre) of **NDI-A** from stock solution and 150 µL (micro litre) of **TBAF** in 2835 µL (micro litre) DCM. It makes addition of 50 equiv. of **TBAF** in **NDI-A** for measurements.

2] 15 µL (micro litre) of **A-NDI-A** from stock solution and 150 µL (micro litre) of **TBAF** in 2835 µL (micro litre) DCM. It makes addition of 50 equiv. of **TBAF** in **A-NDI-**A for measurements.

UV-Vis spectroscopy

Absorption spectra were measured on a UV-vis-1800 Shimadzu absorption spectrometer using 1 cm quartz cells. All solvents were of spectroscopic grade (purchased from Fisher) and stored over 4 Å molecular max was then plotted against the concentration in all λ. The absorption intensity at cases to confirm, by linearity, that the compounds followed Beer's law. Molar extinction coefficients (ε) were determined from the linear plot for each compound (where A = εbc). A 15 µl of **NDI-A**, **A-NDI-A** from 1×10^{-2} M stock solution were transferred to a vial and made up to a final volume of 3 mL (1×10^{-5} M) in DCM. For thin film measurements, samples were prepared using spin coating method.

Fluorescence spectroscopy

Fluorescence emission spectra were measured on an RF-6000 (Shimadzu, Japan) spectrofluorophotometer. All experiments were performed in a quartz cell with a 1 cm path length. Measurement done in the final volume of 3 mL 10^{-5} M in DCM which is made up from 15 µl of 1×10^{-2} M stock solution of **NDI-A** and **A-NDI-A**.

Cyclic voltammetry experiments[4]

The CV measurements were performed at room temperature by using a Power Lab ML160 potentiostat interfaced via a Power Lab4/20 controller to a PC running E-Chem for Windows version 1.5.2. A single compartment three-electrode cell with a glassy counter electrode, a ($Hg_2Cl_2(s) + 2e^-$) Calomel electrode as reference electrode, and a platinum electrode as the

counter electrode. Electrodes were purchased from either BASi, Inc. or CH Instruments. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was purchased from Aldrich and kept dry under vacuum. DCM was taken from Finar solvent company. The compounds of NDI-Adenine solid were dissolved to a concentration of a 0.1 M TBAPF6/DCM electrolyte. Potential sweeps were controlled by a Princeton Applied Research Versastat II potentiostat. The scan rate for CV was 100 mV/s.

E_{ox}^{onset} and E_{red}^{onset} were determined from the onsets of oxidation and reduction, respectively.

E_{HOMO}, E_{LUMO}, and ΔE were determined from equations S1, S2 and S3, respectively.

$E_{HOMO} = - (E^{ox}_{onset} + 4.7)$ eV …….equiv. S1

$E_{LUMO} = - (E^{red}_{onset} + 4.7)$ eV ……..……equiv. S2

$\Delta E = E_{HOMO} - E_{LUMO}$ eV ……..equiv. S3

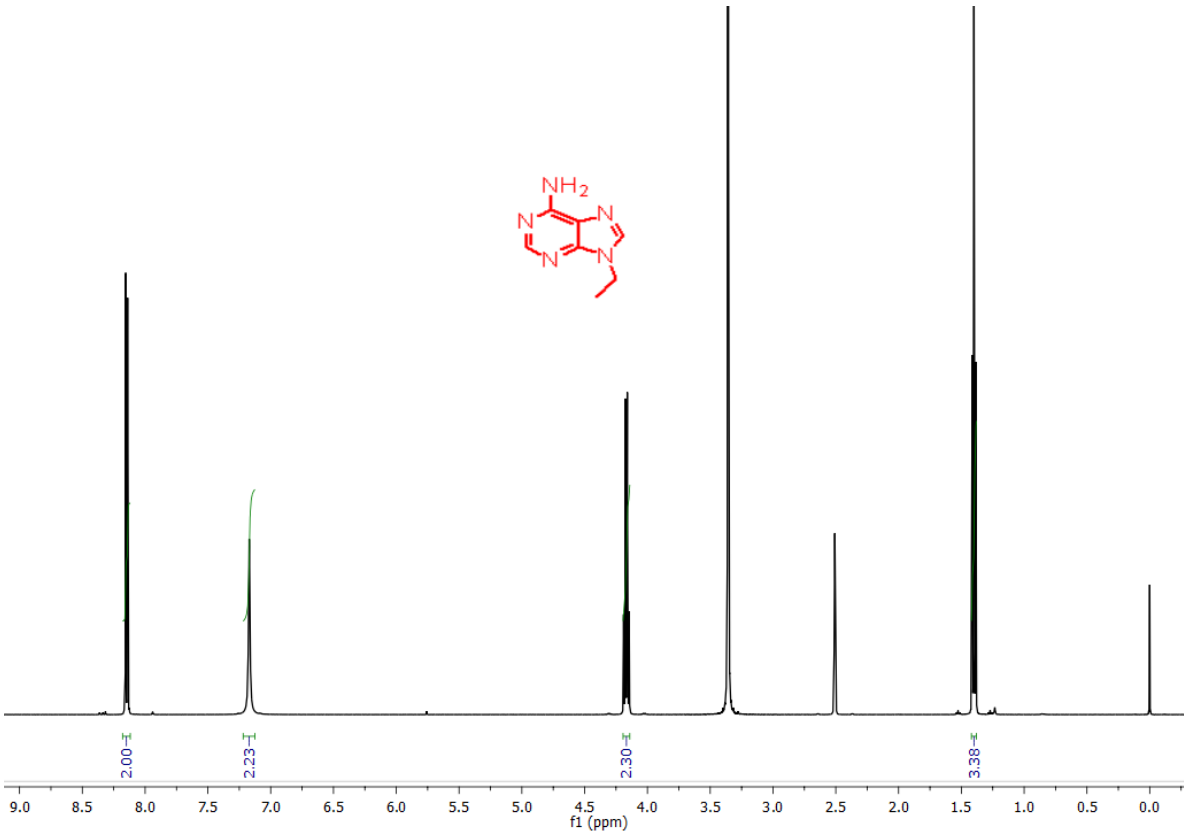


Fig. S1 ^{1}H NMR spectra of **2**.

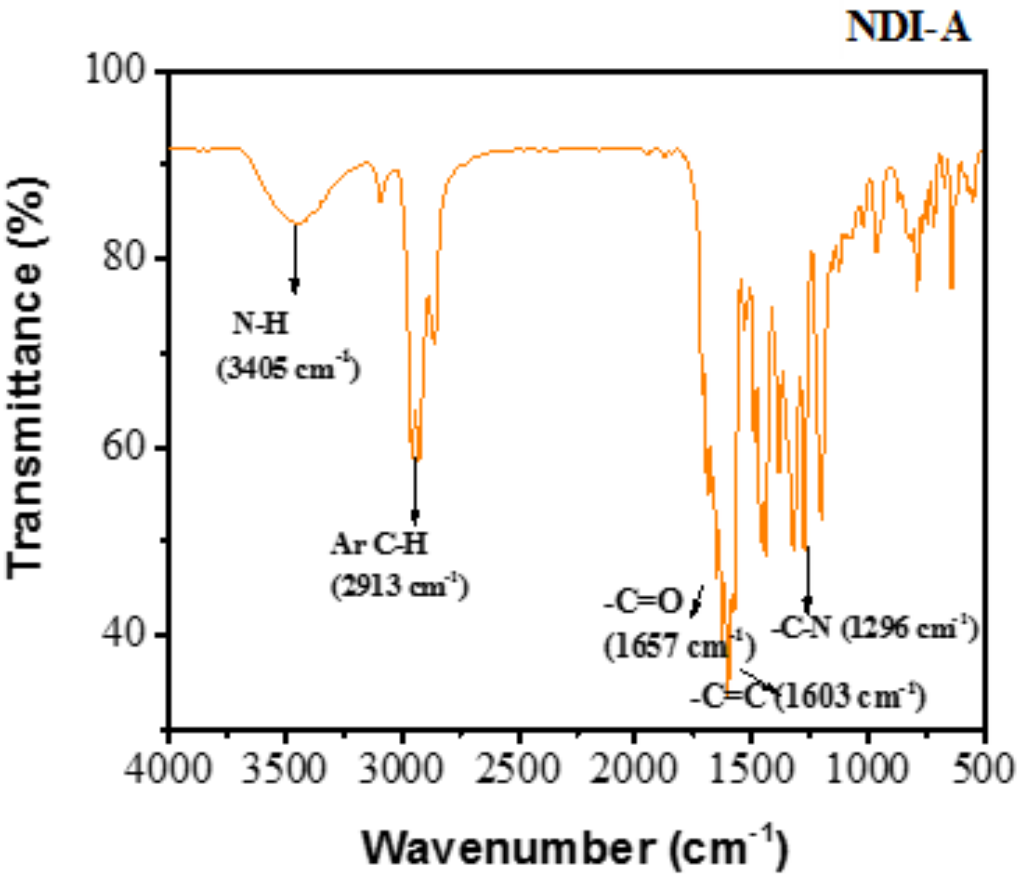


Fig. S2 FT-IR spectra of **NDI-A**

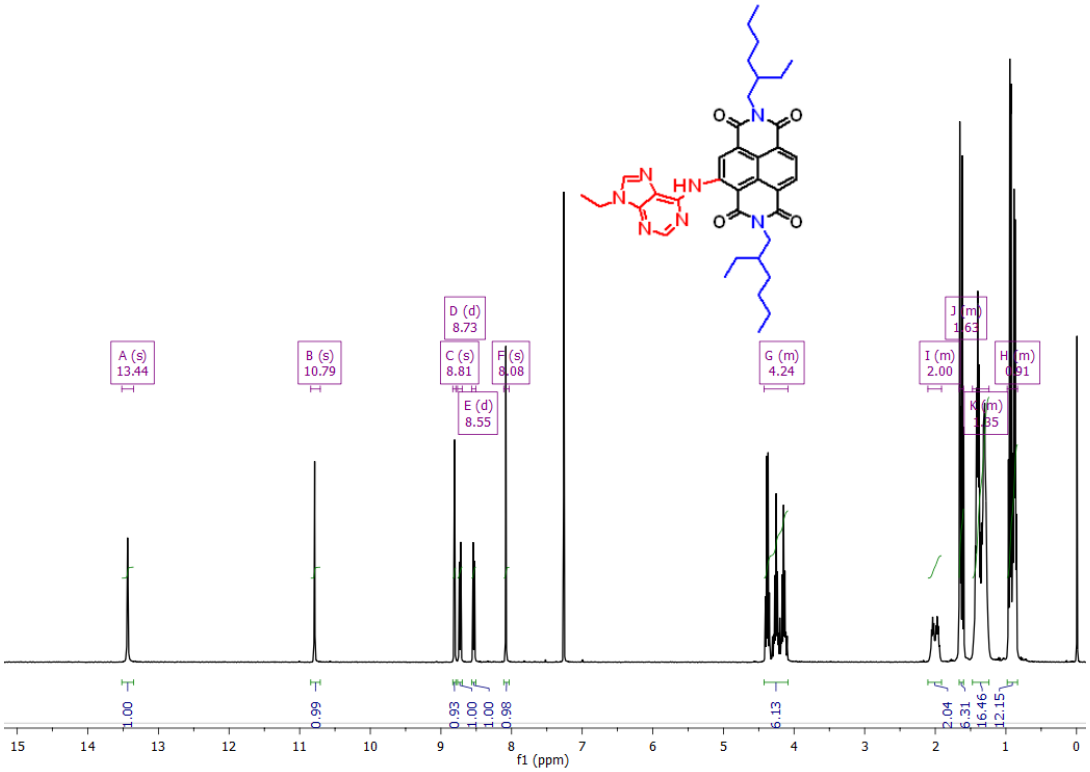


Fig.S3[1]H NMR spectra of **NDI-A**.

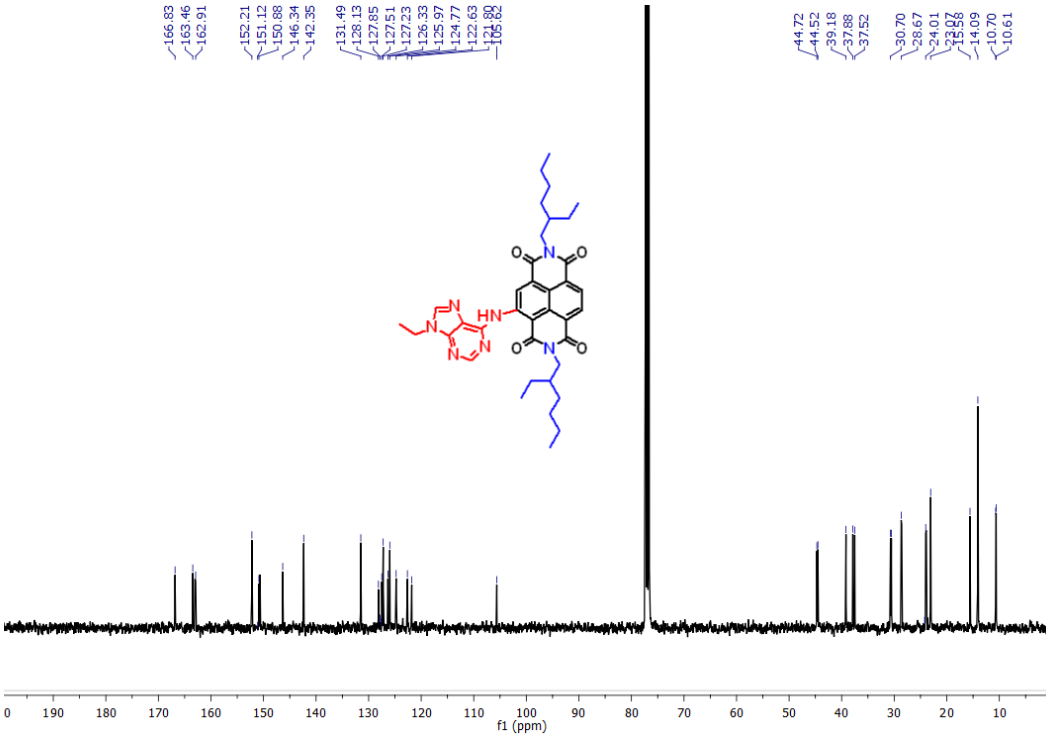


Fig.S4 ^{13}C NMR spectra of **NDI-A**.

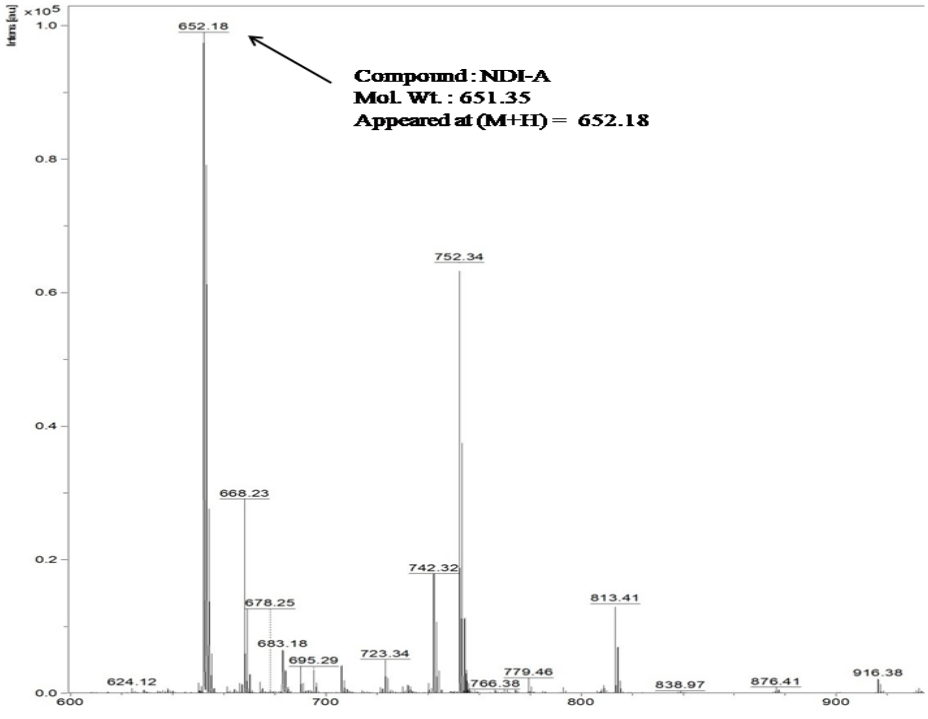


Fig. S5 MALDI-TOF spectrum of compound **NDI-A**.

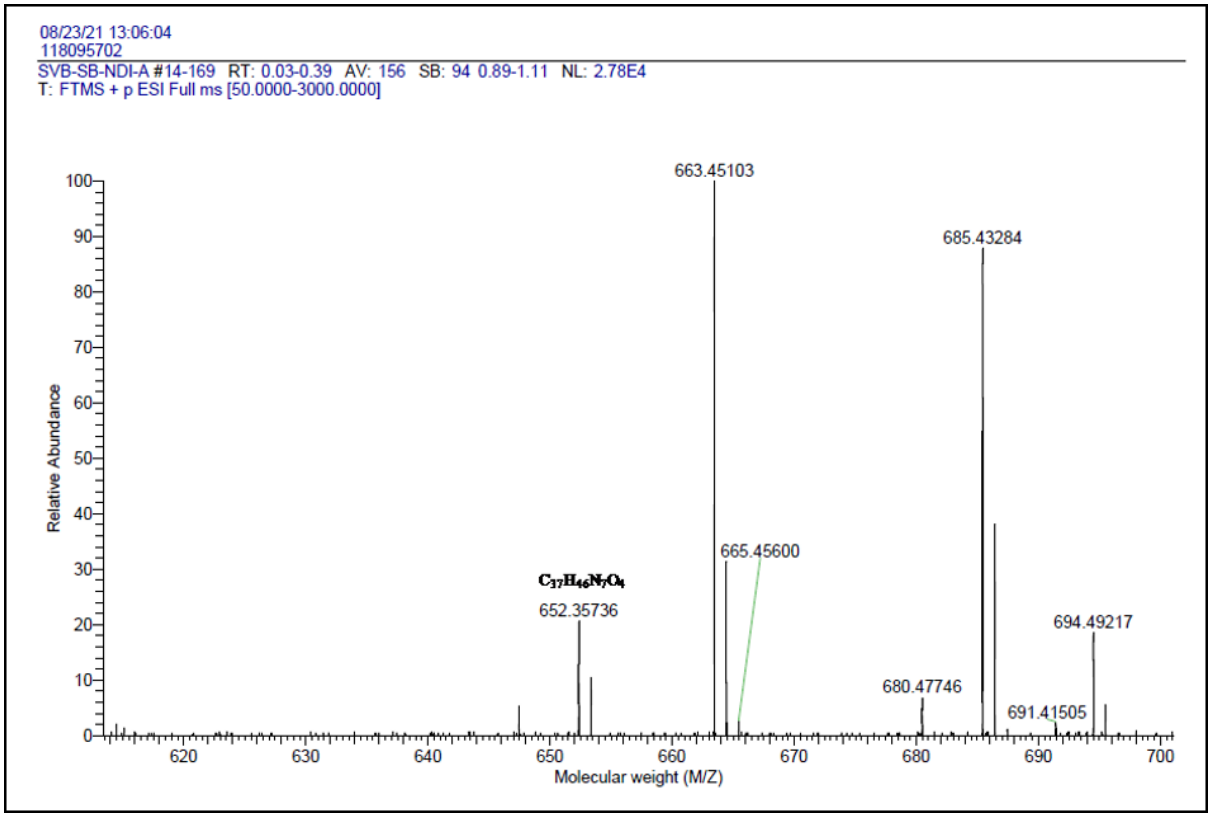


Fig. S6 HRMS spectrum of **NDI-A**

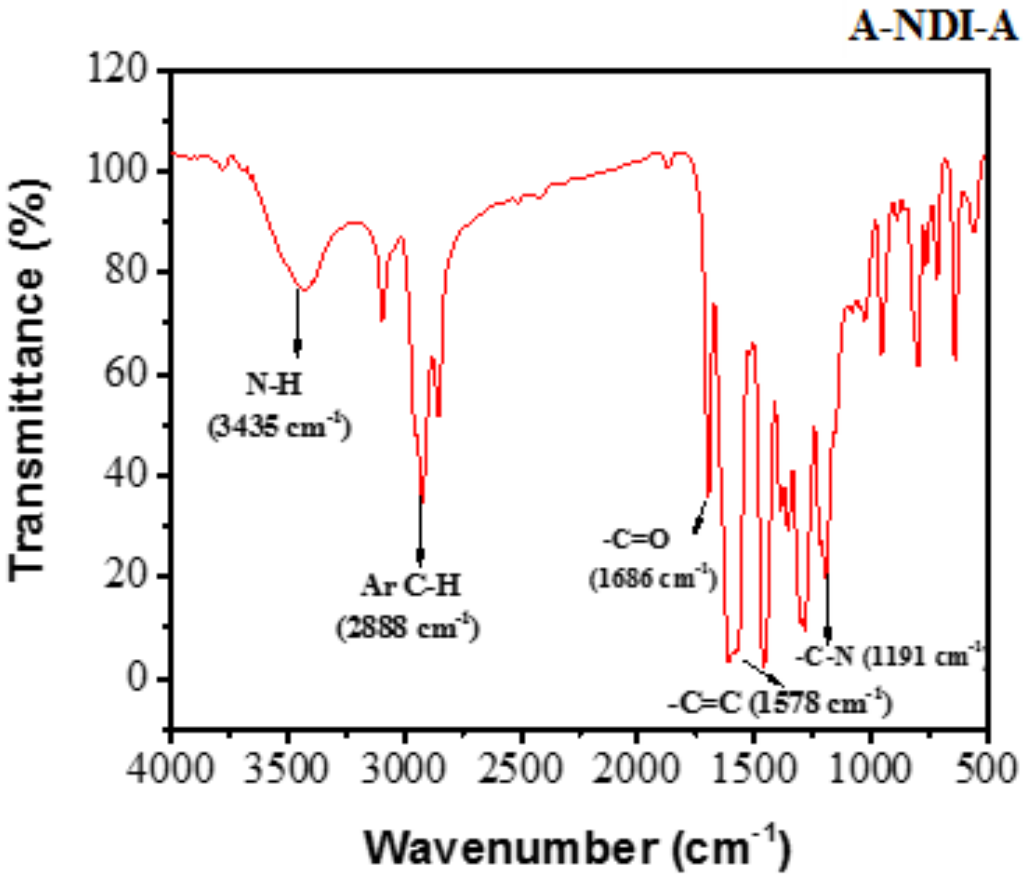


Fig S7FT-IR spectra of **A-NDI-A**

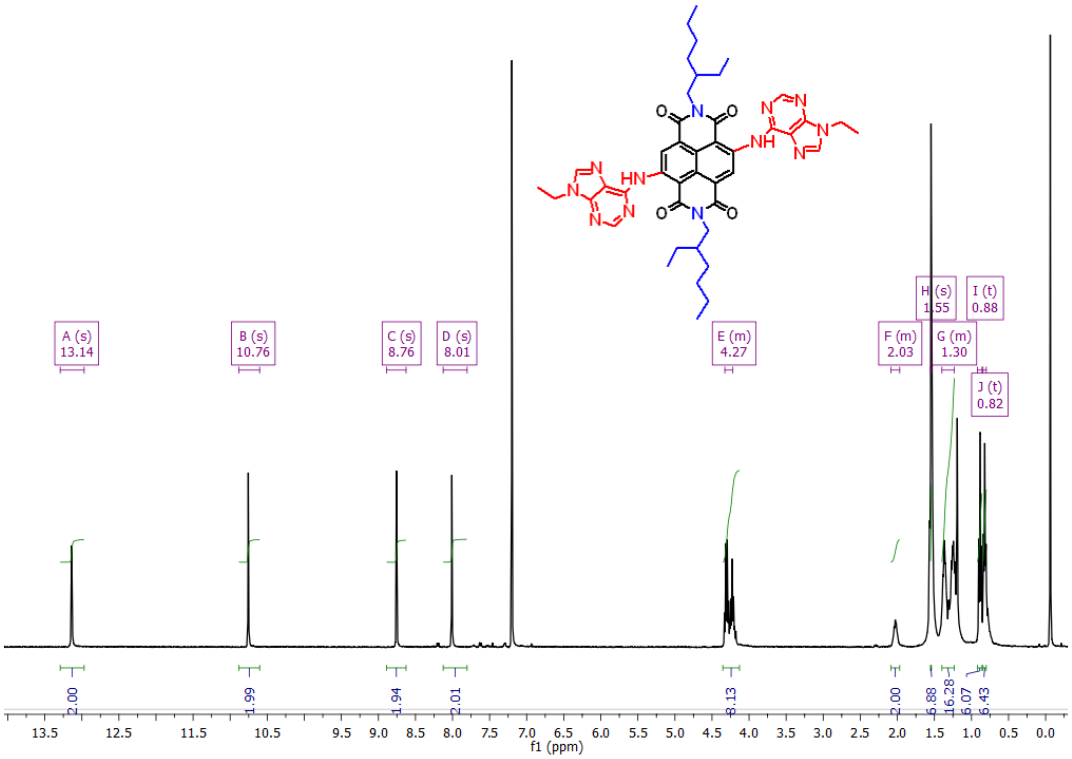


Fig.S8[1]H NMR spectra of **A-NDI-A**.

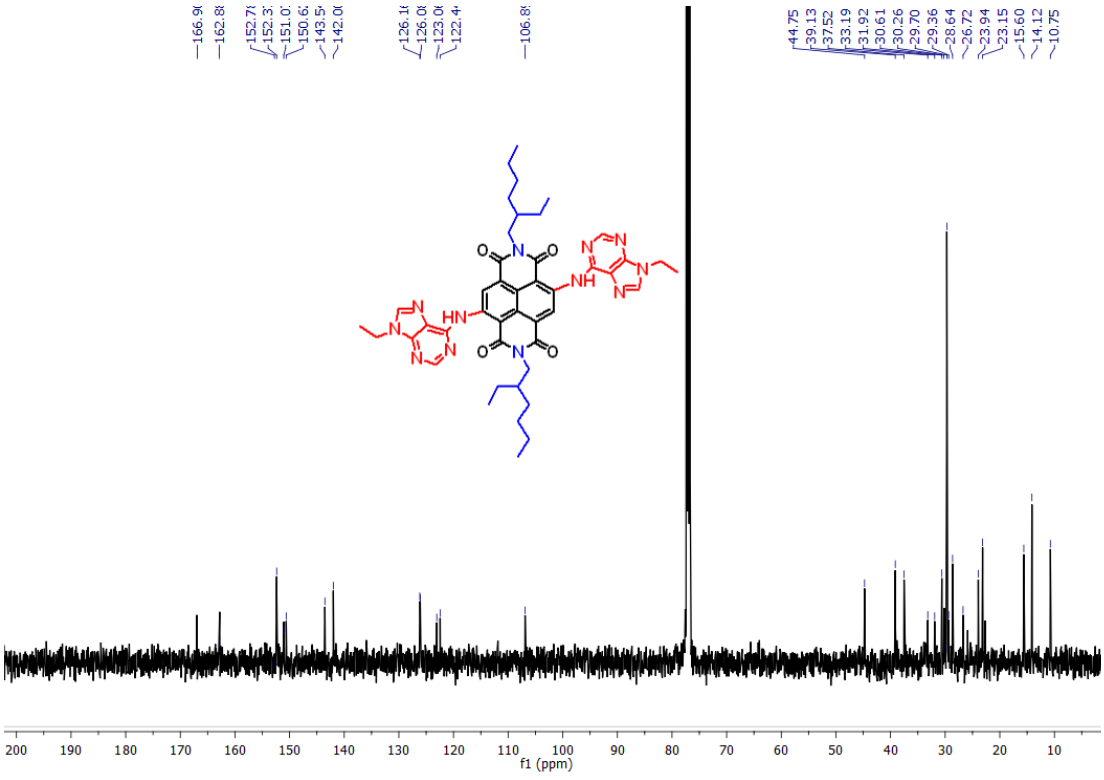


Fig. S9[13]C NMR spectra of **A-NDI-A**.

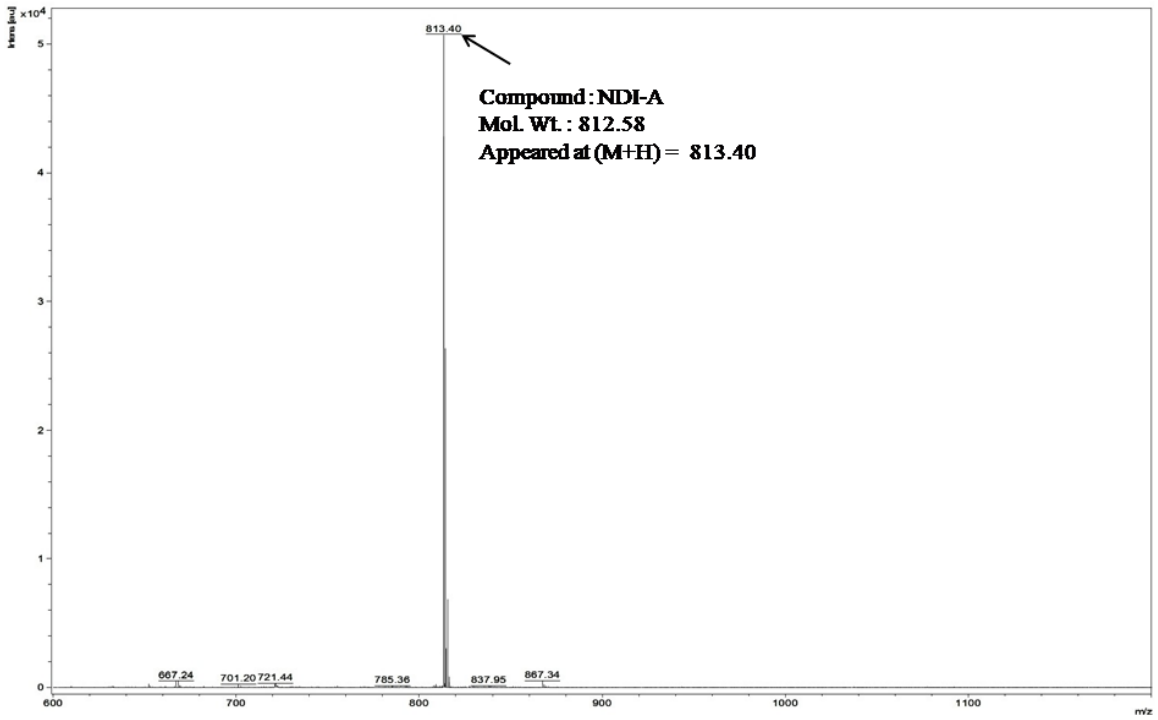


Fig. S10 MALDI-TOF spectrum of compound **A-NDI-A**.

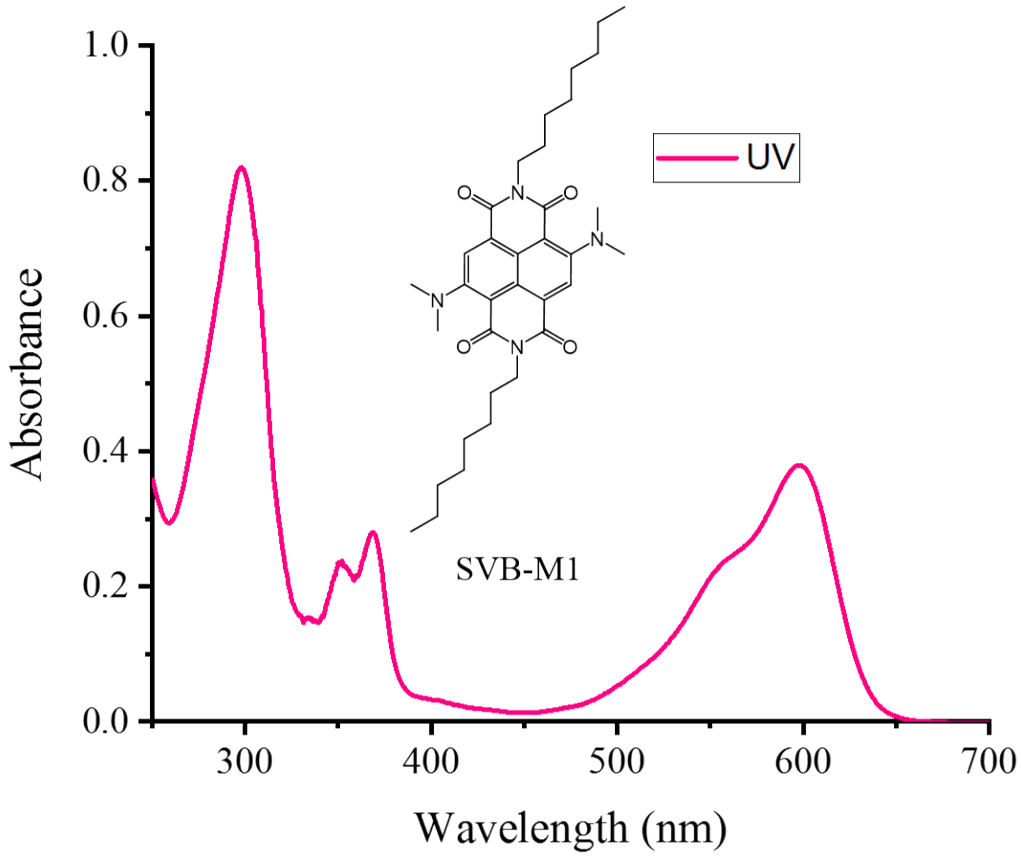


Fig. S11. UV-vis absorption spectra of **SVB-M1** (1 x 10^{-5} M) in dichloromethane.

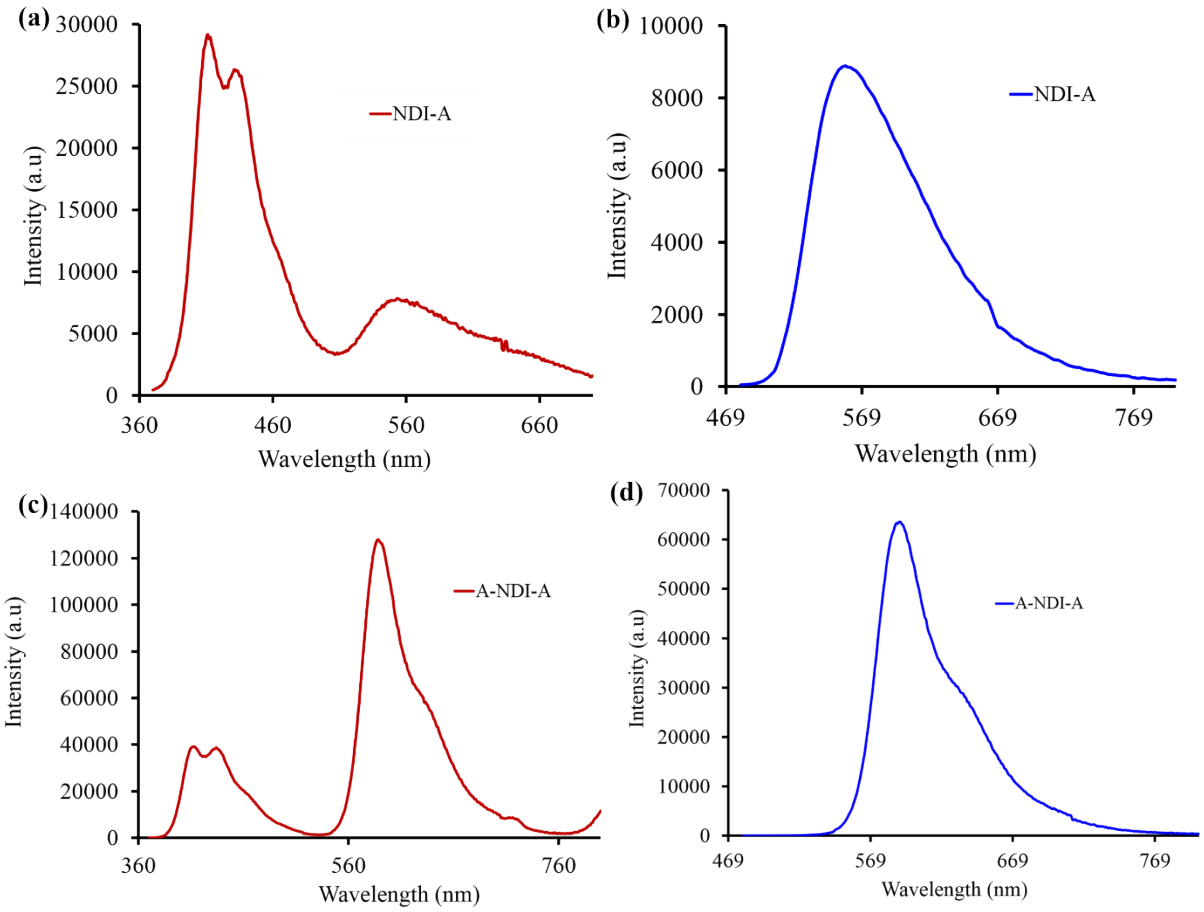


Fig.S12 Fluorescence emission spectra of (a) **NDI-A**(1×10^{-5} M),λ_{ex} = 360 nm; (b)**NDI-A**(1×10^{-5} M),λ_{ex} = 469 nm and (c) **A-NDI-A** (1×10^{-5} M),λ_{ex} = 360 nm; (d) **A-NDI-A** (1×10^{-5} M),λ_{ex} = 469 nm in DCM.

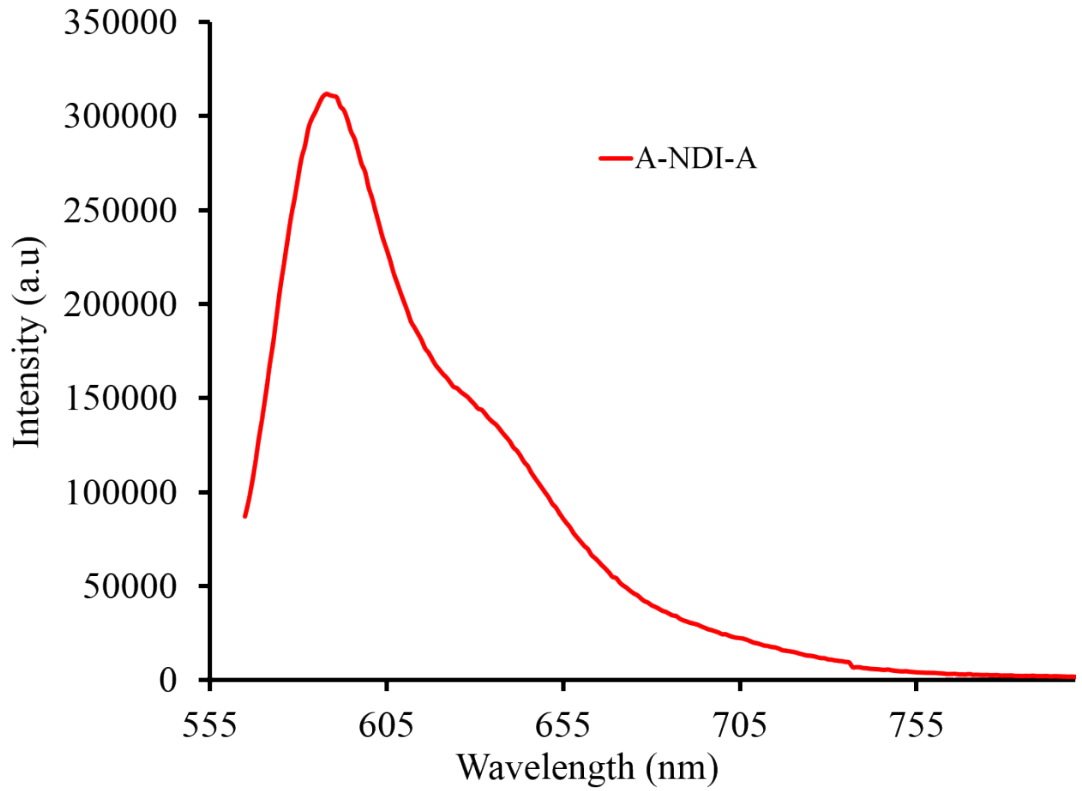


Fig. S13 Fluorescence emission spectra of **A-NDI-A** (1×10^{-5} M) in DCM with the λ_{ex} = 555 nm.

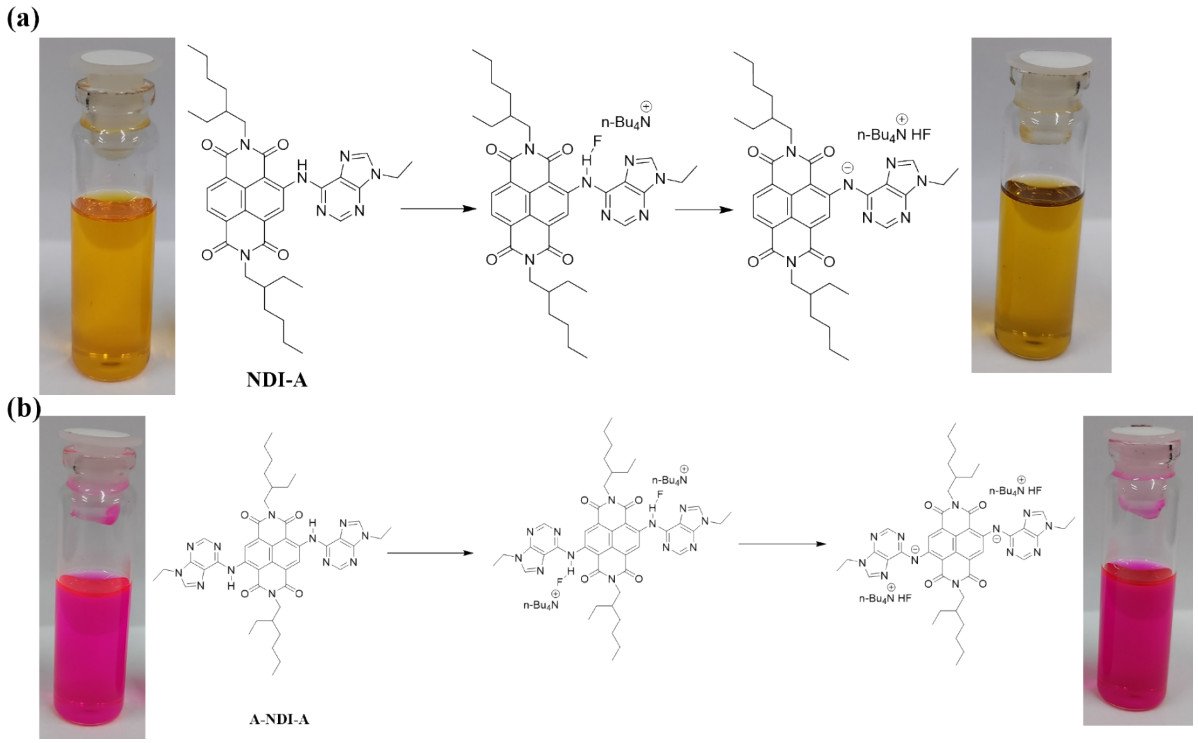


Fig. S14 Colorimetric response of (a) **NDI-A** (0.4 mmol) and (b) **A-NDI-A**(0.4 mmol) in DCM upon addition of tetrabutyl ammonium fluoride (50 equiv.).

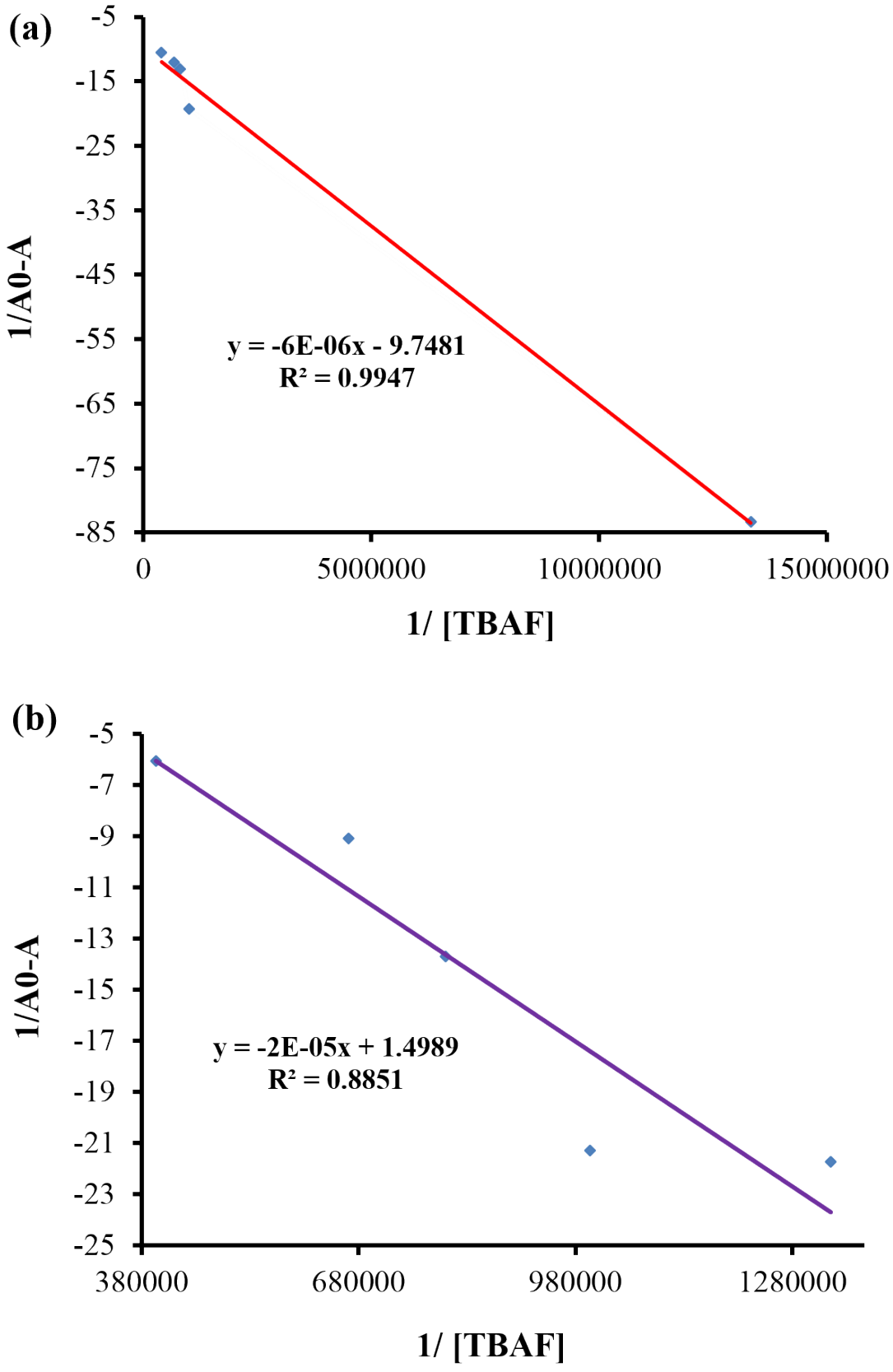


Fig. S15 Benesi-Hildebrand plot for (a) **NDI-A** and (b) **A-NDI-A** upon addition of fluoride anion.

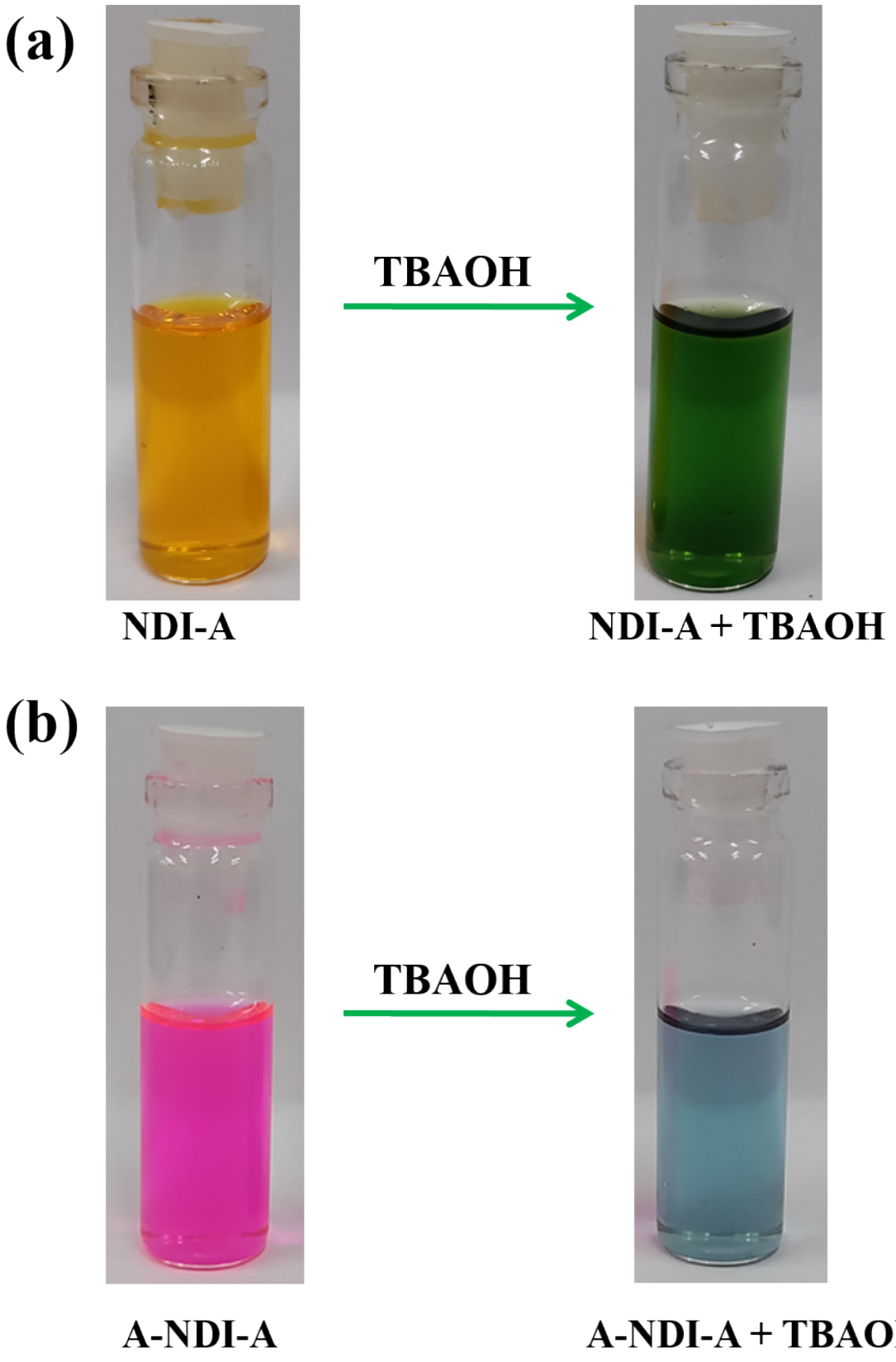


Fig. S16 Colorimetric response of (a) **NDI-A** (0.4 mmol) and (b) **A-NDI-A** (0.4 mmol) in DCM upon addition of tetrabutyl ammonium hydroxide (TBAOH) (50 equiv.).

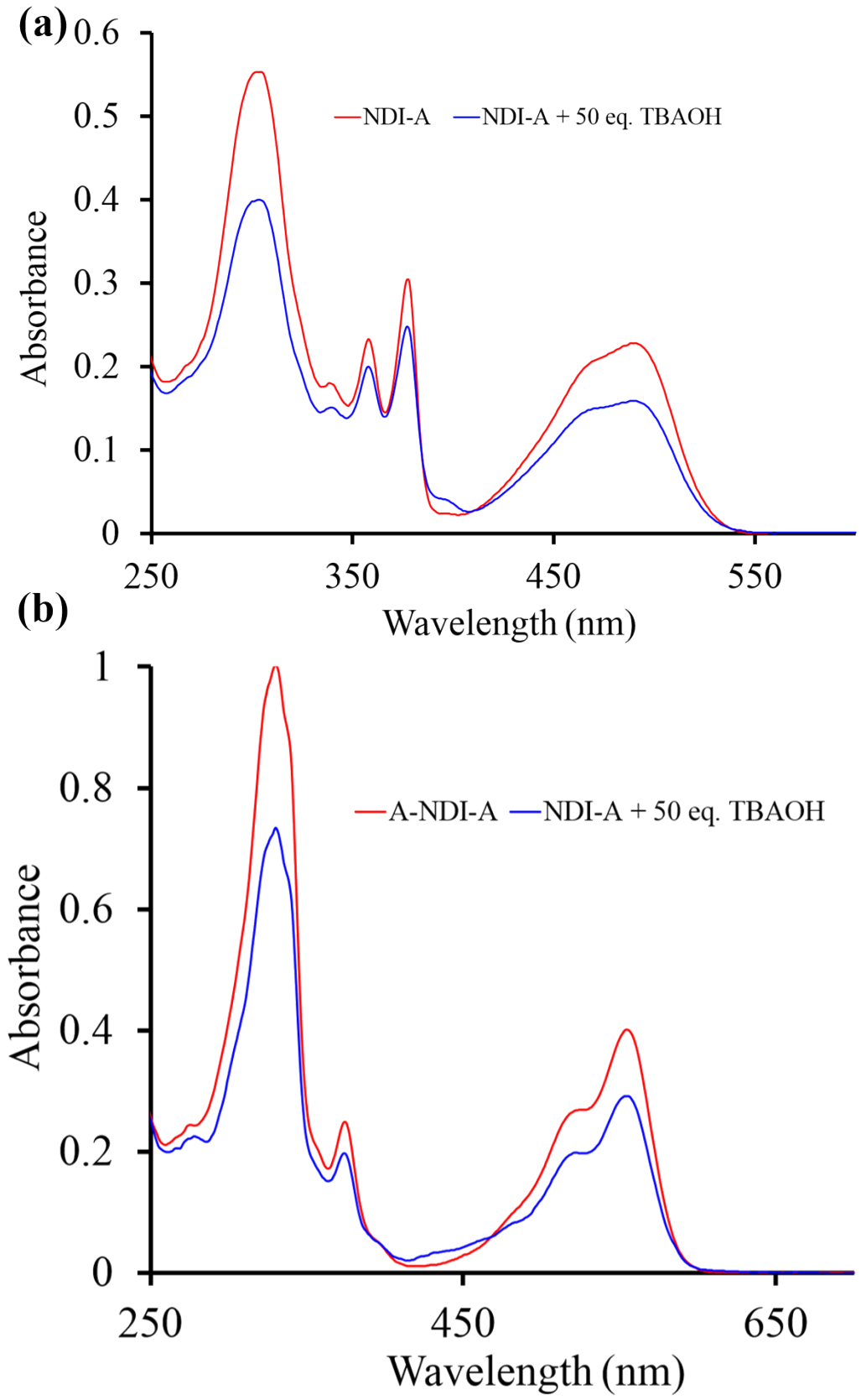


Fig. S17 UV-vis absorption spectra of (a) **NDI-A** (1×10^{-5} M) and (b) **A-NDI-A** (1×10^{-5} M) with the addition of TBAOH in DCM.

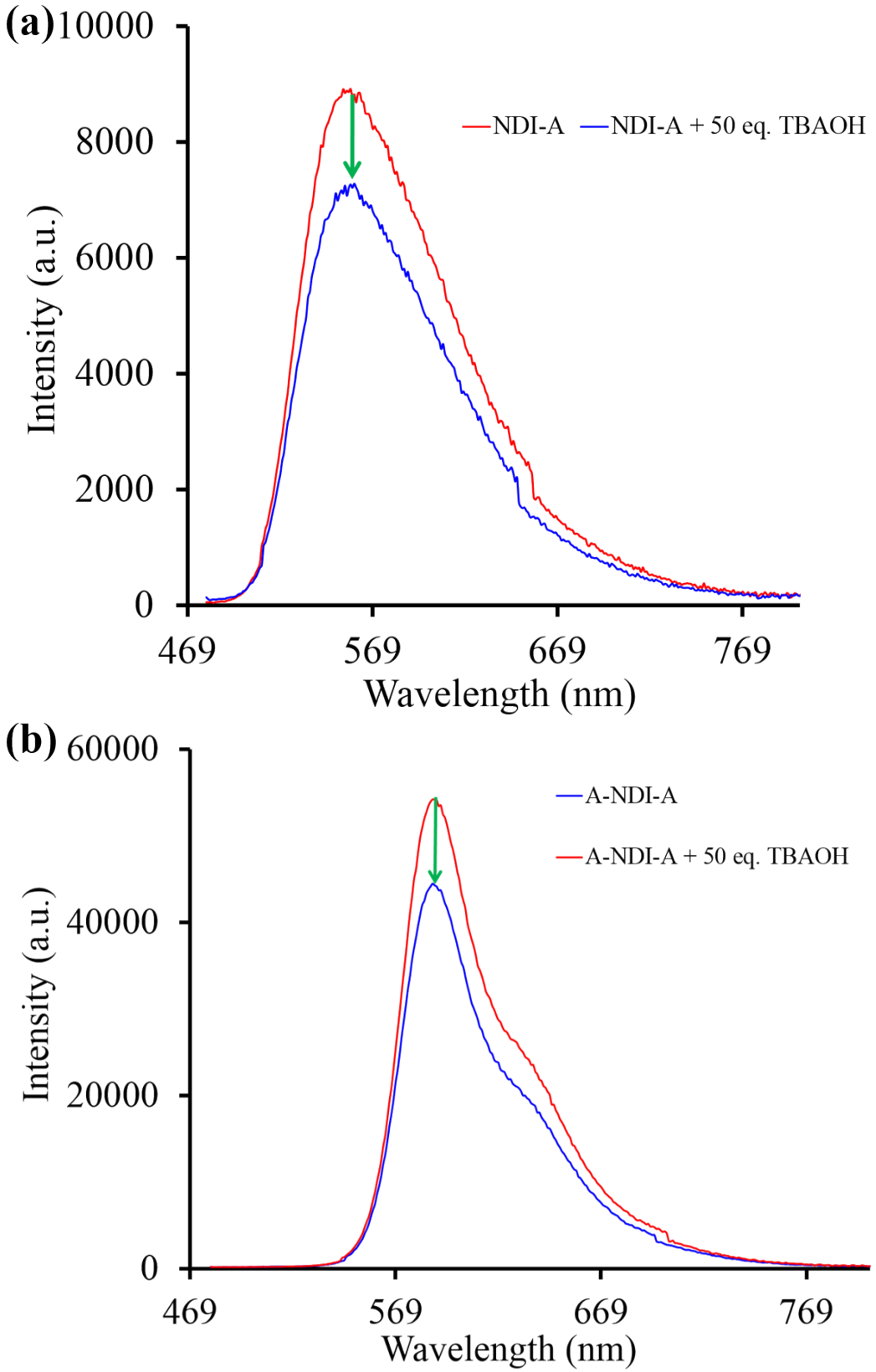


Fig. S18 Fluorescence emission spectra (λ_{ex} = 469 nm) of (c) **NDI-A** (1×10^{-5} M) and (d) **A-NDI-A** (1×10^{-5} M) in DCM upon addition of TBAOH.

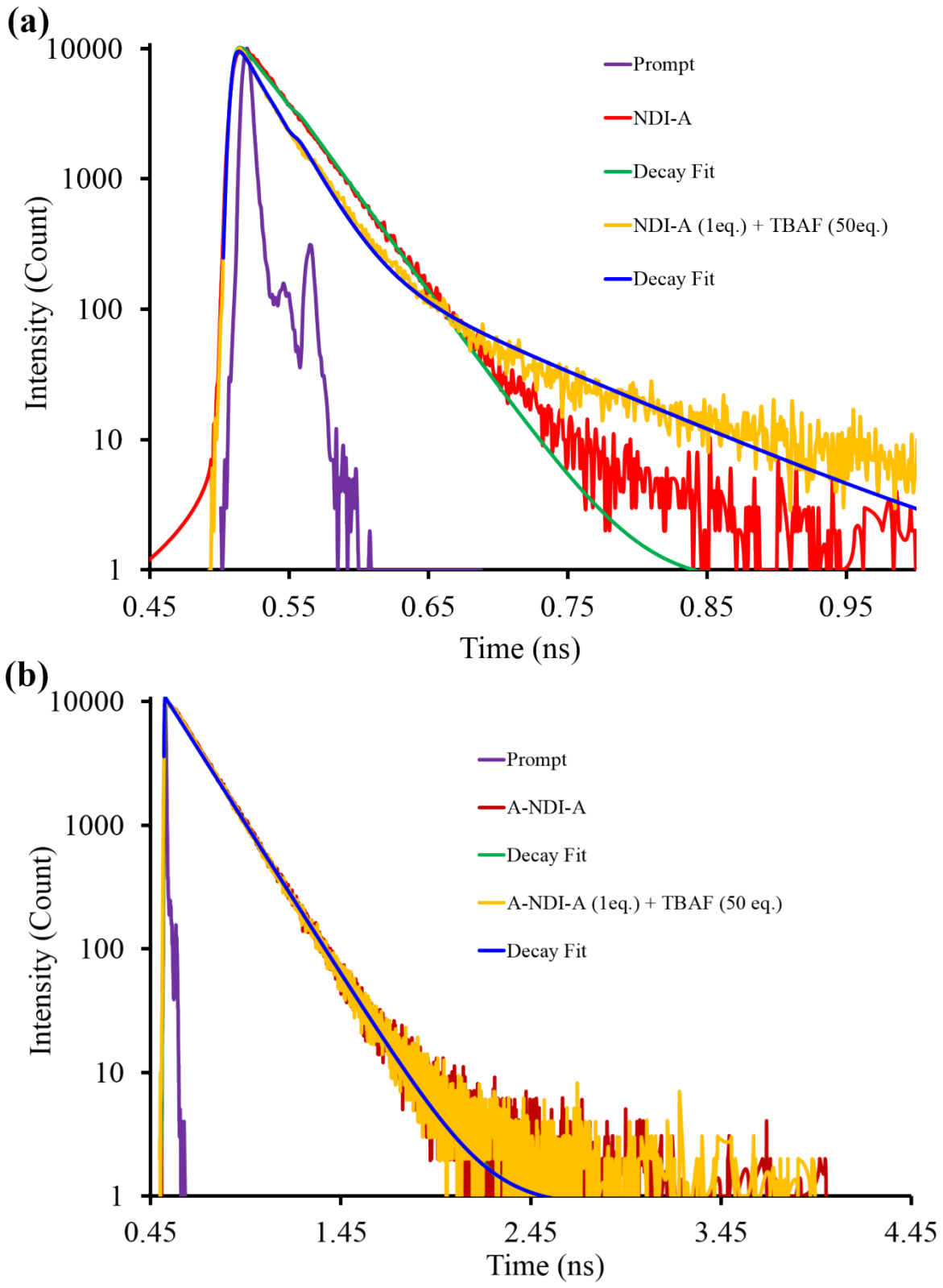


Fig. S19 TCSPC spectra of (a) NDI-A (1×10^{-5} M) and (b) A-NDI-A (1×10^{-5} M) n dichloromethane upon addition of tetrabutyl ammonium fluoride (TBAF) anion.

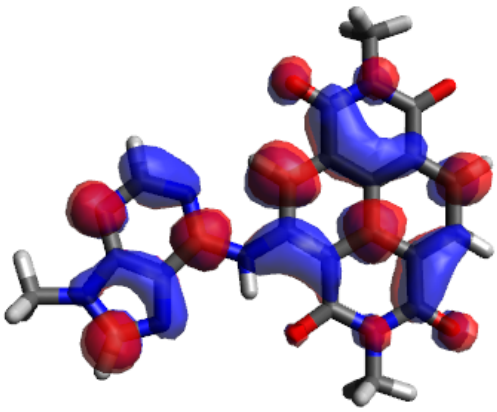
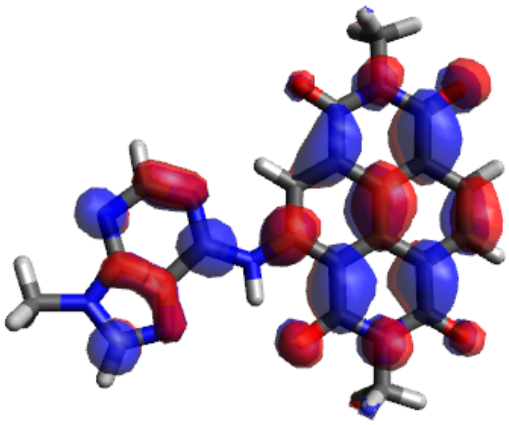
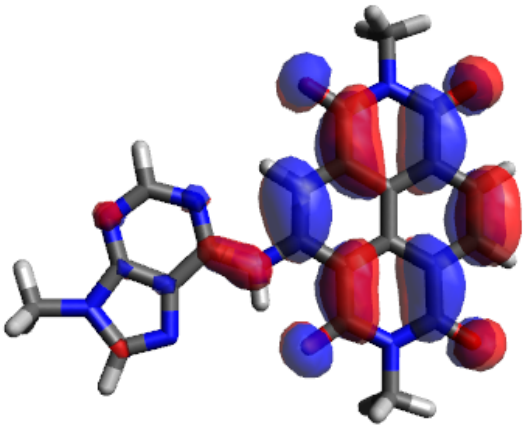
Table S1 Excitation and emission wavelength for TCSPC measurements.

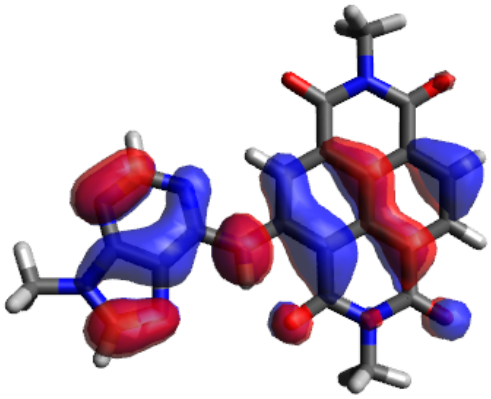
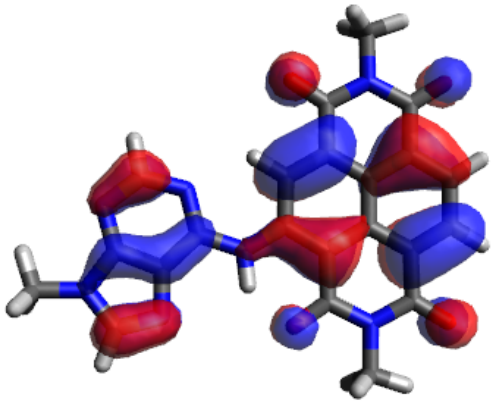
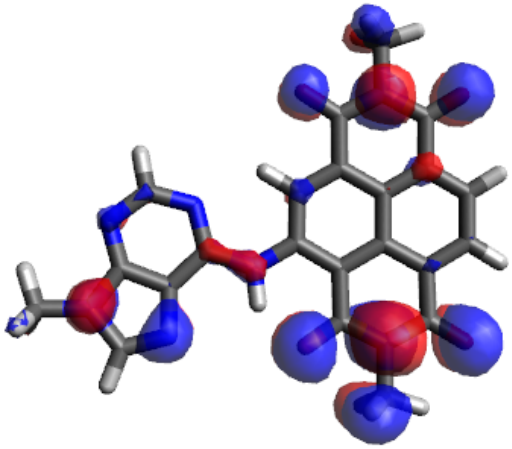
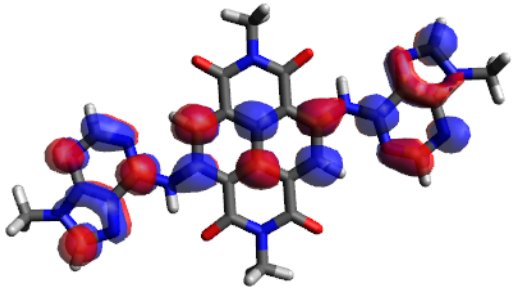
Sr.no.	Compound	Excitation wavelength	Emission wavelength
1.	**NDI-A**	469nm /2.64 eV	560nm /2.21 eV
2.	**A-NDI-A**	469nm/2.64 eV	588nm /2.10 eV

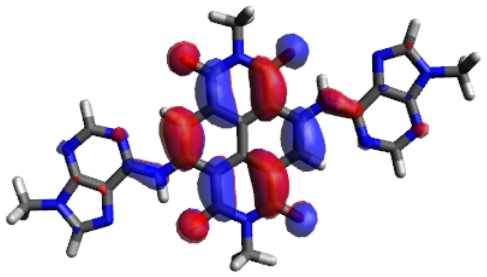
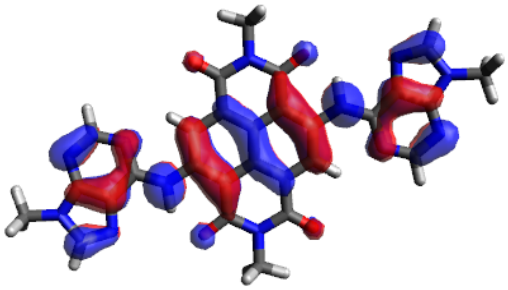
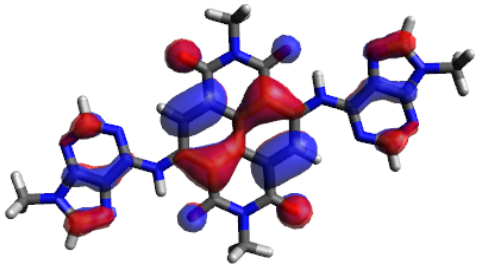
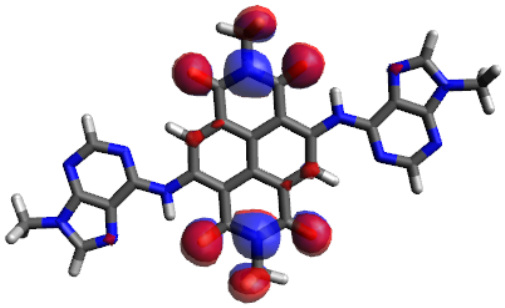
Table S2TCSPC calculation for NDI-A, A-NDI-A and upon addition of TBAF (50 equiv.) and average life time.

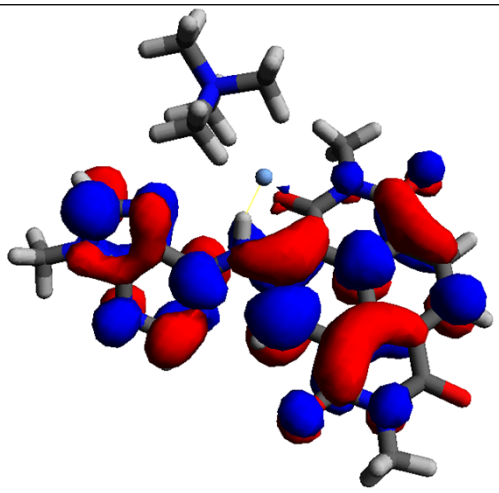
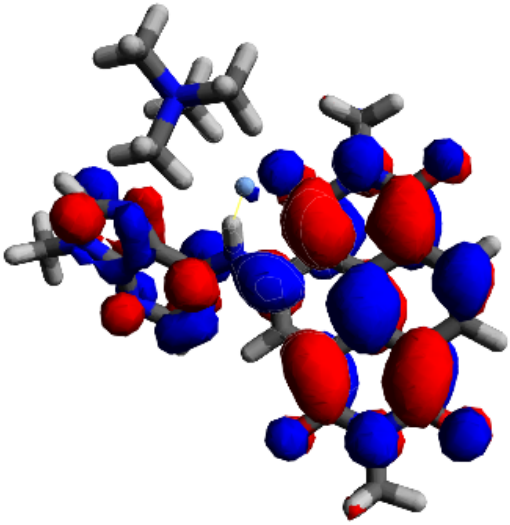
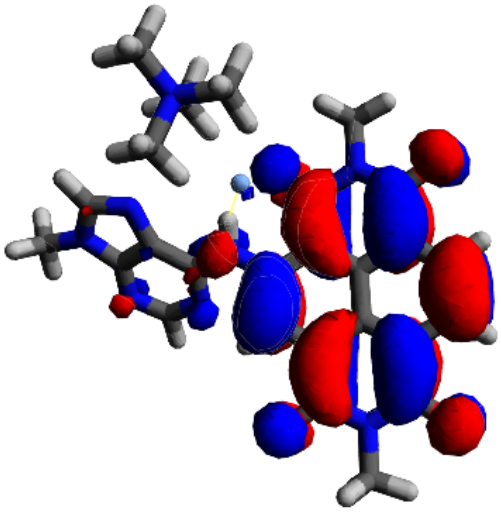
Compound	**τ_1 (nS)**	**Contribution (%)**	**τ_2 (nS)**	**Contribution (%)**	**Average life time**
NDI-A	0.8326	100	-	-	0.8326
NDI-A(1eq.)+TBAF(50eq.)	0.5799	88.69	0.2697	11.31	0.5448
A-NDI-A	0.1831	100	-	-	0.1831
A-NDI-A(1eq.)+TBAF(50eq.)	0.1907	100	-	-	0.1907

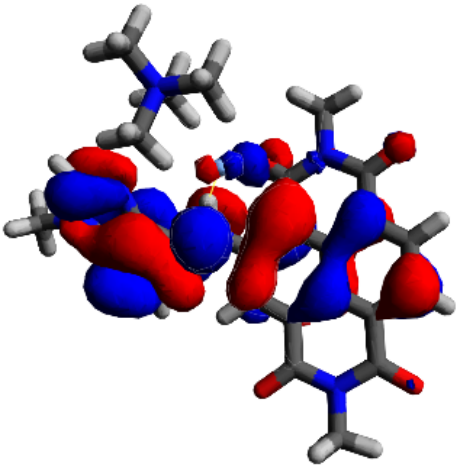
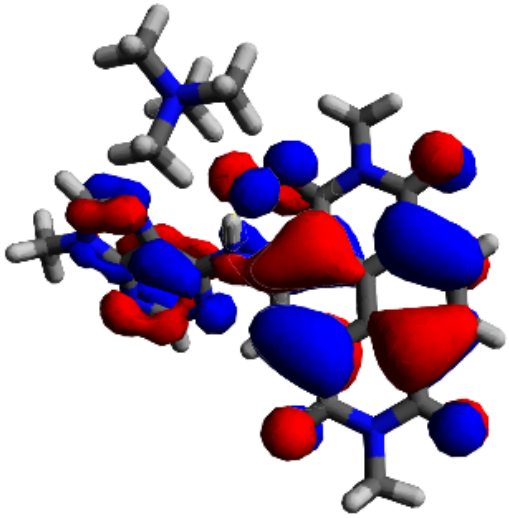
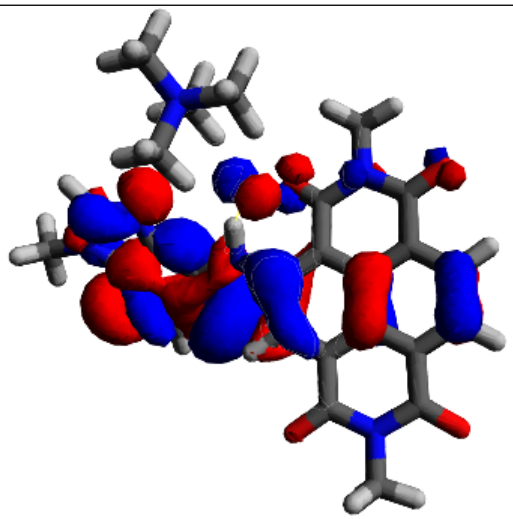
Fig. S20 Frontier molecular orbitals of **NDI-A**, **A-NDI-A**, **NDI-A+TBAF**, and **A-NDI-A+2TBAF** with energy in eV**.**

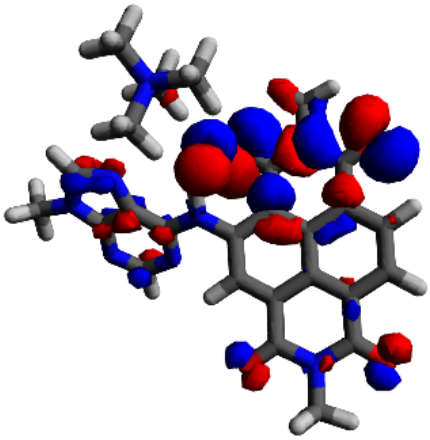
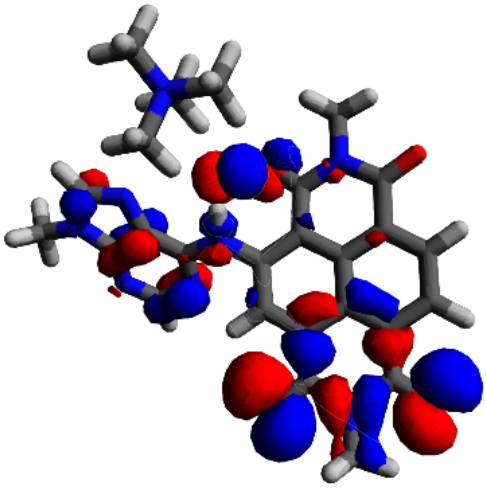
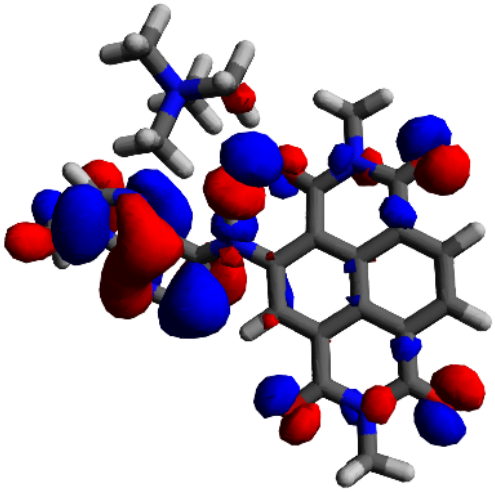
Orbital	**Orbital number**	**Energy (eV)**	**Orbital Picture**
NDI-A			
L+2	117	-1.318eV	
L+1	116	-1.486eV	
L	115	-3.139eV	

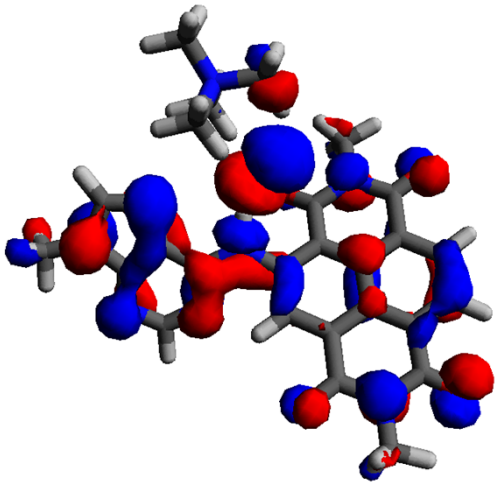
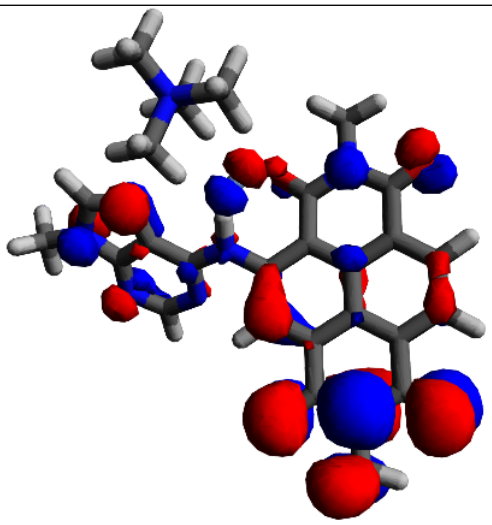
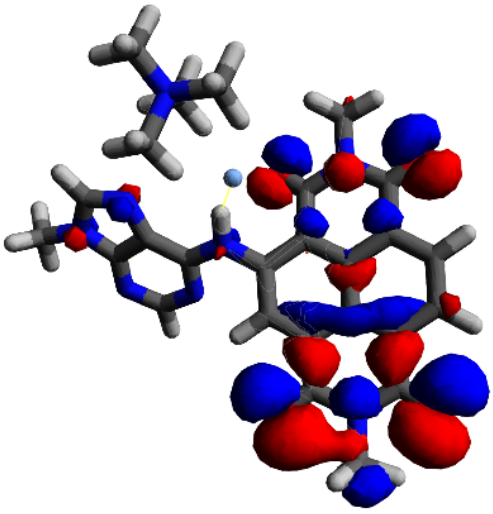
H	114	-6.051eV	
H-1	113	-6.883eV	
H-8	106	- 7.626eV	
A-NDI-A			
L+2	155	1.234eV	

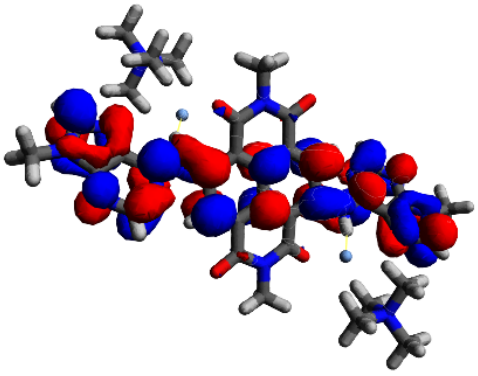
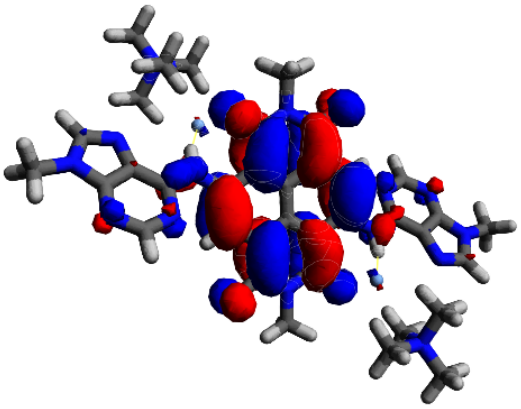
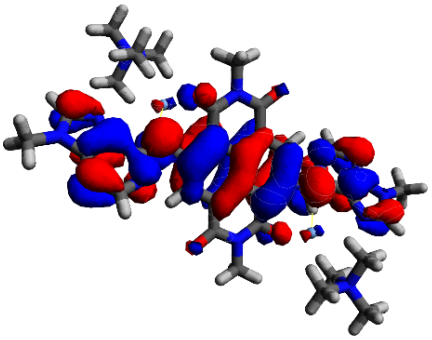
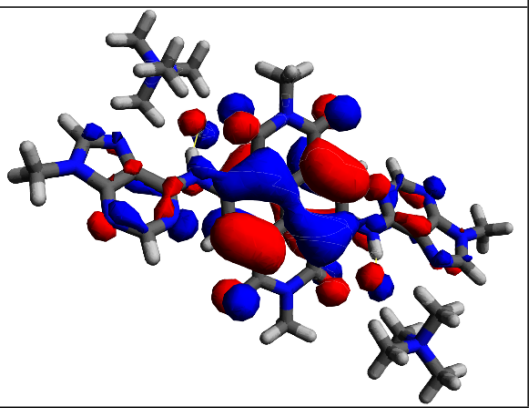
L	153	-2.973eV	
H	152	-5.546eV	
H-2	150	-6.758eV	
H-11	141	-7.535eV	
NDI-A+TBAF			

L+2	143	-0.611eV	
L+1	142	-0.823eV	
L	141	-2.483eV	

H	140	-5.256eV	
H-1	139	-6.163eV	
H-2	138	-6.477eV	

H-3	137	-6.570eV	
H-7	133	-6.857eV	
H-8	132	-6.953eV	

H-10	130	-7.022 eV	
H-11	129	-7.123eV	
H-13	127	-7.468eV	
A-NDI-A+2TBAF			

L+2	207	-0.193eV	
L	205	-1.837eV	
H	204	-4.533eV	
H-2	202	-5.568eV	

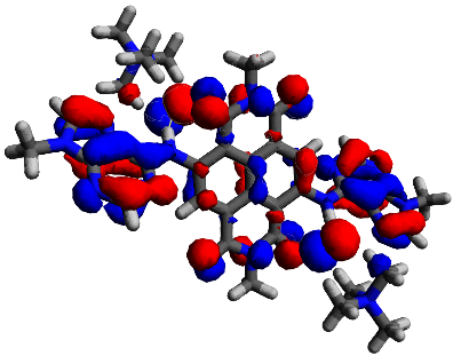
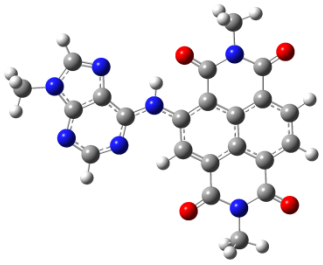
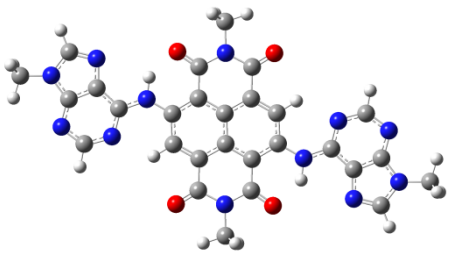
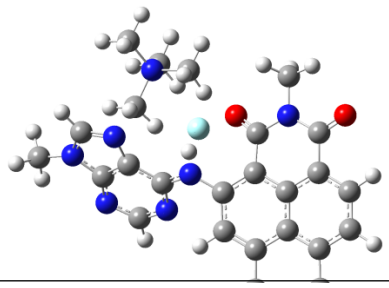
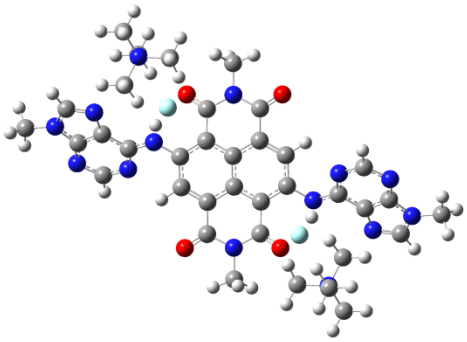
H-9	195	-6.277eV	

Table S3: Optimised structures of **NDI-A**, **A-NDI-A**, **NDI-A+TBAF**, and **A-NDI-A+2TBAF** and their Calculated TD-DFT excitation.

Molecules	**Excitation Wavelength (nm)**	**Oscillator Strength (f)**	**Excitations**	**Percentage Contribution for transition**
NDI-A	480.64	0.2237	114 ->115	HOMO->LUMO (98%)
	362.83	0.2239	113 ->115	H-1->LUMO (95%)
	291.73	0.8109	106 ->115	H-8->LUMO (5%),
			114 ->116	HOMO->L+1 (5%)
			114 ->117	HOMO->L+2 (83%)
A-NDI-A	542.12	0.3831	152 ->153	HOMO->LUMO (99%)
	362.78	0.1629	150 ->153	H-2->LUMO (93%)
			152 ->155	HOMO->L+2 (5%)
	320.21	1.0740	141 ->153	H-11->LUMO (7%),
			150 ->153	H-2->LUMO (4%)
			152 ->155	HOMO->L+2 (87%)
NDI-A+TBAF	525.43	0.1489	140 ->141	HOMO->LUMO (98%)
	369.80	0.1782	133 ->141	H-7->LUMO (2%),
			137 ->141	H-3->LUMO (20%),
			138 ->141	H-2->LUMO (2%)
			139 ->141	H-1->LUMO (70%)
	304.39	0.2255	127 ->141	H-13->LUMO (36%),
			129 ->141	H-11->LUMO (4%),
			130 ->141	H-10->LUMO (2%),

			132 ->141	H-8->LUMO (3%),
			140 ->142	HOMO->L+1 (3%)
			140 ->143	HOMO->L+2 (41%)
A-NDI-A+2TBAF	537.74	0.3300	204 ->205	HOMO->LUMO (98%)
	370.41	0.1945	202 ->205	H-2->LUMO (89%)
			204 ->207	HOMO->L+2 (3%)
	321.25	1.0019	195 ->205	H-9->LUMO (4%),
			202 ->205	H-2->LUMO (3%)
			204 ->207	HOMO->L+2 (85%)

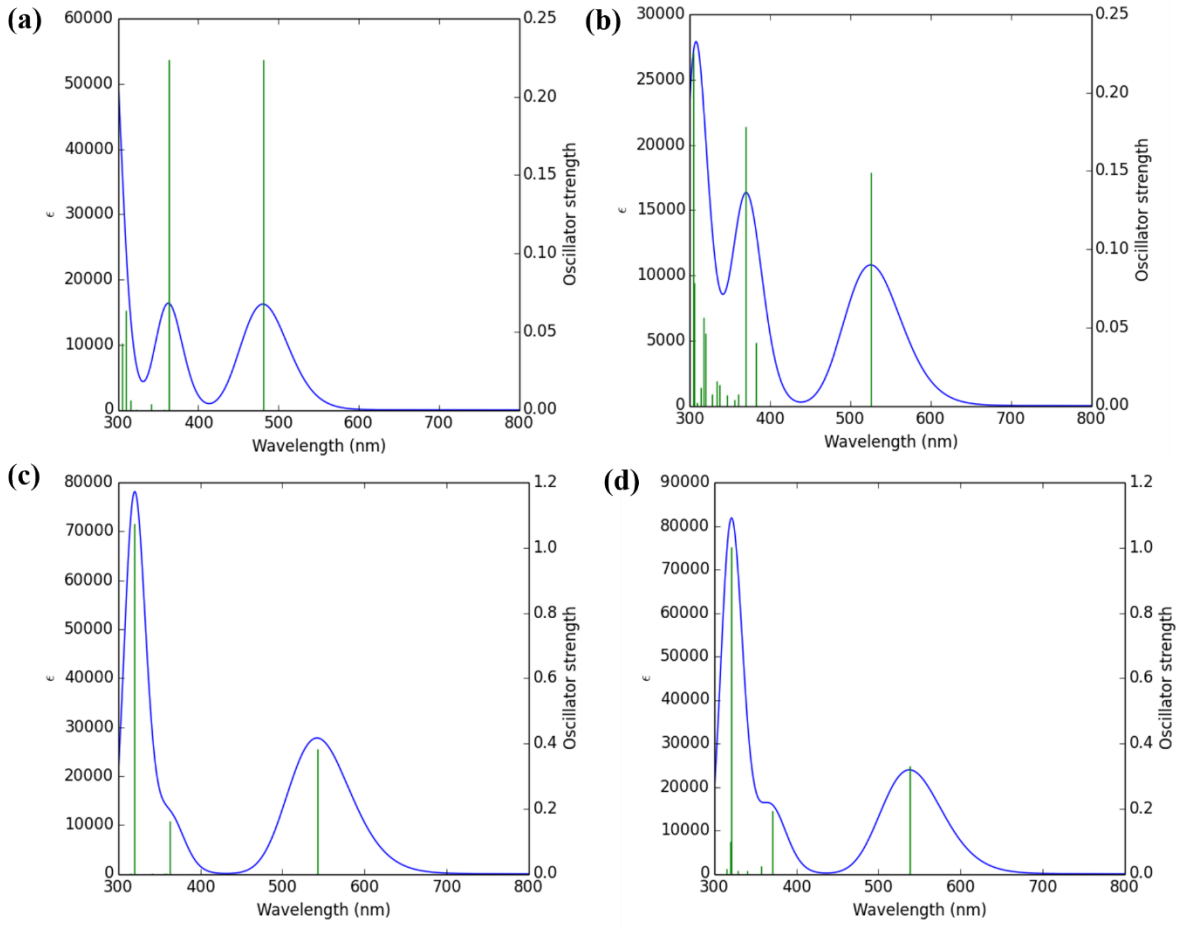


Fig. S21 The computed absorption spectra of(a) **NDI-A**; (b)**NDI-A+TBAF**; (c)**A-NDI-A**and (d) **A-NDI-A+2TBAF**

Experimental							DFT calculation				
Compound	E_{onset}^{ox} (V) ±0.1	E_{onset}^{red} (V) ±0.1	HOMO (eV) ±0.1	LUMO (eV) ±0.1	$E_{g(cv)}$ (eV) ±0.2	E_g Optical (eV) ±0.2	$-\Delta G^o_{ET(CR)}$ (eV)	$-\Delta G^o_{ET(CS)}$ (eV)	HOMO (eV)	LUMO (eV)	E_g (eV)
NDI-A	1.60	-0.69	-6.30	-4.01	2.29	2.33	2.45	0.54	-6.051	-3.139	2.9
A-NDI-A	1.29	-0.76	-5.99	-3.94	2.05	2.11	2.48	0.48	-5.546	-2.973	2.5
NDI-A +TBAF	0.90	-0.40	-5.30	-3.99	1.31	2.33	2.42	0.21	-5.256	-2.483	2.77
A-NDI-A + TBAF	0.81	-0.72	-5.21	-3.67	1.54	2.10	1.95	0.17	-4.533	-1.837	2.70

	ESA, nm (eV)	Life time (τ)	GSB, nm (eV)	Life time (τ)

Table S4. Cyclic voltammetry experimental and DFT calculations for energy gap determination.

Table S5. Summary of the various parameters derived from the $1x10^{-5}$ M solutions of **NDI-A** and **A-NDI-A** in DCM and their mixture with 50 equivalents TBAF transient absorption (TA) spectra and global fitting for lifetime estimation. Transitions are shown as superscript numeral in correlation with Figure 7.

NDI-A	528 (2.34)[1] 760 (1.63)[3]	τ_1 = 85 ps τ_1 = 26 fs τ_2 = 68 ps	616 (2.01)[2]	τ_1 = 110 ps
NDI-A+TBAF	545 (2.24)[1]	τ_1 = 31 ps τ_2 = 118 fs	605 (2.04)[2] 761 (1.62)[4]	τ_1 = 271 fs τ_1 = 350 fs
A-NDI-A	615 (2.01)[1] 733 (1.69)[3]	τ_1 = 477 fs τ_1 = 20 ps τ_2 = 31 ps	550 (2.25)[2]	τ_1 = 85 fs
A-NDI-A+TBAF			555 (2.23)[2] 735 (2.23)[4]	τ_1 = 196 fs τ_1 = 130 fs
SVB-M1	526 762	τ_1 = 300 fs τ_2 = 11 ps τ_1 = 10 ps	597	τ_1 = 186 fs τ_2 = 345 fs

ESA=Excited state emission; GSB=Ground state bleaching

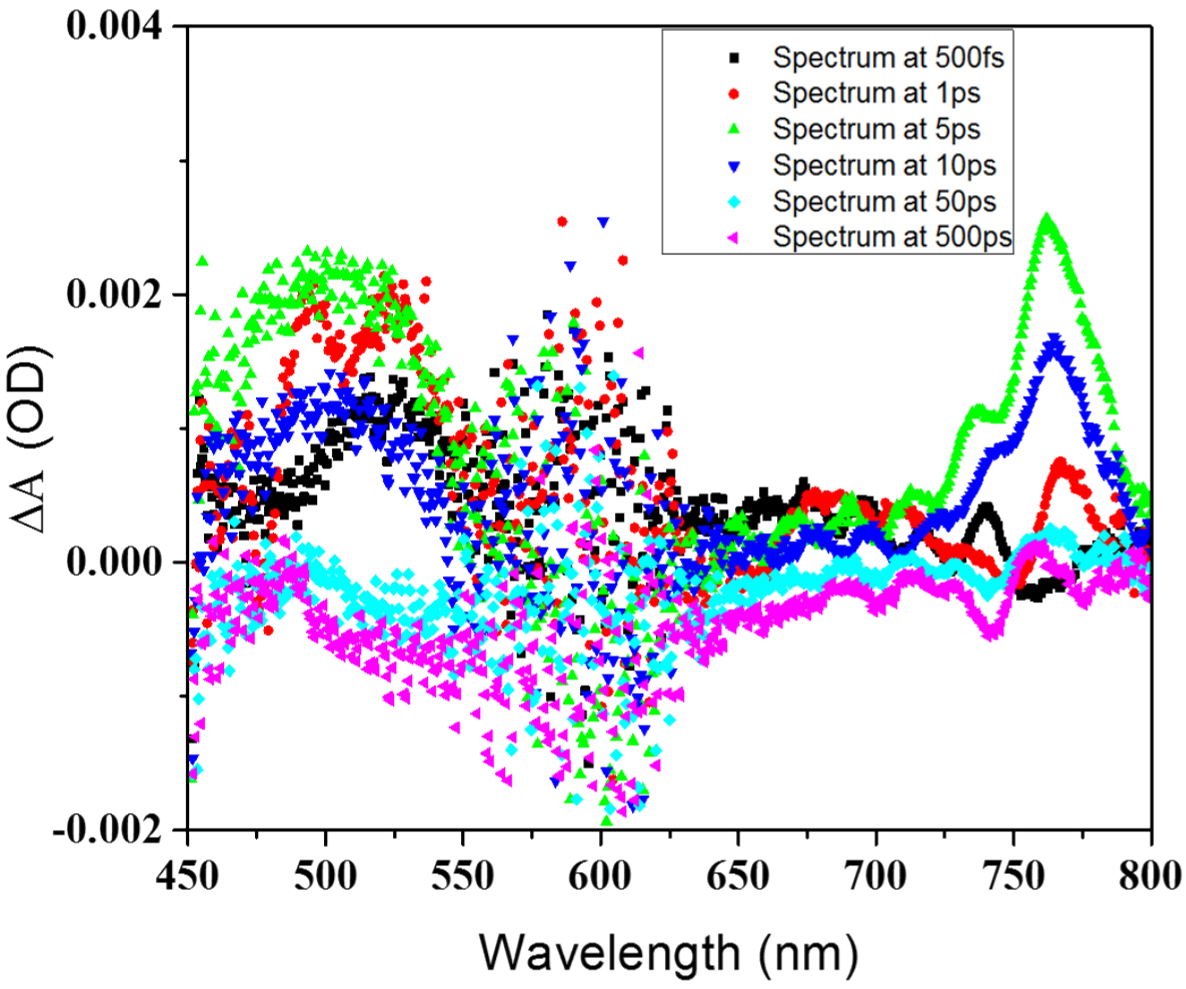


Fig S22 TAS study of **SVB-M1** in visible region

Notes and References

1 A. Robitaille, S. A. Jenekhe and M. Leclerc, *Chem. Mater.,*2018, **30**, 5353−5361.

2 (a) H. Vollmann, H. Becker, M. Corell and H. Streeck, *Justus Liebigs Ann. Chem*., 1937, **531**, 1-159; (b) F. Würthner, S. Ahmed, C. Thalacker and T. Debaerdemaeker, *Chem.–Eur. J.,* 2002, **8**, 4742-4750; (c) S. V. Bhosale, M. B. Kalyankar, S. V. Bhosale, S. J. Langford, E. F. Reid and C. Hogan, *New J. Chem*., 2009, **33**, 2409-2413.

3 D. Egloff, I. A. Oleinich, and E.Freisinger,*ACS Chem. Biol*., 2015, **10**, 547−55