Electronic Supplementary Material (ESI) for Dalton Transactions.

Borylated Perylenediimide: Self-assembly, Photophysics and Sensing Application

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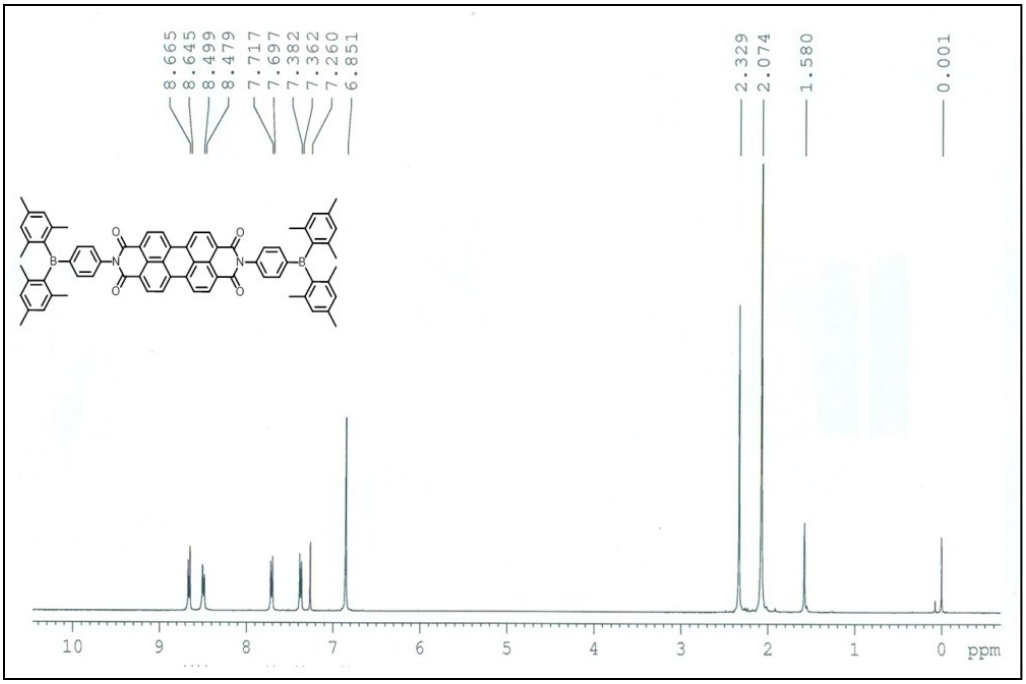

Figure S1. ^{1}H NMR spectra of PDI-TAB

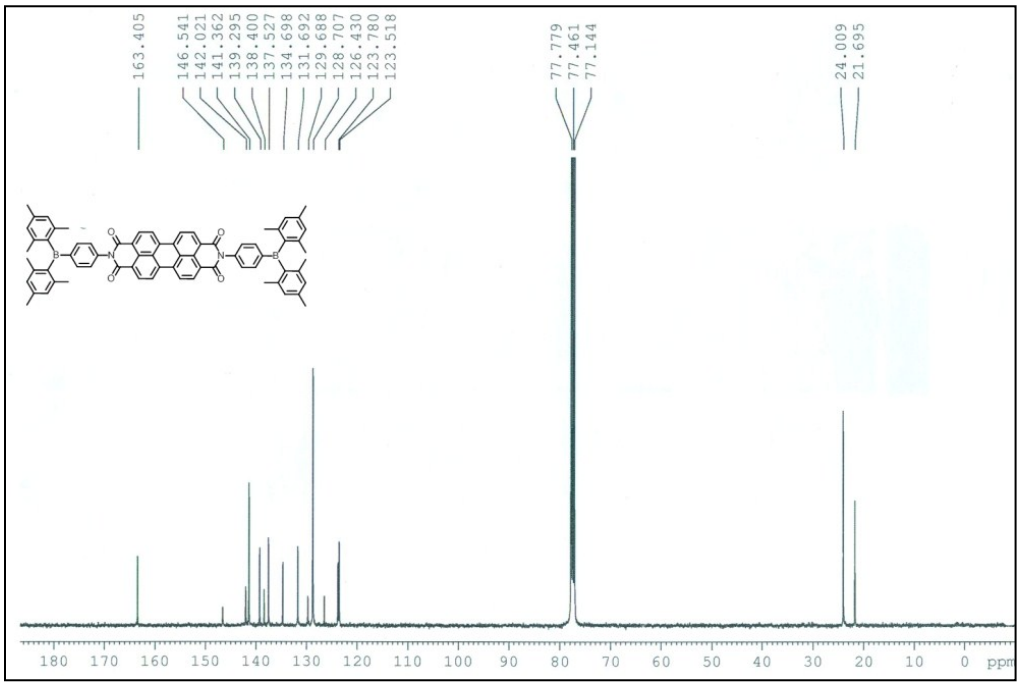

Figure S2. ^{13}C NMR spectra of PDI-TAB

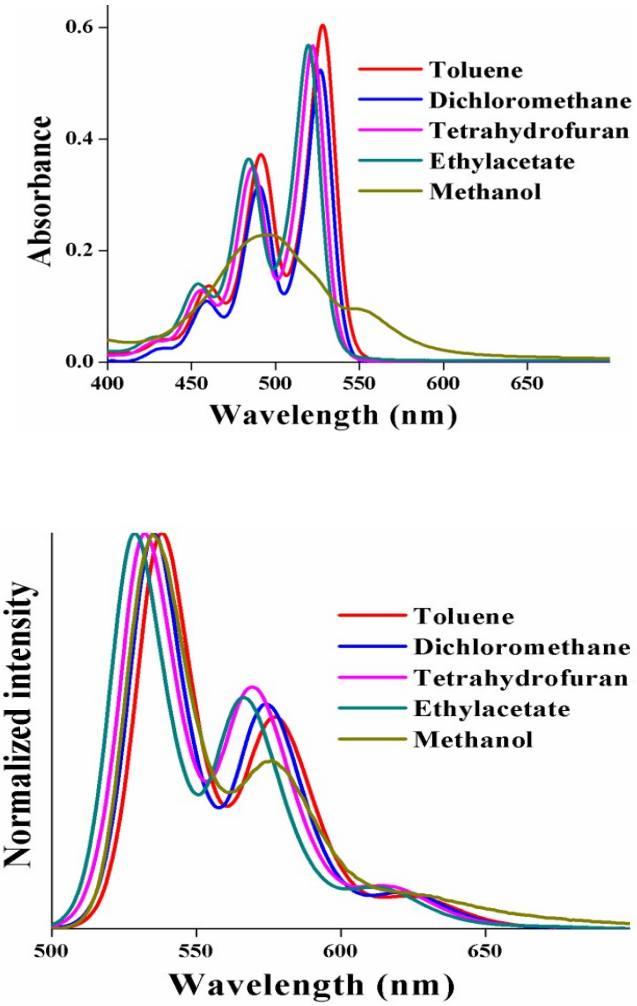

Figure S3. Absorption (top) and emission (bottom) spectra of PDI-TAB in solvents of different polarity (Concentration = 10 μM, λ_{ex} = 490 nm)

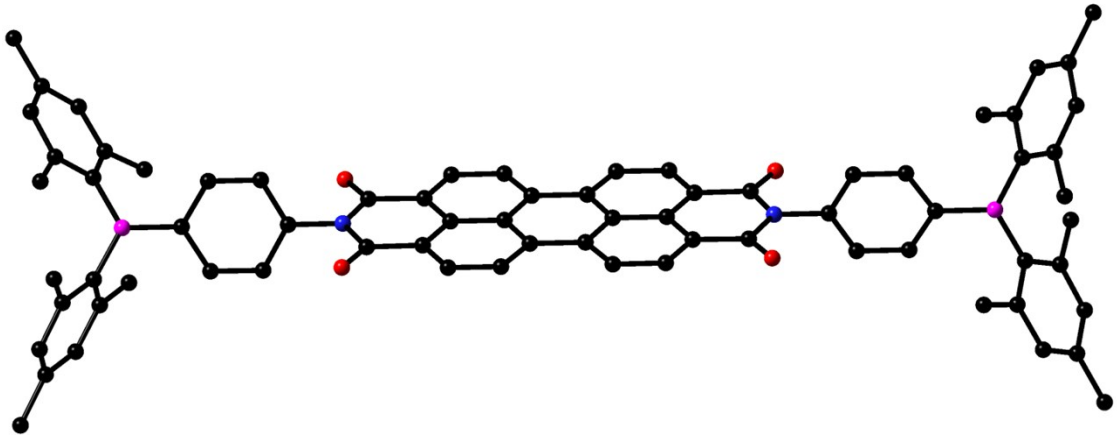

Figure S4. Ground state DFT optimized structure **PDI-TAB** (Atom color codes: C- black, N - Blue, B-Magenta, O – Red and hydrogen atoms are omitted for clarity)

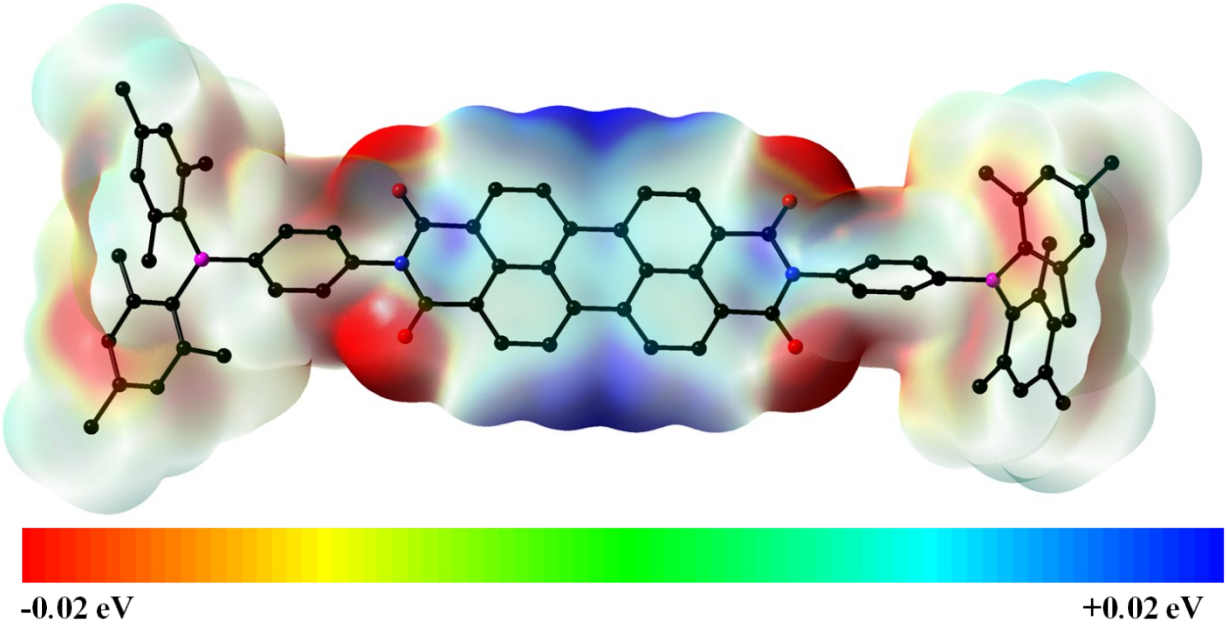

Figure S5. ESP surface diagram of PDI-TAB (Atom color codes: C- black, N - Blue, B-Magenta, O – Red and hydrogen atoms are omitted for clarity)

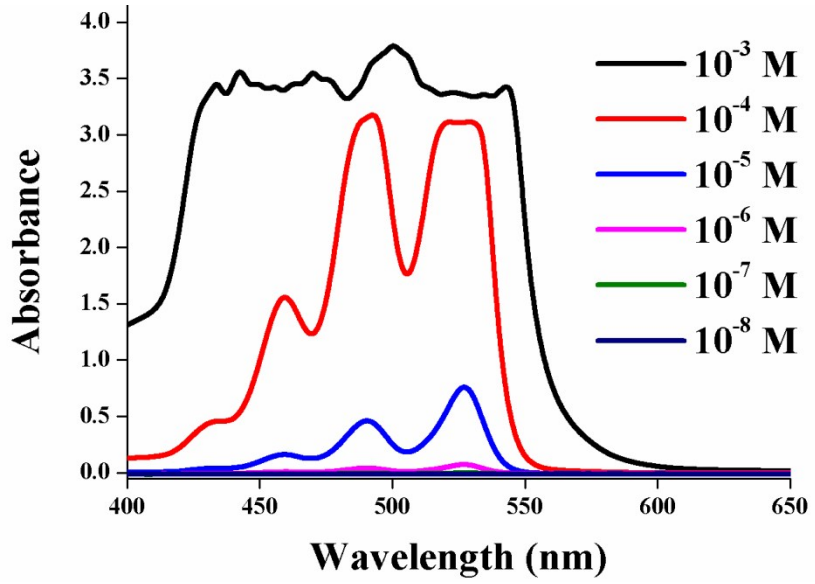

Figure S6. UV-Vis absorption spectra of **PDI-TAB** at different concentrations

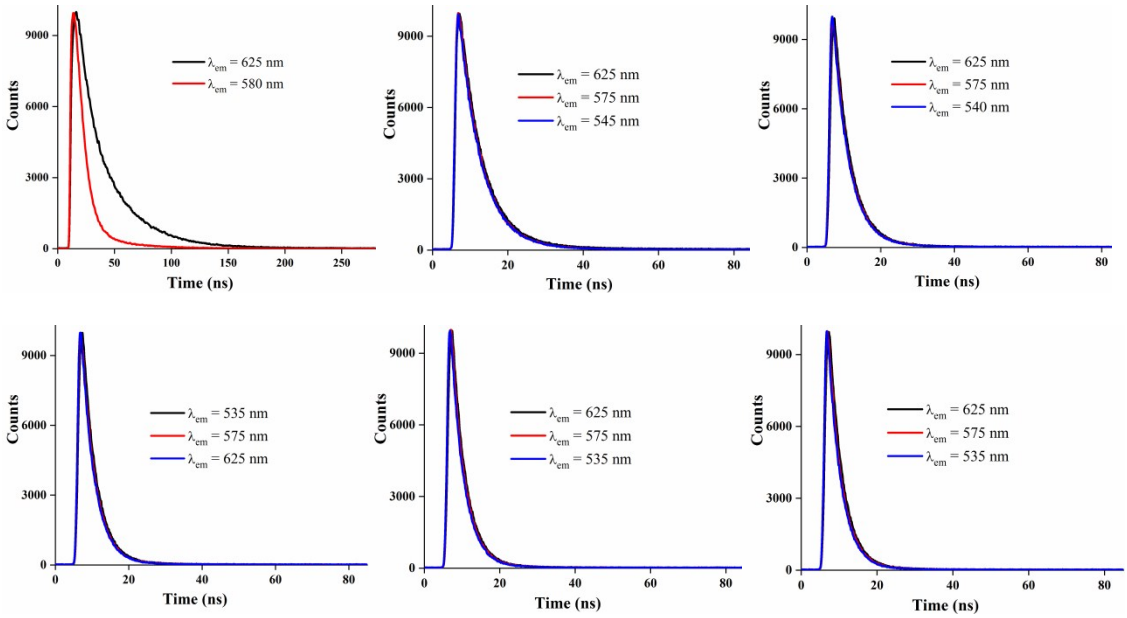

Figure S7. Time resolved emission decay profiles for **PDI-TAB** at different concentrations, 10^{-3} M (top left), 10^{-4} M (top middle), 10^{-5} M (top right), 10^{-6} M (bottom left), 10^{-7} M (bottom middle) and 10^{-8} M (bottom right); (λ_{ex} = 450 nano-LED was used for TRF measurements and the corresponding emission wavelengths are shown in the graphs)

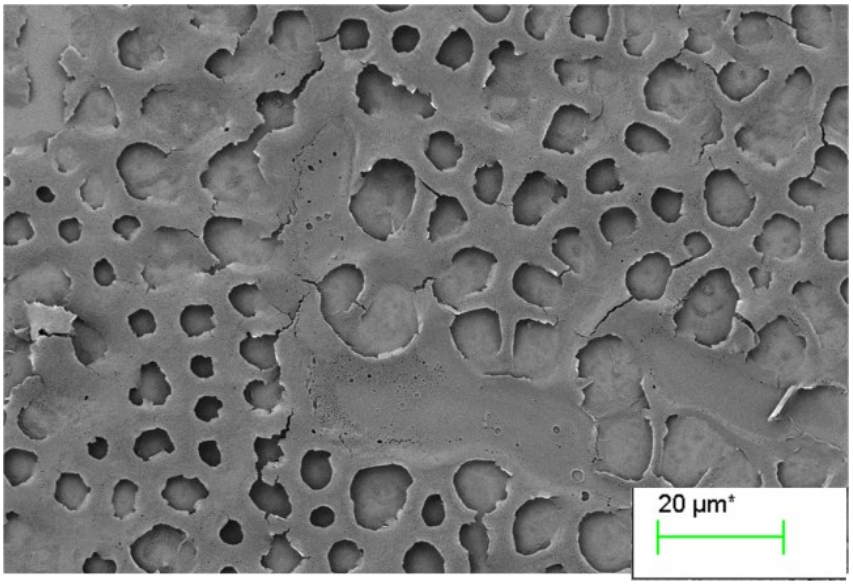

Figure S8. SEM image of thin films of **PDI-TAB. D**rop casted using 10^{-3} M solution in dichloromethane

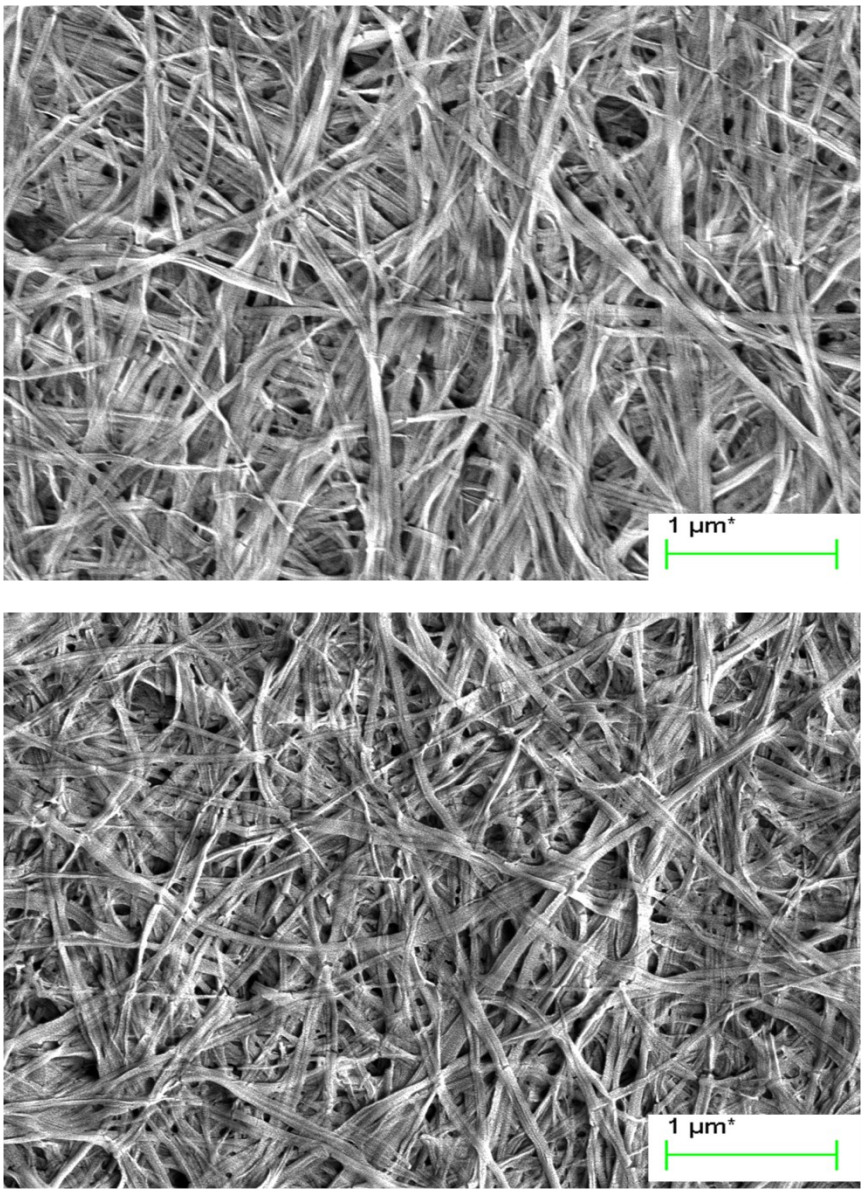

Figure S9. SEM images of self-assemblies of **PDI-TAB** formed by injecting 10^{-4} M (top) 10^{-5} M (bottom) dichloromethane solution to MeOH solvent.

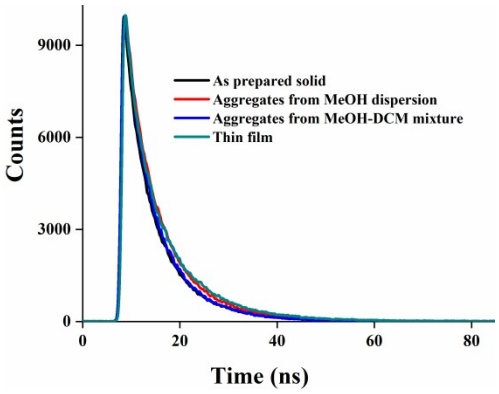

Figure S10. Time resolved emission decay profiles of **PDI-TAB** in the solid state (λ_{ex} = 450 nano-LED was used for TRF measurements)

Table S1. Photophysical data of **PDI-TAB** in solid state (λ_{ex} = 460 nm for emission spectral measurements and 450 nano-LED was used for TRF measurements)

	λ_{em} (nm)	τ/ ns (A, %)	χ^2
As prepared solid of PDI-TAB	688	τ_1 = 5.02 (57%) τ_2 = 10.29 (43%)	1.2
Self–assembly formed by dispersing PDI-TAB in MeOH solvent	694	τ_1 = 4.80 (60%) τ_2 = 10.01 (40%)	1.3
Self–assembly formed by injecting 10^{-3} M DCM solution of PDI-TAB to MeOH solvent	694	τ_1 = 4.61 (45%) τ_2 = 8.88 (55%)	1.2
Thin film (by drop casting 10^{-3} M DCM solution of PDI-TAB)	675	τ_1 = 4.60 (32%) τ_2 = 10.55 (68%)	1.3

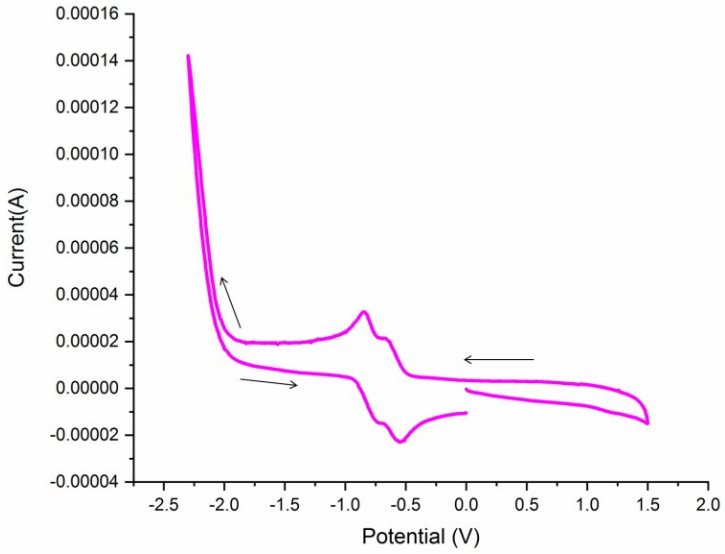

Figure S11. Cyclic voltammogram traces of **PDI-TAB** in DCM with 0.1 M $TBAFPF_6$ as supporting electrolyte. At scan rate of 100 mV/s. Glassy carbon, platinum and calomel were used as working electrode, counter electrode and reference electrode, respectively.

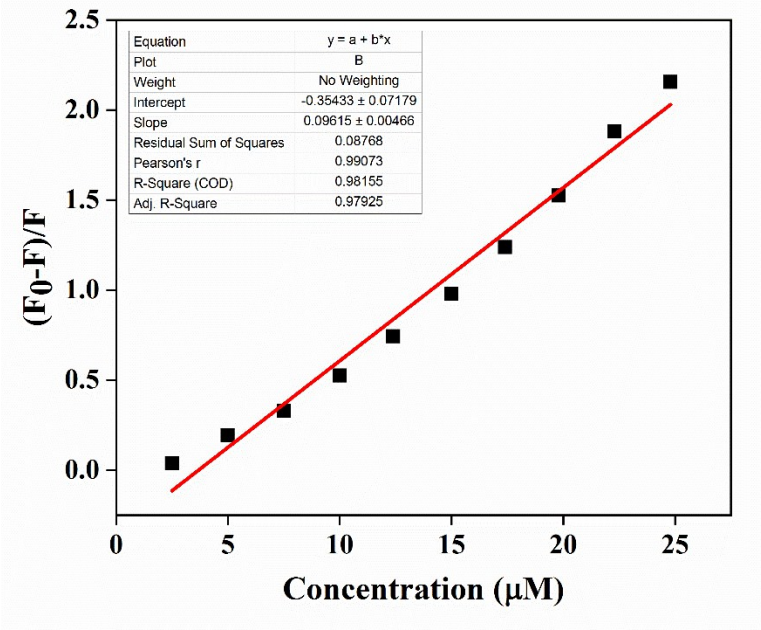

Figure S12. Plot of concentration of TBAF versus relative fluorescence intensity changes of **PDI-TAB** {(F_0-F)/F}, up on addition of increasing concentrations of TBAF.

$$F_0/F = 1 + K_{SV}[Q] ,$$

Where, F_0 and F are the steady-state fluorescence intensities in the absence and presence of the TBAF, respectively. [Q] is the concentration of quencher and K_{SV} is the Stern-Volhmer constant.

Table S2. Photophysical data of PDI-TAB and PDI-TAB++2F$^-$ (PDI-TAB after addition of 5 equivalents of fluoride) in dichloromethane solution (λ_{ex} = 490 nm for emission spectral measurements and 450 nano-LED was used for TRF measurements)

	ϕ_F (%)	τ (ns)	$k_r * 10^6$ (s^{-1})	$k_{nr} * 10^6$ (s^{-1})
PDI-TAB	89.0	4.72	188.70	23.32
PDI-TAB++2F$^-$	11.3	4.37	25.86	202.97

Following equations have been used for the calculation of k_r and k_{nr}; { $\phi_F = k_r/(k_r+k_{nr})$} and {$\tau = 1/(k_r+k_{nr})$}, where ϕ_F is the fluorescence quantum yield, τ is the average life time and k_r and k_{nr} are the radiative and non-radiative decay rate constants, respectively.[1]

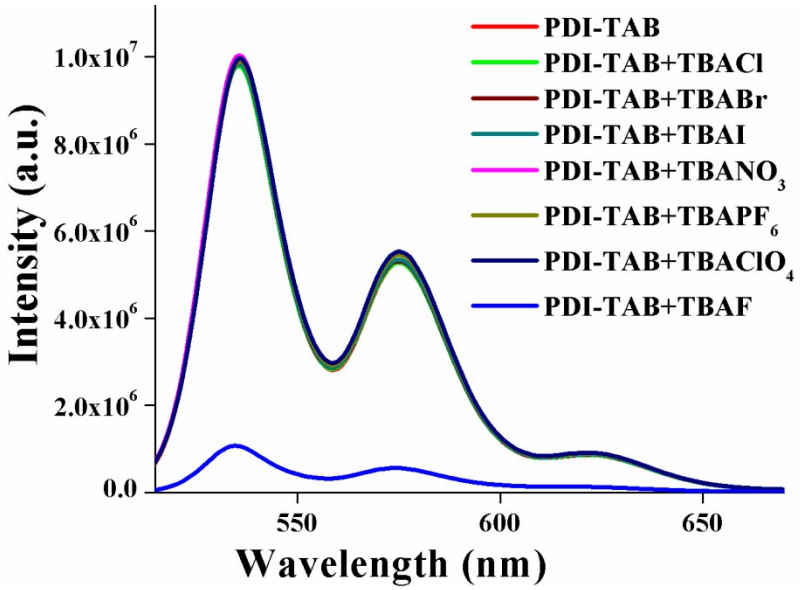

Figure S13. Luminescence changes associated with PDI-TAB (Concentration of PDI-TAB = 10 μM, λ_{ex} = 460 nm) in the presence of various interfering anions (used as their tetrabutylammonium (TBA) salts, 2 μL = 0.5 equivalents).

Table S3. Optimized geometry coordinates of **PDI-TAB** at ground state

C	1.48357557	-1.65085071	-1.71743840
C	2.88173271	-1.63997185	-1.71069995
H	3.43873548	-2.28261830	-2.38352682
C	3.57511183	-0.81020133	-0.84520197
C	3.56968201	0.88789168	0.92255557
C	2.87009365	1.71572752	1.78498661
H	3.42224228	2.36018678	2.46011063
C	1.47168112	1.72259339	1.78605543
H	0.97208291	2.38673436	2.48029715
C	0.73770666	-0.83589308	-0.86326234
C	1.43239595	0.03583269	0.03435385
C	2.86189494	0.03786964	0.03732099
C	0.73133672	0.90553141	0.92901184
C	5.05406554	-0.82322788	-0.86072321
O	5.70592031	-1.53808778	-1.61107477
N	5.70033913	0.04104313	0.04327960
C	5.04897193	0.90479742	0.94359535
O	5.69662505	1.62218754	1.69524575
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C	-2.88387863	1.74197587	1.73812958
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H	-9.76125629	-1.78327027	1.20092044
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C	13.25165254	1.41272093	-1.40065022
C	12.81495230	3.68458000	0.15590916
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C	13.71611956	3.76365148	-0.90715562
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C	13.20500599	-1.50306408	1.34330453
C	12.66392744	-3.74722729	-0.22050370
C	13.80703401	-2.73276388	1.61567164

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H	0.98857879	-2.31632385	-2.41362088
H	-0.99093051	2.43288119	2.42770931

Table S4. Optimized geometry coordinates of PDI-TAB+2F$^-$ at ground state

C	1.40334567	2.34272645	0.93609033
C	2.80012786	2.34226760	1.00988342
H	3.32982319	3.20395190	1.40086546
C	3.52778051	1.24232494	0.58738321
C	3.59463918	-1.01569872	-0.35448638
C	2.93272867	-2.12161790	-0.86110689
H	3.51312256	-2.97840895	-1.18520848
C	1.53716369	-2.13516265	-0.95409532
H	1.06724194	-3.02382287	-1.35698523
C	0.69227843	1.24935899	0.43710067
C	1.42299654	0.10354014	-0.01181077
C	2.85001193	0.11029133	0.07323480
C	0.76146468	-1.04947949	-0.54217280
C	5.00662136	1.27043907	0.68021214
O	5.61659831	2.23951425	1.11502986
N	5.69244412	0.12292068	0.24458088
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H	-1.08349643	3.19745656	1.20898548
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C	-5.09135499	1.19816246	0.13565256
O	-5.75920999	2.15063584	0.51942686
C	7.14021963	0.12367165	0.34142646
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H	7.14609837	-0.51040628	2.39680288
C	9.97545211	0.10081930	0.52989362
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H	-12.31844016	4.41369547	1.39835564
C	12.40740734	-1.36259903	0.59284678
C	11.86922323	-2.58827507	0.11252626
C	13.74640713	-1.42819024	1.08469857
C	12.62590066	-3.77331672	0.12811280
C	14.47444374	-2.62589427	1.07756463
C	13.93455589	-3.82218242	0.60305508
H	12.17057575	-4.68906975	-0.24934311
H	15.49602587	-2.62198260	1.45896576
C	12.24584048	1.33738967	-0.21210045
C	12.20944097	2.68595538	0.25520230
C	12.77390307	1.15192647	-1.51889338
C	12.72036705	3.73829349	-0.51738669
C	13.27240603	2.23151310	-2.26846891
C	13.26853668	3.53820217	-1.78600360
H	12.67822771	4.75130110	-0.11583079
H	13.67212276	2.03814265	-3.26428909
C	-10.51963630	2.56719999	1.02644442
H	-9.80465216	2.55291171	0.19880836
H	-10.36912061	3.49994694	1.58241761
H	-10.23590035	1.74016490	1.68530506
C	-14.59822729	0.30654749	-1.21253398
H	-14.11887451	0.08740797	-2.16833639
H	-14.58000232	-0.62654186	-0.63910532
H	-15.64587447	0.57542994	-1.39115076
C	-14.96689788	4.84205073	0.87627201
H	-15.38704986	5.31602511	-0.02081809
H	-15.81720222	4.56619841	1.51419324
H	-14.38518662	5.60151364	1.41009727
C	-12.75346497	-0.48248497	2.29012229
H	-11.86457636	0.15398349	2.29391353
H	-13.60233963	0.17270673	2.06618217
H	-12.89195172	-0.87060881	3.30644502
C	-11.49242543	-2.67975291	-2.21376560
H	-11.35314904	-3.71485562	-2.54812349
H	-12.13799553	-2.16925082	-2.93308477
H	-10.52375176	-2.17291377	-2.26177239
C	-13.44866957	-5.38028638	1.52111205
H	-14.49254028	-5.58359538	1.24267113

H	-12.84578682	-6.20219200	1.11701961
H	-13.39322899	-5.42709931	2.61473704
C	10.46772221	-2.72815350	-0.45881818
H	9.69144120	-2.56238429	0.29454202
H	10.26789218	-2.01197079	-1.26158991
H	10.32512445	-3.73479505	-0.86882243
C	14.47039744	-0.21855918	1.65211288
H	15.54012824	-0.42977243	1.76851114
H	14.36052611	0.65834593	1.00824940
H	14.06528103	0.06490540	2.62750076
C	14.74232167	-5.10035718	0.57737092
H	14.09450389	-5.98436190	0.57645144
H	15.37574536	-5.16384481	-0.31888868
H	15.41005901	-5.17254912	1.44414040
C	12.83513919	-0.20449093	-2.20115384
H	13.61178512	-0.84773526	-1.77461159
H	11.89486388	-0.75466567	-2.11186128
H	13.05108293	-0.08322857	-3.26945967
C	11.60629532	3.08030090	1.59360998
H	10.60927659	2.65089066	1.72968454
H	12.20644175	2.72606847	2.43586657
H	11.52159955	4.17148189	1.66344436
C	13.79111477	4.69315055	-2.61066280
H	14.43104406	4.34340042	-3.42842059
H	12.97418332	5.27336947	-3.06228302
H	14.37635867	5.39252503	-2.00107423
H	0.88045702	3.22629367	1.28078440
H	-0.89246431	-3.01562958	-1.51413554
F	-11.89270378	0.00426275	-2.11526100
F	11.80056402	0.44383975	2.14530182

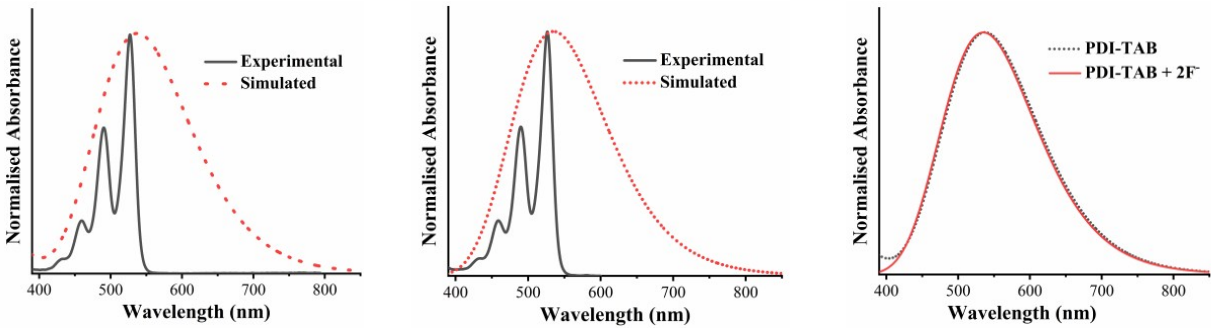

Figure S14. Experimental and simulated absorption spectra of **PDI-TAB**, before (left) and after addition of fluoride anion (middle). Comparison of simulated absorption spectra PDI-TAB before and after complexation of fluoride anion (right).

Table S5. Summary of dominant electronic transitions of **PDI-TAB** and **PDI-TAB+2F$^-$** obtained from TD-DFT calculations

Compound	Excited State	E/eV	E/nm	f	Dominant transitions (percentage contribution)
PDI-TAB	1	2.3075	537.30	1.1289	HOMO ->LUMO (100%)
	2	2.5059	494.78	0.0000	HOMO-1 ->LUMO (100%)
	3	2.5204	491.93	0.0000	HOMO-2 ->LUMO (100%)
	19	3.5369	350.55	0.1121	HOMO-1 ->LUMO+2 (95%)
	20	3.5571	348.56	0.0662	HOMO-15 ->LUMO (5%) HOMO-13 ->LUMO (79%) HOMO-13 ->LUMO (5%) HOMO ->LUMO+6 (5%)
PDI-TAB+2F$^-$	1	1.6949	731.50	0.0000	HOMO ->LUMO (99%)
	2	1.7068	726.43	0.0000	HOMO-1 ->LUMO (99%)
	3	1.8351	675.61	0.0001	HOMO-2 ->LUMO (100%)
	4	1.8363	675.20	0.0001	HOMO-3 ->LUMO (100%)
	11	2.3165	535.21	1.0746	HOMO-10 ->LUMO (100%)
	13	2.6327	470.95	0.0066	HOMO-12 ->LUMO (98%)

Reference

1. B. Kupcewicz and M. Małecka, *Cryst. Growth Des.*, 2015, **15**, 3893-3904.