Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Secondary inner filter effect allows extremely efficient pure white light emission by spatially separated organic fluorophores

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Materials and methods: -

o-Phenylenediamine, 1-Pyrenecarboxaldehyde were purchased from Sigma-Aldrich Chemical Company. Perylene-3,4,9,10-tetracarboxylic dianhydride, 2,6-Diisopropylaniline were purchased from Alfa-Aesar. Zinc acetate dihydate, Imidazole, Nitrobenzene were purchased from Spectrochem. These chemicals were used as received. Spectroscopy grade solvents purchased from Spectrochem were used for spectroscopic analyses. Photophysical studies were undertaken in Q-cuvette (10 mm path length). UV-visible spectra were recorded on Agilent Technologies Cary 3100 UV-Vis-NIR Spectrophotometer. UV-Visible titration analysis of PyBIM (0.1 mM) against TFA, TBAF or PMI were carried out in THF at 298 K. Fluorescence spectra were recorded on Jobin Yvon Horiba's Fluorolog-3-21. All the Nuclear Magnetic Resonance (NMR) spectra were recorded at 298 K in DMSO-d_6 solvent on Bruker Ultra Shield (500 MHz) spectrometer using tetramethylsilane (TMS) as internal standard. Mass spectra were recorded on Micro TOF–Q-II instrument from Bruker Daltonics by using electrospray ionization (ESI) mode. Life time measurements were done on time-correlated single photon counting (TCSPC) spectrometer (Delta Flex-01-DD/ Horiba).

Fluorescence Studies: -

Fluorescence analyses were carried out in THF, and stock solutions of compound (PyBIM = 0.1 mM) were prepared in THF at 298 K, further diluted solutions were used to record the spectra. All the fluorescence spectra were recorded on λ_{ex} = 365 nm. In solution state the relative fluorescence quantum yield was calculated at low concentration (1 μM in THF) for PyBIM, $PyBIM^+$, $PyBIM^-$ using Quninine Sulphate hemisulphate monohydrate (Φ_f = 0.57 in 0.1 N $HClO_4$) as standard. Similarly, Rhodamine 6G (Φ_f = 0.95 in ethanol) was used for calculating quantum yield for PMI. All the white light quantum yield was calculated using Quninine Sulphate hemisulphate monohydrate as standard at their respective concentration at λ_{ex} = 355 nm. The following equation was used to calculate quantum yield. [1]

$$\Phi_{F,x} = \Phi_{F,s} (F_x/F_s) (f_s/f_x) (\eta_x/\eta_s)^2$$

Where-

$\Phi_{F,x}$ = quantum yield of sample, $\Phi_{F,s}$ = quantum yield of standard, F_x and F_s indicate fluorescence integral of sample and standard, η_x and η_s represent the refractive indices of solvent used to measure the fluorescence spectra of the sample and the standard, respectively, f represents the absorption factor at the excitation wavelength ($f = 1\text{-}10^{-A(\lambda_{ex})}$) where $A(\lambda_{ex})$ is the absorbance at the excitation wavelength.

Time-resolved fluorescence measurements: -

Time-resolved fluorescence was performed on time-correlated single photon counting (TCSPC) spectrometer. Photomultiplier tube of picosecond photon detection module was used as detector. Delta diode laser (373 nm) was used for excitation. All decay curves were analysed using non-

linear least-squares iteration method (IBH DAS6, 6.8 version). The quality of fitting was determined by the fitting factor (χ^2).

DFT Calculations: -

The molecular structure optimization of the compounds was performed using DFT at B3LYP level combined with 6-31G(d) basis sets using Gaussian 09 program. [2]

Synthesis and characterization of Pyrene-Benzimidazole PyBIM: -

Synthesis of PyBIM

2-(pyren-1-yl)-1*H*-benzo[d]imidazole (PyBIM, Pyrene-Benzimidazole conjugate) was synthesized via a reported procedure. [3] The purity of PyBIM was verified by HRMS, ^{1}H-NMR studies.

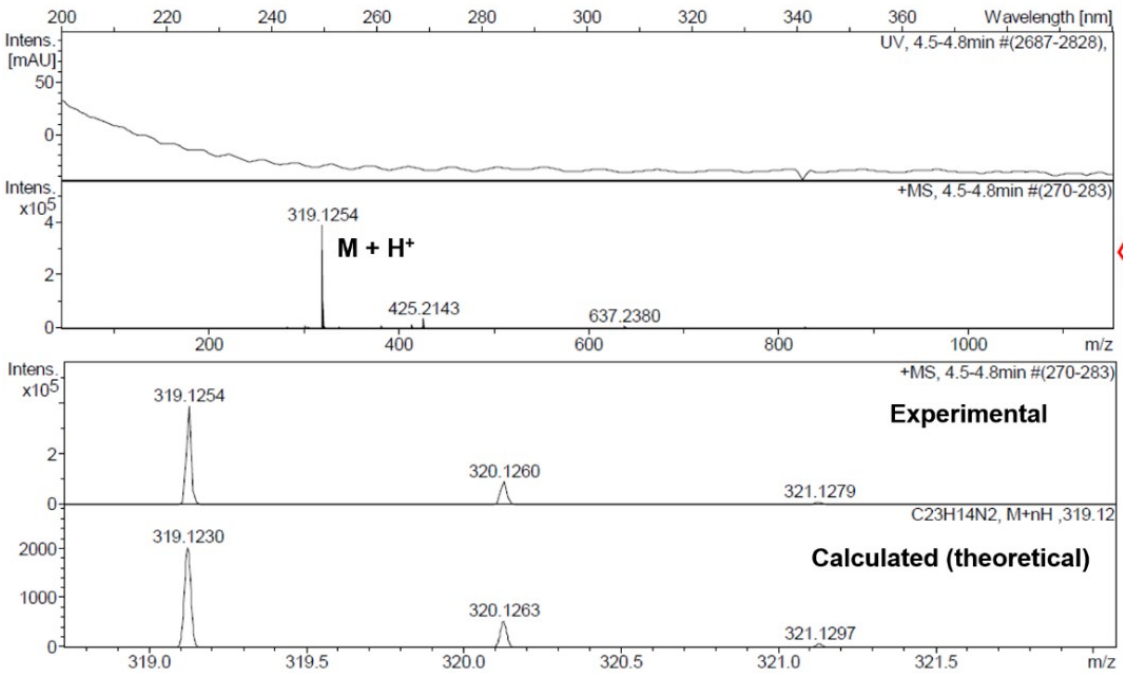


Figure S1. ESI-HRMS spectrum of PyBIM**.**

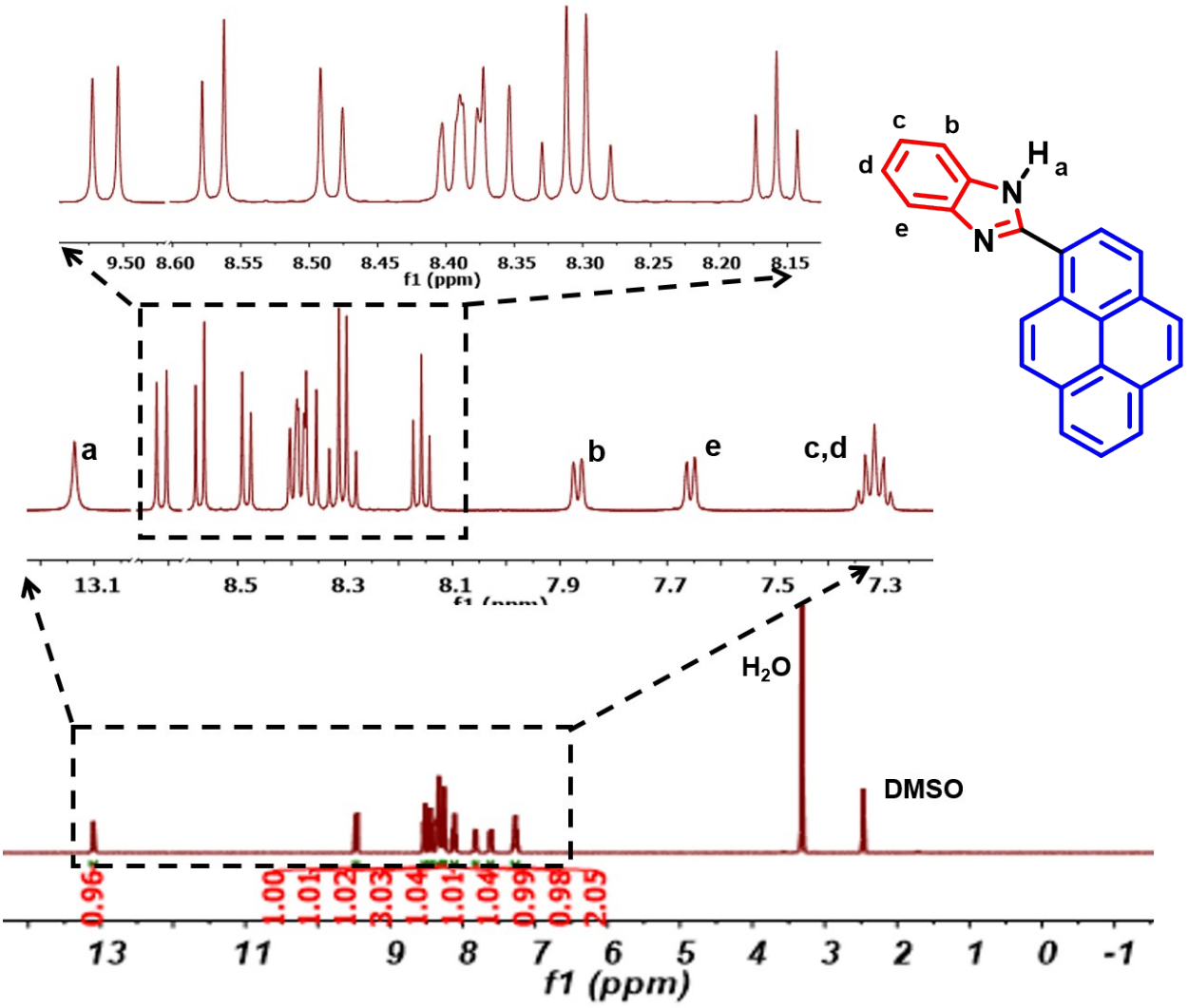


Figure S2. ^{1}H-NMR spectrum of PyBIM in DMSO-d_6 (500 MHz) at 298 K. The region expanded above is highlighted by dashed boxes.

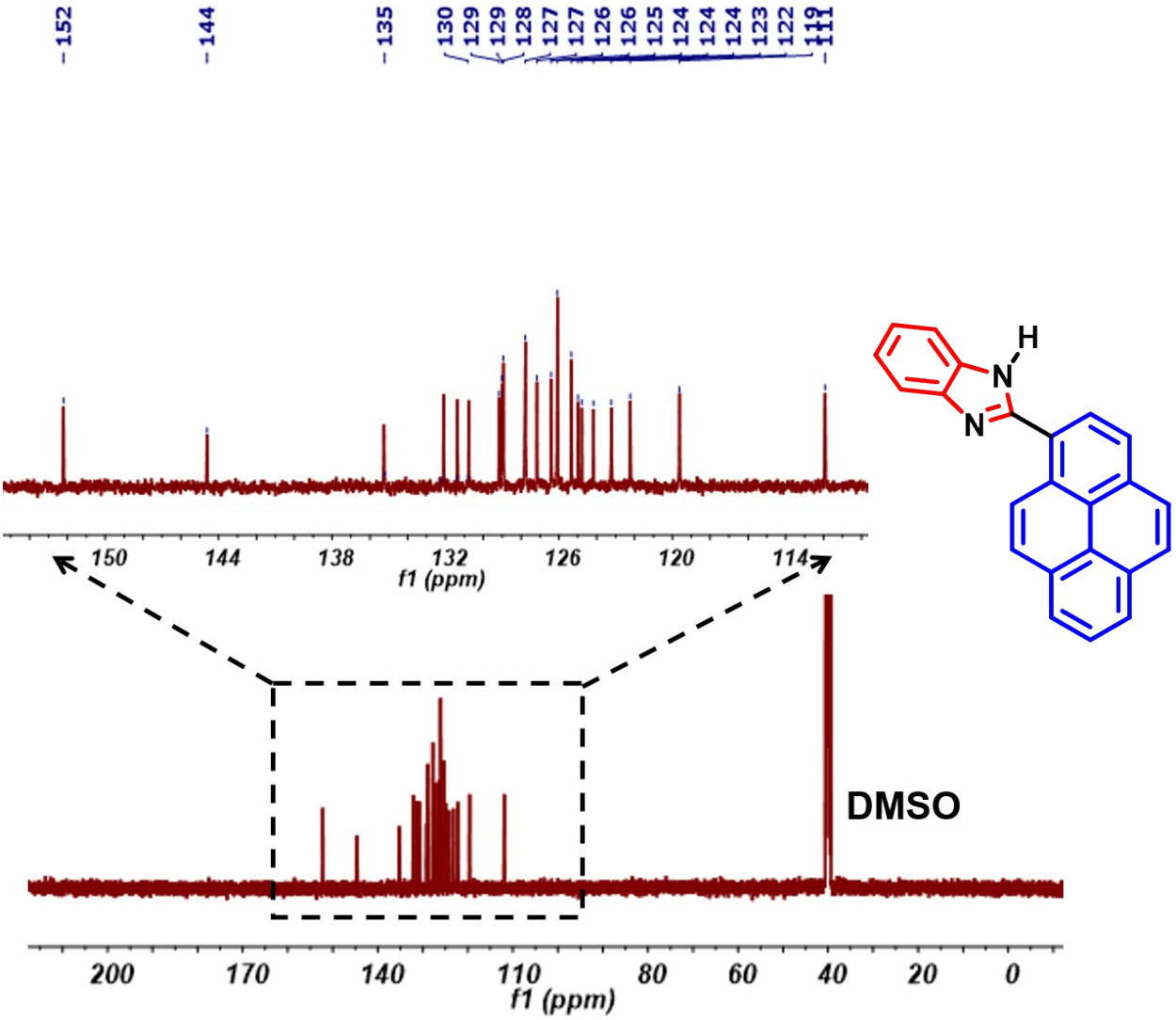


Figure S3. ^{13}C NMR spectrum of PyBIM in DMSO-d_6 (125 MHz) at 298 K. The region expanded above is highlighted by dashed boxes.

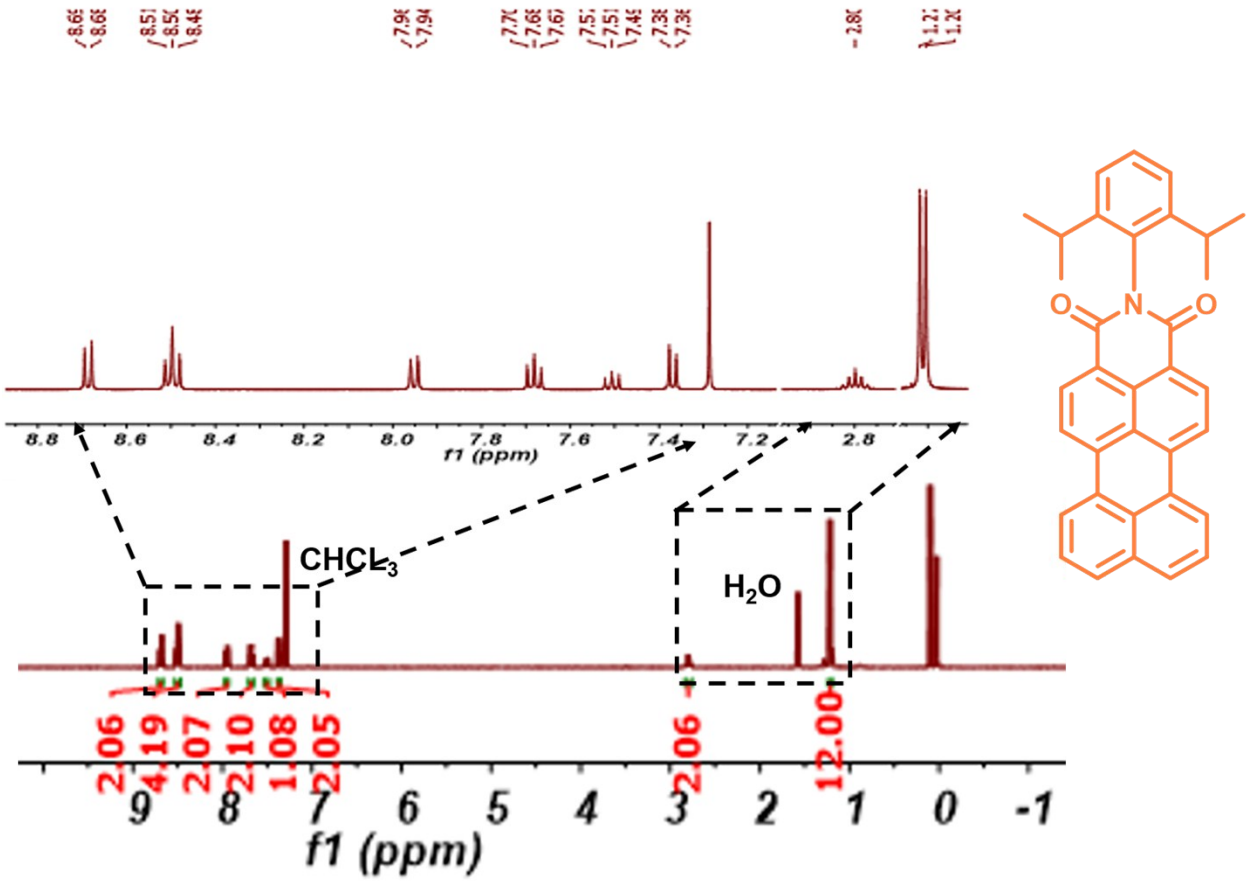


Figure S4. ^{1}H-NMR spectrum of PMI in $CDCl_3$ (500 MHz) at 298 K. The region expanded above is highlighted by dashed boxes.

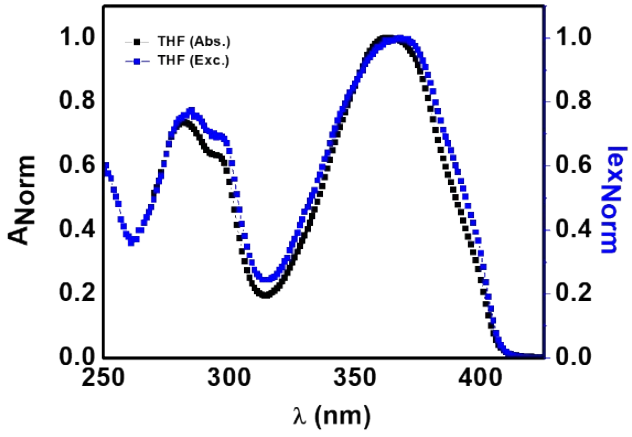


Figure S5. Normalized absorption and excitation spectra of PyBIM (10 μM) in THF monitored at λ_{em} = 405 nm.

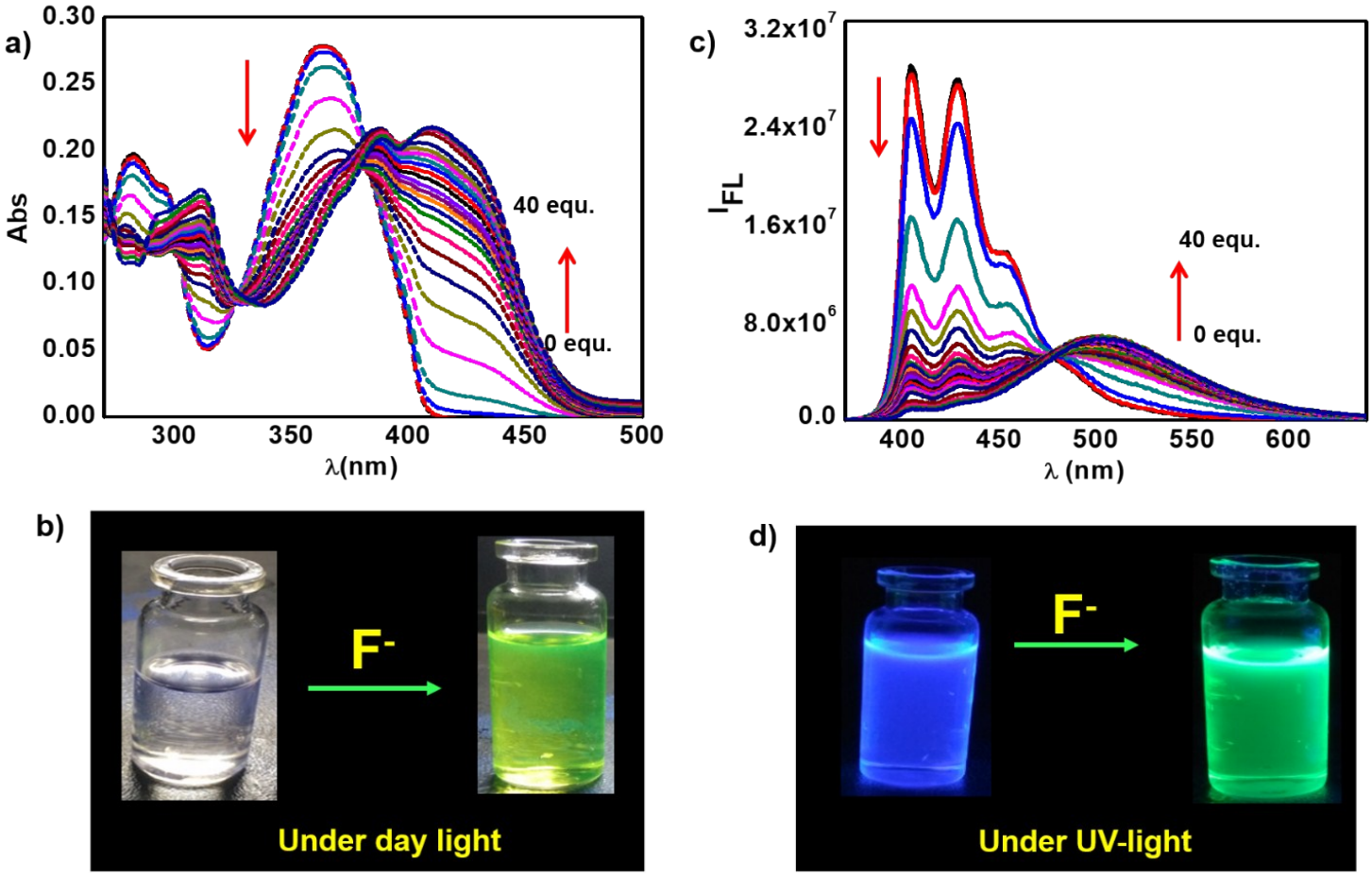


Figure S6. **(a)** UV-Vis titration of PyBIM (10 μM in THF) with TBAF (0-40 eqv.). **(b)** Digital photographs of vials containing PyBIM in THF under daylight illumination before (left) and after (right) addition of TBAF. **(c)** Fluorescence titration of PyBIM with TBAF (0-40 eqv.) at λ_{ex} =365 nm **(d)** Photo of vials containing PyBIM in THF under UV-lamp (365 nm) illumination before and after addition of TBAF.

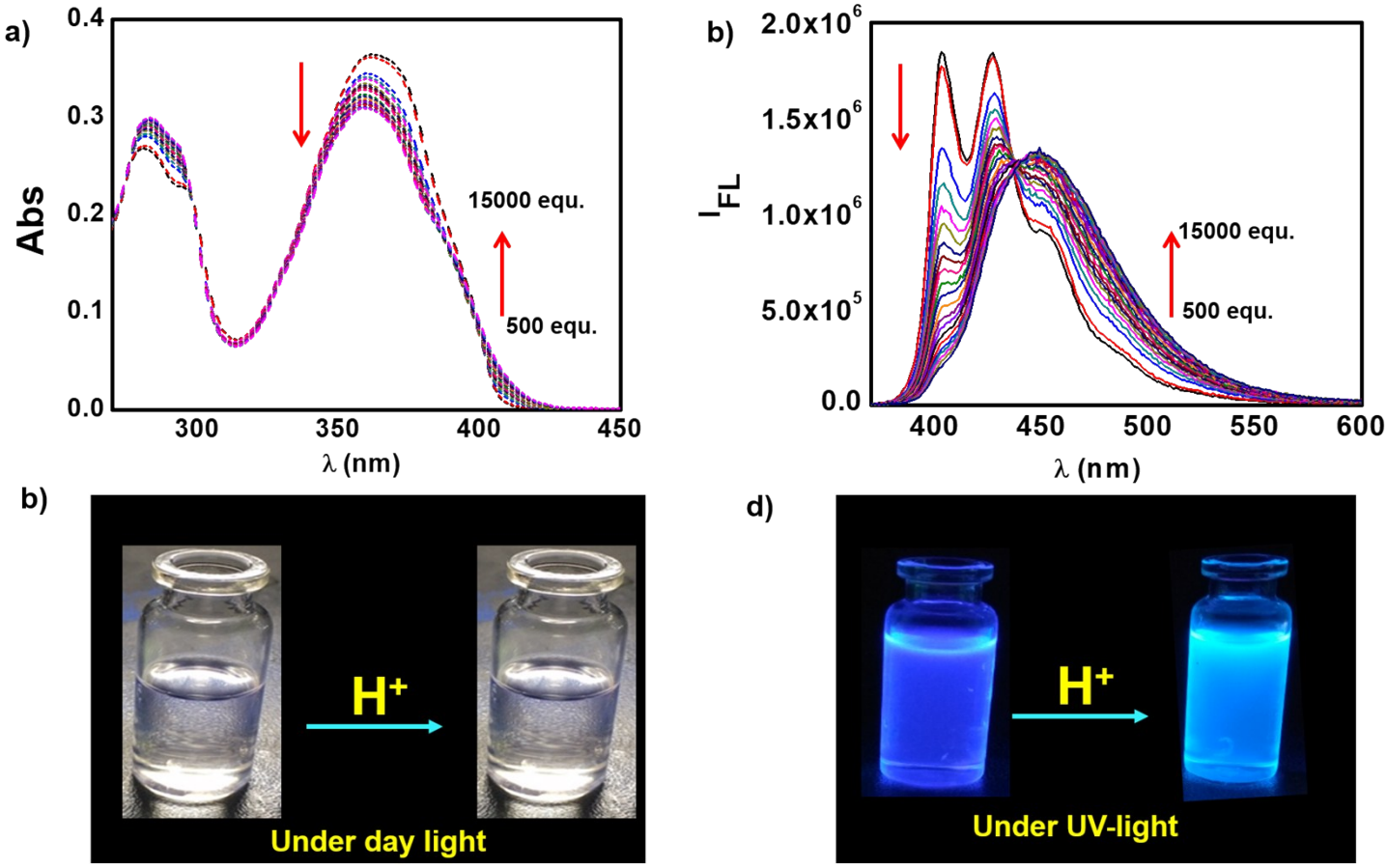


Figure S7. **(a)** UV-Vis titration of PyBIM (10 μM in THF) with TFA (500-15000 eqv.). **(b)** Digital photographs of vials containing PyBIM in THF under daylight illumination before (left) and after (right) addition of TFA. **(c)** Fluorescence titration of PyBIM with TFA (500-15000 equ.) at λ_{ex} =365 nm. **(d)** Photos of vials containing PyBIM in THF under illumination by UV-lamp (365 nm) before and after addition of TFA.

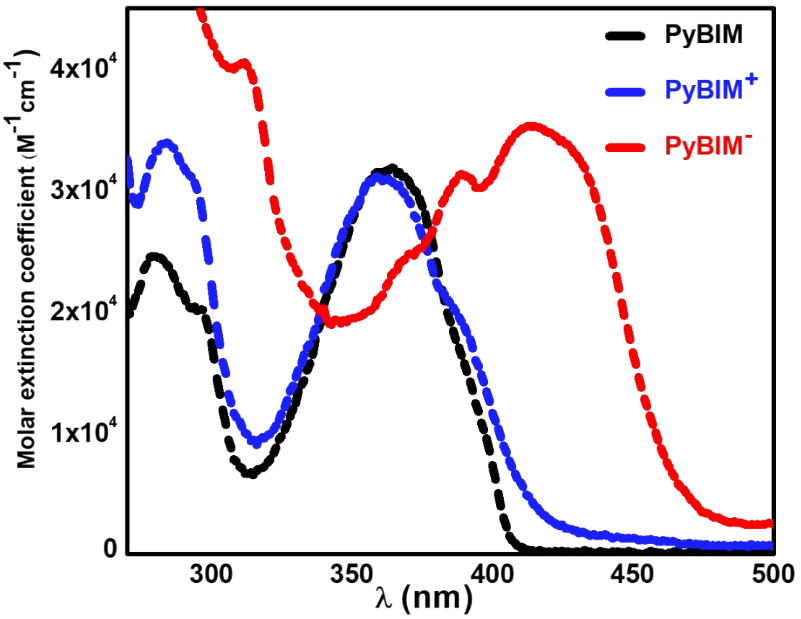


Figure S8. Plots of molar extinction coefficients (ε) against wavelength for PyBIM, $PyBIM^+$, $PyBIM^-$.

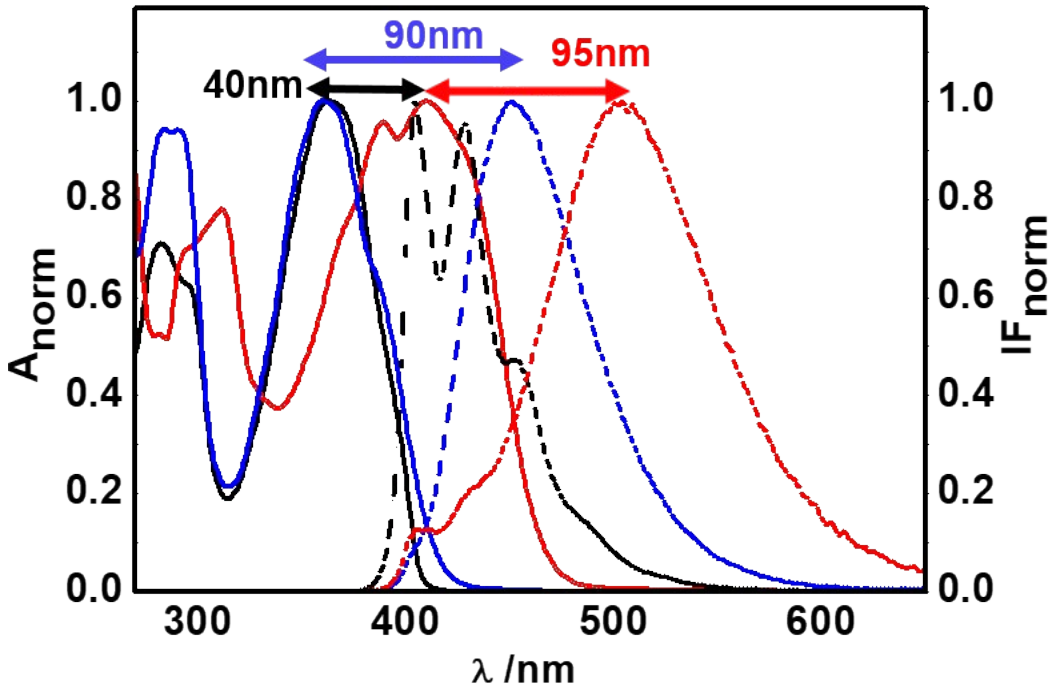


Figure S9. Normalized Absorption (solid lines) and fluorescence (dashed lines) profiles of PyBIM, $PyBIM^+$, $PyBIM^-$ (10 μM in THF). The Stokes shift values for the three are mentioned on top of the graphs.

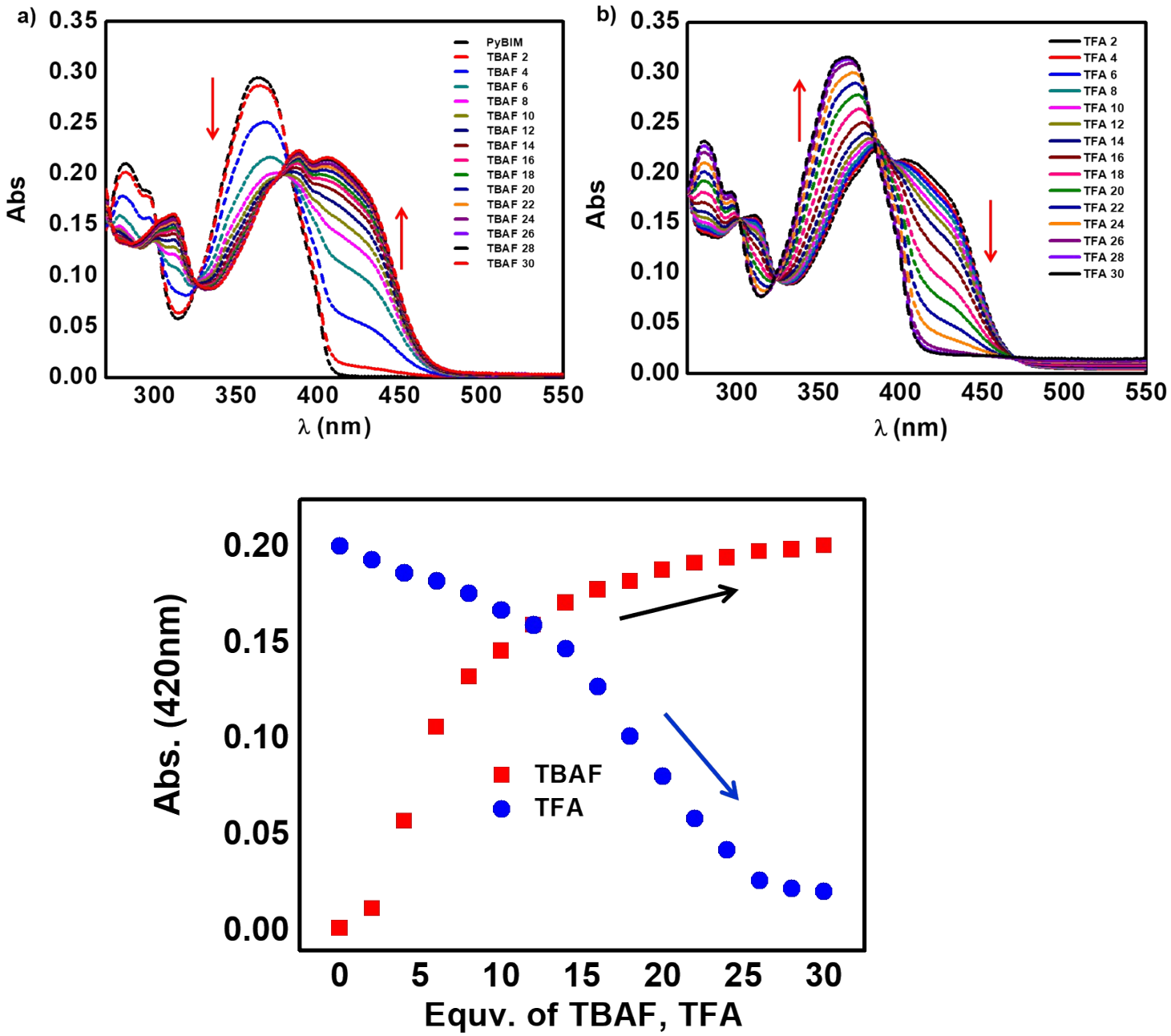


Figure S10. **(a)** UV-Vis titration of PyBIM with TBAF (0 to 30 eqv.). **(b)** UV-vis changes on subsequent addition of TFA (0-30 eqv.) to the same cuvette. **(c)** Plot of absorbance at 420 nm against TBAF and TFA treatment.

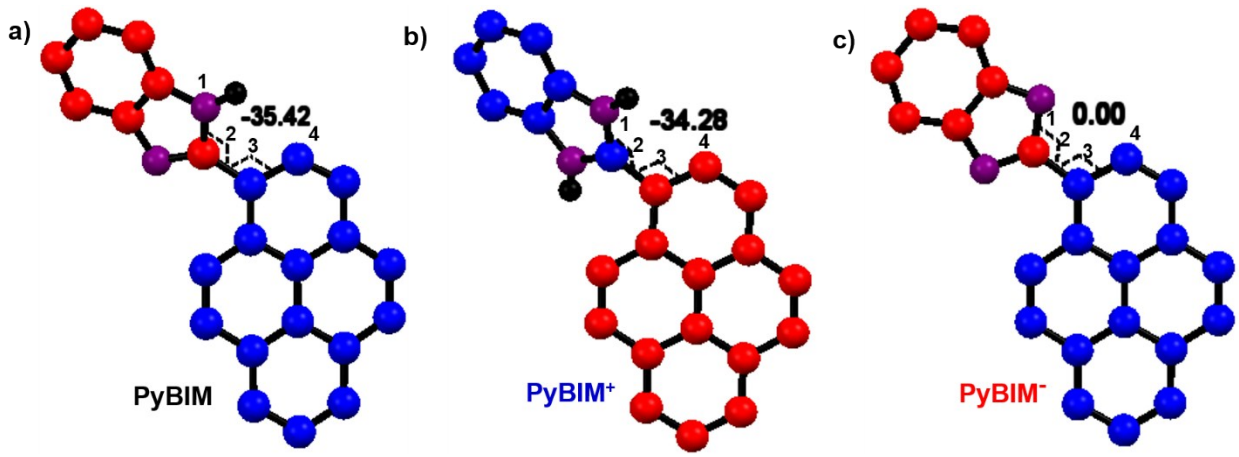
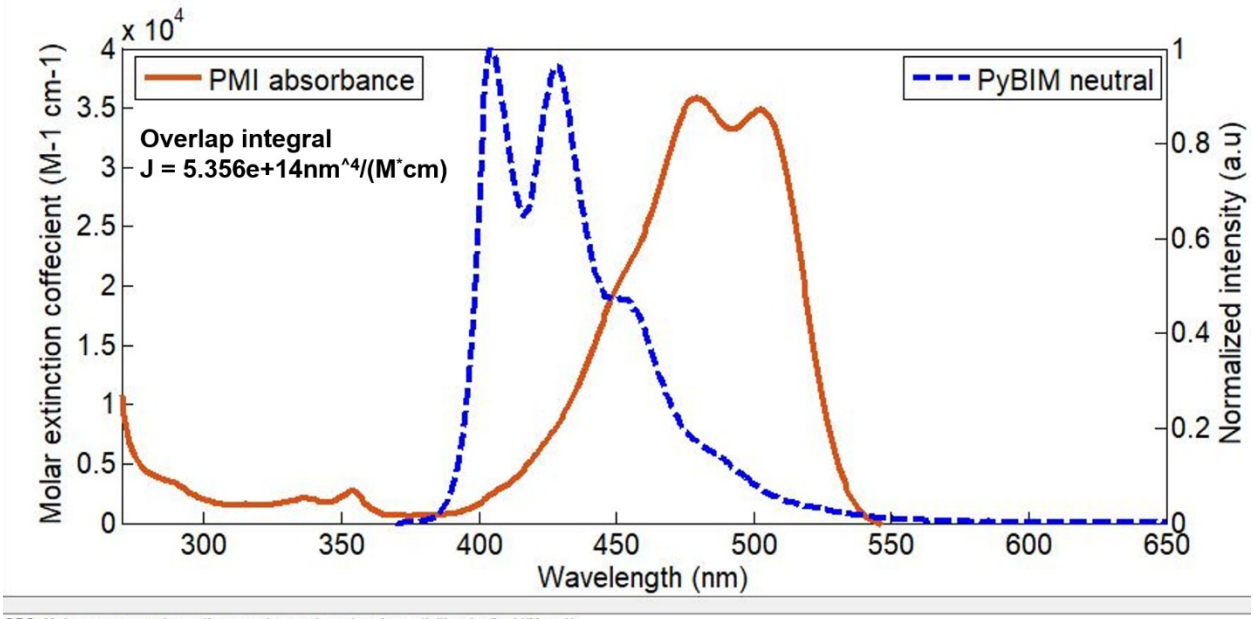


Figure S11. Torsional angle for **(a)** PyBIM, **(b)** $PyBIM^{+}$, **(c)** $PyBIM^{-}$ in between atoms (1, 2, 3, 4) highlighted above calculated by using the method of {B3LYP/6-31G(d)}.

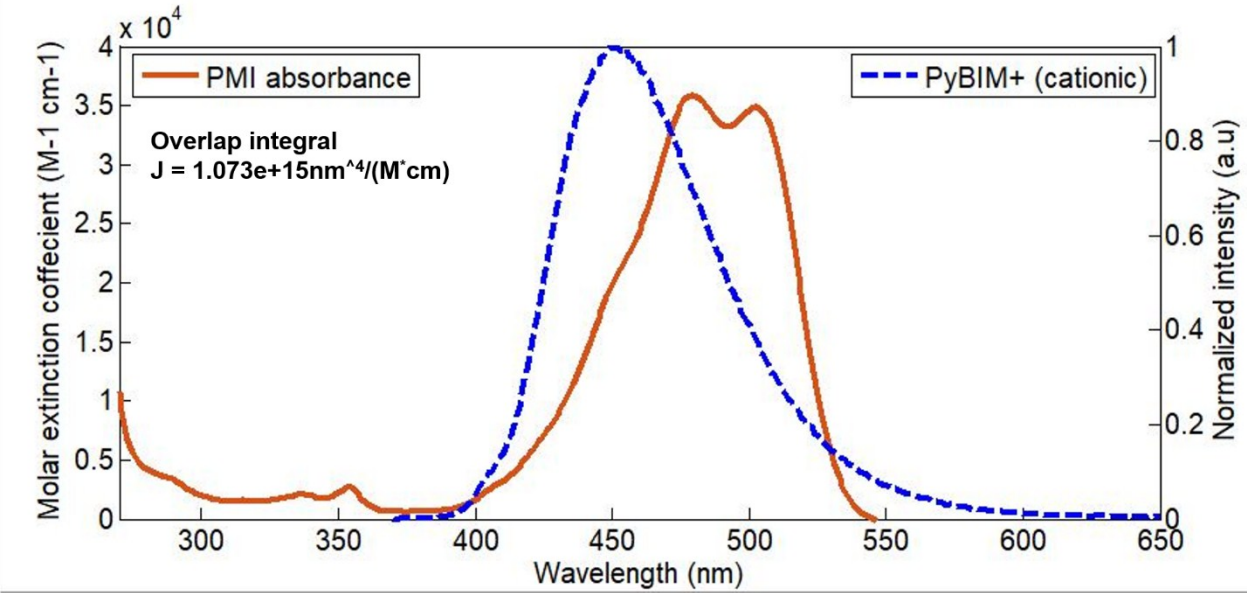
a)



OBS: Make sure your absorption spectra are in molar absorptivities (units 1/(M cm)).

Overlap integral between 'PMI absorbance' and 'PyBIM neutral':
J = 5.356e+14 nm^4/(M*cm)

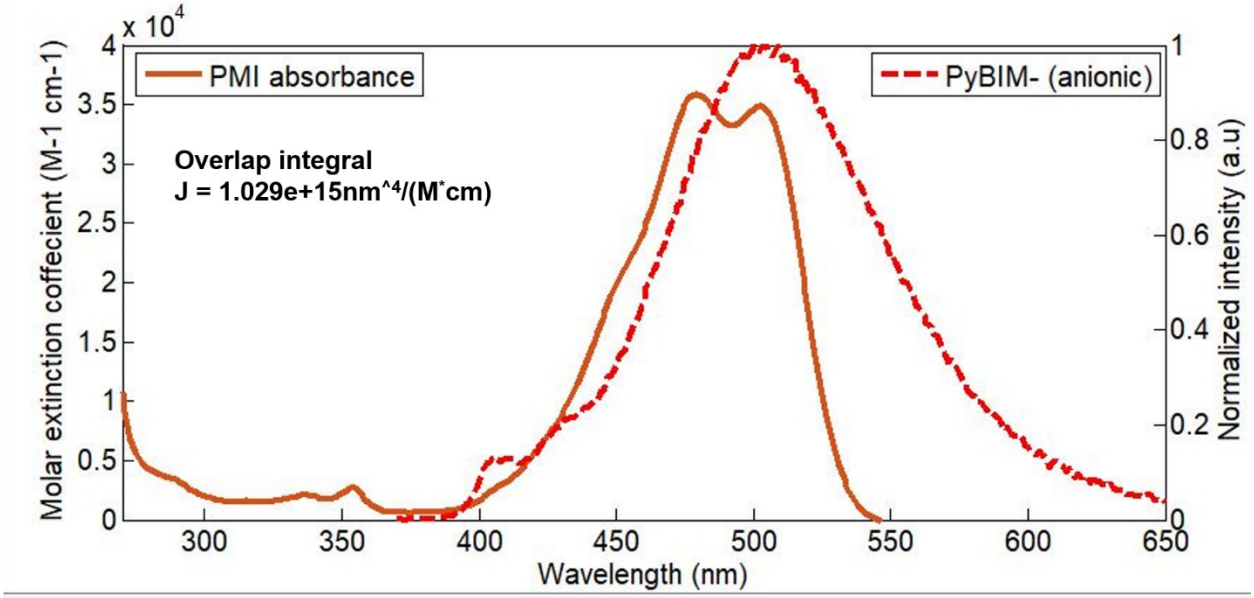
b)



OBS: Make sure your absorption spectra are in molar absorptivities (units 1/(M cm)).

Overlap integral between 'PMI absorbance' and 'PyBIM+ (cationic)':
J = 1.073e+15 nm^4/(M*cm)

c)



OBS: Make sure your absorption spectra are in molar absorptivities (units 1/(M cm)).

Overlap integral between 'PMI absorbance' and 'PyBIM- (anionic)':
J = 1.029e+15 nm^4/(M*cm)

Figure S12. The spectral overlap[1] between the absorption of **(a)** PyBIM, **(b)** $PyBIM^+$, **(c)** $PyBIM^-$ (each 10 μM in THF) with emission of **PMI** in THF.

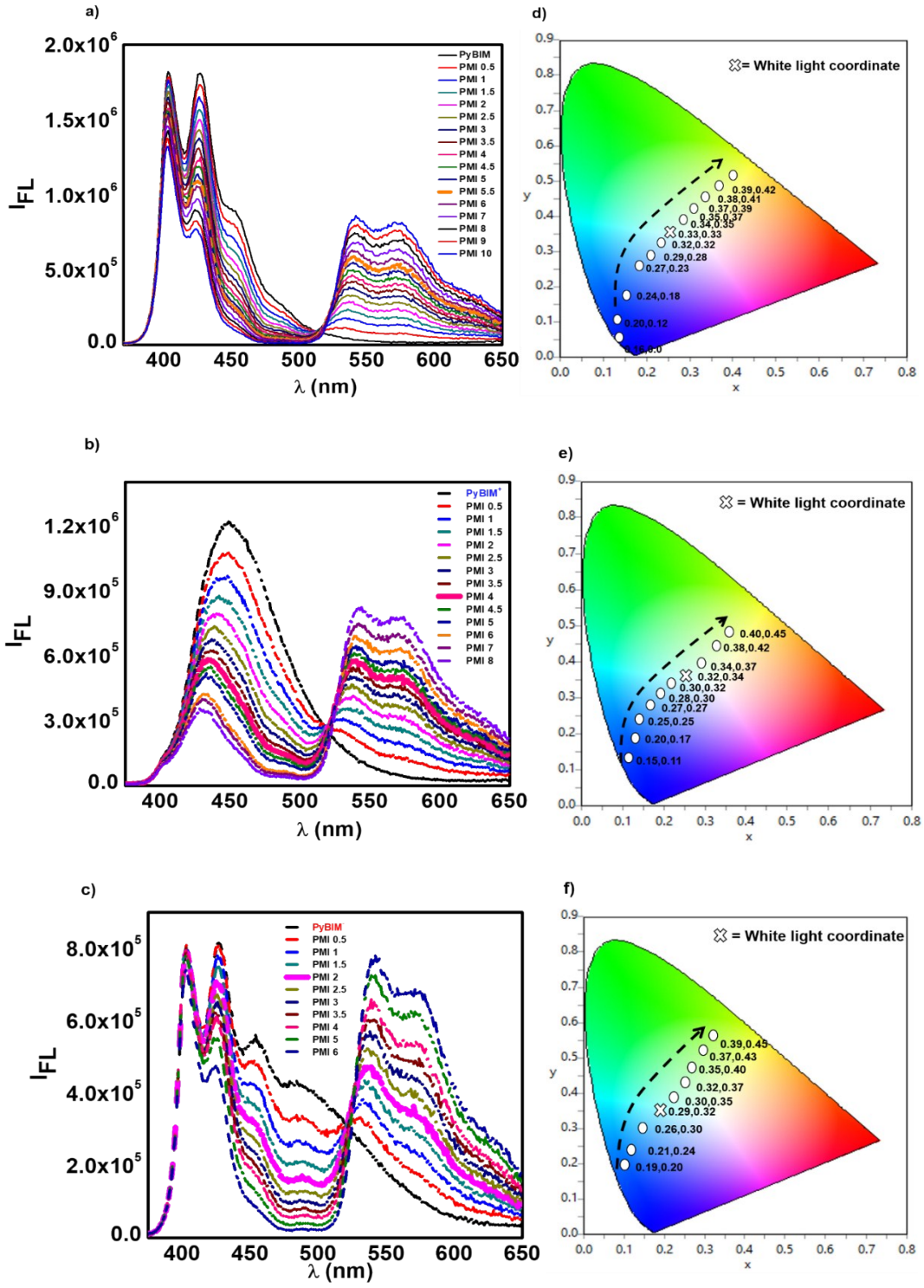
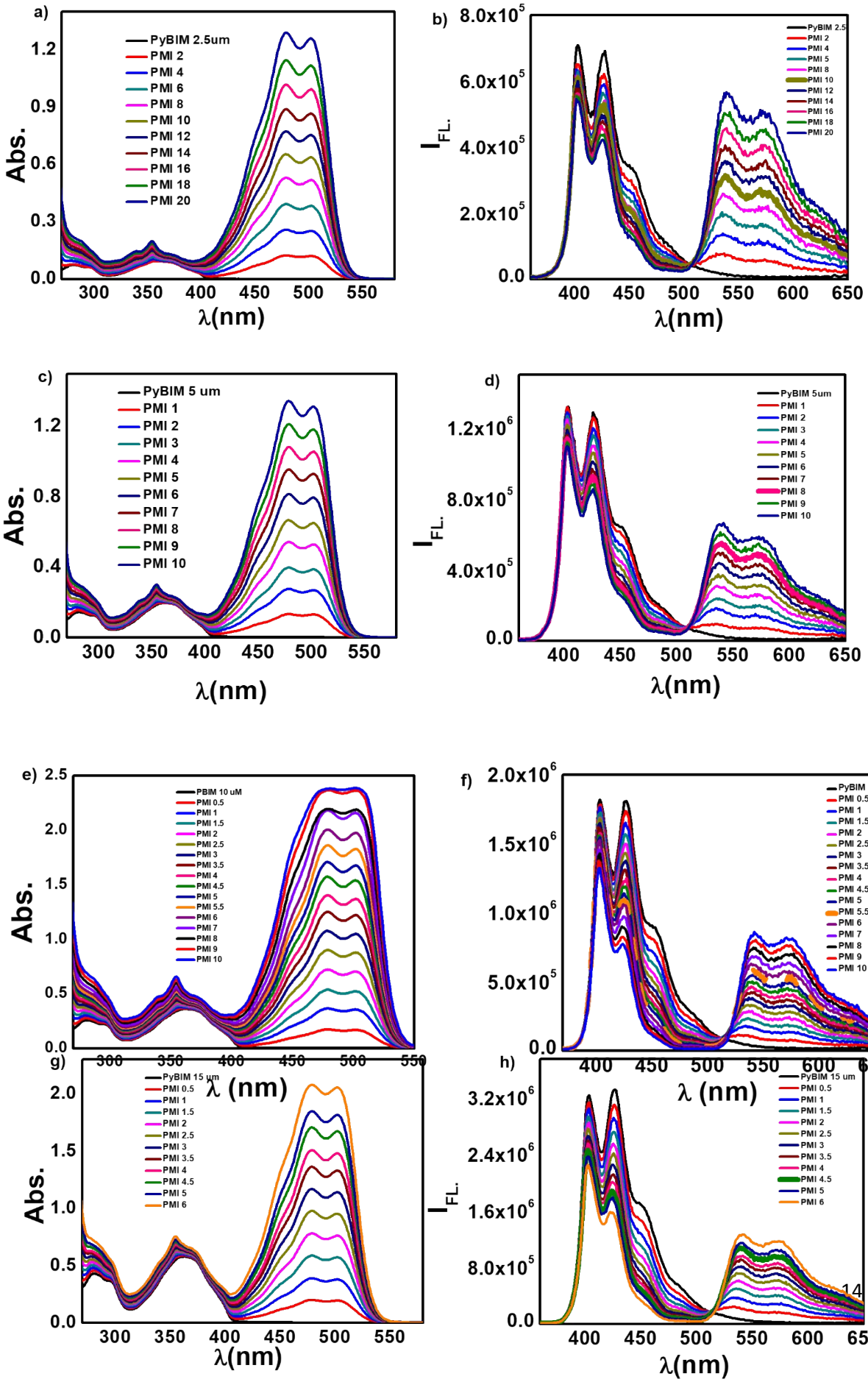


Figure S13. Fluorescence titration of **(a)** PyBIM, **(b)** $PyBIM^{+}$, **(c)** $PyBIM^{-}$ (each 10 μM in THF) with **PMI** in THF at λ_{ex} =355 nm. The white light spectra are shown in bold. Corresponding CIE coordinates are shown by open circle while white light emission (WLE) coordinate shown by cross sign in **(d), (e), (f).**


a)
Abs.
λ(nm)
PyBIM 2.5um
PMI 2
PMI 4
PMI 6
PMI 8
PMI 10
PMI 12
PMI 14
PMI 16
PMI 18
PMI 20
b)
I_FL.
λ(nm)
PyBIM 2.5
PMI 2
PMI 4
PMI 5
PMI 8
PMI 10
PMI 12
PMI 14
PMI 16
PMI 18
PMI 20
c)
Abs.
λ(nm)
PyBIM 5 um
PMI 1
PMI 2
PMI 3
PMI 4
PMI 5
PMI 6
PMI 7
PMI 8
PMI 9
PMI 10
d)
I_FL.
λ(nm)
PyBIM 5um
PMI 1
PMI 2
PMI 3
PMI 4
PMI 5
PMI 6
PMI 7
PMI 8
PMI 9
PMI 10
e)
Abs.
PBIM 10 uM
PMI 0.5
PMI 1
PMI 1.5
PMI 2
PMI 2.5
PMI 3
PMI 3.5
PMI 4
PMI 4.5
PMI 5
PMI 5.5
PMI 6
PMI 7
PMI 8
PMI 9
PMI 10
f)
PyBIM
PMI 0.5
PMI 1
PMI 1.5
PMI 2
PMI 2.5
PMI 3
PMI 3.5
PMI 4
PMI 4.5
PMI 5
PMI 5.5
PMI 6
PMI 7
PMI 8
PMI 9
PMI 10
g)
Abs.
λ (nm)
PyBIM 15 um
PMI 0.5
PMI 1
PMI 1.5
PMI 2
PMI 2.5
PMI 3
PMI 3.5
PMI 4
PMI 4.5
PMI 5
PMI 6
h)
I_FL.
λ (nm)
PyBIM 15 um
PMI 0.5
PMI 1
PMI 1.5
PMI 2
PMI 2.5
PMI 3
PMI 3.5
PMI 4
PMI 4.5
PMI 5
PMI 6

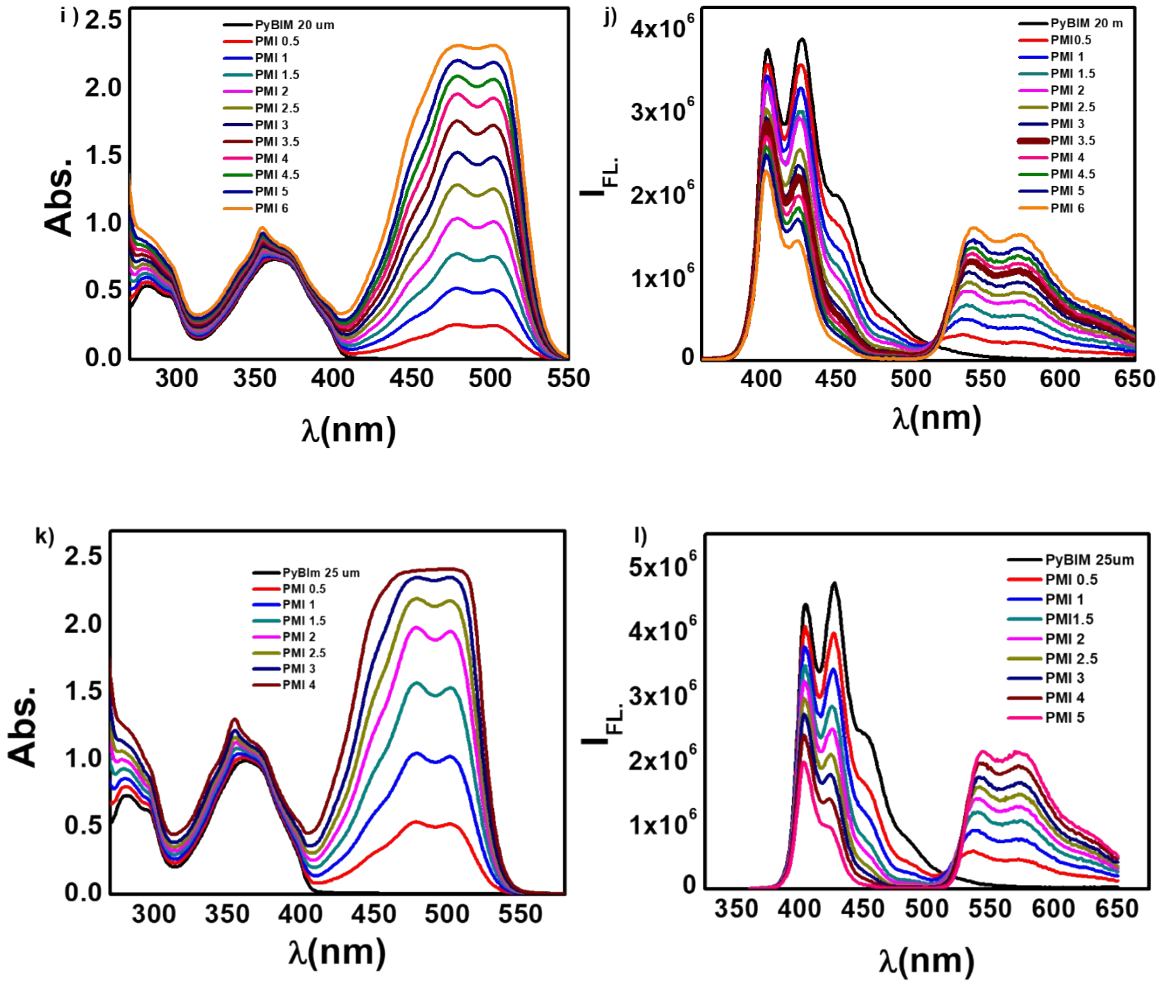


Figure S14. PyBIM was titrated with PMI (in THF) at 2.5 μM, 5 μM **,** 10 μM **,** 15 μM **,** 20 μM , 25 μM their respective UV-Vis is shown in **(a)**, **(c), (e)**, **(g)**, **(i), (k)** and their corresponding fluorescence titration (λ_{ex} =355 nm) are shown in **(b)**, **(d), (f)**, **(h)**, **(j), (l)**. All the WLE spectra are shown bold.

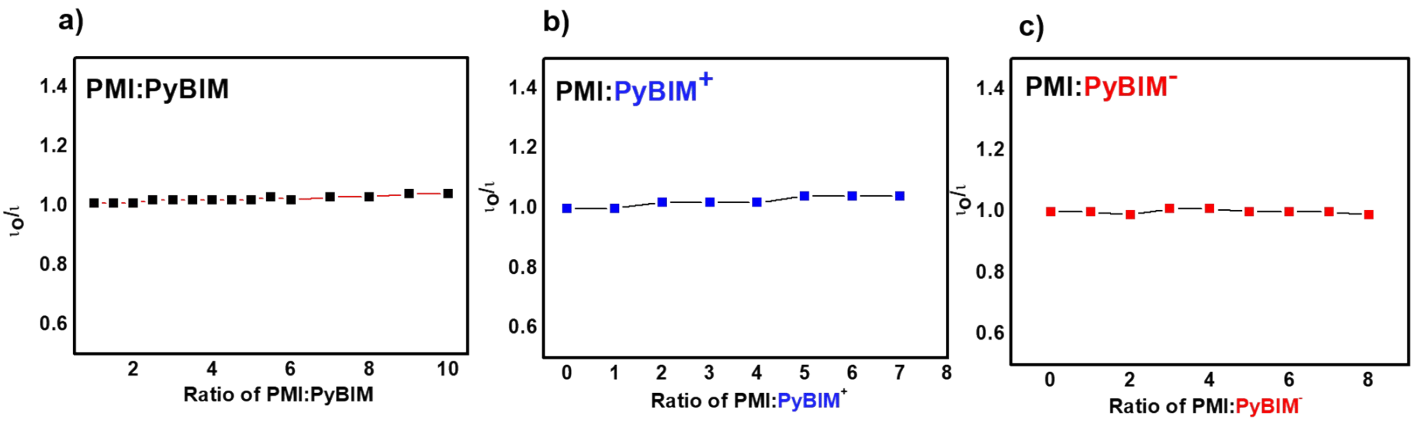
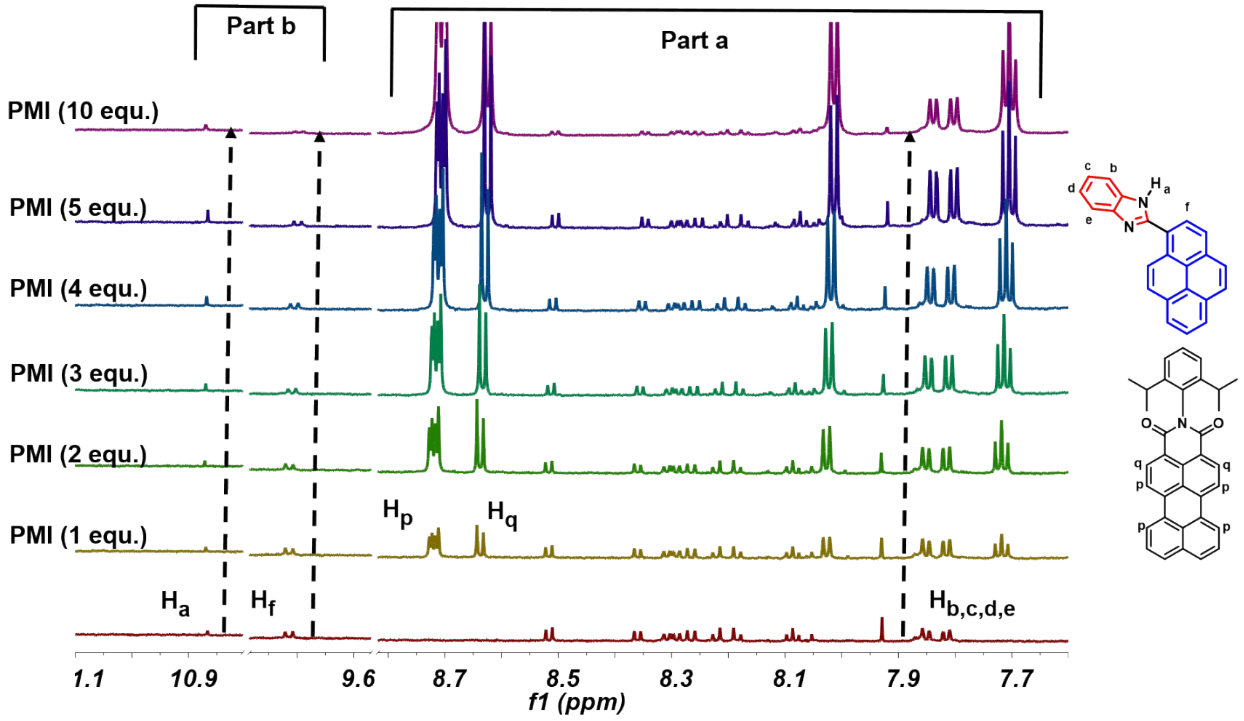


Figure S15. The ratio of lifetime before (τ_o) and on incremental addition of PMI (τ) for **(a)** PyBIM **(b)** $PyBIM^+$ and **(c)** $PyBIM^-$ on incremental with respect to ratio of PMI to PyBIM (or $PyBIM^+$ or $PyBIM^-$).



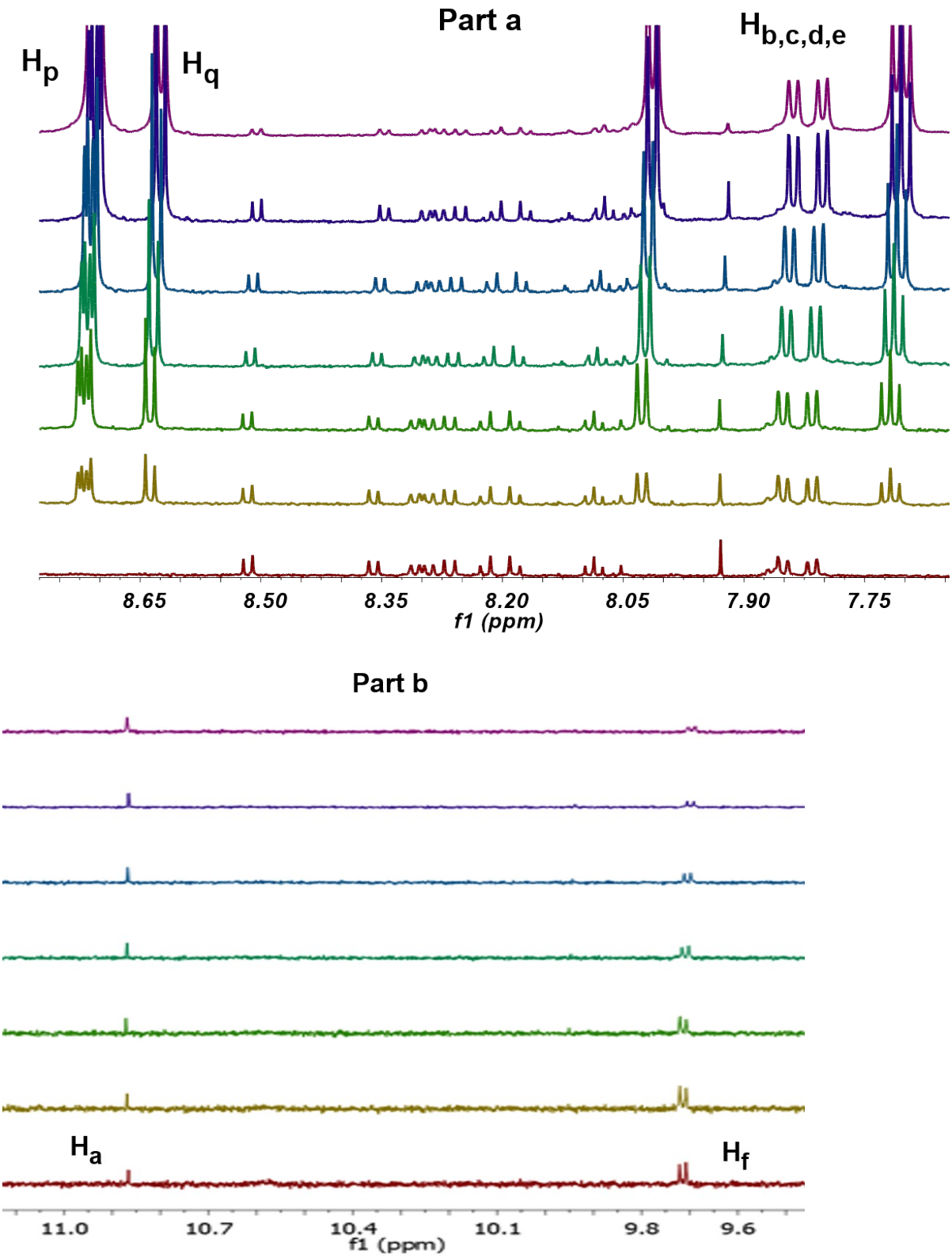


Figure S16. ^{1}H-NMR titration of PyBIM (20 μM) with PMI (20 μM-200 μM) in THF-d_8 at (700 MHz) at 298 K. The region **(a)** and **(b)** expanded and shown below.

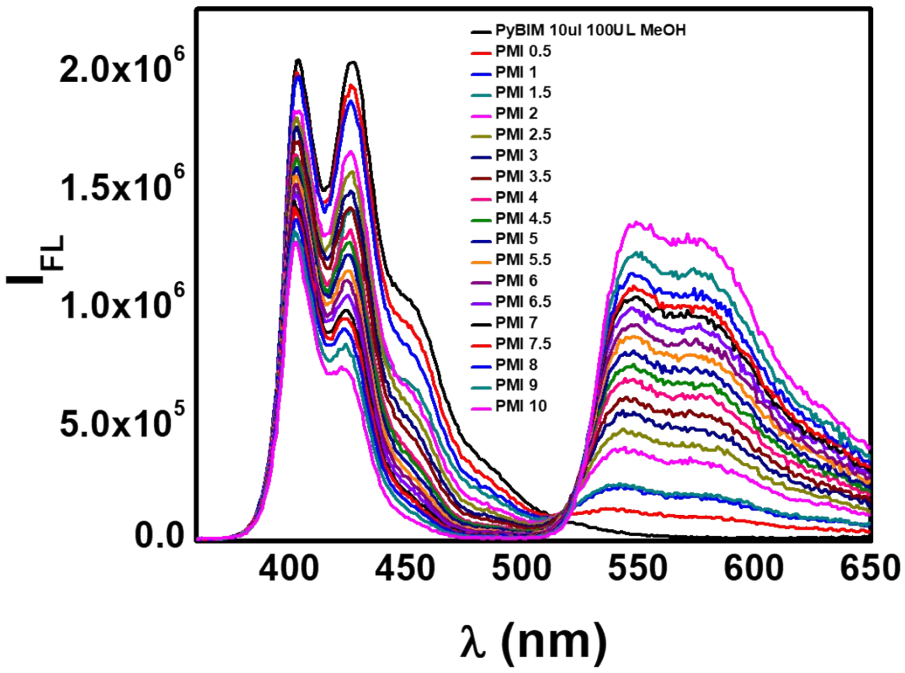


Figure S17. Fluorescence titration of PyBIM (10 μM in 10% v/v MeOH in THF) with PMI at λ_{ex} = 355 nm.

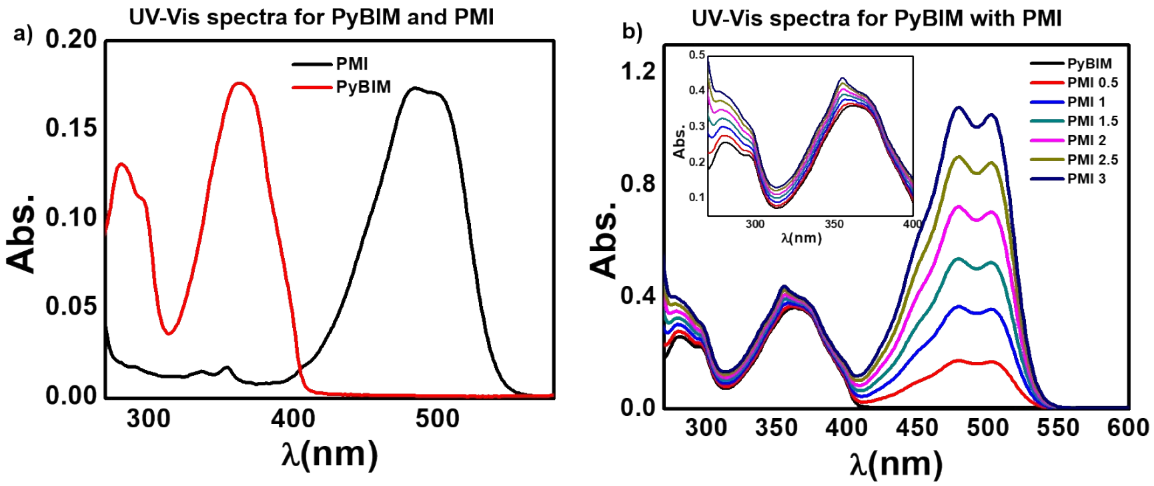


Figure S18. **a)** UV-Vis spectra of PyBIM and PMI recorded independently at 5 μM each in THF; **b)** UV-Vis spectra after titration of PyBIM 10 μM with PMI 5-30 μM (Inset show the enlarged area between λ = 270-400 nm)

Table S1. Lifetime decay data (monitored at 405 nm) for PyBIM (10 μM in THF) on addition of varied amounts of PMI.

PMI (μM)	0	10	20	30	40	50	60	70
τ (ns)	1.69	1.67	1.66	1.66	1.65	1.65	1.65	1.64
χ^2	1.01	1.09	1.14	1.01	1.04	1.07	1.04	1.05

Table S2. Lifetime decay data (monitored at 450 nm) for $PyBIM^+$ (10 μM in THF) on addition varied amounts of PMI.

PMI (μM)	0	10	20	30	40	50	60	70
τ (ns)	2.44	2.42	2.40	2.39	2.38	2.34	2.34	2.34
χ^2	1.10	1.16	1.08	1.13	1.15	1.16	1.19	1.12

Table S3. Lifetime decay data (monitored at 500 nm) for $PyBIM^-$ (10 μM in THF) on addition varied amounts of PMI.

PMI (μM)	0	10	20	30	40	50	60	70
τ (ns)	2.83	2.83	2.86	2.82	2.82	2.82	2.82	2.82
χ^2	1.18	1.12	1.20	1.20	0.98	1.05	1.04	0.99

Table S4. Percentage overlap of emission profile of PyBIM, $PyBIM^+$ and $PyBIM^-$ with the absorption profile of PMI (calculated using Origin-18 software).

Species	Areal Overlap (%)
PyBIM	**33**
$PyBIM^+$	**66**
$PyBIM^-$	**76**

Table S5. Variation of Φ_{WLE} with PyBIM concentration. Equivalents of PMI required for WLE in each case is also provided.

[PyBIM] (μM)	Equ. Of PMI used	CIE coordinate	Φ_{WLE} (%) $\pm$ 3
2.5	8	(0.32,0.33)	56
5	6.5	(0.32,0.33)	59
10	5.5	(0.33,0.33)	62.5
15	3	(0.32,0.32)	66
20	2.5	(0.33,0.33)	70
25	2	(0.33,0.34)	72
30	1.5	(0.34,0.35)	72.5
40	1	(0.33,0.34)	72

Set up for structure optimized of PyBIM

Calculation method = B3LYP

Level of theory = 6-31 G(d)

Charge =0

Spin = Singlet

N1	2.9410	1.0110	-0.6730	N
N2	2.4060	-0.7400	0.5910	N
C3	5.4500	0.6950	-0.7510	C
C4	6.4150	-0.1300	-0.2070	C
C5	6.0780	-1.2260	0.5970	C
C6	4.7650	-1.5170	0.8990	C
C7	3.7760	-0.6800	0.3940	C
C8	4.1330	0.4040	-0.4130	C
C9	1.9330	0.3050	-0.0560	C
C10	0.5570	0.7960	-0.0690	C
C11	0.3160	2.1570	0.0000	C
C12	-0.8990	2.7640	0.1320	C
C13	-2.0200	1.9420	0.1710	C
C14	-3.3450	2.4640	0.3530	C
C15	-4.4200	1.6580	0.3410	C
C16	-4.3020	0.2540	0.1360	C
C17	-5.4050	-0.5900	0.0680	C
C18	-5.2570	-1.9500	-0.1410	C
C19	-3.9890	-2.5010	-0.2750	C
C20	-2.8570	-1.7010	-0.1990	C
C21	-1.5380	-2.2270	-0.3460	C
C22	-0.4410	-1.4340	-0.3130	C
C23	-0.5610	-0.0400	-0.1070	C
C24	-1.8490	0.5400	0.0200	C
C25	-2.9980	-0.3050	-0.0110	C
H26	5.6740	1.4200	-1.3230	H
H27	7.3310	0.0510	-0.3830	H
H28	6.7670	-1.7810	0.9400	H
H29	4.5420	-2.2680	1.4360	H
H30	1.1120	2.8070	-0.0080	H
H31	-1.0040	3.7070	0.1900	H
H32	-3.4640	3.3980	0.4820	H
H33	-5.2810	2.0350	0.4720	H
H34	-6.2770	-0.2280	0.1660	H
H35	-6.0240	-2.5080	-0.1930	H
H36	-3.8960	-3.4350	-0.4200	H
H37	-1.4270	-3.1620	-0.4720	H
H38	0.4190	-1.8240	-0.4210	H
H39	2.8520	1.8200	-1.2230	H

Set up for structure optimized of $PyBIM^+$

Calculation method = B3LYP

Level of theory = 6-31 G(d)

Charge =+1

Spin = Singlet

N1	2.9600	1.1240	-0.5790	N
N2	2.4240	-0.6610	0.5340	N
C3	5.4800	0.7390	-0.6710	C
C4	6.4410	-0.1760	-0.2470	C
C5	6.0950	-1.3280	0.4850	C
C6	4.7730	-1.6150	0.8170	C
C7	3.8120	-0.7000	0.3910	C
C8	4.1580	0.4530	-0.3330	C
C9	1.9130	0.4480	-0.0490	C
C10	0.5380	0.8960	-0.0530	C
C11	0.3160	2.2870	0.0650	C
C12	-0.9600	2.8040	0.1600	C
C13	-2.0830	1.9530	0.1470	C
C14	-3.4110	2.4680	0.2820	C
C15	-4.4930	1.6360	0.2680	C
C16	-4.3390	0.2200	0.1090	C
C17	-5.4420	-0.6490	0.0860	C
C18	-5.2700	-2.0230	-0.0820	C
C19	-3.9930	-2.5570	-0.2330	C
C20	-2.8600	-1.7240	-0.2110	C
C21	-1.5370	-2.2320	-0.3930	C
C22	-0.4440	-1.4130	-0.3580	C
C23	-0.5690	-0.0030	-0.1220	C
C24	-1.8880	0.5420	-0.0010	C
C25	-3.0250	-0.3190	-0.0330	C
H26	5.7490	1.6270	-1.2340	H
H27	7.4830	0.0050	-0.4870	H
H28	6.8780	-2.0110	0.7970	H
H29	4.5090	-2.5040	1.3810	H
H30	1.1640	2.9610	0.1480	H
H31	-1.1040	3.8740	0.2750	H
H32	-3.5420	3.5400	0.3960	H
H33	-5.4960	2.0410	0.3740	H
H34	-6.4420	-0.2380	0.1990	H
H35	-6.1350	-2.6770	-0.0990	H
H36	-3.8620	-3.6270	-0.3720	H
H37	-1.4090	-3.2940	-0.5840	H
H38	0.5300	-1.8420	-0.5680	H
H39	2.8500	1.9530	-1.1490	H
H40	1.8660	-1.2950	1.0910	H

Set up for structure optimized of $PyBIM^-$

Calculation method = B3LYP

Level of theory = 6-31 G(d)

Charge =-1

Spin = Singlet

N1	3.0080	1.3320	-0.0000	N
N2	2.4240	-0.9100	0.0000	N
C3	5.4990	0.9650	-0.0000	C
C4	6.4670	-0.0320	0.0000	C
C5	6.1100	-1.4040	0.0000	C
C6	4.7790	-1.8040	0.0000	C
C7	3.7830	-0.8100	0.0000	C
C8	4.1430	0.5830	-0.0000	C
C9	2.0230	0.3900	-0.0000	C
C10	0.6150	0.8260	-0.0000	C
C11	0.3930	2.2220	0.0000	C
C12	-0.8740	2.7720	0.0000	C
C13	-2.0220	1.9590	0.0000	C
C14	-3.3450	2.5030	0.0000	C
C15	-4.4480	1.7010	0.0000	C
C16	-4.3190	0.2720	0.0000	C
C17	-5.4390	-0.5780	-0.0000	C
C18	-5.2830	-1.9630	-0.0000	C
C19	-4.0110	-2.5300	-0.0000	C
C20	-2.8600	-1.7220	-0.0000	C
C21	-1.5340	-2.2650	-0.0000	C
C22	-0.4280	-1.4680	-0.0000	C
C23	-0.5280	-0.0320	-0.0000	C
C24	-1.8450	0.5410	0.0000	C
C25	-3.0050	-0.2990	0.0000	C
H26	5.7740	2.0190	-0.0010	H
H27	7.5220	0.2400	-0.0000	H
H28	6.8990	-2.1560	0.0010	H
H29	4.5060	-2.8580	0.0010	H
H30	1.2750	2.8520	-0.0000	H
H31	-0.9960	3.8540	0.0000	H
H32	-3.4520	3.5860	0.0000	H
H33	-5.4480	2.1310	0.0000	H
H34	-6.4340	-0.1380	0.0000	H
H35	-6.1620	-2.6050	-0.0000	H
H36	-3.8930	-3.6120	-0.0000	H
H37	-1.4230	-3.3480	-0.0000	H
H38	0.5750	-1.8830	-0.0000	H

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