

Supporting Information for

## **Substitution Effects on the Photoinduced Excited State Dynamics of Perylenemonoimides in Solution and Thin Films**

Suman Dhama<sup>a</sup>, Mst Nasima Khatun<sup>b</sup>, Chaitrali Sengupta<sup>a</sup>, Parameswar Krishnan Iyer<sup>b, c\*</sup>,  
Ravindra Pandey<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology Roorkee, 247667 Haridwar,  
Uttarakhand, India

<sup>b</sup>Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039  
Assam, India

<sup>c</sup>Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati 781039  
Assam, India

**Key words:** Perylene Monoimide, SOCT-ISC, Transient Absorption Spectroscopy, Thin films

\* Author to whom correspondence should be sent: [rpandey@cy.iitr.ac.in](mailto:rpandey@cy.iitr.ac.in), [pki@iitg.ac.in](mailto:pki@iitg.ac.in)

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## S1. Material and Methods

### Sample Preparation:

Reagents and initial materials, such as Perylene-3,4,9,10-tetracarboxylic acid anhydride (PDA), imidazole, Zinc acetate [Zn (OAc)<sub>2</sub>], Bromine, chlorobenzene, and thianthrenyl boronic acid, were procured from Sigma Aldrich (INDIA) in high-quality reagent grade. HPLC-grade solvents were sourced from Fisher Scientific Ltd. and RANKEM. Nuclear magnetic resonance (NMR) spectra, encompassing <sup>1</sup>H, were documented using a Bruker Avance 400 MHz spectrometer. The residual solvent signal served as an internal reference for all solutions employed in the NMR experiments. Mass spectra were acquired through MALDI-TOF spectrometry. The synthetic procedure of perylene monoimide (**PMI**) derivatives (2,6-diisopropylphenyl **PMI**) **PMIB**, (2,5-di-tert-butylphenyl, para bromo PMI) **BrPMITB**, (2,5-di-tert-butylphenyl **PMI**) **PMITB**, (2,5-di-tert-butylphenyl, para thianthren-1-yl PMI) **APITB** will be discussed later.

A 10<sup>-5</sup> M solution of the **PMI** derivatives were prepared in tetrahydrofuran (THF) for steady state and time resolved spectroscopy measurements. Thin films of **PMI** derivatives were deposited on a quartz substrate using thermal evaporation method (HHV Smart Coat 3.0A). The thickness of the thin films was measured using Variable-angle spectral ellipsometry (M 2000, J. A. Woollam) and is found to be 65 ± 13 nm thick. The XRD data was collected using thin film X-ray diffractometer (Rigaku SmartLab). The electrochemical properties of **APITB** were studied using cyclic voltammetry (CH instruments model 700D series). The **APITB** was deposited on a glassy carbon which works as the working electrode, Ag/AgCl as the reference electrode and platinum wire as the counter electrode. A 0.1 M tetra-n-butyl ammonium hexafluorophosphate (TBAP) was prepared in a deaerated acetonitrile solution which was used as a supporting electrolyte. Scan rate was set to 50 mV/s.

### Photophysical Measurements:

The steady state absorption and emission spectra were collected using UV-2600 UV-Vis spectrophotometer (Shimadzu) and FluoroMax-4 (Horiba Scientific) spectrofluorometer, respectively. The time resolved photoluminescence measurements of all **PMI** derivatives in solution and thin films were performed using a time correlated single photon counting (TCSPC) spectrometer (FLS1000 Fluorescence Spectrometer, Edinburgh instruments). The 447 nm

pulsed laser is used for photoexcitation of the samples, with a 74.9 ps pulse width. All measurements were performed at room temperature.

### **Femtosecond (fs) Transient Absorption Spectroscopy:**

The ultrafast transient absorption measurements were carried out using a Ti:sapphire amplifier laser (spectra physics) operated at a 1 kHz repetition rate. The 800 nm amplifier output (pulse duration 120 fs; pulse energy ~7 mJ) splitted into two parts as the pump and probe beam. One part of the amplifier output passes through optical parametric amplifier (OPA) and generates 480 nm pulse that serves as pump pulse for the photoexcitation process. Another part of the amplifier output passes through a CaF<sub>2</sub> crystal and generates supercontinuum in the visible range that serves as a probe pulse. Both the pump and probe beam spatially overlapped on the crystal and the temporal overlap is adjusted using an automatic delay stage. The pump beam is blocked after passing through sample and only spectra of the probe beam is collected with a CCD camera (Newport). The difference absorption spectra are obtained via the modulation of pump on-and-off by a mechanical chopper. All measurements were performed at room temperature. The resulting TA spectra were analysed using a Glotaran software.

### **Theoretical Study:**

We conducted the density functional theory (DFT) calculations to optimise ground-state geometry of **APITB** using BP86 functional and def2-SVP basis set in ORCA software. The optimised geometry and the dihedral angle calculated in **APITB** molecule is shown in Figure 5. The dihedral angle between the **PMI** and thianthrene group was found to be equal to 66°. The spin density surface of optimised triplet state geometry of **APITB** were also calculated at BP86/def2-SVP level with ORCA software.

### **Synthesis of PMI derivatives (PMIB, BrPMITB, PMITB, and APITB)**

#### **Synthetic Route**

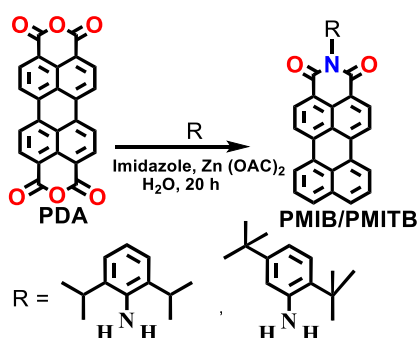
**Synthetic procedures for PMIB and PMITB:** **PMIB** and **PMITB** were synthesized via a straightforward condensation reaction utilizing hydrothermal procedures. In this method, Perylene-3,4,9,10-tetracarboxylic acid anhydride (**PDA**) (2.54 mmol), the corresponding amine (1.35 mmol), Zn (OAc)<sub>2</sub> (1.72 mmol), imidazole (5g), and water (1ml) were incorporated in a

Teflon sleeve and thoroughly mixed to achieve a homogeneous blend. This mixture was then transferred to a hydrothermal autoclave reactor, sealed, and pressurized to 15 bar before being placed in an oven. The temperature within the autoclave reactor was gradually raised to 190 °C over 20 hrs, allowing the reaction to proceed. Following the 20 hr interval, the heat source was deactivated, and the reaction mixture was allowed to cool to room temperature. The resultant dark reddish crude product underwent extraction with a chloroform-water mixture (200 ml chloroform and 50 ml water) under acidic pH conditions. This extraction process was repeated four times for thorough separation. The extracted product underwent four water washes, drying over Na<sub>2</sub>SO<sub>4</sub>, and subsequent filtration. The filtered solution underwent concentration using a rotary evaporator to eliminate the solvent, resulting in a concentrated residue. For further purification, the concentrated residue underwent column chromatography with chloroform as the eluent. This purification process yielded the desired dark reddish compound (400 mg) with a satisfactory 40% yield.

**Characterization data for 2,6-diisopropylphenyl PMI (PMIB).** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.23 (d, 12 H), 7.41 (t, 3H), 7.70 (d, 3H), 8.05 (d, 3H), 8.12 (d, 3H), 8.12 (d, 3H), 8.20 (d, 1H). MALDI-TOF: calculated for C<sub>34</sub>H<sub>27</sub>NO<sub>2</sub>: 481.20 [M]<sup>+</sup>, Found: 481.321 [M]<sup>+</sup>

**Characterization data for 2,5-di-tert-butylphenyl PMI (PMITB):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 1.23 (s, 9H), 1.27 (s, 9H), 6.98 (s, 1H), 7.52 (d, 1H), 7.74 (d, 1H), 7.78 (t, 1H), 8.08 (d, 1H), 8.28 (d, 1H), 8.31 (d, 1H), 8.33 (d, 1H), 8.35 (t, 1H), 8.35 (m, 4H). MALDI-TOF: calculated for C<sub>36</sub>H<sub>31</sub>NO<sub>2</sub>: 509.24 [M]<sup>+</sup>, Found: 510.264 [M+H]<sup>+</sup>

### Synthetic Route



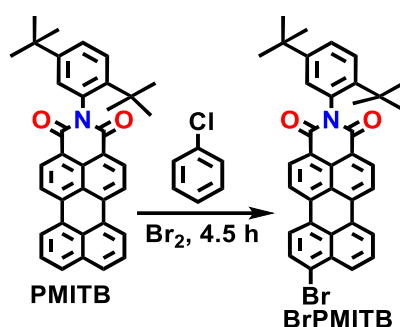
**Scheme S1.** The synthetic method was employed to prepare **PMIB and PMITB**.

**Synthetic procedures for BrPMITB:** **PMITB** (1 mmol) was dissolved in 5 mL of chlorobenzene with mild heating. Following this, bromine (4.5 mmol) was introduced into the solution, and

the ensuing mixture underwent stirring for 4.5 hours at 50 °C. Upon the reaction's completion, chlorobenzene and any residual bromine were evacuated under vacuum. The resultant solid, displaying a distinctive red hue, underwent crystallization with methanol. This crystallization procedure resulted in an impressive 95% yield of the targeted compound.

**Characterization data for 2,5-di-tert-butylphenyl para bromo PMI (BrPMITB):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) 1.25 (s, 9H), 1.28 (s, 9H), 6.88 (s, 1H), 7.32 (d, 1H), 7.64 (d, 1H), 7.98 (t, 1H), 8.12 (d, 1H), 8.29 (d, 1H), 8.38 (d, 1H), 8.69 (t, 1H), 8.57 (m, 4H). MALDI-TOF: calculated for  $\text{C}_{36}\text{H}_{31}\text{NO}_2$ : 509.24  $[\text{M}]^+$ , Found: 510.264  $[\text{M}+\text{H}]^+$

### Synthetic Route

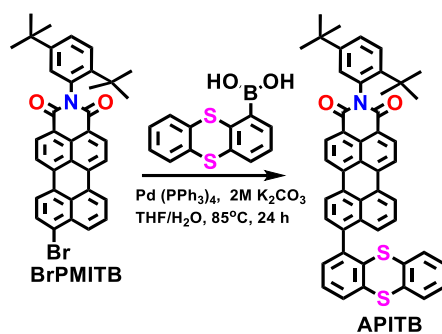


**Scheme S2.** The synthetic method employed to prepare **BrPMITB**.

**Synthetic procedures for APITB:** In a 50 mL round-bottom flask, a blend of compound **BrPMITB** (0.5 mmol) and thianthrenyl boronic acid (1 mmol) was taken along with 5 mg of  $\text{Pd}(\text{PPh}_3)_4$  catalyst. The mixture underwent a 30 min exposure to nitrogen gas to eliminate any residual oxygen. Subsequently, 6 mL of THF (tetrahydrofuran) was introduced into the flask, followed by the addition of 2 mL of a 2.0 M potassium carbonate solution. The resulting mixture was stirred at 85 °C within a nitrogen atmosphere, and the progression of reactions was observed through thin layer chromatography (TLC). After 24 hrs, the solutions were cooled, and  $\text{CHCl}_3$  (chloroform) was employed for extraction. The organic layers were then desiccated using anhydrous sodium sulfate. The solvent was evaporated, and the ensuing product underwent purification through column chromatography, culminating in a 60% yield of the desirable red solid for the **APITB** compound.

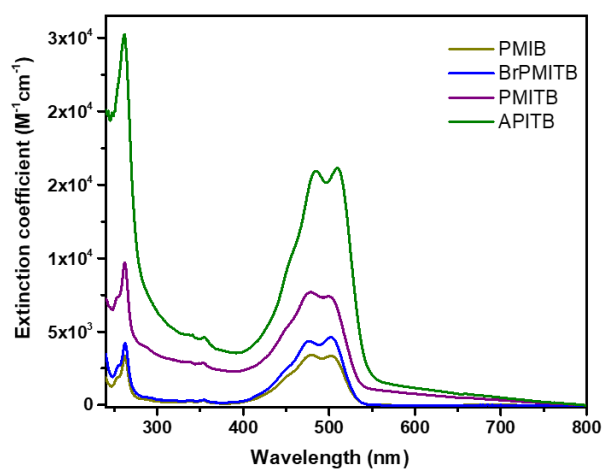
**Characterization data for 2,5-di-tert-butylphenyl para thianthren-1-yl PMI (APITB):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.99 (d, 1H), 7.01 (d, 2H), 7.13 (m, 2H), 7.28 (m, 1H), 7.35 (m, 1H), 7.44 (m, 4H), 7.58 (d, 1H), 8.63 (m, 4H), 8.65 (d, 2H), 8.50 (m, 1H), 8.64 (dd, 2H). MALDI-TOF: calculated for  $\text{C}_{48}\text{H}_{37}\text{NO}_2\text{S}_2$ : 723.23  $[\text{M}]^+$ , Found: 723.701  $[\text{M}]^+$

## Synthetic Route



**Scheme S3.** The synthetic method was employed to prepare **APITB**.

## S2. Steady-state and time resolved spectroscopy



**Figure S1:** Extinction coefficient of **PMIB**, **BrPMITB**, **PMITB**, **APITB** in THF.

**Table S1:** Photophysical properties of **PMI** derivatives

	Absorbance, nm ( $\lambda_{max}$ ) in THF	Emission, nm ( $\lambda_{max}$ ) in THF	Quantum Yield (Q.Y.) in THF	Fluorescence Lifetime, ns ( $\tau$ ) in THF*	Absorbance, nm ( $\lambda_{max}$ ) in Thin Films	Emission, nm ( $\lambda_{max}$ ) in Thin Films	Q.Y. in Thin Films	$\langle\tau_{avg}\rangle$ , ns Thin Films
<b>PMIB</b>	478, 503	545, 573	0.98	4.98 $\pm$ 0.04	487, 521, 556	654	0.003	1.34 $\pm$ 0.05
<b>BrPMITB</b>	477, 502	538, 572	0.98	4.80 $\pm$ 0.04	484, 526	625	0.0013	2.09 $\pm$ 0.04
<b>PMITB</b>	480, 502	541, 571	0.93	4.80 $\pm$ 0.04	487, 527	662	0.02	12.50 $\pm$ 0.2
<b>APITB</b>	484, 509	549, 581	0.08	0.40 $\pm$ 0.01, 4.11 $\pm$ 0.05	494, 527	606	0.02	2.48 $\pm$ 0.05

\*  $\chi^{(2)}$ , value of fluorescence kinetics is in between 1.0 and 1.18

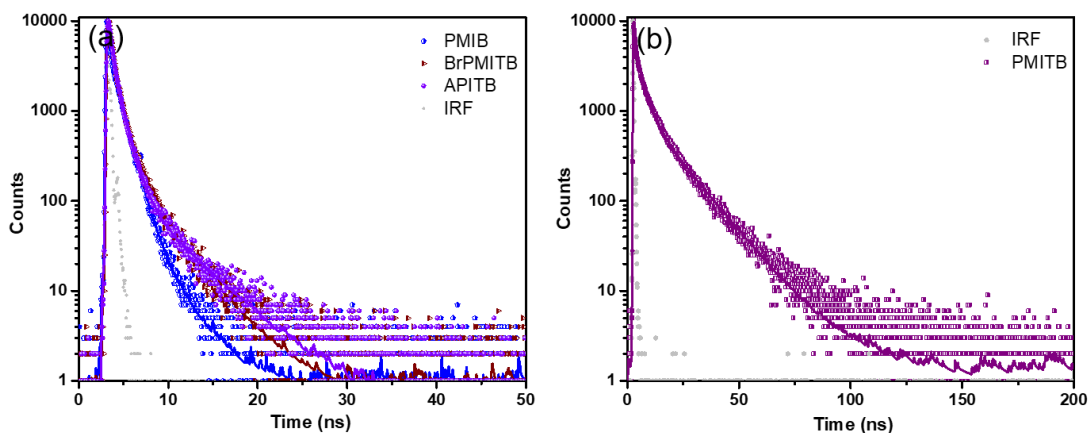
**Table S2.** Band Gap of **PMI** derivatives in solution and thin films

	Eg, eV (THF)	$\lambda$ , nm	Eg, eV (Thin Films)	$\lambda$ , nm
<b>PMIB</b>	2.35	526	2.16	572
<b>BrPMITB</b>	2.38	520	2.18	567
<b>PMITB</b>	2.35	526	2.12	584
<b>APITB</b>	2.34	529	2.20	562

**Table S3.** Fluorescence Lifetimes of **PMI** derivatives in thin films

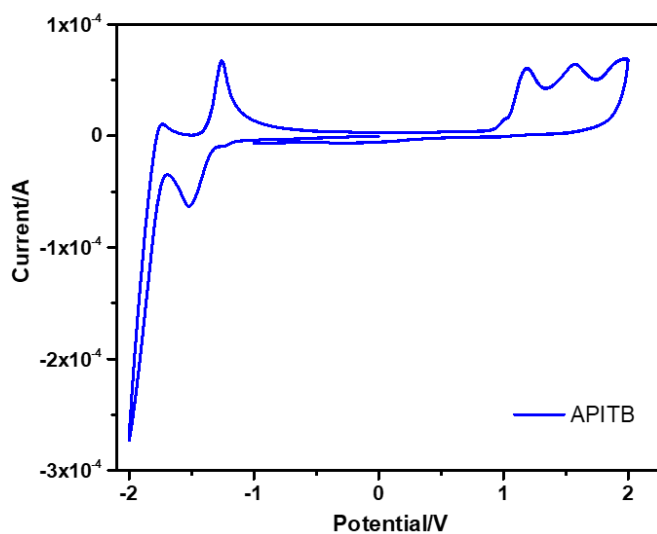
Thin Films	$\tau_1$	$\tau_2$	$\tau_3$	$B_1$	$B_2$	$B_3$	$\chi^2$	Fluorescence Lifetime, ns $\langle\tau_{avg}\rangle$
<b>PMIB</b>	0.05	1.04	2.84	33.76	61.26	4.97	0.87	1.34
<b>BrPMITB</b>	0.19	1.00	3.54	42.29	45.00	12.71	0.91	2.09
<b>PMITB</b>	0.26	3.50	14.42	11.65	40.77	47.58	1.46	12.50
<b>APITB</b>	0.22	1.00	4.68	43.83	47.17	9.00	0.79	2.48





**Figure S2:** Fluorescence decay curve of **PMI** derivatives in thin films

### S5. Electrochemical Study of APITB in THF.



**Figure S3.** Cyclic voltammograms (CV) plot of **APITB**, drop casted on glassy carbon working electrode, Ag/AgNO<sub>3</sub> as the reference electrode, platinum wire as the counter electrode in acetonitrile under the argon gas atmosphere containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Scan rate of 50 mV/s.

**Rhem Weller equation:**

$$\Delta G_S = -\frac{e^2}{4\pi\epsilon_S\epsilon_0 R_{CC}} - \frac{e^2}{8\pi\epsilon_0} \left(\frac{1}{R_D} + \frac{1}{R_A}\right) \left(\frac{1}{\epsilon_{REF}} + \frac{1}{\epsilon_S}\right) \dots\dots\dots S1$$

$$\Delta G_{CS} = e[E_{OX} - E_{RED}] - E_{00} + \Delta G_S \dots\dots\dots S2$$

$$E_{CS} = e[E_{OX} - E_{RED}] + \Delta G_S \dots\dots\dots S3$$

Here,  $\Delta G_{CS}$  is the Gibbs free energy changes,  $\Delta G_S$  is the static Coulombic energy,  $e$  is the electronic charge,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_S$  is the static dielectric constant of the solvent,  $R_{CC}$  is the center-to-center separation distance between the electron donor and electron acceptor in **APITB** molecule.  $R_{CC}$  was determined as 7.59 Å from DFT optimized geometry.  $R_D$  is the radius of the electron donor,  $R_A$  is the radius of the electron acceptor.  $\epsilon_{REF}$  is the static dielectric constant of the solvent used for the electrochemical studies.  $E_{OX}$  is the oxidation potential and  $E_{RED}$  is the reduction potential.  $E_{00}$  is the energy level approximated with the crossing point of UV-vis absorption and emission after normalization, which is equal to 2.34 eV.

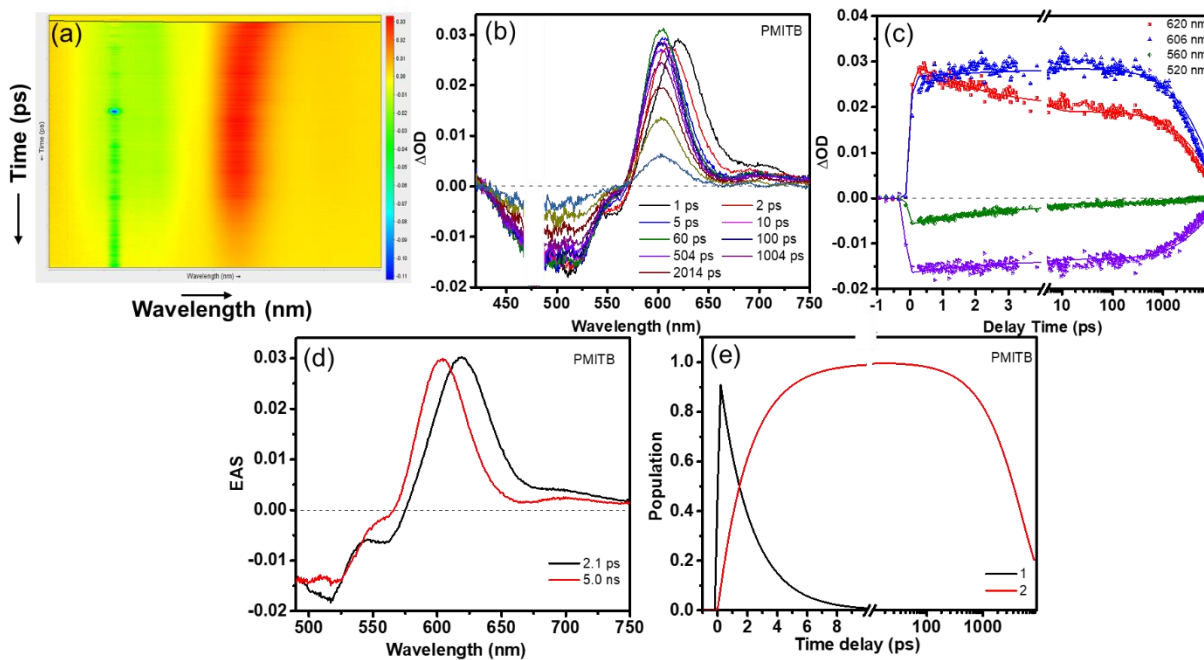
#### S4. Transient Absorption Spectroscopy

**Table S4:** GSB, SE, ESA for **PMI** in THF obtained from TA spectra

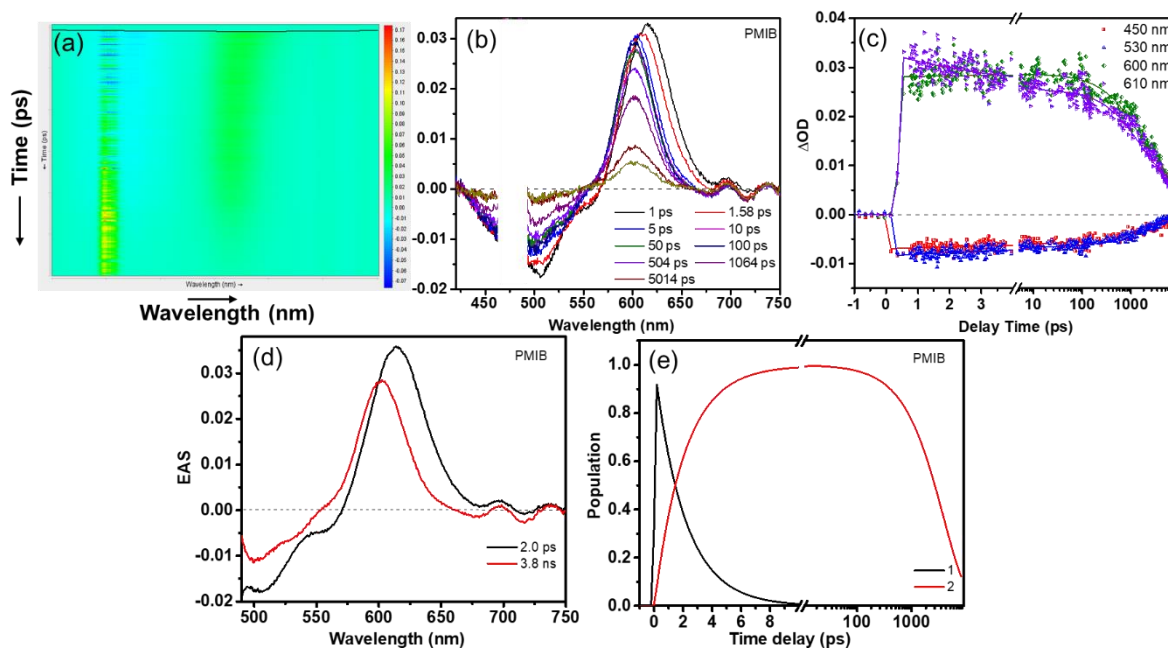
In THF	GSB (nm)	SE (nm)	ESA (nm)
<b>PMIB</b>	506	558	615→610→603→600
<b>BrPMITB</b>	500	564	651→635
<b>PMITB</b>	510	557	619→603
<b>APITB</b>	511	561→537	642→629

**Table S5:** GSB, SE, ESA for **PMI** thin films obtained from TA spectra

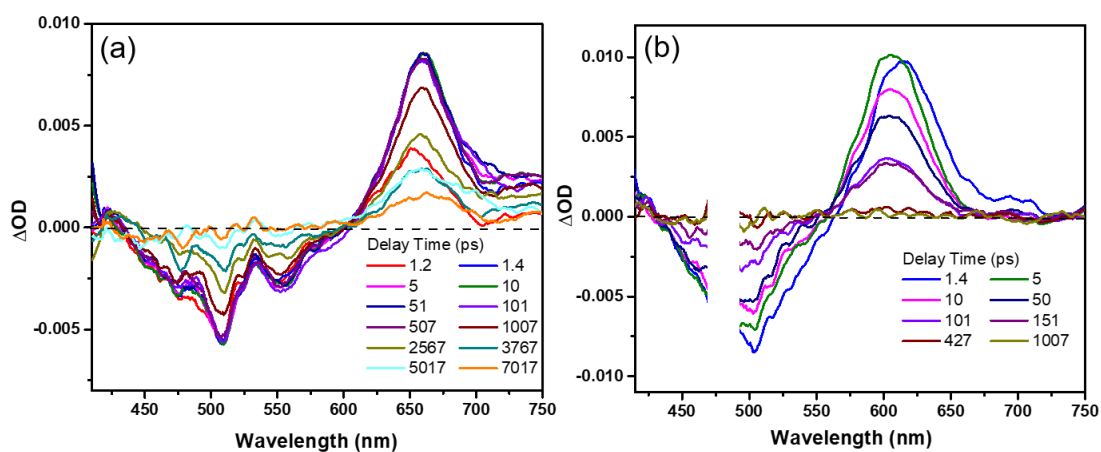
Thin Films	GSB (nm)	ESA (nm)
<b>PMIB</b>	516, 554	593 (564,572,579-750)
<b>BrPMITB</b>	528	660 (559-750)
<b>PMITB</b>	529	625 (550-750)
<b>APITB</b>	529	656 (579-750)



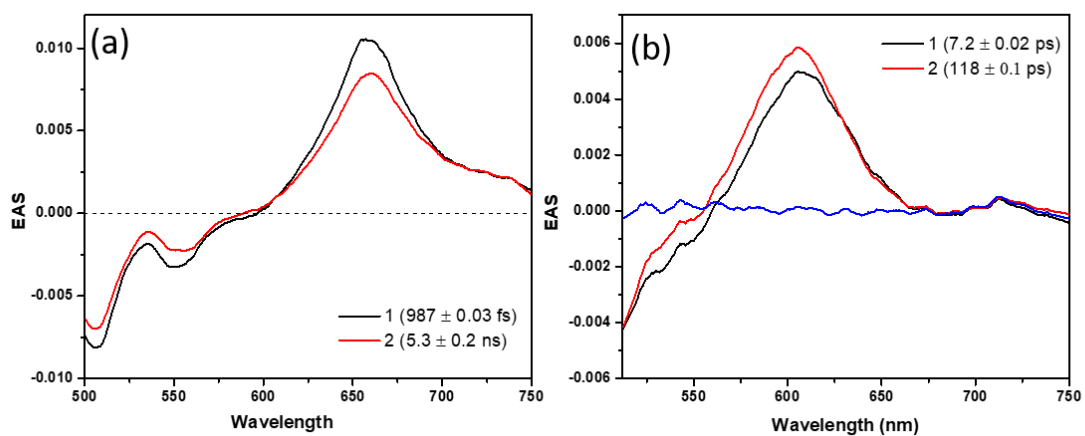
**Figure S4:** (a) Contour plot, (b) fs TA spectra using 480 nm excitation source at selected time delay, (c) kinetics at selected wavelengths, (d) Evolution-associated spectra, and (e) respective population kinetics obtained through global analysis in **PMITB** in THF.



**Figure S5:** (a) Contour plot, (b) fs TA spectra using 480 nm excitation source at selected time delay, (c) kinetics at selected wavelengths, (d) Evolution-associated spectra and (e) respective population kinetics obtained through global analysis in **PMIB** in THF.



**Figure S6:** Femtosecond TA spectra of **APITB** in (a) Hexane and (b) ACN recorded using 480 nm excitation source at selected time delay.

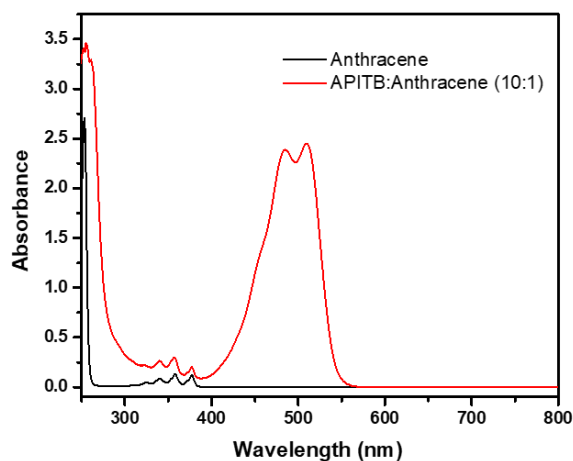


**Figure S7:** EAS spectra of **APITB** in (a) Hexane and (b) ACN.

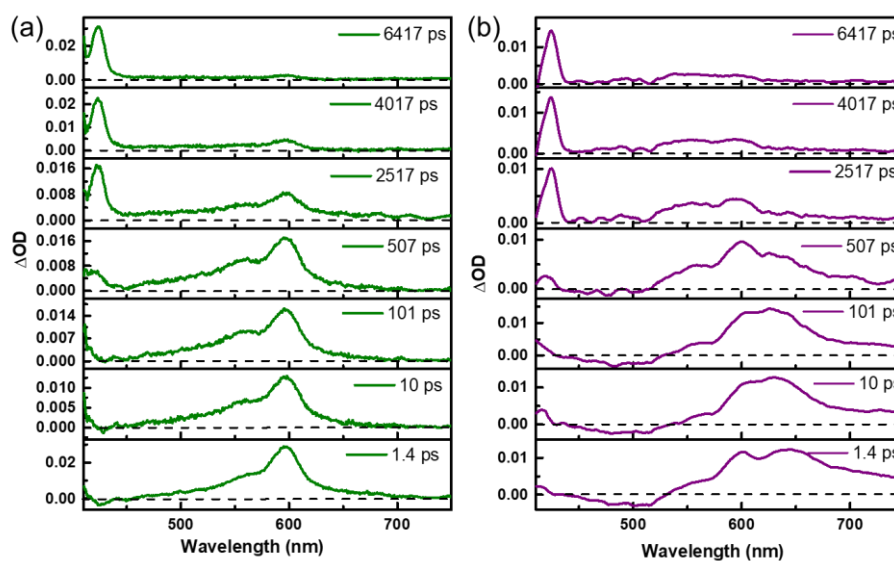
**Table S6:** Time constants obtained for **PMI** in THF from global analysis

In THF	$\tau_1$	$\tau_2$	$\tau_3$
<b>PMIB</b>	$2.0 \pm 0.3$ ps	$3.8 \pm 0.2$ ns	-
<b>BrPMITB</b>	$2.3 \pm 0.1$ ps	$5.5 \pm 0.7$ ns	-
<b>PMITB</b>	$2.1 \pm 0.2$ ps	$5.0 \pm 0.3$ ns	-
<b>APITB</b>	$2.3 \pm 0.2$ ps	$423.0 \pm 0.8$ ps	$> 7$ ns

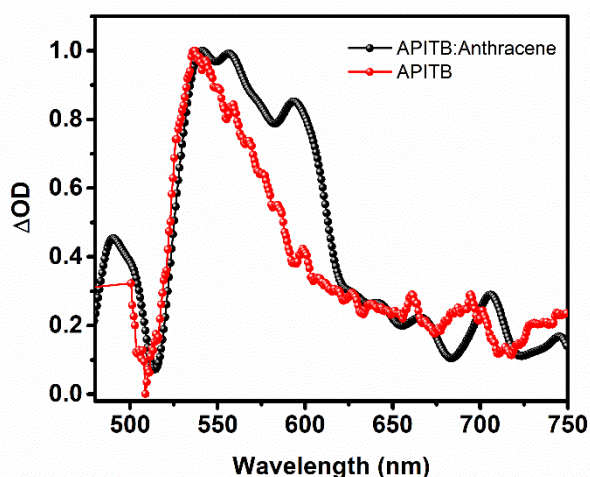
### S5. Sensitization experiments



**Figure S8:** Linear absorption spectrum of anthracene solution (black) plotted alongside the absorption spectrum of a 1:10 doped **APITB**: anthracene solution (red).



**Figure S9:** (a) Transient absorption spectra of anthracene in THF obtained using 380 nm excitation source. (b) Transient absorption spectra of **APITB**: anthracene in THF. The evolution of feature at 540 nm corresponds to the triplet formation in **APITB** using sensitizer. Over tens of picoseconds, anthracene features at 600 nm reduce in amplitude as features from **APITB**  $T_1$  state start to appear at 540 nm as a result of triplet energy transfer from anthracene to **APITB**.



**Figure S10:** Comparison of triplet spectra at 2417 ps obtained from SF (red) in **APITB** solution and triplet sensitization measurements of **APITB**:anthracene (10:1) (black) at 6417 ps. The triplet feature at 540 nm overlap for both the SF and sensitization experiments

### Triplet Quantum Yield

The triplet quantum yield of **APITB** was estimated and determined based on the femtosecond transient absorption spectra and sensitization experiments.<sup>[3,4]</sup>

The triplet quantum yield (Q.Y.) was calculated using the equation,

$$\text{Triplet Q.Y.} = \frac{[T]}{[S]}$$

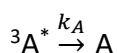
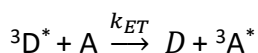
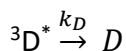
Where [T] and [S] represents the concentration of singlet and triplet states, respectively, determined directly from femtosecond transient absorption spectra using the equation,  $A = \epsilon Cl$ . The concentration is derived from the minimum of the ground state bleach and the maximum of triplet state absorption.

The molar extinction coefficient of triplet excited state ( $\epsilon_A$ ) was determined through the energy transfer method, anthracene as a triplet sensitizer. Triplet energy of anthracene (1.84

eV) is higher than the triplet energy of **APITB** (1.40 eV), making it suitable candidate for sensitizing **APITB**.

A solution of anthracene and **APITB** were mixed in a 1:10 for the sensitization experiments.

The process of triplet energy transfer involves the following steps:



Triplet lifetime of anthracene,  $\tau_D = 6376$  ps

Rate constant of triplet of anthracene,  $k_D = 1/\tau_D$

Triplet lifetime of anthracene after addition of APITB solution,  $\tau_D = 1406$  ps

Rate constant of energy transfer (ET),  $(k_{ET}[A] + K_D) = 1/1406 \text{ ps}^{-1}$

Triplet absorption of anthracene = 0.015

Triplet absorption of **APITB** at 550 nm = 0.002

The probability of energy transfer, PET was calculated using the following equation

$$\text{PET} = \frac{k_{ET}[A]}{k_{ET}[A] + K_D} = 0.788$$

The molar extinction coefficient of triplet state absorption of **APITB** was calculated using the equation,

$$\varepsilon_A = \frac{\varepsilon_D(O_{DA}/O_{DD})}{P_{ET}}$$

(Molar extinction coefficient of anthracene is  $42,000 \text{ M}^{-1} \text{ cm}^{-1}$ .)

$\Delta OD$  of GSB of **APITB** from fs TA spectra at 510 nm = 0.023

Triplet absorption at 550 nm = 0.006

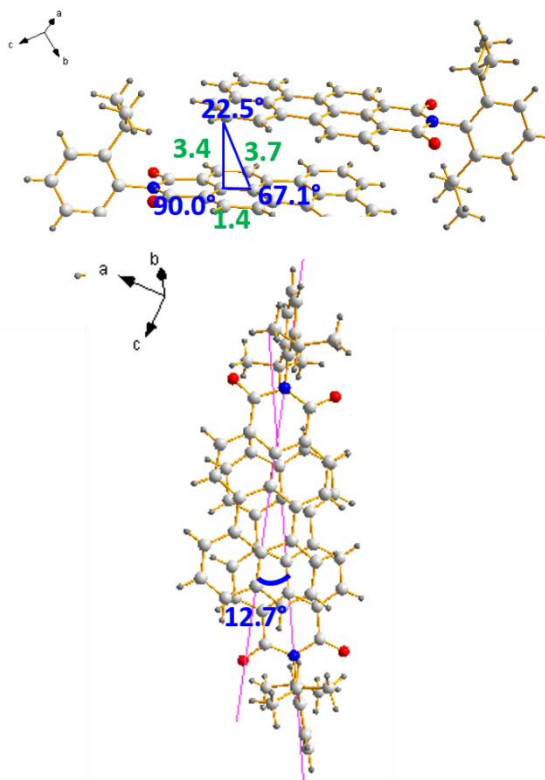
$$\text{Concentration of singlet} = \frac{\Delta OD}{\varepsilon_{@510} \times l}$$

$$\text{Concentration of triplet} = \frac{\Delta OD}{\epsilon_{@500} \times l}$$

$$\text{Triplet Q.Y.} = \frac{[T]}{[S]} = 0.59 = 59 \%$$

The triplet quantum yield of 59 % is an estimation only.

## S6. Single crystal structure



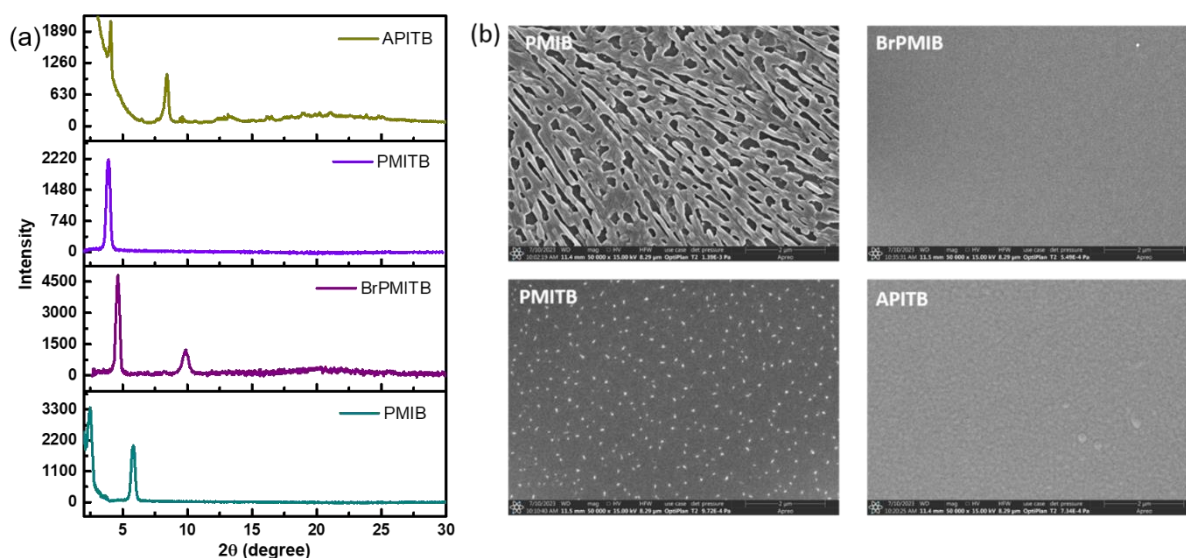
**Figure S11:** Single crystal structure of **PMIB** molecule. (Single crystal data taken from reference<sup>[1]</sup> with CCDC Deposition No. 900321)

The single crystal structures of **PMIB**<sup>[1]</sup> molecules is shown in Figure S1. The single crystal structure of **PMIB** is taken from CCDC (Deposition No. 900321). The unit cell dimensions of the **PMIB** single crystals are  $a=14.59 \text{ \AA}$ ,  $b=8.36 \text{ \AA}$ ,  $c=40.02 \text{ \AA}$ . The **PMIB** molecules in the unit cell forms a  $\pi$ -stacked assembly with a  $3.4 \text{ \AA}$   $\pi$ - $\pi$  distance. A perfect co-facial orientation was inhibited due to the introduction of isopropyl benzene group at the imide position, resulting in the long axis of the **PMIB** being rotated by  $12.7^\circ$ . The twisting has a significant impact in inhibiting excimer formation in thin films, which is a deactivation channel common in dimers.<sup>[2]</sup>



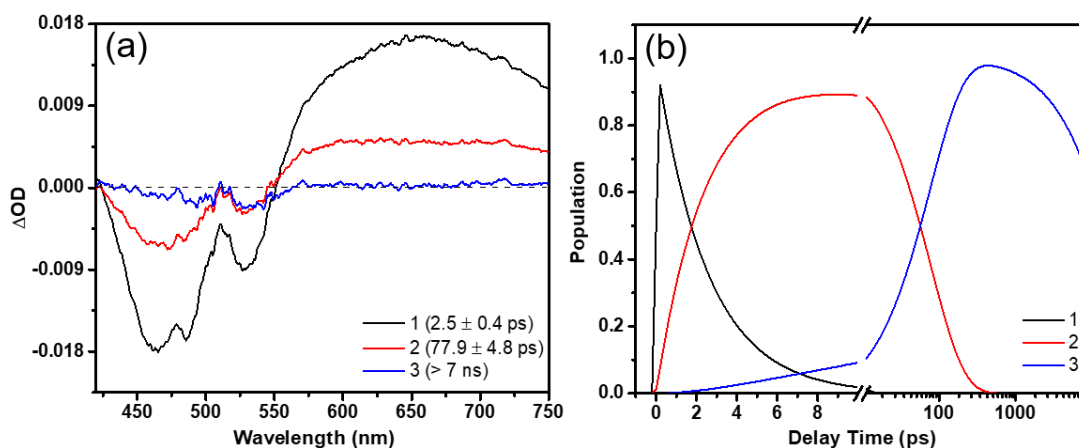
## S7. Thin Films preparation and Characterization

Thin films of **PMI** derivatives were prepared using thermal deposition method. The quartz substrates were first cleaned with detergent then ultrasonically cleaned with deionized water, isopropyl alcohol, and acetone, for 10 min each and dried in a heating oven. The substrates were fixed inside the top of the vacuum chamber using a thermal adhesive tape. Afterward, the material was placed in a metal boat and loaded inside the vacuum chamber. While deposition the pressure was kept at  $10^{-6}$  mbar. The films were deposited at a rate of 0.1-3 Å/min on quartz substrates. After the deposition the samples were cooled and collected. The thickness of the thin films was determined using ellipsometer. Characterisation were done using TF-XRD and FE-SEM techniques. TF-XRD (Figure S11a) confirms the crystalline nature of **PMI** thin films. The broad peak at  $21^\circ$  comes from the quartz substrates. The FE-SEM images are shown in Figure S11b.

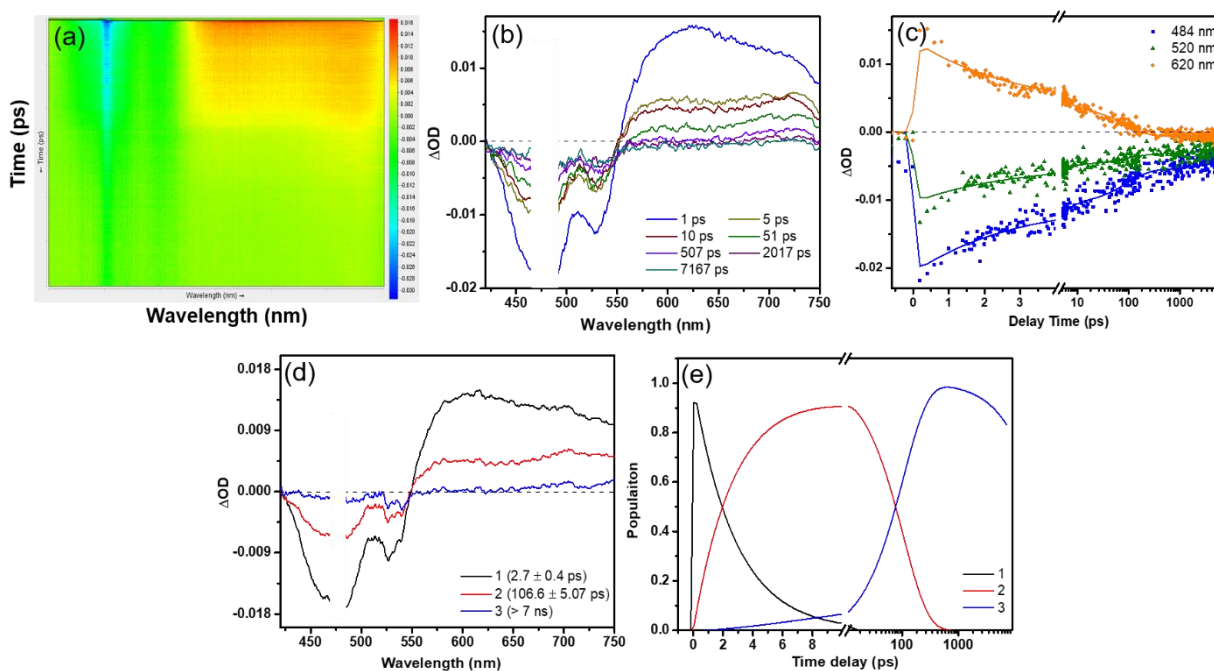


**Figure S12:** (a) TF-XRD and (b) FE-SEM plot of **PMI** thin films.

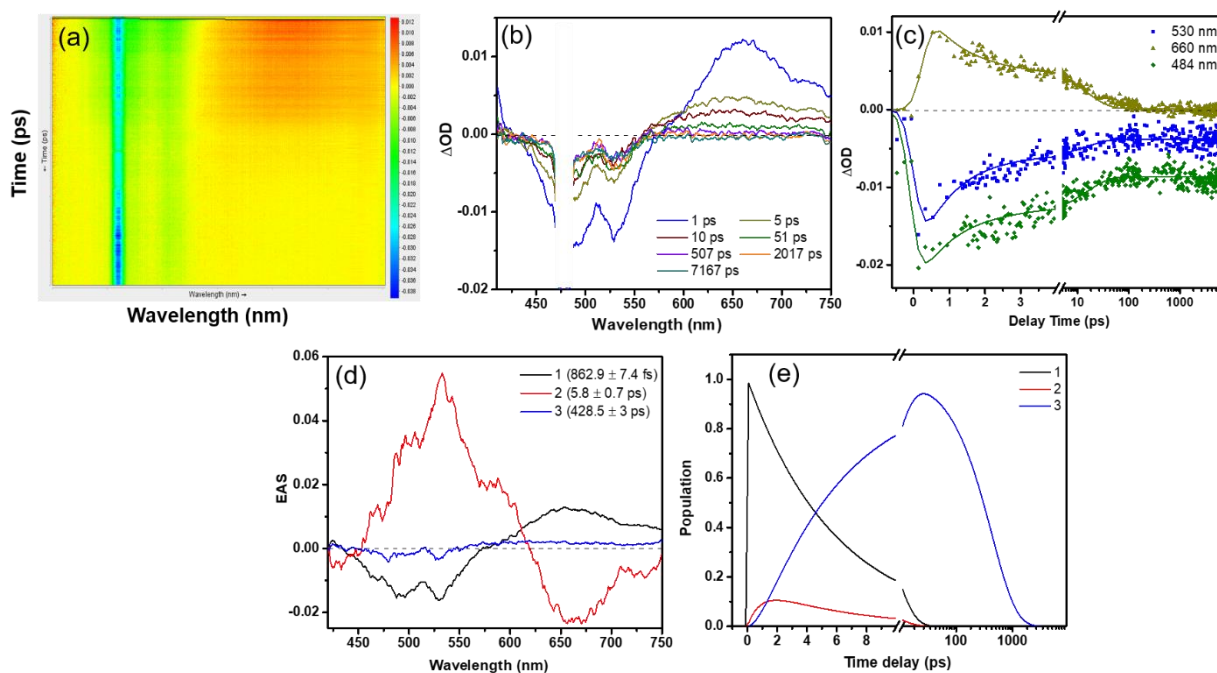
## S8. TA of thin films



**Figure S13:** (a) Evolution-associated spectra and (b) respective population kinetics obtained through global analysis in **BrPMITB** thin films.



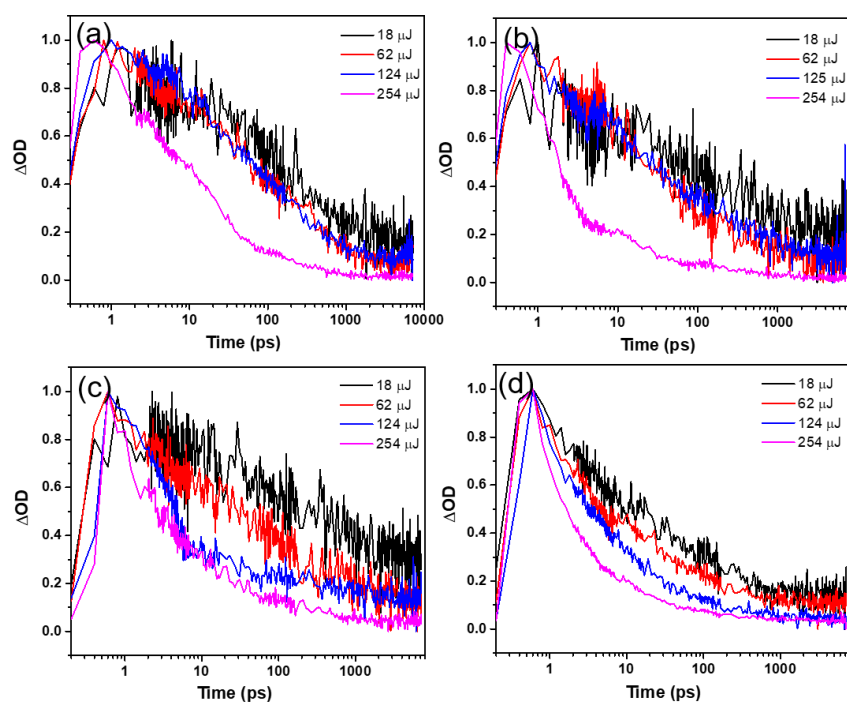
**Figure S14:** (a) Contour plot, (b) fs TA spectra using 480 nm excitation source at selected time delay, (c) kinetics at selected wavelengths, (d) Evolution-associated spectra and (e) respective population kinetics obtained through global analysis in **PMITB** thin films.



**Figure S15:** (a) Contour plot, (b) fs TA spectra using 480 nm excitation source at selected time delay, (c) kinetics at selected wavelengths, (d) Evolution-associated spectra and (e) respective population kinetics obtained through global analysis in **APITB** thin films.

**Table S7:** Time constants of **PMI** thin films obtained through global analysis

Thin Films	$\tau_1$ (ps)	$\tau_2$ (ps)	$\tau_3$	$\tau_4$
<b>PMIB</b>	$11.3 \pm 0.5$	$299.4 \pm 4.1$	$791.2 \pm 9.0$ ps	> 7 ns
<b>BrPMITB</b>	$2.50 \pm 0.4$	$77.94 \pm 4.8$	> 7 ns	-
<b>PMITB</b>	$2.79 \pm 0.4$	$106.60 \pm 5.07$	> 7 ns	-
<b>APITB</b>	$862.93 \pm 7.4$ fs	$5.89 \pm 0.7$	$428.55 \pm 3$ ps	-

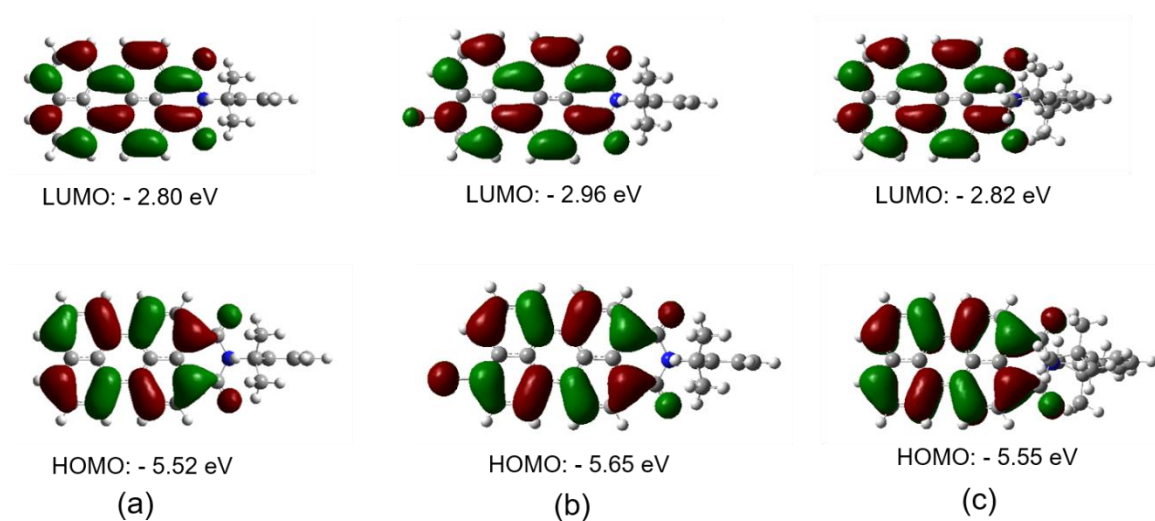


**Figure S16:** TA decay kinetics for (a) **PMIB**, (b) **BrPMITB**, (c) **PMITB**, and (d) **APITB** measured at  $\lambda_{\text{Probe}} = 600 \text{ nm}$ ,  $620 \text{ nm}$ ,  $640 \text{ nm}$  and  $650 \text{ nm}$  respectively. The kinetics are significantly influenced by the annihilation across the range of excitation fluences employed for TA.

**Table S8:** Intersystem crossing (ISC) rate of APITB in THF and PMIB thin film.

	Intersystem crossing (ISC) time, $\tau_{ISC}$ (ps)	ISC rate, $k_{ISC} = 1/\tau_{ISC}$ ( $10^9 \text{ s}^{-1}$ )
APITB in THF	$423.0 \pm 0.8$	2.36
PMIB Thin Film	$791 \pm 9.0$	1.26

## S9. Density Functional Theory calculations



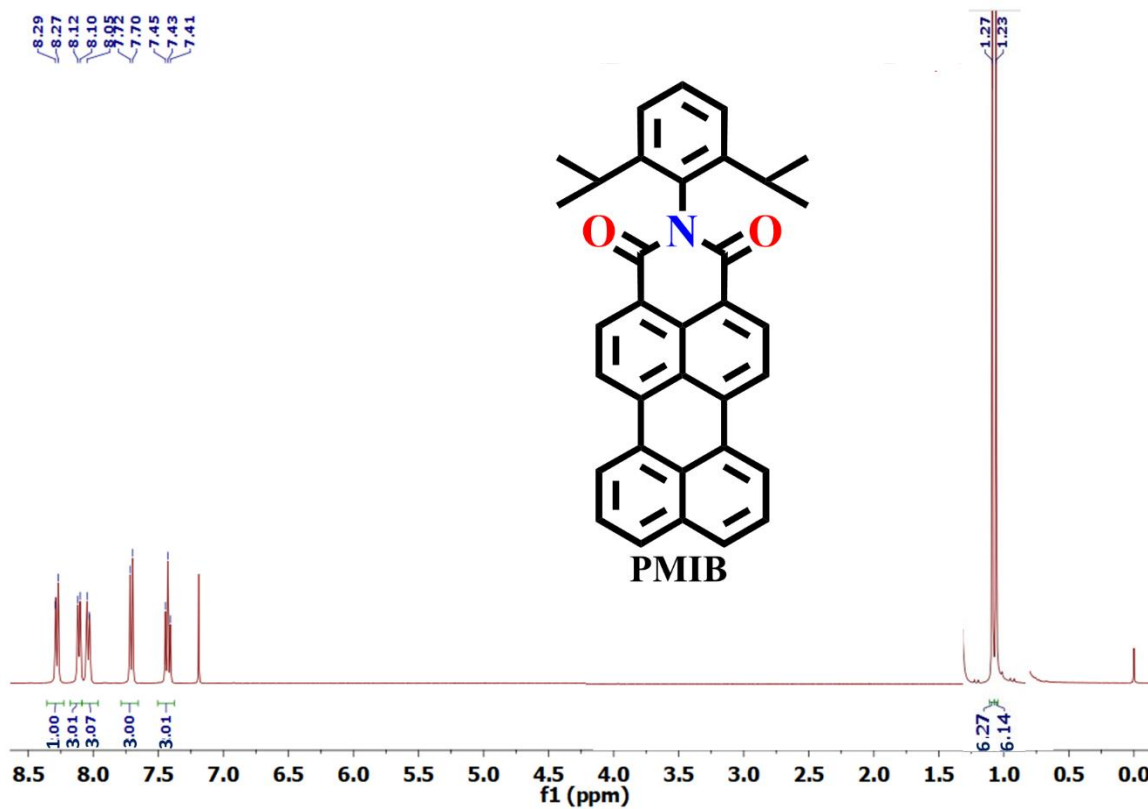
**Figure S17:** The frontier molecular orbitals of the optimized ground-state geometry for (a) **PMIB**, (b) **BrPMITB** and (c) **PMITB**.

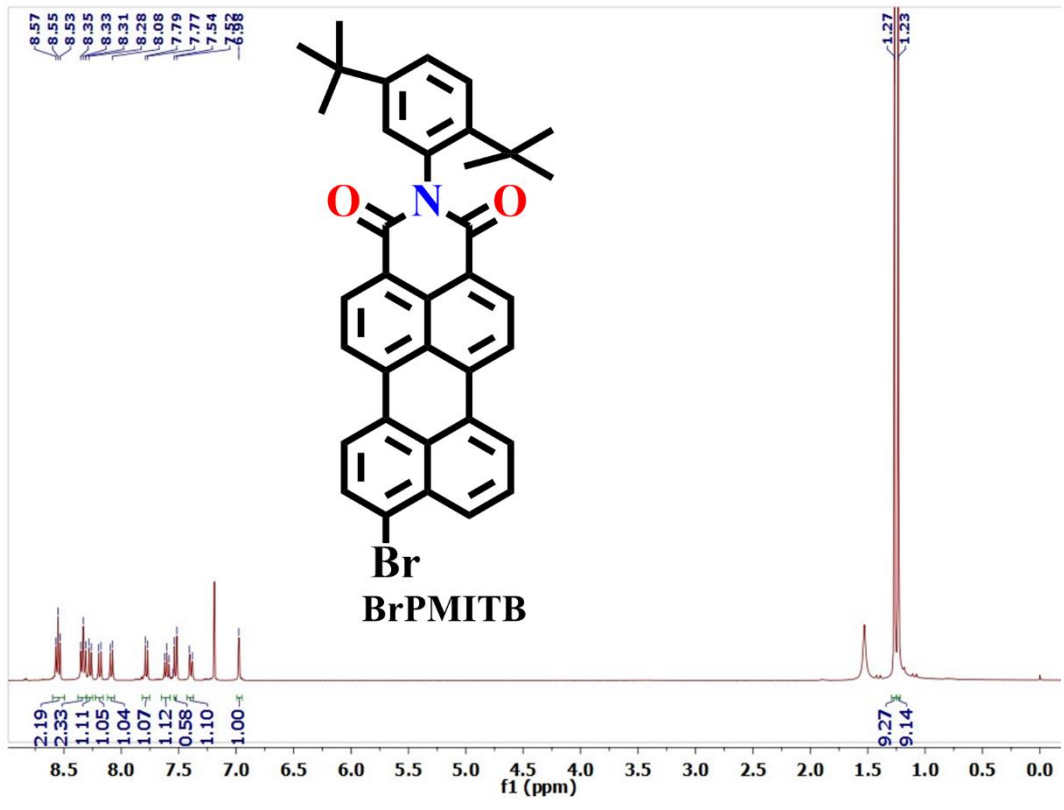
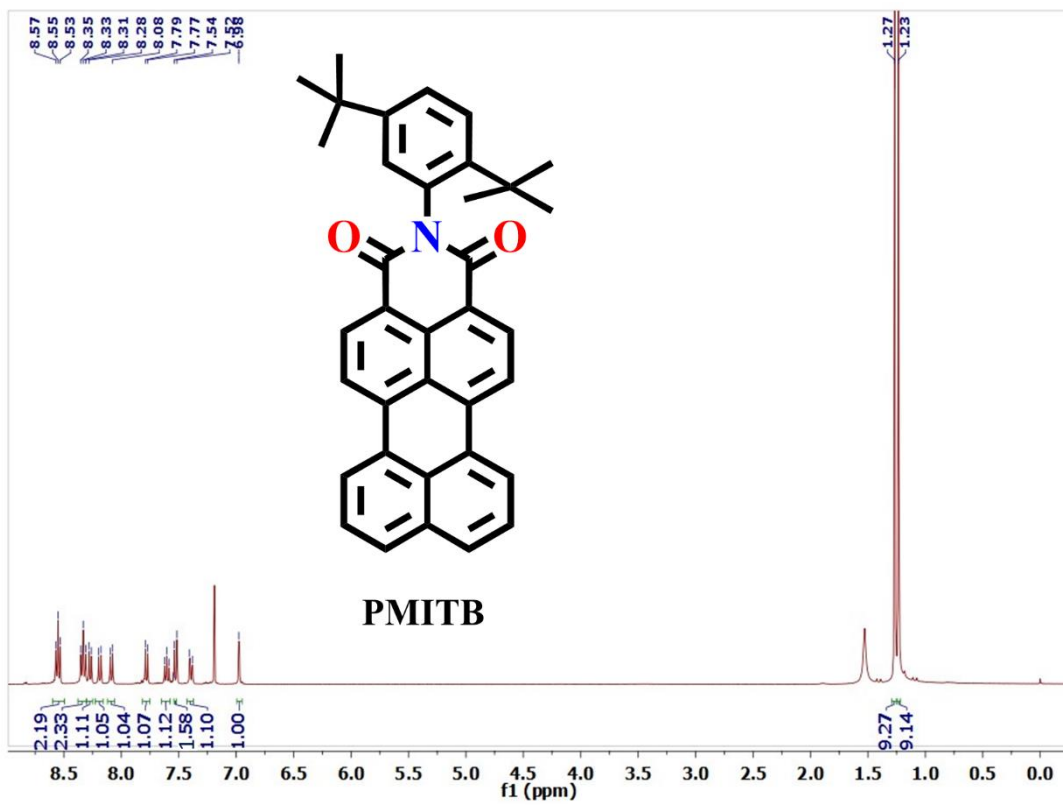
**Table S9:** The singlet and triplet energy levels calculated using TD-DFT calculation.

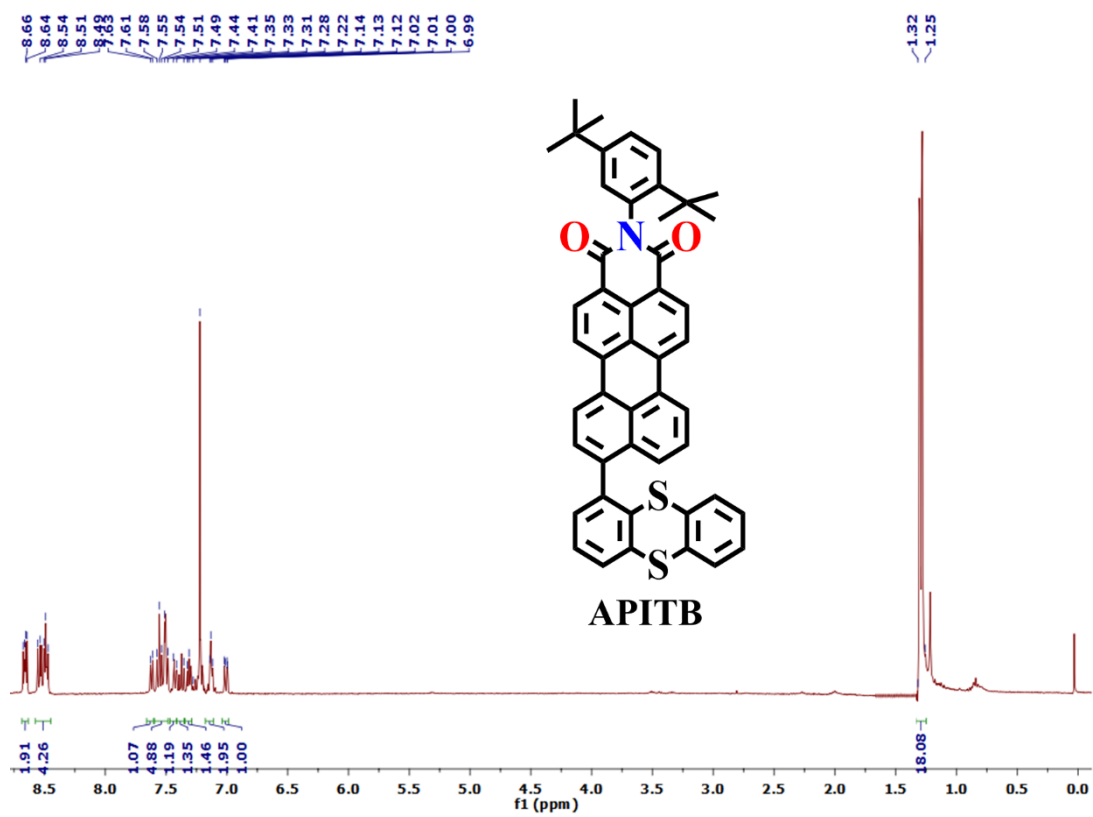
	$S_1$ (eV)	$T_1$ (eV)	$S_2$ (eV)	$T_2$ (eV)
<b>APITB</b>	2.4	1.4	2.6	2.4
<b>PMIB</b>	2.7	1.5	2.8	2.7
<b>BrPMITB</b>	2.6	1.4	2.6	2.5
<b>PMITB</b>	2.6	1.4	2.7	2.6

## Supporting Figures

### $^1\text{H}$ NMR data

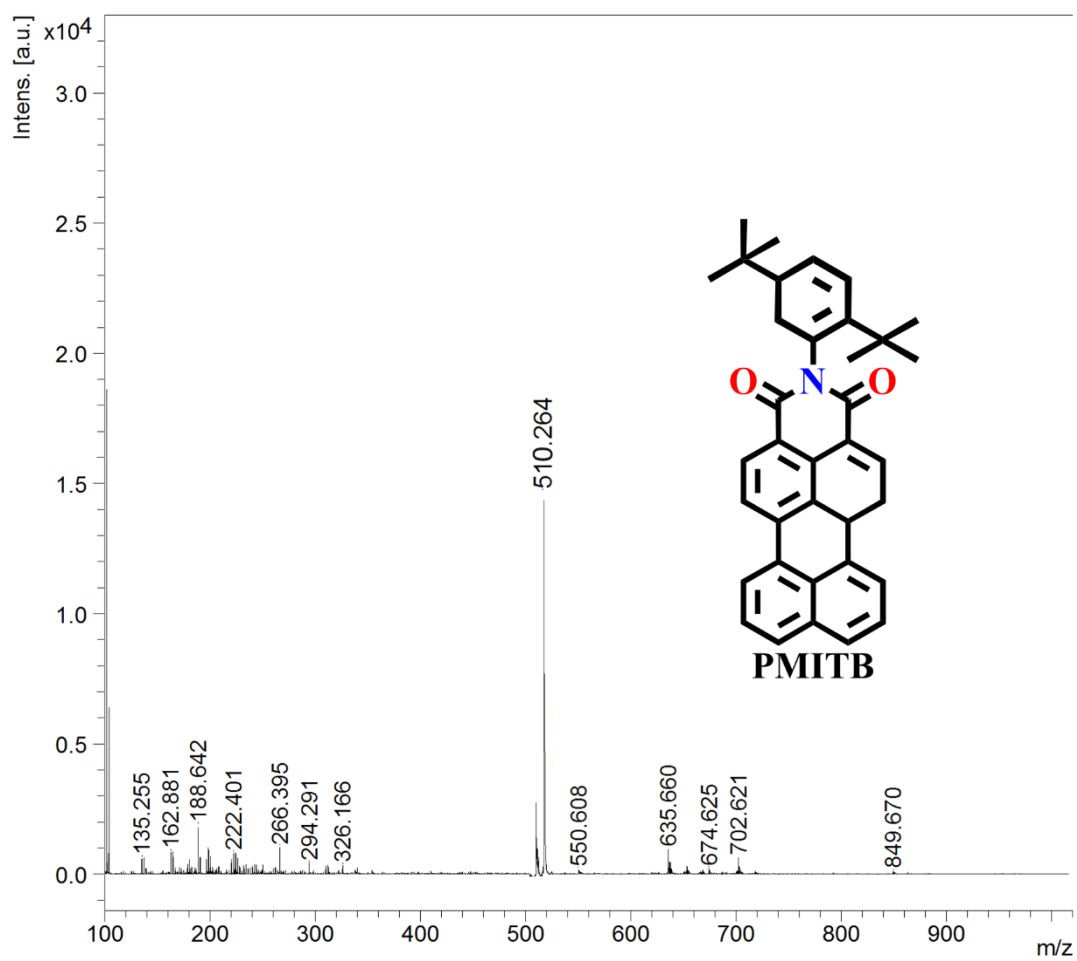
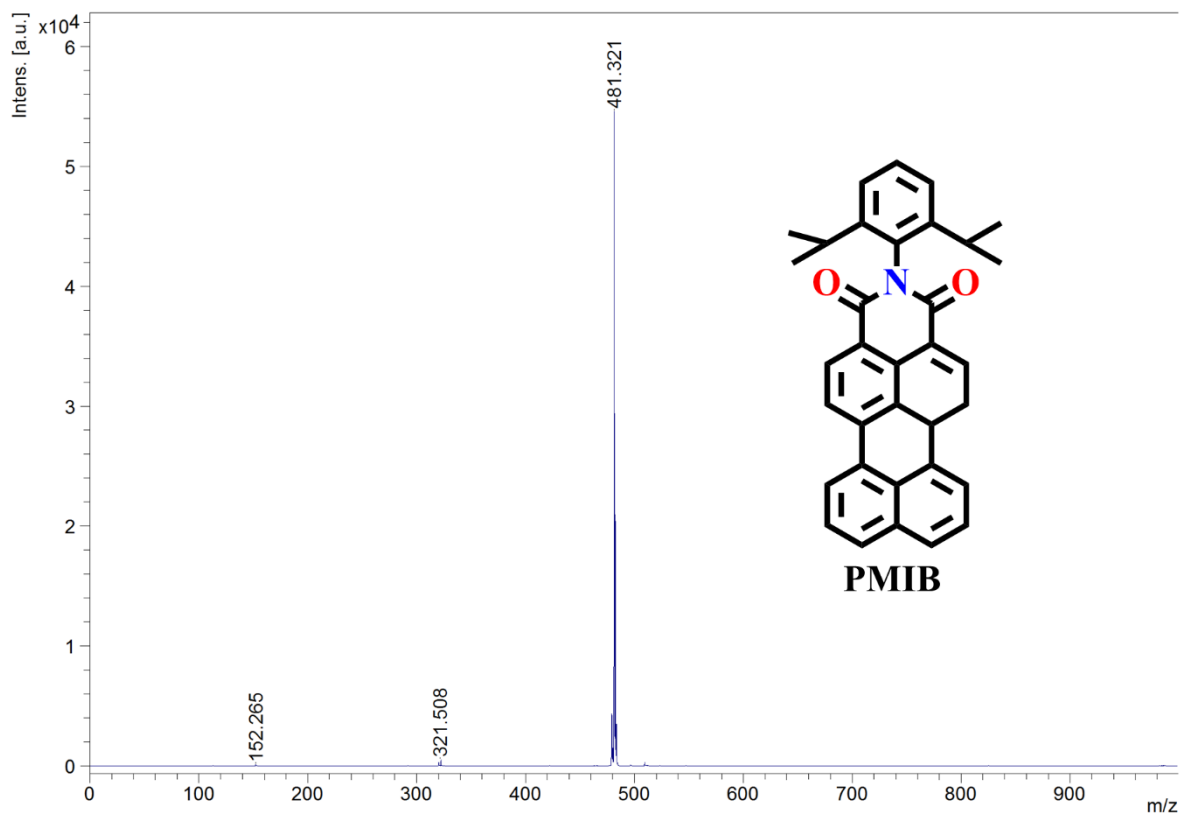


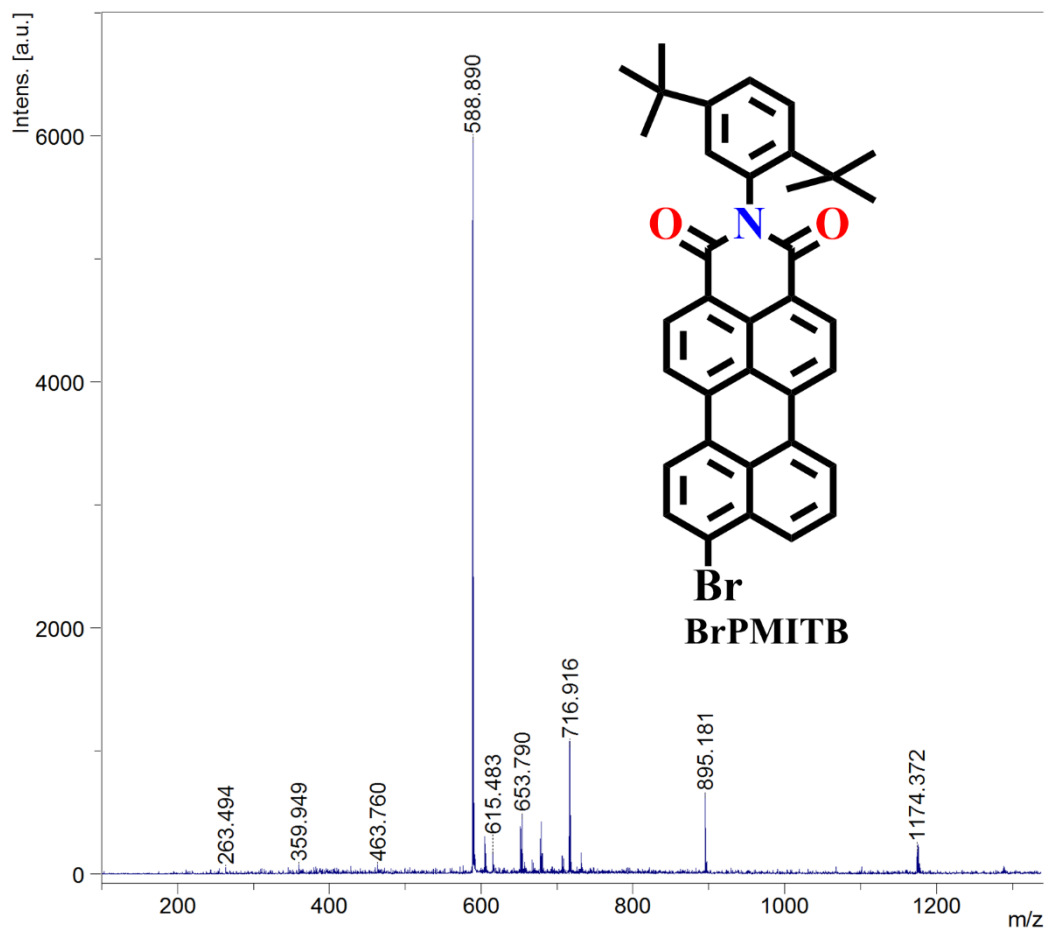


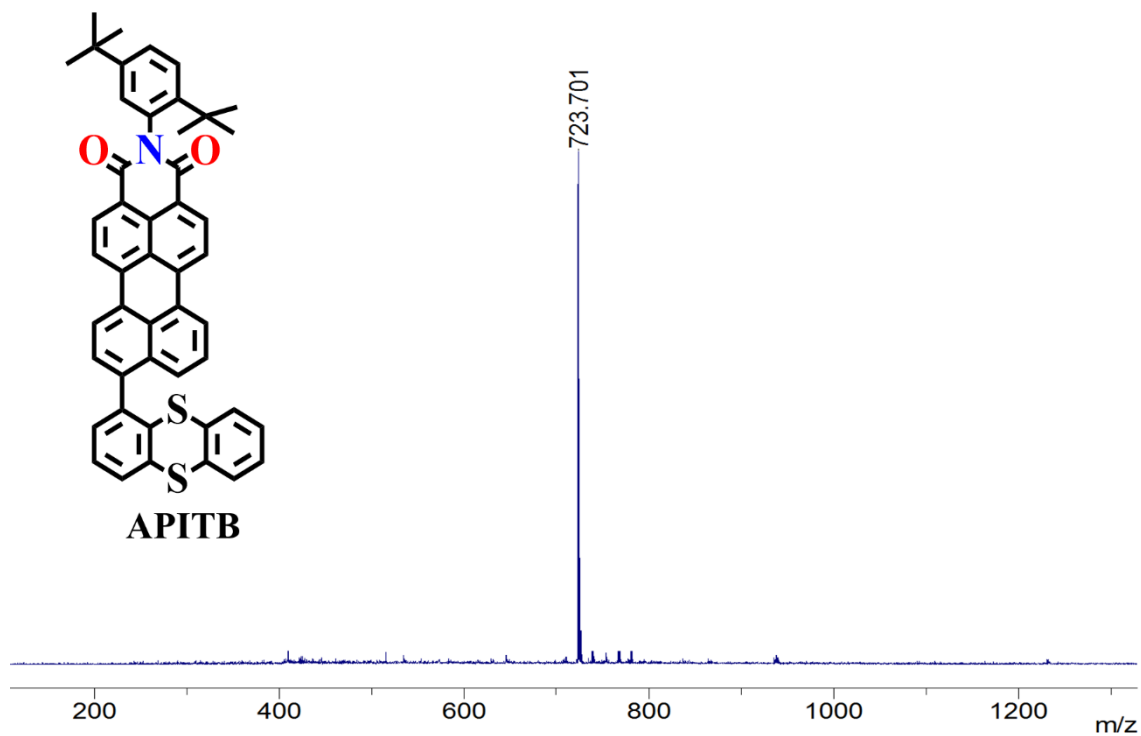


Maldi-TOF data









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*Chem. A* **2016**, *120*, 1867–1875.

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