# Supplementary Information for

# Safeguarding long-lived excitons from excimer traps in H-aggregated dye-assemblies

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## 1. Materials and methods

All reagents were purchased from Sigma Aldrich Chemical Co. and used without further purification, unless specified. Spectroscopic grade solvents were used for photophysical studies.

**NMR spectroscopy** was performed on AVANCE III 500 BRUKER spectrometer and the data were calibrated against TMS.

Mass spectrometry was carried out on Bruker Daltonics UltrafleXtreme using Matrix Assisted Laser Desorption Ionization - Time of Flight (MALDI-TOF) technique on HCCA Matrix. The sample was ionised using Smartbeam-II<sup>™</sup> laser.

**UV/Visible absorption spectroscopy** was performed on a Perkin-Elmer Lambda 35 spectrometer in a 1 cm path length cuvette. **Photoluminescence** (PL) studies were performed on a Perkin-Elmer LS55 spectrophotometer. Spectroscopy on solid samples was carried out by dispersing the sample on a quartz cover slip.

Crystallization was carried out in a 15 ml glass vial. 6 mg of compound **mX-PBI** was taken in 10 ml chlorobenzene and sonicated for 5 minutes. To the resultant deep red colored solution, 2 ml ethanol was added slowly without disturbing the chlorobenzene layer. The vial was placed in a dark, low vibration area at room temperature. After two weeks, red needle shaped crystals were formed.

Single crystal x-ray diffraction data was collected on Oxford Diffraction SuperNova diffractometer using Cu-K<sub> $\alpha$ </sub> (1.54184 Å) radiation and CrysAlisPro software. Suitable crystals of appropriate dimensions were mounted on loops in random orientations. Preliminary unit cell parameters were determined with three sets of total 10 narrow frame scans. Final cell constants were determined by global refinement of reflections from the complete data sets using the Lattice wizard module. Images were indexed and integrated (with "smart" background evaluation) using the CrysAlisPro data reduction package. Data were corrected for systematic errors and absorption using the ABSPACK module: Numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics (according to the point group symmetry using equivalent reflections). The GRAL module and the ASSIGN SPACEGROUP routine of the WinGX suite were used for analysis of systematic absences and space group determination. The structures were solved by the direct methods using SHELXT<sup>1</sup> and refined by the full-matrix least-squares on F<sup>2</sup> using SHELXL<sup>2</sup> which uses a model of atomic scattering based on spherical atoms. Calculations were mainly performed using the Olex2. Non-hydrogen atoms were refined anisotropically. The disorder present in the terminal chain was resolved using free variables and restraints on geometry and anisotropic displacement parameters.

**PL lifetime** measurements on **mX-PBI** crystals were carried out on the FLSP920 spectrometer, Edinburgh Instruments, using EPL-405 pulsed diode laser as an excitation source ( $\lambda_{ex}$  = 400 nm). Crystals were dispersed in ethanol and drop cast on a quartz slide, and cooled to 50 K in ARS cryostat with liquid helium cooling. PL lifetime of monomeric **mX-PBI** was measured in dilute chloroform solution, on a time correlated single-photon-counting setup

(Horiba Jobin Yvon IBH) that uses a picosecond pulsed laser excitation source ( $\lambda_{ex}$  = 408 nm, fwhm < 200 ps, 1 MHz repetition rate), and an MCP photomultiplier tube (Hamamatsu R3809U-50 series) based detector.

**Polarized optical microscopy** was done using Olympus optical microscope equipped with a polarizer and CCD camera. Crystals were dispersed in ethanol, drop cast on a clean glass slide and air-dried.

PL Mueller matrix measurements were performed on a home-built setup<sup>3</sup> equipped with a 540 nm diode laser (PE.B DL.405.50, Pegasus, Shanghai, China) as an excitation source, a polarization state generator (PSG) unit to generate optimized polarization states, a polarization state analyzer (PSA) unit to analyze the corresponding optimized polarization states coupled to a charged coupled device (CCD) spectrometer (Shamrock imaging spectrograph, SR-303i-A, ANDOR technology, USA) in order to spectrally resolved signal detection over a wide spectral window (550 nm-800 nm). A fixed linear polarizer (LPVIS100, Thorlabs, USA) at horizontal state and then a rotatable achromatic guarter wave retarder (WPQ10M-633, Thorlabs, USA) mounted on a computer controlled rotational mount was used to form the PSG unit. The luminescence light is collected from a single mX-PBI crystal and collimated using a lenses assembly to pass through the PSA unit. The PSA unit comprises of a rotatable achromatic quarter wave retarder and a fixed linear polarizer at vertical position. A 550 nm long-pass filter is used to filter out the excitation light and only allow the PL to pass through. Finally a lens was used to relay the emitted light to the spectrograph for recording. The recorded luminescence spectra ( $\lambda_{em}$  = 550–800 nm) for sixteen combination of the PSG and PSA were recorded sequentially by changing the fast axis of the quarter wave retarder by four optimized angles 35°, 70°, 105° and 140°. Used system was eigenvalue calibrated in order to record the complex polarization response of the excitation source, optical components used and the detector. The exact nature of the system PSG and PSA matrices ( $W(\lambda)$  and  $A(\lambda)$ , respectively) and their wavelength response was obtained from eigenvalue calibration.<sup>4</sup> For constructing PL Mueller matrices, the generator matrix  $W(\lambda)$  for 540 nm excitation wavelength and analyzer matrix  $A(\lambda)$  for emission wavelengths (550 nm–800 nm) were used.

**Polarization dependent absorption spectroscopy** on single microcrystals was carried out in a home-built microscopy setup that uses a 35 W xenon lamp (Ocean Optics HPX-2000) as the light source. Incident light is guided through an optical fibre assembly to the sample. Appropriate incident polarization was selected using a linear polarization sheet fixed on a rotation mount, and placed between the fibre cable output and the sample stage. The sample was prepared by casting mX-PBI crystals on a clean class coverslip. The transmitted light through the sample was collected using a long working distance (10.6 mm) objective (Olympus LMPLFLN50X), focussed through a lens assembly into the entrance slit of an imaging spectrometer (Andor Shamrock SR500I-B2) fitted with an electron-multiplying-CCD camera (Andor Ixon 897). Transmission spectra were recorded using a 300 lp/mm grating over 400-700 nm wavelength range, once through a single mX-PBI crystal on glass coverslip,  $I_t(\lambda)$  and also through the coverslip alone,  $I_0(\lambda)$ . The absorbance A was calculated using the formula:  $A = \log_{10}(I_0/I_t)$ .

#### 2. Syntheses and Characterization

#### Compound 1

Perylene monoimide was synthesized following a previously reported procedure.<sup>5</sup>

#### Compound mX-PBI



(a) 3-methylbenzylamine, Imidazole, 130 °C, Ar, 8h

In a 100 ml round-bottom flask, 859 mg (1.5 mmol) of compound **1** and 5 g imidazole were taken, stirred under Ar atmosphere at 130 °C for 30 min. until the mixture turned into a clear solution. To this, 3-methylbenzylamine 187  $\mu$ L (1.5 mmol) in 2 ml n-butanol was slowly added with stirring. The reaction mixture was refluxed under argon at 130 °C for 6 h, cooled to room temperature, 30 ml EtOH and 50 ml 2N HCl solution was added to it and stirred for 12 h. The reaction mixture was filtered to obtain a red precipitate that was washed with cold methanol and water, and further purified using column chromatography (Silica gel 100-200 mesh) (Yield : 0.200g, 85.0 %). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, TMS):  $\delta$  (ppm) = 0.81 (6H, t, *J* = 7.5Hz), 1.24 (16H, m), 1.87 (2H, m), 2.24 (2H, m), 2.33 (3H, S), 5.16 (1H, m), 5.31 (2H, s), 7.06 (1H, d, *J*= 10Hz,), 7.24 (1H, t, *J*=10Hz,), 7.37 (2H, s), 8.34-8.61 (8H, dd,); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  (ppm) = 163.22, 138.15, 136.97, 131.42, 129.74, 128.38, 123.05, 114.05, 54.85, 43.66, 32.38, 31.76, 29.67, 29.23, 26.96, 27, 22, 21, 14. MS (MALDI-TOF): calculated for [C<sub>45</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>], 676.8419, found 676.529.



Figure S1. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298K) spectrum of mX-PBI.



Figure S2. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 298K) of mX-PBI.



Figure S3. <sup>1</sup>H COSY spectrum of mX-PBI.



Figure S4. MALDI-TOF spectrum of mX-PBI.

Formula	$C_{45} H_{44} N_2 O_4$
Temperature (K)	293
Wavelength ( Å )	1.54184
Crystal System	Monoclinic
Space Group	P2 <sub>1</sub> /c
Ζ΄, Ζ	4, 4
a( Å )	27.378(16)
b( Å )	16.404(6)
c( Å )	8.074(4)
α()	90
β()	96.11(5)
γ()	90
Volume (Å <sup>-3</sup> )	3605.6(3)

Table S1. Crystallographic parameters of mX-PBI

#### 3. Additional Figures



**Figure S5.** PL spectrum of **mX-PBI** crystal when compared against that of monomer in CHCl<sub>3</sub> solution shows similar spectral width.



Figure S6. PL decay (left) of mX-PBI crystal monitored at 4 different emission wavelengths (right).

#### Calculation of transition dipole moments for $E_0 \mathcal{D} E_1$ and $E_0 \mathcal{D} E_2$ transitions

In PBI, the  $S_0$ - $S_1$  transition is polarized along the long-axis, along the line joining the two imide N atoms. The cartesian coordinates of N atoms for a pair of  $\pi$ -stacked PBI molecules (N<sub>1</sub>, N<sub>2</sub>, N<sub>3</sub> and N<sub>4</sub>) were used to determine the orientation of two molecular transition dipole moment ( $M_A$ ,  $M_B$ ). The vectors  $M_A$  and  $M_B$  were normalized, such that  $|M_A| = |M_A| = 1$ . Transition dipole moments for  $E_0 \gamma_D E_2$  and  $E_0 \gamma_D E_1$  transitions in the crystal were evaluated from the sum ( $M_A$ + $M_B$ ) and difference ( $M_A$ - $M_B$ ), respectively.



**Figure S7.** A pair of PBI molecules stacked along the *c* axis of the crystal. Cartesian coordinates of N atoms, N<sub>1</sub> and N<sub>2</sub> define the  $S_0$ - $S_1$  transitional dipole moment of molecule A ( $M_A$ ). Likewise N<sub>3</sub> and N<sub>4</sub> coordinates define  $M_B$ . Both  $M_A$  and  $M_B$  are normalized to 1. Transition dipole moments for  $E_0$   $\gamma_0$ ,  $E_2$  and  $E_0$   $\gamma_0$ ,  $E_1$  transitions are given by:  $M_A + M_B$ , and  $M_A - M_B$ , respectively. The unit vectors  $\hat{i}$ ,  $\hat{j}$  and  $\hat{k}$  are along *a*, *b* and *c* axes, respectively.



**Figure S8.** The strongest noncovalent interaction is  $\pi$ -stacking along the *c* axis. Along the *b* axis, there are weaker C– H···O and C–H···H–C interactions (green dotted line) between PBI molecules of neighbouring unit cells. There are no noncovalent interactions along the *a* axis. Based on this, we conclude that **mX-PBI** crystal has a preferred growth axis along the *c* direction. Crystal growth along the *b* axis is comparatively less that gives rise to the width of the crystal. And the least preferred direction of growth is along the *a* direction, which contributes to the crystal thickness. Consequently, **mX-PBI** crystals have a belt-shaped morphology.



Figure S9. A high magnitude of the net depolarization coefficient ( $\Delta > 0.95$ ) determined from the PL Mueller matrix (presented in Figure 3a) confirms the strong depolarizing nature of PL process. Depolarization is primarily caused by multiple scattering of incident as well as the emitted light. Low magnitudes of off-diagonal matrix elements  $M_{23}$ ,  $M_{32}$ ,  $M_{24}$ ,  $M_{42}$ ,  $M_{34}$  and  $M_{43}$  confirm the strong dephasing nature of the PL process.



**Figure S10.** Inter-stack exciton delocalization. There are 6 pairs of short-range C···O interactions (3.23–3.65 Å) between the PBI molecules on adjacent  $\pi$ -stacks (green dashed lines). At such distances there can be a finite HOMO-LUMO overlap<sup>6</sup> that may delocalize the exciton wavefunction across the stacks.

# 4. References

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