

## Supplementary Information

### Perylene diimide with solid-state NIR luminescence for imaging of latent fingerprints (sweat pores)

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#### **Experimental Details**

##### ***Preparation of PDI 2–SiO<sub>2</sub> powder for visualization of LFPs***

PDI 2 and nano porous silica were mixed in different proportions (*w/w*), for example 5, 10, 30 and 50% of PDI 2 in 95, 90, 70 and 50% nano porous silica, in CHCl<sub>3</sub> (5 mL) and mixture was stirred for 30 mins. Subsequently, the mixture was grinded with pestle and mortar to make uniform mixture. The photograph of each mixture (*w/w*) was captured using high pixel camera. The quantum yield was calculated for each mixture (*w/w*) using integrated K-sphere method.

##### ***Development and Imaging of LFPs***

All the LFPs reported in this report were collected from different volunteers aged 18–25 years with their consent. After proper cleaning and drying, sebum rich thumb or finger impressions were collected on various substrates including glass, paper, plastic, leaf, currency, painted metal, compact disk, coin and stainless steel. We have developed these LFPs using PDI 2 powder alone and with nano porous silica powder with 10%, and 30% doping of PDI 2 using powder-dusting method. The powder was uniformly scattered or applied onto the LFPs. Immediately, the excess powder was gently removed by smooth horizontal shaking followed by removal of powder using fine brush. The developed LFPs were visualized either in daylight and under 365 nm UV lamp. The photographs of these LFP were captured by high pixel camera.

##### ***Preparation of samples for DLS and AFM***

The DMSO and HEPES Buffer were filtered through a Millipore membrane filter (Acrodisc syringe filter, 0.2 μm, Supor membrane) to prepare solutions for DLS measurements. The solutions of different concentrations of PDI 2 in binary mixtures of H<sub>2</sub>O–DMSO were prepared and samples were kept for 10 min for thermal equilibration before each measurement for recording DLS. The same solutions were used

to drop-cast the thin films on glass slide for recording the AFM data. The same glass slides were visualized under optical microscope.

### ***Materials and Methods***

Perylene tetracarboxylic dianhydride (PTCDA), 3-aminopentane, propargyl alcohol,  $K_2CO_3$  and  $Br_2$  were obtained from Sigma Aldrich (Merck), Tokyo Chemical Industries and Spectrochem Pvt. Ltd. India and used without further purification. The solvents such as DMSO, DMF, Ether, Acetone, THF,  $CHCl_3$ , Ethyl Acetate, toluene, methyl cyclohexane, hexane, MeOH,  $iBuOH$ ,  $CH_3CN$  and water were of HPLC or AR grade. All reactions were performed under  $N_2$  stream. The progress of the reactions was monitored through thin layer chromatography (TLC). The aluminium sheets coated with silica gel 60 F254 (Merck, Darmstadt, Germany) were used as TLC plates. The column chromatography was performed on silica gel 60-120 mesh for purification of organic compounds. The chloroform was distilled before use in organic synthesis and column chromatography.

### ***Instrumentations***

The Nuclear Magnetic Resonance (NMR) Spectroscopy for proton ( $^1H$ ) and carbon ( $^{13}C$ ) nuclei was performed on BRUKER Biospin AVANCE-III FT-NMR HD-500 and Bruker AVANCE-II FT-NMR AL 400 spectrometers. The NMR peak values are reported in ppm ( $\delta$ ) and coupling constant  $J$  values in Hz. Tetramethyl silane (TMS) was used as an internal standard reference and spectrum were recorded in  $CDCl_3$ . The abbreviations reported for spin multiplicities are s = singlet, d = doublet, and m = multiplet. The UV-Vis experiments were carried out on Cary 5000 UV-VIS-NIR spectrophotometer equipped with Peltier system as temperature controller. The absorbance of various solutions was recorded in quartz cells with 1 cm path length, 2 nm band width and  $140\text{ nm min}^{-1}$  scan rate. The emission experiments were performed using RF 6000 SHIMADZU Spectrofluorophotometer instrument. FT-IR (ATR) spectra were recorded on Perkin Elmer 92035 spectrometer. The wide-angle X-ray diffractions (WXRDs) were measured on a Rigaku diffractometer using  $CuK_\alpha$  ( $\lambda = 1.54\text{ \AA}$ ) emission and spectra were reported in the ( $\theta$ ) range of  $5\text{-}50^\circ$ . The Ni filter was applied to use radiations for spectrum measurement and Bragg Brentano geometry with a flat holder was used for data collection. The thermogravimetric (TGA) studies for PDI **2** and **3** were carried out using HITACHI STA7200 instrument. AFM micrographs of PDI **2** were recorded on Tosca 400 instrument designed by Anton Paar. Dynamic light scattering experiment was recorded using a light scattering apparatus, Nano-ZS, Malvern Instruments (Malvern, U.K.) at  $25.0 \pm 0.1^\circ C$ .

### ***Synthesis of PDI 2 and PDI 3***

To a solution of PDI **1** (50 mg, 0.079 mmol) in  $CHCl_3$  (30 ml),  $Br_2$  (2.5 ml in 50 ml  $CHCl_3$ , 48.5 mmol) was slowly added and reaction mixture was stirred for 2.5 h at  $0^\circ C$ . The progress of the reaction was monitored by TLC performed in  $CHCl_3$ : hexane (7:3, v/v) binary mixture. After this time interval,

Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> was added to quench the bromine and the organic residue was extracted with chloroform. The chloroform layers were collected after washing with brine solution, dried over Na<sub>2</sub>SO<sub>4</sub> and chloroform was evaporated on rotary to afford crude residue. The crude residue was purified by using column chromatography on SiO<sub>2</sub> using chloroform: hexane (7:3 v/v) as mobile phase. Firstly, PDI **3** was eluted as fraction 1 in 21% yield and R<sub>f</sub> = 0.63. Afterwards, PDI **2** was collected in 47% yield, R<sub>f</sub> = 0.38.

**PDI 2** (dark red); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C): δ 9.68 (d, 1H, *J* = 8.4 Hz, perylene ArH), 8.69–8.61 (m, 5H, perylene ArH), 8.46 (s, 1H, perylene ArH), 6.93 (s, 2H, -OCH<sub>2</sub>), 5.42 (s, 1H, vinylic CH), 5.11-5.01 (m, 2H, ethylpropyl), 2.32- 2.20 (m, 4H, CH<sub>2</sub>, ethylpropyl), 1.99-1.88 (m, 4H, CH<sub>2</sub>, ethylpropyl), 0.94-0.90 (m, 12H, CH<sub>3</sub>, ethylpropyl) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C) δ 156.09, 134.35, 134.18, 134.79, 129.50, 129.21, 128.54, 126.97, 125.03, 123.57, 122.14, 121.92, 118.84, 109.19, 70.43, 57.87, 57.60, 25.06, 11.39, 11.38 ppm; IR (ATR): ν = 3079, 2960, 2922, 2855, 2363, 1692, 1655, 1588, 1402, 1327, 1245, 1200, 1066, 984, 805, 746, 656, 447 cm<sup>-1</sup>; HRMS (*m/z*) found 781.4058 [M+K]<sup>+</sup>; calcd 781.1661 [M+K]<sup>+</sup> for [C<sub>37</sub>H<sub>32</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>5</sub>K]<sup>+</sup>; 568.5069 (C<sub>34</sub>H<sub>29</sub>N<sub>2</sub>O<sub>5</sub>Na<sup>+</sup>) due to inductive cleavage of the aromatic ether.

**PDI 3**: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) δ 9.63 (d, 1H, *J* = 8 Hz, perylene ArH), 9.55 (d, 1H, *J* = 8 Hz, perylene ArH), 8.95 (s, 1H, perylene ArH), 8.72 (d, 1H, *J* = 8 Hz, perylene ArH), 8.64 (d, 1H, *J* = 7.5 Hz, perylene ArH), 8.51 (s, 1H, perylene ArH), 6.94 (s, 1H, vinylic CH), 5.41 (s, 2H, -OCH<sub>2</sub>), 5.13-5.05 (m, 2H, ethylpropyl), 2.33- 2.25 (m, 4H, CH<sub>2</sub>, ethylpropyl), 1.99-1.93 (m, 4H, CH<sub>2</sub>, ethylpropyl), 0.97-0.93 (m, 12H, CH<sub>3</sub>, ethylpropyl) ppm; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, 25 °C) δ 155.7, 133.8, 132.9, 132.8, 129.4, 129.2, 128.8-128.78, 127.5, 125.8, 124.2, 121.3, 119.8, 118.8, 113.4, 109.0, 70.4, 57.8, 29.7, 25.0, 24.9, 11.3 ppm; IR (ATR): ν = 3168, 3071, 2967, 2929, 2877, 2363, 2333, 2117, 1699, 1655, 1513, 1454, 1402, 1372, 1327, 1238, 1200, 1066, 984, 917, 895, 857, 805, 701, 649, 611, 552, 514, 418 cm<sup>-1</sup>.

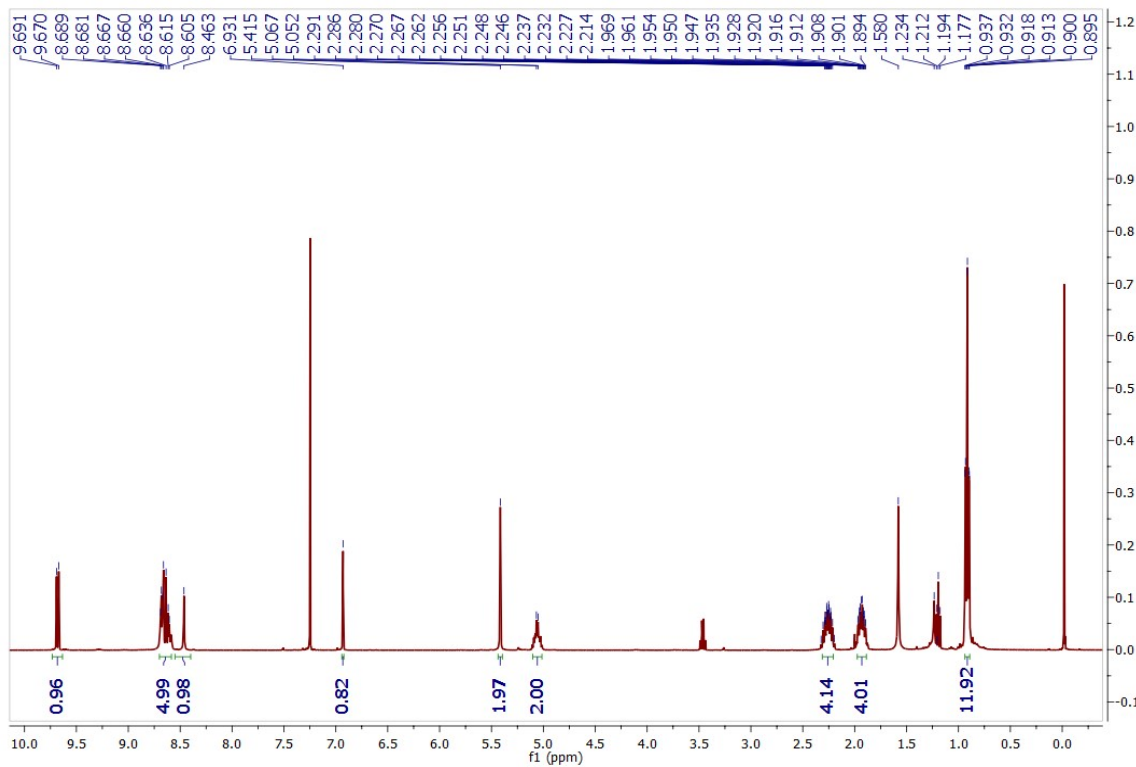


Figure S1a:  $^1\text{H}$  NMR spectrum of PDI 2.

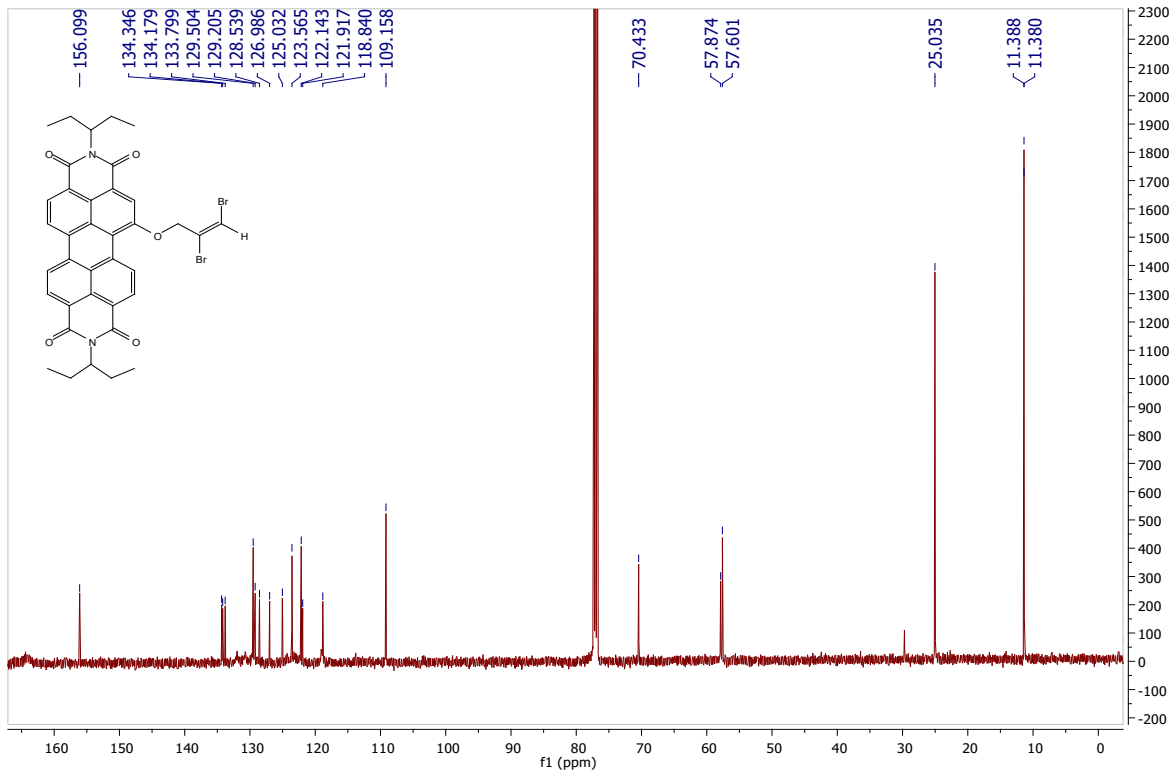
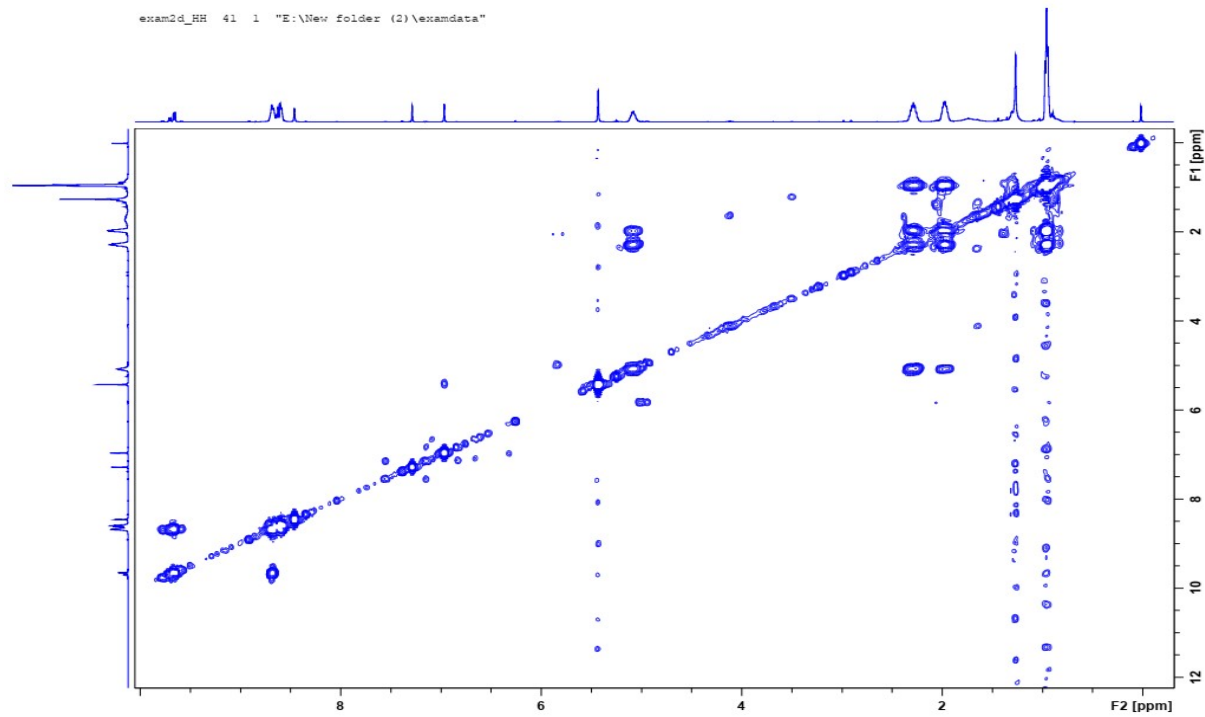
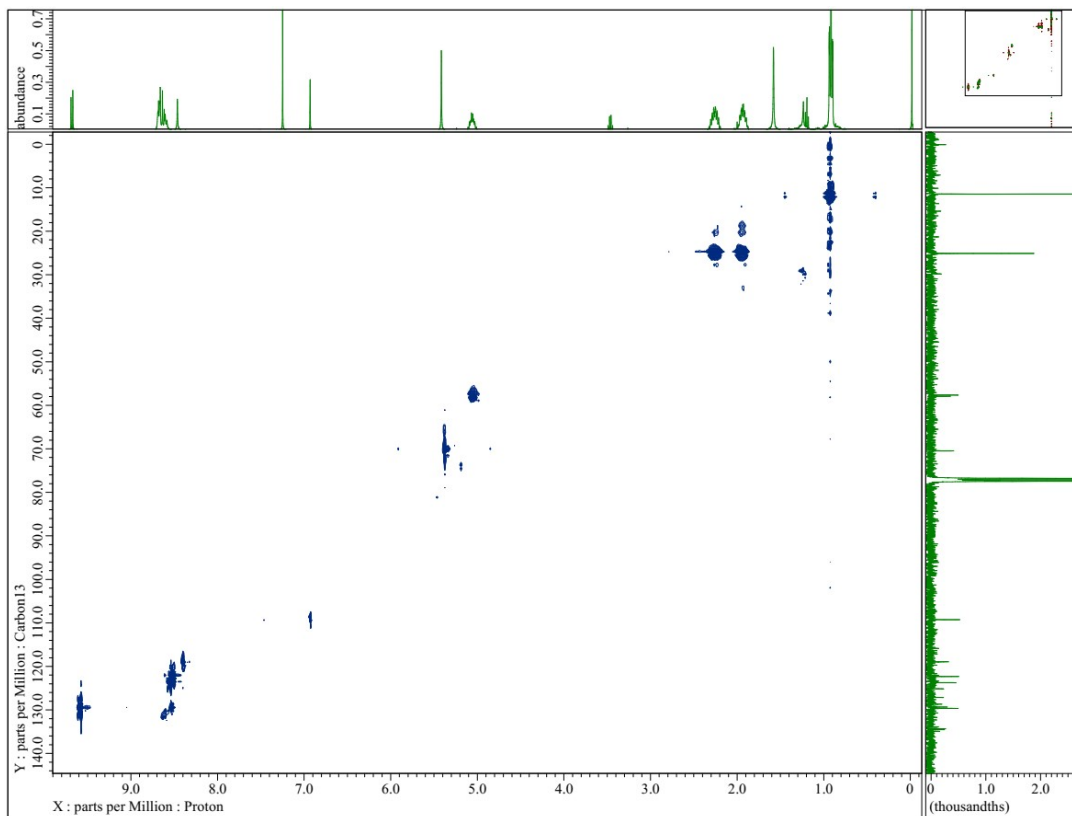


Figure S1b:  $^{13}\text{C}$  NMR spectrum of PDI 2.





**Figure S1e:** The  $^1\text{H}$ - $^1\text{H}$  COSY Spectrum of PDI 2.



**Figure S1f:** The  $^1\text{H}$ - $^{13}\text{C}$  HSQC Spectrum of PDI 2.

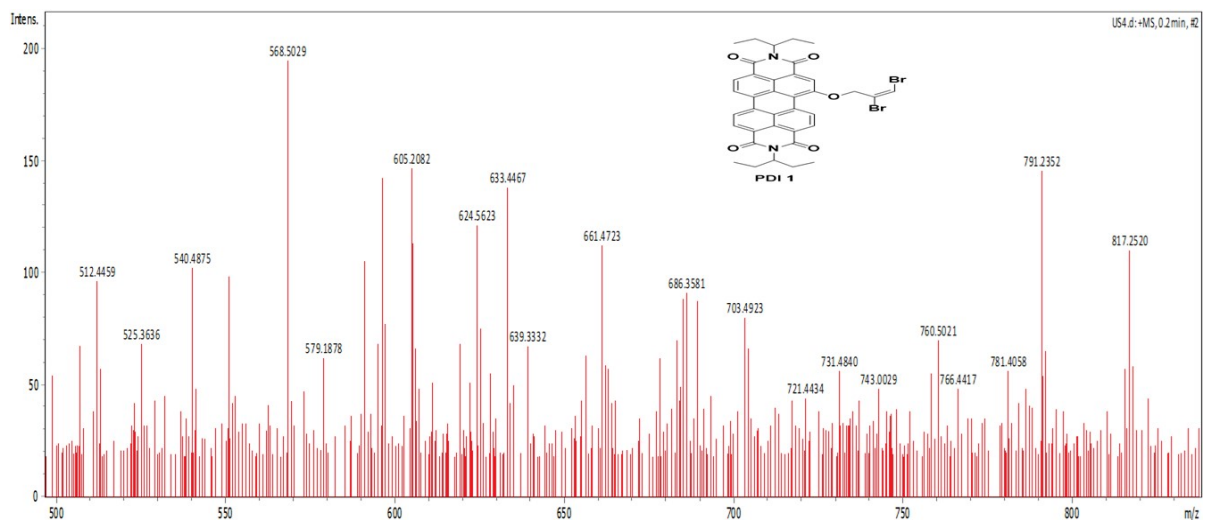


Figure S1g: HRMS spectrum of PDI 2.

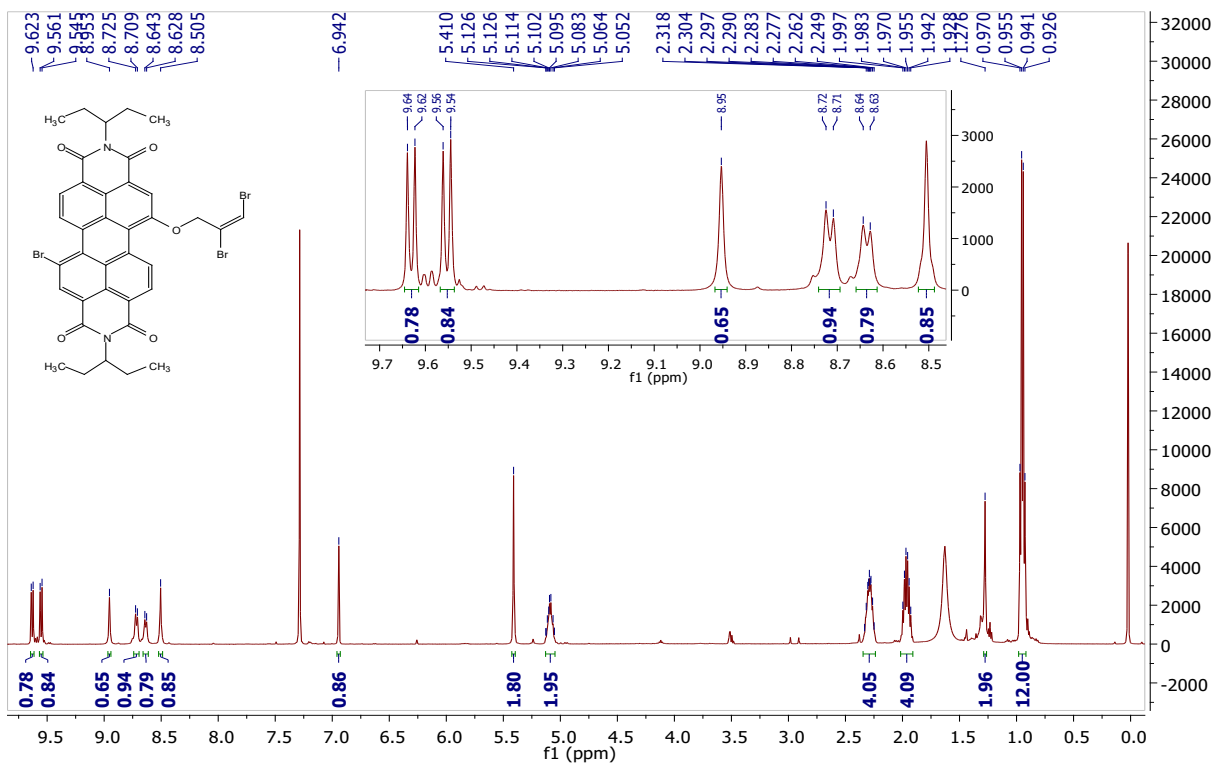


Figure S2a: <sup>1</sup>H NMR spectrum of PDI 3.

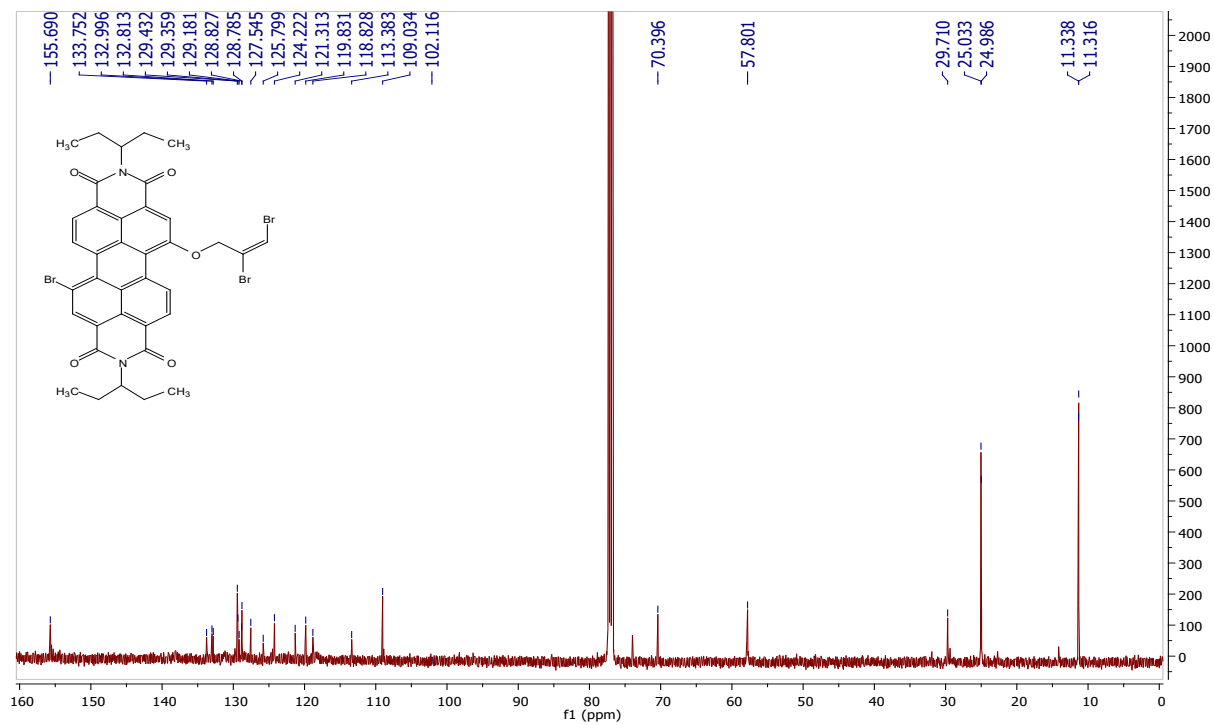


Figure S2b:  $^{13}\text{C}$  NMR spectrum of PDI 3.

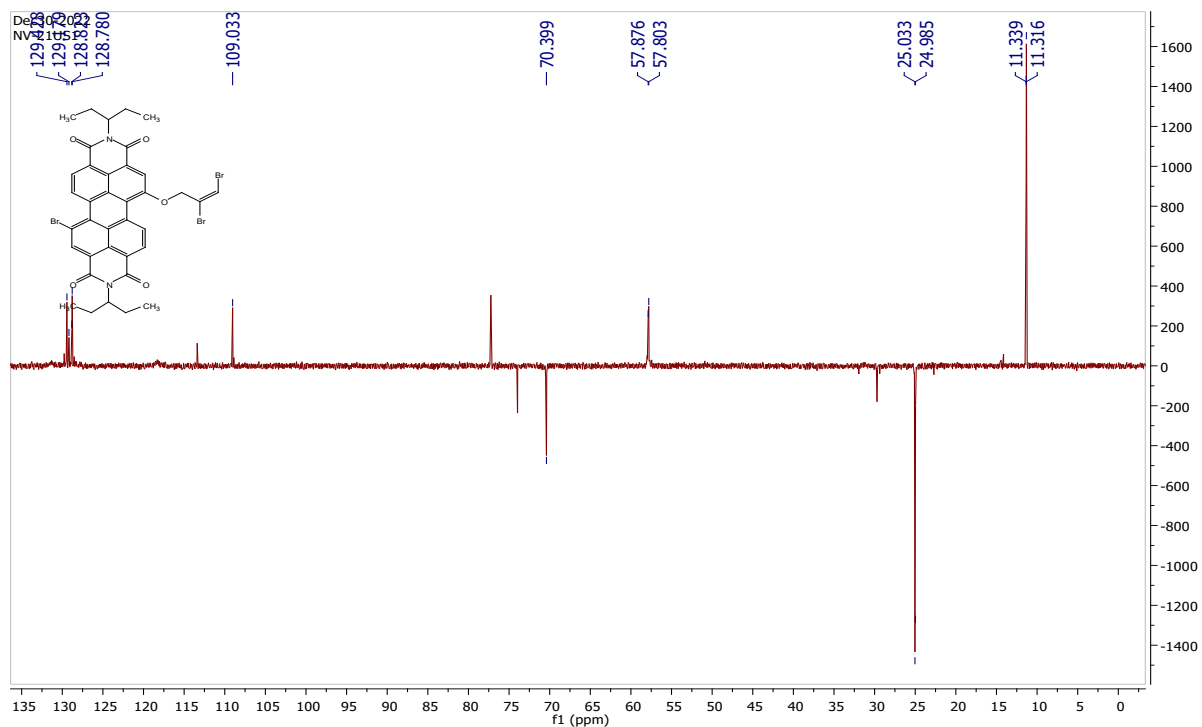


Figure S2c: DEPT-135  $^{13}\text{C}$  NMR spectrum of PDI 3.



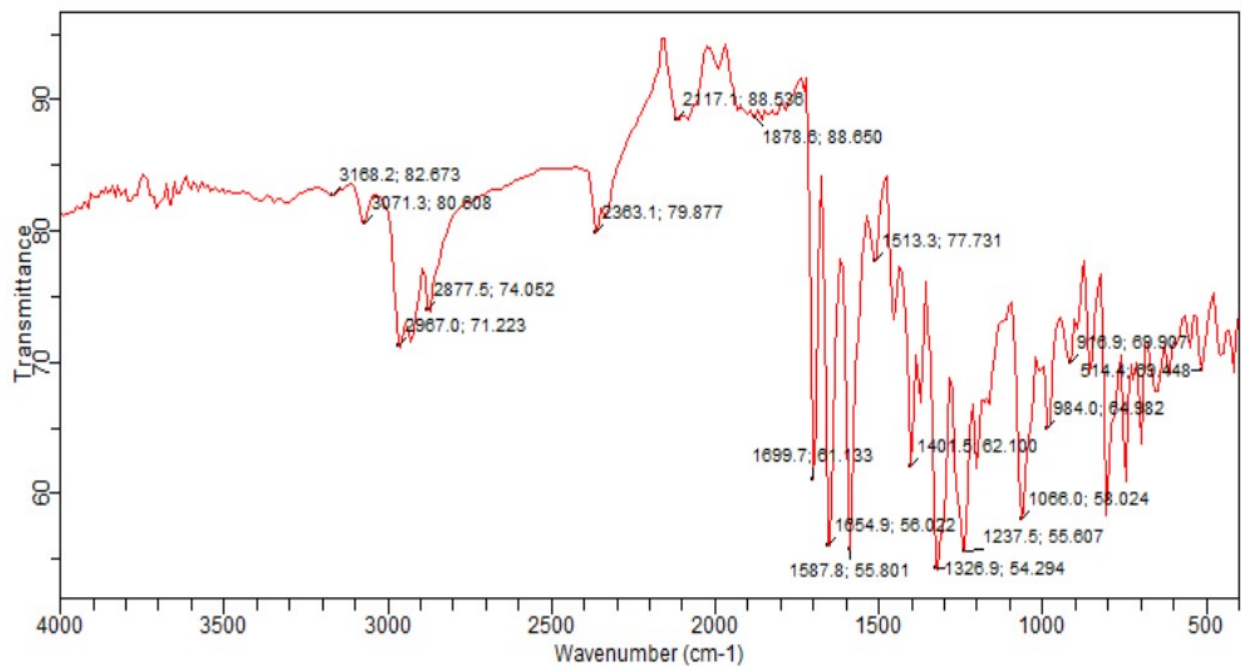


Figure S2d: FTIR (ATR) spectrum of PDI 3.

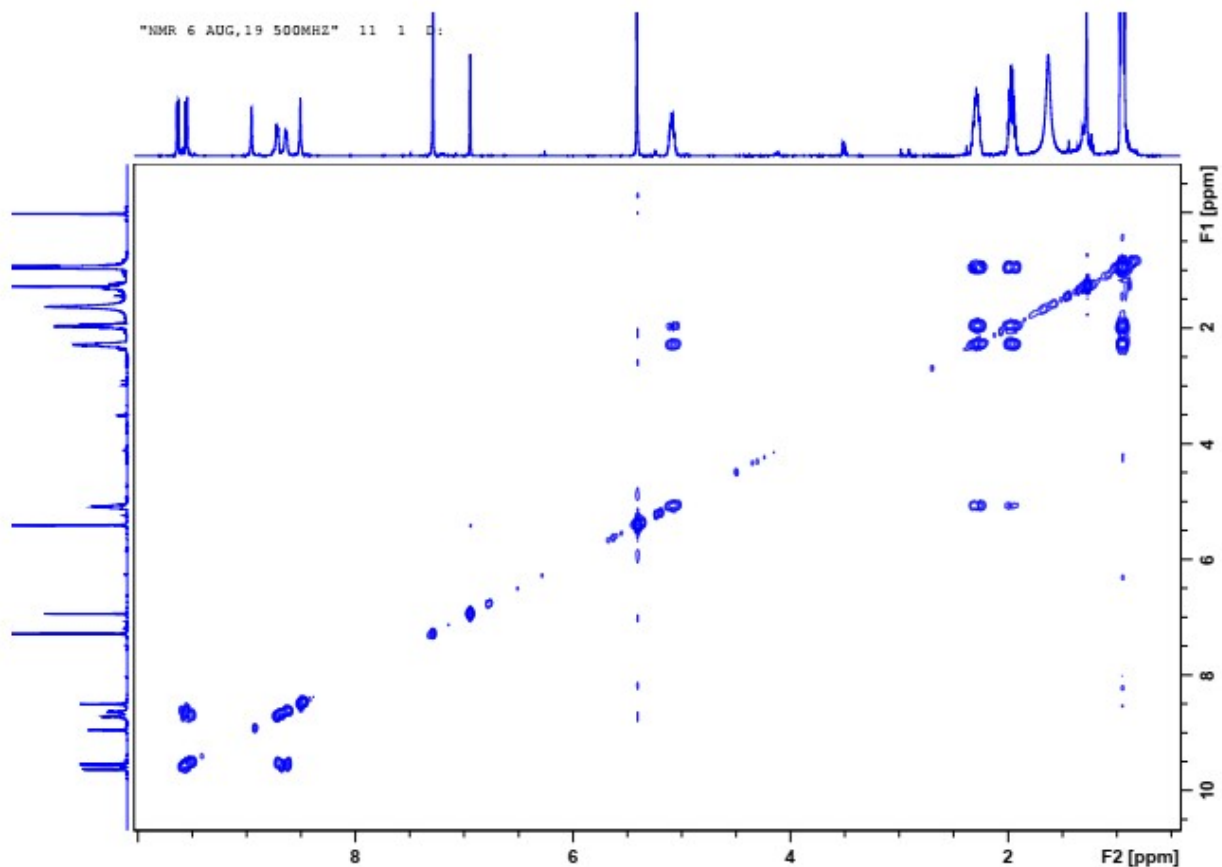
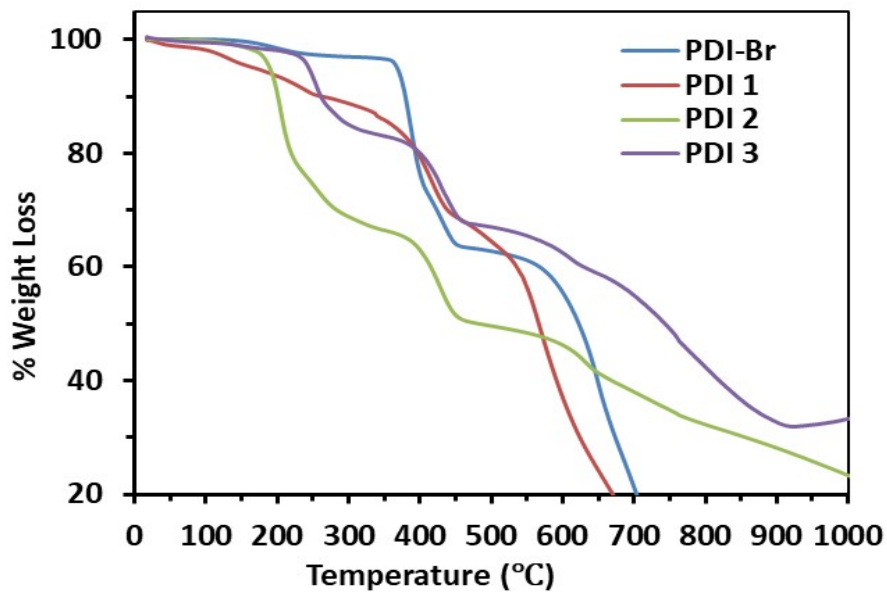
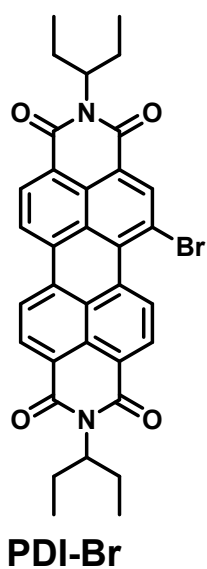
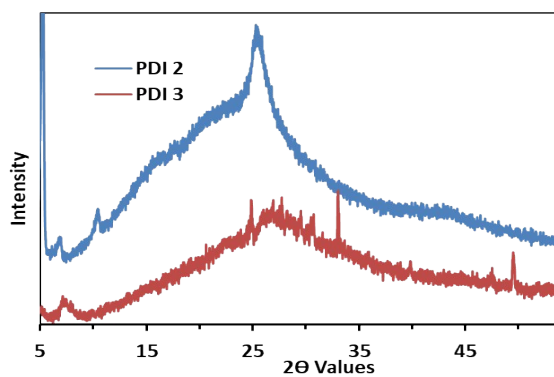


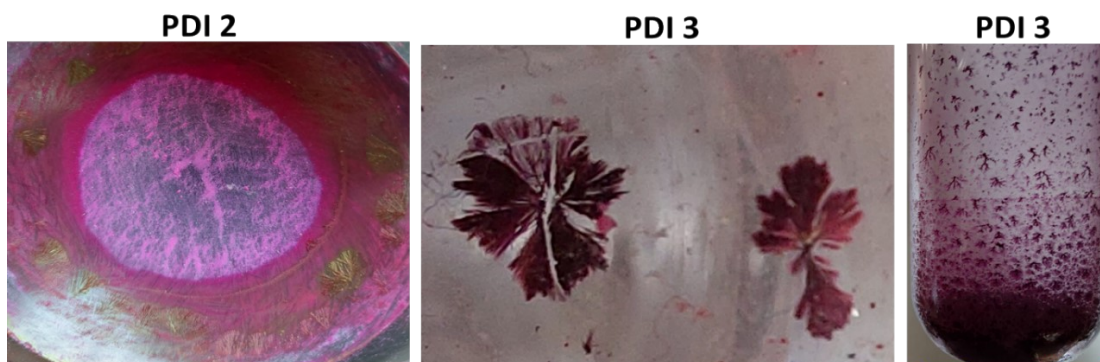
Figure S2e: The <sup>1</sup>H-<sup>1</sup>H COSY Spectrum of PDI 3.



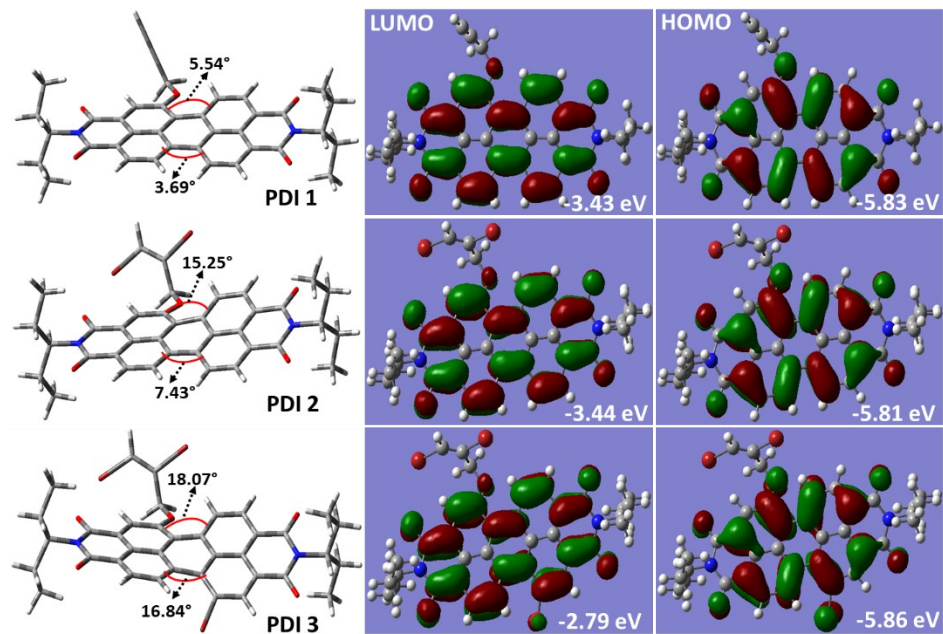
**Figure S3:** (left) Chemical structure of PDI-Br; (right) TGA studies of PDI 1–3 and PDI-Br (as control).



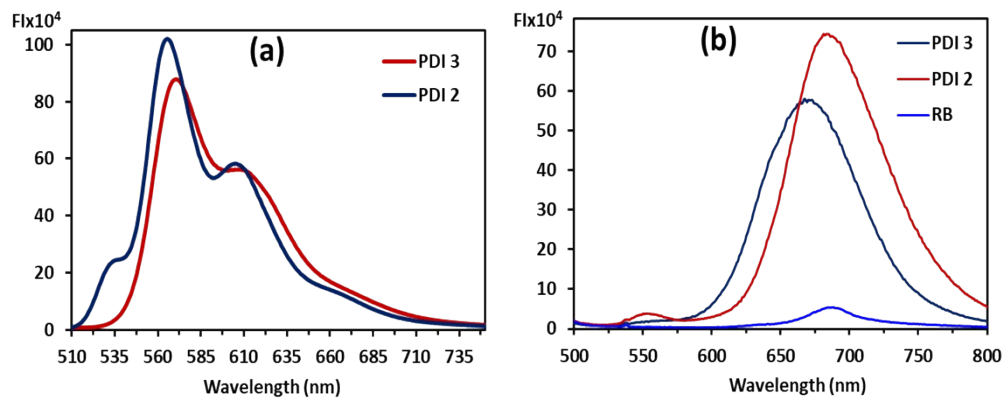
**Figure S4:** XRD studies of PDI 2 and 3.



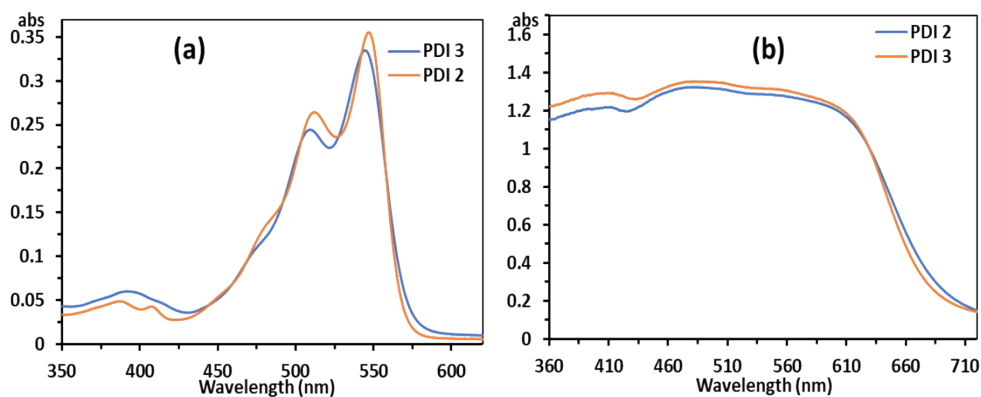
**Figure S5:** Photographs of crystals of PDI 2 and 3 grown for recording the X-ray.



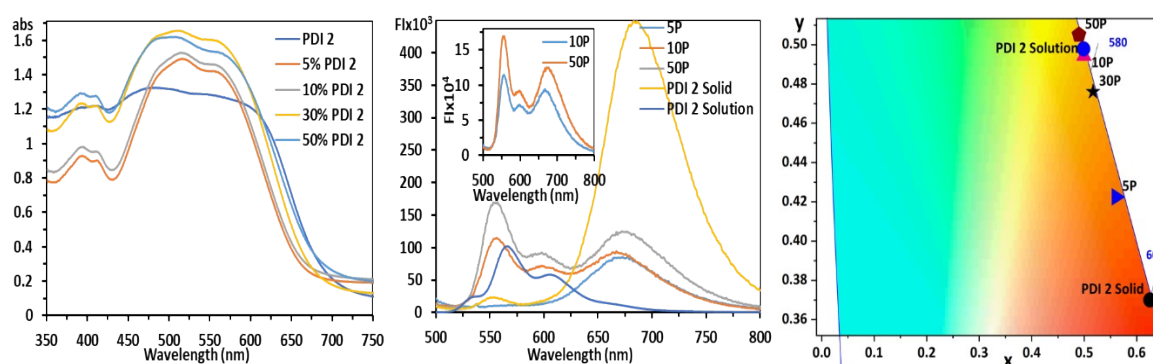
**Figure S6.** The optimized and HOMO, LUMO orbital structures of PDI 1–3 calculated with B3LYP/6-31G\* basis sets using Gaussian 09 package.



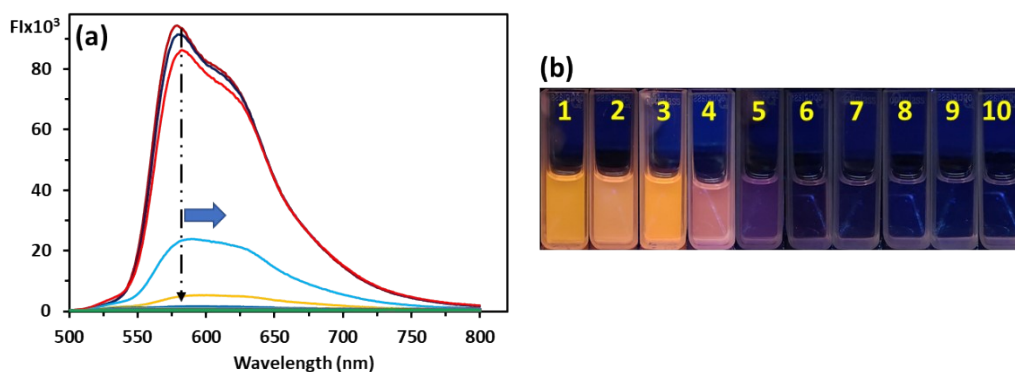
**Figure S7:** The fluorescence spectra of PDI 2 and 3 in (a) solution and (b) solid.



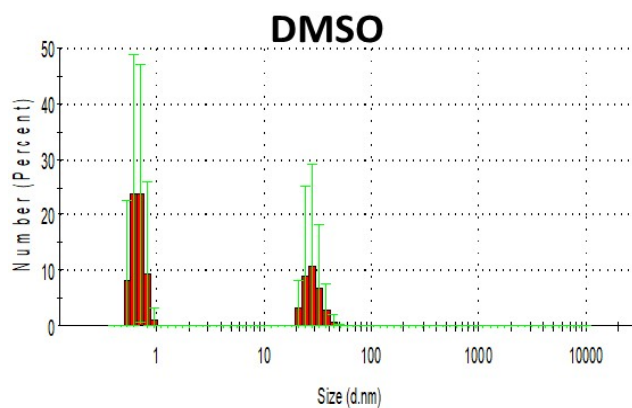
**Figure S8:** The absorbance spectra of PDI 2 and 3 in (a) solution and (b) solid.



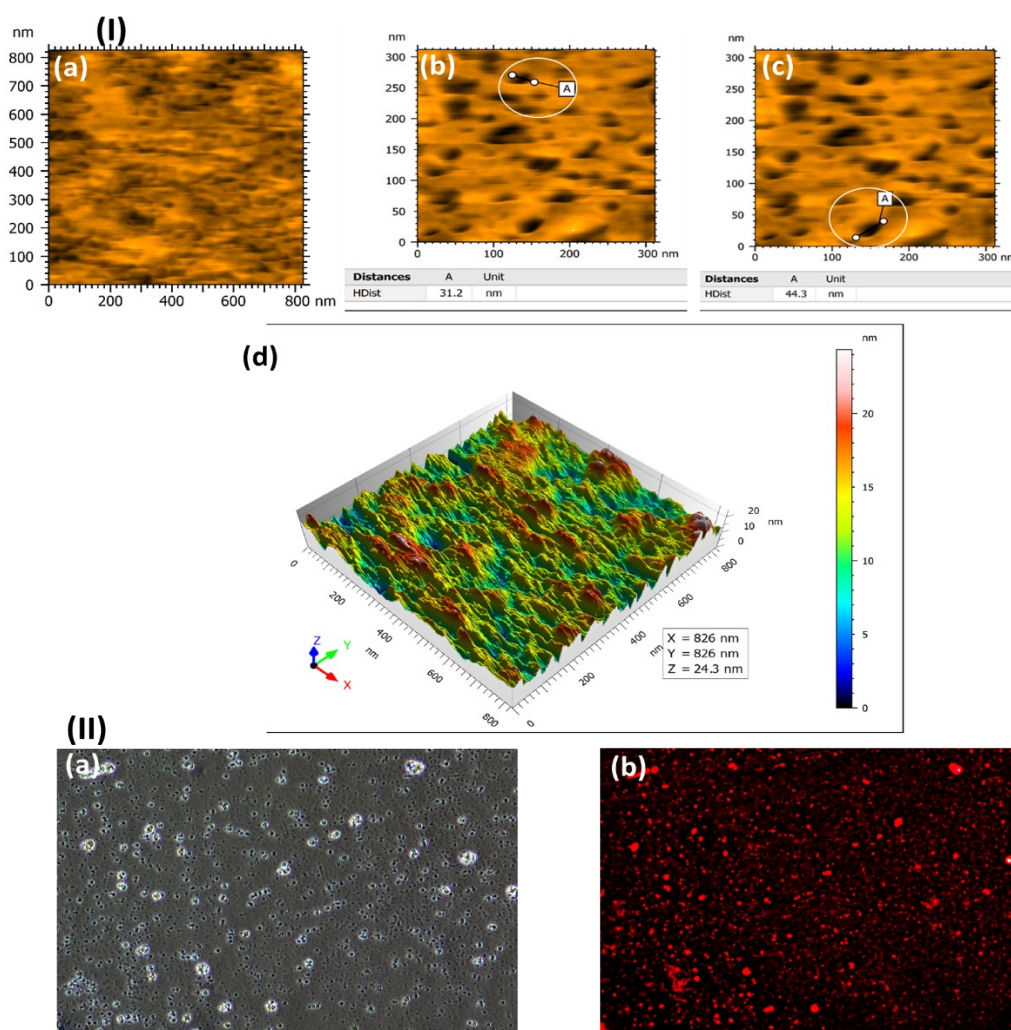
**Figure S9:** The fluorescence spectra of PDI 2 after different loading in silica ( $w/w^0$ ) and their corresponding CIE plot.



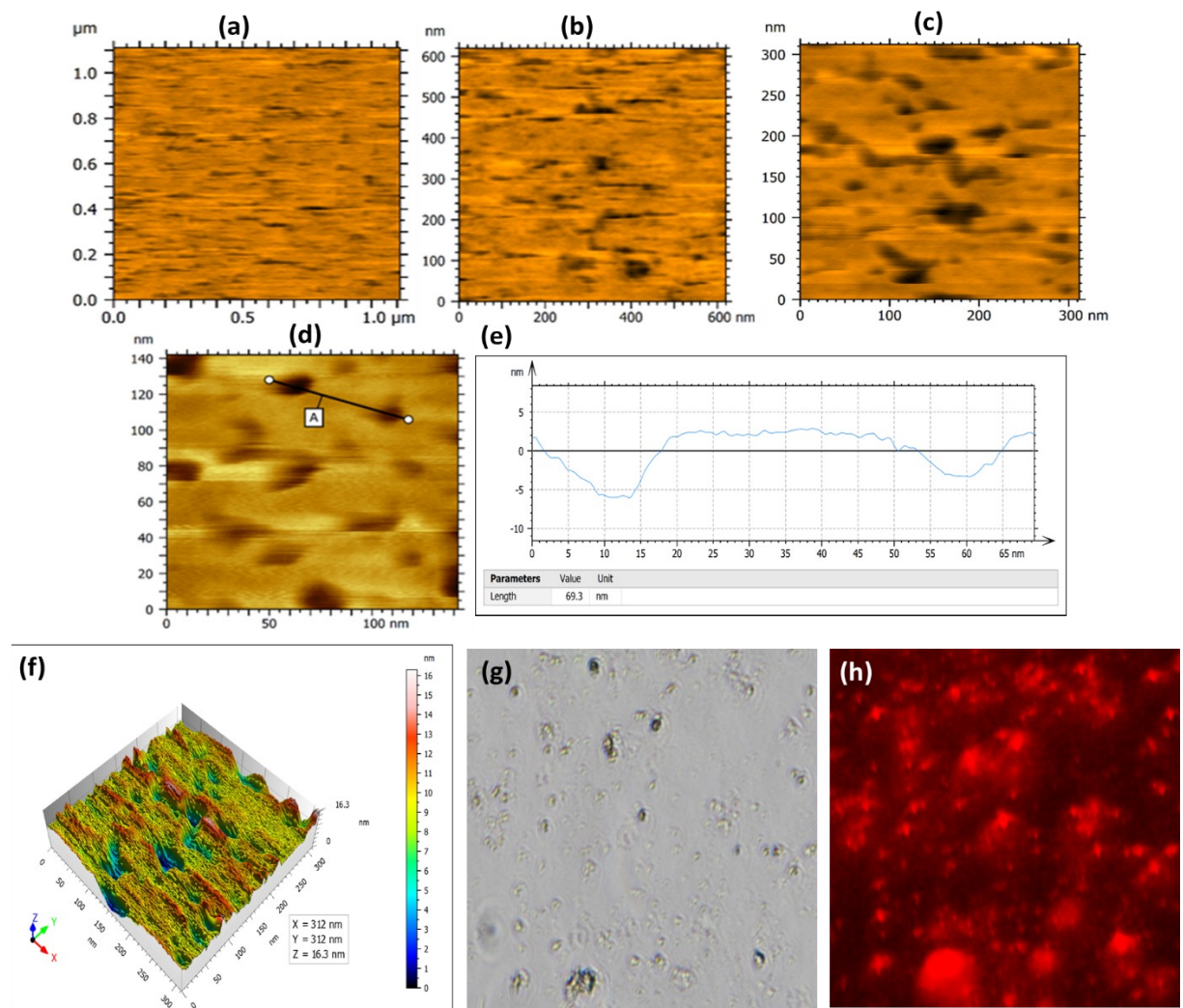
**Figure S10.** (a) Emission spectra of PDI 2 ( $10 \mu\text{M}$ ) in presence of different volume fraction of water content ( $f_w$ ) in DMSO,  $\lambda_{\text{ex}} = 490 \text{ nm}$ , slit widths ( $\lambda_{\text{ex}}/\lambda_{\text{em}}$  10/10); (b) Photographs of PDI 2 in 0–99 %  $\text{H}_2\text{O}$ –DMSO under 365 nm UV illumination. The labels 1–10 in figure S10b corresponds to 0–90%  $\text{H}_2\text{O}$  content in DMSO.



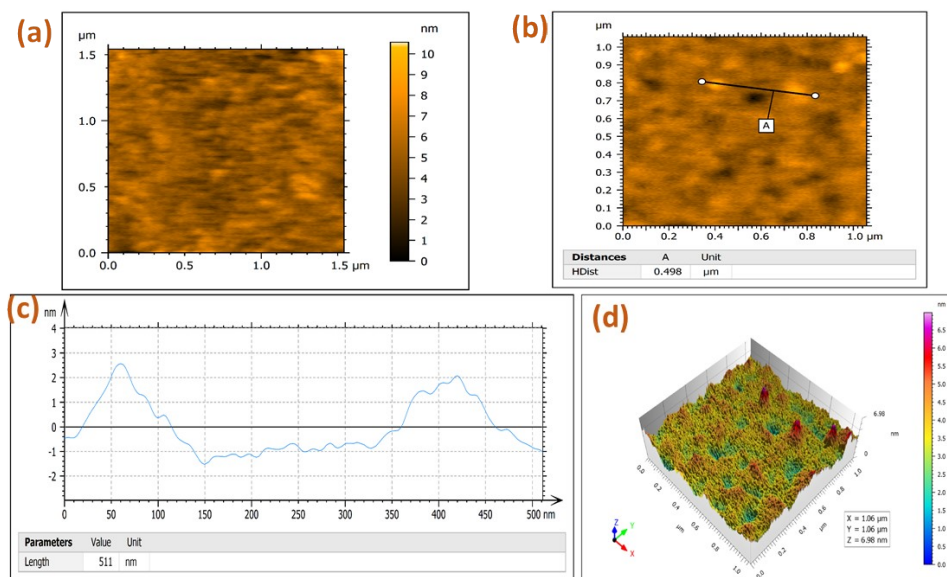
**Figure S11:** DLS plot of PDI 2 (10  $\mu$ M) in DMSO solutions indicating its monomeric form.



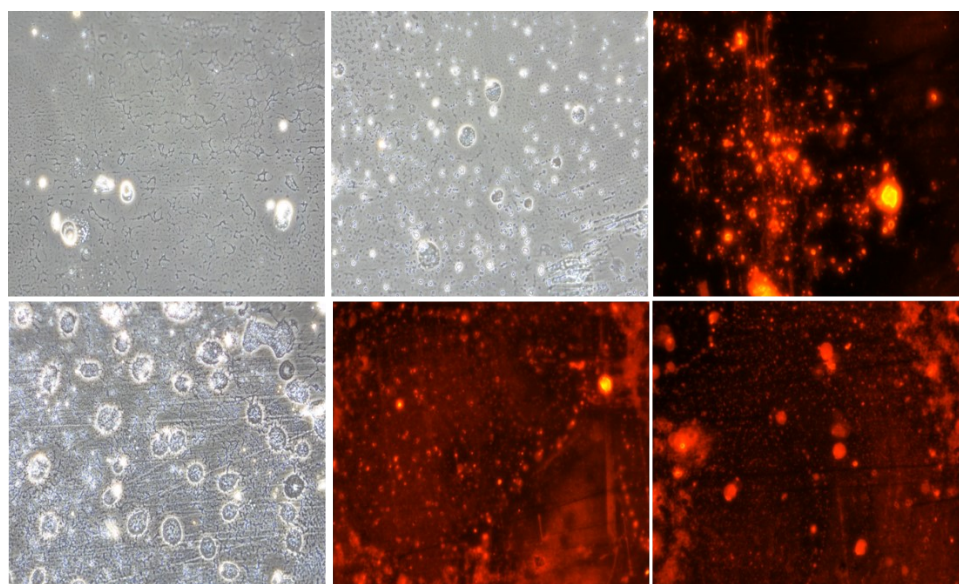
**Figure S12.** (I) (a-c) AFM micrographs (c) 3D plot of PDI 2 (1  $\mu$ M) in 80% H<sub>2</sub>O–DMSO mixture; (II) Optical microscopic imaging of PDI 2 in 80% H<sub>2</sub>O–DMSO solutions (a) brightfield and (b) fluorescence.



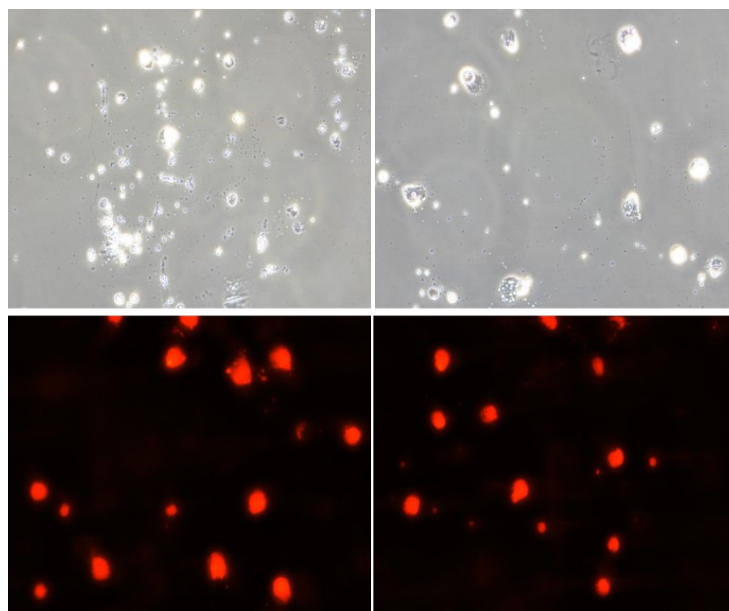
**Figure S13.** (I) (a-d) AFM micrographs; (e) height-profile plot corresponding to image (d); (f) 3D plot of PDI 2 (1  $\mu$ M) in 20% H<sub>2</sub>O–DMSO mixture; (II) Optical microscopic imaging of PDI 2 in 20% H<sub>2</sub>O–DMSO solutions (g) brightfield and (h) fluorescence.



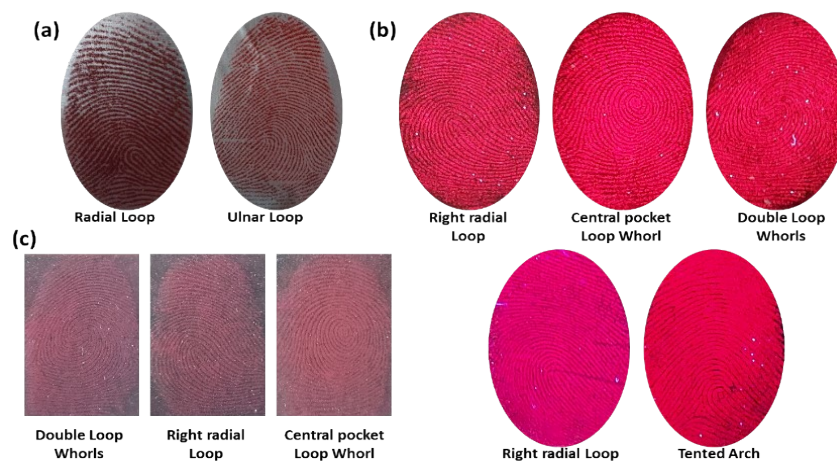
**Figure S14.** (a-b) AFM micrographs; (c) height-profile plot corresponding to image (b); (d) 3D plot of PDI 2 ( $1 \mu\text{M}$ ) in 50%  $\text{H}_2\text{O}$ –DMSO mixture.



**Figure S15:** Optical microscopic imaging of PDI 2 in THF solution (top)  $5 \mu\text{M}$  and (bottom)  $10 \mu\text{M}$  in brightfield and fluorescence.

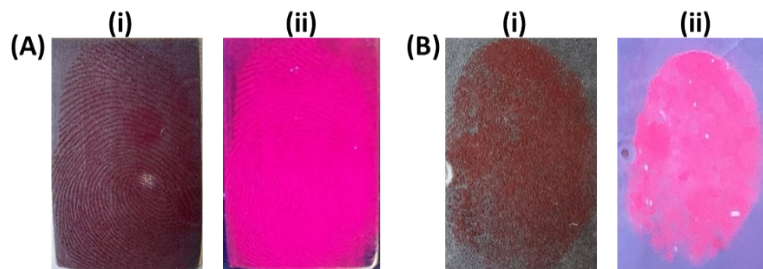


**Figure S16:** Optical microscopic imaging of PDI 2 in DMSO solution (10  $\mu$ M) in brightfield and fluorescence.

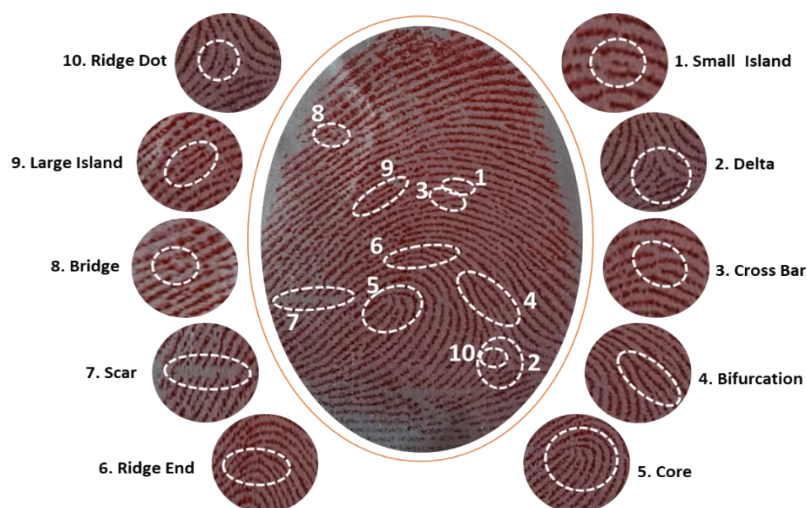


**Figure S17.** The photographs of LFPs developed on (a) aluminum foil and (c) glass slide using PDI 2 powder and visualized in daylight; photographs of LFPs developed on (b) glass slides using PDI 2 powder and visualized under 365 nm UV lamp.

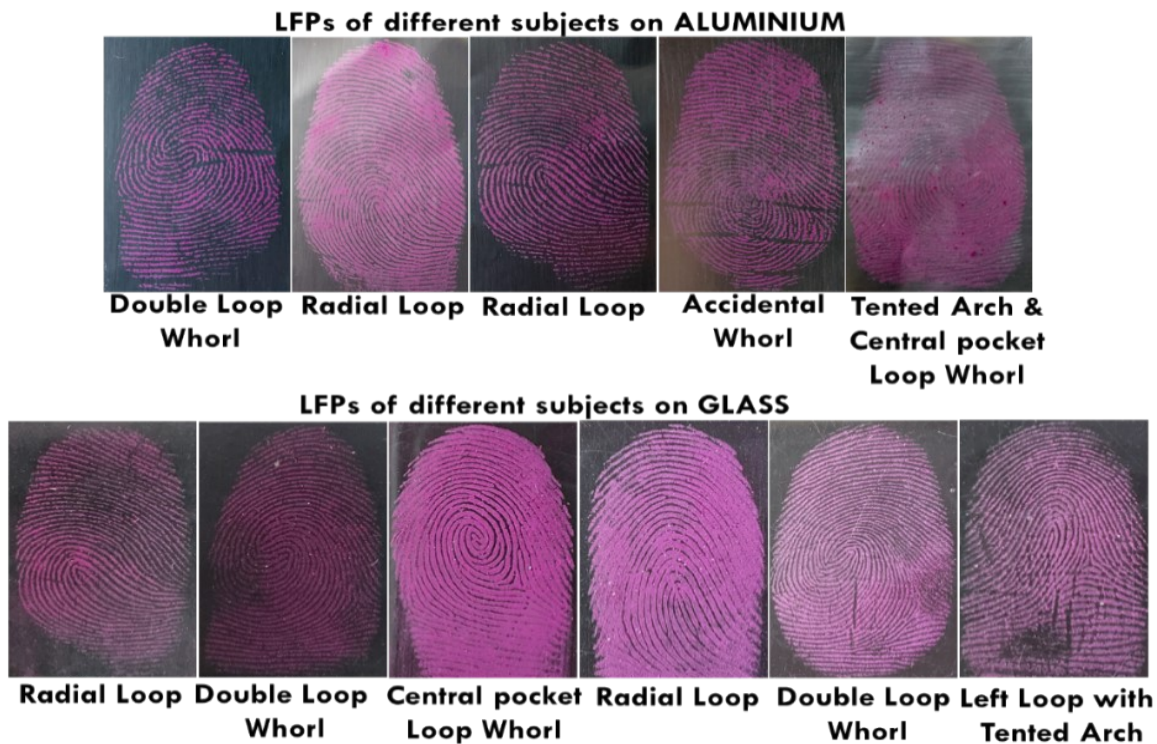




**Figure S18.** The photographs of LFPs developed on (A) stainless steel, (B) rough plastic using PDI 2 powder and visualized in (i) daylight and (ii) under 365 nm UV lamp.



**Figure S19.** The photograph for LFP developed on glass slide using solid powder PDI 2 and visualized in daylight along with description of levels 1–2.



**Figure S20a.** The photographs of LFPs developed using nano porous silica having 10% loading of PDI 2 (w/w) on aluminium and glass slides. The LFPs were visualized in daylight.



**Figure S20b.** The photographs of LFPs developed using nano porous silica having 10% loading of PDI 2 (w/w) on different coloured surfaces. The LFPs were visualized in daylight.