

Note

Metal-free Annulation at Ortho- and Bay- Positions of Perylene Bisimide Leading to Lateral -Extension with Strong NIR Absorption

Ramprasad Regar, Ruchika Mishra, Pradip Kumar Mondal, and Jeyaraman Sankar

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b01303 • Publication Date (Web): 23 Jul 2018

Downloaded from <http://pubs.acs.org> on July 23, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Publications

is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

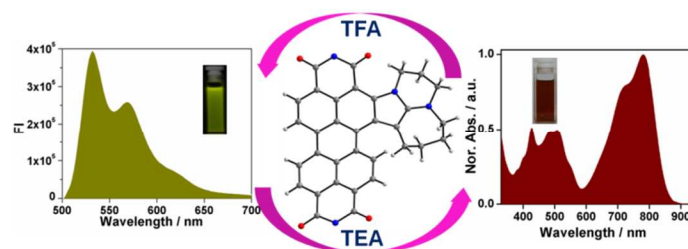
Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Metal-free Annulation at *Ortho*- and *Bay*- Positions of Perylene Bisimide Leading to Lateral π -Extension with Strong NIR Absorption

Ramprasad Regar, Ruchika Mishra, Pradip Kumar Mondal and Jeyaraman Sankar*

Department of Chemistry, Indian Institute of Science Education and Research, Bhopal 462 066, India

Supporting Information Placeholder

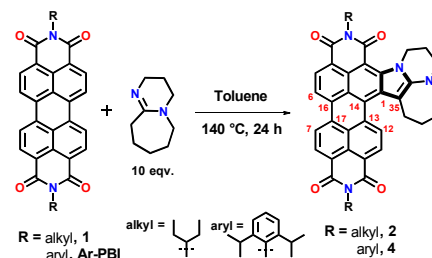


ABSTRACT: A novel *ortho*/*bay* annulation reaction of perylene bisimide (PBI) has been explored in a single step synthetic procedure using perylene bisimide **1** and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) in the absence of any metal catalyst. The single crystal solid state X-ray diffraction structure showed a distorted framework of DBU-fused PBI **2**. Compound **2** exhibited intense near-infrared absorption up to 950 nm. Reversible protonation and deprotonation accompany drastic changes in photophysical characteristics. Further, the reaction of perylene biscalboxyanhydride with DBU offered caprolactam ring-substituted perylene bisimide **3**.

Over the past few years, extensive efforts have been channeled into the development of π -conjugated molecules for various futuristic applications such as organic solar cells, organic field-effect transistors, artificial photo-systems etc.¹ Among the plethora of polyaromatic molecules available, perylene-3,4,9,10-tetracarboxyl bisimides (PBIs) have emerged as the fascinating class of aromatic molecules due to their tunable absorption and emission features with very high thermal and photo-chemical stability.² PBI derivatives find widespread applications in organic photovoltaics,³ organic field-effect transistors,⁴ sensors,⁵ bio-imaging⁶ and supramolecular assemblies⁷ owing to their tunable π -backbone, which is further achieved either by aromatic core extension or expansion. Bay-functionalization⁸ is an practical approach to extend π -framework of PBI, henceforth creating new PBI derivatives with outstanding optoelectronic properties. Core expansion of perylene π -system in longitudinal (N-N axis) manner has provided near-infrared absorbing dyes such as terrylene bisimides up to hexarylene bisimides.⁹ Core expansion along the short molecular-axis of perylene bisimide is another plausible way to influence the aromatic π -cloud of PBIs. The most prevalent methods used to achieve this involve base-mediated cyclization, metal catalyzed cyclization, light-promoted and Diels-Alder cycloaddition.¹⁰ Core expanded PBIs often have benzene rings or heterocyclic rings annulated in the perylene *bay*-region. The resultant chromophores are coronene diimide (CDI), dibenzocoronene diimide, and dinaphthocoronene diimide, which inherit properties from both coronenes and PBIs.¹¹ Expanding the aromatic core in the *bay*-area is comparatively easy and is much exploited. However, functionalization at the *ortho* position is relatively difficult as it requires expensive catalysts and longer reaction times with poor yields.^{12a-i} Meanwhile, an *ortho*-substituted zwitter-

ionic PBI radical was reported using N-heterocyclic carbene.^{12j} Fusion at *bay*/*ortho* positions have been shown to form ladder type oligomers by copper-mediated coupling reactions.^{13a-c} Very recently, a copper-catalyzed *ortho*/*bay* direct diamination of PBIs have also been reported.^{13d} However, metal-free access to simple *ortho*/*bay* annulated systems remain rare. As a result of this, simultaneous fusion at *ortho* and *bay* positions of PBI is challenging and rewarding.

Scheme 1. Synthetic scheme for DBU-annulated perylene bisimide **2** and **4**.



In the current work, we report an interesting annulation reaction of DBU at *bay*- and *ortho*- positions of PBI for the construction of a heteroatom containing 5-membered cyclic unit in a single step synthetic procedure. In this cyclization, the reaction was catalyzed by DBU itself rather than by any metal catalyst. The synthesized compound **2** was non-fluorescent and showed intense absorption across the visible to near-infrared region. The utility of this reaction has been explored to provide a caprolactam tail imide substituted compound **3**. The lateral core-expanded perylene bisimide **2**, formally a DBU appended PBI at *bay*- and *ortho*-positions,

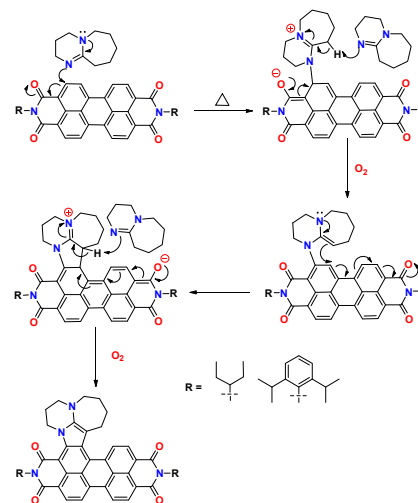
was synthesized through an uncatalyzed, single step reaction of PBI **1** with DBU. In this reaction, DBU acted as a reactant as well as a base and led to the formation of a higher polar brown compound **2**. After repetitive column chromatography using dichloromethane/ethyl acetate solvent mixture, the brown fraction was isolated in 32% yield.

^1H NMR in CDCl_3 at room temperature (Figure S9) indicated three clearly resolved signals from the aromatic PBI core and four well-resolved signals for imide-substituted isopentyl group with a few unresolved signals in the aliphatic region. The absence of resonances for two protons of the aromatic region of PBI hinted at a probable annulation. HRMS-APCI spectra (Figure S17) revealed the molecular ion peak to be a combination of PBI and DBU lacking four protons. Considering this, the brown product was thought to be a DBU-substituted compound **2**, but the room temperature NMR spectra did not support the assignment. A CuI-catalyzed annulation of five-membered heterocyclic ring on naphthalene diimide (NDI) core had been reported earlier.¹⁴ Recently, we have also reported an *ortho*/*bay*-ring annulated 5-membered pyrroloperylene bisimide from alkynyl derivative of PBI with DBU.¹⁵ Taking a cue from this, the brown compound was assumed to be a DBU fused at one *bay* and one *ortho*-position of PBI. The broadening of proton NMR resonances was presumed to be due to the fluxional behavior of the DBU unit. This is due to the flipping of DBU ring that can be arrested at low-temperature. To probe the same, a variable temperature ^1H NMR experiment (Figure S9) was conducted in CDCl_3 . The emergence of new signals between 1.5 and 5.1 ppm was observed, and these signals were assigned to DBU ring protons. No new signals were observed in aromatic region. It was found that at low-temperatures compound **2** shows clearly resolved signals as compared to room temperature spectra. So all the facts discussed above, along with ^{13}C -NMR spectrum confirmed the fusion of DBU at PBI *b/o*-position to form compound **2** (as shown in scheme 1). Compound **2** has good solubility in common organic solvents, such as dichloromethane, chloroform, toluene, and tetrahydrofuran at room temperature. The presence of conjugated aromatic rings along with the presence of the electron-rich amino group would be responsible for the color and strong absorption in the visible region. The melting points of newly synthesized molecules were determined by differential scanning calorimetry technique. Compounds **2** and **3** start melting at 333 and 404 $^\circ\text{C}$, respectively. Further, the present reaction procedure provided DBU fused PBI derivative **4** as shown in scheme 1 with an *N*-aryl PBI derivative. When compound **1** was reacted with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), the reaction did not proceed as expected and resulted in a complicated mixture. The formation of compound **2** probably proceeds by the attack of alkene carbon of DBU at the *ortho*-position of PBI to form a C-C bond followed by oxidation (Scheme 2). Further, an oxidation offers compound **2** by achieving the aromatization.

It was crucial to obtain a solid state structural proof for the formation of compound **2**. To achieve this, suitable crystals for single crystal X-ray diffraction analysis (CCDC No. 1817886) were obtained through vapor diffusion of methanol into a dichloromethane solution of compound **2**. The solid state structure revealed a distorted framework for compound **2**, where DBU has been fused at *b/o*-positions of PBI as shown in figure 1. The two naphthalene units of perylene core deviated from co-planarity due to annulation, probably driven by steric repulsion. The C12C13C14C1 and C13C14C1C35 dihedral angles are 19.72 $^\circ$ and

20.96 $^\circ$, respectively. On the unsubstituted PBI bay side the C6C16C17C7 dihedral angle is 6.36 $^\circ$ as shown in scheme 1.

Scheme 2. Proposed mechanism for the formation of **2** & **4**.



The synthesized molecule **2** showed a broad and intense absorption ranging from visible to near-infrared region. The absorption spectrum recorded in toluene displayed a λ_{max} at 820 nm ($\epsilon = 24000 \text{ M}^{-1} \text{ cm}^{-1}$) and a comparatively less-resolved vibronic absorption feature between 400 and 600 nm (Figure 2, left). The broad and intense band between 580 and 950 nm is a mixture of π - π^* transition for the core extension and charge-transfer (CT) transition, involving the N-heterocyclic aromatic ring and electron-rich dialkylamino group.

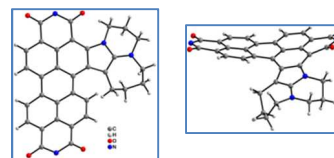


Figure 1. Single crystal X-ray diffraction structure of compound **2** (Alkyl groups on the imide nitrogens have been removed for clarity).

Compound **2** was found to be non-fluorescent as compared to parent PBI **1** owing to strong non-radiative decay, stemming from the structural floppiness of the DBU ring along limited with contribution from a charge transfer (Figure S5). To understand the CT nature, absorption spectra for compound **2** were recorded in toluene, THF, MeOH, DMF and DMSO as shown in figure 2 (right). A bathochromic shift of around 70 nm was observed at the CT band as the polarity of the solvent increased, whereas the splitting of bands in the visible region observed was not typical of unsubstituted PDI **1**. This indicates that the CT state is getting stabilized with increasing solvent polarity.

It is essential to explore the utility of this reaction further. While it is interesting to investigate the reactivity of DBU with PBI, it would be rewarding to understand DBU's reactivity towards the parent insoluble perylene-3,4,9,10-tetracarboxylic dianhydride (PDA). To probe the same, PDA has been subjected to identical reaction conditions (Scheme 4). Surprisingly, DBU underwent nucleophilic reaction¹⁷ to give an unprecedented PBI derivative again. The DBU ring was opened and a caprolactam ring substitut-

ed perylene bisimide **3** was obtained, instead of a ring an annulated product similar to that of compound **2**.

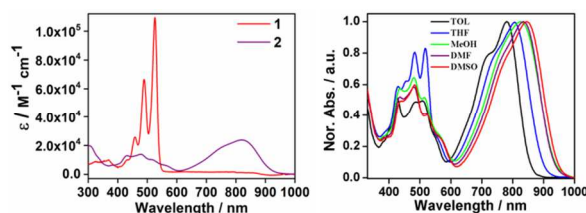


Figure 2. Absorption profiles of compound **2** in toluene (μM) (left) and solvent dependence (right).

To gain further insight into the frontier molecular orbitals of compound **2**, DFT calculations were performed at the B3LYP/6-31g* level using Gaussian 09 suite of programs.¹⁶ These calculations provided insight into the electron delocalization in frontier molecular orbitals. The electron density in HOMO was delocalized over the whole molecule whereas the electron density in LUMO was predominantly spread only over PBI core with contribution from the extended 5-membered heterocyclic ring as shown in figure 3 (A). Hence, the broad band between 580 and 950 nm can be assigned to extension of conjugation and CT transition which originates from HOMO to LUMO transition.

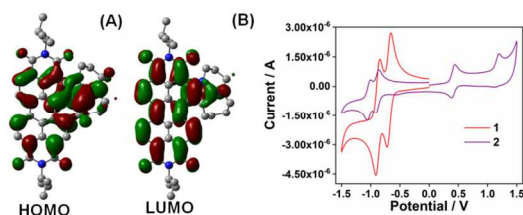
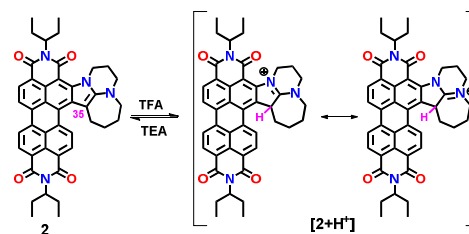


Figure 3. Frontier molecular orbitals (A) and cyclic voltammogram (B) of compound **2** and **1** recorded in dichloromethane at a scan rate of 0.1 V/s with respect to SCE.

In order to understand the redox characteristics of compound **2**, cyclic voltammetric studies were conducted. The experiment was performed under argon in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, with a scan rate of 100 mV/s. Compound **2** exhibited two reversible reductions at -0.88 and -1.03 V whereas PBI **1** showed two reductions at -0.69 and -0.87 V versus SCE. Also, one reversible and one irreversible oxidations each were obtained at 0.43 and 1.23 V, respectively for compound **2** as shown in figure 3 (B). The reversible reductions are expected from electron-deficient PBI core while the oxidations clearly reflect the electron-rich nature of annulated dialkylamino ring. It shows that the compound **2** is both more easy to oxidize and less susceptible to reduce as compared to typical PBI **1**.

To exploit the CT characteristics, a protonation study was conducted. Protonation of the electron-rich carbon atom (C35) should, in turn, affect the CT band by restricting the extended π -conjugation (scheme 3) and therefore should be revealed by absorption and emission spectrum. To verify this, compound **2** in acetonitrile (CH_3CN) was titrated against an acetonitrile solution of trifluoroacetic acid (TFA).

Scheme 3. Protonation and deprotonation of compound **2**.



The successive addition of aliquots of TFA forced the CT band to disappear. Simultaneously, a few peaks emerged at 515, 480 and 450 nm in the absorption spectrum. The fluorescence intensity of bands at 532 and 569 nm increased gradually with the increasing addition of TFA aliquots as shown in figure 4. The protonation resulted in the sharp vibronic feature in the absorption spectra resembling unsubstituted PBI with absorption maxima at 515 nm. The emission spectrum was also similar to parent PBI with emission maxima at 532 nm. This further confirms that the intramolecular charge transfer interactions are suppressed as the electron-rich carbon is getting protonated and the resultant +ve charge being stabilized by the nitrogen atoms in the DBU ring as shown in the scheme 3.

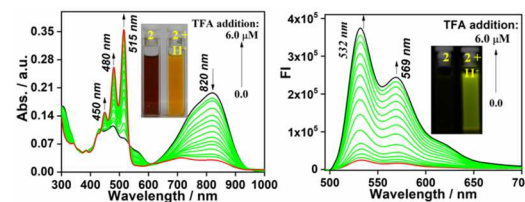
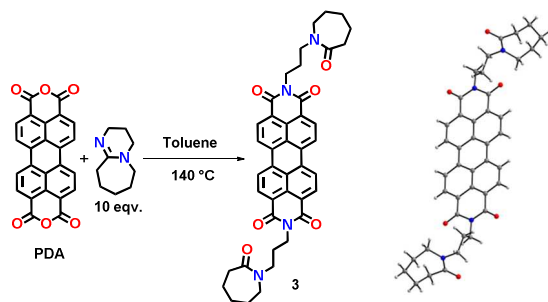


Figure 4. Absorption profile (left), and fluorescence profile excited at 480 nm (right) of compound **2** ($8 \mu\text{M}$) in the presence of different concentrations of TFA in CH_3CN solution.

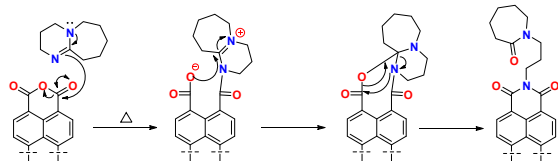
Consequently, the quenched fluorescence was regained after protonation, due to the arrest of intramolecular CT interactions. Therefore, very weakly fluorescent **2** becomes highly fluorescent in the presence of acid. This was further supported by the frontier molecular orbitals of $[\mathbf{2}+\text{H}^+]$. The electron density of HOMO and LUMO are delocalized over the whole PBI core with negligible contribution from extended heterocyclic moiety in $[\mathbf{2}+\text{H}^+]$ (Figure S20) which are of typical PBI-like HOMO and LUMO. The fluorescence turn off can be achieved by deprotonation by the addition of a base such as triethylamine (TEA). The addition of an aliquot of TEA in CH_3CN to the solution of $[\mathbf{2}+\text{H}^+]$ in CH_3CN resulted in the reappearance of CT band between 580 and 950 nm (Figure S2). The fluorescence intensity decreased rapidly at 532 and 569 nm after gradual addition of TEA solution (Figure S3). The switching of fluorescence can be mannered by the alternate additions of TFA and TEA (Figure S4). The reversibility of this switching was performed for several cycles suggesting the chemical robustness of compound **2**. The ^1H NMR showed resonances for all protons upon adding TFA to compound **2** in CDCl_3 at room temperature. The signals which were absent at room temperature were regained upon TFA addition (Figure S10). Also, the appearance of new signal at 5.75 ppm for one proton confirms the protonation at the carbon atom (C35 as shown in scheme 3) in the dialkylamino group. This observation further assures the arrest of fluxionality of DBU unit on protonation.

Scheme 4. Synthetic scheme for imide substitution of DBU and single crystal X-ray diffraction structure for compound **3**.



Compound **3** has been characterized by NMR (Figure S11&S12), and mass (Figure S18) spectrometric analyses. The absorption and fluorescence spectrum of compound **3** resembled that of simple PBI **1** (Figure S6) as functionalization on PBI nitrogens seldom perturbs the frontier orbitals, owing to the presence of a nodal plane along the imide nitrogens (Figure S21). The formation of compound **3** was unambiguously confirmed by single crystal X-ray diffraction structure (CCDC No. 1824653) as shown in Scheme 4. Compound **3** shows a planar conformation.

Scheme 5. Proposed mechanism for the formation of **3**.



The formation of compound **3** can be explained as a nucleophilic attack by nitrogen atom of 6-membered ring of DBU at the carbonyl carbon of anhydride group followed by ring opening (Scheme 5).

In summary, a new DBU annulation reaction on PBI, without the use of any catalyst has been explored in a single synthetic operation. The solid state structure of the molecule **2** revealed a distorted PBI core. The annulation resulted in interesting CT properties of compound **2**. The protonation can manipulate the intramolecular charge transfer interactions. As a result, compound **2**, which is weakly fluorescent, becomes highly fluorescent upon protonation. Hence, compound **2** acts as a pH-sensitive fluorophore with good reversibility and robustness. The utility of this reaction has further been explored to give caprolactam-ring substituted perylene bisimide **3** from PDA. Further, the panchromatic absorption feature makes molecule **2** a promising candidate for organic photovoltaic (OPV) applications. Further studies in this direction are underway in our laboratory.

EXPERIMENTAL SECTION

General Experimental methods: All reactions were carried out under argon atmosphere. Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Unless otherwise noted, the chemicals received from Sigma Aldrich and Alfa Aesar were used without further purification. Samples synthesized were purified by silica gel (100-200 mesh) and neutral alumina column chromatography followed by recrystallisation. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz or 700 MHz spectrometers in CDCl_3 with TMS as internal reference. The chemical shift values have been referenced to the residual solvent signals. HRMS measurements were recorded on a microTOF-QII

high resolution mass spectrometer from Bruker Daltonics coupled to a Waters Acquity UPLC system. Steady state absorption measurements were done on Cary 5000 UV/VIS/NIR spectrophotometer. Steady-state fluorescence emission measurements were done on a Horiba Jobin Yvon fluorolog 3-111. Quartz cell with optical path length of 10 mm was used for all measurements. Cyclic voltammetric measurements were carried out using CH potentiostat from CHI Instruments. CV experiments were done under continuous argon flow and a conventional three-electrode electrochemical cell was used. A glassy carbon working, a platinum wire counter and SCE reference electrodes were used. All the measurements were done in dichloromethane solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as supporting electrolyte. All the voltammograms were recorded at a scan rate of 100 mV/s. Single crystal X-ray diffraction measurements were carried out on a Bruker Apex diffractometer with a CCD detector with Mo-K α radiation. All IR spectra were obtained using Perkin Elmer FTIR system as neat films and selected peaks are reported in cm^{-1} . DFT calculations were performed using Gaussian 09 software suite.

Compound 1:¹⁸ A mixture of pent-3-ylamine (652 μL , 5.612 mmol), perylene-3,4:9,10-tetracarboxylic dianhydride (1000 mg, 2.551 mmol) and imidazole (5204 mg, 76.53 mmol) was stirred at 140 °C for 4 hrs and diluted with ethanol. This was followed by the addition of 2M HCl (100 mL). The reaction mixture was then allowed to settle down. The precipitate thus formed was collected through vacuum filtration and dried in oven. Further purification by silica gel chromatography using chloroform/hexane as eluents provided the desired compound **1** in 80% (1082 mg) yield. ^1H NMR (500 MHz, CDCl_3) δ (ppm) 8.66 (d, J = 7.9 Hz, 4H), 8.59 (d, J = 8.0 Hz, 4H), 5.07 (m, 2H), 2.31 – 2.22 (m, 4H), 1.99 – 1.91 (m, 4H), 0.93 (t, J = 7.5 Hz, 12H). HRMS (APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{31}\text{N}_2\text{O}_4$ 531.2278; found 531.2247.

Compound 2: In a dry sealed tube, a mixture of **1** (200 mg, 0.3773 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (562 μL , 3.773 mmol) in dry toluene (10 mL) was stirred at 140 °C for 24 hrs. Reaction progress was monitored using TLC. After 24 hrs, the reaction mixture was subjected to a water work up and washed with dichloromethane twice. Organic layer was collected over anhydrous sodium sulphate and dried under reduced pressure. Crude mixture was subjected to column chromatography for further purification. The brown compound was purified using alumina column chromatography with dichloromethane/ethyl acetate solvent mixture in 32% (82 mg) yield with remaining unreacted starting material and insoluble fraction. ^1H NMR (500 MHz, CDCl_3 , 253K) δ (ppm) 8.60 – 8.45 (merged doublets, 5H), 7.58 (d, J = 6.9 Hz, 1H), 5.18 – 4.86 (m, 2H), 4.52 (broad t, 1H), 3.93 (t, J = 12.5 Hz, 1H), 3.76 (d, J = 11.0 Hz, 1H), 3.52 (d, J = 21.8 Hz, 2H), 3.42 (d, J = 13.1 Hz, 1H), 2.82 (broad t, 1H), 2.26 (broad m, 5H), 2.07 (broad s, 1H), 1.87 (broad m, 8H), 1.61 (broad s, 1H), 0.87 (m, 12H). ^{13}C NMR (126 MHz, CDCl_3 , 298K) δ (ppm) 164.7, 164.7, 163.9, 163.4, 163.3, 153.8, 135.1, 133.1, 130.2, 129.6, 129.4, 128.8, 128.4, 126.1, 125.6, 124.7, 123.9, 122.1, 120.0, 119.8, 119.5, 93.5, 56.2, 55.9, 52.6, 51.4, 45.9, 45.7, 26.4, 25.9, 24.0, 23.8, 23.4, 22.4, 10.6, 10.3. HRMS (APCI) m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{43}\text{H}_{43}\text{N}_4\text{O}_4$ 679.3279; found 679.3252. IR stretching frequencies (cm^{-1}) 2961, 2926, 2869, 1683, 1644, 1584, 1542, 1338, 1069, 802. The ORTEP diagram and structure refinement data of compound **2** were provided in supporting information (Figure S22 & Table S1).

Compound 3: In a dry sealed tube, PDA (200 mg, 0.5012 mmol) in toluene (10 mL) was degassed with argon for 15 minutes. Then

DBU (760 μ L, 5.102 mmol) was added and stirred at 140 °C for 24 hrs. After which the reaction mixture was subjected to a water workup and washed with chloroform twice. Organic layer was collected over anhydrous sodium sulphate and concentrated under reduced pressure. Crude mixture was subjected to silica-gel column chromatography for purification. After repetitive columns, pure compound was obtained in chloroform/ethylacetate solvent mixture in 20% (71 mg) yield. **¹H NMR** (500 MHz, CDCl₃, 298K) δ (ppm) 8.47 (d, J = 7.9 Hz, 4H), 8.34 (d, J = 8.0 Hz, 4H), 4.19 – 4.12 (m, 4H), 3.52 (t, J = 7.1 Hz, 4H), 3.38 (m, 4H), 2.53 – 2.47 (m, 4H), 1.99 – 1.89 (m, 4H), 1.69–1.64 (m, 12H). **¹³C NMR** (176 MHz, CDCl₃, 298K) δ (ppm) 175.9, 163.4, 134.7, 131.5, 129.4, 126.4, 123.2, 123.1, 49.5, 45.9, 38.5, 37.4, 30.1, 28.7, 26.8, 23.5. **HRMS (APCI)** m/z : [M+H]⁺ calcd for C₄₂H₄₁N₄O₆ 697.3021; found 697.3032. **IR** stretching frequencies (cm⁻¹) 2927, 2855, 1690, 1651, 1592, 1440, 1356, 808. The ORTEP diagram and structure refinement data of compound **3** were provided in supporting information (Figure S23 & Table S1).

Compound Ar-PBI¹⁸ Synthetic procedure is same as that of compound **1** using 2,6-diisopropylaniline. Yield 72% (1306 mg). **¹H NMR** (500 MHz, CDCl₃, 298K) δ (ppm) 8.73 (d, J = 7.9 Hz, 4H), 8.68 (d, J = 7.9 Hz, 4H), 7.44 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 7.8 Hz, 4H), 2.69 (m, 4H), 1.12 (mixed singlets, 24H). **¹³C NMR** (126 MHz, CDCl₃, 298K) δ (ppm) 163.5, 145.6, 135.1, 132.1, 130.5, 130.2, 129.7, 126.8, 124.1, 123.4, 123.3, 29.2, 24.0. **HRMS (APCI)** m/z : [M+H]⁺ calcd for C₄₈H₄₂N₂O₄ 711.3217; found 711.3191.

Compound 4: Synthetic procedure is same as that of compound **2** using **Ar-PBI**. Yield 26% (63 mg). **¹H NMR** (500 MHz, CDCl₃, 253K) δ (ppm) 8.71–8.65 (merged doublets, 2H), 8.61 – 8.50 (m, 3H), 7.63 (d, J = 8.0 Hz, 1H), 7.47 (merged triplets, 2H), 7.38 – 7.28 (m, 4H), 4.57 – 4.44 (m, 1H), 3.95 (t, J = 12.6 Hz, 1H), 3.84 (d, J = 11.0 Hz, 1H), 3.55 – 3.46 (m, 2H), 3.45 – 3.38 (m, 1H), 3.05 – 2.82 (m, 2H), 2.80 – 2.67 (m, 2H), 2.66 – 2.54 (m, 1H), 2.21 – 2.04 (m, 2H), 1.88 (m, 4H), 1.61 (broad s, 1H), 1.14 (broad m, 24H). **¹³C NMR** (126 MHz, CDCl₃, 298K) δ (ppm) 164.7, 164.1, 164.1, 163.6, 155.2, 145.7, 142.4, 136.7, 136.5, 134.4, 132.5, 131.3, 131.3, 131.1, 130.7, 130.1, 129.6, 129.4, 127.7, 126.9, 126.9, 125.8, 124.1, 123.9, 123.9, 121.8, 121.1, 121.0, 120.8, 119.5, 118.5, 102.9, 94.8, 52.7, 47.3, 46.9, 29.7, 29.2, 29.1, 27.6, 27.3, 24.6, 24.1, 24.1, 24.0, 23.9, 23.3. **HRMS (APCI)** m/z : [M+H]⁺ calcd for C₅₇H₅₅N₄O₄ 859.4218; found 859.4248.

ASSOCIATED CONTENT

Supporting Information

Synthetic scheme of precursor, NMR, mass, IR, Frontier MOs, crystallographic data, absorption and fluorescence switching spectra have been provided. The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sankar@iiserb.ac.in

ACKNOWLEDGMENT

The authors thankfully acknowledge Prof. Alakesh Bisai, IISER Bhopal and a reviewer for their insightful suggestions on the mechanism of formation of the compounds. RR thanks DST-INSPIRE for a senior

research fellowship. We sincerely thank Dr. R. V. Ramana Reddy for help in DFT calculations. We acknowledge CREST-MHRD-FAST, IISER Bhopal for funding, and IISER Bhopal for facilities and infrastructure.

REFERENCES

- (a) Facchetti, A. Semiconductors for organic transistors *Mater. Today* **2007**, *10*, 28. (b) Wu, W.; Liu, Y.; Zhu, D. π -Conjugated molecules with fused rings for organic field-effect transistors: design, synthesis and applications *Chem. Soc. Rev.* **2010**, *39*, 1489. (c) Anthony, J. E.; Facchetti, A.; Heeney, M.; Marder, S. R.; Zhan, X. n-Type organic semiconductors in organic electronics *Adv. Mater.* **2010**, *22*, 3876. (d) Zhao, Y.; Guo, Y.; Liu, Y. 25th Anniversary article: recent advances in n-type and ambipolar organic field-effect transistors *Adv. Mater.* **2013**, *25*, 5372. (e) Gsänger, M.; Bialas, D.; Huang, L.; Stolte, M.; Würthner, F. Organic semiconductors based on dyes and color pigment *Adv. Mater.* **2016**, *28*, 3615. (f) Quinn, J. T. E.; Zhu, J.; Li, X.; Wang, J.; Li, Y. Recent progress in the development of n-type organic semiconductors for organic field-effect transistors *J. Mater. Chem. C* **2017**, *5*, 8654.
- (a) Würthner, F. Perylene bisimide dyes as versatile building blocks for functional supramolecular architectures *Chem. Commun.* **2004**, 1564. (b) Wasielewski, M. R. Energy, charge, and spin transport in molecules and self-assembled nanostructures inspired by photosynthesis *J. Org. Chem.* **2006**, *71*, S051.
- (a) Li, C.; Wonneberger, H. Perylene Imides for organic photovoltaics: yesterday, today, and tomorrow *Adv. Mater.* **2012**, *24*, 613. (b) Kozma, E.; Catellani, M. Perylene diimides based materials for organic solar cells *Dyes and Pigments* **2013**, *98*, 160. (c) Wu, Y.; Zhang, Q.; Gao, X. Non-fullerene small molecule acceptors based on perylene diimides *J. Mater. Chem. A* **2016**, *4*, 17604.
- Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. Rylene and related diimides for organic electronics *Adv. Mater.* **2011**, *23*, 268.
- (a) Zhang, L.; Che, Y.; Moore, J. S. One-dimensional self-assembly of planar π -conjugated molecules: adaptable building blocks for organic nanodevices *Acc. Chem. Res.* **2008**, *41*, 1596. (b) Kaloo, M. A.; Mishra, R.; Sankar, J. Perylenebisimide-based multi-modal cyanide recognition: molecular logic gate deciphering magnetic memory units *J. Mater. Chem. C* **2015**, *3*, 1640.
- (a) Peneva, K.; Mihov, G.; Nolde, F.; Rocha, S.; Hotta, J. –I.; Braeckmans, K.; Hofkens, J.; Uji-I, H.; Herrmann, A.; Müllen, K. Water-soluble monofunctional perylene and terrylene dyes: powerful labels for single-enzyme tracking *Angew. Chem. Int. Ed.* **2008**, *47*, 3372. (b) Davis, M.; Jung, C.; Wallis, P.; Schnitzler, T.; Li, C.; Müllen, K.; Bräuchle, C. Photophysics of new photostable rylene derivatives: applications in single-molecule studies and membrane labelling *ChemPhysChem.* **2011**, *12*, 1588. (c) Sun, M.; Müllen, K.; Yin, M. Water-soluble perylenediimides: design concepts and biological applications *Chem. Soc. Rev.* **2016**, *45*, 1513.
- Würthner, F.; Saha-Möller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D. Perylene bisimide dye assemblies as archetype functional supramolecular materials *Chem. Rev.* **2016**, *116*, 962.
- (a) Huang, C.; Barlow, S.; Marder, S. R. Perylene-3,4,9,10-tetracarboxylic acid diimides: synthesis, physical properties, and use in organic electronics *J. Org. Chem.* **2011**, *76*, 2386. (b) Mishra, R.; Lim, J. M.; Son, M.; Panini, P.; Kim, D.; Sankar, J. Tuning the electronic nature of mono-bay alkynyl-phenyl-substituted perylene bisimides: synthesis, structure, and photophysical properties *Chem. Eur. J.* **2014**, *20*, 5576. (c) Shoaee, S.; Eng, M. P.; An, Z.; Zhang, X.; Barlow, S.; Marder, S. R.; Durrant, J. R. Inter versus intra-molecular photoinduced charge separation in solid films of donor-acceptor molecules *Chem. Commun.* **2008**, 4915.
- Avlasevich, Y.; Li, C.; Mullen, K. Synthesis and applications of core-enlarged perylene dyes *J. Mater. Chem.* **2010**, *20*, 3814.
- (a) Usta, H.; Newman, C.; Chen, Z.; Facchetti, A. Dithienocoronediimide-based copolymers as novel ambipolar semiconductors

- for organic thin-film transistors *Adv. Mater.* **2012**, *24*, 3678. (b) Zhou, W.; Jin, F.; Huang, X.; Duan, X.-M.; Zhan, X. A Low-bandgap conjugated copolymer based on porphyrin and dithienocoronene diimide with strong two-photon absorption *Macromolecules*, **2012**, *45*, 7823. (c) Zhou, W.; Zhang, Z.-G.; Ma, L.; Li, Y.; Zhan, X. Dithienocoronene diimide based conjugated polymers as electron acceptors for all-polymer solar cells *Sol. Energy Mater. Sol. Cells* **2013**, *112*, 13. (d) Mishra, R.; Panini, P.; Sankar, J. Novel azepino-terphenylbisimides: synthesis, structure, and properties *Org. Lett.* **2014**, *16*, 3994.
- (11) (a) Rohr, U.; Schlichting, P.; Böhm, A.; Gross, M.; Meerholz, K.; Bräuchle, C.; Müllen, K. Liquid crystalline coronene derivatives with extraordinary fluorescence properties *Angew. Chem., Int. Ed.* **1998**, *37*, 1434. (b) Rohr, U.; Kohl, C.; Müllen, K.; Van de Craats, A.; Warman, J. Liquid crystalline coronene derivatives *J. Mater. Chem.* **2001**, *11*, 1789. (c) Lütke Eversloh, C.; Li, C.; Müllen, K. Core-extended perylene tetracarboxydiimides: the homologous series of coronene tetracarboxydiimides *Org. Lett.* **2011**, *13*, 4148. (d) Jiang, W.; Li, Y.; Yue, W.; Zhen, Y.; Qu, J.; Wang, Z. One-pot facile synthesis of pyridyl annulated perylene bisimides *Org. Lett.* **2010**, *12*, 228.
- (12) (a) Qian, H.; Wang, Z.; Yue, W.; Zhu, D. Exceptional coupling of tetrachloroperylene bisimide: combination of Ullmann reaction and C-H transformation *J. Am. Chem. Soc.* **2007**, *129*, 10664. (b) Shi, Y.; Qian, H.; Li, Y.; Yue, W.; Wang, Z. Copper-mediated domino process for the synthesis of tetraiodinated di(terphenyl bisimide) *Org. Lett.* **2008**, *10*, 2337. (c) Nakazono, S.; Easwaramoorthi, S.; Kim, D.; Shinokubo, H.; Osuka, A. Synthesis of arylated perylene bisimides through C-H bond cleavage under ruthenium catalysis *Org. Lett.* **2009**, *11*, 5426. (d) Nakazono, S.; Imazaki, Y.; Yoo, H.; Yang, J.; Sasamori, T.; Tokito, N.; Cédric, T.; Kageyama, H.; Kim, D.; Shinokubo, H.; Osuka, A. Regioselective Ru-catalyzed direct 2,5,8,11-alkylation of perylene bisimides *Chem. Eur. J.* **2009**, *15*, 7530. (e) Teraoka, T.; Hiroto, S.; Shinokubo, H. Iridium-catalyzed direct tetraborylation of perylene bisimides *Org. Lett.* **2011**, *13*, 2532. (f) Battagliarin, G.; Zhao, Y.; Li, C.; Müllen, K. Efficient tuning of LUMO levels of 2,5,8,11-substituted perylenediimides via copper catalyzed reactions *Org. Lett.* **2011**, *13*, 3399. (g) Battagliarin, G.; Davies, M.; Mackowiak, S.; Li, C.; Müllen, K. Ortho-functionalized perylenediimides for highly fluorescent water-soluble dyes *ChemPhysChem* **2012**, *13*, 923. (h) Li, X.; Wang, H.; Schneider, J. A.; Wei, Z.; Lai, W.-Y.; Huang, W.; Wudl, F.; Zheng, Y. Catalyst-free one-step synthesis of ortho-tetraaryl perylene diimides for efficient OPV non-fullerene acceptors *J. Mater. Chem. C*, **2017**, *5*, 2781. (i) Wu, J.; He, D.; Zhang, L.; Liu, Y.; Mo, X.; Lin, J.; Zhang, H.-J. Direct synthesis of large-scale ortho-iodinated perylene diimides: key precursors for functional dyes *Org. Lett.* **2017**, *19*, 5438. (j) Schmidt, D.; Bialas, D.; Würthner, F. Ambient stable zwitterionic perylene bisimide-centered radical *Angew. Chem., Int. Ed.* **2015**, *54*, 3611.
- (13) (a) Qian, H.; Negri, F.; Wang, C.; Wang, Z. Fully conjugated tri(terphenyl bisimides): an approach to the construction of n-type graphene nanoribbons *J. Am. Chem. Soc.* **2008**, *130*, 17970. (b) Zhen, Y.; Wang, C.; Wang, Z. Tetrachloro-tetra(terphenyl bisimides): an approach towards n-type graphene nanoribbons *Chem. Commun.* **2010**, *46*, 1926. (c) Wang, H.; Chen, L.; Xiao, Y. Heterologous perylene diimide arrays: potential non-fullerene acceptors in organic solar cells *J. Mater. Chem. C* **2017**, *5*, 8875. (d) Kremer, M.; Kersten, M.; Höger, S. Efficient catalytic vicinal diamination of arylene diimides *Org. Chem. Front.* **2018**, *5*, 1825.
- (14) Zhou, C.; Li, Y.; Zhao, Y.; Zhang, J.; Yang, W.; Li, Y. An unusual addition reaction for constructing a novel pH-controlled fluorescence switch *Org. Lett.* **2011**, *13*, 292.
- (15) Regar, R.; Sekhar, A. R.; Mishra, R.; Sankar, J. Bay- and ortho-ring annulated perylenediimides: synthesis and their panchromatic absorption *IJCB*, **2018**, *57B*, 308.
- (16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision A.02*; Gaussian, Inc., Wallingford CT, **2009**.
- (17) Ma, L.; Dolphin, D. Nucleophilic reaction of 1,8-diazabicyclo[5.4.0]undec-7-ene and 1,5-diazabicyclo[4.3.0]non-5-ene with methyl pheophorbide a. Unexpected products *Tetrahedron* **1996**, *52*, 849.
- (18) Langhals, H.; Krötz, O.; Polborn, K.; Mayer, P. A Novel fluorescent dye with strong, anisotropic solid-state fluorescence, small Stokes shift, and high photostability *Angew. Chem., Int. Ed.* **2005**, *44*, 2427.