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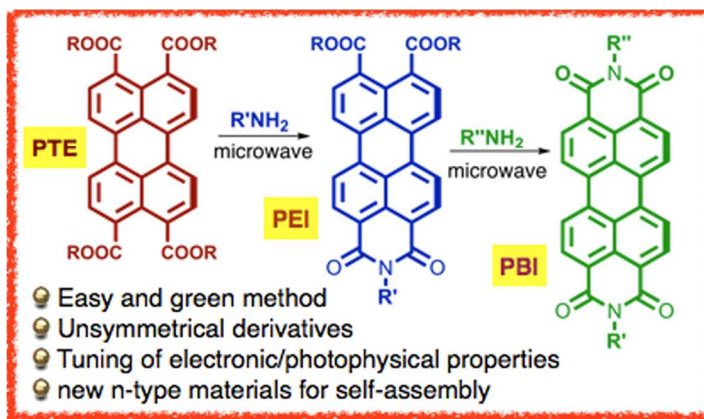
Microwave Assisted-Method for the Synthesis of Perylene Ester Imides as a Gateway Towards Unsymmetrical Perylene Bisimides

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Supporting Information Placeholder



ABSTRACT: A high yielding microwave-assisted synthetic method to obtain unsymmetrical perylene diester monoimide (PEI), by treating the perylene tetrester (PTE) with requisite amine is reported. Perylene-based molecules are widely used in the construction of self-assembled supramolecular structures because of their propensity to aggregate under various conditions. In comparison to perylene bisimides (PBIs), PEIs are less studied in organic electronics/self-assembly due to the synthetic difficulty and low yields in their preparation. PEIs are less electron deficient and have an unsymmetric structure in comparison to PBIs. Further, the PEIs got higher solubility than PBIs. The present method is applicable with a wide range of substrates like aliphatic, aromatic, benzyl amines, PTEs and *bay*-annulated PTEs. This method provides a tuning handle for the optical/electronic properties of perylene derivatives and also provides an easy access to unsymmetrical PBIs from the PEIs.

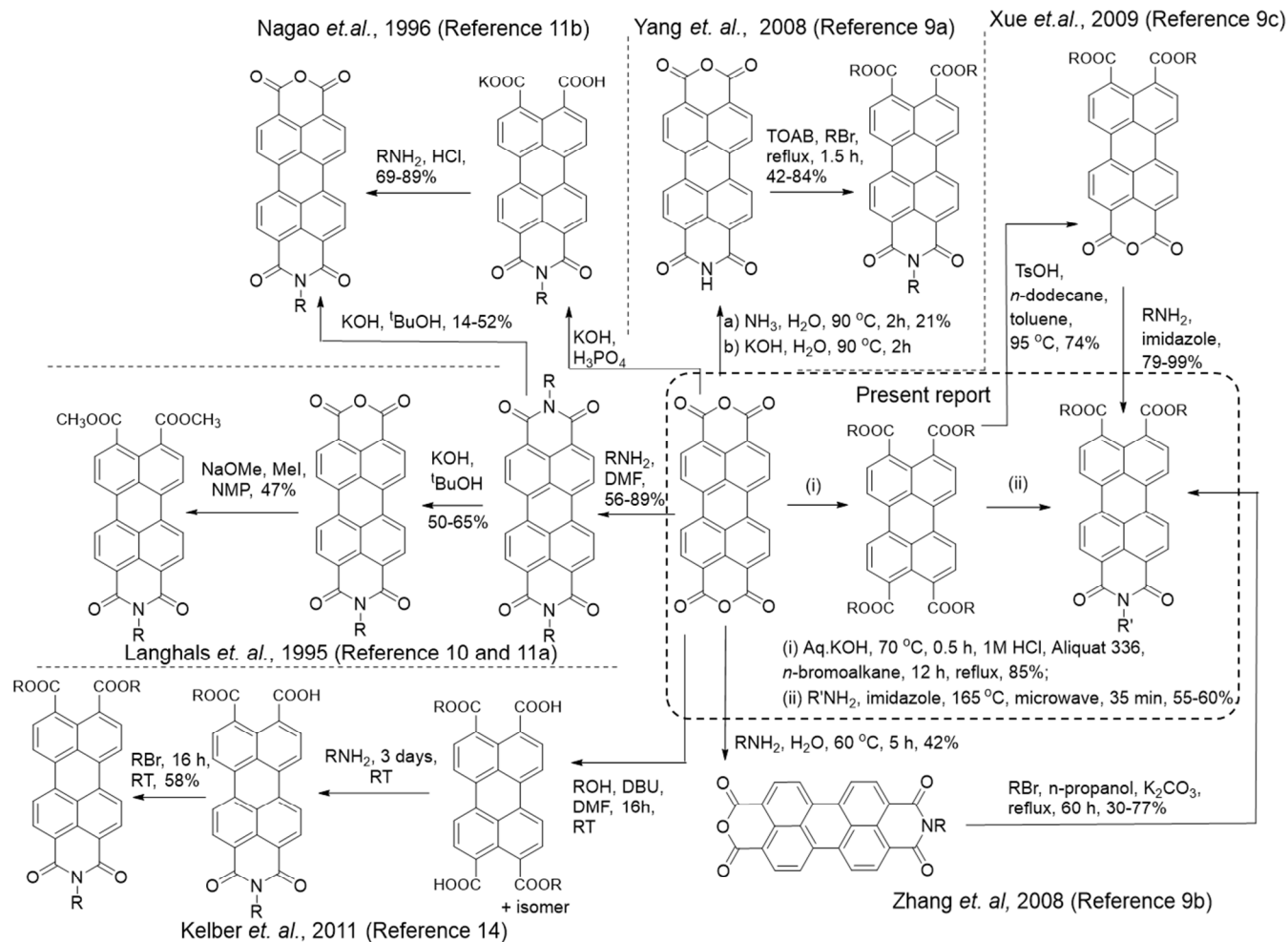
INTRODUCTION

Perylene bisimide (PBI) based molecules are known to exhibit interesting properties and found applications as photo stable dyes, highly luminescent materials, as a component of photoreceptors of photocopiers and laser printers.^{1e} They are also utilized as electron acceptors in organic solar cells (OSCs) or as active components in organic field effect transistors (OFETs), or as building block

1 materials for liquid crystalline and organogel self-assembly.¹ More recently, suitably functionalized PBIs
2 have been utilized for the functionalization of gold nanorods that exhibit unique self-assembly and
3 photophysical behavior.^{1f-i} Further, with the availability of several positions that can be substituted, the
4 photophysical and electronic properties can be modified. The *bay*-substitution of the PBIs had shown to
5 shift the emission towards the red region, with an increase in the Stokes shift and fluorescence life-
6 time.^{2a} The increased stability of such *bay*-substituted PBIs make them potential materials for lasing
7 applications.^{2b} Tetraesters of perylene tetracarboxylic acids (PTEs), which are structurally related to
8 PBIs were also utilized as materials in the area of liquid crystals,³ fluorescent dyes,⁴ electron acceptors
9 in light harvesting antennae,⁵ and organic light emitting diodes (OLEDs).⁶ Similar to PBIs, PTEs have
10 significant electron-accepting ability due to the four carboxylate groups. They are also capable of
11 forming aggregates with strong π - π overlap in both solutions⁷ and the solid state.⁸ Recently, perylene
12 tetracarboxylic diester monoimides (PEIs), are attracting increasing interest due to their intermediate
13 electron deficient nature between PTEs and PBIs as well as higher solubility.⁹ As the name suggests,
14 here an imide and two ester groups are connected to the same perylene core. Nonetheless, in comparison
15 to PBIs, the applications of PTEs and PEIs are relatively limited. Most of the reported PTEs are the
16 symmetrically substituted ones, whereas PEIs that are explored are only limited to simple alkyl
17 derivatives. In comparison, the applications of PBIs have seen steady rise due to their tunability to alter
18 the properties by unsymmetric substitution with various amines. However, the balancing of the
19 electronic levels of organic semiconductors with respect to electrodes is vital for their application in
20 organic electronic devices. The synthesis of PEIs, which are inherently unsymmetric is a bit challenging.
21 An overview of the research done over the past years is presented in Scheme 1. A common approach to
22 obtain alkyl-substituted PEI starts with diimidification of perylene tetracarboxylic acid bisanhydride
23 (PTCBA) with an alkylamine, which is followed by its monohydrolysis under mild conditions.^{10,11}
24 Recently few reports on obtaining PEIs are described. Yang *et al.* recently reported perylene imido-
25 diesters with three *n*-alkyl substituents of same length.^{9a} Their synthetic approach provided
26 unsubstituted perylene tetracarboxylic monoimido-monoanhydride in low-yield, which after isolation
27 subjected to phase-transfer trialkylation of its dipotassium salt. This required an excess amount of the
28 alkyl bromide. In spite of providing access to PEIs, it's drawback is the inability to obtain
29 unsymmetrically substituted PEIs. Zhang *et. al* reported the preparation of PEIs by the reaction of alkyl
30 bromides with perylene tetracarboxylic monoanhydride monoimide.^{9b} Here the perylene tetracarboxylic
31 bisanhydride (PTCBA) was treated with *n*-alkylamine, which results in the formation of two products,
32 *i.e.*, the perylene tetracarboxylic monoanhydride monoimide and the other one is corresponding PBI.
33 After the isolation of monoanhydride monoimide, it is treated with required alkyl bromide to obtain the
34 PEI.^{9b} The yield was varying from 30-77%. Xue *et.al.* prepared perylene tetracarboxylic monoanhydride
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diester from corresponding PTE. This on treatment with *n*-alkyl amine yielded the PEI.^{9c} Although the yields are good, it involves three steps. Earlier, PEIs were also obtained by the controlled hydrolysis of PTCBA with a base to obtain monoanhydride, and its

Scheme 1. Various routes to prepare PEIs/the key intermediates to prepare them over the years.



treatment with alkylamine to get alkyl imidoanhydride which can be further converted to the PEI.^{10,11} Such alkylimidoanhydrides can then be esterified to get PEI, or may be condensed with another amine to obtain PBI.^{12,13} These procedures require the isolation of monoimido monoanhydride (PEA). However, when the monoimido monoanhydride is formed, it possesses an increased solubility in comparison to that of PTCBA. Due to this, its reactivity is increased and often it gives the symmetric PBI. Kelber *et al.* recently approached this problem in a different way.¹⁴ They obtained perylene tetracarboxylic diester from PTCBA, after which they added alkyl amine to obtain imido-ester-acid, which on treatment with bromoalkane yielded imido-diester. However, this reaction depends on the initial solubility of initial starting material in excess alcohol and alkyl bromides, thus it can be used only

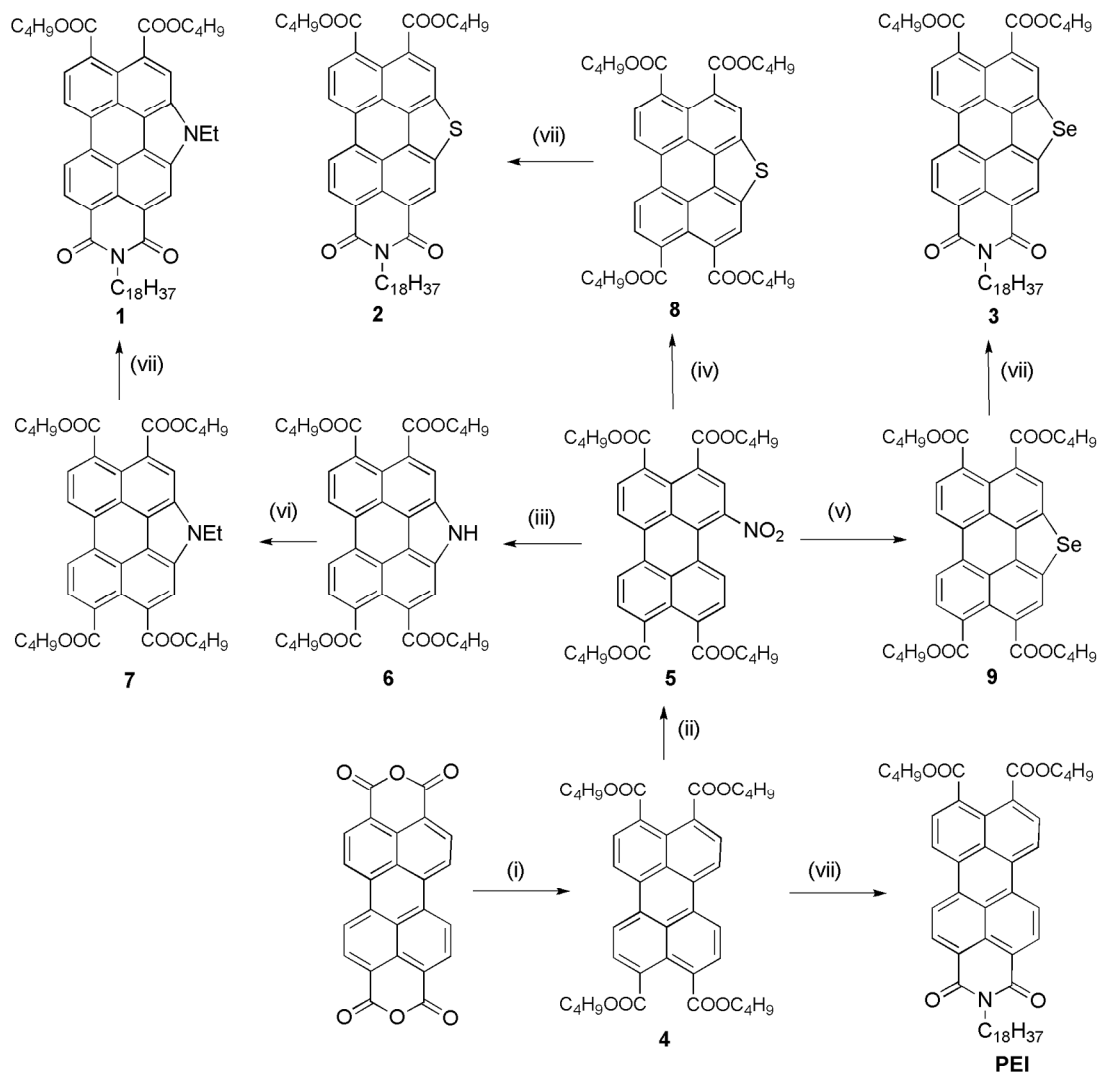
1 for small chain alcohols. In addition, corresponding alkyl bromides are also required in addition to long
2 reaction duration. All these previous investigations made us to investigate the problem of obtaining PEI
3 in a simple, high yielding method. In this report we have presented a high yielding method for the
4 preparation of PEI in two steps, starting from PTCBA. PTCBA is converted to its PTE and later this is
5 treated with the required amine under microwave conditions to yield the requisite PEI (Scheme 2). The
6 PEI obtained can be converted to an unsymmetric PBI if required, thus providing an easy access to
7 unsymmetrical PBIs.
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14 RESULTS AND DISCUSSION

16 Initially we thought of treating PTCBA directly with requisite amine to get corresponding imide
17 anhydride. But this suffers from the insolubility of the starting material in most of the solvents and the
18 increased reactivity of the imide anhydride formed due to its higher solubility than PTCBA, which
19 eventually ends up in the formation of symmetrical PBI. Microwave-assisted synthesis has attracted the
20 material and synthetic chemists, as it provides a green alternative to obtain useful products in higher
21 yields under milder reaction conditions along with higher product purities. Microwaves greatly
22 accelerate the rate of the reactions in comparison to conventional heating.¹⁵ There are few reports on the
23 application of microwave assisted synthesis to obtain symmetrical perylene bisimides.¹⁶ However
24 utilization of microwave assisted synthesis to obtain unsymmetrical derivatives are not reported to the
25 best of our knowledge. The time for the reaction was optimized as 35 min to obtain the maximum yield.
26 Compared to earlier methods, which had several low yielding steps with a difficulty in isolation, this
27 method is straightforward and provides a good yield of 50-55%. The remaining amount of PTE is
28 converted to PBI, which is highly insoluble and remain trapped with the neutral alumina used for the
29 column chromatography. Further we studied the substrate scope of this procedure. The PTE **4** was
30 treated with different aliphatic and aromatic amines (Scheme 3, Table 1) to obtain corresponding PEIs.
31 Further we wanted to test the scope of this reaction in the preparation of perylene tetracarboxylic diester
32 monoimides from *bay*-annulated perylene tetraesters (**7-9**). *Bay*-annulated perylene tetraesters with
33 heteroatoms like nitrogen, sulfur and selenium have shown ordered columnar hexagonal (Col_h) phase
34 over a wide thermal range along with a good luminescence.^{17a-c} The *bay*-substitution and *bay*-extension
35 of perylene derivatives provided an access to modify the photophysical and electrochemical properties
36 of perylene derivatives.¹⁷ Recently we have reported host-guest OLEDs based on *bay*-annulated
37 perylene tetraesters exhibiting room temperature Col_h phase.¹⁹ Thus considering the importance of *bay*-
38 annulated perylene derivatives, we thought of synthesizing the *bay*-annulated PEIs (BAPEIs), by
39 utilizing the corresponding perylene tetraesters (BAPTEs) with four *n*-butyloxy chains.¹⁸ These
40 tetraesters were prepared similarly to the recently published report.¹⁸ These BAPTEs were treated with
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1-aminooctadecane (**14**) under microwave conditions, which yielded the corresponding BAPEIs in good yield (Scheme 2, Table 1).

Scheme 2. Synthesis of PEI and *bay*-annulated PEIs.

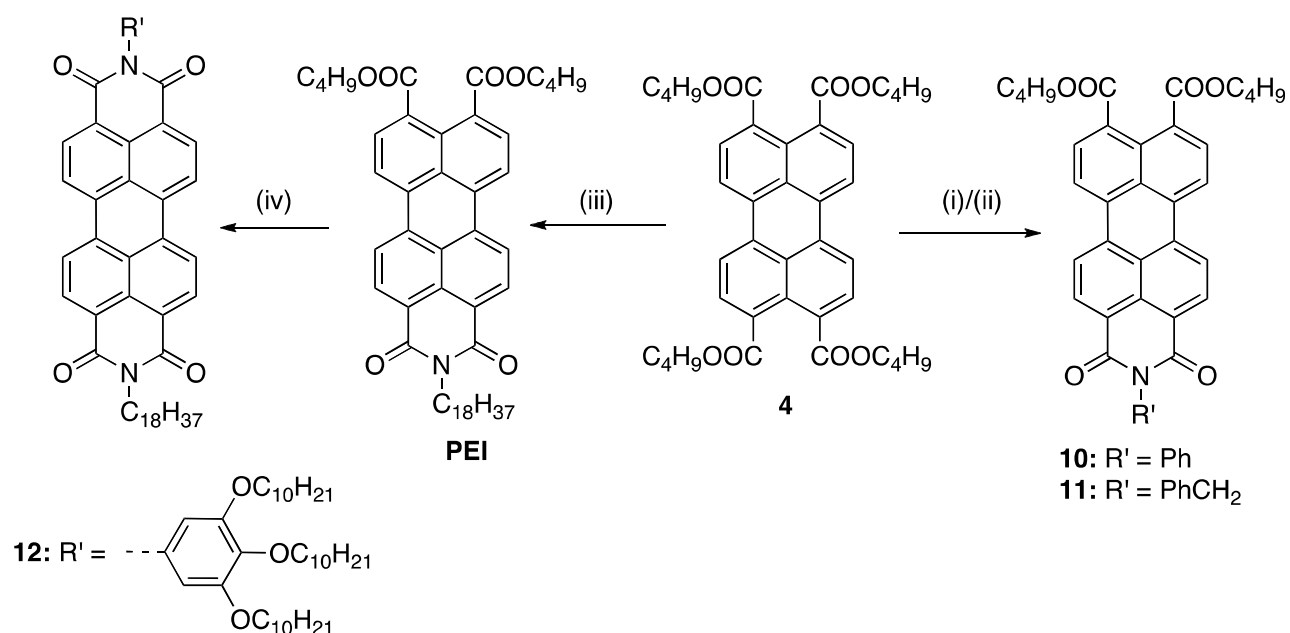


Reagents and conditions. i) KOH, H₂O, 70 °C, 0.5 h, 1M HCl, Aliquat 336, KI, 1-Bromo-butane, reflux, 12 h (76%); ii) NaNO₂, HNO₃, 0 °C, 1h (90%); iii) Triethyl phosphite, 160 °C, reflux, 4 h, N₂ (60%); iv) Sulfur powder, anhyd.NMP, N₂, 70 °C, 0.5 h, 180 °C, 17 h (55%); v) Selenium powder, anhyd. NMP, N₂, 70 °C, 0.5 h, 180 °C, 17 h (55%); vi) NaH, 1-Iodoethane, Dry THF, reflux, 17h (75%); vii) 1-Aminooctadecane, imidazole, 165 °C, microwave, 35 min. (50-55%).

The compound **14** was prepared by Gabriel's phthalimide synthesis (See Scheme 1 in SI).²⁰ An unsymmetrical PBI **12** was also prepared in good yield using the PEI as starting material to show the utility of this method (Scheme 3, Table 1). The synthesized compounds were completely characterized with the help of ¹H, ¹³C NMR, IR spectroscopy and MALDI-TOF mass spectrometry. The ¹H NMR spectra of the BAPEIs were interesting and the effect of the inclusion of the heteroatom in the molecular

structure was evident with the change of the chemical shifts of the aromatic protons. The protons near to the imide group appear in the downfield region, while the protons near the esters resonate in the upfield region in the case of PEI. The *bay* protons (H_c and H_d) appear in between the two sets of protons. Presence of the heteroatoms gives rise to a complex pattern by breaking the symmetry. In the case of compound **1**, H_c and H_d resonate at same position, while protons in *ortho* positions splits to form doublets. In the case of *S*- and *Se*-annulated BAPEIs, H_c and H_d also appear as doublets in addition to the doublets of H_e and H_f . The aromatic signals obtained for compound **3** is similar to that of compound **2** but they appear at upfield (Fig.S31).

Scheme 3. Synthesis of different perylene ester imdides (**10,11**) and an unsymmetrical perylene bisimide **12**.^a



Reagents and Conditions: (i) Aniline, imidazole, 165 °C, 35 min. (55%); (ii) Benzylamine, imidazole, 165 °C, 35 min. (58%); (iii) 1-Aminooctadecane, imidazole, 165 °C, 35 min. (55%); (iv) 3,4,5-tri-*n*-decyloxy aniline, imidazole, zinc acetate, 165 °C, 35 min. (75%).^a all these reactions were done using a microwave reactor.

Table 1. Substrate scope of the present reaction for the synthesis of various PEIs and PBI (**12**).

Starting material	Reactant	Yield (%)
PTE (4) ^a	<i>n</i> -Octyldecylamine	PEI (55)
PTE (4) ^a	Aniline	10 (55)
PTE (4) ^a	Benzylamine	11 (58)
BPTE (7) ^a	<i>n</i> -Octyldecylamine	1 (55)
BPTE (8) ^a	<i>n</i> -Octyldecylamine	2 (55)
BPTE (9) ^a	<i>n</i> -Octyldecylamine	3 (55)
PEI ^b	3,4,5-tri- <i>n</i> -decyloxyaniline	PBI (12) (75)

^aImidazole, 165 °C, microwave, 35 min.; ^bImidazole, Zinc acetate, 165 °C, microwave, 35 min.

1 Photophysical properties of these compounds were explored by obtaining their absorption and
2 emission spectra in micromolar chloroform solutions (Table 2 and Fig.1a, b). The absorption spectra of
3 these **PEI** and **BAPEIs** were well-structured and showed the characteristic vibronic bands. There was
4 not much change observed in the case of **PEI** and *N*-annulated derivative **1** as both of them exhibited an
5 absorption maximum centered at 506 nm. However, the absorption spectra of *S*- and *Se*-annulated
6 derivatives were blue shifted with the absorption maxima centered at 480 and 486 nm respectively. All
7 the PEIs exhibited high molar extinction coefficients at their absorption maxima (ϵ : 11,500 to 15,500
8 $\text{Lmol}^{-1}\text{cm}^{-1}$). The optical band gap calculated from the absorption onset showed that the optical band
9 gap of **PEI** and *N*-annulated derivative **1** were almost similar (2.28-2.33 eV), while that of the *S*- and
10 *Se*-annulated derivatives shown an increase (2.42-2.44 eV). Emission spectra of these compounds
11 showed two main bands, with the high intensity band was in the range of 499-543 nm. The Stokes shift
12 was found to be more for PEI (1347 cm^{-1}) and for other PEIs the value was in the range of $774\text{-}793\text{ cm}^{-1}$.
13 Introduction of hetero atoms led to a blue shifted emission spectra for the *bay*-annulated derivatives.
14 Relative fluorescence quantum yields measured with respect to fluorescein (0.1 M NaOH solution, $Q_f =$
15 0.79), showed a higher quantum yield for **PEI**, **1** and **2**, but a lower quantum yield for compound **3**
16 (Table 2). Both the solution and thin films showed visually perceivable emission under the UV light of
17 long wavelength. A weak emission was noticed for *Se*-derivative **3**, due to the 'heavy atom effect'.^{17c, 19}

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The absorption and emission spectra obtained in thin film state were found to be broad and blue
shifted, while the emission spectra have shown a red-shift (Fig.1d, e), which confirmed the formation of
H-type aggregates,^{21a} though it may not be a classic H-aggregate with an exact overlap of the molecules
one above the other. In the case of perylene based molecules with out any *bay*-substitution, it is quite
common to see that such molecules aggregate one above the other, with their major absorption band
getting blue shifted indicating the predominant H-type excitonic coupling.^{21b} Here, as a consequence of
a rotational displacement of neighboring molecules, the optical transition into the lower energy exciton
state becomes allowed,²² as evidenced by the second absorption band at longer wavelength (Fig.1a and
d, Table 2). The particular arrangement and the concomitant photophysical properties of the aggregates
are strongly dependent on the substituents at *peri*-position.

In literature, for PBIs bearing electronically active rather innocent trialkyl-phenyl substituents, a
relatively long-lived excited state with an appreciably high fluorescence quantum yield of 47% has been
reported,^{21b} which was attributed to the relaxation of the exciton into an excimer.^{21c} As these PEIs are
unsymmetrically substituted, they are slightly rotated from the exact overlap, to accommodate the steric
bulk of ester functional groups. Because of this slight rotation there will not be a perfect overlap as
observed in the case of the classical H-aggregates leading to the complete luminescence quenching. This
is clearly visible in the overlay of the emission spectra of thin films with that of the solutions. A huge

reduction in the emission intensity was observed because of the aggregation caused quenching (Fig. S40).

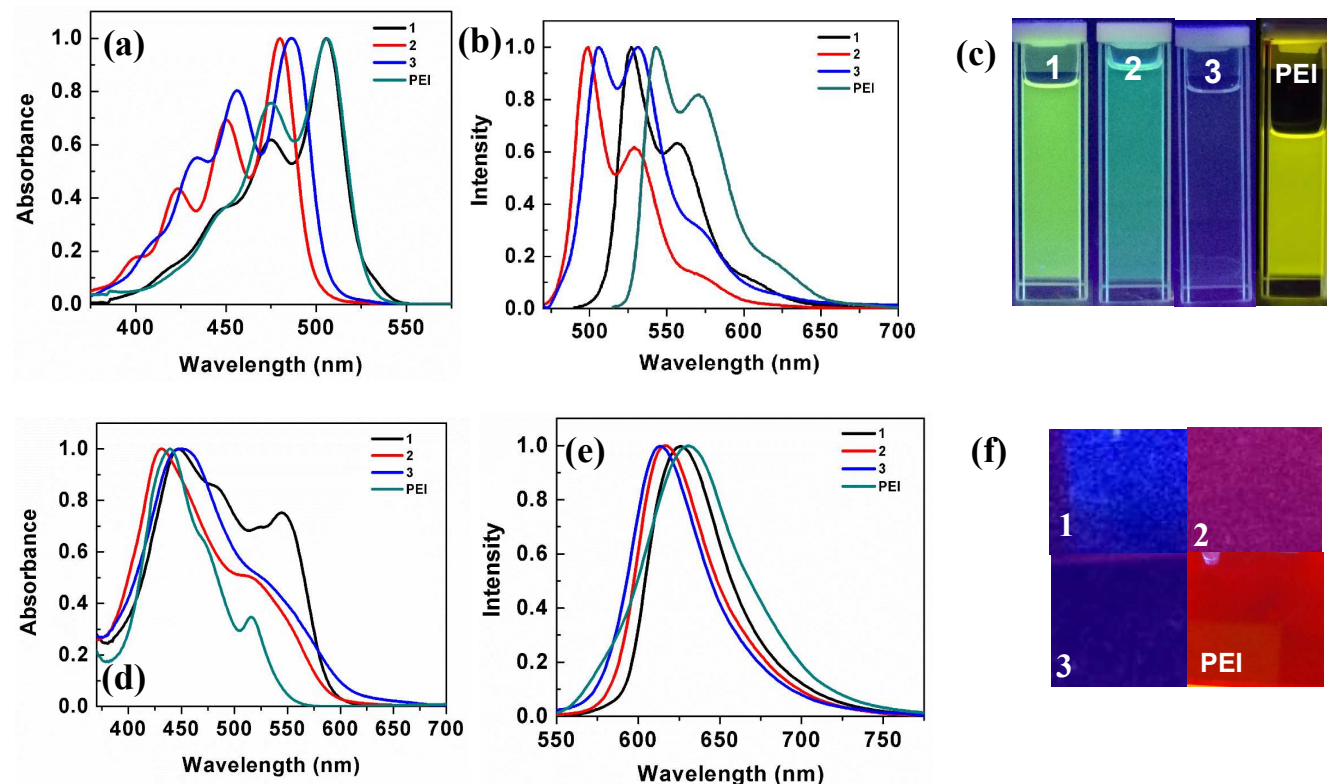


Figure 1. (a) Normalized absorption and (b) emission spectra in micromolar chloroform solution of **1**, **2**, **3** and **PEI** obtained on exciting at their absorption maxima; (c) Images of the same solutions under the UV light of long wavelength ($\lambda = 365$ nm); (d) Normalized absorption and (e) emission spectra of the spin coated films of **1**, **2**, **3** and **PEI** obtained on exciting at their absorption maxima; (f) Images of the same thin films under the UV light of long wavelength ($\lambda = 365$ nm).

Table 2. Photophysical and electrochemical properties of **PEI** and **BAPEIs (1, 2, 3)**.

Entry	Solution ^a					Thin film ^d		Cyclic Voltammetry ^{e,f}		
	Absorption (nm)	Emission ^b (nm)	$\Delta E_{g,opt}$ ^c (eV)	Stokes shift (cm ⁻¹)	ϕ^g	Absorption (nm)	Emission ⁱ (nm)	E_{red} (V)	E_{HOMO}^g (eV)	E_{LUMO}^h (eV)
PEI	506, 475, 446	543, 571, 622	2.33	1347	0.93	439, 516	631	-0.81	-5.86	-3.53
1	506, 475, 448, 417	527, 557, 615	2.28	788	0.89	447, 544	626	-0.96	-5.66	-3.38
2	480, 450, 423, 399	499, 529, 579	2.42	793	0.70	434, 514	616	-0.92	-5.84	-3.42
3	486, 456, 434, 408	505, 531, 577	2.44	774	0.06	451, 533	615	-0.92	-5.86	-3.42

^amicromolar solution in chloroform, ^bexcited at 506 nm for **PEI** and **1**, 480 nm, 486 nm for **2** and **3** respectively, ^ccalculated from the red edge of the longest wavelength in the absorption spectrum ^dprepared from the millimolar solution in chlorobenzene, ^emicromolar solution in dichloromethane, ^fExperimental conditions: Ag/AgNO₃ as reference electrode, Glassy carbon working electrode, Platinum wire counter electrode, TBAP (0.1 M) as a supporting electrolyte, room temperature, ^gEstimated from the formula $E_{HOMO} = E_{LUMO} - \Delta E_{g(UV)}$ eV; ^hEstimated from the formula by using $E_{LUMO} = -(4.8 - E_{1/2, Fc/Fc^+} + E_{red, onset})$ eV; $E_{1/2, Fc/Fc^+} = 0.462$ eV, ⁱrelative quantum yields are calculated with respect to Fluorescein in 0.1M NaOH solution as the standard, $Q_f = 0.79$. ^jexcited at 439 nm for **PEI**, 447 nm for **1**, 434 nm, 486 nm for **2** and **3** respectively.

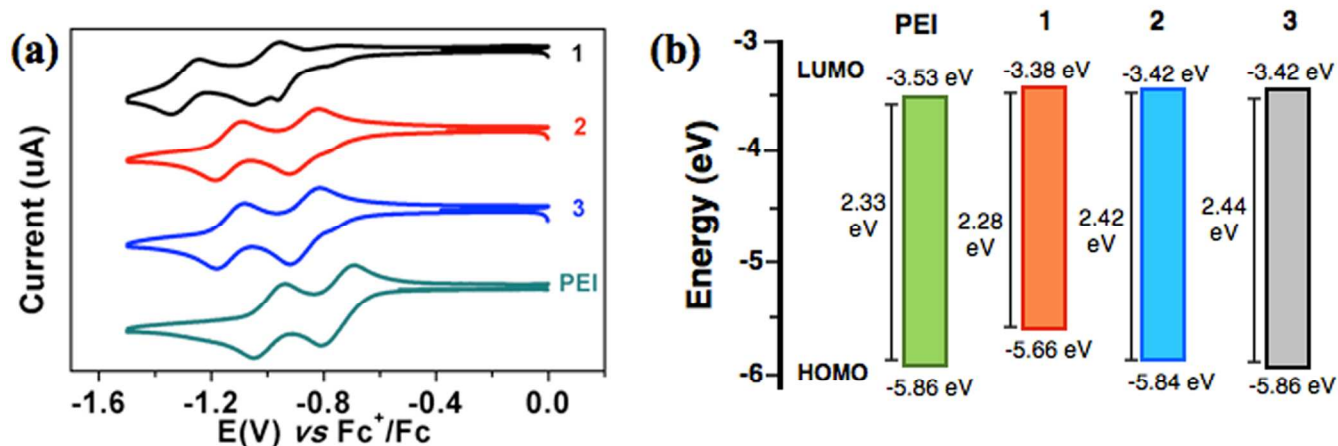


Figure 2. (a) Cyclic voltammograms of **PEI** and *bay*-annulated **PEIs** (**1**, **2** and **3**); (b) Energy band level diagram showing HOMO- and LUMO- energy levels of **PEI** and **BAPEIs**.

Cyclic voltammetry (CV) studies are carried out to understand the electronic energy levels that decide the energy and electron transfer process and reversibility of a redox process. CV studies were carried out in anhydrous dichloromethane solutions (Table 2). PBI is known to be electron deficient n-type semiconductors and known to have high electron affinity.¹ We expected the PEIs to be less electron deficient in comparison to PBIs. All the PEIs exhibited two quasi-reversible reduction peaks, which are due to the reduction of the neutral molecule to a radical anion in the first step and to a dianion in the second step (Fig.2a). The addition of the first electron in the first reduction increases the electron density on the carbonyl of imide. The addition of the second electron in the second reduction is supported by the ability of the core to delocalize this extra electron density to reduce the Coulombic repulsion of the similar charges.²³ It was difficult to obtain the oxidation potentials of these electron deficient compounds even with a CV measurement window up to +1 V vs Ag/AgNO₃. Thus we have estimated the HOMO levels, by subtracting the LUMO energy values from the optical band gap that was obtained from the absorption onset of the respective compounds in solutions. From the CV studies it was found that the *bay*-annulated PEIs showed increased LUMO levels in comparison to **PEI** (Fig.2b). A small increase of 0.15 eV in the LUMO level was noted in the case of **1**, while **2** and **3** displayed a lowering of LUMO levels by 0.11 eV respectively, with respect to the LUMO of **PEI** (Fig.2b). Thus in the case of compound **1**, an increase in the HOMO level was observed, while that of compound **2** and **3** remained fairly unaltered.

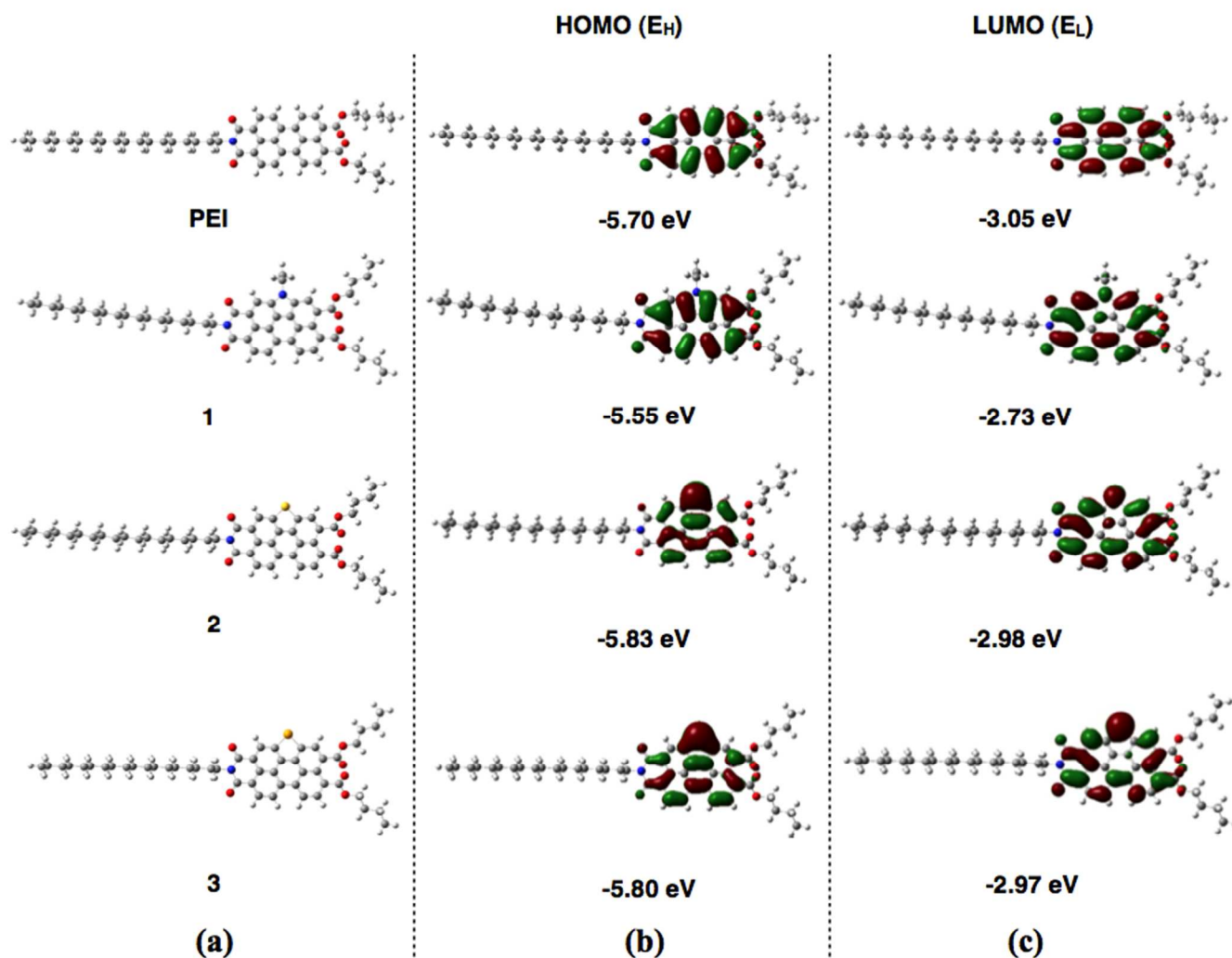


Figure 3. Optimized geometry of compounds **PEI**, **1**, **2** and **3** (a); HOMO (b) and LUMO (c) frontier molecular orbitals of compounds of the same at the B3LYP/6-31G(dp) level. EH and EL denote energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

We further probed the energy levels and their separations with the help of DFT calculations. The energy minimized structures for **PEI**, **1**, **2** and **3** are showed in Fig.3a. Images of frontier molecular orbitals (FMOs) and the differences in their energies offer information about the length of conjugation and the separation of energy levels, which helps in comparing the **PEI** with its *bay*-annulated derivatives. In the energy-minimized structures, we can notice the planarity of the perylene ring remains unchanged after *bay*-annulation. The contours of the HOMO and LUMO of PBIs are shown in Fig. 3b and c. The HOMO-LUMO energy levels of PEIs are distributed on the entire aromatic ring. Imide groups are known to be closed chromophoric (electronically decoupled) systems. This is due to the presence of nodes of the HOMO and LUMO orbitals on imide nitrogen atoms, while some electron density is found to be distributed on the ester group or oxygen atoms. Thus the substitution at imide nitrogen does not alter the optical properties significantly, but the *bay*-annulation is supposed to affect

1 the HOMO-LUMO levels. In the case of *bay*-annulated derivatives, HOMO and LUMOs were found to
2 be spreading over heteroatoms (for compounds **2** and **3**). In the case of compound **1**, only the LUMO
3 was distributed on the *N* atom, which serves as a node for HOMO. In fact, the HOMO and LUMO
4 levels of *bay*-annulated PEIs have increased in comparison to the simple PEI. The HOMO-LUMO
5 separations for **PEI, 1, 2** and **3** were found to be 2.65, 2.82, 2.85 and 2.83 eV respectively.
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10 CONCLUSIONS

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14 We have presented an easy microwave assisted method for the synthesis of unsymmetric PEIs by
15 treating PTEs with requisite amines, in good yield. This microwave assisted synthetic method has a
16 wide substrate scope including various PTEs, *bay*-annulated PTEs, aliphatic amines, aromatic amines
17 and benzyl amines. Especially, application of this method to *bay*-annulated tetraesters, provide *bay*-
18 annulated PEIs, which provide new avenues in organic semiconductors. Photophysical and
19 electrochemical properties of the *bay*-annulated PEIs were studied in comparison with the simple PEI
20 along with the DFT calculations to visualize the electronic energy levels. Moreover, this synthetic
21 method provides an easy access to synthesize unsymmetrical perylene bisimides, which are very
22 important materials from the viewpoint of organic electronics as well as supramolecular self-assembly.
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31 EXPERIMENTAL SECTION

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33 Commercially available chemicals were used without any purification; solvents were dried following
34 the standard procedures. Chromatography was performed using either neutral aluminum oxide. For thin
35 layer chromatography, aluminum sheets pre-coated with silica gel were employed. IR spectra were
36 recorded on a Perkin Elmer IR spectrometer at normal temperature by using KBr pellet. The spectral
37 positions are given in wave number (cm^{-1}) unit. NMR spectra were recorded using Varian Mercury 400
38 MHz (at 298K) or Bruker 600 MHz NMR spectrometer. For ^1H NMR spectra, the chemical shifts are
39 reported in ppm relative to TMS as an internal standard. Coupling constants are given in Hz. Mass
40 spectra were determined from MALDI-TOF mass spectrometer using α -Cyano-4-hydroxycinnamic acid
41 as a matrix or High Resolution Mass Spectrometer (Agilent-QTOF-450). Elemental analysis was carried
42 out with Perkin Elmer-2400, Series II, CHNSO Analyser. UV-Vis spectra were obtained by using
43 Perkin-Elmer Lambda 750, UV/VIS/NIR spectrometer. Fluorescence emission spectra in solution state
44 as well as thin film state were recorded with Horiba Fluoromax-4 fluorescence spectrophotometer or
45 Perkin Elmer LS 50B spectrometer. Cyclic Voltammetry studies were performed using a Versa Stat 3
46 (Princeton Applied Research) Electrochemical workstation. Microwave reactions were performed in
47 CEM discover instrument. All microwave reactions were performed in sealed tube reaction condition
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and the reaction temperatures were monitored by internal probe and the temperature is reached or maintained in each experiment. Other reactions were performed in oil bath condition and reaction temperature was monitored by external probe. The quantum mechanical calculations of molecular properties were performed using DFT by employing the combination of Becke3–Lee–Yang–Parr (B3LYP) hybrid functional and 6-31G(d,p) basis set using the Gaussian09 package²⁴, to obtain the information related to molecular conformation and frontier molecular orbitals (HOMO–LUMO) of all the compounds. Full geometry optimizations were carried out by using the Hatree–Fock method with the 321-G basic set followed by DFT calculations using the B3LYP hybrid functional and the 6-31G(d,p) standard basis set because of the successful application of such methods for larger organic molecules. The absence of imaginary frequency ensured the stable structure of compound.

Tetrakis(butyl) perylene-3,4,9,10-tetracarboxylate (4)¹⁸ Perylene tetracarboxylic dianhydride (2g, 5 mmol, 1 equiv.) was dissolved in 30 mL aqueous KOH (1.5g, 27 mmol, 5.4 equiv.) solution and stirred at 70 °C for 0.5 h. The solution was filtered and pH value of filtrate was adjusted to 8-9 using 10% HCl. Then Aliquat 336 (0.72g, 1.8 mmol, 0.4 equiv.) and KI (0.17g, 1 mmol, 0.2 equiv.) were charged into the solution and then stirred vigorously for 10 min. 1-Bromobutane (4g, 31 mmol, 6 equiv.) was added to this reaction mixture. After the addition the reaction mixture was refluxed for 12 h until a red oil floats on the top and the rest of the solution becomes clear. Subsequently, chloroform (10 mL) was poured into the mixture and filtered through the celite bed to remove unreacted part and the celite bed was washed with chloroform. This chloroform layer was separated and washed twice with 15% sodium chloride solution, dried over sodium sulfate and concentrated *in vacuo* to get a viscous concentrate. Methanol was added to precipitate the compound from this concentrate. The solid was precipitated, filtered and dried in vacuum. Yield of this compound was 76%.

4: $R_f = 0.6$ (20% EtoAc-Hexane); orange solid, yield: 2.48g, 76%; IR (KBr pellet) ν_{\max} in cm^{-1} 2960 (C-H), 2930 (C-H), 2872 (C-H), 1725 (C=O), 1627 (C=C), 1590 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K): 8.04 (d, $J = 7.8\text{Hz}$, 4H, H_{Ar}), 7.90 (d, $J = 7.8\text{Hz}$, 4H, H_{Ar}), 4.36-4.34 (m, 8H, 4 × -OCH₂), 1.82-1.78 (m, 8H, 4 × -OCH₂-CH₂), 1.62-1.49 (m, 8H, 4 × CH₂), 1.02-1.0 (m, 12H, 4 × -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 168.8, 132.9, 130.5, 129, 128.8, 121.5, 65.5, 30.9, 19.5, 14; MALDI-TOF : exact mass calculated for C₄₀H₄₄O₈ (M⁺): 652.3, found: 652.5; HRMS (APCI mode) exact mass calculated for C₄₀H₄₄O₈ (M): 652.3042, found: 652.3297.

Tetrakis(butyl) 1-nitroperylene-3,4,9,10-tetracarboxylate (5)¹⁸ To a solution of **4** (0.9g, 1.4 mmol, 1 equiv.) in dichloromethane (15 mL), added NaNO₂ (0.1g, 0.7 mmol, 1 equiv.) at 0 °C and stirred. To this well stirred suspension, 69% HNO₃ (3.42 mmol, 5 equiv., 10% solution in dichloromethane) was added

dropwise. This mixture was stirred at 0 °C for 1 h. The reaction mixture was poured into water and extracted with dichloromethane (25 mL). Finally, organic layer was dried over anhyd Na₂SO₄ and concentrated. The crude product was purified by column chromatography on neutral alumina. Elution with 50% dichloromethane-hexane yielded the desired product. Yield of this nitro compound was 90%.

5: *R_f* = 0.6 (20% EtoAc-Hexane); red viscous liquid, yield: 0.88g, 90%; IR (KBr pellet) ν_{\max} in cm⁻¹ 2958 (C-H), 2928 (C-H), 2872 (C-H), 1725 (C=O), 1660 (C=C), 1591 (C=C), 1533 (N-O), 1356 (N-O); ¹H NMR (600 MHz, CDCl₃, 299 K): 8.34-8.29 (m, 2H, H_{Ar}), 8.24 (s, 1H, H_{Ar}), 8.18 (d, *J* = 6Hz, 1H, H_{Ar}), 8.10 (d, *J* = 6Hz, 1H, H_{Ar}), 7.95-7.93 (m, 1H, H_{Ar}), 7.86-7.84 (m, 1H, H_{Ar}), 4.37-4.33 (m, 8H, 4 × -OCH₂), 1.81-1.77 (m, 8H, 4 × -OCH₂-CH₂), 1.51-1.46 (m, 8H, 4 × CH₂), 1.01-0.98 (m, 12H, 4 × -CH₃), ; ¹³C NMR (150 MHz, CDCl₃, 298.1K): 168.2, 168, 167.9, 166.8, 146.2, 133.6, 132.3, 132.1, 131.4, 131.3, 130.8, 130.4, 129.9, 129.6, 129.1, 128.5, 128.4, 127.5, 126.6, 125.7, 123.2, 122.7, 66.2, 65.9, 65.8, 65.7, 30.7, 30.7, 29.8, 19.4, 14; MALDI-TOF : exact mass calculated for C₄₀H₄₃NO₁₀ (M⁻): 697.3, found: 697.8; Elemental analysis calcd. (%) for C₄₀H₄₃NO₁₀: C 68.85, H 6.21, N 2.01; found: C 69.19, H 6.26, N 2.11.

Tetrakis(butyl) 1H-phenanthro[1,10,9,8-cdefg]carbazole-3,4,9,10-tetracarboxylate¹⁸(6) A mixture of compound **5** (0.84g, 0.6 mmol) and triethyl phosphite (7 mL) were refluxed for 4 h under argon atmosphere. Reaction mixture was cooled to room temperature and methanol was added to this solution to precipitate the compound. This precipitated product was filtered off and washed with water, dried in vacuum. Further purification was done by repeated recrystallization from dichloromethane-methanol system. Yield of this carbazole was 60%.

6: *R_f* = 0.6 (20% EtoAc-Hexane); yellow solid, yield: 0.48 g, 60%; IR (KBr pellet) ν_{\max} in cm⁻¹ 3458 (N-H), 2959 (C-H), 2927 (C-H), 2853 (C-H), 1722 (C=O), 1637 (C=C), 1593 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K): 9.42 (s, 1H, NH), 8.01 (d, *J* = 7.8 Hz, 2H, H_{Ar}), 7.94-7.92 (m, 4H, H_{Ar}), 4.54-4.5 (m, 8H, 4 × -OCH₂), 1.97-1.92 (m, 8H, 4 × -OCH₂-CH₂), 1.66-1.61 (m, 8H, -CH₂), 1.10 (t, *J* = 7.2Hz, 12H, 4 × -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 169.9, 130.9, 130.1, 128.4, 127.4, 127.1, 122.6, 121.5, 119.2, 117.6, 65.7, 65.6, 31.1, 31.1, 19.6, 19.6, 14.1 ; MALDI-TOF : exact mass calculated for C₄₀H₄₃NO₈ (M⁺): 665.3, found:665.7; Elemental analysis calcd. (%) for C₄₀H₄₃NO₈: C 72.16, H 6.51, N 2.1; found: C 72.06, H 6.45, N 2.08.

Tetrabutyl 1-ethyl-1H-phenanthro [1,10,9,8- cdefg]carbazole-3,4,9,10-tetracarboxylate (7)¹⁸A mixture of compound (**6**, 0.16g, 0.24 mmol, 1 equiv.), sodium hydride (0.03 g, 60% in wax, 0.36 mmol, 3 equiv.) and ethyl iodide (0.06g, 0.18 mmol, 1.53 equiv.) in a dry THF was refluxed for overnight under argon atmosphere. After cooling to room temperature, water (2 mL) was added to the mixture and

1 stirred for 10 min at 0 °C. The resulting mixture was extracted with dichloromethane and the extract was
2 washed with water and brine. Finally, organic layer was dried over anhyd. Na₂SO₄ and concentrated.
3 The crude residue obtained was purified by column chromatography on neutral alumina. Elution with
4 hexane, 50% dichloromethane-hexane solution followed by dichloromethane yielded the desired
5 product with 75% yield.
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10 **7:** *R_f* = 0.6 (15% EtoAc-Hexane); Yellowish solid, yield: 0.126 g, 75%; IR (KBr pellet) ν_{\max} in cm⁻¹
11 2959 (C-H), 2929 (C-H), 2873 (C-H), 1720 (C=O), 1586 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K):
12 8.49 (d, *J* = 7.8Hz, 2H, H_{Ar}), 8.22 (s, 2H, H_{Ar}), 8.18 (d, *J* = 7.8Hz, 2H, H_{Ar}), 4.74-4.7 (m, 2H, -*N*-CH₂),
13 4.45-4.42 (m, 8H, 4 × -OCH₂), 1.87-1.82 (m, 8H, 4 × -OCH₂-CH₂), 1.56-1.5 (m, 8H, 4 × -CH₂), 1.25
14 (bs, 3H, -*N*-CH₂-CH₃), 1.04-1.01 (m, 12H, 4 × -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 169.7,
15 169.3, 131.9, 131.4, 129.2, 128.2, 127.8, 124.4, 123.3, 121.9, 118.1, 117.9, 65.7, 65.6, 40.8, 31, 30.9,
16 29.9, 19.5, 16.7, 14.1, 14.09; MALDI-TOF: exact mass calculated for C₄₂H₄₇NO₈ (M⁺): 693.3, found:
17 693.7; HRMS (APCI mode) exact mass calculated for C₄₂H₄₈NO₈ (MH⁺): 694.3374, found: 694.3371.
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24 **Dibutyl 6-ethyl-9-octadecyl-8,10-dioxo-6,8,9,10-tetrahydroindolo [2',3',4',5':4,10,5] anthra[2,1,9-**
25 **def] isoquinoline-3,4-dicarboxylate (1)** A mixture of compound (**5**, 0.17g, 0.25 mmol, 1 equiv.), 1-
26 amino-octadecane (0.073 g, 0.27 mmol, 1.1 equiv.) and imidazole (1 g) were taken in microwave vessel,
27 flushed with nitrogen and put in microwave reactor. The mixture was heated to 165 °C for 35 minutes at
28 35 W. After cooling, reaction mixture was poured in 2N HCl and extracted with chloroform. Organic
29 mixture was washed with water and saturated sodium chloride solution. The crude compound was
30 purified by neutral alumina column chromatography using 50% chloroform-hexane system yields the
31 desired product.
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39 **1:** *R_f* = 0.4 (20% EtoAc-Hexane); Red waxy solid, yield: 0.11g, 55%; IR (KBr pellet) ν_{\max} in cm⁻¹ 2958
40 (C-H), 2924 (C-H), 2854 (C-H), 1712 (C=O_{ester}), 1695 (C=O_{imide}), 1679 (C=O_{imide}), 1597 (C=C); ¹H
41 NMR (600 MHz, CDCl₃, 299 K): 8.88 (s, 1H, H_{Ar}), 8.81 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 8.75 (s, 2H, H_{Ar}),
42 8.44 (s, 1H, H_{Ar}), 8.37 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 4.85-4.81 (m, 2H, -*N*CH₂), 4.47-4.44 (m, 4H, 2 × -
43 OCH₂), 4.33 (m, 2H, N-CH₂), 1.86-1.83 (m, 6H, CH₂), 1.74 (t, 3H, -NCH₂CH₃), 1.55-1.24 (m, 34H,
44 alkyl chain), 1.03-1.00 (m, 6H, 2 × -CH₃), 0.88-0.86 (m, 3H, -CH₃); ¹³C NMR (150 MHz, CDCl₃,
45 298.1K): 169.3, 168.8, 165, 163.8, 132.7, 132.3, 131.6, 130.5, 130.4, 130.4, 127.8, 126.8, 124, 123.5,
46 123, 122.8, 121.4, 120, 119.9, 119.7, 118.8, 117.8, 117.3, 116.8, 66, 65.9, 41.1, 40.9, 32.1, 31, 30.9,
47 29.9, 29.9, 29.9, 29.9, 29.6, 22.9, 19.6, 19.6, 16.7, 14.3, 14.1; MALDI-TOF exact mass calculated for
48 C₅₂H₆₆N₂O₆ (M⁻): 814.5, found: 814.9; HRMS (APCI mode) exact mass calculated for C₅₂H₆₇N₂O₆
49 (MH⁺): 815.4994, found: 815.4993.
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Tetrakis(butyl) peryleno[1,12-bcd]thiophene-3,4,9,10-tetracarboxylate(8)¹⁸ A mixture of compound (5, 0.17 g, 0.26 mmol) and Sulfur powder (0.083 g, 2.602 mmol) was heated to dissolve in *N*-methylpyrrolidone (10 mL) at 70 °C for 30 min. and then refluxed at 180 °C under Argon atmosphere for overnight by TLC monitoring. After cooling to room temperature, 2 M HCl was added, the precipitate was filtered, washed with water and dried. The crude product was purified by column chromatography on neutral alumina. Elution with 20-30% DCM-Hexanes system followed by 50% DCM-Hexane system yields the desired product. Further purification was done by the addition of concentrated solution of compound in cold methanol.

8: *Rf* = 0.6 (20% EtoAc-Hexane); orange solid, yield: 0.1g, 55%; IR (KBr pellet) ν_{\max} in cm^{-1} 2955 (C-H), 2927 (C-H), 2869 (C-H), 1720 (C=O), 1583 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K): 8.59-8.57 (m, 4H, H_{Ar}), 8.27 (d, *J* = 7.8Hz, 2H, H_{Ar}), 4.44-4.41 (m, 8H, 4 × -OCH₂), 1.87-1.81 (m, 8H, 4 × OCH₂-CH₂), 1.56-1.51 (m, 8H, 4 × CH₂), 1.04-1.01 (m, 12H, 4 × -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 168.9, 168.7, 135.2, 132.1, 130.6, 130, 129.4, 126.3, 125.6, 125.4, 121.9, 65.8, 65.7, 30.9, 30.92, 19.6, 19.5, 14.1; MALDI-TOF : exact mass calculated for C₄₀H₄₂O₈S (M⁺): 682.3, found:682.4; HRMS (APCI mode) exact mass calculated for C₄₀H₄₂O₈S (M⁺): 682.2595, found: 682.2578.

Dibutyl 9-octadecyl-8,10-dioxo-9,10-dihydro-8H-thieno[2',3',4',5':12,1] peryleno[3,4-cd]pyridine-3,4-dicarboxylate (2) A mixture of compound (6, 0.15g, 0.22 mmol, 1 equiv.), 1-amino-octadecane (0.065 g, 0.24 mmol, 1.1 equiv.) and imidazole (1 g) were taken in microwave vessel, flushed with nitrogen and put in microwave reactor. The mixture was heated to 165 °C for 35 minutes at 35 W. After cooling, reaction mixture was poured in 2N HCl and extracted with chloroform. Organic mixture was washed with water and saturated sodium chloride solution. The crude compound was purified by neutral alumina column chromatography using 50% chloroform-hexane to get the desired product.

2: *Rf* = 0.4 (20% EtoAc-Hexane); Orange red waxy solid, yield: 0.097g, 55%; IR (KBr pellet) ν_{\max} in cm^{-1} 2959 (C-H), 2924 (C-H), 2853 (C-H), 1727 (C=O_{ester}), 1697 (C=O_{imide}), 1655 (C=O_{imide}), 1629 (C=C), 1590 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K): 8.94 (s, 1H, H_{Ar}), 8.58 (s, 1H, H_{Ar}), 8.57 (d, *J* = 8.4 Hz, 1H, H_{Ar}), 8.51 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 8.4 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 8.29 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 4.48-4.44 (m, 4H, 2 × -OCH₂), 4.28-4.25 (m, 2H, N-CH₂), 1.9-1.82 (m, 6H, CH₂), 1.59-1.24 (m, 34H, alkyl chain), 1.07-1.03 (m, 6H, 2 × -CH₃), 0.87 (t, *J* = 7.2 Hz 3H, -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 168.3, 168.2, 163.4, 163.1, 137.1, 135, 132.4, 131.1, 130.8, 130.5, 130.3, 129.2, 128.7, 128.5, 126, 125.7, 125.4, 124.8, 124.4, 122.4, 121.1, 120.9, 120.7, 120.5, 66.1, 65.9, 41.1, 32.1, 29.9, 29.9, 29.9, 29.6, 22.9, 19.6, 19.6, 14.3, 14.1, 14.12; MALDI-TOF exact mass calculated for C₅₀H₆₁NO₆S (M): 803.4, found: 803.6; HRMS (APCI mode) exact mass calculated for C₅₀H₆₂NO₆S (M⁺): 804.4292, found: 804.4295.

Tetrakis(butyl) peryleno[1,12-bcd] selenophene-3,4,9,10-tetracarboxylate (9)¹⁸ A mixture of compound (**5**, 0.18g, 0.26 mmol) and Selenium powder (0.21g, 2.602 mmol) was heated to dissolve in *N*-methylpyrrolidone (10 mL) at 70 °C for 30 min. and then refluxed at 180 °C under Ar atmosphere for overnight until the starting material could not be detected by TLC. After cooling to room temperature, 2 M HCl was added, then the precipitate was filtered, washed with water and dried. The crude product was purified by column chromatography on neutral alumina. Elution with 20-30% DCM-Hexanes system followed by 50% DCM-Hexane system yields the desired product. Further purification was done by addition of concentrate solution of compound in cold methanol gives the product.

9: *R_f* = 0.6 (20% EtoAc-Hexane); orange solid, yield: 0.103g, 55%; IR (KBr pellet) ν_{\max} in cm^{-1} 2955 (C-H), 2927 (C-H), 2869 (C-H), 1719 (C=O), 1582 (C=C); ¹H NMR (400 MHz, CDCl₃, 299 K): 8.57-8.53 (m, 4H, H_{Ar}), 8.24-8.23 (m, 2H, H_{Ar}), 4.41 (bs, 8H, 4 × -OCH₂), 1.86-1.82 (m, 8H, 4 × OCH₂-CH₂), 1.55-1.51 (m, 8H, 4 × -CH₂), 1.04-1.01 (m, 12H, 4 × -CH₃); ¹³C NMR (100 MHz, CDCl₃, 298.1K): 168.9, 168.7, 137.6, 133.3, 132.2, 129.9, 129.3, 128.7, 128.7, 127, 125.7, 121.6, 65.8, 65.6, 30.9, 30.9, 19.5, 19.5, 14.1, 14.08; MALDI-TOF : exact mass calculated for C₄₀H₄₂O₈Se(M⁺):730.2, found: 730.8; Elemental analysis calcd. (%) for C₄₀H₄₂O₈Se: C 65.84, H 5.80; found: C 65.74, H 5.80.

Dibutyl 9-octadecyl-8,10-dioxo-9,10-dihydro-8H-selenopheno[2',3',4',5':12,1] peryleno[3,4-cd]pyridine-3,4-dicarboxylate (3) A mixture of compound (**7**, 0.15g, 0.21 mmol, 1 equiv.), 1-amino-octadecane (0.061g, 0.23 mmol, 1.1 equiv.) and imidazole (1g) were taken in microwave vessel, flushed with nitrogen and placed in microwave reactor. The mixture was heated to 165 °C for 35 minutes at 35 W. After cooling, reaction mixture was poured into 2N HCl and extracted with chloroform. Organic mixture was washed with water and saturated sodium chloride solution. The crude compound was purified by neutral alumina column chromatography using 50% chloroform-hexane system to yield the desired product.

3: *R_f* = 0.4 (20% EtoAc-Hexane); Dark red waxy solid, yield: 0.096 g, 55%; IR (KBr pellet) ν_{\max} in cm^{-1} 2959 (C-H), 2924 (C-H), 2853 (C-H), 1724 (C=O_{ester}), 1701 (C=O_{imide}), 1651 (C=O_{imide}), 1597 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K): 8.91 (s, 1H, H_{Ar}), 8.57 (s, 1H, H_{Ar}), 8.52 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 8.42 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 8.31 (d, *J* = 8.4 Hz, 1H, H_{Ar}), 8.25 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 4.47-4.44 (m, 4H, 2 × -OCH₂), 4.26-4.23 (m, 2H, N-CH₂), 1.9-1.81 (m, 6H, CH₂), 1.57-1.24 (m, 34H, alkyl chain), 1.07-1.03 (q, 6H, 2 × -CH₃), 0.87 (t, *J* = 7.2 Hz, 3H, -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 168.4, 168.2, 163.3, 163.1, 139.8, 137.4, 133.3, 132.6, 131.4, 131.1, 130.5, 130, 129.1, 128.4, 128.2, 126.1, 125.7, 124.6, 122.3, 122, 120.8, 120.5, 119.9, 66, 65.9, 41, 32.1, 30.9, 29.9, 29.7, 29.6, 27.6, 22.9, 19.6, 14.3, 14.1; MALDI-TOF exact mass calculated for C₅₀H₆₁NO₆Se (M⁺): 851.4, found: 851.6;

Elemental analysis calcd. (%) for C₅₀H₆₁NO₆Se: C 70.57, H 7.23, N 1.65; found: C 70.29, H 7.44, N 1.57.

2-Octadecylisoindoline-1,3-dione (13)¹⁹ Potassium phthalimide (2.4g, 12.9 mmol) was added to the solution of 1-bromo-octadecane (4g, 12.1 mmol) in DMF. The reaction mixture was stirred at 90 °C for 18 h, cooled the reaction mixture to room temperature, poured the mixture in water and extracted with methylene chloride several times. The combined organic layer was washed with 0.2 N KOH, water, saturated NH₄Cl, dried over anhyd Na₂SO₄ and concentrated under reduced pressure after filtration. The resulting crude compound was purified by column chromatography using methylene chloride as eluent to give white solid in 95% yield.

13: *R*_f = 0.4 (10% EtoAc-Hexane); white solid, yield: 4.55g, 95%; IR (KBr pellet) ν_{\max} in cm⁻¹ 2965 (C-H), 2917 (C-H), 2849 (C-H), 1775 (C=O), 1701 (C=O); ¹H NMR (600 MHz, CDCl₃, 299 K): 7.83-7.82 (m, 2H, H_{Ar}), 7.70-7.69 (m, 2H, H_{Ar}), 3.67-3.65 (m, 2H, -NCH₂), 1.68-1.64 (m, 2H, -NCH₂-CH₂), 1.31-1.23 (m, 30H, alkyl chain), 0.88-0.85 (m, 3H, -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 168.7, 134, 132.4, 123.3, 38.3, 32.1, 29.9, 29.8, 29.7, 29.6, 29.4, 27.1, 22.9, 14.3; HRMS (ESI mode) exact mass calculated for C₂₆H₄₂NO₂ (MH⁺): 400.3210, found: 400.3217.

1-amino-octadecane (14)¹⁹ A mixture of compound (11) (4g, 10 mmol, 1 equiv.) and 80% hydrazine hydrate (1.5g, 30.2 mmol, 3 equiv.) in methanol were stirred at 95 °C for 1 h. after the disappearance of starting imide, methanol was removed under reduced pressure and residue was diluted with dichloromethane and washed with 10% KOH. The combined aqueous layer was extracted with dichloromethane. The combined organic layer was washed with brine and dried over anhyd Na₂SO₄. After removal of solvent the product was obtained as a white solid in 95% yield.

14: *R*_f = 0.3 (20% EtoAc-Hexane); white solid, yield: 2.6g, 95%; IR (KBr pellet) ν_{\max} in cm⁻¹ 3334 (N-H), 2956 (C-H), 2918 (C-H), 2851 (C-H); ¹H NMR (600 MHz, CDCl₃, 299 K): 2.67-2.64 (m, 2H, -NCH₂), 1.41-1.40 (m, 2H, -NCH₂-CH₂), 1.34 (s, 2H, NH₂), 1.24-1.23 (m, 30H, alkyl chain), 0.87-0.84 (m, 3H, -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): 42.5, 34.1, 32.1, 29.9, 29.7, 29.6, 27.1, 22.9, 14.3; HRMS (ESI mode) exact mass calculated for C₁₈H₄₀N (MH⁺): 270.3155, found: 270.3152.

Dibutyl 2-octadecyl-1,3-dioxo-2,3-dihydro-1H-benzo [10,5] anthra[2,1,9-def] isoquinoline-8,9-dicarboxylate (PEI) A mixture of compound (4, 0.3g, 0.46 mmol, 1 equiv.), 1-amino-octadecane (0.138g, 51 mmol, 1.1 equiv.) and imidazole (1.1g) were taken in microwave vessel, flushed with nitrogen and put in microwave reactor. The mixture was heated to 165 °C for 35 minutes at 35 W. After cooling, the reaction mixture was poured in 2N HCl and extracted with chloroform. Organic mixture was washed with water and brine solution. The crude compound was purified by neutral alumina

column chromatography using 50% chloroform-hexane system yields the desired product. This was further purified by recrystallization from DCM-methanol system.

PEI: $R_f = 0.4$ (20% EtoAc-Hexane); Bright orange solid, yield: 0.195g, 55%; IR (KBr pellet) ν_{\max} in cm^{-1} 2958 (C-H), 2923 (C-H), 2852 (C-H), 1714 ($\text{C}=\text{O}_{\text{ester}}$), 1693 ($\text{C}=\text{O}_{\text{imide}}$), 1649 ($\text{C}=\text{O}_{\text{imide}}$), 1618 ($\text{C}=\text{C}$), 1597 ($\text{C}=\text{C}$); ^1H NMR (600 MHz, CDCl_3 , 299 K): δ 8.53 (d, $J = 8.4$ Hz, 2H, H_{Ar}), 8.34 (d, $J = 7.8$ Hz, 4H, H_{Ar}), 8.05 (d, $J = 7.8$ Hz, 2H, H_{Ar}), 4.37-4.34 (m, 4H, $2 \times -\text{OCH}_2$), 4.19-4.17 (m, 2H, $\text{N}-\text{CH}_2$), 1.83-1.73 (m, 6H, CH_2), 1.54-1.24 (m, 34H, alkyl chain), 1.01 (t, $J = 7.2$ Hz, 6H, $2 \times -\text{CH}_3$), 0.88-0.86 (m, 3H, $-\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3 , 298.1K): δ 168.5, 163.7, 135.6, 132.3, 132.1, 131.5, 130.5, 129.4, 129.3, 129.2, 126.1, 122.7, 122.3, 122, 65.8, 40.8, 32.1, 30.8, 29.9, 29.9, 29.86, 29.8, 29.6, 29.58, 28.4, 27.4, 22.9, 19.5, 14.3, 14; MALDI-TOF exact mass calculated for $\text{C}_{50}\text{H}_{64}\text{NO}_6$ (MH^+): 774.5, found: 774.6; HRMS (APCI mode) exact mass calculated for $\text{C}_{50}\text{H}_{64}\text{NO}_6$ (MH^+): 774.4728, found: 774.4730.

Dibutyl 1,3-dioxo-2-phenyl-2,3-dihydro-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-8,9-dicarboxylate (10) A mixture of compound (**4**, 0.1g, 0.15 mmol, 1 equiv.), aniline (0.016g, 0.17 mmol, 1.1 equiv.) and imidazole (0.7 g) were taken in microwave vessel, flushed with nitrogen and put in microwave reactor. The mixture was heated to 165 °C for 35 minutes at 35 W. After cooling, reaction mixture was poured into 2N HCl and extracted with chloroform. Organic mixture was washed with water and saturated sodium chloride solution. The crude compound was purified by neutral alumina column chromatography using 50% DCM-hexane system followed by DCM yields the desired product. This was further purified by recrystallization from DCM-methanol system.

10: $R_f = 0.4$ (20% EtoAc-Hexane); Bright red solid, yield: 0.05g, 55%; IR (KBr pellet) ν_{\max} in cm^{-1} 2959 (C-H), 2931 (C-H), 2872 (C-H), 1707 ($\text{C}=\text{O}_{\text{ester}}$), 1660 ($\text{C}=\text{O}_{\text{imide}}$), 1593 ($\text{C}=\text{C}$); ^1H NMR (600 MHz, CDCl_3 , 299 K): δ 8.63 (d, $J = 7.8$ Hz, 2H, H_{Ar}), 8.44-8.40 (m, 4H, H_{Ar}), 8.10 (d, $J = 8.4$ Hz, 2H, H_{Ar}), 7.60-7.57 (m, 2H, $\text{H}_{\text{Ar-phenyl}}$), 7.52-7.49 (m, 1H, $\text{H}_{\text{Ar-phenyl}}$), 7.38-7.37 (m, 2H, $\text{H}_{\text{Ar-phenyl}}$), 4.38-4.35 (m, 4H, $2 \times -\text{OCH}_2$), 1.83-1.78 (m, 4H, CH_2), 1.54-1.48 (m, 4H, CH_2 CH_3), 1.01 (t, $J = 7.2$ Hz, 6H, $2 \times -\text{CH}_3$); ^{13}C NMR (150 MHz, CDCl_3 , 298.1K): δ 168.4, 164, 136.1, 135.5, 132.3, 132.28, 132, 130.6, 129.8, 129.7, 129.4, 129.3, 129, 128.8, 126.4, 123, 122.4, 122.1, 65.8, 30.8, 19.5, 14; MALDI-TOF exact mass calculated for $\text{C}_{38}\text{H}_{32}\text{NO}_6$ (MH^+): 598.2, found: 598.3; HRMS (APCI mode) exact mass calculated for $\text{C}_{38}\text{H}_{32}\text{NO}_6$ (MH^+): 598.2224, found: 598.2224.

Dibutyl 2-benzyl-1,3-dioxo-2,3-dihydro-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-8,9-dicarboxylate (11) A mixture of compound (**4**, 0.1g, 0.15 mmol, 1 equiv.), benzyl amine (0.018g, 0.17 mmol, 1.1 equiv.) and imidazole (0.7 g) were taken in microwave vessel, flushed with nitrogen and put

in microwave reactor. The mixture was heated to 165 °C for 35 minutes at 35 W. After cooling, reaction mixture was poured in 2N HCl and extracted with chloroform. Organic mixture was washed with water and saturated sodium chloride solution. The crude compound was purified by neutral alumina column chromatography using 50% DCM-hexane system followed by DCM yields the desired product. This was further purified by recrystallization from DCM-methanol system.

11: $R_f = 0.4$ (20% EtoAc-Hexane); Bright orange solid, yield: 0.054g, 58%; IR (KBr pellet) ν_{\max} in cm^{-1} 2960 (C-H), 2933 (C-H), 2873 (C-H), 1720 (C=O_{ester}), 1697 (C=O_{imide}), 1657 (C=O_{imide}), 1594 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K): δ 8.41 (d, $J = 7.8$ Hz, 2H, H_{Ar}), 8.22 (d, $J = 7.8$ Hz, 2H, H_{Ar}), 8.17 (d, $J = 6$ Hz, 2H, H_{Ar}), 8.01 (d, $J = 7.8$ Hz, 2H, H_{Ar}), 7.61 (d, $J = 7.8$ Hz, 2H, H_{Ar-phenyl}), 7.37-7.35 (m, 2H, H_{Ar-phenyl}), 7.29-7.27 (m, 1H, H_{Ar-phenyl}), 5.38 (s, 2H, benzyl-CH₂), 4.36 (t, $J = 6.6$ Hz, 4H, 2 × -OCH₂), 1.83-1.79 (m, 4H, CH₂), 1.54-1.48 (m, 4H, CH₂ CH₃), 1.03-1.00 (m, 6H, 2 × -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): δ 168.4, 163.7, 137.5, 135.6, 132.1, 132.1, 131.6, 130.5, 129.4, 129.3, 129.2, 129.1, 128.7, 127.8, 125.9, 122.8, 122.1, 121.8, 65.8, 43.8, 30.8, 19.5, 14; MALDI-TOF exact mass calculated for C₃₉H₃₄NO₆ (MH⁺): 612.2, found: 612.4; HRMS (APCI mode) exact mass calculated for C₃₉H₃₄NO₆ (MH⁺): 612.2381, found: 612.2385.

2-Octadecyl-9-(3,4,5-tris(decyloxy)phenyl)anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10

(2H,9H)-tetraone (12) A mixture of compound (PEI, 0.042g, 0.05 mmol, 1 equiv.), 3,4,5-tris(decyloxy)aniline (0.034g, 0.06 mmol, 1.1 equiv.), zinc acetate (0.01 g, 0.05 mmol, 1 equiv.) and imidazole (0.5 g) were taken in microwave vessel, flushed with nitrogen and put in microwave reactor. The mixture was heated to 165 °C for 35 minutes at 35 W. After cooling, reaction mixture was poured in 2N HCl and extracted with chloroform. Organic mixture was washed with water and saturated sodium chloride solution. The crude compound was purified by neutral alumina column chromatography using 50% DCM-hexane system, followed by DCM to obtain the desired product.

12: $R_f = 0.4$ (20% EtoAc-Hexane); Dark red waxy solid, yield: 0.048g, 75%; IR (KBr pellet) ν_{\max} in cm^{-1} 2958 (C-H), 2924 (C-H), 2854 (C-H), 1699 (C=O_{imide}), 1662 (C=O_{imide}), 1594 (C=C); ¹H NMR (600 MHz, CDCl₃, 299 K): δ 8.52-8.50 (m, 2H, H_{Ar}), 8.37-8.35 (m, 2H, H_{Ar}), 8.20-8.19 (m, 2H, H_{Ar}), 8.13-8.12 (m, 2H, H_{Ar}), 4.17-4.15 (m, 2H, N-CH₂), 4.06-4.04 (m, 2H, -OCH₂), 3.98-3.96 (m, 4H, 2 × -OCH₂), 1.83-1.73 (m, 8H, CH₂), 1.54-1.24 (m, 74H, alkyl chain), 0.91-0.89 (m, 3H, -CH₃), 0.88-0.85 (m, 9H, -CH₃); ¹³C NMR (150 MHz, CDCl₃, 298.1K): δ 163.4, 163, 153.9, 138.4, 134.2, 133.8, 131.3, 130.8, 130.1, 129.3, 128.7, 125.9, 125.8, 123.4, 123.3, 123.1, 122.9, 107, 73.7, 69.3, 41.1, 32.2, 32.1, 30.7, 30.1, 30, 29.9, 29.92, 29.8, 29.86, 29.72, 29.7, 29.68, 29.65, 29.6, 29.58, 28.3, 27.5, 26.4, 26.4, 23, 22.9, 14.4, 14.3, 14.3; MALDI-TOF exact mass calculated for C₇₈H₁₁₁N₂O₇ (MH⁺): 1187.8386, found:

1187.823; Elemental analysis calcd. (%) for C₇₈H₁₁₀N₂O₇: C 78.88, H 9.34, N 2.36; found: C 78.82, H 9.39, N 2.46.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. ¹H and ¹³C NMR spectra of all new compounds, MALDI-TOF spectra of all new compounds, Experimental details of photophysical and computational studies (PDF)

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