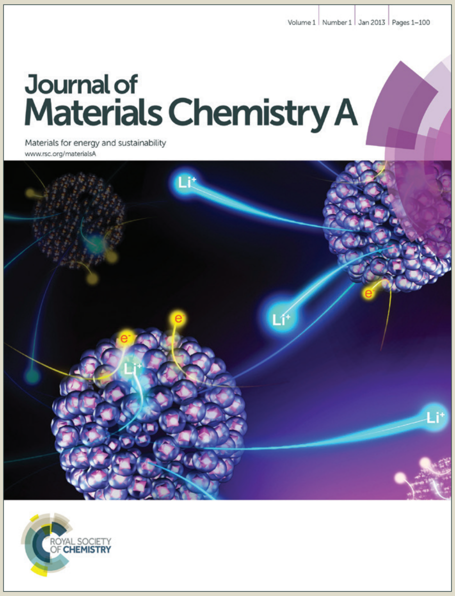
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Synthesis and Study of Electrochemical and Optical Properties of Substituted Perylenemonoimides in Solutions and on Solid Surfaces

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A new and efficient methodology towards the synthesis of 7-pyrrolidinyl and 7, 12-bispyrrolidinyl perylenemonoimide monoanhydrides (PMI monoanhydrides) and their corresponding dicarboxylic acids is devised. The high yields (70-96%) and facile synthesis of PMI monoanhydrides, as compared to traditional methodologies, makes the method attractive and versatile. The reported 7, 12-bispyrrolidinyl PMI monoanhydrides are a new family of peryleneimides, where the both bay-substituents are located towards the anhydride cycle. The electrochemical and optical properties of target molecules and their precursors were investigated using the UV-Vis spectroscopy and differential pulse voltammetry. Atomic charges and electronic properties were calculated using density functional theory (DFT). In addition, self-assembling monolayers of the PMI monoanhydrides and corresponding diacids were successfully formed over ZnO and TiO_2 films. The results of the current study indicate that these molecules are potentially good candidates for various applications in the field of organic electronics and solar cells.

Introduction

Perylene dyes are one of the most versatile and robust chromophores know to be thermally and photophysically stable. Their discovery almost a century ago has not limited the interest of chemists in developing new synthetic methods for their improved applications.[1a, b] Initially used as vat dyes,[2] their applications gradually spread to several high tech fields like sensitizers in organic solar cells,[3] photovoltaics,[4] biosensors,[5] artificial photo synthesis,[6] and several other optical devices.[7]

The functionalization of the perylene core at *peri*-, *bay*- and *ortho*-positions greatly influences the solubility, electronic and morphological properties of the dyes.[8] The substitution at the *peri*-position and its effect on the morphology, solubility and the chrystallochromic properties of the PDI dyes has been reported.[9] Similarly the functionalization of the *bay*-position via halogenation,[10] Pd coupling,[11] catalytic or catalyst free oxidation[12] has also been published. The alkylation,[13] arylation,[14] borylation[15] and halogenation[16] at the *ortho*-positions are well documented.

Since the substitution pattern greatly influences the chemical and physical properties of the perylene dyes, it is crucial to keep these properties in mind while devising the molecules for specific applications. For example, it is known that when perylene derivatives are used as sensitizers in DSSCs, the molecule should have an anchoring group, through which it can bind to the substrate surface and the presence of electron donating groups on perylene core increases the photoconversion efficiency.[17-19] All these molecules carry either aryloxy or thiophenolic substituents in the *bay*-region. In their work, Imahori et al. has reported the synthesis and application of electron donating 1, 7-substituted perylene tetracarboxylic acid derivatives.[20] Recently Sengupta and coworkers have described the synthesis of 1, 7-dibromo perylene monoimide anhydride.[21] All these synthetic strategies are heavily dependent on the presence of good leaving groups at the *bay*-positions. This results in either an isomeric mixture of 1, 7- and 1, 6-substitued products or needs tedious purifications and yield losses.[21, 22] Additionally, a selective conversion of imide to anhydride through a saponification produces low yields and a mixture of mono and bisanhydride.[23a, b]

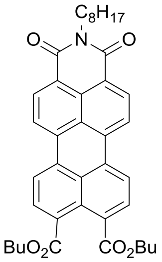
Despite established knowledge about differences in properties of isomeric perylene diimides,[22f, 24] efforts have mostly been focused on the synthesis or purification of 1, 7-substituted isomers of PDIs.[22a, b, 25] This has resulted in a poor knowledge about the properties and potential applications of 1, 6-isomers. Only very recently the synthesis of the preferentially 1, 6-isomer of perylene imide has been reported.[12a, b] So far, only the 1, 7-isomer of the PMI anhydride or its derivatives have been studied as sensitizers in DSSCs[15] leaving 7, 12-substituted perylene monoimides with an anchoring group virtually unknown moieties.

We have recently published, first of this kind, the synthesis of isomerically pure 7- and 7, 12-aminated perylene monoimde diesters (PMI diesters), both under catalytic and catalyst free conditions.[12a] Herein, we report further extension of our methodology towards the synthesis of novel 7- and 7, 12-substitued perylene derivatives having strong electron donating groups in the *bay*-region and anchoring groups at *peri*-positions. The electrochemical and photo physical properties of these compounds were studied both experiminetally and computationally in detail and self-assembling monolayers (SAMs) were prepared over ZnO films and TiO$_2$ nanoparticles. The results of our studies suggest that these compounds can be good candidates for their potential use as sensitizers in DSSCs and related applications.

Results and discussion

Synthesis

We have recently reported the synthesis of precursors **1-3** in 47–96% yields.[12a] A treatment of perylene-3, 4, 9, 10-tetracarboxylic acid bisanhydride (PTCDA) with an alkanol and alkyl halide in a homogeneous solution produced perylene tetraester (PTE).[26] A selective hydrolysis and a subsequent imidization with octyl amine resulted in the formation of perylene monoimide diester PMI (diester) **1**.[12a] The regioselective amination of PMI **1** at 7-, or 7, 12-positions was performed under catalytic or catalyst free conditions.



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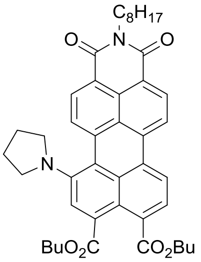

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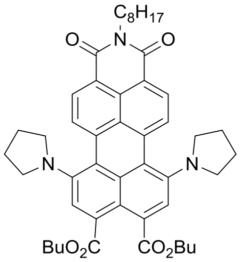
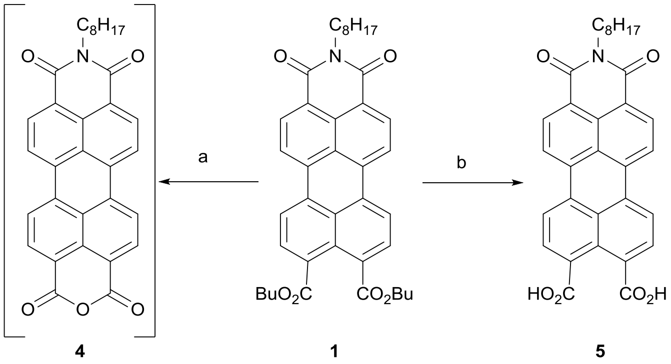


3

With precursors in hand, the hydrolysis of these PMI diesters to dicarboxylic acids was attempted under different conditions. The ester hydrolysis has been reported under acidic, basic and neutral conditions.[27] Most widely used methods for the said purpose is the basic hydrolysis carried out in the presence of aqueous hydroxides and co-solvents at different temperatures. Khurana et al. has reported the facile hydrolysis of esters with potassium hydroxide in methanol at ambient temperatures.[28] However a treatment of PMI diester **2** with KOH in methanol failed to produce the desired diacid product. Similarly the use of trimethylsilyl iodide (TMSI) in various solvents resulted in either partial hydrolysis or decarboxylation of diesters. Same problem was encountered while attempted ester cleavage using sulfuric acid at elevated temperatures. A prolonged treatment of PMI diesters with KOH in a mixture of THF:EtOH:H$_2$O at room temperature or at 50 °C again resulted in a monoacid along with several other spots on TLC. Therefore, we decided to use the procedure described by Terunum et al.[29] PMI diester **1** was heated at reflux for 24 hours with a 6 M aqueous solution of KOH in a 2:1 mixture of THF:EtOH. A removal of solvents and treatment with 3 M HCl gave the desired PMI diacid **5** in 96% yield (Scheme 1)



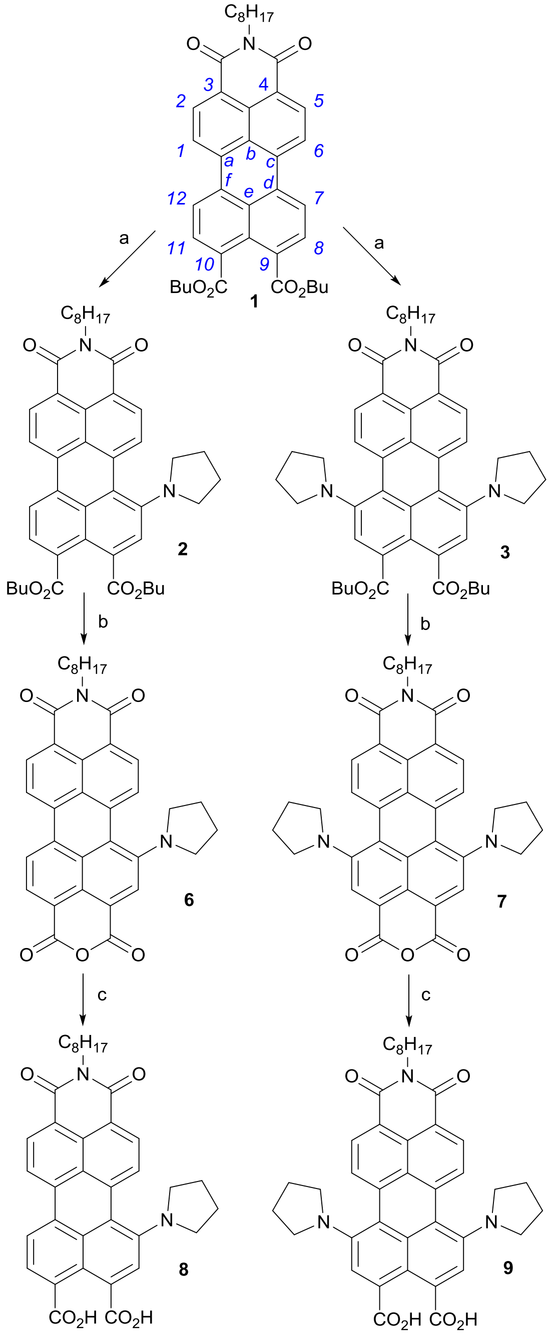
(a) *p*TsOH, Toluene, 90 °C, 4 h; (b) KOH, THF:EtOH, reflux, 24 h

Scheme 1. Synthesis of PMI anhydride **4** and diacid **5**

However, when 7-, or 7, 12-pyrrolidyl PMI diesters **2** and **3** were subjected to similar reaction conditions, it was observed that the pyrrolidinyl substituents at the *bay*-positions greatly influenced the dealkylation process. For example, even longer reaction time did not fully convert the starting material to diacid products. Reaction mixtures contained by-products, which proved to be challenging to separate from the desired compounds. A close vicinity of the two carboxylic groups resulted in the formation of an anhydride during the purification with acidic mixture of organic solvents. In addition, a decomposition of product spots was also observed on the HPTLC plates.

Keeping all the above mentioned limitations in mind, an alternate approach toward desired diacids was needed and a ring closing-opening method was adopted. An acid hydrolysis of PMI diesters **2** and **3** with *p*-toluenesulfonic acid in toluene at elevated temperature[21] yielded novel 7- and 7, 12-substituted PMI monohydrides **6** and **7** in 93 and 75% yields, respectively.

It is well established that this anhydride moiety opens up on adsorption over TiO$_2$, providing strong chemical interactions with TiO$_2$ surfaces and effective electronic coupling.[30] This property of the anhydride moiety makes them excellent anchoring groups for sensitizers in DSSC. The same dicarboxylates functionality was achieved when compounds **6** and **7** were heated at 100 °C with 2 eq. of KOH in tBuOH. The desired diacids **8** and **9** were obtained in 70 and 76% yields respectively (Scheme 2).



(a) $CuCl_2$, pyrrolidine, 1 h or 24 h; (b) *p*TsOH, toluene, 90 °C, 20 h; (c) tBuOH, KOH, 100 °C, 24 h

Scheme 2. Synthesis of PMI anhydrides and acids

Theoretical calculations

In order to clarify the possible reasons for selectivity of substitution, we have run the quantum chemical calculations. In our previous paper we suggested that reaction goes through an anion radical intermediate, and the specificity of the substitution is guided by the charge distribution pattern in the PMI anion radical.[12a] The atomic charges were calculated using two different levels of theory. The calculations predict that the negative charge is mostly localized on the ester side of both the neutral and radical anion species of **1** and **2** and especially on the four carbon atoms: *d*, 7, 8 and 9 or 10, 11, 12 and *f* (see Scheme 2, comp. **1**). This makes the ester side rings prone to an electrophilic attack of the pyrrolidine moiety. Calculations predict that for ester **2**, once the radical anion has formed, carbon 12 becomes the most electronegative in the *bay*-region (-0.366, at both levels of theory; compare with -0.261 or -0.259 for carbon 1). This makes carbon 12 more attractive to the approaching electrophile.

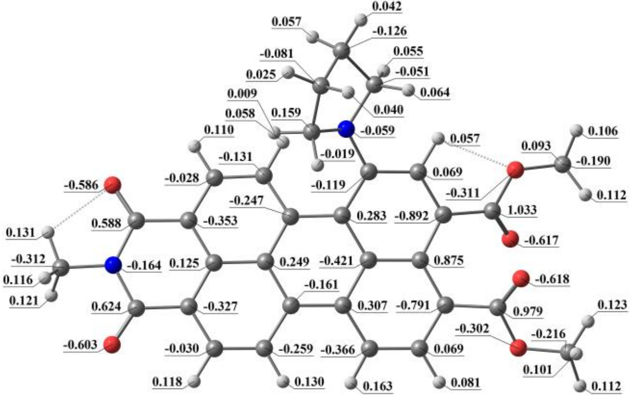


Figure 1. MK charges of a radical anion of **2** calculated at the M062X/6-311++G(d,p)//M062X/6-311++G(d,p) level of theory.

The required level of theory for the quantum chemical calculations has been verified by predicting HOMO/LUMO energies for compounds **1-3**. The theoretical values are in good agreement with the experimental data (-3.6/-5.9 vs -3.6/-6.1 for **1**, -3.1/-5.2 vs -3.1/-5.5 for **2**, and -3.3/-5.0 vs -2.8/-5.2 for **3**). More details on calculations can be found in Supporting Information.

Absorption/Emission Studies

The UV-vis absorption and emission spectra of compounds **1-3** and **5-9** are shown in Figure 2. The spectra of perylene monoimde diesters **1-3** were recorded in $CHCl_3$ while for corresponding PMI anhydrides **6**, **7** and diacids **5, 8** and **9**, measurements were made in ethanol.

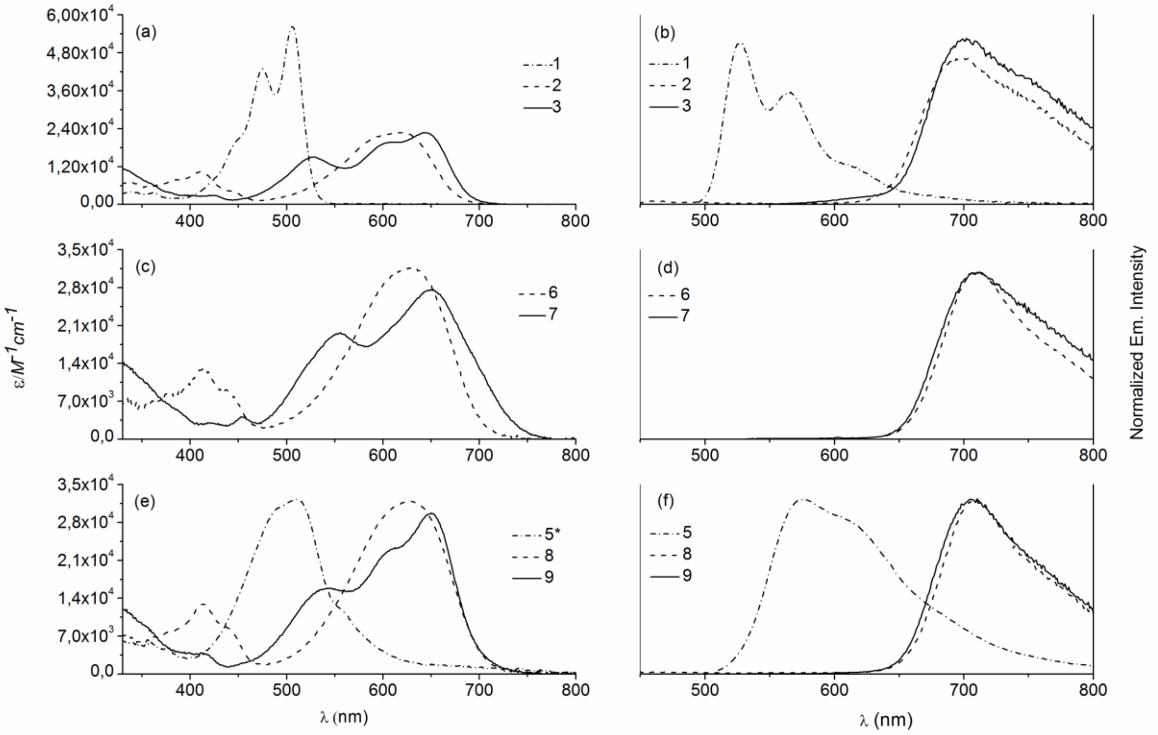


Figure 2. Absorption (a, c, e), and emission (b, d, f) spectra of PMI diesters **1-3** in $CHCl_3$, anhydrides **6**, **7**, and acids **5**, **8**, **9** in ethanol. Abs. of **5*** is normalised due to poor solubility

It is very informative and evident to note the effect of the pyrrolidinyl substituents at the 7- and 12-positions. In the case of unsubstituted PMI diester **1**, two distinct absorption bands at 506 nm and 476 nm are visible (Figure 2a, comp. **1**). One pyrrolidinyl substituent at the 7-position shifts the absorption maximum towards ca 620 nm, and a second absorption band appears at 410 nm (Figure 2a, comp. **2**). In the case of the di-substitution, i.e. 7, 12-pyrrolidinyl PMI diester **3**, the absorption region becomes wider with a maximum at 642 nm and a second absorption band at 528 nm. These features allow us to conclude that the enhanced interaction between the pyrrolidinyl substituents and the perylene core greatly influences the optical properties of compounds. It is visible from the spectra that the subsitituted PMI anhydrides **6**, **7** (Figure 2c) and their corresponding carboxylic acids **8** and **9** (Figure 2e) retain the absorptive features of their corresponding PMI diesters **2** and **3** (Figure 2a). They absorb light in visible region and cover a large part of the spectrum from 475 up to 750 nm. Though substituted PMI diesters, anhydrides and carboxylic acids show similar absorption bands in visible region, the PMI anhydrides **6**, **7** and acids **8**, **9** have the molar extinction coefficients almost two folds higher then the diesters **2**, **3** at low energy (Figure 2).

The emission properties of the substituted PMI diesters, anhydrides, and diacids are almost identical with the emission maxima around 700 nm. The normalized emission spectra of PMI diesters **1-3**, anhydrides **6**, **7** and diacid **5**, **8**, **9** are shown in Figures 2b, d and f.

Electrochemical properties

Several properties and field of applications of peryleneimides and their derivatives depend on the energies of the frontier orbitals HOMO and LUMO. These energies and relative donor-acceptor capabilities of perylenemonoimide diesters **1-3**, PMI monoimide anhydride **6**, and diacid **5** were investigated by differential pulse voltammetry (DPV) in benzonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate as a supporting electrolyte. The obtained redox potentials (V vs. ferrocene) are shown in Table **1** while the calculated HOMO-LUMO energy levels are plotted in Figure 4 (along with the data for TiO_2[31] and fullerene[32] for comparison). The IV curves can be found in the Supporting Information, SI, pages S9-S13.

com	$E_{1\text{red}}$	$E_{2\text{red}}$	$E_{1\text{ox}}$	$E_{2\text{ox}}$	HOMO	LUMO
1	-1.2	-1.5	1.1	-	-5.9	-3.6
2	-1.4	-1.6	0.4	-	-5.2	-3.4
3	-1.5	-1.8	0.25	-	-5.0	-3.3
5	-0.9	-1.2	1.1	1.3	-5.9	-3.9
6	-1.1	-1.3	0.6	1.0	-5.4	-3.7

Table 1. Redox Potentials (*V* vs. ferrocene) of PMIs obtained by DPV and HOMO, LUMO (eV) calculated against vacuum.

The unsubstituted PMI diester **1** and the 12-pyrrolidinyl PMI diester **2** exhibit very similar redox characteristics. Similarly both compounds show a single one-step irreversible oxidation, where the oxidation peak was detected at around +1.1 V and +0.45 V, respectively. The higher value of the oxidation potential for compound **1** (figure 3) compared to the 12-substituted PMI diester **2** means that the unsubtituted PMI diester **1** is a weaker electron donor compared to **2**.

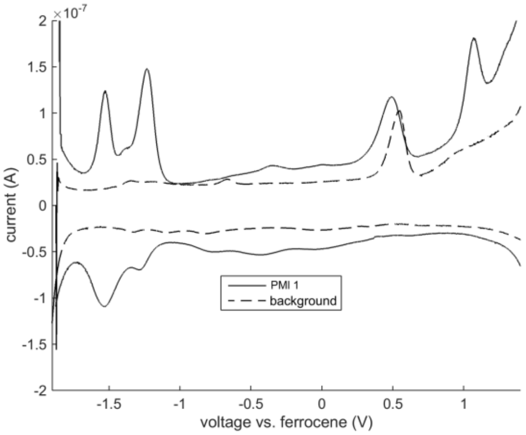


Figure 3. DPV curve of compound **1** vs ferrocene

Similarly, the 7, 12-pyrrolidinyl PMI diester **3** undergoes a two-step reduction and a single-step oxidation. The reduction occurs at around -1.5 V and -1.8 V, whereas the oxidation peak appears at +0.25 V. The oxidation potentials of the 7-pyrrolidinyl PMI diester **2** and 7, 12-pyrrolidinyl diester **3** are quite similar. The unsubtituted PMI diacid **5**, on the other hand, undergoes a three-step reversible reduction, reflecting the first, second and third one-electron reductive processes. The reversible reductions occur at -0.9 V, -1.2 V, and -1.5 V. The diacid **5** shows two irreversible oxidation peaks at higher oxidation potentials of 1.52 and 1.73 V (spectra in SI). The voltamograms of the 12-pyrrolidinyl PMI monoanhydride **6** shows two reversible reductions at -1.1 V and -1.3 V. For the oxidative potentials, it shows two reversible oxidation peaks around 0.6 V and 1.0 V.

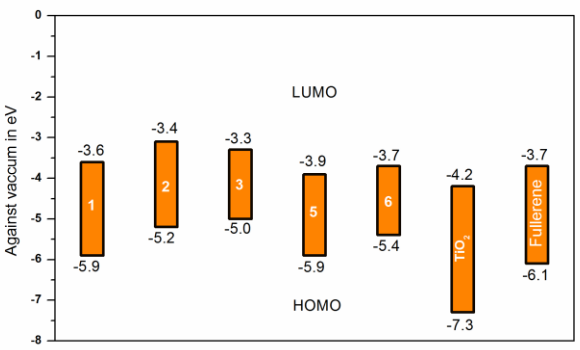


Figure 4. HOMO, LUMO levels of PMIs against TiO_2 and Fullerene.

Self-assembling monolayers

Commercially available indium-tin-oxide (ITO) coated glass substrates were used to prepare ZnO layers using zink acetate and were fabricated according to the literature procedure.[33] Self –assembling monolayers (SAMs) were prepared in a single step. The substrate plates were annealed at 150 °C for 1.5 hours, cooled, and immersed in 0.1 mM solutions of PMI diacid **5**, 7, 12-pyrrolidinyl PMI monoanhydride **7,** and 7, 12-pyrrolidinyl PMI dicarboxylic acid **9** in ethanol. After 60 minutes, the plates were taken out, thoroughly washed with ethanol, dried and the absorption spectra were measured. The spectra for SAMs were obtained by subtracting the absorbance of clean substrates from that of SAMs.

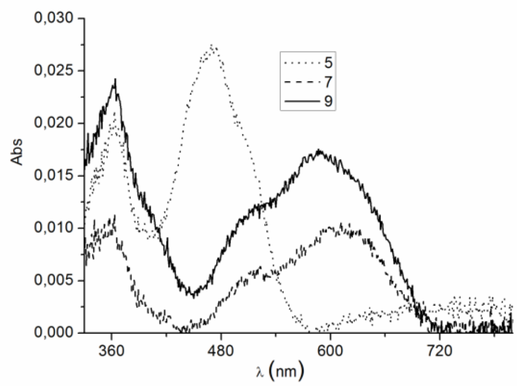


Figure 5. Absorption spectra of SAMs of PMI diacid **5**, monoanhydride **7**, and dicarboxylic acid **9** on ITO/ZnO plates.

The absorption spectra of SAMs of both diacids **5**, **9** and 7, 12-substituted anhydride **7** (Figure 5) differ from those in solution form (Figure 2b and c). Particularly interesting are the absorption features of 7, 12-substituted PMI anhydride **7** and its corresponding diacid **9**. In solution, 7, 12-substituted PMI anhydride **7** shows two major absorption bands at 652 nm and 555 nm plus a weak band at ca 453 nm (Figure 2b). On solid substrate, the major absorption bands shift towards the blue and a new band at higher energy region (ca 364) nm appears (Figure 5). Similarly 7, 12-substituted PMI diacid **9**, in solution, exhibits two absorption bands at 545 nm and 652 nm together with a shoulder at 612 nm. After immobilization on a solid substrate, diacid **9** shows blue shifted absorptions at 588 nm and 514 nm together with a high energy region absorption band at 364 nm. Its important to note that the absorption shape of SAMs of both the 7, 12-substituted PMI anhydride **7** and its corresponding diacid **9** are essentially imitations of each other. This can be explained by their mode of binding to the substrate surface. The dicarboxylic acid **9** reacts strongly with the ZnO surface and forms the desired monolayer. Whereas in the case of 7, 12-substituted PMI anhydride **7**, the anhydride moiety does the anchoring role via ring opening and the resultant dicarboxylates groups bind to the substrate surface, as proved by absorption.[32]

SAM layer formation was also studied on TiO_2 as a substrate. Annealed TiO_2-coated glass plates were immersed into 0.1 mM solutions of PMI diacids **5**, **8**, **9,** and 7, 12-substituted PMI anhydride **7**. In the case of compounds **7**, **8** and **9**, the plates were taken out after 3 hours, washed, dried and absorption spectra were recorded. For the PMI diacid **5**, the deposition time was 24 hours due to its poor solubility and thaerefore a low concentration of the deposition solution. The absorption spectra showed the formation of monolayers (Figure 6).

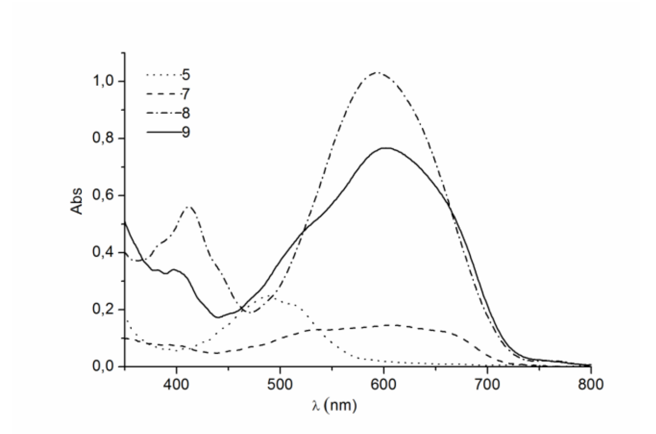


Figure 6. Absorption spectra of SAMs of PMI diacids **5**, **8**, **9** and PMI anhydride **7** over glass/TiO$_2$ plates.

All in all, the formation of monolayers was fast, efficient and simple. Due to the asymmetric structure of PMIs, namely the 7, 12-substitution, the formed layers have an intrinsically anisotropic structure, which might have a beneficial effect in photovoltaic applications. Also, it should be noted that a versatility of substitution on *bay*-rigion and distant from imide side, along with the two possibilities for an anchor (ahydride or bis-acid) makes the proposed PMI template an attractive target for future studies in self-assembled molecular films.

Conclusions

A new and facile route towards the synthesis of novel 7- and 7, 12-bispyrrolidinyl PMI monoanhydride and their dicarboxylic acids is developed. The traditional synthesis of the PMI monoanhydrides heavily depends upon selective saponification of PDIs resulting in low yields due to the absence of the selectivity. Our methodology is free of the selective saponification and thus good to excellent yields for the substituted PMI monoanhydrides are obtained in few steps. These substituted PMI monoanhydrides are easily transformed into either corresponding dicarboxylic acids or unsymmetrical PDIs by introducing second imide functionality on the anhydride cycle. Also, this is the first report of this kind of synheis, where PMI monoanhydrides carry both the amine substituents in 7, 12-positions, distant from the imide cycle. The investigation of their optical and electrochemical properties indicates that this kind of perylene derivatives can be applied in various fields of material chemistry and device preparations. The immobilization studies of the PMI monoanhydrides and diacids clearly indicate their usefulness as building blocks for SAMs. The presences of the electron donating pyrrolidine substituents at the *bay*-region and the presence of the anchoring groups in the form of anhydride/carboxylic acids make them attractive candidates for DSSCs and other types of solar cells.

Experimental Section

General: All commercially available reagents and solvents were purchased either from Sigma Aldrich Co. or from VWR and were used without further purifications unless otherwise mentioned. Purification of the products was carried out either by column chromatography on Silica gel 60 (Merck) mesh size 40-63 µm or on preparative TLC plates (Merck) coated with neutral aluminum oxide 60 F254. NMR spectra were recorded using Varian Mercury 300 MHz spectrometer using TMS as internal standard. HRMS measurements were done with Waters LCT Premier XE ESI-TOF bench top mass spectrometer. Lock-mass correction (leucine enkephaline as reference compound), centering and calibration were applied to the raw data to obtain accurate mass.

Computational methods: Density functional theory (DFT) was applied in all calculations using the Gaussian 09 (Revision D.01) suite of programs.[34] The *n*-octyl and *n*-butyl side chains of the molecules **1**, **2** and **3** were replaced by methyl (CH$_3$) groups in the modelling of the molecular structures. The geometries were optimized and electronic properties calculated using the B3LYP and M062X functionals and the 6-311++G(d,p) basis set. The atomic charges were computed using the same levels of theories with the Merz–Kollman method[35, 36] for the neutral and radical ion models of **1** and **2**.

Synthesis of Precursors 1, 2 and 3

Synthesis and characterization of precursors **1**, **2** and **3** has been reported in our previous article.[12a]

General procedure for synthesis of PMI anhydrides

Perylene monoimide diesters **1**, **2** or **3** (1.0 equiv.) and *p*-toluenesulfonic acid (5.0 equiv.) were taken in toluene (33 mL/mmol PMI diester). The resultant mixture was stirred at 90 °C for 18 hours (in case of precursor **1**, only 4 hours). After cooling to room temperature, the solvent was evaporated. The crude was dissolved in CHCl$_3$ and washed with water (2×). The organic phase was dried over Na$_2$SO$_4$, filtered and concentrated on rotary evaporator. The residue was taken into methanol and refluxed for 2 hours. The precipitates were filtered and washed with methanol to give pure products.

Synthesis of 2-octyl-1,3-dioxo-2,3-dihydro-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-8,9-dicarboxylic acid 5

PMI diester **1** (0.157 mmol, 100 mg) was taken into a 2.53 mL mixture of THF:EtOH (2:1 v/v). To this mixture, 0.835 mL of aq. KOH (6 M) was added and the resultant mixture was heated at 80 °C for 24 hours. The reaction mixture was cooled to room temperature and solvents were removed on rotary evaporator. The pH was adjusted to ca. 4 by adding 3 M HCl over an ice bath. The precipitates were filtered off and dried. The desired PMI diacid 5 was obtained as red solid (80 mg, 97 %).

Data for **5**: ^{1}H NMR (300 MHz, DMSO): δ = 8.69 (d, *J*=8.21 Hz, 2H), 8.63 (d, *J*=7.92 Hz, 2H), 8.45 (d, *J*=8.21 Hz, 2H), 4.04 (t, *J*=7.33 Hz, 2H), 1.69 - 1.57 (m, 2H), 1.39 - 1.18 (m, 10H), 0.86 - 0.81 (m, 3H) ppm. Due to poor solubility, ^{13}C NMR data could not be recorded. MS (ESI-TOF): [M$^+$] calcd for $C_{32}H_{27}NO_6^+$, 520.1777; found, 520.1760.

9-octyl-5-(pyrrolidin-1-yl)-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9H)-tetraone 6

Starting from 7-pyrrolidinyl PMI diester **2** (0.096 mmol, 68 mg), *p*-TsOH.H$_2$O (0.483 mmol, 91 mg), 7-pyrrolidinyl PMI anhydride **6** was obtained as blue solid (51 mg, 91 %).

Data for **6**: ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 8.62 (t, *J*=8.21 Hz, 2H), 8.45 - 8.33 (m, 4H), 7.47 (d, *J*=8.21, 1H), 4.19 (t, *J*=7.62, 2H), 3.74 (br, 2H), 2.75 (br, 2H), 2.12 - 2.02 (m, 4H), 1.74 - 1.70 (m, 2H), 1.44 - 1.25 (m, 6H), 0.89 - 0.84 (m, 3H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$, TMS): δ = 163.80, 163.69, 148.32, 134.95, 134.71, 134.35, 131.18, 131.00, 129.06, 128.55, 127.62, 125.35, 124.86, 124.68, 123.99, 122.54, 121.34, 119.91, 118.89, 118.26, 117.19, 52.83, 40.82, 32.05, 29.91, 29.59, 29,45, 28.38, 27.41, 25.98, 22.86, 14.30 ppm. MS (ESI-TOF): [M$^+$] calcd for $C_{36}H_{32}N_2O5^+$, 572.2350; found, 572.2311.

9-octyl-5,13-di(pyrrolidin-1-yl)-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9H)-tetraone 7

Starting from 7, 12-pyrrolidinyl PMI diester **3** (0.216 mmol, 167 mg), *p*-TsOH.H_2O (1.08 mmol, 205 mg), 7, 12-pyrrolidinyl PMI anhydride **7** was obtained as dark blue solid (105 mg, 75 %).

Data for **7**: ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 8.70 (d, *J*=7.92 Hz, 2H), 8.30 (s, 2H), 7.80 (d, *J*=8.21 Hz, 2H), 4.24 (t, *J*=7.62 Hz, 2H), 3.70 (br, 4H), 2.74 (br, 4H), 1.83 - 1.73 (m, 2H), 1.49 - 1.25 (m, 10H), 0.90 - 0.85 (m, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 164.21, 161.30, 150.01, 135.29, 131.44, 130.41, 129.15, 128.33, 123.89, 119.37, 118.79, 118.60, 117.95, 52.57, 40.74, 32.09, 29.67, 29.48, 28,47, 27.47, 25.91, 22.89, 14.34 ppm. MS (ESI-TOF): [M^+] calcd for $C_{40}H_{39}N_3O5^+$, 641.2897; found, 641.2890.

2-octyl-1,3-dioxo-6-(pyrrolidin-1-yl)-2,3-dihydro-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-8,9-dicarboxylic acid 8

7-pyrrolidinyl PMI anhydride **6** (0.050 mml, 29 mg) and KOH (0.101 mmol, 6 mg) were taken in 3 mL of *t*BuOH. The reaction mixture was heated at 100 °C for 3 hours. After cooling to room temperature, pH of the mixture was adjusted to ca. 6 – 6.5 by adding aqueous NH_4Cl . Precipitates were formed which were filtered off and dried to yield desired product as blue solid (23 mg, 76 %).

Data for **8**: ^{1}H NMR (300 MHz, CD_3OD): δ = 8.58 (d, *J*=8.21 Hz, 1H), 8.52 - 8.46 (m, 3H), 7.97 (s, 1H), 7.90 (d, *J*=7.92 Hz, 1H), 7.11 (d, *J*=7.92 Hz, 1H), 4.19 (t, *J*=7.92 Hz, 2H), 3.81 (br, 2H), 2.81 (br, 2H), 1.77 - 1.72 (m, 2H), 1.43 - 1.31 (m, 10H), 0.93 - 0.87 (m, 3H) ppm. Due to poor solubility, ^{13}C NMR data could not be recorded. MS (ESI-TOF): [M^+] calcd for $C_{36}H_{34}N_2O_6^+$, 641.2897; found, 641.2890.

2-octyl-1,3-dioxo-6,11-di(pyrrolidin-1-yl)-2,3-dihydro-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-8,9-dicarboxylic acid 9

7, 12-pyrrolidinyl PMI anhydride **7** (0.109 mml, 70 mg) and KOH (0.201 mmol, 12 mg) were taken in 6 mL of *t*BuOH. The reaction mixture was heated at 100 °C for 3 hours. After cooling to room temperature, pH of the mixture was adjusted to ca. 6 – 6.5 by adding aqueous NH_4Cl . Precipitates were formed which were filtered off and dried to yield desired product as blue solid (55mg, 76 %).

Data for **9**: ^{1}H NMR (300 MHz, CD_3OD): δ = 8.52 (d, *J*=7.92 Hz, 2H), 8.30 (s, 2H), 7.54 (d, *J*=8.21 Hz, 2H), 4.21 (t, *J*=7.92 Hz, 2H), 3.74 (br, 4H), 2.75 (br, 4H), 1.79 - 1.66 (m, 2H), 1.41 - 1.29 (m, 10H), 0.92 - 0.88 (m, 3H) ppm. ^{13}C NMR (75 MHz, CD_3OD): δ = 164.57, 150.86, 137.70, 137.68, 137.66, 132.20, 130.17, 129.76, 122.02, 121.99, 114.82, 114.14, 111.20, 52.10, 39.98, 31.83, 29.30, 29.19, 27.98, 27.06, 25.48, 22.54, 13.26 ppm. MS (ESI-TOF): [M^+] calcd for $C_{40}H_{41}N_3O_6^+$, 659.3008; found, 659.2996.

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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