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## Alkyl- and aryl-substituted benzo[ghi]perylenetriimides: Synthesis, characterization and comparison of electrochemical and spectroscopic properties



PIGMENTS

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#### 1. Introduction

## In recent years, Perylene-3,4:9,10-tetracarboxylic acid diimides (PDI) have received a great deal of attention due to their widespread industrial applications [1]. The exceptional thermal and photochemical stability of PDIs in combination with their remarkable optoelectronic properties with large fluorescence quantum yields and high molar absorptivities make them as promising organic n-type semiconductors [2]. Today, PDIs are extensively used in field-effect transistors [3], light-emitting diodes [4,5], liquid crystal displays [6,7], biosensors [8], light-harvesting materials [9], optical switches [10], molecular wires [11,12] and as dyes in photodynamic therapy [13]. As a means to replace fullerene electron acceptors in organic solar cells, several efforts were made towards the construction of electron-rich aromatic cores that are capable of acting as good electron acceptors in photovoltaic cells

[14–20]. One such electron acceptor is PDI [1,21–23]. Nevertheless, the solar energy conversion efficiencies achieved for PDI comprised of conjugated polymers and small molecule photovoltaic blends are

## ABSTRACT

Benzo[ghi]peryleneimides constitute a unique class of fluorescent perylene dyes which possesses great synthetic diversity due to the presence of a large number of reactive active sites (availability of third imide region). Taking advantage of this additional active site we synthesized a new series of benzo[ghi] perylenetriimides comprised of alkyl- and aryl-substituents in the third imide region. The core extension of perylene diimides was performed using a Diels-Alder reaction to afford diimido anhydride (3) which provided access to the various triimides with yields ranging from 58% to 69%. The combined spectroscopic and electrochemical studies revealed strong electron accepting properties of the triimides. Potential application of the synthesized triimides for various optoelectronic devices and as non-fullerene electron acceptors in photovoltaics is evident from this study.

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not highly appreciable when compared to the fullerene-based acceptors. Such low efficiency could be attributed to the charge loss existing in PDI molecules [24]. Additionally, one of the drawbacks of PDIs is their low solubility in most organic solvents which adds difficulties in processing and thus limits their use in material science applications. In order to circumvent the solubility issues and increase the potential use of PDIs, various synthetic strategies have been explored with the goal to obtain new soluble PDI derivatives. Recently benzo[ghi]perylenes, representing a more expanded  $\pi$ conjugated system than PDI, have attracted scientists owing to their high photostability and interesting electronic properties [24–28]. Comparison of the skeletal structures of benzo[ghi]pervlenetriimide (BPTI) and PDI suggests that BPTI offers more synthetic diversity owing to the fact that it has three imide regions [24,29–32]. This paves a way for fine-tuning the spectroscopic and electrochemical properties based on the nature and type of substituents. Taking into consideration the synthetic versatility of BPTI and their applications in organic solar cells, we intended to synthesize and examine the properties of a series of benzo[ghi] perylenetriimides containing either an alkyl- or aryl-substituent in the third imide region.

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### 2. Results and discussion

#### 2.1. Synthesis

The chemical structures of benzo[ghi]perylenetriimides **(4a-4g)** and the synthetic routes to obtain such are shown in Scheme 1. The synthesis originated from an imidization of perylene dianhydride **(1)** by reaction with 3-aminopentane in imidazole at 140 °C to afford **2** in an isolated yield of 89%.

A Diels-Alder reaction of PDI (2) with maleic anhydride in the presence of *p*-chloranil as an oxidizing agent and nitrobenzene as the solvent resulted in the formation of the diimido anhydride 3 [24,31]. Attempts were made to obtain the dianhydride (5) under two different reaction conditions: (i) increasing the molar equivalents of maleic anhydride and p-chloranil used and (ii) reacting the formed benzo[ghi]perylenetriimide again with maleic anhydride using similar reaction conditions. Unfortunately, no product was realized in either of the reaction conditions performed. This was presumably due to the presence of the electron-withdrawing group in the 1,12 position that deactivates the benzo[ghi]perylene nucleus preventing the formation of the dianhydride [33]. Additional efforts were also taken towards the bromination of benzo[ghi]perylenetriimide at the 6 or 7 position by refluxing with chlorinated solvents and using a catalytic amount of Lewis acids such as AlCl<sub>3</sub>, Silica or FeCl<sub>3</sub>. However, no conditions resulted in the formation of the desired product. This could also be attributed to the deactivated aromatic core. The solid monoanhydride (3) obtained from the Diels-Alder reaction was poorly soluble in common organic solvents at room temperature and hence used directly in the next step after being washed with copious amount of methanol, ethyl acetate and acetone. The condensation reaction with the amines was performed in DMF and imidazole as the solvent at 140 °C and 160 °C respectively. A relatively higher yield was obtained when DMF was used owing to the higher solubility of the anhydride 3 (Table 1). All of the compounds (4a-4g) were isolated as a yellow solid and were readily soluble in chlorinated solvents, ethyl acetate, THF and DMF at room temperature. The synthesized compounds were characterized by <sup>1</sup>H NMR spectroscopy. The optical and electrochemical properties of the target compounds were determined by UV-Vis, fluorescence and cyclic voltammetric studies.

## Table 1

Reaction	conditions	and isolated	l vields of	benzolgho	lpervlenetriimides.

Yield %
63
68
69
62
58
63
64

#### 2.2. NMR spectroscopy

The <sup>1</sup>H NMR spectra for the target compounds (**4a-4g**) recorded in CDCl<sub>3</sub> are shown in Fig 1. The structure of substituted BPTIs was confirmed by the presence of three distinct downfield signals characteristic of the benzoperylene core. The "H<sub>a</sub>" protons appear as a singlet between 10.07 and 10.45 ppm. The chemical shift of the H<sub>a</sub> protons for alkyl-substituted BPTIs appear slightly downfield relative to those of the aryl-substituted BPTIs. The "H<sub>b</sub>" and "H<sub>c</sub>" protons of all the BPTIs exhibit two separate doublets existing between 8.96 and 9.37 ppm with 4c being an exception in which case a singlet peak equivalent to four protons was obtained. The aromatic proton signals for the corresponding R group were dispersed between 7.0 and 8.7 ppm depending on the substituents attached in the *para* position of the phenyl group. Compounds **4a-4f** display one common multiplet at 5.2 ppm for the methine protons present in 3-aminopentane group. However, the two methine protons present in 4g can be clearly distinguished by the existence of two separate multiplets ( $H_d = 5.7$  ppm - R) and ( $H_e = 5.2$  ppm, 3-



Scheme 1. Synthesis of benzo[ghi]perylenetriimides.



Fig. 1. <sup>1</sup>H NMR spectra of benzo[ghi]perylenetriimide derivatives in CDCl<sub>3</sub>.

aminopentane) in the spectra. Compound **4f** also showed an additional singlet at 5.15 ppm corresponding to the methylene protons of benzylamine.

#### 2.3. Steady-state absorption spectroscopy

The electronic absorption data of compounds 4a-4g were measured in CH<sub>2</sub>Cl<sub>2</sub> or THF and were compiled in Table 2. Fig. 2a compares the electronic absorption spectra of BPTIs 4a, 4e and 4g to that of free PDI, 2. PDI exhibits an absorption spectrum with two intense bands at 523 nm and 488 nm along with a shoulder peak at 457 nm. Compared to the absorption spectral pattern of PDI, the BPTIs exhibited a hypsochromic shift of about 58 nm. All of the target compounds exhibited three bands characteristic of the benzo [ghi]perylene core ( $\lambda$  at 465, 435 and 410 nm). A small hypsochromic shift of about 2 nm occurred for alkyl substituted BPTIs 4f and 4g, which could be attributed to the extended conjugation present in the aryl-substituted compounds. Changing to a relatively polar solvent, CH<sub>2</sub>Cl<sub>2</sub> had only a minor effect on the absorption maximum  $(\lambda_{max})$  displaying a slight bathochromic shift (aryl substituted = 465 nm; alkyl substituted = 464 nm). Hence, it can be concluded that incorporation of an alkyl- or aryl-substituent in the

Table 2	
Spectroscopic data of benzo[ghi]perylenetriimide	es.

Entry	$\lambda_{max}$ (CH <sub>2</sub> Cl <sub>2</sub> ) nm	$\lambda_{\rm max}$ (THF) nm	$\lambda_{emi}\left(CH_{2}Cl_{2}\right)nm$	λ <sub>emi</sub> (THF) nm
4a	465	463	485	485
4b	465	463	485	484
4c	465	463	485	484
4d	465	463	485	484
4e	464	464	488	476
4f	464	461	481	481
4g	464	461	481	481
PDI	523	521	537,573	571

imide region has only a slight effect on the optical properties of the benzo[*ghi*]perylenetriimides.

#### 2.4. Fluorescence spectroscopy

Emission spectra of the target compounds were measured upon excitation at the  $\lambda_{max}$  of the compounds (**4a-4d**:  $\lambda_{463}$ ; **4e**:  $\lambda_{464}$ ; **4f**, **4g**:  $\lambda_{461}$ ). The emission spectra of compounds **4a**, **4e** and **4g**, along with PDI in THF are shown in Fig. 2b and summarized in Table 2 (emission spectra of 4b, 4c, 4d and 4f are provided in the Supplementary Information). As expected from the absorption results, compounds 4a-4g exhibited similar emission characteristics. The emission bands were approximate mirror images of the corresponding absorption bands with a Stokes shift of approximately 20 nm. The aryl-substituted imides (4a-4e) showed a maximum emission peak at 485 nm while the alkyl-substituted compounds display a slight red shift of ~4 nm (481 nm). Moreover the emission spectra reveal another intense band centered around 505 nm along with a shoulder peak existing around 545 nm. No significant effects were realized in the emission spectra by changing the solvent. Combining the absorption and emission spectral data, it can be concluded that the properties of the benzo[ghi]perylenetriimides are not drastically affected by the nature of the substituents attached in the imide region.

#### 2.5. Electrochemical measurements

As a means to identify and compare the redox properties of the benzo[*ghi*]perylenetriimides, electrochemical measurements were performed using cyclic voltammetry. The respective values for the corresponding reductions, optical band gap, and HOMO and LUMO values are depicted in Table 3. Fig. 3 gives the typical voltammograms of compounds **4c**, **4e**, **4f** and **PDI**. All of the benzo[*ghi*]perylenetriimides exhibited three reversible reductions with the exception of NO<sub>2</sub> substituted BPTI showing additional reduction



Fig. 2. (a) UV–Vis spectra (b) emission spectra of benzo[ghi]perylenetriimides in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

Fable 3
Electrochemical potentials and electronic energy levels of benzo[ghi]perylenetriimides.

Entry	$E_g^{a}(eV)$	<sup>1</sup> E1/2 (V vs Ag/AgCl)	<sup>2</sup> E1/2 (V vs Ag/AgCl)	<sup>3</sup> E1/2 (V vs Ag/AgCl)	<sup>4</sup> E1/2 (V vs Ag/AgCl)	$E_{LUMO}^{b}(eV)$	$E_{HOMO}^{c}(eV)$
<b>4</b> a	2.6	-0.574	-0.820	_	-1.265	-3.82	-6.42
4b	2.6	-0.571	-0.822	-0.918	-1.293	-3.82	-6.42
4c	2.6	-0.589	-0.719	-	-1.178	-3.89	-6.49
4d	2.6	-0.643	-0.838	-1.028	-1.297	-3.75	-6.35
4e	2.5	-0.616	-0.841	-0.998	-1.323	-3.78	-6.28
4f	2.6	-0.564	-0.819	-	-1.280	-3.83	-6.43
4g	2.6	-0.562	-0.726	-	-1.297	-3.88	-6.48
PDI	2.3	-0.444	-0.642	-	-	-3.96	-6.26

<sup>a</sup>  $Eg = (E_{abs} + E_{em})/2 = optical band gap [22].$ 

<sup>b</sup>  $E_{LUMO} = 4.4 \text{eV} - E_{red1}$ 

 $^{c}\ E_{HOMO}=E_{LUMO}\text{-}E_{g}\text{.}$ 

peaks. Two of the reversible reductions (-0.4 V and -0.64 V) can be attributed to the PDI core and are slightly negatively shifted with respect to those of PDI.

The difference in the reduction potential between PDI and BPTI ranges from 0.06 V (**4c**) to 0.19 V (**4d**). A gradual shift of the onset potential to a more positive value was realized while moving from aryl-substituted BPTIs (-0.64 V) to alkyl-substituted BPTIs (-0.56 V). This indicates that the alkyl-substituted derivatives possess a stronger electron accepting properties than the arylsubstituted derivatives. Of all the haloaryl-substituted BPTIs, the bromophenyl derivative exhibited a more positive onset potential (-0.50 V) demonstrating a relatively more efficient electron acceptor behavior. The band gaps for all of the BPTI derivatives were calculated to be 2.6 eV with an exception for 4e, the nitrophenyl derivative (2.5 eV) in which case, additional reduction peaks were observed. Based on the obtained electrochemical measurements, it can be confirmed that the benzo[ghi]triimides exhibit excellent acceptor properties that could be potentially applicable in the development of organic solar cells.

#### 3. Experimental section

#### General

Compounds perylenetetracarboxylic dianhydride, benzylamine, 3-aminopentane, phenylethylamine (Sigma Aldrich), *p*-fluoroaniline, *p*-bromoaniline, *p*-chloroaniline, *p*-iodoaniline, *p*-nitroaniline, (TCI America), nitrobenzene, (Alfa Aeser), imidazole (Acros Organics), were purchased from commercial suppliers and used as received or as specified. Reactions were monitored by thin layer chromatography (TLC) on silica gel GF plates (Analtech, No. 21521) and visualized using a hand-held UV lamp. Column chromatography was carried out on silica gel (Sorbent Technologies, 230–400 mesh). Elemental analyses ( $\pm 0.4\%$ ) were performed by Atlantic Microlabs, Inc., Norcross, GA 30071.

#### Spectroscopic measurements

<sup>1</sup>H NMR spectra was measured at 400 MHz in CDCl<sub>3</sub>. Chemical shifts ( $\delta$ ) are referenced to internal (CH<sub>3</sub>)<sub>4</sub>Si and coupling constants (*J*) are given in Hz. FT-IR spectra were run as thin film on NaCl disks using dichloromethane. UV/Vis absorption and Fluorescence emission spectra were recorded on a Cary Eclipse UV–Vis–NIR spectrophotometer in dichloromethane and THF.

#### Electrochemical measurements

Cyclic voltammograms were recorded on a CH instrument (Model: CHI 6017E) by using a three-electrode system. A glassy carbon was used as the working electrode. A platinum wire served as the counter electrode, and Ag/AgNO<sub>3</sub> was used as the reference electrode. Ferrocene–ferrocenium redox couple was used as an internal standard. The voltammograms were performed in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBPF<sub>6</sub> as the supporting electrolyte and at 100 mV<sup>-1</sup> scan rate. All solutions were purged prior to electrochemical measurements using nitrogen gas.



Fig. 3. Cyclic Voltammograms of BPTIs and PDI in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M TBPF<sub>6</sub> as supporting electrolyte at scan rate 100 mV<sup>-1</sup>.

#### 4. Synthesis of compound 3

To a stirred mixture of compound **2** (0.5 g, 9.0 mmol) in nitrobenzene (10 mL) in a 50 mL round bottomed flask were charged *p*-chloranil (1.75 g, 7.0 mmol), maleic anhydride (13.3 g, 130.0 mmol) and heated to 220 °C under argon atmosphere for 24 h. The progress of the reaction was continuously monitored by UV–vis spectroscopy for the disappearance of the absorption band at 523 nm in CH<sub>2</sub> Cl<sub>2</sub> corresponding to the starting material **2**. The reaction mixture was cooled to room temperature and filtered. The resulting solid was made into a slurry with a 1:1 mixture of methanol and ethyl acetate (250 mL) for 30 min and collected the solid by filtration. The filter cake thus obtained was washed with acetone to yield a yellow solid. The yellow crude material was directly taken to the next step without any purification.

# 4.1. A general procedure for the synthesis of substituted benzo[ghi] perylenetriimides (4a-4g)

The anhydride (0.24 mmol) and the corresponding amines (0.72 mmol) were dissolved in 5 mL of DMF and heated in a round bottomed flask at 140 °C for 3–10 h. The progress of the reaction was monitored by TLC using hexane: $CH_2Cl_2$  as the eluent. After completion of the reaction, the reaction mixture was evaporated to dryness. The solid obtained was dissolved in  $CH_2Cl_2$  and washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to yield a yellow solid.

*N1,N2*-Bis(3-pentyl)-*N3*-(4-fluorophenyl)-benzo[*ghi*]perylene-2,3, 8,9,11,12-hexacarboxylic triimide **BPTI-4a**: Reaction time: 6 h; Yield: 86 mg (63%) as a yellow solid, m.p > 300 °C; IR: 1712, 1667, 1317, 811 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  (ppm) 10.29 (s, 2H), 9.19 (d, *J* = 8.0 Hz, 2H), 9.12 (d, *J* = 8.0 Hz, 2H), 7.70–7.73 (m, 2H),

7.43–7.34 (m, 2H), 5.30–5.15 (m, 2H), 2.46–2.32 (m, 4H), 2.12–2.02 (m, 4H), 1.04 (t, J = 7.2 Hz, 12H); Anal. Calcd for C<sub>44</sub>H<sub>32</sub>FN<sub>3</sub>O<sub>6</sub>: C, 73.63; H, 4.49; N, 5.85. Found: C, 73.29; H, 4.10; N, 5.32.

*N1,N2*-Bis(3-pentyl)-*N*3-(4-chlorophenyl)-benzo[*ghi*]perylene-2,3, 8,9,11,12-hexacarboxylic triimide **BPTI-4b**: Reaction time: 6 h; Yield: 93 mg (68%) as a yellow solid, m.p > 300 °C; IR: 1713, 1665, 1317, 811 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  (ppm) 10.07 (s, 2H), 9.03 (d, *J* = 8.2 Hz, 2H), 8.96 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 5.17 (quintet, *J* = 7.2 Hz, 2H), 2.43–2.32 (m, 4H), 2.14–2.04 (m, 4H), 1.07 (t, *J* = 7.2 Hz, 12H); *Anal.* Calcd for C<sub>44</sub>H<sub>32</sub>ClN<sub>3</sub>O<sub>6</sub>: C, 71.98; H, 4.39; N, 5.72. Found: C, 71.75; H, 4.25; N, 5.92.

N1,N2-Bis(3-pentyl)-*N*3-(4-bromophenyl)-benzo[*ghi*]perylene-2,3, 8,9,11,12-hexacarboxylic triimide **BPTI-4c:** Reaction time: 6 h; Yield: 99 mg (69%) as a yellow solid, m.p > 300 °C; IR: 1712, 1664, 1317, 811 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  (ppm) 10.14 (s, 2H), 9.09 (s, 4H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 5.18 (quintet, *J* = 7.2 Hz, 2H), 2.43–2.32 (m, 4H), 2.12–2.03 (m, 4H), 1.06 (t, *J* = 7.4 Hz, 12H); *Anal.* Calcd for C<sub>44</sub>H<sub>32</sub>BrN<sub>3</sub>O<sub>6</sub>: C, 67.87; H, 4.14; N, 5.40. Found: C, 67.96; H, 3.98; N, 5.25.

*N1,N2*-Bis(3-pentyl)-*N3*-(4-iodophenyl)-benzo[*ghi*]perylene-2,3, 8,9,11,12-hexacarboxylic triimide **BPTI-4d:** Reaction time: 7 h; Yield: 96 mg (62%) as a yellow solid, m.p > 300 °C; IR: 1713, 1664, 1317, 810 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  (ppm) 10.25 (s, 2H), 9.17 (d, *J* = 8.1 Hz, 2H), 9.10 (d, *J* = 8.1 Hz, 2H), 8.01 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 5.19 (quintet, *J* = 7.1 Hz, 2H), 2.45–2.32 (m, 4H), 2.13–2.02 (m, 4H), 1.04 (t, *J* = 7.3 Hz, 12H); *Anal.* Calcd for C<sub>44</sub>H<sub>32</sub>IN<sub>3</sub>O<sub>6</sub>: C, 64.01; H, 3.91; N, 5.09. Found: C, 64.21; H, 3.75; N, 5.15.

*N1,N2*-Bis(3-pentyl)-*N3*-(4-nitrophenyl)-benzo[*ghi*]perylene-2,3, 8,9,11,12-hexacarboxylic triimide **BPTI-4e:** Reaction time: 10 h; Yield: 81 mg (58%) as a yellow solid, m.p > 300 °C; IR: 1720, 1661,

1521, 1350, 1318, 812 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  (ppm) 10.28 (s, 2H), 9.21 (d, J = 8.5 Hz, 2H), 9.14 (d, J = 8.5 Hz, 2H), 8.56 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.6 Hz, 2H), 5.20 (quintet, J = 7.3 Hz, 2H), 2.44–2.33 (m, 4H), 2.11–2.03 (m, 4H), 1.05 (t, J = 7.4 Hz, 12H); *Anal.* Calcd for C<sub>44</sub>H<sub>32</sub>N<sub>4</sub>O<sub>8</sub>: C, 70.96; H, 4.33; N, 7.52. Found: C, 71.22; H, 4.19; N, 7.26.

*N*1,*N*2-Bis(3-pentyl)-*N*3-(benzyl)-benzo[*ghi*]perylene-2,3,8,9,11,12-hexacarboxylic triimide **BPTI-4f:** Reaction time: 3 h; Yield: 84 mg (63%) as a yellow solid, m.p > 300 °C; IR: 1709, 1664, 1317, 811 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  (ppm) 10.38 (s, 2H), 9.34 (d, *J* = 8.4 Hz, 2H), 9.15 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 5.22–5.18 (m, 2H), 5.15 (s, 2H), 2.44–2.33 (m, 4H), 2.10–2.0 (m, 4H), 1.01 (t, *J* = 7.4 Hz, 12H); *Anal.* Calcd for C<sub>45</sub>H<sub>35</sub>N<sub>3</sub>O<sub>6</sub>: C, 75.72; H, 4.94; N, 5.89. Found: C, 75.46; H, 5.03; N, 5.66.

*N*1,*N*2-Bis(3-pentyl)-*N*3-(1-phenylethyl)-benzo[*ghi*]perylene-2,3,8, 9,11,12-hexacarboxylic triimide **BPTI-4g:** Reaction time: 3 h; Yield: 87 mg (64%) as a yellow solid, m.p > 300 °C; IR: 1717, 1664, 1317 cm<sup>-1</sup>; <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  (ppm) 10.45 (s, 2H), 9.37 (d, *J* = 8.4 Hz, 2H), 9.16 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 5.86 (q, *J* = 7.3 Hz, 1H), 5.23–5.15 (m, 2H), 2.43–2.31 (m, 4H), 2.18 (d, *J* = 8.5 Hz, 3H), 2.08–2.00 (m, 4H), 1.00 (t, *J* = 7.4 Hz, 12H); *Anal.* Calcd for C<sub>46</sub>H<sub>37</sub>N<sub>3</sub>O<sub>6</sub>: C, 75.91; H, 5.12; N, 5.77. Found: C, 75.78; H, 5.36; N, 5.92.

#### 5. Conclusion

In conclusion, we have successfully synthesized a novel series of benzo[*ghi*]perylenetriimides incorporating an alkyl- or aryl-substituent in the third imide region. The optical properties of the BPTIs as examined by steady state spectroscopic peak measurements revealed a maximum absorption around 465 nm. The electron transfer abilities as estimated by cyclic voltammetric experiments revealed a more positive onset potential for alkyl-substituted derivatives relative to the aryl-substituted BPTIs. The synthesized BPTIs demonstrated better solubility than perylene diimides in common organic solvents such as ethyl acetate, dichloromethane, methanol, DMF and THF. The synthesized benzo [*ghi*]perylenetriimides could be of considerable importance in the development of organic solar cells.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.07.031.

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