

A novel substitution reaction of perylene bisimides with Ph₂PLi at the α -position†

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A novel substitution reaction of perylene bisimides has been developed. The Ph₂PO group was attached to the PBI core at the α -position instead of the usual bay position. This substitution kept the high fluorescence of the PBI dyes and caused the adjacent proton at the bay position and a tertiary proton at the cyclohexyl group to be shifted significantly in the ¹H-NMR spectra.

Introduction

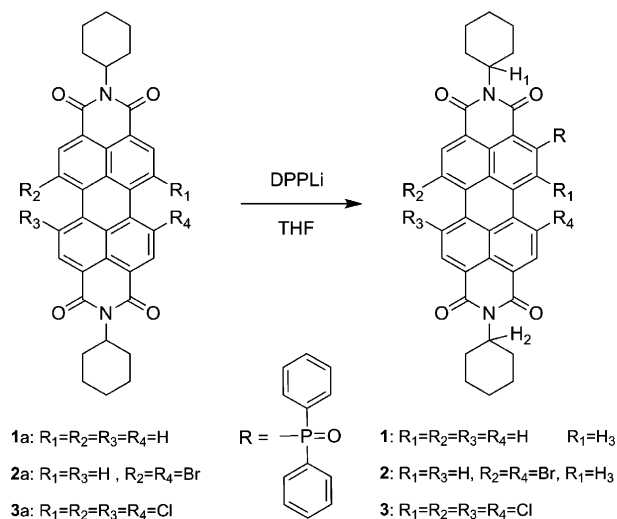
In recent years, functionalized perylene bisimides (PBIs) have received considerable attention for a wide range of applications, for example, as fluorescent dyes for single molecule spectroscopy¹ and bio-imaging² and as organic semiconductors for organic and polymeric light-emitting diodes (OLEDs and PLEDs),³ organic field-effect transistors (OFETs),⁴ and solar cells.⁵ They also have been proven to be good building blocks for constructing supramolecular or giant-molecular systems.⁶ The molecular properties that enable all these applications are the high fluorescent quantum yield, fairly persistent radical anion state, easy accessibility, and outstanding stability of these dyes against environmental influences.⁷ Due to the intrinsic insolubility of perylene bisimides, two different strategies have been developed to modify the dyes. One is introducing solubilizing substituents at the imide nitrogen,⁸ which exhibits usually indistinguishable absorption and emission properties.⁹ Another is introducing substituents at the carbocyclic scaffold in the so-called bay-area (β -position of imide groups). The latter strategy is more elaborate.¹⁰ For example, aryloxy-, cyano-, pyrrolidino, alkoxy and/or alkylthio-substituted PBIs as well as the Suzuki coupling reaction have been investigated. Usually the readily available halogenated PBIs, such as 1,7-dibromo or 1,6,7,12-tetrachloro derivatives, were used as starting materials.^{11,12} As far as we know, it has seldom been reported that the PBI dye was directly modified at α -position of the aromatic core.¹³

Phosphines have been widely used for organic synthesis. For example, organophosphide anions are considered to be powerful nucleophiles. The diphenylphosphide anion (Ph₂P[−]) readily reacts with haloaromatic compounds involving S_{RN}1 mechanism of nucleophilic substitution with both thermal and photochemical initiation steps.¹⁴ And phosphines reduce hydroperoxides, peroxides, disulfides, sulfoxides, epoxides and so on.¹⁵ However, the reaction of Ph₂P[−] with PBI dye has not been reported. Herein, a series of diphenylphosphinoyl (Ph₂PO) group substituted perylene bisimides at the α -position

(**1**, **2** and **3**) were synthesized from corresponding PBIs (**1a**, **2a** and **3a**) following the strategy outlined in Scheme 1.

N,N'-Dicyclohexylperylene-3,4:9,10-tetracarboxylic acid bisimide **1a**, *N,N'*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide **2a** and *N,N'*-dicyclohexyl-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide **3a** were synthesized and purified according to literature procedures.¹⁶ A solution of lithium diphenylphosphide (DPPLi) was prepared from triphenylphosphine in THF.¹⁷ 1,7-Bibromoperylene bisimide **2a** was used to carry out this reaction. Under an argon gas stream, DPPLi in THF was added into the THF solution of **2a**. Originally we aimed to substitute the bromine atoms of **2a**. However, MALDI-TOF mass data suggested that a proton on the perylene core was substituted by a Ph₂PO group instead of substitution of the halogen atom. The suggestion was further confirmed by ¹H-NMR, ¹³C-NMR and ³¹P-NMR spectra. These data indicated that a novel type of substitution reaction of PBIs was developed. This new reaction was also verified by the reactions of DPPLi with **1a** (no halogen substituted) and **3a** (all of the bay positions halogen substituted).

The substitution of the aromatic core of perylene-3,4:9,10-tetracarboxylic acid bisimides generally takes place at bay (β) positions. For 1,6,7,12-tetrachloroperylene bisimide **3a**, four



Scheme 1 The synthesis of compounds **1**, **2** and **3**.

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† Electronic supplementary information (ESI) available: The MS and ¹H-, ¹³C-, ³¹P-NMR spectra of **1**–**3**. See DOI: 10.1039/b9nj00364a

β -positions are occupied by chlorine atoms and no chlorine atom is substituted according to the MS spectrum. Consequently, the Ph_2PO group is incorporated at an α -position of the perylene core. All data from the ^1H -NMR, ^{13}C -NMR and ^{31}P -NMR spectra are consistent with this result. Due to the shielding effect of the Ph_2PO group on compound **3**, the tertiary proton on a nearer cyclohexyl group (H_1 proton, Scheme 1) shifts upfield 0.99 ppm compared with the tertiary proton on another cyclohexyl group (H_2 proton, Table 1). Similar effects are also observed for **1** and **2**. Compared with H_2 proton, the H_1 proton shifts upfield 0.41 and 0.30 ppm, respectively, for **1** and **2**. These values are less than that for **3**. Because the relatively bulky chlorine atom at the adjacent position makes the Ph_2PO group near the H_1 proton, and as a result, the shielding effect of the Ph_2PO group is reinforced for **3** (Fig. 1). The remarkable chemical shifts of the tertiary protons on cyclohexyl groups reveal that the substitutions also take place at the α -positions of the perylene bisimides **1** and **2**.

In addition, an unusual change in ^1H -NMR spectrum of **1** was noted. The adjacent proton of the substituted group at bay position shifts downfield to 9.70 ppm with a large coupling constant of 12.6 Hz (300 M at 25 °C, Table 1). The remarkable increase in chemical shift mainly results from the deshielding effect of Ph_2PO group because this proton locates at a strong induced paramagnetic area of two phenyl groups. The large coupling constant indicates that this proton is split by an adjacent P atom. For compound **2**, a doublet signal at low field of 9.91 ppm with a large coupling constant of 13.7 Hz (far more than the coupling constant of 8.1 Hz at 8.63 ppm for **2a**) is also observed in the ^1H -NMR spectrum, revealing that the adjacent atom of Ph_2PO group is also a proton instead of a Br atom.

In the synthesis of the target compounds, lithium diphenylphosphide was used to react with PBIs. However, it was found that the group incorporated was not Ph_2P but Ph_2PO . In most cases, reactions of alkali metal diphenylphosphide with simple aryl halides produce arylphosphines, which are stable in air.¹⁸ But the incorporation of the large aromatic PBI moiety caused the phosphines to be three-coordinate structures, which are unstable and readily oxidize to penta-coordinate compounds. The experimental phenomena observed in synthesis were that the resulting solutions remained non-fluorescent

Table 1 The special chemical shift of the compounds at 25 °C. (Because of the poor solubility of **1a**, we do not have the NMR chemical shift of **1a**)

	H_1 (ppm)	H_2 (ppm)	H_3 (ppm), J/Hz
1	4.65	5.06	9.70, 12.6
2	4.71	5.01	9.91, 13.7
2a	5.06	5.06	8.63, 8.1
3	4.01	5.00	—
3a	5.02	5.02	—

until separation. After purification with column chromatography, the target compounds obtained were strongly fluorescent. The Ph_2P group can quench the fluorescence of the fluorophore connected due to photo-induced electron transfer (PET) processes. Whereas the PET processes are stopped after the Ph_2P group has been oxidized to a Ph_2PO group.¹⁹ Therefore, it was proposed that non-fluorescent Ph_2P incorporated PBIs were yielded firstly. After the Ph_2P group has been oxidized to the stable Ph_2PO group in the purification procedure,²⁰ the fluorescence of PBIs was restored again due to the hindrance of the PET process.

Spectroscopic grade solvents were used in UV/vis measurements. For the purpose of comparison, the starting materials of perylene bisimides are also included in Fig. 2 and the optical data are summarized in Table 2. Over 400 nm, compounds **1** and **2** show the PBI core absorption band with the same maximum absorption at 534 nm in CHCl_3 , and compound **3** shows the maximum absorption at 528 nm. The absorption maximum of the derivatives are red-shifted by about 8–9 nm after substitution. In the emission spectra of compounds **1**, **2** and **3**, the maximum emission locate at 545 nm, 555 nm and 558 nm, which are red-shifted by 8 nm, 7 nm and 8 nm, respectively, compared to their corresponding PBI starting materials. These results mainly are attributed to the extension of the aromatic system after the substitution. From Fig. 2, we know that the modified PBI dyes have similar absorption and emission profiles to their starting materials. Especially, the absorption and emission bands are not broadened. Whereas the substitution at the bay-area usually results in the maximum absorption and emission bands being red-shifted and broadening of the bands due to the electron-donating effect of the substituted group and the steric twisting of the perylene core.^{6,21}

From Table 2, we know that the fluorescence quantum yield of **1**, **2** and **3** show little difference from the corresponding **1a**, **2a** and **3a**. So the incorporation of the Ph_2PO group to the perylene core at α -position keeps the fluorescence property well. These are in agreement with the calculation results. As clearly shown in Fig. 1, the geometries of compound **1**, **2** and **3** are kept well after the substitution. This is quite different to the substitution at the bay-area, which usually results in a large PDI core twist.²²

In summary, a series of Ph_2PO group substituted perylene bisimides have been synthesized firstly by reaction of lithium diphenylphosphide with corresponding PBI dyes. The substituted group is attached to the PBI core at the α -position instead of the usual substitution of a halogen atom at the bay-area. Owing to the shielding or deshielding effect of the Ph_2PO group, the adjacent proton on the perylene core and

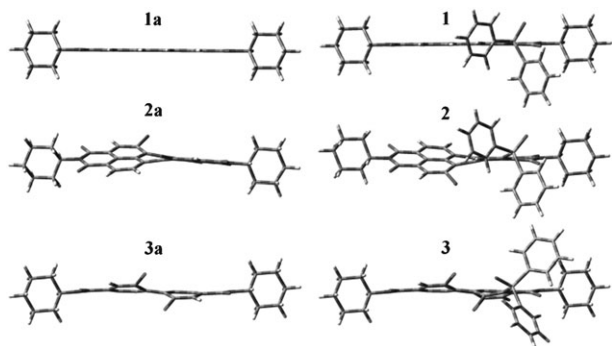


Fig. 1 DFT (B3LYP/6-31G*) geometry-optimized structures of **1a**, **2a**, **3a** and **1**, **2**, **3**. The geometry calculations were performed with Gaussian 03 installed on a Windows PC.

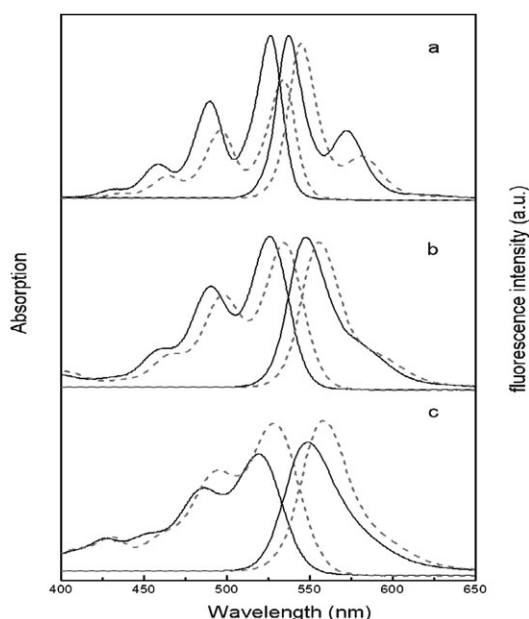


Fig. 2 UV/vis (left axis) and fluorescence (right axis) spectra of the perylene bisimides (10^{-5} M) in chloroform at room temperature. a: **1** (dashed line) and **1a** (solid line), b: **2** (dashed line) and **2a** (solid line), c: **3** (dashed line) and **3a** (solid line).

Table 2 UV/vis absorption and fluorescence emission properties of substituted PBIs and their corresponding PBI starting materials in chloroform

	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	Φ_{fl}^a
1a	526	70 800	527	537	1.00
2a	525	49 600	527	548	0.82
3a	519	27 600	521	550	0.92
1	534	52 100	534	545	1.00
2	534	46 600	535	555	0.83
3	528	34 500	530	558	0.87

^a Determined with *N,N'*-dicyclohexylperylene-3,4:9,10-tetracarboxylic acid bisimide as reference ($\lambda_{\text{ex}} = 527$ nm).

the tertiary proton at a nearer cyclohexyl group shift significantly in the ^1H -NMR spectra. The substitution results in a slight red-shift both in absorption and emission spectra and keeps the high fluorescence of the PBI dyes. This reaction provides a new method to modify PBI dyes.

Experimental

^1H NMR and ^{13}C NMR were measured with Bruker 300 MHz or 600 MHz spectrometers. Mass spectra were recorded on a Bruker BIFLEXIII spectrometer for MALDI-TOF-MS. Infrared spectra were determined with a Bruker Tensor-27 spectrometer. Electronic absorption spectra were measured on a Beijing Purkinje General Instrument Co. Ltd. TU-190 spectrophotometer. The photoluminescence spectra were recorded on a HITACHI FL-4500 spectrofluorometer. Triphenylphosphine, lithium, and THF were purchased from Sinopharm Chemical Reagent Co. Ltd. The THF used was anhydrous THF which was distilled over sodium and benzophenone. Fluorescence quantum yields were measured by the

optically dilute method with *N,N'*-dicyclohexylperylene-3,4:9,10-tetracarboxylic acid bisimide in chloroform solution as reference (using an excitation wavelength of 527 nm).

The solution of lithium diphenylphosphide (DPPLi) was prepared from triphenylphosphine as follows. Triphenylphosphine (5.24 g, 0.02 mol) and lithium (0.84 g, 0.12 mol) which had been washed with hexane and dried carefully with a paper towel were suspended in a three-neck flask containing a magnetic stirring bar and fitted with an argon inlet, and the flask was evacuated and backfilled with argon three times. After the solvent of anhydrous THF (150 ml) had been added, the mixture was stirred vigorously at room temperature for 3 h under an argon gas stream. Then the residual lithium was removed by passing the mixture through a glass tube which was stuffed with glass wool loosely; an argon gas stream was also needed in this step. The red solution of lithium diphenylphosphide (DPPLi) was used directly in the next step of the reaction.

A three-neck flask was charged with *N,N'*-dicyclohexylperylene-3,4:9,10-tetracarboxylic acid bisimide **1a** (280 mg, 0.5 mmol), and the flask was evacuated and backfilled with argon three times. After the solvent of anhydrous THF had been added, the mixture was stirred vigorously at room temperature for 1 h. Subsequently, the solution of lithium diphenylphosphide (DPPLi) was added by syringe with a gentle flow of argon. TLC was used to monitor the reaction. When the reaction was finished, the solvent was removed by rotary evaporation at room temperature. The crude product was purified by silica gel column chromatography with CH_2Cl_2 -THF (50 : 1) as eluent. The main second band was collected, and removal of the solvent yielded 121 mg (32%) as a red-brown solid. MS (MALDI-TOF): m/z 754.2 (M^+). ^1H -NMR (300 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 9.70 (d, 1H, $^3J_{\text{PH}} = 12.6$), 8.66–8.71 (m, 6H), 7.81–7.89 (m, 4H), 7.54–7.56 (m, 2H), 7.28 (m, 4H), 5.06 (m, 1H), 4.65 (m, 1H), 2.57–2.60 (m, 2H), 2.01–2.05 (m, 2H), 1.96–2.01 (m, 2H), 1.76 (m, 4H), 1.47–1.52 (m, 4H), 1.12–1.39 (m, 6H) ppm. ^{13}C -NMR (75 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 163.775, 163.685, 162.982, 162.169, 134.666, 133.983, 133.808, 132.137, 131.772, 131.659, 131.507, 131.406, 131.276, 128.261, 128.096, 124.282, 124.047, 123.990, 123.067, 54.171, 54.089, 52.986, 29.665, 29.336, 29.113, 28.593, 26.528, 26.246, 25.427, 25.159 ppm. ^{31}P -NMR (121 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 34.5403 ppm.

A three-neck flask was charged with *N,N'*-dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide **2a** (360 mg, 0.5 mmol), and the flask was evacuated and backfilled with argon three times. After the solvent of anhydrous THF had been added, the mixture was stirred vigorously at room temperature for 1 h. Subsequently, the solution of lithium diphenylphosphide (DPPLi) was added by syringe with a gentle flow of argon. TLC was used to monitor the reaction. When the reaction was finished, the solvent was removed by rotary evaporation at room temperature. The crude product was purified by silica gel column chromatography with CH_2Cl_2 -THF (50 : 1) as eluent. The main second band was collected, removal of the solvent yielded 198 mg (43%) as a red-brown solid, which was further purified by silica gel column chromatography with toluene-THF (5 : 1) as eluent. The first band was collected, and the solvent was

removed by rotary evaporation to afford 97 mg (49%) of **2** as a red solid. MS (MALDI-TOF): m/z 911.9 (M^+). $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 25 °C): δ = 9.91 (d, 1H, $^3J_{\text{PH}}$ = 13.7), 9.50 (d, 1H, J = 8.2), 8.94 (s, 1H), 8.82 (s, 1H), 8.69 (d, 1H, J = 8.1), 7.74–7.80 (m, 4H), 7.53–7.57 (m, 2H), 7.46–7.48 (m, 4H), 5.01 (m, 1H), 4.71 (m, 1H), 2.51–2.55 (m, 2H), 2.11–2.16 (m, 2H), 1.90–1.93 (m, 2H), 1.73–1.77 (m, 4H), 1.19–1.60 (m, 10H) ppm. $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25 °C): δ = 163.201, 162.621, 161.930, 161.824, 138.730, 137.903, 134.188, 134.030, 133.862, 132.741, 132.361, 132.249, 132.167, 131.638, 131.512, 130.474, 129.910, 129.143, 128.600, 128.495, 128.325, 127.462, 126.901, 126.577, 124.014, 123.622, 123.468, 122.103, 121.454, 54.424, 54.275, 29.067, 28.624, 26.471, 26.217, 25.347, 25.126 ppm. $^{31}\text{P-NMR}$ (121 MHz, CDCl_3 , 25 °C): δ = 2.9746 ppm.

A three-neck flask was charged with 1,6,7,12-tetrachloro-*p*-erylene bisimide **3a** (350 mg, 0.5 mmol), and the flask was evacuated and backfilled with argon three times. After the solvent of anhydrous THF has been added, the mixture was stirred vigorously at room temperature for about 1 h. Subsequently, the solution of lithium diphenylphosphide (DPPLi) was added by syringe with a gentle flow of argon. TLC was used to monitor the reaction. When the reaction was finished, the solvent was removed by rotary evaporation at room temperature. The crude product was purified by silica gel column chromatography with CH_2Cl_2 –THF (50 : 1) as eluent. The main second band was collected, removal of the solvent yielded 190 mg (42%) as a red-brown solid. MS (MALDI-TOF): m/z 891.9 (M^+). $^1\text{H-NMR}$ (600 MHz, CDCl_3 , 25 °C): δ = 8.65 (s, 1H), 8.63 (s, 1H), 8.55 (s, 1H), 8.03–8.06 (m, 2H), 7.62–7.65 (m, 1H), 7.57–7.60 (m, 4H), 7.45–7.48 (m, 1H), 7.38–7.40 (m, 2H), 5.00 (m, 1H), 4.01 (m, 1H), 2.49–2.55 (m, 2H), 1.90–1.92 (m, 2H), 1.70–1.75 (m, 6H), 1.43–1.50 (m, 2H), 1.12–1.37 (m, 8H) ppm. $^{13}\text{C-NMR}$ (75 MHz, CDCl_3 , 25 °C): δ = 162.512, 161.669, 136.342, 135.842, 135.441, 133.317, 132.786, 132.650, 132.098, 131.904, 131.765, 130.933, 130.796, 128.760, 128.586, 128.476, 128.303, 123.987, 123.857, 123.680, 122.675, 55.359, 54.470, 29.068, 29.003, 28.780, 28.328, 26.454, 26.291, 26.062, 25.307, 25.174, 21.382 ppm. $^{31}\text{P-NMR}$ (121 MHz, CDCl_3 , 25 °C): δ = 33.1312 ppm.

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