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# Orientation of bromination in bay-region of perylene diimides

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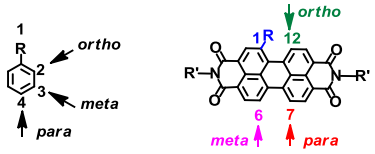
ABSTRACT

We found that the entering position of the bromination in the bay-region (e.g., 1,6,7,12-positions) was precisely determined by the orientation director(s), either individually or cooperatively. In particular, a combination of two directors shows precisely positioning for the third entering bromo with an effect of '1+1>2'.



## 1. Introduction

It is well-known that nature of the first group attached at the benzene nucleus can significantly influence the substituted position and reactivity of the second entering group.[1] Perylene diimides (PDIs) have been paid much attention in the past decades because of their outstanding optoelectronic and self-assembling properties and the potential applications in the fields of organic electronics.[2–6] Because of the nodes of the HOMO and LUMO at the imide nitrogen atoms, substitutions at the bay-region, e.g., 1,6,7,12-positions are the most elaborate synthetic strategy to fine-tune the optoelectronic properties.[2] Since the first introduction by Seybold et al. at BASF in 1987,[7] functionalizations at the bay-region have been well developed. However, the possible orientation of the substitutions at the 1,6,7,12-positions (Scheme 1) has been submerged by the fast advances of perylene diimide chemistry. Understanding the orientation of the first group on the second entering group and further the cooperative effects of the first and second groups on the third entering group are both not only basically important for the advances of perylene diimide chemistry, but it is also a key approach to precisely position functions at the 1,6,7,12-positions and further fine-tune the optoelectronic properties for the utilizations in the organic electronics.




**Scheme 1.** Definitions of the *ortho*-, *meta*-, and *para*-position at the bay-region of a modeling 1-substituted PDI compound, with respect to the conventional nomenclature in the benzene nucleus.

## 2. Results and discussion

To demonstrate the orientation of bromination in the bay-region, we chose 2-methoxyethoxyl (EG) as the electron-donating group, while bromo (Br) and cyano (CN) as the weak and strong electron-withdrawing groups (Scheme 2), respectively. Selection of EG is because the EG-functionalized PDIs are more easily purified than the alkoxyl-substituted ones.[8] The reaction of bromination was conducted at reflux temperature in dichloromethane (DCM) and using bromine as the bromination reagent.[9]

Substitution of monobrominated PDI **2** with EG[8] and CN[10] yielded **3** (Scheme 2) and mono-CN PDI **4** (Fig. S1) in yields of 95% and 99%, respectively. Bromination of **3** preferably gave **5a** in a yield of over 95%, whereas no 6- or 12-brominated isomer (**5b** or **5c**) was detected. We noted that **5a** can be further brominated at its 12-position (vide post), but practically, it can be obtained in a very high yield by controlling the stoichiometric ratio and carefully monitoring the reaction using TLC. This is due to the relative decrease of the electron density at the *ortho*-carbon (−0.210 |e| vs −0.207 |e|) after the *para*-carbon was brominated (**3** vs **5a**, Table S1 vs S2). Structure of **5a** was fully determined by using the $^1$H NMR, NOESY, and HMBC spectra (Figs. S1–S4). Unique formation of **5a** means that the electron-donating EG group is a preferable 1→7

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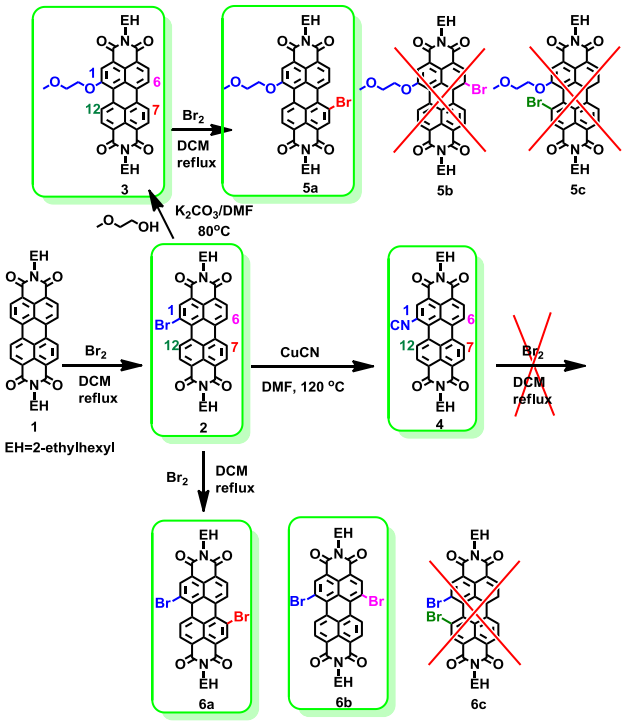
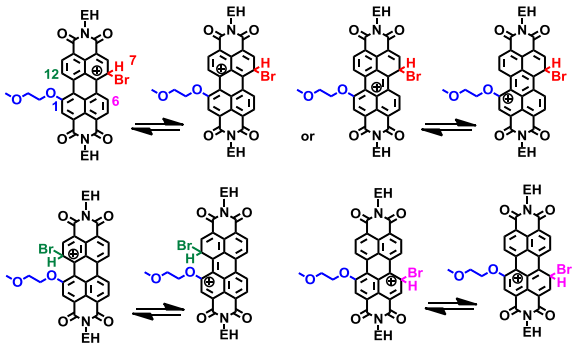



**Scheme 2.** Orientation of bromination at the *ortho*-, *meta*-, and *para*-position of three typical 1-substituted PDI derivatives.

director. Hereafter, we used *ortho*- (12-), *meta*- (6-), and *para*- (7-) to describe the orientation with respect to that director at the 1-position, as similarly used for the benzene nucleus (Scheme 1). Accordingly, EG is a *para*-director.

Further bromination of **2** yielded a mixture of **6a** (1,7-isomer) and **6b** (1,6-isomer) in a total yield of >95%. Because of the very close polarity at TLC, it is very difficult to isolate **6a** and **6b**.[9,11] The ratio of **6a**/**6b** was then estimated from $^1$H NMR spectrum as 70–80% and 20–30%, respectively (Fig. S5). It is well-known that no 1,12-isomer (**6c**) was formed from this reaction.[9,11] Furthermore, as shown vide post, substitutions of the mixture of **6a** and **6b** with the EG and CN groups did not give any clues for the existence of **6c** in the mixture of **6a** and **6b**, further strongly supporting that no **6c** was formed. This indicates that bromo is a *para*-/*meta*-director. In a striking contrast, CN is a strong electron-withdrawing group, and it causes deactivation of the PDI nucleus. No further bromination takes place from **4**.

Similar to the bromination in the benzene nucleus, the orientation of bromination in the bay-region of PDI nucleus can be described by the resonant structures (Scheme 3). The positive charge



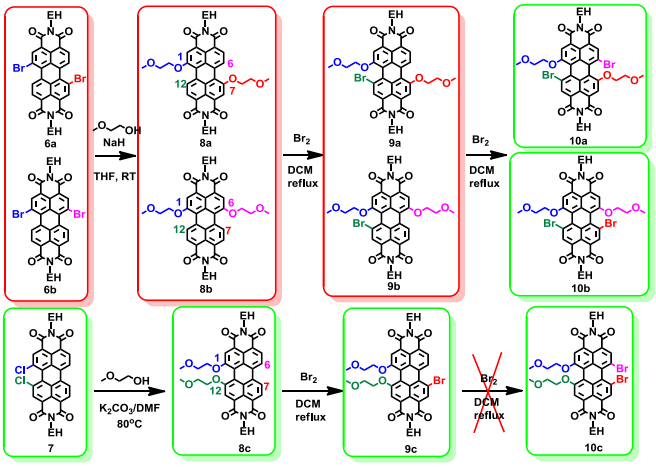

**Scheme 3.** Resonant structures along the PDI nucleus after the *para*-, *ortho*- and *meta*-carbon were attacked by one bromo, respectively.

at the *para*- and *ortho*-position created after attack of one bromo can move to the 1-carbon along the conjugated backbone, where it may be stabilized by the electron-donating EG-oxygen. However, the positive charge created at the *meta*-position cannot.

Quantum chemical calculations (Table S1) revealed that the electron density at the 1-, 6-, 7-, and 12-carbon of PDI **1**, in which the bay-positions are all free of substitutions, was the same, all being −0.204 |e|. Hereafter, this value was used as a reference: higher or lower than this value represents that position may be activated or deactivated by the director(s). When 1-carbon is brominated, affording **2**, the electron density at the *para*- and *meta*-carbon is slightly raised to −0.205 |e|, whereas that at the *ortho*-carbon is slightly down to −0.200 |e|, which is consistent with the *para*-/*meta*-orientation results. Similarly, with respect to the reference value of −0.204 |e|, the electron density at the *para*-, *meta*- and *ortho*-carbon is either increased or decreased slightly after 1-position is substituted with the EG (**3**) or CN (**4**) group, and the changing tendency is all consistent with the experimental observations from the corresponding directors, for example, the *para*-orientation for the EG group. Noted that the electron density at the *ortho*-carbon of **3** is also higher enough for the bromination. Although no *ortho*-brominated products were obtained from **3**, as shown from the following-presented experimental results, the EG group really shows the *ortho*-orientation, and so it is a preferable *para*-director and also an *ortho*-director.

After realizing the orientation of the EG, Br, and CN groups individually, we turned to study the cooperation from both of them. Firstly, we demonstrated the cooperative effect from two same groups.

Scheme 4 displays the cooperative orientation from two EG groups. From the mixture of 1,7- and 1,6-diBr isomers, 1,7- and 1,6-diEG PDIs (**8a** and **8b**) were got in a total yield of over 92%. Their molar ratio was estimated as 80%/20% from the $^1$H NMR spectrum (Fig. S6), consistent well with the molar ratio of the reactants of **6a** and **6b**. The 1,12-diEG derivative (**8c**) was obtained from the 1,12-dichlorinated PDI (**7**).[12]




**Scheme 4.** Cooperative orientation of bromination from the diEG-substituted PDI derivatives.

Full bromination of the **8a**/**8b** mixture yielded 1,7-diEG-6,12-diBr (**10a**) and 1,6-diEG-7,12-diBr (**10b**) PDIs. These two isomers were fully isolated by chromatography, both in yields of 79% (**10a**) and 18% (**10b**) (Fig. S7), respectively, which are both very close to that molar ratio of **6a** and **6b** (80% vs 20%).

We then carefully monitored the bromination of the **8a**/**8b** mixture with TLC and stopped the reaction when most **8b** was likely converted. From this reaction pure **10a** and **10b** were isolated.

Compounds **9a** and **9b** had very close polarity on TLC, and fortunately, a small part of pure **9a** (Fig. S8a) was isolated from the **9a**/**9b** mixture. Yields of **9a** and **9b** were calculated from the $^1$H NMR spectrum (Fig. S8b) and the total quantity of the **9a**/**9b** mixture. Together, about 28% and 69% of **8b** was converted into **9b** and **10b**, respectively, whereas only about 15% and 5% of **8a** converted into **9a** and **10a**, respectively (Table 1). Un-reacted **8a** of 75% was recovered whereas no un-reacted **8b** was isolated. Structures of **8a**, **9a**, and **10a** were further determined by using the $^1$H NMR and HMBC spectra (Figs. S9–S12) as well as the relatively much higher quantity of the isolated product **8a**, **9a**, and **10a** than that of **8b**, **9b**, and **10b**. These reaction results indicate that cooperation of the *ortho*+*para* orientation from the 1,6-EG groups promotes the bromination, with respect to the *ortho*+*meta* combination from 1,7-EG groups.

**Table 1**
Isolated yields of **9a** and **9b** as well as **10a** and **10b**, resulted from the cooperative orientation of two EG groups

| **8a**/**8b** Initial (mmol) | **8a**/**8b** Recovered (mmol) | **9a**/**9b** (mmol) | **10a**/**10b** (mmol) |
|---|---|---|---|
| 0.4:0.1 | 0.3[a]:0 | 0.059:0.028 | 0.020:0.069 |
| Yield (%) | 75[b]:0 | 14.8:28.0 | 5.0:69.0 |

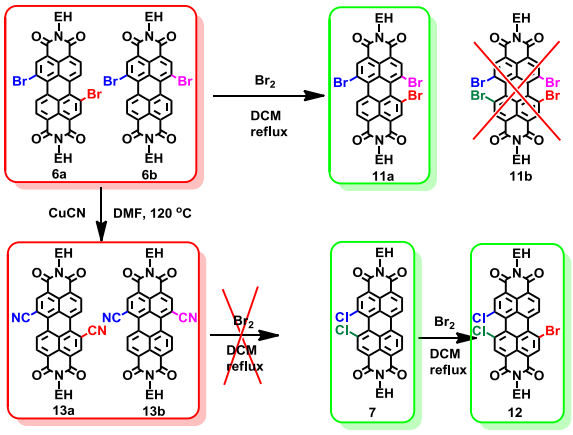
[a] Recovered.
[b] Percentage of recovered versus initial.

These cooperative orientations are originated from the redistributions of the π-electrons when the EG and Br groups are localized at different positions (Table S2). The 1,6-EG groups generate more electron density at the *ortho*- and *para*-position (−0.212 |e|, **8b**) than the 1,7-EG groups do on the *ortho*- and *meta*-carbon (−0.207 |e|, **8a**), indicating that the *ortho*- and *para*-position of **8b** are more active than the *ortho*- and *meta*-position of **8a**. After one bromo is attached at the *ortho*-carbon, affording 1,6-diEG-12-Br isomer (**9b**) and 1,7-diEG-12-Br isomer (**9a**), respectively, the electron density at the *para*-carbon of **9b** is almost retained (−0.211 |e|), whereas that at the *meta*-carbon of **9a** is obviously decreased down to −0.203 |e|, strongly supporting the enhanced reactivity for the further bromination at the fourth position of **9b** with respect to **9a**, and this is in accord with the experimental result that the yield of **10b** is very much higher than that of **10a** (69% vs 5%, Table 1).

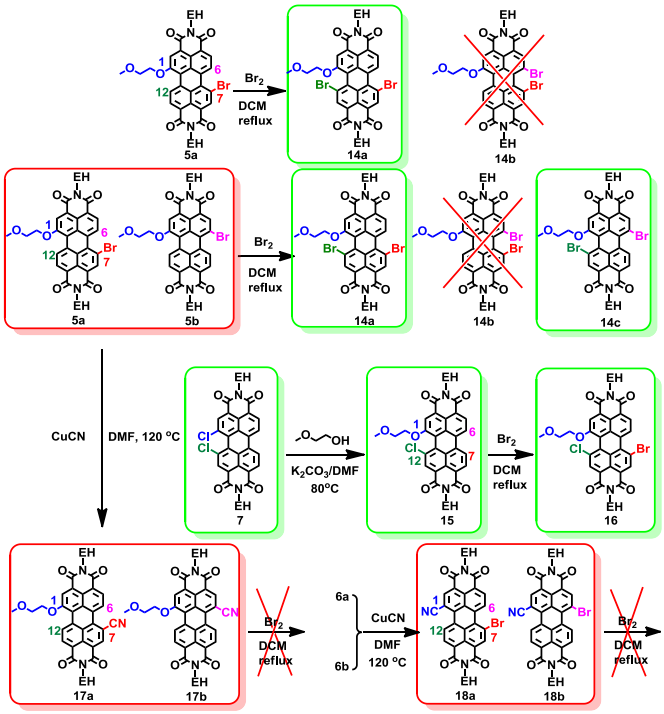
As mentioned above, bromination at the fourth bay-position of **9a** is deactivated. Similarly, bromination of **8c** only yielded monobrominated product of **9c**, while no dibrominated product (**10c**) was detected, meaning that bromination at the fourth bay-position of **9c** is also deactivated. This is in line with the calculation results. The electron density at the *para*- and *meta*-carbon of **8c** is −0.209 |e| (Table S2), being activated for bromination. After **8c** is monobrominated, the electron density at the fourth bay-carbon is decreased down to −0.202 |e|, becoming deactivated.

Further bromination of the **6a**/**6b** mixture only yielded trace of 1,6,7-tribrominated derivative (typically, much less than 1%) and no 1,6,7,12-tetrabrominated PDI (**11b**) was formed (Scheme 5), meaning the *ortho*-carbon of the Br group is strongly deactivated (Table S3). Bromination of 1,12-dichlorinated isomer (**7**) uniquely yielded 1,12-dichloro-7-brominated product (**12**), which is consistent with the *para*- and *meta*-orientation of Cl (similar to Br). In contrasts, dicyano substituted 1,7 and 1,6-isomers, **13a** and **13b**, strongly deactivated the PDI nucleus, no further bromination took place. Quantum chemical calculations indicated that only the *meta*- and *para*-carbon of **7** among these diBr (Cl, CN) PDIs showed a higher electron density (−0.205 |e|) than −0.204 |e| (Table S3).

Secondly, cooperation from two different groups was studied (Scheme 6). From 1-EG-7-brominated isomer (**5a**), only 1-EG-7,12-dibrominated isomer (**14a**) was uniquely formed in a yield of 95%, whereas no 1-EG-6,7-dibrominated isomer (**14b**) was found.




**Scheme 5.** Cooperative orientation of bromination from the diBr-, diCl- or diCN-substituted PDI derivatives.




**Scheme 6.** Cooperative orientation of bromination from the EG/Br (Cl), EG/CN and CN/Br combinations.

Structure of **14a** was assigned from the HMBC spectrum (Fig. S13). Bromination at the 12-position agrees with the cooperative effect from both the *ortho*-orientation of 1-EG and from the *meta*-orientation of 7-Br, showing '1+1>2'.

From the **6a**/**6b** mixture, a mixture of 1-EG-7-Br and 1-EG-6-Br isomers (**5a** and **5b**) was obtained.[8] Full bromination of the **5a**/**5b** mixture, both **14a** and **14c** were, respectively, separated in yields of 68% and 21%, respectively, agreeing well with the molar ratio of **5a** and **5b** (75% vs 25%) (Fig. S14). No 1-EG-6,7-diBr isomer (**14b**) was detected. Structure of **14c** was also determined from the HMBC spectrum (Fig. S15). Clearly, **14a** was from **5a**, and **14c** was from **5b**. Formation of the isomer **14a** agrees with the cooperative *ortho*+*meta* orientation of the EG+Br groups, and formation of **14c** is consistent with the *ortho*+*para* orientation of the EG+Br groups, both showing an effect of '1+1>2'.

Because it was difficult to get the 1-EG-12-Br isomer, we turned to selectively substitute one of the two Cl groups at the 1,12-dichlorinated derivative (**7**) using DMF as the reaction medium

and $K_2CO_3$ as the weak base, affording 1-EG-12-Cl isomer (**15**). Bromination of **15** uniquely yielded 1-EG-7-Br-12-Cl PDI (**16**), also due to the cooperative *para*+*meta* orientation of the 1-EG and the 12-Cl, further supporting the '1+1>2' effect. Structure of **16** was also determined from the HMBC spectrum (Fig. S16).

Calculations revealed that, for **5a** and **5b**, the electron density at the *ortho*-carbon was −0.207 |e| and −0.206 |e|, respectively, both higher than that on the *meta*-carbon of **5a** (−0.198 |e|) and that on the *para*-carbon of **5b** (−0.204 |e|) (Table S4), so the *ortho*-position is activated with respect to the other position. Also, the electron density at the *para*-carbon of **15** reaches to −0.210 |e|, being much higher than that on the *meta*-carbon (−0.203 |e|), also supporting the cooperative *para*+*meta* orientation of 1-EG and 12-Cl in **15**.

We should note that no further brominated product was detected from **14a**, **14c**, and **16**. Substitutions of the 7- and 6-bromo of **5a** and **5b** with CuCN yielded **17a** and **17b**, respectively. Mono-CN substitution of **6a** and **6b** produced **18a** and **18b**, respectively. These mono-CN substituted and diCN-substituted derivatives were all deactivated and no further bromination were observed from derivatives (Scheme 6).

## 3. Conclusion

In conclusions, we have found the precise orientation of bromination in the bay-region (e.g., 1,6,7,12-positions) of the PDI nucleus. The electron-donating EG group shows *para*-/*ortho*-orientation. The weak electron-withdrawing bromo shows the *para*-/*meta*-orientation. However, the strong electron-withdrawing CN group deactivates the PDI nucleus, and no bromination takes place. Cooperation of the EG and EG groups exhibits a '1+1>2' effect. For example, the combined *ortho*+*para* orientation of 1,6-diEG groups accelerates the bromination reaction, with respect to the *ortho*+*meta* combination of the 1,7-diEG groups. Similarly, combination of the *ortho*+*meta*, or *ortho*+*para*, or *para*+*meta* orientation of the EG+Br groups yields precise position for the third entering Br group. The orientation presented herein extends our understandings from the traditional orientation at the aromatic nucleus to the toady's perylene diimide chemistry and this will open opportunities to fine-tune the optoelectronic and self-assembling properties of PDI derivatives through precisely positioning the functional groups at the targeted bay-carbons, and thus pushing further advances for the applications of PDI derivatives in the relative fields.

## 4. Experimental section

### 4.1. General information

All reagents and chemicals were purchased from commercial sources (TCI, Acros, Sigma, or Alfa) and used without further purification except statements. Solvents (toluene and tetrahydrofuran) were distilled by standard procedures before used for organic synthesis. Starting materials are all commercially available reagents and solvents used as received except for statements. Reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel plates (Yantai Shi Huaxue Gongye Yanjiusuo) and visualized using UV irradiation (254 nm). Flash chromatography was performed on silica gel H60 (Qingdao Haiyang Huagongchang). $^1$H, $^{13}$C, NOESY, and HMBC NMR spectra were recorded on a Bruker AVANCE 400 or AVANCE 600 spectrometer with $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. MALDI-TOF mass spectra were recorded by a Bruker BIFLEXIII. Elemental analysis was performed on a flash EA1112 analyzer. The mixture of **6a** and **6b** was synthesized following the literature method.[9] The mixture of **5a** and **5b** and the mixture of **8a** and **8b** were synthesized following our reported procedure.[8] The mixture of **13a** and **13b**, the mixture of **17a** and **17b**, and the mixture of **18a** and **18b** were prepared according to the literature method.[10] PDI **7** was obtained according to the literature procedure.[12]

### 4.2. Synthesis of compound 5a

A mixture of **3** (68.8 mg, 0.1 mmol) and 1 mL of bromine in 20 mL dichloromethane (DCM) was allowed to react under reflux. The reaction was monitored by using TLC for 4 h. The excess of bromine was removed by flow of $N_2$, and the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (DCM/ethanol, 100:1 v/v) to afford compound **5a** as a dark-red solid (73.7 mg, 0.096 mmol, yield=96%). $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.54 (d, $J$=8.00 Hz, 1H), 9.52 (d, $J$=8.00 Hz, 1H), 8.89 (s, 1H), 8.64 (d, $J$=8.00 Hz, 1H), 8.56 (d, $J$=8.00 Hz, 1H), 8.44 (s, 1H), 4.61 (m, 2H), 4.16 (m, 4H), 3.97 (m, 2H), 3.58 (s, 3H), 1.95 (m, 2H), 1.41 (m, 8H), 1.33 (m, 8H), 0.96 (m, 6H), 0.91 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.23, 163.18, 162.51, 156.63, 137.50, 132.94, 132.64, 131.94, 130.79, 128.65, 128.41, 128.16, 127.40, 126.71, 123.69, 122.94, 122.74, 121.70, 121.04, 119.66, 119.16, 117.20, 70.63, 69.19, 59.41, 44.39, 38.03, 30.81, 28.74, 24.08, 23.12, 14.14, 10.62. MS (MALDI-TOF): $m/z$=767.8 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{43}H_{47}BrN_2O_6$: C 67.27, H 6.17, N 3.65; found C 66.93, H 6.20, N 3.65.

### 4.3. Synthesis of compounds 9a, 9b, 10a, and 10b

A mixture of **8a** and **8b** (381.2 mg, 0.5 mmol, **8a**/**8b**=80%:20%) was dissolved into 100 mL of $CH_2Cl_2$, to which 3 mL bromine was dropwise added. The mixture was allowed to react under reflux. The reaction was monitored by using TLC for 2 h. The excess of bromine was removed by flow of $N_2$, and the solvent was removed under vacuum. It was purified by column chromatography on silica gel (DCM/ethanol, 100:1 to 50:1 v/v). The first fraction was collected to afford **10b** as a dark-red solid (63.3 mg, 0.069 mmol). The second fraction afforded **10a** as a dark-red solid (18.4 mg, 0.020 mmol). The third fraction afforded a mixture of **9a** and **9b** as a dark-red solid (72.9 mg, 0.087 mmol, **9a**/**9b**=68%:32%), from which a small part of pure **9a** was fortunately isolated. The last fraction was the un-reacted reactant, being pure **8a** (228.1 mg, 0.3 mmol).

*4.3.1. Compound **10b**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 8.81 (s, 2H), 8.31 (s, 2H), 4.64 (m, 4H), 4.13 (m, 4H), 3.99 (m, 2H), 3.88 (m, 2H), 3.33 (s, 6H), 1.96 (m, 2H), 1.40 (m, 8H), 1.34 (m, 8H), 0.95 (m, 6H), 0.92 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.92, 163.26, 156.90, 136.05, 132.53, 131.54, 124.71, 124.37, 122.72, 120.69, 118.08, 114.90, 70.70, 68.43, 59.42, 44.58, 38.27, 30.86, 28.86, 24.16, 23.17, 14.25, 10.77. MS (MALDI-TOF): $m/z$=920.3 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{46}H_{52}Br_2N_2O_8$: C 60.01, H 5.69, N 3.04; found C 59.56, H 5.72, N 3.04.

*4.3.2. Compound **10a**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 8.72 (s, 2H), 8.41 (s, 2H), 4.60 (m, 4H), 4.16 (m, 4H), 3.99 (m, 2H), 3.88 (m, 2H), 3.33 (s, 6H), 1.96 (m, 2H), 1.40 (m, 8H), 1.34 (m, 8H), 0.95 (m, 6H), 0.92 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.77, 163.39, 156.86, 134.45, 132.26, 131.49, 123.94, 123.76, 121.23, 121.07, 119.28, 116.55, 70.70, 68.50, 59.41, 44.55, 38.15, 30.87, 28.85, 24.16, 23.18, 14.26, 10.77. MS (MALDI-TOF): $m/z$=920.3 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{46}H_{52}Br_2N_2O_8$: C 60.01, H 5.69, N 3.04; found C 59.78, H 5.60, N 3.02.

*4.3.3. Compound **9a**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.43 (d, $J$=8.00 Hz, 1H), 8.73 (s, 1H), 8.55 (d, $J$=8.00 Hz, 1H), 8.44 (s, 2H), 4.66 (m, 2H), 4.57 (m, 1H), 4.50 (m, 1H), 4.15 (m, 4H), 4.03 (m, 1H), 3.95 (m, 2H), 3.90 (m, 1H), 3.56 (s, 3H), 3.38 (s, 3H), 1.95 (m, 2H), 1.40 (m, 8H), 1.32 (m, 8H), 0.96 (m, 6H), 0.90 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 164.19, 163.71, 163.42, 156.58, 156.60, 135.00, 133.27, 132.10, 131.91, 129.94, 128.99, 128.85, 124.12, 123.00, 121.31, 121.12,

120.94, 120.51, 117.11, 116.74, 70.70, 68.50, 59.41, 44.55, 38.15, 30.87, 28.85, 24.16, 23.18, 14.26, 10.77. MS (MALDI-TOF): $m/z$=841.8 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{46}H_{53}BrN_2O_8$: C 65.64, H 6.32, N 3.35; found C 65.29, H 6.31, N 3.32.

*4.3.4. Compounds **9a** and **9b**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.43 (d, $J$=8.00 Hz, 0.68H), 9.37 (d, $J$=8.00 Hz, 0.32H), 8.82 (s, 0.32H), 8.73 (s, 0.68H), 8.64 (d, $J$=8.00 Hz, 0.32H), 8.56 (d, $J$=8.00 Hz, 0.68H), 8.42 (s, 1.36H), 8.33 (s, 0.64H), 4.66 (m, 2H), 4.57 (m, 1H), 4.50 (m, 1H), 4.15 (m, 4H), 4.03 (m, 1H), 3.95 (m, 2H), 3.90 (m, 1H), 3.56 (s, 3H), 3.38 (s, 3H), 1.95 (m, 2H), 1.40 (m, 8H), 1.32 (m, 8H), 0.96 (m, 6H), 0.90 (m, 6H). MS (MALDI-TOF): $m/z$=841.8 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{46}H_{53}BrN_2O_8$: C 65.63, H 6.35, N 3.33; found C 65.29, H 6.31, N 3.32.

*4.3.5. Compound **8a**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.46 (d, $J$=8.00 Hz, 2H), 8.41 (d, $J$=8.00 Hz, 2H), 8.14 (s, 2H), 4.53 (m, 4H), 4.18 (m, 4H), 3.67 (m, 4H), 3.39 (s, 6H), 1.98 (m, 2H), 1.44 (m, 8H), 1.38 (m, 8H), 1.01 (m, 6H), 0.95 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.96, 163.60, 156.11, 133.33, 129.12, 128.90, 128.57, 123.15, 122.89, 121.08, 120.98, 116.51, 70.93, 69.04, 59.54, 44.45, 38.15, 31.00, 28.94, 24.28, 23.26, 14.30, 10.79. MS (MALDI-TOF): $m/z$=763.5 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{46}H_{54}N_2O_8$: C 72.42, H 7.13, N 3.67; found C 72.27, H 7.17, N 3.65.

### 4.4. Synthesis of compounds 15 and 8c

A mixture of **7** (136.4 mg, 0.2 mmol), 2-methoxyethanol (76.1 mg, 1.0 mmol), and potassium carbonate ($K_2CO_3$, 140 mg, 1.0 mmol) in 10 mL dimmethylformamide (DMF) was heated at 80 °C. The reaction was monitored by using TLC for 2 days. Then, the reaction mixture was poured into 30 mL water and the red solid was re-dissolved in 20 mL DCM and washed with 1 N hydrochloric acid and then water each for three times. Then, DCM layer was dried over $Na_2SO_4$. After removal of DCM, the residue was purified by column chromatography on silica gel (DCM/ethanol, 100:1 to 50:1 v/v). The first fraction was collected to afford **15** as a dark-red solid (86.7 mg, 0.12 mmol, yield=60%). The second fraction afforded **8c** as a dark-red solid (30.5 mg, 0.04 mmol, yield=20%).

*4.4.1. Compound **15**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 8.63 (s, 1H), 8.57 (d, $J$=8.00 Hz, 1H), 8.52 (d, $J$=8.00 Hz, 1H), 8.45 (s, 1H), 8.44 (d, $J$=8.00 Hz, 1H), 8.41 (d, $J$=8.00 Hz, 1H), 4.66 (m, 2H), 4.16 (m, 4H), 4.03 (m, 1H), 4.02 (m, 1H), 3.42 (s, 3H), 1.97 (m, 2H), 1.39 (m, 8H), 1.31 (m, 8H), 0.95 (m, 6H), 0.90 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.31, 163.23, 163.14, 162.84, 156.09, 133.92, 133.92, 133.71, 132.75, 131.68, 131.15, 129.53, 128.50, 128.00, 126.17, 124.28, 123.13, 122.77, 122.11, 121.95, 121.58, 121.46, 118.06, 117.40, 70.77, 68.27, 59.40, 44.30, 37.99, 30.78, 28.71, 24.03, 23.13, 14.17, 10.62. MS (MALDI-TOF): $m/z$=723.5 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{43}H_{47}ClN_2O_6$: C 71.40, H 6.55, N 3.87; found C 71.13, H 6.48, N 3.85.

*4.4.2. Compound **8c**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 8.46 (d, $J$=8.00 Hz, 2H), 8.41 (s, 2H), 8.37 (d, $J$=8.00 Hz, 2H), 4.50 (m, 4H), 4.15 (m, 4H), 3.79 (m, 4H), 3.39 (s, 6H), 1.96 (m, 2H), 1.40 (m, 8H), 1.33 (m, 8H), 0.95 (m, 6H), 0.90 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.98, 163.89, 156.19, 133.09, 128.55, 128.21, 123.41, 122.74, 122.38, 121.66, 119.78, 117.97, 71.33, 68.80, 59.35, 44.37, 38.10, 30.93, 28.89, 24.20, 23.21, 14.25, 10.78. MS (MALDI-TOF): $m/z$=763.5 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{46}H_{54}N_2O_8$: C 72.42, H 7.13, N 3.67; found C 72.31, H 7.09, N 3.68.

### 4.5. Synthesis of compound 9c

Compound **8c** (76.3 mg, 0.1 mmol) was dissolved into 20 mL of $CH_2Cl_2$, to which 1 mL bromine was dropwise added. The mixture was allowed to react under reflux. The reaction was monitored by TLC for 4 h. The excess of bromine was removed by flow of $N_2$, and the solvent was removed under vacuum. It was purified by column chromatography on silica gel (DCM/ethanol, 50:1 v/v) to afford compound **9c** as a dark-red solid (79.8 mg, 0.095 mmol, yield=95%). $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.38 (d, $J$=8.00 Hz, 1H), 8.78 (s, 1H), 8.55 (d, $J$=8.00 Hz, 1H), 8.43 (s, 2H), 4.54 (m, 2H), 4.44 (m, 2H), 4.17 (m, 4H), 3.75 (m, 4H), 3.36 (s, 6H), 1.96 (m, 2H), 1.42 (m, 8H), 1.33 (m, 8H), 0.96 (m, 6H), 0.90 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 164.21, 163.87, 163.84, 163.01, 156.50, 156.46, 135.39, 132.16, 131.99, 130.95, 129.98, 127.44, 127.27, 122.92, 122.89, 122.52, 122.18, 121.93, 121.73, 120.34, 119.63, 119.07, 117.55, 117.31, 71.17, 68.91, 59.32, 59.28, 44.51, 44.41, 38.14, 38.11, 30.90, 28.88, 24.20, 23.21, 23.18, 14.25, 10.78, 10.77. MS (MALDI-TOF): $m/z$=842.9 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{46}H_{53}BrN_2O_8$: C 65.63, H 6.35, N 3.33; found C 65.85, H 6.29, N 3.31.

### 4.6. Synthesis of compound 12

A mixture of **7** (68.2 mg, 0.1 mmol) and 1 mL bromine in 20 mL DCM was allowed to react under reflux. The reaction was monitored by using TLC for 12h. The excess of bromine was removed by flow of $N_2$, and the solvent was removed under vacuum. It was purified by column chromatography on silica gel (petroleum ether/DCM, 2:1 v/v) to afford compound **12** as an orange solid (25.1 mg, 0.033 mmol, yield=33%), while 60% of **7** was recovered unchanged. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.46 (d, $J$=8.00 Hz, 1H), 8.92 (s, 1H), 8.71 (d, $J$=8.00 Hz, 1H), 8.69 (s, 2H), 4.16 (m, 4H), 1.95 (m, 2H), 1.40 (m, 8H), 1.32 (m, 8H), 0.95 (m, 6H), 0.91 (m, 6H). MS (MALDI-TOF): $m/z$=762.5 $[M+H]^+$.

### 4.7. Synthesis of compounds 14a and 14c

A mixture of **5a** and **5b** (76.7 mg, 0.1 mmol, **5a**/**5b**=75%:25%) was dissolved into 20 mL of $CH_2Cl_2$, to which 1 mL bromine was dropwise added. The mixture was allowed to react under reflux. The reaction was monitored by using TLC for 3 h. The excess of bromine was removed by flow of $N_2$, and the solvent was removed under vacuum. It was purified by column chromatography on silica gel (DCM/ethanol, 200:1 v/v) to afford compounds **14a** and **14c** as a dark-red solid. The regioisomeric **14a** and **14c** can be separated in yields of 68% (57.4 mg) and 21% (17.7 mg).

*4.7.1. Compound **14a**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.40 (d, $J$=8.00 Hz, 1H), 8.86 (s, 1H), 8.82 (s, 1H), 8.54 (d, $J$=8.00 Hz, 1H), 8.45 (s, 1H), 4.69 (m, 1H), 4.63 (m, 1H), 4.17 (m, 4H), 4.02 (m, 1H), 3.91 (m, 1H), 3.41 (s, 3H), 1.97 (m, 2H), 1.43 (m, 8H), 1.36 (m, 8H), 0.99 (m, 6H), 0.94 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.75, 163.61, 162.85, 162.61, 156.18, 138.28, 138.68, 133.17, 132.42, 131.34, 131.24, 129.72, 128.27, 127.47, 125.39, 124.62, 123.87, 122.78, 122.66, 121.84, 121.13, 120.30, 119.14, 117.23, 70.60, 68.36, 59.32, 44.50, 38.10, 30.77, 28.74, 24.08, 23.11, 14.14, 10.65. MS (MALDI-TOF): $m/z$=846.8 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{43}H_{46}Br_2N_2O_6$: C 61.00, H 5.48, N 3.31; found C 60.75, H 5.53, N 3.33.

*4.7.2. Compound **14c**.* $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.38 (d, $J$=8.00 Hz, 1H), 8.84 (s, 1H), 8.81 (s, 1H), 8.68 (d, $J$=8.00 Hz, 1H), 8.45 (s, 1H), 4.68 (m, 1H), 4.61 (m, 1H), 4.16 (m, 4H), 4.04 (m, 1H), 3.88 (m, 1H), 3.37 (s, 3H), 1.96 (m, 2H), 1.42 (m, 8H), 1.36 (m, 8H), 0.96 (m, 6H), 0.91 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.73, 163.59, 163.45, 163.01, 156.40, 138.84, 136.67, 136.45, 135.78, 131.54, 130.90, 129.56, 128.69, 127.43, 125.60, 124.45, 124.38, 123.63, 122.44, 122.29, 121.91, 121.67, 119.78, 117.37, 70.69, 68.61, 59.50, 44.67, 38.13, 30.90, 28.86, 24.20, 23.22, 14.28, 10.78. MS (MALDI-TOF): $m/z$=846.8 $[M+H]^+$. Elemental analysis: calcd

(%) for $C_{43}H_{46}Br_2N_2O_6$: C 61.00, H 5.48, N 3.31; found C 60.81, H 5.53, N 3.32.

### 4.8. Synthesis of compound 16

A mixture of **15** (68.8 mg, 0.1 mmol) and 1 mL bromine in 20 mL DCM was heated under reflux. The reaction was monitored by using TLC. The excess of bromine was removed by flow of $N_2$, and the solvent was removed under vacuum. It was purified by column chromatography on silica gel (DCM/ethanol, 200:1 v/v) to afford compound **16** as a dark-red solid (75.2 mg, 0.094 mmol, yield=94%). $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ ppm: 9.25 (d, $J$=8.00 Hz, 1H), 8.74 (s, 1H), 8.55 (s, 1H), 8.41 (s, 1H), 8.37 (d, $J$=8.00 Hz, 1H), 4.61 (m, 2H), 4.12 (m, 4H), 3.97 (m, 1H), 3.88 (m, 1H), 3.40 (s, 3H), 1.95 (m, 2H), 1.41 (m, 8H), 1.35 (m, 8H), 0.97 (m, 6H), 0.92 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ ppm: 163.58, 163.40, 162.77, 162.45, 156.59, 137.03, 134.25, 133.43, 132.27, 130.96, 130.91, 130.76, 129.57, 128.05, 127.15, 124.88, 124.55, 122.64, 122.44, 121.64, 121.43, 120.37, 117.79, 117.17, 70.65, 68.47, 59.29, 44.47, 38.05, 30.77, 28.73, 24.07, 23.11, 14.15, 10.67. MS (MALDI-TOF): $m/z$=802.5 $[M+H]^+$. Elemental analysis: calcd (%) for $C_{43}H_{46}BrClN_2O_6$: C 64.38, H 5.78, N 3.49; found C 64.77, H 5.73, N 3.49.

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## Supplementary data

Quantum chemical calculations and copies of $^1$H NMR, $^{13}$C NMR, NOESY and HMBC spectra. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.07.035. These data include MOL files and InChiKeys of the most important compounds described in this article.

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