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Regioisomer-Free C_{4h} β-Tetrakis(*tert*-butyl)metallophthalocyanines: Regioselective Synthesis and Spectral Investigations

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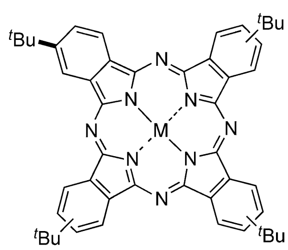
Metal β-tetrakis(*tert*-butyl)phthalocyanines are the most commonly used phthalocyanines due to their high solubility, stability, and accessibility. They are commonly used as a mixture of four regioisomers, which arise due to the *tert*-butyl substituent on the β-position, and to the best of our knowledge, their regioselective synthesis has yet to be reported. Herein, the C_{4h}-selective synthesis of β-tetrakis(*tert*-butyl)metallophthalocyanines is disclosed. Using tetramerization of α-trialkylsilyl phthalonitriles with metal salts following acid-mediated desilylation, the desired metallophthalocyanines were obtained in good yields. Upon investigation of regioisomer-free zinc β-tetrakis-(*tert*-butyl)phthalocyanine using spectroscopy, the C_{4h} single isomer described here was found to be distinct in the solid state to zinc β-tetrakis(*tert*-butyl)phthalocyanine obtained by a conventional method.



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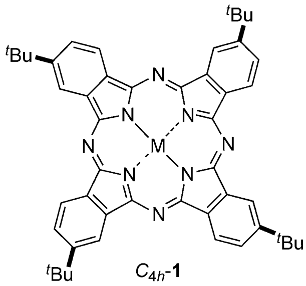
Mixture of four regioisomers
(C_{4h}-**1**, D_{2h}-**1**, C_s-**1**, C_{2v}-**1**)



C_{4h}-**1**

Figure 1. β-Tetrakis(*tert*-butyl)phthalocyanines **1** (mixture) and C_{4h}-**1**.

Phthalocyanines have gained much attention in recent years due to their potential as organic semiconductors, solar cells, liquid crystals, and medicinal agents.[1] Since the first appearance of this macrocycle in 1907,[2] a huge number of phthalocyanine derivatives have been synthesized.[1] The choice of substituted groups on the *peri*-positions of phthalocyanines is extremely important to control/alter the fundamental properties of phthalocyanines, such as aggregation states, intense color in the visible range, and thermal and chemical stability.[3] Among the variety of substituted phthalocyanines that have been examined, β-tetrakis(*tert*-butyl)phthalocyanines (**1**) have been widely investigated because of their chemical robustness, versatility, and high solubility (Figure 1).[4] More than 830 papers and patents have been found for **1** by searching for its structure in SciFinder.[5a] The β-*tert*-butyl isoindoline moiety has also become a standard A-unit for the synthesis of newly designed unsymmetrical A_3B-type phthalocyanines, and more than 1080 compounds have been registered.[5b]

Compound **1** can be synthesized by a standard synthetic protocol (Scheme S1 in Supporting Information)[6] and is thus obtained as a mixture of four regioisomers, C_{4h}, C_s, D_{2h} and C_{2v}-types (Figure 1). The existence of regioisomers is frequently problematic for spectral characterization and inhibits the formation of a single crystal for X-ray crystallographic analysis. Although these four isomers can be separated by HPLC,[7] this task tends to be tedious and sometime even impossible on a practical scale. Consequently, the regoselective synthesis of symmetrical C_{4h}-**1** remains one of the longest-standing challenges in phthalocyanine chemistry, despite their very simple structure and ubiquitous usage. Although several approaches for the regioselective synthesis of α-substituted C_{4h} phthalocyanines have been reported,[8] reports of the regioselective synthesis of β-substituted phthalocyanines are rare. For example, Leznoff et al. reported that during cyclotetramerizations, the reaction of 3-benzyloxy-phthalonitriles produce the α-substituted C_{4h} phthalocyanines.[8g] However, the attempt for β-substituted C_{4h} phthalocyanines required a more complex protocol. They achieved the regioselective synthesis of β-substituted 2,9,16,23-tetraneopentoxy-phthalocyanine in 5% yield by the separation of two regioisomers of the precursor, 1-imino-3-methylthio-6-neopentoxyisoindolenine, following the tetramerization under low reaction temperature at −15 °C for one week.[9] Kobayashi et al. achieved the direct D_{2h} selective synthesis of β-substituted phthalocyanine in 2% yield by using 2,2′-dihydroxy-1L′-binaphthyl linked-phthalonitrile.[10]

In this context, we hypothesized that sterically demanding C_{4h} β-tetrakis-substituted phthalocyanines should be regiose-

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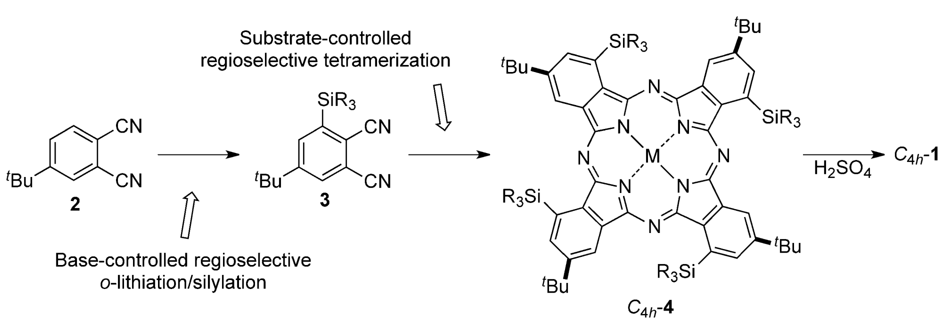
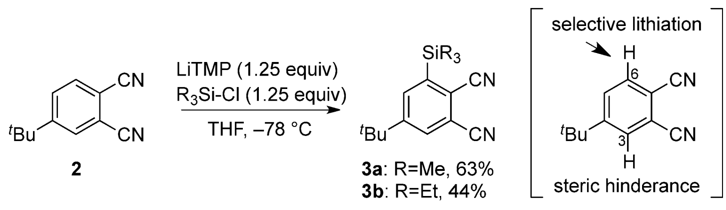
lectively synthesized by assisting the functional group on the α-position. We disclose herein the first regioselective synthesis of metal C_{4h}-tetrakis(*tert*-butyl)phthalocyanines C_{4h}-**1** following the use of α-trialkylsilyl-β-(*tert*-butyl)phthalonitriles (**3**) as substrates. The α-trialkylsilyl group effectively controls the regioselective tetramerization of α-trialkylsilyl-β-(*tert*-butyl)phthalonitriles **3** in the presence of metal ions to corresponding metal C_{4h} phthalocyanines **4**,[8f] and the α-trialkylsilyl moiety on **4** can be easily removed under acid treatment providing C_{4h}-β-tetrakis(*tert*-butyl)phthalocyanines C_{4h}-**1**. This approach is found to be general for a range of C_{4h} tetrakis-β-substituted phthalocyanines, including β-methyl and hexyl substituents, and a variety of metal ions such as Zn, Ni, Co and Fe can be accepted as the central metal of phthalocyanines (Scheme 1). The regioisomer-free Zn C_{4h}-β-tetrakis(*tert*-butyl)phthalocyanine **1** results in very clear ^{1}H and ^{13}C NMR spectra of **1**. The UV/Vis and fluorescence spectra of regioisomer-free C_{4h}-**1** are disclosed for the first time. These first spectral investigations of C_{4h}-**1** have revealed that the UV/Vis spectra of regioisomer-free C_{4h}-**1** in solution are as almost the same as the commonly used **1**, while these of C_{4h}-**1** in the solid state are different from those of conventional **1**.

The trialkylsilyl (R_3Si) group would be suitable as a sterically demanding α-substituent on the phthalocyanines to control regioselectivity, although its removal should be considered. Thus, the regioselective synthesis of **3** was the first requirement. After optimizing the reaction conditions for the trialkylsilylation of 4-(*tert*-butyl)phthalonitrile **2**, the use of sterically demanding lithium tetramethylpiperidide (LiTMP) was found to be effective for the regioselective *ortho*-lithiation of **2** followed by silylation with trimethylsilyl chloride or triethylsilyl chloride in tetrahydrofuran at −78 °C, yielding **3a** (63%) and **3b** (44%), respectively (Scheme 2). The C_6-position was selectively lithiated due to the steric factor between *t*Bu and LiTMP. Other bases such as *n*-butyllithium and lithium diisopropylamide were not effective for this transformation. Consequently, LiTMP was crucial.



Scheme 1. Regioselective protocols for the synthesis of C_{4h}-symmetric **1**.



Scheme 2. Regioselective *ortho*-lithiation of **2** with LiTMP to provide **3**.

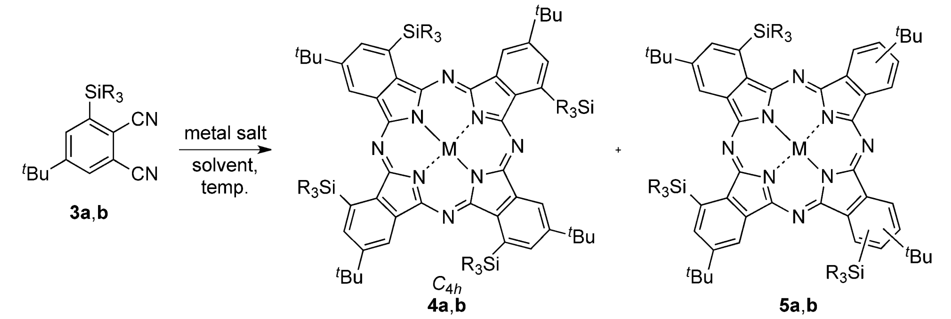
With the key phthalonitriles (**3**) in hand, the regioselective synthesis of C_{4h}-**4** was examined (Table 1). We first attempted the reaction of **3a** under conventional conditions with zinc acetate in *N,N*-dimethyl-2-aminoethanol (DMAE) at 140 °C. However, a complex mixture of fully to partially desilylated phthalocyanines resulted, due to the desilylation of **3a** into **2** (entry 1, Table 1). The desilylation of **3a** could not be avoided under solvent-free conditions at 230 °C (entry 2, Table 1). Gratifyingly, the use of ethylene glycol as a solvent yielded the desired C_{4h}-**4a** (M = Zn) in 29% yield accompanied with a partially (one) desilylated product, **5a** (M = Zn), in 10% yield as a mixture of regioisomers (entry 3, Table 1). The C_{4h}-**4a** (M = Zn) was also obtained by reaction in 1-chloronaphthalene at 230 °C but the yield decreased to 5.0% (entry 4, Table 1).

We next examined the synthesis of C_{4h} phthalocyanines using other metal salts (entries 5–12, Table 1). Under the best conditions, the metal salts of Ni, Co and Fe yielded corresponding Ni–, Co– and Fe–**4a** in 1.5 to 9.1% yield (**4a–2**, M = Ni; entries 5 and 6, Table 1), 33% (**4a–3**, M = Co; entry 8, Table 1) and 11% (**4a–4**, M = Fe; entry 9, Table 1), respectively, with detectable amounts of fully to partially desilylated **5a** (M = Ni, Co). C_{4h} phthalocyanines having copper as a central metal could not be obtained under the same reaction conditions (entries 11–12, Table 1). Only 1-chloronaphthalene as the solvent was effective for the preparation of C_{4h} Co–phthalocyanine **4a–3** (entry 8, Table 1).

Compound **3b** was next investigated for the macrocyclization reaction (entries 13–16, Table 1). Interestingly, the desired C_{4h}-**4b** (M = Zn) having a triethylsilyl group at the α-position was produced in all cases with 1.6 to 18% yields. The formation of a partially desilylated product (**5b**) was suppressed due to the higher thermal stability of the triethylsilyl group than the trimethylsilyl group, except that the reaction took place in ethylene glycol. It should be noted that in all cases, no detectable amounts of the other possible regioisomers of **4a**,**b**, that is, C_s, D_{2h} and C_{2v}-types, were formed.

Next, we applied this methodology for the regioselective synthesis of C_{4h} symmetric phthalocyanines having other alkyl groups at the β-position (Scheme 3). At first, 3-(trimethylsilyl)phthalonitriles with a methyl or hexyl group at the β-position **6a**,**b** were synthesized by regioselective *ortho*-lithiation of **7a**,**b** using LiTMP followed by trimethylsilylation in 33% and 65% yields, respectively. **6a**,**b** were treated with zinc acetate in ethylene glycol at 230 °C affording desired C_{4h}-**8a**,**b** in 14 to 15% yields, respectively.

Table 1. Optimization of reaction conditions for the regioselective synthesis of **4**.[a]



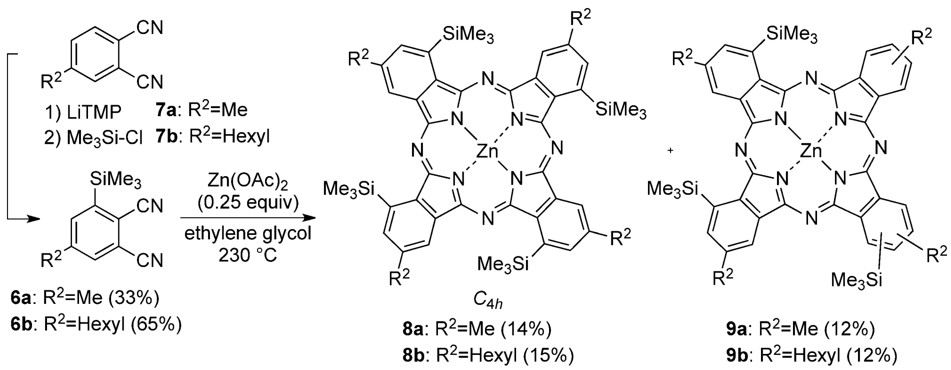
Entry	Metal salt	3	Solvent	Temp [°C]	Yield [%] Compd 4	Compd 5
1	$Zn(OAc)_2$	**3a**	DMAE	140	–[b]	–
2	$Zn(OAc)_2$	**3a**	–	200	trace	–
3	$Zn(OAc)_2$	**3a**	Ethylene glycol	230	29	10
4	$Zn(OAc)_2$	**3a**	Chloronaphthalene	230	5	trace
5	$Ni(OAc)_2$	**3a**	Ethylene glycol	230	9.1	OB[c]
6	$Ni(OAc)_2$	**3a**	Chloronaphthalene	230	1.5	trace
7	$Co(OAc)_2$	**3a**	Ethylene glycol	230	–[b]	–
8	$Co(OAc)_2$	**3a**	Chloronaphthalene	230	33	OB[c]
9	$FeCl_2$	**3a**	Ethylene glycol	230	11	0
10	$FeCl_2$	**3a**	Chloronaphthalene	230	trace	–
11	$Cu(OAc)_2$	**3a**	Ethylene glycol	230	–[b]	–
12	$Cu(OAc)_2$	**3a**	Chloronaphthalene	230	–[b]	–
13	$Zn(OAc)_2$	**3b**	DMAE	140	3.4	0
14	$Zn(OAc)_2$	**3b**	–	200	18	0
15	$Zn(OAc)_2$	**3b**	Ethylene glycol	230	16	OB[c]
16	$Zn(OAc)_2$	**3b**	Chloronaphthalene	230	1.6	0

[a] *Reagents and conditions*: phthalonitrile (1 equiv), metal salt (0.25–0.33 equiv), solvent (0.5–1.0 mL). [b] A mixture of fully to partially desilylated phthalocyanine was observed. [c] OB: **5b** was observed, but it was not fully characterized due to purification difficulties.

the same as another cyano group (0.269 (C_2) vs 0.256 (C_1)), which indicates that their reactivity is similar. On the other hand, the charge distribution of each cyano group in **3b** is rather different (0.405 (C_2) versus 0.234 (C_1)). These computed results suggest that the regioselectivity of **3b** should be higher than that of **3a**. However, the experimental results of the regioselectivity by **3a** and **3b** are the same. Therefore, the regioselectivity of the observed reaction is presumably caused by the steric effect of the trialkylsilyl group (B$\gg$>B′), while the electronic effect is supplemental (A>A′) (Figure 2b). The steric repulsion between two neighboring trialkylsilyl units on dimer units is the main role for the selectivity. This should be the main reason for the success of the regioselective tetramerization even under very high reaction temperature, while the methodology by Leznoff requires very low reaction temperature due to the reactivity controlled between two cyano groups.[9]

The symmetric C_{4h}-**4a** (M=Zn) was easily converted into the target C_{4h}-**1** (M=Zn) in concentrated sulfuric acid at room temperature in 69% yield. Desilylation of **5a** was also attempted under the same conditions to afford **1** as a mixture of regioisomers in 70% yield (Scheme S2 in the Supporting Information).

As expected, the ^{1}H and ^{13}C NMR spectra of C_{4h}-**1** were very different from those of the authentic sample of **1** synthesized by a conventional method. The assignable peaks of ^{1}H and ^{13}C NMR spectra of C_{4h}-**1** are expectedly simple, while those of conventional **1** are complicated (Figure S1 in Supporting Information). The UV/Vis and fluorescence spectra of C_{4h} zinc β-tetrakis(*tert*-butyl)phthalocyanine **1** were compared with those of **1** prepared by a conventional method in dichloromethane. They appear similar, independent of the regioisomers. These spectra show that the position of the *tert*-butyl group on phthalocyanine does not influence the optical properties of **1** in solution (Figure 3).[7a] On the other hand, using a different



Scheme 3. Regioselective synthesis of other symmetric C_{4h} phthalocyanines.

Desilylated analogues **9a,b** were also produced in 12% yield as a mixture of regioisomers.

In order to discuss the high C_{4h} regioselectivity achieved by our methodology, a computation was attempted next. Hanack reported that the regioselectivity of the formation of phthalocyanines depends on the difference in reactivity between two cyano groups of phthalonitrile.[8c] Hence, the charge distributions of two cyano groups on **3a** and **3b** were calculated (DFT/B3LYP/6-31G*) (Figure 2a). In **3a**, the charge distribution of the cyano group next to the trimethylsilyl group was almost

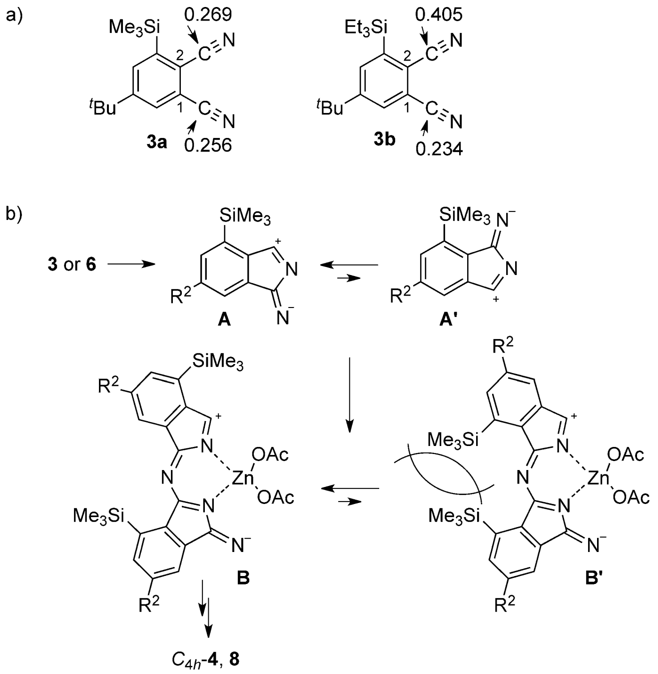


Figure 2. a) Charge distribution of CN groups of **3**. b) A proposed reaction mechanism.

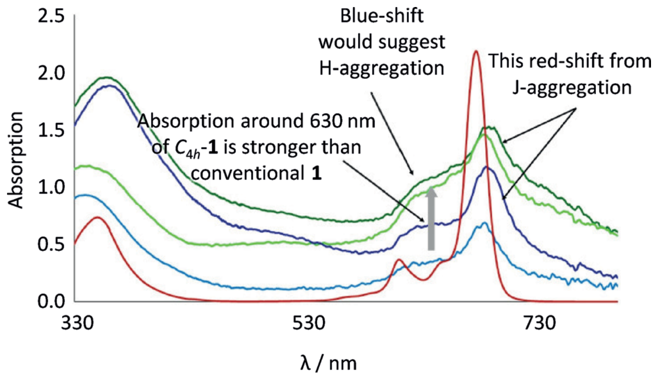


Figure 4. Comparisons between UV/Vis attenuated total reflection (ATR) spectra of C_{4h}-**1** of thin film (green: s-polarized light; light green: p-polarized light), conventional **1** of thin film (blue: s-polarized light; light blue: p-polarized light) and C_{4h}-**1** in dichloromethane (red: 1.0×10^{-5} M).

method such as optical waveguide spectroscopy, the UV/Vis attenuated total reflection (ATR) spectra of C_{4h}-**1** thin films were found to be different from those of conventional **1** thin films (Figure 4). Q-Bands of conventional **1** as thin films are 8 nm red-shifted from those of solution state, and bands of C_{4h}-**1** are 11 nm red-shifted from those of solution state (**1**: 678 nm in CH_2Cl_2; 686 nm in thin film; C_{4h}-**1**: 678 nm in CH_2Cl_2; 689 nm in thin film).

This phenomena could be induced by their J-aggregation, although these shifts are not significant.[11] Namely, **1** and C_{4h}-**1** are aggregation-free in solvents, however, they are J-aggregated as solid states. As can be seen in the red-shifted length, C_{4h}-**1** seems to be more aggregated than **1**. The spectrum of C_{4h}-**1** is much broader than that of conventional **1**, besides, both of them are blue-shifted by comparison with their solution spectra. In particular, the absorption band of C_{4h}-**1** around 630 nm is stronger and broader than that of **1**, which is highly related to the vertical interaction in C_{4h}-**1**. These observations should indicate H-aggregation, and C_{4h}-**1** aggregates more strongly than conventional **1**, which is a mixture of regioisomers.[12] More interestingly, the differences in UV/Vis ATR spectra of conventional **1**, obtained using p-polarized light and s-polarized light, are greater than those of C_{4h}-**1**. This fact indicates that the aggregation state of conventional **1** on the surface is consistent (i.e., J-aggregation), while that of C_{4h}-**1** is rather random (i.e., J and H-aggregation).[13] These aggregation differences in solid states can be explained as follows: C_{4h}-**1** is a single isomer and the vertical interaction of C_{4h}-**1** via π–π stacking is allowable, while the same interactions in conventional **1** are rather difficult due to the steric repulsion of regioisomers. Consequently, both J-aggregation and H-aggregation are allowed in the surface of C_{4h}-**1**, while conventional **1** predominantly exists in J-aggregation.

In conclusion, we have achieved the regioselective synthesis of C_{4h}-tetrakis(*tert*-butyl)metallophthalocyanines for the first time. The key for this transformation is the dual use of steric effects of the trialkylsilyl group in regioselective *ortho*-lithiation/silylation and tetramerization. The trialkylsilyl group can be removed by acid treatment in good yield. The NMR spectra

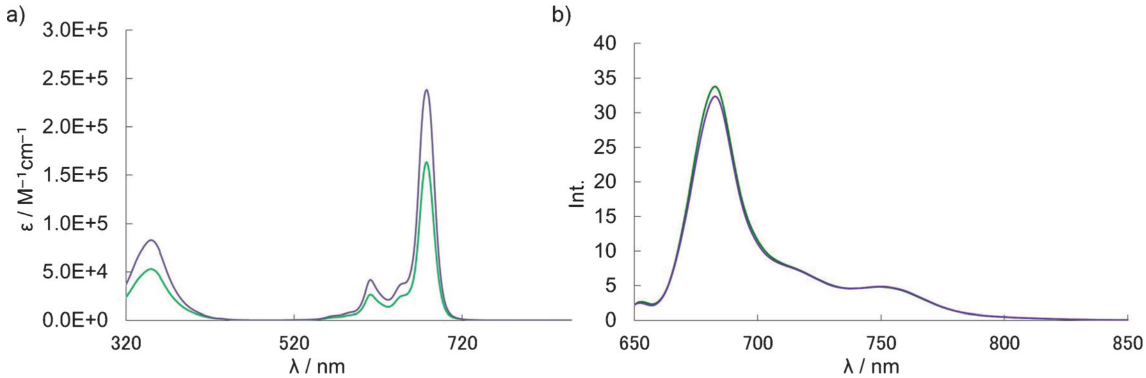


Figure 3. a) Comparisons between UV/Vis spectra of C_{4h}-**1** (green: 1.0×10^{-5} M) and conventional **1** (purple: 1.0×10^{-5} M) in dichloromethane. b) Comparison of fluorescence spectra of C_{4h}-**1** (green) and conventional **1** (purple) in dichloromethane.

of C_{4h}-**1** revealed its high symmetry. It should be mentioned that the UV/Vis ATR spectra of C_{4h}-**1** and conventional **1** in solution are almost the same, and they are even superimposable, while in the thin film, they are different and far from superimposable. In solution, both C_{4h}-**1** and conventional **1** exist as nonaggregates. In thin films, C_{4h}-**1** has a tendency towards random orientation with H- and J-aggregation, while conventional **1** seems to indicate only J-aggregation. Although there might be other interpretations of these spectral differences in a film state, the work reported here represents the first synthesis and spectral investigation of regioisomer-free C_{4h}-tetrakis-(*tert*-butyl)metallophthalocyanines **1**. Since tetrakis(*tert*-butyl)-metallophthalocyanines **1** are among the most popular phthalocyanines, C_{4h}-**1** should be useful for their precise characterization of the aggregation state, and the design of novel materials such as dye-sensitized solar cells. An extension of this methodology for the synthesis of a variety of β-functionalized phthalocyanines is under way.

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Keywords: aggregation · phthalocyanines · protecting groups · regioselectivity · silicon · synthesis

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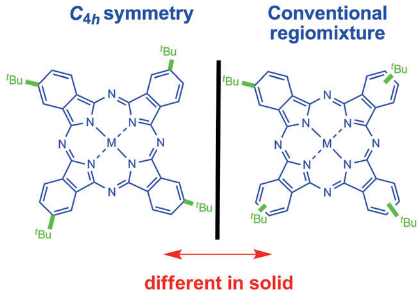
Regioisomer-Free C_{4h} β-Tetrakis(*tert*-butyl)metallo-phthalocyanines: Regioselective Synthesis and Spectral Investigations



A solid case for regioselectivity! The C_{4h}-selective synthesis of β-(*tert*-butyl)-metallophthalocyanines by tetramerization of α-trialkylsilyl phthalonitriles with metal salts following acid-mediated desilylation is disclosed for the first time. Investigation of regioisomer-free zinc β-tetrakis(*tert*-butyl)phthalocyanine using spectroscopy showed that the C_{4h} single isomer is distinct in the solid state to zinc β-tetrakis(*tert*-butyl)phthalocyanine obtained by a conventional method.