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(Phthalocyaninato)copper(II) Complexes Fused with Different Numbers of 15-Crown-5 Moieties – Synthesis, Spectroscopy, Supramolecular Structures, and the Effects of Substituent Number and Molecular Symmetry

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Symmetrical (phthalocyaninato)copper(II) complexes Cu(Pc′) [Pc′ = Pc(15C5), Pc(opp-15C5)$_2$, Pc(adj-15C5)$_2$, Pc(15C5)$_3$; Pc = unsubstituted phthalocyaninate, Pc(15C5) = 2,3-(15-crown-5)phthalocyaninate, Pc(opp-15C5)$_2$ = 2,3,16,17-bis(15-crown-5)phthalocyaninate, Pc(adj-15C5)$_2$ = 2,3,9,10-bis(15-crown-5)phthalocyaninate, Pc(15C5)$_3$ = 2,3,9,10,16,17-tris(15-crown-5)phthalocyaninate] (**2**–**5**) have been prepared by the reaction of corresponding heteroleptic bis(phthalocyaninato)europium complexes Eu(Pc)(Pc′) [Pc′ = Pc(15C5), Pc(opp-15C5)$_2$, Pc(adj-15C5)$_2$, Pc(15C5)$_3$, Pc(15C5)$_4$; Pc = unsubstituted phthalocyaninate] with Cu(OAc)$_2$ in dry dmf at 100 °C. For the purpose of comparative studies, the symmetrical counterparts CuPc (**1**) and CuPc(15C5)$_4$ [Pc(15C5)$_4$ = 2,3,9,10,16,17,24,25-tetrakis(15-crown-5)phthalocyaninate] (**7**) have also been prepared. These monomeric complexes have been characterized by spectroscopic methods in addition to elemental analysis. Having a series of closely related phthalocyanines with a different number and/or disposition of 15-crown-5 groups at the peripheral positions, the effects of 15-crown-5 substituent number and molecular symmetry on the electronic absorption spectra, infra-red (IR) spectra, and supramolecular structure formation induced by K^+ ions have been investigated. Systematic studies on the formation of dimeric supramolecular structures of the series of monomers **2**–**6** reveal and confirm the previously proposed two-step three-stage process of K^+-induced dimerization of phthalocyanines with three or four 15-crown-5 moieties.

Introduction

The design and preparation of supramolecular structures have attracted significant research interest due to their great potential applications in materials science and molecular electronics. Phthalocyanines have been an important class of molecular materials since their first synthesis early in the last century.[1] Crown ethers have also found wide application in molecular electronic devices due to their remarkable recognition and metal-binding properties.[2] The combination of these two functional subunits for the purpose of constructing novel supramolecular structures with novel multi-functional properties has stimulated wide research interest since the 1980s.[3]

The first trial in this direction was the preparation of CuPc(15C5)$_4$ in 1986 by three independent research groups.[3] Subsequently, these crown ether substituted metal-free or metallo-phthalocyanines have been studied for their dimerization in a two-step three-stage process in the presence of potassium ions in a mixed solvent of chloroform and methanol.[4] Since then, significant efforts have been put into adding different numbers of 15-crown-5 voids onto the phthalocyanine skeleton through asymmetric σ-bonded substitution of the peripheral protons. However, most probably because of the absence of a suitable effective separation method for the mono-, bis-, tris-, and tetrakis(15-crown-5)-substituted phthalocyanine compounds, which each have a high and similar polarity, only a few tris(15-crown-5)-substituted phthalocyanine analogues have been isolated.[5] The main target of the present work is to introduce different numbers of 15-crown-5 groups, from one to four, at different peripheral positions of the phthalocyanine ligand of (phthalocyaninato)copper complexes, and then systematically study their spectroscopic and dimeric supramolecular structure formation characteristics.

It is worth pointing out that the effects of lowering the molecular symmetry of phthalocyanine molecules on the spectra have not yet been fully exploited. Most of the studies so far have focused on the spectral properties of phthalocyanine analogues with reduced molecular symmetry because of their lower π-system symmetry than D_{4h},[6] which are obviously significantly affected by the change in the size of the π-system.

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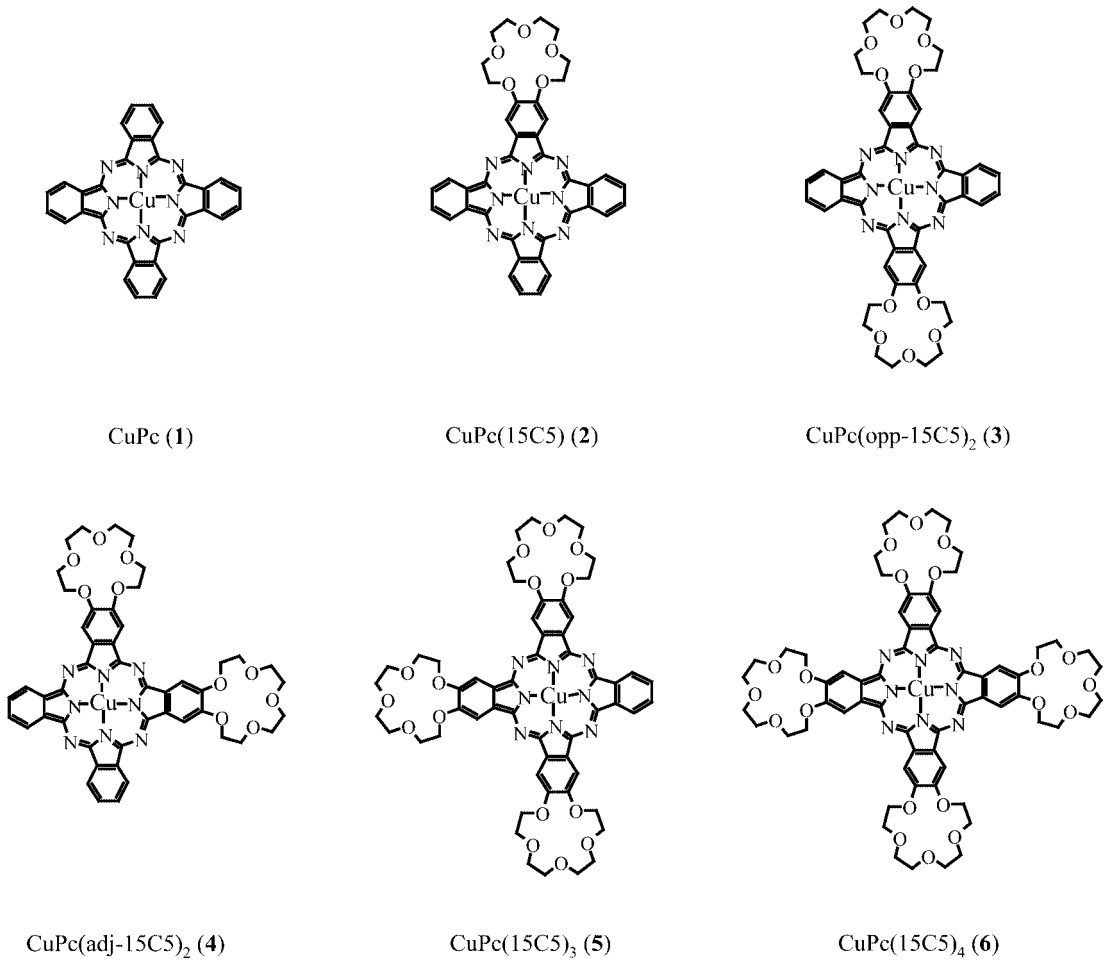

Figure 1. Schematic molecular structures of (phthalocyaninato)copper complexes fused with different numbers of 15-crown-5 moieties.

In this paper, we report the synthesis of a series of unsymmetrical (phthalocyaninato)copper(II) complexes, namely CuPc(15C5) (**2**), CuPc(opp-15C5)$_2$ (**3**), CuPc(adj-15C5)$_2$ (**4**), and CuPc(15C5)$_3$ (**5**) as well as symmetrical CuPc (**1**) and CuPc(15C5)$_4$ (**6**) with zero, one, two, three, and four 15-crown-5 voids attached at different positions of the phthalocyanine ring (Figure 1). Their spectroscopic properties have also been comparatively studied, trying to reveal the effects of lowering the molecular symmetry of phthalocyanines. It is worth mentioning that in spite of the very recent efforts on the heteroleptic bis(phthalocyaninato)europium complexes Eu(Pc)(Pc′) [Pc′ = Pc(15C5), Pc(opp-15C5)$_2$, Pc(adj-15C5)$_2$, Pc(15C5)$_3$, Pc(15C5)$_4$],[7] these effects could not be clearly revealed due to the attenuation and/or covering of such effects by strong π-π interactions in the double-decker molecules, which predominantly control their spectral properties.

Results and Discussion

Synthesis

Two synthetic pathways have been reported so far to prepare unsymmetrical monomeric phthalocyanine analogues. The first method involves a mixed cyclization of two phthalonitrile (or isoindole) precursors in the presence of a metal salt or organic base.[8] As can easily be expected, the separation of a series of closely related and isomeric phthalocyanines obtained in this way has been a great challenge for chemists. As a result, except for the two whole series of phthalocyanine analogues, whose π-system itself has a lower symmetry than D_{4h}, reported by Kenny and Tian,[6a,9] respectively, from the reaction between a tetraazaporphyrin precursor and a phthalocyanine precursor and between a phthalocyanine precursor and a naphthalocyanine precursor, unsymmetrical phthalocyanine derivatives whose π-system itself still maintains the D_{4h} symmetry prepared and isolated with this method as a whole series are still very rare, limited to MPc[(R)$_n$(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_{8-n}$] (M = 2H), to the best of our knowledge.[10] The second pathway involves the ring-expansion reaction of subphthalocyanine. Treatment of a new dinitrile in the isoindole form with a subphthalocyanine led to the formation of phthalocyanine analogues with a 3:1 ratio of the two dinitriles. This method, again, is not practical for the present case. In this work, we employed a novel methodology using heteroleptic bis(phthalocyaninato) rare earth complexes Eu(Pc)(Pc′) [Pc′ = Pc(15C5), Pc(opp-15C5)$_2$, Pc(adj-

Table 1. Analytical and mass spectrometric data for (phthalocyaninato)copper complexes **2**–**7**.[a]

Compound	$[M]^+$ (m/z)[b]	Analysis		
		C	H	N
CuPc(15C5) (**2**)	765.3 (765.2)	[c]	[c]	[c]
CuPc(opp-15C5)$_2$·2CH$_3$OH (**3**)	955.4 (955.2)	58.48 (58.85)	5.11 (5.14)	10.38 (10.98)
CuPc(adj-15C5)$_2$·2CH$_3$OH (**4**)	955.5 (955.2)	58.84 (58.85)	5.22 (5.14)	10.29 (10.98)
CuPc(15C5)$_3$·2CHCl$_3$ (**5**)	1145.7 (1145.3)	50.71 (50.28)	4.15 (4.30)	8.20 (8.20)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. [c] Satisfactory elemental analysis data is not obtained for this compound.

15C5)$_2$, Pc(15C5)$_3$, Pc(15C5)$_4$] as the starting material. Reaction with a large excess of copper acetate in dry dmf at 100 °C for 1.5 h provides two different kinds of (phthalocyaninato)copper compounds Cu(Pc) and CuPc(15C5)$_n$ (n = 1–4) (**2**–**6**) in relatively good yields. Fortunately, all the 15-crown-5-substituted (phthalocyaninato)copper complexes **3**–**6**, except for **2**, could be relatively easily separated and purified from its unsubstituted analogue CuPc (**1**) by simple filtration followed by general neutral alumina column chromatography, due to the presence of 15-crown-5 moieties on the phthalocyanine ring of compounds **3**–**6**. It is worth noting that the symmetrical compound CuPc(15C5)$_4$ (**6**) together with CuPc (**1**) was actually obtained from the simple tetramerization of 4,5-dicyanobenzo-15-crown-5 or unsubstituted dicyanobenzene, in the presence of copper acetate.

Because of the low solubility of CuPc(15C5) (**2**), similar to that of CuPc, complex **2** could not be isolated from the reaction between Eu(Pc)[Pc(15C5)] and Cu(OAc)$_2$. This compound, however, was actually prepared by the reaction between Cu(OAc)$_2$ and metal-free H$_2$Pc(15C5), the latter of which was prepared and separated from mixed ring tetramerization of dicyanobenzene and 4,5-dicyanobenzo-15-crown-5.

All the newly prepared (phthalocyaninto)copper(II) complexes **2**–**5** gave satisfactory elemental analysis results as given in Table 1. They were further characterized by spectroscopic methods. The MALDI-TOF spectra of all these compounds showed the molecular ion $[M]^+$ signals with correct isotopic pattern (Table 1).

Electronic Absorption Spectra

The electronic absorption spectra of the series of (phthalocyaninato)copper complexes **1**–**6** were recorded in CHCl$_3$ and the data are summarized in Table 2. Figure 2 compares the UV/Vis spectra in the range of 300–900 nm of the whole series of compounds. All the absorption spectra show a typical broad Soret band at 340–343 nm, involving a couple of electronic transitions dealing with the third occupied HOMO and the first LUMO. The Q bands for these compounds are observed in the range of 666–677 nm, with two vibrational shoulders at 602–611 and 637–648 nm. In addition, a weak band at 411–435 nm is also observed. Except for the Soret band, both the absorption positions of the Q band and the weak band at 411–435 nm show dependence on the number of 15-crown-5 substituents. The Q band shifts gradually and slightly to the red and the weak band at 411–435 nm to the blue upon an increase in the number of 15-crown-5 substituents. Apart from the absorption position, the appearance of the electronic spectra is also sensitive to the number of 15-crown-5 substituents. For example, the weak band in the range of 411–435 nm for 15-crown-5-containing (phthalocyaninato)copper complexes **2**–**6**, which is absent in the unsubstituted CuPc (**1**), gradually increases in intensity and moves to the higher energy side coinciding with the increase in the number of 15-crown-5 groups from **2** to **6**. This result clearly reveals the origin of this absorption which is associated with the 15-crown-5 substituents. In combination with the fact that a similar band was observed for all the 15-crown-5-substituted monomeric phthalocyanines[3] and even the alkoxy-substituted phthalocyanine derivatives,[11] this absorption can be attributed to the n→π* transitions arising from the oxygen lone pairs of electrons. This assignment is further confirmed by our recent calculation results on the electronic absorption spectra of nonperipherally tetraalkoxy-substituted (phthalocyaninato)lead complexes.[12] It is also noteworthy that for the isomeric complexes **3** and **4**, a very slight shift is still observed for some of the absorption bands, indicating that the electronic absorption properties are also more or less dependent on the substituent positions.

Table 2. Electronic absorption data for (phthalocyaninato)copper complexes **1**–**6** in CHCl$_3$.

Compound	λ_{max} [nm] (log ε)				
1	343 (4.50)		602 (4.22)	637 (4.19)	666 (5.02)
2	341 (4.55)	435 (3.62)	608 (4.24)	644 (4.26)	673 (4.87)
3	340 (4.58)	423 (3.75)	610 (4.29)	646 (4.28)	675 (4.88)
4	340 (4.48)	424 (3.75)	609 (4.17)	646 (4.17)	674 (4.77)
5	341 (4.61)	414 (4.01)	611 (4.35)	647 (4.38)	676 (4.95)
6	341 (4.53)	411 (4.09)	611 (4.26)	648 (4.28)	677 (4.93)

As shown in Figure 2, except for the weak n→π* transition band at ca. 420 nm, all the unsymmetrical (phthalocyaninato)copper(II) complexes **2**–**5** display very similar absorption features, which also resemble their symmetrical counterparts **1** and **6**. This observation reveals that the effect of lowering the molecular symmetry of phthalocyanines only through asymmetric σ-bonded substitution of the peripheral protons is too small to be reflected in their electronic absorption spectra. Phthalocyanines with diminished molecular symmetry through asymmetric σ-bonded substitution of the nonperipheral protons are expected to provide more information in this regard.

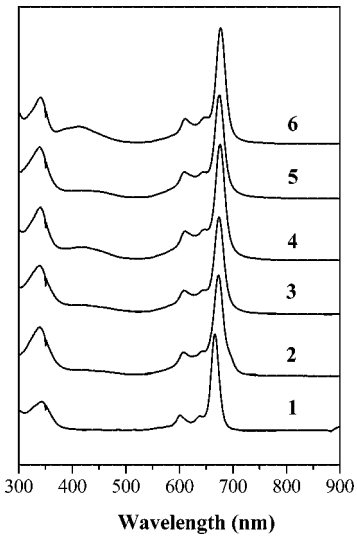

Figure 2. The electronic absorption spectra of CuPc (**1**), CuPc(15C5) (**2**), CuPc(opp-15C5)$_2$ (**3**), CuPc(adj-15C5)$_2$ (**4**), CuPc(15C5)$_3$ (**5**), and CuPc(15C5)$_4$ (**6**) in $CHCl_3$.

IR Spectra

Because of the interest in the sandwich-type (tetrapyrrole)metal complexes related to their potential applications in molecular electronics and magnetism, we have focused our attention on the synthesis and structures of a series of (na)phthalocyaninato and/or porphyrinato rare earth complexes in the past decade.[13–16] IR spectroscopic characteristics of (na)phthalocyanine in these sandwich-type complexes have also been systematically studied for the purpose of investigating the intrinsic properties of these phthalocyanine compounds.[17–19] However, except for the early efforts paid to the metal-free and metalo-phthalocyanines without peripheral substituents and the recent work on the calculated spectra of several phthalocyanine compounds employing the DFT method, systematic investigation of the IR spectroscopy of monomeric phthalocyanine compounds seems not to have been conducted to date. Our compounds in the present work are therefore expected to give representative data for the series of peripherally substituted (phthalocyaninato)metal complexes.

As clearly shown in Figure S1 and Table S1 (Supporting Information), the presence of one, two, three, and four 15-crown-5 moieties on the peripheral positions of the phthalocyanine ring in the molecules of compounds **2**, **3** and **4**, **5**, and **6** increases the number of IR-active modes. The common absorptions for the 15-crown-5-substituted complexes **2**–**6** observed at 2954–2958, 2921–2924, 2871–2872, 2851–2856, 1280–1287, and 1045–1047 cm^{-1}, which are absent in the spectrum of unsubstituted CuPc (**1**), are attributed to the asymmetric and symmetric C–H stretching vibrations and C–O–C stretching vibrations of the 15-crown-5 groups, respectively. Nevertheless, the intensity of all these absorptions has been found to increase along with the number of 15-crown-5 moieties from **2** to **6**.

It is also worth noting that despite of several additional peaks observed for CuPc(15C5)$_4$ (**6**) compared with CuPc (**1**), the characteristic pattern of the IR spectrum of CuPc(15C5)$_4$ (**6**) still remains simple, somewhat simpler than those of **2**–**5**, revealing the relatively higher molecular symmetry of the former compound. The static molecular geometry of CuPc (**1**) and CuPc(15C5)$_4$ (**6**) suggests a D_{4h} point group for their molecule, while **2**, **3**, **4**, and **5**, have a C_{2v}, D_{2h}, C_{2v}, and C_{2v} point group, respectively. This is clearly revealed by the larger number of vibrational modes observed in the IR spectra of **2**–**5** compared with those of either CuPc (**1**) or CuPc(15C5)$_4$ (**6**) (Figure S1 and Table S1; Supporting Information). The difference in the characteristic pattern of IR spectra between the isomers **3** and **4** is clearly due to their different molecular symmetry.

Formation of Dimeric Phthalocyanine Supramolecular Structures

The K^+-induced cofacial dimer formation of monomeric phthalocyanine derivatives substituted with three or four 15-crown-5 voids, in particular CuPc(15C5)$_4$, has been well studied by Kobayashi and co-workers.[4a,5] On the basis of corresponding results, a two-step three-stage process was proposed for cofacial dimer formation of monomeric phthalocyanine derivatives. In the present study, the formation process of K^+-induced dimeric supramolecular structures of 15-crown-5-substituted (phthalocyaninato)metal complexes, *in a two-step three-stage process*, has been clearly revealed and confirmed by studying the formation processes of (phthalocyaninato)copper complexes in $CHCl_3$ mixed with a trace amount of MeOH due to the availability of the series of mono-, bis-, tris-, and tetrakis(15-crown-5)-substituted (phthalocyaninato)copper complexes, in particular CuPc(15C5) (**2**), CuPc(adj-15C5)$_2$ (**4**), CuPc(15C5)$_3$ (**5**), and CuPc(15C5)$_4$ (**6**).

Figure 3 compares the systematic changes in absorption spectra of CuPc(15C5) (**2**), CuPc(adj-15C5)$_2$ (**4**), CuPc(15C5)$_3$ (**5**), and CuPc(15C5)$_4$ (**6**) in $CHCl_3$ upon titration with KOAc in $CHCl_3$/MeOH (9:1, v/v) and the final spectra obtained when [CH_3COOK]/[compound] = 3.0 for all these compounds are listed in Figure S2 (Supporting Information). It can be seen that after adding K^+ ions, the intense Q-band at 673 nm for **2** does not take a blue shift but gradually attenuates in intensity. Moreover, no new peak appears in this Q-band region. These results indicate the formation of linear (or noncofacial) dimeric supramolecular structure [CuPc(15C5)]$(K^+)_1$[CuPc(15C5)][(**2**)$(K^+)_1$-(**2**)]. This is also true for the formation of linear (or noncofacial) dimeric supramolecular structure [CuPc(adj-15C5)$_2$]-$(K^+)_2$[CuPc(adj-15C5)$_2$] [(**4**)$(K^+)_2$(**4**)] when K^+ ions are added to a solution of the (phthalocyaninato)copper compound with two 15-crown-5 moieties at the adjacent peripheral positions according to the experimental results shown in Figure 3 and Figure S2 (Supporting Information).

However, significant change in the electronic absorption spectrum takes place after K^+ ions are added to the solution of compound **5**, see Figure 3 and Figure S2 (Supporting Information). Along with the decrease of the Q-band

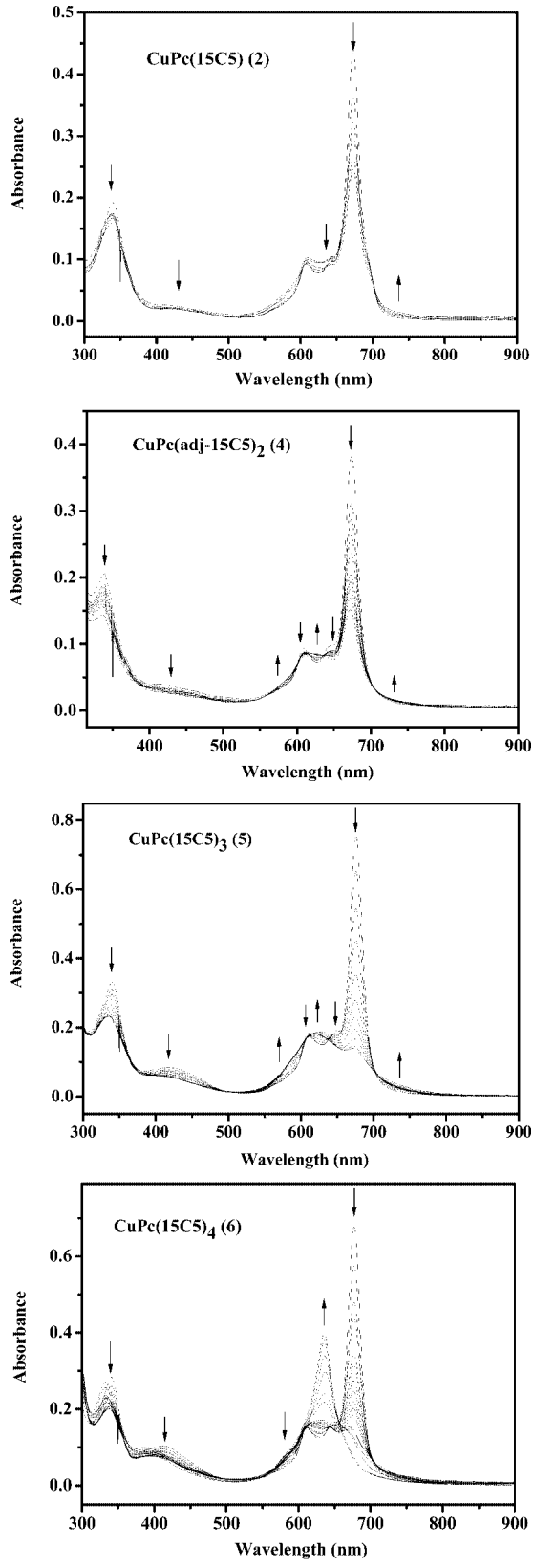

Figure 3. Changes in absorption spectra of CuPc(15C5) (**2**), CuPc(adj-15C5)$_2$ (**4**), CuPc(15C5)$_3$ (**5**), and CuPc(15C5)$_4$ (**6**) in $CHCl_3$ upon titration with KOAc in $CHCl_3$/MeOH (9:1, v/v). Arrows indicate the direction of the spectral changes. The final spectra were obtained when [CH_3COOK]/[compound] = 3.0 (for **2**, **4**–**6**).

of **5** at 676 nm, a new band appears at 624 nm due to the formation of cofacial dimeric supramolecule [CuPc(15C5)$_3$](K^+)$_3$[CuPc(15C5)$_3$] [(**5**)(K^+)$_3$(**5**)]. This is in line with the results found during the formation of K^+-induced cofacial dimerization of phthalocyanine analogues with three 15-crown-5 voids.[4a,5] It is worth noting that the Soret band at 341 nm for **5** also shifts to the shorter wavelength (335 nm) with addition of K^+. In line with the previous reports,[4a,5] cofacial dimeric supramolecular structure [CuPc(15C5)$_4$](K^+)$_4$[CuPc(15C5)$_4$] [(**6**)(K^+)$_4$(**6**)] is formed with addition of K^+.

It is noteworthy that a similar result to that of **5** was observed for compound **3** (Figures S2 and S3; Supporting Information). When no changes occur anymore upon addition of excess K^+ ions, the electronic absorption spectrum can be ascribed to the cofacial dimeric supramolecular structure [CuPc(opp-15C5)$_2$](K^+)$_2$[CuPc(opp-15C5)$_2$] [(**3**)(K^+)$_2$(**3**)].

As a result, it has been found that K^+-induced cofacial dimerization of phthalocyanines with three or four 15-crown-5 voids, for instance compound **5** or **6**, should proceed in the following manner: two monomeric 15-crown-5-substituted phthalocyanine molecules combine with the first K^+ cation to form a linear dimer, which then combines with the second K^+ cation to form a linear or cofacial dimer, and finally transforms into a stable cofacial dimer when the third and/or fourth K^+ cation(s) are combined. In other words, K^+-induced cofacial dimerization of phthalocyanines with three or four 15-crown-5 voids should proceed according to the following three stages:[4a,5] (1) The first involves the formation of a linear (or noncofacial) dimer at a [K^+]/[MPc(15C5)$_4$] value of 0–0.5; (2) the second in the region of $0.5 \leq [K^+]/[MPc(15C5)_4] \leq 1.5$ involves the transition from the linear (or noncofacial) dimer to the cofacial dimer when the second and third K^+ cations are combined; (3) the third involves the complete formation of a cofacial dimer at $[K^+]/[MPc(15C5)_4] \geq 1.5$.

In addition, to monitor the cofacial supramolecular formation for compounds **5** and **3**, the changes in absorption of the so-called monomer band (at 676 nm) and the dimer band (at 592 nm) for **5** (Tables 2 and 3), and monomer band (at 675 nm) and the dimer band (at 593 nm) for **3**, were recorded as a function of [K^+]/[**5**] and [K^+]/[**3**], respectively. As shown in Figure 4 and Figure S4 (Supporting Information), the concomitant change of the two characteristic bands indicates that upon addition of K^+ ions, monomer **5** or **3** is converted exclusively to the dimeric supramolecular

Table 3. Electronic absorption data for the supramolecular dimers (SD) formed from the 15-crown-5-substituted (phthalocyaninato)-copper complexes **2**–**6** in $CHCl_3$ upon titration with KOAc in $CHCl_3$/MeOH (9:1, v/v).

Compound	λ_{max} [nm] (log ε)				
SD2	338 (4.45)		610 (4.19)	643 (4.20)	673 (4.61)
SD3	333 (4.45)		615 (4.31)		673 (4.22)
SD4	335 (4.37)		623 (4.18)		672 (4.36)
SD5	335 (4.44)		624 (4.33)		671 (4.22)
SD6	334 (4.41)	389 (3.98)	637 (4.53)		

structure. The formation process is similar to that of $MPc(15C5)_4$ (M = H_2, Zn, Co, Ni, Cu) in $CHCl_3$. However, probably due to the low solubility of these compounds including complexes **4** and **2**, about a threefold amount of K^+ ions (i.e. $[K^+]/[\mathbf{5}$ or $\mathbf{3}] \approx 3$) is required to reach a steady state (Figure 4 and Figure S4; Supporting Information), instead of the value of 2 observed for other reported monomeric phthalocyanine counterparts.[4a,5]

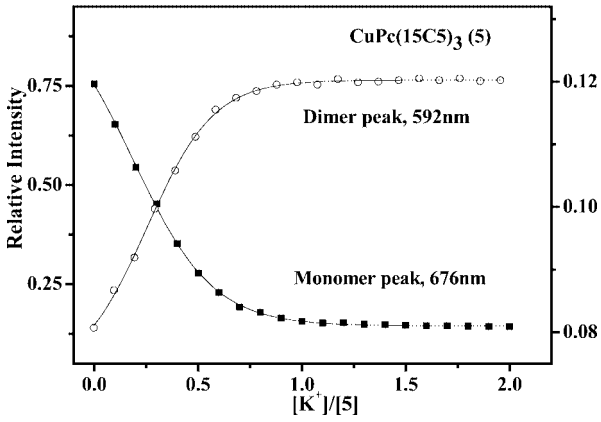

Figure 4. Variation of the absorbance 676 and 592 nm during titration of **5** in $CHCl_3$ with KOAc in $CHCl_3$/MeOH (9:1). The curve going up with $[K^+]$ represents the change at the dimer peak and should be referred to the right-hand axis, while that going down is the change at the monomer peak and should be referred to the left-hand axis.

Equation (1) shows the equilibrium between monomer **5** or **3** (upon addition of K^+ ions) and the corresponding dimer. According to the method described by West and Pearce,[20] the monomer and dimer concentrations could be calculated from the spectral changes during titration, and their relationship be depicted as shown in Figure 5 and Figure S5 (Supporting Information) for the present systems. The region with a slope of ca. 2.0 indicates the dimerization occurs in this region. For these present systems, this includes the data point of $[K^+]/[\mathbf{5}$ or $\mathbf{3}] = 0.5$. When $[K^+]/[\mathbf{5}$ or $\mathbf{3}] > 3$, the slope of the plot approaches zero.

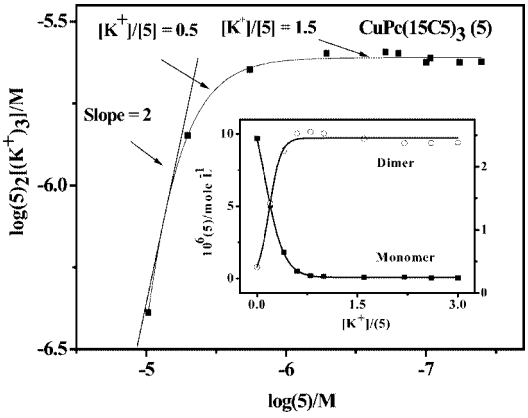

Figure 5. Plots of log[**5**] vs. log[(**5**)$(K^+)_3$(**5**)] for $CuPc(15C5)_3$ (**5**) in $CHCl_3$/MeOH. The inset shows the dependence of monomer and dimer concentrations on $[K^+]/[\mathbf{5}]$.

$$n\ K^+ + 2\ CuPc(15C5)_n \overset{K}{\leftrightarrow} dimer{\cdot}K^+_n \quad (1)$$

It is worth pointing out that for all the crown ether substituted (phthalocyaninato)copper compounds, namely CuPc(15C5) (**2**), $CuPc(opp\text{-}15C5)_2$ (**3**), $CuPc(adj\text{-}15C5)_2$ (**4**), $CuPc(15C5)_3$ (**5**), and $CuPc(15C5)_4$ (**6**), when two $CuPc(15C5)_n$ units bind one K^+ cation and start to form the dimer in the first stage, the monomer–dimer conversion proceeds with a very high formation constant, $K = 3.0 \times 10^{10}$ to 7.0×10^{10} L^2 mol^{-2} with $n = 1$ for Equation (1).[4a]

Conclusions

We have prepared a series of unsymmetrical (phthalocyaninato)copper(II) complexes **2**–**5**, containing different numbers and positions of 15-crown-5 substituents, from the reaction of corresponding heteroleptic bis(phthalocyaninato)europium complexes Eu(Pc)(Pc′) with $Cu(OAc)_2{\cdot}nH_2O$. It has been found that all the unsymmetrical compounds **2**–**5** and the symmetrical analogues **1** and **6** display very similar absorption features, indicating that the electronic absorption spectra of these compounds are not sensitive enough to show the change in the molecular symmetry due to unsymmetrical substitution of 15-crown-5 moieties, which however can be clearly reflected by their IR spectra. Systematic studies over the formation of dimeric supramolecular structures of the series of monomers **2**–**6** clearly reveal and confirm the previously proposed two-step three-stage process of phthalocyanines with three or four 15-crown-5 moieties in $CHCl_3$ with trace amounts of MeOH in the presence of K^+.

Experimental Section

General Remarks: 1,8-Diazabicyclo[5.4.0]undec-7-ene (dbu) and dicyanobenzene were purchased from Aldrich. *n*-Pentanol and *N*,*N*-dimethylformamide (dmf) were freshly distilled from Na and CaH_2, respectively, under nitrogen. Column chromatography was carried out on neutral alumina (SCRC, 200–300 mesh) with the indicated eluents. All other reagents and solvents were used as received. 4,5-Dicyanobenzo-15-crown-5,[4,21] Eu(Pc)(Pc′) [Pc′ = Pc(15C5), $Pc(opp\text{-}15C5)_2$, $Pc(adj\text{-}15C5)_2$, $Pc(15C5)_3$, $Pc(15C5)_4$],[7] CuPc (**1**),[22] and $CuPc(15C5)_4$ (**6**)[4] were prepared according to published procedures. ^{1}H NMR spectra were recorded with a Bruker DPX 300 spectrometer (300 MHz) in [D_6]dmso. Spectra were referenced internally by using the residual solvent resonance (δ = 2.49 for [D_6]-dmso) relative to $SiMe_4$. Electronic absorption spectra were recorded with a Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectra were measured with a Bruker BIFLEX III ultra-high resolution mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences.

Preparation of $H_2Pc(15C5)$: According to a literature method,[23] a mixture of dicyanobenzene (76.8 mg, 0.60 mmol), 4,5-dicya-

nobenzo-15-crown-5 (31.8 mg, 0.10 mmol), and an excess amount of lithium (2.8 mg, 0.40 mmol) in *n*-pentanol (3 mL) was heated to reflux under nitrogen for 2 h. After cooling to room temperature, the resulting green solution was poured into methanol (100 mL) containing a few drops of concentrated HCl. The precipitate was collected by filtration and chromatographed on an alumina column using $CHCl_3$/MeOH (99:1) as the eluent. After eluting the first band containing unsubstituted metal-free H_2Pc, the second green band containing the target compound $H_2Pc(15C5)$ was developed which was collected and the solvent removed in a rotary evaporator. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure $H_2Pc(15C5)$ as a blue powder (12 mg, 16%). MS: calcd. for $C_{40}H_{32}N_8O_5$ $[M]^+$ 704.2; found for $H_2Pc(15C5)$ 704.8.

Preparation of CuPc(15C5) (2): A mixture of $H_2Pc(15C5)$ (12 mg, 0.017 mmol) and $Cu(OAc)_2$ (15 mg, 0.08 mmol) in dry dmf (3 mL) was heated to 100 °C for 1.5 h under a slow stream of nitrogen. After cooling to room temperature, MeOH (30 mL) was poured into the resulting blue solution. The precipitate was collected by filtration and chromatographed on an alumina column using CH_2Cl_2/MeOH (99.5:0.5) as the eluent. The blue band containing the target compound CuPc(15C5) was then collected. Repeated chromatography followed by recrystallization from CH_2Cl_2 and MeOH gave pure CuPc(15C5) as a blue powder (8 mg, 60%). It is worth noting that a satisfactory elemental analysis result could not be obtained for this compound even after repeated purification by column chromatography and recrystallization due to its limited solubility in common organic solvent.

Preparation of CuPc(opp-15C5)$_2$ (3), CuPc(adj-15C5)$_2$ (4), and CuPc(15C5)$_3$ (5): A mixture of Eu(Pc)(Pc′) [Pc′ = $Pc(opp\text{-}15C5)_2$, $Pc(adj\text{-}15C5)_2$, $Pc(15C5)_3$] (20 mg) and a large excess amount of $Cu(OAc)_2$ (15 mg, 0.08 mmol) in dry dmf (3 mL) was heated to 100 °C for 1.5 h under a slow stream of nitrogen. After cooling to room temperature, MeOH (30 mL) was poured into the resulting blue solution. The precipitate collected by filtration was then dissolved in $CHCl_3$. After removing the undissolved CuPc by filtration, the resulting product was then chromatographed on an alumina column using CH_2Cl_2/MeOH (98.5:1.5 for **3** and **4**, 98:2 for **5**) as the eluent. The blue band containing the target compound $CuPc(15C5)_n$ (n = 2–4) (**3**–**5**) was then collected. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure $CuPc(15C5)_n$ as green powders. Yield: $CuPc(opp\text{-}15C5)_2$ (**3**) (8 mg, 56%), $CuPc(adj\text{-}15C5)_2$ (**4**) (7 mg, 53%), and $CuPc(15C5)_3$ (**5**) (10 mg, 61%).

Supporting Information (see footnote on the first page of this article)(see also the footnote on the first page of this article): IR spectra of (phthalocyaninato)copper complexes **1**–**6** in the region of 400–1800 cm^{-1}. UV/Vis absorption spectra of monomers **2**–**5** and corresponding dimers in $CHCl_3$ and in $CHCl_3$/MeOH (9:1, v/v), respectively; changes in absorption spectrum of $CuPc(opp\text{-}15C5)_2$ (**3**) in $CHCl_3$ upon titration with KOAc in $CHCl_3$/MeOH (9:1, v/v); variation of the absorbance at 675 and 593 nm during titration of **3** in $CHCl_3$ with KOAc in $CHCl_3$/MeOH (9:1); plots of log[**3**] vs. log[(**3**)$(K^+)_2$(**3**)] for $CuPc(opp\text{-}15C5)_2$ (**3**) in $CHCl_3$/MeOH; characteristic IR bands (cm^{-1}) of (phthalocyaninato)copper complexes **1**–**6** with 2 cm^{-1} resolution.

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