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Heteroleptic Bis(Phthalocyaninato) Europium(III) Complexes Fused with Different Numbers of 15-Crown-5 Moieties. Synthesis, Spectroscopy, Electrochemistry, and Supramolecular Structure

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A series of heteroleptic bis(phthalocyaninato) europium(III) complexes, namely, Eu(Pc)[Pc(15C5)] (**2**), Eu(Pc)[Pc(opp-15C5)$_2$] (**3**), Eu(Pc)[Pc(adj-15C5)$_2$] (**4**), Eu(Pc)[Pc(15C5)$_3$] (**5**), and Eu(Pc)[Pc(15C5)$_4$] (**6**) [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, Pc(15C5)$_4$ = 2,3,9,10,16,17,24,25-tetrakis(15-crown-5)phthalocyaninate], with one, two, three, and four 15-crown-5 voids attached at different positions of one of the two phthalocyaninato ligands in the double-decker molecules, have been devised and prepared by Eu(Pc)(acac)-induced (Hacac = acetylacetone) mixed cyclization of the two corresponding phthalonitriles in the presence of organic base 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in *n*-pentanol. For the purpose of comparative studies, homoleptic counterparts Eu(Pc)$_2$ (**1**) and Eu[Pc(15C5)$_4$]$_2$ (**7**) have also been prepared. These sandwich double-decker complexes have been characterized by a wide range of spectroscopic methods in addition to elemental analysis. Their electrochemistry has also been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The molecular structure of Eu(Pc)-[Pc(15C5)$_4$] (**6**) has been determined by X-ray diffraction analysis. Their supramolecular structure-formation properties, in particular for compounds **5** and **6** in the presence of potassium ions, have also been comparatively studied for the purpose of future functional investigation.

Introduction

Phthalocyanines have been an important class of dyes and pigments since their first synthesis early in the last century.[1] In particular, bis(phthalocyaninato)−rare earth complexes have been intensively studied as advanced materials for gas sensors, electrochromic displays, photoconductors, and molecular electronics.[2] On the other hand, crown ethers that have remarkable recognition and metal binding properties have also found wide application in molecular electronic devices.[3] The combination of these two functional subunits for the purpose of constructing novel supramolecular structures has stimulated wide research interest since the 1980s.[4]

The first effort was the preparation of crown ether-substituted phthalocyanines, Cu[Pc(15C5)$_4$], in 1986.[4] Their supramolecular structure-formation characteristics were stud-

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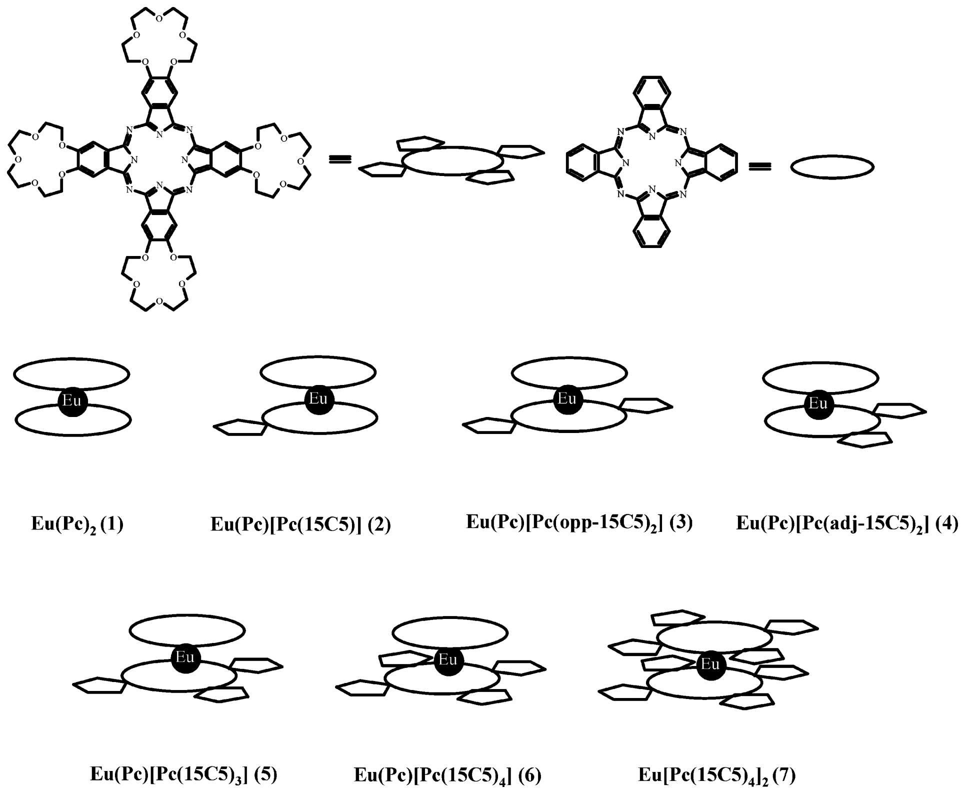

Figure 1. Schematic molecular structures of bis(phthalocyaninato) europium complexes fused with 15-crown-5 moieties.

ied in the presence of potassium in a mixed solvent of chloroform and methanol.[5] Inspired by these studies, Ishikawa introduced one or four 15-crown-5 void(s) onto one phthalocyanine ring in a bis(phthalocyaninato) lutetium complex and investigated their tetrameric structure-formation characteristics, particularly, via ESR technique.[6] Very recently, we have designed and prepared a series of 15-crown-5-substituted phthalocyanine-containing heteroleptic bis- and tris-(phthalocyaninato) rare earth complexes, which were revealed to show unexpectedly good field-effect transistor (FET) properties resulting from the formation of intermolecular J aggregates associated with the four 15-crown-5 moieties in one of the phthalocyanine ligands.[7] In addition, we have also prepared a series of mixed (porphyrinato)-[2,3,9,10,16,17,24,25-tetrakis(15-crown-5)phthalocyaninato] europium double- and triple-deckers and studied their supramolecular formation.[8] For the purpose of extensive studies, we describe herein the synthesis, separation, and molecular structure of a series of heteroleptic bis(phthalocyaninato) europium(III) complexes, namely, Eu(Pc)[Pc(15C5)] (**2**), Eu(Pc)[Pc(opp-15C5)$_2$] (**3**), Eu(Pc)[Pc(adj-15C5)$_2$] (**4**), Eu(Pc)[Pc(15C5)$_3$] (**5**), and Eu(Pc)[Pc(15C5)$_4$] (**6**), with one, two, three, and four 15-crown-5 voids attached at different positions on one of the two phthalocyaninato ligands in the double-decker molecules, Figure 1. Their supramolecular structure-formation properties have also been comparatively studied for the purpose of future functional investigations.

It is worth noting that a significant effort has been made toward the addition of different numbers of alkoxy and 15-crown-5 groups 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 di- (mono), tetra- (bis), hexa- (tris), and octaalkoxy (tetra) (15-crown-5)-substituted phthalocyanine compounds, all of which have similar polarity, only a few tris(15-crown-5)-substituted phthalocyanine analogues have been isolated in the mixed cyclization of 4,5-dicyanobenzo-15-crown-5 with 3,6-diphenylmalonitrile, 3,6-diphenylphthalonitrile, or 1,4-dicyanonaphthalene.[9] The present work therefore seems to represent the first trial to the whole series of phthalocyanines systematically substituted with di- (mono), tetra- (di), hexa- (tri), and octaalkoxy (tetra) groups (15-crown-5 moieties) at the peripheral positions.

Results and Discussion

Synthesis. Three synthetic pathways have been reported thus far for the preparation of rare earth(III) double-decker complexes with two different kinds of phthalocyaninato

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ligands $M(Pc')(Pc'')$. The first method involves a mixed cyclization of two phthalonitrile precursors in the presence of a metal salt.[10] Actually, except for Lu(Pc)[Pc(15C5)], no other heteroleptic bis(phthalocyaninato) rare earth compounds are known to be prepared and isolated by this method. Even for Lu(Pc)[Pc(15C5)], only a trace amount of product could be isolated (8 mg from a reaction of 1.0 g of dicyanobenzo-15-crown-5 and 2.8 g of dicyanobenzene).[6c] The second pathway involves the treatment of $M(acac)_3 \cdot nH_2O$ with two different phthalocyaninates, $H_2/Li_2(Pc')$ and $H_2/Li_2(Pc'')$,[6a,11,12] which again is not practical for the present case. The third route employs the half-sandwich complex $M(Pc')(acac)$ as the template, which induces cyclic tetramerization of a phthalonitrile in the presence of DBU.[13] In this work, we employed the last method using Eu(Pc)(acac) as the template. Reaction with a mixture of dicyanobenzene and 4,5-dicyanobenzo-15-crown-5 in the presence of DBU in refluxing *n*-pentanol led to the formation of a mixture of heteroleptic double-deckers $Eu(Pc)[Pc(15C5)_n]$ ($n = 1-4$) in relatively good yields. As expected, using different ratios of the two dinitriles changed the product distribution, giving Eu(Pc)[Pc(15C5)] (**2**), $Eu(Pc)[Pc(15C5)_2]$ (**3** and **4**), or $Eu(Pc)[Pc(15C5)_3]$ (**5**) as the main product. When only 4,5-dicyanobenzo-15-crown-5 was used, $Eu(Pc)[Pc(15C5)_4]$ (**6**) was isolated as the sole heteroleptic target compound. It is noteworthy that the purification of general phthalocyanine compounds has been a challenge for chemists, not to mention the separation of a series of closely related and isomeric phthalocyanines. Fortunately, in the present case, all the double-deckers, including the two opposite and adjacent isomers **3** and **4**, could be separated and purified by general silica gel column chromatography. For comparative studies, homoleptic analogues $Eu(Pc)_2$ (**1**) and $Eu[Pc(15C5)_4]_2$ (**7**) were also prepared according to published methods.[14,15]

All the newly prepared bis(phthalocyaninto) europium(III) complexes gave satisfactory elemental analysis results, as shown in Table 1. Their sandwich nature was further unambiguously confirmed by various spectroscopic methods. The MALDI-TOF spectra of all these double-deckers showed the molecular ion $(M)^+$ signals with correct isotopic pattern (Table 1).

Table 1. Analytical and Mass Spectroscopic Data for Double-Deckers **2**−**7**[a]

compound	M^+ (m/z)[b]	analysis (%) C	H	N
$Eu(Pc)[Pc(15C5)] \cdot CHCl_3$ (**2**)	1366.9 (1367.3)	59.66 (58.98)	3.53 (3.19)	14.78 (15.08)
$Eu(Pc)[Pc(opp\text{-}15C5)_2]$ (**3**)	1557.1 (1557.3)	61.23 (61.70)	4.01 (3.88)	14.08 (14.39)
$Eu(Pc)[Pc(adj\text{-}15C5)_2]$ (**4**)	1557.3 (1557.3)	61.15 (61.70)	3.81 (3.88)	14.27 (14.39)
$Eu(Pc)[Pc(15C5)_3]$ (**5**)	1748.0 (1747.5)	59.44 (60.48)	4.15 (4.27)	12.49 (12.82)
$Eu(Pc)[Pc(15C5)_4] \cdot CHCl_3$ (**6**)	1936.9 (1937.6)	57.99 (58.02)	4.53 (4.47)	11.14 (11.22)
$Eu[Pc(15C5)_4]_2 \cdot CHCl_3$ (**7**)	2699.0 (2699.3)	54.82 (54.98)	5.27 (5.19)	8.02 (7.95)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry.

Electronic Absorption and Magnetic Circular Dichroism (MCD) Spectra. The electronic absorption and magnetic circular dichroism spectra of double-deckers **1**−**7** were recorded in $CHCl_3$, and the data are summarized in Table 2. Figure 2 compares the UV−vis and MCD spectra in the range of 300−1000 nm of the whole series of compounds. All the absorption spectra show a typical Soret band at 320−335 nm with a shoulder at the lower-energy side, involving a couple of electronic transitions dealing with the third-occupied HOMO and the first LUMO. This is verified by the complicated signals observed in the MCD spectra in this region. It is worth noting that the slight splitting of the Soret band has been observed previously for both homoleptic and heteroleptic bis(phthalocyaninato) rare earth(III) complexes.[14,15] The Q bands for these compounds are observed in the range of 671−677 nm with two vibrational shoulders at 588−590 and 605−612 nm resulting from the transitions from the first semi-occupied HOMO to the second LUMO or from the second fully occupied HOMO to the first LUMO.[16] The Faraday *A*-term-like dispersion in the MCD spectra for the corresponding signals (Figure 2) supports this assignment. In addition, two weak π-radical anion bands at ca. 450 and 908 nm, together with a near-IR band at 1601−1610 nm, are also seen. The latter near-IR band is highly characteristic for tetrapyrrole rare earth(III) double-deckers which contain a hole in one of the ligands.[2] Except for the π-radical anion band at ca. 908 nm attributed to the transition from the semi-occupied HOMO to the LUMO and the near-IR band assigned to the transition from the second HOMO to the first semi-occupied HOMO, the absorption positions of all the remaining bands seem to depend on the number of 15-crown-5 substituents. Along with increasing the number of 15-crown-5 moieties, all these bands shift gradually and slightly to the red. Apart from the absorption position, the appearance of the electronic spectra is also sensitive to the number of 15-crown-5 voids. For example,

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Table 2. Electronic Absorption Data for Double-Deckers **1**−**7** in $CHCl_3$

compound	λ_{max}/nm (log ϵ)									
1	322 (4.78)	342 (4.60)	459 (4.17)			605 (4.21)	671 (4.93)	908 (3.37)	1399 (3.61)	1601 (3.82)
2	324 (4.78)	345 (sh)	458 (4.18)	476 (4.17)	588 (4.10)	606 (4.21)	672 (4.93)	908 (3.37)		1606 (3.82)
3	325 (5.03)	346 (sh)	454 (4.40)	481 (4.45)	588 (4.37)	607 (5.46)	672 (5.16)	908 (3.61)		1604 (4.02)
4	324 (5.02)	346 (sh)	455 (4.41)	480 (4.44)	587 (4.37)	607 (4.46)	672 (5.17)	908 (3.63)		1604 (4.09)
5	326 (4.98)	364 (sh)	449 (4.36)	485 (4.45)	588 (4.32)	607 (4.43)	673 (5.13)	908 (3.58)		1606 (3.96)
6	331 (4.92)	369 (4.75)		489 (4.46)	588 (4.27)	609 (4.38)	674 (5.06)	906 (3.55)		1606 (3.91)
7	335 (5.06)	371 (5.08)		491 (4.64)	590 (4.41)	612 (4.56)	677 (5.22)	907 (3.62)		1610 (4.14)

the shoulder of the Soret bands at the lower energy side gradually gains intensity with the increase of the 15-crown-5 substituent number and becomes more intense compared with the main Soret band in $Eu[Pc(15C5)_4]_2$ (**7**). The most interesting feature is the weak band in the range of 476−491 nm for 15-crown-5-containing double-deckers **2**−**7**, which is absent in the unsubstituted $Eu(Pc)_2$ (**1**). With an increasing number of 15-crown-5 groups (from **2** to **7**), this band gradually gains additional intensity and moves to the lower-energy side, which even covers the weak π-radical anion band at ca. 450 because of the transition from the fourth HOMO to the semi-occupied HOMO, in compounds **6** and **7**. These results clearly reveal the origin of this absorption, which is associated with the 15-crown-5 moieties. In combination with the fact that a similar band was observed for all the 15-crown-5-substituted monomeric phthalocyanines[4] and even the alkoxy-substituted phthalocyanine derivatives,[17] this absorption can be attributed to the n → π^* transitions resulting from the oxygen lone pairs of electrons. This assignment is further confirmed by our recent calculations on the electronic absorption spectra of non-peripherally tetra(alkoxy)-substituted phthalocyaninato lead complexes.[8] It is also noteworthy that for the isomeric double-deckers **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.

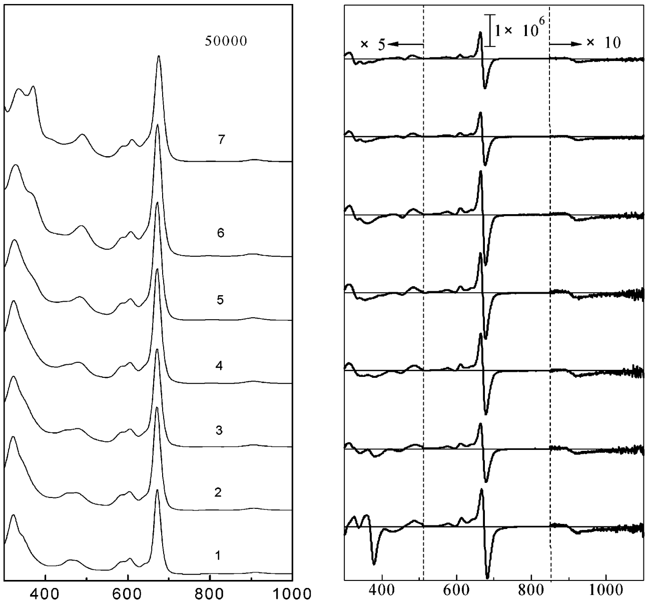

Figure 2. Electronic absorption and MCD spectra of $Eu(Pc)_2$ (**1**), Eu(Pc)-[Pc(15C5)] (**2**), $Eu(Pc)[Pc(opp\text{-}15C5)_2]$ (**3**), $Eu(Pc)[Pc(adj\text{-}15C5)_2]$ (**4**), $Eu(Pc)[Pc(15C5)_3]$ (**5**), $Eu(Pc)[Pc(15C5)_4]$ (**6**), and $Eu[Pc(15C5)_4]_2$ (**7**) in $CHCl_3$.

As shown in Figure 2, all the heteroleptic bis(phthalocyaninato) europium(III) complexes (**2**−**6**) display very similar absorption features, especially in the Q-band region, which also resemble their homoleptic counterparts **1** and **7**. This observation reveals that the electronic absorption spectra of these compounds are dominated by the strong $\pi-\pi$ interactions between the two phthalocyanine rings and therefore give less information about the effect of lowering the molecular symmetry of phthalocyanines by peripheral alkoxy substitutions.

NMR Spectra. ^1H NMR spectroscopy provided strong support for the identity of these compounds. The spectra were recorded in DMSO-d_6 (for compounds **2**−**4**) or DMSO-d_6/$CDCl_3$ (1:1) (for compounds **1** and **5**−**7**) in the presence of ca. 1% hydrazine hydrate, which reduced the double-deckers to the corresponding monoanions.[11b] Double-deckers **2**−**7**, having different numbers or positions of the 15-crown-5 moieties, could be easily distinguished by the aromatic protons' signals. The homoleptic double-decker $Eu[Pc(15C5)_4]_2$ (**7**) simply gave a singlet at δ 10.62 for the 16 equivalent phthalocyanine α ring protons, while the heteroleptic analogue $Eu(Pc)[Pc(15C5)_4]$ (**6**) showed two multiplets at δ 11.20−11.28 and 9.14−9.22 for the α and β ring protons of Pc, respectively, together with a singlet at δ 10.70 for the α ring protons of $Pc(15C5)_4$. Hence the signal(s) for the α protons adjacent to the 15-crown-5 moiety lie(s) between those for the unsubstituted isoindole unit. Figure 3 shows the downfield region of the ^1H NMR spectra of **2**−**5**. It can be seen that the spectrum for **2**, which contains only one 15-crown-5 unit, shows only a singlet (at δ 10.34) for Pc(15C5)-H_α, while the spectrum for the tris(15-crown-5)-containing **5** reveals two sets of $Pc(15C5)_3$-H_α protons (at δ 10.60 and 10.52) in a 1:2 ratio. The opposite and adjacent isomers **3** and **4** can also be differentiated by the presence

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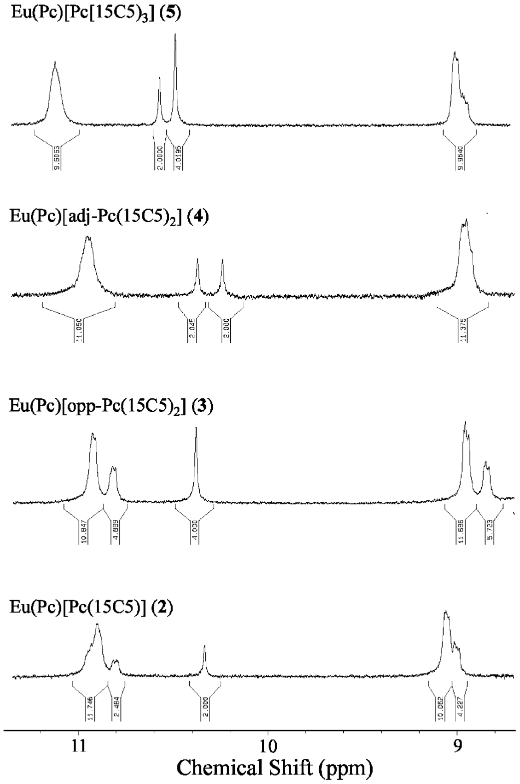

Figure 3. Downfield region of the ^{1}H NMR spectra of **2**−**5** in DMSO-d_6 (for **2**−**4**) or CDCl$_3$/DMSO-d_6 (1:1) (for **5**) with the addition of ca. 1% (by volume) hydrazine hydrate.

of one and two singlets (in a 1:1 ratio) for the Pc(15C5)$_2$-H$_\alpha$ protons, respectively.

The pattern for the crown ether signals for all of these compounds is very similar. Because of the double-decker structure, all the OCH$_2$ protons are diasterotopic.[7] The OCH$_2$CH$_2$ protons nearer the phthalocyanine ring are downfield shifted resonating as four broad multiplets, while the remaining OCH$_2$CH$_2$O protons resonate as two partially overlapped multiplets in ca. 1:3 ratio. The data are compiled in Table 3.

The assignment of these signals was confirmed by various 2D NMR techniques. The ^{1}H−^{1}H COSY spectra for all these compounds clearly revealed the connectivity among the four OCH$_2$CH$_2$ protons nearer the phthalocyanine core. The spectra for **2**−**6** also showed the connectivity between the α- and β-ring protons of the unsubstituted isoindole units in Pc and Pc(15C5)$_n$ (n = 1−3). This is illustrated by the COSY spectrum of Eu(Pc)[Pc(15C5)$_3$] (**5**) given in Figure 4a for exemplification. The NOESY spectra for all these compounds were also recorded. Cross-peaks were clearly shown for the signal(s) of Pc(15C5)$_n$-H$_\alpha$ (n = 1−4) and the two most downfield signals for OCH$_2$ protons, indicating that the latter are from the OCH$_2$ protons nearest to the phthalocyanine core.

To further confirm the assignment, we recorded the total correlation spectroscopy (TOCSY) spectrum of **5** (Figure 4b), in which the cross-peaks indicate correlations between protons that belong to a common spin-system.[19] It can be seen that the broad signals at ca. δ 11.1 and 9.1 are correlated and belong to a common spin-system. Similarly, the four most downfield signals for the OCH$_2$ protons are also correlated and belong to another spin system.

Table 3. ^{1}H NMR Data (δ) for Double-Deckers **1**−**7** in the Presence of ca. 1% Hydrazine Hydrate

compound	^{1}H NMR data (δ)
Eu(Pc)$_2$ (**1**)[a]	11.09−11.11 (m, 16H, Pc-H$_\alpha$), 9.13−9.15 (m, 16H, Pc-H$_\beta$)
Eu(Pc)[Pc(15C5)] (**2**)[b]	10.88−10.96 [m, 12 H, Pc-H$_\alpha$ and Pc(15C5)-H$_\alpha$], 10.80−10.84 [m, 2 H, Pc(15C5)-H$_\alpha$], 10.34 [s, 2 H, Pc(15C5)-H$_\alpha$], 8.98−9.06 [m, 14 H, Pc-H$_\beta$ and Pc(15C5)-H$_\beta$], 5.95−6.03 (m, 2 H, OCH), 5.40−5.48 (m, 2H, OCH), 4.90−4.99 (m, 2H, OCH), 4.67−4.74 (m, 2H, OCH), 4.39−4.45 (m, 2H, OCH), 4.26−4.35 (m, 6H, OCH)
Eu(Pc)[opp-Pc(15C5)$_2$] (**3**)[b]	10.92−10.98 (m, 8H, Pc-H$_\alpha$), 10.83−10.86 [m, 4H, opp-Pc(15C5)$_2$-H$_\alpha$], 10.43 [s, 4H, opp-Pc(15C5)$_2$-H$_\alpha$], 9.05−9.09 (m, 8H, Pc-H$_\beta$), 8.94−8.98 [m, 4H, opp-Pc(15C5)$_2$-H$_\beta$], 5.97−6.05 (m, 4 H, OCH), 5.43−5.53 (m, 4H, OCH), 4.91−5.01 (m, 4H, OCH), 4.66−4.77 (m, 4H, OCH), 4.39−4.47 (m, 4H, OCH), 4.23−4.37 (m, 12H, OCH)
Eu(Pc)[adj-Pc(15C5)$_2$] (**4**)[b]	10.90−11.00 (m, 12H, Pc-H$_\alpha$ and adj-Pc(15C5)$_2$-H$_\alpha$], 10.40 [s, 2H, adj-Pc(15C5)$_2$-H$_\alpha$], 10.28 [s, 2H, adj-Pc(15C5)$_2$-H$_\alpha$], 9.02−9.12 (m, 12H, Pc-H$_\beta$ and adj-Pc(15C5)$_2$-H$_\beta$], 5.94−6.05 (m, 4H, OCH), 5.36−5.47 (m, 4H, OCH), 4.90−5.00 (m, 4H, OCH), 4.64−4.75 (m, 4H, OCH), 4.38−4.46 (m, 4H, OCH), 4.25−4.35 (m, 12H, OCH)
Eu(Pc)[Pc(15C5)$_3$] (**5**)[a]	11.02−11.18 [m, 10H, Pc-H$_\alpha$ and Pc(15C5)$_3$-H$_\alpha$], 10.60 [s, 2H, Pc(15C5)$_3$-H$_\alpha$], 10.52 [s, 4H, Pc(15C5)$_3$-H$_\alpha$], 9.02−9.16 [m, 1 H, Pc-H$_\beta$ and Pc(15C5)$_3$-H$_\beta$], 6.02−6.16 (m, 6H, OCH), 5.40−5.52 (m, 6H, OCH), 4.96−5.04 (m, 6H, OCH), 4.74−4.82 (m, 6H, OCH), 4.40−4.50 (m, 6H, OCH), 4.20−4.38 (m, 18H, OCH)
Eu(Pc)[Pc(15C5)$_4$] (**6**)[a]	11.20−11.28 (m, 8 H, Pc-H$_\alpha$), 10.70 [s, 8H, Pc(15C5)$_4$-H$_\alpha$], 9.14−9.22 (m, 8H, Pc-H$_\beta$), 6.16−6.30 (m, 8H, OCH), 5.48−5.57 (m, 8H, OCH), 5.00−5.12 (m, 8H, OCH), 4.78−4.91 (m, 8H, OCH), 4.46−4.52 (m, 8H, OCH), 4.30−4.53 (m, 24H, OCH)
Eu[Pc(15C5)$_4$]$_2$ (**7**)[a]	10.62 [s, 16H, Pc(15C5)$_4$-H$_\alpha$], 5.98−6.06 (m, 16H, OCH), 5.34−5.44 (m, 16H, OCH), 4.82−4.94 (m, 16H, OCH), 4.65−4.77 (m, 16H, OCH), 4.29−4.41 (m, 16H, OCH), 4.18−4.26 (m, 48H, OCH)

[a] In CDCl$_3$/DMSO-d_6 (1:1). [b] In DMSO-d_6.

IR Spectra. The IR spectra of double-deckers **1**−**7** showed an intense band at 1318−1319 cm^{-1}, which is a marker IR band for the phthalocyanine radical anion.[20] This indi-

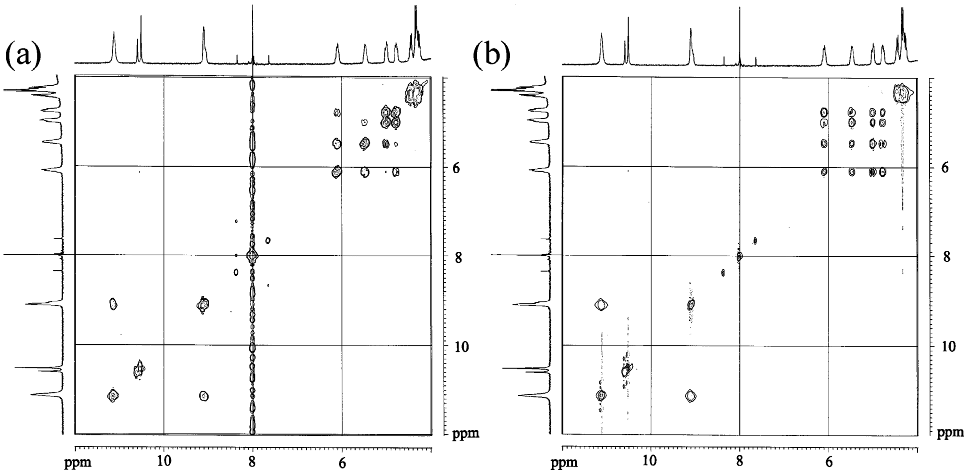

Figure 4. (a) $^1H-^1H$ COSY and (b) TOCSY spectra of Eu(Pc)[Pc(15C5)$_3$] (**5**) in $CDCl_3$/DMSO-d_6 (1:1).

cates the presence of an unpaired electron in one of the phthalocyaninato ligands in these complexes. As found in the IR spectra of the octakis(octyloxy) analogues M[Pc(OC_8H_{17})$_8$]$_2$,[20c−g] the asymmetric C−O−C stretching for **2**−**7** is observed at ca. 1271−1279 cm^{-1}. The intensity of this band increases gradually and reasonably with the increasing number of 15-crown-5 groups, from compound **2** to compound **7**. The spectra for **2**−**7** also showed several strong bands in the region from 2850 to 2925 cm^{-1}, which are attributed to the C−H stretching vibrations of the −CH_2− groups of the 15-crown-5 chains.

Structural Studies. Single crystals of Eu(Pc)[Pc(15C5)$_4$] (**6**) suitable for X-ray diffraction analysis were obtained by slow evaporation of a $CHCl_3$/THF solution of this compound in air. This compound crystallizes in the monoclinic system with a *P2(1)/c* space group with four molecules in one unit cell. The structure also contains solvated $CHCl_3$ and THF from the solvents used for recrystallization. It is worth noting that structurally characterized heteroleptic bis(phthalocyaninato) rare earth complexes remain very rare so far and, to our knowledge, are limited to M(Pc)[Pc(α-OC_5H_{11})$_4$] [M = Sm, Eu, Er; Pc(α-OC_5H_{11})$_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate] reported very recently by our group.[21] Compound **6** thus represents the first heteroleptic bis(phthalocyaninato) complex containing β-substituents that has been structurally characterized.

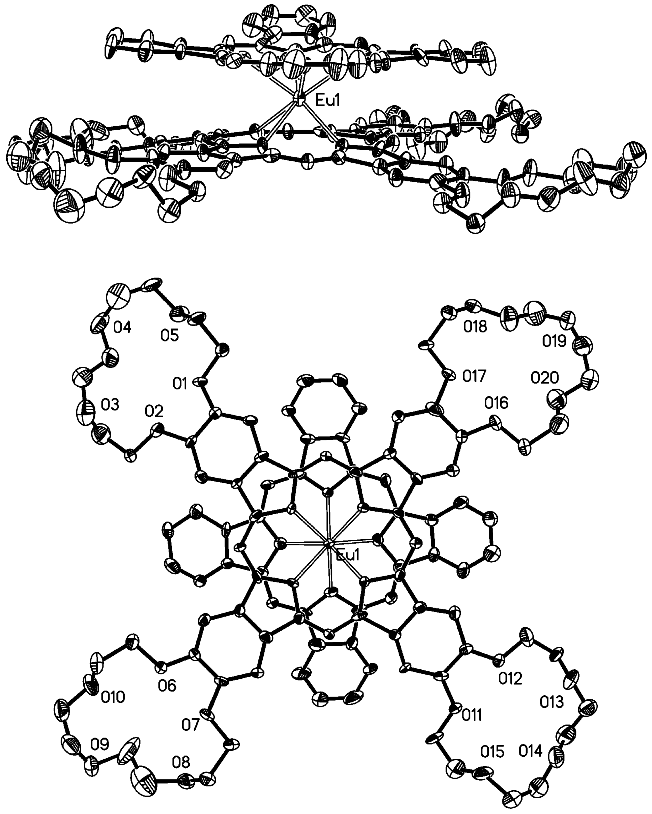

Figure 5. Molecular structure of Eu(Pc)[Pc(15C5)$_4$] (**6**) in the side and top views showing 30% probability thermal ellipsoids for all non-hydrogen atoms.

The molecular structure of Eu(Pc)[Pc(15C5)$_4$] (**6**) in two different perspective views is shown in Figure 5. It can be seen that the europium center is sandwiched between one Pc ligand and one Pc(15C5)$_4$ ring. Both the Pc and Pc(15C5)$_4$ rings adopt a conformation that is domed toward the europium center. The average dihedral angle (ϕ) of the individual isoindole rings with respect to the corresponding N(isoindole)$_4$ mean plane is 7.3 and 7.0° for these two ligands, respectively. The average skew angle of the two rings is 44.9°, showing that the coordination polyhedron of Eu is almost a perfect square antiprism. The displacements of the europium ion from the two N(isoindole)$_4$ mean planes are comparable (Eu−N_4(Pc) = 1.406 and Eu−N_4[Pc(15C5)$_4$] = 1.449 Å), giving a ring-to-ring separation of 2.855 Å.

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Table 4. Half-Wave Redox Potentials of Double-Deckers **1**−**7** in DMF Containing 0.1M $[Bu_4N][ClO_4]$

	Oxd$_1$	Red$_1$	Red$_2$	Red$_3$	Red$_4$	$\Delta E°_{1/2}$[a]	$\Delta E°'_{1/2}$[b]
1	+0.65	+0.29	−1.02	−1.37	−1.68	0.36	1.31
2	+0.61	+0.26	−1.06	−1.39	−1.73	0.35	1.32
3	+0.61	+0.25	−1.04	−1.39	−1.71	0.36	1.29
4	+0.59	+0.24	−1.06	−1.42	−1.79	0.35	1.30
5	+0.62	+0.26	−1.05	−1.39	−1.72	0.36	1.31
6	+0.54	+0.21	−1.05	−1.41		0.33	1.26
7	+0.63	+0.28	−1.04	−1.37		0.35	1.32

[a] $\Delta E°_{1/2}$ = Oxd$_1$ − Red$_1$. [b] $\Delta E°'_{1/2}$ = Red$_1$ − Red$_2$.

Electrochemical Properties. Because of the limited solubility of compounds **2**−**7** in CH_2Cl_2, their electrochemical behavior (as well as that of **1**) was investigated in dry DMF by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). These double-decker complexes displayed an one-electron oxidation labeled as Oxd$_1$ and up to four one-electron reductions labeled as Red$_1$−Red$_4$ within the electrochemical window of DMF. The separation between the reduction and oxidation peak potentials for all the processes lies between 65 and 90 mV, showing their reversible or quasi-reversible nature. All these processes can be attributed to successive removal or addition of one electron to the ligand-based orbitals. The half-wave redox potentials are summarized in Table 4.

The electrochemical properties of all the 15-crown-5-substituted double-deckers, **2**−**7**, are similar to that of the unsubstituted counterpart $Eu(Pc)_2$ (**1**). This can be revealed by the similar potential difference between the first oxidation and the first reduction processes, $\Delta E°_{1/2}$, and between the first reduction and the second reduction processes, $\Delta E°'_{1/2}$, for all the compounds. Both of these values span a very narrow range, 0.33−0.36 and 1.26−1.32 V, respectively, which are also in good agreement with the previously reported results for bis(phthalocyaninato) europium compounds recorded in CH_2Cl_2.[22] The former potential difference is an important value for molecular materials because it predicts some electrical properties such as the thermal activation energy for conduction in the condensed phases derived from these molecular precursors.[23] The latter parameter is related to the potential difference between the first oxidation and first reduction of $[Eu(Pc')_2]^-$, and thus represents the HOMO−LUMO gap of these bis(phthalocyaninato) europium complexes. The present results thus suggest that β-substitution with 15-crown-5 groups does not significantly affect the π−π interactions between the two phthalocyanine rings.

Formation of Tetrameric Phthalocyanine Supramolecular Structures. The K^+- and Rb^+-induced cofacial dimer formation of monomeric phthalocyanine derivatives substituted with three or four 15-crown-5 voids, in a two-step three-stage process, has been well studied by UV−vis, emission, EPR, and NMR techniques.[5a,8] The geometric and electronic structures of K^+-induced tetrameric supramolecular structures of bis(phthalocyaninato) lutetium complexes with one or four 15-crown-5 void(s) {i.e., Lu(Pc)[Pc(15C5)$_4$] and Lu(Pc)[Pc(15C5)]} have also been studied by Ishikawa et al. using the EPR method.[6] In the present study, the formation process of K^+-induced tetrameric supramolecular structures of 15-crown-5-substituted bis(phthalocyaninato) europium complexes, in particular Eu(Pc)[Pc(15C5)$_3$] (**5**) and Eu(Pc)-[Pc(15C5)$_4$] (**6**), has been studied in $CHCl_3$ mixed with a trace amount of MeOH. According to previous studies,[5a,8] K^+-induced cofacial dimerization of phthalocyanines with three or four 15-crown-5 voids is always accompanied by a decrease of the Q band and a concomitant blue shift of this band, as well as the Soret band. Figure 6 shows the changes in the absorption spectra of **5** and **6** from the addition of CH_3COOK dissolved in $CHCl_3$/MeOH (9:1 v/v). It can be seen that, after the addition of the K^+ ions, the intense Q band at 673 or 674 nm gradually attenuates in intensity and a new peak appears at 664 or 661 nm for **5** and **6**, respectively, which can be attributed to the cofacial tetrameric supramolecules {Eu(Pc)[Pc(15C5)$_3$]}$(K^+)_3${Eu(Pc)[Pc(15C5)$_3$]} [(**5**)$(K^+)_3$(**5**)] and {Eu(Pc)[Pc(15C5)$_4$]}$(K^+)_4${Eu(Pc)[Pc-(15C5)$_4$]} [(**6**)$(K^+)_4$(**6**)]. The Soret bands at 326 and 331 nm for **5** and **6** also shift to the shorter wavelength (324 nm) upon addition of K^+. Similar results were observed for double-deckers **2**−**4**, but the changes were less remarkable (Figure S1, Supporting Information). After they remain steady, upon addition of excess K^+ ions, the electronic absorption spectra can be attributed to the tetrameric supra-

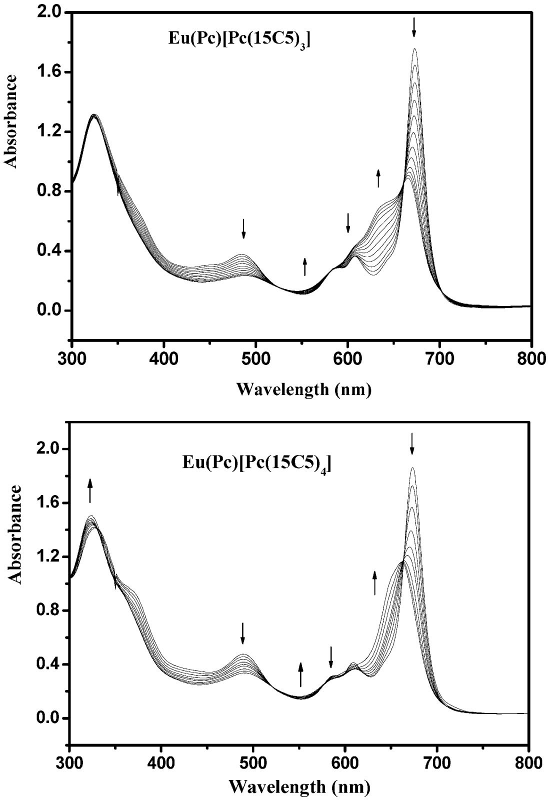

Figure 6. Changes in absorption spectra of Eu(Pc)[Pc(15C5)$_3$] (**5**) and Eu(Pc)[Pc(15C5)$_4$] (**6**) in $CHCl_3$ upon titration with KOAc in $CHCl_3$/MeOH (9:1 v/v). Arrows indicate the direction of the spectral changes. The final spectra were obtained when $[CH_3COOK]/[compound] = 13.0$ (for **5**) or 8.0 (for **6**).

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Table 5. Electronic Absorption Data for the Supramolecular Tetramers (ST) Formed from the Bis(phthalocyaninato) Europium Complexes **2**−**6** in $CHCl_3$ upon Titration with KOAc in $CHCl_3$/MeOH

compound	λ_{max}/nm (log ϵ)									
ST2	324 (4.78)	345 (sh)	460 (5.35)	476 (4.16)	588 (sh)	607 (4.21)		672 (4.88)	904 (3.32)	1604 (3.82)
ST3	327 (4.96)	345 (sh)	456 (sh)	478 (4.22)	588 (sh)		633 (4.76)	671 (4.90)	904 (3.56)	1606 (3.99)
ST4	325 (4.95)	346 (sh)	454 (sh)	478 (4.31)	587 (sh)	610 (sh)	636 (4.55)	672 (4.99)	904 (3.64)	1604 (4.05)
ST5	322 (4.89)	354 (sh)		484 (4.14)	584 (sh)		637 (4.64)	664 (4.77)	904 (3.53)	1594 (3.94)
ST6	324 (4.93)	354 (sh)		491 (4.27)	590 (sh)			661 (4.82)	898 (3.41)	1592 (3.92)

molecular structures. These spectra are given in Figure S2 (Supporting Information), and the data are summarized in Table 5.

It is worth noting that the characteristic near-IR bands were still observed for all the double-deckers (**2**−**6**) after the addition of KOAc (Table 5). This showed that the hole remains in the individual double-deckers in the tetrameric supramolecular structures.

To monitor the supramolecular formation, the changes in absorption of the so-called double-decker band (at 674 nm) and the tetramer band (at 661 nm) for **6** were recorded as a function of $[K^+]/[\mathbf{6}]$. As shown in Figure 7, the concomitant change of the two characteristic bands indicates that upon addition of K^+ ions, double-decker **6** is converted exclusively to the tetrameric supramolecular structure. The formation process is similar to that of $M[Pc(15C5)_4]$ ($M = H_2$, Zn, Co, Ni, Cu) and related phthalocyanine derivatives in $CHCl_3$. However, probably because of the involvement of the large unsubstituted phthalocyaninato ligand and the domed structure of the phthalocyanine rings in **6**, about 4-fold K^+ ions (i.e., $[K^+]/[\mathbf{6}] \approx 4$) are required to reach a steady state (Figure 7), instead of the value of 2 observed for the monomeric phthalocyanine counterparts.[5a,8] The results suggest that the tetrameric supramolecular structure of double-decker **6** is more difficult to form.

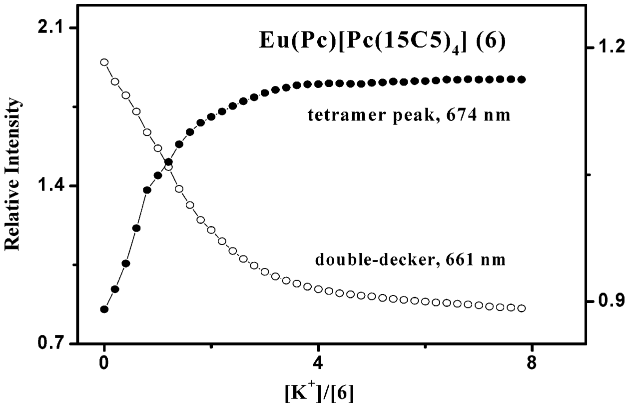

Figure 7. Variation of the absorbance at 674 and 661 nm during titration of **6** in $CHCl_3$ with KOAc in $CHCl_3$/MeOH (9:1). The curve going up with $[K^+]$ represents the change at tetramer peak and should be referred to the right axis, while that going down is the change at double-decker peak and should be referred to the left axis.

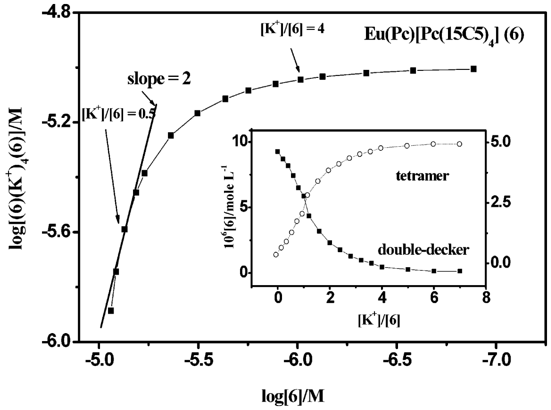

Figure 8. Plots of log [**6**] versus log [(**6**)$(K^+)_4$(**6**)] for $Eu(Pc)[Pc(15C5)_4]$ (**6**) in $CHCl_3$/MeOH. The inset shows the dependence of double-decker and tetramer concentrations on $[K^+]/[\mathbf{6}]$.

Equation 1 shows the equilibrium between double-decker **6** (upon addition of K^+ ions) and the corresponding tetramer. According to the method described by West and Pearce,[24] the double-decker and tetramer concentrations could be calculated from the spectral changes during titration, and their relationship can be depicted as shown in Figure 8 for the present system. The region with a slope of ca. 2.0 indicates that tetramerization occurs in this region. For the present system, this includes the data point of $[K^+]/[\mathbf{6}] = 0.5$. When $[K^+]/[\mathbf{6}] > 4$, the slope of the plot approaches zero, also indicating the difficulty in forming the tetrameric supramolecular structure from **6**.

$$nK^+ + 2Eu(Pc)[Pc(15C5)_4] \leftrightarrow \text{tetramer}\cdot K^+_n \qquad (1)$$

Conclusion

In summary, we have prepared a series of heteroleptic bis(phthalocyaninato) europium(III) complexes with one phthalocyanine ligand containing different numbers and positions of 15-crown-5 substituents. It has been found that all the heteroleptic double-deckers (**2**−**6**) and the homoleptic analogues (**1** and **7**) display very similar absorption features, indicating that the electronic absorption spectra of these compounds are dominated by the strong $\pi-\pi$ interactions between the two phthalocyanine rings. Electrochemical studies confirm that the peripheral substitution with 15-crown-5 groups does not have a significant effect on the $\pi-\pi$ interactions. The cofacial tetrameric supramolecular structures of double-deckers, in particular **5** and **6**, are also formed through a two-step three-stage process in $CHCl_3$ with trace amount of MeOH in the presence of K^+. However, the

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(24) Pearce, S.; West, W. P. *J. Phys. Chem.* **1965**, *69*, 1894−1903.

formation of these supramolecular tetramers occurs less readily than the formation of supramolecular dimers from the monomeric phthalocyanine analogues.

Experimental Section

General Remarks. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and phthalonitrile were purchased from Aldrich. *n*-Pentanol and *N*,*N*-dimethylformamide (DMF), for the voltammetric studies, were freshly distilled from Na and CaH_2, respectively, under nitrogen. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. All other reagents and solvents were used as received. The compounds 4,5-dicyanobenzo-15-crown-5,[5,25] Eu(acac)$_3$·H_2O,[26] Eu(Pc)$_2$ (**1**),[15] and Eu[Pc(15C5)$_4$]$_2$ (**7**)[15] were prepared according to the published procedures.

^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in DMSO-d_6 or $CDCl_3$/DMSO-d_6 (1:1) with the addition of ca. 1% hydrazine hydrate. Spectra were referenced internally using the residual solvent resonance ($\delta = 2.49$ for DMSO-d_6) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Magnetic circular dichroism (MCD) measurements were made with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields (both parallel and antiparallel) of up to 1.09 T. Its magnitude was expressed in terms of molar ellipticity per tesla $[\theta]_M/10^4$ deg mol^{-1} dm^3 cm^{-1} T^{-1}. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh-resolution mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell had inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag$^+$, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe$^+$/Fe) couple [$E_{1/2}$ (Fe$^+$/Fe) = 501 mV vs SCE]. Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in DMF containing 0.5 mmol dm^{-3} of sample was purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rates were 20 and 10 mV s^{-1} for CV and DPV, respectively.

Preparation of Eu(Pc)(acac). A mixture of Eu(acac)$_3$·H_2O (0.10 mmol), dicyanobenzene (0.4 mmol), and DBU (0.5 mmol) in *n*-pentanol (3 mL) was heated at 100 °C for 1.5 h under a slow stream of nitrogen. After the volatiles were removed in vacuo, the residue was chromatographed on a silica gel column with $CHCl_3$ with 2.5% (by volume) of methanol as eluent to give a blue band containing Eu(Pc)(acac) (23 mg, 30%).

Preparation of Compounds 2−6. A mixture of Eu(Pc)(acac) (382 mg, 0.50 mmol), dicyanobenzene (128 mg, 1.0 mmol), 4,5-dicyanobenzo-15-crown-5 (318 mg, 1.0 mmol), and DBU (400 mg, 2.6 mmol) in *n*-pentanol (10 mL) was refluxed for 12 h under a slow stream of nitrogen. Hexane (100 mL) was added into the reaction solution after it had been cooled to room temperature. The precipitate was filtered and washed with hexane, then subjected to chromatography on a silica gel column with $CHCl_3$ as eluent. A trace amount of Eu(Pc)$_2$ (**1**) was removed; then the column was eluted with $CHCl_3$ with 5% (by volume) of methanol to give a green band containing Eu(Pc)[Pc(15C5)] (**2**). This was followed by four other green bands containing Eu(Pc)[Pc(opp-15C5)$_2$] (**3**), Eu(Pc)[Pc(adj-15C5)$_2$] (**4**), Eu(Pc)[Pc(15C5)$_3$] (**5**), and Eu(Pc)-[Pc(15C5)$_4$] (**6**) eluting down with 1, 1.5, 2, and 3% MeOH in $CHCl_3$, respectively. After the solvent was removed in vacuo, the residue was rechromatagraphed under similar conditions followed by recrystallization from $CHCl_3$/hexane to give the target compounds Eu(Pc)[Pc(15C5)] (**2**) (13%), Eu(Pc)[Pc(opp-15C5)$_2$] (**3**) (5%), Eu(Pc)[Pc(adj-15C5)$_2$] (**4**) (8%), Eu(Pc)[Pc(15C5)$_3$] (**5**) (12%), and Eu(Pc)[Pc(15C5)$_4$] (**6**) (11%).

Table 6. Crystallographic Data for **6**

	6·$2C_4H_8O$•$2CHCl_3$
molecular formula	$C_{106}H_{98}Cl_6EuN_{16}O_{22}$
M	2312.66
cryst syst	monoclinic
space group	*P*
a/Å	22.596(8)
b/Å	27.343(9)
c/Å	17.762(6)
β/°	103.777(6)
U/Å^3	10658(7)
Z	4
D_c/Mg m^{-3}	1.441
μ/mm^{-1}	0.817
data collection range/deg	1.75−25.00
reflns measured	53 976
independent reflns	18 436 ($R_{int} = 0.1639$)
params	1360
R1 [$I > 2\sigma(I)$]	0.0787
wR2 [$I > 2\sigma(I)$]	0.1837
GOF	1.009

X-ray Crystallography. Crystal data and details of thedata collection and structure refinement are given in Table 6. Data were collected on a Bruker SMART CCD diffractometer with an Mo Kα sealed tube ($\lambda = 0.71073$ Å) at 293 K, using an ω scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 1290 frames. Final unit cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS was used for integration of intensity of reflections and scaling,[27] and SADABS was used for absorption correction.[28] SHELXL was used for space group and structure determination, refinements, graphics, and structure reporting.[29].

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Supporting Information Available: Changes in the absorption spectra of **2**−**4** in $CHCl_3$ upon titration with KOAc in $CHCl_3$/MeOH (9:1 v/v) and the UV−vis absorption spectra of double-deckers **2**−**6** and the corresponding tetramers in $CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC-274947 contains the supplementary crystallographic data for this paper and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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