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A Decade Journey in the Chemistry of Sandwich-Type Tetrapyrrolato–Rare Earth Complexes

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CONSPECTUS

Phthalocyanines and porphyrins are versatile functional pigments with a wide range of applications. These macrocyclic compounds contain four isoindole or pyrrole nitrogen atoms, which can complex with a range of metal ions. Large rare earth metal ions can bring together these tetrapyrrole derivatives to form sandwich-type double- and triple-decker complexes. Depending on the metal centers and the nature of the macrocyclic ligands, these compounds exhibit tunable spectroscopic, electronic, and redox properties, and different extents of intramolecular $\pi-\pi$ interactions. Some of the properties of the sandwich-type complexes are unique and enable them to be used as advanced materials for various applications. Over the last two decades, a vast number of homoleptic and heteroleptic double- and triple-decker complexes have been synthesized. With improvements in synthetic procedures, researchers have prepared novel sandwich complexes that could not have been prepared by traditional methods.
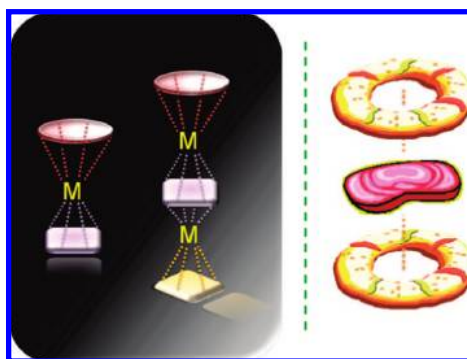
This Account highlights our work over the last decade on this important class of compounds. We have focused both on the development of facile and efficient synthetic methodology and on the various properties and potential applications of these complexes. For both the double- and triple-decker series, we have performed systematic investigations on several series of closely related analogues to reveal the correlations among the structures, electronic properties, spectroscopic characteristics, electrochemistry, and degree of $\pi-\pi$ interactions. We have also performed detailed studies of the self-assembly of amphiphilic analogues in Langmuir–Blodgett films, metal-induced assembly of crown ether containing sandwich compounds, and the use of these complexes in organic field-effect transistors.

Introduction

Tetrapyrrole derivatives such as porphyrins, phthalocyanines, and naphthalocyanines are versatile functional pigments that have found widespread applications.[1] These macrocyclic compounds contain four pyrrole or isoindole nitrogen atoms, which are able to complex with a range of metal ions. With large metal centers that favor octacoordination (e.g., rare earths, actinides, group 4 transition metals, and several main group elements such as In, Sn, As, Sb, and Bi), sandwich-type complexes in the form of double- (A) and triple-deckers (B) can be formed (Figure 1).[2] Due to the intramolecular $\pi-\pi$ interactions and the intrinsic nature of the metal centers, these novel complexes display characteristic features that cannot be found in their nonsandwich counterparts, enabling them to be used in different areas such as field effect transistors,[3] molecular magnets,[4] molecular-based multibit information storage materials,[5] and receptors for metal ions, dicarboxylic acids, and saccharides.[6]
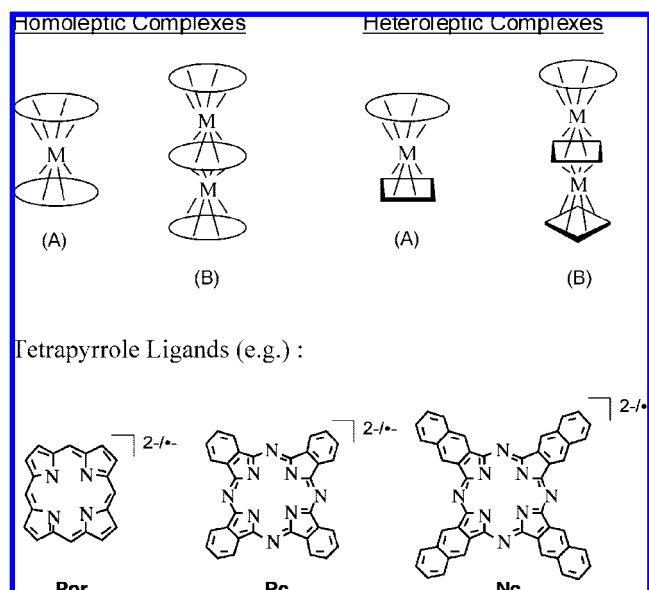
FIGURE 1. Schematic structures of homoleptic and heteroleptic sandwich complexes with tetrapyrrole ligands.

The first bis(tetrapyrrolato)−metal complex [Sn^{IV}(Pc)$_2$] (Pc = phthalocyaninate) was reported as early as in 1936.[7] The bis(phthalocyaninato)−rare earth sandwich analogues have been known since the mid-1960s,[8] while the studies of bis(porphyrinato) counterparts were started in the 1980s.[9] Heteroleptic sandwich compounds with different porphyrinato or phthalocyaninato ligands were not reported till 1986.[10]

Our interest in the chemistry of this class of compounds started in the early 1990s, when we studied a series of homoleptic bis(porphyrinato) rare earth complexes as prospective materials for electronic devices and models for the special pair found in the reaction center protein of photosynthetic bacteria.[11] To facilitate the study of intramolecular $\pi-\pi$ interactions and hole delocalization, we switched our focus several years later to the heteroleptic analogues in which the metal centers are complexed with tetrapyrrole ligands with very different optical and redox properties.[2a] This class of compounds had been extremely rare at that time due to the synthetic barrier. We therefore initiated the work by exploring various facile routes to prepare these compounds, then systematically studied their structural, electronic, optical, and redox properties to reveal the effects of metal centers and the nature of the tetrapyrrole ligands on the $\pi-\pi$ interactions in these double- and triple-decker complexes. Recently, we have also been interested in the supramolecular chemistry of these compounds and their use as advanced materials. With these developed synthetic methodologies, we have recently synthesized a series of amphiphilic analogues and studied their molecular alignment at the liquid−solid interface. The resulting highly ordered supramolecular structures exhibit strong intermolecular $\pi-\pi$ interactions, leading to a superior performance as organic field effect transistors (OFETs).

In this Account, we summarize the progress that we have made over the past decade in the study of this unique class of complexes.

Synthetic Studies

Homoleptic (Na)phthalocyaninato Complexes. Homoleptic bis(phthalocyaninato) rare earth complexes [M^{III}(Pc′)$_2$] (Pc′ = general phthalocyaninate) are usually prepared by cyclic tetramerization of the corresponding phthalonitriles in the presence of rare earth salts and an organic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[12] Alternatively, reactions of [Li$_2$Pc′] or H$_2$Pc′ with rare earth salts in a high-boiling solvent also lead to the formation of these double-deckers.[12a] Homoleptic tris(phthalocyaninato) rare earth complexes [M^{III}$_2$(Pc′)$_3$] can also be prepared in a similar manner but generally in a lower reaction yield.[13,14]

Similarly, the unsubstituted bis(2,3-naphthalocyaninato)lutetium(III) [Lu^{III}(Nc)$_2$] was isolated from the reaction of [Li$_2$Nc] with [Lu^{III}(OAc)$_3 \cdot n$H$_2$O].[15] The substituted analogues including {M^{III}[Nc(tBu)$_4$]$_2$} [M = Y, La−Er except Pm; Nc(tBu)$_4$ = 3(4),12(13),21(22),30(31)-tetra-$tert$-butyl-2,3-naphthalocyaninate] and {Eu^{III}[Nc(SC$_{12}$H$_{25}$)$_8$]$_2$} [Nc(SC$_{12}$H$_{25}$)$_8$ = 3,4,12,13,21,22,30,31-octakis(1-dodecylthio)-2,3-naphthalocyaninate] were prepared by the DBU-promoted cyclization of the corresponding naphthalonitriles in the presence of [M^{III}(acac)$_3 \cdot n$H$_2$O] (acac = acetyl acetonate) in refluxing n-octanol.[16]

Heteroleptic (Na)phthalocyaninato Complexes. There are generally three synthetic methods for double-deckers with two different phthalocyaninato ligands [M^{III}(Pc′)(Pc″)] (Pc″ = another general phthalocyaninate). The first method involves a mixed cyclization of the two corresponding phthalonitrile precursors in the presence of a metal salt, which as expected will lead to a mixture of differently substituted bis(phthalocyaninato) complexes. The second pathway involves the treatment of a rare earth salt with the two macrocycles. As expected, the reaction also produces a substantial amount of the homoleptic complexes [M^{III}(Pc′)$_2$] and [M^{III}(Pc″)$_2$] as the side products. The third route employs the half-sandwich complexes [M^{III}(Pc′)(acac)] as templates, which induce cyclic tetramerization of the other phthalonitriles in the presence of DBU.[17] By using this method, the purification of the desired heteroleptic complexes can be greatly simplified. This pathway can also be used to prepare heteroleptic naphthalocyaninato and phthalocyaninato complexes including {M^{III}(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$]} [M = Y, Sm, Eu; Pc(α-OC$_5$H$_{11}$)$_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate], {Sm^{III}(Nc)-

SCHEME 1. Synthesis of Homo- and Heterodinuclear Tris(phthalocyaninato) Lanthanide Complexes {(Pc)M[III][Pc(β-OC$_8$H$_{17}$)$_8$]M′[III](Pc)}. Reproduced with Permission from Ref 19a. Copyright Wiley-VCH Verlag GmbH & Co. KGaA
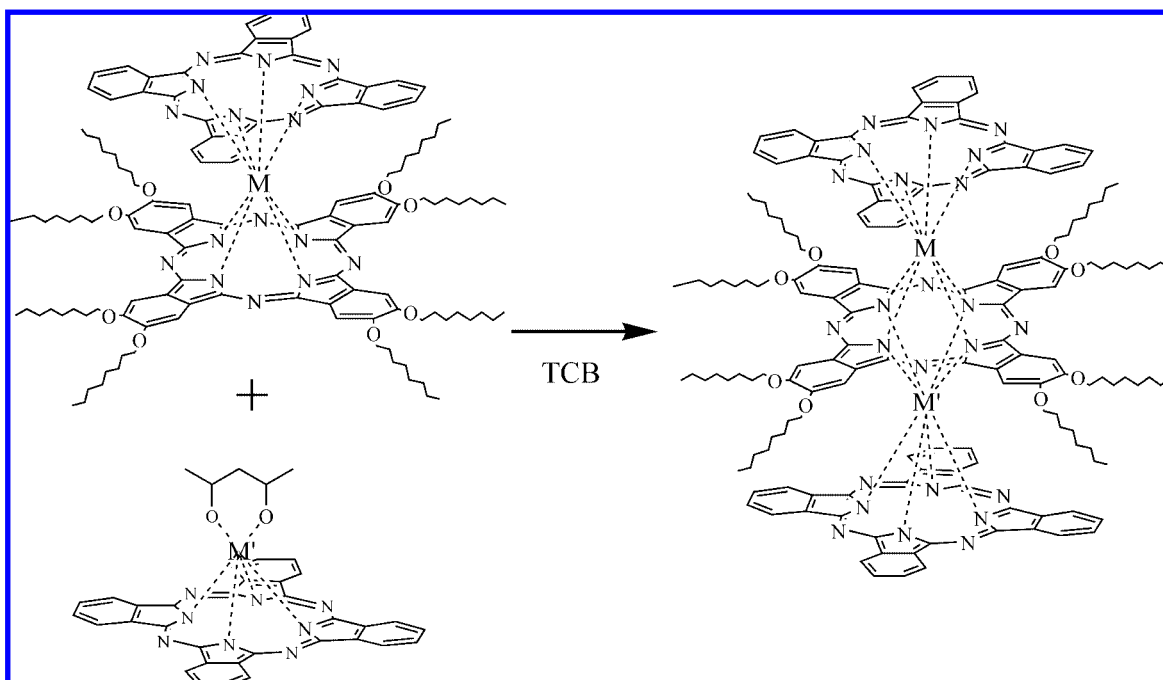
[Pc(β-O$_5$H$_{11}$)$_4$]} [Pc(β-OC$_5$H$_{11}$)$_4$ = 2(3),9(10),16(17),24(25)-tetra-kis(3-pentyloxy)phthalocyaninate], {Sm[III](Nc)[Pc(β-OC$_8$H$_{17}$)$_8$]} [Pc(β-OC$_8$H$_{17}$)$_8$ = 2,3,9,10,16,17,23,24-octakis(1-octyloxy)-phthalocyaninate], and {Sm[III][Nc(*t*Bu)$_4$](Pc)}.[18]

Heteroleptic tris(phthalocyaninato) complexes with two different phthalocyaninato ligands can be prepared by the raise-by-one-story method.[19] For example, the series of complexes {(Pc)M[III][Pc(β-OC$_8$H$_{17}$)$_8$]M′[III](Pc)} (M = M′ = Gd−Lu; M = Lu, M′ = Gd−Yb) were prepared by treating [M[III](Pc)(acac)] with the double-deckers {M′[III](Pc)[Pc(β-OC$_8$H$_{17}$)$_8$]} in refluxing 1,2,4-trichlorobenzene (TCB) (Scheme 1).[19a]

Mixed (Na)phthalocyaninato and Porphyrinato Complexes. Previously, mixed (phthalocyaninato)(porphyrinato)−rare earth double-decker complexes were usually prepared by treating [Li$_2$Pc] with [M[III](Por′)(acac)] (Por′ = general porphyrinate), generated in situ from [M[III](acac)$_3$·*n*H$_2$O] and H$_2$Por′, or the reaction of [Li$_2$Pc] with [M[III](acac)$_3$·*n*H$_2$O] followed by the treatment with H$_2$Por′.[20] However, the aforementioned half-sandwich-template pathway was found to be more convenient and efficient in terms of the reaction yield and the ease of purification. Treatment of [M[III](Por′)(acac)] with an excess of various phthalonitriles in the presence of DBU in amyl alcohol affords the corresponding [M[III](Pc′)(Por′)] readily in good yields.[12b,21] The naphthalocyaninato analogues [M[III](Nc)(Por)] [Por = octaethylporphyrinate (OEP), *meso*-tetrakis(4-*tert*-butylphenyl)porphyrinate (TBPP)] can also be prepared by this method.[22,23]

Treatment of the half-sandwich complexes [M[III](TClPP)(acac)] [*meso*-tetrakis(4-chlorophenyl)porphyrinate (TClPP)] with [Li$_2$Pc] gives a mixture of the mixed triple-deckers [M[III]$_2$(Pc)(TClPP)$_2$] and [M[III]$_2$(Pc)$_2$(TClPP)].[24] Alternatively, the raise-by-one-story procedure can also be used to prepare these complexes. For example, reaction of [M[III](Por′)(acac)] [M = Y, Gd, Lu; Por′ = OEP, *meso*-tetraphenylporphyrinate (TPP)] with the double-deckers [M′[III](Pc)(TPP)] (M′ = La, Ce) affords the corresponding heteronuclear triple-deckers [(TPP)M′[III](Pc)M[III](Por′)] (Por′ = OEP, TPP).[25] The mixed naphthalocyaninato and porphyrinato analogues [M[III]$_2$(Nc)(OEP)$_2$] (M = Nd, Eu) can be prepared similarly.[22]

Effects of the Macrocyclic Ligands and the Metal Centers. The reaction yields of sandwich-type complexes are dependent on both the nature of the tetrapyrrole ligands and the size of the metal centers. For the series of bis(phthalocyaninato) complexes, the yields are lower for those with a larger metal center.[17a] This result is in contrast with the trend observed for the naphthalocyaninato and porphyrinato analogues {M[III][Nc(*t*Bu)$_4$]$_2$}[16a] and [M[III](OEP)$_2$],[2b] and the mixed (naphthalocyaninato)(porphyrinato) complexes [M[III](Nc)(Por′)] (Por′ = OEP, TBPP).[22,23] For the mixed (phthalocyaninato)(porphyrinato) counterparts [M[III](Pc)(TClPP)], the yield increases from 2% (for M = La) to 36% (for M = Y), then decreases steadily to 11% (for M = Lu).[21b] A similar trend was observed for the mixed triple-deckers [M[III]$_2$(Pc)(TClPP)$_2$] and [M[III]$_2$-(Pc)$_2$(TClPP)].[24] The yields are higher for rare earth ions with

SCHEME 2. Synthesis of Protonated and Nonprotonated Double-Decker Complexes. Reproduced with Permission from Ref 27. Copyright Wiley-VCH Verlag GmbH & Co. KGaA
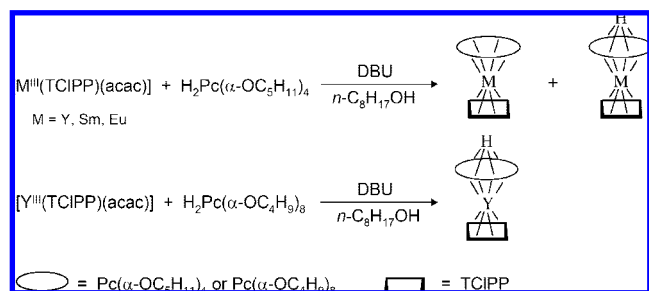
a moderate size, while for both the early and late rare earth analogues, the yields are generally lower. Attempts to isolate the late lanthanide complexes [M_2^{III}(Pc)(TClPP)$_2$] (M = Er to Lu) and [M^{III}_2(Pc)$_2$(TClPP)] (M = Tm to Lu) have not been successful so far.

In addition to the metal centers, the nature of the tetrapyrrole ligands is also important in the preparation of these complexes. In the preparation of bis(phthalocyaninato) double-decker complexes, the use of unsubstituted or β-alkoxy-substituted phthalocyaninato ligands leads to the isolation of [M^{III}(Pc')$_2$] as the sole product. However, when the octa-α-substituted analogue 1,4,8,11,15,18,22,25-octakis(1-butyloxy)-phthalocyanine [H_2Pc(α-OC_4H_9)$_8$] is used, reaction with [Sm^{III}-(Pc)(acac)] gives the protonated double-decker {Sm^{III}H(Pc)[Pc(α-OC_4H_9)$_8$]}.[26] Similarly, treatment of [M^{III}(TClPP)(acac)] (M = Y, Sm, Eu) with the metal-free phthalocyanine [H_2Pc(α-OC_5H_{11})$_4$] results in the isolation of both the nonprotonated double-deckers {M^{III}[Pc(α-OC_5H_{11})$_4$](TClPP)} (M = Y, Sm, Eu) and the protonated analogues {M^{III}H[Pc(α-OC_5H_{11})$_4$(TClPP)} (M = Y, Sm, Eu). However, reaction of [Y^{III}(TClPP)(acac)] with H_2Pc(α-OC_4H_9)$_8$ gives exclusively the protonated double-decker {Y^{III}H[Pc(α-OC_4H_9)$_8$](TClPP)} (Scheme 2).[27] These results clearly show that the α-alkoxy substituents of the phthalocyaninato ligand can stabilize the protonated double-deckers.

Crystallographic Molecular Structures

While the molecular structures of virtually the whole series of homoleptic rare earth double-deckers [M^{III}(Pc)$_2$] have been reported, only a few substituted analogues, namely, {Lu^{III}[Pc(SC_6H_{13})$_8$]$_2$} [Pc(SC_6H_{13})$_8$ = 2,3,9,10,16,17,23,24-octakis(1-hexylthio)phthalocyaninate],[28] {Yb^{III}[Pc(15C5)$_4$]$_2$} [Pc(15C5)$_4$ = tetrakis(15-crown-5)phthalocyaninate],[29] and {Y^{III}[Pc(α-OC_5H_{11})$_4$]$_2$}[30] have been structurally characterized so far. Figure 2 shows the molecular structure of the last given as an example to illustrate the structural features of these complexes. The yttrium center is octacoordinated by the isoindole nitrogen atoms of the two tetra-α-substituted
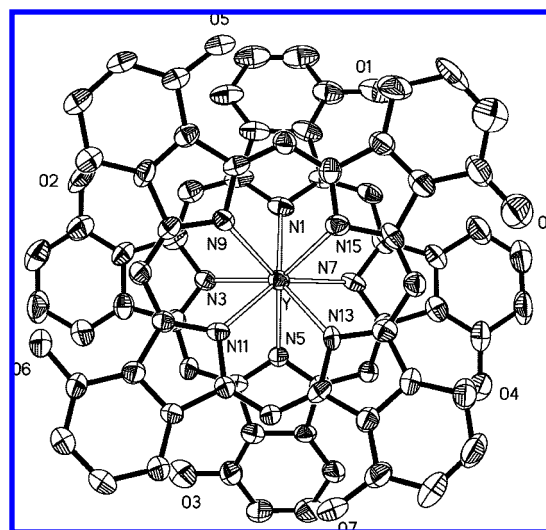

FIGURE 2. Molecular structure of the C_{4h} isomer of {Y^{III}[Pc(α-OC_5H_{11})$_4$]$_2$}. The pentyl groups are omitted for clarity. Reproduced with permission from Ref 30. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

phthalocyaninato ligands. The two ligands are almost fully staggered forming a slightly distorted square antiprism. Thus the compound exhibits a pinwheel-like S_8 symmetry in the solid state. Like the structures of many tetrapyrrole double-decker complexes, the two ligands are not planar and display a saucer shape.

Structurally characterized heteroleptic bis(phthalocyaninato) rare earth complexes are also rare and are limited to {Eu^{III}(Pc)[Pc(15C5)$_4$]},[17b] {M^{III}(Pc)[Pc(α-OC_5H_{11})$_4$]} (M = Sm, Eu, Er),[17a] and {Gd^{III}H(Pc)[Pc(α-OC_4H_9)$_8$]} so far.[31] The last one represents the first structurally determined bis(phthalocyaninato) double-deckers in the reduced form. In the presence of NaOH, the samarium analogue {Sm^{III}H(Pc)[Pc(α-OC_4H_9)$_8$]} forms a new supramolecular structure with a slipped pseudo-quadruple-decker structure in which two anionic double-decker units are linked together by two sodium ions.[26] As shown in Figure 3, each of the two sodium atoms is hexacoordinated by two aza nitrogen atoms and four adjacent butyloxy oxygen atoms from the two Pc(α-OC_4H_9)$_8$ rings, forming a distorted trigonal antiprism. This coordination mode of phthalocyanines is extremely rare.

The triple-decker structures of a series of tris(phthalocyaninato) rare earth compounds including {Lu^{III}_2[Pc(15C5)$_4$]$_3$},[32] {(Pc)M^{III}[Pc(β-OC_8H_{17})$_8$]M^{III}(Pc)} (M = Er, Lu), [19a] {(Pc)Lu^{III}[Pc(β-OC_8H_{17})$_8$]Er^{III}(Pc)},[19a] and {(Pc)M^{III}(Pc)M^{III}[Pc(α-OC_5H_{11})$_4$]} (M = Gd, Lu)[19b] have also been confirmed by single-crystal X-ray diffraction analysis. The molecular structure of {(Pc)Er^{III}[Pc(β-OC_8H_{17})$_8$]Er^{III}(Pc)} is shown in Figure 4 as an example. Each erbium ion is sandwiched between an outer Pc ligand and the central Pc(β-OC_8H_{17})$_8$ ring. The outer Pc rings adopt a dome
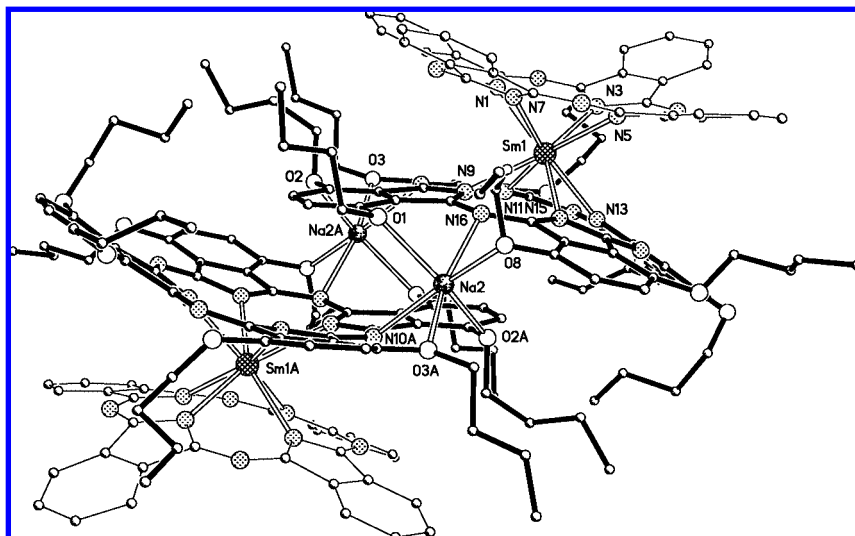
FIGURE 3. Molecular structure of the slipped pseudo-quadruple-decker {NaSm[III](Pc)[Pc(α-OC$_4$H$_9$)$_8$]}$_2$. Hydrogen atoms are omitted for clarity.
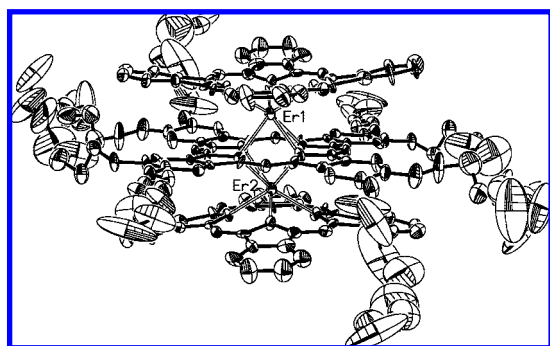

FIGURE 4. Molecular structure of {(Pc)Er[III][Pc(β-OC$_8$H$_{17}$)$_8$]Er[III](Pc)}. Reproduced with permission from Ref 19a. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

FIGURE 5. Plot of the ring-to-ring distance of [M[III](Nc)(OEP)] as a function of the ionic radii of M[III]. The open squares show the positions for hypothetical [Ce[III](Nc)(OEP)] and [Ce[IV](Nc)(OEP)].

shape with a dihedral angle of 9.1° away from the erbium centers. They are staggered with respect to the central Pc(β-OC$_8$H$_{17}$)$_8$ ring by an angle of 43.8°. The average Er−N(Pc) bond distance (2.332 Å) is significantly shorter than the average Er−N[Pc(β-OC$_8$H$_{17}$)$_8$] distance (2.573 Å) because the central [Pc(β-OC$_8$H$_{17}$)$_8$] ligand is shared by two erbium ions while the outer Pc ligands are bound to only one metal ion.

The molecular structures of the whole series of [M[III](Nc)(OEP)] (M = Y, La−Lu except Pm) have also been determined by X-ray diffraction analyses.[22,33,34] They are isostructural, showing a slightly distorted square antiprismatic geometry with two domed ligands. The metal center is octacoordinated by the four isoindole and four pyrrole nitrogen atoms of the Nc and OEP rings, respectively. The ring-to-ring separation between the two domed ligands, as defined by the two N$_4$ mean planes, decreases monotonically from 3.056 to 2.652 Å along the series of La to Lu as a result of lanthanide contraction. As shown in Figure 5, the cerium complex [Ce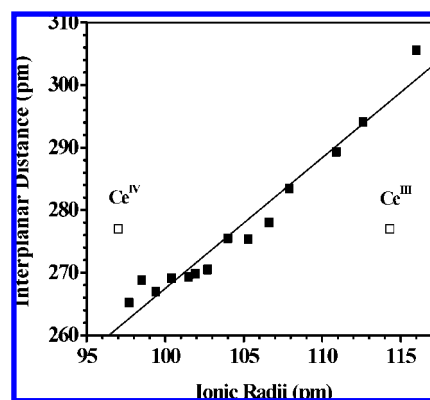(Nc)(OEP)] is the only exception. The line is flanked by two hypothetical points generated by taking the ionic radii of cerium(III) and cerium(IV) ions. The unique behavior of this cerium compound can be attributed to the fact that the cerium center adopts an intermediate valence between +3 and +4, which has been supported by a range of spectroscopic and electrochemical methods.[34] Additionally, the symmetrical molecular structure for the triple-decker [(OEP)Nd[III](Nc)Nd[III](OEP)] has also been established by single-crystal X-ray diffraction analysis.[22]

Probing the π−π Interactions through Spectroscopic and Electrochemical Studies

Systematic studies of the electronic absorption spectra for the whole series of rare earth sandwich complexes are useful in understanding the nature of electronic transitions and the extent of π−π interactions. Taking the absorption spectra of {M[III][Pc(β-OC$_8$H$_{17}$)$_8$]$_2$} (M = Y, La−Tm except Ce and Pm) as examples, they exhibit split Soret bands with maxima around
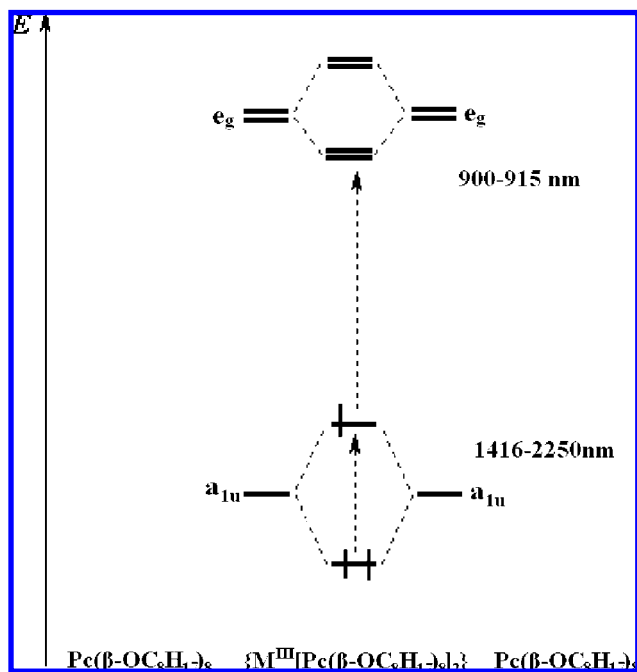
FIGURE 6. A simplified molecular orbital diagram for $\{M^{III}[Pc(\beta\text{-}OC_8H_{17})_8]_2\}$.

FIGURE 7. Plot of the wavenumbers of the two Q bands of $\{(Pc)M^{III}[Pc(\beta\text{-}OC_8H_{17})_8]M^{III}(Pc)\}$ (M = Gd−Lu) (filled symbols) and $\{(Pc)Lu^{III}[Pc(\beta\text{-}OC_8H_{17})_8]M^{III}(Pc)\}$ (M = Gd−Yb) (open symbols) as a function of the ionic radius M^{III} and the mean ionic radius of Lu^{III} and M^{III}, respectively. Reproduced with permission from Ref 19a. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

335−343 and 369−374 nm, an intense Q-band at 672−699 nm, two π-radical related bands at 485−513 and 900−915 nm, and the ring-to-ring charge transfer transition band(s) in the near IR region between 1416 and 2250 nm.[12c] All the absorptions are sensitive to the metal center. Along with the decrease of the ionic radius from La^{III} to Tm^{III}, most of the absorptions, especially the longest-wavelength ring-to-ring charge transfer transition band, are monotonically blue-shifted. A linear correlation exists between the energy of the ring-to-ring charge transfer transition and the M^{III} ionic radius. Similar results were observed for the bis(naphthalocyaninato),[16a] mixed [(na)phthalocyaninato](porphyrinato),[21b,22,23] and reduced bis(phthalocyaninato)[12c] rare earth complexes.

A simplified molecular orbital diagram for $\{M^{III}[Pc(\beta\text{-}OC_8H_{17})_8]_2\}$ constructed from the a_{1u} and e_g orbitals of the two ligands is given in Figure 6.[27] The weak absorption at 900−915 nm, which shifts slightly to the red with decreasing the size of the metal center, is due to the electronic transition from the semioccupied orbital to the degenerate LUMO. The lowest-energy near-IR band at 1416−2250 nm is due to the transition from the second-highest occupied orbital to the semioccupied orbital.[27] The energy involved, which reflects the extent of electronic coupling between the two macrocycles, increases from M = La to Tm. This suggests that the interaction between the two rings becomes weaker as the size of the metal center increases.
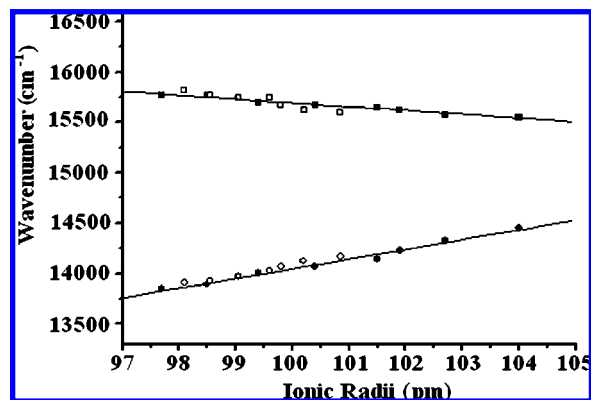
The tris(phthalocyaninato)[19a] and mixed (phthalocyaninato)-(porphyrinato)[24] triple-deckers also have similar spectral features. For example, in the electronic absorption spectra of $\{(Pc)M^{III}[Pc(\beta\text{-}OC_8H_{17})_8]M^{III}(Pc)\}$ (M = Gd−Lu), the phthalocyanine Q bands appear as a very strong absorption around 634−643 nm together with a weak satellite around 692−722 nm.[19a] Along with the decrease in the size of the metal center, the former absorption takes a blue-shift, while the latter is shifted to the red. For the heterodinuclear analogues $\{(Pc)Lu^{III}[Pc(\beta\text{-}OC_8H_{17})_8]M^{III}(Pc)\}$ (M = Gd−Yb), the energies of the two Q bands are also correlated linearly with the mean ionic radius of the two metal centers (Figure 7).

In the IR and Raman spectra of the phthalocyaninato double- and triple-decker complexes, characteristic bands have been observed for the macrocyclic ligands for their different vibrational modes including breathing, isoindole stretching, aza stretching, and coupling of isoindole and aza stretching. Most of these bands also depend on the size of the metal centers, shifting to higher wavenumbers along with the lanthanide contraction. This also indicates an increase in $\pi-\pi$ interactions across the series.[35]

The electrochemistry of several series of double-decker complexes has been systematically studied.[21b,22,36] Figure 8 shows the variation of the redox potentials of $[M^{III}(Pc)_2]$ with the ionic radius of the metal center.[36] The first oxidation and the first reduction potentials are shifted slightly to the negative direction as the size of the metal center decreases. The second oxidation potentials are also dependent linearly on the ionic radius of the metal center, but in an opposite trend. The half-wave potentials of the second, third, and fourth reductions are essentially independent of the metal center. It is
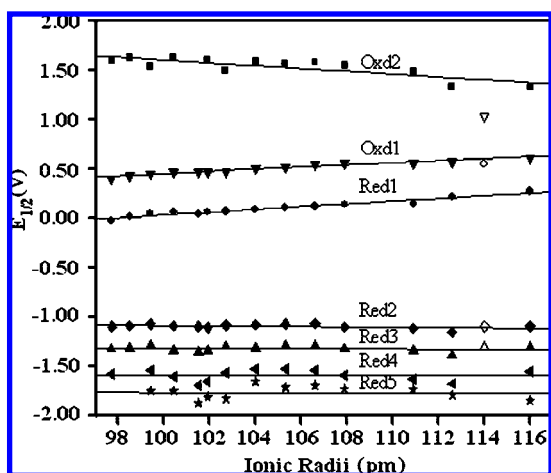
FIGURE 8. Plot of half-wave potentials of the redox processes of $[M^{III}(Pc)_2]$ as a function of the ionic radius of M^{III}. Reproduced with permission from Ref 36. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.
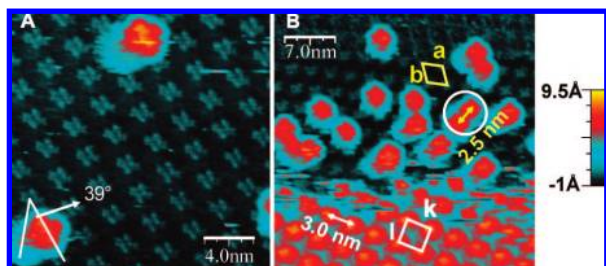

FIGURE 9. STM images of $\{Sm^{III}(Nc)[Pc(\beta-OC_8H_{17})_8]\}$ coadsorbed with $H_2Pc(\beta-OC_8H_{17})_8$ on HOPG: (A) an area of isolated double-decker molecules; (B) an area showing the aggregated double-decker molecules. Red and blue dots correspond to the double-decker and the metal-free phthalocyanine, respectively.

worth noting that the potential difference between the first and second reductions of $[M^{III}(Pc)_2]$ actually corresponds to the potential difference between the first oxidation and the first reduction of $[M^{III}(Pc)_2]^-$. The value, ranging from 1.08 to 1.37 V across the series, gradually diminishes with the decrease of rare earth radius. This clearly indicates an enhanced $\pi-\pi$ interaction in the double-deckers as the size of the metal center decreases. Similar results have also been found for the heteroleptic tris(phthalocyaninato) analogues.[37]

Tuning the Valence of the Cerium Center with Regard to Cerium Double-Decker Complexes

It has been found that except for the series $\{M^{III}[Nc(tBu)_4]_2\}$,[16a] the cerium double-deckers always show different electronic absorption and electrochemical properties from the whole series of tervalent rare earth analogues. To resolve and clarify this issue, a series of cerium double-deckers using a range of tetrapyrrole ligands with different electronic properties have

been synthesized and studied systematically on their electrochemical and spectroscopic properties.[34] The results demonstrate that the valent state of the cerium center varies from III to IV depending on the electronic nature of the two tetrapyrrole ligands. As revealed by X-ray absorption near-edge structure (XANES) study, the valence of the cerium center is 3.59 for $\{Ce[Pc(\beta-OC_5H_{11})_8]_2\}$ and 3.68 for $[Ce(Pc)(TPyP)]$ [TPyP = *meso*-tetra(4-pyridyl)porphyrinate] and $[Ce(Nc)(OEP)]$, while that in $\{Ce[Nc(tBu)_4]_2\}$ is virtually 3.

Location of the Hole and Acid Proton in Double-Decker Complexes

For the rare earth(III) double-decker series (except for cerium), all the neutral complexes can be formulated as $[M^{III}(ring-1^{2-})(ring-2^{\bullet-})]$, which contain a hole in one of the two tetrapyrrole rings. These compounds can be reduced readily to either the monoanions $[M^{III}(ring-1^{2-})(ring-2^{2-})]^-$ or the protonated species $[M^{III}(ring-1^{2-})(Hring-2^-)]$. There has been a considerable interest to reveal the location of the hole and acid proton in the neutral and reduced protonated double-deckers, respectively. By using IR spectroscopy, we have revealed that, on the vibrational time scale, the hole is delocalized over both rings in double-deckers in which the two tetrapyrrole ligands have the same or similar electrochemical characteristics, such as $[M^{III}(Pc)_2]$, $\{M^{III}[Pc(\beta-OC_8H_{17})_8]_2\}$, $[M^{III}(OEP)_2]$, and $[M^{III}(Nc)(OEP)]$. For double-deckers having two electronically distinct tetrapyrrole ligands, the hole is preferentially localized in the ring whose HOMO energy is lower.[35] Recently, we have also performed density functional theory (DFT) calculations on the molecular structures, molecular orbitals, atomic charges, electronic absorption spectra, and infrared spectra of a series of related double-deckers, namely, $[Y^{III}(Pc)(Por)]$, $[Y^{III}(Pc)(Por)]^-$, $[Y^{III}(HPc)(Por)]$, and $[Y^{III}(Pc)(HPor)]$.[38] Through extensive comparable studies, it has been found that the hole in the neutral nonprotonated double-decker is localized on the Pc ring, which is in line with the result obtained from IR study.[35] For the reduced protonated species, the acid proton prefers to localize on the Por ring rather than on the Pc ring.

Supramolecular Structures

At the Liquid—Solid Interface. Controlled assembly of molecular components on surfaces is crucial for the development of many molecular-scale devices. Recently, we have studied the three-dimensional supramolecular structures of these sandwich-type complexes on highly oriented pyrolytic graphite (HOPG) or Au(111).[39] These molecules adsorb on the substrate surface with one tetrapyrrole ligand, usually forming two types of adlayer structures with 4-fold and 6-fold
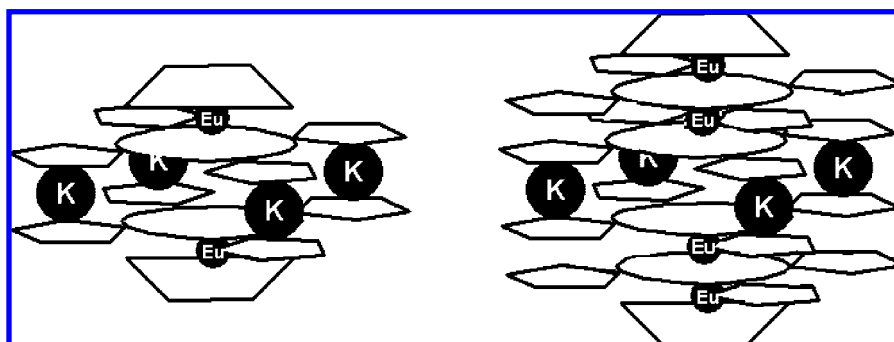
FIGURE 10. Schematic structures of supramolecular tetrameric and hexameric tetrapyrroles formed by K^+-induced dimerization of $Pc(15C5)_4$-containing double- and triple-deckers.
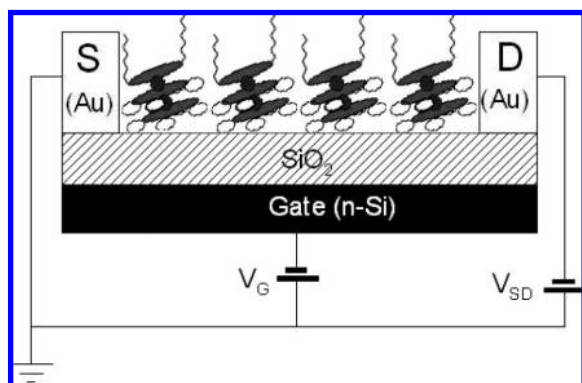

FIGURE 11. Structure of the OFETs with a triple-decker semiconducting layer.

domains. Interestingly, by comparing the supramolecular structures of $\{Lu^{III}(Pc)[Pc(\beta\text{-}OC_8H_{17})_8]\}$ and $\{Sm^{III}(Nc)[Pc(\beta\text{-}OC_8H_{17})_8]\}$ on the HOPG surface, it has been revealed that the top unsubstituted phthalocyanine or naphthalocyanine ligand can affect the intermolecular lattice despite the much larger space occupied by the bottom octa-substituted phthalocyanine ligand.[39a] Studies of coadsorption of the double-deckers with the metal-free phthalocyanine $H_2Pc(\beta\text{-}OC_8H_{17})_8$ on HOPG have also revealed that the two types of molecules independently form well-defined adlayers. The double-decker layers are embedded in rather than being adsorbed on top of the $H_2Pc(\beta\text{-}OC_8H_{17})_8$ layers (Figure 9).

Supramolecular Structures Formed in Solution. Being inspired by the work of Kobayashi[40] and Ishikawa,[41] the K^+-induced dimerization of the 15-crown-5-fused sandwich compounds $\{Eu^{III}(Pc)[Pc(15C5)_n]\}$ ($n = 1\text{−}4$),[17b] $\{Eu^{III}[Pc(15C5)_4](TPP)\}$,[42] and $\{(TPP)Eu^{III}[Pc(15C5)_4]Eu^{III}[Pc(15C5)_4]\}$[42] has also been studied with a range of spectroscopic methods, which clearly reveal the formation of cofacial supramolecular tetramers and hexamers as depicted as Figure 10. The facile formation of these higher arrays of tetrapyrroles is of much current interest and importance.[43]

Applications in Organic Field Effect Transistors

Organic semiconductors have attracted significant research impact since the late 1980s due to their great potential applications in large area and flexible, active-matrix electronic-paper and simple low-cost memory devices. Phthalocyanines have been among the most intensively studied semiconducting materials for organic field effect transistors (OFETs). However, investigations were mainly focused on the unsubstituted metallophthalocyanines including the rare earth double-decker analogues.[44] These phthalocyanine-based OFETs fabricated by vacuum deposition are suitable for laboratory studies but not for large-scale practical industrial manufacturing and commercial applications. The impetus toward solution processable OFETs has stimulated our recent interest in this area.[3,45] We have employed the Langmuir−Blodgett (LB) technique to prepare thin films of the amphiphilic triple-deckers $\{[Pc(15C5)_4]M^{III}[Pc(15C5)_4]M^{III}[Pc(\beta\text{-}OC_8H_{17})_8]\}$ (M = Eu, Ho, Lu) for the fabrication of OFETs (Figure 11). The resulting OFETs show good characteristics with a high carrier mobility ($0.24\text{−}0.60$ cm^2 V^{-1} s^{-1}) in the direction parallel to the phthalocyanine ring and an on/off current ratio of 10^5.[3] Comparative studies on the OFET performance of a series of related triple-deckers indicate that the carrier mobility is dependent on the length of the hydrophobic alkoxy chains due to their effects on the molecular packing and intermolecular interaction in the thin films.[45]

Concluding Remarks

Sandwich-type rare earth complexes represent a unique class of compounds. Apart from their exotic double- and triple-decker structures, these compounds display tunable electronic and optical properties and $\pi\text{−}\pi$ interactions and have found important applications in materials science. Early works in this field focused mainly on the homoleptic unsubstituted phthalocyaninato and porphyrinato complexes. The applications

were confined to electrochromic displays and models to mimic the structure and spectroscopic properties of the "special pair". Only in the last decade, substantial progress has been made during which some useful synthetic pathways have been developed for the preparation of a vast number of these complexes. The accessibility of these compounds has opened up a way to explore their various properties, applications, and inter-relationships. It is believed that the design and synthesis of other novel analogues will continue. The great potential of these compounds in molecular electronics, molecular magnets, and molecular machinery will also continue to draw the attention of scientists. In the coming decade, we are optimistic to see a new phase of advancement of this novel class of complexes.

BIOGRAPHICAL INFORMATION

Jianzhuang Jiang was born in Heilongjiang, China. He received his B.Sc. (1985), M.Sc. (1988), and Ph.D. (1993) (with Tsinglien Chang) from the Peking University. During his doctoral study (1990–1992), he obtained a Fellowship from the Ministry of Culture, Science, and Sport of Japan and carried out his Ph.D. work at the Osaka University under the guidance of Kenichi Machida and Ginya Adachi. He became a Postdoctoral Fellow at the Peking University with Tsinglien Chang (1993–1994), a Visiting Scholar at The Chinese University of Hong Kong with Dennis. K. P. Ng and Thomas C. W. Mak (1995–1996), and a Postdoctoral Fellow at the Queensland University of Technology with Dennis P. Arnold (1998–2000). He joined the Shandong University in 1996 and is presently a Professor and a Cheung Kong Scholar. His current research interests cover a broad range of experimental and theoretical aspects of tetrapyrrole derivatives, especially the sandwich-type porphyrinato or phthalocyaninato rare earth complexes.

Dennis K. P. Ng was born in Hong Kong. He studied chemistry at The Chinese University of Hong Kong, where he received his B.Sc. with first class honors in 1988 and, under the supervision of Tien-Yau Luh, his M.Phil. in 1990. He then joined the research group of Malcolm L. H. Green at the University of Oxford and obtained his D.Phil. in 1993. He became a Research Fellow in Chemistry at the California Institute of Technology working with Seth R. Marder (1993–1994) before returning to his alma mater. He is presently a Professor at The Chinese University of Hong Kong. He received a Faculty Exemplary Teaching Award and Young Researcher Award of the University in 2000 and 2005, respectively. His current research interests lie in the chemistry of functional dyes, particularly phthalocyanines, focusing on their biomedical applications and supramolecular chemistry.

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