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Lu, Fanli and Rintoul, Llew and Sun, Xuan and Arnold, Dennis P. and Zhang, Xianxi and Jiang, Jianzhuang (2004) *Vibrational spectroscopic characteristics of phthalocyanine and naphthalocyanine in sandwich-type phthalocyaninato and porphyrinato rare earth complexes Part 11. Raman spectroscopic characteristics of phthalocyanine in mixed [tetrakis(4-chlorophenyl) orphyrinato](phthalocyaninato) rare earth double-deckers.* Journal of Raman Spectroscopy, 35(10).

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Proofs to Prof. Dr. J. Jiang, address given below.

Vibrational spectroscopic characteristics of phthalocyanine and naphthalocyanine in sandwich-type phthalocyaninato and porphyrinato rare earth complexes
Part 11. Raman spectroscopic characteristics of phthalocyanine in mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) rare earth double-deckers

Fanli Lu^a, Llew Rintoul^b, Xuan Sun^a, Dennis P. Arnold^{b,*}, Xianxi Zhang^a, Jianzhuang Jiang^{a,*}

^aKey Lab for Colloid and Interface Chemistry of State Education Ministry, Department of Chemistry, Shandong University, Jinan 250100, China

^bSchool of Physical and Chemical Sciences, Queensland University of Technology, G. P. O. Box 2434, Brisbane, Qld. 4001, Australia

*Corresponding co-authors. Tel.: +86 531 856 4088; fax: + 86 531 856 5211 (J. Jiang); Tel.: + 61 7 3864 2482; fax: + 61 7 3864 1804 (D. P. Arnold).

E-mail addresses: jzjiang@sdu.edu.cn (J. Jiang), d.arnold@qut.edu.au (D. P. Arnold).

Abstract:

Raman spectroscopic data in the range of 500-1800 cm^{-1} for a series of 15 mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) double-decker complexes with trivalent rare earths $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$ ($\text{M} = \text{Y}, \text{La} \dots \text{Lu}$ except Ce and Pm) and intermediate-valent cerium $\text{Ce}(\text{TCIPP})(\text{Pc})$ have been collected using laser excitation sources emitting at 632.8 and 785 nm. Comparison with the Raman spectra of corresponding bis(phthalocyaninato) rare earths reveals that the Raman characteristics of mixed ring double-deckers are dominated by the phthalocyaninato-metal fragment $\text{M}(\text{Pc})$ and phthalocyanine exists as monoradical anion $\text{Pc}^{\bullet-}$ in $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$ and dianion Pc^{2-} in $\text{Ce}(\text{TCIPP})(\text{Pc})$, respectively. Under excitation at 632.8 nm that is in close resonance with the main Q absorption band of phthalocyanine ligand, typical Raman marker band of the monoanion radical $\text{Pc}^{\bullet-}$ was observed at 1512-1519 cm^{-1} as a weak band resulting from the coupling of pyrrole C=C and aza C=N stretchings. For $\text{Ce}(\text{TCIPP})(\text{Pc})$, a strong band at 1492 cm^{-1} with contributions from both pyrrole C=C and aza C=N stretchings as well as the isoindole stretching was the marker Raman band of Pc^{2-} . When excited with laser radiation of 785 nm, which is far away from the main Q absorption band of the phthalocyanine ligand, the marker Raman band of $\text{Pc}^{\bullet-}$ in $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$ is observed at 1495-1514 cm^{-1} and of Pc^{2-} in $\text{Ce}(\text{TCIPP})(\text{Pc})$ at 1511 cm^{-1} as a strong band.

Keywords: Phthalocyanine; Porphyrin; Raman spectra; Rare earth; Sandwich complexes

1. Introduction

Sandwich-type phthalocyaninato rare earth double-deckers have attracted great attention owing to their potential applications in materials science and molecular electronics [1-3]. The search for novel advanced molecular materials has stimulated intense research into substituted bis(phthalocyaninato), bis(naphthalocyaninato), heteroleptic bis(phthalocyaninato) and mixed porphyrinato-(na)phthalocyaninato metal complexes especially since the beginning of 1990s [4-9]. The wide range of applications arises from the special intense π - π interaction between the conjugated tetrapyrrole ligands in these molecular materials. This recalls the crucial role played by proximate porphyrinoid pigments in photosynthesis and may lead to interesting molecular conductors [1-3]. In this regard, rare earth porphyrin or phthalocyanine sandwich double-decker complexes are attractive models, and understanding of their optical properties may provide insight into how the electronic properties of cofacial dimeric species influence the initial stages of the charge separation process [1a].

It has been proved that vibrational (IR and Raman) spectroscopy is a versatile technique for studying the intrinsic properties of the sandwich bis(phthalocyaninato) rare earth complexes $M(\text{Pc}')_2$ and mixed porphyrinato-phthalocyaninato rare earth double-deckers $M(\text{Por})(\text{Pc}')$ ($\text{Pc}' = \text{Pc}, \text{Pc}^*$; $\text{Pc} =$ unsubstituted phthalocyanine, $\text{Pc}^* =$ substituted phthalocyanine) [10-12]. Recently, we have carried out extensive and systematic studies into the IR and Raman spectra of homoleptic bis[(na)phthalocyaninato] double-deckers of the whole series of rare earth metals, namely $M(\text{Pc})_2$, $M(\text{TBPc})_2$ [TBPc = 3(4),12(13),21(22),30(31)-tetra(*tert*-butyl)phthalocyanine], $M(\text{OOPc})_2$ [OOPc = 3,4,12,13,21,22,30,31-octakis(octyloxy)phthalocyanine] and $M(\text{TBNc})_2$ [TBNc = 3(4),12(13),21(22),30(31)-tetrakis(*t*-butyl)-2,3-naphthalocyanine] [13,14]. Comparative studies on the Raman characteristics of the whole series of rare earth porphyrinato-naphthalocyaninato double-deckers $M(\text{OEP})(\text{Nc})$ and $M(\text{TBPP})(\text{Nc})$ ($\text{Nc} =$ unsubstituted 2,3-naphthalocyanine) have also been conducted [14d,e]. However, trials on the investigation and understanding of the Raman properties

of mixed porphyrinato-phthalocyaninato of rare earths are still limited to some scattered reports. In 1994, Tran-Thi et al. reported on the FT-Raman spectra for a series of phthalocyaninato-porphyrinato gadolinium and cerium double- and triple-decker compounds [12]. Recently we have started to investigate the Raman characteristics of $M(\text{Por})(\text{Pc}')$ by comparing with those of $M_2(\text{Por})_2(\text{Pc}')$ and $M_2(\text{Por})(\text{Pc}')_2$ ($\text{Pc}' = \text{Pc}, \text{Pc}^*$; $\text{Por} = \text{tetraaryl- or octaalkylporphyrin}$) for $M = \text{Ce}$ and Eu [13,14]. To have a more profound and complete understanding of their intrinsic properties, it seems necessary to study systematically the vibrational properties of the mixed porphyrinato-phthalocyaninato sandwich complexes of the whole series of rare earth metals as done previously with the homoleptic bis[(na)phthalocyaninato] or mixed porphyrinato-naphthalocyaninato rare earth counterparts [13,14]. In the present paper, the Raman spectroscopic characteristics of mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) double-decker complexes of the whole series of rare earth metals $M(\text{TCIPP})(\text{Pc})$ ($M = \text{Y}, \text{La} \dots \text{Lu}$ except Pm) (Figure 1) have been systematically investigated by means of excitation with laser sources emitting at 632.8 and 785 nm.

2. Experimental

The sandwich-type mixed ring rare earth complexes were prepared by means of our newly-developed phthalonitrile tetramerization method using $M(\text{TCIPP})(\text{acac})$ as template [6d]. UV-vis spectra were obtained for solutions in CHCl_3 using a Hitachi U-4100 spectrophotometer. Raman spectra were recorded on a few grains of the solid samples with ca. 4 cm^{-1} resolution using a Renishaw Raman Microprobe, equipped with a Spectra Physics Model 127 He-Ne laser excitation source emitting at a wavelength of 632.8 nm and a Renishaw diode laser emitting at 785 nm, and a cooled charge-coupled device (CCD) camera. An Olympus BHZ-UHA microscope was attached and was fitted with three objective lenses ($\times 10$, $\times 20$, $\times 50$). For these experiments, the $\times 10$ objective was employed giving a spot size on the sample of about $5 \mu\text{m}$. Laser power at the sample was approximately 0.08 mW. Spectra of excellent quality were obtained in approximately 3 min,

although fluorescence was a problem for the Tb and Lu complexes excited at 632.8 nm and for cerium double-decker when excited at 785 nm.

3. Results and discussion

3.1 Raman characteristics of $M^{III}(TCIPP)(Pc)$ ($M = Y, La-Lu$ except Ce and Pm) and $Ce(TCIPP)(Pc)$ with excitation by laser line at 632.8 nm

As has been noted previously in some scattered reports [12,14a,b], the Raman spectra of the mixed (porphyrinato)(phthalocyaninato) double-decker compounds of rare earth metals like Gd, Ce and Eu are dominated by the phthalocyanine ligand when exciting laser lines of 1064, 632.8, and 780 nm are employed due to the fact that the phthalocyanine Q absorption bands located near 670 nm are in closer resonance with these laser sources than are the porphyrin Q bands at ca. 550 nm, and the latter are only one-tenth as strong as the former. This is also true for $M(TCIPP)(Pc)$ ($M = Y, La-Lu$ except Ce and Pm). Good correspondence in the Raman features between $M(Pc)_2$ and corresponding $M(TCIPP)(Pc)$ revealed in this work provides more direct evidence that the Raman spectra of $M(TCIPP)(Pc)$ are dominated by the phthalocyaninato-metal fragment $M(Pc)$. The neutral double-decker sandwich complexes of trivalent rare earth ions formally comprise one dianionic and one radical anionic macrocyclic ligand. For these complexes with an unpaired electron in one of the tetrapyrrole ligands, an important intrinsic property is the extent of hole delocalization. Both IR and single crystal structure analysis suggest that the hole for the double-deckers $M^{III}(TCIPP)(Pc)$ is mainly localized on the phthalocyanine ring on the vibrational time scale while for $Ce(TCIPP)(Pc)$ both macrocycles exist as dianions [15]. Therefore the availability of the whole series of rare earth double-decker complexes with mixed tetrakis(4-chlorophenyl)porphyrin and phthalocyanine ligands here also provides a good chance to compare

the Raman vibrational characteristics of phthalocyanine monoanion radical $\text{Pc}^{\bullet-}$ and phthalocyanine dianion Pc^{2-} .

The static molecular geometry of $\text{M}(\text{TCIPP})(\text{Pc})$ shown in Fig. 1 suggests a C_{4v} point group for both the whole molecule and the fragment of $\text{M}(\text{Pc})$ in the mixed ring double-deckers. This has been confirmed by the fact that the mutual exclusion rule was not obeyed between the Raman and IR spectra of $\text{M}(\text{TCIPP})(\text{Pc})$, several phthalocyanine-related Raman frequencies being simultaneously active in the IR spectra [15]. As detailed below from the theoretical expectation, for the C_{4v} symmetrical phthalocyanine metal fragment $\text{M}(\text{Pc})$ containing 57 atoms, there are only 22 A_1 totally symmetric fundamental vibrations active in the spontaneous Raman spectra although the fragment $\text{M}(\text{Pc})$ contains a large number of atoms and thus possesses many possible normal vibrational modes. In the resonance Raman scattering, a number of new frequencies could be attributed to the related $22B_1$, $20B_2$ and $41E$ type in view of the Herzberg-Teller mechanism. The vibrational modes may be summarized as follows, where “IR” and “Ra” represent infrared-active and Raman-active modes, respectively.

$$\Gamma_{\text{vib}} = 22A_1(\text{IR,Ra}) + 19A_2 + 22B_1(\text{Ra}) + 20B_2(\text{Ra}) + 41E(\text{IR}) + 41E(\text{Ra})$$

A_1 modes are both IR- and Raman-active. Half of the E modes are IR-active whereas the remaining half are Raman-active. B_1 and B_2 modes are Raman-active and A_2 modes are vibrationally inactive.

The electronic absorption spectra of $\text{M}(\text{TCIPP})(\text{Pc})$ ($\text{M} = \text{Ce}, \text{Sm}, \text{Ho}$), which are typical representatives of the UV-vis spectra for the intermediate-valent cerium (between III and IV) and light, middle, and heavy trivalent rare earth complexes, respectively, are shown in Fig. 2 [15]. In addition to the strong Pc and TCIPP Soret bands respectively at 328-334 and 398-414 nm, the electronic absorption spectra of $\text{M}(\text{TCIPP})(\text{Pc})$ show a very weak Q band in the region of 689-738 nm for $\text{M} = \text{La}$ to Lu , which is mainly contributed from the major Q absorption of the phthalocyanine monoanion radical by comparing with the absorption features of $\text{M}(\text{Pc})_2$ [1]. This

point actually is indirectly supported by the commonality of the features of the Raman spectra between $M(\text{TCIPP})(\text{Pc})$ and $M(\text{Pc})_2$ with excitation at either 632.8 or 785 nm.

Fig. 3 compares the Raman spectra for two trivalent rare earth compounds $M(\text{TCIPP})(\text{Pc})$ ($M = \text{Sm}, \text{Ho}$) together with that of $\text{Ce}(\text{TCIPP})(\text{Pc})$ obtained with excitation at 632.8 nm. The observed Raman spectroscopic frequencies of phthalocyanine and partial assignments for $M(\text{TCIPP})(\text{Pc})$ are collected in Table 1. Similar to the situation of other conjugated macrocyclic rings, one-to-one association of all the observed vibrational frequencies with the internal vibrational modes in the Raman spectra of $M(\text{TCIPP})(\text{Pc})$ is hindered by the existence of strong coupling. Only groups of characteristic phthalocyanine vibrations could be distinguished. It is worth noting that the assignments given in Table 1 are restricted to characteristic fundamentals based on the previous description of normal modes for phthalocyaninato and especially bis(phthalocyaninato) metal derivatives [10-14], and also with the help of recent preliminary theoretical studies into the monomeric phthalocyanine derivatives [16].

The Raman spectra with excitation at 632.8 nm display similar features in the region of 500-1600 cm^{-1} for the whole series of trivalent rare earth double-deckers from $M = \text{La}$ to Lu . This is in line with the similar electronic absorption characteristics of $M^{\text{III}}(\text{TCIPP})(\text{Pc})$ ($M = \text{Y}, \text{La-Lu}$ except Ce and Pm) revealed in the previous work [15]. The close resemblance of the characteristic features of the Raman spectra of $M(\text{TCIPP})(\text{Pc})$ to those of respective $M(\text{Pc})_2$ [14a] excited at the same frequency undoubtedly verifies the dominant contribution from the phthalocyanine ring to the Raman spectra of $M(\text{TCIPP})(\text{Pc})$.

Similar to those of bis(phthalocyaninato) rare earth complexes, the weak bands in the region 500-1000 cm^{-1} are assigned to the ring radial vibrations of the isoindole moieties and phthalocyanine macrocycle in $M^{\text{III}}(\text{TCIPP})(\text{Pc})$ ($M \neq \text{Ce}, \text{Pm}$). The Pc breathing vibrations were observed at 623-640 and 674-679 cm^{-1} as a weak and medium band, respectively, whose frequencies appear to be slightly sensitive to the ionic radii of the metal center. The medium band observed at ca. 737 cm^{-1} is assigned to aromatic phthalocyanine C-H wagging. The frequencies with

weak and medium intensity observed in the spectral region of 970-1300 cm^{-1} are attributed to the in-plane phthalocyanine C-H bending vibrations except for the medium intense peak of pyrrole breathing at ca. 1140 cm^{-1} . The remaining vibrations in the range 1320-1600 cm^{-1} are isoindole stretch, aza group, and benzene stretch as organized in Table 1. The bands at ca. 1327-1330, 1335-1342 and 1348-1352, 1387-1397 cm^{-1} are attributed to pyrrole stretchings and isoindole stretchings, respectively. The intensity of the one at 1387-1397 cm^{-1} clearly increases along with the rare earth contraction. By analogy with those of $\text{M}(\text{Pc})_2$ under the same excitation [14a], the weak band whose frequency varies in the range from 1512 cm^{-1} for $\text{La}(\text{TCIPP})(\text{Pc})$ to 1519 cm^{-1} for $\text{Lu}(\text{TCIPP})(\text{Pc})$ along with the decrease of rare earth ionic size (attributed to the coupling of pyrrole C=C and aza C=N stretchings) is assigned as the characteristic Raman marker scattering of phthalocyanine monoanion radical $\text{Pc}^{\bullet-}$. This observation corresponds well with that found in the double-deckers $\text{Eu}(\text{TCIPP})(\text{Nc})$ and $\text{RE}(\text{TBPP})(\text{Nc})$ as discussed previously [14b, 14e]. The most intense vibration at ca. 1530-1547 cm^{-1} is attributed to the contribution mainly from the aza C=N stretching, whose energy is linearly blue-shifted along with the decrease in the ionic radius as shown in Fig. 4. This blue shift is caused by the systematic variation in the coordination intensity of the rare earth-central nitrogen bonds along with the decrease in the rare earth ionic radius. In the double-decker phthalocyaninato rare earth complexes, the large central rare earth ion which locates outside the planar phthalocyanine ligand is coordinated by the central N atoms of the phthalocyanine ligands. Along with the decrease in the rare earth ionic radius, the central metal gets closer to the phthalocyanine rings, which favors the coordination between the central rare earth ion and the isoindoline nitrogen atoms and thus reinforces the M-N bonds. Corresponding systematic change is thus expected on the vibrational properties of the aza C=N bonds in the same compounds in association with the corresponding change of these C=N bonds induced by the variation in the M-N bonds, which is reflected by the blue shift observed in the experimental results. Nevertheless, according to our recent preliminary theoretical calculations on the vibrational spectra of monomeric phthalocyanine complex, vibrations in this region actually also contains some contribution,

although not in a large degree, directly from the M-N vibration in addition to the aza C=N stretchings [16b]. Since the M-N bonds are reinforced along with the decrease of the ionic radius, the vibration energy of such vibration mode would thus increase along with the lanthanide contraction. This is believed to add some additional contribution to the blue shift observed for the band at ca. 1530-1547 cm^{-1} . The weak bands at ca. 1570-1600 cm^{-1} are attributed to benzene stretching according to previous work [14]. Notably, satisfactory Raman spectra could not be obtained for M(TCIPP)(Pc) (M = Tb, Lu) due to the strong fluorescence under this condition.

It is worth pointing out that according to our theoretical research [16], the weak band at about 570 and medium intense scattering at ca. 800 cm^{-1} are also attributed to the central macrocycle (Pc) breathing vibrations, Table 1. The intense band at 1340 cm^{-1} was previously assigned to C=C stretching of the pyrrole groups. However, also according to our calculation, not only the C=C bonds of the pyrrole rings but also the C=C bonds of the benzene rings contribute to this scattering. The medium intense vibration at ca. 1307-1318 cm^{-1} also contains the contribution from stretching vibrations of both the C=C bonds of pyrrole rings and the C=C bonds in the benzene rings.

We now move to the cerium compound, whose Raman spectroscopic data are different from those of the rest of the whole series. As shown in Fig. 2, the electronic absorption spectrum of Ce(TCIPP)(Pc) is different from those of trivalent rare earth complexes $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$ but resembles those of $\text{LiM}(\text{TPyP})(\text{Pc})$ or $\text{HM}(\text{TPyP})(\text{Pc})$ (M = Eu, Gd) due to their similar electronic structures [6a,17]. As indicated by the electronic absorption and ^1H NMR spectra, both the porphyrin and phthalocyanine rings exist as dianions in $\text{Ce}(\text{TCIPP}^{2-})(\text{Pc}^{2-})$ despite the XANES results that suggest a valence state intermediate between III and IV for the cerium [4]. This makes this complex differ from other analogues that have the form $\text{M}(\text{TCIPP}^{2-})(\text{Pc}^{\bullet-})$. The close similarity in the Raman spectra between Ce(TCIPP)(Pc) displayed in Fig. 3 and $\text{Ce}(\text{Pc})_2$ [14a] under the same laser excitation reveals the dominant contribution of Pc^{2-} to the Raman characteristics of Ce(TCIPP)(Pc). A comparison of the Raman spectrum of Ce(TCIPP)(Pc) with those of the rest of

the series shows that Ce(TCIPP)(Pc) contains most of the frequencies found in the other complexes, however the relative intensities are obviously different. For example, a weak band appears at 1426 cm^{-1} for Ce(TCIPP)(Pc) (Fig. 3) corresponding to isoindole stretching, but for the other complexes, a medium intense band at the same region is observed. In contrast, a vibrational mode appears at 708 cm^{-1} as a medium band for Ce(TCIPP)(Pc) but a very weak one at 708-711 cm^{-1} has been observed for $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$. Moreover, the marker Raman band of Pc^{2-} at 1492 cm^{-1} with contributions from both pyrrole C=C and aza C=N stretches together with isoindole stretchings is observed as the strongest scattering in the Raman spectrum of Ce(TCIPP)(Pc). This is in good contrast to the very weak Pc^{\bullet} marker Raman band located at 1510-1519 cm^{-1} observed for $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$. It is worth noting that under the same excitation laser line, the Pc^{\bullet} marker Raman band in $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$ was found to locate at the similar region to that in $\text{M}^{\text{III}}(\text{Pc})_2$ [14a,b], but the Pc^{2-} marker Raman band of Ce(TCIPP)(Pc) at 1492 cm^{-1} downshifts about 8 cm^{-1} compared with that in Ce(Pc)₂ [14a] and (OOPc)M(Pc)M(Pc) [14b]. However, this shift corresponds well with that in the triple-deckers $\text{M}_2(\text{Por})_2(\text{Pc})$ and $\text{M}_2(\text{Por})(\text{Pc})_2$ [14a].

3.2 Raman characteristics of $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$ ($\text{M} = \text{Y}, \text{La-Lu}$ except Ce and Pm) and Ce(TCIPP)(Pc) with excitation by laser line at 785 nm

Note that the Raman spectra of Ce(TCIPP)(Pc), Dy(TCIPP)(Pc) and Yb(TCIPP)(Pc) under excitation at 785 nm were of poor quality due to the strong fluorescence. As shown in Fig. 5 and organized in Table 2, the Raman spectroscopic features of $\text{M}(\text{TCIPP})(\text{Pc})$ are very much different from those observed under excitation at 632.8 nm due to the different excitation laser line used [11,14b]. However, they closely resemble those of corresponding $\text{M}(\text{Pc})_2$ under the same conditions [14a], which again confirms that the vibrations of phthalocyanine ligand dominate these spectra, which is in line with the result derived from the Raman characteristics of $\text{M}(\text{TCIPP})(\text{Pc})$ using laser excitation source at 632.8 nm.

With excitation at 785 nm, the typical Raman marker band of the phthalocyanine monoanion radical $\text{Pc}^{\bullet-}$ due to the coupling of pyrrole C=C and aza C=N bond stretches appears as a medium band in the spectra of $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$, which shifts from 1495 cm^{-1} for $\text{M} = \text{La}$ to 1514 cm^{-1} for $\text{M} = \text{Lu}$ along with the decrease in the ionic radius. However, under excitation at 632.8 nm the typical Raman marker band of the monoanion radical $\text{Pc}^{\bullet-}$ was observed at $1512\text{-}1519 \text{ cm}^{-1}$ as a weak band. This is the general phenomenon found in the field of Raman spectroscopy and the difference in the wavenumber derived from the same vibrational modes under different excitation wavelength is attributed to due to the different electron excitation states obtained under different excitation wavelength. In each excitation state, some certain electrons in the occupied orbitals will be excited to certain unoccupied orbitals, the newly-occupied orbitals are different between different excited states obtained using different excitation laser source. Since these orbitals are composed of different sets of atomic orbitals from different sets of atoms, the electron distribution upon each atoms is thus different and both the orders and energies of corresponding bonds involved these atoms are also different between the different excited states. This, in turn, induces the difference in the Raman vibrational energy of the bonds involved. It is noteworthy that the intensity of this scattering also shows dependence on the rare earth ionic size. Along with the lanthanide contraction, this band changes from a very weak scattering for $\text{La}(\text{TCIPP})(\text{Pc})$ to a quite intense one for $\text{Lu}(\text{TCIPP})(\text{Pc})$. Both the intensity and the energy of the aza C=N stretching at ca. 1535 cm^{-1} also increase along with the rare earth contraction, ranging from 1535 cm^{-1} as a medium intensity band for $\text{La}(\text{TCIPP})(\text{Pc})$ to 1551 cm^{-1} as a very strong scattering for $\text{Lu}(\text{TCIPP})(\text{Pc})$.

When exciting the Raman spectrum of $\text{Ce}(\text{TCIPP})(\text{Pc})$ with 785 nm laser line, similar to those of $\text{M}^{\text{III}}(\text{TCIPP})(\text{Pc})$, the vibrations at 672 and 742 cm^{-1} due to the ring radial vibrations and Pc C-H wagging gain intensity, being relatively stronger than those revealed under 632.8 nm excitation. The intense band at 1511 cm^{-1} with contribution from both pyrrole C=C and aza C=N stretches together with isoindole stretchings is the marker Raman band of Pc^{2-} , which upshifts 19 cm^{-1} compared with the band at 1492 cm^{-1} under excitation at 632.8 nm.

4. Conclusion

Good correspondence in the Raman features, excited at either 632.8 or 785 nm, between bis(phthalocyaninato) rare earth complexes $M(\text{Pc})_2$ and mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) rare earth complexes $M(\text{TCIPP})(\text{Pc})$ demonstrates that the Raman spectra of $M(\text{TCIPP})(\text{Pc})$ are dominated by the phthalocyaninato-metal fragment $M(\text{Pc})$. The porphyrin moiety contributes little to the Raman spectra of $M(\text{TCIPP})(\text{Pc})$ under these experimental conditions. Observation of the typical Raman marker band of phthalocyanine monoanion radical $\text{Pc}^{\bullet-}$ at 1512-1519 cm^{-1} as a weak band when excited at 632.8 nm and 1495-1514 cm^{-1} as a medium intense scattering under excitation of 785 nm confirms the existence of the phthalocyanine monoanion radical, $\text{Pc}^{\bullet-}$, in $M^{\text{III}}(\text{TCIPP})(\text{Pc})$. The characteristic Raman band of Pc^{2-} appears at 1492 and 1511 cm^{-1} as a strong scattering under excitation at 632.8 and 785 nm, respectively. The fact that scatterings with contribution from the phthalocyanine breathings, isoindole stretchings, aza group stretchings and the coupling of pyrrole C=C and aza C=N stretchings in $M^{\text{III}}(\text{TCIPP})(\text{Pc})$ all show dependence on the rare earth radius, shifting to higher energy along with the rare earth contraction in the mixed ring double-decker compounds, indicates the increased ring-ring interaction across the series from La to Lu.

Acknowledgments

The authors thank the National Natural Science Foundation of China (Grant No. 20171028, 20325105), National Ministry of Science and Technology of China (Grant No. 2001CB6105-04), Natural Science Foundation of Shandong Province (Grant No. Z99B03), National Educational Ministry of China, The Science Committee of Shandong Province, Shandong University, and the Science Research Centre, Queensland University of Technology for financial support.

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Figure Captions

Fig. 1. Schematic structures of mixed ring rare earth double-decker complexes with tetrakis(4-chloro)phenylporphyrin and phthalocyanine ligands $M(\text{TCIPP})(\text{Pc})$.

Fig. 2. Electronic absorption spectra of $M(\text{TCIPP})(\text{Pc})$ ($M = \text{Ce}, \text{Sm}, \text{Ho}$) in CHCl_3 .

Fig. 3. Raman spectra of $M(\text{TCIPP})(\text{Pc})$ ($M = \text{Ce}, \text{Sm}, \text{Ho}$) with excitation 632.8 nm.

Fig. 4. Plot of wavenumber of the C=N aza stretching scattering of $M(\text{TCIPP})(\text{Pc})$ at ca. 1540 cm^{-1} with excitation of 632.8 nm as a function of the ionic radius of M^{III} .

Fig. 5. Raman spectra of $M(\text{TCIPP})(\text{Pc})$ ($M = \text{Ce}, \text{Sm}, \text{Ho}$) with excitation 785 nm.

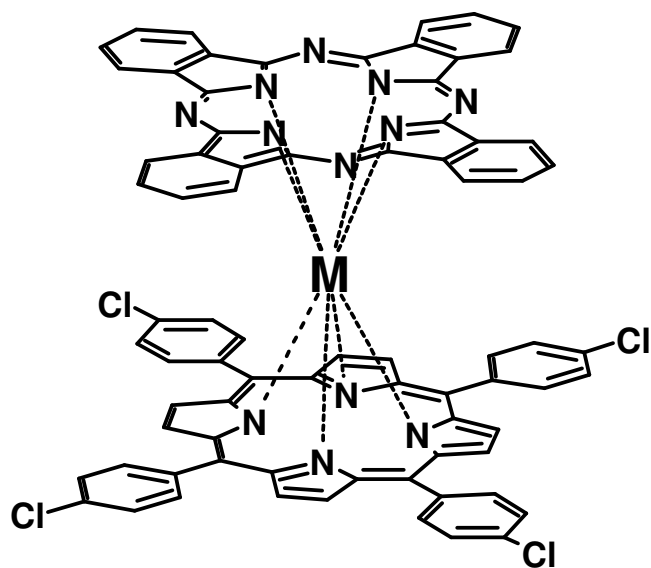


Fig. 1. Schematic structures of mixed ring rare earth double-decker complexes with tetrakis(4-chloro)phenylporphyrin and phthalocyanine ligands $M(\text{TCIPP})(\text{Pc})$.

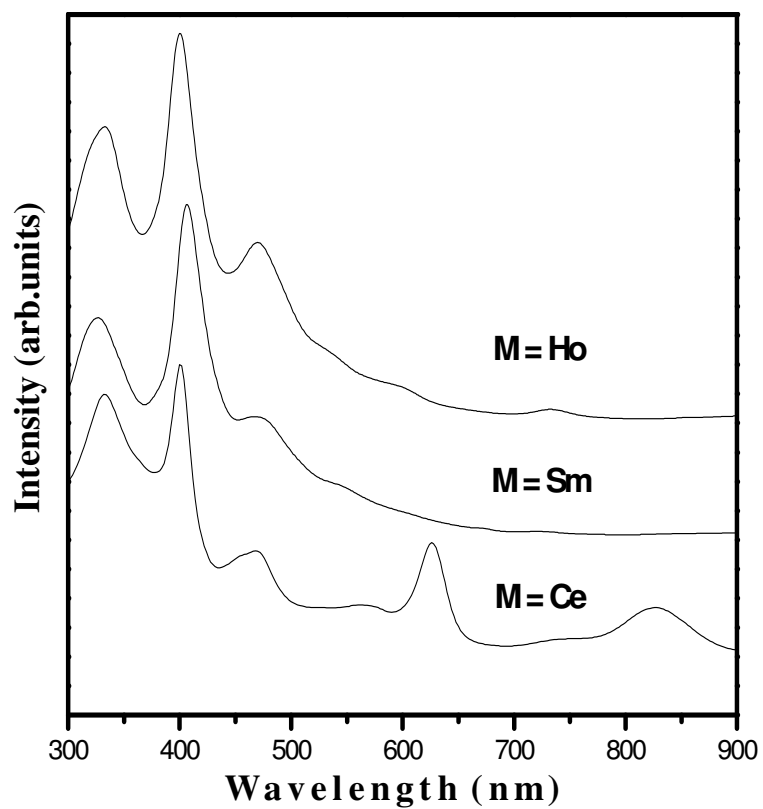


Fig. 2. Electronic absorption spectra of M(TClPP)(Pc) (M = Ce, Sm, Ho) in CHCl₃.

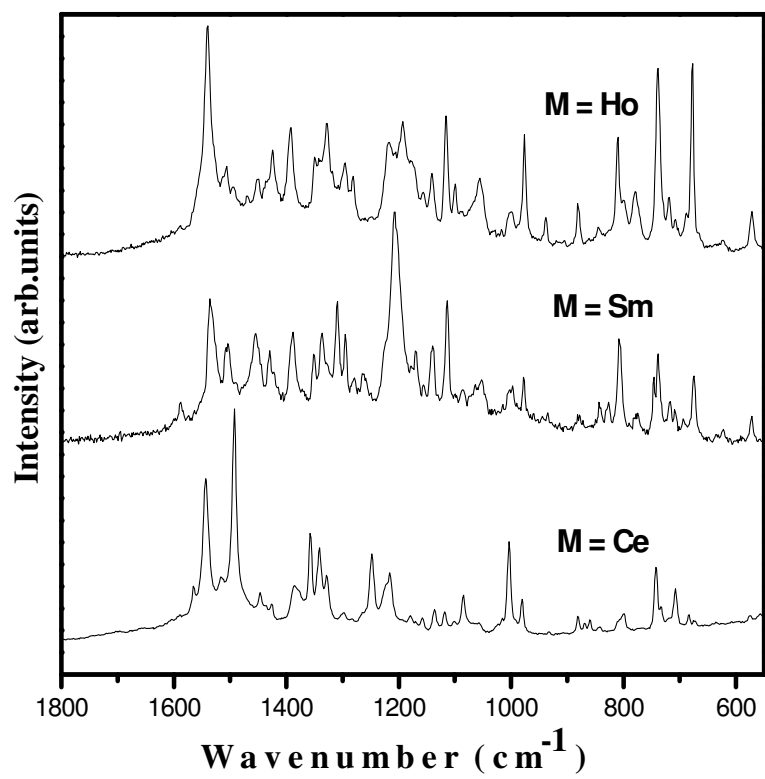


Fig. 3. Raman spectra of M(TCIPP)(Pc) (M = Ce, Sm, Ho) with excitation 632.8 nm.

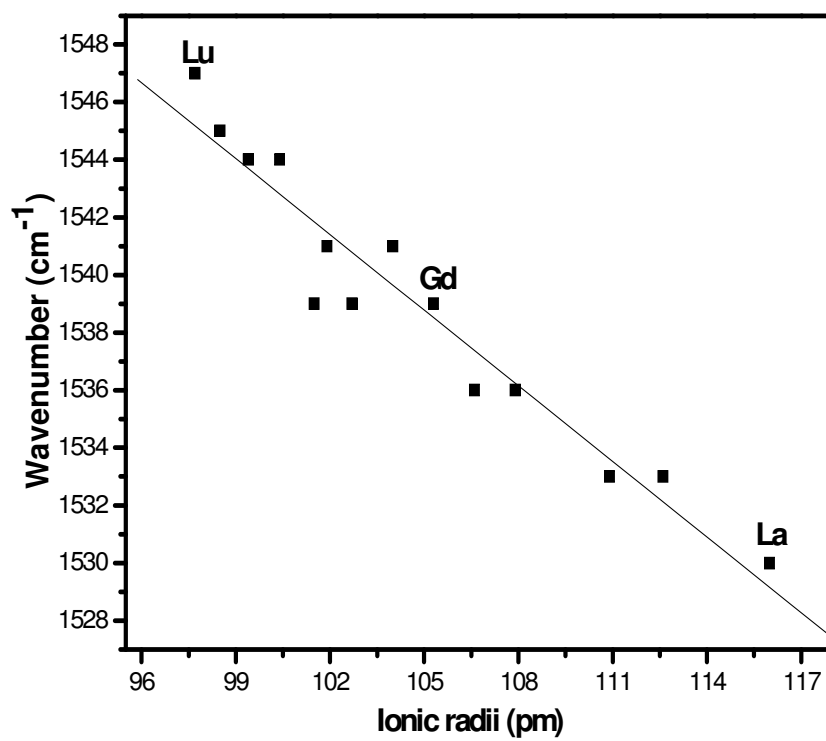


Fig. 4. Plot of wavenumber of the C=N aza stretching scattering of M(TCIPP)(Pc) at ca. 1540 cm⁻¹ with excitation of 632.8 nm as a function of the ionic radius of M^{III}.

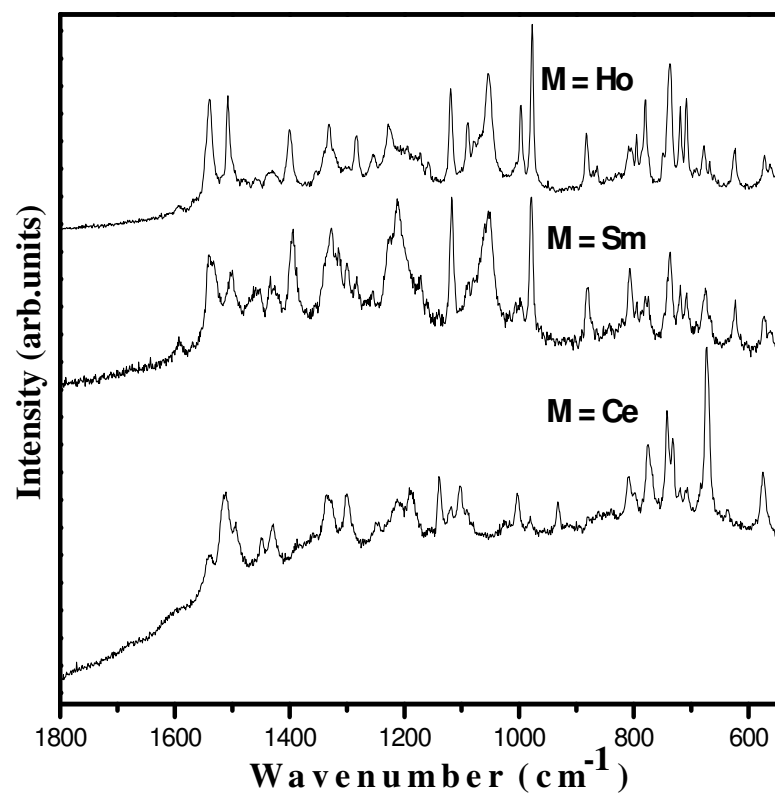


Fig. 5. Raman spectra of M(TCIPP)(Pcc) (M = Ce, Sm, Ho) Ho with excitation 785 nm.

Table 1. Characteristic Raman bands (cm^{-1}) of phthalocyanine for M(TCIPP)(Pc) (M = Y, La...Lu except Pm) ($\lambda_{\text{ex}} = 632.8 \text{ nm}$).

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	assignment
546w	557w	540w	547w	549w	548w	554w	549w	554w	548w	555w	548w	540w	546w	545w	
574w	578w	574w	572w	572w	572w	572w	574w	574w	572w	572m	572m	572m	574w	574w	Pc breathing
623w	636w	635w	635w	636w	636w	632w	636w	637w	634w	636w	635w	633w	633w	640w	Pc breathing
672w	684w	677m	674w	674m	674m	679m	679m	677m	677m	677s	679m	679m	679m	679m	Pc breathing
708w	708m	708w	708w	709w	709w	711sh	708w	707w	708w	708w	706w	708w	708w	710w	
		722m	717m	717w	718m	722m	722m	722m	720w	719m	717w	720w	719m	720m	
737m	743m	740m	738m	738m	740m	741m	738m	737m	741s	738s	737m	741s	738m	738m	C-H wag
781w	799w	781w	774w	775w	775w	793w	780w	778m	778m	780m	778m	780m	780m	780w	C=N aza stretching
806m	811w	807m	806m	809m	807m	809w	802w	809s	809m	810m	810m	810m	809m	810w	Pc breathing
978m	981w	978m	978m	978m	976m	976m	976m	976m	976m	976m	975m	975m	973s	975m	C-H bend
1004w	1004s	998w	996w	998m	999w	998w	1004w	1002m	998m	999m	1001m	1001m	1001m	1001w	C-H bend
1048w	1057w	1054w	1046w	1053w	1054w	1053w	1056w	1053s	1051w	1056m	1050m	1054w	1054s	1053m	C-H bend
1074w	1085m	1083w	1075w	1086w	1098w	1083w	1089w	1098w	1100w	1100m	1100m	1101m	1098w	1098w	C-H bend
1112s	1118m	1114s	1112m	1114s	1115s	1115m	1117m	1117m	1117m	1115m	1117s	1117m	1117s	1117s	C-H bend
1143m	1136m	1138m	1143m	1140m	1143m	1138m	1144m	1143m	1141m	1141m	1140m	1143m	1141m	1141m	pyrrole breathing
1167m	1158w	1168m	1168m	1156w	1158w	1159w	1156w	1156m	1158w	1156w	1155m	1177sh	1153w	1155w	C-H bend
1196sh	1179w	1197sh	1176w	1170m	1170m	1171sh	1171sh	1178sh	1175sh	1192m	1193m	1196s	1193m	1193m	C-H bend
1216m	1216m	1213vs	1210vs	1207vs	1207vs	1207s	1209m	1204vs	1204m	1217m	1219m	1216sh	1219m	1217m	C-H bend

1263w	1248m	1251sh	1252sh	1258sh	1258sh	1252sh	1252w	1257w	1251w	1249w	1253w	1257w	1250w	1250w	
1294m	1297w	1281w	1278w	1279w	1281w	1278w	1280w	1281m	1278m	1282m	1280m	1281w	1280m	1280m	
		1295m	1294m	1295m	1295m	1298sh	1295w	1295m	1298m	1295m	1297m	1295m	1294w	1295w	C-H bend
1307m		1309m	1309m	1309s	1310s	1309m	1311m	1312m	1309m	1318sh	1315sh	1312m	1313w	1313w	C=C pyrrole and benzene stretching
1329m	1329m	1329sh	1327w	1329sh	1326w	1320sh	1328m	1328sh	1329m	1327m	1329vs	1329m	1330s	1330vs	C=C pyrrole and benzene stretching
1339m	1341m	1336s	1335w	1336m	1334sh	1338s	1338m	1333m	1339m	1342w	1338sh	1339sh	1337sh	1337sh	C=C pyrrole and benzene stretching
1348m	1358m	1350m	1348m	1352m	1349m	1350sh	1350m	1352sh	1352m	1350m	1357sh	1352m	1351m	1350sh	isoindole stretching
1387vs	1408w	1388m	1387m	1388m	1391m	1393m	1396s	1397m	1396s	1391m	1397s	1396m	1397s	1397m	isoindole stretching
1423m	1426w	1426m	1426m	1429m	1431m	1425m	1425m	1422m	1425m	1425m	1425m	1428m	1428m	1428m	isoindole stretching
1435m	1439w	1436w	1442sh	1446sh	1446sh		1437w	1434m	1434w	1437w	1435sh	1437sh	1439sh	1440sh	isoindole stretching
1448m	1446m	1449m		1451sh		1448m	1446w	1453sh	1441w	1439w	1448sh	1448sh	1442sh	1449w	
1452m	1462w	1452m	1454m	1454m	1454s	1458sh	1449w	1457m	1452m	1452w	1454w	1454w	1454m	1454sh	isoindole stretching
1490m		1490m	1490sh	1490w	1486w	1480w	1486w	1486w	1487sh	1487sh	1491sh	1483w	1487w	1483w	C=C pyrrole stretching
1512w	1492vs	1510m	1510w	1508sh	1510sh	1512w	1512w	1513w	1513w	1513w	1515w	1512w	1518m	1519w	coupling of pyrrole and aza stretching
1530s	1544s	1533vs	1533s	1536s	1536s	1539vs	1541m	1539m	1541vs	1539vs	1544s	1544vs	1545vs	1547s	C=N aza stretching
1570w	1579w	1565w	1564w	1570w	1570w	1574sh	1577w	1576w	1574w	1575w	1576w	1574w	1578w	1580w	benzene stretching
1587m	1589w	1588w	1588w	1588w	1588w	1580w	1586w	1590w	1586w	1588w	1589w	1588w	1588w	1588w	benzene stretching
1597w	1603w	1602w	1605w	1600w	1600w	1603w	1599w	1603w	1591w	1604w	1601w	1604w	1606w	1603w	benzene stretching

Table2. Characteristic Raman bands (cm^{-1}) of phthalocyanine for M(TCIPP)(Pc) (M = Y, La...Lu except Pm) ($\lambda_{\text{ex}} = 785 \text{ nm}$).

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	assignment
573m	575m	573m	573m	573m	573m	573m	571m	574m	573m	572m	572m	573m	572m	573m	Pc breathing
622m	620w	624m	623m	623m	623m	625m	624m	624m	622m	623m	625m	624m	625m	625m	Pc breathing
680m	672s	675m	676m	675m	676m	676m	679m	681m	678m	678m	678m	678m	678m	679m	Pc breathing
737m	742m	741m	736s	737m	741s	741m	738m	738vs	742m	738s	742s	742m	738m	741s	C-H wag
781m	776m	775w	780m	775m	780m	781m	780m	781m	780m	779m	780m	781m	781m	781m	C=N aza stretching
807m	808m	805m	807s	806s	807m	803m	809m	800m	805m	795m	804m	806m	811m	805m	Pc breathing
980m	980w	980m	979m	978vs	980vs	979vs	979vs	979m	978s	977vs	978vs	977vs	977vs	977vs	C-H bend
1115s	1119w	1116m	1117m	1118s	1119m	1119s	1120s	1120m	1120s	1119s	1119m	1120m	1120m	1120m	C-H bend
1141w	1140m	1144m	1142w	1140w	1146w	1141w	1146w	1147w	1145w	1151w	1146w	1146w	1151w	1147w	pyrrole breathing
1313m	1309sh	1314m	1312m	1315m	1314m	1320sh	1315w	1316w	1316sh	1316sh	1316sh	1316sh	1319w	1318m	C=C pyrrole and benzene stretching
1326m	1335m	1327s	1328m	1327m	1330m	1330s	1332m	1329m	1332m	1331m	1332m	1332m	1334m	1333m	C=C pyrrole and benzene stretching
1394s	1392w	1394s	1391m	1394m	1396m	1398m	1401s	1397m	1399s	1400m	1398m	1400m	1402m	1402m	isoindole stretching
1495w	1511s	1500w	1501w	1500m	1502m	1505m	1506s	1498w	1509m	1508s	1511s	1512s	1513m	1514s	coupling of pyrrole and aza stretching
1535s	1541w	1539s	1538m	1541m	1542m	1543m	1540s	1542w	1543vs	1540s	1545s	1545s	1547m	1551s	C=N aza stretching
1579w	1578w	1581w	1578w	1585w	1572w	1590w	1585w	1580w	1573w	1573w	1573w		1576w	1576w	benzene stretching
1591w	1584w	1584w	1591w	1593w	1593w	1593w	1592w	1589w	1583w	1584w	1584w	1582w	1580w	1591w	benzene stretching
1594w	1596w	1596w	1594w	1602w	1596w	1597w	1599w	1595w	1594w	1594w	1595w	1594w	1595w	1596w	benzene stretching

