

Infrared spectroscopic characteristics of phthalocyanine in mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) rare earth double-deckers

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Abstract

The infra-red (IR) spectroscopic data for a series of 15 mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) rare earth double-decker complexes with trivalent rare earths $M^{III}(\text{TCIPP})(\text{Pc})$ ($M = \text{Y, La, } \dots, \text{Lu}$ except Ce and Pm) and intermediate-valent cerium $\text{Ce}(\text{TCIPP})(\text{Pc})$ have been collected with resolution of 2 cm^{-1} . For $M^{III}(\text{TCIPP})(\text{Pc})$, typical IR marker band of the monoradical anion $\text{Pc}^{\bullet-}$ shows the most intense absorption band whose frequency linearly varies in the range from 1311 cm^{-1} for $\text{La}(\text{TCIPP})(\text{Pc})$ to 1320 cm^{-1} for $\text{Lu}(\text{TCIPP})(\text{Pc})$ along with the decrease of rare earth ionic size. The peaks at $1016\text{--}1023 \text{ cm}^{-1}$ are assigned to C–Cl stretchings. For $\text{Ce}(\text{TCIPP})(\text{Pc})$, a medium band at 1329 cm^{-1} with contribution from pyrrole stretching was the marker IR band of phthalocyanine dianion Pc^{2-} . The $\text{TCIPP}^{\bullet-}$ IR marker band at ca. $1270\text{--}1300 \text{ cm}^{-1}$ was not observed for these compounds. These facts indicate that the hole in these double-deckers is mainly localized at the phthalocyanine ring.

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Keywords: Phthalocyanine; IR spectra; Rare earth; Sandwich-type complexes

1. Introduction

Sandwich-type porphyrinato and/or phthalocyaninato complexes, in which two or three tetrapyrrole ligands are held by rare earth, actinide, and early transition metal or main group metals in close proximity, have been intensively studied over several decades in both fundamental academic and applied fields [1]. They are chemically robust and therefore have been used as dyes, pigments, catalysts for the removal of sulfur in oil, and more recently expanding in many fields such as xerography, photovoltaics, electrochromism, thermochromism, optical discs, laser dyes, liquid crystals, molecular metals, electro-catalysis, chemical sensors, magnetic materials, photochemical hole burning, and photodynamic cancer therapy [2]. These diversified possibilities of phthalocyanines generally stem from their large and flat π -conjugation systems of phthalocyanines and the type of central metal.

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) [3–5]. Recently, we have carried out extensive and systematic studies into the infra-red (IR) spectra of homoleptic bis(phthalocyaninato) double-deckers of the whole series of rare earth metals, namely $M(\text{Pc})_2$, $M(\text{TBPC})_2$ [$\text{TBPC} = 3(4),12(13),21(22),30(31)$ -tetra(*tert*-butyl)phthalocyanine], $M(\text{OOPc})_2$ [$\text{OOPc} = 3,4,12,13,21,22,30,31$ -octakis(octyloxy)phthalocyanine] [6]. However, trials on the investigation and understanding of the IR properties of mixed porphyrinato-phthalocyaninato of rare earths are still limited to some scattered reports. To have a more profound and complete understanding of their intrinsic properties, it is necessary to study systematically the vibrational properties of the mixed porphyrinato-phthalocyaninato sandwich complexes of the whole series of rare earth metals. In the present

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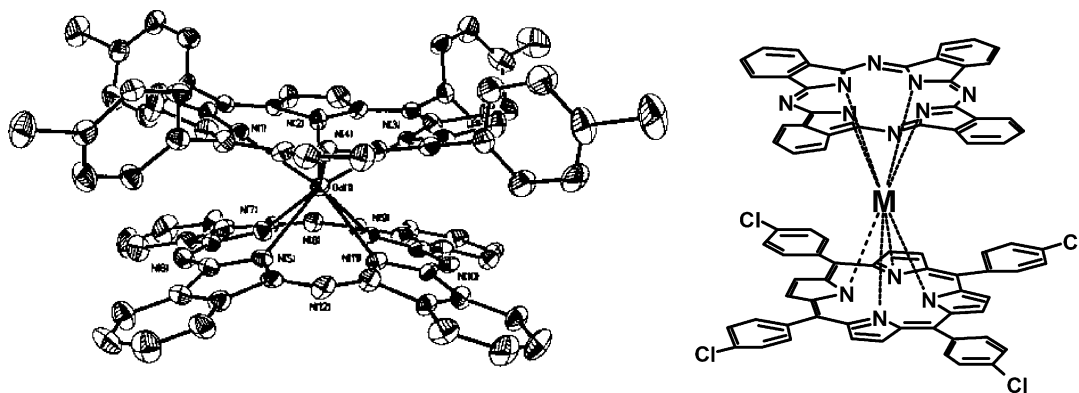


Fig. 1. Side view of the molecular structure [Gd^{III}(Pc)(TCIPP)] and schematic structures of mixed ring rare earth double-decker complexes with tetrakis(4-chloro)phenylporphyrin and phthalocyanine ligands M(TCIPP)(Pc).

paper, the IR spectroscopic characteristics of mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) double-decker complexes of the whole series of rare earth metals M(TCIPP)(Pc) (M = Y, La, . . . , Lu except Pm) (Fig. 1) have been systematically investigated with 2 cm⁻¹ resolution. The influence of the symmetry of mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) molecules and the effects of ionic radius of rare earth metal have also been detailed studied. It is noteworthy that the IR spectra reported here were recorded with 2 cm⁻¹ resolution. This is an improvement on the data obtained with a resolution of 4 cm⁻¹ reported so far.

2. Experimental

The mixed [tetrakis(4-chlorophenyl)porphyrinato](phthalocyaninato) rare earth complexes were prepared by means of phthalonitrile tetramerization method using M(TCIPP)(acac) as template [7,8]. UV–vis spectra were obtained for solutions in CHCl₃ using a HP 8543 spectrophotometer. Their sandwich nature has been established through a series of spectroscopic methods including UV–vis, near-IR, MCD, ESR, and in particularly the X-ray single crystal molecular structure analysis result [8]. Mass spectra, Elemental analysis, and NMR studies of these complexes confirm their identification and purity. IR spectra were recorded in KBr pellets with 2 cm⁻¹ resolution using a BIORAD FTS-3000 spectrometer.

3. Results and discussion

As illustrated by the molecular structure of Gd(TCIPP)(Pc) (Fig. 1), the equilibrium geometry of M(TCIPP)(Pc) can be confirmed to have a C_{4v} point group symmetry according to the X-ray molecular structure analysis [8]. This has been confirmed by the fact that the mutual exclusion rule was not obeyed between the Raman and IR spectra of M(TCIPP)(Pc), several phthalocyanine-related IR frequencies being simultaneously active in the Raman spectra [8,9]. To assist the

interpretation of the observed IR and Raman spectra of mixed (porphyrinato)-(phthalocyaninato) rare earth complexes, a local C_{4v} symmetry for the fragment M(Pc) is reasonably assumed [9]. As detailed below from the theoretical expectation, for the C_{4v} symmetrical phthalocyanine metal fragment M(Pc) containing 57 atoms, there are only 22 A₁ totally symmetric fundamental vibrations active in the IR spectra although the fragment M(Pc) contains a large number of atoms and thus possesses many possible normal vibrational modes. In the IR spectra, only a number of new frequencies could be attributed to the related 41E type in view of the Herzberg–Teller mechanism [5]. The vibrational modes may be summarized as follows, where “IR” and “Ra” represent infrared-active and Raman-active modes, respectively.

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

A₁ modes are both IR- and Raman-active. Half of the E modes are IR-active whereas the remaining half are Raman-active. B₁ and B₂ modes are Raman-active and A₂ modes are vibrationally inactive.

Before describing the IR characteristics of mixed (porphyrinato)-(phthalocyaninato) rare earth complexes, it seems necessary to give a brief description of the porphyrin monianion radical Por^{•-}. In order to distinguish the redox site between the metal and porphyrin ring for metallo-porphyrins, Shimonura et al. developed an effective infrared spectroscopic method, and assigned the band around 1520–1570 and 1270–1300 cm⁻¹ as the IR marker band for the porphyrin π-radicals, OEP^{•-} and TPP^{•-}, respectively [10]. Based on their work, the bands at ca. 1520–1570 and 1270–1300 cm⁻¹ are also assigned to the diagnostic bands for OEP^{•-} and TPP^{•-} in the sandwich-type rare earth complexes [11–14].

It is worth noting that one-to-one matching of observed vibrational frequencies to the internal vibrations cannot be achieved in the vibrational spectra of mixed (porphyrinato)-(phthalocyaninato) rare earth compounds due to the existence of strong couplings of some vibrational coordinates of the large conjugated phthalocyanine rings [6,15]. Therefore, the

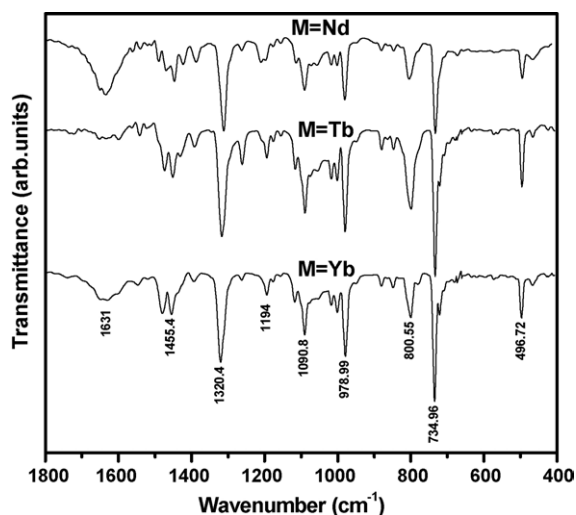


Fig. 2. IR spectra of $M^{III}(\text{TCIPP})(\text{Pc})$ ($M = \text{Nd}, \text{Tb}, \text{Yb}$) in the region of $400\text{--}1800\text{ cm}^{-1}$ with 2 cm^{-1} resolution.

Table 1
Characteristic IR bands (cm^{-1}) of phthalocyanine for $M(\text{TCIPP})(\text{Pc})$ with 2 cm^{-1} resolution

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Assignment
	424w	425w	425w	423w	423w	423w	424w	424w	425w	424w	424w	423w	424w	424w	
465w	467m	463m	467w	468w	466w	466w	467w	467w	467w	467w	467w	467w	467w	466w	
494w	491sh	493w	495m	496w	496m	496m	496m	496m	496m	497m	496m	495w	497m	497m	
672w	673w	673w	672w	674w	672w	674w	678w	678w	678w	679w	679w	673w	673w	674w	Pc breathing
732m	731m	732m	733s	734s	733s	733s	733s	734s	734s	734s	734s	735m	735s	735s	C–H wag
804m	802m	803m	804m	804m	802m	802m	800m	800m	802m	800m	800m	801w	801m	802m	Pc breathing
849w	861w	861w	847w	848w	848w	848w	847w	847w	848w	848w	849w	850w	849w	849w	
878w	883w	878w	881w	881w	881w	880w	880w	881w	881w	881w	880w	876w	881w	879w	Coupling of isoindole deformation and aza stretching
984m	985m	983m	981s	981s	981s	980s	980s	980s	979s	980s	979s	986sh	979s	980s	C–H bend
1005sh		1005sh	1001m	1002m	1002m	1002m	1001m	1001m	1001m	1001m	1002m		1001m	1003w	Pyrrole–N in-plane bending
1019s	1020s	1019s	1018m	1019m	1017m	1019m	1018m	1018m	1016w	1018w	1017w	1023s	1018w	1019w	C–Cl stretching
1066w	1065s	1067sh	1073w	1074w	1073w	1072w	1075w	1075w	1058w	1056w	1054w	1036s	1053w	1072w	Coupling of isoindole deformation and aza stretching
1089m	1090m	1089m	1091m	1091m	1091s	1090s	1090m	1090m	1091m	1090m	1090m	1091s	1091m	1091s	C–H bend
1113sh	1111w	1112sh	1114w	1115w	1116w	1116w	1116w	1117m	1117w	1117w	1117w	1115w	1118w	1115w	Isoindole breathing
		1153w	1156w	1154w	1154w		1156sh	1156w	1157w	1157w	1156w	1157sh	1156w	1153w	Pyrrole breathing
1171w	1178w	1178w	1177w	1177w	1177w	1176w	1176w	1177w	1177sh	1177w	1177w		1178w	1173w	C–H bend
1195w	1202w	1210w	1198w	1197w	1198w	1197w	1194w	1194w	1195m	1195w	1193w	1191sh	1194w	1195w	C–H bend
1263w	1263w	1264w	1263w	1264w	1263w	1264w	1262m	1263w	1264w	1263w	1264w	1263w	1265w	1264w	C–H bend
1311m		1312m	1312s	1314s	1316s	1316s	1318s	1318s	1318s	1318s	1318s	1319m	1320s	1320s	Pyrrole stretching
	1329m														Pyrrole stretching
1386w	1383m	1385w	1387w	1385w	1388w	1384w	1392w	1393w	1393w	1392w	1393w	1384w	1393w	1390w	Isoindole stretching
1422w	1420w	1419w	1423w	1421w	1428w		1431w	1434w	1432w	1434w	1434w	1421w	1425sh	1435sh	Isoindole stretching
1444w	1441w	1440w	1447m	1454w	1451w	1455w	1452w	1452m	1453m	1454m	1453m	1456m	1455m	1455m	Isoindole stretching
1462w	1461m	1460w	1470w	1470w	1473w	1469sh	1474w	1476m	1476m	1476m	1476m	1474sh	1480m	1480m	Isoindole stretching
1489w	1490w	1490w	1489w	1491w	1490w	1489w		1489sh		1489sh		1504w			Coupling of pyrrole and aza stretching
1525w	1524w	1525w	1520w	1524w	1522w	1523w	1523w	1520w	1524w	1520w	1524w	1524w	1520w	1519w	Aza stretching
1543w	1543w	1542w	1540w	1542w	1541w	1542w	1542w	1542w	1543w	1544w	1543w	1544sh	1547w		Benzene stretching
1562w	1563w	1562w	1562w	1564w	1562w	1562w	1563w	1567w	1564w	1567w	1563w	1564sh		1566sh	Benzene stretching
1637m	1638s	1635s	1634s	1635s	1635s	1637s		1630w	1630w	1629w		1633s	1631w	1633s	Benzene stretching
	1645m														Benzene stretching
1652sh	1651sh	1650sh	1650sh	1651sh	1649sh	1652sh	1652w	1651w	1652w	1650w	1652w	1645sh		1647sh	Benzene stretching
1700w	1667w	1699w	1698sh	1699w	1698w	1702w	1680w	1677w		1698w	1700w		1696w	1696sh	Benzene stretching
1719w	1672w	1716w	1717w	1718w	1717w	1724w	1722w	1735w	1736w	1739w	1719w	1739w	1739w	1740w	Benzene stretching

IR spectra of these mixed (porphyrinato)-(phthalocyaninato) complexes are still composed of a relatively small number of fundamentals despite the large number of IR active vibrational modes.

Fig. 2 compares the IR spectra in the range of fundamental frequencies of $400\text{--}1800\text{ cm}^{-1}$ of three compounds $M^{III}(\text{TCIPP})(\text{Pc})$ ($M = \text{Nd}, \text{Tb}, \text{Yb}$) with resolution of 2 cm^{-1} , typical for the light, middle, and heavy rare earths, respectively. In Table 1, characteristic IR vibrational frequencies of the phthalocyanine ligand in mixed (porphyrinato)-(phthalocyaninato) compounds of the series of lanthanides are summarized and their interpretation is proposed by analogy with the IR and Raman spectra of $M(\text{Pc})_2$ and especially $M(\text{TPP})(\text{Pc})$ [6,16]. Due to the similar molecular structure among the whole series of mixed (porphyrinato)-(phthalocyaninato) lanthanide compounds, all these compounds show similar IR characteristics. However, the $\text{TCIPP}^{\bullet-}$ IR marker band at $1270\text{--}1300\text{ cm}^{-1}$

was not seen for these compounds. This suggests that the electron hole in these double-deckers is mainly localized at the phthalocyanine ring. Therefore, the IR spectra of this series of double-deckers is similar to those of $M(\text{Pc})_2$. Good correspondence in the IR features between $M(\text{Pc})_2$ and corresponding $M(\text{TCIPP})(\text{Pc})$ revealed in this work provides more indirect evidence that the IR spectra of $M(\text{TCIPP})(\text{Pc})$ are dominated by the phthalocyaninato-metal fragment $M(\text{Pc})$. 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. Therefore, the availability of the whole series of rare earth double-decker complexes with mixed tetrakis (4-chlorophenyl)porphyrin and phthalocyanine ligands here provides a good chance to compare the IR vibrational characteristics of phthalocyanine monoanion radical $\text{Pc}^{\bullet-}$ and phthalocyanine dianion Pc^{2-} .

Four main IR absorptions corresponding to the C–H wagging at approximately 734 cm^{-1} , C–H bending at $1090\text{--}1264\text{ cm}^{-1}$, pyrrole stretching at $1311\text{--}1320\text{ cm}^{-1}$, and isoindole stretching at $1385\text{--}1480\text{ cm}^{-1}$ have been found to dominate the IR spectra of $M(\text{TCIPP})(\text{Pc})$. In the spectra region from 400 to 1000 cm^{-1} , the remaining weak vibrations have main contributions from the dihedral plane deformation involving the aromatic C–H groups (wagging, torsion, and out-of-plane bending vibrations). Aromatic in-plane C–H bending vibrations are responsible for the IR bands of phthalocyanine molecules in the region of $1000\text{--}1300\text{ cm}^{-1}$, with the exception of the band at 1155 cm^{-1} due to the pyrrole ring breathing. The band at $1113\text{--}1118\text{ cm}^{-1}$ as a weak band is assigned to isoindole breathing together with some C–H bending, and the weak band at $1053\text{--}1075\text{ cm}^{-1}$ due to the coupling of isoindole deformation and aza stretching was observed. Vibrational frequencies in the range of $1300\text{--}1740\text{ cm}^{-1}$ are derived from pyrrole stretching, benzene stretching, isoindole ring stretching, and aza group stretching, for which the pyrrole stretching vibrations appear at $1311\text{--}1320\text{ cm}^{-1}$. Another pyrrole stretching-related vibration couples with the aza stretching and appears at about 1490 cm^{-1} . It should be pointed out that the weak band at $1444\text{--}1456\text{ cm}^{-1}$ in this region is assigned to the isoindole stretching because of its sensitivity to the rare earth ionic size as summarized in Table 1. The ortho-substituted benzene stretchings are observed at approximately at $1630\text{--}1740\text{ cm}^{-1}$.

The strong band whose frequency varies in the range from 1311 cm^{-1} for $\text{La}(\text{TCIPP})(\text{Pc})$ to 1320 cm^{-1} for $\text{Lu}(\text{TCIPP})(\text{Pc})$ along with the decrease of rare earth ionic size (attributed to pyrrole stretching) is assigned as the characteristic IR marker band of phthalocyanine monoanion radical $\text{Pc}^{\bullet-}$ by comparison between the IR characteristics of $M(\text{TCIPP})(\text{Pc})$ and $M(\text{TPP})(\text{Pc})$ [17], clearly showing the rare earth size effect. This observation corresponds well with that found in the double-deckers $\text{Eu}(\text{TCIPP})(\text{Nc})$ and

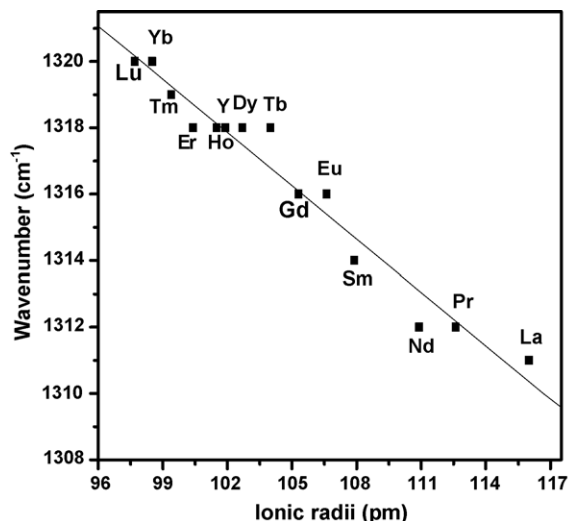


Fig. 3. Plot of wavenumber of the pyrrole stretching absorption band of $M^{\text{III}}(\text{TCIPP})(\text{Pc})$ at ca. 1310 cm^{-1} as a function of the ionic radius of M^{III} .

$\text{RE}(\text{TBPP})(\text{Nc})$ as discussed previously [18]. For instance, a linear correlation exists between the frequency of the pyrrole stretchings at $1311\text{--}1320\text{ cm}^{-1}$ and the trivalent rare earth ionic radii, as shown in Fig. 3. It must be pointed out that the band at $1016\text{--}1023\text{ cm}^{-1}$ is assigned to C–Cl stretching. This observation indirectly verifies our above assignment is correct. Furthermore, one of the most intense bands at around 734 cm^{-1} attributed to the aromatic C–H waggings. The peaks at $672\text{--}679$ and $800\text{--}804\text{ cm}^{-1}$ as a weak and medium band, respectively, are assigned to phthalocyanine ring breathings.

We now move to the cerium compound, whose IR spectroscopic data are different from those of the rest of the whole series, as shown in Fig. 4. The electronic absorption spectrum of $\text{Ce}(\text{TCIPP})(\text{Pc})$ is different from those of trivalent rare earth complexes $M^{\text{III}}(\text{TCIPP})(\text{Pc})$, as shown in Fig. 5, but resembles those of $\text{LiM}(\text{TPyP})(\text{Pc})$ or

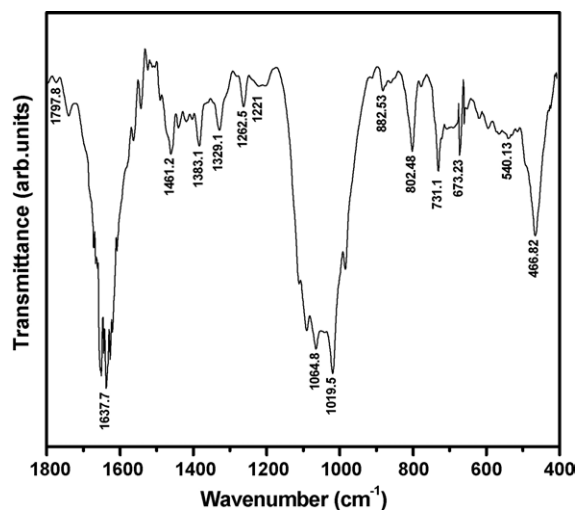


Fig. 4. IR spectra of $\text{Ce}(\text{TCIPP})(\text{Pc})$ in the region of $400\text{--}1800\text{ cm}^{-1}$ with 2 cm^{-1} resolution.

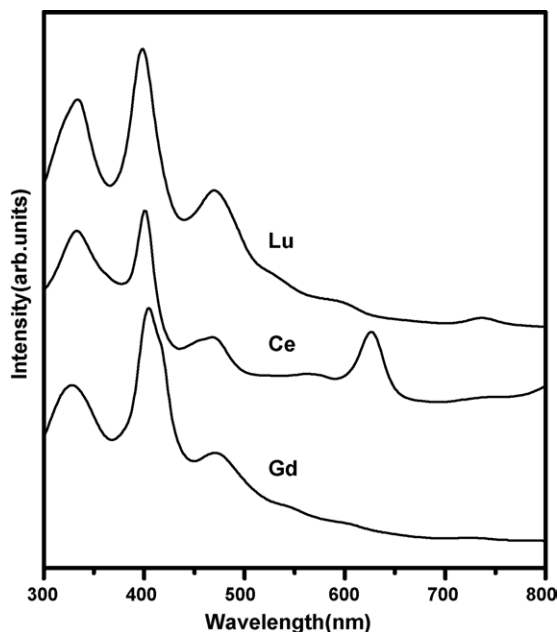


Fig. 5. Electronic absorption spectra of $M(\text{TCIPP})(\text{Pc})$ ($M = \text{Gd}, \text{Ce}, \text{Lu}$) in CHCl_3 .

$\text{HM}(\text{TPyP})(\text{Pc})$ due to their similar electronic structures [19]. 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 [20]. This makes this complex differ from other analogues that have the form $M(\text{TCIPP}^{2-})(\text{Pc}^{\bullet-})$. This is supported by the observation of characteristic IR band of phthalocyanine dianion at 1329 cm^{-1} as a medium band assigned to the pyrrole stretching. The close similarity in the IR spectra between $\text{Ce}(\text{TCIPP})(\text{Pc})$ and $\text{Ce}(\text{Pc})_2$ [6] reveals the dominant contribution of Pc^{2-} to the IR characteristics of $\text{Ce}(\text{TCIPP})(\text{Pc})$. A comparison of the IR spectrum of $\text{Ce}(\text{TCIPP})(\text{Pc})$ with those of the rest of the series shows that $\text{Ce}(\text{TCIPP})(\text{Pc})$ contains most of the frequencies found in the other complexes, however the relative intensities are obviously different. For instance, a strong band appears at 1065 cm^{-1} for $\text{Ce}(\text{TCIPP})(\text{Pc})$ corresponding to the coupling of isoindole deformation and aza stretching, but for the other complexes, a very weak band at $1054\text{--}1075\text{ cm}^{-1}$ is observed. The medium band at 1383 cm^{-1} is assigned to isoindole stretching, while the similar vibration shows very weak absorption around the same region for $M^{\text{III}}(\text{TCIPP})(\text{Pc})$ ($M = \text{Y}, \text{La}, \dots, \text{Lu}$ except Ce and Pm) depending on the rare earth size.

4. Conclusions

According to the IR investigation, typical IR marker band of the monoanion radical $\text{Pc}^{\bullet-}$ shows the strong band attributed pyrrole stretching, whose frequency linearly

varies in the range from 1311 cm^{-1} for La to 1320 cm^{-1} for Lu along with the decrease of rare earth ionic size. For $\text{Ce}(\text{TCIPP})(\text{Pc})$, a medium band attributed to pyrrole stretching appearing at 1492 cm^{-1} was the IR marker band of Pc^{2-} . As expected, the $\text{TCIPP}^{\bullet-}$ IR marker band at ca. $1270\text{--}1300\text{ cm}^{-1}$ was not seen for these compounds. These facts suggest that the hole in these double-deckers is mainly localized at the phthalocyanine ring.

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References

- [1] J. Jiang, K. Kasuga, D.P. Arnold, in: H.S. Nalwa (Ed.), *Supramolecular Photosensitive and Electroactive Materials*, Academic Press, New York, 2001, p. 113.
- [2] J.W. Buchler, D.K.P. Ng, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), *The Porphyrin Handbook*, Academic Press, New York, 1999, p. 245(Chapter 20).
- [3] D. Walton, B. Ely, G. Elliott, *J. Electrochem. Soc.* 128 (1981) 2479.
- [4] C. Clarisse, M.T. Riou, *Inorg. Chim. Acta.* 130 (1987) 139.
- [5] J. Jiang, D.P. Arnold, H. Yu, *Polyhedron* 18 (1999) 2129.
- [6] F. Lu, M. Bao, C. Ma, X. Zhang, D.P. Arnold, J. Jiang, *Spectrochim. Acta. Part A* 59 (2003) 3273.
- [7] T.-H. Tran-Thi, T.A. Mattioli, D. Chabach, A. De Cian, R. Weiss, *J. Phys. Chem.* 98 (1994) 8279.
- [8] F. Lu, X. Sun, R. Li, D. Liang, P. Zhu, C.F. Choi, D.K.P. Ng, T. Fukuda, N. Kobayashi, J. Jiang, *New J. Chem.* 28 (2004) 1116.
- [9] F. Lu, L. Rintoul, X. Sun, D.P. Arnold, X. Zhang, J. Jiang, *J. Raman. Spectrosc.* 35 (2004) 860.
- [10] E.T. Shimomura, M.A. Phillippi, H.M. Goff, W.F. Scholz, C.A. Reed, *J. Am. Chem. Soc.* 103 (1981) 6778.
- [11] J.W. Bucher, K. Elsasser, M. Kihn-Botulinski, B. Scharbert, S. Tansil, *ACS Symp. Ser.* 321 (1986) 94.
- [12] G.S. Girolami, S.N. Milam, K.S. Suslick, *J. Am. Chem. Soc.* 110 (1988) 2011.
- [13] H.-J. Kim, D. Whang, J. Kim, K. Kim, *Inorg. Chem.* 31 (1992) 3882.
- [14] G.S. Girolami, P.A. Gorlin, S.N. Milam, K.S. Suslick, S.R. Wilson, *J. Coord. Chem.* 32 (1994) 173.
- [15] (a) A. Aroca, R.E. Clavijo, C.A. Jennings, G.J. Kovacs, J.M. Duff, R.O. Loutfy, *Spectrochim. Acta* 45A (1989) 957; (b) M.S. Haghghi, A. Franken, H. Homborg, *Z. Naturforsch.* 49b (1994) 812.
- [16] K.M. Kadish, G. Moninot, Y. Hu, D. Dubois, A. Ibnlfassi, J.-M. Barbe, R. Guilard, *J. Am. Chem. Soc.* 115 (1993) 8153.
- [17] R. Guilard, J.-M. Barbe, A. Ibnlfassi, A. Zirneh, V.A. Adamian, K.M. Kadish, *Inorg. Chem.* 34 (1995) 1472.
- [18] Y. Bian, L. Rintoul, D.P. Arnold, N. Pan, J. Jiang, *Vib. Spectrosc.* 31 (2003) 173.
- [19] J. Jiang, W. Liu, X. Sun, D.K.P. Ng, *Chem. Res. Chin. Univ.* 17 (2001) 134.
- [20] Y. Bian, J. Jiang, Y. Tao, M.T.M. Choi, R. Li, A.C.H. Ng, P. Zhu, N. Pan, X. Sun, D.P. Arnold, Z. Zhou, H.-W. Li, T.C.W. Mak, D.K.P. Ng, *J. Am. Chem. Soc.* 125 (2003) 12257.