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Vibrational spectroscopy of phthalocyanine and naphthalocyanine in sandwich-type (na)phthalocyaninato and porphyrinato rare earth complexes Part 13. The Raman characteristics of phthalocyanine in unsubstituted and peripherally octa(octyloxy)-substituted homoleptic bis(phthalocyaninato) rare earth complexes**

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Abstract

The Raman spectroscopic data in the range of 500-1800 cm^{-1} for two series of thirty homoleptic bis(phthalocyaninato) rare earth complexes M(Pc)$_2$ and M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ [M = Y, La-Lu except Pm; H$_2$Pc = unsubstituted phthalocyanine, H$_2$Pc(OC$_8$H$_{17}$)$_8$ = 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyanine] have been collected and comparatively studied using laser excitation sources emitting at 633 and 785 nm. Under both laser excitations, the marker Raman band of Pc^{2-} and [Pc(OC$_8$H$_{17}$)$_8$]$^{2-}$ in the Raman spectra of Ce(Pc)$_2$ and Ce[Pc(OC$_8$H$_{17}$)$_8$]$_2$ appears as a strong scattering at 1498-1501 cm^{-1} with contributions from both pyrrole C=C and aza C=N stretches together with isoindole stretchings. This band has been found to upshift to 1502-1528 cm^{-1} in the Raman spectra of M^{III}(Pc)$_2$ and M^{III}[Pc(OC$_8$H$_{17}$)$_8$]$_2$ as the marker Raman band of phthalocyanine monoanion radicals, Pc$^{\bullet-}$ or [Pc(OC$_8$H$_{17}$)$_8$]$^{\bullet-}$. With laser excitation at 633 nm, Raman vibrations derived from isoindole ring and aza stretchings in the range of 1300-1600 cm^{-1} for both series are selectively intensified. In contrast, when excited with laser radiation of 785 nm, the ring radial vibrations of isoindole moieties and dihedral plane deformations between 500 and 1000 cm^{-1} for M(Pc)$_2$ and M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ intensify to become the strongest scatterings. The present Raman results also reveal that the frequencies of Pc breathing, pyrrole stretching, isoindole stretchings, aza stretchings and coupling of pyrrole and aza stretchings depend on the rare earth ionic size, shifting to higher wavenumbers along with the lanthanide contraction due to the increased ring-ring interaction across the series. Moreover, under these laser excitations, in particular under 785 nm laser line, the Raman spectrum appearance, i.e. the pattern of relative intensities, also changes systematically depending on the rare earth ionic size.

Keywords: Phthalocyanine; Rare earth; Raman; Homoleptic double-decker; Sandwich complex

1. Introduction

Sandwich-type bis(phthalocyaninato) rare earth complexes, in which the conjugated π systems are held in close proximity by rare earth ions, have been extensively studied due to their potential applications as a very important class of advanced molecular materials [1]. Some proposed fields of application include molecular electronic, optronic and iono-electronic devices [1,2]. Vibrational spectroscopies have proved to be versatile methods among various techniques for characterizing thin films of phthalocyanines in solid state devices. In the past several years, the vibrational (IR and Raman) characteristics of (na)phthalocyanine in a wide range of bis[(na)phthalocyaninato] and mixed (porphyrinato)[(na)phthalocyaninato] rare earth complexes have been systematically investigated mainly by Jiang and Arnold [3,4], following the precedent studies of Aroca, Homborg, and Tran-Thi [5-7]. As summarized in our recent papers concerning the vibrational spectroscopic characteristics of sandwich tetrapyrrole rare earth complexes, several series of recently developed novel sandwich double-decker complexes with the whole series of rare earth metals, namely M(TClPP)(Pc) [4g], M(OEP)(Nc) [4d], M(TBPP)(Nc) [4e], M[Nc(*t*Bu)$_4$]$_2$ [4c], and M(Pc)[Pc(α-OC$_5$H$_{11}$)$_4$] [4f] [M = Y, La…Lu except Pm; H$_2$TClPP = 5,10,15,20-tetra(4-chloro)phenylporphyrin, H$_2$OEP = 2,3,7,8,12,13,7,18-octaethylporphyrin, H$_2$TBPP = 5,10,15,20-tetra(4-*t*-butyl)phenylporphyrin, H$_2$Nc(*t*Bu)$_4$ = 3(4),12(13),21(22),30(31)-tetrakis(*t*-butyl)-2,3-naphthalocyanine, H$_2$Pc(α-OC$_5$H$_{11}$)$_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine] have been systematically studied by the Raman technique using laser excitations emitting at 633 and 785 nm, in order to achieve a complete understanding of their intrinsic properties. In contrast, investigation at the same excitation wavelengths of the Raman properties of the most common counterparts, the basic unsubstituted and peripherally octa(alkoxy)-substituted homoleptic bis(phthalocyaninato) rare earth complexes (Figure 1), are still limited to scattered species such as M(Pc)$_2$ (M = Ce, Eu), Eu[Pc(OC$_5$H$_{11}$)$_8$]$_2$, and M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ (M = Ce, Gd, Tb) (λ_{ex} = 633 nm) [4a]. It thus seems opportune to study systematically the Raman spectroscopic properties of these complexes by means of excitation with laser sources emitting at 633 and 785 nm, as for the other series mentioned above. The present work reports these studies.

It is worth noting that we have previously recorded the Raman spectra of the bis(phthalocyaninato) compounds of Ce and Eu, namely M(Pc)$_2$ (M = Ce, Eu) and Ce[Pc(OC$_8$H$_{17}$)$_8$]$_2$, under excitation by 633 nm radiation [4a]. For the purpose of systematic comparison with those under 785 nm laser excitation, the spectra of the complete set of compounds discussed in this paper were re-measured under 633 nm excitation. Note that the Raman spectra of Ce(Pc)$_2$ and Ce[Pc(OC$_8$H$_{17}$)$_8$]$_2$ recorded this time under 633 nm excitation correspond well in band positions, but the relative intensities of some bands differ, compared with those recorded previously [4a]. Nevertheless, the results reported here are confirmed by the systematic and comparative spectra of the whole series of rare earth bis(phthalocyaninato) compounds M(Pc)$_2$ and M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ (M = Y, La…Lu except Ce and Pm), in which the one for Eu(Pc)$_2$ is in good accordance with the previous measurements [4a]. The conclusions are further reinforced by the fact that the Raman spectrum of Ce[Pc(OC$_8$H$_{17}$)$_8$]$_2$ corresponds well with that of Ce(Pc)$_2$ recorded under 633 nm excitation, the former of which is also in line with the previous measurement under excitation by 647 nm radiation [4b].

2. Experimental

Homoleptic bis(phthalocyaninato) rare earth complexes M(Pc)$_2$ and M[Pc(OC$_8$H$_{17}$)$_8$] (M = La-Lu except Pm, Y) were prepared according to published procedures [8]. Their sandwich nature has been well established through a series of spectroscopic methods including high resolution mass, UV-vis, near-IR, and NMR techniques. Resonance 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 633 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 for these experiments the ×10 objective was employed giving a spot size on the sample of about 5 μm. Laser power at the sample was approximately 0.08 mW. Spectra of excellent quality were obtained in approximately 3 min, with the exceptions noted below.

3. Results and Discussion

In bis(phthalocyaninato) rare earth complexes $M(Pc)_2$, the single crystal X-ray diffraction structural data have shown that the rare earth cation is at the center of two Pc ligands facing each other in a staggered arrangement [1,2]. In the solid state, these compounds can be assumed to belong to the D_4 or D_{4d} point-groups depending on the skew angle between the two macrocyclic rings. There has been no crystallographic report on the molecular structure of peripherally octa(alkoxy)-substituted homoleptic bis(phthalocyaninato) rare earth complexes thus far. However, according to the recently reported molecular structures of peripherally octa(hexylthio)- and 15-crown-5 ether-substituted bis(phthalocyaninato) rare earth analogues $Lu[Pc(SC_6H_{13})_8]_2$ and $Yb[Pc(15C5)_4]_2$ [$H_2Pc(SC_6H_{13})_8$ = 2,3,9,10,16,17,23,24-octakis(hexylthio)phthalocyanine, $H_2Pc(15C5)_4$ = 2,3,9,10,16,17,24,25-tetrakis(15-crown-5)phthalocyanine] [9], the skew angle between the two phthalocyanine macrocyclic ligands is 42 and 42.5°, respectively, for these two compounds. The equilibrium geometry of $Lu[Pc(SC_6H_{13})_8]_2$ and $Yb[Pc(15C5)_4]_2$ is therefore D_4. This should also be true for the present alkoxy-substituted analogues $M[Pc(OC_8H_{17})_8]_2$.

It has been found that in the Raman spectra of $Zr[Pc(t\text{Bu})_4]_2$, $M[Nc(t\text{Bu})_4]_2$, and $M(Pc)[Pc(\alpha\text{-}OC_5H_{11})_4]$ [4c,4f,5], only frequencies corresponding to the characteristic fingerprint vibrations of the Pc or Nc macrocycle were observed and side chain vibrations were very weak or absent. This is also true in the present case since both laser lines used in our experiments appear to enhance modes associated with the aromatic macrocycles (see below).

Similar to other large conjugated systems, one-to-one matching of observed vibrational frequencies to the internal vibrations cannot be achieved in the vibrational spectra of homoleptic bis(phthalocyaninato) rare earth compounds due to the existence of strong couplings of some vibrational coordinates [3-7]. Therefore, the Raman spectra of these homoleptic bis(phthalocyaninato) double-decker complexes are still composed of a relatively small number of fundamentals despite the large number of Raman active vibrational modes.

3.1 Raman characteristics of $M(Pc)_2$ and $M[Pc(OC_8H_{17})_8]_2$ (M = Y, La-Lu except Pm) with excitation by laser line at 633 *nm*

The electronic absorption spectra of $M(Pc)_2$ and $M[Pc(OC_8H_{17})_8]_2$ (M = Pr, Tb, Tm) which are typical representatives of the UV-vis spectra for the complexes of tervalent rare earths in each series are shown in Figs. 2 and 3, respectively [8]. All the spectra of $M(Pc)_2$ (M = Y, La-Lu except for Ce and Pm) show a typical B band at 316-325 nm with a very weak shoulder peak at the lower energy side of 342-358 nm [10]. The Q bands for these compounds appear as a strong absorption in the range of 658-689 nm together with the weak vibronic components at 570-596 and 595-618 nm. In addition, a weak band related with the π-radical anion at 420-458 nm is also observed. For the series of $M[Pc(OC_8H_{17})_8]_2$ compounds containing tervalent rare earth metal, the B absorption splits into two bands at 331-343 and 369-378 nm due to the influence of eight octyloxy groups on the phthalocyaninato rings [8d]. Their Q bands appear at 668-699 nm with weak vibronic absorptions at 579-601 and 604-630 nm, respectively. The weak π-radical anion band is seen at 485-513 nm. For both series of compounds, the energies of all the absorption bands mentioned above are sensitive to the metal center. In particular, along with the lanthanide contraction, the Q absorption band for both $M(Pc)_2$ and $M[Pc(OC_8H_{17})_8]_2$ blue-shifts in the same order [8d,10]. These characteristics in their electronic absorption form the basis for the fact that systematic changes are observed in both the frequencies and appearance of the Raman spectra of $M(Pc)_2$ and $M[Pc(OC_8H_{17})_8]_2$ along with the change in the central metal ionic size, as detailed below.

It is worth noting that the Raman spectra of La(Pc)$_2$ and Dy[Pc(OC$_8$H$_{17}$)$_8$]$_2$ with excitation at 633 nm were of poor quality due to the strong fluorescence. Figs. 4 and 5 respectively compare the Raman spectra of three compounds M(Pc)$_2$ and M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ for M = Pr, Tb, and Tm under excitation by 633 nm light. As can be seen, the Raman spectra for both series of compounds M(Pc)$_2$ and M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ seem to be much simpler in comparison with those of M(Pc)[Pc(α-OC$_5$H$_{11}$)$_4$] [4f], revealing the relatively higher molecular symmetry of these compounds than the heteroleptic analogues. In particular, the Raman spectra for the peripherally octa(octyloxy)-substituted bis(phthalocyaninato) rare earth complexes appear to be as simple as, or even simpler than, the corresponding unsubstituted counterparts M(Pc)$_2$, indicating again that only frequencies corresponding to the characteristic fingerprint vibrations of the Pc macrocycle in M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ were observed. Side chain vibrations were very weak or absent under excitation with laser line of 633 nm, and this is also true when using laser excitation emitting at 785 nm (see below). The observed Raman spectroscopic bands of phthalocyanine for these new homoleptic bis(phthalocyaninato) rare earths were partially assigned in Tables 1 and 2, respectively. Note that the assignments given in Tables 1 and 2 are restricted to characteristic fundamentals based on the previous description of normal modes for phthalocyaninato and especially bis(phthalocyaninato) metal derivatives [4,11]. Recent calculations on the vibrational characteristics of monomeric phthalocyanine derivatives also benefit the present assignments [12]. Due to the similar electronic structure and electronic absorption properties among the whole series of bis(phthalocyaninato) rare earth compounds, all members of each series M^{III}(Pc)$_2$ and M^{III}[Pc(OC$_8$H$_{17}$)$_8$]$_2$ (M = Y, La-Lu except Ce and Pm) show similar Raman characteristics.

With laser excitation at 633 nm, which is nearly in resonance with the Q band absorptions of both series of bis(phthalocyaninato) rare earth complexes respectively at 658-689 and 668-699 nm, vibrational frequencies in the range of 1300-1600 cm^{-1} derived from isoindole ring stretchings and the aza group stretching are selectively intensified. For M^{III}(Pc)$_2$, the weak Raman bands at ca. 574-577 and 812-817 cm^{-1} and a band at 678-680 cm^{-1} with medium or strong intensity are attributed to phthalocyanine breathing [4,11], and the frequencies of all these modes seem to show a dependence on the rare earth size, slightly blue-shifted along with the lanthanide contraction. The medium band at ca. 740 cm^{-1} is due to aromatic phthalocyanine C–H wagging of M(Pc)$_2$ [4]. In the range of 1000-1300 cm^{-1}, there are several weak or medium bands lying at ca. 1006, 1030, 1103, 1174, 1196, 1215 and 1301 cm^{-1}, which are assigned to aromatic C-H bending. The pyrrole breathing presents two bands in the region of around 1140 and 1500 cm^{-1}. The former comprises a single peak with medium intensity at ca. 1138-1145 cm^{-1} whereas the latter overlaps with the aza stretching vibration in the same region to form a broad band at 1495-1525 cm^{-1} for the whole series of compounds M^{III}(Pc)$_2$. For the double-deckers with early lanthanide metals, the aza stretching band appears as an unresolved shoulder on the *higher* energy side of the peak. In contrast, for the double-deckers with medium and late lanthanides, the pyrrole breathing band appears as an unresolved shoulder peak on the *lower* energy side of the more intense aza stretching peak. The intense band in the range 1409-1423 cm^{-1} and the weak band in the range 1444-1451 cm^{-1} are attributed to isoindole stretchings. The former intense band discussed above, together with the aza stretching band at 1512-1525 cm^{-1}, show dependence on the rare earth radius, shifting to higher energy along with the rare earth contraction. This is not surprising considering the blue-shifted trend of the Q absorptions at 658-689 nm in the same order.

As shown in Fig. 5 and organized in Table 2, the Raman spectroscopic frequencies of the phthalocyanine core in M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ have been similarly assigned by analogy with those of unsubstituted counterparts M(Pc)$_2$. The Raman spectra observed for M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ are even simpler than those of corresponding M(Pc)$_2$. This is probably due to the fact that the excitation at 633 nm is slightly further away from resonance with the main Q bands of M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ (668-699 nm) than with those of M(Pc)$_2$. This leads to an increased resolution in the Raman spectra of M[Pc(OC$_8$H$_{17}$)$_8$]$_2$, which further benefits the assignments of the frequencies. For instance, unlike for the series of M^{III}(Pc)$_2$, a very good linear correlation can be established between the frequency of the coupled pyrrole and aza stretching modes of M^{III}[Pc(OC$_8$H$_{17}$)$_8$]$_2$ at 1504-1527 cm^{-1} and the tervalent rare earth ionic radii, as shown in Fig. 6. In addition, the band positions of the Pc breathing modes at 561-568 and 683-686 cm^{-1}, the C=N stretch at 782-787 cm^{-1}, the coupled C=C pyrrole and benzene stretching at 1312-1322 cm^{-1} and the isoindole stretching at 1400-1415 cm^{-1} show dependence on the rare earth ionic size. They all shift to higher energy along with the rare earth contraction as for their unsubstituted analogues.

The tervalent yttrium double-deckers are noteworthy. The frequencies of some above-mentioned bands for both $Y^{III}(Pc)_2$ and $Y^{III}[Pc(OC_8H_{17})_8]_2$ deviate from the linear relationship established for the other tervalent rare earth complexes (Tables 1 and 2), due probably to the intrinsic difference between yttrium and the lanthanides, namely the absence of f electrons. This is also true for these two yttrium complexes when using laser excitation emitting at 785 nm, Tables 3 and 4.

As can be expected from the previous studies [4a,4b,4d-f,8d], both $Ce(Pc)_2$ and $Ce[Pc(OC_8H_{17})_8]_2$ show different Raman spectroscopic characteristics from those of the rest of the rare earth series, which is related to the different electronic absorption spectra of these cerium complexes. As indicated by the ^1H NMR spectra, both phthalocyanine rings exist as dianions in $Ce(Pc)_2$ and $Ce[Pc(OC_8H_{17})_8]_2$, despite the XANES results that suggest a valence state intermediate between III and IV for the cerium [13]. These complexes therefore differ from other analogues that have the form $M(Pc'^{2-})(Pc'^{\bullet-})$ [Pc' = Pc, $Pc(OC_8H_{17})_8$]. A comparison of the Raman spectra of $Ce(Pc)_2$ and $Ce[Pc(OC_8H_{17})_8]_2$ with those of the rest of the series shows that these cerium complexes contain most of the frequencies found for the other complexes, however the relative intensities are different. For example, a strong band appears at 1173 cm^{-1} for $Ce[Pc(OC_8H_{17})_8]_2$ (Table 2) corresponding to C-H bending, but for the other complexes, only a weak band in the same region is observed. Moreover, the marker Raman band of Pc^{2-} and $[Pc(OC_8H_{17})_8]^{2-}$ at 1499 and 1501 cm^{-1} with contributions from pyrrole C=C, aza C=N and isoindole stretches is observed as the strongest scattering in the Raman spectra of $Ce(Pc)_2$ and $Ce[Pc(OC_8H_{17})_8]_2$. As noted above, a similar strong band due to $Pc^{\bullet-}$ and $[Pc(OC_8H_{17})_8]^{\bullet-}$ has been found to upshift to 1502-1509 and 1504-1527 cm^{-1} in the Raman spectra of $M^{III}(Pc)_2$ and $M^{III}[Pc(OC_8H_{17})_8]_2$.

3.2 Raman characteristics of $M(Pc)_2$ and $M[Pc(OC_8H_{17})_8]_2$ (M = Y, La-Lu except Pm) with excitation by laser line at 785 nm

Strong fluorescence occurred when trying to record the Raman spectra of $M(Pc)_2$ (M = La, Ce, Lu) using excitation at 785 nm, so these data do not appear in Table 3.

Using the excitation laser line at 785 nm that is far away from resonance with the Q absorption bands, as shown in Fig. 7 and summarized in Table 3, the macrocyclic ring deformation and ring radial vibrations between 500 and 1000 cm^{-1} in the Raman spectra of $M(Pc)_2$ are selectively intensified. This is in good accordance with the Raman characteristics of homoleptic $M(Pc)_2$ reported by Homborg [6b], especially with excitation at 1064 nm. The Pc breathing at 675-679 cm^{-1} and the aromatic C-H wagging at ca. 739 cm^{-1} are the most intense bands. The band locating at 1327-1329 cm^{-1} with medium intensity is assigned to the pyrrole C=C stretchings coupled with benzene C=C stretchings and the weak one at about 1342 cm^{-1} to the isoindole stretchings. Similar to those excited with 633 nm laser line, the frequencies of the coupled pyrrole C=C and aza C=N stretchings in the region of 1507-1521 cm^{-1} overlap to form a broad, unresolved envelope. The vibrations of $M(Pc)_2$ at 675-679 cm^{-1} assigned to the Pc breathings, at 1407-1422 cm^{-1} attributed to the isoindole stretchings, and at 1508-1521 cm^{-1} due to the coupling of aza and pyrrole stretchings are found to shift to higher energy along with the ionic radius contraction.

Under the same laser line excitation of 785 nm, the Raman spectra for the octa(octyloxy)-substituted bis(phthalocyaninato) rare earth analogues $M[Pc(OC_8H_{17})_8]_2$ basically take the same spectroscopic features with corresponding unsubstituted counterparts $M(Pc)_2$. Their Raman spectroscopic frequencies with assignments are tabulated in Table 4. However, this time a systematic but rather more dramatic change could be seen in the appearance of the Raman spectra across the series. Along with the decrease in the ionic size from La to Lu, the band at 1502-1528 cm^{-1} contributed from the coupling of the pyrrole and aza stretchings gradually loses some intensity, changing from a very strong scattering for the light rare earth compounds to a medium and weak one for the heavy rare earth complexes. In the same order, the band at ca. 1060 cm^{-1} assigned to the C-H bendings in contrast gradually gains some intensity to change from a weak band to an intense band. It is worth noting that similar change in the intensity of the latter band at ca. 1050 cm^{-1} due to the C-H bendings was also observed in the Raman spectra of $M^{III}(Pc)_2$ under the same laser line excitation. However, the change in the intensity of the former band for $M^{III}(Pc)_2$ was not so significant. All these results can be clearly exemplified by the Raman spectra of the Pr, Tb, and Tm complexes of the two series shown in Figs. 7 and 8.

When exciting the Raman spectrum of $Ce[Pc(OC_8H_{17})_8]_2$ with 785 nm laser line, similar to the case by means of 633 nm laser line, a Raman spectrum with different characteristics from those of the rest of the rare earth series was obtained. The intense band at 1498 cm^{-1} with contribution from both pyrrole C=C and aza C=N stretches together with isoindole stretchings is the marker Raman band of $[Pc(OC_8H_{17})_8]^{2-}$, which compares with that of $[Pc(OC_8H_{17})_8]^{\bullet-}$ at 1502-1528 cm^{-1} in the Raman spectra of $M^{III}[Pc(OC_8H_{17})_8]_2$ under the same excitation.

4. Conclusions

The Raman spectra for two series of homoleptic bis(phthalocyaninato) rare earth complexes $M(Pc)_2$ and $M[Pc(OC_8H_{17})_8]_2$ have been recorded under excitation with 633 and 785 nm laser lines. The present results are in line with those reported for related series of complexes, namely $M(Pc)[Pc(\alpha\text{-}OC_5H_{11})_4]$ and M(TClPP)(Pc), recorded under similar laser line excitations, in terms of the Raman spectroscopic characteristics of phthalocyanine ligand and the relationship between the phthalcyanine Raman characteristics and the rare earth ionic size. They also provide a good and, more importantly a systematic, experimental basis for further investigation by theoretical chemists in this field.

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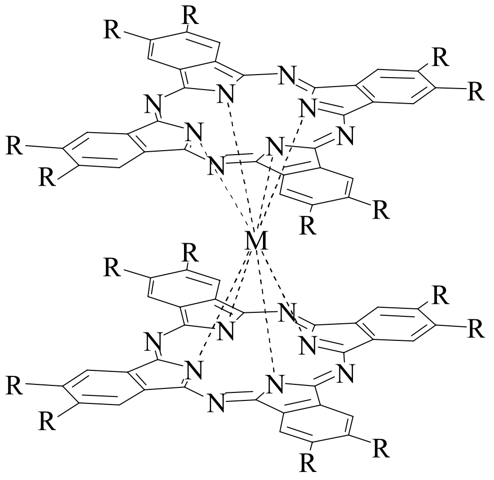

R = H, OC_8H_{17}

Fig. 1. The schematic molecular structure of bis(phthalocyaninato) rare earth sandwich complexes $M(Pc')_2$ [Pc' = Pc, $Pc(OC_8H_{17})_8$].

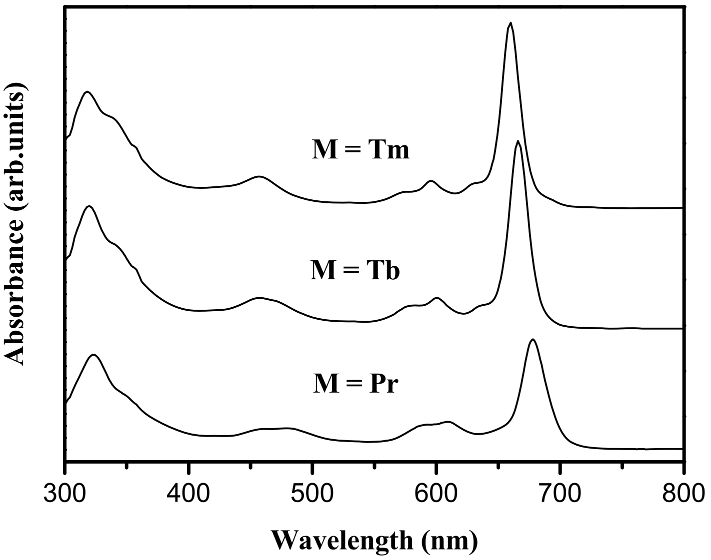

Fig. 2. The UV-vis spectra of $M(Pc)_2$ (M = Pr, Tb, Tm) in $CHCl_3$.

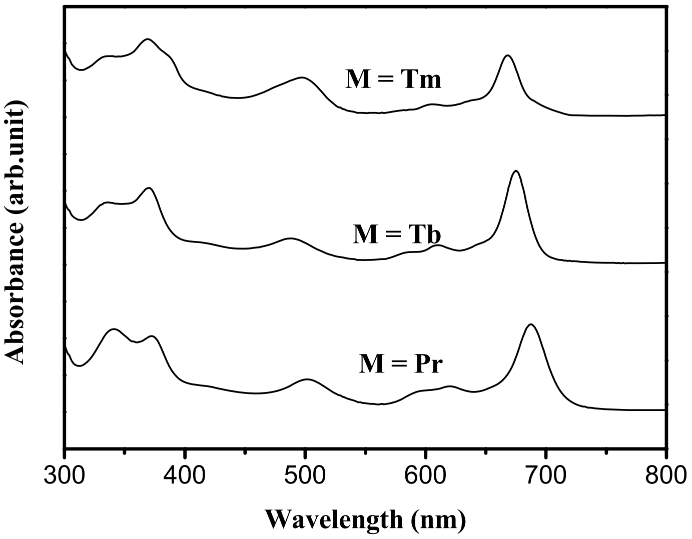

Fig. 3. The UV-vis spectra of M[Pc(OC_8H_{17})$_8$]$_2$ (M = Pr, Tb, Tm) in $CHCl_3$.

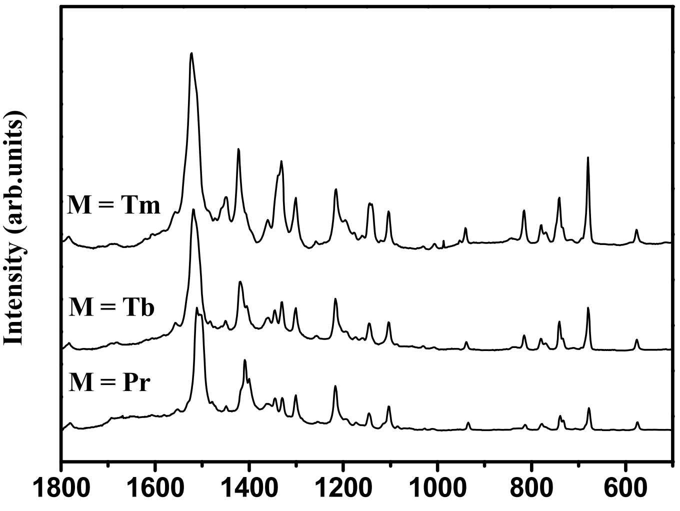

Fig. 4. Raman spectra of M(Pc)$_2$ (M = Pr, Tb, Tm) in the region of 500-1800 cm^{-1} with excitation at 633 nm.

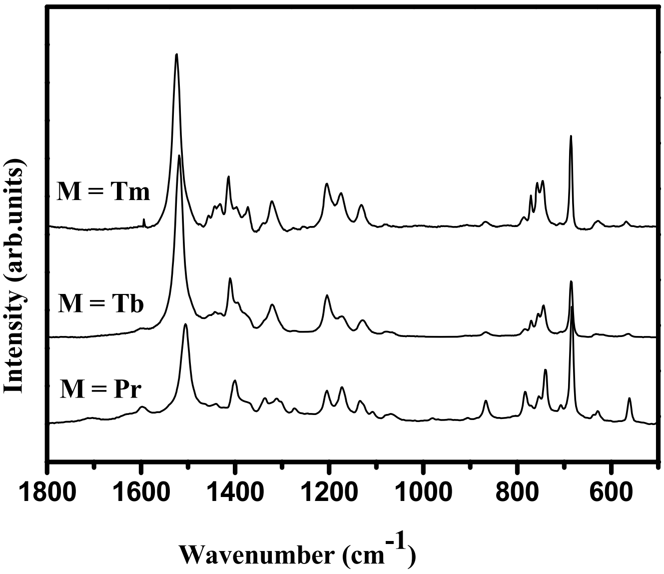

Fig. 5. Raman spectra of M[Pc(OC_8H_{17})$_8$]$_2$ (M = Pr, Tb, Tm) in the region of 500-1800 cm^{-1} with excitation at 633 nm.

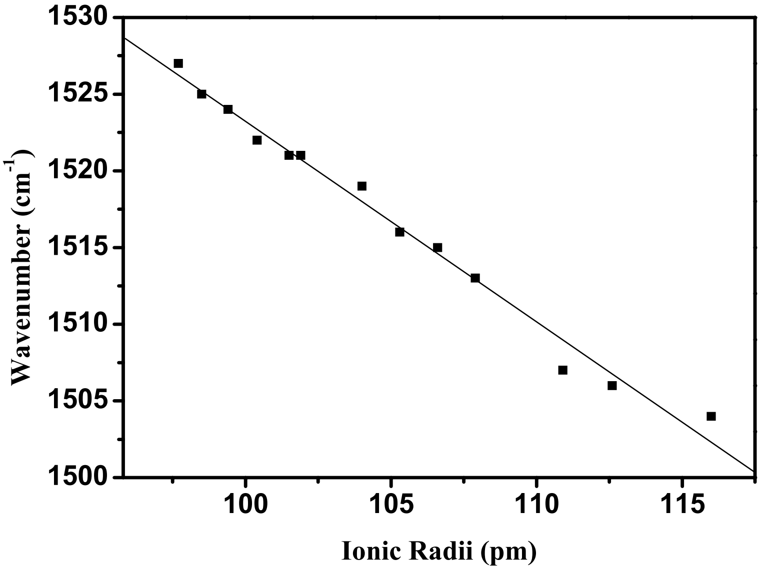

Fig. 6. Plot of wavenumber of the coupling of pyrrole and aza stretching scattering of M[Pc(OC_8H_{17})$_8$]$_2$ at 1504-1527 cm^{-1} with excitation at 633 nm as a function of the ionic radius of M^{III}.

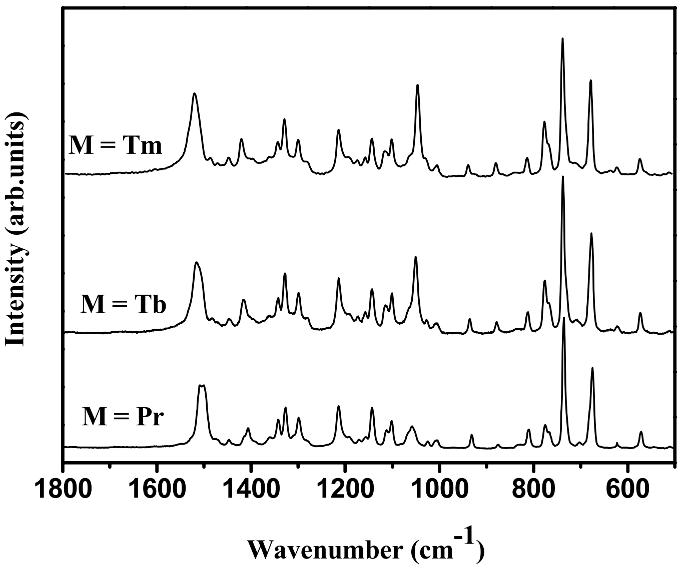

Fig. 7. Raman spectra of M(Pc)$_2$ (M = Pr, Tb, Tm) in the region of 500-1800 cm^{-1} with excitation at 785 nm.

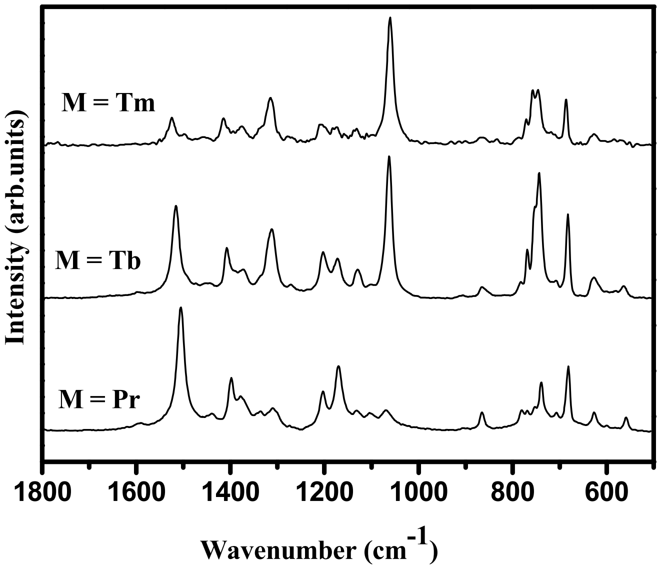

Fig. 8. Raman spectra of M[Pc(OC$_8$H$_{17}$)$_8$]$_2$ (M = Pr, Tb, Tm) in the region of 500-1800 cm^{-1} with excitation at 785 nm.

Table 1. Characteristic Raman bands (cm^{-1}) of phthalocyanines for M(Pc)$_2$ (M = Y, Ce-Lu except Pm) (λ_{ex} = 633 nm).

Ce	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Y**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Assignment**
579w	574w	574w	574w	576w	576w	576w	576w	577w	576w	576w	577w	577w	577w	Pc breathing
677s	678m	678m	678m	678m	678m	680m	678s	680m	680s	680s	680s	680s	680s	Pc breathing
724w														
741m	739w	739m	740m	741m	741m	741m	741m	742m	741s	741s	741m	742m	741m	C-H wag
767w	771[a]	769[a]	770[a]	770[a]	770[a]	770[a]	770[a]	772[a]	769[a]	770[a]	770[a]	771[a]	770[a]	C=N aza stretching
776w	777w	779w	780w	779w	779w	780w	779w	773w	780w	779w	779w	780w	780w	C=N aza stretching
820m	814w	812w	814w	814w	814w	816w	816w	816w	816w	816w	816w	817w	817w	Pc breathing
933w	935w	935w	936w	936w	936w	939w	938w	939w	939w	939w	941w	941w	941w	
1009w	1011w	1006w	1006w	1006w	1006w	1006w	1006w	1006w	1009w	1006w	1006w	1006w	1006w	C-H bend
1026w	1027w	1027w	1029w	1029w	1029w	1031w	1029w		1029w	1031w	1031w	1031w	1031w	C-H bend
1055w														C-H bend
1103m	1104w	1103w	1104w	1103w	1103w	1104w	1103w	1104w	1103w	1103w	1104w	1104w	1103m	C-H bend
1141m	1145w	1138m	1136m	1145w	1144w	1145w	1145w	1138w	1144w	1145w	1144w	1139w	1144m	pyrrole breathing
1173w	1173w	1173w	1175w	1172w	1174w	1174w	1173w	1176w	1173w	1174w	1177w	1177w	1174w	C-H bend
1190w		1196w	1196w	1194w	1196w	1196w	1192w	1196w	1196w	1196w	1196w	1196w	1194w	C-H bend
1206w	1217m	1215m	1215w	1215m	1215m	1217m	1215m	1215w	1217m	1215m	1215m	1215m	1217m	C-H bend
	1255w			1255w	1255w	1257w	1257w			1258w	1258w	1258w	1258w	
1303w	1301m	1299m	1299m	1301m	1301m	1301m	1301m	1301w	1301w	1301w	1301w	1301w	1301w	C-H bend
1332m	1330m	1330m	1331m	1330m	1330m	1330m	1330m	1332m	1330m	1330m	1332m	1332m	1332m	C=C pyrrole and benzene stretching
1338s	1345w	1336m	1336m	1344w	1343w	1345w	1345w	1338m	1344w	1345w	1339m	1338m	1347m	isoindole stretching
1361w	1362w	1360w	1364w	1361w	1357w	1359w	1359w		1361w	1361w	1361w	1361w	1360w	isoindole stretching
1391w	1400[a]	1402[a]	1403[a]	1403[a]	1403[a]	1404[a]	1405[a]	1403[a]	1407[a]	1407[a]	1408[a]		1410[a]	isoindole stretching
1423w	1409s	1409m	1419m	1414s	1414s	1419s	1419s	1423s	1420s	1421s	1423s	1423s	1423s	isoindole stretching
1449m	1449w	1444w	1446w	1449w	1449w	1451w	1449w	1446w	1449w	1451w	1449w	1448w	1449w	isoindole stretching
1499s	1505[a]	1502s	1504s	1510[a]	1511[a]	1513[a]	1512[a]	1509s	1513[a]	1514[a]	1516[a]	1513[a]	1519[a]	coupling of pyrrole and aza stretching
	1512s	1510[a]	1513[a]	1516s	1515s	1519s	1518s		1521s	1521s	1522s	1519s	1525s	aza stretching
1556w	1553w	1553w	1557w	1554w	1554w	1556w	1556w	1561w						benzene stretching

[a] Shoulder band.

Table 2. Characteristic Raman bands (cm^{-1}) of phthalocyanines for $M[Pc(OC_8H_{17})]_2$ (M = Y, La-Lu except Pm and Dy) (λ_{ex} = 633nm).

La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Y**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Assignment**
561w	564w	562m	562w	562w	565w	564w	564w	568w	568w	568w	568w	568w	568w	Pc breathing
628w	625w	629w	629w	629w	634w	634w	632w	628w	629w	628w	628w	628w	636 [a]	Pc breathing
683s	681s	684vs	684s	684s	684s	684s	686s	684s	684s	686s	686s	686s	686s	Pc breathing
741m	741m	741m	741m	742m	744m	744m	744w	745m	745w	745w	745w	747m	745m	C-H wag
753w	750w	755w	756w	755w	756w	756w	756w	757w	756w	756m	758m	758m	758m	
767w				771w	771w	771w	770w	771w	771w	771w	771w	771m	771w	C=N aza stretching
782w	780w	783w	783w	784w	783w	784w	784w	785w	785w	784w	787w	787w	787w	C=N aza stretching
866w	866w	867w	867w	867w	867w	867w	866w	866w	867w	867w	867w	867w	867w	coupling of isoindole deformation
														and aza stretching C-H bend
1067w	1073w	1069w	1064w	1075w	1080w	1078w	1080w	1080w	1081w	1081w	1081w	1080w	1078w	pyrrole breathing
1135m	1135w	1135w	1135w	1132w	1130w	1130w	1128w	1130w	1132w	1130w	1132w	1132w	1132w	C-H bend
1174m	1173s	1173m	1173m	1173w	1173w	1173w	1173w	1174w	1174w	1174w	1174w	1174w	1176w	C-H bend
1205m	1199m	1205m	1205w	1205m	1205m	1205m	1205m	1205m	1205m	1205m	1205m	1205m	1205m	C=C pyrrole and benzene
1316m	1299w	1312w	1312w	1319w	1321m	1321w	1321m	1321m	1321m	1321m	1322m	1322m	1322m	stretching
														isoindole stretching
1335w	1350w	1336w	1339w	1338w										isoindole stretching
								1371w	1371w	1371w	1373w	1373w	1373w	isoindole stretching
1400m	1408m	1400m	1400m	1405s	1408s	1408s	1411s	1411s	1412s	1412s	1414m	1415s	1415m	isoindole stretching
	1434m				1431w	1431w	1432w	1432w	1432w	1432w	1432w	1432w	1432w	isoindole stretching
1444w	1461w	1440w	1443w	1441w	1440w	1441w	1440w	1442w		1443w	1443w	1445w	1444w	isoindole stretching
								1457w	1457w	1457w	1457w	1457w	1457w	coupling of pyrrole and aza
1504vs	1501vs	1506s	1507vs	1513vs	1515vs	1516vs	1519vs	1521vs	1521vs	1522vs	1524vs	1525vs	1527vs	stretching
														benzene stretching
1600w	1599w	1599w	1597w	1599w	1597w	1596w	1594w	1597w	1596w	1594w	1597w	1599w	1590w	

[a] Shoulder band.

Table 3. Characteristic Raman bands (cm^{-1}) of phthalocyanines for M(Pc)$_2$ (M = Y, Pr-Yb except Pm) (λ_{ex} = 785 nm).

Pr	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Y**	**Ho**	**Er**	**Tm**	**Yb**	**Assignment**
572w	572w	572w	573w	573w	574w	573w	574w	575w	574w	575w	574w	Pc breathing
623w	622w	623w	622w	622w	623w	622w	623w	623w	623w	623w	623w	Pc breathing
675s	675s	676s	676s	677s	677s	678s	678s	678s	679s	678s	679s	Pc breathing
736s	737s	738s	738s	738s	738s	738s	739s	739s	739s	739s	739s	C-H wag
775w	775w	775w	776m	776m	776m	776m	777m	776m	777m	777m	777m	C=N aza stretching
810w	811w	812w	813w	813w	812w	813w	813w	814w	814w	814w	814w	Pc breathing
875w	875w	878w	877w	877w	878w	878w	879w	879w	880w	880w	880w	coupling of isoindole deformation and aza stretching
932w	932w	934w	934w	934w	935w	935w	937w	937w	937w	939w	939w	
1005w	1006w	1007w	1007w	1008w	1008w	1008w	1007w	1009w	1006w	1006w	1006w	C-H bend
1025w	1025w	1026w	1026w	1026w	1027w	1026w	1029w	1028w				C-H bend
1058w	1057w	1056m	1052m	1052m	1051m	1049m	1049s	1050s	1048s	1046s	1046s	C-H bend
1101m	1101m	1101w	1101m	1101m	1100m	1101m	1101m	1101m	1101m	1101m	1101m	C-H bend
1113w	1112w	1113w	1113w	1113w	1114w	1114w	1115w	1117w	1115w	1116w	1116w	C-H bend
1143m	1142m	1137m	1143m	1143m	1143m	1143m	1143m	1143m	1143m	1143m	1142m	pyrrole breathing
1157w	1157w	1155w	1157w	1158w	1158w	1158w	1157w	1157w	1158w	1157w	1157w	C-H bend
1172w	1172w	1172w	1172w	1173w	1172w	1172w	1174w	1174w	1175w	1175w	1175w	C-H bend
1215m	1214m	1213m	1215m	1214m	1214m	1215m	1215m	1215m	1214m	1214m	1214w	C-H bend
1299m	1299m	1298m	1299m	1299m	1299m	1300m	1300m	1299m	1300m	1300m	1300w	C-H bend
1327m	1327m	1328s	1328m	1328m	1328m	1328m	1329m	1329s	1329m	1329m	1329m	C=C pyrrole/benzene stretching
1342w	1342w	1336w	1342w	1343w	1342w	1343w	1343w	1343m	1343w	1342w	1342w	isoindole stretching
1407w	1407m	1417m	1412w	1412w	1416m	1417m	1418m	1420m	1420m	1421m	1422m	isoindole stretching
1447w	1446w	1444w	1448w	1449w	1446w	1446w	1447w	1447w	1447w	1448w	1448w	isoindole stretching
1501s	1503s											C=C pyrrole stretching
1508s	1509s	1507s	1513s	1514s	1515s	1517s	1516s	1520m	1519m	1520m	1521m	coupled pyrrole/aza stretchings

Table 4. Characteristic Raman bands (cm^{-1}) of phthalocyanines for $M[Pc(OC_8H_{17})]_2$ (M = Y, La-Lu except Pm) (λ_{ex} = 785nm).

La	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Y**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Assignment**
558w	562w	559w	560w	560w	560w	561w	564w	562w	570w	562w	568w	568w	568w	570w	Pc breathing
626w	623w	627w	626w	627w	627w	626w	627w	630w	630w	630w	630w	627w	625w	627w	Pc breathing
682s	680w	682s	682s	682s	683s	682s	682m	687s	685m	687s	686m	686m	687m	687m	Pc breathing
707w		707w	707w	707w	707w	707w	708w	710m	709w	709w	716w	719w	716w	719w	Pc breathing
739s	740m	739m	740m	740m	741m	743s	743s	742m	746m	742m	746m	746m	748m	747m	C-H wag
751w	751w	752w	752w	751w	754w	753w	753w	757w	757w	758w	756m	757m	758m	758m	
769w	762w	769w	769w	769w	770w	769w	769w	772w	771w	773w	771w	771w	771w	771w	C=N aza stretching
780w	780w	780w	783w	783w	782w	782w	783w	786w	785w	785w	786w	786w	787w	788w	C=N aza stretching
864w	864w	865w	865w	865w	866w	866w	865w	869w	867w	869w	867w	867w	867w	863w	coupling of isoindole deformation and aza stretching
1068w	1071w	1069w	1067w	1069w	1064w	1064s	1063s	1075s	1062s	1074s	1061s	1060s	1060s	1060s	C-H bend
1132w	1132w	1131w	1132w	1133w	1132w	1130w	1129w	1135w	1135w	1136w	1134w	1135w	1137w	1136w	pyrrole stretching
1169m	1172s	1171s	1171s	1171m	1172m	1172m	1172w	1174s	1174w	1174s	1178w	1174w	1178w	1179w	C-H bend
1203m	1198w	1203m	1203m	1203m	1203m	1203m	1203m	1206m	1207w	1205m	1208w	1205w	1206w	1204w	C-H bend
1309w	1298w	1310w	1312w	1312w	1312w	1311m	1312m	1315w	1314w	1314w	1315m	1315n	1315m	1318s	C=C pyrrole and benzene stretching
1334w	1349w	1336w	1335w	1338w	1336w	1336w		1347w	1341w	1346w					isoindole stretching
1369w		1378w	1379w	1381w	1386w	1381w	1373w	1391m	1375w	1392m	1371w	1376w	1377w	1377w	isoindole stretching
1396m	1406s	1398m	1399m	1401m	1403m	1406m	1408m	1408m	1411w	1408m	1412w	1414w	1416w	1416w	isoindole stretching
1439w	1431m	1439w	1439w	1443w	1444w	1445w	1445w	1448w		1445w					isoindole stretching
	1459w														isoindole stretching
1502vs	1498vs	1505vs	1507vs	1510vs	1513vs	1514vs	15 15s	1518s	1520m	1519s	1523w	1525w	1529w	1528w	coupling of pyrrole and aza stretching