Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 251 (2007) 2386–2399

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Synthesis, structure, reactivity and photoluminescence of lanthanide(III) monoporphyrinate complexes

Wai-Kwok Wong [a,b,*], Xunjin Zhu [a], Wai-Yeung Wong [a,b]

[a] *Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, PR China*
[b] *Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Kowloon Tong, Hong Kong, PR China*

Received 22 September 2006; accepted 23 November 2006
Available online 28 November 2006

Contents

Abstract

A series of cationic lanthanide(III) monoporphyrinate complexes of the general formula $[Ln(Por)(H_2O)_3]Cl$ ($Ln = Yb^{3+}$ and Er^{3+}; Por = porphyrinate dianion) were prepared *via* the protonolysis of $Ln(NR_2)_3$ with porphyrin free bases (H_2Por). An unexpected neutral oxalate-bridged Yb porphyrinate dimer $[Yb(Por)(DME)]_2(\mu\text{–}\eta^2\text{:}\eta^2\text{–}O_2CCO_2)$ was isolated and structurally characterized by X-ray crystallography when the protonolysis was carried out in an atmosphere of carbon dioxide. The coordinated aqua molecules of the cationic porphyrinate complexes are very labile and can be easily displaced by good donor solvents such as DMF or anionic tripodal ligand L_2X^- ($L_2X^- = L_{OMe}{}^-$ and $T_p{}^{H-}$) to form the neutral complex $[Ln(Por)(Cl)(DMF)_2]$ or $[Ln(Por)(L_2X)]$, respectively. $[Yb(Por)(H_2O)_3]Cl$ underwent dimerization to give the dimer $[Yb(Por)(\mu\text{-}OH)(H_2O)]_2$ when dissolved in basic solution and $[Yb(Por)(\mu\text{-}Cl)(H_2O)]_2$ in dilute HCl solution. Furthermore, $[Yb(Por)(H_2O)_3]Cl$ behaves as a living catalyst for the cyclotrimerization of phenyl isocyanate to l,3,5-triphenyl-s-triazin-2,4,6-trione. Photoluminescence studies showed that the porphyrinate dianion, acting as an antenna, sensitized Ln^{3+} ($Ln^{3+} = Nd^{3+}$, Er^{3+} and Yb^{3}) ion emission in the near-infrared region, and that $[Ln(TDPAPP)(L_{OMe})]$ complexes exhibited excellent optical limiting capability. Protonolysis of $Ln(NR_2)_3$ with *N*-confused porphyrin free bases (H_2NCP) followed by the addition of the encapsulating tripodal anion, L_{OMe}, gave lanthanide(III) *N*-confused porphyrinate complexes of the general formula $[Ln(NCP)(L_{OMe})]$ ($Ln = Yb^{3+}$ and Er^{3+}; NCP = *N*-confused porphyrinate dianion), whose X-ray structures revealed an η^2 agostic interaction between the metal center and the inner C–H bond of the NCP ligand.

Keywords: Cationic lanthanide monoporphyrinate complexes; Metal-catalyzed cyclotrimerization; Lanthanide porphyrinate dimers; *N*-Confused porphyrin; Near-infrared sensitization; Optical limiting property

---

* *Corresponding author at*: Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, PR China. Fax: +852 3411 5862.
E-mail address: wkwong@hkbu.edu.hk (W.-K. Wong).

0010-8545/$ – see front matter
doi:10.1016/j.ccr.2006.11.014

1. Introduction

Porphyrin undoubtedly represents one of the most widely studied of all known macrocyclic ring systems [1]. Interest in this naturally occurring tetrapyrrolic macrocycle is broadly based and derives in part from its multiple biological functions as well as its ability to function as an excellent metal-complexing ligand. Metalloporphyrins comprise an important class of molecules that serve nature in a variety of ways. They are the active sites of numerous properties whose functions range from oxygen transport and storage (hemoglobin, myoglobin), electron transport (cytochrome *c* oxidase) to energy conversion (chlorophyll) [2–4]. Indeed, there are few compounds found in nature which can compare with the diversity of biochemical functions exhibited by metalloporphyrins [5]. Additionally metalloporphyrins have proven to be efficient catalysts for polymerization of olefin [6], alkane hydroxylation [7], olefin epoxidation [8] and cyclopropanation [9]. Therefore, porphyrin complexes of the main group metals, transition metals, especially of the late transition metals have been continued to attract the attention of researchers for over 50 years [10,11].

Lanthanide(III) porphyrinate complexes were first reported in 1974 [12]. Initially, the desirable qualities of the heme moiety (rigid, well-defined structure, tight binding site in proteins and resistance to demetallation) and the propitious electronic and magnetic properties of trivalent lanthanide ions were chosen to be combined in an effort to develop a potent new dipolar NMR probe for use in biological systems [13], and this work opened up a new area of macrocyclic ligand chemistry of these elements. The general preparative methods of lanthanide monoporphyrinate complexes employ the treatment of $Ln(acac)_3 \cdot xH_2O$ (acac = acetylacetonate) with porphyrin (H_2Por) in high boiling solvent 1,2,4-trichlorobenzene (TCB) at 220 °C for 3–4 h, which gives the product [Ln(Por)(acac)] in 10–30% yields [14]. This method limits the choice of anionic axial ligand as the coordinated diketonates are difficult to displace. The coordinated diketonates can be replaced in subsequent reactions, but high boiling solvents are again required and low isolated yields are typical. For example, by refluxing [Ce(Por)(acac)] with H_2Por in TCB, $[Ce(Por)_2]$ and $[Ce_2(Por)_3]$ were isolated [15]. Thus, most of the works were on the synthesis, characterization and properties of lanthanide(III) homo- and hetero-leptic porphyrinates [15,16], and porphyrin-phthalocyanine heteroleptic [17] double- and triple-decker sandwich complexes.

Currently, there is a great interest in the luminescent properties [18–23], and energy transfer mechanisms [24,25] of Er^{3+}, Yb^{3+} and Nd^{3+} polydentate complexes. These lanthanide(III) ions which emit in the near-infrared (NIR) region, a region where biological tissues and fluids are relatively transparent, have potential for chemosensor and fluoroimmuno essays applications. Direct excitation of lanthanide ions is difficult because of the forbidden nature of their electronic transitions [26]; however, indirect excitation of an organic chromophere (antenna) with close interaction with lanthanide ions can make the energy in the triplet state of the ligand transferring efficiently to the excited state of the lanthanide ion and sensitize lanthanide ion emission [27]. So, the design of molecular systems with binding ability and photosensitizing properties for the construction of efficient photoluminescent lanthanide complexes is the key issue of this active area of research. A number of NIR emitting lanthanide complexes have been reported that have visible light absorbing antennas [28]. Some examples of these sensitizers that absorb in the visible region of the electromagnetic spectrum are fluorescein [23a,29], lissamine [30], porphyrin [31], ferrocene and ruthenium complexes [32]. The ability of porphyrins to accumulate in malignant tumours, to absorb strongly in the UV–vis region and be efficient photo-sensitizers [2] has made lanthanide(III) porphyrinate complexes ideal candidates for luminescence imaging agents. The use of Yb^{3+} monoporphyrinate complex as luminescence contrasting agent was only briefly studied [20].

As the acac anion of [Ln(Por)(acac)] complexes was very difficult to be displaced by other molecules under mild conditions, it was very unfavorable for the modification of final products. Therefore, the luminescent properties and application of these lanthanide ions in porphyrinate dianion coordinated complexes were not fully explored. Recently, [Ln(Por)(acac)] have been used to extract zwitterionic amino acids and applied in CD chirality sensing [33]. The photovoltaic properties and charge transfer process of [Dy(TATBP)(acac)] complexes (H_2TATBP = *meso*-tetraalkyl-tetrabenzoporphyrin) were investigated by surface photovoltage spectroscopy, which reveals that these ligands and complexes are all p-type semiconductor [34]. Application of [Ln(Por)(acac)] complexes (Ln = Er^{3+}, Yb^{3+} and Nd^{3+}) as emitting materials in NIR light-emitting diodes (LEDs) has also been reported [35]. Synthetic routes for the preparation of lanthanide monoporphyrinate complexes with non-diketonate anionic axial ligands have been developed in recent years. Lanthanide-alkyl monoporphyrinate complex [Ln(OEP)(R)] [H_2OEP = octaethylporphyrin; Ln = Lu, Y; R = $CH(SiMe_3)_2$] was prepared *via* the protonolysis of LnR_3 with H_2OEP in toluene [36], and lanthanide-halide monoporphyrinate complexes [Ln(Por)(X)(S)] [X = Cl or I; S = dimethoxyethane or bis(2-methoxyethyl) ether] either *via* the protonolysis of $LnX[N(SiMe_3)_2]_2$ with H_2Por or the interaction of $LnX_3(THF)_4$ with porphyrinate dianions $Li_2(Por)$ [37]. In this review, we will summarize our efforts on the studies of the preparation, structural characterization, reactivity and NIR photoluminescence of lanthanide(III) monoporphyrinate complexes.

2. Synthesis and reactivity of cationic lanthanide(III) monoporphyrinate complexes

2.1. Synthesis and structure

Treatment of an excess amount of $Ln[N(SiMe_3)_2]_3 \cdot x[LiCl(THF)_3]$ (Ln = Yb^{3+}, Er^{3+} and Y^{3+}), generated *in situ* from the reaction of anhydrous $LnCl_3$ with three equivalent of $LiN(SiMe_3)_2$ in tetrahydrofuran, with porphyrin free base (H_2Por) in refluxing bis(2-methoxyethyl) ether for 48 h followed by work up in air gave the cationic monoporphyrinate complexes $[Ln(Por)(H_2O)_3]Cl$ in high yield (Fig. 1) [38]. However, the above synthetic route did not work for lanthanide

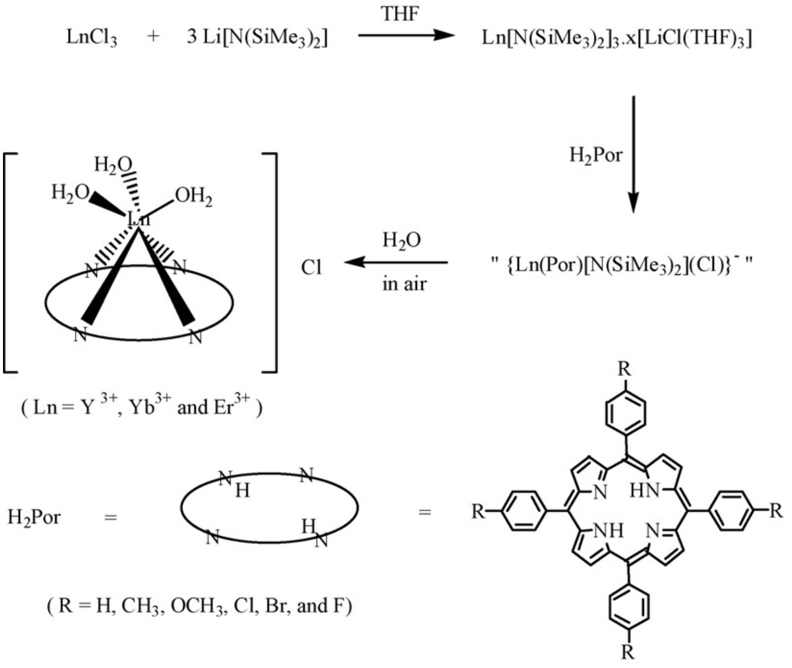

Fig. 1. Synthetic scheme for the cationic lanthanide(III) complexes $[Ln(Por)(H_2O)_3Cl]$.

ions with large ionic radius. For instance, with lighter lanthanide ions, such as Nd^{3+} which has a larger ionic radius, the $[Nd(Por)(H_2O)_3]Cl$ complex which was only observed spectroscopically, was rather unstable and decomposed rapidly *via* de-metallation to re-generate the porphyrin free base upon exposure to air and moisture.

The $[Ln(Por)(H_2O)_3]Cl$ ($Ln = Y^{3+}$, Er^{3+} and Yb^{3+}) complexes are stable in air and in most organic solvents, and can be purified by column chromatography. Their electronic absorption spectra are characteristic of normal metalloporphyrins [13] and are similar to those of the cationic lanthanide monoporphyrinate complexes $[Ln(TMPyP)(acac)]I_4$ [$Ln = Sm^{3+}$, Eu^{3+}, Gd^{3+} and Tb^{3+}; H_2TMPyP = tetrakis(*N*-methylpyridinium-4-yl)porphyrin tetra-cation] [39]. Fig. 2 shows the typical UV–vis spectra for $[Yb(TMPP)(H_2O)_3]Cl$ and tetrakis(*p*-methoxyphenyl)porphyrin (H_2TMPP) in chloroform. The Soret band was observed at *ca*. 425 nm, which was very close to their porphyrin free bases. The *Q* bands for complexes are quite different from free bases. The number of the absorption bands at Q region is reduced from four to two that are centered at 554 and 593 nm. The absorbance at 554 nm is greater than that at 593 nm. This is in agreement with Gouterman's four-orbital model, which predicts that due to an increase in symmetry, the four Q bands of the porphyrin free base will be reduced to two upon the formation of a metalloporphyrin [40]. In the absorption spectra of regular metalloporphyrins there are two Q bands between 500 and 600 nm. The lower-energy band (α band) is the electronic origin Q(0,0) of the lowest singlet excited state S_1. The second band (β band) is its vibrational overtone and is labeled as Q(l,0). The relative intensities of these bands can be a qualitative yardstick of just how stable is the metal ion complex to the four porphyrin nitrogen atoms. Thus, when the intensity of α is greater than β, the metal forms a stable complex with the porphyrin, whereas when α is less than β, the metal is easily displaced by protons. The α/β relative intensity ratio for the cationic complexes ranges from 0.12 to 0.44. The substituents on the phenyl rings of the porphyrinate dianion have little effect on the structure of the complexes, but have some effect on the stability of the complexes. The halo-substituted complexes are much more sensitive to acid hydrolysis during chromatographic separation.

The structures of $[Ln(Por)(H_2O)_3]Cl$ ($Ln = Y^{3+}$, Er^{3+} and Yb^{3+}) complexes were ascertained by X-ray crystallography and are isomorphous [38a]. A perspective drawing of $[Yb(TMPP)(H_2O)_3]Cl$ is shown in Fig. 3. Crystal structure analyses revealed that the lanthanide(III) ions are octa-coordinate,

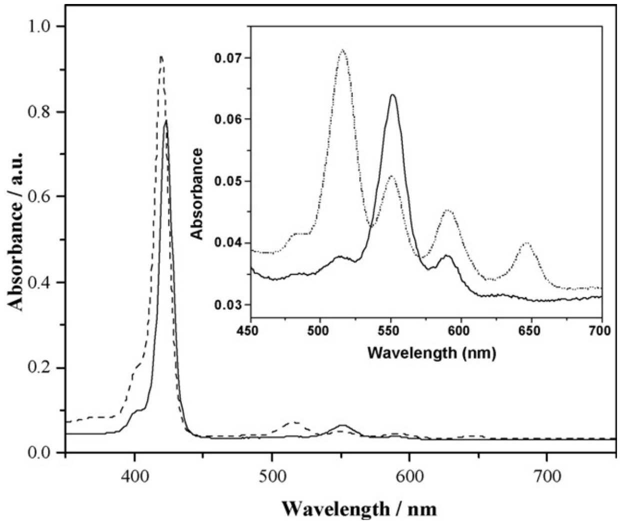

Fig. 2. UV–vis of $[Yb(TMPP)(H_2O)_3]Cl$ (solid line) and H_2TMPP (dot line) in $CHCl_3$ at room temperature. The concentration is 1.5×10^{-6} mol/l.

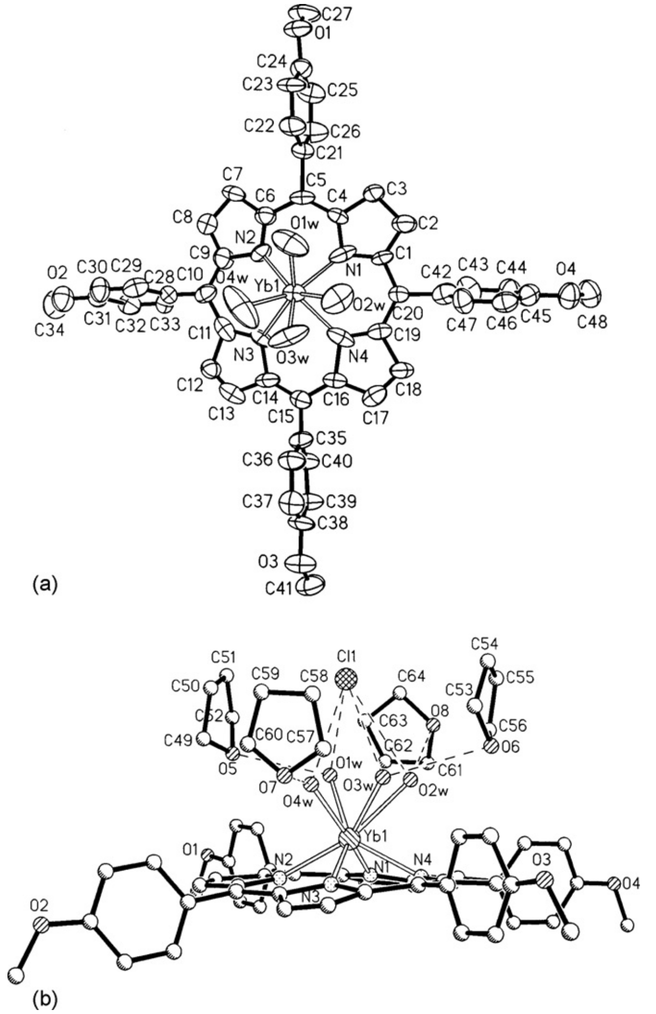

Fig. 3. (a) Perspective view of the cation of $[Yb(TMPP)(H_2O)_3]Cl$. (b) A side view of the molecular structure of the complex. (Reproduced from Ref. [38a] by permission of the Royal Society of Chemistry).

surrounded by four N atoms of the porphyrinate dianion and four aqua ligands in which two are disordered with site occupancy of 0.5, and have a square antiprismatic coordination geometry. The average dihedral angle between a pair of N–Yb–N and O–Yb–O planes is 47.6°. The structural data are similar to that of $[Tb((\beta\text{-}Cl_8TPP)(O_2CMe)(Me_2SO)_2]$ [41], in which the metal also adopts a square antiprismatic coordination geometry with the average dihedral angle between a pair of N–Tb–N and O–Tb–O planes being 46.7°. The average Yb–N and Yb–O bond lengths are 2.301 and 2.307 Å, respectively. The displacement of the Yb atom from the mean planes formed by four N atoms and four O atoms are 1.082 and 1.640 Å, respectively. The two mean planes are almost parallel to each other with a separation of 2.716 Å. The porphyrin ring exhibits a saddle like distortion. As shown by the edge-on view [Fig. 3(b)], the independent solvate THF molecules and the anionic Cl atom form acceptor hydrogen bonds with the aqua ligands.

By varying the nature of the amides, porphyrins and lanthanide metal ions, we could prepare neutral mono- and di-nuclear porphyrinate complexes *via* the above protonolysis reactions (Fig. 4) [42]. The dimer $[Yb(TMPP)(\mu\text{-}OH)(H_2O)]_2$ was the first structurally characterized neutral hydroxy-bridged dinuclear lanthanide(III) bis(porphyrin) complex in which the two porphyrin ligands were unsupported.

The propensity for the formation of lanthanide porphyrinate complexes is highly dependent on the nature of the porphyrins and the lanthanide precursors. A possible mechanism to account for the observations is shown in Fig. 5. It is very likely that the intermediate **A** $[Ln(Por)(NR_2)Cl]^-$ which arises from the protonolysis of the lanthanide-amide *ate* complex, $[Ln(NR_2)_3Cl]^-$ (generated *in situ* from the reaction of $LnCl_3$ with $LiNR_2$) with porphyrin free base H_2Por was involved. Then depending on the nature of the amides, lanthanide(III) metal ions and the porphyrinate dianions, **A** could either lose a chloride group to give the intermediate **B** $[Ln(Por)(NR_2)]$ or lose an amide group to give the neutral monoporphyrinate complex [Ln(Por)Cl]. With (diphenyl)amide, **A** lost the chloride group to give intermediate **B** $[Yb(Por)(NR_2)]$ which hydrolysed to give the neutral dinuclear bis(porphyrin) complex. With bis(trimethylsilyl)amide, **A** lost the amide group to give the neutral monoporphyrinate complex [Yb(Por)Cl]. With an electron donating methoxy or methyl group at the *para*-position of the *meso*-aryls of the porphyrin, [Yb(Por)Cl] underwent further dissociation of the chloride group to give the cationic lanthanide monoporphrinate complex $[Yb^{III}(Por)(H_2O)_3]^+$.

Furthermore, treatment of an excess amount of $Yb[N(SiMe_3)_2]_3{\cdot}x[LiCl(THF)_3]$ with tetrakis(phenyl) porphyrin (H_2TPP) in refluxing bis(2-methoxyethyl) ether solution for 48 h, after work up in air, yielded the unexpected neutral oxalate-bridged dimer $[Yb(TPP)(CH_3OCH_2CH_2OCH_3)]_2(\mu\text{–}\eta^2{:}\eta^2\text{–}O_2CCO_2)$, whose structure has been ascertained by X-ray crystallography (Fig. 6) [43]. Although the origin of the oxalate dianion is not clear, yet experimental results suggest that the oxalate dianion was probably derived from the reductive coupling of carbon dioxide from air during the work up. Reductive coupling of atmospheric carbon dioxide to oxalates in the presence of lanthanide nitrates has been reported [44].

2.2. Reactivity and catalytic activity

The catioinic lanthanide porphyrinate complexes $[Ln(Por)(H_2O)_3]Cl$ are very versatile precursor complexes for the preparation of other lanthanide monoporphyrinate complexes. The aqua molecules of the $[Ln(Por)(H_2O)_3]Cl$ complexes are very labile and can be easily displaced by other good donor solvents. For instance, when dissolved in DMF, the aqua ligands of $[Yb(TPP)(H_2O)_3]Cl$ were substituted by DMF to give a neutral species $[Yb(TPP)(Cl)(DMF)_2]$ in quantitative yield [45]. The $[Ln(Por)(H_2O)_3]Cl$ complexes have a high tendency to form bridging dinuclear complexes [45]. Interaction of the complex $[Yb(TPP)(H_2O)_3]Cl$ with either K_2CO_3 or 4,4′-bipyridine in CH_2C1_2 gave the hydroxyl-bridged dimer $[Yb(TPP)(\mu\text{-}OH)(H_2O)]_2$, and with 8-hydroxyquinaldine (QH) in the presence of K_2CO_3 gave the bridging dinuclear complex $[Yb(TPP)]_2(\mu\text{-}OH)(\mu\text{-}Q)$ in high yield. Biphasic reaction of $[Yb(TMPP)(H_2O)_3]Cl$ in CH_2C1_2 with aqueous HC1 afforded the chloro-bridged dimer $[Yb(TPP)(\mu\text{-}Cl)(H_2O)]_2$ again in good

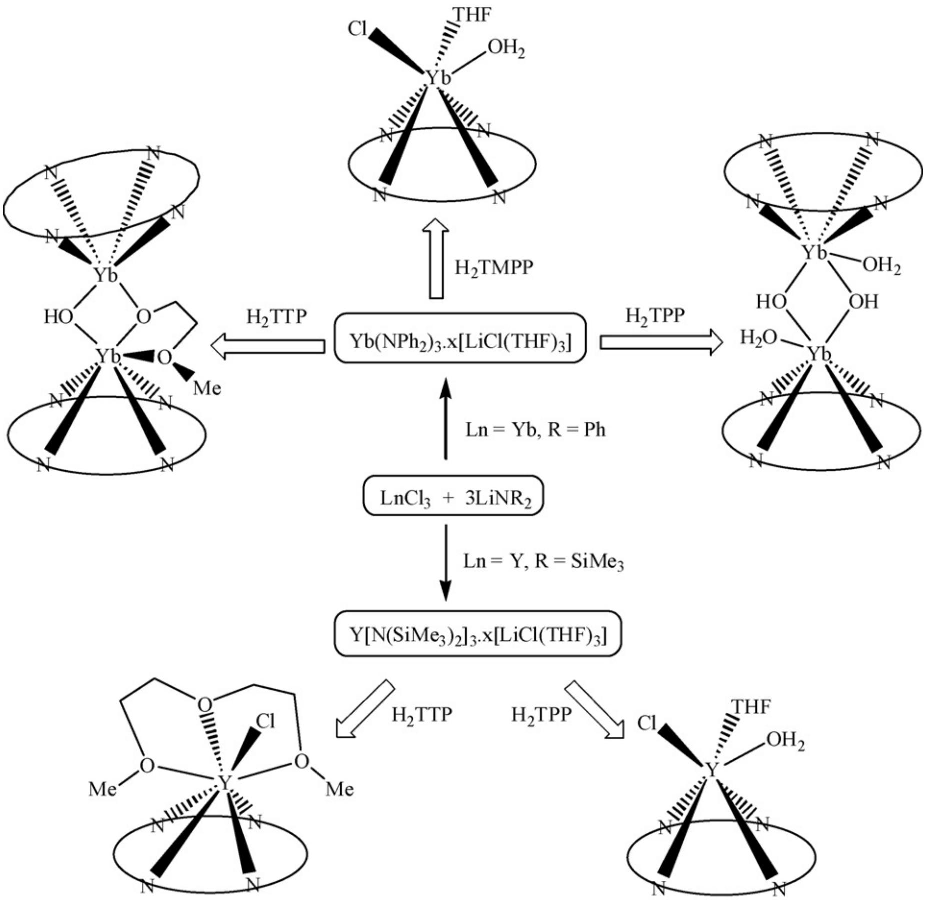

Fig. 4. Reaction scheme of $Ln(NR_2)_3{\cdot}x[LiCl(THF)_3]$ with porphyrin free bases [H_2TPP = tetrakis(phenyl)porphyrin; H_2TTP = tetrakis(*p*-tolyl)porphyrin; H_2TMPP = tetrakis(*p*-methoxyphenyl)porphyrin].

yield. The solid-state structures of these dinuclear complexes were ascertained by X-ray crystallography [45]. Metathesis of $[Yb(TMPP)(H_2O)_3]Cl$ with an excess amount of $AgBF_4$ in tetrahydrofuran led to the disproportionation of Ag(I) to silver metal and Ag(II), and the isolation of silver(II) porphyrin complex $Ag^{II}(TMPP)$ [38a]. The results are summarized in Fig. 7.

The catalytic activity of the cationic lanthanide porphyriante complexes $[Ln(TMPP)(H_2O)_3]Cl$ ($Ln = Yb^{3+}$, Er^{3+} and Y^{3+}) has been briefly examined [38a]. The complex $[Yb(TMPP)(H_2O)_3]Cl$ catalysed the conversion of phenyl isocyanate to its cyclic trimers, l,3,5-triphenyl-s-triazine-2,4,6-trione, quantatitively at 30 °C even at a catalyst to monomer mole ratio as low as 1:600. A possible mechansim for the catalytic process is shown in Fig. 8. The coordinatively unsaturated cationic species, $[Yb(Por)]^+$, generated *in situ*, presumably acting as a Lewis acid, catalyzes the cyclotrimerization of phenyl

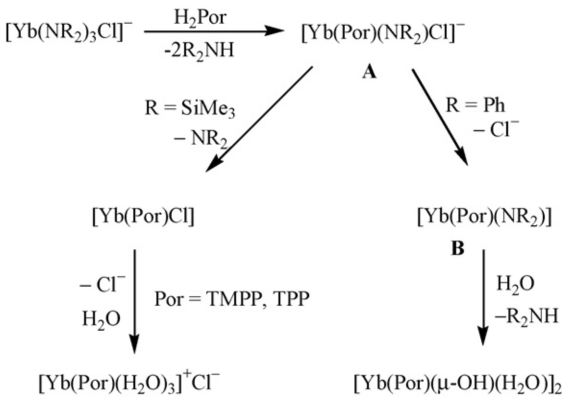

Fig. 5. Proposed mechanism for the formation of ytterbium(III) porphyrinate complexes.

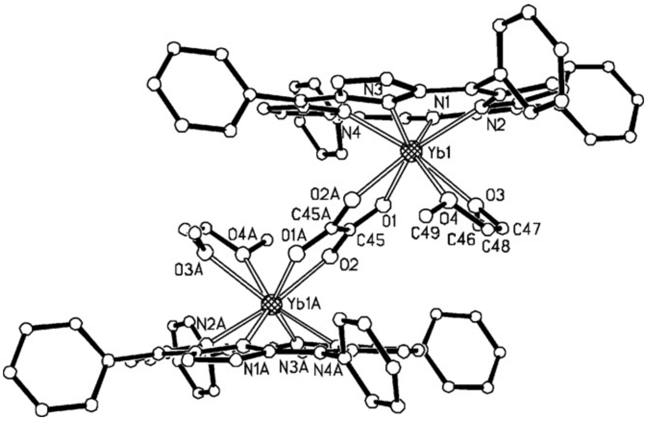

Fig. 6. A perspective drawing of the oxalate-bridged dimer $[Yb(TPP)(CH_3OCH_2CH_2OCH_3)]_2(\mu{-}\eta^2{:}\eta^2{-}O_2CCO_2)$. (Reproduced from Ref. [43] by permission of the Royal Society of Chemistry.)

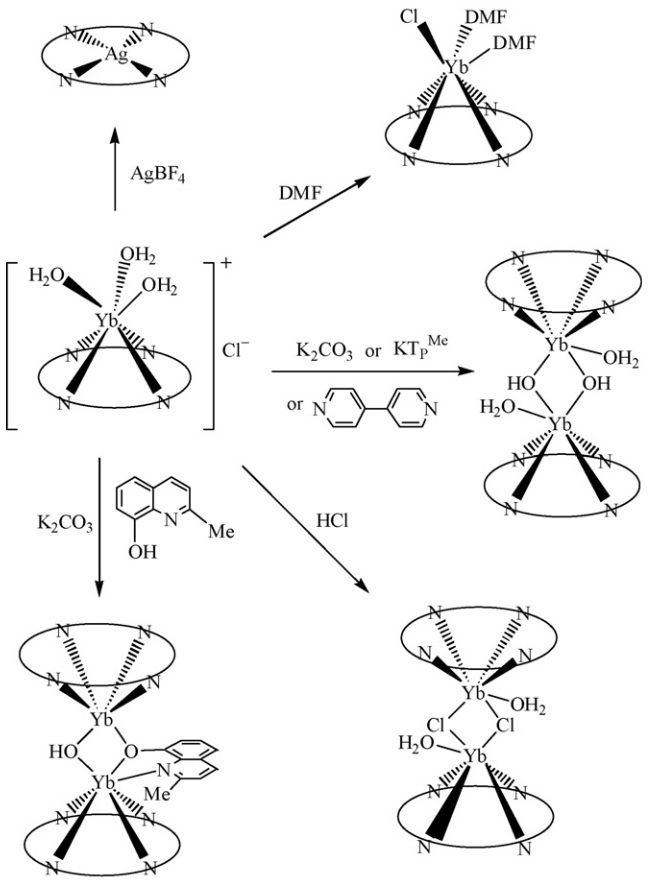

Fig. 7. Reaction scheme of $[Yb(Por)(H_2O)_3]Cl$.

isocyanate [46,47]. However, the corresponding Er^{3+} and Y^{3+} complexes did not catalyze the cyclotrimerization. This may probably be due to the fact the Lewis acidity of Yb^{3+} is higher than that of Er^{3+} and Y^{3+} ions.

3. Synthesis and structure of neutral lanthanide(III) monoporphyrinate complexes

3.1. Synthesis and structure of neutral monoporphyrinate lanthanide(III) complexes containing an anionic tripodal ligand

It is a well known fact that NIR luminescence of lanthanide metal ions can be quenched by O–H vibrations [48]; thus replacement of the aqua molecules of the $[Ln(Por)(H_2O)_3]Cl$ complexes (Ln = Nd^{3+}, Yb^{3+} and Er^{3+}) by ligands that do not contain the OH functional group should be able to enhance the NIR emission of the lanthanide ions. Klaui's O_3-tripodal ligand $L_{OR}{}^-$ [(cyclopentadienyl)tris(dialkylphosphito)cobaltate] [49], and Trofimenko's scorpionate ligands $T_p{}^{R-}$ [hydridotris(pyrazolyl)-borate] [50] are mono-anionic 6e donors isoelectronic with cyclopentadienyl ligands (η^5-C_5R_5). These tripodal ligands are known to stabilize metal ions in high oxidation states and should be able to stabilize oxophilic metal ions such as Ln^{3+} metal ions. These ligands should be ideal ligands to displace the three coordinated aqua molecules of the $[Ln(Por)(H_2O)_3]^+$ complexes, stabilize the resultant lanthanide porphyrinate complexes and enhance their NIR luminescence. At room temperature, the cationic lanthanide porphyrinate complexes $[Ln(Por)(H_2O)_3]^+$ (Ln = Yb^{3+} and Er^{3+}) reacted readily with the anionic tripodal nucleophile $L_{OR}{}^-$ or $T_p{}^{H-}$ to give the neutral complexes $[Ln(Por)(L_{OR})]$ or $[Ln(Por)(T_p{}^H)]$, respectively, in high yield [51a,b]. Although we cannot isolate the unstable cationic $[Nd(Por)(H_2O)_3]Cl$ complexes, yet $[Nd(Por)(L_2X)]$ ($L_2X^- = L_{OR}{}^-$ or $T_p{}^{H-}$) complexes can be prepared in high yield by first protonolysing the lanthanide amide with porphyrin, followed by the addition of tripodal anions before working up in air. The results are shown in Fig. 9 [51]. Presumably, the precursor intermediate $[Nd(Por)(NR_2)Cl]^-$, generated upon protonolysis of the lanthanide amide with porphyrin, underwent nucleophilic displacement reaction with the tripodal anion to form the stable product $[Nd(Por)(L_2X)]$ ($L_2X^- = L_{OR}{}^-$ or $T_p{}^{H-}$) before it hydrolysed to form the unstable cationic complex $[Nd(Por)(H_2O)_3]Cl$. All the neutral $[Ln(Por)(L_2X)]$ (Ln = Nd^{3+}, Yb^{3+} and Er^{3+}) complexes are air-stable and soluble in most organic solvents, and can be purified by column chromatography. Their absorption spectra are similar to that of $[Ln(Por)(H_2O)_3]Cl$ and are characteristic of normal metalloporphyrins [13]. Elemental analyses and positive FAB mass spectra which exhibited the corresponding $(M+1)^+$ molecular ion peak confirmed that the products were 1:1 adducts of lanthanide monoporphyrinate and the anionic tripodal ligand. The ^{31}P NMR spectrum of $[Ln(Por)(L_{OR})]$ complex exhibited a singlet at around δ 184, −166 and 65 ppm. for Nd^{3+}, Er^{3+} and Yb^{3+} complexes, respectively. Recently, $[Ln(Por)(L_{OEt})]$ and $[Ln(Por)(T_p{}^H)]$ complexes had also been prepared by the nucleophilic displacement of halide from $[Ln(Por)(X)(DME)]$ (Ln = Yb, Tm, Er, Ho, Nd, Pr; X = Cl, I; DME = dimethoxyethane) by the anionic tripodal ligands $L_{OEt}{}^-$ and $T_p{}^{H-}$ [37a].

The solid-state structures of $[Ln(Por)(L_{OR})]$ and $[Ln(Por)(T_p{}^H)]$ (Ln = Nd^{3+}, Yb^{3+} and Er^{3+}) complexes were ascertained by X-ray crystallography [51]. Perspective drawings of $[Yb(TMPP)(L_{OEt})]$ and $[Yb(TPP)(T_p{}^H)]$ are shown in Figs. 10 and 11, respectively [51a,b]. The corresponding Nd and Er complexes are iso-structural to the Yb complexes. Selected structural data are summarized in Table 1. Structural analyses revealed that the lanthanide(III) ions are sandwiched between the porphyrin ring and the tripodal ligand. For the $[Ln(Por)(L_{OR})]$ complexes, the lanthanide(III) ions are seven-coordinated, surrounded by four N atoms of the porphyrinate dianion and three O atoms of the three phosphito groups. The $L_{OR}{}^-$ anion caps on the Ln^{3+} ion. The average Ln–N distance is longer than the average Ln–O distance. This reflects that the Ln^{3+} ions have a higher affinity for O atom than N atom. The average Ln–N and Ln–O distances are longer and shorter, respectively, than those of the corresponding cationic complex $[Ln(Por)(H_2O)_3]Cl$ [42]. These data indicate that the lanthanide ions form stronger bonds with the O atoms of the phosphito groups than with the O atoms of the aqua ligands. The three mean planes (C_5 of the cyclopentadienyl ring, N_4 of the porphyrinate ligand and O_3 of the phosphito groups) are almost parallel to one another. The dihedral angles formed

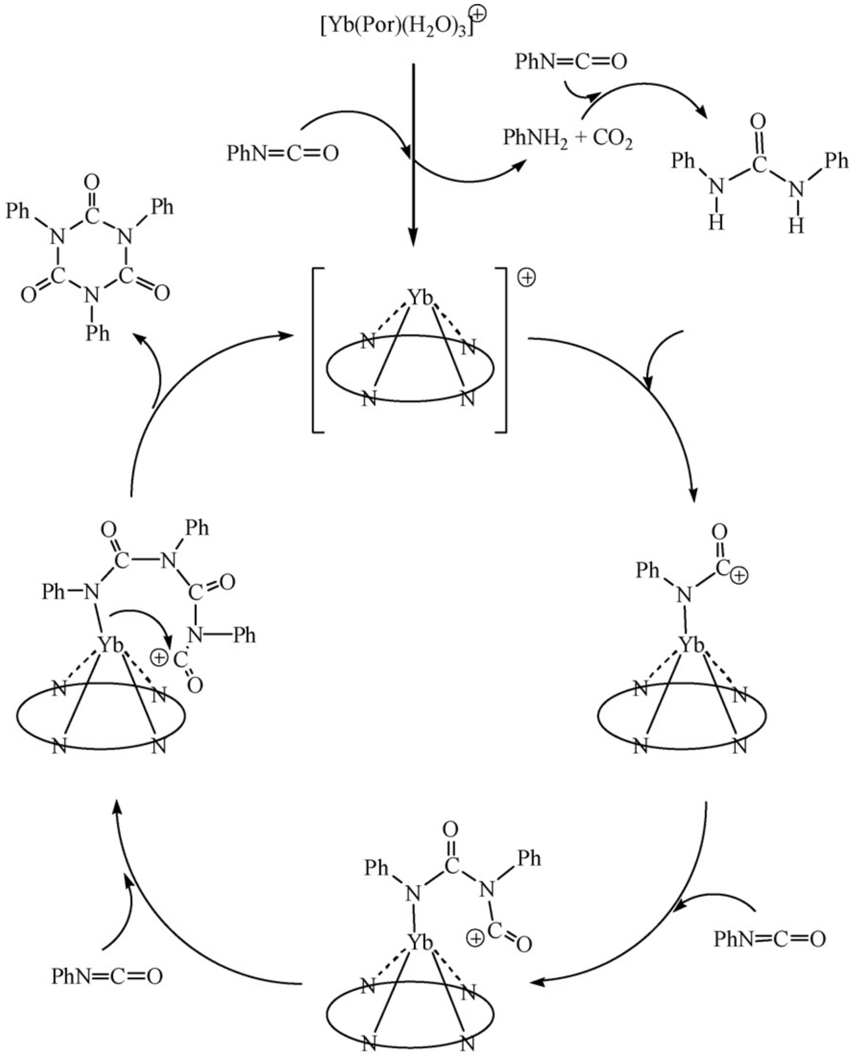

Fig. 8. Proposed mechanism for the cyclotrimerization of phenyl isocyanate.

between the C_5 and O_3 mean planes, O_3 and N_4 mean planes, and C_5 and N_4 mean planes range from 0.5° to 4.8°. The angle formed between the Ln···Co line and the normal of the N_4 plane is in between 2.3° and 3.0°.

For the [Ln(TPP)($T_p{}^H$)] complexes, the lanthanide(III) ions are also seven-coordinated, surrounded by seven nitrogen atoms, four from the porphyrinate dianion and three from the anionic tripodal ligand [51b,d]. The average bond length of

Table 1
Structural comparison of Nd^{3+}, Er^{3+} and Yb^{3+} complexes[a]

Compound	Ln–N(Por)$_{av}$	Ln–O$_{av}$	Ln–N($T_p{}^H$)$_{av}$	d_1[b]	d_2
Nd(TTP)(L_{OMe})	2.450	2.389		1.299	1.677[c]
Er(TPP)(L_{OEt})	2.370	2.261		1.201	1.540
Yb(TMPP)(L_{OEt})	2.352	2.269		1.153	1.540
Nd(TPP)($T_p{}^H$)	2.438		2.602	1.302	1.891[d]
Er(TPP)($T_p{}^H$)	2.373		2.518	1.195	1.800
Yb(TPP)($T_p{}^H$)	2.356		2.495	1.172	1.780
[Er(TMPP)(H_2O)$_3$]Cl	2.329	2.391		1.11	1.650[e]
[Yb(TMPP)(H_2O)$_3$]Cl	2.301	2.307		1.082	1.640

[a] All the measurements are in Å.
[b] Distance to the N_4 mean plane formed by the four nitrogen atoms of the porphyrinate.
[c] Distance to the O_3 mean plane formed by the three oxygen atoms of the L_{OR} ligand.
[d] Distance to the N_3 mean plane formed by the three nitrogen atoms of the $T_p{}^H$ ligand.
[e] Distance to the O_4 mean plane formed by the four oxygen atoms (two of which are disordered with half-site occupancy) of the aqua ligands.

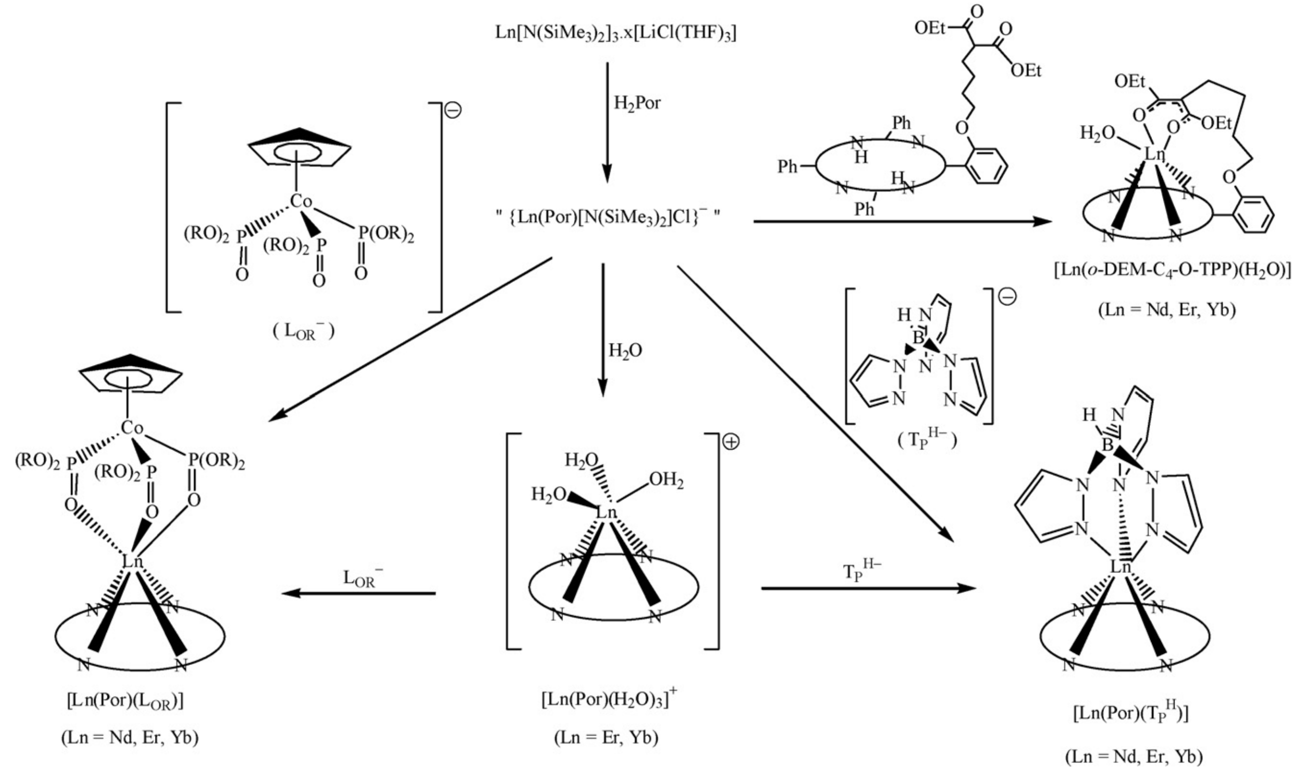

Fig. 9. Synthetic scheme for the preparation of neutral lanthanide(III) monoporphyrinate complexes.

Ln–N(porphyrin) is shorter than that of Ln–N(tripodal ligand). The mean plane N_4 formed by the four nitrogen atoms of the porphyrin dianion is almost parallel to the mean plane N_3 formed by the three nitrogen atoms of the anionic tripodal ligand, with a dihedral angle of 0.4°. The distance of the metal ion to the N_3 mean plane is about 0.6 Å longer than that to N_4 mean plane, so the metal ion is much closer to the N_4 mean plane. The distance of the metal ion to the N_4 mean plane is longer than that

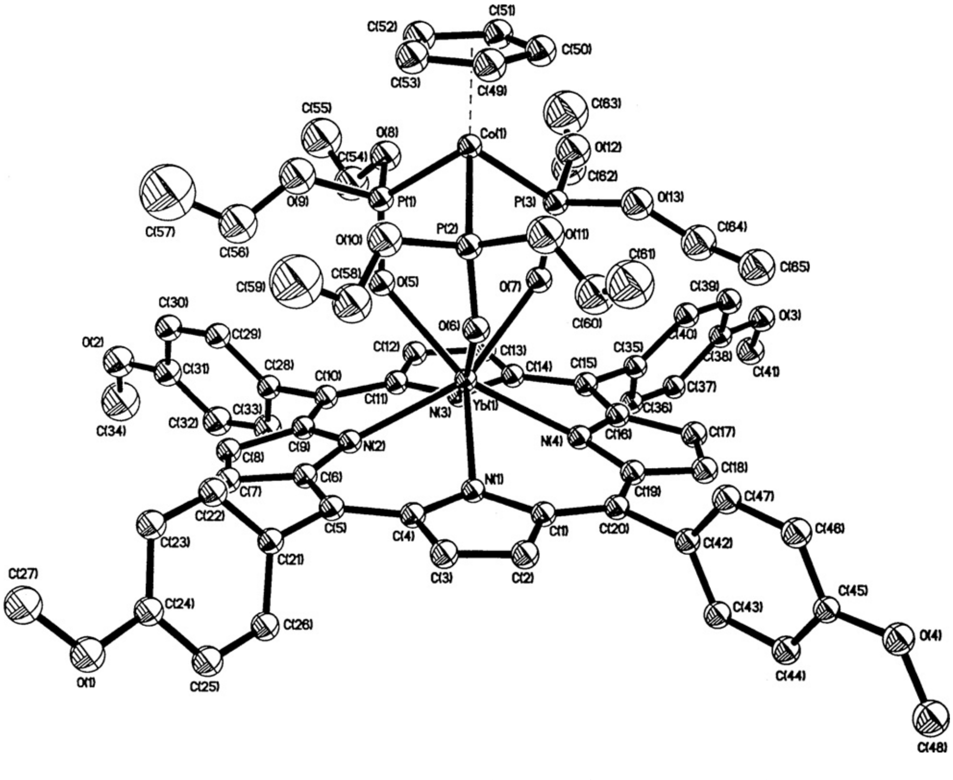

Fig. 10. A perspective drawing of [Yb(TMPP)(L_{OEt})]. (Reproduced from Ref. [51a] by permission of the Royal Society of Chemistry.)

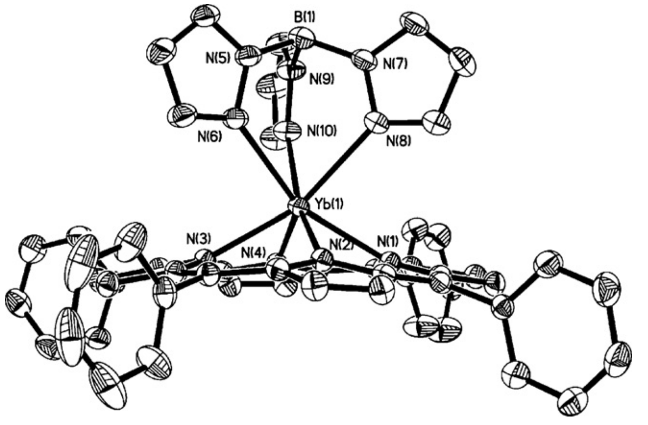

Fig. 11. Perspective views of $[Yb(TPP)(T_p{}^H)]$: (a) side view; (b) top view. (Reproduced from Ref. [51b] by permission of Wiley-VCH.)

of the corresponding $[Ln(porp)(H_2O)_3]Cl$ and shorter than that of $[Ln(porp)(L_{OEt})]$.

The decrease in Ln–N distance in the series $Nd^{3+} > Er^{3+} > Yb^{3+}$ is in agreement with the lanthanide contraction and reflects a decrease in ionic radii: 1.12 > 1.03 > 1.01 Å [52]. The data show clearly that due to the larger radius of Nd^{3+} ion, the distances between Nd^{3+} and porphyrin ring are longer than those of Er^{3+} and Yb^{3+} complexes. This may be the reason why $[Nd(Por)(H_2O)_3]Cl$ complexes are so unstable as compared with the Er^{3+} and Yb^{3+} analogs. Since the lanthanide ions are too large to fit into the cavity of the porphyrinate ring, the porphyrinate ring adopts a domed conformation to maximize the Ln–N interactions. The structures further show that the sterically bulky anions provide a congested environment around the metal center. This would minimize metal–solvent interactions which could reduce the quantum yield for luminescence.

When $[Yb(porp)(H_2O)_3]Cl$ was reacted with sterically bulky nucleophiles such as hydridotris(3,5-dimethylpyrazol-1-yl)borate ($T_p{}^{Me-}$), it gave the μ-OH bridged dimer $[Yb(TPP)(\mu\text{-}OH)(H_2O)]_2$ [45] instead of the expected neutral complex $[Yb(TPP)(T_p{}^{Me-})]$. This implies that there is a competition between the formation of dimers and adducts. When the externally added ligand is sterically hindered, dimerization is preferred even though the N and O atoms in these ligands have strong coordinating ability to the metal ions.

3.2. Synthesis of diethyl malonate appended monoporphyrinate lanthanide(III) complexes

Interaction of an excess amount of $Ln[N(SiMe_3)_2]_3 \cdot x[LiCl(THF)_3]$ (Ln = Yb^{3+}, Er^{3+} and Nd^{3+}) with the porphyrin free base, 5-[2-(5,5′-ethoxycarbonyl)-pentoxy]phenyl-10,15,20-triphenylporphyrin [*o*-DEM(H)–C_4–O–$TPPH_2$] [53] in refluxing bis(2-methoxy-ethyl) ether gave purple air stable lanthanide porphyrinate complexes, [Ln(*o*-DEM–C_4–O–TPP)(H_2O)], which were quite stable toward moisture and could be purified by column chromatography on silica gel (Fig. 9) [54]. Spectroscopic evidence and elemental analyses supported the formulation of [Ln(*o*-DEM–C_4–O–TPP)(H_2O)] for the complexes and that the porphyrin *o*-DEM(H)–C_4–O–$TPPH_2$ behaved as a tri-deprotonated hexadentate ligand with the appended diethyl malonate group coordinated to the lanthanide ion as an anion. The structure of these complexes can be considered as a seven co-ordinated species with four N of the porphyrinate and three O (two from the appended diethyl malonate anion and one from water) co-ordinated to the metal centre. When dissolved in DMF, the coordinated aqua molecule of [Ln(*o*-DEM–C_4–O–TPP)(H_2O)] was displaced by DMF. This is supported IR and mass spectral data. The stability of the [Ln(*o*-DEM–C_4–O–TPP)(H_2O)] complexes which we believe, can only be attributed to the coordination of the appended diethyl malonate anion. This makes us believe that the second ligand is crucial for the preparation of stable monoporphyrinate lanthanide complexes particularly for those metals with large ionic radii.

4. Photophysical properties of lanthanide(III) monoporphyrinate complexes

4.1. Near-infrared sensitization

The electronic absorption, excitation and emission spectra of lanthanide monoporphyrinate complexes in solution at room temperature in the UV–vis region are almost identical and are characteristic of intra-ligand transitions of normal prophyrinate complexes. The absorption bands (Soret and Q bands) and emission peaks in the visible region are typical of the intra-ligand $\pi \rightarrow \pi^*$ transitions of the porphyrinate ligand. The visible emission has a decay time of about 10–15 ns and can be assigned to $S_1 \rightarrow S_0$ ligand centered singlet (^1LC) fluorescence. Fig. 12 shows the absorption, emission (excited at 414 nm) and excitation (monitored at 648 nm) spectra of $[Yb(TPP)(T_p{}^H)]$, which are typical for lanthanide monoporphyriante complexes. The absorption bands at 421, 550 and 588 nm and emission peaks at 648 nm (t = 12.9 ns and $\Phi_{em} = 0.11 \times 10^{-3}$) of $[Yb(TPP)(T_p{}^H)]$ can be assigned to the intra-ligand $\pi \rightarrow \pi^*$ transitions of the

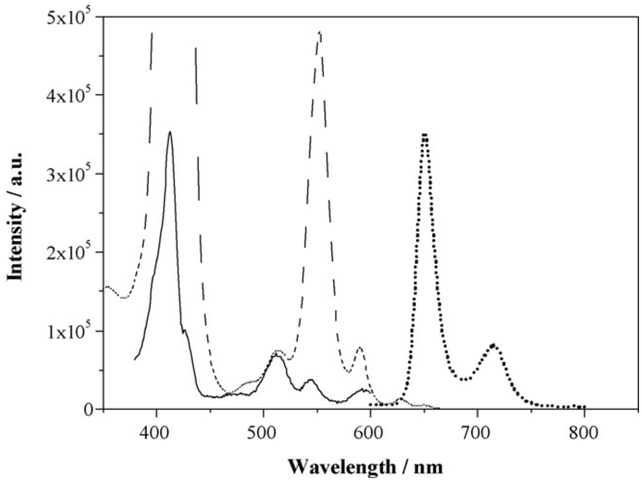

Fig. 12. Room temperature absorption (– – –), emission (···) (excited at 414 nm) and excitation (—) (monitored at 648 nm) spectra of $[Yb(TPP)(T_p{}^H)]$ in $CHCl_3$.

porphyrinate ligand. Other than the visible emission, all Nd^{3+}, Yb^{3+} and Er^{3+} monoporphyrinate complexes also exhibit Ln^{3+} ion emission in the NIR region. For the Nd^{3+} monoporphyrinate complexes, the emissions at 875 and 1068 nm can be assigned to ${}^4F_{3/2} \rightarrow {}^4F_{9/2}$ and ${}^4F_{3/2} \rightarrow {}^4F_{11/2}$ transitions of Nd^{3+}, respectively. For the Yb^{3+} and Er^{3+} monoporphyrinate complexes, the emissions at 1515 and 976 nm can be assigned to the ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} and ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+}, respectively. These NIR emissions are very similar to those reported for Nd^{3+}, Er^{3+} and Yb^{3+}, and the lifetime values are in good agreement with literature values [23a,55]. The NIR luminescence lifetime is about 20 μs for Yb^{3+} complexes and 450–825 ns for Nd^{3+} complexes, and is much longer than the lifetime of the porphyrinate emission. Due to the limitation of our equipment, we were unable to measure the excitation (monitored at 1540 nm) spectrum and the NIR luminescence lifetime of Er^{3+} complexes. The NIR sensitization process was carefully examined using $[Ln(TPP)(L_2X)]$ ($Ln = Nd^{3+}$ and Yb^{3+}; $L_2X = L_{OR}{}^-$ and $T_p{}^H$) complexes as modeled complexes. Fig. 13 shows the NIR emission and the excitation spectrum of $[Yb(TPP)(T_p{}^H)]$. Excitation bands of $[Yb(TPP)(T_p{}^H)]$ in chloroform solution at 298 K (monitored at 980 nm) are observed at 560 and 596 nm, which almost coincide with its visible absorption bands at 550 and 588 nm. This clearly shows that the excitation of the Yb^{3+} ion is originated from the $\pi \rightarrow \pi^*$ transitions of the porphyrinate antenna and excitation of porphyrin is the photophysical pathway leading to the observable NIR luminescence. Photophysical studies showed that the porphyrinate antenna transfers its absorbed visible energy of the Q band to the excited state of the metal ion, which then relaxes through emission in the NIR region. This is consistent with the results of a recent transient absorption study on the electronic structure and lifetime of the emitting states of $[Ln(Por)(L_2X)]$ complexes ($Ln = Yb$, $L_2X = L_{OEt}$ and $T_p{}^H$; $Ln = Nd$, $L_2X = T_p{}^H$) [37a]. Fig. 14 shows a simple, widely accepted photophysical model for the description of the sensitization process [23,28]. In this process, the porphyrin absorbs the light and is excited to its singlet state (S_1). The energy is then transferred to its triplet state (T_1), which is, in part, being transferred to the excited state of lanthanide ion $(Ln^{3+})^*$ and produce the luminescence at last.

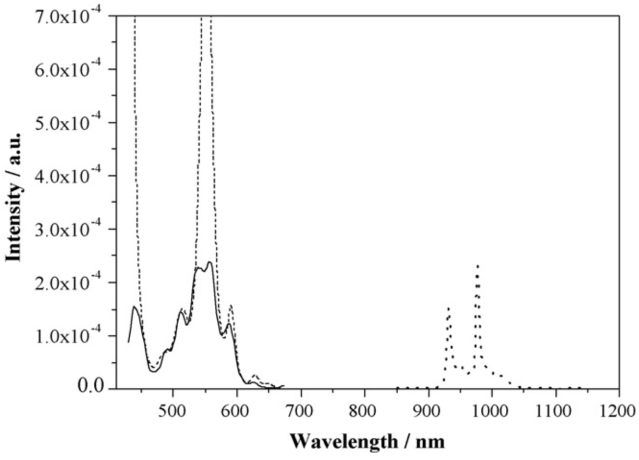

Fig. 13. Room temperature absorption (– – –), NIR emission (···) (excited at 420 nm) and excitation (—) (monitored at 980 nm) spectra of $[Yb(TPP)(T_p{}^H)]$ in $CHCl_3$.

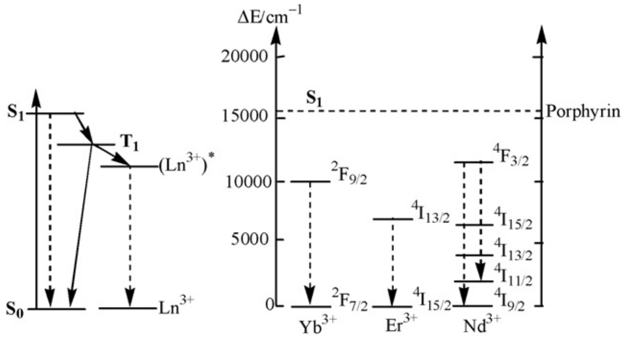

Fig. 14. Schematic energy diagram of $[Ln(Por)(T_p{}^H)]$ complexes. The arrows indicate the excitation mechanism of lanthanide ions by the porphyrin sensitizer ($S_0 \rightarrow S_1$ transition followed by intersystem crossing and energy transfer).

It is known that OH oscillators, e.g. in bound water molecules, OH-containing solvents, could quench the luminescence [48]. In order to investigate the effect of coordinated aqua molecule on luminescence efficiency, we investigated the NIR emission of the $[Yb(Por)(H_2O)_3]Cl$ and $[Ln(TPP\text{-}C_4\text{-}DEM)(H_2O)]$ complexes in different solvents [3,8b,54]. The results showed that the emission intensity was quite weak in methanol and acetone, and quite strong in DMF. The emission enhancement of $[Ln(Por)(H_2O)_3]Cl$ and $[Ln(TPP–C_4–DEM)(H_2O)]$ complexes in DMF could only be attributed to the substitution of coordinated H_2O by DMF. Displacement of the coordinated aqua molecules by tripodal anions also enhanced the NIR emission of the metal ions. For example, the NIR emission intensity of $[Yb(TPP)(T_p{}^H)]$ is more than six times stronger than that of $[Yb(TPP)(H_2O)_3]Cl$ in $CHCl_3$ under the same conditions [51b]. Solvent effect on the NIR luminescence of $[Ln(TPP)(L_{OR})]$ and $[Ln(TPP)(T_p{}^H)]$ was also observed. The emission intensity was found to decrease as the polarity of the solvent increases. The complex exhibits the strongest emission in benzene > chloroform > tetrahydrofuran > DMF > methanol [51b–d].

The NIR emission intensity of the lanthanide porphyrinate complexes follows the trend $Yb^{3+} > Nd^{3+} > Er^{3+}$. The trend is consistent with observations on other luminescent lanthanide complexes and reflects the fact that the efficiency of non-radiative decay increases as the energy of the luminescent state decreases (energy gap law). The emission yields of the $[Ln(TPP)(L_{OR})]$ and $[Ln(TPP)(T_p{}^H)]$ complexes are generally higher than other Yb^{3+}, Nd^{3+} and Er^{3+} complexes [37a,56]. The enhanced emission yields for the $[Ln(TPP)(L_{OR})]$ and $[Ln(TPP)(T_p{}^H)]$ complexes are believed to arise because the coordination environment provided by the porphyrinate in combination with the tripodal anion (L_{OR} or $T_p{}^H$) effectively shield the Ln^{3+} ion from interacting with solvent (C–H) vibrational modes which enhance the rate of non-radiative decay [57]. This premise is supported by the observation that Φ_{em} of $[Yb(TPP)(T_p{}^H)]$ only increases from 0.032 in $CHCl_3$ to 0.034 in $CDCl_3$ [37a]. Recent studies on electroluminescence (EL) devices fabricated by doping $[Ln(TPP)(L_{OR})]$ or $[Ln(TPP)(T_p{}^H)]$ complexes into polymer blends showed that the [Ln(TPP)(L_{OR})] or [Ln(TPP)($T_p{}^H$)] complexes can serve as charge-transport material, the center for electron–hole recombination and the NIR emitter [58].

4.2. Optical limiting property

With the rapid development of laser technology, the damage caused by exposure to sudden intense laser pulses to human eyes, optical sensors, and optical components has driven the search for effective optical limiters that possess fast response speeds and relatively high linear transmissions [59,60]. Optical limiters are materials that are transparent at normal light intensities while opaque to very bright light [61–63]. Over the last decade, interest has focused on materials with weak ground-state absorption and strong excited-state absorption, which achieve optical limiting by a mechanism known as reverse saturable absorption (RSA). An ideal material would have low ground-state absorption over a wide spectral bandwidth and strong excited-state absorption across the same region [64]. Metalloporphyrins are among the most effective optical limiters [64–69] because their ground-state absorption is mostly confined to a few narrow regions (Soret and Q bands), allowing high transmission in the spectral window between these bands. In addition, these macrocycles present a highly developed π-conjugation system which contributes to strong excited-state absorption, high triplet yields and long excited line-like spectra and long luminescence lifetimes. Porphyrins and metalloporphyrins are known to have the RSA at 532 nm.

Recent investigations on metalloporphyrins for optical limiting have focused on the transition metals [65], phosphorus(V) [66], and group III and IV metals [64,67]. Wang has reported a series of pentaazadentate porphyrin-like metal complexes used in optical-limiting materials, where the metal ion is Sm^{3+} or Gd^{3+} [68]. Only a tetraphenylporphyrinate europium(III) complex was reported by Kuznetsova in optical limiting [69]. We have examined the optical limiting capability of [Ln(TDPAPP)(L_{OMe})] (Ln = Gd^{3+}, Er^{3+}, and Yb^{3+}; H_2TDPAPP = 5,10,15,20-tetrakis(*p*-diphenylaminophenyl)-21H,23H-porphyrin) complexes. From the *Z*-scan curves measured in CH_2Cl_2 (Fig. 15), the three monoporphyrinate lanthanide complexes showed excellent optical-limiting behavior [70]. Experiments with CH_2Cl_2 alone afforded no detectable optical-limiting effect. When each sample was far from the focus ($Z/Z_0 = 0$) and the incident irradiance upon it was weak, the transmittance of the sample remained almost constant and showed a linear optical property (obeying the Beer's law). But when the sample was close to the focus and the incident irradiance was strong, the transmittance of the sample decreased quickly and the optical-limiting effect appeared. It is clear that [Er(TDPAPP)(L_{OMe})] showed the strongest optical-limiting capability, superior even to that of C_{60}, which was considered to be an excellent optical limiter. The Gd and Yb complexes also exhibited good optical-limiting properties, comparable to those of C_{60}. Table 2 lists the optical-limiting thresholds of the three monoporphyrinate lanthanide complexes, which is an important parameter in characterizing the merit of these optical limiters. Here, all three monoporphyrinate lanthanide(III) complexes possessed low optical-limiting thresholds at 82% linear transmittance. The complex [Er(TDPAPP)(L_{OMe})] showed a lower optical-limiting threshold than that of the standard fullerene C_{60} [70,71], and was even comparable to those of some state-of-the-art phthalocyanine dyes [72–74].

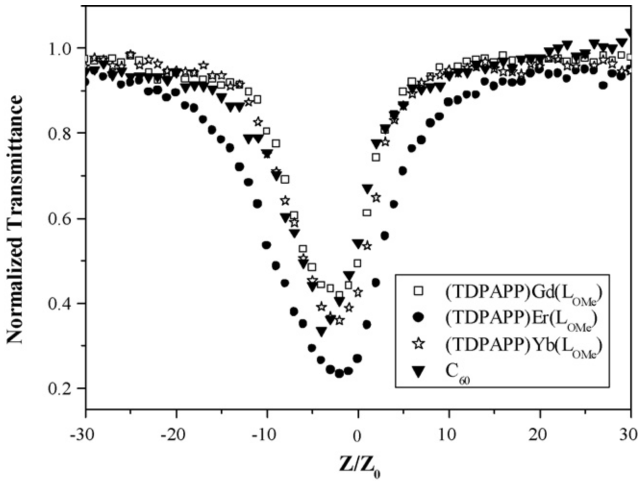

Fig. 15. Open aperture *Z*-scan results for the [Ln(TDPAPP)(L_{OMe})] (Ln = Gd^{3+}, Yb^{3+} and Er^{3+}) complexes and C_{60} solutions at the same linear transmittance of 82%.

Table 2
Comparison of the optical-limiting performance of [Ln(TDPAPP)(L_{OMe})] complexes (Ln = Gd^{3+}, Er^{3+} and Yb^{3+}) with some reported materials

Materials	Optical limiting threshold (J/cm^2)[a]	Linear transmittance (%)	Sample thickness (mm)	References
[Yb(TDPAPP)(L_{OMe})]	0.17	82	1	[70]
[Er(TDPAPP)(L_{OMe})]	0.093	82	1	[70]
[Gd(TDPAPP)(L_{OMe})]	0.30	82	1	[70]
C_{60}	0.15	78	1	[70]
C_{60}	0.18	55	2	[71]
PbPc(β-CP)$_4$	0.070	62	[b]	[72]
CuPcR$_8$[c]	0.30	68	10	[73]
MPc; M = Si, Ge, etc	0.10	84	10	[74]

[a] The optical-limiting threshold is defined as the input light fluence at which the output light fluence is 50% of that predicted by linear transmittance.

[b] Not reported.

[c] R = pentyloxy.

5. Synthesis, structure and spectral features of lanthanide(III) *N*-confused porphyrinate complexes

The successful synthesis of *N*-confused porphyrin in 1994 by two independent research groups has generated a lot of curiosity for the possible existence of new porphyrin isomers with unique properties [75,76]. *N*-Confused porphyrin (H_2NCP), an isomeric porphyrin, has an inverted pyrrole ring joined to the porphyrinic conjugated system through a β-carbon, and exhibits a peripheral pyrrolic nitrogen and an inner core carbon. We have extended our study to *N*-confused porphyrins. When the *N*-confused tetraphenylporphyrin (H_2NCTPP) was treated with an excess amount of $Ln[(N(SiMe_3)_2)_3 \cdot [LiCl(THF)_3]_x$ ($Ln = Yb^{3+}$ or Er^{3+}) under nitrogen in refluxing toluene for 12 h, followed by addition of an excess amount of the tripodal ligand NaL_{OMe} to the reaction mixture at room temperature, work up in air gave green crystals of $[Ln(NCTPP)(L_{OMe})]$ ($Ln = Yb^{3+}$ or Er^{3+}) in 75% yield [77]. These complexes are thermally and air stable and can be purified by column chromatography. However, when the same reaction was carried out without the subsequent addition of $L_{OMe}{}^{-}$, work up only led to the recovery of H_2NCTPP free base. This suggests that the lanthanide *N*-confused porphyrinate intermediate was rather unstable and could be stabilized by the tripodal anion, $L_{OMe}{}^{-}$. These complexes were characterized by elemental analyses and spectroscopic techniques. Electrospray ionization high resolution mass spectrum (ESI-HRMS) of the $[Ln(NCTPP)(L_{OMe})]$ complexes exhibited a peak at *m/z* corresponding to the ($M + 1$) parent peak. The $^{31}P\{^1H\}$-NMR spectrum displayed a single peak at δ 82.8 and −123.2 ppm for the Yb^{3+} and Er^{3+} complex, respectively. Their absorption spectra in CH_2Cl_2 show a Soret band and a broad Q-band at 457 and 670 nm, respectively. These spectral features resemble those observed for related NCP complexes of nickel(II) [78], but are in marked contrast to those of the planar $[Ag^{III}(NCTPP)]$ complex [79], where the Soret band is observed at 447 nm and the Q-band appears with four peaks at 520, 554, 588, and 637 nm.

The solid state structures of the $[Ln(NCTPP)(L_{OMe})]$ complexes were ascertained by X-ray crystallography and shown to be isostructural [77]. A perspective drawing of $[Yb(NCTPP)(L_{OMe})]$ is depicted in Fig. 16. The overall structure of the NCTPP dianion adopts a nonplanar geometry with an inverted pyrrole ring tilted away from the metal and the porphyrin plane defined by N(2)N(3)N(4). The Yb^{3+} ion is eight-coordinate and is bonded to the $NCTPP^{2-}$ and the $L_{OMe}{}^{-}$ ligands. Other than coordinating to the three O atoms of the L_{OMe} ligand, the Yb^{3+} ion is also bound to the three inner N atoms and forms an η^2 agostic bond with the inner C–H edge of the NCTPP ligand. The Yb center sits 1.2461 Å above the mean plane. The distance from Yb(1) to the inner core hydrogen is only 2.568 Å with the inner C–H distance being 0.867 Å. Most interestingly, the solid-state geometry of C(20)–H–Yb(1) in $[Yb(NCTPP)(L_{OMe})]$ is within the bond distance of an agostic interaction. This seems to be in line with the effect due to the coordinatively unsaturated and electron-deficient Yb center that results in stronger three-center two-electron C(20)–H···Yb(1) contact. Similar agostic interaction between transition metal ion and inner C–H bond of NCP has been observed [80]. 2-D COSY ^1H NMR and NIR emission data provide further evidence for the presence of an η^2 agostic interaction between the Yb^{3+} ion and the inner C–H bond of the $NCTPP^{2-}$ ligand [77].

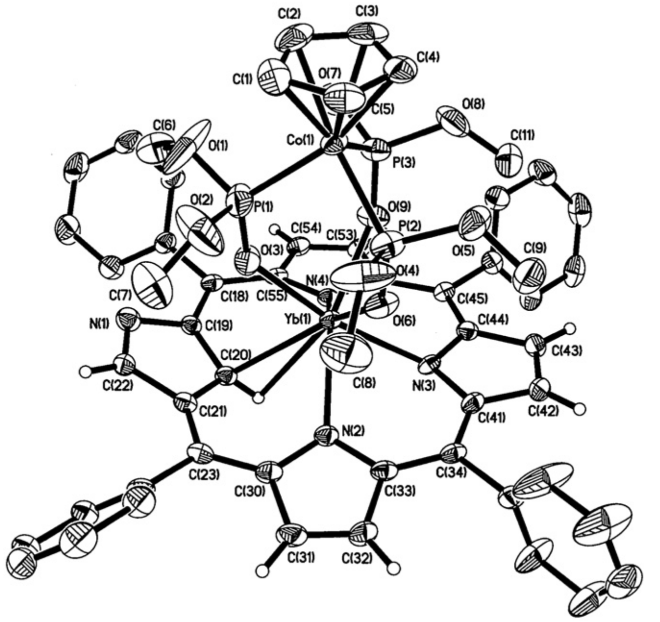

Fig. 16. A perspective drawing of $[Yb(NCTPP)(L_{OMe})]$. (Reproduced from Ref. [77] by permission of the Royal Society of Chemistry.)

6. Summary

We have developed a convenient synthetic route for the preparation of cationic lanthanide(III) monoporphyrinate complexes $[Ln(Por)(H_2O)_3]Cl$ *via* the protonolysis of lanthanide(III) amide with porphyrin free bases. The synthetic route did not work for large lanthanide ions. However, when the protonolysis was carried out in the presence of an encapsulating agent, such as anionic tripodal ligands ($L_{OR}{}^{-}$ and $T_p{}^{H-}$) or an acac group appended to the porphyrinate, stable neutral lanthanide(III) monoporphyriante complex was isolated even with large lanthanide(III) ions, such as Nd^{3+}. The $[Ln(Por)(H_2O)_3]Cl$ complexes have a high tendency to form bridging dinuclear complexes. They formed hydroxyl-bridged dimers when reacted with base, and chloro-bridged dimers with aqueous HCl. The aqua ligands of the $[Ln(Por)(H_2O)_3]Cl$ complexes are very labile and can be easily displaced by anions or donor solvents. When $[Ln(Por)(H_2O)_3]Cl$ was reacted with anionic tripodal ligands, such as $L_{OR}{}^{-}$ and $T_p{}^{H-}$ which served as 6 e donors, stable neutral lanthanide(III) monoporphyrinate complex of the general formula $[Ln(Por)(L_2X)]$ ($L_2X = L_{OR}{}^{-}$ and $T_p{}^{H-}$) was isolated in high yield. Photoluminescence studies of lanthanide(III) monoporphyrinate complexes showed that the porphyrinate anion could sensitize NIR emission of Nd^{3+}, Yb^{3+} and Er^{3+} ions by serving as an antenna that absorbed visible light, transferred the energy to the excited state of the lanthanide(III) ion, which then relaxed through NIR emission. The NIR intensity increased as the number of O–H oscillators within the molecules decreased. The optical limiting property of $[Ln(TDPAPP)(L_{OMe})]$ complexes was also examined. The Er^{3+} complex showed a lower optical-limiting threshold than that of the standard fullerene C_{60}, and was even comparable to those of some state-of-the-art phthalocyanine dyes. We further extended our work to *N*-confused porphyrins and synthesized the first lanthanide(III) *N*-confused porphyrinate complexes $[Ln(NCTPP)(L_{OMe})]$ *via* the protonolysis route. X-ray structural analysis revealed that the lanthanide(III) ion formed an η^2 agostic interaction with the inner C–H bond of the *N*-confused porphyrinate.

Acknowledgements

We thank the Hong Kong Baptist University (FRG/03-04/11-52, FRG/05-06/II-03) and the Hong Kong Research Grants Council (HKBU 2023/00P, HKBU 2021/03P) for financial support.

References

[1] The Porphyrin Handbook, Academic Press, San Diego, 2000.

[2] K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, 1992.

[3] H.S. Cho, H. Rhee, J.K. Song, C.-K. Min, M. Takase, N. Aratani, S. Cho, A. Osuka, T. Joo, D. Kim, J. Am. Chem. Soc. 125 (2003) 5849.

[4] (a) Q. Wang, W.M. Campbell, E.E. Bonfantani, K.W. Jolley, D.L. Officer, P.J. Walsh, K. Gordon, R. Humphry-Baker, M.K. Nazeeruddin, M. Graetzel, J. Phys. Chem. B 109 (2005) 15397;
(b) J.M. Haider, Z. Pikramenou, Chem. Soc. Rev. 34 (2005) 120;
(c) M.K. Nazeeruddin, R. Humphry-Baker, D.L. Officer, W.M. Campbell, A.K. Burrell, M. Graetzel, Langmuir 20 (2004) 6514.

[5] L.R. Milgrom, The Colors of Life: An Introduction to the Chemistry of Porphyrins and Related Compounds, Oxford University Press, 1997.

[6] (a) H. Sugimoto, M. Saika, Y. Hosokawa, T. Aide, S. Inoue, Macromolecules 29 (1996) 3359;
(b) T.E. Patten, B.M. Novak, Macromolecules 26 (1993) 436.

[7] M.J. Gunter, P. Turner, Coord. Chem. Rev. 108 (1991) 115.

[8] W. Nam, S.E. Park, I.K. Lim, M.H. Lim, J. Hong, J. Kim, J. Am. Chem. Soc. 125 (2003) 14674.

[9] Y. Chen, K.B. Fields, X. Zhang, J. Am. Chem. Soc. 126 (2004) 14718.

[10] (a) R. Guilard, K.M. Kadish, Chem. Rev. 88 (1988) 1121;
(b) P. Hambright, Coord. Chem. Rev. 6 (1971) 247;
(c) P.J. Brothers, J.P. Collman, Acc. Chem. Res. 19 (1986) 209;
(d) W.R. Scheidt, Acc. Chem. Res. 10 (1997) 339.

[11] (a) J.W. Buchler, Structure and Bonding, vol. 64, Springer-Verlag, 1987;
(b) J.W. Buchler, Structure and Bonding, vol. 84, Springer-Verlag, 1995.

[12] C.P. Wong, R.F. Venteicher, W.D. Horrocks Jr., J. Am. Chem. Soc. 96 (1974) 7149.

[13] (a) W.D. Horrocks Jr., C.P. Wong, J. Am. Chem. Soc. 98 (1976) 7157;
(b) W.D. Horrocks Jr., E.G. Hove, J. Am. Chem. Soc. 100 (1978) 4386.

[14] C.P. Wong, Inorg. Synth. 22 (1983) 156.

[15] (a) J.W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus, R. Weiss, J. Am. Chem. Soc. 108 (1986) 3652;
(b) J.W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, R. Weiss, Inorg. Chem. 108 (1988) 339.

[16] (a) E.M. Davoras, G.A. Spyroulias, E. Mikros, A.G. Coutsolelos, Inorg. Chem. 33 (1994) 3430;
(b) G.A. Spyroulias, A.G. Coutsolelos, C.P. Raptopoulou, A. Terzis, Inorg. Chem. 34 (1995) 2476;
(c) J.P. Collman, J.L. Kendall, J.L. Chen, K.A. Collins, J.-C. Marchon, Inorg. Chem. 39 (2000) 1661;
(d) S.P. Babailov, A.G. Coutsolelos, A. Dikiy, G.A. Spyroulias, Eur. J. Inorg. Chem. (2001) 303;
(e) G.K. Tsikalas, A.G. Coutsolelos, Inorg. Chem. 42 (2003) 6801;
(f) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, J. Am. Chem. Soc. 125 (2003) 8694;
(g) N. Pan, Y. Bian, T. Fukuda, M. Yokoyama, R. Li, S. Neya, J. Jiang, N. Kobayashi, Inorg. Chem. 43 (2004) 8242.

[17] (a) M. Moussavi, A. De Cian, J. Fischer, R. Weiss, Inorg. Chem. 25 (1986) 2107;
(b) D. Chabach, M. Lachkar, A. De Cian, J. Fischer, R. Weiss, New J. Chem. 16 (1992) 431;
(c) D. Chabach, M. Tahiri, A. De Cian, J. Fischer, R. Weiss, M. El Malouli Bibout, J. Am. Chem. Soc. 117 (1995) 8548;
(d) J. Li, D. Gryko, R.B. Dabke, J.R. Diers, D.F. Bocian, W.G. Kuhr, J.S. Lindsey, J. Org. Chem. 65 (2000) 7379;
(e) T. Gross, F. Chevalier, J.S. Lindsey, Inorg. Chem. 40 (2001) 4762;
(f) K.-H. Schweikart, V.L. Malinovskii, A.A. Yasseri, J. Li, A.B. Lysenko, B.F. Bocian, J.S. Lindsey, Inorg. Chem. 42 (2003) 7431;
(g) K. Padmaja, W.J. Youngblood, L. Wei, D.F. Bocian, J.S. Lindsey, Inorg. Chem. 45 (2006) 5479.

[18] I. Klink, G.A. Hebbink, L. Grave, F.C.J.M. van Veggel, D.N. Reinhoudt, L.H. Slooff, A. Polman, J.W. Hofstraat, J. Appl. Phys. 86 (1999) 1181.

[19] M.H.V. Werts, R.H. Woudenberg, P.G. Emmerink, R. van Gassel, J.W. Hofstraat, J.W. Verhoeven, Angew. Chem. Int. Ed. 39 (2000) 4542.

[20] M.I. Gaiduk, V.V. Grigoryants, A.F. Mironov, V.D. Rumyantseva, V.I. Chissov, G.M. Sukhin, J. Photochem. Photobiol. B 7 (1990) 15.

[21] A. Beeby, R.S. Dickins, S. Faulkner, D. Parker, J.A.G. Williams, Chem. Commun. (1997) 1401.

[22] W.D. Horrocks Jr., J.P. Bolender, W.D. Smith, R.M. Supkowski, J. Am. Chem. Soc. 119 (1997) 5972.

[23] (a) M.H.V. Werts, J.W. Hofstraat, F.A.J. Geurts, J.W. Verhoeven, Chem. Phys. Lett. 276 (1997) 196;
(b) M.H.V. Werts, J.W. Verhoeven, J.W. Hofstraat, J. Chem. Soc., Perkin Trans. 2 (2000) 433;
(c) B.H. Bakker, M. Goes, N. Hoebe, H.J. van Ramesdonk, J.W. Verhoeven, M.H.V. Werts, J.W. Hofstraat, Coord. Chem. Rev. 208 (2000) 3.

[24] F.R. Goncalves e Silva, O.L. Malta, C. Reinhard, H.-U. Gudel, C. Piguet, J.E. Moser, J.-C.G. Bünzli, J. Phys. Chem. A 106 (2002) 1670.

[25] G.A. Hebbink, L. Grave, L.A. Woldering, D.N. Reinhoudt, F.C.J.M. van Veggel, J. Phys. Chem. A 107 (2003) 2483.

[26] (a) R. Reinfeld, C.H. Jorgensen, Lasers and Excited States of Rare Earths, Springer-Verlag, Berlin, 1977;
(b) K.A. Gschneider Jr., L. Eyring, Handbook on the Physics and Chemistry of Rare Earths, vol. 15, North-Holland, Amsterdam, 1979.

[27] (a) N. Sabbatini, M. Guardigli, J.-M. Lehn, Coord. Chem. Rev. 123 (1993) 201;
(b) A. Beeby, R.S. Dickins, S. FitzGerald, L.J. Govenlock, C.L. Maupin, D. Parker, J.P. Riehl, G. Silligardi, J.A.G. Williams, Chem. Commun. (2000) 1183.

[28] Y. Korovin, N. Rusakova, Rev. Inorg. Chem. 21 (2001) 299.

[29] M.P. Oude Wolbers, F.C.J.M. van Veggel, F.G.A. Peters, E.S.E. van Beelen, J.W. Hofstraat, F.A.J. Geurts, D.N. Reinhoudt, Chem. Eur. J. 4 (1998) 772.

[30] S.I. Klink, P. Oude Alink, L. Grave, F.G.A. Peters, J.W. Hofstraat, F.A.J. Geurts, F.C.J.M. van Veggel, J. Chem. Soc, Perkin Trans. 2 (2001) 363.

[31] A. Beeby, R.S. Dickins, S. FitzGerald, L.J. Govenlock, C.L. Maupin, D. Parker, J.P. Riehl, G. Siligardi, J.A.G. Williams, Chem. Commun. (2000) 3092.

[32] S.I. Klink, H. Keizer, F.C.J.M. van Veggel, Angew. Chem. Int. Ed. 39 (2000) 4319.

[33] (a) H. Tsukube, S. Shinoda, Chem. Rev. 102 (2002) 2389;
(b) H. Tsukube, S. Shinoda, H. Tamiaki, Coord. Chem. Rev. 226 (2002) 227;
(c) H. Tsukube, M. Wada, S. Shinoda, H. Tamiaki, Chem. Commun. (1999) 1007;
(d) H. Tsukube, N. Tameshige, S. Shinoda, S. Unno, H. Tamiaki, Chem. Commun. (2002) 2574.

[34] M.-H. Qi, G.-F. Liu, Solid State Sci. 6 (2004) 287.

[35] B.S. Harrison, T.J. Foley, M. Bouguettaya, J.M. Boncella, J.R. Reynolds, K.S. Schanze, Appl. Phys. Lett. 79 (2001) 3770.

[36] (a) C.J. Schaverien, A.G. Orpen, Inorg. Chem. 30 (1991) 4968;
(b) C.J. Schaverien, Chem. Commun. (1991) 458.

[37] (a) T.J. Foley, B.S. Harrison, A.S. Knefely, K.A. Abboud, J.R. Reynolds, K.S. Schanze, J.M. Boncella, Inorg. Chem. 42 (2003) 5023;
(b) T.J. Foley, K.A. Abboud, J.M. Boncella, Inorg. Chem. 41 (2002) 1704.

[38] (a) W.K. Wong, L.-L. Zhang, W.T. Wong, F. Xue, T.C.W. Mak, J. Soc. Chem. Dalton Trans. (1999) 615;
(b) H.S. He, W.K. Wong, K.F. Li, K.W. Cheah, Synth. Met. 143 (2004) 81.

[39] G.A. Spyroulias, M.P. Sioubara, A.G. Coutsolelos, Polyhedron 14 (1995) 3563.

[40] M. Gouterman, in: D. Dolphin (Ed.), The Porphyrins, vol. III, Academic Press, New York, 1978, Chapter 1.

[41] G.A. Spyroulias, A. Despotopoulos, C.P. Raptopoulou, A. Terzis, A.G. Coutsolelos, J. Chem. Soc., Chem. Commun. (1997) 783.

[42] W.K. Wong, L.-L. Zhang, F. Xue, T.C.W. Mak, J. Chem. Soc., Dalton Trans. (1999) 3053.

[43] W.K. Wong, L.-L. Zhang, F. Xue, T.C.W. Mak, J. Chem. Soc, Dalton Trans. (2000) 2245.

[44] D.M.Y. Barrett Adams, I.A. Kahwa, J.T. Mague, New J. Chem. (1998) 919.

[45] H.S. He, X.-J. Zhu, A.-X. Hou, J.-P. Guo, W.K. Wong, W.Y. Wong, K.F. Li, K.W. Cheah, Dalton Trans. (2004) 4064.

[46] J. Mizuya, T. Yokozawa, T. Endo, J. Polym, Sci. Part A: Polym. Chem. 29 (1991) 1545, and refs. therein.

[47] L. Mao, Q. Shen, M. Xue, J. Sun, Organometallics 16 (1997) 3711.

[48] A. Beeby, I.M. Clarkson, R.S. Dickins, S.F. Aulkner, D. Parker, L. Royle, A.S. de Sousa, J.A.G. Williams, M. Woods, J. Chem. Soc. Perkin Trans. 2 (1999) 493.

[49] (a) W. Klaui, Z. Naturforsch, Anorg. Chem. Org. Chem. B 34 (1979) 1043;
(b) W.H. Leung, E.Y.Y. Chan, T.C.Y. Lai, W.T. Wong, J. Chem. Soc. Dalton Trans. (2000) 51, and refs. therein;
(c) T.C.H. Lam, W.L. Mak, W.L. Wong, H.L. Kwong, H.H.Y. Sung, S.M.F. Lo, I.D. Williams, W.H. Leung, Organometallics 23 (2004) 1247;
(d) M. Akita, D.-Q. Ma, S. Hikichi, Y. Moro-oka, J. Soc. Chem. Dalton Trans. (1999) 987, and refs. therein.

[50] (a) S. Trofimenko, Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999;
(b) N. Marques, A. Andrea, J. Takats, Chem. Rev. 102 (2002) 2137;
(c) D. Roitershtein, A. Domingos, L.C.J. Pereira, J.R. Ascenso, N. Marques, Inorg. Chem. 42 (2003) 7666.

[51] (a) W.K. Wong, A. Hou, J. Guo, H. He, L. Zhang, W.Y. Wong, K.F. Li, K.W. Cheah, F. Xue, T.C.W. Mak, J. Chem. Soc. Dalton Trans. (2001) 3092;
(b) H.-S. He, J.-P. Guo, Z.-X. Zhao, W.K. Wong, W.Y. Wong, W.K. Lo, K.F. Li, L. Luo, K.W. Cheah, Eur. J. Inorg. Chem. (2003) 837;
(c) H.-S. He, W.K. Wong, J.-P. Guo, K.F. Li, W.Y. Wong, W.K. Lo, K.W. Cheah, Inorg. Chim. Acta 357 (2004) 4379;
(d) H.-S. He, W.K. Wong, J.-P. Guo, K.F. Li, W.Y. Wong, W.K. Lo, K.W. Cheah, Aust. J. Chem. 57 (2004) 803.

[52] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., Wiley, New York, 1999, p. 1109.

[53] H.S. He, B.S. Fang, J.W. Huang, L.N. Ji, Trans. Met. Chem. 35 (2000) 365.

[54] H.S. He, Z.-X. Zhao, W.K. Wong, K.F. Li, J.-X. Meng, K.W. Cheah, Dalton Trans. (2003) 980.

[55] W.K. Wong, H. Liang, W.Y. Wong, Z. Cai, K.F. Li, K.W. Cheah, New J. Chem. 26 (2002) 275.

[56] J.X. Meng, K.F. Li, J. Yuan, L.L. Zhang, W.K. Wong, K.W. Cheah, Chem. Phys. Lett. 332 (2000) 313.

[57] G.A. Hebbink, D.N. Reinhoudt, F.C.J.M. van Veggel, Eur. J. Org. Chem. (2001) 4101, and references cited therein.

[58] (a) T.-S. Kang, B.S. Harrison, T.J. Foley, A.S. Knefely, J.M. Boncella, J.R. Reynolds, K.S. Schanze, Adv. Mater. 15 (2003) 1093;
(b) B.S. Harrison, T.J. Foley, A.S. Knefely, J.K. Mwaura, G.B. Cunningham, T.-S. Kang, M. Bouguettaya, J.M. Boncella, J.R. Reynolds, K.S. Schanze, Chem. Mater. 16 (2004) 2938.

[59] L.W. Tutt, T.F. Boggess, Prog. Quant. Electron. 17 (1993) 299.

[60] D.G. Mclean, R.L. Sutherland, M.C. Brant, D.M. Brandelick, P.A. Fleitz, T. Potten, Opt. Lett. 18 (1993) 858.

[61] W. Blau, H. Byrne, W.M. Dennis, J.M. Kelly, Opt. Commun. 56 (1985) 25.

[62] G. De La Torre, P. Vázquez, F. Agulló-López, T. Torres, J. Mater. Chem. 8 (1998) 1671.

[63] G.L. Wood, M.J. Miller, A.G. Mott, Opt. Lett. 20 (1995) 973.

[64] A. Krivokapic, H.L. Anderson, G. Bourhill, R. Ives, S. Clark, K.J. McEwan, Adv. Mater. 13 (2001) 652.

[65] (a) K. Sendhil, C. Vijayan, M.P. Kothiyal, Opt. Mater. 27 (2005) 1606;
(b) X.H. Zhong, Y.Y. Feng, S.L. Ong, J.Y. Hu, W.J. Ng, Z.M. Wang, Chem. Commun. (2003) 1882;
(c) G.Y. Yang, S.G. Ang, L.L. Cheng, Y.W. Lee, W.P. Lau, K.S. Lai, H.G. Ang, Chem. Eur. J. 9 (2003) 900;
(d) K.J. McEwan, G. Bourhill, J.M. Robertson, H.L. Anderson, J. Nonlinear Opt. Phys. Mater. 9 (2000) 451;
(e) B. Dupuis, C. Michaut, I. Jouanin, J. Delaire, P. Robin, P. Feneyrou, V. Dentan, Chem. Phys. Lett. 300 (1999) 169;
(f) K. Kandasamy, S.J. Shetty, P.N. Puntambekar, T.S. Srivastava, T. Kundu, B.P. Singh, J. Porphyr. Phthalocyan. 3 (1999) 81.

[66] (a) P.P. Kiran, D.R. Reddy, B.G. Maiya, A.K. Dharmadhikari, G.R. Kumar, N.R. Desai, Appl. Opt. 41 (2002) 7631;
(b) K.P. Prem, R.D. Raghunath, B.G. Maiya, R.D. Narayana, Opt. Mater. 21 (2003) 565.

[67] R.B. Martin, H.P. Li, L.R. Gu, S. Kumar, C.M. Sanders, Y.P. Sun, Opt. Mater. 27 (2005) 1340.

[68] (a) D.Y. Wang, W.F. Sun, S.M. Dong, J.H. Si, C.F. Li, Mater. Res. Soc. Symp. Proc. 479 (1997) 41;
(b) W.F. Sun, C.C. Byeon, C.M. Lawson, G.M. Gray, D.Y. Wang, Appl. Phys. Lett. 74 (1999) 3254;
(c) D.Y. Wang, W.F. Sun, C.F. Wang, F.Q. Guo, Y.H. Zou, Proc. SPIE 3472 (1998) 53.

[69] R.T. Kuznetsova, T.N. Kopylova, G.V. Mayer, L.G. Samsonova, V.A. Svetlichnyi, A.V. Vasil'ev, D.N. Filinov, E.N. Tel'minov, N.S. Kabotaeva, N.V. Svarovskaya, V.M. Podgaetskii, A.V. Reznichenko, Quant. Electron. 34 (2004) 139.

[70] S.-T. Fu, G.-J. Zhou, X.-J. Zhu, C. Ye, W.K. Wong, Z.-Y. Li, Chem. Lett. (2006) 802.

[71] Y.P. Sun, J.E. Riggs, B. Liu, Chem. Mater. 9 (1997) 1268.

[72] J.S. Shirk, R.G.S. Pong, S.R. Flom, F.J. Bartoli, M.E. Boyle, A.W. Snow, Pure Appl. Opt. 5 (1996) 701.

[73] T.C. Wen, I.D. Lian, Synth. Met. 83 (1996) 111.

[74] J.W. Perry, K. Mansour, S.R. Marder, K.J. Perry, D. Alvarez Jr., I. Choong, Opt. Lett. 19 (1994) 625.

[75] P.J. Chemielewski, L. Latos-Grazynski, K. Rachlewicz, T. Glowiak, Angew. Chem. Int. Ed. Engl. 33 (1994) 779.

[76] H. Furuta, T. Asano, T. Ogawa, J. Am. Chem. Soc. 116 (1994) 767.

[77] X.-J. Zhu, W.K. Wong, W.K. Lo, W.Y. Wong, Chem. Commun. (2005) 1022.

[78] P.J. Chmielewski, L. Latos-Grazynski, T. Glowiak, J. Am. Chem. Soc. 118 (1996) 5690.

[79] H. Furuta, T. Ogawa, Y. Uwatoko, K. Araki, Inorg. Chem. 38 (1999) 2676.

[80] (a) H. Furuta, H. Maeda, A. Osuka, Chem. Commun. (2002) 1795;
(b) W.-C. Chen, C.-H. Hung, Inorg. Chem. 40 (2001) 5070.