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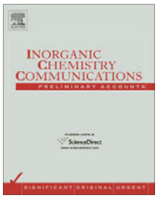

Facile preparation of neutral monoporphyrinate lanthanide complexes with strong near-infrared emission

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ABSTRACT

Ytterbium (III) acetylacetonate reacts with 5,10,15,20-tetraphenylporphyrin (H_2TPP) and 5,10,15,20-tetra(4-bromophenyl)porphyrin (H_2TBrPP) in 1,2,4-trichlorobenzene and forms unexpected acetate-bridged dimer and propionate-coordinated monomer of monoporphyrinate ytterbium (III) complexes, respectively, whereas interaction of ytterbium (III) acetate with H_2TPP gives stable acetate-coordinated monomer with two labile methanol binding directly to metal center. This compound reacts readily with 1,10-phenanthroline derivatives to give eight-coordinate monoporphyrinate ytterbium (III) complexes with strong near infrared emission efficiency.

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Developing facile preparation methods for near-infrared emissive monoporphyrinate lanthanide complexes with high coordination number is critical for the application of lanthanide complexes in diagnostics, photonics and photovoltaics [1–16]. One method that has been widely used was reported by Wong et al. in 1974 [17–21]:

$$H_2Por + [Ln(acac)_3] \rightarrow [Ln(Por)(\eta^2 - acac)(S)_n] + 2Hacac \qquad (1)$$

where Ln is the trivalent lanthanide ion, Por is the pophyrinate dianion, acac is the acetylacetonate anion, and S is the solvent. The number of solvent molecules is one as we determined recently [22]. One disadvantage of this method is the difficulty in substituting the acetylacetonate group for other ancillary ligands, which limits the modification of these complexes for other functionalized materials. Another disadvantage is the pyrolysis of acetylacetonates at high temperature [23,24]. Acetate, the major pyrolytic product, can coordinate to the lanthanide ion *in situ* and form acetate-coordinated monoporphyrinates as reported by Spyroulias et al. [25,26] for halogenated porphyrins:

$$H_2Por + [Tb(acac)_3] \rightarrow [Tb(por)(\eta^2 - OOCCH_3)(DMSO)_2] \qquad (2)$$

In an attempt to utilize this pyrolytic reaction for non-halogenated porphyrinate complexes, we found the reaction products were difficult to predict. When H_2TPP and ytterbium (III) acetylacetonate hydrate are employed in this reaction, a bridging acetate dimer, $[Yb(TPP)(\mu\text{-}OOCCH_3)(CH_3OH)]_2$ (**1**) is obtained (H_2TPP = 5,10,15,20-tetraphenylporphyrin) [27]. The crystal structure of **1** is shown in Fig. 1, in which two ytterbium (III) ions are bridged by two acetate anions. Each ytterbium (III) ion is coordinated by four nitrogen atoms from the porphyrinate dianion plus one oxygen atom from methanol, yielding a seven-coordinate ytterbium (III) center. The two ytterbium (III) TPP units are centrosymmetric and 5.321 Å away from each other indicating there is no direct bond interaction. In another experiment, a propionate-coordinated monomer, $[Yb(TBrPP)(OOCCH_2CH_3)(CH_3OH)_2]$ (**2**), is isolated when H_2TBrPP and ytterbium (III) acetylacetonate hydrate are used (H_2TBrPP = 5,10,15,20-tetrat(4-bromophenyl)porphyrin) [27]. The crystal structure of **2** is shown in Fig. 2. The ytterbium (III) ion is also seven-coordinate with four nitrogen atoms from the porphyrinate dianion, two oxygen atoms from methanol molecules and one oxygen atom from the propionate anion bonded to the metal. The propionate is monocoordinate as the distances between Yb1–O7 and Yb2–O8 are 3.674 Å and 3.705 Å, respectively, indicating this ligand does not chelate the Yb. Two TPP units in the unit cell are hydrogen bonded (dashed lines) to each other with relatively short O–H···O hydrogen bonds ~2.55 Å. Methanol is present as the elutant used during column chromatography.

This structure diversity led us to explore the possibility of other alternative synthetic methods for production of usable Yb-containing starting materials that could be substituted by other ancillary ligands. One method we pursued is the reaction between porphyrin free base and lanthanide acetate [28]:

$$H_2Por + [Ln(OOCCH_3)_3] \rightarrow [Ln(Por)(OOCCH_3)(S)_2] \qquad (3)$$

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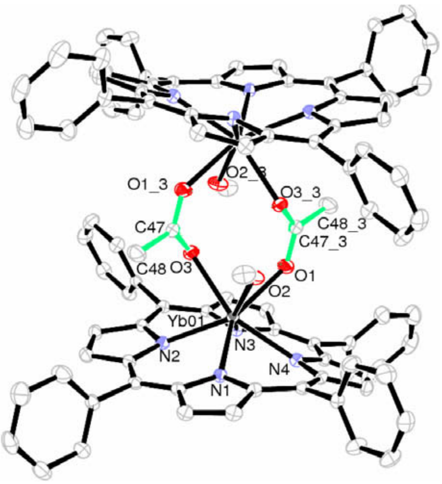

Fig. 1. The ORTEP diagram of $[Yb(TPP)(\mu\text{-}OOCCH3)(CH_3OH)]_2 \cdot 2CHCl_3$ with 50% thermal ellipsoid probability. The $CHCl_3$ and hydrogen atoms are omitted for clarity. Bond lengths (Å): Yb01–N1 2.31454(19), Yb01–N2 2.318(2), Yb01–N3 2.3039(19), Yb01–N4 2.305(2), Yb01–O1 2.3135(18), Yb01–O2 2.3722(18), Yb01–O3 2.3201(17).

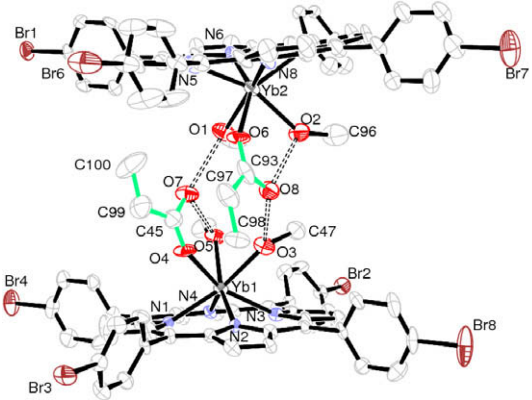

Fig. 2. The ORTEP diagram of $[Yb(TBrPP)(OOCCH_2CH_3)\,(CH_3OH)_2]_2 \cdot 2CH_2Cl_2$ with 50% thermal ellipsoid probability. The CH_2Cl_2 and hydrogen atoms are omitted for clarity. Bond lengths (Å): Yb1–N1 2.323(10), Yb1–N2 2.317(9), Yb1–N3 2.329(11), Yb1–N4 2.331(10), Yb1–O3 2.364(10), Yb1–O4 2.279(9), Yb1–O5 2.339(9), Yb2–O1 2.353(10), Yb2–O2 2.356(11), Yb2–O6 2.243(9).

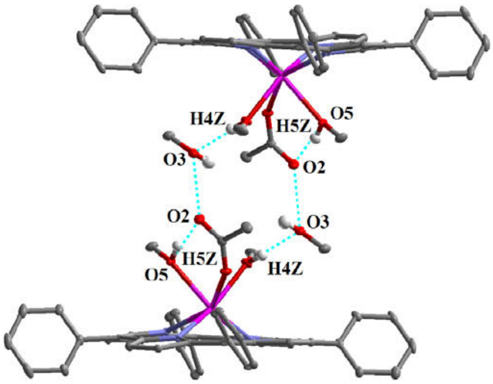

Fig. 3. The ORTEP diagram of $[Yb(TPP)(OOCH_3)(CH_3OH)_2]$ with 50% thermal ellipsoid probability. The hydrogen atoms are omitted for clarity. Bond lengths (Å): Yb1–N1 2.322(3), Yb1–N2 2.331(3), Yb1–N3 2.325(3), Yb1–N4 2.313(3), Yb1–O1 2.272(2), Yb1–O4 2.351(3), Yb1–O5 2.361(3).

The reactions were carried out in 1,2,4-trichlorobenzene at 210 °C under N_2 for 48 h, followed by stirring with methanol at 70 °C for 2 h. The reaction is very easy to handle and only one product is obtained [27]. The Fig. 3 shows the crystal structure of the product $[Yb(TPP)(OOCCH_3)(CH_3OH)_2]$ (**3**) from the reaction between H_2TPP and $Yb(acetate)_3 \cdot 3H_2O$. The ytterbium (III) ion is also seven-coordinate, with four nitrogen atoms from the porphyrinate dianion, two oxygen atoms from coordinated methanol and one oxygen atom from acetate anion occupying the coordination sphere. The distance between Yb1 and O2 is 3.759 Å, indicating the acetate is monocoordinate. The ytterbium (III) is 1.078 Å above the mean plan of N1/N2/N3/N4. One solvated methanol molecule is present in the asymmetric unit, through which two TPP units are hydrogen-bonded. The coordination of the second methanol and its hydrogen bonding with solvated methanol in **3** probably prevents dimerization as was observed in the structure of **1**.

Our results show that two methanol molecules in **3** are labile and can be easily substituted by a variety of bidentate ligands (LL) which form 1:1 stiochiometric adducts. This is of great advantage as a platform to build other highly functionalized Ln complexes:

$$\mathbf{3} + \mathrm{LL} \rightarrow [\mathrm{Yb(TPP)}(\eta^2 - \mathrm{OOCCH_3})(\mathrm{LL})] + 2\mathrm{CH_3OH} \qquad (4)$$

The resulting complexes are bright purple, soluble in dichloromethane, chloroform, toluene, etc. and slightly soluble in methanol. The crystal structure of 4-methyl-1,10-phenanthroline Yb(III) derivative, $[Yb(TPP)(\eta^2\text{-}OOCCH_3)(4\text{-}Me\text{-}phen)]\cdot MeOH$ (**4**), is shown in Fig. 4. Different from its monodentate coordination geometry in **3**, the acetate anion this time chelates to the ytterbium (III) ion, forming an eight-coordinate complex [27]. The phenanthroline backbone is slightly bent to minimize steric interaction with two adjacent phenyl groups of the TPP ring. The ytterbium ion is 1.1671 Å above the mean plan of N1/N2/N3/N4, which is larger than found in the seven-coordinate complexes. One solvated methanol molecule is also present in the asymmetric unit and is hydrogen-bonded to the carbonyl oxygen (O2) of the acetate.

The photoluminescence properties of all complexes have been investigated and reveal emission enhancement in the eight-coordinate diimine complex **4**. All complexes exhibit characteristic near-infrared emission upon irridiation as shown in Table 1. A strong peak centered at 974 nm is observed for all complexes, which can be assigned to characteristic $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. Two shoulders [9,29,30] on the right side of this peak in **1**–**3** have merged into one peak at 1005 nm in **4** with intensity greater than

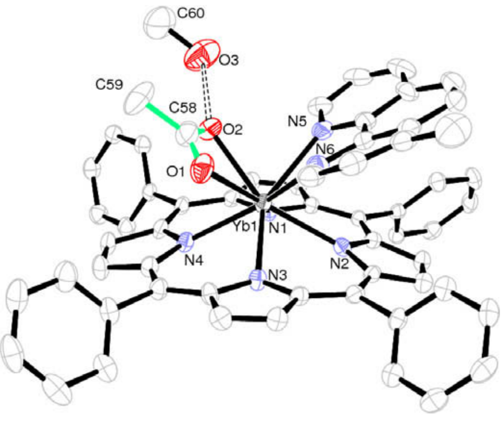

Fig. 4. The ORTEP diagram of $[Yb(TPP)(\eta^2\text{-}OOCCH_3)(4\text{-}Me\text{-}Phen)] \cdot CH_3OH$ with 50% thermal ellipsoid probability. The hydrogen atoms are omitted for clarity. Bond lengths (Å): Yb1–N1 2.351(4), Yb1–N2 2.371(4), Yb1–N3 2.352(4), Yb1–N4 2.359(4), Yb1–N5 2.529(4), Yb1–N6 2.509(4), Yb1–O1 2.368(4), Yb1-O2 2.395(4).

Table 1
Emission and lifetimes of **1**–**4** in CH_2Cl_2 at room temperature

Compound	No. of OH	CN[a]	Em in VIS[b] (nm, ns)	Em in NIR[b] (nm, μs)	Φ_{Yb}(%)[c]
1	1	7	650 (8.42), 717	974 (1.27)	0.064
2	2	7	652 (7.32), 716	974 (2.40)	0.12
3	2	7	647 (8.20), 713	974 (1.56)	0.078
4	0	8	651(6.70), 716	980 (17.29), 1006	0.86

[a] CN: coordination number.

[b] The excitation wavelength is 375 nm from Xe lamp for steady state and from pulsed diode laser for decay, respectively.

[c] $\Phi_{Yb}(\%) = \times 100\ \tau_{obs}/\tau_0$, where τ_0 = 2000 μs for Yb^{III} ion.

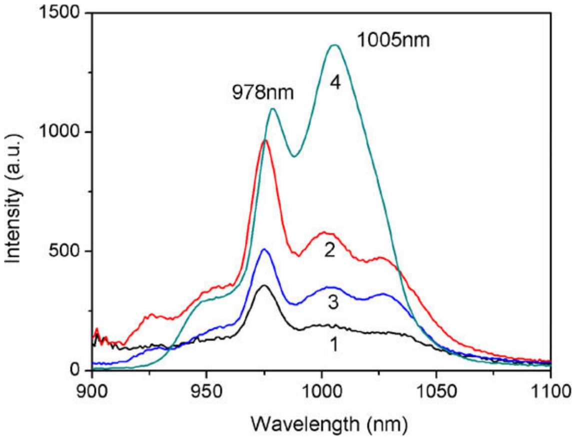

Fig. 5. Near-infrared emission spectra of **1**–**4** in dichloromethane at room temperature. The excitation wavelength is 375 nm. The concentration of the sample is 1.4×10^{-4} mol/L.

in **1**–**3**. The appearance of shoulders can be explained by Stark splitting of $^2F_{7/2}$ level due to the variation of an asymmetric ligand field in these complexes [29]. The NIR emission intensity and lifetime of **4** are 6- and 12-fold larger compared to those of **3** in CH_2Cl_2 at room temperature (see Fig. 5).

In conclusion, a more facile preparation method for monoporphyrinate lanthanide complexes with high coordination number has been developed beginning from ytterbium (III) acetate trihydrate, a commonly available reagent. The resulting octa-coordinate diimine complex exhibits intense near-infrared emisson and a long lifetime. The application of this method for self-assembly of heteronuclear lanthanide complexes as up-conversion materials is ongoing.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.08.004.

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[27] Synthesis of **1**: The solution of 5,10,15,20-tetraphenylporphyrin (H_2TPP) (0.50 g, 0.80 mmol) and ytterbium(III) acetylacetonate hydrate (1.0 g, 2.1 mmol) in TCB (50 mL) was refluxed (~220 °C) under N_2 atmosphere for 4 h. The solvent was then removed under vacuum. The residue was re-dissolved in chloroform, loaded on column (silica gel) and eluted with chloroform-methanol (v/v: 100:5). Collected the second band (the first band was unreacted H_2TPP) and third band. The second band was identified as **1** and third band as [$Yb(TPP)(acac)(H_2O)$]. Yield for 1: 82 mg, 12%. Calc. for $C_{94}H_{70}N_8O_6Yb_2$: C, 64.38; H, 4.02; N, 6.39. Found: C, 64.30; H, 3.95; N, 6.43. Synthesis of **2**: The solution of 5,10,15,20-tetra(4-bromophenyl)porphyrin (H_2TBrPP) (0.22 g, 0.35 mmol) and ytterbium(III) acetate hydrate (0.12 g, 0.34 mmol) in TCB (25 mL) was refluxed (~220 °C) under N_2 atmosphere for 4 h. The solvent was then removed under vacuum. The residue was re-dissolved in chloroform, loaded on column (silica gel) and eluted with chloroform–methanol (v/v: 100:5). Collected the second band and third bands (the first band was unreacted H_2TBrPP). The second band was identified as [$Yb(TBrPP)(acac)(CH_3OH)$] and third band as **2**. Yield for **2**: 52 mg, 18%. Anal. Calc. for $C_{49}H_{37}Br_4N_4O_4Yb$ [$Yb(TBrPP)(OOCCH_2CH_3)(OHCH_3)_2$]: C, 47.52; H, 3.01; N, 4.52; Found: C, 47.58; H, 3.09; N, 4.44. Synthesis of **3**: To a TCB solution (25 mL) of H_2TPP (21.57 mg, 0.35 mmol) was added $Yb(OAc)_3 \cdot 3H_2O$ (12.86 mg, 0.35 mmol). The resulting solution was then heated to 210 °C and magnetically stirred for 48 h under N_2. The solution was cooled to ~70 °C and methanol (10 mL) was added. The resulting solution was stirred for another 2 h at 70 °C. Then all solvent was removed under vacuum on rotary evaporator. The purple solid was re-dissolved in chloroform and loaded on column using silica gel. After removing free base with chloroform as elute, the silica gel was washed with chloroform–methanol (v:v: 100:5) and major band was collected. The final product was re-crystallized from dichloromethane-methanol at room temperature and dried under vacuum at room temperature overnight. Yield for **3**: 12.5 mg, 65%. Anal. Calcd. for $C_{48}H_{39}N_4O_4Yb$ [$Yb(TPP)(OOCCH_3)(OHCH_3)_2$]: C, 63.43; H, 4.33; N, 6.16; found: C, 63.49, H, 4.32, N, 6.52. Synthesis of **4**: To a dichloromethane solution (20 mL) of 3 (28.7 mg, 31.5 mmol) was added excess of 4-methyl-1,10-phenanthroline (67.9 mg, 35.0 mmol). The solution was magnetically stirred at room temperature for 4 h. Then all solvent was removed. The residual was dissolved in chloroform and loaded on column (silica gel). The column was washed with chloroform first to remove tiny amount of H_2TPP from decomposition and then with chloroform–methanol (v:v: 250:3). The major band gave the target complex **4**. Yield for **4**: 26 mg, 81%. Anal Calcd. for $C_{59}H_{45}N_6O_4Yb$ [$Yb(TPP)(OOCCH_3)(4\text{-}Me\text{-}1,10\text{-}Phen)(2H_2O)$]: C, 65.92; H, 4.22; N, 7.82; found: C, 65.79; H, 4.20; N, 8.00. Single crystal X-ray diffraction data were collected on a Bruker SMART CCD diffractometer (λMo Kα = 0.71073 Å), T = 125(2) K, and refined by full-matrix least-squares refinements on F^2 using all data with SHELXL programs. An empirical absorption correction was applied to the data using SADABS. Hydrogen atoms were generated

geometrically and refined with isotropic thermal parameters. Crystal data for $[Yb(TPP)(OOCCH_3)(CH_3OH)]_2{\cdot}2CHCl_3$ (**1**): $C_{96}H_{72}Cl_6N_8O_6Yb_2$, MW = 1992.4, monoclinic, P21/n, $a = 13.2404(5)$ Å, $b = 14.9951(6)$ Å, $c = 21.3514(8)$ Å, $\alpha = 90°$, $\beta = 105.29°$, $\gamma = 90°$, $V = 4089.0(3)$ Å^3, $Z = 2$, $Dc = 1.618$ g cm^{-3}, μ(Mo Kα) = 2.532 mm^{-1}, $T = 125(2)$ K, F(000) = 1988, 48,020 reflections measured with 9900 unique reflections. The final $R = 0.0225$, $wR = 0.0578$ for 7233 observed reflections ($I > 2\sigma(I)$). CCDC 681180. Crystal data for $[Yb(TBrPP)(OOCCH_2CH_3)(OHCH_3)_2]\cdot CH_2Cl_2$ (**2**): $C_{50}H_{37}Br_4Cl_2N_4O_4Yb$, MW = 1324.42, triclinic, P-1, $a = 12.1450(16)$ Å, $b = 19.033(3)$ Å, $c = 21.636(3)$ Å, $\alpha = 98.831(2)°$, $\beta = 94.109(2)°$, $\gamma = 95.744(2)°$, $V = 4898.0(11)$ Å^3, $Z = 4$, $Dc = 1.792$ g cm^{-3}, μ(Mo Kα) = 5.330 mm^{-1}, $T = 125(2)$ K, F(000) = 2564, 46,905 reflections measured with 17,728 unique reflections. The final $R = 0.0824$, $wR = 0.1996$ for 10,726 observed reflections ($I > 2\sigma(I)$). CCDC 682486. Crystal data for $[Yb(TPP)(OOCH_3)(MeOH)_2]\cdot CH_3OH$ (**3**): $C_{49}H_{43}N_4O_5Yb$, MW = 940.91, triclinic, P-1, $a = 11.2696(7)$ Å, $b = 12.5577(8)$ Å, $c = 15.4978(10)$ Å, $\alpha = 73.9610(10)°$, $\beta = 75.2230(10)°$, $\gamma = 80.6060(10)°$, $V = 2028.0(2)$ Å^3, $Z = 2$, $Dc = 1.541$ g cm^{-3}, μ(Mo Kα) = 2.360 mm^{-1}, $T = 125(2)$ K, F(000) = 950, 19,785 reflections measured with 7185 unique reflections. The final $R = 0.0246$, $wR = 0.0563$ for 6409 observed reflections ($I > 2\sigma(I)$). CCDC 681181. Crystal data for $[Yb(TPP)(OOCCH_3)(4\text{-}Me\text{-}1,10\text{-}Phen)]{\cdot}CH_3OH$ (**4**): $C_{60}H_{44}N_6O_3Yb$, MW = 1071.06, triclinic, P-1, $a = 9.8315(5)$ Å, $b = 13.7173(7)$ Å, $c = 17.6627(9)$ Å, $\alpha = 96.5870(10)°$, $\beta = 90.4030(10)°$, $\gamma = 93.1670(10)°$, $V = 2362.5(2)$ Å^3, $Z = 2$, $Dc = 1.506$ g cm^{-3}, μ(Mo Kα) = 2.035 mm^{-1}, $T = 125(2)$ K, F(000) = 1082, 23,291 reflections measured with 8293 unique reflections. The final $R = 0.0364$, $wR = 0.0955$ for 7190 observed reflections ($I > 2\sigma(I)$). CCDC 682748.

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