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Reactivity of Cationic Lanthanide(III) Monoporphyrinates towards Anionic Cyanometallates – Preparation, Crystal Structure, and Luminescence Properties of Cyanido-Bridged Di- and Trinuclear d–f Complexes

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The metathesis reaction between two equivalents of [Ln(tpp)$(H_2O)_3$]Cl (Ln = Yb, Er; tpp^{2-} = tetraphenylporphyrinate dianion) and one equivalent of cyanometallate in dmf at room temperature under nitrogen for 24 hours gave the cyanido-bridged d–f trinuclear complexes [{Ln(tpp)$(dmf)_n$}$_2${(μ-$NC)_2M(CN)_2$}] (Ln = Yb, *n* = 2, M = Ni, **1**; Ln = Er, *n* = 3, M = Ni, **2**; Ln = Yb, *n* = 2, M = Pt, **3**; Ln = Er, *n* = 3, M = Pt, **4**), a trinuclear complex [{Er(tpp)$(dmf)_2$}{(μ-$NC)_2Fe(CN)_4$}{Er(Htpp)$(dmf)_2$}] (**5**), and a dinuclear complex [{Er(tpp)(dmf)(H_2O)}(μ-NC)Ag(CN)] (**6**) when the cyanometallate used was the dianion $[M(CN)_4]^{2-}$ (M = Ni, Pt), the trianion $[Fe(CN)_6]^{3-}$, and monoanion $[Ag(CN)_2]^-$, respectively. The solid-state structures of these complexes were ascertained by X-ray crystallography. Photoluminescence studies of complexes **1**–**4** showed that these complexes displayed photophysical properties characteristic of normal metal–porphyrinato complexes. Their absorption bands and emission peaks in the visible region are typical of the intraligand $\pi\rightarrow\pi^*$ transitions of the porphyrinato ligand. Furthermore, these complexes also exhibited emission characteristic of the lanthanide(III) ion in the near-infrared (NIR) region, which was quenched by the cyanometallates.

Introduction

Porphyrinatolanthanide complexes are continuing to attract considerable research interest, not only for their potential biological and chemical importance, but also for the opportunity they offer to study structure–bonding–reactivity interrelationships.[1–3] Therefore, much effort has been devoted to the synthesis of novel complexes and investigation of their unique properties. Previously, we reported a convenient method for the preparation of cationic monoporphyrinatolanthanide complexes, [Ln(por)$(H_2O)_3$]Cl (por = porphyrinate dianion), by the reaction of Ln[N(Si$Me_3)_2]_3$·*x*[LiCl$(thf)_3$] with porphyrin free base (H_2por) in bis(methoxyethyl) ether.[4,5] X-ray diffraction studies showed that the lanthanide ions are seven-coordinate, surrounded by four N atoms of the porphyrin ring and three O atoms of the aqua ligands. Due to the lability of aqua molecules, these complexes catalyze the cyclotrimerization of phenylisocyanate efficiently[5] and can form adducts with anionic tripodal ligands such as cyclopentadienyltris(dimethylphosphito) cobaltate(I) (L_{OMe}^-) and hydridotris(pyrazole-1-yl)borate (T_p^{H-}) by a displacement reaction under mild conditions.[6] Furthermore, cationic monoporphyrinatolanthanide complexes [Yb(por)$(H_2O)_3$]Cl have a high tendency to form different metal dimers bridged by OH^- ions, chloride ions, or water molecules under different reaction conditions.[7] Therefore, [Ln(por)$(H_2O)_3$]Cl is a very versatile reagent for the preparation of species containing lanthanide porphyrinate and is a good candidate for the investigation of structure–reactivity relationships. Cyanido-bridged d–f complexes exhibit very rich and interesting structural, magnetic, and photophysical properties. Their structural and magnetic properties have been studied extensively;[8,9] however, their photophysical properties were only explored recently.[10] We have been interested in the synthesis and photoluminescence properties of d–f complexes[11] and porphyrinatolanthanide(III) complexes.[12] We would like to extend our study to cyanido-bridged, heterometallic d–f porphyrinato complexes. Cyanido-bridged d–f complexes can be conveniently synthesized by the metathesis reaction between a lanthanide(II or III) salt and a cyanometallate of transition metals in highly polar solvents.[8–10] The cationic lanthanide(III) complex [Ln(por)$(H_2O)_3$]Cl would be an ideal precursor complex for the preparation of such cyanido-bridged d–f porphyrinato complexes. Here we report the characterization and photophysical properties of

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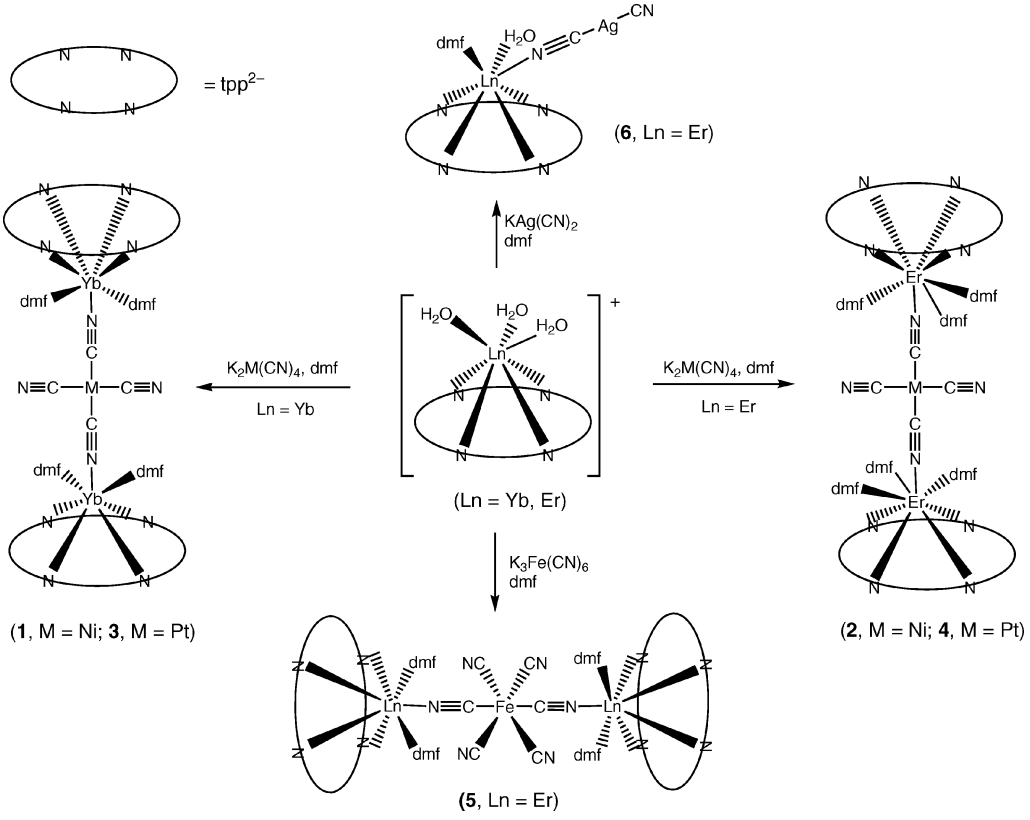
a series of neutral cyanido-bridged, porphyrinato di- and trinuclear d–f complexes prepared by the metathesis of cyanometallates of transition metals with the cationic monoporphyrinatolanthanide complexes $[Ln(por)(H_2O)_3]Cl$ (Ln = Yb, Er) in *N*,*N*-dimethylformamide (dmf).

Results and Discussion

Synthesis and Characterization

The metathesis reaction between two equivalents of $[Ln(tpp)(H_2O)_3]Cl$ (Ln = Yb, Er; tpp^{2-} = tetraphenylporphyrinate dianion) and one equivalent of cyanometallate in dmf at room temperature under nitrogen for 24 hours gave the cyanido-bridged d–f trinuclear complexes $[\{Ln(tpp)(dmf)_n\}_2\{(\mu\text{-}NC)_2M(CN)_2\}]$ (Ln = Yb, *n* = 2, M = Ni, **1**; Ln = Er, *n* = 3, M = Ni, **2**; Ln = Yb, *n* = 2, M = Pt, **3**; Ln = Er, *n* = 3, M = Pt, **4**), a trinuclear complex $[\{Er(tpp)(dmf)_2\}\{(\mu\text{-}NC)_2Fe(CN)_4\}\{Er(Htpp)(dmf)_2\}]$ (**5**), and a dinuclear complex $[\{Er(tpp)(dmf)(H_2O)\}(\mu\text{-}NC)Ag(CN)]$ (**6**) when the cyanometallate was the dianion $[M(CN)_4]^{2-}$ (M = Ni, Pt), the trianion $[Fe(CN)_6]^{3-}$, and the monoanion $[Ag(CN)_2]^-$, respectively (Scheme 1). Complexes **1**–**6** were isolated as air-stable purple crystals in good yields and were characterized by elemental analyses and spectroscopic techniques. Complexes **1**–**6** displayed the characteristic ν(C≡N) band at around 2130 cm^{-1} in their IR spectra. The positive electrospray ionization high-resolution mass spectrum (ESI-HRMS) of **1**–**4** exhibited the $[M + 1]^+$ peak at *m*/*z* = 1871.3261, 1859.3109, 1735.2861, and 1723.2895, which deviated less than 10 ppm from the theoretical values of 1871.3176, 1859.3132, 1735.2969, and 1723.2835, respectively, and their isotopic distribution patterns matched the theoretical distribution patterns as well. For complex **5**, we were unable to obtain an interpretable positive ESI-HRMS, but were able to obtain a negative ESI-HRMS, which displayed the $[M - 1]^-$ peak at *m*/*z* = 1771.2690, deviating less than 10 ppm from the theoretical value of 1771.2828 for $\{[Er(tpp)(dmf)_2]_2[Fe(CN)_6]\}^-$. To balance the charge of complex **5**, it is necessary to have a monocation or one of the porphyrinato ligands protonated. We were unable to locate a monocation in the crystal structure of **5** (vide infra). This suggests that one of the porphyrinato ligands of **5** has been protonated, and complex **5** should be formulated as $[\{Er(tpp)(dmf)_2\}\{(\mu\text{-}NC)_2Fe(CN)_4\}\{Er(Htpp)(dmf)_2\}]$. A similar observation has been reported for bis(porphyrinato)lanthanide(III) complexes, [Ln(tpp)(Htpp)], in which one of the porphyrinate groups has been protonated.[13] The ESI-HRMS of **6**, no matter whether in the negative or positive mode, did not display the molecular ion and was very complex and difficult to interpret.

The solid-state structures of complexes **1**–**6** were ascertained by X-ray crystallography. Crystals of compounds **1**–**6** suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a saturated solution of the respective compounds in dmf at room temperature. Selected



Scheme 1. Reactions of $[Ln(tpp)(H_2O)_3][Cl]$ (Ln = Yb and Er) with cyanometallates of transition metals.

bond lengths and bond angles for the complexes are given in Table 1. Structural analysis revealed that the trinuclear complexes **1**–**4** have very similar structures. The main structural difference between Yb (**1** and **3**) and Er (**2** and **4**) complexes is that Yb is seven-coordinate with two coordinated dmf solvates whereas Er is eight-coordinate with three coordinated dmf solvates. The higher coordination number for Er is probably due to the larger ionic radius of the Er^{3+} ion. Since the structures of **1** and **2** are isomorphous to that of **3** and **4**, respectively, only the molecular structures of **1** and **2** are described here in detail (see Supporting Information for the drawings of **3** and **4**). A perspective view of **1** is shown in Figure 1. The structure reveals that the two seven-fold coordinated Yb(1) and Yb(1′) atoms are connected by a $Ni(CN)_4^{2-}$ bridge in a *trans* fashion. Both Yb^{3+} ions are bound to four N atoms from the porphyrinate dianion, two O atoms from the two dmf molecules, and one N atom from the bridging cyanometallate. The Yb^{3+} ion sits 1.1614 Å above the centroid of the least-squares mean plane defined by the four pyrrole nitrogen atoms with a mean deviation of 0.0196 Å. The Yb–N(por) bond lengths ranging from 2.315(3) to 2.347(3) Å for Yb(1) are shorter than the Yb–N(N≡C) bond length [Yb(1)–

Table 1. Selected bond lengths [Å] and bond angles [°] for compounds **1**–**6**.

1			
Bond lengths			
Yb(1)–N(1)	2.315(3)	Yb(1)–N(2)	2.321(3)
Yb(1)–N(3)	2.315(3)	Yb(1)–N(4)	2.347(3)
Yb(1)–N(5)	2.411(3)	Yb(1)–O(1)	2.343(3)
Yb(1)–O(2)	2.300(3)	Ni(1)–C(46)	1.847(7)
Ni(1)–C(45)	1.852(4)		
Bond angles			
N(1)–Yb(1)–N(2)	76.98(10)	N(1)–Yb(1)–N(3)	139.30(10)
N(4)–Yb(1)–N(1)	77.70(9)	N(2)–Yb(1)–N(3)	77.59(10)
N(4)–Yb(1)–N(2)	122.58(10)	N(4)–Yb(1)–N(3)	75.84(10)
N(4)–Yb(1)–N(5)	121.27(12)	N(1)–Yb(1)–N(5)	158.50(12)
N(2)–Yb(1)–N(5)	97.90(12)	N(3)–Yb(1)–N(5)	73.66(11)
O(2)–Yb(1)–N(1)	99.48(11)	O(2)–Yb(1)–N(3)	119.48(11)
O(2)–Yb(1)–N(2)	159.36(11)	O(2)–Yb(1)–O(1)	78.46(11)
O(2)–Yb(1)–N(4)	75.44(10)	O(1)–Yb(1)–N(4)	144.19(10)
O(2)–Yb(1)–N(5)	77.86(13)		
2			
Bond lengths			
Er(1)–N(1)	2.394(4)	Er(1)–N(2)	2.380(4)
Er(1)–N(3)	2.401(3)	Er(1)–N(4)	2.404(4)
Er(1)–O(1)	2.389(3)	Er(1)–O(2)	2.409(4)
Ni(1)–C(45)	1.860(4)	Ni(1)–C(46)	1.859(7)
Bond angles			
N(1)–Er(1)–N(2)	74.71(12)	N(1)–Er(1)–N(3)	117.57(12)
N(4)–Er(1)–N(1)	74.38(12)	N(2)–Er(1)–N(3)	74.20(12)
N(4)–Er(1)–N(2)	117.65(12)	N(4)–Er(1)–N(3)	74.46(12)
N(4)–Er(1)–N(5)	138.41(13)	N(1)–Er(1)–N(5)	76.67(13)
N(2)–Er(1)–N(5)	81.84(13)	N(3)–Er(1)–N(5)	146.59(13)
3			
Bond lengths			
Yb(1)–N(1)	2.313(5)	Yb(1)–N(2)	2.340(5)
Yb(1)–N(3)	2.343(5)	Yb(1)–N(4)	2.306(5)
Yb(2)–N(9)	2.325(4)	Yb(2)–N(10)	2.332(4)
Yb(2)–N(11)	2.310(5)	Yb(2)–N(12)	2.302(5)
Yb(1)–O(1)	2.316(4)	Yb(1)–O(2)	2.265(4)
Yb(2)–O(3)	2.321(4)	Yb(2)–O(4)	2.314(4)
Yb(1)–N(5)	2.461(5)	Yb(2)–N(13)	2.440(5)
Pt(1)–C(45)	1.983(6)	Pt(1)–C(46)	1.996(7)
Pt(2)–C(97)	1.985(6)	Pt(2)–C(98)	1.995(7)
Bond angles			
N(1)–Yb(1)–N(2)	78.44(16)	N(1)–Yb(1)–N(3)	123.33(16)
N(4)–Yb(1)–N(1)	77.29(16)	N(2)–Yb(1)–N(3)	75.97(17)
N(4)–Yb(1)–N(2)	124.91(16)	N(4)–Yb(1)–N(3)	77.60(16)
N(4)–Yb(1)–N(5)	78.63(16)	N(1)–Yb(1)–N(5)	84.62(16)
N(2)–Yb(1)–N(5)	145.95(17)	N(3)–Yb(1)–N(5)	137.28(17)
N(12)–Yb(2)–N(11)	77.95(16)	N(12)–Yb(2)–N(9)	77.74(15)
N(11)–Yb(2)–N(9)	124.31(16)	N(12)–Yb(2)–N(10)	123.55(16)
N(11)–Yb(2)–N(10)	76.20(15)	N(9)–Yb(2)–N(10)	77.07(15)
N(12)–Yb(2)–N(13)	78.08(16)	N(11)–Yb(2)–N(13)	77.85(16)
N(9)–Yb(2)–N(13)	142.08(16)	C(45)–Pt(1)–C(46)	91.5(2)
C(45)–Pt(1)–C(45)	180.000(1)		

Table 1. *(Continued)*.

4			
Bond lengths			
Er(1)–N(1)	2.393(3)	Er(1)–N(2)	2.403(2)
Er(1)–N(3)	2.414(2)	Er(1)–N(4)	2.397(2)
Er(1)–O(1)	2.419(2)	Er(1)–O(2)	2.360(2)
Pt(1)–C(45)	1.988(3)	Pt(1)–C(46)	1.995(4)
Bond angles			
N(1)–Er(1)–N(2)	74.88(9)	N(1)–Er(1)–N(3)	118.04(9)
N(4)–Er(1)–N(1)	74.53(9)	N(2)–Er(1)–N(3)	73.90(8)
N(4)–Er(1)–N(2)	116.68(9)	N(4)–Er(1)–N(3)	73.98(8)
N(4)–Er(1)–N(5)	81.89(9)	N(1)–Er(1)–N(5)	77.01(9)
N(2)–Er(1)–N(5)	139.89(9)	N(3)–Er(1)–N(5)	145.70(9)
C(45)–Pt(1)–C(46)	88.89(14)		
5			
Bond lengths			
Er(1)–N(1)	2.342(4)	Er(1)–N(2)	2.343(4)
Er(1)–N(3)	2.352(4)	Er(1)–N(4)	2.345(4)
Er(1)–O(1)	2.283(4)	Er(1)–O(2)	2.333(4)
Fe(1)–C(45)	1.943(5)	Fe (1)-C(46)	1.949(7)
Er(1)–N(5)	2.467(4)	N(5)–C(45)	1.155(7)
Bond angles			
N(1)–Er(1)–N(2)	76.20(13)	N(1)–Er(1)–N(3)	121.47(14)
N(4)–Er(1)–N(1)	76.31(13)	N(2)–Er(1)–N(3)	75.12(12)
N(4)–Er(1)–N(2)	121.22(14)	N(4)–Er(1)–N(3)	76.85(14)
N(4)–Er(1)–N(5)	86.23(15)	N(1)–Er(1)–N(5)	83.19(15)
N(2)–Er(1)–N(5)	139.35(13)	N(3)–Er(1)–N(5)	144.54(5)
Er(1)–N(5)–C(45)	157.4(5)	N(5)–C(45)–Fe(1)	175.4(5)
C(45)–Fe(1)–C(46)	91.0(2)	C(45)–Fe(1)–C(46′)	89.0(2)
C(46)–Fe(1)–C(47)	91.7(3)	C(46′)–Fe(1)–C(47)	89.3(3)
6			
Bond lengths			
Er(1)–N(1)	2.342(12)	Er(1)–N(2)	2.343(12)
Er(1)–N(3)	2.353(12)	Er(1)–N(4)	2.340(12)
Er(1)–O(1)	2.339(13)	Er(1)–OW(1)	2.365(11)
Er(1)–N(5)	2.454(16)	Ag(1)–C(45)	2.02(2)
Bond angles			
N(1)–Er(1)–N(2)	77.1(4)	N(1)–Er(1)–N(3)	123.3(4)
N(4)–Er(1)–N(1)	74.53(9)	N(2)–Er(1)–N(3)	76.1(4)
N(4)–Er(1)–N(2)	122.8(4)	N(4)–Er(1)–N(3)	77.4(4)
N(4)–Er(1)–N(5)	160.6(5)	N(1)–Er(1)–N(5)	101.9(5)
N(2)–Er(1)–N(5)	74.8(5)	N(3)–Er(1)–N(5)	117.6(5)
Er(1)–N(5)–C(45)	157.3(16)	C(45)–Ag(1)–C(46)	169.1(11)

N(5), 2.411(3) Å]. The Yb–O distances between Yb and the two dmf molecules are 2.321 Å for Yb(1)–O and 2.316 Å for Yb(2)–O, which are much shorter than that of Yb–O(thf) [3.003(13) Å] reported previously.[5] The Yb–N(N≡C) and Yb–O distances are comparable to the average distances reported for $[(dmf)_{10}Yb_2\{Ni(CN)_4\}_3]_\infty$ (Yb–N, 2.44 Å; Yb–O, 2.30 Å).[8i] The dihedral angles formed between the phenyl rings and the N_4 mean plane are 59.3 [C(21)–C(26)], 79.8 [C(27)–C(32)], 61.1 [C(33)–C(38)], and 78.4° [C(39)–C(44)]. The coordination geometry around the nickel atom is approximately square planar with bond angles of being 90.2(2), 89.8(2) and 180.0(3)° for C(46)–Ni–C(45), C(46)–Ni–C(45′), and C(45)–Ni–C(45′), respectively. The angle Yb(1)–N(5)–C(45) is 161.4(5)°, which is not linear as compared with other lanthanide complexes bridged by transition-metal cyanometallates.[8j] This is most likely, to some extent, due to steric crowding around the Yb^{III} cation (vide infra). The structure of **2** is shown in Figure 2. Similar to that of **1**, the two eight-fold coordinated Er(1) and Er(1′) atoms are connected by a $Ni(CN)_4^{2-}$ bridge in a *trans* fashion. Both Er atoms are bound to four N atoms from the porphyrinate dianion, three O atoms from the three dmf molecules, and one N atom from the bridging cyanometallate. The Er(1) atom lies 1.2403 Å above the porphyrin ring [N(1)–N(4)] with a mean deviation of 0.0022 Å. The Er–N(por) bond lengths, which have an average value of 2.394 Å, are shorter than the Er–N(N≡C) bond length, which is 2.491(4) Å for Er(1)–N(5). The Er–O distances between Er and the three dmf ligands are 2.389(3) Å for Er(1)–O(1), 2.409(3) Å for Er(1)–O(2), and 2.387(4) Å for Er(1)–O(3). The Er–N(N≡C) and Er–O distances are comparable to the average distances reported for $[(dmf)_{10}Er_2\{Ni(CN)_4\}_3]_\infty$ (Er–N, 2.44 Å; Er–O, 2.32 Å).[8i] The dihedral angles formed between the phenyl rings and the N_4 mean plane are 63.2 [C(21)–C(26)], 56.7 [C(27)–C(32)], 68.6 [C(33)–C(38)], and 68.1° [C(39)–C(44)]. In contrast to **1**, the bond angles Er(1)–N(5)–C(45) and Ni(1)–C(45)–N(5) are 174.4(4)°, and 177.5(5)°, respectively, and Er–N–C–Ni is almost linear. A similar structural observation has also been reported for $[(dmf)_{10}Ln_2\{Ni(CN)_4\}_3]_\infty$ (Ln = Yb, Er), in which the Ln–N–C angles range from 156.7(3) to 169.6(3)° for the Yb complex and 170.3(5) to 177.6(5)° for the Er complex.[8i]

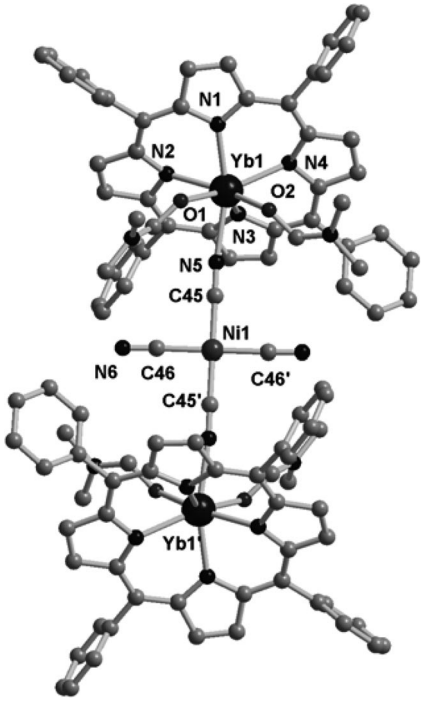


Figure 1. A perspective view of **1**. Hydrogen atoms are omitted for clarity.

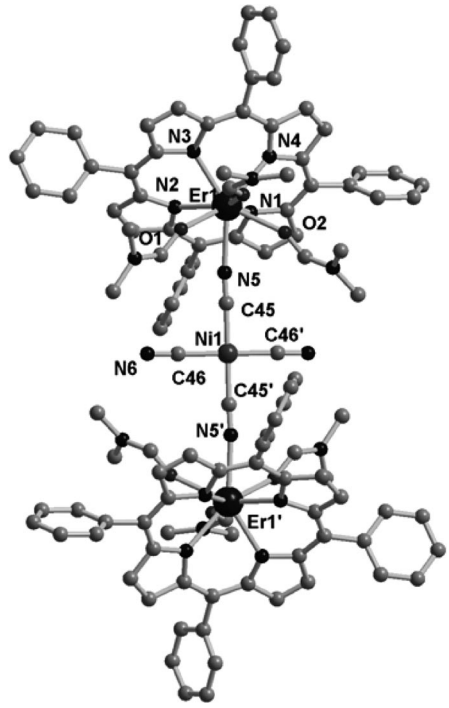


Figure 2. A perspective view of **2**. Hydrogen atoms are omitted for clarity.

The structure of [{Er(tpp)(dmf)$_2$}{(μ-NC)$_2$Fe(CN)$_4$}-{Er(Htpp)(dmf)$_2$}] (**5**) (Figure 3) reveals that the two Er(1) and Er(1′) atoms are connected by an octahedral $Fe(CN)_6^{3-}$ ion, and each is surrounded by four N atoms from the porphyrinate dianion, two O atoms from the two dmf molecules, and one N atom from the bridging cyanido ligand. The Er(1) atom lies 1.1486 Å above the porphyrin ring [N(1)–N(4)]. The average Er–N(por) bond length is 2.345(4) Å and is shorter than the Er–N(N≡C) bond length, which is 2.467(4) Å for Er(1)–N(5). The Er–O distances between Er and the two O atoms of the dmf ligands are 2.283(4) Å for Er (1)–O(1) and 2.333(4) Å for Er (1)–O(2), which are longer than that of the Yb–O distance, which has an average value of 3.302(4) Å. This is probably due to the difference in the ionic radii. The angle for Er(1)–N(5)–C(45) is 157.4(5)°. The dihedral angles formed between the phenyl rings and the N_4 mean plane are 57.6 [C(21)–C(26)], 56.9 [C(27)–C(32)], 70.4 [C(33)–C(38)], and 91.7° [C(39)–C(44)]. Six cyanido ligands surround the Fe^{III} ion in a distorted octahedral environment. The average Fe–

C distance is 1.94 Å, and the bond angles C(46)–Fe–C(45), C(46′)–Fe–C(45), C(46)–Fe–C(47), C(46′)–Fe–C(47), and C(45)–Fe–C(45′) are 91.0(2), 89.0(2), 90.7(3), 89.3(3), and 180.00(1)°, respectively. However, we cannot locate the proton position from the Fourier map.

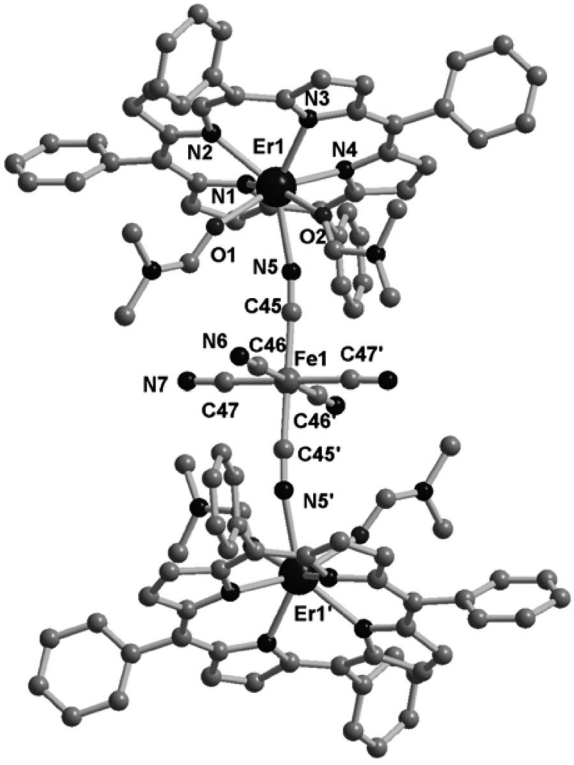


Figure 3. A perspective view of **5**. Hydrogen atoms are omitted for clarity.

A perspective drawing of $[Er(tpp)(dmf)(H_2O)][Ag(CN)_2]$ (**6**) is shown in Figure 4. Structural analysis of **6** reveals that Er is seven-coordinate with four N atoms from the porphyrinate dianion, two O atoms from dmf and H_2O, and one N atom from the bridging cyanido ligand. The Er(1) atom lies 1.1177 Å above the porphyrin ring [N(1)–N(4)]. The Er–N(por) bond lengths, with an average value of 2.344(12) Å, are shorter than the Er–N(N≡C) bond length, which is 2.454(16) Å for Er(1)–N(5). The Er–O distance for the dmf ligand is 2.339(13) Å [Er(1)–O(1)] and is shorter than that for the aqua ligand, which is 2.365(11) Å [Er(1)–O(W1)]. The angle for Er(1)–N(5)–C(45) is 157.3(5)°, which is less linear than that in complexes **1** and **2**.

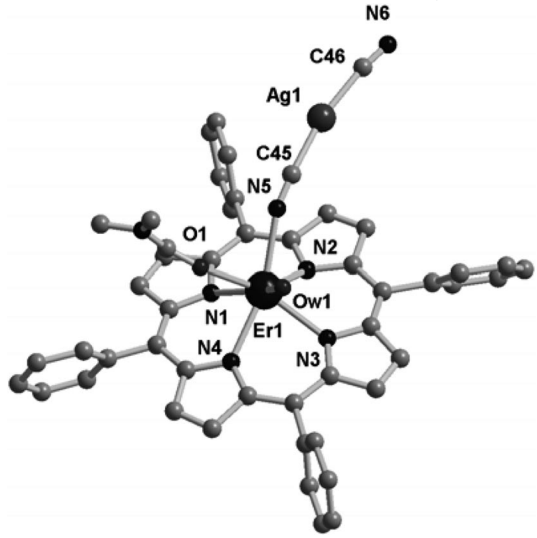


Figure 4. A perspective view of **6**. Hydrogen atoms are omitted for clarity.

Photophysical Properties

Porphyrinatolanthanide complexes display absorption spectra that are typical for "regular metalloporphyrins" (this terminology is derived from Gouterman's original review of the field).[14] Specifically, they feature an intense Soret band near 425 nm, which is due to the allowed $S_0 \rightarrow S_2$ transition, and two weak Q bands [Q(1,0) and Q(0,0)] in the 550–600 nm region arising from the orbitally forbidden $S_0 \rightarrow S_1$ transition. The photophysical data for complexes **1**–**4** are shown in Table 2. The absorption spectra of complexes **1**–**4** are very similar both at the positions around 421, 552, and 588 nm, and in terms of the extinction coefficients of the band maxima (Figure 5). In addition, the Soret bands of complexes **1**–**4** are slightly blueshifted as compared with the parent complex, $[Yb(tpp)(dmf)_2Cl]$. The origin of this effect is yet unclear; it is possibly due to a slight ground state destabilization when the lanthanide ions are coordinated to the cyanometallates. All of the complexes exhibit weak photoluminescence (PL) as several resolved bands in the 600–720 nm region (Figure 6). Presumably, the fluorescence arises from the lowest $^1\pi$–π^* (Q) state of the porphyrin in competition with the intersystem crossing (ISC) to the $^3\pi$–π^* state.[14a] Interpretation of the visible emission intensity of the complexes is rendered difficult due to the complicated system involved. The related fluores-

Table 2. Summary of absorption and fluorescence data for compounds **1**–**4** compared with H_2tpp and $[Yb(tpp)(dmf)_2(Cl)]$.

Compound	Absorption λ_{max} [nm] ($\log\varepsilon$)[a]	Excitation λ_{exc} [nm]	Emission λ_{em} [nm] (τ, $\Phi_{em} \times 10^3$)[b]
1	418 (5.35), 553 (4.41), 592 (4.12)	421	650 (2.71 ns, 1.15), 715, 998 (1.07 μs)
2	418 (5.38), 552 (4.40), 591 (4.14)	421	650 (1.94 ns, 0.55), 715
3	419 (5.67), 552 (4.44), 588 (3.78)	420	650 (1.54 ns, 0.22), 717, 998 (1.03 μs)
4	421 (5.53), 553 (4.28), 590 (3.64)	421	650 (1.93 ns, 0.33), 715
$[Yb(tpp)(dmf)_2(Cl)]$	424 (5.47), 554 (4.29), 593 (3.65)	425	650 (2.33 ns, 0.50), 715, 998 (10 μs)

[a] Photophysical measurements were made in toluene solution at room temperature, and ε is in $dm^3\,mol^{-1}\,cm^{-1}$. [b] The quantum yield standard used in this study was tetraphenylporphyrin (H_2tpp) in outgassed, anhydrous benzene (Φ_F = 0.130 at 298 K).

cence lifetime values are about 1.54–2.71 ns, and [Yb(tpp)(dmf)$_2$Cl] has a similar fluorescence lifetime value of 2.33 ns. This reveals that the C≡N group directly coordinated to the lanthanide center has no obvious effect on the photophysical properties of the porphyrin moiety. Other than the visible emission, complexes **1**–**4** also exhibit an emission band corresponding to the Yb^{3+} or Er^{3+} ion in the near-infrared (NIR) region. The intensity of the NIR emission for the Yb^{3+} complexes (**1** and **3**) is much stronger than that for the corresponding Er^{3+} complexes (**2** and **4**), which is commonly observed in related porphyrinatolanthanide(III) complexes.[12] The NIR emission spectrum obtained in toluene solution of **1** and **2** upon excitation at 600 nm is shown in Figure 7. The emissions centered at around 976 and 1515 nm can be assigned to the $^2F_{5/2}\rightarrow{}^2F_{7/2}$ transition of Yb^{3+} and $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of Er^{3+}, respectively. All of the crystalline samples used for luminescence studies were grown from dmf rather than H_2O and dissolved in dry toluene to minimize the deleterious effects of O–H oscillators on the lanthanide emission.[15] The intensity of the NIR emission of [{Yb(tpp)(dmf)$_2$}$_2${(μ-NC)$_2$-M(CN)$_2$}] (M = Ni, Pt) is much weaker than that of the [Yb(tpp)(dmf)$_2$Cl] complex.[5] This indicates that, to some extent, the tetracyanometallates quenched the NIR emission of the Yb^{3+} ion. It has been shown that bridged cyanometallates could quench Ln^{3+} ion emission.[10a,10d,10i,16] The NIR emission of Nd^{3+}, Er^{3+}, and Yb^{3+} ions was probably quenched by the vibrations of the coordinated cyanido ligands.[10a,10d,10i] The same quenching mechanism may operate here as well. The particularly short luminescence lifetimes of the lanthanide centers are consistent with the weak NIR emission. Luminescence lifetimes for coordinatively saturated Yb^{III} complexes are commonly in the order of microseconds, typically >10 μs for Yb^{III}[17] or more if there are no high-energy oscillators close to the metal center.[18] In our coordination complexes, however, the observed lifetimes are approximately one order of magnitude shorter than those in molecular complexes and many orders of magnitude less than those in oxide/fluoride crystals. We ascribe this to the presence of the relatively high-energy C≡N oscillators at around 2142 cm^{-1}, which are directly coordinated to the lanthanide centers.

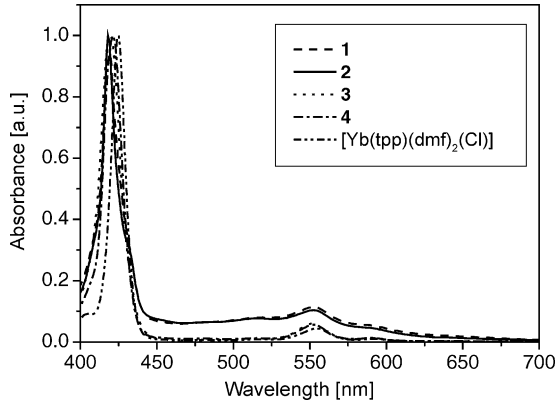


Figure 5. Absorption spectra of complexes **1**–**4** and [Yb(tpp)-(dmf)$_2$(Cl)] in toluene.

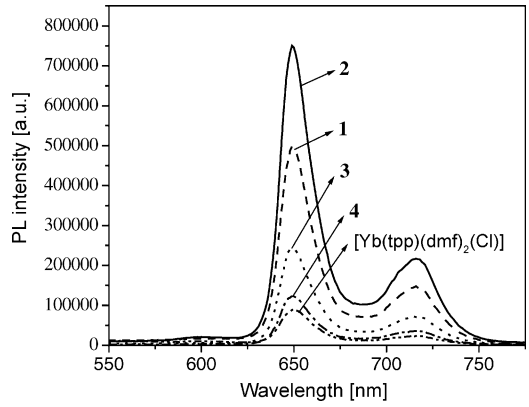


Figure 6. Visible emission spectra of complexes **1**–**4** and [Yb(tpp)(dmf)$_2$(Cl)] in toluene at a concentration of 1×10^{-5} M.

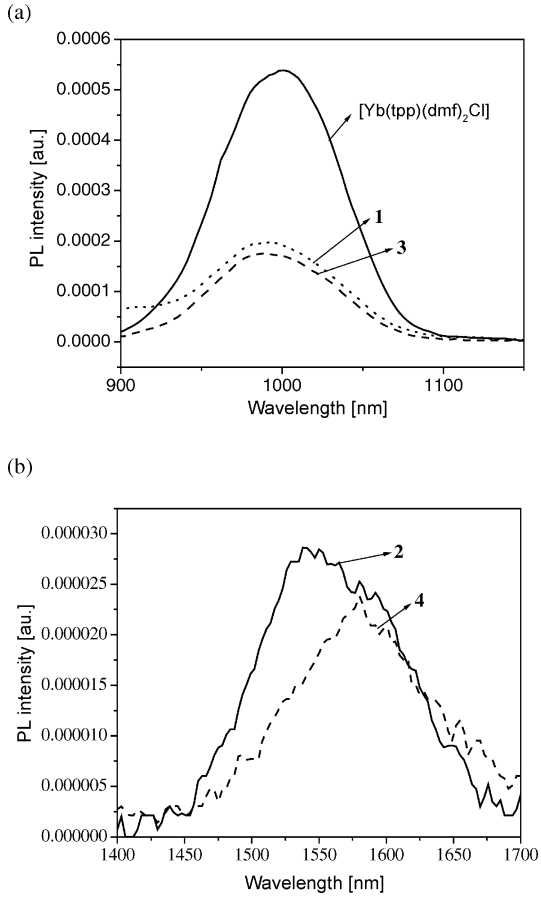


Figure 7. NIR emission of (a) **1**, **3**, and [Yb(tpp)(dmf)$_2$(Cl)] and (b) **2** and **4** in toluene at a concentration of 1×10^{-5} M.

Conclusions

In conclusion, a series of novel neutral di- and trinuclear cyanido-bridged, heterometallic d–f porphyrinato complexes have been synthesized by the metathesis reaction of cationic porphyrinatolanthanide complexes with cyanometallates of transition metals. X-ray structural analysis revealed that for the trinuclear complexes, the two porphyrin-

atolanthanide(III) moieties are linked by a cyanometallate in a *trans* manner. Photoluminescence studies showed that the cyanido bridges quenched the NIR emission of the Yb^{3+} ion.

Experimental Section

General: All reagents and solvents were of the commercial reagent grade and were used without further purification except where noted. Dichloromethane was distilled from calcium hydride. Toluene and thf were distilled under nitrogen in the presence of sodium chips by using benzophenone ketyl as an indicator. The freshly distilled solvents were bubbled with nitrogen for at least 10 min to remove the residual oxygen. Pyrrole was freshly distilled from calcium hydride before use. $[Ln(tpp)(H_2O)_3]Cl$ (Ln = Yb and Er)[5] and $[Yb(tpp)(dmf)_2(Cl)]$[12g] were prepared according to literature methods. Elemental analyses (C, H, N) were performed by Shanxi University, China. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded with a QSTAR mass spectrometer, the electronic absorption spectra in the UV/Vis region with a Hewlett Packard 8453 UV/Vis spectrophotometer, steady-state visible fluorescence and PL excitation spectra with a Photon Technology International (PTI) spectrophotometer. NIR emission was detected by a liquid nitrogen cooled InSb IR detector (EG & G) with a preamplifier and recorded by a lock-in amplifier system. The third harmonics, 355 nm line, of a Nd:YAG laser (Quantel Brilliant B) was used as the excitation light source.

General Procedure for the Preparation of Cyanido-Bridged d–f Complexes: A solution of $[Ln(tpp)(H_2O)_3]Cl$ (0.063 mmol) and $K_x[M(CN)_y]$ (0.032 mmol) in dmf (10 mL) was stirred for 24 h under nitrogen and then filtered. The filtrate was evaporated to dryness, and the residue was flashed on a pad of silica gel by using $CHCl_3$/MeOH as eluent. The first band was collected, evaporated, and redissolved in dmf, then Et_2O was slowly diffused into the dmf solution. Over a period of about four weeks, purple crystals suitable for X-ray diffraction were obtained.

$[\{Yb(tpp)(dmf)_2\}_2\{(\mu\text{-}NC)_2Ni(CN)_2\}]$ (1): $[Yb(tpp)(H_2O)_3]Cl$ (0.063 mmol) and $K_2[Ni(CN)_4]$ (0.032 mmol) were used. Yield: 0.042 g, 78%. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2142, 1664, 1645, 1595, 1480, 1439, 1381, 1201, 1069, 1006, 989, 798, 753, 701 cm^{-1}. ESI-HRMS (positive mode in methanol): calcd. for $C_{92}H_{56}N_{12}NiYb_2$ $[M + 1]^+$ 1735.2969; found 1735.2861. $(C_{92}H_{56}N_{12}NiYb_2)(C_3H_7NO)_4$ (2026.69): calcd. C 61.63, H 4.18, N 11.06; found C 61.64, H 4.16, N 11.09. UV/Vis (toluene, 20 °C): λ_{max} (log ε) [ε in $dm^3\,mol^{-1}\,cm^{-1}$] = 418 (5.35), 553 (4.41), 592 (4.12) nm.

$[\{Er(tpp)(dmf)_3\}_2\{(\mu\text{-}NC)_2Ni(CN)_2\}]$ (2): $[Er(tpp)(H_2O)_3]Cl$ (0.063 mmol) and $K_2[Ni(CN)_4]$ (0.032 mmol) were used. Yield: 0.037 g, 69%. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2118, 1647, 1595, 1479, 1439, 1384, 1198, 1006, 988, 800, 757, 703 cm^{-1}. ESI-HRMS (positive mode in methanol): calcd. for $C_{92}H_{56}Er_2N_{12}Ni$ $[M + 1]^+$ 1723.2835; found 1723.2895. $(C_{92}H_{56}Er_2N_{12}Ni)(C_3H_7NO)_6$ (2161.32): calcd. C 61.13, H 4.57, N 11.67; found C 62.05, H 4.15, N 11.54. UV/Vis (toluene, 20 °C): λ_{max} (log ε) [ε in $dm^3\,mol^{-1}\,cm^{-1}$] = 418 (5.38), 552 (4.40), 591(4.14) nm.

$[\{Yb(tpp)(dmf)_2\}_2\{(\mu\text{-}NC)_2Pt(CN)_2\}]$ (3): $[Yb(tpp)(H_2O)_3]Cl$ (0.063 mmol) and $K_2[Pt(CN)_4]$ (0.032 mmol) were used. Yield: 0.046 g, 78%. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2150, 2132, 1664, 1647, 1595, 1480, 1439, 1382, 1201, 1068, 1006, 989, 800, 753, 702 cm^{-1}. ESI-HRMS (positive mode in methanol): calcd. for $C_{92}H_{56}N_{12}PtYb_2$ $[M + 1]^+$ 1871.3176; found 1871.3261. $(C_{92}H_{56}N_{12}PtYb_2)(C_3H_7NO)_4$ (2163.08): calcd. C 57.75, H 3.91, N 10.36; found C 57.35, H 3.94, N 10.26. UV/Vis (toluene, 20 °C): λ_{max} (log ε) [ε in $dm^3\,mol^{-1}\,cm^{-1}$] = 419 (5.67), 552 (4.44), 588 (3.78) nm.

$[\{Er(tpp)(dmf)_3\}_2\{(\mu\text{-}NC)_2Pt(CN)_2\}]$ (4): $[Er(tpp)(H_2O)_3]Cl$ (0.063 mmol) and $K_2[Pt(CN)_4]$ (0.032 mmol) were used. Yield: 0.048 g, 82%. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2138, 1662, 1595,

Table 3. Crystallographic data for compounds **1**–**6**.

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{108}H_{94}N_{16}NiO_5Yb_2$	$C_{117}H_{115}Er_2N_{19}NiO_8$	$C_{107.5}H_{92.5}N_{16.5}O_5PtYb_2$	$C_{122}H_{126}Er_2N_{22}O_{10}Pt$	$C_{120}H_{119}Er_2FeN_{20}O_8$	$C_{52}H_{44}AgErN_8O_4$
Molecular weight	2100.78	2308.50	2236.65	2590.06	2359.71	1120.08
Crystal size [mm]	0.44×0.32×0.28	0.30×0.20×0.10	0.20×0.15×0.15	0.15×0.15×0.25	0.45×0.20×0.15	0.15×0.15×0.25
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	*P*21/*n*	*P*$\bar{1}$	*P*21/*n*	*P*21/*c*	*P*$\bar{1}$	*P*$\bar{1}$
a [Å]	14.1907(8)	9.9511(10)	17.1312(12)	13.3215(6)	13.121(3)	13.338(2)
b [Å]	14.8861(8)	15.2654(19)	16.3929(12)	26.1840(12)	13.465(3)	13.383(2)
c [Å]	24.8197(14)	19.679(2)	34.302(3)	17.7011(8)	17.496(3)	26.185(5)
α [°]	90	80.164(3)	90	90	83.575(4)	96.588(3)
β [°]	104.6530(10)	81.135(2)	101.3560(10)	110.8100(10)	78.490(3)	92.633(3)
γ [°]	90	71.116(2)	90	90	69.819(3)	90.750(3)
V [Å^3]	5072.5(5)	2771.5(5)	9444.4(12)	5773.1 (5)	2839.9(9)	4637.7(14)
Z	2	1	4	2	1	4
$D_{calcd.}$ [g cm^{-3}]	1375	1383	1573	1490	1.379	1.604
T [K]	293(2)	293(2)	173(2)	223(2)	293(2)	293(2)
μ(Mo-K_α) [mm^{-1}]	2.072	1.733	3.506	2.717	1.655	2.275
F(000)	2124	1178	4444	2612	1205	2236
θ range [°]	1.89 to 28.30	1.42 to 28.28	1.21 to 28.29	1.50 to 28.3	1.88 to 25.00	1.75 to 25.01
Reflections collected	43132	16614	67008	41760	14112	22260
Independent reflections	11868	12122	21758	13343	9821	15832
R_{int}	0.0250	0.0226	0.0517	0.0362	0.0307	0.0437
GoF on F^2	1.060	1.067	1.026	1.059	1.089	1.104
*R*1, *wR*2 [$I > \sigma(I)$][a]	0.0373, 0.1057	0.0399, 0.1025	0.0463, 0.0947	0.0337, 0.0739	0.0572, 0.1509	0.0990, 0.2228
*R*1, *wR*2 (all data)	0.0474, 0.1123	0.0594, 0.1150	0.0773, 0.1132	0.0449, 0.0851	0.0798, 0.1663	0.1421, 0.2420

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

1478, 1439, 1382, 1200, 1068, 1006, 988, 800, 754, 702 cm^{-1}. ESI-HRMS (positive mode in methanol): calcd. for $C_{92}H_{56}N_{12}Er_2Pt$ [M + 1]$^+$ 1859.3132; found 1859.3109. $(C_{92}H_{56}Er_2N_{12}Pt)(C_3H_7NO)_6$ (2297.71): calcd. C 57.50, H 4.30, N 10.97; found C 57.75, H 4.45, N 10.39. UV/Vis (toluene, 20 °C): λ_{max} (log ε) [ε in $dm^3 mol^{-1} cm^{-1}$] = 421 (5.53), 553 (4.28), 590 (3.64) nm.

[{Er(tpp)(dmf)$_2$}{(μ-NC)$_2$Fe(CN)$_4$}{Er(Htpp)(dmf)$_2$}] (5): [Er(tpp)-$(H_2O)_3$]Cl (0.063 mmol) and $K_3[Fe(CN)_6]$ (0.032 mmol) were used. Yield: 0.044 g, 79%. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 3423, 3054, 3021, 2928, 2109, 2088, 2026, 1654, 1596, 1478, 1439, 1384, 1330, 1202, 1106, 1068, 1006, 989, 800, 753, 724, 702 cm^{-1}. ESI-HRMS (negative mode in methanol): calcd. for $C_{94}H_{56}N_{14}Er_2Fe$ [M – 1]$^-$ 1771.2828; found 1771.2690 (error: –7.79 ppm). $(C_{94}H_{57}Er_2FeN_{14})(C_3H_7NO)_4$ (2065.33): calcd. C 61.64, H 4.15, N 12.21; found C 62.03, H 3.95, N 11.96. UV/Vis (toluene, 20 °C): λ_{max} (log ε) [ε in $dm^3 mol^{-1} cm^{-1}$] = 419 (5.67), 552 (4.44), 588 (3.78) nm.

[{Er(tpp)(dmf)(H$_2$O)}(μ-NC)Ag(CN)] (6): [Er(tpp)$(H_2O)_3$]Cl (0.063 mmol) and K[Ag$(CN)_2$] (0.032 mmol) were used. Yield: 0.042 g, 68%. M.p. > 300 °C. IR (KBr): $\tilde{\nu}$ = 2118, 1647, 1595, 1479, 1439, 1384, 1198, 1006, 988, 800, 757, 703 cm^{-1}. $(C_{46}H_{28}AgErN_6)(H_2O)(C_3H_7NO)$ (1031.01): calcd. C 56.77, H 3.60, N 9.46; found C 56.70, H 3.60, N 9.59.

X-ray Crystallography: Single crystals of compounds **1**–**6** suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a saturated solution of the respective compound in dmf at room temperature. X-ray intensity data were collected with a Bruker Axs SMART 1000 CCD area-detector diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT,[19] and an absorption correction was applied (SADABS[20]) to the collected reflections. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses with the software SHELXTL.[21] Structure refinements were made on F^2 by using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective carbon atoms. Pertinent crystallographic data and other experimental details are summarized in Table 3. CCDC-678994, -678995, -678996, -678997, -678998, and -678999 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): X-ray crystal structures of **3** and **4** and decay curves of visible fluorescence and NIR emissions of Yb(tpp)$(dmf)_2$Cl in toluene.

Acknowledgments

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