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Hetero-binuclear near-infrared (NIR) luminescent ZnLn (Ln = Nd, Yb or Er) complexes self-assembled from the benzimidazole-based ligand

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ABSTRACT

With the $[\mathbf{Zn}(\mathbf{HL})_2(\mathbf{Py})]$ compound from the benzimidazole-based ligand $\mathbf{H_2L}$ ($\mathbf{H_2L}$: 2-(1H-benzo[d]imidazol-2-yl)-6-methoxyohenol) as the precursor, the series of four hetero-binuclear ZnLn arrayed complexes $[\mathbf{ZnLn}(\mathbf{HL})_2(\mathbf{Py})(\mathbf{NO_3})_3]$ (Ln = Nd, 1; Ln = Yb, 2; Ln = Er, 3; Ln = Gd, 4) have been obtained by the further reaction with $\mathbf{Ln}(\mathbf{NO_3})_3 \cdot 6H_2O$, respectively. The result of their photophysical properties shows that the strong and characteristic NIR luminescence of Nd³⁺ or Yb³⁺ ion with emissive lifetimes in microsecond range, has been sensitized from the excited state (¹LC and ³LC) of the benzimidazole-based ligand.

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There is currently considerable interest in the near infrared (NIR) luminescent Ln^{3+} ($Ln^{3+} = Nd^{3+}$, Yb^{3+} or Er^{3+}) complexes because of their potential applications in bio-analysis [1] and materials science [2]. However, the f-f transitions for these ions are partially forbidden, absorption coefficients and emissive rates are very low [3]. In order to obtain efficient emissions, many organic (cyclic or acyclic) ligands [4] and d-block metal complexes [5] have been used as antennae or chromophores for the effective sensitization of NIR luminescence of Ln³⁺ ions. For this purpose, in the molecular design of the NIR luminescent Ln^{3+} complexes, besides the complete avoidance or decrease of the luminescent quenching effect arising from OH-, CH- or NH-oscillators around the Ln^{3+} ion [6], another key rule to the high NIR quantum yield should be further considered, requiring the realization of the energy level's match of the excited state of the chromophore to the corresponding Ln³⁺ ion's exciting state for the high-yield energy transfer [7], both are strongly relative to the suitable selection of organic chromophores.

Past studies by our groups have shown that in the formation of the series of ZnLn heterometallic complexes [8] from the compartmental Salen-type Schiff-base ligands with the outer O_2O_2 moieties from MeO groups, the Zn²⁺ complexes based on the Salen-type Schiffbase ligands, as the suitable chromophores, could effectively sensitize

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the NIR luminescence of the centered Ln³⁺ ions. On the other hand, based on the typical Salen-type Schiff-base ligands without the outer O₂O₂ moieties from MeO groups, series of NIR luminescent Zn_2Ln (Ln = Nd, Yb or Er) arrayed complexes have been obtained [9], in which from the viewpoint of enhancement of NIR luminescent properties, the use of the flexible linker while not the rigid one of the typical Salen-type Schiff-base ligands without the outer O₂O₂ moieties, could improve the NIR luminescent quantum efficiency due to the effective intramolecular energy transfer from the ligand-centered ³LC and 1 LC not just 1 LC excited state to the Ln³⁺ ions. Moreover, the occupation of pyridine at the axial position of the Zn^{2+} ion, is helpful for the strong NIR luminescence, which should be due to the complete avoidance of the luminescent quenching effect arising from OH-, CH- or NH-oscillators around the Ln³⁺ ion. As a matter of fact, the use of the Salen-type Schiff-base ligands should not be necessary to bind both Zn^{2+} and Ln^{3+} ions. Especially, the recent report of one magnetic [Cu(HL)₂Tb(NO₃)₃] from the benzimidazole-based ligand H_2L ($H_2L = 2-(1H-benzo[d])$ imidazol-2-yl)-6-methoxyohenol) [10] stimulates us for further exploration on the possibility of its Zn^{2+} and Ln^{3+} luminescent complexes, despite much research on the luminescent Ln^{3+} complexes from the benzimidazole-based ligands [11]. Herein, with the [Zn(HL)₂(Py)] from the benzimidazole-based ligand H₂L as the precursor, series of heterobinuclear ZnLn complexes $[ZnLn(HL)_2(Py)(NO_3)_3]$ (Ln = Nd, 1; Ln = Yb, **2**; Ln = Er, **3**; Ln = Gd, **4**) are obtained, respectively. The sensitization and energy transfer for the NIR luminescence of the Ln^{3+} ions in the ZnLn complexes are discussed.

As shown in Scheme 1, treatment of *o*-phenylenediamine with *o*-vanillin in 1:1 molar ratio in absolute EtOH at ambient temperature

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produced the orange Schiff-base **HL**⁰ with the yield of *ca*. 75%, and the sole presence of pure mono-imine compound was easily recognized in the ¹H NMR spectrum as a result of the presence of single peaks for the – OH, imine and NH₂ groups in a 1:1:2 signal integral ratio. Furthermore, in refluxing absolute EtOH, the mono-imine Schiff-base precursor **HL**⁰ is converted into the off-white benzimidazole-based ligand **H**₂L in good yield. Reaction of the benzimidazole-based ligand **H**₂L and Zn(OAc)₂· 2H₂O in 2:1 molar ratio in the presence of excess absolute pyridine (Py) afforded the precursor [**Zn(HL)₂(Py)**] in good yield of ca. 74%. Further reaction of the precursor [**Zn(HL)₂(Py)**] with the Ln(NO₃)₃· GH₂O (Ln = Nd, Yb, Er or Gd) resulted in the formation of the series of the hetero-binuclear ZnLn complexes [**Zn(HL)₂(Py)Ln (NO₃)₃]** (Ln = Nd, 1; Ln = Yb, 2; Ln = Er, 3 or Ln = Gd, 4), respectively.

It is interesting to note that although the synthesis of the benzimidazole-based ligand H₂L is stepwise, not from the straightforward condensation with o-phenylenediamine and o-vanillin used in the literature [10,11], the higher yield is due to the effective avoidance of possible by-products of the Salen-type Schiff-base ligand and the Nsubstituted benzimidazole ligand. Apart from the ¹H NMR spectrum identification of H₂L in CD₃CN with a sharp singlet at $\delta = 13.27$ ppm for the – OH proton, exhibiting the typical resonance-assisted hydrogen bonded (RAHB) proton of the type O -H…N=C [12], colorless single crystals of H₂L for X-ray crystallography were obtained from an EtOH solution in air at room temperature, and the crystallographic data and the selected bond lengths and angles are given in Tables 1-2S, respectively. As shown in Fig. 1, the ligand H₂L crystallizes in the monoclinic space group P2(1)/n. In the molecule, the fused benzene and imidazole rings are nearly planar, of which the dihedral angle (2.2(2)°) is smaller than that of 6.6(2)° between the benzimidazole moiety and the substituted aryl ring. The molecule is slightly twisted about the C6-C8 bond, with the C5C6C8N2 and C7C6C8N1 torsion angles of 6.9(3)° and 6.2(3)°, respectively. The intra-molecular strong hydrogen bonding between the -OH group and the imine N of the ligand with the N1...O2 distance of 2.586(2) Å, may be responsible for the small twist angles.

The precursor [**Zn(HL)₂(Py**)] and the four ZnLn complexes **1–4** were well characterized by EA, FT-IR, ¹H NMR and ESI-MS. As to the room temperature ¹H NMR spectrum in CD₃CN of complex **1**, one set while large shift (δ from 14.59 to -2.65 ppm) of the photon resonances of the (**HL**)[–] ligands is observed due to the Nd³⁺-induced shift, significantly



Scheme 1. Syntheses of the H₂L, the precursor [Zn(HL)₂(Py)] and the series of heterobinuclear ZnLn complexes 1–4.



Fig. 1. Perspective drawing of H_2L containing intra-molecular hydrogen bonding, H atoms are omitted for clarity.

spread in relative to those of the free H_2L ligand (δ from 13.42 to 3.83 ppm) and the precursor [**Zn(HL)₂(Py**)] (δ from 13.33 to 3.68 ppm). The ESI-MS spectra of the four ZnLn complexes (1–4) exhibit the strongest peak at m/z 954.25 (1), 983.05 (2), 977.27 (3) or 967.26 (4), respectively, corresponding to the major species [**ZnLn(HL)₂(Py)(NO₃)**₃] (Ln = Nd, 1; Ln = Yb, 2; Ln = Er, 3; Ln = Gd, 4), further indicating that the discrete ZnLn (Ln = Nd, Yb, Er or Gd) molecule exists in the respective dilute MeCN solution. Thermogravimetric analysis (TGA) of the four polycrystalline complexes shows the similar weight loss patterns, as shown in Fig. 1S, where a gradual weight loss (about 10%) occurred between 25 and 210 °C, indicative of the loss of solvated molecules, and the frameworks decomposed at *ca*. 308 °C with an observed abrupt weight loss.

X-ray quality crystals of **1**·1.5MeOH·1.5H₂O·0.5Py as the representative of the four ZnLn complexes were obtained, and the tables of selected crystal properties are also given in Tables 1–2S. Complex **1**·1.5MeOH·1.5H₂O·0.5Py crystallizes with two independent heterobinuclear molecules and solvates of MeOH, H₂O and Py in the asymmetrical unit shown in Fig. 1S. As shown in Fig. 2, in both ZnNd molecules, two deprotonated (**HL**)⁻ ligands sandwich one Zn²⁺ ion through their N,O sites and one Nd³⁺ ion through their O₂ site, endowing a relative arrangement close to head-to-head. Each Zn²⁺ (Zn1 or Zn2) ion has a five-coordinate environment and adopts a distorted square pyramidal geometry, composed of the inner N₂O₂ core from two deprotonated benzimidazole-based **HL**⁻ ligands as the base plane, and one N atom



Fig. 2. Perspective drawing of one of the hetero-binuclear part in complex 1.1.5MeOH $\cdot 1.5$ H₂O $\cdot 0.5$ Py, H atoms, the other hetero-binuclear part and solvates are omitted for clarity.

from the coordinated Py at the apical position. The Nd^{3+} ion in both ZnNd molecules is bridged the respective Zn^{2+} ion by two phenoxo oxygen atoms of two $(HL)^{-}$ ligands with the similar Zn···Nd separation of 3.636(3) Å. Each Nd³⁺ ion is ten coordinate. In addition to the four oxygen atoms from two deprotonated benzimidazole-based (HL)⁻ ligands, they complete their coordination environments with six oxygen atoms from three bidentate NO_3^- anions. The lengths (2.026(14)-2.053(14) or 2.019(12)–2.060(10) Å) of Zn-N (the benzimidazole (**HL**)⁻ ligands, N1 and N3 or N11 and N13) bonds are smaller than that (2.083(12) or 2.110(12) Å) of Zn-N (Py, N5 or N15) bond while between those (2.042(8)-2.117(11) or 2.041(9)-2.101(8) Å) of Zn-O (phenoxo, O2 and O3 or O15 and O16) bonds. The Nd-O bond lengths depend on the nature of the oxygen atoms: they vary from 2.354(9)-2.667(9) Å, and the bond lengths from oxygen atoms of NO₃⁻ anions are longer than those from phenoxo oxygen atoms, while slightly shorter than those from -OMe groups. Moreover, all the dihedral angles $(14.8(3)^{\circ})$ and 23.9(3)° or 20.7(3)° and 23.2(3)°) in both ZnNd molecules between the benzimidazole mojeties and the substituted arvl rings, considerably larger than that $(6.6(2)^\circ)$ in the free **H₂L** ligand, should be due to the further coordination of metal ions. Besides the inter-molecular N10-H10...N17 hydrogen bonding with N...N distance of 2.850(2) Å between the solvate Py and one of the ZnNd molecules, as shown in Fig. 2S, the other solvate molecules (MeOH or H₂O) are not bound to the framework and they exhibit no observable interactions with the host structure. It is worth noting that in the formation of ZnNd arrayed complex 1.1.5MeOH.1.5H₂O.0.5Py, incomparable of that of magnetic [Cu(HL)₂Tb(NO₃)₃] [10], the occupation of Py at the axial position of Zn²⁺ ions is considered to completely avoid the further coordination of solvents around the Nd³⁺ ions. As to the bulk purity of the four polycrystalline complexes, it is convincingly established by X-ray powder diffraction measurements. As shown in Fig. 3S, for each of the four complexes, the peak positions of the measured pattern closely match those of the simulated 1.1.5MeOH.1.5H₂O.0.5Py, confirming that a single phase is formed for each complex.

The photophysical properties of the precursor [**Zn(HL)**₂(**Py**)] and complexes **1–4** have been examined in dilute MeCN solution at room temperature or 77 K, and summarized in Table 3S and Figs. 3–5. As shown in Fig. 3, the similar ligand-centered solution absorption spectra (225–231, 298–301 and 339–340 nm) of complexes **1–4** to that (226, 301 and 358 nm) of the precursor [**Zn(HL)**₂(**Py**)] in the UV–visible region are observed, while the lowest energy absorptions of complexes **1–4** are blue-shifted by 18–19 nm upon the further coordination of Ln³⁺ ions. For complexes **1–3**, the similar residual visible emission bands (*ca.* 503 nm and τ <1 ns, almost undetectable) and low quantum yields ($\Phi_{em} < 10^{-5}$) in dilute absolute MeCN solution at room



Fig. 3. UV-vis spectra of precursor $[Zn(HL)_2(Py)]$ and complexes 1-4 in MeCN solution at 2×10^{-5} M at room temperature.



Fig. 4. NIR emission and excitation spectra of complexes 1–3 in MeCN solution at 2×10^{-5} M at room temperature.

temperature are observed, but photo excitation of the antennae at the range of 275–500 nm (λ_{ex} = 377 nm for 1, 384 nm for 2 or 383 nm for 3), as shown in Fig. 4, gives rise to the characteristic emissions of the Nd³⁺ ion (${}^{4}F_{3/2} \rightarrow {}^{4}I_{J/2}, J=9, 11, 13$), the Yb³⁺ ion (${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$) and the Er³⁺ ion (${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$) in the NIR region. For complex **1**, the emissions at 907, 1085 and 1354 nm can be assigned to ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$, ${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$ and ${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$ transitions of the Nd³⁺ ion, respectively. For complexes 2 and 3, the strong emission at 1003 and the weak emission at 1548 cm⁻¹ can be attributed to the ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ transition of the Yb³⁺ ion and the ${}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2}$ transition of the Er³⁺ ion, respectively. The precursor $[Zn(HL)_2(Py)]$ or the complex 4 does not exhibit the NIR luminescence under the same condition, just has the typically strong luminescence ($\lambda_{em} = 528 \text{ nm}, \tau = 1.37 \text{ ns and } \phi = 14.3 \times 10^{-3}$ for the precursor) or weakened ($\lambda_{em} = 503 \text{ nm}, \tau = 0.52 \text{ ns and } \phi = 0.11 \times 10^{-3} \text{ for}$ 4) benzimidazole-based ligand H_2L in the visible region, as shown in Fig. 5. It is worth noting that for complexes 1–3, the similar excitation spectrum (λ_{ex} = 377 nm for 1, λ_{ex} = 384 nm for 2 or λ_{ex} = 383 nm for **3**) monitored at the respective NIR emission peak ($\lambda_{em} = 1085$ nm for 1, $\lambda_{em} = 1003$ nm for 2 or $\lambda_{em} = 1548$ nm for 3) to that ($\lambda_{ex} = 377$ nm for **4**) at the weakened visible emission peak ($\lambda_{em} = 503$ nm), clearly showing that both the visible and NIR emissions are originated from the same $\pi - \pi^*$ transitions of the benzimidazole-based ligand H₂L, suggests that the energy transfer from the antenna to the Ln^{3+} ions takes



Fig. 5. Visible emission and excitation spectra of precursor $[Zn(HL)_2(Py)]$ and complex 4 in MeCN solution at 2×10^{-5} M at room temperature.

place efficiently [13]. Moreover, for complexes 1–2, the respective luminescent decay curves obtained from time-resolved luminescent experiments can be fitted mono-exponentially with time constant of microseconds (1.28 µs for 1 at 1085 nm and 13.4 µs for 2 at 1003 nm), and the intrinsic quantum yield Φ_{Ln} (0.51% for 1 or 0.67% for 2) of the Ln^{3+} emission may be estimated by $\Phi_{Ln} = \tau_{obs}/\tau_0$, where τ_{obs} is the observed emission lifetime and τ_0 is the "natural lifetime", viz 0.25 ms and 2.0 ms for the Nd³⁺ and Yb³⁺ ions, respectively [14], which indicates the presence of single emitting center for both 1 and 2 in dilute MeCN solutions [15]. Due to the limitation of our instrument, we were unable to determine the τ_{obs} value at 1354 nm for Nd³⁺ ion or at 1548 nm for the Er^{3+} ion and thus could not estimate the Φ_{Ln} value for the Er^{3+} ion, besides the reason to the rather weak NIR emission intensity for the Er^{3+} ion in complex **3** with at least one order of magnitude weaker than the corresponding Nd³⁺ or Yb³⁺ ion of complexes 1–2.

As a reference compound, complex 4 allows the further study of the antennae luminescence in the absence of energy transfer, because the Gd^{3+} ion has no energy levels below 32,000 cm⁻¹, and therefore cannot accept any energy from the antennae excited state [16]. In dilute MeCN solution at 77 K, complex 4 displays the stronger antennae fluorescence than that ($\lambda_{em} = 503 \text{ nm}, \tau = 0.52 \text{ ns and } \phi = 0.11 \times 10^{-3}$) at room temperature on the same condition, which shows the higher luminescent intensity ($\lambda_{em} = 486 \text{ nm}$ and 535 nm) and the distinctively longer luminescence lifetimes (1.13 ns and 2.24 ms). This result shows that the sensitization of the NIR luminescence for complexes 1-3 should arise from both the ${}^{1}LC$ (20,576 cm⁻¹) and the ${}^{3}LC$ (18,692 cm⁻¹) excited state of the benzimidazole-based ligand H₂L at low temperature. If the antennae luminescence lifetime of complex 4 is to represent the excited-state lifetime in the absence of the energy transfer, the energy transfer rate (k_{ET}) in the complexes **1–3** can thus be calculated from $k_{\rm ET} = 1/\tau_{\rm q} - 1/\tau_{\rm u}$ [17], where $\tau_{\rm q}$ is the residual lifetime of the Zn²⁺based emission undergoing quenching by the respective Ln³⁺ ion, and τ_{μ} is the weakened while unquenched lifetime in the reference complex **4**, so the energy transfer rates for the Nd^{3+} , Yb^{3+} and Er^{3+} ions in complexes 1–3 may all be estimated to be above $5 \times 10^8 \text{ s}^{-1}$, which could well imply the reason to the effective energy transfer for complexes 1-3. Moreover, from the viewpoint of the energy level match, in spite of the effective energy transfer taking place in complex **3**, the large energy gap between the energy-donating $({}^{3}LC)$ level and the emitting level $({}^{4}I_{13/2}, 6460 \text{ cm}^{-1})$ results in the great nonradiative energy loss during the energy transfer, which should be the reason to the weaker NIR luminescence for complex 3. As to the relatively higher quantum efficiency of **2** than that of **1**, the excited state of the Nd^{3+} ion in complex **1** is more sensitive to quenching by the distant C-H or N-H oscillators of the benzimidazole-based ligand H₂L besides the less opportunities of non-radiative migration from the single emitting transition $({}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2})$ of the Yb³⁺ ion in complex **2** [18], although the energy gap $({}^{4}F_{3/2}, 9217 \text{ cm}^{-1})$ of the Nd³⁺ ion in complex **1** is smaller than that $({}^{2}F_{5/2}, 9970 \text{ cm}^{-1})$ of Yb³⁺ ion in complex **2**. It is interesting to notice that the NIR quantum efficiencies of both 1 and 2 are slightly higher than those (0.34–0.58%) of hetero-trinuclear Zn₂Ln (Ln = Nd or Yb) complexes from the typical Salen-type Schiff-base ligand with the rigid phenylene linker [9], which should be due to the sensitization process just from the ¹LC excited states without the ³LC excited state of the ligand. As compared with the high NIR quantum yields (0.69–1.08%) of the Zn_2Ln (Ln = Nd or Yb) systems from the typical Salen-type Schiff-base ligand with the flexible ethylene linker [9], their lower NIR luminescent efficiencies of complexes 1-2 should be attributed to the larger energy gap between the energy-donating $({}^{3}LC)$ level of the benzimidazole-based ligand H₂L and the corresponding Ln^{3+} ion's exciting state.

In conclusion, with the compound $[Zn(HL)_2(Py)]$ from the benzimidazole-based ligand H_2L as the precursor, a series of heterobinuclear ZnLn complexes $[ZnLn(HL)_2(Py)(NO_3)_3]$ (Ln = Nd, Yb, Er or Gd) with two energy donors around the Ln³⁺ ion are obtained. The results of their photophysical studies show that the strong and characteristic NIR luminescence of Nd³⁺ or Yb³⁺ ion with emissive lifetimes in the microsecond range, has been sensitized from the excited state (both ¹LC and ³LC) of the benzimidazole-based ligand due to the effective intramolecular energy transfer. While in facilitating the NIR sensitization, the specific design of hetero-metallic polynuclear complexes from the benzimidazole-based ligands is now under way.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.05.041.

References

- J.-C.G. Bünzli, Lanthanide luminescence for biomedical analyses and imaging, Chem. Rev. 110 (2010) 2729–2755.
- [2] (a) J. Kido, Y. Okamoto, Organo lanthanide metal complexes for electroluminescent materials, Chem. Rev. 102 (2002) 2357–2368;
 - (b) J.-C.G. Bünzli, S.V. Eliseeva, Lanthanide NIR luminescence for telecommunications, bioanalyses and solar energy conversion, J. Rare Earths 28 (2010) 824–842.
- [3] S. Comby, J.-C.G. Bünzli, in: K.A. Gschneidner Jr., J.-C.G. Bünzli, V.K. Pecharsky (Eds.), Handbook on the Physics and Chemistry of Rare Earths, 37, Elsevier Science B. V, Amsterdam, 2007, p. 235.
- [4] J.-C.G. Bünzli, C. Piguet, Taking advantage of luminescent lanthanide ions, Chem. Soc. Rev. 34 (2005) 1048–1077.
- [5] (a) M.D. Ward, Transition-metal sensitized near-infrared luminescence from lanthanides in d–f heteronuclear arrays, Coord. Chem. Rev. 251 (2007) 1663–1677;
 (b) F.F. Chen, Z.Q. Chen, Z.Q. Bian, C.H. Huang, Sensitized luminescence from lantha-
 - nides in d–f bimetallic complexes, Coord. Chem. Rev. 254 (2010) 991–1010;
 (c) M.D. Ward, Mechanisms of sensitization of lanthanide(III)-based luminescence
 - (c) M.D. ward, McChallish of Sensitization of landhande(m)-based furninescence in transition metal/lanthanide and anthracene/lanthanide dyads, Coord. Chem. Rev. 254 (2010) 2634–2642.
- [6] L. Winkless, R.H.C. Tan, Y. Zheng, M. Motevalli, P.B. Wyatt, W.P. Gillin, Quenching of Er(III) luminescence by C–H vibrations: implications for the use of erbium complexes in telecommunications, Appl. Phys. Lett. 89 (2006) 111115-1-3.
- [7] C.M.G. dos Santos, A.J. Harte, S.J. Quinn, T. Gunnlaugsson, Recent developments in the field of supramolecular lanthanide luminescent sensors and self-assemblies, Coord. Chem. Rev. 252 (2008) 2512–2527.
- [8] (a) W.-K. Wong, H.Z. Liang, W.-Y. Wong, Z.W. Cai, K.-F. Li, K.-W. Cheah, Synthesis and near-infrared luminescence of 3d–4f bi-metallic Schiff base complexes, New J. Chem. 26 (2002) 275–278;
 - (b) W.-K. Lo, W.-K. Wong, J.P. Guo, W.-Y. Wong, K.-F. Li, K.-K. Cheah, Synthesis, structures and luminescent properties of new heterobimetallic Zn-4f Schiff base complexes, Inorg. Chim. Acta 357 (2004) 4510–4521;
 - (c) X.P. Yang, R.A. Jones, Q.Y. Wu, M.M. Oye, W.-K. Lo, W.-K. Wong, A.L. Jolmes, Synthesis, crystal structures and antenna-like sensitization of visible and near-infrared emission in heterobimetallic Zn–Eu and Zn–Nd Schiff-base compounds, Polyhedron 25 (2006) 271–278;
 - (d) W.K. Lo, W.-K. Wong, W.-Y. Wong, J.P. Guo, K.-T. Yeung, Y.-K. Cheng, X.P. Yang, R.A. Jones, Heterobimetallic Zn(II)-Ln(III) phenylene-bridged Schiff base complexes, computational studies, and evidence for singlet energy transfer as the main pathway in the sensitization of near-infrared Nd³⁺ luminescence, Inorg. Chem. 45 (2006) 9315–9325;
 - (e) W.Y. Bi, X.Q. Lü, W.L. Chai, J.R. Song, W.-K. Wong, X.P. Yang, R.A. Jones, Effect of heavy-atom (Br) at the phenyl rings of Schiff-base ligands on the NIR luminescence of their bimetallic Zn–Nd complexes, Z. Anorg. Allg. Chem. 634 (2008) 1795–1800;
 - (f) W.Y. Bi, X.Q. Lü, W.L. Chai, W.J. Jin, J.R. Song, W.-K. Wong, Synthesis, structure and near-infrared (NIR) luminescence of three solvent-induced pseudo-polymorphic complexes from a bimetallic Zn–Nd Schiff-base molecular unit, Inorg. Chem. Commun. 11 (2008) 1316–1319;

- (g) W.Y. Bi, X.Q. Lü, W.L. Chai, J.R. Song, W.-Y. Wong, W.-K. Wong, R.A. Jones, Construction and NIR luminescent property of hetero-bimetallic Zn–Nd complexes from two chiral Salen-type Schiff-base ligands, J. Mol. Struct. 891 (2008) 450–455.
- [9] W.Y. Bi, T. Wei, X.Q. Lü, Y.N. Hui, J.R. Song, W.-K. Wong, R.A. Jones, Hetero-trinuclear near-infrared (NIR) luminescent Zn₂Ln complexes from Salen-type Schiff-base ligands, New J. Chem. 33 (2009) 2326–2334.
- [10] F.Z.C. Fellah, J.-P. Costes, C. Duhayon, J.-C. Daran, J.-P. Tuchagues, Mononuclear Cu and dinuclear Cu–Ln complexes of benzimidazole based ligands including N and O donors: syntheses, characterization, X-ray molecular structures and magnetic properties, Polyhedron 29 (2010) 2111–2119.
- [11] (a) X.P. Yang, R.A. Jones, M.J. Wiester, M.M. Oye, W.-K. Wong, Transformation of a luminescent benzimidazole-based Yb₃ cluster into a one-dimensional coordination polymer, Cryst. Growth & Des. 10 (2010) 970–976;
 - (b) X.P. Yang, R.A. Jones, M.M. Oye, M. Wiester, R.J. Lai, Influence of metal-ligand ratio on benzimidazole based luminescent lanthanide complexes: 3D network structures and chloride anion binding, New J. Chem. 35 (2011) 310–318.
- [12] (a) V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, J. Am. Chem. Soc. 113 (1991) 4917–4925;
 (b) P. Gilli, V. Bertolasi, V. Ferratti, G. Gilli, J. Am. Chem. Soc. 124 (2000) 10405–10417.

- [13] M. Albrecht, O. Osetska, J. Klankermayer, R. Fröhlich, F. Gumy, J.-C.-G. Bünzli, Enhancement of near-IR emissions by bromine substitution in lanthanide complexes with 2-carboxamide-8-hydroxyquinoline, Chem. Commun. (2007) 1834–1836.
- [14] M.J. Weber, Radiative and multiphonon relaxation of rare-ions in Y₂O₃, Phys. Rev. 171 (1968) 283–291.
- [15] J.-C.G. Bünzli, Lanthanide probe in life, chemical and earth sciences, (ch7), in: J.-C.G. Bünzli, G.R. Choppin (Eds.), Theory and Practice, Elsievier Science Pub1. B. V, Amsterdam, 1989, pp. 219–293.
- [16] W.T. Carnall, P.R. Fields, K. Rajnak, Electronic energy levels of trivalent lanthanide aquo ions. II. Gd³⁺, J. Chem. Phys. 49 (1968) 4443–4446.
- [17] D.L. Dexter, A theory of sensitized luminescence in solid, J. Chem. Phys. 21 (1953) 836–850.
- [18] A. Beeby, I.M. Clarkson, R.S. Dockins, S. Faulkner, D. Parker, L. Royle, A.S. de Souda, J.A.G. Williams, M. Woods, Non-radiative deactivation of the excited states of europium, terbium and ytterbium complexes by proximate energy-matched OH, NH and CH oscillators: an improved luminescence method for establishing solution hydration states, J. Chem. Soc. Perkin Trans. 2 (1999) 493–504.