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Three ytterbium(III) complexes with aromatic N-donors: Synthesis, structure, photophysical properties and thermal stability

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Three new ytterbium complexes of the general formula $[\text{YbL}_2\text{Cl}_3]$ with expanded aromatic N-donor based ligands based on 1,10-phenanthroline (dipyrido-[3,2-f:2',3'-h]-quinoxaline (DPQ), 2-methyldipyrido-[3,2-f:2',3'-h]-quinoxaline (MeDPQ) and 1,10-phenanthroline (Phen)) were synthesized and characterized using different structural analysis, simultaneous thermal analysis, and photoluminescence, and UV-Vis-NIR spectroscopy. The compounds were obtained by the reaction of ytterbium(III) chloride hexahydrate and the corresponding aromatic N-donor

through substitution of water from the coordination sphere with the organic ligand. Photoluminescence studies revealed Yb^{3+} -based NIR emission of the corresponding compounds with following luminescence lifetimes $[\text{Yb}(\text{DPQ})_2\text{Cl}_3]$ (1) – 7.8(1) μs , $[\text{Yb}(\text{MeDPQ})_2\text{Cl}_3]$ (2) – 9.3(1) μs , $[\text{Yb}(\text{Phen})_2\text{Cl}_3]$ (3) – 8.7(1) μs . The resulting complexes are stable under atmospheric conditions, exhibit good thermal stability, and start to oxidize only at sufficiently high temperatures: (1) at 470 °C, (2) at 430 °C, and (3) at 395 °C.

Introduction

Trivalent ytterbium, as one of the rare-earth metal ions, exhibits luminescent properties, but unlike typical Ln-emitters in the visible range, such as europium and terbium, its transition $^2F_{7/2} \rightarrow ^2F_{5/2}$ lies in the near-infrared (NIR) region of the spectrum.^[1] This is applied in a wide variety of technological areas, for example, bioimaging, organic light-emitting diodes (OLEDs) and luminescence thermometry.^[2,3] It is known that the intrinsic emission of lanthanide ions is rather weak due to low light uptake according to the forbidden nature of the $f \rightarrow f$ transitions, so various organic ligands with a conjugated aromatic system (“antennas”) can be deployed to gather the light and – subsequent to energy transfer – make the emission more effective.^[4] Good examples of such “antennas” are N-donor organic ligands, such as phenanthroline and quinoxaline derivatives, diazatriphenylene, dipyrido-[3,2-a:2',3-c]-phenazine, and terpyridine derivatives^[5–10] because they also prolong

luminescence lifetimes and give good quantum yields (QY) for both, visible and NIR emitters.^[4,11–13] Ligands of the pyridine series have been shown to give generally better photophysical parameters but have problems with stability on air.

Nevertheless, not only organic ligands were used for the purpose to make luminescence more efficient. There are reports about bimetallic systems with Yb^{3+} , for which energy transfer between metal ions is described.^[14–16] Examples of *bi*-lanthanide Yb^{3+} systems with downconversion have examples of energy transfers $\text{Eu}^{3+} \rightarrow \text{Yb}^{3+}$,^[14] $\text{Tb}^{3+} \rightarrow \text{Yb}^{3+}$,^[15] and $\text{Eu}^{2+} \rightarrow \text{Yb}^{3+}$.^[16] Attempts have also been made to combine *d*-elements such as copper, zinc or iron and rare-earth metals in one complex to combine luminescence, magnetic properties and bioactivity. Indeed, there are publications with $\text{Cu}^+ \rightarrow \text{Er}^{3+}$ ^[17] and $\text{Zn}^{2+} \rightarrow \text{Er}^{3+}/\text{Yb}^{3+}$ ^[18] energy transfers in nanocomposites and zinc-silicate glasses, and monomolecular emitting magnets based on Cu^{2+} cyanide-bridged frameworks with Yb^{3+} .^[19]

At present, numerous trivalent ytterbium complexes are practiced in biomedical research or in luminescent material studies where the corresponding ligands are used, as described above, as well as DNA-intercalators. All complexes mentioned in the literature had a DPQ ligand and its ratio to Yb^{3+} of 1:1^[20] but studies with 2:1 ratio and without coordinated solvent were not reported. In the case of Phen, both 1:1 and 1:2 Ln^{3+} to Phen ratios have occurred.^[21] Neither the crystal structure of the MeDPQ-bearing lanthanide ion nor the aqueous solution of this duo has previously been published even for common emitters such as Eu^{3+} and Tb^{3+} . This report is about the complexes of $\text{Yb}^{3+}:\text{L}$ 1:2 composition that are stable on air, showing great thermal stability and good NIR luminescence, without coordinated solvent and water molecules, and previously unknown crystal structure of the complex with MeDPQ and crystal structure of ligand itself.

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Results and Discussion

Synthesis and Structural Analysis

Pyridyl based ligands on average show better results in photo-physical properties (emission lifetime, QY) but typically demand inert synthesis and storage conditions as well as anhydrous lanthanide's salt as a precursor.^[11–13,22] New Yb³⁺ complexes with the general formula [YbL₂Cl₃] (L=DPQ for 1, MeDPQ for 2, Phen for 3, Figure 1) were synthesized from the hexahydrate of ytterbium(III) chloride and the respective ligands by hydro-thermal reaction in pyridine or MeCN in high yield (Scheme 1) and are stable on air. In the process of producing the target crystals, crystals of MeDPQ were also obtained, and its structure was also determined (orthorhombic space group *Pnma*).

For compound 1, interatomic distances Yb–Cl are in the range of 2.54(3)–2.61(3) Å, for 2 in the 2.54(3)–2.58(3) Å and for 3 2.55(3)–2.60(3) Å, which correlates well with the literature

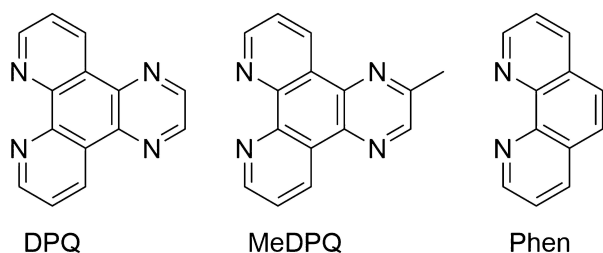
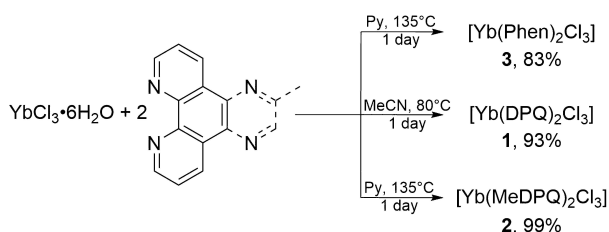


Figure 1. Phen-based aromatic N-donor ligands used in this study.



Scheme 1. Synthetic route of the complexes [YbL₂Cl₃] (1–3).

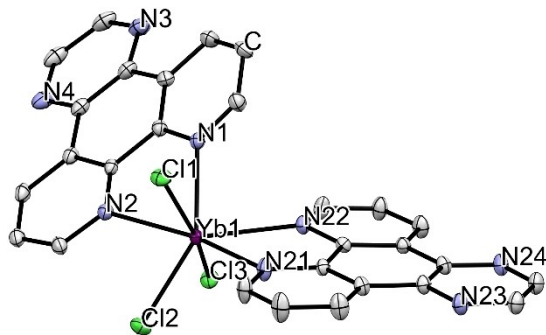


Figure 2. A complex unit of compound 1. Thermal ellipsoids describe a 50% probability level of atoms; hydrogen atoms are omitted for clarity. Yb – purple, N – blue, Cl – green, C – grey.

compounds such as complexes with ptpy, bipy and one coordinated DPQ ligand as they show a range of 2.55–2.62 Å.^[11–13,20–22] Respective Yb–N distances in complex 1 are in the range of 2.42(5)–2.54(5) Å, for 2 in the range of 2.46(5)–2.52(5) Å and 2.46(5)–2.52(5) Å for 3, which is also the literature range for same type complexes as they exhibit values between 2.39–2.58 Å.^[11–13,20–22] A geometry check with Mogul^[23] was provided to find deviations from general trends in complexes reported and nothing unusual has been found. Comparison of the interatomic distances for all compounds can be found in the supporting information (SI).

Compound 1 crystallizes in orthorhombic space group *Pbcn* with Yb³⁺ having a coordination number of seven. Coordinated are two molecules of DPQ and three chloride ions, forming a disordered pentagonal bipyramid (Figure 2). The other two complexes presented have similar molecular structure.

Compound 2 crystallizes in the orthorhombic crystal system as well as 1, but in the space group *Fdd2* as result of the ligands difference by a methyl group (SI, Figure S2). The coordination environment of the ytterbium ion in 2 is similar to complex 1. The packing difference can be a result of the presence of the methyl group and hydrogen bonding between H atoms of the methyl group and a chloride ion. In complex [Yb(MeDPQ)₂Cl₃] (2), the contact H...Cl (2.7725(7) Å) influences more than the π - π interactions (3.4312(43) Å and 3.4280(49) Å) between ligands, as they are much shorter (Figure 3). In addition, there is a distortion of the structure due to the carbon atom of the methyl group and the hydrogen atoms directly bonded to it. Thus, these phenomena provide a different packing and result in a different space group.

Intermolecular interactions are also present in complexes 1 and 3, although the ligand atoms form a rather planar structure through π - π interactions between DPQ or Phen molecules in

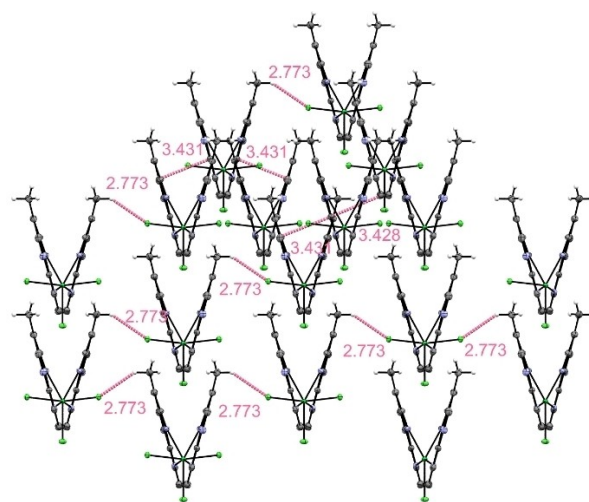


Figure 3. Packing of compound 2, along *a*-axis. It represents molecular interactions such as hydrogen bond H...Cl (2.7725(7) Å) and possible π - π interactions (3.4312(43) Å and 3.4280(49) Å) pink. Thermal ellipsoids describe a 50% probability level of the atoms; hydrogen atoms except methyl ones are omitted for clarity. Yb – dark green, N – blue, Cl – green, C – grey, H – white.

them, so **1** and **3** are thus only more densely packed, as can be seen in a comparison of the calculated crystallographic density of substances. For the **1** and **3** compounds they are quite equal (1.963 g/cm³ and 1.961 g/cm³ respectively), and for compound **2** it is noticeably less (1.892 g/cm³).

Compound **3** crystallizes in the monoclinic space group *P*2₁/*c* with the same coordination environment for Yb³⁺ as in two other presented complexes (SI, Figure S3). Not many complexes of the composition [Ln(Phen)₂Cl₃] are known, and for heavy lanthanides none has yet been reported, whereas light-weight lanthanides tend to form dimeric complexes.^[10,11,24] The iso-constitutional europium complex [Eu(Phen)₂Cl₃], however, crystallizes in a different *C*-centered space group.^[25]

Also, a trivalent bismuth complex [Bi(Phen)₂Cl₃] was reported in the literature,^[26] and despite their significant difference in ionic radii (1.01 Å for Yb³⁺ and 1.17 Å for Bi³⁺, both CN 7),^[27] the bismuth complex is isomorphic to [Yb(Phen)₂Cl₃] as presented here (**3**). Thus, a possibility to obtain bimetallic ytterbium/bismuth compounds by doping/statistical substitution and combination of properties of these two metals seems possible in the future. In particular, Bi³⁺ is used in medicine,^[28,29] thermoelectric materials^[31] and chemical power sources^[30] – which might be very useful in a couple with the optical properties of Yb³⁺.

Powder X-Ray diffraction (PXRD)

For the subsequent determination of the optical and thermal properties of the complexes, they were first checked for phase purity by X-ray powder diffraction (Figure 4). Combined with elemental analysis it can be stated that the synthesized powders are phase pure.

Thermal analysis (DTA-TG)

The thermal properties of complexes **1–3** were investigated by simultaneous differential thermal analysis (DTA) and thermogravimetry (TG) under synthetic air atmosphere. We propose the general oxidizing equation for compounds investigated (Scheme 2).

All compounds obtained endure oxidation of the ligand demonstrating a strong broad exothermic effect and then reaching a plateau on the TG curve (Figure 5). Complexes obtained are oxidized at 470 °C (**1**), 430 °C (**2**), and 395 °C (**3**). Oxidation temperatures of compounds **1–3** are in a correlation with thermal properties of the ligands – and the higher ligand melting point is (332 °C for DPQ,^[31] 271 °C for MeDPQ^[4] and 118 °C for Phen^[32]), the better is the observed corresponding complex stability. For **1** and **3**, oxidation is a clear multi-step process, while for **2**, the mass loss during the oxidation is continuous. After oxidation and cooling, residual powders were analyzed using PXRD and they all consisted only of one phase – Yb₂O₃. Residual mass after experiment corresponds to ytterbium(III) oxide: 24%, 23%, 32% for compounds **1–3** respectively, and calculated residual mass of the Yb₂O₃ accord-

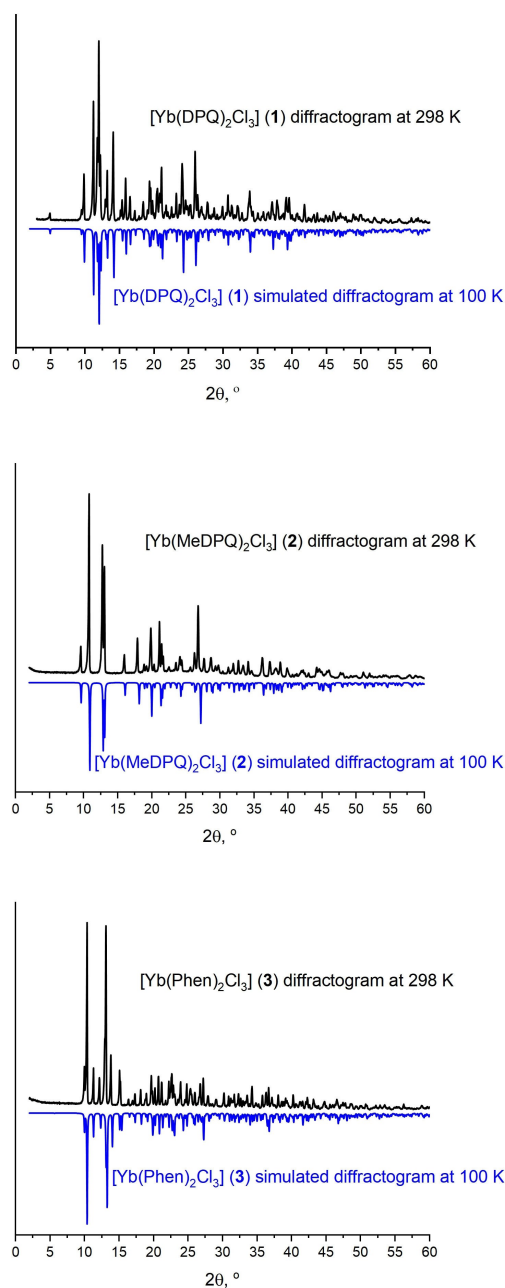
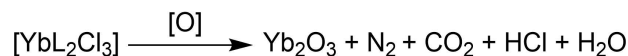


Figure 4. Comparison of experimental and simulated powder diffractograms of complexes **1–3** respectively.



Scheme 2. Possible equation of oxidation of the relative compounds.

ing to proposed equation of oxidation: 27%, 26% and 31% for compounds **1–3** respectively, indicating that all organic parts were released from the samples.

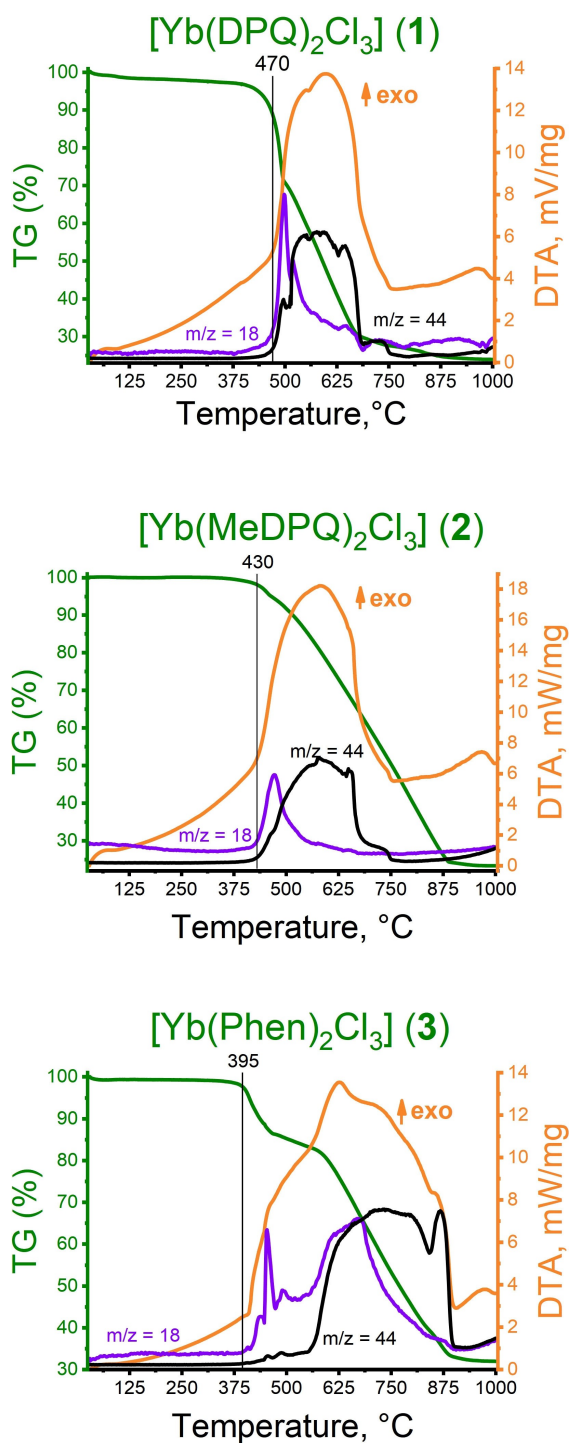


Figure 5. Simultaneous differential thermal analysis (DTA, heat flow, orange), thermogravimetry (TG, green), and ionic currents for $m/z = 18$ (purple) and $m/z = 44$ (black) of compounds 1–3.

Photophysical Properties

Photoluminescence spectroscopy

Since Yb^{3+} has only one ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition in the near-infrared region of the spectrum, the influence of ligands on its

luminescence can be well monitored. All three complexes in solid state and at 23°C exhibit broad band ligand $\pi \rightarrow \pi^*$ luminescence (excitation and emission) as well as an “antenna” effect, with an excitation in the UV ($\lambda_{\text{ex}} = 358 \text{ nm}$ for 1 and 3 or 350 nm for 2) leading to trivalent ytterbium sharp emission lines ($f-f$ transition) in the NIR from 930 to 1045 nm (Figure 6). Multiple emission lines are Stark levels as a result of energy level splitting due to the crystal field. The emission region of these complexes coincides with the trivalent ytterbium complexes described in the literature.^[5,6,11–13,20,33]

The overall emission intensity decay times of the maxima of the ytterbium(III) transition ($\lambda_{\text{em}} = 1015 \text{ nm}$ for the 1, $\lambda_{\text{em}} = 979 \text{ nm}$ for the 2 and $\lambda_{\text{em}} = 977 \text{ nm}$ for the 3) of each complex were measured under the same conditions as the spectra themselves with an excitation in the UV ($\lambda_{\text{ex}} = 358 \text{ nm}$ for 1, 3 and 350 nm for 2 respectively). Investigated trivalent ytterbium lifetimes in the complexes were determined as $7.8(1) \mu\text{s}$ for 1, $9.3(1) \mu\text{s}$ for 2, and $8.7(1) \mu\text{s}$ for 3 and are in good agreement with literature data for Yb^{3+} coordination compounds with aromatic N-donors.^[5–6,11–13,20,33]

UV-Vis-NIR spectroscopy

Together with the emission and excitation spectra, solid-state absorption spectra were collected (Figure 7). The organic part of absorbance of the complexes $[\text{YbL}_2\text{Cl}_3]$ (1–3) is an order of magnitude higher in intensity than for an ytterbium ion in all three cases. Overall, the excitation and absorption spectra of the ligands match well for all three compounds

Conclusion

Three Yb^{3+} complexes with 1,10-phenanthroline derivatives of the general formula $[\text{YbL}_2\text{Cl}_3]$ ($\text{L} = \text{DPQ}$ for 1, MeDPQ for 2, Phen for 3) were synthesized and characterized. Ligands used in this work are well known, affordable and easy to handle: do not degrade under atmospheric conditions and are soluble in polar solvents such as acetonitrile and pyridine. Trivalent ytterbium has coordination number of seven and a similar coordination sphere in all three complexes 1–3. Due to the differences of the ligands, each of the complexes crystallizes in a different space group with a different crystal packing. Additionally, the crystal structure of 2-methyldipyrido-[3,2-f:2',3'-h]-quinoxaline (MeDPQ) was determined for the first time. Compounds 1–3 are obtained in good yield directly from $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and the corresponding organic ligands. The complexes are stable under atmospheric conditions and, for organic-containing compounds, have excellent thermal stability, oxidizing first at 470°C (1), 430°C (2), and 395°C (3). As a part of the photoluminescence studies, emission lifetimes were determined for all complexes 1–3. Upon ligand-based UV-excitation, the complexes presented show a ligand-based emission in UV as well as $f-f$ emission of Yb^{3+} in the NIR.

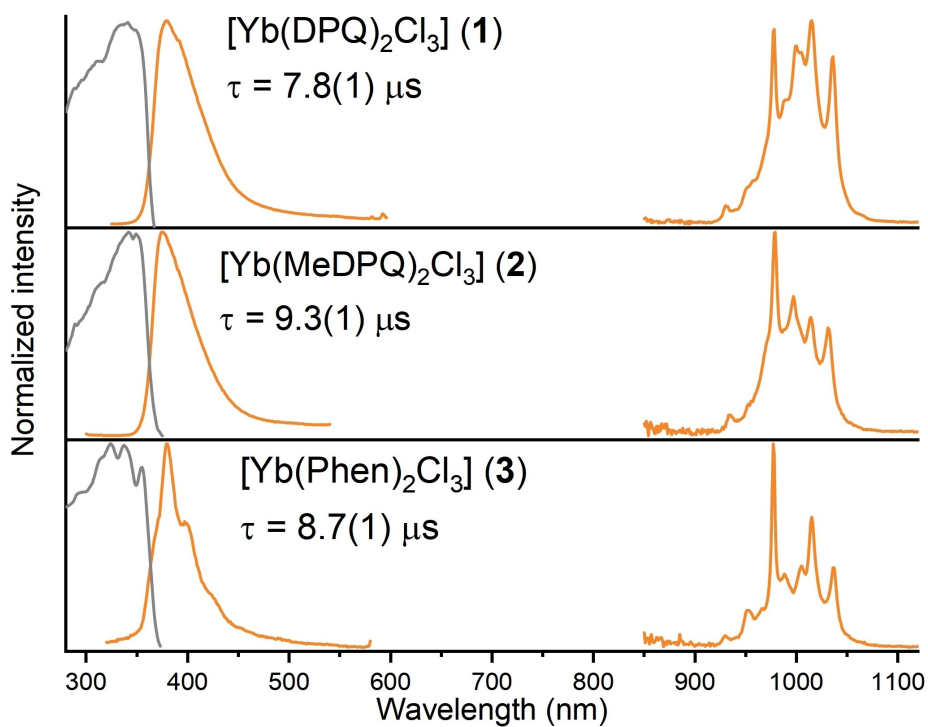


Figure 6. Normalized solid-state photoluminescence spectra of the corresponding compounds at room temperature. Excitation spectra are depicted in grey, emission spectra in orange.

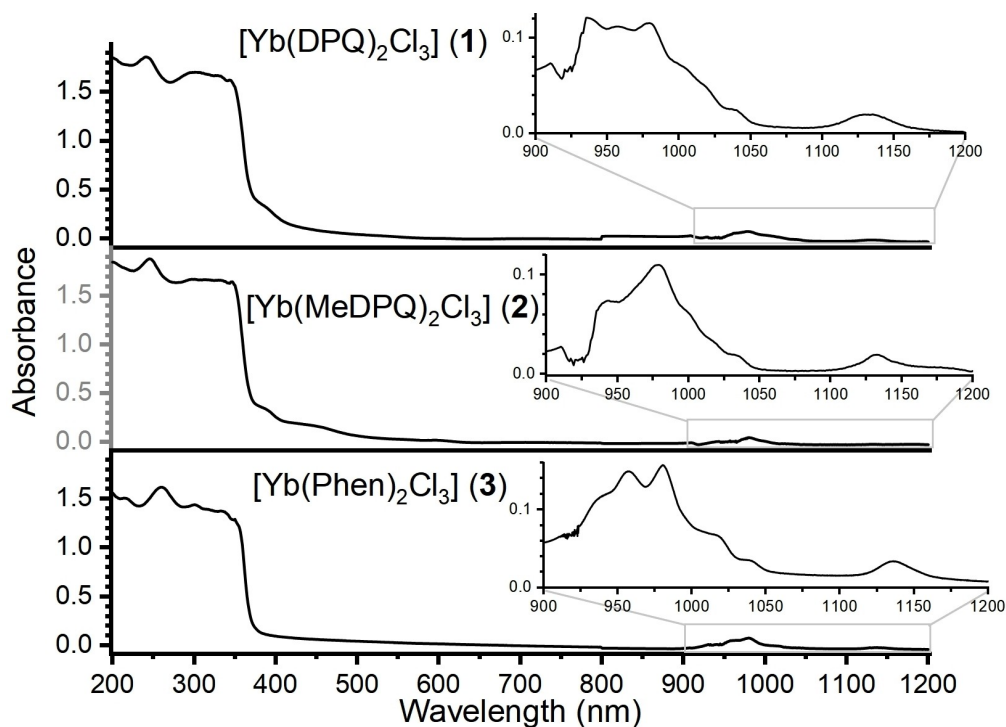


Figure 7. Solid-state absorption spectra of compounds 1–3 at room temperature.

Experimental Section

Analytical Methods

CHN analysis

For carbon, hydrogen, and nitrogen elemental analysis the compounds were placed in a tin crucible with at least one mass equivalent of V_2O_5 , and analyzed using Thermo FlashEA 1112 Series.

Powder X-Ray diffraction

Diffraction data were collected on an STOE STADI P diffractometer with a focusing Ge(111) monochromator and a Dectris MYTHEN 1 K strip detector in Debye-Scherrer geometry using $Cu-K_{\alpha 1}$ radiation. Data collection was done using the STOE Powder Diffraction Software Package WinX^{POW}.

Single-crystal X-Ray diffraction

Single crystals of **1**, **2**, **3**, and MeDPQ were mounted on a goniometer head using a perfluorinated ether (viscosity 1800 cSt, 99.9%, ABCR). Data collection was performed using Mo- K_{α} X-ray radiation on a BRUKER D8 Venture diffractometer equipped with a PHOTON 100 detector at 100 K using the BRUKER APEX3 software package. The structure solution was carried out with direct methods using SHELXT^[34] and the obtained crystal structure was refined with least square techniques using SHELXL^[35] on the graphical platform shelXle.^[36]

CCDC 2175202 (for **1**), 2175212 (for **2**), 2175203 (for **3**) and 2175204 (for MeDPQ) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Photoluminescence spectroscopy

Excitation and emission spectra in UV and visible range (280–800 nm) at $23 \pm 2^\circ C$ (samples were not additionally thermostatted) were recorded with a HORIBA Jobin Yvon Spex Fluorolog 3 spectrometer equipped with a 450 W Xe short-arc lamp (OSRAM), double-grated excitation and emission monochromators, and two photomultiplier tubes (R928P for UV and visible region, R5509-73 cooled down to $-80^\circ C$ for NIR region) using a FluoroEssenceTM software. Solid samples were loaded in spectroscopically pure quartz glass cuvettes on air and examined at specified temperature. Both excitation and emission spectra were corrected for the spectral response of the monochromators and the detector using spectra corrections provided by the manufacturer. Additionally, excitation spectra were corrected for the spectral distribution of the lamp intensity by the use of a photodiode reference detector. When required, an edge filter (Newport) was used during the collection of the data.

Photoluminescence lifetimes were determined using an identical spectrometer equipped with a Time-correlated Single Photon Counting (TCSPC) upgrade (HORIBA) by overall process decay time determination. A microsecond flash lamp was used for sample excitation. Exponential tail fitting was used for the calculation of resulting intensity decay times calculation using Decay Analysis Software 6. The quality of the fit was confirmed by χ^2 value.

UV-Vis-NIR spectroscopy

Solid-state absorption spectra have been acquired on air at room temperature using Cary 5000 Series UV-Vis-NIR spectrophotometer (Agilent Technologies) equipped with the diffuse reflectance accessory Praying MantisTM (Harrick Scientific Products) in double beam mode with reduced slit height using Cary WinUV software (Agilent Technologies). Powdered polytetrafluoroethylene (1 μM , Sigma-Aldrich) was used as a reference material. Both, the reference and the sample, have been ground, filled into the sample cups, and leveled to get a flattened surface. The beam alignment has been checked by putting the light into zero-order. The lamp changeover was set at 350 nm. The detector and monochromator grating changeover was set at 800 nm, leading to a prominent step in the baseline.

Prior to the measurement, the reflectance of the reference material was adjusted to 100% R at 700 nm by balancing beams with an attenuator. Then, the background correction spectrum was recorded. For the sample, the signal intensity has been maximized by increasing or decreasing the height of the sample stage. Afterwards, the sample reflectance was adjusted as well to 100% R at 700 nm. Finally, the reflectance spectrum was recorded for the sample and corrected according to $\%R_{corr}^{sample} = \%R^{sample} / \%R^{reference}$. Spectra collected were recalculated to absorbance using the above-mentioned software according to the Lambert-Beer law.

Simultaneous thermal analysis

Simultaneous differential thermal analysis/thermogravimetry analysis was performed in the dynamic flow of argon (20 ml/min) and synthetic air (30 ml/min) mixture using a NETZSCH STA-409-PC instrument from $25^\circ C$ to $1000^\circ C$ with a heating rate of 5 K/min.

Synthesis and Analytical Data

General information

All synthetic work was done under atmospheric conditions. A Schlenk line was used for sealing ampoules and drying of samples. Details on the crystallographic data, comparison of simulated and recorded powder XRD patterns can be found in the supporting information.

Starting materials

DPQ and MeDPQ were prepared by obtaining 1,10-phenanthroline-5,6-dione according to the literature method^[37] and further condensation with the respective diamine in H_2O and next addition of H_2O_2 . $YbCl_3 \cdot 6H_2O$ (99.9%, ABCR), 1,10-phenanthroline (Phen) (99%, Sigma Aldrich), MeCN (99%, Fisher Scientific), pyridine (99%, Sigma Aldrich) and $CHCl_3$ (99%, Fisher Scientific) were used as it is.

Synthesis of $[YbL_2Cl_3]$

All three complexes were synthesized under similar conditions: 0.1 mmol of $YbCl_3 \cdot 6H_2O$, 0.23 mmol of DPQ, MeDPQ or Phen, respectively, were placed together into Duran[®] culture tubes with a screw cap. Then 2 ml of the solvent (MeCN for **1**, pyridine for **2** and **3**) and stir bar were added. The reaction mixture for (**1**) was heated up to $80^\circ C$ but (**2**) and (**3**) mixtures were heated up to $135^\circ C$, and all of them were left stirring for one day. After the reaction, the tubes were centrifuged, and the solvent was removed. The next step was repeated two times: 1 mL of $CHCl_3$ for the compounds (**1**), (**2**) and acetone for compound (**3**) was added with the following

stirring, the tube was centrifuged again, and the solvent was removed. Then all three powders were dried under vacuum.

Single crystal synthesis

The following methodology was used to synthesize single crystals of **1**, **2**, and **3**: 0.005 mmol of $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.01 mmol of DPQ/MeDPQ/Phen were added to Duran® glass ampoules (outer \varnothing 10 mm, wall thickness 1.5 mm), filled with 0.2–0.3 ml of the solvent (both MeCN or pyridine can be used: single crystal of **1** is obtained from MeCN but single crystals of **2** and **3** are obtained from pyridine) and sealed under vacuum. Ampoules with mixtures to obtain (**1**) and (**2**) were placed into the Büchi B-585 glass oven for 90 hours at 140 °C and then cooled down to room temperature. Ampoule with mixture to obtain (**3**) were placed into the resistance heating oven with thermal control (Eurotherm 2416), heated to 140 °C within 2 hours, then the temperature was held for 8 hours. Afterwards, the oven was cooled down to room temperature in 4 hours. The resulting crystals were suitable for single crystal X-Ray diffraction.

MeDPQ crystals were obtained by recrystallization of several milligrams of the substance from either pyridine or acetonitrile at 140 °C in Duran® glass ampoule.

1 – $[\text{Yb}(\text{DPQ})_2\text{Cl}_3]$. White powder. Yield: 70 mg (93%). Elemental analysis calculated for $\text{C}_{28}\text{H}_{16}\text{Cl}_3\text{N}_8\text{Yb}$: C 45.21%, H 2.17%, N 15.06%. Found: C 44.81%, H 2.17%, N 14.17%.

2 – $[\text{Yb}(\text{MeDPQ})_2\text{Cl}_3]$. Pale yellow powder. Yield: 70.6 mg (99%). Elemental analysis calculated for $\text{C}_{30}\text{H}_{20}\text{Cl}_3\text{N}_8\text{Yb}$: C 46.68%, H 2.62%, N 14.52%. Found: C 46.77%, H 2.57%, N 13.81%.

3 – $[\text{Yb}(\text{Phen})_2\text{Cl}_3]$. White powder. Yield: 61.5 mg (83%). Elemental analysis calculated for $\text{C}_{24}\text{H}_{16}\text{Cl}_3\text{N}_4\text{Yb}$: C 45.05%, H 2.53%, N 8.76%. Found: C 44.33%, H 2.50%, N 8.43%.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: ytterbium(III) · N-donors · NIR luminescence · coordination compounds · thermal stability

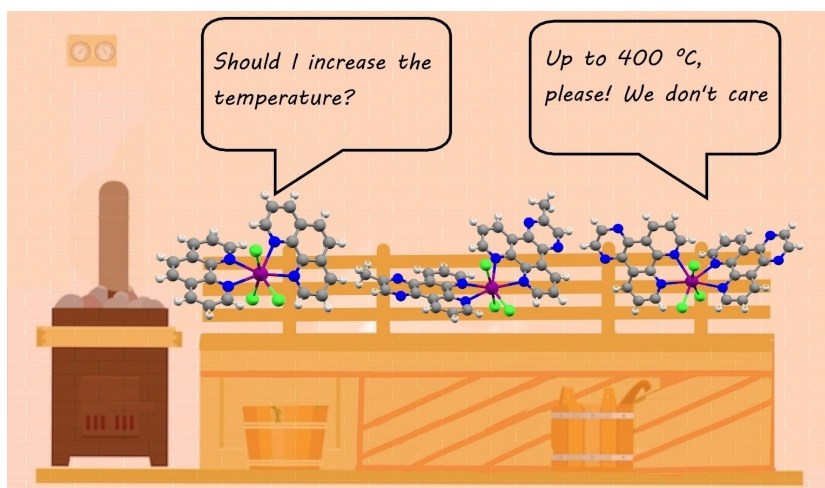
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Three ytterbium(III) complexes with aromatic N-donors: Synthesis, structure, photophysical properties and thermal stability

