# Journal of Materials Chemistry C

# PAPER

Cite this: DOI: 10.1039/d1tc04600d



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25 Received 25th September 2021, Accepted 1st December 2021 DOI: 10.1039/d1tc04600d

rsc.li/materials-c

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# Introduction

At first glance, organic light-emitting diodes (OLEDs) are
devices based on a simple sandwich structure in which an organic semiconductor material is sandwiched between two electrodes for injection of oppositely signed carriers (electrons and holes). The emitting layer, which can also be a composite, acts as both an emitter and a charge transport medium.
Electrons and holes injected from the electrodes form excitons, which are then susceptible to radiative decay. Despite such a simple structure, not all existing OLEDs have suitable device parameters such as efficiency, luminance, operating voltages, and most importantly durability for commercialization.

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 <sup>b</sup> P.N. Lebedev Physical Institute, Leninsky prosp. 53, Moscow, 119992, Russia
 <sup>c</sup> Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P Nr 1410, 50-950 Wroclaw 2, Poland

<sup>e</sup>A.N. Nesmeyanov Institute of Organoelement Compounds, Vavilova St. 28, Moscow, 119334, Russia

# Ytterbium complexes with 2-(tosylamino)benzylidene-N-(2-halobenzoyl)-hydrazones for solution-processable NIR OLEDs<sup>+</sup>

Lyubov O. Tcelykh, <sup>(D)</sup><sup>a</sup> Andrey A. Vashchenko,<sup>b</sup> Alexey V. Medvedko,<sup>a</sup> Łukasz Marciniak,<sup>c</sup> Alexey E. Aleksandrov,<sup>d</sup> Alexander S. Goloveshkin,<sup>e</sup> Leonid S. Lepnev,<sup>b</sup> Egor V. Latipov,<sup>a</sup> Anatoly S. Burlov<sup>f</sup> and Valentina V. Utochnikova <sup>(D)</sup>\*<sup>a</sup>

A series of ytterbium complexes with halogenated 2-(tosylamino)-benzylidene-*N*-(2-benzoyl)hydrazones was obtained for NIR OLED applications. Halogenation resulted in a significant solubility increase, while the photophysical and electronic properties of the obtained complexes almost coincided. High solubility, mobility of charge carriers and, most importantly, the efficiency of luminescence made it possible to successfully use the obtained complexes as host-free emitting layers in a series of OLED devices. The efficiency of the obtained devices correlates with the halogen mass when thick emissive layers are deposited. However, a layer thickness decrease results in an efficiency increase, which for thin layers correlates with charge carrier mobility, the only halogen-dependent parameter. The highest efficiency of pure ytterbium luminescence was reached for the complex with Br-substituted ligands and equaled 430  $\mu$ W W<sup>-1</sup>, which is the highest value obtained to date for Ybbased OLEDs.

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Therefore, scientists around the world are engaged in the optimization of OLEDs, but mainly these are OLEDs emitting in the visible region, while near-infrared (NIR) emitting OLEDs are still in the development stage. However, the number of publications on the topic of NIR OLEDs is growing every year due to the huge importance of NIR OLEDs.<sup>1</sup>

First of all, the 900–1100 nm window coincides with the I and II biological tissue semitransparency windows<sup>2</sup> which makes it interesting for application of NIR OLEDs in a variety of biomedical and biosensing applications such as photodynamic therapy, intracellular imaging, drug delivery systems,<sup>3–5</sup> night vision devices and imaging of finger veins,<sup>6–9</sup> portable thermal imaging cameras for thermal phototherapy<sup>1</sup> and photopolymerization. Second, emission in the solid state at wavelengths beyond 1000 nm is rather weak for organic chromophores, thereby calling into question their use, even in the presence of other advantages such as flexibility, low cost, potential biocompatibility, *etc.* NIR-emitting OLEDs are promising for applications in medical NIR emitters and provide a promising and encouraging outlook for the development of this branch of organic electronics.

Materials based on lanthanide compounds, in particular ytterbium, which are known for their unique optical properties, are the most promising luminescent materials for these applications. Narrow luminescence bands with a constant position

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Q4 <sup>a</sup> M.V. Lomonosov Moscow State University, 1/3 Leninskye Gory, Moscow, 119991, Russia

<sup>&</sup>lt;sup>d</sup> A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Leninsky Prosp. 31, bld. 4, Moscow, 119071, Russia

<sup>&</sup>lt;sup>f</sup>South Federal Institute, Rostov-On-Don, Russia

 <sup>&</sup>lt;sup>1</sup> Electronic supplementary information (ESI) available. CCDC 2060107. For ESI
 and crystallographic data in CIF or other electronic format see DOI: 10.1039/
 d1tc04600d



are ideal for detection. A novel promising class of ytterbium 10 coordination compounds was recently proposed, *i.e.* complexes with 2-(tosylamino)benzylidene-N-aryloylhydrazones. They have already proven themselves as effective NIR emissive materials,<sup>10-12</sup> and despite having generally low solubility, one of them was already tested as the emission layer in 15 OLEDs.<sup>12</sup> However, they do not demonstrate sufficiently high values of the energy conversion efficiency: 50  $\mu$ W W<sup>-1</sup> (8.25  $\mu$ W  $\text{cm}^{-2}$ ) for Yb(L<sup>2</sup>)(HL<sup>2</sup>) at 10 V,<sup>12</sup> which is still higher than those of the previously reported Yb-based OLEDs, operating at high voltages (1.47 µW cm<sup>-2</sup> for Yb(PMIP)<sub>3</sub>TP<sub>2</sub>/Yb(PMBP)<sub>3</sub>Bath at 20 17.8 V,<sup>13</sup> 0.6  $\mu$ W cm<sup>-2</sup> for Yb(TPP)L(OEt) at 15 V,<sup>14</sup> and 10  $\mu$ W  $cm^{-2}$  for Yb(TPP)Tp at 9 V<sup>15</sup>).

Indeed, in order to be used in OLEDs, not only a high quantum yield is required, but also high mobility of charge carriers, solubility, chemical, optical and thermal stability, and, most importantly, the efficiency of luminescence.<sup>16</sup> The purpose of this work is to search for other compounds of this class, capable of more efficient photo- and electroluminescence.

To increase the solubility in organic solvents, we propose the halogenation of the Schiff base ligand. However, the introduction of halogens can affect other properties as well, *i.e.* luminescence efficiency, the mobility of charge carriers, quality of the deposited film, *etc.*<sup>17</sup>

Therefore, the aim of this work was to study the effect of ligand halogenation both on the physicochemical properties of the complexes and on the properties, stability and efficiency of OLED devices.

### Results and discussion

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#### Ligand synthesis and characterization

Schiff base ligands  $H_2L$  were synthesized by a two-step procedure from the corresponding methyl 2-halobenzoates (Scheme 1). The experimental details are given in the ESI.<sup>†</sup> Typically, all hydrazones exist as *anti-/syn*-isomer mixtures in DMSO solution. The ratios are given in Table 3. A single crystal of  $H_2L^F$  was obtained by crystallization from ethanol, and its crystal structure was determined by single-crystal X-ray diffraction (XRD) experiments (Fig. S2, ESI<sup>†</sup>).

50 In this structure, two NH-groups formed intermolecular hydrogen bonds: NH···N and NH···F. The formation of the NH···N bond is typical for these compounds, while NH···F was not realized in the previously studied compounds due to the absence of a fluorine atom. In these unsubstituted derivatives, 55 the molecules formed intermolecular NH···O interactions with

the carbonyl or  $SO_2$  group instead.

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Fig. 1 Structural formula of the selected 2-(tosylamino)-benzylidene-N-(2-halobenzoyl)-hydrazones with various substituents (Hal = F, Cl, Br, I). Protons are numbered to assign <sup>1</sup>H NMR spectra.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were ascribed for all the ligands (Fig. 2 and Fig. S10, ESI<sup>†</sup>), as well as the intermediate products (Fig. S9, ESI<sup>†</sup>), which proved the formation of the desired products with no impurities. All the <sup>1</sup>H NMR spectra of H<sub>2</sub>L are very similar among each other, and the most significant difference is in the shift of the position of the signals of the H<sup>1-</sup> <sup>4</sup> protons in the halogen-substituted ring as a function of the halogen (to a strong field from F to I). Integrated spectra are provided in the ESI<sup>†</sup> (Fig. S12).

The further analysis of the <sup>1</sup>H NMR spectra of  $H_2L$  was performed based on earlier work,<sup>10</sup> where, in particular, H<sup>5</sup> and H<sup>11</sup> proton signals were distinguished based on the COSY data. It is interesting to note that both signals are divided in the spectra of all  $H_2L$ , which we attribute to the rotation of the halogenated phenyl. This results in the formation of the superposition of the two forms, in one of which, unlike the other, a hydrogen bond between H<sup>5</sup> and the halogen is possible. This results in a *ca.* 1 ppm division of the corresponding signal (from 10.80 ppm to 9.80 ppm for  $H_2L^{Cl}$ ), while the signal of H<sup>11</sup>, which is not directly involved in the H···Hal hydrogen bond, only slightly divides (from 12.18 ppm to 12.08 ppm). The correctness of these suggestions is witnessed by the same ratio between the two pairs of signals (both the H<sup>5</sup> and H<sup>11</sup> signals divide into two bands with a ratio 0.76:0.24, Fig. S11, ESI†).

This is also confirmed by the data of ES MS and MALDI MS spectroscopy, performed for  $H_2L$  ( $L = L^F$ ,  $L^{Cl}$ ,  $L^{Br}$ ,  $L^I$ ), which clearly demonstrates the presence of the intense signal with the m/z value, corresponding to the mass of the respective molecule.

#### Complex synthesis and characterization

Complexes Ln(L)(HL) (Ln = Yb, Gd, L = L<sup>F</sup>, L<sup>Cl</sup>, L<sup>Br</sup>, L<sup>I</sup>) were obtained by the reaction between the freshly prepared lanthanide hydroxide and the ligand in ethanol. Gadolinium complexes were obtained to measure the ligand excited state energies (singlet S<sub>1</sub> and triplet T<sub>1</sub>).

$$Ln(NO_3)_3 \cdot 6H_2O + 3NH_3 \cdot H_2O \rightarrow Ln(OH)_3 \downarrow + 3NH_4NO_3 + 9H_2O \qquad 50$$

$$Ln(OH)_3 \downarrow + 2H_2L \rightarrow Ln(L)(HL) \downarrow + 3H_2O$$

Complexes Ln(L)(HL) are insoluble in ethanol, as well as initial  $Ln(OH)_3$ ; therefore, to avoid the impurity of the initial compounds, complexes were synthesized in an excess of the ligand



<sup>10</sup> 

in solution. The precipitate was filtered off, washed with ethanol, and air-dried.

The composition of the obtained complexes was determined using MALDI MS spectroscopy (Fig. 4 and Fig. S16, ESI<sup>+</sup>). All the 15 recorded spectra consist of only one signal, corresponding to the m/z of the corresponding Yb(L)(HL). It is formed from several bands in accordance with the isotopic distribution of the ytterbium ion, significantly different from that of the metalfree organic species (Fig. 3 and Fig. S15, ESI<sup>+</sup>). The only 20 exception corresponds to  $Yb(L^{I})(HL^{I})$  (Fig. S16d, ESI<sup> $\dagger$ </sup>), which also contains a low intensity band with m/z = 1083 of  $[Yb(L^{I})(HL^{I})-I]$ . This indirectly suggests the lowest stability of this complex toward the elimination of the halogen (iodine) atom.

25 It is important to note that the efforts to study these complexes using ES-MS spectroscopy did not succeed since this method resulted in the complete destruction of every complex. So, the only signal, corresponding to the Ybcontaining species according to isotopic distribution, was the 30 signal of ytterbium itself with the maximum at m/z = 174 (Fig. S14, ESI<sup>†</sup>).

The phase composition of Ln(L)(HL) was determined by powder XRD (Fig. 5, Table 1 and see the ESI<sup>+</sup>). Pawley refinement was possible for the powder patterns of Yb(L)(HL) ( $L = L^{Cl}$ , 35  $L^{Br}$ ,  $L^{I}$ ), as well as  $Gd(L^{Cl})(HL^{Cl})$ , which were indexed by the SVD method, proving the formation of the individual compounds (Table 1). According to powder XRD data the Ln = Yb, Gd complexes are isostructural to each other. The obtained cell volumes corresponded to the expected composition of the 40complexes: the independent part of the cell contains one or half Yb(L)(HL), Z' = 1 for triclinic cells and Z' = 1/2 for monoclinic cells, and the Cc space group is also possible, in this case (Z' = 1). It should be noted that in a number of isostructural compounds, Yb(L<sup>Cl</sup>)(L<sup>Cl</sup>) has the lowest volume, Q5 while other compounds have a higher volume, which is due to







Fig. 5 PXRD patterns of Yb(L<sup>Cl</sup>)(HL<sup>Cl</sup>): experimental curve (blue), fitting curve (red), and difference (grey).

the higher size of the lanthanide for Gd(L<sup>Cl</sup>)(L<sup>Cl</sup>) and the higher 25 size of the ligand  $Yb(L^{Br})(L^{Br})$ .  $Yb(L^{I})(L^{I})$  crystallizes in the  $P\overline{1}$ group, and at the same time, the volume of the molecule of  $Yb(L^{I})(L^{I})$  is the maximum.

The powders of the complexes were studied by IR spectroscopy and thermal analysis (TGA) with mass-30 detection. All the IR spectra of Ln(L)(HL) (Ln = Gd, Yb and  $L = L^{F}$ ,  $L^{Cl}$ ,  $L^{Br}$ ,  $L^{I}$ ) contain no –OH vibrations corresponding to water molecules, unlike in the case of the starting H<sub>2</sub>L. Also, vibrations of the -CO-NHR group are present in the IR spectra of the ligands  $(3330-3070 \text{ cm}^{-1})$ , 35 which disappear in the spectra of the complexes, proving the coordination of the ligand with lanthanide via the amide nitrogen atom. The -C=O group vibrations  $(\approx 1605 \text{ cm}^{-1} \text{ and } \approx 1594 \text{ cm}^{-1})$  are present in the IR spectra of the ligands, which degenerate into one vibration  $(\approx 1597 \text{ cm}^{-1})$  in the IR spectra of the complexes, which also confirms complexation. In addition, the coordination of lanthanide ions by ligands leads to a shift of all the vibrations in the IR spectra of the complexes in comparison with the spectra of the protonated ligands. In this case, the 45 IR spectra of the complexes of different metals with the same ligand are identical (Fig. 6 and Fig. S3a-d, ESI<sup>†</sup>).

According to the thermal analysis data, Yb(L)(HL) complexes are stable up to 350 °C, which is important for materials to be used in OLEDs. The complexes are decomposed in two steps (Fig. 7 and Fig. S4, ESI<sup>†</sup>); the calculated mass loss corresponds to the formation of an oxide after decomposition completion. In addition, according to TGA with mass-detection ( $H_2O$  (m/z =18 and 46)), the complexes do not contain coordinated solvent molecules. It is important to note that halogen elimination is also observed upon heating.

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1 Table 1 Cell parameters of Yb(L)(HL)

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	Complex		$Gd(L^{Cl})(HL^{Cl})$	$Yb(L^{Cl})(HL^{Cl})$	$Yb(L^{Br})(HL^{Br})$	Yb(L <sup>I</sup> )(HL <sup>I</sup> )	
5	Space group Cell volume (Å <sup>3</sup> ) Lattice parameters	$\begin{array}{c} a ( \mathring{A} ) \\ b ( \mathring{A} ) \\ c ( \mathring{A} ) \\ \alpha ( ^{\circ} ) \\ \beta ( ^{\circ} ) \\ \gamma ( ^{\circ} ) \end{array}$	$\begin{array}{c} C2/c\\ 4250.6(5)\\ 20.4892(17)\\ 19.4401(13)\\ 10.9973(6)\\ 90\\ 103.979(4)\\ 90\end{array}$	$\begin{array}{c} C2/c\\ 4197.0(6)\\ 20.5929(18)\\ 19.2953(12)\\ 10.8720(8)\\ 90\\ 103.703(4)\\ 90\end{array}$	$\begin{array}{c} C2/c\\ 4233.1(16)\\ 20.654(5)\\ 19.312(4)\\ 10.918(2)\\ 90\\ 103.592(7)\\ 90\end{array}$	$\begin{array}{c} P\bar{1}\\ 2157.0(19)\\ 10.985(6)\\ 14.168(6)\\ 14.276(8)\\ 85.94(2)\\ 81.69(3)\\ 79.14(3) \end{array}$	5
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35 Fig. 7 TGA and DTG data of Yb(L<sup>1</sup>)(HL<sup>1</sup>). Ionic currents are shown in blue (m/z = 18), green (m/z = 46), violet (m/z = 44) and gray (m/z = 127).

Due to the presence of unpaired electrons in lanthanide ions, the signals in the NMR spectra of the complexes with paramagnetic ions can shift and broaden compared to the complexes with diamagnetic ions. The total observed shift  $(\delta_{obs})$  of the signal in the spectrum of the complex with a





paramagnetic ion can be represented as the sum of the diamagnetic associated shift  $\delta_{\rm D}$ , Fermi-contact shift  $\delta_{\rm FC}$ , and pseudo contact shift  $\delta_{\rm PC}$ :

$$\delta_{\rm obs} = \delta_{\rm D} + \delta_{\rm FC} + \delta_{\rm PC} \tag{1}$$

The pseudo contact shift, associated with the incompletely filled 4f-electron shell of the lanthanide cation, can be expressed in the spherical coordinate system  $(r, \theta, \varphi)$  in terms of the magnetic susceptibility tensor  $\chi$ , which depends on the electronic configuration of the lanthanide ion:<sup>18</sup>

$$\delta_{PC} = \frac{1}{12\pi r^3} \left[ \Delta \chi_{ax} \left( 3\cos^2 \theta - 1 \right) + \frac{3}{2} \Delta \chi_{rh} 3\sin^2 \theta \cos^2 2\varphi \right]$$
(2)

Although in some cases this allows estimation of the structure of the complex in solution, usually such an additional shift and broadening complicate the NMR spectra of the lanthanide complexes.

Such an analysis was recently performed in ref. 17 for the lanthanide complexes with unhalogenated 2-(tosylamino)benzylidene-*N*-aryloylhydrazone  $H_2L^H$ . In particular, it was shown that  $Ln(L^H)(HL^H)$  dissociates in DMSO according to the reaction

$$2\mathrm{Ln}(\mathrm{L}^{\mathrm{H}})(\mathrm{HL}^{\mathrm{H}}) \rightarrow [\mathrm{Ln}\mathrm{L}^{\mathrm{H}}]^{+} + [\mathrm{Ln}\mathrm{L}^{\mathrm{H}}_{2}]^{-} + \mathrm{H}_{2}\mathrm{L}$$
<sup>40</sup>

This gives rise to an additional difficulty in the NMR spectra analysis because the signals of three species are present.

In the present work we compared the NMR spectra of the complexes with the spectra of the corresponding ligands H<sub>2</sub>L, 45 as well as with the spectra of  $K[Yb(L^{H})_{2}]$  from ref. 18 (Fig. 8). It is exemplified in the analysis of the spectrum of Yb(L<sup>I</sup>)(HL<sup>I</sup>), since the spectra of all Yb(L)(HL) are similar (Fig. S13a, ESI<sup>+</sup>). In the spectrum of Yb(L<sup>I</sup>)(HL<sup>I</sup>) one can clearly see the superposition of the narrow well resolved signals of the corresponding ligand 50  $H_2L^{I}$ , as well as broad highly shifted bands of the Yb-containing species (Fig. S13b, ESI<sup>†</sup>). This witnesses that in the present case such a dissociation also occurs. Some of the bands can be ascribed to the protons of  $[YbL_2]^-$  based on the comparison with the spectrum of  $K[Yb(L^H)_2]$ , while the remaining signals 55 obviously correspond to the protons of [YbL]+.



Fig. 9 (a) Normalized luminescence spectra of Yb(L<sup>F</sup>)(HL<sup>F</sup>) (1)  $Yb(L^{Cl})(HL^{Cl})$  (2),  $Yb(L^{Br})(HL^{Br})$  (3) and  $Yb(L^{l})(HL^{l})$  (4); (b) light absorption coefficient versus wavelength of Yb(L<sup>F</sup>)(HL<sup>F</sup>).

#### Luminescence properties

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Singlet  $(S_1)$  and triplet  $(T_1)$  excited levels of ligands were determined from the positions of the fluorescence and phos-15 phorescence bands in the luminescence spectra of gadolinium complexes at low (77 K) and room temperature. They were almost independent of the halogen used and equal to  $S_1$  = 20400-20500 cm<sup>-1</sup>,  $T_1 = 18000-18100$  cm<sup>-1</sup> (Fig. S5, ESI<sup>+</sup>). This is very high compared with the resonance level of the Yb<sup>3+</sup>

20 ion (ca.  $10\,000 \text{ cm}^{-1}$ ), but almost exactly coincided with the values obtained earlier for unhalogenated (L<sup>H</sup>)<sup>2-</sup>, which suggests that energy transfer to the ytterbium ion can still be sufficiently high.<sup>11</sup>

Infrared luminescence of ytterbium complexes Yb(L)(HL) 25 was studied upon through-ligand excitation. Luminescence spectra of all the complexes (Fig. 9a) demonstrated only typical  $Yb^{3+}$  ion emission, corresponding to the  ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$  transition. The overall quantum yields (QYs) were determined using the integrating sphere and turned out to be quite close to each

30 other (0.91,...,1.02%, Table 2). These values are quite high for NIR luminescence, as the typical values for powders, emitting at ca. 1000 nm, do not exceed 1% with few exceptions.<sup>19-27</sup> Indeed, the only excited state of ytterbium and the absence of other middle states complicates its sensitization and simplifies

35 its quenching by high-energy vibrations of the X-H (X = O, N, C) bonds in the ligands, in comparison to visible emitting Tb<sup>3+</sup> and Eu<sup>3+</sup>. For the solid samples, the QY values are also limited by the presence of the concentration quenching, which is

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almost not observed for the terbium and europium complexes with bulky organic ligands<sup>28</sup> (rare exceptions were found by us in ref. 29 and 30), while they are common for other lanthanide complexes,<sup>31</sup> including ytterbium.<sup>20</sup> Therefore, the highest QYs of Yb complexes were obtained in diluted solutions,<sup>24,32</sup> while for solid samples,<sup>27</sup> including thin solid films, needed for OLED applications, they are much inferior. The obtained QY values are lower than the OY values of the vtterbium complexes with the unhalogenated  $H_2L^H$  ligand that reached 1.4%.<sup>11</sup> At the same time they coincide with the QYs of Yb complexes with 2-(tosylamino)-benzylidene-N-(isonicotinoyl)hydrazone (0.9  $\pm$ 0.2%) which demonstrates the highest efficiency of solutionprocessed Yb-based OLEDs.<sup>12</sup>

The overall quantum yield QY =  $\eta_{\text{sens}} \cdot Q_{\text{Yb}}^{\text{Yb}}$  is the product of the sensitization efficiency,  $\eta_{\text{sens}}$ , and internal quantum yield, Q  $_{\rm Yb}^{\rm Yb}$ . To understand the factor limiting quantum yield values, quenching or sensitization, we need to calculate both  $\eta_{\text{sens}}$  and  $Q_{\rm Yb}^{\rm Yb}$ . The radiative lifetime,  $\tau_{\rm rad}$ , can be calculated for the  ${}^2{
m F}_{5/2}$  $\rightarrow$  <sup>2</sup>F<sub>7/2</sub> transition of the ytterbium ion from the absorption spectrum using the equation:<sup>33</sup>

$$\frac{1}{\tau_{\rm rad}} = 2303 \cdot \frac{8\pi cn^2 \bar{\nu}^2 (2J+1)}{N_{\rm A} (2J'+1)} \int \varepsilon(\nu) \mathrm{d}\nu$$

where  $N_A$  is Avogadro's number, c is the speed of light in a 25 vacuum (cm s<sup>-1</sup>), *n* is the refractive index, *J* and *J'* are the quantum numbers for the ground and excited states, respectively,  $\varepsilon(\nu)$  is the wave number dependence of absorption, and

$$\bar{\nu} = \frac{\int \nu \cdot \varepsilon(\nu) d\nu}{\int \varepsilon(\nu) d\nu}$$
 is the transition frequency.

The radiative lifetime varied from 0.7 ms to 1.0 ms, which is comparable to those obtained in previous work.<sup>12</sup> Using the value of  $\tau_{rad}$  the internal quantum yield can be calculated using the formula:

$$QY_{Yb}^{Yb} = \frac{k_{rad}}{k_{obs}} = \frac{\tau_{obs}}{\tau_{rad}},$$
<sup>35</sup>

where  $k_{rad}$  and  $k_{obs}$  are constants of radiative and nonradiative relaxation processes. Correspondingly, the sensitization

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1 efficiencies varied from 45% to 70%, meaning that the low internal quantum yield is a factor limiting the overall quantum yield value.

The HOMO energy was measured by photoemission yield 5 spectroscopy. The LUMO energy is calculated as LUMO = HOMO –  $E_g$ , where  $E_g$  is the HOMO–LUMO energy gap.  $E_g$ was calculated from the beginning of the absorption spectra<sup>34,35</sup> (Fig. S7, ESI<sup>†</sup>).

Determination of charge carrier mobility for nonvolatile lanthanide complexes is usually not possible.<sup>36,37</sup> Recently we optimized an approach to charge mobility determination using the photo-CELIV method<sup>36</sup> for the solution processed films of the lanthanide complexes,<sup>38</sup> which was used in the present work. The mobility of charge carriers was estimated by the carrier extraction by the linearly increasing voltage (MIS-CELIV) method with laser pumping (wavelength 405 nm) in structure ITO(100 nm)/SiO<sub>2</sub>(70 nm)/Yb(L)(HL)/Al(100 nm). The mobility was calculated using the formula with a correction factor  $\Delta j \ll j(0)$ :

$$\mu = \frac{d^2 j_{\rm d}}{A t_{\rm max}^2 \Delta j}.$$

where  $\mu$  is the charge carrier mobility, *d* is the sample thickness,  $j_d$  is the current density, *A* is the rate of increase of the applied voltage and  $\Delta j$  is the difference between the maximum current and j(0).



<sup>55</sup> **Fig. 10** (a–c) Electroluminescence spectra, (d–f) *I–V* curves, (g–j) energy conversion efficiencies, (k–m) emitted powers, and (n–p) EQE values of OLEDs in different experiments: (1st) a, d, g, k, n; (2nd) b, e, h, I, o, and (3rd) c, f, j, m, p.

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 The obtained values of electron and hole mobility changed within half of the order of magnitude. It is important to note that the mobility of electrons and holes in all four materials is comparable, so we expect a balanced operation of the devices.
 Complex Yb(L<sup>Br</sup>)(HL<sup>Br</sup>) demonstrated the highest hole and

second highest electron mobility (Table 2). The obtained complexes were highly soluble in THF. Halogenation affects the solubility of the complexes: in the series Yb(L)(HL) the solubility increases in the row I–F–Br–Cl (Table 2).

#### OLEDs based on Yb(L)(HL)

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The complexes of d-elements and one lanthanide complex with *N*-substituted 2-tosylaminobenzylidene have already established themselves as emission layers of organic light emitting

- 15 diodes (OLEDs).<sup>12,39</sup> This fact and the fact that the studied complexes Yb(L)(HL) demonstrated fairly high quantum yields and sufficient solubility allow us to assume that they can be applicable to OLEDs. HOMO and LUMO values and the values of quantum yields of Yb(L)(HL) are almost the same, with a big for the same for the same with a big for the same for the same with a big for the same for the sa
- 20 difference of less than 10% decrease in the series  $I \rightarrow Br \approx F \rightarrow Cl$ , and the largest, though still small, difference corresponds to the mobility of charge carriers, which decrease in the series  $Br \rightarrow I \rightarrow F \rightarrow Cl$ .
- In order to study the impact of the listed parameters and to achieve efficient electroluminescence, all the Yb(L)(HL) complexes were tested in OLEDs with the same heterostructures ITO/PEDOT-PSS/poly-TPD/EML/OXD-7/LiF/Al made under the same conditions, where the EML is pure host-free Yb(L)(HL) (*ca.* 40 nm). HTL (poly-TPD) and ETL layers (OXD-7) were
- 30 selected based on the values of the HOMO and LUMO energies. The balance of the selected heterostructure has already been proven in the literature and studied by our research group.<sup>38</sup> Prior to further investigations, all the obtained OLEDs were tested to verify the absence of the ohmic shortcuts by applying a 35 reverse bias voltage of -6 V. The device was rejected for further measurements when the registered current exceeded 1  $\mu$ A (~10  $\mu$ A cm<sup>-2</sup>).

To compare the OLED efficiency, the value of the energy conversion efficiency (ECE) was used, which is the ratio of the luminous power emitted to the electrical power consumed. It represents the overall efficiency of the device and is analogous to the luminous efficacy (in lumens per watt) for visible LEDs, usually used to describe the characteristics of OLEDs emitting in the near infrared range along with external quantum efficiency (EQE).<sup>40,41</sup>

In the electroluminescence spectra of all the diodes, intense emission bands of ytterbium luminescence corresponding to the  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transitions were observed with no or almost no traces of the broad organic luminescence (Fig. 10a–c and Fig. S8a–c, ESI†). Yb(L<sup>I</sup>)(HL<sup>I</sup>) and Yb(L<sup>Br</sup>)(HL<sup>Br</sup>) have the lowest emitted power, efficiency and intensity. The electroluminescence intensity increases in the I  $\rightarrow$  Br  $\rightarrow$  Cl  $\rightarrow$  F series. The

quantum yields, where  $Yb(L^{I})(HL^{I})$  is in the lead, or with the mobility of charge carriers, where  $Yb(L^{Br})(HL^{Br})$  demonstrates the highest values. At the same time these values correlate with

obtained dependence does not correlate with either of the

the halogen mass: the heavier it is, the lower the efficiency. A literature search revealed an explanation of this behaviour: the halogen-radical elimination is possible in halogenated emitters, followed by their reactions with the materials of other layers, which cause damage, and generate other radicals or further reaction products.<sup>42</sup> This mechanism possibility in the present case is indirectly supported by the thermal analysis data: iodine atom elimination, for example, is observed upon heating Yb(L<sup>I</sup>)(HL<sup>I</sup>) up to 370 °C. Not only can such a temperature be reached during the device operation, but also iodine can be eliminated even at lower temperatures under the action of an electric current. These processes inevitably lead to deterioration in the quality of OLEDs, which is confirmed by electroluminescence data (Fig. 10).

To confirm the assumption of the role of a halogen, we decided to decrease twice the thickness of the emission layers. Typically, OLED efficiency decreases upon a decrease in emission layer thickness, but if the assumption is true, the reverse situation will be observed: the thinner the film, the less halogen it contains, and the more stable and efficient the whole OLED is. Indeed, the sequence of electroluminescence intensities has 06 changed upon a decrease in film thickness:  $Yb(L^{F})(HL^{F})$  electroluminescence intensity did not change at all, while the electroluminescence of the rest of the complexes, containing heavier halogens, increased (Fig. 6b). To make sure that this is the tendency, we further decreased the thickness twice, and again observed an increase in electroluminescence efficiency, except for fluorinated Yb(L<sup>F</sup>)(HL<sup>F</sup>). Moreover, for the thinnest films, the OLED efficiency correlated with the mobility of charge carriers: Br  $\rightarrow$  I  $\rightarrow$  Cl  $\rightarrow$  F. So, Yb(L<sup>F</sup>)(HL<sup>F</sup>) demonstrates the lowest efficiency as a thin film, but as it does not suffer from fluorine radical elimination, it is the only one which operates as a thick film. While the thick film of  $Yb(L^{Br})(HL^{Br})$ demonstrated low efficiency, upon a decrease in film thickness the highest electroluminescence efficiency was achieved for this complex due to the highest mobility. The efficiency reached 430  $\mu$ W W<sup>-1</sup>, and this is the highest value for Yb-based OLEDs, which exceeds the previous record by an order of magnitude.

Its EQE reached 0.12%, which is the second highest value after EQE = 0.21%, which was reached by our group earlier.<sup>20</sup> It is important to note that the highest value was reached only at 12 V, which is very high for NIR luminescence with a low photon energy (*ca.* 1.2 eV). Other reported EQE values do not exceed 0.058%,<sup>43</sup> and were also obtained only at high voltages (> 10 V).<sup>43,44</sup>

# Conclusions

A series of ytterbium complexes with 2-(tosylamino)benzylidene-*N*-(2-halobenzoyl)-hydrazones was obtained and successfully tested in OLEDs thanks to the solubility increase upon halogenation. A thorough study of their physical and photophysical properties revealed that halogenation has almost no effect on the luminescence properties and HOMO/LUMO energies, while charge carrier mobility changes within half an

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order of magnitude. This moderate change in mobility of 1 charge carriers resulted in a significant change in EL efficiency. At the same time, halogenation has a negative effect on the stability of the device at large thicknesses of the EML. High charge mobility together with high solubility and sufficient quantum yield allowed the highest energy conversion efficiency of Yb-based OLEDs to date to be reached, which is equal to 430  $\mu W W^{-1}$ , with the thin film of Yb(L<sup>Br</sup>)(HL<sup>Br</sup>) as the emission layer.

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### **Experimental section**

### Materials and methods

- 15 All solvents and chemicals were purchased from commercial sources. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 25 °C using a Bruker Avance 400 spectrometer with an operating frequency of 400 and 101 MHz, respectively. Chemical shifts are reported in ppm relative to residual solvent signals. Thermal analysis was 20 carried out on a thermoanalyzer STA 449 F1 Jupiter (NETZSCH,
- Germany) in the temperature range of 40-1000 °C in air and at a heating rate of  $10^{\circ}$  min<sup>-1</sup>. The evolved gases were simultaneously monitored during the TA experiment using a coupled QMS 403 Aëolos Quadro quadrupole mass spectrometer
- (NETZSCH, Germany). The mass spectra were registered for 25 the species with the following m/z values: 18 (corresponding to H<sub>2</sub>O), 44 (corresponding to CO<sub>2</sub>), 46 (corresponding to C<sub>2</sub>H<sub>5</sub>OH), 19 (corresponding to F), 35 and 37 (corresponding to Cl), 36 and 38 (corresponding to HCl), 80 (corresponding to
- Br), and 127 (corresponding to I). The IR spectra were recorded 30 on a Thermo Scientific<sup>™</sup> Nicolet<sup>™</sup> iS50 FTIR Spectrometer as powdered at ATR. Absorption spectra of the ligands and Yb(L)(HL) in DMSO solution (l = 10.0 mm) in the range of 800-1100 nm were obtained using a PerkinElmer Lambda 35 35 UV/vis Spectrometer (PerkinElmer). Powder X-ray diffraction
- (PXRD) was performed by using Bruker D8 Advance  $[\lambda(Cu-K\alpha) =$ 1.5418 Å; Ni filter] and Bruker D8 Advance Vario diffractometers  $[\lambda(Cu-K\alpha 1) = 1.54060 \text{ Å}; Ge(111)-monochromator] with$ a step size of  $0.020^{\circ}$ . The patterns were indexed by using the
- 40 SVD-Index<sup>45</sup> as implemented in the TOPAS 4.2 software.<sup>46</sup> Then, the powder patterns were refined by using the Pawley method. Single crystals of C21H18FN3O3S were grown from C<sub>2</sub>H<sub>5</sub>OH. A suitable crystal was selected and kept on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 120 K
- during data collection. Using Olex2,47 the structure was solved 45 with the XS<sup>48</sup> structure solution program using Direct Methods and refined with the XL48 refinement package using Least Squares minimization. The spectra of gadolinium complexes were measured using a HORIBA FluoroMax-4-Plus-C-P. The
- 50 registration of luminescence spectra in the IR range and the measurement of quantum yields were carried out on a Maya 2000 spectrofluorimeter (Ocean Optics) using a Fluorolog FL3-22 (HORIBA) spectrometer at room temperature, excitation was performed through a ligand, and the absolute method in the 55
- integration sphere was used. The electroluminescence spectra were obtained with an Ocean Optics Maya 2000 Pro CCD

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Table 3 Ratios of H<sub>2</sub>L isomers in DMSO solution

Ligand	anti-/syn-ratio
$H_2L^F$	1:0.26
$H_2L^{Cl}$	1:0.43
$H_2L^{Br}$	1:0.44
$H_2L^I$	1:0.36

spectrometer sensitive within 200-1100 nm. Current-voltage characteristics were obtained using two DT 838 Digital multimeters. The OLED optical power was determined using a Coherent FieldMaxII laser power meter with an optic filter removing the visible part of the spectra.

#### Synthesis

General procedure for hydrazide preparation. Methyl 2halobenzoate (10 mmol) was dissolved in methanol (50 ml) and hydrazine hydrate (10 eq.) was added. The solution was refluxed for 8 h, cooled to room temperature and evaporated to dryness. The residue was suspended in water (10 ml), filtered, washed with water and aqueous ethanol, dried and recrystallized from ethanol.

For 2-fluorobenzohydrazide. The residue was suspended in water (3 ml), sodium chloride (1.2 g) was added, and the 25 mixture was extracted with ethyl acetate (3-6 ml). The organic phases were combined, dried over sodium sulfate and evaporated to dryness (Fig. S10a-d, ESI<sup>†</sup>).

General procedure for condensation. The saturated solution of hydrazide in dry ethanol was added to the saturated solution 30 of 2-(tosylamino)benzaldehyde in dry ethanol. The resulting mixture was refluxed for 3 h and cooled to room temperature. The suspension was evaporated to 1/3 of volume and the powder was filtered, washed with dry ethanol, dried in air, and recrystallized from dry ethanol. Typically, all hydrazones exist as anti-/syn-isomer mixtures in DMSO solution. The ratios are given in Table 3.

(Z)-2-Fluoro-N'-((2-((dioxo(p-tolyl)-l7-methyl)amino)phenyl) methylene)benzohydrazide (H2LF). 1H NMR (400 MHz, DMSO $d_6$ , proton numeration in Fig. 1)  $\delta$  ppm 2.33 (s, 3H, DMSO- $d_6$ ) 6.87-7.83 (m, 12H, H<sup>1-4,7-10,12-15</sup>) 8.21-8.55 (m, 1H, H<sup>6</sup>) 9.77- $11.00 \text{ (m, 1H}^{5} \text{)} 11.97 - 12.20 \text{ (m, 1H}^{11} \text{)}.$ 

MALDI MS (ESI): 411.907  $[M]^+$ , 433.936  $[M + Na]^+$ 

(Z)-2-Chloro-N'-((2-((dioxo(p-tolyl)-l7-methyl)amino)

phenyl)methylene)benzohydrazide (H<sub>2</sub>L<sup>Cl</sup>). <sup>1</sup>H NMR (400 MHz, DMSO-d6, proton numeration in Fig. 1)  $\delta$  ppm 2.33 (s, 3H, DMSO-d6) 6.87-7.71 (m, 12H, H<sup>1-4,7-10,12-15</sup>) 8.18-8.50 (m, 1H,  $H^{6}$ ) 9.65–10.98 (m, 1 $H^{5}$ ) 11.99–12.30 (m, 1 $H^{11}$ ).

MALDI MS (ESI): 427.892 [M]<sup>+</sup>, 449.849 [M + Na]<sup>+</sup>, 465.826 [M  $+ K^{+}$ 

(*Z*)-2-Bromo-*N*'-((2-((dioxo(*p*-tolyl)-*l*7-methyl)amino) phenyl)methylene)benzohydrazide (H<sub>2</sub>L<sup>Br</sup>). <sup>1</sup>H NMR (400 MHz, DMSO-d6, proton numeration in Fig. 1)  $\delta$  ppm 2.34 (s, 3H, DMSO-d6) 6.89-7.87 (m, 12H, H<sup>1-4,7-10,12-15</sup>) 8.19-8.46 (m, 1H, H<sup>6</sup>) 9.67-10.88 (m, 1H<sup>5</sup>) 11.94-12.23 (m, 1H<sup>11</sup>).

MALDI MS (ESI):  $495.849 [M + Na]^+$ 

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- 1 (Z)-2-Iodo-N'-((2-((dioxo(p-tolyl)-l7-methyl)amino)phenyl) methylene)benzohydrazide (H2LI). 1H NMR (400 MHz, DMSOd6, proton numeration in Fig. 1)  $\delta$  ppm 2.23–2.41 (m, 3H, DMSO-d6) 6.91-8.06 (m, 11H, H<sup>1-4,7-10,12-15</sup>) 8.20-8.49 (m, 1H<sup>6</sup>) 9.68-10.98 (m, 1H, H<sup>5</sup>) 11.95-12.22 (m, 1H<sup>11</sup>). 5
  - MALDI MS (ESI): 519.737  $[M]^+$ , 541.713  $[M + Na]^+$ Crystal data for  $C_{21}H_{18}FN_3O_3S$  (*M* = 411.44 g mol<sup>-1</sup>). Triclinic, space group  $P\bar{1}$  (no. 2), a = 8.2778(15) Å, b = 10.4591(19) Å, c= 11.303(3) Å,  $\alpha$  = 108.611(3)°,  $\beta$  = 93.498(5)°,  $\gamma$  = 94.266(4)°,
- $V = 921.1(3) \text{ Å}^3$ , Z = 2, T = 120 K,  $\mu(\text{MoK}\alpha) = 0.216 \text{ mm}^{-1}$ ,  $D_{\text{calc}} =$ 10 1.483 g cm<sup>-3</sup>, 12341 reflections measured (3.82°  $\leq 2\Theta \leq$ 61.34°), 5653 unique ( $R_{int} = 0.0726$ ,  $R_{sigma} = 0.0661$ ) which were used in all calculations. The final  $R_1$  was 0.0500 (>2sigma(I)) and  $wR_2$  was 0.1433 (all data).
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### Synthesis of the lanthanide complexes

Ln(L)(HL) was synthesized, where Ln is Yb or Gd and L is  $L^{F}$ , L<sup>Cl</sup>, L<sup>Br</sup> or L<sup>I</sup>. A freshly prepared lanthanide hydroxide (0.25 mmol) was added to a hot solution of 0.2 g (0.55 mmol) H<sub>2</sub>L in 50 ml ethanol. The mixture was heated under stirring for 24 h, resulting in a yellowish precipitate, which was filtered off, washed with ethanol, and air-dried. Therefore, to avoid the impurity of the initial compounds, the Ln(L)(HL) complexes were synthesized in an excess of the ligand in solution.

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## Conflicts of interest

There are no conflicts to declare.

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## Acknowledgements

This work was supported by President's grant MD-2821.2021.1.3. The luminescence study was supported by the Russian Science Foundation (20-73-10053). X-Ray diffraction studies were performed with financial support from the Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition Q7 studies of INEOS RAS.

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