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Tuning White Light Emission in Dinuclear Phenoxo Bridged Dy^{III} **Complexes**

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S Supporting Information



ABSTRACT: A new series of dinuclear dysprosium(III) complexes, $[Dy_2(L^{CH_3})_2(NO_3)_2(MeOH)_2]$ (I), $[Dy_2(L^{CH_3})_2(NO_3)_2(DMF)_2] \cdot 2DMF$ (II), $[Dy_2(L^{CI})_2(NO_3)_2(DMF)_2] \cdot 2DMF$ (III), and $[Dy_2(L^{CH_3O})_2(NO_3)_2(DMF)_2]$ (IV), with 2,2'-[[(2-pyridinylmethyl)imino]di(methylene)]bis(4-R-phenol), where R = CH₃, Cl, and CH₃O, were investigated as potential white light emitters. All octacoordinated dysprosium(III) are phenoxo-bridged species and have a similar coordination environment. Nevertheless, I has a MeOH ligand molecule, while for II-IV a DMF ligand replaces that of MeOH. The nature of the coordinated solvent molecule plays an important role in the behavior of the thermal dependence of the Y/B (yellow/ blue) emission ratio of the Dy^{III} complexes (\mathbf{Y} : ${}^{4}\mathbf{F}_{9/2} \rightarrow {}^{6}\mathbf{H}_{13/2}$, yellow and **B**: ${}^{4}\mathbf{F}_{9/2} \rightarrow {}^{6}\mathbf{H}_{15/2}$, blue transitions), since for I the variation of this ratio is significant, while for the other Dy^{III} complexes with DMF as ligand the ratio remains constant within experimental error. At room temperature the CIE (Commission International d'Eclairage) color coordinates for the Dy^{III} complexes, I (0.286, 0.317), III (0.302, 0.324), and IV (0.322, 0.348) are close to the NTSC (National Television System(s) Committee) standard value for white color. Varying the temperature from 16 to 300 K the CIE coordinates for I change from the blueish to white region of the chromaticity diagram, while those of II present an inverse thermal dependence as compared to I. The CCT (Correlated Color Temperature) values at room temperature for I (8384 K), II (17235 K), and IV (5948 K) permit us to consider these complexes as candidates for white cold light emitters, the high value of II being uncommon. For I and II the CCT values vary strongly with temperature, showing a decrease with increasing temperature for I, and an increase with increasing temperature for II, thus making evident the influence on the photophysical properties of the nature of the coordinated solvent molecule in these complexes.

INTRODUCTION

In recent years, the research of lanthanide (III) complexes has attracted increasing interest due to their potential applications in fields as diverse as luminescence, molecular magnetism, gas separation, catalysis, and adsorption.¹⁻⁸ For photoluminescence, the intense, narrow, and long-lived (up to milliseconds) emission bands encompassing the near-infrared and visible regions observed for the lanthanide ions make them suitable candidates for the development of new luminescent materials.

Using ligands that serve as antenna, many highly luminescent lanthanides complexes have been reported in the literature.^{9–14}

Nowadays, research related to the emission of lanthanide-(III) compounds is being strongly focused on the development of single component white light emitting materials.^{15,16} One of the methods described in the literature is that in which

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lanthanide MOFs are doped with a secondary lanthanide ion.^{17–19} White-light emitting phosphors can be achieved in a single phase, using mixed Ln-MOF, containing Eu^{III} (red emission-R) and Tb^{III} (green emission-G) centers, which combined with the blue emission (B) of an adequate ligand give rise to the RGB trichromic strategy.^{16,20–22} However, taking advantage of the blue luminescence (B) contributed by the ligand-based emission, together with the simultaneous yellow emission (Y) of Dy^{III}, white light emission can be achieved by the balance of Y/B colors (YB dichromic strategy).²³

Alkoxide and aryloxide ligands have been used in both transition metal and lanthanide coordination chemistry due to their variable steric requirements and ligand versatility, including macrocyclic ligands.^{24–29} For example, Xu et al.²⁹ described the synthesis, structures, and photophysical properties of homo- and heteronuclear lanthanide(III) complexes with 2-methyl-8-hydroxyquinoline with the OH group acting as a phenol bridge.

We have been interested in the coordination chemistry of (pyridylamino)phenol ligands toward transition metal ions; mono-, di-, and trinuclear metal complexes have been reported previously,^{30,31} and now we started to study the use of this type of ligand in lanthanide coordination chemistry. We herein present the photophysical characterization of a new series of Dy^{III} complexes, with the tripodal ligands 2,2'-[[(2-pyridinylmethyl)imino]di(methylene)]bis(4-R-phenol) with R = CH₃ (L^{CH₃}), Cl (L^{Cl}), and CH₃O (L^{CH₃O), which behave as single component white light molecular emitters.}

EXPERIMENTAL SECTION

Materials and Reagents. All reagents were reagent grade and used without further purification, unless stated otherwise. Solvents were of HPLC quality and were used as received.

Syntheses. *Synthesis of Ligands.* Ligands were synthesized by a Mannich type reaction as previously reported,³² and details are given as Supporting Information.

Synthesis of Complexes. To a solution of the appropriate ligand (0.5 mmol) in 20 mL of MeOH containing 1 mmol of MeONa, a solution obtained by mixing $Dy(H_2O)_nCl_3$ (1 mmol) in 5 mL of MeOH with KNO₃ (3 mmol) in 60 mL of MeOH was added with stirring at ambient temperature (Scheme 1). The reaction mixture was

Scheme 1. Syntheses of Dy^{III} Complexes



maintained undisturbed for 5–15 days giving the corresponding solid products in yields ranging from 50 to 70%. Alternatively, reacting a solution of the dysprosium nitrate with the ligand under identical conditions, gave the same compounds. $[Dy_2(L^{CH_3})_2(NO_3)_2(DMF)_2]$. 2DMF (II), $[Dy_2(L^{Cl_1})_2(NO_3)_2(DMF)_2]$.2DMF (III), and $[Dy_2(L^{CH_3O})_2(NO_3)_2(DMF)_2]$ (IV) were obtained by recrystallization in hot DMF of the corresponding crude products separated from the reaction mixture. Only in the case of $[Dy_2(L^{CH_3})_2(NO_3)_2(MeOH)_2]$ (I) were crystals suitable for X-ray structural diffraction studies obtained directly from the reaction mixture. The formula of IV is based on elemental analysis and FTIR

data, since single crystals for X-ray diffraction were not obtained. $Y^{\rm III}$ complexes were obtained likewise, and the details are given as Supporting Information.

 $[Dy_2(L^{CH_3})_2(NO_3)_2(CH_3OH)_2]$ (I). Elemental analysis: Exp (Calc) for $C_{46}H_{52}N_6O_{12}Dy_2$: C, 45.5 (45.79); H, 4.2 (4.35); N, 6.8 (6.97)%. FTIR (atr): 1607, 1570, 1492, 1454, 1444, 1381, 1356, 1280, 1248, 1217, 1158, 1127, 1084, 1069, 1060, 1026, 1012 cm⁻¹.

 $[Dy_2(L^{CH3})_2(NO_3)_2(DMF)_2] \cdot 2DMF$ (II). Elemental analysis: Exp (Calc) for $C_{56}H_{72}N_{10}O_{16}Dy_2$: C, 46.5 (46.75); H, 4.95 (5.05); N, 9.4 (9.55) %. FTIR (atr): 1670, 1650, 1606, 1570, 1493, 1464, 1435, 1389, 1319, 1302, 1254, 1225, 1157, 1143, 1127, 1110, 1087, 1067, 1055, 1035, 1015 cm⁻¹.

 $[Dy_2(L^{Cl})_2(NO_3)_2(DMF)_2]2 \cdot 2DMF$ (III). Elemental analysis: Exp (Calc) for $C_{52}H_{60}N_{10}O_{14}Cl_4Dy_2$: C, 41.3 (41.18); H, 3.9 (3.99); N, 9.2(9.24) %. FTIR (atr): 1669, 1648, 1604, 1590, 1570, 1471, 1435, 1416, 1386, 1328, 1286, 1256, 1196, 1088, 838, 792, 763, 742, 669 cm⁻¹.

 $[Dy_2(L^{CH3O})_2(NO_3)_2(DMF)_2]$ (**IV**). Elemental analysis: Exp (Calc) for $C_{50}H_{58}N_8O_{16}Dy_2$: C, 44.8 (44.42); H, 4.5 (4.32); N, 8.1 (8.29) %. FTIR (atr): 1646, 1606, 1573, 1488, 1445, 1429, 1385, 1300, 1266, 1210, 1036, 807, 792, 760, 752, 724, 675 cm⁻¹.

Physical Measurements. Elemental analyses were performed using a Flash 2000 Instrument. Fourier transform infrared spectra (FTIR) were recorded on a Thermo Scientific Nicolet iS5, with an ATR iD5 accessory, in the range 4000 to 650 cm⁻¹. ¹H NMR spectra were recorded in CDCl₃ or DMSO-d₆ on a Bruker AMX-300 NMR spectrometer. Chemical shifts are reported as δ values downfield of an internal Me₄Si reference. The crystal structures were determined by single crystal X-ray diffraction, using a SMART-APEX II CCD diffractometer. Data reduction was done with SAINT.33 Empirical or numerical absorption corrections were applied using SADABS.³⁴ Structure solution by direct methods and completion by difference Fourier synthesis and refinement by least-squares using SHELXL.³¹ The hydrogen atoms positions were calculated after each cycle of refinement with SHELXL using a riding model for each structure, with a C–H distance of 0.93, 0.96, or 0.97 Å. For these cases $U_{iso}(H)$ values were set equal to $1.2U_{eq}$ or $1.5U_{eq}$ of the parent carbon atom. The hydrogen atom for the hydroxyl group of the coordinated MeOH molecule was located in the difference Fourier map and subsequently refined with the hydrogen to oxygen distance to be 0.85 Å. Table S1 shows a summary of structural and refinement details for the reported complexes. Diffuse reflectance spectra of all studied samples were collected on a PerkinElmer Lambda WB1050 spectrophotometer equipped with a Praying Mantis diffuse reflection accessory. Photoluminescence (PL) spectra of the solid samples were measured using a Horiba-Jobin Yvon spectrofluorometer, Model Fluorolog-3 (FL3-221), under excitation with a 450 W Xe lamp and Horiba PPD-850 ps photon detector in the UV-vis region. The excitation and emission slits used were of 1.5 nm. The emission was corrected for the spectral response of the monochromators and the detector using a typical correction spectrum provided by the manufacturer. The $Dy^{\rm III}$ lifetimes were acquired with the same equipment of PL measurements, using a pulse light from a nanoled as excitation source at 340 nm. Low-temperature spectra were obtained, using a closed cycle cryostat model CS202AI-X15 (ARS Cryo) monitoring the temperature with a Lake Shore model 332 controller. All optical measurements were recorded using finely ground powder samples. The Commission International d'Eclairage, (CIE 1931) x, y coordinates and color diagram were calculated, on the basis of a 10° standard observer, from the photoluminescence spectra.³⁶ The values of the correlated color temperature (CCT), were calculated, using the McCamy formula:³⁷ CCT = $-437n^3 + 360n^2 - 6861n +$ 5514.31, where $n = (x - x_c)/(y - y_c)$, x and y the chromaticity coordinates, and $x_c = 0.3320$ and $y_c = 0.1858$; the coordinates of chromaticity epicenter extracted from McCamy et al.³⁷

RESULTS AND DISCUSSION

Structural Characterization. The molecular structure of complexes I, II, and III corresponds to Dy^{III} dinuclear species,



Figure 1. Molecular structure diagram for (a) $[Dy_2(L^{CH3})_2(NO_3)_2(MeOH)_2]$ (I), (b) $[Dy_2(L^{CH3})_2(NO_3)_2(DMF)_2]$ ·2DMF (II-1), and (c) $[Dy_2(L^{Cl})_2(NO_3)_2(DMF)_2]$ ·2DMF (III-1). Atoms are at the 50% level of probability. Hydrogen atoms, except those involved in intramolecular hydrogen bonds, have been omitted for clarity.



Figure 2. (a) Excitation ($\lambda_{emi} = 575 \text{ nm}$) and (b) emission spectra ($\lambda_{exc} = 350 \text{ nm}$) of I (black), II (red), III (blue), and IV (green). A, B, C, D, and E in (a) refer to the Dy^{III} bands. All spectra were collected at room temperature.

assembled around a central and regular Ln_2O_2 parallelogram, with μ -connecting phenoxo oxygen atoms of the ligand. Since all the molecules have a crystallographic inversion center, the molecular point group is C_i with the inversion center in the middle of the parallelogram, which is strictly planar. The phenolate group is not coplanar with the central Ln₂O₂ parallelogram, defining a dihedral angle varying from $45.4(3)^{\circ}$ to $50.7(4)^{\circ}$. Table S2 shows a summary of the most significant bond distances and angles for the studied complexes. The Dy^{III} centers are octacoordinated, with the coordination sphere completed by one pyridyl and one amine nitrogen atoms, three phenoxo oxygens, one oxygen (methanol for I, and N,N'-dimethylformamide for II and III), and a bidentate nitrate ligand. Parts a-c of Figures 1 show the crystal structures of the synthesized complexes. Although the coordination geometry around Dy^{III} is nonregular, a bicapped octahedron is the most accurate description. The methanol molecules which complete the coordination sphere of Dy^{III} centers in I define a rather intimate hydrogen bond with a phenolate oxygen from the neighboring metal center, with D... A of 2.680(4) Å, as shown in Table S3.

The crystal structures of II and III have two very similar but crystalographically nonequivalent molecules of the complexes, subsequently labeled as II-1, II-2, III-1 and III-2. Molecular diagrams for II-2 and III-2 are given as Supporting Information (Figure S1). For I only one crystallographic moiety was detected.

Optical Properties. Solid state absorption spectra and the corresponding analyses are given in the Supporting Information.

Photoluminescence. Figure 2 shows the excitation and emission spectra for Dy^{III} in I–IV. The excitation spectra (Figure 2a), monitoring the emission corresponding to the transition at 575 nm, consist of an intense band centered at 322 (I), 325 (II), 326 (III), and 329 nm (IV) attributed to a transition with π – π * character, between the S₀ and S₁ energy levels of the ligand.²⁹ In addition, the excitation spectra of II and III show several other bands at 360 nm (⁶H_{15/2} \rightarrow ⁶P_{7/2}, $4M_{15/2}$) 386 nm (⁶H_{15/2} \rightarrow ⁴K_{17/2}, ⁴M_{19/2,21/2}, ⁴I_{13/2}, ⁴F_{7/2}), 427 nm (⁶H_{15/2} \rightarrow ⁴F_{9/2}),³⁸ in good agreement with the corresponding diffuse reflectance spectra (Figure S2a). Such bands were not detected in the spectra of the other two complexes.

All emission spectra show characteristic emission bands of Dy^{III} (Figure 2b). No Stark splitting was observed in all the studied Dy^{III} emission spectra. Figure 2b shows that the emission of ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transition is slightly more intense than that arising from the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition. This fact may be due to Dy^{III} ions occupying a low symmetrical environment with an inversion center.³⁹ As shown in Figure 2b, the intensity of the emission bands for I are lower than that for II, the latter having a DMF coordinated instead of methanol as in I. This fact can be explained by the quenching effect of the OH group near to the metal center.

All Dy^{III} spectra also present a rather broad emission in the 380-520 nm region attributed to the ligand. In order to characterize the ligand fluorescence observed in the emission spectra of Dy^{III} complexes, we performed a detailed study of the corresponding Y^{III} complexes (**V**, **VI**, and **VII**) (Figure S3). The emission spectra of Y^{III} complexes show broad bands centered at ca. 440 and 340 nm. The position of the observed bands does not depend on temperature. From Figure S3 we can estimate the triplet and singlet excited states, T₁ and S₁, of the ligands. These are 449 nm (22 258 cm⁻¹) and 344 nm (29 027 cm⁻¹) for **V** and 480 nm (20 830 cm⁻¹) and 350 nm (28 565 cm⁻¹) for **VII**. For **VI** only the triplet excited state T₁ could be determined as 432 nm (23157 cm⁻¹). Figure 3 describes the energy transfer mechanism between the triplet state of the ligands to the ⁴F_{9/2} level of Dy^{III}.



Figure 3. Schematic energy diagram and energy transfer mechanism for I–IV.

According to Latva et al.⁴⁰ one condition for an efficient energy transfer from ligand to metal center is related to the energy gap (ΔE) between the triplet excited state (T_1) and the excited state of Ln^{III} ion. For Dy^{III} ions, $\Delta E[T_1-{}^4F_{9/2}]$ should be between 2500 and 4500 cm⁻¹.⁴¹ For I–IV the $\Delta E[T_1-{}^4F_{9/2}]$ values are 1512, 1554, 2401, and 83 cm⁻¹, respectively. These values are lower than the optimal ligand to metal energy gap for an efficient process as pointed by Xiao et al.⁴¹

Photoluminescence versus Temperature. In order to study the thermal behavior of the emission intensity of the Dy^{III} in compounds I–IV, we performed a series of

luminescence experiments as a function of the temperature. Figure 4 shows the temperature dependence of the emission spectra in the 16–300 K range for I, normalized with respect to the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition intensity. Similar spectra were recorded for III and IV and are presented in Figures S4a,b. In all cases, the bands become more intense as the temperature is lowered. Independent of the temperature, it is possible to observe in the spectra the broad emissions in the 380–520 nm region attributed to the ligands, which become less intense with increasing of temperature.

The luminescence intensity area and ratio between Y (${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$, electric dipole, yellow) and B (${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$, magnetic dipole, blue) for all Dy^{III} complexes, Y/B, are depicted in Figures 5a–c.

Figure 5c shows that only for I a strong variation of the Y/B ratio (1.1 at 16 K to 1.66 at 300 K) is observed, while for the other complexes the ratio remains constant within experimental error in the whole temperature range. These results show that the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ transition is more intense than the ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ transition in I over the entire range of temperature. It is important to bear in mind that I is the only complex with a MeOH in the first coordination sphere, which makes evident the importance of the nature of the coordinated solvent molecules on the emission properties of the studied complexes. In order to explain the observed dependence of the ratio data with temperature, it is possible to assume that the nonradiative decay process induced by the vibration of the OH group of methanol is more thermally dependent compared to that of DMF.

Photoluminescence Lifetime Results and Sensitization. The decay curves at room temperature were fitted with a single and a biexponential functions (Figure S5), being the best results obtained by using the biexponential expression:

$$I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$
(1)

where τ_1 and τ_2 are attenuation times, which determine the decay rate for corresponding exponential components, and A_1 and A_2 are fitting parameters. The average lifetimes were calculated by using the equation:

$$\tau_{\rm AV} = (A_1 \tau_1^2 + A_2 \tau_2^2) / (A_1 \tau_1 + A_2 \tau_2)$$
(2)

The τ and A values at different temperatures are given in Tables S4 and S5. The average lifetime τ_{AV} was calculated to be 8.9(7), 7.6(5), 8.3(6), and 8.1(4) μ s at 16 K and 7.5(7), 8.8(4), 9.1(3), and 8.0(3) μ s at 300 K for I–IV (Table 1). The observed small differences agree with the broadening and splitting of the monitored transitions. The biexponential decay



Figure 4. Dy^{III} emission spectra for I (a) and II (b) from 16 to 300 K. The arrows indicate the temperature variation from 16 to 300 K.



Figure 5. Variation of the integrated area of luminescence intensities against the temperature in I–IV: (a) for ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (B) and (b) for ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$ (Y) transitions, and (c) the Y/B ratio as a function of the temperature. The solid lines in (a) and (b) are used to guides.

Table 1. Photometric Parameters: Experimental Lifetimes τ , Relative Amplitudes A of the Fitted Decay Curves, CIE (x,y) Coordinates, and CCT (K) Values for All Complexes ($\lambda_{exc} =$ 340 nm; $\lambda_{emi} = 575$ nm)

sample	Т	$ \begin{array}{c} au_1 \ (\mu \mathrm{s}) \ (A_1) \end{array} $	$ \tau_{2} (\mu s) \ (A_{2}) $	$ au_{\mathrm{av}}\left(\mu\mathrm{s} ight)$	CIE	CCT (K)
Ι	16	0.40(7)	10.6(2)	8.9(7)	(0.240, 0.255)	21961
		(16.4%)	(83.6%)			
	300	0.27(7)	8.9(5)	7.5(7)	(0.286, 0.317)	8384
		(15.8%)	(84.2%)			
II	16	0.24(2)	9.4(3)	7.6(5)	(0.317, 0.350)	8303
		(20.2%)	(79.8%)			
	300	0.33(2)	11.0(3)	8.8(4)	(0.257, 0.256)	17235
		(20.7%)	(79.3%)			
III	16	0.19(2)	9.8(4)	8.3(6)	(0.289, 0.311)	6142
		(15.9%)	(84.1%)			
	300	0.30(2)	11.1(3)	9.1(3)	(0.302, 0.324)	7189
		(18.1%)	(81.9%)			
IV	16	0.72(1)	8.6(7)	8.1(4)	(0.318, 0.328)	6223
		(12.7%)	(87.3%)			
	300	0.22(2)	9.7(3)	8.0(3)	(0.322, 0.348)	5948
		(17.8%)	(82.2%)			

results indicate that two types of transitions are involved in the observed emissions and have been related by Priya et al.⁴² to the short and longer life times, corresponding to the energy transfer from the ligand to Dy^{III} ions and to the sensitized emission of Dy^{III} , respectively.⁴² As shown in Table 1, the

average τ values for I and II at 16 and 300 K have an inverse thermal dependence, indicating the influence of the coordinated solvent molecule (MeOH versus DMF) on the decay. In contrast, III shows a small variation, while for IV the values are constant within experimental error, illustrating the effect of the substituent on the photophysical properties.

Moreover, the obtained values are comparable to other Dy^{III} compounds reported in the literature, such as $[Dy(2,4'-bpdc)(DMF)_2(NO_3)]_n$ and $\{[Dy(2,4'-bpdc)(1,4-BDC)0.5-(DMF)(H_2O)]\cdot 1.5H_2O\}_n$ (2,4'-H_2bpdc = 2,4'-biphenyldicarboxylic acid, 1,4-H2BDC = 1,4-benzenedicarboxylic acid, DMF = N,N'-dimethylformamide), with average lifetimes of the order of ca. 9.5 μ s.⁴³ However, the obtained values are lower than those reported by Xiao et al.⁴¹ for $[Dy(bipy) (NO_3)_3]_2$; 16.26 μ s at 296 K and 21.07 μ s at 77 K.

CIE Coordinates. CIE 1931 $(x, y)^{36}$ coordinates and color diagram for the Dy^{III} complexes were obtained and are depicted in Figure 6, as a function of temperature, and Table 1 shows the corresponding values at 16 and 300 K. Differences in both CIE 1931 and CCT values could be observed. At room temperature the CIE 1931 color coordinates for I (0.286, 0.317), III (0.302, 0.324), and IV (0.322, 0.348) are close to the NTSC standard value for white color (0.310, 0.316), while the coordinates for II (0.257, 0.256) are shifted to the blue region due to great contribution of ligand emission. For these complexes the CCT values are 8384 (I), 17235 (II), 7189 (III), and 5948 (IV) K.

According to Figure 6a the emission color of I is tunable from light blue to white when the temperature is increased, while for II the emission is tunable from blue to white when the temperature is decreased. The different behavior of these two complexes can be attributed to the different behavior of the emission ligand and metal bands when the temperature is varied. As stated above, this can be explained by the effect of



Figure 6. (a) CIE 1931 chromaticity coordinate diagram for I–IV, with temperature changes from 16 to 300 K and (b) the CCT values as a function of temperature. The arrows indicate the change of temperature from 16 to 300 K.

the coordinated MeOH molecule. Figure 6a also shows that the CIE 1931 coordinates for III and IV do not shift significantly with the temperature, remaining in the white light region. Figure 6b depicts the behavior of the CCT values as a function of temperature for I–IV. The CCT values remain almost unchanged (between 5900 and 7200 K) for III and IV. However, the CCT values for II increase from ca. 8000 K at 20 K to ca. 17 000 K at 300 K, due to the variation of CIE 1931 from white to blue region. The high CCT value at room temperature is due mainly to the contribution of the broad band emission between 375 and 450 nm, and it is not reported in the literature frequently.⁴⁴ However, I possesses an inverse behavior, since at 16 K it presents a CCT value of ca. 22 000 K and at 300 K the CCT value of ca. 8400 K.

It is well established in the literature that the CCT should be greater than 5000 K^{44,45} for cold white light applications for commercial purposes of rare earth luminescent compounds. In this sense, **I**, **III**, and **IV** can be considered as good candidates for white cold light emitters in lightning applications. Besides, nowadays, a search of compounds with extremely high CCT is a new field of research due to the possible applications in the treatment of dementia disease in older people,⁴⁶ or in the wellbeing, functioning and work performance of office workers.⁴⁷ Therefore, the uncommon CCT value (17 235 K) obtained for **II** makes this complex a good candidate.

CONCLUSIONS

The dinuclear Dy^{III} complexes based on the tripodal ligands 2,2'-[[(2-pyridinylmethyl)imino]di(methylene)]-bis(4-R-phenol), where $R = CH_3$, Cl, and CH_3O , exhibit luminescent properties. The Dy^{III} complexes show emissions due to the ligand and the metal center. This fact gives rise to single component white light emitting materials based on Dy^{III} . CIE chromaticity coordinates obtained for the Dy^{III} complexes demonstrate that these materials can be used for white light emitters. The dependence with temperature indicates that I and II show a tunable emission from blue to white and white to blue, respectively. Moreover, III and IV can be considered as white organic light emitting diodes (OLED) in the studied temperature range (16–300 K).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01153.

(PDF)

Accession Codes

CCDC 1902805–1902807 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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