

Organometallic emitting dyes: Palladium(II) Nile Red complexes

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Abstract

The Nile Red dye, H(NR), forms cyclometalated R₂-disubstituted-acetylacetonato square planar Pd(II) complexes (**1–3**; R = CH₃, CF₃, C₆H₅ respectively) whose photophysical properties were tested in cyclohexane, dichloromethane or methanol solutions. In cyclohexane **1–3** emit in the range 580–650 nm with a quantum yield ranging from 0.12 (R = CH₃) to 0.50 (R = CF₃) and lifetimes between 0.88 and 4.46 ns. These complexes form a new family of notably efficient red emitting organometallic dyes which could be of interest for practical applications.

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1. Introduction

Luminescent palladium complexes have been recently proposed for different purposes [1]. Nevertheless, studies concerning the luminescence of Pd(II) complexes at room temperature are not common because most of the palladium compounds suffer from inherent difficulty which hampers an appreciable light emission. This is due to the fact that the lowest-lying excited states of such complexes are usually depleted by thermal population of higher-lying yet thermally accessible metal-centred states (MC) which, geometrically distorted with respect to the ground state, favour a rapid non-radiative deactivation [2]. On the other hand, studies in a rigid matrix at low temperatures allow observation of the luminescence coming from metal-to-ligand charge transfer (MLCT) or ligand-localized (LC) states; this is because thermal population of the MC states is inhibited in these condi-

tions [3]. Some cases of Pd(II) complexes investigated in the solid state have also been reported; however, luminescence was found to originate from intermolecular states produced by pairing interactions in the crystal packing [4].

Recently, we have reported a series of mixed 2-phenylpyridine and 5-substituted-8-hydroxyquinolines Pd(II) complexes which emit in solution at room temperature [5]. In these compounds luminescence arises from an intra-ligand charge-transfer (ILCT) state, which is located at a substantially lower energy with respect to the competing non-emissive MC states (that are therefore not populated). These complexes showed a bluish-green emission and a photoluminescence quantum yield lower than 1%. We have subsequently extended our studies to include other photoluminescent chromophores, and have synthesized a number of organopalladium complexes [6]; among them, the Nile Red derivative, (NR)Pd(acac), **1** in [H(NR) = 9-diethylamino-5H-benzo[a]phenoxazine-5-one, usually reported as Nile Red; H(acac) = acetylacetonate]. Complex **1**,

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partly characterized in dichloromethane solution at room temperature, showed red emission ($\lambda_{\text{em}} = 660$ nm) and a very high fluorescence quantum yield, $\Phi = 0.23$.

In this paper we report the results of an extended investigation carried on **1** and the photophysical properties of two newly synthesized complexes, **2**, (NR)Pd(hfacac) [H(hfacac) = 1,1,1,5,5,5-hexafluoroacetyl acetone] and **3**, (NR)Pd(dpacac) [H(dpacac) = 1,5-diphenylacetylacetone], Chart 1. Remarkably, the obtained results show that the β -diketonato Nile Red cyclometalated Pd(II) complexes form a new family of notably efficient red emitters.

2. Results and discussion

The newly synthesized complexes **2** and **3** were prepared by reacting the cyclopalladated Nile Red acetato-bridged dimer [(NR)Pd(μ -OAc)]₂ with the appropriate β -diketonato ligand and the expected molecular structure (Chart 1) confirmed by mass spectra, IR and ¹H NMR spectroscopies and by elemental analysis (Experimental).

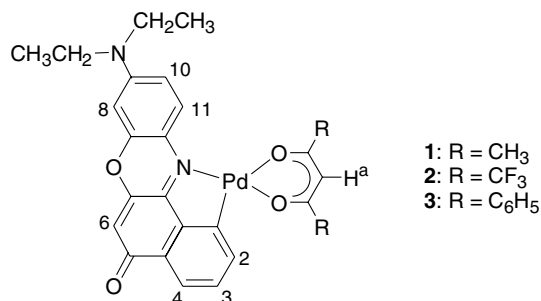


Chart 1.

The photophysical characterization of **1–3** and of the parent ligand **H(NR)** was performed in solution at room temperature (Table 1).

In the absorption spectrum of **2** (Fig. 1), based on comparison with the spectrum for **H(NR)**, we attribute the intense band at 614 nm ($\epsilon = 15,000 \text{ M}^{-1} \text{ cm}^{-1}$) and the 263, 296 and 340 nm features to metal-perturbed LC transitions. It is to notice that the solvatochromism exhibited by the lowest-energy band ($\lambda_{\text{max}} = 588$ nm in cyclohexane, 614 nm in dichloromethane, 618 nm in methanol) is consistent with some degree of CT character for the concerned $\pi\pi^*$ transition (likely involving filled and empty orbitals localized on different aromatic rings) [6]. As for the low-intensity band at 428 nm ($\epsilon = 1770 \text{ M}^{-1} \text{ cm}^{-1}$), absent in the ligand spectrum, the bathochromic shift (from 428 to 452 nm) observed when the 1,1,1,5,5,5-hexafluoroacetylacetone ancillary ligand is replaced by the weaker electron withdrawing acetylacetone group suggests a MLCT assignment [7].

A similar attribution scheme might be proposed for the bands in the electronic spectrum of **3** (Fig. 1). Thus, LC transitions should be responsible for the bands at 258, 325, 364 and 465 nm. For the band at 610 nm, an ILCT character seems likely, based on its solvatochromic behaviour ($\lambda_{\text{max}} = 576$ nm in cyclohexane, 610 nm in dichloromethane, 614 nm in methanol), quite similar to that evidenced by **2**. Finally, the band at 447 nm is ascribed to a MLCT transition (its position is bathochromically shifted with respect to the position of the related band of **2**, but at higher energy with respect to the analogue band of **1**). Interestingly, the absorption band intensities are enhanced by the presence of 1,5-diphenylacetylacetone ancillary ligand.

At room temperature, **2** and **3**, in dichloromethane solution, showed high-yield emission in the red portion of the spectrum (Fig. 2), with an emission maximum at 670 and 660 nm, respectively (Table 1). The solvato-

Table 1
Photophysical data^a of **H(NR)** and **1–3**

| Compound | Solvent | $\lambda_{\text{abs}}^{\text{b}}$ (nm), (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$) | $\lambda_{\text{em}}^{\text{c}}$ (nm) | Φ^{c} (%) | τ^{c} (ns) |
|--------------|-----------------|--|---------------------------------------|-----------------------|------------------------|
| H(NR) | Cyclohexane | 257, 290, 300, 490, 510 | 570, 620* | 60 | 2.95 |
| | Dichloromethane | 262(39,400), 304(9100), 538(42,700) | 602 | 44 | 4.85 |
| | Methanol | 264, 290*, 554 | 638 | 38 | 2.62 |
| 1 | Cyclohexane | 256, 281*, 313, 443*, 465, 534, 578 | 585, 638 | 12 | 0.88 |
| | Dichloromethane | 260(34,900), 296(14,500), 320(12,900), 452(5600), 570*, 608(30,000) | 660 | 23 | 4.6 |
| | Methanol | 260, 296, 322, 455, 590 | 712 | 3 | 1.36 |
| 2 | Cyclohexane | 258, 300*, 360*, 440*, 545, 588 | 595, 650 | 50 | 4.46 |
| | Dichloromethane | 263(12,500), 296(4700), 340(4700), 428(1770), 570*, 614(15,000) | 670 | 35 | 5.95 |
| | Methanol | 264, 305, 340*, 450*, 618 | 705 | 2 | 1.49 |
| 3 | Cyclohexane | 253, 300, 306, 367, 440*, 465, 537, 576 | 587, 636 | 14 | 1.05 |
| | Dichloromethane | 258(67,200), 325(26,700), 364(22,900), 447(9410), 465(9530), 570*, 610(50,100) | 660 | 31 | 4.78 |
| | Methanol | 258, 308*, 348, 460, 614 | 709 | 3.5 | 1.52 |

^a Asterisks indicate shoulders or weak bands.

^b Low solubility in some solvents prevents the accurate determination of ϵ .

^c Excitation performed at 550 nm (for emission spectra) or at 560 nm (for lifetimes); the absorbance at 550 nm of the employed solutions was <0.15.

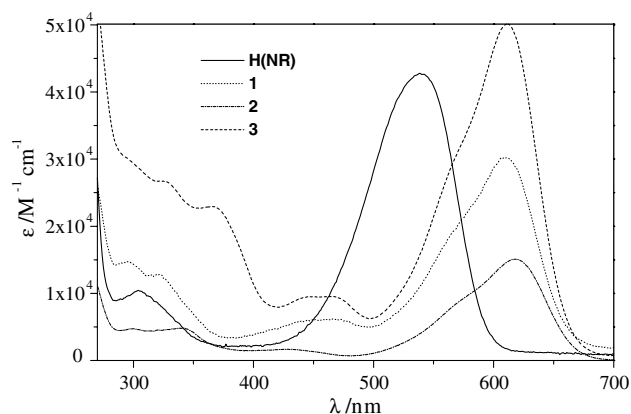


Fig. 1. Absorption spectra of **1–3** and **H(NR)** recorded in dichloromethane solution.

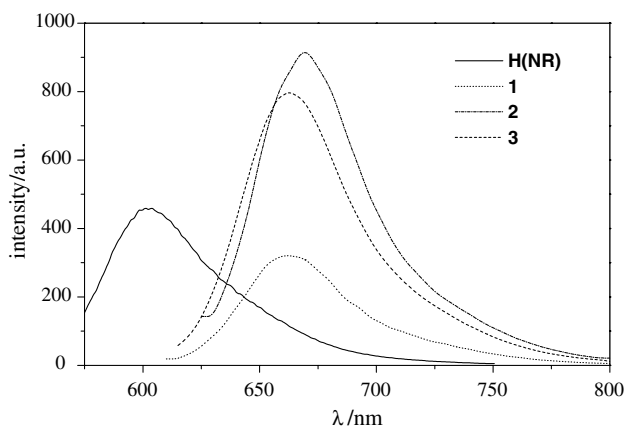


Fig. 2. Emission spectra of **1–3** and **H(NR)** recorded in dichloromethane solution; excitation performed at 550 nm.

chromic behaviour of the emission band (**2**: $\lambda_{em} = 595$ nm in cyclohexane, 670 nm in dichloromethane, 705 nm in methanol; **3**: $\lambda_{em} = 587$ nm in cyclohexane, 660 nm in dichloromethane, 710 nm in methanol), the luminescence lifetime (**2**: $\tau = 5.95$ ns; **3**: $\tau = 4.78$ ns, in dichloromethane solution) and the comparison with the **H(NR)** luminescence features (Table 1) indicate that emission arises from the partially CT $\pi\pi^*$ ligand-localized singlet state. The emission band for **1–3** is bathochromically shifted with respect to the ligand, which is due to the presence of the metal centre; furthermore, this shift increases when electronegative fluorine atoms are present in the β -diketonato chelating ligand.

The particularly high value of fluorescence quantum yield that **1–3** exhibited in solution (Table 1) is related to the photophysical characteristic of the parent Nile Red ligand. The emission spectrum of this dye exhibits shifts to lower energies, upon increasing solvent polarity [8], and in non-polar solvent a notable increase in quantum yield is observed for **2** ($\Phi = 0.50$ in cyclohexane). For the examined complexes, the sensitivity of emission

properties (band shift and quantum yields) to solvent polarity could be explained taking into account the CT character of the emitting state. Actually, CT excited levels are expected to undergo energetic stabilization in polar solvents, which leads to “energy gap law” effects enhancing non-radiative transitions [9].

Regarding the sensitivity of **H(NR)** to the solvent polarity, some authors have proposed the formation of twisted intramolecular charge transfer (TICT) states [10], because the diethylamino group could act as the electron donor group and the quinoid part of the molecule could behave as the electron acceptor [8]. Thus, TICT formation might be involved in the presently investigated compounds even if we could not provide any evidence supporting this hypothesis.

In conclusion, we have shown that the properties exhibited by **H(NR)**, such as red emission, high quantum yield and responsiveness to environmental polarity, are imparted to its square planar Pd(II) complexes **1–3**. This study further indicates that with respect to the CH_3 (**1**) or C_6H_5 (**3**) substituted complexes, in a low-polar solvent as cyclohexane, the presence, on the β -diketonato skeleton, of CF_3 groups (**2**), enhances considerably the fluorescence quantum yield (Table 1). In particular, the value measured for **2** was 50%, which to the best of our knowledge, is the highest reported to date for a Pd(II) complex [11]. Thus, this study proves that complexes **1–3** actually form a new family of efficient red emitting organometallic dyes. Moreover, in spite of the different electronic effects exerted by the groups featuring the ancillary ligand (e.g.: CH_3 in **1**; CF_3 in **2**; C_6H_5 in **3**) the remarkable peculiar features carried by the “(NR)Pd” fragment are preserved. On this basis, this cyclometalated luminophore can be proposed as a versatile moiety that, appended to molecules or macromolecules, confers to them valuable photophysical properties.

3. Experimental

3.1. General procedures

Commercially available chemicals were purchased from Aldrich Chemical Co. and were used without further purification. ^1H NMR spectra were recorded on a Bruker WM-300 (CDCl_3 solutions, Me_4Si internal standard) and IR spectra with a Perkin–Elmer 2000 FT-IR (KBr pellets). Elemental analyses were performed with a Perkin–Elmer 2400 analyzer. The MALDI mass spectra were acquired on a 4700 proteomics analyzer mass spectrometer from Applied Biosystems (Foster City, CA) equipped with a 200 Hz Nd:YAG laser at 335 nm wavelength using 2,7-dimethoxynaphthalene as matrix [12]. The melting points were

determined with a microscope (Zeiss Axioscope) equipped with a Linkam CO 600 heating stage.

Photophysical characterization of the examined compounds was performed at room temperature using spectrofluorimetric grade solvents. Absorption spectra were recorded with a Perkin–Elmer Lambda 900 spectrophotometer; uncorrected emission spectra and excitation spectra (that were found to match the absorption profile) were obtained with a Perkin–Elmer LS 50B spectrofluorimeter, equipped with a Hamamatsu R928 photomultiplier tube. Emission quantum yields were determined using the optically dilute method [13] on aerated solutions and cresyl violet perchlorate in methanol ($\Phi = 0.54$) [14] was the standard. Luminescence lifetimes were obtained with an IBH single-photon counting apparatus equipped with nanoled excitation sources (λ_{exc} was selected 560 nm). The time resolution of the single-photon spectrometer was 0.2 ns. The experimental uncertainty for the band maximum of absorption and luminescence spectra was ± 2 nm, which for the extinction coefficient was within 10%; those for the luminescent intensities and lifetimes were 15% and 8%, respectively.

3.2. Synthesis

Complex **1** was prepared as previously reported [6], similarly **2** and **3** were prepared in MeOH by reacting, in a 1:5 molar ratio, [(NR)Pd(μ -OAc)]₂ [6] with 1,1,1,5,5,5-hexafluoroacetylacetone or 1,5-diphenylacetylacetone at room temperature for six days. Selected analytical data concerning complexes **2** and **3** are:

3.2.1. (NR)Pd(hfacac) (**2**)

Dark blue solid (CHCl₃/MeOH). 61% yield. M.p. > 300 °C. IR (KBr): ν 1020, 1099, 1145, 1210, 1356, 1415, 1472 (sym. C–O acetate), 1590 (asym. C–O acetate), 1637 (C=O ketone), 2985. ¹H NMR (300 MHz, CDCl₃, 298 K, standard TMS): δ 8.34 (d, 1H; H¹¹ $J = 9.25$ Hz), 7.68 (d, 1H, H⁴ $J = 8.15$ Hz), 7.34 (d, 1H, H², $J = 7.39$ Hz), 6.45 (t, 1H, H³, $J_1 = 7.68$, $J_2 = 3.44$ Hz), 6.43 (d, 1H, H¹⁰, $J = 8.88$ Hz), 6.36 (d, 1H; H⁸, $J = 3.02$ Hz), 6.16 (s, 1H, H⁶), 6.14 (s, 1H, H^a), 3.47 (q, 4H, N–CH₂–CH₃), 1.26 (t, 6H, N–CH₂–CH₃). MALDI/TOFMS m/z 630. Anal. Calc. for C₂₅H₁₈N₂O₄F₆Pd: C, 47.60; H, 2.88; N, 4.44. Found: C, 47.56; H, 2.69; N, 4.40%.

3.2.2. (NR)Pd(dpacac) (**3**)

Dark blue solid. 86% yield. M.p. > 300 °C. IR (KBr): ν 1021, 1096, 1121, 1251, 1383, 1451, 1486 (sym. C–O acetate), 1585 (asym. C–O acetate), 1637 (C=O ketone), 2969. MALDI/TOFMS m/z 646. Anal. Calc. for C₃₅H₂₈N₂O₄Pd: C, 64.97; H, 4.36; N, 4.33. Found: C, 65.07; H, 4.52; N, 4.37%. The NMR data are not available because of the low solubility.

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