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Synthesis, crystal structure and optical properties of a series of dipyrrens bearing peripheral coordinating groups and their BODIPYs and Zn(II) complexes

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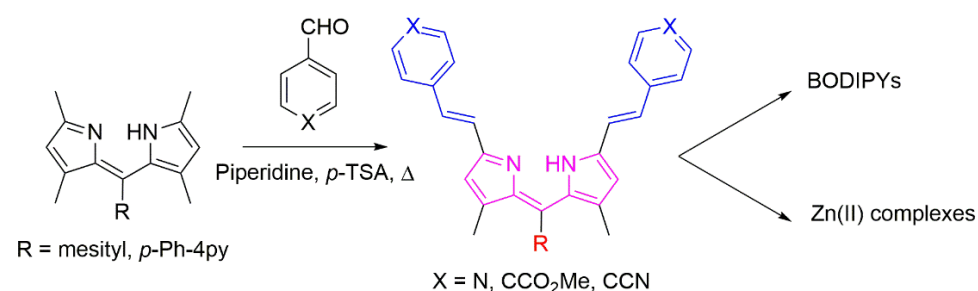
Abstract

A series of dipyrrens bearing peripheral coordinating units has been prepared by Knoevenagel condensation of the appropriate aldehyde with 5-aryl-1,3,7,9-tetramethyldipyrin derivatives (aryl = mesityl or 4-(4-pyridyl)phenyl). Pyridine, benzoic ester and benzonitrile moieties have thus been appended on the bis-pyrrolic backbone *via* vinylic junctions. These compounds have been fully characterized in solution by ¹H-, ¹³C-NMR and UV-Visible spectroscopies, by mass spectrometry and, in the solid state, by single-crystal X-Ray diffraction. For all dipyrrens, an intramolecular hydrogen bond between the two pyrrolic rings and a *trans* organization around the vinylic junctions are observed. The coordination propensity of these ligands has been explored by preparation of the corresponding B(III) and Zn(II) complexes, showing emission in DMF solution.

Keywords

Dipyrren; BODIPY; Zn(II) complexes; Knoevenagel condensation; luminescence.

Graphical abstract



1. Introduction

Over the past two decades, differentiated ligands incorporating several coordinating units have shown their interest in the stepwise construction of heterometallic discrete and infinite architectures [1-6]. With such compounds, coordination of a first metal center affords a metalloligand or metallatecton [7,8] that can be subsequently associated with other metal centers, leading to heterometallic assemblies in a sequential fashion. Among the many coordinating backbones that can be envisioned for further functionalization by additional binding units, dipyrromethene, also known as dipyrin (dpm), is particularly appealing [9-11]. First, under mild basic conditions, this conjugated bis-pyrrolic moiety forms a monoanionic chelate prone to metal binding, yielding a variety of complexes showing catalytic activity [12] or luminescence [13-14], for example. In particular, compounds of the BODIPY type have been extensively investigated for their unique photophysical properties (high quantum yield and tunable emission) [15-18]. Secondly, dpm can also be readily functionalized at the pyrrolic and/or at the *meso* positions to introduce peripheral coordinating sites. Following this strategy, a wide range of metallatectons and assemblies have been described [19-20]. It is worth noting however that this approach has been especially applied using dpm derivatives bearing a coordinating unit solely at the *meso* position [21-27]. Only few examples have described derivatization at pyrrolic sites for the elaboration of metallatectons and heterometallic coordination polymers [28-33]. Recently, our laboratory has reported a dpm equipped with vinyl-benzonitrile groups at positions 1 and 9 and a mesityl unit at position 5 [33], the corresponding BODIPY and its assembly with Ag(I) salts by coordination and Ag- π interactions [34]. Functionalization was performed by Knoevenagel condensation [35] of *p*-cyanobenzaldehyde with dpm **1** (Fig. 1) taking advantage of the slightly acidic nature of methyl groups at the α positions.

In light of this first result, it appeared of interest to develop other ligands and metallatectons as potential building blocks for the construction of heterometallic architectures, modifying the number, position and nature of the peripheral coordinating units. In this contribution, we report the synthesis and characterization of a series of three dpm derivatives bearing pyridyl, benzoic ester or benzonitrile groups at the α -vinyl positions and either a mesityl or a phenylpyridyl moiety at the *meso* position as well as their corresponding B(III) and Zn(II) complexes (Fig. 1).

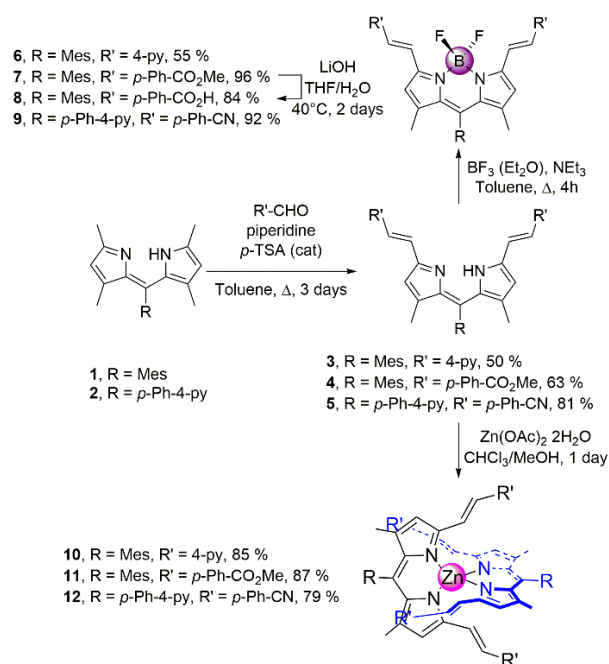


Fig. 1. Synthetic pathway for the preparation of dpms **3-5**, BODIPYs **6-9** and Zn(II) complexes **10-12**.

2. Experimental section

2.1. General

Dipyrin **1** was prepared as described [36]. ¹H- and ¹³C-NMR spectra were recorded at 25 °C on a Bruker AV500 (500 MHz) with the deuterated solvent as the internal reference. NMR chemical shifts and *J* values are given in parts per million (ppm) and in Hertz, respectively. Mass spectrometry was performed by the Service commun d'analyse (University of Strasbourg). UV-visible spectra were recorded on a Perkin Elmer Lambda 650S spectrophotometer using 1.10⁻⁶ M solutions of the compounds. Emission and excitation spectra were recorded on a Perkin Elmer LS 55 spectrometer. Quantum yield were determined using cresyl violet perchlorate as a reference (Φ_s = 0.54 in aerated MeOH solution) [37,38].

2.2 Synthesis

Dipyrin (2): A solution of 4-(formylphenyl)pyridine (2.5 g, 13.6 mmol, 1 eq.) in CH₂Cl₂ (90 mL) was degassed with Ar for 5 min. 2,4-dimethylpyrrole (2.8 mL, 27.3 mmol, 2 eq.) was added, then trifluoroacetic acid (15 drops). The reaction mixture was protected from light and stirred at room temperature under argon for 18h. The resulting orange solution was washed with saturated NaHCO₃ solution with the mixture turning yellow, then with water. The organic layer was dried on MgSO₄, filtered and evaporated. The resulting yellow-brown foam

was dissolved in THF (120 mL), cooled to 0°C and protected from light. A solution of DDQ (3.4 g, 15.0 mmol, 1.1 eq.) in THF (120 mL) was added dropwise and the mixture was stirred at room temperature for 64h. The reaction mixture was concentrated to half volume and the precipitate was dissolved by addition of CH₂Cl₂ and NEt₃ before adsorption on silica for purification by column chromatography (SiO₂, CH₂Cl₂/ NEt₃: 100/1 then CH₂Cl₂/MeOH/ NEt₃: 97/3/1) to afford dipyrin **2** (2.3 g, 48% yield) as a brown solid. δ_{H} (500 MHz, CDCl₃) 13.16 (s, 1H, NH), 8.75 – 8.63 (m, 2H, pyH), 7.75 (d, J = 8.3 Hz, 2H, PhH), 7.64 – 7.56 (m, 2H, pyH), 7.44 (d, J = 8.3 Hz, 2H, PhH), 5.91 (s, 2H, CH₃), 2.36 (s, 6H, CH₃), 1.34 (s, 6H, CH₃). δ_{C} (125 MHz, CDCl₃) 151.99, 150.51, 147.66, 140.24, 139.23, 137.91, 137.82, 136.33, 130.31, 127.15, 121.60, 119.87, 16.18, 14.86. HRMS (ESI): [MH]⁺, found 354.1943. C₂₄H₂₄N₃ requires 354.1965. UV-Vis: λ_{max} (DMF)/nm (ϵ /mol⁻¹.L.cm⁻¹): 449 (35100).

Dipyrin (3): Dipyrin **1** (0.5 g, 1.57 mmol, 1 eq.), 4-pyridinecarboxaldehyde (0.42 g, 3.93 mmol, 2.5 eq.), piperidine (1.5 mL) and *p*-TSA (cat.) were dissolved in distilled toluene (50 mL) under argon. The mixture was stirred at reflux for 3 days. After evaporation under reduced pressure, the residue was purified by column chromatography (SiO₂, CH₂Cl₂/NEt₃: 99/1) affording **3** as a purple solid (0.39 g, 50%). δ_{H} (500 MHz, CDCl₃, 25°C): 8.58 (d, J = 5.5 Hz, 4H, pyH), 7.35 (m, 6H, pyH and C=CH), 7.03 (d, J = 16.2 Hz, 2H, C=CH), 6.93 (s, 2H, PhH), 6.42 (s, 2H, pyrroleH), 2.33 (s, 3H, CH₃), 2.09 (s, 6H, CH₃), 1.37 (s, 6H, CH₃). δ_{C} (125 MHz, CDCl₃, 25°C): 150.44, 150.27, 144.25, 141.42, 139.32, 139.03, 138.50, 135.70, 133.28, 129.32, 129.02, 125.23, 120.98, 119.34, 21.36, 19.82, 14.05. HRMS (ESI): [MH]⁺, 497.2706. C₃₄H₃₃N₄ requires 497.2700. [MH₂]²⁺, 249.1409. C₃₄H₃₄N₄ requires 249.1386. UV-Vis: λ_{max} (DMF)/nm (ϵ /mol⁻¹.L.cm⁻¹): 336 (57600), 557 (39300).

Dipyrin (4): Dipyrin **1** (0.5 g, 1.57 mmol, 1 eq.), methyl 4-formylbenzoate (1.2 g, 7.07 mmol, 4.5 eq.), piperidine (1.5 mL) and *p*-TSA (cat.) were dissolved in distilled toluene (50 mL) under argon. The mixture was stirred under refluxing conditions for 2 days. The resulting mixture was evaporated under reduced pressure and the residue was washed with Et₂O to remove the remaining excess aldehyde. The crude product was purified by column chromatography (SiO₂, CH₂Cl₂/Cyclohexane/NEt₃: 97/2/1) affording **4** as a purple solid (0.6 g, 63%). Single crystals were obtained by *n*-pentane vapor diffusion into a solution of the dipyrin in CHCl₃. δ_{H} (500 MHz, CD₂Cl₂, 25°C): 8.05 (d, J = 8.1 Hz, 4H, PhH), 7.64 (d, J = 8.1 Hz, 4H, PhH), 7.28 (d, J = 16.3 Hz, 2H, C=CH), 7.21 (d, J = 16.3 Hz, 2H, C=CH), 6.98 (s, 2H, PhH), 6.45 (s, 2H, pyrroleH), 3.92 (s, 6H, COOCH₃), 2.35 (s, 3H, CH₃), 2.12 (s, 6H, CH₃), 1.39 (s, 6H, CH₃). δ_{C} (125 MHz, CD₂Cl₂, 25°C): 166.94, 150.91, 141.87, 141.11,

139.59, 138.65, 138.47, 136.03, 130.86, 130.39, 129.79, 129.15, 126.93, 123.81, 119.30, 52.39, 21.33, 19.80, 13.95. HRMS (ESI): $[MH]^+$, 611.2940. $C_{40}H_{39}N_2O_4$ requires 611.2904. UV-Vis: $\lambda_{max}(DMF)/nm$ ($\epsilon/mol^{-1} L cm^{-1}$): 351 (90100), 574 (56700).

Dipyrrin (5): Compound **2** (0.53 g, 1.5 mmol, 1 eq.), 4-cyanobenzaldehyde (0.49 g, 3.75 mmol, 2.5 eq.), piperidine (1.5 mL) and *p*-TSA (cat.) were dissolved in distilled toluene (50 mL) under argon atmosphere. The mixture was stirred under reflux conditions for 3 days. It was then evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2 , $CH_2Cl_2/MeOH/NEt_3$: 97/2/1) affording **5** as a purple solid (0.70 g, 81%). Single crystals were obtained by *n*-pentane vapor diffusion into a solution of the dipyrrin in THF. δ_H (500 MHz, CD_2Cl_2 , 25°C): 8.68 (dd, $J = 4.7$ Hz, $J = 1.6$ Hz, 2H, pyH), 7.83 (d, $J = 8.5$ Hz, 2H, PhH), 7.69 (d, $J = 8.7$ Hz, 4H, PhH), 7.65 (d, $J = 8.7$ Hz, 4H, PhH), 7.63 (dd, $J = 4.7$ Hz, $J = 1.6$ Hz, 2H, pyH), 7.50 (d, $J = 8.5$ Hz, 2H, PhH), 7.29 (d, $J = 16.6$ Hz, 2H, C=CH), 7.16 (d, $J = 16.6$ Hz, 2H, C=CH), 6.51 (s, 2H, pyrroleH), 1.45 (s, 6H, CH_3). δ_C (125 MHz, CD_2Cl_2 , 25°C): 150.78, 150.45, 141.51, 141.32, 140.01, 138.43, 138.38, 138.15, 132.63, 130.14, 130.11, 127.38, 127.06, 124.26, 121.40, 119.37, 118.90, 111.02, 14.80. HRMS (ESI): $[MH]^+$, 580.2481. $C_{40}H_{30}N_5$ requires 580.2496. UV-Vis: $\lambda_{max}(DMF)/nm$ ($\epsilon/mol^{-1}.L.cm^{-1}$): 359 (101800), 575 (57200). IR (ATR): 2218 cm^{-1} (CN).

BODIPY (6): Dipyrrin **3** (0.05 g, 0.10 mmol, 1 eq.) and triethylamine (0.7 mL, 5.0 mmol, 50 eq.) were dissolved in distilled toluene (60 mL) under argon. Then, $BF_3 \cdot Et_2O$ (1.42 g, 10 mmol, 100 eq.) was added dropwise. Under argon atmosphere, the mixture was stirred at reflux and for 4 hours. The reaction was quenched by addition of cold ethanol (100 mL). The resulting mixture was evaporated under reduced pressure and the residue was washed with EtOAc affording BODIPY **6** as a dark solid (30 mg, 55%). δ_H (500 MHz, MeOD- d_4 , 25°C): 8.68 (d, $J = 6.7$ Hz, 4H, pyH), 8.07 (d, $J = 16.0$ Hz, 2H, C=CH), 7.95 (d, $J = 6.7$ Hz, 4H, pyH), 7.58 (d, $J = 16.0$ Hz, 2H, C=CH), 7.12 (s, 2H, PhH), 7.03 (s, 2H, pyrroleH), 2.39 (s, 3H, CH_3), 2.14 (s, 6H, CH_3), 1.55 (s, 6H, CH_3). δ_C (125 MHz, MeOD- d_4 , 25°C): 152.87, 151.33, 146.57, 144.95, 143.91, 141.37, 136.21, 135.74, 133.03, 131.86, 130.70, 127.93, 124.26, 120.90, 21.41, 19.82, 14.07 ppm. HRMS (ESI): $[M+H]^+$, 544.2696. $C_{34}H_{32}BF_2N_4$ requires 544.2719. UV-Vis.: $\lambda_{max}(DMF)/nm$ ($\epsilon/mol^{-1}.L.cm^{-1}$): 339 (131400), 569 (69000), 616 (193300).

BODIPY (7): Dipyrrin **4** (0.27 g, 0.44 mmol, 1 eq.) and triethylamine (3.1 mL, 22 mmol, 50 eq.) were dissolved in distilled toluene (150 mL) under argon atmosphere. Then, $BF_3 \cdot Et_2O$ (6.27 g, 44 mmol, 100 eq.) was added dropwise. The mixture was stirred under reflux and

argon for 4 hours. The reaction was quenched by addition of cold ethanol (300 mL). The resulting mixture was evaporated under reduced pressure and the residue was washed with MeOH affording compound **7** as a dark solid (0.28 g, 96%). Single crystals were obtained by *n*-pentane vapor diffusion into a solution of the BODIPY in CHCl₃. δ_{H} (500 MHz, CD₂Cl₂, 25°C): 8.06 (d, *J* = 8.3 Hz, 4H, PhH), 7.8 (d, *J* = 16.4 Hz, 2H, C=CH), 7.71 (d, *J* = 8.3 Hz, 4H, PhH), 7.33 (d, *J* = 16.4 Hz, 2H, C=CH), 7.02 (s, 2H, PhH), 6.72 (s, 2H, pyrroleH), 3.92 (s, 6H, COOCH₃), 2.36 (s, 3H, CH₃), 2.12 (s, 6H, CH₃), 1.49 (s, 6H, CH₃). δ_{C} (125 MHz, CD₂Cl₂, 25°C): 166.84, 152.27, 142.76, 141.18, 140.63, 139.49, 135.42, 135.09, 133.48, 131.17, 130.51, 130.33, 129.46, 127.58, 121.54, 118.24, 52.44, 21.32, 19.71, 13.84 ppm. HRMS (ESI): [M]⁺, 657.2898. C₄₀H₃₇BF₂N₂O₄ requires 657.2845. UV-Vis.: λ_{max} (CH₂Cl₂)/nm ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 359 (127000), 586 (55900), 635 (156500).

BODIPY (8): To a THF (15 mL) solution of diester **7** (0.1 g, 0.15 mmol, 1 eq.), a H₂O (3 mL) solution of LiOH (0.07 g, 3 mmol, 20 eq.) was added. The mixture was stirred at 40 °C for 2 days before it was evaporated under reduced pressure. The residue was acidified by addition of 37% HCl down to pH = 2 and extracted with AcOEt and water (3 × 50 mL). The organic layers were combined, dried over Na₂SO₄, filtered and evaporated under reduced pressure. The residue was recrystallized in an AcOEt/Cyclohexane mixture affording diacid **8** a dark solid (0.08 g, 84%). δ_{H} (500 MHz, DMSO-*d*₆, 25°C): 13.03 (s, 2H, COOH), 8.02 (d, *J* = 8.4 Hz, 4H, PhH), 7.74 (d, *J* = 8.4 Hz, 4H, PhH), 7.68 (d, *J* = 16.5 Hz, 2H, C=CH), 7.63 (d, *J* = 16.5 Hz, 2H, C=CH), 7.11 (s, 2H, PhH), 7.05 (s, 2H, pyrroleH), 2.34 (s, 3H, CH₃), 2.08 (s, 6H, CH₃), 1.44 (s, 6H, CH₃). δ_{C} (125 MHz, DMSO-*d*₆, 25°C): 166.88, 151.76, 141.67, 140.17, 139.25, 138.65, 135.95, 134.62, 132.42, 130.87, 130.11, 129.45, 128.95, 127.22, 120.12, 118.79, 20.79, 19.13, 13.28. HRMS (ESI): [M]⁺, 629.2498. C₃₈H₃₃BF₂N₂O₄ requires 629.2532. UV-Vis.: λ_{max} (DMF)/nm ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 358 (86900), 585 (40300), 636 (105800). IR (ATR): 2922 cm⁻¹(OH), 1682 cm⁻¹(C=O).

BODIPY (9): Dipyrin **5** (0.1 g, 0.17 mmol, 1 eq.) and triethylamine (1.2 mL, 8.63 mmol, 50 eq.) were dissolved in distilled toluene (65 mL) under argon. Then, BF₃·Et₂O (2.45 g, 17 mmol, 100 eq.) was added dropwise. The mixture was refluxed under argon for 4 hours. The reaction was then quenched by addition of cold ethanol (100 mL). The resulting mixture was evaporated under reduced pressure and the solid was washed with MeOH affording BODIPY **9** as a dark solid (100 mg, 92%). Single crystals were obtained by Et₂O vapor diffusion into a solution of the BODIPY in DMF. δ_{H} (500 MHz, DMSO-*d*₆, 25°C): 8.70 (d, *J* = 5.5 Hz, 2H, pyrH), 8.09 (d, *J* = 8.1 Hz, 2H, PhH), 7.93 (d, *J* = 8.2 Hz, 4H, PhH), 7.87 (d, *J* = 5.5 Hz, 2H,

pyH), 7.80 (d, $J = 8.2$ Hz, 4H, PhH), 7.72 (d, $J = 16.4$ Hz, 2H, C=CH), 7.65 (d, $J = 16.4$ Hz, 2H, C=CH), 7.65 (d, $J = 8.2$ Hz, 2H, PhH), 7.09 (s, 2H, pyrroleH), 1.51 (s, 6H, CH₃). δ_c (125 MHz, DMSO-d₆, 25°C): 162.34, 151.93, 143.93, 142.55, 140.41, 139.22, 136.91, 135.67, 133.22, 133.17, 133.07, 129.69, 128.75, 127.86, 123.58, 120.95, 119.45, 118.85, 111.07, 14.61. HRMS (ESI): [MH]⁺, 628.2495. C₄₀H₂₉BF₂N₅ requires 628.2485. UV-Vis.: λ_{\max} (DMF)/nm ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 361 (75100), 585 (34900), 636 (89600). IR (ATR): 2216 cm⁻¹ (CN).

Zn(II) complex (10): To a CHCl₃ (10 mL) solution of dipyrin **3** (20 mg, 0.04 mmol, 1 eq.), a MeOH (10 mL) solution of Zn(OAc)₂ 2(H₂O) (13 mg, 0.06 mmol, 1.5 eq.) was added. The mixture was stirred at room temperature for 2 days. After evaporation under reduced pressure, the residue was recrystallized from CHCl₃/toluene affording the complex as a dark solid (18 mg, 85%). δ_H (500MHz, DMSO-d₆, 25°C): 8.58 (br s, 8H, pyH), 7.82 (d, $J = 16.1$ Hz, 4H, C=CH), 7.50 (br s, 8H, pyH), 7.27 (d, $J = 16.1$ Hz, 4H, C=CH), 7.03 (s, 4H, PhH), 6.83 (s, 4H, pyrroleH), 2.31 (s, 6H, CH₃), 2.02 (s, 12H, CH₃), 1.27 (s, 12H, CH₃). δ_c (125 MHz, DMSO-d₆, 25°C): 154.91, 150.55, 144.88, 144.37, 144.12, 138.32, 138.017, 135.49, 135.25, 130.38, 129.32, 126.90, 121.18, 119.24. HRMS (ESI): [MH]⁺, 1055.4433 C₆₈H₆₃N₈Zn requires 1055.4462. UV-Vis: λ_{\max} (DMF)/nm ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 339 (32600), 560 (40600), 606 (58100).

Zn(II) complex (11): To a CHCl₃ (10 mL) solution of dipyrin **4** (25 mg, 0.04 mmol, 1 eq.), a MeOH (10 mL) solution of Zn(OAc)₂ 2(H₂O) (14 mg, 0.06 mmol, 1.5 eq.) was added. The solution turned immediately from purple to deep blue and was stirred overnight at room temperature. After evaporation under reduced pressure, the residue was washed with cold MeOH (3x15 mL) and Et₂O (20 mL) and dried in air to afford complex **11** as a dark-blue solid (23 mg, 87% yield). δ_H (500 MHz, CDCl₃, 25°C): 7.81 (d, $J = 8.2$ Hz, 8H, PhH), 7.15 (d, $J = 8.2$ Hz, 8H, PhH), 6.99 (d, $J = 16.0$ Hz, 4H, C=CH), 6.90 (m, 8H, C=CH and PhH), 6.66 (s, 4H, pyrroleH), 3.89 (s, 12H, COOCH₃), 2.34 (s, 6H, CH₃), 1.88 (s, 12H, CH₃), 1.44 (s, 12H, CH₃). δ_c (125 MHz, CDCl₃, 25°C): 166.90, 155.94, 144.56, 143.96, 141.67, 138.78, 138.26, 135.78, 135.25, 131.78, 129.79, 129.10, 128.75, 126.78, 124.21, 118.80, 52.16, 21.32, 19.59, 15.45. HRMS (ESI): [MH]⁺, 1282.4781. C₈₀H₇₄N₄O₈Zn requires 1282.4793. UV-Vis: λ_{\max} (DMF)/nm ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 357 (77800), 578 (82200), 623 (123800).

Zn(II) complex (12): To a CHCl₃ (50 mL) solution of dipyrin **5** (300 mg, 0.52 mmol, 1 eq.), a MeOH (50 mL) solution of Zn(OAc)₂ 2(H₂O) (170 mg, 0.78 mmol, 1.5 eq.) was added. The mixture was stirred at room temperature for 2 days. The resulting mixture was evaporated

under reduced pressure and the residue was recrystallized from a CHCl₃/toluene mixture affording complex **12** as a dark solid (250 mg, 79%). In a test tube, a CHCl₃ (1 mL) solution of dipyrin **5** (0.005 mmol) was layered with a CHCl₃/MeOH (1/1, 2mL) buffer before a solution of Zn(OAc)₂ 2(H₂O) (0.005 mmol) in MeOH (1 mL) was added. After few weeks, single crystals of **12** were obtained. δ_{H} (500 MHz, CDCl₃, 25°C): 8.78 (d, J = 5.1 Hz, 4H, pyH), 7.95 (d, J = 7.9 Hz, 4H, PhH), 7.77 (d, J = 5.1 Hz, 4H, pyH), 7.49 (d, J = 8.1 Hz, 8H, PhH), 7.41 (d, J = 7.9 Hz, 4H, PhH), 7.21 (d, J = 8.1 Hz, 8H, PhH), 6.91 (d, J = 16.3 Hz, 4H, C=CH), 6.84 (d, J = 16.3 Hz, 4H, C=CH), 6.61 (s, 4H, pyrroleH), 1.45 (s, 12H, CH₃). δ_{C} (125 MHz, CDCl₃, 25°C): 156.06, 150.67, 145.28, 143.92, 141.73, 140.27, 139.44, 139.28, 132.53, 131.19, 130.70, 128.00, 127.27, 125.28, 122.07, 119.98, 119.14, 110.97, 16.44. HRMS (ESI): [MH]⁺, 1221.4016. C₈₀H₅₇N₁₀Zn requires 1221.4054. UV-Vis: λ_{max} (DMF)/nm ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$): 358 (60000), 579 (52100), 625 (70200). IR (ATR): 2221 cm⁻¹ (CN).

2.3 X-Ray diffraction

Data were collected on a Bruker SMART CCD diffractometer with Mo-K α radiation. Both structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms [39]. The hydrogen atoms were introduced at calculated positions and not refined (riding model). In the structure of **12**, a CHCl₃ is disordered over two positions that have been modelled accordingly.

CCDC 1903288-19003294 contain the supplementary crystallographic data for compounds **2-5**, **7**, **9** and **12**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Crystal data for **2**: C₂₄H₂₃N₃, M = 353.45, monoclinic, space group $P2_1/n$, a = 7.5682(4), b = 9.8237(5), c = 25.7686(11) Å, β = 95.784(2)°, V = 1906.08(16) Å³, T = 173(2) K, Z = 4, D_c = 1.232 g.cm⁻³, μ = 0.073 mm⁻¹, 21821 collected reflections, 5477 independent (R_{int} = 0.0425), $GooF$ = 1.033, R_1 = 0.0529, wR_2 = 0.1430 for $I > 2\sigma(I)$ and R_1 = 0.0700, wR_2 = 0.1553 for all data.

Crystal data for **3**: C₃₄H₃₂N₄, M = 496.63, orthorhombic, space group $Pbcn$, a = 11.1980(5), b = 12.4554(5), c = 19.3724(8) Å, V = 2702.0(2) Å³, T = 173(2) K, Z = 4, D_c = 1.221 g.cm⁻³, μ

= 0.072 mm⁻¹, 62415 collected reflections, 3995 independent ($R_{\text{int}} = 0.0545$), $Goof = 1.120$, $R_1 = 0.0611$, $wR_2 = 0.1424$ for $I > 2\sigma(I)$ and $R_1 = 0.1110$, $wR_2 = 0.1769$ for all data.

Crystal data for **4**: C₄₀H₃₈N₂O₄, $M = 610.72$, monoclinic, space group Pc , $a = 8.4576(4)$, $b = 24.5157(10)$, $c = 8.0013(3)$ Å, $\beta = 104.099(2)^\circ$, $V = 1609.05(12)$ Å³, $T = 173(2)$ K, $Z = 2$, $D_c = 1.261$ g.cm⁻³, $\mu = 0.081$ mm⁻¹, 36806 collected reflections, 8658 independent ($R_{\text{int}} = 0.0345$), $Goof = 1.048$, $R_1 = 0.0500$, $wR_2 = 0.1235$ for $I > 2\sigma(I)$ and $R_1 = 0.0723$, $wR_2 = 0.1360$ for all data.

Crystal data for **5 (H₂O)**: C₄₀H₂₉N₅O, $M = 595.68$, triclinic, space group $P-1$, $a = 9.3286(4)$, $b = 11.4879(5)$, $c = 14.3862(6)$ Å, $\alpha = 88.789(2)^\circ$, $\beta = 85.395(2)^\circ$, $\gamma = 87.817(2)^\circ$, $V = 1535.37(11)$ Å³, $T = 173(2)$ K, $Z = 2$, $D_c = 1.288$ g.cm⁻³, $\mu = 0.079$ mm⁻¹, 37270 collected reflections, 8290 independent ($R_{\text{int}} = 0.0294$), $Goof = 1.059$, $R_1 = 0.0657$, $wR_2 = 0.1823$ for $I > 2\sigma(I)$ and $R_1 = 0.0891$, $wR_2 = 0.2009$ for all data.

Crystal data for **7**: C₄₀H₃₇BF₂N₂O₄, $M = 658.52$, monoclinic, space group $P2_1/n$, $a = 11.0795(8)$, $b = 12.8631(9)$, $c = 23.4751(17)$ Å, $\beta = 95.628(2)^\circ$, $V = 3329.5(4)$ Å³, $T = 173(2)$ K, $Z = 4$, $D_c = 1.314$ g.cm⁻³, $\mu = 0.092$ mm⁻¹, 39967 collected reflections, 9790 independent ($R_{\text{int}} = 0.0621$), $Goof = 1.016$, $R_1 = 0.0609$, $wR_2 = 0.1350$ for $I > 2\sigma(I)$ and $R_1 = 0.1151$, $wR_2 = 0.1623$ for all data.

Crystal data for **9**: C₄₀H₂₈BF₂N₂, $M = 627.48$, monoclinic, space group $C2/c$, $a = 8.6255(5)$, $b = 28.0408(17)$, $c = 13.8261(7)$ Å, $\beta = 105.3130(10)^\circ$, $V = 3225.3(3)$ Å³, $T = 173(2)$ K, $Z = 4$, $D_c = 1.292$ g.cm⁻³, $\mu = 0.085$ mm⁻¹, 28446 collected reflections, 4734 independent ($R_{\text{int}} = 0.0455$), $Goof = 1.015$, $R_1 = 0.0541$, $wR_2 = 0.1369$ for $I > 2\sigma(I)$ and $R_1 = 0.0938$, $wR_2 = 0.1615$ for all data.

Crystal data for **12 (CHCl₃)₂**: C₈₂H₅₈Cl₆N₁₀Zn, $M = 1461.45$, triclinic, space group $P-1$, $a = 13.8475(6)$, $b = 13.9105(5)$, $c = 20.9147(9)$ Å, $\alpha = 75.296(3)^\circ$, $\beta = 83.923(2)^\circ$, $\gamma = 65.307(2)^\circ$, $V = 3540.4(3)$ Å³, $T = 173(2)$ K, $Z = 2$, $D_c = 1.371$ g.cm⁻³, $\mu = 0.627$ mm⁻¹, 69454 collected reflections, 19122 independent ($R_{\text{int}} = 0.0925$), $Goof = 1.020$, $R_1 = 0.0805$, $wR_2 = 0.2067$ for $I > 2\sigma(I)$ and $R_1 = 0.2140$, $wR_2 = 0.2592$ for all data.

3. Results and discussion

The first class of ligands incorporates a mesityl group at the *meso* position and either pyridyl or methyl-benzoate units at the vinylic positions. Thus, reaction of dipyrin **1**, prepared as described [36], with 4-pyridinecarboxaldehyde or methyl 4-formylbenzoate in the presence of piperidine and a catalytic amount of *p*-toluenesulfonic acid (*p*-TSA) afforded dpms **3** and **4** in

50 and 63% yield respectively (Fig. 1). It was then envisioned to functionalize positions 1 and 9 as well as 5. To that aim, the starting derivative **2** bearing a phenyl-pyridyl group at the *meso* position was prepared, in 48% yield, by reaction of 4-formylphenylpyridine with 2,4-dimethylpyrrole in the presence of trifluoroacetic acid as catalyst, followed by oxidation with DDQ. Condensation of **2** with *p*-cyanobenzaldehyde gave dpm **5** in 81% yield. All new dpms have been characterized in solution by ^1H and ^{13}C -NMR, UV-Visible spectroscopy in DMF (*vide infra*) and high-resolution mass spectrometry. For all compounds, the *trans* organization of the hydrogen atoms of the vinyl groups was confirmed by the value of the corresponding coupling constant ($J_{\text{H-H}} = 16.3\text{-}16.6\text{ Hz}$) in the ^1H -NMR spectra recorded in CDCl_3 or CD_2Cl_2 solution.

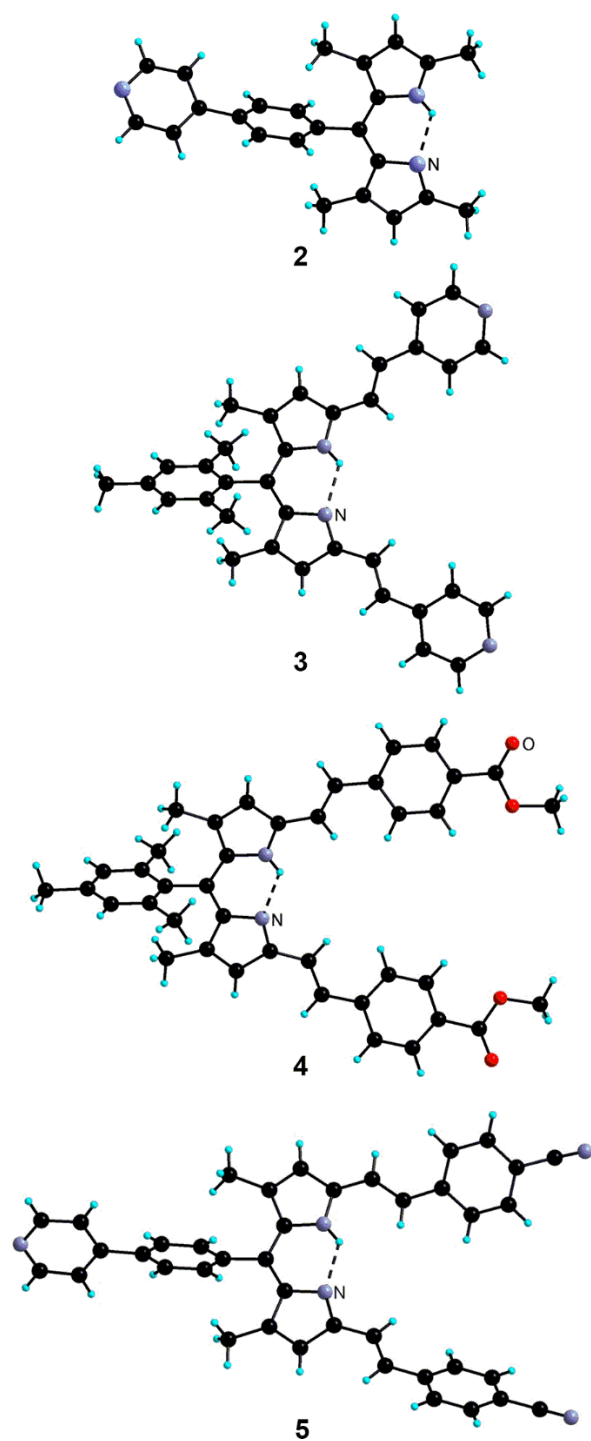


Fig. 2. Crystal structures of dpm 2-5. Solvent molecules have been omitted for clarity.

This is further confirmed in the crystal structure of ligands **3-5** determined by single-crystal X-Ray diffraction (Fig. 2). Crystals of intermediate dpm **2** (Monoclinic $P2_1/n$) were isolated by slow evaporation of a MeOH solution, while crystals of dpm **3** (Orthorhombic $Pbcn$) and **4** (Monoclinic Pc) were obtained by slow diffusion of *n*-pentane vapour into a concentrated CHCl_3 solution of the respective compound. Upon *n*-pentane vapour diffusion into a

concentrated THF solution of **5**, crystals of hydrate (**5**)(H₂O) (Triclinic *P*-1) were obtained. For all four dipyrins, an intramolecular hydrogen bond is observed between the two pyrrolic rings ($d_{N-H\cdots N} = 2.623\text{--}2.660\text{ \AA}$, $\alpha_{N-H\cdots N} = 124.9\text{--}126.4^\circ$) that are almost coplanar. Also, for dpms **2**–**5**, the *meso* group (mesityl or phenyl) is almost perpendicular to the bis-pyrrolic system ($83.2\text{--}89.30^\circ$). Noticeably, for compound **5**, one vinylic group points inward while the other points outward with respect to the dipyrin backbone (Fig. 2) at variance with the other two Knoevenagel condensation products **3** and **4** and what has been reported for the analogue bearing a mesityl at the *meso* position [33].

Reaction of dpms **3**–**5** with an excess of BF₃ Et₂O in toluene in the presence of NEt₃ afforded the corresponding BODIPYs in 92 to 96% yield. BODIPY **8** bearing peripheral benzoic acid was prepared by saponification of the ester analogue **7** with LiOH in a THF/H₂O mixture in 84% yield. All four BODIPYs **6**–**9** were characterized in solution by ¹H- and ¹³C-NMR, UV-Visible and fluorescence spectroscopies (*vide infra*), high-resolution mass spectrometry and, in the solid state, by single-crystal X-Ray diffraction for compounds **7** and **9** (Fig. 3). Crystals of **7** (Monoclinic *P*2₁/*n*) and **9** (Monoclinic *C*2/*c*) were obtained by Et₂O vapor diffusion in a solution of the compound in CHCl₃ or DMF respectively. For both compounds, the boron center is in a tetrahedral environment, bound to the nitrogen atoms of the dipyrinato chelate ($d_{B-N} = 1.537(2)\text{--}1.548(3)\text{ \AA}$) and to two fluoride anions ($d_{B-F} = 1.382(3)\text{--}1.394(3)\text{ \AA}$) as usually observed for such complexes. Interestingly, the arrangement of the two vinyl-benzonitrile units in **9** is the same and similar to other reported BODIPYs incorporating these functional groups [40–42], unlike what is observed for the free ligand **5** (Fig. 2).

Reaction of dpms **3**–**5** with Zn(OAc)₂ 2(H₂O) in a CHCl₃/MeOH (1/1) mixture afforded the corresponding complexes **10**–**12** in 79 to 87 % yield. In light of the observed poor solubility of diacid BODIPY **8**, the saponification of tetraester **11** was not further pursued. The compounds have been characterized in solution by ¹H- and ¹³C-NMR and UV-Visible spectroscopies as well as by mass spectrometry. Crystals of **12** (CHCl₃)₂ (Triclinic *P*-1) were obtained by slow diffusion of a MeOH solution of Zn(OAc)₂ 2(H₂O) into a CHCl₃ solution of ligand **5**. The Zn(II) cation is coordinated to four nitrogen atoms ($d_{Zn-N} = 1.967(3)\text{--}1.976(3)\text{ \AA}$) of two bis-pyrrolic chelates that form an angle of 62.9° . This deviation from a perfect tetrahedral coordination environment is more important than usually observed for this type of complexes [40,43–44], and may result from packing effects, since no interaction could be identified to be specifically responsible for this organization. As for the BODIPY analogue **9**, the vinylic groups are all pointing outward, unlike in the structure of the free dpm **5**.

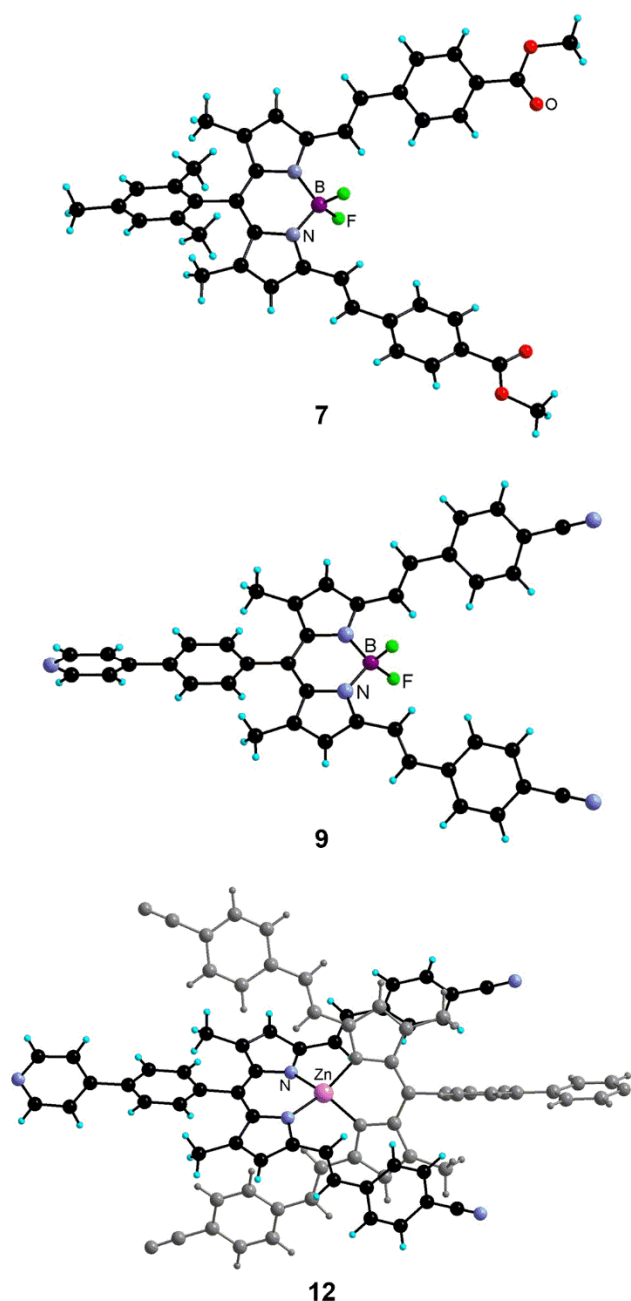


Fig. 3. Crystal structures of BODIPYs **7** and **9** and of Zn(II) complex **12**. For the latter, one of the two ligands is represented in grey. Solvent molecules have been omitted for clarity.

The optical properties of dpms **1-5** have been studied in DMF solution by UV-Visible spectroscopy. All three Knoevenagel adducts feature two strong absorption bands centered around 330-350 nm and 560-580 nm (Table 1, Fig. 4). The high energy band is attributed to the π - π^* transition of the styryl group whereas the low energy one corresponds to the π - π^* transition of the bis-pyrrolic backbone. The latter is bathochromically shifted with respect to the starting dpms **1** and **2** (transition centred around 447-449 nm), owing to the increased conjugation. The nature of the *meso* group does not impact strongly the absorption

wavelength as demonstrated by the comparison of **1** with **2** as well as when comparing **5** with the reported mesityl appended analogue [33]. This is consistent with the limited conjugation between this group and the bis-pyrrolic chromophore, highlighted by the almost perpendicular relative arrangement of these two fragments in the crystalline state (Fig. 2). In contrast, the nature of the styryl-like moiety has an influence as shown by the blue shift observed between the absorption of dpms **3** and **4** resulting from the presence of the pyridyl units. Interestingly, though they present different functional groups at both the *meso* and vinylic positions, dpms **4** and **5** have rather similar absorption features in DMF.

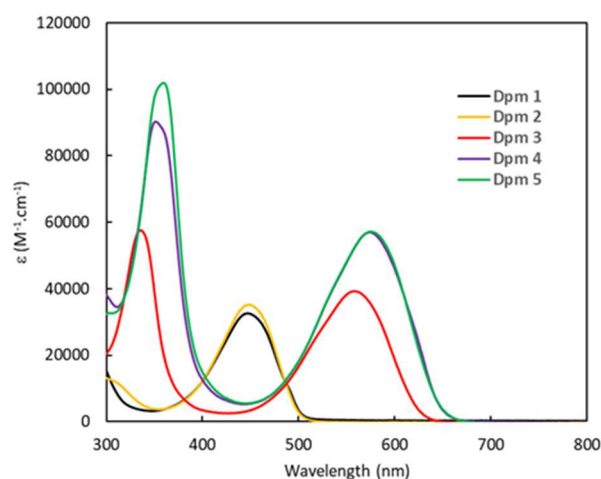


Fig. 4. Absorption spectra of dpms **1-5** in DMF solution at room temperature.

The optical properties of BODIPYs **6-9** and Zn(II) complexes **10-12** were also studied in DMF solution (Table 1, Fig. 5 and 6). For both categories of compounds, three absorption bands are observed that can be attributed to the same transitions as for the free ligands (*vide supra*). Upon excitation at 570 nm, two emission bands are observed for the four BODIPYs **6-9**, that are mirror of the S_0 - S_1 absorption bands. As for the free dpms, a blue shift is observed owing to the presence of pyridyl groups on the vinylic fragment for **6** (Table 1). The quantum yield, Φ_f , for the four BODIPYs was determined using cresyl violet perchlorate as a reference, since it emits in the same region with a comparable Φ_f [37-39]. Compound **6** shows the highest Φ_f resulting from the presence of the electron-withdrawing pyridyl groups. In contrast, saponification of the ester groups results in a less emissive species as seen when comparing **7** and **8** (Table 1). Additionally, the presence of a more freely rotating phenyl-pyridyl group at the *meso* position in **9** results in a lower Φ_f in comparison with the mesityl-appended analogue [33]. This is in agreement with the rotation of the *meso* unit being a favourable non-radiative deactivation pathway [46-49].

Table 1. Optical properties of dpms **1-5** and of BODIPYs **6-9** and Zn(II) complexes **10-12** in DMF, at room temperature.

	$\lambda_{\text{abs}}/\text{nm}$ ($\epsilon/10^3 \text{ M}^{-1}.\text{cm}^{-1}$)	$\lambda_{\text{em}}/\text{nm}^a$	Φ_f^b
1	447 (32.6)		
2	449 (35.1)		
3	336 (57.6), 557 (39.3)		
4	351 (90.1), 574 (56.7)		
5	359 (101.8), 575 (57.2)		
6	339 (131.4), 569 (69.0), 616 (193.3)	626, 684	0.87
7	359 (127.0), 586 (55.9), 635 (156.5)	646, 707	0.71
8	358 (86.9), 585 (40.3), 636 (105.8)	646, 707	0.43
9	361 (75.1), 585 (34.9), 636 (89.6)	648, 709	0.59
10	339 (32.6), 560 (40.6), 606 (58.1)	620, 674	0.14
11	357 (77.8), 578 (82.2), 623 (123.8)	645, 704	
12	358 (60.0), 579 (52.1), 625 (70.2)	647, 710	

^a BODIPYs and Zn(II) complexes have been excited at 570 and 580 nm respectively.

^b using Cresyl Violet perchlorate as reference ($\Phi_s = 0.54$ in MeOH, aerated solution).

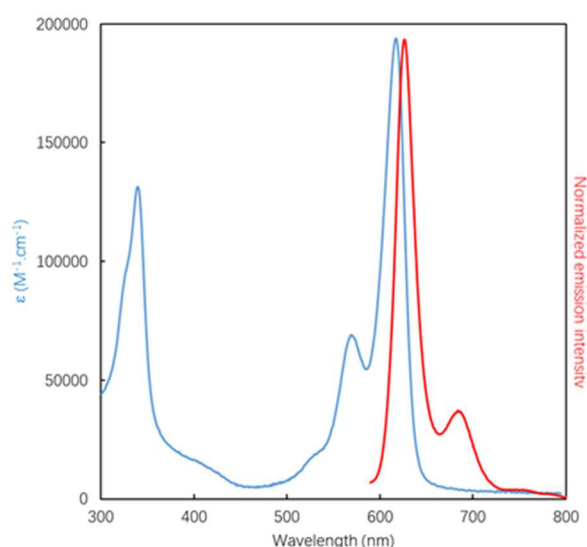


Fig. 5. Absorption and emission spectra of BODIPY **6** in DMF solution at room temperature, upon excitation at 570 nm.

Similar absorption and emission bands with the same trends as for the BODIPYs are measured for complexes **10-12** (Table 3 and Fig. 6). As a representative example, the quantum yield was determined for complex **10** bearing pyridyl groups (Table 1) and it is strongly lowered when compared with the BODIPY analogue **6** ($\Phi_f = 0.14$ vs 0.87) as expected for homoleptic compounds in a polar solvent such as DMF [40,43-44,50-51]. It worth noting that the Stokes shift for the Zn(II) complexes is much larger than for the

BODIPY derivatives *ca.* 20-22 nm vs 10-12 nm, as observed for analogous systems [9, 15-16, 43-44].

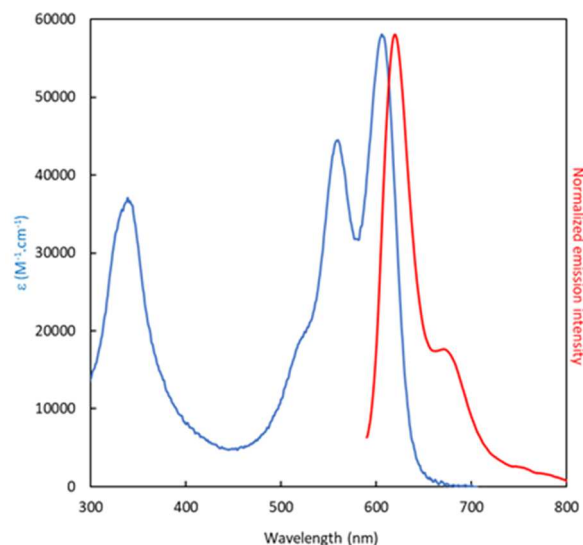


Fig. 6. Absorption and emission spectra of Zn(II) complex **10** in DMF solution at room temperature, upon excitation at 580 nm.

4. Conclusions

In conclusion, using the Knoevenagel condensation, a series of dipyrins bearing peripheral coordinating units has been prepared in good yields, by reaction of the appropriate aldehyde with 5-aryl-1,3,7,9-tetramethyldipyrin derivatives (aryl = mesityl or 4-(4-pyridyl)phenyl). Two types of differentiated ligands have been thus designed and prepared. The first one bears either pyridyl or benzoic ester moieties at the resulting vinylic positions and a non-coordinating mesityl group at the *meso* position. The second one is functionalized by vinyl-benzonitrile units at positions 1 and 9 and a phenyl-pyridyl group at position 5, hence comprising three different kinds of coordinating sites. These compounds have been fully characterized in solution by ^1H -, ^{13}C -NMR and UV-Visible spectroscopies, by mass spectrometry and, in the solid state, by single-crystal X-Ray diffraction. For all compounds, an intramolecular hydrogen bond between the two pyrrolic rings and a *trans* organization around the vinylic junctions were observed.

The coordination of these ligands has been explored by preparation of the corresponding BODIPY and Zn(II) complexes upon reaction with $\text{BF}_3(\text{Et}_2\text{O})$ or $\text{Zn}(\text{OAc})_2 \cdot 2(\text{H}_2\text{O})$ respectively. These species have been characterized in solution by standard analytical techniques. In particular, the crystal structure of BODIPYs **7** and **9** and Zn(II) analogue **12** has been determined by X-Ray diffraction showing the tetrahedral coordination environment of

the B(III) and Zn(II) centers. Furthermore, the photophysical properties of these complexes have been investigated in DMF solution demonstrating that the BODIPYs are, as expected, better emitters than the homoleptic Zn(II) based compounds.

These dipyrins and their complexes represent an interesting class of differentiated ligands and luminescent metallatectons that can be envisioned for the construction of coordination assemblies. These aspects are currently under study in our laboratory.

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Supplementary data

CCDC 1903288-19003294 contain the supplementary crystallographic data for compounds **2-5**, **7**, **9** and **12**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

¹H- and ¹³C-NMR as well as mass-spectra of compounds **2-12** are presented in the supplementary material.

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Highlights

- A series of dipyrins with peripheral coordinating units was prepared by Knoevenagel condensation.
- An intramolecular hydrogen bond between the two pyrrolic rings was observed in the solid state.
- A *trans* organization around the vinylic junctions was observed by ^1H -NMR and X-ray crystallography.
- The corresponding luminescent BODIPY and Zn(II) complexes were prepared.
- In DMF solution, the BODIPYs are better emitters than the homoleptic Zn(II) complexes.