Synthesis and characterisation of D–π–D type Schiff base ligands derived from fluorene and 1,10-phenanthroline and its complexes with ruthenium(II)

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A fluorene derivative, 9*H*-fluoren-9-one(diphenylmethylene)hydrazone has been synthesised from the reaction of 4,5-diazafluoren-9-one with benzophenone hydrazone and a 1,10-phenanthroline derivative, N-[(1E,2E)-3-phenylprop-2-en-1-ylidene]-1,10-phenanthrolin-5-amine has been synthesised from the reaction of 5-amino-1,10-phenanthroline with cinnamaldehyde. Ru(II) complexes of these ligands have been prepared and characterised.

Keywords: Schiff base, D–π–D, complex, fluorene, 1,10- phenanthroline

Schiff bases are often used as ligands in coordination chemistry because their complexes are of considerable interest due to their biological activity,[1,2] catalytic activity,[3,4] ability to reversibly bind oxygen [5] and photochromic properties.[6]

Fluorene compounds have been regarded as excellent fluorescent materials because of their ability to achieve high thermal stability as well as high photoluminescence efficiency.

Recently, substituted fluorene derivatives have been extensively explored in the field of optoelectronics and molecular electronics.[7]

1,10-phenanthroline is a ligand with wide coordination ability and its complexes play a vital role in both analytical and preparative coordination chemistry. As a building block, the 1,10-phenanthroline unit plays an important role in the development of supramolecular chemistry.[8,9]

Ruthenium(II) complexes with polypyridyl ligands have attracted considerable attention, due to a combination of easily constructed rigid chiral structures spanning all three spatial dimensions and a rich photophysical repertoire. In general, ruthenium (II) complexes can bind to DNA in a noncovalent interaction.[10-15] Ruthenium (II) bipyridyl complexes have been extensively studied as a result of their remarkable chemical stability and photophysical properties.[16] These complexes have been used in a wide variety of applications such as solar energy related research, sensors and switches and therapeutic agents.[17-19] Several ruthenium complexes have been reported to be promising as anticancer drugs.[20]

In the present study, we report the synthesis and characterisation of new conjugated Schiff base ligands (D–π–D type), including fluorene and 1,10-phenanthroline units and their Ru(II) complexes. These novel compounds have been characterised by elemental analyses, FTIR, UV-Vis, ^{1}H NMR, MS (LC-MS), TGA-DSC and fluorescence spectra.

Experimental

Measurements and materials

The FTIR spectra were recorded as KBr disks on a Perkin Elmer Spectrum One Bv 5.0 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian UNITY INOVA 500 MHz (DMSO-d$_6$) spectrometer. Mass spectra (LC-MS) were determined on a Finnigan LCQ Advantage MAX spectrometer. Absorption spectra were recorded on an Agilent 8453 UV-visible spectrophotometer. Elemental analyses were determined on a Thermo Finnigan Flash EA 112 instrument. TGA-DSC curves were obtained with a TA SDT Q 600 thermal analyser apparatus using flowing nitrogen gas 100 mL min^{-1}, temperature range 50–1200 °C, at a heating rate of 10 °C min^{-1}. Melting points were obtained with a Büchi Melting point B-540 apparatus in open capillaries. All chemicals were of the highest grade available. The reagent-grade reactants and solvents were used as received from chemical suppliers.

Syntheses

The starting compounds, 4,5-diazafluoren-9-one, 5-amino-1,10-phenanthroline and $[RuCl_2(bpy)_2]\cdot 2H_2O$ were prepared using reported procedures.[21-24]

Synthesis of 9H-fluoren-9-one(diphenylmethylene)hydrazone **(1):** A solution of 4,5-diazafluoren-9-one (0.182 g, 1.00 mmol) in dry ethanol (30 mL) was added to a solution of benzophenone hydrazone (0.196 g, 1.00 mmol) in dry ethanol (30 mL). and the reaction mixture was heated to 60–65 °C under argon for 16 hours with constant stirring. The reaction mixture was cooled down to room temperature and the solvent was removed by using a rotary evaporator under vacuum. The residue was recrystallised from methanol in a few days to give yellow crystals, which were filtered off and dried. Yield 68%, m.p. 183 °C. FTIR (KBr): 3046–3052 (ArCH, w), 1594 (HC=N$_{fluorene}$, s), 1577 (C=N, s). ^{1}H NMR (CDCI$_3$-d$_6$): δ 8.7–7.7 (m, 6H, Ar$_{fluorene}$-H), 7.5–7.1 (m, 10H, ArH). (LC-MS) *m/z*: 361.25 (M + 1, 100%), (360.41 g/mol). Anal. Calcd for $C_{24}H_{16}N_4$: C, 80.00; H, 4.44; N, 15.55. Found: C, 79.90; H, 4.70; N, 15.62%.

Synthesis of N-[(1E,2E)-3-phenylprop-2-en-1-ylidene]-1,10-phenanthrolin-5-amine **(2):** A solution of 5-amino-1,10-phenanthroline (0.195 g, 1.00 mmol) in dry ethanol (30 mL) was added to a solution of cinnamaldehyde (0.13 mL, 1.00 mmol) in dry ethanol (30 mL). The reaction mixture was heated to 60–65 °C under argon for 10 hours with constant stirring. The reaction mixture was cooled down to room temperature and the solvent was removed by using a rotary evaporator under vacuum. The oily residue was dissolved in a small amount of methanol. After distilled water was added to this solution, a yellow precipitate was obtained, which was filtered off and dried. Yield: 56%, m.p. 145 °C. FTIR (KBr): 3024–3032 (ArCH, w), 2926 (–CH–, m), 1627 (H-C=N$_{phen}$, s), 1608 (HC=N, s) cm^{-1}. ^{1}H NMR (CDCI$_3$-d$_6$): δ 8.6 (s, 1H, HC=N) (disappeared with D$_2$O), 9.0–8.2 (m, 7H, Ar$_{phen}$-H), 7.7–6.9 (m, 5H, ArH), 4.8–4.4 (m, 2H, CH). (LC-MS) *m/z*: 310.41 (M + 1, 100%), $C_{21}H_{15}N_3$ (309.36 g/mol). Anal. Calcd For: C, 81.29; H, 5.16; N, 13.54. Found: C, 81.53; H, 5.22; N, 13.58%.

Ru(II) complex of **(1):** A mixture of **(1)** (0.02 g, 0.055 mmol) and $[RuCl_2(bpy)_2]\cdot 2H_2O$ (0.018 g, 0.055 mmol) was heated at reflux in dry ethanol (30 mL) for 4 h under an argon atmosphere. After the solution was cooled, it was diluted with distilled water (50 mL), and treated with an excess of potassium hexafluorophosphate (KPF$_6$). An orange solid was precipitated which was filtered off, washed with diethyl ether and water. Yield 56%; m.p.198–200 °C. FTIR (KBr): 1632 (HC=N$_{fluorene}$), 1578 (C=N), 840 (PF$_6$) cm^{-1}. ^{1}H NMR (500 MHz, ppm, CDCI$_3$): δ 8.6–8.4 (m, 6H, Ar$_{fluorene}$-H), 8.1–8.0 (m, 8H, bpy-H) 7.7–7.6 (m, 10H, ArH). ES-Ms (MeOH): *m/z* 774.51 [M + 1], 918.82 [M–PF$_6$]$^+$, 1063.77 [M–2PF$_6$]$^{2+}$

Ru(II) complex of **(2):** A mixture of **(2)** (0.020 g, 0.064 mmol) and $[RuCl_2(bpy)_2]\cdot 2H_2O$ (0.021 g, 0.064 mmol) was heated to reflux in dry ethanol (30 mL) for 4 hours under an argon atmosphere. After the solution was cooled, it was diluted with distilled water (50 mL), and treated with an excess of potassium hexafluorophosphate (KPF$_6$). A red-brown solid was precipitated which was filtered off, washed with diethyl ether and water. Yield 52%; m.p. 286–288 °C. FTIR (KBr): 1637 (H–C=N$_{phen.}$), 1608 (HC=N), 837 (PF$_6$). ^{1}H NMR (500 MHz, ppm, CDCI$_3$) 8.7–8.5 (m, 7H, Ar$_{phen}$–H), 8.2–8.0 (m, 8H, bpy–H) 7.8–7.6 (m, 5H, ArH), 4.4–3.9 (m, 2H, CH). ES-Ms (MeOH): *m/z* 723.93 [M + 1], 867.12 [M-PF$_6$]$^+$, 1012.78 [M-2PF$_6$]$^{+2}$.

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Results and discussion

The new fluorene **(1)** and 1,10-phenanthroline **(2)** ligands have been synthesised from the reaction of 4,5-diazafluoren-9-one and 5-amino-1,10-phenanthroline with benzophenone hydrazone and cinnamaldehyde in good yield, as shown in Figs 1 and 2. Their ruthenium complexes have synthesised and isolated as the hexafluorophosphate salts (Figs 3 and 4).

IR spectra

In the FTIR spectra of **(1)** and **(2)**, C=N characteristic stretching vibration bands of the fluorene, 1,10-phenanthroline and azomethine groups showed at 1594, 1627 and 1577, 1608 cm^{-1}, respectively. The stretching band of the $-NH_2$ group in the benzophenone hydrazone and C=O in the fluorene groups disappeared in the IR spectrum of **(1)**, and the stretching bands of the $-NH_2$ group in 1,10-phenanthroline and C=O group in cinnamaldehyde disappeared in the IR spectrum of **(2).** This indicates that the condensation reaction has occurred. In the IR spectra of the complexes, the fluorene and 1,10-phenanthroline stretching bands (C=N) at 1594 and 1627 cm^{-1} shift to the higher frequencies 1632 and 1637 cm^{-1}, suggesting the coordination of nitrogen to the metal ions as shown in Figs 3 and 4. The Schiff base C=N stretching bands appear at 1577 and 1608 cm^{-1} for the free ligands; in the complexes, these bands occur in approximately the same range, showing that the nitrogen atom of the $C=N_{azomethine}$ group is not coordinated to the metal ions.

^{1}H NMR spectra

The ^{1}H NMR spectrum of **(1)** and **(2)** were recorded in $CDCl_3$-d_6 solution. The ^{1}H NMR spectrum of **(2)** confirmed the proposed structure showing a D_2O-exchangeble proton at 8.6 ppm as a singlet peak for the HC=N group. The fluorene of **(1)** and 1,10-phenanthroline of **(2)** protons appeared at 8.7–7.7 and 9.0–8.2 ppm as multiplets and phenyl protons at 7.5–7.1, 7.7–6.9 ppm as multiplets, respectively. The bipyridine rings protons appeared at 8.0–8.1 ppm as a multiplet. The Ru(II) complexes of **(1)** and **(2)** give well-defined ^{1}H NMR spectra, which permit unambiguous identification and assessment of purity. The chemical shifts of the signals of the Ru(II) complexes **(1)** and **(2)** are quite similar to those of the free ligands, with the sole exception of fluorene protons and 1,10-phenanthroline protons that move high field due to the diamagnetic currents produced by the bipyridine rings in the pseudooctahedral geometry. The proton chemical shifts are assigned by comparison with those for similar compounds.

Electronic absorption spectra

The ligands and complexes are soluble in common polar organic solvents, such as ethanol, methanol, and chloroform but partially soluble in non-polar organic solvents such as benzene and hexane. The UV-Vis spectra of the ligands and Ru(II) complexes were recorded in methanol (Figs 5 and 6). The absorption spectra of the ligands and complexes exhibit metal-to-ligand charge transfer (MLCT) and ligand-centred (LC) bands. The electronic spectra of the ligands showed two types of transitions, the first appearing in the region of 226 and 303 nm, assigned to π–π* transition due to transitions involving molecular orbitals located on the fluorene and 1,10-phenanthroline. The second type of transitions appeared in the range 336–340 nm and can be assigned to n–π* transitions, due to transitions involving the molecular orbital of the C=N chromophore. In the electronic absorption spectra of the Ru(II) complexes, the n–π* transitions due to the C=N group of fluorene and 1,10-phenanthroline shifted to lower energy compared to the free ligands. The spectra of the complexes show charge- transfer transitions different from the free ligands which can be seen in the range 430–455 nm.

Mass spectra

In the mass spectra, the molecular ion peaks of **(1)** and **(2)** appeared at *m/z*: 361.25 (M+1, 100%) and 310.41 (M+1, 100%) in the LC/MS spectra. Mass spectral data confirmed the proposed structure of ligands. In the ES-MS spectra for [Ru(**1**)(bpy)$_2$] and [Ru(**2**)(bpy)$_2$] complexes, the signals 774.51 [M+1], 918.82 $[M-PF_6]^+$, 1063.77

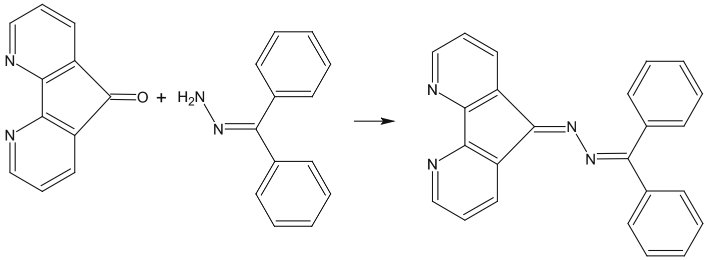

Fig. 1 Formation reaction of **(1)**.

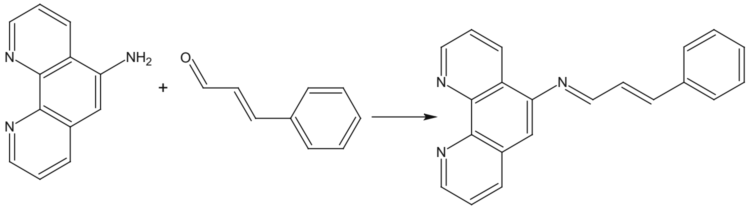

Fig. 2 Formation reaction of **(2)**.

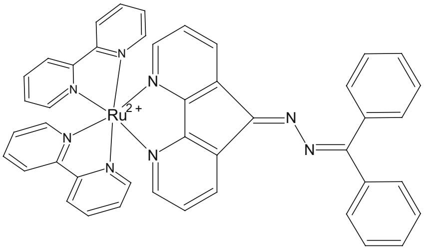

Fig. 3 Proposed structure of [Ru(**1**)(bpy)$_2$].

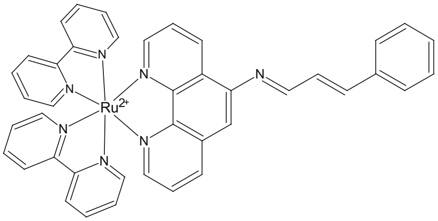

Fig. 4 Proposed structure of [Ru(**2**)(bpy)$_2$].

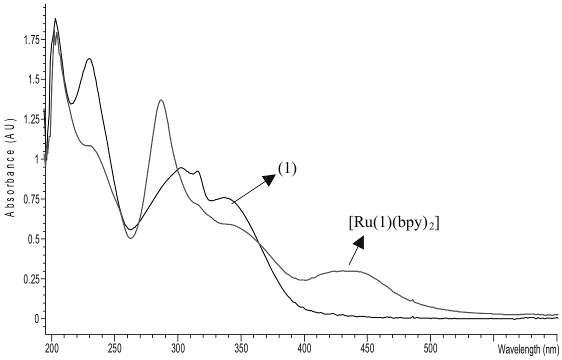

Fig. 5 UV-Vis absorption spectra of **(1)** and [Ru(**1**)(bpy)$_2$].

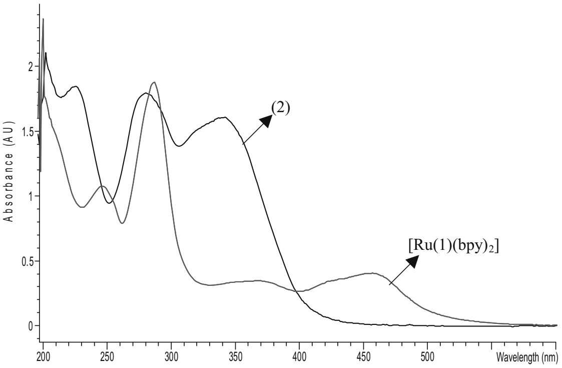

Fig. 6 UV-Vis absorption spectra of **(2)** and Ru(**2**)(bpy)$_2$].

$[M–2PF_6]^{2+}$ and 723.93 [M+1], 867.12 $[M–PF_6]^+$, 1012.78 $[M–2PF_6]^{2+}$ were observed. The measured molecular weights were consistent with expected values. Elemental analysis of the ligands show good agreement with the proposed structures.

Fluorescence spectra

In order to characterise the different emissions observed in various environments, transient fluorescence measurements were carried out for **(1)** and **(2)**. Dimethylsulfoxide (DMSO), ethanol, methanol and chloroform were used as solvents. As a result of several experiments, optimum fluorescence emissions of the **(1)** and **(2)** were obtained in DMSO at room temperature. It was found that the optimum interval of concentration was between 1.10^{-5} M and 1.10^{-6} M. The emission of **(1)** and [Ru(**1**)(bpy)$_2$] did not show good fluorescence emissions but the emission band of **(2)** showed a maximum at 500nm in DMSO. The emission maximum of the [Ru(**2**)(bpy)$_2$] shifted to 650 nm, which is substantially red shifted with respect to the emission spectra of the MCLT.

Thermogravimetric analyses

The thermal analyses of the ligands and complexes were studied by TGA–DSC techniques to give more information on the structure of the investigated materials. The TGA–DSC curves were obtained for **(1), (2)** and their Ru(II) complexes. Samples of **(1)** and its Ru(II) complex were heated from 50 to 1200 °C. Decomposition of **(1)** showed one loss step and it is thermally stable up to 300 °C. The endothermic peak at 183 °C is the melting point. The largest weight loss rate appeared at 315 °C (endothermic) (80.09%). Residue is 0.32%. The thermal analysis curve of the Ru(II) complex of **(1)** shows that decomposition take place in two stages in the 300–1000 °C temperature range. The first weight loss appeared at 333 °C (40.44%) and a second weight loss at 765 °C (48.22%). Reduction of the Ru(II) is shown as endothermic peak at 1063 °C. The final product, at *ca* 1200 °C, consists of metallic ruthenium (Found: 7.75, Calcd: 9.50%).

Samples of **(2)** and its Ru(II) complex were heated from 50 to 1200 °C. Decomposition of **(2)** showed three loss steps and it is thermally stable up to 200 °C. The endothermic peak at 145 °C is the melting point. The largest weight loss rate appeared at 303 °C (endothermic) (43.96%). Residue is 0.98%. The thermal analysis curve of the Ru(II) complex of the **(2)** shows that decomposition take place in four stages in the 100–1200 °C temperature range. The first weight loss appeared at 180 °C (12.05%), a second weight loss appeared at 297 °C (48.81%) and a third at 687 °C (19.31%). A fourth weight loss was not completed by the 1200 °C limit (Residue is 21.52%).

Figures appropriate to the fluorescence and thermogravimetric studies are held by the authors and are available upon request.

Conclusion

The paper describes the synthesis, spectral, and thermal studies of new Schiff base ligands and their Ru(II) complexes derived from fluorene and 1,10-phenanthroline. Schiff bases and Ru(II) complexes have known use in a wide variety of applications, as noted above. We hope that these compounds might be used in the future for such applications.

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