Synthesis, Characterization, and Crystal Structure of a Functionalized Ruthenium(II) Polypyridyl Complex with Fused Triazinone as Ligand

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Introduction

The ability to design molecules rationally which are capable of targeting specific DNA sites offers attractive possibilities in developing both pharmaceuticals and tools for biotechnology.[1,2] Water soluble and photophysically active polypyridyl ruthenium(II) complexes provide a useful tool to probe the drug−DNA interaction.[3] Different from organic molecules and *cis*-Pt(II) based drugs, octahedral polypyridyl ruthenium(II) complexes were found to be bound to DNA enantioselectively and site-specifically. $[Ru(phen)_3]^{2+}$ was the first Ru(II) complex found to bind enantioselectively to CT-DNA, with the Δ-isomer binding more strongly than the Λ-isomer.[4] The molecular "light switch" $[Ru(bpy)_2(dppz)]^{2+}$ (bpy = 2,2′-bipyridine, dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) was found to bind with DNA avidly ($K_b > 10^6$ M^{-1}),[5] while less enantioselectivity was observed.[6] Shape selectivity was improved by the functionalization of the ligand of Rh(III) polypyridyl complex. $[Rh(phen)_2(phi)]^{3+}$ has been shown to recognize open major groove sites through shape selection.[7] Δ,Δ-$[Rh[(R,R)\text{-}Me_2trien]phi]^{3+}$ (Me_2trien = 2,9-diamino-4,7-diazadecane) recognizes the predicated sequence 5′-TGCA-3′ through a mixture of hydrogen bonds and van der Waals contacts.[8]

It is known that 1,2,4-triazine-3,5-dione (6-azauracil) has been proved to possess a broad spectrum of therapeutic effects which include antiviral,[9,10] antitumor,[11,12] and antifungal activities.[13] It has been found that pztp or pytp-based Ru(II) complexes bind to DNA intercalatively (pztp = 3-(pyrazin-2-yl)-1,2,4-triazino-[5,6-*f*]-1,10-phenanthroline and pytp = 3-(pyridin-2-yl)-1,2,4-triazino[5,6-*f*]-1,10-phenanthroline).[14] As a part of ongoing work, we describe here our efforts to explore the effect of ligand functionalizaton on the properties of Ru(II) complex through the construction of the ligand 1,10-phenanthrolino[5,6-*e*]-1,2,4-triazin-3-one (PTZO), which is a fused 1,2,4-triazin-3-one.

Experimental Section

Materials. The complexes *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$,[15] *cis*-$[Ru(phen)_2Cl_2]\cdot 2H_2O$,[16] and 1,10-phenanthroline-5,6-dione (phendione)[17] were prepared according to the literature procedures. Other materials were commercially available. Ammonium acetate was dried in vacuo over calcium chloride before use. All reagents and solvents were purchased commercially and used without further purification unless otherwise noted.

Methods and Instrumentation. Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 240Q elemental analyzer. Absorption spectra were recorded on a Shimadzu MPA-2000 spectrometer. ^{1}H NMR spectra were recorded on a Varian-500 NMR spectrometer with $SiMe_4$ as an internal standard. Fast atom bombardment (FAB) mass spectra were measured on a VG ZAB-HS mass spectrometer with 3-nitrobenzyl alcohol as matrix.

All solutions of complexes **1** and **2** were freshly prepared before use in case of any degradation. Alternating current (ac) or cyclic voltammetry was performed on an EG&G PAR 273 polarographic analyzer and 270 universal programmer. The supporting electrolyte was 0.1 mol dm^{-3} tetrabutylammonium perchlorate in acetonitrile freshly distilled from phosphorus pentaoxide and deaerated by purging with nitrogen. A standard three-electrode system comprising a platinum microcylinder working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE) was used.

Steady-state emission experiments were performed with a Shimadzu RF-4500 fluorescence spectrometer equipped with a PC. Time-resolved emission measurements were conducted on an excimer laser (Lambda Physics EMG 201MSC)−pumped dye laser (Lambda Physics model FL2002) system. The nominal pulse width and the line width of the dye-laser output were 10 ns and 0.18 cm, respectively. The excitation wavelength was fixed at 450 nm. The emission decay of a sample was observed at 600 nm and collected via two lenses in a monochromator, detected by a photomultiplier and processed (10000 data per decay curve) by a two-channel color digital phosphor oscilloscope (Tektronix TDS3032).

Luminescence quantum yields were measured in optically diluted solutions, using $[Ru(bpy)_3]^{2+}$ in oxygen-free CH_3CN ($\phi = 0.06$) as reference emitter. Estimated experimental error in the reported data are as follows: absorption and emission maxima ±2 nm, emission lifetimes and emission quantum yields ±5%.

Syntheses. 1,10-Phenanthroline-5,6-dione Semicarbazone (psc). 1,10-Phenanthroline-5,6-dione (0.5 g, 2.4 mmol) and semicarbazide hydrochloride (0.29 g, 2,6 mmol) were dissolved in 30 mL of methanol under heating, and the mixture was refluxed for 3 h. The solvent was reduced to half, and the yellow solid product was obtained by suction while hot. Yield: 0.51 g, 80%. Anal. Calcd for $C_{13}H_9N_5O_2$: C, 58.4;

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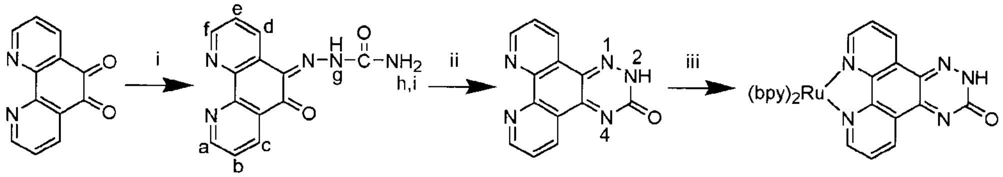
Scheme 1. Synthesis of Complex **1**[a]



[a] Reagents: (i) semicarbazide hydrochloride; (ii) acetic acid, NH_4Ac; (iii) $[Ru(bpy)_2Cl_2]$.

H, 3.37; N, 26.2. Found: C, 58.7; H, 3.52; N, 26.0. FT-IR (ν_{max}/cm^{-1}): 3472 and 3177 ($NH + NH_2$), 1728 (C═O), 1630 and 1581 (C═N). λ_{max}/nm (C_2H_5OH): 248.7, 338 and 385. ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 13.67 (s,1 H), 9.41 (d, 1 H, $J = 7$ Hz), 9.19 (d, 1 H, $J = 5$ Hz), 8.95 (d, 1 H, $J = 4.8$ Hz), 8.77 (d, 1 H, $J = 8.5$ Hz), 7.96 (m, 2 H), 7.56 (br, s, 2 H). FABMS: $m/z = 267$.

1,10-Phenanthrolino[5,6-*e*]-1,2,4-triazin-3-one (PTZO). 1,10-Phenanthroline-5,6-dione semicarbazone (0.5 g, 1.9 mmol) was dissolved in 7 mL of acetic acid, and a 10-fold excess of ammonium acetate (5 g, 19 mmol) was added. The mixture was heated at 120 °C for 6 h and then cooled. The greenish yellow solid was collected by filtration and washed several times with water until the acetic acid was removed. Yield: 0.14 g, 30%. Anal. Calcd for $C_{13}H_7N_5O$: C, 62.7; H, 2.81; N, 28.1. Found: C, 62.2; H, 3.12; N, 28.5. FT-IR (ν_{max}/cm^{-1}): 2987 (NH), 1679 (C═O), 1581 (C═N). λ_{max}/nm (HCl): 258.1, 318.1 and 383.3 (sh). ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 14.14 (br, s, 1 H), 9.20 (dd, 1 H, $J = 4.5$, 2.0 Hz), 9.09 (dd, 1 H, $J = 10$, 1.5 Hz), 9.03 (dd, 1 H, $J = 4.5$, 1.8 Hz), 8.82 (d, 1 H, $J = 7.5$ Hz), 7.83 (dd, 1 H, $J = 8.5$, 4.8 Hz), 7.77 (dd, 1 H, $J = 8.0$, 4.8 Hz). FABMS: $m/z = 249$.

$[Ru(bpy)_2(PTZO)](ClO_4)_2\cdot H_2O$. A mixture of *cis*-$[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (0.5 mmol, 0.261 g), PTZO (0.6 mmol, 0.149 g), and glycol was heated at 90−100 °C under argon for 5 h to give a dark red solution. The solution was diluted with 30 mL of water, and saturated aqueous $NaClO_4$ solution was added dropwise. The product was collected by filtration, purified by column chromatography on alumina using methanol as eluent, and dried in vacuo. Yield: 88 mg, 20%. Anal. Calcd for $[Ru(bpy)_2(PTZO)](ClO_4)_2$: C, 45.0; H, 2.84; N, 14.3. Found: C, 45.4; H, 3.32; N, 14.1. λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) (water): 450 (13350), 285 (60350), and 236 (39110) ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 9.28 (d, 1 H, $J = 7$ Hz), 9.26 (d, 1 H, $J = 6$ Hz), 8.82 (d, 2 H, $J = 7.5$ Hz), 8.80 (d, 2 H, $J = 8.5$ Hz), 8.19 (t, 2 H), 8.10 (t, 3 H), 8.07 (dd, 1 H, $J = 5$, 1.3 Hz), 7.81 (m, 3 H), 7.77 (dd, 1 H, $J = 8$, 5 Hz), 7.71 (t, 2 H), 7.56 (t, 2 H), 7.39 (q, 2 H). FABMS: $m/z = 765$ ($M - ClO_4^- + 3H^+$), 664 ($M - 2ClO_4^- + H^+$), 509 ($M - 2ClO_4^- - bpy + 2H^+$).

$[Ru(phen)_2(PTZO)](ClO_4)_2$. This complex was synthesized in an manner similar to that described for $[Ru(bpy)_2(PTZO)](ClO_4)_2\cdot H_2O$, with 0.5 mmol, 0.226 g of *cis*-$Ru(phen)_2Cl_2\cdot 2H_2O$ in place of *cis*-$Ru(bpy)_2Cl_2\cdot 2H_2O$. Yield: 68 mg, 15%. Anal. Calcd for $[Ru(phen)_2(PTZO)](ClO_4)_2$: C, 48.8; H, 2.53; N, 13.85. Found: C, 49.3; H, 2.81; N, 13.5. λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}) (water): 445 (16600), 263 (87500), and 223 (16600). ^1H NMR (500 MHz, DMSO-d_6): δ (ppm) 9.25 (dd, 1 H, $J = 8$, 1 Hz), 9.23 (dd, 1 H, $J = 7.5$, 1 Hz), 8.76 (dd, 4 H, $J = 15$, 10 Hz), 8.37 (s, 4 H), 8.23 (t, 2 H), 8.03 (q, 4 H), 7.81 (q, 2 H), 7.75 (q, 2 H), 7.70 (dd, 1 H, $J = 5$, 5.3 Hz), 7.65 (dd, 1 H, $J = 7.5$, 5.5 Hz). FABMS: $m/z = 711$ ($M - 2ClO_4^-$).

CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive, and only small amounts of the material should be prepared and handled with great care.

Crystallographic Structure Determination. The red needle crystals of **1** were grown from the mixture of methanol−water (1:1) on standing in air at room temperature. A single crystal of dimensions of 0.3 × 0.05 × 0.03 mm was mounted on glass fiber and placed on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) at 293 K. Crystal data for **1**: $C_{33}H_{26}Cl_2N_9O_{10}$-$Ru\cdot H_2O$, fw = 897.61, tetragonal, space group $P4(3)$, $Z = 4$, $a = 16.620(2)$ Å, $b = 16.620(2)$ Å, $c = 13.020(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3596.4(10)$ Å^3, $D_c = 4$, 1.658 Mg/m∧^{3}; 7741 unique reflections were measured and used in refinement. The structure was solved by direct methods using SHELXTL-97[18] and refined anisotropically on F^2 by the full-matrix least-squares techniques. The final refinement based on F_o for 4526 observations ($F \geq 4.0\ \sigma(F)$) and 441 variables led to convergence. Full details are available in Supporting Information.

Calculations. The energy-minimized structure of the free ligand PZTO was calculated using the semiemprical method CNDO.[19] Calculations of the electronic structures were performed on a PC with the extended Hückel approximation[20] using the HyperChem[21] program as a platform.

Results and Discussion

Synthesis. 1,2,4-Triazin-3-one is a relatively little known compound, which can be prepared via a number of methods. The method widely used is the reaction of a 1,2-dicarbonyl compound with semicarbazide (sc).[22−27] The initially formed semicarbazones can be isolated,[25] but the direct formation of 1,2,4-triazin-3-ones from the starting compounds can be easily carried out by heating the two substances in acetic acid[26] or with a base in ethanolic solution.[27] For instance, 5,6-diphenyl-3-oxo-2,3-dihydro-1,2,4-triazine,[22] phenanthro[9,10-*e*]-1,2,4-triazin-3-one,[23] and 4,7-phenanthro[5,6-*e*]-1,2,4-triazin-3-one[24] can be prepared easily from the corresponding 1,2-dicarbonyl compounds and semicarbazide in 85% acetic acid or in ethanol. However, when 1,10-phenanthroline-5,6-dione (phendione) was heated with semicarbazide hydrochloride (sc) in methanol, 1,10-phenanthroline-5,6-dione semicarbazone was obtained in high yield (80%) as shown in Scheme 1. Furthermore, ring closure could not yet be achieved using 85% acetic acid as solvent in reaction. Therefore the ring closure reaction between phendione and sc appears more difficult than those 1,2-dicarbonyl compounds mentioned above. It is also more difficult than the condensation between 1,2-dicarbonyl compounds and some hydrazidines where 1,2,4-triazines can be obtained easily from their reaction in ethanol or methanol.[14,28] It is found that a very less noted method for the preparation of alyl-triazines[29] using acetic acid and NH_4Ac as reaction medium promoted the ring closure reaction smoothly with the yield being 30%. We noted that aryl-imidazole could be isolated in good yields in similar fashion by the reaction of phendione and aldehydes in the presence of acetic acid and NH_4Ac where 1,10-phenanthroline-5,6-diimine could be a key intermidiate.[30] In our case 1,10-

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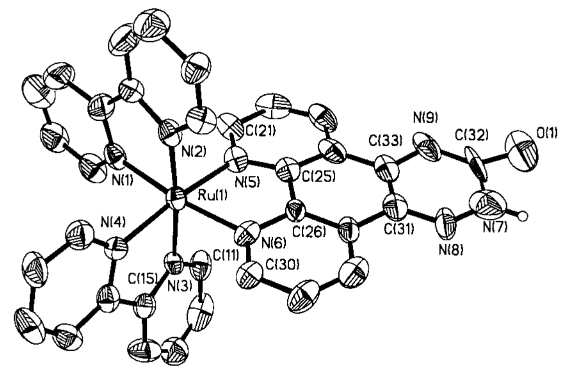

Figure 1. ORTEP drawing (30% probability thermal ellipsoids) of the cation of complex **1.**

phenanthroline-5,6-diimine could also be a key factor facilitating the formation of triazinone, since the rate of reaction for this method depends on the excess of ammonium acetate used.[29]

Preparation of complexes **1** and **2** is according to the established procedures. In comparison with similar reactions, our yields are much lower (10−20%). It is speculated that the carbonyl and N4 (or N2) of PTZO could also act as a binding site for $Ru(bpy)_2Cl_2$ or $Ru(phen)_2Cl_2$ following the formation of the mononuclear complex **1** or **2**.

^{1}H NMR and FAB-MS. The success on the synthesis of the ligand PTZO is confirmed unambiguously by ^{1}H NMR and FAB-MS. Chemical shifts of the protons on psc and PTZO are assigned with the help of ^{1}H−^{1}H COSY and by comparison with related complexes.[14,31,32] The chemical shifts are summarized in Table S1 in the Supporting Information. A broad single peak at 7.56 ppm is assigned to H_h and H_i. The proton H_g in psc appears at 13.67 ppm, which is shifted to downfield by 3.76 ppm with respect to the corresponding proton in an analogue benzilsemicarbazone.[31] Furthermore, the chemical shift of the proton H_g in PTZO (14.14 ppm) is even higher than that in psc and shows a downfield shift of 2−3 ppm with respect to the corresponding protons in other substituted or fused 1,2,4-triazin-3-ones.[32] This downfield shift for proton H_g may be attributed to the more extended aromatic ring system and thus the further delocalization of the π electron system of PTZO.

A peak at $m/z = 249$ (12%) is observed in the fast-atom-bombardment mass spectrum of PTZO. It has been found that a fragment at $m/z = 207$ with the loss of [H−N−C═O] for 5,6-diphenyl-1,2,4-triazin-3-one[33] and 4,7-phenanthrolino[5,6-*e*]-1,2,4-triazin-3-one.[34] However this fragment is not observed for PTZO, suggesting that there be another fractioning mode for PTZO.

Crystal Structure. The molecular structure of $[Ru(bpy)_2(PTZO)](ClO_4)_2\cdot H_2O$ has been confirmed by single-crystal X-ray diffraction analysis. It consists of a $[Ru(bpy)_2(PTZO)]^{2+}$ cation, two disordered ClO_4^- ions, and a water molecule. An ORTEP drawing of the cation with the atomic numbering scheme is depicted in Figure 1. Selected bond lengths and angles are summarized in Table 1.

As shown in Figure 1 the central ruthenium atom is chelated by a PTZO ligand and two bpy ligands orientated in a cis geometry. The coordination geometry about the ruthenium atom is that of a distorted octahedron, with a bite angle of 79.3° averaged over the three bidentate ligands. This distortion from an ideal octahedral geometry is due to the customary narrow bite angles of the bipyridine moieties, as observed in some other ruthenium complexes.[35] The torsion angles between the pyridine pairs of two bpy ligands of the complex are nonequivalent, one being 1.6° and the other 10.5°. Similar cases can be found in some other complexes of this type (1.9−12.3°).[36−38] The PTZO ligand is essentially planar with O1 being slightly out of the triazine plane (0.1024 Å). This observation is similar to that for 7,8-dihydro-8-hdroxy-2-methyl-3*H*,6*H*-[1,3]thiazino[3,2-*b*]-1,2,4-triazin-3-one where the corresponding oxygen is deviated from the triazine plane by 0.08 Å.[39]

Table 1. Selected Bonds Lengths (Å) and Angels (deg) for Complex **1**

Ru(1)−N(1)	2.046(8)	Ru(1)−N(2)	2.002(13)
Ru(1)−N(3)	2.119(13)	Ru(1)−N(4)	2.059(8)
Ru(1)−N(5)	2.055(7)	Ru(1)−N(6)	2.074(7)
N(3)−C(11)	1.288(16)	N(7)−C(32)	1.51(2)
N(7)−N(8)	1.260(16)	N(9)−C(32)	1.35(2)
N(8)−C(31)	1.288(14)	O(1)−C(32)	1.265(14)
N(9)−C(33)	1.385(14)		
N(1)−Ru(1)−N(2)	79.5(4)	N(3)−Ru(1)−N(4)	79.0(4)
N(5)−Ru(1)−N(6)	79.5(3)	N(7)−C(32)−O(1)	103.5(18)
N(7)−C(32)−N(9)	123.3(11)	N(9)−C(32)−O(1)	133(2)

The mean Ru−N bond length (2.059 Å) is a typical value for this type of Ru(II) complex (2.059−2.069 Å)[38,40,41] It is noteworthy that the bond length of N8−C31 (1.288(14) Å) is a typical double bond value[42] and is significantly shorter than that of N9−C33 (1.385(14) Å) and N9−C32 (1.35(2) Å). In fact, the bond lengths of N8−C31 and N3−C11 are nearly the same and the shortest among all the C−N bond lengths in complex **1**. In addition the bond length of N7−N8 (1.260(16) Å) is also a typical value of a double-bond value[42] and significantly shorter than that in many other triazinone compounds and the analogues. For instance, longer N−N bond lengths are found in 6-azauridine (1.369 Å),[43] 7,8-dihydro-8-hydroxy-2-methyl-3*H*,6*H*-[1,3]-thiazino[3,2-*b*]-1,2,4-triazin-3-one (1.32 Å),[39] and 6-azacytidine (1.356 Å).[44] On the other hand, the N7−C32 bond length (1.51(2) Å) is predominant in single-bond character and significantly longer than that found in 6-azauridine (1.386 Å)[43] and 6-azacytidine (1.389 Å).[44] It is interesting that a comparably long C−N bond length was observed in 7,8-dihydro-8-hydroxy-2-methyl-3*H*,6*H*-[1, 3]thiazino[3,2-*b*]-1,2,4-triazin-3-one (1.52 Å).[39] The relatively longer bond length of N7−C32 in the triazinone ring system could be rationalized on the basis of the very short bond lengths of N7−N8 and N8−C31. The O1−C32 distance of 1.265 Å shows that the keto form (H−N−C═O) is predominant in complex **1**. But this C−O bond length is

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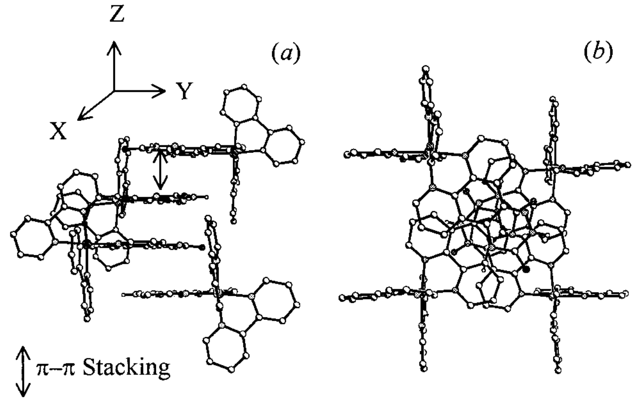

Figure 2. (a) Side view of the packing of the stacking interaction involving PTZO. (b) Top view of the stacking plans.

still slightly lengthened in comparison with that observed in 6-azacytidine (1.246 Å),[44] 6-azauridine (1.217 Å),[43] 6-azauracil (1.224 Å), and 6-azathymine (1.220 Å)[45] and comparable to that found in 7,8-dihydro-8-hydroxy-2-methyl-3*H*,6*H*-[1,3]thiazino[3,2-*b*]-1,2,4-triazin-3-one (1.26 Å).[39] However, a structural resonance of H−N−C═O ⇔ N−C−O−H could also be possible under certain conditions as evidenced by the slightly lengthened O1−C32 double bond.

As hydrogen atoms cannot be located in X-ray crystallography, the tautomeric forms of PTZO will be discussed in the absorption section (vide infra).

The packing of complex **1** created a very simple and closely stacked system (Figure 2). The neighboring molecules of complex **1** are stacked each other head to head in a perpendicular way with a distance of 3.266 Å and create a unique "π-way" along the z axis. It is noteworthy that such a packing scheme is rarely seen for the nucleic acid constituents and their aza analogues where the molecules are usually hydrogen bonding each other in the same sheet with or without stacking interaction between neighboring aromatic planes. For instance, in the crystal of thymine monohydrate or anhydrate, the molecules form hydrogen bonds in the same sheet and are stacked with neighboring sheets with a distance of 3.36 or 3.4 Å.[46] However, such a stacking interaction is absent in the crystal structure of 6-azauracil and 6-azathymine.[45] A packing scheme similar to that of complex **1** was observed for 6-azauridine, where there is no hydrogen bonding in the azathymine molecules and the neighboring heterocycles are stacked each other in an antiparallel way with a distance of 3.3 Å.[43]

Molecular Orbital Calculations. Extended Hückel calculations were performed on the free PTZO ligand using the program HyperChem[21] to rationalize the electrochemical and photophysical results. Figure S1 (Supporting Information) shows the graphical illustrations for the three lowest lying unoccupied orbitals. For this ligand, we made the following observations: (a) The lowest vacant molecular orbital is centered on the triazinone part with the electronic distribution without any significant weight on the coordinating nitrogens. The LUMO is found at −10.44 eV. (b) In contrast, the next vacant MO LUMO+1 lying at higher energy (−9.69 eV) is developed on the bipyridine-type part with a strong weight on the coordinating nitrogens and no more electronic density on the triazinone-type nitrogens. Similarly, the MO LUMO+2 (−9.33 eV) is developed on the phenanthroline-type part and with very little electronic density on the triazinone-type nitrogens.

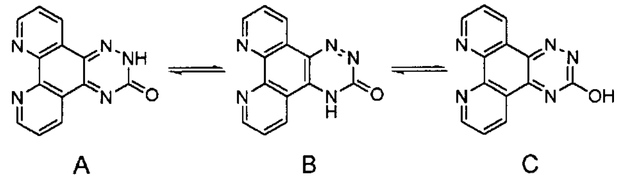

Figure 3. The three possible tautomers for PTZO.

Electrochemistry. Cyclic voltammograms of **1** and **2** in CH_3CN in the −2.0 to +2.0 V potential window (vs SCE) showed four successive waves attributed to one metal-centered oxidation and three ligand-based reductions (Table S2, Supporting Information). The oxidation part of **1** exhibited one quasi-reversible wave at $E_{1/2} = 1.38$ V (vs SCE) for the $Ru^{II}-Ru^{III}$ redox couple, which is comparable to other triazine ligand-based Ru(II) complexes such as $[Ru(bpy)_2(pztp)]^{2+}$ and $[Ru(phen)_2(pztp)]^{2+}$ [14] and 110 mV more positive than that of $[Ru(bpy)_3]^{2+}$.[47] The three reduction processes for **1** occur at potentials of −0.82, −1.45, and −1.76 V, respectively. In contrast with oxidation, the first reduction value −0.82 V is significantly anodically shifted with respect to that of $[Ru(bpy)_3]^{2+}$ (−1.31 V),[47] which stresses the better π-electron acceptor character of the PTZO contained in complex **1**. This is consistent with the addition of one electron on the lowest-energy LUMO mainly localized on the triazinone part of PTZO to give the complex $[Ru(bpy)_2(PTZO)^{\bullet-}]^{+}$. The second and third reduction waves (−1.45 and −1.76 V) appear at almost the same potentials as corresponding reductions of $[Ru(bpy)_3]^{2+}$ (−1.50 and −1.77 V),[47] respectively. These processes are attributed to the simultaneous reductions of one ancillary bipyridine to give first the species $[Ru(bpy)(bpy)^{\bullet-}(PTZO)^{\bullet-}]$ and then $[Ru(bpy)^{\bullet-}(bpy)^{\bullet-}(PTZO)^{\bullet-}]^{-}$. Similar processes are also observed for complex **2** where the first reduction wave at −0.90 V (anodically shifted 450 mV with respect to that of $[Ru(phen)_3]^{2+}$)[48] should involve the species $[Ru(phen)_2(PTZO)^{\bullet-}]^{+}$.

Absorption Spectra. The FT-IR spectrum of psc shows a sharp peak around 3472 cm^{-1} and a peak centered at 3177 cm^{-1} which are assigned to the absorption of the amide.[31] A very strong peak is observed at 1728 cm^{-1} for psc due to the absorption of phendione carbonyl while the absorption is moved to 1686 cm^{-1} for PTZO, which is also consistent with the formation of triazinone.

Psc shows absorption bands at 249, 338, and 385 nm in the UV−vis spectrum where the absorption around 249 nm can be assigned to the $\pi-\pi^*$ transition of psc. This transition is displayed at 258 nm for PTZO as it possesses a more extended π system.

There are three possible tautomers for 1,2,4-triazin-3-one, denoted as forms A, B, and C (Figure 3). Clearly form C is precluded for PTZO since the strong absorption of carbonyl instead of hydroxyl is observed in the IR spectrum of PTZO in solid state. A tentative molecular orbital calculation on the free PTZO ligand using EHMO indicates that form C possesses the highest energy (−37978.1 kcal/mol) and the energies for forms A and B are similar (−38030.7 and −38027.9 kcal/mol, respectively). 5,6-Diphenyl-1,2,4-triazin-3-one has been studied intensively, and form A was considered to be dominant in the solid state on the basis of the comparison of its UV−vis spectrum with those of the methyl derivatives on N^2, N^4, and

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carbonyl.[25,49] It is noted that PTZO has an absorption pattern similar to that of 5,6-diphenyl-1,2,4-triazin-3-one with the $\pi-\pi^*$ transition being at somewhat lower energy. Therefore form A should also be dominant for PTZO.

Both complexes **1** and **2** show absorption bands very similar to those of their parent complexes $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, respectively. Complex **1** displays two absorptions at 236 and 285 nm in the UV region and a broad MLCT band at 450 nm. Two absorptions at 223 and 263 nm and a MLCT band at 445 nm are observed for complex **2** (Figure S2, Supporting Information). Since the MLCT band energy is almost the same for **1** and $[Ru(bpy)_3]^{2+}$, **2** and $[Ru(phen)_3]^{2+}$, respectively, it seems to be difficult to assign the MLCT transition orientations for complexes **1** and **2**. For complex **1**, two transition orientations are possible: one is $Ru(d\pi) \rightarrow bpy(\pi^*)$, and the other is $Ru(d\pi) \rightarrow PTZO(\pi^*)$. The results from electrochemistry together with the molecular orbital calculations strongly indicate that the LUMO is localized on PTZO for both complexes. In addition, emission studies show that the lowest MLCT excited states of the two complexes are different from those of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ (see below). As is seen from Figure S2, the absorption of complex **1** in CH_3CN show an energy band at 336 nm which can be assigned to the intraligand transition of PTZO unambiguously since this absorption cannot be observed in the CH_3CN solution of $[Ru(bpy)_3]^{2+}$.[50] It has been observed that the 1,2,4-triazine ligand pztp based Ru(II) complexes show a red shift of 10−20 nm at MLCT energy band with respect to that of $[Ru(bpy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$. For the pztp-based complexes the MLCT transition is attributed to $Ru(d\pi) \rightarrow pztp(\pi^*)$.[14] Therefore, PTZO and pztp have different influences on the electronic structure of the Ru(II) complexes. This difference should be due to the electron-donating character of carbonyl in PTZO and the electron-accepting property of pyrazyl in pztp.

Luminescence Studies. The emission and absorption data of complexes **1** and **2** are listed in Table 2 and are compared with those of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. It can be seen from Table 2 clearly that the absorption and emission spectra indicate that the MLCT energy band for **1** does not differ substantially from that of $[Ru(bpy)_3]^{2+}$ in acetonitrile and water. This is also true for **2** and $[Ru(phen)_3]^{2+}$. The MLCT bands for $[Ru(bpy)_3]^{2+}$ or $[Ru(phen)_3]^{2+}$ do not show a significant difference in acetonitrile and water,[51,52] while the MLCT bands for **1** and **2** are moved to longer wavelengths by 4−5 nm in CH_3CN with respect to those in water in absorption spectra. In H_2O, the lifetimes for **1** and **2** are somewhat longer than those of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$, but in acetonitrile the lifetimes for **1** and **2** are much shorter than those of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. That is to say, much larger differences for the lifetimes in acetonitrile and water are observed for **1** and **2** in comparison with that of $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$. In addition, the quantum yields for **1** and **2** are lower than those of their parent complexes in both solvents. The pronounced solvent dependent photophysical behavior in emission and absorption of **1** and **2** agrees with the assignment that the lowest MLCT excited states of **1** and **2** should be localized on ligand PTZO.

Table 2. Photophysical Properties of **1**, **2**, and Related Complexes

	abs: λ_{max}		emission[a−c]					
			H_2O			CH_3CN		
complex	H_2O	CH_3CN	λ_{max} (nm)	ϕ_{em}	τ_{em} (ns)	λ_{max} (nm)	ϕ_{em}	τ_{em} (ns)
$[Ru(bpy)_3]^{2+}$	452	452	607	0.042	580	611	0.059	890
$[Ru(phen)_3]^{2+}$	447	447	603	0.072	960	604	0.028	460
1	450	454	610	0.007	687	614	0.013	242
2	445	450	606	0.060	1167	607	0.010	182

[a] In N_2 purged solution at 298 K. [b] Data for $[Ru(bpy)_3]^{2+}$ from ref 51. [c] Data for $[Ru(phen)_3]^{2+}$ from ref 52.

In summary, the synthesis, structural characterization, and spectroscopic investigation of functionalized diimine complexes having very strong intermolecule stacking interactions are presented. Crystal structure analysis on $[Ru(bpy)_2(PTZO)]^{2+}$ indicates that the ligands PTZO are positioned in a parallel manner and stacked very closely head to head via a perpendicular way with a distance of about 3.266 Å. The intensive spectroscopic studies together with molecular calculations imply that the photophysical behavior of the complexes could be dominated by the excited states of PTZO ligand.

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Supporting Information Available: Figure S1 showing graphical illustrations for the three lowest lying unoccupied orbitals, Figure S2 showing the electronic absorption of the complexes in water and acetonitrile, and tables of ^1H NMR data for the ligands and complexes, half-wave potentials of the complexes, atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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