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Review

# Environmental effects on the photophysics of transition metal complexes with dipyrido[2,3-*a*:3′,2′-*c*]phenazine (dppz) and related ligands

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**Contents**



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[1] For ligand abbreviations; see Table 1.

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ABSTRACT

This review primarily covers studies of ruthenium(II) complexes with the dppz (dipyrido[2,3-*a*:3′,2′-*c*]phenazine) ligand; in solution, in polymers and surfactant/lipid media, and when bound to DNA. Related studies with other transition metals, and with extended ligands that can form bimetallic as well as monometallic complexes are discussed. The review focuses on photophysics of these complexes with particular attention devoted to the nature of the excited states that give rise to emission, their dependence on solvent environment, and the behavior of the complexes as luminescent probes for DNA.



## 1. Introduction: dipyrido[2,3-*a*:3′,2′-*c*]phenazine (dppz) and related ligands[1] in coordination chemistry

The synthesis of dipyrido[2,3-*a*:3′,2′-*c*]phenazine (dppz, Table 1) (Fig. 1) as a copper chelator, and of its ethylene-bridged diquaternary salt, were first described in 1970 [1]. The synthesis of $[Ru(dppz)_3]^{2+}$ and its properties in acetonitrile were described in 1984 [2], and the synthesis and excited state properties of $[Ru(bpy)_2dppz]^{2+}$ were described in 1985 [3,4]. These papers observed that $[Ru(L)_2dppz]^{2+}$ emitted in organic solvents but not in water, and had preferential charge transfer to the dppz ligand in the excited state. Following this, a seminal paper [5] on the interaction of $[Ru(bpy)_2dppz]^{2+}$ with DNA appeared in 1990, which demonstrated how the emission of the complex was "turned on" when the dppz ligand moved from an aqueous environment to intercalation between the DNA base pairs; the so-called "light-switch" effect [5]. This heralded an intense period of research activity on this and similar coordination complexes with extended diimine ligands.

Early studies with DNA used the racemic (*rac*-) complex. Since $[Ru(bpy)_2dppz]^{2+}$ is an octahedral complex, it has both left- (Λ-) and right- (Δ-) handed enantiomeric forms (Fig. 2). In homogeneous solution, the stereochemistry has no effect on the photophysical properties of the complex. However, in a chiral environment, *e.g.* when bound to helical DNA, the two enantiomers are distinct entities and must be considered separately [6]. Studies of this complex fall into two areas of particular interest: the binding of these complexes with DNA, and their photophysical behavior. These two areas are strongly interlinked, since dramatic luminescence changes occur upon DNA binding. In this review, we consider developments to date in understanding the photophysical behavior of metal complexes, particularly ruthenium, with dppz and related ligands. We review current the understanding of the excited states in these species, and how the photophysics are influenced by (i) the local environment (including solvent, temperature, and polymers), (ii) the ancillary ligands, (iii) the nature of the transition metal, and (iv) by substituents on the dppz ligand. Binding to DNA [7,8] is not discussed in detail, other than where it pertains to understanding its environmental effect on the photophysics. Neither do we discuss conjugation of these complexes to oligonucleotides for therapeutic and diagnostic applications, nor DNA-mediated electron transfer involving these complexes, since these topics are beyond the scope of this review and are recently described elsewhere [9–11].

The vast majority of studies on this class of metal complexes employ ruthenium(II) as the central metal, with dppz, bdppz/dppn, and alkyl-, halide- modified dppz as ligands [2–98] (Fig. 3). Ruthenium(II) complexes with dppz-related ligands (Fig. 4) have been synthesized with dpqC [99,100], dpp2/dpqp [55,101–103], pydppz/pydppn [104–107], ddz/taptp [108,109], btppz [110], qdppz [111–114], dpqp-OH [115,116], actatp [117], ligands with pteridine (1) [118,119] or ketone [120] functionalities, ligands modified for anion recognition (2) [121,122], and dppz ligands otherwise modified for incorporation in novel materials [123–128].

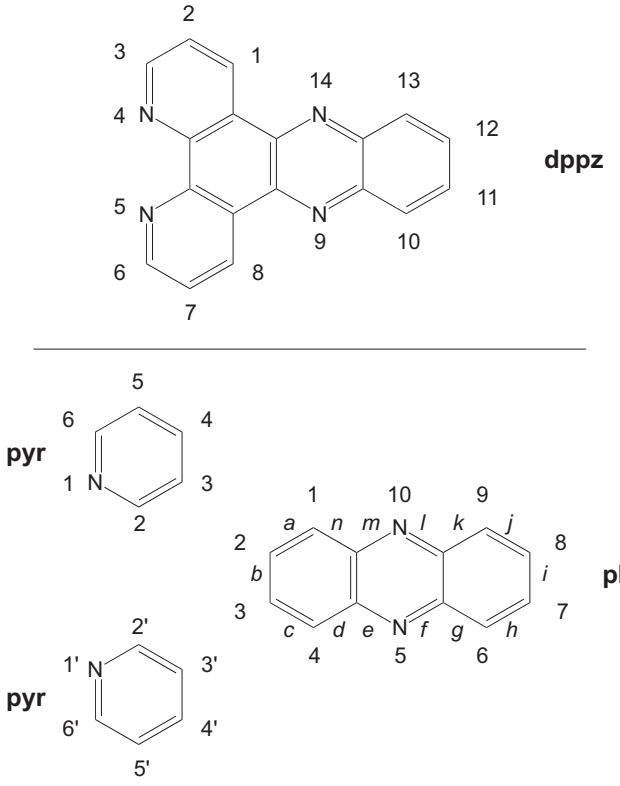


**Fig. 1.** Nomenclature and numbering of the dppz (dipyrido[3,2-*a*:2′,3′-*c*]phenazine) ligand, where pyr represents the pyridine moiety and phz represents phenazine moiety.

*Abbreviations:* phz, phenazine; py, pyridine; bpy, bipyridyl; phen, phenanthroline; EtOH, ethanol; MeOH, methanol; TFE, trifluoroethanol; DCM, dichloromethane; BuCN, butyronitrile; CT-DNA, calf thymus DNA; ss-DNA, single-stranded DNA; $[poly(dA\text{-}dT)]_2$, duplex poly(deoxyadenylic-deoxythymidylic acid); $[poly(dG\text{-}dC)]_2$, duplex poly(deoxyguanylic-deoxycytidylic acid); $[poly(rA\text{-}rU)]_2$, duplex poly(adenylic-uridylic acid); poly(dA).poly(dT), duplex (polydeoxyadenylic acid)(polydeoxythymidylic acid); poly(dG).poly(dC), duplex (polydeoxyguanylic acid)(polydeoxycytidylic acid); P/D ratio, [polynucleotide base]/[dye]; IL, intra-ligand; MC, metal-centred; LC, ligand-centred; MLCT, metal-to-ligand charge transfer; ILET, inter-ligand charge transfer; H-bond, hydrogen bond; TRIR, time-resolved infrared; $TR^2$, transient resonance Raman; $TR^3$, time-resolved resonance Raman; NMR, nuclear magnetic resonance; cmc, critical micelle concentration.

**Table 1**
Abbreviations used for ligands, and references for the origin of different abbreviations where more than one is common for a single ligand.

| | |
|---|---|
| bpy | 2,2′-bipyridine |
| dmb | 4-(4′-Methyl)-2,2′-bipyridine |
| phen | 1,10-Phenanthroline |
| phendione | 1,10-Phenanthroline-5,6-diketone |
| 2,9-dmp | 2,9-Dimethyl-1,10-phenanthroline |
| 4,7-dmp | 4,7-Dimethyl-1,10-phenanthroline |
| dpq | Dipyrido[3,2-*f*:2′,3-*h*]quinoxaline |
| ip | 2-Imidazo[4,5-*f*][1,10]phenanthroline |
| bpz | 2,2′-Bipyrazine |
| tap | 1,4,5,8-Tetraazaphenanthrene |
| hat | 1,4,5,8,9,12-Hexaazatriphenylene |
| ppz | 4,7-Phenanthrolino[6,5-*b*]pyrazine |
| tpy | 2,2′:6′,2″-Terpyridine |
| php | 2-(2′-Pyridyl)-1,10-phenanthroline |
| dppz | Dipyrido[3,2-*a*:2′,3′-*c*]phenazine |
| dpqC | Dipyrido[3,2-*a*:2′,3′-*c*](6,7,8,9-tetrahydro)phenazine |
| dppn | 4,5,9,16-Tetraaza-dibenzo[*a*,*c*]naphthacene [26] |
| bdppz | Benzo[*i*]dipyrido[*a*:3,2-*h*:2′,3′-*j*]phenazine [34] |
| pydppz | 2-(Pyrid-2′-yl)-dipyrido[3,2-*a*:2′,3′-*c*]phenazine [103] |
| dppzp | 6′-(2″-Pyridyl)dipyrido[3,2-*a*:2′,3′-*c*]phenazine [106] |
| pydppn | 3-(Pyrid-2′-yl)-4,5,9,16-tetraaza-dibenzo[*a*,*c*]naphthacene |
| dppp2 | Pyrido[2′,3′:5,6]pyrazino[2,3-*f*][1,10]phenanthroline |
| dppp3 | Pyrido[3′,4′:5,6]pyrazino[2,3-*f*][1,10]phenanthroline |
| dpqp | Pyrazino[2′3′:5,6]pyrazino[2,3-*f*][1,10]phenanthroline |
| hbt | 11*H*,13*H*-4,5,9,10,12,14-Hexaazabenzo[*b*]triphenylene |
| dppm2 | 10-Dimethyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine [26] |
| 10-Medppz | 10-Dimethyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine [91] |
| 11-Medppz | 11-Dimethyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine |
| dppx | 11,12-Dimethyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine [26] |
| 11,12-$Me_2$dppz | 11,12-Dimethyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine [91] |
| 10,13-$Me_2$dppz | 10,13-Dimethyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine |
| bidppz | 11,11′-bi(Dipyrido[3,2-*a*:2′,3′-*c*]phenazinyl) |
| tpphz | Tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2,3‴-*j*]phenazine |
| taptp | 4,5,9,18-Tetraazaphenanthreno[9,10-*b*]triphenylene [109] |
| ddz | Dibenzo[*h*,*j*]dipyrido[3,2-*a*:2′,3′-*c*]phenazine [108] |
| tpac | Tetrapyridoacridine |
| phehat | 1,10-Phenantrolino[5,6-*b*]1,4,5,8,9,12-hexaazatriphenylene |
| tatpp | 9,11,20,22-Tetraazatetrapyrido-[3,2-*a*:2′3′-*c*:3″,2″-*l*:2‴,3‴-*n*]pentacene |
| tatpq | 9,11,20,22-tetraazatetrapyrido-[3,2-*a*:2′3′-*c*:3″,2″-*l*:2‴,3‴-*n*]pentacene-10,21-quinone |
| bqpy | bis′-{Dipyrido[3,2′-*f*:2′,3″-*h*]quinoxalo}′-[2,3′-*e*:2′,3″-*l*]-pyrene |
| actatp | Acenaphtherenol[1,2-*b*]-1,4,8,9-tetraazariphenylence |
| dtpf | 4,5,9,12,16,17,21,25-Octaaza-23*H*-ditriphenyleno-[2,3-*b*:2′,3′-*h*]fluorene |
| dpqp | Dipyrido[2,3-*a*:3′,2′-*c*]quinolino[3,2-*j*]phenazine |
| qdppz | Naphtho[2,3-*a*]dipyrido[3,2-*h*:2′,3′-*f*]phenazine-5,18-dione |
| dpqp-OH | Hydroxy-dipyrido[3,2-*a*:2′,3′-*c*]quinolino[2,3-*h*]phenazine |

The nomenclature for ligands is given in Table 1, including alternative names where they are in common use.

A substantial body of work has also built up in which other metals form coordination complexes with dppz and related ligands, *e.g.*, osmium(II) [22,129–132], rhenium(I) [14,22,52,124,133–140,23,141–146], chromium(III) [147–153], rhodium(II,II) dimers [154–156], iridium(III) [157,158], cobalt(III) [113,121,159–161], iron(II) [161], copper(II) [22,136,138,23,146,162,163], nickel(II) [113,164–166], platinum(II) [22,167–172], palladium(II) [173], molybdenum(0) [22], gold(III) [174], and lanthanides (Eu(III), Gd(III), and La(III)) [175,176]. Of these, the photophysical work with rhenium is most relevant for the topic of this review. The extensive characterization of the excited states of the Re(I) complexes, which differ from those of Ru(II) complexes, provides a deeper insight into the photophysical influence of the dppz ligand in coordination complexes.

A number of monomeric and dimeric transition metal complexes (mainly ruthenium), and also mixed metal complexes, have been synthesized with bridging polyazaaromatic ligands (Fig. 5). These can be rigid ligands such as tpphz, studied in solution [177–186] and with DNA [55,109,187–192], tpac [193–197], phehat [195,198–201], tatpp [202–206], tatpq [202,203], bqpy [202,207]; semi-rigid dppz dimers such as 11,11′-bidppz, studied with DNA [208–217] and in solution [218,219]; and flexible dppz dimers such as C4(cpdppz)$_2$ [220–222]. For many of these dimeric complexes, the primary interest has been in their photophysics and their ability to act as electron or energy transfer dyads [181]; for others, it has been their improved and unusual DNA binding properties that have aroused interest [223]. However, extensive discussion of such complexes is largely beyond the scope of this review. A recent comprehensive review [224] of the past 10–15 years work on metal complexes with phenanthroline-based ligands provides more details about many of these systems.

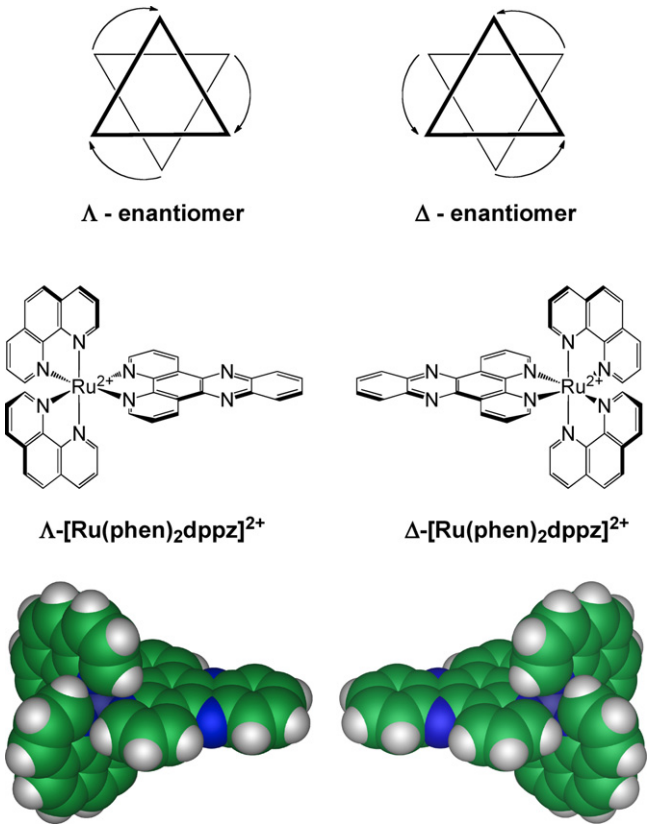


**Fig. 2.** The enantiomers of the octahedral complex [Ru(phen)$_2$dppz]$^{2+}$ rendered as lines and as space-filling models.

## 2. Effects of solvent polarity and environment on the steady-state photophysics of [Ru(L)$_2$dppz]$^{2+}$ and related complexes

### 2.1. The nature of emission

The UV/vis spectrum of [Ru(bpy)$_2$dppz]$^{2+}$ was initially assigned by comparison with the [Ru(bpy)$_3$]$^{2+}$ and uncomplexed dppz [2–4] spectra. With the aid of MO calculations [13], an MLCT absorption was assigned in the visible having $\lambda_{max}$ at ~440 nm, with a superimposed dppz IL transition at ~370 nm, and strong $\pi$–$\pi^*$ bands in the UV for the phen and bpy ligands. Full assignment of the nature and polarisations of the transition moments for [Ru(phen)$_2$dppz]$^{2+}$ has been made by Lincoln et al. using a semi-empirical method [34]. More recently, DFT/TDDFT calculations were performed for

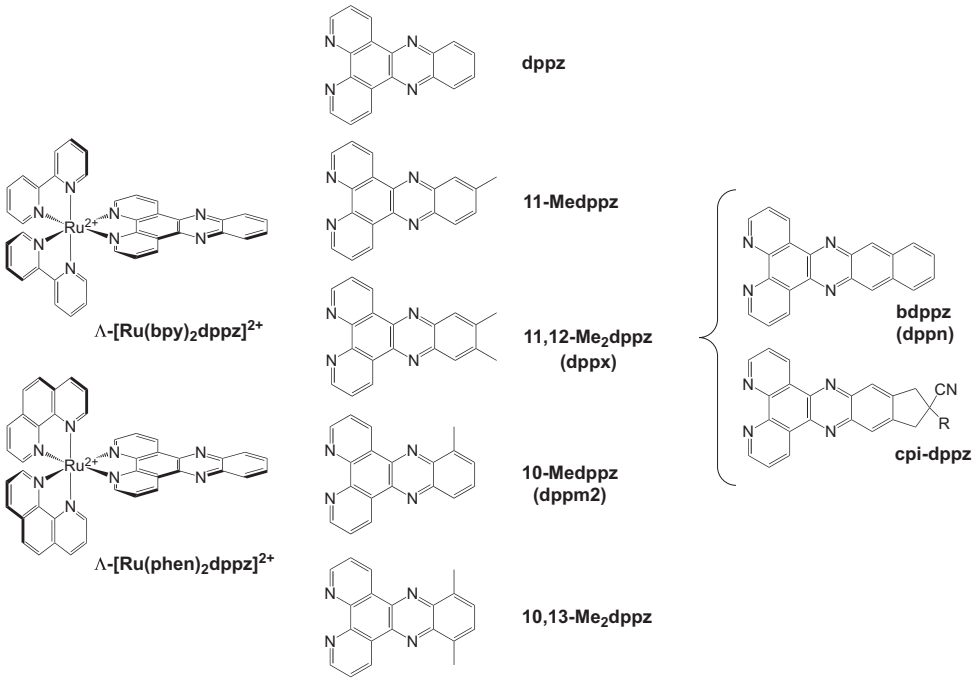


**Fig. 3.** Ruthenium(II) complexes with selected simple extended ligands based on the dppz chromophore. For alternative ligand abbreviations, see Table 1.

$[Ru(phen)_2dppz]^{2+}$ to compare with the experimental data in solution [93,96], and with DNA [95,97].

Early studies on the luminescence of $[Ru(L)_2dppz]^{2+}$ complexes, where L = bpy, phen and dppz, showed emission typical of the $^3$MLCT state of $[Ru(bpy)_3]^{2+}$ state at about 615 nm in organic solvents [2–4,12], micelles [12], and DNA [5]. However, in water, no emission could be observed at any wavelength. A dependence on the polarity of the organic solvent was also noted in these early papers, since emission intensity increased with linear alcohol chain length to propanol before dropping as the chain length was further increased [5,12].

Early studies using cyclic voltammetry [2,4,13], UV/vis [2,4,13] and emission [2,4] spectroscopies, nanosecond transient absorption spectroscopy [4] and EPR [13] also established that the emitting state resulted from a charge transfer from the ruthenium centre to the dppz ligand, in effect producing $[Ru^{III}(bpy)_2(dppz^{\bullet-})]^{2+}$ as the MLCT state. The spectrum of the dppz anion radical matched that of the nanosecond transient absorption of excited state $^*[Ru(bpy)_2dppz]^{2+}$, suggesting that the electron is localized on the dppz in this excited state [4]. These early papers also suggested that $[Ru(bpy)_2dppz]^{2+}$ is made up of two "electronically independent" units, $[Ru(bpy)_3]^{2+}$ and phenazine [3,4], with the phenazine part of the ligand weakly coupled to the ruthenium centre. A HMO perturbation approach suggested there were three close low-lying π-MOs, the lowest localized on the phenazine part of the dppz ligand $b_1$(phz), and two others localized on the α-diimine part, $b_1(\psi)$ and $a_2(\chi)$ [13].

Excited state resonance Raman studies on $[Ru(bpy)_2dppz]^{2+}$ and $[Ru(dmb)_2dppz]^{2+}$ [14] concurred that dppz is the acceptor ligand in the MLCT excited state. The spectra showed evidence of both phen-like and phenazine-like peaks, and were interpreted to imply that the excited electron is delocalized over the entire dppz skeleton.

### 2.2. Water quenching of emission

The absence of $[Ru(L)_2dppz]^{2+}$ mission in water as initially attributed to excited state quenching by $H_2O$, either by H-bond formation with the phenazine nitrogen atoms. The light switch effect for Ru(II) dppz complexes upon binding to DNA was attributed to protection of the phenazine nitrogen atoms from water when dppz is intercalated between the base pairs. [5]. Intensity and lifetime quenching of $[Ru(phen)_2dppz]^{2+}$ in $CH_3CN$ by $H_2O$ and $D_2O$ indicated static quenching, and isotope effects, $k_H/k_D$, of 2.1 (I) and 2.2 (τ) were observed, which are consistent with vibrational deactivation *via* a hydrogen bonding network.

Nair et al. [18] analysed this quenching by water further in a variety of solvents. Stern-Volmer plots were upwards curving, and were best fitted with a Perrin sphere-of-quenching model, with radii in the range 4.5–5.7 Å, decreasing roughly with H-bonding ability (Kamlet–Taft $\alpha$ parameter [225,226]), but also polarity of the solvent. This was consistent with formation of a H-bond (*ca.* 3 Å) in the quenching sphere. An isotope effect, $k_H/k_D$, of 1.5 (τ) was obtained in DMSO.

Demas and coworkers re-examined the quenching of $[Ru(phen)_2dppz]^{2+}$ emission by $H_2O$ in $CH_3CN$, and observed a large difference between quenching of emission intensities and lifetimes. They attributed this to a mix of static and dynamic quenching implying a ground state complex between $H_2O$ and the dppz nitrogen atoms [24], and ruled out the possibility that it could be due to changes in the radiative rate constant as the solvent composition changed. However, $k_r$ values are known to vary significantly with polarity and H-bonding ability of the environment (Section 2.3).

Recent non-linear Stern–Volmer data from our lab [227] also show significant differences between lifetime and intensity quenching of $[Ru(phen)_2dppz]^{2+}$ by oxygen in $CH_3CN$, but no differences in EtOH. Perrin analysis gives quenching radii similar to those of Nair et al. [18], and isotope effects of 1.4 (I)/3.2 (τ) in $CH_3CN$ and 1.2 (I and τ) in EtOH, consistent with previous studies.

Possible protonation of the $^*[Ru(phen)_2dppz]^{2+}$ phenazine nitrogen atoms, which are expected to be more basic in the excited state than the ground state, was tested by adding proton donors, *e.g.* hydroquinone and 2-chlorophenol, in $CH_3CN$ and when the

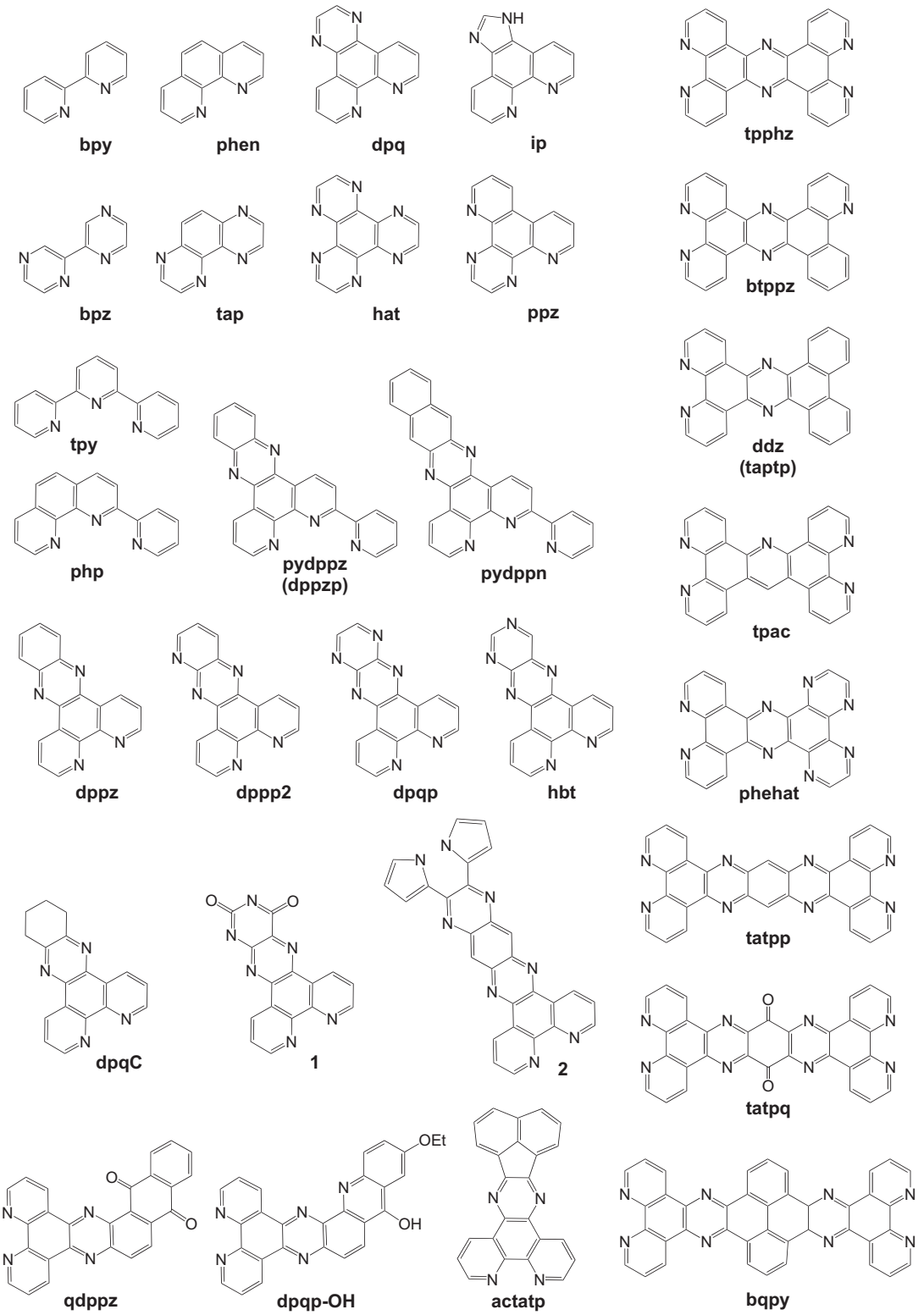


**Fig. 4.** Examples of extended polyazaaromatic ring systems that have been used as coordination ligands for ruthenium(II). For ligand abbreviations, see Table 1.

complex was bound to DNA [31]. Diffusion-controlled quenching with linear Stern–Volmer plots was observed in $CH_3CN$ for quenchers with p$K_a$s in the range 4.5–12; static quenching was observed when the complex was bound to DNA, as well as differential quenching of the long and short lifetimes (see Section 3). However, later time-resolved studies [83] rule out protonation of the excited state as a quenching mechanism. Hence, the reduction of luminescence by these quenchers must have an alternative mechanism.

Although more recent time-resolved studies (see below) have revealed greater detail about excited state dynamics for $^{*}[Ru(L)_2dppz]^{2+}$, steady-state studies provide important information about the behavior of the emissive state in the presence of water molecules.

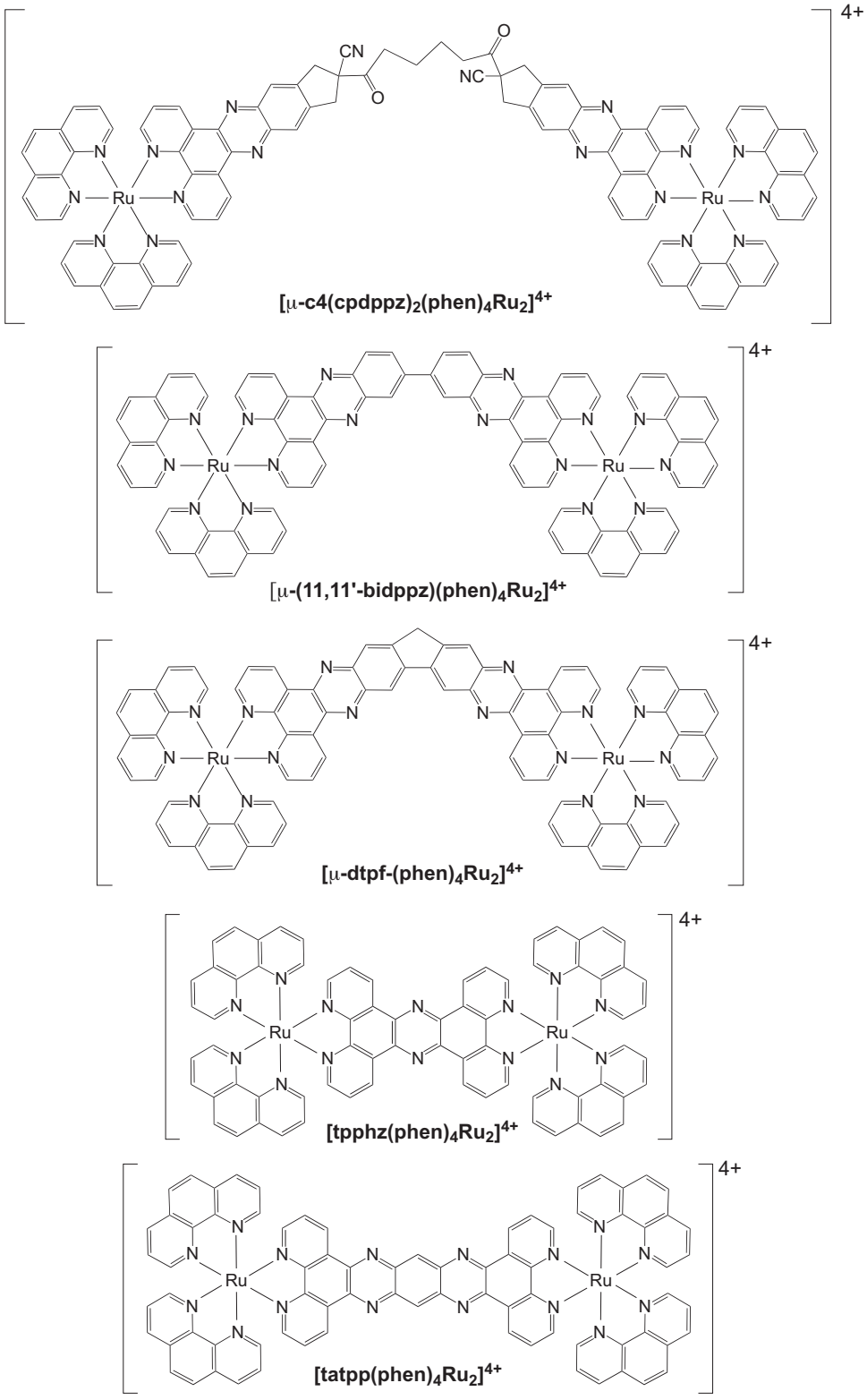


**Fig. 5.** Dimeric ruthenium(II) complexes with dppz-based bridging ligands. For ligand abbreviations, see Table 1.

### 2.3. Effects of solvent polarity on emission

The effect of varying solvent on the spectroscopic properties of $[Ru(phen)_2dppz]^{2+}$ was studied systematically for the first time by Murphy and coworkers [18]. The absorption spectra of the compounds in water and various non-aqueous solvents were very similar, but the emission maxima, lifetimes, and quantum yields were notably solvent-dependent. The wavelength of maximum emission depends on solvent, but without a linear correlation with polarity parameters. No emission was observed in water or in trifluoroethanol (TFE). The emission quantum yield and lifetime showed sensitivity to dissolved oxygen in all solvents, as observed previously [4] in ethanol ($k_q = 8 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$). The emission quantum yield and lifetime also varied with solvent, being reduced

in higher polarity solvents in a manner that correlated reasonably well with the $E_T$ value [225,226], an empirical parameter which reflects both polarity and H-bond-donating ability of the solvent. The radiative rate constant, $k_r$, varied little as a function of either solvent polarity or emission energy, so the change in emission intensity results from variations in the non-radiative rate constant, $k_{nr}$.

There was no clear correlation of $k_{nr}$ with the ground-excited state energy gap, unlike the simple complex $[Ru(bpy)_3]^{2+}$, indicating that the energy gap law does not hold for this complex. Contrary to expectations, based on the premise that H-bonding to the phenazine nitrogen atoms in the excited state quenches emission, $\ln(k_{nr})$ correlates reasonably with $E_T$, better than it does with the simple H-bond-donating ability, $\alpha$ [225,226], of the solvent, indicating that there are more subtle forces at play than were predicted by the early studies.

### 2.4. Effects of ancillary ligands on emission

In a series of four papers, Murphy and coworkers [18–21] illustrated the effect on emission of varying the ancillary ligands to non-aromatic species, and rationalise their observations qualitatively. $[Ru(phen)_2dppz]^{2+}$ is the archetypical light-switch complex [18], and the other complexes can be compared with it.

$[Ru(NH_3)_4dppz]^{2+}$ is non-emissive, either in any solvent or with DNA, and there was no shift in the MLCT absorption maximum when the complex bound to DNA, although hypochromism was observed [19].

$[Ru(CN)_4dppz]^{2-}$ is an anionic dppz complex [21], so it will not bind to DNA.

The MLCT absorption band of this complex shifts significantly with Gutmann acceptor number (a measure of solvent ability to accept electron density [225,226], in this case from the cyano ligands); the colour of the complex thus changes with solvent composition. Emission in ethanol at room temperature resembles that of the dppz ligand alone ($\lambda_{max} \sim 540$ nm), was not sensitive to solvent and was not quenched in water. However, at low temperature, a different spectrum typical of $^3$MLCT emission was observed ($\lambda_{max} \sim 600$ nm).

$[Ru(acac)_2dppz]$ is a neutral complex which is non-emissive in any solvent, like the $NH_3$ analogue [20]. The MLCT absorption maximum is sensitive to solvent, shifting to lower energy with decreasing solvent polarity on the $E_T$ scale [225,226], but with no correlation to H-bonding ability, polarizability, or dielectric constant of the solvent. The absence of emission in any solvent was proposed to be due to the electron-donating ability of the acac ligands which would push electron density towards the dppz ligand.

Minor modifications to ancillary α-diimine ligands, such as methylation of bpy to produce 4,4′-dimethyl-2,2′-bipyridine (dmb), have little effect on the photophysics of $[Ru(L)_2dppz]^{2+}$ [46]. $[Ru(dmb)_2dppz]^{2+}$ shows no emission in water and has significant emission when bound to DNA; however, the quantum yield on binding is about one third that of bound $[Ru(bpy)_2dppz]^{2+}$, which was attributed to increased vibrational deactivation in the methylated complex [46]. Likewise, $[Co(dmb)_2dppz]^{3+}$ showed about half the emission of $[Co(bpy)_2dppz]^{3+}$ when bound to DNA [161]. On the other hand, severe distortion in the coordination sphere of $[Ru(2,9\text{-}dmp)_2dppz]^{2+}$ results in no emission in water, any organic solvent, or when bound to DNA [46].

Modifications to ancillary α-diimine ligands that substantially change their electronic properties can alter the emission characteristics of the $[Ru(L)_2dppz]^{2+}$ complex. For example, $[Ru(TAP)_2dppz]^{2+}$ has strong emission in aqueous solution that is quenched on addition of CT-DNA [49]. Studies with polynucleotides showed that the emission is enhanced 2-fold on binding to $[poly(dA\text{-}dT)]_2$ but almost completely quenched on binding to $[poly(dG\text{-}dC)]_2$. This is attributed to its lowest MLCT state being localized on the TAP ligand rather than dppz, which turns off the light-switch effect, but confers strong oxidising ability on this complex [49,54].

For $[Ru(phendione)_2dppz]^{2+}$, the emission when bound to DNA is much lower than that of $[Ru(phen)_2dppz]^{2+}$ (about 2%) [51]. While the LUMO MLCT state of $[Ru(phen)_2dppz]^{2+}$ is dominated by π-antibonding orbitals localized on dppz, it appears that a subtle shift of this MO to higher energy in $[Ru(phendione)_2dppz]^{2+}$ leads to preferential localization of the electron on the phendione ligands.

$[Ru(IP)_2dppz]^{2+}$ has weak emission in aqueous solution which is enhanced 10-fold, and slightly red-shifted, on binding to DNA. It is unusual in having a mono-exponential lifetime when intercalated with DNA, while other dppz complexes show bi-exponentials (see Section 3) [43]. It is possible that in this complex, the MLCT is localized on the polyazaaromatic ligand IP rather than dppz, although this phenomenon was not studied further.

### 2.5. Effect of metal on emission

Apart from ruthenium(II), several other metal centres produce a light-switch complex when coordinated to dppz, but not all do.

For example, $[Cr(phen)_2dppz]^{3+}$ exhibits metal-centred phosphorescence in solution that is quenched by DNA [148,150,152,153]. Likewise, the emission of $[Ir(bpy)_2dppz]^{3+}$ is quenched by DNA [157].

$[Co(phen)_2dppz]^{3+}$ has its emission increased on binding to DNA, but already has significant emission in aqueous solution [159]. The same behavior is true for $[Co(L)_2(dppz\text{-}7\text{-}NO_2)]^{3+}$, where L: bpy, dmb, and phen [161].

On the other hand, $[Os(phen)_2dppz]^{2+}$ has no emission in water, and is a red-emitting light-switch DNA probe ($\lambda_{max} = 738$ nm) [129], albeit one which has very low quantum yield when bound to DNA and considerably shorter lifetimes (3.4 ns in aerated $CH_3CN$) than $[Ru(phen)_2dppz]^{2+}$ (177 ns in aerated $CH_3CN$ [18]).

The luminescence properties of several Pt(II) complexes with various extended aromatic ligands are described by an interplay of LC, MC, and MLCT states in organic solvents [171]. Weak emission of $[Pt(bdppz)(py)_2]^{2+}$ in aqueous solution was attributed to a mixed LC-MLCT triplet state [172], and enhancement was observed on binding to DNA both in external and intercalative modes. $[Pt(dppz)(4\text{-}aminopyridine)_2]^+$ is non-emissive in aqueous solution, but develops emission on binding to DNA, although with different properties than the emission in $CH_3CN$ [167].

After ruthenium, rhenium is the metal that has been most intensively studied in the excited state with dppz as a ligand.

Several rhenium(I) complexes also exhibit light-switch behavior. *fac*-$[Re(dppz)(CO)_3(py)]^+$ [134,135], *fac*-$[Re(dppz)(CO)_3(4\text{-}Mepy)]^+$ [133], and *fac*-$[Re(dppz)(CO)_3(4,4'\text{-}bpy)]^+$ [142] are light switch complexes that show no significant emission in aqueous solution and have their emission enhanced on binding to DNA. In these complexes the emission was arises predominantly from dppz-based $\pi\pi^*$ states with some MLCT character. Many rhenium(I) complexes have complicated photophysics with subtle inter-relations between ligand-localized and MLCT excited states. Schoonover et al. [14] examined the excited states of *fac*-$[Re(dppz)(CO)_3(Cl)]^+$, and *fac*-$[Re(dppz)(CO)_3(PPh_3)]^+$ and *fac*-$[Re(dppz)(CO)_3(4\text{-}Etpy)]^+$ (where $PPh_3$ = triphenylphosphine, and 4-Etpy = 4-ethylpyridine) and using emission and excited state resonance Raman spectroscopies. *fac*-$[Re(dppz)(CO)_3(Cl)]^+$ is a $^3\pi\pi^*$ emitter at 77 K in 4:1 (v/v) EtOH/MeOH but an MLCT emitter at room temperature; the latter two complexes are $\pi\pi^*$ emitters at both 77 and 298 K. Excited state resonance Raman spectroscopy demonstrated that the lowest excited state in all three complexes is $^3\pi\pi^*$. The difference between the Raman and emission results

was interpreted in terms of a two-state model with a $^3\pi\pi^*$ lowest excited state and a slightly higher energy MLCT state that is thermally populated. Since the MLCT state has shorter radiative and non-radiative lifetimes, it dominates the emission and the excited state decay at room temperature [14].

In studies on a series of rhenium complexes with modified dppz ligands, *fac*-[Re(dppz-11,12-$X_2$)$(CO)_3$(Cl)]$^+$ where X = $CH_3$, H, F, Cl, $CF_3$), Kuimova et al. [144] concur with Schoonover's analysis for *fac*-[Re(dppz)$(CO)_3$(Cl)]$^+$, and further clarify the nature of the MLCT state from TRIR studies (see Section 4.5).

### 2.6. Effect on emission of extending and modifying the dppz ligand

Substituents on the dppz ligand can have a substantial effect on the photophysics of the simple [Ru(L)$_2$dppz]$^{2+}$ complex, where L = bpy, dmb, and phen. The photophysics of complexes of dppz with other metals, *e.g.* Re, can also be significantly influenced by such substituents.

The most common positions for substitution on dppz are the 11- and/or 12-positions (Figs. 3 and 4), although some studies have also modified at the 10- and/or 13-positions [26,55,91,227], at the 1- and/or 8-positions [183], or the 2- and 7-positions [86].

Methylation at the 10-,11-,12-, and/or 13-positions, tends to increase emission lifetimes in water, organic solvents, and DNA compared with [Ru(L)$_2$dppz]$^{2+}$ [26,45,55,87,91,227]. This likely arises from a combination of electronic effects of the electron-donating substituents, steric effects that protect the non-coordinated dppz nitrogen atoms from H-bonding [227], and perturbation of the solvation shell [91]. The limited accessibility to the aza-nitrogen atoms on the phenazine part of the ligand when dppz is methylated can be inferred from the space-filled rendering shown in Fig. 2. Since emission from these complexes can be detected in aqueous solution, these complexes no longer exhibit a classical light-switch effect, even though their luminescence may be enhanced substantially (up to several hundred fold) on binding to DNA [91,227].

1,8-Dimethylation of dppz lengthens lifetimes of [Ru(bpy)$_2$dppz]$^{2+}$ in $CH_3CN$ and MeOH without significantly affecting the absorption spectra or the emission energy [183], suggesting that the methyl groups may protect the non-coordinated nitrogen atoms on dppz from solvent, as well as exerting subtle electronic effects due to their weakly electron-donating character. A similar modification of [Ru(bpy)$_2$tpphz]$^{2+}$ had much less effect on the emission lifetimes, presumably because the non-coordinated nitrogen atoms are already somewhat sterically protected from solvent in this more crowded ligand.

11,12-Dibromination has a much bigger effect on the photophysics of [Ru(tbbpy)$_2$dppz]$^{2+}$ (tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) than does 2,7-dibromination [85,86]. The former modification eliminates emission in $CH_3CN$ [86] although not in DCM [85], while the latter red-shifts the spectrum and doubles the lifetime and quantum yield of the MLCT emission. The former observation is suggested to be due to either a heavy atom effect increasing non-radiative decay to the ground state, or the stabilization of a non-emissive MLCT state localized on the phenazine-part of the dppz ligand by the weakly electron-withdrawing bromines.

By contrast, di-aryl (weakly electron-donating groups) substitution at the 11,12-positions of dppz in [Ru(tbbpy)$_2$dppz]$^{2+}$ [85] results in enhanced emission and longer emission lifetimes for the complex in $CH_3CN$ and DCM, with the lifetimes in DCM about 4-fold larger than those in $CH_3CN$.

[Ru(L)$_2$bdppz]$^{2+}$ (bdppz = dppn), where dppz is extended at the 11,12-carbons with a phenyl ring, was initially reported to have low emission in aqueous solution that was not enhanced on binding to DNA [26]. However, later studies found that it was virtually non-luminescent in water, organic solvents, or with DNA [25,34]. In fact, detailed time-resolved studies [25] established that the lowest excited state of [Ru(bpy)$_2$bdppz]$^{2+}$, and related complexes, was $^3\pi\pi^*$ in all conditions, which explains this observation. [Re(dppn)$(CO)_3$(py)]$^+$, likewise has low emission in aqueous solution that is not enhanced significantly on binding to DNA [134,135].

Similarly, [Ru(pydppn)$_2$]$^{2+}$ and [Ru(tpy)pydppn]$^{2+}$, which are red-emitting, short lifetime light switches, have a lowest pydppn IL $^3\pi\pi^*$ states as their lowest excited states, formed *via* a $^3$MLCT state [104,107].

However, if bdppz is further extended to generate the tpphz ligand, the situation changes again. [Ru(bpy)$_2$tpphz]$^{2+}$ emits strongly in $CH_3CN$ but only weakly in water, although emission is restored on binding to DNA [55,177,190] with a 50-fold increase in emission compared to water; like the methylated complexes it is not quite a light switch complex. [Os(bpy)$_2$tpphz]$^{2+}$ shows similar environment-dependent behavior, but with lower emission quantum yields and a red-shifted emission maxima [177]. Both complexes are observed to aggregate in $CH_3CN$, probably by π–π stacking [109,177]. Intriguingly, the luminescence of DNA-bound [Ru(bpy)$_2$tpphz]$^{2+}$ can be switched off by complexation of metal ions such as $Cu^{2+}$ [187] and $Co^{2+}$ [109].

Extension of dppz to form taptp (also called ddz) produces a complex, [Ru(bpy)$_2$taptp]$^{2+}$, with very similar properties to [Ru(bpy)$_2$tpphz]$^{2+}$; it aggregates in solution, emits weakly in water and more strongly in $CH_3CN$ but shows only a 4-fold increase in emission when bound to DNA [109].

[Ru(bpy)$_2$btppz]$^{2+}$ is a related complex that is pH sensitive [110]. It emits in water at pH 7, and shows a 54-fold emission enhancement on binding to DNA. However, emission is quenched when the btppz ligand is protonated and is insignificant at pH 1.

[Ru(phen)$_2$phehat]$^{2+}$ is a light-switch complex that luminesces in organic solvents but not in water, and has its luminescence restored on binding to DNA [198]. [Ru(phen)$_2$tpac]$^{2+}$, on the other hand, emits in water as well as in $CH_3CN$ and DNA, and has a propensity to be protonated in the excited state [194–196].

Other modifications to the dppz ligand are those which add nitrogen atoms to the ring system without extending it. Hartshorn et al. [26] described [Ru(phen)$_2$(L)]$^{2+}$ complexes with two such ligands, each with one extra nitrogen in the terminal phenyl ring, where L = dppp$^2$ and dppp$^3$. These behave similarly to each other, exhibiting significant MLCT emission in aqueous solution, and little emission enhancement on binding to DNA. Turro and coworkers have performed more detailed studies on [Ru(bpy)$_2$(dppp2)]$^{2+}$ and concur that the emission is little enhanced on DNA binding [55,101]. However, they report that the complex exhibits remarkable solvent-dependence of emission maximum, lifetime and quantum yield [101,102]. For example, its emission shifts from 752 nm in $CH_3CN$ to 653 nm in $CH_2Cl_2$ with a concomitant 19-fold enhancement in quantum yield. This behavior is very different from [Ru(bpy)$_2$(dppz)]$^{2+}$ which displays moderate changes in its luminescence properties as a function of solvent polarity. The behavior with dppp2 is attributed to the relative stabilities of two close-lying MLCT states, as for the parent compound, but with the lower energy state being much more sensitive to solvent polarity than that at higher energy [101,102]. Turro and coworkers have additionally synthesized the complex [Ru(bpy)$_2$dpqp]$^{2+}$, in which the dpqp (dipyrido[2,3-*a*:3′,2′-*c*]quinolino[3,2-*j*]phenazine) ligand has two extra nitrogen atoms in the terminal dppz ring [103]. [Ru(bpy)$_2$dpqp]$^{2+}$ exhibits strong emission in water as well as in $CH_3CN$, similar to [Ru(bpy)$_3$]$^{2+}$, and almost no emission enhancement on binding to DNA, despite strong association [103].

As well as modifications that extend the dppz ligand, one important related ligand is dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (dpq), which is a truncated polyazaaromatic analogue. Without reviewing the entire literature on ruthenium complexes containing this

ligand, which is fairly extensive, certain papers are relevant to the subject of this review, since they deal with the effects of substitution, solvent polarity, and the nature of the excited states of such complexes.

Kelly, Kruger and coworkers [228,229] studied modifications to the dpq ligand in the context of conjugating Ru complexes to oligonucleotides. While $[Ru(phen)_2dpq]^{2+}$ has its emission enhanced 6-fold on binding to DNA, it has significant emission in aqueous solution that is comparable to its emission in organic solvents [228]. Mono- and di-methylated complexes behave similarly, although methylation has a significant effect on the response of emission to the polarity of the solvent [228]. One related complex which does exhibit a light-switch effect on binding to DNA is $Ru(phen)_2(dpq\text{-}CONH(CH_2)_4CH_3)]^{2+}$ [229].

Ambroise and Maiya [230] described ruthenium complexes of the type $[Ru(phen)_n(CN_2\text{-}dpq)_{3-n}]^{2+}$, where $n = 1$–3. Substitution with these strongly electron-withdrawing groups has a considerable effect on the photophysics, such that $[Ru(CN_2\text{-}dpq)_3]^{2+}$ is non-emissive in any solution, the other two complexes behave as molecular light switches with DNA.

In $[Ru(phen)_2dpqC]^{2+}$, the dpq ligand is extended with a cyclohexane ring [100] rather than the phenyl ring that generates dppz. As with dimethylation, this complex is similar to the dpq complex and emits in aqueous solutions with only a modest (~2-fold) enhancement on binding to DNA.

Zaleski and coworkers [231] considered how the light switch effect could be controlled by creating a complex with an extended aromatic system similar to $[Ru(phen)_2dppz]^{2+}$ but with a low energy $^3\pi\pi^*$ state that would mix with the $^3$MLCT, as observed in Re(I) complexes with dppz. This was successfully achieved using an enediyne substituted dpq ligand, giving $[Ru(phen)_2bptt]^{2+}$ where bptt = 2,3-bis(phenylethynyl)-1,4,8,9-tetraazatriphenylene, which exhibits light switch behavior with DNA.

### 2.7. Emission in lipid and polymer environments

Chambron and Sauvage [12] showed that the emission of $[Ru(bpy)_2dppz]^{2+}$ was turned on when SDS was added to solution, maximizing above the cmc, as the dppz groups became buried in the hydrophobic micelles and protected from water. The emission intensity in SDS micelles was similar to that in heavy alcohols [12]. Consequentially, dppz-based light switch complexes make very good probes of lipid environments, including cell membranes [33,63–69]. Lipid membranes have also been used to orient the complexes for polarized spectroscopy [65].

Additionally, the complexes are luminescent in polymer environments with low water activity. $[Ru(bpy)_2dppz]^{2+}$ was incorporated into Nafion coatings [15] and was a sensitive probe of accessible water structures in the perfluorinated ionomer. The photophysics were complicated, with a tri-exponential emission decay that reflected self-quenching as well as local environment. Demas and coworkers [24] examined the emission of $[Ru(phen)_2dppz]^{2+}$ in cross-linked polymethacrylate polymer films, and found that the intensity reflects the water content of the film and therefore environmental humidity.

## 3. Effects of DNA binding on the steady-state photophysics of $[Ru(L)_2dppz]^{2+}$ and related complexes

### 3.1. Racemic complexes with DNA

Friedman et al. [5] were the first to report the binding of *rac*-$[Ru(bpy)_2dppz]^{2+}$ to DNA, and the observation of the light-switch effect, whereby its emission was enhanced from essentially zero in aqueous buffer by a factor of $>10^4$ when intercalcated with DNA. Large emission enhancements were observed with CT-DNA and $[poly(dG\text{-}dC)]_2$, but only a small enhancement with the A-form RNA duplex $[poly(rA\text{-}rU)]_2$. Despite the huge enhancement, the emission quantum yield of the bound complex was low, $\Phi \sim 0.02$ compared to 0.042 for $[Ru(bpy)_3]^{2+}$ in aqueous solution. Luminescence lifetime experiments revealed that *rac*-$[Ru(bpy)_2dppz]^{2+}$ (10 μM) bound to CT-DNA exhibited a bi-exponential decay with a short-lived component of 75 ns and a long-lived component of 259 ns (66% of emission) at a P/D ratio of 10.

Hartshorn et al. [26] studied the luminescence of a series of *rac*-$[Ru(phen)_2L]^{2+}$ complexes, where L = dppz and modified bases, in $CH_3CN$, aqueous solution, and bound to DNA. Apart from $[Ru(phen)_2dppz]^{2+}$, all showed some emission in aqueous solution and could not be classified as light switch probes of DNA. At a P/D ratio of 51, *rac*-$[Ru(phen)_2dppz]^{2+}$ (8.3 μM) exhibited biexponential emission decay of 120 ns ($\alpha = 0.8$) and 750 ns ($\alpha = 0.2$), where $\alpha$ is the pre-exponential factor. The bi-exponential decay was attributed to two binding modes, proposed to be two orientations of the complex bound by intercalation from the major groove, supported by NMR [30], where the non-coordinated nitrogen atoms of the dppz ligand are more exposed to water in the groove in one orientation (responsible for the short lifetime) than in the other (responsible for the long lifetime). Dependence of lifetime on exposure to water was supported by an isotope effect in which changing from $H_2O$ in buffer to $D_2O$ resulted in both lifetimes increasing for $[Ru(phen)_2dppz]^{2+}$ bound to CT-DNA [33]. All the complexes studied bind to DNA by intercalation, and all exhibit bi-exponential emission decays under comparable conditions, although with varying lifetimes and pre-exponential factors.

Jenkins et al. [27] systematically compared the luminescence properties of *rac*-$[Ru(bpy)_2dppz]^{2+}$ and *rac*-$[Ru(phen)_2dppz]^{2+}$ bound to DNA and expanded the work to include a ribo- and deoxyribo-nucleic acids of varying base composition and conformation. Bi-exponential emission decays were observed for both complexes with all nucleic acid materials examined, and subtle differences in lifetimes and pre-exponential factors for the two complexes at a P/D ration of 10 (inferred from comparison of the data in [5] and [26]) were apparent. Generally, luminescence intensity and lifetimes were longer with the phen-complex than with the bpy-complex. For both complexes, emission intensities were lowest with A-form duplexes and highest with triplex DNA, although lifetimes were comparable to those observed with other polynucleotides. Longer lifetimes were apparent with AT-polynucleotides compared to GC-polynucleotides, particularly for the phen-complex; however, relative emission intensities more similar due to variations in pre-exponential factors.

### 3.2. Enantiomers with DNA

Hiort et al. [6] published the first work on the photophysics of the enantiomers of $[Ru(phen)_2dppz]^{2+}$ bound to nucleic acids. This study revealed that analysis of the emission decays of racemic complexes bound to DNA as bi-exponentials was an over-simplification of the photophysics. It was clear that Δ- and Λ-$[Ru(phen)_2dppz]^{2+}$ have different luminescence properties when bound to DNA, even though they intercalate with similar geometries [17,34], and that they must be considered as different species when incorporated in the chiral environment of nucleic acids. For either enantiomer with CT-DNA, or with defined-sequence polynucleotides, the emission decay was biexponential, and the magnitudes of the lifetimes depended on both the enantiomer and the DNA sequence [6]. With mixed-sequence DNA, *e.g.* CT-DNA, for either enantiomer, both the amplitudes and lifetimes of the biexponential decay varied as a function of P/D ratio. The observed trend was for

both the long and the short lifetimes to decrease as the amount of bound complex increased, and for higher proportions of the longer lifetimes as the amount of bound complex increased. The binding model invoked to explain the two lifetimes was that both enantiomers intercalate from the minor groove, with the longer lifetime arising from contiguously bound complexes where the intercalated dppz is well protected from solvent and the shorter lifetime arising from isolated bound complexes where the dppz is more accessible to solvent, *i.e.* groove-bound water [6].

Lim et al. [59] recently reported that the luminescence of $[Ru(bpy)_2dppz]^{2+}$ is sensitive to DNA mismatches and abasic sites at a central GC site in a mixed sequence 27-mer oligonucleotide, and a central AT site in a 12-mer hairpin oligonucleotide. Strong enhancements of steady-state emission were observed in the presence of such defects. At a low [DNA/[Ru] ratio with the 27-mer, neither the long nor the short lifetimes of the bi-exponential emission decay varied greatly with defect for either *rac*-, Δ- or Λ-$[Ru(bpy)_2dppz]^{2+}$. However, in each case, the amplitude of the longer lifetime increased when the defect was present, leading to an increase in observed intensity. It is suggested that the complex intercalates into the mismatched and abasic sites from the minor groove [59].

Biexponential emission decay was also reported for the rhenium light-switch complex *fac*-$[Re(CO)_3(dppz)(4\text{-Mepy})]^+$, where 4-Mepy = 4-methylpyridine, bound to CT-DNA [133]. For this complex, which is non-luminescent in aqueous solution, the emissive state is assigned as $^3IL_{dppz}$ rather than MLCT. The transient absorption of the complex bound to DNA also showed bi-exponential kinetics which were monitored as a function of P/D ratio. As with the enantiomers of $[Ru(phen)_2dppz]^{2+}$, the trend was for both lifetimes to decrease in magnitude as the amount of bound complex increased, and for the amplitude of the long lifetime to increase with increasing amount of bound dye.

It is remarkable that the Ru(II)-dppz and Re(I)-dppz complexes display similar bi-exponential emission decay behavior when intercalated with CT-DNA, despite having different metal centres, ancillary ligands, and excited state natures. Since organic intercalators that have a single intercalative binding mode give mono-exponential emission decays, this suggests that the bi-exponential behavior is a property particular to intercalation of octahedral transition metal complexes with an excited state localized on dppz.

### 3.3. Enantiomers with polynucleotides

In addition to studies of Δ- and Λ-$[Ru(phen)_2dppz]^{2+}$ emission with CT-DNA as a function of P/D ration, Hiort et al. [6] reported the lifetimes for the enantiomers with $[poly(dA\text{-}dT)]_2$ and $[poly(dG\text{-}dC)]_2$ at a P/D ratio of 10. Comparative lifetimes for the Δ-enantiomer are significantly longer than for the Λ-enantiomer. Also, lifetimes with $[poly(dA\text{-}dT)]_2$ are longer than those with $[poly(dG\text{-}dC)]_2$. It is likely that the lifetimes observed with CT-DNA are a convolution of all these lifetimes.

Subsequent work on the emission of Δ- and Λ-$[Ru(phen)_2dppz]^{2+}$ bound to nucleic acids explored the P/D-dependence of the emission with $poly(dA\text{-}dT)]_2$, as well as the effect on the photophysics of varying polynucleotide sequence and conformation at a P/D of 50 where, in the absence of cooperative binding, the complexes should be well separated [35]. A principle aim of that work was to exclude some potential sources of bi-exponential decay. For example, emission decays were studied with non-alternating poly(dA).poly(dT) and poly(dG).poly(dC), which each possess one type of intercalation site (compared to $[poly(dA\text{-}dT)]_2$ and $[poly(dG\text{-}dC)]_2$, which have two types of base pair step each). The observation of two lifetimes with the non-alternating polynucleotides therefore excluded the possibility that different intercalation steps are responsible for the bi-exponential decays. In fact, Δ- and Λ-$[Ru(phen)_2dppz]^{2+}$ both gave bi-exponential decays with all the polynucleotides studied. These results [35] suggest that both Δ- and Λ-$[Ru(phen)_2dppz]^{2+}$ intercalate from the minor groove. This is also supported by NMR studies [47], and seems to exclude the possibility that the two lifetimes arise from intercalation from alternate grooves. The possibility that two different excited states give rise to the two lifetimes when bound to DNA is unlikely, given that the transient absorption and TR$^3$ spectra for the two species are essentially identical (see Section 4). Hence, the observation that the long lifetime amplitude increases with an increase in the density of $[Ru(phen)_2dppz]^{2+}$ bound to $[poly(dA\text{-}dT)]_2$, as it does with CT-DNA, lends weight to the Hiort model [6] that the two lifetimes are linked to adjacency of intercalated molecules.

The emission lifetimes of Δ- and Λ-$[Ru(phen)_2(11,12\text{-}Me_2dppz)]^{2+}$ and $[Ru(phen)_2(10\text{-}Me_2dppz)]^{2+}$bound to CT-DNA and $[poly(dA\text{-}dT)]_2$ have been reported [91] at a P/D ratio of 10. As with the unmethylated complex, bi-exponential decays were observed for all combinations studied and lifetimes for Δ-enantiomers were longer than those for Λ-enantiomers with the same DNA. However, lifetimes for the methylated complexes were significantly longer than those for the unmethylated complex. The data suggest that these complexes also intercalate DNA from the minor groove, and that quenching by water mainly takes place from the groove where the Ru(II) ion resides. This result suggests that the aza-nitrogen atoms of the dppz ligand are rather close to the edge of the base pair that faces the Ru(II) ion. The shorter lifetimes observed for the Λ-enantiomers therefore imply that the dppz ligands of these enantiomers penetrate less deeply into the intercalation site and are more accessible to quenching water molecules. It appears that the steric hindrance of the 10-methyl substituent is of greater importance when bound to DNA than it is in solution. An interesting observation was that the ratio of long and short lifetimes is surprisingly constant in all systems for both enantiomers with a value of $\tau_{LONG}/\tau_{SHORT} \sim 5$, which suggests that the two lifetimes have similar structural origins in all systems. However, the possibility that the two lifetimes have an origin in sequential H-bond formation, to the aza-nitrogen atoms, similar to that observed in diols, is ruled out since the magnitudes of the pre-exponential factors preclude the possibility that the long lifetime is a precursor to the short lifetime [91].

### 3.4. Geometry of intercalated $[Ru(phen)_2dppz]^{2+}$

Intercalation of $[Ru(phen)_2dppz]^{2+}$ is very strong and appears to saturate at P/D = 4 [6,35], which is the limit for nearest-neighbour intercalation. This is surprising for such a large molecule and implies that the complexes are very well packed along the DNA duplex.

To envisage how such packing could occur if the complex is intercalated from the minor groove, Fig. 6 illustrates how this might occur for both Δ- and Λ-$[Ru(phen)_2dppz]^{2+}$ [221]. The graphic shows an energy minimized model of the dimers Λ,Λ- and Δ,Δ-$[\mu\text{-}c4(cpdppz)_2(phen)_4Ru_2]^{4+}$ bound to DNA; these dimers have been show to bis-intercalate by a threading mechanism (as does the Δ,Λ-enantiomer) [220,221]. In the Δ-complex, the ancillary phen ligands lie along the walls of the minor groove while, in the Λ-complex, the phen ligands straddle the groove and are in van der Waals contact at saturation. The model shown in Fig. 6 is consistent with the molecular mechanics predicted geometry of $[Ru(phen)_2dppz]^{2+}$ in the $[poly(dA\text{-}dT)]_2$ minor groove [17], generated taking into account the interpretation of polarised spectroscopy data [34] using calculated transition moment assignments [17].

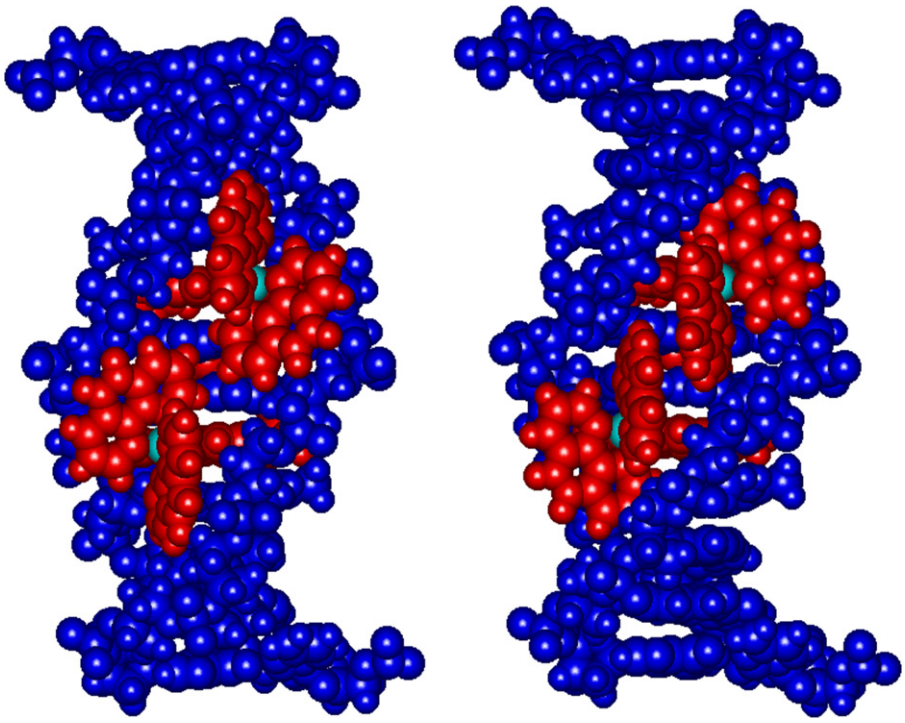

**Fig. 6.** Δ,Δ- (right) and Λ,Λ-[μ-c4(cpdppz)$_2$(phen)$_4$Ru$_2$]$^{4+}$ (left) bound to DNA by bis-intercalation [221], showing the arrangement of the ancillary phen ligands in the minor groove.

## 4. The excited states of [Ru(L)$_2$dppz]$^{2+}$: theory and experiment

### 4.1. The nature of the excited states

Early studies on the steady-state and time-resolved luminescence of [Ru(bpy)$_2$dppz]$^{2+}$ and [Ru(phen)$_2$dppz]$^{2+}$ (see Section 2), suggested that that emission at ~615 nm arose from a $^3$MLCT state similar to that of [Ru(bpy)$_3$]$^{2+}$ and [Ru(phen)$_3$]$^{2+}$. This emission was "switched on" when the complexes were bound to DNA and "switched off" in aqueous solution. It was also "on" when the complexes were dissolved in organic solvents, micelles, lipid membranes, and polymer films; but could be "dimmed" by increasing the polarity and/or H-bonding ability of the solvent, or by increasing the content of water in the non-aqueous phase.

Spectroelectrochemistry and nanosecond transient spectroscopy established that the emissive state resided on the dppz ligand, and it appeared that H-bonding to the phenazine nitrogen atoms in water quenched this emission.

Subsequent application of ultrafast absorption [83,84,86,102], linear dichroism [84], Raman [70–81,136–138,232], and IR spectroscopies [139–141,143,144] to these systems and related systems, in addition to variable-temperature measurements [87–91] and complementary theoretical studies [92–97], have revealed substantially more detail about the nature of the emissive and "non-emissive" excited states in these complexes, although some questions still remain.

### 4.2. Time-resolved spectroscopy of [Ru(L)$_2$dppz]$^{2+}$ excited states

Olson et al. [83] applied picosecond time-correlated single photon counting (TCSPC) emission and transient absorption spectroscopy to [Ru(phen)$_2$dppz]$^{2+}$, in $H_2O$ and $CH_3CN$ solutions, and proposed a mechanism involving two close lying metal to ligand charge transfer (MLCT) states (Fig. 7).

Although both states are emissive, the primary MLCT state (MLCT′, $\lambda_{em}$ = 610 nm) is responsible for the emission in non-aqueous solvents such as $CH_3CN$ ($\tau_b$ = 660 ns), while in an aqueous environment the secondary MLCT state (MLCT″, $\lambda_{em}$ = 800 nm, $\tau_d$ = 250 ps) becomes accessible and dominates the photophysics *via* a rapid MLCT′ → MLCT″ interconversion. This secondary MLCT″ state, though emissive, has an extremely low luminescence quantum yield as a result of a rapid non-radiative decay pathway and, as such, is not observed in steady-state emission spectroscopy. The rate at which the singlet state decayed to the MLCT′ state ($\tau_a$) was determined to be less than 300 fs, limited by the instrument response function, while the internal conversion from MLCT′ to MLCT″ ($\tau_c$) was determined to be approximately 3 ps. This rapid interconversion is responsible for the low quantum yield of emission from MLCT′ of $\Phi$ = 0.3 in $CH_3CN$ [18].

A deuterium isotope effect of $k_D/k_H$ = 2.3 was observed for the rapid radiationless decay of MLCT″ in water. This observation suggests that solvent H-bonds with the phenazine nitrogen atoms are accepting modes for radiationless decay, together with the 3 ps MLCT′ → MLCT″ being a reasonable timescale for H-bond formation. However, the authors [83] point out that a $H_2O/D_2O$ effect of comparable magnitude has been observed for the MLCT state of [Ru(bpy)$_3$]$^{2+}$ [233] which lacks non-coordinated nitrogen atoms on the ligands. Therefore, such isotope effects are not definite proof of H-bond formation.

A femtosecond linear dichroism study of [Ru(phen)$_2$cpdppz(CH$_2$)$_4$NH$_2$]$^{2+}$ in water and DNA by Önfelt et al. [84] adds detail to this model regarding the rate at which the interconversion of states occurs, in addition to the nature of the solvent effect on these processes. In aqueous solution, two excited state processes were observed after equilibration to $S_1$, with lifetimes of 700 fs and 4 ps; the 700 fs process involved a major dichroism change, while the 4 ps process had an associated small anisotropy change. Interestingly, these are approximately the lifetimes measured for reorientational modes of bulk water [234]; rotation of weakly and strongly H-bonded molecules, respectively.

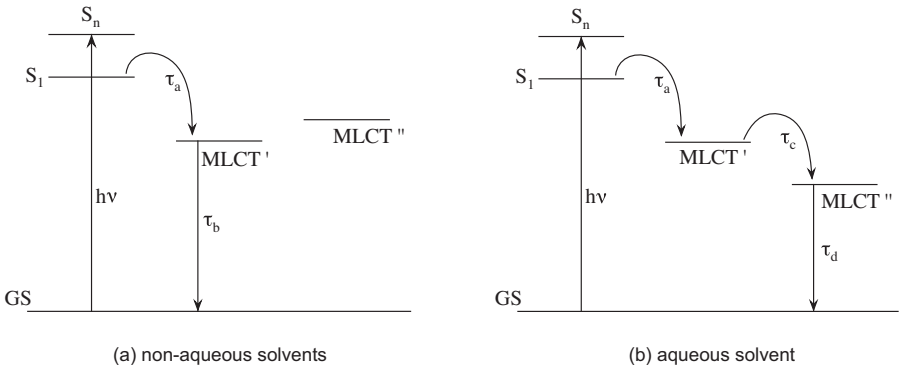


**Fig. 7.** Schematic energy level diagram for the $[Ru(phen)_2dppz]^{2+}$ excited state model proposed by Olson et al. [83].

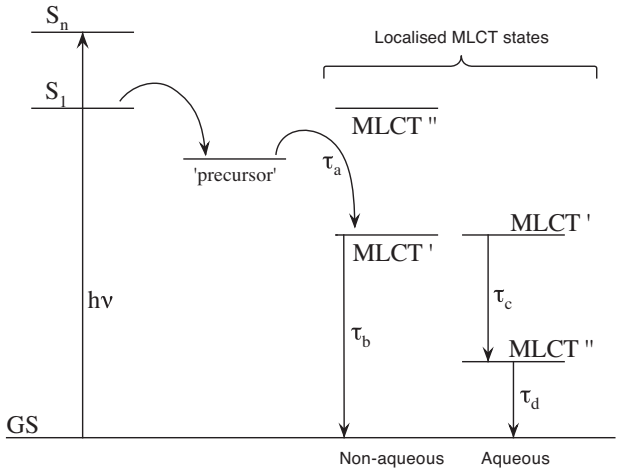


**Fig. 8.** Schematic energy level diagram for the $[Ru(phen)_2dppz]^{2+}$ excited state model proposed from the studies of Önfelt et al. [84] and Coates et al. [79].

The 700 fs process was assigned to an $S_1 \rightarrow$ MLCT process, where $S_1$ is delocalized over the three ligands and MLCT is localized on dppz, with reorientation of $H_2O$ accompanying a $phen^{\cdot -} \rightarrow dppz^{\bullet -}$ charge transfer. The 4 ps process was assigned to an equilibration of the dppz-localized MCLT, $MLCT_{un\text{-}eq} \rightarrow MLCT_{eq}$, accompanied by further solvent reorientation, and involving either formation or reinforcement of H-bonds and the aza lone-pairs of the dppz radical anion. An isotope effect in $H_2O$ ($\tau_H/\tau_D$) for the 4 ps process also correlates well with the isoptope effect measured for the reorientation of water at room temperature [235]. When bound to DNA, slower processes with lifetimes of 7 and 37 ps were observed, and were assigned to structural and electronic equilibration of the Ru(dppz)–DNA complex.

It is likely that $MLCT_{un\text{-}eq}$ and $MLCT_{eq}$ in Önfelt et al's paper [84] correspond with MLCT′ and MLCT″ in Olson's paper [83], so the latter terminology is used in future discussions. They likely also correspond to $MLCT^{prox}$ (proximal) and $MLCT^{dis}$ (distal); terminology used to indicate an MLCT concentrated on the phen part of the dppz, or on the phenazine part, respectively.

Further refinement was proposed by Coates et al. [79] from the results of time-resolved resonance Raman ($TR^3$) studies on $[Ru(phen)_2dppz]^{2+}$ in $H_2O$, $CH_3CN$, and MeOH (Fig. 8). The conclusions obtained in this work were only possible because of the extensive ground-state and transient Raman characterisation of $[Ru(L)_2dppz]^{2+}$ complexes carried out by McGarvey and coworkers [70,71,76–78], which allowed identification of Raman bands that were associated with specific ligands and processes. A so-called 'precursor' state was observed to which the singlet state manifold relaxes following the initial absorption. The precursor state does not itself have radiative properties; instead, radiative effects are observed from one of the two MLCT states. It was found that the lifetime of the precursor state is dependent on the solvent environment, which is consistent with Önfelt et al.'s [84] suggestion that the formation of MLCT′ involves reorientation of the solvent molecules. It was also observed that the rate of radiative decay from MLCT′ depends on the solvent. In water, the lifetime for MLCT′ → MLCT″ conversion was 5–10 ps, and the rate of decay of MLCT″ to the ground state was 250 ps, consistent with the emission results of Olson et al. [83].

In subsequent studies, Olofsson et al. [80] used $TR^3$ to further examine the nature of the "precursor" state for $[Ru(phen)_2dppz]^{2+}$ proposed by Coates et al. [79] in additional solvents and when bound to DNA. This work proposes that the initial Franck-Condon excited state of $[Ru(phen)_2dppz]^{2+}$ is a singlet $^1$MLCT state localized on any one of the three ligands, which converts rapidly (with a lifetime of approximately 100 fs) to a triplet $^3$MLCT state on the same ligand. This is proposed to be the nature of the "precursor" state, and corresponds to the first state observed in the femtosecond linear dichroism studies of Önfelt et al. [84]. After such relaxation, it is proposed that an inter-ligand electron transfer (ILET) occurs, depositing the electron in a $^3$MLCT state localized on dppz. This ILET process results in a large change in the dipole moment of the excited state complex (as well as a large dichroism change), so that the rate of the ILET is strongly influenced by the polarity of the solvent, as well as its rate of reorganisation (which is also influenced by H-bonding and polarizability). For $[Ru(phen)_2dppz]^{2+}$ bound to DNA, it appears that the intercalated environment of dppz is so different from that of the ancillary phen ligands that the excited state is localized on the dppz ligand virually instantaneously, so that no "precursor" state is observed [80].

Kuhnt et al. [86] studied the excited states of $[Ru(tbbpy)_2(Br_2dppz)]^{2+}$, where tbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, in acetonitrile. Di-bromination at the 2,7-positions (one the bpy-part of dppz) stabilizes the bright state so that population of the dark state is reduced compared to the unmodified complex. By contrast, di-bromination at the 11,12-positions (on the phenazine-part of dppz) results in relative stabilization of the dark state with respect to the bright state, and accelerates non-radiative decay to the ground state.

Turro and coworkers examined the ultrafast dynamics of the $^3$MLCT states of the related complex, $[Ru(bpy)_2(dppp2)]^{2+}$ [102], where the extended ligand is more readily reduced than dppz, and there are large solvent effects on emission. Like $[Ru(L)_2(dppz)]^{2+}$, two $^3$MLCT states were observed—$MLCT^{prox}$ and $MCLT^{dist}$. Interconversion between them was on ps timescales in various solvents (26 ps in $CH_3CN$ and 6.7 ps in EtOH), with strong depen-

dence on solvent polarity and H-bonding ability. In contrast to $[Ru(L)_2(dppz)]^{2+}$, the emitting species for this complex is assigned as $^3MCLT^{dist}$.

### 4.3. Temperature dependence of $[Ru(L)_2dppz]^{2+}$ emission

Studies by Brennaman et al. [87,88] of the temperature dependence of $[Ru(bpy)_2dppz]^{2+}$ emission in both aprotic ($CH_3CN$, BuCN) and protic (MeOH) solvents suggested that the light-switch effect is the result of competition between a "bright" state and a "dark" state of the complex, which may be considered to correspond to the MLCT′ and MLCT″ states described in Section 4.2. The light state is associated with the bipyridyl portion of the dppz ligand, while the dark state is located on the phenazine portion. In protic solvents, hydrogen bonding lowers the energy of the dark state, effectively quenching the luminescence. This is supported by the ligand orbital associated with the bright state being similar in size to the corresponding orbital in the $^3$MLCT state of $[Ru(bpy)_3]^{2+}$.

Contrary to previous work, however, the Brennaman model [87] suggests that the dark state is always lower in energy, even in aprotic solvents, and that the "light switch" effect is the result of competition between the entropically favoured bright state and the enthalpically favoured dark state. At low temperatures, the enthalpic (dark) state dominates and lower lifetimes are observed, while at higher temperatures (*e.g.* room temperature) the entropic (bright) state dominates the luminescence. At temperatures higher than room temperature, the luminescence lifetimes reduce again as a result of thermal population of metal-centred dd states, which are about 3100 $cm^{-1}$ higher in energy than $^3$MLCT.

In protic solvents such as MeOH [87], it is proposed that the greatly reduced excited state lifetime is caused by strong preferential stabilization of the dark state such that the temperature required to shift the population to the bright state lies above room temperature, and even above the boiling point of the solvent. The implications of solvent polarity are also described, with a small change in solvent polarity having a profound effect on the energy gap, and hence the equilibrium, between the light and dark states. The origin of the stabilization is proposed to stem from differences in the charge distribution in the two states. If the MLCT electron is localized on the phenazine-part of dppz in the dark state, there will be a large excited state dipole moment, which will be stabilized as solvent polarity is increased. Also, comparative studies with $[Ru(dppz)_3]^{2+}$ [87] demonstrated that this complex must also have an equilibrium between dark and light states, which strongly suggests that $[Ru(bpy)_2dppz]^{2+}$ can be described as a $[Ru(bpy)_3]^{2+}$ core with a phenazine charge acceptor, and that the charge separation is internal to dppz rather than between the bpy and dppz ligands.

In subsequent work, Brennaman et al. [88] continued to explore the temperature-dependent photophysics of these complexes through systematic variation of the dielectric constant of the solvent and chemical modification of the dppz ligands. The excited state model was refined to describe the relationship between the bright–dark state energy gap and $T_{max}$, the temperature at which the maximum luminescence lifetime is observed. Data for $[Ru(bpy)_2dppz]^{2+}$ can be described as a $[Ru(dppz)_3]^{2+}$ with three linear alcohols and three linear nitriles show that $T_{max}$ is correlated to the dielectric constant of the solvent. For a given solvent, $T_{max}$ for $[Ru(dppz)_3]^{2+}$ is shifted to lower temperature than $T_{max}$ for $[Ru(bpy)_2dppz]^{2+}$, although the origin of this difference is unclear. The increase in $T_{max}$ with increasing solvent polarity is consistent with a stabilization of the dark state in more polar solvents, as expected from the previous discussion, above. Stabilization of the dark state would result in a larger energy gap (more negative $\Delta H^\circ$), which would raise the temperature at which the entropic term overcomes the enthalpic term. It would also result in a smaller energy gap between the dark state and the ground state, thus increasing non-radiative decay from the dark state, which would also raise $T_{max}$. The nitriles have lower $T_{max}$ values than the alcohols, the difference probably arising from the ability of alcohols to H-bond to the phenazine nitrogen atoms, which would stabilize the dark state more than solvent polarity alone (Fig. 9).

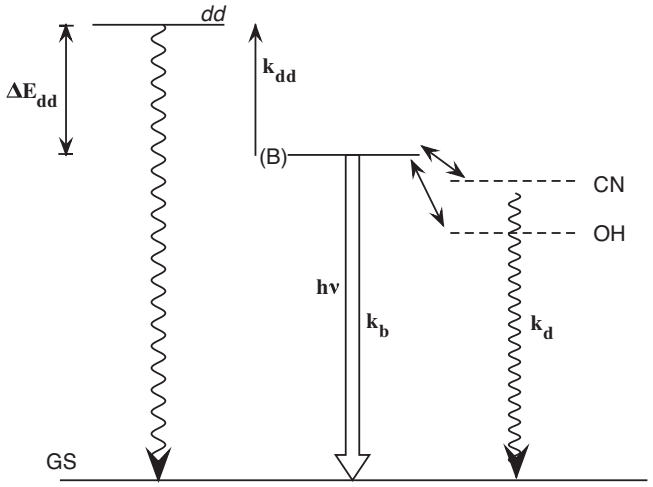


**Fig. 9.** Schematic energy level diagram for the $[Ru(bpy)_2dppz]^{2+}$ excited state model proposed from the studies of Brenneman et al. [87,88].

Similar experiments [88] with $[Ru(bpy)_2(11,12\text{-}Me_2dppz)]^{2+}$ and $[Ru(11,12\text{-}Me_2dppz)_3]^{2+}$ in alcohols indicates that the bright state energy is not affected by di-methylation, but the energy gap between bright and dark states is decreased because the energy of the dark state is raised. This is consistent with the expectation that electron-donating methyl substituents would destabilize an electron in a $\pi^*$ localized on the phenazine-part of the dppz ligand. The luminescent lifetimes of the modified complexes show similar behavior to their unmodified counterparts in alcohols, but in nitriles behave differently. The temperature dependence of $[Ru(bpy)_2(11,12\text{-}Me_2dppz)]^{2+}$ in BuCN closely follows that of $[Ru(bpy)_3]^{2+}$, suggesting that the excited state population remains in the bright state between 150 and 350 K. This could be because the energy gap has become so small that it can be overcome even at low temperatures; alternatively the dark state could be raised in energy above that of the bright state in this complex, which would make the bright state enthalpically favoured.

Studies on the temperature dependence of $[Ru(phen)_2dppz]^{2+}$ emission in glycerol by Önfelt et al. [89] suggested that there are three excited states each with a characteristic luminescence lifetime. State A occurs immediately after excitation whereby the excited electron resides in a $\pi^*$ orbital on one of the three ligands. State B results from conversion of State A, where the electron moves from its initial excited state across the three ligands to lie in a lower energy state on the extended dppz ligand. State C occurs when the solvent has reorganised to H-bond to both phenazine nitrogen atoms. It is accepted that State A decays rapidly into State B, however there is an entropic/enthalpic equilibrium between States B and C, as also suggested by Meyer and coworkers [87,88]. Deconvoluted spectra for the different states indicate that H-bonding to the excited state red-shifts the emission to ~680 nm for State C; so, not as far as the 800 nm emission maximum observed by Olsen et al. [83] for MLCT″.

Later work focused on the question of whether H-bonding to both phenazine nitrogen atoms was necessary to quench the luminescence of the $[Ru(phen)_2dppz]^{2+}$ complexes [90]. This work suggested that, in addition to the primary state populated immediately after excitation (State A), there are two emissive MLCT states, and a third non-emissive MLCT state. These three MLCT states cor-

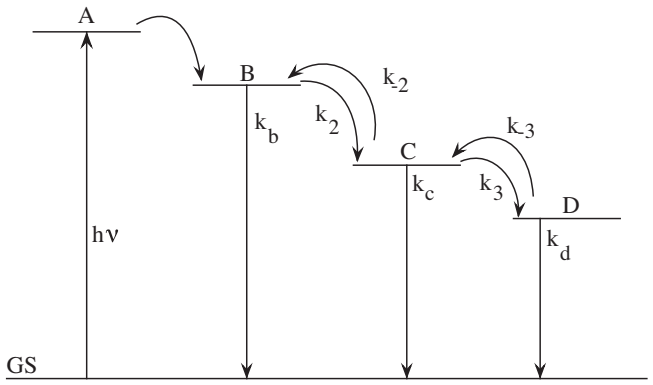


**Fig. 10.** Schematic energy level diagram for the $[Ru(bpy)_2dppz]^{2+}$ excited state model proposed from the studies of Önfelt, Olofsson et al. [89–91].

respond to either both aza-nitrogen atoms H-bonded to the solvent (the dark state), one nitrogen H-bonded (one bright state) or neither nitrogen H-bonded (the other bright state). It was necessary to introduce a third energy level because the energy difference between States B and C was significantly smaller than originally estimated [89]; thus, if State B corresponds to no H-bonds formed, State C must be reassigned to a mono-H-bonded species, inferring the existence of State D where two H-bonds exist. The existence of this non-emissive state is confirmed by kinetic modeling of the temperature dependence of the steady-state concentrations of B and C, a model which necessitates the non-emissive state, D, shown in Fig. 10.

Methylation of dppz (Fig. 3) was also studied in diol solvents as part of the investigation of the "light switch" effect [91]. In this case, it was anticipated that methyl substitution at the 10-position would sterically shield of the aza-nitrogen atoms and that dimethyl substitution at the 11- and 12-positions would also have a significant effect on the photophysics since previous reports indicated that methylation increased the quantum yield in water [26]. Indeed, results obtained from temperature dependence studies suggest that, in all cases, methyl substitution does not primarily affect the enthalpy of making a H-bond, but rather acts to increase the entropy cost of H-bond formation by the solvent to the excited state. 11,12-Dimethyl substitution, despite the more remote location, has almost as pronounced an effect on decreasing the H-bonding as 10-methyl substitution. This effect is attributed to perturbation of the solvation shell around the complex, indicating that the whole solvation shell around the charged dppz ligand is of importance.

### 4.4. Theoretical studies of $[Ru(L)_2dppz]^{2+}$ excited states

In addition to experimental studies, there have been a number of theoretical studies which have examined the origin of the "light switch" effect [92–97]. These have calculated the excited states of the ruthenium complexes using different approaches, and provide varying results.

Time dependent density functional theory (TDDFT, also known as density functional response theory) and self-consistent field (SCF) theory calculations performed by Batista and Martin [94] on $[Ru(bpy)_2dppz]^{2+}$ suggest that there are two nearly degenerate triplet states on the dppz molecule; one ligand based $^3(\pi\rightarrow\pi^*)$ and the other of MLCT character. The dark state in this instance is attributed to the intraligand triplet state, while the $^3$MLCT $(d\rightarrow\pi^*)$ is the radiative bright state. In a general sense, these theoretical results supports the observations of equilibrium between dark and bright states [87,91]. The near degeneracy is such that thermal transfer of electrons between the two levels is possible, although the calculations place the dark state lower in energy which contradicts the results of Brennaman et al. [87,88]. A similar approach confirmed that, from a theoretical perspective, the lowest-lying dark state is predicted to be a dppz-based $^3\pi\pi^*$ state [92].

Brennaman et al. [88] reject the possibility that the dark state is a dppz-based $^3\pi\pi^*$ state, primarily because their results support a state with a large charge-transfer character, which would not be true of a $^3\pi\pi^*$ state. However, from the work of Olson et al. [83], it is known that MLCT′, which corresponds to the "dark" state, is not completely dark but exhibits weak red emission. There is a possibility that this could correspond to the phosphorescence of a H-bonded $^3\pi\pi^*$ state with intraligand charge-transfer character as much as it could to a H-bonded MLCT state. Future theoretical and experimental studies may, in time, resolve this issue.

In a recent study, Atsumi et al. [96] used time-dependent density functional field theory (TD-DFT) to study the nature of the very early stage photophysics of the $[Ru(phen)_2dppz]^{2+}$ complex within 10 ps of excitation. In this work, in addition to identification of absorption transitions, it is reported that the Franck-Condon state is a 'hot' $^1$MLCT state, which quickly relaxes and undergoes subsequent intersystem crossing to the $^3$MLCT state which is available for luminescence, supporting the experimental observations of Olofsson concerning the nature of the precursor state [80].

### 4.5. Related studies with rhenium(I) complexes containing dppz

The excited states of rhenium(I) complexes with a dppz ligand have also been extensively studied. Systematic absorption, emission, EPR and TRIR work on the solvent-dependent photophysics of *fac*-$[Re(CO)_3(11,12\text{-}X_2dppz)py]^+$ (X = H, F or Me) [143] and *fac*-$[Re(CO)_3(dppz\text{-}X_2)Cl]^+$ ($X = CH_3$, H, F, Cl or $CF_3$) [144], coupled with DFT calculations, has provided insight into the effect of environment on these complexes.

For *fac*-$[Re(CO)_3(11,12\text{-}X_2dppz)py]^+$ in acetonitrile, all complexes are similar and the dominant species is $^3IL(\pi\pi^*)$. By contrast in water, the dominant species for the X = H and $CH_3$ derivatives is $^3IL(\pi\pi^*)$, while for X = F, which is non-emissive in water, a mix of $^3IL(\pi\pi^*)$ and MLCT(phz) states occurs. It is proposed that the deactivation mechanism involves solvent H-bonding to the dppz aza-nitrogen atoms, as seen for ruthenium(II) complexes with a dppz ligand [89–91].

For all *fac*-$[Re(CO)_3(dppz\text{-}X_2)Cl]^+$ complexes, the calculations show a lowest unoccupied MO that is dppz-based and localized on the phenazine-part of the ligand. Three excited states, MLCT(phen), MLCT(phz), and $IL(\pi\pi^*)$ are formed depending on the substituent on the ligand and the nature of the solvent. Similar to $[Ru(L)_2dppz]^{2+}$ [87,88], the data suggest that the MLCT(phz) state is stabilized more than MLCT(phen) in more polar solvents, possibly because of greater charge separation in the former. H-bonding ability of the solvent as well as polarity affected the excited state dynamics, and both factors resulted in the lifetime of MLCT(phz) being shortened and altered the dynamics of its formation. The data agree with those for $[Ru(L)_2dppz]^{2+}$ [87–91], that the higher lying MLCT(phen) state is preferentially populated over the lower energy MLCT(phz) state also in these Re(I) complexes. The nature of the excited state could be tuned by varying the electron-withdrawing ability of the substituents X on the dppz ligand. $IL(\pi\pi^*)$ bands are not observed when strongly electron-withdrawing groups such as $-CF_3$ are appended to dppz, as the energy gap between the two MLCT states and the $IL(\pi\pi^*)$ state becomes large, while the gap between MLCT(phz) and MLCT(phen) becomes small.

These studies demonstrate the similarity of the excited states manifolds in dppz complexes of Ru(II) and Re(I). In both cases, the emission is sensitive to the nature of the solvent as well as substituents on the dppz ligands.

## 5. Conclusions and outlook

Over the past 20 years, since the first report of the "light-switch" for $[Ru(bpy)_2dppz]^{2+}$ emission on binding to DNA, a vast array of steady-state and time-resolved spectroscopic techniques have been applied to this system in an attempt to understand the nature of the excited in this complex that give rise to this unusual effect. Recent work that combines DFT calculations with experimental measurements as a function of solvent properties and ligand modification, as well as studies with other metal centres, has thrown some light on the phenomenon, but there remain several outstanding questions. In particular, the role (if any) of triplet interligand $\pi\pi^*$ states on dppz in the $[Ru(L)_2dppz]^{2+}$ emission is suggested by calculations, but not apparent experimentally. Also, the nature of the two emission lifetimes when these complexes bind to DNA remains to be completely resolved. It is likely that answers to these outstanding issues will emerge in the near future, and that tuning of the system to produce switches and probes based on transition metal complexes with dppz and related ligands will continue to be a fertile research area.

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