Molecular Design of pH-Sensitive Ru(II)-Polypyridyl Luminophores

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Abstract: Three new $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions, where bpy represents bipyridyl ligand and X denotes pH-sensitive pyridyl diazolate or pyrazinyl diazolate coordination site, have been computationally designed and synthesised as pH sensitive molecules. The choice of pyridyl and pyrazinyl moieties allows for the nitrogen content to vary, while the influence of the protonation site is quantified by using 1,2-diazolate and 1,3-diazolate derivatives. The absorption and emission properties of the deprotonated and protonated complex ions were characterised by UV-vis and photoluminescence spectroscopy, as well as by time-dependent density functional theory. Protonation causes (1) a strong blue shift in the lowest energy $^3\text{MLCT} \rightarrow \text{S}_0$ emission wavelengths, (2) a substantial increase in the emission intensity and (3) a change in the character of the corresponding $^3\text{MLCT}$ emitting states. The blue shift in the emission wavelength becomes less pronounced when the nitrogen content in the X ligand increases and when going from 1,2- to 1,3-diazolate derivatives. The contrast in the emission intensity of the protonated/deprotonated forms is highest for the complex ion, containing 2-pyridyl derivative of the 1,2-diazolate. The complex ions are suggested as potential pH-responsive materials based on change in the colour and intensity of the emitted radiation. The broad impact of the research is that demonstrate that the modification of the nitrogen content and position within the protonable ligands is an effective approach for modulation of the pH-optosensing properties of Ru-polypyridyl complexes.

Introduction

The emission of light is a powerful probe of chemical information at the molecular level¹⁻³ such that many sensing devices are based on photoemission phenomenon.⁴ For example, in information processing devices the emission light response is switched between two or more states by application of external stimuli such as pressure, temperature and pH.^{5,6} Successful examples of stimuli-responsive luminophores can be found in the family of organometallic complexes.⁷⁻⁹ An advantage of such a hybrid organic-inorganic approach is that the heavy metal functionality gives rise to phosphorescent emissions with relatively long emission lifetime and good quantum yields, which are beneficial for signal detection. Another advantage of the hybrid approach is that the presence of organic functionality implies stronger vibronic coupling effects and gives greater variety in the external stimuli that can be applied. For example, in organometallics the ligands can be designed to be protonable/deprotonable, which allows the use of pH stimulus opening up their potential to become pH sensors.¹⁰⁻¹²

The high potential of the organometallics for the creation of stimuli-responsive materials has led to considerable effort to reveal the fundamental aspects of their photophysical molecular response.^{4,13} Key fundamental aspects in this respect are the derivation of molecular design principles and determination of structure-properties relationships that can be used for the tuning of organometallic emission behaviour. It has been demonstrated that the photophysical response can be significantly altered by changing the central metal ion, while fine tuning of the emission energy, intensity and lifetime can be obtained by ligand modification.¹⁴ However, the principles for the excited state design in organometallics and their relation to the photophysical stimuli responses are not fully understood and are the subject of this study.

The main goal of this investigation is to explain how the photophysical response of organometallic luminophores can be selectively tuned by ligand modification and how it can be switched by using pH as an environmental stimulus. We focus on the family of Ru-polypyridyl luminophores because they have a wide range of applications in dye sensitized solar cells,^{15,16} light-emitting diodes,¹⁷ anti-tumor agents,¹⁸ luminescent sensors,¹⁹ non-linear optical materials,²⁰ molecular switches and machines,^{21,22} and catalysts²³. Another reason to choose Ru-polypyridyl complexes is that they can be molecularly engineered to contain pH-sensitive ligands.^{10,24,25} In particular, we have studied four Ru-polypyridyl complex ions of type $[\text{Ru}(\text{bpy})_2\text{X}]^+$ (**Scheme 1**), where X denotes an anionic protonable/deprotonable ligand: pyrazinyl-1,2-diazolate, pyrazinyl-1,3-diazolate, pyridinyl-1,2-diazolate or pyridinyl-1,3-diazolate. The complex ions of the first three ligands are designed in our laboratory and their acid-base ground and excited state properties are

reported for the first time, while the complex ion of pyridinyl-1,3-diazolate and its pH-optical response have been reported previously²⁶ and is studied here to act as a reference. The selection of the X ligands allows us to reveal how the nitrogen-content and nitrogen-position affect the photophysical response and the pH optosensing properties of $[\text{Ru}(\text{bpy})_2\text{X}]^+$ luminophores.

Scheme 1. Chemical structure and abbreviation of the investigated deprotonated $[\text{Ru}(\text{bpy})_2\text{X}]^+$ and protonated $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions and the corresponding ligands. In compounds notation: 1 is the number of the N-atom in the five-membered ring coordinated to Ru; 2 and 3 denote the presence of N-atom at G₂- or G₃-positions in the five-membered ring; PY and PZ show the presence of pyridine (CH-group at G₄ position) and pyrazine cycle (N-atom at G₄ position) in the X ligand, respectively; AZ denotes diazolate five-membered ring; ²H and ³H denote that proton is attached to the N-atom at G₂- and G₃-positions, respectively. In order to distinguish between the two bpy ligands, they are denoted as L (left) and R (right) depending on their location with respect to the X ligand.

Experimental procedure

All precursor reagents, solvents and high purity NMR solvents were purchased from commercial sources (Sigma Aldrich and Acros) and used as supplied unless otherwise stated. $\text{Ru}(\text{bpy})_2\text{Cl}_2$ (50 mg, 0.1 mmol) was synthesized using method proposed previously²⁷ and one equivalent of the respective ligand were dissolved into a solution of acetone and deionised water in a pressure tube (Scheme 2). The tube was sealed and the solution stirred for 12 hours at reflux. The solution was cooled to room temperature and the acetone removed under a nitrogen flow. A saturated solution of NH_4PF_6 was added dropwise to the solution and the precipitation of the subsequent salt took place. The precipitate was isolated off and dried overnight in a vacuum desiccator. Products were recrystallized using 1:1 water acetone mixtures. All reactions that are air or moisture sensitive were carried out under nitrogen atmosphere using standard Schlenk and vacuum line techniques.

UV/Vis spectra were recorded with a Cary 5000 UV-Vis-NIR spectrophotometer equipped with Pb-Smart detector. All the measurements were carried out in acetonitrile (MeCN) using Hellma suprasil quartz cuvettes (limit 200-2,500 nm spectral range, path length 10 mm, chamber volume 3,500 μL). The photoluminescence spectral data were obtained from a Cary Eclipse spectrometer equipped with a halogen lamp as excitation source. All the excitations were carried out at 285 nm with an auto excitation filter and the emissions were detected in the presence of 430 nm – 1100 nm emission filter. For solution measurements samples Hellma 101-QS cuvettes (Suprasil® quartz, limit 200-2,500 nm spectral range, path length 10 mm, chamber volume 3,500 μL) were used. The solutions were prepared at 10^{-5} M, both base and acid were used to protonate and deprotonate the sample. Trimethylamine (TEA) and trifluoroacetic acid (TFA) were used as base and acid agents, respectively.

Scheme 2. Reaction scheme for the synthesis of Ru-complexes.

Computational procedure

Geometry optimization of the $[\text{Ru}(\text{bpy})_2\text{X}]^+$ and $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions (**Scheme 1**) were performed with the PBE0 functional.²⁸ Pople 6-311G* split-valence basis set²⁹ for the ligand parts and Stuttgart/Dresden (SDD) pseudopotential and basis set for Ru³⁰ were used. The electrostatic interaction with the acetonitrile solvent ($\epsilon_0=35.688$, $\epsilon_\infty=1.807$) was taken into account by using polarizable continuum model (PCM) in its integral equation formalism variant.³¹⁻³³ The frequency analysis confirmed that the optimized ground state structures represent true minima on the potential energy surface. Absorption and emission properties were obtained by the time dependent formulation of density functional theory (TD-DFT)³⁴ with the same functional, basis sets and solvation model as for ground state geometry optimization. The same computational strategy was recently successfully applied in our laboratory in the design of platinum and ruthenium complexes with tunable luminescence properties.³⁵⁻³⁸ All quantum-chemical

calculations were performed with the Gaussian 09 program package.³⁹ The molecular orbitals were visualized with an isosurface value of 0.04 by using GaussView 5 graphical interface.⁴⁰

Results and Discussion

Absorption and emission properties of the deprotonated complex ions $[\text{Ru}(\text{bpy})_2\text{X}]^+$

Comparison between the calculated vertical excitations and experimental absorption spectra can be found in **Table 1**, **Figure 1** and **Figure 2**. From a molecular design perspective, it is important to discuss the possibility to tune the absorption properties of the deprotonated complex ions as a function of the X ligand. Our results reveal that for all $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions the first absorption band originates from the $(\text{d}-\pi_{\text{azo}})-\pi^*_{\text{bpy}}$ transition and that its wavelength varies within a small range depending on the X ligand. In particular, the tunability range for the first absorption band is estimated to be ~33 nm from calculations and ~17 nm from experiment. Despite the relatively small effect of the X ligand, the following tunability trends can be observed: the absorption wavelengths for $(\text{d}-\pi_{\text{azo}})-\pi^*_{\text{bpy}}$ transitions blue shifts when the nitrogen content in the six-membered ring of the X-ligand increases and as 1,2-derivatives > 1,3-derivatives. The observed tunability trends can be explained by the change in the energy of the HOMO ($\text{d}-\pi_{\text{azo}}$) levels as a function of the X-ligand rather than that of the LUMOs (π^*_{bpy}) (**SI, Table S13**). Here, it is important to note that for the deprotonated ions the π^*_{bpy} orbitals are localized on one of the bpy ligands. The dominant UV-vis and UV excitations in the absorption spectra of the $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions represent $\text{d}-\pi^*_{\text{bpy}}$ and $\pi_{\text{bpy}}-\pi^*_{\text{bpy}}$ transitions and therefore do not show high sensitivity on the choice of the X ligand. There is an overall good agreement between calculated and experimentally measured absorption wavelengths for the deprotonated complexes though the theoretical UV maxima are systematically overestimated by ~0.3 eV. The computational results on the first forty excited states for the deprotonated complex ions, as well as a detailed discussion on the most important excitations can be found in the supporting information (**SI, Discussion S1** and **Table S1**).

The experimentally measured emission spectra (**Figure 5, Table 1**) for the $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions show maxima located at 736 nm (12PYAZ), 730 nm (13PYAZ), 710 nm (12PZAZ) and 705 nm (13PZAZ). The calculated emission energies and wavelengths are listed in **Table 1**. The $\text{T}_1 \rightarrow \text{S}_0$ transitions are predicted to be at 865 nm (12PYAZ), 850 nm (13PYAZ), 819 nm (12PZAZ) and 808 nm (13PZAZ). The dominant electronic configuration (**Table 2** and **SI, Table S6**) in all T_1 states one electron excitation from HOMO ($\text{d}-\pi_{\text{azo}}$) to LUMO (π^*_{bpy}). Therefore, our results reveal that for all complex ions the lowest in energy excited state represents metal-to-ligand charge transfer ($^3\text{MLCT}$) transition with $(\text{d}-\pi_{\text{azo}})-\pi^*_{\text{bpy}}$ character.

Table 1. Calculated absorption ($S_0 \rightarrow S_n$) and emission ($T_n \rightarrow S_0$) wavelengths for deprotonated $[\text{Ru}(\text{bpy})_2\text{X}]^+$ and protonated $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions: S_n and T_n denote the number of the excited state in TD-DFT/PCM calculations, λ^{th} [nm] are the calculated wavelengths for vertical excitations, λ^{exp} [nm] experimental wavelengths, E^{th} [eV] are the calculated energies for vertical excitations/emissions, E^{exp} [eV] are the energies of the experimentally measured absorption/emission maxima, f^{th} denotes the calculated oscillator strength. The experimental measurements and theoretical estimations are for acetonitrile.

$S_0 \rightarrow S_n$											
12PYAZ						13PYAZ					
S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	2.31	536	0.0011	2.46	505	1	2.39	519	0.0017	2.51	494
2	2.39	519	0.0112			2	2.43	511	0.0048		
5	2.80	442	0.1205	2.73	454	5	2.78	447	0.1404	2.77	447
39	4.60	270	0.3908	4.28	290	39	4.61	269	0.5238	4.26	291
12PYAZ ² H						13PYAZ ³ H					
S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	2.72	457	0.0008	2.77	448	1	2.67	464	0.0012	2.74	453
2	2.74	452	0.0036			2	2.69	461	0.0009		
5	3.07	404	0.1348	3.00	413	5	3.00	413	0.1600	2.92	425
34	4.62	268	0.6746	4.34	286	36	4.67	266	0.6083	4.32	287
$T_1 \rightarrow S_0$											
12PYAZ						13PYAZ					
T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	1.43	865	NA	1.68	736	1	1.46	850	NA	1.70	730
12PYAZ ² H						13PYAZ ³ H					
T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	1.85	669	NA	1.98	625	1	1.86	667	NA	1.97	630
$S_0 \rightarrow S_n$											
12PZAZ						13PZAZ					
S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	2.39	519	0.0011	2.58	480	1	2.47	503	0.0018	2.54	488 ^{sh}
2	2.47	502	0.0137			2	2.51	494	0.0058		
6	2.89	429	0.1003	2.83	438	5	2.85	435	0.1353	2.75	451
37	4.55	272	0.1986	4.28	290	40	4.61	269	0.5356	4.28	290
40		270	0.1909								
12PZAZ ² H						13PZAZ ³ H					
S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	S_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	2.78	447	0.0013	2.84	436	1	2.77	448	0.0016	2.76	449
2	2.81	441	0.0011			2	2.79	444	0.0008		
7	3.18	390	0.1315	nep	nep	6	3.08	403	0.1055	nep	nep
8	3.22	385	0.1529	nep	nep	8	3.19	389	0.1208	nep	nep
38	4.67	266	0.6495	4.37	284	36	4.63	268	0.7151	4.34	286
$T_1 \rightarrow S_0$											
12PZAZ						13PZAZ					
T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	1.51	819	NA	1.75	710	1	1.53	808	NA	1.76	705
12PZAZ ² H						13PZAZ ³ H					
T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}	T_n	E^{th}	λ^{th}	f^{th}	E^{exp}	λ^{exp}
1	1.87	662	NA	1.99	622	1	1.88	659	NA	1.93	644

NA not available, nep not a clear peak; sh shoulder.

Figure 1. Experimental UV-vis spectra for 12PYAZ and 13PYAZ complex ions (continuous line). The experimental absorption spectra are normalized with respect to the main UV peak. TD-DFT/PBE0/PCM oscillator strengths (bars) and wavelengths are also presented, as well as the molecular orbitals involved in the key electronic excitations. The oscillator strengths are normalized with respect to the most intensive transition.

Figure 2. Experimental UV-vis spectra for 12PZAZ and 13PZAZ complex ions (continuous line). The experimental absorption spectra are normalized with respect to the main UV peak. TD-DFT/PBE0/PCM oscillator strengths (bars) and wavelengths are also presented, as well as the molecular orbitals involved in the key electronic excitations. The oscillator strengths are normalized with respect to the most intensive transition.

Another important aspect is the tunability in the emission properties of the deprotonated complexes ions as a function of the X ligand. The tunability range for the emission wavelengths of the $(d-\pi_{\text{azo}})-\pi^*_{\text{bpy}}$ transitions is estimated to be at ~ 57 nm from calculations and ~ 31 nm from experiment. The following tunability trends can be observed for the $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions: the emission wavelengths blue shift when the nitrogen content in the six-membered ring of the X

ligand increases and as 1,2-derivatives > 1,3-derivatives. The observed tunability trends can be explained again by the change in the HOMO ($d-\pi_{\text{azo}}$) energies as a function of the X ligand rather than that of the LUMO ($\pi^*_{\text{bpy}}^{\text{L}}/\pi^*_{\text{bpy}}^{\text{R}}$) energies. The theoretical and experimental results for the emission properties of the deprotonated complexes are in a qualitative agreement, however, the PBE0 functional systematically underestimates the emission energies with ~ 0.24 eV (average deviation from experiment). Possible explanation of the quantitative differences is the lack of counter ions in our molecular models⁴¹ and the use of linear response approach, as well as by fact that the vibronic structure of the emission bands is not taken into account in the theoretical simulations.

Table 2. Leading MOs in T_1 of the deprotonated complex ions $[\text{Ru}(\text{bpy})_2\text{X}]^+$.

12PYAZ		12PZAZ	
HOMO	LUMO	HOMO	LUMO

13PYAZ		13PZAZ	
HOMO	LUMO	HOMO	LUMO

Absorption and emission properties of the protonated complex ions, $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$

Calculated vertical excitations and experimental absorption spectra for the protonated complex ions are shown in **Table 1**, **Figure 3** and **Figure 4**. The first absorption band in $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions represent $^1\text{MLCT}$ transition with $(d-\pi_{\text{azo}})-\pi^*_{\text{bpy}}$ or $d-\pi^*_{\text{bpy}}$ character. Unlike the case of the deprotonated ions, in the protonated forms the π^*_{bpy} orbitals span both *bpy* ligands. The wavelength of the first absorption band for the $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions blue shifts slightly when the nitrogen content in the six-membered ring of the X ligand increases. The nitrogen position in the five-membered ring also has a small effect on the wavelength of the lowest energy transitions and the later slightly shifts to the red when going from 1,2- to 1,3-derivatives. In summary, the tunability range for the first absorption band of the protonated complex ions amounts to only ~ 17 nm from calculations and experiment. The higher in energy $^1\text{MLCT}$ in $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions are assigned as $d-\pi^*_{\text{bpy}}$, while the inter-ligand and intra-ligand (^1IL) excitations possess $\pi_{\text{bpy}}-\pi^*_{\text{azo}}$ or $\pi_{\text{bpy}}-\pi^*_{\text{bpy}}$ character. Due to their electronic character and the small participation of the diazolate ring, the $d-\pi^*_{\text{bpy}}$ and $\pi_{\text{bpy}}-\pi^*_{\text{bpy}}$ excitations have lower sensitivity to

protonation. The agreement between calculated and experimentally measured absorption wavelengths for the protonated complexes is good though again the theoretical UV maxima are overestimated by ~ 0.3 eV. TD-DFT results on all forty excited states for the protonated complex ions $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ and detailed discussion on the most important excitations are presented in **SI, Table S7** and **Discussion S3**.

The experimentally measured emission spectra of $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions (**Figure 5, Table 1**) reveal maxima at 625 nm (12PYAZ²H), 630 nm (13PYAZ³H), 622 nm (12PZAZ²H) and 644 nm (13PZAZ³H). The TD-DFT emission energies and wavelengths are presented in **Table 1**. The $T_1 \rightarrow S_0$ emission is calculated to be at 669 nm (12PYAZ²H), 667 nm (13PYAZ³H), 662 nm (12PZAZ²H) and 659 nm (13PZAZ³H). The average error in emission energies for the PBE0 functional is about 0.10 eV. Therefore, there is a better quantitative agreement for the emission energies in the case of the protonated forms than in the case of the deprotonated ones. A possible explanation of the better agreement is that counter ion effects are less pronounced when the XH ligand is neutral. The dominant electronic configuration in T_1 states of the protonated complex ions represents one electron excitation from HOMO to LUMO level (**Table 3 and SI, Table S11-S12**). The results indicate that all T_1 excitations possess ³MLCT character, which strongly depends on the XH ligand. For example, T_1 of 12PYAZ²H and 13PZAZ²H possess $(d-\pi_{\text{azo}})-\pi^*_{\text{bpy}}$ charge transfer character, which is similar to case of the deprotonated complex analogues. The only difference with respect to the deprotonated forms is the smaller participation of the diazolate ring in the HOMO of T_1 , 13PZAZ²H. On the other hand, the first triplet excitation in 12PZAZ²H has $(d-\pi_{\text{azo}})-\pi^*_{\text{azo}}$ charge transfer character and therefore a different accepting orbital with respect to 12PZAZ counterpart. Finally, the charge transfer character in T_1 of 13PYAZ³H is $d-\pi^*_{\text{bpy}}$ and it again differs from the deprotonated 13PYAZ analogues. It is interesting to note that such a variety of ³MLCT character as a function of the XH ligand is associated with almost degenerate T_1 states. The different excited state character is also evident from the excited state geometries (**SI, Discussion S4**). The tunability range for the emission wavelength associated with these excitations amounts only to 10 nm from calculations and 22 nm from experiment. Therefore, again it can be concluded that protonation reduces the tunability as a function of the XH ligand.

Figure 3. Experimental UV-vis spectra for 12PYAZ²H and 13PYAZ³H complex ions (continuous line). The experimental absorption spectra are normalized with respect to the main UV peak. TD-DFT/PBE0/PCM oscillator strengths (bars) and wavelengths are also presented, as well as the molecular orbitals involved in the key electronic excitations. The oscillator strengths are normalized with respect to the most intensive transition.

Figure 4. Experimental UV-vis spectra for 12PZAZ²H and 13PZAZ³H complex ions (continuous line). The experimental absorption spectra are normalized with respect to the main UV peak. TD-DFT/PBE0/PCM oscillator strengths (bars) and wavelengths are also presented, as well as the molecular orbitals involved in the key electronic excitations. The oscillator strengths are normalized with respect to the most intensive transition.

pH optical response

The TD-DFT calculations show that the protonation causes a blue shift in the absorption wavelengths of all complex ions and this is in agreement with the experimental observations. The shift for the absorption wavelength of the lowest energy $^1\text{MLCT}$ excitation amounts to 80/55 nm for 12PYAZ/13PYAZ and to 72/55 nm for 12PZAZ/13PZAZ according to the TD-DFT calculations. For comparison, the experimental measurements show the following blue shifts: 57/41 nm for 12PYAZ/13PYAZ and 44/39 nm for 12PZAZ/13PZAZ upon protonation. The absorption wavelength associated with the higher in energy $^1\text{MLCT}$ transition also blue shifts upon H^+ attachment but to a lesser extent with 38/34 nm for 12PYAZ/13PYAZ and 39/32 nm for 12PZAZ/13PZAZ. The measurements reveal 41/22 nm blue shifts for 12PYAZ/13PYAZ. The changes in the higher in energy $^1\text{MLCT}$ absorption bands upon protonation can be explained by the stronger π -donor ability of the X ligands with respect to the XH ones, which results in higher in energy HOMO levels in the deprotonated complex ions with respect to the protonated ones (**SI, Table 13**). A very weak protonation effect is observed for the wavelengths of the ^1IL excitations (≤ 6 nm from calculations and experiment), which can be explained by their $\pi_{\text{bpy}}-\pi_{\text{bpy}}^*$ origin.

The protonation has significant effect on the emission properties of the complex ions. The calculations/experiments show that emission maxima shift to the blue with 149-196 nm/61-111 nm when the H^+ is attached to the X ligand. Both theory and experiment demonstrate that the modulation in the emission maxima upon protonation depends on the X ligand. The blue shifts decreases when the nitrogen content in the six membered ring increases and when going from 1,2- to 1,3-derivatives. Therefore, among all complex ions highest contrast in the emission wavelengths upon protonation is observed for the 12PYAZ, followed by 13PYAZ, 12PZAZ and 13PZAZ. Another important experimental observation is that the emission intensity (**Table 1**) significantly decreases when going from the protonated to deprotonated forms. In the case of 12PYAZ/12PYAZ ^2H couple this decrease is so strong that the emission band of the deprotonated form almost disappears. In the case of 13PYAZ/13PYAZ ^3H , 12PZAZ/12PZAZ ^2H and 13PZAZ/13PZAZ ^3H the decrease in the emission intensity is 32%, 34% and 33%, respectively. These results indicate that the complex ions can serve as a pH-sensitive molecules based on the difference in the wavelength and emission energy intensity. The highest contrast in the emission energy and emission intensity upon protonation is observed for the newly designed 12PYAZ/12PYAZ ^2H couple.

Figure 5. Emission spectra of $[\text{Ru}(\text{bpy})_2\text{X}]^+$ (in the presence of TEA) and $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ (in the presence of TFA) in acetonitrile solution with 10^{-5} M concentration of the complex ions. The excitation wavelength is 285 nm.

Table 3. Leading MOs in T_1 of the protonated complex ions $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$.

12PYAZ ² H		12PZAZ ² H	
HOMO	LUMO	HOMO	LUMO

13PYAZ ³ H		13PZAZ ³ H	
HOMO	LUMO	HOMO	LUMO

Conclusions

We report detailed experimental and DFT/TD-DFT investigation of the optical properties of four Ru-polypyridyl complex ions $[\text{Ru}(\text{bpy})_2\text{X}]^+$ and their protonated analogues $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$, where X (XH) represents 2-pyridyl or 2-pyrazine derivative of 1,2-diazolate (1,2-diazole) and 1,3-diazolate (1,3-diazole). The pH-optosensing properties of the newly designed complex ions are reported for the first time. The selection of the ligands allows us to demonstrate the effect of the nitrogen content and nitrogen position on the absorption and emission properties of the complex ions upon X and XH modification, as well as on the pH optical response of the $[\text{Ru}(\text{bpy})_2\text{X}]^+ / [\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ couples. A strong blue shift in the lowest in energy $^3\text{MLCT} \rightarrow \text{S}_0$ emission wavelengths and a substantial increase in the emission intensity is observed upon protonation of the $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions. The protonation causes also a change in the character of the corresponding $^3\text{MLCT}$ emitting states. At high pH a blue shift is induced, which decreases when the nitrogen content in the X ligand increases and when going from 1,2- to 1,3-diazolate derivatives. Upon protonation the contrast in the emission intensity is highest for the $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ion, containing 2-pyridyl derivative of the 1,2-diazolate. The results demonstrate that the change in the nitrogen content and nitrogen position in the protonable/deprotonable ligand is a successful strategy for modulation of the pH-response Ru-polypyridyl complexes. The investigated complex ions are suggested as a potential pH-sensitive luminophores.

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SUPPORTING INFORMATION

Molecular Design of pH-Sensitive Ru(II)-Polypyridyl Luminophores

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Discussion S1. Absorption properties of the deprotonated complex ions [Ru(bpy)₂X]⁺

Lowest in energy ¹MLCT excitations

The experimental results show absorption bands at 505 nm (12PYAZ), 494 nm (13PYAZ), 480 nm (12PZAZ) and a small shoulder about 488 nm (13PZAZ). The calculations reveal that each deprotonated complex ion is characterized with two very close in energy singlet excited states – S₁ and S₂ (**Table 1**). According to the MO analysis, these excitations involve HOMO→LUMO (S₁) and HOMO→LUMO+1 (S₂) transitions (**Figure 1-2** and **SI, Table S2-S4**). The HOMO of the deprotonated complex ions is localized on the Ru(II) and the azolate rings. The LUMO and LUMO+1 represent π -accepting orbitals, associated with L and the R bipyridine ligands (**Scheme 1**), respectively. Therefore, the S₁ transition is denoted as (d- π_{azo})- $\pi^*_{\text{bpy}}^{\text{L}}$ charge transfer, while S₂ as (d- π_{azo})- $\pi^*_{\text{bpy}}^{\text{R}}$ charge transfer (**Figure 1-2** and **SI, Table S2-S4**). The presence of closely lying in energy S₁ and S₂ excited states can be explained by the stronger interaction of Ru(II) with the R bipyridine ligand than with the L bipyridine ligand

(**SI, Discussion S2**). The calculations also indicate that S_1/S_2 excitations are with relatively low oscillator strength and are located at 536/519 nm (12PYAZ), 519/511 nm (13PYAZ), 519/505 (12PZAZ), and 503/494 nm (13PZAZ).

Higher in energy 1MLCT excitations

The experimental spectra show absorption peaks at 454 nm (12PYAZ), 447 nm (13PYAZ), 438 nm (12PZAZ), and 451 nm (13PZAZ). TD-DFT results for the deprotonated complex ions reveal that the excitations with largest oscillator strength in the UV-vis region are located at: 442 nm (S_5 , 12PYAZ), 447 nm (S_5 , 13PYAZ), 429 nm (S_6/S_7 12PZAZ), and 435 nm (S_5 , 13PZAZ). According to the MO analysis (**Figure 1-2** and **SI, Table S2-S4**), these excitations involve electronic transitions from HOMO-2 to LUMO and from HOMO-2 to LUMO+1. The HOMO-2 is a metal based and will be denoted simply as d-atomic orbital. The LUMO and LUMO+1 are localized on the L and R bipyridine ligands, respectively, and represent $\pi^*_{bpy}^L$ and $\pi^*_{bpy}^R$ molecular orbitals.

1IL excitations

The experimental measurements for the $[Ru(bpy)_2X]^+$ ions show intensive absorption bands located at ~290 nm. The TD-DFT calculations indicate that the complex ions are characterized by very strong absorption in the region above 250 nm (**Table 1**). The UV absorption maxima are calculated at 270 nm (12PYAZ), 269 nm (13PYAZ), 272/270 nm (12PYAZ), and 269 nm (13PZAZ). The lack of sensitivity of the UV maximum on the X-ligand can be explained by looking at the excited states character (**Figure 1-2** and **SI, Table S2-S4**): the MO analysis shows that these excited states involve HOMO-4 or HOMO-5 to LUMO+1 transitions and represent intra-ligand $\pi_{bpy}^L-\pi^*_{bpy}^L$ or $\pi_{bpy}^R-\pi^*_{bpy}^R$ excitations of the bipyridine ligands.

Discussion S2. Ground state geometry of the deprotonated complex ions $[Ru(bpy)_2X]^+$

The optimized ground state bond lengths of $[Ru(bpy)_2X]^+$ complex ions are presented in **Figure S1**. Our calculations demonstrate strong interaction between Ru(II) and the azolate rings. Our results also indicate that the bipyridine coordination sites are structurally identical in all deprotonated complex ion, however, the L bipyridine ligands show weaker interaction with Ru(II) than the R bipyridine ligands. Therefore, despite the apparent identical structure, the two bipyridine ligands can not be regarded as indistinguishable.

Figure S1. Ground state bond lengths [Å] of $[\text{Ru}(\text{bpy})_2\text{X}]^+$. The results are obtained with PBE0/PCM method.

Table S1. TD-DFT/PBE0/PCM wavelengths λ [nm] and oscillator strengths f for the first forty $S_0 \rightarrow S_n$ excitations in deprotonated $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions.

	12PYAZ		13PYAZ		12PZAZ		13PZAZ	
S ₀ →S _n								
S _n	λ	f	λ	f	λ	f	λ	f
1	536	0.0011	519	0.0017	519	0.0011	503	0.0018
2	519	0.0112	511	0.0048	502	0.0137	494	0.0058
3	476	0.0022	481	0.0006	458	0.0082	466	0.0014
4	457	0.0198	473	0.0092	453	0.0059	457	0.0118
5	442	0.1205	447	0.1404	437	0.0288	435	0.1353
6	417	0.0584	421	0.0341	429	0.1003	421	0.0015
7	391	0.0083	401	0.0073	410	0.0863	414	0.0654
8	379	0.0057	394	0.0171	401	0.0019	390	0.0109
9	363	0.0011	372	0.0073	375	0.0265	385	0.0100
10	356	0.0023	364	0.0014	364	0.0467	380	0.0375
11	355	0.0242	356	0.0088	353	0.0015	376	0.0389
12	352	0.0137	347	0.0108	346	0.0034	362	0.0044
13	348	0.0022	344	0.0267	346	0.0081	345	0.0143
14	348	0.0069	341	0.0509	340	0.0047	339	0.0329
15	343	0.0327	339	0.0035	340	0.0019	337	0.0518
16	339	0.0585	335	0.0176	335	0.0692	334	0.0193
17	331	0.0611	333	0.0815	327	0.0130	332	0.0086
18	327	0.0170	330	0.0494	327	0.0477	327	0.0609
19	319	0.0006	325	0.0109	322	0.0817	325	0.0079
20	318	0.0374	322	0.0102	319	0.0129	317	0.0020
21	317	0.0204	319	0.0160	315	0.0017	315	0.0071
22	314	0.0314	318	0.0094	311	0.0095	314	0.0107
23	312	0.0223	313	0.0017	310	0.0148	312	0.0019
24	310	0.0050	312	0.0154	306	0.0271	312	0.0226
25	307	0.0008	311	0.0038	304	0.0030	308	0.0091
26	303	0.0349	309	0.0588	302	0.0092	307	0.0118
27	299	0.0130	305	0.0064	301	0.0224	305	0.0117
28	296	0.0023	302	0.0365	298	0.0291	299	0.1216
29	293	0.0031	300	0.0055	294	0.0047	298	0.0043
30	290	0.0078	297	0.0281	289	0.0443	296	0.0103
31	289	0.0173	290	0.0190	285	0.0036	290	0.0262
32	285	0.0901	288	0.0244	285	0.0047	285	0.0926
33	279	0.0959	288	0.0185	283	0.0960	282	0.0384
34	278	0.0124	280	0.2575	280	0.0098	280	0.0083
35	276	0.0907	276	0.0061	276	0.0032	279	0.0940
36	274	0.1184	275	0.1790	276	0.1549	276	0.0323
37	272	0.0549	272	0.1006	272	0.1986	275	0.1648
38	271	0.2188	271	0.1043	272	0.0036	273	0.0304
39	270	0.3908	269	0.5238	270	0.0468	271	0.1016
40	268	0.0722	267	0.2516	270	0.1909	269	0.5356

Table S2. MOs and CI coefficients for 12PYAZ and 13PYAZ complex ions. The results are obtained in acetonitrile by TD-DFT/PBE0 approach.

12PYAZ			13PYAZ		
λ [nm] (<i>f</i>)	MO involved CI coefficients		λ [nm] (<i>f</i>)	MO involved CI coefficients	
S₁ 536 (0.0011)	127 → 128	0.61159	S₁ 519 (0.0017)	126 → 128	0.26954
	127 → 129	0.31919		126 → 129	0.18561
				127 → 128	0.49102
				127 → 129	0.37164
S₂ 519 (0.0112)	126 → 129	0.18348	S₂ 511 (0.0048)	125 → 129	0.11515
	127 → 128	-0.31094		126 → 128	-0.22361
	127 → 129	0.58778		126 → 129	0.28200
				127 → 128	-0.34284
				127 → 129	0.47069
S₅ 442 (0.1205)	125 → 128	0.58096	S₅ 447 (0.1404)	124 → 128	0.22373
	125 → 129	-0.21127		125 → 128	0.56762
	126 → 129	-0.29128		125 → 129	-0.16815
	127 → 129	0.11645		126 → 128	-0.19530
				126 → 129	-0.14593
				127 → 129	0.17361
S₃₉ 270 (0.3908)	121 → 128	-0.10219	S₃₉ 269 (0.5238)	122 → 128	0.26184
	121 → 129	0.13009		122 → 129	-0.24926
	122 → 128	0.10027		123 → 129	0.51665
	122 → 129	0.54367		124 → 135	-0.17523
	124 → 133	-0.22117		125 → 134	-0.12155
	124 → 134	-0.19205			
	125 → 134	0.11491			

Table S3. MOs and CI coefficients for 12PZAZ and 13PZAZ complex ions. The results are obtained in acetonitrile by TD-DFT/PBE0 approach.

12PZAZ			13PZAZ		
λ [nm] (<i>f</i>)	MO involved CI coefficients		λ [nm] (<i>f</i>)	MO involved CI coefficients	
S₁ 519 (0.0011)	127 → 128	0.62083	S₁ 503 (0.0018)	126 → 128	0.25699
	127 → 129	0.30090		126 → 129	0.17670
				127 → 128	0.50118
				127 → 129	0.36846
S₂ 502 (0.0137)	126 → 129	0.17719	S₂ 494 (0.0058)	125 → 129	0.11562
	127 → 128	-0.29799		126 → 128	-0.20873
	127 → 129	0.60100		126 → 129	0.27705
				127 → 128	-0.34572
				127 → 129	0.47993
S₆ 429 (0.1003)	124 → 128	0.10096	S₅ 435 (0.1353)	124 → 128	0.19004
	125 → 128	0.56999		125 → 128	0.56767
	125 → 129	-0.21776		125 → 129	-0.17799
	126 → 129	-0.29640		126 → 128	-0.22235
	127 → 129	0.10158		126 → 129	-0.13899
				127 → 129	0.16427
S₇ 410 (0.0863)	125 → 128	0.33396			
	125 → 129	0.47007			
	126 → 129	0.25802			
	126 → 130	-0.23966			
S₃₆ 272 (0.1986)	120 → 128	0.16535	S₄₀ 269 (0.5356)	122 → 128	0.32594
	120 → 129	-0.15163		122 → 129	-0.35201
	121 → 128	0.53335		123 → 129	0.41862
	122 → 128	0.16484		124 → 132	0.10157
	124 → 132	-0.22854		124 → 135	-0.12449
	125 → 133	-0.10610		125 → 133	0.10458
S₄₀ 270 (0.1909)	120 → 128	0.20674			
	120 → 129	-0.17651			
	122 → 129	0.46755			
	123 → 129	-0.11800			
	123 → 130	0.14561			
	124 → 132	0.29913			
	124 → 133	-0.11082			

Table S4. MOs for the main $S_0 \rightarrow S_n$ excitations in deprotonated $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions.

12PYAZ					
129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	122 HOMO-5	
13PYAZ					
129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	123 HOMO-4	
12PZAZ					
129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	122 HOMO-5	121 HOMO-6

13PZAZ					
129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	123 HOMO-4

Table S5. MOs and CI coefficients for $T_1 \rightarrow S_0$ transitions in deprotonated $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions. The results are obtained in acetonitrile by TD-DFT/PBE0 approach.

12PYAZ			12PZAZ		
λ [nm]	MO involved CI coefficients		λ [nm]	MO involved CI coefficients	
T₁ 865	123 $\rightarrow$ 128	0.12859	T₁ 819	123 $\rightarrow$ 128	-0.13195
	127 $\rightarrow$ 128	0.67034		127 $\rightarrow$ 128	0.66796
	127 $\rightarrow$ 129	0.12093		127 $\rightarrow$ 129	0.11696
13PYAZ			13PYAZ		
T₁ 850	127 $\rightarrow$ 128	0.66963	T₁ 808	123 $\rightarrow$ 128	0.10143
	127 $\rightarrow$ 129	0.11453		127 $\rightarrow$ 128	0.66773
				127 $\rightarrow$ 129	0.11143

Table S6. MOs associated with $T_1 \rightarrow S_0$ transitions in deprotonated $[\text{Ru}(\text{bpy})_2\text{X}]^+$ complex ions.

12PYAZ		12PZAZ	
128 LUMO	127 HOMO	128 LUMO	127 HOMO
13PYAZ		13PZAZ	
128 LUMO	127 HOMO	128 LUMO	127 HOMO

Discussion S3. Absorption properties of the protonated complex ions $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ *Lowest in energy $^1\text{MLCT}$ excitations*

The experimental measurements show that the first absorption band is located at 448 nm (12PYAZ²H), 453 nm (13PYAZ³H), 436 nm (12PZAZ²H), and 449 nm (13PZAZ³H). Calculations reveal that the $S_0 \rightarrow S_1/S_0 \rightarrow S_2$ transitions in the protonated complex ions are located at 457/452 nm (12PYAZ²H), 464/461 nm (13PYAZ³H), 450/443 nm (12PZAZ²H), 447/441 nm (12PZAZ²H), and 448/444 nm (13PZAZ³H). Similar to the deprotonated complex ions, S_1 and S_2 in the protonated forms are close in energy. However, in the protonated forms the S_1/S_2 splitting is smaller due to the similar in strength interaction between Ru(II) and the L and R bipyridine ligands (**SI**, **Discussion S4**). The TD-DFT results indicate that both $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions possess relatively low oscillator strengths, while the first absorption

band in most of the protonated forms dominates the UV-vis region. The molecular orbital analysis for the protonated forms reveals that $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations are characterized mainly with HOMO to LUMO and HOMO to LUMO+1 transitions, respectively (**SI, Table S8-S9**). In 1,2-protonated derivatives HOMOs represent d- π_{azo} orbitals, which are very similar to the deprotonated analogues but with relatively smaller participation from the X ligand (**Figure 3-4** and **SI, Table S8-S10**). On the other hand, in the case of 1,3-protonated derivatives HOMOs become mainly metal based d-AO. The protonation also affects the LUMOs and LUMO+1 electronic density. In the protonated forms, LUMOs and LUMO+1 are more delocalized and have simultaneous contribution from both bipyridine ligands $\pi_{\text{bpy}}^{*\text{L/R}}$. Therefore, our results show that upon protonation the character of the lowest in energy excited state changes.

Higher in energy $^1\text{MLCT}$ excitations

The experimental measurements for the protonated derivatives indicate absorption peaks at 413 nm (12PYAZ²H), 425 nm (13PYAZ³H). For 12PZAZ²H and 13PZAZ³H there is no clear absorption peak in this wavelength region because the first $^1\text{MLCT}$ excitation dominates the UV-vis region. The TD-DFT results reveal that the most intensive UV-vis excitations for the protonated forms are located at 404 nm (12PYAZ²H), 413 nm (13PYAZ³H), 390/385 nm (12PZAZ²H), and 403/389 nm (13PZAZ³H). The MO analysis shows that the higher in energy $^1\text{MLCT}$ excitations represent HOMO-2 to LUMO or HOMO-2 to LUMO+1 transitions (**SI, Table S8**). HOMO-2 are again mainly metal based d-AO, while LUMO and LUMO+1 are associated simultaneously with both bipyridine ligands - $\pi_{\text{bpy}}^{*\text{L/R}}$ (**Figure 3-4** and **SI, Table S8-S10**).

^1IL excitations

The experimental measurements reveal absorption maxima at 286 nm (12PYAZ²H), 287 nm (13PYAZ³H), 284 nm (12PZAZ²H) and 286 nm (13PZAZ³H), respectively. Our calculations show that all protonated forms are characterized with by strong absorption band at 268 nm (12PYAZ²H), 260 nm (13PYAZ³H), 266 nm (12PZAZ²H), and 268 nm (13PZAZ³H). In 12PYAZ²H and 13PZAZ³H these high energy states are represented by HOMO-4 to LUMO+1 transitions (**Figure 3-4** and **SI, Table S8-S10**). Here, unlike the deprotonated forms the donating and the accepting orbitals spans both bipyridine ligands ($\pi_{\text{bpy}}^{\text{L/R}}$ and $\pi_{\text{bpy}}^{*\text{L/R}}$). In the case of 13PYAZ³H the high energy excitation is from HOMO-3 to LUMO+2, which represent π_{azo} and π_{azo}^* orbitals, respectively. Therefore, for 12PYAZ²H, 13PYAZ³H and 13PZAZ³H it

can be concluded that the character of the high energy excitations remains intra-ligand upon protonation but the ligand participation significantly differs from the corresponding deprotonated analogues. Moreover, the high energy excitation in 12PZAZ²H is a mixed one and it involves HOMO-4 to LUMO+2 and HOMO-3 to LUMO+1 transitions with equal weights. In this case HOMO-4 has contribution from all three ligands with a dominant one from the L bipyridine ($\pi_{\text{azo/bpy}}^{\text{L/R}}$), while LUMO+2 is mainly localized on the XH ligand (π_{azo}^*). On the other hand, HOMO-3 and LUMO+1 span both bipyridine ligands and are $\pi_{\text{bpy}}^{\text{L/R}}$ and $\pi_{\text{bpy}}^{*\text{L/R}}$, respectively. Therefore, it can be concluded that the high energy excitation in 12PZAZ²H possess intra-ligand but also inter-ligand charge transfer character.

Discussion S4. Ground state geometry of the protonated complex ions [Ru(bpy)₂XH]²⁺

Ground state structure

The ground state geometries of the protonated complex ions [Ru(bpy)₂XH]²⁺ are represented in **Figure 3** and will be discussed with respect to the deprotonated analogues. The optimized geometries for [Ru(bpy)₂XH]²⁺ show that the protonation causes an increase in the Ru-N bonds in the azolate rings. This is in line with a decrease in the π -donor ability of the X-ligands upon protonation. The protonation also leads to elongation of the inter-ring bonds in the X ligand. The transformation from [Ru(bpy)₂X]⁺ to [Ru(bpy)₂XH]²⁺ has a negligible effect on the pyridine cycle of the X ligand and its interaction with Ru(II). It is also interesting to note that H⁺ attachment to the X ligand affects the bipyridine ligands. The interaction between Ru(II) and the L/R bipyridine ligands becomes comparable in strength and the similarity between the bipyridine coordination sites is restored upon protonation.

Figure S2. Ground state bond lengths [Å] of $[Ru(bpy)_2XH]^{2+}$. The protonated nitrogen atom is denoted with green dot. The results are obtained with PBE0/PCM method.

Table S7. TD-DFT/PBE0/PCM wavelengths λ [nm] and oscillator strengths f for the first forty $S_0 \rightarrow S_n$ excitations in protonated $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions.

	12PYAZ ² H		13PYAZ ³ H		12PZAZ ² H		13PZAZ ³ H	
S ₀ →S _n								
S _n	λ	f	λ	f	λ	f	λ	f
1	457	0.0008	464	0.0012	447	0.0013	448	0.0016
2	452	0.0036	461	0.0009	441	0.0011	444	0.0008
3	425	0.0009	435	0.0003	436	0.0056	426	0.0014
4	420	0.0081	430	0.0024	411	0.0032	421	0.0038
5	404	0.1348	413	0.1600	408	0.0165	413	0.0122
6	394	0.0152	392	0.0635	399	0.0072	403	0.1055
7	385	0.0896	372	0.0019	390	0.1315	396	0.0509
8	364	0.0015	350	0.0012	385	0.1529	389	0.1208
9	347	0.0794	343	0.0118	359	0.0176	360	0.0387
10	337	0.0153	339	0.0878	332	0.0160	337	0.0079
11	322	0.0030	329	0.0016	317	0.0026	324	0.0021
12	318	0.0034	324	0.0206	316	0.0034	319	0.0200
13	316	0.0119	320	0.0018	315	0.0281	315	0.0017
14	314	0.0044	315	0.0019	311	0.0063	314	0.0021
15	313	0.0014	312	0.0119	309	0.0068	312	0.0023
16	310	0.0040	312	0.0104	307	0.0049	310	0.0015
17	306	0.0307	310	0.0033	303	0.0064	306	0.0129
18	303	0.0035	308	0.0083	300	0.0010	304	0.0042
19	302	0.0294	307	0.0542	300	0.0015	302	0.0075
20	299	0.0309	305	0.0010	297	0.0357	301	0.0029
21	298	0.0095	303	0.0014	296	0.0228	300	0.0117
22	296	0.0121	302	0.0004	293	0.0306	298	0.0022
23	295	0.0166	302	0.0014	291	0.0011	298	0.0787
24	291	0.0399	301	0.0172	290	0.0054	296	0.0017
25	290	0.0075	300	0.0246	287	0.0347	294	0.0042
26	285	0.0131	298	0.0182	287	0.0096	293	0.0114
27	282	0.0015	295	0.0152	284	0.0532	292	0.0147
28	278	0.0135	288	0.0094	278	0.0240	290	0.0171
29	276	0.0063	282	0.0139	276	0.0430	287	0.1332
30	275	0.1228	275	0.1680	275	0.0012	285	0.0135
31	273	0.0047	272	0.0276	273	0.0465	276	0.0439
32	272	0.0615	272	0.0775	272	0.0312	275	0.1253
33	269	0.1966	269	0.3908	272	0.0102	272	0.0598
34	268	0.6746	269	0.1705	270	0.0746	271	0.0193
35	268	0.0170	268	0.0126	269	0.1385	269	0.2193
36	260	0.0023	266	0.6083	268	0.1876	268	0.7151
37	256	0.3887	261	0.0095	267	0.1167	266	0.0042
38	249	0.0075	255	0.0593	266	0.6495	265	0.0565
39	247	0.0021	244	0.0127	265	0.1047	262	0.0398
40	241	0.0105	243	0.0312	259	0.0008	260	0.0012

Table S8. MOs and CI coefficients for **12PYAZ²H** and **13PYAZ³H** complex ions. The results are obtained in acetonitrile by TD-DFT/PBE0 approach.

12PYAZ²H			13PYAZ³H		
λ [nm] (<i>f</i>)	MO involved CI coefficients		λ [nm] (<i>f</i>)	MO involved CI coefficients	
S₁ 457 (0.0008)	127 → 128	0.53141	S₁ 464 (0.0012)	127 → 128	0.58014
	127 → 129	0.44128		127 → 129	0.38654
S₂ 452 (0.0036)	126 → 128	0.11738	S₂ 461 (0.0009)	127 → 128	-0.38938
	126 → 129	-0.14928		127 → 129	0.57994
	127 → 128	-0.42740			
	127 → 129	0.51751			
S₅ 404 (0.1348)	125 → 128	0.62002	S₅ 413 (0.1600)	125 → 128	0.59856
	126 → 129	0.26347		126 → 129	0.36108
	127 → 130	-0.14016			
S₃₄ 268 (0.6746)	122 → 128	-0.30130	S₃₆ 266 (0.6083)	122 → 128	0.17993
	123 → 129	0.47810		123 → 129	-0.22996
	125 → 134	0.19528		124 → 130	0.49735
	125 → 135	0.19037		124 → 131	0.12448
	126 → 133	0.10482		125 → 133	-0.10678
	126 → 141	0.10272		125 → 134	-0.12112
				126 → 135	0.20304

Table S9. MOs and CI coefficients for **12PZAZ²H** and **13PZAZ³H** complex ions. The results are obtained in acetonitrile by TD-DFT/PBE0 approach.

12PZAZ²H			13PZAZ³H		
λ [nm] (f)	MO involved CI coefficients		λ [nm] (f)	MO involved CI coefficients	
S₁ 447 (0.0013)	126 → 130	0.13094	S₁ 447 (0.0016)	127 → 128	0.55423
	127 → 128	0.27051		127 → 129	0.37137
	127 → 130	0.62772		127 → 130	-0.19864
S₂ 441 (0.0011)	127 → 128	0.54503	S₂ 444 (0.0008)	127 → 128	-0.37977
	127 → 129	0.34354		127 → 129	0.58433
	127 → 130	-0.26105			
S₇ 390 (0.1315)	125 → 128	0.51331	S₆ 403 (0.1055)	125 → 128	0.54284
	125 → 130	-0.22746		125 → 130	0.11885
	126 → 128	0.10255		126 → 128	-0.22590
	126 → 129	-0.35548		126 → 129	0.28346
	126 → 130	-0.13042		126 → 130	-0.22996
	127 → 129	0.12508			
S₈ 384 (0.1529)	125 → 128	0.15636	S₈ 389 (0.1208)	125 → 128	0.19289
	125 → 129	0.50326		125 → 129	0.44747
	125 → 130	0.22524		125 → 130	0.34805
	126 → 128	-0.14022		126 → 128	0.14018
	126 → 129	0.22276		126 → 129	-0.30367
	126 → 130	-0.29184		126 → 130	0.11665
S₃₈ 266 (0.6495)	122 → 128	0.17804	S₃₆ 268 (0.7151)	122 → 128	-0.26129
	122 → 129	0.13995		122 → 129	-0.18457
	122 → 130	-0.16457		122 → 130	-0.10239
	123 → 128	-0.16563		123 → 129	0.49515
	123 → 130	0.30881		125 → 134	0.15306
	124 → 129	0.30688		125 → 135	-0.17590
	125 → 133	-0.12970		126 → 133	-0.10874
	125 → 134	0.16239		126 → 135	0.12730
	125 → 135	-0.24096			
	126 → 135	-0.11838			
	126 → 140	0.11016			
	126 → 141	-0.12218			

Table S10. MOs for the main $S_0 \rightarrow S_n$ excitations in protonated $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions.

12PYAZ²H					
	129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	123 HOMO-4
13PYAZ³H					
130 LUMO+2	129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	124 HOMO-3
12PZAZ²H					
130 LUMO+2	129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	124 HOMO-3
12PZAZ ² H	13PZAZ³H				
123 HOMO-4	129 LUMO+1	128 LUMO	127 HOMO	125 HOMO-2	123 HOMO-4

Discussion S4. Excited state geometry of the protonated complex ions $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$

The excited state geometries of the protonated complex ions $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ are represented in **Figure S3**. The results clearly indicate different character of the T_1 states when protonation occurs. The optimized geometries for $12\text{PYAZ}^2\text{H}$ and $13\text{PZAZ}^2\text{H}$ show that the excitation causes a decrease in the Ru-N bonds in the azolate ring and in one of the Ru-N bonds for the R bipyridine ligand. Reduction in Ru-N bonds for the azolate ring is observed also for the $12\text{PZAZ}^2\text{H}$ analogue, however, this time the decrease is much stronger and the Ru-N bonds for the bipyridine ligands are less affected than in the case of $12\text{PYAZ}^2\text{H}$ and $13\text{PZAZ}^2\text{H}$. On the other hand, upon excitation to T_1 in $13\text{PZAZ}^3\text{H}$ an elongation of the Ru-N bond for the azolate ring is observed but strong decrease of one of the Ru-N bonds for the L bipyridine ligand. Therefore, T_1 state of $13\text{PZAZ}^2\text{H}$ also differs from the one in 13PZAZ .

Figure S3. Excited state bond lengths [Å] of $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$. The protonated nitrogen atom is denoted with green dot. The results are obtained with TD-DFT/PBE0/PCM method.

Table S11. MOs and CI coefficients for $T_1 \rightarrow S_0$ transitions in protonated $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions. The results are obtained in acetonitrile by TD-DFT/PBE0 approach.

12PYAZ²H			12PZAZ²H		
λ [nm]	MO involved CI coefficients		λ [nm]	MO involved CI coefficients	
T₁ 669	124 $\rightarrow$ 128	0.16407	T₁ 662	127 $\rightarrow$ 128	0.65611
	127 $\rightarrow$ 128	0.65846		127 $\rightarrow$ 129	-0.15238
13PYAZ³H			13PYAZ³H		
T₁ 667	123 $\rightarrow$ 128	-0.16572	T₁ 659	123 $\rightarrow$ 128	0.17359
	125 $\rightarrow$ 128	0.11925		127 $\rightarrow$ 128	0.65480
	127 $\rightarrow$ 128	0.64876			
	127 $\rightarrow$ 129	-0.10063			

Table S12. MOs associated with $T_1 \rightarrow S_0$ transitions in deprotonated $[\text{Ru}(\text{bpy})_2\text{XH}]^{2+}$ complex ions.

12PYAZ²H		12PZAZ²H	
128 LUMO	127 HOMO	128 LUMO	127 HOMO
13PYAZ³H		13PZAZ³H	
128 LUMO	127 HOMO	128 LUMO	127 HOMO

Table S13. Orbital energies [eV] of the complex ions and the isolated ligands. The results are for ground states (S_0) and are obtained with the PBE0/SDD&6-311G* and the PBE0/6-311G* in acetonitrile, for the complex ions and the isolated ligands, respectively.

COMPLEXES				
	12PYAZ	12PYAZ ² H	13PYAZ	13PYAZ ³ H
LUMO ($\pi_{\text{bpy}}^{\text{R}*}$)	-2.39	-2.63	-2.40	-2.57
HOMO ($d-\pi_{\text{azo}}$)	-5.74	-6.42	-5.86	-6.36
	12PZAZ	12PZAZ ² H	13PZAZ	13PZAZ ³ H
LUMO ($\pi_{\text{bpy}}^{\text{R}*}$)	-2.45	-2.70	-2.45	-2.63
HOMO ($d-\pi_{\text{azo}}$)	-5.86	-6.56	-5.97	-6.50
ISOLATED LIGANDS				
	12PYAZ	12PYAZ ² H	13PYAZ	13PYAZ ³ H
LUMO (π^*)	-0.47	-1.09	-0.37	-0.92
HOMO (π)	-5.40	-6.79	-5.07	-6.37
	12PZAZ	12PZAZ ² H	13PZAZ	13PZAZ ³ H
LUMO (π^*)	-1.04	-1.60	-0.95	-1.45
HOMO (π)	-5.54	6.99	-5.22	-6.54