Electronic Supplementary Material (ESI) for Chemical Science.

Ultrafast transient IR spectroscopy and DFT calculations of ruthenium(II) polypyridyl complexes

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Supporting Information

Synthesis

All starting chemicals were obtained from commercial sources and were used without further purification. $RuCl_3$ was purchased from Fluka, 2, 2'-bipyridine (bpy) and 6-methyl-2, 2'-bipyridine (mbpy) were purchased from Aldrich. 2-methyl-1, 10'-phenanthroline (mphen) was purchased from Shanghai UCHEM Inc.. The complexes $[Ru(bpy)_3]^{2+}$,[1] $[Ru(mbpy)_3]^{2+}$ and $[Ru(mphen)_3]^{2+}$ were prepared by literature methods[2] and precipitated as $[Ru(bpy)_3](PF_6)_2$, $[Ru(mbpy)_3](PF_6)_2$, $[Ru(mphen)_3](PF_6)_2$.

Spectroscopy

FTIR measurement

All the FTIR experiments were performed on KBr pellet with a Biorad Excalibur Instrument. The spectral resolution was set to 1 cm^{-1}. 20 scans were taken for the sample and the background. The KBr pellet was prepared first by grinding approximately 1 mg of ruthenium complexes and 300 mg of KBr (Sigma IR grade potassium bromide) in an agate mortar, and then was pressed at 10 tons of pressure under vacuum.

Kinetic Scheme

The details of the calculation of the SADS

Take a three species:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} D$$

A is the initially excited state (here the ^{3}MLCT state), B the intermediate state, and D the ground state. The observed TRIR spectra of this system are the difference spectra with respect to the ground state $\Delta OD(\lambda, t)$:

$$\Delta OD = OD_A + OD_B + OD_D - OD_{D0} = \varepsilon_A(\lambda)C_A l + \varepsilon_B(\lambda)C_B l + \varepsilon_D(\lambda)C_D l - \varepsilon_D(\lambda)C_0 l \tag{S1}$$

Where the C_i are the concentrations of species "*i*" and the $\varepsilon_i(\lambda)$ the corresponding extinction coefficients, and with the total concentration $C_0 = C_D + C_A + C_B$ we obtain:

$$\begin{aligned}\Delta OD(\lambda,t) &= [\varepsilon_A(\lambda) - \varepsilon_D(\lambda)]lC_A(t) + [\varepsilon_B(\lambda) - \varepsilon_D(\lambda)]lC_B(t) \\ &= \Delta\varepsilon_A(\lambda)lC_A(t) + \Delta\varepsilon_B(\lambda)lC_B(t) = \Delta OD_A(\lambda,t) + \Delta OD_B(\lambda,t)\end{aligned} \tag{S2}$$

$C_A(t)$ and $C_B(t)$ can be obtained according to the chemical reaction kinetics as follows:

$$\begin{aligned}\frac{dC_A(t)}{dt} &= -k_1 C_A(t) \\ \frac{dC_B(t)}{dt} &= k_1 C_A(t) - k_2 C_B(t)\end{aligned} \tag{S3}$$

Solving the above coupled differential equations with initial concentrations $C_A(t=0) = C_0$ and $C_B(t=0) = 0$ gives:

$$\begin{aligned}C_A(t) &= C_0 e^{-k_1 t} \\ C_B(t) &= C_0 \frac{k_1}{k_1 - k_2}\left(e^{-k_2 t} - e^{-k_1 t}\right) \\ C_D(t) &= C_0 - C_A(t) - C_B(t) = C_0\left(1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2}\right)\end{aligned} \tag{S4}$$

The rate constants k_1 and k_2 as well as the species associated difference spectra $SADS_{A/B}(\lambda) = \Delta\varepsilon_{A/B}(\lambda)C_0 l$ can be obtained by least square global fitting to the experimental spectra. For this a home-built program code[3] based on the Matlab software[4] and the built in matrix operations was used.

Computational study

Computational details

Density functional theory (DFT)[5, 6] has been applied to the optimization of the ground-state, the ^{3}MLCT state and ^{3}dd state geometries of $[Ru(bpy)_3]^{2+}$, $[Ru(mbpy)_3]^{2+}$, and $[Ru(mphen)_3]^{2+}$ in the gas phase and with the PCM method in order to take solvent effects into account. The calculations were performed with the Gaussian 09 program package[7] to characterize $[Ru(bpy)_3]^{2+}$, $[Ru(mbpy)_3]^{2+}$ and $[Ru(mphen)_3]^{2+}$ at the mPW1PW91 level in the S_0 ground and in the excited $^3T_1$ state. A LANL2DZ basis set was used for the description of the Ru atom,[8] while of the H, N, C and Ru atoms were described by the D95V basis set.[9] The frequency calculations performed on the optimized geometries showed that they all correspond to real minima (no imaginary frequencies). IR spectra were simulated by convoluting the calculated intensities with Lorentzian functions of FWHM of 10 cm^{-1} using the GaussSum program.[10]

Table S1. Selected bond lengths (Å) in the optimized geometries in acetonitrile (true minima by vibrational analysis) of $[Ru(bpy)_3]^{2+}$ in the S_0 ground state and in the ^{3}MLCT and ^{3}dd states by G09. The * indicates the ligand on which the electron is localised.

Ru-N	S_0	^{3}MLCT	^{3}dd
1	2.07266	2.07433	2.40638
2	2.07299	2.09533	2.13187
3	2.07230	2.09533	2.13182
4	2.07278	2.07434	2.40647
5	2.07252	2.04891*	2.08578
6	2.07242	2.04892*	2.08579

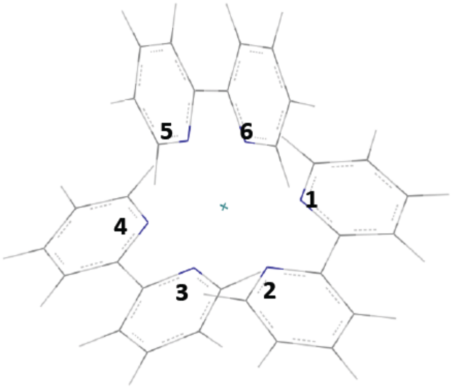


Table S2. Selected bond lengths (Å) in the optimized geometries in acetonitrile (true minima by vibrational analysis) of $[Ru(mbpy)_3]^{2+}$ in the S_0 ground state and in the ^{3}dd states by G09.

Ru-N	S_0	^{3}dd
1	2.08114	2.07758
2	2.15151	2.15821
3	2.13532	2.50581
4	2.06983	2.13332
5	2.06168	2.12842
6	2.13675	2.48641

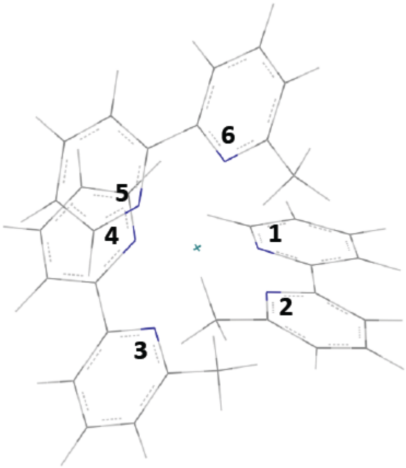


Table S3. Selected bond lengths (Å) in the optimized geometries in acetonitrile (true minima by vibrational analysis) of $[Ru(mphen)_3]^{2+}$ in the S_0 ground state and in the ^{3}MLCT and ^{3}dd states by G09. The * Indicates the ligand on which the electron is localised.

Ru-N	S_0	^{3}MLCT	^{3}dd
1	2.08095	2.10190	2.08142
2	2.15374	2.17611	2.16979
3	2.13737	2.15169	2.50153
4	2.07366	2.06829	2.12679
5	2.06548	2.02447*	2.12839
6	2.14538	2.12483*	2.51246

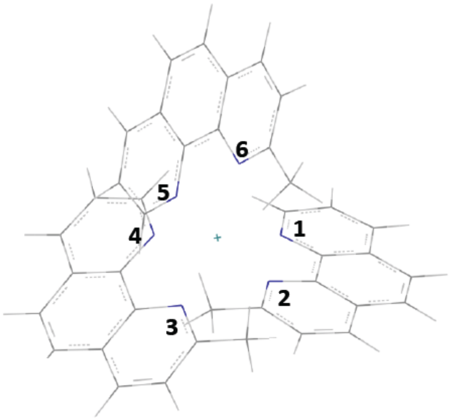


Table S4. Zero-point energy and electronic energy differences (ΔE°, ΔE^{el} in cm^{-1}) between the excited state ^{3}MLCT and ^{3}dd states and the ground state, respectively, of $[Ru(bpy)_3]^{2+}$, $Ru(mbpy)_3]^{2+}$, and $Ru(mphen)_3]^{2+}$ under PCM model in acetonitrile.

G09	ΔE	^{3}MLCT	^{3}dd	ΔE(^{3}dd-^{3}MLCT)
$[Ru(bpy)_3]^{2+}$	ΔE^{el}	16614	18808	2194
	ΔE°	15941	17999	2058
$[Ru(mbpy)_3]^{2+}$	ΔE^{el}	--	14724	--
	ΔE°	--	13854	--
$[Ru(mphen)_3]^{2+}$	ΔE^{el}	16723	14923	-1800
	ΔE°	16164	14126	-2038

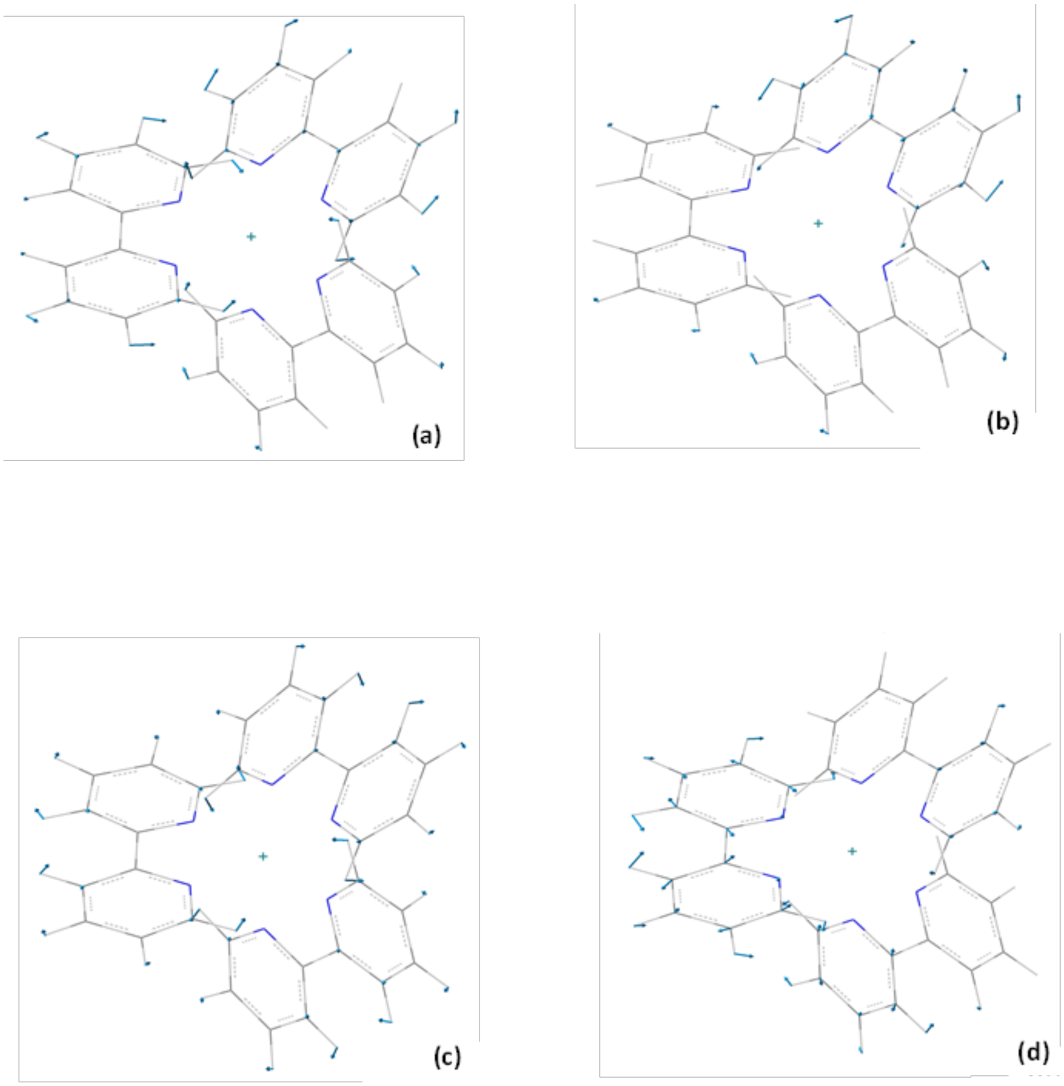


Figure S1. Some selected vibrational modes of $[Ru(bpy)_3]^{2+}$ in the ground state in vacuum at (a) 1416 cm^{-1}, (b) 1436 cm^{-1}, (c) 1450 cm^{-1}, (d) 1607 cm^{-1}.

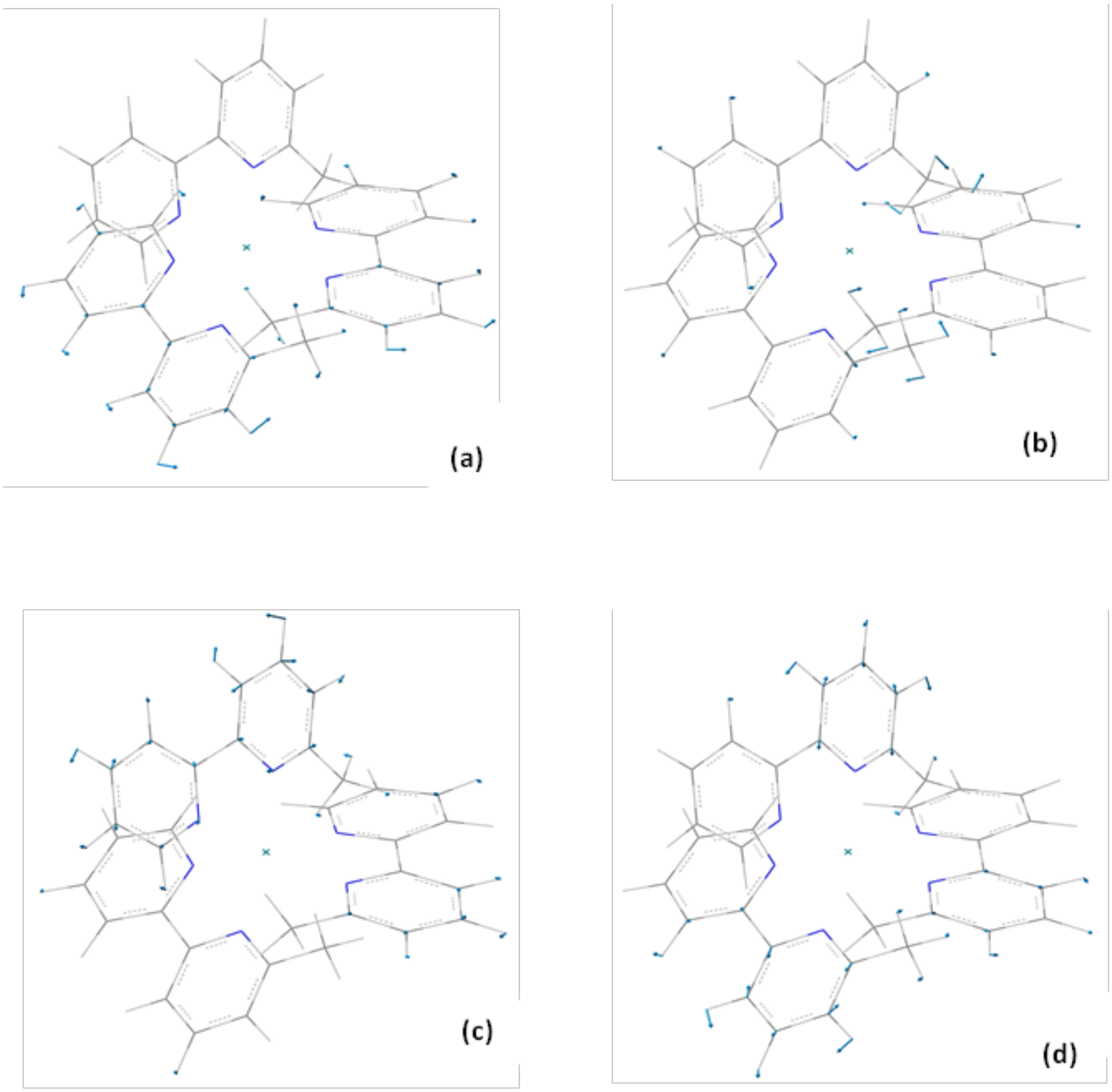


Figure S2. Some selected vibrational modes of $[Ru(mbpy)_3]^{2+}$ in the ground state in vacuum at (a) 1450 cm^{-1}, (b) 1465 cm^{-1}, (c) 1575 cm^{-1}, (d) 1608 cm^{-1}.

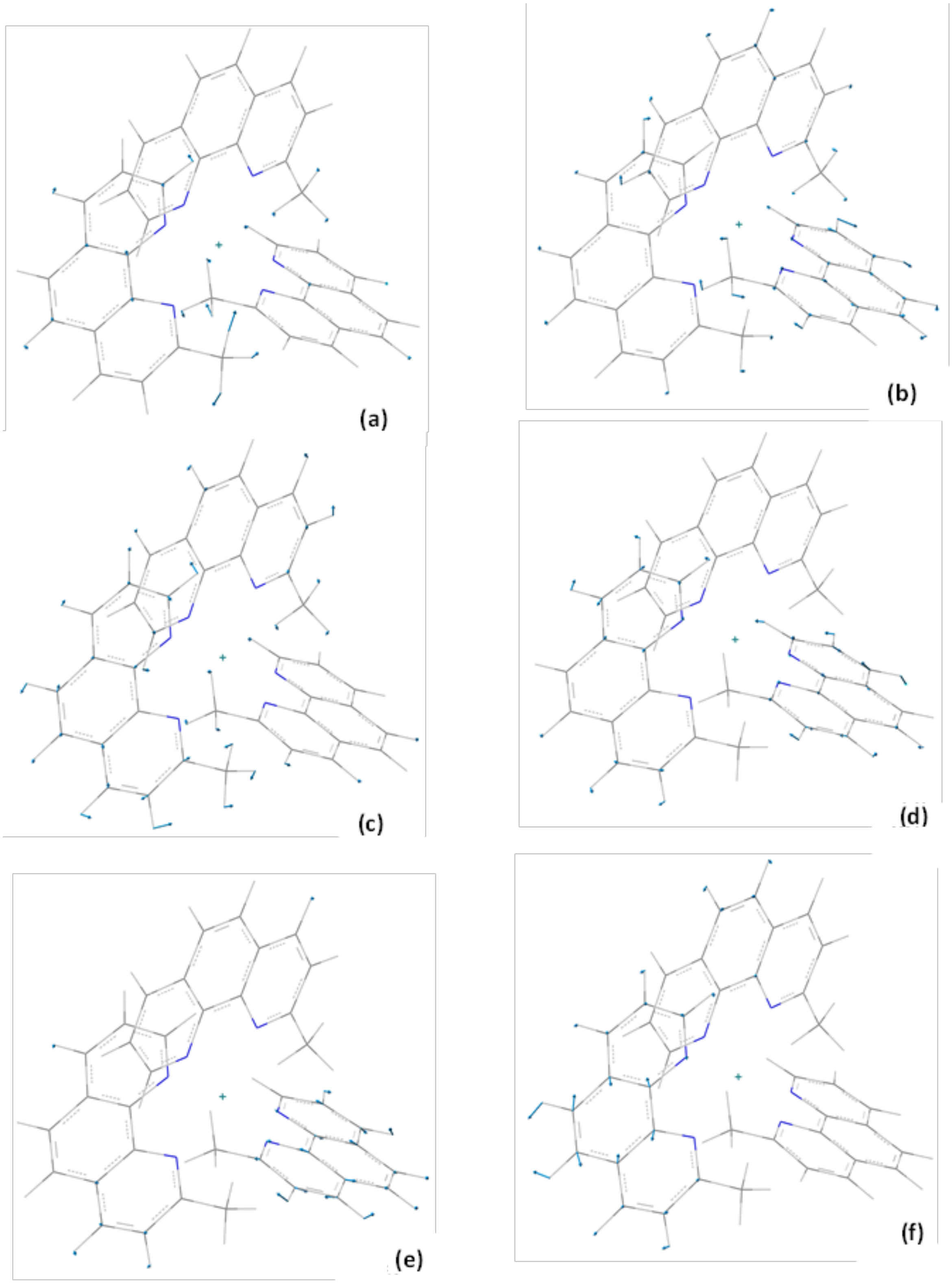


Figure S3. Some selected vibrational modes of $[\mathrm{Ru(mphen)_3}]^{2+}$ in the ground state in vacuum at (a) 1454 $\mathrm{cm^{-1}}$, (b) 1497 $\mathrm{cm^{-1}}$, (c) 1512 $\mathrm{cm^{-1}}$, (d) 1590 $\mathrm{cm^{-1}}$, (e) 1610 $\mathrm{cm^{-1}}$, (f) 1637 $\mathrm{cm^{-1}}$.

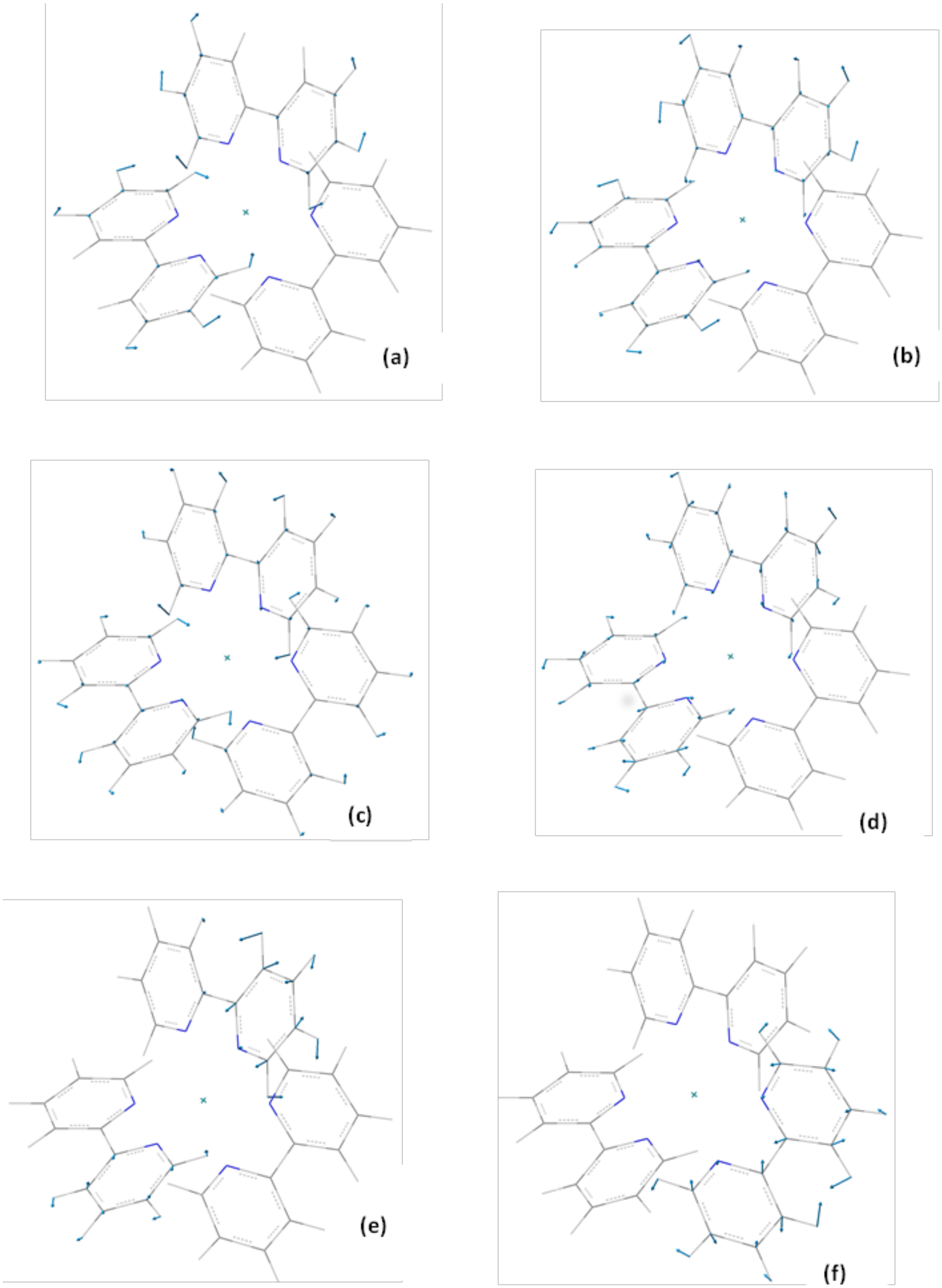


Figure S4. Some selected vibrational modes of $[Ru(bpy)_3]^{2+}$ in the ^{3}dd state at (a) 1416 cm^{-1}, (b) 1426 cm^{-1}, (c) 1450 cm^{-1}, (d) 1575 cm^{-1}, (e) 1592 cm^{-1}, (f) 1610 cm^{-1}.

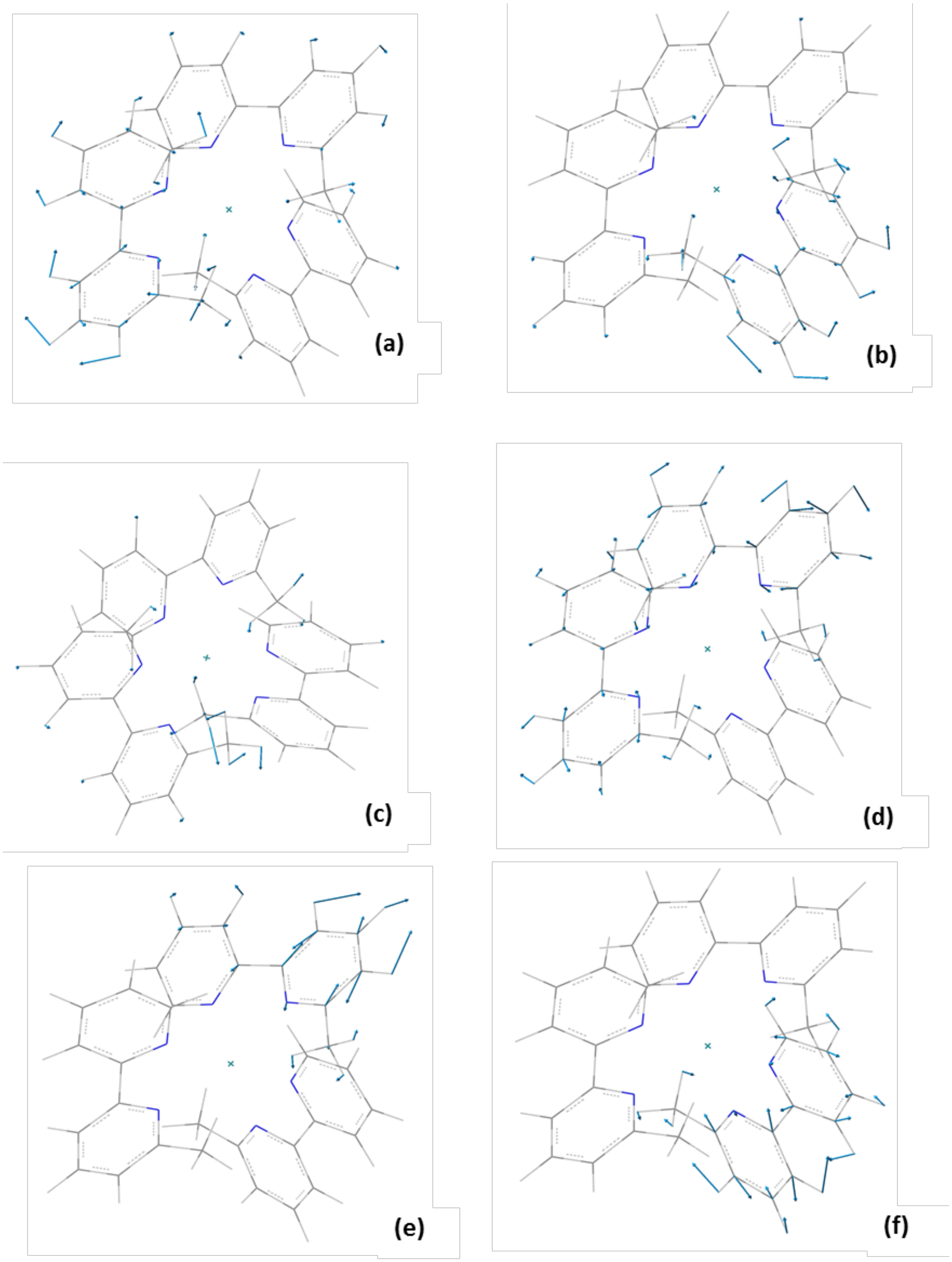
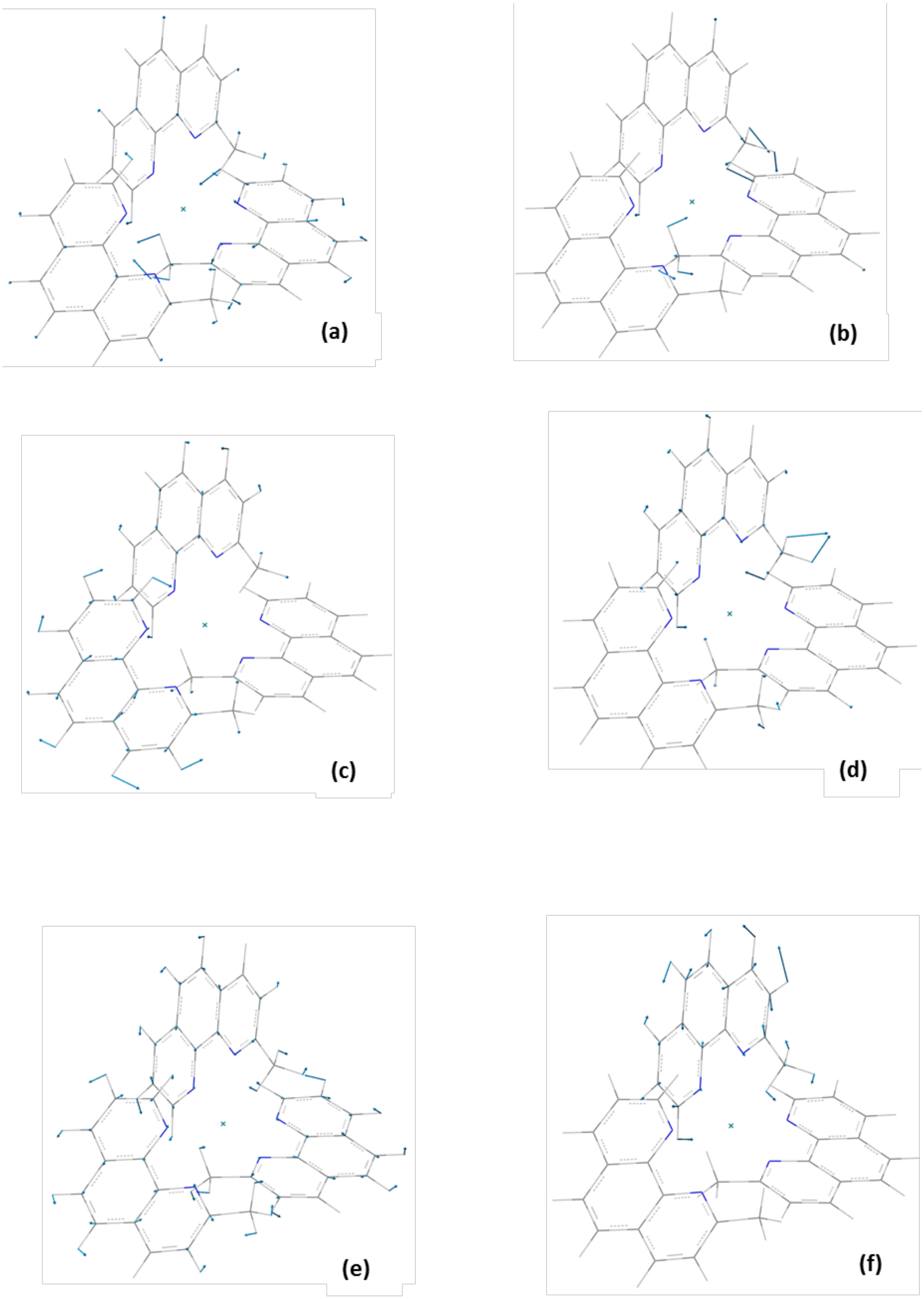


Figure S5. Some selected vibrational modes of $[\mathrm{Ru(mbpy)_3}]^{2+}$ in the ^{3}dd state at (a) 1443 cm^{-1}, (b) 1448 cm^{-1}, (c) 1459 cm^{-1}, (d) 1574 cm^{-1}, (e) 1594 cm^{-1}, (f) 1609 cm^{-1}.


(a)
(b)
(c)
(d)
(e)
(f)

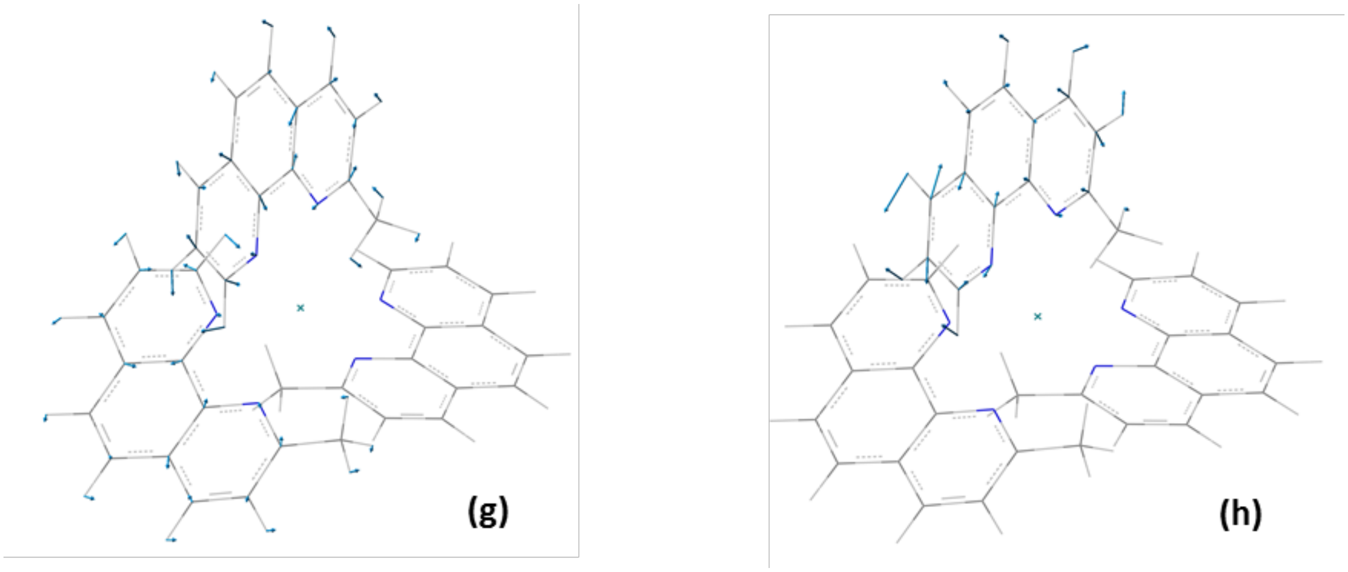


Figure S6. Some selected vibrational modes of $[Ru(mphen)_3]^{2+}$ in the ^{3}dd state at (a) 1382 cm^{-1}, (b) 1394 cm^{-1}, (c) 1428 cm^{-1}, (d) 1442 cm^{-1}, (e) 1496 cm^{-1}, (f) 1508 cm^{-1}, (g) 1561 cm^{-1}, (h) 1588 cm^{-1}.

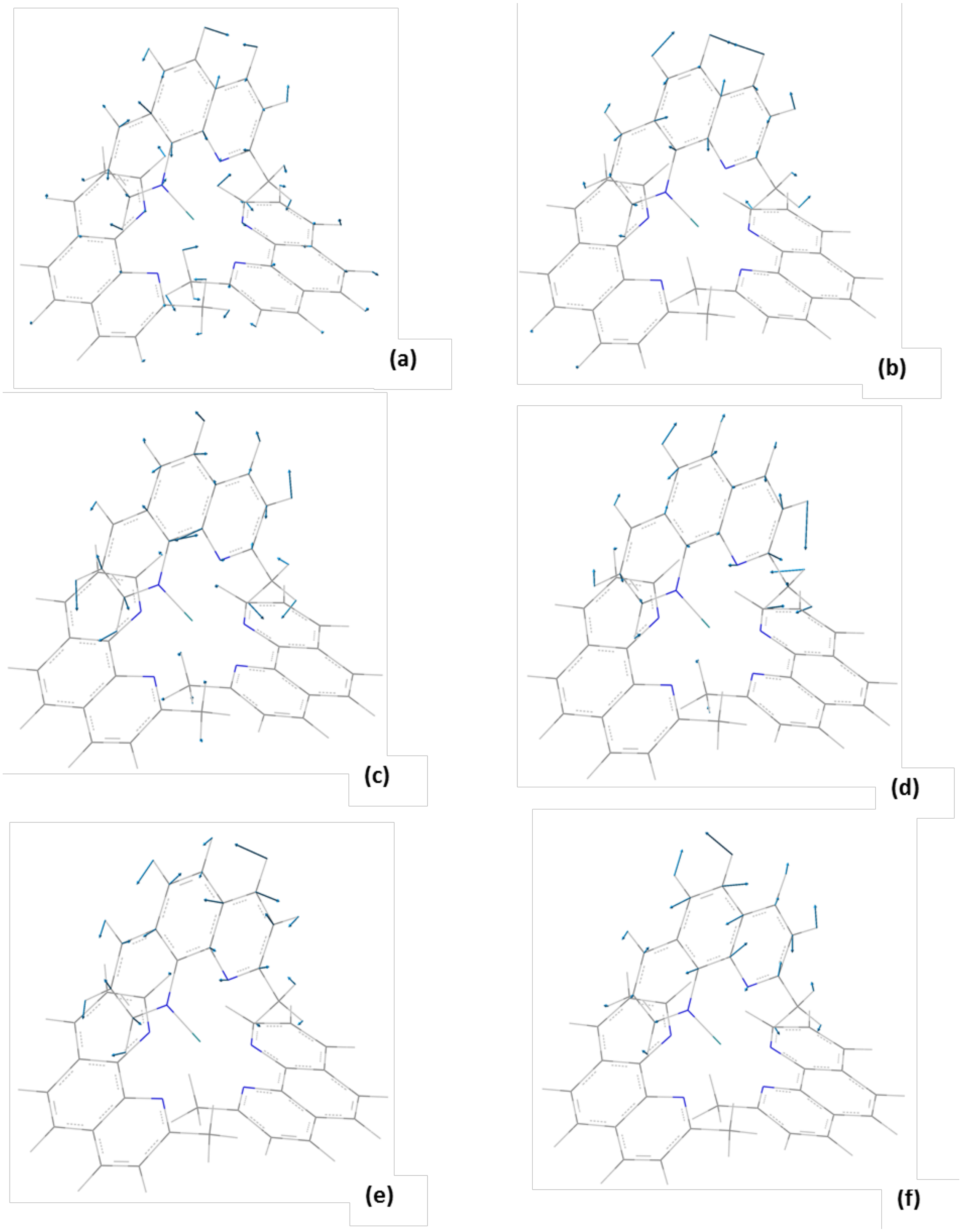


Figure S7. Some selected vibrational modes analysis of $[Ru(mphen)_3]^{2+}$ in the ^{3}MLCT state at (a) 1378 cm^{-1}, (b) 1426 cm^{-1}, (c) 1476 cm^{-1}, (d) 1490 cm^{-1}, (e) 1577 cm^{-1}, (f) 1599 cm^{-1}. The vibrational modes are mainly localized on the negative charged ligand.

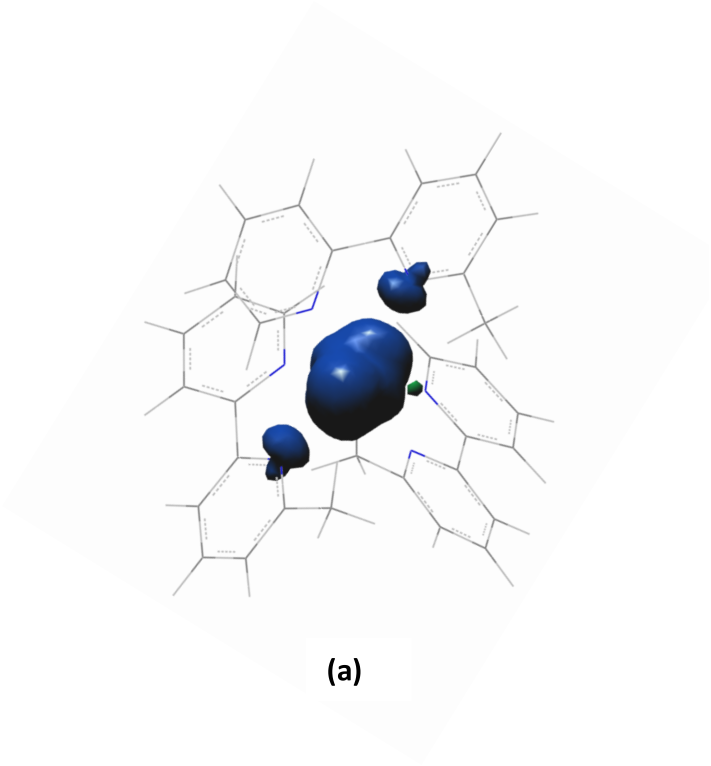


Figure S8. The spin density distribution of ^{3}dd state of [Ru(mbpy)$_3$]$^{2+}$ under PCM model of acetonitrile.

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