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Structure and State-Energy Relationship of Photo-Excited Cu(I) Complex

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Excited $[Cu^I(dmphen)_2]^+$ (dmphen=2,9-dimethyl-1,10-phenanthroline) was studied in terms of its molecular structure. The MLCT (metal-to-ligand charge-transfer) transition energy and phosphorescence lifetime of the copper(I) complex in the solid state were reduced with diminishing the dihedral angle between two dmphen ligands. The results of a DV-Xα molecular orbital calculation were in good agreement with the spectroscopic results. In solution, the non-luminous character of $[Cu^I(phen)_2]^+$ (phen=1,10-phenanthroline), which had no steric-hindered methyl groups retarding the flattening motion, was explained from lowering the lowest excited MLCT state due to a drastic distortion by the photoexcitation.

A number of Cu(I) complexes, which are constructed with 1,10-phenanthroline (phen) derivatives, emit luminescence in solution at room temperature.[1)] The emitting state of Cu(I) complexes is assigned to the MLCT (metal-to-phen charge-transfer) state, because the excited-state absorption spectrum[2)] of $[Cu(dmphen)(PPh_3)_2]^+$ (dmphen=2,9-dimethyl-1,10-phenanthroline; PPh_3=triphenylphosphine) shows a similar profile to that of a dmphen anion radical, and the excited-state resonance Raman[3,4)] exhibits a vibrational mode of a dmphen anion radical.

The $[Cu^I(dmphen)_2]^+$ shows MLCT bands in the visible region, and emits luminescence from the ^{3}MLCT state in a solid. The $[Cu^I(phen)_2]^+$ also shows MLCT bands in the visible region, however, $[Cu^I(phen)_2]^+$ does not emit phosphorescence in a solid. X-Ray crystallographic data of $[Cu(dmphen)_2]^+$ showed that the dihedral angle between two ligands was nearly 90°.[5—8)] However, the molecular symmetry of $[Cu(phen)_2]ClO_4$ was reported to be extremely lower compared with D_{2d}.[9)] This result suggests a correlation between the luminous character of Cu(I) complexes and the molecular geometry.

In this paper, we focus on the relation of the geometry of the complexes and photophysical properties of the lowest excited states. Solid-state absorption and emission measurements show that the lowest excited MLCT states are red-shifted and the emission lifetimes are reduced with decreasing the dihedral angles between two dmphen ligands. We will show by a molecular orbital calculation that the lowest MLCT state largely depends on the dihedral angle. In solution, the absorption spectra of $[Cu(dmphen)_2]^+$ and $[Cu(phen)_2]^+$ exhibit the same profile. Therefore, the molecular structures of both Cu(I) complexes in the ground state are suggested to be in a geometry such as D_{2d} in solution, where the complexes are released from the crystal packing. However, although $[Cu(dmphen)_2]^+$ emits phosphorescence, $[Cu(phen)_2]^+$ is not luminescent. We will discuss the non-luminescence of $[Cu(phen)_2]^+$ in terms of a flattening distortion of the complex in the lowest excited state in solution.

Experimental

Materials. 2,2′-Bipyridine (bpy), 1,10-phenanthroline (phen), and 2,9-dimethyl-1,10-phenanthroline (dmphen) were purchased from Tokyo Kasei Kogyo Co. Ltd. and were used without further purification. 6,6′-Dimethyl-2,2′-bipyridine (dmbpy) was prepared by a literature method.[10)] The $[Cu(dmphen)_2]ClO_4$ was prepared by McMillin's method.[11)] Analogous procedures afforded BF_4^-, NO_3^-, Cl^-, and Br^- salts and $[Cu(dmbpy)_2]ClO_4$ complexes. The $[Cu(phen)_2]ClO_4$ and $[Cu(bpy)_2]ClO_4$ were prepared by a literature method.[12)]

Measurements. The absorption spectra were recorded on a Hitachi spectrophotometer (model 330). Solid-state absorption spectra at room temperature were measured by means of an opal-glass method.[13)] The luminescence emission and excitation spectra were recorded on a Hitachi spectrofluorometer (850) equipped a Hamamatsu photomultiplier (R928). Low-temperature phosphorescence and excitation spectra were measured in a dewer assembly with the samples. The luminescence lifetimes were measured by a single-photon-counting method on a PRA nanosecond fluorometer system. The samples were excited for 5ns duration from a PRA (model 510B) nitrogen-gas lamp through a Jobin–Yvon monochromator (H-10). The photon emission was detected by a Hamamatsu Photonics photomultiplier (R928) and counted on a Norland (model 5300) multichannel analyzer. The lifetime was determined by fitting a decay curve using a least-squares method on a NEC PC-9801F2 interfaced to the multichannel analyzer. The polarized excitation spectra of the Cu(I) complex in ethanol glass at 77 K was measured. The polarization (P) was defined by a literature method.[14)]

DV-Xα Calculation. The calculation was performed on a SONY work station NEWS by a previously described method.[15)] A ligand was substituted by 1,2-ethanediimine (HN=CH–CH=NH) for dmphen, and a z-axis was fixed on a short axis of ethanediimine. Cu: 1s—4p, C: 1s—2p, N: 1s—2p, and H: 1s orbitals were taken into account. The integration points were taken up to 6000 points, and the self-consistency of the orbital population within 0.005e was obtained.

Results and Discussion

The $[Cu(dmphen)_2]^+$ in CH_2Cl_2 exhibits intense visible and UV absorption bands, which were assigned to ^{1}MLCT (Cu(I)-to-dmphen charge-transfer) and $^1(\pi,\pi^*)$ transitions, respectively, and emits luminescence assigned to phosphorescence from ^{3}MLCT state. Figure 1 shows the solid-state absorption spectra measured by the opal-glass method for $[Cu(dmphen)_2]X$ ($X=BF_4^-$, ClO_4^-, NO_3^-, and Cl^-) and $[Cu(phen)_2]ClO_4$. According to X-ray crystallographic data for $[Cu(dmphen)_2]^+$, the dihedral angle between the two ligands is less than 90°, and depends on a counter-anion ($[Cu(dmphen)_2]ClO_4$: 82°,[5,6] $[Cu(dmphen)_2]NO_3$: 67.7°[7]). In the case of $[Cu(phen)_2]ClO_4$, it is the smallest value, 49.7°,[9] and the molecular symmetry is considerably lowered from D_{2d}. Based on a comparison with the solid-state absorption spectra and the geometry of the complexes, there is a tendency for the red-shift of a weak absorption band at 15—20×10^3 cm^{-1} belong with diminishing dihedral angle, especially in the case of $[Cu(phen)_2]ClO_4$, which has the smallest dihedral angle, distinctly splitting MLCT bands (around 17×10^3 and 24×10^3 cm^{-1}) were observed. Figure 1 also shows the emission spectra of the solid samples. The phosphorescence spectra of the $[Cu(dmphen)_2]X$ salts were red-shifted in the order $X=BF_4^- < ClO_4^- < NO_3^- < Cl^-$. The $[Cu(phen)_2]ClO_4$ emitted no luminescence. The order of the emitting ^{3}MLCT band corresponded to the order of the lowest absorption band. The phosphorescence lifetime of $[Cu(dmphen)_2]X$ salts was measured, and the emission decay was fitted as a double-exponential curve. For example, a fast component and a slow one of emission of chloride salt, $[Cu(dmphen)_2]Cl$, were evaluated to be 110 and 480 ns, respectively. As listed in Table 1, the fast component correlates with the MLCT transition energy. X-Ray crystallographic data shows that the distances between the nearest-neighbor copper ions are similar (7.71[5] and 7.20 Å[6] for $[Cu(dmphen)_2]ClO_4$, 7.096 Å[7] for $[Cu(dmphen)_2]NO_3$ and 7.45 Å[9] for $[Cu(phen)_2]ClO_4$, respectively). The energy migration within the excited life-time can be regarded to be similar in the solid samples. Therefore, it should be noted that the fast component reflects the difference of the energy-gap between the MLCT and the ground state, which is caused by a difference in the dihedral angle.[16] The results show that the emission energy and life-time are reduced in the order of the distortion from D_{2d} symmetry.

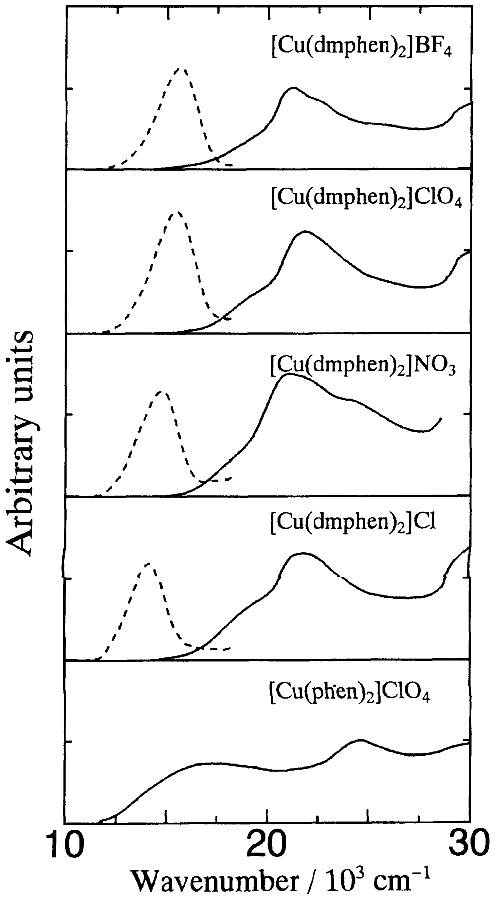

Fig. 1. Solid-state absorption (solid line) and uncorrected emission (broken line) spectra of Cu(I) complexes at room temperature.

As shown in Fig. 2, the luminescence polarization spectrum of $[Cu(dmphen)_2]ClO_4$ was measured in ethanol glass at 77 K. The highest polarization value ($P=0.5$) was obtained at the MLCT absorption maximum (22×10^3 cm^{-1}), and a minimum value ($P=0$) was observed at 26×10^3 cm^{-1}. Crosby also obtained the same result for $[Cu(bcn)_2]^+$ (bcn=2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) in poly(methyl methacrylate) at 77 K.[17] The polarization value ($P=0.5$) shows that the predominant absorption (22×10^3 cm^{-1}) and emission oscillators in the Cu(I) complex are collinear, and that the polarization value is independent of the substituents in the ligands. It is concluded that the transition moments of the MLCT absorption and emission bands are oriented to the same axis (z-axis) in the molecules. A transition at around 26×10^3 cm^{-1}, which was given the lowest value, $P=0$, is predominated by a linear oscillator polarized to the x- or y-axis.

To clarify the relationship between the transition energy and the geometry of the Cu(I) complex, a DV-Xα molecular-orbital calculation on $[Cu^I(ethanediimine)_2]^+$, in which the dihedral angles between the ligands were set at 30—90°, was performed. In the calculation, the 4s and 4p orbitals were taken as the

Table 1. Phosphorescence Lifetime (ns) of $[Cu(dmphen)_2]X$ in the Solid-State at Room Temperature

X	Fast component	Slow component
BF_4^-	290	470
ClO_4^-	200	310
NO_3^-	150	240
Cl^-	110	480

Table 2. The Highest Occupied and the Lowest Unoccupied Molecular Orbitals of $[Cu(ethanediimine)_2]^+$ in the Ground State
Dihedral angle: 60°.

MO	Energy	Occupation	Predominant character in per cent								
			Cu			N		C		H(N)	H(C)
	eV	number	3d	4s	4p	2s	2p	2s	2p	1s	1s
12a	−11.19	2	94	3			1			1	
$11b_1$	−10.74	2	75		4	1	14		4		1
$10b_2$	−10.64	2	66		6	2	14		10	1	1
13a	−10.04	2	86	1			7		6		
$10b_3$	−9.44	2	44		9	4	28		12	1	1
$11b_3$	−7.96	0	11		3	2	54		30		
$11b_2$	−7.74	0	6			1	61		32		
14a	−4.16	0	1				26		74		

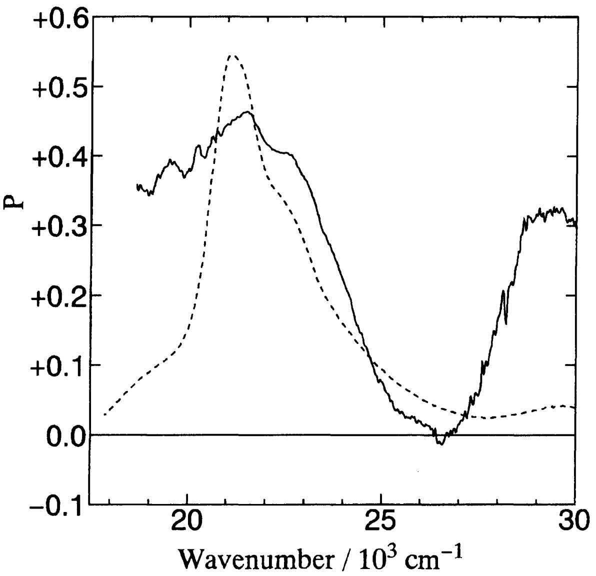

Fig. 2. Luminescence polarization (solid line) and excitation (broken line) spectra of $[Cu(dmphen)_2]ClO_4$ in ethanol at 77 K.

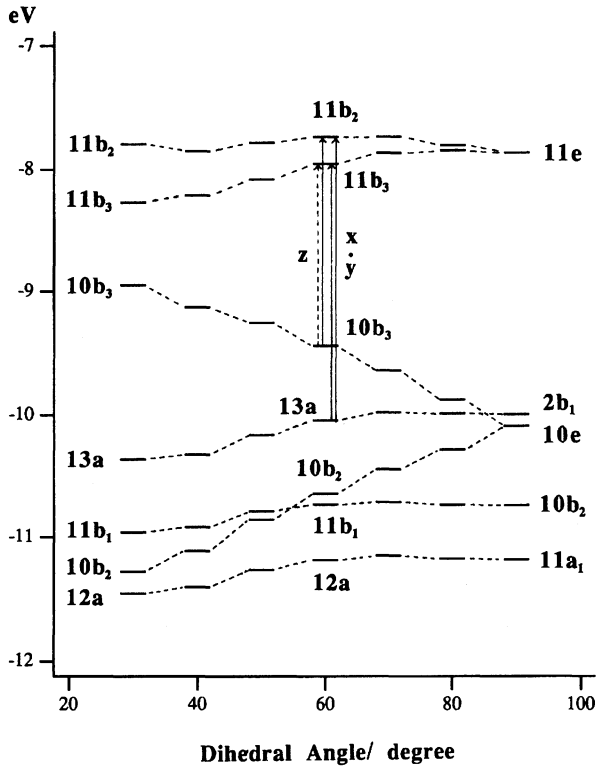

Fig. 3. Energy levels of the highest occupied MO and the lowest unoccupied MO in $[Cu(ethanediimine)_2]^+$ as a function of the dihedral angle.

extra-orbitals of central metal. Table 2 presents the calculated molecular orbitals along with their predominant characters and the energies of some occupied and unoccupied orbitals of $[Cu(ethanediimine)_2]^+$ at a dihedral angle of 60° in the ground state. The highest occupied orbitals ($10b_3$, 13a, and $10b_2$) in D_2 symmetry are localized predominantly on the Cu 3d orbital. The unoccupied orbitals ($11b_3$ and $11b_2$) are localized on the 2p orbitals of C and N atoms in the ethanediimine ligand. This shows that the lowest electronic transitions are undoubtedly due to a charge-transfer transition from the Cu ion to the ethanediimne ligand. Figure 3 shows an energy-level diagram of the highest occupied and the lowest unoccupied orbitals of $[Cu(ethanediimine)_2]^+$ as a function of the dihedral angle. The lowest-allowed MLCT ($10b_3 \rightarrow 11b_2$) transition energies decrease in the following order: $90° > 60° > 30°$. This is in good agreement with the experimental results in which the absorption spectrum of $[Cu(dmphen)_2]X$ was red-shifted with diminishing the dihedral angle. Table 3 presents the transition energies and atomic populations in the excited state calculated by using the transition-state method.[15] The lowest allowed transition state, B_1 ($10b_3 \rightarrow 11b_2$), is polarized in the direction of the short axis of the ethanediimine ligands (z-axis) and the other allowed transition state, B_3 ($13a \rightarrow 11b_2$) and B_2 ($13a \rightarrow 11b_3$), which are at a higher energy than the B_1 state, are x- and y-polarized, respectively. The transition to the A state ($10b_3 \rightarrow 11b_3$) is symmetry-forbidden. The calculation results are in agreement with the polarization spectrum of $[Cu(dmphen)_2]^+$ in ethanol glass.

The transition energies of the A state (1.74 eV at 60°) are lower than those of the B_1 state (1.93 eV at 60°). The flattening distortion causes a decrease in the energy

Table 3. Transition Energies and Atomic Populations in the Excited State
Dihedral angle: 60° (upper) and 30° (lower).

State	A	$\mathrm{B_1}(z)$	$\mathrm{B_3}(x)$	$\mathrm{B_2}(y)$
transition	$10\mathrm{b_3}\rightarrow 11\mathrm{b_3}$	$10\mathrm{b_3}\rightarrow 11\mathrm{b_2}$	$13\mathrm{a}\rightarrow 11\mathrm{b_3}$	$13\mathrm{a}\rightarrow 11\mathrm{b_2}$
energy/eV	1.69	1.98	2.77	3.08
Population/e				
Cu 3d	9.42	9.42	9.34	9.35
4s	0.59	0.59	0.59	0.59
4p	0.62	0.59	0.72	0.69
Net charge	+0.37	+0.38	+0.35	+0.37
N 2s	1.48	1.48	1.50	1.49
2p	3.74	3.75	3.73	3.74
Net charge	−0.22	−0.23	−0.23	−0.23
C 2s	1.12	1.12	1.13	1.13
2p	2.95	2.95	2.93	2.94
Net charge	−0.07	−0.07	−0.06	−0.07
H(N) 1s	0.74	0.74	0.74	0.74
Net charge	+0.26	+0.26	+0.26	+0.26
H(C) 1s	0.81	0.81	0.81	0.81
Net charge	+0.19	+0.19	+0.19	+0.19

State	A	$\mathrm{B_1}(z)$	$\mathrm{B_3}(x)$	$\mathrm{B_2}(y)$
transition	$10\mathrm{b_3}\rightarrow 11\mathrm{b_3}$	$10\mathrm{b_3}\rightarrow 11\mathrm{b_2}$	$13\mathrm{a}\rightarrow 11\mathrm{b_3}$	$13\mathrm{a}\rightarrow 11\mathrm{b_2}$
energy/eV	0.73	1.29	2.74	3.37
Population/e				
Cu 3d	9.44	9.44	9.33	9.35
4s	0.61	0.61	0.60	0.61
4p	0.60	0.55	0.71	0.63
Net charge	+0.35	+0.40	+0.36	+0.41
N 2s	1.49	1.48	1.50	1.50
2p	3.74	3.75	3.73	3.75
Net charge	−0.23	−0.23	−0.23	−0.25
C 2s	1.13	1.13	1.13	1.13
2p	2.93	2.94	2.93	2.93
Net charge	−0.06	−0.07	−0.06	−0.06
H(N) 1s	0.74	0.74	0.74	0.74
Net charge	+0.26	+0.26	+0.26	+0.26
H(C) 1s	0.81	0.81	0.81	0.81
Net charge	+0.19	+0.19	+0.19	+0.19

of both the allowed $\mathrm{B_1}$ states and the forbidden A state (see Table 3 dihedral angle: 30°). The energy of the forbidden A state is greatly affected by the dihedral angle, compared with the lowest symmetry-allowed MLCT state, $\mathrm{B_1}$. Therefore, it is suggested that the emission lifetime is shortened with lowering from D_{2d} symmetry. However, the $\mathrm{B_3}$ state does not depend very much on the dihedral angle, and the $\mathrm{B_2}$ state is slightly raised by the flattening distortion. The $\mathrm{B_1}$ and $\mathrm{B_2}$ (and/or $\mathrm{B_3}$) states correspond to the lower and higher energy components of the observed splitting MLCT bands for $[\mathrm{Cu(phen)_2}]\mathrm{ClO_4}$, respectively. The net charges on the Cu metal atom at 60° are +0.28, +0.37, +0.38, +0.35, +0.37 in the ground state, A, $\mathrm{B_1}$, $\mathrm{B_2}$, and $\mathrm{B_3}$ MLCT excited states, respectively; the central metal atom is neutralized by a redistribution of the electron donations in the MLCT states. Kobayashi et al. calculated $[\mathrm{Cr(bpy)(CO)_4}]$ and predicted the same results: that the charge in the central metal atom in the MLCT excited state did not change compared with that in the ground state.[15]

The phosphorescence lifetime and quantum yield of $[\mathrm{Cu(dmphen)_2}]^+$ in $\mathrm{CH_2Cl_2}$ at 25 °C were reported to be 80 ns and approximately 10^{-4}, respectively.[18] Figure 4 shows absorption (solid line) and emission (dotted line) spectra of $[\mathrm{Cu(dmphen)_2}]^+$ (A) and $[\mathrm{Cu(dmbpy)_2}]^+$ (B) in $\mathrm{CH_2Cl_2}$. The emission lifetime of $[\mathrm{Cu(dmbpy)_2}]^+$ was determined to be 20 ns and shorter than that of $[\mathrm{Cu(dmphen)_2}]^+$. The difference in the excited lifetime of the complexes was accounted for by the energy-gap between the MLCT and ground states.[19] As shown in Fig. 4, the absorption spectra of $[\mathrm{Cu(phen)_2}]^+$ (A: broken line) and $[\mathrm{Cu(bpy)_2}]^+$ (B: broken line) in $\mathrm{CH_2Cl_2}$ are very similar to those of $[\mathrm{Cu(dmphen)_2}]^+$ and $[\mathrm{Cu(dmbpy)_2}]^+$, respectively. This implies that the MLCT transition energies of $[\mathrm{Cu(phen)_2}]^+$ and $[\mathrm{Cu(dmphen)_2}]^+$ are approximately the same. The complexes seem to be nearly in the D_{2d} symmetry in solution, according to the results of a DV-Xα molecular orbital calculation, in which the MLCT transition energy is fixed by the molecular structure. Despite the same structure, emission was observed only for dimethyl substituted ligand systems. This result suggests that the emission lifetime is shortened by a lowering of the energy of the lowest excited state of $[\mathrm{Cu(phen)_2}]^+$ com-

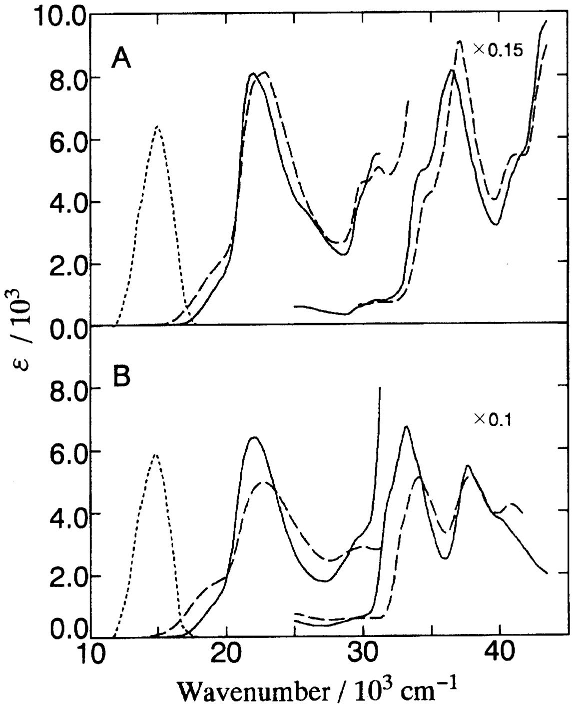

Fig. 4. Absorption (solid line) and emission (dotted line) spectra of Cu(I) complexes in $\mathrm{CH_2Cl_2}$ at room temperature. A: $[\mathrm{Cu(dmbpy)_2}]^+$ and $[\mathrm{Cu(bpy)_2}]^+$ (broken line); B: $[\mathrm{Cu(dmphen)_2}]^+$ and $[\mathrm{Cu(phen)_2}]^+$ (broken line). Emission of $[\mathrm{Cu(bpy)_2}]^+$ and $[\mathrm{Cu(phen)_2}]^+$ could not be observed.

pared with that of $[\mathrm{Cu(dmphen)_2}]^+$ in solution. On the base of the results of the solid-state measurements and DV-Xα molecular orbital calculation, it is suggested that $[\mathrm{Cu(phen)_2}]^+$ in the excited MLCT state is largely distorted, since the complex has no steric-hindered methyl groups retarding the flattening motion. The same suggestion can be given for $[\mathrm{Cu(bpy)_2}]^+$. It is concluded that the MLCT excitation, which changes the electronic configuration of the central metal from $3\mathrm{d}^{10}$ to $3\mathrm{d}^9$, causes the dynamic flattening-distortion from D_{2d} to planer.

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