

Multiple Anti-Kasha Emissions in Transition Metal Complexes

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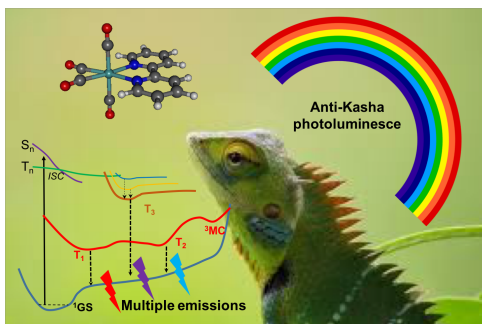
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ABSTRACT. In this manuscript we present a from-first-principles evidence that several higher-lying excited states are responsible for the emission spectrum of $[M(CO)_4(bpy)]$ ($M = Cr, Mo, W$ and $bpy=2,2'$ -bipyrimidine) complexes. These results highlight the violation of Kasha's rule, which states that after irradiation molecules emit light with appreciable yield only from its lowest energy excited state. Furthermore, in $[W(CO)_4(bpy)]$ and $[Mo(CO)_4(bpy)]$, the breaking of Kasha's rule is two-fold, because at least two different excited states besides T1 are involved in emission. To our knowledge, these are the first transition metal complexes unambiguously demonstrated to display simultaneous equilibrated and non-equilibrated anti-Kasha emissions. This work also highlights the complexity of the emissive processes of tetracarbonyl-diimine transition metal complexes, which are controlled via a subtle interplay of electronic and

geometrical effects along the excited state deactivation dynamics.

TOC GRAPHICS

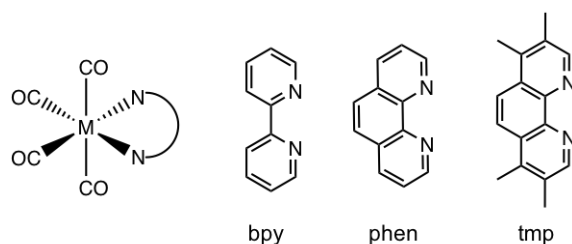


KEYWORDS Kasha rule – Photophysics – Computational Photochemistry – Photodeactivation kinetics – TDDFT – DLPNO-CCSD(T)

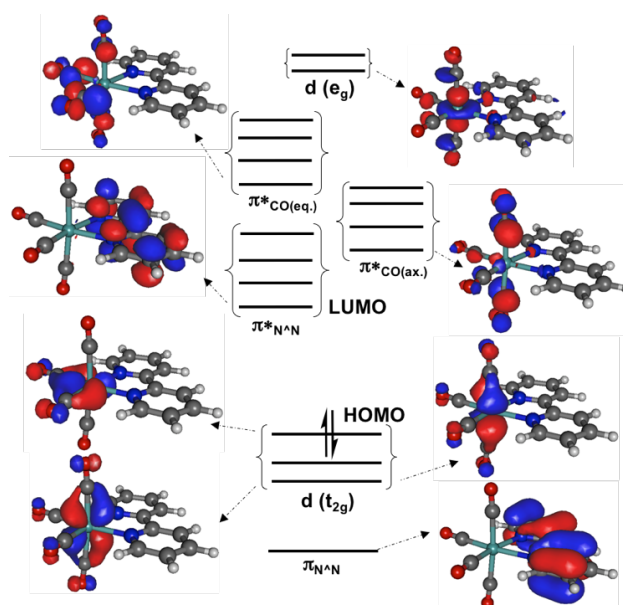
Observation of believed scientific rules being broken leads often to new knowledge and promisingly to important applications. Kasha rule states that “*the emitting electronic level of a given multiplicity is the lowest excited level of that multiplicity*”.¹ The initial formulation of Kasha’s rule was later extended to include not only emission processes but also excited state reactivity, that is “*polyatomic molecular entities react with appreciable yield only from the lowest excited state of a given multiplicity*”.² According to Itoh,³ anti-Kasha events can be classified into thermally or non-thermally equilibrated cases. In general, as kinetic control is always at play in photochemistry, most of the molecular systems behave in a Kasha-like manner. This is because higher-lying excited states (ES) are extremely short-lived, due to the ultrafast relaxation by internal conversion (IC) to the lowest ES; and thus, photoreactions and/or photoluminescence from the higher-lying ES (i.e., non-thermally equilibrated case) are generally not fast enough to compete with IC; but also because the possibility of having close-lying ESs (within the $k_B T$ energy window) near the lowest ES is unlikely (i.e., thermally equilibrated case).

While examples of molecular systems breaking Kasha rule are known since the late 50's, such as e.g., azulene,^{4,5} those examples were believed to be a few exceptions. This was so because these “hot” photochemical reactions were difficult to track experimentally, but also because low-lying dark excited states are silent to many spectroscopic techniques. In steady-state photoluminescence experiments, the presence of a single emission band does not guarantee *per se* its occurrence from the lowest-lying ES. Thus, the observance or violation of Kasha rule needs further experimental evidences. For instance, excitation wavelength- and/or temperature-dependent emissive features are characteristic footprints for anti-Kasha photoluminescence. Sometimes, a simple inspection of the steady-state emission spectrum can hint to violations of Kasha rule, as e.g., when dual (or multiple) emissions are observed. However, photoreactions might also lead to dual emissions scenarios.⁶ The latter cases are strictly not violating Kasha rule because different chemical species (i.e., products and reactants) are responsible for the different emissive bands. In recent years, with the progresses in both experimental and computational techniques to unambiguously track ES species and their photodeactivation dynamics, more molecular systems have been proven to violate Kasha rule.⁷ There is still some controversy in some of the systems claimed to behave in an anti-Kasha manner. For instance, Catalán and coworkers recently claimed that Kasha rule still holds true for the majority of the investigated organic compounds.⁸ Conversely, transition metal complexes (TMCs), due to their higher density of excited states of different spin and character, often display more complex and chameleonic photochemical properties than those of organic compounds.⁹ Their ES photodeactivation dynamics are also more intricate, since intersystem crossing (ISC) often occur in the ultrafast regime (i.e., from few femtoseconds to the picosecond regime) and thus, ISC directly competes with IC. Hence, TMCs can undergo a plethora of interconnected ES

deactivation processes, which compete to each other, and which are controlled by geometrical and electronic factors. Intrinsic factors such as the character and spin of the involved ESs along with their effective couplings and their energetic alignment determine the preferred ES deactivation channels and/or the branching of the ES population. Furthermore, the situation of having multiple close-lying ES is not rare for TMCs, and the combination of all these characteristics leads in many cases to complex ES decay kinetics at different timescales. To showcase this complexity, dual emissive scenarios have been reported for TMCs, including Ag(I),¹⁰ Ir(III),^{11,12,13} Pt(II),^{14,15} Rh(I),¹⁶ Os(II)¹⁷ and Ru(II).^{18,19} Both dual singlet-triplet and triplet-triplet scenarios have been reported.



Scheme 1. $M(CO)_4L$ ($M = Cr, Mo, W$; $L = bpy, phen, tmp$) complexes.



Scheme 2. Qualitative molecular orbital diagram for $M(CO)_4L$ complexes.

The electrochemical, photophysical and photochemical properties of group 6 complexes of the type $M(CO)_4L$ (where $M=Cr, Mo, W$; and L is a α -diimine ligand, such as e.g., 2,2'-bipyrimidine(bpy) or 1,10'-phenantroline (phen)), see Scheme 1, were examined with experimental techniques,^{20,21} including ultrafast time-resolved ones,^{22,23} but also computationally.^{24,25} In terms of applications, these complexes have recently emerged as efficient electrocatalysts for CO_2 reduction, especially in the case of the Mo and W complexes.^{26,27} Thus, due to their rich physical and chemical aspects but also due to their relative molecular simplicity, these complexes are excellent model systems to test novel experimental and theoretical approaches. The group 6 complexes of the type $M(CO)_4L$ possess many common electronic features.^{28,29} In Scheme 2 is shown a qualitative molecular orbital (MO) diagram, which includes the most relevant orbitals involved in their photochemistry. The three highest occupied MOs (HOMOs) are located in an energetically narrow range and mainly correspond to the set of t_{2g} metal d orbitals, while HOMO-4 is a $\pi_{N\wedge N}$ orbital. The lowest unoccupied MOs (LUMOs) of $M(CO)_4L$ complexes correspond to $\pi^*_{N\wedge N}$ orbitals, see for instance LUMO in Scheme 2. Higher in energy appear in increasing energetic order the set of $\pi^*_{CO(ax.)}$ and $\pi^*_{CO(eq.)}$ MOs. Finally, much higher in energy appear the set of e_g metal d orbitals. The diversity of MOs in a narrow energy range leads to a manifold of close-lying ES of different character, i.e., from metal-to-ligand charge transfer (MLCT) involving both CO and L ligands as well as ligand-centered (LC) or metal-centered (MC) ESs. Experimentally, in terms of photoreactivity, these complexes undergo excitation wavelength-dependent photochemical substitution of an axial CO ligand,²⁹ being the yields of this reaction strongly dependent on the nature of i) the central atom and ii) the L ligand, but also on other extrinsic effects, such as temperature, pressure and environmental conditions

(solvent). Concerning their emission properties, they generally exhibit multiple photoluminescence features in room temperature solutions and in low-temperature glasses, leading to two emission bands separated by ca. 4000 cm^{-1} , and which are identified as high-energy (HE) and low-energy (LE) bands.^{20,29} All emitting states responsible of these bands possess considerable triple character.²⁹ For some of the wolframium complexes, i.e., $\text{W(CO)}_4(\text{phen})$ and $\text{W(CO)}_4(\text{tmp})$ (tmp=3,4,7,8-tetramethyl-1,10'-phenantroline), time-resolved emission spectra were recorded.³⁰ For these complexes, the HE emission is very short-lived (<36 ns), and it is excitation wavelength-dependent, since it fully develops only upon UV excitation. It likely originates in several radiative transitions for these complexes.³⁰ The LE band is thermally-equilibrated, it displays biexponential photoluminescence decay and it is longer-lived than the HE band (i.e., the measured lifetimes for $\text{W(CO)}_4(\text{phen})$ are 150 and 487 ns). In addition, the time-resolved experiments highlighted that the emitting states responsible for the HE and LE bands are not in thermal equilibrium, regardless of the temperature.³⁰ The assignment of the ES responsible of the LE and HE bands is more controversial. Early stage investigations²⁰ pointed to several triplet $^3\text{MLCT}$ states involving the $\text{N}^{\wedge}\text{N}$ ligand ($^3\text{MLCT}_{\text{N}^{\wedge}\text{N}}$) to be responsible of the LE band while ^3MC state(s) being responsible for the HE band. Later investigations,³⁰ which also included time-dependent density functional theory (TD-DFT) calculations at the Franck-Condon region, concluded that the lowest-lying $^3\text{MLCT}_{\text{N}^{\wedge}\text{N}}$ states are likely responsible for the LE band, but conversely the HE band likely originates from $^3\text{MLCT}$ states involving the CO ligands ($^3\text{MLCT}_{\text{CO}}$). In this contribution we aim at shedding some light into this controversy by identifying the ES unambiguously involved in the emission process and by rationalizing the origins of the anti-Kasha behavior in these complexes. Towards this end, high-level *ab initio* coupled-cluster and TD-DFT calculations are performed.

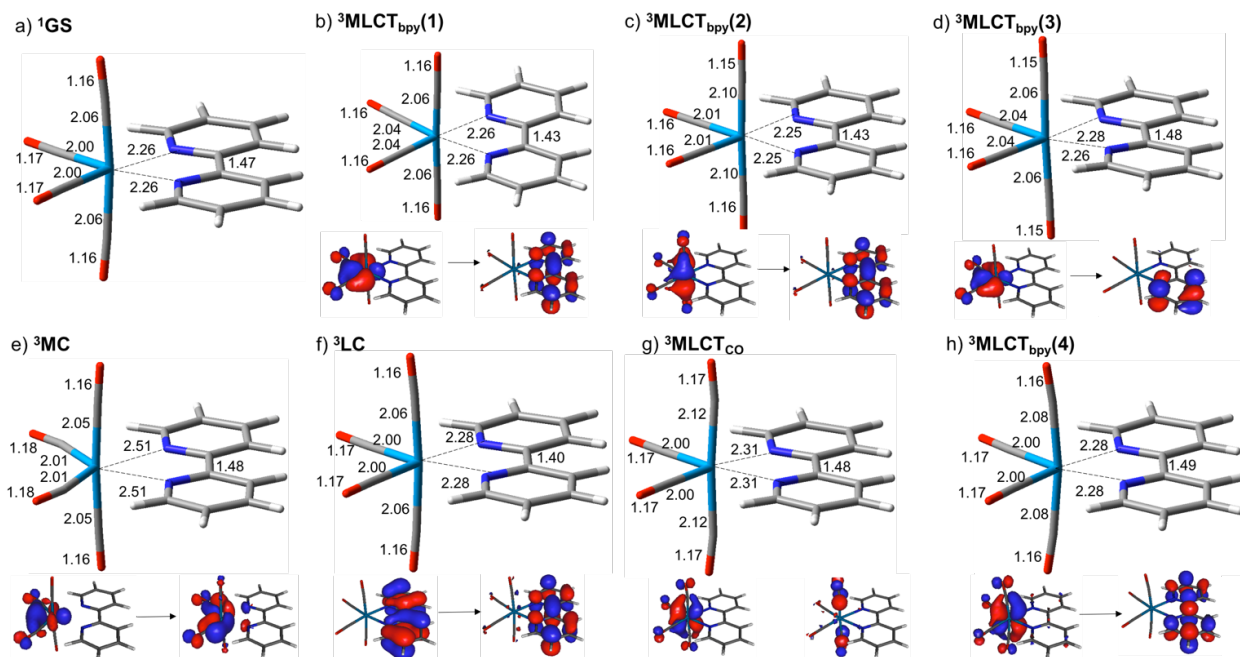


Figure 1. Main geometrical features of the optimized structures of ^1GS , $^3\text{MLCT}_{\text{bpy}}(1)$, $^3\text{MLCT}_{\text{bpy}}(2)$, $^3\text{MLCT}_{\text{bpy}}(3)$, ^3MC , ^3LC , $^3\text{MLCT}_{\text{CO}}$ and $^3\text{MLCT}_{\text{bpy}}(4)$ for $\text{W}(\text{CO})_4(\text{bpy})$. Below each optimized structure are shown the orbitals involved in their corresponding TD-DFT electronic transitions. Bond distances are given in Å.

Owing to the common photophysical properties of group 6 $\text{M}(\text{CO})_4\text{L}$ complexes, we herein focus our computational efforts on the following bpy derivatives: $\text{W}(\text{CO})_4(\text{bpy})$ and $\text{Mo}(\text{CO})_4(\text{bpy})$. As discussed above, the photophysical properties of these complexes were investigated experimentally (see in Table 1 their emission data) and with TD-DFT,³⁰ but these studies were restricted at the Franck-Condon region. Herein, we go beyond in complexity by exploring the triplet ES potential energy surface (PES), so that important geometric relaxation effects along the ES photodeactivation dynamics can be captured. Due to the presence of a high density of close-lying ESs of different character, many of those ESs might be responsible for the measured emission bands. Therefore, we performed TD-DFT optimizations of the first twenty-

five triplet excited states to locate ES minima (see computational details in the SI). With this *brute force* protocol to explore the triplet ES PESs we were able to optimize the geometries of seven different triplet excited states for both Mo(CO)₄(bpy) and W(CO)₄(bpy). The other trials were either unsuccessful or ended up in the wells of those seven ES minima. The optimized geometries of the seven triplet excited state minima and of the ground state (¹GS) for W(CO)₄(bpy) are shown in Figure 1, while those of Mo(CO)₄(bpy) are found in Figure S1. The assignment of the character of the electronic states is based on the analysis of the orbitals involved in their corresponding TD-DFT electronic transitions, see Figures 1 and S1. For W(CO)₄(bpy) we obtained the following ES minima: four different ³MLCT states involving the bpy ligand (³MLCT_{bpy}(1-4)); one ³MLCT state involving the axial CO ligands (³MLCT_{CO}); one ³LC state; and one ³MC state. ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) correspond to the lowest-lying triplet states. The optimized structures of the ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) states closely resemble the ¹GS geometry with regard to the octahedral coordination (see e.g., Figures 1a-c). ³MLCT_{bpy}(1) is characterized by stretched equatorial M-CO bond distances (2.04 Å), while stretched axial M-CO bond distances (2.10 Å) are observed in the optimized geometry of ³MLCT_{bpy}(2). In addition, and due to the population of a π^*_{bpy} orbital, the bpy bond ring distances strongly differ in the ³MLCT_{bpy}(2) and ¹GS optimized structures (compare e.g., 1.47 with 1.43 Å for the central C-C bond). In the following we discuss the optimized geometries of the rest of higher-lying states. First, the ³MLCT_{bpy}(3) state displays similar features to those of ³MLCT_{bpy}(1). However, the optimized ³MLCT_{bpy}(3) structure is less symmetric than that of ³MLCT_{bpy}(1). This is because in the former complex only one pyridyl unit participates in π^*_{bpy} (see Figure 1d). Consequently, the optimized ³MLCT_{bpy}(3) geometry displays asymmetric M-N bond distances (i.e., 2.26 and 2.28 Å). The optimized ³MC structure is characterized by strong geometric

distortions with respect to the ^1GS structure. Importantly both M-N bond distances are significantly stretched (amounting up to 2.51 Å at ^3MC , see Figure 1e) and the equatorial C-O bond distances are slightly stretched due to mixing of equatorial π^*_{CO} orbitals with the e_g -like metal d orbital. Conversely, the optimized ^3LC structure displays very similar features to those of the ^1GS structure. Not surprisingly, the main geometric distortions affect the bpy ligand. The optimized $^3\text{MLCT}_{\text{CO}}$ structure involves the axial CO ligands (see Figure 1g), and therefore stretched axial M-CO distances are observed with respect to the ^1GS structure. Thus, the $^3\text{MLCT}_{\text{CO}}$ state is likely involved in the excitation wavelength-dependent photochemical substitution of an axial CO ligand. Finally, the $^3\text{MLCT}_{\text{bpy}}(4)$ states involves a lower-lying t_{2g} d orbital and a higher-lying π^*_{bpy} orbital. However, its optimized structure displays similar geometric characteristics to those observed for other $^3\text{MLCT}_{\text{bpy}}$ states. For $\text{Mo}(\text{CO})_4(\text{bpy})$ we also obtained seven ES minima: $^3\text{MLCT}_{\text{bpy}}(1-4)$, ^3MC , ^3LC and $^3\text{MLCT}_{\text{CO}}/^3\text{MC}$ (see Figure S1). Five ($^3\text{MLCT}_{\text{bpy}}(1-3)$, ^3MC and ^3LC) out of the seven ES minima are analogous to those of $\text{W}(\text{CO})_4(\text{bpy})$. Conversely, for $\text{Mo}(\text{CO})_4(\text{bpy})$, the $^3\text{MLCT}_{\text{CO}}$ state is mixed with a ^3MC state (see the orbitals involved in Figure S1) and the ES minima of two different asymmetric $^3\text{MLCT}_{\text{bpy}}$ states were found ($^3\text{MLCT}_{\text{bpy}}(1-3)$). We recall that only one was found for $\text{W}(\text{CO})_4(\text{bpy})$.

Table 1. Emission Maxima for $\text{M}(\text{CO})_4(\text{bpy})$ Complexes in Benzene at 298 K.^a

	HE band	LE band
$\text{W}(\text{CO})_4(\text{bpy})$	17030	12970
$\text{Mo}(\text{CO})_4(\text{bpy})$	17300	12940

^aFrom ref. 20

Table 2. Computed adiabatic relative energies for the different ES minima (with respect to the ¹GS minimum, in eV); TD-DFT, Δ SCF-DFT and Δ SCF-DLPNO-CCSD(T) emission energies (in cm⁻¹); and computed phosphorescence rates from selected ES minima (in s⁻¹).

W(CO)₄(bpy)	TD-DFT (UDFT) Relative Energies [eV] ^a	TD-DFT (PCM-TD- DFT) emission energy [cm ⁻¹]	Δ SCF-DFT (PCM- Δ SCF- DFT) emission energy [cm ⁻¹]	Δ SCF-DLPNO- CCSD(T) (solv)emission energy [cm ⁻¹]	k_r [s ⁻¹]
³ MLCT _{bpy} (1)	1.29 (1.61)	8756 (10693)	10934 (12010)	7990 (9066)	8.92×10 ³
³ MLCT _{bpy} (2)	1.47 (1.68)	9859 (11604)	10661 (11723)	8103 (9166)	1.21×10 ⁴
³ MLCT _{bpy} (3)	2.27	16002 (18243)	-	-	3.12×10 ⁴
³ MC	1.69 (2.23)	-2930 (-2445)	2331(2808)	-	-
³ LC	2.75	19077(19000)	-	-	2.70×10 ²
³ MLCT _{CO}	3.00	22339 (20818)	-	-	-
³ MLCT _{bpy} (4)	4.16	32883 (32107)	-	-	-
Mo(CO)₄(bpy)					
³ MLCT _{bpy} (1)	1.41 (1.74)	9521 (11499)	11043 (12036)	9172 (10164)	-
³ MLCT _{bpy} (2)	1.56 (1.82)	10394(12210)	11704 (12713)	9207 (10217)	-
³ MLCT _{bpy} (3)	2.38	16885(19153)	-	-	-
³ MLCT _{bpy} (4)	2.51	17984 (19890)		-	-
³ MC	1.72	-2645 (-2165)	-	-	-
³ LC	2.74	18858 (18839)	-	-	-
³ MLCT _{CO} / ³ MC	2.78	18831 (18898)	-	-	-

The seven TD-DFT optimized geometries served as initial guesses for subsequent UDFT optimizations (see computational details in the SI). With the latter computational protocol, for $\text{W(CO)}_4(\text{bpy})$ only three (i.e., $^3\text{MLCT}_{\text{bpy}}(1)$, $^3\text{MLCT}_{\text{bpy}}(2)$ and ^3MC) out of the seven triplet states converged into their original triplet ESs. Conversely, the optimizations starting from the other four higher-lying states ended up in lower-lying ES minima due to the variational collapse of the wavefunction at the UDFT level. In the case of $\text{Mo(CO)}_4(\text{bpy})$, only the re-optimizations for the $^3\text{MLCT}_{\text{bpy}}(1)$ and $^3\text{MLCT}_{\text{bpy}}(2)$ states were successful. Similar geometric features are observed between the TD-DFT and UDFT optimized geometries (see Figures S2-S3 for comparisons). Thus, the analysis of these results hints that $^3\text{MLCT}_{\text{bpy}}(1)$, $^3\text{MLCT}_{\text{bpy}}(2)$ and ^3MC are true minima in the lowest adiabatic triplet PES, at least for $\text{W(CO)}_4(\text{bpy})$, while the other minima belong to higher-lying triplet PESs. In Table 2 we collect the computed i) adiabatic relative energies between all the states, ii) the emission energies from all possible triplet ES minima for $\text{W(CO)}_4(\text{bpy})$ and $\text{Mo(CO)}_4(\text{bpy})$ and iii) the computed radiative rates for selected ES minima. The radiative rates have been computed with quadratic response (QR)-TD-DFT calculation (see details in the SI). The adiabatic relative energies further confirm that $^3\text{MLCT}_{\text{bpy}}(1)$ and $^3\text{MLCT}_{\text{bpy}}(2)$ are the lowest-lying triplet ESs. They are adiabatically located within 0.07 and 0.08 eV (see UDFT values in Table 2), so that both states are likely thermally-equilibrated at room temperature. In Table 2 are also collected both the gas phase and solvent corrected i) TD-DFT emission energies for all possible emitting states; ii) $\Delta\text{SCF-DFT}$ emission energies for the $^3\text{MLCT}_{\text{bpy}}(1)$, $^3\text{MLCT}_{\text{bpy}}(2)$ and ^3MC states. The variational collapse of the wavefunction for the other four states refrain us to compute their $\Delta\text{SCF-DFT}$ emission energies. An inspection of the computed emission energies reveals that the ^3MC is not responsible for any of the experimentally observed emission bands simply because the computed values are too low (see e.g., the PCM-

Δ SCF-DFT values of 2808 cm⁻¹ for W(CO)₄(bpy)). Indeed, ³MC states are generally believed not to be involved in emission processes. Instead, they play an important role in non-radiative deactivation mechanisms,³¹ mediated *via* ³MC/¹GS minimum energy crossing points.^{32,33} Therefore, in view of the computed values, the states responsible for the LE band are the lowest-lying ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) states. Very similar PCM- Δ SCF-DFT emission energies are computed for these two states, compare e.g., 12010 and 11723 cm⁻¹ for the ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) states of W(CO)₄(bpy); values which are in good agreement with the LE band maximum (12970 cm⁻¹). Conversely, the computed PCM-TD-DFT values are slightly underestimated with respect to the PCM- Δ SCF-DFT values and the experimental values. Further theoretical insights towards unambiguously assigning the LE band are presented in the following. More in details, single point singlet and triplet DLPNO-CCSD(T)/CBS calculations on the ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) optimized geometries were performed (see the computed energy values in Table 2 and the computational details in the SI). The DLPNO-CCSD(T) method is considered to be the gold-standard method for transition metal complexes,³⁴ and has shown to yield accurate results provided the investigated systems lack of multireference character.³⁵ Our DLPNO-CCSD(T)/CBS emission energies are slightly underestimated with respect to the experimental values but also point to both ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) to be responsible for the LE band for both complexes. Besides the energetic criteria discussed above, the radiative rates computed at the latter ES minima should be of the same order of magnitude to make the thermally-equilibrated dual emission scenario feasible. Indeed, the computed rates at the ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) minima are 8.92×10³ and 1.21×10⁴ s⁻¹, respectively; and thus, they corroborate this hypothesis. In a nutshell, the emissions from the ³MLCT_{bpy}(1) and ³MLCT_{bpy}(2) states overlap and result in a single band in the experimental spectra, but indeed

two different lifetimes are experimentally measured for the LE band; which are likely due to the slight differences between their radiative decay rates.

We now turn the discussion to the assignment of the HE band. As discussed above, previous investigations hypothesized the ^3MC and $^3\text{MLCT}_{\text{CO}}$ to be responsible for this band. Instead, in view of our computed adiabatic relative energies and the PCM-TD-DFT emission energy values the $^3\text{MLCT}_{\text{bpy}}(3)$ state is likely responsible for the HE band (compare e.g., the computed emission maxima of 18243 and 19153 cm^{-1} with the experimental values of 17030 and 17300 cm^{-1} for $\text{W}(\text{CO})_4(\text{bpy})$ and $\text{Mo}(\text{CO})_4(\text{bpy})$; respectively). Other possible emissive states (i.e., $^3\text{MLCT}_{\text{CO}}$, $^3\text{MLCT}_{\text{CO}}/^3\text{MC}$, ^3LC and $^3\text{MLCT}_{\text{bpy}}(4)$) are in principle ruled out since they are adiabatically located above $^3\text{MLCT}_{\text{bpy}}(3)$ (see their relative energies in Table 2) but also in view of their larger computed emission energies (in most of the cases). In addition, we also computed the radiative rates from the first two higher-lying emissive states of $\text{W}(\text{CO})_4(\text{bpy})$ (i.e., $^3\text{MLCT}_{\text{bpy}}(3)$ and ^3LC). $^3\text{MLCT}_{\text{bpy}}(3)$ yielded the largest k_r value among all possible ES minima ($3.12 \times 10^4 \text{ s}^{-1}$), while the k_r value for the ^3LC state is rather small (2.70×10^2), as one might could have expected due to negligible spin-orbit coupling (SOC) contributions to the decay rate for ligand-based ES. In a nutshell, both the energetic and kinetic criteria further support the assignment of the $^3\text{MLCT}_{\text{bpy}}(3)$ state as being responsible for the HE band. Indeed, experimentally the HE emission is very short-lived,³⁰ a fact which is in agreement with the computed fast radiative deactivation. For the phenanthroline-based $\text{W}(\text{CO})_4(\text{phen})$ and $\text{W}(\text{CO})_4(\text{tmp})$ complexes, time-resolved experiments concluded that the HE likely originates in several radiative transitions.²⁵ However, in the case of our bpy complexes this option appears less plausible in view of the computed evidences; since only one triplet ES minimum was obtained in the 2.2-2.4 eV energy window, i.e., $^3\text{MLCT}_{\text{bpy}}(3)$ state. In a nutshell, these theoretical

investigations highlight that the breaking of Kasha's rule in $[\text{M}(\text{CO})_4(\text{bpy})]$ complexes is at least two-fold, because two different excited states besides T_1 are involved in emission.

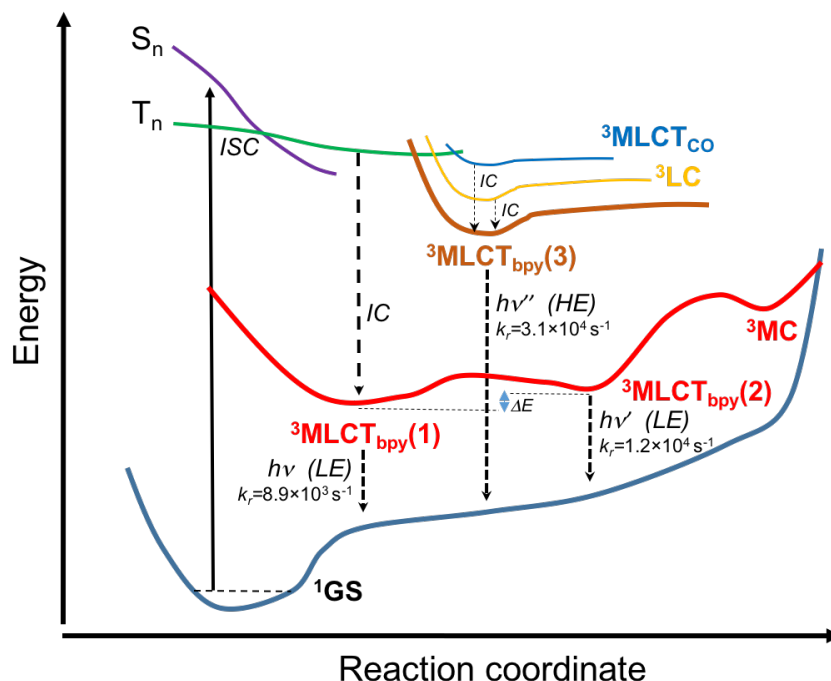


Figure 2. Schematic Jablonski diagram for $[\text{W}(\text{CO})_4(\text{bpy})]$

In the following we discuss the likely origins for the anti-Kasha emissions observed in $[\text{W}(\text{CO})_4(\text{bpy})]$ and $[\text{Mo}(\text{CO})_4(\text{bpy})]$. Exemplarily, the schematic Jablonski diagram displaying all possible triplet ES minima for $[\text{W}(\text{CO})_4(\text{bpy})]$ is shown in Figure 2. Note that $^3\text{MLCT}_{\text{bpy}}(4)$ is disregarded in view of its large adiabatic relative energy (>4.0 eV) and thus, it will likely not be populated under the experimental conditions. The lowest adiabatic triplet PES is depicted in red. Upon excitation of the manifold of singlet ES (S_n) relatively fast ISC processes populating the manifold of triplet ESs (T_n) occur. From there two possibilities arise: i) population of the lowest adiabatic triplet PES through IC processes and ii) population of the wells of different higher-lying triplet ES (i.e., $^3\text{MLCT}_{\text{bpy}}(3)$; ^3LC and $^3\text{MLCT}_{\text{CO}}$ in the case of $[\text{W}(\text{CO})_4(\text{bpy})]$). The large

adiabatic energy gaps between these three states and the lowest triplet ES (of ca. >0.8 eV, see Table 2) are responsible for slowing down the IC processes to the lowest triplet ES. Therefore, emission of a photon from $^3\text{MLCT}_{\text{bpy}}(3)$, which is the lowest adiabatic state in the high-energy window, is competitive with IC, leading to the HE band (see Figure 2). Note that for this band, emissions arising from the ^3LC and $^3\text{MLCT}_{\text{CO}}$ are less plausible due to their smaller (but non-negligible) energy gaps with $^3\text{MLCT}_{\text{bpy}}(3)$, which on the one hand side promote fast IC processes to $^3\text{MLCT}_{\text{bpy}}(3)$, and on the other hand side prevent that those triplet ES will be thermally equilibrated with $^3\text{MLCT}_{\text{bpy}}(3)$; but also due to their smaller k_r values. $[\text{Mo}(\text{CO})_4(\text{bpy})]$ shows very similar features, differing only in the character of some of the higher-lying ESs; so that the above discussion is also valid for this complex. The above discussed HE emission can be catalogued as a non-thermally equilibrated anti-Kasha scenario. This scenario also explains the experimentally observed excitation wavelength-dependent emissive characteristics of $[\text{M}(\text{CO})_4(\text{bpy})]$ complexes. Besides these “hot” photoemissions, some of the ES population will decay to the lowest adiabatic triplet PES through IC, from where emission from the $^3\text{MLCT}_{\text{bpy}}(1)$ and $^3\text{MLCT}_{\text{bpy}}(2)$ states will occur, leading to the LE band. Dual emission from the $^3\text{MLCT}_{\text{bpy}}(1)$ and $^3\text{MLCT}_{\text{bpy}}(2)$ states is feasible due to i) the small energy gap between these states ($\Delta E < 0.08$ eV), so that these states are thermally equilibrated at room temperature and ii) the rather similar radiative decay rates from both states. Therefore, this second anti-Kasha scenario corresponds to a thermally-equilibrated one. In a nutshell, $[\text{M}(\text{CO})_4(\text{bpy})]$ ($\text{M} = \text{Mo}, \text{W}$) complexes are demonstrated to display both equilibrated and non-equilibrated anti-Kasha emissions. To complete their complex photoreactivity, we note that other triplet ES besides the emissive states might be populated on the course of photodeactivation. These alternative “hot” photoreactivity channels might be involved e.g., in the nonradiative deactivation to the ^1GS (through e.g., the

^3MC state, see Figure 2) or in the experimentally observed excitation wavelength-dependent photochemical substitution of an axial CO ligand (through e.g., the population of the $^3\text{MLCT}_{\text{CO}}$ state and/or other possible dissociative states). To conclude, despite their apparent structural simplicity, $[\text{M}(\text{CO})_4(\text{bpy})]$ ($\text{M} = \text{Mo}, \text{W}$) complexes possess rich and chameleonic photochemical properties, which make them the ideal case studies for in-depth theoretical investigations. In this contribution, the triplet ES PES of these complexes have been explored with high-level *ab initio* coupled-cluster and TD-DFT calculations. Our investigations have helped to unambiguously unravel the origins of their complex emissive characteristics. These studies highlight that in the $[\text{M}(\text{CO})_4(\text{bpy})]$ series, the breaking of Kasha's rule is at least two-fold. Hence, different anti-Kasha scenarios (equilibrated vs non-equilibrated ones) are demonstrated to simultaneously coexist. Thus, to our knowledge, these are the first transition metal complexes unambiguously demonstrated to display simultaneous equilibrated and non-equilibrated anti-Kasha emissions, besides the Kasha-like emission from T_1 . This work also highlights the complexity of the photodeactivation channels in transition metal complexes and it contributes to put on firmer grounds anti-Kasha events, which are still a matter of debate in the community partially due to the lack of in-depth experimental photochemical investigations performed on a routine basis (e.g., excitation wavelength- and temperature-dependent emission experiments). From a theoretical viewpoint, we remark the capability of UDFT and TD-DFT methods to studying complex emissive scenarios involving not only the lowest adiabatic triplet ES (accessible with UDFT) but also higher-lying ESs (accessible with TD-DFT). Due to the increasing number of reported violations of Kasha rule in the literature, it also raises an urgent debate in the theoretical inorganic photochemistry community on the need to exhaustively explore higher-lying ES PES in a routine basis to model emissive processes. Currently, the common strategy in the community

consists of optimizing only the geometry of T_1 , from where Kasha-like emission is always believed to take place. As shown here, this latter strategy is not appropriate in complex photochemical scenarios, such as those of e.g., $[M(CO)_4(bpy)]$ complexes, but also in the case that the lowest ES is a dark state.³⁶

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge. Computational details, Figures S1-S3 and the cartesian coordinates of all optimized structures.

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