

A TDDFT description of the low-energy excited states of copper and zinc metalloenediynes†

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Time-dependent density functional theory shows that the photoreactivities of copper and zinc metalloenediynes derive from multi-configurational excited states involving the enediyne and pyridine π systems.

Photo-Bergman cyclization of enediynes has considerable potential in optical polymerization¹ and biomedical applications² due to the ability to photo-generate reactive radical intermediates. Indeed, enediynes have been shown to have several reactive excited state pathways at high energy. These include (i) alkyne-localized $\pi\pi^*$ states that promote in-plane geometric distortion and lead to the *para*-benzynes intermediate; (ii) ene localized states that cause either an out-of-plane geometric distortion *via* rotation about the double bond, leading to *cis*–*trans* isomerization, or localization of unpaired electron density at the alkyne termini, promoting photoreduction of an alkyne unit.^{3,4} The desire for lower energy routes to photo-Bergman cyclization has sparked interest in designing structures with extended chromophores,⁵ or alternative strategies such as pH-sensitive triggers,⁶ and photochemically generated thermal reactants to initiate Bergman cyclization.⁷

Recently, photo-Bergman cyclization of copper metalloenediynes has been shown to occur *via* metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge transfer excited states that serve as conduits to reactive enediyne-centered electronic configurations.⁸ Photolysis ($\lambda \geq 395$ nm) of d^{10} [Cu(bpod)₂]⁺ (bpod = 1,8-bis(pyridine-3-oxy)oct-4-ene-2,6-diyne) or its d^9 Cu(II) analogue results in ~ 50% yield of Bergman cyclized product. In contrast, direct photolysis ($\lambda \geq 395$ nm) of either the free bpod ligand or the d^{10} Zn(II) complex results in no reactivity, whereas triplet sensitization of the Zn(II) complex results in *cis*–*trans* isomerized product.^{3,9}

To understand this type of rare photoreaction, we have employed time-dependent density functional theory (TDDFT) to study the geometric and electronic structures of bpod (1), Cu(bpod)NH₃Cl (2), Cu(bpod)Cl₂ (3), and Zn(bpod)Cl₂ (4) model systems (Fig. 1). Geometries of 1–4 were optimized

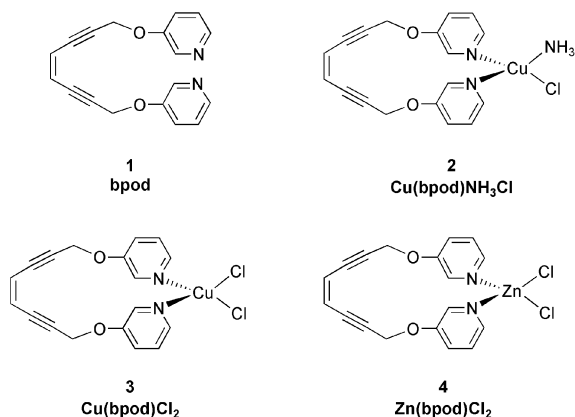


Fig. 1 Representative structures of 1–4.

† Electronic supplementary information (ESI) available: Cartesian coordinates of optimized structures and tables of the TDDFT configurations for each excited state. See <http://www.rsc.org/suppdata/cc/b3/b308633j/>

using the (U)B3LYP density functionals with Gaussian 98.¹⁰ The 6-31G* basis was used for C, H, N, and O, while the LANL2 pseudopotential with the LANL2DZ basis was applied to Cl, Cu, and Zn. Time-dependent (U)B3LYP calculations of the first 20 excited states of 1–4 were performed with the same functionals/basis at the optimized geometries.†

The optimized ground state structure of 1 has an alkyne termini separation of 4.59 Å, which large, but in the range expected for acyclic enediynes.⁵ Metalloenediynes 2–4 have pseudo-tetrahedral geometries consistent with the d^9 *cis*-CuN₂Cl₂ core and the d^{10} electronic configurations of Cu(I) and Zn(II).^{11,12} As a consequence, their alkyne termini separations do not deviate significantly from that of the free ligand.

The wave functions of the excited states of 1–4 are presented as superpositions of excitations (configurations) within the ground state orbital manifold. Examples of the orbitals that compose the dominant configurations of select excited states of 2 and 3 are illustrated in Fig. 2, while the excited state energies and the respective percent contributions of the dominant

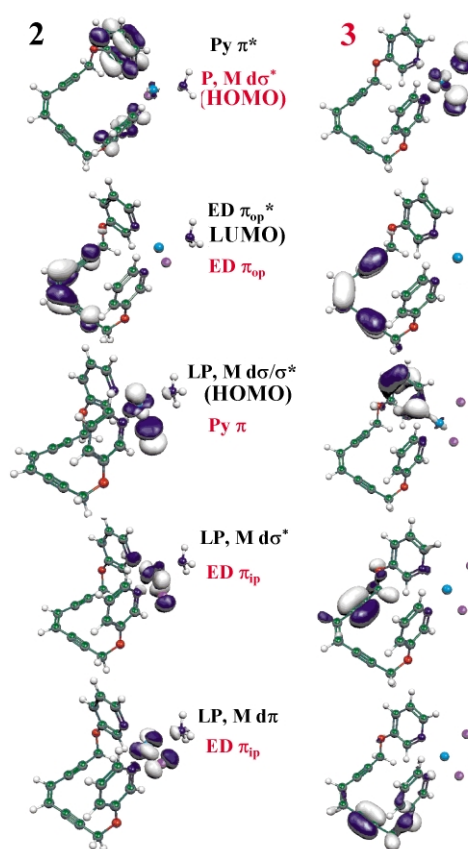


Fig. 2 Subset of (U)B3LYP molecular orbitals of Cu(bpod)NH₃Cl (2) (#92–96) and Cu(bpod)Cl₂ (3) (#74–75, 78, 80, 93) that contribute to the electronic transitions of each complex. The character of the molecular orbitals is presented in black (for 2, left) and red (for 3, right). Atom designations: carbon (green), oxygen (red), nitrogen (blue), copper (teal), chloride (purple).

configurations (the squares of the configuration coefficients) are presented in Table 1. The energy difference between some of the π orbitals is small (< 1 kcal mol⁻¹) and therefore detailed interpretation of the frontier orbital energies is inappropriate. The electronic structure of **1** is very similar to that of the simplest enediyne, *cis*-1,5-hexadiene-3-ene (1,5-hd), but with additional electronic transitions between the pyridine and enediyne π systems. The lowest energy excited state of **1** is an ene-localized $^3\pi\pi^*$ state (2.36 eV) that is known to lead to *cis*-*trans* isomerization in 1,5-hd. To higher energy (> 3.75 eV) lie the traditional pyridine and alkyne localized $\pi\pi^*$ singlet and triplet states.

Chelation of bpod to either Cu(I) or Cu(II) leads to several low energy (< 3.0 eV) MLCT and LMCT states. In particular, Cu(bpod)NH₃Cl, **2**, exhibits six ¹MLCT states between 2.35 and 3.0 eV that are composed of two distinct configurations. These are represented as transitions from the metal *d* orbitals to the lowest energy π^* orbitals of the enediyne (ED π_{op}^*) and pyridine (Py π^*) frameworks (Fig. 2, left). In the case of Cu(bpod)Cl₂, **3**, several multi-configurational LMCT states are observed between 2.24 and 3.26 eV that are the result of excitations from the highest occupied enediyne (ED π_{ip} , π_{op}) and pyridine π (Py π) orbitals to the singly occupied Cu *d* HOMO (Fig. 2, right).

The TDDFT description of the excited states of Zn(bpod)Cl₂, **4**, reveals mainly ligand-localized states that are very similar to those of uncomplexed **1**, as evidenced by a parallel, low-energy enediyne $^3\pi\pi^*$ state at 2.35 eV and its pyridine counterpart at 3.63 eV (Table 1). Due to the poor energetic overlap between the Zn(II) *d* orbitals and the pyridine σ or π orbitals, **4** exhibits no low energy charge transfer states. The TDDFT results are consistent with the reactivity of a [Zn(bpod)₂]²⁺ which undergoes *cis*-*trans* isomerization of the bpod ligand upon triplet photosensitization. Thus, population of an ene-localized

$^3\pi\pi^*$ state on the enediyne facilitates reactivity that parallels that of acyclic organic enediynes.

How then, do charge transfer excited states of **2** and **3** lead to photochemical Bergman cyclization? The multi-configurational nature of the charge transfer excited states of **2** and **3** indicate that the photoexcitations are, in general, distributed over both the pyridine π and the enediyne π moieties, despite the lack of direct orbital overlap between the metal and enediyne π system. Thus, absorption into these excited states is facilitated by the strong spatial and energetic overlap between the pyridine π and metal *d* orbitals. In **2**, the MLCT states populate the lowest energy unoccupied ED π_{op}^* orbital on the vinyl unit. The charge transfer character of the excitation in **2** leads to an approximate bond order of 1.5 about the ene unit, while $^3\pi\pi^*$ diyl excitation in 1,5-hd reduces the π bond completely and leads to *cis*-*trans* isomerization. In addition, it is unlikely that the terminal alkyne carbons obtain excess unpaired electron density in this excited state since charge transfer essentially delocalizes only one electron onto the enediyne ligand, reducing the potential for photoreduction products.

A similar TDDFT description of the excited states of **3** is observed. Here, several LMCT states result from a superposition of configurations that represent ED π_{ip} , π_{op} and Py π -to-metal *d* excitation. Thus, the highest occupied enediyne π orbitals (mainly π_{op}) are depopulated, which decreases the overall π bond order at both the -ene and -yne units. The net photoreactivity is expected to be similar to that observed upon MLCT excitation of **2** since the competitive excited state reaction pathways should have higher activation barriers than Bergman cyclization because of the electronic similarities between the excited MLCT or LMCT configuration and the cyclization transition state electronic structure. This description is conceptually parallel to but is distinct from enediyne cyclization along ionic potential surfaces.¹³ In general, these calculations show that metal-ligand charge transfer involving the enediyne π -system, either directly or *via* delocalized excitation as is the case here, is a sufficient trigger to drive Bergman cyclization of metalloenediynes. Overall, the results illustrate the intriguing opportunities available for using metal-ligand charge transfer to electronically initiate diradical formation for photodynamic therapy applications.

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Table 1 Multiplicity, energy, dominant configuration, and % contribution (square of configuration expansion coefficients) of low-energy excited states of **1**-**4**, calculated with TD (U)B3LYP

State	2S + 1	$\Delta E/eV$	Configuration	$\Sigma(C^2 \times 100)$ (%)
bpod (1)				
1	3	2.36	ED $\pi \rightarrow$ ED π^*	58.0
2	3	3.78	PY $\pi \rightarrow$ PY π^*	52.5
4	1	3.88	PY $\pi \rightarrow$ ED π^*	47.1
Cu(bpod)NH₃Cl (2)				
5	1	2.57	<i>d</i> π ,LP \rightarrow ED π^*	48.1
			<i>d</i> π ,LP \rightarrow PY π^*	1.5
8	1	2.77	<i>d</i> π ,LP \rightarrow ED π^*	46.0
			<i>d</i> π ,LP \rightarrow PY π^*	1.3
14	1	2.95	<i>d</i> π ,LP \rightarrow ED π^*	10.8
			<i>d</i> π ,LP \rightarrow PY π^*	33.8
Cu(bpod)Cl₂ (3)^a				
6	2	2.08	ED $\pi \rightarrow$ <i>d</i> π , Cl LP	16.5
			PY $\pi \rightarrow$ <i>d</i> π , Cl LP	16.4
			<i>d</i> \rightarrow <i>d</i>	61.5
7	2	2.24	PY $\pi \rightarrow$ <i>d</i> π , Cl LP	33.8
			<i>d</i> \rightarrow <i>d</i>	14.4
			ED $\pi \rightarrow$ <i>d</i> π , Cl LP	12.8
11	2	2.61	ED $\pi \rightarrow$ <i>d</i> π , Cl LP	11.8
			PY $\pi \rightarrow$ <i>d</i> π , Cl LP	3.9
			ED+PY $\pi \rightarrow$ <i>d</i> π , LP	51.3
Zn(bpod)Cl₂ (4)				
1	3	2.35	ED $\pi \rightarrow$ ED π^*	64.7
2	3	3.63	PY $\pi \rightarrow$ PY π^*	48.1
6	1	4.06	Cl LP \rightarrow ED π^*	46.0

^a Pure *d*-*d* transitions omitted for clarity.

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