

# The Dog That Didn't Bark: A New Interpretation of Hypso porphyrin Spectra and the Question of Hypso corroles

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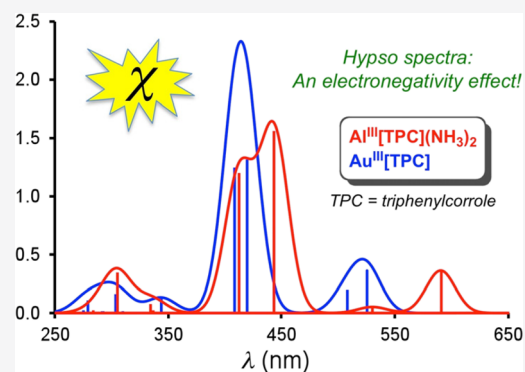


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**ABSTRACT:** Nearly a half-century after Gouterman classified the UV–vis–NIR spectra of porphyrin derivatives as normal, hyper, or hypso, we propose a heretofore unsuspected “mechanism” underlying hypso spectra. Hypso porphyrins, which exhibit blueshifted optical spectra relative to normal porphyrins (such as Zn porphyrins), typically involve  $d^n$  transition metal ions, where  $n > 6$ . The spectral blueshifts have been traditionally ascribed to elevated porphyrin  $e_g$  LUMO (lowest unoccupied molecular orbital) energy levels as a result of antibonding interactions with metal  $d_\pi$  orbitals. Herein, we have found instead that the blueshifts reflect a lowering of the  $a_{2u}$  HOMO (highest occupied molecular orbital) energy levels. Electronegative metals such as Pd and Pt transfer smaller quantities of electron density to the porphyrin nitrogens, compared to a more electropositive metal such as Zn. With large amplitudes at the porphyrin nitrogens, the  $a_{2u}$  HOMOs of Pd(II) and Pt(II) porphyrins accordingly exhibit lower orbital energies than those of Zn(II) porphyrins, thus explaining the hypso effect. Hypso spectra are also observed for corroles: compared with six-coordinate Al(III) corroles, which may be thought of exhibiting normal spectra, Au(III) corroles, for instance, exhibit blueshifted or hypso spectra.



## 1. INTRODUCTION

The famous four-orbital model,<sup>1,2</sup> which explained the electronic absorption spectra of simple porphyrins, was devised

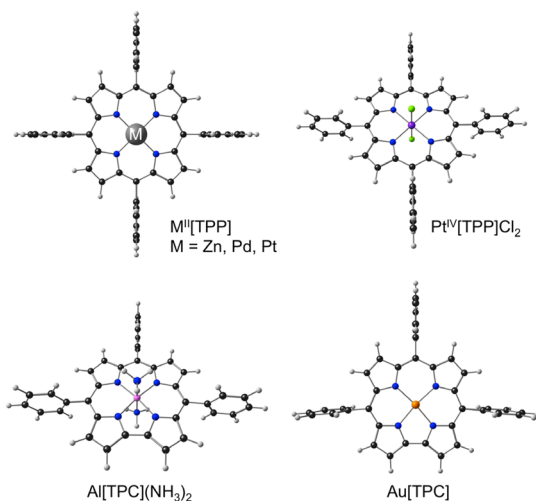


Figure 1. Molecules studied in this work.

by Gouterman in the early 1960s, while he was an Assistant Professor at Harvard. According to this model, the two highest occupied molecular orbitals (HOMOs) ( $a_{1u}$  and  $a_{2u}$  under  $D_{4h}$  symmetry) and the two lowest unoccupied molecular orbitals

(LUMOs) ( $e_g$ ) are energetically well-separated from all other occupied and virtual molecular orbitals (MOs). The Q and Soret bands are then explained by transitions between these four MOs, taking configuration interaction into account. Some 15 years later, now on West Coast, he presented an optical taxonomy of porphyrins in a lengthy chapter in Dolphin's multivolume work *The Porphyrins*.<sup>3</sup> He classified porphyrins into three major classes—normal, hypso, and hyper. Normal porphyrins exhibit electronic absorption spectra that can be largely accounted for with the four-orbital model. Hypso porphyrins exhibit blueshifted spectra, typical examples including  $d^n$  metalloporphyrins for  $n > 6$ . In contrast, hyperporphyrins exhibit redshifted optical spectra and/or extra absorption bands above 300 nm. Typical examples include  $d^n$  metalloporphyrins with  $n < 6$ , which in turn include many heme proteins and their intermediates and model compounds. Substituents and other structural perturbations can also lead to hyper spectra.<sup>4</sup>

Many, but not all, hypso porphyrins, especially the noble metal porphyrins, are moderately to strongly phosphorescent.<sup>5–7</sup> Their long-lived triplet states have been exploited for oxygen

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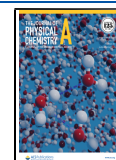


Table 1. Comparison of TDDFT and Experimental Absorption Maxima (nm)<sup>a</sup>

compound	Q (nm)					Soret (nm)					HOMO–LUMO gap (eV)			
	OLYP	B3LYP	B3LYP*	CAMY-B3LYP	Expt	OLYP	B3LYP	B3LYP*	CAMY-B3LYP	Expt	OLYP	B3LYP	B3LYP*	CAMY-B3LYP
Zn[TPP]	564.3	531.2	542.0	540.4	589	454.3	432.6	441.8	424.8	425	1.94	2.90	2.63	4.42
Pd[TPP]	534.9	507.0	515.6	512.7	554	445.6	422.1	430.7	412.2	418	2.09	3.04	2.78	4.58
Pt[TPP]	519.7	493.7	500.2	494.5	539	437.5	413.2	420.7	400.3	493	2.19	3.14	2.89	4.68
Pt[TPP]Cl <sub>2</sub>	673.1	600.3	583.2	523.3	570	445.7	423.8	431.4	414.8	421	1.81	2.87	2.72	4.50
	544.0	516.3	524.5	516.5										
Au[TPC]	554.4	525.9	534.6	530.3	575	449.4	419.4	429.8	408.1	418	1.85	2.75	2.51	4.26
	537.8	508.3	516.7	507.4	560	441.2	408.4	418.5	391.8					
Al[TPC](NH <sub>3</sub> ) <sub>2</sub>	631.7	590.7	607.6	600.7	620	471.8	443.4	455.9	436.4	432	1.55	2.46	2.20	3.94
	570.9	530.4	544.2	528.1	582	445.4	413.0	424.3	398.0	412				

<sup>a</sup>The experimental data quoted are obtained from refs 40–44.

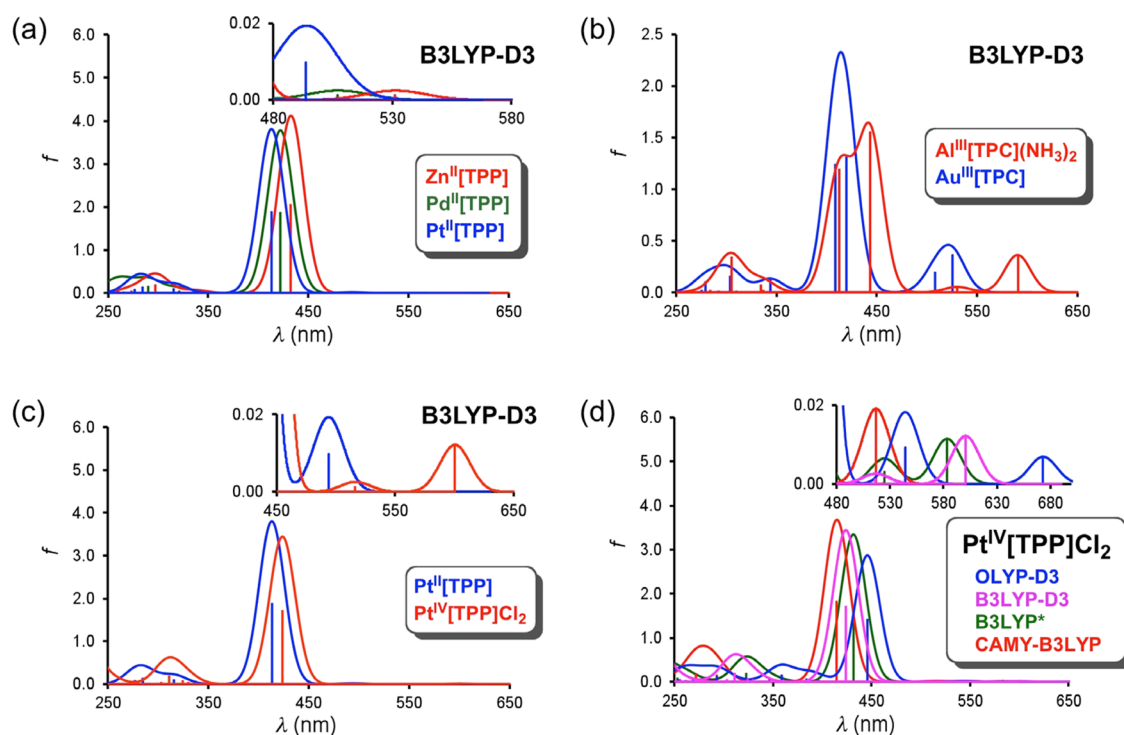


Figure 2. TDDFT (COSMO/dichloromethane) simulated spectra of the metalloporphyrins studied.

sensing and photodynamic therapy.<sup>8–12</sup> Gouterman and co-workers famously exploited platinum(II) porphyrins to devise pressure-sensitive paints for airplane wings.<sup>13–16</sup> More recently, Sd metallocorroles,<sup>17–21</sup> including ReO,<sup>22–24</sup> OsN,<sup>25,26</sup> Ir,<sup>27–29</sup> Pt,<sup>30,31</sup> and Au<sup>20,32–35</sup> corroles, have been found to exhibit NIR phosphorescence under ambient conditions, raising the question whether they, or at least some of them, should be described as hypso-corroles.

Remarkably, in spite of their broad importance, few hypso and hyper spectra have been examined by means of modern quantum chemical methods, such as time-dependent density functional theory (TDDFT) calculations,<sup>36–38</sup> which prompted us to undertake a first such investigation of selected hypso-porphyrin systems. Thus, we examined several M<sup>II</sup>[TPP] derivatives (where M = Zn,<sup>39,40</sup> Pd,<sup>41</sup> and Pt<sup>41</sup>), Pt<sup>IV</sup>[TPP]Cl<sub>2</sub>,<sup>42</sup> and two corroles, Al<sup>III</sup>[TPC](NH<sub>3</sub>)<sub>2</sub><sup>43</sup> and Au<sup>III</sup>[TPC]<sup>34</sup> (Figure 1). Of these, only Pd<sup>II</sup>[TPP] and Pt<sup>II</sup>[TPP] are clearly hypso-porphyrins, while Au[TPC] is a potential hypso-corrole. The other complexes are included for comparison.

The hypso effect has traditionally been explained in terms of metal(*d<sub>π</sub>*)–porphyrin(LUMO) orbital interactions.<sup>3</sup> By engaging in backbonding interactions with the porphyrin e<sub>g</sub> LUMOs, the *d<sub>xz</sub>* and *d<sub>yz</sub>* orbitals are stabilized. The corresponding antibonding MOs, that is, the LUMOs, the theory goes, are destabilized, which results in an elevated HOMO–LUMO gap, explaining the hypsochromic shifts of the Q and Soret bands. To our surprise, the present reinvestigation provided no support whatsoever for this long-held picture, suggesting instead an entirely different “mechanism” underlying hypso spectra.

## 2. COMPUTATIONAL METHODS

All calculations were carried out with the ADF<sup>44</sup> 2018 program with all-electron ZORA-STO-TZ2P basis sets, fine meshes for numerical integration of matrix elements, and adequately tight convergence criteria for both SCF and geometry optimization cycles. Molecular geometries were optimized with OLYP<sup>45,46</sup>-D3,<sup>47</sup> with *D*<sub>4h</sub> and *C*<sub>2v</sub> symmetry constraints for the porphyrin and corrole derivatives, respectively. These optimized geo-

**Table 2.** B3LYP-D3/STO-TZ2P TDDFT Results, Including Transition Energies ( $E$ ) and Wavelengths ( $\lambda$ ), Oscillator Strengths ( $f$ ), MO Compositions, and Symmetries

molecule	peak	$E$ (eV)	$\lambda$ (nm)	$f$	MO composition		weight (%)	state symmetry
					from	to		
Zn[TPP]	Q	2.33	531.2	0.001	HOMO	LUMO	55	$E_u$
					HOMO - 1	LUMO	45	$E_u$
Pd[TPP]	Soret	2.87	432.6	2.061	HOMO - 1	LUMO	54	$E_u$
					HOMO	LUMO	49	$E_u$
	Q	2.45	507.0	0.001	HOMO - 1	LUMO	50	$E_u$
					HOMO	LUMO	49	$E_u$
Pt[TPP]	Soret	2.94	422.1	1.891	HOMO	LUMO	49	$E_u$
					HOMO - 1	LUMO	49	$E_u$
	Q	2.51	493.7	0.010	HOMO - 1	LUMO	55	$E_u$
					HOMO	LUMO	44	$E_u$
Pt[TPP]Cl <sub>2</sub>	Q	2.07	600.3	0.012	HOMO	LUMO	100	$A_{2u}$
					HOMO	LUMO + 1	55	$E_u$
	Soret	2.93	423.8	1.722	HOMO - 1	LUMO + 1	44	$E_u$
					HOMO - 1	LUMO + 1	54	$E_u$
					HOMO	LUMO + 1	42	$E_u$
					HOMO	LUMO + 1	42	$E_u$
Au[TPC]	Q	2.36	525.9	0.362	HOMO	LUMO	88	$B_2$
					HOMO - 1	LUMO + 1	11	$B_2$
					HOMO - 1	LUMO	81	$A_1$
					HOMO	LUMO + 1	18	$A_1$
	Soret	2.96	419.4	1.312	HOMO	LUMO + 1	80	$A_1$
					HOMO - 1	LUMO	17	$A_1$
					HOMO - 1	LUMO + 1	87	$B_2$
					HOMO	LUMO	11	$B_2$
Al[TPC](NH <sub>3</sub> ) <sub>2</sub>	Q	2.10	590.7	0.362	HOMO	LUMO	91	$B_2$
					HOMO - 1	LUMO + 1	8	$B_2$
					HOMO - 1	LUMO	60	$A_1$
					HOMO	LUMO + 1	39	$A_1$
	Soret	2.80	443.4	1.561	HOMO	LUMO + 1	59	$A_1$
					HOMO - 1	LUMO	39	$A_1$
					HOMO - 1	LUMO + 1	91	$B_2$
					HOMO	LUMO	7	$B_2$

metries were then used for TDDFT calculations with the OLYP-D3, B3LYP\* (15% exact exchange), and CAMY-B3LYP<sup>48–50</sup> functionals. B3LYP<sup>51,52</sup>-D3-optimized geometries were used for the TDDFT calculations with the B3LYP functional. The COSMO<sup>53</sup> solvation model (with dichloromethane as the solvent) was used throughout.

### 3. RESULTS AND DISCUSSION

**3.1. Theoretical Model.** We began by examining to what extent TDDFT calculations reproduce known trends in relative positions of the absorption maxima of the compounds studied. As mentioned above, four exchange-correlation functionals were examined—OLYP-D3, B3LYP-D3, B3LYP\*, and CAMY-B3LYP—with solvation (dichloromethane) taken into account with the COSMO model. Table 1 lists calculated and experimental absorption maxima and calculated HOMO–LUMO gaps, while Figure 2 presents selected simulated spectra, mostly from B3LYP-D3 calculations. It is immediately obvious that all the exchange-correlation functionals do a qualitatively good job of reproducing key trends in experimental absorption maxima. Thus, both the Q and Soret bands of Pd<sup>II</sup>[TPP] and Pt<sup>II</sup>[TPP] are hypsochromically shifted relative to those of Zn<sup>II</sup>[TPP], with larger blueshifts for Pt, just as experimentally observed.<sup>39–41</sup> The calculations also predict a substantial spectral blueshift for Au<sup>III</sup>[TPC] relative to Al[TPC](NH<sub>3</sub>)<sub>2</sub>,

mirroring a qualitatively similar blueshift for Au<sup>III</sup>[TPFPC] relative to Al<sup>III</sup>[TPFPC](py)<sub>2</sub>.<sup>33,43</sup> Finally, the calculations predict a spectral redshift for Pt<sup>IV</sup>[TPP]Cl<sub>2</sub> relative to Pt<sup>II</sup>[TPP], again in qualitative accord with experimental results.<sup>41,42</sup>

Interestingly, the lowest-energy Q band of Pt<sup>IV</sup>[TPP]Cl<sub>2</sub> appears to pose a peculiar challenge for some of the functionals. Thus, the calculated lowest-energy transition for this compound (experimental value: 570 nm<sup>42</sup>) is not a true Q band but a HOMO( $a_{2u}$ ) → LUMO( $a_{1g}$ ) transition, where the  $a_{1g}$  LUMO corresponds to the empty  $d_{z^2}$  orbital of the Pt(IV) center. Table 1 shows that while OLYP unduly redshifts this feature, CAMY-B3LYP results in an undue blueshift, whereas B3LYP-D3 and B3LYP\* perform just about right.

**3.2. MO Analysis.** A first step toward understanding the hypsochromic effect is to examine the MO composition of the various calculated spectral features. This information is provided in Table 2 for the B3LYP-D3 functional, while key MOs are depicted in Figure 3 for one of the complexes, Pt<sup>II</sup>[TPP]. To our considerable surprise, we found that the four frontier MOs of all the complexes examined, except Pt<sup>IV</sup>[TPP]Cl<sub>2</sub>, correspond to classic Gouterman MOs, with little or no metal d character. Even for the two corrole derivatives, the four frontier MOs for Au<sup>III</sup>[TPC] (Figure 4) and Al<sup>III</sup>[TPC](NH<sub>3</sub>)<sub>2</sub> look essentially identical. This finding, reminiscent of the Sherlock Holmes story (*Silver Blaze*) about “the dog that didn’t bark in the night-time”,

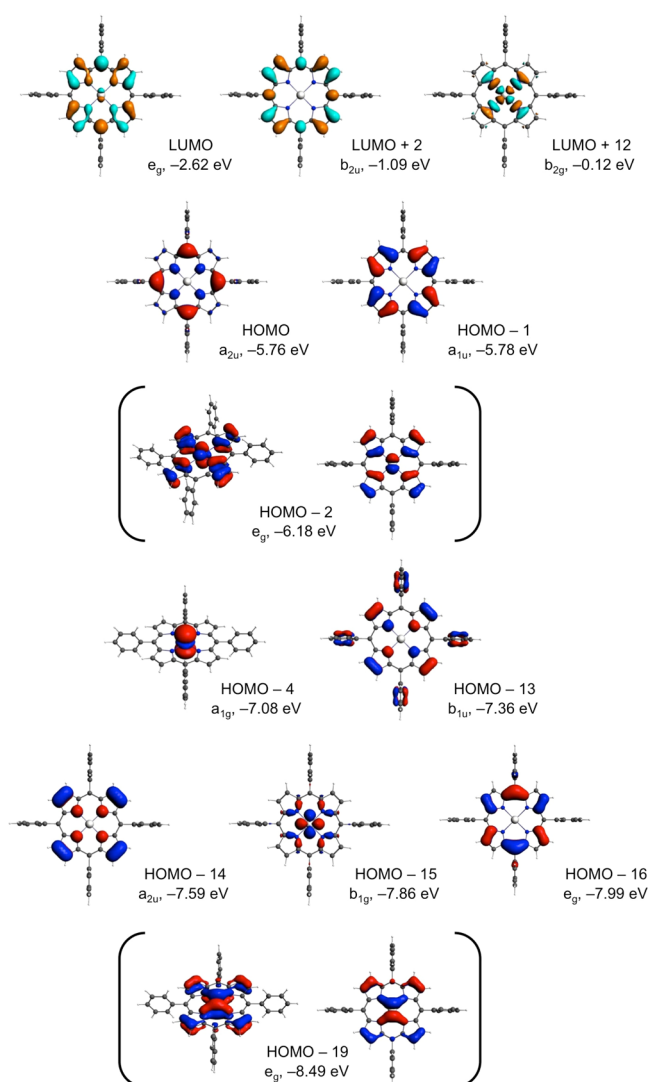


Figure 3. Selected B3LYP-D3 frontier MOs of Pt<sup>II</sup>[TPP].

flies in the face of—and indeed invalidates—the conventional explanation for the hypso-porphyrin effect, namely, that a  $\pi$ -antibonding interaction with the metal  $d_{\pi}$  orbitals is responsible for an elevation of the orbital energies of the  $e_g$  LUMOs.

A comparative study of the frontier MO energy levels (Figures 5 and 6) came to our rescue. While the LUMO energy levels were found to be almost identical across all the porphyrin (or corrole) derivatives studied, the hypso-porphyrins examined exhibit lower orbital energies for the  $a_{2u}$  HOMOs (or for the topologically similar  $b_1$  HOMOs of corroles). This, then, appears to be the new explanation for the hypso-porphyrin effect.

**3.3. Molecular Charge Distributions.** The question as to why hypso-porphyrins such as Pd<sup>II</sup>[TPP] and Pt<sup>II</sup>[TPP], as well as hypso-corroles such as Au<sup>III</sup>[TPC], should exhibit lower “ $a_{2u}$ ” energy levels is a somewhat subtle one, because, as mentioned, there is little difference in the shape of these orbitals relative to those of the normal porphyrin Zn<sup>II</sup>[TPP] [and the normal corrole Al<sup>III</sup>[TPC](NH<sub>3</sub>)<sub>2</sub>]. An examination of the atomic Mulliken and Hirschfeld charges, as well as of the nitrogen 1s orbital energies (Table 3), suggests a plausible explanation. Hypso-porphyrins appear to involve less electropositive metals that transfer less electron density to the porphyrin/corrole ligands as a whole and specifically to the macrocycle nitrogens.

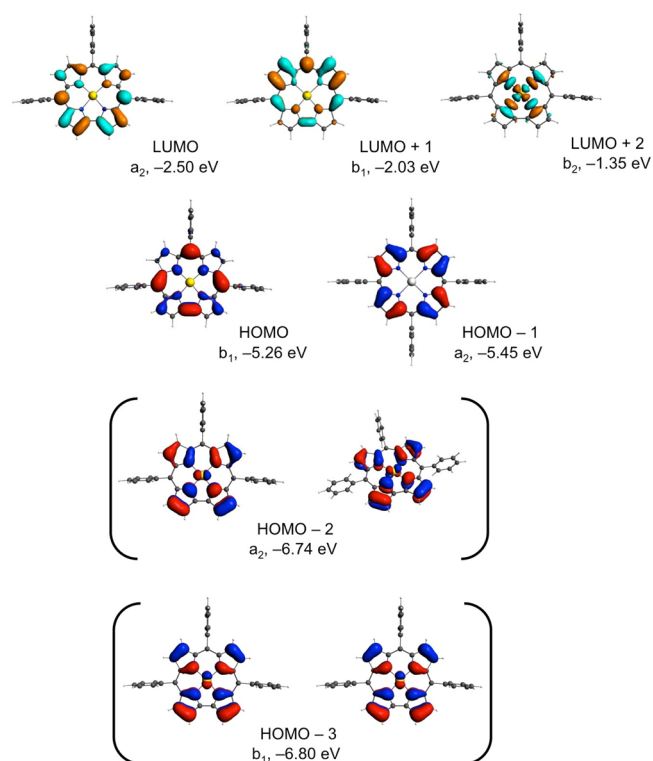


Figure 4. Selected B3LYP-D3 frontier MOs of Au<sup>III</sup>[TPC].

Thus, both the macrocyclic ligands as a whole and their central nitrogens carry less negative Hirschfeld charges in the case of the hypso-porphyrins, relative to the normal porphyrin Zn<sup>II</sup>[TPP]. As a result, the nitrogen 1s orbital energies are also relatively more negative, which would translate to higher XPS ionization potentials, for the hypso-porphyrins. Given that the  $a_{2u}$  HOMO has large amplitudes on the macrocycle nitrogens, it follows that hypso-porphyrins should also exhibit lower  $a_{2u}$  orbital energies, which accounts for the hypso-porphyrin effect.

The above argument might suggest that a Pt(IV) porphyrin would exhibit a stronger hypsochromic shift than a Pt(II) porphyrin. As shown in Table 1, the opposite is observed. A recent, combined X-ray absorption spectroscopy and density functional theory (DFT) study has shown that a Pt(IV) porphyrin entails substantial oxidation of the porphyrin ligand as a whole.<sup>54</sup> That systemic oxidation results in a lowering of not only the  $a_{2u}$  HOMO, but also an even greater lowering of the  $e_g$  LUMOs, which explains the lack of a hypso-porphyrin spectrum for Pt<sup>IV</sup>[TPP]Cl<sub>2</sub>.

#### 4. CONCLUSIONS

DFT and TDDFT calculations indicate that the hypso-porphyrin effect (blueshifted Q and Soret bands) does not result from elevated porphyrin LUMO ( $e_g$ ) energy levels as a result of antibonding interactions with metal  $d_{\pi}$  orbitals. Instead the observed blueshifts reflect a lowering of the  $a_{2u}$  HOMO energy level. Electronegative metals such as Pd and Pt transfer smaller quantities of electron density to the porphyrin nitrogens, compared to a more electropositive metal such as Zn. As a result, the nitrogens in Pd and Pt porphyrins exhibit higher electrostatic potentials, more negative N 1s orbital energies, and higher N 1s ionization potentials. With large amplitudes at the porphyrin nitrogens, the  $a_{2u}$  HOMOs of Pd(II) and Pt(II) porphyrins also exhibit lower orbital energies (mirroring the behavior of the N 1s

Table 3. Selected Mulliken and Hirschfeld Charges and N 1s Orbital Energies (eV) for the Compounds Studied

		Mulliken		Hirschfeld		N 1s energy	
		OLYP	B3LYP-D3	OLYP	B3LYP-D3	OLYP	B3LYP-D3
Zn <sup>II</sup> [TPP]	M	0.815	0.817	0.479	0.481		
	ligand	-0.815	-0.817	-0.479	-0.481		
	N	-0.517	-0.519	-0.160	-0.170	-381.668	-390.126
	C $\alpha$	0.228	0.228	0.024	0.029		
	C $\beta$	0.236	0.190	-0.068	-0.067		
	C $m$	-0.020	-0.034	-0.005	-0.004		
Pd <sup>II</sup> [TPP]	M	0.991	0.901	0.437	0.472		
	ligand	-0.991	-0.901	-0.437	-0.472		
	N	-0.550	-0.547	-0.158	-0.174	-382.396	-390.790
	C $\alpha$	0.221	0.227	0.019	0.024		
	C $\beta$	0.241	0.196	-0.066	-0.065		
	C $m$	-0.016	-0.032	-0.007	-0.006		
Pt <sup>II</sup> [TPP]	M	0.975	0.933	0.249	0.263		
	ligand	-0.975	-0.933	-0.249	-0.263		
	N	-0.582	-0.571	-0.124	-0.138	-382.644	-391.036
	C $\alpha$	0.228	0.226	0.022	0.028		
	C $\beta$	0.247	0.200	-0.065	-0.064		
	C $m$	-0.014	-0.030	-0.005	-0.004		
Pt <sup>IV</sup> [TPP]Cl <sub>2</sub>	M	1.040	1.075	0.510	0.555		
	ligand	-0.355	-0.344	0.072	0.033		
	N	-0.515	-0.513	-0.113	-0.132	-383.100	-391.404
	C $\alpha$	0.250	0.244	0.030	0.035		
	C $\beta$	0.262	0.216	-0.054	-0.053		
	C $m$	-0.016	-0.029	0.000	0.000		
Au <sup>III</sup> [TPC]	M	1.461	1.362	0.551	0.583		
	ligand	-1.461	-1.362	-0.551	-0.583		
	N2	-0.629	-0.607	-0.130	-0.142	-382.740	-391.090
	N1	-0.594	-0.573	-0.136	-0.150	-382.663	-391.089
	C $\alpha$	0.209	0.200	0.012	0.016		
	C $\beta$	0.219	0.182	-0.072	-0.072		
	C $m$	-0.056	-0.068	-0.017	-0.017		
Al <sup>III</sup> [TPC](NH <sub>3</sub> ) <sub>2</sub>	M	1.660	1.640	0.390	0.424		
	ligand	-1.826	-1.817	-0.929	-0.938		
	N2	-0.635	-0.634	-0.155	-0.170	-381.014	-389.439
	N1	-0.548	-0.559	-0.159	-0.175	-381.191	-389.621
	N (NH <sub>3</sub> )	0.237	0.163	-0.167	-0.186	-381.875	-390.341
	C $\alpha$	0.203	0.192	0.016	0.022		
	C $\beta$	0.196	0.157	-0.087	-0.086		
	C $m$	-0.074	-0.072	-0.022	-0.020		

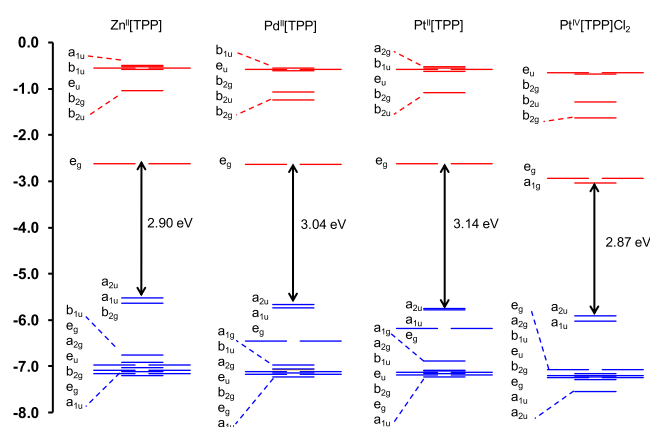


Figure 5. B3LYP-D3 MO energy level diagrams for key TPP derivatives studied.

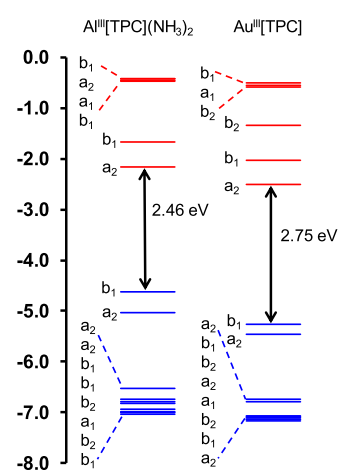


Figure 6. B3LYP-D3 MO energy level diagrams for key TPC derivatives.



orbitals) than Zn(II) porphyrins, thus explaining the hypsochromic spectra.

The hypsochromic concept also appears to extend to corroles. With blueshifted spectral features relative to six-coordinate Al(III) corroles, Au(III) corroles appear to be justifiably described as hypsochromic. It may be recalled that examples hyperchromic, likewise, have also been documented in the literature.<sup>55</sup>

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c08425>.

Optimized Cartesian coordinates (PDF)

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### Notes

The authors declare no competing financial interest.

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