# **Inorganic Chemistry**

# Charge Transfer Properties of Triarylamine Integrated **Dimolybdenum Dyads**

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**S** Supporting Information

ABSTRACT: Three quadruply bonded dimolybdenum complexes equipped with a triarylamine pendant,  $[(DAniF)_3Mo_2(\mu-O_2CC_6H_4N (C_6H_4CH_3)_2$  (DAniF = N,N'-di(p-anisyl) formamidinate; [OO-ph-N]),  $[(DAniF)_{3}Mo_{2}(\mu - OSCC_{6}H_{4}N(C_{6}H_{4}CH_{3})_{2}]$  ([OS-ph-N]), and  $[(DAniF)_{3}Mo_{2}(\mu - S_{2}CC_{6}H_{4}N(C_{6}H_{4}CH_{3})_{2}]$  ([SS-ph-N]), have been synthesized and characterized by single crystal X-ray diffraction. In electrochemical measurements, the redox couple for the organic amine group becomes irreversible, reflecting the substantially strong electronic interaction between the dimetal center and organic redox site. The potential difference for the two successive redox events, ca.  $\Delta E_{1/2}(E_{1/2}(2)(N/N^{\bullet+}) - E_{1/2}(1)(Mo_2^{IV/V}))$ , falls in the range of 0.5-0.8 V as estimated from the differential pulse voltammograms. For the monocation radicals [OO-ph-N]<sup>+</sup>, [OS-ph-N]<sup>+</sup>, and [SS-ph-N<sup>+</sup>, obtained by chemical oxidation of the neutral precursor, a broad



ligand (amine) to metal  $(Mo_2)$  charge transfer (LMCT) absorption band is observed in the near-IR region. Interestingly, analogous to the intervalence charge transfer (IVCT) bands for mixed-valence complexes, the LMCT absorption bands, which are solvent dependent, decrease in energy and bandwidth as the electronic coupling between the two redox sites increases in an order of increasing S content in the chelating group. The electronic coupling matrix elements  $(H_{ab})$  are determined by optical analyses from the generalized Mulliken-Hush (GMH) theory, falling in the range of 400-800 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>. These results indicate that in these radical cations the charge is localized. Time-dependent DFT calculations show that the frontier molecular orbitals for these asymmetrical donor-acceptor systems have unbalanced distribution of electron density, and the LMCT bands arise from an electronic transition from the pendant ligand-based to metal-based molecular orbitals, corresponding to donor (N)-acceptor  $(Mo_2)$  charge transfer.

# INTRODUCTION

Study of charge transfer spectra is of fundamental importance in chemistry because it provides an indispensable approach to probe the electronic structures of the molecule or molecular system, on the basis of which its chemical and chemically related properties are elucidated. Intensive research practices in this direction have developed an active intersection of modern chemistry for experimentalists and theorists, that is, donoracceptor electron transfer (ET) crossing a significant distance,<sup>1-3</sup> which is ubiquitous in artificial and naturally existing compounds, materials, and systems. Long-distance electron transfer has been studied using the simplest mixedvalence model (MV) compounds, of which the reduced redox site serves as the electronic donor (D) and the oxidized one as the acceptor (A), and ET proceeds crossing the bridge (B) connecting D and A.4,5 According to the Marcus-Hush theory,<sup>1,6</sup> electron transfer may occur nonadiabatically (optically) or adiabatically (thermally) depending on the D-A electronic coupling, which is quantitatively evaluated by the electronic coupling matrix element  $H_{ab}$ . A strong research motivation in this field is to derive the kinetic data, e.g., activation energy ( $\Delta G^*$ ) and rate constant ( $k_{et}$ ), for D–A

electron transfer by optical analyses of the intervalence charge transfer (IVCT) absorption band.4,7,8 Aiming at this goal, interpretation of the spectroscopic behavior of various D-B-A systems, in terms of electronic and vibronic transitions from the ground state to the excited state, are the essentials of investigation.4,9,10

The majority of the studied D-B-A systems are dinuclear metal MV complexes with the Creutz–Taube ion,  $[(NH_3)_{S}Ru$ - $(pyrazine)Ru(NH_3)_5]^{5+}$ , as the prototypes.<sup>11,12</sup> MV compounds consisting of two organic redox termini, typically bridged tertiaryl diamine,<sup>5,13</sup> become an important subgroup of this array. With two identical chemical motifs as the donor and acceptor, most of the D-B-A systems are structurally symmetrical. Asymmetrical MV D-B-A systems may result from heterodinuclear metal centers with similar electronic configurations, such as Ru–Os,<sup>14</sup> Ru–Fe,<sup>15</sup> and organic radicals in which the two different structural termini have the same redox centers.<sup>16,17</sup> Asymmetrical D–B–A systems also include metal-organic hybrids<sup>18</sup> and various redox active molecular

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dyads,<sup>19</sup> which strictly speaking, may not be termed as mixedvalence compounds. Overall, relative to symmetrical systems, studies of asymmetric D-B-A systems are much less documented, especially those with mixed inorganic–organic redox sites. Therefore, we are not quite knowledgeable on the nature of charge transfer between the two distinct redox partners and the pertinent electronic and vibronic transitions. While development of novel D-B-A systems has long been a research focus in the hope of expanding the libraries, creation and investigation of structurally and electronically well-defined asymmetrical electro-active donor–acceptor systems are of particular interest.

For the reasons mentioned above, we are interested in the study of electronic coupling and electron transfer in asymmetrical MV D-B-A systems. Recently, by employing a guadruply bonded Mo<sub>2</sub> unit as the electron donor and acceptor, we have investigated the thermally induced electron transfer in weakly coupled asymmetrical [Mo2]-bridge-[Mo2] systems by optical analyses within the semiclassical theoretical framework, which validates the existing theories.<sup>20</sup> We also explored the mixed-valence properties for three strongly coupled asymmetrical Mo2 dimers.<sup>21</sup> In these systems, symmetrical IVCT absorption bands are observed, which correspond in energy to the electronic transition between two  $\delta$ -based molecular orbitals. Significantly, it is found that in these strongly coupled systems, donor-acceptor electron transfer occurs because the redox asymmetry creates two chargeunbalanced Mo2 centers, in contrast to symmetrical Class III systems in Robin-Day's scheme,<sup>22</sup> in which charge is equally distributed over the two redox centers.

In this report, a series of three dimolybydenum compounds with mixed inorganic–organic redox centers was developed by integrating a triarylamine group via a carboxylate or thiolated carboxylate chelating group, which are  $[(DAniF)_3Mo_2(\mu - O_2CC_6H_4N(C_6H_4CH_3)_2)]$  (DAniF = N,N'-di(p-anisyl)-formamidinate) ([OO-ph-N]),  $[(DAniF)_3Mo_2(\mu - OSCC_6H_4N(C_6H_4CH_3)_2)]$  ([OS-ph-N]), and  $[(DAniF)_3Mo_2(\mu - S_2CC_6H_4N(C_6H_4CH_3)_2)]$  ([SS-ph-N]). These compounds were characterized by single crystal X-ray diffractions; the molecular skeleton for the series is shown in Figure 1. The monocation radicals,  $[OO-ph-N]^+$ , [OS-ph-



Figure 1. A molecular skeleton for the studied  $[Mo_2(DAniF)_3][N-(C_6H_4CH_3)_2]$  ( $\mu$ -O<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>) ([OO-ph-N]),  $[Mo_2(DAniF)_3][N-(C_6H_4CH_3)_2](\mu$ -OSCC<sub>6</sub>H<sub>4</sub>) ([OS-ph-N]), and  $[Mo_2(DAniF)_3][N-(C_6H_4CH_3)_2](\mu$ -S<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>) ([SS-ph-N]) complexes.

N<sup>+</sup>, and [SS-ph-N]<sup>+</sup>, were obtained by one-electron chemical oxidation of the neutral compounds. Our study shows that this electro-active donor-acceptor system can be treated as asymmetrical mixed-valence systems, in terms of donor-acceptor charge transfer behavior. For each of them, a broad ligand (amine) to metal (Mo<sub>2</sub>) charge transfer (LMCT) absorption band with significant vibronic IVCT band characters, which is absent in the neutral precursors, was observed in the near-IR spectra. Optical analyses based on the generalized Mulliken-Hush (GMH) theory<sup>23</sup> gave the electronic coupling constants  $(H_{ab})$  falling in the range of 400–800 cm $^{-1}$ . In the series, the electronic coupling increases with increasing the S content, as indicated by the electrochemical and spectroscopic properties and the magnitude of  $H_{\rm ab}$ . DFT calculations show that the LMCT band arises from electronic transition between the molecular orbitals (MOs) involving the two redox centers, which corresponds to  $N(\pi) \rightarrow N(\pi)$  $Mo_2(\delta)$  charge transfer, analogous to the IVCT bands in MV systems. This study offers detailed understanding on the donor-acceptor charge transfer characteristics in metalorganic electro-active D-B-A systems.

#### RESULTS AND DISCUSSION

Molecular Design and Synthesis. With well-defined redox properties, both the quadruply bonded Mo<sub>2</sub> complex unit<sup>8</sup> and organic triarylamine group<sup>13</sup> are favorable components for construction of D–B–A assembling for the study of mixed valency and electron transfer.<sup>8,24,25</sup> The involvement of these symmetrical Mo<sub>2</sub>-Mo<sub>2</sub> and bridged diamine compounds has increased the diversity of the D-B-A systems and enriched the chemistry in these field. In an attempt to incorporate these two different redox sites to a single molecule to create the inorganic-organic D-B-A system, the triarylamine moiety should be functionalized with a chelating group that is able to bind to a Mo<sub>2</sub> unit by equatorial coordination. Obviously, carboxylate is the most suitable candidate that can be readily introduced. Thus, 4-(di-p-tolylamino)benzoic acid  $HO_2CC_6H_4N(C_6H_4CH_3)_2$  is considered to be a free ligand for assembling with a Mo2 unit. Stepwise thiolation of the carboxylic group yields the derivatives, which changes redox potentials of the Mo<sub>2</sub> unit. This strategy has been successfully used to expand the family of Mo<sub>2</sub> dimers in our recent study, because the energy of the  $\delta$  electrons of the Mo–Mo quadruple bond is very sensitive to variation of the coordination environment. The free acidic ligands in this study can be generally denoted as  $HEE'CC_6H_4N(C_6H_4CH_3)_2$  (EE' = OO (4), OS (6), or SS (9)) and were synthesized as schematized in Figure 2.

Acid 4 can be easily prepared by hydrolysis of the methyl ester 3 that can be synthesized by the coupling reaction of di-*p*-tolylamine 1 with *p*-iodo-methylbenzoate (2) in the presence of the copper catalyst.<sup>26</sup> Preparation of the thiobenzoic acid 6 started with 4, which was first converted to the chloride derivative 5 using oxalyl chloride. Thiolation of 5 with thioacetamide gave the target molecule in good yield.<sup>27</sup> For 9, the dithiocarboxylic group was introduced by the Grignard precursor 8 reacting with CS<sub>2</sub>.<sup>28</sup> For these reactions (Figure 2), generally good yields can be obtained as long as the necessary reaction conditions are retained. For example, for the reaction with the Grignard reagent involved, the solvents and reagents used must be dried thoroughly. With the availability of these free ligands, a general procedure was adopted for preparation of the Mo<sub>2</sub> complexes with an arylamine pendant,



**Figure 2.** (i) Cu, anhydrous  $K_2CO_3$ , crystalline iodine, *p*-xylene, 200 °C reflux, 24 h. (ii, a) KOH, 60 °C, 12 h (b) HCl. (iii) (COCl)<sub>2</sub>, DCM, r.t., 15 h. (iv, a) CH<sub>3</sub>CSNH<sub>2</sub>, THF, r.t., 12 h; (b) NaOH, HCl. (v) Mg, crystalline iodine, THF, 80 °C reflux, 2 h. (vi) (a) CS<sub>2</sub>, r.t., 2 h; (b) HCl.

 $[Mo_2(DAniF)_3(\mu-EE'CC_6H_4N(C_6H_4CH_3)_2], [OO-ph-N] (E = E' = O), [OS-ph-N] (E = O, E' = S), and [SS-ph-N] (E = E' = S), described as follows:$ 

$$\begin{split} & [\mathrm{Mo}_{2}(\mathrm{DAniF})_{3}(\mathrm{O}_{2}\mathrm{CCH}_{3})] + \mathrm{HEE'CC}_{6}\mathrm{H}_{4}\mathrm{N}(\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{CH}_{3})_{2} \\ & + \mathrm{NaOCH}_{3} \rightarrow [\mathrm{Mo}_{2}(\mathrm{DAniF})_{3}(\mu\text{-}\mathrm{EE'CC}_{6}\mathrm{H}_{4} \\ & \mathrm{N}(\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{CH}_{3})_{2}] + \mathrm{CH}_{3}\mathrm{CO}_{2}\mathrm{Na} + \mathrm{CH}_{3}\mathrm{OH} \end{split}$$

The usage of the mixed-ligand  $Mo_2$  complex  $[Mo_2(DAniF)_3(O_2CCH_3)]$  as the starting material guarantees a convergent assembling between the two redox components under mild reaction conditions, a procedure similar to preparation of the dicaboxylate bridged  $Mo_2$  dimers.<sup>29</sup>

Molecular Structures. Single crystals suitable for crystallographic studies were obtained by slow diffusion of ethanol into a dichloromethane solution of the compound. Crystals of [OO-ph-N] and [OS-ph-N] belong to the triclinic *P*<sub>1</sub> space group with the molecules residing in a general position (Z = 2)in the unit cell, while with the [SS-ph-N] crystal, the molecule sits in a special position of the monoclinic C2/c space group (Z = 4). The molecular structures are shown in Figure 3. The crystallographic data and refinement parameters are given in Table S1, and the selected bond parameters are summarized in Table S2. The Mo-Mo bonds of these three complexes are about 2.10 Å in length, as expected for the quadruple bond<sup>24</sup> and increase slightly with introduction of the S atom(s) to the chelating ligand. In [OO-ph-N], the Mo-O bonds (2.143(4) and 2.136(4) Å) are significantly longer than those of [OSph-N (2.106(4) Å). A plausible reason for this is the degree of  $d(\delta)-p(\pi)$  orbital interaction between atoms Mo and O in the thiolated species. A similar phenomenon is also observed for the Mo-S bonds of [OS-ph-N] (2.483(2) Å and [SSph-N] (2.446(2) Å). The triarylamine segment of the three compounds adopts the common propeller-shaped structure.<sup>25a</sup>

The sum of the bond angles  $(\angle C - N - C)$  about the amine N atom in [OO-ph-N], [OS-ph-N], and [SS-ph-N] is about 360°, which is compatible with the triarylamine structures in other systems,<sup>18,19</sup> indicating that the amine N atom adopts essentially an sp<sup>2</sup> hybridization which endows a significant participation in the N-Mo2 charge-transfer. It is also noted that there is a small dihedral angle  $(\phi_1)$  defined by the Mo<sub>2</sub> chelating ring and the phenyl group, 9.0° for [OO-ph-N],  $6.1^{\circ}$  for [OS-ph-N], and  $12.0^{\circ}$  for [SS-ph-N]. Relatively large torsion angles  $(\phi_2)$  between the central phenyl group and the plane defined by the three N-C bonds, 39.6°, 31.5°, and 59.4°, are found for [OO-ph-N], [OS-ph-N], and [SS-ph-N], respectively. The smallest  $\phi_1$  and  $\phi_2$  in [OS**ph**–**N**] is an indication of better conjugation of this compound along the charge transfer axis at least in the solid state. The C(4)-N(7) distances, ~5.7 Å, which may be defined as the "edge to edge" distance with respect of the two redox sites, are close for the three compounds. As expected, the "center to center" distance between the two redox sites increases in order as the S atom is stepwise introduced, that is, 8.435 Å for OOph-N], 8.657 Å for [OS-ph-N], and 8.949 Å for [SS-ph-N].

**Electrochemical Studies.** Figure 4 shows the cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) for [**OO**–**ph**–**N**], [**OS**–**ph**–**N**], and [**SS**–**ph**–**N**] in CH<sub>2</sub>Cl<sub>2</sub>. All compounds display two redox processes within the measuring window, one reversible redox couple at 0.3–0.35 V and one irreversible peak separated by 0.5–0.75 V. The half-wave potentials are estimated from the DPVs and summarized in the Table 1. As is known, both the Mo<sub>2</sub> complex unit and arylamine segment are electrochemically reversible redox centers in the symmetrical systems.<sup>30</sup> Oxidation of Mo<sub>2</sub> complexes [Mo<sub>2</sub>(DAniF)<sub>3</sub>(EE′CC<sub>6</sub>H<sub>5</sub>)] (EE′ = O, S) occurs at 0.4–0.7 V, increasing as the carboxylate group is stepwise thiolated (Figure S1). The half-wave potentials ( $E_{1/2}$ ) for acidic





Figure 3. X-ray crystal structures for [OO-ph-N] (top), [OS-ph-N] (middle), and [SS-ph-N] (below).

ligands HEE'CC<sub>6</sub>H<sub>4</sub>N(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub> (EE' = O, S) range from 0.9 to 1.1 V and decrease with the acidic group changing from carboxylic to dithiocarboxylic (Figure S1). By referring to these data, it is clear that the low potential one-electron oxidation is due to the  $Mo_2^{4+} \rightarrow Mo_2^{1.5+}$  process, which is reversible. Notably, by assembling with the  $Mo_2$  unit, the  $N/N^{\bullet+}$  redox process of the amine component becomes irreversible. Presumably, significant N  $\rightarrow$   $Mo_2^{\,5+}$  charge transfer occurs in the electrochemically generated radical species, and thus, the irreversibility is attributed to electronic interaction between the two redox centers. This hypothesis is supported by the better  $N/N^{\bullet+}$  redox reversibility for [SS-ph-N] (Figure 4), because



Figure 4. CVs and DPVs of [OO-ph-N] (red), [OS-ph-N] (blue), and [SS-ph-N] (green).

Table	1.	Data	from	the	Electrochemical	Measurements
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compound	$E_{\rm vir}$ (1 · V)	$E_{\rm vir}$ (2 · V)	$\Delta E_{\rm vir}$ (mV)	$K_{-a}^{a}$				
compound	$L_{1/2}$ (1, 1)	$L_{1/2}$ (2, •)	$\Delta L_{1/2}$ (mv)	r.c				
[OO-ph-N]	0.29	0.81	520	$6.5 \times 10^{8}$				
[OS-ph-N]	0.28	1.03	750	$5.1 \times 10^{12}$				
[SS-ph-N]	0.36	0.97	610	$2.1 \times 10^{10}$				
<sup>a</sup> Comproportionation constant $K_{\rm C}$ was determined as $K_{\rm c} = e^{\Delta E_{1/2}/25.69}$ .								

the dithio chelating group is able to lower the electron deficiency of the Mo<sub>2</sub><sup>5+</sup> center. Therefore, the electrochemical data indicate that in the monocation radicals, the organic redox center serves as the electron donor, while the Mo<sub>2</sub> center is the acceptor.

The potential differences  $(\Delta E_{1/2})$  between the two redox centers, 0.52 V for [OO-ph-N], 0.75 V for [OS-ph-N] and 0.61 V for [SS-ph-N], are determined by Taube-Richardson methods from the DPV working curves.<sup>31</sup> It is noted that in the series, the monothiolated species, rather than [SS-ph-N], has the largest  $\Delta E_{1/2}$  value, in disagreement with the trend observed in other O/S series with Mo2 centers.<sup>8</sup> For the asymmetrical systems, there are three major terms that contribute to the  $\Delta E_{1/2}$  value, that is, electrostatic interaction, electron resonance, and internal potential difference. The electron resonance effect accounts for the electronic coupling, whereas the internal potential difference between the donor and acceptor defines the redox asymmetry. When similar Mo<sub>2</sub>... N separation is assumed for the series, the electrostatic effect should be similar for the three complexes. The internal potential difference  $(\Delta E_{\rm IP})$  refers to the redox potential difference between the noninteracting donor and acceptor, which corresponds to the free energy difference  $(\Delta G^{\circ})$  for the diabatic states. One of the practical ways to determine  $\Delta E_{\rm IP}$  is to measure the potential difference for the reference compounds which are structurally and electronically similar to the donor and acceptor.<sup>32</sup> In this study, complexes [Mo<sub>2</sub>(DAniF)<sub>3</sub>(EE'CC<sub>6</sub>H<sub>5</sub>)] and free ligands HEE'CC<sub>6</sub>H<sub>4</sub>N- $(C_6H_4CH_3)_2$  (EE' = OO, OS, and SS) can be used as the reference compounds for the Mo<sub>2</sub> and arylamine redox centers, respectively. Then, the  $\Delta E_{\mathrm{IP}}$  values are estimated to be 0.75 ([OO-ph-N]), 0.65 ([OS-ph-N]), and 0.25 V ([SS-ph-**N**]) (Figure S1). Clearly, the smallest  $\Delta E_{IP}$  for [SS-ph-N] lowers its  $\Delta E_{1/2}$  value to less than that for [OS-ph-N].

Valence Complexes. As shown in Figure 5, the electronic



Figure 5. Electronic absorption spectra of [OO-ph-N] (red), [OS-ph-N] (blue), and [SS-ph-N] (green).

spectra of these three compounds are quite simple, showing only one pronounced absorption band in the visible region. This band is likely due to the  $\delta(Mo_2)$  to  $\pi^*(bridging ligand)$ transitions (MLCT) according to prior studies.<sup>8,24,33</sup> The MLCT energies ( $E_{\rm ML}$ ) decrease and the intensities increase as the S content increases, in a trend parallel to the reported results.<sup>8</sup> For [**OO**-**ph**-**N**], the intense absorption is observed at 407 nm with an extinction coefficient ( $\varepsilon_{\rm ML}$ ) of 14 410 M<sup>-1</sup> cm<sup>-1</sup>, and at 514 nm ( $\varepsilon_{\rm ML}$ , 17 040 M<sup>-1</sup> cm<sup>-1</sup>) for [**OS**-**ph**-**N**], and at 605 nm ( $\varepsilon_{\rm ML}$ , 30 093 M<sup>-1</sup>cm<sup>-1</sup>) [**SS**-**ph**-**N**], as listed in Table 2. An additional absorption band at 407 nm is observed

Table 2. Spectroscopic Data of the IVCT Bands for  $[OO-ph-N]^+$ ,  $[OS-ph-N]^+$ , and  $[SS-ph-N]^+$  in Different Solvent

compound	solvent	$(\text{cm}^{-1})$	$\Delta  u_{1/2} \left( \mathrm{IV}  ight) \ (\mathrm{cm}^{-1})$	$(M^{-1}cm^{-1})$	$(\mathrm{cm}^{-1})^{a}$			
[00-ph-	DCM	11680	4570	3280	442			
$N]^+$	THF	13850	4675	2580	403			
	ACTONE	14513	5000	2950	499			
[OS-ph-	DCM	10245	3655	6900	701			
$N]^+$	THF	11862	4025	3647	444			
	ACTONE	12593	3699	4510	549			
[SS-ph-	DCM	8605	3118	10350	739			
$N]^+$	THF	9479	3448	6270	553			
	ACTONE	10370	3470	6538	581			
<sup><math>a</math></sup> Calculated by eq 1.								

for [SS-ph-N], which can be assigned as the intraligand charge transfer within the pendent triarylamine ligand on the basis of DFT calculation (*vide infra*).

Single electron oxidation of these compounds with one equivalent of ferrocenium hexafluorophosphate yielded the corresponding radical monocation  $[OO-ph-N]^+$ ,  $[OS-ph-N]^+$ , and  $[SS-ph-N]^+$ . These radial species were characterized by X-band electron paramagnetic resonance spectra (EPR). The EPR signals of  $[OO-ph-N]^+$ ,  $[OS-ph-N]^+$ , and  $[SS-ph-N]^+$  were recorded in situ at 173 K, as shown in Figure 6. All the species show symmetrical isotropic EPR signals with a *g* factor less than 2.0023 for an organic radical. In the series, species with more S atom(s) have a larger *g* value, 1.945 for  $[OO-ph-N]^+$ , 1.955 for  $[OO-ph-N]^+$ , and 1.960 for  $[SS-Ph-N]^+$ , and 1.960 for  $[SS-Ph-N]^+$ .



Figure 6. X-band EPR spectra of the radical cations generated by single oxidation of the neutral compounds. Samples were measured in  $CH_2Cl_2$  solution.

**ph**–**N**]<sup>+</sup>. These results show that for each of them, the odd electron is localized on the metal-based orbital, rather than the amine N center, consistent with the electrochemical analyses. This is different from asymmetrical Ru–N mixed-valence systems reported by the Zhong group,<sup>18a,b</sup> in which a single electron resides on the  $p_{\pi}$  orbital of the amine group. The variation trend of *g* values indicates that the extent of charge delocalization increases in order as the chelating group changes from OO to OS to SS. Furthermore, the *g* values for this series are larger than those for symmetrical and asymmetrical Mo<sub>2</sub> MV complexes,<sup>20,24</sup> indicating a significant valence detrapping effect due to the donor–acceptor electronic coupling.

The absorption spectra of the monocation radials are shown in Figure 7, and the spectral data are summarized in Table 3. All



Figure 7. Vis–Near-IR absorption spectra for  $[OO-ph-N]^+$  (red),  $[OS-ph-N]^+$  (blue), and  $[SS-ph-N]^+$  (green).

the radical species display an absorption band in the range of  $16\ 000-25\ 000\ \mathrm{cm}^{-1}$  with the energy and intensity similar to those for the MLCT band for the neural compound; accordingly, this band is assigned to the MLCT transition. For  $[\mathbf{OO}-\mathbf{ph}-\mathbf{N}]^+$  and  $[\mathbf{SS}-\mathbf{ph}-\mathbf{N}]^+$ , the MLCT band is slightly red-shifted relative to that for the neutral precursor (Figure S2). For the two thiolated complexes  $[\mathbf{OS}-\mathbf{ph}-\mathbf{N}]^+$  and  $[\mathbf{SS}-\mathbf{ph}-\mathbf{N}]^+$  and  $[\mathbf{SS}-\mathbf{ph}-\mathbf{N}]^+$ 

Table 3.	Calculated	Energy	Levels	of the	e Selected	l Frontier	<sup>·</sup> Molecula	r Orbitals	by DFT	//TD-DFT	Calcula	tions
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		MLCT		LMCT			
		calcd (	(nm)		calcd (cm <sup>-1</sup> )		
compound	$E_{\rm ML}~({\rm cm}^{-1})$	$E_{\rm ML}({\rm ex})^a$	$\Delta E_{\mathrm{H-L}}$	$E_{\rm LM}~({\rm cm}^{-1})$	$E_{\rm LM}({\rm ex})^a$	$\Delta E_{\mathrm{H-1-H}}$	
[OO-ph-N]	24570	23740	23390			10645	
[OS-ph-N]	19455	20210	19920			10080	
[SS-ph-N]	16530	16800	17180			7905	
$[OO-ph-N]^+$	23180	21700		11680	10010		
[OS-ph-N] <sup>+</sup>	19420	18250		10245	9890		
[SS-ph-N] <sup>+</sup>	16080	15800		8605	7940		
	1			1 4 17	1.07	1 1 .	

 ${}^{a}E_{ML}(ex)$  and  $E_{LM}(ex)$  represent the excitation energies calculated by TD-DFT.  $\Delta E_{H-L}$  and  $\Delta E_{H-1-H}$  are the energy differences between the two orbitals.

24 810 and 21 900 cm<sup>-1</sup>, respectively. The assignment of this band is based on the DFT calculations (*vide infra*).

All these metal-organic radical cations exhibit a broad absorption band in the near-IR region, which is absent for the neutral complexes, as shown in Figure 7. We can safely assign this band to the LMCT absorption due to the charge transfer from the pendant amine ligand to the oxidized Mo<sub>2</sub><sup>5+</sup> center. In previous work, it was observed that a LMCT band appears upon one-electron oxidation of the bridged Mo<sub>2</sub> dimers, ascribable to the electronic transition from the high-lying bridging ligand orbital to the singly occupied  $\delta$  orbital, and the transition energy  $(E_{LM})$  decreases as donor-acceptor coupling increases. For the phenylene bridged Mo2 dimers, stepwise thiolation of the bridging ligand shifts the IVCT band toward low energy by 800  $\text{cm}^{-1.8}$  Here, introducing the S atom onto the chelating group lowers the LM transition energy by about 1500 cm<sup>-1</sup>, while the band intensity increases. For each of the three complexes, the LMCT band is appreciably broader than the MLCT band (Figure 7; Table 2). The highest transition energy ( $E_{\rm IT}$ , 11682 cm<sup>-1</sup>) and lowest band intensity ( $\varepsilon_{\rm IT}$ , 3380  $M^{-1}cm^{-1}$ ) and broadest band profile ( $\Delta \nu_{1/2}$ , 4570 cm<sup>-1</sup>) are observed for [OO-ph-N]<sup>+</sup>; for [SS-ph-N]<sup>+</sup>, these band parameters vary toward the opposite direction (Table 2). Interestingly, the LMCT bands show vibronic transition features, resembling an IVCT band in the MV analogues. The Gaussian-shaped band profile is also similar to that for asymmetrical MV compounds,<sup>21,34</sup> while the "cut-off" of IVCT bands is generally observed for moderately strongly coupled symmetrical MV Mo<sub>2</sub> dimers,<sup>8a,c,33,35</sup> as predicted from the two-state model.<sup>36</sup>

Solvent dependence of the IVCT absorption is a practical criterion for distinguishing Class II and III mixed-valence systems. In this study, in addition to dichloromethane, more polar solvents THF and acetone were also used for the spectroscopic measurements of the obtained monoradical cations. As shown in Table 2, all three complexes show solvent dependence of the LMCT band, similar to the spectral property of the IVCT band for Class II MV compounds. Notably, in contrast, the MLCT bands do not show similar solvent dependences. It is found that in the polar solvents, the transition energy  $(E_{LM})$  is increased and the absorption band is broadened (Figure S3). For each of the complex systems, the LMCT band in acetone is higher in energy and broader (Table 2). Furthermore, solvent polarity affects the band parameters of these complexes to different extents, which reflects roughly the coupling strength of the complex. For example, for [OO-ph-N]<sup>+</sup>, the difference of  $E_{LM}$  in acetone and CH<sub>2</sub>Cl<sub>2</sub> is 2899 cm<sup>-1</sup>, and 2326 cm<sup>-1</sup> for [OS-ph-N]<sup>+</sup>, and 1791 cm<sup>-1</sup> for [SS-phN]<sup>+</sup>. Therefore, the observed solvent dependences of spectra for the series demonstrate that unlike the MLCT band, the LMCT band shows a vibronic IVCT band character and signals the extent of electronic coupling between the dimetal and amine redox centers.

**Calculation of Electronic Coupling Matrix Elements**  $H_{ab}$ . Considering the vibronic features of the LMCT bands in the spectra, the generalized Mulliken–Hush (GMH) theory (eq 1), which is applicable for both symmetric and asymmetric MV compounds,<sup>17,34,37,38</sup> is employed to determine the electronic coupling matrix element ( $H_{ab}$ ) from the LMCT band parameters.

$$H_{\rm ab} = \frac{|\mu_{\rm ab}|}{er_{\rm ab}} \nu_{\rm max} \tag{1}$$

$$\mu_{\rm ab} = \sqrt{\frac{3hc\varepsilon_0 \ln 10}{2000\pi^2 N}} \frac{9n}{\left(n^2 + 2\right)^2} \int \frac{\varepsilon}{\tilde{\nu}} \,\mathrm{d}\tilde{\nu} \tag{2}$$

In eq 1,  $|\mu_{ab}|$  is the diabatic transition dipole moment of the IVCT band,  $\nu_{\rm max}$  is the absorption maximum (cm<sup>-1</sup>) of the IVCT band, e (esu) is the elementary charge of an electron, and  $r_{ab}$  (Å) is the effective ET distance. The  $|\mu_{ab}|$  can be calculated from eq 2, in which h is Planck's constant, c is the speed of light,  $\varepsilon_0$  is the permittivity of the vacuum, N is the Avogadro's number, *n* is the refractive index of the solvent,  $\varepsilon$  is the extinction coefficient, and the integration part is the integrated intensity of the IVCT band. In principle, making good use of this equation requires reasonable estimation of the effective electronic coupling distance  $(r_{ab})$ . The distance between the two redox sites is usually used as the ET distance, which would lead to an underestimated  $H_{ab}$  value because the effective distance is shorter than the geometric D-A separation.<sup>39</sup> For the three complex systems, the N(amine)-C(4) distance (ca. 5.7 Å), or the "edge to edge" separation, is used as the effective electron transfer distance to calculate the  $H_{\rm ab}$  considering  $d(\delta)-p(\pi)$  conjugation within the [Mo<sub>2</sub>] complex unit. The corresponding H<sub>ab</sub> values in CH<sub>2</sub>Cl<sub>2</sub>, THF, and acetone are determined in the range of  $400-800 \text{ cm}^{-1}$ , as listed in Table 2. In the series, the variation trend of  $H_{ab}$  is in accordance with the coupling strength predicated from the S content on the chelating group. For example, in dichloromethane, the smallest one (442 cm<sup>-1</sup>) is found for  $[OO-ph-N]^+$  and the largest  $H_{ab}$ (739 cm<sup>-1</sup>) for  $[SS-ph-N]^+$ . The  $H_{ab}$  values for present series are compatible with those for phenylene bridged Mo2 dimers  $\{[Mo_2(DAniF)_3]_2(\mu$ -EE'CC<sub>6</sub>H<sub>4</sub>CEE') $\}^+$ , namely, [OO-ph- $OO]^+$  ( $H_{ab}$ , 560 cm<sup>-1</sup>),  $[OS-ph-OS]^+$  ( $H_{ab}$ , 730 cm<sup>-1</sup>), and  $[SS-ph-SS]^+$   $(H_{ab}, 870 \text{ cm}^{-1})$ .<sup>8b</sup> The smaller  $H_{ab}$  values for these inorganic-organic radical systems reflect the weaker



Figure 8. DFT calculated frontier molecular orbitals of [SS-ph-N], [OS-ph-N], and [OO-ph-N] models.



Figure 9. TD-DFT calculated frontier molecular orbitals and dominant transitions for [OO-ph-N]<sup>+</sup>, [OS-ph-N]<sup>+</sup>, and [SS-ph-N]<sup>+</sup> models.

coupling in comparison with the related Mo<sub>2</sub> dimers because the redox asymmetry increases the charge localization. In the symmetrical series,  $[SS-ph-SS]^+$  is considered in the Class II–III transition regime, judged by the half cutoff of IVCT band at  $2H_{ab}$ .<sup>4,8b</sup> In our recent study on strongly coupled asymmetrical series { $[Mo_2(DAniF)_3]_2(\mu$ -EE'CCEE')}<sup>+</sup> (E, E' = O, S),<sup>21</sup>  $H_{ab}$  values of 1098, 1600, and 1615 cm<sup>-1</sup> are estimated from eq 1 for complexes  $[OO-OS]^+$ ,  $[SS-OO]^+$ , and  $[SS-OS]^+$ , respectively. These results validate the generalized Mulliken–Hush expression (eq 1) for determination of  $H_{ab}$  constants for metal–organic D–B–A systems, in combining with the application of eq 2, which accounts for the charge transfer bandwidth and intensity.

**DFT and TD-DFT Calculations.** To gain insights into the ground state geometries, electronic structures, and nature of frontier molecular orbitals (FMOs) for the series, DFT and time-dependent DFT (TD-DFT) calculations on the simplified molecular models were performed assuming an S = 0 spin state. The calculation models  $Mo_2(NHCHNH)_3[\mu$ -EE'CC<sub>6</sub>H<sub>4</sub>N-(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>] (EE' = OO, OS, or SS) are derived by replacing

the *p*-anisyl groups in the DAniF ligands with H atoms. Figure 8 shows that the HOMO is constructed mainly by the  $\delta$  bonding orbital of the model  $[Mo_2(HNCHNH)_3]$ , while LUMO is dominated by the  $\pi^*$  orbital of bridging moiety  $-\text{EE}'\text{CC}_6\text{H}_4-$  (E/E' = O or S). HOMO-1 involves the  $p_{\pi}$  orbital of the triarylamine nitrogen center (-NAr<sub>2</sub>, Ar =  $-\text{C}_6\text{H}_4\text{CH}_3$ ) with some admixture of the phenylene  $\pi$  orbitals. The composition of the HOMO confirms that the lower redox potential wave (~0.3 V) in electrochemical measurements is attributed to the Mo<sub>2</sub><sup>5+/4+</sup> redox process. Importantly, the frontier orbitals prove that the complex monocations are electronically redox active D–B–A systems with an amine N donor and a Mo<sub>2</sub> acceptor.

For each of the neutral complex models, the energy gap between the HOMO and LUMO ( $\Delta E_{H-L}$ ) corresponds to energy of the pronounced absorption band (MLCT) in the spectrum (Table 3). TD-DFT calculations confirm that this band arises from the HOMO  $\rightarrow$  LUMO transition, thus showing the MLCT character (Table S3). The intense high energy absorption (407 nm) for [SS-ph-N] corresponds to the HOMO-1  $\rightarrow$  LUMO transition in energy, as shown in Figure 8, and thus is due to the charge transfer within the pendant ligand, or internal ligand charge transfer (ILCT). For [OO-ph-N] and [OS-ph-N], this band does not exhibit in the spectra because the transition energies are high. Furthermore, in symmetric Mo<sub>2</sub> dimeric systems, the electronic coupling between two Mo<sub>2</sub> centers increases with the HOMO-1-HOMO energy gap ( $\Delta E_{H-1-H}$ ). Large  $\Delta E_{H-1-H}$  is found in Class III, which corresponds to the IVCT band energy.<sup>3</sup> However, this criterion is not valid for the asymmetrical [EEph-N] systems, although the orbital interactions in the frontier MOs are established in a similar manner. Here, the  $\Delta E_{H-1-H}$ value is correlated to the measured LMCT band energy  $(E_{LM})$ but decreases as the coupling strength increases in the series, as shown in Table 3. These theoretical results reflect the electronic nature of the asymmetrical, metal-organic radical systems, with a substantial difference from the bridged Mo<sub>2</sub> dimers.

The electronic properties and optical behaviors of the singly oxidized complexes were studied by TD-DFT calculations on the radial cation models (S = 1/2). The calculated excitation energies for  $[OO-ph-N]^+$ ,  $[OS-ph-N]^+$ , and  $[SS-ph-S]^+$ are listed in Table 3. For the radical species,  $\alpha$ - and  $\beta$ -MOs are named for orbitals in different electron spin states, as shown in Figure 9. For example, the HOMO of the neutral model corresponds to  $\alpha$ -HOMO and  $\beta$ -LUMO, while the HOMO-1 becomes  $\alpha$ -HOMO-1 and  $\beta$ -HOMO. It is noted that the  $\alpha$ -LUMOs for the three models of the series are not in the same order. For  $[OO-ph-N]^+$  and  $[OS-ph-N]^+$ ,  $\alpha$ -LUMO+1 shows the bridging  $\pi$  orbital character, whereas for [SS-ph-N<sup>+</sup>, the corresponding orbital is  $\alpha$ -LUMO. Therefore, metal (Mo<sub>2</sub>) to bridging ligand ( $\pi^*$ ) charge transfer (MLCT) absorption corresponds to the transition of  $\alpha$ -HOMO  $\rightarrow \alpha$ -LUMO for the dithiolated species, but for the other two, this band is due to the  $\alpha$ -HOMO  $\rightarrow \alpha$ -LUMO+1 transition. The  $\beta$ -HOMO  $\rightarrow \beta$ -LUMO transition corresponds to the LMCT absorption in energy and electron density distribution as well, as shown in Figure 9. For all three systems, the calculated transition energies  $E_{\rm LM}(ex)$  are in excellent agreement with the observed LMCT band energies  $(E_{LM})$ ; for the series, both of the calculated and measured energies decrease with increases of the electronic coupling (Table 3). The electron density on the  $\beta$ -HOMO is spread over the three phenyl groups surrounding the central sp<sup>2</sup> N atom and extended to the chelating group (Figure 9). This indicates that this MO is contributed by the fourth ligand of the Mo<sub>2</sub> center and has nothing to do with the DAniF ligands. On this basis, the assignment of the LMCT band to the  $\beta$ -HOMO to  $\beta$ -LUMO transition is confirmed. Calculations show that the intense band at 21 900 cm<sup>-1</sup> for [SS-ph-N]<sup>+</sup> results from linear combinations of two transitions,  $\alpha$ -HOMO-1  $\rightarrow \alpha$ -LUMO and  $\beta$ -HOMO  $\rightarrow \beta$ -LUMO+1 characters, as shown in Figure S4 and Table S4. Since the MOs involved in these transitions are contributed by the triarylamine pendant ligand, this band may be termed as intraligand charge transfer (ILCT) absorption. Similarly, for [OS-ph-N]<sup>+</sup> and [OO-ph-N]<sup>+</sup>, linear combinations of  $\alpha$ -HOMO-1  $\rightarrow \alpha$ -LUMO+1 and  $\beta$ -HOMO  $\rightarrow \beta$ -LUMO+1 characters give rise to the ILCT band.

Interestingly, the TD-DFT calculations show that the vertical transition energy matches well with not only the observed charge transfer energy but also the charge transfer between the ground and excited states. For the monoradicals, the  $\beta$ -HOMO and  $\beta$ -LUMO may be viewed as the ground and excited states, respectively, which have the electron density concentrated on the amine and dimolybdenum sites, respectively. The  $\beta$ -HOMO to  $\beta$ -LUMO transition leads to the charge transfer from the donor (N) to the acceptor  $(Mo_2)$ . Consistently, the LMCT absorption band shows IVCT band characters for the Mo<sub>2</sub> MV analogues. Therefore, these results conform well to the two-state model in semiclassical theory.<sup>2-4</sup> However, it should be noted that this correlation between computational and experimental results does not exist for symmetrical, moderately strongly coupled MV systems because the derived symmetrical electronic states (MOs) do not account for the dynamic process of charge transfer. The LMCT band appears with vibronic features of IVCT bands because the pendant ligand is redox noninnocent and the redox center is geometrically far from the dimetal unit and the LM electronic transition states are coupled with the vibrational states.

# CONCLUSIONS

In the present work, assembling a quadruply bonded Mo<sub>2</sub> unit with an arylamine segment has generated a series of three compounds with a general formula of  $[Mo_2(DAniF)_3(\mu EE'CC_6H_4N(C_6H_4CH_3)_2$ ] (EE' = OO, OS, or SS), which are all characterized by X-ray diffraction. To achieve equatorial linkage of the amine pendant to the Mo2 center, the organic moiety is functionalized with a carboxylate or thiocarboxylate group; meanwhile, variation of this chelating group tunes the electronic communication between the two redox sites. Single oxidation of these compounds allowed systematic examination of the optical behavior and electronic properties of the asymmetrical D-B-A systems in which the amine and the Mo<sub>2</sub> redox sites serve as the electron donor and acceptor, respectively. In this series, the dimetal and amine redox sites are moderately strongly interacted, which reduces the reversibility of the redox couple for the amine site  $(N/N^{\bullet+})$ . The inorganic–organic conjugation through  $\delta - \pi$  orbital interaction increases with increasing the S content of the chelating group, as expected. Both of the neutral and radiccal complexes exhibit a characteristic metal ( $\delta$ ) to bridging ligand ( $\pi^*$ ) charge transfer absorption band with similar transition energies. The monoradical species display a low energy, solvent-dependent LMCT absorption band due to electronic transition from the pendant amine ligand to the Mo<sub>2</sub> center. The transition energy of this band decreases from 11680 to 8605 cm<sup>-1</sup> with

decreasing bandwidth and increasing intensity as the S atom is introduced stepwise. Therefore, the LMCT band presents significantly vibronic features of an IVCT band in MV systems. The generalized Mulliken-Hush (GMH) formalism has been employed to estimate the electronic coupling matrix elements  $H_{ab}$  falling in the range of 400–800 cm<sup>-1</sup>. DFT and TD-DFT calculations on the reasonably simplified models show that the key molecular orbitals are asymmetrical with unequal distribution of the electron density over the two redox centers. Remarkably, for all three complex systems, the observed LMCT band energy is in good agreement with the calculated HOMO-1 (amine based) to HOMO (metal based) transition energy, corresponding to  $N(\pi) \rightarrow Mo_2(\delta)$  charge transfer. Therefore, in this metal-organic radical system, the LMCT band is analogous to the vibronic IVCT band in mixed-valence systems. This study demonstrates that the same methods of optical analysis used for MV compounds can also be used to study the charge transfer bands in donor-acceptor compounds.

## EXPERIMENTAL SECTION

**Materials and Methods.** All manipulations were performed in a nitrogen-filled glovebox or by using standard Schlenk-line techniques. All solvents were freshly distilled over appropriate drying agents and collected for further use under a nitrogen atmosphere. 4-Bromo-4',4"-dimethyltriphenylamine is obtained from a commercial resource. HDAniF<sup>40</sup> and Mo<sub>2</sub>(DAniF)<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sup>29</sup> were synthesized according to published methods.

Physical Measurements. UV-vis-near-IR spectra were measured in CH<sub>2</sub>Cl<sub>2</sub> solutions using IR quartz cells with a light path length of 2 mm on a Shimadzu UV-3600 UV-vis-near-IR spectrophotometer. Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were performed using a CH Instruments Model-CHI660D electrochemical analyzer in a 0.10 M CH<sub>2</sub>Cl<sub>2</sub> solution of "Bu<sub>4</sub>NPF<sub>6</sub> with a Pt working and auxiliary electrodes, a Ag/AgCl reference electrode, and a scan rate of 100 mV/s<sup>-1</sup>. All potentials are referenced to the Ag/AgCl electrode. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 300 spectrometer. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. EPR spectra were measured using a Bruker A300-10-12 electron paramagnetic resonance spectrometer. Measurements for the mixed-valence complexes were carried out in situ after single oxidation of the corresponding neutral compounds using ferrocenium hexafluorophosphate (Cp<sub>2</sub>FePF<sub>6</sub>).

X-ray Structure Determinations. Single-crystal data for  $[OS-ph-N]\cdot CH_2Cl_2$  were collected on an Agilent Xcalibur Nova diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 173 K and for  $[OO-ph-N]\cdot CH_2Cl_2$  and [SS-ph-N], the data were collected on an Agilent Gemini S Ultra diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å) at 173 K. The empirical absorption corrections were applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.<sup>41</sup> All the structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions in the final structure refinement. Structure determination and refinement were carried out using SHELXS-2014 and SHELXL-2014 programs, respectively.<sup>42</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters.

**Computational Details.** The ORCA 2.9.1 software package was used for all DFT computations.<sup>43</sup> The geometry of the model complexes was optimized in the gas phase without imposing any symmetry constraints. Geometry optimizations for the complexes were converged to the S = 0 or 1/2 spin and employed the Becke–Perdew (BP86) functional<sup>44</sup> and the SV(P) (Ahlrichs split valence polarized) basis with the SV/J auxiliary basis for all atoms except for S, N, O, and Mo atoms where the larger TZVP (Ahlrichs triple-valence polarized) basis in conjunction with the TZV/J auxiliary basis was used.<sup>45</sup> For Mo atoms, the scaled-ZORA (zeroth-order regular approximation)

Hamiltonian was used to take account of the relativistic effect in the calculations.<sup>46</sup>These calculations employed the resolution of identity (RI) approximation developed by Neese.<sup>47</sup> The coordinates of all DFT energy minimized models of the complexes presented in this study are included in Tables S5–S10. Electronic transition energies and intensities were computed for neutral model compounds as well as oxidized model compounds using the time-dependent DFT (TD-DFT) method within the Tamm–Dancoff approximation.<sup>48</sup> These calculations employed the B3LYP functional<sup>49</sup> and ZORA (Mo), TZVP (S, O, and N), and SVP (C and H) basis sets. Forty excited states were calculated by including all one-electron excitations within an energy window of ±3 hartree with respect to the HOMO/LUMO energies. Isosurface plots of molecular orbitals were generated using the gOpenMol program using isodensity values of 0.04.

**Preparation of 4-(Di***p***-tolylamino)-benzoic acid (4).** 4-(Di*p*-tolylamino)-benzoic acid (4) was synthesized by a similar procedure in the literaure.<sup>26</sup> Di-*p*-tolylamine (0.90 g, 4.56 mmol), *p*-iodo-methylbenzoate (1.20 g, 4.58 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (0.74 g), copper bronze (0.23 g), *p*-xylene (0.5 mL), and a small amount of iodine crystals were mixed in a 100 mL flask. Under an argon atmosphere and in the dark, the mixture refluxed at 200 °C for 24 h. The reaction mixture was cooled down to room temperature and filtered. The solid materials were washed with diethyl ether. The filtrate was evaporated under reduced pressure, yielding a sticky oil product. Purification by column chromatography (DCM/*n*-hexane = 1:1) gave 1.21 g of the compound (3) as viscous yellow oil (yield, 80%). <sup>1</sup>H NMR δ (ppm in CDCl<sub>3</sub>): 7.88 (d, 2H, aromatic C–H), 7.15 (q, 8H, aromatic C–H), 6.99 (d, 2H, aromatic C–H), 3.90 (s, 3H, –COOCH<sub>3</sub>), 2.38 (s, 6H, –CH<sub>3</sub>).

A solution of 3 (1.21 g, 3.82 mmol) in ethanol (30 mL) was mixed with KOH solution (1 M, 30 mL). The mixture was stirred at 60 °C for 12 h. After completion of the reaction, the solvents were removed under reduced pressure. To the mixture, HCl solution (1.0 M) was added to neutralize the excess KOH by controlling pH = 2. The solution was extracted with ethyl acetate (3 × 20 mL), and the collected extract was dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent gave compound 4 as a white solid. Yield: 0.93 g, 80%. <sup>1</sup>H NMR  $\delta$  (ppm in CDCl<sub>3</sub>): 7.90 (d, 2H, aromatic C–H), 7.14 (q, 8H, aromatic C–H), 6.96 (d, 2H, aromatic C–H), 2.36 (s, 6H, –CH<sub>3</sub>).

**Preparation of 4-(Di-***p***-tolylamino)-thiobenzoic acid (6).** To a solution of compound 4 (1.08 g, 3.46 mmol) in  $CH_2Cl_2$  (30 mL) was added oxalyl chloride (0.72 mL, 4.20 mmol) followed by few drops of DMF at 0 °C under a nitrogen atmosphere. The color of the mixture changed to yellow immediately. After stirring the mixture at room temperature for 15 h, the solvent was removed under reduced pressure, which gives a yellow solid of compound 5. This material was directly used for the next step without further purification.

The crude product of **5** was mixed with thioacetamide (0.65 g, 8.6 mmol) in 30 mL of THF at room temperature and stirred for 12 h. After that, NaOH solution (1M, 30 mL) was added, and the reaction was stirred for another 1 h. Then, solvents were removed under reduced pressure, and HCl solution (1.0 M) was added to neutralize the excess NaOH by controlling pH = 2. The solution was extracted with ethyl acetate (3 × 20 mL), and the collected extract was dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent gave compound **6** as a green solid. The solid was purified by column chromatography (EtOAc/*n*-hexane = 1:15). Yield: 0.87 g, 75%. <sup>1</sup>H NMR  $\delta$  (ppm in CDCl<sub>3</sub>): 7.73 (d, 2H, aromatic H), 7.15 (q, 8H, aromatic H), 6.92 (d, 2H, aromatic H), 2.37 (s, 6H,–CH<sub>3</sub>).

**Preparation of 4-(Di**-*p*-tolylamino)-dithiobenzoic Acid (9). 4-(Di-*p*-tolylamino)-dithiobenzoic acid (9) was synthesized by a similar procedure in the literature.<sup>28</sup> Magnesium (0.09 g, 3.69 mmol) and a small amount of iodine crystals were introduced in a three-neck roundbottomed flask. A solution was prepared separately by dissolving 4bromo-4',4"-dimethyltriphenylamine (1.07 g, 2.84 mmol) in 5 mL of dry THF. A volume of 1 mL of this solution was added to the Mg and I<sub>2</sub> containing flask under a nitrogen atmosphere. The mixture was heated at 80 °C to reflux to initiate the reaction; then, the remaining solution was added. The reaction was heated for an additional 2 h. The reaction mixture was cooled down to room temperature, and carbon disulfide (3 mL) was added. The mixture was stirred for another 2 h at room temperature. After completion of the reaction, HCl solution (1.0 M) was added to control the pH = 2. The solution was exacted with ethyl acetate (3 × 20 mL), and the collected extract was dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent gave compound 9 as a brown oil. Yield: 0.82 g, 83%. <sup>1</sup>H NMR  $\delta$  (ppm in CDCl<sub>3</sub>): 7.06 (m, 12H, aromatic C–H), 2.33 (s, 6H, –CH<sub>3</sub>).

General Procedure for Preparation of [OO-ph-N], [OS-ph-N], [SS-ph-N]. A solution of sodium methoxide (0.50 mmol) in 10 mL of methanol was transferred to a solution of  $Mo_2(DAniF)_3(O_2CCH_3)$  (0.25 mmol) and 4-(di-*p*-tolylamino)-benzoic acid (0.25 mmol) for [OO-ph-N] or (4-(di-*p*-tolylamino)-thiobenzoic acid for [OS-ph-N] or 4-(di-*p*-tolylamino)-dithiobenzoic acid for [SS-ph-N] in 30 mL of THF. The solution was stirred at room temperature for 5 h. All volatiles were removed under a vacuum, and the residue was extracted with 20 mL of dichloromethane and filtered through a Celite-packed funnel. After removal of the solvent from the filtrate, the residue was washed with ethanol (3 × 15 mL) and collected by filtration. The resulting product was dried under a vacuum.

Yield of [OO-ph-N]: 0.21 g (67%). Yellow powder. <sup>1</sup>H NMR  $\delta$  (ppm in CDCl<sub>3</sub>): 8.48 (s, 1H, -NCHN-), 8.38 (s, 2H, -NCHN-), 8.14 (d, 2H, aromatic C-H), 7.10 (q, 10H, aromatic C-H), 6.64 (q, 16H, aromatic C-H), 6.48 (d, 4H, aromatic C-H), 6.27 (d, 4H, aromatic C-H), 3.74 (d, 18H, -OCH<sub>3</sub>), 2.34 (s, 6H, -CH<sub>3</sub>). UV-vis,  $\lambda_{max}$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 407 (30387). Anal. Calcd for C<sub>66</sub>H<sub>63</sub>N<sub>7</sub>O<sub>6</sub>O<sub>2</sub>Mo<sub>2</sub>: C, 63.67; H, 5.06; N, 7.88. Found: C, 63.57; H, 5.13; N, 7.91.

Yield of [**OS**-**ph**-**N**]: 0.24 g (74%). Red powder. <sup>1</sup>H NMR δ (ppm in CDCl<sub>3</sub>): 8.46 (s, 1H, -NCHN-), 8.37 (s, 2H, -NCHN-), 8.13 (d, 2H, aromatic C-H), 7.11 (q, 8H, aromatic C-H), 6.97 (d, 2H, aromatic C-H), 6.63 (m, 20H, aromatic C-H), 6.20 (m, 4H, aromatic C-H), 3.73 (t, 18H, -OCH<sub>3</sub>), 2.35 (s, 1H, -CH<sub>3</sub>). UV-vis,  $\lambda_{max}$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 514 (35521). Anal. Calcd for C<sub>66</sub>H<sub>63</sub>N<sub>7</sub>O<sub>6</sub>OSMo<sub>2</sub>: C, 62.07; H, 4.94; N, 7.68. Found: C, 62.00; H, 4.89; N, 7.81.

Yield of [**SS**-**ph**-**N**]: 0.28 g (85%). Green powder. <sup>1</sup>H NMR  $\delta$  (ppm in CDCl<sub>3</sub>): 8.46 (s, 1H, -NCHN-), 8.33 (s, 2H, -NCHN-), 8.24 (d, 2H, aromatic C-*H*), 7.10 (q, 8H, aromatic C-*H*), 6.95 (d, 2H, aromatic C-*H*), 6.64 (q, 16H, aromatic C-*H*), 6.44 (d, 4H, aromatic C-*H*), 6.12 (d, 8H, aromatic C-*H*), 3.74 (d, 18H, -OCH<sub>3</sub>), 2.35 (s, 6H, -CH<sub>3</sub>). UV-vis,  $\lambda_{max}$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 604 (60522). Anal. Calcd for C<sub>66</sub>H<sub>63</sub>N<sub>7</sub>O<sub>6</sub>S<sub>2</sub>Mo<sub>2</sub>: C, 60.49; H, 4.81; N, 7.49. Found: C, 60.41; H, 4.30; N, 7.62.

#### ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00913.

<sup>1</sup>H NMR spectra and DFT calculations data (PDF)

#### Accession Codes

CCDC 1551557–1551559 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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