

Probing Triplet State Properties of Organic Chromophores via Design and Synthesis of Os(II)-Diketonate Complexes: The Triplet State Intramolecular Charge Transfer

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Received: October 14, 2004

We report the probe of specific triplet state properties of organic chromophores that are otherwise inaccessible in low viscous solution. The prototypical example demonstrated here is [Os(CO)₃(Cl)(NDP)] (**1**) ((NDP)H = 2-naphthyl-7-dimethylanilino-1,3-propanedione), which, upon electronic excitation, undergoes intramolecular charge transfer in both S₁ and T₁ manifolds of NDP. The dipolar changes in S₁ and T₁ monitored via the solvatochromism for both fluorescence and phosphorescence were deduced to be 18.0 and 11.9 D, respectively. The appreciable difference in the dipolar change can be qualitatively rationalized by different extents of charge-transfer character between S₁ and T₁ states. The results led to the probe of other reactions in triplet manifold feasible.

Third-row heavy metal containing luminescent complexes have increasingly gained attention due to their potential applications in electroluminescent devices.¹ The strong spin–orbit coupling effectively promotes an intersystem crossing from singlet excited states to lower triplet emitting states, namely ³MLCT, ³ππ*, or a mixture of the two.² The resulting materials are suitable for use in the preparation of OLEDs with unprecedented phosphorescence efficiencies attained by harnessing both triplet and singlet excitons, theoretically giving 100% internal quantum efficiency.³

We here would like to advance another angle of approach toward probing the fundamentals of the triplet-state properties based on the design of Os(II) complexes. Our strategy is to functionalize ligands connected to the heavy metal, so that the lowest triplet-state energy level can be fine tuned and thus lie mainly in the ππ* (or nπ*) chromophore of the designated ligand. On this basis, one can ingeniously design a special type of triplet-state reaction, the associated properties of which can thus be dictated by the prominent phosphorescence. A case in point is the triplet state intramolecular charge transfer (TSICT) reaction,⁴ the investigation of which is rare due to the spin forbidden nature of the T₁ → S₀ transition. Several methods have been employed to circumvent the lack of phosphorescence in solution. The micelle or polymer encapsulated organic chromophore, together with the external heavy atom effect, may resolve room-temperature phosphorescence.⁵ However, the resulting heterogeneous and rigid environments make studies of the solvation-associated properties impractical. As a result, photophysical properties associated with TSICT, such as the solvation relaxation dynamics as well as the steady-state consequence, e.g., the phosphorescence solvatochromism, are not attainable in low viscous solvents. To achieve this goal, we have designed and synthesized an asymmetrical β-diketonate ligand, composed of an *N,N*-dimethylaniline moiety that serves as the electron donor,⁶ and obtained the corresponding Os(II) carbonyl–metal complexes. The addition of back π-bond

donating carbonyl ligands should further increase the d–d energy gap,⁷ so that the organic chromophore of interest, i.e., β-diketonate, is expected to lie in the lower-lying excited states. The β-diketonate ligand with both donor and acceptor substituents was synthesized through a Claisen condensation reaction, in which treatment of 2-acetonaphthone and 4-dimethylanilino-benzoic acid ethyl ester in the presence of a strong base NaH gives the desired diketone, 2-naphthyl-7-dimethylanilino-1,3-propanedione (NDP)H. To prepare the Os(II)–metal complexes, we selected the literature method designed for the related dibenzoylmethanate complex [Os(CO)₃(tfa)(dbm)], tfa = CF₃CO₂[−] and (dbm)H = dibenzoylmethane.⁸ In this approach, heating the finely pulverized solid-state mixture of (NDP)H and osmium dimer [Os₂(CO)₆(tfa)₂] afforded [Os(CO)₃(tfa)(NDP)] (**1a**). Treatment of **1a** with NaCl in refluxing THF solution afforded the ligand substitution product [Os(CO)₃(Cl)(NDP)] (**1**) in ~80% yield. Moreover, treatment of (NDP)H with BPh₃ in THF solution at room temperature gave the respective BPh₂ complex **2** in 90% yield (see Supporting Information).

Figure 1 shows absorption and emission spectra of complex **1** in various solvents. As solvent polarity increased, in contrast to a slight bathochromic shift of the absorption spectral features, a drastic solvatochromic dependence in emission spectra was observed. In aerated cyclohexane, **1** exhibited distinct dual emission with λ_{max} at 470 and 570 nm. While the intensity of the 470 nm band remained unchanged, the 570 nm band revealed drastic O₂-concentration dependence and became dominant in the degassed solution (see Figure 1). The O₂ quenching rate was calculated to be as large as 1.4 × 10⁹ M^{−1} s^{−1} (Supporting Information). Accordingly, the 470 and 570 nm bands in **1** unambiguously are ascribed to the fluorescence and phosphorescence, respectively. Table 1 lists the photophysical properties of the studied complexes. In degassed cyclohexane the phosphorescence lifetime for **1** was measured to be ~60 μs. This, in combination with a near unity of the phosphorescence quantum yield, renders a radiative lifetime of ~60 μs, which is much shorter than that of the triplet ππ* for the free NDPH ligand (~0.1 s measured in the 77 K methylcyclohexane glass). The results support the enhancement of the T₁ → S₀ transition

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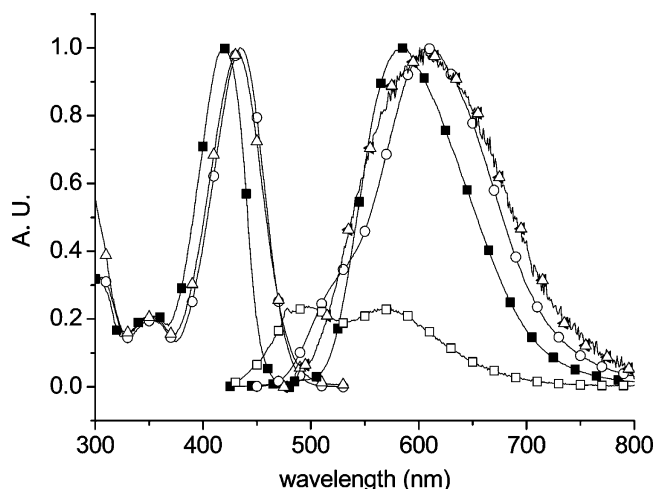


Figure 1. Absorption and steady-state emission spectra of **1** at 298 K degassed cyclohexane (■), dichloromethane (○), and acetonitrile (△). (□) denotes the emission spectrum of **1** in aerated cyclohexane.

TABLE 1: Photophysical Properties of Complexes 1, 1a, and 2

		λ_{abs}	$\lambda_{\text{em}}^{\text{max } a}$ (nm)	$\lambda_{\text{em}}^{\text{max } b}$ (nm)	$\Phi^{b,c}$	τ_f^a	τ_p^b
1	C ₆ H ₁₂	424	470, 570	574	~1	15.4 (ps) ^d	60 (μ s)
	C ₆ H ₆	432	508	593	0.84	15.6 (ps) ^d	125 (μ s)
	THF	430	537	609	0.40	104 (ps)	74 (μ s)
	CH ₂ Cl ₂	436	543	611	0.58	110 (ps)	86 (μ s)
	CH ₃ CN	422	580	649	0.005	22.0 (ps) ^d	70 (μ s)
1a	C ₆ H ₁₂	419	497, 583	577	~1	5.13 (ps) ^d	105 (μ s)
	CH ₂ Cl ₂	435	532	603	0.61	113 (ps)	201 (μ s)
	CH ₃ CN	432	575	646	0.015	8.52 (ps) ^d	50 (μ s)
2	C ₆ H ₁₂	434	467	467	0.12	1.23 (ns)	
	CH ₂ Cl ₂	461	537	537	0.39	1.07 (ns)	
	CH ₃ CN	466	572	572	0.005	0.21 (ns)	

^a Data were obtained in aerated solution. ^b Data were obtained in degassed solution (via three freeze–pump–thaw cycles). ^c Quantum yield was obtained for fluorescence plus phosphorescence. ^d Due to the system response of 30 ps, these values obtained from curve fitting are subject to large uncertainties.

dipole in **1** due to the Os heavy atom effect. Conversely, the fluorescence lifetime of **1** in cyclohexane is beyond the system response of 30 ps (see Table 1). In comparison, the boron complex **2** (see Scheme 1) bearing the same NDP ligand exhibits a unique fluorescence, the lifetime of which is as long as 1.23 ns in cyclohexane. Assuming that the relaxation dynamics of S₁ in **1** is dominated by rate of S₁ → T_n, the results also manifest the enhancement of spin–orbit coupling on the S₁ → T_n intersystem crossing due to the Os heavy atom effect.

In degassed, polar solvents, fluorescence and phosphorescence strongly overlap, giving rise to a broad emission (Figure 1). Fortunately, as shown in Table 1, the different relaxation dynamics of fluorescence and phosphorescence allow us to temporally resolve each component (Supporting Information). In the degassed solution, the spectrum taken at a delayed time of 5 μ s after the excitation ensures the acquisition of phosphorescence free from fluorescence interference. Conversely, gating the time-resolved spectrum at the first ~10 ns should obtain a nearly phosphorescence-free fluorescence. The results shown in Figure 2 clearly reveal remarkable solvent dependency, and the plot of peak frequency for both fluorescence and phosphorescence is linearly proportional to solvent polarity (Δf)⁹ (see inset of Figure 2). Accordingly, changes in dipole moment with respect to the ground state were deduced to be 18.0 and 11.9 D for S₁ and T₁, respectively, with the Lippert–Mataga equation.^{10,SI}

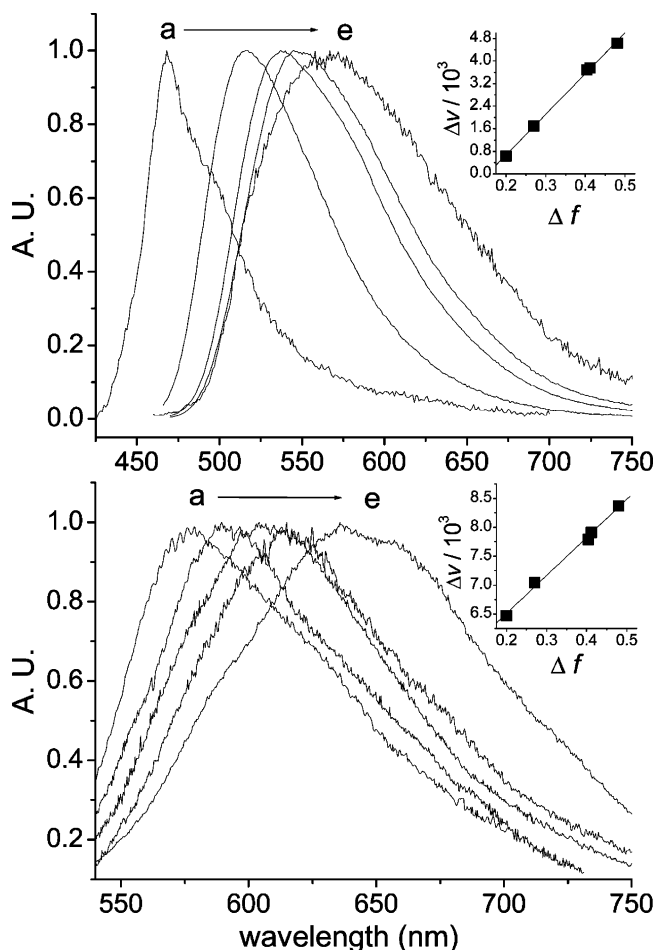


Figure 2. Time-gated fluorescence (upper) and phosphorescence (lower) of **1** in degassed (a) C₆H₁₂, (b) C₆H₆, (c) CH₂Cl₂, (d) THF, and (e) CH₃CN. (inset) The plot of peak frequency versus solvent polarity Δf .

SCHEME 1: Complexes 1–2 and the Proposed Prototypes to Study Charge (3) and Proton (4) Transfer in the Triplet State

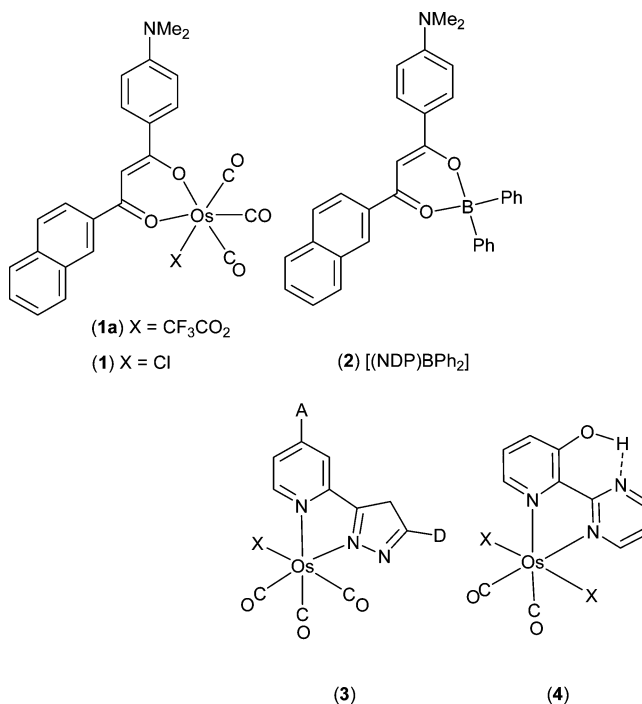
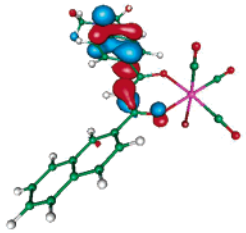
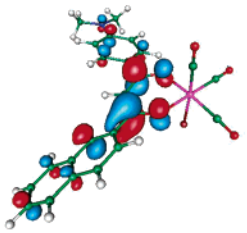
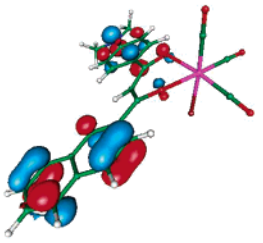
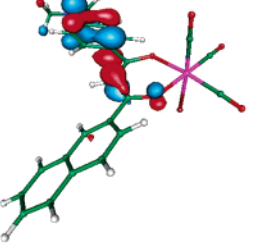
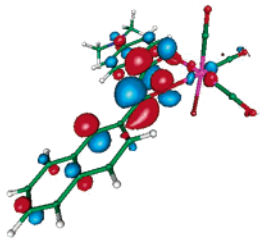


TABLE 2: Calculated Electronic Transitions and Associated Frontier Orbitals for Complex **1**^a

A	Transition	Energy Gap, eV	Molecular Orbital Contribution	Oscillator Strength
	S ₁	3.10	HOMO → LUMO	0.6075
		(HOMO)		(LUMO)
				
B	Transition	Energy Gap, eV	Molecular Orbital Contribution	Oscillator Strength
	T ₁	1.74	HOMO → LUMO (90%) HOMO-1 → LUMO (10%)	N/A
		(HOMO-1)	(HOMO)	(LUMO)
				

^a A. TD-B3LYP method based on the geometry optimized S₀ state (B3LYP). B. TD-B3LYP method based on the geometry optimized T₁ state (UB3LYP).

As shown in Table 1, a similar ICT reaction was observed for **1a**, in which the axial ligand in **1** is replaced by CF₃CO₂[−], and the dipolar changes for S₁ and T₁ were derived to be 17.8 and 11.8 D, respectively. In comparison, only fluorescence solvatochromism resulting from ICT in the excited singlet state was observed for boron complex **2**, and the calculated dipolar change of 18.4 D is consistent with that in **1** (or **1a**) (Supporting Information).

The appreciable difference in the dipolar change is intriguing, as it may imply the intrinsic difference in the electron density distribution between S₁ and T₁ for both **1** and **1a**. To show such a possibility, Table 2 depicts the composition and structures of the crucial frontier molecular orbitals for **1** involved in the transition of low-lying excited states using the TD-B3LYP//B3LYP/6-31G(d', p') method (Supporting Information). With this method, the Franck–Condon excitation energy from the ground state to the S₁ state was calculated to be 3.1 eV (400 nm), which is qualitatively consistent with the corresponding experimental results of 424 nm (S₁) in cyclohexane. Since the phosphorescence originates from the geometry-relaxed T₁ state, we also performed the geometry optimization of the T₁ state, followed by a single-point calculation of the T₁–S₀ transition. As shown in Table 2, differences in the frontier orbital configuration between S₁ and T₁ are immediately discernible. The HOMO and LUMO frontier orbitals in the singlet manifold

possess a π configuration in the amino phenyl ligand and a π^* pattern mainly in the 2-naphthyl ligand. One thus would expect that the S₀ → S₁ transition incorporated an electron-transfer process from the amino phenyl group to the 2-naphthyl moiety.¹¹ In contrast, although to a large extent (90%) similar HOMO and LUMO are involved in the S₀ → T₁ transition, contribution from other frontier orbitals are also substantial. The involvement of HOMO-1 orbital possessing a π configuration of the 2-naphthyl and MLCT is ~10% (Supporting Information). Different extents of charge transfer character render distinctly different solvatochromism effects, as observed experimentally.

The success in probing TSICT in complexes **1** and **1a** warrants the design of other TSICT prototypes, among which complex **3** bearing various degrees of donor/acceptor substituents (Scheme 1) should receive considerable attention due to their facile syntheses.¹² The Os(CO)_n fragment can thus be exploited as a building block to probe other types of reactions in the triplet manifold. For example, theoretical approaches have predicted that, relative to the fast excited-state proton transfer (ESPT) in the singlet state, the triplet-state proton transfer should be much slower due to the decrease in proton acidity.¹³ Unfortunately, cases of triplet state proton transfer are very rare¹⁴ because of the fast, dominant proton-transfer process in the singlet-excited state. If the rate of S₁ → T_n ISC can compete with the proton-transfer rate in a singlet manifold, studies of

the triplet-state proton-transfer become feasible. Accordingly, a proposed structure like complex **4**, in which the phenol-ligand is expected to undergo ESPT, forming a quinone isomer,¹⁵ should be intriguing to probe the proton-transfer dynamics in the triplet state manifold. We thus believe that results presented in this study can spark a broad range of interest in both fundamental approach and synthetic field relevant to third-row transition metal complexes.

Acknowledgment. This work was supported by the National Science Council, Taiwan, R.O.C. (NSC93-2119-M-002-002). We thank the National Center for High-Performance Computing, Taiwan, for the use of their facility.

Supporting Information Available: Syntheses, photophysical experimental details, the Lippert–Mataga plot, and crystal data of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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