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1000-Fold Enhancement of Luminescence Lifetimes via Energy-Transfer Equilibration with the T_1 State of Zn(TPP)

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The new zinc porphyrin/tungsten alkylidyne dyad Zn(TPP)−C≡CC_6H_4C≡W(dppe)$_2$Cl (**1**) possesses novel photophysical properties that arise from a tunable excited-state triplet−triplet equilibrium between the porphyrin and tungsten alkylidyne units. Dyad **1** exhibits $^3(d_{xy} \leftarrow \pi^*(\mathrm{WCR}))$ phosphorescence with a lifetime that is 20 times longer than that of the parent chromophore W(CC_6H_4-CCPh)(dppe)$_2$Cl (**2**). The triplet−triplet equilibrium can be tuned by the addition of ligands to the Zn center, resulting in phosphorescence lifetimes for **1**(L) that are up to 1300 times longer than that of **2**. The "lifetime reservoir" effect exhibited by **1**(L) is approximately 1 order of magnitude larger than previously reported examples of the phenomenon.

Controlling the excited-state lifetimes of luminescent transition-metal compounds is essential for optimizing them for applications such as artificial photosynthesis, sensing, and optoelectronics. One general approach to enhancing emission lifetimes is to append to the emissive complex a chromophore that possesses a longer-lived excited state of energy comparable to that of the emitting state, such that thermal equilibrium between the emissive and longer-lived pendant states enables the latter to serve as a "lifetime reservoir".[1] Nearly all prior examples of this phenomenon have employed aromatic hydrocarbons as reservoirs because their long-lived triplet states are energetically well matched to the emissive metal-to-ligand charge-transfer (MLCT) states of the ubiquitous metal diimine luminophores [e.g., Ru(bpy)$_3^{2+}$].[1] Emission lifetimes in weakly coupled assemblies of this type are typically extended by 2−40-fold relative to the parent complexes and, in a few cases, by up to 100-fold.[2] These effects can be further modulated by designing systems in which more than two excited states are in equilibrium.[3]

In considering the development of lifetime reservoirs suitable for use with other metal luminophores, zinc porphyrin complexes stand out as interesting candidates: they possess long-lived triplet states [$\tau(T_1) \sim 1$ ms] whose energies are compatible with those of common red-emitting chromophores;[4] unlike conventional organic lifetime reservoirs, their excited-state energies can be finely tuned via zinc ligation;[5] they can be fashioned into a wide variety of efficient light-harvesting assemblies.[6,7] We are aware of only one prior report of the use of a metalloporphyrin as a lifetime reservoir; in this system, the emission lifetime of the appended luminophore was lengthened slightly (2.5-fold).[8] In view of the desirable features noted above, however, further exploration of zinc porphyrin reservoirs seems justified. Here we report the photophysical properties of dyad **1** (Chart 1), which consists of a zinc tetraphenylporphyrin [Zn(TPP)] moiety attached to the phosphorescent tungsten alkylidyne unit W(≡CC_6H_4-CCC_6H_4−)(dppe)$_2$Cl [hereafter, W(CAr)(dppe)$_2$Cl, where

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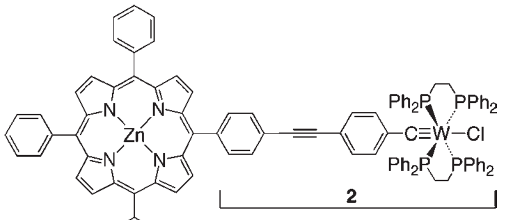
Chart 1. Dyad **1** and Model Compound **2**



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dppe = 1,2-bis(diphenylphosphino)ethane], and of its zinc-ligated derivatives **1**(L). These assemblies exhibit extremely large “lifetime reservoir” effects, with emission lifetime enhancements of up to 1300 times.

Dyad **1** was prepared by the palladium-catalyzed coupling of Zn(TPP-mono-*p*-I)[9] with $W(CC_6H_4CCH)(dppe)_2Cl$,[10] purified by column chromatography, and characterized by ^1H, ^{13}C, and ^{31}P NMR and elemental analysis.[10] The compounds Zn(TPP) and $W(CC_6H_4CCPh)(dppe)_2Cl$[10] (**2**; Chart 1) were used as model chromophores for the two subunits of the dyad.

The porphyrin and $W(CAr)(dppe)_2Cl$ units of **1** are weakly electronically coupled, as evidenced by the fact that the electronic absorption spectrum of **1** (Figure 1) is essentially a composite of the spectra of Zn(TPP) and **2**. Specifically, the spectrum exhibits porphyrinic Q (λ_{max} = 590 and 551 nm) and Soret bands (425 nm) at wavelengths within 2 nm of those observed for Zn(TPP) and, from the $W(CAr)(dppe)_2Cl$ unit, a shoulder at ~370 nm arising from the $^1(\pi \rightarrow \pi^*)$ transition and a weak tail at λ > 625 nm due to the $^1(d_{xy} \rightarrow \pi^*)$[11] transition, similar to those for **2** at 386 and 604 nm, respectively. The facts that the electronic transitions of Zn(TPP) and **2** are only subtly perturbed in **1** and that no new features are observed (apart from a slight broadening of the Soret band) indicate that the emission properties of **1** are likely to be derived from excited states analogous to those of Zn(TPP) and **2** rather than from a new excited state delocalized across **1**.

In accordance with this expectation, **1** exhibits dual emission bands in toluene solution at room temperature (Figure 2) that are attributable to fluorescence from the porphyrin moiety and phosphorescence from the $W(CAr)(dppe)_2Cl$ unit. The fluorescence band maxima (598 and 648 nm) are similar to those for Zn(TPP) (600 and 649 nm), but the quantum yield is > 100 times smaller [$\phi_{fl} < 10^{-4}$ versus 0.033 for Zn(TPP) in toluene];[12] quenched fluorescence in other zinc porphyrin compounds with transition-metal substituents has been attributed to enhanced intersystem crossing between the porphyrin S_1 and T_1 states.[7] The phosphorescence band due to the tungsten center (λ_{max} = 805 nm and $\phi_{ph} = 3.2 \times 10^{-3}$) closely resembles the $^3(d_{xy} \leftarrow \pi^*)$ band observed for **2** (λ_{max} = 776 nm and $\phi_{ph} = 5.4 \times 10^{-3}$), and its excitation spectrum matches the absorption spectrum of **1** over the 350−600 nm wavelength range. This latter result indicates that the excitation energy is transferred efficiently from porphyrin excited states to the phosphorescent tungsten excited state because the absorbance across most of this region is >99% porphyrin-localized.

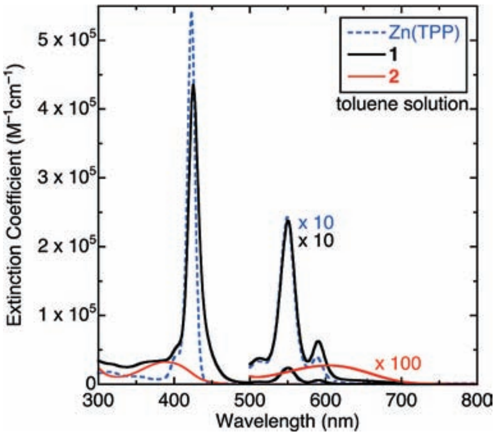

Figure 1. Electronic absorption spectra of **1** and model compounds Zn(TPP) and **2** in toluene solution at room temperature.

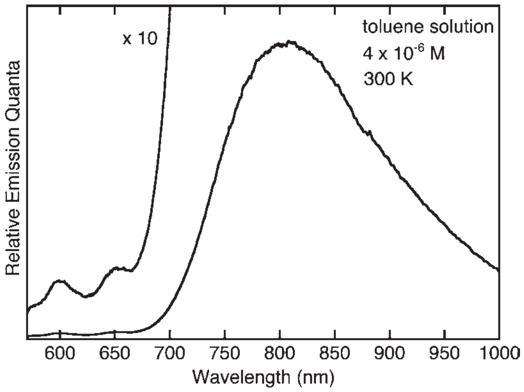

Figure 2. Emission spectrum of **1** in toluene solution at room temperature.

A striking feature of the phosphorescence of **1** is that its lifetime (τ_{ph} = 2.0 μs, toluene, 21 °C) is nearly 20 times longer than that of parent complex **2** (τ_{ph} = 106 ns) and more than double that of any previously reported metal alkylidyne complex (M = Mo, W, Os) with an emissive $^3(d_{xy} \leftarrow \pi^*)$ state.[11] The enhanced lifetime of **1** compared to **2** can be accounted for by a thermal equilibrium between the emissive $^3(d_{xy} \leftarrow \pi^*)$ state of the tungsten fragment and the longer-lived (τ = 1.25 ms),[4] nonemissive T_1 state of the porphyrin moiety. Given that the onset of the phosphorescence of **1** is in the 700−750 nm region, it is inferred that the T_1 state of Zn(TPP) [$E(T_1)$ = 12 985 cm^{-1}][5a] lies ca. 400−1300 cm^{-1} lower in energy than the $^3(d_{xy} \leftarrow \pi^*)$ state. Application of the standard kinetic model for “lifetime reservoir” systems[1] provides a calculated triplet−triplet energy gap of 600 cm^{-1}, consistent with the spectroscopic estimate and indicates that the triplet-state population of the Zn(TPP) and $W(CAr)(dppe)_2Cl$ units lies in the ratio 19:1.[10] Consistent with this, the transient absorption spectrum of **1** is dominated by a broad absorption (λ_{max} = 475 nm) similar to that observed for the T_1 state of Zn(TPP)[13] but with a lifetime identical with that of the tungsten emission. Transient absorptions attributable to the $W(CAr)(dppe)_2Cl$ unit are not observed.

In view of the fact that the excited-state energies of Zn(TPP) are modestly perturbed ($\Delta E \cong$ 1000 cm^{-1}) upon the

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Table 1. Spectroscopic and Photophysical Properties of **1** and **1**(L)[a]

	absorption (nm)			emission		
compound	Soret	Q(1,0)	Q(0,0)	λ_{fl} (nm)	λ_{ph} (nm)	$\tau_{\mathrm{ph}}{}^{b}$ (μs)
1	425	551	590	598, 649	805	2.0
1(py)	431	563	604	613, 667	784	103
1(dmap)	433	566	608	623, 670	777	139
1(pic)	432	564	605	618, 671	783	77
1(im)	433	566	608	623, 671	783	78

[a] Samples of **1**(L) were prepared from the following mixtures of **1** and L. **1**(py): 3×10^{-6} M **1** and 2.2×10^{-2} M pyridine. **1**(dmap): 1×10^{-5} M **1** and 1.7×10^{-2} M 4-(dimethylamino)pyridine. **1**(pic): 1×10^{-5} M **1** and 1.6×10^{-2} M 4-picoline. **1**(im): 2×10^{-5} M **1** and 6.2×10^{-3} M imidazole. [b] $\lambda_{\mathrm{ex}} = 532$ nm.

addition of ligands to the Zn center,[5a,14] it seemed reasonable to expect that ligation to zinc in **1** would provide a means to control the triplet−triplet energy gap and, thus, optimize the "lifetime reservoir" effect. This hypothesis was investigated using the ligands pyridine, 4-picoline (pic), 4-(dimethylamino)pyridine (dmap), and imidizole (im), which coordinate to Zn(TPP) with binding constants of 10^3-10^4.[15] The electronic spectra of **1** in toluene in the presence of sufficient ligand to produce >99% **1**(L) exhibit shifted Q, Soret, and porphyrin fluorescence bands that lie within 2−3 nm of those for Zn(TPP)(L) (Table 1). All **1**(L) complexes exhibit phosphorescence bands arising from the W(CAr)(dppe)$_2$Cl unit; phosphorescence excitation spectra reproduce the shifted **1**(L) absorption bands, demonstrating that the emission arises from these adducts and not unligated **1**. Strikingly, the phosphorescence lifetimes of **1**(L) at room temperature are much longer again than those of **1**, lying in the 77−139 μs range (Table 1). These effects are reversible; removal of the ligand in vacuo restores the 2.0 μs lifetime of **1**. Relative to the 106 ns lifetime of **2**, the lifetimes of **1**(L) are lengthened by 700−1300-fold. This "lifetime reservoir" effect is 1 order of magnitude larger than any previously reported for a weakly coupled luminophore−reservoir system.[1] We are presently examining the details of the energy-transfer processes of **1** and **1**(L) using time-resolved spectroscopy.

Enhancement of the emission lifetime of **2** over a 3 order of magnitude range in **1** and **1**(L) indicates that Zn(TPP) is a useful and tunable lifetime reservoir for red-emitting luminophores. Given the broad synthetic control that can be exerted over metalloporphyrin excited-state energies, their excellent light-harvesting properties, and the variety of ways in which metal complexes may be peripherally coordinated to porphyrins,[16] the construction of luminophore−porphyrin assemblies should be an especially flexible and powerful means to optimizing the luminescence properties of metal compounds for applications.

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Supporting Information Available: Synthetic procedures and characterization data for **1** and **1**(L) and kinetic analysis of the triplet−triplet equilibrium of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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