

Structural Control of the Excited-State Dynamics of Bis(dipyrrinato)zinc Complexes: Self-Assembling Chromophores for Light-Harvesting Architectures

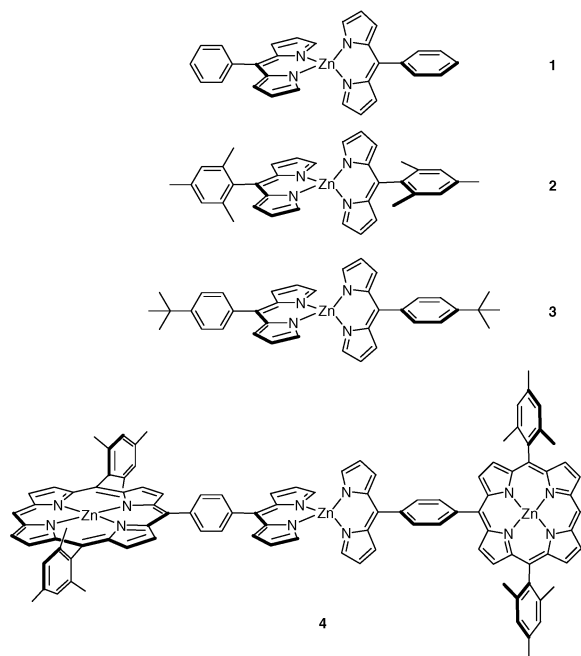
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We have been exploring the photophysical properties of bis(dipyrrinato)metal complexes to elucidate their potential as self-assembling antenna pigments and structural elements in synthetic light-harvesting architectures.¹ Bis(dipyrrinato)-metal complexes, first reported by Fischer in 1924,² have generally been regarded as nonfluorescent. We show here that replacement of the phenyl rings at the 5,5'-positions of bis(dipyrrinato)zinc complex **1** with mesityl groups in **2** (Chart 1) transforms the molecule from a very weak emitter that deactivates within ~ 100 ps of photoexcitation to a highly fluorescent chromophore with a multianosecond singlet excited-state lifetime. In contrast, the 5,5'-(*p*-*tert*-butylphenyl)-substituted complex **3** has properties virtually identical to those of **1**. These results demonstrate that steric constraints on aryl-ring internal rotation dramatically alter the excited-state properties of 5,5'-aryl-substituted bis(dipyrrinato)metal complexes. These insights establish the foundation for tuning the photophysical properties of these chromophores for use in diverse photochemical applications.

Chart 1



One approach to emulate natural photosynthetic antenna complexes is to utilize chromophores that self-assemble into persistent

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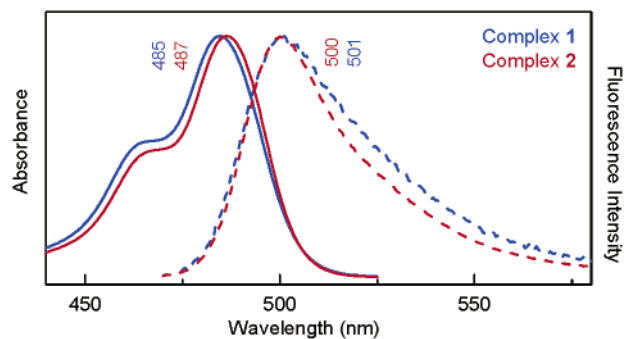


Figure 1. Absorption spectra (—) and fluorescence spectra (---) obtained using 480 nm excitation for **1** (blue) and **2** (red) in toluene at room temperature.

organized architectures. Porphyrins have been widely employed in synthetic light-harvesting systems,³ both alone and in combination with accessory pigments to increase spectral coverage.⁴ Recently, we found that porphyrins bearing a 5-phenyl-substituted dipyrrin in the presence of zinc acetate spontaneously form triad **4** composed of two porphyrins and an intervening bis(dipyrrinato)zinc complex.¹ The zinc dipyrrin moiety absorbs light between the porphyrin near-UV and visible bands, and transfers excited-state energy to the porphyrins in ~ 2 ps with 99% yield. Thus, the bis(dipyrrinato)-zinc complex in such triads serves the dual roles of a self-assembling architectural element (linker) and an accessory pigment.

As a foundation for extending this strategy, we have undertaken studies of simple 5,5'-aryl-substituted bis(dipyrrinato)metal complexes (e.g., **1**–**3**)¹ to elucidate their photophysical properties.^{5,6} The replacement of phenyl with *p*-*tert*-butylphenyl or mesityl groups has relatively small effects on the absorption characteristics of the bis(dipyrrinato)zinc complexes. The intense ($\epsilon \approx 115\,000\text{ M}^{-1}\text{ cm}^{-1}$) absorption band lies in the range 482–487 nm in toluene at room temperature (Figure 1; —). The fluorescence profile for each complex is approximately mirror symmetric to the absorption contour, although the apparent vibronic overtone feature is less prominent in emission (Figure 1; ---). In each case, although there is modest absorption-emission overlap, there is a considerable Stokes shift between the maxima (660, 580, 940 cm^{-1} for **1**, **2**, **3** in toluene). These and other observations indicate that the chromophores undergo excited-state relaxations (conformational, vibrational, electronic) prior to a substantial fraction of the photon output observed in the steady-state emission spectrum. In this regard, the absorption and emission widths and Stokes shift are somewhat reduced for **2** as compared to **1** (and **3**), reflecting less conformational freedom in the ground or excited states or both due to the steric hindrance present in **2**.

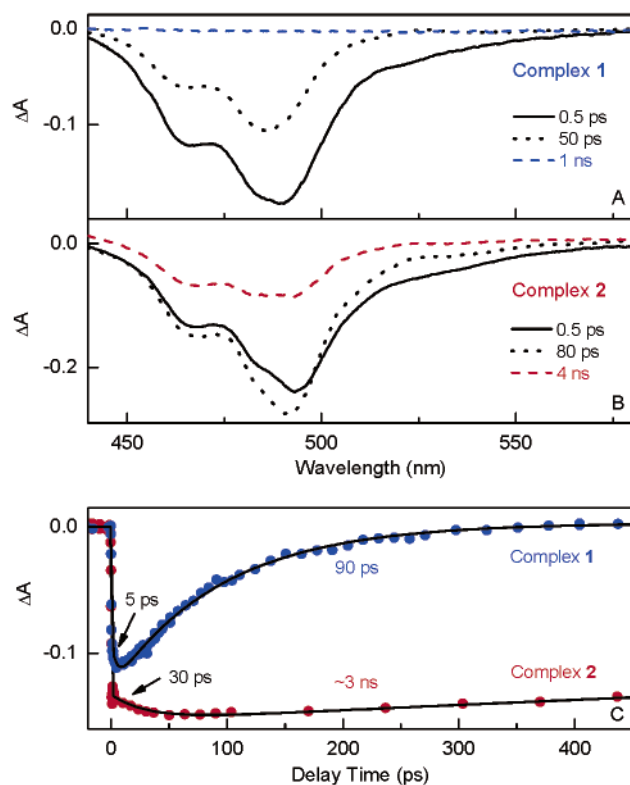


Figure 2. Transient absorption data for complexes in toluene at room temperature. Absorbance difference spectra from combined data sets using 130-fs excitation flashes (A) at 454 and 500 nm for **1** or (B) 456 and 500 nm for **2**. (C) Kinetic profiles and fit (convolution of instrument response, two exponentials, and a constant) for data taken to 4 ns at 483 nm for **1** and at 486 nm for **2**. The average time constants given in the text were obtained using several probe wavelengths.

Complex **3** has virtually the same low fluorescence quantum yield as the parent **1** ($\Phi_f = 0.007$ versus 0.006 in toluene), whereas complex **2** emits strongly with an ~ 50 -fold larger fluorescence yield ($\Phi_f = 0.36$). The key difference is that the 2,6-dimethyl groups on the aryl ring in **2** strongly hinder internal rotation of this ring with respect to the dipyrin framework. Analogous differences are found for the excited-state lifetime of **2** versus **1** and **3** (Figure 2). In particular, a lifetime of 90 ± 10 ps (in toluene) was determined for **1** from transient absorption measurements. In contrast, the same measurements for **2** gave a lifetime of 3 ± 1 ns, in good agreement with the value of 2.7 ± 0.3 ns determined by fluorescence decay.

The time-resolved absorption studies also revealed significant differences in the rates and yields of the nonradiative excited-state decay pathways for **2** as compared to **1** (and **3**). The salient features of the transient absorption spectra are as follows:

(1) At very short times (0.5 ps) after a 130-fs excitation flash, **1** and **2** exhibit similar absorption difference spectra that contain bleaching of the ground-state absorbance bands plus excited-state stimulated emission (Figure 2A and 2B; -). The initial spectrum for each complex is assigned primarily as the Franck-Condon form of the S_1 excited state, which gives way to the relaxed state (50–80 ps spectra in Figure 2A and 2B; •••) in 9 ± 3 ps for **1** and 25 ± 5 ps. This relaxation for **2** is accompanied by little competing deactivation to the ground state, as is evidenced by undiminished bleaching of the ground-state absorption bands.

(2) The relaxed S_1 excited state of **1** subsequently decays with a 90 ps time constant. This lifetime is dominated (>90%) by internal conversion to the ground state, which is evidenced by the uniform collapse of the difference spectrum to $\Delta A = 0$ between 50 ps and 1 ns (Figure 2A). In contrast, the relaxed S_1 excited state of **2** decays

in ~ 3 ns. This decay encompasses not only ground-state repopulation, but also formation ($\sim 30\%$ yield) of a longer-lived transient state that contributes substantially (along with the residual S_1 state) to the spectrum at 4 ns in Figure 2B (---). Based on the reduced stimulated emission relative to ground-state bleaching, a >5 ns lifetime, and the fact that charge-transfer states should be at high energy in these systems, the longer-lived transient is mostly likely the lowest triplet excited state, T_1 .

The rate constants for the fluorescence, internal conversion, and intersystem crossing decay pathways of the S_1 excited state can be estimated from the yields and S_1 lifetime for each molecule. For example, as compared to **1**, complex **2** has an ~ 2 -fold greater radiative rate [$0.36 \times (2.7 \text{ ns})^{-1}$ vs $0.006 \times (90 \text{ ps})^{-1}$] and an internal conversion rate that is at least 75-fold lower [$0.34 \times (2.7 \text{ ns})^{-1}$ vs $>0.9 \times (90 \text{ ps})^{-1}$]. Thus, the preponderant structural/electronic effect of hindered internal rotation of the 5,5'-aryl rings with respect to the dipyrin framework (by the mesityl groups in **2** vs phenyl groups in **1**) is to substantially slow nonradiative relaxation to the ground state. The consequence is to transform the bis(dipyrinato)zinc complex from one with very weak emission and a rapidly deactivating excited state to a strong emitter with a multianosecond excited-state lifetime. The dramatic increase in lifetime overcomes a potential limitation of the bis(dipyrinato)-metal complexes and affords greater latitude in the incorporation of these complexes into larger assemblies where high yields of energy transfer are desired.

The bis(dipyrinato)metal complexes are cousins of the dipyrinato-boron difluoride dyes (containing one boron complexed to a single dipyrin),⁷ which are highly fluorescent and have been widely used in biological applications. The bis(dipyrinato)metal complexes have heretofore been excluded from such applications because of their negligible fluorescence. On the other hand, the bis(dipyrinato)-metal complexes have the distinct advantage over the dipyrinato-boron difluoride dyes in self-assembling under mild conditions with a variety of transition metals. The ability to tune the excited-state characteristics of the bis(dipyrinato)metal complexes via relatively minor structural alterations should open the door to a number of applications, particularly where the combination of self-assembly and intense absorption/fluorescence in the visible region are desirable attributes.

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