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Article

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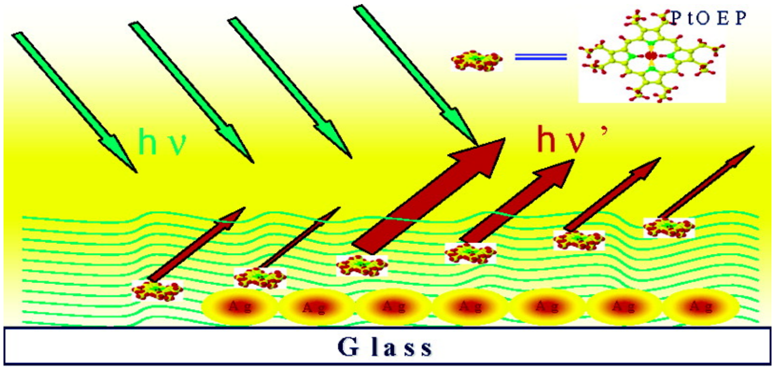

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Enhancement of Platinum Octaethyl Porphyrin Phosphorescence near Nanotextured Silver Surfaces

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Abstract: We observe more than a 200-fold increase in the photoexcited phosphorescent emission of PtOEP (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrin platinum II) in a polystyrene film on nanotextured silver surfaces, coincident with a reduction in the triplet state lifetime by a factor of 5. The large enhancement results in films with apparent luminescence quantum yields much greater than unity and can be understood in terms of increased radiative rates due to interactions between the molecules and the electron plasma in nearby silver nanoparticles. We study the photoluminescence efficiency, excitation spectrum, and decay dynamics as a function of film thickness and silver density. We use a model of the photophysics to decompose the phosphorescent enhancement into contributions from increases in absorption, emissive rate, and quenching. Quenching increases in importance for very thin films, and we conclude that ~3 nm spacing between metal and chromophore leads to the largest photoluminescence enhancement.

Introduction

Radiative processes in molecules can be dramatically altered when they are near rough metallic surfaces. The collective response of electrons in metal nanoparticles to optical fields, so-called plasmon resonance,[1−2] strongly affects the spectroscopy of nearby molecules.[3−6] Modifications of radiative rates can be understood in terms of local field enhancements near the metal particles or in a picture where the molecule borrows oscillator strength from the huge transition dipole of the plasmon resonance.[5] Very large enhancements of molecular fluorescence and Raman scattering have been observed since local fields can be increased by more than 3 orders of magnitude under ideal circumstances.[7−10] Therefore, optical processes linear in light intensity, such as absorption and emission, can in principle be accelerated by more than 6 orders of magnitude. Raman processes that involve both incident and scattered fields can be enhanced by 12 orders of magnitude, the underlying basis for the recent discovery of single molecule Raman scattering.[11−12]

It would be desirable to exploit electromagnetic enhancement phenomena by plasmons for biomolecular sensing or for fabrication of improved emissive devices, such as lasers or organic light-emitting diodes (OLEDs). In the context of biomolecular sensing, it may be possible to endow essentially nonemissive molecules of importance with good fluorescence quantum yield or to improve fluorescent tags that already have near unit quantum yields by effectively enhancing their absorption cross-sections. The latter strategy has the additional benefit of reducing the excited-state lifetime due to radiative rate enhancement, thereby reducing excited-state reactions that result in permanent photobleaching.[13] In the arena of emissive devices, such as OLEDs, it would be highly desirable to choose molecules on the basis of their stability under current flow or perhaps on the basis of their emission spectrum with less consideration of whether they have high luminescence quantum yield. In particular, enhancement of triplet emission would have high impact since spin statistics favor recombination to the molecular triplet state in OLEDs.[14] Speeding up phosphorescence in triplet-based OLEDs[15−20] is also desirable to avoid-

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saturation of emissive sites at high current, triplet−triplet annihilation, and triplet quenching by O_2.

A number of examples of emissive enhancement near silver surfaces have been documented[21−30] in a wide variety of systems varying from DNA[27] to erbium complexes[28] to CdSe quantum dots.[30] There is also theoretical work considering how molecular emission is affected near silver nanoparticles.[5] Nevertheless, the experimental observations are complicated by excited-state quenching processes such as electron transfer and dissipative energy transfer that are also introduced when molecules are placed near metals. Moreover, one expects radiative rate enhancement for both absorption and emission to play a role in increasing photoluminescence. For applications like enhancement of OLED emitters, it is important to separate these contributions since absorption enhancement is irrelevant when excited states are created by charge recombination. Previous work, however, has not adequately disentangled effects of absorption and emission enhancement on the observed luminescence. Many other important fundamental questions also remain unanswered, such as how the metallic plasmon resonance affects the molecular absorption and emission spectra and how the molecule should be situated with respect to the surface to optimize the tradeoff between quenching and enhancement.

In the present paper, we address these questions for the molecule PtOEP,[14,16,18−20] an important phosphorescent emitter in OLED technology that has well characterized spectroscopy and photophysics. PtOEP luminescence has also been used for oxygen pressure sensing[31] and as a temperature sensor.[32] We measure the absorption, photoluminescence, luminescence excitation spectra, and excited-state decay dynamics of films of PtOEP in a polymer binder that are made by spin casting onto nanotextured silver surfaces. In some cases, we observe 200 times greater enhancements in phosphorescence relative to that of analogous films without silver, leading to apparent quantum yields far exceeding unity. In the case of 200-fold increase in luminescence, we ascribe it to approximately 40 times absorption enhancement and 5 times enhancement due to increased phosphorescent rate with little quenching introduced by the silver. Film thickness dependent measurements suggest the optimal distance of the chromophores from the silver to be around 3 nm, and the spectroscopic data show that the enhancement factor is linked to the silver plasmon resonance spectrum.

Experimental Section

A detailed description of our substrate cleaning procedure can be found elsewhere.[33] We chose the Tollens "mirror" reaction to apply silver to glass substrates prior to spin casting polystyrene/PtOEP films on them. The Tollens reaction produces bare silver and can be adjusted to produce nanometer scale texture optimal for electromagnetic field concentration. Briefly, concentrated ammonium hydroxide was added to 30 mL of silver nitrate (0.1 M) while stirring. After the initially formed brown precipitate dissolved, 15 mL of 0.8 M KOH was added and additional concentrated ammonium hydroxide was added slowly to dissolve the precipitates. For nanotextured silver nanoparticle growth, equal amounts of the above solution and 0.5 M dextrose were mixed together and immediately drop cast on a clean glass substrate. Optically thick films form in 5 min under these conditions at room temperature. The density of the silver film was controlled by regulating reaction time. Exposure times were between 5 s and 2 min. We found that using starting solutions that had been stored in a refrigerator (at ∼5 °C) increased the observed luminescence enhancements relative to that of films made from solutions stored at 20 °C.

Toluene solutions with 0.05% PtOEP (0.48 mmol/L, porphyrin product, Frontier Scientific, MW = 727.84) codissolved with polystyrene (MW = 44 000, Aldrich Chemical) were used for film preparation where the film thickness is well controlled by adjusting the polymer concentration and spin casting speed to get desired film thickness. Spectroscopic ellipsometry of films cast as above onto silicon wafers was used to calibrate thickness and typically showed that each percent of polystyrene adds 2.7 nm thickness at a spin casting speed of 4000 rpm.

Extinction spectra were recorded using a Perkin-Elmer Lambda 19 UV−vis−NIR spectrometer with 2 nm resolution. Steady-state phosphorescence excitation spectra were taken with a SPEX Fluorolog-3 fluorimeter at 2 nm resolution. Decay dynamics of the phosphorescence were recorded with a photomultiplier tube and digital storage oscilloscope (Lecroy 9450A). The excitation for the transient measurements was with pulsed lasers. For S_0−S_1 excitation, we used a 10 Hz frequency doubled Nd:YAG laser (Spectra Physics DCR2, 532 nm, 10 ns pulse duration), and for S_0−S_2 excitation, we used a 2 Hz nitrogen laser-pumped dye laser (Photochemical Research Associates LN1000 and LN102, 366 nm, 200 ps pulse duration) with 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1-3,4-oxadiazole (PBD) dye in 1:1 toluene/ethanol. All photoluminescence data were taken with excitation and emission from the film side of the substrate.

Results and Discussion

1. PtOEP Spectroscopy and Photophysics. The absorption spectrum of PtOEP in solution (Figure 1) shows three well-resolved peaks.[34] The one around 380 nm is attributed to the S_0−S_2 transition (Q2 band), and the one at 530 nm is assigned to the S_0−S_1 transition (Q1 band). The small absorption around 490 nm is from the vibrational structure associated with carbon double-bond stretching in S_1. The emission spectrum of PtOEP is dominated by a strong red band at 650 nm that originates from the $T(0,0)$ triplet level,[35] with quantum yield reported to be about 45% and lifetime around 90 μs.[36−37] Due to the heavy Pt atom, strong spin−orbit coupling leads to intersystem crossing yields close to 100%, and singlet emission is not observed. The

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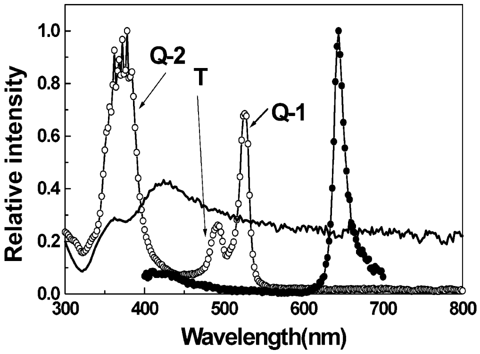

Figure 1. PtOEP absorption (○) and emission (●) spectra in toluene solution. Bands are labeled according to the designations of ref 35. A typical extinction spectrum of a nanotextured silver film prepared by the Tollens reaction is shown for reference (—).

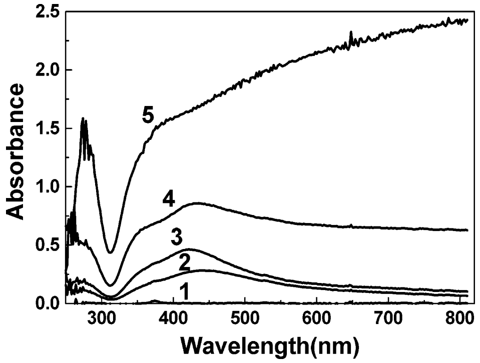

Figure 2. Extinction spectra of substrates coated with nanotextured silver and 15 nm PtOEP/polystyrene films. The increasing density of silver particles in the films from samples 1−5 is controlled by the exposure time to the Tollens reaction, as described in the text.

relative sharpness of the bands and minimal vibronic structure in the transitions are consequences of the rigidity of the porphyrin.

The extinction spectrum of a typical nanotextured silver film prepared by the Tollens reaction on glass is included in Figure 1 for reference. The measured attenuation of light in this case can be ascribed to both absorption and scattering. The silver spectrum is much broader and less structured than that of individual silver nanoparticles in solution,[38] and its breadth reflects an inhomogeneous distribution of plasmon frequencies characteristic of interacting nanostructures. The absorption and emission bands of PtOEP are therefore all resonant with parts of the plasmon distribution and potentially subject to local field enhancement and excited-state quenching if the molecules are situated appropriately.

2. Silver Spectroscopy and Film Morphology. Atomic force micrographs of our silver surfaces (Supporting Information) indicate hard films composed of nanoparticles of ≤50 nm regardless of reaction time, presumably limited by the size that rapidly precipitates from the suspension. For reaction times of 2 min or less, discontinuous silver particle assemblies with various density can be prepared, and Figure 2 shows the extinction spectra of several with different reaction times used in our experiments. The optical density of the silver films at 400 nm varies from around 0.2 up to 2.0 for the substrates used in our experiments. The spectrum evolves from having more isolated particle plasmon feature around 400 nm to having a broad inhomogeneous distribution of plasmon resonance frequencies, the increase in the red tail reflecting interactions between the plasmons of many particles and the increased reflection of the silver film. These interactions are responsible for large local electromagnetic field enhancements in “hot spots” between particles. The local geometries for these hot spots are not well understood but are probably associated with inhomogeneous size distribution and discontinuous morphology,[39] so that the plasmon cannot propagate, and the electromagnetic energy remains confined to a small area. For these particular surfaces, we have shown that the roughness scales with fractal dimensionality[40] ($D \sim 1.5$), allowing for focusing of energy from larger to smaller length scales.[9]

Each of the samples shown in Figure 2 was coated by a 15 nm thick PtOEP/polystyrene film, while the silver formation reaction times were 5, 15, 30, 60, and 90 s, respectively. AFM topographic and phase images (Supporting Information) after the film is applied on top of silver assemblies indicate that the film surface has changed from stiff to viscoelastic. At the same time, the film is slightly smoother, indicating that the spin cast film is not perfectly conformal. We can use the data of Figure 2 to provide an upper limit for the enhancement of PtOEP absorption by silver. The PtOEP absorbance in the film without silver is approximately 0.02 at 380 nm and 0.012 at 535 nm. Because much of the extinction is due to scattering by the nanotextured silver and because scattered light can subsequently excite PtOEP without creating an obvious PtOEP spectral feature in the absorbance, it is not straightforward to use the extinction near 535 nm in Figure 2 to estimate the actual increase in PtOEP absorption in films on silver. Nevertheless, we can say that the absorption by the PtOEP at 535 nm is certainly less than the entire observed extinction at 535 nm, corresponding to an absorbance around 0.75 for film number 4. This leads to an upper limit for the increase in absorption by PtOEP to be a factor slightly greater than 60 at 535 nm and slightly greater than 25 at 380 nm. These are clearly overestimates but are nevertheless important because we can use them to prove that our observed luminescence enhancement data below cannot be explained without invoking enhanced rates for phosphorescence.

3. Excitation Wavelength Dependence and Absorption Enhancement. Phosphorescence excitation spectra for PtOEP/polystyrene films with 15 nm average thickness are reported in Figure 3. Increasing the silver density on the substrate prior to spin casting the emissive film results in a dramatic increase in luminescence followed by a decrease to a value lower than that obtained for films without silver on the substrate. The luminescence spectrum is essentially unchanged and remains such as that in Figure 1 with a maximum near 650 nm. Optimal luminescence is obtained for silver films with optical densities between 0.4 and 0.7 near the single particle plasmon peak at 420 nm. For excitation at 535 nm, increases in photoluminescence of a factor of 75 are observed for 15 nm thick films. Effects of that magnitude cannot be explained by increased reflectivity or by multiple scattering leading to longer effective excitation path length. On the basis of the upper limit for absorption enhancement derived in the previous section, the

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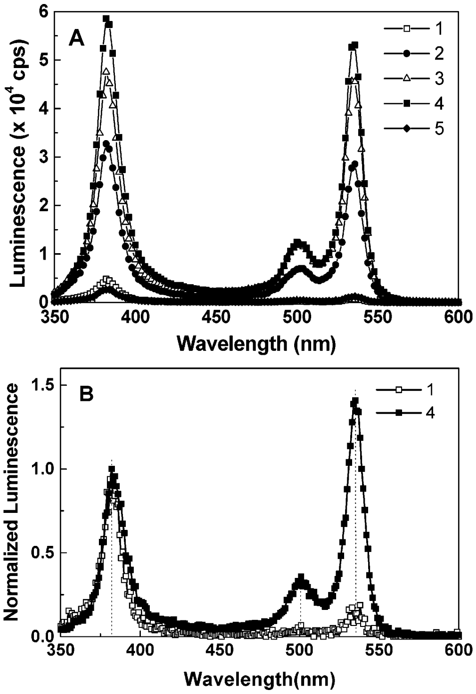

Figure 3. Excitation wavelength dependence of emissive enhancement. (A) Phosphorescence excitation spectra of the 15 nm PtOEP/polystyrene films on silver whose extinction spectra were presented in Figure 2. The emission is monitored at 650 nm. (B) Normalized phosphorescence excitation spectra for film 1 (no silver, □) and film 4 (largest enhancement, ■). The emission intensity for 380 nm excitation is set to unity.

photoluminescence enhancement also cannot be explained without increased emissive yield for the triplet state. The fact that decreases in luminescence can also be observed in thick films (cf. film 5) suggests that discontinuous silver morphologies, where plasmons cannot propagate so that optical field energy remains localized, are essential to the enhancement.[39]

The excitation spectrum of the PtOEP without silver is a good approximation to the PtOEP absorption spectrum. On silver, however, it is significantly changed. For moderate amounts of silver (surfaces 2−4), the magnitude of the excitation spectrum increases at all wavelengths, reflecting overall enhancement of the phosphorescence. A substantial change in the shape of the excitation spectrum is also observed, indicating variation in the amount of absorption enhancement versus excitation wavelength. The magnitude of absorption enhancement does not track the plasmon spectra for the underlying silver films. For example, the surface facilitating the highest emission (#4 in Figures 2 and 3) has about the same value of extinction at 380 and 535 nm, yet the relative enhancement in phosphorescence for 535 nm excitation is over 6-fold as large (Figure 3B). We nevertheless believe that local field enhancement due to interaction with metal nanostructure plasmons is the root cause of the increase in phosphorescence. The changes in the excitation spectrum do not directly correlate to the silver film spectrum for several fundamental reasons. First, the largest field enhancements are near aggregates of silver nanoparticles, and these have much redder extinction spectra than those of the isolated silver particles due to interactions between plasmons in different nanoparticles constituting the aggregate. Second, our measurement is biased toward regions with redder plasmon absorption because we are collecting luminescence at 650 nm and the vacuum field responsible for spontaneous emission at that wavelength is most enhanced by aggregates with redder plasmon emission, as well. For this reason, local absorption enhancement at 535 nm is likely to be larger than at 380 nm. Finally, the silver extinction spectrum represents both scattering and absorption, but the part due to scattering is more closely related to local field enhancement. Scattering increases in importance relative to absorption for larger particle sizes whose plasmon absorption is redder.

We show below that the excited-state lifetime is independent of excitation wavelength, so that the contribution of increase in emission rate cannot explain the relatively larger enhancement for 535 nm excitation (∼75-fold versus ∼12.5-fold for 380 nm). Therefore, the ratio of enhancement at 535 nm to that at 380 nm (∼75/12.5 = 6 for 15 nm films on surface #4) represents a lower limit on the contribution of absorption enhancement to the overall increase in observed photoluminescence for 535 nm excitation.

4. Distance Dependence of Plasmon Enhancement. The largest local field enhancement is expected to be for regions extremely close to the metal nanoparticles, but charge transfer quenching of the molecular excited state is very efficient under these circumstances. Maximum fluorescent enhancement is therefore observed when there is some distance between the fluorophore and the silver. Previous experiments on fluorescent enhancement that investigated the dependence of the molecule on metal separation have been done using various spacer designs. Due to the extremely rough topology of typical surfaces supporting enhancement, it is difficult to develop a rigorous approach to control distance and orientation. In the present work, we study the surface plasmon-enhanced phosphorescence by changing the PtOEP/polystyrene layer thickness rather than by attempting to make uniform spacers. The thickness can be well controlled by changing the concentration of polystyrene or spin casting speed without changing the concentration of PtOEP in the solution to be spin cast onto the silver substrate. The thickness of these films is estimated using ellipsometric measurements of analogous films spun onto silicon substrates.

While atomic force micrographs indicate that we obtain approximately conformal films, it should be said at the outset that the geometry we enforce, using this procedure, is not well characterized. The silver roughness is substantially greater than the film thickness, and the PtOEP is distributed throughout the film. Thus, we can only meaningfully speak of average distances between chromophore and silver and can only obtain semiquantitative estimates of optimal distance. Having said that, we believe that our methodology tends to underestimate the magnitude of luminescence enhancement due to plasmons since it represents a wide distribution of geometries, including many PtOEP molecules that are too close to the silver and are quenched. It should be noted, however, that there is some increase in surface area due to the roughness of the silver films, so that more PtOEP is accommodated than on a substrate without silver. On the basis of experiments where we reverse our procedure and deposit silver on top of films containing the emitter, instead, we estimate this effect to be less than a factor of 2. We also believe that our approach overestimates the optimal spacer thickness since a larger fraction of molecules in thinner films will be lost to quenching because the distance is not precisely controlled.

Table 1 summarizes data like those of Figure 3 for a variety of PtOEP/polystyrene film thicknesses. We report both the

Table 1. PtOEP/Polystyrene Film Thickness Dependence of the Enhanced Phosphorescence[a]

film thickness (nm)	$I_{380\text{ nm}}$	$I_{535\text{ nm}}$	$I_{380\text{ nm(Ag)}}$	$I_{535\text{ nm(Ag)}}$	$I_{380\text{ nm(Ag)}}/I_{535\text{ nm(Ag)}}$
2	5	1	158	133	1.2
6	17	3	452	645	0.7
15	40	7	251	272	0.9
30	80	15	325	278	1.2
65	178	34	376	227	1.7
130	352	66	402	159	2.5

[a] Normalized values of PtOEP phosphorescence at 650 nm are reported for various PtOEP film thicknesses when excited at 380 and 535 nm. Phosphorescence for films on nanotextured silver coatings like those of sample 4 in Figures 2 and 3 having optical density of ~1.0 near 400 nm is compared to phosphorescence from nominally identical films on substrates without silver coatings. All intensities are normalized to the observed luminescence for 535 nm excitation of a 2 nm thick PtOEP/polystyrene film on glass.

values of enhancement relative to the case with no silver and the ratio of 535/380 nm enhancement that we have discussed in the previous section. The largest increase in luminescence with silver as well as the largest increase in ratio between 535 and 380 nm occurs for films around 6 nm in thickness, suggesting optimal spacing between PtOEP and silver of around 3 nm. This is consistent with conclusions of previous work and almost certainly correct to within a factor of 2. Given the modest length scale, it is plausible that well-defined supramolecular structures containing chromophores, silver particles, and spacers could be made synthetically that would exhibit giant plasmonic enhancement of photoluminescence.

The falloff with increasing film thickness is much slower than one would expect in a spacer experiment for two reasons. First, even the small fraction of molecules within a few nanometers of the silver make a large contribution to the overall film luminescence since the plasmonic enhancements are so large. Second, the silver film roughness is on the order of 10 nm and is not entirely negligible even for thick films. Molecules can therefore fill crevices so that the average molecule is much closer to metal than would be the case for a strictly planar geometry. Conversely, because the silver surfaces producing the largest enhancements are discontinuous, it is still possible to observe enhanced emission from molecules that fall between silver particles even when there is no spacer. Hence, our 2 nm films still show net enhancement even though our time-resolved data show that there is undoubtedly a large amount of quenching. We have documented dramatic spatial inhomogeneity of the enhancement in previous work on luminescent enhancement of ruthenium complex emission.[33]

5. Excited-State Decay Dynamics of Plasmon-Enhanced Emission. Normalized time-resolved photoluminescence data are presented for several PtOEP/polystyrene film thicknesses on silver in Figure 4. The decay lifetime decreases substantially when the PtOEP has been cast onto silver-modified substrates even though the measured luminescence yield increases substantially. Thus, at least some of the explanation for reduced lifetime must be enhancement of the radiative rate since quenching by the silver could not account for increases in photoluminescence. The thinnest film, however, has the shortest lifetime but not the highest quantum yield, so that quenching must also be significant in that case. Not surprisingly, the decays are nonexponential since they represent averaging over molecules with a large distribution of enhancement and quenching. For purposes of modeling, we assign a single lifetime that corresponds to the time after which only 1/*e* of the integrated luminescence remains to be emitted. This gives effective lifetimes of ~30 μs for the film without silver (curve e), ~25, 15, and 5 μs for the 47, 6, and 2 nm films on silver (curves d, c, and b), respectively. The instrument response (<1 μs) is shown by curve a. The observed lifetimes are nearly the same for excitation at 366 or 532 nm, confirming that the differences between the absorption and excitation spectral shapes (cf. Figures 1 and 3) are primarily due to the wavelength dependence of absorption enhancement. It is worth noting that we observe large total luminescence enhancement for all observation angles (Supporting Information), a result that rules out cavity effects that might have only resulted in a fortuitous angular redistribution of emission that mimics enhancement.[41−42] These data also indicate that scattering from the nanotextured silver that could cause improved outcoupling of the emission ordinarily waveguided in the substrate is not an important factor in our observed enhancement.

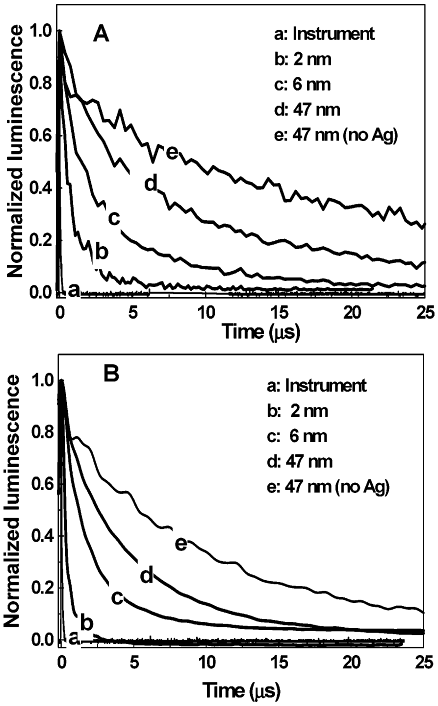

Figure 4. Normalized photoluminescence decay dynamics of PtOEP phosphorescence excited by short laser pulses. (A) At 366 nm dye laser excitation. (B) At 532 nm Nd:YAG second harmonic excitation. Data are presented for several PtOEP/polystyrene films with thickness as indicated in the figure legend. The nanotextured silver films have optical density around 1.0 near 400 nm similar to those of sample 4 in Figures 2 and 3.

6. Analysis of Contributions to Overall Luminescence Increase. Several excellent theoretical treatments of plasmon-enhanced luminescence for molecules near rough metallic surfaces were presented in the early 1980s.[5,43−47] Prior experi-

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mental studies of enhanced photoluminescence have generally not attempted to decompose the enhancement by plasmons into the underlying contributing factors, namely, absorption enhancement, emissive rate enhancement, and increases in quenching. Those studies that address experimental data have relied on specific models of the metal particle shape and dielectric function to infer some of the necessary parameters required to separate these factors.[43,45] The approach we have taken to modeling our data contains the same physics but relies on using additional measurements such as the excited-state lifetimes and excitation spectra that obviate the need for a model of the complex local geometry. Beyond academic interest, the ability to separate absorption, emissive rate enhancement, and quenching is important for at least two reasons. First, there are circumstances under which all three do not contribute to enhancement where one would like to know how much enhancement can be expected. Examples of this would be emission in organic light-emitting diodes or cathodoluminescence, where absorption enhancement plays no role since the relevant emitting states are created via electrical excitation. Second, in designing optimized supramolecular structures to enhance luminescence, one wants to know how quenching, emissive rate enhancement, and absorption enhancement each vary independently with distance from metal nanoparticles.

We have developed a quantitative procedure for approximately separating the various contributions to the photoluminescence enhancement based on the data in Figures 3 and 4. We express the photophysics in terms of five parameters, the local field enhancements at the absorption and emission wavelengths, $E^2(\lambda_1)$ and $E^2(\lambda_2)$, the excited-state decay rates due to quenching through interactions with the metal k_Q, other nonradiative processes that relax the emissive state k_{NR}, and the radiative rate k_R^0 in the absence of silver. We have four experimental observations to determine these, the observed increase in photoluminescence with silver (PL/PL^0), the excited-state lifetimes with and without silver (τ and τ^0), and the phosphorescence quantum yield without silver (Φ_P^0). Our reasoning goes as follows. The values of Φ_P^0 and τ^0 are used to determine the radiative and nonradiative rates in the absence of silver through the standard relationships $k_R^0 = \Phi_P^0\tau^0$ and $(k_{NR} + k_R^0)^{-1} = \tau^0$. We assume that nonradiative decay rate k_{NR} is unaffected by local field enhancement. Our experimentally observed lifetime in the presence of silver τ then specifies a set of possible emissive rate enhancements $E^2(\lambda_2)$ and quench rates k_Q that could account for the reduction in lifetime. If we choose a particular k_Q, then the absorption enhancement $E^2(\lambda_1)$ is determined. While this does not uniquely determine the entire set of parameters, we can set fairly narrow bounds on what the absorption enhancement can be from additional experimental data. The maximum absorption enhancement can be determined by comparing total extinction with and without silver near the sharp PtOEP absorption (section 2). The minimum possible absorption enhancement is determined from our photoluminescence excitation spectra to be at least the ratio between enhancement at 535 nm to enhancement at 366 nm since the difference between these can only be accounted for by absorption enhancement (section 3).

The above approach can be condensed into the following set of formulas:

$$PL/PL^0 = (\text{absorption enhancement}) \times (\text{phosphorescence yield enhancement}) \times (\text{quench fraction}) \tag{1}$$

where

$$\text{absorption enhancement} = E^2(\lambda_1) \tag{1a}$$

$$\text{phosphorescence yield enhancement} = \Phi_P/\Phi_P^0 = E^2(\lambda_2)k_R^0\tau/k_R^0\tau^0 = E^2(\lambda_2)\tau/\tau^0 = E^2(\lambda_2)\,(k_{NR} + k_R^0)/(k_{NR} + E^2(\lambda_2)\,k_R^0 + k_Q) \tag{1b}$$

and

$$\text{quench fraction} = f_Q = k_Q\tau \tag{1c}$$

The lifetime we observe for PtOEP/polystyrene without silver is about a factor of 3 shorter than the literature lifetime for PtOEP, and we ascribe this to oxygen quenching since we have not tried to encapsulate our films or regulate their environment. We can extract the radiative rate for PtOEP phosphorescence from the literature[36,37] ($\tau = 90$ μs, $\Phi_P = 0.45$), giving us estimates of $k_R = 5 \times 10^3$ s^{-1}, $k_{NR} = 4.5 \times 10^4$, and 0.15 for our film's luminescence quantum yield Φ_P^0 in the absence of silver. Enhancements of a factor of 215 for 6 nm PtOEP/polystyrene films excited at 535 nm (Table 1) cannot be rationalized solely on the basis of emissive rate enhancement since the phosphorescence per absorbed photon can only increase ~6.7 (1/0.15) times. The observed increase in photoluminescence on silver must therefore be at least partly due to absorption enhancement.

Using the formalism above and the photoluminescence enhancement results from Table 1, we can generate a series of curves representing different possible ways to deconvolute the observed photoluminescence enhancement into contributions from changes in absorption, phosphorescence rate, and quenching due to silver. These curves (Figure 5) have been generated from our model by choosing a fraction of triplet states that are quenched by interactions with silver, $f_{Q,}$ and computing the field enhancements required to explain the observed spectroscopy and decay dynamics. In constructing these curves, permissible values of f_Q are constrained by the following requirements. (1) Local field enhancements at the incident and emitted wavelengths, $E^2(\lambda_1)$ and $E^2(\lambda_2)$, are greater than or equal to unity. (2) The true quantum yield Φ_P for PtOEP in the presence of silver must be less than or equal to unity (i.e., $\Phi_P/\Phi_P^0 < 6.7$). (3) $E^2(\lambda_1)$, $E^2(\lambda_2)$, and Φ_P/Φ_P^0 have positive values. Plots of the points satisfying these criteria are illustrated in Figure 5 for the 2, 6, and 47 nm films.

Consider the photoluminescence enhancement of 215 observed for 535 nm excitation of the 6 nm thick PtOEP/polystyrene film. Choosing a quench fraction $f_Q = 0$ requires that we have roughly 11 times phosphorescence rate enhancement $E^2(\lambda_2)$ and almost 40-fold absorption enhancement $E^2(\lambda_1)$ to account for our observed luminescence and excited-state lifetime. Phosphorescent rate enhancement of 11 times with no quenching ($f_Q = 0$) corresponds to triplet emission probability Φ_P of nearly unity. At the other extreme, we can assume a quenching fraction of 0.75 to account for the observed excited-state lifetime reduction and would conclude that there is no

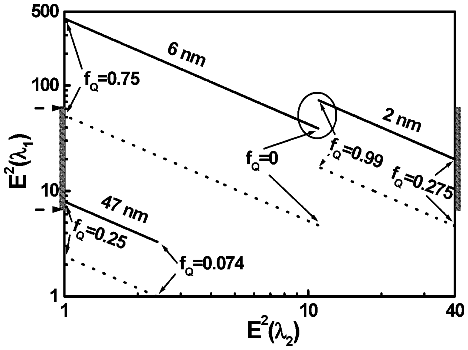

Figure 5. Possible ways to deconvolute the contributions of absorption enhancement $E^2(\lambda_1)$ and emissive rate enhancement $E^2(\lambda_2)$ to the experimentally observed PtOEP phosphorescence increases on nanotextured silver. The slanted lines represent the values of $E^2(\lambda_1)$ and $E^2(\lambda_2)$ derived from the theory described in the text given a fraction of triplets that are quenched, f_Q, for the range of possible choices of f_Q. Solid lines represent the results for 535 nm excitation and dotted ones for 380 nm. The maximum and minimum possible values of f_Q consistent with the observed overall enhancement are labeled at the ends of the lines. Excited-state lifetimes are derived from the results of Figure 4, and the total enhancements as excited at 380 and 535 nm are from the results in Table 1. The shaded region between the two arrows along the vertical axis indicates the possible range of absorption enhancement contributions to the total phosphorescent enhancement as excited at 535 nm. These are estimated as described in the text. The circular region outlined on the plot indicates the set of values deemed most likely for our 2 and 6 nm films excited at 535 nm, as explained in the text.

phosphorescent rate enhancement but over 400-fold absorption enhancement. We think that the former assumption, $f_Q \approx 0$, is probably close to the truth. If we were to assume sizable quenching for the 6 nm film, it would lead to the unphysical conclusion that the absorption enhancement factor in the 6 nm film is larger than that for the 2 nm film (cf. Figure 5). It would also be necessary to exceed our conservative estimate of the maximum absorption enhancement of around 60 (cf. section 2) that was based on the assumption that all of the extinction at 535 nm is due to silver particle scattering and results in PtOEP absorption.

The opposite reasoning applies to the likely quenching fraction for the 2 nm films. In that case, the average local field enhancements are almost certainly greater than those for 6 nm films, and Figure 5 indicates that this can only be the case if f_Q is quite large (>0.8). Such efficient quenching is quite plausible for average distances of PtOEP from silver of around 1 nm, half the film thickness. At the high end of the quench fraction scale ($f_Q = 0.99$), absorption enhancement would need to be around 70 and phosphorescent rate enhancement around 17 at 535 nm to explain the data. Modeling results of the 47 nm film in Figure 5 following the same theory are less meaningful in that we believe that a large fraction of the PtOEP molecules are too far from silver to see substantial radiative enhancement and a uniform treatment is no longer a reasonable approximation. However, there is still significant enhancement due to the irregular texture of the silver. Given that the best enhancement was obtained from the 6 nm thick PtOEP/polystyrene film, we conclude that approximately 3 nm spacing between metal and chromophore is optimal for photoluminescence enhancement in PtOEP.

We note that the ideal spacing will be different for molecules with higher or lower emissive quantum yield. For low quantum yield species, reducing distance from silver would increase the fraction of states that decay radiatively in the absence of quenching until $k_R = E^2(\lambda_2)k_R{}^0 \gg k_{NR}$. Thus, while quenching would naturally increase closer to the silver, there would still be some compensation from increased emissive rate. The same reasoning would mean that ideal spacings will be larger for higher quantum yield emitters. In a similar fashion, the theory predicts that the ideal spacing will depend on the excited-state lifetime in the absence of silver since short-lived species will tend to be less affected by quenching processes. The benefits of proximity to the silver will therefore be more pronounced for molecules with already short excited-state lifetimes, and shorter spacers will be helpful in improving emission.

It is worth pointing out that our model of the photophysics and silver enhancement does not account for heavy atom effects associated with silver that might affect phosphorescent and nonradiative decay rates for the triplet state. The theoretical justification for this is that heavy atom effects are quite short range since they require wave function overlap. Effects of the silver are likely to be much smaller than those of the Pt atom embedded in the porphyrin. Experimentally, we can rule out the importance of these effects since we do not observe enhancement on uniform evaporated silver films nor on films that become essentially continuous, as for the thickest films in Figure 2.

Conclusions and Future Prospects

We have shown that very large enhancements of photoluminescence can be observed in films of the phosphorescent emitter PtOEP when they are put onto nanotextured discontinuous silver substrates. The mechanism is that local enhancement of the incident electromagnetic field causing absorption and of the vacuum field causing spontaneous emission leads to increased radiative rates for molecules near the silver. This picture is equivalent to coupling of the molecular transition dipole to that of the nanotextured silver plasmons, so that the molecular transitions effectively borrow oscillator strength from that of the electron plasma in the silver. We have estimated the relative contributions of absorption enhancement, phosphorescent rate enhancement, and quenching to the overall increase in photoluminescence using a simple model of the photophysics. Phosphorescent rate enhancement is responsible for reducing the excited-state lifetimes substantially, and for the case of PtOEP, we believe that the fraction of triplet states that emit in our most enhanced case is close to unity. There are obvious potential applications of this increase in luminescence efficiency to low threshold photopumped organic film lasers or organic light-emitting diodes. Absorption enhancement has an even larger effect on photoluminescence enhancement than do emissive rate increases in our experiments. This may, in part, be due to the fact that there is an upper limit on emissive enhancement for a material such as PtOEP with reasonably high quantum yield and in part due to the placement of the PtOEP absorption with respect to the silver plasmon resonance. Quenching appears to play little role even for films as thin as 6 nm, and we have concluded that ~3 nm spacing between metal and chromophore leads to the largest photoluminescence enhancement.

As with the present study, work on silver plasmon enhancement of molecular spectroscopy has largely relied on placing molecules in random orientation on disordered silver substrates. This generally results in poorly defined geometries where the effects at play will not be optimized. Hence, even large enhancements such as the factors of 200 we report are probably much smaller than what is achievable. Synthesis of chromophores where silver nanoclusters are covalently incorporated into supramolecular structures could therefore lead to substantial breakthroughs for improved emissive devices and luminescent tags. We hope that our work will inspire creative synthetic chemists to take up that challenge. Much work remains to be done to define optimal configurations and quantify the expected improvements in luminescence, but the large effects observed even for highly inhomogeneous circumstances such as the one presented here show that there is great promise in pursuing that approach.

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Supporting Information Available: Atomic force micrographs of nanotextured silver surfaces and PtOEP/polystyrene covered silver surfaces. Angular dependence of photoluminescence decay dynamics of PtOEP/polystyrene on glass and nanotextured silver-coated glass. This material is available free of charge via the Internet at http://pubs.acs.org.

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