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Photoswitched Singlet Energy Transfer in a Porphyrin−Spiropyran Dyad

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Abstract: A photochromic nitrospiropyran moiety (Sp) has been covalently linked to a zinc (P_{Zn}) and to a free-base (P_{H2}) porphyrin. In the resulting dyads (P_{Zn}−Sp_c and P_{H2}−Sp_c), the porphyrin first excited singlet states are unperturbed by the closed form of the attached spiropyran. Excitation of the spiropyran moiety of either dyad in the near-UV region results in ring opening to a merocyanine form (P−Sp_o) that absorbs at 600 nm. The open form re-closes thermally in 2-methyltetrahydrofuran with a time constant of 20 s, or following irradiation into the 600 nm band. Excitation of the zinc porphyrin moiety in the merocyanine form of the dyad yields $^1P_{Zn}$−Sp_o. The lifetime of the zinc porphyrin excited state is reduced from its usual value of 1.8 ns to 130 ps by singlet−singlet energy transfer to the merocyanine moiety to give P_{Zn}−^1Sp_o. The quantum yield of energy transfer is 0.93. Quenching is also observed in the free base dyad, where $^1P_{H2}$−Sp_o and P_{H2}−^1Sp_o exchange singlet excitation energy. This photoswitchable quenching phenomenon provides light-activated control of the porphyrin excited states, and consequently control of any subsequent energy or electron-transfer processes that might be initiated by these excited states in more complex molecular photonic or optoelectronic devices.

Introduction

Porphyrins absorb light strongly in the visible and near-UV, are often fluorescent with reasonably long excited singlet state lifetimes, and undergo reversible one-electron redox reactions. They are readily synthesized, and their properties are easily tuned by substitution and metalation. A large number of porphyrin-based multicomponent molecular systems that demonstrate efficient singlet energy transfer, triplet energy transfer, and photoinduced electron transfer to yield energetic charge-separated states[1−6] have been reported. These serve as mimics of the primary energy conversion steps of photosynthesis, as molecular photovoltaics that transduce light energy into electrochemical energy, and as the basis for prototype molecular-scale mechanical, photonic, and optoelectronic switches and wires.[7−20] In such systems, the photonic or optoelectronic process is initiated by a porphyrin excited singlet state. These can serve as donors of singlet excitation energy in photonic and light-gathering antenna systems or as electron donors or acceptors, or undergo intersystem crossing to triplet states, which can also initiate energy and electron-transfer processes. Thus, control of the lifetime of the porphyrin first excited singlet state provides a mechanism for modulation of various photonic and optoelectronic processes. In principle, such control can be exerted by quenchers that shorten the lifetime of the porphyrin excited state, rendering it ineffective in other photochemical or photophysical processes.

Energy transfer is an attractive mechanism for such quenching because it does not directly produce redox-active ions that could lead to photodamage or other undesirable processes. Quenching of the porphyrin first excited singlet state by singlet−singlet energy transfer requires an acceptor whose first excited singlet state lies at a lower energy than that of the porphyrin. Thus, one approach to a light-controlled photonic or optoelectronic molecular switch would be to associate with a porphyrin a second chromophore which could be switched with light

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(1) Gust, D.; Moore, T. A. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: New York, 2000; Vol. 8, pp 153−190.

(2) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461.

(3) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198−205.

(4) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849−866.

(5) Maruyama, K.; Osuka, A.; Mataga, N. *Pure Appl. Chem.* **1994**, *66*, 867−872.

(6) Sakata, Y.; Imahori, H.; Tsue, H.; Higashida, S.; Akiyama, T.; Yoshizawa, E.; Aoki, M.; Yamada, K.; Hagiwara, K.; Taniguchi, S.; Okada, T. *Pure Appl. Chem.* **1997**, *69*, 1951−1956.

(7) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2001**, *34*, 40−48.

(8) Gust, D.; Moore, T. A.; Moore, A. L. *IEEE Eng. Med. Biol.* **1994**, *13*, 58−66.

(9) Ashton, P. R.; Johnston, M. R.; Stoddart, J. F.; Tolley, M. S.; Wheeler, J. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1128−1131.

(10) Bissell, R. A.; de Silva, A. P.; Gunaratne, H. N.; Lynch, P. M.; Maguire, G. E.; Sandanayake, K. S. *Chem. Rev.* **1992**, *92*, 7−195.

(11) Debreczeny, M. P.; Svec, W. A.; Wasielewski, M. R. *Science* **1996**, *274*, 584−587.

(12) Gunter, M. J.; Johnston, M. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1163−1165.

(13) Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707−1716.

(14) Mirkin, C. A.; Ratner, M. A. *Annu. Rev. Phys. Chem.* **1992**, *43*, 719−754.

(15) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D. J.; Gaines, G. L. I.; Wasielewski, M. R. *Science* **1992**, *257*, 63−65.

(16) Shiratori, H.; Ohno, T.; Nozaki, K.; Yamazaki, I.; Nishimura, Y.; Osuka, A. *Chem. Commun.* **1998**, 1539−1540.

(17) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocian, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996−3997.

(18) Chambron, J.-C.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 7419−7425.

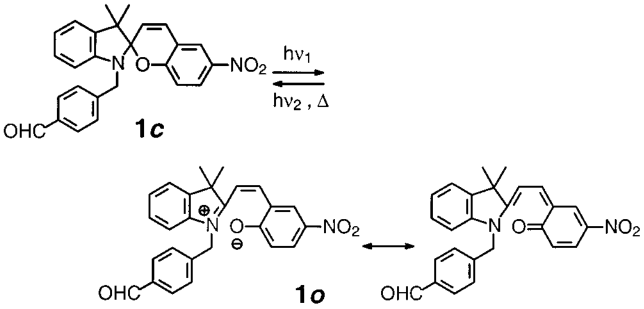
(19) Chambron, J.-C.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1993**, *115*, 6109−6114.

(20) Linke, M.; Chambron, J.-C.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1997**, *119*, 11329−11330.

10.1021/ja010058t CCC: $20.00

between a short-wavelength-absorbing form (incapable of quenching the porphyrin) and a long-wavelength-absorbing form capable of accepting singlet excitation energy from the porphyrin. In a few reports, photochromic moieties including dithienylethenes[21,22] and fulgides[23] have been linked to chromophores, and switching of the photochromic unit has been shown to affect the emission properties of the chromophore. In these cases, the quenching mechanism is either unknown or a process other than energy transfer to the photochromic moiety. However, these studies suggest that the approach mentioned above might be feasible.

Spiropyrans are promising candidates for such light-controlled quenchers. Spiro[indoline-benzopyran] molecules such as **1** exist in nonpolar environments in a "closed" spiro form (**1*c***) that does not absorb above 400 nm. When excited, this form undergoes an intramolecular rearrangement to an "open", merocyanine form (**1*o***), which absorbs in the visible in the 500−700 nm region. As indicated in the structural drawing, the open form is a resonance hybrid of a polar, zwitterionic structure and a less polar, quinonoid form. Thus, the three bonds in the linkage joining the indolino and phenolic rings have some double-bond character. This suggests that **1*o*** can exist as an equilibrating mixture of 8 isomeric forms. Irradiation of the open form induces ring closure, regenerating the closed spiro form. Thermal reversion to the closed form is also observed, with time constants as large as many minutes. The lifetime is a function of the conditions and the substituents on the spiropyran skeleton.[24] The open form of the spiropyran is considerably more polar than the closed form, and this polarity change has been exploited for the photonic control of molecular interactions with electrode surfaces[25−30] and for various possible separation applications.[31−35]



1*c*

1*o*

In various classes of photochromic molecules, the difference in conjugation between the two forms has been used as the basis for control of electron-transfer rates, redox potentials, and nonlinear optical properties.[21,36−44]

In the present application, the difference in energy of the first excited singlet states of the two forms of a spiropyran is exploited. In the closed form, the spiropyran first excited singlet state is too high in energy to quench the porphyrin first excited singlet state by energy transfer. The absorption and emission spectra of the open form, however, overlap those of a typical porphyrin, suggesting the possibility of energy transfer.

Herein, we report the synthesis and photophysical properties of zinc porphyrin−spiropyran dyad **2**, free base analogue **3**, and related model compounds. As described in detail below, the spiropyran in the closed form has no effect on the photophysics of the first excited singlet state of the attached porphyrin. In the open, merocyanine form, however, efficient energy transfer quenching of the porphyrin is observed, demonstrating the desired photoswitching phenomenon.

Results

Synthesis. Porphyrin−spiropyran **3** was prepared according to the sequence depicted in Figure 1. Fischer's base was benzylated with methyl 4-(bromomethyl)benzoate. Base-induced conversion of the intermediate salt gave **4**. Condensation of **4** with 5-nitrosalicyaldehyde produced **5** in good yield. Reduction of the methyl ester with lithium aluminum hydride and reoxidation of the resulting alcohol **6** with manganese dioxide yielded **1**, which bears the requisite aldehyde for formation of the porphyrin. Reaction of **1** under conditions developed by Lindsey and co-workers[45] gave the expected mixture of porphyrin-containing products, which were separated by column chromatography to yield free-base porphyrin−spiropyran dyad **3**. Insertion of zinc to give **2** was accomplished by stirring **3** overnight with zinc acetate in chloroform.

Cyclic Voltammetry. Electrochemical measurements were undertaken to investigate the redox properties of the dyads. The zinc porphyrin moiety of dyad **2** in benzonitrile solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate and ferrocene as an internal redox standard was found to exhibit a first oxidation potential of 0.34 V (0.74 V vs SCE) and a first reduction potential of −1.85 V (−1.46 V vs SCE) in the closed form. The spiropyran moiety in **2** showed a first oxidation potential of 0.79 V (1.20 V vs SCE) and a first reduction potential of −1.67 V (−1.25 V vs SCE). Irradiation of **2** with ultraviolet light at wavelengths known to open the spiropyran

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(21) Fernandez-Acebes, A.; Lehn, J.-M. *Chem.−Eur. J.* **1999**, *5*, 3285−3292.

(22) Norsten; T. B.; Branda, N. R. *J. Am. Chem. Soc* **2001**, *123*, 1784−1785.

(23) Walz, J.; Ulrich, K.; Port, H.; Wolf, H. C.; Wonner, J.; Effenberger, F. *Chem. Phys. Lett.* **1993**, *213*, 321−324.

(24) Bertelson, R. C. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1998; Vol. 1, pp 11−83.

(25) Kaganer, E.; Pogreb, R.; Davidov, D.; Willner, I. *Langmuir* **1999**, *15*, 3920−3923.

(26) Katz, E.; Itzhak, N.; Willner, I. *Langmuir* **1993**, *9*, 1392−1396.

(27) Katz, E.; Willner, B.; Willner, I. *Biosens. Bioelectron.* **1997**, *12*, 703−719.

(28) Katz, E.; Willner, I. *Langmuir* **1997**, *13*, 3364−3373.

(29) Patolsky, F.; Filanovsky, B.; Katz, E.; Willner, I. *J. Phys. Chem. B* **1998**, *102*, 10359−10367.

(30) Willner, I.; Rubin, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 367−385.

(31) Garcia, T.; Cherian, S.; Park, J.; Gust, D.; Jahnke, F.; Rosario, R. *J. Phys. Chem. A* **2000**, *104*, 6103−6107.

(32) Ino, M.; Tanaka, K.; Otsuki, J.; Araki, K.; Seno, M. *Colloid. Polym. Sci.* **1994**, *272*, 151−158.

(33) Przystal, F.; Ruduloph, T.; Phillips, J. P. *Anal. Chim. Acta* **1968**, *41*, 391−394.

(34) Sunamoto, J.; Iwamoto, K.; Mohri, Y.; Komiya, H. *J. Am. Chem. Soc* **1982**, *104*, 5502−5504.

(35) Winkler, J. D.; Deshayes, K.; Shao, B. *J. Am. Chem. Soc.* **1989**, *111*, 769−770.

(36) Fernandez-Acebes, A.; Lehn, J.-M. *Adv. Mater.* **1998**, *10*, 1519−1522.

(37) Tsivgoulis, G. M.; Lehn, J.-M. *Adv. Mater.* **1997**, *9*, 39−42.

(38) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem.−Eur. J.* **1995**, *1*, 275−284.

(39) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J.-M. *Chem.−Eur. J.* **1995**, *1*, 285−293.

(40) Tsivgoulis, G. M.; Lehn, J.-M. *Angew.e Chem., Int. Ed. Engl.* **1995**, *34*, 1119−1122.

(41) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *246*, 323−326.

(42) Fraysse, S.; Coudret, C.; Launay, J. P. *Eur. J. Inorg. Chem.* **2000**, 1581−1590.

(43) Launay, J. P.; Coudret, C. *Chemical Approaches of Molecular Switches*; New York Academy of Sciences: New York, 1998; pp 116−132.

(44) Khairutdinov, R. F.; Giertz, K.; Hurst, J. K.; Voloshina, E. N.; Voloshin, N. A.; Minkin, V. I. *J. Am. Chem. Soc.* **1998**, *120*, 12707−12713.

(45) Littler, B. J.; Ciringh, Y.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 2864−2872.

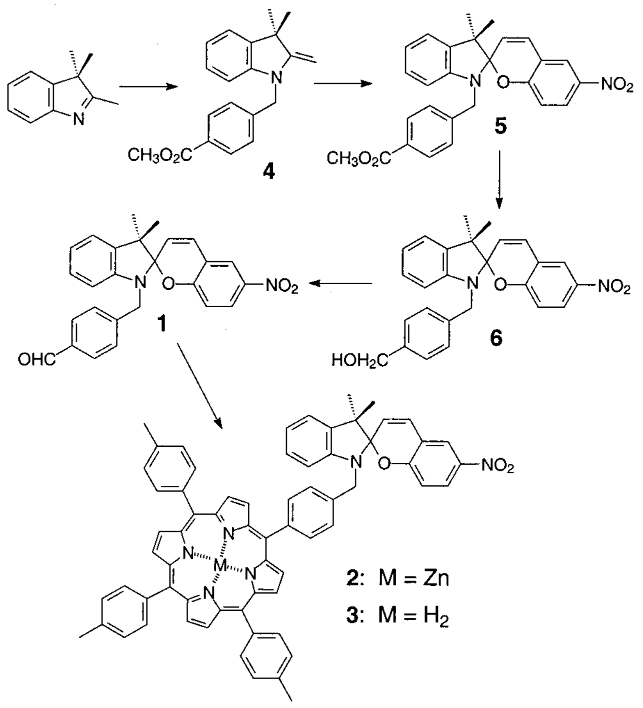

Figure 1. Synthetic scheme for preparation of the porphyrin−spiropyran dyads. Details are given in the Experimental Section.

moiety to the merocyanine form resulted in no observable change in the redox behavior. It has been reported that for very similar spiropyrans, partial conversion of the sample to the open form with UV light does not reveal any more easily oxidized or reduced species.[46,47] Similar experiments with free base dyad **3** gave a first oxidation potential for the porphyrin of 0.55 V (0.96 V vs SCE). The spiropyran moiety was oxidized at 0.79 V (1.20 V vs SCE). A reduction wave at −1.60 V (−1.20 V vs SCE) corresponded to reduction of both the spiropyran and the porphyrin at nearly the same potential. The values for both compounds are close to those for model spiropyrans and porphyrins, indicating little effect on redox potentials due to linking the chromophores.

Absorption Spectra. The absorption spectrum of zinc dyad **2***c* (closed form) in 2-methyltetrahydrofuran is shown in Figure 2a. The maxima in the Q-band region are at 597, 557, and 518 (sh) nm, and the maximum of the Soret occurs at 420 nm. These absorption bands are essentially identical to those observed for zinc *meso*-tetraphenylporphyrin. There is an additional absorption band at 330 nm (not shown). This is ascribed to the closed form of the spiropyran chromophore by reference to the absorption spectrum of model spiropyran **1***c*, whose longest wavelength absorption band is in this region (Figure 3). Similarly, the absorption spectrum of free base dyad **3***c* is similar to that of *meso*-tetraphenylporphyrin, with maxima at 648, 592, 549, 514, and 416 nm (Figure 2b). The spectrum also features the 330 nm absorption characteristic of the closed spiropyran. Thus, the absorption spectra of the dyads are essentially superpositions of the spectra of the porphyrin and spiropyran chromophores, and show no significant perturbations indicative of strong interactions between the linked moieties.

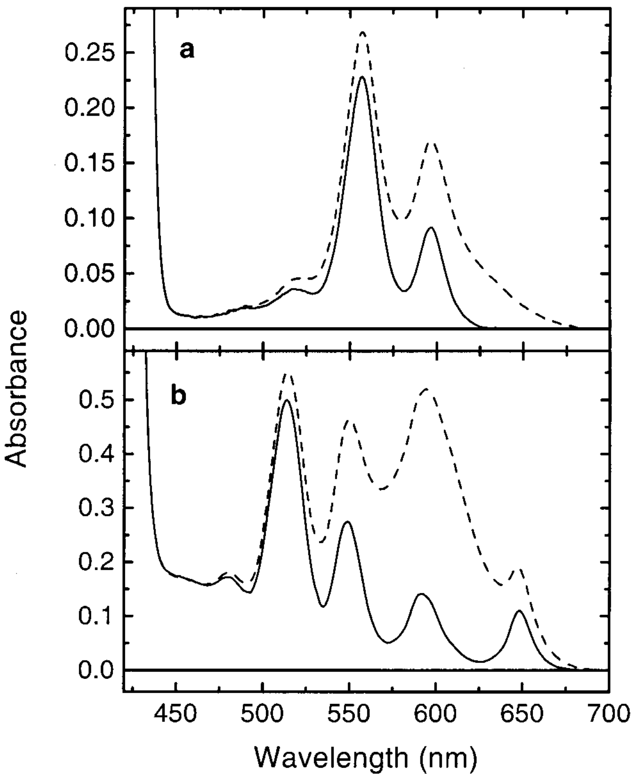

Figure 2. Absorption spectra of (a) zinc dyad **2** and (b) free base dyad **3** in deoxygenated 2-methyltetrahydrofuran: (—) samples kept in the dark prior to spectra, (− −) samples irradiated at ~360 nm prior to spectra, converting the spiropyran to the open, merocyanine form.

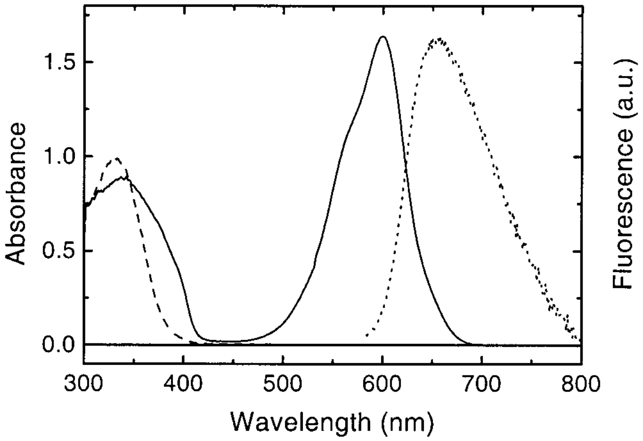

Figure 3. Spectra from a 2-methyltetrahydrofuran solution of model spiropyran **1**: (− −) absorption spectrum of the closed spiropyran from a sample kept in the dark, (—) absorption spectrum of the solution after irradiation at 340 nm to generate the open, merocyanine form, and (···) emission of the irradiated solution containing the merocyanine form, with excitation at 580 nm.

A 2-methyltetrahydrofuran solution of dyad **2***c* was irradiated in the near-UV at ~360 nm, where the spiropyran moiety absorbs, and the absorption spectrum was again measured (Figure 2a). The main absorption bands of the zinc porphyrin are still apparent, but the absorption is enhanced in the 600-nm region. The reason for the enhancement is apparent from Figure 3, which shows the absorption spectrum of the model spiropyran **1** following similar UV excitation. The absorption in the 330-nm region has decreased, and new absorption has appeared in the 380 and 600 nm regions. The new absorption is due to the open, merocyanine form of the spiropyran (**1***o*), which features significantly extended conjugation relative to the spiro form. Clearly, UV irradiation of dyad **2***c* has led to opening of the spiropyran moiety, and its visible absorption underlies the porphyrin Q-bands, resulting in the observed enhancement in

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(46) Zhi, J.-F.; Baba, R.; Hashimoto, K.; Fujushima, A. *Chem. Lett.* **1994**, *1994*, 1521−1524.

(47) Zhi, J.-F.; Baba, R.; Hashimoto, K.; Fujushima, A. *J. Photochem. Photobiol. A* **1995**, *92*, 91−97.

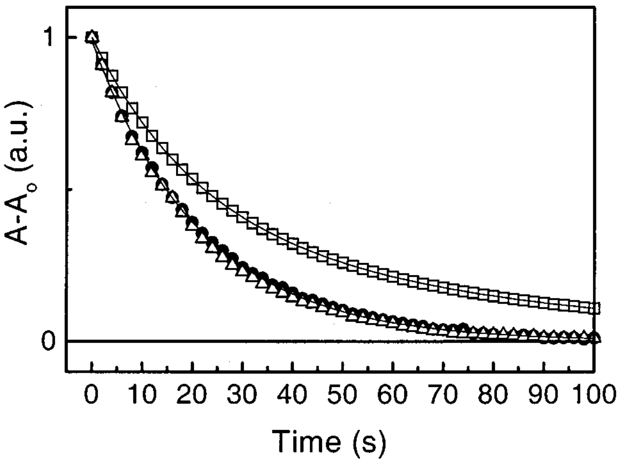

Figure 4. Decay of the transient absorption of solutions of model spiropyran **1** (□) and dyads **2** (●) and **3** (△) in 2-methyltetrahydrofuran at 600 nm following irradiation at ∼360 nm to generate the merocyanine form. The solid lines are calculated decays with time constants of 20 s for **2** and **3** and 20 (60%) and 70 s (40%) for **1**. The ordinate is the total absorbance at 600 nm minus any (invariant) absorbance due to the porphyrin at that wavelength.

Figure 2a. The enhancement is maximal at 600 nm, which is the maximum of the merocyanine absorption. A similar effect is observed for free base dyad **3** (Figure 2b). After irradiation at ∼360 nm, the four Q-bands are still apparent, but the spectrum is strongly perturbed by the merocyanine absorption of **3*o*** at 600 nm.

The spectral perturbations resulting from UV irradiation of **2** and **3** decay with time after irradiation ceases (Figure 4), and the original spectrum is recovered. The decay is exponential, and fitting yields a time constant of 20 s for each molecule. This decay is ascribed to thermal closing of the merocyanine to regenerate the spiro form. Closing is more rapid if the molecule is irradiated in the 600-nm region. Repetitive cycling of either **2** or **3** leads to the appearance of degradation products, as is the case with most spiropyrans. The degradation rate was not investigated quantitatively, but such degradation could obviously limit the ultimate utility of practical devices employing this spiropyran. Model spiropyran **1** shows similar opening and closing behavior (Figures 3 and 4), in common with related spiropyrans. The thermal closing of merocyanine **1*o*** can be fitted with two exponential components with time constants of 20 (60%) and 70 s (40%). The decay of the merocyanine form of many spiropyrans is not a single-exponential process.[48]

Emission Spectra. No significant fluorescence emission was observed upon irradiation of the closed form of the model spiropyran, **1*c***. During steady-state irradiation of the sample with light from a 500 W xenon arc lamp passed through a 340-nm filter with a 10-nm band-pass, which generates the open, merocyanine form **1*o***, excitation at 580 nm produced readily detectable fluorescence (Figure 3). The emission spectrum was relatively broad and featureless, with a maximum at 657 nm.

Fluorescence experiments were also carried out with the dyads. Figure 5a shows the emission of dyad **2*c*** in 2-methyltetrahydrofuran (with the spiropyran in the closed form). Excitation was at 430 nm, where the porphyrin absorbs strongly (Figure 2a), but the absorption of both the closed and open forms of the spiropyran moiety is negligible (Figure 3). The emission is essentially identical to that of zinc 5,10,15,20-tetrakis(4-methylphenyl)porphyrin, with maxima at 607 and 657 nm. Furthermore, the amplitude of the emission is essentially identical to that of a solution of the model zinc porphyrin with an equal absorbance at 430 nm. Thus, the closed form of the spiropyran has no effect on the emission properties of the porphyrin moiety.

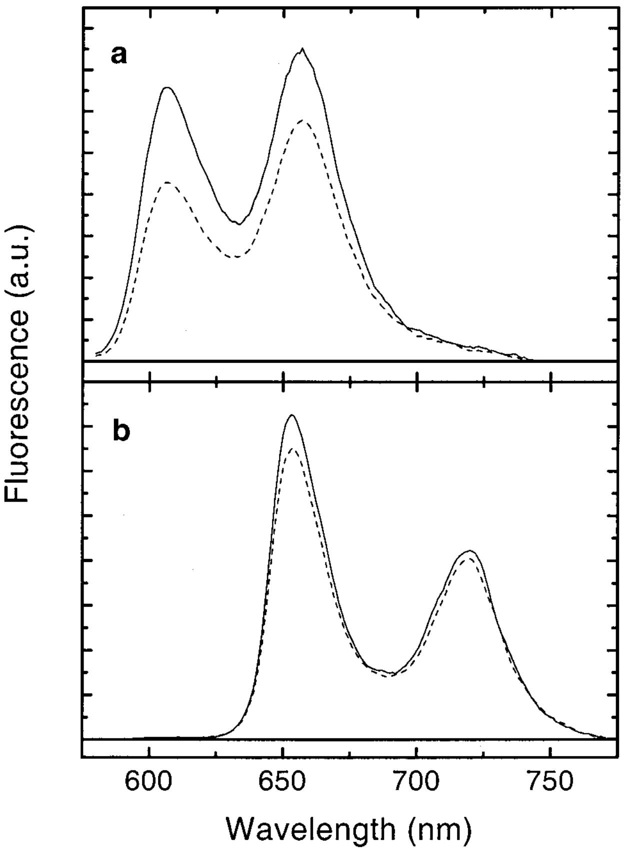

Figure 5. Corrected fluorescence spectra of dyads **2** (a) and **3** (b) in 2-methyltetrahydrofuran solution, with excitation into the porphyrin at 430 nm; (—) samples kept in the dark prior to spectrum, (– –) same samples irradiated at 340 nm to generate the open, merocyanine form.

The emission spectrum was measured again after irradiation of the sample at 340 nm; the irradiation was stopped before the spectrum was measured. The emission spectrum after irradiation (Figure 5a) is significantly reduced in amplitude. This result provides additional evidence that the spiropyran moiety undergoes photoinduced ring opening even in the presence of the porphyrin. In addition, it indicates that the zinc porphyrin excited singlet state is quenched by the open form of the spiropyran. It will be noted that the decrease in amplitude in the open form is greater in the 610-nm region than in the 655-nm region. There are two reasons for this effect. The spectrum was measured by scanning from shorter to longer wavelengths after the 340-nm radiation was turned off. Thus, thermal reversion to the closed form **2*c*** is occurring during the measurement, leading to enhanced porphyrin emission at longer wavelengths. Second, any emission from the merocyanine chromophore at 657 nm will also enhance the total emission amplitude at these wavelengths.

Similar experiments were performed with free base dyad **3**. Emission from a 2-methyltetrahydrofuran solution of the closed form **3*c*** following irradiation at 430 nm was observed with maxima at 653 and 720 nm (Figure 5b). The spectral shape and emission intensity are essentially identical with those of a solution of 5,10,15,20-tetrakis(4-methylphenyl)porphyrin having the same absorbance at 430 nm. After partial conversion to the open form **3*o*** by irradiation at 340 nm, quenching of the

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(48) Pimienta, V.; Lavabre, D.; Levy, G.; Samat, A.; Guglielmetti, R.; Micheau, J. C. *J. Phys. Chem.* **1996**, *100*, 4485−4490.

porphyrin fluorescence is again observed. However, the quenching is not as great as in the zinc analogue. The spectrum is distorted for the reasons mentioned above.

These results show that the zinc and free base dyad porphyrin first excited singlet states are quenched by more than 35% and 10%, respectively, by the open form of the spiropyran. However, these estimates are not quantitative for several reasons. Because both the open and closed forms of the spiropyran moiety absorb at 340 nm, irradiation at this wavelength produces a photostationary state of the spiro and merocyanine forms, rather than driving the system totally to one isomer. As mentioned above, irradiation was not performed during collection of the emission spectra, and thermal reversion to the closed form was occurring before and during data collection. Finally, the fluorescence quenching is partially offset by fluorescence from the open form of the spiropyran in the same wavelength region.

To obtain more quantitative information concerning the excited-state properties of the dyads, time-resolved emission experiments were carried out using the single photon timing technique. A ~1 × 10^{-5} M solution of dyad **2*c*** in 2-methyltetrahydrofuran was excited with 2 ps laser pulses at 430 nm (porphyrin absorption), and the emission was monitored at 15 wavelengths in the 580−760 nm region. Global analysis of the resulting data as a single-exponential decay gave a satisfactory fit ($\chi^2 = 1.11$) with a lifetime of 1.80 ns, which is a typical lifetime for a zinc tetraarylporphyrin of this type.[49] The lack of lifetime quenching in **2*c*** is consistent with the unquenched steady-state emission spectra discussed above. Similar experiments were carried out with some of the spiropyran in the open form. The sample of **2** was irradiated for ~1 min at 340 nm as discussed above. The irradiation source was turned off, and time-resolved emission data with excitation at 430 nm were collected for ~25 s. Data collection was stopped, the sample again irradiated at 340 nm, and the cycle repeated until useable signal-to-noise was obtained. Some sample degradation was noted after a number of cycles. Data were collected at 14 wavelengths in the 580−720 nm region, and analyzed globally. A satisfactory fit ($\chi^2 = 1.12$) was obtained with two exponential components with lifetimes of 130 ps and 1.78 ns. These are shown as decay-associated spectra in Figure 6a. The 1.78-ns component has the emission spectrum and lifetime of the unperturbed zinc porphyrin first excited singlet state, and is assigned to the closed form of the dyad **2*c***. The 130-ps component also has the general shape of zinc porphyrin emission, perhaps distorted slightly by a small contribution from the merocyanine emission band at ~657 nm. The 130-ps component is associated with the open form of the dyad, **2*o***, and the short lifetime is qualitatively consistent with the quenched steady-state emission spectrum.

Similar time-resolved emission experiments were performed on free base dyad **3**. Irradiation of the closed form **3*c*** at 430 nm with measurements at 15 wavelengths in the 580−760 nm region gave decays that were analyzed globally to yield a single-exponential process with a lifetime of 10.5 ns ($\chi^2 = 1.07$). Model chromophore 5,10,15,20-tetrakis(4-methylphenyl)porphyrin gave a lifetime of 10 ns under the same conditions, indicating that the attached closed spiropyran has no significant effect on the lifetime of the free base porphyrin singlet state. Decays were also obtained after irradiation of **3** at 340 nm to open the spiropyran ring, as described above. Data from measurements at 14 wavelengths in the 630−760 nm region were fitted globally ($\chi^2 = 1.08$) to yield three exponential components with lifetimes of 11 ns, 1.0 ns, and 85 ps (Figure 6b). The 11-ns component has the emission spectrum and lifetime of the free base porphyrin, and is attributed to the closed form of the dyad, **3*c***. The other two components have spectral shapes suggesting a mixture of emissions from both quenched porphyrin and merocyanine chromophores.

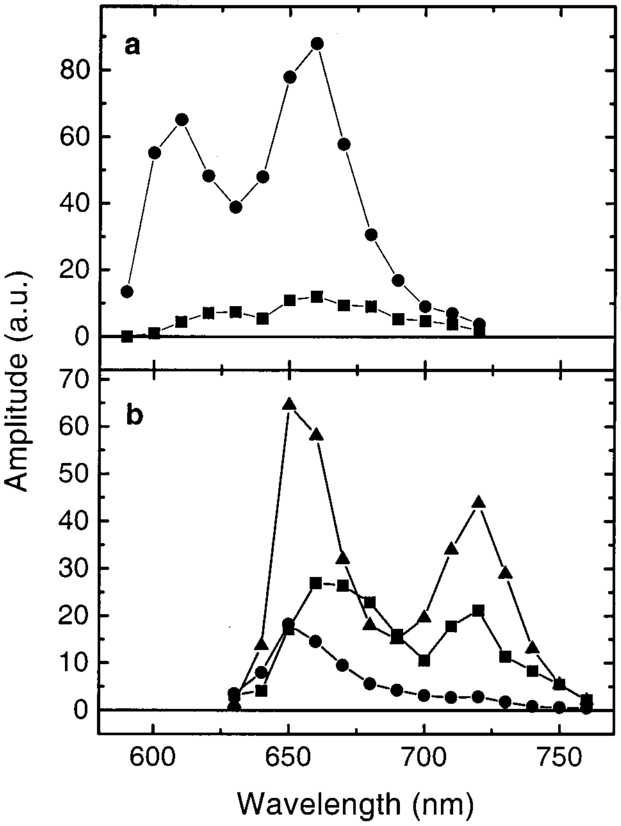

Figure 6. Decay-associated fluorescence spectra of dyads **2** and **3** in 2-methyltetrahydrofuran solution following irradiation at 340 nm to generate the open, merocyanine form as described in the text. Excitation was at 430 nm, where absorption is due to the porphyrin moiety. (a) Zinc dyad **2** ($\chi^2 = 1.12$): (●) 1.8 ns, (■) 130 ps. (b) Free base dyad **3** ($\chi^2 = 1.08$): (▲) 11 ns, (●) 1 ns, (■) 85 ps.

Time-resolved emission studies of model spiropyran **1** were undertaken to aid in the interpretation of the results for the dyads. No emission was observed from the closed, spiro form of the molecule, **1*c***. A ~1 × 10^{-5} M solution of **1** in 2-methyltetrahydrofuran was irradiated with light from a 500-W xenon arc lamp passed through a 340-nm interference filter with a 10-nm band-pass, the light was turned off, and time-resolved fluorescence spectra of the resulting mixture of **1*c*** and **1*o*** were obtained by the single photon timing method as described above. Excitation was at 620 nm using ~7 ps laser pulses. Global analysis of data at 10 wavelengths in the 580−760-nm region as a 4-exponential process ($\chi^2 = 1.26$) gave significant lifetimes of 15, 45, and 120 ps (Figure 7). A very minor component with a lifetime of 2 ns was also noted. Although the 15-ps component appears as a decay at 630 nm and below, it has a negative amplitude at 640 nm and above. This represents a grow-in of emission at these wavelengths with time. The 45-ps component appears to have approximately the same spectral shape as the 15-ps component above 640 nm, whereas the 120-ps transient is weak, and shows an emission maximum around 700 nm.

Transient Absorption Measurements. Additional information on the merocyanine form of the model compound, **1*o***, was obtained by the pump−probe transient absorption technique, with the sample under continuous irradiation at 340 nm to

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(49) Gust, D.; Moore, T. A.; Moore, A. L.; Macpherson, A. N.; Lopez, A.; DeGraziano, J. M.; Gouni, I.; Bittersmann, E.; Seely, G. R.; Gao, F.; Nieman, R. A.; Ma, X. C.; Demanche, L. J.; Luttrull, D. K.; Lee, S.-J.; Kerrigan, P. K. *J. Am. Chem. Soc.* **1993**, *115*, 11141−11152.

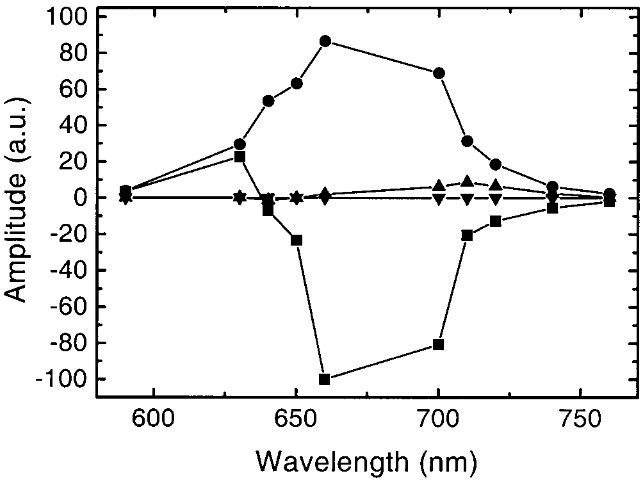

Figure 7. Decay-associated fluorescence spectra of model spiropyran **1** in 2-methyltetrahydrofuran solution following irradiation at 340 nm to generate the open, merocyanine form as described in the text. Excitation was at 620 nm ($\chi^2 = 1.20$): (■) 15 ps, (●) 45 ps, (▲) 120 ps, (▼) 2 ns).

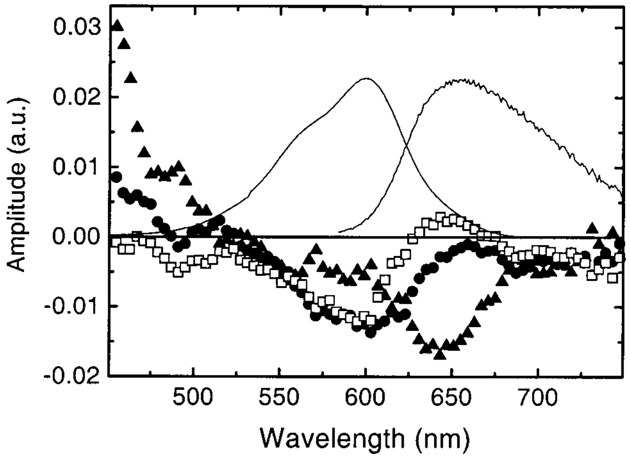

Figure 8. Decay-associated absorption spectra of model spiropyran **1** in 2-methyltetrahydrofuran solution following irradiation at 340 nm to generate some of the open, merocyanine form as described in the text. Excitation was at 600 nm:(●) 20 ps, (▲) 45 ps, (□) 140 ps. Shown for comparison are the absorption and emission spectra of the merocyanine form, **1*o***, from Figure 3.

produce some merocyanine form of the molecule. Excitation of a ~1 × 10^{-3} M solution in 2-methyltetrahydrofuran employed ~100 fs laser pulses at 600 nm, which excite only the open form. Global analysis of these data shows absorption difference decay components with lifetimes of 20, 45, and 140 ps (Figure 8). These correspond, within experimental error, to the 15, 45, and 120 ps lifetimes determined by fluorescence techniques. Although all three components display bleaching of the merocyanine ground state in the 550−600-nm region, only the 45-ps component shows significant stimulated emission near the maximum of merocyanine fluorescence around 657 nm. Note that a component with the same lifetime dominates the time-resolved emission spectrum in Figure 7.

Discussion

Energetics. The energies of the first excited singlet states of the various chromophores may be estimated as the frequency-domain average of the long-wavelength absorption and short-wavelength emission maxima. Thus, the porphyrin first excited singlet states $^1P_{Zn}$ and $^1P_{H2}$ lie at 2.06 and 1.91 eV, respectively, above the ground states. The situation with the spiropyran chromophores is somewhat more complex (vide infra), but the absorption and emission spectra for the open, merocyanine form of model compound **1*o*** in Figure 3 give a value of 1.98 eV for ^1Sp_o. The closed form of the spiropyran is not emissive, but from the absorption spectrum, the energy of ^1Sp_c may be roughly approximated as ~3.8 eV. These data suggest that in zinc dyad **2*o***, $^1P_{Zn}-Sp_o$ lies 0.08 eV above $P_{Zn}-{}^1Sp_o$, while $^1P_{H2}-Sp_o$ is 0.07 eV lower in energy than $P_{H2}-{}^1Sp_o$. The energy differences between the ground states of the closed and open forms of the dyads cannot be determined from the spectroscopic data, but are not relevant to the discussion that follows.

Singlet state quenching by electron, as well as energy, transfer must be considered. We can estimate the energies of $P_{Zn}^{\bullet+}-Sp_c^{\bullet-}$ and $P_{H2}^{\bullet+}-Sp_c^{\bullet-}$ (the lowest energy charge-separated states) as 1.99 and 2.21 eV above the ground states, respectively, in polar solvents based on the cyclic voltammetric data given earlier. Thus, $^1P_{H2}$ at 1.91 eV lies at significantly lower energy than the charge-separated state, and its formation on the picosecond time scale is unlikely. These estimates place $^1P_{Zn}-Sp_c$ ~0.07 eV above $P_{Zn}^{\bullet+}-Sp_c^{\bullet-}$, and photoinduced electron transfer is in principle possible. However, neither $^1P_{Zn}$ nor $^1P_{H2}$ are quenched in the closed forms of the dyads, so it may be concluded that photoinduced electron transfer does not occur in 2-methyltetrahydrofuran. As mentioned above, the open, merocyanine form of the spiropyran does not display observable reduction behavior in cyclic voltammetry at potentials less negative than those of the closed form, so photoinduced redox processes involving this moiety are also unlikely. The energy of ^1Sp_o is lower than that of $^1P_{Zn}$, so its involvement in photoredox processes is also improbable. These arguments suggest that photoinduced electron transfer is unlikely as a quenching mechanism. Thus, singlet−singlet energy transfer is the most probable cause of the quenching. This conclusion is supported by the time-resolved emission spectra measured for **3** (Figure 6b), which have features characteristic of merocyanine emission, even though only the porphyrin chromophore was excited.

Model Spiropyran 1. Although the focus of this work is on the excited-state properties of the porphyrin moieties of the dyads, understanding these properties requires some consideration of the photochemistry of the spiropyran. We will therefore now discuss the spectroscopic results for the model spiropyran **1**. The absorption and emission data in Figure 3 illustrate that in common with other closely related spiropyrans, the closed, spiro form of **1*c*** absorbs only in the ultraviolet region, and has no strong fluorescence. Upon irradiation in the near-UV region, the molecule isomerizes to an open, merocyanine form with strong absorption at 600 nm and emission at 657 nm. This form slowly reverts thermally to the closed form. Irradiation of the merocyanine form with visible light enhances the reversion rate, as is true for other spiropyrans. The time-resolved fluorescence results (Figure 7) indicate that the open molecule, **1*o***, exists in at least three major isomeric forms, with lifetimes of 15, 45, and 120 ps. This is confirmed by the transient absorption data in Figure 8, where three components with similar lifetimes were observed. The species with the 15 ps lifetime emits relatively weakly in the 600−630-nm region, and its decay is apparent in Figure 7. However, at longer wavelengths, where the main spiropyran emission occurs, this component appears as a *rise* in emission intensity with time. Thus, the species responsible for this component is evidently converted into the species having the 45-ps lifetime with a time constant of 15 ps. The 45-ps component is responsible for most of the fluorescence emission, whereas the third component with the lifetime of 120 ps is only weakly emissive around 700 nm.

These results might be taken to suggest that the component with the 120-ps lifetime is of minor importance. However, the transient absorption results in Figure 8 show that this is not necessarily the case. All three components demonstrate significant ground-state bleaching in the region of the merocyanine absorption around 600 nm. If they all have comparable extinction coefficients in this region, then all three are present in considerable amounts. Only the component with a lifetime of 45 ps shows significant stimulated emission around 657 nm, and this is consistent with the time-resolved fluorescence results.

We interpret these results in terms of at least three conformationally isomeric forms of **1*o***. There have been many reports of conformational heterogeneity in the open form of spiropyrans and related photochromic compounds.[50−57] The conformers are usually ascribed to slow rotation about the carbon−carbon bonds in the linkage joining the two rings on the time scale of the observation. The resonance forms of the merocyanine suggest that all three of these bonds have double-bond character, which would pose a significant barrier to rotation. As mentioned above, 8 stereoisomeric forms could exist in principle. In addition, studies of related donor−acceptor substituted stilbene derivatives have been interpreted to show that the excited states of these molecules evolve into emissive twisted intramolecular charge transfer states and nonemissive biradicaloid states via rotations about the corresponding bonds. Thus, generating several transient states after excitation of the merocyanine is fully consistent with previous findings. In addition, it must be remembered that repeated cycling of the spiropyran between the open and closed forms (necessary to obtain the time resolved data) eventually leads to some degradation products that may contribute to the spectra.

Dyads 2 and 3. Because the spiropyran moiety absorbs at shorter wavelengths than the porphyrin in the closed forms of the dyads, energy transfer quenching of the spiropyran singlet state by the porphyrin is thermodynamically possible. However, it is obvious from the spectroscopic results that significant energy transfer does not occur; the spiropyran opens in the usual way to generate the merocyanine. This is consistent with the lack of fluorescence emission from the closed spiropyran and the short lifetimes for the excited singlet states of these and similar photochromic molecules as observed in transient absorption experiments,[58] as both factors would make the closed spiropyran excited singlet state a poor energy donor.

In both **2** and **3**, the merocyanine form closes thermally to the spiro form in an exponential fashion with a rate constant of 3.5×10^{-2} s^{-1} in deoxygenated 2-methyltetrahydrofuran at ambient temperatures. Thus, the open form has a long lifetime relative to any of the other processes of interest in this work, and the ring closure process will be ignored in the kinetic analyses that follow.

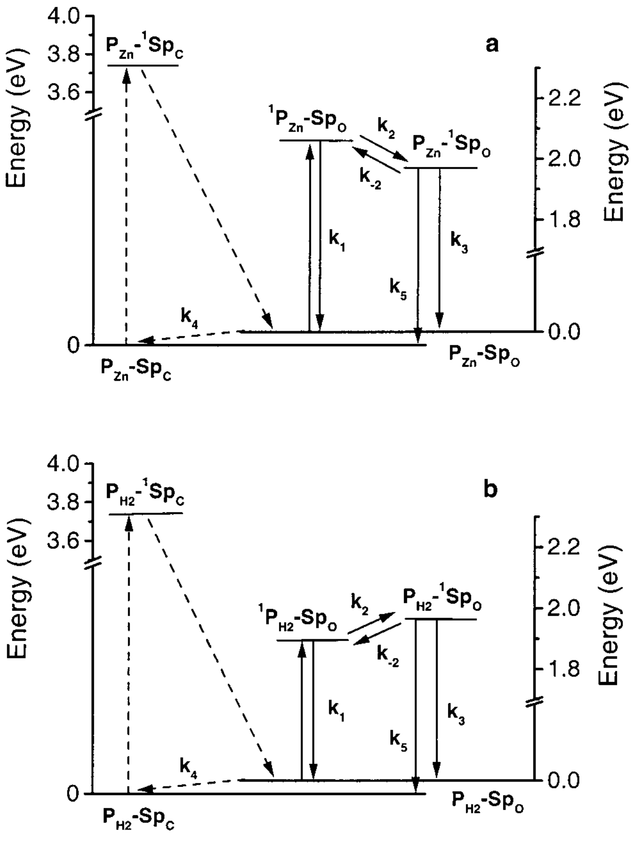

Figure 9. Energies and relevant interconversion pathways for high-energy states of (a) zinc dyad **2** and (b) free base dyad **3**. Excited-state energies are calculated from spectroscopic data, as described in the text.

Dyad 2. Figure 9a shows the relevant ground- and excited-state species for zinc dyad **2** and associated interconversion pathways. The energies are derived from the spectroscopic results given above. In the closed form of zinc dyad, **2*c***, the fluorescence lifetime of the zinc porphyrin first excited singlet state is 1.80 ns, which is essentially identical with that of a model zinc tetraarylporphyrin. Thus, $^1P_{Zn}-Sp_c$ decays by the usual photophysical pathways of internal conversion, intersystem crossing, and fluorescence.

When the sample is irradiated in the UV where the spiropyran absorbs, the steady-state absorption and emission results show that the sample is partially converted to the merocyanine form, $P_{Zn}-Sp_o$. Excitation of this open form at 430 nm, where only the porphyrin absorbs, reveals a quenching of the porphyrin emission, relative to $P_{Zn}-Sp_c$. As photoinduced electron transfer seems unlikely for the reasons mentioned avove, the most reasonable quenching mechanism is singlet−singlet energy transfer to the merocyanine.

The time-resolved emission experiments provide more quantitative information. Continuous irradiation at 340 nm of a sample of **2** in 2-methyltetrahydrofuran generated a mixture of the closed and open forms of the spiropyran. Excitation of this mixture at 430 nm after turning off the continuous light necessarily generated only the porphyrin first excited singlet states. The global analysis of the time-resolved fluorescence emission data yielded only two components, with lifetimes of 1.78 ns and 130 ps (Figure 6a). The 1.78-ns component shows

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(50) Heiligman-Rim; R.; Hirshberg, Y.; Fischer, E. *J. Phys. Chem.* **1962**, *66*, 2465−2477.

(51) Yuzawa, T.; Ebihara, K.; Hiura, H.; Ohzeki, T.; Takahashi, H. *Spectochim. Acta* **1994**, *50A*, 1487−1498.

(52) Takahashi, H.; Yoda, K.; Isaka, H.; Ohzeki, T.; Sakaino, Y. *Chem. Phys. Lett.* **1987**, *140*, 90−94.

(53) Hobley, J.; Malatesta, V. *Phys. Chem. Chem. Phys.* **2000**, *2*, 57−59.

(54) Abe, Y.; Nakao, R.; Horii, T.; Okada, S.; Irie, M. *J. Photochem. Photobiol. A* **1996**, *95*, 209−214.

(55) Cottone, G.; Noto, R.; La Manna, G.; Fornili, S. L. *Chem. Phys. Lett.* **2000**, *2000*, 51−59.

(56) Wilkinson, F.; Worrall, D. R.; Hobley, J.; Jansen, L.; Williams, S. L.; Langley, A. J.; Matousek, P. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1331−1336.

(57) Marevtsev, V. S.; Zaichenko, N. L. *J. Photochem. Photobiol. A* **1997**, *104*, 197−202.

(58) Malatesta, V. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum: New York, 1999; Vol. 2, pp 68−75.

emission maxima characteristic of the zinc porphyrin first excited singlet state, and a lifetime characteristic of the unperturbed porphyrin excited state; it is ascribed to $^1P_{Zn}-Sp_c$. This material is present in relatively large amount because some is present in the photostationary state during irradiation with the 340-nm light, and more is formed as the open form of the spiropyran isomerizes to the closed form during time-resolved data acquisition. The 130-ps component has the general emission profile of the zinc porphyrin first excited singlet state, with possibly some contribution from the open spiropyran moiety around 650 nm. This component is assigned to molecules having the open, merocyanine form of the spiropyran, $P_{Zn}-Sp_o$. The substantial quenching of the zinc porphyrin emission relative to the molecule in the closed form is attributed to singlet−singlet energy transfer to the merocyanine (step 2 in Figure 9a). The rate constant for energy transfer may be estimated from eq 1, where τ is the lifetime of $^1P_{Zn}-Sp_o$. Substituting $\tau = 130$ ps and $k_1 = 5.6 \times 10^8$ s^{-2} (from the 1.80-ns lifetime of the unperturbed zinc porphyrin first excited singlet state) yields a

$$1/\tau = k_1 + k_2 \tag{1}$$

value of 7.1×10^9 s^{-1} for k_2. The quantum yield of singlet−singlet energy transfer is given by eq 2, and equals 0.93.

$$\Phi = k_2/(k_1 + k_2) \tag{2}$$

The $P_{Zn}-{}^1Sp_o$ formed by the singlet−singlet energy transfer process should also emit, as suggested by the fluorescence of model spiropyran **1*o*** (Figure 3). The time-resolved fluorescence results for **1*o*** indicate that the only strongly emissive form of the merocyanine has an excited-state lifetime of 45 ps. However, as this decay rate of $P_{Zn}-{}^1Sp_o$ is significantly faster than its formation rate (130 ps), the concentration of $P_{Zn}-{}^1Sp_o$ is always small, and no contribution from a short decay lifetime was observed in the decay-associated spectra.

In principle, $P_{Zn}-{}^1Sp_o$ could decay not only to the ground state and $P_{Zn}-Sp_c$ but also by reverse energy transfer to the zinc porphyrin, yielding $^1P_{Zn}-Sp_o$ (step −2 in Figure 9a). If this process occurred, additional lifetime components in the decay-associated spectra would be expected (see below), but none were observed. The reason is that k_{-2} is small, relative to the rate constants for other processes. The energy difference between $^1P_{Zn}-Sp_o$ and $P_{Zn}-{}^1Sp_o$ based on the absorption and emission data given above is 0.08 eV, yielding an equilibrium constant of 23 at ambient temperature. This and the value for k_2 estimated above give a nominal value for k_{-2} of 3×10^8 s^{-1}. This value is less than 4% of the rate constant for even the slowest decay process measured for model spiropyran **1** in the open form. Thus, $P_{Zn}-{}^1Sp_o$ decays by other pathways, and endergonic energy transfer by the reverse of step 2 may be ignored.

Dyad 3. Turning our attention to free base dyad **3**, the energetics and interconversion pathways are shown in Figure 9b. When the spiropyran is in the closed form, the $^1P_{H2}-Sp_c$ state has a lifetime of 10.5 ns, which is similar to that of a porphyrin model compound. Thus, this state is not quenched by the attached spiropyran. Irradiation of the compound in the UV results in opening of some of the spiropyran to yield $P_{H2}-Sp_o$, as shown by the absorption spectra in Figure 2b and the emission spectra in Figure 5b. The emission spectrum with excitation into the porphyrin (430 nm) from the solution previously irradiated at 340 nm is less intense than that from pure $P_{H2}-Sp_c$, suggesting that the porphyrin first excited singlet state is quenched by the open spiropyran.

In the time-resolved emission data for **3o** (Figure 6b), three components were observed, with lifetimes of 11 ns, 1.0 ns, and 85 ps. The 11-ns component has the spectral features and typical lifetime of the unperturbed free base porphyrin first excited singlet state, and is attributed to $^1P_{H2}-Sp_c$ whose ground state is present during steady-state UV excitation and forms by thermal isomerization during data collection. The other two components may be ascribed to the merocyanine form, $P_{H2}-Sp_o$.

Turning to Figure 9b, it is evident that the lifetime of the porphyrin first excited singlet state can be shorter than 11 ns only if there is some quenching by the open form of the spiropyran. Quenching by singlet−singlet energy transfer is an endergonic process because $P_{H2}-{}^1Sp_o$ lies at slightly higher energy (1.98 eV) than $^1P_{H2}-Sp_o$ (1.91 eV), based on the absorption and emission data reported above. The energy difference between $^1P_{H2}-Sp_o$ and $P_{H2}-{}^1Sp_o$ yields an equilibrium constant of 0.065. This relatively small energy difference, coupled with the relatively long (11 ns) lifetime of the free base porphyrin first excited singlet state, suggests that singlet−singlet energy transfer will be significant for **3*o***.

In the general case of two excited states rapidly undergoing exchange of singlet excitation, two fluorescence lifetimes will be observed. The reciprocals of these lifetimes, γ_1 and γ_2, do not correspond to any rate constants, but are related to the rate constants in Figure 9b according to the following equations:

$$\gamma_1 = \frac{(X + Y) + \sqrt{(X - Y)^2 + 4k_1k_3}}{2} \tag{3}$$

$$\gamma_2 = \frac{(X + Y) - \sqrt{(X - Y)^2 + 4k_1k_3}}{2} \tag{4}$$

where

$$X = k_1 + k_2 \tag{5}$$

$$Y = k_3 + k_{-2} \tag{6}$$

and the rate constants are defined as per Figure 9b. The time-resolved fluorescence results for **3o** in Figure 6b show that two decay components (85 ps and 1.0 ns) are indeed observed, in addition to the 11-ns component due to porphyrin emission from the closed, spiro form $^1P_{H2}-Sp_c$. If we assign the reciprocals of γ_1 and γ_2 to these lifetimes, we can solve eqs 3−6 for k_2 and k_{-2} if we have values for k_1 and k_3. The value of k_1 is 9.5×10^7 s^{-1}, based on the 10.5-ns lifetime of the unperturbed free base porphyrin first excited singlet state in **3*c***. Choosing a value for k_3 is more problematic, as three lifetimes were found for the mixture of isomeric merocyanine structures in the open form of model spiropyran **1*o***: 15 ps, 45 ps, and ∼140 ps (Figures 7 and 8). One or several of these could be involved in the exchange of singlet excitation energy with the free base porphyrin in **3o**. As it turns out, solutions for eqs 3−6 could only be found using the 140-ps lifetime ($k_3 = 7.1 \times 10^9$ s^{-1}). Using this lifetime, $k_2 = 9.7 \times 10^8$ s^{-1} and $k_{-2} = 4.6 \times 10^9$ s^{-1}. These values in turn give an equilibrium constant $K = k_2/k_{-2} = 0.2$. This is larger than the nominal value of 0.065 calculated from the absorption and emission spectra of **3*o*** and model compounds, but still in relatively good agreement considering that the absorption and emission spectra observed for model **1*o*** are actually composites of the spectra of at least three isomeric forms of the merocyanine, each of which has its own unique spectral properties. Some of the corresponding isomers in **3*o*** may not be directly involved in the energy transfer process. Thus, the energy of the merocyanine first excited singlet state involved in the energy transfer process is somewhat uncertain. On the basis of the rate constants reported above, kinetic simulations show that singlet−singlet energy transfer quenches the fluorescence emission of ^{1}P−Sp$_o$ to 14% of its value in the closed form of the dyad, or a comparable model porphyrin. Of course, the emission in Figure 5b is not quenched to this degree because a substantial amount of the compound in the sample is in the closed, unquenched form.

In both dyads, the open form of the photochromic moiety closes to the spiropyran both thermally and photochemically. Singlet−singlet energy transfer from the porphyrin to the merocyanine would therefore enhance the overall rate of closing. The degree to which this occurs depends on the yields of the various photochemical and isomerization processes, and has not been investigated.

Conclusions

These experiments demonstrate that in both the zinc, **2**, and free base, **3**, porphyrin−spiropyran dyads, the porphyrin first excited singlet states are unperturbed by the attached spiropyran when it is in the closed form. Conversely, even in the presence of the porphyrin moiety, the excited state of the closed spiropyran chromophore formed by UV excitation still opens smoothly to yield the merocyanine, which in turn closes to the spiro form thermally, with a time constant of 20 s, or upon irradiation into its visible absorption band. In the merocyanine form of the zinc dyad, **2o**, the porphyrin first excited singlet state is quenched by the merocyanine with a quantum yield of 0.93, reducing the lifetime from 1.8 ns to 130 ps. The quenching is most reasonably assigned to singlet−singlet energy transfer. In the free base dyad, strong quenching is also observed, even though the energy transfer reaction is slightly endergonic. Thus, in these dyads, the spiropyran is a light-activated “switch” that controls the lifetime of the porphyrin first excited singlet states. As such, it could be used to turn on or off photochemical processes arising from the porphyrin excited singlet or triplet states, including photoinduced electron transfer, singlet energy transfer, and triplet energy transfer. Linking electron or energy donors and/or acceptors to the porphyrin moiety would allow realization of this potential.

Experimental Section

Instrumental Techniques. The ^{1}H NMR spectra were recorded on Varian Unity spectrometers at 300 or 500 MHz. Unless otherwise noted, samples were dissolved in deuteriochloroform with tetramethylsilane as an internal reference. Low-resolution mass spectra were obtained on a Varian MAT 311 spectrometer operating in EI mode or a matrix-assisted laser desorption/ionization time-of-flight spectrometer (MALDI-TOF), as indicated. High-resolution mass spectra were determined on a Kratos MS50 mass spectrometer operating at 8 eV in FAB mode. Steady-state ultraviolet−visible spectra were measured on a Shimadzu UV2100U UV−vis spectrometer.

Steady-state fluorescence emission spectra were measured using a SPEX Fluorolog-2 and corrected. Excitation was produced by a 450-W xenon lamp and single grating monochromator. Fluorescence was detected at 90° to the excitation beam via a single grating monochromator and an R928 photomultiplier tube having S-20 spectral response operating in the single-photon-counting mode.

Fluorescence lifetime measurements were made using the single-photon-timing method. Two different laser systems were used. For excitation between 570 and 630 nm an ultrafast dye laser system was used. It included a frequency-doubled, mode-locked Coherent Antares Nd:YAG laser, which synchronously pumped a cavity-dumped Coherent 700 dye laser. The pulse width was ca. 7 ps, and the average power was ca. 100 μW. The excitation beam was attenuated as needed to obtain 1000−5000 fluorescence counts per second. For excitation at 380−440 nm, a Spectra Physics Tsunami laser was used. Its fundamental output was doubled by a Spectra Physics Model 3980 frequency doubler and pulse selector. The pulse width was 2 ps, and the average power was ca. 1 μW. Fluorescence emission was detected at the magic angle using a single-grating monochromator and a microchannel plate photomultiplier (Hamamatsu R2809U-11). The instrument response time was ca. 35−50 ps, as verified by scattering from Ludox AS-40. The spectrometer was controlled by software based on the LabWindows program from National Instruments.

The femtosecond transient absorption apparatus consists of a kilohertz pulsed laser source and a pump−probe optical setup. The laser pulse train was provided by a Ti:Sapphire regenerative amplifier (Clark-MXR, Model CPA-1000) pumped by a diode-pumped CW solid-state laser (Spectra Physics, Model Millennia V). The typical laser pulse was 100 fs at 790 nm, with a pulse energy of 0.9 mJ at a repetition rate of 1 kHz. Most of the laser energy (80%) was used to pump an optical parametric amplifier (IR-OPA, Clark-MXR). The excitation pulse was sent through a computer-controlled optical delay line. The remaining laser output (20%) was focused into a 1.2 cm rotating quartz plate to generate a white light continuum. The continuum beam was further split into two identical parts and used as the probe and reference beams, respectively. The probe and reference signals were focused onto two separated optical fiber bundles coupled to a spectrograph (Acton Research, Model SP275). The spectra were acquired on a dual diode array detector (Princeton Instruments, Model DPDA-1024).

Synthesis. All reactions were run under an argon atmosphere. The 4-tolyldipyrrolemethane was prepared according to a literature procedure,[59] and was used immediately after recrystallization.

1-(4-Carbomethoxybenzyl)-*exo*-methyleneindoline (4). A solution of commercially obtained 2,3,3-trimethyl-3*H*-indole (7.26 g, 45.7 mmol) and methyl 4-bromomethylbenzoate (10.0 g, 45.7 mmol) in 35 mL of 3-methyl-2-propanone was stirred at 85 °C for 24 h. Upon cooling the solution to room temperature, a viscous sludge formed at the bottom of the flask. Upon addition of ether to the supernatant, additional salt precipitated. This material was dissolved in chloroform and washed with aqueous sodium hydroxide (pH 10). After drying the chloroform solution and removing the volatiles by distillation at reduced pressure, chromatography (silica gel, dichloromethane) was employed to isolate 5.6 g of the product (40%): ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.06 (2H, d, J = 8 Hz, Ar 3,5H), 7.36 (2H, d, J = 8 Hz, Ar2,6H), 7.22 (1H, d, J = 7.2 Hz, indoline-ArH), 7.14 (1H, t, J = 7 Hz, indoline-ArH), 6.87 (1H, t, J = 7 Hz indoline-ArH), 6.54 (1H, d, J = 7.2 Hz, indoline-ArH), 4.79 (2H, s, CH$_2$-Ar), 3.94 (2H, s, −CH$_2$), 3.91 (3H, s, COOCH$_3$), 1.49 (6H, s, indoline-CH$_3$); MS (EI) *m*/*z* 307 (M$^+$).

1′-(4-Carbomethoxybenzyl)-6-nitroindolinospirobenzopyran (5). A solution of **4** (3.0 g, 9.8 mmol) and 5-nitrosalicyaldehyde (1.6 g, 9.8 mmol) in 60 mL of ethanol was refluxed for 2 h. After the mixture was cooled to room temperature, the solvent was removed by distillation at reduced pressure, and the residue was dissolved in dichloromethane. Chromatography (silica gel, dichloromethane) yielded 3.5 g of **5** (79%): ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.04 (1H, d, J = 8 Hz, 7H), 7.98 (1H, s, 5H), 7.95 (2H, d, J = 8 Hz, Ar3,5H), 7.35 (2H, d, J = 8 Hz, Ar2,6H), 7.13 (1H, d, J = 8 Hz, 8H), 7.07 (1H t, J = 7.5 Hz, 6′H), 6.90 (1H, t, J = 7.5 Hz, 5′H), 6.90 (1H d, J = 10 Hz, 4H), 6.78 (1H, d, J = 7.5 Hz, 4′H), 6.29 (1H, d, J = 7.5 Hz, 7′H), 5.90 (1H, d, J = 10 Hz, 3H), 4.54 (1H, d, J = 16 Hz, −CH$_2$−), 4.26 (1H, d, J = 16 Hz, −CH$_2$−), 3.91 (3H, s, −OCH$_3$), 1.35 (3H, s, 3′-CH$_3$), 1.31 (3H, s, 3′-CH$_3$); MS (MALDI-TOF) *m*/*z* 456 (M$^+$).

1′-(4-Hydroxymethylbenzyl)-6-nitroindolinospirobenzopyran (6). A portion of **5** (3.0 g, 6.6 mmol) was dissolved in 50 mL of dry tetrahydrofuran at 0 °C, and excess lithium aluminum hydride was added slowly. After being stirred for 1 h the solution was poured into dichloromethane and washed with dilute citric acid. The organic layer was dried over sodium sulfate, filtered, and concentrated by distillation of the solvent at reduced pressure. Chromatography (silica, dichloromethane containing 2% methanol) was employed to isolate 2.27 g

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[59] Littler, B. J.; Miller, M. A.; Hung, C.-S.; Wagner, R. W.; O’Shea, D. F.; Boyd, P. D. W.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.

of **6** (81%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.02 (1H, d, $J = 7.2$ Hz, 7H), 7.97 (1H, d, $J = 3$ Hz, 5H), 7.29 to 7.25 (4H, m, ArH), 7.12 (1H, d, $J = 7.2$ Hz, 8H), 7.07 (1H, t, $J = 7.5$ Hz, 6′H), 6.88 (1H t, $J = 7.5$ Hz, 5′H), 6.86 (1H, d, $J = 10$ Hz, 4H), 6.78 (1H, d, $J = 7.5$ Hz, 4′H), 6.34 (1H, d, $J = 7.5$ Hz, 7′H), 5.87 (1H, d, $J = 10$ Hz, 3H), 4.67 (2H, d, $J = 6$ Hz, CH_2OH), 4.50 (1H, d, $J = 16.5$ Hz, $-CH_2-$), 4.21 (1H, d, $J = 16.5$ Hz, $-CH_2-$), 1.60 (1H, m, −OH), 1.34 (3H, s, 3′-CH_3), 1.30 (3H, s, 3′-CH_3); MS (MALDI-TOF) *m*/*z* 428 (M^+).

1′-(4-Formylphenyl)-6-nitrospirobenzopyran (1). Excess manganese oxide was added to a solution of **6** (2.0 g, 4.7 mmol) in 40 mL of dichloromethane. After the mixture was stirred at room temperature for 24 h, the suspension was filtered through Celite and concentrated by distillation at reduced pressure. A short silica gel column (dichloromethane containing 0.5% methanol) was employed to remove traces of unreacted starting material. A total of 1.52 g of **1** was isolated (76%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.98 (1H, s, −CHO), 8.04 to 7.99 (2H, m, 5H and 7H), 7.83 (2H, d, $J = 7.8$ Hz, Ar3,5H), 7.47 (2H, d, $J = 7.8$ Hz, Ar2,6H), 7.15 (1H, d, $J = 7$ Hz, 8H), 7.08 (1H, t, $J = 7.6$ Hz, 6′H), 6.91 (1H, t, $J = 7.6$ Hz, 5′H), 6.91 (1H, d, $J = 10.5$ Hz, 4H), 6.78 (1H, d, $J = 7.6$ Hz, 4′H), 6.30 (1H, d, $J = 7.6$ Hz, 7′H), 5.92 (1H, d, $J = 10.5$ Hz, 3H), 4.56 (1H, d, $J = 16.8$ Hz, $-CH_2-$), 4.30 (1H, d, $J = 16.8$ Hz, $-CH_2-$), 1.37 (3H, s, 3′-CH_3), 1.34 (3H, s, 3′-CH_3); MS (MALDI-TOF) *m*/*z* 426 (M^+).

Porphyrin−Spiropyrans (2 and 3). A solution of **4** (1.20 g, 2.85 mmol), 4-methylbenzaldehyde (0.342 g, 2.85 mmol), and *meso*-(4-methylphenyl)dipyrromethane (1.35 g, 5.70 mmol) was prepared in 570 mL of $CHCl_3$. After the solution was purged with argon for 15 min, BF_3OEt_2 (0.23 mL, 1.9 mmol) was added by syringe. The solution was stirred at room temperature in the dark for 1 h, and 2,3-dichloro-5,6-dicyanobenzoquinone (0.98 g, 4.3 mmol) was added. After being stirred for an additional 1 h, the solution was concentrated by distillation at reduced pressure, and the residue was purified by flash chromatography on a short silica column using chloroform as the eluant. All fluorescent bands were collected. The porphyrin-containing products were then separated by chromatography (silica gel, dichloromethane containing 35% petroleum ether). Free base dyad **3** was isolated as purple crystals in 5% yield (138 mg). It was characterized after quantitative conversion to zinc-containing dyad **2** by stirring a solution of **3** overnight with an excess of $Zn(OAc)_2$ in chloroform and chromatographing the product on a short silica gel column: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 to 8.81 (8H, m, pyrrole-H), 8.17 to 8.10 (10 H, m, 7H, 5H, Ar3,5H, por-10,15,20-Ar-2,6H), 7.67 (2H, d, $J = 7.8$ Hz, Ar2,6H), 7.57 (6H, d, $J = 7.7$ Hz, por-10,15,20-Ar-3H,5H), 7.31 to 7.22 (2H, m, 6′H and 8H), 7.03 (1H, t, $J = 7.6$ Hz, 5′H), 7.03 (1H, d, $J = 10.5$ Hz, 4H), 6.92 (1H, d, $J = 7.6$ Hz, 4′H), 6.72 (1H, d, $J = 7.6$ Hz, 7′H), 6.15 (1H, d, $J = 10.5$ Hz, 3H), 4.86 (1H, d, $J = 16$ Hz, $-CH_2-$), 4.54 (1H, d, $J = 16$ Hz, $-CH_2-$), 2.72 (9H, s, por-CH_3), 1.45 (3H, s, 3′-CH_3), 1.43 (3H, s, 3′-CH_3); MS (MALDI-TOF) *m*/*z* 974 (M^+). Dyad **2**: FAB-HRMS, calcd 1038.3236, found 1038.3202 (M^+).

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