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Opening a Spiropyran Ring by Way of an Exciplex Intermediate

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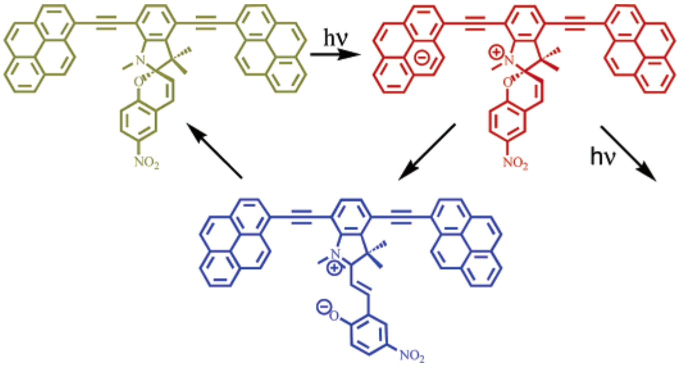

A molecular dyad has been synthesized in which the main chromophore is a 1,4-diethynylated benzene residue terminated with pyrene moieties, this latter unit acting as a single chromophore. A spiropyran group has been condensed to the central phenylene ring so as to position a weak electron donor close to the pyrene unit. Illumination of the pyrene-based chromophore leads to formation of a fluorescent exciplex in polar solvents but pyrene-like fluorescence is observed in nonpolar solvents. The exciplex has a lifetime of a few nanoseconds and undergoes intersystem crossing to the pyrene-like triplet state with low efficiency. Attaching a 4-nitrobenzene group to the open end of the spiropyran unit creates a new route for decay of the exciplex whereby the triplet state of the spiropyran is formed. Nonradiative decay of this latter species results in ring opening to form the corresponding merocyanine species. Rate constants for the various steps have been obtained from time-resolved fluorescence spectroscopy carried out over a modest temperature range. Under visible light illumination, the merocyanine form reverts to the original spiropyran geometry so that the cycle is closed. Energy transfer from the pyrene chromophore to the merocyanine unit leads to an increased rate of ring closure and serves to push the steady-state composition in favor of the spiropyran form.

Introduction

The term photochromism refers to the reversible transformation of a compound between two forms having disparate absorption spectral profiles, with at least one of the formation reactions being driven by light absorption.[1] Although a great number of molecules,[2] including naturally occurring substances,[3] display photochromism, the so-called spiropyrans[4] have received intensive study over many decades. Indeed, a wide variety of important applications have been found for photochromic spiropyrans. Such uses range from transient data storage,[5] to optical filters for eye protection,[6] to self-developing photography.[7] Of late, considerable interest has been given to the

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development of optical data storage systems with novel read-write features.[8] Other applications involve photochemical switching,[9] ion transfer through membranes,[10] and surface modulation and 3-D imaging.[11] Paramount to all such applications is the light-induced conversion of the colorless spiropyran (SP) to the colored merocyanine (MC) form.[12] This transformation leads to a large increase in dipole moment, a feature that allows the optical properties to be probed by both polarity and electrical field effects, and a marked change in geometry.[13] Conversion of the ring-opened MC to ring-closed SP is accomplished by illumination with visible light, although there is often a slow dark reaction that restores the SP form.[14]

The mechanisms and rates of the two photochemical steps have been subjected to detailed examination by theoretical[15] and spectroscopic study.[16] Evidence has accumulated to show that photoconversion of the SP to MC forms can take place via both singlet[17] and triplet[18] excited states but the reverse process seems to occur exclusively by way of the singlet manifold. The triplet mechanism allows sensitization of the ring-opening step and, in turn, this leads to a marked improvement in the optical properties of the light-absorbing unit.[19] Alternatively, the rate of ring opening can be influenced by changes in solvent polarity.[20] Here, we have sought to develop a different route for the SP to MC conversion that allows for a wide choice of chromophore and retains the polarity dependence. This new approach to ring opening makes use of the amino donor site inherent to the SP moiety to form an exciplex intermediate with a covalently attached polycyclic aryl hydrocarbon.[21] Provided the energy levels are carefully balanced, intersystem crossing within the exciplex provides a means by which to populate the triplet excited state localized on the SP unit. Once formed, this latter species acts as the precursor for the MC form.

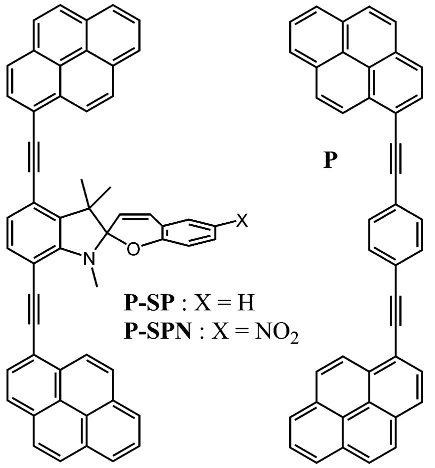

FIGURE 1. Molecular formulas for the spiropyrans and pyrene-based reference compound studied here.

As a test of this ring-opening strategy we have synthesized a T-shaped, pyrene-based SP derivative whereby the ancillary chromophore is provided by a highly delocalized polycyclic hydrocarbon. The two molecular fragments are connected by way of a rigid framework that brings the pyrene subunit into close proximity with the amino donor that is an integral part of the SP function. The resultant system, **P-SP** (Figure 1), has been characterized in full detail. To activate the ring-opening step, the SP unit has been functionalized with a nitro group on the terminal phenylene ring, forming **P-SPN** (Figure 1). Our studies have shown that illumination into the pyrene-based chromophore leads to ring opening and transient formation of the MC species. This latter geometric form, which is fluorescent and highly colored, has a lifetime of ca. 20 s in methyltetrahydrofuran at 20 °C but returns to the closed form via both thermal and photodriven processes. We now examine the mechanisms of the ring-opening and ring-closing events in the context of developing a next-generation Write-Read-Erase optical system. It is also interesting to consider this system in terms of its dual fluorescence properties, bearing in mind that the fluorescence spectral profile is sensitive to the composition of the equilibrium mixture and that intramolecular energy transfer can take place within the open form.

Results and Discussion

Synthesis. The general procedures used in the preparation of spiropyran-based molecular systems are very well documented, and represent a convergent synthetic approach.[22] The formation of the linking sp^3 spiro carbon center generally involves condensation of a methyl indolinium salt and an appropriately functionalized aromatic aldehyde.[23] To this end, we devised a synthetic strategy utilizing this well-established procedure. However, care has to be taken regarding which unit is functionalized. That is to say, we chose to graft the

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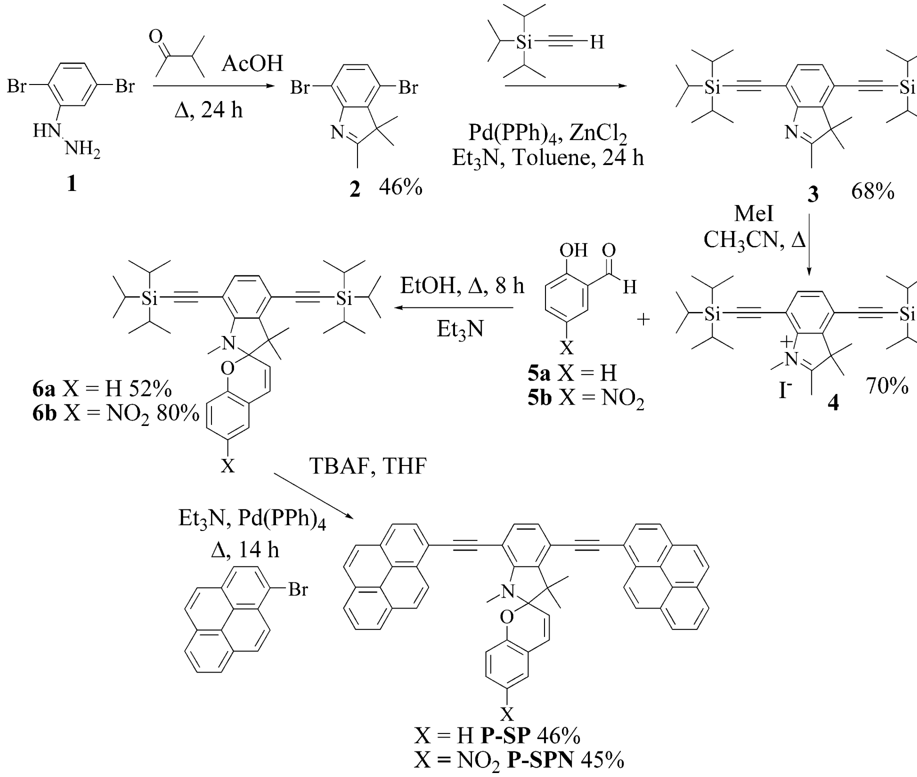
SCHEME 1. General Methods Used in the Preparation of the T-Shaped Dyads



photoactive unit onto the benzene ring of the methyl indolinium function, rather than at the nitrogen atom—the latter being the normal site for attachment of functionalizing groups.[24] The main gain from our approach is that it opens up the possibility for making a wide range of spiropyran dyads. It should be noted that this approach minimizes the number of model compounds needed for photophysical characterization. The main reference compound required, 1,4-bis(pyrenylethynyl)benzene (**P**), is easily prepared from 1,4-bis(trimethylsilylethynyl)benzene by deprotection with *tert*-butylammonium fluoride and palladium-catalyzed cross-coupling with 2-bromopyrene.

Illustrated in Scheme 1 is a breakdown of the procedures used to prepare the molecular dyads: note well, these systems are termed dyads in that the pyrene-based chromophore and the spiropyran-based switch are the two active components. The starting point is the preparation of 4,7-dibromo-2,3,3-trimethyl-3*H*-indole **2**, since it was expected that the bromo groups could be substituted later in the synthetic procedure with acetylene groups under the usual cross-coupling conditions. Following the standard Fisher indole synthesis[25] reaction of 1 equiv of 2,5-dibromophenylhydrazine, **1**, with 2 equiv of 3-methyl-2-butanone in dry acetic acid under reflux afforded, after workup, compound **2** in 46% yield. The cross-coupling of **2** with (triisopropylsilyl)acetylene under conventional Sonogashira[26] coupling conditions was problematic, and a great number of side products were isolated. However, the reaction of **2** with (triisopropylsilyl)acetylene with a Negishi-type[27] palladium catalyzed cross-coupling reaction in refluxing toluene gave 2,3,3-trimethyl-4,7-bis[triisopropylsilyl)-ethynyl]-3*H*-indole **3**, in excellent yield. It should be noted that toluene as solvent is essential since use of lower boiling point solvents (e.g., THF) gave rise to the monoethynylated product. Methylation at the 1-position of the indole ring with iodomethane afforded the tetramethyl indolinium iodide salt **4** in good yield. The precursor-protected spiropyrans (**6a**,**b**) are formed by condensation of **4** with the appropriate salicylaldehydes (**5a**,**b**) in ethanol in the presence of triethylamine. Introduction of the required pyrene units was achieved by in situ fluoride triisopropylsilyl deprotection of **6a**,**b** and palladium catalyzed cross-coupling with 2-bromopyrene. The dyads were readily soluble in standard organic solvents.

Photophysical Properties of the P-SP Dyad. The electronic absorption spectrum of the pyrene-based reference compound (**P**) shows a series of well-resolved bands with maxima between 320 and 450 nm. The spectral shape and position are quite insensitive to changes in solvent polarity and the onset of absorption is located at ca. 425 nm. There are marked similarities between absorption spectra recorded for **P** and the corresponding dyad **P-SP** in cyclohexane solution. The most notable differences are a modest red shift and a general loss of spectral resolution for the dyad. The less intense absorption bands associated with the SP moiety located at ca. 350 nm are obscured by pyrene-based electronic transitions. Hence, it is not possible to selectively illuminate into the SP unit for any of these dyads but, in contrast, the pyrene-based excited singlet state can be accessed with complete selectivity. Fluorescence is observed for both compounds in deoxygenated cyclohexane. In each case,

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TABLE 1. Photophysical Properties of the Various Pyrene-Based Compounds Measured in Deoxygenated Solution at Room Temperature

property	solvent	**P**	**P-SP**	**P-SPN**
Φ_F[a]	cyclohexane	0.67	0.62	0.66
	MeTHF	0.62	0.52	0.040
	MeCN[e]	0.65	0.39	0.004
τ_F/ns[b]	cyclohexane	2.2	1.7	1.3
	MeTHF	2.1	2.2	0.19 (84%) 4.7 (16%)
	MeCN	2.4	3.4	0.07 (95%) 2.8 (5%)
τ_T/μs[c]	cyclohexane	90	85	80
	MeTHF	80	80	80
	MeCN	80	70	65
SS/cm^{-1} [d]	cyclohexane	400	730	700
	MeTHF	420	1280	1150
	MeCN	480	2140	1900

[a] Fluorescence quantum yield, ±8%. [b] Fluorescence lifetime, ±5%. [c] Triplet lifetime, ±10%. [d] Stokes shift, ±80 cm^{-1}. [e] Acetonitrile.

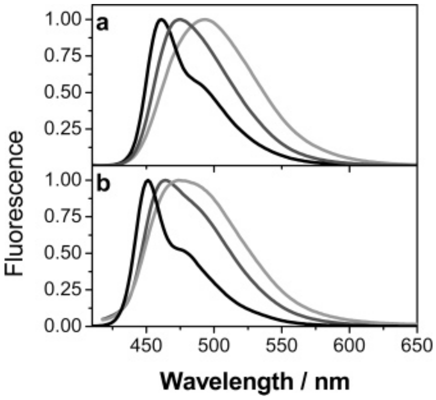

FIGURE 2. Normalized fluorescence spectra recorded for (a) **P-SP** and (b) **P-SPN** in cyclohexane (black), MeTHF (dark gray), and acetonitrile (gray) at room temperature following excitation into the pyrene-based chromophore.

the corrected excitation spectrum matches well with the absorption spectrum but the Stokes' shift increases from 400 cm^{-1} for **P** to 730 cm^{-1} for **P-SP**. Again, fluorescence from the dyad is somewhat less well resolved than that from **P**. The fluorescence quantum yields (Φ_F) and lifetimes (τ_F), however, are comparable (Table 1).

For **P-SP**, the fluorescence maximum shifts progressively toward longer wavelength with increasing polarity of the solvent: appearing at 461, 473, and 493 nm, respectively, in cyclohexane, MeTHF, and acetonitrile (Figure 2). Indeed, the Stokes' shift (SS) increases markedly with increasing solvent polarity (Table 1). There is a progressive decrease in Φ_F but a slight increase in τ_F (Table 1) and further loss of vibrational fine structure (Figure 2) with increasing solvent polarity. In each solvent, fluorescence decay occurs by way of a monoexponential process. The fluorescence spectral properties are independent of concentration over the range of interest and there are no indications for intermolecular interactions. The fluorescence spectral profile and intensity recorded for **P-SP** in MeTHF remain independent of temperature on progressively cooling the solution from 298 to 150 K. Below 150 K the spectral profile evolves steadily toward that found in cyclohexane; at 80 K, the 0,0 transition is at 465 nm (see the Supporting Information). Phosphorescence was not detectable at 80 K, even when 10% v/v iodoethane was added.

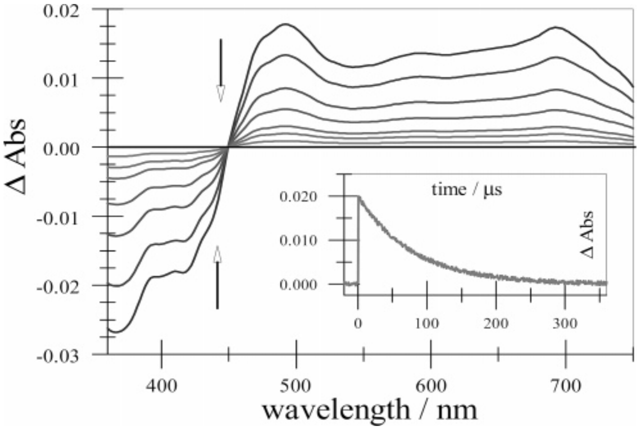

FIGURE 3. Transient differential absorption spectra recorded after laser excitation (λ = 355 nm) of **P-SP** in deoxygenated MeTHF. The insert shows a decay profile recorded at 490 nm.

Laser flash photolysis studies carried out with **P-SP** in deoxygenated solution at room temperature show a weak signal that could be attributed to transient formation of the π,π^* excited triplet state (Figure 3). Transient bleaching is observed in the region where the pyrene chromophore absorbs while weak absorption is seen over the range from 440 to 760 nm. Addition of 10% v/v iodoethane enhances the signal by a factor of about 4-fold but decreases the lifetime from 80 to 20 μs in acetonitrile. Molecular oxygen quenches the signal. All indications point to the transient species being the π,π^* triplet state localized on the pyrene unit,[28] as confirmed by comparison to spectra recorded for **P** under the same conditions (see the Supporting Information). The quantum yield (Φ_T) for formation of the triplet state is ca. 0.10 in cyclohexane but increases to around 0.20 in both MeTHF and acetonitrile. The triplet lifetime remains comparable in all solvents at low laser intensity but there are indications for triplet−triplet annihilation at higher laser power.

Our understanding of the **P-SP** excited-state manifold can now be summarized as follows: Excitation in cyclohexane gives rise to a first-excited singlet state that is pyrene-like and is primarily of π,π^* character. This species is highly fluorescent but possesses increased charge-transfer character relative to pyrene, probably due to interaction with a high-lying charge-transfer state.[29] Increasing the polarity of the solvent leads to stabilization of this charge-transfer state such that it now lies at lower energy than the corresponding pyrene-based π,π^* state. The charge-transfer state, which is destabilized below the glass transition temperature due to the restriction in solvent reorientation,[30] can be considered to be a further example of the well-known exciplex family formed between pyrene and amine donors.[31] There is no indication in any of the spectral records to suggest that the SP ring is opened following illumination. Indeed, absorption bands due to the SP function are obscured

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TABLE 2. Results from the Time-Resolved Fluorescence Studies Carried out with P-SPN in Deoxygenated MeTHF as a Function of Temperature

temp/K	t_1/ps	t_2/ns	A_1/%	$k_F{}^a$	$k_B{}^b$	$k_D{}^c$	ΔE^d
323	110	0.83	87	6.1	11.4	10.8	4.5
318	130	0.89	88	5.0	9.1	10.0	4.5
313	160	1.00	89	3.7	7.2	8.6	4.3
308	190	1.05	89	2.9	6.3	7.9	3.9
303	120	1.04	92	5.8	6.9	8.6	5.4
298	180	1.10	91	3.2	5.5	7.8	4.4
293	150	1.10	92	4.3	5.7	8.0	4.9
288	170	1.49	93	3.6	4.9	5.4	4.8
283	190	1.88	94	3.1	4.1	4.0	4.7
278	160	1.50	96	4.1	2.9	6.0	6.1
273	170	1.60	95	3.7	3.6	5.3	5.3
268	200	1.65	96	2.9	2.6	5.3	5.4
263	220	1.75	97	2.5	1.8	5.1	5.7
258	180	1.80	97	3.5	2.1	5.0	6.0
254	230	1.87	98	2.3	1.2	4.9	6.3

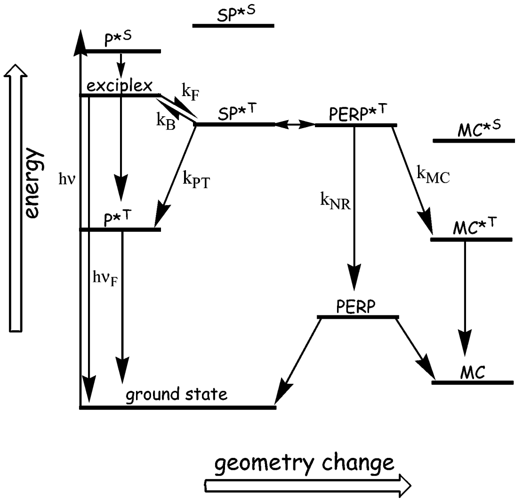
[a] ±8%, units 10^9 s^{-1}. [b] ±8%, units 10^8 s^{-1}. [c] ±12%, units 10^8 s^{-1}. [d] ±20%, units kJ mol^{-1}.

by π,π^* transitions localized on the pyrene-like chromophore and it is clear that photons collected by this latter chromophore are not used to open the SP ring in either polar or nonpolar solvent.

Photophysical Properties of P-SPN. The electronic absorption spectrum of **P-SPN** remains remarkably similar to that of **P-SP** in each of the three solvents investigated. Likewise, the fluorescence spectra of the two compounds are closely comparable, except for a slight blue shift noted for **P-SPN** (Figure 2). This leads to a small reduction in the size of the Stokes' shift (Table 1). It is notable that both Φ_F and τ_F for **P-SPN** remain similar to those of **P-SP** in deoxygenated cyclohexane (Table 1), where ring opening does not take place, and where the fluorescence is pyrene-like. Under such conditions, the corrected fluorescence excitation spectrum is in good agreement with the absorption spectrum while fluorescence decay profiles are strictly monoexponential at all monitoring wavelengths. The close similarity between the photophysical properties of the two compounds can be used to argue that the same species is responsible for the observed fluorescence in each case. Fluorescence decay leads to partial formation of the π,π^* triplet state localized on the pyrene-like chromophore, Φ_T being around 0.10, but no other transient species are observed in the spectral records.

However, in polar solvents Φ_F is much lower for **P-SPN** than for **P-SP** (Table 1). In MeTHF, Φ_F is reduced a factor of 13-fold whereas acetonitrile leads to a 100-fold decrease in Φ_F relative to **P-SP**. In both solvents, the fluorescence decay profiles were dual-exponential. In MeTHF, for example, the decay profiles were dominated by a short-lived component of ca. 0.2 ns but there was clear evidence for a minor contribution from a longer lived species (Table 1). Again, corrected fluorescence excitation spectra were in good agreement with the corresponding absorption spectrum and the fluorescence decay profiles were independent of both monitoring and excitation wavelengths. It was clear, however, that the contribution of the longer lived component increased progressively with increasing temperature while both derived lifetimes increased with decreasing temperature (Table 2). Repeated purification of the sample and solvent had no effect on the time-resolved fluorescence decay profiles. Furthermore, time-gated fluorescence spectra[32] were identical for the short- and long-lived components. The simplest explanation for this latter finding is that, in a polar solvent, the exciplex lies in thermal equilibrium with a lower lying excited state that itself undergoes fast nonradiative decay to a dark state.[33]

SCHEME 2. Outline for the Ring-Opening Processes That Follow Illumination into the Pyrene-Based Chromophore Present in P-SPN



$$I_F(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + (1 - A_1) \exp\left(-\frac{t}{\tau_2}\right) \qquad (1)$$

$$K = \frac{k_F}{k_B} = \exp\left(-\frac{\Delta E}{RT}\right) \qquad (2)$$

The time-resolved fluorescence (I_F) results can be analyzed in terms of eq 1, where τ_1 and τ_2 are the two lifetimes and A_1 refers to the fractional contribution of the shorter lived species. In turn, the derived parameters can be used to calculate[33] rate constants for conversion of the exciplex into the new state (k_F), for the corresponding reverse process (k_B) whereby the exciplex is repopulated from the new state, and for nonradiative decay of the new state (k_D). Furthermore, the energy gap (ΔE) between the exciplex and the new state can be derived by virtue of eq 2, where K refers to the equilibrium constant for the reversible interchange between the exciplex and the new state (Scheme 2). The parameters derived for MeTHF over a modest temperature range are collected in Table 2. Similar behavior was found in acetonitrile, albeit over a smaller temperature range, where it was found that k_F, in particular, is much higher than in MeTHF.

From this analysis it appears that there is a slight tendency for both k_F and k_D to decrease on lowering the temperature whereas k_B is somewhat more sensitive to changes in temperature. Because k_F and k_B show disparate temperature effects, it follows that the corresponding equilibrium constant increases with decreasing temperature and this, in turn, means that the

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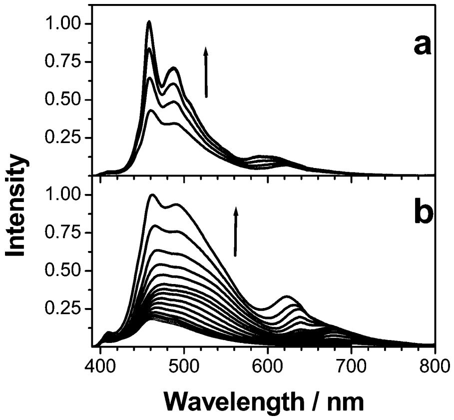

FIGURE 4. Effect of decreasing temperature on the fluorescence spectrum of **P-SPN** in MeTHF recorded at 10-deg intervals over the range (a) 80−120 and (b) 120−300 K. Note the slit widths were decreased from (b) 5 to (a) 2 nm to offset the effects of increased intensity.

energy gap (ΔE) between the exciplex and the reservoir state increases slightly as the temperature is lowered (Table 2). Since the fluorescence maximum noted for the exciplex is insensitive to changes in temperature, at least over the relevant range, it seems likely that the energy of the reservoir state must decrease progressively with decreasing temperature. The net effect is small and it is clear the exciplex and reservoir states are close in energy.

The steady-state fluorescence spectral profiles also exhibit interesting temperature effects. On rapid cooling of the MeTHF solution to 80 K the fluorescence spectrum changes from that typical of the exciplex at room temperature to the pyrene-like emission in the glassy matrix.[34] The fluorescence quantum yield and lifetime measured at 80 K are 0.51 and 2.6 ns, respectively. No other fluorescent species could be seen under these conditions. This behavior is to be contrasted with that observed on slowly cooling the solution and recording spectra at regular temperature intervals (Figure 4). Here, the fluorescence intensity increases progressively until around the freezing point of MeTHF (−136 °C) where the spectral profile begins to sharpen. Below the glass transition temperature (ca. 120 K) the fluorescence spectrum is reminiscent of the pyrene-like π,π^* emission seen for **P-SP** under these conditions. An additional feature of these emission spectra is the development of new fluorescence bands at long wavelength (Figure 3). At 250 K, there are two such bands with peaks at 678 and 640 nm but the emission spectrum evolves in favor of the higher energy band as the temperature is lowered. At temperatures below ca. 180 K, the fluorescence maximum shifts progressively from 640 nm to around 600 nm although the 678 nm band is still evident (Figure 4).

These new fluorescence features arise from photolysis into the pyrene-like band, as can be demonstrated by steady-state illumination at fixed temperature. Corrected excitation spectra indicate that both bands are due to ring-opened MC forms. Based on earlier work[9c,16a,18a,35] with the parent SP module, the species responsible for fluorescence around 678 nm is most likely the cis isomer while the higher energy fluorescence can be attributed to the corresponding trans isomer. At ambient temperature, the cis isomer converts rapidly into the trans form[16a,35c] but this structural change becomes progressively more difficult as the temperature is lowered. Literature work indicates that the trans isomer reconverts, both thermally and photolytically, to the original SP geometry.[14,36] It is notable that the energy gaps between the exciplex and the MC forms, taken simply as the respective emission maxima, far exceed the ΔE values derived from the time-resolved fluorescence spectra. This means that the reservoir state, which in any case is a dark species, is not a ring-opened MC.

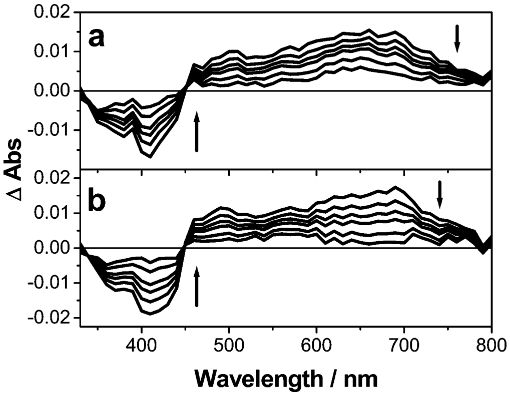

FIGURE 5. Transient differential absorption spectra recorded for **P-SPN** in deoxygenated (a) MeTHF and (b) acetonitrile at delay times 10, 25, 45, 60, 100, and 160 μs following laser excitation at 355 nm.

A more likely assignment for the reservoir state is the lowest energy triplet localized on the SP moiety. It is known that ring opening of SP can be effected by triplet sensitization[19] and we have shown that a triplet state is involved in the formation of the MC form. The corresponding SP singlet excited state lies at an energy above that of the pyrene-based singlet state and therefore well above the energy level associated with the exciplex. The energy of the SP triplet state (SP^{*T}) should be close to that of the exciplex such that k_F can be assigned to intersystem crossing from the exciplex to SP^{*T} while k_B refers to the reverse step (Scheme 2). Consequently, k_D must refer to the sum of all other processes leading to deactivation of SP^{*T} ($k_D = k_{NR} + k_{PT} + k_{MC}$).

Laser flash photolysis studies carried out with 4-ns excitation pulses delivered at 355 nm, where the pyrene-like chromophore is the only absorbing species, show that the pyrene-like triplet (P^{*T}) excited state is present (Figure 5). This species has a characteristic differential absorption spectrum, already identified from studies made with **P-SP**, and seen clearly from its absorption at long wavelengths. This species decays with a lifetime of 80 μs in deoxygenated MeTHF at room temperature. Other species are also evident in the transient records. One such contributor appears as a permanent product on the available time scale (<10 ms) (Figure 5) and can be identified from its characteristic absorption spectrum as being the ring-opened MC form.[9c,16a,18a] It is known that this latter species reverts to the SP form with a lifetime of ca. 20 s under these conditions. A second contributor decays with a lifetime of ca. 5 μs (Figure 6). The differential absorption spectrum of this latter species

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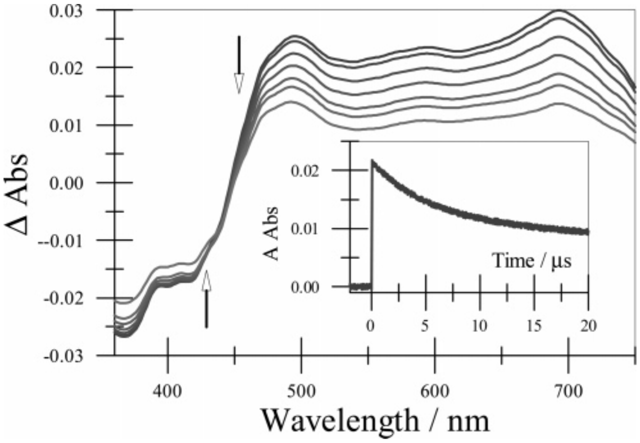

FIGURE 6. Transient differential absorption spectra recorded for **P-SPN** in deoxygenated MeTHF at delay times 0.1, 0.2, 0.5, 1, 2, 5, and 10 μs following laser excitation at 355 nm. The insert shows a decay profile recorded at 500 nm.

can be resolved by removal of the P^{*T} spectrum, normalizing at 700 nm, and is consistent with that expected for the triplet state of the MC form.[37] At room temperature, we expect the trans isomer to be the dominant, if not the only, MC form present so the derived spectrum can be assigned to the triplet state of this species.

Confirmation of this assignment was obtained from a two-color experiment in which the sample was first subjected to preirradiation at 355 nm to build up the MC form, before laser photolysis at 560 nm (see the Supporting Information). Under such conditions, the MC form is the only species able to absorb at 560 nm and the resultant transient absorption spectrum, which decays with a lifetime of 7 μs in deoxygenated MeTHF at 200 K, can be assigned to the corresponding triplet state. Both spectrum and lifetime are consistent with the assignment made on the basis of the 355-nm excitation studies.

It appears, therefore, that the SP^{*T} formed from the exciplex decays to form a mixture of P^{*T} and the ring-opened MC form (Scheme 2). Presumably, the latter species is formed by way of the so-called perpendicular triplet state ($PERP^{*T}$),[16a,18a,35b] which itself decays to form a mixture of cis and trans MC isomers. As already mentioned,[14,36] the cis isomer rapidly converts to the more stable trans isomer at room temperature but can be seen by fluorescence spectroscopy at low temperature. As such, k_D can be partitioned into the three individual rate constants leading to formation of P^{*T} (k_{PT}), MC^{*T} (k_{MC}), and the ground state PERP (k_{NR}).

Mechanism for Ring Opening. Relying heavily on earlier work[9d,16a−d] carried out with simpler SP derivatives, the ring opening process for **P-SPN** can be summarized in terms of Scheme 2. The unusual feature of this scheme concerns the key role played by the exciplex. Also, the onset of delayed fluorescence due to thermal repopulation of the exciplex from the dark reservoir state, now identified as the SP^{*T}, allows additional energy levels and rate constants to be quantified. A key feature is that the SP^{*T} lies at slightly lower energy than the exciplex such that it can be populated by intersystem crossing. The energy level of this triplet state seems to be slightly dependent on temperature, which might reflect a modest structural change. Once formed, the SP^{*T} converts rapidly to $PERP^{*T}$, with the later triplet being responsible for ring opening. For **P-SP**, ring opening is too slow to compete with decay of $PERP^{*T}$ and, since formation of P^{*T} is far from quantitative, there must be an escape route to reform the ground state via nonradiative decay. For **P-SPN**, however, $PERP^{*T}$ partitions between P^{*T} and ring opening.[38] It is clear that these two triplets are not in thermal equilibrium and population of P^{*T} does not facilitate ring opening. Since the triplet state of the ring-opened form can be detected at early times in the flash photolysis records following excitation of the pyrene-like chromophore, it follows that there must be a direct link between $PERP^{*T}$ and MC^{*T}.

Solvent polarity plays an important role in formation of the MC form.[20] In nonpolar solvents, the mechanism is switched-off since exciplex formation is inefficient and the photophysics are localized on the pyrene-like unit. In moderately polar solvents, such as MeTHF, ring opening is able to compete with formation of P^{*T} and the MC form is formed in modest yield. On moving to more polar solvents, such as acetonitrile, there is a significant increase in k_F but a reduction in the yield of the ring-opened MC form. This finding suggests that partitioning favors formation of P^{*T} in polar solvents, probably because the energy of the MC-based triplet states will increase in polar solvents.[39] (Note well, the energy level for MC^{*T} remains unknown since this species does not show phosphorescence after rapid cooling to 77 K.) The transient absorption spectral records show the presence of the latter species (MC^{*T}) at the end of the laser pulse. Although the open form accumulates during repetitive laser flashing, it is still possible to detect MC^{*T} in a flow cell where each laser shot is directed to a fresh aliquot of solution. This means that the MC^{*T} must arise, at least in part, directly from the $PERP^{*T}$. Finally, to allow for formation of the cis isomer, it is necessary to consider that the SP^{*T} and/or $PERP^{*T}$ undergo(es) nonradiative decay to give a mixture of open and closed forms in their respective ground state geometries.

Ring Closing To Reform the Spiropyran. It has been shown that the ring-opened MC form of **P-SPN** reverts back to the corresponding SP form on standing in the dark. The lifetime of the MC form is ca. 20 s in deoxygenated MeTHF at 20 °C and the activation energy for ring closure is ca. 60 kJ mol^{-1}.[22] These values seem to be in line with results collected for the parent SP unit in various solvents.[40] Thermal reformation of the SP form is very much slower ($\tau \approx 36$ min) in sucrose octaacetate glass, no doubt due to the greatly increased viscosity although ring opening is still highly efficient and light-induced ring closure occurs readily. The ring-opened forms, both cis and trans isomers, fluoresce at ambient temperature and also form relatively long-lived excited triplet states. On illumination into the pyrene-like absorption bands, the ring-opened form accumulates in solution but quickly reaches a steady-state value

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[38] The role of the nitro group in promoting ring opening is unclear. Ring opening does not take place when the nitro group is replaced with either a hydrogen atom or a cyano group. Replacing pyrene with perylene lowers the excitation energy of the exciplex to below that of the SP^{*T} and again there is no ring opening. The nitro group might facilitate intersystem crossing, because of its efficient spin orbit coupling properties, or weaken the bond around the spiro center, as shown by X-ray crystallography. Further research is required to fully explore this effect. Note well, the perylene derivative of **P-SPN** was particularly insoluble and limited analytical data are collected in the Supporting Information.

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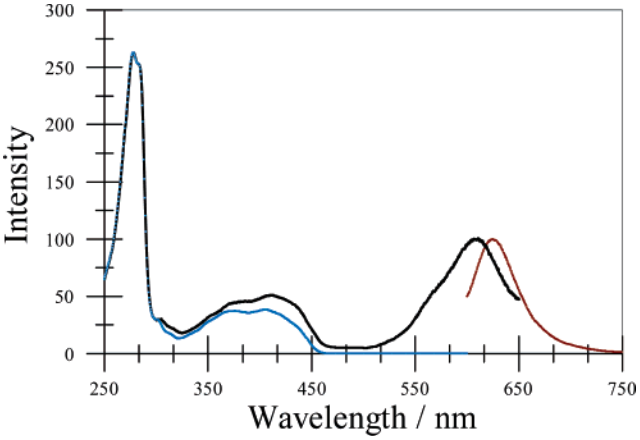
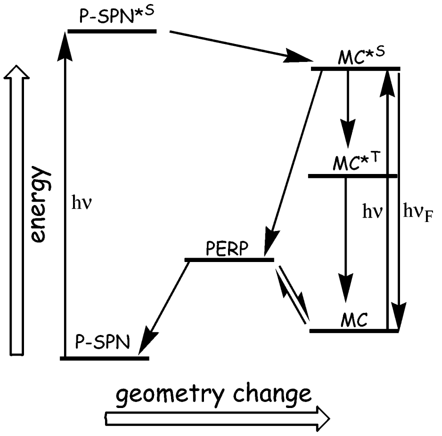


FIGURE 7. Fluorescence (red) and corrected excitation (black) spectra recorded for the MC form in deoxygenated MeTHF at 200 K and the absorption spectrum recorded for the pyrene-like chromophore.

SCHEME 3. Proposed Outline for the Ring Closure Step, Allowing for Both Light-Activated and Thermal Processes and for Sensitization by the Pyrene-like Excited Singlet State



that is comprehensively on the side of the SP form. Prolonged irradiation causes gradual decomposition of the material but does not improve the steady-state composition. Illumination into the MC absorption bands causes fast conversion to the original SP geometry such that ring closure must be light activated (Scheme 3). Since the triplet lifetime is not unusually short for a MC dye, it can be argued that photoisomerization occurs from the singlet excited state of the ring-opened species.

In deoxygenated MeTHF at 200 K, where thermal ring closure is relatively slow, the corrected fluorescence excitation spectrum recorded for emission from the trans MC isomer clearly shows that photons absorbed by the pyrene-like chromophore are transferred to the MC form (Figure 7). This requires intramolecular singlet energy transfer and is most likely to involve the Förster dipole−dipole mechanism.[41] Such a process is favored by spectral overlap between pyrene-like emission and absorption by the MC form and by their close proximity. Energy transfer of this type decreases the amount of the ring-opened form in the steady-state composition. It should be noted that, because of the respective absorption spectral profiles, Förster energy transfer from exciplex to the ring-closed SP form is extremely unlikely.

The ring-opened form should be more polar than the corresponding SP form[42] and the extent of resonance polarity might be affected by the nature of the surrounding solvent.[43] Increased polarity, or the increased contribution of zwitterionic resonance forms, will lead to slower rates of ring closure. It is also likely that such polar species will minimize the role of the tertiary amine as an electron donor for the pyrene moiety. As such, a further effect of ring opening might be to switch-off exciplex emission and restore pyrene-like fluorescence. This situation is very difficult to verify experimentally because of the low concentration of MC forms present in the equilibrium mixture.

Concluding Remarks

Ring opening has been achieved via an exciplex state that makes direct use of the tertiary N atom as the primary electron donor. The mechanism works only in moderately polar solvents; the exciplex is not formed in nonpolar environments while there is a reduced yield of MC in strongly polar solvents. Although the choice of chromophore is restricted to UV-absorbing materials it is far wider than that available to conventional triplet sensitization[19] where the singlet−triplet energy gap has to be considered. Because SP-based triplet excited states are involved, ring opening is affected by the presence of dissolved oxygen. Temperature is not a limiting factor and the various forward steps show small activation energies. This leads to a high overall rate of ring opening in fluid solution. A limitation of the present system involves the onset of intramolecular energy transfer from the pyrene fluorophore to the ring-opened MC form. In viscous media, where ring closure is relatively slow, this latter process provides an unusual means for fluorescence modulation.[44] Thus, in the absence of preirradiation with an intense UV pulse, only exciplex fluorescence is observed. After preirradiation, fluorescence is observed in the far red region for both UV and visible illumination. It is also important to note the dual fluorescence found for the exciplex in certain solvents. This allows the energy gap between exciplex and reservoir states to be measured accurately.

This latter situation can be considered in terms of a Write-Read-Erase protocol.[45] A UV pulse is used to write the signal. The far red fluorescence provides the means by which to read the signal. The intensity, peak wavelength, decay rate, dipole moment, and absorption spectral change provide critical information about the system under interrogation. An alternative way to read the signal could involve monitoring the MC^{*T} in deoxygenated media. Additional benefits might accrue from the use of Stark spectroscopy,[46] electric field effects,[47] or fluorescence correlation spectroscopy.[48] An important advantage of this system, perhaps unique in the field, is that a second UV pulse, or a visible light pulse, can be used for fast erasure of the signal. The entire cycle could be operable within times as short as 10

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ns. Ongoing research with **P-SPN** dispersed in solid media[49] are aimed at expanding on this aspect of the work and taking advantage of the high fatigue resistance inherent to polymer-bound material.

Experimental Section

General experimental methods are reported in the Supporting Information. Preparations described below were carried out under a N_2 atmosphere unless stated otherwise.

Preparation of 2,5-Dibromophenylhydrazine (1). To concentrated HCl (110 mL) at 0 °C in a conical flask was added 2,5-dibromoaniline (10 g, 39.7 mmol). The mixture was stirred for 30 min, followed by the dropwise addition at 0 °C of $NaNO_2$ (3.01 g, 43.67 mmol) in water (20 mL). The initial light brown suspension turned yellow and the reaction mixture, maintained at a temperature of 0 °C, was stirred for a further 1 h. Urea (0.15 g, 2.49 mmol) was added and, after stirring for 10 min, $SnCl_2$ (18 g, 79.8 mmol) in concentrated HCl (30 mL) that had been cooled to −30 °C was added slowly, causing the reaction mixture to turn a cream/beige color. The reaction was stirred for 3 h and finally left in a refrigerator overnight. The resultant precipitate was filtered and added to an ice bath and the pH was adjusted to above 10. The crude product was extracted into ethyl acetate, which was washed with dilute NaOH (50 mL). The separated organic fraction was removed under vacuum to give a tan solid that was washed with petroleum ether to afford the product. Yield 7.00 g, 66%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.28 (d, 1H, $J = 2.1$ Hz), 7.23 (d, 1H, $J = 8.4$ Hz), 6.76 (dd, 1H, $J = 8.3$ Hz, $J' = 2.1$ Hz), 5.72 (s, br, 1H), 3.62 (s, br, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 148.5, 133.2, 122.4, 122.1, 115.4, 105.9. FT-IR (cm^{-1}) 3341, 3239, 3177, 3115, 3080, 1614, 1575, 1558, 1486, 1449, 1398, 1296, 1284, 1269, 1144, 1101, 1079, 1015, 940, 880, 836, 784, 734. EI-MS *m/z* 266 (M^+). Elemental analysis calcd (found) for $C_6H_6Br_2N_2$: C 27.10 (27.07), H 2.27 (2.25), N 10.53 (10.26). Mp 90 °C.

Preparation of 4,7-Dibromo-2,3,3-trimethyl-3*H*-indole (2). 2,5-Dibromophenylhydrazine (3.12 g, 11.73 mmol) and 3-methyl-2-butanone (2.02 g, 23.46 mmol) were added to acetic acid (50 mL) and the mixture was heated under reflux temperature for 24 h. The solvent was removed and the reaction mixture was extracted with ethyl acetate (50 mL). The combined organics were washed with aqueous Na_2CO_3 solution (2 × 30 mL) and brine (1 × 30 mL). The organic layer was separated and dried over $MgSO_4$ and the solvent was removed to afford the crude product. Column chromatography on silica gel with ethyl acetate/petroleum ether (3:1) as eluant afforded the pure product as a pale yellow solid. Yield 1.70 g, 46%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.32 (d, 1H, $J = 8.4$ Hz), 7.16 (d, 1H, $J = 8.4$ Hz), 2.31 (s, 3H) 1.45 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 190.7, 154.1, 144.5, 132.7, 130.5, 116.6, 113.5, 58.5, 19.7, 15.7. EI-MS *m/z* (%) 317 (80) [M^+], 302 (56) [$M - CH_3$]$^+$. FT-IR (cm^{-1}) 2979, 2967, 2928, 2866, 1597, 1579. Elemental analysis calcd (found) for $C_{11}H_{11}Br_2N$: C 41.67 (41.75), H 3.50 (3.53), N 4.42 (4.32). Mp 132 °C.

Preparation of 2,3,3-Trimethyl-4,7-bis[(triisopropylsilyl)ethynyl)]-2,3,3-trimethyl-3*H*-indole (3). 4,7-Dibromo-2,3,3-trimethyl-3*H*-indole (2.20 g, 7.17 mmol) was added to a Schlenk flask charged with a suspension of zinc(II) chloride (1.59 g, 11.68 mmol) and triethylamine (20 mL) in toluene (20 mL). The reaction mixture was degassed thoroughly and [Pd(PPh_3)$_4$] (0.828 g, 0.72 mmol) and (triisopropylsilyl)acetylene (3.14 g, 17.21 mmol) were added. The reaction mixture was heated at reflux for 24 h. The solvent was removed under vacuum and the residue was extracted with ethyl acetate (50 mL), before being washed with water (2 × 30 mL) and brine (1 × 30 mL). The organic layer was separated and dried over $MgSO_4$ and the solvent was removed. Column chromatography on silica gel, using EtOAc/petroleum ether (4:100) as eluant, gave the product as a pale cream oily solid. Yield 2.54 g, 68%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.32 (d, 1H, $J = 7.8$ Hz), 7.17 (d, 1H, $J = 8.1$ Hz), 2.29 (s, 3H), 1.45 (s, 6H), 1.16 (m, 42H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 189.5, 155.7, 146.4, 131.8, 129.4, 117.9, 116.1, 104.2, 104.1, 97.4, 96.9, 55.2, 20.3, 18.9, 15.6, 11.7. EI-MS *m/z* (%) 519 (32) [M]$^+$, 476 (100) [$M - CH(CH_3)_2$]$^+$. FT-IR (cm^{-1}) 2940, 2888, 2862, 2144, 1583, 1479. Elemental analysis calcd (found) for $C_{33}H_{53}NSi_2(H_2O)_{0.5}$: C 74.93 (75.23), H 10.29 (10.23), N 2.65 (2.56). Mp 82 °C. [Note well, the oily nature of the solid made accurate elemental analysis difficult even after constant drying.]

Preparation of 1,2,3,3-Tetramethyl-4,7-bis[(triisopropylsilyl)-ethynyl)]-1*H*-indolinium Iodide (4). Methyl iodide (4.25 g, 29.91 mmol) was added to 2,3,3-trimethyl-4,7-bis[(triisopropylsilyl)-ethynyl)]-3*H*-indole (2.55 g, 4.88 mmol) in acetonitrile (40 mL), and the mixture was heated overnight under reflux. The solvent was removed under vacuum and the residue was purified by washing with diethyl ether (15 mL), before being filtered to afford the product as a yellow solid. Yield 2.26 g, 70%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.49 (d, 1H, $J = 9.0$ Hz), 7.44 (d, 1H, $J = 9.0$ Hz), 4.54 (s, 3H), 3.17 (s, 3H), 1.82 (s, 6H), 1.11 (m, 42H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 198.3, 142.6, 140.7, 135.7, 133.7, 120.0, 112.5, 105.4, 101.3, 100.45, 52.0, 39.55, 20.6, 18.7, 11.5. MALDI-MS *m/z* (%) 534.5 (100) [$M - I$]$^+$. FT-IR (cm^{-1}) 2941, 2889, 2862, 2151, 1486. Elemental analysis calcd (found) for $C_{34}H_{56}INSi_2$: C 61.70 (61.57), H 8.53 (8.51), N 2.12 (2.03). Mp >178 °C dec.

General Method for the Preparation of Bis(triisopropylsilylethynyl)spiropyrans (6a,b). 6a: 1,2,3,3-Tetramethyl-4,7-bis-[(triisopropylsilyl)ethynyl)]-1*H*-indolinium iodide (0.100 g, 1.51 × 10^{-4} mol) was dissolved in ethanol (88 mL) containing salicylaldehyde **5a** (0.11 g, 9 × 10^{-4} mol) and triethylamine (1 mL). The reaction mixture was refluxed for 8 h then cooled and the solvent was removed under vacuum. The residue was dissolved in ethyl acetate (40 mL) and washed with aqueous Na_2CO_3 (3 × 40 mL) and brine (1 × 30 mL). The organic fraction was collected and dried over $MgSO_4$ and the solvent was removed under vacuum. The crude material was purified by column chromatography on silica gel, using petroleum ether/diethyl ether (20:1) as eluant to afford the required compound as an oily solid. Yield 0.050 g, 52%. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.19 (d, 1H, $J = 8.1$ Hz), 7.14 (dt, 2H, $J = 7.8$ Hz, $J' = 1.3$ Hz), 7.05 (dd, 1H, $J = 7.5$ Hz, $J' = 1.5$ Hz), 6.86 (m, 2H), 6.78 (d, 1H, $J = 8.1$ Hz), 5.63 (d, 1H, $^3J = 10.2$ Hz), 3.31 (s, 3H), 1.60 (s, 3H), 1.29 (s, 3H), 1.15 (m, 42H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 154.8, 148.4, 138.4, 133.9, 130.1, 129.9, 126.9, 124.4, 120.3, 119.2, 118.9, 118.7, 115.2, 106.2, 105.3, 97.1, 95.5, 52.2, 31.2, 23.3, 20.1, 19.1, 11.9. EI-MS *m/z* (%) 637 (100) [M]$^+$, 594 (13), [$M - CH(CH_3)_2$]$^+$. Accurate mass calcd (found) for $C_{41}H_{59}NOSi_2$ 637.4135 (637.4134). FT-IR (cm^{-1}) 2941, 2889, 2863, 2147, 2136, 1557, 1486. Elemental analysis calcd (found) for $C_{41}H_{59}NOSi_2(H_2O)_{0.5}$: C 76.10 (76.32), H 9.35 (9.26), N 2.16 (1.81). Mp 67 °C.

6b: Yield 0.54 g, 80%. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.04 (dd, 1H, $J = 9.0$ Hz, $J' = 2.7$ Hz), 7.99 (d, 1H, $J = 2.7$ Hz), 7.17 (d, 1H, $J = 8.1$ Hz), 6.92 (d, 1H, $J = 10.2$ Hz), 6.87 (d, 1H, $J = 8.1$ Hz), 6.81 (d, 1H, $J = 8.7$ Hz), 5.79 (d, 1H, $J = 10.5$ Hz), 3.26 (s, 3H), 1.54 (s, 3H), 1.26 (s, 3H), 1.10 (m, 42H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 159.9, 147.7, 141.6, 137.5, 134.1, 128.7, 126.1, 125.0, 122.9, 121.5, 119.0, 118.6, 115.7, 106.7, 105.6, 104.8, 104.0, 97.7, 96.3, 52.7, 31.2, 30.8, 23.3, 21.9, 18.9, 11.8, 11.7. EI-MS *m/z* (%) 682 (100) [M]$^+$, 652 (14) [$M - 2\ CH_3$]$^+$. FT-IR (cm^{-1}) 2941, 2890, 2863, 2144, 1578, 1522, 1464. Elemental analysis calcd (found) for $C_{41}H_{58}N_2O_3Si_2$: C 72.09 (71.80), H 8.56 (8.54), N 4.10 (3.83). Mp 97 °C.

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(49) Preliminary Write-Read-Erase experiments were carried out on **P-SPN** dispersed in sucrose octaacetate glass. Thus, pulsed illumination of a **P-SPN** impregnated glass with short wavelength light ($\lambda_{max} = 400$ nm) caused the development of the usual colored product. The so-formed MC species could be detected by absorption spectroscopy. Subsequent illumination with a long wavelength pulse ($\lambda_{max} = 600$ nm) bleached the colored spot and restored the original spectrum from the pyrene moiety. Repeated cycling was possible by exposure of the glass to the two different wavelengths (see the Supporting Information).

General Method for the Preparation of Dyads. To a refluxing mixture of the spiropyran (**6a**,**b**) (0.400 g, 0.613 mmol), $[Pd(PPh_3)_4]$ (0.075 g, 0.065 mmol), and 2-bromopyrene (0.34 g, 1.21 mmol) in THF (20 mL) were added over 10 h triethylamine (10 mL) and tetrabutylammonium fluoride (1.8 mmol) in THF (10 mL). After 14 h, the solvent was removed and the residue dissolved in CH_2Cl_2 (100 mL), which was washed with water (1 × 50 mL), separated, and dried over $MgSO_4$. Removal of the solvent afforded the crude product, which was purified by column chromatography on silica gel eluting with CH_2Cl_2/petroleum ether (1:2). **P-SP**: Yield 0.21 g, 46%. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.64 (2d, 2H, $J = 9.0$ Hz), 8.09 (m, 15H), 7.57 (d, 1H, $J = 8.1$ Hz), 7.24 (d, 2H, $J = 8.1$ Hz), 7.17 (m, 1H), 7.09 (m, 1H), 6.94 (d, 1H, $J = 10.2$ Hz), 6.88 (m, 2H), 5.87 (d, 1H, $J = 10.5$ Hz), 3.50 (s, 3H), 1.78 (s, 3H), 1.48 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 155.7, 149.5, 139.3, 134.1, 133.0, 132.9, 132.48, 132.44, 132.30, 132.26, 132.18, 131.1, 131.0, 130.4, 130.04, 129.5, 129.3, 129.2. 129.03, 128.3, 127.26, 127.22, 126.66, 126.61, 126.55, 125.75, 125.55, 124.9, 121.3, 119.91, 119.86, 119.61, 119.13, 116.1, 105.6, 104.6, 95.52, 95.27, 94.6, 94.1, 68.94, 54.3, 53.4, 26.7, 24.7, 21.5. MALDI-MS *m*/*z* 725 $[M]^+$. Elemental analysis calcd (found) for $C_{55}H_{35}NO$: C 91.01 (90.74), H 5.04 (5.02), N 1.93 (2.16). Mp 226 °C.

P-SPN was purified by three consecutive column chromatography separations on silica gel with first petroleum ether/diethyl ether (1:1) as eluant, then petroleum ether/THF (2:1), and finally petroleum ether/CH_2Cl_2 (1:2). Yield 0.29 g, 45%. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.66 (d, 1H, $J = 9.3$ Hz), 8.62 (d, 1H, $J = 9.3$ Hz), 8.13 (m, 18 H), 7.59 (d, 1H, $J = 8.1$ Hz), 7.27 (d, 1H, $J = 8.4$), 7.01 (d, 1H, $J = 10.2$ Hz), 6.90 (d, 1H, $J = 8.7$ Hz), 5.92 (d, 1H, $J = 10.2$ Hz), 3.52 (s, 3H), 1.78 (s, 3H), 1.49 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) δ 160.1, 148.2, 141.8, 137.7, 133.6, 132.38, 132.23, 131.9, 131.8, 131.7, 131.6, 129.7, 129.4, 129.2, 128.9, 128.8, 128.5, 127.6, 126.7, 126.6, 126.4, 126.1, 125.9, 125.8, 125.1, 124.9, 123.1, 121.5, 119,3, 118.8, 118.6, 118.1, 115.9, 107.1, 104.4, 94.9, 94.1, 93.8, 93.3, 53.6, 53.2, 31.7, 27.3, 24.0, 20.6. MALDI-MS *m*/*z* (%) 770 (14) $[M]^+$, 621 (100) $[M - (CH)OC_6H_3NO_2]^+$, $[M - CH_3 - (CH)OC_6H_3NO_2]^+$. Elemental analysis calcd (found) for $C_{55}H_{34}N_2O_3$: C 85.69 (85.54), H 4.45 (4.57), N 3.63 (3.73). Mp >180 °C dec.

Preparation of 1,4-Bis(pyrenylethynyl)benzene (P). To 1,4-bis(trimethylsilylethynyl)benzene (0.200 g, 7.39×10^{-4} mol) in THF (20 mL) were added triethylamine (10 mL), $[Pd(PPh_3)_4]$ (0.085 g, 0.0736 mmol), and 2-bromopyrene (0.42 g, 11.49 mmol). The reaction mixture was brought to reflux and a solution of tetrabutylammonium fluoride (0.57 g, 2.20 mmol) in THF (10.2 mL) was added over 8 h. After an additional 10 h of reflux, the solvent was removed and the residue dissolved in chloroform (100 mL), which was washed with water (50 mL), separated, and dried over $MgSO_4$. Removal of the solvent afforded a crude product that was purified by column chromatography on silica gel with petroleum ether/diethyl ether (2:1) as eluant, followed by a second column with petroleum ether/THF (1:1) to afford the required product. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.63 (d, 2H, $J = 9.0$ Hz), 8.12 (m, 16H), 7.73 (s, 4H).

Spectroscopic grade solvents were obtained from commercial sources and redistilled from appropriate drying agents. All solutions were purged with a stream of dried nitrogen gas. All measurements were made at 20 °C, unless stated otherwise, using N_2-purged spectroscopic grade solvent. Quantum yields were measured relative to Coumarin 153 in cyclohexane[50] and were corrected for changes in refractive index as necessary.[51] Variable temperature emission spectroscopy was carried out with a cryostat and a commercial fluorimeter, allowing 15 min equilibration at each temperature. Emission lifetimes were measured at room temperature with a spectrophotometer and at variable temperatures with a time-correlated, single photon counting spectrometer. For all time-resolved fluorescence measurements, the instrumental response function was deconvoluted from the experimental decay record before calculating the fluorescence lifetime. All emission studies were made with optically dilute solutions having an absorbance of ca. 0.08 at the excitation wavelength. A sample of **P-SPN** dispersed in a glass was made by grinding together ca. 1 mg of the sample and recrystallized sucrose octaacetate in a mortar. The solid was transferred to a glass cuvette and melted at ca. 110 °C. Slow cooling of the cuvette afforded a clear glass.

Transient differential absorption spectra were recorded with a standard flash photolysis setup. The sample was deoxygenated by a constant stream of N_2 and irradiated with pulses (fwhm = 4 ns) delivered with a frequency-tripled, Nd:YAG laser. The monitoring beam was a pulsed Xe arc lamp, filtered as appropriate, and directed to a high radiance monochromator. Spectra were compiled point-by-point with 3 individual spectra being averaged at each wavelength. Kinetic measurements were made at a single wavelength by averaging 50 individual traces. Control experiments were carried out to estimate the efficiency of intersystem crossing in **P-SP**. Thus, sufficient iodoethane was added to reduce Φ_F by a fixed amount in deoxygenated cyclohexane solution. Comparing the differential absorption spectral signals observed before and after addition of iodoethane, and allowing for the noted effect on the fluorescence yield, we conclude that the quantum yield for formation of the triplet state is about 0.1 in cyclohexane. Similar measurements were made in other solvents.

To make spectroscopy measurements on the ring-opened form, the N_2-purged solution was preirradiated with light of $\lambda = 355$ nm. For fluorescence measurements, the sample was cooled in a thermostated cell prior to preirradiation for 30 s with monochromatic light from a Xe arc lamp, delivered through an optical fiber. During illumination, the spectrometer slits were blocked by mechanical shutters so as not to saturate the detector. Fluorescence and excitation spectra were recorded on fast scan rates and averaged. Such measurements were made at low temperature where the MC form is relatively stable. The radiative lifetime for the MC form, believed to be the trans isomer, was estimated from the Strickler–Berg expression[52] by using measured absorption and fluorescence spectra and with the molar absorption spectrum at the peak maximum in MeTHF being taken as 52 000 M^{-1} cm^{-1}.[32] For the corresponding transient absorption spectral studies the laser excitation wavelength was 560 nm, as obtained with a frequency-tripled, Nd:YAG laser fitted with an OPO. The sample was housed in an optical cryostat set to a particular temperature and preirradiated as above. The concentration of the MC form present in the sample was measured by transmittance spectroscopy with a laser diode/photocell system. Transient differential absorption spectra were obtained in a single shot with a pulsed Xe lamp and cooled CCD setup. Kinetic measurements were made at fixed wavelength with a high radiance monochromator and PMT.

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Supporting Information Available: ^1H NMR spectra for all new compounds; figures showing the temperature dependence for **P-SP** fluorescence, a triplet absorption spectrum for **P**, absorption spectra for **P-SPN** in different solvents, and a triplet absorption spectrum for the MC form. This material is available free of charge via the Internet at http://pubs.acs.org.

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