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Modulation of Unconventional Fluorescence of Novel Photochromic Perimidine Spirodimers

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Abstract: Fluorescence modulation by a class of photochromic perimidine spirodimers, which exhibit a characteristic fluorescence associated with their photochromic reactions, has been described. Upon irradiation using 365 nm light, these non-fluorescent spiro molecules undergo a thermally-reversible ring opening at their spiro junction resulting in the generation of strong fluorescence. The fluorescing species is distinctly different from both the stable ring-closed and the ring-opened compounds, though it appears to have been formed from and remains in equilibrium with the photochemically generated ring-opened form. While the fluorescing species possesses a narrow absorption band with its maximum centered at 500 nm, the ring-opened form exhibits a broad absorption across the visible region with two maxima centered at 410 and 650 nm, respectively. After initiating the photochromic reactions in these molecules using 365 nm light, purely photochemically-controlled fluorescence modulation can be carried out using two wavelengths in the visible region, that is, 500 and 700 nm, while the equilibrium concentration of the ring-opened form and the fluorescing species is controlled. Fluorescence modulation is attained also by controlling the ratio of the ring-closed and ring-opened forms by photochemical ring-opening and thermal ring-closing reactions. The study on the effect of substitution of these molecules suggests that by extending the conjugation of the perimidine core in the ring-opened form the molecule is rendered non-fluorescent and hence it can be assumed that the perimidine core forms the fluorescing entity of the molecule.

Keywords: fluorescence · photochromism · photoswitching · spiro compounds

Introduction

The design and development of novel organic photochromic molecules[1–4] have become increasingly significant with the advent of technologies based on light-triggered molecular and supramolecular devices,[5–7] where a reversible change of the optical properties of the involved photochromic molecule forms the basic principle. More importantly, when their photochromic reactions are associated with a reversible change in a phenomenon such as fluorescence, the systems become more functional.[8,9] In a recent review, Raymo et al. have described the developments in the area of photochromism-based fluorescence modulation, highlighting the various underlying mechanisms involved.[10] Among the numerous organic photochromic molecules known, the ones associated with a reversible fluorescence change are rather scarce. Efficient fluorescence switching has been demonstrated using various photochromic molecules; however, in all of them the origin of fluorescence has been either due to one of the isomers of the photochromic system,[11–16] their molecular aggregates[17–19] or occurs from a fluorophore tagged[19–25] to or mixed[26,27] with the photochromic molecule. Generally, photochromic systems that are capable of fluorescence modulation possess one of the following mechanisms:[10] a) photochromic molecules where at least one of the interconvertible isomers is fluorescent;[11,13–15] b) photoinduced change in the conjugation between a tagged fluorophore and a photochromic molecule;[25,28,29] c) photoinduced change in the dipole moment of a photochromic molecule that affects the fluorescence of a linked fluorophore;[30,31] d) photoinduced electron transfer between a photochromic molecule and an attached fluorophore;[32,33] e) intramolecular transfer of the excitation energy from a fluorophore to a photochromic group in a dyad;[16,34,35] f) photoinduced filter

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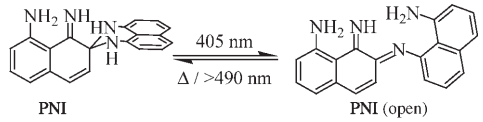
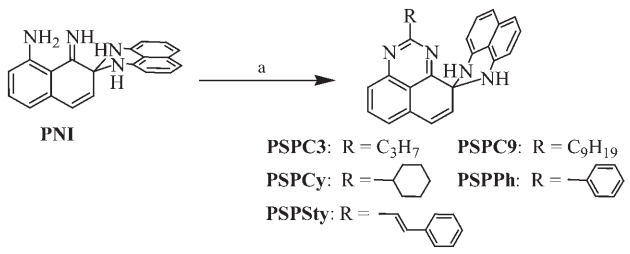
effects, where intermolecular energy transfer between an uncoupled fluorescing species and photochromic molecule occurs due to a favorable overlap of the emission band of the fluorophore with the absorption band of one of the isomers of the photochromic molecule.[8,36,37] In all of the above cases the modulated fluorescence band corresponds to either that of an isomer of a photochromic molecule or to that of a fluorophore.

Recently we had reported the photochromic properties of a new class of perimidine-based spiroheterocyclic compounds, in which the initial ring-closed form is transformed to a ring-opened form upon photolysis (Scheme 1).[38] These derivatives exhibit thermally reversible photochromism with good photofatigue resistance; in addition their photochemically generated ring-opened form shows an unusual broad absorption in the visible region.



Scheme 1. Photochromic reaction of perimidine-based spiroheterocycle.

In this report we describe the photochromism of a novel class of perimidine spirodimers (Scheme 2) and the switching process of its unique fluorescence property. Perimidine spirodimers were prepared from 2,3-dihydro-2-spiro-7′-[8′-imino-7′,8′-dihydronaphthalen-1′-amine]perimidine, PNI, by a simple reaction with acid chlorides. The current derivatives like its precursor molecule, PNI, exhibit a thermally reversible photochromism and follow a similar mechanism. However, the photochromic reactions in the case of the derivatives with aliphatic substitutions on one of the perimidine units—unlike PNI—are coupled with a reversible fluorescence change, where the fluorescence intensity is proportional to the concentration of the photogenerated ring-opened form. A key novelty here is that the observed fluorescence originates from an unconventional species, which is formed from the ring-opened form and remains in an equilibrium with it. The results suggest that the perimidine ring in the ring-opened form is the fluorescent moiety. The photochromic reaction of the system is initiated by UV light (365 nm) but the fluorescence of the system can be switched by a second photochemical process where the ratio of the ring-opened form and the fluorescent species is selectively controlled using only visible light (500 and 700 nm).



Scheme 2. Syntheses of the perimidine spirodimers: a) RCOCl, THF, 25 °C, 3 h.

Results and Discussion

Synthesis and structure: We synthesized derivatives of PNI using butyryl, decanoyl, cyclohexanecarbonyl, benzoyl and cinnamoyl chloride (Scheme 2) to yield a novel class of photochromic perimidine spirodimers, PSPC3, PSPC9, PSPCy, PSPPh and PSPSty, respectively (see Experimental Section).

The structures of all compounds were unequivocally confirmed with the general characterization techniques and by single crystal X-ray diffraction.[39] Figure 1 shows the ORTEP diagram of PSPC9. The molecule consists of two perimidine units fused orthogonally at the spiro junction. The perimidine unit involving two sp^2 hybridized nitrogen atoms (N3 and N4) and bearing the alkyl chain is planar with the torsional angle between planes bearing the atoms C17-C18-N4-C21 being 179.9(2)°. The second perimidine unit possessing two sp^3 hybridized nitrogen atoms (N1 and N2) is non-planar with the torsional angle of 158.2(2)° between planes bearing the atoms C4-C5-N1-C11.

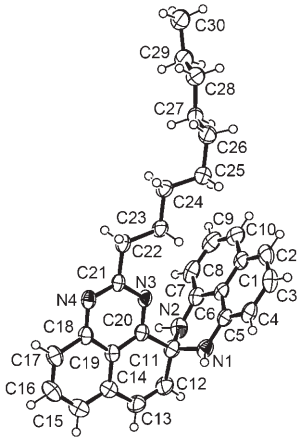


Figure 1. ORTEP diagram of PSPC9.

Photochromism: The perimidine spirodimers exhibit efficient photochromic behavior. Figure 2 depicts the absorption spectral changes associated with the photochromic behavior of PSPC3. Upon irradiation at 365 nm, the pale yellow toluene solution of PSPC3 turns dark green. The changes in the absorption band are a decrease in the absorbance of the band centered at 347 nm ($\varepsilon = 17\,700\ cm^{-1}$) and a concomitant increase in that of two bands centered at 410 and 650 nm, respectively. The observed absorption spectral changes were found to be reversible both thermally ($\tau_{27\,°C} =$ 21 min) and photochemically.

The photochromic behavior of these derivatives has close similarities to its precursor, PNI.[38] In the dark, these derivatives remain in its stable ring-closed form and hence the photochromic reactions are initiated only photochemically, in contrast to similar molecules where a spontaneous thermal equilibrium between ring-closed and ring-opened forms is attained in non-polar solutions.[40,41] The mechanism of the photochromic reactions observed in the perimidine spirodimers is assumed to be similar to that of its precursor pho-

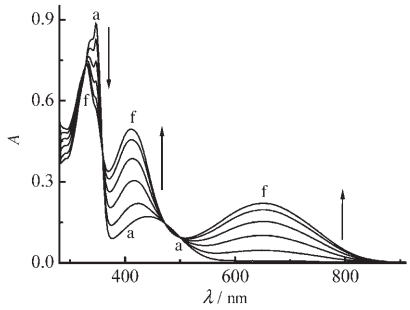
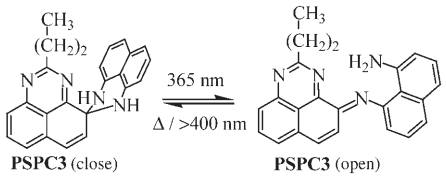


Figure 2. Changes in the absorption spectrum of PSPC3 in toluene ($c = 5\times10^{-5}$ M) upon irradiation using 365 nm light; a) 0; b) 10; c) 30; d) 60; e) 120; f) 360 s.

tochrome, PNI and as established for related molecules studied by Minkin et al.[1,38,40,42] The photochromic reactions of the perimidine spirodimers are shown in Scheme 3.



Scheme 3. Photochromic reactions of perimidine spirodimers.

Using ^{1}H NMR analysis, the 365 nm photostationary state (PSS) mixture of PSPC3 in toluene was found to possess 65% of the ring-opened form similar to that of its precursor, PNI.[39] The quantum yield of photoisomerization of PSPC3 was estimated to be 0.03, which is one-half of that of PNI. The photochromic properties and the related spectral changes of all the other derivatives in the current report are similar to that of PSPC3.[39]

Fluorescence switching: The photochromic reactions of the perimidine spirodimers with aliphatic substitutions (PSPC3, PSPC9 and PSPCy) are coupled with a reversible fluorescence change. The photoinduced ring-opening reaction, upon 365 nm irradiation, leads to generation of fluorescence ($\lambda_{max} = \sim 576$ nm), the intensity of which increases with the time of irradiation. Figure 3A shows the fluorescence spectra of a toluene solution of PSPC3 recorded at various time intervals during the photoirradiation. It has to be noted that the precursor photochromic molecule PNI does not exhibit any such fluorescence effect. Upon thermally or photochemically reverting to the stable ring-closed form, the intensity of fluorescence was seen to proportionally decrease. The fluorescence intensity could thus be switched on and off and its reproducibility has been observed over several continuous ring close-open-close cycles (Figure 3B). However, in the case of the derivatives with aromatic substitution (PSPPh and PSPSty) their identical photochromic changes were not coupled with any fluorescence effect.

Although the fluorescence change was interesting and consistent, it was surprising that the fluorescence did not

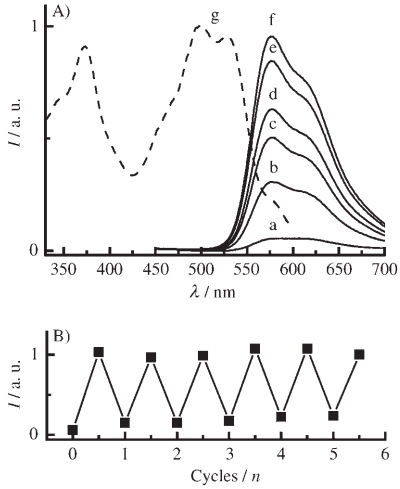


Figure 3. A) Fluorescence change of a toluene solution of PSPC3 ($c = 5\times10^{-5}$ M) upon irradiation using 365 nm light; a) 0; b) 10; c) 30; d) 60; e) 120; f) 360 s (PSS). (λ_{ex}, 365 nm) and g, excitation spectrum of a PSS solution (λ_{em}, 620 nm). B) Fluorescence switching cycles showing the emission intensity change at 576 nm after repeated cycles of 365 nm irradiation and heating at 85 °C for about 30 min.

occur from any of the major isomers of the photochromic molecule. The excitation spectrum of the 365 nm PSS toluene solution of PSPC3, shown in Figure 3A (curve g), possesses wavelength maxima at 380, 500 and 530 nm, which is widely different from the absorption spectra of both the ring-closed and ring-opened forms. Specifically, this shows that the observed fluorescence indeed does not arise from the ring-opened form but from yet another species.

The system possesses an additional unusual characteristic. When a PSS (365 nm) solution of PSPC3 was kept in the dark for about 1 min and then re-introduced in the light path, an immediate bright fluorescence was observed which gradually diminished and equilibrated to constant fluorescence intensity. This effect was visually perceivable and could be followed using a spectrofluorometer (Figure 4A). In Figure 4A the solution at time $t = 0$ is a PSS (365 nm) solution kept in the dark for 1 min. It may be noted that this effect of fluorescence occurs in about 1 min and hence while recording the fluorescence spectra (in Figure 3A), the fluorescence intensity observed is from an equilibrated state and is reproducible. This loss of fluorescence in the presence of light is attributed to a light-induced change in the concentration of the fluorescing species. The above-mentioned photochemical depletion of fluorescence recovers thermally, $\tau_{27°C} = 3$ min and was also observed using a spectrofluorometer (Figure 4B). In Figure 4B the solution at time $t = 0$ is an immediately obtained PSS (365 nm) solution possessing a photochemically equilibrated fluorescence. The latter time trace was obtained using low intensity excitation light (365 nm) in order to reduce the photochemical depletion of fluorescence.

Mechanism: All these observations pave way to make a few suggestions on the origin of fluorescence and the nature of

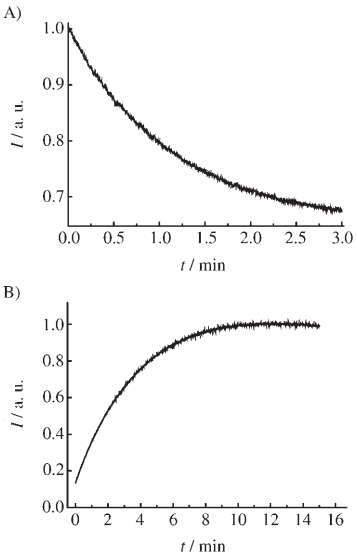
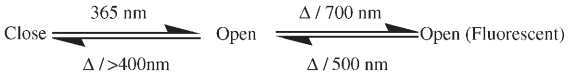


Figure 4. Time dependent photochemical and thermal change in fluorescence of a toluene solution of PSPC3 ($c = 5 \times 10^{-5}$ M). A) Time trace depicting depletion of fluorescence upon continuous photolysis of the solution using 365 nm light. B) Thermal growth of fluorescence after photochemical equilibration; $\lambda_{ex} = 365$ nm and $\lambda_{em} = 600$ nm.

the fluorescing species. Scheme 4 describes the relationship of the fluorescing species with respect to the isomers of the photochromic molecule.



Scheme 4. Relationship between the isomers and the various processes involved in the photochromism based fluorescence modulation.

The ring-closed form is non-fluorescent as seen in Figure 3A (curve a). However, the weak fluorescence observed from an unirradiated solution may be due to irradiation by the excitation light (365 nm) while recording the fluorescence spectrum. With the increase in time of irradiation the concentration of the ring-opened form increases; due to the proportional increase in the fluorescence intensity it may be assumed that the fluorescing species is formed from the initial ring-opened form. At the PSS, the ring-closed and -opened forms reach a photochemical equilibrium, while the open form attains a photochemical equilibrium with the fluorescent species. The depletion of the fluorescence upon irradiation and its recovery in the dark confirm that the fluorescent species attains a thermal equilibrium with the ring-opened form. The changes in the absorption spectrum during the ring closing–opening photochromic reactions (Figure 2) do not show the absorption band characteristics of the fluorescent species indicating its formation in very low concentration. Hence, upon the photochemical depletion and thermal growth of fluorescence (shown in Figure 4) no significant change is observed in the absorption spectrum of the solution. Further evidence of the formation of the fluorescent isomer from the initial ring-opened form was obtained by observing an efficient on/off photoswitching of fluorescence over several cycles by alternate irradiation using wavelengths of light at 500 and 700 nm. Figure 5 depicts the photochemical fluorescence switching using

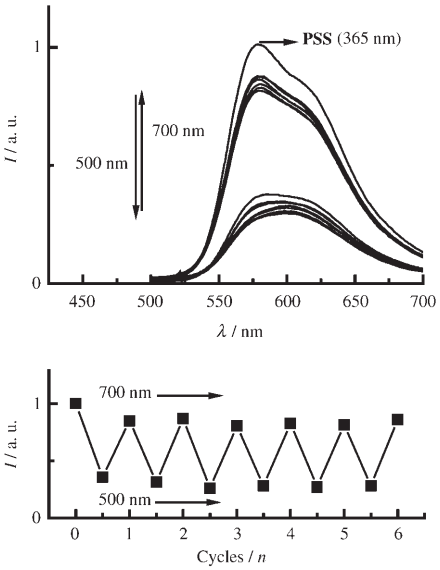


Figure 5. Photoswitching of fluorescence of a toluene solution of PSPC3 ($c = 5 \times 10^{-5}$ M) using wavelengths of light at 500 and 700 nm.

PSPC3. Upon irradiation of a PSS (365 nm) solution of PSPC3 using 500 nm light, the fluorescence intensity considerably diminishes but the same recovers by further irradiation using 700 nm light. Upon irradiation using 500 nm light, the fluorescent isomer is converted to the non-fluorescent open-form and by irradiation using 700 nm, which is absorbed only by the non-fluorescent open-form, the concentration of the fluorescent isomer is recovered.

Although further studies are required to exactly predict the structure of the fluorescing species, it may be suggested that the photochemically generated ring-opened form undergoes a photochemical and thermal *cis–trans* isomerization about the imine (C=N) bond to form a lesser stable ring-opened form having comparable energies. Closely related imine bond photoisomerization of the ring-opened merocyanine forms of spirooxazines have been studied.[43,44] By comparing the properties of the aliphatic and aromatic substituted derivatives it is evident that upon extension of conjugation provided by the aromatic substitution, the fluorescence effect is nullified. The initial ring-opened form of the molecule is expected to be fairly planar resulting in an extended conjugation, which is evident from the bright green color of the irradiated solution. The initial ring-opened form is non-fluorescent and the extension of conjugation by aromatic substitution quenching the fluorescence effect, together lead to the possibility that the perimidine core with the imino group could be the fluorescent species. In the fluorescent isomer formed from the initial ring-opened form, the amino

naphthalene moiety is expected to be out-of-plane with the perimidine core due to a possible steric hindrance causing a restricted conjugation and hence results in fluorescence of the perimidine core. The excitation spectrum of PSPC3 solution (Figure 3A, curve g) clearly reveals that the fluorescent species absorbs in the short wavelength region possessing a considerably narrow absorption band when compared with the initial ring-opened form. This appears to be a result of the loss in extended conjugation. The photoinduced ring-opening of the spiro-form and a further isomerization about the imine bond in these molecules basically exposes the fluorophoric segment of the molecule. Such a generation of fluorescence and its modulation is considered distinct from related systems following mechanisms involving a photoinduced conjugation change or those having at least one fluorescent isomer of the photochromic molecule.

Conclusion

We reported on the photochromic nature of a novel class of perimidine spirodimers, the photochromism of which is coupled with a reversible change in fluorescence. The fluorescing species in this system is rather unique and the fluorescence is understood to arise practically from one-half of the molecule, the perimidine core of the ring-opened form. This finding is well supported by the obtained results and the role of aromatic and aliphatic substitutions on the fluorescence effect. Hence, the system is assumed to form yet another mechanism of photochromism-based fluorescence modulation. Contrarily, in most other systems, either one of the isomers of a photochromic molecule is fluorescent or a fluorescent molecule is tagged to a non-fluorescent photochromic molecule. The system provides two modes of fluorescence switching, one being photo(365 nm)-thermal and the other being purely visible light (500 and 700 nm) induced switching.

Photoinduced reversible control of molecular structure and their associated properties have been exploited in the development of technologies based on photonic materials. The current findings contribute to our understanding of photochromism-based fluorescence switching; the molecules described are expected to be useful candidates in the areas such as materials chemistry and bioorganic chemistry for the development of innovative optical switches, sensors and devices.

Experimental Section

Instrumentation and materials: Absorption spectra were recorded on an Agilent diode array (8453) UV-visible spectrophotometer. Photolysis of solutions was carried out using 365 nm-filtered light from a 500 W USHIO high-pressure mercury lamp. Monochromated 500 and 700 nm light sources from a 500 W USHIO high-pressure Xenon lamp were used for visible light photolysis. Fluorescence spectra were recorded on a Jasco FP-777 spectrofluorometer. Single crystal analysis was carried out by using a Bruker SMART-CCD diffractometer, structure determination and refinement with SAINT (SAINTPLUS Version 6.22, Bruker AXS, Madison, WI, USA) and SHELXTL[45] software packages, empirical absorption correction with SADABS[46] program. NMR spectra were recorded on either a Variant (300 MHz) or Bruker (600 MHz) spectrometer. The intensity of light source, for the estimation of quantum yield of photoisomerization, was determined using potassium ferric oxalate actinometery.[47] Rate constants were calculated using the first order fit performed using the software Origin version 7.0.

Dry THF and acid chlorides were purchased from Wako Chemicals Ltd and TCL Chemicals Ltd, Japan, respectively, and were used without any further treatment.

Synthesis and characterization

General procedure: A dry THF solution (10 mL) of the corresponding acid chloride (1.5 equiv) was added dropwise to a dry THF solution (50 mL) of 2,3-dihydro-2-spiro-7′-[8′-imino-7′,8′-dihydronaphthalen-1′-amine]perimidine (PNI)[38] (100 mg, 0.32 mmol) at room temperature. The reaction mixture was stirred for 3 h at room temperature. The crude product was extracted using dichloromethane, washed with water, dried over sodium sulfate and then concentrated under reduced pressure. Column chromatography over silica gel using ethyl acetate/hexane 1:4 gave pure orange colored product with nearly 35% yield in all cases.

2,3-Dihydro-2-spiro-4′-[2′-nonyl-4*H*-perimidine]perimidine (PSPC9): ^{1}H NMR (600 MHz, [D$_6$]acetone, 25°C, TMS): δ = 0.89 (t, J=7.32 Hz, 3H), 0.99–1.31 (m, 14H), 2.63–2.66 (m, 2H), 6.19 (br, NH), 6.36 (d, J=9.9 Hz, 1H), 6.50 (d, J=7.3 Hz, 2H), 6.96 (d, J=9.9 Hz, 1H), 7.11 (d, J=7.3 Hz, 2H), 7.18–7.20 (dd, 2H), 7.46 (d, J=6.9 Hz, 1H), 7.74 (d, J=8.8 Hz, 1H), 7.86–7.88 (dd, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 14.32, 23.31, 28.09, 29.79, 32.61, 40.05, 64.43, 64.49, 106.64, 106.68, 113.78, 115.12, 117.34, 118.48,125.04, 127.53, 128.16, 131.54, 134.88, 135.00, 140.41, 151.36, 168.93, 169.39; ESIMS: m/z: calcd for C$_{30}$H$_{33}$N$_4$: 449.27, found 449.28 $[M+H]^+$; elemental analysis calcd (%) for C$_{30}$H$_{32}$N$_4$: C 80.32, H 7.19 N 12.49; found C 79.93, H 7.13, N 12.16.

2,3-Dihydro-2-spiro-4′-[2′-propyl-4*H*-perimidine] perimidine (PSPC3): ^{1}H NMR (600 MHz, [D$_6$]acetone, 25°C, TMS): δ = 0.58 (t, J=7.32 Hz, 3H), 1.25–1.32 (m, 2H), 2.65 (t, J=7.32 Hz, 2H), 6.19 (br, NH), 6.37 (d, J=9.8 Hz, 1H), 6.50 (d, J=6.9 Hz, 2H), 6.95 (d, J=9.8 Hz, 1H), 7.11 (d, J=8.4 Hz, 2H), 7.18 (t, J=7.38 Hz, 2H), 7.45 (d, J=6.9 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H), 7.86–7.88 (dd, 1H); ^{13}C NMR (150 MHz, CDCl$_3$): δ?13.78, 21.27, 30.21, 41.84, 64.56, 106.72, 113.75, 115.25, 117.32, 125.06, 126.37, 127.55, 128.11, 131.55, 134.91, 135.04, 135.13, 140.44, 151.32, 168.78, 169.13; ESIMS: m/z: calcd for C$_{24}$H$_{21}$N$_4$: 365.18, found 365.20 $[M+H]^+$.

2,3-Dihydro-2-spiro-4′-[2′-cyclohexyl-4*H*-perimidine]perimidine (PSPCy): ^{1}H NMR (600 MHz, [D$_6$]acetone, 25°C, TMS): δ = 0.73–0.79 (m, 2H), 0.86–0.95 (m, 1H), 1.08–1.14 (m, 2H), 1.36–1.39 (m, 2H), 1.45–1.48 (m, 3H), 2.50–2.54 (m, 1H), 6.15 (br, 2H), 6.35 (d, J=9.8 Hz, 1H), 6.49 (d, J=7.3 Hz, 2H), 6.99 (d, J=9.9 Hz, 1H), 7.12–7.19 (m, 4H), 7.45 (d, J=6.9 Hz, 1H), 7.73 (d, J=8.4 Hz, 1H), 7.84 (dd, 1H); ESIMS: m/z: calcd for C$_{27}$H$_{25}$N$_4$: 405.20, found 405.22 $[M+H]^+$.

2,3-Dihydro-2-spiro-4′-[2′-phenyl-4*H*-perimidine]perimidine (PSPPh): ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25°C, TMS): δ = 6.34 (d, J=9.9 Hz, 1H), 6.42 (d, J=7.3 Hz, 2H), 7.06 (br, 2H), 7.08–7.11 (m, 3H), 7.16 (t, J=7.32 Hz, 4H), 7.32 (t, J=7.32 Hz, 1H), 7.58–7.60 (m, 3H), 7.88 (d, J=8.46 Hz, 1H), 7.96 (dd, 1H); ESIMS: m/z: calcd for C$_{27}$H$_{19}$N$_4$: 399.16, found 399.17 $[M+H]^+$.

2,3-Dihydro-2-spiro-4′-[2′-styryl-4*H*-perimidine]perimidine (PSPSty): ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25°C, TMS): δ = 6.31 (d, J=9.5 Hz, 1H), 6.44 (d, J=7.3 Hz, 2H), 6.48 (d, J=15.7 Hz, 1H), 7.04 (d, J=15.7 Hz, 1H), 7.05–7.07 (m, 3H), 7.13 (d, J=8.0 Hz, 2H), 7.19 (t, J=7.32 Hz, 2H), 7.28–7.31 (m, 1H), 7.35–7.36 (m, 4H), 7.54 (d, J=6.9 Hz, 1H), 7.78 (d, J=8.4 Hz, 1H), 7.92 (dd, 1H); ESIMS: m/z: calcd for C$_{29}$H$_{21}$N$_4$: 425.17, found 425.19 $[M+H]^+$.

Crystal data for 2,3-dihydro-2-spiro-4′-[2′-nonyl-4*H*-perimidine]perimidine (PSPC9): C$_{30}$H$_{32}$N$_4$, M=448.6, monoclinic, space group $P2(1)/c$, a=14.761(4), b=19.822(6), c=8.316(2) Å, $\alpha=\gamma=90°$, β=94.638(5)°, V=2425.1(12) Å^3, Z=4, ρ_{calcd}=1.229 Mg m^{-3}, μ=0.073 mm^{-1}, 14131 reflec-

tions collected, 5513 unique (R_{int} = 0.0482), final R indices[$I>2\sigma(I)$] $R1$ = 0.0618, $wR2$ = 0.1424, R indices (all data) $R1$ = 0.1436, $wR2$ = 0.1835.

CCDC-282478 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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