Tetrahedron Letters 49 (2008) 4292–4295

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: http://www.elsevier.com/locate/tetlet

Selenospiropyrans incorporating appended pyrene chromophores

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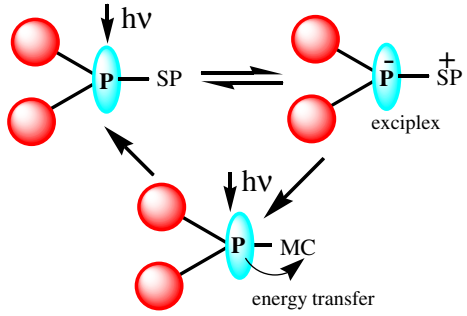
ARTICLE INFO

Article history:
Received 28 February 2008
Revised 16 April 2008
Accepted 23 April 2008
Available online 27 April 2008

ABSTRACT

The synthesis of two pyrene-based selenospiropyran dyads is described along with their absorption profiles in various solvents.

Major developments have been seen over the past twenty years or so in molecular-scale assemblies that are capable of using photons to initiate the passage of information in a controlled manner.[1] The tenet is that molecular-based systems will find applications in the emerging field of photonics where fast optical responses are required.[2] The basic structure commonly comprises a donor–relay–acceptor motif, in which the relay acts as the conduit for passage of, for example, electrons, but can be altered in some manner to perturb information flow.[3] In general, a switching unit incorporated into the relay is the controller, and can operate by breaking π-conjugation,[4] or perturbing the energy levels of the HOMO/LUMOs within the relay.[5] Identification of ultimate switching units has seen the evolution of different groups including fulgides, diarylethenes and dihydroindolizines.[6] In particular, the spiropyran (SP) group has been targeted since it is readily ring-opened by light to the merocyanine (MC) form.[7] The reverse process can be thermally induced or initiated by a light of long wavelength. As well as the clear colour change, the MC form also promotes increased conjugation through the double-bond backbone. In previous work, we devoted attention to using such a switching action to manipulate energy migration in a T-shaped array.[8] An upshot from this work was the development of pyrene-based systems that could be ring-opened via an exciplex (Scheme 1).[9] The interest here was that direct illumination of the spiropyran was avoided, which sometimes can be difficult in multi-chromophoric systems for which the SP absorption band is obscured. However, one disadvantage of the molecular system was the fast ring closure, MC to SP, induced by energy transfer from the pyrene to the singlet state of the MC unit. Having established that the singlet state of the MC was predominantly responsible for efficient ring closure, the next stage in development was to endeavour to circumvent this problem. It is well established that heavy atom incorporation (e.g., S, Se) into merocyanine dyes promotes efficient singlet to triplet inter-system crossing.[10] Thus, we devised a strategy to produce selenospiropyrans in the expectation that triplet formation



Scheme 1.

would compete with MC to SP ring closure. We noted that the only previous examples of selenium-based molecular systems, reported by Miyashita et al.,[11] showed enhanced yields of the MC form and displayed good switching action. A second design feature was to extend the nitro-containing ring to increase delocalization to see if this had any effect on the strength of the spiro C–O bond; a weaker bond would hopefully favour the MC over the SP arrangement.

The procedures used to prepare the two prototype selenospiropyran derivatives, **P1** and **P2**, are shown in Scheme 2. The starting material **1** was specifically targeted since the 6,8 substitution pattern at the pyrene centre is consummate for appending other redox or photoactive groups. The first task was to convert the alcohol group of **1** to a good leaving group for reaction with commercially available 2-methylbenzoselenazole.

The compound **1**[12] could be readily converted to several derivatives containing OMs (**2b**), Cl (**2c**), I (**2d**) and Br (**2e**) in good yields. All attempts to prepare **2a**, the OTs derivative, failed to give the desired product. Rather disappointingly, no conditions could be found to convert **2b–d** to the corresponding 2-methylselenazolium salts.[13] However, by careful control of the temperature and reaction times, the heating of **2e** with neat 2-methylbenzoselenazole at 100 °C for 5 d produced a workable quantity of **3a** as the bromide salt. As illustrated in Scheme 2, the reaction also produced

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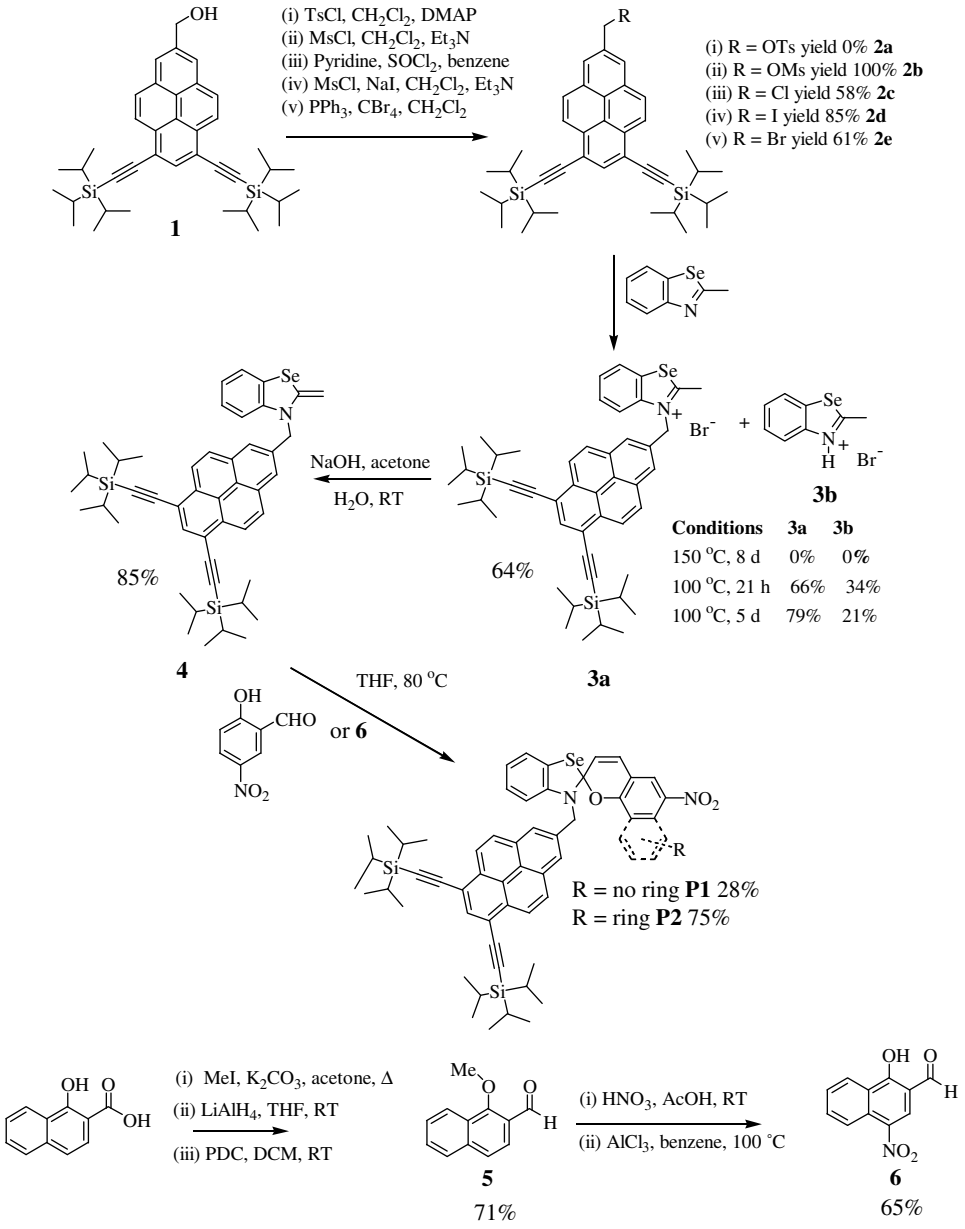
doi:10.1016/j.tetlet.2008.04.134



Scheme 2.

the protonated salt side product **3b**, which was carried through in the preparation as its separation from **3a** was difficult. Deprotonation of the methyl group within **3a** with NaOH in water/acetone (1:10) afforded the derivative **4** in excellent yield. Refluxing of **4** with 2-hydroxy-5-nitrobenzaldehyde in THF afforded, after thorough chromatography (silica gel, DCM/MeOH, 100:0 then 98:2), the desired derivative **P1**. Synthesis of the corresponding naphthalene analogue required the preparation of compound **6**. This material was obtained by an adaptation of literature procedures[14] starting from 1-hydroxynaphthalene-2-carboxylic acid. Thus, in three steps this material was converted to the aldehyde **5** in an overall 71% yield. Under mild nitration conditions **5** was selectively converted to 1-methoxy-4-nitronaphthalene-2-carbaldehyde and finally deprotected to afford **6**. The refluxing of **6** with **4** in THF afforded after purification (silica gel, CH_2Cl_2) the compound **P2** in good overall yield (75%). The somewhat high yield of this latter compound would suggest enhanced reactivity of the aldehyde for the naphthalene precursor **6**. Accurate MALDI-MS and ES-MS along with ^{1}H NMR spectroscopy and sharp melting points confirmed the identity and purity of the two compounds (Supplementary data). The two final compounds were soluble in a wide range of solvents, especially very low polarity solvents (e.g., cyclohexane) presumably because of the appended pyrene unit.

The ratio of SP:MC in a steady-state mixture is highly dependent, along with other factors (i.e., temperature), on the polarity of the solvent.[15] Inspection of the ^{1}H NMR spectrum can be rather revealing, since the *J*-coupling constants and chemical shifts for the two adjacent alkene protons are indicative of a cis geometry (SP) or trans geometry (MC). Thus, ^{1}H NMR spectra were recorded for **P1** and **P2** in $CDCl_3$ at room temperature. Considering the only main difference between the two compounds is the additional benzene ring, the ^{1}H NMR spectra for the two are very informative in terms of ground-state geometries. Illustrated in Figure 1 is the spectrum for **P1** along with the corresponding peak assignments that were corroborated by COSY. The *J*-coupling constants for the two signals associated with the alkene protons (H_{15}, H_{16}) are 9.9 Hz, and

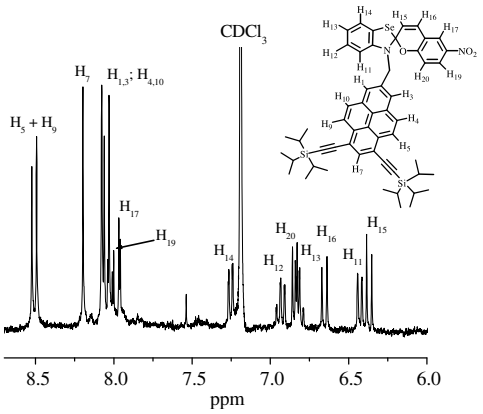


Figure 1. Selected 300 MHz ^{1}H NMR spectrum for **P1** in $CDCl_3$ at rt, and the corresponding peak assignments.

consequently consistent with the cis geometry, as shown, for the closed SP form. There is some evidence of minor resonances on the baseline (<5%) that almost certainly represent the open MC form. In view of the NMR data, the limit for the SP:MC ratio is assigned tentatively to 95:5. By comparison, the ^{1}H NMR spectrum for **P2** in $CDCl_3$ at room temperature (Supplementary data) contains no discernable resonances in the region 6–7 ppm, that correspond to alkene protons H_{15} and H_{16}. Furthermore, a number of downfield signals are broad, which would indicate a dynamic process taking place in solution. This hypothesis was tested by collecting ^{1}H NMR spectra for **P2** in CD_2Cl_2 at low temperatures; this solvent was chosen to avoid aromatic signals being obscured by the residual solvent peak. The 500 MHz ^{1}H NMR spectrum at −50 °C (Fig. 2) contains far more detail and well-resolved peaks, and their assignments are especially instructive. The proton resonance for H_{15} is well downfield (9.0 ppm) and the *J*-coupling constant is 13.5 Hz. The peak at 7.70 ppm is assigned readily to H_{16} with an identical *J*-coupling constant. These large *J*-values are fully consistent with a trans alkene geometry, as expected for the open MC form. Once again minor resonances on the baseline can be assigned to the closed SP form. The SP:MC ratio is assigned tentatively to 5:95, which is the converse of the case for **P1**. It would appear that a relatively subtle structural change can greatly influence the SP:MC ratio.

The unmistakable structural difference between **P1** and **P2** is evident in their UV–visible spectra recorded in CH_2Cl_2 (Supplementary data). The structured absorption bands in the 300–400 nm region are assigned readily to π–π* transitions of the pyrene group. The long wavelength broad absorption band at ca. 600 nm is associated with electronic transitions for the open MC

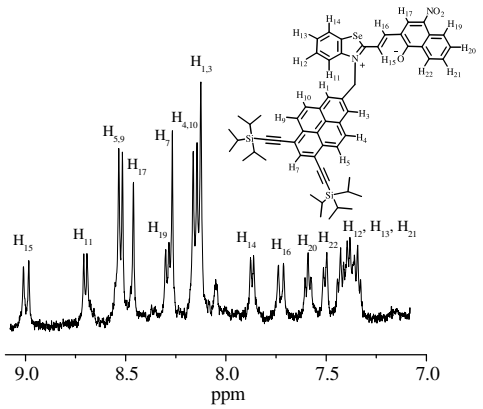


Figure 2. Partial 500 MHz ^{1}H NMR spectrum for **P2** in CD_2Cl_2 at −50 °C and the peak assignments.

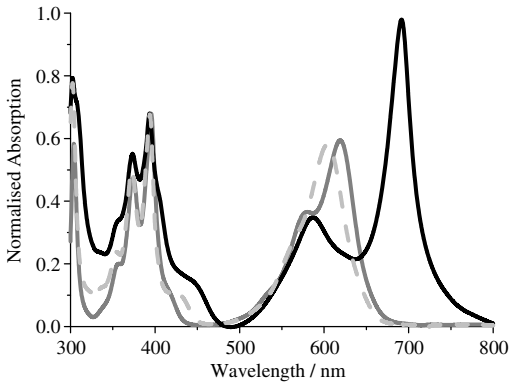


Figure 3. Absorption spectra recorded for **P2** in cyclohexane (black), toluene (grey) and CH_2Cl_2 (dashed) at room temperature.

form.[16] That the long-wavelength absorption band for **P1** is only just observable from the baseline is in agreement with the proposed SP form dominating the steady-state mixture. The most significant finding regarded the alteration in the absorption spectrum for **P2** when recorded in a very low polarity solvent (Fig. 3). Even though it is recognized that solvent polarity plays an important role in controlling the MC absorption maximum,[17] the appearance of a new near-IR band at ca. 700 nm in cyclohexane is unprecedented. It should be noted that the usual absorption band attributed to the MC is still visible. The cause of the new band is not at this stage completely understood, but may arise from excimer/exciplex formation involving the pyrene and naphthalene units. Future studies will be required to resolve this issue.

In previous literature reports it has been shown that illumination at the MC long wavelength absorption band brings about ring closure.[18] Under steady state conditions the irradiation of **P2** at ca. 600 nm in N_2-purged CH_2Cl_2, toluene or cyclohexane solutions afforded no observable changes in the respective absorption spectra. Illumination of a sample of **P2** in cyclohexane at ca. 700 nm, however, led to a gradual decrease in the intensity of this band along with the band at 600 nm (Supplementary data). No precipitate could be detected in the sample cuvette after prolonged irradiation times. Thus, it appears possible to selectively facilitate the ring closure, MC to SP, by long-wavelength excitation of **P2** in cyclohexane. Rather curiously, irradiation of the sample at wavelengths between 350 and 450 nm did not bring about restoration of the original absorption spectrum.

Two new pyrene-based molecular dyads have been produced, which incorporate benzoselenazole in the basic structures. The full extent of the effect of the selenium on controlling the SP:MC ratio is not at present fully clear, and future work will be needed to address this issue. Preliminary evidence is encouraging that the new systems display disparate behaviour in solution and hence should find applications in future photonic-based systems.

Acknowledgements

We thank the Leverhulme Trust for financial support and the ESPRC sponsored Mass Spectrometry Service at Swansea for collecting electrospray mass spectra.

Supplementary data

Detailed description of the synthesis and characterization for selected intermediates and final products. Proton NMR of **P2** in $CDCl_3$, absorption spectra for **P1** and **P2** in CH_2Cl_2 and irradiation absorption spectra. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.04.134.

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