Revisiting Perkin's dye(s): the spectroscopy and photophysics of two new mauveine compounds (B2 and C)†

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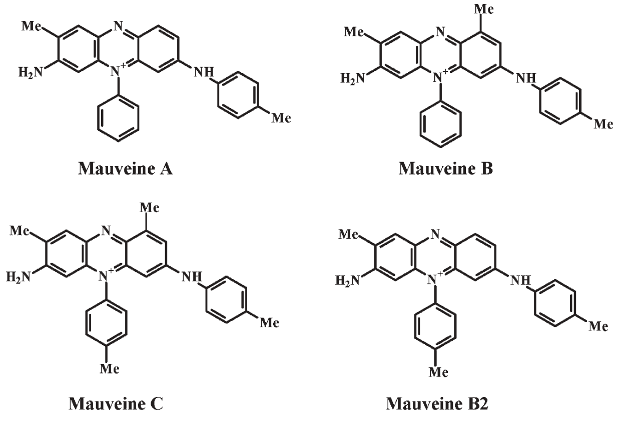
Two new components have been identified in an early sample prepared according to the original recipe of Perkin, and perhaps even by Perkin himself around 1860 – a new isomer of Perkin's mauveine B (designated as mauveine B2) together with a new mauveine compound (mauveine C) – and these compounds were synthesized again using starting materials chosen to reproduce Perkin's original synthesis and isolated by HPLC-DAD, identified by ^{1}H NMR, MS and their spectroscopic (UV/Vis and emission) and photophysical behaviour investigated.

Perkin's mauveine dye is considered to be a chemical icon and is often associated with the pioneering times of the British chemical industry.[1–4] The rich history of mauveine is also related to its magnificent colour: a colour that fascinated Queen Victoria and the Empress Eugenie of France. Nowadays there are thousands of synthetic dyes. However, in antiquity only a few dozen dyes were known and all were of natural origin.[5] This symbolic molecule mauveine was the first purely synthetic organic dye, had never been observed in nature, was a great commercial success and is, thus, rightly considered as a landmark in the history of chemistry and the dye industry. The year 2006 celebrated the 150th anniversary of the birth of mauveine, which resulted from a pioneering synthesis by the 18-year-old William Perkin. The story is well known and resulted from a fortuitous event, since the young Perkin was trying to synthesize the anti-malarial pharmaceutical quinine; Perkin's serendipity did the rest.[1,6] However, as was shown in 1994, analysis of Perkin's original samples[3] with modern NMR techniques[7] led to the conclusion that Perkin's dye (initially called Tyrian purple, then from 1859 mauve, and in 1863 given the scientific name mauveine) involved not just a single molecule but two compounds, which were both different from the commonly accepted chemical structure of mauveine.[7]

The general lack of information on the electronic spectra and photophysics of this historic dye was the initial driving force of our study. Remarkably, in spite of the significant number of publications related to the history of mauveine's discovery,[1,3,8–10] very little is known concerning the origin of its colour or the effect of interaction of light with this dye. As its purple-like colour is one of its most important characteristics, it is intriguing why so little exists in the literature on, for example, its absorption maxima, its fluorescence (or lack of it), its photostability (mauveine is known to be a very stable molecule), *etc*. One possible explanation might lie in the fact that this dye is no longer used in dyeing processes and is thus only referred to within its historical context.[3,4] However, its position in mankind's history clearly warrants a deeper spectroscopic and photophysical insight. Because of the relevance of the interaction of mauveine with light, in this work we describe a detailed spectroscopic and photophysical solution study on two new mauveine compounds, which are also present in a series of different samples collected by P. J. T. Morris (Science Museum, London).[11] A detailed investigation of all the components of several historic Perkin samples, with the objective of fingerprinting their origin, is currently underway.[11] In a previous study of historic mauveine samples, two products were identified: mauveine A and mauveine B, see Scheme 1.[7] Using starting materials that could reproduce Perkin's conditions,[12,13] several mauveine-like products were obtained in the present synthesis, namely mauveine derivatives with two (mauveine A), three (mauveines B and B2) and four methyl (mauveine C) groups, see Scheme 1, Fig. 1 and Supplementary Information (ESI). The mauveine B2 isomer was found to be the dominant product under the reported synthetic procedure, Fig. 1B.[13] A description of the synthesis and characterization of the four main constituents obtained can be found in the ESI section. The identification and separation of the compounds was made by HPLC-DAD (Fig. 1), FD MS and ^{1}H NMR (ESI). The four major mauveine compounds (violet, $\lambda_{\max}$ = 550 nm) were isolated by HPLC and were identified as: mauveine A, mauveine B, mauveine B2 and mauveine C. The compounds discussed in the present study are the two new (identified)


Mauveine A
Mauveine B
Mauveine C
Mauveine B2

Scheme 1 Chemical structures of mauveines A, B, B2 and C.

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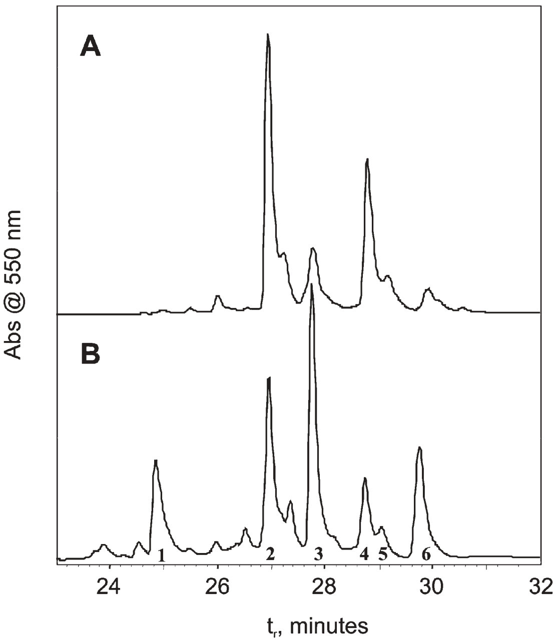

Fig. 1 Chromatograms obtained at λ = 550 nm, for **A**: historic sample from the Science Museum Collection and **B**: sample synthesized in this paper; both samples were dissolved in methanol. The major compounds identified correspond to the numbered peaks: **2** – mauveine A, **3** – mauveine B2, **4** – mauveine B, **6** – mauveine C.

compounds: mauveine B2, an isomer of mauveine B, and mauveine C.

In Fig. 1 the chromatograms for the two samples (historic sample from the Science Museum, London and mixture resulting from the synthesis) are shown. It should be emphasized that these two new compounds are also present in Perkin's Mauve historic samples,[11] as can be clearly seen by comparison between the chromatograms A and B in Fig. 1 and ESI.

Fig. 2 shows the absorption and fluorescence emission and excitation spectra of mauveine B2 in methanol. The absorption spectrum shows two intense bands: one in the UV (281 nm) and the other in the visible region of the spectrum (550 nm), with a pronounced minimum between the two. These can be attributed to the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transitions of mauveine B2. With excitation in the visible band, the obtained ϕ_F values are very low ($\sim 10^{-4}$), see Table 1. The purity of the compound was confirmed by the match of the excitation spectra with the absorption spectra (see Fig. 2), showing this is not due to impurities.

With the two mauveine dyes we were unable to detect any transient triplet absorption by laser flash photolysis (with ns time resolution) and did not observe any singlet oxygen sensitization (singlet oxygen quantum yield, $\phi_\Delta \approx 0$). Although there are reports of fast decay of the triplet state of some polypyridines (with lifetimes of less than 10 ns),[14] we are unaware of any reports of triplet states of nonpolymeric organic compounds deactivating faster than the limiting value of 20 ns used in our experiments (which excludes the possibility of a very fast deactivation of the triplet state in the studied mauveines). Since we have recently been able to determine ϕ_Δ values of *ca.* 10^{-3}–10^{-4} for indigo – and a triplet intersystem crossing quantum yield for indigo $\phi_T = 0.0066$[15] – and some of its derivatives,[16,17] these two complementary pieces of experimental evidence establish an upper limit of *ca.* 10^{-4} for the ϕ_Δ and ϕ_T values of mauveine B2 (and C). In this situation, it is possible to establish the balance $\phi_F + \phi_{IC} \approx 1$ which then allows the determination of the internal conversion quantum yield ϕ_{IC} (see Table 1).

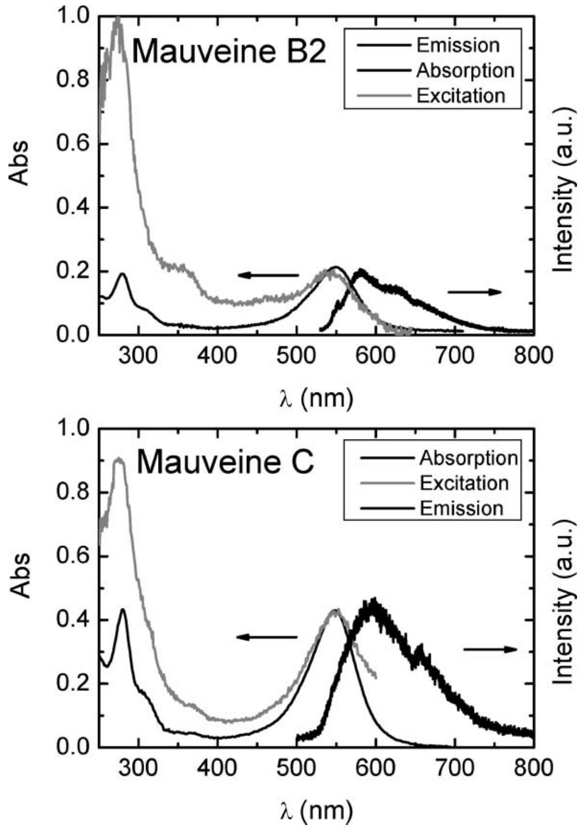

Fig. 2 Absorption and fluorescence emission and excitation spectra for mauveine B2 and mauveine C in methanol at T = 293 K.

From Table 1 it is also clear that the radiative rate constant (k_F) is *ca.* 2000–3000 lower than the radiationless rate constant (k_{NR}). Since the triplet state is a non-efficient radiationless channel for mauveines B2 and C, it seems clear that more than 99.99% of the quanta are lost through the internal conversion channel, enabling a fast and effective dissipation of energy of the excited state.

The high stability of some dyes – one example is indigo, also of great historical interest – has been linked to the predominance of internal conversion over the other deactivation pathways. Proton transfer in the excited state (ESPT) could possibly be linked to the fast internal conversion due to the presence of the N–H donor groups in mauveines B2 and C (presumably with the methanol as the hydrogen bonding acceptor). However, and without excluding ESPT, a second possible explanation for the observed fast internal conversion rate constant values lies in the small energy difference between the ground and lowest singlet excited state of mauveines B2 and C. The golden rule for radiationless transitions[18] states that a small value in the S_1–S_0 energy gap ($\Delta E_{S_1-S_0}$) favours a nonradiative *vs.* radiative decay pathway by increasing the vibrational overlap (Franck–Condon integrals) of the wave functions for the nonradiative modes of these two states. Particularly when small energy gaps are involved the Franck–Condon factors are dominated by skeletal vibrations,[18] which are clearly the dominant modes in mauveine. The small $\Delta E_{S_1-S_0}$ gives

Table 1 Spectroscopic and photophysical parameters obtained for mauveine B2 and mauveine C in methanol at $T = 293$ K

Compound	λ_{abs}/nm	ε^{a}/M^{-1} cm^{-1}	λ_{em}/nm	$\phi_F{}^{b}$	$\tau_F{}^{c}$/ps	$\phi_{IC}{}^{d}$	$k_F{}^{e}/10^9$ s^{-1}	$k_{NR}{}^{f}/10^9$ s^{-1}
B2	550	33000	581	0.00049	4.7	0.9995	0.1047	214
C	549	36500	596	0.00034	2.9	0.9997	0.1177	347

[a] Calculated for a formate counter ion. [b] Data resulting from 4 independent determinations with associated errors of ±2%. [c] Major component (> 90% of the overall decay) of a biexponential decay. [d] Assuming that $\phi_T \approx 0$ and thus $\phi_F + \phi_{IC} \approx 1$, see text for further details. [e] $k_F = \phi_F/\tau_F$. [f] $k_{NR} = (1 - \phi_F)/\tau_F$.

mauveine's violet colour and is also likely to be responsible for its photostability.

In summary, Perkin's mauveine dye was synthesized and four major products (mauveines A, B, B2 and C) were isolated and identified. The two new mauveine compounds, B2 and C, were characterized and studied for the first time. These were spectroscopically and photophysically characterized. It was found that the internal conversion radiationless pathway is the major channel for electronic deactivation dissipation. As with other dyes, such as indigo[16,17,19] and purple,[16,19] this predominance of the $S_1 \rightsquigarrow S_0$ radiationless deactivation over all other excited state deactivation pathways is found with the mauveine dyes, and may be relevant to their high stability.

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