doi:10.2533/chimia.2022.869 Chimia 76 (2022) 869–870

Chemical Education

A CHIMIA Column

Topics for Teaching: Chemistry in Nature

Dragonflies that Change Colour: Nature's Hidden Redox Chemistry[a]

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Abstract: The colour distinction between male and female, and between young and mature male dragonflies of the genera *Crocothemis* and *Sympetrum* arises from simple redox chemistry. This natural phenomenon has inspired the development of a class of electrochromic devices.

Keywords: Chemical education · Natural colour changes · Redox chemistry

In an earlier *CHIMIA* Chemical Education Column, we described how the violet iridescence in purple emperor butterflies arises from structural order in the wing-scales (structural colour) while coloured chemical species such as anthocyanins, carotenoids and flavones are responsible for the colours of many flowers, fruit and vegetables.[1] In the present article, we look at how Nature has learnt the physics or chemistry that allows animals to change their colours. Perhaps the best known example is the chameleon in which structural colour plays an important role.[2] In this Column, we focus on the chemistry underlying the change of colour of some male dragonflies from yellow to red as they reach sexual maturity.

The broad scarlet dragonfly (*Crocothemis erythraea*) is common in Africa, western Asia and in southern (especially Mediterranean) regions of Europe. Mature males are brilliant red in colour (Fig. 1a) while females and young males are yellow or brown-yellow (Fig. 1b). Further east in Asia, the broad scarlet is replaced by the oriental scarlet (*Crocothemis servilia*), and again, a spectacular colour change from yellow to vivid red is observed as males reach sexual maturity. This is known as a nuptial colour change. Colour differentiation between males and females not only allows partner distinction for mating, but also permits territorial male dragonflies to recognize competing males. Visual differentiation between the sexes is most critical for mature, rather than young, males. The darters (genus *Sympetrum*) comprise another family of dragonflies having red males and yellow females (Fig. 2). Like the *Crocothemis* family, many males of the genus *Sympetrum* are yellow when young and undergo a change to red upon reaching maturity.

(a) (b)

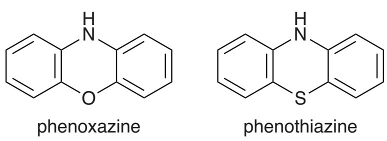
Fig. 1. The broad scarlet dragonfly (*Crocothemis erythraea*). (a) Mature males are bright red and (b) young males and females are yellow. Credit: Edwin Constable.

(a) (b)

Fig. 2. The red-veined darter (*Sympetrum fonscolombii*) is known as the nomad in Africa: (a) male and (b) female. Credit: Edwin Constable.

In 2012, Futahashi *et al*. demonstrated that the origin of the nuptial colour change in *Crocothemis* and *Sympetrum* dragonflies was a simple chemical redox reaction.[3] They first identified the ommochrome pigments which gave rise to the red and yellow colours. Ommochromes occur widely in invertebrates, especially in the eyes of insects,[4] and the core building blocks are phenoxazine or phenothiazine units (Scheme 1). Using 0.5% hydrochloric acid in methanol, Futahashi *et al.* extracted the epidermal pigments from mature male and female dragonflies *C. servilia*, *S. frequens* and *S. darwinianum*. Analysis using high-performance liquid chromatography (HPLC) and mass spectrometry showed that all the dragonflies contained the ommochrome pigments xanthommatin and decarboxyated xanthommatin (Scheme 2), although the ratio of the two compounds varied between the genera and from male to female *C. servilia*; decarboxylated xanthommatin was dominant in *Sympetrum* dragonflies and in the females of *C. servilia*, while male *C. servilia* contained similar amounts of xanthommatin and decarboxylated xanthommatin.

Since ommochromes were known to be redox active (Scheme 2) with associated colour changes, Futahashi *et al.* investigated the effects of adding $NaNO_2$ (which acts here as an oxidizing agent) and ascorbic acid (a reducing agent) to pigments extract-



Scheme 1. Structures of phenoxazine or phenothiazine, the building blocks of ommochromes pigments.

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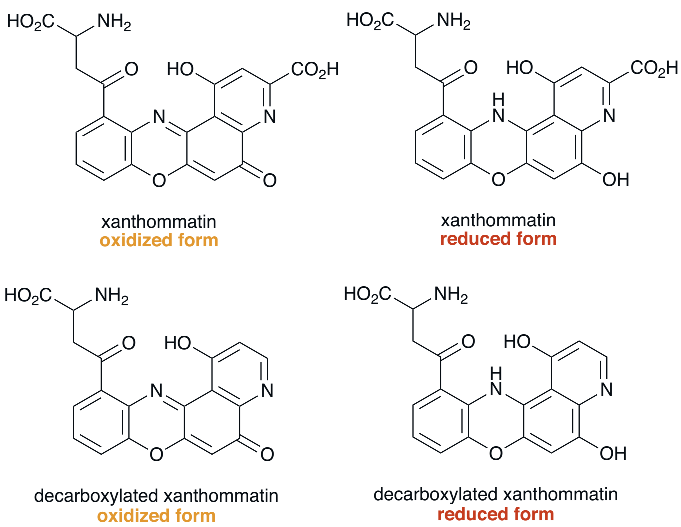

Scheme 2. Structures of the ommochromes in dragonflies in the genus *Crocothemis* and *Sympetrum* studied by Futahashi *et al*.[3] Compounds are drawn in the pyridin-4-ol form rather than the tautomeric pyridin-4(1H)-one.

ed from young and sexually mature male dragonflies. Initial *in vitro* experiments showed that the red pigment extracted from a mature male *C. servilia* turned yellow on treatment with $NaNO_2$. In contrast, the yellow pigment from an immature male *C. servilia* turned red on treatment with ascorbic acid. These colour changes were also triggered *in vivo*. Thus, red coloration is associated with the reduced forms of the ommochrome pigments, and yellow with the oxidized forms (Scheme 2). This applies to both xanthommatin and decarboxylated xanthommatin. The absorption maximum (λ_{max}) of the reduced form of xanthommatin is 500 nm, while λ_{max} for the oxidized form is 430 nm.[5] By using an electrochemical technique, Futahashi *et al*. were able to assess the relative amounts of the reduced and oxidized forms of the pigments in the dragonflies. The results confirmed that in red mature males of each of *C. servilia*, *S. frequens* and *S. darwinianum*, the pigments were essentially entirely present in their reduced forms. In females and immature males, both reduced and oxidized forms were present, leading to the observed yellow-brown colour (Figs. 1b and 2b). The difference between the brilliant red of male dragonflies from the *Crocothemis* genus (Fig. 1a) versus the duller red of those of the *Sympetrum* genus (Fig. 1b) arises from the presence of the reduced form of xanthommatin and decarboxylated xanthommatin in the former, but predominantly the reduced form of decarboxylated xanthommatin in the latter.

There are innumerable examples in which Nature motivates experimental science, and the redox chemistry of xanthommatin in dragonflies is no exception. In 2018, inspired by the results of Futahashi *et al*. as well as the role played by xanthommatin as a pigment in arthropods and cephalopods,[5] Deravi and coworkers designed electrochromic devices (ECDs) based on the redox-mediated, reversible colour change of xanthommatin.[6] The pigment was combined with the polymer poly(3,4-ethylene dioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, a common component in optoelectronic devices) in ECDs which had the device architecture shown in Fig. 3. By altering the concentration of xanthommatin in the polymer and applying a low bias across the device, the colour of the device could be tuned and could be cycled between various shades of red and yellow under reducing and oxidizing potentials.

In this column, we have described how redox-active organic pigments are responsible for the change in colour of male dragonflies of *Crocothemis* and *Sympetrum* genera as they reach sexual maturity. This simple chemistry has inspired the development of electrochromic devices using the same natural pigments as occur in the dragonflies – an example of how Nature can inspire experimental materials chemistry.

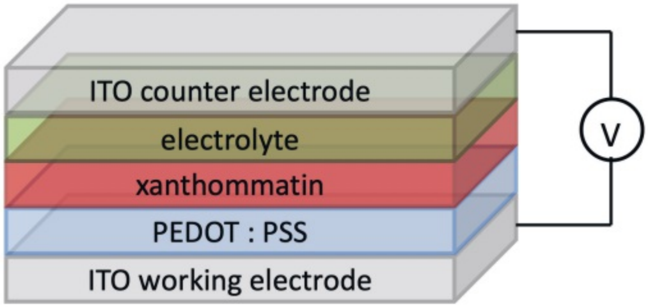

Fig. 3. Device architecture for the xanthommatin-based ECDs reported by Deravi.[6]

Received: August 12, 2022

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[a]This column is one of a series designed to attract teachers to topics that link chemistry to Nature and stimulate students by seeing real-life applications of the subject.