

Nature inspired dyes for the sensitization of titanium dioxide photocatalyst

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Introduction

Solar energy is not only environmentally clean, it may also be most effectively utilised within the restrictions imposed by the second law of thermodynamics. Light may provide free energy to drive endergonic reactions, directly, or indirectly by being transformed into electric energy, as in photosystems in green plants or bacteria, or in manmade solar cells. It might also be applied to overcome energetic barriers in exergonic reactions, as in photocatalysis. However, there are no perfect substances that would absorb and utilise the entire visual solar radiation spectrum (350–700 nm, equivalent to 3.5–1.8 eV or better to near infrared, 1240 nm corresponding to 1 eV).

Plant and bacterial photosystems rely on chlorophylls, porphyrin macrocycles, exhibiting outstandingly high absorbance in the visible and ultraviolet region. Solar energy is harvested by antennae from where it is relayed into the special-pair of the photosystem, where it drives electron transfer, i.e., is transformed into electric energy. To broaden the spectrum range, plants use not only chlorophylls but also polymethine dyes, like carotenoids and xanthophylls. *Halobacteria*, (*Archea*, not bacteria, as their name would deceptively imply) [1] and some real bacteria [2] use light but in an entirely different way. The protein used to capture light, Bacteriorhodopsin, contains retinal, a molecule responsible for vision in almost all animals, also humans. Retinal is a polymethine molecule, half the length of carotene (or xanthophyll), and terminated by an aldehyde group, typically bound in a Schiff base. Retinal in its ground state is *all-trans*. In *Halobacteria*, photoexcited retinal immediately undergoes *trans-cis* isomerisation, upon which literally mechanically throws a proton out into the extracellular side of the membrane creating a proton concentration gradient, and hence the proton-motive force, analogous to electromotive force in galvanic cells. This can drive various processes, the synthesis of ATP, above all. Some bacteria have additionally a light-harvesting antenna with carotenoid molecules that widen the spectrum range [3].

The energy of absorbed photons might correspond directly to the free or Gibbs energy that is used provided they exactly match and there are no mediators required. However, in real systems, upon photo-excitation, the electron goes vertically to a higher than needed vibrational level or when mediators are used, the electron must gain an excess energy to drive its further transfer in subsequent processes. This excess energy is dispersed. Using a broader range of spectrum for a given process means that only the energy equivalent to the lowest energy photon could be utilised, and it also has its advantages. More photons could be used and although part of the harvested photon energy is lost, it is easier to control systems of lower energy to avoid the degradation of more sensitive molecules. It is how photosystems I and II work. The Gibbs energy required for photosynthesis is divided into two parts [4].

Beside the free energy elevation provided by the absorption of photons, there is another condition that has to be met for redox reactions to occur, namely, the electron donor must have lower potential than that of the acceptor. This must be taken into account

in designing solar cells and photocatalytic systems, particularly dye-sensitised [5]. The most popular solar cells are titanium dioxide based. This semiconductor has a wide bandgap of 3.03 eV and 3.20 eV, depending on its crystalline form, rutile or anatase, respectively [6–8]. Thus, TiO₂ requires ultraviolet radiation to get electrons in its conductance band. This would leave most of the solar radiation unused. Such a high free energy, ca. 300 kJ mol⁻¹ for one-electron processes, is rarely needed. Even water electrolysis (a two-electron process!) can be effected with about half that voltage. Electrons originating from elsewhere, but having sufficient energy to get to the conductance band of TiO₂ may do the task. These electrons could come from a photoexcited molecule, a dye-sensitiser LUMO, in contact with TiO₂, provided their energy is higher than that of the conductance band edge of TiO₂ of ca. -3.8 eV (for anatase at pH 7 [6, 9] or in non-aqueous environments [7]). After the photoexcited dye molecule has injected the electron into TiO₂, it may receive it back from an electrolyte mediator (most commonly iodide anion [10]) having its electrons at the potential lower than the HOMO potential of the dye. The oxidised mediator (triiodide anion) is reduced at the counter electrode and this process sets the potential of this electrode. In this way the useful voltage of the solar cell would be equal to the difference between the potential of the TiO₂ conductance band and the redox potential of the mediator (I⁻/I₃⁻). Dye-sensitised solar cells have higher conversion efficiencies than plant photosystems, though there is a theoretical limit of ca. 30% to their efficiency [11]. The highest known conversion efficiency of 15% was achieved in a solar cell that employs an organic-inorganic hybrid perovskite (CH₃NH₃PbI₃) as a sensitising dye [12].

Cyanine dyes are most known and studied among the artificial polymethine dyes [13]. They contain a polymethine chain that couples two nitrogen centres, of which one is positively charged, and thus pulls electrons in, while the other one pushes them out. Hence these systems are often called “push-pull” alkenes. Generally they have an all-trans structure. Upon photoexcitation, like the described natural dyes, they undergo extremely fast *trans-cis* isomerisation within picoseconds [14], but also very rapidly, within milliseconds, return to their all-trans structure when the light is switched off [15].

The properties of these dyes depend on the length of the polymethine chain and the type of terminal nitrogen groups. A general rule applies to all polymethine dyes that the longer the chain, the lower the HOMO-LUMO energy gap and the lower the difference between the first reduction and oxidation potentials. It was shown that some cyanine dyes with indoline terminal groups exhibit suitable redox potentials to be used as sensitisers for TiO₂ based solar cells and photocatalysts [16]. This type of dyes were also tested as TiO₂ sensitisers in photocatalytic I⁻ oxidation [17]. It appeared that their activity was related to the length of the polymethine chain, the longer the chain, the higher the activity.

Here we demonstrate that polymethine dyes with indoline end groups containing additional substituents in the middle of the chain are efficient sensitisers of titania.

Experimental

Samples of dyes used were generously donated by Prof. A.A. Ishchenko from the Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv. Their synthesis was published [18].

Electrochemical measurements were conducted using a BAS 100B/W Electrochemical Workstation (Bioanalytical Systems) with a standard three-electrode cell in 0.1 M tetra-n-butylammonium tetrafluoroborate solutions. The working electrode was a 1.6 mm diameter glassy carbon electrode (Mineral) and platinum wire was the auxiliary electrode. All potentials were measured and quoted against an Ag/AgCl (3 M NaCl) reference. All measurements were done under dry argon atmosphere. Voltammograms were registered at 100 mVs⁻¹ scan rate. Ferrocene was added at the end of each measurement series as an internal standard. In acetonitrile $E_{1/2}(\text{Fc}^+/\text{Fc}) = 0.44$ V vs. employed reference electrode. For the energy calculations it was assumed that $E^0(\text{Fc}^+/\text{Fc}) = 0.40$ V vs. SHE and that the absolute potential of SHE equals +4.44 V [16, 19].

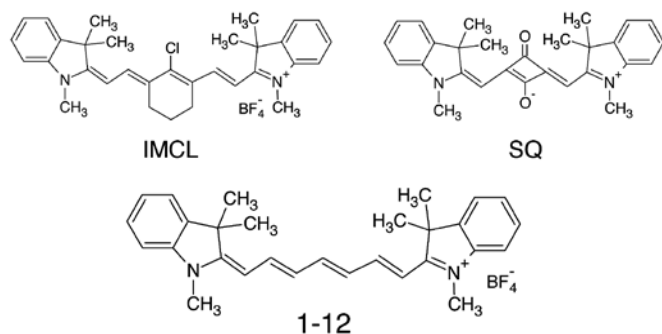
Spectra were taken with a fibre optics OceanOptics USB 2000-XR spectrometer.

Degussa P-25 titania was used to prepare the photocatalysts and its properties are described [20]. Titania powder was soaked with a solution of the dye in methanol and the solvent was evaporated. Afterwards, the surface was covered with polyepoxypropylcarbazole (0.1 mg/g TiO₂) film to protect the dye from leaching when used in photocatalytic tests. The photocatalysts contained 2 μmoles dye per g TiO₂.

Photocatalytic tests were carried out in a thermostated (18°C) glass reactor filled with aqueous 0.1 M KI solution, 1 g photocatalyst per L solution added, open to the air, and irradiated with a 500 W lamp kept at a fixed distance of 170 mm from the reactor. The reactor was wrapped in Al foil leaving open only a window that was covered with a filter cutting off the radiation of $\lambda < 480$ nm. The progress of the reaction was monitored by UV-Vis spectroscopy.

Results and discussion

Three polymethine dyes were used with various groups in the middle of the polymethine chain, the structures and symbols of which are given below.



IMCL and 1-12 dyes are cationic with BF₄⁻ as a counterion, SQ has zwitterionic structure. Their spectra, presented in Figure 1, are determined by the presence of a conjugated polymethine chain and hence are the same in character. The peak position is related to the HOMO-LUMO energy gap in the dye. As can be seen, the presence of substituents in the middle of the chains shifts the absorption band. The introduction of a chlorine atom apparently increases the coupling, shifting the band bathochromically from 741 nm in 1-12 to 775 nm for IMCL. SQ is a squaraine type dye with a four-membered squaric acid ring in the middle, which could increase the degree of coupling, but contains less methine groups, which would counter this effect. However, comparing it with a dye analogous to 1-12, but containing one ethylene unit less [16] shows that unexpectedly its absorption is shifted hypsochromically from 637 nm to 628 nm for SQ.

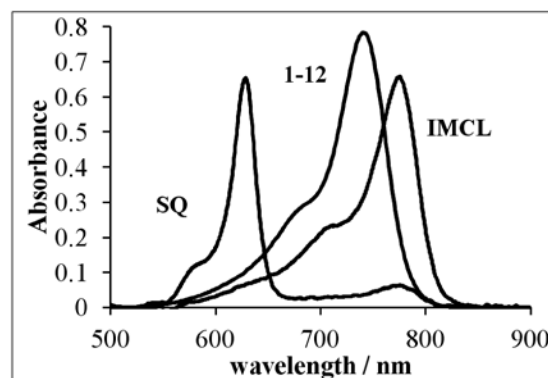


Fig. 1. UV-Vis spectra of the used dyes in 25 μM solution in acetonitrile

The studied polymethine dyes exhibited well-defined CV reduction and oxidation waves, as presented in Figure 2. IMCL and SQ dyes show quasi-reversible first reduction and oxidation processes. It was checked that first oxidation and reduction processes for 1-12, despite being irreversible because of the lack of the reverse waves, are diffusion controlled and hence could be applied for the calculation of energy levels.

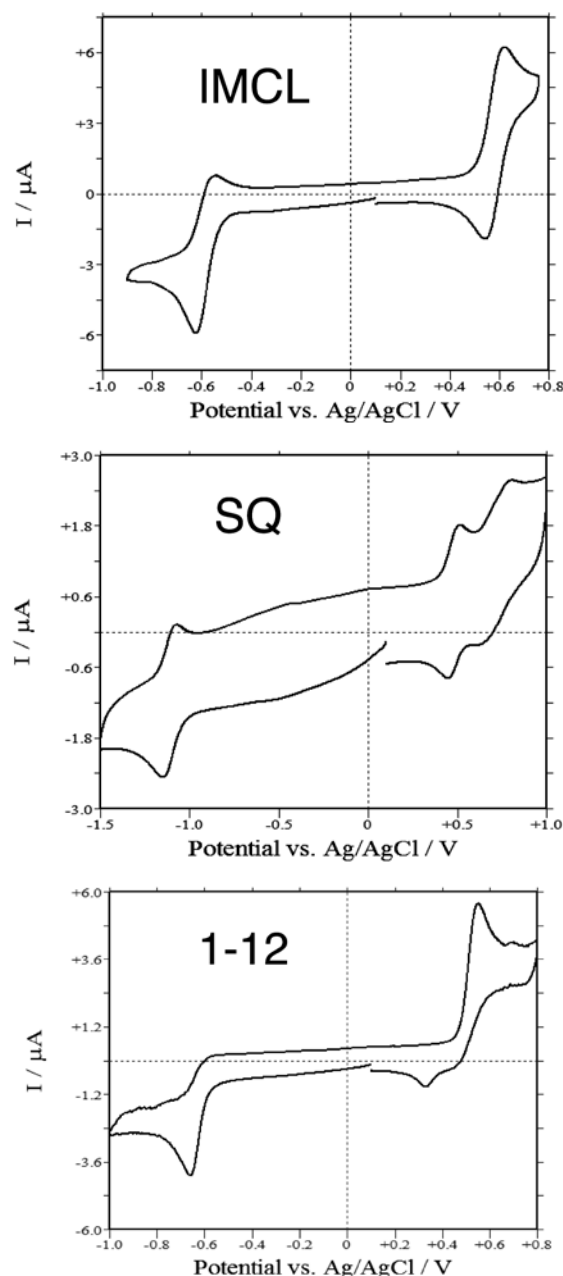


Fig. 2. Cyclic voltammograms of the studied dyes in acetonitrile

This pattern of well-defined first oxidation and reduction waves is characteristic of polymethine dyes. It may be assumed that the electron goes from the highest occupied orbital (HOMO) upon oxidation and to the lowest unoccupied orbital (LUMO) upon reduction. The potentials of these processes in the absolute scale should be equal to the potentials of the electron in respective orbitals. When multiplied by the electron charge they yield the energy of HOMO and LUMO. To get the energies expressed in electron-volts it is enough to multiply the potentials by -1 . Table I summarises the cyclic voltammetry results, and HOMO and LUMO energy levels.

Table I

First oxidation and reduction potentials of the studied dyes in dichloromethane and acetonitrile, and HOMO and LUMO energies based on oxidation and reduction potentials, respectively

| Dye | Solvent | $E_{1/2}^{ox}$ vs. SHE / V | $E_{1/2}^{red}$ vs. SHE / V | HOMO / eV | LUMO / eV |
|------|---------------------------------|----------------------------|-----------------------------|-----------|-----------|
| IMCL | CH ₂ Cl ₂ | 0.59 | -0.68 | -5.03 | -3.76 |
| | CH ₃ CN | 0.55 | -0.62 | -4.99 | -3.82 |
| SQ | CH ₂ Cl ₂ | 0.53 | -1.08 | -4.97 | -3.36 |
| | CH ₃ CN | 0.44 | -1.15 | -4.88 | -3.29 |
| I-12 | CH ₂ Cl ₂ | 0.52 | -0.68 | -4.96 | -3.76 |
| | CH ₃ CN | 0.47 | -0.68 | -4.91 | -3.76 |

The difference in energies between HOMO and LUMO may also be calculated from spectroscopic data. As can be seen in Table 2, the energies thus obtained are significantly higher than those based on electrochemical measurements. It is chiefly due to different environments, the presence of the base electrolyte stabilising the charged species, and to the fact that upon electrochemical processes the charge of the entire molecule changes, which is generally contributes to a change in the energy of the orbitals. The LUMO energies may also be calculated by adding to the HOMO energy the HOMO-LUMO energy gap obtained from spectral data. In this case all the values would be higher than those based only on electrochemical data. In summary, all the dyes have LUMO energies higher than the conduction band edge energy of anatase (except for IMCL based on electrochemical data in acetonitrile), which means that all of them meet the thermodynamic requirements to act as sensitisers for TiO₂.

Table 2

Absorption maxima and HOMO-LUMO energy gaps calculated from spectroscopic and electrochemical data, and the differences between the gap energy values obtained from both methods

| Dye | Solvent | λ_{max} / nm | $\Delta E_{(LUMO-HOMO)}$ / eV | | Difference between calculated $\Delta E_{(LUMO-HOMO)}$ / eV |
|------|---------------------------------|----------------------|-------------------------------|----------------|---|
| | | | from λ_{max} | from $E_{1/2}$ | |
| IMCL | CH ₂ Cl ₂ | 785 | 1.58 | 1.27 | 0.31 |
| | CH ₃ CN | 775 | 1.60 | 1.17 | 0.43 |
| SQ | CH ₂ Cl ₂ | 632 | 1.96 | 1.61 | 0.35 |
| | CH ₃ CN | 628 | 1.97 | 1.59 | 0.38 |
| I-12 | CH ₂ Cl ₂ | 756 | 1.64 | 1.20 | 0.44 |
| | CH ₃ CN | 741 | 1.67 | 1.15 | 0.52 |

It is interesting to note that in a more polar solvent, acetonitrile, the HOMO-LUMO gap energies obtained from λ_{max} are slightly higher for all the studied dyes. The same values based on electrochemical data show the opposite effect.

The photocatalytic activity of the dye-TiO₂ systems was tested in the oxidation of iodide anions to triiodide. The test results are shown in Figure 3.

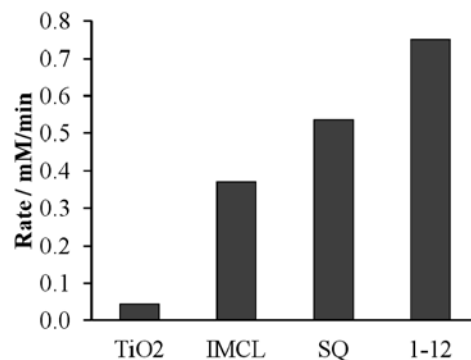
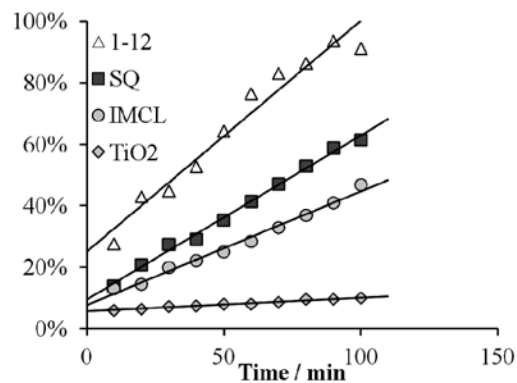


Fig. 3. Photocatalytic oxidation of iodide to triiodide anions; TiO₂ denotes pure titania; dye symbols denote TiO₂-dye systems. a) progress of the reaction as percent conversion of the initial iodide; b) comparison of steady-state reaction rates

The most active appeared to be TiO₂ sensitised by I-12 dye, the least active was the system with chlorine-substituted dye, IMCL, however, it was still nearly 8 times more active than TiO₂ without added sensitiser. After a rapid start, the reaction goes to steady-state characterised by a constant rate. These rates were compared in Figure 3b. There seems to be no clear reason for the highest activity of I-12 dye. Its absorption coefficient is the highest among the studied dyes, but not enough to justify the observed differences in the activity. Its LUMO energy based on spectral data may be much higher than that of IMCL, but still, SQ dye has the highest lying LUMO. It seems that the photocatalytic activity is governed by a combination of factors.

Conclusions

Polymethine dyes with indoline end groups with and without substituents in the middle of the chain show similar spectroscopic and electrochemical properties. In the visible spectrum one band with a shoulder at shorter wavelengths could be seen. Cyclic voltammetry revealed the presence of well-defined, oxidation and reduction processes, quasi-reversible for the dyes with substituents in the polymethine chain. The first oxidation and reduction waves are all diffusion controlled and the electrochemical data may be used to calculate free-energies and to estimate the HOMO and LUMO levels, which was done for all the studied dyes.

The calculated LUMO energies are higher than the conduction band edge of anatase TiO₂, which indicates that they all may act as sensitisers for titania. Testing the photocatalytic activity in the oxidation of iodide to triiodide anions demonstrated that the most active sensitiser was the dye without any substituents in the chain, and the least active, the dye with Cl in the middle of the polymethine chain.

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