Dyes for Fluorescent Solar Collectors

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The energy crisis of 1973 and the ensuing energy debate have made people aware of the importance of obtaining primary energy in technology. One energy source that has only been used to a small extent so far, but is available in practically unlimited quantities, is solar energy. A direct use of solar power (and thus solar energy) is hindered by the fact that, in contrast to the other primary energy sources used today, it is distributed over large areas. In the case of purely thermal use, the low power density (AM1 spectrum1) at full incidence of light2) approx. 800 $W \cdot m^{-2}$) interferes because the practically achievable temperatures are too low for most applications. For energy conversion systems such as photovoltaic cells, the low power density is also a problem because these expensive systems have to be applied over large areas. Economical solar systems therefore need concentrators for solar power density, which are connected upstream of the actual useful system. So far, mirrors (and to a lesser extent lenses) have been used for this purpose, systems that achieve light concentration with geometric optics. However, geometrical optics3) can only concentrate directed radiation, but not diffuse radiation, for thermodynamic reasons4) (it is generally known that a burning glass can no longer be used even under dimly cloudy skies). Concentrators with geometrical optics are therefore suitable at best for desert regions with direct solar radiation. In temperate zones, where a large part of the solar radiation is diffuse, plants of this type can hardly be used economically.

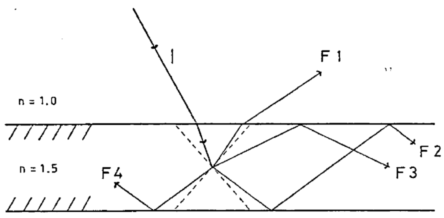


Figure 1. Mode of operation of the fluorescent solar collector. I: incident light beam, F_1 ... F_4: fluorescent light.

A way out is offered by the fluorescent solar collector developed by Garvin5) and improved by Götzberger and Greubel,3) which is able to concentrate even diffuse light radiation. The fluorescent solar collector3) consists of a plane-parallel plate of highly refractive material (e.g., Plexiglas with $n_D^{20} \approx 1.5$) homogeneously dyed with a fluorescent dye (Figure 1). Light radiation I hitting the surface of the plate from all directions can penetrate (under refraction) into the optically denser material, where it is absorbed by the homogeneously dissolved dye. The subsequent fluorescence F_1 ... F_4 is emitted (statistically) almost isotropically in all spatial directions. Of the emitted fluorescence light, however, only the smaller share can leave the plate again directly, which hits the plate surface more steeply than in the critical angle of total reflection. The majority of the fluorescent light is guided by total reflection in the plate and can only leave it again at the edge surface. Since the area of the plate is much larger than the edge area, this results in a light concentration. In practice, concentration factors of up to 200 can be expected.3) The maximum achievable concentration factor is $exp(h\Delta\nu/(k_BT))$, where $\Delta\nu$ is the Stokes' shift of the fluorescent dye used.4)

This fluorescent solar collector system requires fluorescent dyes with the following properties, which must be present simultaneously:

1. homogeneous solubility in organic matrix,
2. very high light fastness (photostability),
3. fluorescence quantum yields close to 100%,
4. low overlap between absorption and fluorescence spectra,
5. adaptation to all required spectral ranges of visible or near IR radiation.

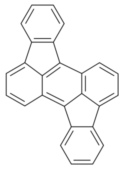
Points 1 to 5 seem to be (at least partially) mutually exclusive and pose a challenge to dye chemistry. Dyes that combine all of these properties are not currently known. However, the applicability of fluorescent solar collectors depends critically on the synthesis of suitable dye systems.

For points 1 to 5, at least partial solutions have been worked out so far, which lead to the expectation that dyes can be synthesized which can fulfill the requirements synchronously.

Solubility

The solubility of aromatic systems in organic solvents is known to decrease with increasing number of linked ring systems,6) and with sufficient number of rings such systems are finally completely insoluble in common organic solvents at room temperature. Aromatic polycyclic systems, however, are needed as chromophores for absorption in the long-wave visible or near-IR region. In dying technology, such dyes can be used in most cases as pigments (e.g., the indanthrene dyes in textile dyeing), where their poor solubility is a welcome side effect. In the fluorescence collector, however, the pigment particles form scattering centers that lower the efficiency of the system. For this application, homogeneous solubility is therefore a condition for all dyes.

In connection with the work on fluorescent dyes for solar collectors, it was found[7)] that when an aromatic system is substituted with *tert*-butyl groups, the solubility in organic solvents is drastically increased. This principle has been successfully applied to dyes of very different structures. Replacing one hydrogen in the molecule with a *tert*-butyl group increases the solubility of the compound by a factor of about 10, almost independently of the solvent. By introducing one to eight *tert*-butyl groups, compounds known to be completely insoluble can therefore be homogeneously brought into solution.



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The rubicene system (**1**, CAS RN 197-61-5) can be listed here as an example. In which the basic body is very sparingly soluble in aliphatic solvents and sparingly soluble in aromatic solvents. The introduction of four *tert*-butyl groups (with unknown substitution site) increases the solubility of the system in common solvents by a factor of about 10^4. The introduction of *tert*-butyl groups still has special advantages, since they do not adversely affect the photostability of dyes, hardly change the absorption and fluorescence spectrum and usually (slightly) increase the fluorescence quantum yield. Moreover, they can be readily introduced into the dye itself or its precursors by electrophilic or nucleophilic substitution.

Photostability

For solar collectors to be economically viable, they should have a minimum lifetime of five to 20 years. Under simplifying assumptions and considering the special properties of the fluorescent collector system, a quantitative relationship can be established between quantum yields of photobleaching reactions of the dyes used and lifetime of the system.[8)] As can be seen from Figure 2, the quantum yields for photobleaching reactions must not exceed 10^{-8} to 10^{-9}.

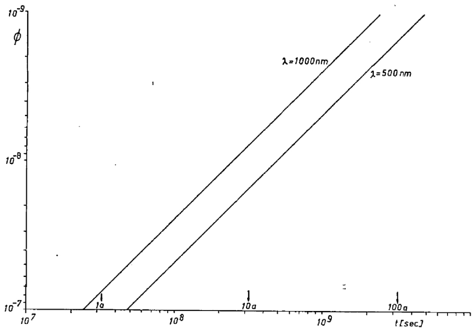
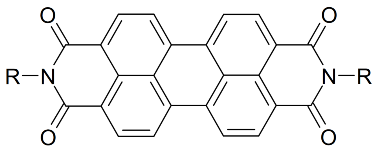


Figure 2. Relationship between lifetime of solar collectors and quantum yields of photobleaching reactions of the dyes used. The straight lines refer to the average absorption wavelengths of 500 and 1000 nm, respectively.

In addition, photolysis products must not quench fluorescence. Dye systems meeting these conditions have been obtained by combining very photostable chromophores with very photostable auxochromic groups. The experience available from the preparation of stable vat dyes serves as a basis. For example, it is known that the perylene backbone is particularly suitable for the formation of photostable dyes. On this basis, perylene dyes (**2**), for example, have been synthesized[9)] that reasonably meet the requirements for fluorescent collectors.



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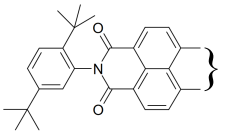
To obtain sufficient solubility in organic matrix, R is a phenyl group with *tert*-butyl substituents.[10)] A dye with the substitution according to (**3**) has turned out to be a favorable compromise between quantum yield, photostability and solubility.



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A key position in photobleaching reactions appears to be singlet oxygen, which can destroy the chromophore in certain cases by Diels-Alder analogous or *en* reactions. The singlet oxygen is formed by the dye itself via its T_1 state by sensitization.[11)] Now, to protect the dye against its bleaching effect, singlet oxygen quenchers such as 1,4-diazabicyclo[2.2.2Joctane[12)] can be used, which in one experiment were able to double the lifetime of dyes. To optimize the protection against singlet oxygen, one could think of fixing the quencher directly to the dye molecule.

Quantum yield

Little is known about the relationship between chemical structure and fluorescence quantum yield. The main competing processes to fluorescence are non-radiative deactivation and inter system crossing to the triplet state.[13)]

To avoid nonradiative deactivations via predissociation,[13)] dyes should not contain groups with weak bonds such as nitro or methoxy groups. Other deactivations that should be avoided are brought in by conformationally labile groups or by groups that consume excitation energy via a proton shift. To keep the inter system crossing low, the dye should not contain heavy atoms such as bromine. Furthermore, there should be no restriction by lacking overlap of orbitals (for excitation or fluorescence an electronic π-π^* transition is generally favorable). Of particular importance is the degree of purity of the dyes, since impurities from the synthesis can sometimes be very efficient fluorescence quenchers. Taking this into account, dyes with fluorescence quantum yields up to 100% have been obtained.

Overlap between absorption and fluorescence

The fluorescent light is collected over long distances in the solar collector (in practice, distances between 1 and 5 m are expected). Reabsorption of the fluorescent light should not lead to any loss of light. Fluorescent solar collectors therefore require fluorescent dyes with absorption and fluorescence spectra that are as well separated as possible (minimum spectral overlap). However, as can be seen from the Jablonski diagram in Figure 3, the 0-0 transition in absorption and fluorescence is identical. This inevitably results in a spectral overlap of the absorption and fluorescence spectra. A mathematical model has been developed for a quantitative description of the overlap.[14)]

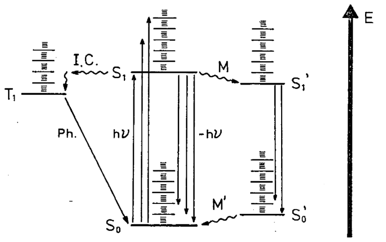

Figure 3. Jablonski's diagram for absorption and fluorescence. M, M': modification of the dye.

One way to eliminate this overlap is to modify the dye after excitation (Figure 3). The whole process can be done in a cycle:

1. Excitation by absorption ($S_0 \rightarrow S_1$).
2. Modification M under energy lowering ($S_1 \rightarrow S_1'$).
3. Fluorescence ($S_1' \rightarrow S_0'$).
4. Modification M' to the ground state ($S_0' \rightarrow S_0$).

Double modification M and M' results in a shift of the fluorescence spectrum to longer wavelengths and thus a separation between absorption and fluorescence spectra. The most important modification processes that can be considered are a relaxation of the solvate shell (when the dye changes its dipole moment upon excitation), a deprotonation-protonation according to the Förster mechanism,[15)] a change in molecular geometry, or an energy transfer mechanism.

Fluorescence by long-wave excitation

For the shorter wavelength regions, dyes have already been obtained that reasonably meet the requirements. Problems are currently encountered in the long wavelength visible and IR regions. It has not yet been possible to obtain photostable dyes that fluoresce in the IR region with high quantum yields. It is hoped that fluorescent dyes with appropriate properties can be obtained from vat dyes.

Outlook

A universal solution has been found for point 1. Points 2 and 3 have been realized for individual dye systems, and the resulting results can be transferred to other dye classes. General solutions for points 4 and 5 are still pending, but with the approaches already available, realization can be expected. Thus, it can be expected that the fluorescent solar collector can be used in practice in the next few years. Then it has to be examined in which areas its use for the generation of solar energy is economical.

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