



non-radiative deactivation, the latter two leading back to the ground state molecule A. Note that the term luminescence summarizes fluorescence, phosphorescence, as well as chemiluminescence.^[46] The product P does not necessarily need to be a ground state molecule but can also be the outcome of a transformation into another excited state, such as triplet states. Each process in Figure 2.9 is called a *primary process* for which a

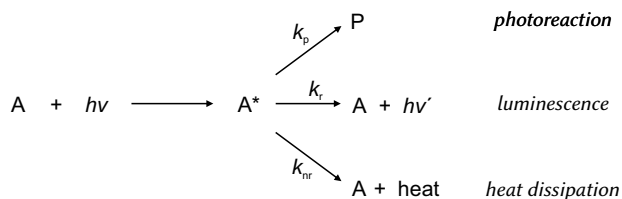


Figure 2.9. Primary steps after the interaction between light with the energy $h\nu$ and a molecule A. A chemical reaction with the rate constant k_p leads to the formation of product P (top). Luminescence associated with the rate k_r to the ground state A and release of a photon with energy $h\nu'$ (middle). Non-radiative deactivation can occur *via* heat dissipation with a rate k_{nr} (bottom).

quantum yield (Φ_i) can be defined by Equation (2.17a) and Equation (2.17b). As such, Φ_i represents the efficiency of a photochemical process.

$$\Phi_i = \frac{\text{Number of molecules undergoing process } i}{\text{Total number of photons absorbed}} \quad (2.17a)$$

$$\Phi_p = \frac{k_p}{k_p + k_r + k_{nr}} \quad (2.17b)$$

Another important quantity is the *lifetime* $\tau(A^*)$ of the respective excited state A^* , as given by Equation (2.18). It is the inverse of the sum of all rate deactivation rate constants.

$$\tau(A^*) = \frac{1}{k_p + k_r + k_{nr}} \quad (2.18)$$

Φ_i and τ of the respective primary steps are correlated *via* k_i (refer to Equation (2.19)).

$$k_i = \frac{\Phi_i}{\tau(A^*)} \quad (2.19)$$

Rigorous treatment of photochemical processes with quantum chemistry results in the so-called transition dipole moment M_{if} of an initial state i and a final state f (see first line of Equation (2.20)).^[43] M_{if} answers the question whether a photochemical process is in principle possible or not. Ψ_i and Ψ_f are the wave functions of the initial and the final state, respectively and $\hat{\mu}$ the *dipole-moment operator*.



$$\begin{aligned}
 M_{if} &= \int \Psi_i \hat{\mu} \Psi_f d\tau \\
 &= \int \phi_i \hat{\mu} \phi_f d\tau_e \int S_i S_f d\tau_s \int \theta_i \theta_f d\tau_N
 \end{aligned}
 \tag{2.20}$$

The *Born–Oppenheimer* approximation enables the separation of the electronic wave function from the wave function of the nuclei, which is denoted as θ .^[47] Further split of the electronic wave function into a one electron wave function ϕ and a spin function S leads to the expression given for M_{if} in the second line of Equation (2.20). The first integral called the *electronic transition moment*, the middle one the *spin overlap integral*, while the square of the third integral is known as the *Franck–Condon* factor (FCF).^[48]

For a specific transition $i \rightarrow f$ to occur, the transition dipole moment must be non-zero. The selection rules for electronic transitions are the result of the *electronic transition moment*. The *spin overlap integral* states that during an electronic transition, the spin multiplicity must be preserved. In cases where this rule is violated, the transition is called *spin forbidden*. This is especially relevant for molecules containing heavy atoms, like some of the metal complexes used in the present thesis. The intensity of the actual transition can be estimated *via* the FCF, which is known as the *Franck–Condon* principle.^[48a,b,49]

When applying the *Born–Oppenheimer* approximation, it is possible to visualize the energy of the ground and excited electronic state with respect to the nuclear coordinates.^[47] An example is depicted in Figure 2.10a). The potential energy curves of the ground and the excited state are visualized by the bold lines in yellow and red, respectively. An absorption results in a so-called *vertical transition*, which reflects the fact that the nuclei are considered at fixed position during electronic excitations in the *Born–Oppenheimer* approximation. The nuclei coordinates of the relaxed energies of the ground state differ from those of the excited state, leading to an intensity pattern of the possible transitions into various vibrational states as shown on the left side of the energy axis. The intensity distribution of the various transitions can be calculated by the FCF.

While the picture drawn in Figure 2.10a) may be illustrative for small molecules, it fails with increasing molecular size. A suitable presentation of such systems is obtained by the so-called *Jablonski* diagram.^[50] An example is depicted in Figure 2.10b) with the energy levels of the various excited states relative to the ground state S_0 in yellow. The gray lines represent excited vibrational states.

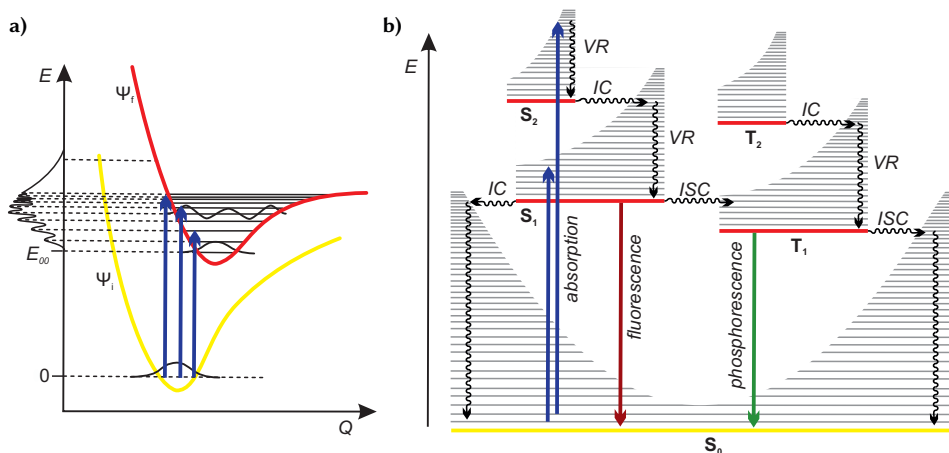


Figure 2.10. a) Schematic explanation of vertical electronic transitions from a ground state Ψ_0 to an excited state Ψ_1 . E is the energy scale and Q the nuclear coordinates of the respective molecule. E_{ab} represents the energy of a vibronic transition from $\Psi_{v=a} \leftarrow \Psi_{v=b}$. b) *Jablonski diagram*, depicting the energy levels of a molecule with the possible intramolecular photo processes as described in the text. Adapted with permission from [43]. © 2014 Wiley-VCH Verlag GmbH & Co. KGaA.

Excitation from the S_0 state into excited singlet states S_1 or S_2 can occur upon irradiation.^(a) The distribution into the respective vibrational levels is dictated by the FCFs. The combination of an electronic and vibrational transition is referred to as *vibronic transition*. Fast *vibrational relaxation* (VR) brings the excited molecules to the lowest vibrational level in the respective state. From a here, *internal conversion* (IC) denotes the isoenergetic radiationless transition between two electronic states having the same multiplicity, e.g. from S_1 to S_0 . On the other hand, *intersystem crossing* (ISC) describes the isoenergetic radiationless transition between two electronic states of different multiplicity, e.g. from T_1 to S_0 . The spontaneous emission of a photon from the molecule in the excited state is termed *fluorescence*, if the spin multiplicity is retained. The corresponding process involving a change in spin multiplicity is termed *phosphorescence*, which typically involves a transition from the first excited triplet state T_1 . As this transition is *spin-forbidden*, phosphorescence occurs on a much longer timescale than fluorescence. Fluorescence, as well as phosphorescence are following the *Kasha–Vavilov rule*, which states that quantum yield of the luminescence is independent of the excitation wavelength, i.e. the process occurs from the lowest vibrational level of the respective excited state.^[51] As in the case of singlet excited states, ISC can also occur from a triplet state into a singlet state.

^(a) Single photon excitations mainly occur into the S_1 state, although higher order excitations are possible if allowed *via* the selection rules.



Table 2.1 summarizes the above described photophysical processes together with their corresponding timescales.

Table 2.1. Summary of the photophysical processes described in the text and their corresponding time scales. Reproduced with permission from [46]. © 2009 John Wiley & Sons, Ltd.

Process	Abbreviation	Time scale / s
Absorption	–	10^{-15}
Internal conversion	IC	10^{-12} – 10^{-6}
Intersystem crossing (S → T)	ISC	10^{-12} – 10^{-6}
Intersystem crossing (T → S)	ISC	10^{-9} – 10^1
Vibrational relaxation	VR	10^{-13} – 10^{-12}
Fluorescence	–	10^{-9} – 10^{-7}
Phosphorescence	–	10^{-6} – 10^{-3}

2.2.2 Photochromic molecules

The first reports of the phenomenon later called “photochromism” date back to the end of the 19th century, where Fritzsche described a molecular photochromism.^[52] These observations have been termed *phototropy* and *phototropism*,^[53] while the term *photochromism* was suggested by Hirshberg in 1950.^[54]

Photochromic molecules respond to light as an external stimulus. Upon irradiation, the molecule undergoes a reversible transformation in geometry, polarity, as well as charge distribution.^[55] Light as the stimulus has the advantage that it does not contaminate the system, is orthogonal to most other processes and non-toxic. In addition, light can be delivered with high spatial and temporal control, precise wavelength, as well as defined intensity.^[56]

The photodynamic system of a photochromic molecule allows the population of a less stable or metastable state, as compared to the thermal ground state.^[57] Figure 2.11 illustrates the differences between thermal and photodynamic equilibrium. In the thermal case (a), the two energy levels (I) and (II) are populated according to the Boltzmann distribution and is given by the equilibrium constant K_{eq}^{Δ} . Forward and backward reactions take place *via* the same transition state on the same potential energy surface (principle of microscopic reversibility).

In the dark case of the photodynamic system (b), the activation barrier is too high for thermal transformations. Upon irradiation with a suitable wavelength (c), the molecule can transit into an excited state, from which it can relax into state (III). The backward



reaction can either take place spontaneously in the dark, or *via* irradiation with a different wavelength (d). As such, the equilibrium involves two different pathways and can involve

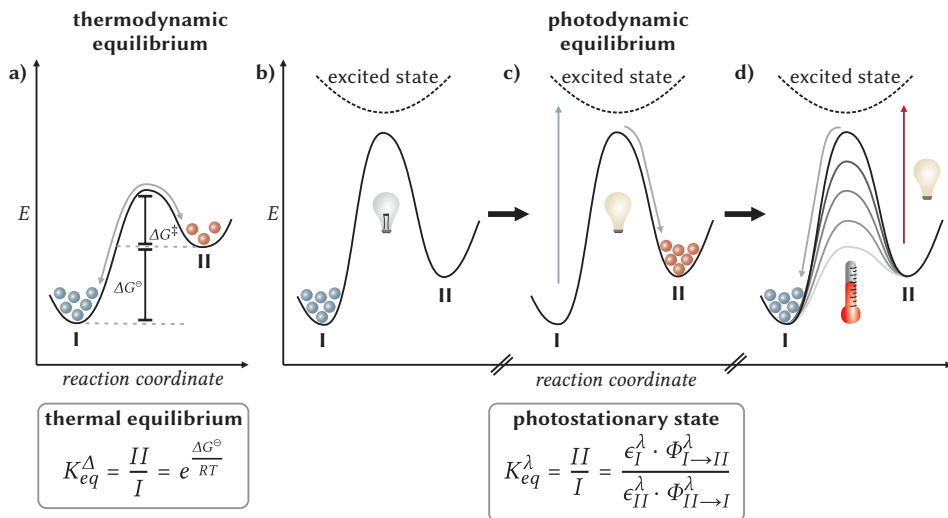


Figure 2.11. Comparison between thermodynamic (a) and photodynamic (b–d) equilibria. The Boltzmann distribution dictates the population of the energy levels (I) and (II) in the thermal case (a) with the equilibrium constant K_{eq}^{Δ} . The difference between the energy levels is given by ΔG^{\ddagger} and ΔG° . (b) Exclusive population of state (I) in the dark as a result of a high energy barrier. (c) Transition into an excited state upon irradiation and relaxation into state (II). (d) Depopulation of state (II) *via* thermal fading (T-type photochromism) or photo excitation (P-type photochromism). The photodynamic equilibrium constant K_{eq}^{λ} in this case is depicted below the graph and depends on the molar extinction coefficients and the quantum yields of the for- and backward reaction. [57] – Adapted with permission of The Royal Society of Chemistry.

the potential energy surface of an excited state, i.e. the principle of microscopic reversibility does not apply. The equilibrium constant for the resulting photostationary state (PSS) in the absence of thermal fading, i.e. the ratio between (I) and (II) under continuous irradiation with wavelength λ is given by K_{eq}^{λ} , which depends on the molar extinction coefficients ϵ_I^{λ} and ϵ_{II}^{λ} , as well as the quantum yields $\Phi_{I \rightarrow II}^{\lambda}$ and $\Phi_{II \rightarrow I}^{\lambda}$ of the two reactions. Depending on the energy barrier for the (II) to (I) backward reaction, photochromic molecules are classified as either *P-type* or *T-type*. For *P-type* molecules, the activation barrier is too high for a thermal reaction, resulting in a thermally bistable system. In contrast, *T-type* molecules are thermally labile, i.e. exhibit thermal depopulation of state (II).

Figure 2.12 gives an overview over photochromic molecules. Two examples of *P-type* photochromic molecules are diarylethenes^[58] and fulgides.^[59] In these systems, the



transformation in both directions is based on the electrocyclic $[2\pi+2\pi+2\pi]$ rearrangement, i.e. both isomerizations are photochemical reactions. Azobenzene^[60] and flavylum systems^[61] exhibit a $(E)\rightleftharpoons(Z)$ double-bond isomerization and belong to the *T-type* photochromic molecules. Finally, SPs and spirooxazins^[62] are also *T-type* photochromes, but undergo reversible photo activated cyclization/ring-opening reactions.

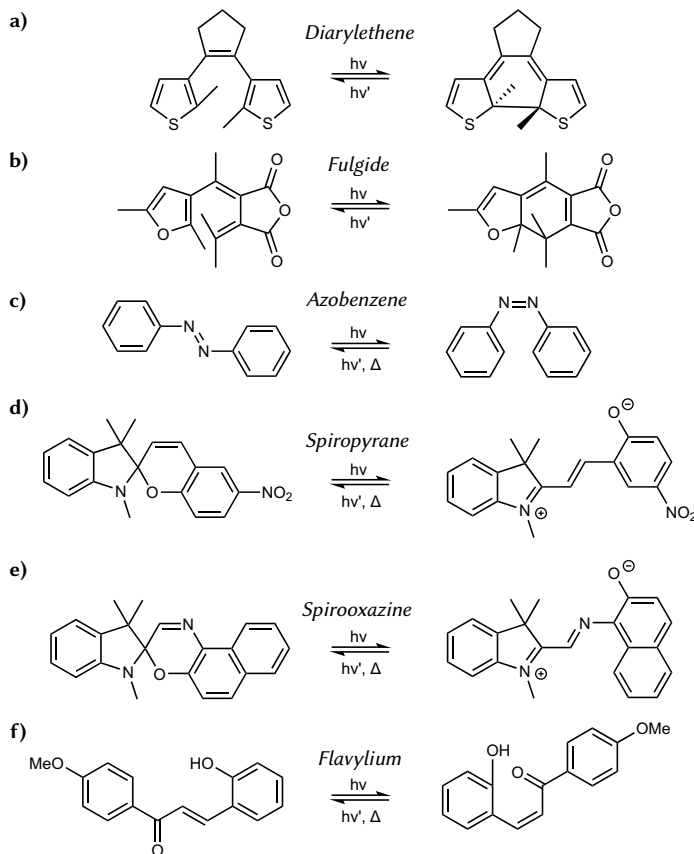


Figure 2.12. Most prominent families of molecular photochromic molecules. Diarylethenes (a) and fulgides (b) are examples of *P-type* photochromic molecules that isomerize *via* electrocyclic rearrangements. *T-type* photochromic molecules are for example azobenzenes (c) or flavylium molecules (f), which undergo $(E)\rightleftharpoons(Z)$ double-bond isomerizations. Spiropyrans (d) and spirooxazins (e) are also *T-type* photochromes, but with reversible cyclization/ring-opening isomerizations.

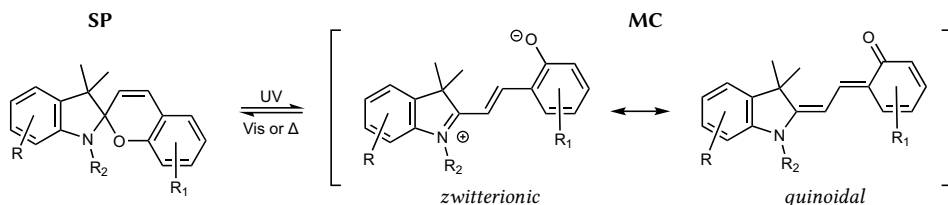
Every class of photochromic molecules described above has its unique set of properties, which can be tuned to take into account the desired applications. Parameters include the quantum yields Φ , the molar extinction coefficients ϵ , the spectra shape of the absorption,



the position of the PSS, the speed of switching and thermal stability of both isomers, and the resistance towards degradation (fatigue) of the photochrome.^[56] The following section describes the photochemistry of SPs in more detail, which was exploited in Chapter 4 and 5 of the present thesis.

2.2.2.1 Spiroprans

Fischer and Hirshberg were the first who described the photochemistry of SPs in the early 1960s.^[63] The general structure of SPs and their photochromism is depicted in Scheme 2.3. The close-ring isomer is abbreviated as “SP”, while the open-ring isomer is abbreviated as “MC”, from the analogy to the structure of merocyanines. The MC form can either be drawn as a zwitterionic or a quinoidal structure, while the real structure is a hybrid of both.



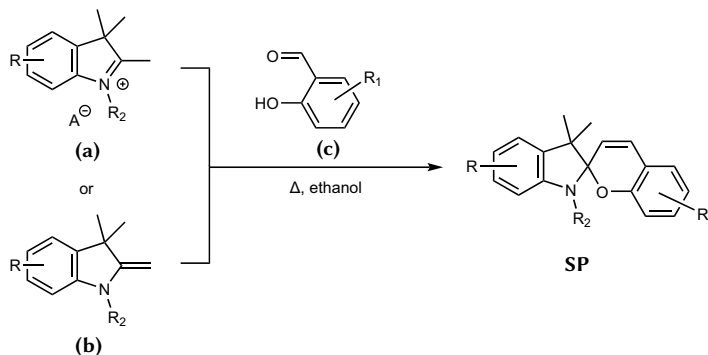
Scheme 2.3. General structure motif of the photochromic SP molecule and its open-ring MC isomer.

The unique properties of SPs compared to other photochromic molecules arise from the vastly different properties of the two isomers. First, the charge separation in the MC form results in a large electric dipole moment compared to the SP isomer.^[64] Secondly, the structural differences between SP and MC geometries results in less occupied volume of the SP as compared to the MC form.^[62c] Thirdly, the SP isomer is mostly transparent in the visible light region, whereas the MC form exhibits a strong absorption between 450–650 nm. In addition, the MC form shows strong fluorescence, while the SP form does not show significant emission.^[65] Fourthly, the MC isomer is significantly more basic than the SP isomer and can be protonated at the oxygen atom.^[66] Finally, the MC form also exhibits more affinity to other chemical species, such as metal ions or other zwitterionic species.^[62c]

Synthesis The synthesis of SP molecules is straightforward and has been reviewed extensively.^[53,62b,d,67] The most common methods are the condensation of a *N*-heterocyclic quaternary ammonium salt with a vicinal alkyl group with respect to the nitrogen



(a) or the corresponding methylene base (b) with a 2-hydroxyarenealdehydes (c), i.e. salicylaldehydes, in refluxing ethanol solutions (see Scheme 2.4).^[62c]



Scheme 2.4. The two most common synthesis strategies towards SP molecules. Condensation of a cyclic quaternary ammonium salt (a) or the corresponding methylene base (b) with a salicylaldehyde (c).

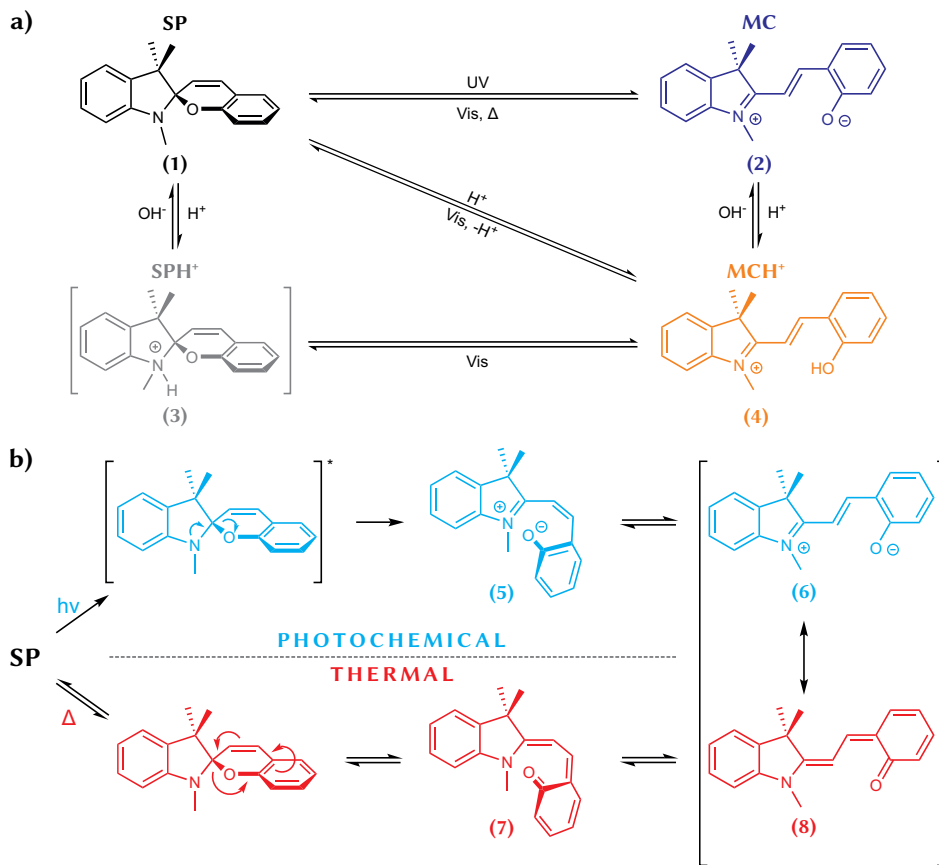
Isomerization mechanism The $SP \rightleftharpoons MC$ isomerization can not only be triggered by light, but also by other stimuli, such as temperature^[62d] (*thermochromism*), pH^[68] (*acidochromism*), solvent polarity^[69] (*solvatochromism*), metal ions,^[70] redox potential^[71] (*electrochromism*), or mechanical force^[62d] (*mechanochromism*).

The *photochromism* and *acidochromism* of SPs is depicted in Scheme 2.5a).^[62c] Transformation of SP (1) to MC (2) occurs *via* irradiation with UV light, while the reverse reaction is possible through irradiation with visible light or thermal fading. Upon protonation, the SP form (1) can be protonated towards SPH^+ (3). However, this species is not stable in solution and quickly ring-opens towards the protonated MCH^+ species (4), which is also indicated by the direct transformation of SP to MCH^+ in the middle. MCH^+ is also accessible *via* the MC form (2) at low pH values.

A comparison between the thermal and photochemical pathway of the SP to MC interconversion is illustrated in Scheme 2.5b). In the photochemical path on the top, irradiation with UV light around 365 nm gives rise to the MC isomer in a first-order process.^[72] The heterolytic cleavage of the spiro C–O bond forms the *cis*-MC (5) isomer, which transforms into the *trans*-MC species (6) upon rotation about the central C–C bond. Interestingly, this ring-opening can also be achieved *via* two-photon excitation using near-infrared (NIR) irradiation,^[70b,73] which will be exploited in Chapter 5 of the current thesis.



On the bottom half of Scheme 2.5b), the thermal SP to MC interconversion is depicted. In this case, the mechanism is a 6π electrocyclic ring-opening, which first results in the formation of the quinoidal form of the *cis*-MC isomer (7). Rotational isomerization towards *trans*-MC species (8) completes the transformation. The final MC structure is a hybrid of the two resonance structures (6) and (8).

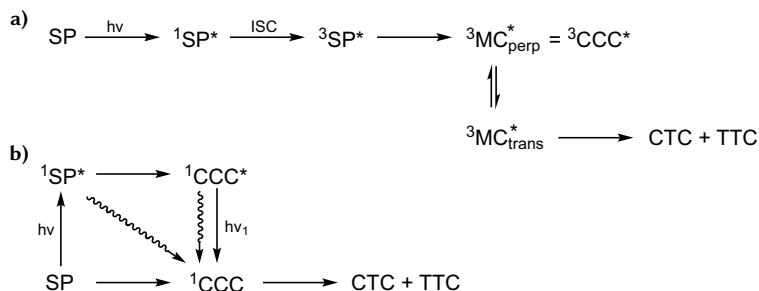


Scheme 2.5. a) Photochromism and acidochromism of SP molecules. Reversible transformations between the four states: SP (1), MC (2), protonated SP SPH^+ (3), and protonated merocyanine MCH^+ (4). b) Comparison between photochemical (top) and thermal ring-opening (bottom) mechanism. The resultant MC forms (6) and (8) are resonance structures of each other. [62c] – Adapted by permission of The Royal Society of Chemistry.

The mechanism and the involved excited species for the photochemical transformation has been investigated in great detail and can be divided in SP molecules without a nitro-group in the 6-position of the benzopyrane ring and those without substituents (see



Scheme 2.6a) and b), respectively).^[68b,70a,74] For 6-nitro substituted SPs, excitation of SP into the singlet state is followed by ISC into $^3\text{SP}^*$. From here, ring-opening occurs towards the triplet state $^3\text{MC}_{\text{perp}}^*$, which transforms into $^3\text{MC}_{\text{trans}}^*$ through rotation. Additional ISC and IC results in the MC isomers CTC and TTC (for the description of the abbreviations, see Scheme 2.7 and discussion thereof). This mechanism is also called the *Görner–Chibisov* mechanism.^[62a] In contrast, no triplet states are involved for SP



Scheme 2.6. a) *Görner–Chibisov* mechanism of the photo triggered ring-opening of SPs with a nitro-group in the 6-position of the benzopyran ring, involving triplet states. b) Ring-opening mechanism for SP molecules without an electron-withdrawing group in the 6-position only occurs via singlet excited states. Adapted with permission from [62d]. © 2004 American Chemical Society.

molecules without electron withdrawing groups in the 6-position of the benzopyrane ring (see Scheme 2.6b). Here, the SP can either directly ring-open towards the ^1CCC isomer (thermal way), or, upon irradiation, undergo the ring-opening from the $^1\text{SP}^*$ state towards the $^1\text{CCC}^*$ excited state, from which IC or irradiation with another wavelength results in the ^1CCC isomer. From here, rotational isomerization finally also results in the CTC and TTC MC isomers.^[62a,d]

Scheme 2.7 illustrates the different possible isomers and their interconversion.^[62a] Electrocyclic 6π ring-opening (thermally) or heterolytic C–O bond cleavage (photochemically) of (*R*)-SP in the top line yields a sterically strained intermediate, which rapidly converts to the nearly planar CTT MC isomer. The abbreviations highlighted in green are referring to the orientation relative to the two double bonds (*cis*, *trans*; C and T) and the central single bond (*s-cis*, *s-trans*; C, T). Only the *s-trans* isomers are depicted in Scheme 2.7, because the *s-cis* conformers are significantly higher in energy.^[62b] Consecutive rotational isomerizations result in the formation of the CTC, TTC, and TTT isomers, from which the CTC and TTC are the thermodynamically most stable ones. Final ring-closure from the TTT form yields the (*S*)-SP stereoisomer. As depicted in the