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On the Versatility of Electronic Structures in Polymethine Dyes

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ABSTRACT

This article provides an overview of the photophysical behavior diversity of polymethine chromophores which are ubiquitous in biological imaging and material sciences. One major challenge in this class of chromophore is to correlate the chemical structure to the observed optical properties, especially when symmetry-breaking phenomena occur. With the constant concern for rationalization of their spectroscopy, we propose an extended classification of polymethine dyes based on their ground state electronic configuration using three limit forms namely: *cyanine*, *dipole* and *bis-dipole*. The chemical modifications of the dye and the influence of exogenous parameters can promote dramatic spectroscopic changes that can be correlated to significant electronic reorganization between the three-abovementioned forms. The deep understanding of such phenomena should allow to identify, predict and take advantage of the versatile electronic structure of polymethines.

Keywords: Polymethine, near-infrared dyes, cyanine, dipole, bis-dipole, spectroscopy, electronic absorption

1. INTRODUCTION

Polymethines are π -conjugated molecules featuring an odd number of sp^2 carbon atoms. An incredible wide variety of polymethines have been reported since the 1850's,[1] with a length comprised between 1 and 13 C atoms and with various electron-donating and/or withdrawing extremities resulting in the formation of neutral, positively or negatively charged dyes.[2-5] The most common derivatives possess a positive charge perfectly delocalized between electron-donating indole moieties through the conjugated bridge which confer the polymethine dyes their unique structural and optical properties. This *ideal polymethine state* is generally referred to as the *cyanine* state. It is accompanied by an equalization of the bond lengths and is characterized by sharp "solitonic" absorption and emission in the red, near-infrared region, reminiscent of polyacetylene conductors. This last feature accounts for the craze for polymethines and their use in a vast range of applications such as biological imaging,[6-8] photovoltaic devices[9] or as electroluminescent switches.[10, 11] In that framework, some of the most recent breakthroughs have been made in the field of nonlinear optics in the near infrared spectral range, where the usefulness of polymethines has clearly been demonstrated in the context of optical limiting,[12, 13] all-optical switching,[14-16] electro-optic modulation[17, 18] and biphotonic bio-imaging applications.[19, 20] However, a major issue with polymethines is the difficulty to explain and predict the nature and magnitude of the changes in optical properties that take place upon structural variations such as: chain elongation,[21] functionalization[22] or under the influence of their environment.[23, 24] Therefore it appears necessary to get a better understanding of these structure-to-properties relationships using an appropriate model.

2. CHEMICAL AND ELECTRONIC DEFINITIONS OF POLYMETHINE DYES

2.1 Chemical classification of polymethine dyes

In the 60-70's, Dähne proposed a classification of organic unsaturated chromophores, distinguishing three classes, as depicted in Figure 1: *aromatic* cycles; *polyenes* with an even number of carbon atoms; *polymethines* with an odd number of carbon atoms.[25] Both aromatic and polymethine states possess a strong resonance and a bond length alternation

(BLA) equal to zero.[26] Conversely, the polyene state is characterized by an alternation of single and double bonds along the π -conjugated backbone. This early classification attempts to correlate chemical structures and electronic properties but does not give account of the strong modifications of the electronic configuration for a given chemical structure under the influence of external parameters.[27] For instance, under certain circumstances, polymethine can display electronic/spectroscopic properties almost undistinguishable from those of polyenes, and *vice-versa*.

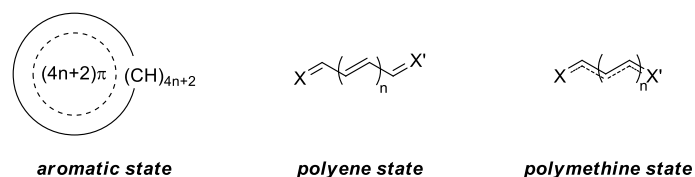


Figure 1. Three classes of organic unsaturated compounds introduced by Dähne.

In their reference review, Behera et al. proposed a more accurate description of the diversity of the polymethine family. This classification however, was still based on exclusive structural considerations (Figure 2).[2] Thus, four classes were distinguished, according to their charge state: (i) cationic cyanines, (ii) anionic oxonols, (iii) neutral merocyanines and (iv) zwitterionic (charge separated) cyanines. This classification has been very popular among chemists because it is based on the schematic representation of the dye. But once again, it does not fully account for the variety of spectroscopic characteristics of polymethines: although these four families exhibit different structures, it is well established that they can all reach identical electronic properties.

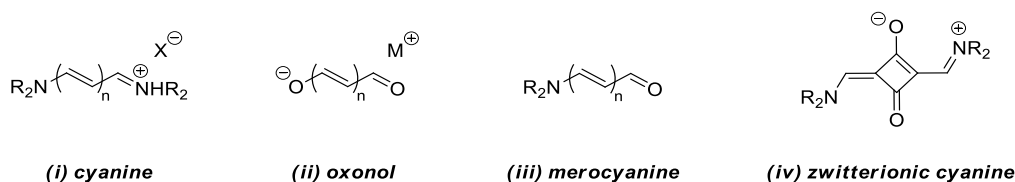


Figure 2. Four families of polymethine dyes according to their charge introduced by Behera et al.[2]

2.2 Electronic classification of polymethine dyes

To tackle this drawback, a first alternative classification based on the electronic structure has emerged which provides a more accurate description and rationalization of their spectroscopic properties.[28-30] According to this model, highlighted in Figure 3, symmetrical and unsymmetrical polymethines can be stabilized under two different forms depending on their charge (de)localization. The *dipole* structure corresponds to a polarized form where one end of the polymethine possesses a higher electronic density than the other extremity. The dipole is characterized by a non-zero BLA and a particularly broad and solvatochromic linear absorption spectrum. In the case of an unsymmetrical chemical structure, this form can be stabilized under either neutral or zwitterionic configurations. Conversely, when the charge is perfectly delocalized through the polymethine bridge, the *cyanine* electronic structure is reached: the BLA vanishes and the linear absorption spectrum displays a typical intense, narrow and not solvatochromic transition. This classification allows explaining that a given structure can exhibit various electronic configurations hence spectroscopic properties under the influence of various external stimuli or chemical modifications, as illustrated by the upcoming selected examples.

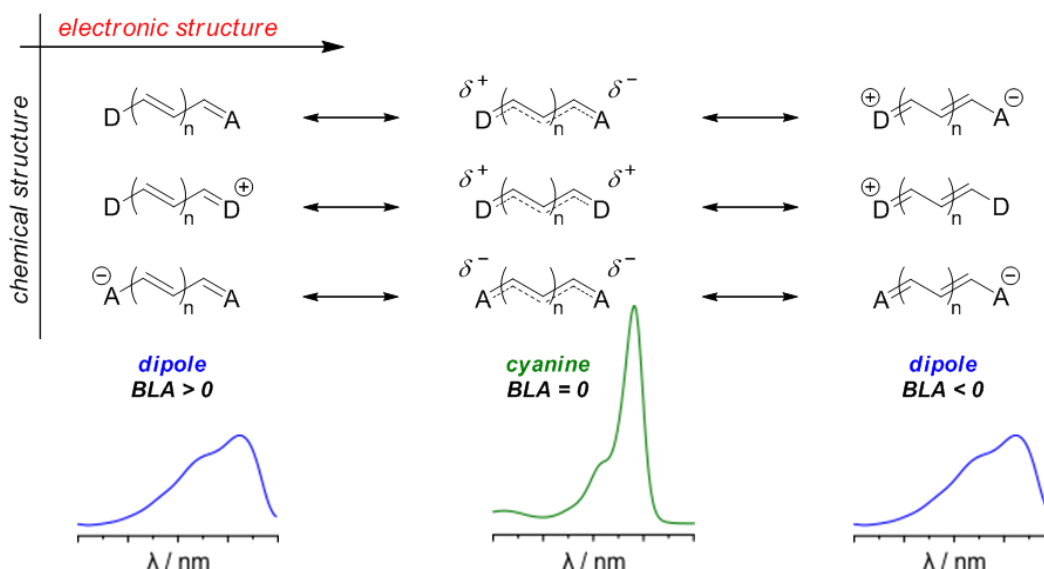


Figure 3. Resonance structures and absorption profiles of symmetrical and unsymmetrical polymethines.

3. TRANSITIONS BETWEEN DIPOLE AND CYANINE ELECTRONIC CONFIGURATIONS

The transition between cyanine and dipole forms has been punctually reported and appears to be sensitive and generally unexpected. This phenomenon occurs upon chemical modification or under the influence of exogenous parameters such as pH or polarity. The modulation of the electronic structure is always characterized by easily observable changes of the optical properties.

3.1 Transition induced by chemical modification

The pioneering Brooker experiment consists in increasing the length of a symmetrical cyanine dyes: a strong bathochromic shift of the cyanine transition is observed upon elongation, by about 100 nm per vinyl moieties, until a critical limit is reached where a broadening of the absorption band is observed.[31] This behavior was eventually explained by Tolbert in a benchmark studies,[21] as a consequence of loss of the cyanine character due to symmetry breaking for longer chains (Peierls-type distortions). This hypothesis was further confirmed by theoretical calculations, which demonstrated that the elongated polymethine dyes adopt a dipolar electronic configuration.[32-34]

In 1997, Würthner and co-workers studied the variation of the electro-donating strength of the donor extremity in the case of a series of unsymmetrical polymethines (Figure 4).[35] The dyes that incorporate weak donor groups were shown to display broad dipole-type absorption whereas increasing the strength of the donor resulted in a red shift of the absorption band featuring ultimately the sharp solitonic profile characteristic of a cyanine electronic structure. This transition from dipole-to-cyanine was explained on the basis of the increased delocalization along the π -conjugated skeleton resulting in the equalization of the electronic density at both extremities and a vanishing of the BLA. Consequently an unsymmetrical polymethine structure can present a symmetrical cyanine-type electronic configuration.

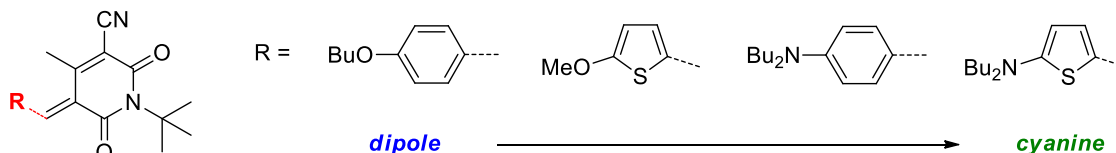


Figure 4. Unsymmetrical polymethines incorporating various donors reported by Würthner et al.[35]

3.2 Transition induced by solvent polarity

This dipole-to-cyanine transition has also been described in the case of a single unsymmetrical polymethine (Figure 5) under the influence of the solvent.[36] When increasing the solvent polarity, a strong bathochromic and hyperchromic shift is observed which can be rationalized as followed. In less polar solvent, the transition is broad and typical of a dipolar structure. In a more polar solvent the absorption becomes sharper and presents the characteristic profile of a cyanine electronic structure. Finally, as the solvent polarity still increases (case of CH_3CN), the absorption band becomes less intense and broader. This last behavior corresponds to a charge separation in highly polar solvent and illustrates the transition from a cyanine to a zwitterionic dipole (Figure 3). This unique example describes a double transition from a dipole-to-cyanine and then from a cyanine-to-(charge separated) dipole. Similarly, multiple studies about unsymmetrical polymethines close to the cyanine limit underline the possibility to stabilize these compounds under their cyanine structure by influence of solvent polarity.[18, 29, 37-40]

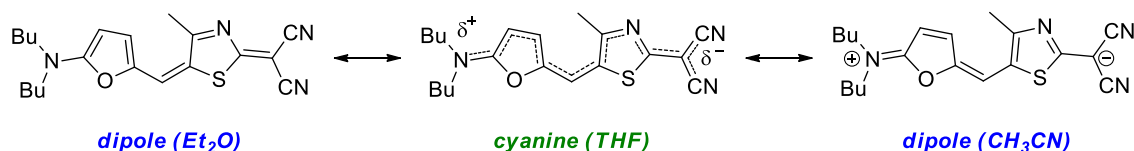


Figure 5. Various electronic configuration reached by an unsymmetrical polymethine under the influence of the solvent polarity.[36]

The influence of the solvent polarity has also been explored in the case of symmetrical polymethines. A representative example is described by Lepkowicz in 2004 using a dye containing 11 conjugated carbon atoms (Figure 6).[41] In low polarity solvent this polymethine exhibits a characteristic cyanine absorption band but as the polarity increases a broad band appears at lower energy. The authors rationalized this behavior by an increased contribution in more polar solvent of the asymmetric electronic configuration. Using the present classification, this behavior illustrates a cyanine-to-dipole transition induced by the solvent.

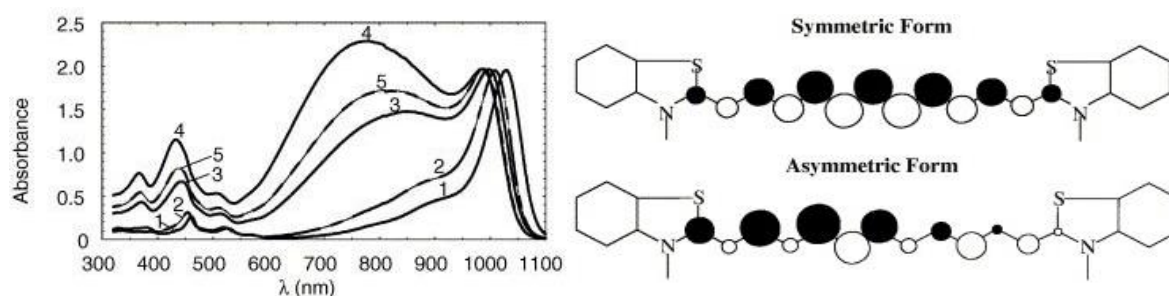


Figure 6. Absorption spectra of undecamethine reported by Lepkowicz et al. (left) in *o*-dichlorobenzene (1), dichloromethane (2), ethanol (3), acetonitrile (4) and methanol (5). Determined symmetric and asymmetric forms (right). Figure adapted from ref. [41].

3.3 Transition induced by protonation

The protonation is also an elegant way to promote dipole-to-cyanine transition. In 2000, Cooper and co-workers reported the pH-dependent optical properties of an unsymmetrical pentamethine with one non-alkylated indole extremity (Figure 7).[42] In basic conditions, this dye displays a broad absorption spectrum (dipole type) whereas in acidic medium, the transition is dramatically red-shifted and becomes sharper and more intense (cyanine type). This cyanine electronic structure is simply reached because of the protonation of the free-base indole extremity. A positive charge is then generated and is perfectly delocalized along the conjugated skeleton. Several analogous polymethines have been reported more recently: these pH probes took advantage of a non-fluorescent dipolar form whereas the protonated cyanine form exhibited an intense red fluorescence.[43-46]

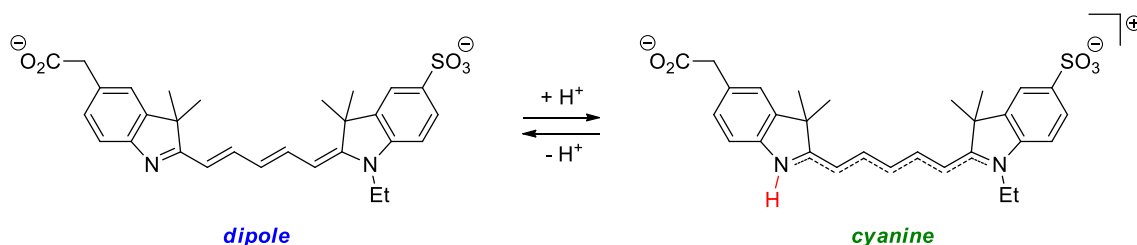


Figure 7. pH-sensitive pentamethine dye developed by Cooper et al.[42]

3.4 Transition induced by ion-pairing

Finally, our group demonstrated that the optical properties of symmetrical cationic heptamethine can be strongly influenced by the nature of the counter-anion.[24, 47] A strong ion-pair is formed with small counter-anions in a non-dissociative solvent or at the solid state resulting in a localization of the cationic charge at one extremity of heptamethine **DD[Br]** and consequently a polarization of the conjugated backbone. Consequently, this loss of symmetry favours a dipole electronic structure, with a non-zero BLA in the X-ray structure and a broad absorption profile in apolar solvent (Figure 8). Increasing the dissociative character of the solvent or the bulkiness of the counter-anion prevents the ion-pairing phenomena which restores the cyanine electronic structure. This study showed that ion-pairing phenomena can also trigger the cyanine-to-dipole transition.

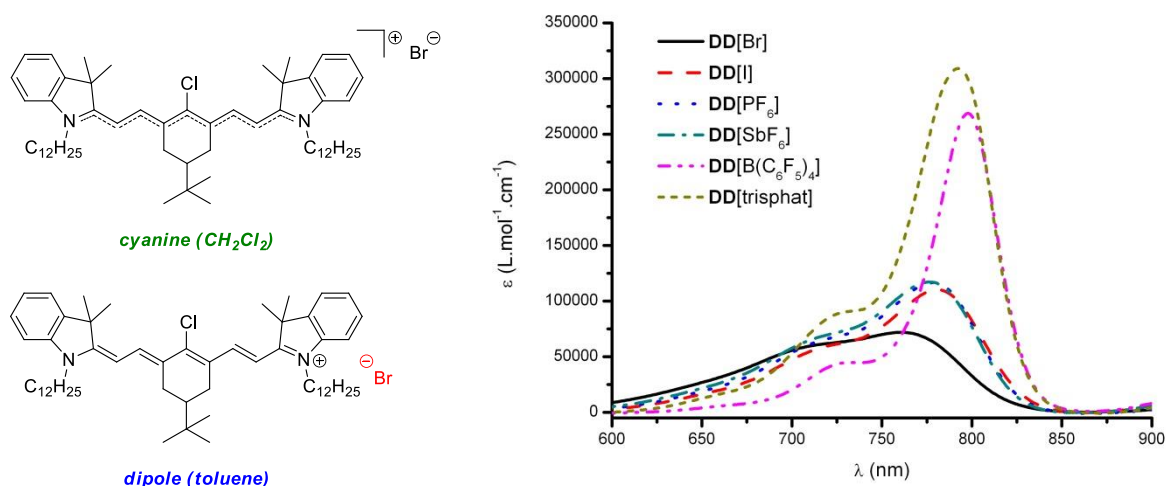


Figure 8. Influence of ion-pairing effect on the absorption spectra of heptamethine dye DD[Br] in toluene.[47]

In conclusion, all these examples illustrate the electronic versatility of symmetrical or unsymmetrical polymethine dyes, under the influence of chemical modification or exogenous parameters and highlighted the interest of the electronic classification for the interpretation and rationalization of the observed optical modifications. However it appears that the dipole and cyanine models are not always sufficient to explain all the observed phenomena and that this first classification remains incomplete.

4. THE BIS-DIPOLE ELECTRONIC CONFIGURATION: A PARTICULAR CASE OF CHARGE LOCALIZATION

4.1 Preliminary study: the amino-heptamethine

In particular the modification of the central position of polymethine dyes has raised questions during the last decade. Peng and co-workers reported in 2005 the optical properties of a symmetrical heptamethine featuring a secondary amine at the central position.[22] The replacement of the usual central chlorine atom by an amine led to a dramatic blue shift of

the electronic absorption as illustrated in Figure 9 (using analogous **DD-Cl** and **DD-NHPr**). In the case of **DD-NHPr**, both absorption and emission are broad with a larger Stokes shift. Immediately this class of molecules has become very popular for bio-imaging applications due to their high quantum yield and larger Stokes shift.[48-51] However, the influence of the central functionalization on optical properties remains not fully understood: although the cyanine character is clearly lost, no clear explanation was proposed, the authors putting forward the hypothesis of a charge transfer at the excited state. Therefore we have undertaken a systematic study of the role of the central substitution of heptamethines in order to explain this loss of cyanine character.[52]

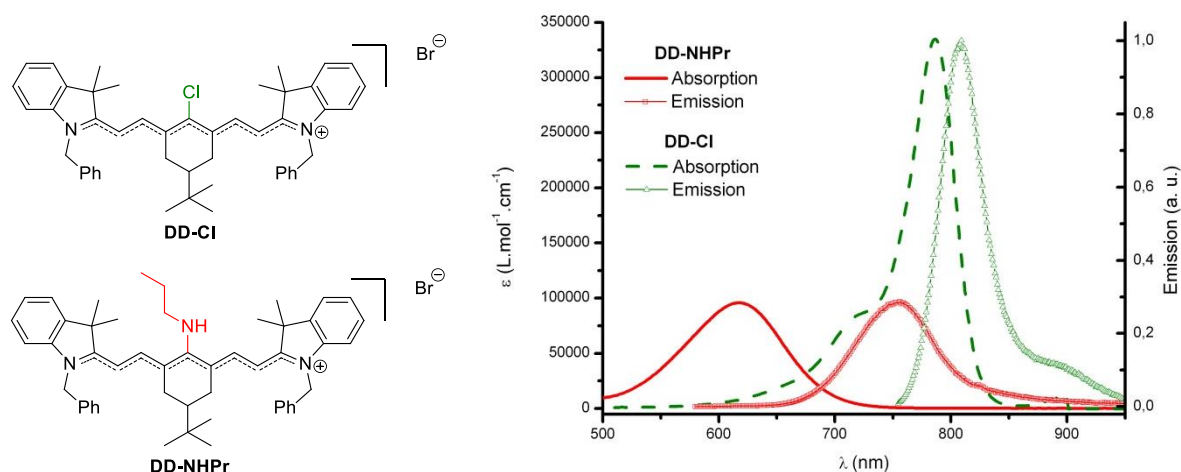


Figure 9. Structure and optical properties in methanol of heptamethines **DD-Cl** and **DD-NHPr**.

4.2 Electronic absorption of polymethines substituted at the central position

A series of 17 heptamethine dyes (Figure 10) incorporating various central functionalization was thus prepared by nucleophilic substitution.[30, 53-56] These compounds incorporate central functions such as halogens (**DD-Cl**, **DD-Br**), amines (**DD-NEt₂**, **DD-Pip**, **DD-NHPr**), imines (**DD=NPr**, **DD=NPh**), ketone (**DD=O**), ester (**DD-OAc**), (thio)phenol (**DD-OPh**, **DD-SPh**)... Such substituents allow screening the influence of different electro-donating strength, particularly in the case of the aniline series (**DD-NO₂**, **DD-AnCF₃**, **DD-AnH**, **DD-AnOMe**).

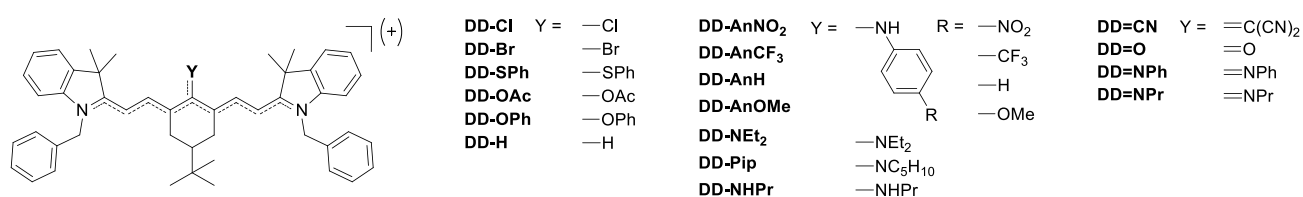


Figure 10. Series of heptamethines substituted on the central position.

The absorption spectra of the heptamethine were recorded in dichloromethane solution and are presented on Figure 11 (left). A first observation is that the central functionalization has a strong influence on the transition wavelengths and allows tuning the absorption from the UV-visible region towards the near-infrared region (350-850 nm). Two behaviors are highlighted: some heptamethines present characteristic cyanine transition localized around 800 nm (**DD-SPh**, **DD-Br**, **DD-Cl**, **DD-OAc**, **DD-H**, **DD-OPh**) whereas the other functionalized heptamethines exhibit broad and less intense absorption band, blue-shifted up to 350 nm. Considering the localization of the band and the nature of the central substituent, it appears that the more electro-donating the latter is, the more blue-shifted the absorption is.

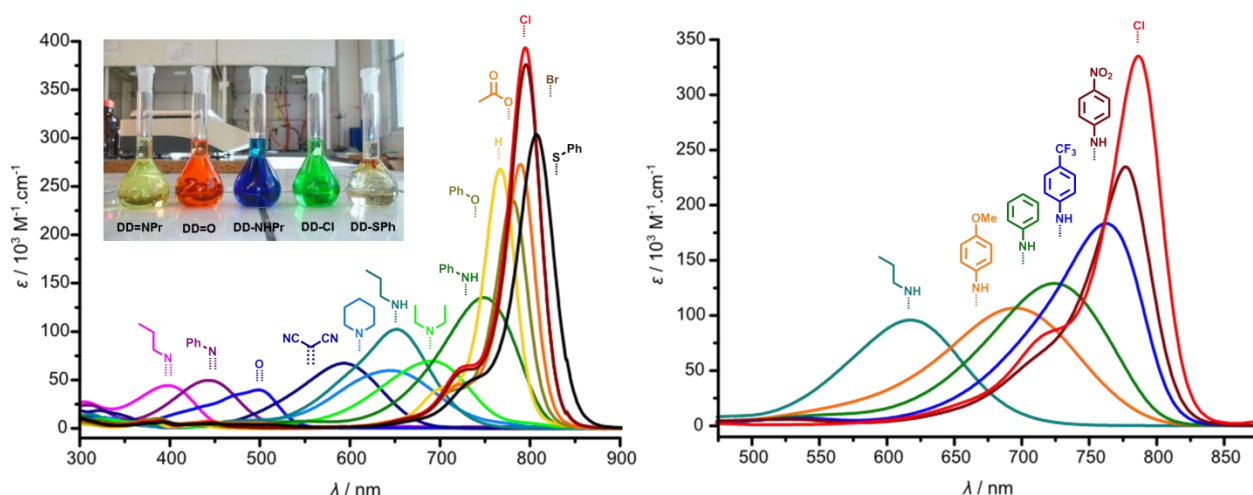


Figure 11. Electronic absorption spectra of heptamethines in dichloromethane (left) and in methanol (right). The inset is a picture of selected compounds in dichloromethane solutions (ca. 0.04 mg.L⁻¹).

In order to rationalize these observations, we proposed a model (Figure 12), where the electro-donating central substituent contributes in stabilizing the cationic charge of the heptamethine at the central position. The progressive localization of the charge is responsible for the shift of the electronic structure away from the cyanine configuration towards a new electronic configuration that we defined as *bis-dipole*. In the extreme case of heptamethines with a central double bond (**DD=CN**, **DD=O**, **DD=NPh**, **DD=NPr**), the substituent can be depicted in a limit form, in which an anionic central substituent (*i.e.* with the highest electro-donating effect) faces the centered cationic charge, leading to the most blue-shifted absorption bands.

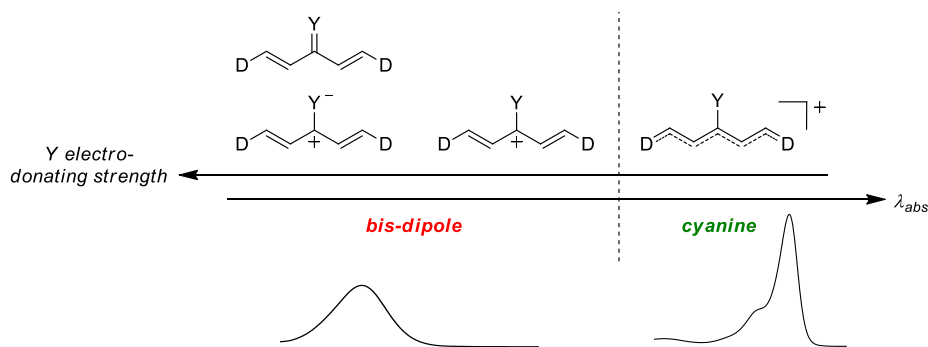


Figure 12. Model describing the electronic structure and absorption shape of a polymethine as the cationic charge is progressively localized towards the central position.

To test this hypothesis, we synthesized a series of aniline substituted dyes **DD-AnX** (X = NO₂, CF₃, H, OMe) whose absorption is located at the frontier between the two electronic behaviours. Consequently, minor alterations of the electron-donating ability of the aniline substituent are sufficient to lead the chromophore to adopt either of these two configurations. The absorption spectra of the aniline series (Figure 11, right) show that the decrease of the electron density on the aniline moieties (NO₂ > CF₃ > H > OMe) lead to a hyperchromic and bathochromic shift of the transition, bridging the gap between the bis-dipole and the cyanine forms. The existence of the bis-dipole electronic configuration and the bis-dipole-to-cyanine transition were also unambiguously confirmed by the linear correlations between the absorption energy and ¹³C NMR, BLA or local charge (the last two parameters being obtained by DFT calculations).[52] This correlation between optical observation and parameters representative of the electronic delocalisation further validates the choice of the electronic rather than structural classification of polymethines.

5. CONCLUSION

In conclusion, this article demonstrated that polymethine dyes can be best described according to a classification using not two but three electronic configurations (Figure 13): (i) the symmetrical cyanine with a perfectly delocalized charge, (ii) the unsymmetrical dipole with a charge localized at one extremity and (iii) the bis-dipole with a charge localized at the central position. This classification allows an easier rationalization of the spectroscopy of this whole chromophore family: for a given structure and environment (solvent, pH, counter-ion...) the electronic configuration of the dye can shift from one to the other limit electronic configuration, or more realistically, consists in a combination of these three forms with variable ponderations. In a more general perspective, we believe that these three-forms model can not only be helpful to improve one's understanding of the versatile optical properties of polymethines but can also constitute a useful toolbox to develop new responsive-probes or switches.

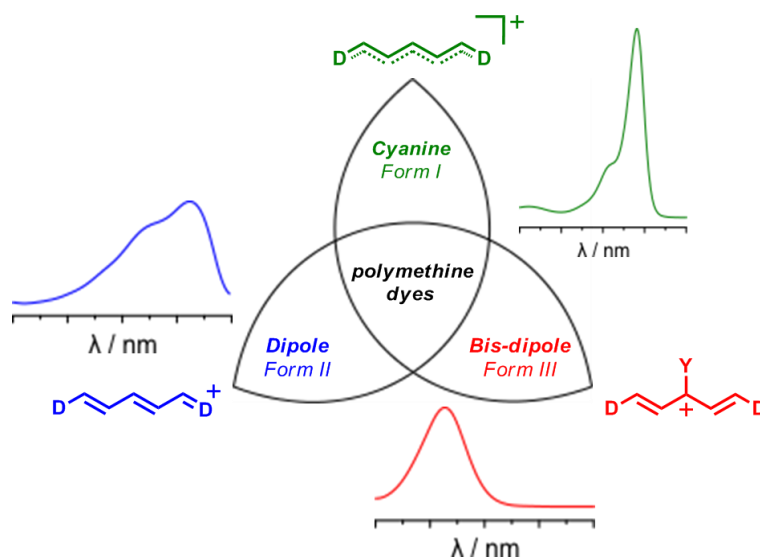


Figure 13. Complete electronic classification of polymethine dyes.

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