

Transient absorption of symmetrical carbocyanines

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Abstract

Transient absorption in several symmetrical cyanine and carbocyanine dyes is measured by time-resolved spectroscopy with subpicosecond white-light continuum in a wide spectral range (0.35–1 μm). The results are compared with data available in the literature on ultrashort and long-lived transients. The linear shift law observed here for the S_1S_n absorption bands in the wavelength scale allows one to predict the main induced absorption bands for members of several carbocyanine families (vinylogous series) which have not yet been studied. In the case of the shortest methine chains (cyanines and monocarbocyanines) a few transient absorption bands are assigned to the formation of photoisomers. The absolute values of the excited-state or photoisomer cross sections of polymethine carbocyanines are evaluated by global spectral analysis, from the measured differential optical density spectra. Several cases of large values (higher than 10) of the absorption cross section ratio (excited/ground state) are found at new wavelengths, which allows applications of photo-induced absorption to photonics and laser technologies over a broad spectral range. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Carbocyanine dyes have been extensively studied for more than a century, mainly as photosensitizers in photography [1]. In the late 60's the use of carbocyanines as saturable absorbers, mode-lockers and gain molecules in laser technology added a new interest to their study. The carbocyanine dye chemistry was reviewed [2,3]. More recently carbocyanine dyes received attention as potent sensitizers for photodynamic therapy [4] (and Refs. therein), as probes of micelle structure [5], as initiators in photopolymerization [6], or else as IR absorbing films for optical-disk recording [7]. Photoisomer and triplet-triplet transient absorption were studied under strong flashlamps or laser excitation mainly with relatively long pulses: nanoseconds to microseconds or longer. Transient states or species were observed in solution and assigned to the formation of photoisomers which revert to the more stable form in micro- or milliseconds at room temperature. The formation of triplet states by intersystem crossing from the lowest excited singlet state was found to be small or negligible as a rule in this type of compounds. In these works the S_1S_n absorption (from the lowest-excited singlet state S_1 to a higher singlet S_n) was not studied. Rather the photoisomerization reaction and its back process to the

initial stable form was discussed as a type of thermally activated process. It is still the object of increasing interest in relation to the study of ultrafast vibrational relaxation and excited state chemical reactions in solution by femtosecond spectroscopy in cyanine compounds [8–10].

With powerful and tunable subpicosecond laser pulses significant population of the lowest excited singlet state S_1 can now be obtained easily, even for the short S_1 lifetimes (a few picoseconds) sometimes met in cyanine dyes. The absorption and emission transitions from the excited state S_1 can thus be studied. Following the excitation to any excited S_n state, a variety of reversible transient intermediate states or species can be formed during the relaxation process to S_0 , such as hot vibrational states, other singlet or charge transfer states, excimers, intermediate photoisomer forms in their excited or ground states, etc. Moreover, because of the large vibronic transition band widths in solution, the electronic spectra often overlap. This makes the S_1 absorption spectroscopy not straightforward. The pioneering works using the ultrafast pump-probe technique at one wavelength (that of the available lasers) led to discrepancies in the measurement of relaxation times of the excited states [11]. An easier approach is now possible thanks to time-resolved spectroscopy using near-UV to near-IR ultrafast continuum technique. It allows one to detect the absorption regions which have different time behavior before trying to analyze each of

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the dynamic processes at the best possible wavelengths. A literature survey shows that the main transient S_1S_n absorption bands are still not known for most available carbocyanines.

In this work we compare the information reported on transient absorption of symmetrical carbocyanines, excluding the triplet absorption (for a review see Ref. [12]), and we bring new experimental results to complete data for several members of eight families (i.e., vinylogous series) of polymethine carbocyanines. The main purpose is to see whether a systematic state correlation for the strong S_1S_n transitions can be obtained as a function of the polymethine chain length, as is the case for the ground state absorption wavelengths for each family. If so, this could provide a way to predict the S_1S_n absorption wavelength for compounds not yet synthesized. This is the only possible predictive approach since reliable theoretical calculations of the energy and oscillator strength of upper singlet states, at 3 or 4 eV above the ground state, of large molecules (more than 50 atoms, including a few heteroatoms) appear to be too complex in the state of the art.

There are practical interests in knowing about the strong transitions from the excited singlet states for ultrafast laser and photonics technologies. In particular, the S_1S_n absorption is expected to be more rapidly photo-induced than the chemical photochromism (e.g., in spiro compounds) which is often slow to appear and to revert (the chemical reaction may involve a triplet state). When the excited singlet state absorption is more probable than the ground-state absorption at a given wavelength, the solution crossed by a laser beam will present a photo-induced absorption, varying nonlinearly with the incident intensity. Materials with fast and strong transient absorption are sought for optical limiting. Such compounds, sometimes called 'reverse saturable absorbers', can also be used for ultrafast laser pulse energy stabilization and beam profile smoothing [13]. Inversely, transient photo-induced absorption is a drawback for saturable absorbers or gain dyes and needs to be known or if possible predicted for chemical engineering purposes.

2. The polymethine carbocyanines

2.1. Structure

The main chromophore of the carbocyanines is the polymethine resonant chain, which by itself constitutes the strongly absorbing streptocyanine cationic dye family, sketched in Fig. 1, where R is an alkyl group. The odd number of 'methine' group ($-C=$) in the chain can be up to 13 or more. Streptocyanines are not chemically very stable and can suffer irreversible bleaching in solutions. Polymethine cyanine dyes are more stable because of the presence of heterocyclic groups at both ends of the chain such as the 8 end-group types shown in Fig. 1. Several distinct isomers can be formed by rotation around the bonds of the polymethine chain. All formulas given here (see inserts in Figs. 2–12 and 15) are drawn in the 'all-trans' isomer conformation which are gen-

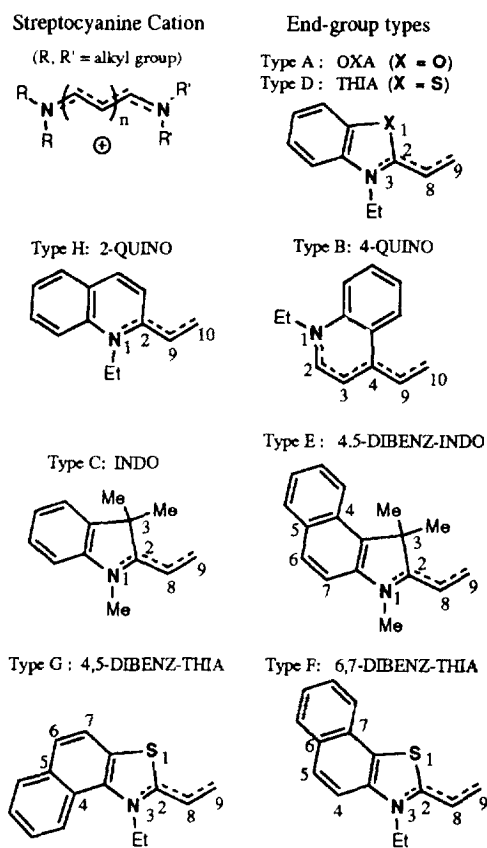


Fig. 1. Formula of the streptocyanines and of 8 end-group types in cyanines and carbocyanines.

erally thought to be more stable at room temperature. Isomers can be formed by photoexcitation and remain stable at low temperature [14,15]. These isomers present in general slightly shifted absorption spectra and weaker intensity bands [16,17]. They can be sometimes separated but only when adsorbed on a substrate [16]. The number of isomers formed in solution, as well as their formation and back reaction rates, either in the excited or the ground state, depend on the existence and height of a barrier in the potential curves. Measurements of barrier heights were done in a few cases [18,19]. Care must be taken to avoid ambiguity in the nomenclature of the possible multi-cis isomers [20]. A few cyanines and carbocyanines present good enough chemical stability in solution for practical use. For longer polymethine chains, stability is improved with 'rigidified' structures in which the possible rotation around the chain bonds is blocked by appropriate substituents [21]. Several such compounds, e.g., tri-carbocyanine, are known as 'IR dye' series [22] and a few are commercially available.

2.2. Nomenclature

According to the number n of additional groups ($-C=$ in the chain, the molecule is called a cyanine (for $n=0$), a carbocyanine (for $n=1$) and a di- to heptacarbocyanine (for $n=1$ to 7). We shall consider here only the 'symmetri-

Table 1

Double entry table of the ground-state absorption wavelength (nm) of symmetrical carbocyanines

End-group type	N = 4 Cyanine n = 0	6 Carbocyan. n = 1	8 Dicarbo. n = 2	10 Tricarbo. n = 3	12 Tetracarbo. n = 4	14 Pentacarbo. n = 5
A: oxa	<u>OCY</u> 375	<u>DOC</u> 483 D9C 489 TDO 502	<u>DOD</u> 580	<u>DOT</u> 682 <u>DMO</u> ^M 681	<u>DOR</u>	<u>DOP</u>
B: 4-quinol	–	–	<u>4CY</u> 590 (Cyanine) n = 0	<u>CRY</u> 707 (Carbo) n = 1	<u>DDC</u> 814 DC4 798 (Dicarbo) n = 2	<u>DT4</u> 928 (Tricarbo) n = 3
C: indo	<u>HCY</u> ^M 433	<u>HIC</u> ^M 545 <u>IC2</u> 549 ^h <u>HIF</u> ^M 558 ^e <u>BIF</u> ^S 559 ^s	<u>HID</u> ^M 638 <u>TID</u> 671 ^p TIF 685 ^p	<u>HIT</u> ^M 739 <u>HII</u> ^M 741 <u>III</u> 743 IRI to IRL ^d	<u>HIQ</u> ^M 848 ⁸	<u>HIP</u> ^M 956 ⁸
D: thia	<u>TCY</u> 423	<u>DTC</u> 557 <u>MTC</u> ^M 555 ⁱ DME ^M 540 ^c TMT ^M 536 ^c DMI 543 ^j TTC 547 ^k ETC 598 ^o	<u>DTD</u> 652 NTD 653	<u>DTT</u> 759 DNC 765 ^c IRA 788 ^e	<u>DTQ</u> 870 ^a DAT	<u>DPC</u> 1000 ^f <u>DNT</u> 1010 ^a <u>DXC</u> 1130 ^p <u>DHC</u> 1250 ^p
E: 4,5-dibenzindo	<u>BCY</u>	<u>HBC</u> 586	<u>HBD</u> 676	<u>HBT</u> 778 IRB 750 <u>IRC</u> 782 ^b	<u>HBQ</u>	<u>HDC</u> 1000 ^a
F: 6,7-dibenzthia	<u>ZCY</u>	<u>B6C</u> 593 DMC 572 TDC 578	<u>DB6</u> 684 CB6 680	<u>D6C</u> 792 M6C ^x (IRE) ^r 811 ^b	<u>D6Q</u>	<u>D6P</u> DND 1050 ^a
G: 4,5-dibenzthia	<u>5CY</u> 452	<u>B4C</u> 595 TDB ^t 577 DDB ^z 571	<u>DB4</u> 698	<u>D4C</u> 795 IRD 845 ^e	<u>D4Q</u>	<u>D4P</u>
H: 2-quinol	<u>PIC</u> 523 ⁿ (ECY 516) ^q (MCY 564) ^q	<u>PIN</u> 608 <u>DCC</u> 606 ^v	<u>DDI</u> 707 MDI ^M 707 ^y DC2 ^w 697 BDI ^v 690	<u>DT2</u> 817 <u>DTP</u> 824 ⁿ MT2 817 ^y	<u>DQ2</u> DAQ 928 ^d	<u>D2P</u>

The dyes are organized by end-group type A to H (first column) and by the number of bonds *N* between the two resonant nitrogen atoms (first row). The end-group rows are ordered (from A to H) by increasing absorption (averaged) wavelengths (given in nm). The underlined dyes have unsubstituted polymethine chain. Most dyes have ethyl-substituted nitrogen atoms.

^hMethyl substituted, indicates a methyl group on the two nitrogen atoms: ^adichloroethane; ^b[24]; ^cethanol; [25]; ^dethylene carbonate + propylene carbonate (3:1); [26]; ^eethanol, this work; ^fdichloroethane; [27]; ^gethanol; [28]; ^h[29] (1,1'-diethyl); ⁱ[30]; ^j(9-methyl); ^kmethanol (9-ethyl); ^lethanol [30], (3,3',9-triethyl); ^mpropylene carbonate + ethylene glycol; [31]; ⁿpropanol; (10-fluoro); [32]; ^oethanol [33], (bridged cycles); ^p(5,6-dibenzthia); ^qbenzene, (1-butyl on nitrogens); PF6 [34]; ^r(9-ethyl), Br⁻; ^s(11-chloro); ^tCl⁻; [35]; ^u(11-chloro), Br⁻; ^vethanol, (11-methyl), this work; ^w11-bromo; [36]; ^x(9-methyl); [37]; ^yethanol; [3]; ^zmethylene chloride; [38]; ¹[39]; ²IRI (775 nm); IRJ (768 nm); IRK (780 nm); IRL (792 nm) [40]; ³Benzeno, PF6 [41]; ⁴[42]; ⁵8,10-ethylene- [42].

The reference numbers are given in square brackets.

Codes in italics correspond to hypothetical dyes. (For code meaning see Table 7 in Section 7 (Appendix).)

Unless otherwise specified, the solvent is methanol and the wavelength values come from NKS [23].

cal' compounds in which both end-groups are identical. They absorb more strongly than the asymmetrical carbocyanines.

We have studied the 8 types of end-groups shown in Fig. 1, namely, benzoxazolyl (type A), 4-quinolyl (B), indolyl (C), benzothiazolyl (D), 4,5-dibenzindolyl (E), 6,7-dibenzthiazole (F), 4,5-dibenzthiazole (G) and 2-quinolyl (H). Following a common use we shall abbreviate these names and will refer to the corresponding 8 families respectively as: oxa-, 4-quinol-, indo-, thia-, 4,5-dibenzindo-, 6,7-dibenzthia-, 4,5-dibenzthia- and 2-quinol-, the prefix quinolyl

(or quinol-) being often wholly omitted in the common names of the symmetrical carbocyanines. In this paper we shall label these families from A to H as shown in Fig. 1 and Table 1 which comprise for each family about 5 to 15 members differing from each other by the number of vinyl groups (vinylologous series), and/or by substitution along the polymethine chain. For convenience, each dye will be given an arbitrary code of three alphanumeric characters. The codes, common names and synonyms of the 83 dyes mentioned here are listed in Table 7.

3. Ground-state absorption of carbocyanines

Absorption spectra of carbocyanine compounds in solution are characterized by a specific, often single, strong and relatively narrow band, 600 to 1500 cm^{-1} FWHM, lying between 0.35 and 1.1 μm , and due to a $S_0 \rightarrow S_1$ vibronic transition from the ground singlet state to the first excited singlet state. One secondary maximum occurs only for the 2-quino- family, with a $\sim 1300 \text{ cm}^{-1}$ vibrational interval. The position of the first band, expressed in nanometers, was shown [44] to be related, for 4 families and $n=0$ to 3, to the length of the polymethine chain by the linear law expected from the simple metallic electron theory [48]. The short methine chain cyanines ($n=0$ and 1) are characterized by a broadening of the first band ($\sim 1500 \text{ cm}^{-1}$) with respect to the di- and tricarbocyanines ($n=2$ and 3) with unsubstituted chain. This broadening is probably related to the non planar conformation of the quino-cyanines 2CY and 4CY which are found by X-ray crystallography to be twisted by 40 to 60° (angle between the planes of the heterocyclic rings) [2]. The thia-cyanine TCY, where the sterical hindrance is smaller, has an angle of less than 15°, similar to the case of the thiocarbocyanine and thiadibocarbocyanine DTC and DTD (the formula of the dyes are given in Table 7).

The wavelengths of the band maxima of 83 known symmetrical cyanine and carbocyanine dyes are given in the double entry Table 1 as a function of both the end-group nature and the 'resonance path length' (total number of bonds (N) between the two resonant nitrogen atoms). The end-group types are ordered by increasing mean bathochromic shift of the absorption in the parent unsubstituted chain compounds of each family. The 4-quino family is a particular case because the 'resonance path length' (N) between the two nitrogen atoms includes 6 bonds within the cyclic end-groups instead of only 2 as for the other cyanine end-groups, so the chromophore chain of the 4-quinones comprises 4 more bonds (see formula of the dyes CRY, DDC and DT4 in the inserts in Figs. 5 and 11 and Fig. 12). Dyes in the same cell in Table 1 have their absorption maxima in a spectral interval of less than about 30 nm as they differ only by the substituents on the polymethine chain or on the end-groups, or else, in a few cases, by the counter ion. The effect of the latter (such as I^- , ClO_4^- , ...) on the photophysical properties of the cation is usually negligible in polar solvents [4]. In addition Table 1 is completed by 11 hypothetical dyes (not yet synthesized to our knowledge) the absorption band wavelengths of which will be predicted by extrapolation in Table 3 for both S_0S_n and S_1S_n transitions.

In all cases the long-wavelength absorption band is the strongest of the whole UV to IR spectrum. It mainly arises, in the Hückel Molecular Orbital model, from electronic excitation from the highest occupied (HO) to the lowest unoccupied (LU) molecular orbital, and the transition moment is along the longitudinal molecular axis. The reduced vibrational structure shows that the excited-state potential curve is not shifted much along the nuclear coordinate axis. The fol-

lowing two higher-energy electronic transitions are degenerate in the simple HMO picture, but split into two separate transitions when electron interaction is taken into account (see Ref. [3], Chap. XII). They are both allowed but have much lower transition probabilities than the first band.

The excited state of polymethine cyanines presents in the 'perp' form (90° rotation around one of the polymethine bonds) a charge transfer character which may correspond to a minimum in the S_1 potential energy surface [49]. This could play an important role in the non radiative deactivation of the excited state and the photoisomerization reaction. The existence of such a well was assumed, by a discussed [49] but fruitful analogy with polyenes, to explain the complex relaxation behavior of the photoexcited monocarbocyanine DOD (DODCI) [50].

4. Experimental and analysis methods

4.1. Laser system

Sub-picosecond pulses are obtained with an alternative short pulse generation technique [51], which leads to an unconventional ultrafast laser type already described in detail [52]. It uses presently a seeded Q-switch, 6 ns, pump Nd:YAG laser at 532 and 355 nm, and an efficient photonic system for pulse shortening from 6 ns down to subpicosecond in cascaded short-cell dye oscillators combined with saturable dye amplifiers and extracavity absorbers. Two beams of jitter-free subpicosecond pulses, independently tunable, can be obtained by selection, with interference filters and tunable Fabry Perot etalons, of the continuum generated by focusing 500 fs, 200 μJ laser pulses in a water cell. Additional dye amplifiers increase the pulse energies in both beams up to several hundreds of microjoules. The whole short pulse generation system is pumped by the same nanosecond Nd:YAG laser.

4.2. Subpicosecond spectrophotometer

The transient absorption and gain spectra were measured by the pump-probe double-beam technique with subpicosecond 'white' light continuum, described previously [53,54]. Typically, a first tunable beam of 10 to 100 μJ , 500 fs pulses, linearly polarized at the magic angle (54.7°) with respect to the probe beam, is focused on an $\sim 1 \text{ mm}^2$ spot to pump the sample 1 mm cell (20 ml recirculating solution). A second beam at 600 or 700 nm is focused in a 1-cm water cell to generate the probe continuum beam which is split into two sub-beams, one for probing the sample cell at an angle of about 10° with the pump beam, and one for reference. The sample and reference probe beams collected after the cells by optical fibers are sent onto the slit of a small polychromator. The spectral width of the slit is about 3 nm. The two spectra are recorded on two cooled 512-photodiode arrays. When necessary, corrections for the chirp of the continuum during

propagation in the water cell and the optical components were calculated from measured values by two-photon absorption in 1 mm of liquid 1-chloro-naphthalene in the blue region and extrapolation to longer wavelengths.

4.3. Absolute cross section values and excited state populations

The medium is described by a generalized two level (ground (S_0) and lowest-excited (S_1) singlet electronic states) system, each level being characterized by an effective extinction coefficient taking into account the actual relaxed vibrational population distribution and the associated Frank-Condon factors. The generalized 'optical density' (positive or negative) of the sample at time t after the pumping pulse reads

$$D(\lambda, t) = (\varepsilon_u - \varepsilon_c)C_1(t) + \varepsilon_a C_0(t) L \quad (1)$$

where the (positive) molar 'extinction' coefficients are denoted $\varepsilon_a(\lambda)$ for the $S_0 \rightarrow S_1$ absorption, $\varepsilon_u(\lambda)$ for the absorption from the S_1 state to the upper states S_n , and $\varepsilon_c(\lambda)$ for the stimulated emission from S_1 to S_0 ; $C_0(t)$ and $C_1(t)$ are space-averaged molar concentrations; L is the path length in the medium.

Defining a molar gain coefficient $\varepsilon_g = (\varepsilon_u - \varepsilon_c)$, the variation of the sample absorbance $\Delta D(t) = D - D_0$ due to excitation is

$$\Delta D(t) = (\varepsilon_g - \varepsilon_a)C_1(t)L, \quad (2)$$

and the non-excited sample absorbance is $D_0 = \varepsilon_a CL$, C being the total molar concentration.

The spectrum of the molar decadic absorption/gain coefficient ε_g can be obtained from the experimental ΔD and D_0 spectra with

$$\varepsilon_g(\lambda, t) = \frac{1}{CL} \left(D_0(\lambda, t) + \frac{\Delta D(\lambda, t)}{q(t)} \right) \quad (3)$$

where $q(t) = C_1(t)/C$ is the unknown ratio of excited molecules at time t . The procedure aims at finding the parameter $q(t)$ on a microcomputer in order to visually suppress from the calculated ε_g spectrum the contribution of the vibrational structure of the S_0 state absorption, as detailed in Ref. [54].

We stress here the fact that vibrationally equilibrated levels should lead to a unique value of $\varepsilon_g(\lambda)$ at all times t if no more than two populations contribute to the transmission measured. In this work we shall generally assume that at delays of 1 to 5 ps, according to the dye and to the excess energy of the excitation, we have only two contributions (ε_u and ε_c) from the vibrationally equilibrated populations of the ground and the excited states. If there is a third population involved, for example if there is formation of a photoisomer, it is often possible to use the same relation at long delays (more than several S_1 lifetimes) when only the ground states of both isomers are populated.

Table 2

Typical experimental conditions for measurements of differential absorption spectra $\Delta D(\lambda)$ at room temperature with subpicosecond excitation pulse

Dye code	Concentration ($\times 10^{-5}$ M)	λ_{excit} (nm)	Probe delay (ps)	λ_{D} ^{max} (nm)	ΔD ^{max} (OD)
4CY	8	608	2	490–550	0.008
			10	630	0.015
CRY	3	710	3	543	0.07
D4C	7 ^a	740	1	564	0.35
D6C	5	708	3	575	0.12
DDC	5	710	3	566	0.11
DDI	4	710	3	535	0.12
DME	7	550	2	425	0.07
DNT	3 ^a	740	2	625	0.55
DOC	31	305	20	392	0.7
DOD	3	553	2	442	0.1
DOT	4	610	3	464	0.05
DT2	5.6	710	3	572	0.3
DT4	4.8 ^a	740	3	607	0.16
DTC	5.4	305	5	444	0.07
DTD	5	603	3	482	0.2
DTT	3	708	3	525	0.3
HID	2.6	604	1	497	0.1
HIT	6	736	3	523	0.18
IRA	5	712	3	565	0.3
IRB	5	712	3	558	0.47
IRC	5.7	712	3	548	0.32
IRD	6 ^a	740	3	577	0.25
IRK	4.6	740	2	520	0.22
PIC	15	305	30	552	0.008
PIN	4.4	610	1	470–500	0.05
			50	633	0.01
TCY	1.2	425	< 1	370–410	0.02
			100	452	0.04

Some typical $\Delta D(\lambda)$ values (in optical density units) are given in the last column.

The solvent is ethanol, or acetone when marked with a sign ^a.

4.4. Measurement parameters

Typical experimental conditions used in this work for the measurement of the differential optical density spectra $\Delta D(\lambda, t)$ are given in Table 2 for 26 dyes in solution at room temperature. The solvent is ethanol, unless specified. The subpicosecond excitation wavelength and pump-probe delays as well as a few of the main peaks of the differential absorption are given as directly read on the chirp corrected $\Delta D(\lambda, t)$ spectra. More complete results for ΔD bands and/or cross section values are given in Tables 3 and 4 for dye families A to H.

5. Excited state and photoisomer absorption in cyanine dyes

5.1. Excited state cross section spectra

Typical transient cross section spectra (ε_g) obtained after global treatment are presented in this section in Figs. 2–12,

Table 3.

Absorption data on symmetrical poly methine carbocyanines, at room temperature unless otherwise specified. Each of the 8 following tables contains dyes of the 8 end-group types as listed in Table 1. In the first column, *n* is the carbocyanine type (0 for cyanine, 1 to 5 for mono to penta-carbocyanine), *N* is the number of bonds between the two resonant nitrogen atoms; underlined codes indicate dyes with unsubstituted polymethine chain. The second column gives the wavelengths λ_i of the ground-state maximum absorption cross section, and the corresponding extinction coefficient ϵ_i in $\text{mM}^{-1} \text{cm}^{-1}$ units (i.e., $10^3 \times \text{M}^{-1} \text{cm}^{-1}$). The third column gives the transient absorption data of the lowest excited singlet state (λ_p, ϵ_p) from this work and from literature. The wavelengths of the shoulders are indicated by sh. The symbol DD in place of the ϵ_p value indicates that only the Differential Optical Density maximum is known at λ_{DD} . The wavelength λ_i indicates the region ($\pm 10 \text{ nm}$) of an isosbestic point (where $\sigma_s \sim \sigma_p$) observed in this work; τ_i (in nanoseconds) is the initial decay time of the main S_1S_0 absorption band estimated by fitting a monoexponential decay. The last column gives data, mainly from the literature, on the ground state photoisomer (λ_p, ϵ_p); τ_{PS} (in milliseconds) is the lifetime of the back reaction from the Photoisomer form to the Normal form. The sign @ indicates that the cross section value is measured at this wavelength, generally not a band maximum. Solvent abbreviations: act. acetone; bz. benzene; dcc. 1,2-dichloroethane; eg. ethylene glycol; coh. ethanol; dms. dimethylsulfoxide; gol. glycerol; hxx. hexanol; mcl. methylene chloride; moh. methanol; pc. propylene carbonate; prh. propanol. The reference numbers are given in square brackets.

<i>n</i> (<i>N</i>)	Code	S_0S_1 absorption		Isosbestic		S_1S_0 absorption		Photoisomer absorption		
		λ_i (nm)	ϵ_i ($\text{mM}^{-1} \text{cm}^{-1}$), Slv Ref.	λ_i (nm)	λ_p (nm)	ϵ_p ($\text{mM}^{-1} \text{cm}^{-1}$), Slv Ref.	τ_i (ns)	λ_p (nm)	ϵ_p ($\text{mM}^{-1} \text{cm}^{-1}$), Slv Ref.	τ_{PS} (ms)
A. OXA end-group type										
0 (4)	<i>OCY</i>	375	76, moh [NKS, personal communication (1996)]		392	DD, coh ^c	0.3	502	91, coh [20]	~250
1 (6)	<i>DOC</i>	482	140, moh [17]	435				490	141, moh ^a [17]	165 ^b
		482	157, moh ^a [17]					486	moh [55]	290
2 (8)	<i>D9C</i>	489	143, coh [56]							
	<i>TDO</i>	502	moh [23]	525			0.9	621	104, eg [58]	
	<i>DOD</i>	582	238, coh [33]					620	DD, moh [59]	1.3
		582	223, coh [25]					620	184, coh [61]	
								620	180, coh + h2o [63]	
								618	120, moh [58]	
3 (10)	<i>DOT</i>	685	193, coh ^c	565			2	@630	coh [50]	1.2
		700	dms [66]					@630	coh [18]	4
								@630	coh [19]	0.12
	<i>DMO</i>	682	198, coh [25]					730	220, dms [66]	
^a At 210 K; ^b extrapolated from Fig. 8 in [55]; ^c this work.										
B. 4-QUINO end-group type										
0 (18)	<i>4CY</i>	590	89, moh [NKS, personal communication (1996)]	525	500-540	18, coh ^a	"	610	80, coh ^a	~0.01
					@470	15, coh ^b	0.003	621	DD, coh [67]	
					500, 450	DD, hxx ^d [8]		621	DD, coh [68]	
					510, 425	DD, hxx ^e [8]	0.009 ^b	620	DD, hxx [8]	
					@650	hxx [8]		@650	hxx [8]	

Table 3 (continued)

Dye	$S_{0,1}$ absorption		Isosbestic		$S_{1,2}$ absorption		Photoisomer absorption		
	λ_a (nm)	ϵ_a (mM ⁻¹ cm ⁻¹), Slv Ref.	λ_i (nm)	λ_u (nm)	λ_u (nm)	ϵ_u (mM ⁻¹ cm ⁻¹), Slv Ref.	λ_p (nm)	ϵ_p (mM ⁻¹ cm ⁻¹), Slv Ref.	τ_{ps} (ms)
1 (10)	CXY	706	605	543	70, coh ^g				0.088
		706		452	40, eoh ^g				0.086
		708		404	35, eoh ^g				0.095
		710		575, 440	DD, moh [36]				
2 (12)	DDC	813	640	581, 440	DD, moh [43]				
		815		@694	26, dms [70]				
				566	66, eoh ^g				0.14
				516	50, eoh ^g				0.14
3 (14)	DC4	797	660	816	20, eoh ^g				
	D74	924		610	70, eoh ^g				0.12
		928							
		928		550 sh	50, eoh ^g				
C: INDO end-group type	HCY	433		465	20, eoh ^g				
				812	72, act [13]				
	HIC	544		730 sh	44, act [13]				
	IC2	549		607	93, act [13]				0.11
	HIF (PF ₆)	558		579 sh	80, act [13]				
	BIF (PF ₆)	559		549 sh	55, act [13]				
	HID	639							
	TID	671		480, 430	DD, bz ^c [6]				0.25
	TIF	685		479, 435	DD, bz ^b [34]				
	HII	741		497	DD, bz ^c [6]				0.01
	(HIT, I ⁻)	742		447	DD, bz ^b [34]				> 10 ⁻³
3 (10)		750	550	497	120, eoh ^f				1.2
				447	122, eoh ^f				
				760?	300?, dms [72]				
				540 sh	18, moh [73]				
			493	26, moh [73]					0.2
			415	7, moh [73]					
			550, 500	DD, moh [36]					

^a In ethanol (8.4 × 10⁻³ M) the decay time of the total fluorescence excited at 560 nm was measured with a ps camera to be 3.4 ps; ^b a three-component decay is reported in Ref. [18] at $\lambda_{exc} = 510$ nm: 1.25 ps (39%), 8.6 ps (60%), 109 ps (1%); ^c a three-component decay is reported in Ref. [8] at 650 nm: 0.2 ps (56%), 5.3 ps (40%), 200 ps (4%); ^d with $\lambda_{exc} = 590$ nm, probe delay: < 300 fs [8]; ^e with $\lambda_{exc} = 590$ nm, probe delay: 1 ps [8]; ^f $\lambda_{exc} = 608$ nm, probe delay: 10 ps; ^g this work.

Table 3 (continued)

Dye <i>n</i> (<i>N</i>)	Code	S_{01} absorption		Isosbestic λ_i (nm)	S_{12} absorption		Photoisomer absorption	
		λ_a (nm)	ϵ_a (mM ⁻¹ cm ⁻¹), Slv Ref.		λ_m (nm)	ϵ_m (mM ⁻¹ cm ⁻¹), Slv Ref.	λ_p (nm)	ϵ_p (mM ⁻¹ cm ⁻¹), Slv Ref.
4 (12)	HIT (ClO ₄)	743	215, eoh (a)	600	546 sh, 493	DD, moh [43]	0.9	
		743	281, moh [39]		518, 485 sh	DD, moh [75]		
					533	39, moh [76,77]		
5 (14)	HIT to IRL	743	moh [23]		@694	29, dms [70]		
		784	240, eoh [13]		@532	63, moh [78]		
					@532	37, eoh [79]		
4 (12)	HIQ	848	eoh [28]		523	128, eoh [13]		
		956	eoh [28]		486	132, eoh [13]		
					@532	115, eoh [13]		
5 (14)	HIP				@532	212, eoh [65]		
					@355	83, eoh [65]		
					520	154, eoh [13]		
5 (14)	HIP				567	94, eoh [13]		
					@532	129, eoh [13]		

^a Assumed to be equal to HIT (HIT.I); ^b PF₆ counterion, excited at 532 nm, probe delay: 18 ps [34]; ^c excited at 532 nm, probe delay: 10 ns [34]; ^d IRI (775 nm), IRI (768), IRL (792) [40]; ^e PF₆ counterion, excited at 532 nm, probe delay: 60 ps [6]; ^f this work.

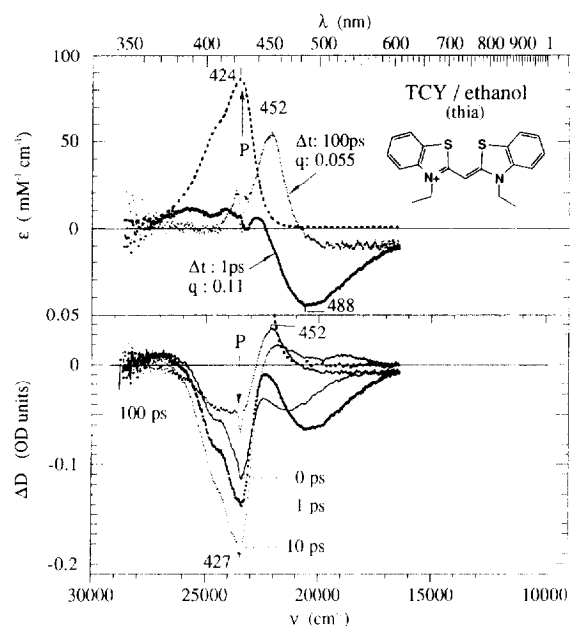


Fig. 2. Top frame: Ground state absorption extinction coefficient (ϵ_g) spectrum (broken line). S_1S_0 absorption/gain extinction coefficient (ϵ_g) spectrum at 1 ps pump-probe delay Δt (thick line), and transient absorption extinction coefficient spectrum of a photoisomer at larger delays (thin line). Lower frame: Transient difference absorption spectra (ΔD) measured at various pump-probe delays. The pump wavelength (P) is indicated by an arrow.

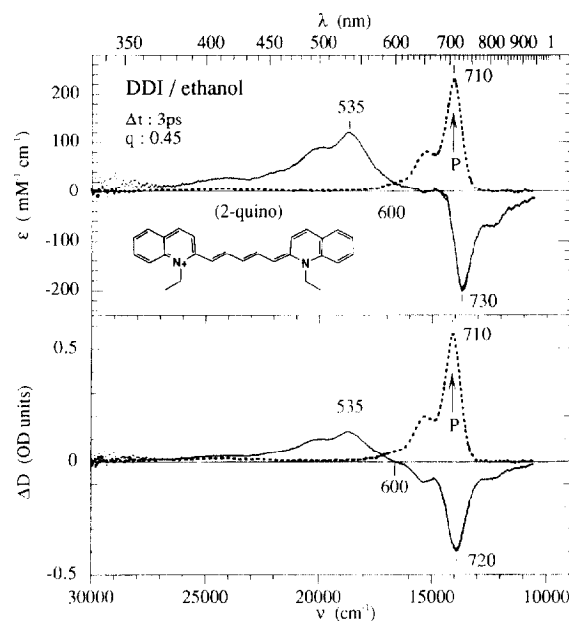


Fig. 4. Top frame: Ground state absorption extinction coefficient (ϵ_g) spectrum (broken line). S_1S_0 absorption/gain extinction coefficient (ϵ_g) spectrum at 3 ps pump-probe delay Δt (thick line), and transient absorption extinction coefficient spectrum of a photoisomer at larger delays (thin line). Lower frame: Transient difference absorption (ΔD) spectra measured at various pump-probe delays. The pump wavelength (P) is indicated by an arrow. The isosbestic point is indicated in both frames.

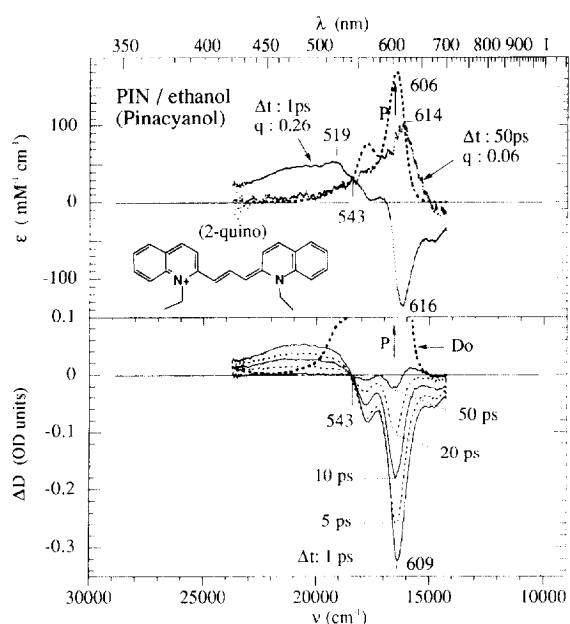


Fig. 3. See caption Fig. 2.

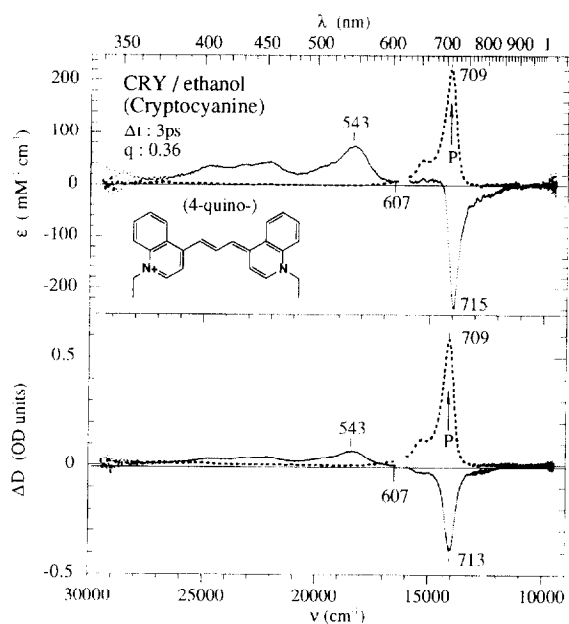


Fig. 5. See caption Fig. 4.

together with the corresponding transient optical density spectra ΔD . In some cases the results were obtained from rapid tests or with early versions of the experimental devices; the full spectra and decay times were not always measured. To estimate the ϵ values a global treatment of the ΔD and D_0 spectra was done and the ϵ_g values were adjusted by varying the parameter $q = C_1/C$ of relation (3) so that the maximum negative value of the ϵ_g becomes equal to the value of ϵ_g .

taking into account a guessed value of ϵ_u at the wavelength of the maximum (negative) ϵ_g . This procedure is based on the assumption that, for delays of about 1 to 5 ps, the vibrationally relaxed S_1 state reached after S_0S_1 absorption has not undergone a significant conformational evolution. Then the maximum cross section value of the (vibrationally relaxed) S_1S_0 stimulated emission should be nearly equal to that of the (vibrationally relaxed) ground state absorption. This

Table 4 (continued)

<i>n</i> (<i>N</i>)	Dye	S_0S_1 absorption		S_0S_2 absorption		Isosbestic		S_1S_2 absorption		Photoisomer absorption		
		λ_a (nm)	ϵ_a (mM ⁻¹ cm ⁻¹)	λ_a (nm)	ϵ_a (mM ⁻¹ cm ⁻¹)	λ_i (nm)	λ_j (nm)	λ_a (nm)	ϵ_a (mM ⁻¹ cm ⁻¹)	λ_p (nm)	ϵ_p (mM ⁻¹ cm ⁻¹)	τ_{PS} (ms)
		1008	179, mol NKS; Personal communication (1996)	638 ^a	DD, dms ^a							
6 (16)	<i>DXC</i>	1020	[00, pyr [2]	626 ^a	DD, act [13]							0.1
7 (18)	<i>DHC</i>	1130	mol [38]									
		1250	mol [38]									
^a With $\lambda_{exc} = 305$ nm, delay: 5 ps; ^b iodide; ^c tetrafluoroborate; ^d at 190 K; ^e with $\lambda_{exc} = 305$ nm, delay: 100 ps; ^f bromide; see also Ref. [30]; ^g chloride; ^h a new permanent absorption appears during the measurement of this strong transient; ⁱ this work.												
F. 4,5-dibenzimidazo end-group type												
1 (6)	<i>HBC</i>	586	mol [23]									
2 (8)	<i>HBD</i>	676	mol [23]									
3 (10)	<i>HBT</i>	780	231, coh [31]									
		746	123, dms [22]	635	105, coh ^a							0.7
		(IR 144)	141, coh [25]		471	32, coh ^a						0.54
		786	194, coh [24]	635	549	110, coh ^a				830	DD, coh [86]	0.6
		(IR 125)	196, dms [22]		474	42, coh ^a				835	DD, dms [86]	0.7
		1010	638	560	DD, dms ^a							
4 (14)	<i>HDC</i>		coh [27]									
^a This work.												
F. 6,7-dibenzthia end-group type												
1 (6)	<i>B6C</i>	593	mol [23]									
		572	mol [23]									
		578	mol [23]									
2 (8)	<i>D86</i>	684	mol [23]									
		680	mol [23]									
3 (10)	<i>D6C</i>	796	180, coh ^b									
			[44]									
		828	165, dms [22]									
		814	160, coh [22]							885	DD, coh [86]	
4 (14)	<i>DND</i>	1050	dec [23]									
^a 5,6-dibenzthia; ^b this work.												
G. 4,5-dibenzthia end-group type												
0 (4)	<i>5CY</i>	452	78, coh [42]									
1 (6)	<i>B4C</i>	595	coh [30]									
		596	141, coh [42] ^a									
		577	mol [23]									
		571	coh [37]									
2 (8)	<i>D84</i>	698	mol [23]									
3 (10)	<i>D4C</i>	798	act [13]									
		798	196, coh [25]									
		844	170, act [13]									
		855	~200 eg ⁺ dms [46]									
				662	564	130, act [13]				855	170, dms [66]	0.86
				720	578	110, act [13]						0.73
				579	579	DD, coh ^b						
				585	585	DD, dms ^b						

^a Toluene sulfonate; ^b this work.

Table 4 (continued)

Dye	<i>n</i> (<i>N</i>)	Code	$S_{0,1}$ absorption		ϵ_s (mM ⁻¹ cm ⁻¹), Slv Ref.	Isosbestic	$S_{1,2}$ absorption		ϵ_s (mM ⁻¹ cm ⁻¹), Slv Ref.	τ_u (ns)	Photoisomer absorption		τ_{PS} (ms)	
			λ_a (nm)	λ_b (nm)			λ_a (nm)	λ_b (nm)			λ_p (nm)	ϵ_p (mM ⁻¹ cm ⁻¹), Slv Ref.		
H, 2-QUINO end-group type														
0 (4)		<i>PIC</i>	523 525		77, moh [42] ^a 78, coh [NKS, Personal communication (1996)] 54, coh [33]		400–450		~ 15, coh ^{a,†}	~ 0.002	540 545	53, coh ^{b,†} DD, moh [88]		
1 (6)		<i>ECY</i> <i>MCY</i> <i>P/N</i> (I)	516 523 605 606		90, coh [33] 20, coh [33] 125, moh [67] 170, coh [25]	540	519 470 sh ≤ 540	54, coh [†] 46, coh ^{a,†} DD, coh [92]	0.014 0.013 0.016	614 630 632 635 635	100, coh ^{a,†} DD, coh [81] 156, moh [67] 133, coh [90] 128, coh [68] moh [89]	~ 0.01 0.050 0.025		
2 (8)		<i>DCC</i> (CI)	602		189, moh [12]						640 640	193, [92] DD, moh [93]	0.00038 0.016	
		606 607			200, coh [35] 124, coh [33]									
		<i>DDI</i>	710		230, coh [25]	600 600	540, 505 535, 498 535 500 sh 415	DD, moh [43] DD, coh ^{a,†} 115, coh [†] 80, coh [†] 25, coh [†]	0.1–0.4 0.03	721	DD, coh ^{a,†}			
3 (10)		<i>MDI</i> <i>DC2</i> <i>BDI</i> <i>DT2</i> (I)	707 697 690 817 820		254, moh [39] moh [23] moh [43] 238, moh [NKS, Personal communication (1996)] 250, coh [39]	640	505, 405 625 sh	DD, moh [43] 20, coh [†]						
		<i>MT2</i> <i>DTP</i> (ClO ₄)	816 824		234, moh [39] 262, pc+eg [94]		570 530 sh 472 sh 438 sh 416 sh	130, coh [†] 100, coh [†] 40, coh [†] 22, coh [†] 21, coh [†]	0.04 0.04					
4 (12)		<i>DAQ</i>	928		95, pc+eg [26]									

^a 1 ps delay; ^b 30 ps delay; [†] 100 ps delay; [‡] 3 ps delay; [§] 900 ps delay; [¶] this work.

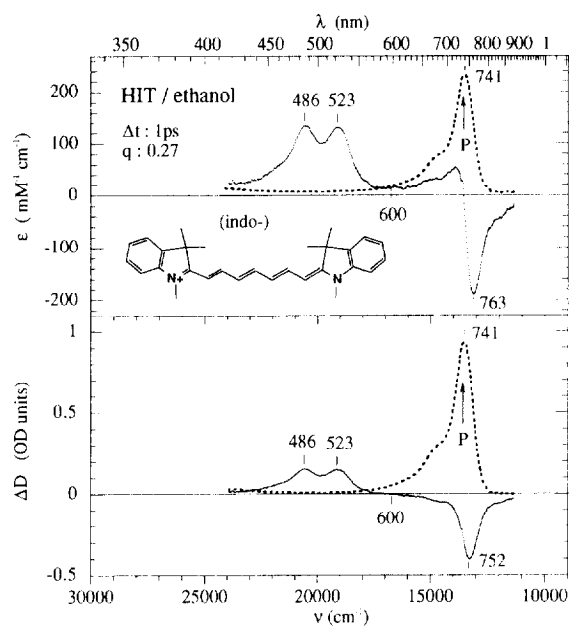


Fig. 6. See caption Fig. 4.

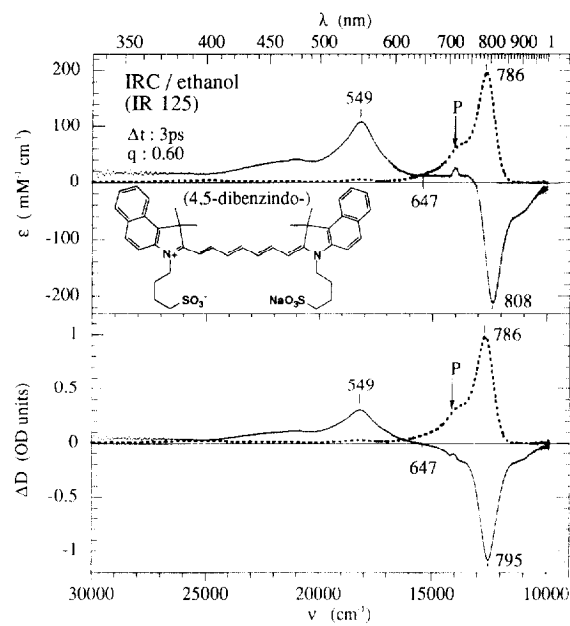


Fig. 8. See caption Fig. 4.

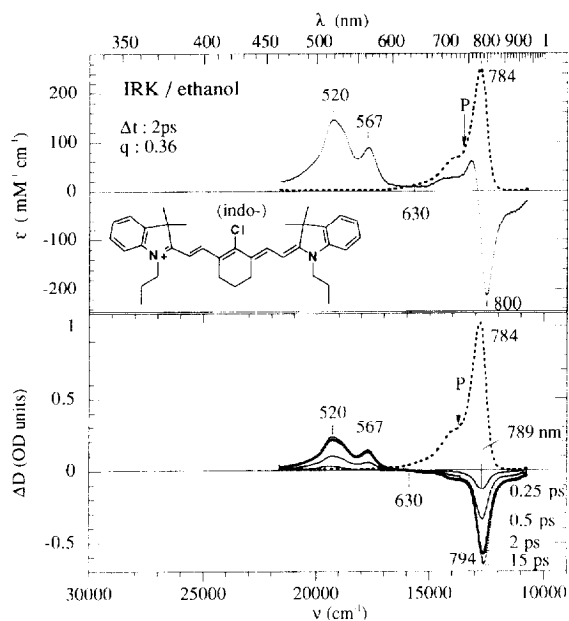


Fig. 7. See caption Fig. 4.

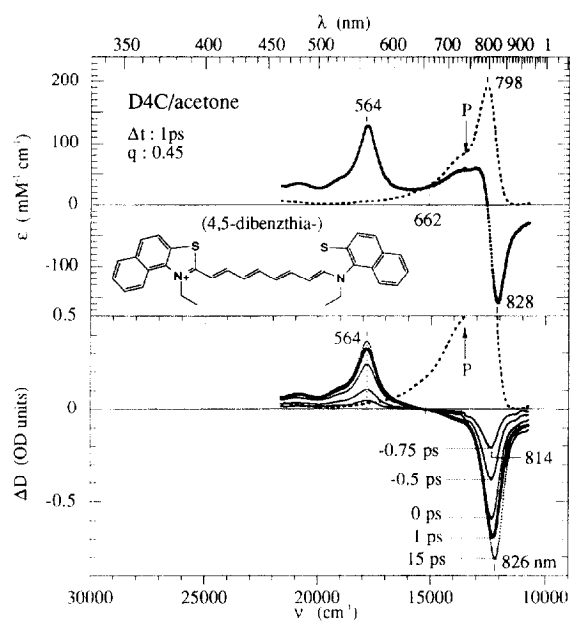


Fig. 9. See caption Fig. 2.

assumption is not valid in all cases. In particular it is likely to be incorrect for nonplanar cyanines (e.g., the 2-quinocyanine *PIC*, see Fig. 15), and for short chain polymethines (e.g. the 2-quinocarbocyanine *PIN* (see Fig. 3), and the thiocarbocyanine *DME*, with a 9-ethyl substitution in the chain, see Fig. 15), because strong driving forces due to stereo hindrance can probably induce very fast conformational relaxation after a Frank–Condon transition to the excited singlet state.

5.2. Dicarboxyanines and longer chain dyes

At small pump-probe delays (a few picoseconds), the ϵ_g cross-section spectrum of the largest resonant chain dyes

($N \geq 8$) exhibits two types of transient bands (see top frames in Figs. 4–12). The first type is constituted by one or two strong transient absorption bands appearing on the blue side of the S_0S_1 absorption band and assigned to S_1S_n transition(s). These S_1S_n bands present little or no shift as a function of the pump-probe delay. The corresponding ΔD spectra are given for nine dyes in the lower frames of Figs. 2–11. In a few cases the ΔD curves measured at different delays are also given.

The second type of transient band is a strong gain band (similar to the reversed mirror-image of the S_0S_1 absorption first band) but with a 'stimulated Stokes shift' (SSS) generally smaller than the usual Stokes shift of the fluorescence

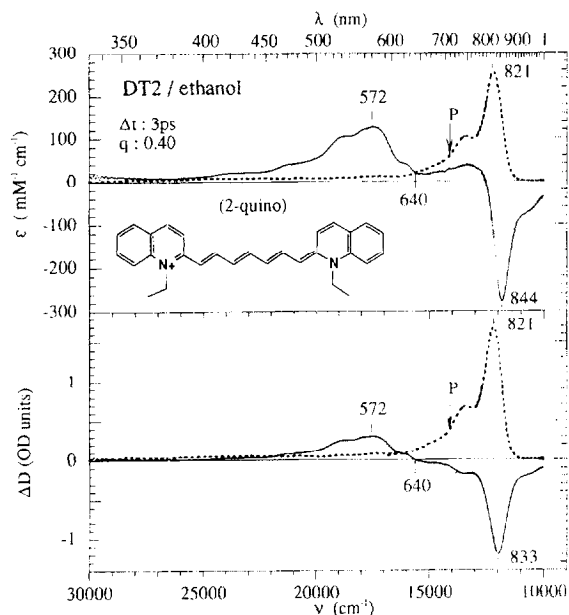


Fig. 10. See caption Fig. 4.

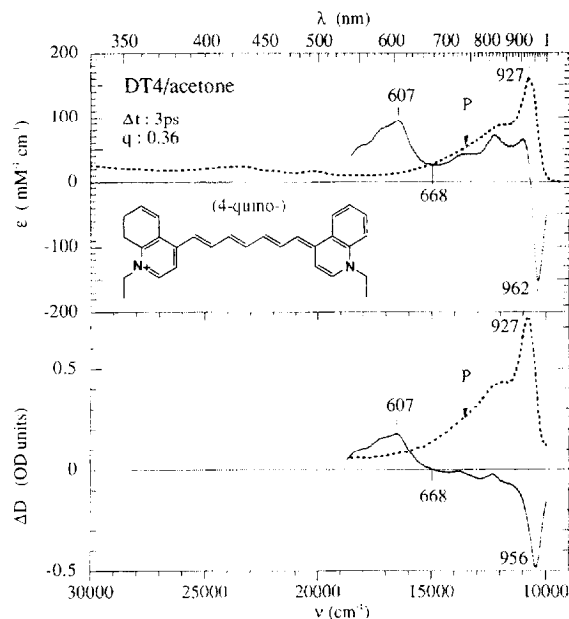


Fig. 12. See caption Fig. 4.

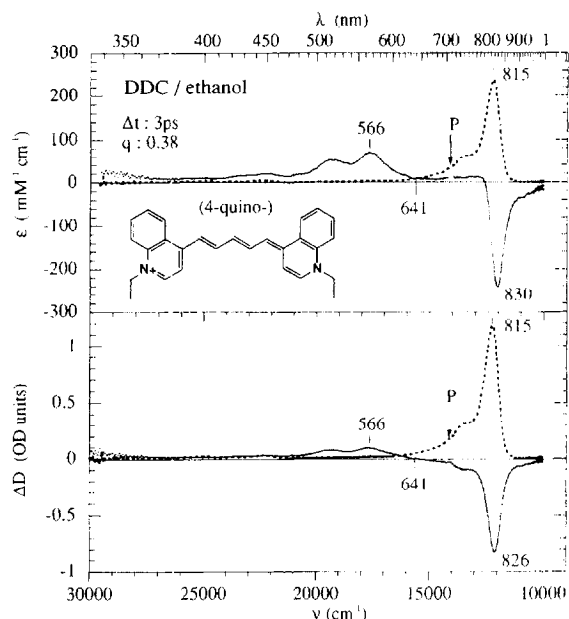


Fig. 11. See caption Fig. 4.

spectra (about one half). The SSS value varies, according to the carbocyanine, from 120 cm^{-1} (for *CRY*/Cryptocyanine, see Fig. 5) to 1300 cm^{-1} (for *IRB*/IR144, see Fig. 15). It seems to be related to the vibronic band width since it remains in the range of 0.75 ± 0.25 times the HWHM (measured in the red side half-width) of the absorption band. The factor two between the Stokes shift and the SSS measured in several dyes at short delay times is not really understood but is assumed to be due to the various relaxation processes occurring during the fluorescence lifetime and involving intramolecular vibrations, solvation (in ethanol where the solvation time τ_s is 16 ps) [31], and/or conformation (photoisomer or 'perp' state). These points will need more detailed exper-

iments, as well as appropriate spectral analysis treatments in the difficult cases where three or more time-dependent populations are involved. As an example we show the case of the indo-tricarbocyanine *IRK*, with a 'rigidified' chain, in ethanol (Fig. 7). The rise of the negative ΔD bands at 794 nm persists up to 15 ps with a weak red shift (5 nm) of the peak. For the 4,5 dibenzthia-tricarbocyanine *D4C*, with an unsubstituted chain, in acetone (Fig. 9), the red shift is larger (12 nm) while the S_1S_n ΔD band does not shift at any time.

At long pump-probe delays (nanoseconds), photoisomer absorption bands were reported in the literature to be observed for many dyes after long pulse excitation on the red side of the ground state absorption (see Tables 3 and 4). These isomers might contribute to the distortion of the time-dependent ' ϵ_2 ' gain curve obtained, as shown in Fig. 13, for the dye *D4C* at several pump-probe delays from 15 ps to 800 ps. In this figure the values of the parameter $q = C_1/C$ were arbitrarily chosen for all delays larger than 15 ps so that the ϵ_2 (560 nm) value remains at its 15 ps value. This procedure, which is correct only if no photoisomer absorption is assumed to take place at this wavelength, evidenced a distortion of the ϵ_2 curve in the gain region, and therefore indicates the presence of more than two varying populations. This distortion could be due to either a new absorption from a photoisomer in the ground state, which does not exclude the presence of some gain band from an excited photoisomer. Again this point would require knowledge of the involved population values.

5.3. Cyanines and monocarbocyanines

For smaller dyes (see Figs. 2 and 3) a strong transient band appears in the ϵ_2 spectrum on the red side of the ϵ_1 absorption band after only a few picoseconds, and is assigned to rapid formation of a photoisomer in its ground state. At the same

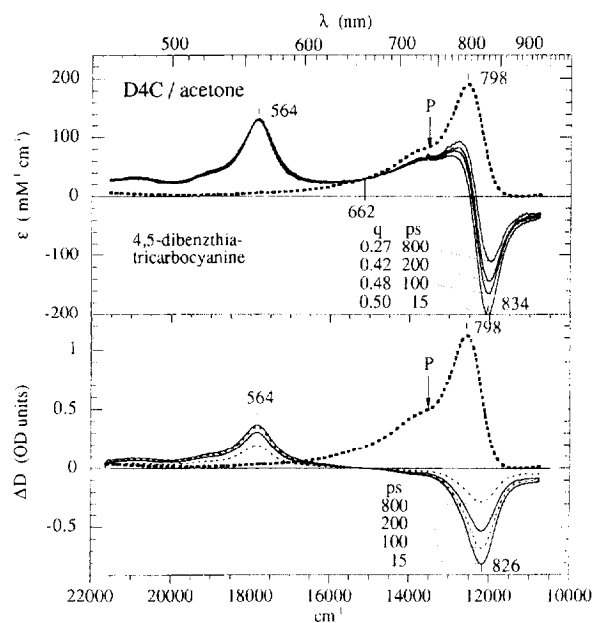


Fig. 13. Variation of the ϵ_2 extinction coefficient spectrum of the 4,5-dibenzthiatricarboyanine D4C as a function of the population dependent ΔD curves measured at different pump-probe delay times. The values of the coefficient $q = C_1/C_2$ given in the insert, are adjusted for superposition of the ϵ_2 curves in the S_1S_n absorption region around 560 nm.

time the gain red-wing part of the negative ΔD curve shifts considerably and quickly in the thia-cyanine *TCY* (Fig. 2), which could be interpreted by the formation of an excited photoisomer with a strong gain cross section. For the 2-quinocarbocyanine *PIN* (Fig. 3), the maxima of the gain and of the ground-state photoisomer absorption coincide, and only a small shift occurs. An extreme case is the 4-quinocyanine *4CY* (formula in Fig. 15) for which the process seems to be so fast that no gain can be detected in our experiment, but only a transient absorption at 610 nm, assigned to a photoisomer, which reaches a maximum at 10 ps (Table 3B). The S_1S_n absorption bands at small delays (< 1 ps) appear quite broad, in contrast to the case of larger carbocyanine dyes. A shift with a 1.2-ps time constant was reported with the 4-quinocyanine *4CY* after a 20-fs excitation [8] and assigned to the accumulation time of the molecules at the bottom of the S_1 state potential ('perp' configuration).

5.4. Comparison of all available data: Tables 3 and 4

Early works by flash or laser photolysis on transient absorption in carbocyanine dyes were performed with long pulse excitation from nano to microseconds and gave information on the photoisomers and triplet states [61,66,74,72]. Less data are available concerning the energies of the higher singlet states which can be observed only by allowed absorption transitions from the lowest excited state S_1 . This state is often of short (subnanosecond) lifetime for carbocyanines and a few picoseconds or less for cyanines. A few transient

absorption bands observed were assigned to S_1S_n transitions by comparing their decay times with that of the fluorescence [85,43,36,73]. The S_n energies thus obtained do not correspond well to those given by the weak S_0S_n absorption bands in the short wavelength range and must correspond to other excited singlet states. Results obtained with subpicosecond pulse excitation should allow one to discriminate more easily between the transient chemical species formed in cascade.

Tables 3(A–C) and 4(D–H) give the differential absorption data assigned to transient S_1S_n absorption bands as found in the literature for cyanine and carbocyanine dyes, grouped by end-group types and methine chain lengths, together with new data measured during the last few years in this group either for different preliminary tests or for more detailed studies, but all obtained after subpicosecond excitation. In addition Tables 3 and 4 give some of the reported ground-

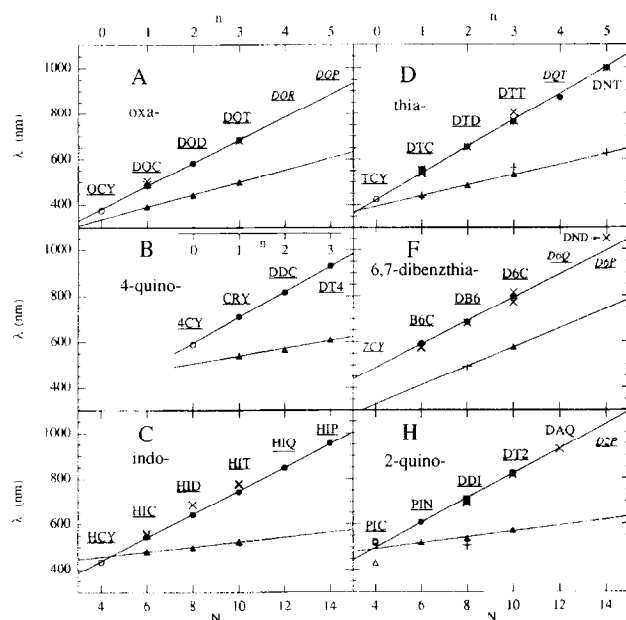


Fig. 14. Plot of measured S_1S_n (triangles) and S_0S_1 (circles) transition band maxima for cyanines (empty marks) and carbocyanine (filled marks) dyes showing the linear shift dependence in a wavelength scale within each end-group family A to H. Unsubstituted chain dye codes are underlined. The substituted dyes are represented by (+) for S_1S_n and by (x) for S_0S_1 bands but are not labelled. Only filled triangles and circles (unsubstituted carbocyanines) are used for the fits.

Table 5

Wavelength increments (per added bond pair in the chain) of the main S_0S_1 ($\Delta\lambda_n$) and S_1S_n ($\Delta\lambda_n$) bands for six symmetrical carbocyanine families

Family	$\Delta\lambda_n(S_0S_1)$ (nm)	$\Delta\lambda_n(S_1S_n)$ (nm)
A: oxa-	101	54
B: 4-quinocyanine	112	33
C: indo-	100	22
D: thia-	117	47
E: 6,7-dibenz-thia-	102	(83) ^a
G: 2-quinocyanine	108	25

^a S_1S_n data for type F (6,7-dibenzthia) are to be confirmed.

Table 6

Wavelengths (± 3 nm) of strong S_1S_n bands (arranged by increasing order) as measured or predicted (^a) in acetone, methanol or ethanol

$S_1S_n \lambda_n$ (nm)	Dye code	$S_nS_1 \lambda_n$ (nm)
330 ^a	7CY	460 ^a
337 ^a	OCY	375
390 ^a	TCY	424
392	DOC	483
395 ^a	DMC	572
397 ^a	D9C	489
399 ^a	TDC	578
407 ^a	TDO	502
410 ^a	B6C	593
422 ^a	ECY	516
422 ^a	TMT	536
425	DME	540
426 ^a	DMI	543
429 ^a	MCY	523
430	PIC	525
430 ^a	TTC	547
439 ^a	MTC	555
440	DTC	557
442	DOD	580
454 ^a	HCY	433
467 ^a	HIC	544
471 ^a	IC2	549
472 ^a	ETC	598
479 ^a	BIF	559
479 ^a	HIF	558
483	DTD	653
483 ^a	NTD	653
490 ^a	DB6	684
493	CB6	680
497 ^a	HID	639
498 ^a	DMO	681
500	DOT	682
505 ^a	4CY	591
512 ^a	IRJ	768
517 ^a	IRI	775
518	HII	741
519 ^a	DCC	606
519	PIN	606
520	IRK	784
522 ^a	TID	671
524	HIT	743
524 ^a	TII	743
525 ^a	DC2	697
528 ^a	IRL	792
533 ^a	DTT	760
533 ^a	MDI	707
533 ^a	TIF	685
535	DDI	710
536 ^a	DNC	765
541 ^a	HIQ	848
543	CRY	708
549	IRC	782
552 ^a	DOR	784 ^a
558 ^a	M6C	772 ^a
563 ^a	HIP	956
563 ^a	IRA	803
564	D4C	798
566	DDC	815
567 ^a	MT2	816
569 ^a	DTP	824

Table 6 (continued)

$S_1S_n \lambda_n$ (nm)	Dye code	$S_nS_1 \lambda_n$ (nm)
570	DT2	817
576	D6C	796
576 ^a	DAT	881 ^a
577	IRD	844
578 ^a	DTQ	886
589 ^a	<i>DQ2</i>	928 ^a
589 ^a	IRE	814
593 ^a	DAQ	928
606 ^a	<i>DOP</i>	886 ^a
610	DT4	930
617 ^a	<i>D2P</i>	1035 ^a
626	DNT	1010
626 ^a	DPC	1000
657 ^a	D6Q	922 ^a
668 ^a	DXC	1130
714 ^a	DHC	1250
736 ^a	DND	1050
741 ^a	D6P	992 ^a

^a Predicted values of the S_1S_n or S_nS_1 bands. They were obtained by extrapolation with the linear law of the 6 dye families shown in Fig. 14 and Table 4.

Italics designate hypothetical dyes.

state absorption extinction coefficients (ϵ_n). The rather large discrepancies can be partly assigned to the fact that gravimetric preparation of quantitative solutions is complicated by the difficulty in removing the crystallization solvents or the absorbed water by hygroscopic dyes [42]. Finally Tables 3 and 4 also gives all the transient bands we could find in the literature which were assigned to one (or several) photoisomer form(s), in the ground state. They often differ from the S_1S_n bands by their longer decays, in the micro or millisecond range for carbocyanines at room temperature. In general, the ϵ values for the S_1S_n bands measured in this work should be considered only as tentative and have in some cases a large uncertainty of the order of $\pm 50\%$.

5.5. Shift law of the strong S_1S_n absorption transition

Inspection of the transient absorption and gain bands for all dyes shows a close similarity of their relative position with respect to that of the ground state absorption band. This suggests that the regular shift law as a function of the chain length, well-known for the ground state absorption, could also hold for the S_1S_n absorption.

Several values of the wavelength maximum of the main S_1S_n bands (Tables 3 and 4, λ_n column) are plotted in Fig. 14, for 6 carbocyanine families (A to H), as a function of the 'resonance' chain length (N). For five of the carbocyanine families A, B, C, D and H, enough data are available to have a plot of the chain dependence of the S_1S_n transition wavelength. The straight lines drawn for each family are the linear fits based on 3 to 5 unsubstituted methine chain dyes (underlined codes). For the F (6,7-dibenzthia) family only two

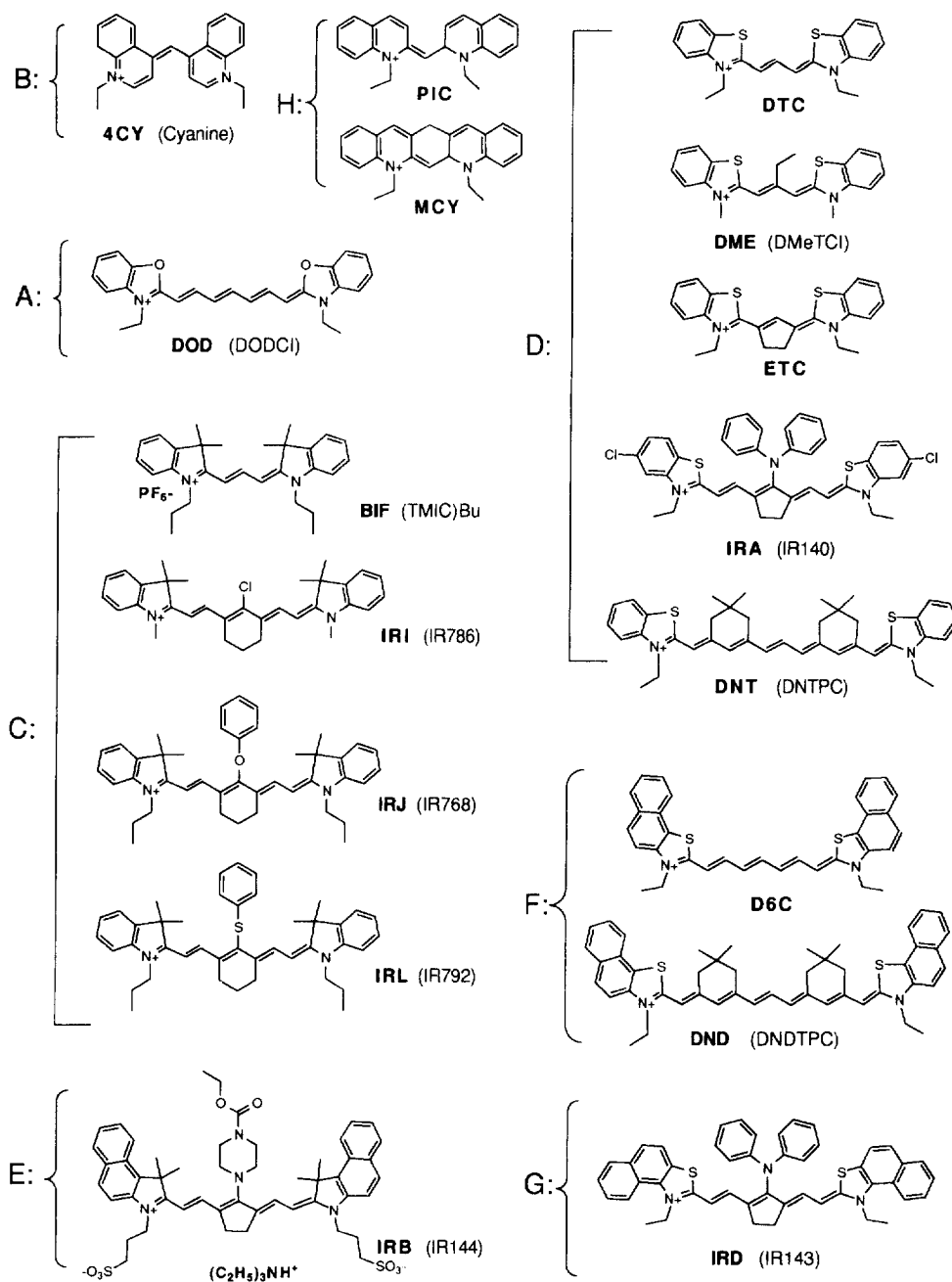


Fig. 15. Example of molecular structures of cyanine and carbocyanine dyes with end-groups of types A to H.

points are available for the S_1S_n transition and the fit is only tentative. In addition, data from substituted dyes are added (but not labeled) to visualize the generally weak effects of the substituents.

From these graphs we conclude that a linear wavelength shift also occurs for the S_1S_n main band as a function of N , but with a smaller slope than for the ground-state absorption, the slope value being much more dependent on the end-group type for the S_1S_n band. The slopes of the shifts for each carbocyanine family are expressed in Table 5 in nm per added bond pair in the chain.

5.6. Prediction of unknown S_1S_n absorption bands wavelengths

From these results an estimation of the positions of the not yet measured strong S_1S_n absorption bands of any other symmetrical carbocyanine can be predicted within each family from their known (or extrapolated) ground-state absorption wavelengths. Some minor proportional corrections were applied to estimate the band wavelengths of the substituted chain compounds by comparison with the shifts of the S_0S_1 bands for the unsubstituted parent dyes. The results are given

in Table 6 where all the measured and predicted S_1S_n absorption bands are ordered by increasing wavelengths for the 83 known dyes listed here and for 9 hypothetical unsubstituted dyes (not synthesized to our knowledge); in the latter case the S_0S_1 absorption band wavelength is predicted by extra- or interpolation.

6. Summary and conclusion

There is a general agreement on the S_1S_n absorption wavelength regions of the carbocyanine dyes reported in the literature, but large discrepancies (up to two orders of magnitude) on the cross section values obtained by different methods, in particular by indirect methods based on propagation measurements at a single wavelength and more or less a priori level models. From the procedure used here to evaluate the excited-state population the accuracy of the present cross section values is estimated to be better than $\pm 50\%$.

The spectral position of the main S_1S_n bands can be empirically well predicted with a few structural parameters, such as:

- the length of the methine chain (which shifts the main band by steps of 20 nm to 50 nm per added bond pair, according to the end-group type),
- the end-group nature, which can be chosen among the six well-known group types used here (or among a few others) and shifts the bands by up to a few tens of nanometers,
- the choice of the solvent, which also shifts the wavelength up to two tens of nanometers,
- the substitution by electron donating or withdrawing groups which can shift the S_1S_n spectra to either side, and allows a chemical tuning of the bands by a few nanometers.

For practical application, the addition of chain rigidifying substituents has the advantageous effect of maintaining narrow band spectra and therefore high extinction coefficients, while reducing the number of isomers, the chemical degra-

dation and the photolysis. The carbocyanine compounds present a weak overlap of the main S_0S_1 and S_1S_n absorption bands. This is a favorable case to produce, at specific wavelengths, strong 'induced absorption' as is required for optical limiting or other photonic applications.

The lifetime of the S_1 state, as measured by the S_1S_n band decay, generally follows a single exponential law in contrast to both the ground state recovery and the gain band decay, during the first tens of picoseconds. The complex dynamic behavior of cyanine and monocarbocyanine dyes, when probed in the ground state absorption or in the gain band, might be due to three main causes: (1) the time dependent solvation in polar solvents of long solvation times [95] due to the increased polarity of the dyes in the S_1 state. (Quinocarbocyanines have a negligible permanent dipole moment in S_0 .) [96]; (2) the formation of photoisomers in their ground state for long S_1 lifetime dyes (e.g., 2 ns for most dicarbocyanines) and the slow back reaction allowing large accumulation of isomers under long pulse excitation; and (3) the ultrafast formation of photoisomers in a charge transfer excited state of low radiative power (for cyanines and distorted monocarbocyanines).

The S_1S_n data in Tables 3 and 4 and estimations in Table 6 can serve as a guideline in the future search of strong transient bands with appropriate decay times as required for opto-optic applications, for example in ultrafast photonic and laser technologies. It is to be noted that the high S_1S_n extinction coefficient of carbocyanines potentially allows their study by time resolved resonance Raman spectroscopy. This technique could provide interesting data on the structural conformation of the S_1 state, and hopefully of the photoisomers.

7. Appendix

Examples of molecular structures of cyanine and carbocyanine dyes are given in Fig. 15; the common chemical names are given in Table 7.

Table 7

Common chemical names of known symmetrical cyanine and carbocyanine dyes, with their abbreviations and synonyms used in literature and/or commercial catalogues, placed in alphabetic order of the arbitrary codes used in this work

No.	Codes	Names/Synonyms [Ref.]	T	n	N	Common chemical names (CC = carbocyanine, Me = methyl, Et = ethyl)
1	4CY	NK6/Cyanine	B	0	8	1,1'-diEt-4,4'-cyanine iodide
2	5CY	Ref. [42]	G	0	6	3,3'-diEt-2,2'-(4,5,4',5'-dibenzo) thiacyanine chloride
3	B4C	NK382	G	1	6	3,3'-diEt-2,2'-(4,5,4',5'-dibenzo) thiaCC iodide
4	B6C	NK467	F	1	6	3,3'-diEt-2,2'-(6,7,6',7'-dibenzo) thiaCC iodide
5	BDI	Ref. [36]	H	2	2	1,1'-diethyl-11-bromo-2,2'-diCC iodide
6	BIF	(TMIC)Bu, PF6/Ref. [34]	C	1	6	1,1'-dibutyl-3,3,3',3'-tetraMe-indoCC hexafluorophosphate
7	CB6	Ref. [43]	F	2	6	3,3'-diEt-10-chloro-2,2'-(6,7,6',7'-dibenzo)thiadiCC iodide
8	CRY	NK5/Cryptocyanine/DCI	B	1	10	1,1'-diEt-4,4'-CC iodide
9	D4C	NK427/DDTTCI	G	3	10	3,3'-diEt-2,2'-(4,5,4',5'-dibenzo)thiatriCC iodide
10	D6C	NK1887	F	3	10	3,3'-diEt-2,2'-(6,7,6',7'-dibenzo)thiatriCC iodide
11	D9C	D9MOCI	A	1	6	3,3'-diEt-9-Me-oxaCC iodide
12	DAQ	NK1161.P/DaQTeC/Ref. [44]	H	4	12	1,1'-diEt-13-acetoxy-2,2'-tetraCC perchlorate or iodide

No.	Codes	Names/Synonyms [Ref.]	T	n	N	Common chemical names (CC = carbocyanine, Me = methyl, Et = ethyl)
13	DAT	DaTTeC/Refs. [44,45]	D	4	12	3,3'-diEt-12-acetoxy-2,2'/1'-thiatetraCC perchlorate
14	DB4	NK2409	G	1	6	3,3'-diEt-2,2'-(4,5,4',5'-dibenzo)thiadiCC
15	DB6	NK2627	F	1	6	3,3'-diEt-2,2'-(6,7,6',7'-dibenzo)thiadiCC
16	DC2	NK1150	H	2	8	1,1'-diEt-11-chloro-2,2'-diCC bromide
17	DC4	NK78	B	2	12	1,1'-diEt-11-chloro-4,4'-diCC iodide
18	DCC	Pinacyanol Cl/Ref. [33]	H	1	6	1,1'-diMe-2,2'-CC chloride
19	DDB	DDBCl/Ref. [37]	G	1	6	3,3'-diEt-9-Me-2,2'-(4,5,4',5'-dibenzo) thiaCC iodide
20	DDC	NK1144/DDC1-4	B	2	12	1,1'-diEt-4,4'-diCC iodide
21	DDI	NK1456/DDI	H	2	8	1,1'-diEt-2,2'-diCC iodide
22	DHC	Ref. [38]	D	7	18	3,3'-diEt-2,2'-thiaheptaCC iodide
23	DMC	NK462	F	1	6	3,3'-diEt-9-Me-2,2'-(6,7,6',7'-dibenzo)thiaCC iodide
24	DME	DMeTC1/Ref. [30]	D	1	6	3,3'-diMe-9-Et-thiaCC iodide
25	DMI	NK77	D	1	6	3,3'-diEt-9-Me-thiaCC iodide
26	DMO	NK199/DMOTCI	A	3	10	3,3'-diMe-2,2'-oxatriCC iodide
27	DNC	DNTTC1 Ref. [31]	D	3	10	3,3'-diEt-9,11-neopentylene-thiatriCC iodide
28	DND	DNP-1040/DNDTPC-P/[23]	F	5	14	3,3'-diEt-9,11,15,17-dineopentylene-(6,7,6',7'-dibenzo)thiapentaCC perchlorate
29	DNT	DNP-1020/DNTPC-P/[23]	D	5	14	3,3'-diEt-9,11,15,17-dineopentylene-thiapentaCC perchlorate
30	DOC	NK85/DOCI	A	1	6	3,3'-diEt-2,2'-oxaCC iodide
31	DOD	NK1533/DODCI	A	2	8	3,3'-diEt-2,2'-oxadiCC iodide
32	DOT	NK1511/DOTCI	A	3	10	3,3'-diEt-2,2'-oxatriCC iodide
33	DPC	Ref. [27]	D	5	14	3,3'-diEt-2,2'-thiapentaCC iodide
34	DT2	NK123/Ref. [44]	H	3	10	1,1'-diEt-2,2'-triCC iodide
35	DT4	NK124/DQTICI	B	3	14	1,1'-diEt-4,4'-triCC iodide
36	DTC	NK76/DTCI	D	1	6	3,3'-diEt-2,2'-thiaCC iodide
37	DTD	NK136/DTDCI	D	2	8	3,3'-diEt-2,2'-thiadiCC iodide
38	DTP	DTP/Ref. [31]	H	3	10	1,1'-diEt-2,2'-triCC perchlorate
39	DTQ	Ref. [39]	D	4	12	3,3'-diEt-2,2'-thiatetraCC iodide
40	DTT	NK126/DTTCI	D	3	10	3,3'-diEt-2,2'-thiatriCC iodide
41	DXC	Ref. [38]	D	6	16	3,3'-diEt-2,2'-thiahexaCC iodide
42	ECY	Ref. [33]	H	0	4	1,1'-ethylene-2,2'-cyanine iodide
43	ETC	Refs. [16,42]	D	1	6	3,3'-diEt-8,10-ethylene thiaCCtoluene sulfonate (R = 1,3,3,1',3',3'-hexaMe-2,2'-)
44	HBC	NK2610	E	1	6	R-(4,5,4',5'-dibenzo)indoCC iodide
45	HBD	NK2929	E	2	8	R-(4,5,4',5'-dibenzo)indodiCC perchlorate
46	HBT	NK2014/HDITCP	E	3	10	R-(4,5,4',5'-dibenz)indotriCC perchlorate
47	HCY	NK3212	C	0	4	R-indocyanine perchlorate
48	HDC	Ref. [27]	E	5	14	R-(4,5,4',5'-dibenzo)indopentaCC iodide
49	HIC	NK79/HICI	C	1	6	R-indoCC iodide
50	HID	NK529/HIDCI	C	2	8	R-indodiCC iodide
51	HIF	HIC.PF6/Ref. [41]	C	1	6	R-indoCC hexafluorophosphate
52	HII	NK125/HITCI	C	3	10	R-indotriCC iodide
53	HIP	Ref. [28]	C	5	14	R-indopentaCC iodide
54	HIQ	Ref. [28]	C	4	12	R-indotetraCC iodide
55	HIT	NK2421/HITCP	C	3	10	R-indotriCC perchlorate
56	IC2	DiIC ₂ (3)/Ref. [29]	C	1	6	1,1'-diEt-3,3,3',3'-tetraMe-2,2'-indoCC iodide
57	IRA	IR140 P/Ref. [22]	D	3	10	5,5'-dichloro-11-diphenylamino-3,3'-diEt-10,12-ethylene thiatriCC perchlorate
58	IRB	IR144/Ref. [22]	E	3	10	anhydro-11-(4-ethoxycarbonyl-1-piperazinyl)-10,12-ethylene-3,3,3',3'-tetraMe-1,1'- di(3-sulfopropyl)-4,5:4',5'-dibenzoindotriCC hydroxide, triethylammonium salt
59	IRC	IR125 1/Ref. [22]	E	3	10	3,3,3',3'-TetraMe-1,1'-di(4-sulfobutyl)-4,5:4',5'-dibenzo indotriCC iodide, monosodium salt
60	IRD	IR143 P/Refs. [22,46]	G	3	10	11-diphenylamino-3,3'-diEt-10,12-ethylene-4,5:4',5'-dibenzothiatriCC perchlorate
61	IRE	IR132/Ref. [22]	F	3	10	3,3'-di(3-acetoxypropyl)-11-diphenylamino-10,12-ethylene-5,6:5',6'- dibenzothiatriCC perchlorate
62	IRI	IR786/Ref. [40]	C	3	10	[2-[2-[2-chloro-3-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)ethylidene]-1- cyclohexen-yl]ethenyl]-1,3,3-trimethylindolium perchlorate]
63	IRJ	IR768/Ref. [40]	C	3	10	[2-[2-[3-(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene)ethylidene]-1- cyclohexen-1-yl]ethenyl]-3,3-dimethyl-1-propylindolium iodide]
64	IRK	IR780/Ref. [40]	C	3	10	[2-[2-[2-chloro-3-(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene)- ethylidene]-1-cyclohexen-1-yl]ethenyl]-3,3-dimethyl-1-propyl-indolium perchlorate]

No.	Codes	Names/Synonyms [Ref.]	T	<i>n</i>	<i>N</i>	Common chemical names (CC = carbocyanine, Me = methyl, Et = ethyl)
65	IRL	IR792/Ref. [40]	C	3	10	[2-[2-[3-[(1,3-dihydro-3,3-dimethyl-1-propyl-2H-indol-2-ylidene)-ethylidene]-2-(phenylthio)-1-cyclohexen-1-yl]ethenyl]-3,3-dimethyl-1-propyl-indolium perchlorate]
66	M6C	NK2166/Ref. [44]	F	3	10	3,3'-diEt-2,2'-(6,7,6',7'-dibenzo)-11-Me-thiatriCC iodide
67	MCY	Ref. [33]	H	0	4	1,1'-methylene-2,2'-cyanine iodide
68	MDI	Ref. [39]	H	2	8	1,1'-diMe-2,2'-diCC iodide
69	MT2	Ref. [39]	H	3	10	1,1'-diMe-2,2'-triCC iodide
70	MTC	Refs. [30,47]	D	1	6	3,3'-diMe-2,2'-thiaCC iodide, or tetrafluoroborate
71	NTD	NK1836/Ref. [30]	D	2	8	3,3'-diEt-9,11-neopentylene-2,2'-thiadiCC iodide
72	OCY	NK863/DOI	A	0	4	3,3'-diEt-2,2'-oxacyanine iodide
73	PIC	NK757/PIC	H	0	4	1,1'-diEt-2,2'-cyanine iodide
74	PIN	NK3/DCI-2/Pinacyanol I	H	1	6	1,1'-diEt-2,2'-CC iodide
75	TCY	NK88	D	0	4	3,3'-diEt-2,2'-thiacyanine iodide
76	TDB	NK716	G	1	6	3,3',9-triEt-2,2'-(4,5,4',5'-dibenzo)-thiaCC bromide
77	TDC	NK1056	F	1	6	3,3',9-triEt-2,2'-(6,7,6',7'-dibenzo) thiaCC iodide
78	TDO	NK1538	A	1	6	3,3',9-triEt-5,5'-diphenyl-2,2'-oxaCC iodide
79	TID	Ref. [32]	C	2	8	1,1'-diEt-3,3,3',3'-tetramethyl indodiCC perchlorate
80	TIF	Ref. [32]	C	2	8	1,1'-diEt-3,3,3',3'-10-fluoro-tetraMe-indodiCC perchlorate
81	THI	NK1414	C	3	10	1,1'-diEt-3,3,3',3'-tetraMe-2,2'-indotriCC iodide
82	TMT	Ref. [30]	D	1	6	3,3',9-triMe-2,2'-thiaCC iodide
83	TTC	NK737/Ref. [30]	D	1	6	3,3',9-triEt-2,2'-thiaCC iodide

The column T gives the end group type (A to H).

Column *n* gives the number of conjugated bond pairs added in the methine chain (0 for cyanines, 1 to 7 for carbocyanines).

Column *N* gives the shortest conjugated path measured by the number of bonds between the two resonant nitrogen atoms.

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