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Structure and properties of new classes of coupled polymethine dyes

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Dedicated to Professor Dr. Achim Mehlhorn on the occasion of his 60th birthday.

Abstract

The structure and the energy spectra of new classes of coupled polymethines (**CP**) (coupled cyanines, merocyanines and oxonoles) were investigated theoretically. The **CP**s may be considered as being composed of two identical or two different streptopolymethine fragments or as derivatives of poly(peri-naphthylene)s. All **CP**s display low-energy $^1S_o \rightarrow ^1S_1$ transitions with a high transition probability. The transition energies are comparable with those of the streptopolymethine substructures. The similarity of the energy spectra of streptopolymethines and **CP**s is determined by the symmetry of the frontier MOs of the streptopolymethine fragments and the **CP**s. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

After Williams [1] introduced the term cyanines (1856), and König (1922) [2] defined the class of polymethine compounds, these species were the subject of intense theoretical and experimental investigations [3].

The basic chromophores of polymethine dyes are the streptopolymethines—the oxonole anions **1**, the cyanine cations **2**, and the neutral merocyanines **3** (except for special cases, hereafter and below only one mesomeric formula of the corresponding molecules is given):

$$^{-}O-(CH=CH)_m-CH=O \quad (1)$$

$$R_2N-(CH=CH)_m-CH=N^+R_2 \quad (2)$$

$$R_2N-(CH=CH)_m-CH=O \quad (3)$$

The carbanions (carbocations, radicals) **4**:

$$CH_2-(CH=CH)_m-CH=CH_2]^{-(+)()} \quad (4)$$

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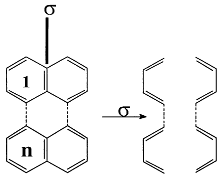
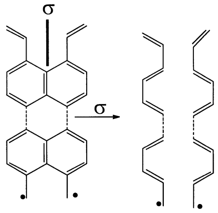
also belong to the polymethines, being at the same time a major structural unit of **1–3**. The polymethines can be considered to be derivatives of the simplest one-dimensional (1-D) π-systems, namely odd polyenes, i.e. the polymethine dyes are α,ω-substituted odd polyenes.

The poly(peri-naphthylene)s (**PPN**) and their derivatives **P**



PPN (n)



P (n)

are 1-D π-systems whose topology is similar to the topology of even polymethines–polyenes and odd polyenes, respectively. The symmetry groups of **PPN**s and **P** are D_{2h} and C_{2v}, respectively (here, and below, we consider the symmetry of the π-electron framework). The frontier MOs, the HOMO and LUMO of **PPN**s ($n = 1, 2, 3, ...$), belong to the irreducible representation a_u (HOMO) and b_{3g} (LUMO), i.e. they are asymmetric with respect to the reflexion at the symmetry plane σ. The frontier MOs of the **P**s ($n = 1, 2, 3, 4$) are characterized by the irreducible representation b_1, i.e. they are also asymmetric with respect to the reflexion at the symmetry plane σ. For both π-systems, the mirror plane σ is a nodal plane, and the frontier MOs are composed only from the 2p AOs of the π-centers along the periphery of **PPN**s and **P**s.

The MOs constituting the frontier (HOMO and LUMO) bands of **PPN**s with cyclic boundary conditions (symmetry group $D_{(2n)h}$), investigated in Refs. [4,5], belong to the irreducible representation E_{j-}:

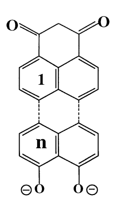
$$\{E_{j-}\} = \{E(2\chi)u\} \cup \{E(2\chi + 1)g\}$$

The characters of these representations with respect to the mirror symmetry plane (σ_h) perpendicular to the symmetry axis ($\mathbf{C}_{2n}$) have a value $\chi(\sigma_h) = -1$. Therefore, the MOs belonging to E_{j-} are asymmetric with respect to the reflexion at σ_h.

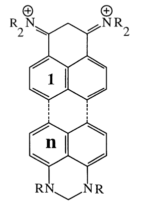
Because the **PPN**s and **P**s are alternant π-systems, it follows that

$$\text{E(HOMO)} = -\text{E(LUMO)}$$

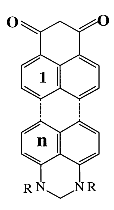
The HMO frontier orbitals a_u and b_{3g} of **PPN(n)**s are isoenergetic with the orbitals of even polyenes with $2n$ double bonds. This means that in topological (HMO) approximation the HOMO–LUMO gap ΔE of **PPN(n)**s is identical with those of even polyenes, and the HOMO–LUMO gap ΔE of **P**(n)s is identical with those of odd polyenes (polymethines). It is remarkable that the derivatives of **PPN**s, namely the coupled **PPN**-polymethines (**CP**) with C_{2v} symmetry have the same symmetry properties as the **P**(n)s:



Ox-Ox



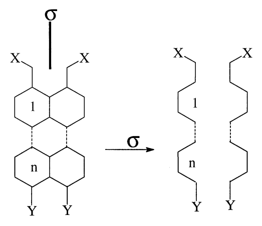
Cy-Cy



Me-Me

CP-C_{2v}

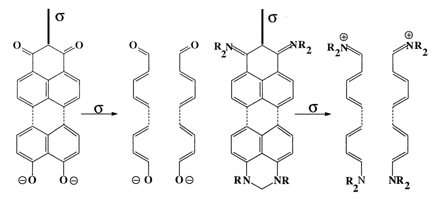
A general formula of the **CP**s with C_{2v} symmetry can be written in the following manner:



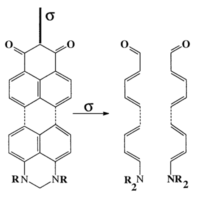
The frontier MOs of this class of molecules belong to the irreducible representation b_1, i.e. they are also asymmetric with respect to the reflexion at the symmetry plane σ.

Hence, the HOMO–LUMO gap ΔE of the three classes of polymethines **Ox–Ox**, **Cy–Cy** and **Me–Me** is identical with the HOMO–LUMO gap ΔE of the corresponding streptopolymethineoxonoles

Ox, streptopolymethinecyanines **Cy** and streptopolymethinemerocyanines **Me**, respectively:

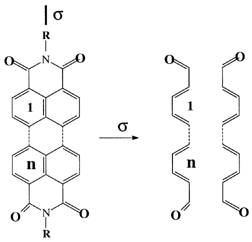


Ox-Ox **Ox** **Cy-Cy** **Cy**



Me-Me **Me**

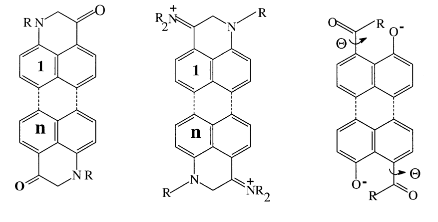
The synthesis and the spectral properties of the dyes **A**(n) with R = hydrogen, alkyl or aryl:



A(n) **D(n)**

are well known [6] (see also Refs. [7,8]). The HOMOs and LUMOs of this class of π-systems are also asymmetric with respect to the reflexion at the symmetry plane σ. However, the molecules **A**(n) do not belong to the polymethine dyes because the number of the methine groups in the polyenedione substructure **D**(n) is even.

Theoretically more attractive are the spectral properties of the **CP**s whose sub-structures are streptopolymethines with N π-centers and $(N+1)$ π-electrons [3]. There are two sub-groups of polymethines which are derivatives of **PPN**s. The molecules of the first sub-group **Ox–Ox**, **Cy–Cy**, and **Me–Me** belong to the symmetry group C_{2v}. The molecules with C_{2h} symmetry (**CP**-C_{2h}):

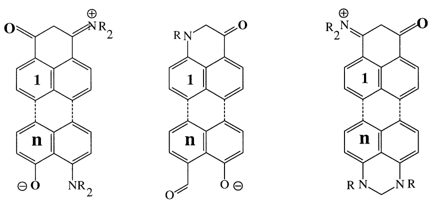


Me-Me (C_{2h}) **Cy-Cy (C_{2h})** **Ox-Ox (C_{2h})**

CP-C_{2h}

form a second sub-group of coupled polymethines which are isomeric with the molecules of the first group.

The molecules with the symmetry C_s, **CP**-C_s:



Ox-Cy **Ox-Me** **Cy-Me**

CP-C_s

belong to a third sub-group of **CP**s.

The symmetry properties of the frontier MOs (HOMO and LUMO) of the molecules of the second and the third sub-group are different in comparison with the molecules of the first sub-group, but all the three sub-groups are **CP**s.

The **PPN** polymethines can be considered to be coupled polymethines from the standpoint of Dähne's polymethine conception [9] (see also the papers of Fabian et al. [10,11]. The theoretical investigation of the structure and the energy spectra of this new class of polymethines is the aim of the present paper.

2. Methods of investigations

The energies of the singlet–singlet π–π* electronic transitions have been calculated by means of the PPP method using a geometry optimized with the quantum-chemical all-valence electron AM1 method [12,13].

A set of parameters was used [14]: $\beta_0(\mathrm{C-C}) = -2.318\,\mathrm{eV}$ at $R_0 = 1.40\,\text{Å}$; $\beta_{\mathrm{CN}} = -2.30\,\mathrm{eV}$, and

$\beta_{CO} = -2.6$ eV. The relationship between the resonance integrals between neighboring carbon atoms on the bond lengths R has been calculated using Mulliken's formula [15]: $\beta(R) = \beta_0\ S(R)/S_0$, where S are the overlap integrals (calculated with $Z_C = 3.25$).

The two-center Coulomb integrals have been calculated using Mataga–Nishimoto potentials [16] with $\gamma_{CC} = 10.84$ eV, $\gamma_{NN} = 11.42$ eV and $\gamma_{OO} = 14.52$ eV. The configuration interaction includes all mono-excited singlet configurations. The following values of the valence state ionization potentials were used: $I_C = 11.42$ eV, $I_N = 19.42$ eV, and $I_O = 15.42$ eV.

3. Numerical results and discussion

3.1. Equilibrium geometry

A characteristic feature of the structure of streptopolymethines is the equalization of bond lengths within the polymethine chain. This concept of König [2] was confirmed later by Kuhn [17] and by Dähne et al. [18] (see also the references given in Ref. [3] and the paper of Mehlhorn et al. [19]) on the basis of quantum-chemical calculations, and experimentally by X-ray analyses [20,21]. The bond length equalization between the carbon atoms is typically expressed in the structures of streptopolymethinecyanines and streptopolymethineoxonoles with all-*trans* configuration [18,20,21]. The streptopolymethinemerocyanines show a more a polyene-like molecular geometry with alternating C–C bond lengths [3,18].

The nonamethineoxonole sub-structure **Ox**, the nonamethinecyanine sub-structure **Cy**, and the nonamethinemerocyanine sub-structure **Me** of the investigated **CPs** shown in Fig. 2 have a *trans*, *cis*, *trans*, *cis*, *trans*, *cis*, *trans*, *cis* configuration. Nevertheless, the bond lengths correspond qualitatively to those of the streptopolymethines with all-*trans* configuration, with the tendency of bond length equilization. For all **CPs** investigated in this paper, the bond lengths along the periphery of the peri-naphthylene framework show a more marked alternation.

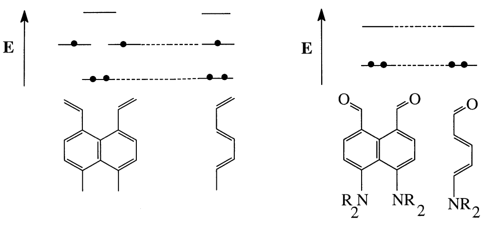


Fig. 1. MO scheme of **P(1)** and the odd polyene **4** (m = 2), and of the **CP**-C_{2v} (n = 1) merocyanine and the streptopolymethinemerocyanine **3** (m = 2).

3.2. Electronic excitation energies

In Tables 1–5 are collected the results of the calculated values of the longest-wavelength singlet–singlet transitions ΔE ($S_0 \rightarrow S_1$) of the different types of **CPs** with different polymethine chain lengths (peri-naphthylene units n). The corresponding values of the streptopolymethines are

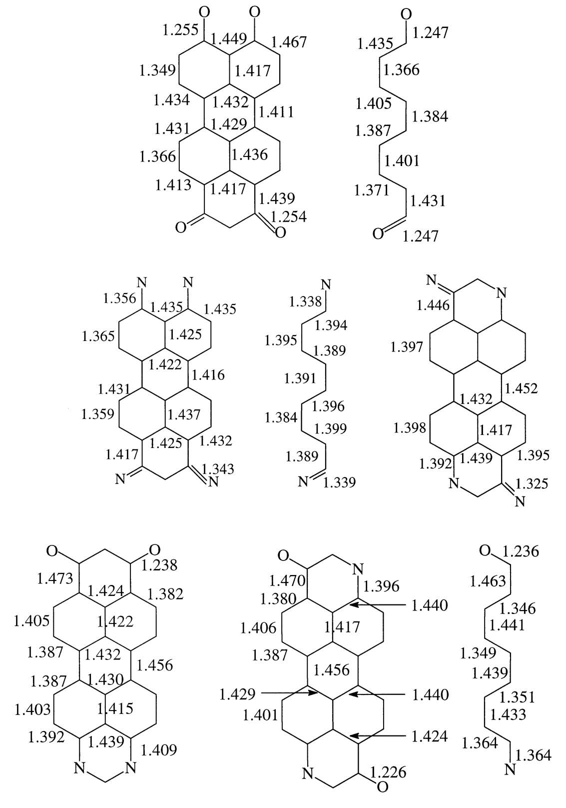
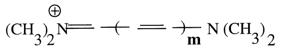


Fig. 2. Equilibrium geometry of different types of **CPs** obtained by means of the AM1 method (bond length in Å).

Table 1
Calculated values ΔE ($S_0 \rightarrow S_1$) (in eV) of the longest-wavelength singlet–singlet transitions and the oscillator strengths f of **Cy–Cy** polymethines, and calculated ΔE(**2**) and experimental values ΔE_{exp}(**2**) [30] of streptopolymethinecyanines **2**.



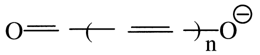
$(CH_3)_2\overset{\oplus}{N}{=}\left(-{=}-\right)_m N(CH_3)_2$

2

n	ΔE(**Cy–Cy**)	f	ΔE(**2**)	m	f	ΔE_{exp}(**2**)
1	2.728	0.263 [a]	2.982	2	1.311	2.981
2	2.223	1.389	2.096	4	2.038	1.984
3	1.927	2.180	1.622	6	2.628	1.462
4	1.737	2.864	1.321	8	3.068	–

[a] The transition $S_0 \rightarrow S_4$ has a value $f = 1.617$.

Table 2
Calculated values ΔE ($S_0 \rightarrow S_1$) (in eV) of the longest-wavelength singlet–singlet transitions of **Ox–Ox** polymethines, calculated ΔE(**1**) and experimental values ΔE_{exp}(**1**) [30] of streptopolymethineoxonoles **1**. **f** is the oscillator strength



$O{=}\left(-{=}-\right)_n O^{\ominus}$

1

n	ΔE(**Ox–Ox**)	f	ΔE(**1**)	m	f	ΔE_{exp}(**1**)
1	3.111	0.179 [a]	3.273	2	1.139	3.421
2	2.479	1.098	2.280	4	1.820	2.265
3	2.086	2.013	1.777	6	2.382	–
4	1.816	2.698	1.472	8	2.820	–

[a] The transition $S_0 \rightarrow S_4$ has a value $f = 1.617$.

Table 3
Calculated values ΔE ($S_0 \rightarrow S_1$) (in eV) of the longest-wavelength singlet-singlet transitions of **Me–Me–C**$_{2v}$ polymethines and calculated ΔE(**3**) and experimental values ΔE_{exp}(**3**) [30] of streptopolymethinemerocyanines **3**. f is the oscillator strength

$R_2N - (CH{=}CH)_m - CH{=}O$

3

n	ΔE(**Me–Me**)	f	ΔE(**3**)	m	f	ΔE_{exp}(**3**)
1	3.141	0.627	3.513	2	1.038	3.430
2	2.490	1.351	2.792	4	1.474	2.681
3	2.112	1.946	2.494	6	1.872	2.420
4	1.887	2.498	2.356	8	2.291	–
5	1.750	3.012	2.285	10	2.740	–

Table 4
Calculated values ΔE ($S_0 \rightarrow S_1$) (in eV) and oscillator strengths f of the longest-wavelength singlet–singlet transitions of **Me–Me**–C_{2h} (ΔE-Me) and **Cy–Cy**-C_{2h} (ΔE-Cy) polymethines and experimental values of the longest-wavelength singlet-singlet transitions of **A**(**2**) and **A**(**4**) [7]

n	ΔE(Me)	f	ΔE(Cy)	f	ΔE_{exp} [**A**(n)]
1	3.006	0.630	2.427	0.703	
2	2.288	1.148	1.486	0.744	2.340
3	2.033	1.793	1.236	0.898	
4	1.869	2.448	1.179	1.239	1.627

also given in the Tables for comparison. All the coupled polymethines display low-energy $^1S_0 \rightarrow {}^1S_1$ transitions with a high transition probability. The oscillator strength is $f > 1$ for $n \geqslant 2$. The lowest electronic excitation for all **CP**s is a strongly allowed transition to the $^1\mathbf{A}_1$ excited state. As in the case of streptopolymethines, the longest-wavelength transition is the HOMO–LUMO transition. The dominant electronic configuration corresponds to the HOMO–LUMO one-electron excitation. The contribution of other configurations is small. This is illustrated by the CI wave function of the $^1\mathbf{A}_1$ state for **Cy–Cy** with $n = 2$:

$$\Phi \approx 0.967 < 1 \mid 14 \rightarrow 15 \mid -0.131 < 1 \mid 13 \rightarrow 16 \mid - 0.119 < 1 \mid 12 \rightarrow 17 \mid$$

where $< 1 \mid i \rightarrow j \mid$ are the singlet electronic configurations corresponding to an excitation from the ith to the jth MO.

The longest-wavelength transition of **CP**s with $\mathbf{C}_{2h}$ and $\mathbf{C}_s$ symmetry, respectively, has also a HOMO-LUMO character.

In all cases, the transition energies of the **CP**s are comparable and not essentially different from the transition energies of the streptopolymethine sub-structures. This is an indication that the streptopolymethines which compose the **CP**s are the basic chromophores, i.e. the **CP**s may be considered as being composed of two streptopolymethine moieties.

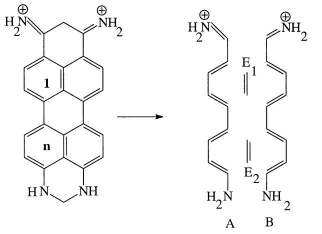
These qualitative considerations can be illustrated quantitatively using the MIM (molecule in

Table 5
Calculated values ΔE ($S_0 \rightarrow S_1$) and oscillator strengths f of the longest-wavelength singlet–singlet transitions of **Cy–Me** (ΔE-CM) with *Cs* symmetry[a]

n	ΔE(CM)	f
1	2.438	0.432
2	1.977	1.419
3	1.621	2.253
4	1.375	2.955

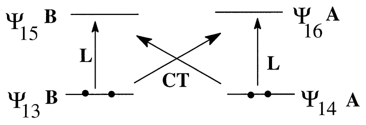
[a] The structures of other **CP**s with *Cs* symmetry, namely **Ox–Cy** and **Ox–Me** are not realistic.

molecule) method developed by Longuet-Higgins and Murrell [22] (see also Ref. [23]). We denote by **A**, **B** and $\mathbf{E}_{1(2)}$ the subunits which constitute the **Cy–Cy**($n = 2$) molecule:



The analysis of the CI wave functions, which involves the MOs of the **A**, **B** and $\mathbf{E}_{1(2)}$sub-units as basic functions, shows that the streptopolymethine-cyanines **A** (**B**) are the basic chromophore of the **Cy–Cy**($n = 2$) molecule.

The frontier SCF MOs are degenerate and asymmetric (with respect to the reflexion at the symmetry plane σ). They are constructed only from the 2p AOs of the fragment **A**: Ψ_{14} and Ψ_{16}, and from the 2p AOs of the fragment **B**: Ψ_{13} and Ψ_{15}:



There are two degenerate "Local Excitations" [22,23] **L** within the unit **A** and within the unit **B**, respectively. The correct CI wavefunctions:

$$\Phi(1) \approx 0.680 < 1 \mid 14 \rightarrow 16 \mid -0.704 < 1 \mid 13 \rightarrow 15 \mid$$

and

$$\Phi(2) \approx 0.695 < 1 \mid 14 \rightarrow 16 \mid +0.664 < 1 \mid 13 \rightarrow 15 \mid$$

correspond to the excitation energies: $\Delta E(1) = 1.637$ eV ($f = 0.019$) and $\Delta E(2) = 2.450$ ($f = 2.029$).

There are two degenerate "Charge Transfer Excitations" [22,23] **CT** from unit **B** to unit **A**, and from unit **A** to unit **B**, described by the CI wavefunctions:

$$\Phi(3) \approx 0.995 < 1 \mid 14 \rightarrow 15 \mid$$

and

$$\Phi(4) \approx 0.995 < 1 \mid 13 \rightarrow 16 \mid$$

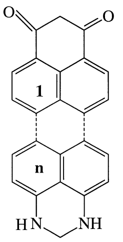
with an excitation energy $\Delta E(3) = \Delta E(4) = 1.975$ eV and $f = 0$.

3.3. Electronic properties

The uncharged **CP** molecules **Me–Me** display very large dipole moments. The values calculated using the AM1 method are collected in Table 6.

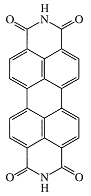
The static electronic polarizabilities in the ground and excited states are molecular characteristics

Table 6
Calculated values of the dipole moments μ (in Debye units) in the ground state of **Me–Me CP**s calculated by means of the AM1 method



n	μ
1	6.68
2	8.17
3	9.11
4	9.42
5	9.91

connected with the electronical and optical properties of extended π-electron systems [24,25]. The first-order and higher-order polarizabilities of streptopolymethines in the ground and excited electronic states were investigated theoretically in Ref. [26]. A systematical investigation of the electronic polarizabilities of **CP**s is in progress [27]. Here, we want to compare the results of the theoretically determined polarizabilites in the ground and the excited singlet states of **CP**s-C_{2v} with those of compound **A**(**2**), which has been investigated experimentally by Langhals [28].



A(2)

The calculations were carried out in π-electron approximation, i.e. only the π-components of the polarizabilities of first and higher orders were determined. The sum over states (SOS) approach [29] was realized within the PPP-CI algorithm described in detail in Ref. [26].

The input geometry for the calculation of the polarizabilities in the ground state was obtained by means of the AM1 method. This geometry was also used for the calculation of the polarizabilities in excited states.

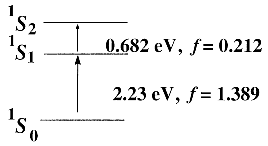
Table 7 shows data for the change of the polarizability upon excitation from the ground to the first and second excited singlet states for the **CP**s-C_{2v} and the molecule **A**(**2**).

Table 7
π-Electron components of the polarizability (α in Å^3) in ground ($^1S_0$), first ($^1S_1$) and second ($^1S_2$) excited singlet states for different **CP** and **A**(2) molecules

Molecule	α ($^1S_0$)	α ($^1S_1$)	α ($^1S_2$)
Cy–Cy ($n = 2$)	77.04	255.03	−145.66
Ox–Ox ($n = 2$)	65.89	90.05	92.82
Me–Me ($n = 2$)	59.37	57.87	57.16
A(2)	69.07[a]	69.07	51.14

[a] $\alpha(^1S_0)_{\text{exp}} = 224$; Ref. [28].

The significant change of the polarizability in the excited states in relation to the ground state of **Cy–Cy** is determined by the closely lying $^1S_1$ and $^1S_2$ excited states



A more correct calculation of the polarizabilities in the excited states requires a geometry optimization, investigations of which are in progress [27].

4. Conclusions

Based on Dähne's polymethine concept, poly (peri-naphthylene) polymethines can be considered as coupled polymethines which are composed of streptopolymethines. The bond lengths along the periphery of the peri-naphthylene framework show a more marked alternation, while the streptopolymethinecyanines and streptopolymethineoxonoles are characterized by an equalisation of the bond lengths within the polymethine chain. As in the case of the streptopolymethines, the longest-wavelength transitions of poly(peri-naphthylene) polymethines are HOMO–LUMO transitions. The transition energies and the oscillator strengths of the coupled polymethines investigated in this paper are in the same order of magnitude as those of the corresponding streptopolymethines. Therefore, the streptopolymethines are the basic chromophores of the poly(peri-naphthylene) polymethines. The uncharged dyes composed of streptopolymethinemerocyanines display very large dipole moments. In the case of the coupled cyanines, the π-components of the first-order static electronic polarizabilities change significantly in the excited singlet states in relation to the ground state.

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References

[1] Williams CHG. Trans Roy Soc Edinburgh 1856;21:377.
[2] König W. J Prakt Chem 1926;112:1.
[3] Tyutyulkov N, Fabian J, Mehlhorn A, Dietz F, Tadjer A. Polymethine dyes—structure and properties. Sofia: St. Kliment Ohridski University, 1991.
[4] Bredas JL, Baughman RH. J Chem Phys 1985;83:1316.
[5] Baumgarten M, Karabunarliev S, Koch K-H, Müllen K, Tyutyulkov N. Synth Met 1992;47:21.
[6] Zollinger H. Color chemistry. Weinheim (Germany): VCH, 1991.
[7] Quante H, Müllen K. Angew Chem 1995;107:1487.
[8] Geerts Y, Quante H, Platz H, Mahrt R, Hopmeier M, Böhm A, Müllen K. J Mater Chem 1998;8:2357.
[9] Dähne S, Leupold D. Angew Chem 1966;78:1029.
[10] Fabian J, Tröger-Naake G. J Prakt Chem 1976;318:801.
[11] Fabian J. J Prakt Chem 1978;320:361.
[12] Stewart JJP. MOPAC 6.00, QCPE, No 455.
[13] Spartan, version 3.0. Irvine (CA): Wavefunction, Inc.
[14] Radeglia R, Gey E, Nolte K-D, Dähne S. J Prakt Chem 1970;312:877.
[15] Mulliken RS. J Chem Phys 1949;46:497.
[16] Mataga N, Nishimoto K, Z Phys Chem 1953;13:140.
[17] Kuhn H. Helv Chim Acta 1957;34:1308.
[18] Dähne S, Moldenhauer F. In: Progress in physical organic chemistry, vol. 15. New York: Wiley, 1985. p 1.
[19] Mehlhorn A, Fabian J, Tyutyulkov N. Compt Rend Acad Bulg Sci 1982;35:335.
[20] Zedler A, Kulpe S. J Prakt Chem 1975;317:38.
[21] Ziemer B, Kulpe S. J Prakt Chem 1975;317:185.
[22] Longuet-Higgins HC, Murrell JN. Proc Phys Soc 1955;A68:601.
[23] Fabian J, Mehlhorn A, Dietz F, Tyutyulkov N. Monatsh Chem 1984;115:21.
[24] Andre J, Morley J, Zyss J. In: Marshal J, editor. Molecules in physics, chemistry, and biology, vol. 2. Dordrecht, (The Netherlands): Kluwer, 1988. p. 615.
[25] Andre J, Delhale J. Chem Rev 1991;91:843.
[26] Kanev I, Monev V, Dietz F, Tyutyulkov N. Molecular Engineering 1992;2:233.
[27] Dietz F, Tyutyulkov N. Unpublished data.
[28] Langhals H. Chem Phys Lett 1988;150:321.
[29] Buckinham A, Orr B. Quart Rev Chem Soc 1967; 21: 195.
[30] Malhotra SS, Whiting MC. J Chem Soc 1960:3812.