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First Examples of Dyes of the Pyridopyrylo- and Pyridopolycarbo-cyanine Series: Synthesis and Special Spectral–Luminescent Properties

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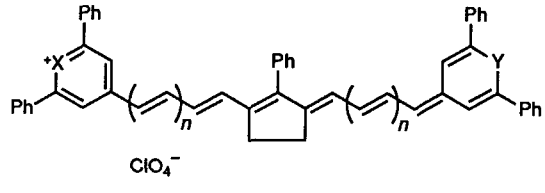
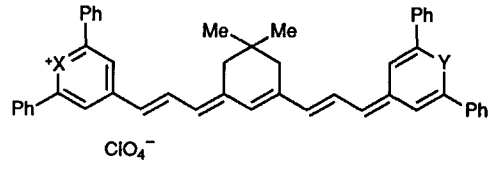
Pyridopyrlo- and pyridotri-, tetra- and penta-carbo-cyanines displaying unusual spectral–luminscent properties for polymethine dyes have been synthesized.

Attempts to obtain cyanine dyes with high electron asymmetry, containing a long polymethine chain (PC) and two heterocyclic residues, the electron-donor capacity of the former being much higher and that of the latter being much lower than average, have so far been unsuccessful. This is mainly due to difficulties encountered in the synthesis of such dyes by traditional cyanine condensation methods, since heterocycles of high and low electron-donor capacity undergo these reactions under incompatible conditions.[1]



1; X = NMe, Y = O, *n* = 0
3; X = NMe, Y = O, *n* = 1
4; X = Y = NMe, *n* = 0



2; X = NMe, Y = O
5; X = Y = NMe

This paper presents the first compounds of this series, pyridopyrylotri-, tetra- and penta-carbo-cyanines **1–3** prepared in good yields by treatment of the corresponding symmetric pyrylocyanines dissolved in acetonitrile or methylene chloride with excess of methylamine. This is quite unexpected for dyes with a long PC and low-electron-donor heterocyclic residues, for they display the maximum displacement of the positive charge from the heteroatom into the polymethine chromophore.[2] For this reason, the reactivity of the dye's heterocyclic residues towards nucleophiles should decrease substantially, compared with pyrylium salts, and the reactivity of the PC should be high. On heating the initial pyrylocyanines with excess of methylamine in dimethyl sulphoxide (DMSO) at 80–90 °C for 0.5–1.0 h, the symmetrical pyridotri- and tetracarbocyanines **4**, **5** are obtained. Dye **5** is the first in the series of symmetric tetracarbocyanines containing heterocyclic residues of high electron-donor strength. Owing to the high sensitivity

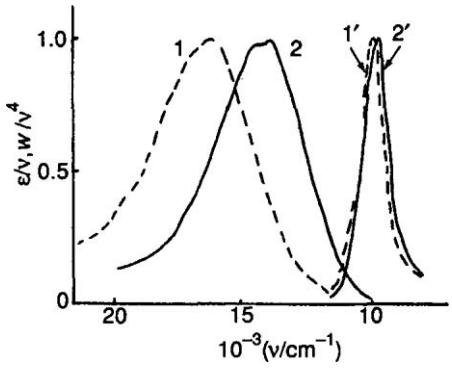


Fig. 1 Absorption (1, 2) and fluorescence (1′, 2′) spectra for dye **2** in acetonitrile (1, 1′) and dichloromethane (2, 2′)

of the dye solutions to traces of moisture, carbon dioxide and oxygen, we did not succeed in sufficiently precise measurement of the mala-absorption coefficients of compounds **4** and **5**. It should be noted that we were unable to prepare analytically pure 1,3-dimethylbenzimidazotetracarbocyanine *via* the usual cyanine condensation, and the electron-donor ability of its end-residues is much the same as that of the pyridine end-residues.[3,4] Thus the method presented here is preferable for preparing not only unsymmetric pyridopolycarbocyanines, but symmetric ones as well.

It is necessary to point out, that the vinylene shifts of the unsymmetric pyridopyrylocyanines **3–5**, unlike the corresponding symmetric dyes, converge with increasing chain length, and thus their absorption maxima lie near the long-wave limit of carotenoid absorption.[3] This suggests that the bond order alternation in the ground state of dyes **1–3** is of the same order of magnitude as that of polyenes.[3] Such a pronounced bond order alternation is caused by the strong electronic asymmetry of pyridopyrylocyanines **1–3**. The value of the spectral deviation serves as a quantitative measurement of this asymmetry.[3] In fact the deviation values (D^a) of dyes **1–3** substantially exceed those of the most electronically unsymmetrical cyanines known at present.[5] Thus compounds **1–3** are the most extreme polymethine dyes known in terms of their electronic asymmetry.

The data in Table 1 confirm that pyridopyrylocyanines **3–5** show strong solvatochromism, which increases uniformly on lengthening the PC. For pentacarbocyanine **3**, the solvatochromic shift in fact exceeds the highest known value of unsymmetric polymethines,[5] and also that for many highly solvatochromic merocyanines.[6]

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Table 1 Yields, melting points (T_m), absorption maxima (λ^a_{max}) and fluorescence (λ^f_{max}) bands, deviations of these maxima (D^a and D^f), molar absorption coefficients (ϵ) and Stokes shifts (ΔS) for dyes **1–5**

Dye	Yield/%	T_m/°C	Solvent	λ^a_{max}/nm	D^a/nm	$(\epsilon/mol^{-1}\ dm^3\ cm^{-1}) \times 10^{-4}$	λ^f_{max}/nm	D^f/nm	ΔS/nm
1	78	256–258	CH_2Cl_2	730	235	7.12	970	66	240
			MeCN	635	309	6.12	965	50	330
2	40	232–233	CH_2Cl_2	704	319.5	7.06	1030	60	326
			MeCN	610	387.5	6.74	1020	35	410
3	50	251–252	CH_2Cl_2	760	440	6.33			
			MeCN	625	545	6.44			
4	67	208–210	CH_2Cl_2	945			1012		67
			MeCN	920			995		75
5	65	178–180	CH_2Cl_2	1015			1070		55
			MeCN	990			1040		50

Pyridopyrylocyanines **1** and **2** demonstrated the largest Stokes shifts yet observed for an organic dye (see Table 1).

It was also found from the fluorescence spectra that passing from the unsymmetric tricarbocyanine **1** to the tetracarbocyanine **2** is accompanied by a marked bathochromic shift, contrary to the hypsochromic shift observed for the absorption spectra. The absolute value of the bathochromic shift is of the same order of magnitude as that for the series of corresponding symmetric dyes. The deviations in the fluorescence spectra are much smaller than those for absorption (see Table 1). The band shapes are similar in the fluorescence and absorption spectra, though the former are much narrower (Fig. 1). The solvatofluorochromic effects for the pyridopyrylocyanines are substantially weaker than the solvatochromic effects.

The low deviations and small solvatochromism found in the fluorescence spectra of the unsymmetric dyes indicates that the excited state structures are energetically more symmetric and they resemble the symmetric cyanines in spite of their extremely high asymmetry in the ground state. This conclusion agrees well with HMO quantum-chemical calculations for pyridopyrylocyanines analogous to those carried out in ref. 5, indicating that the atomic charges and bond orders in the dye cations become much more uniform on excitation. For instance, the net charges on the pyridinium and pyrylium residues of the tetracarbocyanine **2** are 0.910 and 0.274, respectively, in the ground state and 0.634 and 0.467 in the excited state. The bond order alternation parameter introduced in ref. 7 is 0.159 for the S_0 state and 0.116 for the S_1 state. The very large difference between the ground and excited states with respect to the electron density distribution leads to the large Stokes shifts observed for the unsymmetric dyes. The charge equalization which occurs on excitation weakens the Coulomb interactions between the dye and the solvent molecules and hence the solvatofluorochromic shifts are considerably smaller than the solvatochromic shifts. The fact that the bond orders in the excited state are more uniform than those in the ground state explains why the fluorescence spectra of the synthesized pyridopyrylocyanines show decreased deviations, narrow emission bands and an increase in the vinylene shifts relative to those of the absorption spectra.

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