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Synthesis of Amphiphilic Styrylpyridinium and Styrylquinolinium Hemicyanines and Merocyanines

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ABSTRACT

Amphiphilic polymethine dyes are synthesized by alkylation of 4-methylpyridine and 4-methylquinoline and consequent condensation with hydroxy- or amino-substituted aromatic aldehydes. The resulting dyes are characterized with respect to their absorption and emission spectra. The synthetic approach is generic in that it allows adjustment of the physical properties of the respective dyes (absorption, fluorescence, charge transfer, lipophilicity) and provides chromophores useful for the preparation of Langmuir–Blodgett films with non-linear optical properties and as potential sensitive dyes in analytical chemistry.

1 INTRODUCTION

Polymethine dyes based on hydroxy- and aminostyrylpyridinium salts have been known for decades and have been thoroughly investigated in terms of solvatochromism and structure–colour relationships.[1] These dyes have now gained increasing interest not only because of the effect of solvent polarity on their optical properties, but also because of their potential applicability in non-linear optics, as optical sensors, and in physiology/biochemistry areas.

Hydroxystyrylpyridinium dyes in their deprotonated phenolbetaine form have been used for the investigation and quality control of solvents,

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due to their marked solvatochromism.[2] Of the dyes exhibiting betaine structure, ET 30 as a non-polymethine compound has found widespread application in scientific research.[3]

Aminostyrylpyridinium halides have been utilized in physiology studies for the investigation of cells and axons and transport mechanisms through cell membranes. Depending on the potential inside and outside the cell, either the charge of the dye fixed in the cell membrane or the dye itself moves between the aqueous and organic membrane interface, causing changes in its optical properties.[4,5]

Dyes with related structures have also found application in optical sensing of ionic species in aqueous samples. The so-called optodes are obtained by entrapment of solvatochromic 'potential-sensitive dyes' (PSDs) and selective carriers in a plasticized PVC membrane coated onto a polymer support. Again, the combined ion exchange or co-extraction of analyte ion and charged indicator between the aqueous and organic interphase is responsible for the analyte-induced signal change.[6–8]

Finally, polymethine dyes with significant charge shift between ground and excited state, particularly hemicyanines,[9] have been shown to exhibit non-linear optical properties such as second or third harmonic generation. These effects, which can be observed in both solutions and organized systems such as LB layers and crystals render these dyes promising candidates in the development of optical data storage systems or optical switching devices.[10]

In view of the usefulness of solvatochromic hemicyanine and merocyanine dyes, new compounds with easily varied structures and physical properties have been synthesized in this study. The dyes have been characterized with respect to their optical properties (absorption and fluorescence).

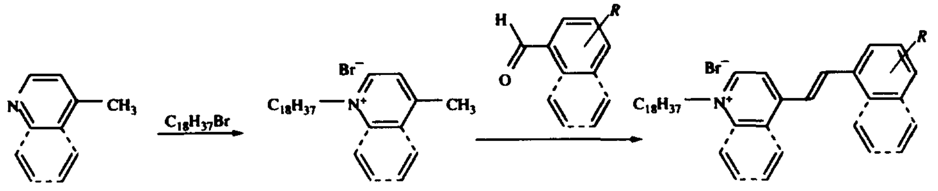
2 EXPERIMENTAL

2.1 Apparatus

Absorption spectra were recorded on a Perkin Elmer PE Lambda 16 UV/VIS spectrophotometer; fluorescence spectra were recorded on a PE LS 50 spectrofluorometer. Melting points were determined on a Kofler apparatus and are uncorrected.

2.2 Reagents

The reagents used for the synthesis of the dyes were of synthetic grade. The chemicals used for spectroscopic investigations were of analytical



Scheme 1

reagent grade. Absorption and fluorescence spectra of the dyes were recorded using trichloromethane and acetonitrile as solvents, and the acid and base forms were obtained by the addition of trace amounts of 70% perchloric acid or triethanolamine, respectively.

2.3 Synthetic procedure

The dyes were obtained following the general Knoevenagel condensation mechanism. The educts were reacted via two routes: (a) in methanol or absolute ethanol with piperidine as the catalyst; or (b) in acetic anhydride. The dyes obtained via route (a) were usually precipitated after reacting the respective aldehyde and the CH-acid by refluxing for 8 h and cooling the mixture to room temperature (Scheme 1). The dyes obtained via route (b) were also reacted for 8 h at reflux in acetic anhydride and then cooled to −15°C in order to precipitate the product. Products were washed twice, with acetic acid and diethyl ether, and dried in air at ambient temperature.

The crude reaction products from both routes were usually recrystallized from methanol, in some cases with addition of 5% of distilled water. For dyes containing a deprotonable aromatic hydroxy group, water was replaced with 48% hydrobromic acid in order to obtain the protonated form of the dyes.

2.3.1 4-Methyl-1-octadecylpyridinium bromide

4-Methylpyridine (2·8 g) was reacted with 10·0 g octadecylbromide at 130–140°C for 3 h. The resulting melt was recrystallized from 200 ml ethyl acetate to yield 11·5 g of the pale white product (m.p. 91°C). Calculated/found for $C_{24}H_{44}NBr + H_2O$: C 64·84/64·73; H 10·43/10·14; N 3·15/3·37.

2.3.2 4-Methyl-1-octadecylquinolinium bromide

4-Methylquinoline (4·3 g) was reacted with 10·0 g octadecylbromide at 130–140°C for 3 h. The resulting melt was recrystallized from 600 ml ethyl acetate to yield 5·5 g of the pale blue product (m.p. 75°C). Calculated/found for $C_{28}H_{46}NBr + H_2O$: C 68·00/67·79; H 9·78/9·72; N 2·83/3·49.

*2.3.3 4-[2-(4-Aminophenyl)-ethenyl]-1-octadecylchloride (**1a**)*

(i) 4-[2-[4-Acetamidophenyl]ethenyl]-1-octadecylbromide was obtained by the reaction of 1·95 g 4-acetamidobenzaldehyde with 5·00 g 4-methyl-1-octadecylpyridinium bromide and 1·0 ml piperidine in 30 ml methanol; this yielded 4·5 g of an orange amorphous compound which was recrystallized from 70 ml methanol (m.p. 237–243°C). Calculated/found for $C_{33}H_{51}N_2OBr$: C 69·33/69·52; H 8·99/9·43; N 4·90/4·78.

(ii) Hydrolysis of the acetyl group was performed by refluxing 3·0 g of compound **9** in a solution of 30 ml concentrated hydrochloric acid and 30 ml ethanol for 2 h. After treating the resulting mixture with a saturated solution of aqueous sodium carbonate, the orange dye (2·4 g) precipitated in crystalline form (m.p. 245–250°C). Calculated/found for $C_{31}H_{49}N_2Cl$: C 76·74/76·29; H 10·18/9·46; N 5·77/5·56.

*2.3.4 4-[2-(4-Diethylaminophenyl)-ethenyl]-1-octadecylpyridinium bromide (**1b**)*

Compound **1b** was prepared by following route (a), and reacting 0·21 g 4-diethylaminobenzaldehyde with 0·5 g 4-methyl-1-octadecylpyridinium bromide and 0·15 ml piperidine in 4 ml methanol; the m.p. of the red crystalline compound (0·48 g) was 211–214°C. Calculated/found for $C_{35}H_{57}N_2Br$: C 71·87/71·81; H 9·83/9·98; N 4·79/4·69.

*2.3.5 4-[2-(Julolid-4-yl)-ethenyl]-1-octadecylpyridinium bromide (**1c**)*

Following route (a), 0·47 g julolid-4-ylaldehyde[11] was reacted with 1·0 g 4-methyl-1-octadecylpyridinium bromide and 0·2 ml piperidine in 6 ml methanol; the m.p. of the red crystalline compound (1·26 g) was 135–142°C. Calculated/found for $C_{37}H_{57}N_2Br$: C 72·88/72·57; H 9·42/9·50; N 4·59/4·47.

*2.3.6 4-[2-(4-Dimethylaminonaphth-1-yl)-ethenyl]-1-octadecylpyridinium bromide (**1d**)*

Compound **1d** was obtained via route (a), by reaction of 0·34 g 4-dimethylaminonaphthaldehyde with 0·7 g 4-methyl-1-octadecylpyridinium bromide and 0·14 ml piperidine in 5 ml methanol; the m.p. of the orange crystalline compound (0·40 g) was 195–201°C. Calculated/found for $C_{37}H_{55}N_2Br$: C 73·12/73·09; H 9·12/9·45; N 4·61/4·48.

*2.3.7 4-[2-(Julolid-4-yl)-ethenyl]-1-octadecylquinolinium bromide (**1e**)*

Compound **1e** was obtained via route (b), by reacting 0·21 g julolid-4-ylaldehyde with 0·5 g 4-methyl-1-octadecylquinolinium bromide in 3 ml acetic anhydride; the m.p. of the blue crystalline compound (0·43 g) was 174–182°C. Calculated/found for $C_{41}H_{59}N_2Br + CH_3COOH$: C 71·47/71·75; H 8·82/8·69; N 3·91/3·93.

*2.3.8 4-[4-(4-Dimethylaminophenyl)-1,3-butadienyl]-1-octadecylpyridinium bromide (**1f**)*

Compound **1f** was obtained via route (a), by reaction of 0·41 g 4-dimethylaminocinnamic aldehyde with 1·0 g 4-methyl-1-octadecylpyridinium bromide and 0·2 ml piperidine in 6 ml methanol to yield a dark red amorphous compound (0·67 g); m.p. 205–210°C. Calculated/found for $C_{35}H_{55}N_2Br$: C 72·86/71·56; H 9·50/9·78; N 4·80/4·67.

*2.3.9 4-[2-(4-Dimethylaminophenyl)-ethenyl]-1-octadecylquinolinium bromide (**1g**)*

Compound **1g** was obtained via route (a), by reacting 0·31 g 4-dimethylaminobenzaldehyde with 1 g 4-methyl-1-octadecylquinolinium bromide and 0·2 ml piperidine in 5 ml methanol; the m.p. of the purple compound (0·55 g) was 98–105°C. Calculated/found for $C_{37}H_{55}N_2Br$: C 73·12/73·43; H 9·12/9·40; N 4·61/4·46.

*2.3.10 4-[2-(7-Diethylamino-2-oxo-2H-benzopyran-3-yl)-ethenyl]-1-octadecylpyridinium bromide (**2a**)*

Compound **2a** was obtained via route (b), by reacting 0·5 g 7-diethylamino-3-formyl-2-oxo-2H-benzopyran[12] with 0·87 g 4-methyl-1-octadecylpyridinium, bromide in 6 ml acetic anhydride (0·70 g); m.p. 201–206°C. Calculated/found for $C_{38}H_{57}N_2O_2Br$: C 69·81/69·43; H 8·79/8·89; N 4·28/4·14.

*2.3.11 4-[2-(7-Diethylamino-2-oxo-2H-benzopyran-3-yl)-ethenyl]-1-octadecylquinolinium bromide (**2b**)*

Compound **2b** was obtained via route (b), by reacting 0·5 g 7-diethylamino-3-formyl-2-oxo-2H-benzopyran[13] with 0·97 g 4-methyl-1-octadecylquinolinium bromide in 6 ml acetic anhydride (0·74 g); m.p. 101–104°C. Calculated/found for $C_{42}H_{59}N_2O_2Br + H_2O$: C 69·88/70·24; H 8·52/8·75; N 3·88/3·53.

*2.3.12 4-[2-(Indol-3-yl)-ethenyl]-1-octadecylpyridinium bromide (**3**)*

Compound **3** was obtained via route (a), by reaction of 0·35 g indol-3-carbaldehyde, 1·0 g 4-methyl-1-octadecylpyridinium bromide and 0·2 ml piperidine in 6 ml absolute ethanol; the m.p. of the orange crystalline compound (0·85 g) was 252–260°C. Calculated/found for $C_{33}H_{49}N_2Br$: C 71·59/71·27; H 8·92/8·94; N 5·06/4·85.

*2.3.13 4-[2-(4-Hydroxyphenyl)-ethenyl]-1-octadecylpyridinium bromide (**4a**)*

Compound **4a** was obtained via route (a), by reacting 0·6 g 4-hydroxybenzaldehyde with 2·0 g 4-methyl-1-octadecylpyridinium bromide and 0·4 ml piperidine in 12 ml methanol; the m.p. of the yellow product (1·58 g) was 260–265°C. Calculated/found for $C_{31}H_{48}NOBr + H_2O$: C 67·87/67·53; H 9·19/9·17; N 2·55/2·53.

*2.3.14 4-[2-(4-Hydroxyphenyl)-ethenyl]-1-octadecylquinolinium bromide (**4b**)*

Compound **4b** was obtained via route (a), by reacting 0·56 g 4-hydroxybenzaldehyde with 2·0 g 4-methyl-1-octadecylquinolinium bromide and 0·4 ml piperidine in 12 ml methanol; the m.p. of the resulting orange compound (1·5 g) was 190–196°C. Calculated/found for $C_{35}H_{50}NOBr$: C 72·39/72·12; H 8·68/8·57; N 2·41/2·55.

*2.3.15 4-[2-(4-Hydroxynaphth-1-yl)-ethenyl]-1-octadecylquinolinium bromide (**4c**)*

Compound **4c** was obtained via route (a), by reacting 0·5 g 4-hydroxynaphthaldehyde[14] with 1·4 g 4-methyl-1-octadecylquinolinium bromide and 0·25 ml piperidine in 10 ml ethanol; the m.p. of the dark red crystalline product (0·95 g) was 170–175°C. Calculated/found for $C_{39}H_{52}NOBr$ + $2H_2O$: C 70·25/70·19; H 8·47/8·53; N 2·10/2·11.

*2.3.16 4-[2-(2-Hydroxyphenyl)-ethenyl]-1-octadecylpyridinium bromide (**4d**)*

Compound **4d** was obtained via route (a), by reacting 0·50 g salicylaldehyde with 2·0 g 4-methyl-1-octadecylpyridinium bromide and 0·4 ml piperidine in 12 ml methanol; the m.p. of the yellow crystalline compound (1·6 g) was 205–214°C. Calculated/found for $C_{31}H_{48}NOBr$: C 70·17/71·06; H 9·12/9·47; N 2·64/2·75.

*2.3.17 4-[2-(4-Hydroxy-3,5-dimethoxyphenyl)-ethenyl]-1-octadecylpyridinium bromide (**4e**)*

Compound **4e** was obtained via route (a), by reacting 0·85 g 4-hydroxy-3,5-dimethoxybenzaldehyde with 2·0 g 4-methyl-1-octadecylpyridinium bromide and 0·4 ml piperidine in 12 ml methanol. The orange product (1·4 g) melted at 138–141°C. Calculated/found for $C_{33}H_{52}NO_3Br$: C 67·10/66·54; H 8·87/8·86; N 2·37/2·45.

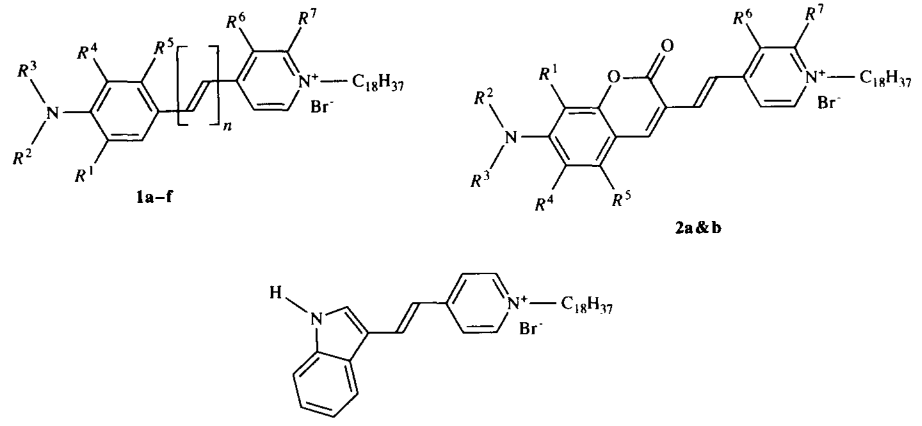
*2.3.18 4-[2-(2-Hydroxynaphth-1-yl)-ethenyl]-1-octadecylpyridinium bromide (**4f**)*

Compound **4f** was obtained via route (a), by reacting 0·4 g 2-hydroxy-1-naphthaldehyde with 1·0 g 4-methyl-1-octadecylpyridinium bromide and 0·2 ml piperidine in 6 ml ethanol; the m.p. of the orange compound (0·67 g) was 141–148°C. Calculated/found for $C_{35}H_{50}NOBr$: C 72·39/71·90; H 8·68/8·71; N 2·41/2·33.

3 RESULTS AND DISCUSSION

3.1 Synthetic strategy

The aim of this work was to use a generic synthetic route which would provide a wide range of amphiphilic solvatochromic hemicyanine and



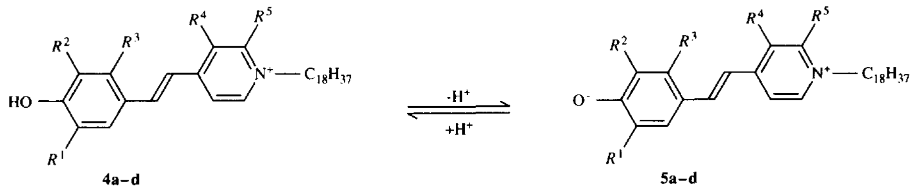
	R^1	R^2	R^3	R^4	R^5	R^6	R^7	n
1a	H	H	H	H	H	H	H	1
1b	H	C_2H_5	C_2H_5	H	H	H	H	1
1c	$(CH_2)_3$		$(CH_2)_3$		H	H	H	1
1d	H	CH_3	CH_3	$(CH{=}CH)_2$		H	H	1
1e	$(CH_2)_3$		$(CH_2)_3$		H	$(CH{=}CH)_2$		1
1f	H	CH_3	CH_3	H	H	H	H	2
1g	H	CH_3	CH_3	H	H	$(CH{=}CH)_2$		1
2a	H	C_2H_5	C_2H_5	H	H	H	H	1
2b	H	C_2H_5	C_2H_5	H	H	$(CH{=}CH)_2$		1

Scheme 2

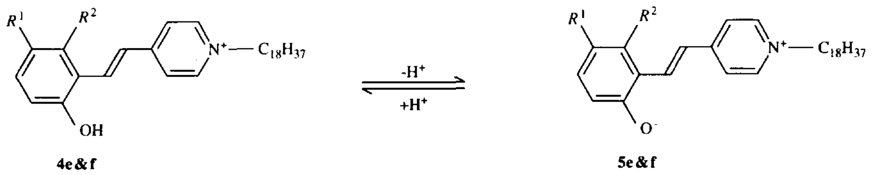
merocyanine dyes, or their protonated stilbazolium salt counterparts, by using readily available synthons to afford molecules which contain both long alkyl chains and a reactive CH-acid group in order to couple the educts to any available substituted aldehyde. Synthons were obtained using 4-methylpyridine and 4-methylquinoline, which can be easily converted into the respective lipophilic derivatives by reacting them with appropriate alkylhalogenides. The resulting 4-methyl-1-alkylpyridinium bromides and 4-methyl-1-alkylquinolinium bromides were then reacted with derivatives of benzaldehyde and comparable compounds (Schemes 2 and 3). The properties of the dyes could be adjusted to their respective application by reacting the CH-acid substances with sultones, halogen carbonic acids, alkyl halides, trimethylammoniumalkyl halogenides, and similar compounds.[15]

3.2 Optical properties and structure–colour relationship

The absorption and emission spectra of the compounds synthesized are given in Table 1. The wavelength of the lowest energy transition of the



	R^1	R^2	R^3	R^4	R^5
4a/5a	H	H	H	H	H
4b/5b	H	H	H	$(CH=CH)_2$	
4c/5c	H	$(CH=CH)_2$		$(CH=CH)_2$	
4d/5d	CH_3O	CH_3O	H	H	H



	R^1	R^2
4e/5e	H	H
4f/5f	$(CH=CH)_2$	

Scheme 3

amino-substituted cyanine dyes varies between 440 nm and 600 nm, depending on the length of the donor–acceptor chromophore and is more pronounced on further benzo-condensation or substitution of the chromophore.

A surprising observation was the absence of any vinylene shift between **1b** and **1f**. The vinylene shift is usually significantly smaller with hemicyanines compared with more ideal cyanines.[16] However, its complete absence, together with a hypochromic effect, requires an explanation. It might indicate a high conformational flexibility which effectively shortens the chromophore.

The remarkably large Stokes shift of **1f** in acetonitrile compared with trichloromethane as solvent indicates a considerable geometric relaxation of the S_1 state in a solvent of high polarity. The relaxation of the S_1 state will be further studied.

The betaines represent merocyanines with large solvatochromism, due to solvent sensitive mesomerism between the quinoid and aromatic π-electron distributions. Upon protonation, the aromatic structure becomes dominant, thus causing a hypsochromic shift of the absorption and a decrease in the solvatochromism. These observations fit well to known

TABLE 1
Spectroscopic Data for Compounds **1–5**

Compound	*Acetonitrile*			*Trichloromethane*		
	λ_{max} *(nm)*	ε *(l mol^{-1} cm^{-1})*	λ_{fmax} *(nm)*	λ_{max} *(nm)*	ε *(l mol^{-1} cm^{-1})*	λ_{fmax} *(nm)*
1a	439	34400	578	439	n.d.	547
1b	487	49700	619	508	57300	598
1c	517	37600	651	537	57600	615
1d	448	20100	660	476	16500	624
1e	600	37800	n.f.	607	41500	692
1f	485	38200	703	507	35500	615
1g	541	31200	694	553	34700	652
2a	500	48100	650	520	46500	633
2b	545	52900	715	556	55400	691
3	428	38200	537	437	33400	519
4a	383	28600	499	402	17500	492
5a	533	45600	604	606	66600	n.f.
4b	428	28200	557	440	21500	557
5b	655	66900	n.f.	674	90100	n.f.
4c	473	16300	628	492	15100	624
5c	682	43600	n.f.	690	34300	n.f.
4d	376	24600	511	393	16700	506
5d	531	24800	n.f.	588	26400	n.f.
4e	408	31000	563	424	30900	532
5e	637	78300	n.f.	665	84900	n.f.
4f	415	20400	497	437	13100	493
5f	598	53600	n.f.	625	57500	n.f.

n.f. No fluorescence detectable.
n.d. Not determined due to poor solubility.

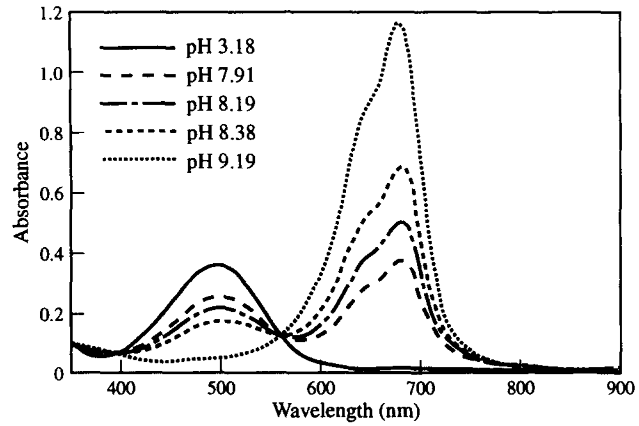


Fig. 1. Absorption spectra of compounds **4c** and **5c** as a function of pH.

observations and conclusions as first discussed by Hünig.[1] Figure 1 shows an example (for substance **4c**) of the absorption spectra as a function of pH in an ethanol/water (1:1 per volume) mixture; we determined a pK_a of 8·23 ± 0·01 for **4c**.

Measurements of the first and second hyperpolarizability values are in progress. The results will be published, together with quantum chemical calculations, in a forthcoming paper.

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