Organometallics in Cyanine Chemistry − Synthesis, Reactivity and Photophysical Properties of some Heptamethine Merocyanine Dyes

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A one-pot reaction between lithium reagents of ketones and pentamethine cyanine dyes affords a series of seven-carbon merocyanines in good to excellent yields. In subsequent reactions with "soft" organolithium reagents they can be easily converted into anionic cyanine dyes, oxonols. The synthetic potential and limitations of this reaction are discussed. Absorption and fluorescence behavior of the studied merocyanines were found to depend on their substitution patterns and the solvent used. Based on the relationship between the absorption maxima and ET(30) (= solvent polarity parameter) constants, a different nature of the absorbing state in protic and non-protic solvents can be assumed.

Introduction

The continually growing interest in the synthesis, design and reactivity of cyanine dyes stems from their large range of applications, widely documented in numerous papers, patents and reviews.[1] Depending on the charge on the polymethine unit, cyanine dyes can be classified into three main groups: cationic (cyanine and hemicyanine) dyes, anionic (oxonol) dyes and neutral (merocyanine) dyes.

In the search for a new synthetic application of organometallic reagents, known to be of fundamental importance for a multitude of chemical transformations, we recently examined the reactivity of organolithium reagents towards cationic pentamethine cyanine dyes. It was established that the factors governing the regioselectivity of the nucleophilic addition (C1/C5 vs. C3 attack on the alternate charged polymethine chain) are more steric than electronic in nature. Within 1,5-aryl-substituted cyanines the addition of "soft" lithium reagents (benzyl cyanide and phenylacetic acid derivatives) occurred regioselectively to the central C3 carbon atom thus furnishing easily, and in high yields, a new series of ramified tripodand ligands.[2] When 1,5-nonsubstituted cyanine dyes were used, quantitative addition of both "soft" and "hard" organometallic nucleophiles to the C1/C5 terminal carbon atom, followed by a spontaneous or silica gel accelerated Hoffman elimination reaction, gave new access to hexatrienes with lengthened carbon chains and different functionalities.[3]

The fast and convenient one-pot experimental procedure, mild reaction conditions, high yields and easy access to a variety of 1,5-nonsubstituted pentamethine cyanine dyes[3−4] directed our efforts to the synthesis, by the use of lithium reagents of ketones with an activated methyl group, of a series of heptamethine merocyanines with different substitution patterns. It is noteworthy that although the nucleophilic replacement of the end group of cyanines by CH-acidic compounds is recognized as a method for the merocyanine synthesis,[5,6] to the best of our knowledge lithium enolates have not been used as specific nucleophiles.

This goal was justified for several reasons. The molecular design of merocyanines, "push-pull" systems bearing electron donating and electron withdrawing groups, has attracted much attention since they are crucial materials for non-linear optics (NLO), laser technology, telecommunications, data storage, photosensitizers and the photodynamic therapy of cancer etc.[7,8] Another important application, related to the pronounced solvatochromism of the merocyanine dyes, is their use as probes for solvent polarity.[9]

Having merocyanines with different donor and acceptor groups at our disposal, we investigated the relationship between their molecular structures and spectroscopic behavior (UV/Vis absorption and fluorescence spectra) in solvents with different polarities.

Finally, since the merocyanine dyes are known to be stable intermediates in the cyanine synthesis[10] we also targeted our research towards the reactivity studies of the heptamethine merocyanines obtained. Herein we report the results of our studies in these areas.

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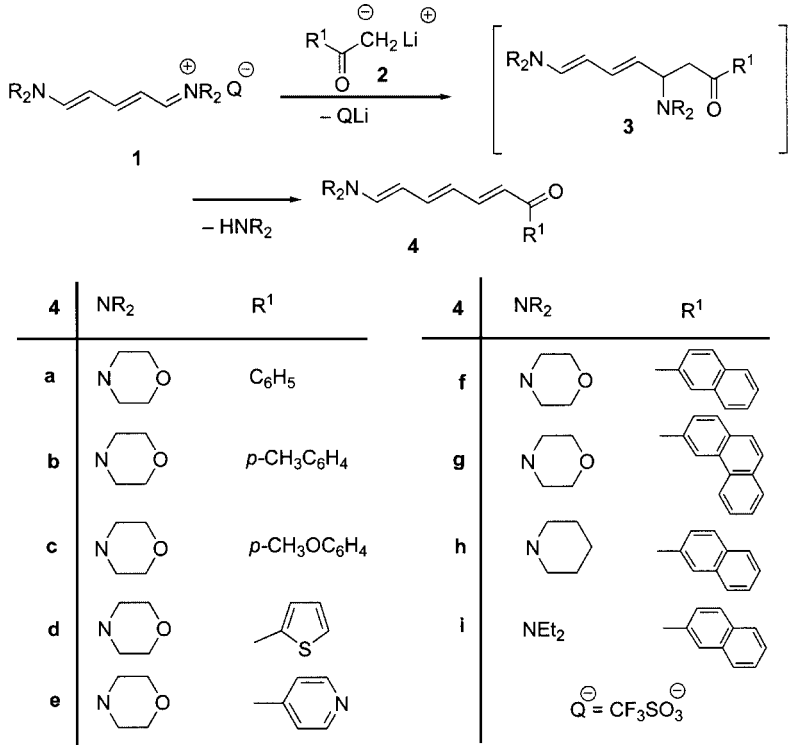


4	NR_2	R^1
a	N O	C_6H_5
b	N O	*p*-$CH_3C_6H_4$
c	N O	*p*-$CH_3OC_6H_4$
d	N O	S
e	N O	N
f	N O	
g	N O	
h	N	
i	NEt_2	

$Q^{\ominus} = CF_3SO_3^{\ominus}$

Scheme 1. Syntheses of the merocyanines **4a**−**4i**

Results and Discussion

The syntheses of the merocyanines **4a**−**i** are presented in Scheme 1.

Utilizing our previous experience of the reactivity of organometallic reagents towards polymethinium salts,[2,3] the reactions were performed in THF at low temperature. Thus, to the lithium enolate of the corresponding methyl aryl or methyl heteroaryl ketone prepared in THF at −78 °C, a solution of the polymethinium salt in the same solvent was introduced. The addition reaction leading to the unstable key intermediates **3** occurred very fast as evidenced by the immediate disappearance of the deep red-brownish color of the cyanine dye. Simultaneously, TLC monitoring of the reaction mixture showed full consumption of the cyanine salt. The process of elimination of the amino moiety was accompanied by a deep-red coloration of the reaction mixture, observed instantaneously after the removal of the cooling bath. After evaporation of the solvent at reduced pressure, the pure products were isolated by flash chromatography on silica gel in good to excellent yields.

The merocyanines are red to deep-red solids or gum-like substances. They have limited stability at room temperature, but can be stored for months at −15 °C. Their structures were established by means of elemental analysis, IR spectroscopy, ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The unambiguous assignment of ^1H and ^{13}C NMR chemical shifts was done using different NMR experiments such as DEPT (Distortionless Enhancement by Polarization Transfer), COSY (Correlated Spectroscopy) and HMQC (Heteronuclear Multiple-Quantum Coherence).

The ^1H NMR spectra of all products exhibited one set of well-resolved peaks for the methine chain protons, which is an indication of the conformational homogeneity in solution. Their coupling constants, which were within 12−15 Hz, confirmed the all-*trans* configurations of the polymethine units. The alternate charge distribution for the chain carbons observed in the ^{13}C NMR spectra is a characteristic feature for cyanine and merocyanine dyes.[11]

All the investigated merocyanines absorb in solution at room temperature in the visible region of the spectrum. Their longest wavelength absorption bands in ethanol show maxima between 22000 and 20000 cm^{-1} with molar absorptivities in the range of 17000−43000 (Table 1, Figure 1). The solvent polarity and proton donating ability as well as the nature of the substituents in positions 1 and 7 have a pronounced effect on the energy of the $S_0 - S_1$ transition. Passing from ethanol to acetonitrile to chloroform, a hypsochromic shift of about 1000 cm^{-1} can be observed. The presence of electron donating substituents in the *para*-position of the phenyl ring (compounds **4b** and **4c**) did not lead to remarkable changes in the energy of the first absorption transition. On the contrary, the replacement of the phenyl

group with the thiophene and pyridine heterocycles shifted the longest wavelength absorption maxima to the red by 400−1400 cm^{-1} (Table 1). Upon extension of the conjugated system by changing phenyl to naphthyl and phenanthryl (compounds **4a**, **4f**, **4g**) a bathochromic shift (500 cm^{-1}) can be observed. Similar to other merocyanine dyes[12] the energies of the $S_0 - S_1$ transitions of the studied compounds strongly depend on the type of N-containing substituent in position 7. When the morpholino group (compound **4f**) is replaced by piperidino (compound **4h**) or diethylamino (compound **4i**), which increases the electron density at this position, a significant decrease in the $S_0 - S_1$ transition energy by more than 1100 cm^{-1} is observed (Table 1).

Table 1. Absorption characteristics of the studied merocyanines: $\tilde{\nu}_{abs}$ − frequencies of the longest wavelength absorption Franck−Condon transitions in cm^{-1} at 293 K; ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$) − molar absorptivity. The numbers of the compounds correspond to those given in Scheme 1

	Ethanol		Acetonitrile		Chloroform	
	$\tilde{\nu}_{abs}$	ε	$\tilde{\nu}_{abs}$	ε	$\tilde{\nu}_{abs}$	ε
4a	21500	17400	22270	16200	22590	17000
4b	21710	18200	22370	19000	22770	15000
4c	21900	30800	22400	33300	22760	29800
4d	21170	20200	22000	23000	22180	29800
4e	20070	38000	21180	43200	21290	35300
4f	21180	36000	22100	38400	22400	41600
4g	21040	42500	21610	48200	21980	50000
4h	20190	36000	20880	36000	20930	32000
4i	20020	43200	20760	50400	20540	30400

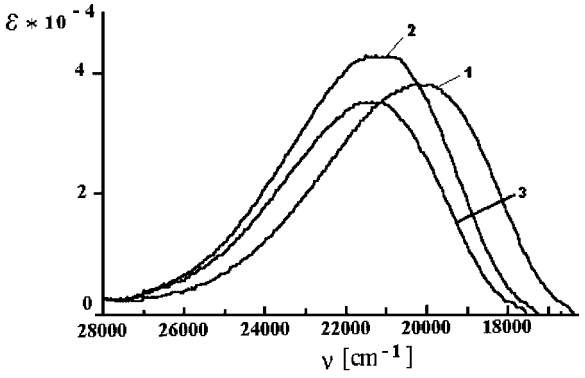


Figure 1. Absorption spectra ε ($dm^3 \cdot mol^{-1} \cdot cm^{-1}$) of compound **4e** at 293 K: curve 1 − in ethanol; curve 2 − in acetonitrile; curve 3 − in chloroform

The longest wavelength absorption maxima of the studied compounds (e.g. **4e**, **4f** and **4g** − Table 2) in aprotic solvents shift monotonically to the red with increasing solvent polarity. A sharp drop in the energies of the $S_0 - S_1$ absorption transitions is observed between acetonitrile and 1-butanol despite their similar polarity. The relationship between the orientational polarizability Δf of the solvents, which is a function of the dielectric constant (ε_r) and the refractive index (**n**), [13] and the energy of the absorption maxima was studied. No linear correlation between the absorption frequency of these compounds and the Δf (ε_r, **n**) constants for protic solvents was found, whereas such correlation was present for aprotic solvents (Figure 2). This fact indicates that the significant bathochromic shift of the absorption maxima of the studied merocyanines in protic solvents could not be explained by their higher polarity alone.

Table 2. Absorption characteristics of compounds **4e**, **4f** and **4g** in solvents with different ET(30) parameters (in kcal·mol^{-1}) at 293 K; $\tilde{\nu}_{abs}$ − energy of the absorption maximum in cm^{-1}. The numbers of the compounds corresponds to those given in Scheme 1

Solvent	*ET*(30) [kcal·mol^{-1}]	**4e** $\tilde{\nu}_{abs}$[cm^{-1}]	**4f** $\tilde{\nu}_{abs}$[cm^{-1}]	**4g** $\tilde{\nu}_{abs}$[cm^{-1}]
1 Toluene	33.9	22140	22750	22600
2 Benzene	34.5	21810	22600	22370
3 Chloroform	39.1	21290	22400	21980
4 Acetone	42.2	21400	22210	21890
5 Acetonitrile	46	21180	22100	21610
6 2-Propanol	48.6	20080	21260	21200
7 1-Butanol	50.7	19930	21340	21080
8 Ethanol	51.9	20070	21175	21040
9 Methanol	55.5	19880	21050	20730

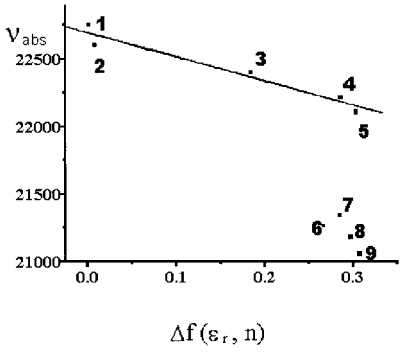


Figure 2. Energy of the absorption maxima ($\tilde{\nu}_{abs}$ in cm^{-1}) of compound **4f** at 293 K vs. Δf constants of the solvents. The numbers of solvents correspond to those given in Table 2

Contrary to the above mentioned results, two different linear correlations were obtained for the relationship between the absorption frequencies of the investigated compounds and the ET(30) constants of the solvents,[14] one for protic and another for aprotic solvents (Figure 3). The presence of two correlation lines indicates that the nature of the absorbing states in protic and aprotic solvents is different. This spectral behavior could be explained, as in the case of other cyanine dyes,[15] by the possible formation of intermolecular hydrogen bonds in the ground state between the substance and the protic solvents.

All the studied merocyanines fluoresce in solution at room temperature between 18000 and 16000 cm^{-1} (Table 3). The energies of the fluorescence Franck−Condon transitions decreases upon passing from chloroform to acetonitrile to ethanol. The fluorescence quantum yields of all compounds are rather low − between 0.001 and 0.06 in ethanol and less than 0.001 in acetonitrile and chloroform.

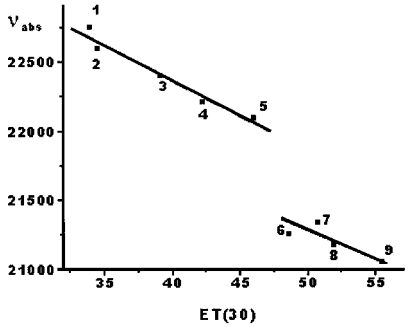


Figure 3. Energy of the absorption maxima of compound **4f** [$\tilde{\nu}_{abs}$ in cm^{-1}] at 293 K vs. the solvent polarity parameter ET(30) (in $kcal \cdot mol^{-1}$). The numbers of the solvents correspond to those given in Table 2

Bearing in mind the structures of the studied merocyanines, i.e. two heavy fragments connected by a polymethine chain, the most probable explanation for the low Q_F in solution at room temperature is the presence of intramolecular vibrations with large amplitudes in the fluorescent excited states. This conclusion is also supported by the fluorescence measurements in frozen ethanol matrices at 77 K. It was found that under these conditions, the fluorescence intensities of the investigated merocyanines were between 20- and 50-fold higher.

Table 3. Fluorescence characteristics of the studied merocyanines at 293 K: $\tilde{\nu}_{fl}$ – frequencies of the fluorescence Franck–Condon transitions in cm^{-1}; Q_F – fluorescence quantum yield

	Ethanol		Acetonitrile	Chloroform
	$\tilde{\nu}_F$	Q_F	$\tilde{\nu}_F$	$\tilde{\nu}_F$
4a	1727	0.008	17050	18290
4b	17330	0.05	17660	18440
4c	1746	0.06	17830	18660
4d	16970	0.013	17140	17900
4e	16370	0.01	16360	17330
4f	16820	0.001	16930	17930
4g	16710	0.002	16740	17860
4h	16730	0.002	16870	17560
4i	16810	0.003	16950	17660

Having a variety of readily available heptamethine merocyanines to hand, we further explored their reactivity potential. It was considered that the transformation of the heptamethine merocyanines into non-symmetrical cyanine dyes might be of interest. Our synthetic plan included obtaining an intermediate chloro equivalent, followed by reaction with an amino moiety (Scheme 2, pathway A).[16]

The first reaction step was predicted to occur smoothly by analogy with the recently reported conversion of pentamethine merocyanines to hemicarboxonium salts under the action of acid chlorides.[17] Unfortunately, our attempts to obtain chloro hemicarboxonium salts failed. Two selected representatives of merocyanines **4a** (with a terminal phenyl group) and **4f** (with a terminal β-naphthyl group) were found to show different behavior towards phosphorus oxychloride. Thus, **4a** was consumed over 3 h at 0 °C (TLC monitoring), while **4f** disappeared upon boiling the reaction mixture. In both cases however the reaction mixtures were too complicated and neither the expected chloro equivalent nor the cyanine dye from the sequential reaction with amine were isolated or characterized (^{1}H NMR and mass spectra).

In an attempt to rationalize the difference in the reactivity of the penta- and hepta-oxo merocyanines we calculated the partial charge distribution using the AM1 method in the case of **4a**. According to the results obtained, the partial positive charge on the keto carbon atom does not differ dramatically from that calculated for the penta analog (0.296 vs. 0.360), so the difference observed is presently unclear.

Our efforts to convert the merocyanines into cyanine dyes by treatment with amines and triflic acid[3] resulted in highly unstable ethereal type dimeric dications (Scheme 2, pathway B). The process was completed by obtaining a small quantity of the starting pentamethinium salt, probably due to a degradation process which is typical for longer-chain polymethines.[18]

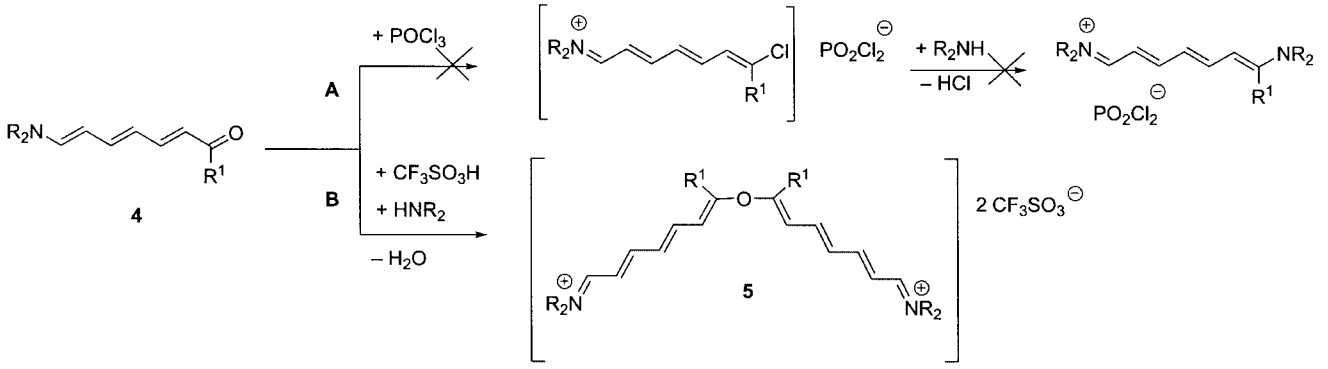
The structures of the dimeric salts were established by means of ^{1}H NMR spectroscopy. It was found that the same transformation occurred without participation of the amine. Clearly the amine moiety is not involved in this reaction mechanism, which most probably includes protonation of the charge-separated form of the starting merocyanine in acidic media, followed by a dehydration reaction (Scheme 3). This case is different from the very stable previously obtained dimeric ethers[17] in which the use of anhydrides instead of acids necessitated the intervention of a protic amine to generate the anionic charge on the oxygen atom, with the subsequent formation of an acetamide salt.

Furthermore, we examined the possibility for conversion of the heptamerocyanines into nine-carbon chain analogs by means of reaction with CH-acidic compounds such as malononitrile and diethylthiobarbituric acid under a variety of conditions using the Knoevenagel reaction.[19] Under mild conditions (toluene, room temperature and the presence of a catalytic amount of 2,2,6,6-tetramethylpiperidine) a successful condensation with malononitrile occurred. The reaction, however, stopped at the addition step and further attempts at elimination of water led to complicated reaction mixtures.

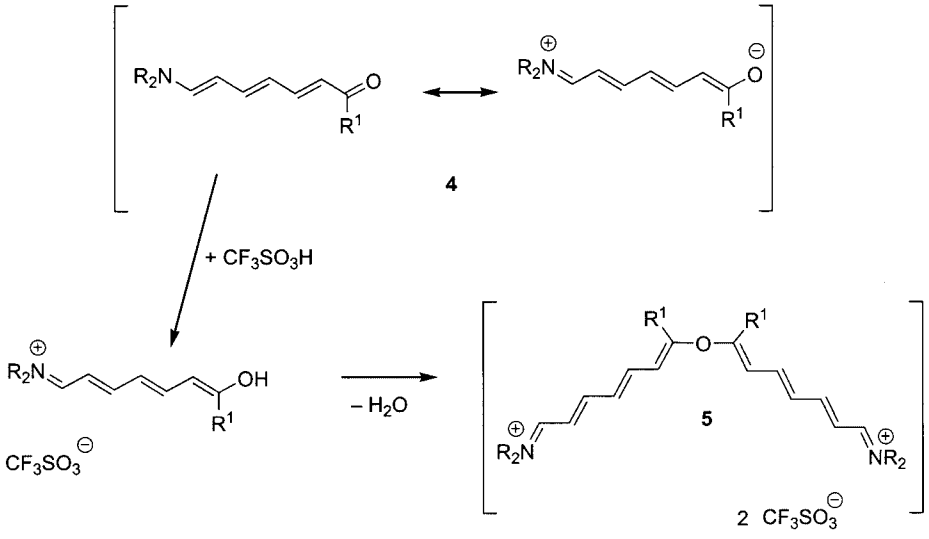
An interesting result was obtained when the lithium reagent of malononitrile was utilized. Within 2 h at room temperature **4f** was fully consumed (TLC monitoring), the process being accompanied by a change in the color of the reaction mixture from deep red to deep blue. The workup procedure (see Exp. Sect.) afforded a dark-blue crystalline product, which proved to be an anionic polymethine cyanine dye, oxonol **6a**, with a nine-carbon chain.

The proposed reaction mechanism pathway includes an aldol condensation step, followed by elimination of LiOH and subsequent hydrolysis of the terminal enamino group (Scheme 4).

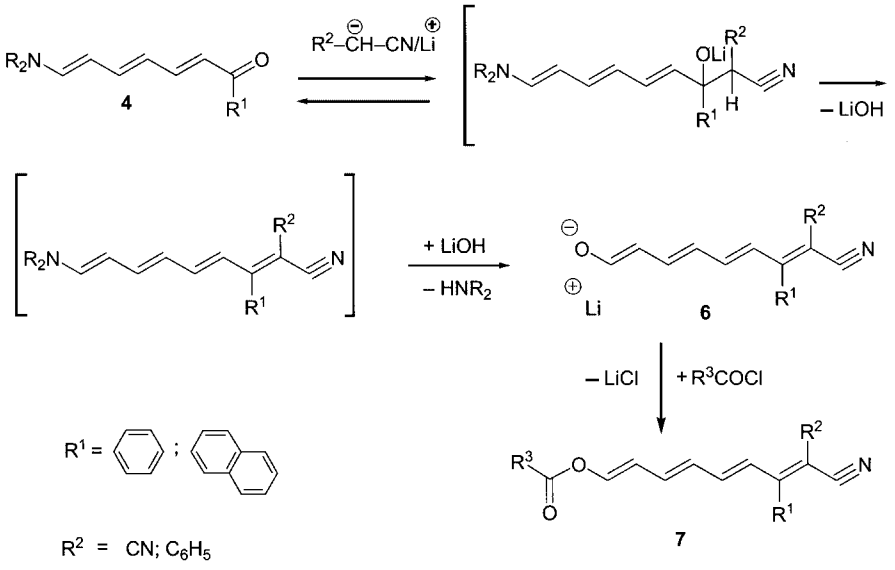
With the aim of defining the synthetic potential and limitations of the above one-pot reaction we examined the be-



Scheme 2. Transformation of the merocyanines in acidic media



Scheme 3. Proposed mechanism for the formation of the dimeric salts **5**



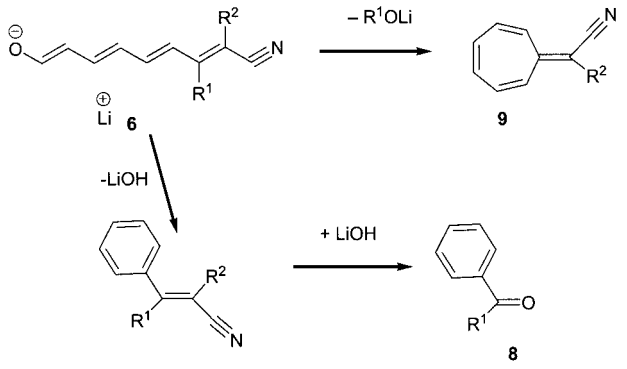
Scheme 4. Reaction pathway to oxonols **6** and their ester derivatives **7**

havior of the merocyanines towards different organolithium reagents under standard reaction conditions. It was established that the reactivity of the merocyanines depends on two main factors namely the type of metal reagent and the amino-subunit involved in the merocyanine molecule. Thus, the reaction of **4f** with lithiated malononitrile was complete after 2 h, while with the lithium reagent of benzyl cyanide the necessary reaction time was 6 h. On the contrary, **4f** failed to react with the lithium enolate of acetophenone. On the other hand, the reactivity of the merocyanines with the same R^1 substituent (producing the same oxonol) towards lithiated malononitrile decreased strongly in the order **4f** (morpholino) >> **4h** (piperidino) = **4i** (diethylamino). For example the reaction of **4f** was complete after 2 h but more than 24 h were necessary in the cases of **4h** and **4i**.

It is difficult to unambiguously interpret the first observation. In general, if we consider merocyanines as vinylogs of α-enones, the addition to the carbonyl group must occur under charge control[20] and the order of reactivity of carbanions will be reversed i.e. malonitrile < benzyl cyanide < acetophenone in accordance with the increase of the negative charge on the nucleophilic carbon from 0.280 and 0.306 to 0.422 (calculated with B3LYP 6−31 G**).

The second fact is obviously connected with the different rates of hydrolysis of the terminal enamino group[21] which, for the definite R^1, seems to be the rate-determining step of the reaction. The faster hydrolysis in the case of morpholine compared with piperidine or diethylamine residues is due to the electron attracting effect of the oxygen atom from the morpholine cycle, which increases the partial charge on the C−N carbon atom thus facilitating the coordination with LiOH in the transition state of the reaction.

The newly synthesized anionic dyes with participation of malononitrile as the CH-acidic component are crystalline or gum-like, deeply blue-colored substances. We failed to purify the products by varying solvents and conditions of crystallization, obviously due to their poor crystallization properties. Dyes with satisfactory purity were obtained by washing the crude oxonols with an appropriate solvent at boiling point (see Exp. Sect.). The structures of the oxonols were unambiguously confirmed by their spectroscopic data. Thus, in the ^{1}H NMR spectra, we detected signals for the chain protons and values for the coupling constants are consistent with all-*trans* configurations of the polymethine carbon chains. Additional evidence for the oxonol structures comes from their conversion into the corresponding esters in the reaction with acid chlorides.[4] When benzyl cyanide was used (oxonol **6b)** we could not detect protons for the cyanine carbon chain in the ^{1}H NMR spectrum. This fact is most probably due to the specificity of the molecular structure. Despite this, oxonol dye formation was detected spectroscopically by the intense long-wavelength absorption maximum at 17700 cm^{-1} and confirmed by obtaining the derived ester (15%) in the reaction with an acid chloride. It is noteworthy that **6b** has rather limited stability. Thus, it looses its deep blue color rapidly in open-air, becoming brown. Mass-spectral analysis of this mixture (EI, 9 eV) gave several basic peaks which can be attributed to fragmentation of derivatives from the spontaneous transformation of **6**, mainly **8** and **9**, as shown in Scheme 5.



Scheme 5. Spontaneous transformation reactions of the oxonol dyes **6**

This fact drew our attention to oxonols produced with participation of malononitrile. Repeat recordings of the mass spectra of the products several months later exhibited fragmentation suggesting analogous processes where the ketone **8** seems to be predominant. An additional argument for such a cyclization is the increase in the integral intensity for the aromatic proton signals compared with those of the methane chain protons in ^{1}H NMR spectroscopy.

The longest wavelength absorption maxima of the anionic dyes in ethanol are red shifted by about 2700 cm^{-1} in comparison with the merocyanine precursors in accordance with the increasing of the polymethine chain length.

Conclusion

An efficient one-pot synthesis of seven-carbon chain merocyanine dyes with different substitution patterns, based on the reaction between pentamethinium salts and organolithium reagents of methyl aryl or methyl heteroaryl ketones has been developed. Under acidic conditions the merocyanines have been found to form unstable ethereal-type dimeric salts. In subsequent reactions with "soft" lithium reagents they undergo intriguing one-pot conversions into nine-carbon chain oxonols. Thus, by the use of suitable organolithium reagents the starting cationic pentamethine cyanines can be subsequently converted into neutral cyanine dyes, merocyanine, and anionic cyanine dyes, oxonols, with elongation of the carbon chain at each stage with two carbon atoms.

The absorption and fluorescence characteristics of the merocyanines in solvents with different polarities and proton donating abilities are strongly dependent on the type of solvent and the nature of the N-containing substituent in position 1. The relationship between the energy of the absorption maxima and the *ET*(30) constants of the solvents indicates that the nature of the absorbing state in protic and non-protic solvents is different, probably due to the formation of intermolecular hydrogen bonds.

Experimental Section

General Remarks: Air-sensitive reactions were performed under dry argon using oven-dried flasks equipped with a rubber septum for introduction of the reagents with a syringe. THF was distilled from $LiAlH_4$ prior to use. Dichloromethane, toluene and acetonitrile were distilled from CaH_2 and kept over molecular sieves (3Å). LDA was prepared before use according to the standard procedure from *n*BuLi (1.6 M in hexane, Fluka). Starting ketones were obtained from commercial suppliers and used without further purification. Pentamethinium salts were obtained as described.[3]

Flash column chromatography purification of products was carried out using silica gel particle size 0.035−0.070 mm. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60F-254 plates and the spots were visualized with a UV lamp. Melting points were determined with a Kofler apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were measured using a Bruker DRX-250 spectrometer operating at 250.13 MHz for ^1H and 62.50 MHz for ^{13}C with TMS as an internal reference standard. Coupling constants are given in Hz. IR spectra were recorded with a Bruker FTR-113 V spectrometer using KBr pellets. Mass spectra were obtained with a Hewlett−Packard 5973 mass spectrometer. Absorption spectra were recorded with a Specord M40 (Carl Zeiss, Jena) UV/Vis spectrophotometer and the corrected fluorescence spectra with a Perkin−Elmer MPF44 spectrofluorimeter. The solvents used were of fluorescence grade. The emission spectra were corrected using a standard tungsten lamp, while the excitation spectra were corrected with rhodamin B. The fluorescence quantum yields (Q_F) were determined relative to that of 5-amino-3-[4-(dimethylamino)phenyl]-1(3*H*)-isobenzofuranone (Q_F = 0.4 in ethanol)[22] according to Equation (1), where the superscripts **X** and **ST** refer to the sample and the standard, respectively, **n** is the refractive index of the solvent, **S** is the integrated area under the corrected fluorescence spectrum, **A** denotes the optical density at the excitation wavelength and **SS** is a characteristic of the spectrofluorimeter.

$$\mathbf{Q_F}^{X} = \frac{\mathbf{Q_F}^{ST} \cdot (\mathbf{n}^{X})^2 \cdot \mathbf{S}^{X} \cdot \mathbf{SS}^{ST} \cdot \mathbf{A}^{ST}}{(\mathbf{n}_{ST})^2 \cdot \mathbf{S}^{ST} \cdot \mathbf{SS}^{X} \cdot \mathbf{A}^{X}} \quad (1)$$

General Procedure for the Preparation of Merocyanines 4a−4i: To a solution of BuLi (1.0 mL, 1.65 mmol, 1.6 M in hexane) in dry THF (1.5 mL) was added diisopropylamine (0.23 mL, 1.65 mmol) at room temperature. After cooling to −78 °C a solution of the corresponding ketone (1.5 mmol) in the same solvent (3 mL) was introduced dropwise at stirring. The reaction mixture was kept at this temperature for 30 min and then the starting pentamethinium salt (1 mmol) dissolved in THF (5 mL) was added with a syringe. The addition resulted in immediate disappearance of the deep red-brownish color of the cyanine salt. After stirring for an additional 15 min the cooling bath was removed and the reaction mixture was warmed to room temperature over 3 h, the process being accompanied by a deep-red coloration of the solution. The solvent was evaporated under vacuum and the crude merocyanines were purified by means of flash column chromatography on silica gel.

Starting from the corresponding ketones (1.5 mmol) and cyanine salts (1 mmol) according to the general reaction procedure the following compounds were obtained:

7-(Morpholin-4-yl)-1-phenylhepta-2,4,6-trien-1-one (4a): Yield 220 mg (82%); **4a** was isolated after flash chromatography (silica gel, dichloromethane/methanol, 19:1) as a dark-red solid. R_f = 0.55 (ether). M.p. 91−93 °C. $C_{17}H_{19}NO_2$ (269.35): calcd. C 75.81, H 7.11, N 5.20; found C 75.43, H 7.30, N 5.52. MS (EI, 30 eV): *m*/*z* = 269 [M^+]. IR (KBr): $\tilde{\nu}$ = 1623 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 3.14 [t, 4 H, $N(CH_2CH_2)_2O$], 3.69−3.73 [m, 4 H, $N(CH_2CH_2)_2O$], 5.34 (dd, *J* = 13.0, 11.3 Hz, 1 H, H-6), 6.17 (dd, *J* = 14.2, 11.6 Hz, 1 H, H-4), 6.45 (d, *J* = 13.0 Hz, 1 H, H-7), 6.70 (dd, *J* = 14.2, 11.3 Hz, 1 H, H-5), 6.76 (d, *J* = 14.4 Hz, 1 H, H-2), 7.44−7.55 (m, 4 H, H-4 + C_6H_{5ortho} + C_6H_{5para}), 7.91−7.95 (2 H, C_6H_{5meta}) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT, HMQC): δ = 48.5 [$N(CH_2CH_2)_2O$], 66.1 [$N(CH_2CH_2)_2O$], 100.6 (C-6), 118.9 (C-2), 121.1 (C-4), 128.1, 128.3, 128.4, 128.5, 128.8 (C_6H_5), 139.2 ($C_{quat.}$), 145.3 (C-5), 147.4 (C-3 + C-7), 190.3 (CO) ppm.

7-(Morpholin-4-yl)-1-(*p*-tolyl)hepta-2,4,6-trien-1-one (4b): Yield 218 mg (77%); **4b** was isolated after flash chromatography (silica gel, diethyl ether/hexane, 4:1) as a viscous red-orange oil. R_f = 0.25 (diethyl ether/hexane, 2:1). $C_{18}H_{21}NO_2$ (283.37): calcd. C 76.30, H 7.47, N 4.94; found C 76.58, H 7.64, N 4.68. MS (EI): *m*/*z* = 283 [M^+]. IR (KBr): $\tilde{\nu}$ = 1613 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 2.38 (s, 3 H, CH_3), 3.08−3.16 [m, 4 H, $N(CH_2CH_2)_2O$], 3.63−3.73 [m, 4 H, $N(CH_2CH_2)_2O$], 5.32 (dd, *J* = 13.6, 13.0 Hz, 1 H, H-6), 6.15 (dd, *J* = 14.6, 14.6 Hz, 1 H, H-4), 6.42 (d, *J* = 13.0 Hz, 1 H, H-7), 6.67 (dd, *J* = 14.6, 13.6 Hz, 1 H, H-5), 6.75 (d, *J* = 14.6 Hz, 1 H, H-2), 7.20−7.28 (m, 2 H, $CH_3-C_6H_{4meta}$), 7.53 (dd, *J* = 14.6, 14.6 Hz, 1 H, H-3), 7.81−7.84 (m, 2 H, $CH_3-C_6H_{5ortho}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT, HMQC): δ = 21.5 (CH_3), 48.4 [$N(CH_2CH_2)_2O$], 66.1 [$N(CH_2CH_2)_2O$], 100.5 (C-6), 118.8 (C-2), 121.1 (C-4), 128.2, 129.0 (C_{ortho} + C_{meta}) 136.4 ($C_{quat.}$), 142.5 ($C_{quat.}$), 145.1 (C-5), 147.1 (C-3), 147.3 (C-7), 189.9 (CO) ppm.

1-(4-Methoxyphenyl)-7-(morpholin-4-yl)-2,4,6-trien-1-one (4c): Yield 225 mg (75%); **4c** was isolated after flash chromatography (silica gel, ether) as a red-orange solid. M.p. 112−114 °C. R_f = 0.43 (ether). $C_{18}H_{21}NO_3$ (299.37): calcd. C 72.22, H 7.07, N 4.68; found C 72.60, H 7.35, N 4.24. MS (EI): *m*/*z* = 299 [M^+]. IR (KBr): $\tilde{\nu}$ = 1671 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 3.11 [t, 4 H, $N(CH_2CH_2)_2O$], 3.68 [t, 4 H, $N(CH_2CH_2)_2O$], 3.85 (s, 3 H, OCH_3), 5.33 (dd, *J* = 13.6, 13.0 Hz, 1 H, H-6), 6.16 (dd, *J* = 14.3, 14.3 Hz, 1 H, H-4), 6.43 (d, *J* = 13.0 Hz, 1 H, H-7), 6.68 (dd, *J* = 14.3, 13.6 Hz, 1 H, H-5), 6.78 (d, *J* = 13.6 Hz, 1 H, H-2), 6.60−6.95 (m, 2 H, $CH_3-C_6H_{5meta}$) 7.53 (dd, *J* = 14.3, 13.6 Hz, 1 H, H-3), 7.92−7.98 (m, 2 H, $CH_3O-C_6H_{5ortho}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT, HMQC): δ = 48.4 [$N(CH_2CH_2)_2O$], 55.3 (OCH_3), 66.1 [$N(CH_2CH_2)_2O$], 100.5 (C-6), 113.5 ($CH_3-C_6H_{5meta}$), 118.6 (C-2), 121.2 (C-4), 130.2 ($CH_3-C_6H_{5ortho}$), 131.8 ($C_{quat.}$), 144.7 (C-5), 146.5 (C-3), 147.1 (C-7), 162.6 ($C_{quat.}$), 188.5 (CO) ppm.

7-(Morpholin-4-yl)-1-(thiophen-2-yl)hepta-2,4,6-trien-1-one (4d): Yield 260 mg (95%); **4d** was isolated after flash chromatography (silica gel, dichloromethane/methanol, 19:1) as a dark-orange solid. M.p. 73−75 °C. R_f = 0.57 (dichloromethane/methanol, 19:1). $C_{15}H_{17}NO_2S$ (275.36): calcd. C 65.43, H 6.22, N 5.09; found C 65.68, H 6.40, N 5.35. MS (EI): *m*/*z* = 275 [M^+]. IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1} (CO). ^1H NMR (250 MHz, CD_3CN, COSY): δ = 3.14 [t, 4 H, $N(CH_2CH_2)_2O$], 3.63 [t, 4 H, $N(CH_2CH_2)_2O$], 5.42 (dd, *J* = 14.3, 13.6 Hz, 1 H, H-6), 6.14 (dd, *J* = 14.3, 14.2 Hz, 1 H, H-4), 6.62 (d, *J* = 13.6 Hz, 1 H, H-7), 6.73 (d, *J* = 14.4 Hz, 1 H, H-2), 6.82 (dd, *J* = 14.3, 14.2 Hz, 1 H, H-5), 7.16 (dd, *J* = 5.0, 4.0 Hz, 1 H, $H\text{-}3_{thioph.}$) 7.46 (dd, *J* = 14.4, 14.3 Hz, 1 H, H-3), 7.69 (dd, *J* = 5.0, 1.2 Hz, 1 H, $H\text{-}5_{thioph.}$), 7.77 (dd, *J* = 4.0, 1.2 Hz, 1 H, $H\text{-}4_{thioph.}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT, HMQC): δ = 49.2 [$N(CH_2CH_2)_2O$], 66.5 [$N(CH_2CH_2)_2O$], 100.7 (C-6), 117.9 (C-2), 120.3, (C-4), 129.1, 131.3, 133.5 ($C_{thioph.}$), 147.3 (C-3), 147.7 ($C_{quat.}$), 148.3 (C-5), 149.5 (C-7), 182.2 (CO) ppm.

7-(Morpholin-4-yl)-1-(pyridin-4-yl)hepta-2,4,6-trien-1-one (4e): Yield 143 mg (53%); **4e** was isolated after flash chromatography (silica gel, dichloromethane/methanol, 19:1) as a deep-red shiny solid. M.p. 151−153 °C. R_f = 0.44 (dichloromethane/methanol, 19:1). $C_{16}H_{18}N_2O_2$ (270.33): calcd. C 71.09, H 6.71, N 10.36; found C 71.48, H 6.95, N 10.21. MS (EI): *m*/*z* = 270 [M^+]. IR (KBr): $\tilde{\nu}$ = 1621 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 3.21 [t, 4 H, N(CH_2CH$_2$)$_2$O], 3.71 [t, 4 H, N(CH$_2$CH_2)$_2$O], 5.37 (dd, *J* = 13.6, 12.8 Hz, 1 H, H-6), 6.17 (dd, *J* = 14.1, 11.4 Hz, 1 H, H-4), 6.54 (d, *J* = 12.8 Hz, 1 H, H-7), 6.63 (d, *J* = 14.5 Hz, 1 H, H-2), 6.77 (dd, *J* = 13.6, 11.4 Hz, 1 H, H-5), 7.56 (dd, *J* = 14.5, 14.1 Hz, 1 H, H-3), 7.68−7.75 (m, 2 H, $H_{py\text{-}ortho}$), 8.73−8.83 (m, 2 H, $H_{py\text{-}meta}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT, HMQC): δ = 48.5 [N(*C*H$_2$CH$_2$)$_2$O], 66.1 [N(CH$_2$*C*H$_2$)$_2$O], 100.3 (C-6), 117.3 (C-2), 120.4, (C-4), 121.4 ($C_{py\text{-}ortho}$), 145.8 6 ($C_{quat.}$), 147.8 (C-5), 148.5 (C-7), 149.6 (C-3), 150.2, 150.8 ($C_{py\text{-}meta}$), 188.9 (CO) ppm.

7-(Morpholin-4-yl)-1-(naphthalen-2-yl)hepta-2,4,6-triene-1-one (4f): Yield 277 mg (87%); **4f** was isolated after flash chromatography (silica gel, dichloromethane/methanol, 19:1) as a dark-red solid. M.p. 108−111 °C. R_f = 0.34 (ether). $C_{21}H_{21}NO_2$ (319.41): calcd. C 78.97, H 6.63, N 4.39; found C 78.75, H 6.50, N 4.35. MS (EI): *m*/*z* = 319 [M^+]. IR (KBr): $\tilde{\nu}$ = 1619 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 3.12 [t, 4 H, N(CH_2CH$_2$)$_2$O], 3.67 [t, 4 H, N(CH$_2$CH_2)$_2$O], 5.33 (dd, *J* = 13.6, 13.2 Hz, 1 H, H-6), 6.21 (dd, *J* = 13.6, 12.9 Hz, 1 H, H-4), 6.42 (d, *J* = 13.2 Hz, 1 H, H-7), 6.71 (dd, *J* = 13.6, 13.6 Hz, 1 H, H-5), 7.46 (dd, *J* = 14.4, 14.1 Hz, 1 H, H-3), 6.91 (d, *J* = 13.1 Hz, 1 H, H-2), 7.64 (dd, *J* = 13.1, 12.9 Hz, 1 H, H-3), 7.50−7.52, 7.84−8.49 (m, 7 H, $CH_{naphth.}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT, HMQC): δ = 48.4 [N(*C*H$_2$CH$_2$)$_2$O], 66.1 [N(CH$_2$*C*H$_2$)$_2$O], 100.5 (C-6), 118.8 (C-2), 121.0, (C-4), 124.5, 126.4, 127.6, 127.7, 128.0, 129.9, 129.3 (*C*$H_{naphth.}$), 132.5 ($C_{quat.}$), 135.0 ($C_{quat.}$), 136.5 ($C_{quat.}$), 145.5 (C-5), 147.4 (C-3), 147.5 (C-7), 189.9 (CO) ppm.

7-(Morpholin-4-yl)-1-(phenanthren-2-yl)hepta-2,4,6-trien-1-one (4g): Yield 320 mg (86%); **4g** was isolated after flash chromatography (silica gel, dichloromethane/methanol, 30:1) as a dark-red solid. M.p. 70−73 °C. R_f = 0.61 **(**dichloromethane/methanol, 19:1). $C_{25}H_{23}NO_2$ (369.47): calcd. C 81.27, H 6.27, N 3.79; found C 81.03, H 6.54, N 3.55. MS (EI): *m*/*z* = 369 [M^+]. IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 3.11 [t, 4 H, N(CH_2CH$_2$)$_2$O], 3.67 [t, 4 H, N(CH$_2$CH_2)$_2$O], 5.32 (dd, *J* = 13.1, 12.5 Hz, 1 H, H-6), 6.21 (dd, *J* = 14.2, 14.1 Hz, 1 H, H-4), 6.41 (d, *J* = 12.5 Hz, 1 H, H-7), 6.71 (dd, *J* = 14.2, 13.1 Hz, 1 H, H-5), 6.95 (d, *J* = 14.5 Hz, 1 H, H-2) 7.62−8.72 (m, 10 H, H-3 + $CH_{phenan.}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 48.4 [N(*C*H$_2$CH$_2$)$_2$O], 66.1 [N(CH$_2$*C*H$_2$)$_2$O], 100.5 (C-6), 118.8 (C-2), 121.1, (C-4), 122.8, 123.2, 125.6, 126.8, 127.4, 127.5, 128.6, 129.1 *C*$H_{phenan.}$), 129.7 ($C_{quat.}$), 132.6 ($C_{quat.}$), 132.7 ($C_{quat.}$), 137.0 ($C_{quat.}$), 147.5 (C-5), 147.6 (C-3 + C-7), 160.9 ($C_{quat.}$), 189.8 (CO) ppm.

1-(Naphthalen-2-yl)-7-(piperidin-1-yl)hepta-2,4,6-trien-1-one (4h): Yield 275 mg (87%); **4h** was isolated after flash chromatography (silica gel, dichloromethane/methanol, 19:1) as a dark-red solid. M.p. 82−85 °C. R_f = 0.65 (dichloromethane/methanol, 19:1). $C_{22}H_{23}NO$ (317.43): calcd. C 83.24, H 7.30, N 4.41; found C 83.14, H 7.43, N 4.58. MS (EI): *m*/*z* = 317 [M^+]. IR (KBr): $\tilde{\nu}$ = 1617 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 1.53 (s, bd, 6 H, 3′ (5′)-$H_{pip.}$, 4′-$H_{pip.}$), 3.10 (s, bd, 2 H, 2′ (5′)-$H_{pip.}$), 5.25 (dd, *J* = 13.1, 12.3 Hz, 1 H, H-6), 6.10 (dd, *J* = 14.0, 12.8 Hz, 1 H, H-4), 6.47 (d, *J* = 12.3 Hz, 1 H, H-7), 6.70 (dd, *J* = 14.0, 13.1 Hz, 1 H, H-5), 6.75 (d, *J* = 13.3 Hz, 1 H, H-2), 7.56 (dd, *J* = 13.3, 12.8 Hz, 1 H, H-3), 7.45−7.49, 7.77−8.40 (m, 7 H, C$H_{naphth.}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 23.9, 25.2, 49.5, ($CH_{pip.}$), 98.6 (C-6), 116.8 (C-2), 118.8, (C-4), 124.4, 126.2, 127.5, 127.8, 128.2, 128.6, 129.1, (*C*$H_{naphth.}$), 132.4 ($C_{quat.}$), 134.7 ($C_{quat.}$), 136.7 ($C_{quat.}$), 147.3 (C-5), 148.1 (C-3), 148.6 (C-7), 189.6 (CO) ppm.

7-Diethylamino-1-(naphthalen-2-yl)hepta-2,4,6-trien-1-one (4i): Yield 293 mg (96%); **4i** was isolated after flash chromatography (silica gel, ether) as a dark-red viscous oil. R_f = 0.68 (dichloromethane/methanol, 19:1). $C_{21}H_{23}NO$ (305.42): calcd. C 82.59, H 7.59, N 4.59; found C 82.47, H 7.70, N 4.70. MS (EI): *m*/*z* = 305 [M^+]. IR (KBr): $\tilde{\nu}$ = 1617 cm^{-1} (CO). ^1H NMR (250 MHz, $CDCl_3$, COSY): δ = 1.14 (t, *J* = 7.2 Hz, 6 H, N(CH$_2$CH_3)$_2$], 3.17 (q, *J* = 7.2 Hz, 4 H, N(CH_2CH$_3$)$_2$], 5.23 (dd, *J* = 12.6, 11.2 Hz, 1 H, H-6), 6.16 (dd, *J* = 14.0, 11.7 Hz, 1 H, H-4), 6.57 (d, *J* = 12.6 Hz, 1 H, H-7), 6.76 (dd, *J* = 14.0, 11.2 Hz, 1 H, H-5), 6.85 (d, *J* = 14.3 Hz, 1 H, H-2), 7.66 (dd, *J* = 14.3, 11.7 Hz, 1 H, H-3), 7.44−7.62, 7.83−8.43 (m, 7 H, $CH_{naphth.}$) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 13.2 [N(CH$_2$*C*H$_3$)$_2$], 45.9 [N(*C*H$_2$CH$_2$)$_2$], 98.3 (C-6), 116.6 (C-2), 118.2 (C-4), 124.6, 126.2, 127.5, 127.6, 127.9, 128.7, 129.2, (*C*$H_{naphth.}$), 132.6 ($C_{quat.}$), 134.8 ($C_{quat.}$), 136.9 ($C_{quat.}$), 147.3 (C-7), 147.8 (C-5), 148.5 (C-3), 189.8 (CO) ppm.

"**Dimeric" Salt 5a:** To a stirred solution of **4a** (135 mg, 0.5 mmol) in dry methanol (7 mL) was added triflic acid (113 mg, 0.067 mL, 1.5 equiv.) at room temperature. After stirring for 24 h, the solvent was removed under vacuum and the resultant viscous oil was purified by flash chromatography using dry solvents (silica gel, dichloromethane/methanol, 19:1) thus affording **5a** as a dark-brown oil (80 mg, 40%). R_f = 0.33 (dichloromethane/methanol, 19:1). ^1H NMR (250 MHz, CD_3CN): 3.81−3.92 (m, 16 H, 2 × N(CH$_2$CH$_3$)$_2$], 6.52 (dd, *J* = 13.9, 11.1 Hz, 2 H), 6.66 (dd, *J* = 14.2, 11.7 Hz, 2 H), 7.31 (dd, *J* = 14.2, 11.7 Hz, 2 H), 7.44−8.15 (m, 16 H, 2 × C_6H_5 + chain protons) ppm.

General Procedure for the Preparation of Oxonols 6: To the lithium reagent of the CH-acidic compound (1.5 mmol) prepared in dry THF (3 mL) at −78 °C for 30 min as described above, was introduced a solution of the corresponding merocyanine (1 mmol) dissolved in the same solvent (3 mL) with stirring using a syringe. After 15 min the cooling bath was removed and the reaction mixture was allowed to reach room temperature. The warming was accompanied by a change of the deep-red color due to the starting merocyanine, to dark-blue. After completion of the reaction which was monitored by the consumption of the starting merocyanine (TLC), the solvent was evaporated at reduced pressure and the crude oxonol was purified as described below.

Oxonol 6a (R^1 = β-naphthyl, R^2 = CN) [Lithium Salt of the 8,8-Dicyano-7-(naphthalen-2-yl)octa-1,3,5,7-tetraen-1-ol Anion]: Following the general experimental procedure from malononitrile (100 mg, 1.5 mmol) and **4f** (319 mg, 1 mmol) after 2 h at room temperature, crude **6a** was obtained as shiny blue-dark crystals. The product was consecutively treated with boiling dry dichloromethane (3 × 10 mL) and boiling dry diethyl ether (3 × 10 mL) to remove the excess of malononitrile, morpholine eliminated in the course of the reaction and traces of unchanged merocyanine. This procedure, after drying at high vacuum, afforded **6a** as a shiny deep-blue powder (0.260 g, 87%). M.p. 70−73 °C. UV/Vis: $\tilde{\nu}_{abs}$ (ethanol) = 18490 cm^{-1}. MS (EI, 9 eV): *m*/*z* = 255 [M^+(297) − C_2H_2O], 170 [M^+ − $C_{10}H_7$], 155 [M^+ − $C_{10}H_7$ − CH_3], 127 [$C_{10}H_7]^+$, 57 [C_2H_2O + $CH_3]^+$, 42 [$C_2H_2O]^+$. IR (KBr): $\tilde{\nu}$ = 2194 cm^{-1} (CN). ^1H NMR (250 MHz, [D$_6$]DMSO, COSY, HMQC): δ = 5.83 (dd, *J* = 13.7, 11.6 Hz, 1 H, H-6), 6.10 (dd, *J* = 13.5, 12.1 Hz,

1 H, H-4), 6.63 (d, J = 13.7 Hz, 1 H, H-7), 6.83 (d, J = 14 Hz, 1 H, H-2), 6.89 (dd, J = 13.5, 11.6 Hz, 1 H, H-5), 7.54−8.02 (m, 8 H, H-3 + $CH_{naphth.}$) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO, DEPT, HMQC): δ = 111.6 (C-6), 114.9 (C-2), 118.1(C-4), 125.3, 127.5, 128.5, 128.7, 128.8, 129.4, 130.1 ($CH_{naphth.}$), 130.4 ($C_{quat.}$), 135.7($C_{quat.}$), 138.0 ($C_{quat.}$), 150.4 (C-7), 150.9 (C-3), 151.4 (C-5), 188.8 [C=C(CN)$_2$] ppm.

Oxonol 6b (R^1 = β-naphthyl, R^2 = C$_6$H$_5$): According to the general experimental procedure from benzyl cyanide (176 mg, 1.5 mmol) and **4f** (319 mg, 1 mmol) after 6 h at room temperature, crude **6b** was isolated as a dark solid. Triturating with dry diethyl ether (4 × 10 mL) in a mortar and drying in high vacuum afforded **6b** as shiny black crystals (0.250 g, 72%). UV/Vis: $\tilde{\nu}_{abs}$ (ethanol) = 17700 cm^{-1}. MS (EI, 9 eV)**:** m/z = 232, 205, 170, 155, 117, 90, 71, 57, 42. Mass spectral fragmentations are in agreement with the presumed cyclization of **6b** according to Scheme 5. IR (KBr): $\tilde{\nu}$ = 2183 cm^{-1} (CN).

Oxonol 6c (R^1 = 2-thiophenyl, R^2 = CN): Following the general experimental procedure from malononitrile (73 mg, 1.1 mmol) and **4d** (275 mg, 1 mmol) after 4 h at room temperature, crude **6c** was obtained as a dark-blue sticky product. The crude oxonol was treated with boiling hexane (3 × 10 mL) thus affording, after drying at high vacuum, **6c** as gum-like deep-blue substance (0.260 g, 87%). UV/Vis: $\tilde{\nu}_{abs}$ (ethanol) = 18450 cm^{-1}. MS (EI, 9 eV): m/z = 252 [M$^+$ − 1]: 237, 209, 188, 171, 153, 126, 111, 84, 66, 43. IR (KBr): $\tilde{\nu}$ = 2193 cm^{-1} (CN). ^1H NMR (250 MHz, [D$_6$]DMSO, COSY, HMQC): δ = 5.63 (dd, J = 13.7, 11.7 Hz, 1 H, H-6), 5.94 (dd, J = 13.8, 12.0 Hz, 1 H, H-4), 6.54 (d, J = 13.7 Hz, 1 H, H-7), 6.64 (d, J = 14.0 Hz, 1 H, H-2), 6.85 (dd, J = 13.8, 11.7 Hz, 1 H, H-5), 6.94−7.82 (m, 4 H, H-3 + $CH_{thioph.}$) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO, DEPT): δ = 72.4 [C(CN)$_2$]. 110.0 (C-6), 114.2 (C-2), 116.5 (C-4), 128.5, 130.1, 132.6 ($CH_{thioph.}$), 144.9 (C-7), 147.2 (C-3), 147.5 ($C_{quat.}$), 148.8 (C-5), 180.0 (C=C(CN)$_2$] ppm.

General Procedure for Preparation of the Esters 7: To a solution of the starting oxonol (1 mmol) in dry pyridine (5 mL) was added the corresponding acid chloride (1.5 mmol) slowly at 0 °C with stirring. The color of the solution changed immediately from deep-blue to red. The reaction mixture was kept at this temperature for 15 min, poured into ice-cold water (30 mL) and extracted with dichloromethane (4 × 10 mL). The combined organic extracts were washed with water, dried ($MgSO_4$) and the solvent was evaporated.

8,8-Dicyano-7-(naphthalen-2-yl)-1,3,5,7-tetraenyl Benzoate (7a): Following the general experimental procedure from **6a** (304 mg, 1 mmol) and benzoyl chloride (280 mg, 2 mmol), **7a** was obtained as a red-brown solid after column chromatography on silica gel (dichloromethane) (290 mg, 52%). M.p. 237−240 °C. R_f = 0.5 (dichloromethane). $C_{27}H_{18}N_2O_2$ (402.46): calcd. C 80.58, H 4.51, N 6.96; found C 80.14, H 4.83, N 6.58. MS (EI, 9 eV): m/z = 402 [M$^+$]. IR ($CHCl_3$): $\tilde{\nu}$ = 1695 cm^{-1} ($COOC_6H_5$), 2228 cm^{-1} (CN). ^1H NMR (250 MHz, [D$_6$]DMSO): δ = 6.70−6.89 (m, 1 H), 6.90−7.12 (m, 2 H), 7.28−8.28 (m, 15 H) ppm. ^{13}C NMR (62.5 MHz, [D$_6$]DMSO, DEPT): δ = 112.6 (CN), 114.5 (CN), 117.8, 122.4, 124.4, 127.1, 127.5, 127.7, 128.7, 129.4, 130.3, 130.8 ($C_{quat.}$), 132.8 ($C_{quat.}$), 133.4 ($C_{quat.}$), 133.6, 134.6, 137.5, 150.5 ($C_{quat.}$), 151.5, 162.2, 164.3 ($COOC_6H_5$) ppm.

8-Cyano-7-(naphthalen-2-yl)-8-phenylocta-1,3,5,7-tetraenyl Acetate (7b): Starting from **6b** (304 mg, 1 mmol) and acetyl chloride (160 mg, 2 mmol), **7b** was isolated after flash chromatography of the crude product (silica gel, dichloromethane) as an orange oil (113 mg, 29%). R_f = 0.7 (dichloromethane). $C_{27}H_{21}NO_2$ (391.46): calcd. C 82.84, H 5.41, N 3.58; found C 82.37, H 5.70, N 3.78. MS (EI, 9 eV): m/z = 391 [M$^+$]. IR ($CHCl_3$): $\tilde{\nu}$ = 1752 cm^{-1} ($COOCH_3$), 2222 (CN). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, $COOCH_3$), 6.54−7.86 (m, 18 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 20.8 (CH_3), 112.6, 116.9 (CN), 117.3, 120.4, 122.0, 124.0, 125.5, 126.7, 126.8, 127.6, 128.5, 128.6, 129.0, 129.3 ($C_{quat.}$), 130.0, 130.7, 131.2 ($C_{quat.}$), 133.2 ($C_{quat.}$), 133.4 ($C_{quat.}$), 133.7 ($C_{quat.}$), 133.8, 140.9, 141.0, 148.4 ($C_{quat.}$), 168.7 ($COOCH_3$) ppm.

8,8-Dicyano-7-(thiophen-2-yl)octa-1,3,5,7-tetraenyl Benzoate (7c) Starting from **6c** (260 mg, 1 mmol) and acetyl chloride (160 mg, 1 mmol), **7c** was isolated after flash chromatography of the crude product (silica gel, dichloromethane) as an orange oil (53 mg, 15%). R_f = 0.72 **(**dichloromethane). $C_{21}H_{14}N_2O_2S$ (358.41): calcd. C 70.37, H 3.94, N 7.82; found C 70.60, H 3.72, N 7.68. MS (EI, 9 eV): m/z = 358 [M$^+$]. IR ($CHCl_3$): $\tilde{\nu}$ = 1739 cm^{-1} ($COOC_6H_5$), 2223 (CN). ^1H NMR (250 MHz, $CDCl_3$): δ = 6.65 (d, J = 13.3 Hz, 1 H), 6.65−8.26 (m, 20 H) ppm. ^{13}C NMR (62.5 MHz, $CDCl_3$, DEPT): δ = 77.1 [C(CN)$_2$], 115.6 (CN), 126.3, 128.0, 128.3, 128.9, 129.5, 130.4, 130.9 ($C_{quat.}$), 131.5, 132.8, 134.3, 136.8 ($C_{quat.}$), 139.6, 149.6, 158.9, 164.0 ($COOC_6H_5$), 167.1 (C=C(CN)$_2$] ppm.

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