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Fluorescent Streptocyanine Dyes: Synthesis and Photophysical Properties – Synthesis of a New Hemicarboxonium Salt

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Seven new nonacarbon chain carboxonium salts were synthesized from variously substituted arylethanones, except a few which were too deactivated to react. By the action of several amines, thirteen new nonacarbon chain streptocyanine dyes were synthesized. Photophysical properties of these new dyes were evaluated to highlight that they all absorb around 700 nm and emit fluorescence above 720 nm. As the purity of the intermediary carboxonium salt was improved (up to 98 %), a new nonacarbon chain hemicarboxonium salt was synthesized and fully characterized by X-ray crystallography.

Introduction

The development of new fluorescent dyes is an important challenge in various fields such as single-molecule imaging, non linear optics, and biological probes. These fluorophores must show a strong absorption, high fluorescence quantum yield, weak bottleness into triplet states, and high thermal, solvato- and photostability. Streptocyanines dyes, part of the group of polymethinium dyes, fulfil most of these conditions. These organic compounds are cationic and contain a chain that is made up of an odd number of carbon atoms and ended by two nitrogen atoms. When the nitrogen atoms are included in conjugated heterocycles, the dye is called a cyanine, otherwise it is a streptocyanine. Numerous applications are already known for dyes of this type:[1] photographic sensitizers[2], optical recording devices[3], nonlinear frequency doublers[4], drugs[5], and biological probes[6] mainly by using their fluorescence properties. It is of primary interest to synthesize dyes emitting fluorescence above 600 nm in order to avoid the interference of fluorescence of complex media such as biological ones.

In recent years we have developed the synthesis of streptocyanine dyes from the reaction of penta-[7], hepta-[8] and nonacarbon chain (9-C) carboxonium salts[9] with various nitrogen nucleophiles. So, the absorption wavelengths of these dyes can be tuned across the visible and near-infrared spectrum by changing the length of the conjugated chain and/or the terminal substituents.

Only one 9-C carboxonium salt was described previously and its reaction with amines or hydrazone led to 9-C streptocyanines as near-infrared fluorescent dyes.[9] One of them was used to study the diffusion of single streptocyanine molecules in the nanoporous network of sol-gel glasses.[10] To extend the family of 9-C streptocyanine dyes, it was necessary to synthesize a larger number of 9-C carboxonium salts. That is why we have studied the generalization of their synthetic pathway.

Results and Discussion

Synthesis

9-C carboxonium salts are obtained from a mixture of arylethanone, 2-chloro-3-(hydroxymethylene)cyclohex-1-ene-1-carbaldehyde and triethoxymethane in a tetrafluoroboric acid medium (Scheme 1). A byproduct identified as a 1,9-diketone, which is also an intermediate in the reaction, is always present with the carboxonium salt. The 1,9-diketone does not disrupt the synthesis of nonacarbon chain streptocyanine dyes and it is filtered off from the mixture at the end of the reaction.

Table 1 shows the influence of the substituent of the arylethanone on the carboxonium salt/diketone proportion and on the yield of the carboxonium salt.

With 4-halogenophenylethanone we have been able to reach a purity of 98 %. Carboxonium salt **5** obtained from 4-phenylphenylethanone is too sensitive to hydrolyze to determine its purity by ^{1}H NMR analysis with good precision, so it is not reported in Table 1. Moreover, this study highlights that this synthetic method cannot be generalized to deactivated arylethanones since we did not obtain the corresponding 9-C carboxonium salts with 4-nitrophenylethanone and pentafluorophenylethanone. Consequently,

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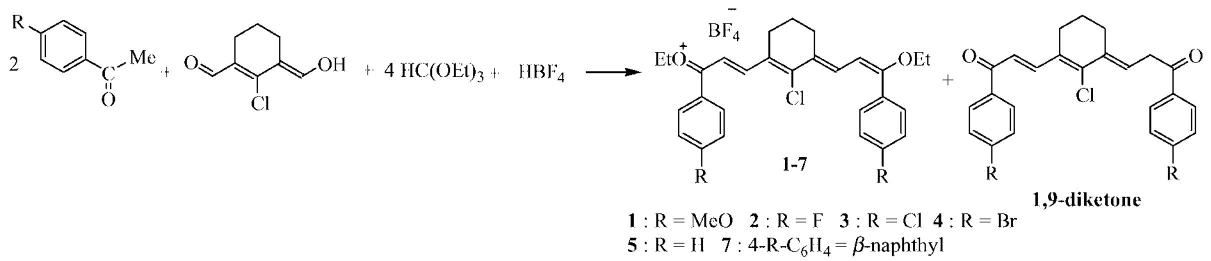
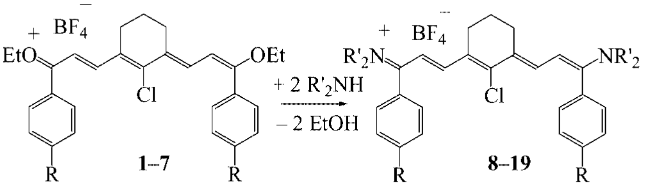


Scheme 1. Synthesis of the 9-C carboxonium salts **1**–**7**.

Table 1. Purity and corrected yield (taking into account the presence of the 1,9-diketone) of new 9-C carboxonium salts. The 4-methylphenylethanone derivative is in italics.[9]

R	*Me*	MeO	F	Cl	Br	H	β-Naph
Carboxonium salt [%]	*85*	77	98	97	97	52	75
Diketone [%]	*15*	23	2	3	3	48	25
Corrected yield [%]	*48*	63	38	36	38	26	20

only streptocyanine dyes **8**–**20** were synthesized from pure carboxonium salts **1**–**7** by the addition of 2 equiv. of dimethylamine, diethylamine, or morpholine (Scheme 2).



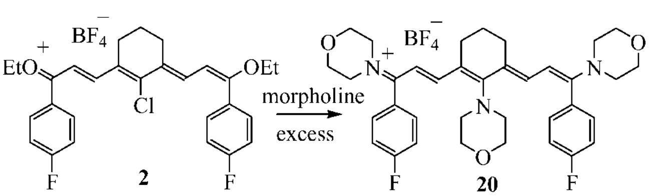
	8	**9**	**10**	**11**	**12**	**13**
R	MeO	F	Cl	Br	Ph	H
NR'_2	NEt_2	NEt_2	NEt_2	NEt_2	NEt_2	NEt_2

	14	**15**	**16**	**17**	**18**	**19**
R	4-R-C_6H_4 = β-naphthyl	F	Cl	Br	MeO	F
NR'_2	NEt_2	NMe_2	NMe_2	NMe_2	morpholino	morpholino

Scheme 2. Syntheses of streptocyanine dyes **8**–**19**.

Under the same reaction conditions (solvent, temperature) the addition of an excess of morpholine to carboxonium salt **2** leads to 1,5,9-trisubstituted streptocyanine **20** (Scheme 3). This reaction does not occur with other amines.

Dye **8** was characterized by X-ray diffraction (Figure 1).



Scheme 3. Synthesis of streptocyanine dye **20**.

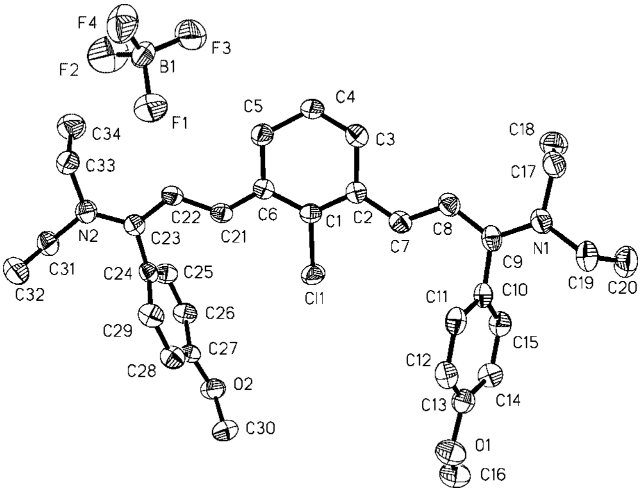
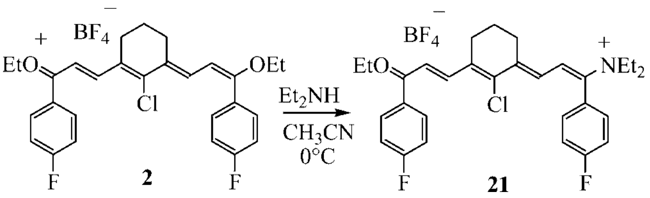


Figure 1. X-ray crystal structure of **8**; selected bond lengths [Å] and angles [°]:N1–C9 1.338(3), C9–C8 1.409(3), C8–C7 1.383(3), C7–C2 1.411(3), C2–C1 1.399(3), C2–C3 1.503(3), C1–C6 1.410(3), C6–C5 1.505(3), C6–C21 1.387(3), C21–C22 1.397(3), C22–C23 1.398(3), C23-N2 1.346(3), C23–C24 1.487(3), C9–C10 1.482(4), C21–C6–C1 121.9(2), C22–C21–C6 127.7(2), C21–C22–C23 121.0(2), C7–C8–C9 122.3(3), C23–N2–C33 122.7(2), C8–C7–C2 126.5(3), C1–C2–C7 122.2(2), C23–N2–C31 122.6(2), C9–C10–C11 119.6(2), C23–C24–C29 121.3(2), C22–C23–N2 123.4(2), C8–C9–N1 122.2(3), C8–C9–C10–C11 69.2, C22–C23–C24-C29 87.8; mean deviation of the carbon chain from the mean plane: 0.190 Å.

As for one 7-C[8] and three 9-C streptocyanines[4c,9] X-ray structures previously obtained, the X-ray resolved structure of **8** shows a mean C–C length that lies in between a single and a double bond; this is the case for the C–N bond length as well. It expresses the conjugation and the delocalization of the positive charge of the nonacarbon chain. This structure, moreover, confirms the "*all trans*" conformation of the nonacarbon chain. Bond angles are all around 120°, in agreement with an sp^2 hybridization for the carbon atoms. The mean deviation towards the best plane formed with all atoms of the nonacarbon chain between N1 and N2 is 0.190 Å. This value is ten times greater than the one corresponding to streptocyanine **9** (0.016 Å)[4c] and shows that the nonacarbon chain geometry is approximately planar. However, dihedral angles (69.2° and 87.8°) describing the position of the aryl groups compared with the carbon chain highlight that the two aryl groups are not parallel to one another and point almost perpendicularly to the carbon chain. This observation could be in agreement with the weak influence of the phenyl groups on the photophysical properties in solution of the various 9-C streptocyanine dyes.

As the purity of intermediary carboxonium salts has been improved, we have also been able to synthesize 9-C hemicarboxonium salt **21** by adding 1 equiv. of diethylamine to fluorosubstituted 9-C carboxonium salt **2** in acetonitrile at 0 °C (Scheme 4). This hemicarboxonium salt is still reactive towards amines and can be potentially used in this way for labeling molecules with amino groups. The structure of **21** was determined by X-ray diffraction (Figure 2).



Scheme 4. Synthesis of the hemicarboxonium salt **21** from the carboxonium salt **2**.

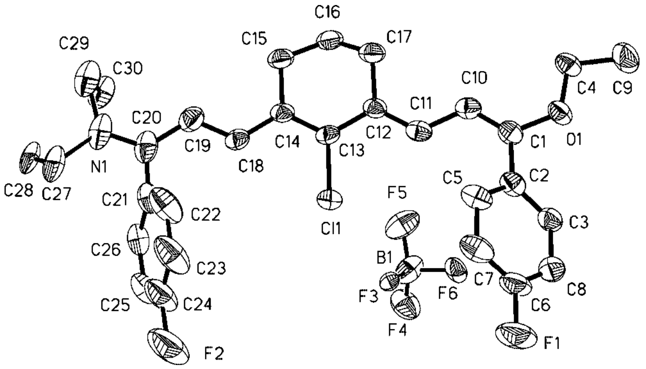


Figure 2. X-ray crystal structure of **21**; selected bond lengths [Å] and angles [°]:O1–Cl 1.388(9), C1–C10 1.335(8), C10–C11 1.434(8), C11–C12 1.355(4), C12–C13 1.446(8), C12–C17 1.503(8), C13–C14 1.374(8), C14–C15 1.507(8), C14–C18 1.418(8), C18–C19 1.352(8), C19–C20 1.433(8), C20–N1 1.285(16), C20–C21 1.469(9), C1–C2 1.484(14), N1–C20–C19 129.4(13), C20–C19–C18 122.9(6), C19–C18–C14 125.3(6), C18–C14–C13 122.1(6), C14–C13–C12 124.7(5), C13–C12–C11 122.6(5), C12–C11–C10 128.0(6), C11–C10–C1 124.0(7), C10–C1–O1 124.0(7), C10–C1–C2 126.7(8), C19–C20–C21 118.5(6), C10–C1–C2–C5 40.0, C19–C20–C21–C22 61.4.

The X-ray structure of **21** shows a polymethine chain that is less conjugated relative to the corresponding streptocyanine dye,[4c] with alternating quasisingle and quasidouble carbon–carbon bonds. Moreover, this polymethine chain is no longer planar and it curves somewhat with the meso carbon atom C13 as a maximum (the deviation towards planarity is 0.31 Å for this atom). The aryl groups are no longer perpendicular to the polymethine chain plane, which is contrary to the case of streptocyanine dyes. At last, regarding the length of the C–O (1.388 Å) and the C–N bonds (1.285 Å), we can say that the positive global charge is located to a greater extent on the nitrogen side of the molecule than on the oxygen side.

Photophysical Properties and Studies of Stability

Table 2 shows the absorption and emission wavelengths of these new dyes. It must be mentioned that from 200 to 1000 nm, only one absorption peak is observed.

Table 2. Absorbance and fluorescence data for dyes **8**–**21** (CH_2Cl_2, 20 °C).

	λ_{max} [nm]	ε [$M^{-1}cm^{-1}$]	$\lambda_{em.}$ [nm]	$\lambda_{exc.}$ [nm]	Δ Stokes [nm]	Φ [%]
8	698	254000	724	687	26	5.5
9	696	248000	726	684	30	7.2
10	698	269000	725	684	27	4.3
11	699	275000	732	684	33	3.5
12	700	205000	732	684	32	3.3
13	694	280000	717	684	23	7.3
14	701	285000	736	684	35	5.9
15	694	220000	721	684	27	3.0
16	697	240000	730	684	33	3.6
17	697	230000	728	684	31	3.8
18	710	195000	745	652	35	6.3
19	706	216000	736	670	30	3.0
20	613	76000	721	605	108	4.1
21	552	3000	–[a]	–[a]	–[a]	–[a]

[a] No fluorescence.

All new dyes **8**–**19** absorb with very high molar extinction coefficients (above 2×10^5 $M^{-1}cm^{-1}$) and emit fluorescence in the red region. 1,5,9-Trimorpholino streptocyanine **20** absorbs at about 100 nm lower than corresponding *meso*-chlorosubstituted dye **19** and shows a larger Stokes shift (108 nm). The molar extinction coefficient is also three times weaker (0.76×10^5 $M^{-1}cm^{-1}$). Similar effects where described for cyanine dyes in previous works.[11,12] For example, substitution of the *meso*-chlorine atom of a 9-C cyanine dye by a morpholino group induces a blueshift (82 nm) in the absorption spectrum.[11] It is of great interest to synthesize dyes with large Stokes shifts in order to allow easier detection and to avoid spectra recovering, which may lead to distortions in the emission spectrum and a decrease of its intensity.[12,13] Table 2 also highlights that for one type of amine (diethylamine, for instance) changing the atom in the 4-position of the phenyl groups results in a small change (4 nm) in the absorption wavelength (compounds **8**–**13**). For a fixed aromatic substituent (F, for instance), alteration of the amino group leads to a small change (about 12 nm) in the absorption wavelength (compounds **9**, **15**, and **19**). The fluorescence wavelength can be modulated in the same way from 717 nm to 736 nm. The absorption spectrum of hemicarboxonium salt **21** shows important hypso- and hy-

Table 3. Absorbance and fluorescence data for **9** in various solvents at 20 °C.

Solvent	MeOH	EtOH	CH_3CN	DMF	CH_2Cl_2	AcOEt
λ_{max} [nm]	687	688	686	693	696	687
ε [$M^{-1}cm^{-1}$]	183000	286000	152000	234000	230000	74000
$\lambda_{em.}$ [nm]	715	719	715	720	726	710
$\lambda_{exc.}$ [nm]	679	672	677	683	684	667
Δ Stokes [nm]	28	31	29	27	30	23
Φ [%]	3.9	5.3	3.1	6.2	7.2	3.9

Table 4. Absorbance and fluorescence data for dyes in MeOH and DMF at 20 °C.

Dye		**8**	**9**	**10**	**12**	**13**	**19**	**20**
MeOH	$\lambda_{\text{abs.}}$ [nm]	688	687	689	691	685	694	613
	ε [$\text{M}^{-1}\,\text{cm}^{-1}$]	202000	183000	177000	188000	400000	127000	72000
	$\lambda_{\text{em.}}$ [nm]	720	715	719	723	713	726	713
	ΔStokes [nm]	32	28	30	32	28	30	100
	Φ [%]	4.2	3.9	2.6	2.6	3.2	1.9	2.6
DMF	$\lambda_{\text{abs.}}$ [nm]	693	693	696	697	692	702	620
	ε [$\text{M}^{-1}\,\text{cm}^{-1}$]	193000	234000	196000	155000	178000	111000	66000
	$\lambda_{\text{em.}}$ [nm]	727	720	724	727	717	736	723
	ΔStokes [nm]	33	27	28	30	26	34	103
	Φ [%]	6.6	6.2	8.0	6.0	7.5	4.2	5.2

pochromic effects compared to those of the streptocyanines. Moreover, this salt is not fluorescent.

The influence of the polarity of the solvent on the absorption spectrum has been studied for **9** (Table 3). It highlights weak solvatochromism from methanol to dichloromethane.

In order to compare the data with those of recent cyanine dyes,[14a,b] Table 4 indicates absorbance and fluorescence data of our streptocyanine dyes in methanol and *N*,*N*-dimethylformamide.

Negative solvatochromism of about 6 nm was observed for our compounds when the solvent was changed from methanol to *N*,*N*-dimethylformamide. In the same solvents, Peng et al.[14a,14b] described a negative solvatochromism of about 15 nm for 9-C cyanine dyes.

The evolution of absorbance of **9** in different solvents ($c \approx 10^{-6}\,\text{mol}\,\text{L}^{-1}$) was evaluated for 12 h at 20 °C. Good stability was observed in methanol, ethanol, acetonitrile, and *N*,*N*-dimethylformamide.

Over the course of 15 h, we examined the stability of different streptocyanines at 20 and 40 °C in three solvents (methanol, *N*,*N*-dimethylformamide, and acetonitrile) that are widely used for their synthesis and for other purposes. For streptocyanine dyes **8**–**10**, **12**, and **13**, which are synthesized from diethylamine, no significant change in the absorbance was observed; this implies that no degradation occured. Up to 40 °C, streptocyanine dyes synthesized from diethylamine can be used for any application in most common solvents.

In conclusion, the synthetic method previously described[9] was extended to new carboxonium salts with the use of halogenated arylethanones and with less diketonic impurities. New fluorescent 9-C streptocyanines were obtained, as well as the first 9-C hemicarboxonium salt. This last compound opens the door to dissymmetrical streptocyanines and can be grafted onto biomolecules with amino groups. The stability of most of the streptocyanines in usual solvents up to 40 °C for 15 h may allow for them to be used in biological media.

Experimental Section

General Remarks: All experiments were performed under dry conditions (argon atmosphere, anhydrous solvents) to avoid degradation of the carboxonium salt. Melting points were determined with a Büchi capillary apparatus. ^{1}H- and ^{13}C-NMR spectra were recorded with Bruker AC 200, Bruker AC 250, AM 300 WB, or AM 400 WB spectrometers. Chemical shifts are given in ppm from TMS. Mass spectra were obtained with a Perkin–Elmer SCIEX API 365 apparatus with electrospray (positive mode, CH_3CN) and a Nermag R10–10 apparatus for DCI. UV/Vis spectra were obtained with a Hewlett–Packard 8453 UV/Vis spectrophotometer. Excitation and fluorescence emission spectra were obtained with a Perkin–Elmer LS 50B spectrofluorimeter fitted with a xenon pulsed lamp (20 kW, flash-time 8 µs) and a Hamamatsu R 928 photomultiplicator. Fluorescence quantum yields were measured at 25 °C with a Cary Eclipse Varian Spectrophotometer equipped with a xenon flash lamp and by using a red sensitive photomultiplier tube detector. UV/Vis absorption spectra were recorded with a Shimadsu UV-2401PC, UV/Vis recording spectrophotometer. 3,3′-Diethylthiadicarbocyanine iodide was used as a reference (Fluka, Φ_f = 0.36 in methanol).[15] Elemental analyses were performed by the microanalysis service from the Laboratoire de Chimie de Coordination (LCC) in Toulouse.

Synthesis of the Carboxonium Salts 1–7: 9-C carboxonium salts were synthesized by extension of the synthetic pathway previously developed in the laboratory.[9] To a solution of 2-chloro-3-(hydroxymethylene)cyclohex-1-ene-1-carbaldehyde[16] (0.6 g, 3.47 mmol) in triethoxymethane (2.3 mL, 13.88 mmol) was added dropwise a mixture of arylethanone (6.94 mmol) and 54% tetrafluoroboric acid in diethyl ether (0.472 mL, 3.47 mmol). The solution turned purple and viscous. After stirring for 10 min, diethyl ether (200 mL) was added in order to precipitate the product. The product was filtered off after 4 h of stirring to obtain a purple powder.

5-Chloro-1,9-diethoxy-1,9-bis(4-methoxyphenyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (1): From 4-methoxyphenylethanone: Purple powder (77%), carboxonium salt/diketone proportion, 63:37. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.53 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3CH_2O), 1.93 (quint, $^3J_{H,H}$ = 5.5 Hz, 2 H, $H^{5'}$), 2.73 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H, $H^{4'-6'}$), 3.88 (s, 6 H, CH_3O), 6.46 (d, $^3J_{H,H}$ = 13.0 Hz, 2 H, H^{2-8}), 7.01 and 7.59 (AB syst., $^3J_{H,H}$ = 8.7 Hz, 8 H, H_{arom}), 8.16 (d, $^3J_{H,H}$ = 13.0 Hz, 2 H, H^{3-7}) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$, 25 °C): δ = 14.5 (CH_3CH_2O), 20.5 ($C^{5'}$), 26.9 ($C^{4'-6'}$), 55.9 (CH_3OAr), 69.2 (CH_3CH_2O), 107.8 (C^{2-8}), 114.6 (C_{arom}), 127.5 (C^{4-6}), 132.8 (C_{arom}-C^{1-9}), 133.1 (C_{arom}), 155.0 (C^{3-7}), 158.4 (C^5), 164.3 (C_{arom}-OCH_3), 181.4 (C^{1-9}) ppm.

5-Chloro-1,9-diethoxy-1,9-bis(4-fluorophenyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (2): From 4-fluorophenylethanone: Purple powder (34%), carboxonium salt/diketone proportion, 98:2. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = 1.57 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, OCH_2CH_3), 1.98 (quint, $^3J_{H,H}$ = 6.1 Hz, 2 H, $H^{5'}$), 2,81 (t, $^3J_{H,H}$ = 6.1 Hz, 4 H, $H^{4'-6'}$), 4,56 (q, $^3J_{H,H}$ = 6.9 Hz, 4 H, OCH_2CH_3), 6,61 (d, $^3J_{H,H}$ = 13.1 Hz, 2 H, H^{2-8}), 7,21 (t,

${}^{3}J_{\mathrm{H,H}}$ = 8.3 Hz, 4 H, H$_{\mathrm{arom}}$), 7.61 (m, 4 H, H$_{\mathrm{arom}}$), 8.18 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.1 Hz, 2 H, H$^{3-7}$) ppm. ^{13}C{^{1}H} NMR (63 MHz, CDCl$_3$, 25 °C): δ = 14.3 (*C*H$_3$CH$_2$O), 20.4 (C$^{5'}$), 26.9 (C$^{4'-6'}$), 69.6 (CH$_3$*C*H$_2$O), 108.3 (C$^{2-8}$), 116.3 (d, ${}^{2}J_{\mathrm{C,F}}$ = 21.9 Hz, CH$_{\mathrm{arom}}$), 123.2 (C$^{4-6}$), 129.6 (C_{arom}-C$^{1-9}$), 165.5 (d, ${}^{1}J_{\mathrm{C,F}}$ = 256.6 Hz, C$_{\mathrm{arom}}$-F), 156.5 (C$^{3-7}$), 160.8 (C^{5}-Cl), 164.0 (*C*H$_{\mathrm{arom}}$), 181.4 (C$^{1-9}$) ppm.

5-Chloro-1,9-bis(4-chlorophenyl)-1,9-diethoxy-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (3): From 4-chlorophenylethanone: Blue powder (36%), carboxonium salt/diketone proportion, 97:3. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.56 (t, ${}^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 6 H, OCH$_2$C*H*$_3$), 1.97 (quint, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 2 H, H$^{5'}$), 2.81 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 4 H, H$^{4'-6'}$), 4.56 (q, ${}^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 4 H, OC*H*$_2$CH$_3$), 6.63 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.1 Hz, 2 H, H$^{2-8}$), 7.49 and 7.55 (AB syst., ${}^{3}J_{\mathrm{H,H}}$ = 8.9 Hz, 8 H, H$_{\mathrm{arom}}$), 8.19 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.1 Hz, 2 H, H$^{3-7}$) ppm.

1,9-Bis(4-bromophenyl)-5-chloro-1,9-diethoxy-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (4): From 4-bromophenylethanone: Blue powder (38%), carboxonium salt/diketone proportion, 97:3. ^{1}H NMR (250 MHz, CD$_3$CN, 25 °C): δ = 1.56 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, 6 H, OCH$_2$C*H*$_3$), 1.96 (quint, ${}^{3}J_{\mathrm{H,H}}$ = 5.9 Hz, 2 H, H$^{5'}$), 2.80 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, 4 H, H$^{4'-6'}$), 4.54 (q, ${}^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, 4 H, OC*H*$_2$CH$_3$), 6.60 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.0 Hz, 2 H, H$^{2-8}$), 7.38 and 7.74 (AB syst., ${}^{3}J_{\mathrm{H,H}}$ = 8.5 Hz, 8 H, H$_{\mathrm{arom}}$), 8.19 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.0 Hz, 2 H, H$^{3-7}$) ppm.

5-Chloro-1,9-bis(4-phenylphenyl)-4,6-(propane-1,3-diyl)nona-2,4,6-trien-1,9-dione (5): Carboxonium salt **5** is too sensitive to hydrolyze and the NMR spectrum could not be recorded. Only the ^{1}H NMR spectrum of the diketone resulting from its hydrolysis is given here. 4-Phenyl streptocyanine **12** is synthesized in one-pot. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.88 (quint, ${}^{3}J_{\mathrm{H,H}}$ = 6.4 Hz, 2 H, H$^{5'}$), 2.58 (m, 4 H, H$^{4'-6'}$), 3.93 (d, ${}^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 2 H, H^{2}), 6.71 (m, 1 H, H^{3}), 7.10 (d, ${}^{3}J_{\mathrm{H,H}}$ = 15.5 Hz, 1 H, H^{7}), 7.26–7.72 (m, 8 H, H$_{\mathrm{arom}}$), 8.04 (m, 8 H, H$_{\mathrm{arom}}$), 8.28 (d, ${}^{3}J_{\mathrm{H,H}}$ = 15.3 Hz, 1 H, H^{8}) ppm.

5-Chloro-1,9-diethoxy-1,9-diphenyl-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (6): From phenylethanone: Blue powder (26%), carboxonium salt/diketone proportion, 52:48. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.57 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, 6 H, OCH$_2$C*H*$_3$), 1.95 (m, 2 H, H$^{5'}$), 2.78 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.1 Hz, 4 H, H$^{4'-6'}$), 4,52 (q, ${}^{3}J_{\mathrm{H,H}}$ = 6.9 Hz, 4 H, OC*H*$_2$CH$_3$), 6.54 (d, ${}^{3}J_{\mathrm{H,H}}$ = 12.9 Hz, 2 H, H$^{2-8}$), 8,26 (d, ${}^{3}J_{\mathrm{H,H}}$ = 12.9 Hz, 2 H, H$^{3-7}$), 7.54 (m, H$_{\mathrm{arom}}$) ppm.

5-Chloro-1,9-diethoxy-1,9-bis(β-naphthyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (7): From β-naphthylethanone: Blue powder (20%), carboxonium salt/diketone proportion, 75:25. ^{1}H NMR (250 MHz, CDCl$_3$, 25 °C): δ = 1.61 (t, ${}^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 6 H, OCH$_2$C*H*$_3$), 2.03 (quint, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 2 H, H$^{5'}$), 2.86 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 4 H, H$^{4'-6'}$), 4.60 (q, ${}^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 4 H, OC*H*$_2$CH$_3$), 6.70 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.0 Hz, 2 H, H$^{2-8}$), 7.59 (t, ${}^{3}J_{\mathrm{H,H}}$ = 8.0 Hz, 4 H, H$_{\mathrm{arom}}$), 7.64 (d, ${}^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 2 H, H$_{\mathrm{arom}}$), 7.90 (d, ${}^{3}J_{\mathrm{H,H}}$ = 10.4 Hz, 4 H, H$_{\mathrm{arom}}$), 7.93 (d, ${}^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 2 H, H$_{\mathrm{arom}}$), 8.12 (s, 2 H, H$_{\mathrm{arom}}$), 8.31 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.0 Hz, 2 H, H$^{3-7}$) ppm.

Synthesis of Streptocyanine Dyes 8–20: To a solution of carboxonium salt (1.17 mmol) in acetonitrile (20 mL) was added freshly distilled diethylamine (0.25 mL, 2.40 mmol) (or an excess of dimethylamine or exactly 2 equiv. of morpholine). After stirring for 24 h at room temperature, the solution was filtered off to eliminate the diketone. The solvent was then removed under reduce pressure, and the crude product was recrystallized from ethanol. For trimorpholino substituted dye **20**, a large excess of morpholine (8 equiv.) was added and washing with pentane was realized before crystallization. Dyes **9** and **13** are described in ref.[4c]

5-Chloro-1,9-(diethylamino)-1,9-bis(4-methoxyphenyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (8): Green needles (75%). M.p. 208–210 °C (dec.). ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ = 1.22 [t, ${}^{3}J_{\mathrm{H,H}}$ = 7.3 Hz, 12 H, (C*H*$_3$-CH$_2$)$_2$N], 1.78 (quint, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 2 H, H$^{5'}$), 2.46 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 4 H, H$^{4'-6'}$), 3.48 [m, 8 H, (CH$_3$-C*H*$_2$)$_2$N], 3.82 (s, 6 H, CH$_3$O-Ar), 5.98 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.2 Hz, 2 H, H$^{2-8}$), 6.93 (m, 4 H, H$_{\mathrm{arom}}$), 7.06–7.25 (m, 6 H, H$^{3-7}$ and H$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 25 °C): δ = 13.4 [(*C*H$_3$CH$_2$)$_2$N], 21.0 (C$^{5'}$), 26.8 (C$^{4'-6'}$), 46.9 [(CH$_3$*C*H$_2$)$_2$N], 55.5 (CH$_3$O-Ar), 106.0 (C$^{2-8}$), 114.2 (C$_{\mathrm{arom}}$), 124.1 (C$^{4-6}$), 125.2 (C_{arom}-C$^{1-9}$), 130.1 (C$_{\mathrm{arom}}$), 149.9 (C$^{3-7}$), 150.6 (C^{5}), 160.8 (C_{arom}-OCH$_3$), 167.6 (C$^{1-9}$) ppm. UV/Vis (23 °C, CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon_{\max}$, M^{-1}cm^{-1}) = 643 (shoulder), 698 (254000) nm. Fluorescence spectrometry (23 °C, CH$_2$Cl$_2$): $\lambda_{\mathrm{em.}}$ = 724 nm. MS (Electrospray): *m*/*z* (%) = 547.4 [M]$^+$, 549.4 (40) [M + 2]$^+$. C$_{34}$H$_{44}$BClF$_4$N$_2$O$_2$ (634.99): calcd. C 64.31, H 6.98, N 4.41; found C 64.03, H 7.00, N 4.52. *Crystal Data for* **8***:* C$_{34}$H$_{44}$BClF4N$_2$O$_2$, *Fw* = 634.97, monoclinic, $P2_1/c$, a = 15.305(1) Å, b = 13.370(1) Å, c = 16.207(1) Å, α = 90°, β = 93.948(2)°, γ = 90°, V = 3308.3(5) Å^3, Z = 4, λ = 0.71073 Å, T = 193(2) K, 14678 reflections (4743 independent, R$_{\mathrm{int}}$ = 0.0496) were collected at low temperatures by using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer. The structure was solved by direct method (SHELXS-97)[17] and 403 parameters were refined by using the least-squares method on F^2.[18] Largest electron density residue 0.233 eÅ^{-3}, R_1 [for $I > 2\sigma(I)$] = 0.0380 and wR_2(all data) = 0.0845 with $R_1 = \Sigma|F_o|-|F_c|/\Sigma|F_o|$ and $wR_2 = \mathrm{w}[\Sigma w\,(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

5-Chloro-1,9-bis(4-chlorophenyl)-1,9-diethylamino-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (10): Green needles (51%). M.p. 231 °C. ^{1}H NMR (250 MHz, CD$_3$CN, 25 °C): δ = 1.18 [t, ${}^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, 12 H, N(CH$_2$C*H*$_3$)$_2$], 1.74 (quint, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 2 H, H$^{5'}$), 2.51 (t, ${}^{3}J_{\mathrm{H,H}}$ = 6.0 Hz, 4 H, H$^{4'-6'}$), 3.44 [m, 8 H, N(C*H*$_2$CH$_3$)$_2$], 6.08 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.3 Hz, 2 H, H$^{2-8}$), 6.96 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.3 Hz, 2 H, H$^{3-7}$), 7.23 and 7.51 (AB syst., ${}^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 8 H, H$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (63 MHz, CD$_3$CN, 25 °C): δ = 13.4 [(*C*H$_3$CH$_2$)$_2$N], 21.7 (C$^{5'}$), 27.4 (C$^{4'-6'}$), 47.8, [(CH$_3$*C*H$_2$)$_2$N], 107.0 (C$^{2-8}$), 124.8 (C$^{4-6}$), 129.9 (CH$_{\mathrm{arom}}$), 131.2 (CH$_{\mathrm{arom}}$), 132.9(CH$_{\mathrm{arom}}$-C$^{1-9}$), 136.4 (C$_{\mathrm{arom}}$-Cl), 149.7 (C$^{3-7}$), 150.0 (C^{5}-Cl), 167.4 (C$^{1-9}$) ppm. UV/Vis (23 °C, CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon_{\max}$, M^{-1}cm^{-1}) = 640 (shoulder), 698 (269000) nm. Fluorescence spectrometry (23 °C, CH$_2$Cl$_2$): $\lambda_{\mathrm{em.}}$ = 725 nm. MS (Electrospray, positive mode, CH$_3$CN): *m*/*z* (%) = 555.2 (97.8) [M]$^+$, 557.2 (100) [M + 2]$^+$, 559.2 (42.4) [M + 4]$^+$. C$_{32}$H$_{38}$BCl$_3$F$_4$N$_2$ (642.21): calcd. C 59.70, H 5.95, N 4.35; found C 59.65, H 5.63, N 4.16.

1,9-Bis(4-bromophenyl)-5-chloro-1,9-diethylamino-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (11): Green needles (38%). M.p. 240 °C. ^{1}H NMR (250 MHz, CD$_3$CN, 25 °C): δ = 1.18 [t, ${}^{3}J_{\mathrm{H,H}}$ = 7.0 Hz, 12 H, N(CH$_2$C*H*$_3$)$_2$], 1.75 (quint, ${}^{3}J_{\mathrm{H,H}}$ = 5.9 Hz, 2 H, H$^{5'}$), 2.51 (t, ${}^{3}J_{\mathrm{H,H}}$ = 5.9 Hz, 4 H, H$^{4'-6'}$), 3.46 [m, 8 H, N(C*H*$_2$CH$_3$)$_2$], 6.08 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.3 Hz, 2 H, H$^{2-8}$), 6.98 (d, ${}^{3}J_{\mathrm{H,H}}$ = 13.3 Hz, 2 H, H$^{3-7}$), 7.17 and 7.68 (AB syst., ${}^{3}J_{\mathrm{H,H}}$ = 8.6 Hz, 8 H, H$_{\mathrm{arom}}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN, 25 °C): δ = 13.4 [(*C*H$_3$CH$_2$)$_2$N], 21.7 (C$^{5'}$), 27.4 (C$^{4'-6'}$), 47.8, [(CH$_3$*C*H$_2$)$_2$N], 107.0 (C$^{2-8}$), 124.4 and 124.6 (C$_{\mathrm{arom}}$-Br and C$^{4-6}$), 131.4 (CH$_{\mathrm{arom}}$), 132.9 (CH$_{\mathrm{arom}}$),133.4 (C$_{\mathrm{arom}}$-C$^{1-9}$), 149.8 (C$^{3-7}$), 150.1 (C^{5}-Cl), 167.5 (C$^{1-9}$) ppm. UV/Vis (23 °C, CH$_2$Cl$_2$): $\lambda_{\max}$ ($\varepsilon_{\max}$, M^{-1}cm^{-1}) = 640 (shoulder), 699 (275000). Fluorescence spectrometry (23 °C, CH$_2$Cl$_2$): λ_{em} = 732 nm. MS (Electrospray, positive mode, CH$_3$CN): *m*/*z* (%) = 643.3 (43.6) [M]$^+$, 645.3 (100) [M + 2]$^+$, 647.3 (76.9) [M + 4]$^+$, 649.3 (16.7) [M + 6]$^+$. C$_{32}$H$_{38}$BBr$_2$ClF$_4$N$_2$ (732.73): calcd. C 52.45, H 5.23, N 3.82; found C 52.55, H 4.89, N 4.02.

5-Chloro-1,9-diethylamino-1,9-bis(4-phenylphenyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (12): Green powder (60%). M.p. 220 °C (dec.). ^{1}H NMR (250 MHz, CD_3CN, 25 °C): δ = 1.22 [m, 12 H, $N(CH_2CH_3)_2$], 1.76 (quint, $^{3}J_{H,H}$ = 5.9 Hz, 2 H, $H^{5'}$), 2.51 (t, $^{3}J_{H,H}$ = 5.9 Hz, 4 H, $H^{4'-6'}$), 3.47 [m, 8 H, $N(CH_2CH_3)_2$], 6.09 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{2-8}), 7.04 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{3-7}), 7.28 and 7.71 (AB syst, $^{3}J_{H,H}$ = 8.6 Hz, 8 H, H_{arom}), 7.41 (m, 6 H, H_{arom}), 7.61 (m, 4 H, H_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR (63 MHz, CD_3CN, 25 °C): δ = 12.5[$(CH_3CH_2)_2N$], 20.8 ($C^{5'}$), 26.6 ($C^{4'-6'}$), 46.8 [$(CH_3CH_2)_2N$], 106.1 (C^{2-8}), 123.7 (C^{4-6}), 126.7–129.1 (CH_{arom}), 132.3 (C_{arom}-C^{1}), 139.4 (C_{arom}), 142.2 (C_{arom}-Ph), 148.9 (C^{3-7}), 149.0 (C^{5}), 167.5 (C^{1-9}) ppm. UV/Vis (23 °C, CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 640 (shoulder), 700 (205300) nm. Fluorescence spectrometry (23 °C, CH_2Cl_2): $\lambda_{em.}$ = 732 nm. MS (Electrospray, positive mode, CH_3CN): *m/z* (%) = 639.55 (100) $[M]^+$, 641.55 (43.6) $[M + 2]^+$. $C_{44}H_{48}BClF_4N_2$ (727.13) calcd. C 72.68, H 6.65, N 3.85; found C 72.10, H 6.23, N 3.42.

5-Chloro-1,9-diethylamino-1,9-bis(2′-naphthyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (14): Green marbles (50%). M.p. 158 °C (dec.). ^{1}H NMR (250 MHz, CD_3CN, 25 °C): δ = 1.20 [t, $^{3}J_{H,H}$ = 6.7 Hz, 12 H, $N(CH_2CH_3)_2$], 1.75 (quint, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, $H^{5'}$), 2.52 (t, $^{3}J_{H,H}$ = 6.0 Hz, 4 H, $H^{4'-6'}$), 3.49 [m, 8 H, $N(CH_2CH_3)_2$], 6.13 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{2-8}), 6.92 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{3-7}), 7.24–7.28 (2d, $^{3}J_{H,H}$ = 8.6 Hz, 2 H, H_{arom}), 7.54 (m, 4 H, H_{arom}), 7.72 (s, 2 H, H_{arom}), 7.80–8.01 (m, 6 H, H_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ = 13.4 [$(CH_3CH_2)_2N$], 21.7 ($C^{5'}$), 27.5 ($C^{4'-6'}$), 47.9 [$(CH_3CH_2)_2N$], 107.1 (C^{2-8}), 124.5 (C^{4-6}), 126.4 (CH_{arom}), 128.1 (CH_{arom}), 128.5 (CH_{arom}), 128.7 (CH_{arom}), 129.1 (CH_{arom}), 129.2 (CH_{arom}), 129.5 (C_{arom}), 129.7 (C_{arom}), 133.4 (C_{arom}-C^{1-9}), 133.9 (C_{arom}), 149.8 (C_5-Cl), 149.7 (C^{3-7}), 168.6 (C^{1-9}) ppm. UV/Vis (23 °C, CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 640 (shoulder), 701 (285000) nm. MS [DCI (NH_3), CH_3CN]: *m/z* (%) = 587.0 (7.1) $[M]^+$, 589.0 (3.7) $[M + 2]^+$. $C_{40}H_{44}BClF_4N_2$ (675.05) calcd. C 71.17, H 6.57, N 4.15; found C 70.39, H 6.23, N 3.86.

5-Chloro-1,9-bis(4-fluorophenyl)-1,9-bis(dimethylamino)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (15): Golden needles (83%). M.p. 219 °C (dec.). ^{1}H NMR (250 MHz, CD_3CN, 25 °C): δ = 1.77 (quint, $^{3}J_{H,H}$ = 6.2 Hz, 2 H, $H^{5'}$), 2.52 (t, $^{3}J_{H,H}$ = 6.2 Hz, 4 H, $H^{4'-6'}$), 3.12 [s, 12 H, $N(CH_3)_2$], 6.06 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{2-8}), 7.05 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{3-7}), 7.24–7.30 (m, 8 H, H_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ = 20.8 ($C^{5'}$), 26.5 ($C^{4'-6'}$), 42.2 [$(CH_3)_2N$], 106.5 (C^{2-8}), 116.2 (d, $^{2}J_{C,F}$ = 23.4 Hz, CH_{arom}), 124.1 (C^{4-6}), 131.0 (C_{arom}-C^{1-9}), 131.7 (CH_{arom}), 148.4 (C^{3-7}), 148.9 (C^{5}-Cl), 165.2 (d, $^{3}J_{C,F}$ = 249 Hz, C_{arom}-F), 167.8 (C^{1-9}) ppm. UV/Vis (23 °C, CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 640 (shoulder), 694 (220100) nm. Fluorescence spectrometry (23 °C, CH_2Cl_2): $\lambda_{em.}$ = 721 nm. MS (Electrospray, positive mode, CH_3CN): *m/z* (%) = 467.25 (100) $[M]^+$, 469.15 (37) $[M + 2]^+$. $C_{28}H_{30}BClF_6N_2$ (554.81) calcd. C 60.62, H 5.45, N 5.05; found C 60.41, H 5.24, N 5.40.

5-Chloro-1,9-bis(4-chlorophenyl)-1,9-bis(dimethylamino)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (16): Green powder (54%). M.p. 236 °C (dec.). ^{1}H NMR(250 MHz, CD_3CN, 25 °C): δ = 1.77 (quint, $^{3}J_{H,H}$ = 6.1 Hz, 2 H, $H^{5'}$), 2.52 (t, $^{3}J_{H,H}$ = 6.1 Hz, 4 H, $H^{4'-6'}$), 3.12 [s, 12 H, $N(CH_3)_2$], 6.06 (d, $^{3}J_{H,H}$ = 13.6 Hz, 2 H, H^{2-8}), 7.05 (d, ^{3}J = 13.6 Hz, 2 H, H^{3-7}), 7.24 and 7.53 (AB syst., $^{3}J_{H,H}$ = 8.6 Hz, 8 H, H_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR (63 MHz, CD_3CN, 25 °C): δ = 21.7 ($C^{5'}$), 27.4 ($C^{4'-6'}$), 43.2 [$(CH_3)_2N$], 107.3 (C^{2-8}), 125.2 (C^{4-6}), 130.0 (CH_{arom}), 131.6 (CH_{arom}), 133.0 (C_{arom}-C^{1-9}), 136.8 (C_{arom}-Cl), 149.4 (C^{3-7}), 150.0 (C^{5}-Cl), 168.5 (C^{1-9}) ppm. UV/Vis (23 °C, CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 640 (shoulder), 697 (240000) nm. Fluorescence spectrometry (23 °C, CH_2Cl_2): $\lambda_{em.}$ = 730 nm. MS (Electrospray, positive mode, CH_3CN): *m/z* (%) = 499.4 (97.8) $[M]^+$, 501.4 (100) $[M + 2]^+$, 503.4 (31.9) $[M + 4]^+$. $C_{28}H_{30}BCl_3F_4N_2$ (587.72) calcd. C 57.22, H 5.14, N 4.77; found C 57.12, H 4.70, N 4.57.

1,9-Bis(4-bromophenyl)-5-chloro-1,9-bis(dimethylamino)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (17): Green needles (52%). M.p. 240 °C (dec.). ^{1}H NMR (250 MHz, CD_3CN, 25 °C): δ = 1.76 (quint, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, $H_{5'}$), 2.52 (t, $^{3}J_{H,H}$ = 6.0 Hz, 4 H, $H_{4'-6'}$), 3.12 [s, 12 H, $N(CH_3)_2$], 6.05 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H_{2-8}), 7.05 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H_{3-7}), 7.17 and 7.68 (AB syst., $^{3}J_{H,H}$ = 8.6 Hz, 8 H, H_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ = 21.7 ($C_{5'}$), 27.4 ($C_{4'-6'}$), 43.2 [$(CH_3)_2N$], 107.3 (C_{2-8}), 125.0 and 125.2 (C_{4-6} and C_{arom}-Br), 131.7 (CH_{arom}), 133.0 (CH_{arom}), 133.4 (C_{arom}-C_{1-9}), 149.3 (C_{3-7}), 150.0 (C_5-Cl), 168.5 (C_{1-9}) ppm. UV/Vis (23 °C, CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 697 (230000) nm. Fluorescence spectrometry (23 °C, CH_2Cl_2): λ_{em} = 728 nm. MS (Electrospray, positive mode, CH_3CN): *m/z* (%) = 587.0 (41.1) $[M]^+$, 589.0 (100) $[M + 2]^+$, 591.0 (67.6) $[M + 4]^+$, 593.0 (14.8) $[M + 6]^+$. $C_{28}H_{30}BBr_2ClF_4N_2$ (676.62) calcd. C 49.70, H 4.47, N 4.14; found C 49.78, H 4.40, N: 3.97.

5-Chloro-1,9-(dimorpholino)-1,9-bis(4-methoxyphenyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (18): Green needles (49%). M.p. 255–257 °C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.79 (quint, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, $H^{5'}$), 2.54 (t, $^{3}J_{H,H}$ = 7.6 Hz, 4 H, $H^{4'-6'}$), 3.58 (t, $^{3}J_{H,H}$ = 5.7 Hz, 8 H, CH_2N), 3.78 (t, $^{3}J_{H,H}$ = 5.7 Hz, 8 H, CH_2O), 3.83 (s, 6 H, CH_3O-Ar), 6.20 (d, $^{3}J_{H,H}$ = 13.2 Hz, 2 H, H^{2-8}), 6.96 and 7.21 (AB syst., $^{3}J_{H,H}$ = 8.6 Hz, 8 H, H_{arom}), 7.26 (d, $^{3}J_{H,H}$ = 13.2 Hz, 2 H, H^{3-7}) ppm. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$, 25 °C): δ = 21.0 ($C^{5'}$), 26.8 ($C^{4'-6'}$), 50.9 (CH_2N), 55.6 (CH_3O-Ar), 66.7 (CH_2O), 108.1 (C^{2-8}), 114.4 (C_{arom}), 124.9 (C^{4-6}), 127.2 (C_{arom}-C^{1-9}), 131.4 (C_{arom}), 149.3 (C^{3-7}), 149.8 (C_5-Cl), 161.5 (C_{arom}-OCH_3), 167.9 (C^{1-9}) ppm. UV/Vis (23 °C, CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 357 (14000), 654 (shoulder), 710 (195000) nm. Fluorescence spectrometry (23 °C, CH_2Cl_2): $\lambda_{em.}$ = 745 nm. MS (Electrospray): *m/z* (%) = 575.2 (100) $[M]^+$, 577.2 (42) $[M + 2]^+$. $C_{34}H_{40}BClF_4N_2O_4$ (662.95) calcd. C 61.60, H 6.08, N 4.23; found C 61.42, H 5.74, N 4.32.

5-Chloro-1,9-bis(4-fluorophenyl)-1,9-dimorpholino-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (19): Green needles (65%). M.p. 243 °C (dec.). ^{1}H NMR (250 MHz, CD_3CN, 25 °C): δ = 1.77 (quint, $^{3}J_{H,H}$ = 5.9 Hz, 2 H, $H^{5'}$), 2.54 (t, $^{3}J_{H,H}$ = 5.9 Hz, 4 H, $H^{4'-6'}$), 3.52 (t, $^{3}J_{H,H}$ = 4.7 Hz, 8 H, N-CH_2), 3.72 (t, $^{3}J_{H,H}$ = 4.7 Hz, 8 H, O-CH_2), 6.23 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{2-8}), 7.13 (d, $^{3}J_{H,H}$ = 13.3 Hz, 2 H, H^{3-7}), 7.21–7.35 (m, 8 H, H_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR (75 MHz, CD_3CN, 25 °C): δ = 20.8 ($C^{5'}$), 26.5 ($C^{4'-6'}$), 50.7, (CH_2-N), 66.4 (CH_2-O), 107.5 (C^{2-8}), 116.1 (d, ^{2}J = 22.6, CH_{arom}), 125.9 (C^{4-6}), 129.2 (C_{arom}-C^{1-9}), 131.9 (CH_{arom}), 148.8 (C^{3-7}), 149.1 (C^{5}-Cl), 163.7 (d, $^{1}J_{C,F}$ = 249.0, C_{arom}-F), 167.0 (C^{1-9}) ppm. UV/Vis (23 °C, CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 640 (shoulder), 706 (216000) nm. Fluorescence spectrometry (23 °C, CH_2Cl_2): $\lambda_{em.}$ = 736 nm. MS (Electrospray, positive mode, CH_3CN): *m/z* (%) = 515.3 (10.1) $[M - HCl]^+$, 551.3 (100) $[M]^+$, 553.3 (44) $[M + 2]^+$. $C_{32}H_{34}BClF_6N_2O_2$ (638.88) calcd. C 60.16, H 5.36, N 4.38; found C 59.74, H 5.00, N 4.24.

1,9-Bis(4-fluorophenyl)-1,5,9-trimorpholino-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (20): Green needles (26%). M.p. 223 °C (dec.), ^{1}H NMR (250 MHz, CD_3CN, 25 °C): δ = 1.64 (quint, $^{3}J_{H,H}$ = 6.5 Hz, 2 H, $H^{5'}$), 2.33 (t, $^{3}J_{H,H}$ = 6.5 Hz, 4 H, $H^{4'-6'}$), 3.56 (t, $^{3}J_{H,H}$ = 4.8 Hz, 8 H, N-CH_2), 3.71 (t, $^{3}J_{H,H}$ = 4.8 Hz, 8 H, O-CH_2), 5.89 (d, $^{3}J_{H,H}$ = 12.4 Hz, 2 H, H^{2-8}), 6.56 (d,

$^3J_{H,H}$ = 12.4 Hz, 2 H, H$^{3-7}$), 7.28 (m, 8 H, H$_{arom}$) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN, 25 °C): δ = 20.4 (C$^{5'}$), 26.5 (C$^{4'-6'}$), 50.7, (*C*H$_2$-N), 66.1 (*C*H$_2$-O), 101.6 (C$^{2-8}$), 115.9 (d. $^2J_{C,F}$ = 22.6. CH$_{arom}$), 122.2 (C$^{4-6}$), 130.4 (C$_{arom}$-C$^{1-9}$), 132.0 (CH$_{arom}$), 146.8 (C$^{3-7}$), 163.5 (d, $^1J_{C,F}$ = 248.3, C$_{arom}$-F), 163.8 (C^5-N), 173.6 (C$^{1-9}$) ppm. UV/Vis (23 °C, CH$_2$Cl$_2$): λ_{max} (ε_{max}, M^{-1} cm^{-1}) = 590 (shoulder), 613 (76000) nm. Fluorescence spectrometry (23 °C, CH$_2$Cl$_2$): $\lambda_{em.}$ = 721 nm. MS (Electrospray, positive mode, CH$_3$CN): *m*/*z* (%) = 602.3 (100) [M]$^+$. $\mathrm{C_{36}H_{42}BF_6N_3O_3}$ (689.54) calcd. C 62.71, H 6.14, N 6.09; found C 62.67, H 6.31, N 6.29.

Synthesis of Hemicarboxonium Salt 21: To a solution of carboxonium salt **2** (0.50 g, 0.88 mmol) in anhydrous acetonitrile (20 mL), was added freshly distilled diethylamine (0.07 mL, 0.68 mmol) at 0 °C, under an argon atmosphere. Immediately at the end of the addition, the solvent was evaporated after filtration. The crude product was washed with water and extracted from dichloromethane. The residue was then recrystallized from toluene/acetonitrile, 1:1.

5-Chloro-1-ethoxy-9-diethylamino-1,9-bis(4-fluorophenyl)-4,6-(propane-1,3-diyl)nona-1,3,5,7-tetraenylium Tetrafluoroborate (21): Red needles (51%). Because of the dissymmetry of the molecule and the presence of conformers in solution, ^{1}H- and ^{13}C-NMR spectra are difficult to solve and are not given. MS (Electrospray, positive mode, CH$_3$CN): *m*/*z* (%) = 496.15 (100) [M]$^+$, 498.2 (45.2) [M + 2]$^+$. UV/Vis (23 °C, CH$_2$Cl$_2$): λ_{max} (ε_{max}, M^{-1} cm^{-1}) = 552 (3000) nm. *Crystal Data for* **21***:* $\mathrm{C_{37}H_{41}BClF_6NO}$, *Fw* = 675.97, triclinic, $P\bar{1}$, a = 10.378(2) Å, b = 11.874(2) Å, c = 16.177(2) Å, α = 92.526(3)°, β = 104.263(3)°, γ = 113.152(3)°, V = 1754.1(4) Å^3, Z = 2, λ = 0.71073 Å, T = 133(2) K, 7837 reflections (5009 independent, R$_{int}$ = 0.0361) were collected at low temperatures by using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer. The structure was solved by direct method (SHELXS-97)[17] and 645 parameters were refined by using the least-squares method on F^2.[18] Largest electron density residue 0.433 e Å^{-3}, R_1 [for $I > 2\sigma(I)$] = 0.0715 and wR_2 (all data) = 0.2122 with $R_1 = \Sigma|F_o|-|F_c|/\Sigma|F_o|$ and $wR_2 = w[\Sigma w\ (F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

CCDC-610543 for **8** and -610544 for **21** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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