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Synthesis and Optical Properties of Trioxatriangulenium Dyes with One and Two Peripheral Amino Substituents

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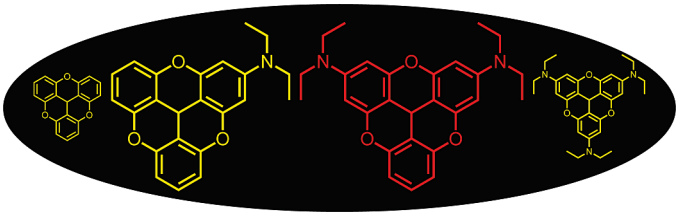

Several derivatives of two new dye systems, with one or two dialkylamino donor groups attached to resonant positions at the periphery of a trioxatriangulenium ion, were synthesized. The mono- and bis-dialkylamino trioxatriangulenium salts ($\mathbf{A_1}$-**TOTA**$^+$ and $\mathbf{A_2}$-**TOTA**$^+$) were prepared from methoxy-substituted triphenylmethylium (TPM) compounds by aromatic nucleophilic substitution with secondary amines and subsequent intramolecular ring closure. The optical properties of the new triangulenium dyes and their TPM precursors were investigated and compared to those of known TPM and xanthenium dyes. The optical properties were found to be dependent on symmetry and charge localization in the conjugated framework. The trioxatriangulenium dye with two amino groups ($\mathbf{A_2}$-**TOTA**$^+$) was found to be a strong fluorophore with properties as a blue-shifted rhodamine B. The mono-substituted compound ($\mathbf{A_1}$-**TOTA**$^+$) was found to be only weakly fluorescent. We assign the weak fluorescence of $\mathbf{A_1}$-**TOTA**$^+$ to an efficient but reversible formation of a nonfluorescent conformation in the excited state, favored by the large degree of charge localization in this dye with only one donor group.

Introduction

The triangulene (4,8,12-trioxa-4,8,12,12c-tetrahydrodibenzo[*cd,mn*]pyrene) compounds share a structure consisting of six aromatic rings arranged in a triangular fashion.[1,2] The all-carbon triangulene is not a stable molecule but can exist as either biradical or dianion.[3,4] The synthesized triangulenes contain heteroatoms and can be divided into two groups depending on the nature of the central atom. Figure 1 shows the charged triangulenium[5−10] compounds (**A**) where the central atom is carbon, and the heterotriangulenes (**B**) with nitrogen[11−16] or phosphor[17,18] in the central position. Triangulenium compounds

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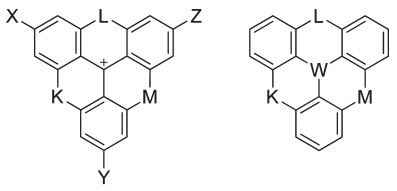

A B

FIGURE 1. Planar triangulenium ions (**A**) and bowl-shaped heterotriangulenes (**B**). **A**: K, L, M can be nitrogen or oxygen; X, Y, Z can be hydrogen, alkyl, hydroxy, or dialkylamino. **B**: W can be nitrogen or phosphorus; K, L, M can be oxo groups or oxygen.

have also been synthesized with saturated carbon and oxo groups in the bridge positions.[1,4,7,19−21]

The triangulene compounds are highly symmetric, which makes the electronic structure interesting.[4,7,19−24] The physical chemical properties of the triangulene compounds have been investigated, with focus on crystal packing[8,10,18,25,26] and cation stability.[8,10,27] Because of the planar and rigid triangular structure, triangulene compounds has found use in supramolecular assemblies,[28−33] as chiral platforms,[33−35] and as DNA intecalators.[36−39]

The charged triangulenium compounds (**A** in Figure 1) have been shown to be extremely stable carbocations and excellent fluorescent dyes.[8−10,27,40−44] The azaoxa-triangulenium dyes, with no donor group in the position *para* to the formal cation center (X, Y, Z = hydrogen), are medium strength fluorophores, where triangulenium compounds with strong donor groups on the periphery are strong absorbers and excellent fluorescent dyes with high brigthness.[8,27,43,45] Tris-(dialkylamino)-trioxatriangulenium (X, Y, Z = dialkylamino) and trihydroxy-trioxatriangulenium (X, Y, Z = hydroxyl) are 3-fold symmetric extensions of rhodamines[46]/rosamines[47]and fluorescein,[48] respectively. Fluorescien can be considered a hetero bridged version of a triphenylmethylium (TPM) dye (phenolphthalein). The same is true for rhodamines and for tris(dialkylamino)-trioxatriangulenium. The latter is a hetero bridged version of crystal violet, where the bridging of all *ortho* positions provides rigidity and planarity, giving excellent fluorescence properties. Tris(dialkylamino)-trioxatriangulenium has 3-fold symmetry. This introduces degenerate transitions that give characteristic absorption properties.[42,43] So far, all the donor substituted triangulenium derivatives synthesized have been 3-fold symmetric, with either three oxygen or three nitrogen donor groups at the periphery (X, Y, Z positions). Here, the synthesis and fluorescence properties of two new asymmetric amino-trioxatriangulenium salts, with only one or two nitrogen donor groups, are reported.

Recent results from the trihydroxy-trioxatrianguelnium[45] system showed interesting, symmetry dependent behavior, and it was decided to synthesize the dialkylamino-trioxatriangulenium (**8**, $\mathbf{A_1}$**-TOTA**$^+$, 2-dialkylamino-4,8,12-trioxa-4,8,12,12c-tetrahydro-dibenzo[*cd*,*mn*]-pyrenylium) and bis(dialkylamino)-trioxatriangulenium (**9**, $\mathbf{A_2}$**-TOTA**$^+$, 2,6-bis(dialkylamino)-4,8,12-trioxa-4,8,12,12c-tetrahydro-dibenzo[*cd*,*mn*]-pyrenylium) dyes, the structures of which are shown in Figure 2. The synthesis was adapted from the synthetic route used in the preparation of tris(dialkylamino)-trioxatriangulenium ($\mathbf{A_3}$**-TOTA**$^+$, 2,6,10-tris-(dialkylamino)-4,8,12-trioxa-4,8,12,12c-tetrahydro-dibenzo[*cd*,*mn*]-pyrenylium).[8,27,28] The intermediates in these syntheses are triphenylmethylium dyes with one or two *para* amino groups similar to malachite green and sunset orange,[49,50] yet with all *ortho* positions carrying methoxy groups. These new hexamethoxy-TPM dyes are isolated in the synthesis of $\mathbf{A_1}$**-TOTA**$^+$ and $\mathbf{A_2}$**-TOTA**$^+$ and allowed for a comparison of the spectroscopic properties of TPM dyes with a varying number and type of donor groups. While the $\mathbf{A_2}$**-TOTA**$^+$ target molecules show good fluorescent dye properties, comparable to those of rhodamine, the $\mathbf{A_1}$**-TOTA**$^+$ dyes display unexpected excited state properties.

Results and Discussion

Synthesis. The previously reported synthesis of $\mathbf{A_3}$**-TOTA**$^+$ salts is based on the unique chemistry of the tris(2,4,6-trimethoxyphenyl)-methylium ion ($(TMP)_3C^+$), which due to the steric shielding of the central carbenium atom by the six *o*-methoxy groups, undergoes aromatic nucleophilic substitution (S_NAr) in the *para* positions (Scheme 1).[8,27,51] In the final step,

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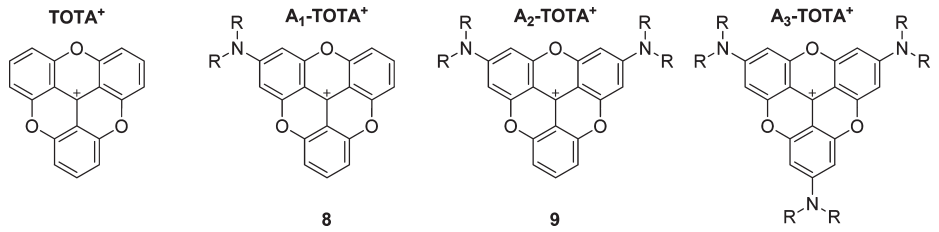
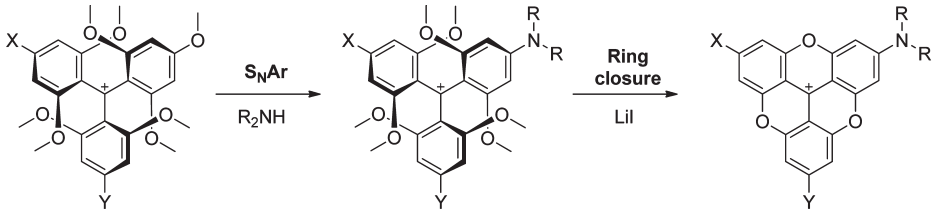


FIGURE 2. Amino-triangulenium dyes: trioxatriangulenium (**TOTA**$^+$), mono(dialkylamino)-trioxatriangulenium (**A$_1$-TOTA**$^+$, **8**), bis-(dialkylamino)-trioxatriangulenium (**A$_2$-TOTA**$^+$, **9**), and tris(dialkylamino)-trioxatriangulenium (**A$_3$-TOTA**$^+$).

SCHEME 1. General Synthetic Route to Amino-trioxatriangulenium Dyes



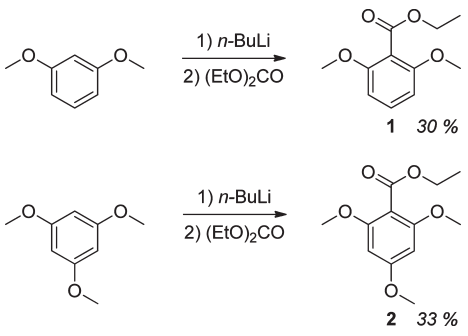
the same *o*-methoxy groups form the oxygen bridges in the trioxatriangulenium system, by a ring-closure reaction facilitated by an ether cleaving reagent (e.g., LiI). In order to apply this strategy in the synthesis of the two asymmetric amino-trioxatriangulenium dyes **A$_1$-TOTA**$^+$ (**8**) and **A$_2$-TOTA**$^+$ (**9**), the heptamethoxy- and octamethoxy-substituted TPM salts **3** and **4** were required.

The synthesis of the starting materials, heptamethoxy-triphenylmethylium tetrafluoroborate (**3**, bis(2,6-dimethoxyphenyl)-(2,4,6-trimethoxyphenyl)-methylium·BF_4) and octamethoxy-triphenylmethylium tetrafluoroborate (**4**, (2,6-dimethoxyphenyl)-bis(2,4,6-trimethoxyphenyl)-methylium·BF_4), differs from the synthesis of the symmetric nonamethoxy-triphenylmethylium ($(TMP)_3C^+$) starting material used to make **A$_3$-TOTA**$^+$, as they are of lower symmetry.[5,8,51,52]

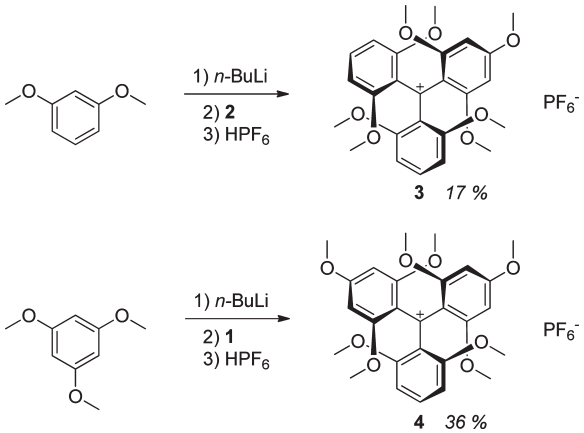
The syntheses of the symmetric hexa- and nona-methoxy TPM compounds were achieved via lithiation of the corresponding di- or trimethoxy benzene and reaction with an appropriate carbonyl compound, e.g., diethyl carbonate, to yield a triphenylcarbinol, which in turn can be isolated[5,51] or directly reacted to the triphenylmethylium salts.[8,10] To obtain the asymmetric TPM compounds **3** and **4**, the carbonate was exchanged for di- or trimethoxy ethyl benzoate **1** or **2,** respectively. The simple syntheses of these compounds are based on quenching of the lithiated di- and trimethoxybenzenes with excess diethylcarbonate (Scheme 2). From **2** and **1** respectively, **3** and **4** are prepared as shown in Scheme 3. The crude products are obtained in good yields and used in the subsequent reactions steps without further purification. If 99.9% pure materials are needed the overall yields drop to 17% and 36% for **3** and **4**, respectively, due to loss of material in the consecutive recrystallizations.

The products from aromatic nucleophilic substitution reactions, where the *p*-methoxy groups in **3**, **4**, and $(TMP)_3C^+$ is exchanged with dialkyl amines, are analogues of well-known

SCHEME 2. Synthesis of 2,6-Dimethoxybenzoic Acid Ethyl Ester (1) and 2,4,6-Trimethoxybenzoic Acid Ethyl Ester (2)



SCHEME 3. Synthesis of Heptamethoxy-triphenylmethylium Salt 3 and Octamethoxy-triphenylmethylium Salt 4



TPM dyes, with the addition of six *o*-methoxy groups. The symmetrically substituted tris(dialkylamino)-hexamethoxy-TPM$^+$ compound can be considered a crystal violet derivate. Crystal violet is tris(4-dimethylaminophenyl)-methylium, and tris(dialkyl)amino-hexamethoxy-TPM$^+$ is

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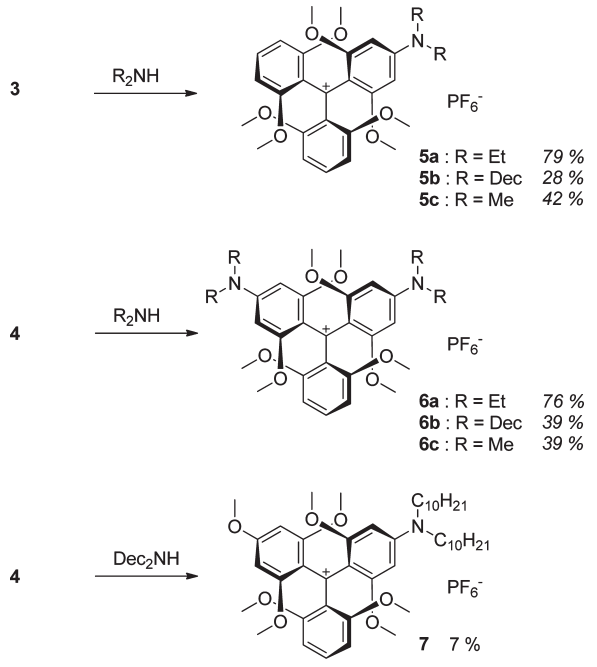
SCHEME 4. Synthesis of Monoamino-hexamethoxy-triphenylmethylium Salt 5, Diamino-hexamethoxy-triphenylmethylium Salt 6, and Amino-heptamethoxy-triphenylmethylium Salt 7

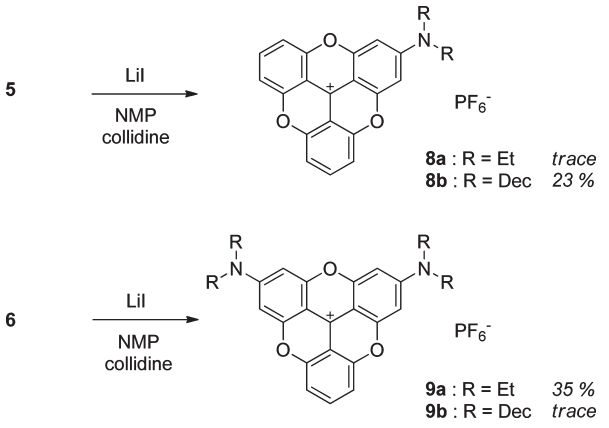


tris(4-dialkylamino-2,6-dimethoxyphenyl)-methylium. The bis-(dialkylamino)-hexamethoxy-TPM$^+$ salt **6** (bis(4-dialkylamino-2,6-trimethoxyphenyl)-(2,6-dimethoxyphenyl)-methylium) is by analogy a malachite green (bis(4-dimethylaminophenyl)-phenylmethylium) derivative, and the monoamino-hexamethoxy-TPM$^+$ derivative **5** (4-dialkylamino-2,6-dimethoxyphenyl)-bis(2,6-dimethoxyphenyl)-methylium) is a sunset orange (4-dimethylaminophenyl-diphenyl-methylium)-type compound.[53−55] Several derivatives of the new trioxatriangulenium dyes **5** and **6** were obtained by reaction of **3** and **4** with various secondary amines in acetonitrile solutions as outlined in Scheme 4. The S_NAr reaction is practically quantitative for the more nucleophile amines, but difficult purification results in moderate yields for some derivatives (28−79%).

The driving force in the S_NAr reactions is the cationic nature of the TPM substrates, and reactivity decreases as more and stronger stabilizing donor groups are introduced.[8] The reactivity of **3** follows this trend in the sense that the first, and only, substitution is fast even with low nucleophilic didecylamine.[28] Compound **4** is less reactive and the difference in reactivity between first and second substitution allows for preparation of the intermediate product **7**. In all reactions the very strong MALDI-TOF mass spectrometric signals,[10,56] from the stable and permanently charged carbenium ions, were use to monitor the progress of the reactions and to determine when to work up the desired products.

The amino-trioxatriangulenium target molecules (**8** and **9**) were obtained from **5** and **6** by a ring-closure reaction. Initially the conditions reported for triamino-trioxatriangulenium system were tried, using LiI in NMP.[8] However, this

SCHEME 5. Synthesis of Dialkylamino-trioxatriangulenium · PF_6 (8) and Bis(dialkylamino)-trioxatriangulenium · PF_6 (9)



method failed to produce the target molecules. The target molecules were formed according to MALDI-TOF MS, but before the reaction had run to completion (with consumption of all the starting material and intermediates), the target compound was converted into unidentified decomposition products. Using MALDI-TOF MS as monitoring technique, several reaction conditions were tested, including LiI/NMP, LiCl/NMP, LiI/NMP/Collidine, LiCl/Collidine, LiI/MeCN, and HCl/AcOH. All combinations of nucleophile/solvent were tested at various temperatures. No reaction conditions were found that fully solved the issues. The best conditions found were LiI in NMP at 140 °C with 10−50% collidine as cosolvent, resulting in moderate to low yields as shown in Scheme 5. In all cases the methyl derivatives **5c** and **6c** decomposed much faster than the ethyl and decyl derivatives and no fully ring-closed triangulenium compounds were obtained from these compounds. This observation suggests that dealkylation is the first step in the decomposition,[8,28] as the methyl groups are cleaved from anilines much more quickly by nucleophiles than, e.g., ethyl groups.[57] The positive effect of collidine suggests that *in situ* methylation by methyl iodide generated in the ring closure also may contribute to the degradation.[27] The main pathway of degradation in the amino-trioxatriangulenium compounds is through dealkylation of the aminogroups. The large degree of decomposition in **8** and **9**, compared to **A_3-TOTA$^+$**, is believed to be due to a larger partial positive charge on the amino groups in these systems. The fewer donor groups increases the charge on the amino groups in **8** and **9**, which leads to a higher reactivity in nucleophilic dealkylation reactions. Thus, the chemical stability of the amino-trioxatriangulenium dyes increase as the number of donor groups is increased. This also explains why **8a** is less stable than **9a**. The apparent low yield of **9b** is not due to chemical degradation but is a result of difficult purification (see Experimental Section).

Optical Properties of Triphenylmethylium Derivatives. Triphenylmethylium (TPM) dyes are nonfluorescent, potent dyes and colorants.[49,58] Figure 3 shows the absorption spectra of the hexamethoxy-TPM dyes with one to three *p*-methoxy or nitrogen donor groups. The data from the spectra are compiled in Table 1 that gives the symmetry, absorption maximum, molar absorption coefficient, and *para* substituent pattern of the

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individual dyes. For comparison, literature values for analogous TPM dyes without the *o*-methoxy groups are compiled in Table 2.

In order to understand the spectral properties of these dyes, it is in each case necessary to identify the active chromophore unit. For these systems the chromophore units consist of the cationic center and between one and three of the donor-substituted phenyl rings. A coplanar orientation of the sp^2 hybridized central carbon atom and the phenyl rings will provide optimal charge delocalization and resonance stabilization. However, steric interactions prevent all three phenyl substituents to be coplanar simultaneously. This competition between steric and electronic factors may lead to decoupling of phenyl groups with weak or no donor groups, in favor of more coplanarity with the stronger donor groups. Such conformations will results in an effective reduction of the length/size of the chromophore unit and consequently a blue shift of the first electronic transition. This is exactly what is observed for the TPM dyes with only one donor-substituted phenyl group. Thus, the first electronic transitions in compounds **3**, **5**, and sunset orange display significantly lower absorption coefficients and higher transition energies compared to that of the $(DMP)_3C^+$ system with no *para* donor groups. In the latter, symmetry favors a π-system conjugated over the entire molecule. In the compounds with two and three donor groups, the conjugation pathway is extended to at least two phenyl arms, and a high absorption coefficient and low transition energy is observed. As expected, a higher absorption coefficient and a lower transition energy is observed when going from weaker methoxy to the stronger nitrogen electron donor.[59]

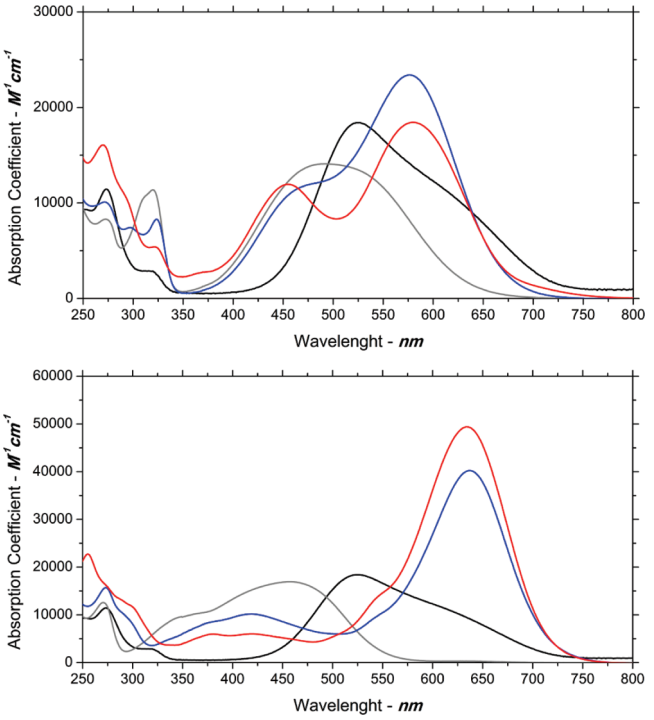
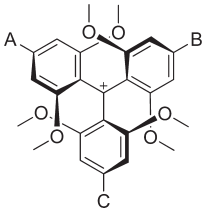


FIGURE 3. Absorption spectra of methoxy (top) and dimethylamino (bottom) donor substituted hexamethoxy-triphenylmethylium dyes in acetonitrile. The compounds have 0 *para* donor groups (black), 1 donor (gray), 2 donors (blue), and 3 donors (red).

The effect of the *o*-methoxy groups can be estimated by comparison of Tables 1 and 2. The direct effect is a small red shift of the absorption maxima and a factor 2 decrease in the absorption coefficient. The decrease can be explained by the higher twist of the conjugation pathway, lowering the transition probability. Within each type of donor groups the trends are similar and exemplified by the compounds in Table 2. The absorption maximum does not change much between two and three donor groups, as the length of the chromophore unit is unchanged. However, the absorption coefficient still increases, as a new degenerate transition is added in the dyes with 3-fold symmetry.

Optical Properties of Amino-trioxatriangulenium Derivatives. The normalized absorption spectra of the amino-trioxatriangulenium dyes in dichloromethane are shown in Figure 4. Trioxatriangulenium (**TOTA**$^+$, black curve) and tris(dialkylamino)-trioxatriangulenium (**A$_3$-TOTA**$^+$, red curve) have high symmetry, and the two lowest transitions are, in theory, degenerate. The symmetry is lifted in **TOTA**$^+$, resulting in a broad peak arising from two close-laying transitions.[42] The spectrum of **A$_3$-TOTA**$^+$ shows one degenerate transition.[43] Going to the less symmetric **A$_2$-TOTA**$^+$ the degenerate transition is split into

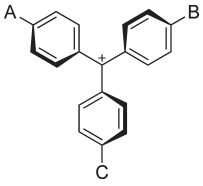
TABLE 1. Spectral Properties of *o*-Hexamethoxy-triphenylmethylium Dyes



compound[a]	symmetry	solvent	A	B	C	λ_{max} (nm)	ε (M^{-1} cm^{-1})
$(DMP)_3C^{+b}$	D_3	MeCN	H	H	H	524	18,400
3	C_2	MeCN	H	H	OMe	491	14,100
4	C_2	MeCN	H	OMe	OMe	580	18,400
$(TMP)_3C^{+c}$	D_3	MeCN	OMe	OMe	OMe	577	23,400
5	C_2	MeCN	H	H	NR_2	457	16,900
6	C_2	MeCN	H	NR_2	NR_2	637	40,200
$(R_2N\text{-}DMP)_3C^{+c}$	D_3	MeCN	NR_2	NR_2	NR_2	634	49,400
7	C_1	MeCN	H	OMe	NR_2	512	19,700
$(R_2N\text{-}DMP)(TMP)_2C^{+c}$	C_2	MeCN	OMe	OMe	NR_2	534	27,400

[a]DMP = 2,6-dimethoxyphenyl, TMP = 2,4,6-trimethoxyphenyl. [b]Synthesized as described in ref 10. [c]Synthesized as described in ref 8.

TABLE 2. Spectral Properties of Triphenylmethylium Dyes



compound	symmetry	solvent	A	B	C	λ_{max} (nm)	ε (M^{-1} cm^{-1})
TPM^+	D_3	$HFSO_3/SbF_5$	H	H	H	429[a]	38,900[a]
sunset orange	C_2	H_2O/AcOH	H	H	NR_2	463[b]	13,300[c]
malachite green	C_2	H_2O/AcOH	H	NR_2	NR_2	621[a]	105,000[a]
crystal violet	D_3	H_2O/AcOH	NR_2	NR_2	NR_2	589[b]	112,000[a]

[a]From ref 58. [b]From ref 54. [c]From ref 55.

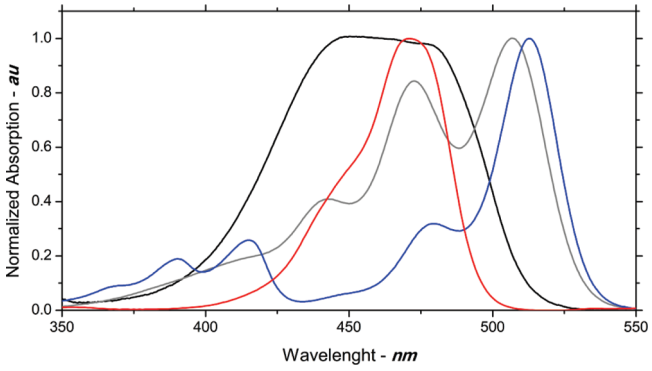


FIGURE 4. Normalized absorption spectra of the amino-trioxatriangulenium dyes in dichloromethane: **TOTA**$^+$ (black), **A$_1$-TOTA**$^+$ (gray), **A$_2$-TOTA**$^+$ (blue), and **A$_3$-TOTA**$^+$ (red).

two transitions as shown by the blue curve in Figure 4, one blue-shifted band at 400 nm and one red-shifted at 510 nm. The high energy transitions borrows intensity from the low energy transitions, resulting in a lower than expected intensity of the main absorption in **A$_2$-TOTA**$^+$. The compound is essentially a rhodamine type chromophore and an absorption coefficient of 80,000−100,000 M^{-1} cm^{-1} was expected. The observed absorption coefficient is 60,000 M^{-1} cm^{-1}. This is possible in **A$_2$-TOTA**$^+$ as the structure is planar. Compared to rhodamines **A$_2$-TOTA**$^+$ has two additional hetero bridges, thus allowing for the high energy band to have significant intensity. In rhodamines/rosamines the low energy band is all dominating, and usually the only band observed in the visible region of the spectrum.[47,60]

A$_1$-TOTA$^+$ similarly shows two bands at 425 and 500 nm, in this system the high energy band is hidden in the pronounced vibrational structure of the low energy band. The absorption coefficient is 42,000 M^{-1} cm^{-1}, comparable to other small donor−acceptor systems.[59]

A$_3$-TOTA$^+$ is an excellent fluorophore, with optical properties comparable to those of rhodamine.[8,43] The symmetry of the structure result in two degenerate transitions in this extended xanthenium system. Consequently it is expected that the less symmetric **A$_2$-TOTA**$^+$ and **A$_1$-TOTA**$^+$ systems should be regarded as diamino-xanthenium and monoamino-xanthenium dyes, as

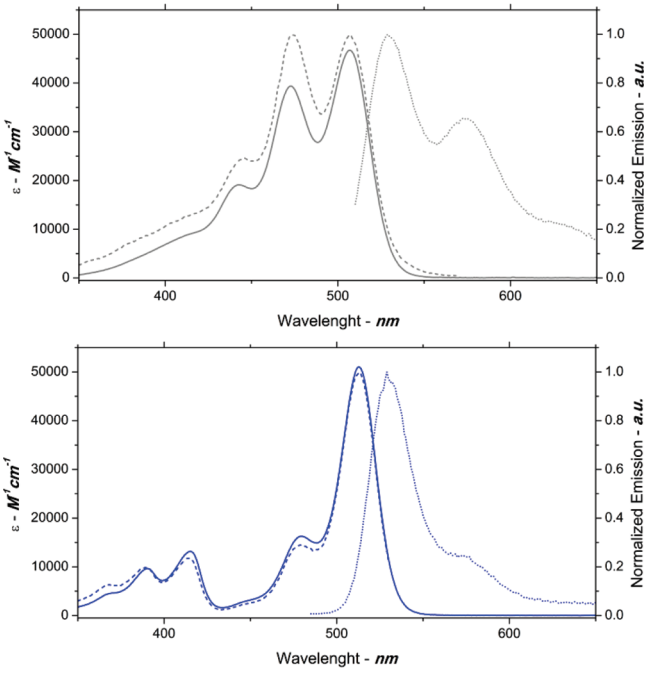


FIGURE 5. Absorption (line), fluorescence excitation (dash), and emission (dot) spectra of **A$_1$-TOTA**$^+$ in dichloromethane (top, gray) and **A$_2$-TOTA**$^+$ (bottom, blue).

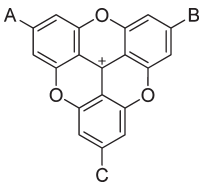
these structures are the obvious chromophores in the two compounds.

The emission and excitation spectra of **A$_1$-TOTA**$^+$ and **A$_2$-TOTA**$^+$ are shown in Figure 5. The mirror image rule is obeyed by both species. The excitation and absorption spectra are identical, albeit the excitation and absorption spectra of **A$_1$-TOTA**$^+$ differs in the intensity of the vibrational bands. These observations show that the observed emission originates from the chromophore responsible for the absorption spectrum and that only this species is emitting. However, significant deviations from ordinary fluorophore behavior become clear when the quantum yields and fluorescence lifetimes of **A$_1$-TOTA**$^+$ are taken into account.

The fluorescence properties of the amino-trioxatriangulenium dyes are a compiled in Table 3. To enable comparison, values for **TOTA**$^+$ and **A$_3$-TOTA**$^+$ in dicholoromethane are included. The unsubstituted system (**TOTA**$^+$) is markedly different, with lower absorption coefficient, longer excited state lifetime, and overall lower oscillator strength of the

(59) Griffiths, J. *Colour and Constitution of Organic Molecules*; Academic Press: New York, 1976.
(60) Brackmann, U. *Lambdachrome Laser Dyes*; 3rd ed.; Lambda Physik: Goettingen, Germany, 2000.

TABLE 3. Photophysical Properties of the Amino-trioxatriangulenium Dyes



compound		A	B	C	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{fl} (nm)	ϕ_{fl}[c] (%)	τ (ns)	τ^0 (ns)
TOTA$^+$	DCM[a]	H	H	H	475	8,200	520	11	11.7	106
A_1-TOTA$^+$	DCM	NR_2	H	H	507	41,700	529	5.1	4.2	82[d]
	MeCN	NR_2	H	H	502	39,800	541	1.6	4.03	250[d]
	EtOH	NR_2	H	H	499	37,900	530	2.8	3.73	140[d]
A_2-TOTA$^+$	DCM	NR_2	NR_2	H	513	59,700	544	100	4.16	4.2[e]
	MeCN	NR_2	NR_2	H	512	46,000	541	44	1.34	3.0[e]
	EtOH	NR_2	NR_2	H	512	46,600	537	55	1.8	3.3[e]
A_3-TOTA$^+$	DCM[b]	NR_2	NR_2	NR_2	471	132,900	494	67	3.6	5.4

[a]From ref 42. [b]From ref 43. [c]The error is estimated to be 10% of the nominal value. [d]The radiative lifetime assuming no excited state reactions occurring. [e]These values are within the error of the quantum yield determination identical.

main transition.[42] The addition of one nitrogen donor on the periphery (**A_1-TOTA$^+$**) increases the oscillator strength significantly, resulting in a molar absorption of 40,000 M^{-1} cm^{-1} at 509 nm. However, the emission quantum yield is surprisingly low (1−5%). A low fluorescence quantum yield and high oscillator strength is expected to result in a short fluorescence lifetime.[61] Yet we find a lifetime (τ) of ~4 ns, resulting in a radiative lifetime (τ^0) between 80 and 250 ns, depending on the solvent (Table 3). The radiative lifetime is much too long for an optical transition with this intensity. A radiative lifetime of ~7 ns is expected on the basis of the absorption intensity, according to the Strickler−Berg equation.[61] To find an explanation for these unusual properties, we consider that the **A_1-TOTA$^+$** fluorophore is likely to have similar pathways and rates of nonradiative energy dissipation as rhodamines.[46,62−68] Thus the difference in absorption and excitation spectrum, the anomalous long radiative lifetime, and low quantum yield is explained by a very efficient formation of a twisted internal charge transfer or TICT state on the excited state potential surface.[68] The process is expected to be more favorable in **A_1-TOTA$^+$**, due to the presence of only one donor group, which results in a cation with more charge localization compared to rhodamines and **A_3-TOTA$^+$**.[27] The good mirror image relationship suggests that the emission indeed originates from the xanthenium chromophore. When the long radiative lifetime is taken into account, this emission must be due to a repopulation of the absorbing and emitting state from the dark TICT state. As the only degree of freedom present is rotation of the donor group, the TICT state formation is the most plausible explanation for the unusual observation of simultaneous long radiative lifetime, high oscillator strength, and good mirror image relationship. The observed solvatochromatic effects can be explained by the stabilization of the TICT state in agreement with the proposed model.

The addition of the second donor group gives the system properties close to those of rhodamine B. **A_2-TOTA$^+$** has a high quantum yield and a fluorescent lifetime as would be expected. Table 3 includes data for three different solvents. The change in properties of **A_2-TOTA$^+$** follows the observations for other amino-xanthenium dyes such as rhodamine B.

Conclusions

New amino-trioxatriangulenium dyes with one and two amino donor groups on the periphery were synthesized along with their TPM precursors. In the final ring-closure reactions pronounced N-dealkylation was encountered emphasizing the increased charge density on the nitrogen donor groups in these compound compared to the previous reported tris-(dialkylamino)trioxatriangulenium systems (**A_3-TOTA$^+$**).

The optical properties of monoamino-trioxatriangulenium and diamino-trioxatriangulenium were also found to be strongly influenced by the degree of cation stabilization/localization. Thus, **A_1-TOTA$^+$** was found to be a surprisingly poor fluorophore. The proposed explanation is a very efficient formation of a TICT state in the system. **A_2-TOTA$^+$** was shown to a good fluorescent dye with strong emission at 540 nm. This dye may be considered as a blue-shifted version of rhodamine B.

The optical properties of the *o*-methoxy-substituted TPM dye intermediates were determined. They were found to depend on the twist in the conjugated system and the type and number of donor groups on the periphery.

Experimental section

All materials were used as received. Solvents were HPLC grade unless otherwise noted. Experiments were run under ambient conditions (20−24 °C) except where noted. The fluorescence lifetimes were measured using a TC-SPC setup and the decay data fitted with standard software.

Ethyl 2,6-Dimethoxybenzoate (1).[69] To a solution of dimethylresorcinol (13.8 g, 0.1 mol) in ether/benzene 1:1 (100 mL) was

(61) Turro, N. J. *Modern Molecular Photochemistry*: University Science Books: Sausalito, 1991.
(62) Lippert, E.; Rettig, W.; Bonacickoutecky, V.; Heisel, F.; Miehe, J. A. *Adv. Chem. Phys.* **1987**, *68*, 1.
(63) Vogel, M.; Rettig, W.; Fiedeldei, U.; Baumgartel, H. *Chem. Phys. Lett.* **1988**, *148*, 347.
(64) Vogel, M.; Rettig, W.; Sens, R.; Drexhage, K. H. *Chem. Phys. Lett.* **1988**, *147*, 452.
(65) Vogel, M.; Rettig, W.; Sens, R.; Drexhage, K. H. *Chem. Phys. Lett.* **1988**, *147*, 461.
(66) Plaza, P.; Hung, N. D.; Martin, M. M.; Meyer, Y. H.; Vogel, M.; Rettig, W. *Chem. Phys.* **1992**, *168*, 365.
(67) Rettig, W. In *Electron Transfer I*; Springer-Verlag: Berlin: Berlin, 1994; Vol. 169, p 253.
(68) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899.
(69) Arrieta, A.; Garcia, T.; Palomo, C. *Synth. Commun.* **1982**, *12*, 1139.

added a 1.6 M solution of *n*-BuLi in hexane (65 mL, 0.104 mol) at room temperature. After the reaction mixture was stirred for 3 h, the reaction was quenched by addition of diethylcarbonate (61 mL, 0.5 mol) and was left to stand overnight. The reaction mixture was poured onto water (100 mL) and extracted with ether (3 × 100 mL), and the combined organic layers were washed with water (3 × 100 mL) and dried over $MgSO_4$. The solvent was removed to produce a yellow oil. Recrystallization in heptanes/toluene 3:1 yielded **1** (6.3 g, 30%) as white crystals. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.30 (t, J = 8.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.80 (s, J = 5.2 Hz, 9H), 1.33 (t, J = 7.1 Hz, 3H). GC-MS m/z 210 (M^+, 20%), 165 (100).

Ethyl 2,4,6-Trimethoxybenzoate (2).[70] To a solution of trimethylphloroglucinol (16.8 g, 0.1 mol) in ether/benzene 1:1 (100 mL) was added a 1.6 M solution of *n*-BuLi in hexane (65 mL, 0.104 mol) at room temperature. After the reaction mixture was stirred for 3 h, the reaction was quenched by addition of diethylcarbonate (61 mL, 0.5 mol) and was left to stand overnight. The reaction mixture was poured onto water (100 mL) and extracted with ether (3 × 100 mL), and the combined organic layers were washed with water (3 × 100 mL) and dried over $MgSO_4$. The solvent was removed to produce a yellow oil. Recrystallization in heptanes/toluene 3:1 yielded **1** (7.8 g, 33%) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 6H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 162.6, 158.7, 106.6, 90.9, 61.2, 56.2, 55.6, 14.4. GC-MS m/z 240 (M^+, 25%), 195 (100). Anal. Found: C, 60.3; H, 6.7. Calcd for $C_{12}H_{16}O_5$: C, 60.0; H, 6.7.

Bis(2,6-dimethoxyphenyl)-(2,4,6-trimethoxyphenyl)-methylium Hexafluorophosphate (3). To a solution of dimethoxybenzene (6.9 g, 50 mmol) in dry ether (50 mL) was added a 1.6 M solution of *n*-BuLi in hexane (31.5 mL, 50 mmol) at room temperature. After 48 h of stirring a solution of **2** (4.8 g, 20 mmol) in ether (100 mL) was added, and the reaction was left overnight. The reaction mixture was poured onto 1 M KOH (100 mL), the reaction mixture was extracted with ether (3 × 100 mL), and the combined organic layers were washed with water (3 × 100 mL) and dried over $MgSO_4$. The solvent was removed, the residue was taken up in methanol (25 mL), and a 60% aqueous HPF_6 (4 mL, 28 mmol) was added followed by 0.2 M KPF_6(aq) (300 mL). The product was extracted with dichloromethane (3 × 100 mL), the organic phase was dried over $MgSO_4$, and the solvent volume was reduced in vacuum. Precipitation with ether allowed for isolation of crude **3** (4.8 g, 56%) as a dark blue powder with a metallic sheen. This material was used for synthesis without further purification. Analytical samples of **3** for spectroscopy and analysis was obtained by repeated recrystallization from methanol, yielding dark blue needle-like crystals (2.0 g, 17%). ^{1}H NMR (400 MHz, DMSO) δ 7.36 (t, J = 8.4, 2H), 6.64 (d, J = 8.4, 4H), 6.30 (s, 2H), 4.21 (s, 3H), 3.58 (s, 6H), 3.48 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.9, 157.2, 128.7, 128.7, 125.44, 124.7, 122.6, 104.1, 100.0, 55.8, 55.2, 48.6. ^{19}F NMR (376 MHz, DMSO) δ 9.12, 7.23. ^{31}P NMR (162 MHz, DMSO) δ −132.20, −138.07, −143.93, −149.80, −155.67. MALDI-TOF (Dithranol matrix) m/z 452.96 (M^+). λ_{max}(CH_3CN)/nm 492 (log(ε) 4.15), 320 (4.06), 311sh (4.03), 272 (3.92). Anal. Found: C, 52.5; H, 4.9. Calcd for $C_{26}H_{29}F_6O_7P$: C, 52.2; H, 4.9. V_2O_5 added.

(2,6-Dimethoxyphenyl)-bis(2,4,6-trimethoxyphenyl)-methylium Hexafluorophosphate (4). To a solution of trimethoxybenzene (8.4 g, 50 mmol) in dry ether (50 mL) was added a 1.6 M solution of *n*-BuLi in hexane (31.5 mL, 50 mmol) at room temperature. After 48 h of stirring a solution of **1** (4.2 g, 20 mmol) in ether (100 mL) was added, and the reaction was left overnight. The reaction mixture was poured onto 1 M KOH (100 mL), the product was extracted with ether (3 × 100 mL), and the combined organic layers were washed with water (3 × 100 mL) and dried over $MgSO_4$. The solvent was removed, the residue was taken up in methanol (25 mL), and a 60% aqueous HPF_6 (4 mL, 28 mmol) was added followed by 0.2 M KPF_6(aq) (350 mL). The product was extracted with dichloromethane (3 × 100 mL), the organic phase was dried over $MgSO_4$, and the solvent volume was reduced in vacuum. Precipitation with ether allowed for isolation of the crude **4** (8.5 g, 68%) as a deep blue powder. This material was used for synthesis without further purification. Analytical samples of **4** for spectroscopy and analysis were obtained by recrystallization from methanol, yielding dark blue powder (4.5 g, 36%). ^{1}H NMR (400 MHz, DMSO) δ 7.35 (t, J = 8.4, 1H), 6.63 (d, J = 8.4, 2H), 6.24 (s, 4H), 4.01 (s, 6H), 3.52 (s, 12H), 3.49 (s, 6H). ^{13}C NMR (101 MHz, CD_3CN) δ 174.2, 171.0, 167.0, 160.4, 134.8, 124.4, 122.0, 106.2, 93.6, 58.2, 57.9, 57.4. ^{19}F NMR (376 MHz, DMSO-d_6) δ 9.10, 7.21. ^{31}P NMR (162 MHz, DMSO-d_6) δ −132.20, −138.07, −143.93, −149.80, −155.67. MALDI-TOF (Dithranol matrix) m/z 482.82 (M^+). λ_{max}(CH_3CN)/nm 576 (log(ε) 4.37), 472sh (4.07), 323 (3.92), 297 (3.87), 271 (4.00). Anal. Found: C, 51.7; H, 5.0. Calcd for $C_{27}H_{31}F_6O_8P$: C, 51.6; H, 5.0. V_2O_5 added.

General Procedure to 5, 6, and 7. To a solution of the appropriate starting material (2 mmol), **3** for **5** and **4** for **6**/**7**, in acetonitrile (5 mL) was added dialkylamine (0.1 mol). The reaction was stirred at room temperature until MALDI-TOF MS showed complete reaction of the starting material. The reaction mixture was then poured onto 0.2 M KPF_6(aq) (350 mL), and the crude product was collected by filtration and washed with water. Recrystallization from methanol was used to obtain the pure product unless another method for purification is mentioned.

(4-Diethylamino-2,6-dimethoxyphenyl)-bis(2,6-dimethoxyphenyl)-methylium Hexafluorophosphate (5a). Isolated as a dark orange powder (840 mg, 78.7%) ^{1}H NMR (400 MHz, CD_3CN) δ 7.24 (t, J = 8.4 Hz, 2H), 6.56 (d, J = 8.4 Hz, 4H), 5.82 (s, 2H), 3.75 (q, J = 7.2 Hz, 4H), 3.51 (s, 12H), 3.49 (s, 6H), 1.33 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 166.2, 160.8, 157.3, 154.0, 130.1, 124.4, 122.0, 104.2, 90.6, 56.5, 55.9, 46.7, 13.1. MALDI-TOF (Dithranol matrix) m/z 494.18 (M^+). λ_{max}-(CH_3CN)/nm 457 (log(ε) 4.23), 365sh (4.01), 271 (4.10). Anal. Found: C, 54.6; H, 5.6; N, 2.2. Calcd for $C_{29}H_{36}F_6NO_6P$: C, 54.5; H, 5.7; N, 2.2. V_2O_5 added.

(4-Didecylamino-2,6-dimethoxyphenyl)-bis(2,6-dimethoxyphenyl)-methylium Tetrafluoroborate (5b). Recrystallized from ethyl acetate to yield a yellow microcrystalline powder (120 mg, 28%). ^{1}H NMR (400 MHz, DMSO) δ 7.19 (t, J = 8.3, 2H), 6.48 (d, J = 8.4, 4H), 5.80 (s, 2H), 3.69 (t, J = 7.6, 4H), 3.55 (s, 12H), 3.51 (s, 6H), 1.73 (m, 4H), 1.31 (m, 28H), 0.87 (t, J = 6.7, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 162.0, 158.0, 154.6, 130.8, 125.3, 122.7, 104.5, 90.6, 56.5, 53.3, 32. 1, 29.7, 29.7, 29.6, 29.5, 28.6, 27.0, 22.9, 14.3. ^{19}F NMR (376 MHz, DMSO-d_6) δ −3.55. MALDI-TOF (Dithranol matrix) m/z 718.71 (M^+). λ_{max}-(CH_3CN)/nm identical to **5a**. Anal. Found (on PF_6 salt): C, 62.6; H, 8.2; N, 1.4. Calcd for $C_{45}H_{68}F_6NO_6P$: C: 62.6, H: 7.9, N: 1.6. V_2O_5 added.

(4-Dimethylamino-2,6-dimethoxyphenyl)-bis(2,6-dimethoxyphenyl)-methylium Hexafluorophosphate (5c). Isolated as a red powder (95 mg, 42%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.23 (t, J = 8.4, 2H), 6.51 (d, J = 8.4, 4H), 5.71 (s, 2H), 3.53 (s, 12H), 3.51 (s, 6H), 3.43 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.7, 162.0, 157.2, 154.0, 130.1, 128.8, 128.2, 125.3, 124.4, 122.1, 104.3, 91.0, 56.4, 55.9, 41.9. ^{31}P NMR (162 MHz, DMSO) δ −132.20, −138.07, −143.93, −149.80, −155.67. MALDI-TOF (Dithranol matrix) m/z 466.12 (M^+). λ_{max}(CH_3CN)/nm identical to **5a**. Anal. Found: C: 53.1, H: 5.3, N: 2.5. Calcd for $C_{27}H_{32}F_6NO_6P$: C: 53.0, H: 5.3, N: 2.3. V_2O_5 added.

Bis(4-diethylamino-2,6-dimethoxyphenyl)-(2,6-dimethoxyphenyl)-methylium Hexafluorophosphate (6a). Isolated as a dark blue powder (0.862 g, 76%). ^{1}H NMR (500 MHz, CD_3CN) δ

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7.22 (t, J = 8.3, 1H), 6.57 (d, J = 8.3, 2H), 5.78 (s, 4H), 3.57 (q, J = 7.1, 9H), 3.51 (d, J = 11.0, 6H), 3.47 (s, 11H), 1.24 (t, J = 7.1, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) 164.4, 158.5, 156.2, 155.1, 130.4, 124.2, 117.6, 104.9, 88.9, 77.5, 77.2, 77.0, 56.8, 56.2, 45.9, 13.2. MALDI-TOF (Dithranol matrix) m/z 565.26 (M^+). λ_{max}(CH_3CN)/nm 634 (log(ε) 4.69), 547sh (4.15), 421 (3.78), 380 (3.78), 300sh (4.07), 255 (4.36). Anal. Found: C, 56.0; H, 6.1; N, 3.9. Calcd for $C_{33}H_{45}F_6N_2O_6P$: C, 55.8; H, 6.4; N, 3.9. V_2O_5 added.

Bis(4-didecylamino-2,6-dimethoxyphenyl)-(2,6-dimethoxyphenyl)-methylium Hexafluorophosphate (6b). The compound co-crystallizes with a didecylamine as a dark purple wax (0.85 g, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, J = 8.3 Hz, 1H), 6.51 (d, J = 8.4 Hz, 2H), 5.68 (s, 4H), 3.57 (s, 6H), 3.54 − 3.40 (m, J = 24.1 Hz, 20H), 2.65 (t, 4H), 1.82 − 1.60 (m, J = 33.8 Hz, 12H), 1.59 − 1.45 (m, 4H), 1.41 − 1.19 (m, 80H), 0.88 (t, J = 6.9 Hz, 18H). MALDI-TOF (Dithranol matrix) m/z 1013.72 (M^+). λ_{max}(CH_3CN)/nm identical to **6a**.

Bis(4-dimethylamino-2,6-dimethoxyphenyl)-(2,6-dimethoxyphenyl)-methylium Hexafluorophosphate (6c). Dark violet powder (200 mg, 39%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.19 (t, J = 8.3, 1H), 6.57 (d, J = 8.3, 2H), 5.85 (s, 4H), 3.47 (s, 6H), 3.44 (s, 12H), 3.20 (s, 12H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.2, 157.7, 157.2, 155.5, 129.6, 123.9, 117.0, 104.8, 89.2, 56.3, 55.9, 40.4. ^{19}F NMR (376 MHz, DMSO) δ 9.10, 7.21. ^{31}P NMR (162 MHz, DMSO) δ = −132.20, −138.07, −143.93, −149.80, −155.67. MALDI-TOF (Dithranol matrix) m/z 509.30 (M^+). λ_{max}(CH_3CN)/nm identical to **6a**. Anal. Found: C, 53.1; H, 5.7; N, 4.5. Calcd for $C_{29}H_{37}F_6N_2O_6P$: C, 53.2; H, 5.7; N, 4.3.

(4-Didecylamino-2,6-trimethoxyphenyl)- (2,6-dimethoxyphenyl)-(2,4,6-trimethoxyphenyl)-methylium Tetrfaluoroborate (7). Isolated as a dark violet powder (40 mg, 7.1%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.19 (s, 1H), 6.49 (d, J = 8.4, 2H), 6.04 (s, 2H), 5.73 (d, J = 11.6, 2H), 3.83 (s, 3H), 3.64 (s, 4H), 3.57 (s, 12H), 3.53 (s, 6H), 1.26 (s, 32H), 0.86 (d, J = 6.5, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.6, 163.0, 161.1, 159.3, 157.7, 130.4, 130.4, 123.9, 122.9, 104.2, 90.8, 89.9, 89.9, 56.3, 56.2, 56.1, 56.0, 55.3, 52.7, 31.8, 29.40, 29.35, 29.23, 29.16, 28.2, 28.1, 26.7, 22.6, 14.0. MALDI-TOF (Dithranol matrix) m/z 748.68 (M^+). Hi-Res ESI-TOF Found: 748.5121. Calcd for $C_{46}H_{70}NO_7^+$: 748.5152. λ_{max}(CH_3CN)/nm 511 (log(ε) 4.29), 418sh (4.10), 371sh (4.04), 269 (4.12).

Diethylamino-trioxatriangulenium Hexafluorophosphate (8a). A solution of **5a** (100 mg, 0.16 mmol) in *N*-methylpyrrolidone (50 mL) was heated to 140 °C, and collidine (5 mL) and LiI (1 g, 7.5 mmol) were added. The reaction was followed on MALDI-TOF, and when the peak at m/z 402 disappeared, corresponding to the two times ring-closed intermediate, the reaction mixture was cooled and poured onto 0.2 M aqueous KPF_6 (300 mL). The crude product is collected by filtration and dried. Flash chromatography on silica with dichloromethane/methanol 1:20 afforded the pure compound in trace amounts as yellow hair crystals (< 3%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.08 (t, J = 8.5 Hz, 2H), 7.56 − 7.37 (m, 4H), 6.81 (s, 2H), 3.70 (q, J = 7.3 Hz, 4H), 1.41 (t, J = 7.2 Hz, 6H). MALDI-TOF (Dithranol matrix) m/z 355.89 (M^+). Hi-Res ESI-TOF Found: 356.1280. Calcd for $C_{23}H_{18}NO_3^+$: 356.1281. λ_{max}(CH_3CN)/nm identical to **8b**.

Didecylamino-trioxatriangulenium Hexafluorophosphate (8b). A solution of **5b** (50 mg, 0.06 mmol) in *N*-methylpyrrolidone (3 mL) was heated to 140 °C, and collidine (3 mL) and LiI (0.4 g, 3.0 mmol) were added. The reaction was followed on MALDI-TOF, and when only the product was observed, the reaction mixture was cooled and poured onto 0.2 M aqueous KPF_6 (250 mL) with 50% aqueous KPF_6 (1 mL). The product was extracted with dichloromethane (3 × 100 mL), and the organic phase was washed with 0.2 M aqueous KPF_6 (2 × 200 mL) and dried over $MgSO_4$. Recrystallization from ethyl acetate/*n*-heptane afforded the product (10 mg, 23%) as hair thin yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (t, J = 8.5 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 6.76 (s, 2H), 3.59 (s, 4H), 1.76 (s, 4H), 1.42 (s, 8H), 1.29 (s, 20H), 0.89 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.5, 152. 9, 152.3, 139.0, 119.3, 112.2, 104.4, 96.2, 53.0, 31.8, 29.6, 29.5, 29.3, 29.3, 27.2, 26.9, 22.7, 14.1, (incomplete, the quaternary carbon missing). MALDI-TOF (Dithranol matrix) m/z 580.22 (M^+). Hi-Res ESI-TOF Found: 580.3791. Calcd for $C_{39}H_{50}NO_3^+$: 580.3785. λ_{max}-(CH_3CN)/nm 502 (log(ε) 4.60), 475 (4.57), 441sh (4.29), 302.5 (4.45), 268.5 (4.57), 235 (4.83). Anal. Found: C, 64.8; H, 7.0; N, 1.9. Calcd for $C_{39}H_{50}F_6NO_3P$: C, 64.5; H, 6.9; N, 1.9. V_2O_5 added.

Bis(diethylamino)-trioxatriangulenium Hexafluorophosphate (9a). A solution of **6a** (180 mg, 0.25 mmol) in *N*-methylpyrrolidone (3 mL) was heated to 140 °C, and collidine (3 mL) and LiI (0.8 g, 6.0 mmol) were added. The reaction was followed on MALDI-TOF, and when only the product was observed, the reaction mixture was cooled and poured onto 0.2 M aqueous KPF_6 (250 mL) with 50% aqueous KPF_6 (1 mL). The product was extracted with dichloromethane (3 × 100 mL), and the organic phase was washed with 0.2 M aqueous KPF_6 (2 × 200 mL) and dried over $MgSO_4$. Recrystallization from ethyl acetate/dichloromethane afforded the product (50 mg, 35%) as orange platelets. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (t, J = 8.4 Hz, 1H), 7.28 (t, J = 6.0 Hz, 2H), 6.66 (d, J = 1.8 Hz, 2H), 6.58 (s, 2H), 3.60 (q, J = 7.1 Hz, 8H), 1.34 (t, J = 7.2 Hz, 12H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.5, 154.7, 154.2, 152.6, 138.4, 133.0, 112.2, 104.3, 96.5, 95.5, 95.3, 46.2, 12.9. MALDI-TOF (Dithranol matrix) m/z 427.00 (M^+). Hi-Res ESI-TOF Found: 427.1986. Calcd for $C_{27}H_{27}N_2O_3^+$: 427.2016. λ_{max}(CH_3CN)/nm 511 (log(ε) 4.66), 478.5sh (4.35), 412.5 (4.25), 388.5 (4.03), 367.5sh (3.73), 317 (3.96), 305sh (3.87), 244.5 (4.58), 235 (4.58). Anal. Found: C, 48.0; H, 4.7; N, 4.9. Calcd for $C_{27}H_{27}F_6N_2O_3P$: C, 56.7; H, 4.8; N, 4.9. Incomplete combustion even with V_2O_5 added. This is commonly observed as a too low carbon value for this compound class.[8]

Bis(didecylamino)-trioxatriangulenium Hexafluorophosphate (9b). A solution of **6b** (850 mg, 0.75 mmol) in *N*-methylpyrrolidone (3 mL) was heated to 140 °C, and collidine (3 mL) and LiI (3 g, 22 mmol) were added. The reaction was followed on MALDI-TOF, and when only the product was observed, the reaction mixture was cooled and poured onto 0.2 M aqueous KPF_6 (300 mL) with 50% aqueous KPF_6 (1 mL). The product was extracted with dichloromethane (3 × 100 mL), and the organic phase was washed with 0.2 M aqueous KPF_6 (2 × 200 mL) and dried over $MgSO_4$. The crude product (900 mg) was collected by filtration and dried; the main impurities were free amine and monodealkylated product. Repeated recrystallizations from methanol/dichloromethane afforded the pure product in trace amounts as a dark red powder. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.90 (t, J = 8.4 Hz, 1H), 7.35 (d, J = 22.0, 8.6 Hz, 2H), 6.60 (s, 4H), 3.50 (t, J = 15.2, 7.1 Hz, 8H), 1.79 − 1.49 (m, 8H), 1.31 (dd, J = 45.1, 31.4 Hz, 24H), 0.90 (t, 12H). MALDI-TOF (Dithranol matrix) m/z 875.05 (M^+). Hi-Res ESI-TOF Found: 875.7026. Calcd for $C_{59}H_{91}N_2O_3^+$: 875.7024. λ_{max}-(CH_3CN)/nm identical to **9a**.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all prepared compounds. This material is available free of charge via the Internet at http://pubs.acs.org.