

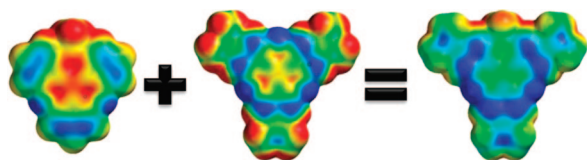
Synthesis of Super Stable Triangulenium Dye

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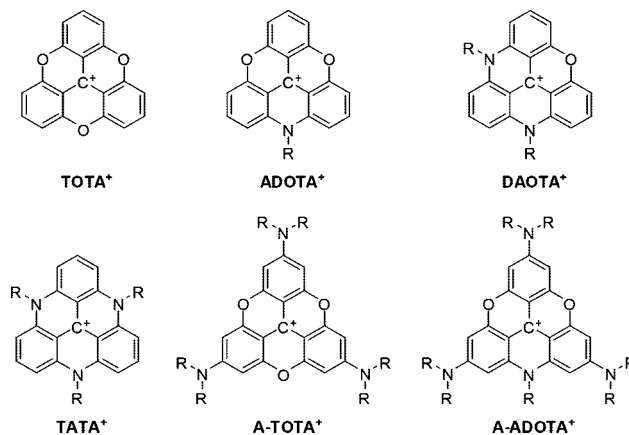
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The super stabilized tris(dialkylamino)-azadioxatriangulenium carbenium ion (A-ADOTA⁺) **4** has been synthesized and characterized. As a result of extended delocalization of the positive charge in the planar triangulenium system and the presence of several strongly electron-donating groups, the A-ATOTA⁺ ion displays extreme cation stability with a pK_{R+} value close to 25. Furthermore the A-ATOTA⁺ ion shows excellent dye properties with intense absorption at 458 nm and high fluorescence quantum yield.

Triangulenium ions are highly stabilized carbenium ions, which from a structural point of view may be described as a triphenyl methylum ion rigidified and made planar by bridging of all *ortho* positions by hetero atoms (Scheme 1). The triangulenium ions have been studied because of their properties as highly stable carbenium ions,^{1–3} dyes,^{4–9} DNA intercalators,^{5,10} phase-transfer catalysts,¹¹ and building blocks for the construction of macrocyclophanes,^{12–14} stable triplet π biradicals,^{15–17} and chiral structures.^{18,19} Very recently triangulenium ions have been applied as self-assembling surface anchoring platforms²⁰ and in columnar packed Langmuir monolayers.²¹ In most of these applications unique effects or functions may be ascribed to the most striking property of the triangulenium ions: their extreme cation stability. The high cation stability is assigned

SCHEME 1. General Structures and Acronyms of Various Triangulenium Ions



to efficient charge delocalization facilitated by the planar structure and the electron-donating hetero atoms.^{1–3,22}

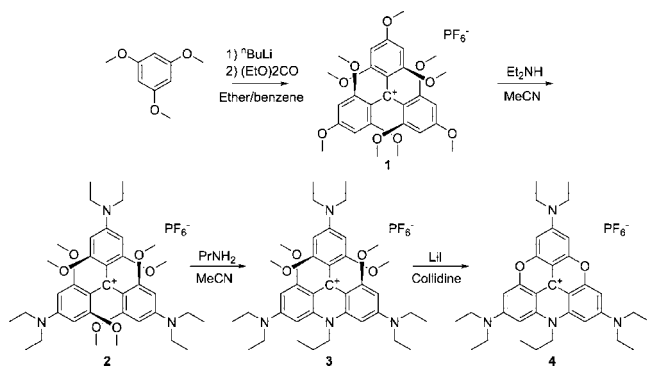
The first triangulenium ion to be studied was the trioxatriangulenium ion TOTA⁺ synthesized by Martin and Smith in 1964.³ Over the past decade we have synthesized and investigated a number of new triangulenium salts. Thus we have previously shown that adding three dialkylamino groups to the TOTA⁺ system, as in the tris(dialkylamino)trioxatriangulenium ion (A-TOTA⁺) (Scheme 1), raises the cation stability by 10 orders of magnitude² and generates an efficient rhodamine-like fluorescent dye.⁸ Comparable large enhancements in carbenium stability is obtained by replacing the oxygen bridges by nitrogen, as in the azaoxatriangulenes: AzaDiOxaTriAngulenium (ADOTA⁺), DiAzaOxaTriAngulenium (DAOTA⁺), and TriAzaTriAngulenium (TATA⁺).^{1,23}

In this paper a new class of triangulenium ions is presented combining the peripheral amino substitution of A-TOTA⁺ with the presence of one internal nitrogen bridge, as in the ADOTA⁺ ion. This combination of electron-donating groups makes the new tris(dialkylamino)-azadioxatriangulenium ion (A-ADOTA⁺) the most stable triangulenium ion ever made.

The synthesis of A-ADOTA⁺ is achieved following the pathway used in the preparation of A-TOTA⁺ salts² and

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SCHEME 2. Synthetic Route to A-ADOTA·PF₆

inserting an *ortho* substitution step, as in the synthesis of ADOTA⁺ (Scheme 2).¹ Following the general strategy used in the synthesis of the A-TOTA⁺ systems, the readily available tris(trimethoxyphenyl)carbenium ion **1**^{2,24} is reacted with diethyl amine to give **2** by selective nucleophilic aromatic substitution of the three *p*-methoxy groups.² At this stage the nitrogen bridge is introduced by reaction with large excess of propyl amine, substituting two of the *o*-methoxy groups and yielding the aminoacridinium compound **3**. Compared to the formation of the nitrogen bridge in ADOTA⁺ the *ortho* substitution reaction of **2** is very slow, days compared to minutes.¹ However, **3** is isolated in excellent yields of 70–80% after reaction for 4 days at room temperature. The relative low reactivity of **2** is expected on the basis of the presence of the three electron-donating diethyl amino groups, which stabilize the carbenium ion and thus reduce the reactivity toward nucleophiles.^{1,2}

The high stability of acridinium compound **3** prohibits further *ortho* substitution, which potentially would lead to formation of the even more stabilized amino-triangulenium ions with two and three nitrogen bridges. Raising the temperature led to decomposition rather than formation of the desired products, and the diaza compound was only observed as traces in the reaction mixture.

The ring closure from **3** to **4** was first attempted using LiI in NMP as reported for A-TOTA⁺.² However, this method led to a significant amount of byproducts that was difficult to remove. The byproducts were identified as A-ADOTA⁺ isomers in which one, two, or three ethyl groups were exchanged by methyl groups. We believe that these products are formed by the methyl iodide generated during the demethylation of the *o*-methoxy groups in the ring-closure reaction. Methylation and subsequent dealkylation leads to the overall replacement of the ethyl substituents. In agreement with this mechanism the problem was solved by replacing the solvent NMP by collidine, which acts as a methyl iodide scavenger. The fact that this problem was only encountered with the ring closure of **3** and not with that of **2** to A-TOTA⁺ illustrates the strong electron-donating power of the acridinium system. The enhanced stabilization of cation **3** results in a lowering of the partial positive charge on the diethyl amino groups, making them more nucleophilic and thus susceptible to methylation. The ring closure of **3** to **4** with LiI in collidine gave after ion exchange with KPF₆ (aq), column chromatography, and recrystallization A-ADOTA·PF₆ (**4**·PF₆) in 75% yield.

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TABLE 1. Summary of pK_{R+} Values for Triangulenium Ions

Compound	pK _{R+}	ref
TOTA ⁺	9.1	3
ADOTA ⁺	14.5	1
DAOTA ⁺	19.4	1
A-TOTA ⁺	19.7	2
TATA ⁺	23.7	1, 23
A-ADOTA ⁺	~25	this study

The stability of carbenium ions, trivalent carbocations, is measured by the pK_{R+} value of the system.^{25–27} The pK_{R+} value is based on the equilibrium constant for the equilibrium between the carbenium ion and the corresponding carbinol of a given system. The pK_{R+} value reports the pH at which 50% of the carbinol is converted into the carbenium ion. For the TOTA⁺ ion this value is 9.1.³ However, for the more stable triangulenium ions the pK_{R+} values are above 14 and have to be measured in strongly basic nonaqueous solution. By applying a solvent system of tetramethylammonium hydroxide/DMSO/water, the pK_{R+} values of the highly stabilized A-TOTA⁺ and azatriangulenium ions have been measured (Table 1).^{1,2,23} When applying this method to determine the pK_{R+} value of the new A-ADOTA⁺ ion, we find that it is even more stable than the TATA⁺ ion (pK_{R+} = 23.7) and that the very basic conditions required to generate the carbinol is outside the range where this solvent system provides accurate values.¹ In these very basic solutions the measurements are compromised by irreversible reaction of the carbenium ion.^{1,25} However, by careful measurements we are able to give a reasonable estimate of the pK_{R+} value of 25 (see Supporting Information for details).

Despite the lack of accurate pK_{R+} measurements, these results clearly show that the new A-ADOTA⁺ ion is the most stable triangulenium ion synthesized so far and comparable in stability to the most stable carbenium ions ever reported.^{1,25,28,29} The super stable A-ATOTA⁺ ion is obtained by changing just one of the oxygen bridges in the A-TOTA⁺ system to a nitrogen bridge, increasing the cation stability by 5 orders of magnitude. Behind this significant increase in stability is a major redistribution of the charge density in the cationic system. This is clearly seen in the plots of charge distribution in the A-TOTA⁺ and A-ADOTA⁺ ions shown in Figure 1, generated from DFT calculations (see Supporting Information for details). From the charge distribution plots it is evident how the introduction of the aza bridge in the A-ADOTA⁺ ion increases the electron density on the central carbon atom and thereby raises the pK_{R+} value. In addition it is noticed that the electron density on the dialkyl amino groups also increases, as more of the positive charge is localized on the aza bridge, in perfect agreement with the enhanced nucleophilicity observed for these groups during our synthetic work.

The presence of peripheral dialkylamino groups in A-TOTA⁺ and A-ADOTA⁺ makes these carbenium ions potent dyes. Thus the A-TOTA⁺ dyes show absorption and fluorescence properties resembling those of the rhodamines, yet with a significant blue shift of the lowest electronic transition ($\lambda_{\text{abs}} = 471$ nm and $\lambda_{\text{fl}} = 506$ nm).⁸ The new A-ADOTA⁺ dye **4** also shows very intense absorption and fluorescence, which is even further blue-

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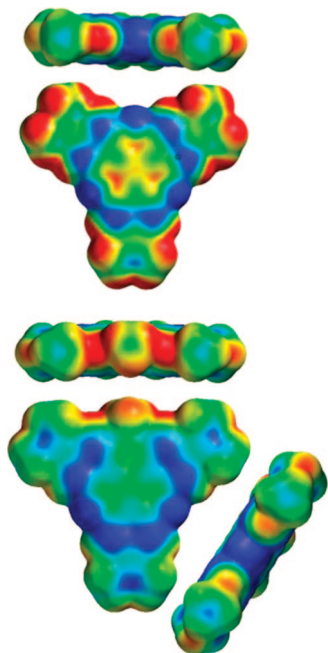


FIGURE 1. Calculated electron density plots for the A-TOTA⁺ (top) and A-ADOTA⁺ (bottom) cations (all R-groups = methyl). Red is positive, and blue is negative relative charge (see Supporting Information for details).

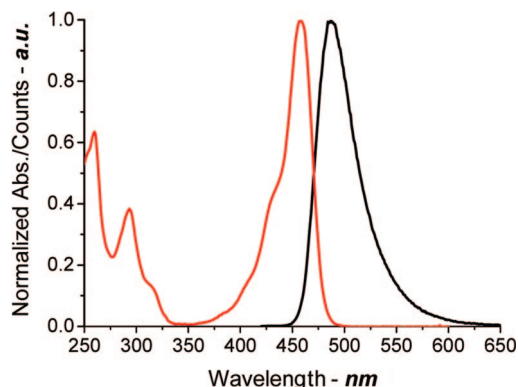


FIGURE 2. Absorption and fluorescence spectra of A-ATOTA⁺ (4·PF₆) in acetonitrile solution. Concentration in the absorption measurement was 5.54×10^{-6} M.

shifted (Figure 2). In acetonitrile solution 4·PF₆ has absorption maximum at 458 nm ($\epsilon = 120,000 \text{ M}^{-1} \text{ cm}^{-1}$). The intense fluorescence peaks at 486 nm, and the quantum yield was measured to 0.64 ± 0.5 in acetonitrile solution, which is even better than that of the A-TOTA⁺ dyes and comparable to that of rhodamines.³⁰

The blue-shifted transitions of the A-ADOTA⁺ system compared to the A-TOTA⁺ dyes is similar to the shift when going from rhodamine to aminoacridinium dyes and in agreement with the general observation regarding the structure and color of carbenium dyes, generally known as Dewar's rule.³¹ The excellent fluorophore properties (intense absorption and high

fluorescence quantum yield) of the new A-ADOTA⁺ dye is worth noticing since few dyes with such intense transitions are found in the spectral region below fluorescein ($\lambda_{\text{abs}} = 494 \text{ nm}$).

In conclusion, we have reported the synthesis and spectral properties of the new super stable tris(dialkylamino)-azadioxatriangulenium carbenium ion (A-ADOTA⁺). The synthesis is based on a combination of controlled nucleophilic substitutions in the *para* and *ortho* positions of the tris(trimethoxyphenyl)-methylum ion **1** and represents the first example where both types of substitution are applied in the same synthetic sequence. The cation stability given by a $\text{p}K_{\text{R}^+}$ value close to 25 makes the A-ADOTA⁺ ion the most stable triangulenium ion so far, comparable to the most stable carbenium ions ever reported. The new triangulenium salt shows promising dye properties with intense absorption at 458 nm and efficient ($\phi_{\text{fl}} = 0.64$) fluorescence at 486 nm in acetonitrile solution.

Experimental Section

The synthesis of compounds **1**·BF₄ and **2**·PF₆ are reported elsewhere.²

9-(4-Diethylamino-2,5-dimethoxyphenyl)-10-propyl-2,7-bis-(diethylamino)-4,5-dimethoxyacridinium Hexafluorophosphate (3·PF₆). Tris(4-diethylamino-2,5-dimethoxyphenyl)-methylum hexafluorophosphate **2**·PF₆ (1.0 g, 1.28 mmol) was dissolved in 10 mL of acetonitrile, and *n*-propylamine (8 g, 136 mmol) was added. The reaction mixture was stirred for 96 h at room temperature. Solvent and propylamine was removed by evaporation, and the residue was recrystallized from methanol (120 mL) to yield 0.70 g (70%) of **3**·PF₆ in a mixture of orange powder and needles. ¹H NMR (CDCl₃, 250 MHz): δ 6.20 (2H, d), 6.16 (2H, d), 6.03 (2H, s), 4.39 (2H, t), 3.93–3.41 (14H, m), 2.11 (2H, m6), 1.37–1.23 (21H, m). ¹³C NMR (CDCl₃, 63 MHz): δ 162.8, 157.1, 153.9, 149.6, 149.4, 144.4, 111.6, 110.0, 93.37, 90.41, 87.13, 56.81, 56.40, 52.21, 45.76, 45.40, 20.23, 13.10, 13.04, 11.66. MALDI-TOF: $M^+ m/z = 631$. Anal. Calcd: C, 58.74; H, 7.08; N, 7.21. Found: C, 58.71; H, 7.02; N, 7.11.

2,6,10-Tris(diethylamino)-4-propyl-4-aza-8,12-dioxatriangulenium Hexafluorophosphate (4·PF₆). 3·PF₆ (0.5 g, 0.64 mmol) was dissolved in collidine (40 mL), and LiI (1.0 g, 7 mmol) was added. The reaction mixture was heated to reflux under argon for 2 h. The reaction mixture was allowed to cool to room temperature and was diluted with heptane (150 mL). The crude product was collected by filtration and redissolved in methanol. The product was precipitated with aqueous KPF₆ solution (100 mL, 0.2 M), collected, and washed repeatedly with water. Column chromatography with dichloromethane/ether 2:1 yielded the product as a yellow powder in a yield of 350 mg (80%). Further purification can be obtained by recrystallization from methanol, in this case yielding 330 mg (75%) of yellow powder. ¹H NMR (CDCl₃, 250 MHz): δ 6.38 (2H, s), 6.34 (2H, s), 6.17 (2H, s), 4.13 (2H, t, $J = 7$ Hz), 3.48–3.60 (12H, m), 1.89 (2H, m6, 7 Hz), 1.30–1.35 (18H, m), 1.14 (3H, t, $J = 10$ Hz). ¹³C NMR (acetone-*d*₆, 101 MHz): δ 155.93, 155.56, 155.52, 154.31, 154.11, 142.37, 131.94, 98.06, 94.49, 94.29, 90.97, 48.24, 46.32, 46.20, 20.22, 12.87, 12.77, 11.54. MALDI-TOF: $M^+ m/z = 532$. Anal. Calcd: C, 59.64; H, 6.28; N, 8.18. Found: C, 59.58; H, 6.28; N, 8.16.

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Supporting Information Available: Spectroscopic details and $\text{p}K_{\text{R}^+}$ determinations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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