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Base-Assisted One-Pot Synthesis of *N,N′,N″*-Triaryltriazatriangulenium Dyes: Enhanced Fluorescence Efficiency by Steric Constraints

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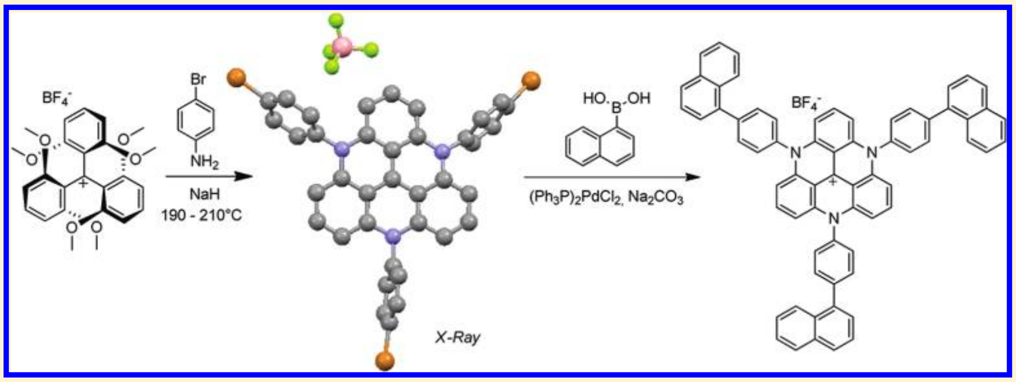
S *Supporting Information*



ABSTRACT: In this paper we report the first synthesis of cationic *N,N′,N″*-triaryltriazatriangulenium dyes (Ar$_3$-TATA$^+$). Previously, only alkyl-substituted triazatriangulenium derivatives (R$_3$-TATA$^+$) were known, a consequence of the low reactivity of anilines in the aromatic nucleophilic substitution reaction leading to the formation of the TATA$^+$ core. The synthesis of Ar$_3$-TATA$^+$ was achieved by heating the tris(2,6-dimethoxyphenyl)methylium ion (DMP$_3$C$^+$) in various anilines in the presence of NaH. In the solvent-free reaction all three aryl substituents could be introduced despite the low reactivity of the anilines. The symmetric Ar$_3$-TATA$^+$ derivatives with Ar = phenyl (**2**), 4-methoxyphenyl (**3**), and 4-bromophenyl (**4**) were synthesized. Single crystal structures of **2** and **4** were obtained as BF$_4^-$ salts, where torsional angles larger than 80° were observed between the TATA$^+$ chromophore and the aryl substituents. The photophysical properties were studied in solution and in thin films. The results show that the Ar$_3$-TATA$^+$ dyes have a surprising 3-fold increase in fluorescence quantum yields when compared to the parent alkyl-substituted R$_3$-TATA$^+$ salts. With a high quantum yield (>50%) and emission in the red (λ_{fl} = 560 nm) the Ar$_3$-TATA$^+$ dyes represent a promising new addition to the family of superstable cationic triangulenium dyes. Additionally, the synthesized tribromo derivative **4** is shown to be a potential triagonal synthon for polymers and other macromolecules.

INTRODUCTION

Triazatriangulenium (TATA$^+$) belongs to the large group of charged fluorescent dyes of which the most prominent are fluorescein and rhodamine. The investigation of known derivatives and the synthesis and characterization of new derivatives of these fluorophores is an ongoing process.[1−6] In the past decades the focus has been more that of application: The fluorescent dyes act as reporters of sensing events in artificial or biological systems[7−14] and as stains to image biological systems.[15−19] TATA$^+$ has yet to be used in these application, mainly because of a quantum yield of only 20%, which makes TATA$^+$ the least fluorescent of the triangulenium dyes.[20] The fluorescent triangulenium dyes fall in two groups: (1) the donor-substituted amino-trioxatriangulenium dyes,[21−26] which have photophysics similar to that of rhodamines and fluoresceins,[27] but with a manifold increase in cation stability and with high symmetry and (2) the unsubstituted azaoxa-triangulenium dyes,[28−33] which constitute a unique class of fluorophores, with long fluorescence lifetime, emission in the red, and a high quantum yield. On the synthetic pathway to the triangulenium dyes, helical cationic dyes are found.[34,35] Of these especially dimethoxyquinacridinium (DMQA$^+$) has been investigated.[35−40]

Recently, the cationic nature of TATA$^+$ has been exploited to form self-assembled ionic supramolecular assemblies, where the combination of charge and other molecular properties has been used to control the nanostructure of materials.[41−44] A similar approach to that of in ionic self-assembly (ISA), where distinct properties of anions and cations combined with their mutual

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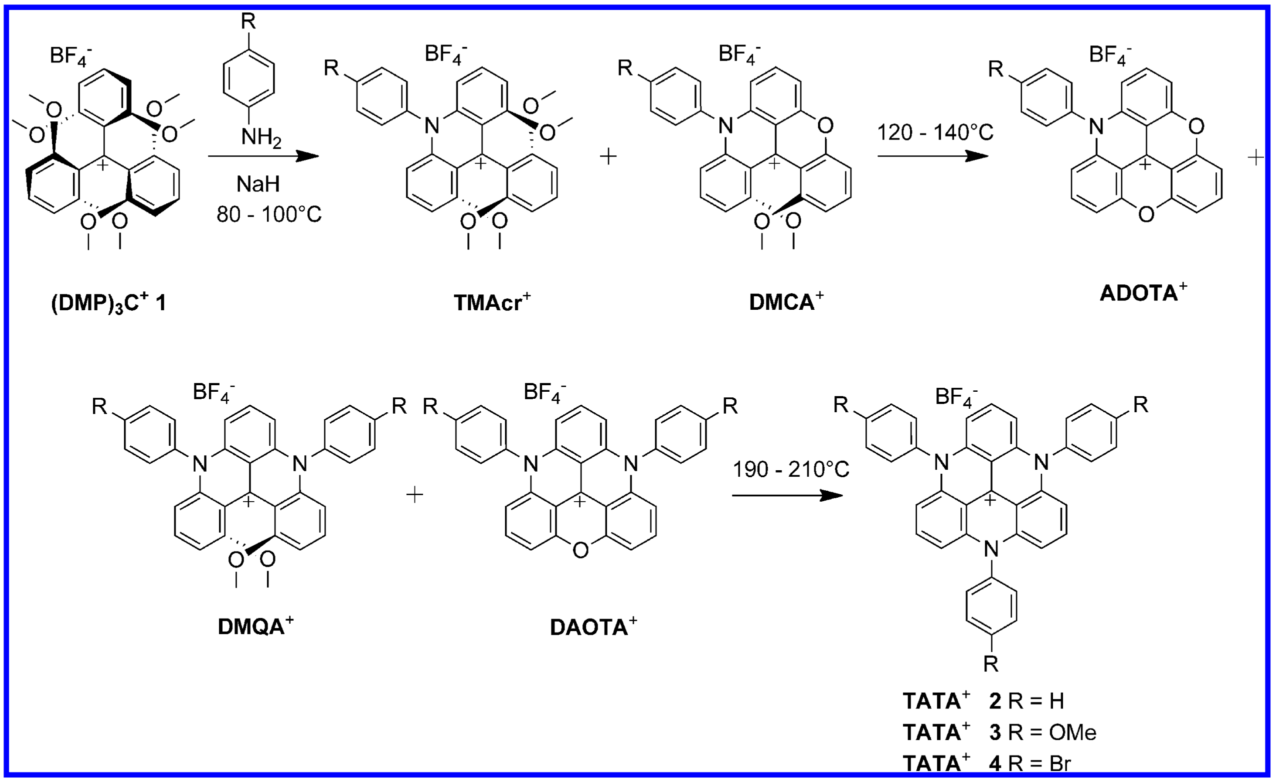
Scheme 1. Synthesis of Phenyl-TATA$^+$ 2 (36%), 4-Methoxyphenyl-TATA$^+$ 3 (24%), and 4-Bromophenyl-TATA$^+$ 4 (22%)



Coulomb attraction are used to form unique materials.[45,46] The unique cation stability of the triangulenium salts allow them to form materials where the cations are stacked on top of each other, resulting in segregation of cations and anion.[47,48] In the case of *N,N′,N″*-trialkyltriazatriangulenium (R_3-TATA$^+$), the molecular conformation does, however, not allow for a continuous, cofacial columnar stack of the planar cations and only dimers are formed. For the bromide and tetrafluoroborate salts this leads to a rare lamellar bilayer structure that self-organizes with segregation of the alkyl side chains and the ions. The result is that the TATA$^+$ dimers are ordered in an infinite 2D lattice isolated between layers of alkyl chains.[31,49] The high symmetry and triangular nature of the triangulenium salts has been exploited to form chiral and supramolecular structures.[50−55] The cationic nature has been used to add functional structures directly to the center carbon.[56−59]

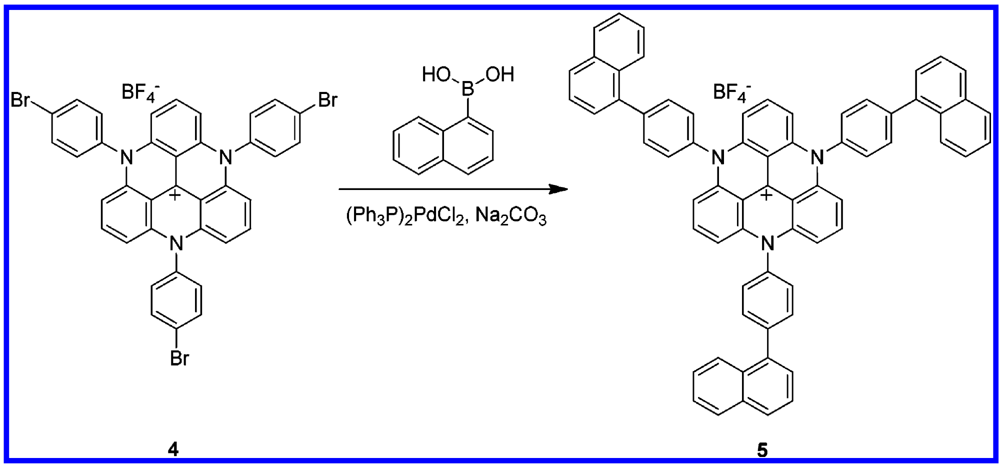
In this paper we report on the synthesis and fluorescence properties of a new series of TATA$^+$ salts, where the three substituents on nitrogen are aryl groups. The *N,N′,N″*-triaryltriazatriangulenium (Ar_3-TATA$^+$) dyes have higher quantum yields than the *N,N′,N″*-trialkyltriazatriangulenium (R_3-TATA$^+$) dyes, and the dyes are relatively insensitive to functionalization on the aryl arms. We show the possibility of using Ar_3-TATA$^+$ as a trigonal building block in, e.g., porous polymers,[60−64] by demonstrating the possibility of metal-catalyzed polymerization of the tribromo derivative. Metal-catalyzed cross-couplings have previously been shown to be compatible with the triangulenium skeleton.[65,66] Through crystal structures and thin film absorption spectra we show that the bulk of the phenyl groups in Ar_3-TATA$^+$ inhibit the formation of closely packed cofacial $\pi-\pi$ dimers that otherwise dominates the solid-state packing of other TATA$^+$ salts.

■ RESULTS AND DISCUSSION

Synthesis of Ar_3-TATA$^+$ Salts. Symmetric TATA$^+$ cations were synthesized in a one-pot procedure from the readily available tris(2,6-dimethoxyphenyl)carbenium ion ($(DMP)_3C^+$ **1**) (Scheme 1), by three consecutive aromatic nucleophilic substitution (S_NAr) reactions with primary amines.[29,30] In the first step the amine attacks the carbenium ion **1** and replaces two of the *o*-methoxy groups, forming a tetramethoxyacridinium ion (TMAcr$^+$).[67] For simple aliphatic amines the first reaction is fast and proceeds readily at room temperature. Introduction of the second and third nitrogen bridge requires an increasing excess of the amine and elevated temperatures. However, the low nucleophilicity of anilines have limited the products to compounds with only one aryl group.[30,50,65,66] Refluxing **1** in pure aniline yields Ph-ADOTA$^+$, the product of one amine S_NAr substitution and two intramolecular ring-closing oxa-bridge-forming reactions. To overcome this limitation the reactivity of the anilines was enhanced by using a strong base (NaH), essentially reacting **1** with the sodium anilide.

In this way Ar_3-TATA$^+$ can be prepared directly from **1** using a large excess of the appropriate aniline and sodium hydride. The reaction mixture was gradually heated from room temperature to 200 °C. As the temperature increases three substitutions (a total of six MeO groups are substituted with three anilines) were achieved. With each substitution a distinct change in color and gas evolution was observed. Using this procedure, the possible Ar_3-TATA$^+$ derivatives are limited as anilines that can be applied in large quantities and have boiling points above 180 °C are required. From the reaction with aniline, triphenyl-TATA$^+$ **2** was isolated in a yield of 36% (71% per reaction) along with the double substitution product diphenyl-DMQA$^+$ in a yield of 15%. Scheme 1 includes the expected intermediates/byproducts in the Ar_3-TATA$^+$ syn-

Scheme 2. Suzuki Aryl−Aryl Coupling To Make Naphthalene-phenyl-TATA$^+$ 5, 55%



thesis. If the temperature was set between 90 and 130 °C we observed TMAcr$^+$ and DMCA$^+$ as the major products (observed by MALDI-TOF mass spectrometry, not isolated). At temperatures between 130 and 180 °C, DMQA$^+$ and DAOTA$^+$ are the dominating products (observed by MALDI-TOF mass spectrometry, not isolated). In this study, we did not optimize the synthesis of the mono and double substituted carbenium ions TMAcr$^+$ and DMQA$^+$. However, our observations suggest that these compounds and their oxygen ring-closed analogues can be obtained using the same procedure reported here, but using lower temperatures. To further functionalize the new Ar$_3$-TATA$^+$ system, functional groups on the aryl side groups were introduced. From the reaction of **1** with 4-methoxyaniline, tris(4-methoxyphenyl)-TATA$^+$ **3** was isolated in a yield of 24%. In the case of 4-bromoaniline the reaction needed a longer period of time at high temperature and gave tris(4-bromophenyl)-TATA$^+$ **4** in a yield of 22%. The observed order of reactivity and intermediates in the NaH-assisted reaction with anilines clearly indicates that the introduction of the aniline moieties indeed takes place via the S$_N$Ar mechanism.

To investigate post-modification of the functionalized Ar$_3$-TATA's, **4** was modified by a triple Suzuki coupling reaction, using naphthalene-1-boronic acid and (Ph$_3$P)$_2$PdCl$_2$ in refluxing toluene (Scheme 2). The 4-naphthyl-phenyl substituted tris(4-(naphthyl)-phenyl)-TATA$^+$ **5** were obtained in a yield of 55% (82% per reaction). This demonstrates that the TATA$^+$ ions are compatible with the Suzuki coupling conditions as was previously shown for the ADOTA$^+$ system.[65]

Spectroscopy. The photophysical properties of the aryl-substituted triazatriangulenium dyes are at first glance very similar to those of the trialkyl-TATA$^+$ salts. The absorption and emission spectra of triphenyl-TATA$^+$ and trioctyl-TATA$^+$ are shown in Figure 1. A small red shift of 5 nm is observed in both absorption and emission accompanied by a broadening of the absorption and narrowing of the emission band. An increased absorption in the region 200−300 nm, corresponding to the absorption of the many isolated aniline and diaminophenylenes, is not surprisingly observed for the Ar$_3$-TATA$^+$ compounds. All spectra are included as Supporting Information. The photophysical properties are compiled in Table 1. It is evident that substitutions on the aromatic *N*-substituents do not alter the absorption or the emission spectrum of TATA$^+$. Both Ar$_3$-TATA$^+$ and R$_3$-TATA$^+$ show very little solvatochromism.[49] The increase in observed absorption coefficient seen in Table 1 is due to a narrowing of the bands in dichloromethane compared to acetonitrile. The integrated absorption is constant. Only compound **5** behaves slightly different, with a higher absorption coefficient in acetonitrile than in dichloromethane. This is most likely due to solvation effects, as the TATA$^+$ chromophore in this case is flanked by three large aromatic plates.

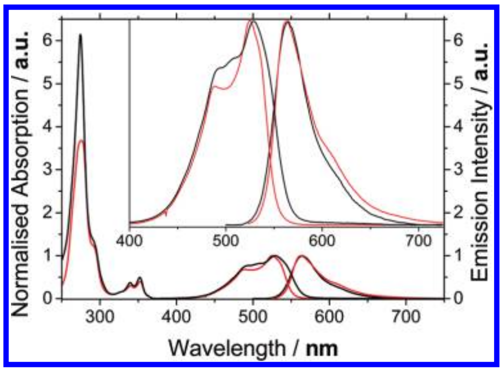


Figure 1. Absorption and emission spectra of triphenyl-TATA$^+$ 5 (black) and trioctyl-TATA$^+$ (red) in acetonitrile solution. Both absorption and emission spectra are normalized to the peak of the main band.

Table 1. Photophysical Properties of Trioctyl-TATA·BF$_4$ and Triaryl-TATA·BF$_4$ 2−5 in Solution

compound	solvent	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{fl} (nm)	ϕ_{fl} (%)
Oct-TATA$^+$	acetonitrile	523	20,300	560	16
Ph-TATA$^+$ 2	acetonitrile	528	20,400	564	53
	dichloromethane	535	23,800	558	55
4-BrPh-TATA$^+$ 3	acetonitrile	529	19,800	566	27
	dichloromethane	535	23,800	562	30
MeOPh-TATA$^+$ 4	acetonitrile	530	21,100	565	62
	dichloromethane	535	24,600	558	59
4-NpPh-TATA$^+$ 5	acetonitrile	530	21,500	567	45
	dichloromethane	530	20,500	561	38

The key feature of the Ar$_3$-TATA$^+$, when compared to R$_3$-TATA$^+$, is the large increase in the fluorescence quantum yield. The replacement of the simple alkyl chains in R$_3$-TATA$^+$ by phenyl (**2**) or 4-methoxyphenyl (**4**) changes the fluorescence quantum yield from 16% to 55−60% (Table 1), corresponding to more than a 3-fold increase. Thus, this substitution of alkyl groups with aryl groups changes a mediocre fluorescent dye to an excellent dye. This effect is surprising as the aryl groups must have limited electronic overlap with the TATA$^+$ chromophore and it is known that such non-coplanar π systems most often favors non-radiative deactivation. The observed reverse effect for the Ar_3-TATA$^+$ dyes we attribute to the increased symmetry and structural constraints imposed on the TATA chromophore by aryl relative to alkyl substituents. As seen from the X-ray structures (discussed below) the aryl groups are decoupled from the TATA chromophore due to steric interactions between the two subsystems. The steric interaction is also present in the alkyl derivatives.[31] However, for the alkyl derivatives the result is a symmetry lowering as the alkyl chains can be located only on one side of the TATA chromophore. This structural distortion will not be present in the Ar_3-TATA$^+$ dyes because the aryl substituents are symmetric with respect to the plane of the chromophore. We speculate that this may be part of the reason for the enhanced fluorescence efficiency of these dyes. Introduction of more flexible groups, as in **5**, or heavy atoms, as in **3**, reduces the quantum yield again.[68,69] Most pronounced is the heavy atom effect in **3**.

Solid State Structures. The molecular structure of triphenyl-TATA$^+$ (**2**) and tris(4-bromophenyl)-TATA$^+$ (**4**) was confirmed by single-crystal X-ray diffraction of their BF_4^- salts (Figure 2). Crystals suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution of the compound in a mixture of dichloromethane and toluene at room temperature. Selected crystallographic data are shown in Table 2.

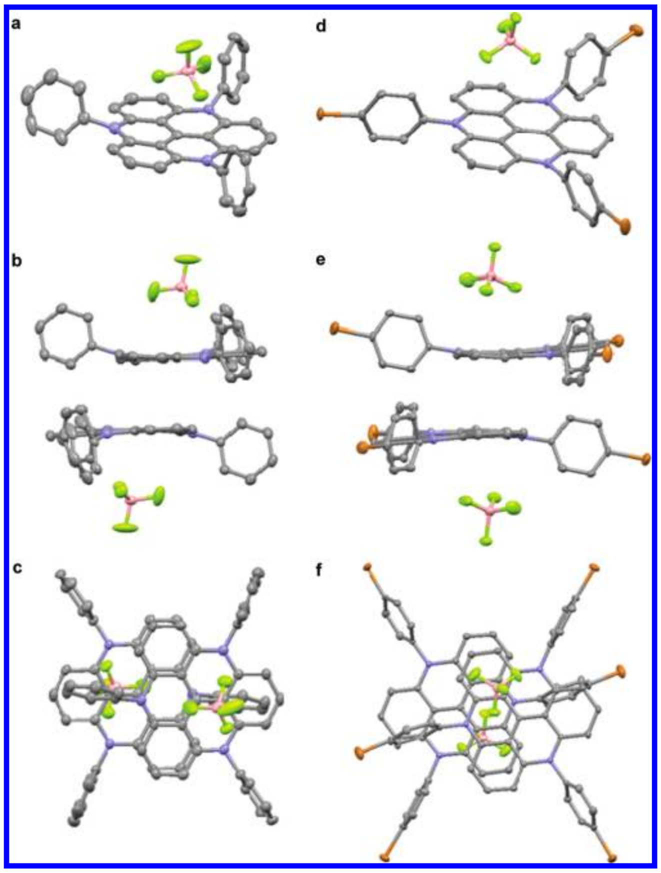


Figure 2. X-ray structures of triphenyl-TATA$^+$ (**2**, a−c) and tris(4-bromophenyl)-TATA$^+$ (**4**, d−f) with 50% of probability ellipsoids. All hydrogen atoms are omitted for clarity (nitrogen, blue; bromine, orange; fluorine, green; boron, pink).

Table 2. Selected Crystallographic Data for Triphenyl-TATA·BF_4 2 and Tris(4-Bromophenyl)-TATA·BF_4 4

	2·BF_4	**4**·BF_4
formula	$C_{37}H_{24}BF_4N_3$	$C_{37}H_{21}BBr_3F_4N_3$
CCDC	CCDC 865387	CCDC 865823
M_w	597.41	834.10
crystal system	monoclinic	monoclinic
space group	$P21/n$	$P21/c$
a [Å]	14.75	14.52
b [Å]	10.62	10.94
c [Å]	18.40	19.67
α [deg]	90.00	90.00
β [deg]	99.04	101.56
γ [deg]	90.00	90.00
Z	4	4
V [Å^3]	2847.7	3061.2
T [K]	122	122
F^2	5.23	6.17
R_{int}	0.1059	0.1431
D_{calcd} [g/cm]	1.393	1.810
crystal size [mm]	0.06 × 0.18 × 0.28	0.03 × 0.15 × 0.41

Ar_3-TATA$^+$ is an equilateral triangle with three flanking phenyl rings; see Figure 2a and c. The aryl substituents are oriented at an angle almost perpendicular to the TATA$^+$ cores; in the highly strained structure the phenyls adopt an average angle of 80.5° with the plane of the TATA$^+$ core. The large torsion angle is a result of the intrinsic steric repulsion.[31]

The molecular packing of compound **2** and **4** in the obtained crystals are characterized by a face-to-face arrangement of the TATA$^+$ cores in slipped dimers with moderate overlap as shown in Figure 2b,c and 2e,f. This is in contrast to the symmetric alkyl-substituted R_3-TATA·BF_4 salts that pack in close cofacial dimers surrounded by the BF_4^- counterions in the same plane.[29,31,70] The packing of alkyl-TATA is possible because the alkyl chains can all pack on the same side of the TATA$^+$ core and away from the dimer. In the Ar_3-TATA·BF_4 salts the aryl groups must occupy space on both sides of the TATA$^+$ core. The result is the slipped packing shown in Figure 2, where one of the aryl groups is located above the TATA$^+$ core of the neighbor. The many competing forces in the crystal packing result in an almost pyramidal aryl nitrogen and a reduced overlap between the two TATA systems in the would-be dimer. A further consequence of the steric demands of the aryl groups is a larger TATA−TATA distance in this unit. For all reported R_3-TATA·BF_4 salts close contact-dimers with a stacking distance of 3.30 Å are found. In phenyl-TATA$^+$ (**2**) and 4-bromophenyl-TATA$^+$ (**4**) the distance is significantly increased to 3.58 and 3.79 Å.

The restricted dimer packing motif is also evident in the absorption spectra of thin films of the Ar_3-TATA·BF_4 salts (Figure 3). In thin films of R_3-TATA·BF_4 a large red shift of the first absorption band (λ_{max}(solution) = 525 nm vs λ_{max}(thin film) = 548 nm) is observed accompanied by a new band around 425 nm. Both effects are assigned to the formation of close cofacial TATA−TATA contact-dimers.[31] For Ar_3-TATA·BF_4 only a small red shift and a broadening are observed. A very important observation is that no increased

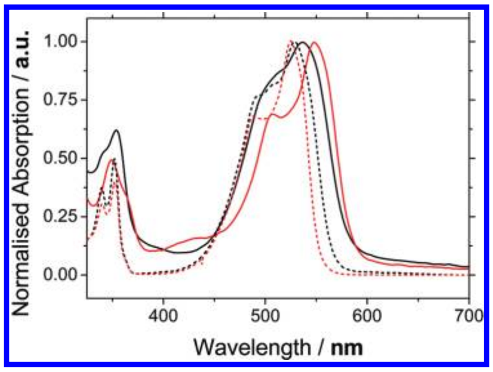


Figure 3. Absorption spectra of triphenyl-TATA$^+$ **2** (black) and trioctyl-TATA$^+$ (red) in acetonitrile (dash) and as thin films spin-casted from 5 mg/mL dichloromethane solution (full lines).

absorption is seen around 425 nm. This implies that the changes in the spectrum relative to solution is due to the crystal field and not formation of a new absorbing species, as is the case for thin films of R_3-TATA·BF_4. The bulk of the aryl groups prevents the formation of dimers, despite the fact that it is energetically favorable from an electronic point of view. The result is the contorted molecular structures observed in the single crystal structures of compound **2** and **4**.

To summarize, we have reported the synthesis and photophysical properties of the first *N,N′,N″*-triaryltriazatriangulenium (Ar_3-TATA$^+$) salts. The introduction of aromatic side groups on the TATA core results in a 3-fold increase in fluorescence quantum yield, making the new Ar_3-TATA$^+$ salts potent fluorophores. The bulk of the phenyl groups also prevents formation of close contact-dimers in the solid state, thus imposing monomer-like optical properties to spin-cast films of Ar_3-TATA$^+$ salts. We further showed that Ar_3-TATA$^+$ can take part in metal-catalyzed cross-couplings, which will make these compounds useful as a unique triangular platform for fluorescent materials.

■ EXPERIMENTAL SECTION

Unless otherwise stated, all starting materials were obtained from commercial suppliers and used as received. Solvents were HPLC grade and were used as received. Ground state absorption spectroscopy was routinely recorded with a double beam spectrophotometer. Steady state fluorescence was recorded with a standard L-configuration fluorimeter with single grating monochromators. The absorbance at the excitation wavelength was kept low, to avoid inner filter effect and intermolecular interactions. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz instrument (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). Proton chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) and carbon chemical shifts in ppm downfield of TMS, using the resonance of the solvent as internal standard. Melting points were measured on a Gallenkamp apparatus and are uncorrected. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a vertical reflector instrument. Dry column vacuum chromatography was performed on Kieselgel 60 (0.015−0.040 mm particle size). Thin layer chromatography was carried out using aluminum sheets precoated with silica gel 60F.

General Method. *N,N′*-Diphenyl-DMQA Tetrafluoroborate and *N,N′,N″*-Triphenyl-TATA Tetrafluoroborate (2). A mixture of aniline (20 mL) and starting material tris(2,6-dimethoxyphenyl)-methylium tetrafluoroborate (**1**) (2.0 g, 3.9 mmol)[29] was placed in a 500 mL round-bottom flask equipped with a large magnetic stir bar and a reflux condenser. NaH (60% w/w, 0.6 g, 15.0 mmol) was added, and the round-bottom flask was placed in an oil bath and heated from room temperature to 200 °C over a period of 20 min. During the reaction the color changes from purple to red and then back to dark purple. Furthermore, three violent gas evolutions were observed of which the last at 180 °C was handled with concern (hence the 500 mL flask). The reaction mixture was allowed to reach room temperature, then quenched by slow addition of H_2O (100 mL), and extracted with CH_2Cl_2 (3 × 100 mL). The extracts were washed with brine (100 mL) and evaporated to dryness *in vacuo*. The title compound was further purified by dissolving in CH_2Cl_2 and precipitation by addition of Et_2O. The residue was subjected to dry column vacuum chromatography (heptane/toluene/EtOH with 5% increment of EtOH in toluene). Two compounds were isolated, one blue (DMQA$^+$) and one red (TATA$^+$). Phenyl-DMQA$^+$ was precipitated/crystallized in CH_2Cl_2/toluene by slow evaporation of CH_2Cl_2 yielding blue crystals. Yield: 330 mg, 15%; mp >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83 (m, 4H), 7.76 (t, 2H, J = 7.5 Hz), 7.69 (m, 3H), 7.45 (m, 4H), 6.93 (d, 2H, J = 8.0 Hz), 6.66 (d, 2H, J = 8.0 Hz), 6.60 (d, 2H, J = 8.0 Hz), 3.87 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.9, 144.9, 143.9, 139.7, 137.8, 137.5, 135.7, 132.4, 131.4, 130.9, 129.3, 128.0, 117.9, 113.1, 108.8, 106.7, 103.6, 56.0; MS (MALDI-TOF) *m/z*: calcd for $C_{33}H_{25}N_2O_2^+$ 481.56, found 481.03. Anal. Calcd for $C_{33}H_{25}BF_4N_2O_2$: C, 69.74; H, 4.43; N, 4.93. Found: C, 70.01; H, 4.55; N, 5.02.

Phenyl-TATA$^+$ **2** were precipitated/crystallized in CH_2Cl_2/toluene by slow evaporation of CH_2Cl_2 yielding red crystals. Yield: 851 mg, 36%; mp >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (t, 6H, J = 8.6 Hz), 7.72 (t, 3H, J = 7.6 Hz), 7.56 (t, 3H, J = 8.4 Hz), 7.45 (d, 6H, J = 8.3 Hz), 6.38 (d, 6H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ142.34, 142.02, 137.85, 137.20, 132.30, 130.71, 128.55, 110.19, 107.30; MS (MALDI-TOF) *m/z*: calcd for $C_{37}H_{24}N_3^+$ 510.61, found 509.98. Anal. Calcd for $C_{37}H_{24}BF_4N_3$: C, 74.39; H, 4.04; N, 7.03. Found: C, 74.46; H, 3.90; N, 6.81.

***N,N′,N″*-Tris(4-methoxyphenyl)-TATA Tetrafluoroborate (3).** The compound was prepared as in the case of compound **2**, starting from 4-methoxyaniline (5.0 g, 40.6 mmol), starting material **1** (2.0 g, 3.9 mmol), and NaH (60% w/w, 0.6 g, 15.0 mmol). The residue was subjected to dry column vacuum chromatography (heptane/toluene/EtOH with 5% increment of EtOH in toluene) and yielded a red compound. Precipitation/crystallization in CH_2Cl_2/toluene by slow evaporation of CH_2Cl_2 yielded red crystals. Yield: 540 mg, 24%; mp >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (t, 3H, J = 8.5 Hz), 7.34 (d, 6H, J = 9.0 Hz), 7.29 (d, 6H, J = 9.0 Hz), 6.43 (d, 6H, J = 8.5 Hz), 3.96 (s, 9H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 160.86, 142.26, 137.29, 129.99, 129.80, 117.38, 110.13, 107.35, 55.91; MS (MALDI-TOF) *m/z*: calcd for $C_{40}H_{30}N_3O_3^+$ 600.7, found 600.3. Anal. Calcd for $C_{40}H_{30}BF_4N_3O_3$: C, 69.88; H, 4.40; N, 6.11. Found: C, 69.54; H, 4.32; N, 5.97.

***N,N′,N″*-Tris(4-bromophenyl)-TATA Tetrafluoroborate (4).** The compound was prepared as in the case of compound **2**, starting from 4-bromoaniline (10 g, 58.1 mmol), starting material **1** (2.0 g, 3.9 mmol), and NaH (60% w/w, 0.6 g, 15.0 mmol). The residue was subjected to dry column vacuum chromatography (heptane/toluene/EtOH with 5% increment of EtOH in toluene) and yielded a red compound. Precipitation/crystallization in CH_2Cl_2/toluene by slow evaporation of CH_2Cl_2 yielded red crystals. Yield: 640 mg, 22%; mp >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.92 (d, 1H, J = 8.6 Hz), 7.56 (t, 1H, J = 8.5 Hz), 7.41 (d, 1H, J = 8.6 Hz), 6.38 (d, 1H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.66, 141.84, 137.04, 136.83, 135.54, 130.75, 124.77, 110.55, 107.21; MS (MALDI-TOF) *m/z*: calcd for $C_{37}H_{21}Br_3N_3^+$ 747.3, found 748.0. Anal. Calcd for $C_{37}H_{21}BBr_3F_4N_3$: C, 53.28; H, 2.54; N, 5.04. Found: C, 53.40; H, 2.43; N, 4.89.

***N,N′,N″*-Tris(4-naphthalen-1-yl-phenylene)-TATA Tetrafluoroborate (5).** To a flame-dried 100 mL three-necked round-bottom flask equipped with a rubber septum and a reflux condenser were added 4-bromophenyl-TATA **4** (100 mg, 0.12 mmol), naphthalene-1-boronic acid (100 mg, 0.58 mmol), and toluene (150 mL). The mixture was heated to 80 °C to dissolve 4-bromophenyl-TATA **4**. K_2CO_3 (3 g) and H_2O (100 mL) was added, and the mixture was degassed for 10 min via a syringe through the rubber septum. $(PPh_3)_2PdCl_2$ (50 mg, 0.07 mmol) was added, and the mixture was heated to reflux for 12 h. The reaction mixture was allowed to reach room temperature and extracted with CH_2Cl_2 (3 × 100 mL). The residue was subjected to dry column vacuum chromatography (heptane/toluene/EtOH with 5% increment of EtOH in toluene). Precipitation/crystallization in CH_2Cl_2/toluene by slow evaporation of CH_2Cl_2 yielded red crystals. Yield: 65 mg, 55%; mp >300 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.09−8.04 (m, 1H), 8.03−7.96 (m, 4H), 7.78 (t, J = 8.4 Hz, 1H), 7.71−7.58 (m, 6H), 6.66 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 143.30, 142.57, 142.19, 138.39, 137.20, 136.92, 133.93, 133.79, 131.24, 128.73, 128.63, 127.37, 126.66, 126.19, 125.47, 110.63, 107.44; MS (MALDI-TOF) m/z: calcd for $C_{67}H_{42}N_3^+$ 889.07, found 888.09. Anal. Calcd for $C_{67}H_{42}BF_4N_3$: C, 82.46; H, 4.34; N, 4.31. Found: C, 82.57; H, 4.49; N, 4.42.

Selected Crystallographic Data. Crystallographic data is summarized in Table 2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H (1D and COSY) and ^{13}C NMR for all compounds, crystal structures for compound **2** and **4** in CIF format, absorption spectra for all compounds, solution fluorescence emission and excitation spectra, and solid state emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Han, J.; Burgess, K. *Chem. Rev.* **2009**, *110*, 2709.
(2) Wu, L. X.; Burgess, K. *J. Org. Chem.* **2008**, *73*, 8711.
(3) Wu, L. X.; Burgess, K. *Org. Lett.* **2008**, *10*, 1779.
(4) Jose, J.; Burgess, K. *J. Org. Chem.* **2006**, *71*, 7835.
(5) Best, Q. A.; Xu, R.; McCarroll, M. E.; Wang, L.; Dyer, D. J. *Org. Lett.* **2010**, *12*, 3219.
(6) Kenmoku, S.; Urano, Y.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2007**, *129*, 7313.
(7) Minta, A.; Kao, J. P. Y.; Tsien, R. Y. *J. Biol. Chem.* **1989**, *264*, 8171.
(8) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
(9) Giepmans, B. N. G.; Adams, S. R.; Ellisman, M. H.; Tsien, R. Y. *Science* **2006**, *312*, 217.
(10) Lavis, L. D.; Raines, R. T. *ACS Chem. Biol.* **2008**, *3*, 142.
(11) Ueno, T.; Urano, Y.; Setsukinai, K.; Takakusa, H.; Kojima, H.; Kikuchi, K.; Ohkubo, K.; Fukuzumi, S.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 14079.
(12) Urano, Y.; Kamiya, M.; Kanda, K.; Ueno, T.; Hirose, K.; Nagano, T. *J. Am. Chem. Soc.* **2005**, *127*, 4888.
(13) Mineno, T.; Ueno, T.; Urano, Y.; Kojima, H.; Nagano, T. *Org. Lett.* **2006**, *8*, 5963.
(14) Amelia, M.; Lavie-Cambot, A.; McClenaghan, N. D.; Credi, A. *Chem. Commun.* **2011**, *47*, 325.
(15) Dedecker, P.; Flors, C.; Hotta, J. I.; Uji-I, H.; Hofkens, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 8330.
(16) Ameloot, R.; Roeffaers, M.; Baruah, M.; De Cremer, G.; Sels, B.; De Vos, D.; Hofkens, J. *Photochem. Photobiol. Sci.* **2009**, *8*, 453.
(17) Willig, K. I.; Rizzoli, S. O.; Westphal, V.; Jahn, R.; Hell, S. W. *Nature* **2006**, *440*, 935.
(18) Hell, S. W. *Science* **2007**, *316*, 1153.
(19) Nolan, E. M.; Lippard, S. J. *Acc. Chem. Res.* **2009**, *42*, 193.
(20) Dileesh, S.; Gopidas, K. R. *J. Photochem. Photophys. A: Chem.* **2004**, *162*, 115.
(21) Laursen, B. W.; Krebs, F. C.; Nielsen, M. F.; Bechgaard, K.; Christensen, J. B.; Harrit, N. *J. Am. Chem. Soc.* **1998**, *120*, 12255.
(22) Laursen, B. W.; Reynisson, J.; Mikkelsen, K. V.; Bechgaard, K.; Harrit, N. *Photochem. Photobiol. Sci.* **2005**, *4*, 568.
(23) Laursen, B. W.; Sørensen, T. J. *J. Org. Chem.* **2009**, *74*, 3183.
(24) Westerlund, F.; Hildebrandt, C. B.; Sørensen, T. J.; Laursen, B. W. *Chem.—Eur. J.* **2010**, *16*, 2992.
(25) Sørensen, T. J.; Laursen, B. W. *J. Org. Chem.* **2010**, *75*, 6182.
(26) Westerlund, F.; Elm, J.; Lykkebo, J.; Carlsson, N.; Thyrhaug, E.; Akerman, B.; Sørensen, T. J.; Mikkelsen, K. V.; Laursen, B. W. *Photochem. Photobiol. Sci.* **2011**, *10*, 1963.
(27) Wysocki, L. M.; Lavis, L. D. *Curr. Opin. Chem. Biol.* **2011**, *15*, 752.
(28) Nicolas, C.; Bernardinelli, G.; Lacour, J. *J. Phys. Org. Chem.* **2010**, *23*, 1049.
(29) Laursen, B. W.; Krebs, F. C. *Angew. Chem., Int. Ed.* **2000**, *39*, 3432.
(30) Laursen, B. W.; Krebs, F. C. *Chem.—Eur. J.* **2001**, *7*, 1773.
(31) Sørensen, T. J.; Hildebrandt, C. B.; Elm, J.; Andreasen, J. W.; Madsen, A. O.; Westerlund, F.; Laursen, B. W. *J. Mater. Chem.* **2012**, *22*, 4797−4805.
(32) Nicolas, C.; Lacour, J. *Org. Lett.* **2006**, *8*, 4343.
(33) Martin, J. C.; Smith, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 2252.
(34) Guin, J.; Besnard, C.; Lacour, J. *Org. Lett.* **2010**, *12*, 1748.
(35) Herse, C.; Bas, D.; Krebs, F. C.; Bürgi, T.; Weber, J.; Wesolowski, T.; Laursen, B. W.; Lacour, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3162.
(36) Laleu, B.; Mobian, P.; Herse, C.; Laursen, B. W.; Hopfgartner, G.; Bernardinelli, G.; Lacour, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 1879.
(37) Mobian, P.; Banerji, N.; Bernardinelli, G.; Lacour, J. *Org. Biomol. Chem.* **2006**, *4*, 224.
(38) Villani, C.; Laleu, B.; Mobian, P.; Lacour, J. *Chirality* **2007**, *19*, 601.
(39) Guin, J.; Besnard, C.; Pattison, P.; Lacour, J. *Chem. Sci.* **2011**, *2*, 425.
(40) Conreaux, D.; Mehanna, N.; Herse, C.; Lacour, J. *J. Org. Chem.* **2011**, *76*, 2716.
(41) Haketa, Y.; Takayama, M.; Maeda, H. *Org. Biomol. Chem.* **2012**, *10*, 2603.
(42) Haketa, Y.; Sasaki, S.; Ohta, N.; Masunaga, H.; Ogawa, H.; Mizuno, N.; Araoka, F.; Takezoe, H.; Maeda, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 10079.
(43) Maeda, H.; Terashima, Y. *Chem. Commun.* **2011**, *47*, 7620.
(44) Bando, Y.; Sakamoto, S.; Yamada, I.; Haketa, Y.; Maeda, H. *Chem. Commun.* **2012**, *48*, 2301.
(45) Kadam, J.; Faul, C. F. J.; Scherf, U. *Chem. Mater.* **2004**, *16*, 3867.
(46) Zakrevskyy, Y.; Smarsly, B.; Stumpe, J.; Faul, C. F. J. *Phys. Rev. E* **2005**, *71*, 021701.
(47) Simonsen, J. B.; Kjaer, K.; Howes, P.; Nørgaard, K.; Bjørnholm, T.; Harrit, N.; Laursen, B. W. *Langmuir* **2009**, *25*, 3584.
(48) Simonsen, J. B.; Westerlund, F.; Breiby, D. W.; Harrit, N.; Laursen, B. W. *Langmuir* **2011**, *27*, 792.
(49) Sørensen, T. J.; Hildebrandt, C. B.; Glyvredal, M.; Laursen, B. W. Submitted for publication.
(50) Mobian, P.; Nicolas, C.; Francotte, E.; Bürgi, T.; Lacour, J. *J. Am. Chem. Soc.* **2008**, *130*, 6507.
(51) Narasimhan, S. K.; Kerwood, D. J.; Wu, L.; Li, J.; Lombardi, R.; Freedman, T. B.; Luk, Y.-Y. *J. Org. Chem.* **2009**, *74*, 7023.
(52) Narasimhan, S. K.; Lu, X.; Luk, Y. Y. *Chirality* **2008**, *20*, 878.

(53) Lofthagen, M.; Siegel, J. S. *J. Org. Chem.* **1995**, *60*, 2885.

(54) Lofthagen, M.; Vernonclark, R.; Baldridge, K. K.; Siegel, J. S. *J. Org. Chem.* **1992**, *57*, 61.

(55) Lofthagen, M.; Chadha, R.; Siegel, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 8785.

(56) Kubitschke, J.; Nather, C.; Herges, R. *Eur. J. Org. Chem.* **2010**, 5041.

(57) Kuhn, S.; Baisch, B.; Jung, U.; Johannsen, T.; Kubitschke, J.; Herges, R.; Magnussen, O. *Phys. Chem. Chem. Phys.* **2010**, *12*, 4481.

(58) Baisch, B.; Raffa, D.; Jung, U.; Magnussen, O. M.; Nicolas, C.; Lacour, J.; Kubitschke, J.; Herges, R. *J. Am. Chem. Soc.* **2009**, *131*, 442.

(59) Kuhn, S.; Jung, U.; Ulrich, S.; Herges, R.; Magnussen, O. *Chem. Commun.* **2011**, *47*, 8880.

(60) Chen, Q.; Luo, M.; Hammershøj, P.; Zhou, D.; Han, Y.; Laursen, B. W.; Yan, C.-G.; Han, B.-H. *J. Am. Chem. Soc.* **2012**, *134*, 6084.

(61) Chen, Q.; Wang, J.-X.; Wang, Q.; Bian, N.; Zhou, D.; Li, Z.-H.; Yan, C.-G.; Han, B.-H. *Macromolecules* **2011**, *44*, 7987.

(62) Zhao, Y.-C.; Zhou, D.; Chen, Q.; Zhang, X.-J.; Bian, N.; Qi, A.-D.; Han, B.-H. *Macromolecules* **2011**, *44*, 6382.

(63) Chen, Q.; Luo, M.; Wang, T.; Wang, J.-X.; Zhou, D.; Han, Y.; Yan, C.-G.; Zhang, C.-S.; Han, B.-H. *Macromolecules* **2011**, *44*, 5573.

(64) Chen, Q.; Wang, J.-X.; Yang, F.; Zhou, D.; Bian, N.; Zhang, X.-J.; Yan, C.-G.; Han, B.-H. *J. Mater. Chem.* **2011**, *21*, 13554.

(65) Krebs, F. C. *Tetrahedron Lett.* **2003**, *44*, 17.

(66) Krebs, F. C.; Spanggaard, H.; Rozlosnik, N.; Larsen, N. B.; Jørgensen, M. *Langmuir* **2003**, *19*, 7873.

(67) Laleu, B.; Herse, C.; Laursen, B. W.; Bernardinelli, G.; Lacour, J. *J. Org. Chem.* **2003**, *68*, 6304.

(68) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, 1991.

(69) Lewis, G. N.; Calvin, M. *Chem. Rev.* **1939**, *25*, 273.

(70) Laursen, B. W. Ph.D. Thesis, Risø National Laboratory, 2001.