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Highly-Substituted Δ^3-1,2,3-Triazolines: a New Class of Solid State Emitters with Electrofluorochromic Behavior

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Abstract: Highly-substituted Δ^3-1,2,3-triazolines can be prepared by reaction of triarylvinyl Grignard reagents with functionalized organic azides. The heterocycles are fluorescent in solid state, and – depending on the substituents – they can display aggregation-induced emission. Upon oxidation, the triazolines form stable radical cations with altered photophysical properties. Therefore, they represent rare examples of solid state emitters with intrinsic electrofluorochromic behavior.

The attachment of multiple phenyl groups to small heterocycles can lead to molecules with interesting photophysical properties.[1] A well-known example is hexaphenylsilole (HPS, Figure 1a).[2] This compound is strongly luminescent in the solid state. Efficient solid state emission is unusual, because aromatic luminophores typically show aggregation-caused quenching (ACQ). HPS is weakly luminescent in solution, and studying the properties of HPS kick-started the now burgeoning field of aggregation-induced emission (AIE).[3]

Following the studies on HPS, numerous other polyphenylated heterocycles were synthesized, and some of them were found be good solid state emitters as well.[1,3] Examples include luminophores based on thiophene dioxides,[4] phosphole oxides,[5] pyrroles,[6] pyrazines[7] and others (Figure 1b–e).[1] It is assumed that the propeller-shaped geometry of these molecules helps preventing π-π stacking interactions in the solid state, and thus self-quenching.[1,3]

Below, we describe a new class of solid state emitters containing an unusual Δ^3-1,2,3-triazoline heterocycle (Figure 1f). A unique feature of these compounds is the possibility to convert them into stable radical cations, which are non-emissive. Therefore, they represent rare examples of electrofluorochromic compounds with intrinsic redox activity.[8,9]

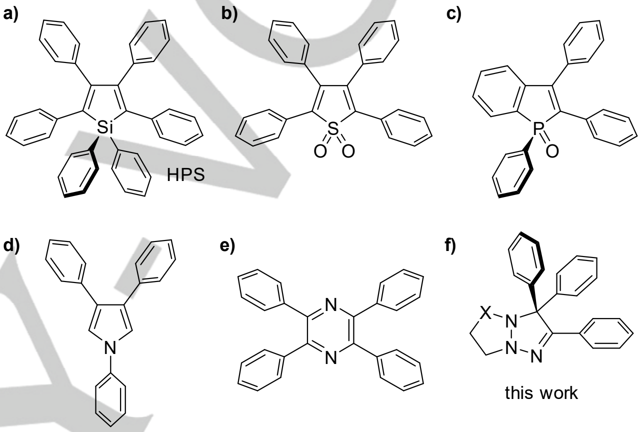
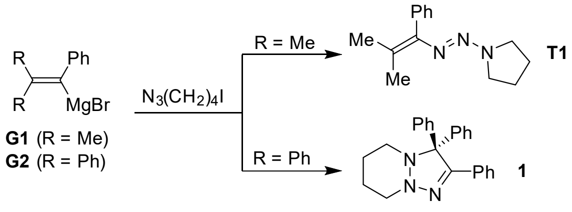


Figure 1. Examples of polyphenylated heterocycles, which are luminescent in the solid state.

The fluorophores described in this work were discovered by accident. We have recently studied the synthesis of triazenes from organomagnesium reagents and functionalized organic azides.[10] The reaction between **G1** and 1-azido-4-iodobutane lead to the formation of triazene **T1** in high yield (Scheme 1). Surprisingly, when the Grignard reagent **G2** was used instead of **G1**, we observed the formation of the triazoline **1** instead of a vinyl triazene. We assume that the electron-withdrawing effect of the two additional phenyl groups in **G2** is responsible for the different reactivity (see SI for mechanistic proposal).



Scheme 1. Substrate-dependent formation of a triazene (**T1**) or a triazoline (**1**).

In the literature, there are only few scattered reports about 2,5-dihydro-1H-1,2,3-triazoles, or Δ^3-1,2,3-triazolines,[11,12] and the photophysical and electrochemical properties of these compounds are largely unexplored. We therefore decided to investigate the scope of the new synthetic procedure.

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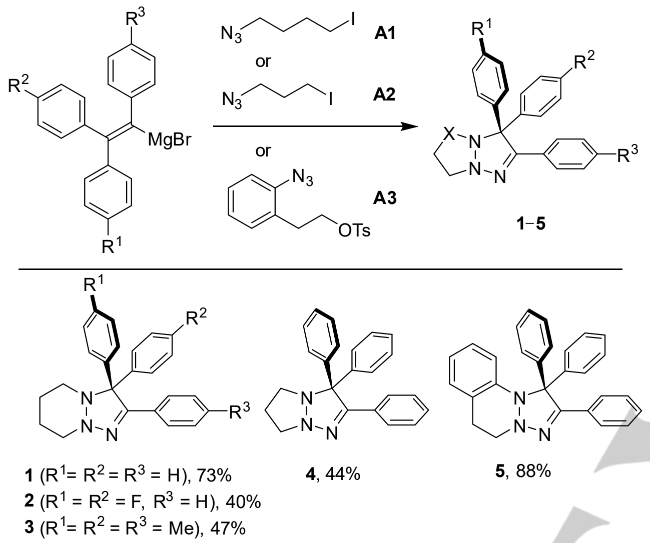
Vinyl Grignard reagents with *p*-tolyl or *p*-fluorophenyl groups gave the corresponding triazolines **2** and **3**, albeit in lower isolated yield of 40 and 47%, respectively (Scheme 2). The azide reagent **A2** with a shorter C_3H_6 linker gave triazoline **4** in 44% yield. Using an azide with a longer C_5H_{10} linker, on the other hand, gave rise to a complex mixture of products. Interestingly, the aromatic azide **A3** is well suited for this type of reaction, and coupling with **G2** gave the corresponding triazoline **5** in 88% yield. It is worth noting that the presence of three aryl substituents on the vinyl Grignard reagent seems to be crucial, because other vinyl magnesium compounds gave triazenes instead of triazolines.[10]



1 ($R^1 = R^2 = R^3$ = H), 73%
2 ($R^1 = R^2$ = F, R^3 = H), 40%
3 ($R^1 = R^2 = R^3$ = Me), 47%
4, 44%
5, 88%

Scheme 2. Synthesis of the triazolines **1**–**5**. Reaction conditions: Grignard reagent (1.0 equiv.), azide (1.2–1.5 equiv.), THF (0.2 M), 50 °C, 4 h, then aqueous workup.

The new compounds **1**–**5** have been characterized by NMR spectroscopy, high-resolution mass spectrometry (HRMS), UV-Vis and fluorescence spectroscopy, cyclic voltammetry, and – in the case of **1**, **4**, and **5** – by single-crystal X-ray crystallography.[13]

The electrochemical investigations (CH_2Cl_2, 0.1 M $TBAPF_6$) revealed that all triazolines undergo a reversible one-electron oxidation at potentials between $E_{1/2}$ = 0.02 and 0.16 V versus the Fc/Fc^+ redox couple (Figure 2a and Table S6). The cyclic voltammetry data suggested that it should be possible to oxidize the triazolines with mild oxidants. Indeed, we were able to convert **1** into the radical cation [**1**]$^{\bullet+}$ by reaction with $Ag(NTf_2)$ in THF. The triazolinium salt **1(NTf₂)** was isolated in 80% yield as a dark red crystalline solid. The salt was found to be stable when stored under nitrogen.[14,15] In THF solution in the presence of oxygen, **1(NTf₂)** slowly decomposed with a half-life around 24 h.

Electron paramagnetic resonance (EPR) studies revealed the presence of a nitrogen-centered radical of **1(NTf₂)** (Figure 2c; for a simulation see the SI). The high stability of **1(NTf₂)** allowed us to perform a crystallographic analysis, and a graphic representation of the radical cation [**1**]$^{\bullet+}$ is depicted in Figure 2d. Due to the trigonal planar geometry of the central N-atom, the heterocyclic ring in [**1**]$^{\bullet+}$ is nearly planar. In contrast, the neutral triazoline **1** shows an envelope-like structure for the heterocyclic ring system (SI, Figure S8.1).

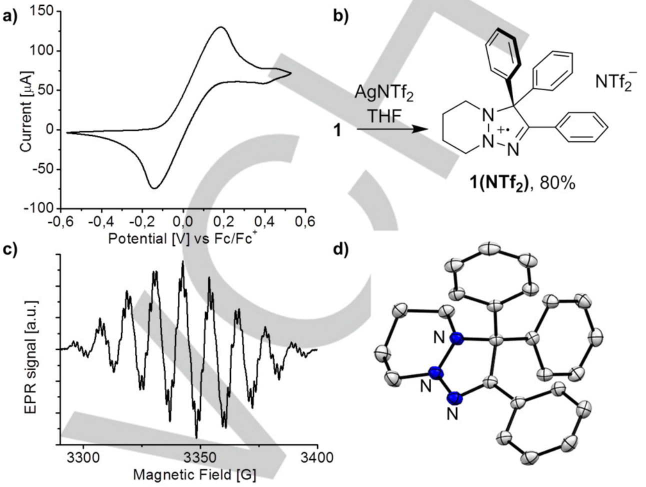


Figure 2. Cyclic voltammogram of **1** (a), synthesis of **1(NTf₂)** (b), EPR spectrum of **1(NTf₂)** in THF (c), and structure of [**1**]$^{\bullet+}$ in the solid state (NTf_2^- and hydrogen atoms are omitted) with thermal ellipsoids at 50% probability (d).

For comparison, we have also converted triazoline **5** into the radical cation [**5**]$^{\bullet+}$ by reaction with $Ag(NTf_2)$. The resulting salt **5(NTf₂)** was characterized by X-ray crystallography and EPR spectroscopy (for details, see SI).

The electronic structure of the radical cations [**1**]$^{\bullet+}$ and [**5**]$^{\bullet+}$ was examined at the ωB97X-D3/def2-TZVP level, including implicit solvation in THF (SMD model). The spin density of both radical cations is centered on the triazoline ring with the highest amplitudes on the N1, N2, N3 and C4 atoms.

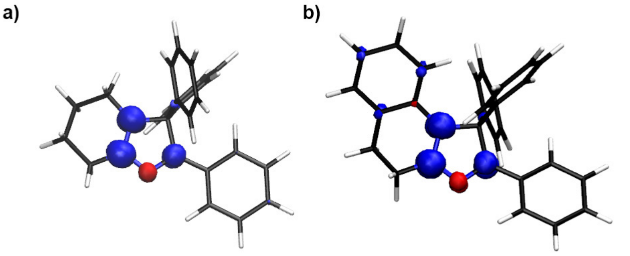


Figure 3. Spin density (blue: positive spin density; red: negative spin density; isovalue: 0.01 $e^-/Bohr^3$) of [**1**]$^{\bullet+}$ (a) and [**5**]$^{\bullet+}$ (b). Computations are at the ωB97X-D3/def2-TZVP level.

Next, we investigated the photophysical properties of the new heterocyclic compounds. First tests revealed minor differences between the structurally related compounds **1**, **2**, and **3**. For more detailed investigations, we thus focused on the triazolines **1**, **4**, and **5**. All three compounds were found to be fluorescent in solid state with comparable quantum yields of 3.0, 6.1 and 2.6%, and decay times between 0.6 and 2.0 ns (Table 1).

Pronounced differences between the triazolines were observed in solution (THF). The best solid state emitter, compound **4**, was non-emissive, whereas the quantum yield for **1** in solution was higher than in the solid state. The contrasting behavior between **1** and **4** was surprising, given that the structures differ by only one CH_2 group. A close inspection of the geometries of **1** and **4** in the crystal revealed a possible explanation. For triazoline **4**, the phenyl ring at C4 position is further apart from the two geminal phenyl groups at C5 position, allowing for a more independent rotation (for details, see the SI). The rotational freedom of the phenyl group in **4** can lead to increased non-radiate decay.[3]

Table 1. Photophysical properties of the triazolines **1**, **4** and **5**.^{a}

#	λ_{em} [nm] in THF (solid)	Φ [%] in THF (solid)	τ [ns] (solid)^b
1	510 (512)	5.0 (3.0)	0.7 (94%), 2.0 (6%)^c
4	NE (489)	NE (6.1)	1.0
5	500 (492)	0.2 (2.6)	0.6 (50%), 2.0 (50%)^c

^{a} λ_{ex} = 340 nm. The solid state spectra were acquired using an integrating sphere. NE = non-emissive. ^{b} λ_{ex} = 405 nm. ^{c} the best fit obtained for a biexponential decay.

Triazoline **1** displays positive solvatochromism with a bathochromic shift of 54 nm when going from apolar hexane (λ_{max} = 484 nm) to polar MeCN (λ_{max} = 538 nm). A Stokes shift of 194 nm is observed in acetonitrile (10859 cm^{-1}), which is a very large value for an organic fluorophore.[16]

The radical cations $[\mathbf{1}]^{\bullet+}$ and $[\mathbf{5}]^{\bullet+}$ and their precursors **1** and **5** show markedly different optical properties. Solutions of **1** and **5** in THF are colorless and yellow, whereas **1(NTf₂)** and **5(NTf₂)** absorb in the visible range, and solutions appear orange/red and green respectively (Figure 4).[17]

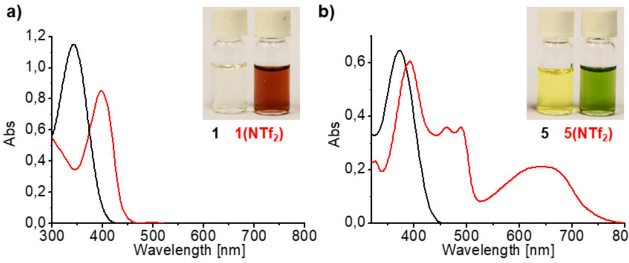


Figure 4. Absorption spectra of **1**, **1(NTf₂)** (a) and **5**, **5(NTf₂)** (b) in THF (ca. 0.1 mM). Insets: photos of **1**, **1(NTf₂)** (left) and **5**, **5(NTf₂)** (right) solutions.

The computational analysis of the absorption properties of **1** and **5** shows that the spectrum in the experimental energy range is characterized by an unique bright state (an essentially pure HOMO→LUMO transition) for the neutral species, whereas multiple bright states of mixed character dominate the spectrum of the radical cations (for details, see SI). In contrast to molecule $[\mathbf{1}]^{\bullet+}$, where the density on the cyclohexane ring remains unperturbed upon excitation, the electronic transitions of $[\mathbf{5}]^{\bullet+}$ are characterized by a depletion of the π-electron density on the additional benzene ring. The contribution of the benzene electron density to the excitation modify decisively the optical properties of $[\mathbf{5}]^{\bullet+}$ with respect to $[\mathbf{1}]^{\bullet+}$.

The fluorescence of **1** and **5** is nearly fully quenched upon oxidation. Consequently, triazolines **1** and **5** classify as electrofluorochromic compounds. It is worth noting that most electrofluorochromic compounds are dyads comprised of a redox-active group, a spacer, and a fluorophore.[8] Fluorophores with intrinsic redox-activity are much less common,[8,9] and solid state electrofluorochromic emitters are scarce.[9e,18]

In conclusion, we have shown that highly-substituted Δ^3-1,2,3-triazolines can be prepared by reaction between triarylvinyl Grignard reagents and organic azides. The new triazolines are solid state emitters with a unique characteristic: it is possible to convert them at low potential into non-fluorescent radical cations. The radicals display good stability, allowing for a structural and spectroscopic analysis. The high stability of the two redox states suggests that these compounds could be used for preparing novel electrofluorochromic devices. Furthermore, compounds which are both redox-active and luminescent are of interest for applications in imaging using a combined scanning electrochemical and fluorescence microscope.[19]

Acknowledgements

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Keywords: electrofluorochromism • triazolines • fluorescence • radicals • aggregation-induced emission

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[13] Crystallographic data have been deposited to the CCDC and correspond to the following codes: **1** (1895508), **4** (1895510), **5** (1895509), **1(NTf$_2$)** (1895511), **1(NTf$_2$)-2** (1900662) and **5(NTf$_2$)** (1895512). Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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COMMUNICATION

Abdusalom A. Suleymanov, Albert Ruggi, Ophélie Marie Planes, Anne-Sophie Chauvin, Rosario Scopelliti, Farzaneh Fadaei Tirani, Andrzej Sienkiewicz, Alberto Fabrizio, Clémence Corminboeuf, and Kay Severin

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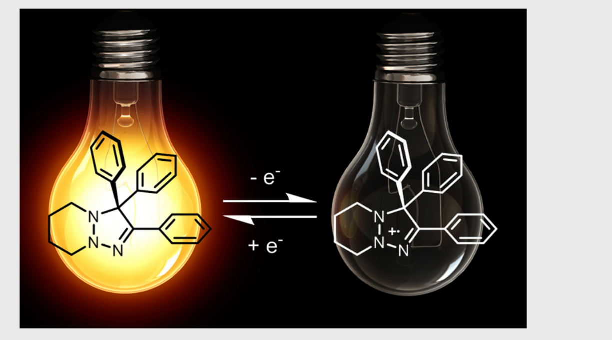

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