

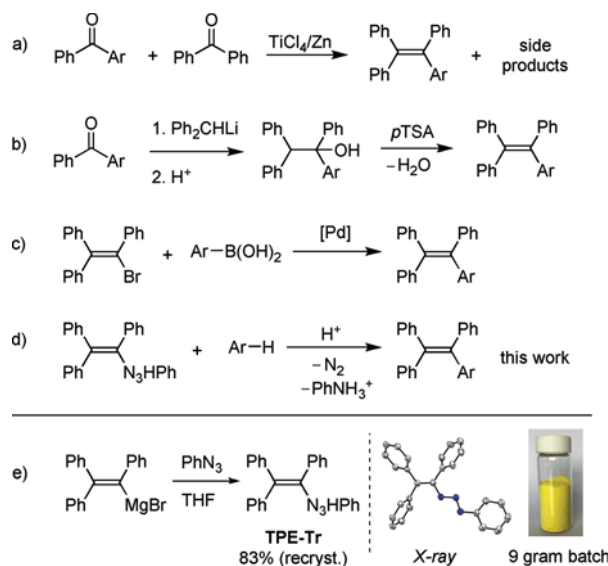
Synthesis of Tetraarylethene Luminogens by C–H Vinylation of Aromatic Compounds with Triazenes

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Abstract: Tetraarylethenes are obtained by acid-induced coupling of vinyl triazenes with aromatic compounds. This new C–H activation route for the synthesis of aggregation-induced emission luminogens is simple, fast, and versatile. It allows the direct grafting of triarylethenyl groups onto a variety of aromatic compounds, including heterocycles, supramolecular hosts, biologically relevant molecules, and commercial polymers.

Compounds showing aggregation-induced emission (AIE) properties have found numerous applications in analytical chemistry, imaging, materials sciences, and biology.^[1] Tetraarylethenes are particularly popular in this context.^[2] These AIE luminogens are easy to functionalize, and the optical properties can be modulated by steric and electronic effects.

Symmetric tetraarylethenes are conveniently obtained by McMurry couplings.^[3] However, unsymmetrical tetraarylethenes with different aryl groups are needed for many applications. Unsymmetrical tetraarylethenes such as aryltriphenylethenes can also be obtained by McMurry couplings of benzophenone derivatives (Scheme 1a), but competing homocoupling reactions compromise the yield and require chromatographic purification.^[4] The most popular route for the synthesis of unsymmetrical aryltriphenylethenes is depicted in Scheme 1b. Coupling of benzophenone derivatives with lithiated diphenylmethane gives tertiary alcohols, which can be dehydrated to give the desired olefins (Scheme 1b). This method was developed by Rathore and co-workers,^[5] and it is widely used for the preparation of AIE luminogens. Its substrate scope is limited by the utilization of a highly reactive organolithium reagent. Functionalized aryltriphenylethenes can be obtained by Pd-catalyzed cross-coupling reactions between triphenylethenyl bromide and arylboronic acids (Scheme 1c). There are several other methods for the synthesis of asymmetric and symmetric tetraarylethenes,^[6] but these procedures are rarely used in the context of AIE studies.



Scheme 1. a–d) Different routes for the synthesis of aryltriphenylethenes. e) Synthesis of triazene TPE-Tr.

We show that aryltriphenylethenes and other unsymmetrical tetraarylethenes are accessible by acid-induced vinylation of aromatic and heteroaromatic compounds with triazenes (Scheme 1d). This new C–H activation route is facile and versatile. Importantly, it can be used for the direct attachment of AIE luminogens to supramolecular hosts, to biologically relevant molecules, and to polymers.

Recently, we started to explore the chemistry of alkynyl and vinyl triazenes.^[7] During these investigations, we found that cyclobutenyl triazenes can be coupled under acidic conditions to arenes, such as mesitylene and thiophene.^[7e] The C–C coupling reactions are triggered by acid-induced cleavage of the triazene function. This finding prompted us to explore if vinyl triazenes can be used more widely for the electrophilic vinylation of aromatic compounds. In particular, we were interested in seeing if we could use triazenes for the synthesis of tetraarylethenes.

The triphenylethenyl triazene **TPE-Tr** is easily accessible by reaction of triphenylethenyl magnesium bromide with phenyl azide (Scheme 1e).^[8,9] In 1967, Jones and Miller reported that the addition of oxo acids (HOR) to **TPE-Tr** results in substitution of the triazene group by OR groups.^[8] These results demonstrated that **TPE-Tr** can be used as an electrophilic vinylation reagent, but there were only few subsequent studies, all of which focused on reactions with oxo acids.^[10]

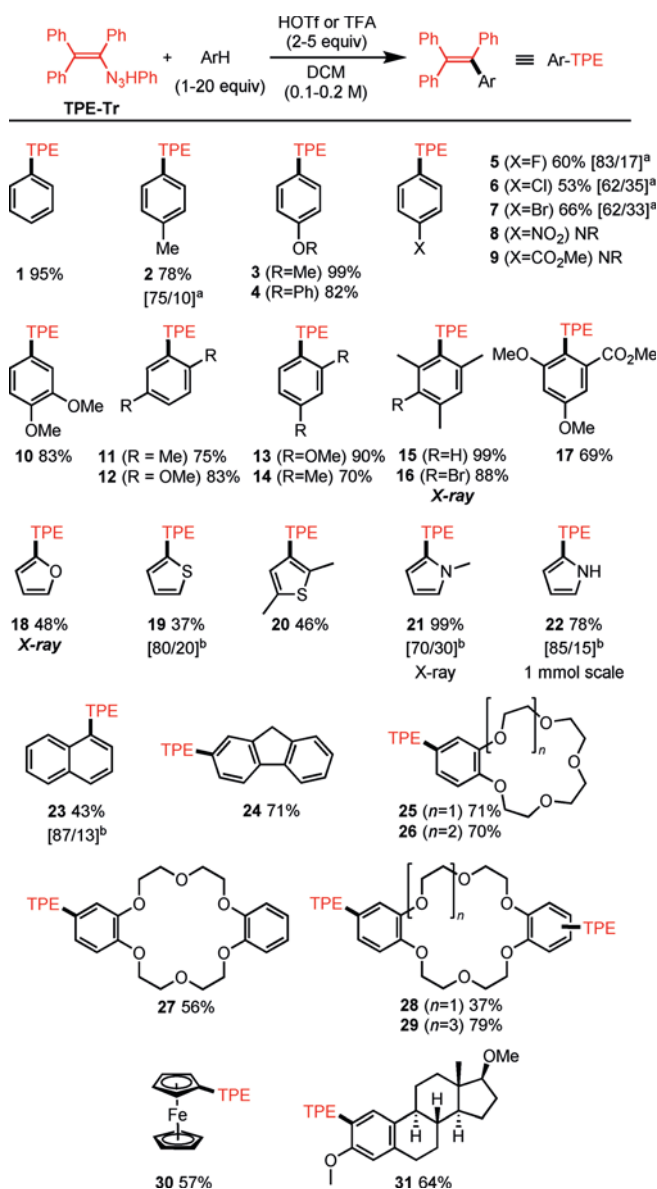
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To test if **TPE-Tr** was suited for the vinylation of aromatic compounds, we investigated the reaction of **TPE-Tr** with benzene, which was used as solvent. Different Brønsted and Lewis acids were used to induce cleavage of the triazene function (for details, see the Supporting Information). Utilization of triflic acid (HOTf, 5 equiv) gave tetraphenylethene (**1**) in almost quantitative yield. Clean and fast (<10 min) formation of **1** was also observed when the reaction was performed in DCM (0.2M) with 20 equivalents of benzene.

For reactions of **TPE-Tr** with oxoacids, it was proposed that that acid-induced cleavage of the triazene gives a vinyl cation, which then reacts with the oxo acid.^[8,10] An analogous mechanism is conceivable for the C–H vinylation of benzene.^[11] It is worth noting that the triazene function is apparently cleaved in a highly regioselective fashion, because we were only able to detect vinylation and not phenylation products (or compounds derived from PhN₂⁺).

Next, we investigated the scope of the reaction using different aromatic compounds (Scheme 2). Monosubstituted benzenes gave the desired tetraarylethenes **2–7** in yields between 53 and 99%. Reactions with anisole and diphenyl ether afforded the products **3** and **4**, respectively, in the form of a single isomer, whereas mixtures of *para* and *ortho* isomers were observed for the other substrates. It is worth noting that halobenzenes are competent coupling partners, even though the yields are slightly lower (**5–7**). Unsuccessful coupling reactions were observed for electron-deficient arenes such as nitrobenzene and methyl benzoate. Di-, tri-, and tetrasubstituted arenes gave the corresponding products as single isomers in high yields (**10–16**). Even though methyl benzoate was not a suitable reaction partner, 3,5-dimethoxy-substituted methyl benzoate could be converted into the corresponding product **17** in good yield.

Heterocyclic AIE emitters have found many applications because of their unique electronic and structural properties.^[12] The coupling of **TPE-Tr** with standard five-membered-ring heterocycles using HOTf as a cleavage agent gave complex mixtures of products. However, utilization of the weaker trifluoroacetic acid (TFA) instead of HOTf allowed the preparation of the desired TPE derivatives **18–22** (Scheme 2). For the reactions with furan, thiophene, and dimethylthiophene, triphenylethenyl trifluoroacetate was observed as a side product, compromising the yields of the products **18–20**. The compound **18** was additionally characterized by single-crystal X-ray diffraction. Electron-rich *N*-methyl pyrrole gave the TPE derivative **21** in quantitative yield as a mixture of positional isomers ($\alpha/\beta = 70:30$). To our surprise, unprotected pyrrole gave also the desired C–C coupling product, **22**, which was synthesized on a 1 mmol scale and isolated in 78% yield with a high α/β ratio. Notably, **22** is described in the literature as a precursor for the synthesis of AIE-active BODIPY fluorophores with near-infrared emission.^[13] The previous synthesis for **22** is based on a two-step procedure involving a Pd-catalyzed cross-coupling between triphenylethenyl bromide and *N*-Boc-pyrrole-2-boronic acid, followed by Boc removal, whereas our procedure allows direct vinylation of free pyrrole without a transition-metal catalyst.



Scheme 2. Synthesis of aryltriphenylethenes by coupling of **TPE-Tr** with different arenes. [a] *para/ortho* isomers. [b] α/β isomers.

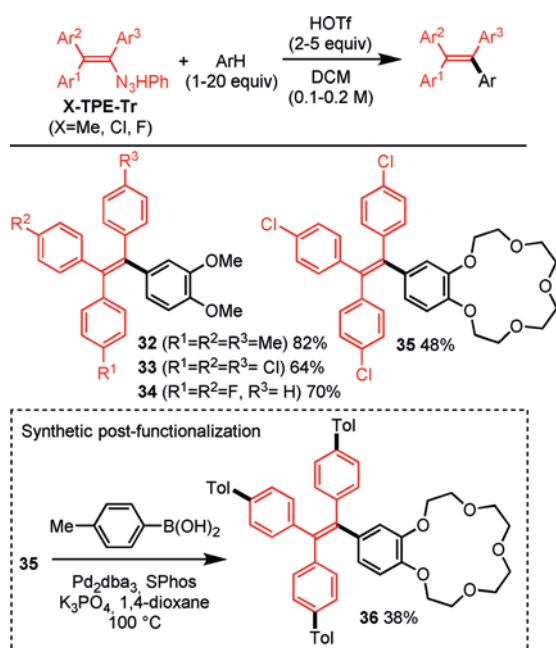
The replacement of one or more phenyl groups in tetraphenylethene by polycyclic aromatic hydrocarbons is of interest because the resulting compounds can display superior electroluminescence properties.^[14] Our new method is suited to prepare such compounds, as evidenced by the synthesis of the naphthalene derivative **23** and the fluorene-containing **24** (Scheme 2). The latter was isolated as a single regioisomer.

The functionalization of supramolecular receptors with AIE-active groups is attractive because the resulting conjugates can potentially be used for the optical detection of guest molecules.^[15] An advantage of our new synthetic methodology is the possibility to convert existing receptors in one step into AIE luminophores, given that the receptors contain appropriate aromatic groups. To demonstrate this point, we performed coupling reactions between **TPE-Tr** and five commercially available benzo-crown ethers (Scheme 2). The corresponding TPE derivatives **25–27** were obtained in

moderate to good yields as single isomers (selective coupling at the *meta* position). Twofold coupling reactions are also possible, as evidenced by the syntheses of **28** and **29**. Ferrocene was found to be compatible with our vinylation protocol, and triphenylethenylferrocene (**30**) was isolated in 57% yield. The compound **30** is nonfluorescent in the solid state, presumably because the redox-active ferrocenyl groups acts as an intramolecular quencher.

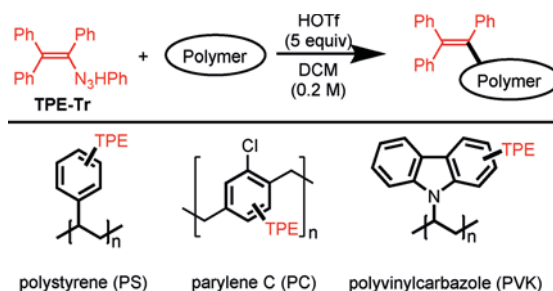
Conjugates between biomolecules and AIE luminophores are of interest for medicinal and analytical applications.^[1,16] Following our procedure, we were able to install the TPE moiety on a β -estradiol derivative (Scheme 2). The corresponding product, **31**, was isolated in good yield as a single isomer.

The scope of the coupling reaction was extended to different aryl-substituted vinyl triazene reagents (**X-TPE-Tr**) using 1,2-dimethoxybenzene as the coupling partner (**32–34**, Scheme 3). To demonstrate that our approach allows building complex TPE derivatives in a few steps, we synthesized the chlorinated benzo-crown ether **35**, which was further functionalized using a Suzuki cross-coupling reaction with tolyl boronic acid to give the compound **36**.



Scheme 3. Scope of vinyl triazenes used for the synthesis of the tetraarylethenes **32–36** and post-functionalization reactions.

Finally, we applied our vinylation procedure to the functionalization of polymers.^[17] Polymers containing AIE groups have been investigated extensively over the last years, and numerous applications have emerged.^[18] Typically, multi-step syntheses are required to prepare polymer-AIEgen conjugates. Our method allows the direct grafting of TPE groups to polymers containing arenes (side or main chain; Scheme 4). When triflic acid was added to a suspension of crosslinked polystyrene beads (1% divinylbenzene) in a solution of **TPE-Tr** (10 mol%) in DCM, an instantaneous reaction was observed (evidenced by gas evolution). Filtra-



Scheme 4. Covalent grafting of TPE groups to commercial polymers.

tion and extensive washing of the polymer gave a highly fluorescent **TPE-PS** conjugate. The latter showed a fluorescence quantum yield (QY) of 24% in the solid state with an emission maximum at 500 nm ($\lambda_{\text{ex}} = 320$ nm). The QY is comparable to that of tetraphenylethene (QY = 18%, $\lambda_{\text{em}} = 460$ nm, $\lambda_{\text{ex}} = 320$ nm) and clearly different from the starting crosslinked polystyrene (QY = 10%, $\lambda_{\text{em}} = 360$ nm, $\lambda_{\text{ex}} = 320$ nm). Furthermore, we modified parylene C, which is used as protective coating for microelectronic and medical devices. A film of parylene C was dipped in a DCM solution of **TPE-Tr** (0.2M), followed by addition of TfOH. The resulting TPE-functionalized parylene C film (**TPE-PC**) showed strong blue fluorescence, whereas the starting polymer is almost nonemissive under UV-365 nm.^[19] Polyvinylcarbazole (PVK) has numerous applications in materials science as a conducting polymer.^[20] In a similar fashion as described above, we transformed commercially available PVK into **TPE-PVK**, which showed strong fluorescence in the solid state.

The swelling behavior of crosslinked polystyrene beads is strongly dependent on the nature of the solvent. We hypothesized that the degree of swelling would affect the conformational freedom of the TPE groups, and thus the fluorescence intensity. Indeed, suspensions of **TPE-PS** in different organic solvents showed vastly different emission intensities (Figure 1). Nonswelling solvents such as methanol or *n*-hexane gave rise to a bright emission, whereas highly swelling solvents such as toluene gave poor emission. **TPE-PS** therefore allows easy optical differentiation of solvents.

To conclude, we have developed a simple, fast, and versatile protocol for the preparation of asymmetric tetraarylethene luminogens. The new methodology relies on the acid-induced conversion of vinyl triazenes into highly electrophilic vinylation reagents. A key feature of our procedure is

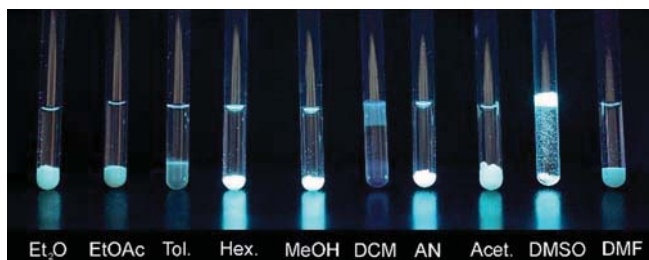


Figure 1. The polymer **TPE-PS** in different organic solvents under UV 366 nm (20 mg of polymer in 0.5 mL of solvent).

the possibility to use plain aromatic or heteroaromatic compounds as coupling partners. It is thus possible to convert nonfunctionalized aromatic compounds in a single step into solid-state emitters. For example, we have been able to attach TPE groups to commercially available crown ethers and polymers. Further studies towards new applications of this new coupling procedure are ongoing in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aggregation · tetraralyethenes · fluorescence · synthetic methods · vinylation

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