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Fluorinated Tetraarylethenes: Universal Tags for the Synthesis of Solid State Luminogens

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Abstract: The aggregation-induced emission properties of tetraarylethenes (TAEs) have led to numerous applications in chemistry, biology, and materials science. Herein, we describe two fluorinated tetraarylethenes, which can be employed as universal tags for the synthesis of solid state luminogens. The tags are accessible in one or two steps from commercially available starting materials. Facile coupling reactions with ubiquitous substrates such as thiols, alcohols, amines, phosphines, aldehydes, and enamines allow preparing a wide range of TAE conjugates, including tagged amino acids, peptides, carbohydrates, steroids, and commercial polymers.

Tetraarylethenes (TAEs) are solid state luminogens with aggregation-induced emission (AIE) properties.[1] TAE conjugates have found applications in diverse areas such as chemical sensing,[2] OLEDs,[3] bioimaging,[4] and cancer treatment[5] (Figure 1a). Various strategies to build TAEs have been established.[6] They can be synthesized *de novo* by the McMurry coupling of diarylketones,[7] diarylmethyl lithium–benzophenone coupling,[8] Suzuki cross-coupling,[9] and other methods.[10] The abovementioned reactions allow preparing functionalized TAEs, which can be used for further conjugation with molecules of interest using condensation, addition, and cross-coupling reactions.[11,12] These methods have limitations with regard to functional group compatibility and reaction conditions (e.g. high temperature, use of metal catalysts, activating agents). More versatile 'click reactions' have also been employed in this context, such as Cu-catalyzed azide-alkyne cycloadditions,[13] maleimide-thiol couplings,[14] and reactions of amines, thiols, or alcohols with TAEs containing an ynone functionality.[15] Drawbacks of these 'clickable' TAE tags are the required synthetic efforts (typically 3–4 steps from commercial chemicals), the lack of universality, the need for pre-functionalized coupling partners (azides/alkynes for triazole-based conjugates), or the low selectivity towards biologically relevant functional groups (ynone-based tags).[15] To overcome some of these issues, we decided to develop simple and universal TAE tags for efficient conjugation reactions.

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In the design of our tags, we were inspired by applications of perfluoroarylated compounds in chemical biology and materials science.[16] Nucleophilic substitution reactions with pentafluorophenyl compounds (RC_6F_5) occur selectively at *para* position under mild conditions.[17] The reactivity towards various nucleophiles can be tuned by the choice of base, solvent, and temperature.[18] Perfluoroaryl azides ($RC_6F_4N_3$), on the other hand, can form stable Staudinger reaction adducts with phosphines,[19] and they readily react with aldehydes[20] and enamines.[21] Reactive singlet nitrenes generated by N_2 elimination from perfluoroaryl azides can be used for C–H functionalization of inert polyolefins.[22] Below, we describe the synthesis of two TAE tags containing a C_6F_5 and a $C_6F_4N_3$ group. These easy-to-access compounds can be used for selective conjugation reactions with a vast variety of coupling partners, including amino acids, peptides, carbohydrates, and commercial polymers (Figure 1b).

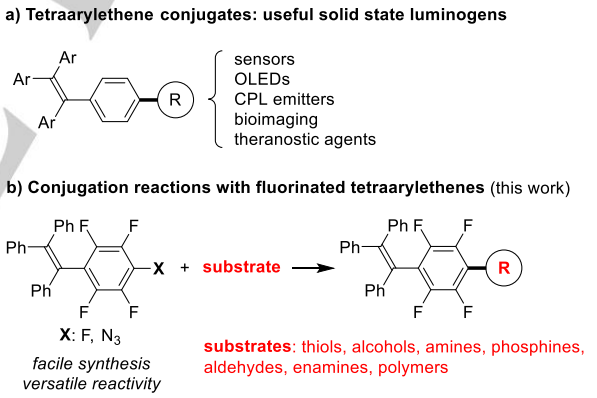


Figure 1. General structure of tetraarylethene conjugates and selected applications (**a**), and the fluorinated TAE tags described in this work (**b**).

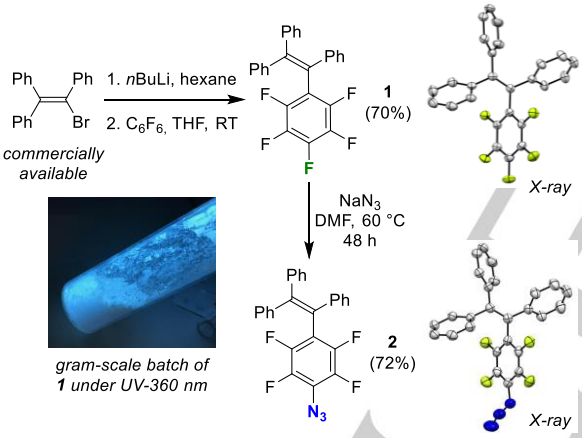
Our previous work on the synthesis of tetraarylethenes focused on the utilization of triphenylvinyl triazenes as electrophilic vinylation agents.[23] For the synthesis of tag **1**, we have employed an electronically inversed reaction: the coupling of a triphenylvinyl carbanion with hexafluorobenzene (Scheme 1). Lithiation of commercially available bromotriphenylethene with *n*BuLi in hexane at room temperature resulted in the formation of a bright yellow precipitate, which was used directly for the reaction with hexafluorobenzene. This simple one-pot procedure gave the coupling product **1** in 70% yield after regular workup. The reaction could be scaled up to 10 grams without compromising the yield. While our work was in progress, an alternative synthesis of **1** was reported by Miljanić and co-workers.[24] They employed 1,2-dibromo-1,2-diphenylethene as

starting material. Cu-catalyzed coupling with C_6F_5H followed by Pd-catalyzed coupling with $PhSnBu_3$ gave **1** in only 42% overall yield.

Compound **1** is a stable colorless solid. It shows bright blue fluorescence in the solid state with an emission quantum yield of 20%. This value is comparable to what has been reported for other tetraarylethenes.[23] Compound **1** demonstrates aggregation-induced emission (AIE) in different water/organic solvent mixtures (solvents: DMF, DMA, EtOH, $MeOCH_2CH_2OH$). When **1** was dissolved in THF, no AIE was observed when an excess of water was added.[24] The special role of THF for the AIE behavior of tetrarylethenes was also noted by Bai and co-workers.[25]

In addition to a standard characterization by NMR spectroscopy and high resolution mass spectrometry (HRMS), the solid state structure of **1** was determined by single-crystal X-ray diffraction (XRD) (Scheme 1, top right).

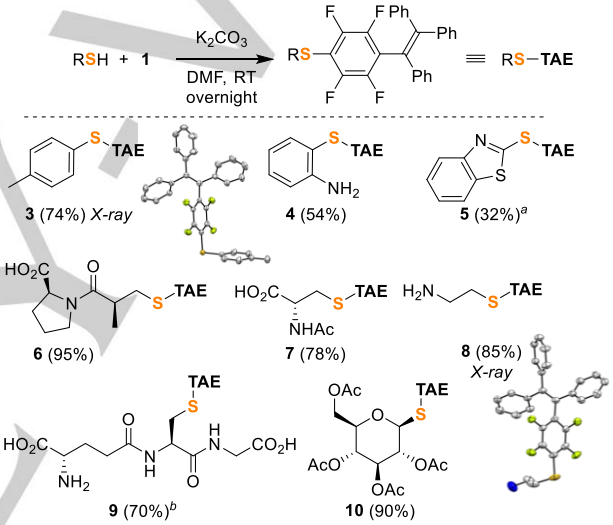
Tag **2** was obtained in 72% isolated yield by reaction of **1** with sodium azide in DMF (Scheme 1). As in the case of **1**, a gram scale synthesis can be accomplished without problems. Compound **2** was also characterized by NMR spectroscopy, HRMS, and single crystal XRD. It is worth noting that **2** is not luminescent in the solid state (in contrast to its reaction products; see below).



Scheme 1. Synthesis of the fluorinated tetraarylethenes **1** and **2**. The structures are based on crystallographic analyses. The thermal ellipsoids are at 50% probability and hydrogen atoms are not shown for clarity.

We started reactivity studies by investigating nucleophilic substitution reactions of **1** with thiols. When **1** was combined with 4-methylbenzenethiol in DMF in the presence of K_2CO_3, the coupling product **3** was formed in good yield (74%) after stirring the mixture overnight at room temperature (Scheme 2). Under similar conditions, thioether **4** was obtained from 2-aminothiophenol. The reaction was found to be highly chemoselective, and coupling with the NH_2 group was not observed. The heterocyclic 2-mercaptobenzothiazole did not react with **1** at room temperature. However, by increasing the temperature to 100 °C, we were able to obtain the C–S coupling product **5** in 32% yield.

Next, we examined reactions with aliphatic thiols. Captopril, a drug used for hypertension treatment, readily reacted with **1**, providing thioether **6** in almost quantitative yield. N-Acetyl L-cysteine gave cleanly the substitution product **7**. The reaction with cysteamine occurred selectively at SH position, leaving the NH_2 group intact. The corresponding thioether **8** was isolated in 85% yield, and it could be employed for further functionalizations through the NH_2 handle. We have been able to tag the natural tripeptide glutathione in a highly chemoselective fashion, giving the C–S coupling product **9** in 70% yield after purification by HPLC (for details see SI). Protected thioglucose showed very efficient coupling and afforded **10** in 90% yield. The thioethers **3**–**10** were all found to be luminescent in the solid state, with emission maxima at 450–500 nm, and photoluminescence quantum yields ranging from 20% (for **3**) to 50% (for **6**) (for details, see the Supporting Information).

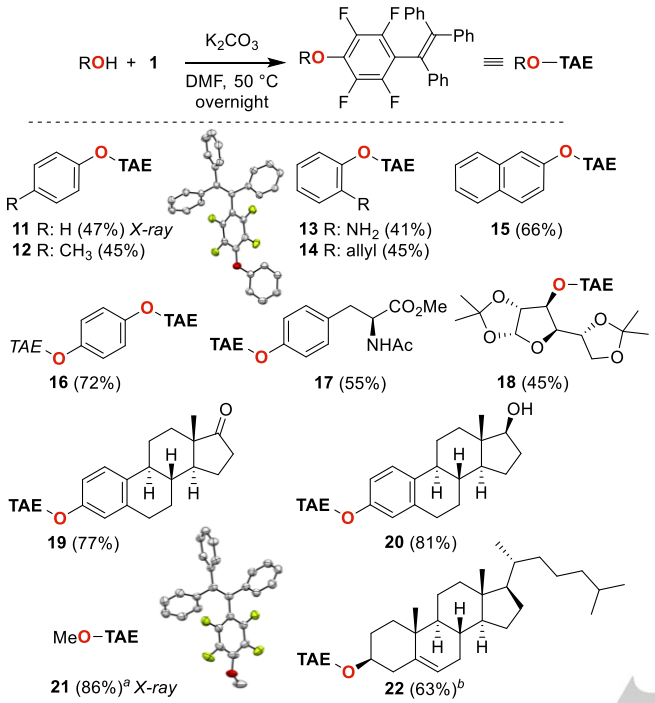


Scheme 2. Conjugation reactions of **1** with thiols. [a] The reaction was performed at 100 °C. [b] The product was isolated by preparative HPLC. NMR yield reported.

Next, we tested alcohols as reaction partners. Phenols readily reacted with **1** when heated at 50 °C (DMF, K_2CO_3), and the desired products **11**–**16** were isolated in moderate to good yields (Scheme 3). The reaction with 2-aminophenol was found to be chemoselective, with preferential reaction of the alcohol (**13**). The N,O-protected amino acid tyrosine gave the product of O–C coupling **17** in 55% yield. A coupling reaction with a carbohydrate, diacetone-D-glucose, afforded **18** in 45% yield. The hormones estrone and estradiol were selectively functionalized at the phenolic OH group. Notably, the enolizable keto group in **19** and the aliphatic OH group in **20** did not interfere in these reactions.

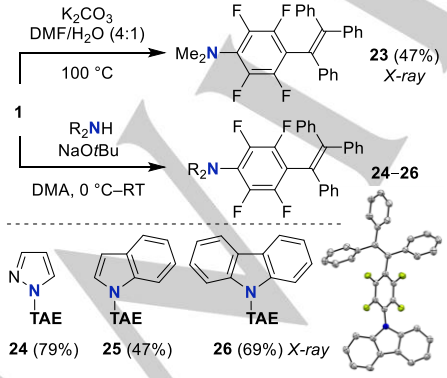
Our attempts to perform the coupling of **1** with aliphatic alcohols such as MeOH under standard conditions (DMF, 50 °C, K_2CO_3) were not successful. However, we found that using the sodium salt of the corresponding alcohol in THF allows for C–O coupling reactions. For NaOMe, we obtained the methoxyether **21** in 86% yield after overnight stirring at 60 °C. The same strategy allowed coupling of the aliphatic OH group of cholesterol to give

conjugate **22** in 63% yield. Compound **22** is an interesting candidate for CPL emissive liquid crystalline materials.[26]



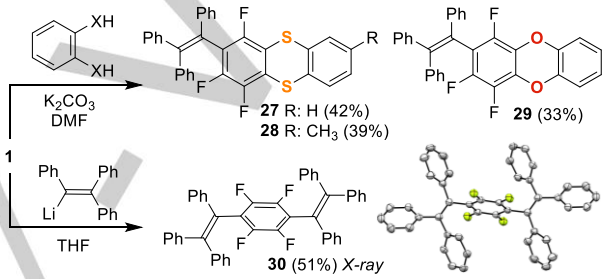
Scheme 3. Conjugation reactions of **1** with phenols and alcohols. [a] Conditions: MeONa, THF, 60 °C. [b] Conditions: cholesterol, NaH, THF, 50 °C.

While optimizing the reaction conditions for thiols and alcohols, we found that heating **1** in DMF/H_2O (1:1) at 100 °C resulted in the formation of the Me_2N adduct **23** (Scheme 4), with the amine originating from hydrolysis of DMF. In order to expand the scope of reactions with N-nucleophiles, we have optimized the conditions for coupling with aromatic heterocycles such as pyrazole, indole, and carbazole. Using NaO*t*Bu as the base in DMA led to the formation of the desired products **24**–**26** in good yields (Scheme 4).

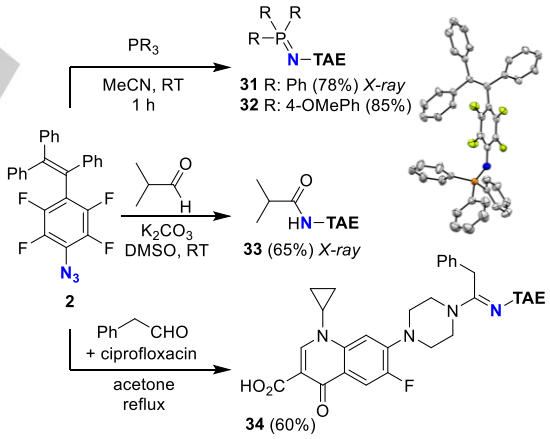


Scheme 4. Conjugation reactions of **1** with N-nucleophiles.

Double nucleophilic substitution with aromatic 1,2-dithiols gave AIE-active thianthrenes **27** and **28** (Scheme 5). Interestingly, we observed a highly regioselective coupling for the methyl-substituted dithiol, which allowed us to isolate **28** as a single regioisomer. It is worth noting that thianthrenes are known to form stable radical cations.[27] Therefore, **27** and **28** might find applications as redox-switchable AIE luminogens.[28] For the reaction of **1** with catechol, we also obtained a double substitution product, **29**, which could be isolated in 33% yield. The scope of the substitution reactions with **1** was extended towards carbon nucleophiles. We have synthesized 1,4-bis(triphenylvinyl)tetrafluorobenzene **30** by *para*-fluoro nucleophilic substitution reaction of **1** with triphenylvinyl lithium in good isolated yield (51%). The structure of **30** was confirmed by single crystal XRD.



Scheme 5. Coupling products of **1** with 1,2-dithio- and 1,2-dihydroxybenzenes (**27**–**29**), and triphenylethenyl lithium (**30**).

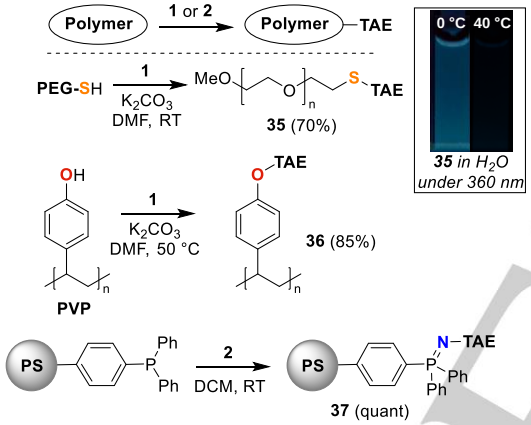


Scheme 6. Coupling reactions of the azide tag **2**.

The azide-containing tag **2** rapidly reacts with triarylphosphines at room temperature, as evidenced by the formation of gas bubbles.[19] After 1 hour, the coupling products **31** and **32** could be isolated in good yields (Scheme 6). Enolizable aldehydes react with perfluoroaryl azides under mild conditions to give amides.[20] Accordingly, the coupling of isobutyraldehyde and **2** afforded amide **33** in 65% yield. The structure of the product was confirmed by single-crystal X-ray analysis. Perfluoroaryl azides can also be used as coupling partners in multicomponent reaction with amines and aldehydes.[21] In analogy to a reported

procedure,[21a,b] we have synthesized the TAE conjugate **34** with phenylacetaldehyde and the antibiotic ciprofloxacin. In contrast to what was found for precursor **2**, the coupling products **31**–**34** all show strong solid state emission.

Conjugation reactions with tags **1** and **2** were extended to polymeric substrates (Scheme 7). The reaction of thioethyl-PEG monomethyl ether (MeO-PEG-SH, MW: ca. 10 kDa) with **1** gave coupling product **35** in 70% yield. The conjugate is amphiphlic, and shows a temperature-dependent luminescence in water (molecular thermometer).[29] Functionalization of commercially available polyvinylphenol (PVP, MW: ca. 1.8 kDa) with **1** gave polymer **36**. It shows a bright blue solid state emission, which is of potential use for chemical sensing or for display applications of PVPs.[30] The TAE group was also installed onto commercial polymer-bound triphenylphosphine beads.[31] The TAE-functionalized beads **37** are highly fluorescent. Considering the popularity of triphenylphosphine in chemical synthesis and organocatalysis,[32] one can envision applications of emissive PPh_3 polymer beads in optical monitoring of reaction progress.



Scheme 7. Functionalization of polymers (PEG = polyethyleneglycol; PVP = polyvinylphenol; PS = polystyrene).

In summary, we have developed two universal tags for the coupling of tetraarylethenes to a diverse range of substrates. Tag **1** can be obtained on a gram scale in a one-pot reaction from commercial reagents. It contains a reactive C_6F_5 group, which allows for chemoselective coupling reactions with S-, O-, N- and C-nucleophiles. Tag **2** is available in one step from **1**. The $C_6F_4N_3$ group of **2** can be used for conjugation reactions with phosphines, aldehydes and enamines. Using either tag **1** or **2**, it is possible to convert a wide variety of substrates into solid state luminogens, including amino acids, peptides, carbohydrates, steroids, and commercial polymers. Given the technological importance of tetraarylethene luminogens, we think that the new conjugation method will enable new applications.

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Keywords: aggregation-induced emission • fluorination • bioconjugation • nucleophiles • tetraarylethens • perfluoroarylazide • polymers

[1] For general reviews on AIE, see: a) H. Zhang, Z. Zhao, A. T. Turley, L. Wang, P. R. McGonigal, Y. Tu, Y. Li, Z. Wang, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Adv. Mater.* **2020**, 2001457; b) Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2015**, *115*, 11718–11940; c) S. Xu, Y. Duan, B. Liu, *Adv. Mater.* **2020**, *32*, 1903530; d) D. Ding, K. Li, B. Liu, B. Z. Tang, *Acc. Chem. Res.* **2013**, *46*, 2441–2453; e) F. Würthner, *Angew. Chem. Int. Ed.* **2020**, *59*, 14192–14196; For reviews on AIE of tetraarylethenes, see: f) D. D. La, S. V. Bhosale, L. A. Jones, S. V. Bhosale, *ACS Appl. Mater. Interfaces* **2018**, *10*, 12189–12216; g) Z. Zhao, J. W. Y. Lam, B. Z. Tang, *Curr. Org. Chem.* **2010**, *14*, 2109–2132.

[2] a) D. Dai, J. Yang, Y.-W. Yang, *Chem. Eur. J.* **2022**, *28*, e202103185; b) G. Niu, R. Zhang, X. Shi, H. Park, S. Xie, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *TrAC Trends Anal. Chem.* **2020**, *123*, 115769; c) M. Gao, B. Z. Tang, *ACS Sens.* **2017**, *2*, 1382–1399.

[3] a) Z. Zhao, J. W. Y. Lam, B. Z. Tang, *J. Mater. Chem.* **2012**, *22*, 23726–23740; b) Z. Zhao, S. Chen, C. Deng, J. W. Y. Lam, C. Y. K. Chan, P. Lu, Z. Wang, B. Hu, X. Chen, P. Lu, H. S. Kwok, Y. Ma, H. Qiu, B. Z. Tang, *J. Mater. Chem.* **2011**, *21*, 10949–10956; c) S. Chen, W. Qin, Z. Zhao, B. Z. Tang, H.-S. Kwok, *J. Mater. Chem.* **2012**, *22*, 13386–13390.

[4] a) X. Cai, B. Liu, *Angew. Chem. Int. Ed.* **2020**, *59*, 9868–9886; b) J. Mei, Y. Huang, H. Tian, *ACS Appl. Mater. Interfaces* **2018**, *10*, 12217–12261.

[5] a) Y. L. Balachandran, X. Jiang, *CCS Chem.* **2022**, *4*, 420–436; b) G. Feng, B. Liu, *Acc. Chem. Res.* **2018**, *51*, 1404–1414.

[6] a) D. Yan, Q. Wu, D. Wang, B. Z. Tang, *Angew. Chem. Int. Ed.* **2021**, *60*, 15724–15742; b) M. Zhang, W. Zhao, *Aggregate.* **2021**; *2*, e60.

[7] Selected examples: a) X. Fang, Y.-M. Zhang, K. Chang, Z. Liu, X. Su, H. Chen, S. X.-A. Zhang, Y. Liu, C. Wu, *Chem. Mater.* **2016**, *28*, 6628–6636; b) X.-F. Duan, J. Zeng, J.-W. Lu, Z.-B. Zhang, *J. Org. Chem.* **2006**, *71*, 9873–9876.

[8] Selected examples: a) X. Chen, X. Y. Shen, E. Guan, Y. Liu, A. Qin, J. Z. Sun, B. Z. Tang, *Chem. Commun.* **2013**, *49*, 1503–1505; b) M. Banerjee, S. J. Emond, S. V. Lindeman, R. Rathore, *J. Org. Chem.* **2007**, *72*, 8054–8061; c) R. Rathore, C. L. Burns, S. A. Abdelwahed, *Org. Lett.* **2004**, *6*, 1689–1692.

[9] Selected examples: a) M. Zhang, Y. Yao, P. J. Stang, W. Zhao, *Angew. Chem. Int. Ed.* **2020**, *59*, 20090–20098; b) G.-F. Zhang, H. Wang, M. P. Aldred, T. Chen, Z.-Q. Chen, X. Meng, M.-Q. Zhu, *Chem. Mater.* **2014**, *26*, 4433–4446.

[10] Selected examples: a) G. Tan, L. Zhu, X. Liao, Y. Lan, J. You, *J. Am. Chem. Soc.* **2017**, *139*, 15724–15737; b) C. Song, Y. Sun, J. Wang, H. Chen, J. Yao, C.-H. Tung, Z. Xu, *Org. Chem. Front.* **2015**, *2*, 1366–1373.

[11] For reviews on conjugation and supramolecular assembly reactions with TAEs, see: a) H. Liu, L.-H. Xiong, R. T. K. Kwok, X. He, J. W. Y. Lam, B. Z. Tang, *Adv. Optical Mater.* **2020**, 2000162; b) F. Wu, X. Wu, Z. Duan, Y. Huang, X. Lou, F. Xia, *Small* **2019**, *15*, 1804839.

[12] a) W. Chen, C. Zhang, X. Han, S. H. Liu, Y. Tan, J. Yin, *J. Org. Chem.* **2019**, *84*, 14498–14507; b) K. C. Chong, F. Hu, B. Liu, *Mater. Chem. Front.* **2019**, *3*, 12–24.

[13] a) H. B. Shi, R. T. K. Kwok, J. Z. Liu, B. G. Xing, B. Z. Tang, B. Liu, *J. Am. Chem. Soc.* **2012**, *134*, 17972–17981.

[14] Selected examples: a) Z. Y. Wang, P. F. Zhang, H. X. Liu, Z. Zhao, L. H. Xiong, W. He, R. T. K. Kwok, J. W. Y. Lam, R. Q. Ye, B. Z. Tang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 17306–17312; b) M. Z. Chen, N. S. Moily, J. L. Bridgford, R. J. Wood, M. Radwan, T. A. Smith, Z. G. Song,

B. Z. Tang, L. Tilley, X. H. Xu, G. E. Reid, M. A. Pouladi, Y. N. Hong, D. M. Hatters, *Nat. Commun.* **2017**, *8*, 474; c) Y. Liu, Y. Yu, J. W. Lam, Y. Hong, M. Faisal, W. Z. Yuan, B. Z. Tang, *Chem. Eur. J.* **2010**, *16*, 8433–8438.

[15] a) C. Liu, H. Bai, B. He, X. He, J. Zhang, C. Chen, Y. Qiu, R. Hu, F. Zhao, Y. Zhang, W. He, J. H. C. Chau, S. Chen, J. W. Y. Lam, B. Z. Tang, *Angew. Chem. Int. Ed.* **2021**, *60*, 12424–12430; b) X. Hu, X. Zhao, B. He, Z. Zhao, Z. Zheng, P. Zhang, X. Shi, R. T. Kwok, J. W. Lam, A. Qin, *Research* **2018**, 3152870.

[16] For selected reviews, see: a) W. D. G. Brittain, C. R. Coxon, *Chem. Eur. J.* **2022**, *28*, 10–23; b) S. Xie, M. Sundhoro, K. N. Houk, M. Yan, *Acc. Chem. Res.* **2020**, *53*, 937–948; c) L.-H. Liu, M. Yan, *Acc. Chem. Res.* **2010**, *43*, 1434–1443; d) J. W. Bartels, C. Cheng, K. T. Powell, J. Xu, K. L. Wooley, *Macromol. Chem. Phys.* **2007**, *208*, 1676–1687. For selected publications, see: e) W. J. Ong, T. M. Swager, *Nature Chem.* **2018**, *10*, 1023–1030; f) E. A Qian, A.I Wixtrom, J. C Axtell, A. Saebi, D. Jung, P. Rehak, Y. Han, E. H. Moully, D. Mosallaei, S. Chow, M. S Messina, J. Y. Wang, A. T. Royappa, A. L. Rheingold, H. D. Maynard, P. Král, A. M. Spokoyny, *Nature Chem.* **2017**, *9*, 333–340; g) A. Alsbaiee, B. J. Smith, L. Xiao, Y. Ling, D. E. Helbling, W. R. Dichtel, *Nature* **2016**, *529*, 190–194; h) C. Zhang, M. Welborn, T. Zhu, N. J. Yang, M. S. Santos, T. Van Voorhis, B. L. Pentelute, *Nature Chem.* **2016**, *8*, 120–128; i) A. M. Spokoyny, Y. Zou, J. J Ling, H. Yu, Y.-S. Lin, B. L. Pentelute, *J. Am. Chem. Soc.* **2013**, *135*, 5946–5949; j) P. M. Imbesi, N. V. Gohad, M. J. Eller, B. Orihuela, D. Rittschof, E. A. Schweikert, A. S. Mount, K. L. Wooley, *ACS Nano* **2012**, *6*, 1503–1512; k) J. Ma, C. Cheng, K. L. Wooley, *Macromolecules* **2009**, *42*, 1565–1573; l) R. Breslow, B. Gabriele, J. Yang, *Tetrahedron Lett.* **1998**, *39*, 2887–2890.

[17] For reviews, see: a) G. Delaittre, L. Barner, *Polym. Chem.* **2018**, *9*, 2679–2684; b) C. Liu, B. Zhang, *Chem. Rec.* **2016**, *16*, 667–687.

[18] For reviews, see: a) Y. Du, Q. Zeng, L. Yuan, L. He, *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2021**, *58*, 521–538; b) S. Agar, E. Baysak, G. Hizal, U. Tunca, H. Durmaz, *J. Polym. Sci., Part A: Polym. Chem.* **2018**, *56*, 1181–1198; c) Quanyi Yin, PhD Thesis, Chapter 1, pp. 7–50. *Université de Lyon* **2018** Link: https://tel.archives-ouvertes.fr/tel-02000999.

[19] a) M. Sundhoro, J. Park, M. Yan, *Macromolecules* **2018**, *51*, 4532–4540; b) M. Sundhoro, S. Jeon, J. Park, O. Ramström, M. Yan, *Angew. Chem. Int. Ed.* **2017**, *56*, 12117–12121. For a recent review about the Staudinger ligation: C. Bednarek, I. Wehl, N. Jung, U. Schepers, S. Bräse, *Chem. Rev.* **2020**, *120*, 4301–4354.

[20] S. Xie, Y. Zhang, O. Ramström, M. Yan, *Chem. Sci.* **2016**, *7*, 713–718.

[21] a) S. Xie, J. Zhou, X. Chen, N. Kong, Y. Fan, Y. Zhang, G. Hammer, D. G. Castner, O. Ramström, M. Yan, *Mater. Chem. Front.* **2019**, *3*, 251–256; b) S. Xie, S. Manuguri, G. Proietti, J. Romson, Y. Fu, A. K. Inge, B. Wu, Y. Zhang, D. Häll, O. Ramström, M. Yan, *Proc. Natl. Acad. Sci. USA* **2017**, *114*, 8464-8469; c) S. Xie, S. A. Lopez, O. Ramström, M. Yan, K. N. Houk, *J. Am. Chem. Soc.* **2015**, *137*, 2958−2966.

[22] B. McVerry, A. Polasko, E. Rao, R. Haghniaz, D. Chen, N. He, P. Ramos, J. Hayashi, P. Curson, C.-Y. Wu, P. Bandaru, M. Anderson, B. Bui, A. Sayegh, S. Mahendra, D. Di Carlo, E. Kreydin, A. Khademhosseini, A. Sheikhi, R. B. Kaner, *Adv. Mater.* **2022**, *34*, 2200254; b) K. Siegmann, J. Inauen, R. Sterchi, M. Winkler, *Surf. Interface Anal.* **2018**, *50*, 205–211; c) K. Siegmann, J. Inauen, D. Villamaina, M. Winkler, *J. Appl. Surf. Sci.* **2017**, *396*, 672–680.

[23] A. A Suleymanov, M. Doll, A. Ruggi, R. Scopelliti, F. Fadae-Tirani, K. Severin, *Angew. Chem. Int. Ed.* **2020**, *59*, 9957–9961.

[24] Z. Zhang, T. Lieu, X. Wang, O. Daugulis, O. Miljanic, *ChemPhotoChem* **2022**, e202200011.

[25] A similar phenomenon was noted by Miljanic *et al* (ref. 24) and by Bai *et al* for substituted tetrarylethene aggregates formed in THF/water mixtures: H. Yao, M. Zhou, X. Yu, M. Bai, *Chem. Commun.* **2022**, *58*, 4985–4988.

[26] Examples of tetraaryethene-cholesterol conjugates: a) S. Jiang, S. Zhou, Y. Chen, H. Guo, F. Yang, *Chin. Chem. Lett.* **2022**, *33*, 2442–2446; b) Y.-X. Yuan, J.-B. Xiong, J. Luo, M. Hu, H. Jiang, M. Liu, Y.-S. Zheng, *J. Mater. Chem. C* **2019**, *7*, 8236–8243.

[27] J. Beck, T. Bredow, R. T. Tjahjanto, *Zeitschrift Naturforsch. B* **2009**, *64b*, 145–152.

[28] Electrofluorochromic AIE luminogens: A. A Suleymanov, A. Ruggi, O. M. Planes, A.-S. Chauvin, R. Scopelliti, F. Fadae-Tirani, A. Sienkiewicz, A. Fabrizio, C. Corminboeuf, K. Severin, *Chem. Eur. J.* **2019**, *25*, 6718–6721.

[29] Selected examples of molecular thermometer: a) T. Qin, B. Liu, K. Zhu, Z. Luo, Y. Huang, C. Pan, L. Wang, *Trends Anal. Chem.* **2018**, *102*, 259–271; b) L. Tang, J. K. Jin, A. Qin, W. Z. Yuan, Y. Mao, J. Mei, J. Z. Sun, B. Z. Tang, *Chem. Commun.* **2009**, 4974–4976; c) S. Uchiyama, Y. Matsumura, A. P. de Silva, K. Iwai, *Anal. Chem.* **2003**, *75*, 5926–5935.

[30] J. M. Nasrullah, S. Raja, K. Vijayakumaran, R. Dhamodharan, *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 453–461, and references cited therein.

[31] The coupling to polymers without reactive groups can potentially be achieved via C-H insertion of a photochemically generated nitrene (see ref 22).

[32] H. Guo, Y. C. Fan, Z. Sun, Y. Wu, O. Kwon, *Chem. Rev.* **2018**, *118*, 10049–10293.

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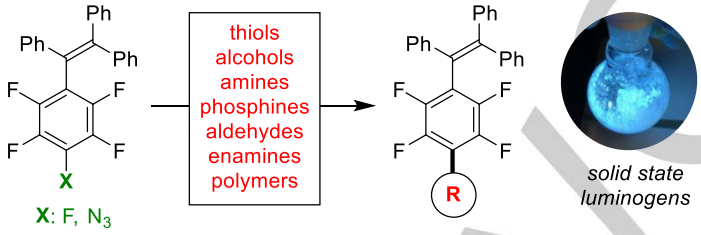
COMMUNICATION

A simple method for the coupling of fluorinated tetraarylethens to a wide range of substrates is described. The approach allows converting amino acids, bioactive compounds, carbohydrates, steroids, and polymers in one step into solid state luminogens.



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Fluorinated Tetraarylethenes: Universal Tags for the Synthesis of Solid State Luminogens

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