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Cite this: *Chem. Commun.*, 2022, **58**, 3306

Received 27th January 2022,
Accepted 10th February 2022

DOI: 10.1039/d2cc00548d

rsc.li/chemcomm

Synthesis, properties and chemical modification of a persistent triisopropylsilylethynyl substituted tri(9-anthryl)methyl radical†

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In studies aimed at developing new organic spin materials, we prepared a triisopropylsilylethynyl substituted tri(9-anthryl)methyl (TAntM) radical. The TIPS-ethynyl group in this radical effectively suppresses its reactivity, resulting in extremely high stability in air for at least one month. Chemical modification of the radical using [4+2] Diels–Alder reaction proceeds even at room temperature. Because harsh conditions and metal-catalyzed reactions are not required, this post-modification strategy should be highly versatile for use in constructing unique spin-labelled molecules.

Highly persistent neutral organic radicals have attracted great attention recently. Various radicals of this type have been synthesized to explore their physical and photophysical properties and utilization as functional materials in organic magnets,[1] batteries,[2] magnetic resonance imaging systems,[3] and doublet emission-based light emitting diodes[4] and in dynamic nuclear polarization (DNP) studies.[5] To enable them to be highly persistent, organic radicals usually contain nitrogen or oxygen atoms to provide thermodynamic stability.[6,7] Alternatively, the stabilities of purely hydrocarbon radicals can be enhanced by incorporating bulky substituents at positions bearing high spin densities to inhibit their reactivities[8,9] (Fig. 1). For example, perchlorotriphenylmethyl (PTM)[10] and tetrathiatriarylmethyl (TAM)[11] radicals are well known persistent aromatic hydrocarbon radicals that gain stability from kinetic protection of their spin-localized central sp^2 carbons by halogen or sulfur atoms. Owing to the presence of embedded heteroatoms at high spin density locations, PTM and TAM radicals have relatively large *g*-anisotropies. However, persistent non-heteroatom-embedded hydrocarbon radicals with small *g*-anisotropies are the most ideal candidates for use in various spintronic materials.[12] Unfortunately, the library of stable hydrocarbon radicals not containing heteroatoms remains small because of structural limitations and synthetic issues.

We recently prepared the purely hydrocarbon mesityl-substituted tri(9-anthryl)methyl (**TAntM**) radical,[8e] in which the central sp^2 carbon is sterically protected by three 9-anthryl groups. In addition, we demonstrated that the **TAntM** radical displays extremely high persistence, undergoing only slight decay after more than a month in an air-saturated solution (Fig. 2). Because no heteroatoms are present, the **TAntM** radical is expected to have small *g*-anisotropy and, therefore, its functionalized derivatives should be attractive targets in efforts aimed at developing and applying new organic spin materials.

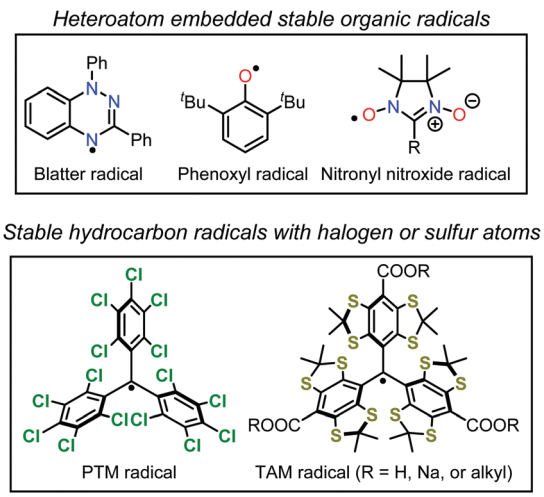

Fig. 1 Stable neutral organic radicals embedded with heteroatoms for gaining thermodynamic stability (top) and stable hydrocarbon radicals with halogen or sulfur atoms for gaining kinetic stability (bottom).

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† Electronic supplementary information (ESI) available. CCDC 2123624, 2123625 and 2149932. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d2cc00548d

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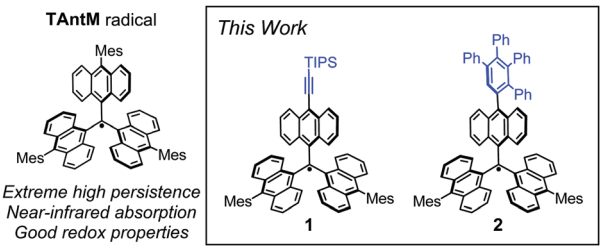


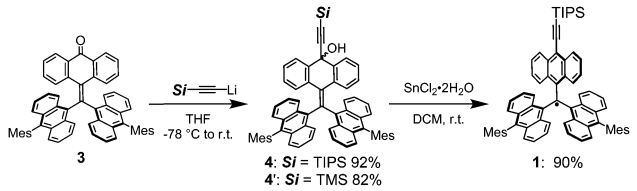
Fig. 2 The structures of the **TAntM** radical (left) and functionalized **TAntM** radicals **1** and **2** (right).

In the investigation described below, whose overall goal is to increase the scope and versatility of hydrocarbon radicals for organic-based materials, we prepared the **TAntM** radical **1** containing a triisopropylsilyl (TIPS) ethynyl group because the TIPS ethynyl group enhances the stability of radical species,[13] and assessed its properties and chemical reactions. The results show that the TIPS-ethynyl group in **1** effectively enhances its stability in air. Moreover, we demonstrated that modification of **1** by a Diels–Alder reaction can be utilized to produce the related tetraphenylphenyl substituted **TAntM** radical **2**.

The route employed to synthesize **1**, shown in Scheme 1, begins with the 10-alkylidene-9-anthrone derivative **3**, which was prepared using a reported procedure.[8e] Reaction of **3** with TIPS-ethynyl lithium generated the corresponding alkynyl–carbinol **4** in high yield (92%). Treatment of **4** with tin(ii) chloride dihydrate then efficiently (90%) produced the target radical **1**. Although the steric hindrance provided by the TIPS-ethynyl unit should be less than that by the mesityl group, it is worth noting that the radical **1** has a stability that matches that of the **TAntM** radical, even to the extent of allowing purification by silica gel chromatography in air.

The structure of radical **1** was unambiguously confirmed by using X-ray crystallographic analysis (Fig. 3 and Fig. S1, ESI†). Analysis of the X-ray data shows that radical **1** has a C–C bond distance between the central sp^2 carbon C1 and the anthryl carbon C2 (C1–C2) of 1.452(3) Å, which is slightly shorter than the C1–C3 (1.478(2) Å) and C1–C4 (1.473(2) Å) distances. Also, the anthryl unit twist angle $\theta1$ (37.4°) is smaller than $\theta2$ (48.5°) and $\theta3$ (47.5°), indicating that the distribution of unpaired electrons on the TIPS ethynyl-substituted anthryl unit is slightly larger than that on the other mesityl-substituted anthryl units.

Radical **1** has a C_2-like structure in the crystal state. Quantum chemical calculations on its TMS-analog **1′** show that it has only a slight spin distribution on the ethynyl unit (Fig. 4a and Fig. S3, ESI†). Yet, the ESR spectrum of **1** contains a narrow



Scheme 1 Synthesis of **4**, **4′** and **1**.

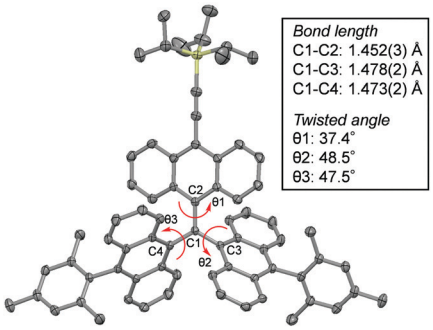


Fig. 3 Plot of single crystal X-ray data of **1** and its structural factors (bond lengths and twist angles). Protons are omitted for clarity.

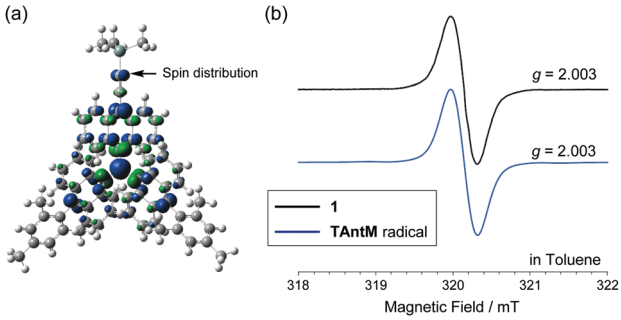


Fig. 4 (a) Spin density map of **1′** (UBLYP/6-31G**//ωB97XD/6-31G**). (b) ESR spectra of **1** (black line) and the **TAntM** radical (blue line).

peak (Fig. 4b) that has a width that is identical to that of the peak in the spectrum of the **TAntM** radical, which has D_3 symmetry. Thus, the spin distribution of **1** is similar to that of the **TAntM** radical because the anthryl units can undergo ready rotation in a solution.

The UV-vis-NIR spectrum of **1** is similar to that of the **TAntM** radical (Fig. 5a). The differences consist of a slight red-shift of the maxima from those of the **TAntM** radical in the visible region (600–> 620 nm) and near-infrared region (1020–> 1100 nm) caused by the presence of the TIPS-ethynyl unit. These effects are also reflected in the results of TD-DFT calculations (Fig. S4, ESI†). The effect of TIPS-ethynyl substitution is also seen in the redox properties of radical **1**. The cyclic

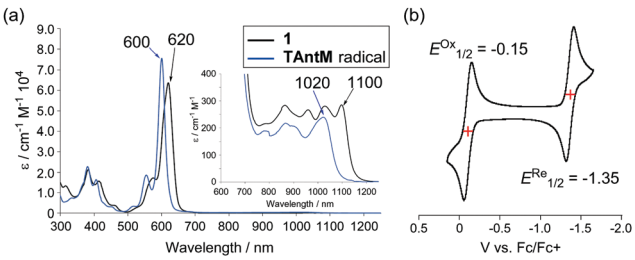


Fig. 5 (a) UV-Vis-NIR spectra of **1** and the **TAntM** radical in CH_2Cl_2 (inset: Expansion from 600 to 1250 nm). (b) Cyclic voltammograms of **1**. Measurement conditions: 0.1 M $^nBu_4NPF_6$ in CH_2Cl_2, scan rate = 100 mV s^{-1}.

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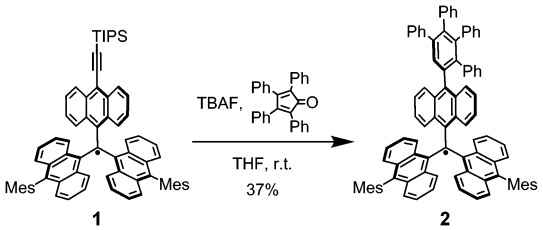
voltammogram (CV) of **1** contains reversible oxidation and reduction waves at $E^{Ox}_{1/2}$ = −0.15 V and $E^{Re}_{1/2}$ = −1.35 V, respectively (Fig. 5b). In contrast, CV waves of the **TAntM** radical ($E^{Ox}_{1/2}$ = −0.19 V and $E^{Re}_{1/2}$ = −1.48 V, Fig. S5, ESI†) show that the oxidation and reduction potentials are slightly positively shifted by the TIPS-ethynyl unit.

The stability of radical **1** in an air-saturated solution was assessed by monitoring the decay of the absorption maximum at 620 nm. Surprisingly, no significant decomposition was observed to take place for at least one month (Fig. S6, ESI†).

Although the steric protection provided by its TIPS-ethynyl unit is less than that of a mesityl group, **1** has a stability that is comparable with that of the **TAntM** radical. To ascertain reason(s) for this persistence, the related radical **1′** containing a smaller TMS-ethynyl substituent was prepared. The solution of formed **1′** has a green color initially, but the color slowly changes to red along with formation of an orange precipitate. Quantitative analyses such as ^{1}H- and ^{13}C NMR, MS, IR, and single crystal X-ray measurements revealed that in solution, **1′** efficiently reacts to generate an allene-type tail-to-tail **1′** dimer in 75% yield (Scheme 2a and Fig. S7–S10, ESI†). Quantum chemical calculations indicate that the σ-dimer is energetically highly favorable (−25.5 kcal mol^{-1}, Fig. S11, ESI†). For comparison purposes, the TMS-ethynyl substituted fluorenyl radical reacts to only form the asymmetric head-to-tail σ-dimer (allene–ethynyl) (Scheme 2b)[14] probably because the fluorenyl moiety is sterically less hindered than the **TAntM** unit. The combined results indicate that the TIPS-ethynyl unit in **1** stabilizes the radical both through a steric effect and electronically by delocalization of the unpaired electron.

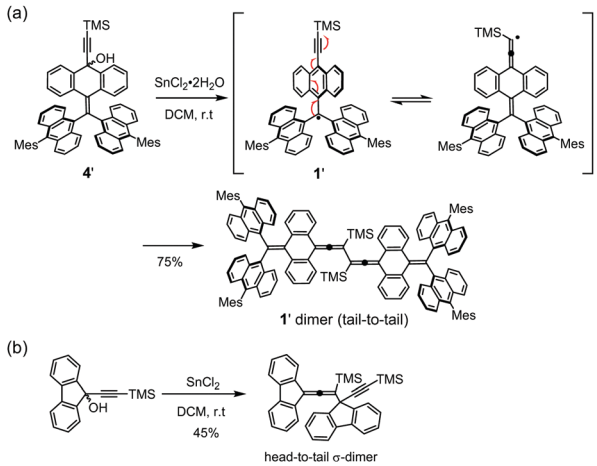
Finally, the chemical reactivity of radical **1** was probed to evaluate its versatility in the preparation of new organic spin materials. Direct introduction of a radical group in a molecular skeleton is an attractive strategy for creation of spin-based materials. The use of a nitronyl nitroxide radical[15] exemplifies this approach. However, to use trityl-based persistent hydrocarbon radicals in this strategy, a functional group would need to be introduced before generating the radical (pre-modification) for avoiding rapid decomposition,[16] and the post-modification of the persistent radicals is still limited.[17] To explore this strategy, we examined reactions of radical **1** involving *in situ* removal of the silyl group using TBAF and subsequent [4+2] Diels–Alder reaction using tetraphenylcyclopentadienone (tetracyclone) (Scheme 3). We observed that this process leads to formation of the tetraphenylphenyl substituted **TAntM** radical **2** in 37% yield. Surprisingly, although Diels–Alder reactions usually require relatively high temperatures (>100 °C), the one involved in generation of **2** takes place at room temperature.



Scheme 3 Diels–Alder reaction of **1** to form radical **2**.

Significantly, tetraphenylphenyl substituted radical **2** has almost the same properties as the **TAntM** radical. X-Ray crystallographic analysis of **2** shows that its C1–C2 bond length is longer and the $\theta 1$ twist angle is larger than that of **1** (Fig. 6 and Fig. S2, ESI†), making it have close to the D_3 propeller structure of the **TAntM** radical. In fact, the UV-vis and ESR spectra, and CV of **2** are almost identical to those of the **TAntM** radical (Fig. S12–S14, ESI†). Due to steric bulkiness provided by the tetraphenyphenyl (TPB) unit, the twist angle $\theta 4$ between the anthryl and TPB units is 76.9°. As a result, the stability of **2** is also comparable to that of **TAntM** radical and **1** (Fig. S15, ESI†). This result indicates that the radical **2** retains the properties of the **TAntM** radical.

In summary, in the study described above, we synthesized TIPS-ethynyl substituted **TAntM** radical **1** and evaluated its properties. The results of studies with the analogous TMS-ethynyl substituted **TAntM** radical **1′** gave important information that has led to an understanding of the stability/reactivity of the ethynyl moiety. Post-modification of radical **1** employing



Scheme 2 (a) Reaction of **1′** to form **1′** dimer. (b) Reaction of the TMS-ethynyl substituted fluorenyl radical.[15]

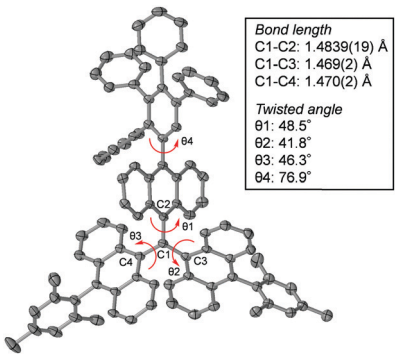


Fig. 6 Plot of single crystal X-ray data of **2** and its structural factors (bond lengths and twist angles). Protons are omitted for clarity.

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[4+2] Diels–Alder reaction with tetracyclone was found to occur effectively even at room temperature. In contrast to approaches often utilized to introduce radical groups into other molecules, the strategy developed in this effort avoids harsh reaction conditions and metal-catalyzed reactions that lead to decomposition and contamination with residual metals. In addition, tetracyclone, a model reactant in this study, can be readily modified such as by attaching emissive or amphiphilic components, utilized for unique NIR-emissive dyes, DNP, or spin-embedded self-assembled materials. Therefore, the facile post-modification process involving a room-temperature Diels–Alder reaction could become a highly versatile method to introduce **TAntM** radicals into substances used as organic spin-labelled materials. Further development of this overall strategy is ongoing.

This study was supported by a Grant-in-Aid for Scientific Research (C) (JSPS KAKENHI Grant Number JP20K05475, T. N.) and Transformative Research Areas (A) (Grant Number JP20H05865, T. K.). Quantum chemical calculations were performed at the Research Center for Computational Science, Okazaki, Japan. T. N. thank Prof. Shuichi Suzuki (Graduate School of Engineering Science, Osaka University) for acquisition of HR-MS spectra.

Conflicts of interest

There are no conflicts to declare.

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