

Thermally Ultrarobust $S = 1/2$ Tetrazolinyl Radicals: Synthesis, Electronic Structure, Magnetism, and Nanoneedle Assemblies on Silicon Surface

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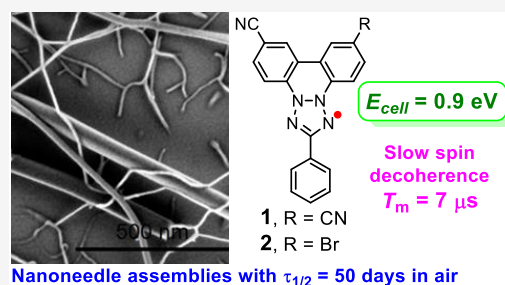


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Supporting Information

ABSTRACT: Open-shell organic molecules, including $S = 1/2$ radicals, may provide enhanced properties for several emerging technologies; however, relatively few synthesized to date possess robust thermal stability and processability. We report the synthesis of $S = 1/2$ biphenylene-fused tetrazolinyl radicals **1** and **2**. Both radicals possess near-perfect planar structures based on their X-ray structures and density-functional theory (DFT) computations. Radical **1** possesses outstanding thermal stability as indicated by the onset of decomposition at 269 °C, based on thermogravimetric analysis (TGA) data. Both radicals possess very low oxidation potentials <0 V (vs. SCE) and their electrochemical energy gaps, $E_{\text{cell}} \approx 0.9$ eV, are rather low. Magnetic properties of polycrystalline **1** are characterized by superconducting quantum interference device (SQUID) magnetometry revealing a one-dimensional $S = 1/2$ antiferromagnetic Heisenberg chain with exchange coupling constant $J'/k \approx -22.0$ K. Radical **1** in toluene glass possesses a long electron spin coherence time, $T_m \approx 7 \mu\text{s}$ in the 40–80 K temperature range, a property advantageous for potential applications as a molecular spin qubit. Radical **1** is evaporated under ultrahigh vacuum (UHV) forming assemblies of intact radicals on a silicon substrate, as confirmed by high-resolution X-ray photoelectron spectroscopy (XPS). Scanning electron microscope (SEM) images indicate that the radical molecules form nanoneedles on the substrate. The nanoneedles are stable for at least 64 hours under air as monitored by using X-ray photoelectron spectroscopy. Electron paramagnetic resonance (EPR) studies of the thicker assemblies, prepared by UHV evaporation, indicate radical decay according to first-order kinetics with a long half-life of 50 ± 4 days at ambient conditions.



INTRODUCTION

Recent advances in the design and synthesis of thermally robust high-spin di- and triradicals based on the Blatter radical^{1–6} have expedited the preparation of organic radical thin films via controlled evaporation under ultrahigh vacuum (UHV).^{1,4–6} Notable developments include thin films of an $S = 1/2$ Blatter radical derivative exhibiting magnetic ordering⁷ and a high-spin ($S = 1$) Blatter-based diradical with robust stability and electrical conductivity.⁶ In addition, robustness and synthetic availability of $S = 1/2$ Blatter radicals⁸ enabled their recent applications as paramagnetic liquid crystals,^{9,10} batteries,¹¹ and potential molecular spin qubits.¹² Likely, other novel properties will emerge from the remarkable Blatter radical; however, we are in search of new $S = 1/2$ building blocks for future development.

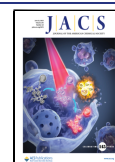
2,2'-Biphenylene-fused tetrazolinyl (BFTZ) monoradicals, or so-called phototetrazolinyl radicals,¹³ have attracted our attention because of their exceptional stability and, most importantly, the potential to achieve relatively large spin densities at the *para*-positions (and *ortho*-positions) with respect to the nitrogens of the tetrazolinyl moiety (Figure 1). Large spin densities at the *para/ortho* positions are the

essential prerequisite in the design of high-spin polyradicals with large energy gaps between the high-spin ground state and low-spin excited state.^{14–17}

Spin densities at the *para/ortho*-positions may be derived from experimental ¹H hyperfine couplings via the McConnell linear relationship,¹⁸ that is, a larger hyperfine coupling corresponds to a greater spin density. For example, in the BFTZ radical (R = Ph, X = Y = H), the hyperfine coupling at the *para*-position is $|A(^1\text{H})| = 5.2$ MHz.¹⁹ In other nitrogen-centered stable radicals, analogous values of *para* $|A(^1\text{H})|$ are 5.0 MHz (*p*) and 1.6 MHz (*p'*) in the Blatter radical,^{20,21} 1.8 MHz in the oxo-verdazyl radical,²² 3.1 MHz in the verdazyl radical,²³ and only 2.7 MHz in simple tetrazolinyl radicals.²⁴

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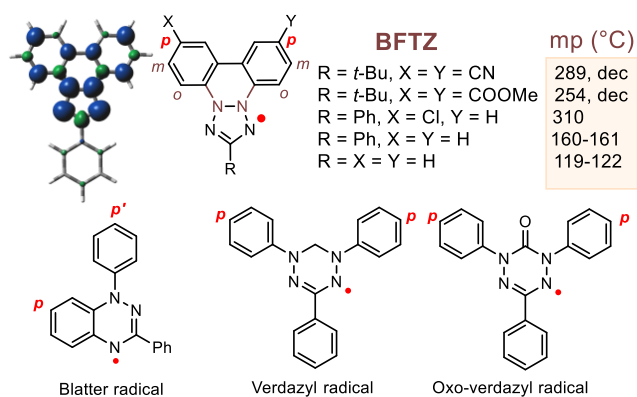


Figure 1. Top: 2,2'-Biphenylene-fused tetrazolanyl (BFTZ) radicals and spin density map at the UB3LYP/6-31G(d)+ZPVE level. Bottom: Blatter and verdazyl radicals. *Para*-positions are indicated with a red symbol *p* or *p'*.

BFTZ radicals possess exceptional thermal stability. While the parent radical (R = X = Y = H) melts at about 120 °C,²⁵ its derivatives (R = *t*-Bu, X = Y = CN or CO₂Me) melt with decomposition at temperatures >250 °C, according to the literature.²⁴ Remarkably, a BFTZ derivative (R = Ph, X = Cl, Y = CN) was reported to melt at temperatures as high as ~300 °C.^{20,21} Some of these radicals could be prepared not only in good yields but also with nearly quantitative spin concentrations. Also, they were found to be monomeric in the solid state and in solution.^{13,19,24–26} In more recent studies, the mechanism of photochemical formation and ultrafast excited-state dynamics of tetrazolanyl radicals and 2,2'-biphenylene-fused tetrazolium cations (Figure 1: R = Ph, X = Y = H) were elucidated.^{27,28}

Here, we report the synthesis and comprehensive characterization of *S* = 1/2 2,2'-biphenylene-fused tetrazolanyl radicals **1** and **2** (Figure 2). Radicals **1** and **2** are designed to take

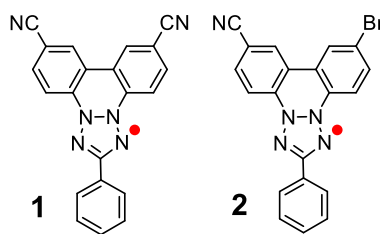


Figure 2. Radicals **1** and **2**.

advantage of the exceptional stability of the BFTZ backbone, with the long-term goal of thermally and magnetically robust high-spin radicals. In particular, Br-substituted **2** would likely enable cross-coupling chemistry.

Both radicals were prepared as crystalline solids with near-perfect spin concentrations and characterized by X-ray crystallography, electron paramagnetic resonance (EPR) spectroscopy (including electron spin relaxation properties for **1**), superconducting quantum interference device (SQUID) magnetometry, voltammetry, UV–vis–NIR absorption spectroscopy, and thermogravimetric analysis (TGA). Radical **1** was evaporated under UHV, forming, under the present preparation conditions, nanoneedles, as shown by scanning electron microscopy (SEM). The nanoneedles' UHV- and air-

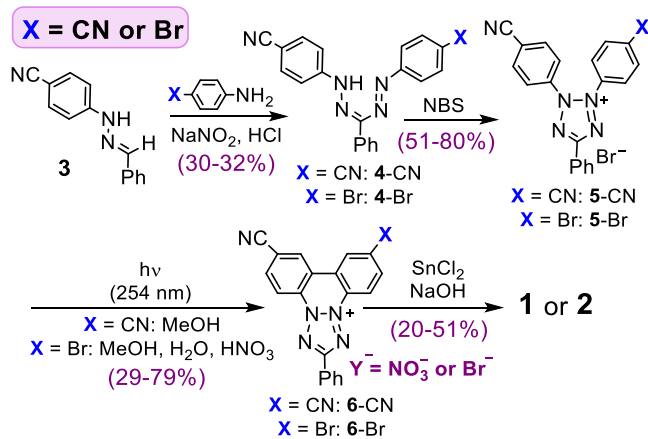
stability were further investigated by using X-ray photoelectron spectroscopy (XPS) and EPR spectroscopy.

The nanoneedle morphology is very interesting for nanoelectronics applications because of device miniaturization and the favorable ratio between surface and bulk that is beneficial for various devices such as sensors and transistors.^{29–32} Several examples of small diamagnetic molecules, *p*- and *n*-type semiconductors, have been shown to grow following this morphology.^{32–37} However, to our knowledge, among adequately characterized thin films of radicals, only the tris(2,4,6-trichlorophenyl)methyl radical shows a mixed morphology, with the coexistent presence of islands and fibers when grown on graphene.³⁸ Conversely, radical **1** shows a distinct nanoneedle self-assembled morphology under the present preparation conditions.

RESULTS AND DISCUSSION

Synthesis. Formazans **4** are synthesized using a phase transfer catalysis approach,^{39–41} in which suspensions of diazonium salts, prepared in situ from 4-cyano- or 4-bromoaniline, are added to hydrazone **3** in a mixture of dichloromethane (DCM) and water in the presence of tetraalkylammonium salt (Scheme 1). Oxidation of formazans **4** with *N*-

Scheme 1. Synthesis of Radicals **1** and **2**



bromo-succinimide (NBS) provides the tetrazolium salts **5**.^{24,41} Photochemical ring closure of **5** gives fused tetrazolium (phototetrazolium) salts **6**.^{24,25} Finally, reduction of salts **6**, using SnCl₂ under basic conditions in water/benzene under inert atmosphere,²⁶ yields radicals **1** and **2**. Spin concentrations for all prepared samples of radicals are summarized in the Supporting Information (SI).

X-ray Crystallography. The structures of radicals **1** and **2** are confirmed by X-ray crystallography (Figure 3). In both radicals, the tetrazolanyl-and-biphenyl-fused moieties are planar. As illustrated by the small values of the dihedral angles, the phenyl substituent connected to C1 is approximately co-planar with the planes defined by the phenyl group (C14–C19) and the tetrazolanyl/biphenyl (C1–C13, C20, C21, N1–N6, Br1) tilted relative to each other by 10.18(9) and 1.2(2)° in **1** and **2**, respectively.

Both **1** and **2** crystallize in the monoclinic space group *P*2₁/*n*. However, one molecule of benzene per formula unit is co-crystallized with **1**. The crystals of **2** that are obtained from either pentane/toluene (0.17-mm-long needle) or pentane/ethyl acetate (0.87-mm-long needle) possess identical

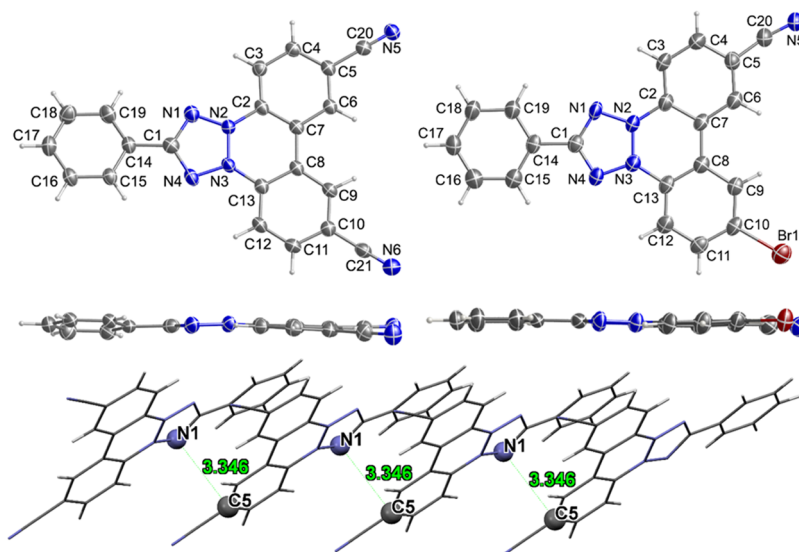


Figure 3. Molecular structure and crystal packing of **1** at 100 K and of **2** at 153 K. For **1**, a molecule of co-crystallized benzene is omitted. Top and Middle: Ortep plots (top and side views) with carbon, nitrogen, and bromine atoms depicted with thermal ellipsoids set at the 50% probability level (top and side views). For **1**, a molecule of co-crystallized benzene is omitted and for **2**, Br/CN disorder is not shown. Bottom: tetramer of molecules of **1** forming a one-dimensional (1-D) chain along the crystallographic *a*-axis with short intermolecular contacts, N1...C5 = 3.346 Å. Further details are reported in Tables S1–S3 and Figures S1–S6, SI.

structures at 153 and 296 K, respectively; in both structures, the Br and CN groups are disordered over two positions.

In the crystal of **1** at 100 K, the molecules are π -stacked, forming one-dimensional (1-D) chains along the crystallographic *a*-axis, with an average plane-to-plane distance of 3.28(9) Å, with planes defined by the C/N atoms of the entire molecule (Figure 3). Because intermolecular close contacts, such as N1...C5 = 3.346 Å,⁴² primarily involve atoms with positive spin densities, significant intermolecular antiferromagnetic interactions are anticipated in crystalline radical **1**. Also, co-crystallized molecules of benzene magnetically isolate the 1-D chains (predominantly along the *c*-axis).

In the crystal of **2** at 153 K, the molecules are also π -stacked, forming alternating 1-D chains along the crystallographic *a*-axis, with plane-to-plane distances of 3.24(4) and 3.35(4) Å, when Br/CN disorder is not considered (planes defined by the Br/C/N atoms of the entire molecule). In the crystal of **2** at 296 K, 1-D chains with an average plane-to-plane distance of 3.40(4) Å are found, when Br/CN disorder is taken into account. For the nearest-neighbor molecules, intermolecular contacts, such as N1...C5 = 3.407 Å, are found. Thus, we anticipate that intermolecular antiferromagnetic interactions in **2** will be relatively weak and, most likely not 1-D, because of the spatial proximity of 1-D chains in the crystal.

Density-Functional Theory (DFT) Computations. DFT (UB3LYP-D3BJ/6-31G(d,p)/PCM-UFF+ZPVE) optimized geometries for **1** and **2** in benzene (or DCM) indicate perfectly planar structures with C_{2v} and C_s symmetry, respectively.⁴³ In these computations, the UB3LYP functional is augmented with Grimme's empirical dispersion correction (D3 version)⁴⁴ and with the Becke–Johnson damping function.⁴⁵

Based on the relatively small value of the lowest vibrational frequency of 16 cm⁻¹ (A_2 -symmetric mode) in **1**, primarily involving twisting of the phenyl group at C1 (Figure 3), we suspect that small distortions from planarity observed in the solid state structures of especially **1** are due to crystal packing effects. (For comparison in **2**, the lowest vibrational frequency

of 22 cm⁻¹ is computed.) Both radicals follow the typical Aufbau rule, with electrons in their singly occupied molecular orbital (SOMOs) at higher energy, compared to electrons in the corresponding highest occupied molecular orbitals (HOMOs), in contrast to the SOMO/HOMO inversions found in selected nitrogen-centered radicals.^{46–52}

EPR Spectroscopy. The purity of samples for radicals **1** and **2** is determined by EPR spectroscopic spin counting (SI). In addition, treatment of **1** with HCl in methanol/water at room temperature gives cleanly the 1-electron-oxidized product, i.e., diamagnetic tetrazolium cation **6-CN**.

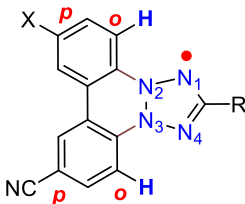
Neugebauer and Russell carried out ¹⁵N labeling in symmetrically substituted BFTZ (X = Y) derivatives (Figure 1)⁵³ and established that the values of $A(^{14}\text{N}) \approx 11$ MHz associated with N1 and N4 (Table 1) were almost independent of substitution; the values of $A(^{14}\text{N}) \approx 22$ –16 MHz associated with N2 and N3 (Table 1) were following the relationship, $\text{CH}_3 > \text{H} > \text{CO}_2\text{CH}_3 > \text{CN}$.^{19,24,53} Also, in the un-substituted derivatives (X = Y = H), values of $A(^1\text{H})$ at the *ortho* and *para* positions (Figure 1) were identical.¹⁹

Due to significant spin densities at the four nitrogens of the tetrazolanyl moiety and at the *ortho*-carbons (and protons), CW EPR spectra of radicals **1** and **2** in benzene at room temperature show resolvable isotropic ¹⁴N and ¹H hyperfine couplings, $A(^{14}\text{N})$ and $A(^1\text{H})$ (Figure 4 and Table 1).⁵⁴

The inclusion of unresolved ⁷⁹Br- and ⁸¹Br-hyperfine couplings at natural isotopic abundance,⁵⁴ which serves as an effective additional line broadening contribution, provides an improved spectral fit for **2** (Figure S21, SI). The resultant value of $A(^{79}\text{Br}) = 0.78$ MHz indicates a non-negligible amount of spin density on bromine, which is in qualitative agreement with the DFT-computed $A(^{79}\text{Br}) = 1.7$ MHz (Table S4, SI).

We evaluate electron spin relaxation properties of **1** in frozen dilute toluene solution as a function of temperature. Longitudinal relaxation properties are measured using inversion recovery and fitted with an exponential recovery $V(T) = a - b \exp(-T/T_1)$, yielding the longitudinal relaxation time T_1 (Figure S22, SI). As shown in Figure SA, the relaxation

Table 1. Summary of DFT-Computed (UB3LYP-D3BJ/6-31G(d,p)/PCM-UFF+ZPVE in Benzene) and Experimental Hyperfine Coupling Constants (A in MHz)



	1R = Ph X = CN		2R = Ph X = Br		R = <i>t</i> -Bu X = CN
	DFT	EPR	DFT	EPR	
N_1	11.9	10.5	11.6	10.4	10.7
N_2	10.9	15.8	13.8	20.1	15.7
N_3	10.9	15.8	10.0	14.8	15.7
N_4	11.9	10.5	11.9	10.4	10.7
H(o)	-7.2	5.8	-7.1	5.6	5.0
			-7.9	6.0	
N (CN)	1.6		1.8		

^aRef 24.

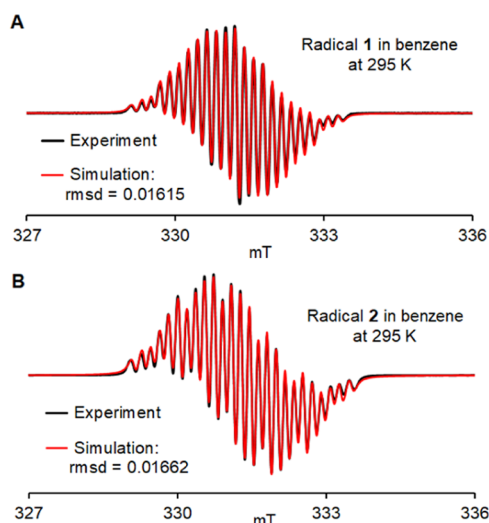


Figure 4. EPR spectra of radicals 0.29 mM **1** and ~0.2 mM **2** in benzene. (A) 9.2918 GHz, modulation amplitude = 0.02 mT; simulation:⁵⁴ $g = 2.0042$, $A(^{14}\text{N}) = 15.79$ MHz ($n = 2$), $A(^{14}\text{N}) = 10.51$ MHz ($n = 2$), $A(^1\text{H}) = 5.74$ MHz ($n = 2$), linewidths peak-to-peak (lwpp), Gaussian = 0.00043 mT and Lorentzian = 0.1179 mT; (B) 9.2956 GHz, modulation amplitude = 0.04 mT; simulation:⁵⁴ $g = 2.0046$, $A(^{14}\text{N}) = 20.10$ MHz ($n = 1$), $A(^{14}\text{N}) = 10.40$ MHz ($n = 2$), $A(^{14}\text{N}) = 14.79$ MHz ($n = 1$), $A(^1\text{H}) = 6.02$ MHz ($n = 1$), $A(^1\text{H}) = 5.64$ MHz ($n = 1$), lwpp, Gaussian = 0.00146 mT and Lorentzian = 0.1225 mT; g -values are uncorrected. Further details are in the SI: Table S4 and Figures S19–S21.

rate, $1/T_1$, shows a steep monotonic increase with temperature, progressing from 0.033(5) ms^{-1} at 19 K to 2.3(5) ms^{-1} at 160 K.

To quantify the transverse relaxation, Hahn echo decays are measured and fitted with a stretched exponential decay $V(2\tau) = V(0) \exp(-(2\tau/T_m)^\xi)$, yielding the electron spin phase memory (or coherence) time T_m and the stretch exponent ξ . The Hahn echo decays show substantial modulations due to ^{14}N (see Figure S23, SI), which are neglected in the stretched exponential model. As shown in Figure 5B, $1/T_m$ shows a nonmonotonic temperature dependence, in which it initially

decreases to a minimum of about 0.14(1) μs^{-1} around 60 K (corresponding to $T_m \approx 7 \mu\text{s}$), before it increases until about 120 K. Values of $1/T_m$ above 120 K are unreliable and associated with large uncertainties, since in this range the echo decay is on the same time scale as the period of the strong ^{14}N nuclear echo modulation. We tentatively attribute the increased transverse relaxation rate at very low temperatures to the dynamics of the methyl groups of the solvent molecules (toluene- h_8). Protons on these methyl groups are responsible for enhancing decoherence. Such effects have been observed in a variety of other methyl-containing systems.^{55–58} The decrease of the stretch exponent at low temperatures corroborates this interpretation.

One of the key prerequisites for the use of paramagnetic molecules as spin qubits for potential quantum sensing applications is a long coherence time T_m .^{59,60} For **1** in toluene- h_8 , the value of $T_m \approx 7 \mu\text{s}$ in the 40–80 K temperature range is comparable to $T_m = 7.2 \mu\text{s}$ for a Blatter radical derivative measured in toluene- d_8 at 25 K.⁶¹ The value of $T_m \approx 7 \mu\text{s}$ is significantly longer than $T_m = 3$ –4 and 4–5 μs in the 40–80 K range for typical *gem*-dimethyl and optimized spirocyclic pyrroline nitroxide radicals, respectively,⁵⁸ or $T_m = 4$ –6 μs and $T_m < 4 \mu\text{s}$ in the 40–80 K range for Blatter radicals immobilized on silica and optimized vanadium complexes in protiated solvents/matrices, respectively.^{12,59,60}

SQUID Magnetometry. Polycrystalline **1** and **2** are studied by SQUID magnetometry (Figures S24–S27, SI). We focus on the study of radical **1** (Figure 6) because **1** exhibits much stronger exchange interactions, compared to **2**, as indicated by the values of mean-field parameters ($|l|$) differing by a factor of 3 (Figure S26, SI). The value of $\chi T_{\text{max}} = 0.351$ emu K mol⁻¹ in the high-temperature plateau (280–320 K) is in excellent agreement with a spin concentration of 94%, as determined by EPR spin counting. At lower temperatures, the χT vs. T plot shows a profound downward turn, with crystal defects (magnetically isolated $S = 1/2$ radicals), significantly contributing to the values of χT (and χ) at 1.8 K. The χ vs. T plot has a characteristic broad maximum at $T_{\text{max}} \approx 14$ K, suggesting a low-dimensional magnetic behavior. Three sets of χ vs. T data may be well fit to one-dimensional (1-D) $S = 1/2$ antiferromagnetic Heisenberg chain,^{62–64} to provide the coupling constant, $J'/k = -21.85 \pm 0.70$ K (mean \pm SE, $n = 3$). The common relationship for such 1-D chains, $T_{\text{max}}/|J'/k| = 0.641$, is well satisfied for radical **1**.⁶² Notably, another limiting model for such intermolecular antiferromagnetic coupling, such as pairs of $S = 1/2$ radicals (dimers),¹⁵ gives much inferior fits for the χ vs. T data (Figure S25, SI).^{4,65,66}

Electrochemistry. Cyclic, differential pulse, and square-wave voltammograms (SWV) for radical **1** present approximately reversible processes with the oxidation and reduction peaks at $E^{+/0} \approx -0.14$ V and $E^{-/0} \approx -1.07$ V vs. SCE.⁶⁷ Because radical **2** is derived from **1** by replacing one of the strongly electron-withdrawing cyano groups with bromine, it is easier to oxidize at $E^{+/0} \approx -0.28$ V to the diamagnetic cation and slightly more difficult to reduce at $E^{-/0} \approx -1.14$ V (Figure 7).

The highly negative oxidation potentials (e.g., $E^{+/0} \approx -0.3$ V for **2**) may impede its Pd-catalyzed cross-coupling reactions, as already observed for Blatter radicals with $E^{+/0} \approx +0.1$ – (+0.3) V,^{68,69} requiring a highly reactive Pd-catalyst,⁵ compared to oxo-verdazyl radicals with $E^{+/0} \approx +0.8$ V.^{70,71}

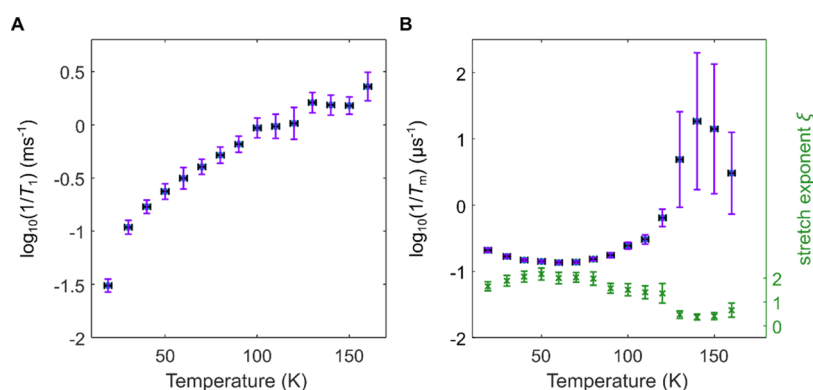


Figure 5. Relaxation properties of **1** at X-band (9.70 GHz, 346 mT). (A) Temperature dependence of $1/T_1$ (blue circles) with experimental errors of temperature (black) and 95% confidence intervals of $1/T_1$ (purple). (B) Temperature dependence of $1/T_m$ (blue circles, left axis) and the stretch exponent ξ (green crosses, right axis), including 95% confidence intervals. Values are listed in Table S5, SI.

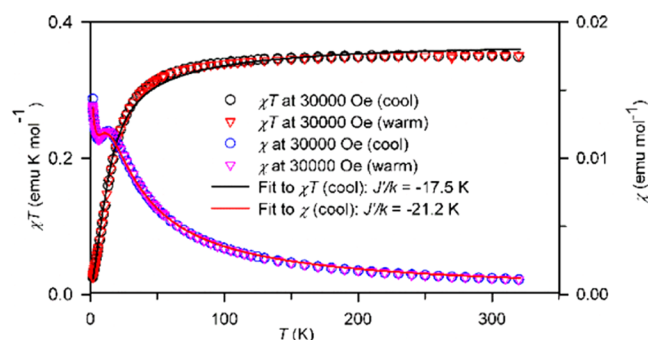


Figure 6. SQUID magnetometry of polycrystalline radical **1**: experimental data plotted as χT vs. T and χT vs. T and the selected numerical fits to one-dimensional $S = 1/2$ antiferromagnetic Heisenberg chain (eq S1A,B, SI). Fitting parameters, such as J/k and weight factors, and relevant statistical parameters are summarized in Table S6, and illustrated in Figures S24–S27, SI.

For radicals **1** and **2**, electrochemical band gaps, $E_{\text{cell}} = E^{+/0} - E^{-/0}$, are rather low with $E_{\text{cell}} = 0.935 \pm 0.015$ and 0.866 ± 0.003 eV, respectively. Because E_{cell} may be related to the gas phase IP – EA and to disproportionation energies for the $2R^{\bullet} \rightarrow R^+ + R^-$ reaction, the low values of E_{cell} are one of the favorable factors in the design of neutral radical conductors.^{6,72–75}

UV–Vis–NIR Spectroscopy. UV–vis–NIR spectra of **1** and **2** in dichloromethane (DCM) show the longest-wavelength bands at $\lambda_{\text{max}} = 717\text{--}729$ nm with broad absorption envelopes (Figure 8). The spectrum for **1** can be reasonably well reproduced by time-dependent density-functional theory (TD-DFT) computations (after shifting the computed band positions by -0.6 eV, Figure S7, SI).⁴³ Plots of molar absorbance (extinction coefficient), ϵ , vs. wavenumber, $\tilde{\nu}$, for radical **1** in DCM and in benzene demonstrate that the longest-wavelength band at $\lambda_{\text{max}} \approx 730$ nm (the lowest-wavenumber band at $\tilde{\nu}_{\text{max}} \approx 13,700$ cm^{-1}) is symmetrical, and it shows negligible solvent dependence (Figure 8, inset).

For radical **1** in DCM or benzene, the optical band gap, $E_g = 1.12 \pm 0.002$ eV, is slightly higher, compared to $E_g = 1.09$ eV for radical **2** in DCM (Figures S9–S12, SI), which parallels the trend in the values of E_{cell} ; though for **1** in DCM, the longest-wavelength band, $\lambda_{\text{max}} = 726\text{--}729$ nm, possesses a bathochromic shift, compared to corresponding $\lambda_{\text{max}} = 717$ nm for **2** in DCM. For comparison, BFTZ ($R = t\text{-Bu}$, $X = Y = \text{CN}$) radical in dioxane was reported to possess $\lambda_{\text{max}} = 695$ nm.²⁴

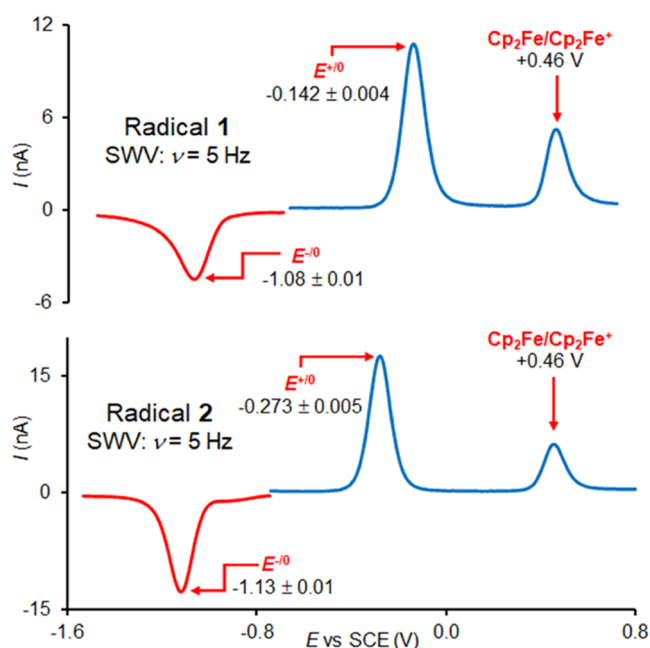


Figure 7. Square-wave voltammetry (SWV) of radicals **1** and **2** in 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane at room temperature. Redox potentials are given as mean \pm stddev with $n = 4\text{--}9$ (**1**) and $6\text{--}9$ (**2**). For further details, including cyclic and differential pulse voltammograms; see the SI, Figures S15–S18.

Diamagnetic cations (salts) **6-CN** and **6-Br**, precursors to **1** and **2**, possess much higher $E_g = 2.50$ and 2.00 eV, respectively (Figures S13 and S14).

Stability of Radicals by TGA. Thermogravimetric analysis (TGA) data indicate that the onset of thermal decomposition of **1**, corresponding to a 1% mass loss, is at 269 $^{\circ}\text{C}$. At 301 $^{\circ}\text{C}$, the decomposition rate reaches a sharp maximum (with a shoulder at ~ 290 $^{\circ}\text{C}$). In contrast, for **2**, the primary decomposition has the onset and maximum rate temperatures that are by $50\text{--}80$ $^{\circ}\text{C}$ lower, and the secondary decomposition possesses a maximum rate at 338 $^{\circ}\text{C}$ (Figure 9).

We note that radical **1** in benzene at room temperature is quite persistent with about 3% (vs. TEMPONE) and 5% decrease of double-integrated intensity of its EPR spectrum in one and two weeks, respectively; this corresponds to a half-life of the order of 5–6 months. As mentioned before, radical **1** in the presence of a strong acid, such as concentrated HCl in

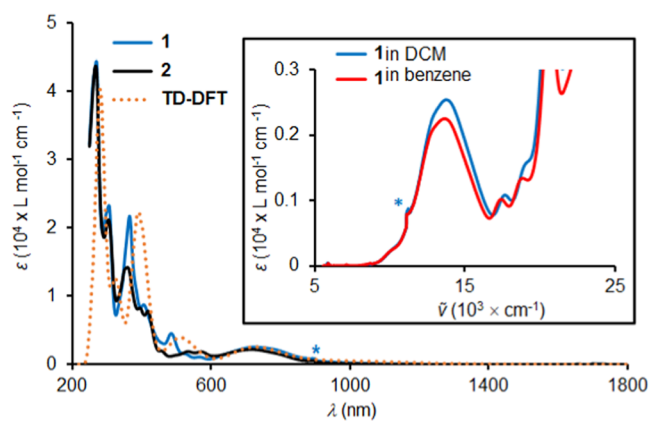


Figure 8. Main plot: UV-vis-NIR (294 K) absorption spectra for 0.31 and 0.30 mM radicals **1** and **2** in DCM, as well as TD-DFT-computed spectrum for **1** in DCM solvent model. For **1**, bands at $\lambda_{\max} = 270, 306, 365, 406, 485,$ and 729 nm have the following extinction coefficients ($\text{L mol}^{-1} \text{cm}^{-1}$): $\epsilon_{270} = 4.4 \times 10^4$, $\epsilon_{306} = 2.3 \times 10^4$, $\epsilon_{365} = 2.2 \times 10^4$, $\epsilon_{406} = 8.7 \times 10^3$, $\epsilon_{485} = 4.5 \times 10^3$, and $\epsilon_{729} = 2.5 \times 10^3$. The values of ϵ are not corrected for spin concentration of the radicals. Inset plot: Expanded spectra for **1** in DCM and benzene, plotted vs wavenumbers ($\tilde{\nu}$) and showing the longest-wavelength band at $\lambda_{\max} \approx 730$ nm. The feature at $\lambda \approx 900$ nm, marked with a blue asterisk, is an instrumental artifact (change of grating). Further details may be found in the SI: Figures S7–S14.

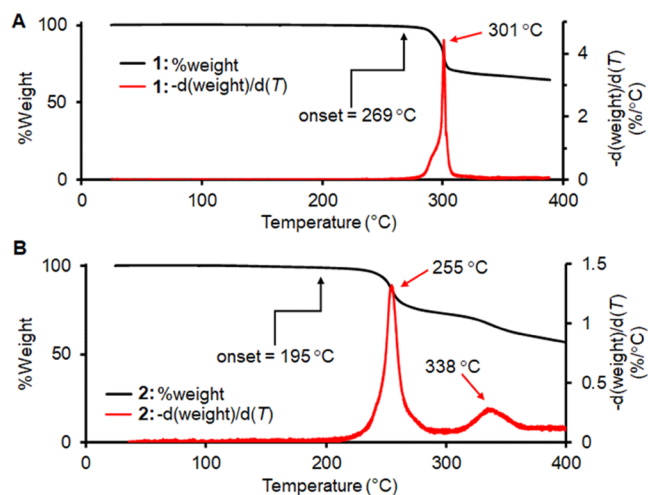


Figure 9. Thermogravimetric analysis (TGA) of radicals **1** (A) and **2** (B) under N_2 ; heating rate = 5 $^\circ\text{C min}^{-1}$. Further details may be found in the SI: Figures S28–S31.

methanol/water, at room temperature undergoes a nearly quantitative conversion to the precursor tetrazolium salt **6-CN** (see SI, Section 1e).

Controlled Deposition of Radical 1 on $\text{SiO}_2/\text{Si}(111)$ Wafers. Using a well-established method,^{76,77} we evaporated radical **1** on native SiO_2 on $\text{Si}(111)$ wafers. We used organic molecular beam deposition (OMBD) which allows precise control of the evaporation parameters.⁷⁸ The radical assemblies were investigated, without breaking the vacuum, by using XPS. This experimental technique, based on the photoelectric effect, can be used to determine quantitatively the concentration of the elements adsorbed onto a surface.^{79,80} The intensity and binding energies of the spectroscopic lines are sensitive to the chemical environment of the elements forming the radicals.⁷⁹ Thus, we were able to: (1) compare the core-level spectra of

the assemblies with those of the powder (i.e., with the signal from radical **1** that did not undergo evaporation, Figure 10); (2) calculate the stoichiometry of the obtained assemblies, comparing them to the molecular stoichiometry (Table S7, SI); and (3) fit the main spectroscopic line adopting a fit procedure that we developed for radicals⁸¹ that allows assessing the integrity of the molecules and, therefore, their radical character (Figure 10).

Looking in detail at the C 1s and N 1s core-level spectra, we found that the main lines have a complex shape that mirrors the different chemical environments of each atom in the radical. The carbon atoms have two main different chemical environments: the emitted photoelectrons have different binding energies depending on whether they are bound to other carbon atoms and hydrogen atoms or to a nitrogen atom (see; the molecular structure in Figure 2, the fit analysis in Figure 10, and the corresponding Tables S8 and S9, SI). This is signaled by the C 1s spectroscopic line showing two contributions, the one at higher binding energy being the component due to photoemission of electrons from carbon atoms bound to nitrogen atoms. In a very simplified model, this can be understood in terms of electronegativity. Nitrogen atoms are more electronegative than carbon atoms. This moves the electronic cloud toward them, requiring more energy to emit an electron. A similar argument also holds for the N 1s spectroscopic line that, with its complex shape, mirrors the presence of the tetrazole ring, with four different chemical environments of the nitrogen atoms and the presence of the cyano groups (see the molecular structure in Figure 2, the fit analysis in Figure 10, and Tables S10 and S11, SI). The fit assignment is also in very good agreement with previously investigated radical and closed-shell thin films.^{1,61,82} In addition to the effects due to the different chemical environment, we also observe the presence of several satellite features, the so-called shake-up satellites, typical features in photoemission that appear as an effect of the relaxation processes, caused by the core hole left behind by the photoemitted electron. Taking into account their intensity is mandatory to gain reliable information on the stoichiometry of the investigated systems.^{79,80,83}

The comparison of the spectra of the assembly with the spectra of the powder does not show new or different features (see Figure 10).

In the tetrazolanyl ring, the chemical environments of the four nitrogen atoms are very similar, thus, within the experimental resolution, we expect a single asymmetric line, as it is the actual case both for powders and assemblies. This is consistent with previously published results on the diamagnetic tetrazole-based systems.^{84–88} The main line at around 400 eV shows a pronounced shoulder. This suggests a stronger delocalization/screening of the core hole created upon photoemission in one of the nitrogen atoms. Considering the crystal structure of radical **1** (Figure 3), we can infer that the intermolecular contact $\text{N1}\cdots\text{C5}$ is short enough^{42,89–91} to enhance the screening of the core hole in N1, pushing the binding energy of the N1 photoemitted electrons toward the lower-energy range. This behavior is the same for the assemblies and the powder (polycrystalline **1**). This observation suggests that the nanoneedles are characterized by an arrangement of the molecules similar to the one of polycrystalline **1**.

The result of this approach indicates that evaporation and deposition do not change the chemical structure of the

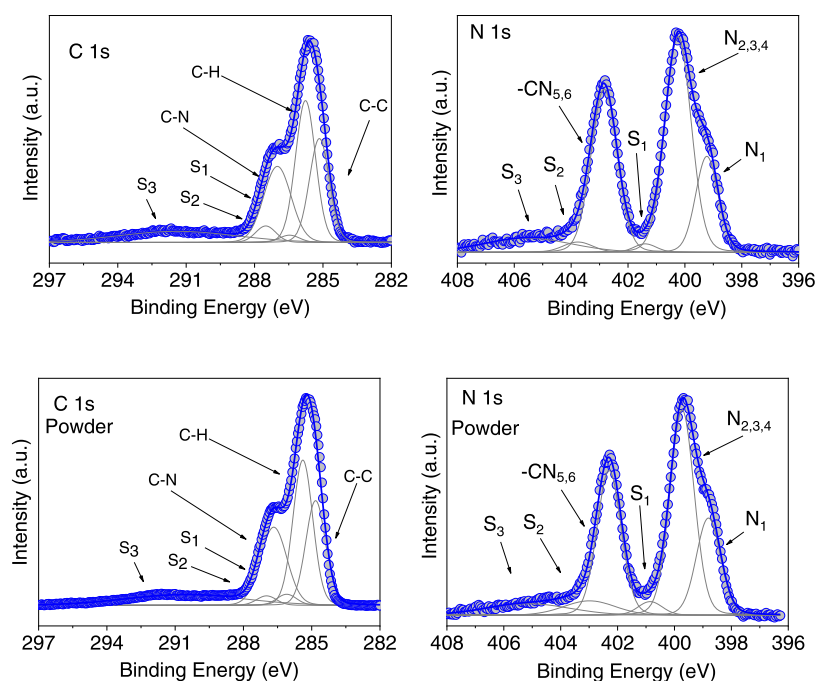


Figure 10. (Top) C 1s and N 1s core-level spectra of a thicker assembly of radical **1** deposited on SiO₂/Si(111) substrate compared to the (bottom) powder spectra, together with their fit components. For the fit details, see the [Supporting Information](#).

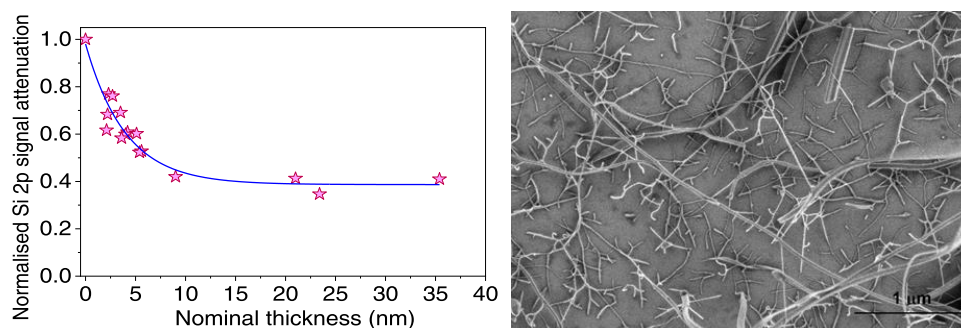


Figure 11. (Left) Attenuation of the Si 2p XPS signal, normalized to the corresponding substrate signal at zero adsorbate thickness as a function of radical **1** nominal thickness, during the deposition at room temperature of radical **1**. The exponential decay line is a guide to the eye. (Right) Typical SEM image showing the radical **1** nanoneedles (see also [Figure S32](#) in the Supporting Information for additional SEM images).

molecules in the assemblies, i.e., the radical character and the molecules are wholly intact in the assembly, i.e., the deposition of radical **1** occurred without degradation. The assemblies were also investigated by using EPR spectroscopy that confirmed their radical character.

XPS is also a powerful spectroscopic method to assess the growth modes of adsorbates onto a substrate. An advantage of this method is that the investigation occurs in real time, without breaking the vacuum, by monitoring the decay of the substrate signal versus the nominal thickness of the adsorbate during evaporation ([Figure 11](#)). We note that the substrate signal, Si 2p in this case, follows an exponential decay with increasing the assembly nominal thickness, which indicates either Stranski–Krastanov (layer(s) + islands) or Volmer–Weber growth modes (islands). However, the decay at higher thickness is different in the two cases: for pure island nucleation and growth, the substrate signal intensity is still very high as in the present case. Thus, XPS hints at the Volmer–Weber growth mode. This growth mode is favored by weak molecule–substrate interactions and the selected thermodynamical conditions determined by substrate and

evaporation temperatures. To shed light on the assembly morphology we used scanning electron microscopy (SEM). The SEM images ([Figures 11](#) and [S32](#), SI) are very surprising. On the one hand, they confirm the XPS finding of island growth, on the other hand, the islands have a specific morphology: they are needles. We have never observed this morphology in our previously investigated radical and multiradical systems. This specific morphology justifies, and it is the reason why, in this case, we prefer to use the word “assembly” rather than the word “film” to describe the adsorbate. In general, the needle morphology is generated by the asymmetry of the diffusion and traverse step-edge potential barriers seen by the molecules landing on the nucleated island during evaporation.³⁵ The diffusion barrier along the plane perpendicular to the needle axis is high, hindering the growth in those directions while the growth along the needle axis is facilitated. We also observe that in some cases the diffusion barrier relaxes giving rise to branches that follow a dendritic growth. The nanoneedles are stable when exposed to air: we monitored their core-level signals upon prolonged air exposure

by using XPS and did not observe changes (see Figures S33 and S34, SI).

Persistence of Assemblies of Radical 1 on Silicon Surface by EPR Spectroscopy. We studied the nanoneedle assemblies of **1** on SiO₂/Si(111) by EPR spectroscopy. Their typical EPR spectra show two components, that is, a narrow $S = 1/2$ isotropic peak, which is superimposed on a broader anisotropic $S = 1/2$ peaks; these peaks correspond to radical **1** and the well-known paramagnetic defect site in the Si substrate, respectively (Figure 12A). This is confirmed by

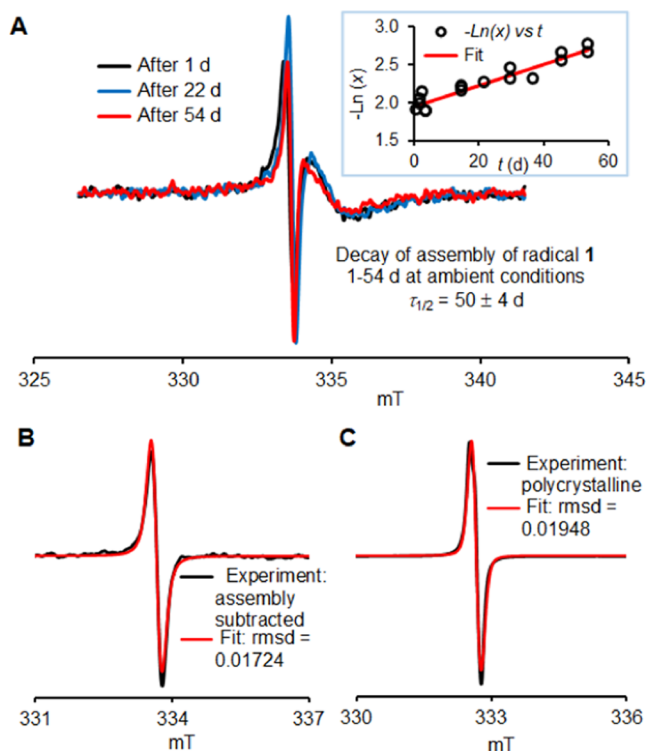


Figure 12. EPR spectroscopy of assemblies of radical **1** at ambient conditions: assemblies on SiO₂/Si(111) (A, B) and polycrystalline (C). Additional details may be found in the SI: Table S12 and Figures S35–S40.

the spectra of empty SiO₂/Si(111) substrate (SI). Numerical fits of the spectra of the assemblies provide the ratios for the two components, which allow for a calculation of the molar fraction of radical **1**, x (Table S12, SI), assuming that the intensity of the spectrum for the Si-defect site is constant. Decay of x follows first-order kinetics with a half-life, $\tau_{1/2} = 50 \pm 4$ days (d) (Figure 12A).

For the freshly prepared assemblies on SiO₂/Si(111), the spectral subtraction (adsorbate minus the substrate), provides a narrow line spectrum with $g = 2.0036$ and a peak-to-peak linewidth (lwpp) of about 0.17 and 0.12 mT for Gaussian and Lorentzian components (Figure 12B). This spectrum may be compared to similar spectra of polycrystalline radical **1**, for which $g = 2.0034$ and lwpp = 0.18 mT (Gaussian) and 0.05 mT (Lorentzian) are obtained (Figure 12C). Since nanoneedle assemblies have a line-shape intermediate between Gaussian and Lorentzian, this may suggest an even more pronounced 1-D character for exchange coupling, compared to the polycrystalline solid.⁹²

CONCLUSIONS

We successfully synthesized two new tetrazolinyl-based (BFTZ) radicals **1** and **2** with excellent spin concentrations. X-ray crystallography of **1** and **2** shows nearly perfectly planar structures. DFT computations reveal perfectly planar structures with C_{2v} (for **1**) and C_s (for **2**) point groups of symmetry. Dicyano-substituted radical **1** shows long electron spin coherence times in frozen solution. Polycrystalline **1** has an ultrarobust thermal stability as suggested by its onset of decomposition in TGA at >260 °C. We were able to evaporate radical **1** under controlled conditions to form nanoneedles with intact radical character. The nanoneedles are also stable under air. This specific morphology might enable using radical **1** with the purpose to achieve precise lateral control of deposition, growth, and positioning of radical nanostructures in nano-devices. Combination of ultrarobust thermal stability, nanoneedle morphology, low electrochemical band gap, and relatively long electron spin coherence times makes radical **1** exceptional.

We envisage tetrazolinyl-based (BFTZ) radicals as superior building blocks for the next generation of thermally and magnetically robust high-spin diradicals and triradicals.

EXPERIMENTAL SECTION

X-ray Crystallography. Crystals of **1** and **2** for X-ray studies were prepared by slow evaporation from organic solvents. Data collections were performed at Indiana University, using Mo $K\alpha$ radiation. Final cell constants were calculated from the xyz centroids of strong reflections from the actual data collection after integration (SAINT);⁹³ intensity data were corrected for absorption (SADABS).⁹⁴ The space group, $P2_1/n$, was determined based on intensity statistics and systematic absences. The structures were solved and refined using the SHELX suite of programs.^{95,96} Intrinsic-methods solutions were calculated, which provided most non-hydrogen atoms from the E-maps. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining nonhydrogen atoms. All nonhydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Crystal and structure refinement data for **1** and **2** are in the Supporting Information and the CCDC deposited files in CIF format.

Synthesis. Standard techniques for synthesis under inert atmosphere (argon or nitrogen), using custom-made Schlenk glassware and custom-made double-manifold high-vacuum lines, were employed. Chromatographic separations were carried out using normal-phase neutral alumina or silica gel.

Electron Spin Relaxation. Pulse EPR data were recorded at X-band on a Bruker E580 spectrometer equipped with an MD4 dielectric resonator and a Bruker/ColdEdge cryogen-free sample cooling system. The sample in 4 mm O.D. was prepared in toluene with a concentration of 200 μ M, validated by spin quantification. The sample was purged with argon for 3 minutes before freezing. Longitudinal relaxation times T_1 were determined from inversion recovery data recorded with a $\pi-T-\pi/2-\tau-\pi-\tau$ -echo sequence, with a constant $\tau = 200$ ns and four-step phase cycling. Phase memory times T_m were obtained from fitting a stretched exponential to Hahn echo decay curves, obtained with a $\pi/2-\tau-\pi-\tau$ -echo sequence, with an initial $\tau = 200$ ns and two-step phase cycling. All pulses are rectangular pulses. The length of the $\pi/2$ pulse ranges from 14 to 16 ns. A nutation experiment and an echo-detected field sweep were measured at each temperature for optimizing pulse length and magnetic field, respectively. The sample temperature was controlled via a Mercury iTC controller (Oxford Instruments) utilizing a Cernox sensor mounted on the resonator body.

Assemblies on SiO₂/Si(111) Wafers. The preparation of the radical assemblies and the XPS measurements were carried out under

ultrahigh-vacuum conditions. A three-chamber UHV-System was used equipped with a monochromatic Al K α source (SPECS Focus 500) and a SPECS Phoibos 150 MCD hemispherical electron analyzer, attached directly to the OMBD and sample preparation chambers. To grow the radical assemblies on SiO₂/n-Si(111) wafers, we followed our approach to film deposition by OMBD.^{78,97} The substrate was cleaned in an ultrasonic bath in acetone and methanol for one hour each. After annealing at around 500 K for several hours, the wafer surface was examined for contaminants by XPS. The radical molecules were evaporated and deposited on the substrate kept at room temperature (evaporation rate: 0.1–0.7 nm/min). The evaporation rate was monitored by a quartz crystal microbalance. In parallel, the nominal thickness was estimated from the XPS data, investigating the attenuation of the substrate Si 2p signal after deposition. The XPS survey spectra were recorded at 50 eV pass energy and the high-resolution core-level spectra at 20 eV pass energy. All measured binding energies were calibrated by taking the substrate Si 2p_{3/2} signal at 99.8 eV as a reference.⁹⁸ The energy resolution was 0.4 eV. All photoemission measurements were performed in normal emission. The SEM images were acquired ex situ by using a Hitachi SU 8030 SEM.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.3c03402>.

General procedures and materials, additional experimental and computational details for **1** and **2**, including XPS fit parameters and stability investigations of assemblies of **1** (PDF)

Accession Codes

CCDC 2253237–2253239 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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