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Tetraarylsuccinonitriles as Mechanochromophores to Generate Highly Stable Luminescent Carbon-Centered Radicals

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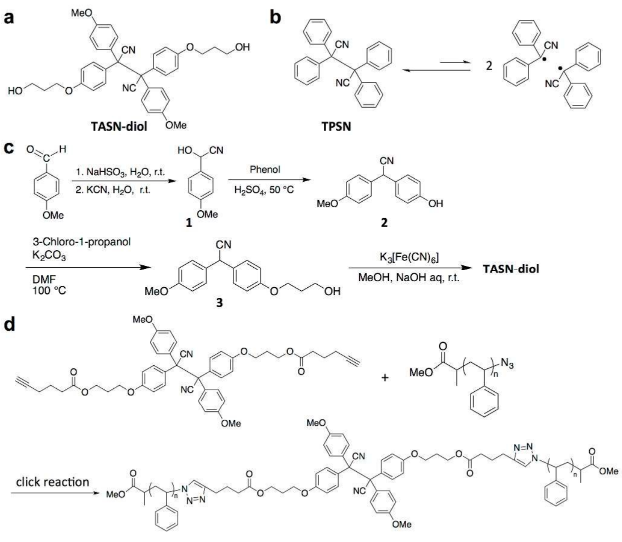
This paper reports on the design and synthesis of mechanochromophores with dynamic covalent system composed of tetraarylsuccinonitrile skeleton that generate metastable organic luminescent carbon radical. The mechanically generated radical species showed pink color and yellow light emission under UV irradiation. Unusually high stability of luminescent carbon-centered radicals was also observed in a polymer system.

Mechanochromic luminescent materials,[1] which exhibit simple and/or luminescent color changes in response to external mechanical stimuli such as shearing, stretching, and compressing, often in a reversible manner, have been attracting considerable research interests because of their potential applications in optoelectronic devices, sensors, probes, and optical data storage devices.[2-4] Many mechanochromic luminescent materials have been developed so far, utilizing organometallic complexes,[5] organic crystalline compounds,[6,7] liquid crystalline compounds,[8] and force-sensitive molecules (i.e., mechanophores).[9–11] In these systems, color changes and/or luminescent color changes are usually associated with changes in the chemical structures or formation/deformation of aggregation structures owing to non-covalent interactions, e.g., π-π interactions. These systems are often irreversible because the luminescent changes originate from changes to more stable states in response to mechanical stress. In some cases, however, the changed structure can be reverted to the original thermodynamically stable one, although thermal energy or solvent assistance is required. Dynamic covalent systems that generate metastable organic radicals are promising candidates as mechanochromic or mechanoluminescent systems, because the systems can autonomously go back to the thermodynamically stable original states without generating any byproduct.[12–17] However, the example of photostable radical with luminescent property is extremely limited and easily degrades upon photoexcitation.[18–20] Therefore, developing a mechanochromic luminescent molecule based on radical systems will expand the scope of mechanochemistry[21–23] and luminescent organic radicals in scientific research.

We focused on tetraarylsuccinonitrile (TASN) derivatives as promising candidates for mechanochromophores, which can potentially generate radical species (Scheme 1a). The simplest TASN, tetraphenylsuccinonitrile (TPSN), usually exists in a dimer form at room temperature but attains equilibrium with the corresponding radical species at moderate temperatures in solution (Scheme 1b).[24,25] Structural characterization of TPSN and TASN derivatives have been investigated and their reactivity have been studied.[26–30] The carbon-centered radicals generated are highly stable at room temperature unlike conventional carbon-centered radicals, but they dimerize to form more stable TASN structures. Furthermore, TPSN can act as an “iniferter” (initiator–transfer agent–termination) agent



Scheme 1. (a) Chemical structure of TASN-diol, (b) equilibrium between TPSN and corresponding radical species, (c) synthetic scheme for TASN-diol, and (d) synthetic scheme for a TASN-centered polystyrene.

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for radical polymerization at elevated temperatures.[25,26] Recently, Scaiano *et al.* revealed that the radical species generated from TPSN has high tolerance to oxygen[24,25] and that the bond dissociation energy (BDE) of the central C‒C bond in TPSN is quite low (109.6 kJ mol^{-1}).[25] In addition, TASN derivatives showed thermochromic behavior based on dissociated radicals.[25,31] However, the luminescent property of the radicals generated and mechanochromic behavior of TASN derivatives have never been investigated, despite the low BDE of TASN derivatives being expected to induce mechanical dissociation[12] and the carbon-centered radicals being analogous to photoluminescent diphenylmethyl radicals.[18]

Herein, we report the mechanochromic property of TASN derivatives based on homolytic cleavage of central carbon–carbon covalent bonds and chromic properties and stability of the radical spices generated. A dihydroxy-functionalized TASN derivative (TASN-diol) was designed and synthesized due to its facile introduction into polymer systems, and the preparation of a TASN-containing polystyrene and its mechanoresponsive behavior were demonstrated (Scheme 1c,d).

The designed TASN-diol was synthesized according to Scheme 1c. 4-Methoxymandelonitrile (**1**), prepared from *p*-anisaldehyde and KCN, was condensed with phenol under acidic conditions; the obtained compound (**2**) with a phenolic hydroxy group was converted to precursor **3** with an aliphatic hydroxy group to extinguish the reactivity against radicals. Finally, oxidative coupling of **3** was performed to afford TASN-diol as a white powder in 50% overall yield. The chemical structure of TASN-diol was fully characterized by ^{1}H and ^{13}C NMR and FT-IR spectroscopies and fast atom bombardment mass spectrometry (FAB-MS) (Figures S1 and S2).

TASN-diol, a white powder was ground using a mixing mill at room temperature to investigate its mechanoresponsive property. The powder changed in color from white to pink after grinding (Figure 1a) and then the color gradually faded within a few hours (Figure S5). Importantly, the pink color could be induced repeatedly by regrinding after complete disappearance of the previous color. On the other hand, no color change was observed with heating from 20 °C to 70 °C. Therefore, this chromic behavior is not derived from local thermal stimulus but from mechanical one. To confirm the generation of a radical species by the grinding process, electron paramagnetic resonance (EPR) spectroscopic analysis was undertaken before and after grinding. As shown in Figure 1a, drastic increase in the peak intensity was observed after grinding. Furthermore, the estimated g value (2.003) was consistent with the generation of a carbon-centered radical, indicating that the central carbon–carbon bond in TASN-diol can undergo homolytic bond cleavage in response to mechanical stress and generate the corresponding radical species with pink color. The simulated stable structure by density-functional theory (DFT) calculations (Figure S6) strongly supported this result, and the spin density is distributed on the central carbon atom and also on the cyano and phenyl moieties. On the other hand, TPSN powder showed no significant color change after being ground by the same procedure (Figure S7). EPR measurements suggested a dissociation ratio of 0.028 % for TASN-diol after grinding, nearly 5 times as large as that of TPSN (5.5×10^{-3}%) with good reproducibility (Figure S7). The difference in mechanoresponsiveness might be due to the so-called "captodative stabilization effect,"[32] thus, the electron-donating alkoxy functions at the para-position of phenyl rings in TASN-diol was considered to play a key role in stabilizing the generated radical. These results suggested that the observed disappearance of pink color was due to the recombination of mechanically generated radicals to afford the original dimer form, TASN-diol. Indeed, the pink color disappeared immediately on adding a good solvent for TASN-diol.

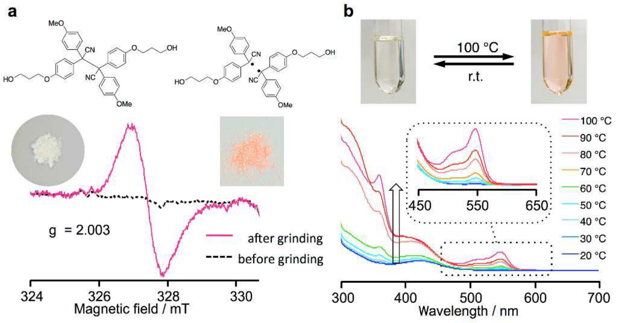

Fig. 1 (a) EPR spectra for TASN-diol before and after grinding. (b) Reversible change in dissociation–association equilibrium during heating–cooling cycles from rt to 100 °C and the UV-vis spectra for TASN-diol in DMAc.

To evaluate the mechanoresponsive color change and estimate the BDE of the central C–C bond of TASN-diol, UV-Vis absorption spectroscopy was used in DMAc at various temperatures between 20 and 100 °C. With increasing temperature, new absorption peaks arose at around λ_{max} = 350 nm and 550 nm and increased (Figure 1b); these peaks showed reversibility on increasing/decreasing the temperatures. The absorption peak at 550 nm corresponds to the pink color based on the dissociated radical owing to extension of the conjugated system. The BDE of the central C–C bond in TASN-diol was estimated as the enthalpy change (ΔH_{UV}) in the van't Hoff plot to be 92.9 kJ mol^{-1} (Figure S9). It value was slightly smaller than that previously reported for TPSN (109.6 kJ mol^{-1}), in accordance with the abovementioned EPR results. To further verify the obtained value, variable-temperature EPR measurements were obtained in solution, and the g value of 2.003 completely agreed with that for a mechanically induced one in solid state (Figures 2a, S10, and S11). The calculated parameters are summarized in Table S1. It was concluded that the estimated BDE value is authentic and selective scission of the central C–C bond in TASN-diol occurred both in solution and the bulk state.

Considering previously reported diphenylmethyl radical systems,[18–20] the absorption peak observed at around λ_{max} = 350 nm in UV-vis spectrum was ascribed to the excitation absorption of the generated radical species. Indeed, the TASN-diol solution emitted yellow photoluminescence under UV irradiation at 365 nm (Figure S12). The fluorescence spectrum of the DMAc solution (1×10^{-5} M) of TASN-diol exhibited an

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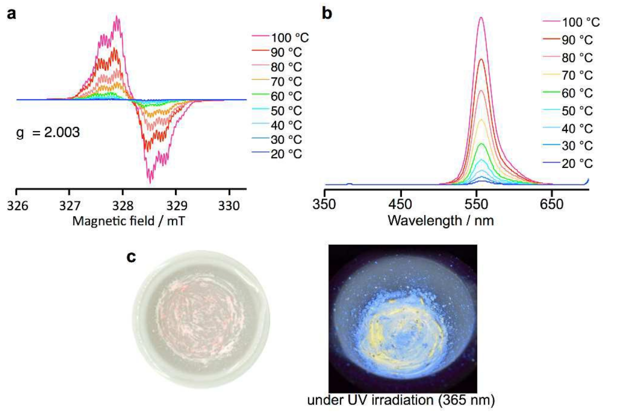

Fig. 2. (a) EPR spectra for TASN-diol in DMAc at various temperatures. (b) Fluorescence spectra for TASN-diol in DMAc. (c) Images of ground TASN-diol under UV irradiation at 365 nm.

emission peak at $\lambda_{max,em}$ = 560 nm; the heating obviously augmented the emission (Figure 2b, Figure S13). In accordance with the variable-temperature EPR measurements, the yellow photoluminescence could be attributed to the activated radicals arising from TASN-diol because the emission signal intensity strongly depended on the amount of radicals generated. In fact, the yellow photoluminescence was only observed from the grinding part of the pink-colored region (Figure 2c). Moreover, the luminescence spectrum of TASN-diol before and after grinding was measured at room temperature. The luminescence was only observed from ground TASN-diol, and the maximum emission peak exhibited at 565 nm as similar to solution state (Figure S14). Here, the absolute photoluminescence quantum yield of the ground TASN-diol was measured to be 39%. Thus, TASN-diol not only shows mechanochromism with color change, but also potentially shows yellow-emitting photoluminescence under UV irradiation.

Based on these findings, we designed and synthesized a mechanochromic polymer including a TASN unit at the center of the polymer chain (Scheme 1d). To evaluate the stability of the yellow-emitting activated radicals in solid state, the glassy polystyrene (PS) chain was chosen as it was expected to suppress radical recombination.[33,34] TASN-containing PS was prepared by combining atom transfer radical polymerization (ATRP) and a click reaction. Alkyne-difunctionalized TASN was prepared by esterification of TASN-diol and 5-hexynoyl chloride; ω-terminated azide polystyrene (PS-N_3, M_n = 31.8 kg/mol) was prepared by ATRP of styrene and subsequent conversion of the bromo-terminal by treatment with sodium azide. After the click reaction of TASN with two alkyne groups and PS-N_3, the SEC showed two distinct peaks for the linked product and the residual PS-N_3. PS with one TASN at the center of the polymer chain (PS-TASN-PS) was successfully isolated by fractional precipitation using tetrahydrofuran (THF)/acetone and showed a sharp SEC peak (M_w/M_n = 1.09) and an expected molecular weight (M_n= 63.8 kg/mol), in good agreement with the theoretical value ($M_{ntheo.}$ = 64.1 kg/mol) and that calculated from the ^{1}H NMR spectrum (M_{nNMR} = 63.4 kg/mol) (Figure S3, S4).

The color of PS-TASN-PS dramatically turned from white to passion pink in response to mechanical force exerted using a mixing mill at room temperature similar to TASN-diol, and the pink-colored polymer showed strong yellow photoluminescence under UV irradiation (Figure 3a and S15). Unlike the case of TASN-diol, the pink color was retained even after several months, but it disappeared immediately on the addition of THF, a good solvent for PS, due to rapid increase in chain mobility and radical recombination. The white powder reprecipitated from this THF solution showed mechanochromism to passion pink again on grinding. The ground sample displayed EPR signals, and the estimated g value was 2.003, indicating the generation of carbon-centered radical similar to as for the ground TASN-diol sample (Figure 3b). On the other hand, no EPR signal was observed for the ground PS homopolymer (M_n = 64.0 kg/mol), indicating that TASN moieties incorporated into the mid-chains were selectively cleaved. An interesting comparison can be made between the TASN-containing PS and TASN-diol. PS-TASN-PS had only one TASN unit in each chain, but the dissociated TASN ratio for PS-TASN-PS (5.08%) was 168 times of that of TASN-diol (2.79×10^{-2} %). Moreover, the ratio of dissociated TASN radical in a blend sample of TASN-diol and PS homopolymer was comparable to that of TASN-diol (Figure S8). Therefore, the TASN-containing polymer system successfully functioned as a mechanochromic polymer and mechanical stress effectively transferred to the TASN unit through the polymer chains due to an increase of intermolecular entanglements compared with TASN-diol[33,35–38].

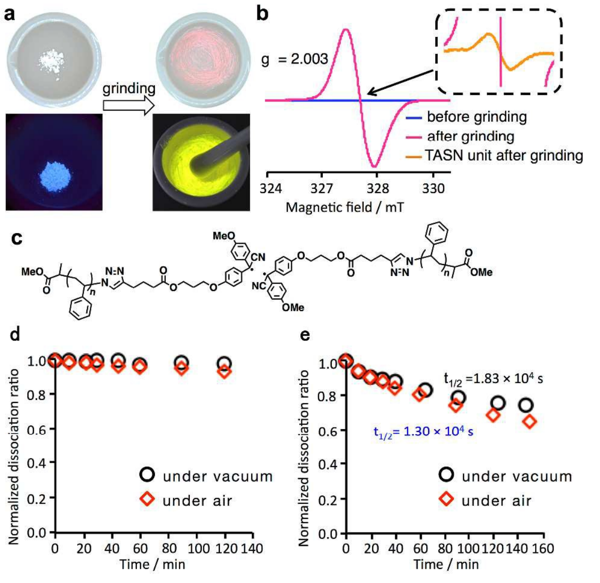

Fig. 3. (a) Photographs of PS-TASN-PS before and after grinding and ground sample under UV irradiation. (b) EPR spectra for PS-TASN-PS before and after grinding. (c) Schematic representing cases before and after grinding PS-TASN-PS. (d) Radical intensity transitions in EPR measurements and (e) those under UV irradiation after grinding PS-TASN-PS.

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Finally, we evaluated the stability of the activated radicals in ground PS-TASN-PS (Figure 3c) by monitoring the peak intensity under UV irradiation using EPR spectroscopy. Oxygen tolerance in solid state was first evaluated without irradiation: decay of the radical intensity was comparable in air and in vacuum (Figure 3d). Then, we investigated the photostability of radical species mechanically induced from PS-TASN-PS under UV irradiation at 360 nm. The half-life ($t_{1/2}$) of the radical attenuation in air was estimated to be 1.30×10^4 s, close to that in a sealed condition (1.83×10^4 s) (Figure 3e). This unusually high stability might be attributed to the stabilized singly occupied molecular orbital (SOMO) level resulting from the electron-withdrawing cyano group directly combined with the carbon-centered radical and electron-donating alkoxy functions.[39,40] Thus, the mechanically induced TASN radical had high stability not seen in other luminescent organic radical compounds.

In conclusion, we successfully demonstrated that the designed TASN functioned as a novel color-changing and yellow-light-emitting mechanochromophore based on reversible homolytic cleavage of the central dynamic C–C covalent bond under mechanical stress. The TASN-containing polymer system also displayed a passion pink color and yellow photoluminescence in response to mechanical stress, and the mechanoresponsiveness of the TASN mechanochromophore connected to polymer chains was enhanced remarkably. We also revealed the peculiar stability of the dissociated TASN radical in air and demonstrated the potential of TASN as a functional unit in various smart materials for highly sensitive visualization and quantitative detection.

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Conflicts of interest

There are no conflicts to declare.

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