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Electronic Supplementary Information (ESI)

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

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Supporting Information

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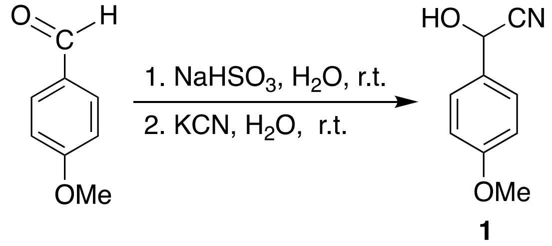
1. General Information

All solvents and reagents used were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, or Kanto Chemical and used as received, unless otherwise noted. 5-Hexyoyl chloride was synthesized according to the literature.[1] 1,4-Dioxane was purified by basic alumina column (Merck KGaA) to remove the stabilizer prior to use. Styrene was distilled under reduced pressure over CaH_2 before used. Benzene, triethylamine, and pyridine were dried over 4A molecular sieves. CuBr was purified by washing with acetic acid. All the reactions were carried out in dehydrated solvents under nitrogen atmosphere. ^{1}H NMR spectra were measured at 25 °C using a 300 MHz Bruker spectrometer with tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) or dimethyl sulfoxide-d_6 (DMSO-d_6). IR spectra were obtained with a Perkin-Elmer Spectrum One infrared spectrometer as thin films with KBr. Elemental analysis was carried out with Elementar Vario EL. Variable-temperature electron paramagnetic resonance (VT EPR) measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller. VT UV–vis absorption spectra were measured with JASCO V-550 spectrophotometer equipped with JASCO ETC-505T temperature controller. Fluorescence measurements were carried out using a spectrofluorometer (JASCO FP-6500) equipped with a temperature controller (JASCO ETC-273T) between 360 and 800 nm. Absolute photoluminescence quantum yields and fluorescence spectra were obtained on a Hamamatsu Photonics, Absolute PL Quantum Yield Measurement System, C9920-02G. Size exclusion chromatography (SEC) measurements were carried out at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards ($M_n = 4430-3242000$; $M_w/M_n = 1.03-1.08$) were used to calibrate the SEC system. DFT calculations were executed using the Gaussian09 program package. TDDFT calculations were performed using UB3LYP with the 6-31G* basis set.

2. Synthetic Procedure

2.1. TASN-diol

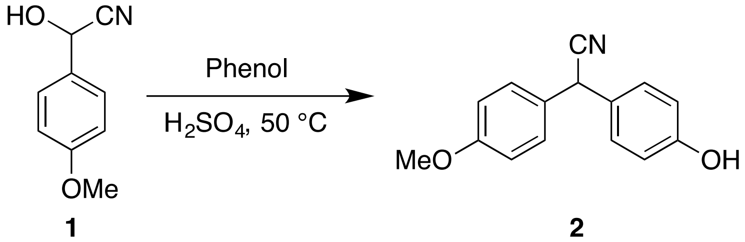
2.1.1. 4-Methoxymandelonitrile (1)



The solution of sodium bisulfite (66.6 g, 640 mmol) in water (230 mL) was added dropwise into *p*-anisaldehyde (35.0 mL, 288 mmol) at room temperature and allowed to stir for 2.5 h. Then, a KCN (41.7 g, 640 mmol) aqueous solution (156 mL) was added dropwise into the solution at 0 °C, and the reaction mixture was allowed to stir at room temperature for 2 h. After extracting with ethyl acetate, the organic layer was washed with brine, dried with Na_2SO_4 and evaporated the solvent. The residue was filtrated, washed with hexane, and dried *in vacuo* to give **1** as a white powder (39.8 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.49–7.44 (m, 2H, aromatic), 6.98–6.93 (m, 2H, aromatic), 5.49 (s, 1H, –C*H*(CN)OH), 3.84 (s, 3H, $–OCH_3$), 2.45 (s, 1H, –OH).

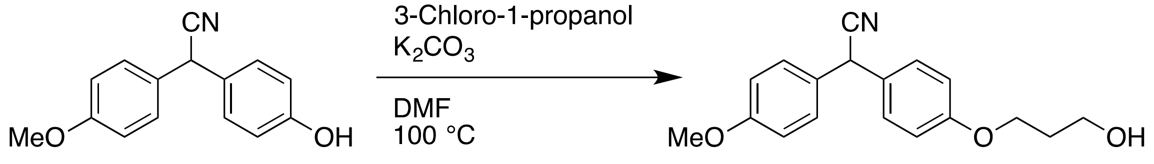
2.1.2. 2-(4-Hydroxyphenyl)-2-(4-methoxyphenyl)acetonitrile (2)



In a 300 mL two necked round bottom flask, 35% sulfuric acid (32.7 mL), compound **1** (6.52 g, 40.0 mmol), and phenol (9.05 g, 288 mmol) were added, and the mixture was allowed to stir at 50 °C for 21 h. After cooling to room temperature, the remaining liquid was decanted and the residual solid was dissolved in ethyl acetate. The organic layer was washed with brine and water, and evaporated. The residue was reprecipitated from THF to water, filtrated, and dried in vacuo to give compound **2** as a white powder (8.88 g, 93%).

^{1}H NMR (300 MHz, DMSO-d_6): δ/ppm 9.56 (br, 1H, –OH), 7.28–7.25 (m, 2H, aromatic), 7.16–7.13 (m, 2H, aromatic), 6.96–6.93 (m, 2H, aromatic), 6.78–6.75 (m, 2H, aromatic), 5.57 (s, 1H, –CH(CN)–), 3.73 (s, 3H, –OCH$_3$).; ^{13}C NMR (75 MHz, DMSO-d_6) : δ/ppm 158.87, 157.20, 129.23, 128.70, 128.67, 121.07, 115.93, 114.52, 55.19. FT-IR (KBr, cm^{-1}): 3466, 3021, 2955, 2904, 2839, 2370, 2337, 2243, 2046, 1886, 1765, 1604, 1511, 1445, 1350, 1299, 1256, 1224, 1180, 1110, 1026, 969, 825, 766, 692, 594, 536, 518. FAB-MS (*m*/*z*): [M]$^+$ calcd. for $C_{15}H_{13}NO_2$, 239.095; Found, 239.095.

2.1.3. 2-(4-(3-hydroxypropoxy)phenyl)-2-(4-methoxyphenyl)acetonitrile (3)

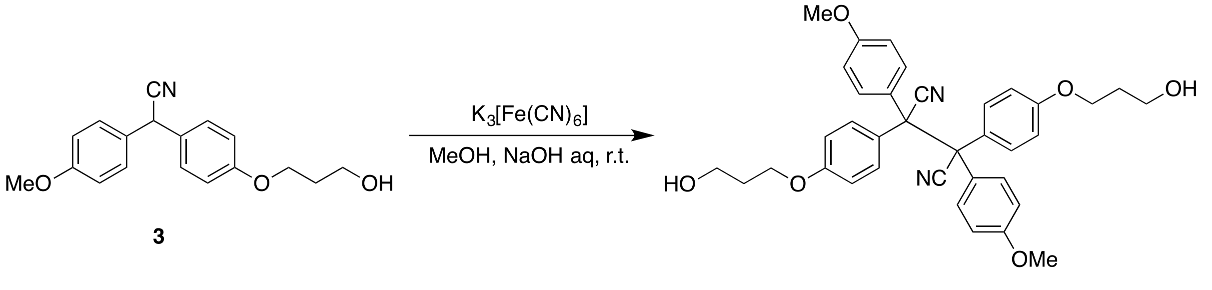


2 **3**

In a 300 mL round bottom flask, a mixture of compound **2** (15.6 g, 65.0 mmol), potassium carbonate (18.0 g, 130 mmol), and DMF (163 mL) was heated to 100 °C for 1 h. 3-Chloro-1-propanol (10.8 mL, 130 mmol) was added to the reaction mixture, the mixture was allowed to stir at 100 °C for 1.5 h. After extracting with ethyl acetate and washed with brine and water, the organic layer was dried with Na_2SO_4 and evaporated. The residue was isolated by column chromatography using silica gel and ethyl acetate/hexane (1/1, v/v) as eluents to give **3** as pale yellow oil (13.5 g, 70%).

^{1}H NMR (300 MHz, CDCl$_3$): δ/ppm 7.24–7.20 (br, 4H, aromatic), 6.90–6.86 (br, 4H, aromatic), 5.03 (s, 1H, –CH(CN)–), 4.08 (t, *J* = 6.0 Hz, 2H, –OC*H*$_2$CH$_2$–), 3.82 (q, *J* = 6.0 Hz, 2H, –CH$_2$C*H*$_2$–OH), 3.78 (s, 3H, –OCH$_3$), 2.16 (t, *J* = 6.0 Hz, 1H, –CH$_2$CH$_2$–O*H*), 2.01 (quint, *J* = 6.0 Hz, 2H, –CH$_2$C*H*$_2$CH$_2$–).; ^{13}C NMR (75 MHz, CDCl$_3$): δ/ppm 159.32, 158.61, 128.76, 128.59, 128.33, 128.22, 120.01, 115.02, 114.47, 65.41, 59.75, 31.91. FT-IR (NaCl, cm^{-1}): 3428, 2945, 2883, 2842, 2553, 2244, 2051, 1888, 1609, 1509, 1467, 1302, 1252, 1179, 1114, 1035, 952, 829, 590, 548, 417. FAB-MS (*m*/*z*): [M]$^+$ calcd. for $C_{18}H_{19}NO_3$, 297.137; Found, 297.137.

2.1.4. TASN-diol



3

A 5 M NaOH aqueous (57.9 mL) solution of potassium ferricyanide (6.36 g, 19.3 mmol) was added dropwise into **3** (5.22 g, 17.6 mmol) in methanol (140 mL) under water bath. The reaction mixture was allowed to stir for 5 min. After filtration of the reaction mixture, the solid product was washed with water and reprecipitated from chloroform solution to hexane three times. The obtained white powder was dried in vacuo at room temperature to give TASN-diol as a white powder (4.96 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.18–7.15 (br, 8H, aromatic), 6.77–6.75 (br, 8H, aromatic), 4.09 (t, J = 6.0 Hz, 2H, –OCH_2CH$_2$–), 3.84 (br, 4H, –CH$_2$CH_2–OH), 3.79 (s, 6H, –OCH$_3$), 2.04 (quint, J = 6.0 Hz, 4H, –CH$_2$CH_2CH$_2$–), 1.74 (br, 2H, –CH$_2$OH).; ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 159.38, 158.64, 131.35, 129.43, 129.26, 121.53, 113.83, 113.34, 65.51, 60.06, 58.44, 55.35, 31.98. FT-IR (KBr, cm^{-1}): 3416, 3048, 2948, 2844, 2558, 2374, 2337, 2243, 2048, 1890, 1744, 1607, 1509, 1468, 1301, 1256, 1185, 1127, 1036, 952, 827, 632, 598, 545. FAB-MS (m/z): [M]$^+$ calcd. for $C_{36}H_{37}N_2O_6$, 593.265; Found, 593.269.

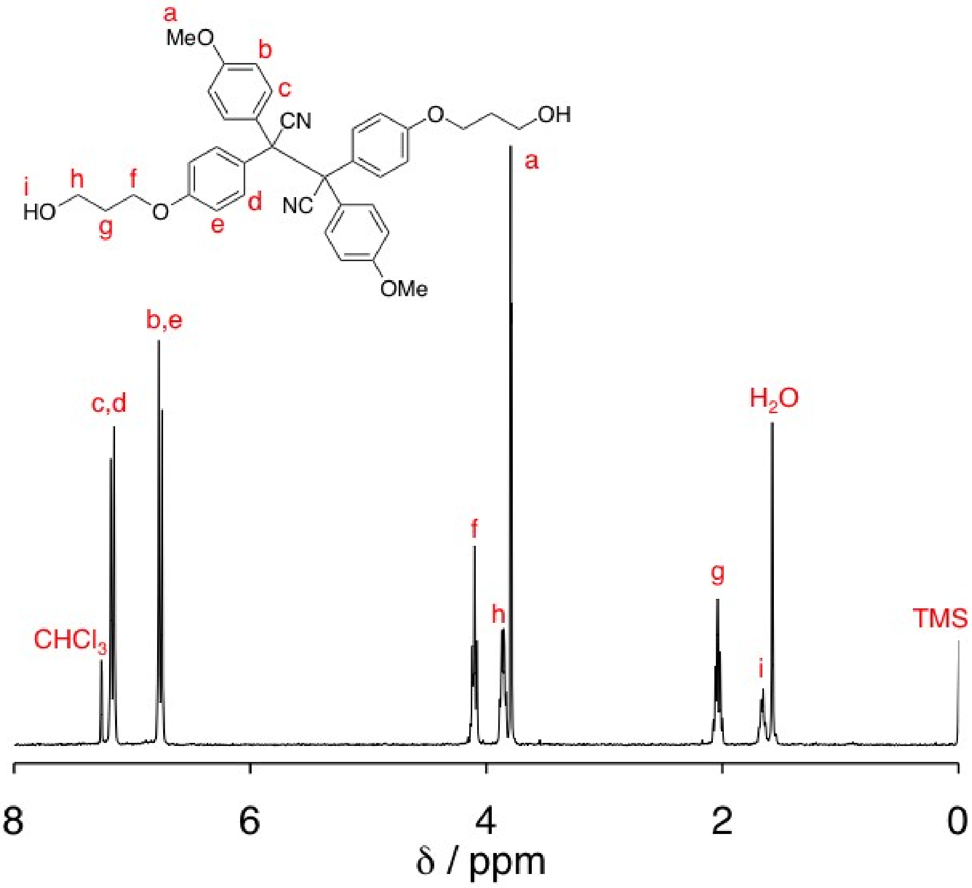


Figure S1. ^{1}H NMR spectrum of TASN-diol (in $CDCl_3$).

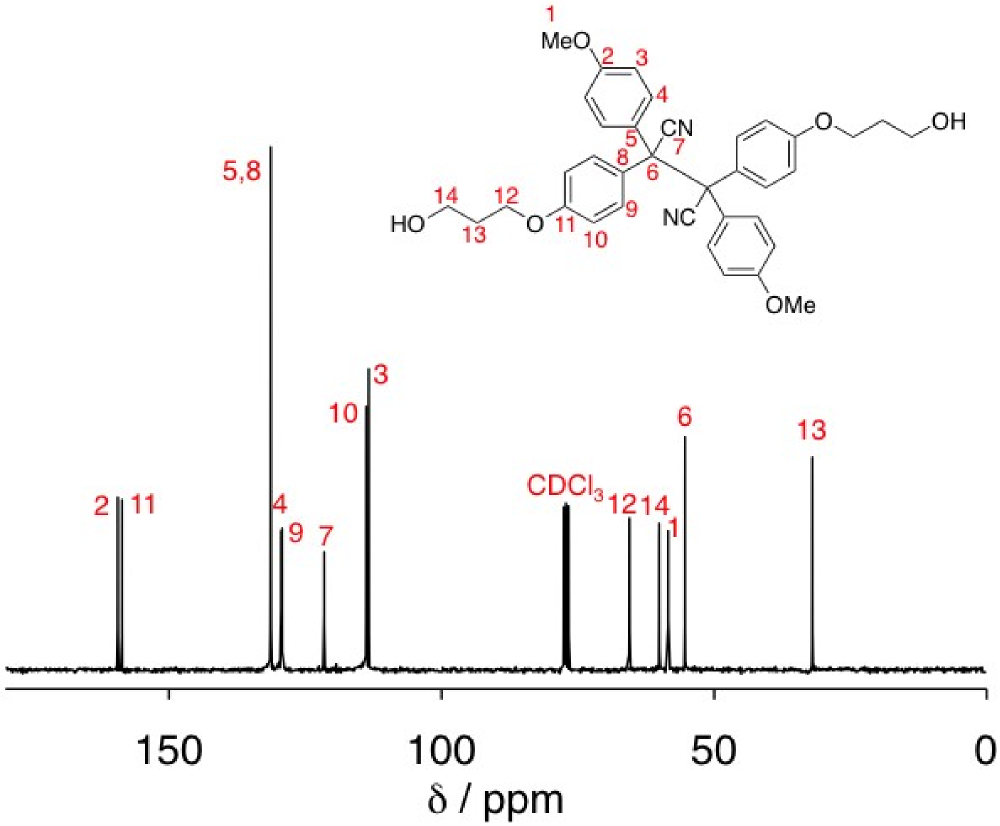
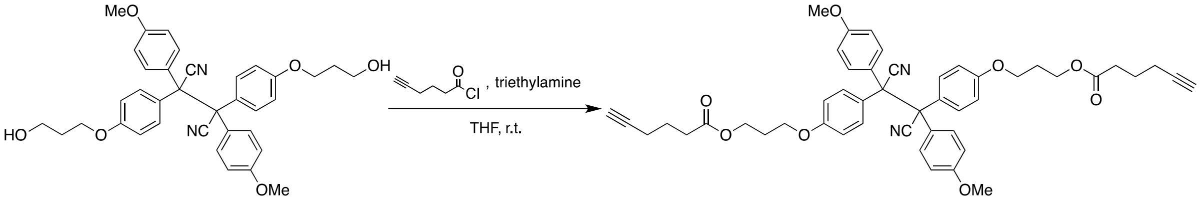


Figure S2. ^{13}C NMR spectrum of TASN-diol (in CDCl$_3$).

2.2. PS-TASN-PS

2.2.1. TASN-dialkyne



TASN-diol (119 mg, 0.20 mmol) and triethylamine (0.223 mL, 1.60 mmol) were dissolved in dry THF (2.00 mL) and cooled to 0 °C in an ice bath. A hexynoyl chloride (0.192 mL, 1.60 mmol) was added dropwise through syringe at 0 °C, and the reaction mixture was warmed to r.t and stirred for 5 h. After the reaction, it was poured into water, extracted with dichloromethane. The organic layer was washed with brine and dried with Na$_2$SO$_4$, filtrated, evaporated, and the residue was purified by silica gel column chromatography using ethyl acetate/hexane (1/6, v/v) as eluents and dried in vacuo to give TASN-dialkyne as a yellow oil (139 mg, 0.178 mmol, 89% yield). ^{1}H NMR (300 MHz,

$CDCl_3$): δ/ppm 7.18–7.15 (m, 8H, aromatic), 6.78–6.74 (br, 8H, aromatic), 4.27 (t, *J* = 6.0 Hz, 4H, –OC*H*$_2$CH$_2$OC(O)–), 4.02 (t. *J* = 6.0 Hz, 4H, –OC*H*$_2$CH$_2$CH$_2$O–), 3.79 (s, 6H, –OCH$_3$), 2.47 (t, *J* = 6.0 Hz, 4H, –OC(O)C*H*$_2$CH$_2$–), 2.29-2.24 (m, 4H, –CH$_2$C*H*$_2$CCH), 2.11 (quint, *J* = 6.0 Hz, 4H, –OCH$_2$C*H*$_2$CH$_2$O–), 1.97 (t, *J* = 2.6 Hz, 2H, –CCH), 1.85 (quint, *J* = 6.0 Hz, 4H, –OC(O)CH$_2$C*H*$_2$CH$_2$–).; ^{13}C NMR (75 MHz, $CDCl_3$): δ/ppm 173.14, 159.37, 158.58, 131.39, 129.44, 129.27, 121.55, 113.78, 113.34, 83.29, 69.35, 64.38, 61.27, 58.41, 55.38, 32.89, 28.62, 23.63, 17.91. FT-IR (KBr, cm^{-1}): 3293, 2957, 2842, 2558, 2347, 2240, 2116, 1889, 1733, 1607, 1510, 1466, 1365, 1301, 1256, 1186, 1036, 828, 758, 640, 544, 449.

2.2.2. ω-Azide-terminated polystyrene (PS-N_3)

In a round bottom flask, a mixture of styrene (70.0 mL, 609 mmol), toluene (46.9 mL), methyl 2-bromopropionate (113 mL, 1.02 mmol), and *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA) (21.2 mL, 1.02 mmol) was formed. The mixture was bubbled with nitrogen for 25 minutes, CuBr (146 mg, 1.02 mmol) was added, and the resulting solution was allowed to stir at 80 °C for 24 h. The reaction was stopped via exposure to air at 0 °C and dilution with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. After evaporation and precipitating into methanol, the resulting precipitate was collected by filtration and dried in vacuo to give ω-bromo-terminated polystyrene (PS-Br) as a white powder (26.9 g, 42% yeild). The M_n and M_w/M_n values were determined by SEC with polystyrene standards. M_n = 32000 g mol^{-1}, M_w/M_n = 1.15. ^{1}H NMR (300 MHz, $CDCl_3$) : δ/ppm 7.26–6.26 (br, aromatic), 4.40 (br, –C*H*Ph–Br), 3.51–3.38 (br, –OCH$_3$), 2.31–1.00 (br. backbone).

To a 200 mL round bottom flask with magnetic stir bar was added PS-Br (32 000 g mol^{-1}, 26.9 g, 0.840 mmol) and DMF (108 mL) was formed. Sodium azide (697 mg, 8.40 mmol) was added into the flask and the mixture was allowed to stir at room temperature for 24 h. After precipitation into methanol/water mixture (1/1, v/v), the resulting precipitate was collected by filtration and dried in vacuo to give ω-azido-terminated polystyrene (PS-N_3) as a white powder (26.7 g, 99% yield). M_n = 32000 g mol^{-1}, M_w/M_n = 1.17. ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 7.32–6.27 (br, aromatic), 3.93 (br, –C*H*Ph–N$_3$), 3.56–3.39 (br, –OCH$_3$), 2.32–1.00 (br. backbone).

2.2.3. PS-TASN-PS

TASN-dialkyne (46.9 mg, 60 μmol), PS-N_3 (32 000 g mol^{-1}, 4.03 g, 0.126 mmol), and PMDETA (12.5 mL, 0.600 mmol) were dissolved in DMF (12.6 mL) and then the solution was purged with a nitrogen atmosphere for 25 min. Cu (30.4 mg, 0.480 mmol) and CuBr (17.3 mg, 0.120 mmol) were added carefully, and the reaction mixture was allowed to stir at room temperature for 3 h. The reaction was quenched by exposing to air at 0 °C and diluted with $CHCl_3$. The polymer solution was filtered through a neutral alumina, and the solvent was removed, precipitated into methanol, and filtered. The SEC profile of the reaction mixture exhibited two peaks corresponding to the target PS-TASN-PS and the residual PS-N_3 used in excess. The PS-TASN-PS was isolated in 10% yield by fractional precipitation using acetone/THF and reprecipitated from THF to methanol and dried in vacuo. M_n = 64 000 g mol^{-1}, M_w/M_n = 1.09. ^{1}H NMR (300 MHz, $CDCl_3$) : δ/ppm 7.38–6.26 (br, aromatic), 5.06 (br, =CH(N)–), 4.22 (br, $–CH_2CH_2OC(O)–$), 3.98 (br, $–OCH_2CH_2CH_2O–$), 3.76 (br, $–OCH_3$), 3.55–3.38 (br, $–C(O)OCH_3$), 2.40–1.02 (br. backbone).

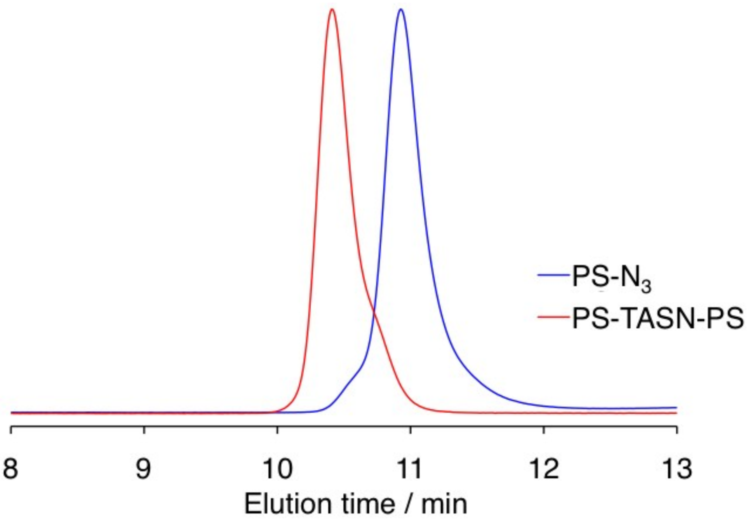


Figure S3. SEC charts of after isolated PS-TASN-PS and here used PS-N_3.

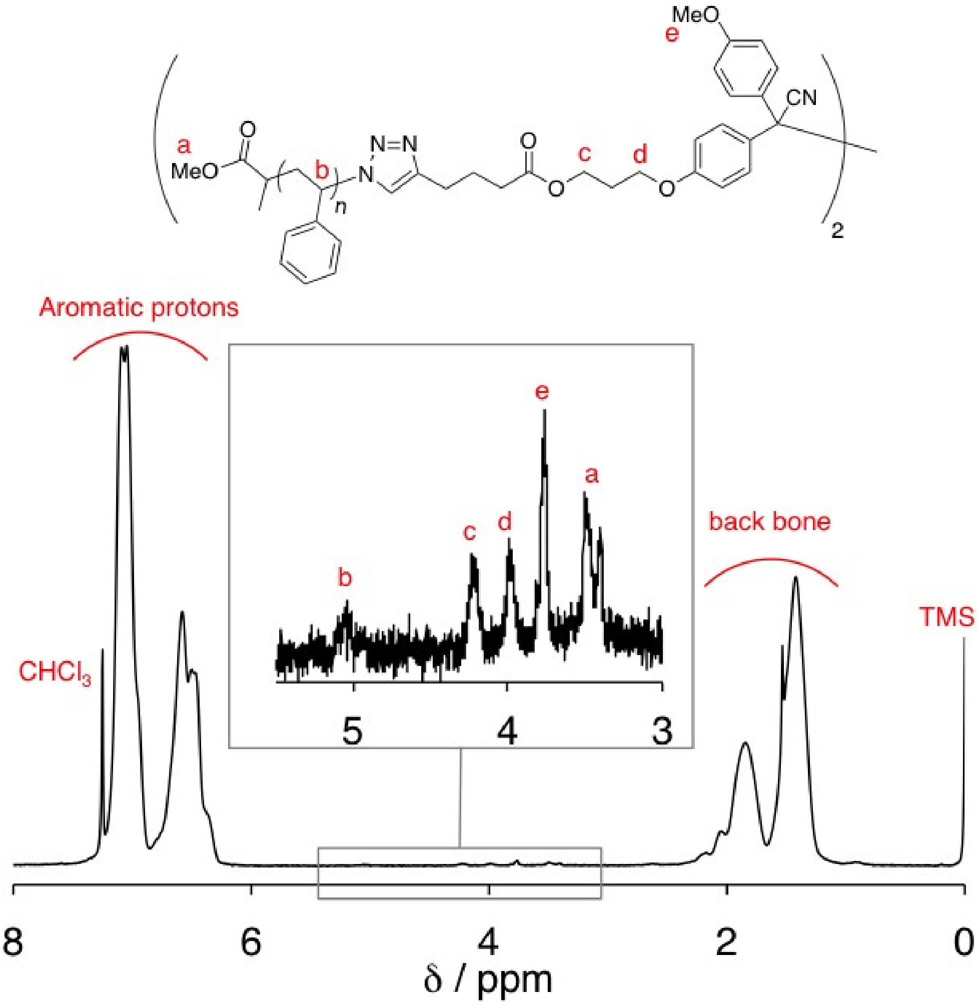


Figure S4. ^{1}H NMR spectrum of PS-TASN-PS (in $CDCl_3$).

3. Grinding Tests and EPR Study (solid state)

Grinding tests were performed using mixer mill machine (Retsch MM 400). The mechanical energy was controlled by the frequency of the screw-top grinding jars. The powder sample (50 mg) was placed in the jar and ground for 5 min at 25 Hz. The ground sample was transferred into an EPR glass capillary and weighted, and the capillary was sealed after being degassed. The spectra were measured using a microwave power of 0.1 mW and a field modulation 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.25 mT/s. The concentration of the formed radicals was determined by comparing the area of the observed integral spectrum with a 0.06 mM solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) in benzene under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard. The *g* value was calculated according to the following equation:

$$g = h\nu/\beta H$$

where h is the Planck constant, ν is the microwave frequency, β is the Bohr magneton and H is the magnetic field.

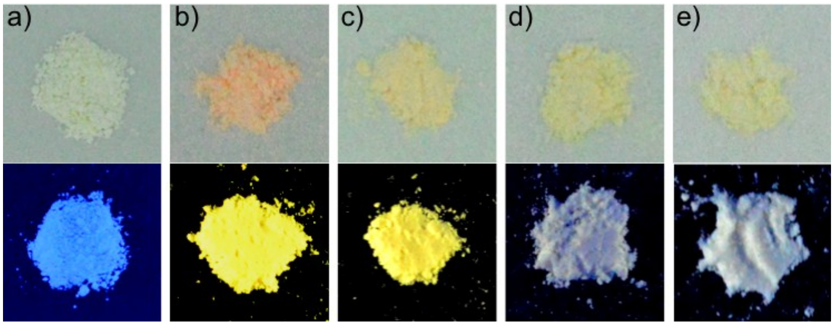


Figure S5. Photographs of time-dependence color change of ground TASN-diol a)before grinding, b)after grinding, c) after 1 h, d) 2 h, and e) 3 h (upper side: appearance, lower side: under 365 nm UV irradiation).

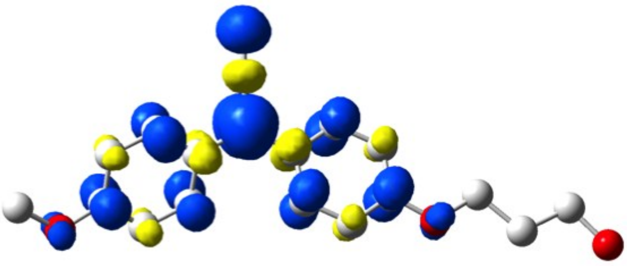


Figure S6. Spin density distribution calculated using DFT (UB3LYP/6-31G*).

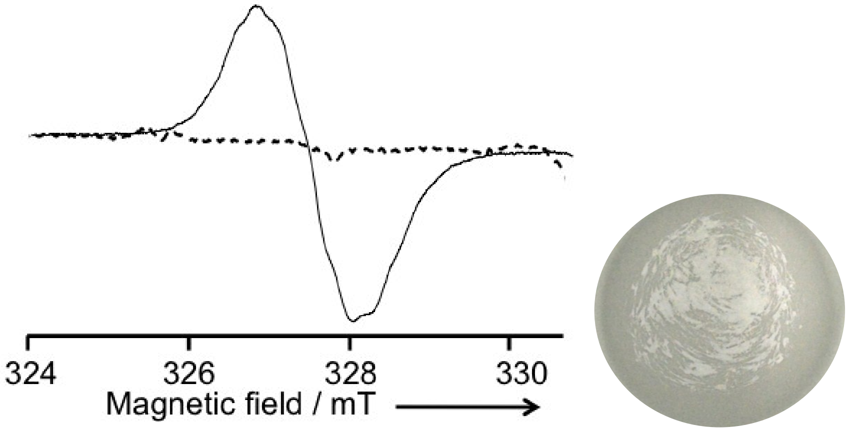


Figure S7. EPR spectra of TPSN before (dashed line) and after (solid line) grinding, and the photograph of after grinding TPSN.

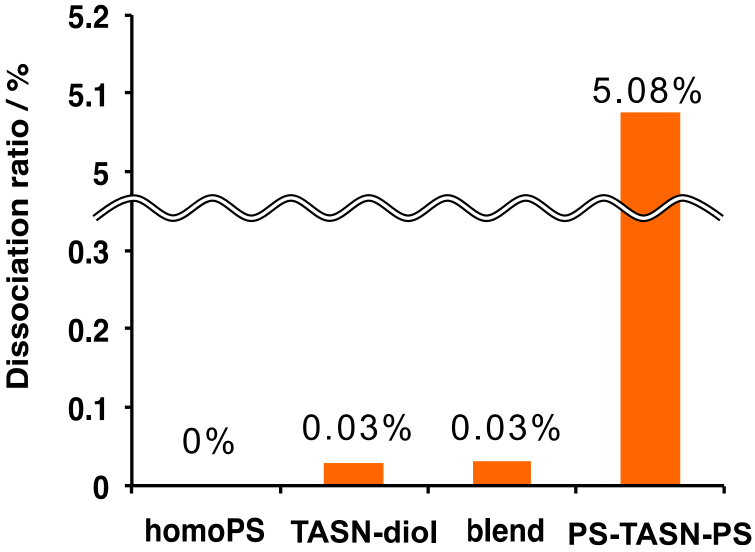


Figure S8. Dissociation ratio of polystyrene (homoPS), TASN-diol, blend sample of homoPS and TASN-diol, and PS-TASN-PS.

4. Variable Temperature UV–vis Spectroscopy

The measurements were carried out with a 1.0 mM DMAc solution of TASN-diol at from 20 to 100 °C. Spectra were measured after waiting for 5 min at each temperature, using a quartz cell with an optical path length of 1 mm.

The K_{eq} was calculated from the following equation and van't Hoff plot was prepared. The bond dissociation enthalpy (ΔH) and entropy (ΔS) were also calculated from the above-mentioned equation.

$$K_{eq} = 2A^2/\varepsilon l\ (2\varepsilon l - A)$$

where A is absorbance at 548 nm, ε is the molar absorbance constant each temperature at 548 nm, l is the optical path length.

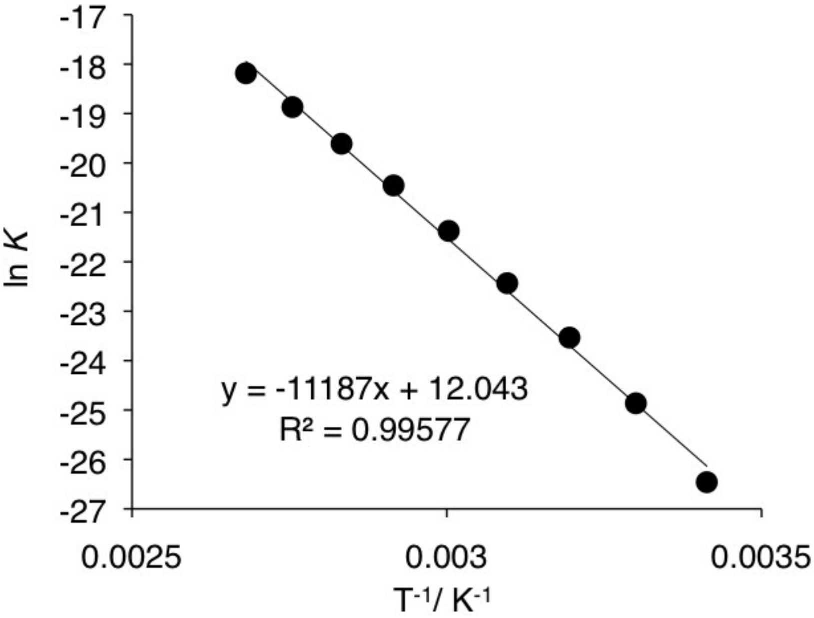


Figure S9. van’t Hoff plot for the dissociation of TASN-diol.

5. EPR Study (solution state)

A 50 mM dioxane solution of TASN-diol was charged in a 5 mm glass capillary with more than 43.5 mm height (the effective measuring range), and the capillary was sealed after being degassed. The spectra were measured using a microwave power of 0.7 mW and a field modulation 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.25 mT/s. In variable temperature measurements from 0 to 90 °C range, the spectra were measured after waiting for 5 min at each temperature. The concentration of the formed radicals was determined by comparing the area of the observed integral spectrum with a 0.06 mM solution of TEMPOL in the same solvent under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard. The *g* value was calculated according to the following equation:

$$g = h\nu/\beta H$$

The ratio of dissociated TASN-diol was calculated from the peak intensity using TEMPOL as a standard. van't Hoff plot was prepared, and the bond dissociation enthalpy (ΔH) and entropy (ΔS) were calculated from the following equation:

$$\ln K = -\Delta H/RT + \Delta S/R$$

where R is the gas constant and T is the measurement temperature.

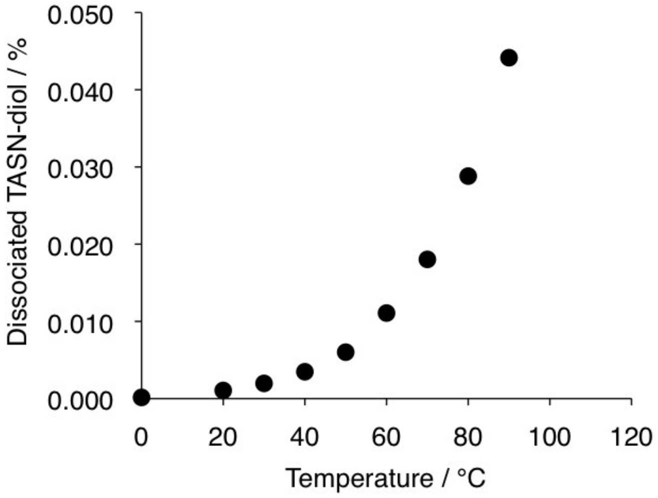


Figure S10. Percentage of dissociated TASN-diol.

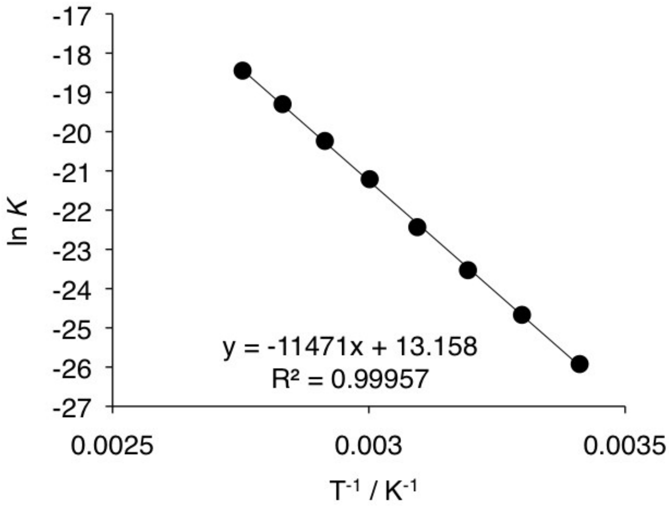


Figure S11. van’t Hoff plot for the dissociation of TASN-diol.

Table S1. Bond dissociation enthalpy and entropy of TASN-diol.

ESR		UV-vis	
Δ*H* (kJ/mol)	Δ*S* (J/K•mol)	Δ*H* (kJ/mol)	Δ*S* (J/K•mol)
95.4	107.9	92.9	100.0

6. Variable Temperature Fluorescent Spectroscopy

The measurements were carried out with a 1×10^{-5} M DMAc solution of TASN-diol at from 20 to 100 °C. The excitation wavelength at 350 nm was selected using interference filters, and the fluorescence emission was observed at 561 nm.

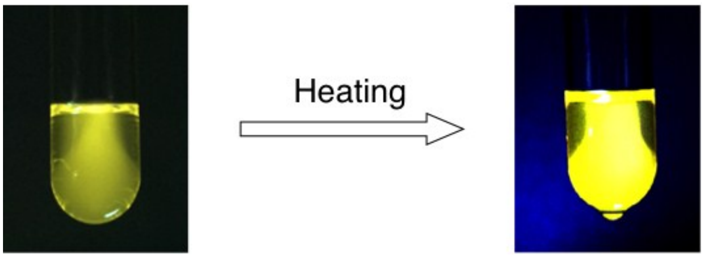


Figure S12. Photographs of before and after heating of TASN-diol under UV light at 365 nm.

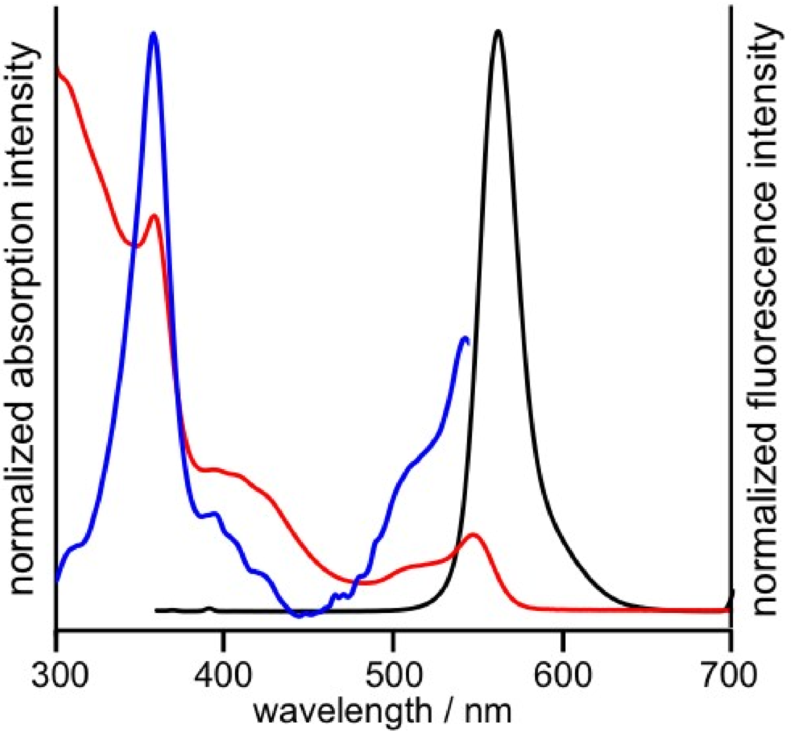


Figure S13. UV-Vis absorption (red), excitation (blue) and fluorescence (black) spectra of TASN-diol in DMAc at 100 °C.

7. Fluorescent Spectroscopy (solid state)

The measurements were carried out using before and after grinding TASN-diol and PS-TASN-PS. The excitation wavelength at 350 nm was selected, and the each of fluorescence emission was observed at 565 and 555 nm, respectively.

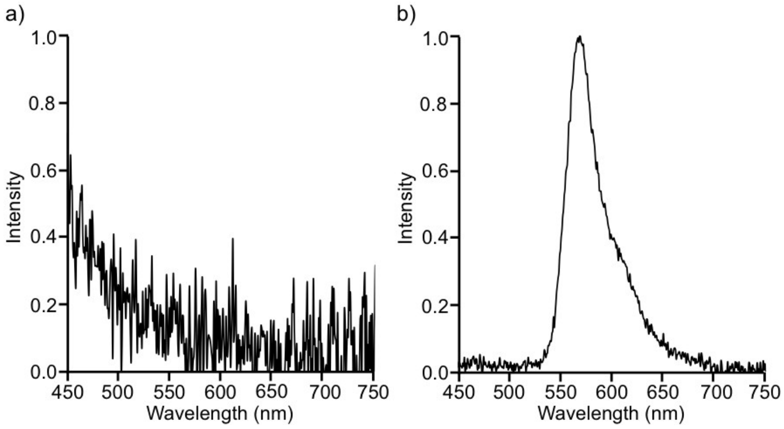


Figure S14. Fluorescent spectra of before and after grinding TASN-diol with excitation at 350 nm.

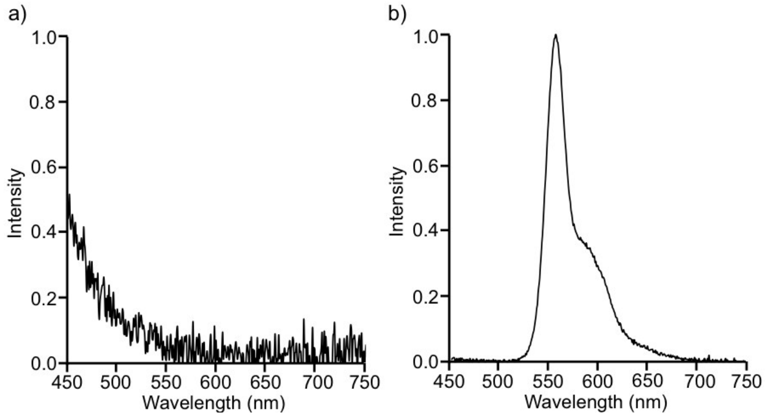


Figure S15. Fluorescent spectra of before and after grinding PS-TASN-PS with excitation at 350 nm.

8. Photostability Study

The powder sample (50 mg) was placed in a screw-top grinding jar and was ground for 5 min at 25 Hz using mixer mill machine (Retsch MM 400). The ground sample was transferred into an EPR glass capillary and weighed, and the capillary was sealed after being degassed or used intact. The sample was irradiated under UV light (USHIO ES-UXL500, 500 W Xe lamp equipped with cutoff filters (U-360 and HA-50, JEOL) of transmission range from 300 to 400 nm and maximum at 365 nm, 10 mW cm^{-2}) maintained at 25 °C with temperature controller. The EPR spectra were measured using a microwave power of 0.1 mW and a field modulation 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.25 mT/s. The concentration of the formed radicals was determined by comparing the area of the observed integral spectrum with a 0.06 mM solution of TEMPOL in benzene under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard.

9. Reference

1. R. A. Earl, K. P. C. Vollhardt, *J. Org. Chem.* **1984**, *49*, 4786–4800.