Supporting Information

A Nonconjugated Radical Polymer with Stable Red Luminescence in the Solid State

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Content

1. General information

4-hydroxy-2,2,6,6-tetramethylpiperidin-N-oxy (TEMPO-OH) and epichlorohydrin was purchased from J&K. Tetrabutylammonium hydrosulfate (TBA) and ascorbic acid were purchased from Sigma-Aldrich. Potassium *tert*-butoxide was purchased from Meryer. 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-N-[methoxy-(polyethylene glycol) (DSPE-PEG) was purchased from Xi'an Ruixi Biological Technology Co., Ltd. LysoTracker Green (LTG) were purchased from ThermoFisher Scientific. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. Other reagents and solvents were used as received from Sigma-Aldrich and J&K used without further purification. Water used was ultra-pure water purified by Milli-Q® Reference Water Purification System.

2. Characterization

Relative number-average (M_n) and weight-average (M_w) molecular weights and polydispersity indices (M_w/M_n) of the polymers were estimated on a Waters gel permeation chromatography (GPC) system equipped with a Waters 486 wavelength-tunable UV-vis detector using THF as an eluent. Details about the sample preparation and the experimental setup can be found in our previous publications.[1,2] Absolute molecular weights were obtained by tandem GPC experiments using a system equipped with an isocratic pump (Waters 2414), a Down HELEOS multi-angle laser light scattering (MALLS) detector and an Optilab rEX refractive index detector (Wyatt technology, Santa Barbara, CA). The separations were carried out using size-exclusion columns (400 Å, 103 Å and 104 Å phenogel columns, 5 µm, 300 × 7.8 mm, Phenomenex, Torrance, CA) connected in series at 45 °C with DMF containing 0.1 M LiBr as the mobile phase. The MALLS detector was calibrated by pure toluene without external polymer standards. The absolute M_w of polymers were calculated by their d_n/d_c values determined offline using the internal calibration system (ASTRA V software, version 5.1.7.3, Wyatt Technology, Santa Barbara, CA).

High resolution mass spectra (HRMS) were performed on a Finnigan MAT TAQ 7000 mass spectrometer system operating in matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF) mode. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70 FTIR spectrometer with attenuated total reflection (ATR) mode. The thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer TGA 7 analyzer and a TA Instruments DSC Q1000, respectively, at a heating rate of 10 °C/min under nitrogen. Electron paramagnetic resonance (EPR) spectroscopy experiments were completed using a JES-FA200 EPR spectrometer at room temperature. ^1H NMR spectrum was measured on a Bruker AV 400 NMR spectrometer in $(CD_3)_2SO$.

UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda spectrophotometer. Photoluminescence (PL) spectra of solid was recorded a Horiba FluoroLog-3 fluorescence spectrophotometer. Absolute fluorescence quantum yield was measured on a Hamamatsu Quantaurus-QY C11347. Fluorescent photos were taken by Olympus BX 41 upright biological microscope with fluorescent accessories and CCD camera. Powder X-ray diffraction (PXRD) pattern was collected on an X’per Pro (PANalytical) instrument with Cu Kα radiation (λ = 1.5418 Å) at 25 °C (scan range: 5–30°). The samples for XRD measurements were prepared by casting powders on glass wafer.

The temperature-dependent PL spectrum were collected with a two-lens system and detected using an optical fiber positioned at the focus of lens. The spectra were recorded with an Andor Shamrock SR-500i spectrometer with silicon detector cooled down to -60 °C. The samples were mounted in a liquid helium continuous flow cryostat. The sample temperature was controlled via an active feedback heater and temperature controller.

3. Organic Synthesis

Synthesis of GTEMPO

The monomer, GTEMPO, was synthesized as reported.[3] Briefly, TEMPO-OH was purified by recrystallization before use. Sodium hydroxide (NaOH) (8 g) was gradually added to deionized water (16 mL) in a 250 mL round-bottom flask under vigorous stirring. After NaOH was completely dissolved, epichlorohydrin (10 mL, 120 mmol) and TBA (1.5 g, 4.6 mmol) were added. A solution of TEMPO-OH (4.12 g, 24 mmol) in 20 mL tetrahydrofuran (THF) was then added dropwise into the mixture. The resulting solution was stirred at room temperature overnight. The reaction mixture was poured into 200 mL of ice water and then extracted with ethyl acetate (EA). The organic layer was washed with sodium chloride (NaCl) aqueous solution and then extracted with ethyl acetate again. The combined organic layers were then dried over anhydrous sodium sulfate. After filtration, the filtrate was evaporated under reduced pressure and the crude product was purified on a silica gel column using hexane/EA (8/1, v/v) as the eluent. The oily product obtained was freeze-dried for 1 day to yield the monomer, GTEMPO, as a red crystalline solid.

Synthesis of PGTEMPO

The polymerization of the monomer was achieved using a procedure optimized from the literature.[4] GTEMPO was further dried under reduced pressure for one day before use and stored in glove box. Inside a glove box, a mixture of GTEMPO (300 mg, 1.31 mmol) and potassium *tert*-butoxide (12 mg) were added into a 10 mL Schlenk tube with a stirring bar, which was already dried in a hot oven overnight. Then, the tube was sealed with a rubber stopper. The reaction mixture was heated at 80 ° C for 2 hours without solvent and then was injected with 2 mL anhydrous THF for another 8 hours. The mixture was vortexed after addition of solvent to make sure the mixture was well dissolved in THF. After cooling down to room temperature, NaCl aqueous solution was added to mixture, followed by extraction with chloroform for three times. The organic solvent was removed under reduced pressure and the crude polymer dissolved with a small volume of THF. The crude polymer solution was passed through a simple column filled with neutral Al_2O_3 powder and precipitated in hexane. The precipitates were collected by ultracentrifugation (7000 rpm for 3 min). This protocol was repeated for three times to remove excess unreacted monomer. The polymer was dried overnight in a vacuum oven at room temperature to obtain an orange solid. M_n = 5,400; M_w = 8,800; M_w/M_n = 1.63 (GPC, polystyrene calibration).

TEMPO-doped and PGTEMPO-doped commercial polymer

To achieve the TEMPO-doped polystyrene (PS), PS was dissolved in toluene with TEMPO, at the mole ratio of 1:1, in which the polymer was calculated by unit molecular weight. After stirring and sonication, the mixture was evaporated under reduced pressure and an orange solid product was obtained.

To achieve the PGTEMPO-doped PS, PGTEMPO and PS were dissolved in chloroform respectively. After vortexing and sonication, the two solutions were mixed together. Then, the mixture solution was vortexed and sonicated again. At last, the solvent was evaporated under reduced pressure and the solid was dried under vacuum. The light orange product was obtained. The doping percentage of PGTEMPO is 10%.

4. Single crystal data and structure refinement

Single crystals of GTEMPO were grown by vapor diffusion of *n*-hexane solution at low temperature. Single-crystal XRD measurements were conducted on a Bruker-Nonius Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation. Absolute fluorescence quantum yield was measured on a Hamamatsu Quantaurus-QY C11347.

Table S1. Crystal data and structure refinement for GTEMPO.

Identification code	zwang1CuLT
Empirical formula	C12H22NO3
Formula weight	228.30
Temperature/K	100.2(8)
Crystal system	monoclinic
Space group	P21/m
a/Å	5.81660(10)
b/Å	11.4718(2)
c/Å	9.5696(2)
α/°	90
β/°	103.897(2)
γ/°	90
Volume/Å3	619.86(2)
Z	2
ρcalcg/cm3	1.223
μ/mm-1	0.703
F(000)	250.0
Crystal size/mm3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.52 to 146.662
Index ranges	-7 ≤ h ≤ 6, -13 ≤ k ≤ 13, -9 ≤ l ≤ 11
Reflections collected	3277
Independent reflections	1266 [Rint = 0.0099, Rsigma = 0.0105]
Data/restraints/parameters	1266/0/96
Goodness-of-fit on F2	1.047
Final R indexes [I>=2σ (I)]	R1 = 0.0357, wR2 = 0.0924
Final R indexes [all data]	R1 = 0.0368, wR2 = 0.0931
Largest diff. peak/hole / e Å-3	0.25/-0.17

5. Nanoparticle synthesis and cell culture, staining, and imaging

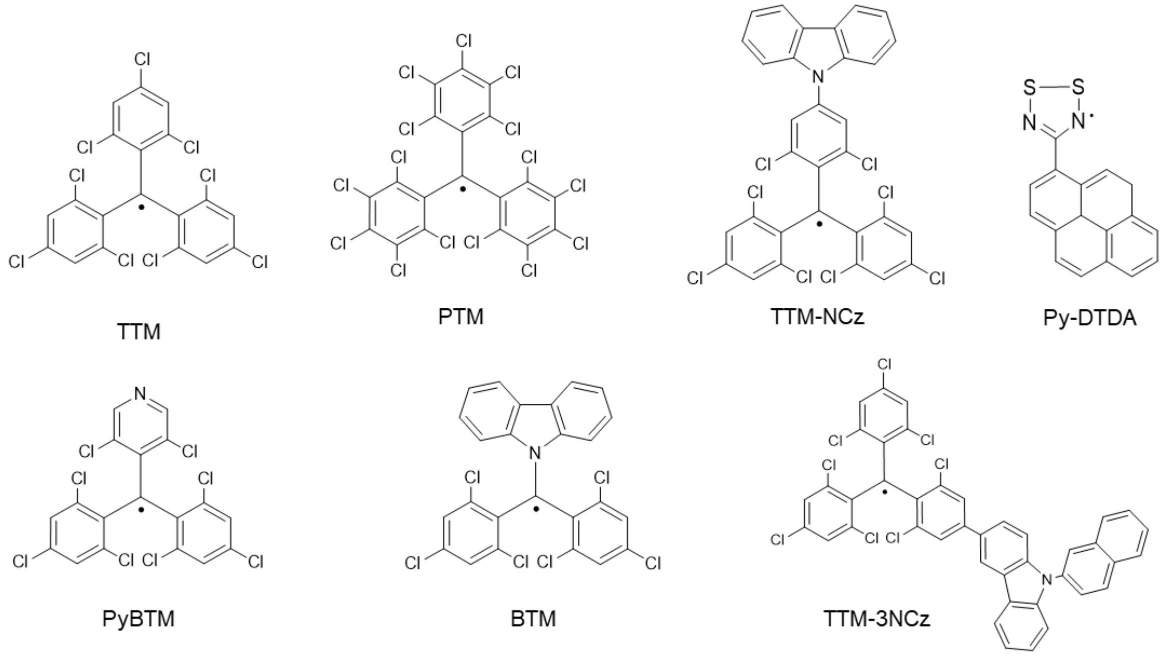
A solution of PGTEMPO (2 mg) and DSPE-PEG (M_w: 2000, 10 mg) in distilled THF (1 mL) were added drop-by-drop into 10 mL distilled-deionized water under continuous sonication. The mixture solution were passed through a 0.45 μm filter membrane. Then, the mixture was stirred under blowing of compressed air until the total volume was concentrated to 4 mL. The PGTEMPO NPs dispersed in water was used for further characterization. Dynamic light scattering (DLS) data were obtained at room temperature using dynamic light Scattering particle size analyzer (Malvem Zetasizer Nano ZS). The TEM imaging was performed on a Philips Tecnai 12 transmission electron microscope.

Cell culture: Adenocarcinomic human alveolar basal epithelial cells (A549) were grown in Dulbecco's Modified Eagle Medium supplemented with 10% fetal bovine serum (FBS) and 1% penicillin and streptomycin in a 5% CO_2 incubator at 37 °C.

Cell staining experiment: A549 cells were placed on glass coverslips and allowed to adhere for 48 h. A549 cells were incubated with PGTEMPO NPs (10 μg/mL) in DMEM at 37 °C for 4 h. After taken confocal images, A549 cells were incubated with ascorbic acid medium solution (1.5 mg/mL) for 15 min.

Co-staining experiment: LTG was dissolved in DMSO at a stock concentration of 100 μM. To confirm the location of PGTEMPO NPs in lysosome, A549 cells were firstly incubated with10 μg/mL PGTEMPO NPs for 4 h, then stained with 0.2 μM LysoTracker Green (LTG) for 15 min. Excitation: 488 nm for LTG and 561 nm for PGTEMPO NPs. Emission: 500-550 nm for LTG and 610-700 nm for PGTEMPO NPs.

Fluorescence imaging: The confocal fluorescent images were obtained with Zeiss LSM 800 confocal laser scanning microscope. The co-localization coefficient of the images was determined by the software with Zeiss LSM 800 confocal microscope.


TTM PTM TTM-NCz Py-DTDA

PyBTM BTM TTM-3NCz

Figure S1. Examples of reported luminescent radicals.

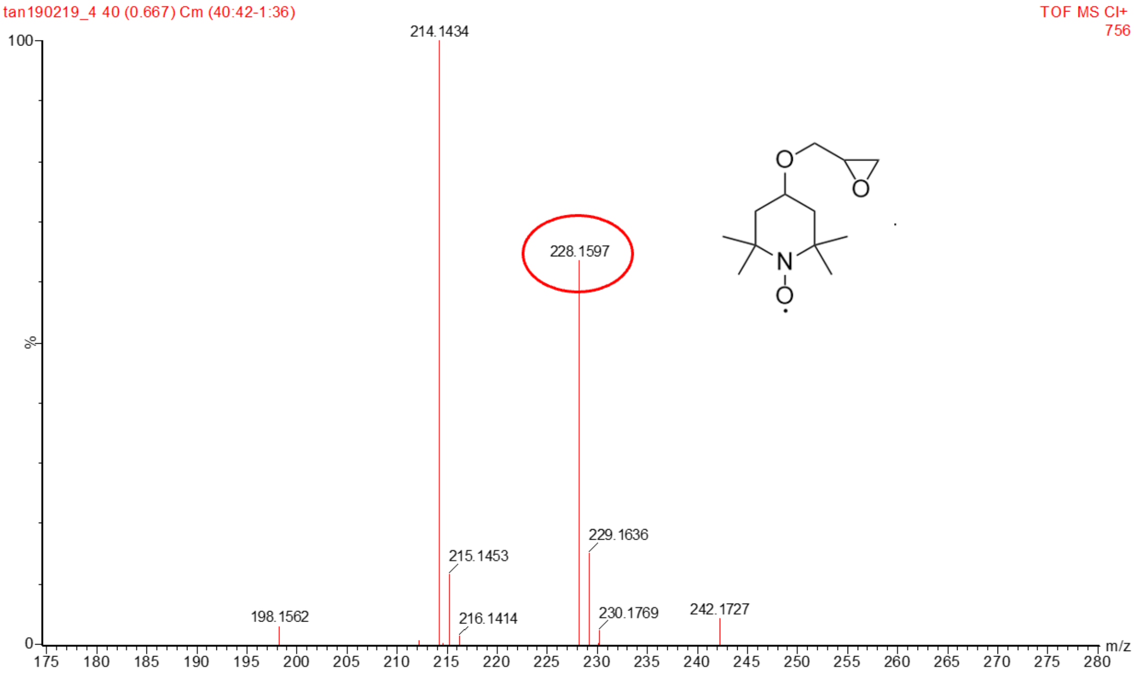


Figure S2. HRMS spectrum of GTEMPO. m/z = 228.1600 (calculated), 228.1597 (found).

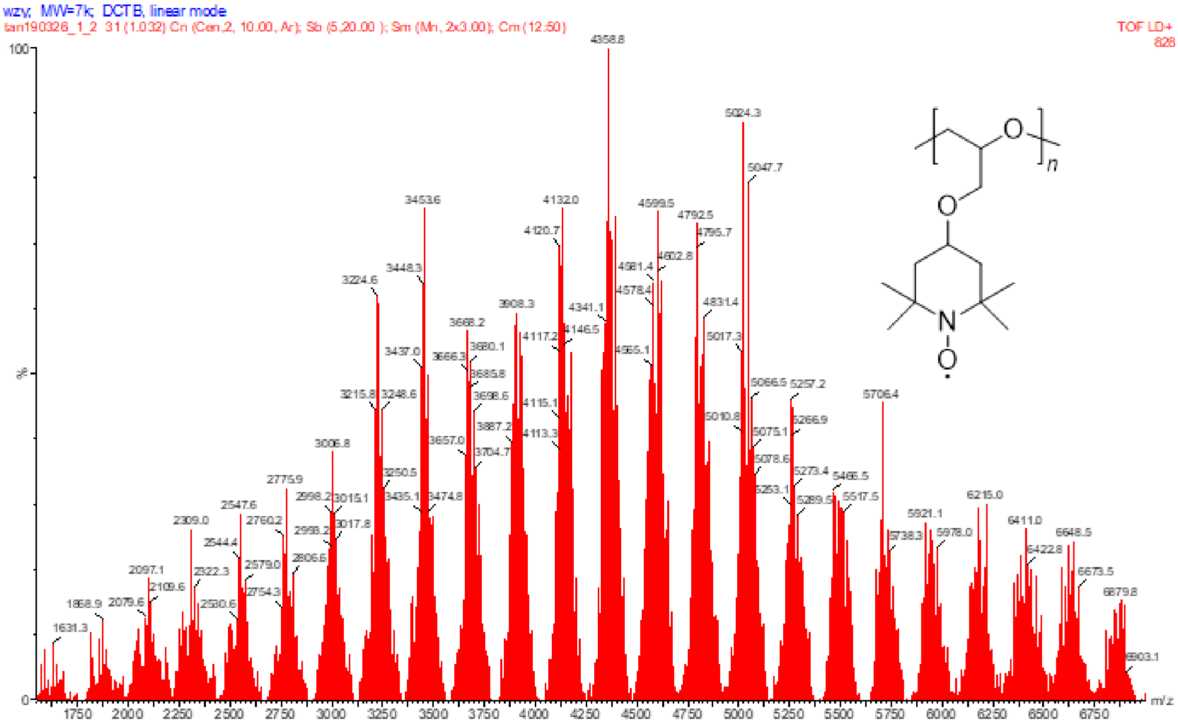


Figure S3. HRMS spectrum of PGTEMPO.

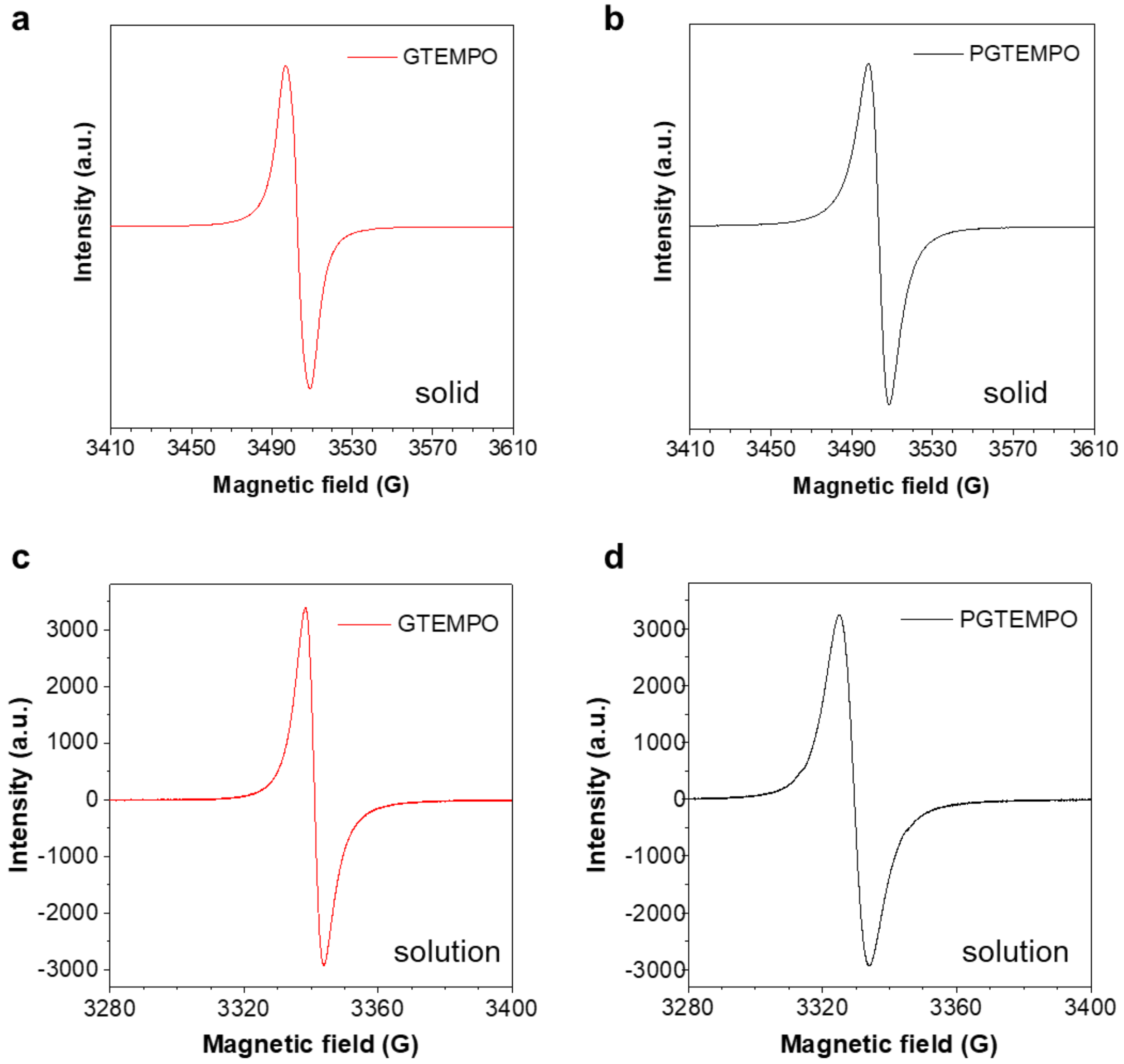


Figure S4. a-b, The EPR spectroscopy signal of (a) GTEMPO and (b) PGTEMPO in solid state. c-d, The EPR spectroscopy signal of (c) GTEMPO and (d) PGTEMPO in THF solution at the concentration of 0.1 M.

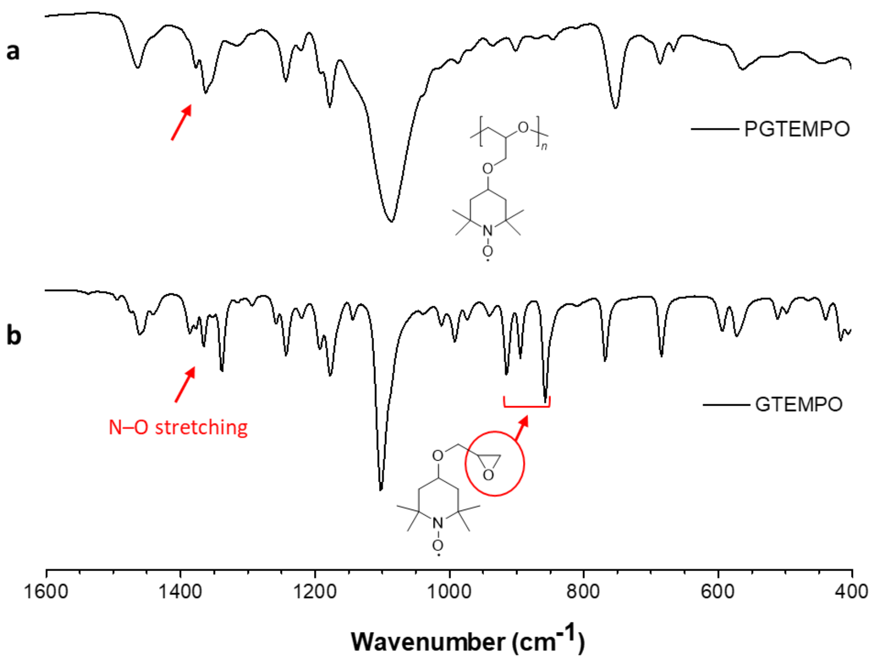


Figure S5. ATR-FTIR spectra of (a) PGTEMPO and (b) GTEMPO.

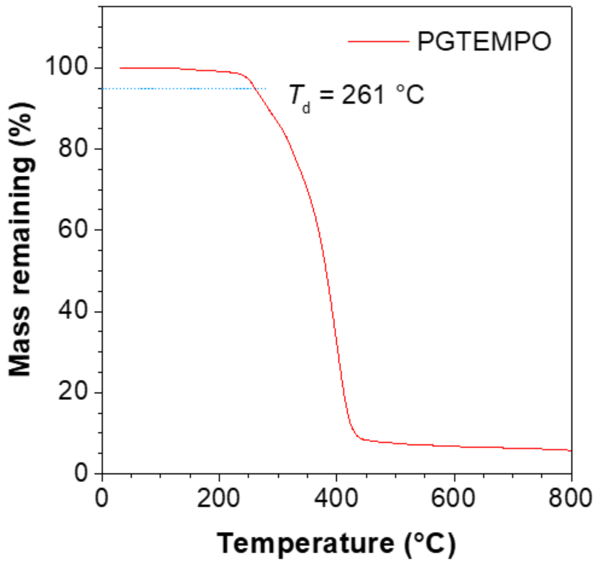


Figure S6. TGA curves of PGTEMPO recorded under nitrogen at a heating rate of 10 °C/min. The onset decomposition temperature (T_d) of PGTEMPO at 5% weight loss is 261 °C.

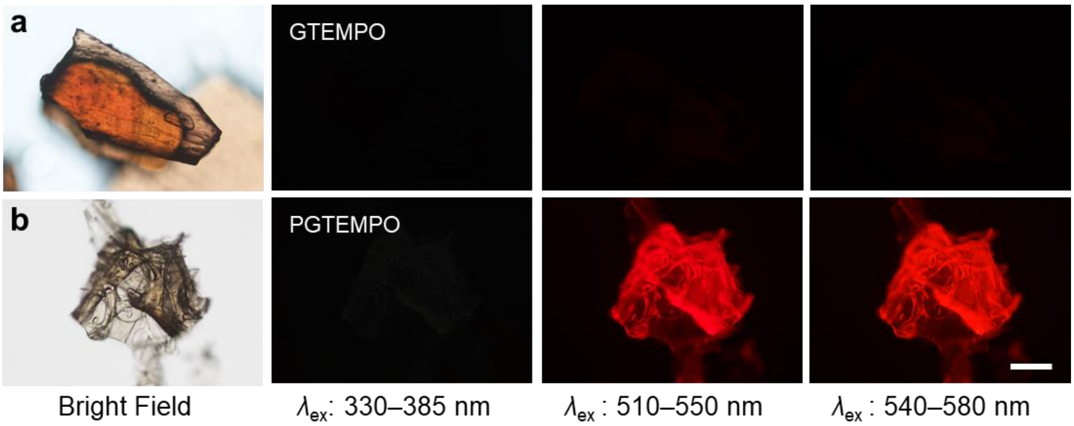


Figure S7. Photographs of (a) GTEMPO crystal and (b) PGTEMPO solid on glass slide taken with fluorescence microscope under bright field (transmission light) and under various excitation (330–385 nm; 510–550 nm; 540–580 nm). Scale bar: 200 μm.

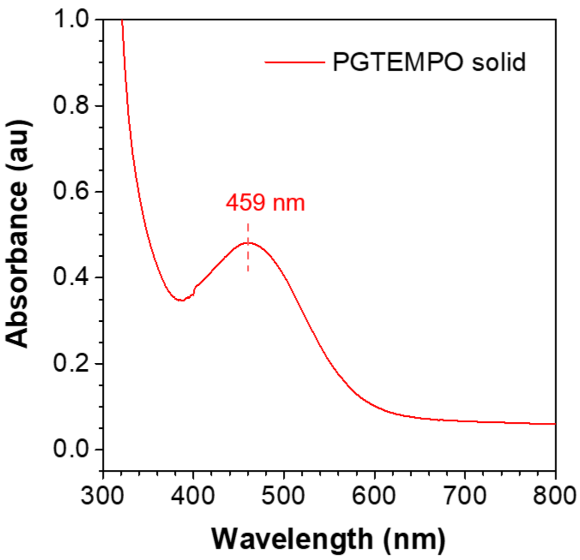


Figure S8. UV−vis spectrum of PGTEMPO in the solid state. Sample was prepared by pressing a bulk of PGTEMPO on quartz.

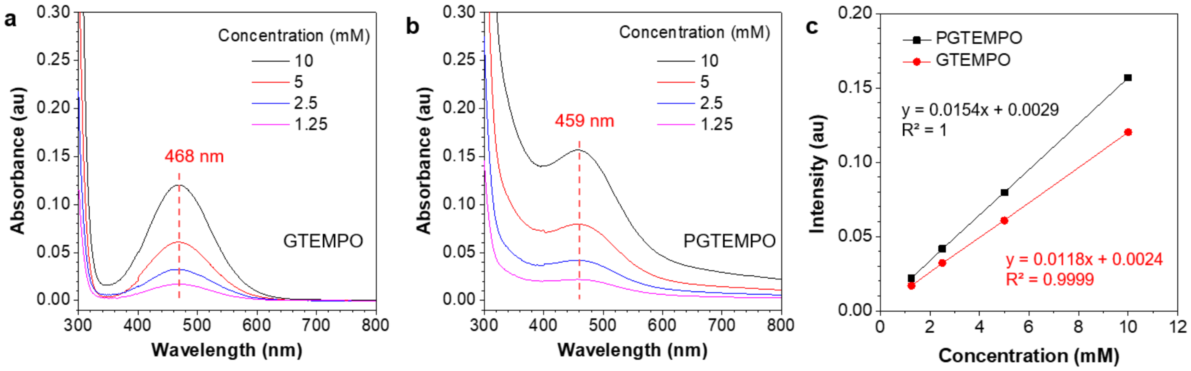


Figure S9. UV absorptivity of GTEMPO and PGTEMPO. a-b, UV−vis spectra of (a) GTEMPO and (b) PGTEMPO in THF at a solution concentration from 1.25 to 10 mM. c, Absorbance intensity at 468 nm and 459 nm versus concentration of GTEMPO (ε = 12.02 $mol^{-1}\cdot L\cdot cm^{-1}$) and PGTEMPO ($\varepsilon$ = 15.68 $mol^{-1}\cdot L\cdot cm^{-1}$).

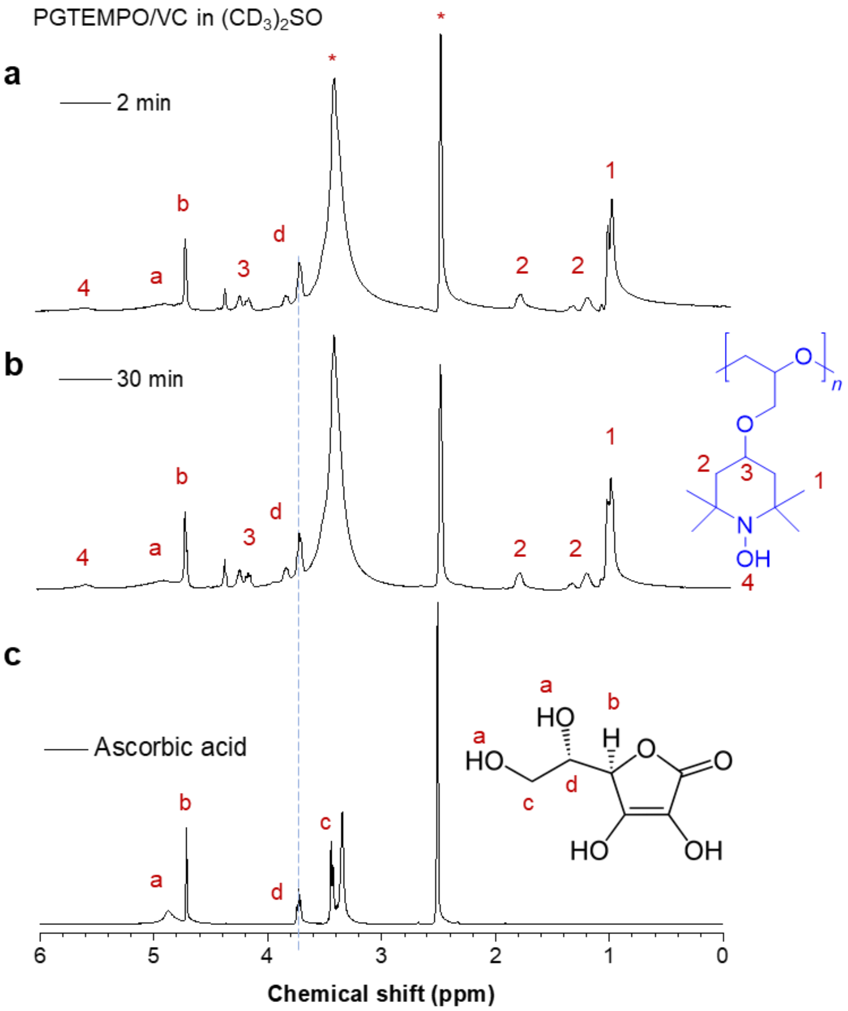


Figure S10. ^{1}H NMR spectra. a-b, ^{1}H NMR spectra of the mixture of PGTEMPO and VC in $(CD_3)_2SO$ after 2 min and 30 min. c, ^{1}H NMR spectrum of VC.

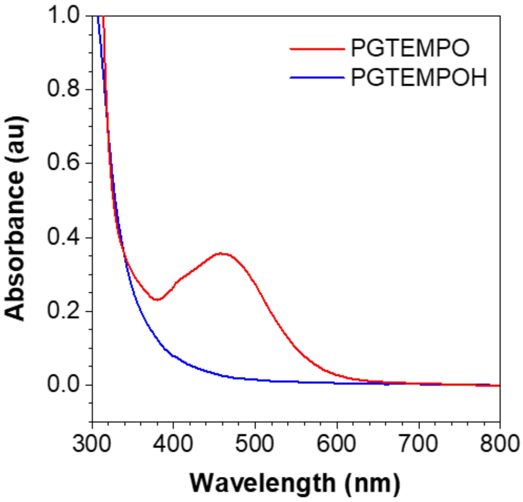


Figure S11. UV−vis spectra of PGTEMPO and PGTEMPOH in DMSO (20 mM).

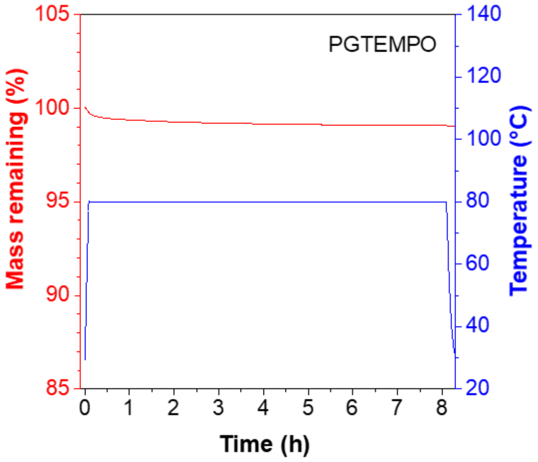


Figure S12. TGA curves of PGTEMPO recorded under nitrogen holding at the temperature of 80 °C for 8 hours. The mass losing is less than 1% to demonstrate the thermostability under 80 °C.

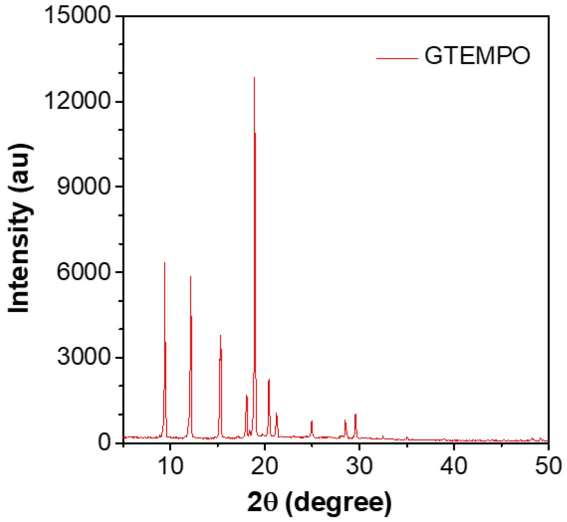


Figure S13. XRD spectra of GTEMPO powder on glass substrate.

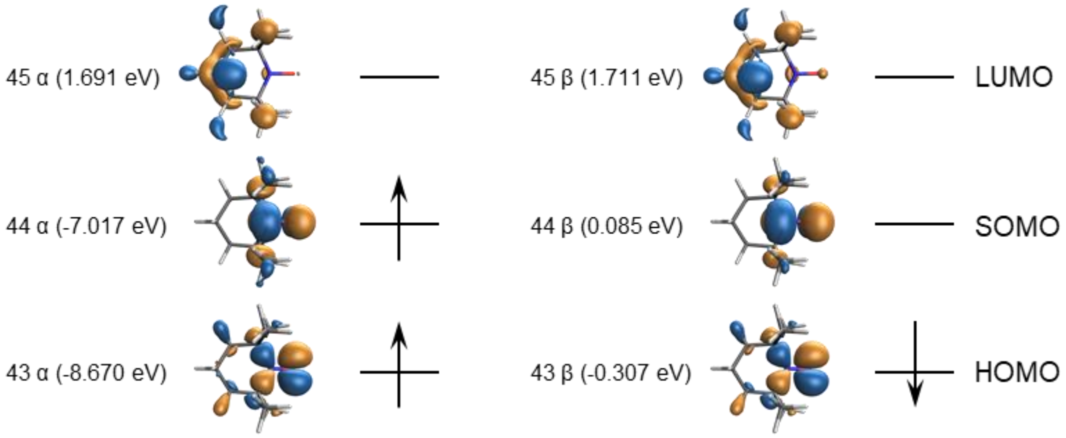


Figure S14. Active molecular orbitals of TEMPO calculated by CAM-B3LYP-D3/def2-TZVP. The calculated absorption ($D_0 \rightarrow D_1$) is 459 nm, which is the HOMO-SOMO transition and corresponds to the strong absorption at 468 nm in the UV-Vis spectrum.

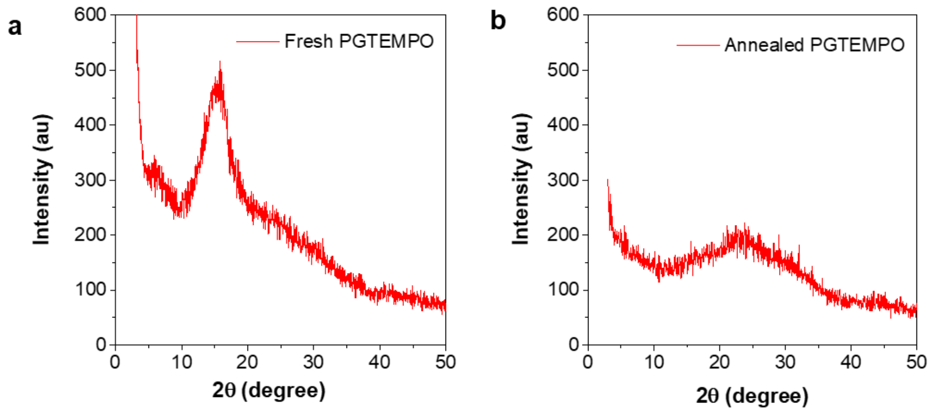


Figure S15. Powder XRD spectra of fresh and annealed PGTEMPO.

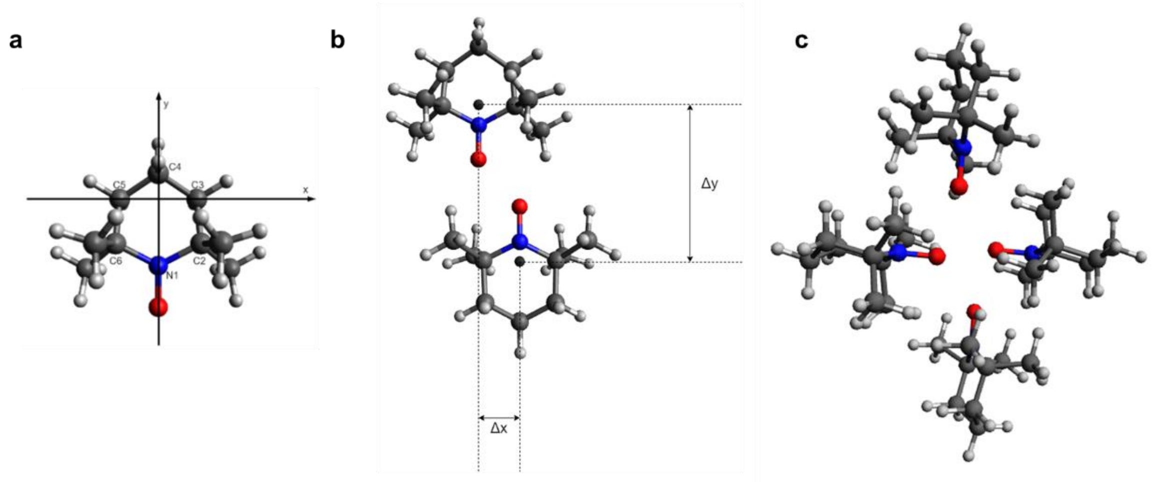


Figure S16. a, Definition of Cartesian coordinate axes of the geometries. X-axis is defined by the line running through atoms C3 and C5, while y-axis is defined by the line running through N1 and C6. The axes are guaranteed to be perpendicular because of the axisymmetricity of TEMPO molecule. b, Definition of Δx and Δy in the TEMPO dimer model. These parameters are defined by horizontal and vertical distances respectively for Δx and Δy between the center of mass of each monomer. c, Geometry of tetramer model built up from dimer with Δy = 6.0 Å.

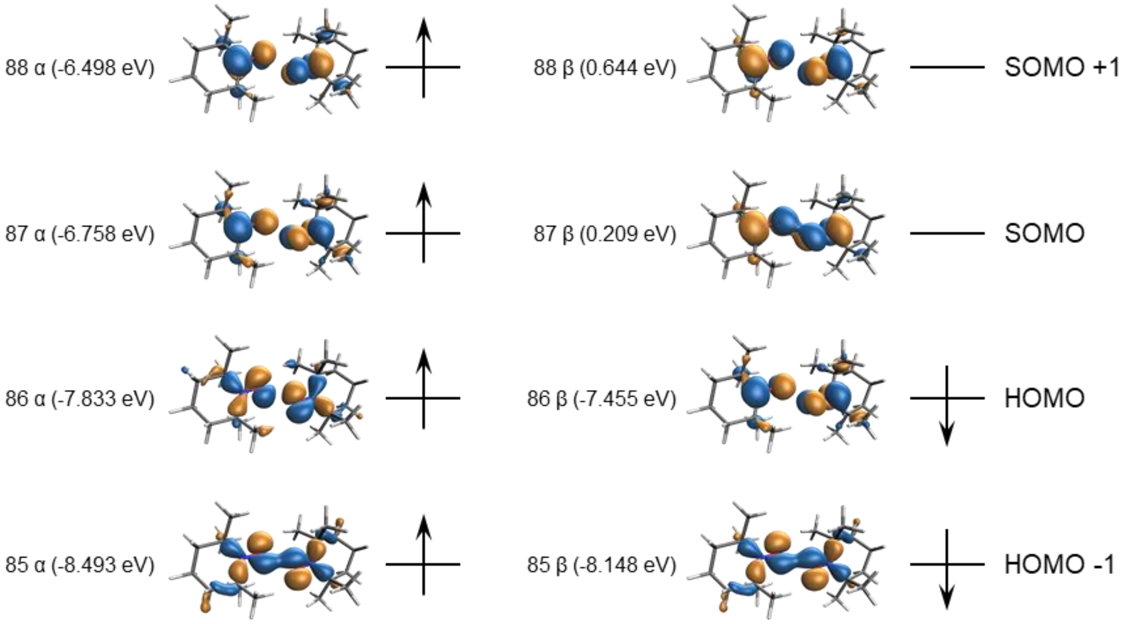


Figure S17. Frontier molecular orbitals of the head-head TEMPO dimer model with Δx = 1.5 Å and Δy = 5.7 Å. The distance between two oxygen on TEMPO is 2.289 Å.

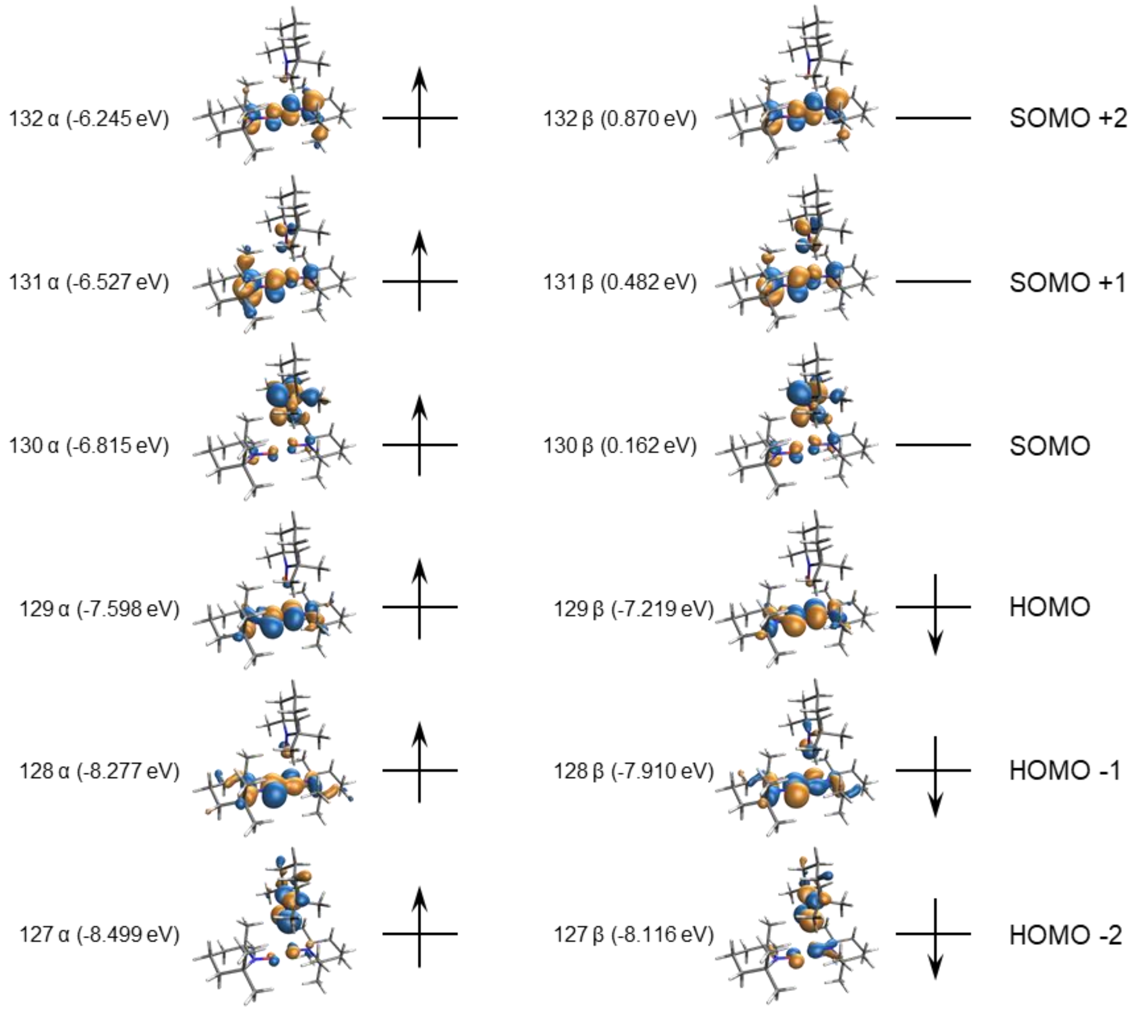


Figure S18. Frontier molecular orbitals of the TEMPO trimer model built up from head-head dimer model with $\Delta y = 5.7$ Å.

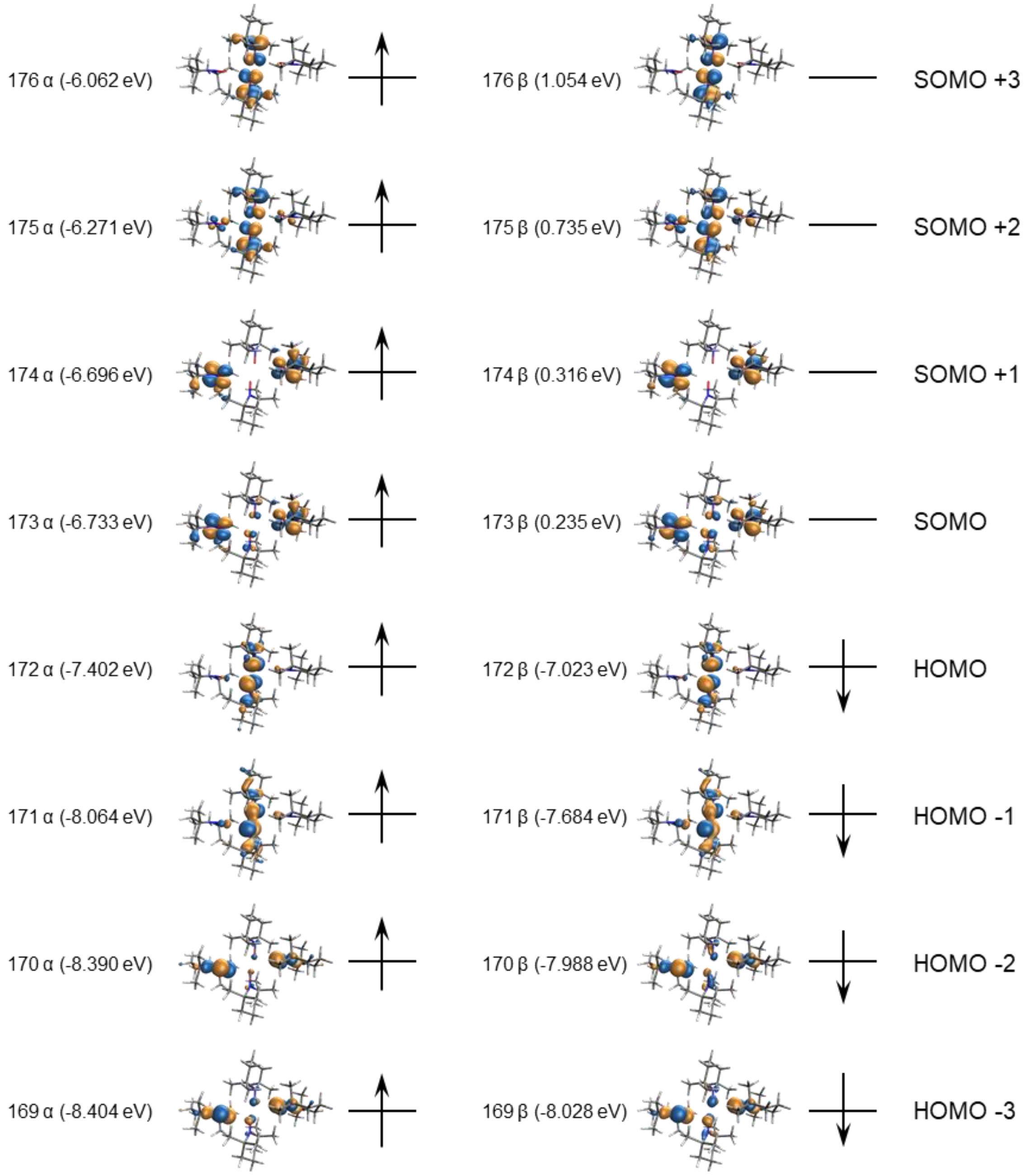


Figure S19. Frontier molecular orbitals of the TEMPO tetramer model built up from head-head dimer model with Δy = 5.7 Å.

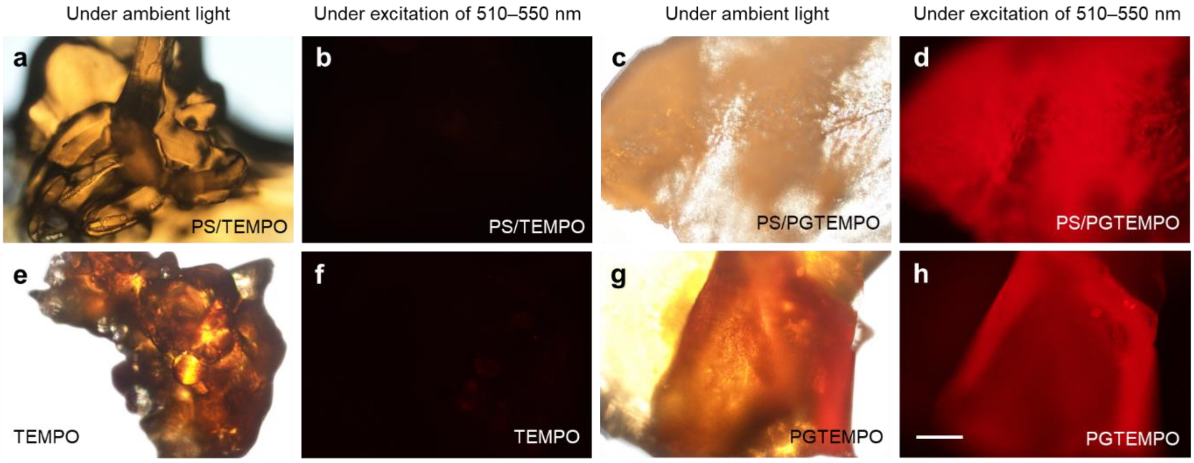


Figure S20. (a-d) Photographs of PS doped with (a-b) small molecule, TEMPO, and (c-d) PGTEMPO taken with fluorescence microscope (a, c) under bright field (transmission light) and (b, d) under the excitation of 510–550 nm. (e-h) Photographs of (e-f) TEMPO and (g-h) PGTEMPO solid on glass slide taken with fluorescence microscope (e, g) under bright field (transmission light) and (f, h) under the excitation of 510–550 nm. Scale bar: 200 µm. All photos were taken under the same conditions. The doping percentage of TEMPO and PGTEMPO are 50% and 10% respectively.

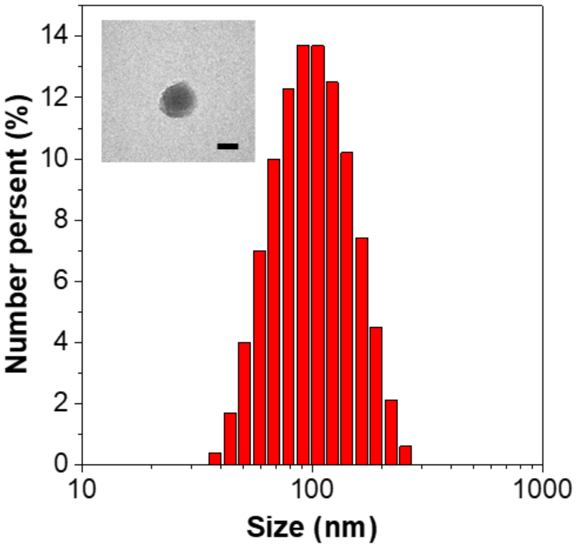


Figure S21. Particle size distribution measured by DLS and TEM image of PGTEMPO NPs. Scale bar: 50 nm.

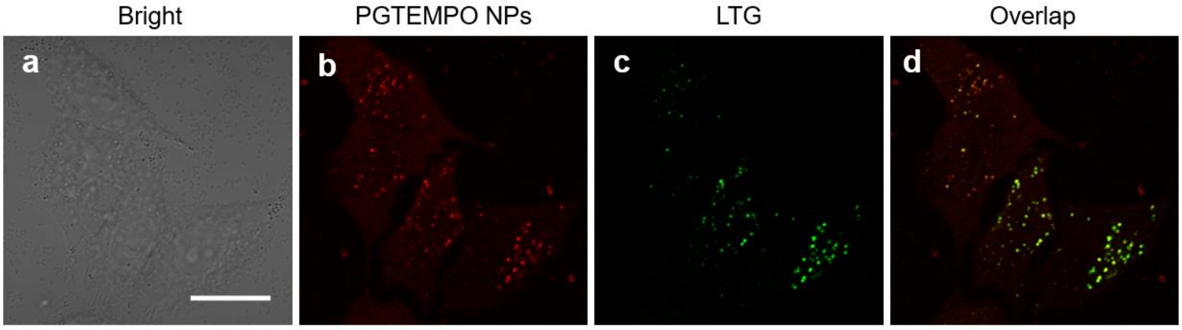


Figure S22. Colocalization of PGTEMPO NPs with LTG. a, Bright field image. A549 cells were co-stained with (b) PGTEMPO NPs (10 μg/mL) for 4 h, and (c) LTG (0.2 μM) for 15 min. d, Overlap image. Excitation: 561 nm for PGTEMPO NPs and 488 nm for LTG. Scale bar: 20 μm. Emission: 500-550 nm for LTG and 610-700 nm for PGTEMPO NPs. The overlap coefficients were calculated to be 0.52.

6. Quantum chemical calculation

All calculations were performed with the Q-Chem 5.1[5] software package.

6.1 Building TEMPO cluster model system

In this work, we have constructed model systems of clusters of TEMPO units using Avogadro 1.2.0[6], which is similar to the general approach of references[7,8]. The geometry of TEMPO is optimized with B3LYP/def2-TZVP[9,10]. To construct TEMPO dimer model systems, the TEMPO molecule is rotated about the x-axis by 180° as defined by Figure S18a, and then translated by Δx and Δy on x-axis and y-axis respectively (Figure S17b). Δx is fixed at 1.5 Å to minimize collision, and Δy is chosen to be values between 5.5 Å and 6.0 Å with step size of 0.1 Å to model systems with different distance between nitroxide radicals.

For trimers, the third molecule is defined by rotating the first molecule by 90° about x-axis and then 15° about z-axis, then translating by vector (2.75 Å, $0.5\Delta y$, 4.0 Å). For tetramers, the fourth molecule is defined as the mirror image of the third. The resulting tetramer model is sketched in Figure S17c.

All model systems have not been further optimized other than the optimization of the TEMPO monomer. This is because these model systems or any head-to-head TEMPO dimers are not stable in gas phase and would separate apart upon optimizing. Such orientation of TEMPO units would only exist in polymers like PGTEMPO, where the backbone of polymer can force less stable orientation of TEMPO units to persist.

6.2 Calculation of model systems

Time dependent density functional theory (TDDFT) calculations were performed on TEMPO monomer and all model systems constructed above with CAM-B3LYP/def2-TZVP[11] with Grimme’s D3 dispersion correction[12] to obtain the excitation energies. For all model systems, there exists 2 excited states within the visible light area, and we chose to plot the excitation energies of 1st excited state of each system. The molecular orbitals are plotted with IQmol 2.13 from the orbital information from the calculation results. From the plots of molecular orbitals, there are no severe interference between moieties other than nitroxide radical, so we argue that the geometries constructed in 4.1 is physically viable.

Cartesian coordinates:

<u>Dimer model in Figure S17</u>

H	-3.54919181	3.18314236	0.81802452
H	-4.01400712	2.50429755	-1.54918799
H	-1.86501048	2.80818383	0.40752248

C	-2.78438043	2.40431516	0.82537979
H	-5.38553788	1.44356186	0.30460073
H	-2.59223026	2.11742765	1.86029118
H	1.68695979	3.16707908	-0.77161322
C	-3.40781422	1.60054718	-1.46523325
H	-2.42108223	1.80342512	-1.88033824
C	-3.27691818	1.20062713	0.01533087
H	2.4541082	2.81496636	1.58806442
H	-4.56017208	0.72733124	1.6771602
C	-4.61966756	0.71630812	0.58428324
H	-3.88128128	0.82339104	-2.06409545
H	0.47361218	1.93649204	-0.37284549
C	1.46383794	2.09874203	-0.7924687
H	4.17395236	2.68795144	-0.27440511
H	1.45296381	1.76747724	-1.83189792
C	2.43164555	1.72819334	1.48956172
H	1.4932576	1.360462	1.90346185
H	-5.13733586	-0.71796434	-0.9545097
H	-5.96257339	-0.97108729	0.56673594
O	-1.03686297	0.47811353	-0.07816007
N	-2.24286865	0.12282773	0.14336134
C	-5.00245235	-0.68633482	0.12992203
C	2.53160775	1.34088557	0.00324406
H	3.8606731	1.65796414	-1.65972701
C	3.92101277	1.66610857	-0.56687108
H	3.25218786	1.32182098	2.07977397
H	-3.2521898	-1.32181436	-2.07977392
C	-3.92101471	-1.66610195	0.56687113
H	-3.86067504	-1.65795752	1.65972706
C	-2.53160968	-1.34087896	-0.00324401
H	5.13733391	0.71797096	0.95450975
H	5.96257144	0.97109391	-0.5667359
O	1.03686103	-0.47810691	0.07816012
N	2.24286671	-0.12282112	-0.14336129

C	5.00245041	0.68634144	-0.12992198
H	-1.4932314	-1.36055134	-1.90346251
C	-2.4316475	-1.72818672	-1.48956168
H	-1.45293761	-1.76756658	1.83189727
H	-4.17392616	-2.68804079	0.27440445
C	-1.46383988	-2.09873542	0.79246874
H	-0.47361412	-1.93648542	0.37284554
H	3.88127934	-0.82338442	2.0640955
C	4.61966562	-0.71630151	-0.58428319
H	4.56017014	-0.72732463	-1.67716015
H	-2.45411014	-2.81495974	-1.58806437
C	3.27691624	-1.20062052	-0.01533082
H	2.42110843	-1.80351445	1.88033758
C	3.40781228	-1.60054056	1.46523331
H	-1.68696173	-3.16707246	0.77161327
H	2.59225646	-2.11751698	-1.86029183
H	5.38556408	-1.44365119	-0.30460138
C	2.78437849	-2.40430855	-0.82537974
H	1.86500854	-2.80817721	-0.40752243
H	4.01400518	-2.50429093	1.54918803
H	3.54918987	-3.18313575	-0.81802447

Trimer model in Figure S18

H	4.76727693	-2.53095879	-2.02441769
H	4.45362948	-0.16046279	-2.77471938
H	2.9969674	-2.54433111	-1.91765654
C	3.91514893	-2.36827516	-1.36186636
H	6.08120721	-0.62491827	-0.88314298
H	3.96612371	-3.09288066	-0.54785398
H	-0.6312891	-2.93285416	-2.82345138
C	3.75199073	0.05821993	-1.96777212
H	2.7374076	-0.03524879	-2.3537725
C	3.96319112	-0.93824635	-0.81382702
H	-0.77704013	-4.84896239	-1.2147673

H	5.55226676	-1.58976096	0.48339831
C	5.31046838	-0.70429319	-0.11285802
H	3.90984227	1.09061452	-1.6578964
H	0.42358342	-2.21184818	-1.59342416
C	-0.60226429	-2.28141229	-1.94804096
H	0.18687206	0.89743437	-2.96704654
H	-2.9338839	-3.86101365	-2.11741432
H	-0.92869001	-1.28436022	-2.24737544
C	-0.96238593	-4.19033502	-0.36439099
H	-0.02126209	-4.02420824	0.15886748
H	5.1465286	1.42944762	0.22370639
H	6.2996503	0.62697416	1.26563885
O	1.69424454	-1.19423882	-0.23506705
N	2.83900534	-0.79820152	0.16795481
C	5.31796713	0.51581491	0.79909346
C	-1.52437793	-2.84690326	-0.86288476
H	-3.18306461	-2.12653688	-2.03004247
C	-2.94254895	-3.01073589	-1.43138931
H	0.05035688	0.02088292	-1.43127473
C	0.15526565	1.00548733	-1.88127991
H	1.10155481	1.43432854	-1.54826346
H	-1.64762212	-4.7010972	0.31114732
H	-2.31825212	0.90414441	-2.89714888
H	-1.11305402	3.10604627	-3.27386565
H	0.17481601	3.57501155	-2.17860544
H	2.95393084	2.0360997	0.12821648
C	4.24885766	0.34573839	1.87075311
H	4.48937332	-0.53846062	2.46940627
C	2.83068665	0.18190575	1.30224856
C	-0.87389862	3.26427579	-2.21961426
C	-2.3413762	1.22376786	-1.85379457
C	-1.01453808	1.91652841	-1.49501396
H	-4.99334158	-3.29197166	-0.82627505
H	-3.84021989	-4.09444512	0.2156574

C	-4.01165843	-3.18081242	-0.35972966
O	-0.38793583	-1.47075868	0.67443084
N	-1.53269662	-1.86679599	0.27140899
H	-2.48034034	0.34578967	-1.22375133
H	1.32752804	1.35925303	0.28057621
C	2.26869464	1.52533751	0.80375479
H	2.23495596	-1.380595	2.68681913
H	4.24014985	1.19605844	2.55685801
H	-3.20034158	1.88118346	-1.7243298
C	1.908573	-0.38358522	2.38740475
H	0.88272529	-0.45314933	2.03278796
H	-1.5903119	5.29800895	-2.17854032
H	-2.60353355	-3.75561202	2.09726019
C	-1.73470645	4.36941445	-1.62123863
N	-0.95180732	2.11900387	-0.0109753
C	-4.00415966	-1.96070432	0.55222182
H	-4.24595807	-1.07523654	-0.04403451
O	-0.82433051	1.06051222	0.6912317
H	2.08334884	2.18396488	1.6541311
C	-2.65688241	-1.72675116	1.25319081
H	-2.79609657	4.1219249	-1.7071758
H	-1.43114165	-2.62970642	2.7932162
C	-2.44568202	-2.72321743	2.40713592
H	1.93759781	0.26785665	3.26281517
H	-0.29726756	4.88446083	-0.11907127
H	-2.65985775	0.42792545	0.98729767
H	-4.77494126	-2.04003694	1.32258667
C	-1.34541284	4.57214442	-0.16256595
C	-2.60884022	-0.29672235	1.80123016
H	-1.69065869	-0.12066639	2.35702034
C	-1.51754014	3.31173591	0.69940328
H	0.33265579	3.567069	1.80616434
H	-3.14732077	-2.50453471	3.21408317
H	-3.62491061	3.05883406	0.12790891

H	-1.93076012	5.37416735	0.29349189
C	-3.00018188	3.05113947	1.02034081
C	-0.73595504	3.47752142	2.00679694
H	-3.46096822	-0.13403872	2.46378148
H	-3.1065385	2.082714	1.50812661
H	-0.88868382	2.62555867	2.66542417
H	-1.06993008	4.38350454	2.5159315
H	-3.37101294	3.82425053	1.69566715

Tetramer model in Figure S19

H	6.33071502	-0.83999408	2.04474765
H	5.55468293	1.40505905	2.84355405
H	3.94699946	0.65621104	2.8312075
H	4.72512185	-1.5021215	1.6958558
H	2.92659732	-2.96242646	2.46117157
C	4.65631768	1.23756062	2.24652232
C	5.54208095	-0.90434188	1.29295135
H	7.04421381	1.21946925	0.74390332
H	5.95003507	-1.41840738	0.42341699
H	0.67323914	-3.92396137	2.98881361
H	4.20361807	2.20475812	2.02337805
C	5.03430352	0.50837583	0.95305622
H	2.04080924	-1.43393039	2.3041626
C	2.41150588	-2.30094706	1.76210923
C	6.1010096	1.31994656	0.20156476
H	2.07606759	-5.0442055	1.19440149
H	3.13058607	-1.95656956	1.01739751
H	5.82678048	2.3788227	0.24183318
H	0.43126906	1.86095644	3.13407873
C	0.20058287	-3.4174161	2.14543299
H	-0.27455264	-2.50654127	2.50828959
H	6.6005026	-0.12453114	-1.33368489
C	1.264884	-3.06423669	1.09107662
H	2.13947784	3.00131494	1.69804813

O	2.75747087	-0.05075947	0.72498764
H	2.75356133	-4.06764056	-0.09612463
C	1.81919755	-4.32627366	0.4119251
N	3.79067761	0.39687229	0.12344028
C	6.26026084	0.91160859	-1.25729579
H	-0.57192672	-4.07592959	1.74999959
H	7.0300544	1.52303084	-1.73405919
H	0.46807726	0.61094849	1.87642303
C	-0.03038244	1.51987485	2.20558339
H	4.89567062	-1.62005777	-1.53759317
H	-2.43356305	-0.80813335	2.96141103
H	0.10859099	4.32757903	2.44591953
H	-1.07632901	1.28271828	2.40563399
C	1.55958576	2.84003369	0.78755569
H	1.94755014	1.95775332	0.27944485
H	3.17003374	-1.79953817	-1.1964498
C	0.86423314	-4.93971067	-0.60400477
N	0.65884188	-2.1511325	0.0682103
O	0.37384442	-0.97373461	0.47102551
H	1.31474743	-5.82977567	-1.04958747
H	-0.05623463	-5.27274957	-0.11716768
C	3.78515833	0.26947203	-1.37022666
C	3.90601464	-1.21724656	-1.74996566
C	4.93006008	1.09599766	-1.9762823
C	0.07901456	2.623402	1.14827657
H	-1.49226732	3.65390237	2.19783293
C	-0.55942573	3.91303479	1.68724675
H	-1.61500202	-0.21020807	1.50607014
C	-2.44307577	-0.81427023	1.86988208
H	-2.29414919	-1.83956637	1.52803914
H	1.70626952	3.7038348	0.1401685
H	4.65441599	2.15460271	-1.93864571
H	-3.71630882	1.34000809	2.81778125
H	-5.01353737	-0.8310956	3.03294775

H	5.01353912	0.83109503	-3.03294483
H	3.71631057	-1.34000867	-2.81777834
H	-4.65441424	-2.15460328	1.93864863
H	-1.70626777	-3.70383537	-0.14016558
H	2.29415093	1.83956579	-1.52803622
C	2.44307752	0.81426966	-1.86987917
H	1.61500377	0.2102075	-1.50606722
C	0.55942749	-3.91303536	-1.68724383
H	1.49226907	-3.65390295	-2.19783002
C	-0.07901281	-2.62340257	-1.14827365
C	-4.93005833	-1.09599824	1.97628521
C	-3.90601289	1.21724598	1.74996857
C	-3.78515659	-0.26947261	1.37022958
N	-0.65884014	2.15113193	-0.06820739
O	-0.37384267	0.97373404	-0.47102259
C	-0.86423139	4.93971009	0.60400769
H	0.05623638	5.272749	0.1171706
H	-1.31474568	5.82977509	1.04959039
H	-3.17003199	1.7995376	1.19645272
H	-1.94759912	-1.95773725	-0.27952649
C	-1.55958401	-2.84003426	-0.78755277
H	1.07628002	-1.28270221	-2.40571562
H	-0.10863998	-4.32756296	-2.44600116
H	2.4335648	0.80813277	-2.96140812
H	-4.89566888	1.62005719	1.53759608
C	0.03038419	-1.51987543	-2.20558047
H	-0.46807551	-0.61094906	-1.87642011
H	-7.03005265	-1.52303142	1.73406211
H	0.57192847	4.07592902	-1.74999667
N	-3.79067586	-0.39687286	-0.12343736
C	-6.26025909	-0.91160916	1.25729871
C	-1.8191958	4.32627308	-0.41192219
H	-2.75355958	4.06763998	0.09612754
O	-2.75746912	0.0507589	-0.72498473

H	-2.13947609	-3.00131552	-1.69804521
C	-1.26488225	3.06423611	-1.0910737
H	-6.60050085	0.12453056	1.3336878
H	0.27450365	2.50655734	-2.50837122
C	-0.20058112	3.41741552	-2.14543008
H	-0.43126731	-1.86095702	-3.13407581
H	-5.82677873	-2.37882327	-0.24183026
H	-3.13063506	1.95658563	-1.01747914
H	-2.07611658	5.04422157	-1.19448312
C	-6.10100785	-1.31994714	-0.20156184
C	-2.41150413	2.30094648	-1.76210632
H	-2.04080749	1.43392982	-2.30415968
C	-5.03430178	-0.5083764	-0.9530533
H	-4.20361633	-2.2047587	-2.02337513
H	-0.67323739	3.9239608	-2.9888107
H	-5.95003327	1.4184068	-0.42341408
H	-7.04421206	-1.21946982	-0.74390041
C	-5.54207915	0.90434131	-1.29294843
C	-4.65631593	-1.23756119	-2.2465194
H	-2.92659557	2.96242589	-2.46116866
H	-4.72512009	1.50212093	-1.69585288
H	-3.94699771	-0.65621162	-2.83120459
H	-5.55468119	-1.40505963	-2.84355113
H	-6.33071327	0.83999351	-2.04474474

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