Electronic Supplementary Information

Stable metallic state of $(TTPCOO)_2NH_4$ with mobile dopant

Takeshi Terauchi,[a] Satoshi Sumi[a], Yuka Kobayashi,*[a] Toshikazu Nakamura,[b] Ko Furukawa,[b,‡] and Yohji Misaki[c]

[a]Polymer Materials Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba,305-0047 (Japan). [b]Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan. [c]Department of Applied Chemistry, Graduate School of Science and Engineering, Ehime University, Matsuyama, Ehime 790-8577, Japan. ‡Current address is Nigata Univ.
E-mail: kobayashi.yuka@nims.go.jp; Tel: +81-29-859-2154.

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1. General

^1H nuclear magnetic resonance (NMR) spectrum for a solution was recorded on Bruker AVANCE system (600 MHz). Infrared (IR) spectrum was measured with a Thermo Fisher SCIENTIFIC/Nicolet 6700. Diffuse reflectance spectra was measured from 200 to 2500 nm using polycrystalline solids on a JASCO V-670DS spectrophotometer and then transformed to absorption one by adopting Kubelka–Munk theory.[S1]

Ammonium hydroxide solution, 28%, dimethyl sulfoxide-d_6, 99.96 atom% D, were purchased from Sigma-Aldrich Japan. Diethyl ether, 1,4-dioxane, and tetrahydrofuran (THF) were purchased from KANTO CHEMICAL.

2. Sample preparation

$(TTPCOO)_2NH_4$: Finely-ground TTPCOOH (140 mg, 0.330 mmol) was suspended by a mixture of 1,4-dioxane (31.5 ml), THF (31.5 ml) and Et_2O (7.0 ml) and sonicated for 15 seconds. 28% Aqueous ammonia (2.8 ml) was added to the mixture and then sonicated for additional 15 second. After vigorously stirring at room temperature for 14 hours, the reaction mixture was cooled at +5°C for one hour. The precipitation was collected by filtration using a membrane filter (H010A047A, ADVANTEC) and washed with deionized water, THF and Et_2O. The resulting polycrystalline solid were dried in vacuo to afford dark brown crystals, $(TTPCOO)_2NH_4$ (134 mg, 92%). ^1H NMR (600 MHz, DMSO-d_6): δ 6.69 (s, 1H), 6.79 (s, 2H), 6.96 (s, 4H); Anal. calcd. for (TTFCOOH:NH_3=2:1; $C_{22}H_{11}O_4NS_{16}$): C, 30.50; H, 1.28; N, 1.62. Found: C, 30.56; H, 1.03; N, 1.41.

3. ^{1}H NMR spectra

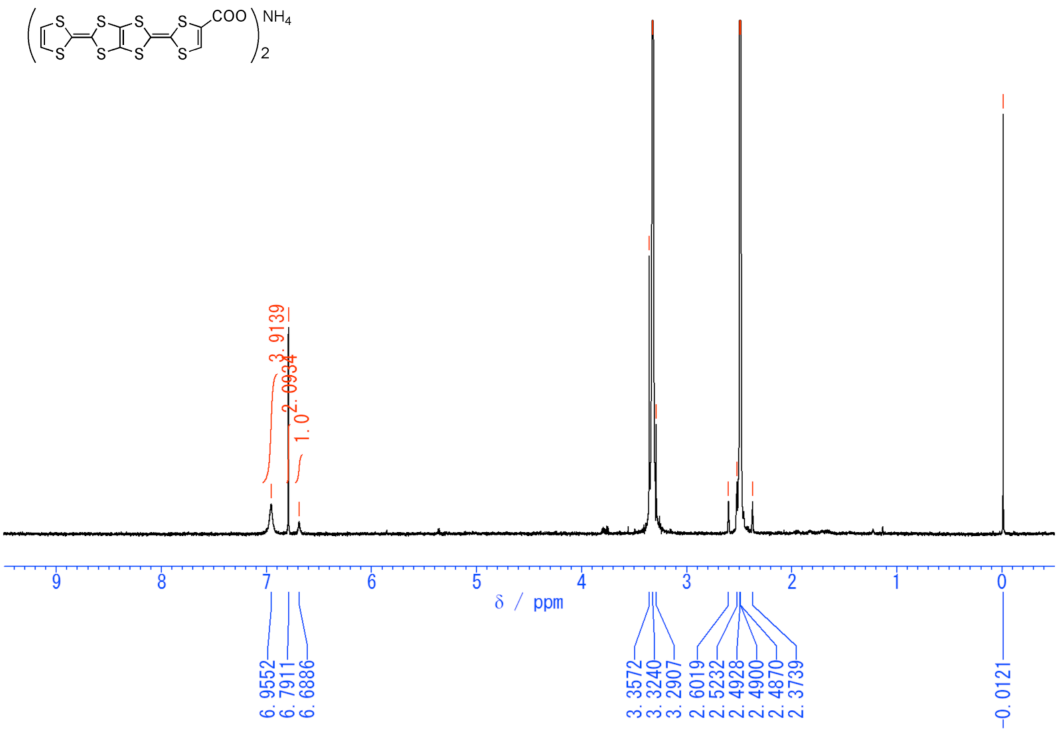

Fig. S1. ^{1}H NMR spectrum of $(TTPCOO)_2NH_4$ in DMSO-d_6.

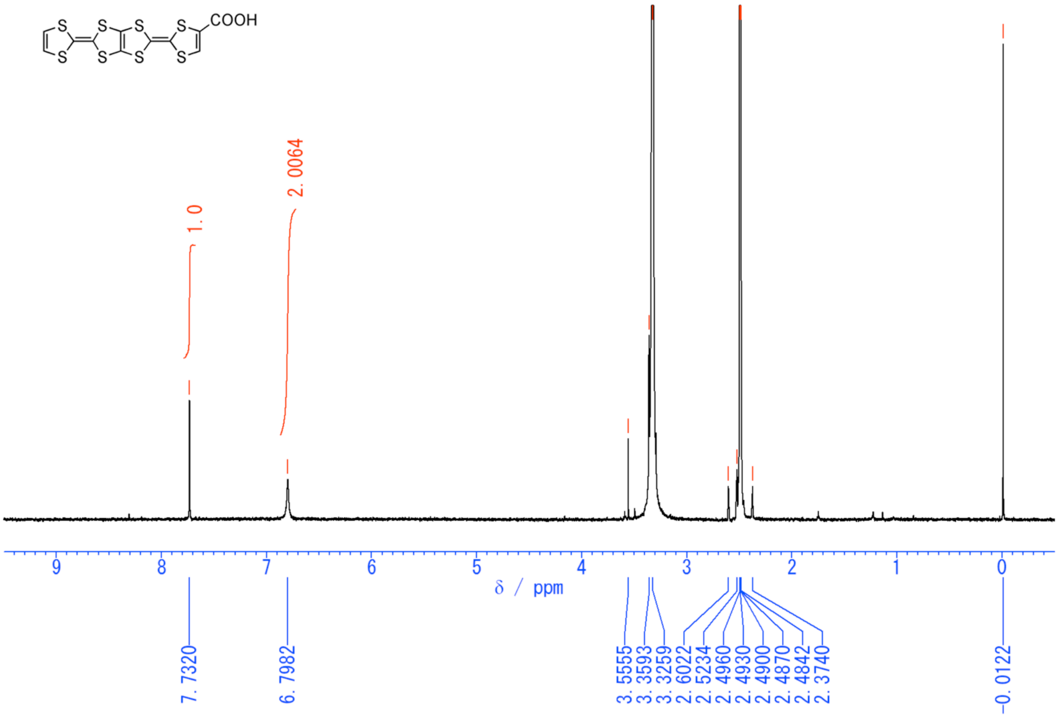

Fig. S2. ^{1}H NMR spectrum of TTPCOOH in DMSO-d$_6$.

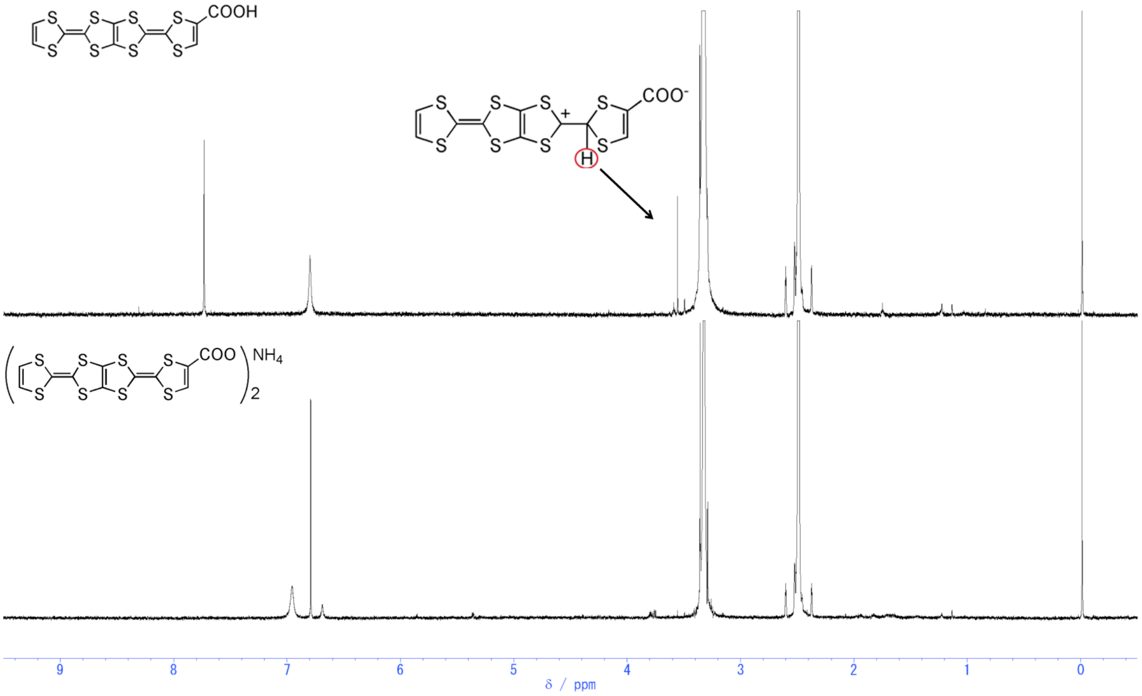

Fig. S3. Comparison of ^{1}H NMR spectra of TTPCOOH and $(TTPCOO)_2NH_4$ in DMSO-d_6.

Figure S3 indicates that TTPCOOH is converted into the ammonium salt completely from the disappearance of the singlet peak at 7.73 ppm in the bottom chart. Moreover, $TTPH^+COO^-$ species is found only in the upper chart with the ratio of ca 30%, which is considered to play a role to keep charge neutrality in TTPCOOH. Note that the chemical shift of the proton in $TTFH^+$ is also upfiled-shifted in CD_3CN solution.[S4]

4. Physical measurements.

XPS analysis.

XPS spectrum was obtained by monochromatic Al *K*α X-ray excitation at 45° take-off angle and 55 eV pass energy, with the energy scan in 0.1 eV steps. The curve fitting of the spectrum was performed by adopting a symmetrical Gaussian–Lorentzian linear combination line with a Shirley-type background.[S2]

ESR analysis.

ESR spectra were measured for crystalline powder with a JEOL JES-FA100 instrument. The spin concentration was evaluated by comparison with the peak area of 2,2-diphenyl-1-(2,4,6-trinitrophenyl)hydrazino (DPPH) radical.[2a]

Transport measurements.

DC conductivity was measured using physical properties measurement system (Quantum design PPMS-9). Magnetic susceptibility was measured on the magnetic property measurement system (Quantum design MPMS-7). Polycrystalline solids (10.708 mg for [$(\mathrm{TTPCOO})_2\mathrm{NH}_4$], and 9.618 mg for TTPCOOH) were enveloped with a plastic wrap using a ceramic pincette, and set into plastic straw in magnetic susceptibility measurement. Diamagnetic component in the samples was subtracted by adopting Pascal's constant[S3], and the contribution of the plastic wrap and straw, which was evaluated by blank measurement without samples, was subtracted from the total susceptibility carefully.

EMF was measured by means of the hydrogen concentration method using a pellet with 1 mm thickness at rt. Carbon(C)/platinum(Pt) sheet (EC-20-10-7, Pt20C80wt%, Pt 1mg/cm^2, ElectroChem Inc.) was bonded on both faces of the sample with polymer glue as an electrode material. Each electrode was attached with two gold lead wires, one of which was connected to a potentiostat and the other of which was connected to an electrometer, as shown in Fig. 3a. The sample was exposed to the atmosphere with a constant partial pressure of hydrogen gas diluted by argon gas.

5. XPS Spectrum

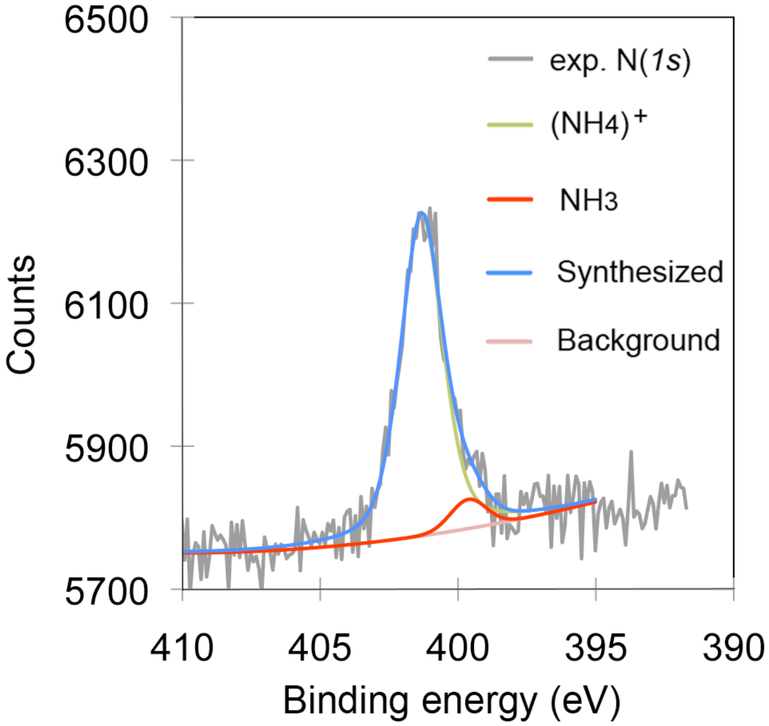

Fig. S4. XPS spectrum for N*1s* core level of $(TTPCOO)_2NH_4$.

6. ESR spectra

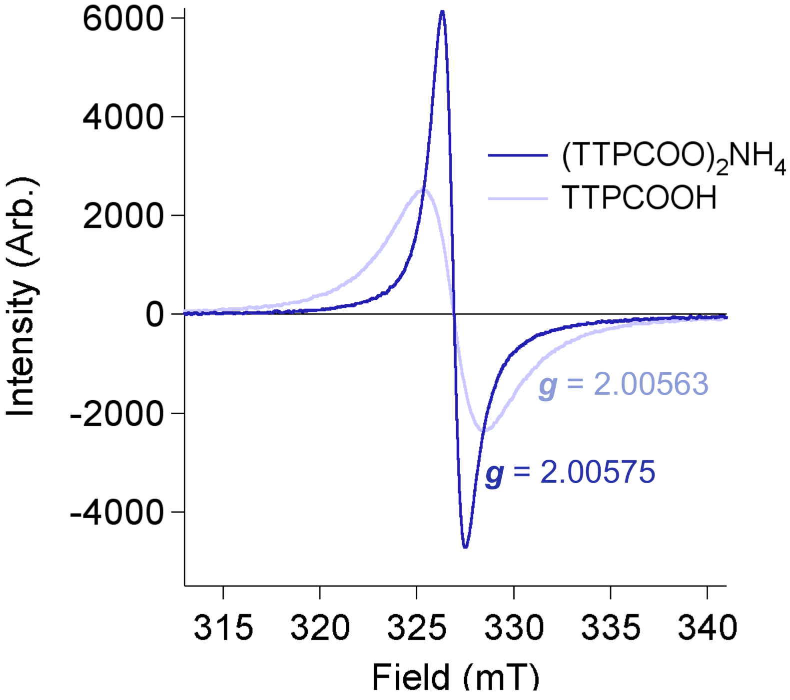

Fig. S5. ESR spectra of polycrystalline solids of $(TTPCOO)_2NH_4$ and TTPCOOH, which were measured at room temperature.

The spin concentration was evaluated to be 32 % for $(TTPCOO)_2NH_4$ (see text) and 37 % for TTPCOOH. The shape of the signal of TTPCOOH is broadened even with considering anisotropy of crystals, which suggests a possibility of the mixture of multiple radical species.

7. Reference

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