Supporting Information

Dielectric Response of 1,1-Difluorosumanene Caused by an In-Plane Motion

Minghong Li,^a JianYun Wu,^b Kohei Sambe,^b Yumi Yakiyama,^{*a,c} Tomoyuki Akutagawa,^{b,d} Takashi Kajitani,^e Takanori Fukushima,^{f,g} Kazunari Matsuda,^h and Hidehiro Sakurai^{a,c}

^aDivision of Applied Chemistry, Graduate School of Engineering, Osaka University 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

^bGraduate School of Engineering, Tohoku University 6-6 Aramakiazaaoba, Aoba-ku, Sendai 980-8579, Japan

^cInnovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University

2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

^dInstitute of Multidisciplinary Research for Advanced Materials (IMRAM) , Tohoku University 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

^eOpen Facility Development Office, Open Facility Center, Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^fLaboratory for Chemistry and Life Science, Institute of Innovative Research, Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^gDepartment of Chemical Science and Engineering School of Materials and Chemical Technology, Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^hInstitute of Advanced Energy, Kyoto University Gokasho, Uji, Kyoto 611-0011, Japan

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1. General experimental information

All chemicals were reagent grade and used as received if not mentioned. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-ECS400 NMR spectrometer (¹H: 400 MHz and ¹³C: 100 MHz). Chemical shift (δ) are expressed relative to the resonances of the residual non-deuterated solvent for ¹H (CDCl₃: ¹H(δ) = 7.26 ppm, (CD₃)₂CO: ${}^{1}H(\delta) = 2.50$ ppm) and for ${}^{13}C$ (CDCl₃: ${}^{13}C(\delta) = 77.0$ ppm, (CD₃)₂CO: ${}^{13}C(\delta) = 39.52$ ppm). High resolution mass spectra (HRMS) were measured using electron impact mode (EI) methods on JEOL JMS-777V spectrometer. Infrared spectra and UV-vis absorption spectra were recorded on a JASCO FTIR-4100 spectrometer and a JASCO V-670 spectrometer, respectively. VT-IR measurement was performed on a JASCO FTIR-4200 spectrometer with JASCO IRT-5000 FTIR microscope system. Electrochemical measurements were performed on a BAS ALS660A Electrochemical Measurement System for cyclic voltammetry. A standard three-electrode cell incorporating a glassy carbon (GC) as a working electrode, a Pt counter electrode and an Ag/AgNO₃ reference electrode was employed for electrochemical measurements. Specific heat measurement was carried out on a Perkin Elmer DSC 8500 differential scanning calorimeter, where temperature and enthalpy were calibrated with In (156.6 °C, 28.450 J/g) standard sample in a sealed Al pan. Specific heat profile was analyzed using the Perkin Elmer Pyris software. TG-DTA was carried out using a Rigaku Thermo Plus TG8120 thermal analysis station with Al2O3 reference under N2. Differential scanning calorimetry (DSC) analysis was performed on a Mettler thermal analysis DSC1-TS station using an Al₂O₃ reference under N₂. Temperature-dependent powder X-ray diffraction patterns were collected on a Rigaku Rint-Ultima III diffractometer using Cu K α radiation at $\lambda = 0.154187$ nm. Temperature-dependent dielectric constants were measured using the two-probe AC impedance method between 1000 and 1000×10^3 Hz (HP 4194A impedance/gain-phase analyzer, Hewlett-Packard). Electrical contacts were prepared using gold paste (Tokuriki 8560) to attach the 10 μ m ϕ gold wires to the single crystal and the 25 μ m ϕ gold wires to the 3 mm ϕ compressed pellet. Temperature control between 298 and 423 K was carried out using a Linkam LTS350 hot stage. Melting points were determined on a Standford Research Systems Optimelt MPA100 and were uncorrected. The preparative TLC (PTLC) purification was conducted using Wakogel B-5F PTLC plates. Elemental analyses were measured on a J-Science Micro corder JM10 at the Analysis Center in Osaka University.

2. Synthesis

4,7-dihydrospiro[tricyclopenta[def,jkl,pqr]triphenylene-1,2'-[1,3]dithiane] (4)



To a solution of sumanene-1-one^[S1] (80.0 mg, 0.287 mmol) in dry CH_2Cl_2 (132 mL) was added 1,3-Dithiopropane (0.820 mL, 8.18 mmol, 28.5 equiv.) and Boron trifluoride etherate (1.66 mL, 13.4 mmol, 46.7 equiv.). The reaction mixture was stirred at 23 °C for 1.5 h. After quenched with 10% NaOH aqueous solution, the organic layer was washed with sat. NaHCO₃ aq., dried over anhydrous Na₂SO₄, filtered and

concentrated under reduced pressure. The residue was purified by silica gel chromatography by a eluent of Hexane: DCM = 2:1 to give the target product **4** as a white solid (97.0 mg, 92%).

mp: 59 °C; ¹H NMR (CDCl₃): δ (ppm) 7.37 (d, J = 8.0 Hz, 2H), 7.14 (s, 2H), 7.12 (d, J = 8.0 Hz, 2H), 4.71 (d, J = 20.0 Hz, 2H), 3.46 (d, J = 20.0 Hz, 2H), 3.32 (m, 4H), 2.34 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 154.94, 150.79, 149.00, 148.91, 148.85, 144.73, 124.15, 123.67, 121.76, 60.73, 41.91, 29.52, 28.82, 24.80; IR (KBr): 3047(s), 2949(s), 2938(s), 2893(vs), 1556(w), 1416(s), 1389(vs), 1268(vs), 1235(s), 1076(s), 914(s), 796(vs), 776(vs), 747(vs), 675(w), 630(s), 611(s), 566(s), 516(w); HRMS (EI) *m/z*: Calcd. for C₂₄H₁₆S₂ [M]⁺ 368.0693, found: 368.0688.

1,1-difluoro-4,7-dihydro-1*H*-tricyclopenta[*def.jkl,pqr*]triphenylene (1,1-Difluorosumanene) (1)



A carefully dried PP-tube was charged with *N*-iodosuccinimide (29.0 mg, 0.129 mmol, 2.48 equiv.) and purged with N₂. CH_2Cl_2 (10.0 mL) was added by syringe and the mixture was cooled to -30 °C. Pyridine hydrofluoride (0.033 mL, 1.27 mmol, 24.4 equiv.) was added in one portion, then followed by the dropwise addition of **4** (19.0 mg, 0.052 mmol) in 4.00 mL dichloromethane. The mixture was stirred at -30 °C for 30 min. Then water and dichloromethane (30 mL) were added and the organic phase was washed

with sat. NaHCO₃ aq., dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by PTLC (Hexane/DCM = 2:1) to give the compound **1** as a white solid (12.0 mg, 77 %). Single crystal of **1** was obtained by the slow evaporation method using chloroform solution of **1**.

mp: 226 °C (dec.); ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.20 (d, J = 8.0 Hz, 2H), 7.16 (s, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.72 (d, J = 20.0 Hz, 2H), 3.49 (d, J = 20.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) 154.10, 149.24, 149.00, 148.79, 145.93 (dd, ${}^{3}J_{C-F} = 8.0, 3.0$ Hz), 142.94 (t, ${}^{2}J_{C-F} = 27.0$ Hz), 126.48 (t, ${}^{1}J_{C-F} = 258$ Hz), 124.61, 124.03, 122.35, 42.01; ¹⁹F-NMR ((CD₃)₂CO, 376 MHz): δ (ppm) –91.55 (d, J = 263 Hz), -117.05 (d, J = 244 Hz); IR (KBr): 3048(s), 2931(s), 2886(vs), 1570(w), 1446(w), 1393(vs), 1219(vs), 1189(vs), 1171(s), 1068(vs), 1035(vs), 906(s), 816(s), 804(vs), 288(vs), 739(s), 672(w), 607(s), 566(s), 543(w), 475(w); HRMS (EI) *m/z*: Calcd. for C₂₁H₁₀F₂ [M]⁺ 300.0751, found: 300.0750. Elemental Analysis: Calcd. for C₂₁H₁₀F₂(H₂O)_{0.2} C, 83.00; H, 3.45; Found: C, 83.12; H, 3.68.

3. NMR data of 4 and 1.

 1 H NMR data of **4**



¹³C NMR data of 4





¹³C NMR data of 1





4. X-ray Crystal Structure Analysis

The diffraction data for 1 (at 100 K) was recorded on a DICTRIS PILATUS3 X CdTM 1M Detector System ($\lambda = 0.43158$ Å) at 100 K at SPring-8 BL02B1. The diffraction images were processed by using RIGAKU RAPID AUTO.^[S2]

The diffraction data for 1 (at 413 K) was recorded on an ADSC Q210 CCD area detector with a synchrotron radiation ($\lambda = 0.70000$ Å) at 2D beamline in Pohang Accelerator Laboratory (PAL). The diffraction images were processed by using HKL3000.^[S3]

All the structures were solved by direct methods (SHELXT-2015, 2018/2)^[S4a] and refined by fullmatrix least squares calculations on F^2 (SHELXL-2018/3)^[S4b] using the Olex2^[S5] program package.

CCDC 2119515 (1 at 100 K) and 2119514 (1 at 413 K) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (https://www.ccdc.cam.ac.uk/).

1 (at 100 K): $C_{21}H_{10}F_2$, trigonal, space group *R3c* (No. 161), a = b = 16.735(2) Å, c = 7.889(2) Å, V = 1913.5(7) Å³, $\rho_{calcd} = 1.564$ g/cm³, Z = 6, 874 unique reflections out of 972 with $I > 2\sigma(I)$, 82 parameters, $3.43^{\circ} < \theta < 38.00^{\circ}$, $R_1 = 0.0372$, w $R_2 = 0.0964$, GOF = 1.037.

1 (at 413 K): $C_{21}H_{10}F_2$, trigonal, space group *R3c* (No. 161), a = b = 16.872(2) Å, c = 8.169(2) Å, V = 2013.9(7) Å³, $\rho_{calcd} = 1.486$ g/cm³, Z = 6, 1156 unique reflections out of 1504 with $I > 2\sigma(I)$, 82 parameters, $4.387^{\circ} < \theta < 33.115^{\circ}$, $R_1 = 0.0580$, w $R_2 = 0.1652$, GOF = 1.070.

5. Supporting Figures



Fig. S1. Energy diagram of 1, 2 and 3 with the Kohn-Sham MO representations of each orbital calculated at B3LYP/6-31G(d,p) level of theory.



Fig. S2. UV-vis spectra of **1**. a) Simulated data calculated at TD-B3LYP/6-31G++(d,p)) level of theory. b) Experimentally obtained spectrum. 1.0×10^{-5} M in CH₂Cl₂. UV-vis spectra of **2** and **3** (1.0×10^{-5} M in CH₂Cl₂) is also shown.



Fig. S3. Cyclic voltammogram of THF solution of **1** $(2.0 \times 10^{-3} \text{ M})$ measured at 294 K in the presence of $[n-Bu_4N]^+[ClO_4]^-(0.1 \text{ M})$ supporting electrolyte. Scan rate: 0.1 V s⁻¹. The ferrocene/ferrocenium couple (Fc⁰/Fc⁺) was used as a reference.



Fig. S4. a) TGA and b) DSC data for 1.



Fig. S5. The specific heat measurement for 1.



Fig. S6. a) Temperature dependent VT-PXRD peak intensity change at around $2\theta = 25^{\circ}$ (corresponding to 202 reflection). b) The crystal plane (one of (101) plane, red) and the crystal structure relationship.



Fig. S7. Crystal structures of 1 at 413 K. a) Thermal displacement ellipsoid plot of 1 in the crystal structure at 50% probability (Both F1 and F2 have Occ. 0.33). b) View from the *a* axis. c) View from the *c* axis. Blue and red dotted lines indicate the shortest C (aromatic)…C(benzylic) and F…F distances, respectively. Gray: C; light green: F. Hydrogen atoms are omitted for clarity.



Fig. S8. Bond length and the displacement ellipsoid size differences in 1 at 100 K and 413 K.



Fig. S9. a) Energy frameworks representing the total interaction energies in the crystal structure of **1** at 413 K. b) The output files of energy framework calculations and averaged interaction energies of **1** at 413 K with colour codes.

The calculation was performed using CrystalExplorer 21.5.^[S6] The "energy framework" was constructed based on the crystal symmetry, and the energies are estimated from B3LYP/6-31G(d,p) molecular wave functions calculated at the crystal geometry, summing up the electrostatic, polarization, dispersion, and exchange-repulsion terms based on a calculated at the crystal geometry, summing up the electrostatic, polarization, dispersion, and exchange-repulsion terms based on a scaling factor of 1.057, 0.740, 0.871, and 0.618, respectively. The dispersion force mainly contributed to the stabilization and the contribution from coulombic interaction was small.



Fig. S10. VT-IR spectra of **1** measured at 74 °C ~110 °C. All the data was obtained by using ϕ 7 mm KBr pellet of **1** on a heater-attached Cu plate. Sample temperature was obtained by using a thermocoupler directly attached onto the pellet. a) IR spectra showing C–F stretching (blue) and C–H out-of-plane bending (red) modes. All peaks indicated with arrows showed lower wavenumber shift by heating. b) Magnified figure of each region. c) Temperature dependent wavenumber change at the peak top position of each absorption band.

791.5

791.0

790.5

100 110 120

90

Temperature

Wavenumber



Fig. S11. Dielectric response of crystalline powder of 1. a) The real and b) the imaginary parts of the dielectric constant of 1 obtained via heating process.



Fig. S12. Dielectric response of crystalline powder of 3. a) The real and b) the imaginary parts of the dielectric constant of 3 obtained via heating process.



Fig. S13. Arrhenius plot of the relaxation time τ as a function of inverse temperature for **1** in a) powder crystalline pellet and b) single crystalline sample, where the τ -value is the inverse of measurement *f*-values of the $\tau = 1/(2\pi f)$. The dotted line represents the least-squares fit of the data.



Fig. S14. Sample photos applied for the single-crystal-based dielectric measurement. a) Single crystal photo of **1**. b) Measurement setting for the dielectric response measurement in the long axis direction. c) Measurement setting for the dielectric response measurement in the short axis direction.

6. Cartesian Coordinates of Optimized Structures

All theoretical calculations were conducted by Gaussian09.^[S7] The ground state structure optimization were performed at the B3LYP/6-31G(d,p) level of theory. Simulation of UV-vis spectrum were performed by TD-DFT (time-dependent density functional theory) at the B3LYP/6-31G++(d,p) level of theory using the optimized coordinates.

a) Optimized cartesian coordinates of 1

С	-0.72807	0.428827	1.408445	Н	-0.46523	2.509762	3.610947
С	-0.76868	-0.77111	0.719841	Н	0.9536	-0.59868	4.159419
С	-0.17103	-1.92834	1.221208	Н	0.903171	-2.71028	2.927244
С	0.056953	-2.86406	0	С	-0.76868	-0.77111	-0.71984
С	-0.17103	-1.92834	-1.22121	С	-0.72807	0.428827	-1.40845
С	0.379507	-1.85974	-2.50067	С	-0.08488	0.55525	-2.64801
С	0.411167	-0.62104	-3.21784	С	0.198928	2.068334	-2.85551
Н	0.903171	-2.71028	-2.92724	С	-0.04885	2.658975	-1.43994
Н	0.9536	-0.59868	-4.15942	С	0.4875	3.729063	-0.71512
С	-0.70008	1.671284	-0.69379	С	0.4875	3.729063	0.715116
С	-0.70008	1.671284	0.693793	Н	1.224745	2.244169	-3.19482
С	-0.04885	2.658975	1.439937	Н	-0.46523	2.509762	-3.61095
С	0.198928	2.068334	2.855508	Н	1.032977	4.524418	-1.21683
С	-0.08488	0.55525	2.648005	Н	1.032977	4.524418	1.216827
С	0.411167	-0.62104	3.21784	F	-0.80176	-3.93402	0
С	0.379507	-1.85974	2.500672	F	1.318809	-3.39181	0
Н	1.224745	2.244169	3.194816				

a) Optimized cartesian coordinates of 2

2.970651	0.958107	3.120097	Н	1.409983	-0.6845	0.013492	С
-0.71648	-0.68451	1.214202	С	0.716476	-0.68451	1.214202	С
-1.40998	-0.6845	0.013492	С	1.214665	-0.06667	2.3657	С
-2.65633	-0.06665	-0.13098	С	0	0.186263	3.303022	С
-2.86048	0.186006	-1.6517	С	-1.21467	-0.06667	2.3657	С
-1.44129	-0.06671	-2.23476	С	-2.51725	0.438276	2.279584	С
-0.71558	0.43843	-3.31974	С	-3.23296	0.438454	1.040134	С
0.71558	0.43843	-3.31974	С	-2.97065	0.958107	3.120097	Н
-1.21683	0.958537	-4.13245	Н	-4.18741	0.958554	1.012607	Н
1.21683	0.958537	-4.13245	Н	-0.69331	-0.68449	-1.22737	С
0	-0.48695	4.171147	Н	0.693313	-0.68449	-1.22737	С
0	1.207898	3.696913	Н	1.441288	-0.06671	-2.23476	С
3.201984	1.207442	-1.84903	Н	2.860477	0.186006	-1.6517	С
3.611889	-0.48771	-2.08569	Н	2.656325	-0.06665	-0.13098	С
-3.20198	1.207442	-1.84903	Н	3.232955	0.438454	1.040134	С
-3.61189	-0.48771	-2.08569	Н	2.517245	0.438276	2.279584	С
				4.187409	0.958554	1.012607	Н

c) Optimized cartesian coordinates of 3

2.892172	3.089247	-0.96424	Н	1.412196	0.017142	0.836277	С
-0.72064	1.214478	0.836266	С	0.720636	1.214478	0.836266	С
-1.4122	0.017142	0.836277	С	1.218828	2.346079	0.18084	С
-2.64141	-0.11748	0.181185	С	0	3.278476	-0.06975	С
-2.839	-1.63926	-0.07007	С	-1.21883	2.346079	0.18084	С
-1.42215	-2.22847	0.181289	С	-2.48438	2.261021	-0.39288	С
-0.71598	-3.2827	-0.39139	С	-3.20056	1.020951	-0.39279	С
0.71598	-3.2827	-0.39139	С	-2.89217	3.089247	-0.96424	Н
-1.22941	-4.05071	-0.96166	Н	-4.12177	0.960101	-0.96406	Н
1.229414	-4.05071	-0.96166	Н	-0.69136	-1.23089	0.83618	С
0	3.775405	-1.34038	F	0.691356	-1.23089	0.83618	С
0	4.359268	0.76996	F	1.422151	-2.22847	0.181289	С
3.775889	-2.18102	0.767675	F	2.839003	-1.63926	-0.07007	С
3.267849	-1.88624	-1.34139	F	2.641409	-0.11748	0.181185	С
-3.26785	-1.88624	-1.34139	F	3.200559	1.020951	-0.39279	С
-3.77589	-2.18102	0.767675	F	2.484383	2.261021	-0.39288	С
				4.121771	0.960101	-0.96406	Н

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