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Electrochemical sum frequency generation spectroscopic studies on the interface of room temperature ionic liquid - octathio[8]circulene (sulflower) thin-film

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【序】 Octathio[8]circulene (sulflower), shown in fig. 1, possesses high thermal stability, low solubility in common organic solvents, and redox potentials within the range needed for organic electronic devices. Recently, thin films of sulflower were shown to have organic field-effect transistor (OFET) properties¹ in an electrochemically gated device where low-voltage switching was enabled by the high electrical field present at the double layer of an electrically polarized room temperature ionic liquid (RTIL) interface. In this study, we use infrared-visible sum frequency generation spectroscopy (IV-SFG) to examine an RTIL/sulflower thin-film interface on a polycrystalline platinum electrode within the same range of applied potentials as reported for the electrochemically-gated RTIL-OFET.

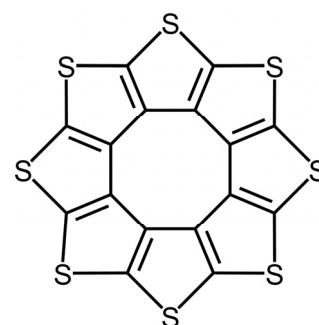


Fig. 1. Sulflower

【実験】 Room-temperature ionic liquids used in this study purchased from from Kanto Chemicals ($H_2O \leq 18$ ppm, halogens < 5 ppm) and used without further purification. Being liquid salts, RTILs consist of a [cation][anion] pair. [bmim] represents the 1-butyl-3-methylimidazolium cation, [TfSA] the bis(trifluoromethylsulfonyl)imide anion, and [OTf] the trifluoromethanesulfonate anion. Samples of sulflower used in this study were synthesized by the method used in reference 3. Thin films of sulflower were sublimed onto the polished surface of platinum electrodes under 1×10^{-4} Pa at a rate of $1-3$ nm min^{-1} inside an ULVAC VTR-300M evaporation system to a nominal thickness of 50 nm as determined by QCM.

Our (sealed) three-electrode electrochemical SFG (EC-SFG) cell uses a $\phi 10 \times 5$ mm polycrystalline Pt disc working electrode, a coiled Pt wire counter electrode, and a Ag/Ag⁺ type reference electrode (0.1 M AgOTf in [bmim][OTf]). The cell design allows the surface of the working electrode to be pressed tightly against a BaF₂ window, through which SFG measurements can be taken. An HZ-5000 Automatic Polarization System (Hokuto Denko) was used for both control and measurement of the applied potentials.

A mode-locked ps Nd:YAG laser (EKSPLA, 10 Hz, 25 ps) with a difference frequency generation (DFG) unit was used to generate a visible (532 nm) and a tunable 2.5 – 10 μ m infrared beam. Visible and infrared beams are overlapped spatially and temporally on the electrode surface to generate a sum-

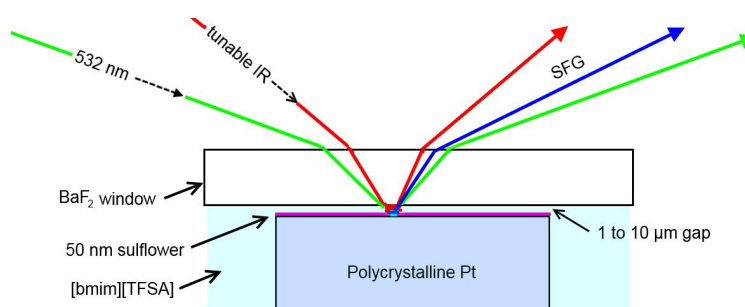


Fig. 2 Schematic of electrochemical cell and SFG geometry

frequency beam of $\omega_{SFG} = \omega_{IR} + \omega_{VIS}$. SFG measurements were performed at 20 °C with ssp (denoting the s-polarized sum-frequency, s-polarized visible, and p-polarized infrared beams,

respectively) and ppp polarization combinations. All SFG spectra were obtained at a quasi-equilibrium condition, which was confirmed by monitoring the sum-frequency signal intensity during the 1 mV s^{-1} potential change and for 15 minutes after each potential step.

Gaussian 03 was used for all the density functional theory (DFT) calculations, which were done at the B3P86/UB3P86 level of theory using the 6-31G(d,p) basis set. Optimization and frequency analysis were done for the neutral, monocation (singlet), and dication (triplet) forms of sulflower.

【結果と考察】

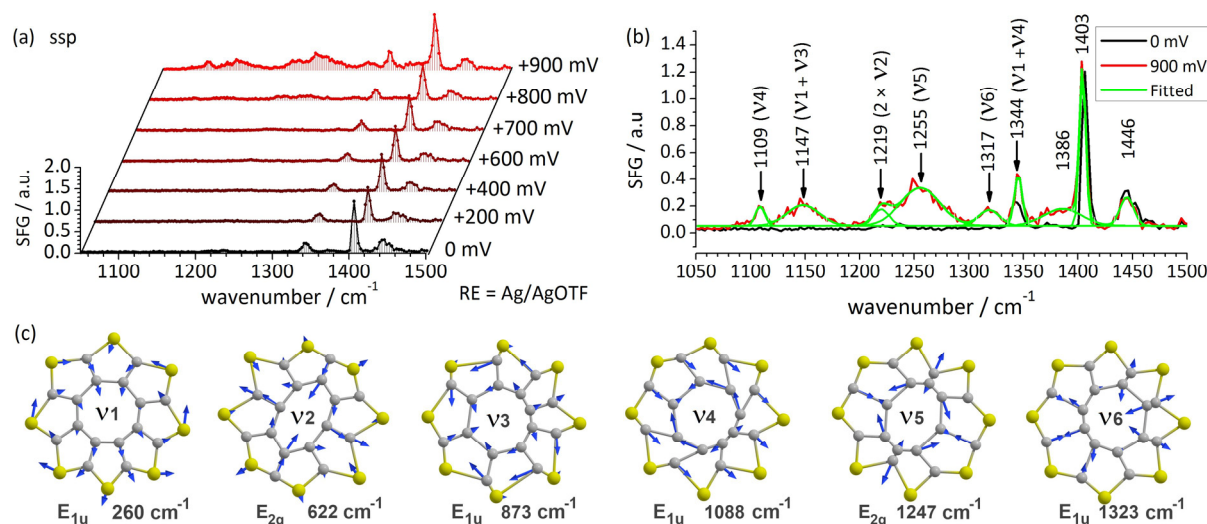


Fig. 3 (a) ssp SFG spectra of [bmim][TfSA]-sulflower -Pt interface at stepped potentials. (b) Gaussian fitting of +900 mV SFG emission (c) double-length eigenvectors, symmetry species, wavenumber of dication vibrational modes

The trend in SFG emission in the ssp polarization combination is shown in fig. 3a. From 0 mV to +700 mV we only observed 3 peaks. We interpret these as belonging to the neutral species of sulflower. Spectra obtained in the ppp combination were similar. At a threshold voltage in the range of +700 to +800 mV additional peaks appear, and these continued to gain intensity until +900 mV. In terms of the OFET device described by Fujimoto et al.¹, this threshold voltage corresponds to the gate potential where an approximately 25% rise in current was observed.

SFG is based on a second-order nonlinear optical process which can only occur when the q^{th} vibrational mode is both IR and Raman active. We performed density functional analysis and obtained the normal mode frequencies, IR intensities, and Raman scattering activities of the neutral (singlet), monocation (doublet), and dication (triplet) forms of sulflower. Only the triplet dication possessed vibrational modes with both significant IR and Raman activity. Eigenvector images were generated in Chemcraft, allowing the symmetry species of each vibrational mode to be identified within the D_{8h} character table. Our peak assignments are shown in figs. 3b and 3c.

The study published by Bukalov et al.² in which peak assignments for experimental IR and Raman spectra were made, was helpful in our assignment of the SFG peak at 1219 cm^{-1} to an overtone of an E_{2g} vibration. We noted that the neutral form has an E_{2g} Raman peak 616 cm^{-1} . A slight blueshift of this vibration would allow it to match $1219 \div 2 = 609.5 \text{ cm}^{-1}$.

【文献】

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