Electrical Rectification by Monolayers of Three Molecules

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Summary: Rectification, i.e. asymmetrical electrical conduction by a Langmuir-Blodgett monolayer of dicyano{4-[1-cyano-2-(1-hexadecylquinolin-1-ium-4-yl)vinyl]phenyl} methanide (**1**), occurs between both Al and Au electrodes: this rectification arises from the asymmetry of the molecule, and the interplay between the zwitterionic ground state D^{+}-π-A^{-} and the less dissociated first electronic excited state D^{0}-π-A^{0}. Two more monolayer rectifiers have been found: 1-butyl-2,6-bis{2-[4-(dibutylamino)phenyl] vinyl}pyridin-1-ium iodide (**2**) is an interionic rectifier with back charge transfer between the iodide ion and the pyridinium ring. 1a-[4-(dimethylamino)phenyl]-1a*H*-1a-aza-1(2)a-homo(C_{60}-I_h)[5,6]fullerene (**3**) is a moderate rectifier, with a rectification ratio of 2.

Keywords: Aviram-Ratner proposal; electrical conduction through molecules; Langmuir-Blodgett monolayers; unimolecular rectification

Introduction

"Molecular electronics" *(sensu stricto),* or "molecular-scale electronics" is the study of electrical and electronic processes measured or controlled on a molecular scale.[1] A second, much wider, definition of molecular electronics *(sensu lato*), or "molecule-based electronics" encompasses electronic processes by molecular assemblies of any scale, including crystals and conducting polymers.[1] This review falls within the former, narrower definition of the field, and focuses on our own work on electrical rectification, or asymmetric conduction, through a monolayer of organic molecules.

We have "reached out and touched" individual molecules with two metal electrodes, and exploited their structure, to control the flow of electrical signals from them and to them. We have measured electrical rectification, or asymmetrical conductivity, in Langmuir-Blodgett monolayers of three molecular species: first, dicyano{4-[1-cyano-2-(1-hexadecylquinolin-1-ium-4-yl)vinyl]phenyl} methanide, ($C_{16}H_{33}$Q-3CNQ, **1**; Fig. 1), a zwitterionic D^{+}-π-A^{-} molecule,[2-4] second, 1-butyl-2,6-bis{2-[4-(dibutylamino)phenyl]vinyl}pyridin-1-ium iodide (($Bu_2N\varphi V)_2BuPy^{+}I^{-}$, **2**; Fig. 1), a charge-transfer salt,[5] and third, 1a-[4-

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(dimethylamino)phenyl]-1a*H*-1a-aza-1(2)a-homo(C_{60}-I_h)[5,6]fullerene (DMAn-NC_{60}, **3**; Fig. 1), a D-σ-A molecule.[6]

These results are an experimental realization of a molecular rectifier proposed in 1974 by Aviram and Ratner (AR).[7] The interest in such systems is due to the hope that molecular-scale electronics, in one embodiment or other, will become practical for integrated circuits. The four-decade-old progressive miniaturization (and concomitant increase in speed) of integrated circuits uses silicon and inorganic semiconductors, and is well described by Moore's "law", which has seen a remarkable doubling in circuit speeds, at first every 2 years, then every 18 months or so.[8] The increased processor and memory speeds have been driven by market forces, but may fail in the future at some scale of miniaturization (50 nm or 10 nm between adjacent circuit elements?), because of cost, or inherent limitations on inorganic materials, or limitations in electron-beam lithography.

The AR Ansatz

The first concrete suggestion for unimolecular electronics was the 1974 AR proposal that a one-molecule rectifier could be achieved with a D-σ-A molecule **4**, where D is a good one-electron donor, with relatively low first ionization potential, where σ is some saturated covalent "sigma" bridge, and where A is a good one-electron acceptor, with relatively high electron affinity, when this molecule is placed between two appropriate metal contacts M_1 and M_2 [7]. The σ bridge should partially decouple the molecular orbitals mostly localized on the donor moiety D from the molecular orbitals mostly localized on the acceptor moiety A, yet allow for intramolecular charge-transfer band. The molecular ground state of D-σ-A has a low dipole moment (written as D^0-σ-A^0), while the first excited state is much more polar, and is written as the zwitterion D^+-σ-A^-.

The suggested mechanism consists of two, not necessarily simultaneous, resonant electron transfers across metal-organic interfaces:

$$M_1 + D^0\text{-}\sigma\text{-}A^0 + M_2 \rightarrow M_1^- + D^+\text{-}\sigma\text{-}A^0 + M_2 \qquad (1)$$

$$M_1^- + D^0\text{-}\sigma\text{-}A^0 + M_2 \rightarrow M_1^- + D^+\text{-}\sigma\text{-}A^- + M_2^+ \qquad (2)$$

This creates the excited state D^+-σ-A^-. To restore the molecule to the initial state, there is an inelastic down-hill intramolecular electron transfer:

$$M_1^- + D^+\text{-}\sigma\text{-}A^- + M_2^+ \rightarrow M_1^- + D^0\text{-}\sigma\text{-}A^0 + M_2^+ \qquad (3)$$

Overall, one electron has migrated from M_2 to M_1. This intramolecular electron transfer requires that the molecule has reasonable oscillator strength in the optical intervalence transfer (IVT) band linking D^0-σ-A^0 to D^+-σ-A^-.

In their proposed molecule **4,** Aviram and Ratner suggested D = tetrathiafulvalene, A = tetracyanoquinodimethane, because these were, respectively, a good organic donor D, and one of the best organic acceptors A. The AR mechanism uses an IVT electronic transition, which is fast (ps to ns), compared with translations, conformational transitions, or molecular rearrangements.

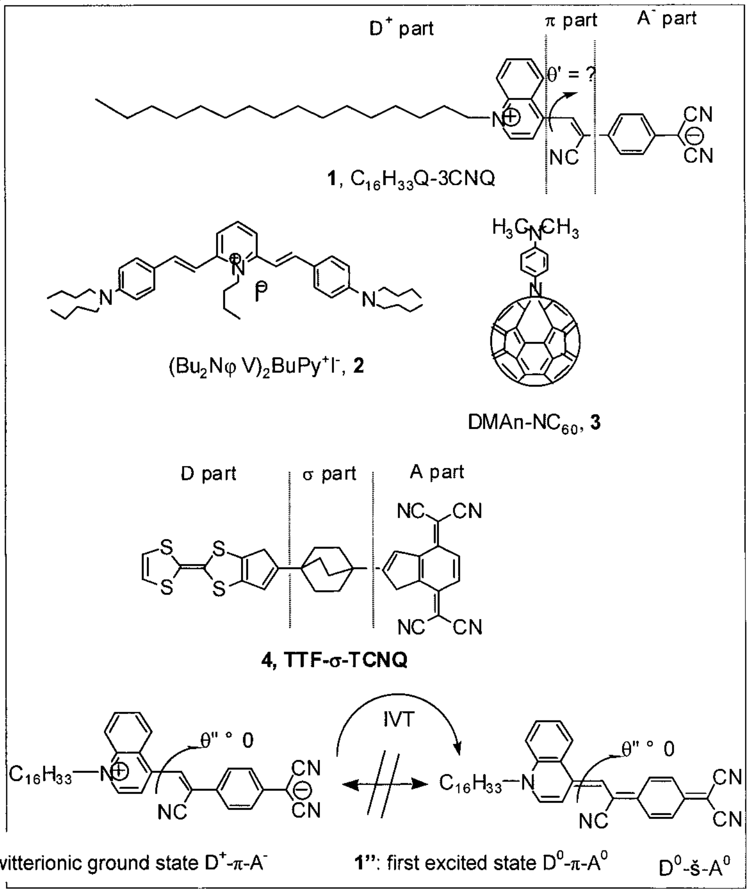

Figure 1. Relevant molecular structures.

Assembly

To design unimolecular rectifiers or, some day, unimolecular transistors, one must choose how the designed molecules will be assembled and measured. The molecules can be placed on an electrode surface by either physisorption or chemisorption. Physisorption includes the random deposition from a vapor onto a solid substrate ('chemical vapor deposition'), or the transfer of an ordered monolayer (Langmuir film or Pockels-Langmuir[9] monolayer) from the air-water interface to a solid substrate, forming a Langmuir-Blodgett (LB) monolayer or, if the transfer is repeated, an LB multilayer. The unimolecular rectifiers described below were assembled as LB films. Chemisorption forms a covalent bond between molecule and electrode, (e.g. thiols and similar compounds bonded to gold, or chlorosilanes bonded to hydroxyl-covered silicon surfaces ("self-assembled monolayers").

The Top Electrode

It is easy enough to transfer an organic monolayer or multilayer atop a sufficiently flat metal layer either by the LB method,[10] or by chemisorption.[11] It is much more difficult to then put a second metal electrode atop the organic layer without damaging the organic layer. J. Roy Sambles made dramatic improvements, first by using Mg as the top electrode,[12-16] then by using the "cold gold" method.[17] Samples showed that **1** rectified when sandwiched between Pt and Mg.[11,12]

Rectification of $C_{16}H_{33}Q$-3CNQ

We confirmed unimolecular rectification by **1**; we avoided asymmetries in the current-voltage plots due to electrodes of dissimilar metals: we used the same metallic electrode on both sides of an LB monolayer or multilayer of **1** (at first Al [2,18,19], now Au [3-6]). We also characterized what in **1** is responsible for rectification, both chemically and spectroscopically.[6,20] Compound **1** is slightly soluble in polar solvents and forms microcrystallites; a single-crystal structure determination was not possible.[2] Its cyclic voltammogram showed a reversible reduction at $E_{1/2}$ = -0.54 V vs SCE (this potential resembles that of the weak acceptor 1,4-benzoquinone, **8**) [2]. The ground-state static electric dipole moment of **1** is $\mu_{GS} = 43 \pm 8$ D at infinite dilution in CH_2Cl_2 [2]. There is an intense, hypsochromic absorption band; this is the intervalence transfer (IVT) band [2,20]. The near-infrared fluorescence lifetime of the first excited state **1"** in solution is as short as 1.4 ps [21]. Using the Stokes shift or theory, the excited-state dipole moment is between 3 and 9 D [20]. **1** is clearly zwitterionic in the ground state (D^+-π-A^-, **1'**), and less dissociated (D^0-π-A^0, **1"**) in the first excited state. The twist angle θ' in structure **1** is non-zero for steric reasons, and prevents the π electron bridge from allowing complete mixing of the quinolinium electrons with the electrons on the 3CNQ part, i.e. states **1'** and **1"** are non-degenerate. Molecule **1** forms amphiphilic Pockels-Langmuir monolayers at the air-water interface, with a collapse pressure of 34 mN m^{-1} and a collapse area of 50 Å^2 at 20 °C [2]. It transfers well on the upstroke, with transfer ratios around 100 % onto hydrophilic glass, quartz, or aluminum [2] or fresh hydrophilic Au [3,4]. It transfers poorly on the downstroke onto HOPG graphite (transfer ratio ≈ 50 %) [2]. Successive layers transfer onto HOPG on the upstroke, with 100% transfer ratios, forming Z-type LB multilayers [2].

The LB monolayer thickness of **1** is 23 Å [2] and 29 Å [4] by X-ray diffraction, 23 Å by spectroscopic ellipsometry, 22 Å by surface plasmon resonance [2,22], and 25 Å by X-ray photoelectron spectrometry (XPS) [22], yielding an average monolayer thickness of 23 Å. Using the calculated maximum molecular length of 33 Å, one estimates a tilt angle of $\cos^{-1}(23 / 33) = 46^\circ$ from the surface normal [2]. The XPS spectrum of one monolayer of **1** on Au shows two N(1s) peaks, one attributable to the quinolinium N, and one attributable to the three CN species [22]. Molecules of **1**, adhering by the two terminal CN groups onto a hydrophilic substrate, are tilted about 45° from the surface normal, and present alkyl chains to the air. This is confirmed by a grazing-angle FTIR study of **1** on Al [2] or on Au [22]. LB multilayers of **1** exhibit an intense IVT absorption band at 575 nm [2].

To perform rectification measurements, LB monolayers and multilayers of **1** were sandwiched between macroscopic Al electrodes [2], or between Au electrodes [3,4]. In both cases, the sample holder was cryo-cooled to 77 K. For Au deposition, 10^{-3} Torr of Ar gas was added to the evaporation chamber [17], to cool the Au atom vapor, and the substrate was shielded from direct thermal radiance from the heated Au source [3,4].

As expected, a monolayer or multilayer of arachidic acid, $C_{19}H_{39}COOH$, sandwiched between Al or Au electrodes, has a sigmoidal and almost symmetrical curve under both positive bias and negative bias [2,4]. When a monolayer of **1** is placed between Al electrodes (with their inevitable patchy and defect-ridden covering of oxide), then a dramatically asymmetric current is seen (Fig. 2). The rectification ratio, RR, is defined as the current at a positive bias V divided by the absolute value of the current at the corresponding negative bias $-V$:

$$\mathrm{RR}(V) = I(V) / | I(-V) | \qquad (4)$$

For **1**, RR = 26 at 1.5 V [2]; this corresponds to a current $I = 0.33$ electrons molecule^{-1} s^{-1} [2]. This same asymmetry is seen also for multilayers of **1**, for a sample covered by Mg pads topped by Al pads [2] (as before [12]), for monolayers and multilayers of **1** on graphite studied by scanning tunneling spectroscopy [2], and even for a solution of **1** in dimethyl sulfoxide placed in the scanning tunneling microscope [2]. The RR varies somewhat from pad to pad, as does the total current, in part because these are two-probe measurements, with all electric resistances (Al, Ga/In or Ag paste, wires, etc.) in series. A thorough review of all data suggested that any molecule which exhibits RR < 2 at maximum bias V should not be considered a rectifier [18]. Some samples of **1** between Al electrodes have enhanced currents, albeit smaller, under negative bias, instead of positive bias [18]. As high potentials are scanned repeatedly, the I-V curves show progressively less asymmetry; the rectification ratios decrease gradually with measurement, i.e. with repeated cycling of the bias across the monolayer. Putting 1.5 V across a monolayer of thickness 2.3 nm creates an electrical field of 0.65 GV m^{-1}; under such large fields, many zwitterionic molecules in the monolayer may turn around, end over end, to minimize the total energy. Measurements of the temperature dependence of rectification of **1** between Al electrodes in the range $105\ K < T < 390\ K$ established that the asymmetry is not temperature-dependent [19].

Although it seemed clear that with symmetrical Al electrodes we had measured the rectification of several molecules in parallel (unimolecular rectification) [2], some asked whether the oxide covering of the Al electrodes could somehow be responsible for the I-V asymmetry. Using the cold-gold evaporation technique [17], the current rose dramatically, and asymmetric conduction was seen again (Figs 3 and 4) [3,4]. Figure 3 shows the best rectification ratio at 2.2 V (RR = 27.53), obtained with Au electrodes [4]. The maximum current registered was 90,400 electrons $molecule^{-1}$ s^{-1} [4]. Some pads exhibit, as in Fig. 4, a saturation in the forward current [4] predicted by physical models for conduction through a molecule or monolayer of molecules (e.g. the AR model [7]). Rectification by a one-molecule thick layer of $C_{16}H_{33}Q$-3CNQ **(1)** is an established fact.

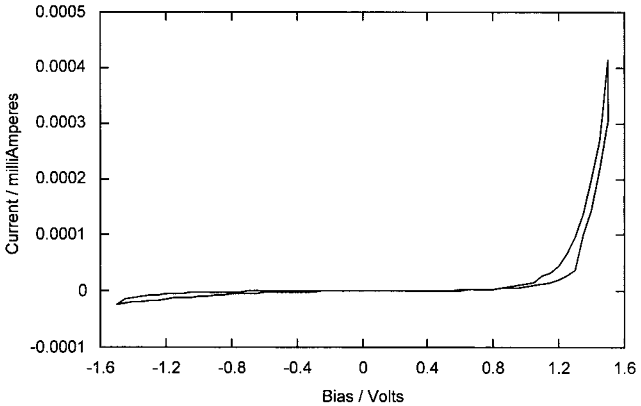

Figure 2. Plot of the DC current I versus the DC applied voltage V (I-V plot) through a single monolayer of $C_{16}H_{33}Q$-3CNQ **(1)** sandwiched between Al electrodes (top Al pad area 4.5 mm^2, thickness 100 nm), using Ga/In eutectic and Au wires. The DC voltage is swept at 10 mV s^{-1}[2].

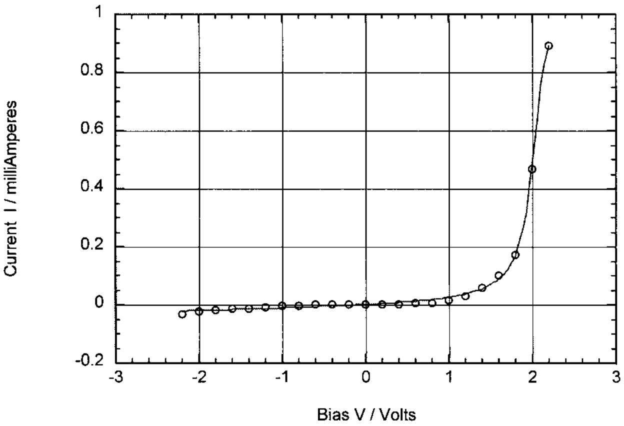

Figure 3. Current-voltage (*I-V*) plot for a cell Au | $C_{16}H_{33}Q$-3CNQ (**1**) monolayer | Au. The resistance at 2.2 V is $R = 2.47$ kΩ; the current at 2.2 V is $I = 9.83 \times 10^3$ electrons molecule^{-1} s^{-1}. The rectification ratio at 2.2 V is RR = 27.53 in the first cycle (shown), but decreases to 10.1, 4.76, 2.44, and 1.86 in cycles 2, 3, 4, and 5, respectively (not shown). [4].

A plausible mechanism for rectification by **1** is a minor change in the AR proposal, so that Eqs. (1), (2), and (3) are replaced by:

$$M_1 + D^+\text{-}\pi\text{-}A^- + M_2 \rightarrow M_1 + D^0\text{-}\pi\text{-}A^0 + M_2 \quad (5)$$

$$M_1 + D^0\text{-}\pi\text{-}A^0 + M_2 \rightarrow M_1^- + D^+\text{-}\pi\text{-}A^- + M_2^+ \quad (6)$$

where the first step is the electric field-driven excitation from ground to excited state, followed by electron transfer across the two molecule | metal interfaces [2].

Two New Rectifiers

Recently, two more molecules were found: 1-butyl-2,6-bis{2-[4-(dibutylamino)phenyl]vinyl}pyridin-1-ium iodide $(Bu_2N\varphi V)_2BuPy^+I^-$, **2** [6], and an azafullerene, 1a-[4-(dimethylamino)phenyl]-1a*H*-1a-aza-1(2)a-homo(C_{60}-*I*h)[5,6]fullerene, DMAn-NC_{60}, **3** [5].

$(Bu_2N\varphi V)_2BuPy^+I^-$ (**2**) forms a PL film at the air-water interface, and transfers to hydrophilic substrates as a Z-type multilayer. The monolayer thickness was 0.7 nm by spectroscopic ellipsometry, and 1.15 nm by surface plasmon resonance ($\lambda = 532$ nm), and 1.3 nm by X-ray diffraction [6]. The films exhibit an absorption maximum at 490 nm (which is slightly hypsochromic in solution), attributable to iodide-to-pyridinium back charge transfer, and a second harmonic signal $\chi^{(2)} = 50$ pm V^{-1} at normal incidence (λ =1064 nm) and 150 pm V^{-1} at 45° [6]. XPS of a multilayer of **2** on Au finds only 30 % of the expected signal from the iodide; the iodide anion may be partially replaced by a more abundant hydroxide anion during LB transfer [6]. The rectification (Fig. 5) shows a decrease of rectification upon successive cycles. Some cells have initial rectification ratios as high as 60. The favored direction of electron flow is from the gegenion to the pyridinium ion, i.e. in the direction of back charge transfer; the rectification in **2** is attributed to an interionic process, rather than to an intramolecular process [5].

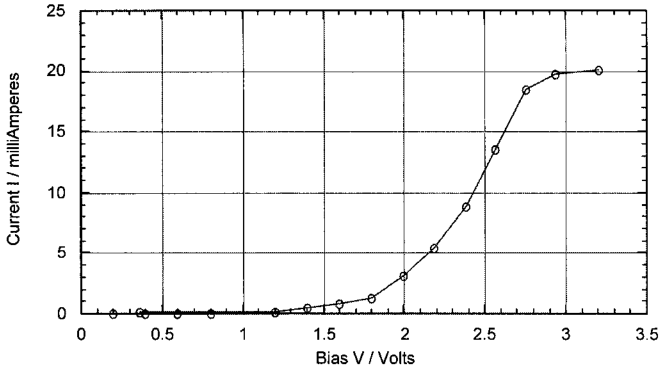

Figure 4. *I-V* plot for a cell Au | $C_{16}H_{33}Q$-3CNQ (**1**) monolayer | Au that shows saturation in the forward current $I = 20$ mA at 3.2 V (this cell broke down at 3.4 V) [4].

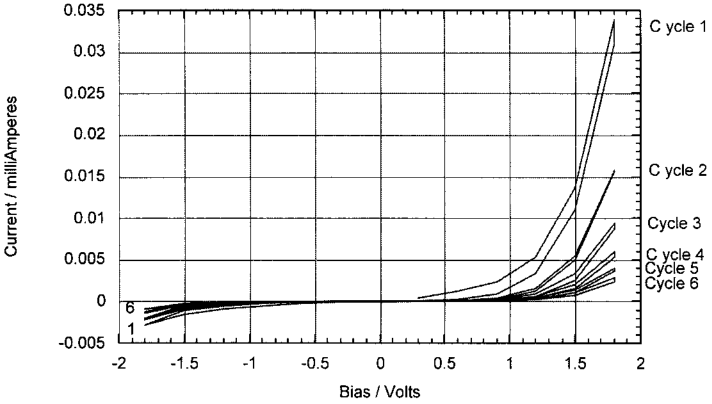

Figure 5. *I-V* plots for $(Bu_2N\varphi V)_2BuPy^+I^-$ (**2**) measured in an Au | LB monolayer of **2** | Au cell, for six successive cycles of measurement. The rectification ratios are RR = 12, 7, 5, 4, 3, 3, for cycles 1 through 6, respectively [6].

The azafullerene (DMAn-NC_{60}, **3**) consists of a weak electron donor (*N,N*-dimethylaniline) bonded to a moderate electron acceptor (N-capped C_{60}). It is a blue compound, with a significant IVT peak at 720 nm [5]. Molecules **3** probably transferred onto Au in a staggered mode, since the measured molecular area at the transfer pressure (22 mN m^{-1}) is only 70 $Å^2$, whereas the area of C_{60} is about 100 Å^2 [5]. The XPS film thickness is 2.2 nm [5]. Angle-resolved N(1s) XPS spectra confirm that the two N atoms are closer to the bottom Au electrode than is the C_{60} cage [5]. The monolayer was covered with 17 nm thick Au pads deposited by the cold-gold technique. The current-voltage plot shown in Fig. 6 shows a "marginally" rectifying current [18] in the forward direction, with RR = 2 [5].

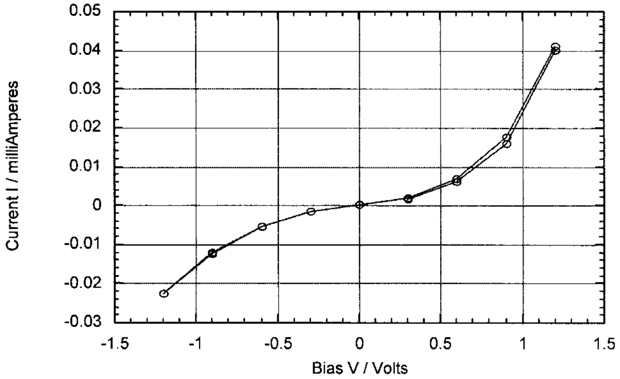

Figure 6. Current-voltage plots for DMAn-NC_{60} (**3**) measured in a Au | LB monolayer of **3** | Au cell, in which the current stays small: this is probably the current due to the molecules **3** and not to the Au filaments [5].

Caution

Not all asymmetric currents seen in metal | molecule | metal cells are due to asymmetries in the molecular energy levels, however. At any molecule | metal interface a set of dipoles may form, that become Schottky barriers. Also, if a chromophore is placed asymmetrically within a metal | molecule | metal sandwich, a current asymmetry will be produced [23].

Conclusion

Unimolecular rectification, a quarter century after it was proposed, is now a reality.

Acknowledgments

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