

Electrical rectification from a fullerene[60]-dyad based metal–organic–metal junction†

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Langmuir–Blodgett monolayer films of C₆₀-didodecyloxybenzene dyad, with a C₆₀ acceptor and didodecyloxybenzene donor, exhibit rectification with high rectification ratios of 87–158 at 3 V.

The advent of organic molecules to act as conductors began in 1973 when Ferraris *et al.*¹ demonstrated electron transfer in the organic metal tetrathiafulvalene. Soon after this discovery, the idea of molecular rectification with the sequence metal|donor–bridge–acceptor (D–B–A)|metal by Aviram and Ratner² led to a search for such molecular junctions containing dyads. In molecular junctions of the form metal|molecule|metal, electrical rectification is defined in terms of the absence of inversion symmetry, $I(V) \neq -I(-V)$, where I and V are the measured current and the applied voltage, respectively. The absence of structural mirror symmetry gives rise to rectification; the dominant factors inducing rectification are geometric asymmetry in the molecular junction and the spatial profile of the electrostatic potential.^{3,4} In the past decade, D–B–A diodes have been synthesized and rectifying behaviour has been measured on molecular layers formed by the Langmuir–Blodgett (LB) route.^{5,6} Molecular rectification was also observed successfully in dyad chromophores aligned by self-assembly.^{7–9} Recently, organic rectifying junctions were fabricated by the assembly of ionic acceptors and donors, yielding an optimum rectification ratio (RR) of 100 at ± 1 V.¹⁰ Rectification behaviour has also been observed in derivatives^{11–13} of fullerene[60] acting as a super-rectifier¹¹ when operated between +2 to –2 V with a RR = 20 000 at 1.5 V. In this work, we report the rectifying behaviour of a monolayer LB film of fullerene C₆₀-didodecyloxybenzene dyad sandwiched between two gold electrodes, corroborated by theoretical predictions.

The dyad molecule was synthesized as a pure [6,6] isomer, confirmed by HPLC, NMR and other standard techniques.¹⁴ The dyad molecule is maroon-red in the solid state and brown in most solvents. The absorption spectrum of the dyad showed a feature at 431 nm, characteristic of [6,6]-bridged mono-adducts. Furthermore, a weak absorption at 697 nm was assigned to the 0–0 transition. Another broad feature in the 450–650 nm region represented the visible transitions in the dyad. The *ab initio* geometry optimized (B3LYP/3-21G*) dyad, 1-(3-carboxy-(3,4-di(dodecyloxy)benzoic acid)-4-carboxyphenyl ester)propyl-1-phenyl [6,6]-C61, with a hydrophobic–hydrophilic–hydrophobic

(C₆₀–bridge–didodecyloxybenzene) network, is depicted in Fig. 1. The geometry optimization and single point energy calculations gave the conformation shown in Fig. 1, leading to a total dipole moment of 8.9 D with the bridge benzene and the donor benzene being planar with respect to each other. The binding energy was –21.784 kcal mol^{–1} and the heat of formation was 571.647 kcal mol^{–1}, with the HOMO and LUMO amplitudes localized on the donor and acceptor moieties, respectively. The HOMO–LUMO gap, estimated as 1.6 eV, compares reasonably with the overestimated calculated value of 2.3 eV from DFT B3LYP/3-21G*. It was fairly well established that the molecule forms a ground state intramolecular charge transfer complex from the absorption, emission and electrochemical studies.¹⁴

Analysis of the spatial extent and the energy levels of the frontier orbitals is essential in order to understand the mode of electron transport through the dyad molecule. More specifically, the spatial orientations of the LUMOs can provide clues of electrical rectification in this molecular system. For an active molecular device such as a rectifier diode, the electron flow is controlled when the unoccupied molecular orbitals provide channels for electron conduction through the molecule. For the chemically-bonded donor–spacer–acceptor dyad molecule, the potential drop is thus defined as the energy difference (ΔE) between the unoccupied orbitals localized on the donor and acceptor moieties.¹⁵

Fig. 2 shows the spatial orientations of the HOMO, LUMO and higher order LUMOs of the dyad molecule, clearly showing the LUMO of the dyad to be localized on its acceptor, while the LUMO + 7 of the dyad is localized on the donor. Thus, a potential drop of $\Delta E_{\text{LUMO}} = E_{\text{LUMO}+7} - E_{\text{LUMO}} [-1.4 - (-3.4)] = 2$ eV resulted, which when applied as a bias voltage would facilitate the tunnelling of electrons from the acceptor end to the donor end of the dyad molecule. By adopting *ab initio* calculations, Majumder

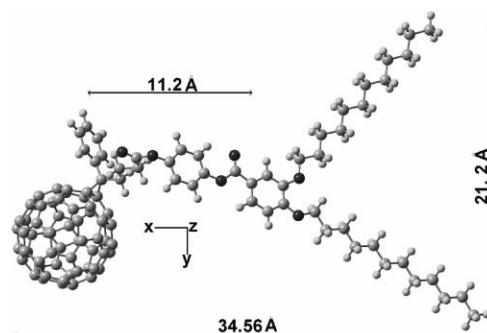


Fig. 1 *Ab initio* (B3LYP/3-21G*) geometry-optimized structure of the dyad showing the bridge and donor benzene rings to be planar (shading codes: dark grey = carbon, light grey = hydrogen, black: oxygen).

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† Electronic supplementary information (ESI) available: Cyclic voltammograms of the dyad monolayer film and I – V characteristics of a Y-type film of two monolayers. See DOI: 10.1039/b602203k

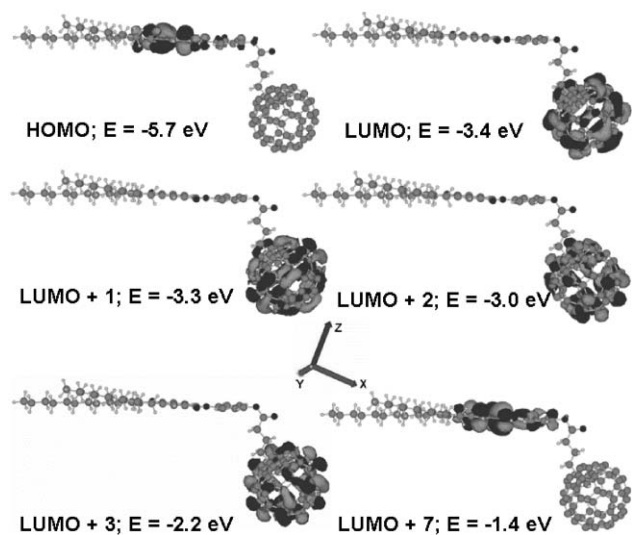


Fig. 2 Orbital spatial orientations of HOMO, LUMO, LUMO + 1, LUMO + 2, LUMO + 3 and LUMO + 7 of the dyad molecule with associated orbital energies.

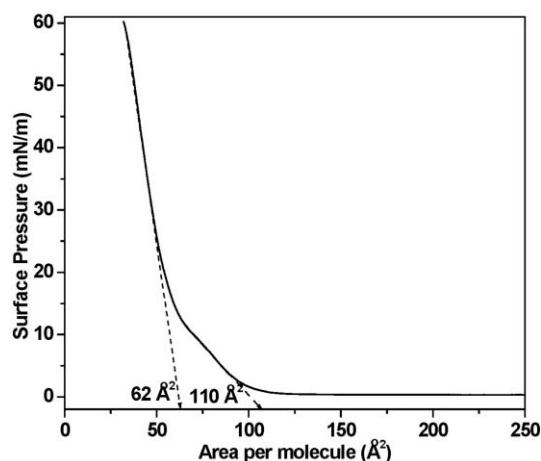


Fig. 3 Pressure–area isotherm of the dyad at the air–water interface, showing two distinct phases for a 1 mM concentration at 298 K.

et al. reported the geometric and electronic structures of polyphenyl-based conjugated D–B–A molecules as potential candidates for molecular rectifying devices.¹⁶ The rectifier was modelled by combining the donor (benzene ring substituted with $-\text{NH}_2$, $-\text{CH}_3$ or $-\text{OCH}_3$) and the acceptor (benzene ring substituted with $-\text{NO}_2$, $-\text{CN}$ or $-\text{CF}_3$) molecules through methylene or ethylene spacer groups. The estimated potential differences amounted to 1.56 and 2.05 eV, respectively, for the two spacers. The high value of the potential drop in the present investigation is due to the presence of the σ -spacer in the molecule, which may enable it to act as a robust rectifier.

Fig. 3 shows the pressure–area (π – A) isotherm of the dyad at a 1 mM concentration, recorded at 298 K. In contrast to C_{60} , which forms a multi-layer, the isotherms show distinct phases, withstanding a surface pressure of $\sim 60 \text{ mN m}^{-1}$. As can be seen, the dyad displays a very short liquid-like region below 3 mN m^{-1} , followed by a short range region up to 14 mN m^{-1} , a short condensed phase. Extrapolation of this condensed portion of the

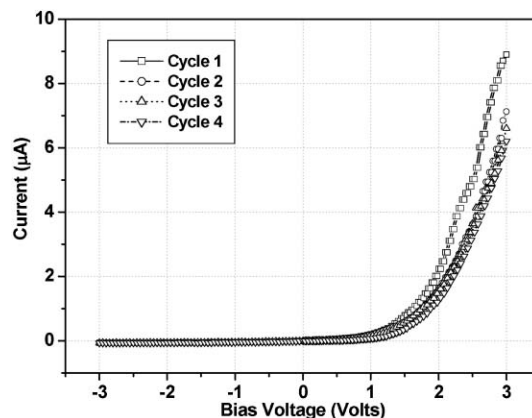


Fig. 4 The I – V curves for cell ii. Four successive I – V scans within the voltage limits of $\pm 3 \text{ V}$ are shown for the dyad monolayer deposited at 10 mN m^{-1} .

isotherm led to a surface area of 110 \AA^2 , agreeing well with the reported areas for various fullerene derivatives,¹⁷ indicating the formation of a monolayer. The morphological properties of the dyad Langmuir film and LB films are reported elsewhere.¹⁸ The monolayers were transferred at 10 mN m^{-1} onto ITO (indium tin oxide) and Au substrates for electrochemical and current–voltage (I – V) studies, respectively.

Electrochemistry of the dyad film was done in an acetonitrile solvent, which has negligible dyad solubility. The cyclic voltammograms of the dyad monolayer film (ESI, Fig. S1†) were reproducible, showing two irreversible waves on the reduction side corresponding to C_{61}^{1-} at 1.03 V and C_{61}^{2-} at 1.15 V. The electroactivity of C_{61}^{1-} decreased on continuous scanning and disappeared completely after 10 scans.

A high current for C_{61}^{1-} for the first scan of potential scanning subsided with a gradual increase in the current magnitude for C_{61}^{2-} . Such an observation is typical for films of methanofullerene derivatives and the LB films of fulleropyrrolidines.¹⁹ A probable electrical rectification can be inferred owing to the irreversible nature of the dyad monolayer. The surface coverage of the dyad monolayer deposited at 10 mN m^{-1} onto the ITO electrode area of 0.5 cm^2 was estimated from the peak current as $4.76 \times 10^{-10} \text{ mol cm}^{-2}$, in good agreement with reported coverages.²⁰

I – V measurements in the present investigation were performed on the monolayer electrode, using the two probe technique. Metal–organic monolayer–metal (MOM) junctions were fabricated with a bottom Si|Cr|Au electrode and a top Au electrode. Around fifteen MOM assemblies, labelled cell i to xv, were measured; five of which were short-circuited, maybe due to the inability to control the thickness of the top Au electrode, and two of which did not yield any results.²¹ The remaining eight had rectifying behaviour in the voltage range $\pm 3 \text{ V}$.

Fig. 4 shows the I – V behaviour of one of the cells prepared with the dyad monolayer deposited at 10 mN m^{-1} . At an applied forward bias of $\sim 1.5 \text{ V}$, a rise in current, as against a negligible current under the reverse bias condition, implies that the monolayer behaves as a rectifier. This threshold voltage matches well with the calculated potential drop of 2 eV obtained from the analysis of the spatial extent of the dyad LUMO.

Table 1 Current vs. voltage data for the dyad monolayer deposited at 10 mN m⁻¹

Cell no.	Cycle	V_{\max}/V	RR @ 3 V	I @ 3 V/ μA
ii	1	3	158.01	9.37
	2	3	107.54	7.13
	3	3	105.61	6.21
	4	3	96.20	6.6
	5	3	89.23	6.05
v	1	3	141.43	9.66
	2	3	139.80	8.64
	3	3	135.61	9.52
	4	3	131.54	9.09
	5	3	128.98	8.99
xii	1	3	132.75	9.12
	2	3	95.70	6.68
	3	3	92.38	6.19
	4	3	91.23	6.35
	5	3	87.57	6.20

The RR reached a maximum of 158 at 3 V, and the I - V data for three such cells, labelled ii, v and xii, are summarised in Table 1. Thus, with the HOMO localized on the donor ring and the LUMO on the acceptor C₆₀ moiety, the dyad molecule behaves as a rectifying diode when electrons injected from the cathode to the acceptor LUMO are transported to the LUMO localized on the donor moiety upon application of a bias voltage equivalent to the potential drop.

Furthermore, it is important to prove the molecule induced rectification and show evidence that this arose from the D-B-A sequence. To do this, we deposited two monolayers of similar electrode configuration as constructed for the monolayer electrode. Since the dyad formed Y-type films, the system should not rectify since it is centrosymmetric. This was indeed the case and the system revealed symmetric I - V curves (ESI, Fig. S2†). Thus it is proved that the dyad shows molecule-induced rectification.

In conclusion, a rectifying junction operating at an applied bias voltage of ± 3 V with an optimum RR of 158 at 3 V has been obtained from a LB monolayer film of C₆₀-didodecyloxybenzene dyad. The molecular rectification was verified from the symmetrical I - V curves of centrosymmetric bilayers of the dyad. The above results corroborate well with theoretical predictions and electrochemical experiments. The RRs obtained in our experiments are comparable with the recently reported values of 50–150 from a D-B-A diode.^{10,22} Further, Langmuir-Schaefer monolayer films¹² of fullerene-bis-(4-diphenylamino-4''-(*N*-ethyl-*N*-2'''-ethyl)amino-1,4-diphenyl-1,3-butadiene)-malonate, sandwiched between two Au electrodes, exhibited pronounced rectification in the voltage range from 3.0 to 5.4 V, with RRs up to 16.5.

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