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Large scale assembly of ordered donor-acceptor heterojunction molecular wires using the Langmuir-Blodgett technique[†]

Richard Charvet,*^a Katsuhiko Ariga,^a Jonathan P. Hill,^a Qingmin Ji,^a Ali Hossain Khan^b and Somobrata Acharya*^b

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Unidirectionally aligned photoconductive donor-acceptor heterojunction molecular wires spanning over fifty square microns are fabricated using the Langmuir-Blodgett technique.

The fabrication of highly ordered architectures composed of electronic donor-acceptor pair molecules using a supramolecular approach is a subject of critical importance for organic photovoltaic devices (OPVs).^{1,2} Increasing the width of the photoactive region by forming wide area heterojunctions consisting of precisely ordered donor and acceptor components can lead to improved photocarrier generation efficiency while creating pathways for nontrivial charge migration. Long range charge carrier separation and transport have been demonstrated via the formation of photoconductive one dimensional (1D) nanostructures consisting of supramolecular donor/acceptor heterojunctions.^{2,3} Nevertheless, deposition of such structures on solid substrates leads to disordered arrays containing large void areas, which breaks down long range charge carrier transport. Advantageously, the Langmuir-Blodgett (LB) technique offers sophisticated processability since the packing, orientation and long range ordering of a molecular assembly on a surface can be precisely tailored with perfect control and reliable thickness.^{4,5} Here we report the fabrication of large area close packed photoconductive molecular wires using a newly designed amphiphilic zinc porphyrin-fullerene dyad with the aid of the LB technique.⁶⁻⁸ The molecular wire assembly spans over fifty-square microns retaining tight spatial registry and alignment, which, to our knowledge, has not been reported previously for any bottom up technique on the macroscale.9

Zinc porphyrin–fullerene dyad **1** consists of an electronacceptor fullerene moiety connected to an electron-donor porphyrin through a rigid 4,4'-substituted-diphenylacetylene bridge to a 5,15-bis-phenyl porphyrin core, a geometry which



Fig. 1 (a) Structure of 1. (b) AFM micrographs of aligned molecular wires of 1 spanning over ~ $20 \times 20 \ \mu\text{m}^2$ area with tight packing density. The frame represents a part of ~ $50 \times 50 \ \mu\text{m}^2$ aligned area. (c) Higher resolution AFM images showing aligned triangular domains in the form of molecular wires, monolayer film deposited onto freshly cleaved mica lifted by the LB method at a surface pressure of 15 mN m⁻¹ at 19 °C. Inset shows an AFM image of an equilateral triangular block.

prevents ground-state electronic interactions and promotes charge separation between the photoactive entities. The zinc porphyrin moiety is substituted with a relatively flat and cone-like unit containing terminal triethylene glycol (TEG) chains, which can be regarded as a tapered hydrophilic segment (or dendritic wedge). Thus, **1** can be seen as a cone-like amphiphilic molecule with TEG chains forming hydrophilic tails while C_{60} acts as a hydrophobic head (Fig. 1a and see the ESI⁺).

We used the LB technique to organize the amphiphilic donor-acceptor pairs into long range macromolecular objects in a controllable and efficient way. The uniaxial compression promotes the irreversible formation of an aggregate of 1 as evidenced by the large hysteresis in the isotherm cycle (see Fig. S1, ESI†). Compression to higher surface pressure essentially results in unidirectional alignment in the form of molecular wires as evidenced by atomic force micrographs (AFM) (Fig. 1b and 1c). Uniformly aligned and tightly packed molecular wires spanning over a ~50 \times 50 μ m² area are

^a World Premier International (WPI) Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), JST, CREST, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan. E-mail: racharvet@yahoo.com

^b Centre for Advanced Materials (CAM), Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India. E-mail: camsa2@iacs.res.in

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obtained. The optimum alignment has been achieved in the surface pressure range of $10-18 \text{ mN m}^{-1}$ with full retention of registry. The aligned layer can be transferred in a single step onto a variety of substrates (see Fig. S2 and S3, ESI†) to yield large scale parallel molecular wire arrays.

The higher resolution AFM image (Fig. 1c) shows finely structured wires that are essentially composed of nearly equilateral triangular blocks aligned unidirectionally in the form of molecular wires. The edge length of triangular blocks is ~ 60 nm leading to an area of around 1.5 μ m² per block (inset of Fig. 1c). Within each molecular wire, the triangular blocks are decked in a side-by-side tilted configuration defining the molecular wire diameter of ~ 60 nm (Fig. 1c and Fig. S4a, ESI[†]). The molecular wires are exceeding 30 µm in length defining an aspect ratio of greater than 500 (Fig. 1a). The AFM height profile (see Fig. S4, ESI⁺) of the triangular blocks is less than 4 nm, therefore less than the actual upright length of 1, suggesting a tilted configuration at the air-water interface as also evidenced from the π -A isotherms. The triangular structure likely results from the trigonal packing of the fullerene groups and the cone-like structure of the hydrophilic TEG chains adjacently packed together under the proximal surface pressure. TEG chains remain disordered and in a stretched configuration in the hydrated state, which accounts for the 4 nm height of the aggregated triangular blocks.

The electronic absorption spectrum of a solution of 1 shows characteristic fullerene bands at 254 and 310 nm, and characteristic porphyrin bands at 417 nm (Soret band), 540 and 585 nm (Q-bands) respectively. In contrast, a significant broadening and overall Stokes shift of the porphyrin absorption bands are observed in the absorption spectrum of an ordered LB film (Fig. 2a). Furthermore, appearance of a new band at 463 nm indicates the formation of porphyrin J-aggregates.^{10a,4a} We followed the dynamics of this aggregation process by monitoring the on-trough UV-vis absorption of the Langmuir monolayer with increasing surface pressure (Fig. 2b). Gradual appearance of the new band at 465 nm with increasing pressure indicates formation of J-aggregates upon compression. Increase in absorption intensity implies that a large number of aggregates are dragged by the surface pressure at the footprint of the beam while the Langmuir film remains stable.



Fig. 2 (a) Absorption spectra of solution of **1** (1 μ M) in chloroform (red curve) and a 7-layer LB film (blue curve) lifted at $\pi = 10 \text{ mN m}^{-1}$ at temperature 19 °C. (b) Monitoring of the aggregation process using on-trough UV-vis absorption by changing the surface pressure.



Fig. 3 (a) A 3D molecular structure of **1** and its equivalent cartoon. (b) A schematic model of **1** aggregation showing an arm of a triangular block with porphyrin J-aggregate stacking. (c) Segregated fullerenetilted porphyrin J-aggregates and entangled TEG chains forming a triangular block.

Based on AFM observation and spectral evidences, we modeled the triangular domain structures and their long range ordering in the form of molecular wires (Fig. 3b and 3c). Notably, Z-type deposition of LB films implies that hydrophilic TEG chains are first attached onto a mica surface, while hydrophobic fullerene moieties are facing outwards in a trigonal configuration. Implicit here is the existence of stronger interactions among hydrophilic-hydrophilic and hydrophobic-hydrophobic groups and rigidity of the spacer introduced between donor/acceptor chromophores, leading to a phase-segregation phenomenon and aggregates at the supramolecular level. The triangular structures appear to form with zinc porphyrin units appended with disordered hydrophilic TEG chains on the base side, while hydrophobic C_{60} entities are exposed at the other extremity. Interestingly, the arms of the triangular blocks can be realized via porphyrin J-aggregate stacking (Fig. 3b) while the arm length depends on the number of 1 (Fig. 3a) and extent of spreading of TEG chains. Well-known strong $\pi - \pi$ electronic interactions between C₆₀ moieties, the J-aggregate formation of zinc porphyrin blocks and hydrogen bonding between TEG chains are leading to densely packed aggregates of **1** into triangular blocks.¹⁰ Owing to the directionality nature of hydrogen bonding between the inter 1 TEG chains and $\pi-\pi$ interactions of C₆₀ moieties, adjacent triangular blocks are coupled and decked at a certain angle resulting in long range interactions in the form of molecular wires.^{10b} The preferential orientation perpendicular to the compression direction originates from the reduced pressure gradient along this direction.

The characterized heterojunction obtained with precisely organized donor and acceptor domains on large area prompted us to perform preliminary studies of the photoconductive properties. A complete quenching of the porphyrin emission in ordered LB films indicates a highly efficient photoinduced electron transfer (PET) between donor and acceptor components.¹¹ Furthermore, the unidirectionally aligned wires display robust photocurrent properties owing to higher absorption cross sections. A linear current–voltage response upon white light irradiation was measured (see Fig. S5, ESI[†])



Fig. 4 (a) Photocurrent generation from molecular wires deposited on ITO with Al as a counter electrode illuminated with white light at an illumination flux of 30 mW cm⁻² for different duration times. Inset, a plot of conductance *versus* illumination time. (b) Dynamic on–off photocurrent switching response under an irradiance power of 30 mW mm⁻² with a frequency of 25 mHz and a duty cycle of 50%.

with linearly increasing photocurrent upon increasing incident light intensity while the conductance also varied linearly upon variation of illumination flux intensity (see Fig. S6, ESI†).¹⁰

The photocurrent was found to increase gradually with the illumination time (Fig. 4a). The conductance increased immediately following commencement of light irradiation and reached saturation after an extended irradiation time (inset in Fig. 4a). Repetitive on–off device response to white illumination flux was found to be sharp and repeatable over successive on/off irradiation cycles (Fig. 4b). A plot of conductance *versus* time response reveals a similar trend over multiple cycles (see Fig. S7, ESI†).

Donor-acceptor molecules 1 form well-defined triangular blocks which pack in the form of ordered molecular wire arrays over large area under applied pressure. The separation of donor and acceptor entities by the rigid 4,4'-diphenylacetylene bridge at the molecular level in 1 leads to high concentrations of electrons and holes on either side of the interface, which generates a large chemical potential under illumination. The chemical potential in combination with built-in potential and charge delocalization within the densely packed and precisely ordered domains lead to promising photoconductive properties. Our results illustrate an intimate relationship between charge carrier mobility and efficient supramolecular packing between functional entities favorable to the delocalization of the photogenerated charges. Our method is quite flexible since the ordered assembly can be precisely controlled in the sub-micron range by varying the applied surface pressure. The presented approach for the fabrication of large area molecular heterojunction devices

may lead to potential OPVs with high photon conversion efficiencies.

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