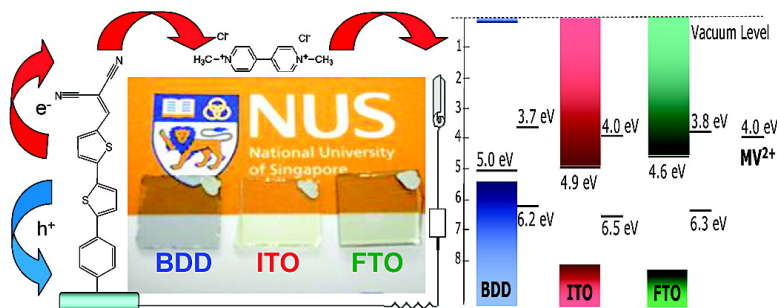Communication

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Diamond-Based Molecular Platform for Photoelectrochemistry

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Photoelectrochemistry is one of the major field of studies for molecular-based platforms due to the ease of tailoring highly efficient photodevices via organic chemistry.[1] There are numerous reports on architectured donor–acceptor molecules or polymers on indium tin oxide (ITO) targeting photovoltaic applications,[2] photoswitching applications, and electrogenerated chemiluminescence (ECL).[4] In terms of the performance criteria of these molecular-based platforms, generic issues such as efficient charge transfer between the electrode and organic interface as well as photostability of the platforms are fundamental to all applications.

Interest in boron-doped diamond (BDD) thin films as a signal transduction platform for sensing applications[5] stems from its excellent properties such as chemical robustness, wide electrochemical potential window, biocompatibility, and optical transparency. Due to its intrinsic high carrier mobilities and wide band gap, diamond electronic devices can potentially deliver outstanding performance in power diodes and high-frequency field effect transistors. In the past few years, there has been tremendous progress in the chemical vapor deposition (CVD) of nanocrystalline diamonds (NCDs) prepared on large area glass[6] and polymer substrate,[7] which opens up many new technological possibilities. NCDs can be boron-doped to metallic levels, and specific resistivity as low as 0.005 Ω cm can be achieved. The B-doped NCD layers deposited on quartz and glass possess very high optical transparency in the 300 to 1000 nm spectral range.[6] In addition, the electron affinity of diamond can be tuned by controlling its surface termination[8] and organic molecules can be attached[5] via chemically stable C–C bonding, which are advantageous for efficient charge transfer and robust applications. Previous work on the photoconductive properties of BDD focused mainly on the charge generation mechanism from the bare substrate.[9,10] Here we report the spectrophotochemical characteristics of a light harvesting molecular platform constructed on BDDs using a donor–acceptor molecular wire.

An optically transparent diamond electrode was fabricated by the CVD of a thin layer of BDD film on glass substrate (160 nm thick, boron concentration 7×10^{20} cm^{-3}). The construction of the diamond-based molecular platform begins with the functionalization of the BDD thin film with arylboronic ester or arylhalide which acts as a synthon for subsequent Suzuki coupling to target light harvesting molecules. We have successfully coupled two donor–acceptor molecules: bithiophene-C$_{60}$ (**2TC$_{60}$**) and bithiophene-dicyano (**2T(CN)$_2$**) as summarized in Figure 1. Photoelectrochemical measurements were performed in 0.1 M Na$_2$SO$_4$ solution containing 5 mM methyl viologen (MV^{2+}) as the electron carrier,

using a three electrode system: the diamond-based molecular platform as working electrode, a platinum mesh counter electrode, and a Ag/AgCl reference electrode, under 1 sun irradiation (100 mW/cm^2, AM 1.5G). From the action spectra in Figure 1a, the arylboronic ester functionalized BDD shows a small photocurrent peak at 310 nm due to the arylboronic ester groups; in contrast the H-terminated BDD shows minimal photocurrent. After coupling to **2TC$_{60}$**, a large photocurrent peak centered at 360 nm is observed. The photocurrent peak is shifted bathochromically to 440 nm for **2T(CN)$_2$** owing to the extended conjugation length of the dicyano group which also acts as the electron acceptor. This photocurrent peak correlates well with the UV–vis absorption spectrum of 2(dicyanovinyl)-5-iodobithiophene (**I-2T(CN)$_2$**) as shown in Figure S2.
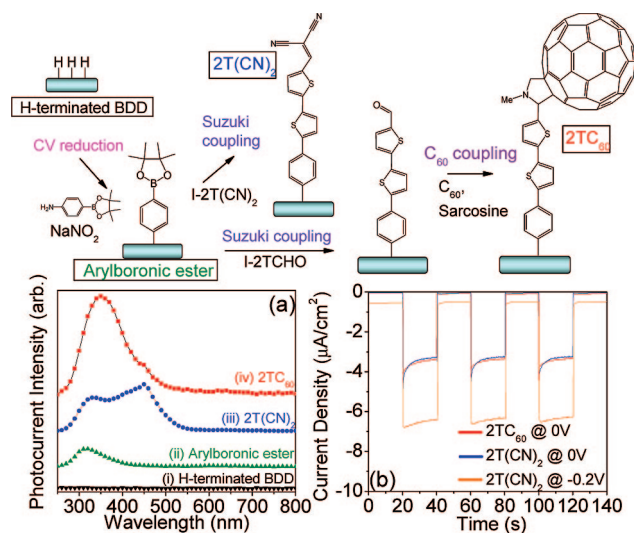

Figure 1. Surface functionalization and Suzuki coupling scheme of: bithiophene-C$_{60}$ (**2TC$_{60}$**) and bithiophene-dicyano (**2T(CN)$_2$**) on boron-doped diamond (BDD) thin film. (a) Action spectrum of (i) H-terminated BDD, (ii) arylboronic ester functionalized BDD, (iii) **2T(CN)$_2$**, and (iv) **2TC$_{60}$** molecular platform on BDD at 0 V (vs Ag/AgCl). (b) Photocurrent response at 0 V (vs Ag/AgCl) of **2TC$_{60}$** (red) and **2T(CN)$_2$** (blue, at −0.2V: orange) and **4T(CN)$_2$** (blue) under 1 sun (100 mW/cm^2, AM 1.5G) illumination.

From Figure 1b, the photocurrent of **2TC$_{60}$** and **2T(CN)$_2$** on BDD under board solar spectrum (AM 1.5G) illumination yields similar values despite a dissimilar action spectrum. On application of a negative bias (−0.2 V vs Ag/AgCl), an ∼80% increase in photocurrent could be produced compared to zero potential, although there was a slight accompanied increase in the dark current due to the reduction of MV^{2+} (redox peak at −0.6 V vs Ag/AgCl).

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The negative bias favors the flow of electron from the donor (bithiophene) to the acceptor (dicyano) group.

To benchmark our BDD electrode against common transparent electrodes such as tin-doped indium oxide (ITO) and fluoride-doped tin oxide (FTO), similar coupling reactions were applied to graft **2T(CN)₂** onto these electrodes. From Table S1, it is apparent that, for the CVD diamond samples used in this work, the conductivity, optical transparency, and the density of grafted **2T(CN)₂** on BDD thin film are of lower values than that of ITO or FTO. An estimation of the surface coverage of **2T(CN)₂** based on the XPS calibration of the S $2p$ intensity versus that of a dodecanethiol self-assembled monolayer on Au gives a surface coverage of 0.44 for BDD, 0.60 for ITO, and 0.55 for FTO. Despite these limiting parameters, we found that the photocurrent (Figure 2b) generated on the diamond-based molecular platform recorded under that same condition was 2.3 and 3 times larger than that on ITO and FTO, respectively. The photocurrents have been normalized against the respective surface coverage of **2T(CN)₂**. The surface roughness of clean BDD was found to be similar to FTO (Supporting Information S6). This implies that the surface roughness of electrodes is not the main factor affecting the photoconversion efficiency. It is clear from Figure 2a that the BDD thin film outperformed ITO and FTO at all applied voltages.
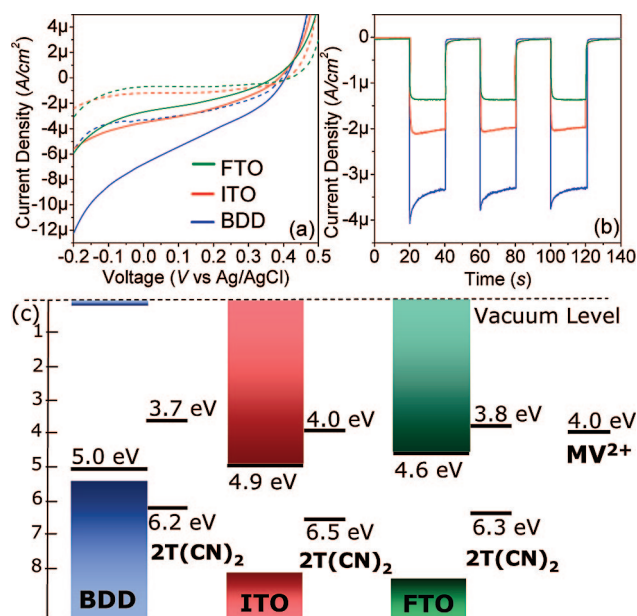

Figure 2. (a) I−V plot and (b) photocurrent response at 0 V (vs Ag/AgCl) of bithiophene-dicyano (**2T(CN)₂**) on FTO (green), ITO (red), and BDD (blue) in the dark (dotted line) and under 1 sun (100 mW/cm,² AM 1.5G) illumination (solid line). (c) Energy alignment (HOMO/LUMO) of **2T(CN)₂** on BDD (blue), ITO (red), and FTO (green). Color strips represent valence band and conduction band of respective electrodes.

To understand the superior performance of BDD film, the energy alignment of the HOMO/LUMO of **2T(CN)₂** was compared with the Fermi level in the three substrates (Figure 2c). The positions of the HOMO and Fermi level were determined using Ultraviolet Photoelectron Spectroscopy (UPS). The Fermi level of BDD is placed at ∼5.0 eV below the vacuum level. Compared to FTO and ITO, it is separated farthest from the redox level of MV^{2+} located at 4.0 eV and gives rise to the largest open circuit voltage (V_{OC}). The n-doped ITO and FTO have Fermi levels that are placed closer to the redox level of MV^{2+}. Upon photogeneraton of exciton, the electron is transferred to MV^{2+} from the acceptor and the hole is

transferred to the working electrode from the donor; hence a match between the HOMO of the donor molecule with the valence band of the electrode is vital for efficient hole injection. For BDD, its valence band is situated closest (1.2 eV) to the HOMO of grafted **2T(CN)₂**, thus favoring hole injection from **2T(CN)₂** to the diamond. On the other hand, the valence band lies farthest away from the LUMO of the molecule, thus preventing electron injection into the LUMO which will result in undesired electron−hole recombination.

Electrochemical Impedance Spectroscopy (EIS) was applied to provide insights to the impedance contribution of different interfaces on the frequency domain. The molecular-diamond platform behaves like an ideal capacitor in the dark as judged from the near 90° phase angle. Upon illumination, the charge transfer resistance decreased drastically due to photoinduced exciton creation and electron transfer process (Supporting Information Figure S7). Comparing the EIS data (Figure S8) of **2T(CN)₂** on BDD, ITO, and FTO at 0 V (vs Ag/AgCl) where there was minimal dark current, the results show that the BDD thin film exhibited the lowest photoinduced electron transfer resistance.

Lastly, the photostabilities of the three electrodes coupled to **2T(CN)₂** were compared after 2 h of continuous illumination in air-saturated electrolyte under 1 sun (100 mW/cm², AM 1.5G) illumination. The drop in photocurrent for BDD was only 10% compared to 40% and 36% drop for ITO and FTO, respectively. Clearly, the inertness of the diamond electrode[11] and the robustness of the interfacial bonding contributed to the higher stability of the diamond-based molecular device.

In summary, we have constructed donor−acceptor molecular wires on diamonds via facile functionalization with aryldiazonium salts followed by Suzuki coupling. The BDD thin film exhibited relatively higher photoconversion efficiency and photostability compared to ITO and FTO, due to the matching energy levels as well as strong C−C bonding at the organic−diamond interface. Further optimization of the physical properties of the diamond in terms of its optical transparency, doping, and attainment of higher charge carrier mobility by minimizing grain-boundary scattering will be expected to afford an even stronger performance from this material.

Supporting Information Available: Experimental section, reaction scheme, comparison table, and EIS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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