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Subject: Opinion of Dr. Michael Londesborough on the Doctoral Thesis of Martin Hladík, entitled "Nanostructures for solar cells: controlling the surface electronic properties by monolayers of carborane molecules".

In general, the chosen topic for research is highly relevant and of importance to a world currently experiencing a fundamental shift in its sourcing of energy. There seems to be a political consensus for the requirement to end our dependency on fossil fuels, and so the field of solar energy is one that is deserved of concerted research effort. As such, Mr. Hladík's chosen area of work is, I believe, highly appropriate for a Doctoral Thesis.

In the main, solar cells are reliant on semiconducting devices fabricated by the doping of Si via the introduction of impurity atoms into the crystal lattice through an *in situ* doping process during growth or ion implantation after growth. However, incorporation of impurities into Si has several inherent deficiencies, such as poor steerability and potential damage to the crystal structure. In addition, with the scaling down of silicon-based electronics to smaller dimensions, the surface/interface properties of Si become a dominating factor that can significantly impact the electronic properties. Presumably with this in mind, Mr. Hladík has set to explore computationally an alternative semiconductor production via the surface charge transfer doping (SCTD) of Si with thiolated carborane molecules. SCTD is emerging as a simple yet efficient technique to achieve reliable doping in a non-destructive manner, which can modulate the carrier concentration by injecting or extracting the carrier charges between the surface dopant and semiconductor due to the work-function difference. SCTD is particularly useful for low-dimensional nanostructures that possess high surface area and single-crystalline structure. To this, there is a growing body of work on the immobilisation of thiolated carborane molecules on (mainly) gold and silver surfaces. The $C_2B_{10}H_{10}(SH)_2$ icosahedral molecule exists in various isomers, and the polarity of the molecule can be manipulated by choice of the positions of thiolation on the carborane cage. Thus, opposite dipoles of thiolated carborane can be made, and have been shown to self-organise on surfaces, and, indeed, are known to alter the work-function of these surfaces accordingly.

Mr. Hladík has, in his Thesis, investigated, theoretically, various conformations of both gold-carboranethiol and silicon-carboranethiol junctions and their isolated subsystems, examining both their structural and electronic properties. These calculations have resulted in hypotheses for the driving mechanism determining junction geometry and preferred modes of chemisorption, as well as offering a rationalisation of what surface-modificant structural changes lead to more stable junctions. All these considerations allow for the reasonable predictions of the effect that surface modification of Si by carboranethiols has on the material's work-function.

Mr. Hladík's Doctoral Thesis is clear and well-structured, and is written in very good English. The work he has produced within the scope of the Thesis has resulted in two publications (with a third paper in preparation) and have been presented in a number of international conferences. In summary, the work presented in the Thesis maps out the potential impact of Si-carboranethiol junctions on photovoltaic devices, which I believe to be a very worthy contribution to the field. I hope that this work will be of inspiration to experimental physical chemists, who may persist to fabricate devices based on the theoretical ground work of Mr. Hladík.

Therefore, it is a pleasure to declare that it is my opinion that Mr. Hladík's Doctoral Thesis is of sufficient quality and enterprise to prove the author's ability for independent creative scientific work.

Yours sincerely,

Dr. Michael G. S. Londesborough, Ph.D M.B.E.