# EXECUTIVE SUMMARY OF THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

**PROJECT TITLE:**

## "Molecular Design and Synthesis of Push-Pull Type Perylene Dyes for Dye Sensitized Solar Cells"

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## 1. Design and Identification of new push-pull perylene dye molecule

Structural design and optimization of dyes are most essential to gain insight into the geometrical, electronic and optical properties of the dyes. For this purpose we have done TD-DFT and DFT calculations for starting materials and various push-pull type perylene dyes using Gaussian 09 software with basis set 6-31G. The following molecules were studied using DFT theoretical calculation:

1. *N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (PMI)
2. *N*-(2,5-di-tert-butylphenyl)-9-bromoperylene-3,4-dicarboximide (BRPMI)
3. 9-(piperidin-1-yl) perylene-3,4-dicarboxylic anhydride (PIPDA)
4. 9-(pyrrolidin-1-*yl*)perylene-3,4-dicarboxylic anhydride (PIPDA)
5. 9-naphthyl-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (NPMI)
6. *N*-(2,5-di-tert-butylphenyl)terrylene-3,4-dicarboximide (TMI)
7. *N*-(2,5-di-tert-butylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide (TBRPMI)
8. 1,6-(di-4-tert-butyl-phenoxy)-N-(2,5-di-tert-butylphenyl)-9-bromoperylene-3,4-dicarboximide (DPBPMI)
9. 9-(amino) perylene-3,4-dicarboxylic anhydride (APDA)

## 2. Synthesis of push-pull type perylene dyes

Theoretically predicted perylene dyes were synthesized and characterised using spectral techniques. according to the references and are demonstrated here. PMI was synthesized to use as starting materials for the synthesis of push-pull type perylene dyes.

(i) *N*-(2,5-di-*tert*-butylphenyl)perylene-3,4-dicarboximide (PMI)

(ii) *N*-(2,5-di-tert-butylphenyl)-9-bromo perylene 3,4-dicarboximide (BRPMI)

(iii) *N*-(2,5-di-tert-butylphenyl)-9-(piperidin-1-yl)perylene-3,4-dicarboximide (PIPMI)

(iv) 9-(piperidin-1-yl) perylene-3,4-dicarboxylic anhydride (PIPDA)

(v) *N*-(2,5-di-tert-butylphenyl)-9-(piperidin-1-yl)perylene-3,4-dicarboximide (PYPMI)

(vi) 9-(Pyrrolidin-1-yl)perylene-3,4-dicarboxylic anhydride (PYPDA)

(vii) *N*-(2,5-di-tert-butylphenyl)-9-(1,1-dimethylpropan-2-ol-amino) perylene 3,4-dicarboximide (OAPMI)

(viii) 9-naphthyl-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (NPMI)

(ix) *N*-(2,5-di-tert-butylphenyl)-1,6,9-tribromoperylene-3,4-dicarboximide (TBRPMI)
(x) 1,6-[bis(4-tert-octylphenoxy)]-9-bromo-N-(2,5-di-tert-butylphenyl)perylene-3,4-dicarboximide (DOBPMI)
(xi) 1,6-(di-4-tert-butyl-phenoxy)-*N*-(2,5-di-tert-butylphenyl)-9-bromoperylene-3,4-dicarboximide (DPBPMI)
(xii) 1,6-(di-4-tert-butyl-phenoxy)-*N*-(2,5-di-tert-butylphenyl)- 9-(piperidin-1-yl)perylene 3,4-dicarboximide (DPPIPMI)
(xiii) 1,6-(di-4-tert-butyl-phenoxy)-9-(piperidin-1-yl)perylene-3,4- dicarboxylic anhydride (DPPIPDA)
(xiv) 1,6-(di-4-tert-butyl-phenoxy)-*N*-(2,5-di-tert-butylphenyl)-9-(pyrrolidin-1-yl)perylene-3,4-dicarboximide
(xv) 1,6-(di-4-tert-butyl-phenoxy)-9-(pyrrolidin-1-yl)perylene-3,4-dicarboxylic anhydride (DPPYPDA)
(xvi) 1,6-(di-4-tert-butyl-phenoxy)-*N*-(2,5-di-tert-butylphenyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene-3,4-dicarboximide (DPBAPMI)

## 3. Study of aggregation behaviour of synthesized push-pull type perylene dyes on $TiO_2$ nanoparticle surface

The synthesized molecules such as PIPDA and PYPDA adsorbed on $TiO_2$ nanoparticle surface by chemisorption using various solvents like $CHCl_3$, DCM, ethanol and DMF. The aggregation of chemisorbed dye molecules on $TiO_2$ surface were analyzed by UV-vis and fluorescence spectroscopic techniques. The sodium salt of PIPDA and PYPDA were synthesized to demonstrate the performance of respective dyes on $TiO_2$ nanoparticle surface.

## 4. DSSC fabrication and testing using synthesized push-pull type perylene dyes

PIPDA and PYPDA molecules were utilized for DSSC device fabrication. The other molecules have to be utilized for DSSC fabrication. IPCE measurements were carried out for fabricated devices. The current conversion efficiency has to be improved.

## 5. Additional Novel Outcomes of this Project

The synthesized perylene compounds such as 9-(piperidin-1-yl) perylene-3,4-dicarboxylic anhydride (PIPDA), 9-(Pyrrolidin-1-yl)perylene-3,4-dicarboxylic anhydride (PYPDA), *N*-(2,5-di-tert-butylphenyl)-9-(1,1-dimethylpropan-2-ol-amino) perylene 3,4-dicarboximide (OAPMI) were utilized for hydrogen production using solar water splitting. The molecules are attached to graphene surface through imidation and are utilized for making composites. The prepared composites were used to absorb light in the visible region which is aiding the water splitting. This work related to objectives of this project such as solar energy utilization for green fuel hydrogen production. Further, the same compounds were used to capture green house gas $CO_2$ also.