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研究課題名（和文）低電荷注入障壁に着目した近赤外領域に高い光電変換効率を持つ色素に関する研究

研究課題名（英文）Investigation of suitable dye molecular framework focusing small driving force for electron injection and dye regeneration in NIR dyes for efficient photoconversion

研究代表者

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研究成果の概要（和文）：近赤外光吸収出来る増感色素の設計および開発のために、理論及び実験的な方法を組み合わせて適用した。 遠赤色素を用いて、エネルギー及び電子吸収スペクトルの計算と実験値との差を最小にする計算パラメータの最適化にTD-DFT理論計算を実施した。それを実現するにスクアリル系色素利用し、HOMOのエネルギーについては0.1eV、吸収最大については40nm-60nmの差であることが分かりました。電子注入および色素再生の最小エネルギー障壁はそれぞれに対して0.15eV及び0.12eVが必要である事を見出さした。この結果近赤外波長の1060nmまで光収色素の設計することが可能であると結論した。

研究成果の概要（英文）：Combined theoretical and experimental approaches have been applied for the design and development of novel sensitizing dyes aiming towards the NIR photon harvesting. Utilizing a model far-red sensitive squaraine dye, TD-DFT theoretical calculations were performed to optimize the best calculation parameters giving minimum possible error between the calculated and experimental values of the energetics and electronic absorption spectrum. Optimization of calculation parameters gave only an error of 0.1 eV for the energy of HOMO and 40-60 nm in the absorption maximum tested for a series of squaraine dyes. It has also been found that it is possible to have facile electron injection and dye regeneration with the minimum energy barrier of 0.15 eV and 0.12 eV, respectively. This led to conclude that it is possible to design novel sensitizers having photon harvesting up to 1060 nm.

研究分野：　化学（複合化学）

キーワード：　Structural optimization　TD-DFT calculations　Far-red sensitizers　Squaraine dyes　Energy barrier mapping

1. 研究開発の背景

Dye-sensitized solar cells (DSSCs) have emerged as one of the cheap and environment friendly alternatives to the conventional silicon photovoltaics as demonstrated by efficiency > 10 % by development Ruthenium complex or efficient organic sensitizers having nearly quantitative photon harvesting in the visible wavelength region (400-600 nm). A perusal of photon harvesting behaviour by sensitizers based on organic/inorganic or Perovskite in spite very high photon harvesting in visible region (< 750 nm), they still lack of effective light absorption as well as photon harvesting in the NIR wavelength region which is highly desired for further enhancement in the photoconversion efficiency. The dyes having efficient photon harvesting only in NIR-IR (700-900 nm) wavelength are highly required for fabrication of efficient hybrid DSSCs using a vast variety of available visible dyes having nearly quantitative photon harvesting in 500-700 nm wavelength range. Efficient NIR dyes (700-900 nm) without having visible light absorption and photon harvesting are unfortunately not available and need a logical and careful molecular design. Minimization of energy barriers of electron injection and dye regeneration are highly required for the development sensitizers covering the wide wavelengths of solar spectrum from visible NIR region which in-turn controls final attainable photoconversion efficiency. In the case of most commonly utilized ruthenium based sensitizers a driving force of 0.3-0.4 eV and 0.5-0.6 eV are needed for effective electron injection and dye regeneration respectively, compelling the utilization dyes absorbing the light and harvesting the photons effectively up to 750 nm and the majority of experimental results have witnessed this also. Therefore, development of novel class of dyes with relatively small driving force for the effective electron injection and dye regeneration are one of crucial requirements towards the development of efficient NIR Dyes. Understanding of the limiting factors associated with electron injection and dye regeneration and their relation on the dye molecular framework are expected to assist the design and development of efficient sensitizing dyes having intense absorption in the wavelength region of 700- 900 nm.

2. 研究の目的

Aim of this proposal is to find out and propose the most suitable dye molecular frameworks with sharp and intense absorption and efficient photon harvesting in the in the higher wavelength (600-900 nm) regions. In order to attain this targeted goal, logical efforts will be directed towards the identification of limiting factors like minimum energy barrier for efficient electron injection and dye regeneration for dye-sensitized solar cells.

3. 研究の方法

To accomplish the proposed work successfully, the research work to be conducted has been broadly divided in to two major categories where first one is related to the fundamental aspects of computer assisted design and development of the novel NIR sensitizers in the light of our findings and knowledge till date. On the other hand, second task related to the investigations pertaining to the electron injection, transport and recombination dynamics in order to propose the optimum molecular frameworks having relatively small driving force for electron injection and dye regeneration.

Task 1. Design of novel NIR dyes based on quantum chemical calculations.

Task 2. Synthesis and Characterization of novel and potential NIR dyes based on quantum chemical Calculations.

Task 3. Validation of photon harvesting of designed sensitizers by the fabrication of dye-sensitized solar cells measurement of photovoltaic performance

Research plan for year 2014.

In this fiscal year research was conducted as follows:

(1) Structural optimization and UV-visible spectral computation by time dependent density functional theory (TD-DFT) using

suitable functional and basis sets as implemented in Gaussian G09 package.

(2) Comparison between the experimental and calculated values of energetics and electronic absorption spectra using a model far-red sensitive squaraine dye

(3) Synthesis, purification and characterization of potential dyes after feed-back from theoretical calculation.

Research plan for year 2015-2016.

(4) In the case of mismatch between experimental and calculated values, further optimization in calculation techniques by varying the functional and basis sets in G03 program package.

(5) Estimation of experimental HOMO and LUMO of designed and synthesized dyes by photoelectron yield spectroscopy and optical absorption measurements, respectively.

(6) Testing of sensitization behaviour of newly designed and developed dyes by fabricating the DSSC and evaluating its performance under simulated solar irradiation at global AM 1.5 condition.

(7) Fine tuning of dye molecular structure in order to estimate the minimum energy barrier needed for the electron injection and dye regeneration.

(8) Proposal of potential sensitizers having intense absorption in NIR to IR region by mapping of energetics

4. 研究成果

Year [2014]

First of all Gaussian program was used to assist the molecular design using a model unsymmetrical squaraine dye which was designed and subjected structural optimization and calculation of electronic absorption spectra and energy of HOMO and LUMO. To make a balance between computation cost and accuracy, density functional theory (DFT) under 6-311G basis set was utilized in order to get the optimum functional for the prediction of energetics along with the electronic absorption spectrum using TD-DFT. In parallel, the designed sensitizers were synthesized, characterized and subjected to photophysical characterizations also. This was performed to compare and correlate the values obtained experimentally and calculated theoretically.

Theoretical calculations reveal that a logical selection of optimum functional is required depending on the physical properties under consideration. For example, functional like LSDA, PBE1 and MPW1 gives relatively better similarity with the experimentally determined HOMO energy level. On the other hand, functional like LSDA, HCTH, THCTH and BPV86 gives better result for the absorption maximum. At the same time, if we are interested in the calculation of energy band gap, B3LYP and B3PW91 are found to be optimum.

In order to determine the minimum offset energy for electron injection and dye regeneration, there is need for fine turning of molecular structure controlling the energetics. To achieve this goal, four model squaraine dyes bearing same pi-conjugated framework and alkyl chain length were designed based on theoretical calculations, synthesized, characterized and used as sensitizers for the fabrication of DSSC. Results have revealed that simply by creating molecular asymmetry and positional variation of substituents, it is possible to control the energy level of the sensitizers at 0.1 eV level.

Year [2015]

Several far-red sensitizing squaraine dyes were designed using Gaussian program package taking TD-DFT under 6-311G basis set along with the synthesis and photophysical characterizations. A perusal of the experimental and results pertaining to the calculation of their energy band gap, HOMO/LUMO energies and electronic absorption spectra revealed that functional like LSDA and MPW1 were able accurately predict the HOMO energy level within the accuracy of ± 0.1 eV. On the other hand, LSDA functional was able to accurately predict the absorption maximum with a very small difference of 30-50 nm only as compared to the experimental data. At the same time, utilization of polarization continuum model (PCM) model in TD-DFT and B3PW91 functional gives comparative values of the results in terms of the energy of HOMO and absorption maximum as obtained by gas phase calculations using LSDA but

energy band gap and energy of LUMO were rather more accurate but needs relatively higher computation cost.

Efforts were also directed to determine the minimum energy barriers for electron injection from excited dye molecules to the TiO_2 conduction band. A number of symmetrical and unsymmetrical squaraine dyes with varying alkyl and fluoroalkyl substituents were designed, synthesized and subjected to estimation of their photon harvesting after DSSC fabrication. Implementing these combined theoretical and experimental approaches, it has been found that it is possible to inject the electron from excited dye molecules to the conduction band of TiO_2 with minimum energy barrier of 0.15 eV where far-red photon harvesting was clearly observed even with such a small driving force for electron injection.

Year [2016]

As a next step such combined theoretical and experimental approaches were also applied for the determination of minimum energy barrier of dye-regeneration by subtle molecular design, their successful synthesis and characterization along with utilization as sensitizers for DSSC using mesoporous TiO_2 as electron transporter and most commonly utilized iodine based electrolyte I^-/I_3^- for dye regeneration. Good match between theoretical and calculated results for energetics and electronic absorption spectra of newly designed unsymmetrical squaraine dyes was observed. Upon utilization of these dyes as sensitizers of DSSCs, all of them appreciably good far-red photon harvesting.

Comparing the energetics of the dye HOMO with the redox energy level of I^-/I_3^- electrolyte, a very good photon harvesting in the far-red wavelength region was observed with smallest energy barrier of 0.12 eV. This clearly indicates the facile dye regeneration with such a small driving force for dye regeneration. Therefore, considering this minimum driving force for electron injection (0.15 eV) and dye regeneration (0.12 eV), it can be concluded that using this squaraine class of sensitizers, it possible to design NIR dyes with minimum energy band gap of 1.17 eV having capability of photon harvesting in the NIR wavelength region up to 1050 nm. Efforts were also directed to design and develop NIR sensitive unsymmetrical squaraine dyes by extending the p-conjugation of the terminal aromatic ring. Hampered photon harvesting in our previously designed NIR dyes was clarified by TD-DFT calculations and explained due to poor coupling of excited electron density in the LUMO of the dye with TiO_2. This has led us to propose new dye molecular structures having good diversion of electron density at the anchoring group of dye in the excited state.

Finally attempts have also been made to design and develop long wavelength absorbing dyes towards their application as sensitizer for DSSCs using Cobalt complex redox electrolytes. Cobalt complex based redox electrolytes are not only preferable due to their less corrosive nature as compared to Iodine but also due to their relatively deeper redox potential providing the attainment of higher open circuit voltage. In spite of such good points of cobalt complex based electrolyte they suffer from enhanced charge recombination owing to their slow diffusion due relatively bulkier size. This make it necessary for strict control of not only the efficient surface passivation but also design of new sensitizers having multiple and large number of long alkyl chain. Considering these points new far-red sensitive squaraine dyes were also designed used for DSSC fabrication. It has been found that surface passivation of both of conducting FTO and mesoporous TiO_2 is necessary for preventing the charge recombination. At the same time, a combination of compact TiO_2/MgO was found to more effective for the surface passivation.

5. 主な発表論文

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(図書)（計０件)

(産業財産権)

出願状況（計０件）

取得状況（計０件）

(その他)

ホームページ

6.研究組織

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