

Rational Design of Organic Materials for Solar Energy Applications

Hiroshi Imahori^{1,2}

¹Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

²Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Introduction

Organic materials have attracted much attention due to their potential applications in organic electronics. In this regard, charge-transporting properties of organic thin films have found to be important in organic transistors, whereas excellent charge separation and charge-transporting properties of organic thin films are essential for organic photovoltaics (OPVs). In this preprint I will describe some of our recent representative examples of organic functional materials for artificial photosynthesis and solar energy applications.¹⁻⁴

Results and Discussion

As a donor phthalocyanines are some of the most widely investigated self-assembling molecules in discotic liquid crystals (DLCs). On the other hand, as an acceptor fullerenes have been successfully incorporated into LC systems to give various LC phases. Besides, some of the covalently functionalized fullerenes are known to form different columnar phases. Therefore, a simultaneous application of phthalocyanine and fullerene to LCs is highly attractive to form such donor-acceptor (D-A) heterojunction structures. Nevertheless, so far there have been a few examples of mesogenic phthalocyanine-fullerene linked dyads. As such, relationships between the LC structures and charge-transporting properties have yet to be examined. We have examined close relationship between LC and charge-transporting properties of a zinc phthalocyanine (ZnPc)-C₆₀ dyad.¹ We expected that due to the strong π - π interaction between the C₆₀ molecules and the covalent linkage the C₆₀ molecules would be arranged successively along the ZnPc one-dimensional (1D) DLC column, leading to D-A bicontinuous structure in the LCs. Actually, the D-A heterojunction structure of ZnP-C₆₀ molecules was found to exhibit highly efficient ambipolar charge-transporting properties. Such relationship between the LC structures and charge-transporting properties will provide basic and fundamental information on the rational design of high-performance LC materials in organic electronics.

Charge-transporting properties within as well as between grains of organic thin films have found to be crucial in the device performances. In this context, constructing bicontinuous D-A arrays in nanoaggregates is a major challenge toward realization of high performance OPVs. Such D-A arrays are expected to improve charge separation (CS) and charge collection efficiencies in the nanoaggregates. Self-assembly of covalently linked D-A dyads is a promising strategy to tailor the D-A arrays with a hope that the covalent constraint would assist their formation. Although elegantly designed D-A dyads have proven to form nanotubes, nanofibers and LC film with bicontinuous D-A arrays, the photocurrent generation efficiency remains poor owing to dilemma of introducing extra self-assembling units that show insulating properties. Moreover, the charge transport is limited by the D-A nanoaggregate boundaries, resulting in the low photocurrent output. Therefore, a new method minimizing self-assembling units and enhancing electrical contact between D-A nanoaggregates is necessary to improve device performances. A novel self-assembly method to build up

bicontinuous D-A nanoaggregates and simultaneous molecular wiring has been developed for efficient photocurrent generation.² Semiflexible methylene linkage of porphyrin (D)-C₆₀ (A) successfully allowed us to form ellipsoid-shaped nanoaggregates in a good-poor solvent mixture. The porphyrin-C₆₀ molecules in the nanoaggregates were found to yield bicontinuous D-A arrays, making it possible to achieve efficient intra charge-transport within the nanoaggregates. More importantly, functionalized-SWNT wiring between the nanoaggregates also rendered inter charge-transport efficient, leading to the highest incident photon-to-current efficiency (IPCE=22%) ever reported for analogous photoelectrochemical devices utilizing covalently linked D-A dyads. Such hierarchical self-assembly of D-A linked molecules with molecular wires will be a promising method to achieve high device performances in OPVs and transistors.

Core to photosynthesis is the multistep electron transfer (ET) of supramolecularly assembled photofunctional chromophores in protein. Such well-organized multistep ET systems allow photosynthesis to achieve efficient solar energy conversion. To mimic the multistep ET, various attempts have been made in artificial systems. However, it is still a challenge to organize suitable organic/inorganic materials in a bottom-up manner, forming a hierarchical ET cascade on an electrode without impairing the intrinsic structures and functions. We have exploited an approach to construct a multistep ET system exhibiting efficient photocurrent generation.³ It utilizes porphyrin (ZnP), zinc oxide nanoparticle (ZnONP), and reduced graphene oxide (RGO) as D-A components. They are sequentially organized on an electrode, that is, i) anchoring of the ZnONP on RGO as a two-dimensional (2D) scaffold, ii) adsorption of ZnP on the ZnONP on RGO, iii) electrophoretic deposition of the resulting organic/inorganic composites onto sintered SnO₂ nanoparticles on an FTO electrode (denoted as FTO/SnO₂). The electrophoretically deposited film exhibited remarkably high photocurrent generation (IPCE = 70%) compared with the reference device without RGO sheets as well as ZnONP. These results will provide fundamental clue for the bottom-up construction of artificial photosynthetic systems utilizing organic/inorganic assemblies.

Porphyrins are an important class of potential sensitizers for highly efficient dye-sensitized solar cell (DSSC) owing to their photostability and high light-harvesting capabilities as seen in natural photosynthesis. Porphyrins possess an intense Soret band at 400 nm and moderate Q bands at 600 nm. Nevertheless, the poor light-harvesting properties relative to the ruthenium complexes have limited the cell performance of porphyrin-sensitized TiO₂ cells. Elongation of the π -conjugation and loss of symmetry in porphyrins cause broadening and redshift of the absorption bands together with an increasing intensity of the Q bands relative to that of the Soret band. On the basis of the strategy, the cell performance of porphyrin-sensitized solar cells has been improved intensively by the enhanced light absorption. Actually, some of our π -extended porphyrins have disclosed a remarkably high efficiency (6-8%) that was close to that of the ruthenium complexes.⁴

References

- (1) Hayashi, H.; Nihashi, W.; Umeyama, T.; Matano, Y.; Seki, S.; Shimizu, Y.; Imahori, H. *J. Am. Chem. Soc.* **2011**, *133*, 10736.
- (2) Umeyama, T.; Tezuka, N.; Kawashima, F.; Seki, S.; Matano, Y.; Nakao, Y.; Shishido, T.; Nishi, M.; Hirao, K.; Lehtivuori, H.; Tkachenko, N. V.; Lemmetyinen, H.; Imahori, H. *Angew. Chem., Int. Ed.* **2011**, *50*, 4615.
- (3) Hayashi, H.; Lightcap, I. V.; Tsujimoto, M.; Takano, M.; Umeyama, T.; Kamat, P. V.; Imahori, H. *J. Am. Chem. Soc.* **2011**, *133*, 7684.
- (4) Imahori, H.; Umeyama, T.; Ito, S. *Acc. Chem. Res.* **2009**, *42*, 1809.