

Hydrogen bonding effect on photocurrent generation in porphyrin–fullerene photoelectrochemical devices†

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A hydrogen bonding effect on photocurrent generation has been evaluated successfully in a mixed film of porphyrin and fullerene with hydrogen bonding on an ITO electrode, which exhibits efficient cathodic photocurrent generation as compared to the reference system without hydrogen bonding.

The utilization of non-covalent bonding such as hydrogen bonding, coordination bonding, electrostatic interactions and van der Waals interactions has recently merited increasing attention as simple but sophisticated methodology to assemble supramolecular architectures.^{1,2} In particular, a variety of non-covalently bonded donor–acceptor (D–A) systems have been constructed in solutions to mimic photoinduced energy and electron transfer processes in photosynthesis.^{2–4} Such methods may be applied to bulk heterojunction molecular photoelectrochemical devices^{5–7} in which the nano-morphology of D–A blends exhibiting an interpenetrating network^{8,9} is achieved in the photoactive films by non-covalent bonding. However, there have so far been few examples where a non-covalent bonding strategy has been employed in a mixed film of donor and acceptor to improve photocurrent generation efficiency in photoelectrochemical devices.¹⁰

Here, we report the first mixed films of porphyrin and fullerene with hydrogen bonding on an ITO electrode to reveal efficient photocurrent generation. The compounds used in this study are shown in Fig. 1. A combination of porphyrin as a donor and fullerene as an acceptor was chosen because such a D–A system is known to exhibit a long-lived charge-separated state with a high quantum yield.¹¹ Taking into account the fact that porphyrins form

an intermolecular complex with fullerenes in the solid state due to the π – π interaction,¹² we can expect fast photoinduced charge separation in the mixed film. More importantly, the resulting electron and hole pair should be separated between the acceptors and the donors, respectively, to suppress charge recombination. Such an electron or hole-transporting highway would be constructed with the help of hydrogen bonding. To evaluate the hydrogen bonding effect on the photoelectrochemical properties of the D–A systems, carboxyl and ethoxycarbonyl groups were introduced to C₆₀ to yield a C₆₀ acid and a C₆₀ ester, respectively, as acceptors (Fig. 1).¹³ Porphyrin (ZnP)¹⁴ was employed as a donor.

An equimolar THF or benzonitrile (PhCN) solution of porphyrin and/or fullerene was cast or spin-coated on an ITO electrode.† Fig. 2 displays absorption spectra of a mixed film of ZnP and C₆₀ acid (denoted as ZnP + C₆₀ acid/ITO), a film of ZnP (denoted as ZnP/ITO), and the equimolar PhCN solution of ZnP and C₆₀ acid (denoted as ZnP + C₆₀ acid). The Soret bands of ZnP + C₆₀ acid/ITO and ZnP/ITO are broadened and red-shifted relative to that of ZnP + C₆₀ acid in PhCN due to the interaction between the porphyrins (see Electronic Supplementary Information, S1†). In addition, the broad long wavelength absorption of ZnP + C₆₀ acid/ITO in the 600–700 nm region is diagnostic of the charge-transfer absorption band due to the π -complex formed between the porphyrin and the C₆₀.¹⁵ The peak frequencies for the CO₂H group in the IR spectra of ZnP + C₆₀ acid and of the C₆₀ acid reveal a characteristic value (1717 cm⁻¹) for the hydrogen

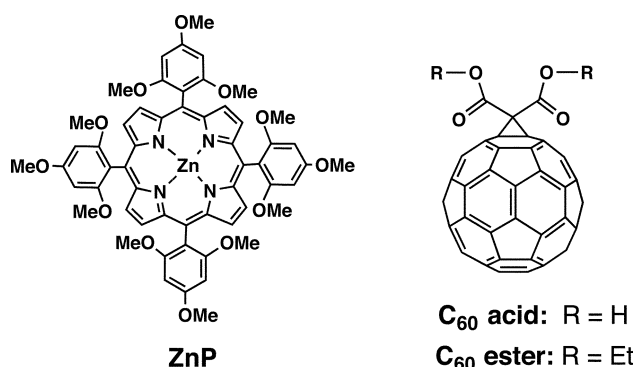


Fig. 1 Donor and acceptor molecules used in this study.

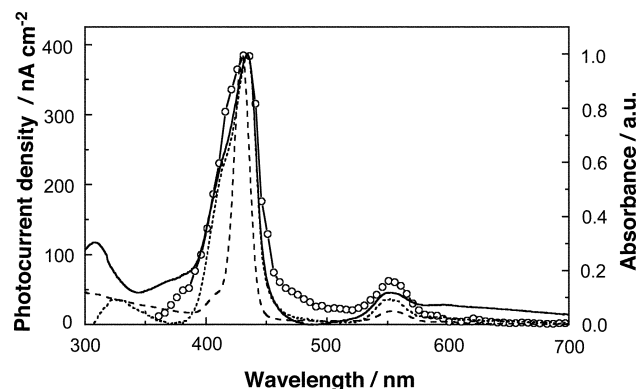


Fig. 2 UV–visible absorption spectra of a mixed film of ZnP and C₆₀ acid (solid line), a film of ZnP (dotted line), the equimolar PhCN solution of ZnP and C₆₀ acid (dashed line), and the action spectrum of an ITO/ZnP + C₆₀ acid/MV²⁺/Pt system (solid line with open circles); input power: 210 $\mu\text{W cm}^{-2}$ ($\lambda_{\text{ex}} = 434 \text{ nm}$); applied potential: $-0.1 \text{ V vs. Ag/AgCl (sat. KCl)}$; an air-saturated 0.1 M Na₂SO₄ aqueous solution containing 5 mM MV²⁺. The spectra are normalized at the Soret band for comparison.

† Electronic supplementary information (ESI) available: spectra (absorption and IR) and AFM images of ZnP and C₆₀ acid. See <http://www.rsc.org/suppdata/cc/b4/b404690k/>

bonding of carboxylic acid, suggesting the formation of a dimer or higher aggregates of the C_{60} acid (see ESI, S2†). The AFM image of $ZnP + C_{60}$ acid/ITO is compared to those of $ZnP + C_{60}$ ester/ITO, ZnP /ITO and C_{60} acid/ITO (see ESI, S3†). The image of $ZnP + C_{60}$ acid/ITO is much smoother than those of $ZnP + C_{60}$ ester/ITO, ZnP /ITO and C_{60} acid/ITO. In particular, the image of $ZnP + C_{60}$ acid/ITO reveals a small domain structure with a regular size (30–70 nm) in comparison with those of $ZnP + C_{60}$ ester/ITO, ZnP /ITO and C_{60} acid/ITO. These results indicate that the porphyrin and the C_{60} are uniformly mixed in the film with the help of hydrogen bonding together with the π -complexation, leading to the smooth morphology on the surface.

Photoelectrochemical measurements were performed in an air-saturated 0.1 M Na_2SO_4 aqueous solution containing 5 mM methylviologen (MV^{2+}) as an electron acceptor using $ZnP + C_{60}$ acid/ITO as the working electrode, a platinum counter electrode, and an Ag/AgCl (sat. KCl) reference electrode (hereafter represented by ITO/ $ZnP + C_{60}$ acid/ MV^{2+} /Pt system, where / denotes an interface). A stable cathodic photocurrent from the ITO electrode to the electrolyte appeared immediately upon irradiation of the ITO electrode (Fig. 3). The photocurrent fell instantly when the illumination was cut off. The cathodic photocurrent increases with increasing negative bias to the ITO electrode from +0.20 V to -0.10 V vs. Ag/AgCl (sat. KCl), whereas the dark current remains almost constant, as shown in Fig. 3. The agreement of the action spectrum with the absorption spectrum of $ZnP + C_{60}$ acid/ITO (Fig. 2) demonstrates that photocurrent flows from the ITO to the electrolyte via the excited state of the porphyrin moiety.

The internal quantum yields (ϕ) of photocurrent generation were compared between ITO/ $ZnP + C_{60}$ acid/ MV^{2+} /Pt, ITO/ $ZnP + C_{60}$ ester/ MV^{2+} /Pt and ITO/ ZnP / MV^{2+} /Pt systems under the same conditions (applied potential: -0.10 V vs. Ag/AgCl (sat. KCl)). The ϕ value ($4.0 \pm 0.6\%$) of the ITO/ $ZnP + C_{60}$ acid/ MV^{2+} /Pt system is larger by a factor of 5–7 than the ϕ value of the ITO/ $ZnP + C_{60}$ ester/ MV^{2+} /Pt ($0.60 \pm 0.10\%$) and ITO/ ZnP / MV^{2+} /Pt ($0.76 \pm 0.03\%$) systems. These results reveal that photocurrent generation efficiency is much improved in the mixed system with hydrogen bonding as compared to the reference system.

Such an ET process is confirmed by the comparison of picosecond fluorescence lifetime measurements for the $ZnP + C_{60}$ acid/ITO, $ZnP + C_{60}$ ester/ITO and ZnP /ITO systems. The fluorescence lifetimes on the ITO surfaces were measured by a picosecond single-photon counting technique at an emission wavelength of

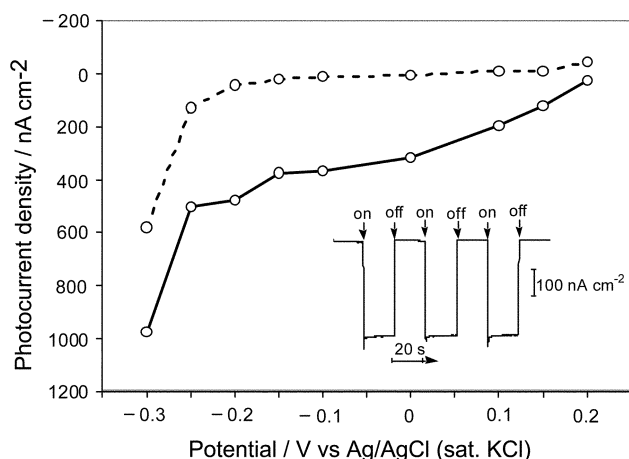


Fig. 3 Photocurrent vs. applied potential curves of the ITO/ $ZnP + C_{60}$ acid/ MV^{2+} /Pt system. The dark currents are shown as a dashed line with open circles. $\lambda_{ex} = 434$ nm ($210 \mu W cm^{-2}$); an air-saturated 0.1 M Na_2SO_4 aqueous solution containing 5 mM MV^{2+} . The photoelectrochemical response is shown as an inset; applied potential: -0.10 V vs. Ag/AgCl (sat. KCl).

650 nm due to the porphyrin moiety having an excitation at 400 nm. The decay curve of the fluorescence intensity could be fitted as a single exponential. The fluorescence lifetimes of $ZnP + C_{60}$ acid/ITO (56 ps) and $ZnP + C_{60}$ ester/ITO (54 ps) are shorter by a factor of 1/2 than that of ZnP /ITO systems (117 ps), which is much shorter than that of ZnP in solution (~ 2 ns). These results suggest the occurrence of photoinduced electron transfer from the porphyrin singlet excited state to the C_{60} moiety rather than self-quenching of the porphyrin excited state due to the aggregation to yield the charge-separated state, which eventually leads to the photocurrent generation. No significant difference in the fluorescence lifetimes of the $ZnP + C_{60}$ acid/ITO and the $ZnP + C_{60}$ ester/ITO also supports that the separated electron in the ITO/ $ZnP + C_{60}$ acid/ MV^{2+} /Pt system is transported more efficiently than that in the ITO/ $ZnP + C_{60}$ ester/ MV^{2+} /Pt system, leading to the relatively efficient photocurrent generation in the former, with the help of the hydrogen bonding.

Based on the energetics of the photoactive and radical ion species involved in the ITO/ $ZnP + C_{60}$ acid/ MV^{2+} /Pt system, the mechanism of cathodic photocurrent generation is proposed. First, an electron transfer takes place from $^1ZnP^*$ (-1.44 V vs. Ag/AgCl) to C_{60} (-0.62 V vs. Ag/AgCl),¹¹ yielding the porphyrin radical cation ($ZnP^{+\cdot}$) and the C_{60} radical anion ($C_{60}^{\cdot-}$). The reduced $C_{60}^{\cdot-}$ gives an electron to MV^{2+} (-0.62 V vs. Ag/AgCl)¹¹ to yield $MV^{\cdot+}$, while the ITO electrode donates an electron to $ZnP^{+\cdot}$ (0.63 V vs. Ag/AgCl) to generate a cathodic photocurrent.

In conclusion, we have successfully observed the hydrogen bonding effect on the photoelectrochemical properties in a porphyrin and fullerene mixed system, which exhibits efficient photocurrent generation relative to the reference systems. Further improvement on the photovoltaic properties may be made by modulating the hydrogen bonding of donors and/or acceptors in the photoactive film.

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Notes and references

† Thicknesses of the films were determined to be 10–20 nm by the surface profiler P-15 (KLA-Tencor).

- J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995.
- F. Diederich and M. Gómez-López, *Chem. Soc. Rev.*, 1999, **28**, 263.
- T. Hayashi and H. Ogoshi, *Chem. Soc. Rev.*, 1997, **26**, 355.
- Electron Transfer in Chemistry*, ed. V. Balzani, VCH, Weinheim, 2001, vol. 3.
- L. Sanchez, M. T. Rispen and J. C. Hummelen, *Angew. Chem., Int. Ed.*, 2002, **41**, 838.
- J. J. González, S. González, E. M. Priego, C. Luo, D. M. Guldi, J. de Mendoza and N. Martín, *Chem. Commun.*, 2001, 163.
- E. H. A. Beckers, A. P. H. J. Schenning, P. A. van Hal, A. El-gayoury, L. Sanchez, J. C. Hummelen, E. W. Meijer and R. A. J. Janssen, *Chem. Commun.*, 2002, 2888.
- G. Yu, J. Gao, J. C. Hummelen, F. Wudl and A. J. Heeger, *Science*, 1995, **270**, 1789.
- J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498.
- L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend and J. D. Mackenzie, *Science*, 2001, **293**, 1119.
- H. Imahori, Y. Mori and Y. Matano, *J. Photochem. Photobiol., C*, 2003, **4**, 51.
- D. Sun, F. S. Tham, C. A. Reed and P. D. W. Boyd, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 5088.
- L. Pasimeni, A. Hirsch, I. Lamparth, M. Maggini and M. Prato, *J. Am. Chem. Soc.*, 1997, **119**, 12902.
- K. Ichimori, H. Ohya-Nishiguchi and N. Hirota, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 2753.
- T. Hasobe, H. Imahori, P. V. Kamat and S. Fukuzumi, *J. Am. Chem. Soc.*, 2003, **125**, 14962.