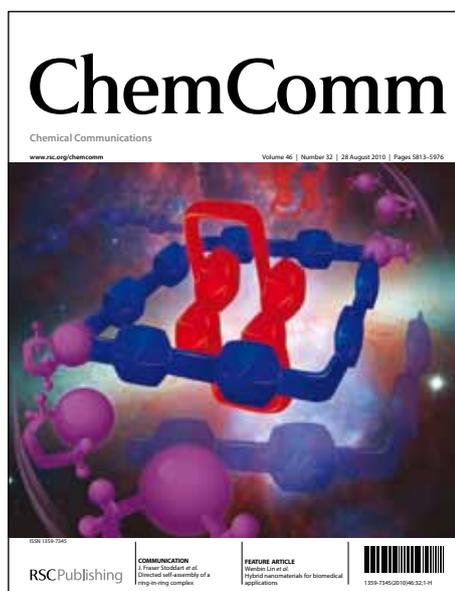


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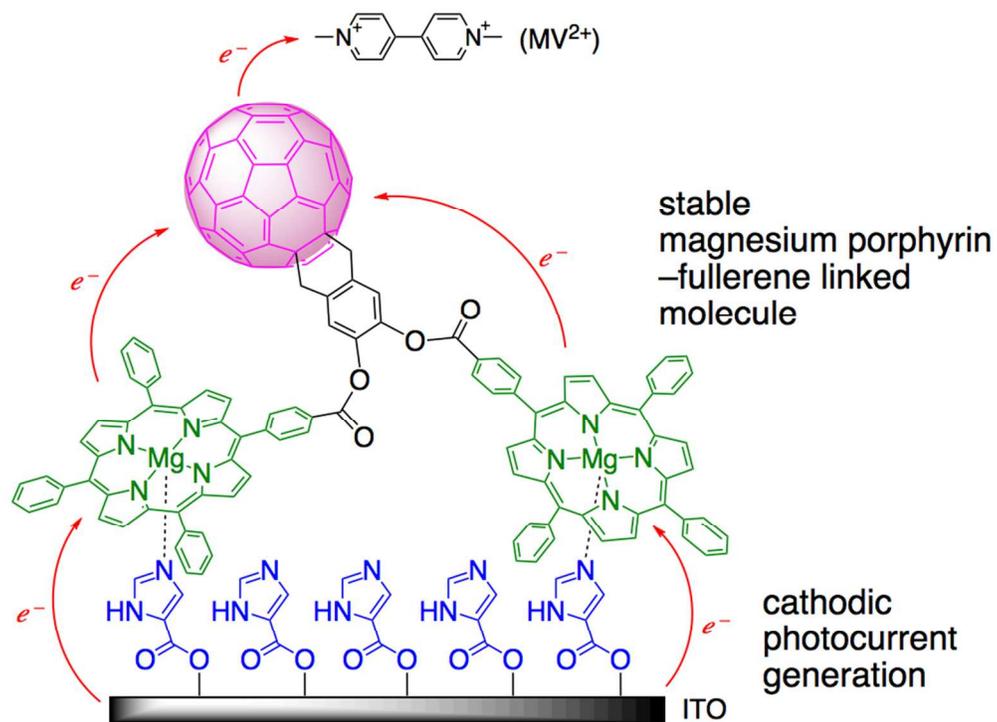
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## Photostability of a dyad of magnesium porphyrin and fullerene and its application to photocurrent conversion

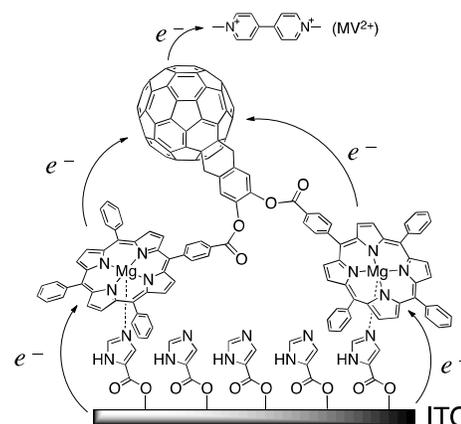
Takahiko Ichiki, Yutaka Matsuo,\* and Eiichi Nakamura\*

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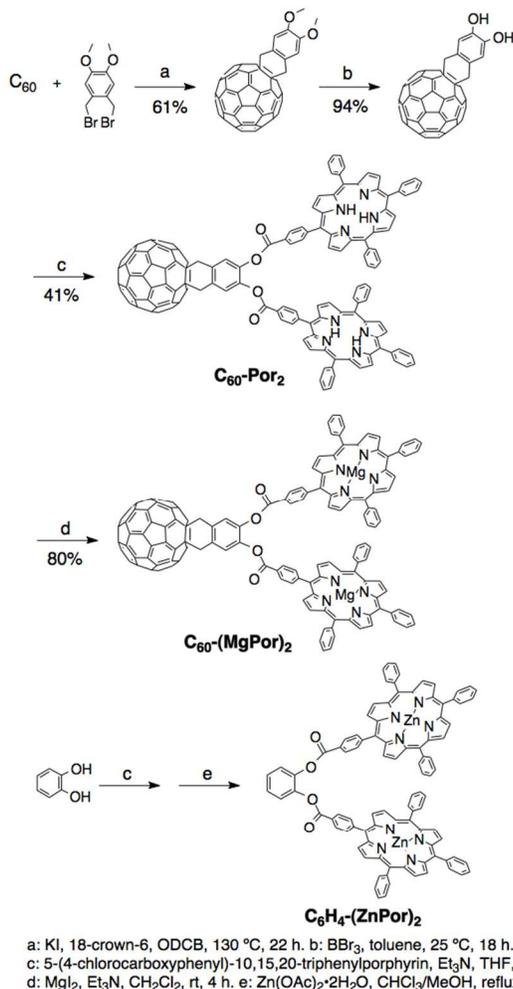
A new type of acceptor–donor<sub>2</sub> dyad system containing two magnesium porphyrin molecules and a fullerene molecule is much more stable than magnesium porphyrin itself. When it is fabricated into a binary system using imidazole carboxylic acid as a linker to indium tin oxide, the molecule effects efficient photocurrent generation that surpasses the device using the corresponding zinc porphyrin.

Magnesium porphyrinoid (chlorophyll)<sup>1</sup> plays the central role in photosynthesis.<sup>2</sup> Likewise, magnesium porphyrin has attracted interest in a man-made photo devices<sup>3</sup> because it offers several advantages over the widely studied zinc porphyrins such as higher fluorescence quantum yields and longer excited-state lifetime (5–10 ns for magnesium porphyrins versus 2–2.5 ns for zinc porphyrins).<sup>4</sup> In general, however, magnesium porphyrins have a crucial disadvantage, that is their instability. Because magnesium porphyrins have high-lying HOMO levels due to their ionic bonding nature, magnesium porphyrins tend to be easily oxidized by singlet oxygen that generates through energy transfer from photoexcited magnesium porphyrin to triplet oxygen.<sup>5</sup> We conjectured the possibility of rapidly quenching the photoexcited magnesium porphyrin via electron transfer to [60]fullerene,<sup>6,7</sup> thereby both increasing the stability of the magnesium porphyrin and achieving efficient photon-to-electron conversion. We report here the synthesis and properties of a acceptor–donor<sub>2</sub> (A–D<sub>2</sub>) dyad system of fullerene and two molecules of magnesium porphyrin (**C<sub>60</sub>-MgPor<sub>2</sub>**)<sup>8,9</sup> and a binary photoelectric device composed of **C<sub>60</sub>-MgPor<sub>2</sub>** and imidazole carboxylic acid (ICA), which in turn is layered on an indium tin oxide (ITO) surface (Scheme 1). The **C<sub>60</sub>-MgPor<sub>2</sub>** was found to be quite stable, particularly when imidazole or pyridine is coordinated to the magnesium atom. Thus, the **C<sub>60</sub>-MgPor<sub>2</sub>:ICA:ITO** device shows much higher performance than the corresponding device using zinc porphyrin (**C<sub>60</sub>-ZnPor<sub>2</sub>**).



**Scheme 1** Schematic drawing of a photo-current conversion system of a fullerene–magnesium porphyrin A–D<sub>2</sub> dyad on a self-assembled monolayer of imidazole carboxylic acid.

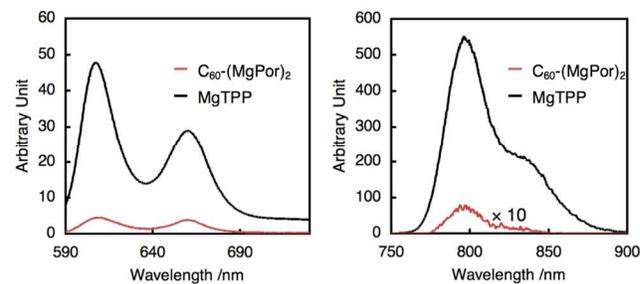
The new fullerene–fullerene A–D<sub>2</sub> dyad (**C<sub>60</sub>-Por<sub>2</sub>**) was synthesized first from fullerene in four linear steps (Scheme 2). After the Diels–Alder reaction of an *in situ*-generated *o*-quinodimethane and deprotection, the fullerene diol was esterified with two porphyrin carboxylic acids to obtain **C<sub>60</sub>-Por<sub>2</sub>**. Introduction of magnesium(II) atoms into the two porphyrin units was achieved by the known procedure using magnesium iodide and triethylamine.<sup>10</sup> Interestingly, unlike magnesium tetraphenylporphyrin (MgTPP), which is unstable, **C<sub>60</sub>-(MgPor)<sub>2</sub>** can be purified by silica gel chromatography under air and ambient light without demetalation or decomposition, indicating its stability under aerobic and mildly acidic conditions.



**Scheme 2** Synthesis of a fullerene–magnesium porphyrin A–D<sub>2</sub> dyad and a reference molecule.

The UV/vis absorption spectrum of **C<sub>60</sub>-(MgPor)<sub>2</sub>** in *o*-dichlorobenzene (ODCB) showed a sharp Soret band at 429 nm and two *Q*-bands at 566 and 607 nm (Fig. S1). The spectrum of **C<sub>60</sub>-(MgPor)<sub>2</sub>** was similar to that of MgTPP, suggesting that there is little interaction between the porphyrin and fullerene in the ground state. In the cyclic voltammetry (CV) measurements (Fig. S2), **C<sub>60</sub>-(MgPor)<sub>2</sub>** showed two-electron oxidation and one-electron reduction for each porphyrin moiety as well as two reduction waves for the fullerene part. No electrochemical interaction between the two magnesium porphyrin units was observed. The first oxidation peak assigned to the magnesium porphyrin moieties of **C<sub>60</sub>-(MgPor)<sub>2</sub>** was slightly shifted to the positive side in comparison with that of MgTPP. This result indicates that the fullerene has an electron-withdrawing effect on the magnesium porphyrin moiety, thereby lowering the HOMO level to stabilize against oxidation. Emission properties were investigated by fluorescence and phosphorescence spectroscopies (Fig. 1). These data suggest that the emission from the porphyrin moieties is effectively suppressed by the presence of the fullerene moiety, as judged by the comparison with MgTPP, which is highly emissive under the same conditions. We surmise that the formation of a charge-separated state is favored over the emission and intersystem

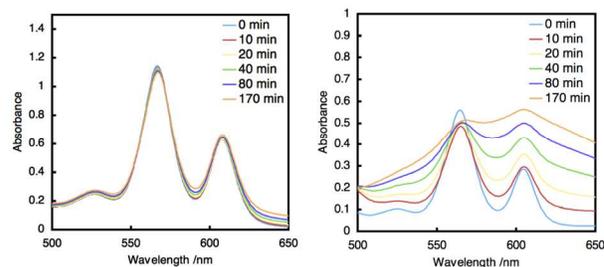
crossing processes in the presence of the fullerene unit.



**Fig. 1** Fluorescence spectrum in ODCB at room temperature (left) and phosphorescence spectrum in EtOH/toluene at 77 K (right) for **C<sub>60</sub>-(MgPor)<sub>2</sub>** (1.0 μM, red line) and MgTPP as a reference (2.0 μM, black line).

To investigate the stabilizing effect of ligand coordination, we titrated **C<sub>60</sub>-(MgPor)<sub>2</sub>** with pyridine (Fig. S3). The changes in the UV/vis spectrum were analyzed as a function of ligand concentration according to the method of Jaffe and Orchin.<sup>11</sup> The slope of the fitted line indicated the formation of a 1:1 coordination complex with a binding constant of  $6.0 \times 10^4 \text{ M}^{-1}$ , which agrees with the data known for MgTPP coordinated to pyridine.<sup>12</sup> In this concentration range, **C<sub>60</sub>-(MgPor)<sub>2</sub>** is five-coordinated. The CV data for the pyridine coordination to **C<sub>60</sub>-(MgPor)<sub>2</sub>** showed a positive shift of the oxidation wave of the porphyrin moiety, indicating that the pyridine coordination lowers HOMO and hence stabilizes the porphyrin against oxidation (Fig. S4).

Next, photooxidation of MgTPP (Fig. 2, left) and **C<sub>60</sub>-(MgPor)<sub>2</sub>** with and without pyridine upon irradiation of incandescent light (60 W) under air was studied spectroscopically (Fig. 2, left, and S5). Whereas MgTPP immediately decomposed, **C<sub>60</sub>-(MgPor)<sub>2</sub>** was much more stable under the same conditions (Fig. S5), and its pyridine complex was much more stable against photooxidation (Fig. 2, right).

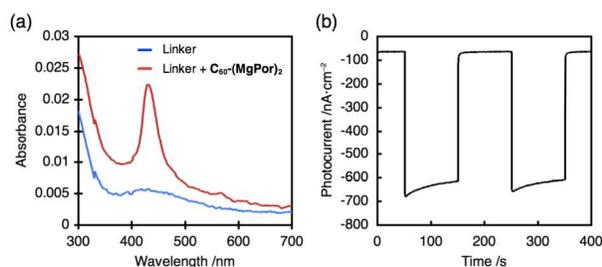


**Fig. 2** Comparison of spectral changes during photooxidation of the stable **C<sub>60</sub>-(MgPor)<sub>2</sub>**-pyridine complex (left) and MgTPP (right). ODCB solutions (38 μM) were irradiated under aerobic conditions.

With information on the photostability and the ability of six nitrogen atoms to coordinate to the two magnesium atoms in **C<sub>60</sub>-(MgPor)<sub>2</sub>**, we next examined the **C<sub>60</sub>-(MgPor)<sub>2</sub>**/ICA/ITO device. First, an ITO substrate was immersed in a DMF solution of ICA (0.1 M) for 3 days; after washing with DMF and ODCB, it was then immersed in an ODCB solution of **C<sub>60</sub>-(MgPor)<sub>2</sub>** (0.01 M) for 3 h. UV/vis measurements provided evidence of the presence of **C<sub>60</sub>-(MgPor)<sub>2</sub>** on the functionalized ITO substrate (Fig. 3a), and the surface

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coverage of  $C_{60}$ -(MgPor)<sub>2</sub> was 0.017 nmol/cm<sup>2</sup>, as estimated from the peak height in the UV/vis spectrum (Fig. 3a). This value is consistent with the formation of a monolayer of  $C_{60}$ -(MgPor)<sub>2</sub>.<sup>13</sup>



**Fig. 3** (a) UV/vis spectrum of the ITO substrate functionalized by ICA (imidazole carboxylic acid linker) (blue line) and  $C_{60}$ -(MgPor)<sub>2</sub> (red line). (b) Photocurrent generation of  $C_{60}$ -(MgPor)<sub>2</sub>/ICA/ITO system in the presence of MV<sup>2+</sup> in aqueous solution containing Na<sub>2</sub>SO<sub>4</sub> at -100 mV applied bias voltage vs Ag/AgCl reference electrode.

Photocurrent generation experiments were carried out in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution containing 50 mM methyl viologen (MV<sup>2+</sup>) as an electron acceptor. The  $C_{60}$ -(MgPor)<sub>2</sub>/ICA/ITO device was used as the working electrode in a cell with a platinum counter-electrode and an Ag/AgCl (saturated KCl) reference electrode. In the presence of MV<sup>2+</sup>, a stable cathodic photocurrent was observed upon light irradiation ( $\lambda_{ex} = 430 \pm 10$  nm, with a power of 207  $\mu$ W) at an applied potential of -100 mV versus Ag/AgCl (Fig. 3b). A photocurrent action spectrum at a bias of -100 mV versus Ag/AgCl was measured (Fig. S6) and found to match well with the corresponding absorption spectrum of  $C_{60}$ -(MgPor)<sub>2</sub> in solution, indicating that  $C_{60}$ -(MgPor)<sub>2</sub> fixed on the substrate was responsible for the photocurrent.

The quantum yield of the photocurrent conversion was 7.8%, a respectable value for self-assembled monolayer/ITO systems.<sup>14</sup> We compared this result with those obtained for the corresponding zinc compound  $C_{60}$ -(ZnPor)<sub>2</sub> and a no-fullerene reference compound  $C_6H_4$ -(ZnPor)<sub>2</sub> (Table 1; the values were estimated from the data in Figs S7–S10). The  $C_{60}$ -(MgPor)<sub>2</sub>-based device was over 10 times more efficient than the Zn-based and no-fullerene devices. We consider that the longer lifetime of the singlet excited state and the higher energy levels of HOMO and LUMO of the magnesium porphyrin is responsible for the efficient charge separation and hence better performance.

**Table 1** Quantum yield and surface coverage of A–D<sub>2</sub> dyad and reference systems.

Compound	Quantum Yield (%)	Surface Coverage <sup>c</sup> (nmol/cm <sup>2</sup> )
$C_{60}$ -(MgPor) <sub>2</sub>	7.8 <sup>a</sup>	0.017
$C_{60}$ -(ZnPor) <sub>2</sub>	0.64 <sup>b</sup>	0.016
$C_6H_4$ -(ZnPor) <sub>2</sub>	0.043 <sup>b</sup>	0.032

<sup>a</sup> Measured with 430 nm irradiation. <sup>b</sup> Measured with 425 nm irradiation. <sup>c</sup> Estimated from the peak area of UV/vis spectrum.

In conclusion, we found that covalent connection of a fullerene molecule to magnesium porphyrin stabilized the intrinsically photo-unstable magnesium porphyrin, probably by the rapid quenching of the photoexcited state of the magnesium porphyrin. Construction of a binary photocurrent conversion system using ICA as a linker between  $C_{60}$ -

(MgPor)<sub>2</sub> and ITO resulted in efficient photocurrent generation. The results illustrate how one can utilize the magnesium porphyrin for useful applications through stabilization against oxidation by the use of an intramolecular excited-state quencher and a nitrogen ligand that lowers the HOMO level and creates a supramolecular array, which is reminiscent of the photosynthesis system in nature.

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## Notes and references

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- † Electronic Supplementary Information (ESI) available: Procedures for Synthesis and self-assembled monolayer formation as well as data for photophysical, electrochemical, photoelectrochemical properties. See DOI: 10.1039/b000000x/
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