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Efficient Bidirectional Photocurrent Generation by Self-Assembled Monolayer of Penta(aryl)[60]fullerene Phosphonic Acid

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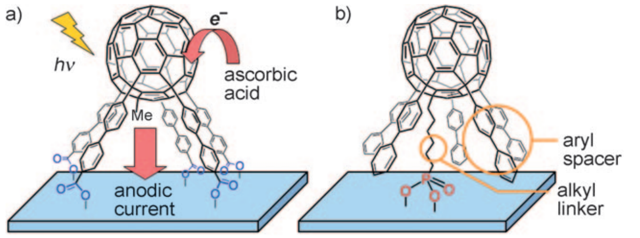
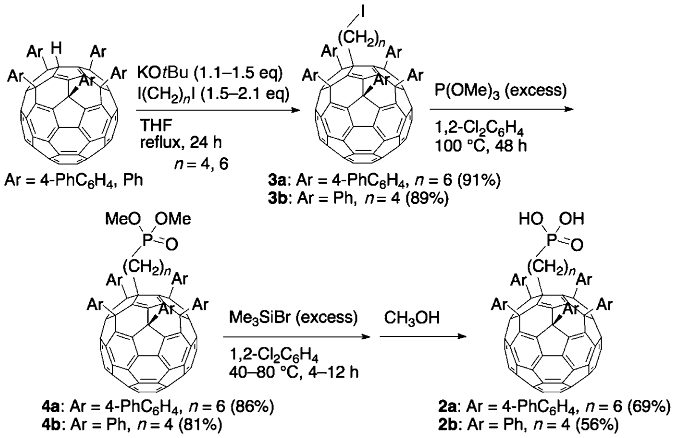


1 2a

Figure 1. SAMs of penta(organo)[60]fullerenes on a metal oxide electrode. a) Penta(biphenyl)[60]fullerene pentacarboxylic acid **1** (pentapod fullerene) attached to the electrode generates anodic photocurrent only and not cathodic current. b) Phosphonic acid **2a** generates both anodic and cathodic photocurrent under reductive and oxidative environment, respectively. The hexyl linker was chosen in consideration of the size of the aryl spacer to secure stable binding of the molecule to the substrate surface.

Photocurrent-generating self-assembled monolayer (SAM) of photoactive molecules on an electrode[1,2] is an archetypal device to achieve photoelectric conversion.[3] Each molecule in the assembly represents a molecular device that absorbs light and generates photocurrent by giving or receiving electrons to or from the electrode. Among such molecules, fullerene derivatives[2] are particularly interesting for their high electron affinity[4] for a long-lived triplet excited state, small reorganization energy,[5] and good electron-transporting ability.[6] However, the propensity of fullerene derivatives to aggregate poses a problem in SAM formation, because it causes excited state annihilation and low efficiency of photocurrent generation. We recently reported a simple molecular design that effectively solves this problem (Figure 1 a); that is, a penta(biphenyl)[60]fullerene pentacarboxylic acid **1** resembling an Apollo lunar landing module generated an anodic (and not cathodic) photocurrent with a quantum efficiency of up to 18% under 400 nm irradiation.[7] The unidirectional photocurrent generation is unique among other fullerenes that are generally known to be bidirectional, and are thus worthy of careful investigations. In addition, the role of the five aryl groups as a space- and orientation-controlling anchor needs to be confirmed. One practical problem was that the SAM on ITO is not very stable and did not tolerate the use of organic medium. To investigate these issues, we have studied phosphonic compounds (**2a** and **2b**, Scheme 1) that bear aryl spacer groups but lack the carboxylic acid groups. We found that these molecules form stable SAM on ITO and SnO_2 both in an aqueous and organic medium, and effectively generate both anodic and cathodic currents. The results suggest that polarization of the pentaarylfullerene molecule **1** caused by the five acid



Scheme 1. Synthesis of [60]fullerene phosphonic acid derivatives.

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groups is a factor responsible for the unidirectional photocurrent generation property of this molecule.

The phosphonic acid fullerene derivatives **2a** and **2b** started from the penta-adducts, $C_{60}Ar_5H$ (Ar = biphenyl and phenyl) as shown in Scheme 1.[8] Deprotonation of the penta-adduct with KO*t*Bu in THF generated a cyclopentadienyl anion,[9] which was alkylated with excess 1,6-diiodo hexane or 1,4-diiodo butane to obtain the iodoalkyl adducts **3a** and **3b**. Michaelis–Arbuzov reaction converted the terminal iodine atom into the dimethyl phosphate group in derivatives **4a** and **4b**. Demethylation of the methyl esters of **4a** and **4b** with bromotrimethylsilane followed by methanolysis afforded the desired phosphonic acid derivatives **2a** and **2b** as an air-stable orange powder in good overall yield. The products were characterized by NMR and atmospheric-pressure chemical ionization mass spectrometry (APCI-MS), and the molecular structure of **4b** was determined unambiguously by X-ray crystallography (Figure 2). To our knowledge, this is the first phosphonic acid derivative of a fullerene to be used for photocurrent generation on an electrode surface.

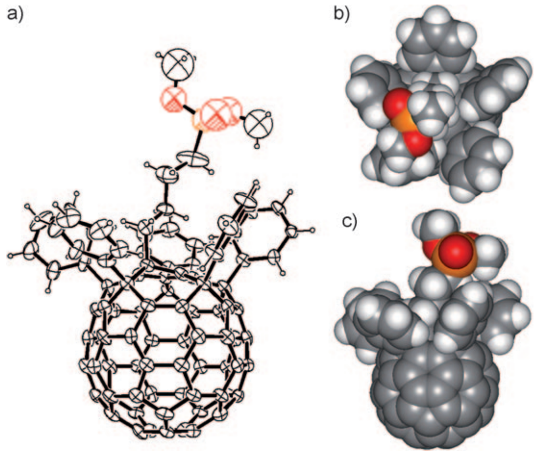

Figure 2. Crystal structure of dimethylphosphonate **4b**. a) The ORTEP drawing with 30% probability level ellipsoids. b) Top view of the CPK model. c) Side view of the CPK model.

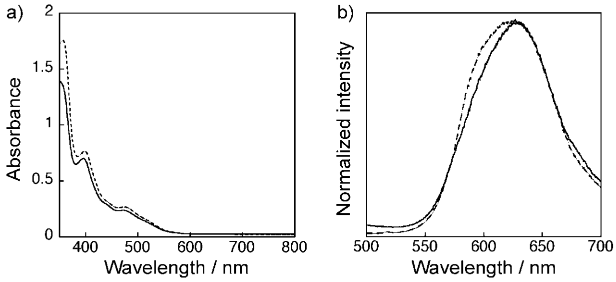

Figure 3. Photophysical properties. a) UV/Vis absorption spectra of solutions of compounds **2a** in 1,2-$Cl_2C_6H_4$ (dotted line) and **2b** in 1,2-$Cl_2C_6H_4$/ethanol (1:1 v/v%, solid line). b) Emission spectra of solutions of dimethyl phosphates **4a** (dotted line) and **4b** (solid line).

The compounds **2a** and **2b** showed essentially the same photophysical and electrochemical properties in solution as the carboxylic acid **1**. The UV/Vis absorption maximum appears at 397 nm ($\varepsilon = 16800\,\text{M}^{-1}\text{cm}^{-1}$, Figure 3a, assigned to the π–π* excitation of the fullerene core). The emission peak wavelength (excitation wavelength 400 nm) was 630 and 627 nm for **4a** and **4b**, respectively (Figure 3b). The photoluminescence quantum yield was very small [$(1.5 \pm 0.1) \times 10^3$] as for the penta(organo)[60]fullerenes in general,[10] because of extremely efficient intersystem crossing from the singlet excited state to the triplet excited state. The electrochemistry of the dimethyl phosphates **4a** and **4b** instead of the phosphonic acid **2a** and **2b** were performed, because the acidic hydrogen atom interferes with the measurements. The cyclic voltammograms exhibited two reversible one-electron reduction processes at $E = -1.49$ V and -1.94 V (**4a**) versus Fc/Fc^+ (Figure S1 in the Supporting Information).

Photoelectrochemical studies of the SAMs of the penta(aryl)[60]fullerenes **2a** and **2b** were performed by irradiation at $\lambda^{ex} = 400$ nm (244 µW). The SAMs were prepared on ITO and SnO_2 by immersion of the electrode into a solution of the compound. Quartz crystal microbalance measurements[11] indicated that the SAM deposition saturates after 10 min immersion time. As shown by the data in Table 1, the phosphonic acid molecules generated both anodic and cathodic photocurrents under reductive and oxidative environments, respectively.

In the presence of the sacrificial donor ascorbic acid (AsA), the SAMs of the biphenyl compound **2a** showed anodic photocurrent with quantum yields of 4.5% and 11% without and with an applied bias voltage of 0.1 V, respectively (Table 1, entries 1 and 2). The phenyl compound **2b** showed 0.5% and 1.9% yield under the same conditions

Table 1. Photocurrent generation characteristics of the SAMs of **2a** or **2b**.[a]

Entry	Cmpd	Sacrificer	Solv.	Substrate	Bias[b]	Direction	Quantum yield [%]
1	**2a**	AsA	H_2O	ITO	0	anodic	4.5
2	**2a**	AsA	H_2O	ITO	0.1	anodic	11.0
3	**2b**	AsA	H_2O	ITO	0	anodic	0.5
4	**2b**	AsA	H_2O	ITO	0.1	anodic	1.9
5	**2a**	MV^{2+}	H_2O	ITO	–0.1	cathodic	1.5
6	**2b**	MV^{2+}	H_2O	ITO	–0.1	cathodic	0.2
7	**2a**	AsA	H_2O	SnO_2	0.1	anodic	2.1
8	**2a**	MV^{2+}	H_2O	SnO_2	–0.1	cathodic	5.8
9	**2a**	TEA	CH_3CN	ITO	0	anodic	17.6
10	**2a**	TEA	CH_3CN	ITO	–0.1	anodic	11.8

[a] Conditions: sacrificing reagents, 50 mM; excitation wavelength, 400 nm. [b] Applied bias potentials vs an Ag/AgCl reference electrode (filled with saturated aqueous KCl solution). Applied bias potentials vs a Ag/Ag^+ reference electrode for the non-aqueous systems.

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(entries 3 and 4), and was found to be generally less effective (data not shown). Figure 4a shows an on–off profile of the anodic photocurrent generation (150 nA cm^{-2}). The action spectrum of the ITO/**2a**/AsA/Pt system (Figure 4b) is in good agreement with the absorption spectrum of compound **2a** (Figure 3a), indicating that **2a** is responsible for the anodic photocurrent generation. In the presence of the sacrificial acceptor methyl viologen dication (MV^{2+}), the SAMs of compounds **2a** and **2b** generated cathodic photocurrent with 1.5 % and 0.2 %, respectively under −0.1 V applied bias potential (Table 1, entries 5 and 6).

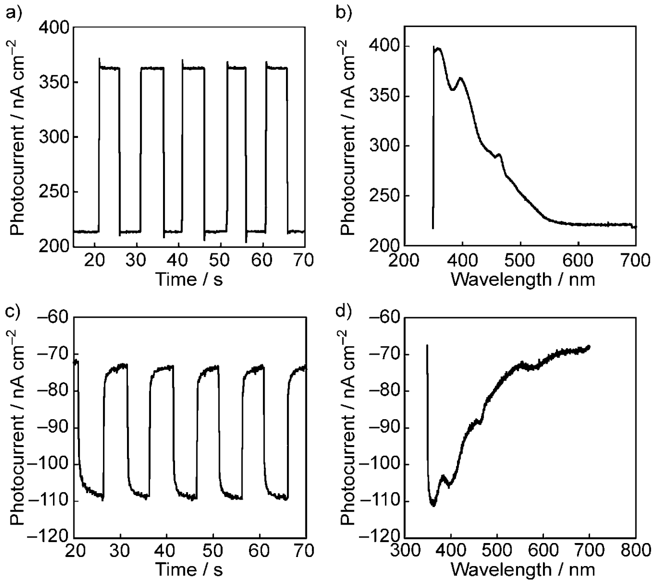

Figure 4. Photoelectrochemical measurements were performed upon irradiation at $\lambda^{\text{ex}} = 400$ nm (244 μW) in an argon-saturated 0.1 M Na_2SO_4 aqueous solution containing AsA (50 mM) or oxygen/MV^{2+} (50 mM) as sacrificing reagents using ITO/**2a** as a working electrode, a platinum counterelectrode, and a Ag/AgCl (KCl saturated) reference electrode. a) Photocurrent response for anodic photocurrent in the presence of AsA under 0.1 V bias potential vs Ag/AgCl (KCl saturated). b) Corresponding action spectrum. c) Photocurrent response for cathodic photocurrent in the presence of MV^{2+} under −0.1 V bias potential vs Ag/AgCl (KCl saturated). d) Corresponding action spectrum.

The SAMs of compound **2a** on SnO_2 were prepared with the same immersion procedures. The SnO_2/**2a** system exhibited higher cathodic (quantum yield, 5.8 %, entry 8) than anodic photocurrent (2.1 %, entry 7), likely because of the lower work function of SnO_2 (4.75 eV)[12] than that of ITO (4.95 eV),[13] which facilitates electron transfer from the electrodes.

The phosphonic acid compounds bind tightly to the ITO surface and can be used in an organic solvent system as opposed to the carboxylic acid **1**, which is easily depleted in an organic solvent. Triethanolamine (TEA) was found to be a good sacrificial donor to be used in an organic solvent (CH_3CN). Photocurrent generation measurements of the ITO/**2a** system in CH_3CN resulted in 17.6 % and 11.8 % photocurrent quantum yields under 0 V and −0.1 V bias potentials, respectively (Table 1, entries 9 and 10). Note that the −0.2 V bias potential is effectively comparable to the 0 V bias in an aqueous system since the Ag/Ag$^+$ couple (non-aqueous) is about 0.2 V lower than the Ag/AgCl couple (aqueous). The observed efficiency is comparable to the best value reported for fullerene derivatives on the ITO system (19.5 %).[2c]

We suggest a rationale for the anodic and cathodic photocurrent generation in Figure 5. The redox potential of the excited state of the penta(organo)[60]fullerene can be calculated by the equation $E^{0'}_{\text{ex}} = E^{0'} + E^{\text{gap}}$, where $E^{0'}_{\text{ex}}$ is the reduction potential of the excited state (i.e., redox couple of $C_{60}{}^{*}R_5$), E^0 is the reduction potential of the ground state (redox couple of $C_{60}R_5$; Figure S1 in the Supporting Information), and E^{gap} is the energy gap for excitation. The energy gap between the ground state and the singlet excited state was derived from the peak top of the emission spectra of compound **2a** in solution (Figure 3b). The energy gap between the triplet state and the ground state was taken from

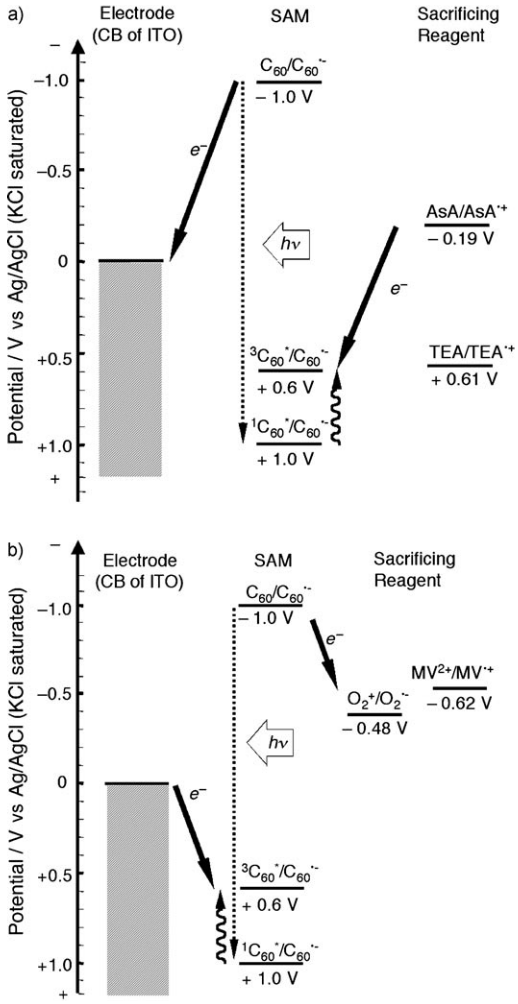

Figure 5. Mechanisms of photocurrent generation. a) Anodic current. b) Cathodic current. The fullerene molecules are simplified as C_{60}.

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the literature.[10] Arrows indicate the electron flows after photo-excitation. The first step is the generation of the singlet excited state of the fullerene. This singlet species is known to be rapidly and quantitatively converted into the triplet species.[10] The excited fullerene is naturally easier to reduce than the neutral molecule. The triplet fullerene (+0.6 V) receives an electron from the donor AsA (−0.19 V), and the resulting fullerene radical anion (−1.0 V) then donates its electron to the ITO electrode, leading to the anodic photocurrent generation.

Figure 5b illustrates the cathodic photocurrent generation process. Upon photoirradiation, the triplet fullerene receives an electron from the ITO, and the resulting fullerene radical anion (redox couple: −1.0 V) donates an electron to MV^{2+} (redox couple: −0.62 V) or molecular oxygen (redox couple: −0.48 V) to generate the cathodic photocurrent.[2b] This energy diagram accounts for the bidirectional photocurrent generation by compound **2**. As the effect of the carboxylic acid groups on the electronic properties of the fullerene core is known to be rather small (e.g., ca. 0.1 eV lowering of the fullerene LUMO),[7] we consider that the polarization effect of these electron-withdrawing groups caused the shutdown of the cathodic current generation in **1**. A related polarization effect was suggested for Grätzel cells and for organic modulation of the work function.[14]

In summary, we have synthesized fullerene phosphonic acids $C_{60}(Ar)_5(CH_2)_nPO(OH)_2$ (Ar = Ph, biphenyl; $n = 4$ and 6) and examined the photoelectrochemical behavior of their stable SAMs. This very simple system performs as efficiently as the prototype **1** with photocurrent quantum yield up to 17% on ITO or SnO_2 in aqueous and organic systems, suggesting that the bulky cone-shaped spacer—a feature common to **1** and **2a**,**b**—contributes to aggregation of the molecules on the electrode surface. However, the new phosphonic acid compounds are bidirectional photocurrent-generating devices in contrast to **1**, which is unidirectional. Thus, the carboxylic acid groups in **1** change the characteristics of the fullerene-SAM devices—useful implications for the design of molecular devices. Besides such mechanistic implications, the molecules were found to be of higher practical values for their easier synthesis and fabrication of the SAM.

Experimental Section

Preparation of self-assembled monolayers on ITO: The ITO electrodes, which were treated beforehand with O_3/UV, were immersed in the 1,2-dichlorobenzene solution of fullerene derivatives (0.02 mM) for 10 min. The substrates were taken from the solution and rinsed with 1,2-dichlorobenzene to remove excess molecules from the surface. Then they were rinsed also with fresh dichloromethane to remove 1,2-dichlorobenzene and finally dried in an argon stream. The immersion time was determined to 10 min from the data of quartz crystal microbalance measurements (Affinix-Q, Initium).[11]

Typical measurements of photocurrent generation: Photocurrent was measured by a HOKUTO DENKO electroanalyzer HZ-5000, and irradiation was performed by a HITACHI fluorescence analyzer F-4500. Photocurrent measurements were conducted in argon-saturated aqueous solutions containing Na_2SO_4 (50 mM) electrolyte and sacrificing reagents (50 mM; AsA and MV^{2+}) in a quartz photoelectrochemical cell equipped with an Ag/AgCl (filled with saturated aqueous KCl solution) reference electrode and a platinum wire counterelectrode (diameter 0.5 mm). The SAM-modified ITO electrodes were used as working electrodes. The surface area of the electrode was 0.20 cm^2. The light intensity at 400 nm was 244 μW. Quantum yields (ϕ) of anodic and cathodic photocurrent were obtained by the following equation: $\phi = (i/e)/[I\ (1–10^{A})]$, where $I = (W\lambda/hc)$. I is the number of photons per unit area and unit time, A is the absorbance of the adsorbed dyes at λ nm, i is the photocurrent density, e is the elementary charge, W is the light power irradiated at λ nm, λ is the wavelength of light irradiation, h is the Planck constant, and c is the speed of light. A was estimated from the next equation, $A = \varepsilon c'l$, where ε was measured from the UV/Vis spectrum of the compound in solution and the surface coverage $c'l$ was estimated from cyclic voltammetry.

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Keywords: fullerenes • molecular devices • phosphonic acid • photocurrent generation • self-assembled monolayers

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