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Synthesis of a porphyrin–C_{60} dyad for potential use in solar energy conversion

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Abstract

A convenient procedure for the synthesis of a new porphyrin–C_{60} dyad via the reaction between 5-(4-aminophenyl)-10,15,20-tris(4-methoxyphenyl) porphyrin and a C_{60} carboxylic acid is described. The results of preliminary photoelectrochemical studies on nanostructured SnO_2 electrodes coated with the new dyad suggest that the resultant substrate is suitable for solar energy conversion devices. © 2001 Published by Elsevier Science Ltd.

Keywords: Porphyrin–C_{60}; Fullerene; Synthesis; Solar energy conversion

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1. Introduction

One approach to mimicking energy conversion via photosynthesis involves the construction of a synthetic system containing chromophores, electron donors and electron acceptors linked by covalent bonds [1,2]. Many of the synthetic systems employ porphyrin derivatives as light receptors in energy conversion and in the design of molecular-scale electronic devices [3,4]. Porphyrins have also been used in solar energy conversion, which takes place in the spectral sensitization of wide band gap semiconductors [2,5,6]. The energy difference between the conduction band edge of an n-type semiconductor and the oxidation potential of the excited adsorbed dye provides the driving force for photo-induced charge injection [7,8]. Therefore, the synthesis of well-defined asymmetric porphyrin derivatives is of great interest for the development of new molecular structures [1,2].

In other studies, fullerene (e.g. C_{60}) derivatives proved capable of multiple electron reductions, and were good electron-acceptors in systems mimicking electron transfer during photosynthesis [9–12]. Taking into account the properties of porphyrins and C_{60}, a solid-state double-layer photoelectrochemical cell was developed [13]. In this system, the light-induced electron transfer from porphyrin to C_{60} was the primary mechanism for photocurrent generation at the porphyrin–C_{60} interface. Studies involving the covalent attachment of C_{60} [14,15] to porphyrins have opened the possibility of constructing artificial systems, in which light-induced electron or energy transfer from a porphyrin donor to a fullerene acceptor occurs.

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The present work pertains to the synthesis of porphyrin dyad **7**, in which the porphyrin moiety is attached to C_{60} via an amide bond. To this end, aminoporphyrin **3** was synthesized by the dipyrromethane method, which appears to offer advantages in porphyrin synthesis [16]. The methoxy groups in the *para* positions of the peripheral phenyl rings enhance the electron-donating character of the porphyrin macrocycle. In addition, C_{60} was functionalized to give carboxylic acid **6**, which is suitable for introducing an amide linkage [17]. Thus, the asymmetrical dyad **7** is characterized by donor–acceptor properties and can undergo light-induced electron transfer [10]. Preliminary studies involving spectral sensitization of a nanostructure having wide band-gap semiconductor (SnO_2) electrodes coated with dyad **7** showed good light harvesting capacity and incident-photon-to-photocurrent efficiency. Nearly complete quenching of porphyrin fluorescence in solution and when adsorbed on SnO_2 nanostructure was observed with dyad **7**, indicating that the photocurrent generation mechanism probably involves the formation of a light-induced charge separation state. The results showed that this porphyrin–C_{60} dyad could be used as a substrate for light energy conversion [18].

2. Experimental

2.1. General

Absorption spectra were recorded on Shimadzu UV-2401PC spectrophotometer. NMR spectra (300 MHz) were recorded on a Varian Gemini spectrometer and mass spectra were recorded on Varian Matt 312 (70 eV) and Vestec Laser Tec (laser desorption) instruments. TLC Uniplate silica gel plates type GHLF (250 microns) from Analtech and silica gel (230–400 mesh) for column chromatography from Aldrich Chemicals were used. Fluorescence spectra were recorded on a Spex FluoroMax fluorimeter. The fluorescence quantum yields (ϕ_f) were calculated by comparison of the area below the corrected emission spectrum, in deoxygenated toluene, with that of tetraphenylporphyrin ($\phi_f = 0.11$) as a fluorescence standard, exciting at $\lambda_{ex} = 550$ nm [10]. Cyclic voltammetry was performed using the previously described equipment [6], and were carried out in 1,2- dichloroethane containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

All chemicals obtained from Aldrich were used without further purification, except for hydroquinone, which was recrystallised from toluene. Toluene, dichloromethane and chloroform (GR grade) were obtained from Merck and were distilled and stored over 4 Å molecule sieves.

2.2. Synthesis

2.2.1. meso-(4-Methoxyphenyl) dipyrromethane (1)

A solution of 4-methoxybenzaldehyde (1.2 ml, 9.8 mmol) and pyrrole (32.0 ml, 460 mmol) was degassed by bubbling with argon for 15 min, and $BF_3{\cdot}O(C_2H_5)_2$ (320 μl, 2.6 mmol) was added. The solution was stirred for 20 min at room temperature, at which point no starting aldehyde was evident by TLC analysis (cyclohexane/ethyl acetate/triethylamine 80:20:1). The mixture was diluted with dichloromethane (100 ml), washed with aqueous 0.1 M NaOH (50 ml) and then washed with water. The organic phase was dried ($MgSO_4$) filtered, and the solvent was removed under reduced pressure. The excess pyrrole was removed by vacuum distillation at 40 °C and the crude product was purified by flash column chromatography (silica gel, cyclohexane/ethyl acetate/triethylamine 80:20:1), giving pure **1** (2.1 g, 85%). TLC analysis: $R_f = 0.41$. ^1H NMR ($CDCl_3$, TMS) δ [ppm]: 4.06 (*s*, 3H); 5.40 (*s*, 1H, *meso*-H); 5.90 (*m*, 2H, pyrrole-H); 6.15 (*q*, 2H, pyrrole-H); 6.70 (*m*, 2H, pyrrole-H); 6.92 (*d*, 2H, $J = 8.7$ Hz); 7.41 (*d*, 2H, $J = 8.7$ Hz); 7.96 (*s*, *brs*, 2H, pyrrole NH). EI–MS [*m*/*z*]: 252.1 (M^+) (252.13 calculated for $C_{16}H_{16}N_2O_1$). Anal. calc.: C 76.17, H 6.39, N 11.10. Found: C 76.28, H 6.30, N 11.14.

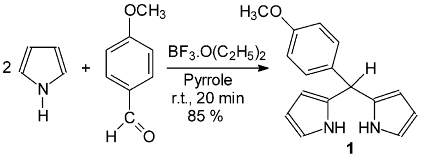
2.2.2. 5-(4-Aminophenyl)-10,15,20-tris(4-methoxyphenyl) porphyrin (3)

A solution of 4-methoxybenzaldehyde (325 mg, 2.39 mmol), 4-acetamidobenzaldehyde (486 mg, 2.98 mmol) and compound **1** (1.20 g, 4.76 mmol) in 250 ml of chloroform was purged with argon for 15 min. Then $BF_3{\cdot}O(C_2H_5)_2$ (1.40 mmol, 0.56

ml of 2.5 M stock solution in chloroform) was added. The solution was stirred for 80 min at room temperature, DDQ (700 mg, 3.08 mmol) was added, and the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and flash column chromatography (silica gel, dichloromethane/methanol gradient) afforded 328 mg (18%) of pure 5-(4-acetamidophenyl)-10,15,20-tris(4-methoxyphenyl) porphyrin (2) as the second porphyrin band. TLC analysis (dichloromethane/methanol 5%): $R_f = 0.52$. EI–MS [*m*/*z*]: 761.3 (M^+) (761.30 calculated for $C_{49}H_{39}N_5O_4$).

To a solution of porphyrin **2** (150 mg, 0.20 mmol) in THF/methanol (90 ml, 2:1) was added KOH (20 ml, 50%). The reaction mixture was stirred under an argon atmosphere for 22 h at 60 °C, and the mixture was diluted with dichloromethane and washed with aqueous sodium carbonate (1%). Removal of the organic solvent under reduced pressure followed by flash column chromatography (silica gel, dichloromethane) afforded porphyrin **3** (108 mg, 75%). TLC (silica gel): R_f (dichloromethane/methanol 5%) $= 0.86$. ^1H NMR ($CDCl_3$, TMS) δ [ppm]: 2.76 (*brs*, 2H, pyrrole N–H); 4.00 (*s*, *brs*, 1H, $ArNH_2$); 4.08 (*s*, 9H, Ar-OCH_3); 7.04 (*d*, 2H, $J = 8.3$ Hz, 5 Ar 3,5-H); 7.26 (*d*, 6H, $J = 8.6$ Hz, 10,15,20-Ar 3,5-H); 7.98 (*d*, 2H, $J = 8.3$ Hz, 5 Ar 2,6-H); 8.10 (*d*, 6H, $J = 8.6$ Hz, 10,15,20-Ar 2,6-H); 8.76–8.95 (*m*, 8H, pyrrole). EI–MS *m*/*z* 719.3 (M^+) (719.30 calculated for $C_{47}H_{37}N_5O_3$). Anal. calcd.: C 78.42, H 5.18, N 9.73. Found: C 78.31, H 5. 26, N 9.68.

Porphyrin **2** was also synthesized by a modified Alder method [19]. Thus, a solution of 4-methoxybenzaldehyde (1.22 g, 9 mmol) and 4-acetamidobenzaldehyde (489 mg, 3 mmol) in propionic acid (75 ml) was stirred at 90 °C as pyrrole (1.43 ml, 20 mmol) was slowly added. The resultant mixture was stirred under reflux for 1 h, at which time it was poured into water (300 ml) containing 12 g NaCl. The green precipitate was collected by vacuum filtration and dried under vacuum at 65 °C for 48 h to remove propionic acid. The solid (2.5 g) was dissolved in 95 chloroform/5 methanol (150 ml) and filtered through short column (45 mm) of alumina (50 g) and then through the same size silica gel column. The solvent was removed under reduced pressure and the solid was stirred for 2 h with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (908 mg, 4 mmol) in chloroform (200 ml). The solvent was removed and the residue was powdered. Gravity controlled column chromatography column (silica gel, chloroform/methanol gradient) afforded 68 mg (3%) of pure porphyrin **2** as the second band.



Scheme 1. Synthesis of dipyrromethane **1**.

2.2.3. C_{60}-acid (*6*)

This intermediate was prepared according to a previously described method [20].

2.2.4. Porphyrin–C_{60} dyad (7)

Aminoporphyrin **3** (22 mg, 0.030 mmol) and C_{60}-acid 6 (20 mg, 0.025 mmol) were dissolved in dry bromobenzene (PhBr) (6 ml). This solution was stirred under argon for 10 min and 1,3-dicyclohexylcarbodiimide (DCC) (6 mg, 0.030 mmol), 1-hydroxybenzotriazole (BuOH) (4 mg, 0.030 mmol), triethylamine (TEA) (4 μl, 0.030 mmol) and 4-(dimethylamino)pyridine (DMAP) (4 mg, 0.0032 mmol) were added. The reaction mixture was stirred for 24 h at room temperature. Flash column chromatography (silica gel) of the entire reaction mixture using toluene (for PhBr removal) and then dichloromethane, afforded pure **7** (32 mg, 73%). TLC (silica gel): R_f (97 dichloromethane/3 methanol) $= 0.84$ and R_f (dichloromethane) $= 0.64$. ^1H NMR ($CDCl_3$, TMS) δ [ppm]: 2.76 (*brs*, 2H, pyrrole N–H); 4.10 (*s*, 9H, Ar–OCH_3); 4.89 (*s*, 1H, methine); 7.31 (*d*, 6H, $J = 8.4$ Hz, 10,15,20-Ar 3,5-H); 7.51 (*s*, *brs*, 1H, NHCO); 7.83 (*d*, 2H, $J = 8.5$ Hz, 5 Ar 2,6-H); 8.13 (*d*, 6H, $J = 8.4$ Hz, 10,15,20-Ar H-2,6); 8.34 (*d*, 2H, $J = 8.5$ Hz, 5 Ar H-2,6); 8.87–8.95 (*m*, 8H, pyrrole). LD–MS *m*/*z* 1479 (M^+) (1479.2848 calculated for $C_{109}H_{37}N_5O_4$). Anal. calcd.: C 88.43, H 2.52, N 4.73. Found: C 88.31, H 2.65, N 4.78.

2.3. Preparation of SnO_2 nanocrystalline films

Optically transparent electrodes were prepared from indium tin oxide (ITO) coated glass plates

(1.3 mm thickness, 100 Ω/square) obtained from Delta Technologies. A suspension of SnO_2 (1.5%) was prepared by diluting the commercial suspension of SnO_2 (20–30 Å, 15%, from Alfa Chemicals) with water containing a surfactant (0.01% Triton X-100, Aldrich). ITO/SnO_2 electrodes were prepared by using a published procedure [21]. In this regard, 0.1 ml of the SnO_2 suspension was spread onto a clean ITO surface (3.5 cm^2) and the coating was dried over a warm plate. The SnO_2 films were annealed at 450 °C for 1 h and the resultant films, which were transparent in the visible region, gave a strong absorption in the UV region near 355 nm. This absorption corresponded to a bulk band gap of 3.5 eV.

Dyad adsorption onto the semiconductor film was accomplished by soaking the annealed film in a saturated solution of dyad **7** in *n*-hexane or petroleum ether. The amount of adsorbed dye was controlled by the soaking time (~30 min in the case shown in Fig. 2). A wire was connected to the ITO surface using an indium solder.

2.4. Photoelectrochemical measurements

Photoelectrochemical experiments were conducted in aqueous hydroquinone (0.01 M), with phosphate buffer (pH = 5.2) prepared from NaH_2PO_4 (0.05 M). A pH = 5.2 was attained by adding NaOH (0.05 M). This solution was thoroughly degassed by bubbling with Ar and the Ar atmosphere was maintained in the top of the cell using a continuous stream. The measurements were carried out in a 10-mm quartz photoelectrochemical cell equipped with Ag/AgCl as reference and Pt foil as the auxiliary electrode. A battery operated low noise potentiostat, constructed in our laboratory, was used in all photoelectrochemical measurements, which were recorded on a Radiometer-Copenhagen X-t recorder. Action spectra for dye-coated SnO_2 electrodes were obtained by sending the output of a 150 W high-pressure Xe lamp (Photon Technology Instrument) through a high intensity grating monochromator and recording the resultant steady-state photocurrent. The electrodes were placed at the focus of the monochromator output (illuminated area = 1 cm^2) and all photoelectrochemical measurements were made in front face configuration. The incident light intensities at different wavelengths were measured with a Coherent Laser-Mate Q radiometer.

3. Results and discussion

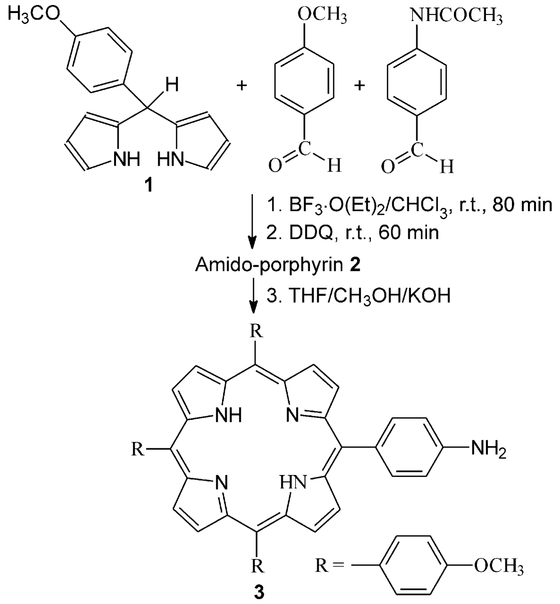
3.1. Porphyrin synthesis

4-Methoxybenzylaldehyde and pyrrole (1:47 aldehyde/pyrrole mole ratio) afforded crude *meso*-(4-methoxyphenyl) dipyrromethane **1** via an acid-catalyzed condensation. The reaction resulted in complete consumption of the aldehyde in 20 min at room temperature, with pyrrole serving as a reactant and the solvent. Flash column chromatography of the crude product on silica gel, using cyclohexane/ethyl acetate/triethylamine (80/20/1) as the eluent, gave pure dipyrromethane **1**. The use of triethylamine in the eluent prevented the decomposition of the dipyrromethane on the slightly acidic silica column. Compound **1** was stable in the purified form on storage at 0 °C under nitrogen and in the absence of light. Highly pure dipyrromethane is essential for its use in the synthesis of the target porphyrin **2**.

Porphyrin **2** was synthesized by the acid-catalyzed condensation of dipyrromethane **1** and a mixture of 4-methoxybenzaldehyde and 4-acetamidobenzaldehyde (Scheme 2). An optimum yield was obtained when the mixed-benzaldehyde–dipyrromethane condensation was performed using a 2.2:1.4:1 molar relationship of dipyrromethane **1**, 4-methylbenzaldehyde and 4-acetamidobenzaldehyde, respectively.

The condensation step employed a catalytic amount of $BF_3{\cdot}O(Et)_2$ and this was followed by oxidation of the reaction mixture with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). This 2-step sequence gave a mixture of three porphyrins, viz. 5,10,15,20-tetra(4-methylphenyl) porphyrin, 5-(4-acetamidophenyl)-10,15,20-tris(4-methoxyphenyl) porphyrin (**2**), and 5,15-bis(4-acetamidophenyl)-10,20-bis(4-methoxy phenyl) porphyrin. Porphyrin **2** was obtained in 18% yield by flash column chromatography.

Using a published method [19], porphyrin **2** was also synthesized by heating a mixture of 4-



Scheme 2. Synthesis of amino-porphyrin **3**.

acetamidobenzaldehyde, 4-methoxybenzaldehyde and pyrrole in propionic acid for 1 h at 90 °C. Due to difficulties with the subsequent removal of propionic acid and the tarry substance, only a 3% yield was obtained.

Thus, the dipyrromethane method offered two main advantages for the synthesis of AB_3-porphyrins over the modified Alder method [19], viz. easier work up and higher yield. Also, the present procedure is a two-step one-flask process that may be used to prepare porphyrin derivatives bearing only one different peripheral phenyl substituent.

Amido-porphyrin **2** was hydrolyzed to amino-porphyrin **3** by heating the former in an alkaline medium (Scheme 2).

3.2. C_{60}-acid formation

Carboxylic acid **6** (C_{60}-acid) was prepared according to a previously described method (Scheme 3) [20]. Reaction of C_{60} and (ethoxycarbonyl)methyl diazoacetate (**4**) gave a mixture of isomers that was equilibrated to the thermodynamic product methanofullerene ester **5**, by heating in toluene. Ester **5** was converted to **6** by treatment with boron tribromide (Scheme 3).

3.3. Dyad synthesis

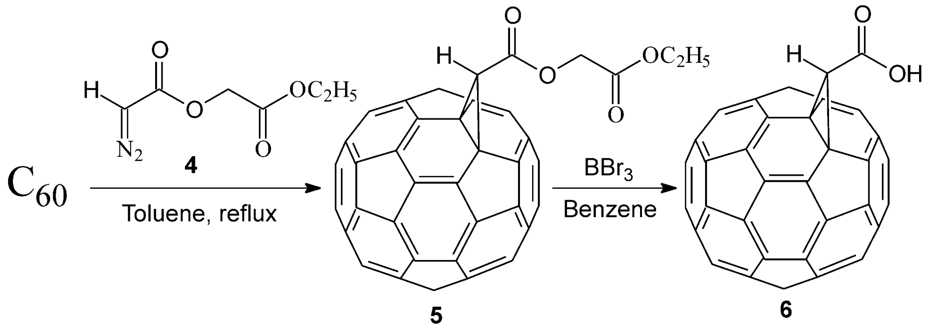
Porphyrin–C_{60} dyad **7** was synthesized by a dicyclohexylcarbodiimide-mediated condensation of C_{60}-acid (**6**) and amino-porphyrin **3** (Scheme 4). The yield after work up was 73%.

3.4. Absorption spectra

The absorption spectra of amido-porphyrin **2**, C_{60}-ester **5** and porphyrin–C_{60} dyad **7** are shown in Fig. 1. The spectra of **2** and dyad **7** exhibited a *Q*-band maxima at 518, 555–556, 593–594 and 650–651 nm. The spectrum of **7** is essentially a linear combination of the spectra of the precursors, which is consistent with only a weak interaction between the two chromophoric systems.

3.5. Steady-state fluorescence spectra

When corrected emission spectra were recorded in toluene, exciting the sample at 550 nm, the amido-porphyrin **2** gave maxima at 658 and 722 nm. The fluorescence quantum yield of porphyrin **2** (ϕ_{f2}) was calculated by steady state comparative method using tetraphenylporphyrin as a reference, giving $\phi_{f2}=0.19$ in deoxygenated toluene. Dyad **7** showed only very weak emission from the porphyrin moiety, indicating strong quenching of the porphyrin excited singlet-state by the attached fullerene moiety. The fluorescence quantum yield for the porphyrin moiety in dyad **7** (ϕ_{f7}) was 3.4×10^{-3} in toluene, and the ϕ_{f2}/ϕ_{f7} ratio increased to $\sim10^2$ in dichloromethane. This decrease in the fluorescence quantum yield of dyad **7** in polar solvents suggests that a new quenching pathway occurred in these solvents, possibly the formation of a charge separated species. The ability of dyad **7** to form a charge-separated state is enhanced by the presence of methoxy groups in the *para*-position of the peripheral phenyl rings of the porphyrin moiety. These groups increase the electron-donor character of the porphyrin, as indicated by the oxidation potentials of **2** (0.86 V vs SCE). This value is 50 mV less positive than that of the corresponding amide-substituted porphyrin having methyl groups rather than methoxy groups [6].



Scheme 3. Formation of C_{60} carboxylic acid **6**.

3.6. Photoelectrochemistry

Our results from determining the photoelectrochemical properties of dyad **7** adsorbed on a semiconductor SnO_2 electrode nanostructure demonstrated that the SnO_2 modified film gave a photoresponse in the visible region with good light harvesting capacity [21,22]. The incident-photon-to-photocurrent efficiency (IPCE) was obtained by measuring the photocurrent when the electrodes were illuminated with monochromatic light, by using Eq. (1),

$$\mathrm{IPCE}(\%) = 100(i_{sc}1240)/(I_{inc}\lambda) \qquad (1)$$

where i_{sc} is the short circuit photocurrent (A cm^{-2}), I_{inc} is the incident light intensity (W cm^{-2}), and λ is the excitation wavelength (nm) [5]. The photocurrent action spectrum closely matches the absorption spectrum of the ITO/SnO_2/dyad **7** electrode (Fig. 2). A maximum IPCE of 9% was found for this system at 422 nm. The fact that there is good correlation between the photocurrent action spectrum and the absorption spectrum of the electrodes confirms that light absorption by dyad **7** is the initial step in the charge transfer mechanism, which is consistent with previous work [5]. Moreover, Fig. 2 shows that anodic photocurrent is generated in the region where C_{60} is the mainly responsible of the light absorption, i.e. below 380 nm. In control experiments, ITO/SnO_2/C_{60} electrodes do not produce an appreciable anodic photocurrent [23], which suggests that the charge transfer process involves the porphyrin moiety. On the other hand, ITO/SnO_2/dyad **7** electrodes are non-fluorescent and produce comparable or higher photoelectric effects than the

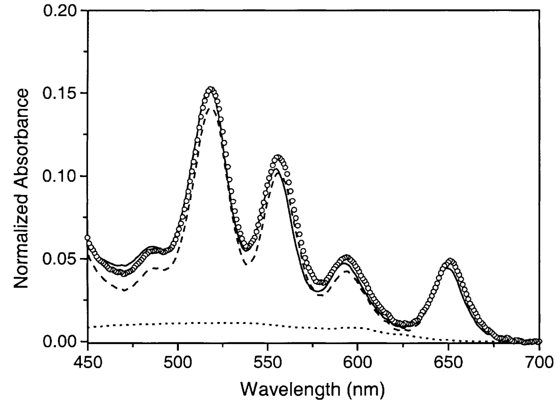


Fig. 1. Normalized absorption spectra (in dichloromethane) for amido-porphyrin **2** (dashed curve), C_{60}-ester **5** (dotted curve), dyad **7** (solid curve) and a linear combination of the spectra of **2** and **5** (open circles).

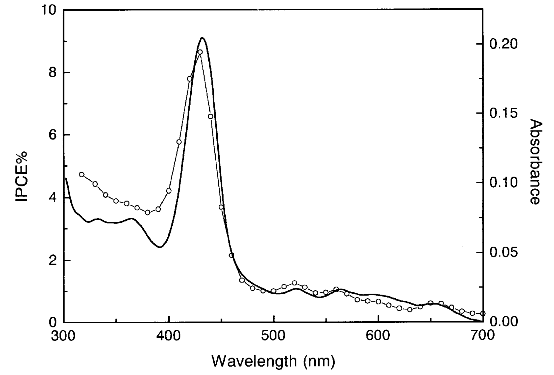
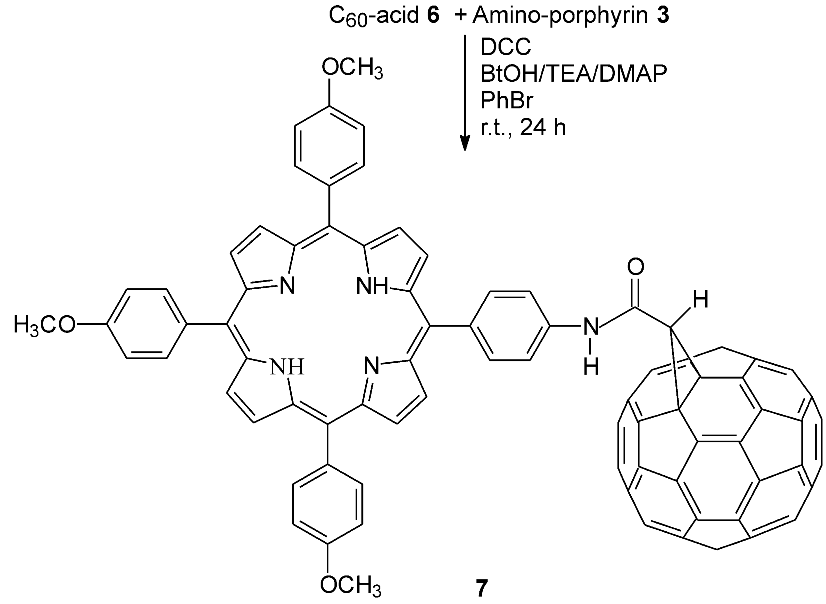


Fig. 2. Absorption spectrum (solid curve) and photocurrent action spectrum (open circles) for electrode ITO/SnO_2/dyad **7**.



Scheme 4. Synthesis of porphyrin–C_{60} dyad **7**.

fluorescent SnO_2 electrodes modified by the porphyrin moiety, when are illuminated in the spectral region where porphyrin is excited. This indicates that a mechanism other than direct electron injection from the excited porphyrin to SnO_2 nanoparticles is involved, probably involving an intramolecular charge separation state.

4. Conclusions

An amido-porphyrin bearing an acetamidophenyl group and three 4-methoxyphenyl groups can be conveniently obtained by condensing dipyrromethane with appropriate benzaldehydes. The corresponding amino-porphyrin can be converted to a porphyrin–C_{60} dyad by a DCC-mediated amidation reaction involving C_{60}-acid. The new dyad contains an electron acceptor C_{60} structure and a porphyrin moiety having electron donor groups. Fluorescence quenching of the porphyrin moiety is believed to occur by electron transfer from the porphyrin to the C_{60} structure to yield a charge-separated species. While it has been demonstrated previously that covalently linked related chromophores can undergo electron transfer in high yield, evidence for electron transfer from a porphyrin to the C_{60} moiety in dyad 7 is important in establishing the mechanism of photocurrent generation in this system.

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