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Synthesis and Properties of 9,10-Anthrylene-substituted Phenyleneethynylene Dyes for Dye-sensitized Solar Cell

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A series of 9,10-anthrylene-substituted phenyleneethynylenes having Ph_2N and CN groups were synthesized. A dye-sensitized solar cell fabricated by both Ph_2N- and CN-substituted derivative exhibited the highest performance of photo-to-current energy conversion.

Photovoltaics has attracted great attention as a sustainable energy resource.[1] Since Grätzel achieved a high solar light-to-electricity conversion efficiency (η) by invoking ruthenium bipyridyl complex,[2] a number of metal-free organic dyes have been developed for fabrication of low-cost and high-performance dye-sensitized solar cells (DSSCs): coumarins,[3] merocyanines,[4] polyenes,[5] oligothiophenes,[6] indolines,[4] and porphyrins[7] have been synthesized. In order to achieve high performance of DSSCs, UV–vis absorption in a wide range of wavelength, a high molar extinction coefficient (ε) and an efficient intramolecular charge transfer upon excitation are required for a sensitizer. We have been involved in synthesis of phenyleneethynylene derivatives and revealed that amino- and cyano-substituted phenyleneethynylenes underwent effective charge separation in the excited state.[8] Because molar extinction coefficient (ε) and wavelength of absorption maximum (λ_{max}) of phenyleneethynylene can be tuned by changing the aryl group and π-conjugation length, we envisioned that amino- and cyano-substituted phenyleneethynylenes would serve as efficient sensitizers for DSSC. We present herein synthesis of 9,10-anthrylene-substituted phenyleneethynylenes with Ph_2N and/or CN group(s) **1**–**3** (Chart 1), their UV–vis absorption spectra, and preliminary results of light-to-electricity conversion using **1**–**3** as sensitizers.

We designed a sensitizer **1** on the basis of the following premise: (i) amino and cyano groups facilitates photoinduced charge separation; (ii) anthrylene-substituted phenyleneethynylene array achieves high molar extinction coefficient (ε) and proper wavelength of absorption maximum (λ_{max}) which enable taking advantage of solar light efficiently; and (iii) substitution with branched long alkoxy groups ((±)-3,7-dimethyloctyloxy) improves solubility of the dye and retards their aggregation induced by π–π interaction between enlarged π-systems.

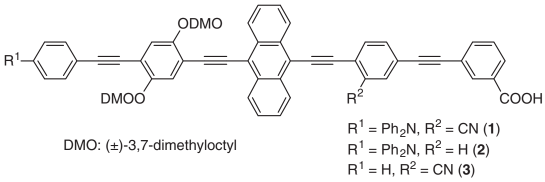
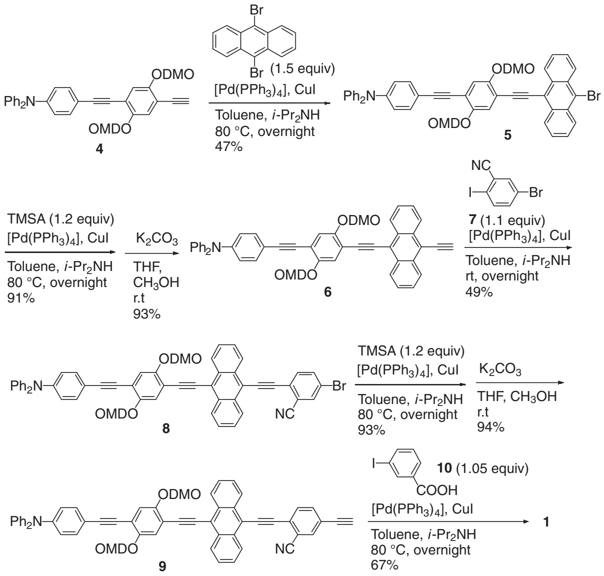


Chart 1.



Scheme 1.

Anthrylene-substituted phenyleneethynylenes with Ph_2N and/or CN group **1**–**3**, were prepared by the iterative Sonogashira coupling of aryl halide with terminal ethyne derivatives and deprotection of terminal ethynes, a representative synthetic route for **1** being shown in Scheme 1. The Sonogashira coupling of 9,10-dibromoanthracene with terminal acetylene **4** having an electron-donating Ph_2N group gave **5** in 47% yield. The Sonogashira coupling of **5** with trimethylsilylacetylene (TMSA) followed by deprotection of the TMS group under basic conditions afforded **6**. Terminal ethyne **9** was obtained through **8** by successive coupling of **6** with **7** and TMSA followed by removal of the TMS group. The desired acetylenic dye **1** was synthesized by coupling of **9** with **10** in 67% yield.[9,10] Although the final coupling produced a mixture of the desired compound **1** and its salt **1**$\cdot$*i*-Pr_2NH, the salt was transformed smoothly to free acid **1** by treatment with silica gel in $MeOH/CH_2Cl_2$. A second column chromatography on silica gel provided **1** as red powder in a pure form (mp: 195–198 °C). ^{13}C NMR of **1** indicated eight signals for acetylene carbons from 85.9 to 100.5 ppm.

In order to assess optical properties of **1**–**3**, UV–vis absorption spectra were recorded in toluene (1.0×10^{-4} M) as shown in Figure 1. All the dyes exhibit high molar extinction coefficients (ε) at the wavelengths of λ_{max}: ε_{max} 7.2×10^4

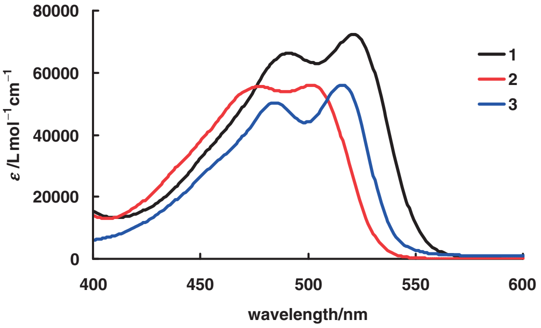


Figure 1. UV–vis absorption spectra of **1**–**3** in toluene.

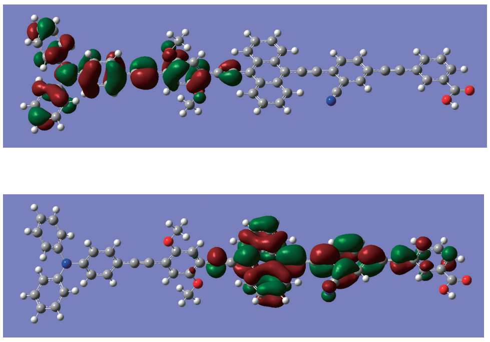


Figure 2. HOMO and LUMO of **1** calculated by B3LYP/6-31G(d). MeO groups were attached instead of DMOO groups for simplicity.

$\mathrm{L\,mol^{-1}\,cm^{-1}}$ ($\lambda_{\max}$ 521 nm) for **1**, 5.6×10^4 (502 nm) for **2**, 5.6×10^4 (516 nm) for **3**. These results indicate that these three dyes could harvest solar light efficiently for photo-to-current energy conversion. Cyanoacetylenic dyes **1** and **3** exhibit longer wavelengths of $\lambda_{\max}$ than **2**, demonstrating that cyano substituent provides a bathochromic shift. Substitution with amino and cyano groups gives rise to a hyperchromic effect, and dye **1** exhibits the highest molar extinction coefficient in comparison to amino- **2** and cyano-substituted dye **3**.

DFT calculations were carried out for dye **1** in order to get further insight to its electronic state in the ground state.[11] In Figure 2 are indicated the HOMO and LUMO of dye **1** in which alkoxy-substituted phenylene and anthrylene are located in a twisted form. The HOMO is located mainly on the $\mathrm{Ph_2N}$ side, while the LUMO on the cyano side, giving rise to a charge-separated excited state of **1**. The LUMO is expanded on 9,10-anthrylene moiety with large coefficients suggesting the anthrylene moiety serves as an efficient light-harvesting group. TDDFT calculations on this conformation of **1** suggested strong UV absorption at 541 nm (oscillator strength $f = 1.68$) which is ascribable to transition from HOMO−1 to LUMO, and this result is rather consistent with the longest wavelength of $\lambda_{\max}$ (521 nm) observed in Figure 1.

The photovoltaic performance was measured to evaluate the potential application of these three organic dyes for DSSCs.[9] Figure 3 shows action spectra of incident photon to current conversion efficiency (IPCE) for DSSCs using a $\mathrm{TiO_2}$ electrode with 6 µm thickness and 0.2399 $\mathrm{cm^2}$ working area by an aperture mask. The IPCE data of the DSSCs based on these dyes exhibit a plateau over 50% in the range from 450 to 620 nm.[12] An IPCE spectrum of a DSSC based on the dye **2** exhibits blue shift in accordance with the absorption spectrum of dye **2**. The maximum value of IPCE spectrum of **2** decreases by ca. 7% in comparison with that of **1**, while dye **3** demonstrates a similar IPCE spectrum to that of dye **1**. These results indicate that the electron-withdrawing cyano group plays a pivotal role for achieving high photo-to-current energy conversion in this series of acetylenic dyes.

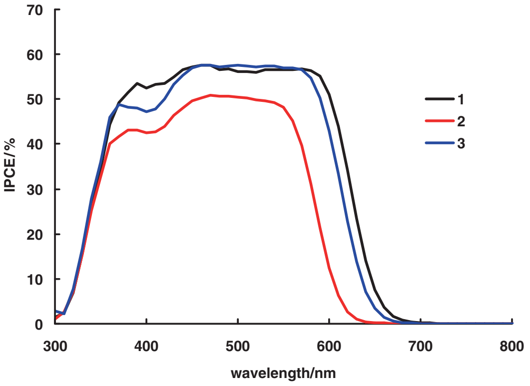


Figure 3. Action spectra of IPCE for DSSCs based on dyes **1**–**3**.

Under standard global AM 1.5G irradiation (100 $\mathrm{mW\,cm^{-2}}$), a solar cell based on dye **1** gave the best performance in a series of acetylenic dye-based solar cells: photo-to-current conversion efficiency $\eta = 4.1\%$, short circuit current density $J_{\mathrm{sc}} = 7.8$ $\mathrm{mA\,cm^{-2}}$, open circuit voltage $V_{\mathrm{oc}} = 0.74$ V, and fill factor $FF = 0.71$. Under the same conditions, solar cells based on **2** and **3** show $\eta = 2.9\%$ and 3.8%, $J_{\mathrm{sc}} = 5.8$ and 7.3 $\mathrm{mA\,cm^{-2}}$, $V_{\mathrm{oc}} = 0.70$ and 0.72 V, $FF = 0.70$ and 0.72, respectively.

These acetylenic dye-based solar cells demonstrate rather high open circuit voltages V_{oc} without any coadsorption such as deoxycholic acid, although they all have a 9,10-anthrylene π-system which aggregates easily through π–π interaction. Long DMOO groups on benzene would retard effectively these dyes from aggregation. The mechanism for high performances of dyes **1**–**3** is under further investigation.

We succeeded in synthesis of a series of 9,10-anthrylene-substituted phenyleneethynylene dyes having $\mathrm{Ph_2N}$ and/or CN groups by the repeating Sonogashira coupling between the corresponding aryl halides and terminal ethynes. The 9,10-anthrylene-substituted phenyleneethynylenes exhibited strong absorption bands in UV–vis spectroscopy, and theoretical calculations suggested that phenyleneethynylene π-conjugated systems expanded by the 9,10-anthrylene moiety induce large molar extinction coefficients. A dye-sensitized solar cell fabricated from $\mathrm{Ph_2N}$- and CN-substituted derivative **1** served well by irradiation of simulated solar light and exhibited a rather high performance ($\eta = 4.1\%$). Because these new dyes based on phenyleneethynylene π-linkage have a high potential for application to DSSCs, the optimization of cell-fabrication conditions such as electrolyte, $\mathrm{TiO_2}$ thickness, and so on are under investigation in order to achieve higher photo-to-current conversion efficiency.

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9 Representative synthetic procedure for **1**, the DSSC preparation method, and UV–vis absorption spectra of dyes **1**–**3** adsorbed on TiO_2 film were shown in Supporting Information. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

10 Syntheses, characterization, and spectral data of **2** and **3** and their properties will be described fully in the following full paper.

11 The theoretical calculations of **1**–**3** were performed with the Gaussian 09 software package.

12 Photo-to-current energy conversion of DSSCs based on dyes **1**–**3** was observed in a range of long wavelength where UV–vis absorption was not observed in toluene, because UV–vis absorption spectra of the dyes adsorbed on TiO_2 underwent bathochromic shift. See Supporting Information.