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Dye-sensitized Solar Cells Based on Novel Diphenylpyran Derivatives

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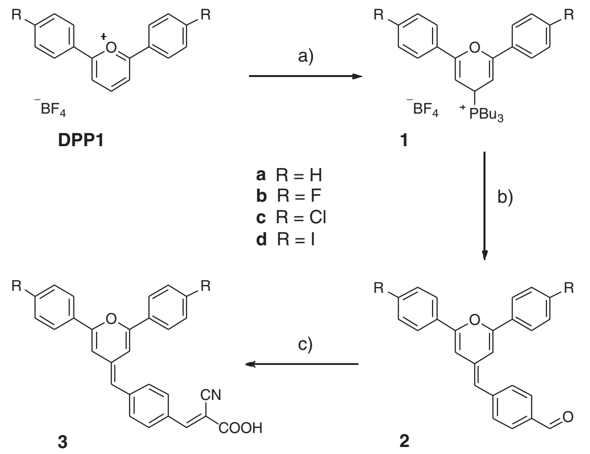
We have prepared a series of novel diphenylpyran derivatives as photosensitizers of dye-sensitized solar cells (DSSCs) for the first time. Nonsubstituted dye **3a** shows an energy conversion efficiency of 2.3% and iodine-substituted dye **3d** shows a higher efficiency of 2.9% due to the tuned energy levels and steric effect.

Worldwide concerns about energy provision and development of recyclable energy source has made dye-sensitized solar cells (DSSCs)[1,2] an important area of research in new energy utilization. A dye-sensitized system was long ago reported by Moser et al. in 1887, explaining a charge-transfer phenomenon from dye to semiconductor through optical excitation.[3] DSSCs have made remarkable progress due to contributions by Grätzel et al. since 1991.[2] Although well-known Ru-based DSSC materials researched by Grätzel et al. have already achieved noteworthy power conversion efficiency up to 11–12%,[4] use of rare metal and environmental issues restrict their further development for practical application. On the other hand, development of metal-free organic materials for DSSCs have attracted much attention due to their appealing advantages such as low-cost production, flexibility, and light weight. Compared with Ru-based materials, pure organic dyes have further advantages such as larger molar extinction coefficients, easier preparation, and more controllable energy levels. Various organic dyes have recently been developed, which are anticipated to be applied for colorful transparent production.[5] Up to date, conversion efficiency as high as 10.1% has been achieved on organic dyes based on ethylenedioxythiophene and dithienosilole blocks.[6] However, these performances are still not good enough for real application when compared with traditional silicon solar cells. Development of new organic dyes is still very important for progress of this field to explore new materials as well as to investigate the relationship between structure and device performance.

In general, broad UV–vis absorption extending to the near-infrared region and well-matched energy levels with the conduction band of TiO_2 electrode and iodine/iodide redox potentials are desirable for achieving excellent energy-conversion efficiencies in DSSCs. The electron donor part of DSSC organic dye is largely responsible for the absorption spectrum and HOMO energy level of materials. Diphenylpyran is electron-donating, but this unit has not been used in DSSC organic dyes until now. According to our previous report,[7] compounds containing the diphenylpyran part have intense absorptions in the visible region as well as proper HOMO energy levels adjustable by introducing substituents at the end of the phenyl groups. Moreover, organic dyes with the diphenylpyran moiety can be simply prepared and various π-conjugated parts can be inserted between the donor and acceptor parts to extend the absorption region. We present herein the synthesis, physical properties, and DSSC device performances of novel diphenylpyran dye **3a** and its halogen-substituted derivatives **3b**–**3d** to investigate the influence of halogen groups introduced at the termini of organic dyes.



Reagents: a) Tributylphosphine, MeCN. b) Terephthalaldehyde, *t*-BuOK, dry THF. c) Cyanoacetic acid, piperidine, MeCN.

Scheme 1. Synthesis of dyes **3a**–**3d**.

The synthesis was accomplished in only three steps as shown in Scheme 1. Addition of tributylphosphine to an acetonitrile solution of 2,6-diphenylpyrylium tetrafluoroborate (**DPP1a**)[7] gave tributyl(2,6-diphenyl-4*H*-pyran-4-yl)phosphonium tetrafluoroborate (**1a**), which produced aldehyde **2a** by a Wittig reaction in good yield. The aldehyde **2a** was condensed with cyanoacetic acid to give the final product **3a**. Other dyes **3b**–**3d** were similarly prepared.

The UV–vis absorption spectra of dyes **3a**–**3d** measured in dichloromethane are shown in Figure S1.[14] The absorption edges of the dyes are extended to 594–566 nm due to intramolecular charge transfer. Compared with dye **3a**, the absorption maxima of halogen derivatives **3b**–**3d** are a little blue-shifted from 497 to 491, 488, and 487 nm, respectively, due to the minutely changed oxidation potentials as shown in Table 1. The molar extinction coefficients also decreased according to the size of halogen atom at the end of the phenyl groups. The redox potentials were measured by cyclic voltammetry in DMF. The first oxidation potential of dye **3a** was observed at 1.09 V, which is more positive than the iodine/iodide redox potential of 0.4 V. The excited state oxidation potential of **3a** of −0.99 V is more

Table 1. Photophysical^{a} and electrochemical^{b} properties of the diphenylpyran dyes in solution

	Dye			
	3a	**3b**	**3c**	**3d**
λ_{max}/nm^{a}	497	491	488	487
$\varepsilon/10^4\,M^{-1}\,cm^{-1}$	3.3	2.3	1.2	0.9
E_{0-0}/eV^{c}	2.08	2.14	2.17	2.19
E_{ox}/V vs. NHE	1.09	1.11	1.13	1.13
E^{*}_{ox}/V vs. NHE^{d}	−0.99	−1.03	−1.04	−1.06

^{a}In CH_2Cl_2. ^{b}Measured by cyclic voltammetry in DMF. ^{c}Obtained from the edge absorptions. ^{d}Estimated by subtracting E_{0-0} from E_{ox}.

Table 2. Photovoltaic performances^{a} of the solar cells sensitized with dyes **3a–3d**

	Dye			
	3a	**3b**	**3c**	**3d**
J_{sc}/mA cm^{-2}	6.5	5.0	6.3	6.9
V_{oc}/V	0.51	0.54	0.56	0.56
FF	0.70	0.71	0.72	0.75
η/%	2.3	1.9	2.5	2.9

^{a}Illumination: 100 mW cm^{-2} simulated AM 1.5 G solar light. Electrolyte solution comprising 0.6 M DMPImI, 0.1 M LiI, 0.2 M I_2, and 0.5 M TBP (in acetonitrile).

negative than the conduction band of TiO_2, −0.5 V.[8] This suggests that the electron injection from the dye to TiO_2 and the electron transfer from I_3^- to the cation-radical state of dye are thermodynamically favorable. The molecular orbital calculations for **3a** were carried out using Gaussian 03 program at the B3LYP/6-31G(d) level of theory. The HOMO orbital exists on the phenyl rings as shown in Figure S2.[14] Introducing halogen atoms makes the oxidation potentials more positive. The excited state oxidation potential is the most negative in the iodine derivative **3d**.

The UV–vis absorption spectra of diphenylpyran dyes on TiO_2 thin films (Figure S3[14]) are a little blue-shifted compared with those in CH_2Cl_2 solution. This might result from weak intermolecular interactions between the dye molecules and/or different energy levels caused by deprotonation of the carboxylic acids.[9] The iodine derivative **3d** shows the absorption maximum on TiO_2 at a longer wavelength than those of **3b** and **3c**, suggesting the presence of a comparatively stronger intermolecular interaction in **3d**.

The action spectra of incident photo-to-current conversion efficiency (IPCE) for DSSCs based on **3a**–**3d** are shown in Figure S4.[14] The IPCE values are lower than 60%. This may be due to the planar structures of diphenylpyran units resulting in dye-aggregation on TiO_2. The maximum value of the IPCE spectra increases in order **3b** (46%) < **3c** (50%) < **3d** (54%) < **3a** (56%). This order is consistent with their maximum absorption bands shifting to the longer wavelength on TiO_2 films as shown in Figure S3.[14] Although the maximum IPCE for the cell based on **3a** is a little higher than that of **3d**, the IPCE spectrum for **3d** is broader than that of **3a** at 600 to 700 nm.

The photovoltaic performances of the DSSCs were measured at 100 mW cm^{-2} under simulated AM 1.5 G solar light conditions. The *I*–*V* curves for DSSCs are shown in Figure S5[14] and the performance data are summarized in Table 2. The short-circuit photocurrent densities (J_{sc}) of DSSCs based on **3b** and **3c** are lower than that of **3a** owing to the blue-shifted absorption spectra caused by their larger electronegativity. J_{sc} of **3d** is a little higher than that of **3a** due to the broader IPCE spectrum.[10] The open-circuit voltage (V_{oc}) and fill factor (*FF*) values of halogen derivatives **3b**–**3d** are higher than those of **3a**. This might be caused by the decrease of charge recombination[11] and/or faster dye regeneration due to the tuned energy levels.[12] Among them, **3d** shows further improved performance than **3b** and **3c**, probably due to the influence of the bigger size of iodine at the end of phenyl groups, which might be leading to steric effects preventing I_3^-/I_2 from approaching the TiO_2 surface.[13] As a result, dye **3d** sensitized solar cell gave the highest overall conversion efficiency of 2.9%.

In summary, we designed and synthesized a class of novel diphenylpyran derivatives **3a**–**3d** and used them as organic sensitizer of DSSCs for the first time. Introducing halogen groups at the end of phenyl groups was found to improve V_{oc} and *FF* due to the tuned energy levels and steric effect. The DSSC based on the iodine derivative gave the highest overall efficiency of 2.9%. The energy conversion efficiency would be further improved by modification of the diphenylpyran and the spacer units.

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