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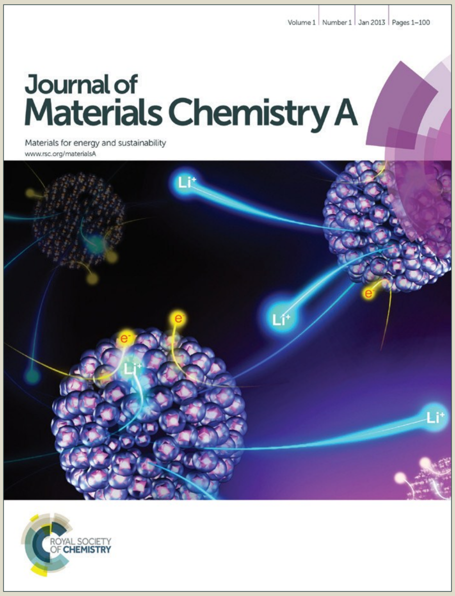

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Graphical Abstract

The high positive potentials for oxidation and long-wavelength absorption properties of tetra-β-cyanoporphyrins make them good candidates for sensitizers in photoelectrosynthetic cells for water splitting. A new synthetic procedure for preparation of these porphyrins that gives high yields under relatively mild conditions has been developed and used to evaluate two tetra-β-cyanoporphyrins as sensitizers for photoanodes of photoelectrochemical cells.

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A new method for the synthesis of β-cyano substituted porphyrins and their use as sensitizers in photoelectrochemical devices

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β-Cyanoporphyrins have high positive potentials for oxidation and absorb light at longer wavelengths than most porphyrins, making them potential candidates for sensitizers in photoelectrosynthetic cells for water oxidation. In order to begin to evaluate this potential, two Zn(II) tetra-β-cyanoporphyrins have been synthesized and evaluated as sensitizers in dye sensitized solar cells using I^-/I_3^- as the redox mediator. To prepare such specialized β-cyanoporphyrins, a new synthetic method has been developed. This approach involves reaction of $Zn(CN)_2$ with β-brominated zinc porphyrins in the presence of tris-(dibenzylideneacetone)dipalladium. The tetra-cyanation reaction is complete under milder conditions as compared to those usually employed in previous methods and gives improved yields of up to ~50%. The procedure allows for the cyanation of porphyrins with relatively sensitive functional groups. Examples of its application to a range of substituted tetra-arylporphyrins are reported, and the absorption and electrochemical properties of the compounds prepared are given. The results from using two of the molecules as sensitizers in dye sensitized solar cells are presented. It was found that the porphyrins produced no photocurrents in nanoparticulate TiO_2-based cells, but both molecules produced photocurrents in SnO_2-based cells, and are potential candidates for sensitizers in photoelectrosynthetic cells for water oxidation.

Introduction

In this energy dependent society, it is important to find sustainable and clean alternative energy sources to reduce our dependence on fossil fuels. Sunlight is a viable source of energy as it is globally available and delivers enough energy to the Earth's surface to not only exceed current global energy requirements, but to meet the energy demands for the foreseeable future. Methods to convert sunlight to a usable energy source have been widely sought. A system that can convert sunlight directly into chemical fuels would be most advantageous because such fuels would provide a practical energy source that could be stored and transported.[1] Hydrogen gas is one such energy source, but in order to use hydrogen for our energy needs, a sustainable method to generate it must be found. One promising route is through photochemical water oxidation. While promising, this method has proven difficult to develop, in part because it requires combining single-photon excitation with multiple electron and proton transfer events to drive the half reactions.[2–7] One of the more difficult steps of this process is the oxidation of water.

One approach to achieving photochemical water oxidation is through the design of dye-sensitized photoelectrosynthetic cells. Such cells couple the fundamental chemistry of the dye-sensitized nanoparticulate wide band gap solar cell to catalysts for water oxidation and hydrogen evolution.[5,8–10] The pioneering report[11] by O'Regan and Grätzel in 1991 has generated a huge number of investigations of approaches to dye sensitized solar cells (DSSC) for electricity production with a view toward improving performance.[12–15] The knowledge gained from these studies can be applied to the design of efficient photoelectrosynthetic cells for water splitting, although water splitting requires an aqueous environment, specific wavelength sensitivity, and the generation of suitable redox potentials. The excited state redox potential of the sensitizer must have the thermodynamic driving force necessary to inject an electron into the conduction band of a semiconductor such as TiO_2 or SnO_2, and the radical cation produced by such injection must be able to accept an electron from the water-oxidation catalyst.

Of the many types of sensitizers for DSSC that have been investigated,[16–31] porphyrins have recently been found to be particularly promising. Porphyrins have long been used as light absorbers and electron donors in artificial photosynthetic molecules, as many of the properties of synthetic porphyrins are generally similar to those of their natural chlorophyll relatives,[32–42] and porphyrins have given some of the highest efficiencies yet observed for DSSC.[16,43] Porphyrins absorb in the UV and visible regions of the solar spectrum with several

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distinctive bands typically from 400 to 650 nm which arise from π-π* transitions.[42,44] Porphyrins are electroactive and can undergo multiple redox processes, and the potentials at which these processes occur can be tailored for different applications, as they depend on several factors including the substituents, the planarity of the macrocycle, and the type and oxidation state of a central metal ion.[45] However, most porphyrins have several shortcomings as ideal dyes for water oxidation. For example, the most common porphyrins do not absorb light in the far red and infrared spectral regions, and sunlight at these wavelengths is wasted, thus reducing efficiency. In addition, the radical cations of most common porphyrins are not oxidizing enough to drive catalysts for water oxidation.

Porphyrins with cyano groups in β-positions absorb light at longer wavelengths than most porphyrins lacking such substituents, and thus in principle can make more efficient use of the solar spectrum in energy conversion applications. Furthermore, addition of electron withdrawing cyano groups at the β-positions of a porphyrin stabilizes both the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). As a result, cyanoporphyrins are more easily reduced than their unsubstituted analogs, making them well suited as electron acceptors in photoinduced electron transfer reactions. They can replace more commonly used electron acceptors such as fullerenes or quinones.[46] Their radical cations are very strong oxidants, which could in principle make them useful for driving water oxidation in solar fuel production systems.

In spite of these advantages, β-cyanoporphyrins have been little explored for such uses, due mainly to the difficulty of preparing them, and the synthetic methods available have limited the selection of substituents to serve as anchoring groups to semiconductors. The first tetrasubstituted β-cyanoporphyrin was reported by Callot in 1973.[47] Bromination of 5,10,15,20-tetraphenylporphyrin with N-bromosuccinimide (NBS) yielded a porphyrin with bromine atoms at four β-positions, and treatment of the nickel derivative of this compound with CuCN in pyridine yielded the tetracyano analog. Using the same synthetic method, Callot and coworkers synthesized various cyanoporphyrins.[48–51] In 1991, Crossley and coworkers reported that the tetrabromo-, and consequently the tetracyano-tetraarylporphyrins formed in this way have the 2,3,12,13 substituent pattern, wherein substitution occurs only on transannular double bonds, opposite one another on the porphyrin macrocycle.[52] A few additional reports of the synthesis of tetracyanoporphyrins have appeared since that time.[53,54]

In these previous reports, the same basic method was employed to prepare the porphyrins. The method requires harsh conditions which are unsuitable for some kinds of substituted porphyrins. The cyanation step necessitates a copper catalyst, and if free base porphyrins or porphyrins containing zinc or other easily replaced metals are used in the cyanation step, copper is introduced into the macrocycle during the reaction. Removal of the copper requires the use of concentrated sulfuric acid. Bhyrappa *et al.* avoided the copper insertion by first incorporating nickel into the porphyrin,[54] but removal of the Ni(II) also requires strong acid. We found this cyanation method to give low yields and produce a number of side products which complicated purification. We therefore sought another synthetic route to β-cyanoporphyrins.

It is known that aromatic halides may be converted to nitriles via palladium-catalyzed cross-coupling reactions,[55–69] and in 2006 Liu and Chen[70] reported synthesis of a β-trifluoromethylated porphyrin from a tetra-β-bromoporphyrin using such a reaction.[70] Based on these reports, we have investigated the preparation of β-cyanoporphyrins via palladium-catalyzed cross coupling. The palladium-catalyzed cyanation we have developed gives yields of ca. 50% for simple porphyrins. The conditions of the reaction are relatively mild, employing temperatures up to 110°C. This method (Fig. 1) eliminates the use of CuCN, which avoids the insertion of copper into the porphyrin macrocycle, and therefore eliminates the copper demetallation step, which requires harsh conditions. The new approach opens up the synthesis of β-cyanoporphyrins that have relatively sensitive functional groups.

Using this new method, several β-cyanoporphyrins were synthesized and two were investigated for use in DSSC applications. The investigations were geared to test the β-cyanoporphyrins for their eventual use in light-driven water-oxidation systems. First, we investigated the spectroscopic and electrochemical properties of model porphyrins bearing either three or four β-cyano groups, and their zinc analogs, in order to determine which were most suitable for DSSC applications. Based upon these results, we selected two porphyrins as sensitizers for DSSC. These two compounds differ in the position of the carboxylic acid group that serves to link the porphyrin to the semiconductor oxide. It has been hypothesized that having the anchoring group at a *meta* position to the macrocycle on a *meso*-aryl ring can allow for more efficient net electron injection into the semiconductor than can be obtained with a *para* linkage.[18,71,72] Finally, we prepared and tested several electrochemical cell types in order to determine whether or not β-cyanoporphyrins could function in DSSC.

Results and discussion

General cyanation method

The general method of synthesis of the β-cyanoporphyrins from the corresponding β-bromoporphyrins is illustrated in Fig. 1. The catalyst is generated *in situ* from tris(dibenzylideneacetone)dipalladium(0) and a ligand such as triphenylarsine, tri-(*o*-tolyl)phosphine, or 1,1'-bis(diphenylphosphino)ferrocene (dppf). Such catalysts are commonly used for cyanation of aromatic bromides.[56,67] The dppf resulted in the highest yields in our hands, and this ligand was used for most of the preparations. This ligand has been found to enhance the yields in other cyanation reactions.[56,65,69]

A variety of additional considerations had to be taken into account in order to obtain reasonable yields. One contribution

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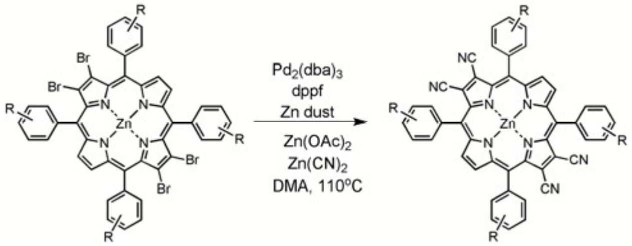

Fig. 1. General synthetic scheme for cyanation of β-bromoporphyrins.

to low yields with this catalyst is deactivation by oxygen, and so the reaction was carried out under an argon atmosphere. We also employed zinc dust and zinc acetate, which have been shown to help keep the catalyst active during the course of the reaction.[62,69,73]

Catalyst deactivation is also caused by reaction with cyanide ion to form a palladium cyanide complex.[58,59,73,74] We employed $Zn(CN)_2$ in our work, as the metal-cyanide bond is less ionic than that of the more commonly employed NaCN or KCN, and this reduces the formation of the palladium cyanide complex.[60,75] Potassium ferrocyanide was also used as a source of cyanide, and worked successfully in several reactions.

The choice of solvent is very important. The solvent must dissolve the organic precursor and catalyst, and in addition the cyanide source, which is a salt. If the solvent is too non-polar, sufficient cyanide will not dissolve. On the other hand, too much cyanide ion in solution can exacerbate the problem of catalyst cyanation.[57,58,60,61] Although dimethylformamide (DMF) is often used as a solvent for reactions of this type, we observed significant debromination of the porphyrin precursor with this solvent, resulting in the formation of porphyrin side products. It has been reported that DMF can be a hydride source in palladium catalyzed reactions.[59] In addition, it is known that the thermal and base catalyzed decomposition of dimethylformamide gives dimethylamine and carbon monoxide,[59,74,76] and that in the presence of secondary acyclic amines, the reduction of aryl bromides occurs under Pd(0) catalysis.[59] It is possible that these reactions also contribute to the debromination. After investigation of several solvent possibilities, N,N-dimethylacetamide (DMA) purified by distillation from barium oxide was found to give the best yields. The reactions were carried out at 110 °C. Yields are the best when the β-bromoporphyrin component is very soluble in DMA, and solubility is in general facilitated by substituents on the phenyl rings.

The demetallation of the zinc β-cyanoporphyrins was carried out using a 10% (v/v) solution of trifluoroacetic acid (TFA) in dichloromethane and the free base porphyrins were obtained in nearly quantitative yields. Some of the β-cyanoporphyrins were prepared bearing methoxycarbonyl groups on *meso*-aryl rings. It was found that to obtain the corresponding carboxylic acid, the ester must be hydrolyzed under base-promoted conditions while the Zn(II) is still in the center of the macrocycle in order to prevent hydrolysis/degradation of the cyanide groups.

Synthesis of β-cyanoporphyrins

The overall scheme for preparation of β-cyanoporphyrins is shown in Fig. 2, and the compounds prepared are depicted in Fig. 3. The requisite dipyrromethanes **A** were prepared from the corresponding aromatic aldehyde and pyrrole by addition of trifluoroacetic acid (TFA), and then triethylamine. Condensation of the dipyrromethane with the appropriate aldehydes under the conditions described previously[40-42] yielded the porphyrins **B**. Treatment of the porphyrins with recrystallized N-bromosuccinimide (NBS) in chloroform or dichloromethane solution beginning with one addition of 4.5 mol equivalents of NBS per mol of porphyrin in solution, followed by several portions of ~2.5 equivalents of NBS (with the number of portions varying among the different porphyrins) until a complete reaction was observed, yielded the 2,3,12,13-tetrabromoporphyrins. The introduction of zinc yielded the zinc 2,3,12,13-tetrabromoporphyrins **C**, which were converted to the corresponding zinc β-cyanoporphyrins **D** as discussed above. In the case of the compounds where the R_1 groups are aryl groups bearing methoxycarbonyl substituents, hydrolysis of **D** with base as discussed above yielded the corresponding acid derivatives. Finally, removal of the zinc with TFA gave the free base porphyrins **E**.

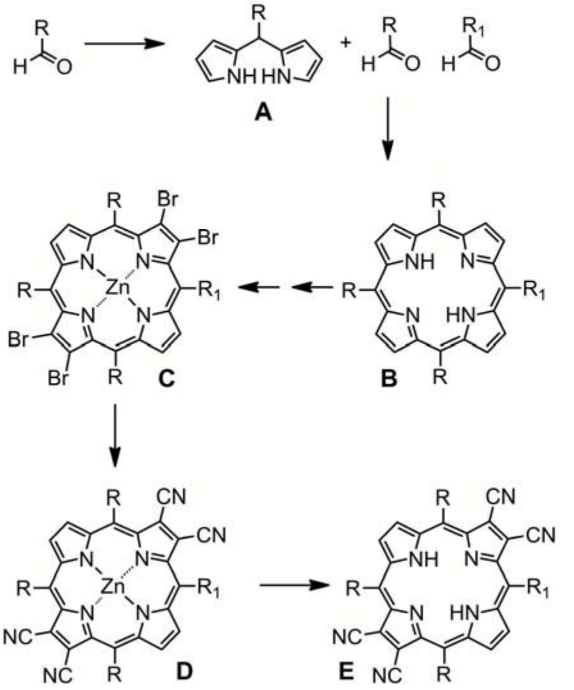

Fig. 2. Synthetic scheme for zinc and free base β-cyanoporphyrins. See the text for reagents and conditions.

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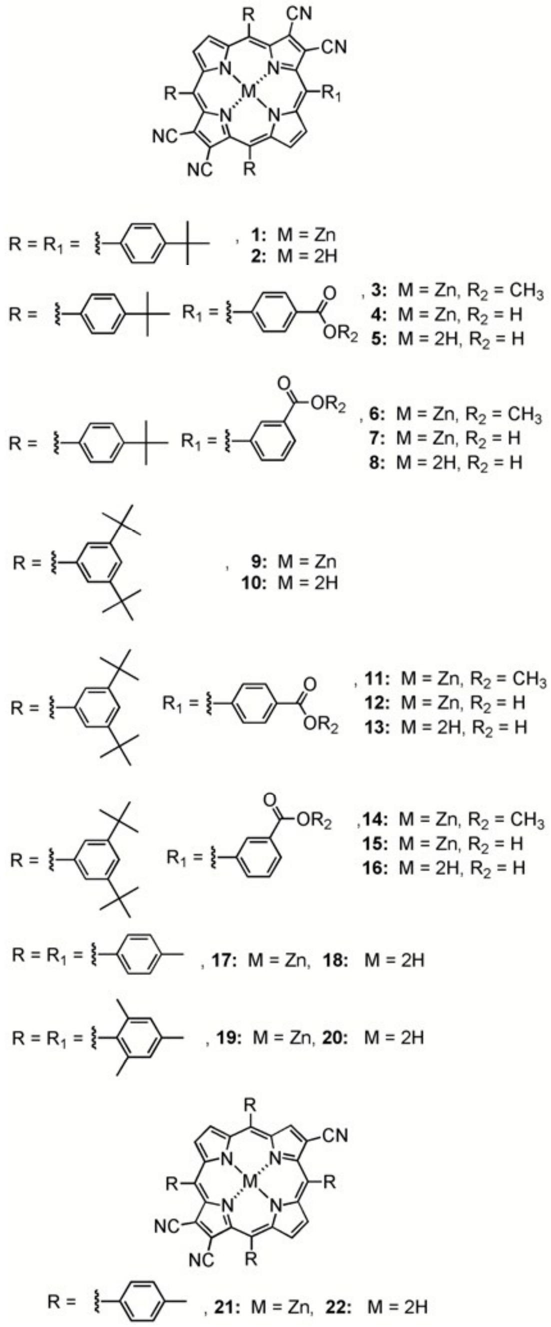

Fig. 3. Porphyrins prepared using the cyanation procedure.

Electrochemical and spectroscopic properties

We determined the absorption and emission spectra and selected electrochemical properties of the compounds synthesized, as these properties are relevant for possible applications of these materials to solar energy conversion and other optoelectronic applications.

The electrochemical properties of the cyanoporphyrins were studied by cyclic voltammetry, and the redox potentials are reported vs. SCE in Table 1. The potentials for acid derivatives **4** and **7** were not measured, but are assumed to be essentially identical to those of the corresponding esters **3** and **6**, based on studies of other porphyrins. Cyclic voltammetry was performed under an argon atmosphere in purified dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. A Pt disc working electrode, Pt mesh counter electrode, and an Ag^+/Ag quasi-reference electrode were employed. Potentials were determined using a ferrocene internal standard and the results were converted to SCE by referencing peaks to the first oxidation wave of ferrocene, which is assigned to be 0.45 V vs SCE in this solvent.[77] A typical voltammogram, that for free base compound **20**, is shown in Fig. 4. The free base cyanoporphyrins show two reversible reduction waves. The first oxidation wave is reversible. When higher potentials are applied, a quasi-reversible second oxidation wave is also observed, and the peaks for the first oxidation are no longer of equal intensity (Fig. 4). The potentials show the anticipated[45,50,52,78] anodic shift due to the electron withdrawing cyano groups. For example, the potential for the first oxidation of 5, 10, 15, 20-tetrakis-(4-methylphenyl)porphyrin is 0.94 V vs SCE and the potential for the first reduction is -1.27 V.[79] The corresponding numbers for **22**, with three cyano groups, are 1.19 V and -0.53 V vs SCE. Thus addition of the three cyano groups has a very large effect on the stabilization of a negative

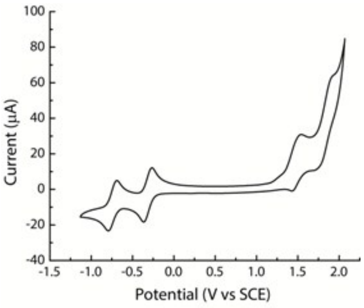

Fig. 4. Cyclic voltammogram of free base porphyrin **20** in dichloromethane obtained under the conditions described in the text.

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Table 1
Spectroscopic and cyclic voltammetric data for the synthesized β-cyanoporphyrins

Cmpd	Soret By[a] λ_{max} (nm)	Soret Bx[a] λ_{max} (nm)	Q bands[a] λ_{max} (nm)	Emission[b] λ_{max} (nm)	Ox_1 ($E_{1/2}$, V vs SCE)	Ox_2 ($E_{1/2}$, V vs SCE)	Red_1 ($E_{1/2}$, V vs SCE)	Red_2 ($E_{1/2}$, V vs SCE)
1	443	459	660, 685	740	1.01	1.42	-0.59	-0.98
2	441	454	556, 600, 670, 738	781	1.22	--	-0.34	-0.61
3	443	454	657, 677	739	1.19	--	-0.38	-0.75
4	443	458	659, 681	--	--	--	--	--
5	445	459	555, 602, 672, 738	781	1.32		-0.31	-0.61
6	443	459	661, 685	737, ~827 (sh)	0.94	--	-0.64	-1.02
7	443	460	662, 689	--	--	--	--	--
8	441	453	556, 601, 668, 735	781	1.27	--	-0.42	-0.69 (E_p)
9	443	458	655, 677	711, ~776 (sh)	1.04	--	-0.62	-1.02
10	440	453	553,599, 667, 730	768	1.41	--	-0.38	-0.67
11	443	458	655, 679	713	1.18	--	-0.45	-0.88
12	443	458	657, 681	--	1.10	--	-0.54	-0.92
13	441	452	554, 599, 667, 729	768	1.38	--	-0.32	-0.62
14	444	456	655, 680	709	1.22	--	-0.48	-0.93
15	445	460	661, 685	712	--	--	--	--
16	443	453	555, 600, 669, 730	767	~1.29	1.47	-0.37	-0.65 (E_p)
17	441	458	659, 680	737	~0.87	1.47	-0.47	-0.88
18	441	453	556, 601, 679, 737	783	1.28	1.51	-0.30	-0.58
19	444	460	662, 686	703, 770	1.22	1.65	-0.49	-0.95
20	439	451	552, 599, 673, 733	742, ~823 (sh)	1.48	1.80	-0.32	-0.75
21	444		632	695	1.02	1.41(E_p)	-0.69	-1.05
22	445		544, 586, 650, 708	755	1.19	1.40(E_p)	-0.53	-0.89
PF_{10}	416		510, 543, 587, 641	646, 709	1.33	1.54	-0.97	-1.35
PF_{10Zn}	415		545, 578	590, 642	1.11	1.35	-1.15	-1.57

[a] Spectra were obtained in dichloromethane. For the porphyrins bearing a carboxylic acid, a solution containing 2% methanol was used to prevent aggregation.

[b] Emission spectra were obtained in dichloromethane, with excitation into the Soret band. For the porphyrins bearing a carboxylic acid, a solution of 2% methanol in dichloromethane was used.

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charge on the porphyrin during reduction, and a smaller but still substantial effect on oxidation. Addition of the fourth cyano group in **18** increases the effect with a ~230 mV shift positive for the first reduction and about ~100 mV shift positive for the first oxidation, relative to **22**. Addition of zinc to the porphyrin makes the macrocycle somewhat easier to oxidize and more difficult to reduce, as can be seen in Table 1 by comparing free base porphyrins with their zinc analogs. Addition of an electron withdrawing carboxyl group to one of the *meso*-aryl rings has little effect on the potentials for oxidation and makes the potentials for reduction more negative by less than 100 mV. Table 1 also shows data for 5-(4-methoxycarbonylphenyl)-15-(4-carboxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin, **PF$_{10}$**, and its zinc analog **PF$_{10Zn}$** which have been explored for use in light-driven water oxidation due to their strong oxidizing ability.[80,81] The tetracyanoporphyrins are roughly comparable to the PF$_{10}$ compounds in terms of oxidation, whereas reduction of the cyanoporphyrins is considerably more facile. This last fact suggests that cyanoporphyrins may be useful as electron acceptors in molecular artificial photosynthetic reaction centers and related compounds in place of the more usually employed quinones or fullerenes. Such applications have been recently demonstrated.[46,82,83]

The UV-visible absorption and emission maxima for the cyanoporphyrins in dichloromethane are given in Table 1. The absorption spectrum of **13** is shown in Fig. 5. In general, the UV-visible maxima of the cyanoporphyrins are shifted to longer wavelengths as compared to porphyrins without β-substituents. Due to the electron withdrawing β-substituents, the longest wavelength Q-band of **18** has a maximum at 737 nm, whereas typical free base *meso*-tetra-arylporphyrins have this maximum around 650 nm. In **17** the Soret bands appear in the same spectral region as those of **18**, but the longest-wavelength Q-band absorption is at 680 nm. As can be seen in Fig. 5, the Soret band is split into two peaks. In terms of the Gouterman four orbital theory,[44] the Soret band is due to electronic transitions from the b_2 orbital (HOMO) to the c_1 and c_2 LUMO orbitals. These transitions consist of two transition dipole moments in directions along a set of axes, *x* and *y*, on the porphyrin which pass through the two sets of opposing pyrrole rings. At room temperature these transitions are observed as a single peak in most porphyrins.[44] Due to the electronic effects of the 4 cyano substituents on the antipodal β-pyrrole positions on only one axis, the energies of the c_1 and c_2 orbitals are no longer degenerate in these compounds, and this in turn leads to the observed split in the Soret band. The cyanoporphyrins with only three cyano groups do not show the splitting of the Soret band, and have less pronounced shifts of the Q-bands to longer wavelengths (see literature[84] and Experimental Section). The fluorescence spectrum of **13** is also shown in Fig. 5. The spectrum features a relatively large Stokes shift and is not the mirror image of the longest-wavelength Q-band. This is in contrast to most porphyrins, which show small Stokes shifts, and indicates that the relaxed excited singlet state has significant electronic differences from the ground state. It may indicate some charge-transfer character in the excited state. It should be noted that the cyanoporphyrins absorb at significantly longer wavelengths than the fluorinated porphyrins and thus have lower-energy excited states.

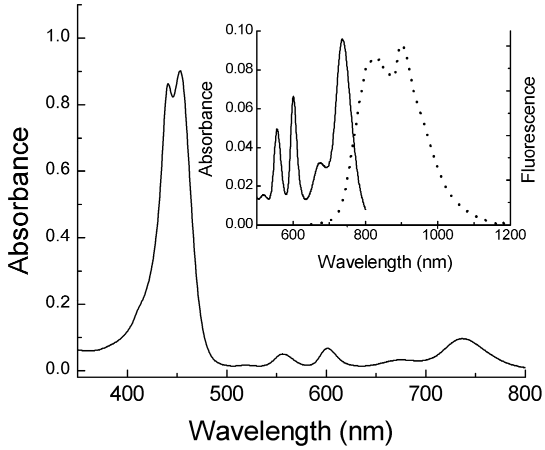

Fig. 5. Spectrum of **13** in dichloromethane. The inset shows absorbance (solid line), and fluorescence with excitation at 451 nm (dotted line).

Photoelectrochemical cells

Both DSSC and photoelectrosynthetic cells for water splitting share the concept of a dye-sensitized nanoparticulate wide band gap semiconductor as a photoanode. Thus, we have evaluated the cyanoporphyrins as sensitizers for DSSC as a step toward their use in water splitting cells. The redox potential for water oxidation at pH 0 is 0.99 V vs SCE, and at pH 8 it is 0.52 V. Thus, from Table 1 it is clear that from a thermodynamic point of view, any of the tetra-β-cyanoporphyrins investigated can oxidize water, and they have significant excess oxidizing power to supply reasonable overpotentials to drive the reaction. The sensitizer must also be able to inject an electron into the CB of the semiconductor. This ability is a function of both the potential for the first oxidation and the excited state energy. Table 2 shows the excited state potentials for oxidation of the various porphyrins. It also shows the thermodynamic driving force values for electron injection into the conduction bands of nanoparticulate TiO$_2$ and SnO$_2$ based on the CB potentials of the semiconductors. These data show that with the possible exception of **21**, none of the porphyrins are expected to be able to sensitize TiO$_2$. With the exception of **18**, all of the porphyrins have some driving force for electron injection into the CB of SnO$_2$. On the other hand, the tri-β-cyanoporphyrins, especially **21**, do not absorb at especially long wavelengths compared to other tetra-arylporphyrins, and thus do not have the advantage of absorbing more of the solar spectrum. We decided to evaluate the zinc tetra-β-cyanoporphyrins as potential sensitizers for DSSC. We also decided to examine both the commonly used TiO$_2$ and the less common SnO$_2$ as semiconductors. Because the CB potentials of nanoparticulate semiconductors are difficult to determine and are a function of the solvent in the cell, and because trap states below the CB

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may be present, we decided to study sensitization of both semiconductors.

Table 2. Longest wavelength absorption maximum in dichloromethane (^{1}P (nm)), energy of the first excited singlet state (^{1}P (eV)), excited state potentials for oxidation vs SCE (*Ox), and free energy changes (ΔG° (eV)) for injection into the conduction bands of TiO_2 and SnO_2 for selected porphyrins.

Cmpd	^{1}P (nm)	^{1}P (eV)^a	*Ox^b	ΔG° TiO_2^{c}	ΔG° SnO_2^{d}
17	680	1.75	-0.55	+0.32	-0.36
18	737	1.59	-0.311	+0.56	-0.12
21	632	1.87	-0.85	+0.02	-0.66
22	708	1.70	-0.51	+0.36	-0.32
3	677	1.75	-0.56	+0.31	-0.37
6	685	1.75	-0.57	+0.30	-0.38
PF$_{10}$	641	1.93	-0.60	+0.27	-0.41
PF$_{10Zn}$	578	2.12	-1.01	-0.14	-0.82

[a] Calculated from the wavenumber average of the longest wavelength absorption maximum and shortest wavelength emission maximum.

[b] The excited state potentials for oxidation were estimated by subtracting the energy of the first excited singlet state from Ox_1.

[c] Calculated using the literature value of -0.63 V vs. SHE for the CB of nanoparticulate TiO_2 at pH 8.[85]

[d] Calculated using the literature value of 0.05 V vs. NHE for the CB of nanoparticulate SnO_2 at pH 8.[80]

The sensitizer dye in a DSSC must bear at least one substituent that serves to bind the sensitizer to the semiconductor nanoparticle. Although various choices are possible,[18] we selected carboxylic acid moieties, as these have been extensively employed in the DSSC literature.[18,71,86,87] The effect of the position of the anchoring group on the macrocycle has been studied and it has been hypothesized that having the anchoring group at the *meta* position on a *meso*-phenyl group allows the porphyrin to lie flatter on the semiconductor surface than does a substituent at the *para* position, and that this increases the efficiency of electron injection.[71,72] Therefore, we have studied both **4** and **7** as sensitizers.

For construction of the cells, the photoanode featured nanoparticulate TiO_2 or SnO_2 deposited on glass substrates bearing a coating of conductive fluorine-doped tin oxide (FTO). After sensitizing the photoanode from a solution of dye, the electrode was used in preparation of a DSSC device that employed a platinized FTO cathode and the I^-/I_3^- redox couple in an acetonitrile-based electrolyte. The DCCS cells were prepared using one of two slightly different protocols. Details of cell construction are given in the Experimental Section.

The absorption maxima of the sensitizers on both TiO_2 and SnO_2 were slightly shifted to longer wavelengths relative to the spectra in solution. Fig. 6a shows the light harvesting efficiency for electrodes sensitized with **7** and **4**. The absorption spectra from which these plots were derived were corrected for scatter and absorbance by the unsensitized electrode. The electrodes for the two sensitizers were prepared under identical conditions, but electrodes bearing **4** consistently showed slightly stronger absorption than those sensitized with **7**. This is likely because the *para* carboxylate linkage group on **4** allows the molecules to attach to the semiconductor oxide with the macrocycle plane more perpendicular to the local semiconductor surface than does the *meta*-carboxylate linkage in **7**, and thus **4** achieves a greater packing density.

Fig. 7 shows the current-voltage plots for DSSC with a TiO_2 photoanode sensitized with **7** and two cells with SnO_2 electrodes sensitized with either **7** or **4** and prepared using the electrodes characterized in Fig. 6. The TiO_2 cell was prepared according to protocol 1 (see Experimental Section) and the SnO_2 cells were prepared according to protocol 2. Illumination was carried out with simulated AM 1.5 G sunlight. The TiO_2-based cell produced no significant photocurrent. This is consistent with the positive ΔG° value for injection of an electron into the conduction band of the semiconductor shown in Table 2.

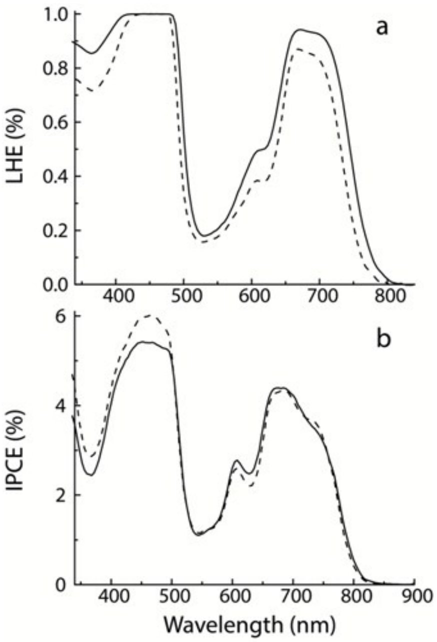

Fig. 6. (a) Light-harvesting efficiency (LHE) of SnO_2 electrodes bearing **7** (dashed) and **4** (solid). The absorption spectra were corrected by subtraction of the spectra of the corresponding unsensitized electrodes. (b) Incident photon to current efficiency (IPCE) as a function of wavelength for DSSC constructed using the electrodes whose LHE are shown in (a). The curves are from electrodes bearing **7** (dashed) and **4** (solid).

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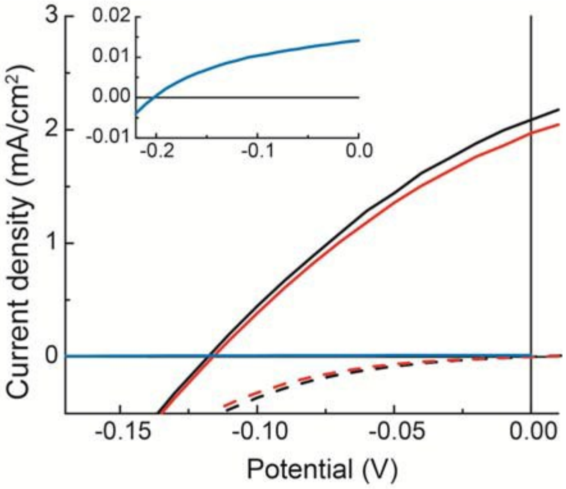

Fig. 7. Current density-voltage plots for DSSC with SnO_2 photoanodes sensitized by **7** (red) and **4** (black). The solid lines show performance under illumination (simulated AM 1.5 G solar irradiation) and the dotted lines show behavior in the dark. The blue curve shows the behavior of a DSSC using **7** deposited on a TiO_2 electrode. The inset is an expansion of the vertical axis for **7** on TiO_2.

The SnO_2 electrodes, on the other hand, both produced photocurrents. The *para*-linked compound **4** produced slightly more photocurrent than the *meta*-linked **7**. For **4**, the short-circuit photocurrent density J_{sc} was 2.09 mA cm^{-2} whereas for **7** J_{sc} was 1.97 mA cm^{-2}. The open-circuit voltages V_{oc} for the cells were nearly identical at 0.118 V for **4** and 0.116 V for **7**, and the fill factor (FF) was 0.31 for both cells. These values give a very slightly higher efficiency η for **4** (0.08%) than for **7** (0.07%).

More detailed information concerning performance comes from the incident photon to current efficiency (IPCE) plots shown in Fig. 6b. In the Soret band region around 430 nm where both electrodes absorb essentially all of the available photons, *meta* sensitizer **7** performs slightly better than the *para* isomer **4**. This increase is consistent with the findings of other workers for other porphyrins sensitizing TiO_2, as mentioned above.[18,71,72] On the other hand, the *para* isomer **4** has efficiencies comparable to or greater than those of **7** in the region from ca. 550 – 800 nm due to the increased LHE in this spectral region shown in Fig. 6a. Thus, in all spectral regions **7** is more efficient than **4** in net electron injection into the cell circuit, but **4** achieves higher packing density on the electrode.

The efficiencies of **4** and **7** reported above are significantly less than those observed for porphyrins in TiO_2-based dye sensitized solar cells. This is expected, as DSSC based on SnO_2 are in general less efficient than those based on TiO_2, and especially those that use an I^-/I_3^-electron mediator.[94,95,96] However, the performance of **4** and **7** is similar to that obtained in similarly-constructed, SnO_2-based DSSC using Zn(II) 5-(4-carbomethoxyphenyl)-15-(4-carboxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin as sensitizer.[80] Optimized SnO_2-based anodes are theoretically advantageous for use in photoelectrochemical cells for water oxidation because electron injection into the SnO_2 conduction band is thermodynamically more facile than injection into TiO_2. This in turn permits the use of more oxidizing long wavelength light absorbing sensitizers than can be used with TiO_2.

Experimental

Synthesis

Synthetic details are reported in the Electronic Supplementary Information.

DSSC preparation and testing

Two related protocols were used to prepare and evaluate the cells.

Protocol 1. A titanium dioxide based electrode was used for constructing DSSC. Transparent conductive fluorine-doped tin oxide (FTO) glass electrodes (Hartford Glass) were coated with a TiO_2 paste[97] and sintered at 450 °C for 45 min. After sintering, the FTO-semiconductor electrode was allowed to cool in air, and was then immersed in a porphyrin solution in ethyl acetate while still warm. Electrodes were soaked for at least 18 h.

A DSSC was constructed using the TiO_2 electrode in combination with a platinum-coated FTO counter electrode. Heat shrink film (Solaronix) was used to seal the electrodes together. Electrolyte was introduced to the internal volume of the cell via holes drilled in the FTO-Pt counter electrode. The electrolyte consisted of an acetonitrile:valeronitrile (1:1 by volume) mixture containing 0.2 M lithium iodide, 0.05 M iodine, 0.2 M tetrabutylammonium iodide, and 0.5 M 4-*t*-butyl pyridine. A mask with a 0.2 cm^2 opening placed over the solar cell defined the illuminated area used for photo-based measurements. A 350 W Xenon arc lamp (Osram) light source with a 400 nm cutoff filter (Thor Labs) and an AM 1.5 solar spectrum filter (Oriel) was used to provide 100 mW cm^{-2} illumination. The 400 nm cutoff filter was used to avoid direct bandgap excitation of the semiconducting layer. A Keithley Sourcemeter was used for photocurrent and photovoltage experiments. A monochromator (Jobin-Yvon) was placed between the Xe lamp and solar cell to provide monochromatic light for incident photon to current (IPCE) measurements. The light intensity at each wavelength used in the IPCE measurements was determined using a silicon photodiode (Newport).

Protocol 2. Conductive FTO-coated glass (TEC 7, Hartford Glass) was cleaned by sonication in acetone and then water, and rinsed with ethanol. Using tape (Scotch® magic tape) as a mask and spacer to outline a defined area on the FTO, a film of SnO_2 paste was spread using a glass rod. The film was dried at 80 °C for 9 min, and the process was repeated to produce a double layer. This layer was sintered (temperature ramped from 180 °C to 370 °C, held for 10 min, ramped from 180 °C to 470 °C, held for 30 min, and slowly cooled). An additional SnO_2 layer was added as described above, and the sintering step repeated. The thickness of the nanoparticulate porous SnO_2 films was ~ 12 μm as determined using profilometry (Tencor Alpha-step 200). The colloidal SnO_2 paste used in this experiment was prepared using a modification of the

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procedure of Ito and co-workers.[97] Acetic acid (200 µL) and water (1 mL) were added to 1.2 g of Sn(IV) oxide nanoparticles (Nanoarc - Alfa Aesar, 13-19 nm). Once the particles were hydrated, 10 mL of ethanol was added and the mixture was sonicated using a sonic horn (Branson 450 with ¼" tip; 30 s × 3, 50% duty cycle, power level 4). α-Terpineol (4 mL, Alfa Aesar) was added, and the mixture was sonicated using the sonic horn (30 s × 3, 50% duty cycle, power level 4). In 20 mL ethanol was dissolved 300 mg of ethylcellulose (Acros Organics, 22 cps) and 300 mg of ethylcellulose (Acros Organics, 10 cps), and the resulting solution was added to the colloid. The colloid was sonicated using the sonic horn (30 s × 3, 50% duty cycle, power level 4). Under reduced pressure, the volatile ethanol was removed from the colloid by evaporation to yield a viscous paste. The SnO_2 electrodes were sensitized in 0.150 mM solutions of porphyrin in ethyl acetate overnight, rinsed, and dried under a nitrogen atmosphere in the absence of light. A defined electrode area was formed by removal of the undesired SnO_2 film using a plastic razor blade. Platinized FTO was prepared by adding a drop of 20 mM H_2PtCl_6 in ethanol to FTO coated glass (TEC 7, Hartford Glass), drying the glass in air, and then heating it at 450 ^oC for 30 min. A hole was drilled in the FTO to allow for incorporation of electrolyte.

DSSC devices were prepared by sandwiching a 25 µm thermoplastic spacer (Surlyn, Solaronix) between the dye-sensitized electrode and the counter electrode and sealing at 115 ^oC for 45 s. Electrolyte (600 mM LiI, 50 mM I_2, 10 mM *t*-butylpyridine in acetonitrile) was introduced into the device by vacuum-assisted addition, and the Pt/FTO hole was sealed using Surlyn®.

Incident photon to current efficiency (IPCE) was measured by using monochromatic light from a xenon lamp and single-grating monochromator. Power density was determined using a calibrated silicon diode (Newport 818-UV). Current-voltage (I-V) curves were obtained under simulated sunlight at 100 mW cm^{-2} at the electrode by filtering light from a xenon arc lamp with an AM 1.5 G filter (Newport Corp). The power density was determined using a calibrated silicon diode (ASTM E948-09 / ASTM E1021-06). The IPCE and I-V data were obtained using a Keithley 2400 Sourcemeter and LabView software.

Conclusions

We have reported an improved synthesis of β-cyanoporphyrins and carried out photoelectrochemical experiments to determine whether porphyrins bearing β-cyano groups could act as sensitizers in DSSC, with a view toward their eventual use in photoelectrosynthetic cells for water splitting or other solar fuel production. The newly developed method for the synthesis of β-cyano substituted porphyrins is better suited for the production of specialized β-cyano substituted porphyrins containing sensitive functional groups than previously known methods. This new method uses a palladium catalyzed reaction to give yields of up to ca. 50%, while employing milder conditions than the previous methods used for cyanation of β-tetrabromoporphyrins. Like previous methods, this approach still requires the use of more than a catalytic amount of palladium in order to obtain high yields.

The β-tetracyanoporphyrins have absorption maxima at considerably longer wavelengths than do their unsubstituted analogs. For example, as shown in Table 1, the longest-wavelength Q-bands in the free base compounds are found around 740 nm. Absorption in this region is important for solar energy-harvesting applications, as there is ample sunlight in this spectral region that is not captured by many other common dyes. In addition, these porphyrins, especially the freebase versions, are very good electron acceptors; indeed they are better acceptors than the quinones that are found in natural photosynthesis and have often been used in artificial photosynthetic molecules.

The results from using the cyanoporphyrins as sensitizers in DSSC show that the zincated tetra-β-cyanoporphyrins can inject electrons into the conduction band of nanoparticulate SnO_2, but are not thermodynamically competent to inject into TiO_2. This is due to a combination of the relatively long wavelength absorption of the porphyrin Q-bands, which decreases the energy of the first excited singlet state relative to many other porphyrins, and the high potentials for oxidation of these molecules, which is due to the electron withdrawing properties of the cyano groups. The performances of the DSSC prepared here are inferior to those of optimized TiO_2 based cells, but are similar to those obtained in similarly constructed DSSC with Zn(II) 5-(4-carbomethoxyphenyl)-15-(4-carboxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin.[80] No attempt was made to optimize the cells reported here, but in general, cells made with SnO_2 electrodes perform more poorly than those that use TiO_2.[94,95] Losses in efficiency relative to TiO_2 cells could be related to inefficient injection of electrons into the semiconductor, enhanced recombination between the semiconductor conduction band and the oxidized porphyrin, or enhanced recombination reactions involving the I^-/I_3^- mediator.[96] The use of cobalt complexes as mediators would be expected to increase V_{oc} in such cells; however, our efforts are toward incorporation of these molecules into photoelectrosynthetic devices.[98]

These same properties – long wavelength absorption and strong oxidizing power – make the cyanoporphyrins good candidates for use in photoelectrosynthetic cells for solar fuel production. Their redox potentials ensure that their radical cations possess significant overpotential for water oxidation via suitable catalysts. The long wavelength absorption ensures that they can absorb significant amounts of light at longer wavelengths than can most porphyrin sensitizers. These two properties are especially promising for the application of these porphyrins in tandem photoelectrosynthetic cells for solar fuel production.

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