ORGANIC LETTERS

2007
Vol. 9, No. 5
797−800

Phosphorus(V) Porphyrins with Axial Carbazole-Based Dendritic Substituents

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Received December 9, 2006

ABSTRACT

Three phosphorus(V) porphyrins with axial carbazole-based dendritic substituents (D-A-D) have been designed and synthesized, which are nonfluorescent due to their effective electron transfer from the carbazole dendron to the excited porphyrin within the dendritic matrix. The incident photon to current conversion efficiencies (IPCE) spectra demonstrate that the molecular structure of the dendrimers can significantly affect the photovoltaic response to the visible light.

Because of their outstanding photophysical and redox properties, porphyrins have been widely used as building blocks in the construction of π-conjugated systems for their potential applications in molecular electronics, photochemical energy conversion and storage, switches, etc.[1] Recently, various rigid and flexible dendritic structures have been designed to connect with porphyrin cores as artificial molecular systems to investigate their energy and/or electron transfer. Most of these dendritic porphyrins reported so far are modified by the functional substitutes in the peripheral *meso*- or *pyrrole*-β position via covalent linkages, which may require extensive synthetic efforts.[2−4] However, the "axial-bonding" strategy appears to be an attractive approach for the facile preparation of porphyrin arrays with well-tunable photo- and electrochemical properties through changing the π-orbital interactions.[5,6] [P(TPP)Cl_2]Cl is a well-known axial-bonding building block, and the P−Cl bonds are reactive toward phenols and alcohols.[7] On the other hand, carbazole is also an appealing molecule because of its intense luminescence, electron efficiency, and potential for dendritic construction.[8,9] Our group has previously reported photo-induced intramolecular energy transfer in the porphyrins with four monodisperse dendritic carbazole arms.[10] Therefore, the

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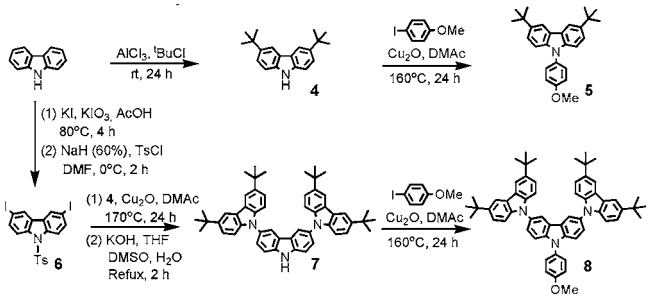
10.1021/ol062979k CCC: $37.00
Published on Web 02/01/2007

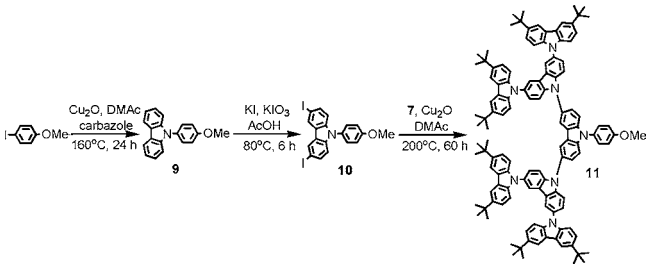
synthesis of D-A-D-type molecules based on carbazole dendron-derived phosphorus(V) porphyrins, which are strong electron acceptors, may lead to novel materials with fascinating photo- and electrophysical properties. To the best of our knowledge, there is no example of an axially linked phosphorus(V) porphyrin with a rigid dendron. Herein, we present the preparation and characterization of novel phosphorus(V) porphyrins with axial monodisperse dendritic carbazoles **1**−**3**. Notably, a photovoltaic response to the visible light is observed in the incident photon to current conversion efficiencies (IPCE) spectra.

Scheme 1. Syntheses of Cz-G1-OMe and Cz-G2-OMe



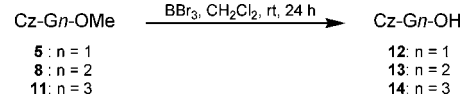
The synthetic routes for the carbazole dendrons **12**−**14** are shown in Schemes 1, 2, and 3, respectively. To improve

Scheme 2. Synthesis of Cz-G3-OMe



the solubility and stability of the molecules, *t*-butyl groups were introduced into the 3,6-positions of the peripheral

Scheme 3. Syntheses of Cz-G*n*-OH



carbazoles in the dendrons. 3,6-Di(*t*-butyl)carbazole **4** was prepared in a yield of 54% by Friedel−Crafts alkylation of

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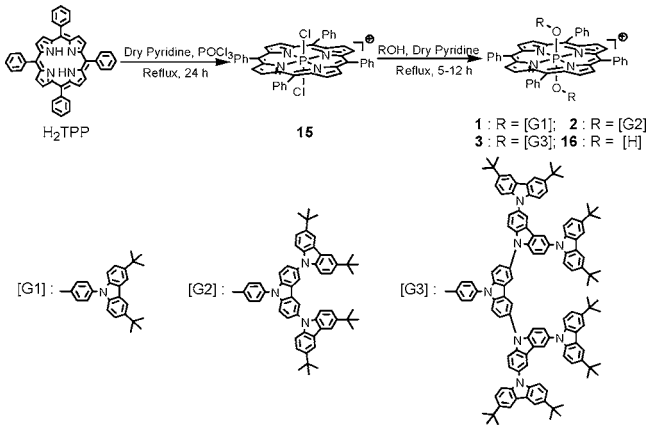
carbazole, adapting a published procedure.[11] The Ullmann condensation reaction between compound **4** and 1-iodo-4-methoxybenzene, which was catalyzed by Cu_2O in *N*,*N*-dimethylacetamide (DMAc) at 160 °C for 24 h, gave the first generation of the carbazole dendron, **5** (Cz-G1-OMe), in a yield of 83%.[3i,4o,8b,c,10] The second generation of the carbazole dendron, **8** (Cz-G2-OMe), was achieved from compound **7** and 1-iodo-4-methoxybenzene under similar conditions with a yield of 76%. Compound **7** was synthesized from compounds **4** and **6** via Ullmann coupling reaction, followed by the cleavage of the N−Ts bond under a basic environment (70%, two steps).[3i,4o,8b,c,10]

Significantly, a high yield was achieved in the preparation of **5** and **8** based on the modified Ullmann condensation reaction, and we were encouraged to synthesize the third generation of the carbazole dendron, **11** (Cz-G3-OMe).[8c,10] The synthetic route of compound **11** is shown in Scheme 2. The iodination of compound **9**, which was obtained from the Ullmann condensation reaction of carbazole with 1-iodo-4-methoxybenzene, was pursued to give compound **10**. Then, the Ullmann condensation reaction between compounds **10** and **7** was carried out at 200 °C for 60 h to yield the carbazole dendron **11**, which was recrystallized from EtOH/THF (1:2, v/v) over four times with a yield of 64% after flash chromatography using THF as eluent. Generally, the preparation of dendritic oligocarbazoles of a higher generation was more difficult and the yield was not high (12−37%), which was probably due to their lower reactivity and easier oxidation.[8b,c] The methyls in O−CH_3 of compound **5**, **8** and **11** were easily removed by BBr_3 to give the corresponding phenols **12**, **13**, and **14** with yields of 80∼90% (Scheme 3).[12]

The phosphorus(V) porphyrins with axial dendritic carbazoles were synthesized from [P(TPP)Cl_2]Cl **15** and the phenols (**12**−**14**). As shown in Scheme 4, the dry pyridine solution with H_2TPP (5,10,15,20-tetraphenylporphyrin)[13] was refluxed for 24 h in the presence of excess $POCl_3$ with a good yield (74%) of compound **15**.[7a] It was reactive toward water and a variety of phenols in the presence of pyridine, although air stable in both solid state and solution. Then, the obtained phenols **12**−**14** were converted into the corresponding axial dendritic porphyrins [P(TPP)(O-G*n*-Cz)$_2$]Cl (**1**−**3**) in dry pyridine containing compound **15** under reflux for 5−8 h with a yield of 79, 71, and 63%, respectively.[7] It was found that the degree of demetalation would be promoted, as the condensation time between **15** and phenols increased, probably as a result of HCl generated during the reaction. The obtained axial dendritic porphyrins [P(TPP)-(O-G*n*-Cz)$_2$]Cl (**1**−**3**) were soluble in chloroform, THF, toluene, and CH_2Cl_2, and the solubility of these dendrimers

Scheme 4. Syntheses of [P(TPP)(O-G*n*-Cz)$_2$]Cl (**1**−**3**) and Compound **16**



increased with the generation. In addition, the reference compound **16** was prepared by adding excess water to the pyridine solution containing compound **15** under reflux for 12 h (Scheme 4).[7a] The intermediates and target molecules were purified with column chromatography on silica gel and characterized by FT−IR, ^{1}H NMR, and MALDI-TOF mass spectrometry (see Supporting Information).

The UV−vis spectra of **1**−**3** in $CHCl_3$ and the film were including two Q-bands in the range of 500−700 nm (consistent with a reported phosphorus(V) porphyrin), together with the Soret band at ca. 440 nm, and others in the UV region (250−350 nm) due to the carbazole units (Figure 1). The absorbance of the carbazole units was clearly

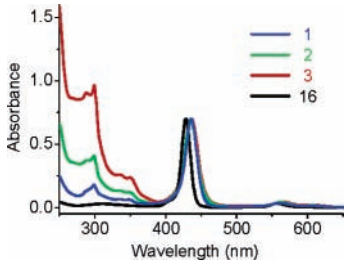


Figure 1. UV−vis absorption spectra (normalized at the Soret bands) of **1**−**3** and **16** in $CHCl_3$.

proportional to their increased number in each generation, which indirectly reflected the flawless or perfect structures of the as-synthesized dendrimers. Notably, there was no distinct spectral shift or spectral broadening of the absorption bands of the carbazole units and porphyrin core with increasing generation.[8d] It was suggested that the electronic structures of the axial porphyrins did not change when the generation increased. As shown in Figure S1 (Supporting Information), the Soret bands for the porphyrin cores of compounds **1**−**3** in films were red-shifted compared with those in solution, which was due to the aggregation effect.

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The degree of red shifts depended on the generation number of the dendrimers: the absorptions of **1**, **2**, and **3** in films were red-shifted by 13, 8, and 5 nm, respectively; in other words, the higher the generation was, the smaller the red shift moved in the absorption (Table 1). It was deduced that

Table 1. Comparison of the UV−vis Spectroscopic Data of **1**−**3**

	1	**2**	**3**
λ_{max}[a] [nm]	436	436	436
λ_{max}[b] [nm]	449	444	441
$\Delta\lambda_{max}$[c] [nm]	13	8	5

[a] In $CHCl_3$. [b]In spin-coated film. [c]λ_{max}(film) − λ_{max}(solution).

the dendrons in the higher-generation dendrimers had a larger site-isolation effect on the porphyrin core.[6a] Compared to our previous results, the axial dendritic substituents suppressed cofacial intermolecular excitonic interactions more efficiently than the *meso*-position dendritic substituents.[10b] The site isolation could also be confirmed by the polarity of these dendrimers, which decreased with the generation, because the R_f values were enlarged when the generation increased (Figure S2, Supporting Information).

The fluorescence spectrum of compound **16** in $CHCl_3$ showed a strong emission at 613 and 665 nm excited at 436 nm, which were typical values for phosphorus(V) porphyrins.[7] When carbazole dendrons were introduced into the axial direction of phosphorus(V) porphyrin, however, the emission was strongly quenched (>99%) (Figure S3, Supporting Information). It was suggested that the attachment of carbazole dendrons to the axial direction of porphyrins imparted a fast deactivation of the porphyrin singlet excited state through electron transfer.[7g,j] Because porphyrins possessed broad absorption in the visible region, these phosphorus(V) porphyrins with axial carbazole-based dendritic substituents [P(TPP)(O-G*n*-Cz)$_2$]Cl (**1**−**3**) might be potentially applied in the solar cell.[7j,14]

To examine the potential of the (D-A-D) triads **1**−**3** as photovoltaic materials, their sandwich devices with a configuration structure of Al/organic film/ITO glass were fabricated. As shown in Figure S4 (Supporting Information), the wavelength-dependent IPCE spectra of the devices based on compounds **1**−**3** were in rough accordance with the electronic absorption spectra of the porphyrin chromophores. Compared to the [P(TPP)(O-G1-Cz)$_2$]Cl (**1**) device, the [P(TPP)(O-G2-Cz)$_2$]Cl (**2**) device produced a more effective photovoltaic response to the visible light owing to the lower oxidation potential of the larger carbazole dendron,[8c] which could lower the energy level of the charge separated state, and the subsequent long-distance charge separation also contributed to the generation of the photocurrent.[14b] According to this, the [P(TPP)(O-G3-Cz)$_2$]Cl (**3**) device should produce the most effective photovoltaic response because compound **3** had the lowest oxidation potential and the longest distance of charge separation. However, a poorer photovoltaic performance than the [P(TPP)(O-G2-Cz)$_2$]Cl (**2**) device was observed, and it could be explained as followed: because compound **3** had the largest site-isolation effect, the resulting anion radical of porphyrin cores might be surrounded by the carbazole dendron, which forbade the electron from flowing.

In conclusion, three axial phosphorus(V) porphyrins with dendritic carbazoles [P(TPP)(O-G*n*-Cz)$_2$]Cl **1**−**3** have been designed and synthesized. Their nonfluorescence caused by the photoinduced electron transfer may lead to potential applications as photovoltaic materials in solar cells. The IPCE spectra of these dendrimers demonstrate that the structure of the dendrimers could significantly affect their photovoltaic response to the visible light. Further investigation on the detailed transient absorption spectra and fluorescence decay profiles of compounds **1**−**3** to study the electron-transfer process is underway.

Acknowledgment. This work is financially supported by the National Natural Science Foundation of China (NNSFC, No. 20574027) and the Program for New Century Excellent Talents in University (NCET).

Supporting Information Available: Experimental procedures and characterizations of the key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL062979K

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