# Synthesis, Structure, and Optical and Electrochemical Properties of Star-Shaped Porphyrin–Triarylamine Conjugates

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ABSTRACT

3 R = H
4 R = CH$_3$
5 R = OCH$_3$
6 R = Cl
7 R = CN
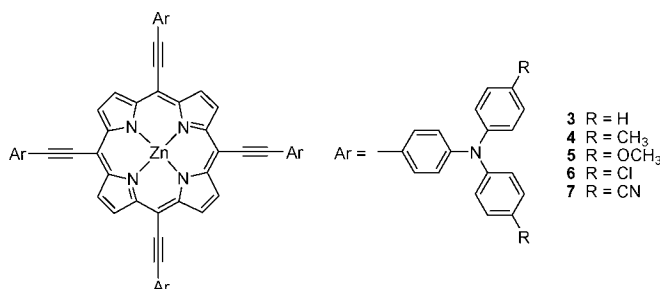
A series of novel star-shaped porphyrin–triarylamine conjugates were synthesized by palladium-catalyzed cross-coupling reactions. The spectroscopic and electrochemical studies show that π-conjugation of the porphyrin core is extended to the triarylamine moieties.

There has been continuous interest in the synthesis of porphyrins because they are widespread in nature[1] and have promising applications in electronic materials.[2] The physical and chemical properties of porphyrins can be precisely controlled by proper functionalization of the porphyrin core. In the *meso*-tetraarylporphyrins, the electronic perturbation is only moderate since the aryl groups twist out of the porphyrin plane resulting in the interruption of the π-conjugation.[3] To increase the electronic interaction, numerous linkers have been used to bridge the aryl groups and the porphyrin.[4] It has been reported that acetylenic types of linkers exhibit effective π-conjugation between aryl groups and the porphyrin core.[4]

Triarylamine-based oligomers and dendrimers have been intensively studied because of their potential applications in the field of organic light-emitting diode, information storage

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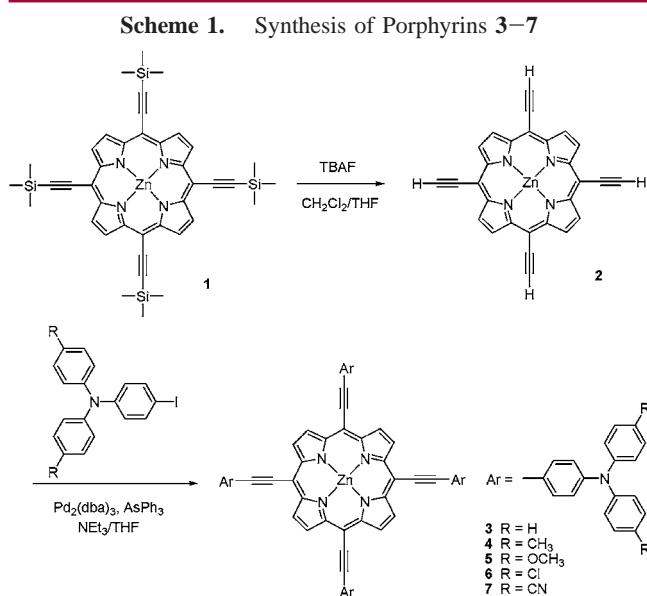**Table 1.** Absorption, Emission, and Redox Data for Compounds **1** and **3**−**7**[a]

	fwhm, B-band/ cm^{-1} (nm)[b]	f_B[c]	fwhm, Q-band/ cm^{-1} (nm)	f_Q[d]	λ_{em}[e] (nm)	oxidation (V)			reduction (V)	
						$E_{1/2}$(ox1)	$E_{1/2}$(ox2)	$E_{1/2}$(ox3)	$E_{1/2}$(red1)	$E_{1/2}$(red2)
1	379 (458)	1.22[f]	481 (646)	0.09[g]	652, 716	1.24			−0.90	−1.38
3	1371 (500)	1.65	1019 (702)	0.39	727, 801	0.87	1.09		−0.94	−1.37
4	1420 (503)	1.58	1018 (709)	0.32	736, 801	0.84	0.99	1.26	−0.92	−1.34
5	1830 (504)	2.04	1174 (713)	0.41	742, 799	0.76	0.94	1.03	−0.97	−1.35
6	1181 (497)	1.26	932 (696)	0.22	716, 800	0.90	1.12		−0.90	−1.32
7	918 (490)	1.78	800 (684)	0.24	700, 799	1.06	1.42[h]		−0.78	−1.23

[a] The absorption and emission spectra were taken in CH$_2$Cl$_2$ and electrochemical data were recorded in THF. [b] fwhm is the full width at half-maximum height; the number in parentheses is the absorption maximum. [c] Oscillator strengths calculated over the region from 400 to 600 nm. [d] Oscillator strengths calculated over the region from 600 to 800 nm. [e] Emission maximum. [f] Oscillator strengths calculated over the region from 400 to 500 nm. [g] Oscillator strengths calculated over the region from 500 to 700 nm. [h] Irreversible reaction.

devices, hole-transporting materials, field-effect transistors, and photovoltaic cells.[5] In recent years, significant interest has focused on the synthesis of hybrid molecules containing triarylamine moiety.[6] However, only a few examples of porphyrin−triarylamine hybrids have been reported.[7] Our group has previously reported the synthesis of porphyrin−triarylamine conjugates, in which two triarylamine units are attached to the porphyrin core via ethynyl linkers.[8] The electrochemical studies showed that the triarylamine units display strong coupling via the diethynylporphyrin bridge. In this Letter we report a synthetic route to star-shaped porphyrin−triarylamine conjugates and their spectroscopic and electrochemical properties are presented.

While the synthesis and properties of *meso*-substituted tetraarylporphyrins have been intensively studied, the studies on the *meso*-tetraarylethynylporphyrins are relatively rare.[9] Usually, 5,10,15,20-*meso*-tetraarylethynylporphyrins were synthesized from the reaction of pyrrole with the corresponding arylpropynal under Lindsey's conditions.[10] To avoid the multistep syntheses of arylpropynal, we have developed a simple approach to this type of porphyrins by coupling of 5,10,15,20-tetraethynylporphyrin to the appropriate aryl iodides.[11] We extended the palladium-catalyzed

coupling method to the synthesis of star-shaped porphyrin−triarylamine conjugates. As shown in Scheme 1, deprotection

Scheme 1. Synthesis of Porphyrins **3**−**7**

of porphyrin **1** by TBAF afforded the key intermediate porphyrin **2**, which was then coupled to 4-(*N*,*N*-diarylamino)-phenyl iodides to give the desired porphyrins **3**−**7**. The coupling process proceeded efficiently for both electron-donating and electron-withdrawing substrates. The new compounds were characterized by various spectroscopic methods.

The electronic interaction between the triarylamine units and porphyrin macrocycle was investigated by UV−vis absorption spectroscopy. The electronic absorption data for porphyrins **3**−**7** and reference porphyrin **1** are summarized in Table 1. The absorption spectra of these conjugates are very different from the sum of their respective components, porphyrin **1** and the corresponding triarylamines, and show peak broadening, peak shifts, and changes in the oscillator

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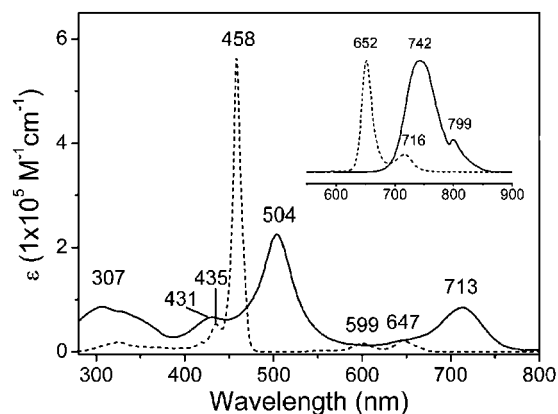(11) Kuo, M.-C.; Yen, W.-N.; Lo S.-S.; Yeh, C.-Y. Manuscript in preparation.

Figure 1. The absorption of **5** (solid) and **1** (dash) in CH₂Cl₂. Inset: Emission spectra, excited at 504 and 458 nm for **5** and **1**, respectively.

Figure 2. The cyclic voltammograms of **1** and **4** in THF containing 0.1 M TBAPF$_6$. Dashed lines show narrower scanned ranges.

strength of absorptions.[12,13] As an example, Figure 1 shows the UV−vis spectra of compounds **1** and **5**. In CH₂Cl₂, porphyrin **5** shows a Soret band at 504 nm, representing the longest wavelength for a planar single porphyrin, together with a smaller Q-band at 713 nm. The full width at half-maximum height (fwhm) of the Soret bands is much larger for **5** (1830 cm^{-1}) than for **1** (379 cm^{-1}), indicative of strong electronic interaction between the porphyrin and triarylamine units. The large red shifts of both the Soret and Q-bands indicate a decreased energy gap between the HOMO and LUMO orbitals as a consequence of the expanded π-conjugation.[14,15] It should be noted that compounds **3**−**7** exhibit significantly enhanced oscillator strength of the Q-band, which is consistent with an enhanced energy splitting between the a$_{1u}$ and a$_{2u}$ orbitals, or the E$_g$ orbitals.[13,14] The absorption spectra suggest that incorporation of triarylamine units via the carbon−carbon triple bonds produces profound perturbation to the ground-state properties of the porphyrin. The fluorescence spectra of porphyrins **1** and **5** are shown in the inset of Figure 1. The enlargement of the π-conjugation exhibits the emission characteristics. This is manifested in a red shift of the emission maximum as the π-delocalization increases. This finding is consistent with the similar trend observed in the absorption spectra.

The effective π-conjugation of the triarylamine moieties via acetylene bridges is expected to reflect on the electrochemical behavior of porphyrins **3**−**7**. The electrochemical data of the porphyrin−triarylamine conjugates are listed in Table 1. It is well-known that both the porphyrin and triarylamine units are redox active. In general, the former has two oxidation and two reduction processes and the latter
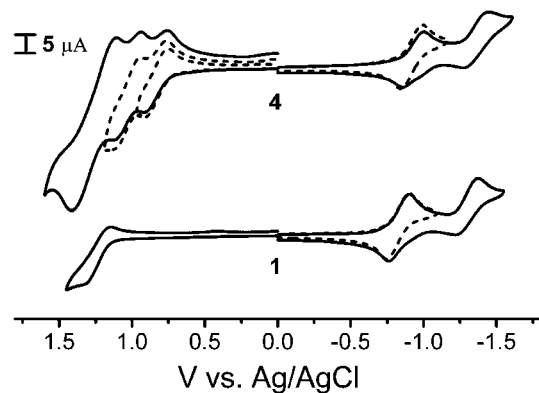
exhibits one reversible oxidation. Figure 2 shows the cyclic voltammograms of porphyrins **1** and **4**. For porphyrin **4**, the first two one-electron oxidations at $E_{1/2}$ = +0.84 and +0.99 V can be assigned to porphyrin-centered processes, which were further comfirmed by spectroelectrochemistry as will be discussed later on. The two-electron process at $E_{1/2}$ = +1.26 V corresponds to the oxidation for two of the triarylamine units. As compared to that of porphyrin **1**, the first oxidation of porphyrin **4** is anodically shifted by 400 mV, indicating that the triarylamine units can stabilize the oxidized porphyrin core. Interestingly, except for porphyrin **7** the reduction processes of **3**−**6** exhibit slight shift in the range 0 to 70 mV relative to those of porphyrin **1**, suggesting that the LUMO energy is only slightly perturbed as the π-conjugation is expanded. In agreement with the absorption and emission measurements, the potential difference between the HOMO and LUMO gap (estimated by $\Delta E = E_{1/2}(\text{ox1}) - E_{1/2}(\text{red1})$) decreases with increasing π-conjugation. For example, the voltammetric HOMO-LUMO gap of +1.76 V for porphyrin **4** is smaller by 380 mV than that of porphyrin **1**. The contraction of the HOMO-LUMO energy gap in **4** is attributed to the elevated HOMO energy.

Substituent effects of porphyrins **3**−**7** on the redox potentials were observed. For example, the first oxidation for porphyrin **5** occurred at $E_{1/2}$ = +0.76 while that for porphyrin **7** was observed at $E_{1/2}$ = +1.06. Considering the long distance of about 12 Å between the substituents of the triarylamine units and the porphyrin core, such a large difference in the redox potential is remarkable.

The electrochemical reactions of our compounds were also studied by spectroelectrochemistry. The spectral changes of compound **4** at applied potentials of $E_{\text{appl.}}$ = +0.90 and +1.15 V show a sharp decrease in the Soret band, indicating that the oxidations occur at the porphyrin ring. The most striking feature of the spectra for both one- and two-electron oxidized species is the presence of the broad near-IR band, which can be ascribed to the charge transfer between the triarylamine units and the porphyrin cation/dication.[7c,8] The first two one-electron oxidation processes are reversible. How-

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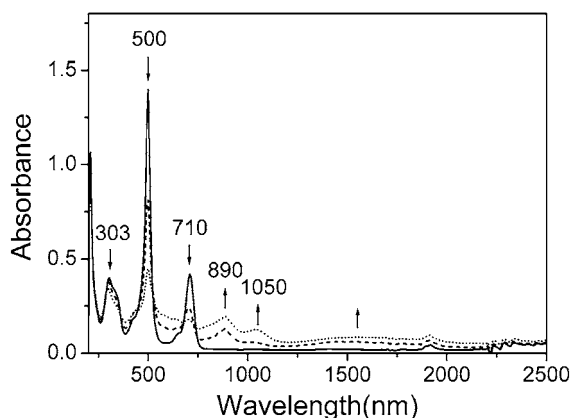
Figure 3. Spectral changes of **4** in THF containing 0.1 M TBAPF$_6$ at applied potentials of +0.70 (solid), +0.90 (dash), and +1.15 V (dot).

ever, further oxidation at an applied potential of +1.35 V leads to decomposition of the complex.

Figure 4 shows the ORTEP diagram of compound **3**. The zinc ion is coordinated to a THF molecule. The bond distances and angles in the porphyrin ring are similar to those observed in the 5,10,15,20-tetraarylporphyrin system.[15,16] The porphyrin framework is essentially planar. The acetylene carbons slightly deviate from the mean plane of the porphyrin in the range 0.008 to 0.136 Å. Strong electronic interaction requires efficient π-orbital overlap and this can be examined by the dihedral angles between the aromatic rings. The dihedral angles between the acetylene-bonded benzene rings and the porphyrin macrocycle are 15.41°, 15.41°, 18.69°, and 24.78°, respectively, which are smaller than those of 29.7° and 59.5° observed in *meso*-tetra(4-butylphenyl-ethynyl)porphyrin zinc.[4a] The distances of carbon−carbon triple bonds fall into the range 1.193−1.201 Å, indicating that there is no cumulenic character in this compound. It is noteworthy that the porphyrin shows strong π−π interaction with a plane−plane distance of 3.30 Å, which is shorter by 0.26 Å than that observed in *meso*-tetra(4-butylphenyl-ethynyl)porphyrin zinc.[4a]

In conclusion, we have successfully synthesized a series of star-shaped porphyrin−triarylamine conjugates. Their optical and electrochemical properties show that the introduction of triarylamine units via acetylene bridges signifi-

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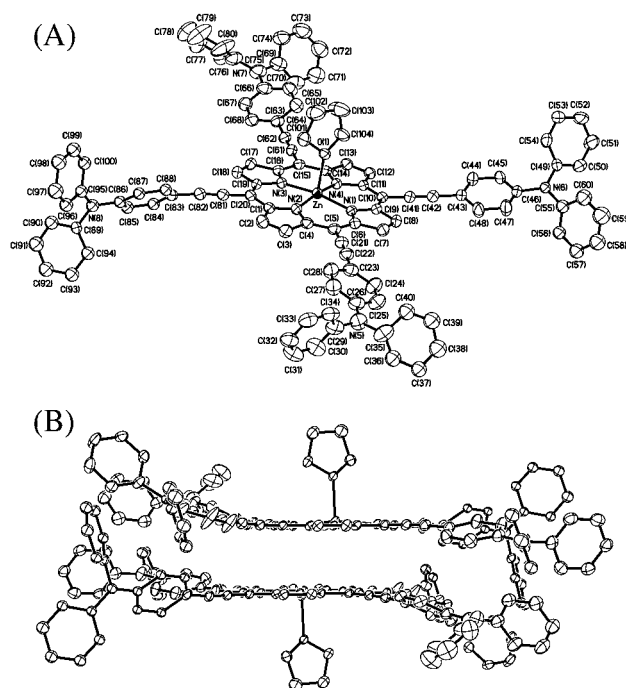
Figure 4. (A) Crystal structure of **3**. (B) Stacking pair of **3** with a plane−plane distance of 3.30 Å. Thermal ellipsoids were drawn at 50% probability levels.

cantly extends the π-conjugation of the porphyrin core. These new compounds exhibit large red shifts of Soret and Q-bands and these studies may lead to the development of new photosensitizers for applications in photodynamic therapy. The strong π−π interaction of **3** in the solid state suggests that upon proper modification this type of porphyrin may form columnar stacking supramolecules, which can be considered as "molecular wires" and may be used for charge-transporting or light-harvesting. Study along this line is currently underway in our laboratory.

Supporting Information Available: Synthetic procedures, spectral data, and cyclic voltammograms for new compounds, and crystallographic data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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