Organic LETTERS
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Synthesis and Electrochemical Properties of Porphycene–Diketopyrrolopyrrole Conjugates

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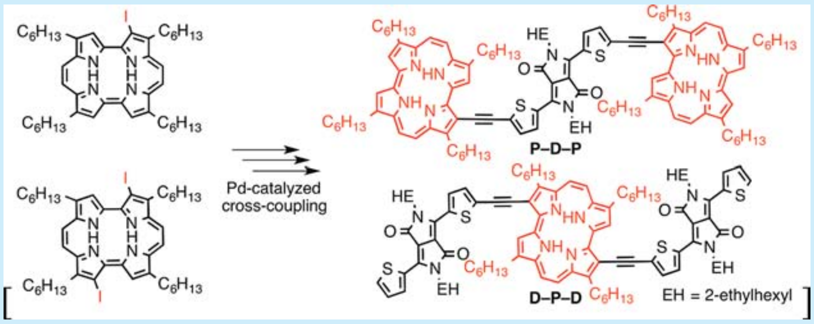
Supporting Information



ABSTRACT: The selective iodination of 2,7,12,17-tetrahexylporphycene **1** was successfully accomplished by using *N*-iodosuccinimide in the presence of activators to give 3-iodoporphycene **2** and 3,13-diiodoporphycene **3a**. These iodinated porphycenes can be used as the substrates for palladium-catalyzed coupling to prepare porphycene–diketopyrrolopyrrole conjugates in two steps. The connection of the diketopyrrolopyrrole units to porphycenes broadened their absorption spectra and increased the intensity of the Q-bands due to the electronic interactions between the porphycene and diketopyrrolopyrrole moieties.

Porphycene, which consists of two bipyrrole units and two ethylene bridges, is a constitutional isomer of porphyrin.[1] Porphycene has a lower LUMO level and smaller HOMO–LUMO difference than porphyrin since its molecular symmetry is lower than that of porphyrin.[2] These properties have allowed us to explore the possible applications of porphycenes in the fields of photodynamic therapy (PDT),[3] photoinactivation of viruses and bacteria,[4] protein mimicry,[5] nonlinear optics,[6] and catalysis.[7] We recently reported solution-processed organic solar cells, based on tetrabenzoporphycene[8] as the p-layer and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) as the n-layer, with a power-conversion efficiency (PCE) of 1.54%.[9] The feature of the lower LUMO level of porphycene is suitable for use in electron-accepting materials. Jux, Guldi and co-workers have reported porphycene derivatives which function as electron acceptors in the composites with graphene oxide or nano-graphene.[10] Porphycenes therefore have potential as organic semiconducting materials exhibiting unique electronic properties, even though such materials have seldom been reported. To make a variety of porphycene derivatives, it is necessary to develop synthetic substrates for versatile reactions. In porphyrin chemistry, various cross-coupling reactions have led porphyrins to various functional materials;[11−14] however, there have been no reports of the palladium-catalyzed cross-coupling reactions of porphycenes.

Here we report the preparation of porphycene–diketopyrrolopyrrole (DPP) conjugates by the selective iodination and cross-coupling reaction of porphycenes. We have designed three porphycene–DPP conjugates; **P–D**, **P–D–P**, and **D–P–D**, where **P** is porphycene and **D** is DPP, with ethynyl linkages at the 3- or 3,13-positions of the porphycenes (Figure 1). The absorption of the DPP unit appears at around 450–550 nm, while porphycene has an absorption valley around 400–550 nm. The ethynyl linkages have increased the planarity of the molecules and thus also enhanced the electronic conjugation with attached functional groups. Therefore, the combination of DPP and porphycene via ethynyl linkages is expected to generate absorption covering the visible to NIR regions of the spectrum. Along this line, DPP-linked porphyrin derivatives exhibit good absorption abilities in the UV–vis–NIR range and have functioned as the excellent p-type semiconducting materials in an organic solar cell (OSC) with a power-conversion efficiency of over 7%.[15] In addition, DPP-linked bisporphyrin shows strong two-photon absorption.[16]

We initially investigated the reaction conditions necessary for the iodination of porphycene. Hisaeda et al. reported bromination of 2,7,12,17-tetraalkyl-porphycene by bromine.[17] By controlling the ratio of equivalents of bromine to porphycene, the mono-, di-, tri-, and tetra-brominated porphycenes were prepared. Waluk et al. also demonstrated the preparation of 2,7,12,17-tetra-*tert*-butyl-3,13-diiodoporphycene, using *N*-iodo-

Received: May 20, 2014
Published: June 17, 2014

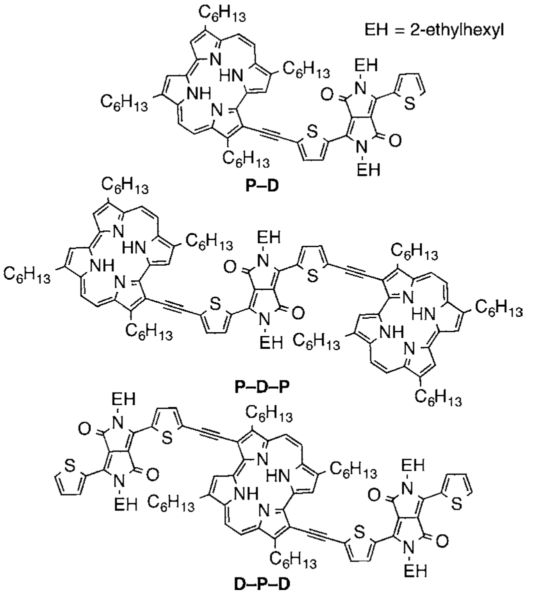
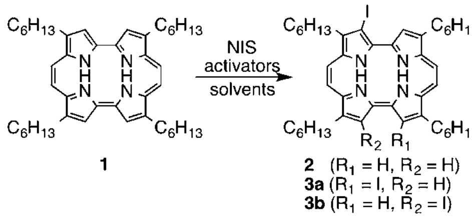


Figure 1. Structures of porphycene–DPP conjugates **P–D**, **P–D–P**, and **D–P–D**.

succinimide (NIS) as an iodonium cation source.[18] This reaction, however, gave a mixture of 3,13-diiodoporphycene and 3-bromo-13-iodoporphycene because the used NIS reagent included a small amount of *N*-bromosuccinimide (NBS) as a contaminant.

We attempted to optimize the iodination conditions by referring to Waluk's conditions (Table 1). The reaction of 2,7,12,17-tetrahexylporphycene **1** and NIS (1.1 equiv) in THF gave a mixture of 3-monoiodoporphycene **2** in 36% yield and diiodoporphycenes **3a** and **3b** (entry 1) (Figure S1). Fortunately, 3,16-diiodoporphycene **3b** could be removed by repeated recrystallizations from chloroform/hexane to give pure 3,13-diiodoporphycene **3a**. Even though the amount of NIS was increased to 2.5 equiv, the porphycene **1** was not completely consumed nor were tri- and tetra-iodinated porphycenes obtained (entry 4). These results suggested that the low reactivity induced by the steric hindrance associated with the large iodonium cation prevents the multi-iodination reaction. The activation of the iodonium cation by TFA[19] or silica gel,[20] which are well-known efficient activators of NIS and NBS, was then attempted. By addition of an excess amount of TFA with 1.1 equiv of NIS, **2** was predominantly obtained in 66% yield (entry 2), while the reaction of **1** and 2.5 equiv of NIS in the presence of TFA gave a mixture of **3a** and **3b** in 35% and 12% yields, respectively. Interestingly, the yield of **3a** was increased to 54% by using silica gel as the activator. In addition, the product ratio of **3a** to **3b** varied from 35/12 when using TFA to 54/13 when using silica gel. The positions of the iodine atoms in **3a** were unambiguously elucidated by crystal X-ray diffraction analysis (Figure S2).

Table 1. Synthetic Conditions for Iodinated Porphycenes

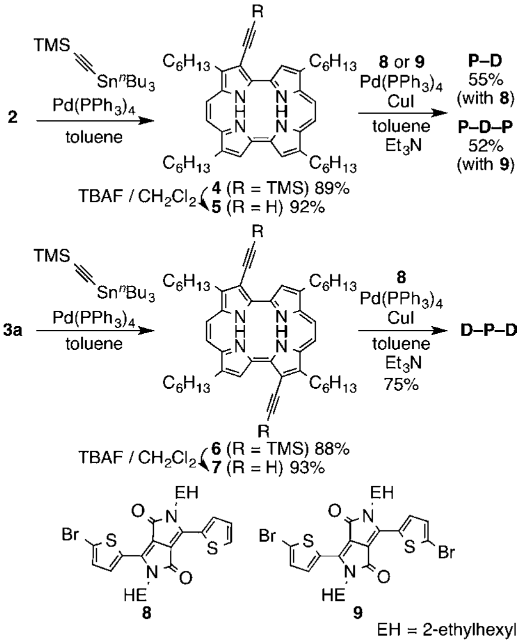


entry	NIS (equiv)	activator	yield (%) 2	yield (%) 3a[c]	yield (%) 3b[d]
1	1.1	none[a]	36	12	3
2	1.1	TFA[a]	66	trace	trace
3	1.1	silica gel[b]	29	20	5
4	2.5	none[a]	42	7	1
5	2.5	TFA[a]	trace	35	12
6	2.5	silica gel[b]	trace	54	13

[a] In THF. [b] In CH_2Cl_2. [c] Purification by recrystallization from $CHCl_3$/hexanes three times. [d] **3b** yields were determined by ^1H NMR spectroscopy.

We then attempted to synthesize ethynyl-linked porphycene–DPP conjugates, applying the reaction procedure as shown in Scheme 1. The trimethylsilyl (TMS) ethynyl group was introduced to **2** and **3a** by Stille coupling with tributyl(trimethylsilylethynyl)tin to give **4** and **6** in 89% and 88% yields, respectively. The structure of **6** was elucidated by crystal X-ray diffraction analysis, as presented in Figure S3. When the reaction of **3a** was instead attempted by Sonogashira coupling with trimethylsilylacetylene, the yield of **6** was only 6% and porphycenic enyne products were obtained after purification by GPC (see Supporting Information, Figure S4).[21]

Scheme 1. Synthesis of Porphycene–DPP Conjugates P–D, P–D–P, and D–P–D



Subsequently, deprotection of the TMS groups of **4** and **6** by tetrabutylammonium fluoride (TBAF) gave **5** and **7**, respectively. The porphycene–DPP dyad (**P–D**) was prepared from **5** by Sonogashira coupling with monobrominated dithienyl-DPP **8** in 55% yield. The porphycene–DPP triads, **P–D–P** and **D–P–D**, were synthesized by the same procedures: **P–D–P** from **5** and **9** in 52% yield and **D–P–D** from **7** and **8** in 75% yield, respectively. These three obtained porphycene–DPP conjugates were characterized by ^1H NMR spectroscopy and high-resolution matrix assisted laser desorption/ionization time-of-flight (HR MALDI-TOF) mass spectrometry. The thermal stabilities of **P–D**, **P–D–P**, and **D–P–D** were measured by thermogravimetric analysis (TGA) (Figure S5). **P−D** showed the onset of melting point at 184.3 °C, while **P−D−P** and **D−P−D** exhibited weight loss starting above 300 °C, indicating that these conjugates possess highly thermal stability.

The UV−vis absorption spectra of **P−D**, **P−D−P**, and **D−P−D** in $CHCl_3$ are shown in Figure 2 and summarized in Table 2.

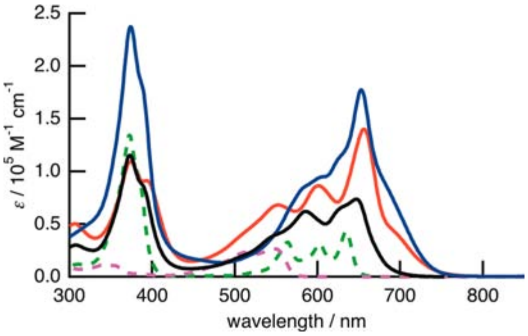


Figure 2. UV−vis absorption spectra of **P−D** (black solid line), **P−D−P** (blue solid line), **D−P−D** (red solid line), **1** (green dashed line), and **DTh−DPP** (pink dashed line) in $CHCl_3$.

Table 2. Optical and Electrochemical Properties of P−D, P−D−P, and D−P−D[a]

	λ_{abs} (nm) ($\log \varepsilon$)[b]	E_{ox} (V)	E_{red} (V)
P−D	373 (5.06), 550 (4.60), 586 (4.79), 647 (4.87)	0.43, 0.66, 0.84	−1.30, −1.52, −1.75
P−D−P[c]	374 (5.38), 603 (4.98), 653 (5.25)	0.35, 0.49, 0.66	−1.30, −1.51, −1.56, −1.80
D−P−D	374 (5.04), 393 (4.96), 552 (4.83), 601 (4.94), 656 (5.15)	0.41, 0.53, 0.77	−1.17, −1.32, −1.68

[a] Potential values were measured by cyclic voltammetry in dichlorobenzene/acetonitrile (5:1) with 0.1 M $^{n}Bu_4NPF_6$. The ferrocene/ferrocenium cation redox couple was used as the internal standard. Scan rate = 100 mV s^{-1}. [**P−D−P** and **D−P−D**] = saturated, [**P−D**] = 0.5 mM, and [**1** and **DTh−DPP**] = 1.0 mM. Working electrode: glassy carbon. Counter electrode: Pt wire. Reference electrode: Ag/$AgNO_3$. [b] In $CHCl_3$. [c] The oxidation and reduction potentials were determined by DPV.

The absorption spectra of **1** and dithienyl−DPP (**DTh−DPP**) in $CHCl_3$ are also provided in Figure 2 for reference purposes. The absorption of **1** exhibits a typically intense Soret-like band and broad Q-like bands with moderate intensity. The absorption peak of **DTh−DPP** is observed at 548 nm. The maximum absorption peaks of the porphycene−DPP conjugates **P−D**, **D−P−D**, and **P−D−P** all show the Soret-like and Q-like bands in similar wavelength regions similar to those observed for **1** and the absorption edges of **D−P−D** and **P−D−P** extend to 750 nm. The molar absorption coefficient of **P−D−P** at the Soret band is almost twice as high as those of **1**, **P−D**, and **D−P−D** because **P−D−P** contains two porphycene moieties in each molecule. The intensities of the Soret bands of **P−D** and **P−D−P** are similar to that of **1**. Interestingly, the intensities of the Q-bands are significantly increased for all three porphycene−DPP conjugates compared to the parent porphycene **1**. In particular, the molar absorption coefficient of **P−D−P** exhibits a maximum of 178 000 M^{-1} cm^{-1} at 653 nm. In addition, the absorption of the DPP components of all three of these compounds are not clearly evident within the range of 500−600 nm. These results indicate that electronic interactions occur between the DPP and porphycene moieties.

The electronic properties of the three porphycene−DPP conjugates and the reference compounds were studied by cyclic voltammetry and differential pulse voltammetry in *o*-dichlorobenzene/acetonitrile (5:1) containing 0.1 M $^{n}Bu_4NPF_6$ at room temperature (Figure 3). The reference compound **1** exhibits reversible peaks at 0.47 V (vs ferrocene/ferrocenium cation) for oxidation and −1.45 V for reduction. **DTh−DPP** shows reversible oxidation and reduction peaks at 0.47 and −1.70 V, respectively, while **P−D** has three reversible oxidation peaks (0.43, 0.66, and 0.84 V) and three reduction peaks (−1.30, −1.52, and −1.75 V).

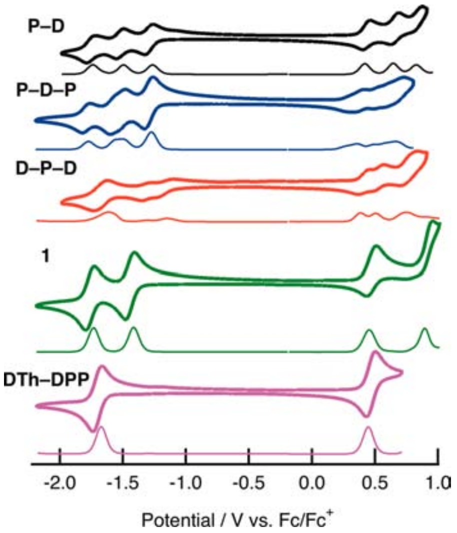


Figure 3. Cyclic voltammograms (solid lines) and differential pulse voltammograms (thin lines) of **P−D** (black), **P−D−P** (blue), **D−P−D** (red), **1** (green), and **DTh−DPP** (pink) in *o*-dichlorobenzene/acetonitrile (5:1) with 0.1 M $^{n}Bu_4NPF_6$. Scan rate = 100 mV s^{-1}.

In order to further elucidate the structure and electronic properties of these compounds, DFT calculations were performed using the Gaussian 09 program package at the B3LYP/6-31G* level.[22] The structures of **P−D**, **D−P−D**, and **P−D−P** were simplified by substituting methyl groups for the hexyl and 2-ethylhexyl groups in the molecules. The results demonstrated that the HOMO of the dyad **P−D** is distributed over the DPP moiety, while the LUMO is distributed over the porphycene core. Similarly, the orbitals of the **D−P−D** and **P−D−P** triads are primarily situated on the DPP portion in the case of the HOMO and at the porphycene in the case of the LUMO. Considering the redox potentials and DFT calculations results for the porphycene−DPP conjugates and reference compounds, the first oxidation and reduction peaks of the conjugates are assigned to the DPP and porphycene portions, respectively. This result indicates that porphycene behaves as an electron acceptor, while DPP is the electron donor in the porphycene−DPP conjugate systems. **P−D−P** and **D−P−D** also exhibit redox properties based on the donor (DPP)−acceptor (porphycene) systems.

In summary, we were successful in achieving the selective iodination of porphycene to give 3-iodo- and 3,13-diiodoporphycenes for the first time. Activators such as TFA and silica gel were found to be important with regard to improving the yield and selectivity of these reactions. The synthesis of these iodoporphycenes allowed us to carry out palladium-catalyzed cross-couplings to prepare the three porphycene−DPP conjugates **P−D**, **D−P−D**, and **P−D−P**. The introduction of DPP units through ethynyl linkages to porphycene resulted in broadened absorption bands in the visible to NIR regions and enhancement of the molar absorption coefficients of the Q-band regions. The electrochemical properties of these porphycene−DPP conjugates showed that multiredox properties were obtained based on the donor−acceptor structures of the molecules. The optical and electrochemical properties of these porphycene−DPP conjugates are expected to allow these compounds to exhibit superior performance as the OSC materials. Extension of this synthetic strategy by the palladium-catalyzed cross-couplings of 3,13-diiodoporphycene and applications of the resulting porphycene−DPP conjugates in the OSC devices are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and computational details, and characterization data for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid (No. 25288092 to H.Y.), the Green Photonics Project in NAIST, and the Program for Promoting the Enhancement of Research Universities in NAIST sponsored by the Ministry of Education, Culture, Sports, Science and Technology, Japan. We also acknowledge Nippon Synthetic Chem. Ind. (Osaka, Japan) for a gift of ethyl isocyanoacetate, which was used for the preparation of the starting pyrroles.

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