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Triptycene as a rigid, 120° orienting, three-pronged, covalent scaffold for porphyrin arrays

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ABSTRACT

The synthesis of novel porphyrin trimers covalently linked by one central, rigid triptycene unit is described. Reaction of 2,6,14-triiodotriptycene, generated in a three-step synthesis from triptycene, with borylated porphyrins under Suzuki cross-coupling conditions afforded porphyrin trimers. In addition, Sonogashira cross-coupling conditions could be successfully applied for the synthesis of trimeric porphyrin arrays as well.

Porphyrin assemblies with highly conjugated π systems have attracted considerable attention as promising organic materials for electronic devices,[1,2] and there has been increasing interest in the design and construction of porphyrin arrays with well-defined geometries for this purpose.[3] Multi-porphyrin architectures are desirable systems as they provide rigid molecular machinery frameworks via relatively straightforward synthetic pathways. In nature, the antenna chlorophylls in photosynthetic bacteria are arranged as macrorings to absorb and transfer solar energy efficiently.[4] This biological importance of circularly arranged multi-porphyrin arrays makes them an attractive research target.

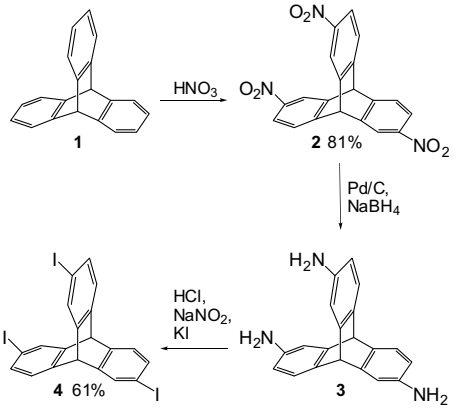
Whilst significant advances in this area have been made with regard to synthetic methodology, the current focus is more on rational building strategies and the use of appropriate scaffold units that define the orientation of the chromophores in space, and can be used as components for molecular machineries. In this context, the triptycene unit is a convenient molecular scaffold to construct rotationally oriented light harvesting devices.

The first porphyrins with triptycene substituents were reported by Wasielewski and Niemczyk in 1984.[5] A quinone substituent was incorporated into the triptycene group, such that the functionalised molecules possessed a porphyrin electron donor and a quinone electron acceptor. The resulting porphyrins were used for the study of photoinduced electron transfer reactions, as they represented model systems with well-defined donor–acceptor distances and orientations.[6–8] Osuka et al. later described the first porphyrin oligomer in which three porphyrin units were attached to one benzene ring.[9a] The porphyrin trimers were obtained after an 11-step synthesis in overall yields of 13%.

Herein, we describe a straightforward synthetic pathway for the preparation of porphyrin trimers in which each porphyrin unit is covalently linked to one central triptycene residue via Suzuki or Sonogashira cross-coupling reactions.[9b]

First, commercially available triptycene **1** was reacted with nitric acid under reflux conditions to give 2,6,14-trinitrotriptycene **2** in 81% yield according to a procedure by Zhang and Chen[10] The nitro residues were subsequently reduced to amino groups to afford 2,6,14-triaminotriptycene **3**. Finally, Sandmeyer reaction of **3** resulted in the formation of 2,6,14-triiodotriptycene **4** in an overall yield of 61% (Scheme 1).

In the past, Suzuki cross-coupling reactions with borylated porphyrins as synthons had been successfully carried out.[11–14] The requisite borylated porphyrins **8**–**10** were prepared from bromoporphyrins **5** to **7**[15] via Pd-catalysed reaction with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane). Debromination of the starting material was a competitive reaction, thus a ten-fold excess of pinacolborane was used. The borylated porphyrins **8**–**10** were obtained in 51%, 29% and 48% yields, respectively.[16] In the



Scheme 1. Three-step synthesis of 2,6,14-triiodotriptycene **4**.

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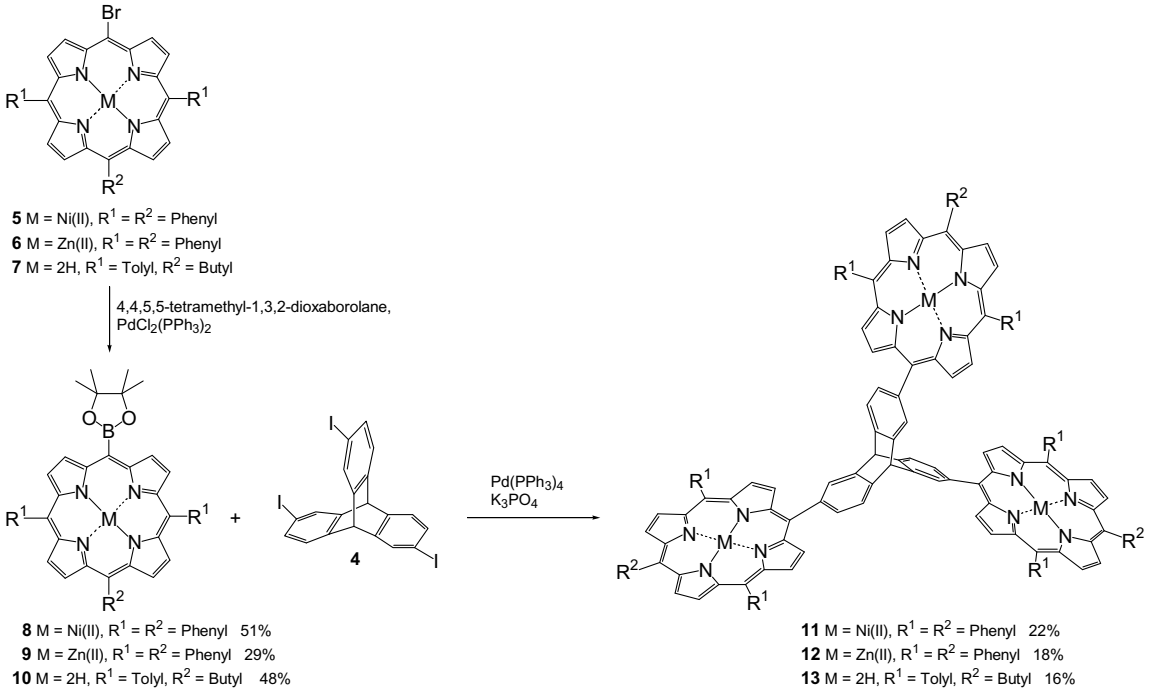
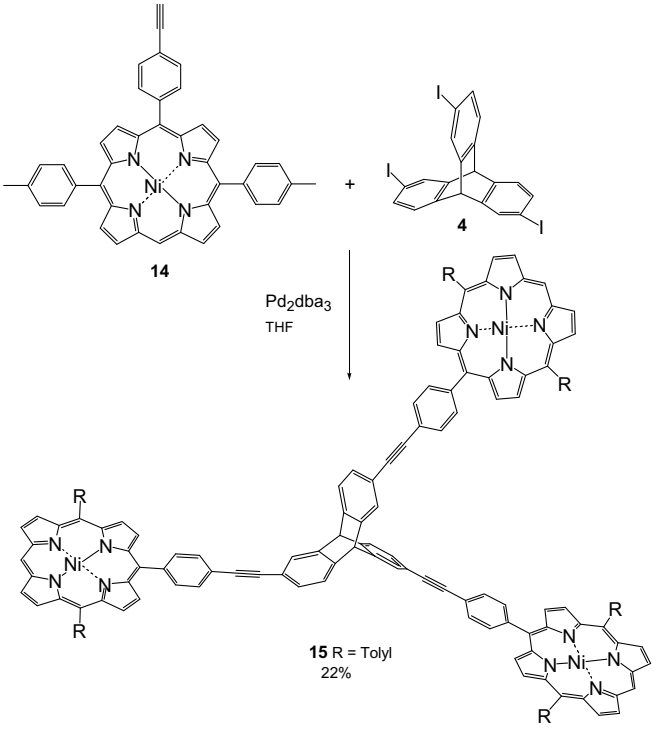


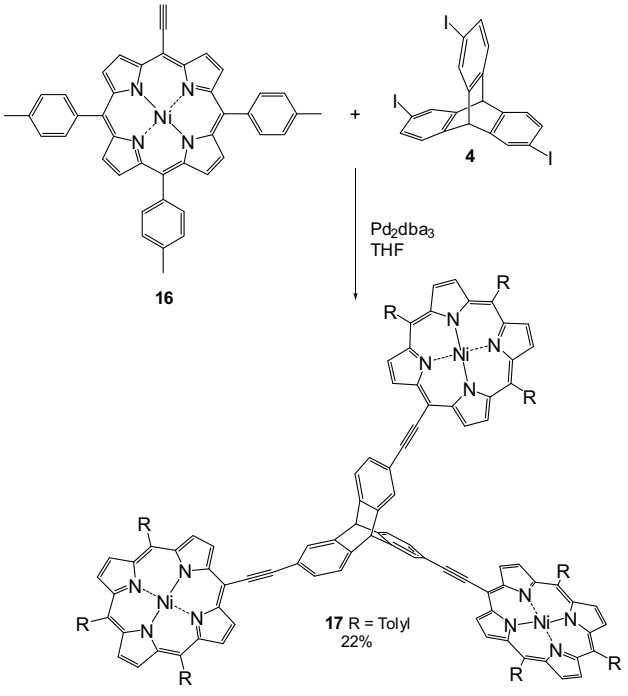
Scheme 2. Synthesis of triptycenyl-linked porphyrins via Suzuki cross-coupling reaction with 2,6,14-triiodotriptycene.

next step, compounds **8**–**10** were reacted with 2,6,14-triiodotriptycene **4** under Suzuki cross-coupling conditions. Following work-up, the desired porphyrin trimers **11**–**13** were isolated in 22%, 18% and 16% yields, respectively[17] (Scheme 2). The yield of the free base trimer is comparable to that of the metallated trimers, which implies that this reaction is generally applicable to different porphyrin systems.

As a second pathway for the synthesis of porphyrin trimers covalently linked by one triptycene unit, Sonogashira cross-coupling conditions were employed. Sonogashira reactions with porphyrins have been applied widely, and proved successful here as well.[18–21] The ethynylporphyrins **14** and **16** were used as porphyrin units[15] and reacted with 2,6,14-triiodotriptycene **4**. The reactions were carried out with Pd_2dba_3 as catalyst in dry THF at reflux under an argon atmosphere (Schemes 3 and 4). The desired porphyrin trimers **15** and **17** were both isolated in 22% yield.[22]



Scheme 3. Synthesis of porphyrin trimer **15** via Sonogashira cross-coupling.



Scheme 4. Synthesis of porphyrin trimer **17** via Sonogashira cross-coupling.

The results indicate that it is not important for the outcome of the reaction how close the ethynyl group is to the porphyrin moiety. It also shows the potential utility of this approach to prepare even larger porphyrin arrays using this method by attaching oligoporphyrins to the triptycene unit.

In summary, 2,6,14-triiodotriptycene **4** was generated in a three-step synthesis from commercially available triptycene. Treatment of the borylated porphyrins **8**–**10** with **4** under Suzuki cross-coupling conditions afforded the desired porphyrin trimers **11**–**13** in unoptimised yields of 16–22%. Likewise, the reaction of the ethynylporphyrins **14** and **16** under Sonogashira conditions gave the target compounds **15** and **17** in unoptimised yields of 22%. These synthetic pathways therefore provide a straightforward approach for the design of rigid porphyrin trimers, and have opened up access to a new class of porphyrin arrays. We are currently optimising the reactions, extending them to the coupling of oligoporphyrins and the use of such units in dendritic porphyrin arrays.

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16. (a) All new compounds reported herein showed spectral data consistent with the assigned structures. Selected data: For compound **8**: Yield: 201.5 mg (0.28 mmol, 51%); mp 230 °C; R_f = 0.53 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.72 (s, 12H, CH_3), 7.71 (m, 9H, Ar_H), 8.02 (m, 6H, Ar_H), 8.70 (d, 2H, ^3J = 4.9 Hz, H_β), 8.74 (d, 2H, ^3J = 4.9 Hz, H_β), 8.86 (d, 2H, ^3J = 5.1 Hz, H_β), 9.79 (d, 2H, ^3J = 5.1 Hz, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 24.73, 84.39, 118.25, 126.38, 127.23, 127.29, 131.12, 131.86, 132.61, 133.18, 133.26, 133.54, 140.33, 140.44, 141.25, 141.45, 142.48, 146.44 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 413 nm (5.27), 528 (4.21), 569 (3.78); HRMS (ES+) [$C_{44}H_{35}BN_4NiO_2$+H]: calcd 721.2285, found 721.2272. For compound **9**: Yield: 108.7 mg (0.15 mmol, 29%); mp 148 °C; R_f = 0.17 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 1.83 (s, 12H, CH_3), 7.72 (m, 9H, Ar_H), 8.17 (m, 6H, Ar_H), 8.83 (d, 2H, ^3J = 4.7 Hz, H_β) 8.85 (d, 2H, ^3J = 4.9 Hz, H_β), 8.99 (d, 2H, ^3J = 4.7 Hz, H_β), 9.83 (d, 2H, ^3J = 4.7 Hz, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 25.02 ppm, 84.91, 120.64, 122.30, 126.20, 127.13, 127.19, 131.24, 131.85, 132.56, 132.69, 134.02, 134.17, 142.44, 142.55, 149.02, 149.69, 150.09, 154.10 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 417 nm (5.13), 546 (4.27), 581 (3.57); HRMS (ES+) [$C_{44}H_{35}BN_4O_2Zn$+H] calcd 727.2223, found 727.2206. For compound **10**: Yield: 207.3 mg (0.308 mmol, 48%); mp 260 °C; R_f = 0.37 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$,20 °C): δ = 1.14 (t, 3 H, ^3J = 7.40 Hz, CH_2–CH_3), 1.84 (s, 14H, CH_3 + CH_2–CH_3), 2.55 (m, 2H, CH_2–CH_2–CH_2), 2.76 (s, 6H, C_6H_4–CH_3), 5.04 (t, 2H, ^3J = 7.91 Hz, CH_2–CH_2–CH_2–CH_3), 7.59 (d, 4H, ^3J = 7.78 Hz, Ar_H), 8.10 (d, 4H, ^3J = 7.78 Hz, Ar_H), 8.92 (d, 2H, ^3J = 4.77 Hz, H_β), 8.95 (d, 2H, ^3J = 4.77 Hz, H_β), 9.49 (d, 2H, ^3J = 4.77 Hz, H_β), 9.82 (d, 2H, ^3J = 4.77 Hz, H_β) ppm; ^{13}C NMR (100.6 MHz, $CDCl_3$, 20 °C): δ = 14.24, 21.58, 23.71, 25.33, 35.28, 40.94, 85.06, 119.58, 122.50, 127.29, 134.45, 137.24, 139.67 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 417 nm (5.35), 517 (4.22), 549 (3.79), 589 (3.77), 644 (3.53); HRMS (ES+) [$C_{44}H_{45}BN_4O_2$+H]: calcd 673.3714, found 673.3685.; A potential rational for the initially low yields is the reduction of the bromoporphyrin as noted by Balaban et al.: (b) Balaban, T. S.; Bhise, A. D.; Fischer, M.; Schaetzel-Linke, M.; Roussel, C.; Vanthuyne, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2140–2144; (c) Balaban, T. S.; Goddard, R.; Linke-Schaetzel, M.; Lehn, J. M. *J. Am. Chem. Soc.* **2003**, *125*, 4233–4239.
17. (a) All new compounds reported herein showed spectral data consistent with the assigned structures. Selected data: For compound **11**: Yield: 20.6 mg (0.01 mmol, 22%); mp >310 °C; R_f = 0.47 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 5.96 (s, 1H, *CH*), 6.10 (s, 1H, *CH*), 7.71 (m, 30H, Ar_H), 8.05 (m, 21H, Ar_H), 8.18 (s, 1H, Ar_H), 8.25 (s, 1H, Ar_H), 8.33 (s, 1H, Ar_H), 8.78 (m, 16H, H_β), 8.92 (m, 8H, H_β) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C): δ = 13.99, 22.56, 29.24, 29.58, 31.80, 53.97, 54.01, 118.83, 118.84, 118.87, 118.91, 118.96, 122.43, 126.69, 126.71, 127.56, 129.43, 131.16, 132.02, 132.06, 132.29, 132.36. 132.42, 133.57, 138.02, 140.80 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 418 nm (5.54), 528 (5.06); HRMS (MALDI LD+) [$C_{134}H_{80}N_{12}Ni_3$]: calcd 2030.4689, found 2030.4666. For compound **12**: Yield: 18.3 mg (0.009 mmol, 18%); mp >310 °C; R_f = 0.09 (CH_2Cl_2/*n*-hexane, 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 6.16 (s, 1H, *CH*), 6.31 (s, 1H, *CH*), 7.81 (m, 30H, Ar_H), 8.30 (m, 21H, Ar_H), 8.51 (s, 1H, Ar_H), 8.59 (s, 1H, Ar_H), 8.69 (s, 1H, Ar_H), 9.03 (m, 18H, H_β), 9.22 (m, 6H, H_β) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C): δ = 14.01, 22.59, 29.26, 29.56, 29.60, 31.83, 36.26, 121.01, 121.07, 121.12, 122.27, 126.47, 127.40, 130.53, 131.89, 131.92, 132.00, 132.29, 134.35, 134.38, 140.04, 142.79, 144.09, 144.92 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 424 nm (5.49), 549 (4.92), 587 (4.32). For compound **13**: Yield: 8.9 mg (0.005 mmol, 16%); mp 237 °C; R_f = 0.13 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ = −2.64 (s, 2H, N*H*), −2.61 (s, 2H, N*H*), −2.57 (s, 2H, N*H*), 1.16 (t, 9H, ^3J = 7.31 Hz, CH_3), 1.85 (m, 6H, CH_2–CH_3), 2.57 (m, 6H, CH_2–CH_2–CH_2), 2.77 (m, 18H, C_6H_5–CH_3), 5.06 (m, 6H, CH_2–CH_2–CH_2–CH_3), 6.13 (s, 1H, *CH*), 6.26 (s, 1H, *CH*), 7.61 (m, 12H, Ar_H), 8.14 (m, 18H, Ar_H), 8.48 (s, 1H, Ar_H), 8.53 (s, 1H, Ar_H), 8.60 (s, 1H, Ar_H), 8.91 (m, 5H, H_β), 8.99 (m, 13H, H_β), 9.51 (m, 6H, H_β) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C): δ = 13.97, 14.06, 21.41, 22.54, 23.51, 29.21, 29.56, 31.79, 35.11, 40.75, 54.17, 119.25, 119.46, 119.53, 120.29, 122.34, 127.19, 128.69, 130.47, 130.75, 132.04, 134.33, 137.05, 137.08, 137.15, 139.30, 139.43, 144.11, 144.87 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 422 nm (5.40), 446 (5.01), 518 (4.44), 554 (4.25), 593 (4.04), 649 (4.05); HRMS (ES+) [$C_{134}H_{110}N_{12}$+2H]: calcd 1888.9133, found 1888.9158.
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22. All new compounds reported herein showed spectral data consistent with the assigned structures. Selected data: For compound **15**: Yield: 7.2 mg (0.003 mmol, 22%); mp >310 °C; R_f = 0.45 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 2.96 (s, 18H, CH_3), 5.61 (s, 1H, *CH*), 5.62 (s, 1H, *CH*), 7.42 (d, 4H, ^3J = 7.65 Hz, Ar_H), 7.53 (d, 15H, ^3J = 7.56 Hz, Ar_H), 7.79 (m, 2H, Ar_H), 7.86 (d, 6H, ^3J = 7.83 Hz, Ar_H), 7.95 (d, 12H, ^3J = 7.56 Hz, Ar_H), 8.04 (d, 6H, ^3J = 7.91 Hz, Ar_H), 8.80 (m, 6H, H_β), 8.85 (m, 6H, H_β), 8.95 (m, 6H, H_β), 9.16 (m, 6H, H_β), 9.86 (s, 3H, H_{meso}) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C): δ = 21.06, 29.27, 88.35, 90.05, 104.21, 118.01, 118.38, 120.03, 122.33, 123.56, 126.63, 127.18, 128.92, 129.62, 131.27, 131.65, 131.84, 132.23, 133.26, 133.30, 137.01, 137.49, 140.75, 141.59, 142.35, 142.48, 142.54, 144.18, 144.28 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 410 nm (5.14), 522 (4.17), 553 (3.68); HRMS (MALDI LD+) [$C_{146}H_{92}N_{12}Ni_3$]: calcd 2186.5628, found 2186.5596. For compound **17**: Yield: 4.8 mg (0.002 mmol, 22%); mp >310 °C; R_f = 0.61 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ = 2.65 (s, 9H, CH_3), 2.67 (s, 18H, CH_3), 5.82 (s, 1H, *CH*), 5.87 (s, 1H, *CH*), 7.51 (m, 20H, Ar_H), 7.73 (m, 4H, Ar_H), 7.89 (m, 18H, Ar_H), 8.14 (s, 1H, Ar_H), 8.16 (s, 1H, Ar_H), 8.19 (s, 1H, Ar_H), 8.70 (m, 12H, H_β), 8.84 (m, 6H, H_β), 9.59 (m, 6H, H_β) ppm; ^{13}C NMR (150.9 MHz, $CDCl_3$, 20 °C): δ = 21.05, 29.27, 89.29, 96.52, 98.41, 119.35, 119.95, 127.21, 130.91, 131.62, 131.84, 132.51, 133.15, 137.05, 137.22, 137.30, 141.95, 142.25, 142.79, 144.24, 144.43 ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 437 nm (5.68), 545 (4.84), 584 (4.84); HRMS (MALDI LD+) [$C_{149}H_{98}N_{12}Ni_3$]: calcd2228.6098, found 2228.6174.