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Synthesis of a single-molecule nanotruck

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Abstract—We report the synthesis of a new nanovehicle, a porphyrin-based nanotruck. The porphyrin inner core was designed for possible transportation of metals and small molecules across a surface.

In recent years, miniaturization of machines and devices has generated new molecular machines including motors, switches, scissors, gyroscopes, elevators, and walkers and transporters.[1] To further develop this new field, we designed molecular machines called nanocars that can be manipulated at the single-molecule-level using the electric field of a scanning tunneling microscope (STM).[2] With the demonstration of the nanocar and its fullerene-based wheel-like rolling motion across a surface, we have expanded our research goals to design and synthesize new versions of nanovehicles.[3] Transporters within molecular-sized systems have been reported including the molecular shuttle[4] and a cyclodextrin abacus.[5] Transportation of liquids via surface conformation changes brought about through an array of molecules is known.[6,7] Individual molecule trapping and moving using the STM tip have been reported.[8] Our eventual goal, however, is to introduce single molecules with inherent machine-like function, namely, the porphyrin-based nanotruck **1** (Fig. 1), to transport metals and small molecules across a surface (Fig. 2). Here we disclose the synthesis of the target molecular system.

Nanotruck **1** has two new components: First are the *p*-carborane wheels rather than the former fullerene-based wheel system.[2] Carboranes greatly facilitate the synthesis since they are very soluble and need not be incorporated at the final step; unlike fullerenes, carboranes do not inhibit transition metal-catalyzed cross-coupling reactions. While carborane–porphyrin systems have been studied in the past,[9] our required wheel/axle system requires a rigid backbone separating the two moieties. The other new component featured in this design is

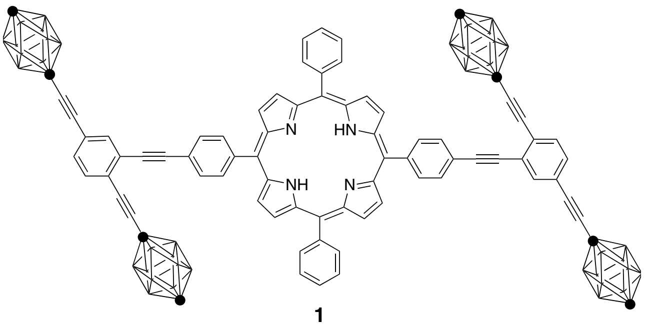

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Figure 1. Porphyrin-based nanotruck **1** with carborane wheels. The *p*-carborane have BH at every intersection except at the points denoted by (●), which represents C and CH positions, *ipso* and *para*, respectively. The porphyrin inner-core serves as transporter of metals and small molecules on the surface.

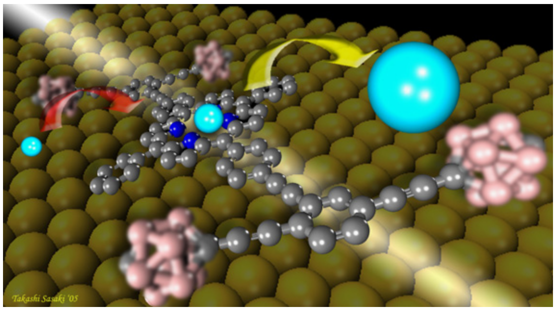

Figure 2. The picture depicts the transport of metal atoms across a surface using some field-induced influence to move the nanocars.

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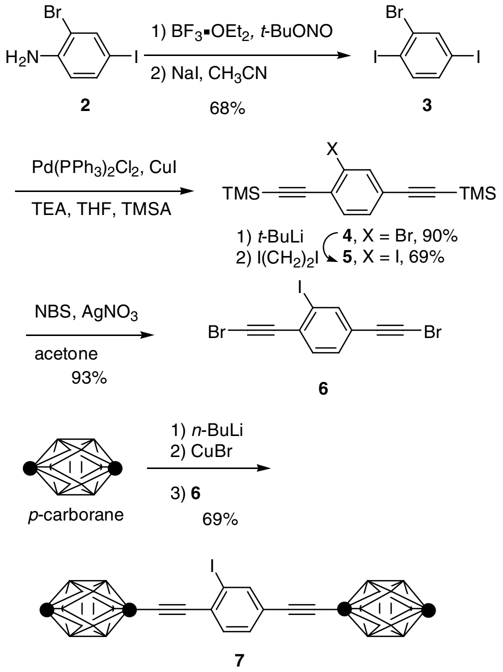
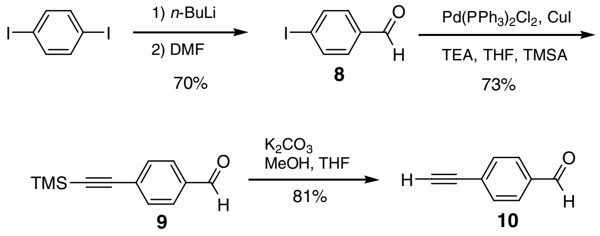


Scheme 1. Synthesis of axle **7**.

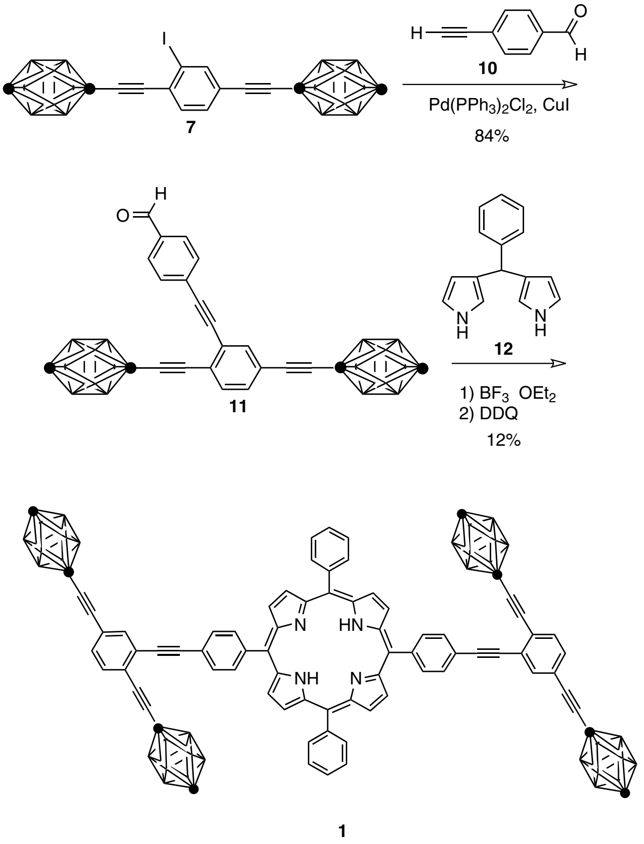
the porphyrin inner core. Porphyrins and metal-complexed porphyrins have been observed using STM,[10] thus making them suitable to design features from the standpoint of imaging and the requisite transport 'loading bay'.

The synthesis of the porphyrin-based nanotruck **1** started with the wheel/axle component (Scheme 1). The dihaloaniline **2** was diazotized and further converted to bromodiiodide **3**. Both of the iodo groups were selectively substituted with trimethylsilylacetylene (TMSA) by means of Sonogashira coupling to afford **4**; the bromide remained intact. The aryl bromide was then converted to iodide **5**.[11] The TMS-protected alkynes were converted to the alkynyl bromides in **6**.[12] The attachment of the carborane wheels to the axle was performed by lithiating *p*-carborane followed by transmetallating with CuBr. Compound **6** was then added to afford **7** as the wheel/axle section of the nanotruck.[13,3a]

The remaining chassis section was synthesized from 1,4-diiodobenzene by first lithium halogen exchange and quenching with DMF to afford the corresponding iodoaldehyde **8**.[14,15] Coupling **8** with TMSA using standard Sonogashira conditions yielded **9**;[16,17] this was followed by proto-desilylation to afford the desired 4-ethynylbenzaldehyde (**10**) (Scheme 2).



Scheme 2. Synthesis of aldehyde linker **10**.



Scheme 3. Synthesis of single-molecule nanotruck **1**.[22]

The final assembly of the nanotruck was performed (Scheme 3) by Sonogashira coupling of the wheel/axle system **7** to alkynylaldehyde **10** to obtain the penultimate aldehyde intermediate **11**. Again, the amenability of *p*-carborane wheels is underscored since insolubility was not an issue and they did not inhibit the required organometallic coupling. The synthesis of the porphyrin inner core involved the preparation of phenyldipyrromethane **12** in one step by condensing benzaldehyde and pyrrole in acetic acid.[18–20] At this point all the individual components were prepared for assembly. Aldehyde **11** and dipyrromethane **12** were condensed and then oxidized to afford the porphyrin-based nanotruck **1**.[21,22]

In summary, we have designed and successfully synthesized a new nanovehicle. Nanotruck **1** bears a porphyrin inner core that should allow for the incorporation of metals and then the subsequent transportation of other small molecules across the surface and allow for its monitoring by STM. This experiment and imaging of surface rolling motion of the carborane wheel-based system is currently underway.

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22. All reactions were performed under an atmosphere of nitrogen unless stated otherwise. Reagent grade tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Triethylamine (Et_3N) was distilled over CaH_2. Boron trifluoride diethyl etherate was obtained from Aldrich. Flash column chromatography was performed using 230–400 mesh silica gel from EM Science. Compound **11**. A 100 mL round bottom flask was charged with **10**[16,17] (28 mg, 0.212 mmol), **7**[3a] (114 mg, 0.212 mmol), bis(triphenylphosphine)palladium(II) chloride (2 mg, 0.003 mmol), and CuI (1 mg, 0.005 mmol). Dry THF (20 mL) and Et_3N (5 mL) were added and the solution was stirred at room temperature for 24 h. The reaction was quenched with NH_4Cl and the organic phase was extracted with methylene chloride several times. The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography using hexane/ethyl acetate (9:1, v/v) to provide 101 mg (84%) of the title compound as a white solid. FTIR 3058, 2829, 2611, 2732, 2250, 1699, 1600, 1203, 1062, 907, 825, 732 cm^{-1}; ^1H NMR (400 MHz $CDCl_3$) δ 10.1 (s, 1H), 7.92 (d, 2H, $J = 8.8$ Hz), 7.70 (d, 2H, $J = 8.8$ Hz), 7.45 (d, 1H, $J = 1.8$ Hz), 7.25 (d, 1H, $J = 8.8$ Hz), 7.18 (dd, 1H, $J = 8.8$ Hz, $J = 1.8$ Hz); ^{13}C NMR (100 MHz $CDCl_3$) δ 191.8, 136.2, 135.6, 132.7, 132.6, 131.9, 130.0, 129.2, 126.2, 124.6, 122.5, 93.6, 91.8, 90.5, 88.5, 78.1, 77.7, 69.4 (x2), 60.8 (x2); MALDI-TOF NS *m/z* calcd for $C_{23}H_{30}B_{20}O$ 539.4279, found 539.4290 (M^+).

    Nanotruck **1**. Degassed chloroform (15 mL) was added to a 100 mL round bottom flask charged with **12**[18–20] (47.9 mg, 0.22 mmol) and **11** (116 mg, 0.22 mmol). The solution was stirred for 1 h at room temperature. To the slightly reddish orange solution was added DDQ (37 mg, 0.16 mmol) and the mixture stirred for another 1 h. The solvent was then removed in vacuo, and the residue was redissolved in methylene chloride, and passed through a long silica gel plug. The residue was then purified via silica gel flash chromatography using hexane/methylene chloride (9:1, v/v) to collect the fourth spot as 38 mg (12%) of the title compound as a purple semi-solid. FTIR 3317, 3054, 2917, 2844, 2606, 2216, 1592, 1397, 1350, 1209,

1061 cm^{-1}; ^{1}H NMR (400 MHz CDCl$_3$) δ 8.92 (m, 8H), 8.30 (d, 4H, $J = 9$ Hz), 8.27 (m, 4H),7.98 (d, 4H, $J = 9$ Hz), 7.78 (m, 6H), 7.60 (d, 2H, $J = 2$ Hz), 7.33 (d, 2H, $J = 9$ Hz), 7.23 (dd, 2H, $J = 9$ Hz, $J = 2$ Hz), 3.6–1.8 (m, 44H), −2.73 (s, 2H). ^{13}C NMR (100 MHz CDCl$_3$) δ 143.2, 142.5, 135.6, 135.1, 135.0, 132.6, 131.5, 130.6, 128.2 (x2), 127.2 (x2), 124.6, 122.6, 122.5, 121.0, 120.9, 119.8, 119.7, 94.9, 91.7, 88.3, 88.0, 78.4, 78.2, 69.8, 69.5, 60.9, 60.8; MALDI-TOF NS *m*/*z* calcd for $C_{76}H_{80}B_{40}N_4$ 1482.0407, found 1479.9954 (M^{+}−2H).