Tetrahedron 64 (2008) 8522–8529

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

The assembly line: self-assembling nanocars☆

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ARTICLE INFO

Article history:
Received 7 March 2008
Received in revised form 13 May 2008
Accepted 16 May 2008
Available online 21 May 2008

ABSTRACT

Certain molecular structures that have controlled rolling properties on surfaces have been termed as nanocars. The syntheses of nanocars are generally multi-stepped. We report here the synthesis of two nanocars by a process resembling an assembly line where front and rear portions are attached using hydrogen bonding and metal complexation. Nanocars **1a** and **2a,b** were designed using 2-pyridone moieties for hydrogen bonding and terpyridyl ligands for metal complexation, respectively.

1. Introduction

In recent years there have been significant advancements and increased attention in the field of molecular machinery.[1] To further develop nanomachines and devices, researchers have looked for information and solutions in nature and its biological processes. The concept of self-assembly is a 'bottom–up' approach that has inspired scientist to generate numerous new structures.[2] However, there are ideas that are not reminiscent of biological systems. In our present work, our inspiration comes from both the process of self-assembly and the concept of an assembly line. In our efforts to develop machines and devices at the molecular level, our research has recently focused on the synthesis and manipulation of surface-rolling molecular machines, which are called the nanocars.[3] To facilitate the syntheses and to further understand and develop new-generation nanocars, we have integrated the ideas of assembly lines and self-assembly to construct new nanocar models.

There are a wide range of noncovalent interactions such as hydrogen bonding, π–π stacking, van der Waals forces, hydrophobic/hydrophilic interactions, Coulombic interactions, and metal complexation that have been used to generate impressive structures[4] in applications such as bioactive systems, sensors, field-effect transistors (FETs), thermoplastic elastomers, and optoelectronic devices.[5–9] In particular, hydrogen-bond and metal–ligand interactions are attractive for obtaining well-defined supramolecular structures due to their spatial arrangement and directionality.[10] Reported here are the syntheses of self-assembled nanocars via hydrogen bonding and metal complexation (Fig. 1).

Well-defined hydrogen-bonding structures are realized through DNA nucleotide-like molecules offering multiple binding sites for increased binding strength and organization.[11] However, simpler hydrogen-bonding molecules should not be overlooked for generating self-assembled structures. 2-Pyridones and their tautomers, hydroxypyridines, are well documented for their ability to form hydrogen-bonded dimeric structures in both solution and solid phases.[12] Therefore, the 2-pyridone moiety has been incorporated into the design of nanocar **1a** (Scheme 1).

2. Results and discussions

The synthesis of the hydrogen-bonded nanocar **1a** started by coupling trimethylsilylacetylene (TMSA) via palladium-catalyzed Sonogashira coupling with 2-hydroxy-5-iodopyridine to afford **3**. The TMS-protecting group was removed by treatment with tetrabutylammonium fluoride (TBAF) and the resulting crude product was used immediately for coupling with wheel/axle molecule **4**,[3d,f,g] a common component used in prior carborane-wheeled nanocars, to afford the half-car **1**. Incorporation of the *p*-carborane wheel into the nanocar structures has proven to be useful because of its stability, its ease of imaging by STM,[3a,13] and its compatibility with the required Pd-catalyzed coupling reactions.[3,14]

Half-car **1** was characterized by MALDI-TOF (Fig. 2), which showed no monomer peaks for **1** but showed only the self-assembled nanocar **1a** at peak *m*/*z* 1056 (M^+). Thus we were able to successfully construct a system that spontaneously self-assembled into a hydrogen-bonded nanocar **1a**. Solvent such as methanol is known to break the hydrogen-bonded dimer of pyridones[12] and spectral analysis of **1** by EI-HRMS showed only the monomer.

To retain a relatively rigid chassis as well as a molecule compatible with palladium-catalyzed Sonogashira couplings, terpyridines were used in an initial strategy to synthesize a metal-complexing nanocar. Due to the electrochemical properties and

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doi:10.1016/j.tet.2008.05.074

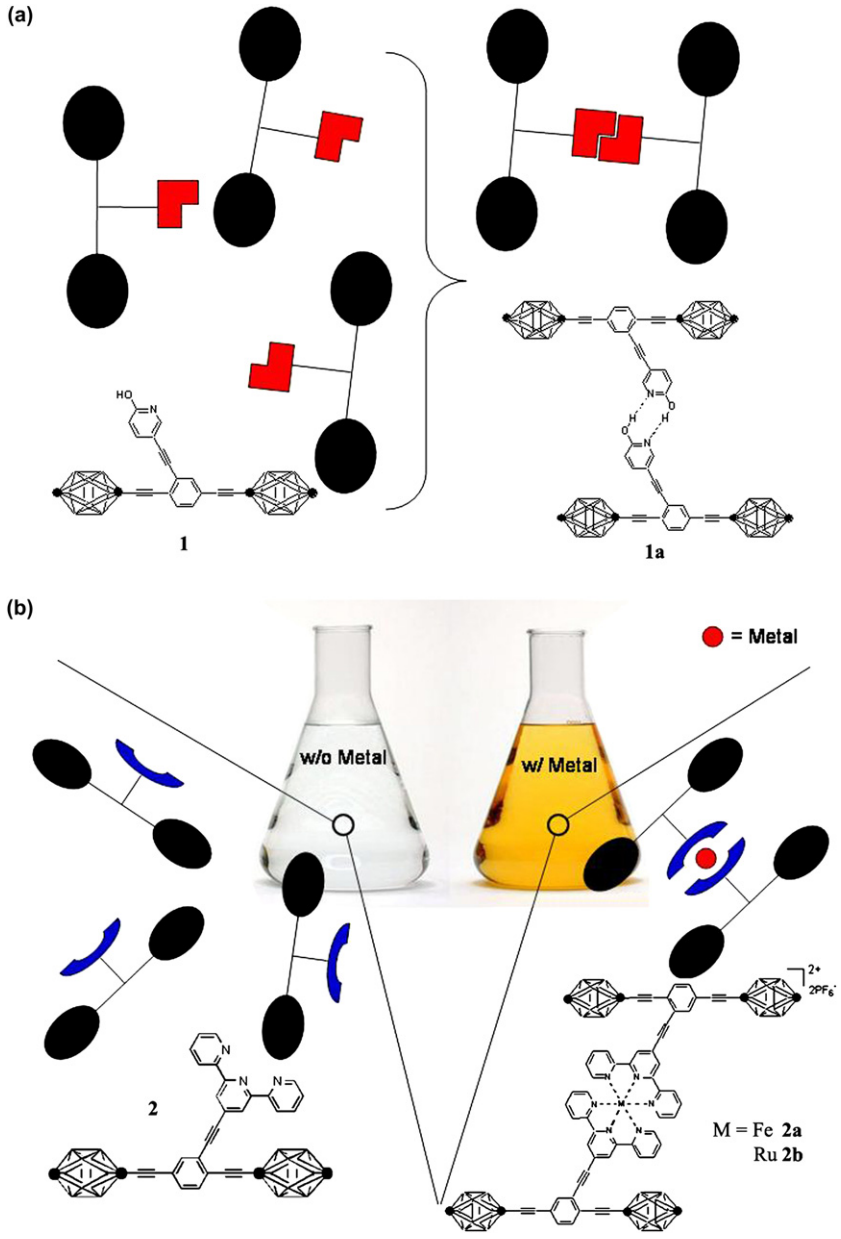
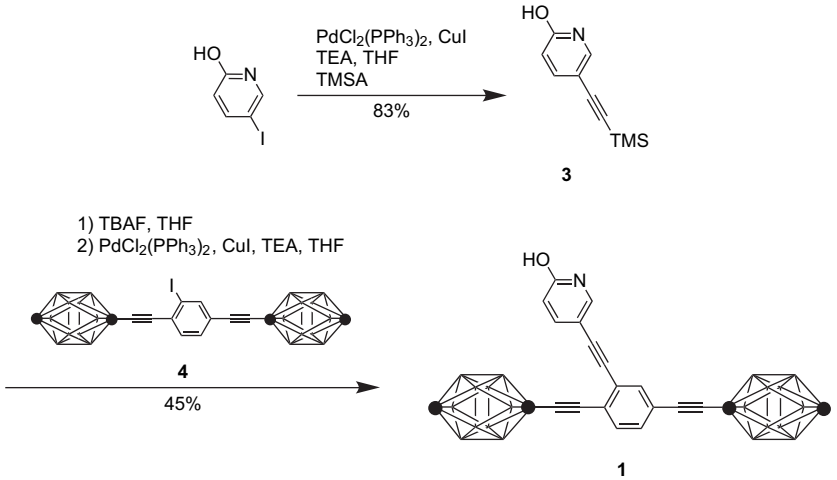


Figure 1. Illustration of the self-assembled (a) hydrogen-bonding nanocar **1a** and (b) metal complex nanocar **2a** and **2b**. The *p*-carborane moieties have BH at every intersection except at the points denoted by ●, which represents C and CH positions, *ipso* and *para*, respectively.



Scheme 1. Synthesis of hydroxypyridine half-car **1**.

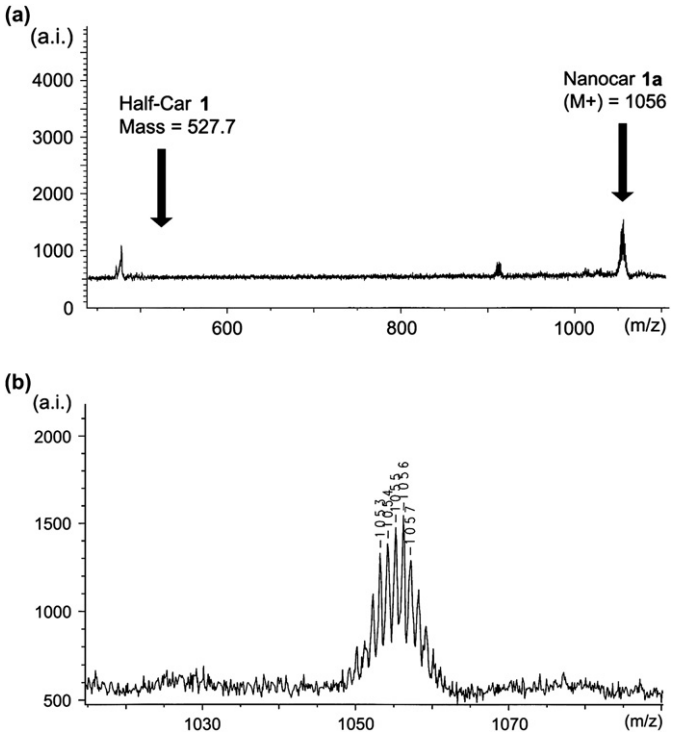


Figure 2. MALDI-TOF mass spectrometry of hydrogen-bonding nanocar **1a**. (a) There is no peak that would correspond to the exact mass for the half-car **1** while the peak for the exact mass of nanocar **1a** is clearly discernable; (b) an expansion of the exact mass peak for **1a**.

ease of isolation with different metals, terpyridyl ligands are used in a variety of applications such as redox polymers, electrocatalysis, photovoltaics, and electrochromic devices.[15–17] The most attractive metals for complexation of the self-assembling nanocars **2a** and **2b** were iron and ruthenium due to their simple solution complexation at room temperature.

The terpyridyl ligand suitable for the half-car **2** was synthesized using the known protocols (Scheme 2) to form the OTf–terpyridine **7**.[18] Under Sonogashira conditions, **7** was coupled to TMSA to form **8**, which was immediately deprotected with TBAF in THF to afford **9**. To complete the synthesis, the alkyne **9** and the carborane wheel/axle **4** were again coupled to afford half-car **2**.

The self-assembled nanocar **2a** was obtained by mixing a 2.5:1 ratio of **2** to $FeCl_2$ in ethanol at room temperature for 1 h followed by adding the counter ion tetrabutylammonium-hexafluorophosphate (NBu_4PF_6).[18] Characterization using ^1H NMR (Fig. 3) showed clear differences between the half-car **2** and complexed **2a**. Due to the presence of iron in the complex, the T_2 relaxation time is shortened thus producing line broadening of the peaks. Similarly, the ruthenium complex **2b** was synthesized by mixing a 2.5:1 ratio of **2** and $RuCl_3$, respectively, in MeOH. After adding a drop of 1-ethylpiperidine, the mixture was heated to reflux for 24 h. NBu_4PF_6 was added as the counter ion and the reaction mixture was heated to reflux for an additional 2 h. Analysis by NMR resulted in similar ^1H NMR broadening with the terpyridyl peaks being slightly more downfield in the ruthenium complex than in the iron complex.

From the visible absorption spectrum (Fig. 4a), a new band was formed after the addition of Fe(II) to a solution of **2** in CH_3CN that is indicative of metal-to-ligand charge transfer (MLCT). Changes at 570 nm shown in Figure 4b indicate that the formation of **2a** is complete after a stoichiometric amount (0.5 equiv) of Fe(II) is added. Gradual formation of monoterpyridyl Fe(II) results from further addition of Fe(II), as evidenced by the slight decrease in the absorption spectra. The small shoulder formed at ~375 nm is due to changes in the π–π^* transition.[19] The two distinct maxima (315 nm and 325 nm) observed are blue shifted compared to our past optical studies on carborane-containing conjugated molecules.[3g] The blue shift can be attributed to the steric hindrance between the carborane wheels and the terpyridyl core, which leads to a high dihedral angle between the axle and the core.

Two terpyridine ligands are known to show perpendicular orientation (octahedral) around the metal centers.[14–17] However, the ability to freely rotate about the alkyne bond will enable each terpyridyl ligand to rotate about 45° in relation to the mean plane of the molecule to minimize the interaction with the surface. The distances from the end of the ligand to the chassis and the radius of the carborane wheel[20] (Fig. 5) are approximately the same. Moreover, the flexibility of the chassis might allow the bending of each ligand to afford wheel rotation with little dragging of the inner core. In order to have better ground clearance of the inner core to alleviate any dragging, the synthesis of a less rigid more nearly planar metal complex is planned in the future.

Fluorescent optical studies of carboranes are scarcely reported,[3g] but fluorescent imaging could be an alternate to STM for discerning movement of these molecules on surfaces. The emission spectrum of **2** in CH_3CN (Fig. 6), when excited at 315 nm, gave rise to an emission band in the UV–blue region. The quenching behavior as a result of $FeCl_2$ addition is due to the coordination of Fe(II) to the terpyridyl units (Fig. 6a). When $RuCl_3$ was added to the half-car **2** in CH_3CN, in addition to the decreasing emission intensity, three distinctive bands were observed (Fig. 6b). The individual peaks correspond to free ligand **2** (355 nm), Ru-complexed nanocar **2b** (366 nm), and possible mono-complexed species (390 nm).[21] The emission spectrum of **2b** showed one peak at 366 nm with varying concentrations. The three separate species arise because the reaction conditions for complexation requires heating.

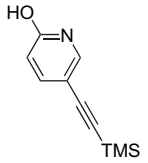
3. Conclusions

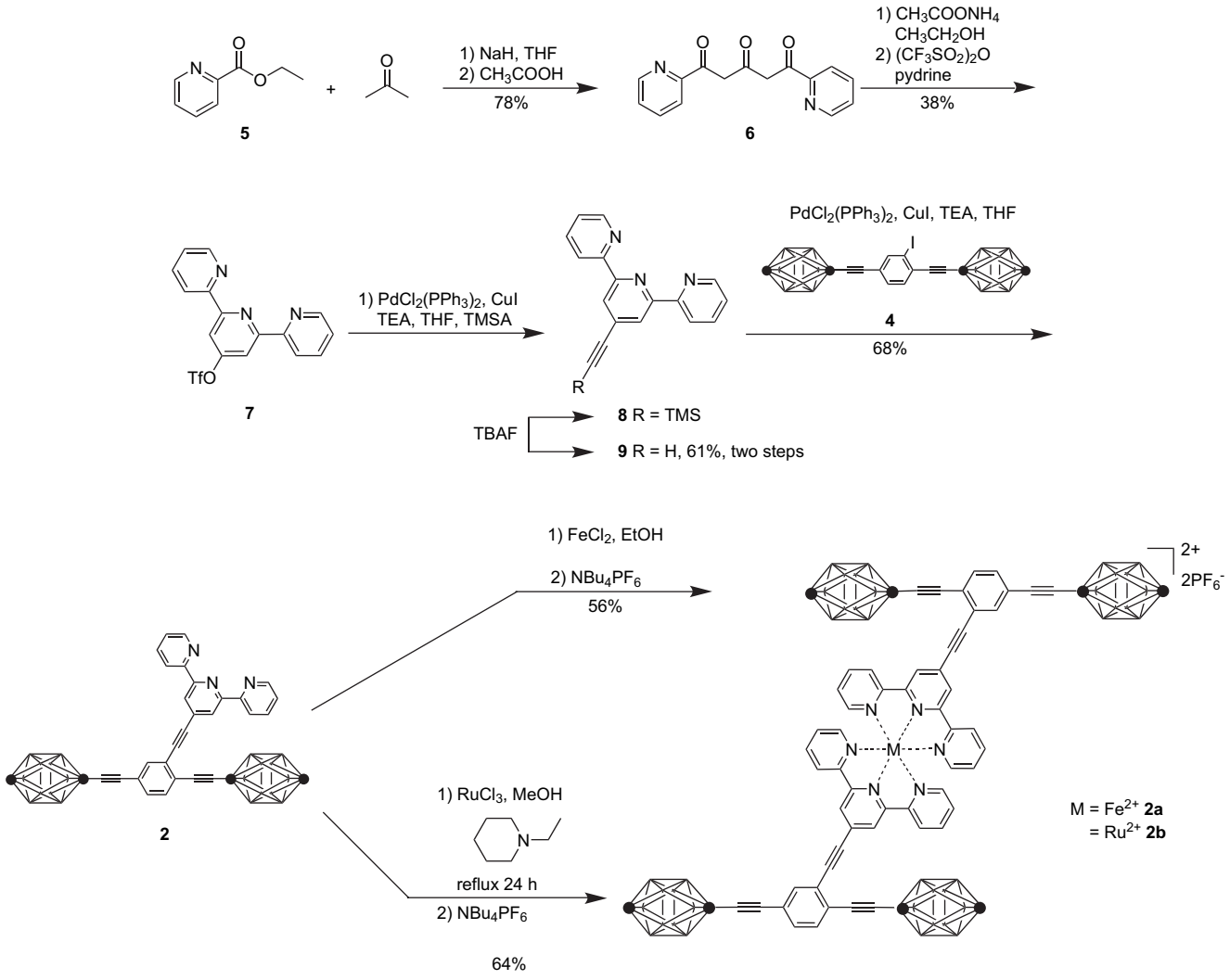
In summary, incorporating an assembly line approach to the synthesis of two types of self-assembled nanocars has been successful. Work continues on assembling these molecules on surfaces to demonstrate both self-assembly and rolling of these nanocars. With the use of these simple moieties for self-assembly, one can envision other complex nanomachine architectures such as nanotrains being constructed through a similar complexation process.

4. Experimental

4.1. General methods

All reactions were performed under an atmosphere of nitrogen unless otherwise stated. Reagent grade tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Triethylamine (Et_3N) was distilled over CaH_2. Flash column chromatography was performed using 230–400 mesh silica gel from EM Science or using 50–200 micron aluminum oxide activated-neutral from Acros. Thin layer chromatography (TLC) was performed using glass plates precoated with silica gel 40 F_{254} purchased from EM Science.

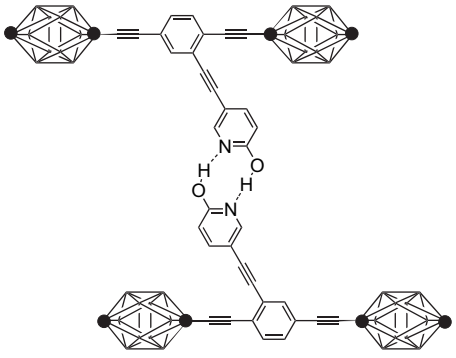




Scheme 2. Synthesis of metal-complexed nanocars **2a** and **2b**.

4.2. Compound (3)

To an oven-dried round-bottom flask equipped with a magnetic stir bar were added 2-hydroxy-5-iodopyridine (0.250 g, 1.131 mmol), $PdCl_2(PPh_3)_2$ (0.032 g, 0.046 mmol), and CuI (0.017 g, 0.089 mmol). THF (150 mL) and TEA (5 mL) were added followed by TMSA (0.40 mL, 2.828 mmol) and the mixture was stirred at 45 °C overnight. Upon completion, the reaction was quenched with a saturated solution of NH_4Cl. The organic layer was then diluted with hexanes and was washed with water or saturated NH_4Cl (1×). The combined aqueous layers were extracted with hexanes and CH_2Cl_2 (2×). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed from the filtrate in vacuo to afford the crude product, which was purified by SiO_2 column chromatography using 5% ethyl acetate in hexanes. After the starting material was eluted, the eluent was increased to 50% ethyl acetate in hexane to produce fractions containing the product. Removing the solvent in vacuo afforded a slightly colored solid **3** (0.179 g, 83%). Mp 105–107 °C. FTIR 3057, 2949, 2899, 2850, 2155, 1657, 1613, 1437, 1249, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 13.71–12.60 (s, 1H), 7.54 (d, 1H, J=2.4 Hz), 7.47 (dd, 1H, J=2.4, 9.4 Hz), 6.50 (d, 1H, J=9.4 Hz), 0.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 144.2, 138.7, 120.0, 103.7, 100.1, 95.3, −0.2; MALDI-TOF MS m/z (direct ionization) calcd for $C_{10}H_{13}NOSi$ 191.30, found 382.6 (dimer). EI-HRMS m/z calcd for $C_{10}H_{13}NOSi$ 191.3019, found 191.3016.



4.3. Hydrogen-bonding nanocar (1a)

To an oven-dried flask equipped with a stir bar were added the crude product from treatment of **3** with TBAF in THF (0.022 g, 0.1855 mmol), **4** (0.110 g, 0.2041 mmol), $PdCl_2(PPh_3)_2$ (0.005 g, 0.007 mmol), and CuI (0.003 g, 0.016 mmol). THF (40 mL) and TEA (5 mL) were added and the mixture was stirred at 45 °C overnight. Upon completion, the reaction was quenched with a saturated solution of NH_4Cl. The organic layer was then diluted with hexanes and was washed with water or saturated NH_4Cl (1×). The

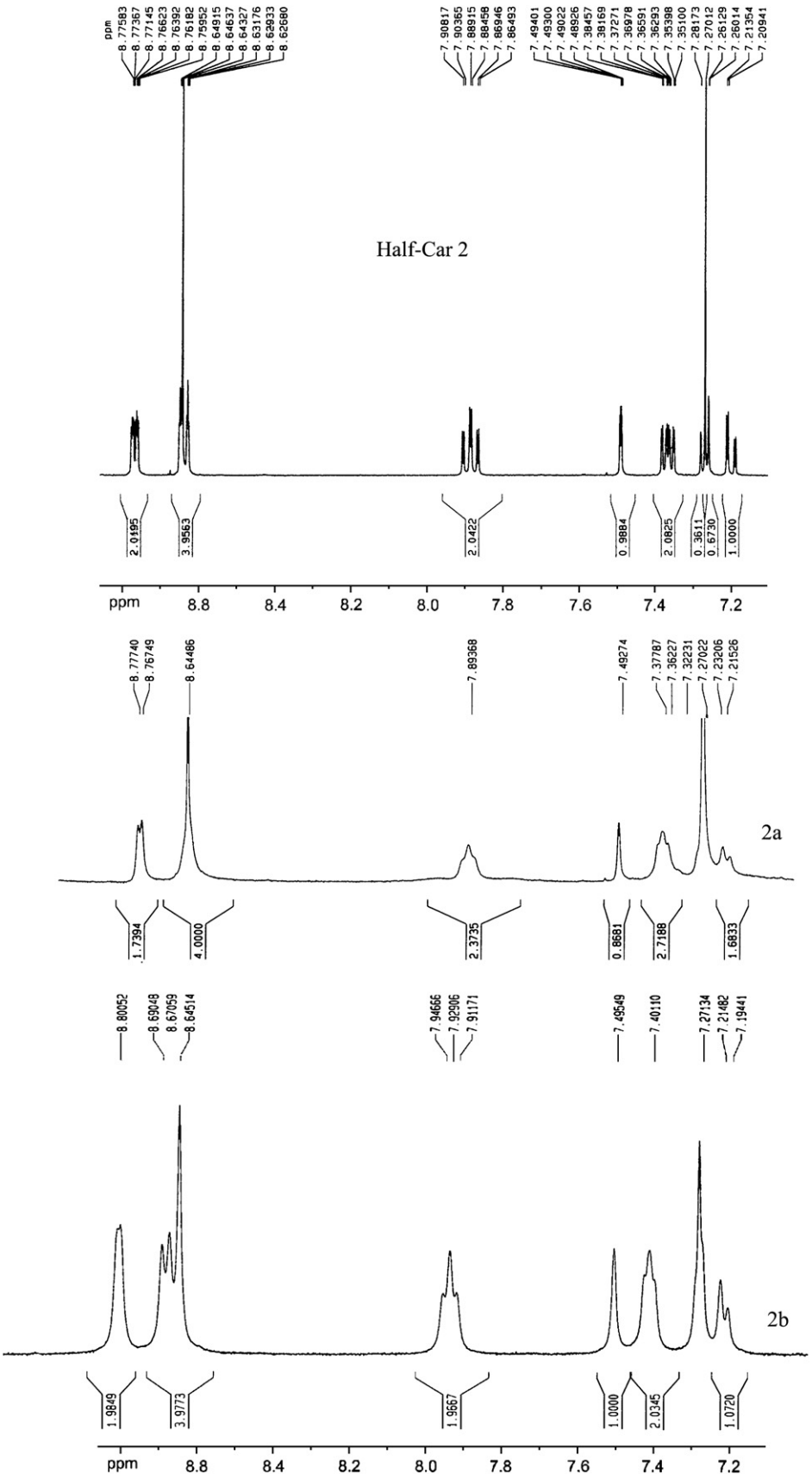


Figure 3. Evidence for the formation of nanocars **2a** and **2b**; ^{1}H NMR aromatic region of the half-car **2** (top); ^{1}H NMR of the aromatic region of nanocar **2a** with peak broadening due to the presence of iron (middle); ^{1}H NMR of the aromatic region of nanocar **2b** with peak broadening due to the presence of ruthenium (bottom).

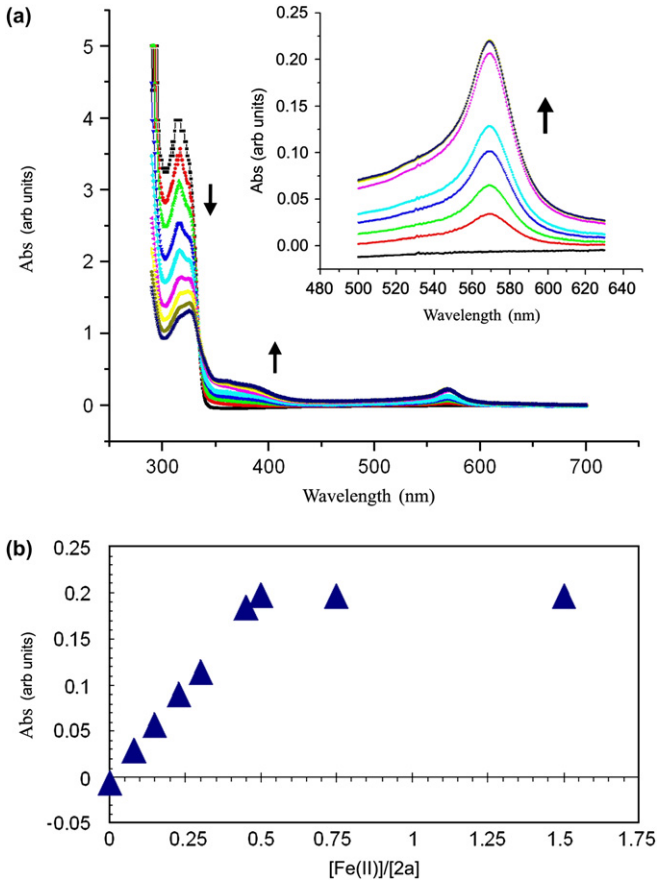
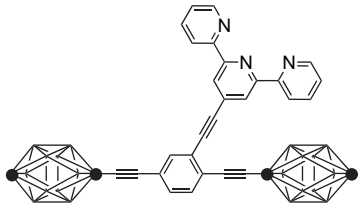


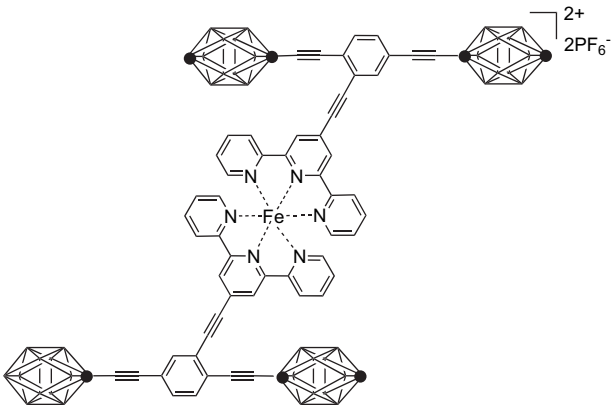
Figure 4. (a) Absorption spectra of **2** (2.0×10^{-4} M) in CH_3CN with increased amount of $FeCl_2$ in CH_3CN. (b) Changes observed at MLCT at 570 nm from 0 → 1.5 equiv of Fe(II) added.

combined aqueous layers were extracted with hexanes and CH_2Cl_2 (2×). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed from the filtrate in vacuo to afford the crude product, which was purified by SiO_2 column chromatography using 100% hexanes. After the starting material eluted, the eluent was increased to 50% ethyl acetate in hexane. Fractions containing the product were combined and the solvent was removed in vacuo to afford a white solid **1** (0.044 g, 45%). Mp >250 °C (dec). FTIR 3317, 3061, 3010, 2945, 2613, 2216, 1692, 1609, 1486, 1255, 1212, 1059, 767, 666 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (d, 1H, J=2.1 Hz), 7.57 (dd, 1H, J=2.2, 9.29 Hz), 7.37 (dd, 1H, J=0.5, 1.6 Hz), 7.21 (dd, 1H, J=0.6, 8.1 Hz), 7.14 (dd, 1H, J=1.7, 8.1 Hz), 3.31–1.48 (m, 22H); unfortunately, the solubility of the product was too low for ^{13}C NMR. MALDI-TOF MS m/z (direct ionization) calcd for $C_{12}H_{29}B_{20}NO$ 527.68, found 1055.4 (dimer). EI-HRMS m/z calcd for $C_{12}H_{29}B_{20}NO$ 527.6811, found 527.6813.



4.4. Terpyridyl half car (2)

To an oven-dried flask equipped with a stir bar was added **4** (0.036 g, 0.0662 mmol), **9** (from **7**[18] in 61% yield, 0.019 g, 0.0728 mmol), $PdCl_2(PPh_3)_2$ (0.003 g, 0.004 mmol), and CuI (0.006 g, 0.032 mmol). THF (10 mL) and TEA (2 mL) were added and the mixture was stirred at room temperature overnight. Upon completion, the reaction was quenched with a saturated solution of NH_4Cl. The organic layer was then diluted with hexanes and was washed with water or saturated NH_4Cl (1×). The combined aqueous layers were extracted with hexanes and CH_2Cl_2 (2×). The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed from the filtrate in vacuo to afford the crude product, which was purified by alumina column chromatography using 5 → 10% ethyl acetate in hexanes. Removing the solvent in vacuo afforded a white solid **2** (0.033 g, 68%). Mp 239–240 °C. FTIR 3060, 3006, 2924, 2847, 2610, 1580, 1463, 1390, 1060 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.76 (m, 2H), 8.63 (m, 4H), 7.87 (m, 2H), 7.48 (dd, 1H, J=0.6, 1.6 Hz), 7.36 (m, 2H), 7.26 (dd, 1H, J=0.5, 8.1 Hz), 7.19 (dd, 1H, J=1.7, 8.1 Hz), 3.49–1.55 (m, 22H); ^{13}C NMR (100 MHz $CDCl_3$) δ 155.7, 155.6, 149.3, 136.8, 135.5, 132.5, 132.1, 131.5, 125.8, 124.4, 123.9, 123.0, 122.0, 121.1, 92.2, 91.6, 90.1, 88.0, 77.7, 77.2, 69.3, 69.0, 60.34, 60.33. EI-HRMS m/z calcd for $C_{31}H_{35}B_{20}N_3$ 669.4692, found 669.4690.



4.5. Metal complex nanocar (2a)

To an oven-dried flask equipped with a stir bar was added **2** (0.019 g, 0.029 mmol) in hot (boiling) ethanol (5 mL). To the hot

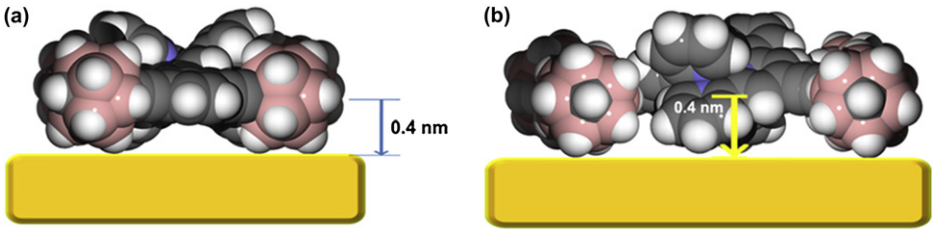


Figure 5. Front view, center of wheel to ground 0.4 nm (a), and side view, center of terpyridyl ligand to surface 0.4 nm (b), of minimal surface interaction conformation of the terpyridyl complexed nanocar.

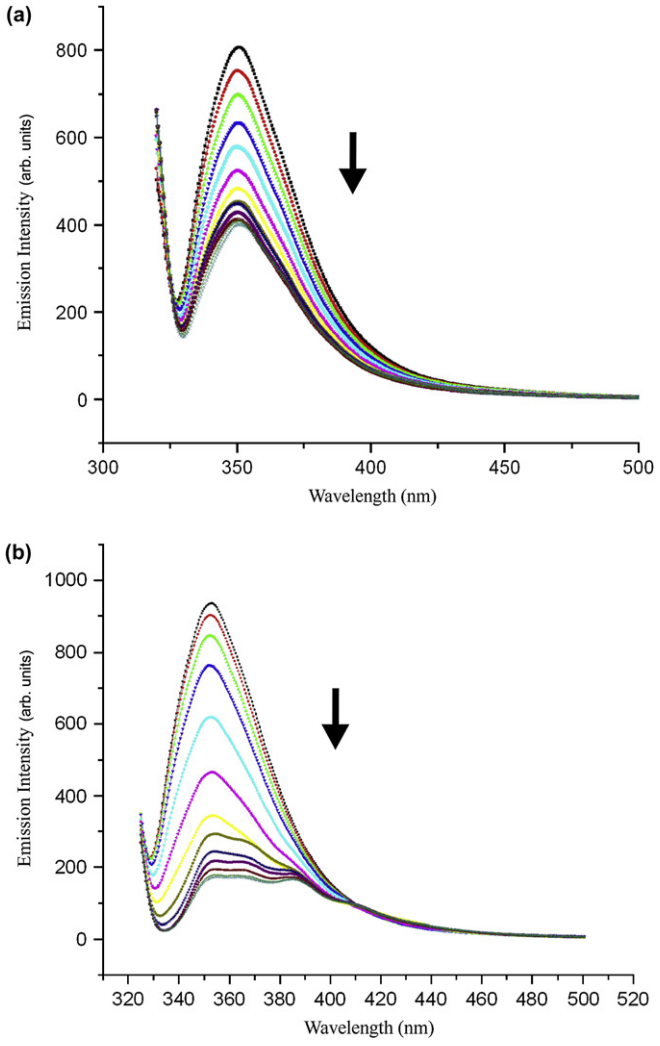
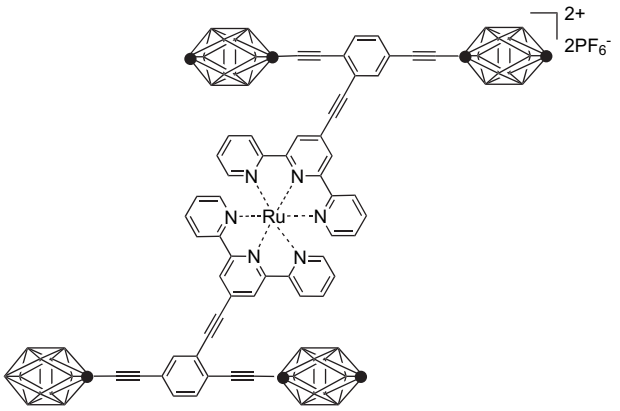


Figure 6. (a) Emission spectra of **2** (5.0×10^{-7} M) in CH_3CN excited at 315 nm with increased amounts of $FeCl_2$ in CH_3CN. (b) Emission spectra of **2** (7.0×10^{-7} M) in CH_3CN excited at 315 nm with increased amount of $RuCl_3$ in CH_3CN.

stirring mixture was added $FeCl_2$ (0.002 g, 0.012 mmol) in water (0.5 mL). The reaction mixture was gradually permitted to cool to room temperature and the mixture was stirred overnight. Finally, the counter ion ammonium hexafluorophosphate (0.006 g, 0.015 mmol) was added and the mixture was stirred at room temperature overnight to produce a purple precipitate. The reaction mixture with purple solids was purified by passing it through an alumina plug, first using ethyl acetate to elute the starting materials,



followed by MeOH to elute **2a** (0.010 g, 56%). Mp >250 °C (dec). FTIR 3202, 2960, 2930, 2873, 2614, 1708, 1463, 1386, 1064, 841, 752, 662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.77 (d, 2H, J=4.0 Hz), 8.64 (s, 4H), 7.89 (br t, 2H), 7.49 (s, 1H), 7.38 (t, 2H, J=6.6 Hz), 7.27 (br d, 1H, overlapped with $CDCl_3$), 7.21 (d, 1H, J=7.4 Hz), 3.50–1.20 (m, 22H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.5, 149.2, 136.7, 135.4, 132.3, 132.0, 131.4, 125.6, 124.3, 123.8, 122.9, 121.9, 121.0, 92.1, 91.5, 90.0, 87.9, 77.6, 77.5, 70.1, 70.0, 60.3, 60.2. MALDI-TOF MS m/z (direct ionization) calcd for $C_{62}H_{70}B_{40}F_{12}FeN_6P_2$ 1677.47, calcd for $[M-PF_6]^+$ 1532.51, found $[M-PF_6]^+$ 1532.5.

4.6. Metal complex nanocar (2b)

To an oven-dried flask equipped with a stir bar were added **2** (0.017 g, 0.025 mmol), $RuCl_3$ (0.003 g, 0.013 mmol), and methanol (15 mL). After adding one drop of 1-ethylpiperidine, the solution was heated at reflux for 24 h. After adding the counter ion ammonium hexafluorophosphate (0.007 g, 0.018 mmol), the reaction mixture was heated at reflux for additional 2 h. After the reaction mixture was cooled back down to room temperature, the resulting solid was filtered, redissolved, and passed through a short silica plug, to remove excess ruthenium, to afford a whitish purple solid **2b** (0.015 g, 64%). Mp >250 °C (dec). FTIR 3413, 2957, 2927, 2873, 2610, 1486, 1459, 1386, 1317, 1300, 1130, 1057, 838, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.80 (br d, 2H), 8.67 (m, 4H), 7.93 (t, 2H, J=7.0 Hz), 7.50 (s, 1H), 7.40 (br t, 2H), 7.27 (br d, 1H, overlapped with $CDCl_3$), 7.20 (d, 1H, J=8.2 Hz), 3.50–1.20 (m, 22H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 155.1, 149.0, 137.3, 135.5, 132.7, 132.1, 131.6, 125.6, 124.4, 123.3, 122.1, 121.4, 92.0, 91.6, 90.4, 88.0, 77.7, 77.2, 69.3, 69.0, 60.4, 60.3. MALDI-TOF MS m/z (direct ionization) calcd for $C_{62}H_{70}B_{40}F_{12}RuN_6P_2$ 1722.70, calcd for $[M-PF_6]^+$ 1577.73, found $[M-PF_6]^+$ 1577.7.

Acknowledgements

We thank the Welch Foundation, Zyvex Corporation, American Honda Motor Co., NSF 07111302, and NSF Penn State MRSEC for financial support. The NSF, CHEM 0075728, provided partial funding for the 400 MHz NMR. We thank Dr. I. Chester of FAR Research, Inc. and Dr. R. Awartari of Petra Research, Inc. for providing TMSA.

Supplementary data

FTIR, ^1H NMR, ^{13}C NMR, and mass spectrometry for compounds **1a**, **2**, **2a**, **2b**, and **3**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.05.074.

References and notes

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