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Carbon-rich supramolecular metallacycles and metallacages

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ABSTRACT

Coordination-driven self-assembly via the directional-bonding approach utilizes rigid transition metal acceptors and electron-rich donors to allow for complex, nanoscale 2D polygons and 3D polyhedra to be prepared under mild conditions and in high yields. To ensure proper rigidity and directionality, many acceptor and donor precursors contain largely carbon-rich aromatic and/or acetylenic moieties. This article introduces self-assembly as an alternative means of synthesizing carbon-rich materials and discusses the development, design, synthesis, and applications of carbon-rich supramolecular metallacycles and metallacages as well as the self-assembly of new diastereomeric carbon-rich supramolecular triangles.

1. Introduction

Carbon-rich materials[1] have attracted the interest and attention of chemists ever since the extraction and identification of polycycles during petroleum analysis began in the late 1800s. In the intervening years, seminal studies, led initially by Glaser, Scholl, and Clar, have transformed the science of carbon-rich materials from one primarily of analysis to one of planned preparation.[2,3] Whereas it was once a distinct challenge to synthesize even a relatively simple polycyclic aromatic hydrocarbon (PAHs) such as naphthalene—a challenge originally overcome by Radziszewski[4] in 1878—it is now possible to carry out a chemical synthesis of such highly-complex PAHs as C_{60}, as was done by Scott and co-workers[5] in 2001. Even so, as the field of carbon-rich molecules expands further, continually branching out into new areas with new applications, there is a persistent need for new and innovative ways of preparing these important compounds. Recent advances in coordination-driven self-assembly have provided such a means and have enabled a wide variety of carbon-rich metal–organic supramolecules to be prepared.

Over the past 150 years a variety of methods have been devised for preparing carbon-rich compounds. Originally, most techniques relied upon fairly harsh conditions typically requiring high temperatures and/or strong oxidizing agents and often resulted in low yields. Milder, higher yielding methods have since been developed such as Clar's Zn-dust reductions,[2] oxidative couplings of terminal alkynes,[6] Scholl-type intramolecular cyclodehydrogenation,[7] $h\nu$-induced ring closures,[8] cyclodehydration,[9] and Diels–Alder cycloaddition,[10] just to name a few. High temperature flash vacuum pyrolysis (FVP), however, remains a very popular means of preparing carbon-rich molecules despite its often-poor yields. Self-assembly, on the other hand, is a synthetic technique that is typified by mild reaction conditions and high yields.

1.1. Coordination-driven self-assembly of carbon-rich supramolecules

Molecular self-assembly[11] is a process through which properly designed, complementary molecular subunits spontaneously assemble according to the specific noncovalent 'information' encoded within their structures. The use of noncovalent interactions (e.g., hydrogen-bonding, π–π, donor–acceptor, charge–charge, etc.) to direct self-assembly enables product formation to be thermodynamically controlled. Individual building-blocks are able to continually and reversibly assemble in a variety of ways until the most thermodynamically stable product is obtained. Such dynamic[12] self-assembly processes often result in one highly symmetric, thermodynamically stable product in high and often quantitative yield. With appropriate planning, individual precursor building-blocks may be designed such that they lead specifically to a single desired supramolecule possessing unique architectural or topological[13] characteristics. While many examples of self-assembled supramolecules involve flexible, significantly saturated carbon backbones[11c–f] and, thus, may not fit the typical definition of being carbon-rich compounds, there are also myriad ways of using the virtues of self-assembly (high yield, mild conditions, complex architectures) to prepare carbon-rich molecules.

As a design and synthesis methodology, coordination-driven[14] self-assembly is especially useful for preparing carbon-rich molecules. Coordination-driven self-assembly relies upon the use of

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dative metal–organic interactions between electron-poor transition metal acceptors and electron-rich organic donors and is often used in conjunction with the directional-bonding[14f,15] approach to self-assembly. According to the directional-bonding protocol, discrete supramolecular assemblies will be formed in accordance with the specific geometric information—the 'directionality'—stored within the pre-defined angles and symmetry of rigid precursors and the stoichiometric ratio in which those precursors are mixed. Rigid acceptor and donor precursors are necessary so that they retain their directionality, increasing the likelihood of a successful self-assembly, i.e., one that results in a high yield of a single discrete product as opposed to a mixture of polymeric, oligomeric, or other side products. With these design criteria in mind, the vast majority of examples that follow the directional-bonding approach to coordination-driven self-assembly utilize largely aromatic and/or alkynyl building-blocks. The resulting self-assembled metal–organic supramolecules are often quite carbon-rich.

1.2. Carbon-rich polygons and polyhedra

The use of coordination-driven self-assembly in the synthesis of carbon-rich compounds has many advantages. When precursors are carefully designed it is possible to self-assemble 2D metallacyclic polygons and 3D metallacage polyhedra while exerting precise control over the often highly-complex structures of the supramolecular products. Representative collections of 2D and 3D metallacycles that can be prepared by the directional-bonding approach are shown in Figures 1 and 2, respectively. It would likely prove exceedingly difficult, if not altogether impossible, to prepare analogous structures in high yields by traditional synthetic methods. Dynamic self-assembly, on the other hand, as a thermodynamically controlled process, enables such complex structures to be prepared in significantly fewer synthetic steps and often in near quantitative yields. Preparation of these highly symmetric polygons and polyhedra is very modular, enabling both their architecture and properties to be easily manipulated simply by changing the size, shape, coordination number, and/or functionality of individual building units.

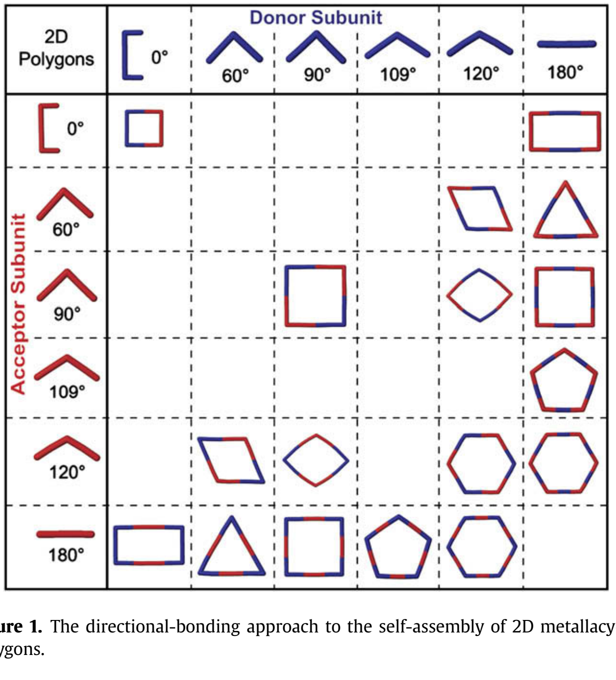


Figure 1. The directional-bonding approach to the self-assembly of 2D metallacyclic polygons.

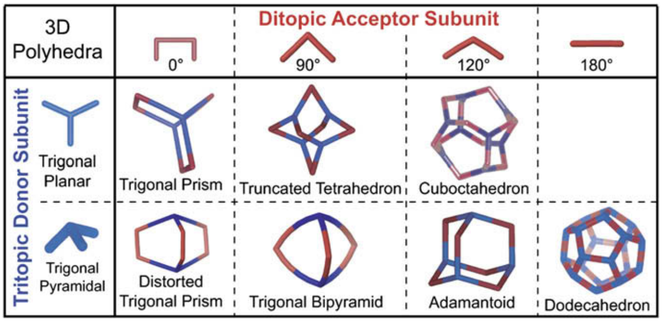


Figure 2. The directional-bonding approach to the self-assembly of select 3D metallacages.

2. Metallacyclic polygons

While earlier examples of metal–organic self-assembled metallacages exist, most notably from Maverick and Klavetter[16] in 1984, it wasn't until about 1990 that systematic approaches to metallacycles began to appear.[17] Most initial examples of self-assembled metallacycles took the form of supramolecular squares. One of the most commonly utilized protocols for designing a supramolecular square calls for a combination of four linear ditopic units (L^2) and four complementary angular ditopic units (A^2), generating a square of type $A^2{}_4L^2{}_4$. Square planar Pt(II) and Pd(II) metals have provided the basis for 90° angular corner units of myriad carbon-rich supramolecular squares in conjunction with rigid pyridyl or nitryl substituted linear donors.[18–22] Examples of carbon-rich angular and linear components are shown in Figure 3, while Scheme 1 summarizes the self-assembly of a number of $A^2{}_4L^2{}_4$ supramolecular squares.

It is also possible to form related squares of type $A^2{}_2A^2{}_2$ wherein two sets of ditopic 90° angular units, one donor and one acceptor, are combined in a 1:1 ratio.[23]

By employing ditopic donor and/or acceptor building-blocks with turning angles that deviate from 90°, a variety of other carbon-rich 2D metallacycles can be prepared (Fig. 1). Representative examples of ditopic acceptors and donors used in the construction of carbon-rich supramolecular rectangles,[24–26] rhomboids,[26–28] triangles,[29] pentagons,[30] and hexagons[27,28,31,32] are shown in Figure 4. As can be seen in Scheme 2, the variety of complementary angular and linear ditopic building units provides access to a series of metallacyclic polygons.

Rigid supramolecular rectangles can be prepared upon mixing the 0° molecular 'clip' with linear donor ligands such as **4**, **10**, **11**, and **13**. Given the close proximity of the two Pt(II) acceptors in **14**, care must be taken when designing a linear donor ligand because of steric crowding. Given that a rhomboid can be defined as any four sided parallelogram that is neither a square nor a rectangle, a variety of donor and acceptor combinations may be used to prepare metallacyclic rhomboids. Carbon-rich supramolecular rhomboids have thus been prepared using 180° donor bis(pyridyl)-substituted perylene diimide **13** as well as 120° donors **21**–**23**. It is possible to form a rhomboid structure using the linear donor **13** because its length, ~3.5 nm, confers enough overall flexibility to self-assemble when combined with a 90° metal acceptor.

Combining three ditopic 60° phenanthrene-based Pt(II) acceptors (**15**) with three ditopic 180° 4,4′-bipyridyl linear donors (**4**) results in a metallacyclic triangle.[29] Changing the acceptor unit from a 60° phenanthrene-based **15** to a 120° benzophenone-based Pt(II) acceptor (**17**) results in a carbon-rich supramolecular hexagon when mixed with the same linear donor (**4**) in a 1:1 molar ratio.[31] The modularity of the coordination-driven directional-bonding approach is easily seen when comparing some of the many carbon-

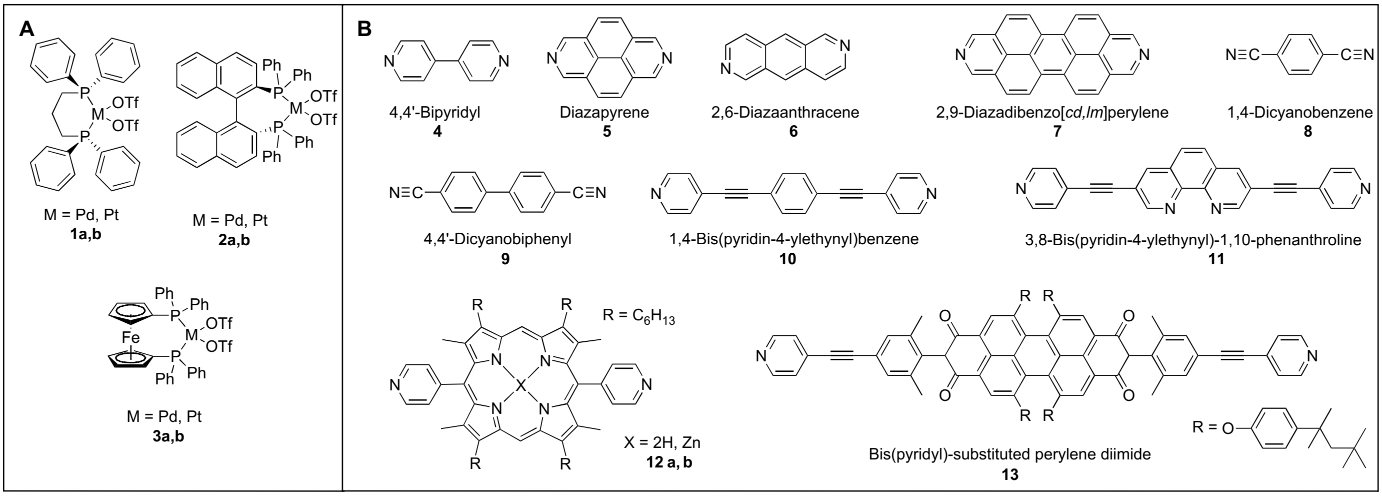
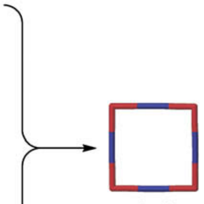


Figure 3. Carbon-rich ditopic 90° metal acceptors (A) and ditopic 180° donors (B).

Ref.	Acceptor		Donor
(19)	**1a,b**	+	**4**
(20)	$M(PEt_3)_2(OTf)_2$	+	**5**
(20)	$M(PEt_3)_2(OTf)_2$	+	**7**
(20)	**1a**	+	**8**
(20)	**1a**	+	**9**
(21)	**3a,b**	+	**5**
(22)	**2a,b**	+	**6**
(23)	**1a,b**	+	**12a,b**


$A^2{}_4L^2{}_4$

Scheme 1. The self-assembly of carbon-rich metallacyclic squares. In all cases, the acceptor and donor are mixed in a 1:1 molar ratio; M=Pt, Pd.

rich metallacyclic hexagons that have been self-assembled. Hexagons of type $A^2{}_3A^2{}_3$, which are devoid of linear building-blocks, have been prepared.[27] Similarly, large hexagons of type $A^2{}_6L^2{}_6$ composed of complementary pairs of 120° acceptors with 180° donors, or analogous 120° donors with 180° acceptors, have also been prepared. Pentagonal metallacycles may be formed by using a slightly more flexible 109° acceptor, however, they are often in competition with related hexagonal metallacycles.

3. Metallacage polyhedra

More recently, considerable attention has been paid to the expansion of these coordination-driven self-assembly techniques to the third dimension. The protocol for preparing 3D metallacages only requires the preparation of donor and/or acceptor precursors with greater than two binding sites. As shown in Figure 2, combining carbon-rich tritopic and ditopic building units allows for the

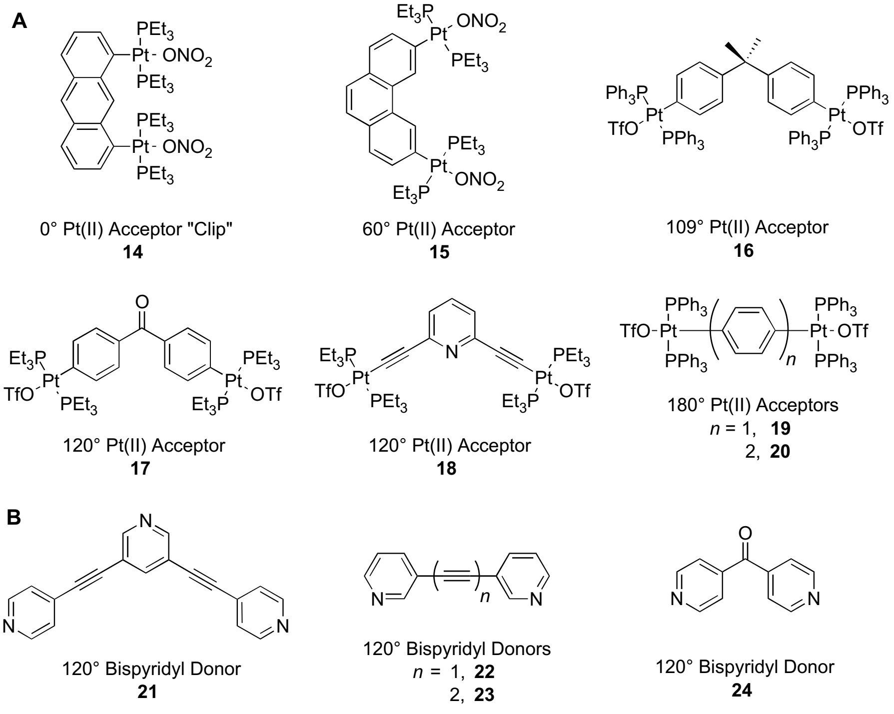
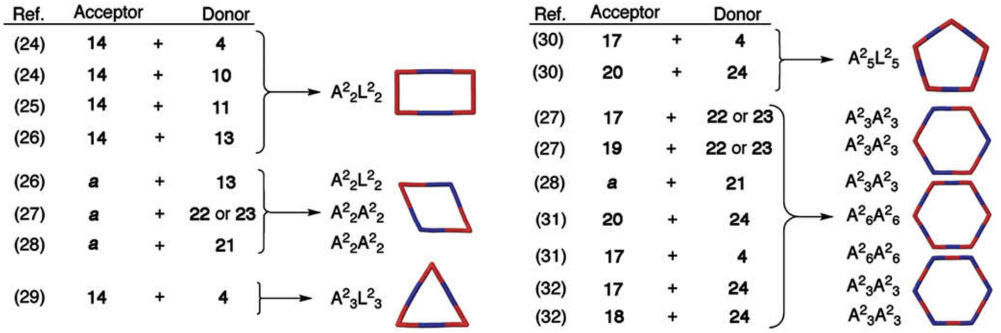
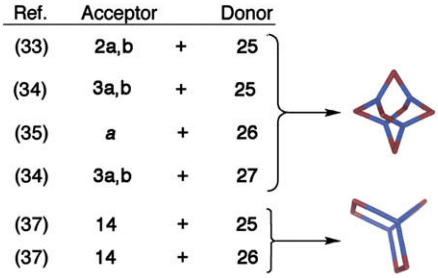


Figure 4. Carbon-rich Pt(II) acceptors with turning angles of 0°, 60°, 109°, 120°, and 180° (A) as well as non-linear ditopic donors (B).



Scheme 2. Summary of protocols for self-assembling a variety of carbon-rich 2D polyhedra. In each case, the donor and acceptor precursors are mixed in a 1:1 molar ratio; **a**=Pt(PMe$_3$)$_2$(OTf)$_2$.



Scheme 3. Use of trigonal planar tritopic donors to self-assemble carbon-rich truncated tetrahedra and trigonal prisms; **a**=Pt(PMe$_3$)$_2$(OTf)$_2$.

construction of metallacages with truncated tetrahedral, distorted and non-distorted trigonal prism, cuboctahedral, adamantoid, and dodecahedral geometries (Scheme 3).[14b,c,e] Combining carbon-rich, threefold symmetric planar tritopic donors or acceptors (Fig. 5) with complementary 90° units in a 3:2 ratio allows the self-assembly of truncated tetrahedral assemblies.[33–35] In addition to these carbon-rich examples, Fujita and co-workers have also prepared related nitrogen-rich analogues based on tritopic trispyridyl donors with a triazabenzene core.[36] If the self-assembly involving donor **25** or **26** is performed with a 0° molecular 'clip' rather than a 90° acceptor, also in a 3:2 ratio, the result becomes a trigonal prism.[37,38] An alternative method for preparing a carbon-rich trigonal prism has been achieved by Fujita using a combination of two tritopic trigonal planar donors, three ditopic linear donors, and six 90° metal acceptors.[39]

Other trigonal prism geometries may be formed using three carbon-rich tetratopic donors that function as planar 'walls' that are linked using six 90° metal acceptors as 'corners' as shown in Scheme 4. Tetrapyridyl-substituted porphyrins[40] as well as tetrapyridyl-substituted benzene and cyclobutadiene–cyclopentadieneyl cobalts[41] have been used as the carbon-rich walls of such trigonal prism geometries. In the case of tetratopic donor **34**, restricted rotation of pyridyl ligands in a trigonal prism renders the assembly helically chiral with *MMM* and *PPP* enantiomers.

An entirely different geometry, that of a cuboctahedron, is obtained when planar tritopic units such as carbon-rich donor **25** or acceptor **28** are combined in an 8:12 ratio with complementary 120° ditopic units (Scheme 5).[42] Robson and co-workers[43] have self-assembled a metallacage with cuboctahedral geometry by

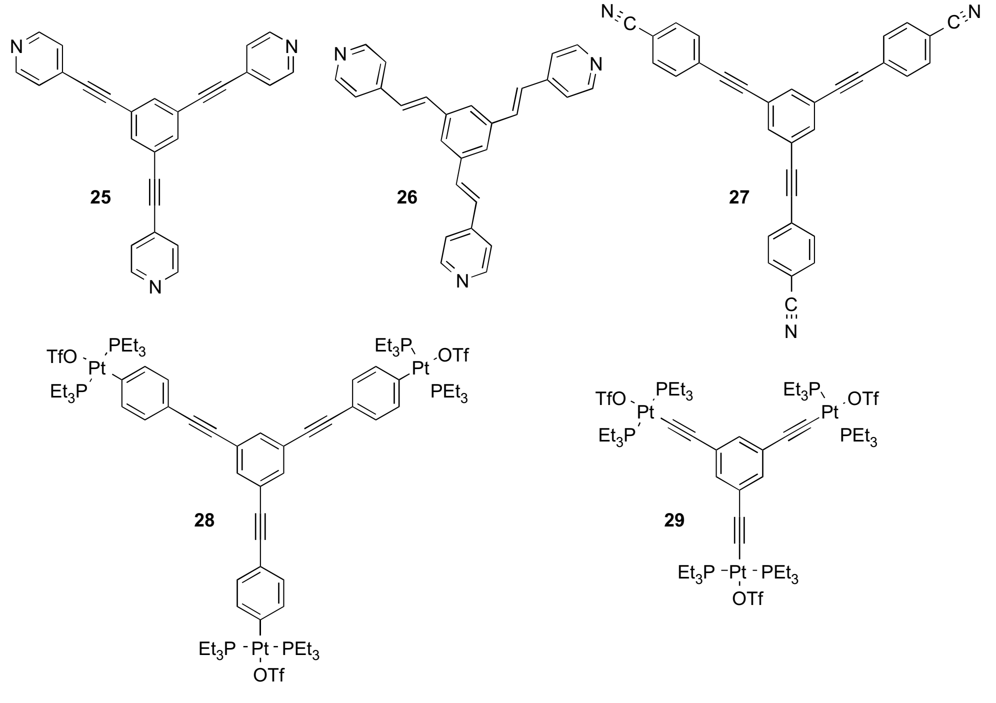
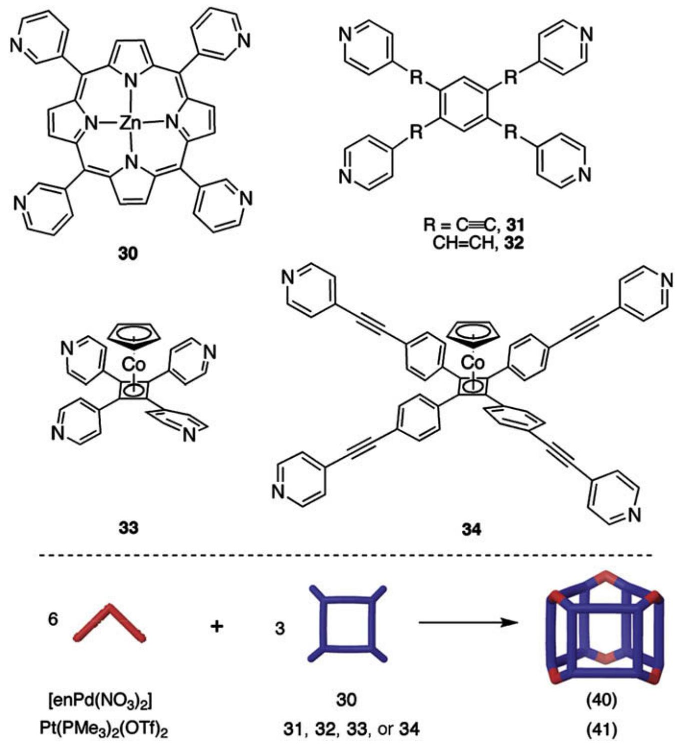
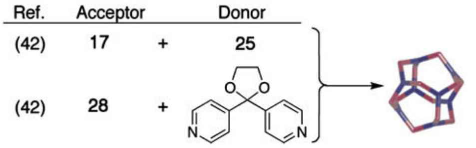


Figure 5. Trigonal planar tritopic donors and acceptors.



Scheme 4. The self-assembly of ‘walled’ trigonal prism geometries using carbon-rich tetratopic donors and 90° metal acceptors in a 3:6 molar ratio.



Ref.	Acceptor		Donor
(42)	17	+	25
(42)	28	+	

Scheme 5. The self-assembly of cuboctahedra from 12 ditopic 120° precursors and 8 complementary tritopic trigonal planar precursors.

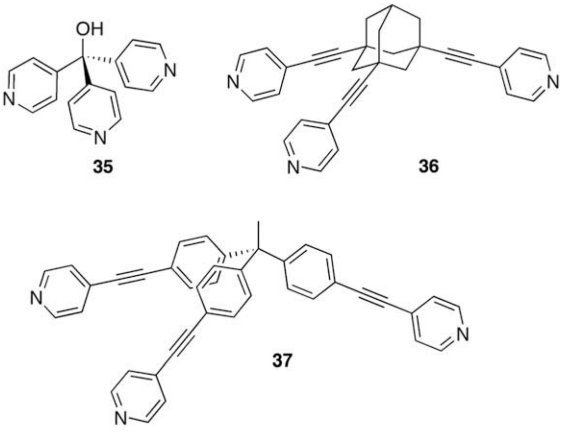
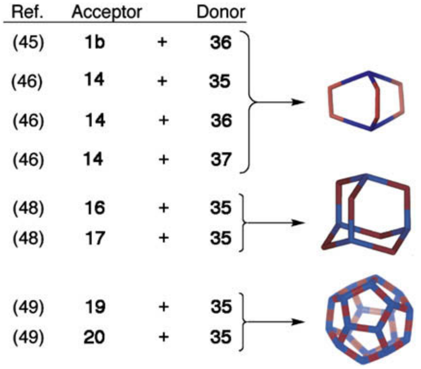


Figure 6. Examples of three carbon-rich trigonal pyramidal tritopic donors.



Ref.	Acceptor		Donor
(45)	1b	+	36
(46)	14	+	35
(46)	14	+	36
(46)	14	+	37
(48)	16	+	35
(48)	17	+	35
(49)	19	+	35
(49)	20	+	35

Scheme 6. Self-assembly of trigonal bipyrimidal, adamantoid, and dodecahedral polygons. Component acceptor and donor precursors are mixed in 3:2, 6:4, and 30:20 molar ratios, respectively.

combining a 2,4,6-triazophenyl-1,3,5-trioxybenzene trianion and $Cu(NO_3)_2$ in a 2:3 molar ratio. By using ‘naked’ Pd metals in conjunction with 120° dipyridyl donors, Fujita and co-workers[44] have prepared a variety of cuboctahedral complexes of the form $M_{12}L_{24}$. The large variety of carbon-rich 3D architectures available simply using planar tritopic of tetratopic units with 0°, 90°, or 120° units—resulting in assembly geometries that range from truncated tetrahedral to trigonal prisms, to cuboctahedra, respectively—demonstrates the power and modularity of the directional-bonding, coordination-driven approach.

Using non-planar tritopic donors (Fig. 6) opens the door to an even greater variety of 3D metallacages. Combining trigonal pyramidal tritopic donors with 0° or 90° acceptors in a 2:3 molar ratio results in the formation of distorted trigonal prisms[45,46] or, more precisely, trigonal bipyramids (Scheme 6). The extent of distortion from a ‘planar’ trigonal prism geometry is controlled by the size and geometry of the tritopic donor and the angle of the acceptor, with a greater acceptor angle resulting in greater distortion from a trigonal prism geometry.

Fujita has self-assembled a ‘double-square’ metallacage[47] by combining 4 equiv of a tritopic trispyridyl methyl donor derivative with 6 equiv of a 90° Pd(II) acceptor. Whereas a 90° Pd(II) acceptor in the previous case is used to prepare a double-square, a 109–120° Pt(II) can be combined with a related tritopic trispyridyl methyl derivative (**35**) to self-assemble an adamantoid structure (Scheme 6).[48] We have also prepared a variety of carbon-rich dodecahedral assemblies using a trispyridylmethanol tritopic donor and different sized 1,4-substituted benzene and 4,4′-biphenyl substituted Pt(II) linear (180°) ditopic acceptors.[49] Combining the tritopic donors and ditopic acceptors in a 30:20 ratio results in carbon-rich supramolecular metallacages with dodecahedral geometries. These dodecahedra, with diameters ranging from 5–7 nm, represent some of the largest discrete supramolecular assemblies prepared to date.

4. Materials applications

As with many other carbon-rich molecules, which have found applications in materials such as organic field-effect transistors (OFETs), artificial photosynthetic systems, and luminescent devices, the potential materials applications of carbon-rich supramolecular assemblies have also been explored. Our phenanthroline-containing supramolecular rectangle,[25] for example, has been shown to function as an optical sensor for Ni(II), Cd(II), and Cr(III). Fujita and co-workers have demonstrated the ability of a carbon-rich supramolecular tetrahedron cage to selectively recognize and bind sequence-specific peptides[50] and, in the case of a supramolecular trigonal prism, capable of folding an Ala-Ala-Ala tripeptide in to a β-turn on account of hydrophobic encapsulation.[51] The use of largely aromatic moieties in various precursors enables many supramolecular cages to act as hosts for other aromatic guests through a combination of π–π and hydrophobic interactions.[39,52] Both Hupp and co-workers[53] and Mirkin and co-workers[54] have recently used porphyrin-based supramolecular rectangles as catalysts for epoxidation and acyl transfer reactions, respectively.

4.1. Microporous molecular materials

In addition to aforementioned host–guest applications, rigid supramolecular 2D polygons offer unique opportunities to be used as highly-selective nanofilters. The size and shape of nanoscale cavities present in metallacyclic polygons can be easily modified in order to allow for size-specific discrimination of various molecular permeants. Hupp and Dinolfo[55] have extensively explored the use of metal–organic supramolecules as selective nanofilters. Small and large supramolecular squares, for example, composed of Re(I) $Cl(CO)_3$ corners and either pyrazine or dipyridyl porphyrin edges, respectively, were shown capable of filtering planar and spherical permeants based upon their size.[56] Further studies utilizing thin-films of Mn(I) and Re(I) carbon-rich rectangles demonstrated that only those molecular permeants that were narrow in at least one dimension, similar to the metallacyclic rectangles, were able to pass through the intramolecular rectangular cavities whereas permeants lacking a narrow dimension were blocked.[57] In addition to applications as highly-modular nanofilters, the gas adsorption properties of carbon-rich supramolecular metal–organic assemblies are currently being explored.[58]

4.2. Higher-order self-assembly on surfaces

Recently, in collaboration with Wan and co-workers, we have explored the self-assembly of supramolecular assemblies on Au(111) and HOPG surfaces. Both polygonal (rectangular[59] and square[60]) and polyhedral (trigonal bipyramid[60] and chiral trigonal prism[61]) structures have been assembled onto surfaces and their structures characterized. Results of these studies have shed considerable light on the factors that influence the orientation of these supramolecules on various surfaces. For example, one carbon-rich supramolecular rectangle investigated adopts an edge-down orientation on HOPG while the same rectangle adopts a face-down orientation on Au(111).[59] In the case of chiral trigonal prisms, deposition of a racemic mixture of supramolecular assemblies resulted in spontaneous symmetry breaking and formation of enantiomerically segregated chiral domains.[61] Furthermore, we have demonstrated the ability of using a molecular template[62] to promote the formation of a well-ordered, monodisperse monolayer of molecular rectangles on Au(111) whereas without the template only a disordered adlayer is observed. Having the ability to prepare well-ordered arrays of these carbon-rich supramolecules and control their orientation on surfaces may lead to a variety of applications as sensors, electronic, photonic, or magnetic materials, or catalysis, especially in the case of chiral 2D assemblies, which may have a range of heterogeneous stereoselective synthetic applications.

4.3. Functionalized metal–organic assemblies

Another development in the use of carbon-rich supramolecular metallacycles and metallacages has been in their functionalization. The rigid structures and precise, unique geometries of many supramolecular assemblies makes them very effective ‘scaffolds’ for a variety of functionalities simply by preparing derivatized donors and/or acceptors. Given the rigid structural characteristics of precursor building-blocks and the fact that donors and acceptors are mixed in specific ratios, the location and stoichiometry of covalently linked functional moieties attached to carbon-rich supramolecules can be precisely controlled. We have recently prepared 120° donors functionalized with Frechét-type dendritic,[63] crown-ether,[64] and ferrocenyl[65] moieties attached. Combining these donors with complementary 90°, 120°, or 180° Pt(II) acceptors allows for the formation of bisfunctionalized rhomboids as well as tris- and hexakisfunctionalized hexagons, respectively. We have further demonstrated the ability of crown-ether derivatized assemblies to act as hosts for multiple dibenzylammonium cations[64] and have explored the electrochemistry of ferrocenyl metallacycles, which may have applications as multiple electron redox catalysts or as electron sponges.[65] Fujita and co-workers[66] have also successfully prepared carbon-rich 3D cuboctahedra that have been functionalized endohedrally with azobenzene,[66a,c] oligo(ethyleneglycol),[66a] polyfluoro,[66b] and polymerizable methyl methacrylate units[66d] and exohedrally with saccharide moieties.[66e] These 3D assemblies have found uses in a variety of host–guest applications.

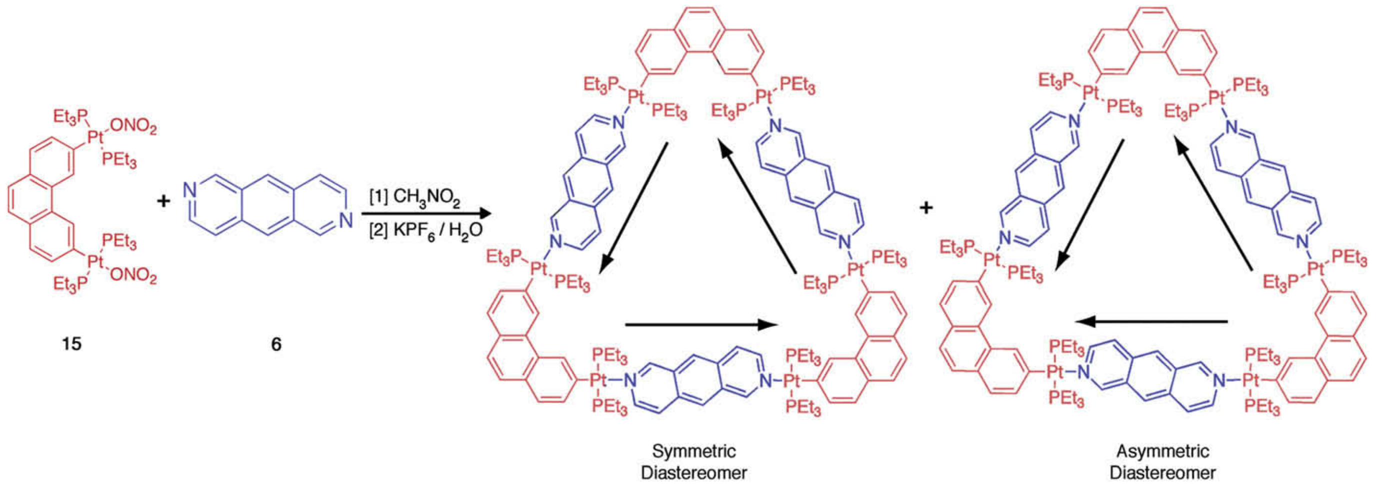
5. Novel stereoisomeric supramolecular triangles

Chirality is a ubiquitous and important phenomenon throughout nature in general and chemistry in particular. The general lack of tetrahedral carbon atoms throughout most carbon-rich compounds usually rules out the possibility of synthesizing carbon-rich molecules with point chirality. There are, however, ways to introduce chirality into carbon-rich molecules by means of helicity. For example, beginning in 1967, Martin and co-workers[67] prepared helically chiral hepta-, octa-, and nonahelicene. Building upon these purely aromatic helically chiral structures, in 1972 Staab and co-workers[68] prepared a carbon-rich helically chiral benzannulene structure composed solely of benzene and acetylene moieties. Since that time a rich chemistry of chiral benzannulene compounds has been developed.[69] Similarly, chirality can be introduced into carbon-rich systems through the incorporation of chiral moieties, such as binaphthyl units.

Coordination-driven self-assembly techniques provide a means of synthesizing stereoisomers of carbon-rich supramolecules in high yield under thermodynamic control. In the mid-1990s, Stang and co-workers used a chiral binaphthyl-substituted 90° Pt(II) acceptor to prepare optically active carbon-rich 2D metallacyclic squares[21] and 3D metallacage truncated tetrahedra.[33] It is also possible to use self-assembly to synthesize carbon-rich supramolecules from completely achiral building-blocks. To demonstrate the utility of coordination-driven self-assembly we report herein the design and synthesis of stereoisomeric carbon-rich metallacyclic triangles.

The combination of 2,6-diazaanthracene (**6**) and the 60° Pt(II) acceptor **15** in a 1:1 ratio results, theoretically, in the formation of two possible $A^2{}_3L^2{}_3$ metallacyclic triangle diastereomers (Scheme 7), which are both *meso* compounds. The diastereomers differ in the relative orientations of their donor components as indicated by arrows in the scheme. In the symmetric diastereomer, all three donor moieties are oriented in the same direction while in the asymmetric diastereomer, one donor moiety is oriented opposite the other two. Rotation around the Pt–N bonds in each assembly is restricted,[70] preventing direct interconversion between stereoisomers through dynamic bond rotations.

Stirring **6** and **15** in dry CH_3NO_2 for 2 h results in a homogeneous yellow solution. Following the exchange of the NO_3^- counterions for weakly coordinating PF_6^- counterions the formation of the new metallacyclic triangles was initially investigated by ^{31}P and ^{1}H NMR spectroscopy. Analysis of the carbon-rich triangles with $^{31}P\{^{1}H\}$ NMR revealed the presence of a sharp signal around 13.7 ppm, indicating the formation of discrete supramolecules as opposed to oligomeric species. Close examination of the sharp signal, however, revealed that it is in fact composed of two peaks: one high intensity signal at 13.69 ppm and another lower intensity signal at 13.59 ppm (Fig. 7). The observation of two peaks indicates that both carbon-rich diastereomers are present in solution, though more of one stereoisomer is formed than the other. Both peaks are upfield shifted by about 5.3 ppm as compared to the starting 60° acceptor **15** due to back donation from the platinum atoms. Further evidence of back donation and Pt–N coordination was also observed by the



Scheme 7. Self-assembly of 'symmetric' and 'asymmetric' diastereomers of a carbon-rich supramolecular triangle from achiral building-blocks.

decrease in coupling of the ^{195}Pt satellite peaks (ΔJ=109 Hz). Examination of the ^{1}H NMR spectrum also revealed the presence of highly symmetric species, though proton signals were broadened slightly as a result of the presence of two different stereoisomers. It was further observed that hindered Pt–N rotation gives rise to nonequivalent signals for donor **6**, the four protons that point inward with respect to the core of the supramolecular triangle display are shifted slightly relative to the four that point outward (see Supplementary data). Further confirmation of the formation of discrete supramolecular triangles was provided by electro-spray ionization mass spectrometry (ESI-MS). A peak was found at m/z=986.8, corresponding to the $[M-4PF_6^-]^{4+}$ peak of the carbon-rich $A^2{}_3L^2{}_3$ triangle, and the distribution of peaks matched their theoretical values (see Supplementary data) establishing the molecularity of the assembly.

The observation of two peaks of different intensity in the ^{31}P NMR spectrum of the carbon-rich supramolecular triangle can be rationalized through molecular modeling studies. The supramolecular structures of both diastereomers were built within the input mode of the program Maestro v8.01.10 and were subjected to a 1.0 ns molecular dynamics simulation (MMFF force field, 300 K, gas phase) in order to equilibrate their structures, followed by energy minimization to full convergence (Fig. 8). The fully equilibrated and minimized structure of the 'symmetric' supramolecular triangle, having all three donor moieties oriented in the same direction, was found to be 6.9 kcal/mol more stable than the asymmetric supramolecular triangle. This difference in stability likely arises from differences in strain energy induced by the relative orientations of the donor moieties in the two diastereomers. In the asymmetric diastereomer, two of the three donors are oriented opposite to each other, increasing the structural strain in the supramolecule and causing the asymmetric triangle to deviate from a perfectly triangular structure as shown in Figure 8. The aligned arrangement of the three donor moieties in the symmetric triangle distributes and equalizes any strain, resulting in a more stable, and more triangular, structure (Fig. 8). The differences in structural strain can be seen, in part, in comparing the distances between neighboring phenanthrene units as measured from molecular modeling: all three distances are 1.46 nm in the symmetric diastereomer while in the asymmetric diastereomer they range from 1.43 to 1.49 nm. Due to the energetic difference between the two

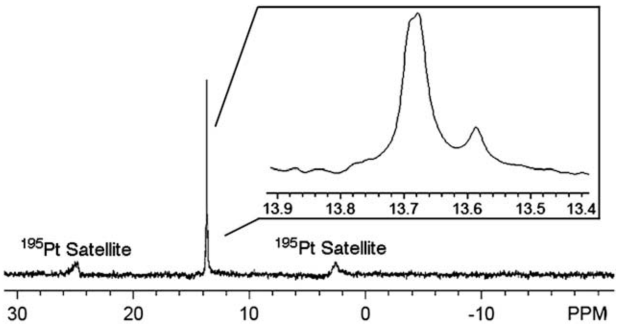


Figure 7. ^{31}P NMR spectrum (121.5 MHz, CD_3COCD_3, 298 K) of the self-assembled carbon-rich supramolecular diastereomers. The inset shows that what appears to be a single sharp peak is actually composed of two peaks of differing intensity, indicating one diastereomer is formed preferentially.

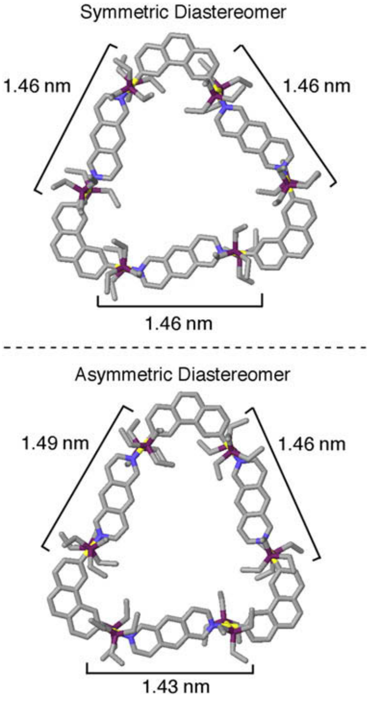


Figure 8. Structures of symmetric and asymmetric diastereomers obtained from molecular modeling. Measurements of the distance between neighboring phenanthrene units partially demonstrates differences in structural strain between the diastereomers. Color scheme: C=grey, N=blue, P=purple, Pt=yellow.

diastereomeric carbon-rich triangles it is likely that the symmetric triangles are formed preferentially, giving rise to the ^{31}P NMR signal of higher intensity, while the less stable asymmetric triangles can be accounted for by the ^{31}P NMR signal of lower intensity.

These results demonstrate how self-assembly may be used to prepare different stereoisomers of carbon-rich supramolecular assemblies from achiral precursors. Though not the first examples of chiral carbon-rich molecules or supramolecules, the preferential formation of one stereoisomer at the expense of another indicates that it may be possible to prepare enantiomerically pure carbon-rich supramolecular assemblies by coordination-driven self-assembly. In addition to structural strain it may be possible to use other driving forces such as electrostatics to bias the formation of one desired stereoisomer. Having the ability to prepare novel, enantiomerically pure carbon-rich compounds in high yield under the mild reaction conditions of self-assembly is very desirable. Experiments aimed at such chiral discrimination during self-organizing self-assembly are currently underway.

6. Conclusions

In conclusion, these examples demonstrate many of the ways in which coordination-driven self-assembly can be used to prepare carbon-rich supramolecular 2D and 3D assemblies. The key characteristics of metal–ligand self-assembly—mild reaction conditions, high yields, thermodynamic control, and a high degree of modularity—combine to make the directional-bonding approach to self-assembly a very valuable addition to the many other synthetic protocols available for the synthesis of carbon-rich materials. While carbon-rich molecular polygons and polyhedra have also been prepared via traditional covalent means—from triangles[71] and rectangles[72] composed purely of aromatic and acetylenic moieties, to molecules such as Kohnkene,[73] to Diederich's synthesis of expanded cubane[74]—the overall number of synthetic steps and yields of such synthesis often limit their practicality. Self-assembly allows access to related supramolecular systems at significantly lower synthetic cost. It has also been demonstrated that coordination-driven self-assembly can be used to prepare diastereomeric supramolecular triangles and that the structural characteristics of these metallacyclic systems are able to bias the formation of one stereoisomer over another. Such observations may lead to the development of methods that utilize self-assembly to form enantiomerically pure carbon-rich supramolecules. Furthermore, the unique geometries and physical, electronic, and magnetic properties of these metal–organic structures open a wide range of potential applications. It is likely that as their solution, solid-state, and surface-confined properties continue to be studied, and as new functionalized examples of this already important class of compounds continue to be investigated, researchers will find an ever widening number of applications in materials and nanosciences. They are certainly a welcome recent addition to the diverse world of carbon-rich materials.

7. Experimental

7.1. Self-assembly of diastereomeric supramolecular triangles

The 2,6-diazaanthracene donor **6** and 60° Pt(II) acceptor **15** were prepared according to the literature procedures.[21,29] In a glass vial equipped with a magnetic stir bar was placed **15** (32.2 mg, 0.0277 mmol). In another glass vial was placed solid **6** (5.0 mg, 0.0277 mmol). Donor **6** was then dissolved in 0.5 mL dry CH_3NO_2, transferred to the vial with acceptor **15**, and then washed with additional CH_3NO_2 (3×0.5 mL) to ensure quantitative transfer. The suspension was stirred for 5 h at room temperature, resulting in a homogeneous clear yellow solution. The solvent was removed under reduced pressure, the NO_3^- counterions were exchanged for PF_6^- using a concentrated aqueous solution of KPF_6, and the resulting precipitate was dried to completeness. Yield 39 mg (yellow solid), 93%. ^{1}H NMR (CD_3COCD_3, 300 MHz): δ 10.43 (s, 3H, H_e), 10.42 (s, 3H, $H_{e'}$), 9.58 (s, 3H, H_f), 9.54 (s, 3H, $H_{f'}$), 9.20–9.13 (m, 6H, H_H), 9.03–8.93 (m, 6H, H_g), 8.61 (br, 6H, H_a), 7.86 (d, 6H, H_b, J=7.7 Hz), 7.75 (d, 6H, H_c, J=7.7 Hz), 7.71 (s, 6H, H_d), 1.42 (m, 72H, PCH_2CH_3), 1.19 (m, 108H, PCH_2CH_3). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 121.4 MHz): δ 13.7 (major), 13.6 (minor) ($^1J_{Pt-P}$=2662.7 Hz). MS (ESI) calcd for $[M-4PF_6]^{4+}$ m/z 986.8, found 986.8.

The majority of synthetic procedures outlined in Schemes 1–6 involve the self-assembly of pyridyl or nitryl donors and Pt(II) metal acceptors as either their OTf^- or NO_3^- salts. The following two synthetic self-assembly protocols, one for a Pt(II) triflate salt and one for a Pt(II) nitrate salt, serve as representative examples of the procedures used to prepare 2D and 3D supramolecules.

7.2. Self-assembly of supramolecular rectangles[24]

In a glass vial equipped with a magnetic stir bar were placed solid 1,8-bis(*trans*-$Pt(PEt_3)_2(NO_3)$)anthracene (**14**) (20.0 mg, 0.0172 mmol) and an equimolar amount of the appropriate linear bridging ligand (e.g., **4**, **10**, **11**, **13**). Next, 0.5 mL of CD_3COCD_3 and 0.5 mL of D_2O were added to the vial, which was then sealed with Teflon tape and heated in an oil bath at 50–55 °C, with stirring. After 10–15 h, the initial pale yellow suspension gradually turned bright orange and became homogeneous. The orange solution was then transferred to an NMR tube for analysis. The product was precipitated with KPF_6, collected on a frit, washed with excess water, and dried in vacuo.

7.3. Self-assembly of an $A^2{}_6L^2{}_6$ supramolecular hexagon[30]

In a glass vial equipped with a magnetic stir bar were placed solid bis(4-*trans*-$Pt(PEt_3)_2(OTf)_2$)methanone (**17**) (20.0 mg, 0.0149 mmol) and 4,4′-bipyridyl (**4**) (2.3 mg, 0.0149 mmol). Next, 1.0 mL of CD_2Cl_2 was added to the vial, which was then stirred at 298 K for 30 min, resulting in quantitative formation (as observed by ^{1}H and ^{31}P NMR spectroscopy) of the desired supramolecular hexagon.

For details of the synthetic procedures used in the preparation of **1**–**37** please see the original texts.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.08.062.

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