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Performance of energy storage devices: potential areas for dendritic chemistry involvement

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US007250534B1

(12) **United States Patent**
Newkome

(10) **Patent No.:** **US 7,250,534 B1**
(45) **Date of Patent:** **Jul. 31, 2007**

(54) **PERFORMANCE OF ENERGY STORAGE
DEVICES: POTENTIAL AREAS FOR
DENDRITIC CHEMISTRY INVOLVEMENT**

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(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 240 days.

- (21) Appl. No.: **10/049,259**
(22) PCT Filed: **Jul. 20, 2000**
(86) PCT No.: **PCT/US00/40431**

§ 371 (c)(1),
(2), (4) Date: **Apr. 23, 2002**

- (87) PCT Pub. No.: **WO01/07497**
PCT Pub. Date: **Feb. 1, 2001**

Related U.S. Application Data

- (63) Continuation-in-part of application No. 09/646,737,
filed on Nov. 22, 2000, now Pat. No. 6,399,717.
(60) Provisional application No. 60/145,785, filed on Jul.
27, 1999.
(51) **Int. Cl.**
C07C 209/16 (2006.01)
C07C 209/34 (2006.01)
C07C 213/02 (2006.01)
(52) **U.S. Cl.** **564/495; 528/422; 528/495;**
977/754
(58) **Field of Classification Search** **525/451**
See application file for complete search history.

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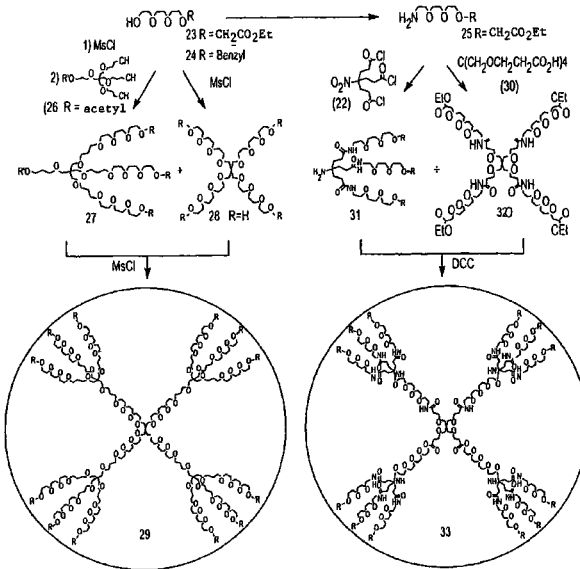
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(57) **ABSTRACT**

A compound consists of a fractal-like, plain or organometallic array useful for energy storage devices. A dendrimer useful in the synthesis of the fractal-like compound includes a single ligating moiety bound to a surface of each quadrant of the dendrimer. A method of making metallo-based (macro) molecules includes the steps of combining monomers selected from the group consisting of bipyridal- and terpyridal-based ligands with connecting metals and self assembling macrocycles wherein the monomers are interconnected by the metals.

2 Claims, 10 Drawing Sheets



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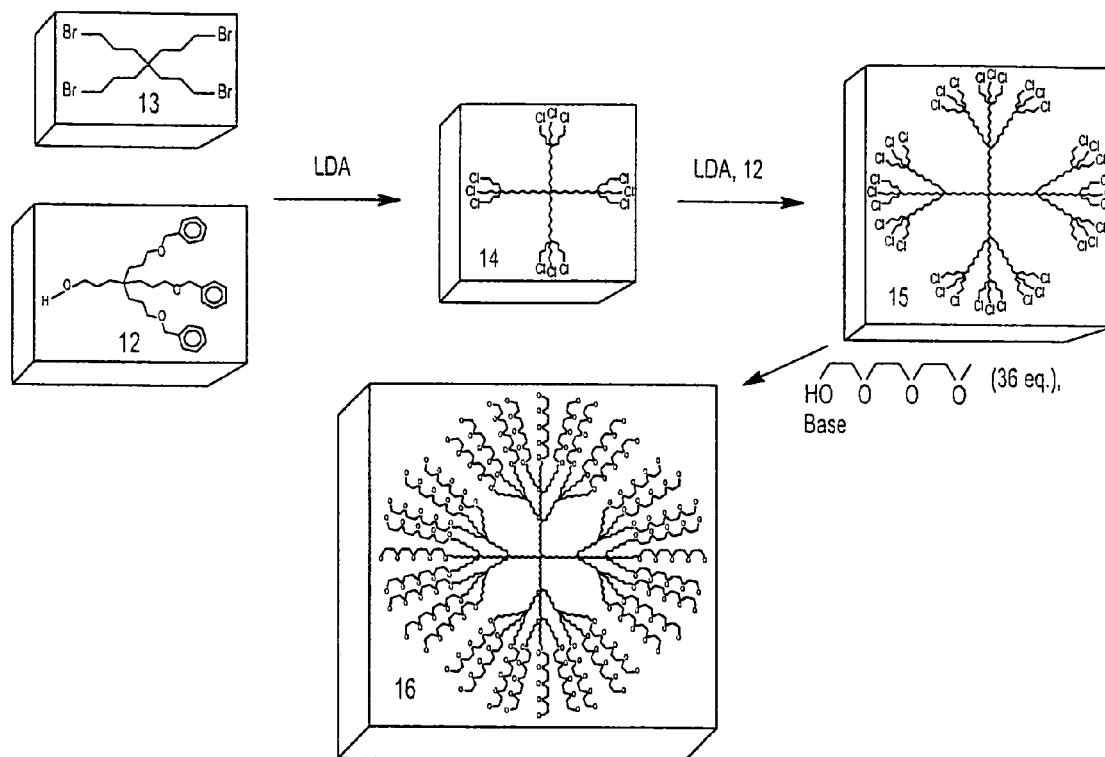


Figure 1

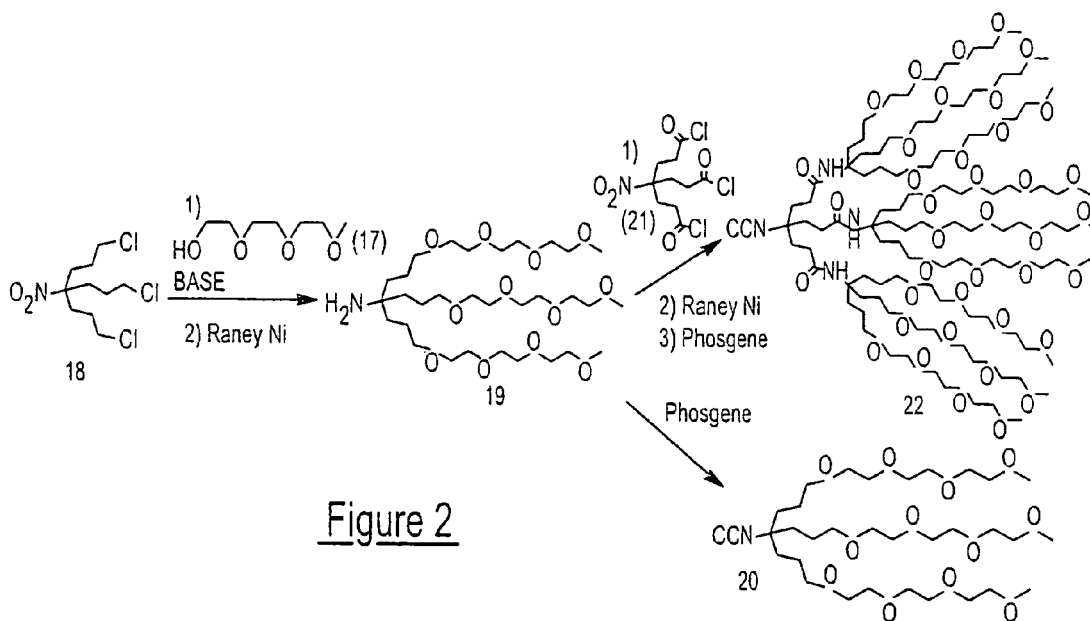


Figure 2

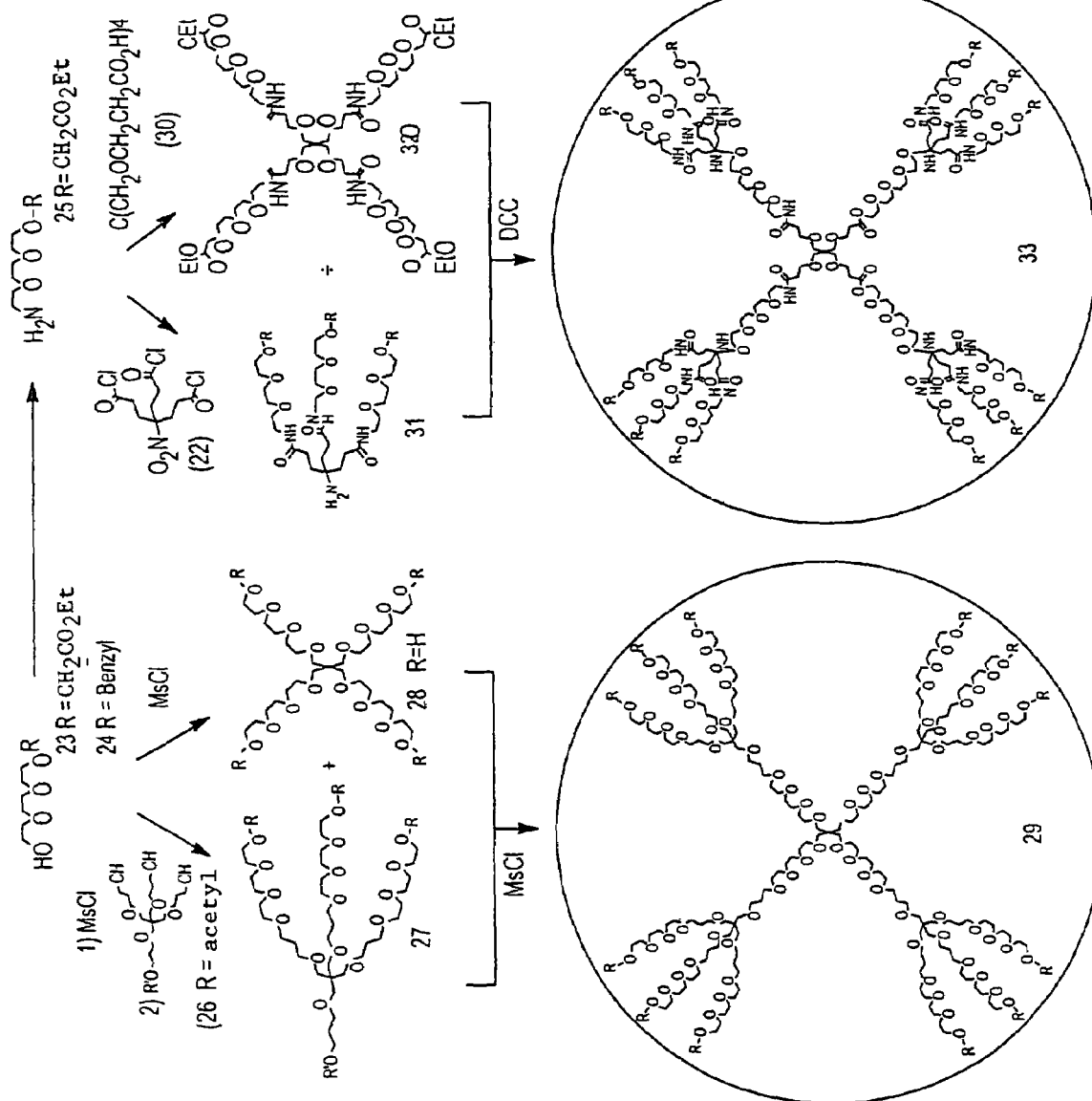
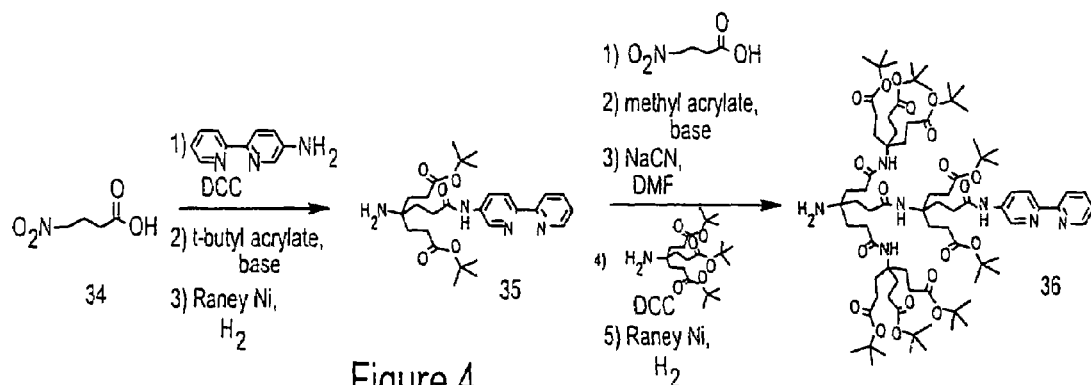
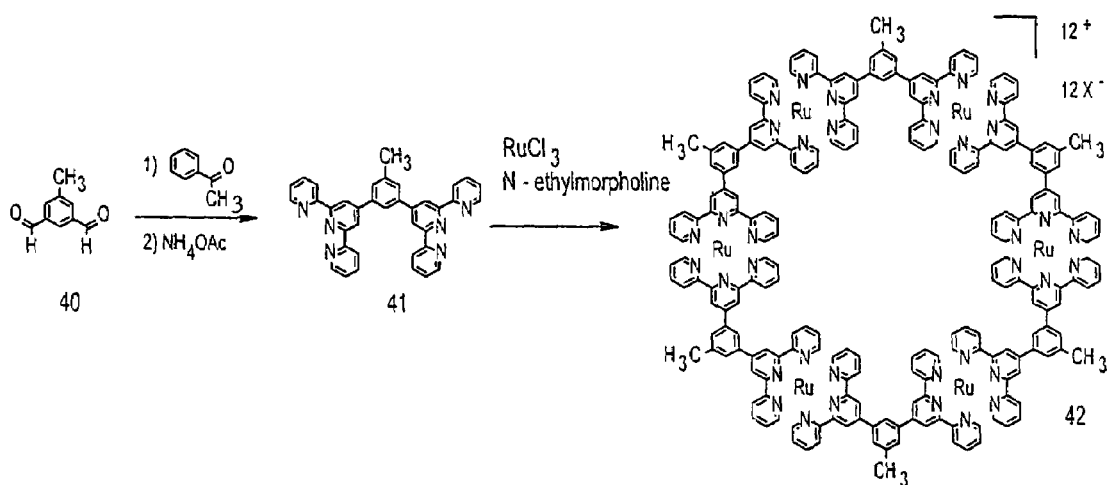


Figure 3

Figure 4Figure 6

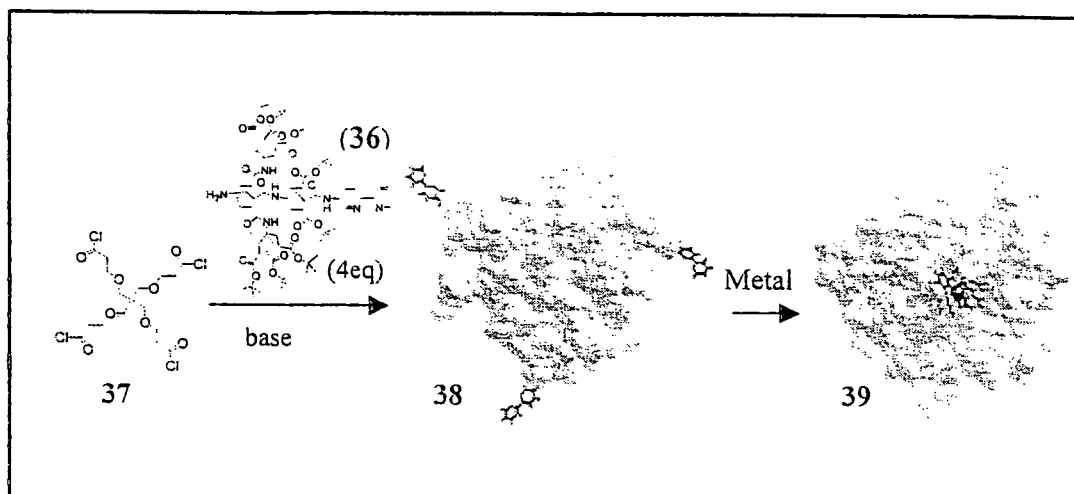


Figure 5

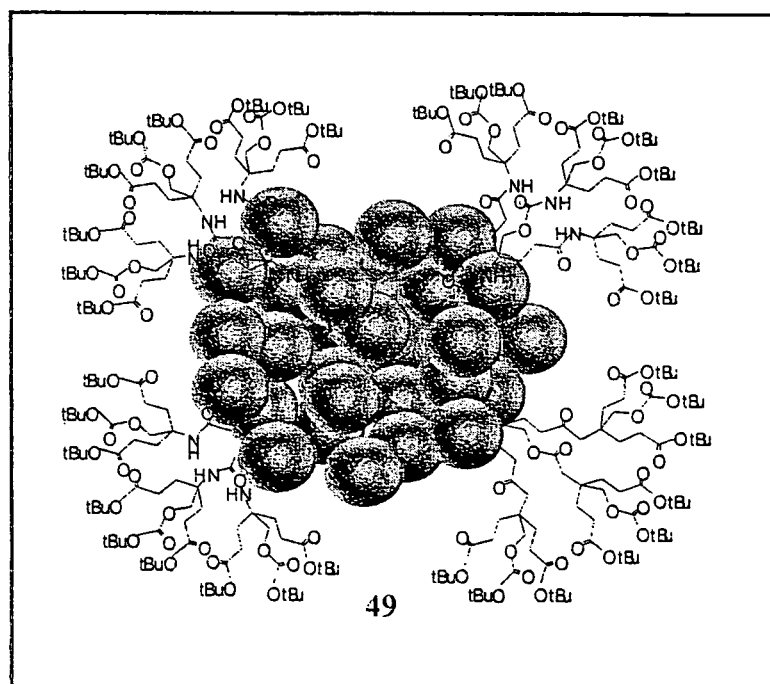
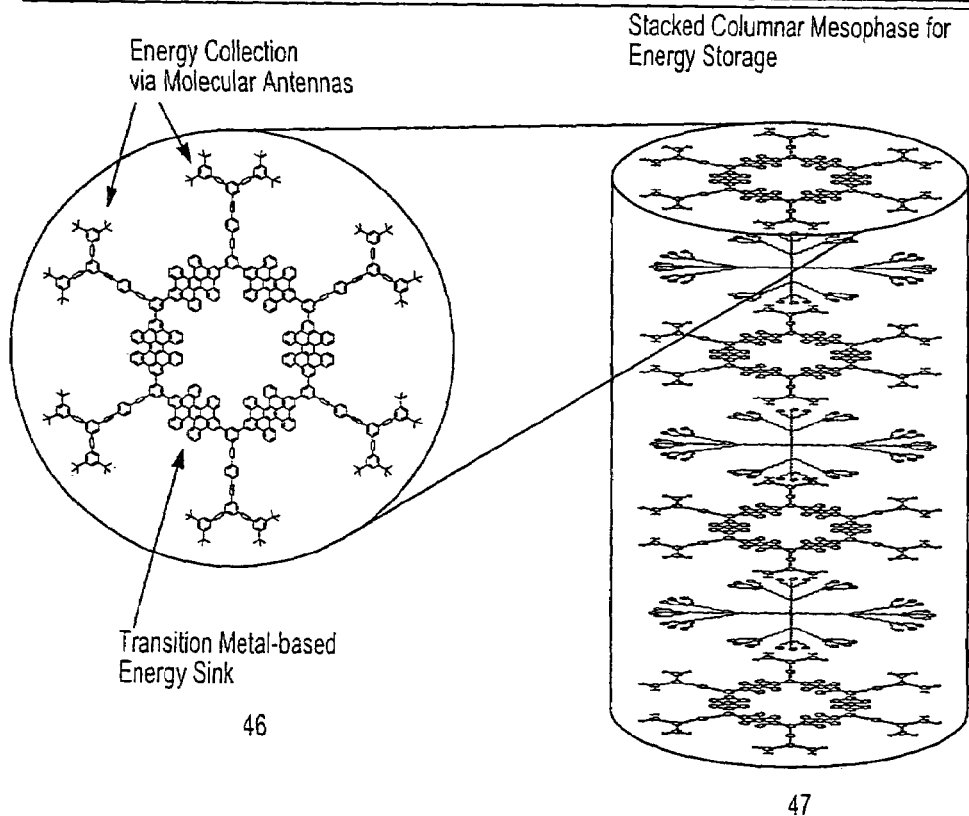
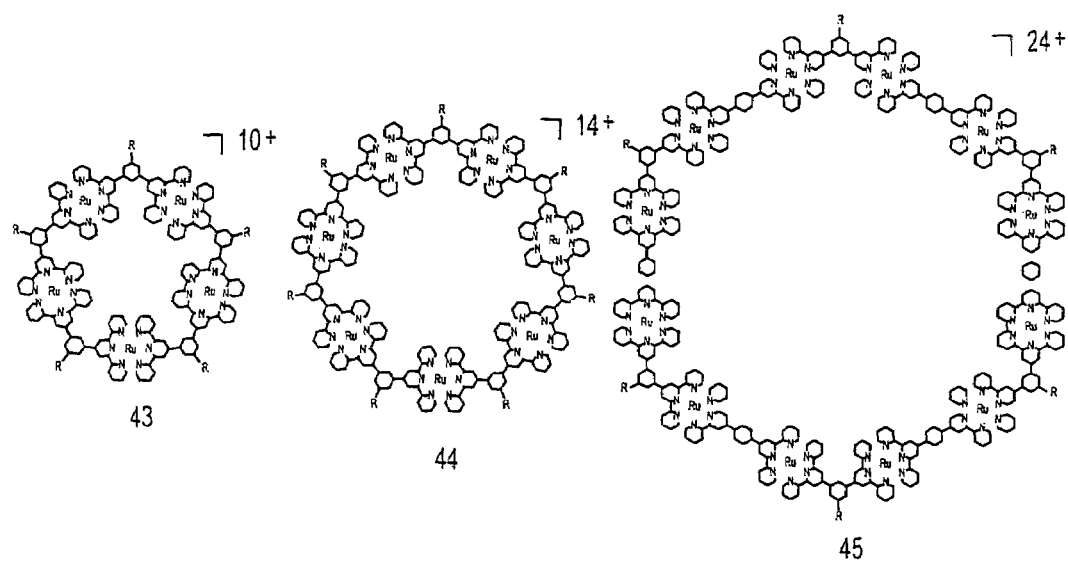
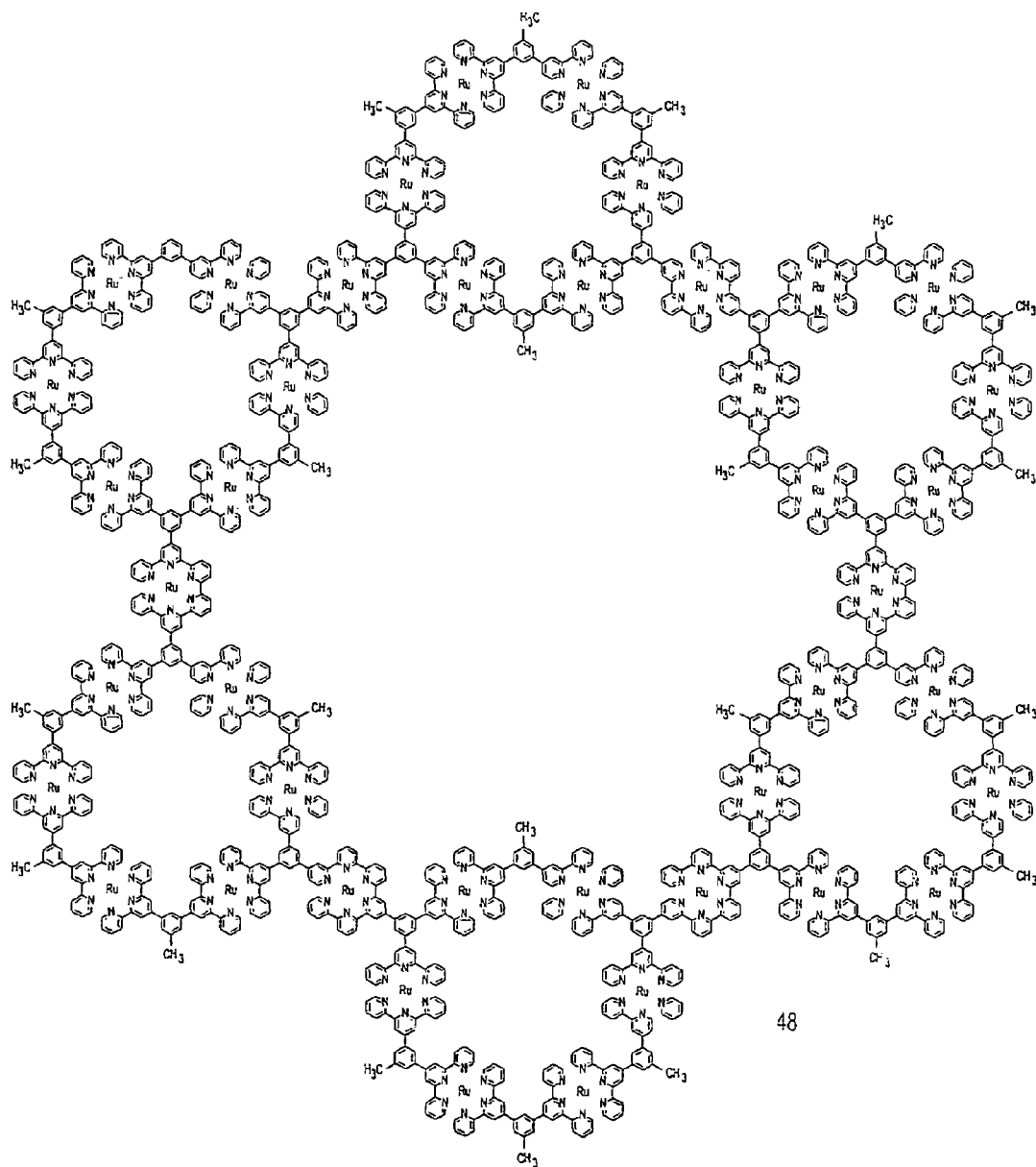


Figure 9

Figure 7

Figure 8

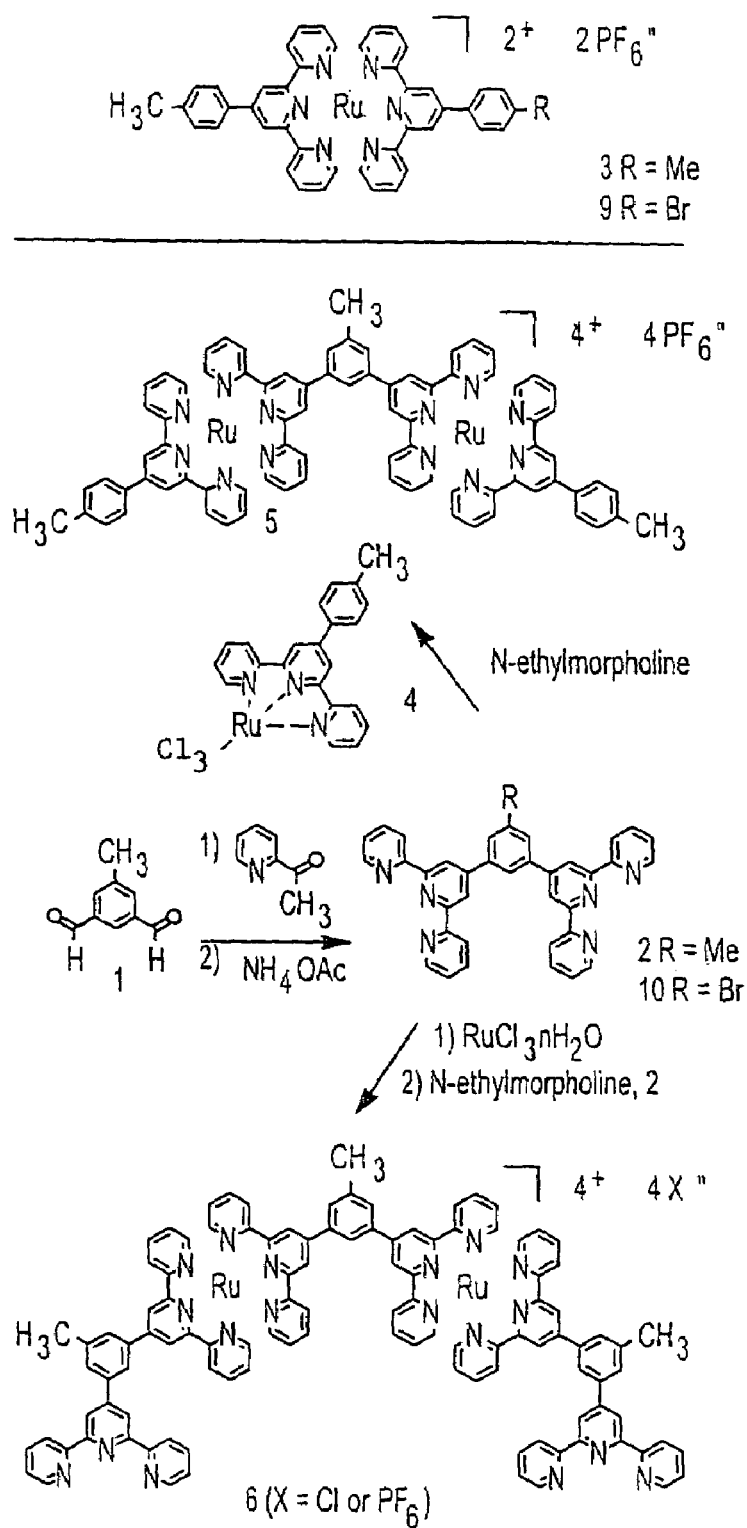


Figure 10

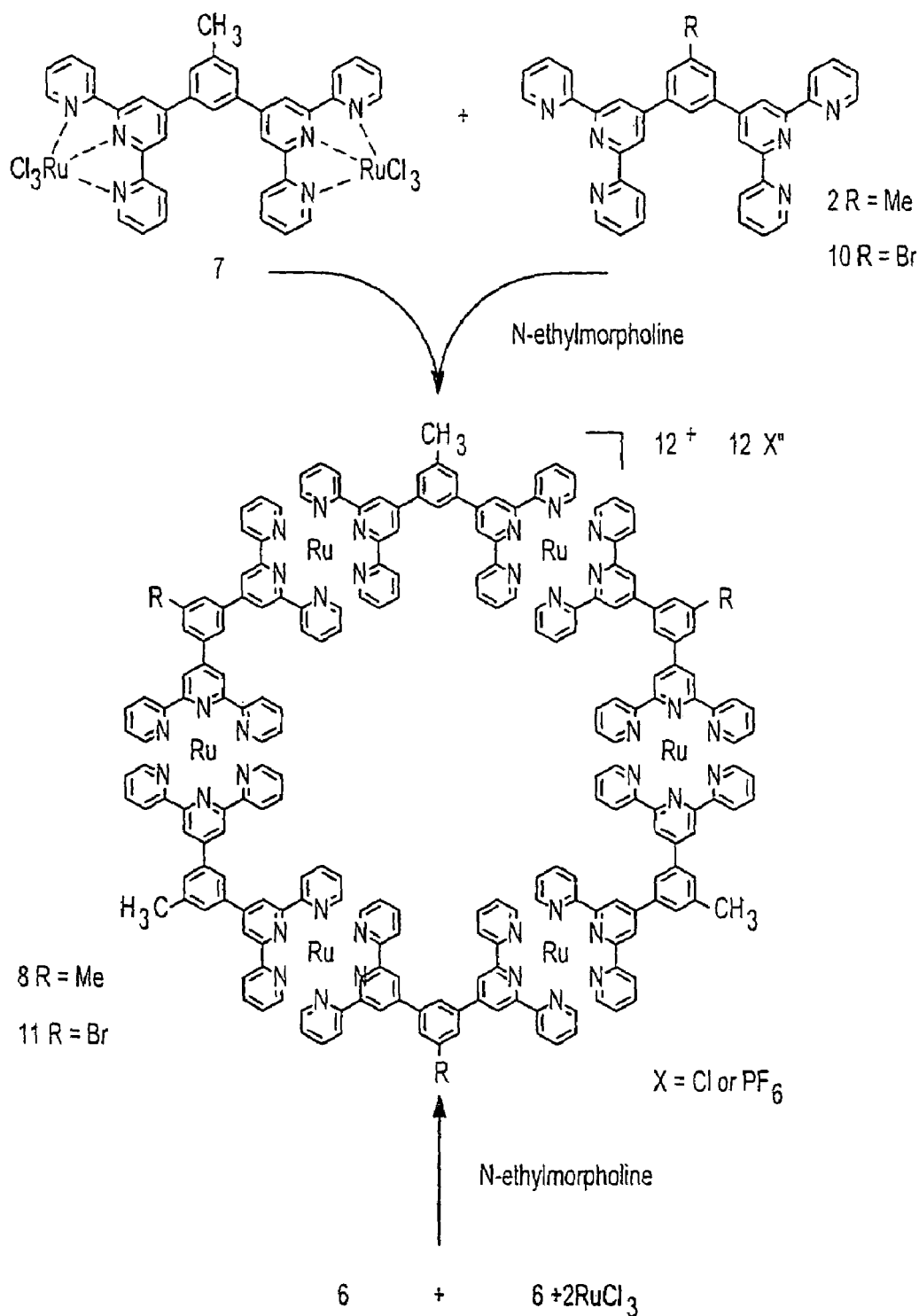
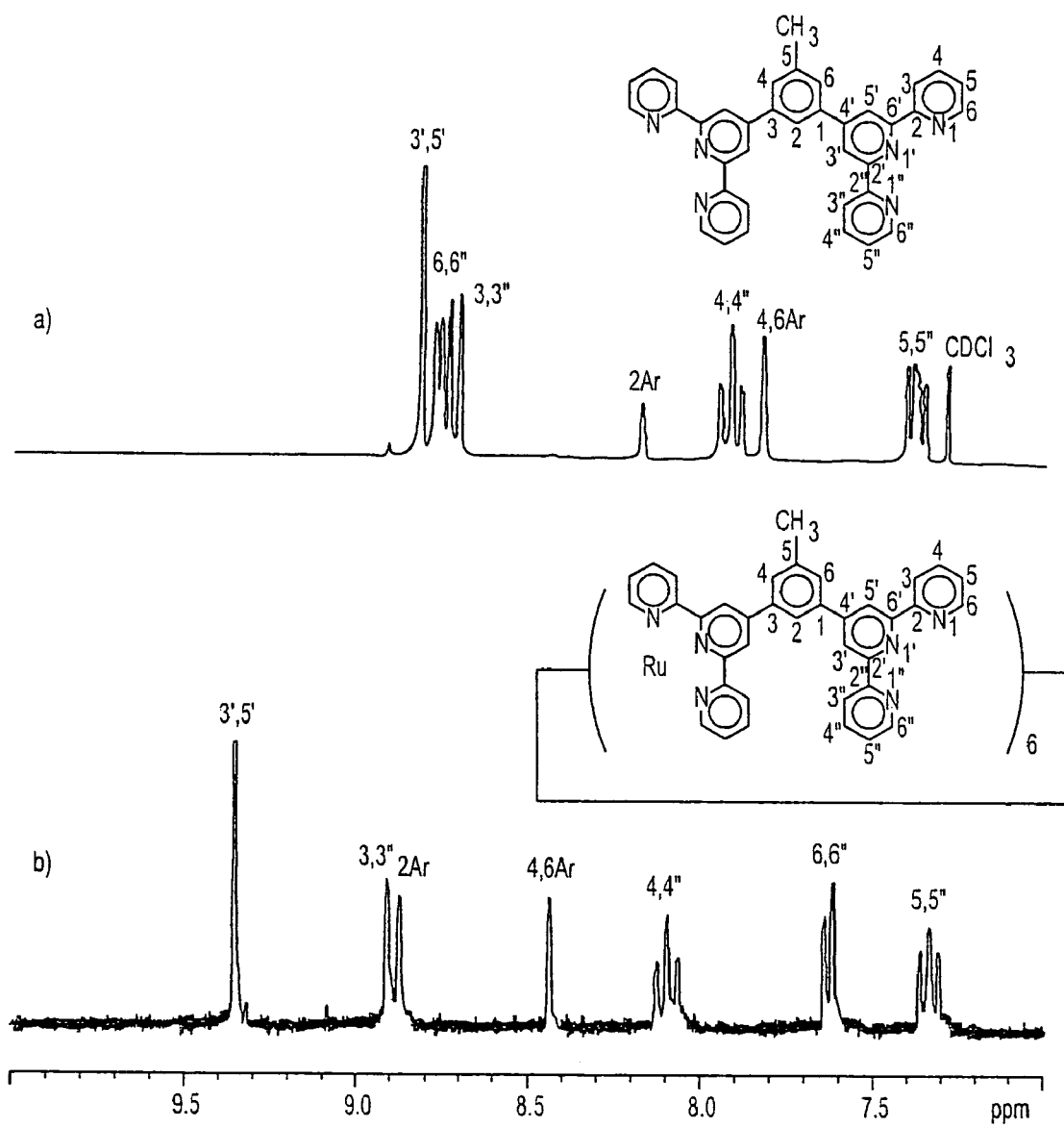


Figure 11



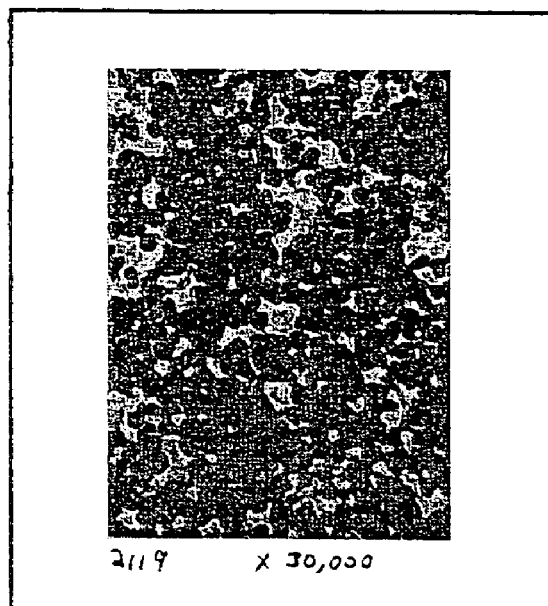


Figure 12A

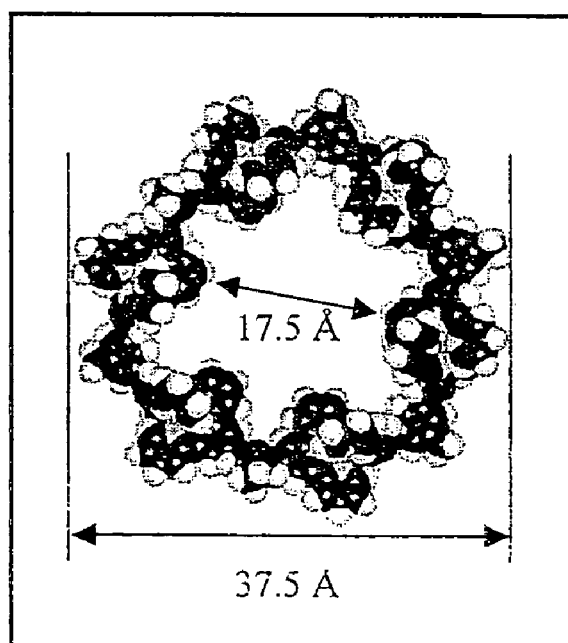


Figure 12B

PERFORMANCE OF ENERGY STORAGE DEVICES: POTENTIAL AREAS FOR DENDRITIC CHEMISTRY INVOLVEMENT

CROSS REFERENCE TO RELATED APPLICATIONS

The present application is the National Stage State, under 35. U.S.C. 371, of PCT/US00/40431, filed Jul. 20, 2000, which claims the benefit of priority to U.S. Provisional Patent Application No. 60/145,785, filed Jul. 27, 1999, and is also a continuation-in-part of U.S. patent application Ser. No. 09/646,737, filed Nov. 22, 2000 now U.S. Pat. No. 6,399,717, which claims the benefit of priority to U.S. Provisional Patent Application No. 60/079,413, filed Mar. 26, 1998, all of which are incorporated herein by reference.

TECHNICAL FIELD

The present invention relates to dendritic materials for use in energy storage devices. More specifically, the present invention relates to branched macromolecules for use as enhanced electrolyte and electrocomponents in solid state energy storage devices.

BACKGROUND OF THE INVENTION

The present invention relates to the melding of iterative synthetic protocols with more mature research arenas for the production of is utilitarian materials. Accordingly, the present invention combines the areas of dendrimers, combinatorial chemistry, and dendrimer-based electrolyte material chemistry and applies the same to the utilitarian arena of electrocomponents and enhanced electrolyte capability in solid state energy storage devices. Hence, each of these fields is addressed as the present invention provides improvements resulting from a synergy of advancements in each of these fields in combination.

By way of background, rapid advancement in the field of "dendritic chemistry" (Newkome et al., VCH: Weinheim, Germany, 1996) has afforded scientists with a new arsenal of techniques for the construction of utilitarian materials. Testament to interest in this burgeoning area is evidenced by ubiquitous literature reports on the subject since its discovery (1978) and commencing rise (mid-1980s). Central to dendritic chemistry is the "iterative synthetic methodology", which has afforded new pathways to the construction of complex, high molecular weight molecules.

The realization of "dendrimers", and related constructs such as "hyperbranched" polymers (Hult et al., 1999) and "dendrimer-polymer hybrids", (Roovers et al., 1999) has thus facilitated advances in the ability to design and build architecturally homogeneous branched molecular assemblies.

There are inherent limitations imposed on these structures due primarily to 1) the repetitive application of a single building block for tier construction leading to functional group uniformity on the surface, as well as the interior, of the branched structure and 2) a lack of interchangeable monomers that would facilitate the incorporation of diverse application oriented functionality and thus allow the creation of utilitarian assemblies.

These limitations are addressed via 1) the development of a "modular" set of application-oriented branched building blocks for dendritic synthesis (Young et al., 1994) aimed directly at enhanced solid-state energy storage and release devices (e.g., lithium battery performance); 2) the use of combinatorial-based tier construction techniques (Newkome et al., Isocyanate-Based Dendritic Building Blocks: Combinatorial Tier Construction and Macromolecular Property

Modification, *Angew. Chem., Int. Ed. Engl.*, 1998) for the creation of unimolecular, multi-component assemblies whereby the individual components can act in concert to produce a desired physicochemical effect, and 3) use of branched architectures to fabricate, template, and stabilize metal and non-metal particles, composites, and clusters.

Specifically, advancement in lithium- and lithium rocking chair-battery efficiency (Lipkowski et al., 1994; Owen, J. R., 1997) is shown to result from 1) improved electrolyte materials based on highly stable, polyethylene glycol functionalized, saturated hydrocarbon-type dendrimers, and 2) significantly reduced inter-electrode separations. Ultimately, this has led to branched assemblies possessing mutually compatible and synergistic units capable of triggered electrochemical discharge. This forms the basis of a logical evolution of iterative chemistry that melds the maturity of classical polymer, organic, and inorganic chemistries, as well as emerging fields that include "C₆₀" technology, with the strengths of dendritic chemistry.

To date, a diverse set of branched monomers have been crafted for the introduction of 1) high-density surfaces and 2) "latent" functionality to be used, or activated, after primary dendritic construction, including: terpyridine (Newkome, et al., *J. Mater. Chem.* 1997; Newkome et al., *Chem. Commun.* 1998) arylamine hexaester; (Newkome et al., Synlett 1992) arylaminoterpyridyltriester, (Newkome et al., *Chem. Commun.* 1999) and arylinitroanthraquinonoid (Narayanan et al., 1999; Newkome et al., *Designed Monomers and Polymers*, 1999; Newkome et al., *Macromolecules*, 1999; Newkome et al., *Macromolecules*, 1997).

Additionally, applicants have recently reported the preparation of β -cyclodextrin branched building blocks has recently reported (5) for use in self-assembly studies predicated on molecular recognition and host-guest inclusion. (Newkome et al., *Chem. Commun.*, 1998).

A novel family of isocyanate, 1 \rightarrow 3 branched buildings blocks has been developed and reported (Newkome et al., U.S. Pat. No. 4,154,853, 1992; Newkome et al., *Angew. Chem., Int. Ed. Engl.*, 1991; Newkome et al., *Chem. Commun.*, 1996; Newkome et al., *Tetrahedron Lett.*, 1997; Newkome et al., *Designed Monomers and Polymers*, 1997) that allows 1) rapid physicochemical modifications of diverse macromaterials (Newkome et al., *Chem. Commun.*, 1996) and 2) "combinatorial-based" multiple functional group incorporation. (Newkome et al., *Combinatorial Chem.*, 1999; Newkome et al., U.S. Pat. No. 5,886,126, 1999; Newkome et al., U.S. Pat. No. 5,886,127, 1999). Each member of this series relies on an isocyanate moiety for monomer connectivity. Steric demands associated with the adjacent branch junctures give rise to unprecedented isocyanate stability. These materials are generally solids that are stable in air, which facilitates handling and storage. For example, the isocyanatotriester is a white crystalline solid (mp 60–62° C.) that reacts readily with amines and requires slightly more vigorous conditions to react with alcohols; its crystal structure has been reported. (Newkome et al., *Tetrahedron Lett.*, 1997).

Eloquent work in the area of self-assembly by Stang (1), Lehn (2), and many others (3–7), has prompted our investigation of the potential to spontaneously construct Ru-based (macro)molecules. More specifically, our goal involved the design and preparation of polyterpyridyl ligands that would form the basis of a "modular building block set" (8) capable of being used to access "higher order" (fractal) architectures. We herein report the construction of a bis(terpyridine) monomer that facilitates the preparation of hexaruthenium macrocycles.

Linear bis(terpyridyl) monomers have been employed for the formation of layered polyelectrolyte films (9), Ru(II)-based dendrimers (10), helixing ligands (11), grids (12),

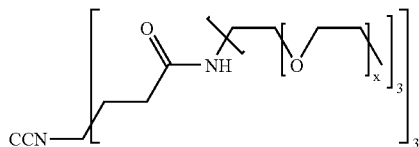
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racks (13), and photoactive molecular-scale wires (14), to mention but a few. Whereas, progress in directed synthesis of cyclic rigid structures can be found in "shape persistent" phenylacetylenes (15-17), diethynylbenzene macrocycles (18), and a 24 phenylene hexagon (19), advances via self-assembly has yielded, for example, chiral (20) and achiral (21) circular helicates, cylindrical cage structures (22), Pt-coordinated bipyridyl squares (23), and metal-templated [2]catenanes (24, 25), and cyclic porphyrin trimers (26).

In view of the above, it is desirable to develop further compounds, and in the larger sense, various means for improving and enhancing electrolyte and electrocomponents in solid state, energy storage devices. It would be desirable to be able to meld together iterative processes utilized in dendritic chemistry with combinatorial processes which have also been highly developed in dendritic chemistry towards multiple unit positioning within dendritic structures and other architectures in order to obtain improvements and enhancements.

SUMMARY OF THE INVENTION

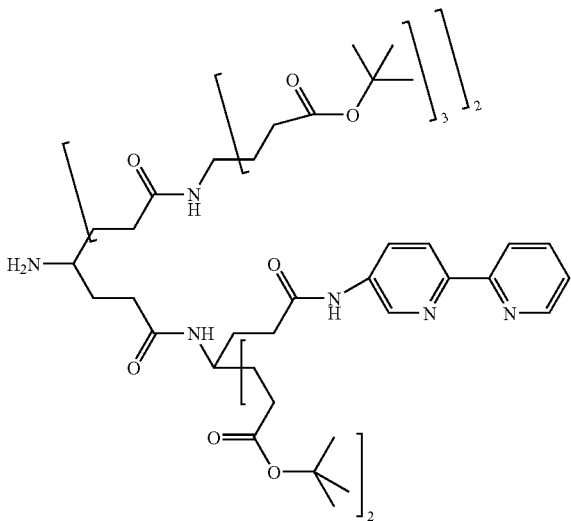
According to the present invention, there is provided a compound of the formula



wherein x is an integer from 1 to 4.

A method of making dendrimer frameworks includes the steps of reacting and converting a triethylene glycol and then coupling it and subsequently reducing the building block, followed by forming a dendrimer core and reacting the building block with the dendrimer core to yield a first generation dendrimer.

The present invention further provides a monomer of the formula



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More generally, a dendrimer is provided including a single ligating moiety bound to a surface of each quadrant of the dendrimer.

A dendrimer is further provided which is a nanocrystallite.

A method of making metallo-based (macro)molecules includes the steps of providing monomers selected from the group consisting of bipyridyl- and terpyridyl-based ligands with connecting metals and self-assembling macrocycles wherein the monomers are interconnected by the metals.

Finally, a compound is provided which consists of a fractal-like, planar organometallic array.

BRIEF DESCRIPTION OF THE DRAWINGS

Other advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

FIG. 1 shows the construction of PEG-terminated hydrocarbon-based dendrimers;

FIG. 2 shows the preparation of isocyanate-based, branched PEG monomers;

FIG. 3 shows the synthesis of PEG dendrimer framework;

FIG. 4 shows the synthesis of a second generation bipyridyl-capped monomer;

FIG. 5 shows the synthesis of a tetrabipyridine-terminated dendrimer for investigating macromolecular torsional behavior, the fourth, uncomplexed bipyridine not being shown;

FIG. 6 shows the self-assembly synthesis of a hexa-Ru(II) cluster;

FIG. 7 shows structures for energy collection and storage made in accordance with the present invention;

FIG. 8 shows a second generation fractal polymer made in accordance with the present invention;

FIG. 9 shows a dendritic nano-cluster templating and stabilization made in accordance with the present invention;

FIG. 10 shows the synthesis of the key monomer and primer for macro cycle construction in accordance with the present invention;

FIG. 11 shows the self- and directed-synthesis of macro cycles in accordance with the present invention;

FIG. 12 shows the ¹H NMR spectra of the bis(terpyridine) ligand and self assembled hexaRu(II) complex made in accordance with the present invention;

FIG. 12A shows an electron micrograph of a regularly shaped aggregate; and

FIG. 12B shows a computer generated cpk model of a macro cycle made in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Generally, the present invention provides several generic concepts and several further specific compounds and methods of making compounds, all in combination significantly advancing the art of electrolyte and electrocomponents in solid state, energy storage devices. The methods disclosed below are useful for manufacturing either monomers used as building blocks to create compounds or the compounds per se, which are useful as electrolytes in energy storage devices. Such compounds useful in energy storage devices are capable of encapsulating, entraining, and stabilizing metal and non-metal nanoclusters for use in electromaterials and surfaces. Such materials, by use of combinatorial-based

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synthetic techniques, are disclosed herein which allow for the preparation and rapid testing of heterogeneously functionalized branched assemblies with tunable physiochemical properties. Such tunable physiochemical properties allow for the maximization of enhanced electrolyte capability of stackable compounds capable of energy storage and release through the metals retained thereby.

While numerous routes and electrolyte architectures can be envisioned, four approaches are described which allow access to these materials. More specifically, dendritic polymer-based electrolyte materials, as shown in FIG. 1, are predicated on the use of the process for construction of all-saturated hydrocarbon dendrimers (Newkome et al., U.S. Pat. No. 5,154,853, 1992; Newkome et al., *Unimolecular micelles*, Angew. Chem., Int. Ed. Engl., 1991; Newkome et al., *Alkane Cascade is Polymers Possessing Micellar Topology: Micellanoic Acid Derivatives*, Angew. Chem., Int. Ed. Engl. 1991) (i.e., **14** and **15** that are prepared from monomers **12** and **13** via sequential alkylation, reduction, and halogenation) and the attachment of polyethylene glycol units on the dendrimer surface. Polyethylene glycol (PEG) units can be easily attached to dendrimers and building blocks via the well established Williamson synthesis (Buckmann et al., 1981; Burns et al., 1999) to afford PEG-modified dendrimers (**16**). Examination of these materials in concert with added "free" salts (Lipkowski et al., 1994; Owen, J. R., 1997; Salomon, M., 1998; Cisak et al., 1993) [e.g., LiClO_4 , LiCF_3SO_3 , LiPF_6 , $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, and $\text{LiC}(\text{SO}_2\text{CF}_3)_3$] is planned. PEG commercial availability allows access to a variety of chain lengths.

Saturated hydrocarbon frameworks are effectively inert towards oxidizing and reducing conditions. Hence, it is expected that improved electrolyte stability, more efficient Li-ion transport, and decreased electrolyte layer thickness will result in greater specific energy, energy density, and battery cycle life. (Owen, J. R., 1997) Specific present pitfalls (Lipkowski et al., 1994) addressed by this technology are (a) stability towards highly oxidizing and reducing environments [i.e., at the anode and cathode interfaces due to the absence of reactive functional groups such as NH , OH , etc.]; (b) electrolyte crystallinity and brittleness [i.e., such as found with LiI and some other polymeric matrices]; (c) mechanical strength; (d) charge and discharge temperature range operation; (e) electrolyte layer thickness [inter-electrode gaps corresponding to $\sim 10^{-8}$ to 10^{-9} m are envisioned assuming a dendrimer radius of 20–25 Å]; (f) lithium plating [“dendrite” formation should be reduced in a more electrochemically stable electrolyte region]; and (f) safety [environmental as well as operational].

Synthesis of branched PEG architectures is shown in FIG. 2. Monomers allowing for attachment of the polyether moieties to a wide array of surfaces and preconstructed dendrimers are prepared by employing the branched monomer design and isocyanate technology. (Newkome et al., *Isocyanate-Based Dendritic Building Blocks: Combinatorial Tier Construction and Macromolecular Property Modification*, Angew. Chem., Int. Ed. Engl. 1998; Newkome et al., *Designed Monomers and Polymers*, 1997; Newkome et al., U.S. Pat. No. 5,773,551, 1998) For example, monomethylated triethylene glycol (**17**: prepared via reaction of the glycol with 1 equivalent of MeI) can be reacted with the known nitrotrichloride (**18**) (Newkome et al., *Synthesis*, 1991) to give the nitrotris (triethylene glycol) (not shown) that can be reduced to afford the corresponding amine **19**. Treatment of this amine with phosgene (or a phosgene equivalent such as di- or triphosgene) yields isocyanate **20**. A second generation dendron can be accessed via coupling

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of amine **19** with nitrotris (acid chloride) **21**. Subsequent reduction of the nitro moiety and treatment with phosgene gives an isocyanate monomer possessing 9 PEG units (**22**).

Triethylene glycol units were prepared possessing terminally modified, complementary reactive and inert moieties (FIG. 3). Triethylene glycol was reacted separately with ethyl diazoacetate and benzyl chloride to afford ester **23** and benzyl ether **24**, respectively. The free hydroxyl group of monofunctionalized glyco (**23**) was then converted to the corresponding amine via established procedures. Thus treatment of alcohol **23** sequentially with mesyl chloride (MsCl) and sodium azide (NaN_3) followed by catalytic hydrogenation ($\text{Pd}-\text{C}, \text{H}_2$) yielded amine **25**.

PEG-based dendrimers, possessing polyether units throughout the dendritic structure, are accessible via use of these modified polyethers. For example transforming alcohol **24** to the 1→3 branched monomer **27** via conversion of **24** to the mesylate and reaction triol **26** (obtained by reduction of the corresponding tetraacid followed by treatment with one equivalent of acetyl chloride; a monosubstituted pentaerythritol can also be employed). Reaction of the same mesylate with pentaerythritol followed by reductive debenzoylation should yield core **28**. Basic deprotection of the acetyl moiety on monomer **27**, transformation to the mesylate, and attachment to tetraol **28** provides the first tier polyether dendrimer **29**. Repetition of the sequence allows access to higher generations.

In a complementary scheme, PEG-based dendrimer **18** is constructed using amide-based monomer connectivity. Amide versus ester based connectivity was chosen due to the greater stability of the $\text{C}(\text{O})-\text{N}$ bond. Thus, coupling aminoester **25** with nitrotris(acid chloride) **21** and subsequently reducing the nitro group should afford aminotriester **31**. The corresponding core **32** can then be accessed by reaction of the traacid **30** with four equivalents of amino **25**. Selective ester hydrolysis of core **32** followed by coupling of monomer **31** is anticipated to yield the first generation dendrimer **33**.

Based on the high yields (generally 80–90%) of the reactions to access the building blocks and dendrimers in Scheme 3 and the commercial availability of diverse polyethylene glycol homologs, a wide latitude in structural design is attainable.

In view of the above, the present invention provides novel PEG dendrimer frameworks and methods of making the same. It should be noted that such methods can be utilized in homologous synthesis; that is, such methods can be utilized to synthesize homologues by modifications of a method well known in the art.

Further, the above methods demonstrate the ability of the present invention to produce a wide array of surfaces and preconstructed dendrimers employing branched monomer design and isocyanate technology developed by applicants. Such compounds can have a flat architecture capable of stacking, such being inert towards oxidizing and reducing conditions. Thus, they can provide improved electrolyte stability and more efficient Li-ion transport and decreased electrolyte layer thickness. This results in greater specific energy, energy density, and battery cycle life, as demonstrated by the prior art discussed above.

The present invention further provides combinatorial methods utilized toward the synthesis of multiple unit positioning.

While intra- and inter-molecular “multiple structural element positioning” is in its infancy, foundations rooted in such areas as molecular recognition and other non-covalent interactions suggest a host of potential architectures. For

example, structural units can be held in precise juxtaposition via rigid control units (Zhang et al., 1992; Zhang et al., 1994) that bind branched units via H-bond-based molecular recognition (Newkome et al., *Chem. Commun.*, 1996) or, more simplistically, an 'event' (chemical or physical) can be effected via absorption of molecular guests that fill internal void regions and cause branch chain movement. A simple analogy is found in well known polymer swelling. Competition for binding sites and compartments can form the basis for "molecular triggers."

Additionally, a fundamental property of branched macromolecules that is useful for the construction of "next generation" materials is revealed via consideration of the allowed bond rotations (torsions) within these structures. (Newkome et al., *Combinatorial Chem.*, 1999, in press) This suggests molecular surfaces that are "dynamic" whereby terminal units can at one instant be separated as far as physically possible and in another moment these same units are nearest adjacent neighbors. Essentially, movement of terminal groups or units about the surface of the branched superstructure is predicated on simple bond rotations which can be effected by "logical constants." This dynamic property, which conceptually imparts a "Rubik's sphere" character to these unique molecules, can be controlled by the use of logical constraints (i.e., site-specific molecular recognition, disruption of internal H-bonding, swelling in void regions, etc.) to facilitate construction of macromolecular assemblies with controllable functional unit positions.

"Combinatorially" prepared structures (Newkome et al., Isocyanate-Based Dendritic Building Blocks: Combinatorial Tier Construction and Macromolecular Property Modification, *Angew. Chem., Int. Ed. Engl.*, 1998; Newkome et al., *Combinatorial Chem.*, 1999) whereby tiers are constructed by using a mixture of equally reactive, complementary monomers are integral elements for the ultimate construction of tunable networks.

As proof of the concept that branched architectures are dynamic with respect to functional group position, a dendrimer was constructed with a single ligating moiety bound to the surface of each quadrant of a dendrimer prepared using a tetravalent core. The key monomer **36** possessing a single bipyridine unit can be accessed via standard reactions (FIG. 4). Starting with 4-nitrobutyric acid (**34**), the bipyridyl diester **35** can be afforded by coupling of the aminobipyridine unit (Newkome et al., *J. Org. Chem.* 1997) followed by Michael-type addition of tert-butyl acrylate and nitro moiety reduction. (Dominguez et al., 1961) Amine acylation of **35** (DCC) addition of methyl acrylate, methyl ester deprotection (McMurray, J., 1976) (NaCN, DMF), and coupling (DCC) of the aminotriester precursor to **6** with subsequent reduction of the nitro group to an amine (Weis et al., 1995) affords the desired homologated aminobipyridine **36**. Acylation of four equivalents of **36** with tetraacyl chloride **37** yields dendrimer **38** (FIG. 5; the fourth bipyridine is not depicted), whereupon metal addition (Issberner et al., 1997) (e.g. RuCl₃, under reducing conditions) in dilute solution the trisbipyridine metal complex [e.g., Ru(II)] **39** is expected. Other ligating species can be envisioned to function analogously, such as the siderophore-based dihydroxybenzene. (Tor et al., 1987) Standard analyses using UV, NMR, and mass spectrometry techniques are expected to confirm the presence of one free bipyridine and three complexed ligands. The structural proof-of-concept, for the Rubik's sphere model, (Tor et al., 1987) although synthetically lengthy, is critical to the demonstration that randomly placed functionalities on a dendron, sphere, or surface can contact, influence, or affect each other. The "Rubik's sphere

concept has far reaching ramifications related to the incorporation of dendritic monomers that can rotate to favorable orientations to stabilize metals, clusters, and composites.

In view of the above, the present invention provides a monomer useful in the construction of dendrimers for investigating macromolecular torsional behavior. Such torsional behavior of branch architectures which are capable of being dynamic with respect to functional positioning groups. Such rotatable dendritic monomers capable of stabilizing metals, clusters and composites are used as "switches" for transferring ions or controlling ion transfer. Control can be obtained by the use of changing environments wherein the environment itself, whether hydrophobic and hydrophilic, high ionicity, low ionicity, etc. can induce torsional changes which result in bringing ions or the like into or out of proximity with each other thereby able to either transfer or not transfer ionic moieties. Hence, the present invention provides significant utility in the molecular or electronics field. Likewise, such "Rubik's" sphere capability is useful in electrodes and solid state electronics.

The present invention further provides means for making novel nanoscale metallomacrocycles. As part of efforts to develop nanoscale and molecular-sized energy storage devices, the potential self-assembly of polymetallic architectures for energy collection was investigated. These macrocycles are the first in a series of unique fractal polymers capable of molecular stacking and metal positioning. Synthesis of these novel materials is illustrated in FIG. 6 whereby a hexaruthenium ring is targeted. Beginning with the known dialdehyde **40** the primary bisterpyridine building block **41** was crafted via treatment with 2-acetylpyridine followed by reaction with NH₄OAc. Hexa-metallo ring **42** can then be accessed by a simple, one step, high yield, self-assembly of bisterpyridine **41** and six equivalents of RuCl₃·H₂O in the presence of N-ethylmorpholine. Ruthenium connectivity was initially employed to prove the self-assembly process but other metals work in a comparable fashion. Also, rigid structural control facilitates the introduction of alternating metals. As well, 1,3,5-versus 2,4,6-external substituents can be incorporated, in a precise manner, affording a series of architecturally related materials.

Different sized rings (**43-45**; FIG. 7) and derivatization of the peripheral methyl moieties via free radical halogenation (Newkome et al., *Synthesis*, 1984) and Suzuki-type coupling (Xu et al., Stiff Dendritic Macromolecules: Extending Small Organic Chemistry to the Nanoscale Regime, *Polym. Prep.*, 1993; Xu et al., Synthesis and Characterization of a High Molecular Weight Stiff Dendrimer, *Angew. Chem., Int. Ed. Engl.*, 1993) of rigid or flexible appendages to facilitate "network" positioning of the poly-metal centers were investigated.

For example, the branch modified structure **46**, which is easily accessed via attachment of known, pre-formed polyphenylacetylene dendrons, (Xu et al., 1994) possesses structural requirements known to promote columnar mesophase (**47**) formation (Markovitsi et al., 1988) (i.e., near planarity and lipophilic arms positioned in a symmetrical cyclic array). Further, the phenylacetylene dendritic arms act as "molecular antennas," as reported in the literature, (Kopelman et al., 1998; Shortreed et al., 1997; Xu et al., 1994) for energy direction and concentration towards the electron-poor poly-metallic rings. Interestingly, stacked assemblies using anionic-terminated, hydrocarbon dendrimers as counter ions and "insulators" suggest their use in a number of areas of molecular electronics (i.e., LEDs, photodiodes, and thin film transistors) due to the potential to form alternating conducting and non-conducting layers.

(Luryi et al., 1999; Krummenacker et al., 1995; Barnes et al., 1999) Although the first members of this series are depicted in FIG. 5, the creation of higher generations via the incorporation of additional terpyridine moieties can also be accomplished (48; FIG. 8).

In view of the above, the present invention provides compounds consisting of fractal-like, planar organometallic arrays. The term "fractal" is used in its accepted meaning, fractal geometry being concerned with the quantitative description of complex structures and the way in which the structures transform under a change of lens scales. The most simple fractals are self-similar or scale invariant structures that are invariant to an isotropic change of length scales. That is, they "look the same" under different magnifications. Familiar examples of such fractals are coastlines, clouds, and biological structures, such as the vascular system and nerve cells. During the past few years, these ideas have become widely disseminated and apply to a very broad range of materials and phenomena.

The fractals of the present invention provide for stackable, is planar organometallic arrays, especially in higher generations of the fractals, capable of encapsulating, entraining, and stabilizing metal and non-metal nanoclusters for use as stacked electrode materials.

The fractals, as well as the previously disclosed dendrimers can be utilized in combination with various metals having the appropriate ionic properties for use in energy collection and storage devices. Examples of such metals, are Cu, Fe, Ru, Os, Zn, Co, Ni, Mn, Pd, Pt, Rh, Re, W, Ir, Au, and Ag.

Use of dendritic chemistry for the creation of new and improved anode and cathode materials is provided herein. Both "lithium"- and "lithium-rocking-chair"-type electrodes are targeted. Dendritic "void volume" employed in concert with internal and external metal or non-metal coordination sites as well as aqueous and non-aqueous chemical equilibria provide a wide range of options for their construction.

Essentially, the unique, branched architecture of dendrimers simply provide a molecular-sized reaction vessel for component polymerization or colloidal stabilization and solubilization. Polymerization and particle stabilization using micelles and vesicles are well known. (Fendler et al., 1975; Fendler et al., 1994) Metal coordination to the interior of dendritic framework has been demonstrated in labs employing alkyne, (Newkome et al., Unimolecular micelles, *Angew. Chem., Int. Ed. Engl.*, 1991; Newkome et al., Alkane Cascade Polymers Possessing Micellar Topology: Micellanoic Acid Derivatives, *Angew. Chem., Int. Ed. Engl.*, 1991; Newkome et al., Chemistry within a Unimolecular Micelle Precursor: Boron Superclusters by Site- and Depth Specific Transformations of Dendrimers, *Angew. Chem.*, 1994; Newkome et al., Chemistry Within a Unimolecular Micelle Precursor: Boron Superclusters by Site- and Depth-Specific Transformations of Dendrimers, *Angew. Chem., Int. Ed. Engl.*, 1994) bipyridine, (Newkome et al., Synthesis of Unsymmetrical 5,5'-Disubstituted 2,2'-Bipyridines, *J. Org. Chem.*, 1997; Newkome et al., Cascade Infrastructure Modification Via Integration of Application-Based Monomers, *Polym. Mater. Sci. Eng.*, 1995; Newkome et al., Design, Syntheses, Complexation, and Electrochemistry of Polynuclear Metallodendrimers Possessing Internal Metal Binding Loci, *Chem. Eur. J.*, 1999) and terpyridine moieties, (Newkome et al., Electroactive Metallomacromolecules via Tetrakis(2,2':6'2"-Terpyridine)ruthenium(II) Complexes: Dendritic Networks towards Constitutional Isomers and Neutral Species without External Counterions, *Chem. Commun.*, 1998; Newkome et al., Neutral highly branched met-

allomacromolecules: Incorporation of (2,2':6'2"-terpyridine) ruthenium(II) complex without external counterions, *Chem. Commun.*, 1999; Newkome et al., Construction of Dendritic Assemblies: A Tailored Approach to Isomeric Metallomacromolecules by Means of Bis(2,2':6'2"-terpyridine) ruthenium(II) Connectivity, *Macromolecules*, 1998) while coordination and subsequent reaction have produced "nanoparticles" (i.e., zero valent Pt clusters [Zhao et al., Dendrimer-Encapsulated Pt Nanoparticles: Synthesis, Characterization, and Applications to Catalysis, *Adv. Mater. (Weinheim, Fed. Repub. Ger.)*, 1999; Chechik et al., 1999; Zhao et al., Homogeneous Hydrogenation Catalysis with Monodisperse, Dendrimer-Encapsulated Pd and Pt Nanoparticles, *Angew. Chem. Int. Ed.*, 1999] and CuS₂ [Balogh et al., 1998; Tan et al., 1999; Dagani, R., 1999]).

Dendrimers can be used as templates (49; FIG. 9) for the preparation of uniform, nanocrystallite materials such as hydrous RuO₂, (Ru—Ti) O_x (Kriesel et al., 1999; Long et al., 1999) and organic-based binary material such as polyethyleneoxide-dihydrophenazine block copolymer. (Tran et al., 1998) Use of dendrimers for construction of nanocrystallites for electrode materials allows for high surface area and near uniform dimensions thereby enhancing electrode stability, conductivity, and capacity. The concept of dendrimer nanocrystallite formation is predicated on the preparation of semiconductor crystallites via "arrested precipitation" techniques, or templated polymerization, using structured reaction media such as zeolites, ionomers, porous glass, vesicles, micelles, and gels. (Steigerwald et al., 1990) More recently, CdS clusters have been derivatized with pyridine units and fabricated into superarrays, (Steigerwald, et al., Semiconductor Crystallites: A Class of Large Molecules, *Acc. Chem. Res.*, 1990) and superlattices, (Que et al., 1988; Que et al., 1990) thus electronically coupling the individual clusters for enhanced luminescence emission properties. Thus, use of the "void volume" inherent in dendritic assemblies and components affords an ideal method for preparation of crystallites with a high degree of purity and monodispersity, as well as at sizes relevant to the "quantum effect" (i.e., 50 Å or less). (Que et al., 1988; Que et al., 1990; Weller, H., 1993)

In view of the above, the present invention most generally provides a dendrimer nanocrystallite.

The present invention further provides a method of preparing polyterpyridyl ligands in a self-assembling manner. By "self-assembling" it is meant that the combination of the components will, without further chemical or physical prompting assemble into a higher order (fractal) architecture.

More specifically, the present invention provides a preparation of a bis(terpyridine) monomer possessing a 120° concave angle with respect to the two ligating moieties. This would facilitate the assembly of six building blocks with six connecting metals in the ubiquitous benzenoid architecture. The potential to synthesize such constructs, with little equilibration (metal-ligand exchange) under mild physiochemical conditions, is predicated on the unique strength of the terpyridine-Ru coordination.

Synthesis of the requisite building block began via treatment of the known dialdehyde (28) 1 (FIG. 9) with excess 2-acetylpyridine (29) followed by NH₄Oac to afford (66%) of the desired angular (1200) bis(terpyridine) 2. Confirmation of this structure included ¹H NMR absorptions at 7.38 (dd; 5,5"), 7.82 (s; 4,6 Ar), and 8.83 ppm (s; 3', 5') Reaction of hexagonal precursor 2 with two equivalents of RuCl₃·nH₂O produced the minimally soluble, paramagnetic bis[Ru(II)] adduct 7 (FIG. 10) which was treated without further

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purification with one equivalent of monomer **2** under reducing conditions (N-ethylmorpholine) to yield (85%) the self-assembled, diamagnetic, hexameric Ru(II) complex **8** (Table 1). The ^1H NMR spectrum (FIG. 11) of the purified material revealed a single absorption at 2.90 ppm (CH_3) suggesting the presence of only one type of monomeric unit in contrast to that expected for a linear oligomer. Other diagnostic spectral attributes (^1H NMR) included upfield and downfield shifts, respectively, of the 6,6' signals (δ 7.62; Δ 1.13) and the 3',5' signals (δ 9.37; Δ 0.54). COSY and HETCOR spectra of the bis(ligand) and the self-assembled macrocycle verified the peak assignments and coupling patterns. Hexamer **8**, isolated as the 12 Cl $^-$ salt, exhibited solubility in MeOH and hot H $_2$ O while conversion to the 12 PF $_6^-$ facilitated solubilization in acetonitrile, acetone, and dimethylsulfoxide.

In order to ensure structural verification of macrocycle **8**, a stepwise, directed route to the material was devised. Initially, further characterization of the key monomer **2**, as well as the bis(terpyridyl)-Ru(II) connective moieties, was provided by the formation of the mono- and di-Ru(II) complexes **3** and **5** (FIG. 9). Reaction of 4'-(4-methylphenyl)-2,2':6,2''-terpyridine (**30**) with RuCl $_3$ ·nH $_2$ O followed by addition of the unmetallated mono- and di-terpyridine ligands (**4** and **2**, respectively) afforded the desired complexes. As in the case of hexamer **8**, constructs **3** and **5** exhibited a downfield shift (^1H NMR) of the 3',5' proton resonances (δ 9.20; Δ 0.46) and an upfield shift of the 6,6' signals (δ 7.62; Δ 1.07). Bis(Ru) complex **5** was also prepared employing ligand **7** followed by capping with the free monoterpyridine precursor to **4**.

Subsequently, the diamagnetic tris(oligomer) **6** was prepared from building block **2** via sequential treatment with two equivalents of RuCl $_3$ ·nH $_2$ O and then unmetallated monomer **2**. The ^1H NMR spectrum of trimer **6** showed a complex pattern of broadened absorptions in the aromatic region (δ 9.76–7.40) as well as the two anticipated singlets arising from the non-equivalent methyl groups (δ 2.79, 3H, 2.94, 6H). Finally, reaction of the oligomer **6** with one equivalent of its bis[terminal Ru(III)] adduct yielded a material possessing identical spectral and physical characteristics to that of the self-assembled hexamer **8**. Notably, a silica TLC of the macrocycle **8**, eluting with a mixture of CH $_3$ CN and aqueous KNO $_3$, clearly showed the absence of any starting materials, while the UV spectrum extinction coefficients (E) exhibited a 5.1, 5.5, and 5.8 fold increase for λ_{max} at 290, 312 and 496 nm, respectively (Table 2), when compared to analogous measured coefficients for the monoRu(II) complex **3**.

An electron micrograph (EM) of 8 $^{+12}$ (12 PF $_6^-$) revealed a regular, packing morphology with particle sizes ranging from \approx 160 to 350 Å (FIG. 12a) while powder X-ray diffraction showed only short-range order with determined d-spacings at 7.99, 6.24, and 4.32 Å. Powder diffraction spectra of bis[Ru(II)] complex **5** exhibited a similar pattern (d-spacings; 10.11, 7.58, 5.80 and 4.32 Å). Molecular modeling of macrocycle **8** (FIG. 12b) indicated a diameter of 37.5 Å, a minimum inner void distance of 17.5 Å and a distance between adjacent Ru metals of 13.5 Å.

In an effort to modify the generally poor solubility of macrocycle **8**, as well as provide organizational scaffolding for non-bonded network formation, the counter ions in 8 $^{+12}$ (12 Cl $^-$) were exchanged with a dodecarboxylate-terminated dendrimer (**31**) to give 8 $^{+12}$ [C(CH $_2$ OCH $_2$ CH $_2$ CONHC(CH $_2$ CH $_2$ CO $_2^-$) $_3$) $_4$], which is an extremely insoluble assembly. However, a 1:1 mixture of hexamer **8** and a third generation carboxylate-terminated dendrimer gave 8 $^{+12}$

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(G3-108-CO $_2^-$), which produced a deep red D $_2$ O solution (25° C.) allowing verification of aqueous solubility via ^1H NMR. The use of compact, charge concentrated, (psuedo) spherical dendrimers possessing uniquely positioned anionic counterion character affords a convenient circumvention of the spatial randomness of traditional simple counterions in such complexes.

These results have led to the construction of heteroleptic macrocycles. Bromo analogs of monomethyl terpyridine **2** and the p-methyl monoterpyridine **4** were prepared starting with 5-bromo-m-xylene or 4-bromobenzaldehyde, respectively. Reaction of the bromomonoterpyridyl ligand (not depicted) with Ru(III) adduct **4** gave the anticipated Ru(II) complex **9** exhibiting nearly identical ^1H and ^{13}C NMR spectra to that of complex **3**. While addition of the bromo building block **10** to the bis[Ru(II)] adduct **7** afforded the mixed monomer macrocycle **11**. Evidence for its formation includes a symmetrically similar yet expectedly broadened ^1H NMR spectrum corresponding exactly to that of the hexamethyl analog **8**. HETCOR experiments further support the structure.

In conclusion, the iterative synthetic method combined with fundamental properties of branched macromolecular architecture allows the realization of new materials to promote advances in energy storage devices and their components. Construction of a modular set of building blocks or monomers is essential and key to the realization of the chemistry discussed herein.

Dendrimer-based electrolyte materials enhance solid state lithium-type batteries via improvements in such properties as electrode separation, electrolyte solubility, and ion conduction, and safety.

Operational temperature ranges increase due to better electrolyte solubility and matrix stability.

Improved anode and cathode materials to result via the potential for branched architectures to be employed for the preparation and stabilization of metal and non-metal colloids and composites. Use branched architectures for binders in existing materials improve surface areas and retard polarization gradients thereby enhancing ion diffusion and overall conduction.

Metal encapsulation with branched architectures finds utility in many areas of battery technology and molecular electronics. Ramifications include the ability to produce smaller particles with greater cumulative surface areas that ultimately facilitate better ion diffusion within is the electrode and at the electrode-electrolyte interface. Use of dendritic vessels as molecular reactors, in a similar fashion as micelles are employed for polymerizations, allow the investigation of new organic- and organometallic-based copolymers and composites.

The single-step construction of new fractal-like, planar organometallic arrays provides new methods of energy storage and conduction via the potential to precisely position metals within large networks. Combinatorial methods of macromolecular construction are proposed that ultimately lead to the creation of single molecules possessing the capability of energy storage and release (i.e., molecular batteries). Creation of molecules with the capacity to take advantage of multiple environmental interactions at multiple sites within the superstructure provides vast opportunity for the examination and evaluation of materials related to energy storage devices.

The overall unifying theme presented in this proposal relates to the melding of iterative synthetic protocols with more mature research arenas for the production of utilitarian materials. Ultimate control of macromolecular structural

features leads to ultimate control of macromolecular properties and thereby lead to tunable macroscopic material properties.

Throughout this application, various publications, including United States patents, are referenced by author and year and patents by number. Full citations for the publications are listed below. The disclosures of these publications and patents in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this invention pertains.

The invention has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is, therefore, to be understood that within the scope of the described invention, the invention may be practiced otherwise than as specifically described.

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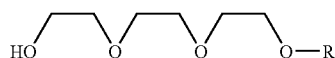
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What is claimed is:

1. A method of yielding dendrimer frameworks by the steps of:

reacting triethylene glycol separately with ethyl diazoacetate and benzyl chloride to separately yield an ester and benzyl ether of the formula



wherein R is $\text{CH}_2\text{CO}_2\text{Et}$ or benzyl;

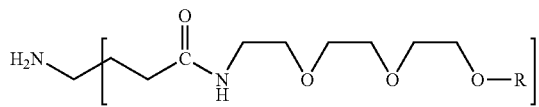
converting a free hydroxyl of the ester to an amine; coupling the amine with a nitrotris (acid chloride) and subsequently reducing the nitro group to form an aminotriester;

forming a dendrimer core by reacting pentaerythritol with the amine;

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and

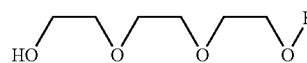
performing selective ester hydrolysis of the core followed by coupling of a monomer of the formula



thereby yielding a first generation dendrimer of Formula 31.

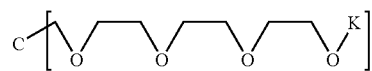
2. A method of yielding dendrimer frameworks by the steps of:

reacting triethylene glycol separately with ethyl diazoacetate and benzyl chloride to separately yield an ester and benzyl ether of the formula



wherein K is $\text{CH}_2\text{CO}_2\text{Et}$ or benzyl, followed by conversion to a mesylate;

then reacting the mesylate with pentaerythritol to yield a core of the formula;



and

deprotecting an acetyl moiety of Formula 27, transforming the moiety to a corresponding mesylate and attaching to the core thereby forming a first tier polyether dendrimer.

* * * * *