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Recent progress and applications for metallodendrimers†‡

Seek-Ho Hwang,[a] Carol D. Shreiner,[a] Charles N. Moorefield[c] and
George R. Newkome*[ab]

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Progress in metallodendritic architectures is discussed as it relates to catalysis, luminescence, sensors, and molecular switches. It is intended that the reader will gain an appreciation for the different roles that metals can play in dendritic connectivity as well as their vast potential for application-oriented nanoscale device construction.

I Introduction

In recent decades, highly branched macromolecular architectures[1,2] and self-assembly processes have become two of the more popular and fascinating research areas, both of which have become global, fundamental topics for chemists, scientists, and chemical engineers. Utilizing advances in both fields simultaneously has led to astounding progress in nano-scale science, which has given rise to various potential utilitarian applications. One can cite numerous reasons for the rapid materialization developing from these merged fields, for instance: exceptional positioning of structural units, facile construction, superior and tunable solubility features permitting characterization and further alteration, and the overwhelming collection of documented evidence that proves such species can be assembled for useful as well as aesthetic purposes. However using the current mass spectroscopy techniques, it is often the case to find substandard purity and flawed branching leading to the hyperbranched arena. But with dendrimer chemistry, perhaps one of the more important aspects is its potential to be incorporated into, or merged with, other established chemical disciplines.

The union of supramolecular chemistry, defined as "chemistry beyond the molecule" by Lehn,[3] and dendrimer chemistry, specifically that of metallodendrimers, directly led to "supramacromolecular" chemistry.[4] The integration of metal ions into dendritic architecture was pioneered by the research groups of Balzani[5–7] and Newkome[8,9] in the early 1990s, either by the use of metallo-branching centers or by interior metal coordination and encapsulation at precise chelating site(s), respectively. Metallodendrimers can be categorized (Fig. 1), such as when metal centers are positioned at the infrastructure's core, connectors between branching centers or act as

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[a] *Department of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA. E-mail: newkome@uakron.edu; www.dendrimers.com*
[b] *Department of Chemistry, The University of Akron, Akron, OH 44325-3909, USA*
[c] *Maurice Morton Institute for Polymer Science, The University of Akron, Akron, OH 44325-3909, USA*

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‡ The HTML version of this article has been enhanced with colour images.

Seok-Ho Hwang was born in Incheon, Korea in 1968. He received his Bachelor of Science Degree in the Department of Chemical Engineering at Soongsil University, Korea in 1992, where he also was granted a Masters of Science in 1994. From 1994–2000, he worked as a Researcher in the Korea Institute of Industrial Technology. In 2001, he joined the Department of Polymer Science at the University of Akron in Ohio, where he joined the research group of Professor George R. Newkome. In 2006, he was granted his PhD based on his dissertation titled, Design and Construction of Nanoarchitectures Using Smart Building Blocks. Currently, he is a Senior Researcher at the Korea Institute of Industrial Technology in Korea.

Charles N. Moorefield was born in Arlington, VA. He received his Bachelor of Science Degree in 1982 at the University of Central Florida, where he also received a Master of Science Degree in 1984 in Industrial Chemistry. In 1991, he was granted a PhD from the University of South Florida under the direction of Professor George R. Newkome. During his graduate research, he received the Theodore and Jennette Askounes–Ashford Fellowship for Outstanding Achievement as a Doctoral Student, a University of South Florida Author and Artist Award, and the Outstanding Doctoral Student Award. In 1996, he worked at the La Belle Institute at the University of Strasbourg, in France. Currently, he is an Associate Research Scientist in the Maurice Morton Institute of Polymer Science at the University of Akron.

terminal groups. Metal centers can also be integrated as structural auxiliary points within the dendritic framework by their incorporation after dendrimer construction. While there are numerous contemporary reports concerning metallodendrimers,[10–15] this review will attempt to account for recent developments in the chemistry and potential applications of metallodendrimers as well as consider selected multi-branched, metal-based constructs with less than three generations, which has been defined[16] as the threshold that must be achieved to be strictly considered a dendrimer.

II General structures and their potential applications

1 Catalysts

The potential application of metallodendrimers to the realm of catalysis appears to embrace significant promise,[10,17–31] since the dendritic infrastructure can be fabricated to ensure a tailored size, shape, critical surface, and framework composition. The ability to modify the surface is more often, than not, possible and a necessary action in order to attain the desired solubility characteristics; advantages of homogeneous and heterogeneous catalysis can also be investigated without losing the well-defined molecular features.[32] In 1994, the first publication on the topic appeared[33] in which organometallic and inorganic catalysts were made using organic macromolecules and an inorganic polymer[33] thus introducing diverse microenvironments that can give rise to a host of opportunities for specific applications.

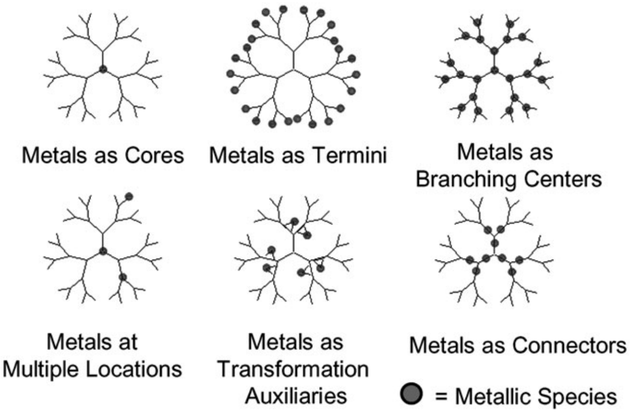

Fig. 1 The different roles metals can play in metallodendrimers.

1.1 Ni-based dendritic catalysts. One of the earliest models of a catalytic metallodendrimer[33] utilized monoanionic chelating "*N–C–N*"-type pincer moieties, which were attached to the termini of a carbosilane dendrimer, followed by Ni(II) complexation.[25,27,34,35] These carbosilane-based metallodendrimers (**1**, Fig. 2) were employed in a Kharasch-type addition[36] to catalyze the reaction between an olefin and polyhalogenated alkane. These dendritic catalysts possess a uniqueness that arises from the low Ni(II)/Ni(III) redox potential ($E_{1/2}$ = 0.14 V *vs.* SCE)[37] of the [(*N*,*C*,*N*)NiX] group; however, as the generation of the metallodendrimer increased, the catalytic activity decreased as demonstrated by the addition of CCl_4 to methyl methacrylate (MMA) under typical reaction conditions. The decrease in catalytic activity was suggested to be due to the irreversible oxidation from Ni(II) to Ni(III) as a result of a reaction between the Ni(III) sites with an intermediate radical (Cl_3C–MMA$^\bullet$) or initial radical ($Cl_3C^\bullet$). The Ni–Ni inter-site distance in these metallodendrimers was small based on molecular modeling calculations,[38] which suggested that the Cl-bridging in these mixed-valance intermediates was, in part, responsible for the loss of efficiency in the more congested members of this family. Preliminary analysis of these metallodendritic systems within a membrane reactor by the van Koten group[39] has shown another promising application,[37] that is the use of amino acid–based dendrons, as molecular scaffolds, for urea-mediated attachment of the catalytic organometallic Ni "pincer" complexes.

Carol D. Shreiner completed her BS in chemistry in 1999 at The University of Pittsburgh, Pittsburgh, PA. In 2004, she earned a PhD in chemistry at The University of Akron. Her graduate research focused on porphyrin/polyphenylene dendritic systems and transition-metal terpyridyl systems as artificial photosynthetic reaction centers. During her graduate career, she was awarded the Noveon Research Award for research excellence and was a Flexsys Fellowship award recipient (1999–2003). She is a member of Iota Sigma Pi, the national honor society of women in chemistry. Dr Shreiner is currently a Postdoctoral Research Associate with Dr George R. Newkome studying novel shape-persistent transition-metal terpyridyl complexes and dendritic macromolecules. In the Fall of 2007 she will become an assistant Professor of Chemistry at Hiram College.

George R. Newkome received his BS and PhD in chemistry from Kent State University. He joined Louisiana State University in 1968 becoming a full professor in 1978 and Distinguished Research Master in 1982. In 1986, he moved to the University of South Florida as Vice President for Research and Professor of Chemistry, becoming a Distinguished Research Professor in 1992. In 2001, he was appointed as Oelschkager Professor of Science and Technology at the University of Akron, where he is also Professor of Polymer Science and Chemistry. He has over 400 publications and is Vice President for Research and is President of the Universities Research Foundation. His research is currently focused on supra(macro)molecular chemistry, molecular assemblies, nanochemistry, inorganic–organic interfaces, molecular inclusion chemistry, molecular electronics, and photonics.

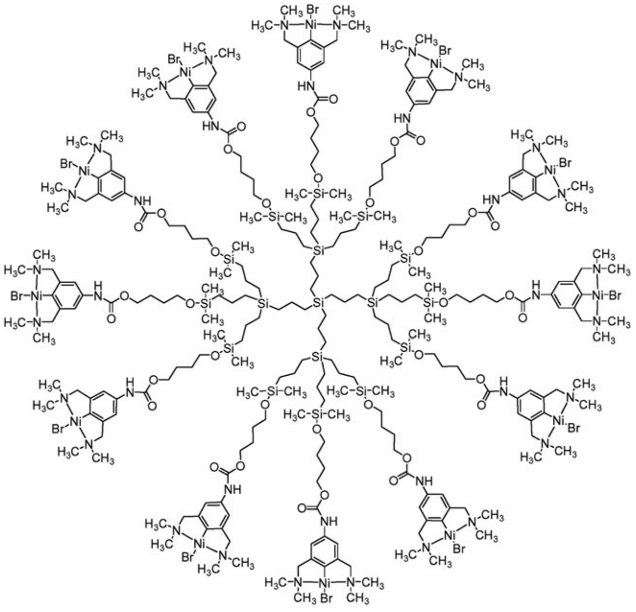

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Fig. 2 The Ni-containing metallodendrimer of van Koten and co-workers used as a Kharasch addition reaction catalyst.

Nickel complexes, derived from *o*-diphenylphosphinophenols,[40] are known to catalyze the oligomerization of ethylene *via* the Shell Higher Olefins Process.[41] Recently, van Leeuwen's group demonstrated the advantage of a nickel catalyst embedded at the core of a carbosilane dendrimer (**2**, Fig. 3) over the conventional method for ethylene oligomerization.[42] The superior nature of the metallodendritic system comes from the enhanced stability of the bis(*P*,*O*)–Ni complexes due to the dendron-based *P*-ligands, compared to the corresponding parent ligand in toluene. This metallodendrimer proves that, although rare, core-functionalized dendritic catalysts can be far more active than parent complexes because of catalytic center isolation.

1.2 Cu-based dendritic catalysts. Chow and Mak[43] designed a Cu(II)–bis(oxazoline) dendritic catalyst, (**3**, Fig. 4) which was shown to accelerate the Diels–Alder reaction between cyclopentadiene and crotonyl imide. A kinetic study supporting a two-step mechanism was established in which the reversible binding of crotonyl imide to the copper complex was followed by the rate-determining step between the resulting dienophile-catalyst complex and cyclopentadiene. These results showed that the initial complexation constant for this dienophile-catalyst complex gradually decreased with increasing dendrimer generation (G0–G3). While the Diels–Alder reaction rate constant remained similar through the G2 catalysts, it decreased notably at G3,[44] presumably due to the back-folding of the dendritic arms inhibiting access to the catalytic center. Thus, the increased surface size hindered both the reactivity and binding profile at the catalytic center. These results were described as an exo- to endo-active site transition that prohibited the diene from approaching the dienophile-catalyst complex.[43,45]

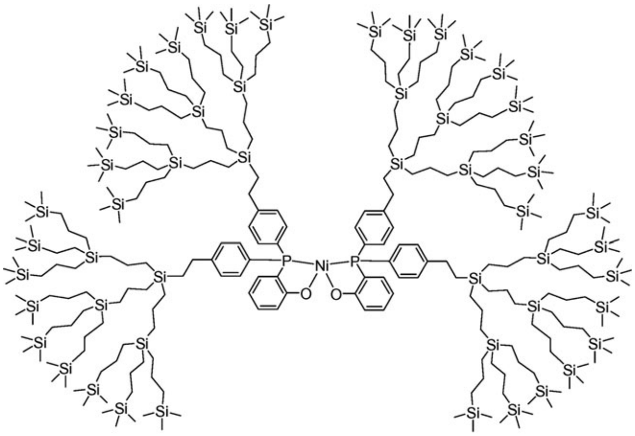

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Fig. 3 A Ni-containing metallodendrimer prepared by van Leeuwen and co-workers[42] used for the oligomerization of ethylene.

Buckminsterfullerene [C_{60}] has been utilized as a spherical core in the assembly of globular dendrimers[46–48] and lipofullerenes having an octahedral pattern.[49–51] Adducts having C_{60} as the core possess T_h symmetry,[52] as well as C_{2v}, C_s and C_3 symmetries. Enantiomerically pure C_3-symmetrical fullerene dendrimers, such as the *all-R-^{f}A*, *all-S-^{f}C*, *all-R-^{f}C*and *all-S-^{f}A*, as well as all-*S-^{f}A* and *all-S-^{f}C* lipofullerenes having an octahedral [3 : 3] addition pattern (**4**, Fig. 5) were synthesized by Hirsch and co-workers.[53] The unique near-core assimilation of the bis(oxazoline) groups that subsequently formed the internal Cu(II) complexes was able to act as catalytic sites for the cyclopropanation of styrene with ethyl diazoacetate.[54] These prototypes, termed dendrizymes, yielded poor stereoselectivity when compared to other *bis*(oxazoline) catalysts for the cyclopropanation of styrene. For example, the % ee-*trans* values using *all-S-^{f}A* and *all-S-^{f}C* in the presence of Cu(OTf), as a co-catalyst, were determined to be 2 and 1, respectively; whereas, the % ee-*cis* values were found to be 9 and 7, respectively, for other bis(oxazoline) catalytic systems.

1.3 Rh-based dendritic catalysts. Hydroformylation has been commonly used in homogeneous catalysis processes for the preparation of aldehydes and alcohols.[55] Reek and co-workers[56] reported the hydrosilylation of a family carbosilane dendrimers[57] with $HSiMe_2Cl$ or $HSiMeCl_2$, followed by reaction with $LiCH_2PPh_2 \cdot (N,N,N',N'$-tetramethylethylenediamine) (TMEDA),[58] in order to create ligands for the Rh-catalyzed hydroformylation of 1-octene. The catalytic activity of these rhodium metallodendrimers was shown to be dependent on the dendrimer size and flexibility. These results agreed with the observations of Alper and co-workers [59] utilizing bidentate, phosphine-functionalized polyamidoamine dendrimers on silica coordinated to the rhodium-complexes.

Polypropylenimine (PPI) dendrimers were introduced as core sites by Reetz *et al.*[60] for building phosphine-coated constructs that could complex with $Rh(COD)BF_4$, where COD = 1,5-cyclooctadiene, to introduce the desired catalytic component. The hydroformylation of 1-octene with these metallodendrimers was shown to have turnover numbers (TON) that were equivalent of the monomeric analogues. It

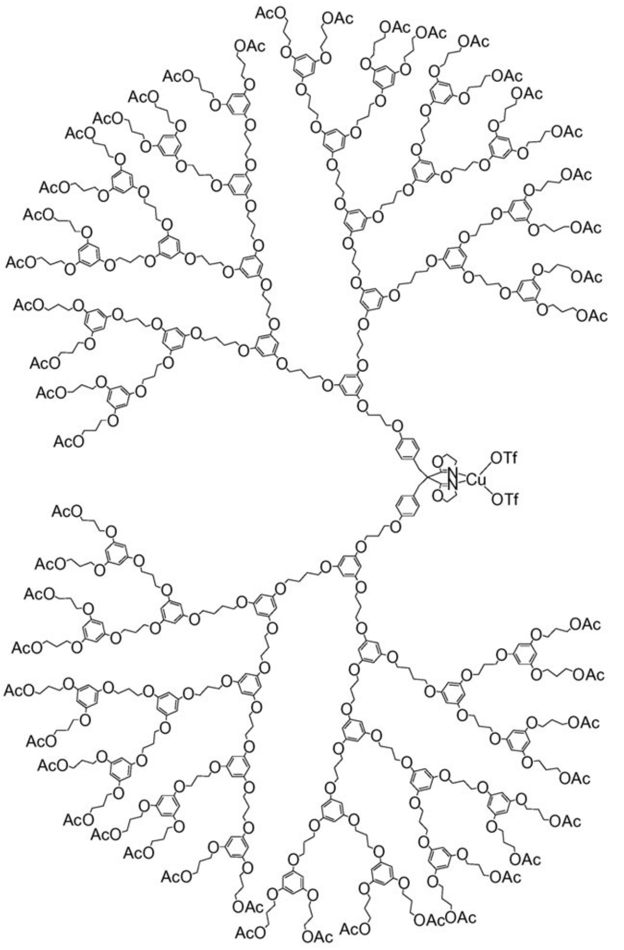

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Fig. 4 The copper(II)-bis(oxazoline) metallodendrimer of Chow and Mak for use in Diels–Alder reactions.

was also mentioned that these catalysts could be recovered using membrane separation technology.[61] A similar transformation using a water-soluble, phosphonated dendritic ligand, based on the PAMAM framework, was produced by Gong *et al.*[62] These water-soluble metallodendritic catalysts were tested in a two-phase hydroformylation using either styrene or 1-octene under mild conditions (40 °C, 20 atm). In the presence of styrene, the Rh(I) complexes demonstrated a higher selectivity to form branched-type (2-phenylpropionaldehyde) over linear-type (hydrocinnamaldehyde) products. In contrast, the standard hydroformylation using 1-octene was shown to favor linear-type (1-nonanal) products.

Dendrimers, utilizing a polyhedral oligosilsesquioxane (POSS) core, with up to 72 termini have been developed by Jeffrès and Morris.[63] A polyhedral oligosilsesquioxane core was also employed by Cole-Hamilton and co-workers[64–66] to construct alkylphosphine-coated dendrimers capable of complexing either [Rh(acac)(CO)$_2$] or [Rh$_2$(OAc)$_4$]. Using the G1 dendritic ligand (**5**, Fig. 6), the hydrocarbonylation of propen-1-ol gave products (butane-1,4-diol and 2-methylpropan-1-ol) similar to those reported elsewhere;[67] however, the formation of the linear alcohol (butane-1,4-diol) clearly occurred in two-steps: initial hydroformylation to form 4-hydroxybutan-1-al and subsequent reduction. The construction of 2-methylpropan-1-ol most likely occurred *via* a hydroxycarbene intermediate with intermolecular protonation of the acyl moiety.[64]

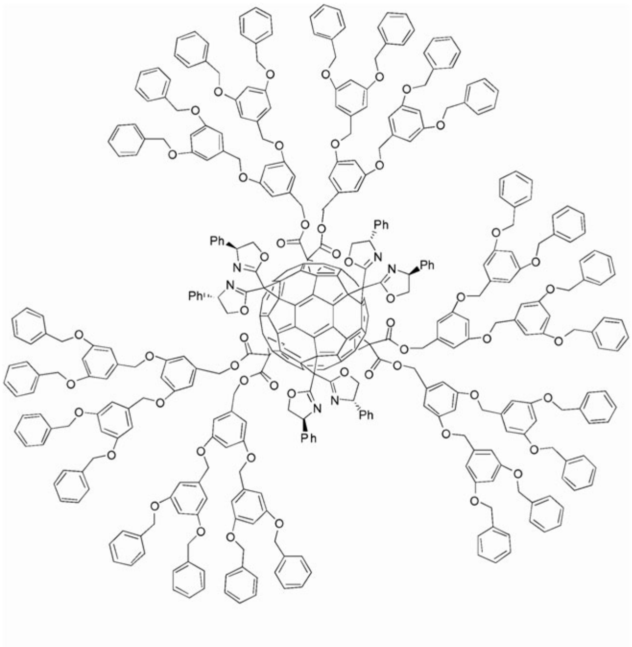

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Fig. 5 The fullerene-based dendrimer of Hirsch and co-workers was complexed with Cu(II) and used to catalyze the cyclopropanation of styrene with ethyl diazoacetate.

Higher linear selectivity (14 : 1) was found using a dendrimer possessing 16 Ph$_2$P-termini when compared with its linear monomeric analogues (3 : 1 and 4 : 1) in the Rh(I) catalyzed hydroformylation of oct-1-ene.[65,66] Molecular modeling calculations for this metallodendrimer showed that the *P*-centers were separated by 4–7 Å within a dendron and 5–10 Å between dendrons. Analogous metallodendrimers containing two CH$_2$

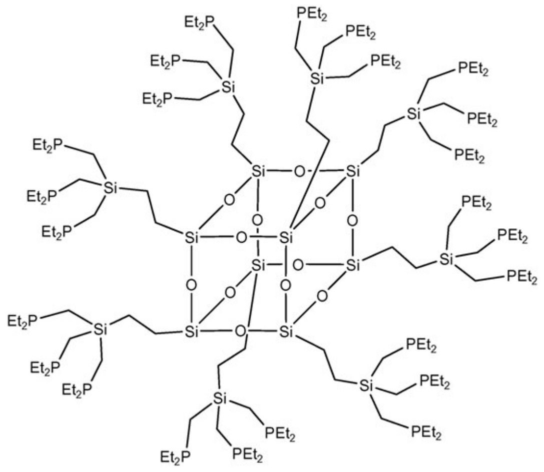

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Fig. 6 The dendrimer of Cole-Hamilton and co-workers, possessing a polyhedral oligomeric silsesquioxane core and phosphine termini, used to complex Rh.

units between the Si and P atoms failed to demonstrate superior selectivity over the monometallic catalysts. The positive dendritic enhancement was envisioned to be a result of steric crowding, along with reduced arm length, thus inducing an eight-membered bidentate coordination that favored linear selectivity.

The divergent synthesis of a series of organophosphine dendrimers comprised of both a phosphorus core and branching centers utilizing [–OSiMe$_2$O–] connectivity, as well as terminal hydroxy groups, was reported by Kakkar and co-workers.[68,69] The addition of [Rh(μ-Cl)(η^4-1,5-COD)]$_2$ to these multi-tiered *P*-centers produced metallodendrimers containing both internal and external organometallic centers; such complexes demonstrated an ability to catalyze the hydrogenation (25 °C, 20 bar H$_2$, 30 min, THF) of 1-decene in a 1 : 200 metal-to-substrate ratio. However, the larger Rh(I)$_{46}$ (where 46 represents the number of Rh atoms) metallodendrimer showed a slight decrease in turnover frequencies. After one hydrogenation cycle using this Rh(I)$_{46}$ metallodendrimer, the dendritic catalyst was separated, recrystallized, and reused with only a 5% loss in catalytic activity [resulting in a TON of *ca.* 200 $\text{mol}_{\text{prod}}(\text{mol}_{\text{cat}})^{-1}$ and turnover-frequency of *ca.* 400 $\text{mol}_{\text{prod}}(\text{mol}_{\text{cat}})^{-1}\ \text{h}^{-1}$], which was found to be totally comparable to the analogous monometallic complex. Treatment of organophosphine dendrimers with [Rh(COD)Cl]$_2$ led to the formation of other metallodendrimers[69] by means of a bridge-splitting procedure. The catalytic hydrogenation of 1-decene with these 3,5-dihydroxybenzyl alcohol-based organometallic dendritic materials[70] under standard reaction conditions (25 °C, 20 bar H$_2$) was found to be dependent upon reaction time and structural generation, with maximum conversion being accomplished in 5 h.

The use of dendrimers in the preparation of network carriers containing cavities of predetermined size and disposition has appeared.[71] Rossell and co-workers[72] reported the construction of cationic, Rh-containing carbosilane metallodendrimers; the catalytic activity of these dendrimers was tested in the hydrogenation of 1-hexene (25 °C, 10 bar H$_2$, 1 h, Me$_2$CO) in an 1 : 500 metal-to-substrate ratio. There was a slight decrease in TON with the larger Rh(I) metallodendrimers; the results were comparable to those of Kakkar's group.[68]

A new bicarbazolediol-based,[73] chiral monodentate phosphoramidite ligand, developed by Reek and co-workers,[74] possessed *N*-sites in the bicarbazole skeleton permitting the facile introduction of desired metal centers. The asymmetric hydrogenation of methyl 2-acetamidocinnamate using the Rh-catalyst was evaluated, as a model reaction. Utilizing a ligand to metal ratio of 2 : 2, the resulting enantioselectivity from the rhodium complex (**6**, Fig. 7) was 93% at full conversion, which is similar to the results obtained by Feringa and co-workers.[75,76] These observations confirmed the ability of the bicarbazole bidentate metal center to produce products possessing a high degree of enantioselectivity.

Arya, Alper and co-workers demonstrated a novel approach for minimizing the costs associated with using Rh catalysts in hydroformylation reactions by immobilizing the dendritic ligands on either silica gel[59,77] or polystyrene-based beads.[78,79] *p*-Methoxystyrene was selected as a model reagent in order to observe the recycling behavior of the polystyrene-supported Rh catalyst in hydroformylation. The catalyst derived from the G1 dendrimer was found to be extremely reactive up to the 4th cycle (99%); however, product conversion decreased to 56% for the 5th cycle. The G2 catalyst demonstrated equal reactivity up to the 4th cycle (>99%), but unlike with the G1 catalyst, continued reactivity was observed for the 5th cycle (>85%). In general, it was hypothesized that polymer-supported catalysts are less reactive compared to homogeneous catalysts. Although, the results found by Arya, Alper and co-workers emphasize the improved recycling capability, since this approach assisted in the recovery of the catalyst using various size exclusion techniques.

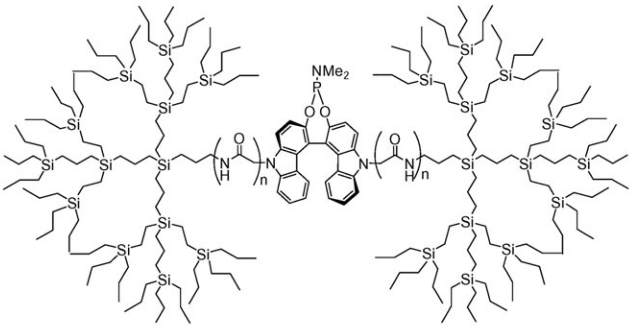

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Fig. 7 A dendritic phosphoramidite ligand designed by Reek and co-workers for Rh-mediated asymmetric hydrogenations.

Busetto *et al.*[80–83] reported the preparation and catalytic properties of different rhodium complexes of the type [Rh{C$_5$H$_4$CO$_2$(CHR)$_2$OH}(L,L)], [R = H, Me, Ph; L,L = 2CO, 2,5-norbornadiene (NBD)]. For example, [Rh{(1*R*,2*S*)-CpCO$_2$(CHMe)$_2$OH}(NBD)] and [Rh{(1*S*,2*S*)-CpCO$_2$(CHMe)$_2$OH}(NBD)], where Cp = η^5-C$_5$H$_5$, are well-known to be active catalysts for the hydroformylation of hex-1-ene. A new family of DAB-*dendr*-[NH(O)COCH$_2$CH$_2$OC(O)C$_5$H$_4$Rh(NBD)$_n$] (*n* = 4, 8, 16, 32, 64, DAB = diaminobutane)[84] metallodendrimers was synthesized by treatment of the PPI dendrimers with alkoxycarbonylcyclopentadienyl complexes of Rh(I).

One of the most widely used ligands for asymmetric catalytic hydrogenation of C=C and C=O bonds is that of chiral diphosphine ligands.[85] 3,4-Bis(diphenylphosphino)pyrrolidine (pyrphos), which can be prepared from natural tartaric acid, contains an amino group, which can be used for attachment to either organic or inorganic supports. Rh–pyrphos complexes and their derivatives demonstrated 99% ee[86,87] when used for the asymmetric hydrogenation of dehydroamino acid. Chan and co-workers[88] prepared a novel chiral dendritic diphosphine precursor for the Rh(I)–catalyzed asymmetric hydrogenation of α-acetamidocinnamic acid, as a model reaction. The G1–G4 dendritic pyrphos-Rh catalysts showed a dramatic change in catalytic activity for the transition from the G3 and G4 dendrimer, which could possibly be a result of a change in structural shape of the metallodendrimer from a flattened, pancake-like motif to a more globular structure associated with the 4th generation.

N-Heterocyclic carbene ligands have become increasingly popular in both homogeneous catalysts and organometallic

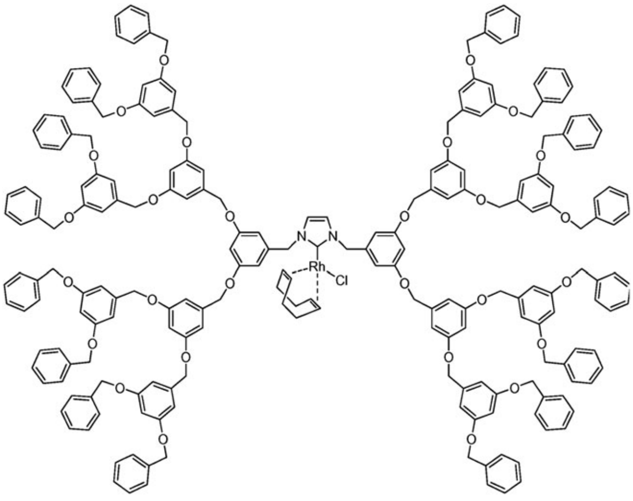

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Fig. 8 A Rh(I)-coordinating *N*-heterocyclic carbene complex crafted by Tsuji and co-workers to examine hydrosilylation reactions.

chemistry because of their strong coordination to metals centers, compared to conventional ligands, such as phosphines.[89,90] Tsuji and co-workers[91] investigated the consequences that the dendritic effect had on the catalytic activity of imidazolium salts connected to Fréchet-type polybenzyl ether dendrons for the hydrosilylation of ketones (**7**, Fig. 8). The dendritic effect was found to be positive in certain solvents, such as benzene and CH_2Cl_2, based on the dendron's aromatic character interacting with the rhodium metal, as well as the influence of concentration. The yield of 1-phenylethanol decreased considerably (to 44%) after 46 h using the G1 dendron catalyst, while the yields were unaffected for the hydrosilylation of acetophenone with G2–G4 catalysts.

Fan and co-workers[92] synthesized a dendritic monodentate phosphoramidite ligand by the substitution of the dimethylamino moiety in monophos with Fréchet-type dendritic wedges and then studied the asymmetric hydrogenation of α-dehydroamino acid esters and dimethyl itaconate. High enantioselectivities (up to 97.9% ee) and catalytic activities (up to 4850 h^{-1} TOF) were shown. The G3 dendritic catalyst gave slightly lower catalytic activity relative to those of lower generation. The steric shielding by the dendron's environment stabilized the rhodium complex against decomposition caused by hydrolysis in the protic solvent.

1.4 Pd-based dendritic catalysts. Olefin oxidation has continued to attract interest ever since the successful application of the Wacker process[93] for the industrial manufacturing of acetaldehyde. The catalyst utilized in this reaction normally consists of an acidic solution of a palladium salt with a copper(I) salt and air, as an oxidant, in an aqueous environment; however, the application of the Wacker process to longer chain alkenes has been challenging due to the alkene's low solubility in aqueous media. This has led to the exploration of biphasic systems that include the use of tetraalkylammonium salts,[94] polyethylene glycols,[95] as well as cyclodextrins.[96,97]

Alper and co-workers[98,99] placed Pd-modified PAMAM-like dendrons onto a silica backbone and evaluated the carbonylation of iodobenzene in MeOH to produce methyl benzoate under low CO pressures at 100 °C. Product yields were found to be generally high, and the catalyst was recycled 4–5 times without considerable loss of activity. This Pd-modified complex was also employed in the oxidation of terminal alkenes to generate methyl ketones under mild conditions.[100]

The retention of diaminopropyl-type dendrimers bearing palladium phosphine complexes on ultra- or nano-filtration membranes was described by Brinkmann, Kragl and co-workers;[101] these metallodendrimers were also studied as a catalyst for allylic substitution in a continuously operating chemical membrane reactor. Their results confirmed a practical method for catalyst recovery in that these metallodendrimers, which act as catalyst supports, offer the advantage of having a low solution intrinsic viscosity, thereby facilitating filtration.

Screttas and co-workers[102] prepared a PPI dendrimer possessing iminophosphines on the periphery, DAB-*dendr*-[1,2-$(N{=}CHC_6H_4PPh_2)]_{32}$ ("DAB-32-imiphos"), as well as the corresponding reduced aminophosphine-terminated dendrimer, DAB-*dendr*-[1,2-$(NHCH_2C_6H_4PPh_2)]_{32}$ ("DAB-32-amiphos"). The ability of these *P*,*N*-ligands to catalyze a Heck reaction, by coordination with Pd, was then evaluated using the conversion of C_6H_5Br into stilbene, as a model reaction.[103] Using palladium acetate (1%) in the presence of 3 equivalents of DAB-32-imiphos, LiOAc, and a mixture of tri-*n*-butylamine and AcOH at 130 °C for 15.5 h, complete conversion occurred generating a mixture of *ca.* 90% *trans*-stilbene and *ca.* 10% isomers. It was shown that for higher [dendritic ligand : Pd] ratios, lower conversions were realized and became zero for ratios >15. This result suggested a lack of competition between the metal and ligand, as a result of a strong inter-arm interaction within the dendrimer to which the metal was coordinated.[104] These catalytic systems were found to be unrecoverable as a result of thermal degradation and Pd black precipitation.

Reek and van Leeuwen and co-workers[58,105] synthesized a series of Ph_2P-terminated carbosilane dendrimers, then the corresponding Pd-complexes. Similar to previous work,[101] these Pd-functionalized dendrimers were used to investigate their catalytic activities in continuously operated membrane reactors. The *P*-terminated dendrimers were metallated with $[PdCl(\eta^3\text{-}C_3H_7)]_2$ to afford either bidentate palladium phosphine metallodendrimers or mixtures of monodentate and bidentate coordination. These metallodendrimers were subsequently used as catalysts in the allylic alkylation of allyl trifluoroacetate and diethyl methylsodiomalonate. Using 0.2% of catalyst, the yield was greater than 80% after 30 min, and only a minor variation of reaction rates was observed for the related monodentate and bidentate catalysts. The metallodendrimer having 12 chelated palladium atoms was examined for use in a continuous process. This catalyst had 98.1% retention in the membrane reactor corresponding to a mere 25% decrease in activity after flushing the reactor 15 times.

The Sonogashira reaction[106,107] between an aryl or vinyl halide and a terminal alkyne has widespread synthetic appeal by circumventing the synthesis of an organometallic intermediate. Astruc and co-workers[108,109] synthesized a series of bis(*tert*-butylphosphine)- and bis(cyclohexylphosphine)-functionalized Pd(II) monomers and PPI-coated catalysts and investigated C–C bond formation under efficient copper-free conditions. Their *tert*-butyl metallodendrimer series demonstrated an ability to catalyze the Sonogashira reaction of iodoarenes with phenylacetylene at 25 °C; however, the reaction times were significantly longer than with usual monomeric catalysts. The cyclohexyl-counterparts required heat (80 °C) activation but maintained the same catalytic efficiency after five cycles; it was easier to recover, than the *tert*-butyl series, as a result of solubility considerations.

van Koten's group[110] studied the aldol condensation of benzaldehyde and methylisocyanate catalyzed by cationic cyclopalladated carbosilane dendrimers, serving as Lewis acids, to yield oxazoline. It was shown that up to the 2nd generation, the reaction selectivity was not affected, but the reaction rate decreased with increasing generation, which was rationalized by the steric congestion at the dendrimer's periphery.

Moberg and co-workers[111] prepared the G1–G4 dendrons, using the divergent synthetic approach, based on 2,2-bis(hydroxymethyl)propionic acid and (1*R*,2*S*,5*R*)-menthoxyacetic acid. The dendrons were joined with 2-(hydroxymethyl)pyridinooxazoline and bis[4-(hydroxymethyl)oxazoline] and were evaluated in Pd-catalyzed allylic alkylation reactions. Introduction of a chiral dendritic substituent on the pyridinooxazoline ligand demonstrated little enantioselectivity [(*R*)- and (*S*)-chiral dendron ligands each resulted in 79% ee]; however, substitution of the bis(oxazoline) ligand with the same chiral dendron gave the (*S*,*S*)-chiral dendron ligand with 94% ee. The higher degree-of-enantioselectivity with the bis(oxazoline) series was proposed to be a result of the dendritic wedges being close enough to the catalytic center to effect both stereoselectivity and reactivity, therefore, leading to increased stereoselectivity but decreased catalytic activity.

Recently, van Koten and co-workers[112] designed a branched architecture having encapsulated catalytic sites (**8**, Fig. 9). The OH-functionalized carbodiazasilane macrocycles were attached to a simple core, which was subsequently treated with $Pd(dba)_2$ to afford a novel, multi-caged structure having remote $–Si(Ph_2)–$ sites for further extension of the dendritic infrastructure. This metallodendritic complex was used in the aldol condensation of benzaldehyde and methyl isocyanoacetate; the rate-of-reaction was found to be higher using the tricyclopalladated catalyst than with other mononuclear models that were tested. The sterically hindered, chiral environment around the Pd center did not, however, influence the diastereoselectivity of the resultant reaction.

Canovese, Chessa *et al.*[113] synthesized Pd(II) allyl and Pd(0) fumaronitrile complexes having pyridyl-dithioether-based metallodendrimers, as ancillary ligands. The reactivity of these complexes was tested with respect to the allyl amination using piperidine. The transformation from a nondendritic model to the G2 dendritic substrates showed no macroscopic effects; however, notable variation in the observed rate and equilibrium constant was observed when using the G3 complex. It followed that an increase in the steric hindrance at the allyl fragments from the higher generation dendritic complex caused a rearrangement and related distortion of the ligand environment at the metal core.

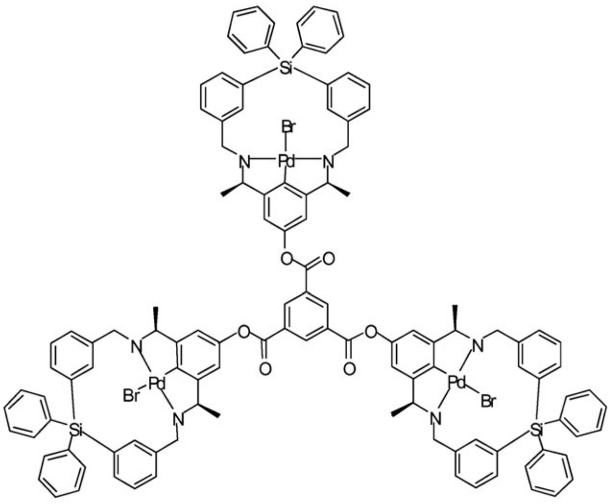

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Fig. 9 Encapsulated N–C–N-based Pd complexes of van Koten and co-workers designed for aldol condensation reactions.

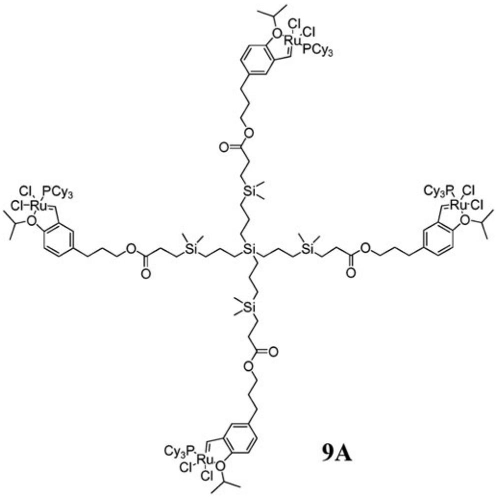
Heck olefin arylation[104] is one of the most extensively used reactions in synthetic organic chemistry and has been successfully accomplished in solution with diverse aryl iodides, bromides and chlorides, using several catalytic dendritic systems. Dahan and Portnoy[114] constructed the first poly(aryl benzyl ether) dendronized polystyrene resin decorated with $Pd(dba)_2$. Reacting bromobenzene and methyl acrylate under typical Heck conditions using the G2 and G3 catalysts proved superior in all parameters when compared to the monodendron analogue; catalyst selectivity increased with higher dendron generation.[115]

Kaneda and co-workers[116] prepared a dendrimer-bound Pd(II) complex by the treatment of DAB-*dendr*-$[N(CH_2PPh_2)_2]_{16}$ with $PdCl_2(PhCN)_2$. This catalyst demonstrated selectivity in the hydrogenation of conjugated dienes with H_2 under atmospheric pressure, was easily recovered, and could be reused without loss in catalytic efficiency. Allylic amination using Pd(0) and Pd(II) complexes was also investigated;[117–119] these catalysts gave products with high stereoselectivity, which was credited to surface congestion.

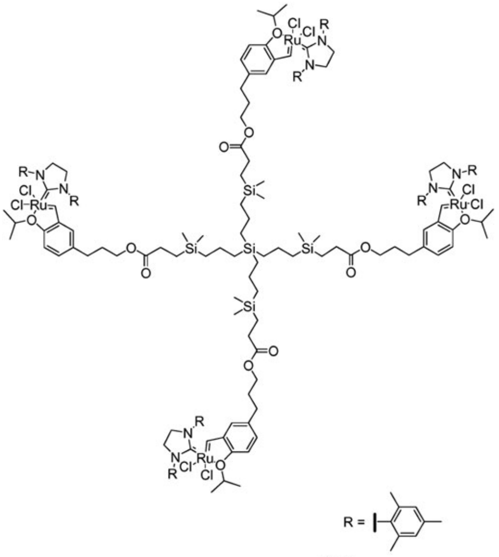
Gade and co-workers[120] described a strong dendritic effect when using pyrphos-palladium-functionalized PPI and PAMAM dendrimers for asymmetric catalysis in the allylic amination of 1,3-diphenyl-1-acetoxypropene with morpholine. A significant and unmatched increase in selectivity was observed as a function of dendrimer generation. The enhanced ee-values for these allylic aminations were less notable for the PPI-derived Pd-catalysts than for the corresponding PAMAM-catalysts, which demonstrated an increase from 9% ee for a mononuclear reference system to 69% ee for the Pd_{64}-dendrimer.

Although there is significant difficulty surrounding the topic, synthesizing artificial active sites,[121–125] as hosts for transition metal catalysts, with unique reactivity properties has become an important venture. Gagné and co-workers[126] synthesized a novel polymerizable amino-acid containing a diphosphine ligand with eight styrene moieties, which was used in the synthesis of a series of P_2PdX_2 complexes (X_2 = (*R*)-BINOL, (*S*)-BINOL, Cl_2 and 1,3-Ph_2allyl^+). The metallomonomers derived from these ligands were used as co-monomers in the synthesis of permanently porous ethylene dimethacrylate (EDMA)-based polymers, which were used as catalysts for the alkylation of allylic acetates. After the polymerization was complete, removal of the large ligands from the metallodendrimer guaranteed that the catalyst had sufficient room at the active site to hold the reactants necessary to accomplish catalysis.

1.5 Ru-based dendritic catalysts. Hoveyda *et al.*[127] synthesized two efficient and recyclable dendritic Ru-based metathesis catalysts (**9A**, Fig. 10) that differed from Grubbs catalyst, $[Ru(PPh_3)_2Cl_2({=}CHPh)]$,[128,129] in that a chelating carbene (2-isopropoxystyrene) replaced the benzylidene and one phosphine. The $[–(CH_2)_3SiMe_2(CH_2)_3OC(O)(CH_2)_2–]$ branches in this four-directional Si-centered dendrimer were connected to a styrenyl ether ligand. The model ring-closing metathesis of $TsN(CH_2CH{=}CH_2)_2$ using only 5 mol% of Ru-based dendritic catalyst was shown to proceed at 99% conversion; when the catalyst was recovered; however, there was a 13% Ru loss. Continuous use of the dendritic catalyst yielded 91% complete conversion of $TsN(CH_2CH{=}CH_2)_2$. The high level of activity was suggested to result, in part, from the release of a highly active monophosphine Ru complex into solution, which was thought to be trapped again by a styrenyl ether ligand arm of the dendrimer. An analogous four-directional metallodendrimer (**9B**, Fig. 10) was prepared wherein the phosphine ligand was replaced by the diaminocarbene ligand used in the Grubbs catalyst.[130] This metallodendritic catalyst demonstrated greater activity than the former in that it promoted trisubstituted allylic alcohol formation and was recovered with only an 8% Ru loss. Also, it was shown to catalyze tandem ring-opening or -closing metathesis and was more easily separated from reaction mixtures due to its high molecular weight and polarity.



9A



9B

Fig. 10 Ru-based dendritic metathesis catalysts designed by Hoveyda and co-workers.

Alonso and Astruc[131] positioned 32 or 64 $[Ru_3(CO)_{11}]$ groups onto the 32-branched dendritic polyphosphine prepared by Reetz *et al.*[60] by means of the double phosphine-methylation of a G3 PPI dendrimer[132] with PPh_2CH_2OH.[133] The bis(phosphine) end units, having two cyclohexyl groups on each phosphorus, were treated with monoruthenium carbine complexes, synthesized by the replacement of PPh_3 with PCy_3.[127,134] These constructs offered four generations of novel metallodendrimers possessing terminal ruthenium-benzylidene units.[135] The G4 metallo-dendrimer containing 32 ruthenium-benzylidene peripheral units, however, was found to have poor solubility in common organic solvents attributed to steric congestion unlike the earlier generations that contained 4-, 8- and 16-ruthenium-benzylidene moieties. The G1–G3 metallodendrimers, as well as the model complex, demonstrated their catalytic efficiency for the ring-opening metathesis polymerization of norbornene under ambient conditions to yield dendrimer-cored star-shaped polymers having molecular weights that were close to theoretical, indicating efficient polymerization of the branches.

Moss and co-workers[136] studied the Fischer–Tropsch synthesis[137] using a silica-supported hexa-branched ruthenium metallodendrimer with each dendritic branch having [RuCp $(CO)_2$(alkyl)] termini. The ''time-on-stream'' behavior of this catalyst, when compared to an impregnated Ru/SiO_2 catalyst, in the CO hydrogenation showed no Fischer–Tropsch product pattern, which was confirmed by the rate-of-formation of specific hydrocarbons. This study indicated that a single ruthenium site was insufficient for this type of reaction.

Majoral and co-workers[138] utilized a G3 metallodendrimer containing 24 terminal Ru–diphosphine complexes in the Knoevenagel condensation[139] of malononitrile and cyclohexanone. The activity of this catalyst, when compared with that of the simple monomeric complexes, was often higher, and catalyst recycling was possible without significant loss of activity.

The catalytic hydrogenation of organic compounds is a commonly studied chemical transformation.[140] An alternative

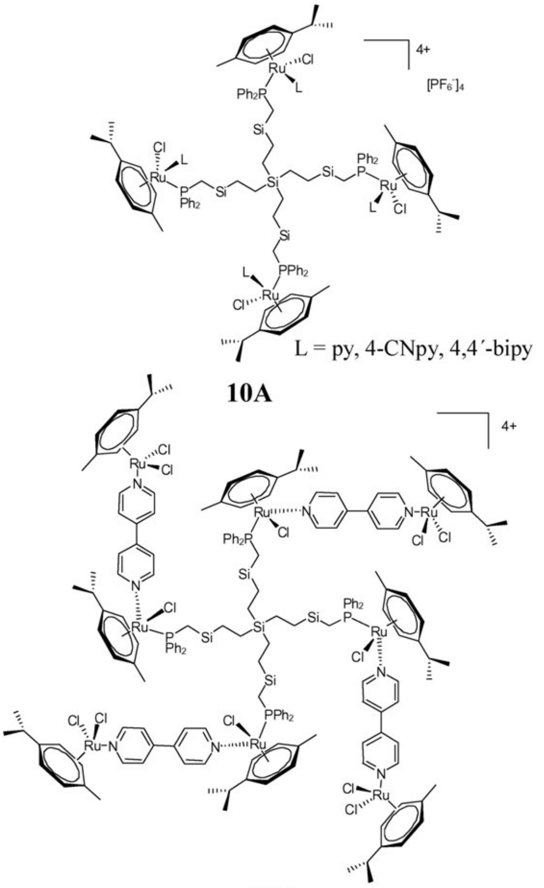


Fig. 11 Ruthenium metalloconstructs possessing a single and double metallic layer crafted by Rossell and co-workers for hydrogen-transfer reductions.

method, which avoided the use of hydrogen (gas), was provided by hydrogen-transfer processes, in which the hydrogen came from a hydride donor (such as: cyclohexadiene or formic acid) that is oxidized (dehydrogenation) during the course of the reaction. The catalytic systems used in this instance are relatively stable, environmentally friendly, and easily handled.[141,142] Rossell and co-workers[143] prepared a series of metallodendrimers by treating phosphanyl-terminated carbosilane dendrimers, having a single phosphorus ligand per arm, with [$RuCl_2$(*p*-cymene)]$_2$ (**10A**, **10B**, Fig. 11). The activity of the multi-(η^6-arene)ruthenium(II) species, compared to the corresponding Ru(II) mononuclear complexes, was found to be lower in the reduction of cyclohexanone by hydrogen-transfer. Among the G1 metallodendrimers, as well as for the mononuclear species, the neutral species was more active than the corresponding cationic analog. Under standard conditions, the cationic species resulted in a 62% conversion, indicating possible catalytic decomposition. The G3 metallodendrimer was found to be less active than the 1st generation; however, these systems demonstrated higher activities than other dendritic systems reported.[144]

A series of dendritic chiral diphosphines with tunable dihedral angels has been synthesized by Fan and Shuai,[145] and used in the Ru-catalyzed asymmetric hydrogenation of β-ketoesters. These dendritic catalysts exhibited very good catalytic activities while the enantioselectivities changed dramatically. These results demonstrated that the dihedral angles of Ph_2P-type diphosphine ligands can be fine-tuned through the systematic adjustment of the size of the dendritic wedges, which consequently influence the stereoselectivity of the catalytic reaction.

1.6 Ti-based dendritic catalysts.

Kriesel and Tilley[146–150] prepared a series of Ti-containing dendritic catalysts for the epoxidation of cyclohexene which demonstrated higher selectivity and activity, in terms of yields and initial rates, then the Shell catalyst[151] made by the treatment of silica with [Ti(O^{i}Pr$_4$)$_4$]. The G2 and G3 alkoxysilyl-terminated carbosilane dendrimers were used as key components in the synthesis of high surface area xerogels. The acid-catalyzed hydrolysis of $Si[(CH_2)_3Si(CH_2CH_2Si(OEt)_3)_3]_4$ and $Si\{(CH_2)_3Si[(CH_2)_3Si(CH_2CH_2Si(OEt)_3)_3]_3\}_4$ in benzene generated monolithic gels with surface areas of 600 and 800 $m^2\ g^{-1}$, respectively, where the surface area of these xerogels increased with increasing dendritic radii. These gels were treated with Ti(O^{i}Pr)$_4$ to afford the desired catalytic systems for the epoxidation of cyclohexene and were shown to be highly selective and considerably more active (in terms of yield and initial rate) then the traditional Shell catalyst.

Seebach *et al.*[152,153] synthesized a hexa-armed dendrimer bearing the $Ti(OCHMe_2)_4$ complexed ligand, TADDOL (α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol), at the periphery. Enantiomeric addition[154] of Et_2Zn to benzaldehyde proceeded with similar enantioselectivity (ee, 97%) as that of the monomeric chiral catalyst. Since this metallodendrimer had a molecular weight of only 3833 Da, it was necessary to perform column chromatography to recover the catalyst, rather then ultrafiltration. To simplify this process, Fréchet-type dendrons having styrenyl end groups were used to cross-link the catalyst into a polystyrene support.[152,155–158] This polymeric catalyst showed: (1) an enantioselectivity above 9 : 1 for all polymers of low loading (*i.e.*, 0.1 mmol TADDOL per g polymer), only the dendritic polymer demonstrated a selectivity of 98 : 2 in 20 sequential applications; (2) the catalytic efficiency decreased with increasing spacer-chain length between the TADDOL core and polymer backbone; (3) the swell properties of the low-loaded dendritic catalyst beads with the shortest spacer remained high, even after 20 runs, while others did not swell even after multiple cycles; and (4) using the beads of dendritic catalyst that had the shortest spacer, the rate-of-reaction was the same with or without stirring under standard conditions. Rheiner and Seebach[159] also employed Ti-TADDOLate-dendritic catalysts of the G1–G4 Fréchet-type dendrons in the enantioselective addition of Et_2Zn to benzaldehyde. There was no obvious decrease in selectivity (98 : 2) up to G2; whereas, the rates decreased slightly up to the 3rd generation.

Pu and co-workers[160,161] used 4,4′,6,6′-tetrabromo-1,1′-bi-2-naphthol to create a series of cross-conjugated, rigid optically active dendrimers. Upon complexation with Ti(O^{i}Pr)$_4$, the chiral dendrimer demonstrated high enantioselectivity in the reaction between 1-naphthaldehyde with Et_2Zn; notably, with this catalyst, the reaction proceeded with 100% conversion and 90% ee in 5 h devoid of by-products. The advantage of this metallodendrimer over BINOL is the facile separation from the reaction mixture by precipitation with MeOH.

Optically active Ti–1,1′-binaphthol metallodendrimers, using (*R*)-6,6′-dibromo-1,1′-binaphthol, containing poly(benzyl ether) wedges at the 6,6′-positions were prepared by Yoshida and co-workers.[162] The Ti-binaphthol-catalyzed allylation of an aldehyde and allyl stannane, as the model reaction,[163] demonstrated constant enantioselectivity with increasing generation up to G3 (90 ± 2% ee; nondendritic parent, 87% ee).

New significance has been placed on β-diketiminato transition metal complexes due to the ligand's ability to stabilize coordinatively unsaturated complexes,[164] which can catalyze non-metallocene olefin polymerizations.[165] Gómes and co-workers[166,167] described the synthesis and ethylene polymerization using mixed cyclopentadienyl(β-diketiminato) complexes having either titanium or zirconium catalytic sites surrounded with G1 carbosilane dendritic wedges connected to the β-diketiminato ligand (**11**, Fig. 12). These catalysts showed an improvement over the performance of metallocene complexes ($(\eta^5\text{-}C_5H_5)MCl_3$ (M = Ti, Zr), but they displayed somewhat higher activities than their non-dendritic counterparts.

1.7 Fe-based dendritic catalysts. The iron-based redox catalyst $[Fe(II)(\eta^5\text{-}C_5H_4CO_2^-)(\eta^6\text{-}C_6Me_6)][PF_6]$ was the first organometallic catalyst to effect the catalytic reduction of nitrate.[18,168] Astruc and co-workers[169] synthesized a water-soluble hexametallic redox catalyst using the $CpFe^+$ moiety to induce hexaallylation of hexamethylbenzene. The kinetics of an $[FeCp(arene)]^+$-centered star were found to be an order of magnitude lower than the kinetics of such a star with the catalyst on the periphery.

The metallodendrimers of Togni and co-workers[170] utilized a cyclophosphazene core and 16 peripheral chiral ferrocenyl ligands (**12**, Fig. 13). $[Rh(COD)_2][BF_4]$ was then added to the periphery of these ferrocenyldiphosphine metallodendrimers to instill the desired catalytic properties necessary to reduce dimethyl itaconate. These metallo-constructs showed 98% ee, which were comparable to the 99% ee achieved with monomeric Rh-based josiphos catalysts.

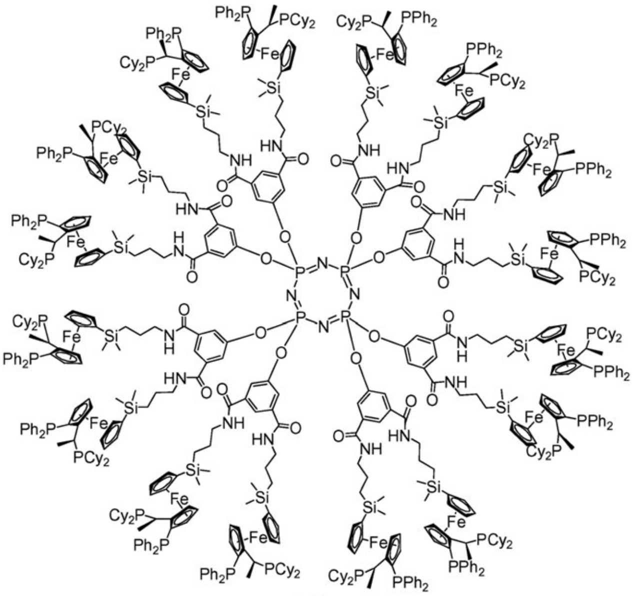


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Fig. 13 Ferrocenyldiphosphine dendritic ligand designed by Togni and co-workers for rhodium complexation and reduction of dimethyl itaconate.

1.8 Co-based dendritic catalysts. Breinbauer and Jacobsen[171] reported dendrimer-bound [Co(III)–(salen)] complexes, generated from the G0–G2 PAMAM cores and demonstrated improved catalytic activity in the hydrolytic kinetic resolution of terminal epoxides (**13**, Fig. 14). A mechanism has been proposed for asymmetric ring-opening reactions involving the simultaneous activation of both epoxide and nucleophile by these metallodendrimer's different metal-salen units.[172] This

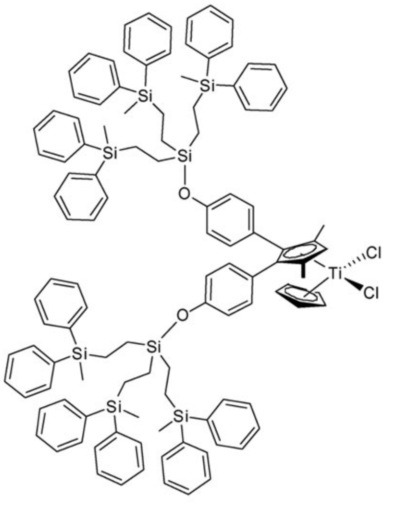

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Fig. 12 A titanium β-diketiminato dendritic complex prepared by Gómes and co-workers for ethylene polymerization.

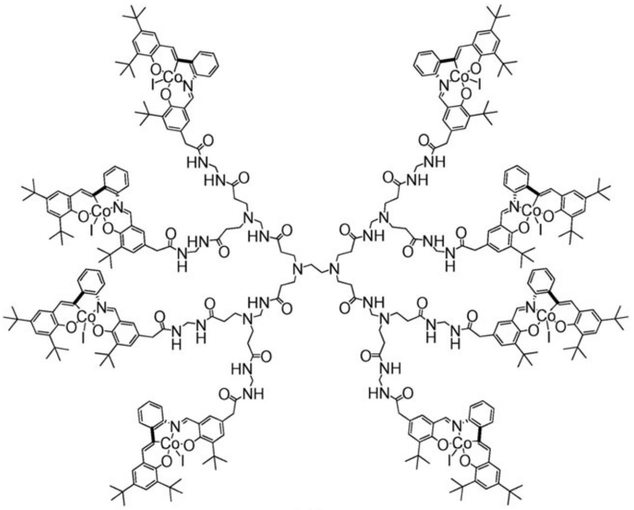

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Fig. 14 Dendritic PAMAM–Co(salen) complex prepared by Jacobsen and co-workers for the hydrolytic resolution of epoxides.

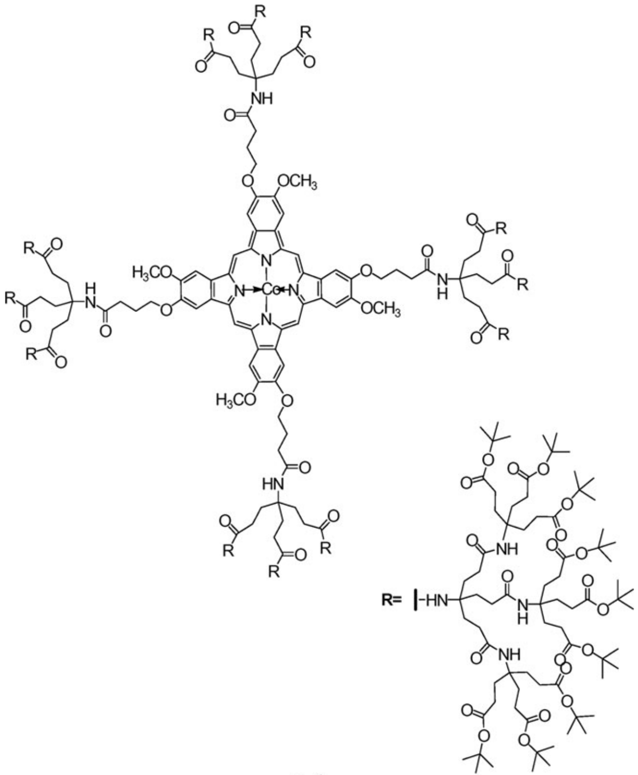

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Fig. 15 Metallophthalocyanine dendrimer prepared by Kimura *et al.* for the oxidation of mercaptoethanol.

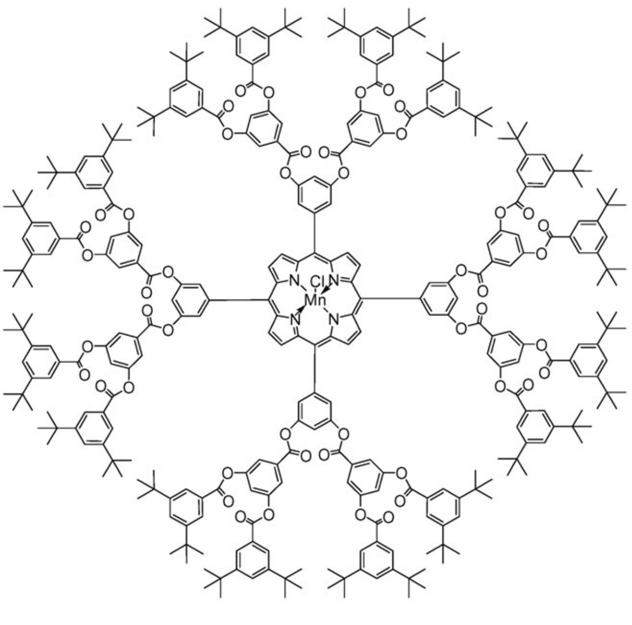

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Fig. 16 Chloromanganese(III) porphyrin dendrimer of Suslick and co-workers for alkene epoxidation.

catalytic system demonstrated a positive dendritic effect as a result of cooperation in the principal mechanistic step whereby a coordinated nucleophile attacks an epoxide coordinated to an adjacent cobalt atom.

Kimura *et al.*[173] took advantage of the attractive properties of phthalocyanines and their metal complexes[174] by synthesizing a phthalocyanine-centered dendrimer possessing Newkome-type dendrons.[175] Subsequently, they used the G2 cobalt-metallated phthalocyanine dendrimer to catalyze the oxidation of mercaptoethanol by dioxygen (**14**, Fig. 15). The influence of phthalocyanine aggregation, resulting from strong intermolecular stacking, led to increased catalytic activity, as well as enhanced catalytic stability.

For investigating the Pauson–Khand [2 + 2 + 1] cycloadditions,[176] Dahan and Portnoy[177] modified a dendronized support with 2- and 4-(diphenylphosphino)benzoic acid groups, followed by the incorporation of $Co_2(CO)_8$. A notable amplification in catalytic activity and selectivity for this reaction was found for the Co complexes immobilized on the G2 and G3 dendron-functionalized polystyrene support, when compared with the same non-dendronized support.

1.9 Mn-based dendritic catalysts. Suslick and co-workers[178–180] fashioned dendritic chloromanganese(III) porphyrins, as catalysts for alkene epoxidation with iodosyl benzene (**15**, Fig. 16). The dendritic wedges were derived from the G1 and G2 aromatic polyesters, which offered a confined setting to obtain better intra- and intermolecular regioselectivities than with the unsubstituted 5,10,15,20-tetraphenylporphyrinatomanganese(III) cation. The preferential epoxidation of the least hindered double bond of unconjugated dienes, such as found in 1,4-heptadiene and limonene, was favored. Using a G2 dendritic metalloporphyrin, epoxidation of a terminal monoalkene and cyclooctene mixture demonstrated a two- to three-fold greater selectivity towards the 1-alkenes relative to a nondendritic catalyst; however, when compared to the classical picket-fence porphyrin, 5,10,15,20-tetrakis(2′,4′,6′-triphenylphenylporphyrin), the regioselectivity was considerably reduced.[181,182]

Kawi and co-workers[183] anchored different PAMAMs onto ultrafine silica followed by the surface immobilization of a Mn(II) salen complex to afford a bound dendritic catalyst for olefin epoxidation. Activity improved with increasing generation indicating the significance of the peripheral amino group concentration as well as the Mn loading. The length of the dendritic backbone was also a significant factor as demonstrated by the increasing catalytic activity due to the improved accessibility of the active sites and reactant species.

1.10 Polyoxometalate (POM)-based dendritic catalysts. The groups of Newkome and Hill prepared two dendritic tetra-POM molecules with $[HP_2V_3W_{15}O_{59}]^{5-}$ units covalently bonded to a four-armed core and used them as a recoverable catalyst in the oxidation of tetrahydrothiophene to its sulfoxide by *tert*-BuOOH and H_2O_2.[184] The order of catalytic reactivity is tetra-POM + (H^+) > tetra-POM + *p*-MeC_6H_4-SO_3H (a strong MeCN-soluble Brønsted acid) > *p*-MeC_6H_4-SO_3H alone > tetra-POM + $(Bu_4N^+$ salt) alone ≫ no catalyst. Significantly, these catalysts can be easily recovered (Et_2O precipitation and filtration) and reused without loss in catalytic activity.

To build the supramolecular assembly of the dendritic oxidation catalysts in which each POM trianion is connected to a trication, Astruc and co-workers have designed polymethylarenes in which each methyl group can be transformed with three allyl groups by using the temporary complexation/activation by the 12-electron fragment $[CpFe]^+$.[185] The catalysts were precipitated from the organic phase by the addition of pentane leaving a clear solution in the case of the tris- and tetra-POM catalysts; whereas, precipitation of the mono-POM catalyst was tedious and left a white colloidal solution. When these catalysts were exposed to air, their catalytic activity was suppressed. Also, the G1 and 2 rigid dendrimers, based on polyphenylated adamantane cores with four or sixteen peripheral phosphonate moieties, were designed by Neumann and co-workers.[186] Further reaction of these dendritic phosphonates with tungstic acid in the presence of hydrogen peroxide led to the stepwise *in situ* formation of mono- and dinuclear phosphoperoxotungstates. These assemblies were active and selective for the epoxidation of simple alkenes with hydrogen peroxide. Recently, Astruc and co-workers[187] reported an elegant synthesis of a series of 9- and 27-armed polyoxometalate-centered metallodendrimers that bear epoxy, *n*-propyl and aryl sulfide end groups (**16**, Fig. 17). These catalysts were air-stable, efficient, recoverable, and reusable catalysts in the (1) epoxidation of cyclooctane, (2) selective oxidation of sulfides to sulfones, and (3) oxidation of cyclohexanol to cyclohexanone with H_2O_2. A study of the concentration effects showed that the dendritic structure increased the stability of the POM species and facilitated the recovery of the catalyst up to eight cycles; whereas, increased bulk around the POM center led to a negative kinetic effect. The results obtained with POM-cored metallodendrimers *vs.* tetraalkylammonium POMs ($[\{n\text{-}(C_8H_{17})_3\text{-}NCH_3\}^+]_3[PO_4\{WO(O_2)_2\}_4]^{3-}$ and $([\{[n\text{-}C_{18}H_{37}\ (75\%) + n\text{-}C_{16}H_{33}\ (25\%)]_2N(CH_3)_2\}^+]_3[PO_4\{WO(O_2)_2\}_4]^{3-})$ clearly revealed that these dendritic structures are more stable then their nondendritic counterparts. After the reactions were complete, the metallodendritic catalysts were recovered and recycled without a discernable lost of activity.

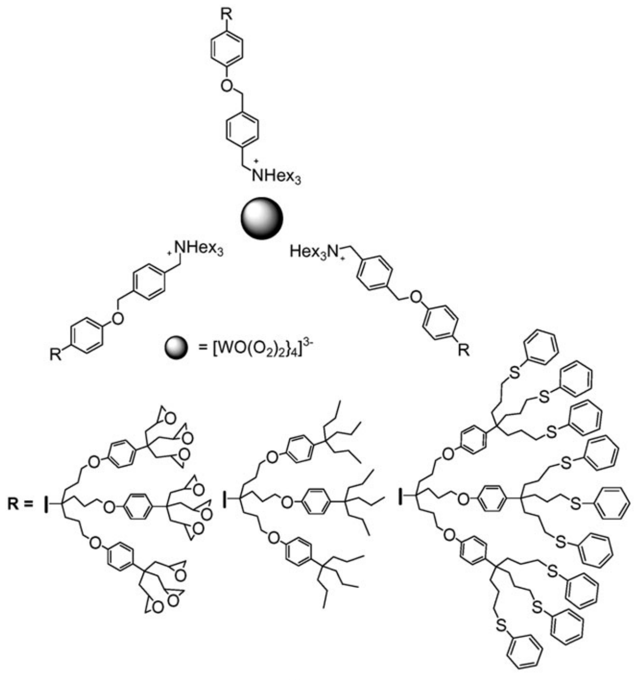

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Fig. 17 Metallodendrimers based on a tetrakis(diperoxotungsto)phosphate-core designed by Astruc and co-workers for use in epoxidations and oxidations.

2 Luminescence

Luminescence is commonly defined as light emission (in the broad sense of ultraviolet, visible or near-infrared radiation) by the electronic excited states of atoms or molecules and is an invaluable phenomenon for examining excited state behavior[188] and it is found in utilitarian applications (*e.g.*, lasers, displays, sensors, *etc.*).[189] Since dendrimers are structurally complex, multifunctional constructs possessing well-defined structures with a high degree-of-order, the selective incorporation of specific moieties for example luminescent moieties at predetermined sites within their structure is not only possible but in vogue. In this section, we will review recent advances in the field of luminescent metallodendrimers.

2.1 Ru-based metallodendrimers. Since the discovery of the unique photophysical properties of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine), the light absorbing properties of this and numerous related metal-centered chromophores have been widely studied.[190,191] Recent focus has been on the development of metallic supramolecular systems intended to absorb light and achieve transformations such as the conversion of light energy to electrical or chemical energy.[192]

Three bipyridine constructs each possessing two dendrons have been reacted with $RuCl_3$ or $[Ru(bpy)_2Cl_2]$ to generate a $[Ru(bpy)_3]^{2+}$-type core composed of up to 24 4′-*tert*-butylphenyloxy or 48 benzyl units.[193] The resultant complexes showed that the characteristic luminescent excited state was protected against quenching by dioxygen by the mere presence of the dendritic canopy. The electrochemical behavior and excited state quenching *via* electron-transfer of three different compounds containing the 4′-*tert*-butylphenyloxy peripheral units were studied. The metallodendrimer exhibited electrochemical behavior characteristic of encapsulated electroactive units; the value of the luminescence quenching rate constant, with three different electron acceptors (methylviologen dication, tetrathiafulvalene, and anthraquinone-2,6-disulfonate anion) decreased with increasing number and size of the dendritic branches.

Campagna *et al.*[194] examined photophysical properties of several racemic species, including $[(phen)_2Ru(phen\text{-}5,6\text{-}dione)(PF_6)_2]$ (where, phen = 1,10-phenanthroline), $[(phen)_2Ru(phen\text{-}5,6\text{-}diamine)(PF_6)_2]$, $[Ru(phen\text{-}5,6\text{-}dione)_3(PF_6)_2]$, $[(phen)_2Ru(tpphz)(PF_6)_2]$ (where, tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*:2″,3″-*j*]phenazine), $[(phen)_2Ru(\mu\text{-}tpphz)Ru(phen)_2(PF_6)_4]$ and $[\{(phen)_2Ru(\mu\text{-}tpphz)\}_3Ru(PF_6)_8]$, as well as the dinuclear species $\Delta\Delta\text{-}[(phen)_2Ru(\mu\text{-}tpphz)Ru(phen)_2(PF_6)_4]$, $\Lambda\Lambda\text{-}[(phen)_2Ru(\mu\text{-}tpphz)Ru(phen)_2(PF_6)_4]$ and $\Delta\Lambda\text{-}[(phen)_2Ru(\mu\text{-}tpphz)Ru(phen)_2(PF_6)_4]$, and the dendritic tetranuclear complexes $[(\Delta\text{-}(phen)_2Ru(\mu\text{-}tpphz))_3\text{-}\Delta\text{-}Ru(PF_6)_8]$, $[(\Delta\text{-}(phen)_2Ru(\mu\text{-}tpphz))_3\text{-}\Lambda\text{-}Ru(PF_6)_8]$ and $[(\Lambda\text{-}(phen)_2Ru(\mu\text{-}tpphz))_3\text{-}\Lambda\text{-}Ru(PF_6)_8]$ (**17**, Fig. 18). In all cases, luminescence decay was shown to be non-exponential with lifetimes in the range of 10^{-5} to 10^{-8} s; energy transfer

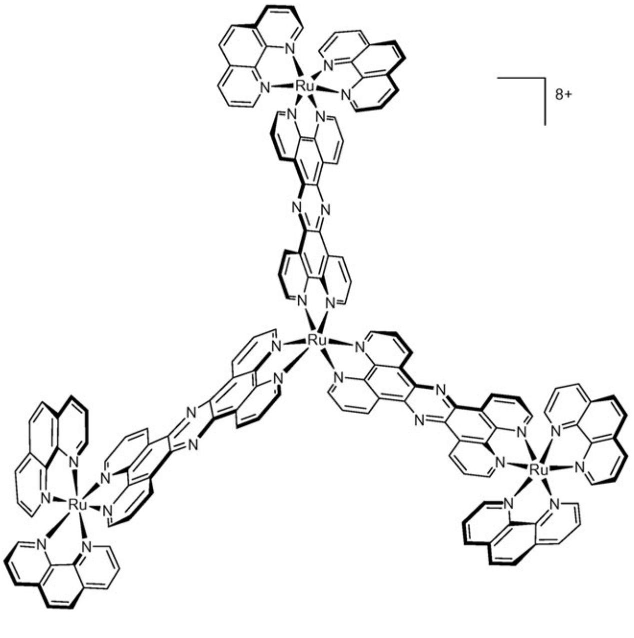

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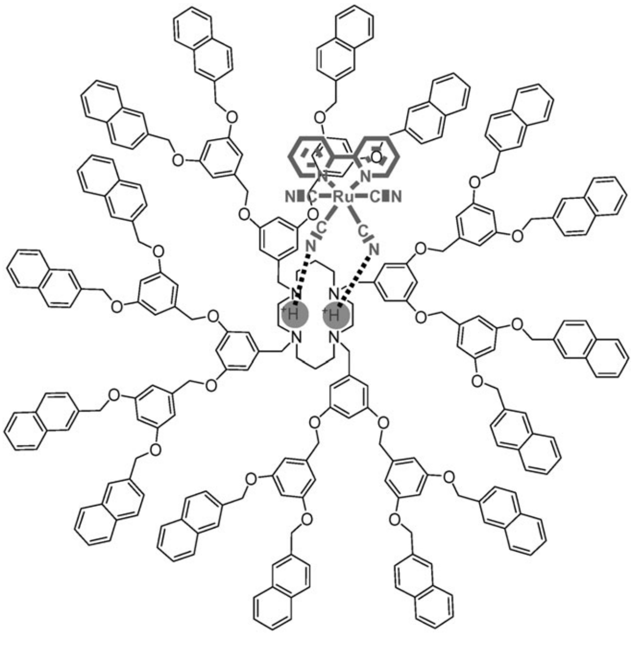
Fig. 18 Tetranuclear Ru(II) complex prepared by Campagna *et al.*



18

Fig. 19 $[Ru(bpy)(CN)_4]^{2-}$ complex with a protonated cyclam core prepared by Vögtle and co-workers for luminescence studies.

was found to occur from the core to periphery in the case of dendritic tetranuclear complexes.

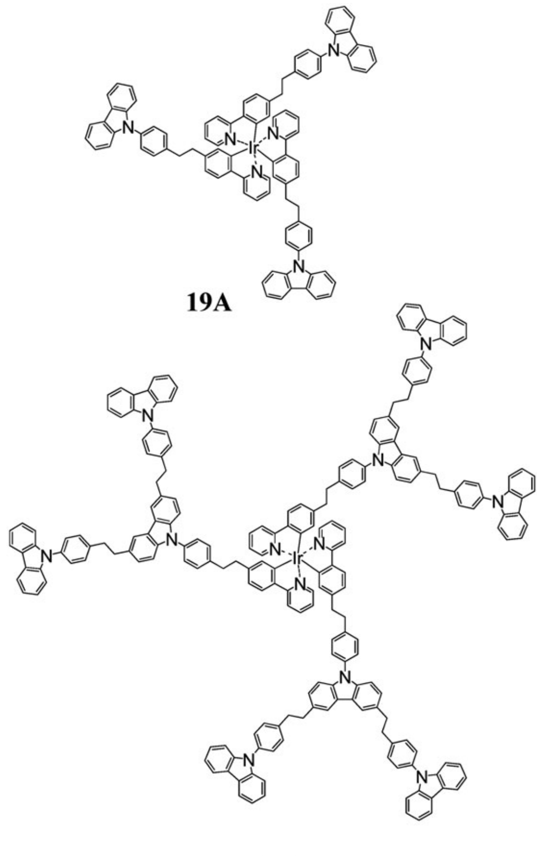
Vögtle and co-workers[195] illustrated that the luminescent cyclam-based hosts, 1,4,8,11-tetrakis(naphthylmethyl)cyclam (**A**) or 1,4,8,11-tetrakis{3,5-bis[3′,5′-bis(2″-oxymethylnaphthyl)benzyloxy]}benzyl-1,4,8,11-tetraazacyclotetradecane (**B**), can be constructed with the luminescent complex $[Ru(bpy)(CN)_4]^{2-}$ by a process that effects major changes in the luminescence properties (**18**, Fig. 19). In the $\{[Ru(bpy)(CN)_4]^{2-}(2H^+)[\mathbf{A}]\}$ and $\{[Ru(bpy)(CN)_4]^{2-}(2H^+)[\mathbf{B}]\}$ adducts, very efficient energy transfer occurred from the naphthyl units of (**A**) and (**B**) to the metal complex. Interestingly, the $\{[Ru(bpy)(CN)_4]^{2-}(2H^+)[\mathbf{A}]\}$ and $\{[Ru(bpy)(CN)_4]^{2-}(2H^+)[\mathbf{B}]\}$ adducts can be disordered by specific chemical additives, namely, DABCO (1,4-diazabicyclo[2.2.2]octane) yielding $[Ru(bpy)(CN)_4]^{2-}$ and **A** or **B**. The addition of triflic acid also caused this type of disassociation forming $(\mathbf{A}\cdot 2H)^{2+}$ or $(\mathbf{B}\cdot 2H)^{2+}$ and the protonated forms of $[Ru(bpy)(CN)_4]^{2-}$.

Kim and co-workers[196] reported the surface coating of a metallodendrimer with electrochemiluminescent (ECL) polypyridyl Ru(II) complexes, *dendr*-4-[Ru(L)$_2$(L′)] (L = bpyCO–; L′ = mbpy(CH$_2$)$_3$CO–, where, mbpy = 4′-methyl-2,2′-bipyridine). The electrochemistry of the Ru(II) metallodendrimers containing the 4-carboxypropyl-4′-methyl-2,2′-bipyridine moiety was similar with those of the parent $[Ru(bpy)_3(PF_6)_2]$ complex; however, the ECL intensity of *dendr*-4-[Ru(bpy)$_2$(mbpy(CH$_2$)$_3$CO–)(PF$_6$)$_8$] was considerably larger than that of the corresponding Ru(II) complexes containing an *o*-phenyl ligand and $[Ru(bpy)_3(PF_6)_2]$ complex. The spacer unit between the complex and dendrimer affected the ECL intensity and the *dendr*-4-[Ru(bpy)$_2$(mbpy(CH$_2$)$_3$CO–)] was proven to be a very efficient ECL material.

2.2 Ir-based metallodendrimers. Bis- and triscyclometalated Ir(III) complexes are of interest due to their potential applications as phosphorescent materials in organic light emitting devices (OLEDs).[197–199] Burn and co-workers[200] designed a metallodendrimer possessing phenylene dendrons, a *fac*-tris(2-phenylpyridine) iridium core, and a 2-ethylhexyloxy surface. This unique metallodendrimer was incorporated into a device prepared using a neat solution-processed method containing the emissive iridio dendrimer with an evaporated 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-based electron-transport/hole-blocking layer. The device exhibited intense green luminescence with a turn-on voltage of 4.5 V and peak brightness of 1680 cd m^{-2} at 12 V; however, the maximum efficiency of the device was minimal, reaching only 0.14 lm W^{-1} (0.47 cd A^{-1}) at 9.5 V.

Solution-processable phosphorescent metallodendrimers with biphenyl-based dendrons and *fac*-tris(2-phenylpyridyl)iridium(III) core have been prepared through a facile, convergent procedure.[201] The quantum yield of the neat metallodendrimer film increased with increasing generation suggesting that the metallodendritic architecture can start to control intermolecular interactions. Recently, films of the phenylene- and carbazole-based dendron, *fac*-tris(2-phenylpyridine)iridium(III)–cored metallodendrimer with 2-ethylhexyloxy surface groups, were reported and the triplet–triplet annihilation studied.[202] By evaluating the neat film state, the triplet exciton diffusion length was found to be between 2 and 10 nm based on dendron size.

Tokito and co-workers[203] prepared the G1 and G2 metallodendrimers with hole-transporting phenylcarbazole-based dendrons and the *fac*-tris(2-phenylpyridine)iridium(III) core (**19A** and **19B**, Fig. 20). When incorporated into an OLED device with 1,3-bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole-2-yl]-



19A

19B

Fig. 20 Dendritic Ir(III) tris(bpy) complexes prepared by Tokito and co-workers for use in OLEDs.

benzene, as an electron-transporting material, the device exhibited greater efficiency than those using a neat metallodendrimer film. The current is higher in the OLED using the neat G1 level system than those using the dendrimer consisting of the Ir(ppy)$_3$ core and phenylene-based dendrons[204] indicating that the dendrimer's hole drift mobility was enhanced by the hole-transporting dendrons.

Balashev and co-workers[205] synthesized Ir-based complexes [Ir(C^N)$_2$(G1-bpy)(PF$_6$)], where C^N is a cyclometallating ligand derived from 2-(2′-thienyl)pyridine and 2-phenylpyridine, and G1-bpy is 4,4′-bis[3″,5″-bis(benzyloxy)phenylethyl]-2,2′-bipyridine. Their studies demonstrated that the luminescence behavior of the mixed-ligand Ir(III) complexes with a dendritic bipyridine ligand strongly depended on the cyclometalating ligand, temperature, and matrix (effect of the hardness and polarity).

Cheng and Wang[206] designed an iridio dendrimer with G1 and G2 carbazole dendrons, as the rigid hole-transporting materials. With a device structure of ITO/poly(3,4-ethylenedioxythiphene):poly(styrenesulfonic acid)/neat dendrimer/1,3,5-tris(2-*N*-phenylbenzimidazolyl)benzene/LiF/Al, a maximum external quantum efficiency (EQE) of 6.8 (G1) and 10.3% (G2) and a maximum luminous efficiency of 23.2 (for G1) and 34.7 cd/A (for G2) were realized. The turn-on voltage slightly increased from 3.0 V for G1 to 3.5 V for G2. By doping the dendrimers into a carbazole-based host, the maximum EQE can be further increased to 16.6%; however, even with the G2 dendron, there were still significant intermolecular interactions in the film that caused photoluminescence quenching. To obtain the best device performance, the doping material into *N*-(4-([9,3′;6′,9″]tercarbazol-9′-yl)phenyl)carbazole (TCCz) and controlled under the concentration of 40 and 50 wt% for G1 and G2, respectively, should be used.

2.3 Lanthanide-based metallodendrimers. Lanthanide ions are known to have long luminescence lifetimes, which is a useful asset for specific applications,[207] such as in sensors[208–210] and fluoroimmunoassays.[211] As a result of their forbidden electronic transitions, lanthanide ions have weak absorption properties, which can be a severe disadvantage for applications based on luminescence. Attaching dendrimers or dendrons containing strong chromophores can help circumvent this problem. For example,[212–215] in solution, these complexes have proven that: (1) the absorption spectrum of the dendrimer was unaffected; (2) fluorescence from dansyl groups was quenched; (3) the quenching effect was best for Nd^{3+} and Eu^{3+}, moderate for Er^{3+} and Yb^{3+}, small for Tb^{3+}, and minimal for Gd^{3+}; and (4) for Nd^{3+}, Er^{3+} and Yb^{3+}, the quenching of the dansyl fluorescence was accompanied by a sensitized, near-infrared emission of the lanthanide ion. These observations were clarified by using the energy levels and redox potentials of both dendrimer (**20**, Fig. 21) as well as metal ions.

Fréchet-type dendrons comprised of carboxylate-focal unit were self-assembled around Er^{3+}, Tb^{3+} or Eu^{3+} ions leading to dendrimer **21** shown in Fig. 22.[216–220] Luminescence experiments conducted in toluene revealed that excitation of the chromophores in the branches caused sensitized emission of the lanthanide ion, most probably by energy-transfer based on the Förster mechanism.[221] These metallodendrimers revealed

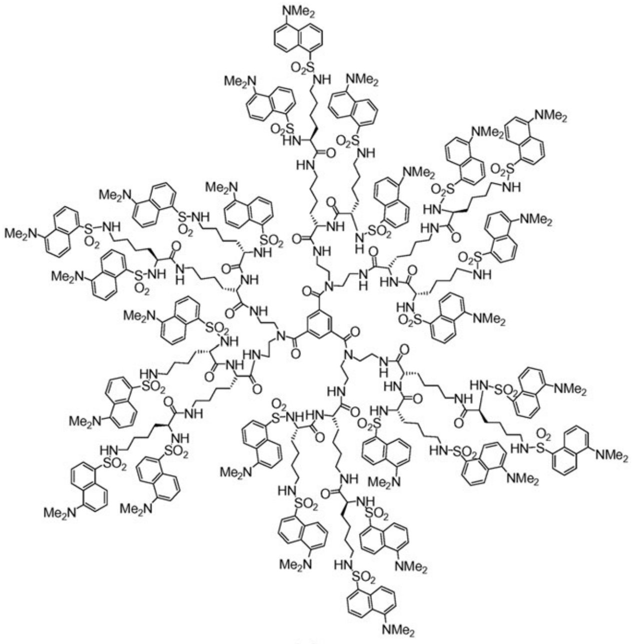


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Fig. 21 A dendritic polylysine ligand for lanthanide ion complexation.

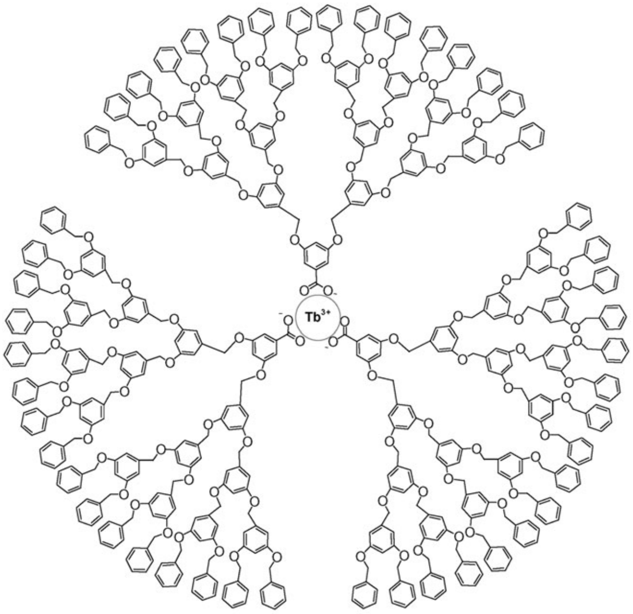

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Fig. 22 Tb-cored metallodendrimer prepared for luminescence studies.

enhanced luminescence properties as the shell size increased, which was attributed to both an "antenna effect" (energy transfer from the ligand to the core), and a "shell effect" (site isolation of the steric emission effect that keeps the Ln^{3+} cores apart from one another leading to a decrease in their rate of self-quenching).

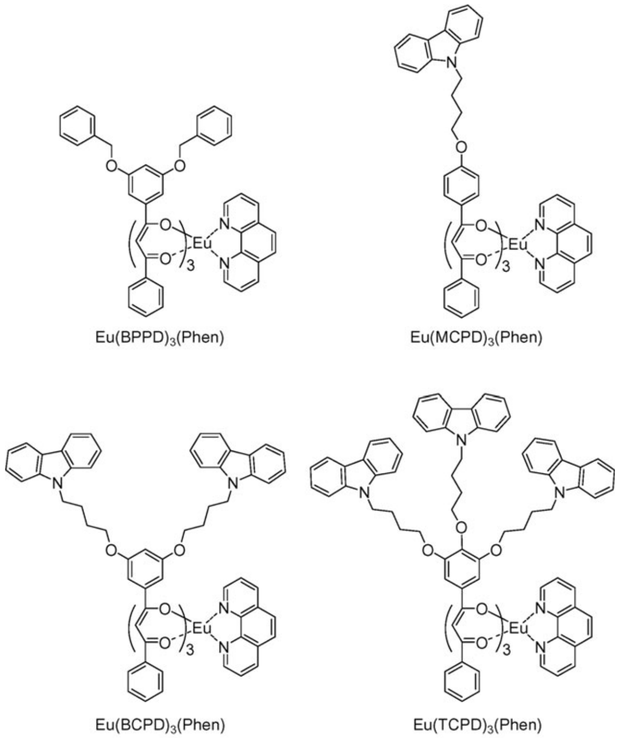

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Fig. 23 Photoluminescence efficiencies were reported for these dendritic Eu(III) complexes.

Tian and co-workers[222,223] designed Eu-based dendritic complexes bearing carbazole units on the periphery (**22**, Fig. 23). Upon indirect excitation of the carbazole units, a red emission peak was observed at 615 nm, characteristic of the Eu(III) ion transition ($^5D_0 \rightarrow {}^7F_2$). As a result of the light-harvesting and site-isolation properties of carbazole dendrons, the photoluminescence efficiencies of [Eu(MCPD)$_3$(phen)], [Eu(BCPD)$_3$(phen)] and [Eu(TCPD)$_3$(phen)] in the film state were increased by 3.3, 7.9 and 4.5 fold, respectively, (where, MCPD = 1-{4-[4-(9*H*-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3-dione, BCPD = 1-{3,5-bis[4-(9*H*-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3-dione, TCPD = 1-{3,4,5-tris[4-(9*H*-carbazol-9-yl)butoxy]phenyl}-3-phenylpropan-1,3-dione). The EL device, ITO/NPB/CBP:Eu(TCPD)$_3$(Phen)/BCP/Mg:Ag (where, NPB = *N*,*N*′-bis(1-naphthyl)-*N*,*N*′-diphenyl-1,1′-diphenyl-4,4′-diamine), showed white light emission with a maximum external quantum efficiency of more than 1.1% and maximum brightness of 229 cd m^{-2}.

Lanthanide ion-cored (Er^{3+} and Tb^{3+}) metallodendrimers were synthesized by the self-assembly of three fluorinated dendrons having a carboxyl anion focal group surrounding the lanthanide ion.[224] Spectroscopic evidence showed that energy transfer from the peripheral fluorinated phenyl moieties of the dendrons to the lanthanide cation for the Eu^{3+}- and Tb^{3+}-cored metallodendrimers occurred in solution. The excitation of perfluorinated aromatic groups was found to decay with *ca.* 0.7 ns and a longer decay with lifetimes in the range 1–1.5 ms over a wide concentration range (μM–mM). Antenna effects and light harvesting from the surface of the metallodendrimer, followed by energy transfer to the core, were the main mechanisms for luminescence in the cationic-lanthanide metallodendrimers.

2.4 Mixed metals-based metallodendrimers and others.

The synthesis of mono- or polynuclear transition metal complexes and the evaluation of their appealing photo- and electrophysical properties, have attracted substantial attention in support of their extensive potential practical applications.[19,20,225–230] Balzani and co-workers[231] constructed a dendritic nanometric polynuclear metal complex, based on an Os(II) core and containing 21 Ru(II)-based complexes within the branches, using both convergent and divergent techniques.[227] The Os(II) moiety gave the dendrimer ambient temperature luminescent properties, and the absorption cross-section increased with increasing nuclearity.

Campagna and co-workers[232] reported a series of new trinuclear dendrons: $[Cl_2Os\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2]^{4+}$, $[Cl_2Os\{(\mu\text{-}2,3\text{-dpp})Os(bpy)_2\}_2]^{4+}$ and $[(bpy)Ru\{(\mu\text{-}2,3\text{-dpp})Os(bpy)_2\}_2]^{6+}$, where bpy = 2,2′-bipyridine and 2,3-dpp = 2,3-bis(2-pyridinyl)pyrazine. The photophysical properties of the subunit(s) dominated the luminescence properties, whereby the lowest-lying excited state was localized, indicative of fast intercomponent energy transfer. However, the lowest-lying excited state of the intermediate chromophore(s) was higher in energy than the lowest-lying excited states of the central and peripheral chromophores; consequently, periphery-to-center energy transfer was not achieved. To overcome this, alternative metals, such as Os(II) and Pt(II), that facilitate efficient periphery-to-center energy transfer in larger species were introduced.[233]

One of the most widely investigated ligands in coordination chemistry is 1,4,8,11-tetraazacyclotetradecane (cyclam).[234,235] Cyclam and its 1,4,8,11-tetramethyl derivative can be mono- and di-protonated in aqueous solution and is capable of coordinating numerous metal ions, such as: Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). Several studies have been conducted on metal ion interactions of cyclam-cored dendrimers with Fréchet-type dendrons, as the peripheral units.[236–239] Complexation with Zn^{2+} occupied the N-lone pairs thereby preventing exciplex formation and resulting in an intense naphthyl fluorescence.[238] Using this strong emission signal, dendrimer–metal complex formation could be determined from titration experiments. Additionally, a study involving the complexation of dendritic ligands with lanthanide ions (Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}) has led to similar results; an increase of the naphthyl emission band at 337 nm and the disappearance of the exciplex signal at 480 nm were observed.[236]

Sha and co-workers[240] prepared a dendritic 8-hydroxyquinoline ligand, based on a PAMAM-type dendron, which was coordinated with Zn(II) (**23**, Fig. 24). The luminescence intensity of the G2 dendron was higher than that of G1, and upon complexation with Zn(II), a bathochromic shift was observed; the intensity of the Zn(II) complexes was found to be higher than that of the analogous ligands.

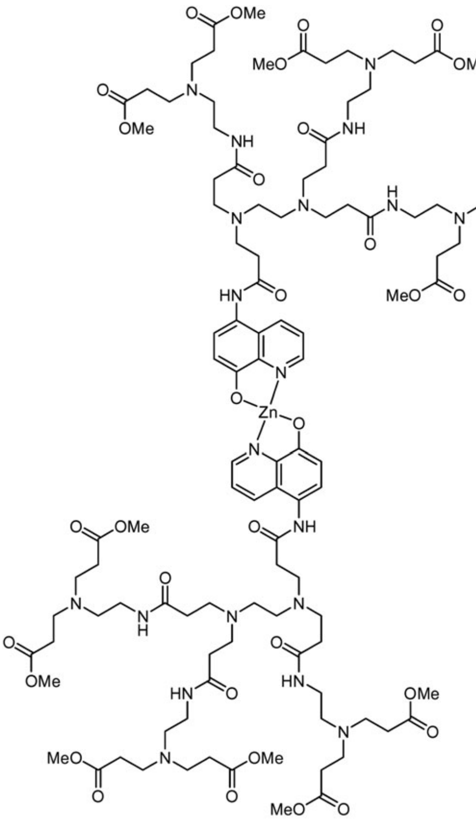

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Fig. 24 Dendritic 8-hydroxyquinoline–Zn(II) complex prepared by Sha and co-workers.

Kim and co-workers[241] synthesized complexes for optical amplification based on erbium(III)-cored metalloporphyrins or dendritic counterparts. The complex having a Pt(II)-metallated porphyrin showed a higher intensity near-infrared emission for the Er^{3+} ion than that of the Zn(II)-metallated porphyrin complex. The Er(III)-cored complex with Pt(II)-porphyrin bearing G2 Fréchet-type dendrons displayed an intensity seven times greater than that of its parent Pt(II)-porphyrin. The emission lifetimes of the Pt(II)-porphyrin Er(III)-cored complex and the Er(III)–cored dendritic complex were found to be 30 and 40 μs, respectively, in deoxygenated THF solution. These results indicated that energy transfer from the metalloporphyrins to the Er^{3+} core occurred through a triplet state.

Halet and co-workers[242] prepared the Re(I)–alkynyl precursors, [1,3-$(HC{\equiv}C)_2$-5-{(N^N)$(CO)_3$ReC≡C}C_6H_3] (N^N = ^{t}Bu$_2$bpy, Me$_2$bpy or bpy), and the trinuclear branched [Re(I)–Pd(II)]-alkynyl complexes, [1,3-{Cl$(PEt_3)_2$PdC≡C}$_2$-5-{(N^N)$(CO)_3$ReC≡C}C_6H_3] in order to achieve strong fluorescence properties. An intense, low-energy absorption at *ca.* 410–430 nm was observed and assigned to the [dπ(Re) → π*(diimine)] MLCT transition possibly mixed with some alkynyl-to-diimine [π(C≡C) → π*(diimine)] LLCT character.

3 Sensors

Metallodendrimers have been utilized for various sensing applications, as a result of their polyvalent characteristics, such as ion detection, gas sensing, and redox-active switches.[243]

Recently, Castellano and co-workers[244] described a luminescence lifetime-based sensor for cyanide ion as well as other counterions using Ru(II) diimines having metal-to-ligand charge transfer (MLCT) excited states with anion recognition capabilities of the 2,3-di(1*H*-2-pyrrolyl)quinoxaline moiety. The viability as a lifetime-based sensor for anions has been tested using time-resolved photoluminescence decay techniques. Significant changes to the UV-Vis and steady-state emission properties upon addition of various ions (*e.g.*, fluoride, cyanide and phosphate) were detected.

The use of ferrocene to detect CO through coordination has been exploited by Kim and co-workers.[245] Their metallodendrimer sensor showed a 10-fold linear increase up to a volume concentration of 40%, above which, it became saturated. The transient responses exhibited a delay time of 50 s, a rise time of 150 s, and a decay of 420 s, which was reasonable for a gas sensor when considering the gas diffusion time into the chamber and the continuous reaction with the remaining gas in the chamber after the initial gas introduction had ceased.

Since phosphorescence quenching is very sensitive to, and selective for, oxygen, phosphorescence quenching of dissolved molecular oxygen (O_2) for quantification is a well-established process.[243,246–248] Vinogradov and co-workers[249–251] designed a novel metallodendrimer consisting of encapsulated Pd or Pt porphyrins, which are commonly used as basic phosphors. Diffusion barriers for oxygen and other quenchers in solution have been increased using the protective canapé of the

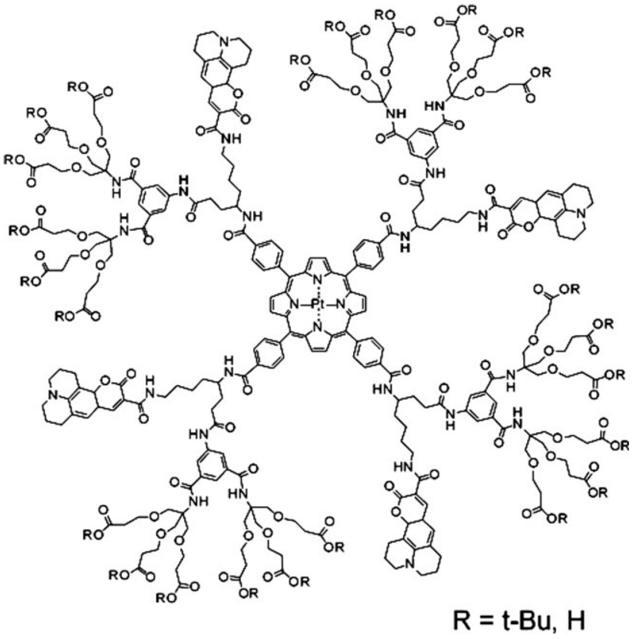

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Fig. 25 Pt-containing dendritic porphyrin prepared by Vinogradov and co-workers that displays phosphorescence.

dendritic shell to isolate the luminescent chromophore(s). Recently, a phosphorescent oxygen nanosensor utilizing a combination of dendritic architecture and two-photon absorbing antennae (**24**, Fig. 25) has been reported,[252] in which the intramolecular energy transfer, followed by intersystem crossing within the acceptor chromophore group, induced its phosphorescence.

van Koten and co-workers[253–256] synthesized a series of square-planer platinum(II) complexes [PtX(4-E-2,6-$\{CH_2NRR'\}_2C_6H_2$)] (X = Cl, Br, I, tolyl; R, R′ = Et, Me; E = H, OH, $OSiMe_2{}^tBu$) based on a *N*,*C*,*N*′-tridentate, monoanionic "pincer" ligand. These complexes demonstrated spontaneous adsorption of gaseous SO_2 to form pentacoordinated adducts. The formation of these adducts in either the solid- or solution-state was fast, reversible and had a characteristic material-color change from colorless to bright orange. This novel complex possessed several key prerequisites of sensor materials for repetitive, submillimolar to molar, diagnostic SO_2 detection. The response capacity to gas detection was tunable by both electronic and steric modifications of the ligand, for example, by introducing different *N*-substituents. When the active detection sites were anchored to the periphery of these metallodendrimers, full recovery, necessary for repetitive uses, of the sensor materials was possible. A recent report described a signal detection technique using a quartz crystal microbalance (QMB),[257,258] wherein substrate binding was detected by changes of the net mass of the surface (host–guest complex *vs.* host only).

Dendrimers having nanoparticle cores can also be used as sensing materials. One novel route to such composites involved the assembly of dendrons onto gold nanoparticles, ultimately giving rise to stable nanoparticle-cored dendrimers (**25**, Fig. 26).[259–262] Using cyclic voltammetry, these metallodendrimers were demonstrated to selectively distinguish oxo-anions and ATP^{2-} even in the presence of other less interacting anions, such as hydrogensulfate, chloride or the anion of the supporting electrolyte (BF_4^- or PF_6^- in large quantity). A surface-modified platinum electrode was also found to act as an efficient sensor; upon washing the sensor-modified electrode with CH_2Cl_2, the ATP^{2-} was removed, showing only the original cyclic voltammetry wave of the dendrite, demonstrating the potential for repeated use.

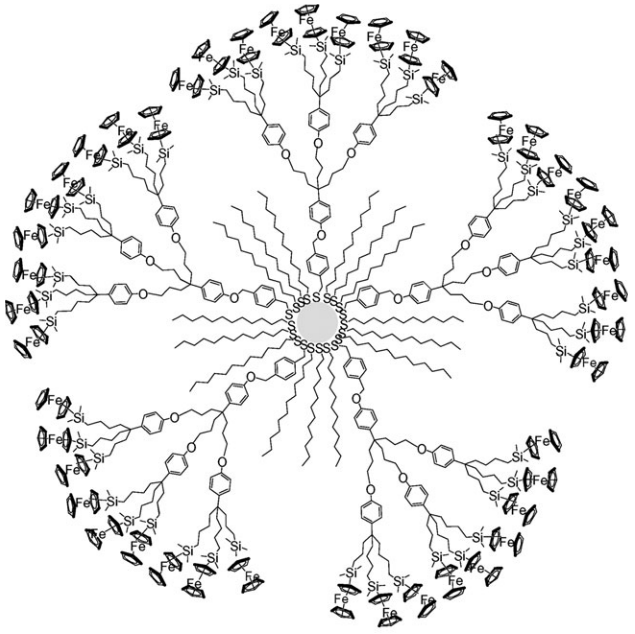

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Fig. 26 Dendronized gold colloids shown to sense oxo-anions and ATP^{2-}.

Recently, Beer and Cormode[263] developed a surface-enhanced optical anion sensor based on the modification of gold nanoparticles in which dodecanethiol-stabilized gold nanoparticles were subjected to ligand substitution with a disulfide-substituted zinc porphyrin, providing 30 and 80 receptor sites per nanoparticle. Enhanced binding affinities of the surface bound porphyrin receptor site were demonstrated to be two orders of magnitude greater for chloride ions and dihydrogenphosphate ions in DMSO compared to that of the free metalloporphyrin.

4 Molecular switches

Molecular switches based on photochromic behavior,[264–273] optical control of chirality,[274,275] fluorescence,[276,277] intersystem crossing,[278] electrochemical and photochemical changes in liquid crystals,[279,280] thin films,[281] and electron- as well as energy-transfer[282–285] have been investigated. Generally, porphyrins have been utilized in molecular switching systems because of their tunable electrochemical and spectral properties associated with the incorporation of different metals within the porphyrin. Also, porphyrins can potentially create arrays with four-fold symmetry. Lindsey and co-workers[286] designed a pentamer having four Zn(II)-porphyrins (Zn–Por)s around a central free-based porphyrin (FBPor) (**26**, Fig. 27), in

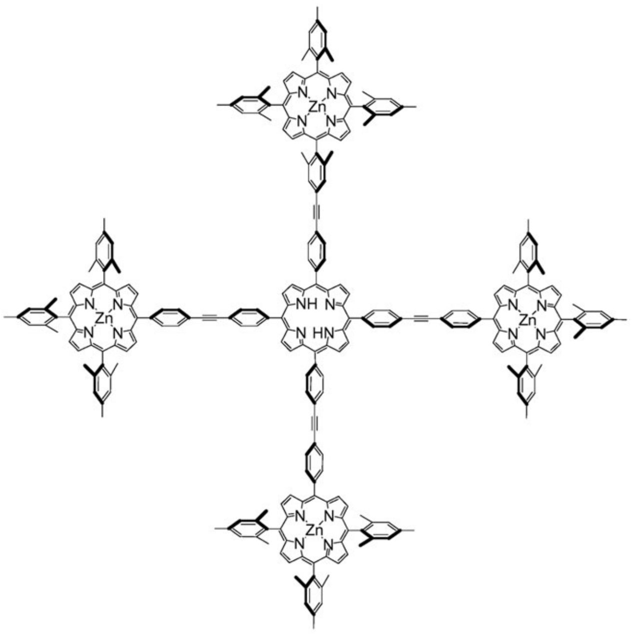

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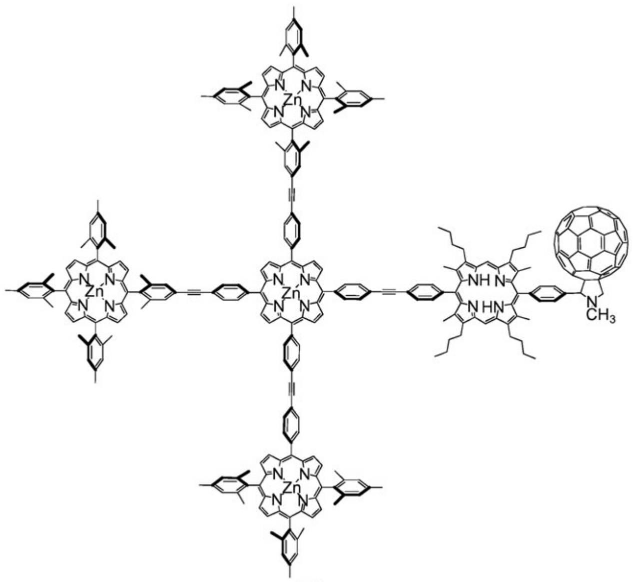
Fig. 27 Pentameric porphyrin–Zn(II) complex prepared by Lindsey and co-workers.

which energy transfer from Zn–Por to FBP or occurred with a quantum yield of *ca.* 90% based on the Zn–Por emission quenching.

An example of a molecular switch utilizing energy transfer in porphyrin arrays is the optoelectronic gate also synthesized by Lindsey and co-workers.[287] Three porphyrins and a light-absorbing dye were arranged in either a linear or branched array. The branched arrangement consisted of a trisubstituted Zn–Por with a boron dipyrromethane dye (BDPY) and magnesium-porphyrin (Mg–Por) with a FBPor on the periphery. Excitation of BDPY with 485 nm light initiated a stepwise energy transfer; the energy was localized on the FBPor and radiatively dissipated with an emission maximum at 650 nm. The quantum yield was *ca.* 0.8 for both these arrays. The activation of a non-radiative decay pathway within the architecture can, however, alter the emission. For example, the Mg–Por has the lowest oxidation potential ($^{+1}E_{1/2}$ = 0.34 V *vs.* SCE); therefore, vacancy in the highest-occupied molecular orbital can be induced electrochemically or with an oxidizing agent, such as iron perchlorate [(Fe)(ClO$_4$)$_3$]. Once oxidized, energy transfer to the Mg–Por$^+$ occurred. The fluorescence signal was fully restored by reducing the porphyrin back to its original state. This system established the capacity to modulate energy transfer in large arrays; however, diffusional processes, which are relatively slow compared to the energy transfer events, governed the "ON/OFF" fluorescence switching.

Gust and co-workers[288] created a synthetic antenna capable of electron transfer-induced energy transfer. Four Zn–Por chromophores were covalently attached to a FBP or electron donor, which was linked to a C$_{60}$ electron acceptor (**27**, Fig. 28). Excitation of the Zn–Por chromophores resulted in an energy transfer (τ = 240 ps) to the FBPor with a quantum yield of 0.69, followed by an electron transfer (τ = 3 ps) to yield the charge-separated Zn–Por$_4$–FBPor$^+$–C$_{60}{}^-$ state (τ = 1 ns). The choice of metal in the porphyrin chromophore is vital in determining the rate and yield of energy transfer, in that the metal controlled both the electrochemical properties and the excited state energy and lifetime. A through-bond energy transfer mechanism dominants in most antenna complexes; therefore, the nature of the link between the participating moieties is critical in order to have sufficient electronic coupling between sites.



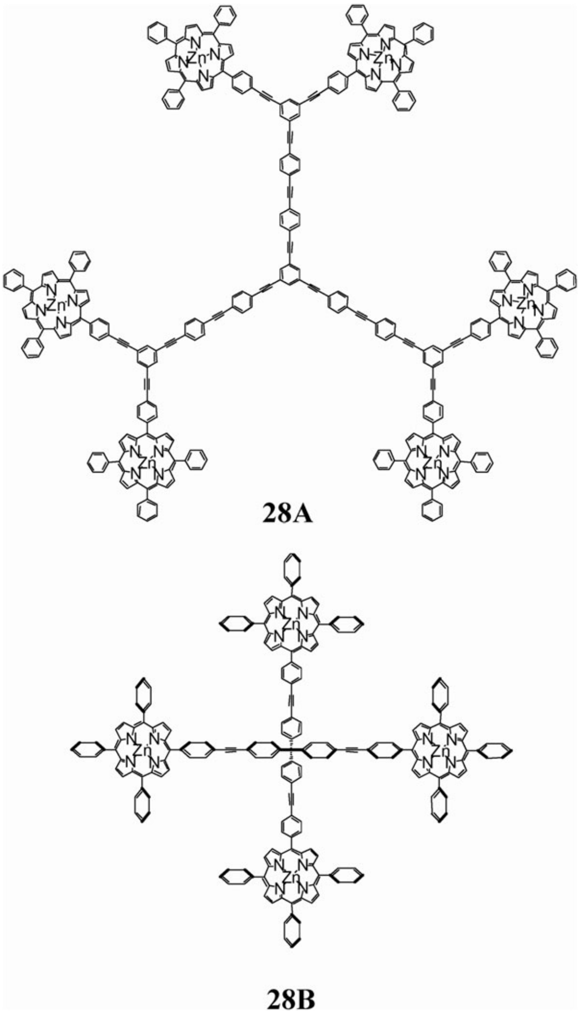
27

Fig. 28 C$_{60}$–porphyrin Zn(II) complex designed by Gust and co-workers as a molecular antenna.

Vauthey and co-workers[289] synthesized trigonal and tetrahedral metallomacromolecular systems from which energy transfer-based molecular switches might be crafted. The Zn–Por to FBPor distance is 35.5 Å (**28A**, Fig. 29) along the shortest line and 67.5 Å along the bonded pathway; energy transfer was found to occur primarily *via* a through-space mechanism. When the bonded pathway distance became small ($<$45 Å), a shift to a through-bond mechanism was observed. However, in components where the interchromophore distance was 27 Å along the shortest line and 32 Å along the bonded pathway (**28B**, Fig. 29), the through-space mechanism was still dominant.

5 Others

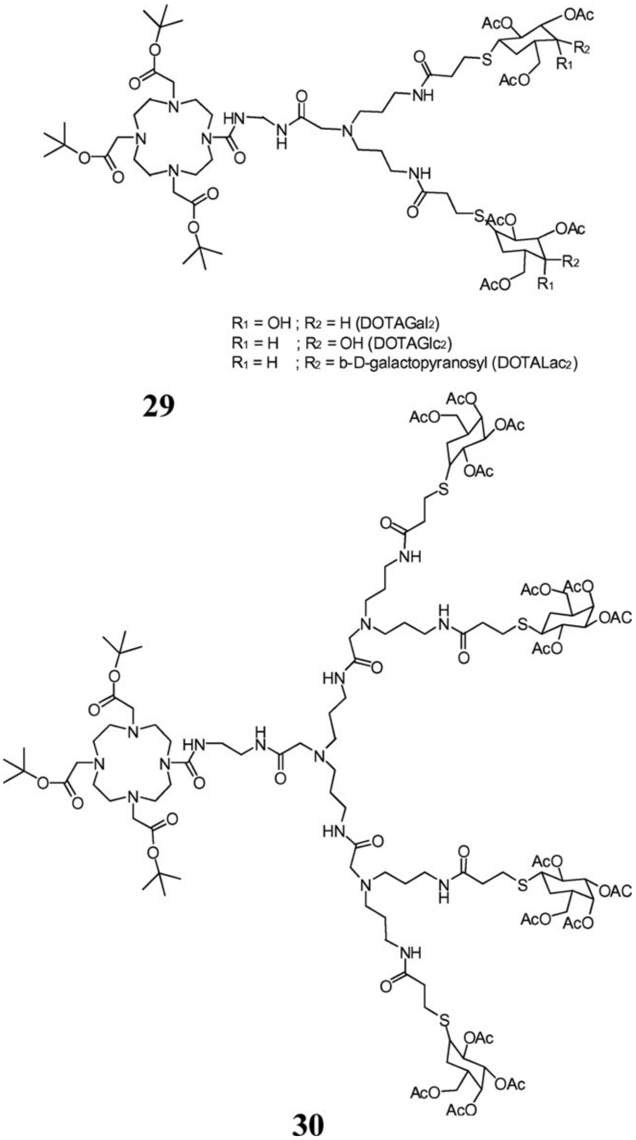
Metallodendrimers have played an active role with regards to biomedical applications.[290,291] Dendritic magnetic resonance imaging (MRI) contrast agents have been developed in which Gd(III) was chelated by 2-(4-isothiocyanatobenzyl)-6-methyldiethylenetriaminepentaacetic acid; the Gd(III) complex was then anchored to different amino-terminated PAMAM dendrimers.[292] The PAMAM-based Gd(III) complexes were found to be more effective contrast agents when compared with other readily available macromolecule-chelated complexes, such as those formed using albumin, polylysine and dextrin. Also using the PAMAM framework, Tóth and co-workers[293–295]



28A

28B

Fig. 29 Trigonal and tetrahedral shaped Zn(II)-porphyrins crafted by Vauthey and co-workers as molecular switches.



R_1 = OH ; R_2 = H (DOTAGal$_2$)
R_1 = H ; R_2 = OH (DOTAGlc$_2$)
R_1 = H ; R_2 = b-D-galactopyranosyl (DOTALac$_2$)

29

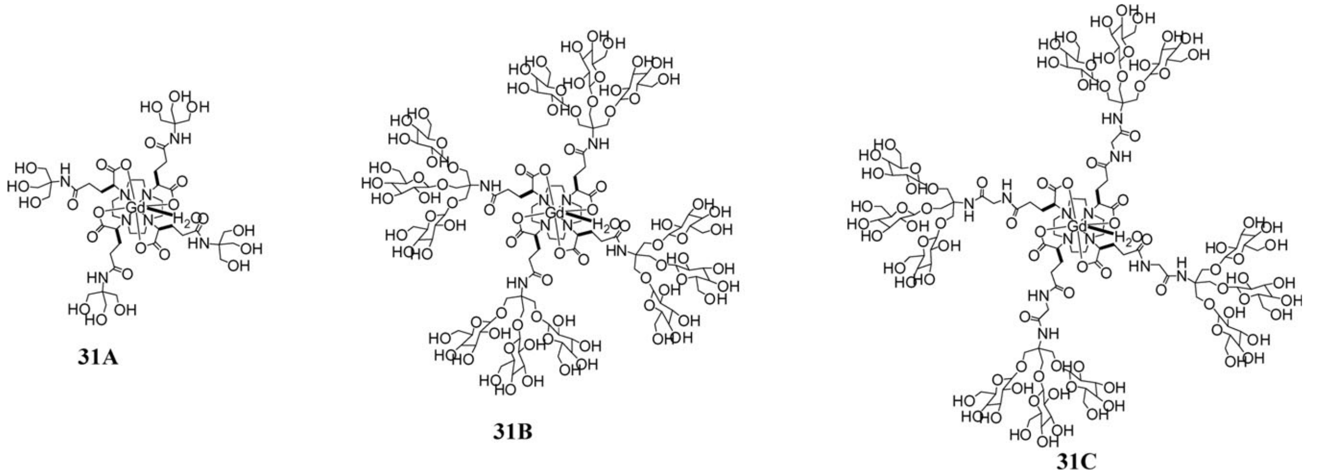
30

Fig. 30 DOTA–Glycoconjugate ligands prepared by Tóth and co-workers for lanthanide(III) complexation.

prepared a series of multivalent lanthanide(III)–glycoconjugates, possessing 1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane (DOTA) monoamide functionalized chelators, (**29**, **30**, Fig. 30) which were known to form Ln(III) complexes possessing high thermodynamic and kinetic stability, a property of crucial importance for *in vivo* applications.[296] The probability of *in vivo* MRI applications, based on receptor binding, generally depends on the concentration of the receptor as well as the receptor-bound species relaxivity. However, the relaxivity of the Gd(III) complexes of the glycodendrimer in solution had a lower value than expected as a result of restrictions imposed by the flexibility and molecular weight of the dendrimer. In spite of these limits, the lectin–glycoconjugated interaction was capable of retarding the tumbling rate considerably, therefore increasing the relaxivity of the Gd(III) complexes.

Meijer and co-workers[297] synthesized gadolinium–diethylenetriaminepentaacetic acid (Gd-DTPA)-terminated PPI dendrimers as contrast agents. The efficiencies of these dendritic contrast agents, expressed in terms of longitudinal (r_1) and transverse (r_2) relaxivities, were determined at 1.5 T at 20 °C. The r_1 and r_2 values increased considerably with increasing generation of Gd–DTPA-terminated dendrimer. The G5 contrast agent displayed the highest ionic relaxivities (per gadolinium), $r_1 = 19.7\ \mathrm{mM^{-1}\ s^{-1}}$ and $r_2 = 27.8\ \mathrm{mM^{-1}\ s^{-1}}$, which are substantially higher than the ionic relaxivities of the parent Gd–DTPA. Such complexes have also used to study the interaction of avadin and biotin based on the relaxivity of the metallodendrimer.[298–300]

Hermann and co-workers[301] reported the relaxometric characterization of the fully loaded conjugate, containing 16 gadolinium chelates on the surface of a G2 PAMAM dendrimer. The proton relaxivity of this system was found to be pH-dependent and, at pH < 6, it increased to *ca.* 24.8 $\mathrm{mM^{-1}\ s^{-1}}$. As the relaxivity of Gd–DO3AP^{ABn} ⟨H$_4$DO3AP^{ABn} = 1,4,7,10-tetraazacyclododecane-4,7,10-triacetic-1-{methyl[(4-aminophenyl)methyl]phosphinic acid}⟩ was constant in the 2.5 to 12 pH range,[302] the observed behavior has to be related to an effect associated with the protonation of donor groups on the dendrimer backbone. The protonation of the


31A

31B

31C

Fig. 31 Glycoconjugates with gadolinium complexes prepared by Parker and co-workers for use as MRI contrast agents.

ethylenediamine core of the dendrimer as well as branching tertiary amine centers may rigidify the dendrimer's backbone[303] and/or induce the formation of H-bonds with neighboring oxygen atoms of the Gd-chelates. The occurrence of these intra-branch interactions would lead to a decrease in the internal mobility of each paramagnetic complex and, in turn, an increase of their observed relaxivity. In case of ionic pairs between the negatively charged G2 Gd_{16} metallodendrimer and polycationic species, the relaxation enhancement was not primarily associated with formation of multimeric structures involving cross-linking of more polyaminoacid chain by a single unit of the dendritic conjugate. Rather, the independence of the relaxivity enhancement observed from the length and nature of the polyaminoacid chain indicated that the polycationic species acted as "glue" that reduced the internal mobility of the Gd-chelates, in a way analogous to that surmised above for the protonation of the dendritic backbone.

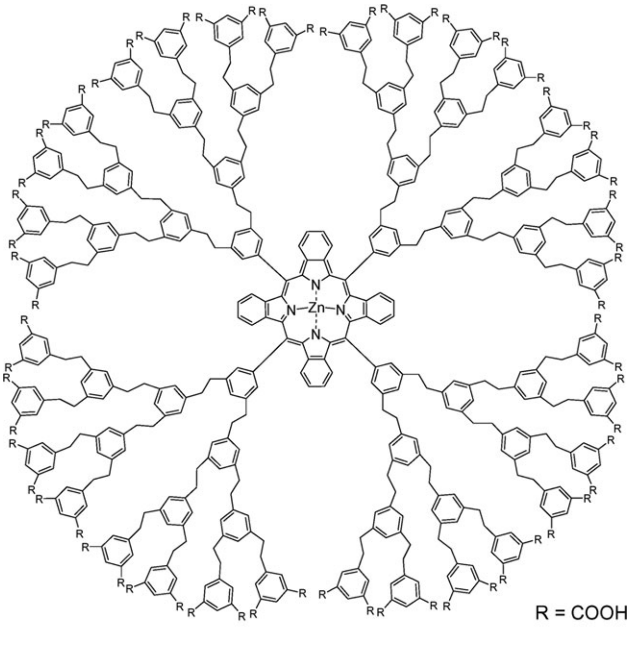
Parker and co-workers[300,304] synthesized the C_4 symmetric, medium molecular weight conjugates incorporating 12 glucose or galactose groups linked *via* four dendritic wedges to a central Gd complexes (**31A–C**, Fig. 31). The water exchange rate at the Gd center (by a variable-temperature ^{17}O NMR study) showed a similar rate for **31B** and **31C** (the water exchange lifetime, τ_M = 198 and 221 ns, respectively, at 298 K) although exchange was about twice as fast with **31A** (τ_M = 93 ns). From those values, the relaxivities for **31B** and **31C** were determined to be 23.5 and 19.6 mM^{-1} s^{-1} (298 K, pH = 7, 20 MHz), respectively.

Metallodendrimers containing metal elements that can provide robust redox activity can be used as electron-reservoirs for molecular batteries[305–307] or molecular electronics.[308–314] Astruc and co-workers[315] designed and synthesized metallodendrimers containing 54 ferrocenyl units using a specific convergent sequence. Other metallodendrimers, resulting from divergent construction and containing theoretically 81 and 243 ferrocenyl groups, were also created.[306] The Fc/Fc^+ potential for these ferrocenyl metallodendrimers was found to be too low to allow electron storage. It was later discovered that grafting $[FeCp(\eta^6\text{-}C_6Me_6)]^{+/0}$ onto a G5 PPI dendrimer (theoretically 64 amine termini) using the chlorocarbonyl complex $[Fe(\eta^5\text{-}C_5H_4COCl)(\eta^6\text{-}C_6Me_6)(PF_6)]$ to generate the corresponding amido-based dendrimer *dendr*-$\{[(NHCOC_5H_4)\text{-}Fe(\eta^6\text{-}C_6Me_6)(PF_6)]\}_{64}$ gave an excellent electron-reservoir system. Reduction of the metallodendritic complex to its 19-electron Fe(I) form was possible using the prototype 19-electron, electron-reservoir complex $[Fe(I)Cp(\eta^6\text{-}C_6Me_6)]$. When the latter complex was introduced to 64 equivalents of C_{60}, single exergonic electron transfer from each Fe(I) site to C_{60} occurred yielding the *dendr*-$\{[(NHCOC_6H_4)Fe(II)(\eta^6\text{-}C_6Me_6)(C_{60}^{-})]\}_{64}$ hybrid, which was characterized *inter alia* by its Mössbauer and EPR spectra.[307]

Photodynamic therapy (PDT) is a promising method for the contained treatment of tumors, in which numerous photosensitizers have been recently examined in preclinical and clinical trials.[316–321] Absorbed energy can be conveyed over comparatively long distances using dendritic porphyrin architectures, thus mimicking the antenna complex in bacteriochlorophyl photosystems.[322,323] Several porphyrins have been known to effectively produce highly toxic singlet oxygen with selective excitation at a characteristic wavelength, making them ideal photosensitizers for PDT (**32**, Fig. 32).

Kataoka and co-workers[324] prepared the G3 aryl ether dendritic porphyrin with either 32 quaternary ammonium groups (32[+]DPZn) or 32 carboxylic groups (32[−]DPZn) and studied their effectiveness as photosensitizers for PDT. Notably, higher singlet oxygen-induced cytotoxicity against LLC cells was attained by 32[+]DPZn than from protoporphyrin IX, demonstrating the highly selective photosensitizing effect and reduced systemic toxicity of these novel metallodendrimers.

A new concept for the treatment of choroidal neovascularization (CNV) using a combination of dendritic photosensitizer (DP) and polymeric micelles was introduced by the Kataoka group.[325] The DP-loaded micelle achieved a highly selective accumulation of DP in the CNV lesions, and a lower energy of light was sufficient to occlude the CNV lesions. This might be attributed to the unique characteristic of DP; the aggregation of the core porphyrin was sterically prevented even at a remarkably high concentration. The DP-loaded micelles significantly enhanced the efficiency of PDT while



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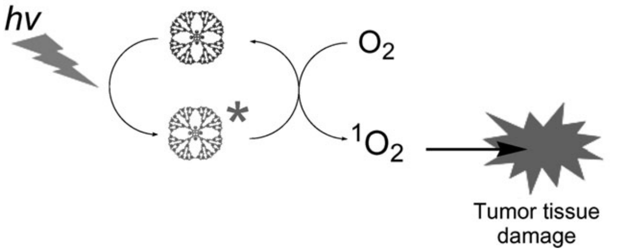

Fig. 32 Depiction of a 'photodynamic therapy' (PDT) process, developed by the Kataoka group, using a dendrimer with a protoporphyrin photosensitizer core, which upon irradiation with light and subsequent reaction with oxygen creates tissue damaging singlet oxygen.

still circumventing the side effects to the normal retinal and choroidal vessels and skin. This protocol was shown to be applicable to the PDT of solid tumors.

Since Grätzel introduced the dye-sensitized solar cells (DSSCs),[326,327] they have become an attractive, low-cost type of solar cell, which offers high conversion performance.[328–331] Yamamoto and co-workers[332] developed a DSSC using a metallodendrimer made of a charge-separable and hole-transporting phenylazomethine with a triphenylamine (TPA) core and complexed $SnCl_2$. Electrochemical oxidation of the TPA core showed that these dendrons have 0.35 of the attenuation factor (β) in the electron transfer. The complexation between triphenylamine with dendritic phenylazomethine (TPA–DPA) and $SnCl_2$ took place—stepwise in an outward radial fashion, following the basicity gradient of the imines within the dendrimer. The increase in radius and association with I_3^- contributed exponentially to the retardation of back-electron-transfer based on β values differences. Since back-electron-transfer increased exponentially with voltage, this contribution was shown to be beneficial for improving the open-circuit voltage.

III Concluding remarks

The unique features surrounding dendritic architectures and the rich chemistry of transition metal complexes have merged to create a wide range of prospective utilitarian materials and applications. As this merger continues, there is no doubt that new vistas in these varied topics will be explored particularly in the areas of biomedical applications such as new contrast agents for MRI, drug application and delivery, and biosensors for advanced disease detection. Metallodendrimers, with their ability to precisely position large numbers of metal centers, will surely find new uses in the fields of molecular sensors, switches and electronic devices, such as those now being developed in templated quantum dots.[333,334] Perhaps one of the more exciting aspects of this merging is also the ability to probe and make use of the interior of the macromolecular architectures. Thus, continued exploration of these "void regions" in metallodendritic catalysis, combined with the techniques of supramolecular chemistry and other areas of nanotechnology, such as lithography, should yield exciting new materials and constructs.

Acknowledgements

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