Dendrimers

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Tris(2,2′-bipyridyl)ruthenium(II) with Branched Polyphenylene Shells: A Family of Charged Shape-Persistent Nanoparticles[**]

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Dedicated to Professor Klaus Hafner on the occasion of his 80th birthday

Polyphenylene dendrimers with poly(pentaphenylbenzene)[1,2] branches (PPDs) are special within dendrimer chemistry because of their stiff, mostly radial arms that do not allow backfolding, thus rendering the molecules shape-persistent.[3] As a result, their overall shapes are defined by the geometry of the particular core unit, and different cores (Figure 1 a–c) have been proven to generate structural diversity.[4]

The highest core symmetry that approaches spherical PPDs[5] has, however, been limited to a four-armed, tetrahedral tetraphenylmethane core (Figure 1 c), since higher symmetries, such as octahedral, are challenging to achieve in organic chemistry. A powerful tool for building structures with controlled symmetry is instead provided by the use of organometallic complexes as core units such as the well-known tris(2,2′-bipyridyl)ruthenium(II) complex ($\{Ru(bpy)_3\}$, Figure 1 d).[6] This complex has already been employed as a functional core in a variety of non-shape-persistent dendrimers,[7–9] mainly for investigating the effect that site isolation has on the properties of the ruthenium-based chromophore[8] (for example, excited-state lifetimes) or for the design of light-harvesting systems.[9] Moreover, it possesses an almost perfect octahedral coordination geometry[10] and is shape-persistent itself, and thus can serve as the desired PPD core when dendritic wedges are attached to the six positions *para* to its nitrogen atoms (Figure 1 d).

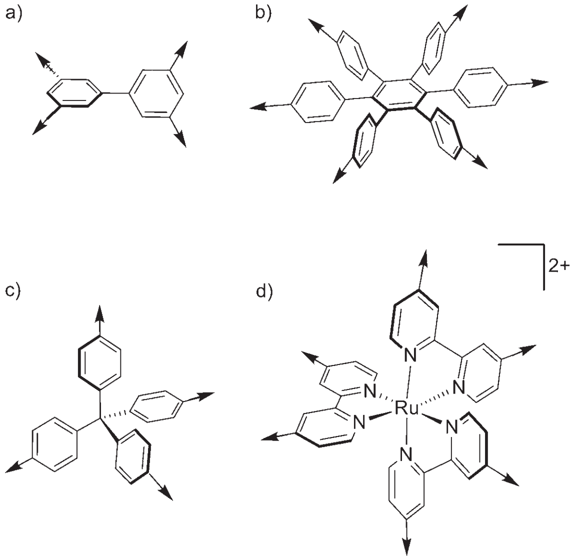

Figure 1. PPD cores (the arrows indicate the positions for dendrimer growth): a) biphenyl, b) hexaphenylbenzene, c) tetraphenylmethane (Td), and d) $\{Ru(bpy)_3\}$.

In addition, the $\{Ru(bpy)_3\}$ core provides valuable synthetic handles: First, it introduces two positive charges within the center of the stiff and nonpolar PPD backbone, thus giving the dendrimer the character of a large, weakly coordinating dication. Second, this core is constructed by metal complexation, which is expected to deliver a facile and versatile tool for the synthesis of desymmetrized PPDs if the ligand (dendron) attachment is performed stepwise.

The reaction sequence established for the synthesis of high-generation, monodisperse polyphenylene dendrimers is based on a [4+2] Diels–Alder cycloaddition of a triisopropylsilyl (TIPS) protected ethynyl-substituted cyclopentadienone branching unit to an ethynyl-substituted core or dendrimer, followed by removal of the TIPS groups, which activates the molecule for further growth.[2] Since 2,2′-bipyridine has no known reactivity under Diels–Alder conditions, it offers the opportunity to either grow the dendrimer divergently or to synthesize the polyphenylene dendrons first and then build the dendrimer by metal complexation in the final step ("convergent" approach).

The key component in the two synthetic strategies for $\{Ru(bpy)_3\}$-cored PPDs is 4,4′-bis(ethynyl)-2,2′-bipyridine (**1**). The reported synthesis of **1** consists of six steps and is complicated by weakly soluble 2,2′-bipyridine (bpy) intermediates.[11] Therefore, a new five-step synthesis was devel-

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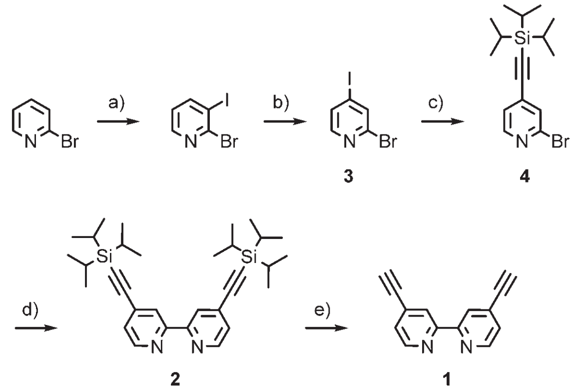
oped for **1**, which is more convenient since the bpy moiety is formed in the penultimate step (Scheme 1).

Starting from 2-bromopyridine, 2-bromo-4-iodopyridine (**3**) was prepared in two steps.[12] Subsequent selective Sonogashira–Hagihara coupling gave **4**, which was converted into bipyridine **2** by employing a Stille coupling procedure.[13] Removal of the TIPS groups of **2** with tetrabutylammonium fluoride (TBAF) gave 4,4′-bis(ethynyl)-2,2′-bipyridine (**1**) in 26% overall yield from 2-bromopyridine.



Scheme 1. Synthesis of 2,2′-bipyridine **1**: a), b)[12]; c) TIPS-acetylene, [$PdCl_2(PPh_3)_2$], CuI, NEt_3, toluene, 0 °C, 18 h, 67%; d) [$Sn_2(nBu)_6$], [$Pd(PPh_3)_4$], toluene, 120 °C, 7 days, 65%; e) TBAF, THF, RT, 30 min, 89%. TBAF = tetrabutylammonium fluoride.

A series of dendrons (**5**–**8**) was prepared for the synthesis of dendrimers by "convergent" metal complexation. These dendrons were prepared from **1** by utilizing the iterative reaction sequence of Diels–Alder cycloadditions and TIPS deprotections described above (Scheme 2). The building blocks **10**[2] and **11**[14] were prepared by literature methods.

To obtain the desired PPDs, dendrons **5**–**7** were treated with [$RuCl_2(dmso)_4$][15] in DMF at 140 °C for three to four days, which led to the formation of the first ([G1]) to third ([G3]) generation dendrimers **16**–**18** (Scheme 3). The synthesis of the corresponding [G4] dendrimer, derived from the largest bpy derivative **8**, was unsuccessful.

Divergent dendrimer synthesis required the use of the [G1] TIPS-ethynyl-functionalized 2,2′-bipyridine **12**. The [G1] {$Ru(bpy)_3$}-based dendrimer **19** was then formed upon complexation of **12** with [$RuCl_2(dmso)_4$] in DMF at 140 °C (Scheme 4). Further dendrimer synthesis was again achieved by iterative Diels–Alder cycloadditions with cyclopentadienone **11** and cleavage of the TIPS groups. The crucial point is that the {$Ru(bpy)_3$} core survives the reaction cycles, thereby enabling growth to higher generations. As for the convergent strategy, synthesis was successful up to the [G3] dendrimer **23**, but the corresponding [G4] species was not obtained. Interestingly, both strategies are apparently limited to the synthesis of the third generation and, moreover, both were found to give comparable overall yields.

The size, shape, and polyphenylene density of the [G3] {$Ru(bpy)_3$}-cored dendrimer **18** were compared with those of the related [G3] species with a tetraphenylmethane (Td) core (Figure 2).[4] Diffusion NMR measurements revealed a hydrodynamic radius of 2.5 nm for dendrimer **18**, which is slightly larger than that determined for the Td species (2.2 nm).[4] This finding indicates a decrease in the large voids between branches, as the physical radii are almost identical. Whereas the tetrahedral dendrimer distributes 144 phenylene rings within the hydrodynamic volume, the density of the {$Ru(bpy)_3$}-cored dendrimer is increased to 216 aromatic rings. Therefore, it is likely that the surface crowding, beyond which defined dendrimer growth no longer occurs, is reached earlier for the herein presented octahedral PPDs than for the Td-cored species, which were obtained up to the fourth generation.

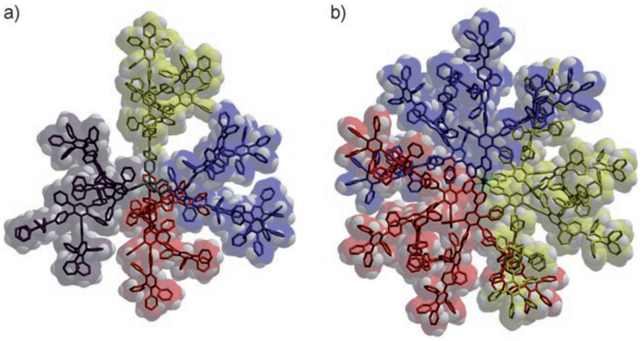


Figure 2. Illustrations of a) [G3] Td-cored PPD[4] and b) [G3] {$Ru(bpy)_3$}-cored PPD **18**.

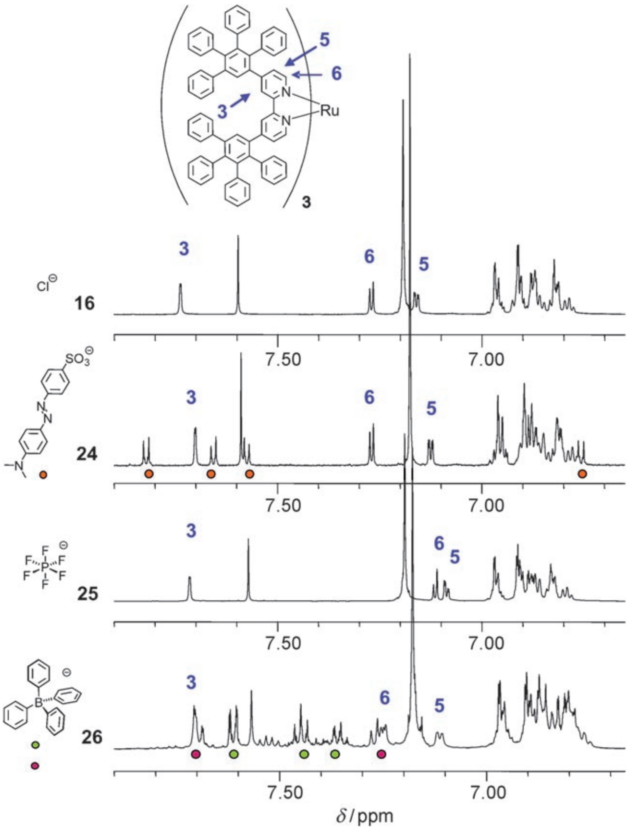
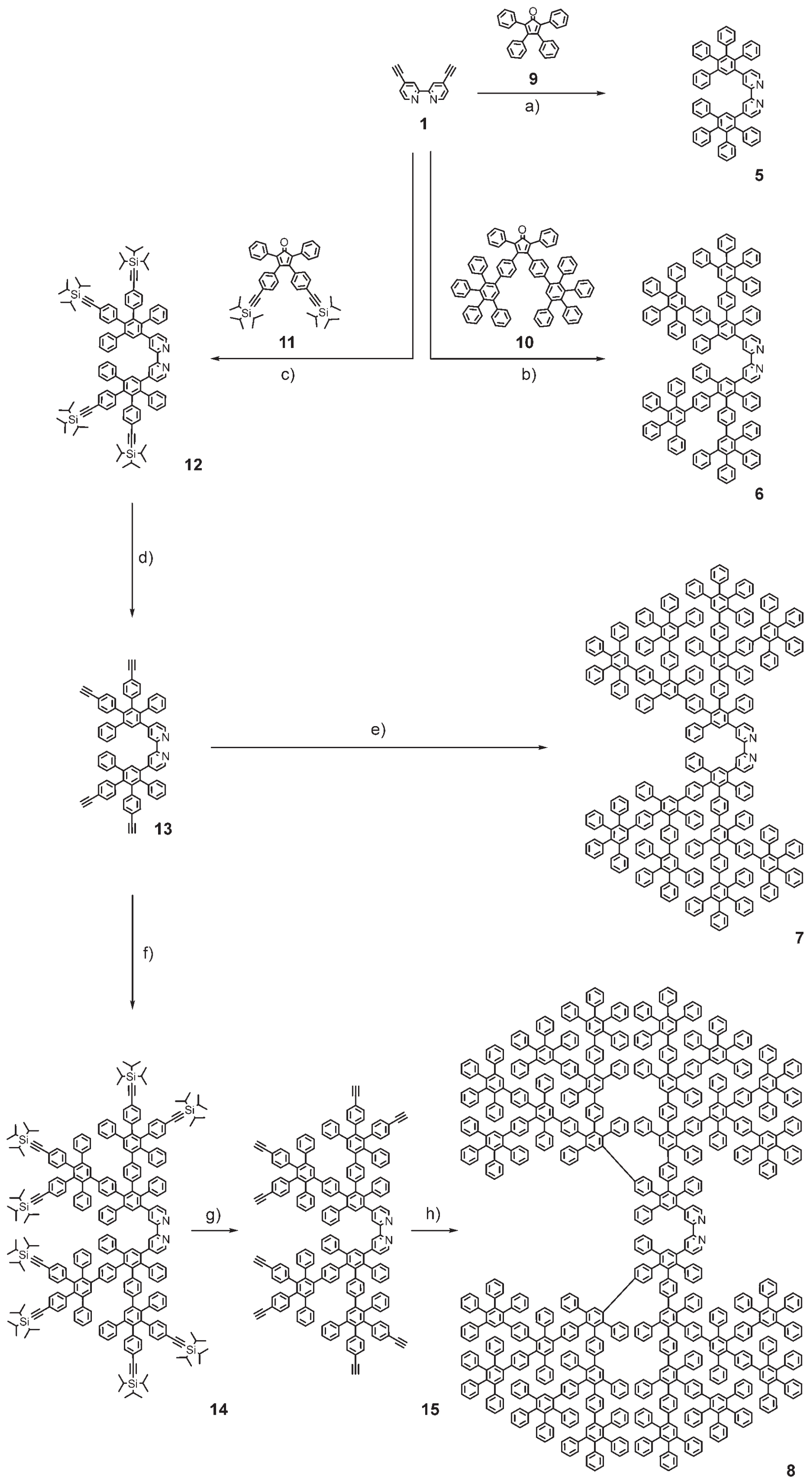


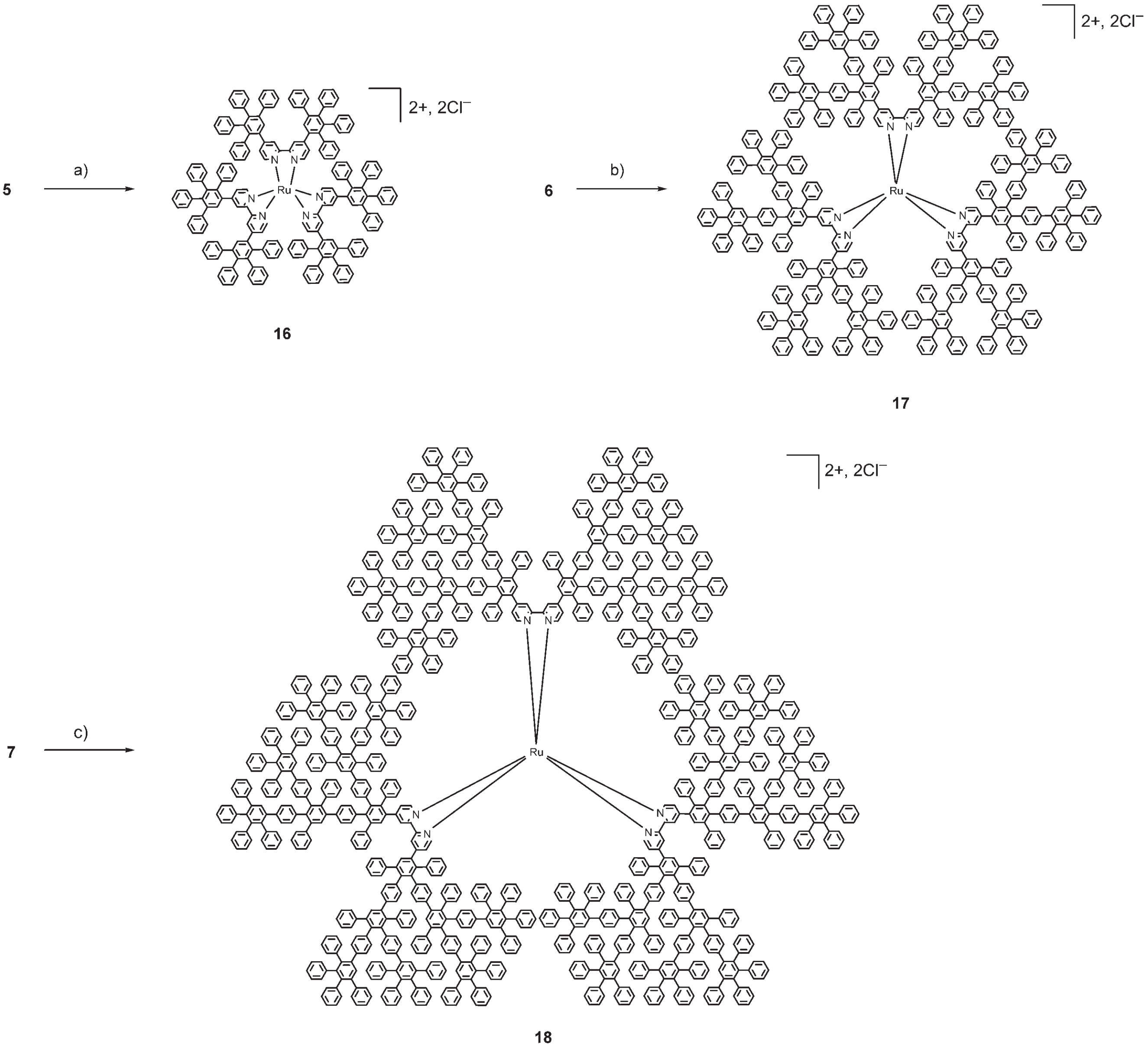
Figure 3. ^1H NMR spectra (700 MHz, CD_2Cl_2, 303 K) of [G1] dendrimers **16**, **24**, **25**, and **26**.



Scheme 2. Syntheses of 2,2′-bipyridylpolyphenylene dendrons **5**–**8**: a) **9**, *o*-xylene, 140 °C, 20 h, 97 %; b) **10**, *o*-xylene, 140 °C, 2 days, 90 %; c) **11**, *o*-xylene, 140 °C, 20 h, 48 %; d) TBAF, THF, RT, 1 h, 98 %; e) **10**, *o*-dichlorobenzene, 175 °C, 3 days, 45 %; f) **11**, *o*-xylene, 140 °C, 2 days, 90 %; g) TBAF, THF, RT, 1 h, 98 %; h) **10**, *o*-dichlorobenzene, 175 °C, 3 days, 32 %.

In addition to their increased density, the {Ru(bpy)$_3$}-cored dendrimers differ from previously reported PPDs since they carry the positive charges of the metal complex within their center. The TIPS-protected species **19**, **21**, and **23** were found to be completely soluble in hydrocarbon solvents, which suggests that only the dendrimer surface defines the solubility properties, whereas the positive charge together with the chloride counterions are shielded within the dendrimer backbone. The counterions of the [G1] dendrimer **16** were efficiently exchanged upon treatment with the sodium salt of methyl orange, ammonium hexafluorophosphate, or sodium tetraphenylborate to give the new salts **24**, **25**, and **26**, respectively. As can be seen from the ^{1}H NMR spectra (Figure 3), the bpy resonances of the dendrimer are sensitive to the anion exchange, whereas the polyphenylene regions remain unaffected. The resonances that are most influenced are H5 and H6 of bpy, which suggests their proximity to the anions in cases where coordination is strong (for example, chloride). The tetraphenylborate salt is a different case, and the complexity of the spectrum suggests interactions with dendrimer aryl groups. A future challenge is the combination of these nanoscale dications with anions of a similar size to construct large dendrimer salts. The introduction of charge would add an additional tool for the assembly of complex supramolecular architectures.[16]

Two other strategies to influence the supramolecular behavior of such charged PPDs involve the modification of their shape or the generation of inhomogeneous dendrimer surfaces. Both goals are reached by a desymmetrization of the dendrimer core through the attachment of different dendrons. Since desymmetrized PPDs have so far only been accessible by statistical approaches,[17] the applicability of a stepwise formation of a {Ru(bpy)$_3$} derivative as a potential controlled route for desymmetrization was evaluated. Therefore, the dichloro-



Scheme 3. "Convergent" syntheses of {Ru(bpy)$_3$}-cored PPDs **16**–**18**: a)–c) [RuCl$_2$(dmso)$_4$], DMF, 140°C, 3 days. a) 55%, b) 23%, c) 44%.

ruthenium compound **27** was synthesized and treated with the [G2] dendron **6**, which led to the formation of macromolecule **28** (Scheme 5) in 34% overall yield from [RuCl$_2$(dmso)$_4$]. This result establishes the ease of this desymmetrization strategy and further work, concentrating on the design of dumbbell-type and amphiphilic structures,[16] is in progress.

In summary, this is the first description of shape-persistent dendrimers that are based on octahedral symmetry, and moreover, possess a positively charged transition-metal complex at their center. The molecules are accessible with structural perfection up to the third generation by either a partly convergent synthesis or a divergent strategy in which the metal complex proved to be stable to high temperature Diels–Alder conditions. The {Ru(bpy)$_3$}-based dendrimers were shown to possess a strongly enhanced global density of aromatic rings compared to the related tetrahedral structure; nevertheless, efficient counterion exchange was demonstrated for the first generation dendrimers. The resulting opportunity to combine the salts with larger anions and the possibility of the stepwise attachment of dendrons gives access to various dendrimer salts and charged desymmetrized PPDs, which are of interest for further investigations of the self-assembly of shape-persistent polyphenylene structures.

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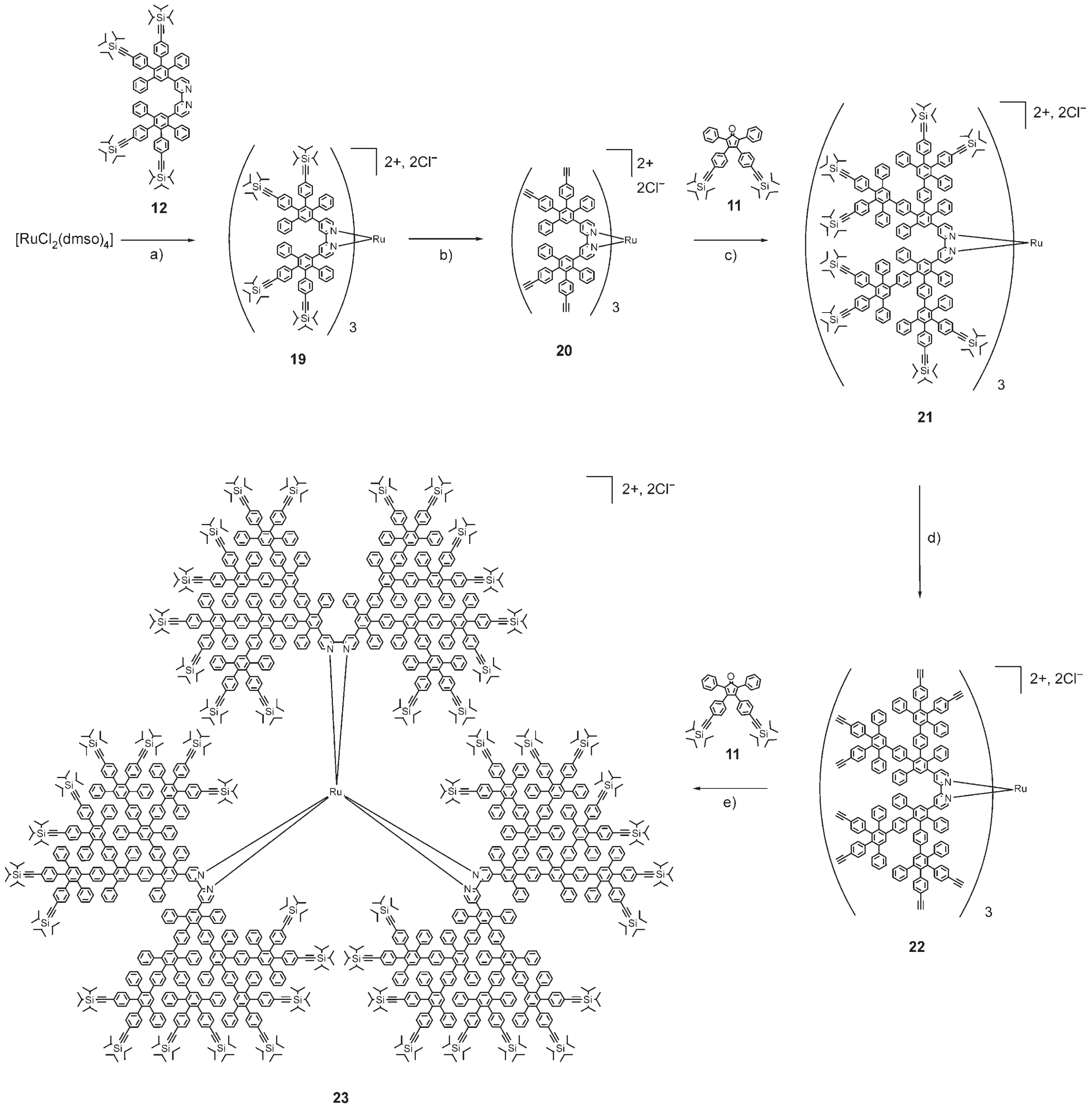
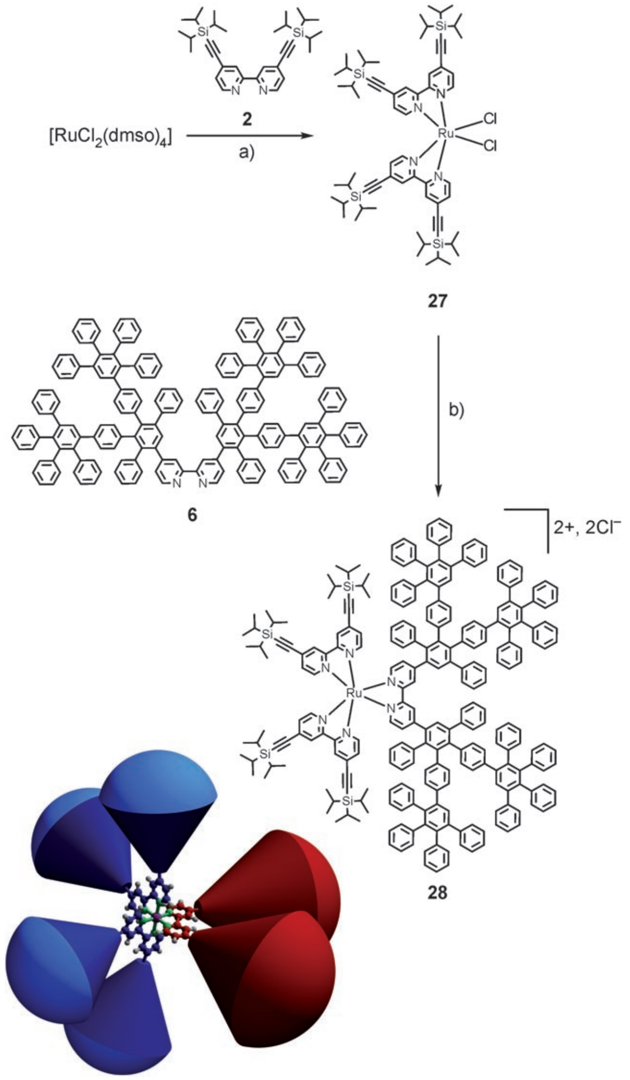


Scheme 4. Divergent syntheses of {Ru(bpy)$_3$}-cored PPDs **19**–**22** a) DMF, 140 °C, 4 days, 48 %; b) TBAF, THF, RT, 1 h, 82 %; c) **11**, ethylene glycol, *o*-xylene, 140 °C, 3 days, 55 %; d) TBAF, THF, RT, 1 h, 60 %; e) **11**, ethylene glycol, *o*-xylene, 140 °C, 4 days, 81 %.



Scheme 5. Synthesis and schematic representation of desymmetrized compound **28**: a) DMF, 140 °C, 3 days, 64 %; b) EtOH/CHCl$_3$, 90 °C, 6 days, 46 %.

Keywords: coordination modes · dendrimers · ruthenium · supramolecular chemistry · synthetic methods

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