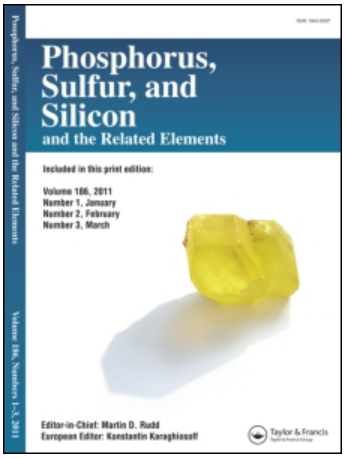

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PHOSPHORUS DENDRIMERS: A NEW CLASS OF MACROMOLECULES

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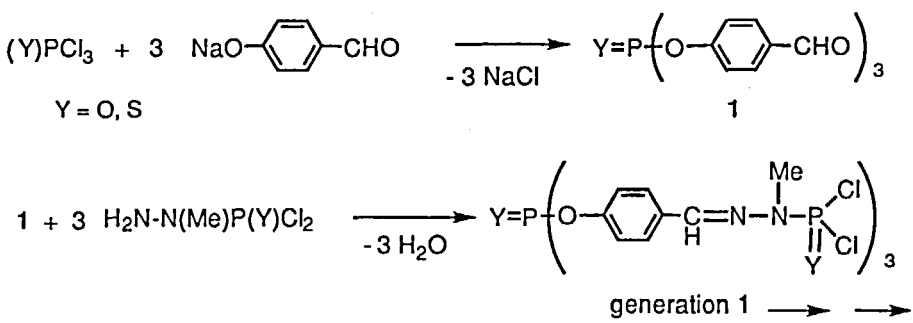
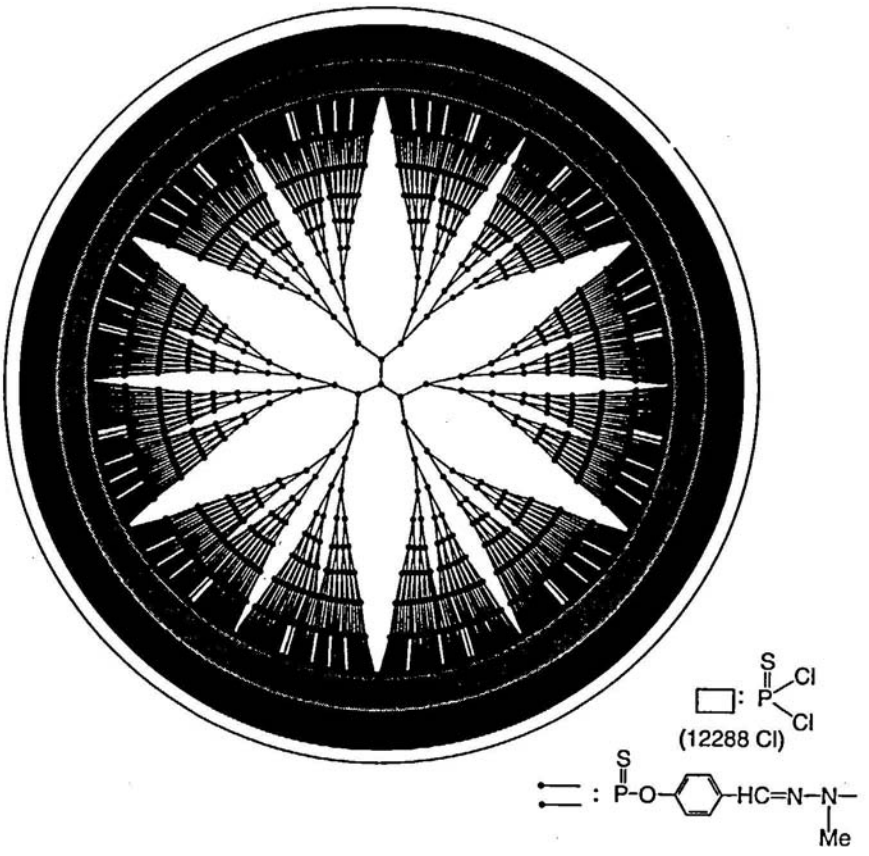
Abstract Two ways of synthesis of phosphorus dendrimers are elaborated up to the twelfth generation for one of them, to give a molecule which possesses 12288 functions. Examples of the reactivity of some dendrimers are described.

INTRODUCTION

Dendrimers are high molecular weight, highly branched multifunctional molecules which incorporate structural repetitions in an ordered manner.[1] Despite the fact that a variety of organic dendrimers have been synthesized in the past few years,[1a,b] only one phosphorus dendrimer (cationic)[2] was described before our work. We published last year the divergent synthesis of the first neutral phosphorus dendrimer,[3] and we described very recently a second approach.[4] A few recent papers concern dendrimers having cyclotriphosphazene in the cascade structure[5] and the formation of small organophosphine dendrimers.[6]

The first phosphorus dendrimers we reported[3] were built by a simple two steps synthesis, which gives alternatively P-Cl and aldehyde functions on the surface of the molecules.[7] Reiteration of the same sequence of reactions now allows us to elaborate dendrimers up to the twelfth generation, which is the highest generation currently known for a dendrimer. This compound possesses 12288 chlorine at the periphery, a molecular weight of more than 3 millions, and a diameter of roughly 190 Å.

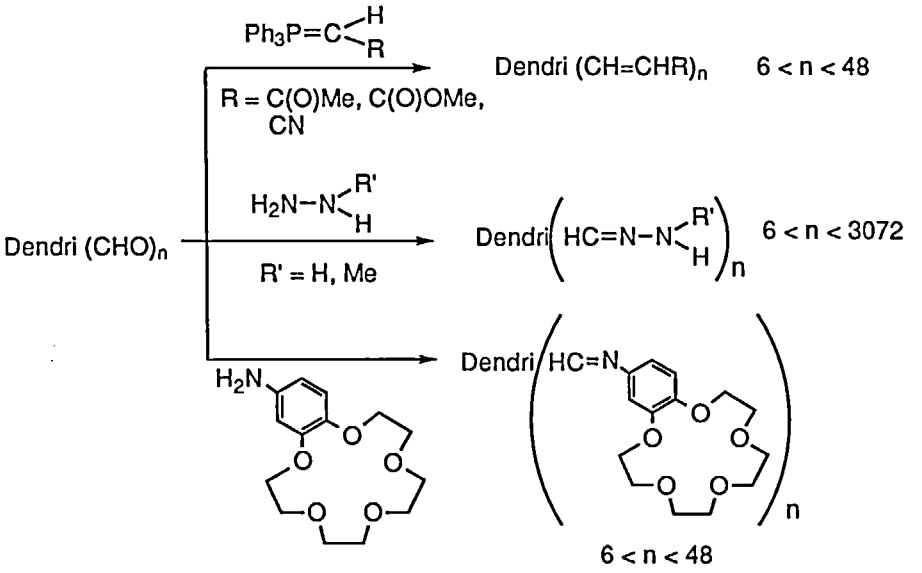




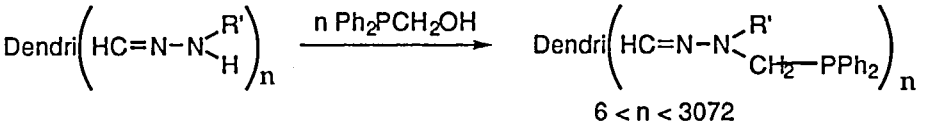
Schematic drawing of the twelfth generation of the dendrimer

Our second way to obtain phosphorus dendrimers consists in a three steps synthesis which gives alternatively aldehyde, NH, and phosphine functions at the periphery. Dendrimers were elaborated in this way up to the third generation, with either up to 24 phosphines at the periphery starting from a tridirectional core, or up to 48 aldehyde functions starting from an hexadirectional cyclotriphosphazene core.[4]

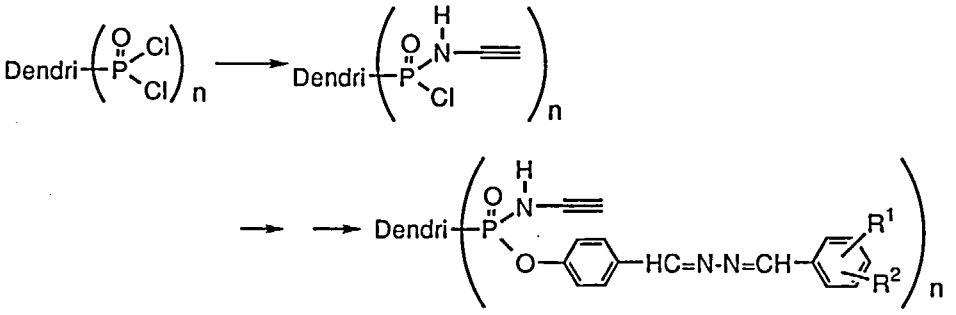
The presence of reactive functions at the periphery of dendrimers prompted us to study the reactivity of these highly functionalized molecules and to graft new functions able to meet precise requirements. Starting from aldehyde functions, we performed Wittig reactions, as well as condensations with hydrazines or imines which gave for example a compound with up to 48 crown-ether functions.[7]



NH and NH_2 functions react with Ph_2PCH_2OH leading to polyphosphines which are isolated up to the tenth generation. This is the largest polyphosphine of defined structure ever known (3072 phosphines!) which can be complexed with 3072 gold atoms.[8]



Starting from $P(S)Cl_2$ functions, we can selectively substitute only one chlorine on each phosphorus, in order to obtain dendrimers which have for the first time two, three, four or even five different and compatible functions at the periphery.



Studies on physical and chemical properties, and potential applications of these new families of macromolecules are underway.

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