DOI: 10.1002/ejoc.201101376

Molecular and Macromolecular Engineering with Viologens as Building Blocks: Rational Design of Phosphorus–Viologen Dendritic Structures

Nadia Katir,[a,b] Jean Pierre Majoral,*[a,b] Abdelkrim El Kadib,*[a] Anne-Marie Caminade,[b] and Mostapha Bousmina[a,c]

Dedicated to the memory of Dr. Robert Wolf[‡]

Keywords: Viologens / Dendrimers / Dendrons / Phosphorus / Synthesis design

The design of symmetric or asymmetric diversely functionalized monomer, dimer, or trimer viologens and the design of phosphorus building blocks allows the synthesis of unique types of mix phosphorus–viologen dendrimers. Strategies for the preparation of dendrimers of generations 0 and 1 are presented as are those for various dendrons. These methods exhibit broad applicability, high efficiency and usability, and are compatible with the presence of various functional groups (aldehyde, cyano, phenol, phosphonate, brominated groups).

Introduction

Dendrimers are a class of well-defined monodisperse nanostructured macromolecules with a modifiable multivalent surface. A key advantage of dendrimers emanates from the multiplicity and additive effects that can be achieved by manipulating the densely packed end groups, thus allowing a vast number of applications in different fields ranging from biomedical applications to material science, catalysis, etc.[1] The nature of the internal branches as well as that of the core strongly also influences the behavior and the properties of dendrimers, as frequently demonstrated.[1]

The different types of dendrimers that contain photoactive and/or electroactive moieties such as the 4,4′-bipyridinium ion (viologen) are attracting interest due to the properties of these dicationic species. Indeed, viologens are well-known electroactive compounds that undergo two successive one-electron reversible reduction processes and exhibit peculiar spectroscopic features in both their dicationic and radical cation forms.[2] Moreover, viologens are known to give strong donor–acceptor complexes with electron-donating species. These behaviors were exploited by several authors describing the formation of host–guest complexes and the electrochemical properties of symmetric and asymmetric dendrimers incorporating viologen units.[3,4] In a completely different field it can be also mentioned that structure–activity relationships of a series of viologen units and dendrimers as antiviral agents were recently reported, pointing out an unexpected biological aspect of viologen dendrimers as novel HIV-1 replication inhibitors.[5] Up to now, viologen units were incorporated at the focal point,[4,6] or at the core, the branches, and the periphery[7] of a very few types of purely organic dendrimers.[8]

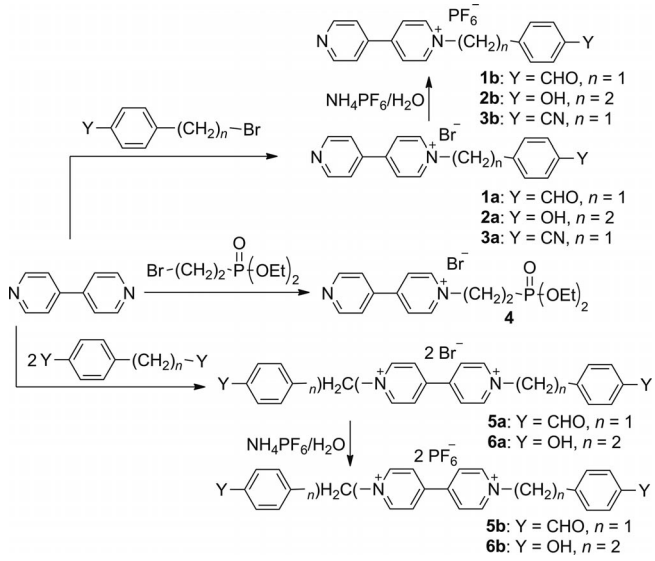
Similarly, phosphorus dendrimers, and especially those we are developing, are extremely versatile macromolecules with unique properties and applications. These dendrimers allow the design of a new class of biosensors displaying high efficiency both in terms of their sensitivity and stability.[9] Phosphorus dendrimers bearing two-photon absorption (TPA) chromophores at the core, the branches, or the surface constitute a new class of "soft" nontoxic and biocompatible fully organic chromophores exhibiting exceptional one- or two-photon brightness outperforming the best quantum dots without suffering from the drawbacks of the latter (blinking, toxicity, insolubility).[10] Phosphorus dendrimers allow the template preparation of polyelectrolyte multilayer nanotubes based only on charged dendrimers and displaying an excellent detection limit for DNA hybridization up to 10^{-18} mol in certain cases.[11] Phosphorus dendrimers with phosphonic end groups (poly-

[a] INANOTECH Institute of Nanomaterials and Nanotechnology – MAScIR (Moroccan Foundation for Advanced Science, Innovation and Research), ENSET, Avenue de l'Armée Royale, Madinat El Irfane, 10100 Rabat, Morocco
E-mail: a.elkadib@mascir.com
[b] Laboratoire de Chimie de Coordination du CNRS, BP 44099, 205 Route de Narbonne, 31077 Toulouse cedex 4, France
Fax: +33-5-61553003
E-mail: majoral@lcc-toulouse.fr
[c] Hassan II Academy of Science and Technology Rabat, Rabat, Morocco
[‡] Deceased November 3, 2011.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101376.

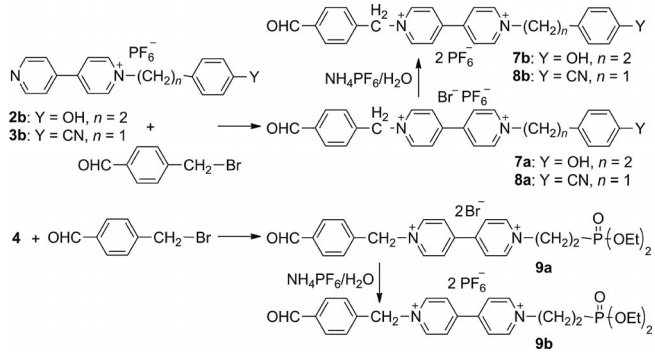
anionic dendrimers) appear as new nanotools promoting an anti-inflammatory and immunosuppressive activation of human monocytes and thus prove to be good candidates for innovative anti-inflammatory immunotherapies.[12] Polycationic phosphorus dendrimers have a strong anti-prion activity reducing prion replication both in vitro and in vivo; these dendrimers did not bear any specific therapeutic agents.[13]Among other unique properties of phosphorus dendrimers,[14] their key roles as catalysts in some reactions of industrial interest with a so-called "strong dendritic effect"[15] and their utility in the synthesis of so-called "organic–inorganic hybrid materials" should be noted.[16]

In light of these examples on the properties and applications of both viologens and phosphorus dendrimers, which are far from exhaustive, it appeared to us of great interest to develop new methodologies for the preparation of dendrimers by mixing viologen units and phosphorus linkages into the same framework. The goal was not to propose a strategy that would be one more synthetic pathway to dendrimers with a limited extension, but to propose a large panel of possibilities to build and tailor the dendrimers through multistep synthesis and by using a variety of original building blocks, "*mixed*" dendrons and dendrimers, and related macromolecules, which, taking into account the properties briefly reported above, would be fruitful nano-objects for new applications.

We report herein (i) the synthesis of symmetric or asymmetric new viologen monomers, dimers, and trimers; (ii) the design of original dendrimers of generation 0 and 1 bearing both phosphorus linkages and viologen units by using convergent syntheses and different strategies; and (iii) the elaboration of several dendrons. In all cases, the solubility and functionalization of these original systems can be modulated by allowing the preparation of diversely multifunctionalized dendritic structures.



Scheme 1. Synthesis of 4,4′-bipyridin-1-iums **1a**–**3a**, **1b**–**3b**, and **4** and symmetrical viologens **5a**, **6a**, **5b**, and **6b**.



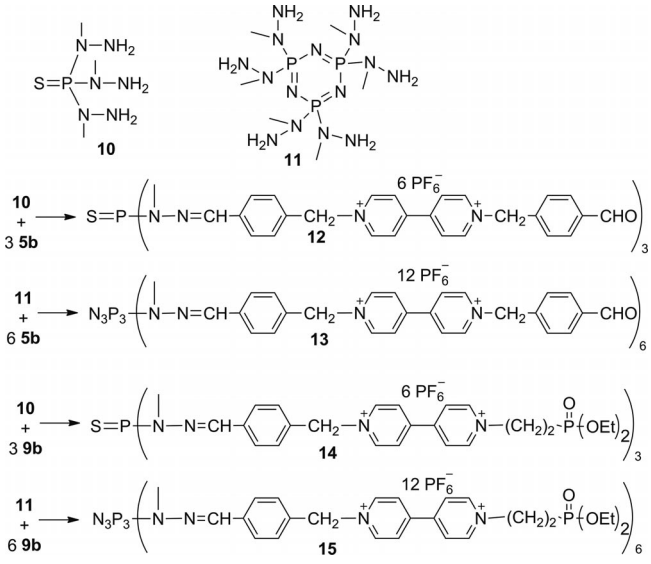
Scheme 2. Synthesis of asymmetric viologens **7a**–**9a** and **7b**–**9b**.

Results and Discussion

In practice, the synthetic sequence of all these methodologies was initiated by the single alkylation of 4,4′-bipyridine with various halogenated reagents leading selectively to water-soluble 4,4′-bipyridin-1-ium bromides **1a**–**3a** and **4**. The corresponding hydrosoluble symmetrical [4,4′-bipyridine]-1,1′-diiums **5a**–**6a** were obtained by a double alkylation reaction involving two equivalents of the brominated aldehyde or phenol. Anion exchange with KPF_6 allowed the formation of **1b**–**3b**, **5b**, and **6b** from **1a**–**3a**, **5a**, and **6a**, respectively, which are soluble in organic solvents such as acetonitrile and acetone (Scheme 1). Asymmetric viologens were prepared through alkylation of **2b**, **3b**, or **4** with 4-(bromomethyl)benzaldehyde at 78–80 °C over 12–24 h; the resulting water-soluble monomers **7a**, **8a** (anion = PF_6^- and Br^-), and **9a** (anion = Br^-) were then treated with NH_4PF_6 to give asymmetric compounds **7b**–**9b** (anion = PF_6^-) presenting good solubility in organic solvents (Scheme 2).

Trihydrazidophosphane sulfide **10** and hexahydrazidocyclotriphosphazene **11** were intensively used in our hands as a core for the preparation of phosphorus dendrimers incorporating viologen units. They can be readily prepared by substitution reactions of the corresponding tri- or hexachloro derivatives with methylhydrazine in the presence of a base.[17] Condensation of **10** or **11** with 3 or 6 equiv. of dialdehyde viologen **5b** proceeds smoothly at room temperature overnight to give selectively generation-0 dendrimers **12** and **13** (soluble in organic solvents) bearing three or six aldehyde end groups in excellent yields; only one of the two aldehyde groups of **5b** reacted with each hydrazido unit and no cross-coupling resulting in the formation of insoluble material was observed (Scheme 3). This is supported by analysis of the ^1H and ^{13}C NMR spectra revealing the presence of a singlet for the remaining aldehyde groups (10.07, 191.09 ppm for **12**) and by electrospray mass spectrometry (m/z = 2051.6 [M – PF_6]). The same reactions were conducted with asymmetric viologen **9b** and either **10** or **11**: dendrimers **14** and **15** bearing two different phos-

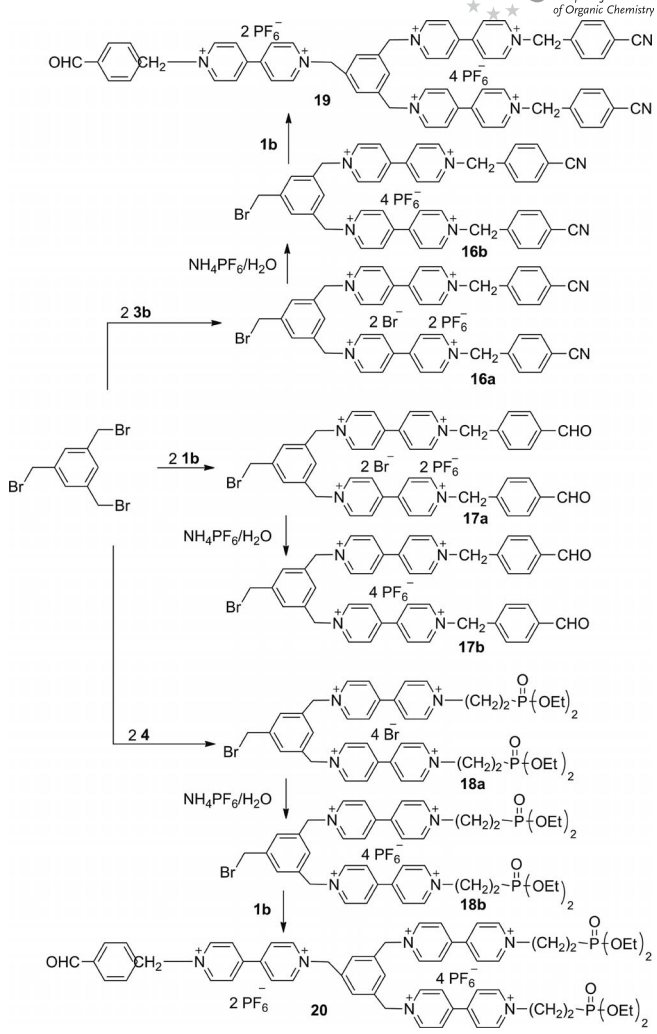
phorus units (cyclotriphosphazene unit as core and phosphonate as end groups) were thus quantitatively obtained (Scheme 3).



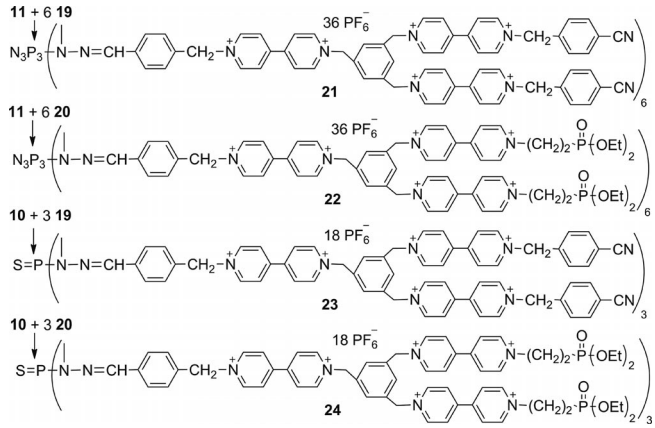
Scheme 3. Synthesis of generation-0 dendrimers **12**–**15**.

In order to access higher multivalent functionalities and higher dendrimer generations, several strategies were elaborated. The first access to a dendrimer of generation 1 by mixing phosphorus linkages and viologens involves, as a preliminary step, the preparation of trifunctionalized viologens: this can be done through double alkylation of 1,3,5-tris(bromomethyl)benzene, selectively performed on monomer **1b**, **3b** or **4**. Indeed, disubstitution with 2 equiv. of monomers **1b**, **3b** and **4** afforded diviologens **16a**–**18a** in good yields, which, after treatment with NH_4PF_6, gave rise to polycationic species **16b**–**18b**. The presence of a remaining CH_2Br function in **16b** and **18b** allows a second reaction with pyridine–pyridinium monomer **1b** leading to the formation of asymmetric trisviologens **19** and **20** in satisfactory yields (from 53% for **19** to 70% for **20**, Scheme 4). These trifunctionalized trisviologens contain an aldehyde function and either two cyano or two phosphonate groups. They can be used as building blocks for the formation of generation-1 dendrimers. For example, condensation of **19** or **20** with **11** leads directly to generation-1 dendrimers **21** and **22** (Scheme 5).

These unprecedented types of dendrimers are equipped with hexahydrazidocyclotriphosphazene linkage at the focal point, trisubstituted benzene units as branching points, 18 viologens within the dendritic structure, 12 phosphonate (or cyano) end groups, and 36 PF_6 anions. The same type of experiment can be performed with **10** instead of **11** (Scheme 5): in this case, generation-1 dendrimers **23** and **24** are also formed in high yields and were fully characterized by NMR and IR spectroscopy and mass spectrometry (see the Experimental Section and Figure 1 for NMR assignment).



Scheme 4. Synthesis of asymmetric bisviologens **16a**–**18a** and trisviologens **19** and **20**.



Scheme 5. Synthesis of generation-1 dendrimers.

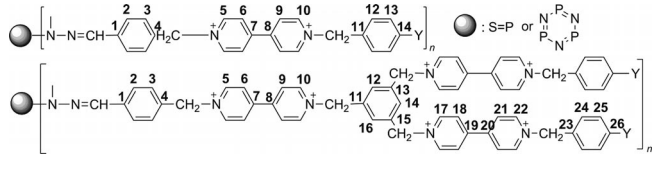


Figure 1. Numbering used for NMR assignments.

Conclusions

New symmetric and asymmetric viologen monomers, dimers, and trimers have been shown to be versatile building blocks for the synthesis of a number of polycationic dendrimers incorporating linear and (or) cyclic phosphorus units. In all cases, divergent points of each generation are different and can be cyclotriphosphazene, thiophosphotrihydrazido, or di- or trisubstituted benzene linkages. These different ways of preparation of mixed phosphorus–viologen-containing dendrimers illustrated the potentiality of these methodologies for the design of new types of dendritic structures. Several properties and applications of these dendritic structures are under active investigation as is the extension of these methods to the design of dendrimers of higher generations.

Experimental Section

13: To a solution of **5b** (0.25 g, 0.365 mmol) in acetonitrile (10 mL) was added a solution of **11** (0.025 g, 0.06 mmol) in acetonitrile (3 mL). This mixture was stirred overnight. The solvent was removed in vacuo. An orange solid was obtained (0.25 g, 95%). ^{1}H NMR (300 MHz, CD_3CN): δ = 3.29 (s, 18 H, CH_3-N), 5.79 (s, 12 H, C^{11}-CH_2), 5.93 (s, 12 H, C^4-CH_2), 7.45 (d, $^3J_{H,H}$ = 8.4 Hz, 12 H, H^3), 7.68 (d, $^3J_{H,H}$ = 8.1 Hz, 24 H, H^{13}, H^2), 7.72 (br. s, 6 H, CH=N), 8.03 (d, $^3J_{H,H}$ = 8.4 Hz, 12 H, H^{12}), 8.37–8.43 (m, 24 H, H^6, H^9), 8.83–8.96 (m, 12 H, H^5), 9.00 (d, $^3J_{H,H}$ = 7.1 Hz, 12 H, H^{10}), 10.07 (s, 6 H, CHO) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_3CN): δ = 31.94 (CH_3-N), 64.12 (C^{11}-CH_2), 64.44 (C^4-CH_2), 127.12 (C^2), 127.47, 127.64, 127.69 (C^6, C^9), 129.79 (C^3), 129.84 (C^{13}), 130.33 (C^{12}), 132.22 (C^1), 137.43 (C^4, C^{11}), 137.76 (CH=N), 138.48 (C^{14}), 145.52, 145.87 (C^5, C^{10}), 150.31, 150.56 (C^7, C^8), 192.14 (CHO) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_3CN): δ = 18.16 ppm. MS (ESI): m/z = 2056.4 $[M - 2PF_6]^{2+}$. IR (neat): $\tilde{\nu}$ = 1695 (C=O), 1637 (C=N) cm^{-1}.

21: To a solution of **19** (0.09 g, 4.98 10^{-2} mmol) in acetonitrile (10 mL) was added **11** (0.0034 g, 8.395×10^{-3} mmol). The mixture was stirred overnight. The solvent was removed in vacuo to yield (0.90 g, 96%) as an orange solid. ^{1}H NMR (300 MHz, CD_3CN): δ = 3.29 (br. d, $^3J_{P,H}$ = 8.9 Hz, 18 H, CH_3-N), 5.85 (s, 12 H, C^4-CH_2), 5.89 (s, 36 H, C^{11}-CH_2, C^{13}-CH_2, C^{15}-CH_2), 5.93 (s, 24 H, C^{23}-CH_2), 7.36–7.51 (m, 12 H, H^3), 7.57–7.70 (m, 36 H, H^{24}, H^2), 7.69 (br. s, 6 H, CH=N), 7.76 (s, 18 H, H^{12}, H^{14}, H^{16}), 7.84 (d, $^3J_{H,H}$ = 8.5 Hz, 24 H, H^{25}), 8.37–8.50 (m, 72 H, H^6, H^9, H^{18}, H^{21}), 8.96–9.10 (m, 72 H, H^5, H^{10}, H^{17}, H^{22}) ppm. ^{13}C{^{1}H} NMR (75 MHz, CD_3CN): δ = 31.92 (br. d, $^2J_{P,C}$ = 9.6 Hz, CH_3-N), 63.57 (C^{11}-CH_2, C^{13}-CH_2, C^{15}-CH_2), 63.73 (C^{23}-CH_2), 64.29 (C^4-CH_2), 113.41 (C^{26}), 118.02 (CN), 127.02 (C^2), 127.44, 127.54, 127.64 (C^6, C^9, C^{18}, C^{21}), 129.67 (C^3), 129.93 (C^{24}), 131.79 (C^{12}, C^{14}, C^{16}), 132.32 (C^1), 133.26 (C^{25}), 134.95, 135.03 (C^{11}, C^{13}, C^{15}), 136.20 (br. d, $^3J_{P,C}$ = 13.5 Hz, CH=N), 137.52 (C^{23}), 137.80 (C^4), 145.59, 145.86, 145.93 (C^5, C^{10}, C^{17}, C^{22}), 150.31, 150.43, 150.51, 150.65 (C^7, C^8, C^{19}, C^{20}) ppm. ^{31}P{^{1}H} NMR (121 MHz, CD_3CN): δ = 17.06 ppm. MS (ESI): m/z = 1711.9 $[M - 6PF_6]^{6+}$. IR (neat): $\tilde{\nu}$ = 2233 (CN), 1637 (C=N) cm^{-1}.

22: To a solution of **20** (0.10 g, 5.25 10^{-2} mmol) in acetonitrile (20 mL) was added **11** (0.0035 g, 8.64×10^{-3} mmol). The mixture was stirred overnight. The solvent was removed in vacuo to yield **22** (0.098 g, 95%) as an orange solid. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.27 (t, $^3J_{H,H}$ = 6.0 Hz, 72 H, OCH_2-CH_3), 2.59 (dt, $^2J_{P,H}$ = 18.1 Hz, $^3J_{H,H}$ = 7.3 Hz, 24 H, CH_2-CH_2P), 3.30 (br. s, 18 H, CH_3-N), 4.02–4.12 (m, 48 H, OCH_2-CH_3), 4.90 (dt, $^3J_{P,H}$ = 14.8 Hz, $^3J_{H,H}$ = 7.3 Hz, 24 H, CH_2-CH_2P), 5.85 (s, 12 H, C^4-CH_2), 5.90 (s, 36 H, C^{11}-CH_2, C^{13}-CH_2, C^{15}-CH_2), 7.46 (d, $^3J_{H,H}$ = 7.7 Hz, 12 H, H^3), 7.69 (d, $^3J_{H,H}$ = 7.7 Hz, 12 H, H^2), 7.74 (s, 18 H, H^{12}, H^{14}, H^{16}), 7.78 (br. s, 6 H, CH=N), 8.46 (d, $^3J_{H,H}$ = 5.1 Hz, 72 H, H^6, H^9, H^{18}, H^{21}), 9.04 (d, $^3J_{H,H}$ = 5.5 Hz, 72 H, H^5, H^{10}, H^{17}, H^{22}) ppm. ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ = 15.67 (d, $^3J_{P,C}$ = 5.9 Hz, OCH_2-CH_3), 26.53 (d, $^1J_{P,C}$ = 140.6 Hz, CH_2-CH_2P), 31.91 (br. s, CH_3-N), 56.61 (CH_2-CH_2P), 62.39 (d, $^2J_{P,C}$ = 6.4 Hz, OCH_2-CH_3), 63.57 (C^{11}-CH_2, C^{13}-CH_2, C^{15}-CH_2), 64.31 (C^4-CH_2), 127.09 (C^2), 127.00, 127.44, 127.53 (C^6, C^9, C^{18}, C^{21}), 129.81 (C^3), 131.77 (C^{12}, C^{14}, C^{16}), 132.39 (C^1), 135.00 (C^{11}, C^{13}, C^{15}), 136.45 (br. d, $^3J_{P,C}$ = 14.8 Hz, CH=N), 137.77 (C^4), 145.59, 145.89, 146.14 (C^5, C^{10}, C^{17}, C^{22}), 150.32, 150.41, 150.55 (C^7, C^8, C^{19}, C^{20}) ppm. ^{31}P{^{1}H} NMR (162 MHz, CD_3CN): δ = 17.29, 23.63 ppm. MS (ESI): m/z = 1809.8 $[M - 6PF_6]^{6+}$.

Supporting Information (see footnote on the first page of this article): Synthesis and characterization of **1a**–**3a**, **4**, **5a**–**9a**, **5b**–**9b**, **12**, **14**, **15**, **16a**–**18a**, **16b**–**18b**, **19**, **20**, **23**, and **24**.

Acknowledgments

Thanks are due to the Moroccan Foundation for Advanced Science, Innovation and Research (Rabat, Morocco) and to Centre National de la Recherche Scientifique (CNRS) (France) for financial support.

[1] a) G. R. Newkome, C. D. Shreiner, *Polymer* **2008**, *49*, 1–173; b) P. Niederhafner, M. Reiniš, J. Šebestík, J. Ježek, *J. Pept. Sci.* **2008**, *14*, 556–587; c) A.-M. Caminade, C.-O. Turrin, J.-P. Majoral, *Chem. Eur. J.* **2008**, *14*, 7422–7432; d) A.-M. Caminade, P. Servin, R. Laurent, J.-P. Majoral, *Chem. Soc. Rev.* **2008**, *37*, 56–67; e) A.-M. Caminade, A. Hameau, J.-P. Majoral, *Chem. Eur. J.* **2009**, *15*, 9270–9285; f) S. Svenson, *Eur. J. Pharm. Biopharm.* **2009**, *71*, 445–462; g) D. Astruc, E. Boisselier, C. T. Ornelas, *Chem. Rev.* **2010**, *110*, 1857–1959; h) A.-M. Caminade, C.-O. Turrin, J.-P. Majoral, *New J. Chem.* **2010**, *34*, 1512–1524; i) A.-M. Caminade, J.-P. Majoral, *Chem. Soc. Rev.* **2010**, *39*, 2034–2047; j) G. R. Newkome, C. Shreiner, *Chem. Rev.* **2010**, *110*, 6338–6442; k) R. S. Navath, A. R. Menjoge, B. Wang, R. Romero, S. Kannan, R. M. Kannan, *Biomacromolecules* **2010**, *11*, 1544–1563; l) J. M. Oliveira, A. J. Salgado, N. Sousa, J. F. Mano, R. L. Reis, *Prog. Polym. Sci.* **2010**, *35*, 1163–1194; m) M. Calderón, M. A. Quadir, M. Strumia, R. Haag, *Biochimie* **2010**, *92*, 1242–1251; n) J. Sebestik, P. Niederhafner, J. Jezek, *Amino Acids* **2011**, *40*, 301–370; o) M. A. Mintzer, M. W. Grinstaff, *Chem. Soc. Rev.* **2011**, *40*, 173–190.

[2] W. Sliwa, B. Bachowska, T. Girek, *Curr. Org. Chem.* **2007**, *11*, 497–513.

[3] F. Marchioni, M. Venturi, A. Credi, V. Balzani, M. Belohradsky, A. M. Elizarov, H.-R. Tseng, J. F. Stoddart, *J. Am. Chem. Soc.* **2004**, *126*, 568–573.

[4] a) C. A. Schalley, C. Verhaelen, F.-G. Klärner, U. Hahn, F. Vögtle, *Angew. Chem.* **2005**, *117*, 481–485; *Angew. Chem. Int. Ed.* **2005**, *44*, 477–480; b) V. Balzani, H. Bandmann, P. Ceroni, C. Giansante, U. Hahn, F.-G. Klärner, U. Müller, W. M. Müller, C. Verhaelen, V. Vicinelli, F. Vögtle, *J. Am. Chem. Soc.* **2006**, *128*, 637–648.

[5] S. Asaftei, E. De Clercq, *J. Med. Chem.* **2010**, *53*, 3480–3488.

[6] a) T. H. Ghaddar, J. F. Wishart, D. W. Thompson, J. K. Whitesell, M. A. Fox, *J. Am. Chem. Soc.* **2002**, *124*, 8285–8289; b) W. Wang, A. E. Kaifer, *Angew. Chem.* **2006**, *118*, 7200–7204; *Angew. Chem. Int. Ed.* **2006**, *45*, 7042–7046; c) P. Bhattacharya, A. E. Kaifer, *J. Org. Chem.* **2008**, *73*, 5693–5698.

[7] a) S. Heinen, L. Walder, *Angew. Chem.* **2000**, *112*, 811–814; *Angew. Chem. Int. Ed.* **2000**, *39*, 806–809; b) C. M. Ronconi, J. F. Stoddart, V. Balzani, M. Baroncini, P. Ceroni, C. Giansante, M. Venturi, *Chem. Eur. J.* **2008**, *14*, 8365–8373.
[8] L.-C. Cao, M. Mou, Y. Wang, *J. Mater. Chem.* **2009**, *19*, 3412–3418.
[9] a) V. Le Berre, E. Trévisiol, A. Dagkessamanskaia, S. Sokol, A. M. Caminade, J. P. Majoral, B. Meunier, J. François, *Nucleic Acids Res.* **2003**, *31*, e88; b) E. Trévisiol, V. Le Berre-Anton, J. Leclaire, G. Pratviel, A.-M. Caminade, J.-P. Majoral, J. M. Francois, B. Meunier, *New J. Chem.* **2003**, *27*, 1713–1719.
[10] a) O. Mongin, T. R. Krishna, M. H. V. Werts, A.-M. Caminade, J.-P. Majoral, M. Blanchard-Desce, *Chem. Commun.* **2006**, 915–917; b) T. R. Krishna, M. Parent, M. H. V. Werts, L. Moreaux, S. Gmouh, S. Charpak, A.-M. Caminade, J.-P. Majoral, M. Blanchard-Desce, *Angew. Chem.* **2006**, *118*, 4761–4764; *Angew. Chem. Int. Ed.* **2006**, *45*, 4645–4648.
[11] a) D. H. Kim, P. Karan, P. Göring, J. Leclaire, A.-M. Caminade, J.-P. Majoral, U. Gösele, M. Steinhart, W. Knoll, *Small* **2005**, *1*, 99–102; b) C. L. Feng, X. H. Zhong, M. Steinhart, A. M. Caminade, J. P. Majoral, W. Knoll, *Adv. Mater.* **2007**, *19*, 1933–1936.
[12] a) L. Griffe, M. Poupot, P. Marchand, A. Maraval, C.-O. Turrin, O. Rolland, P. Métivier, G. Bacquet, J.-J. Fournié, A.-M. Caminade, R. Poupot, J.-P. Majoral, *Angew. Chem.* **2007**, *119*, 2575–2578; *Angew. Chem. Int. Ed.* **2007**, *46*, 2523–2526; b) M. Poupot, L. Griffe, P. Marchand, A. Maraval, O. Rolland, L. Martinet, F.-E. L′Faqihi-Olive, C.-O. Turrin, A.-M. Caminade, J.-J. Fournié, J.-P. Majoral, R. Poupot, *FASEB J.* **2006**, *20*, 2339–2351; c) M. Hayder, M. Poupot, M. Baron, D. Nigon, C. O. Turrin, A. M. Caminade, J. P. Majoral, R. A. Eisenberg, J.-J. Fournié, A. Cantagrel, R. Poupot, J. L. Davignon, *Sci. Transl. Med.* **2011**, 81ra35.
[13] J. Solassol, C. Crozet, V. Perrier, J. Leclaire, F. Beranger, A.-M. Caminade, B. Meunier, D. Dormont, J.-P. Majoral, S. Lehmann, *J. Gen. Virol.* **2004**, *85*, 1791–1799.
[14] a) A.-M. Caminade, B. Delavaux-Nicot, R. Laurent, J.-P. Majoral, *Curr. Org. Chem.* **2010**, *14*, 500–515; b) C.-L. Feng, A.-M. Caminade, J.-P. Majoral, D. Zhang, *J. Mater. Chem.* **2010**, *20*, 1438–1441; c) M. Bardají, A.-M. Caminade, J.-P. Majoral, B. Chaudret, *Organometallics* **1997**, *16*, 3489–3497; d) M. Slany, A.-M. Caminade, J. P. Majoral, *Tetrahedron Lett.* **1996**, *37*, 9053–9056; e) S. Merino, L. Brauge, A.-M. Caminade, J.-P. Majoral, D. Taton, Y. Gnanou, *Chem. Eur. J.* **2001**, *7*, 3095–3105; f) A. V. Maksimenko, V. Mandrouguine, M. B. Gottikh, J. R. Bertrand, J. P. Majoral, C. Malvy, *Eur. J. Gen. Med.* **2003**, *5*, 61–71; g) L. Brauge, G. Magro, A.-M. Caminade, J.-P. Majoral, *J. Am. Chem. Soc.* **2001**, *123*, 6698–6699; h) F. Terenziani, V. Parthasarathy, A. Pla-Quintana, T. Maishal, A.-M. Caminade, J.-P. Majoral, M. Blanchard-Desce, *Angew. Chem.* **2009**, *121*, 8847–8850; *Angew. Chem. Int. Ed.* **2009**, *48*, 8691–8694.
[15] A. Ouali, R. Laurent, A.-M. Caminade, J.-P. Majoral, M. Taillefer, *J. Am. Chem. Soc.* **2006**, *128*, 15990–15991.
[16] a) Y. Brahmi, N. Katir, A. Hameau, A. Essoumhi, E. Essassi, A.-M. Caminade, M. Bousmina, J. P. Majoral, A. El Kadib, *Chem. Commun.* **2011**, *47*, 8626–8628; b) P. Reinert, J.-Y. Chane-Ching, L. Bull, R. Dagiral, P. Batail, R. Laurent, A.-M. Caminade, J.-P. Majoral, *New J. Chem.* **2007**, *31*, 1259–1263; c) A.-M. Caminade, J. P. Majoral, *J. Mater. Chem.* **2005**, *15*, 3643–3649; d) A. El Kadib, N. Katir, M. Bousmina, J. P. Majoral, *New J. Chem.* **2012**, DOI: 10.1039/clnj204436.
[17] C. Galliot, A.-M. Caminade, F. Dahan, J.-P. Majoral, *Angew. Chem.* **1993**, *105*, 1508–1510; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1477–1479.

Received: September 20, 2011
Published Online: December 2, 2011

