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Viologen-based dendritic macromolecular asterisks: synthesis and interplay with gold nanoparticles[†]

Nadia Katir,^a Abdelkrim El Kadib,*^a Vincent Collière,^b Jean Pierre Majoral*^b and Mosto Bousmina^{ac}

The viologen-skeleton reacts with a hydrazine-terminated cyclotriphosphazene core to provide novel dendritic macromolecular asterisks that efficiently exchange, deliver and stabilize gold nanoparticles for up to eight months.

Owing to their various properties, 4,4'-bipyridinium derivatives better known as viologens constitute staple building blocks in electro-chemistry as well as in coordination and supramolecular chemistry.¹ Thanks to their cationic character and their ability to undergo two successive one-electron reversible reductions, viologen-based macromolecular systems have applications in several fields, including medicinal chemistry and materials science, mainly as interacting charges with cells and living organisms,² reducing agents for active metal particles,³ switchable ionic liquids,⁴ photo-and electrochromic materials⁵ and as mediators for charge-induced energy transfer in photovoltaic devices.⁶ Their introduction into classical linear polymers and dendrimers offers additional opportunities in imparting specific properties to these macromolecular structures. Dendrimers are of particular interest due their well-designed and ramified structure, their nanometric size, periodically alternated diverging and well-separated branches and the presence of multifunctional end groups.⁷

The incorporation of the viologen skeleton within the framework of dendritic nanostructures⁸ has been shown to bring specific photo- and bio-activity relationship. However, to the best of our knowledge no report is available on viologen macromolecular asterisks⁹ assembled around an inorganic core.¹⁰

Herein, we report a novel approach allowing the design of such new ambiphilic viologen-based dendritic-macromolecular

asterisks incorporating three types of phosphorus units: a cyclotriphosphazene core, phosphonates end groups and hexafluorophosphate as counteranions. Interestingly, standard organic reactions and easy work-up procedures provide a library of mono-, bis-, tris- and tetrakis-viologen-based molecular and macromolecular building blocks that can react with a functional cyclotriphosphazene core to generate photo-reactive phosphorus-viologen macromolecular asterisks. These soft scaffolds were used here to efficiently stabilize nanosized gold particles.

The first step in constructing these architectures consists in the synthesis of a viologen terminated with aldehyde on one side and a phosphonate on the other side. Thereafter, a set of 4,4'-pyridin-pyridinium featuring terminal phosphonates (P1 and P3) or aldehyde extremities (P5 and P7) that are prone to single alkylation were isolated in good yields (71 to 89%). Alkylation of P1 and P3 by 4-(methylbromo)benzaldehyde followed by ionic exchange with NH₄PF₆ affords mono-viologen 1V and bis-viologen 2V in good yields (73-75%) as their hexafluorophosphate salts. Selective mono-alkylation of P3 by 1,4-bisbromomethylbenzene provides bromo-ended P4 (yield: 58%) that can condensate to mono-substituted viologens P5 and P7. This quaternization followed by ionic exchange enables quantitative access to 3V (89%) and 4V (84%) as their hexafluorophosphate salts (Scheme 1). These novel precursors, presenting good solubility in acetone and acetonitrile, were unambiguously characterized by ¹H, ¹³C and ³¹P NMR and mass spectroscopy (see S1 and S2, ESI[†]).

Owing to their reactive aldehyde extremity, nV (n = 1 to 4) easily react with hexahydrazidocyclotriphosphazene used as a core¹¹ to provide quantitatively **D1V**, **D2V**, **D3V** and **D4V** (Scheme 2). ³¹P NMR shows two signals: a single symmetrical signal of the (P=N)₃ ring at 17 ppm (instead of the one observed at 29 ppm for the starting core)¹¹ and a second signal at around 23–25 ppm assignable to the peripheral phosphonate of the viologen framework. Combining these results with those of ¹H and ¹³C NMR – in which the disappearance of aldehydes has been ascertained – unequivocally demonstrates that the ring core and the viologen asterisks are chemically linked *via* a

^a Euro-Mediterranean University of Fez (UEMF), Fès-Shore, Route de Sidi harazem, Fès, Morocco. E-mail: a.elkadib@ueuromed.org

^b Laboratoire de Chimie de Coordination, Centre National de la Recherche Scientifique, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

^c Hassan II Academy of Science and Technology, Avenue Mohammed VI, 10222 Rabat, Morocco

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(iii) 1,4-bis (bromomethyl)benzene, acetonitrile, 40°C; (iv) 4,4-bipyridine, acetonitrile, 40°C Scheme 1 Multi-step synthesis of **1V** to **4V**.



Scheme 2 Synthesis of D1V to D4V.

hydrazido linkage [in ¹³C NMR, C—N resonates at 136–137 ppm (d, ³*J*_{PC} = 13 to 15 Hz); in IR: ν (C—N) = 1638 cm⁻¹ (see S1 to S3, ESI†)]. All these syntheses were notably performed using metal-free routes, making them particularly adapted for biological applications.

Expectedly, owing to the presence of viologens in these dendritic substructures, UV-visible spectroscopic analysis shows a broad band at 264 to 280 nm wavelength ascribed to π - π * transition, with a hyperchromic effect (the intensity is proportional to the number of the viologen units: see S4, ESI†). Fluorescence studies reveal a substantial shift in the fluorescence maxima,

being more significant when comparing **D1V** and **D2V** (540 nm) with **D3V** and **D4V** (495 to 507 nm) (see S5, ESI[†]). This hypsochromic effect might emanate from the difference in the supramolecular organization of these macromolecular asterisks, which probably results in shielding or crowding the photo-responsive viologen motifs in different electronic environments.¹²

Considering the ability of viologens to interact with metallic species,³ the aim was to verify if the number of viologen units grown in each asterisk accounts for the interplay with gold particles (asterisk effect). To this end, D1V, D2V, D3V and D4V were subjected to a stoichiometric reaction with HAuCl₄ (with respect to the number of viologen units in each dendrimer) and the reaction was monitored by UV-visible spectroscopy. In the absence of any reducing agent, besides the well-recognized absorption band of the viologen motifs, a new band appeared at 227 nm assignable to AuCl₄⁻. Compared to the starting neutral gold complex HAuCl₄ that exhibits a broad band at 215 nm, the new band is narrowed and 12 nm red shifted as a result of its exchange with a viologen (formation of viologen⁺-AuCl₄⁻). Upon addition of NaBH₄, a redshift in the viologen band is observed (reaching 30 nm for D3V@Au and D4V@Au) and the clear yellow solutions turned purplish red indicative of the formation of gold nanoparticles (Fig. 1). This has been additionally ascertained by the apparition of a broad surface plasmon resonance (SPR) band centered at 523-535 nm, typical of gold nanoparticles.^{3c,13} The intensity of the plasmonic band increased slightly after 4 days and even continues to rise 6 days after. This indicates that regardless of the number of molecular units in each branch, viologen fragments act as anchoring sites to firstly exchange and then smoothly transform molecular gold to nanosized particles. The absence of the second SPR band at around 650 nm proves the formation of isotropic particles thereby excluding any preferential growth at the asterisk branching direction built from sequential viologen units (anisotropic nanoparticles).^{3c}

HRTEM analysis revealed nanosized particles without any presence of bulky aggregates (Fig. 2 and S6, ESI⁺). The average



Fig. 1 Digital photos of DnV (left) and DnV@Au NPs (right).



Fig. 2 TEM images of **D2V@Au**, **D3V@Au** and **D4V@Au**. Onset: single particle at higher magnification.

Table 1 UV-visible and fluorescence measurements of DnV before and after the reaction with HAuCl₄·3H₂O

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	Viologen– ${\rm PF_6}^{-a,b}$	Viologen ⁺ -AuCl ₄ ^{- a}	Viologen@AuNPs ^c	AuNPs ^d (nm)
D1V	282 (540)	282, 227	289 (530)	45
D2V	266 (540)	266, 227	269 (535)	8.5
D3V	264 (507)	264, 227	293 (523)	7.5
D4V	265 (495)	264, 226	294 (528)	7

^{*a*} UV-visible analysis (nm). ^{*b*} The value between brackets correspond to the fluorescence measurements (nm). ^{*c*} UV-Visible upon addition of NaBH₄ (nm). (The value between brackets corresponds to the characteristic band of gold nanoparticles (nm)). ^{*d*} Average particle size measured using HRTEM.



Fig. 3 (a) SAED pattern showing the planes of **D4V@Au**. (b) Size distribution of gold nanoparticles in **D4V@Au** calculated from HRTEM. (c) EDX cartographic mapping of P (green) and Au (red) of **D1V@Au** showing homogeneous distribution of metallic and dendritic phases.

size of gold nanoparticles varies from 7 to 45 nm, with the smallest dendrimer **D1V** being the least efficient to limit the growth of the metallic objects (Table 1 and S7, ESI[†]). However, regardless of the nature of the dendrimer used, no further growth, bulky aggregates or metal precipitation can be observed for up to eight months witnessing consequently the efficiency of these dendrimers in long-term stabilization of gold nanoparticles (Fig. 2 and S6, ESI[†]).

The SAED pattern shows a periodicity of d = 0.23 nm that corresponds to the [111] plane of symmetry attributed to crystalline gold nanoparticles (Fig 3a and S8, ESI†). The homogeneity of the nanocomposite **DnV@Au** has been assessed by means of EDX mapping, looking at the amount of P, N and Au at different regions. Nicely, an intimate dispersion and distribution of the nanosized gold particles within the dendritic phase resulted in continuous regular organic–inorganic hybridization at the nanoscale, with neither phase separation nor clustering of any single phase (Fig. 3c and S9, ESI†).

To sum up, a series of linear and dendritic sub-structures in which the number of viologen units varies from 1 to 24 have been successfully prepared and isolated. These macromolecular asterisks provide novel building blocks that couple the specificity of viologen "molecular recognition" and "sterical hindrance" of dendrimers to efficiently exchange, deliver and stabilize (for *up to eight months*) nanosized gold particles (S9 in ESI[†]). Considering the broad spectrum of utilization of viologen motifs, the importance of phosphonate terminal groups in biological applications^{2c} and for hybrid material synthesis,¹⁴ and the outstanding catalytic and optical properties of gold nanoparticles, promising applications can emerge from these nanocomposite "ternary" hybrid systems.

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