Tetrahedron Letters 54 (2013) 303–307

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Aminoacidic units wired on poly(aryleneethynylene) platforms as highly selective mercury-responsive materials

Antonella Ricci [a], Marco Chiarini [a], Maria Teresa Apicella [a], Dario Compagnone [a], Michele Del Carlo [a], Claudio Lo Sterzo [a,b,*], Luca Prodi [c], Sara Bonacchi [c], Diego Villamaina [c,†], Nelsi Zaccheroni [c,*]

[a] Dipartimento di Scienze degli Alimenti, Facoltà di Agraria, Università degli Studi di Teramo, Via Carlo R. Lerici 1, 64023 Mosciano S. Angelo (Teramo), Italy
[b] Istituto CNR di Metodologie Chimiche (IMC-CNR), Sezione Meccanismi di Reazione, Dipartimento di Chimica, Università La Sapienza, 00185 Roma, Italy
[c] Dipartimento di Chimica 'G. Ciamician', Latemar Unit, Università degli Studi di Bologna, 40126 Bologna, Italy

ARTICLE INFO

Article history:
Received 2 August 2012
Revised 31 October 2012
Accepted 7 November 2012
Available online 14 November 2012

Keywords:
Poly(aryleneethynylene)s
Aminoacids
Fluorescence
Mercury ion
Sensors

ABSTRACT

Novel highly ethynylated materials carrying aminoacidic side arms on poly(aryleneethynylene) (PAE) conjugated backbones have been prepared and fully characterized. The luminescent sensing properties of these materials toward metal ions were investigated. All compounds showed high selectivity toward Hg(II) ions, and a signal amplification in Hg(II) detection was observed for the polymeric compound in comparison with other molecular ligands.

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The widespread role of metal ions in human health ranges from the requirement of daily intake of essential elements, to the toxicity due to metal overload.[1] Because of their large presence in the environment, as a result of human activities such as farming, industry or from contamination during food processing and storage, sources of metal ingestion might be contaminated drinking water, seafood, breast milk, smoking, together with plants and animals used in the diet. In this respect, frequent exposure, although below current admitted levels, may result in accumulative effects and, with the extension of lifespan in the western world, the total accumulation in the body over a lifetime, with special attention to heavy metals, should be taken into serious account.[2]

Therefore, the development of selective and tunable practical sensors for the detection and quantification of metal ions is the subject of considerable research efforts.[3–5]

In nature, metal binding is achieved with an unsurpassed degree of selectivity using aminoacids and peptides.[6–9] In principle, mimicking nature, one could thus succeed in designing and tuning the selectivity of peptides to achieve the desired sensing properties.[10] Despite these premises, only recently sensing systems using aminoacidic and peptide moieties as recognition units for metal sensing have started to appear.[11–17]

In the past few years we entered this field proposing a new synthetic access to highly conjugated small molecules and polymers characterized by poly(aryleneethynylene)s backbones (PAEs), and their use as sensing material in the construction of efficient chemo- and bio-sensors.[18–20] In particular[20] we reported the preparation of co-polymers made of alternating arylene and phenanthroline or bithiophene moieties spaced by ethynylene units, and their sensing properties toward metal ions.

More recently, we presented our preliminary results obtained with the use of further elaborated structures made of aminoacidic recognition sites covalently linked to conjugated PAEs backbones, and their effectiveness toward metal ion sensing.[21] The good selectivity and sensitivity obtained for the Hg(II) ion, an environmental heavy metal pollutant of major concern,[22] encouraged us to foster the development of the sensing potential of highly ethynylated platforms decorated with aminoacids.

In this Letter we present the synthesis of different PAE structures carrying leucine moieties as side arms, and the investigation of their photophysical behavior upon interaction with metal ions.

Starting from the commercially available terephthalic acid bromides **1** and **2**, formation of derivatives **5** and **6** bearing L-leucine pendants was achieved in two steps by adapting literature procedures (Scheme 1).[23] Subsequently, formation of the conjugated structures **DLM**, **TLM**, and **DLP** was achieved by the use of the Stille

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[*] Corresponding authors. Tel.: +39 0861 266904; fax: +39 0861 266915 (C.L.S.).
E-mail addresses: closterzo@unite.it (C.L. Sterzo), nelsi.zaccheroni@unibo.it (N. Zaccheroni).

[†] Present address: University of Geneva, Department of Physical Chemistry, CH 1211.

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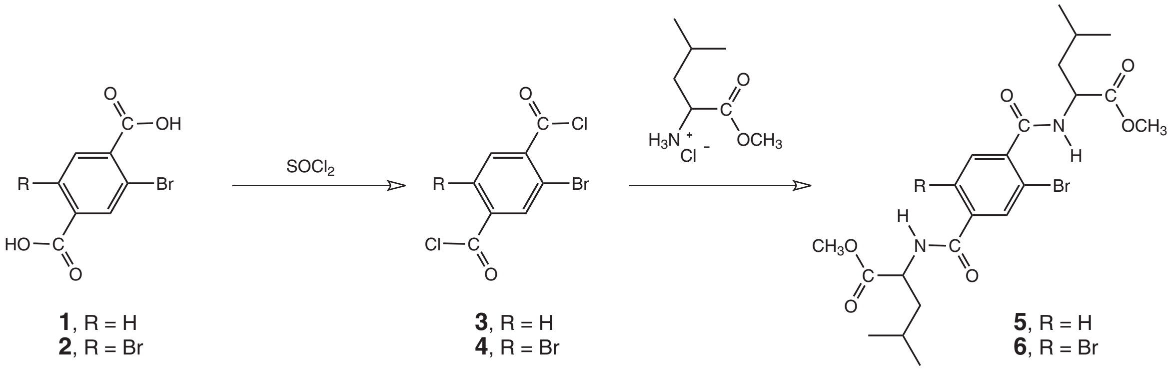
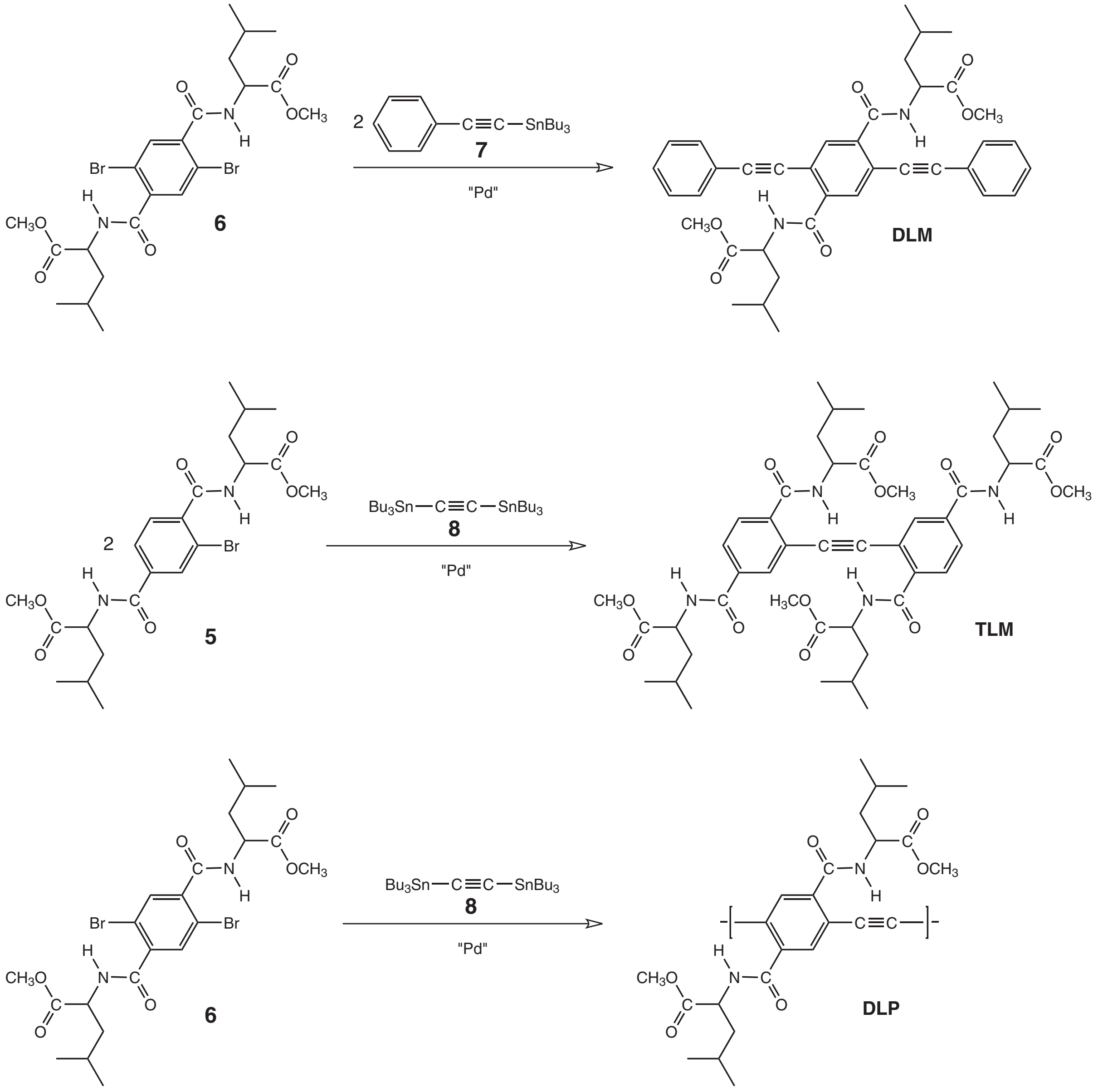
http://dx.doi.org/10.1016/j.tetlet.2012.11.034



Scheme 1. Schematic representation of the synthesis of aromatic bromides carrying leucine side arms.

Pd-promoted cross coupling reaction[19,24] between the tributylethynyltin derivatives **7** and **8** and the aryl halides **5** and **6**, in the presence of tetrakis(triphenylphosphine)palladium(0) catalyst (Scheme 2).

The model compounds *N*,*N*′-[2,5-bis(phenylethynyl)terephthaloyl](L,L)di-leucine methyl ester (**DLM**) and *N*,*N*′,*N*″,*N*‴-[(2,2′-ethyne-2,1-diyl)diterephthaloyl](L,L,L,L)tetra-leucine methyl ester (**TLM**), presenting, respectively, two and four leucine units



Scheme 2. Synthetic scheme of the leucine functionalized conjugated materials **DLM**, **TLM**, and **DLP**.

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