

## Abstract

More than twenty new bis(*tpy*)oligothiophenes (*tpy* stands for 2,2':6',2''-terpyridin-4'-yl) with unsubstituted as well as substituted (with methyl, hexyl, bromohexyl or 6-(4-methoxyphenoxy)hexyl groups) central blocks comprising one to four thiophene rings have been prepared as building blocks (unimers) for constitutional dynamic metallo-supramolecular polymers (MSPs) soluble in common organic solvents. In addition a series of ionic unimers soluble in alcohols and partially in water have been prepared by modification of bromohexyl unimers with trimethylamine or triethylphosphine.

Spectroscopic studies have shown that the steric hindrances prevail over the electronic effects of substituents as regards the impact on the delocalization of electrons along unimer chains. Unimers with high steric hindrances in the middle of the central oligothiophene block were found to behave nearly like the unimers with half central block.

Three stages of the assembly of MSPs from unimers and metal ions in solutions were characterized by the UV/vis and fluorescence spectroscopy, viscometry and size exclusion chromatography: (i) formation of dimers  $U-Mt^{2+}-U$  in the early stages of assembling, (ii) assembly to longer MSPs chains, and (iii) end-capping with surplus metal ions and partial decomposition of MSPs chains.

The observed changes in optical absorption spectra indicate a significantly increased extent of the delocalization of electrons upon binding the unimer molecules into polymer chains. On the other hand, a blue shift of luminescence emission in thin films of the most of MSPs compared to parent unimers indicates that the bulky *tpy*- $Mt^{2+}$ -*tpy* linkages suppress efficient planarization of unimer units in thin films of MSPs. Fe-MSPs exhibit MLCT band giving them typical blue color and are non-emissive in contrast to Zn-MSPs.

Evidences from spectroscopic, viscometric and SEC techniques proved fast constitutional dynamic for Zn-MSPs while very slow for Fe-MSPs. Slow dynamic in  $Fe^{2+}$ /unimer systems allowed the molecular-mass characterization of these systems by SEC. Remarkable influence on stability of MSPs was found by experiments in different solvents.