The study shows strong influence of the conformation of the main chains of polythiophenes in solutions on their spectroscopic properties. The conformational changes affect strength of interactions between neighboring chains and lead to the formation of aggregates of stacked polythiophene chains. Stacked chains show red shift of the optical absorption and lead to visible vibronic structure of absorption bands. Multilayered systems prepared by periodic adsorption of the cationic and anionic polythiophene polyelectrolytes on various substrates show proportionality of the overall layer thickness to the number of coatings, which allows a control of the layer thickness. Adsorption of the conjugated polyelectrolytes on the anatase form of titanium dioxide show better penetration of the anionic polythiophene to porous anatase. The adsorption of polymer into the mesoporous structure is not complete: maximum adsorption of PTTA (poly(thiophene-3-ylacetic acid)) adsorbed on anatase do not correspond to the inner surface of mesoporous anatase. Alternating adsorption from the solutions of polythiophene with anionic and cationic side groups on mesoporous anatase allows preparation of the Graetzel-like photovoltaic cell provided that the adsorption process starts with the anionic polythiophene and the layers are deposited from sufficiently diluted solutions. The absorption should be ceased before reaching the saturation, which can be explained by a blockage of the substrate mesopores with superfluous PTTA. Also it was shown that the absorption of cationic polythiophene on the layer of anionic polythiophene is strongly affected by Coulombic interactions that do not allow good ordering of the cationic polymer layer to stacked structures. As a result, the molar absorption coefficient of the polymer layer is lower than it might be expected on the basis of known absorption coefficients of parent polythiophene polyelectrolytes. The absorption maximum of layered system is blue-shift compared to the absorption maxima of layers of their constituents. The layered system prepared was subject to test of photovoltaic efficiency which has proved its functionality. The tests performed include volt-ampere characteristics measured in the dark and under illumination as well as photoelectric characterization of the systems. They have shown rather low efficiency of the system, in particular, at increased temperature; nevertheless, the system has a potential of further tuning.