Synthesis of azobenzene based probes for reversible metal ion binding and releasing

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Abstract

Azobenzene is one of the simplest example of molecular machine. Azobenzene can exist in two isomeric forms, namely *trans* (*E*-isomer) and in *cis* (*Z*-isomer). Azobenzene based systems under the external stimuli (light) reversibly isomerize between the two isomers. This property of reversible photoisomerization of azobenzene using light, preferably at different wavelengths led to the generation of many molecular switches that can potentially be used in variety of fields such as data storage, molecular recognition, molecular machines.

In our current investigation, we set our goal towards synthesizing a azobenenze based probe for reversibly binding and release of metal ions. The reversibility of this probe could be controlled by external stimuli, light in this case. Since sulphur atoms are found to have strong affinity towards soft metal ions, we designed and incorporated thiophene connected azobenzene systems in this regard. Amide linkage has been used for connecting the thiophene to the azobenzene moiety.

Two target probe molecules were synthesized using azobenzene dicarboxylic acids (4,4'- and 3,3'-isomers), followed by acid-amine coupling with a common secondary amine containing two thiophene units. For understanding the light induced reversibility of the probe, photoswitching experiments were perfomed in solution. However, we observed only a partial photoswitching. Apart from that, we also investigated the possibility of metal ion binding with zincperchlorate. Both *E*- and *Z*-isomers exhibited only broadening without strong shifts in the absorption bands. Since both the target molecules were partially switching and also the shifts were not strong, the results were inconclusive. Connectivity pattern may be tuned to exhibit better switching characteristics. The synthesis, photoswitching and the metal-ion binding experiments have been given in detail.