The development of ratiometric fluorescence sensor for heavy metal ions based on Suzuki-miyaura Cross-coupling reaction

（鈴木一宮浦クロスカップリングを活用した変色型蛍光重金属イオンセンサーの創製）

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Introduction

With the high development of industry, monitoring and determination of heavy metal ions are of great significance to both the environment and public health. Transition metal ions have especially received considerable concern due to their importance in biological and environmental processes. In recent years, the study of chemosensors in which 1,5-diphenylcarbazide (DPC) and DPC derivatives are used to detect heavy metal ions has been reported. Nevertheless, most of these probes are based on colorimetric measurements. Given the high sensitivity and selectivity of fluorescent probes, the aims of this study were to (1) synthesize a kind of novel carbazide (heavy metal ions recognition site in DPC)-containing fluorescent solvatochromic dye (acetylthiophenyl including); to (2) analysize the photophysical properties, and to (3) investigate the capability of selectively detecting heavy metal ions fluorimetrically.

Methods

The synthetic approaches started from protecting the amino group of 4-bromoaniline with Boc. A strong electron withdrawing group was introduced to benzene ring through Suzuki cross-coupling reaction two times to synthesize a typical solvatochromic fluorescent dye. After deprotecting Boc from the amino group, diazotization conducted to synthesize 1-(5-(4-hydrazineylphenyl)thiophen-2-yl)enthan-1-one. This compound was reacted with triphosgene in CH_2Cl_2 to obtain the target product N', 2-bis(4-(5-acetylthiophen-2-yl)phenyl)hydrazine-1-carbohydrazide. The target product was analysized and evaluated by ^{1}H NMR, ^{13}C NMR and IR spectra.

Results and Discussion

The results showed that the desired DPC-based fluorescent solvatochromic dye which is a kind of dark yellow solid was successfully synthesized. The overall synthesis route was easy to operate. Simultaneously, it showed different fluorescence color (i.e. fluorescence wavelength) in different solvents. The emission color was blue in low polarity solvents such as toluene, and presented yellow in high polarity solvents such as ethyl acetate and acetone. The fluorescence wavelength demonstrated a red-shift tendency increasing the solvent polarity.

Contrary to expectation, the target fluorescent dye did not show chromogenic reaction with Cr^{6+} in DMF and acetone. Whether the oxidation reaction of the carbazide fraction was strongly affected by thiophene functional group or relevant to the solubility still need to be further explored. We expect that this kind of DPC-based fluorescent dye could selectively recognize other heavy metal ions with the improvement of experiment.