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Determination of Methamphetamine Hydrochloride by highly fluorescent polyfluorene with NH_2-terminated side chains

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ABSTRACT

Three different poly{9,9-bis[6′(–NHBoc, $–NH_3^+$ and $–NH_2$)hexyl]fluorene}s (PF-NHBoc, PF-NH_3^+ and PF-NH_2) have been synthesized and characterized. Both UV–Vis and fluorescence spectroscopic results supported the interaction between the polyfluorenes and Methamphetamine Hydrochloride (MAPA) was derived from the different terminals of hexyl side chains. Among the three polyfluorenes, PF-NH_2 exhibited the best sensory response to Methamphetamine Hydrochloride (MAPA) in THF arising from its $–NH_2$ terminals. The fluorescence of PF-NH_2 was immediately quenched once the MAPA was added, and the detection limit of MAPA was determined to be ~25 ng/mL. Fluorescence quenching experiments of PF-NH_2 by NH_4Cl and other metal ions confirmed that electrostatic interaction should make contributions to the quenching behavior, in addition, upward non-linear curvature and much higher quenching constant (K_{sv}) in the Stern–Volmer plots for MAPA suggested some other interactions such as hydrophobic or/and hydrogen-bonding interactions dominated the analyte-induced aggregation, and such hydrophobic interaction was responsible for the sensitive selectivity. The fluorescent quenching experiments upon adding other drugs such as Pethidine Hydrochloride (PTD) and Ephedrine Hydrochloride (EPD) confirmed such selectivity, especially under the high concentration of the Stern–Volmer plots. The high sensitivity, selectivity, and its simple and fast character, made it a new and effective way for drug detection.

1. Introduction

In the past decades, the usage of abused drugs such as methamphetamine-like stimulants, cocaine and morphine has spread widely on the global scale, which brings on serious consequence for human health and social behavior [1–3]. Clandestine illegal drug production laboratories driven by the high commercial profit produce a lot of hazardous waste resulting in great pollutions to environment [4,5]. Meanwhile, many of these laboratories are temporary and capable of producing large quantities of prohibited drugs in production cycles that can often span less than 48 h, making timely discovery essential. By this time, various methods have been developed to the detection of the abused drugs including liquid chromatography/mass spectrometry (LC/MS) [6,7], immunoassays [8,9], capillary electrophoresis (CE) [10], infrared spectrometry (IR) [11], and ion mobility spectrometry (IMS) [4,12]. However, most of them suffer from problems of time-consuming, expensive apparatuses, or tedious sample pre-workup. Developing efficient, rapid and simple detection methods of such drugs are still of great interest in public safety field.

Fluorescent conjugated polymers (CPs) have attracted considerable attentions as chemical and biological sensors for their unique optical properties [13,14]. The CPs have been used as the optical platforms in highly sensitive chemical and biological sensors such as the detection of metal ions, explosives, small biomolecules, proteins and DNA [15–27]. It is well known that the backbone of the conjugated polymers contains a large number of chromic repeat units, and the fluorescence intensity will change dramatically upon binding of the analyte resulted in the amplification of fluorescent signals. The most widely exploited mechanism for the amplification of fluorescent signals is quenching of the inherent fluorescence through electron/energy transfer between the CPs and an analyte [14,28]. However, another mechanism, namely analyte-induced aggregation has attained an increasing interest recently, which directly causes fluorescence self-quenching resulting from interchain electrostatic or hydrophobic interactions [29–33]. Formation of tight aggregates named π-stacking aggregation of CPs generally gives rise to new, broad emission peaks at longer wavelength and reduction of fluorescent quantum yields (Φ_f) [15,18,24,30,34–37].

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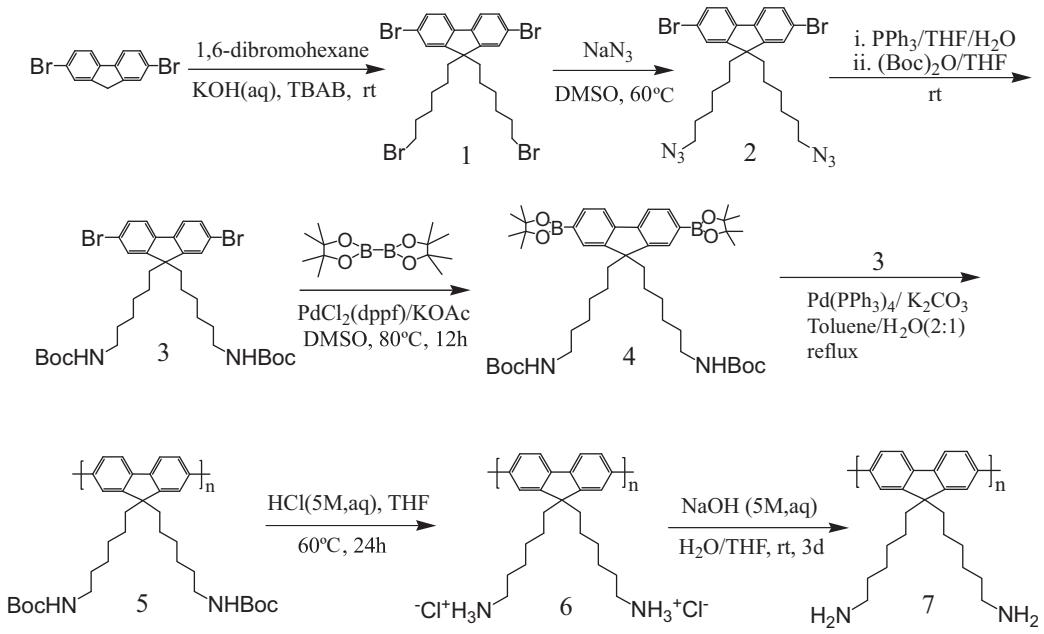

Scheme 1. Synthetic route of poly{9,9-bis(6′-aminohexyl)fluorene}.

Because of the facile modifying the side groups of the CPs, this quenching mechanism usually takes advantage of the interaction between analytes and side-chain functional groups inducing the planarization/deplanarization of the polymer backbone [18,22,31]. Nevertheless, most of the CPs used in this process are conjugated polyelectrolytes (CPEs), which are characterized with multiple ionic units. CPEs usually have lower Φ_f for the tendency of aggregations in common solvents, the lower Φ_f is responsible for lower sensitivity [22,24,32,38]. Therefore, it is necessary to develop CPs with higher Φ_f and sensitivity. In the contribution of Wang and co-workers' work, cationic polyfluorenes have been used as fluorescent sensors widely [24,31,39]. Unlike cationic polyfluorene, we utilize amino functionalized side-chain of polyfluorene (PF-NH_2, high photoluminescent quantum efficiency) in MAPA detection for MAPA is a cationic and it is capable to form static electric or/and hydrogen-bonding interaction between cationic MAPA and amino units. We investigated the sensory response of three polyfluorenes with different side-chain terminals to MAPA and found that the interaction between MAPA and PF-NH_2 led to a significantly fluorescent quenching response. The interaction mechanism was proposed by control experiments under different conditions.

2. Experimental

2.1. Materials and measurements

All solvents and reagents were obtained from commercial sources and used as received. The ^{1}H NMR spectra were obtained from a Brucker DRX500 instrument, and tetramethylsilane (TMS) was used as an internal standard. Mass spectra were recorded on a BIFLEX III MALDI-TOF (Brucker Daltonics Inc.) mass spectrometer. UV–vis absorption and fluorescence spectra were performed on a Jasco V-670 spectrophotometer and a Jasco FP 6500 spectrometer respectively. The time-resolved fluorescence data were collected on an Edinburgh FLS920 spectrofluorimeter. The gel permeation chromatography (GPC) measurements were performed on a PL-GPC 50 Plus integrated system with tetrahydrofuran (THF) as eluent, and polystyrene was used as standard. The IR spectra were recorded on a Brucker IR spectrometer (TENSOR 27, RT-DLaTGS detector).

2.2. Synthesis

A general synthetic procedure was outlined in Scheme 1. Detailed synthesis process was described in supporting information and the monomers used in the Suzuki-coupling reaction were synthesized according to the literature [39]. PF-NHBoc (**5**) was synthesized by Suzuki-coupling reaction of monomers **3** and **4**, and the infrared spectrum (film) of PF-NHBoc (**5**) exhibited the expected strong carbonyl absorption at 1700.89 cm^{-1} and amide absorption band at 3358.74 and 1509.78 cm^{-1}. The strong carbonyl absorption at 1700.89 cm^{-1} disappeared and the amide absorption band was found at 3420.51 and 1609.07 cm^{-1} while treatment of PF-NHBoc (**5**) with 5 M aqueous of HCl in THF solution to afford PF-$NH_3^+Cl^-$ (**6**) (yield, 89%). PF-NH_2 (**7**) was obtained from the reaction between **6** and 5 M NaOH aq in 70% yield. In contrast with PF-$NH_3^+Cl^-$ (**6**), the infrared spectrum (film) of PF-NH_2 (**7**) exhibited a strong C–N band at 1021.17 cm^{-1} suggested the reaction was conduced suc-

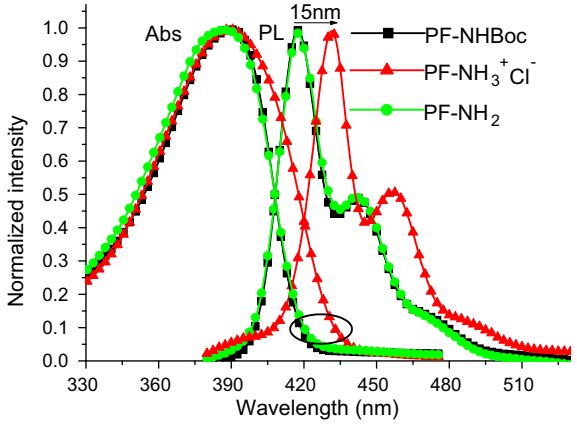

Fig. 1. UV–Vis and PL spectra of PF-NHBoc, PF-$NH_3^+Cl^-$ and PF-NH_2 in THF solution (10^{-7} M), the excitation wavelength was at 370 nm.