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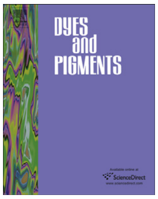

TCNE-decorated triphenylamine-based conjugated polymer: Click synthesis and efficient turn-on fluorescent probing for Hg^{2+}

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A type of triphenylamine-based conjugated polymer with cyano-containing chromophore in side chain, poly[(9,9-dioctyl)-2,7-fluorene-co-N-4-(1,1,4,4-tetracyanobuta-1,3-dienyl)-4,4′-triphenylamine] (**P3**) was successfully synthesized by catalyst-free and efficient click reaction between poly[(9,9-dioctyl)-2,7-fluorene-co-N-4-ethynyl-4,4′-triphenylamine] (**P2**) and tetracyanoethylene (TCNE). Chemical structures of intermediates and target polymer were verified by FT-IR and ^{1}H NMR analyses. Fluorescence of **P3**'s THF solution was specifically quenched by the introduction of I^-, accompanied by the change of its apparent color from pale brown to light yellow. With the introduction of Hg^{2+}, fluorescence of **P3**/I^- complex recovered quickly and even exceeded the initial intensity of pristine **P3** (when the concentration of Hg^{2+} above ~6.65 × 10^{-5} M). Other common cations brought very slight interference for **P3**/I^- complex's response of Hg^{2+}, and the detection limit of Hg^{2+} reached ~6.9 nM for such probing system.

1. Introduction

Hg^{2+} is a type of tremendous poisonous pollutant and the high-efficiency detection of Hg^{2+} by practical-simple and low-cost protocol is still a challenging issue [1–4]. Considerable efforts have been devoted to detect Hg^{2+} *via* different approaches, such as neutron activation analysis [5], anodic stripping voltammetry [6,7], inductively coupled plasma mass spectrometer [8], optical probes [9–12] and so on. Among these reported methods, optical probes, especially conjugated polymers (CPs)-based optical probes sprung up in recent years displayed interesting advantages, such as good optical stability [13,14], high sensitivity and excellent selectivity [15–17], and thus have drawn increasing attention. Despite of the great advance achieved in recent years, most of reported CPs-based Hg^{2+} probes are turn-off mode, and the fluorescence turn-on detection is much more preferable than the quenching mechanism due to the ease of detection and less interference [18–20]. Recently, Iyer et al. reported a type of thiazole-containing CP as a visual and fluorometric sensor for I^- (turn-off mode) and Hg^{2+} (turn-on mode) [21]. It was also reported by our group that triphenylamine or carbazole-containing CPs can be utilized as selective turn-off fluorescent probes for I^-, moreover, owing to the high association constant and matching ratio between I^- and Hg^{2+}, theses probes can realize the efficient turn-on detection for Hg^{2+} [22,23]. These materials represent a series of promising probing substrates and the detection limit for Hg^{2+} reached ~2.4 × 10^{-7} M [22]. How to further modify their probing performance is an interesting issue remains to be solved, which might be explored by investigating the relationship between the chemical structure-probing properties of these polymeric fluorescent sensors.

Recently, Kaur et al. reported a charge-transfer compound of cyano-containing *N*-methylpyrrole derivative [24], which exhibits good selectivity and reasonably sensitivity (with detection limit of ~10 ppm) for Hg^{2+}. The intramolecular charge-transfer (ICT) in this compound was quenched due to the interaction between dicyano-substituted olefinic carbon atom and Hg^{2+}, which is responsible for the alteration of its optical properties [24]. This finding give us an inspiration that the introduction of electron-withdrawing cyano groups into Hg^{2+}-responsive CPs might simultaneously tune their electron energy and modify the interaction between these CPs and Hg^{2+}. Tetracyanoethylene (TCNE) is one type of typical cyano-containing strong electron acceptors and has been successfully introduced into carbazole and thiophene-based CPs by catalyst-free, ethynyl-TCNE addition click reaction [25–29]. But to the best of our knowledge, although the TCNE-decorated small-molecular triphenylamine derivatives have been

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successfully synthesized [30,31] and applied as the optical probe for cysteine [31], the introduction of TCNE to triphenylamine-based CP as well as using it as Hg^{2+} optical probe has not been reported up to now.

Inspired by above-mention knowledge and in order to modify the turn-on Hg^{2+} probing performance of triphenylamine-based CPs, a kind of triphenylamine-based CP with chromophore in side chain, poly[(9,9-dioctyl)-2,7-fluorene-co-*N*-4-(1,1,4,4-tetracyanobuta-1,3-dienyl)-4,4′-triphenylamine] (**P3**), was successfully synthesized by catalyst-free and efficient click reaction between acetylene (≡C–H) pendent-substituted precursor polymer, poly [(9,9-dioctyl)-2,7-fluorene-co-N-4-ethynyl-4,4′-triphenylamine] (**P2**) and TCNE. The sensing properties of **P3** to I^- and the further **P3**/I^- complex to Hg^{2+} was investigated systematically in this effort.

2. Experimental section

2.1. Measurements and characterization

IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets. ^1H NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating at 400 MHz in deuterated chloroform solution with tetramethylsilane as the internal standard. UV–visible absorption spectra were recorded on a SHIMADZU UV-2450 UV–*vis* spectrophotometer. PL spectra were recorded on SHIMADZU RF-5301pc spectrophotometer. Number-average (M_n) and weight-average (M_w) molecular weights were determined by UltiMate3000 in THF using a calibration curve of polystyrene standards. Cyclic voltammogram were carried out on a CHI660D electrochemical workstation with platinum electrodes at scan rate of 50 mV/s against saturated calomel reference electrode (SCE) with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) in CH_3CN.

2.2. Materials

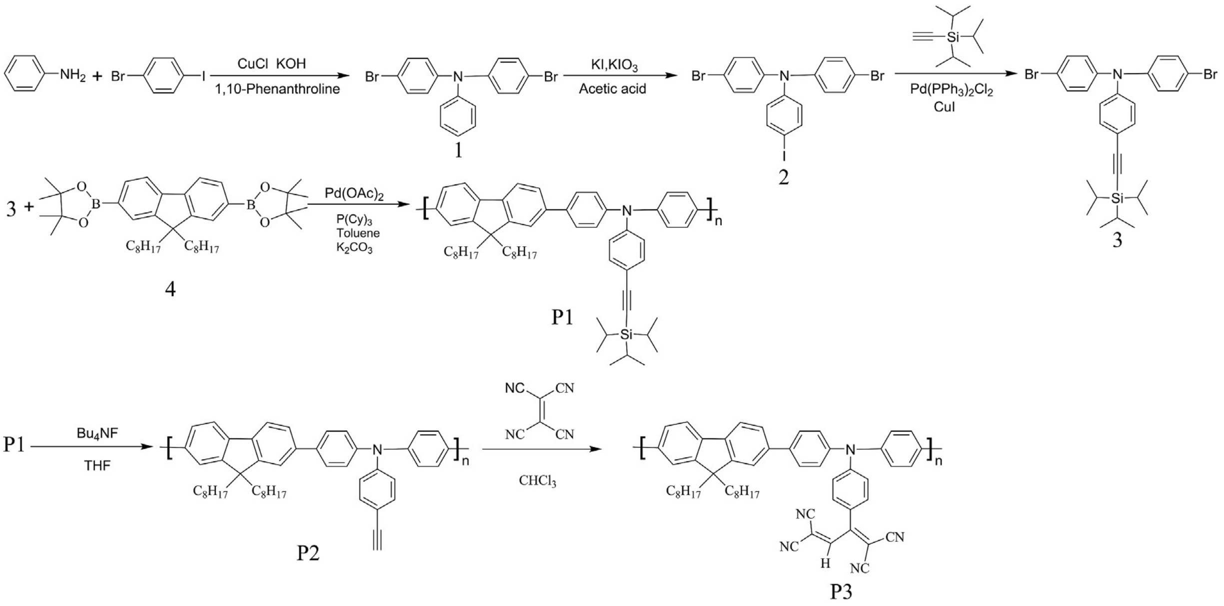
All reagents, unless otherwise specified, were purchased from Aldrich, Acros and TCI Chemical Co. and used without further purification. Tetrahydrofuran (THF) and toluene were distilled from sodium at the presence of benzophenone and degassed before use. *N, N*-bis(4-bromophenyl)-4-(triisopropylsilyl-alkynyl)aniline (**3**) was synthesized according to the method reported previously by our group [32]. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) was synthesized according to reported literature [33].

Solutions of F^-, Cl^-, SO_4^{2-}, HCO_3^-, SCN^-, $H_2PO_4^-$, CO_3^{2-}, NO_3^- and I^- were prepared from their sodium salts. Br^- and Ac^- were prepared from their potassium salts. Solutions of Ba^{2+}, Al^{3+}, Cu^{2+}, Co^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+} Pb^{2+}, Fe^{3+}, Cd^{2+}, Ag^+ and Ca^{2+} were prepared from their nitrate salts. Hg^{2+} was prepared from its acetate salt. Concentrations of above-mentioned solutions were controlled at 10^{-1} M in deionized water and were diluted subsequently to different concentration stocks for next use.

2.3. Synthesis

2.3.1. Synthesis of poly[(9,9-dioctyl)-2,7-fluorene-co-N-4-triisopropylsilyl-alkynyl-4,4′-triphenylamine] (**P1**)

N, N-bis(4-bromophenyl)-4-(triisopropylsilyl-alkynyl)aniline (**3**) (0.350 g, 0.60 mmol), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**4**) (0.360 g, 0.60 mmol) were added in toluene (16 mL) and 0.2 M potassium carbonate aqueous solution (3.0 mL). Under nitrogen, $Pd(OAc)_2$ (0.006 g, 0.026 mmol) and 3 drops of Aliquat 336 were placed. The above mixture was degassed for several times, tricyclohexyl phosphine (0.012 g, 0.042 mmol) was added afterward. The reaction mixture was refluxed for 3 days under nitrogen before it was cooled to room temperature. The crude product was reprecipitated into methanol (250 mL) and the formed precipitate was purified by flash column chromatography using toluene as eluant. The target polymer was obtained by reprecipitation in methanol and dried in vacuum at 50 °C overnight (0.400 g, 79%). FT-IR (KBr, cm^{-1}): 3033, 2925, 2860, 2150 (C≡C), 1597, 1504, 1486, 1381, 1315, 1285 (C–N), 1178, 1071, 883, 817, 668. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81–7.72 (m, 1.98H), 7.64–7.52 (m, 6.02H), 7.39–7.33 (m, 4.05H), 7.18–7.07 (m, 2.94H), 7.04–6.98 (m, 2.18H), 6.95–6.91 (m, 1.18H), 2.15–1.93 (m, 4.00H, fluorene $-CH_2-$), 1.19–1.09 (m, 45.28H, alkyl H), 0.85–0.78 (m, 6.06H, alkyl H). Gel permeation chromatography (GPC): $M_w = 11{,}822$, $M_n = 9173$, and $M_w/M_n = 1.29$.



Scheme 1. Synthesis of monomers and polymers.