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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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ABSTRACT

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 ^1H 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

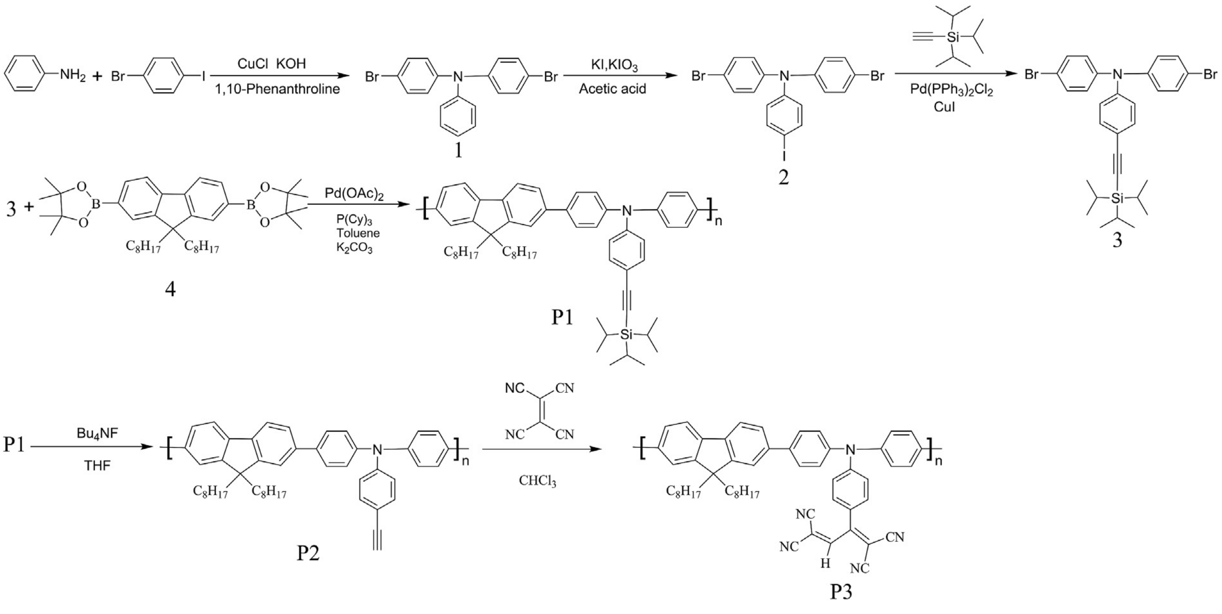
All reagents, unless otherwise specified, were purchased from Aldrich, Acros and TCI Chemical Co. and used without further purification. Tetrahydrofuran (THF) and toluene were distilled from sodium at the presence of benzophenone and degassed before use. *N, N*-bis(4-bromophenyl)-4-(triisopropylsilyl-alkynyl)aniline (**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.

*2.3.2. Synthesis of poly[(9,9-dioctyl)-2,7-fluorene-co-N-4-ethynyl-4,4′-triphenylamine] (**P2**)*

A solution of **P1** (0.211 g, 0.25 mmol) in anhydrous THF (10 mL) was vigorously stirred under nitrogen in a round-bottom flask and n-tetrabutylammoniumfluoride (n-Bu_4NF) (1 M in THF, 1.27 mL, 1.27 mmol) was added to this solution. The mixture was stirred at room temperature overnight. The crude product was purified by flash column chromatography, using toluene as an eluant, then concentrated and reprecipitated in methanol. The final product was obtained after vacuum drying at 50 °C overnight (0.190 g, 90%). FT-IR (KBr, cm^{-1}): 3293 (≡C–H), 3032, 2923, 2851, 2104 (C≡C), 1597, 1504, 1462, 1315, 1285 (C–N), 1267, 1176, 1071, 887, 815, 644. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.81–7.73 (m, 1.80H), 7.65–7.51 (m, 6.74H), 7.43–7.33 (m, 3.87H), 7.18–7.12 (m, 1.96H), 7.06–7.00 (m, 2.11H), 6.98–6.88 (m, 0.98H), 3.10–3.00 (m, ≡C–H, 1.07H), 2.12–1.87 (m, 4.00H, fluorene –CH_2–), 1.22–0.98 (m, 24.35H, alkyl H), 0.80–0.74 (m, 5.86H, alkyl H).

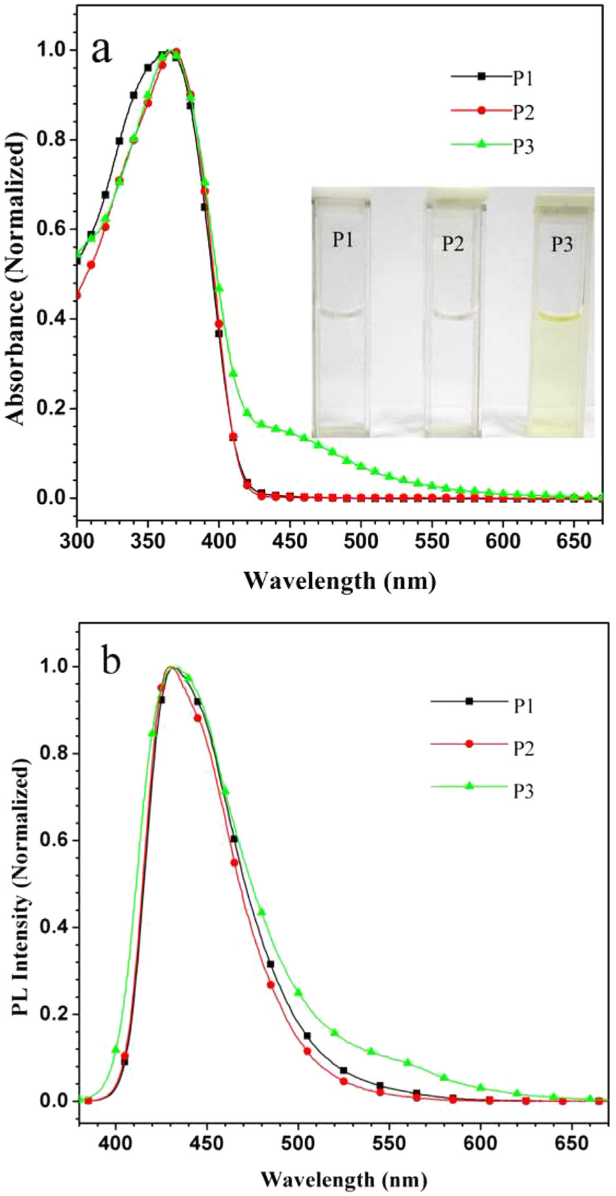


Fig. 1. Normalized UV–*vis* (**a**) and PL spectra (**b**) of **P1**, **P2** and **P3** in THF (~1.0×10^{-5} M) (inset in (a) is the visual photograph of polymers solutions).

*2.3.3. Synthesis of poly[(9,9-dioctyl)-2,7-fluorene-co-N-4-(1,1,4,4-tetracyanobuta-1,3-dienyl)-4,4′-triphenylamine] (**P3**)*

TCNE (4.5 mg, 0.035 mmol) was added to a solution of **P2** (24.0 mg, 0.035 mmol) in $CHCl_3$ (5.0 mL). After stirring at room temperature for 1 h under nitrogen, the solvent was vacuum-evaporated to yield the desired product as brown-black solid (27.9 mg, 98%). FT-IR (KBr, cm^{-1}): 3032, 2922, 2850, 2220 (C≡N), 1590, 1486, 1321, 1285 (C–N), 1267, 1182, 1070, 887, 814, 620. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09–8.00 (m, 1.08H), 7.84–7.64 (m, 4.92H), 7.63–7.45 (m, 5.26H), 7.45–7.31 (m, 4.15H), 7.18–7.10 (m, 2.07H), 7.08–6.98 (m, 0.96H), 6.89–6.71 (m, 0.64H), 2.19–1.84 (m, 4.00H, fluorene –CH_2–), 1.31–0.95 (m, 24.14H, alkyl H), 0.81–0.74 (m, 6.22H, alkyl H).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route of intermediates and target polymer is shown in Scheme 1. **P1** was successfully obtained *via* Suzuki coupling reaction and deprotected by the disilylation of n-Bu_4NF in THF at room temperature to afford acetylene-pendent substituted polymer, **P2**, with high yield (90%). The target polymer, **P3**, was synthesized by using **P2** and TCNE as starting materials *via* atom-economic click postfunctionalization at room temperature without the involvement of any catalyst and demonstrated excellent yield (98%). The number-average molecular weight of **P1** was measured by means of gel permeation chromatography (GPC) analysis using THF as eluant against polystyrene standards, to be 9173 and with the polydispersity of 1.29. Considering that the backbone of **P1** should not be affected by subsequent disilylation and click reaction, the molecular weight of **P2** and **P3** should be close to that of **P1**.

The chemical structures of **P1**, **P2** and **P3** were verified by FT-IR and ^1H NMR analyses. As shown in Fig. S1, notable difference appears in FT-IR spectra between **P1** and **P2**, i.e., in the spectrum of **P2**, absorption signal intensity at ~2104 cm^{-1} (corresponds to the C≡C stretching vibration) weakened significantly as compared to that of **P1** (at ~2150 cm^{-1}), and a new band at ~3293 cm^{-1} appears, which can be assigned to the typical stretching absorption signal of ≡C–H [34,35]. This indicates that the disilylation of triisopropylsilyl (TIPS) groups successfully occurred. The ≡C–H stretching vibration signal fades significantly in the spectrum of **P3**, and there is a new absorption signal appears at ~2220 cm^{-1}, which

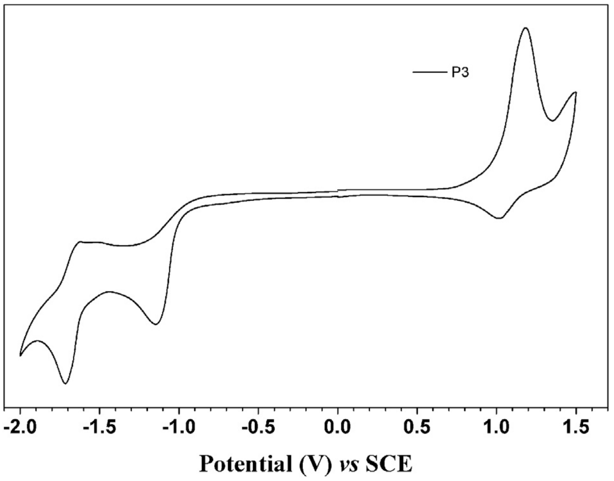


Fig. 2. Cyclic voltammogram of **P3** in CH_3CN with 0.1 M n-Bu_4NPF_6 at room temperature.

corresponds to the C≡N stretching vibration of the cyano groups in **P3** [27].

^{1}H NMR spectra of polymers are shown in Fig. S2. ^{1}H NMR spectra of **P1** and **P2** are similar to each other as a whole, except that a proton signal at ~δ 3.08 ppm appears exclusively in the spectrum of **P2**, which corresponds to the signal of deprotected acetylene (≡C–H) groups [34,35]. This result is consistent with the finding in FT-IR analysis, by which one can conclude that the desilylation reaction happened successfully. From spectrum of **P3** one can find that the proton signal at ~δ 3.08 ppm almost vanishes. Meanwhile, a new proton signal emerges at ~δ 8.04 ppm in the spectrum of **P3** but not present in the spectra of **P1** and **P2**, which corresponds to the characteristic signal of olefin–hydrogen in 1,1,4,4-tetracyanobuta-1,3-dienyl [31]. FT-IR and ^{1}H NMR analyses strongly support that **P3** has been successfully synthesized by click reaction between **P2** and TCNE.

3.2. *Optical properties*

Optical properties of three polymers were investigated in THF (with the concentration of ~1×10^{-5} M) by ultraviolet–visible (UV–*vis*) absorption and fluorescence spectrometry. Fig. 1a displays the UV–*vis* spectra of these polymers in normalization. From Fig. 1a one can find that the absorption maxima of these three polymers locate at ~365 nm, which stem from the π–π* transition along polymer backbones. Different from other polymers, a new absorption band between 400 and 600 nm appears exclusively in the spectrum of **P3**, which might be due to the interaction between the electron-withdrawing 1,1,4,4-tetracyanobuta-1,3-dienyl pendent and electron-donating triphenylamine moiety in polymer backbone [27]. Solutions of **P1** and **P2** are close to colorless, and the apparent color of **P3** is pale brown (seen from the inset in Fig. 1a). Fig. 1b displays corresponding emission spectra of polymers in THF solution. Spectra of **P1**, **P2** and **P3** are similar to each other and display emission maxima at ~431 nm.

3.3. *Electrochemical properties*

Electrochemical redox properties of **P1**, **P2** and **P3** have been investigated *via* cyclic voltammogram (CV) using n-tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$, 0.1 M) as supporting electrolyte in acetonitrile at room temperature to reveal

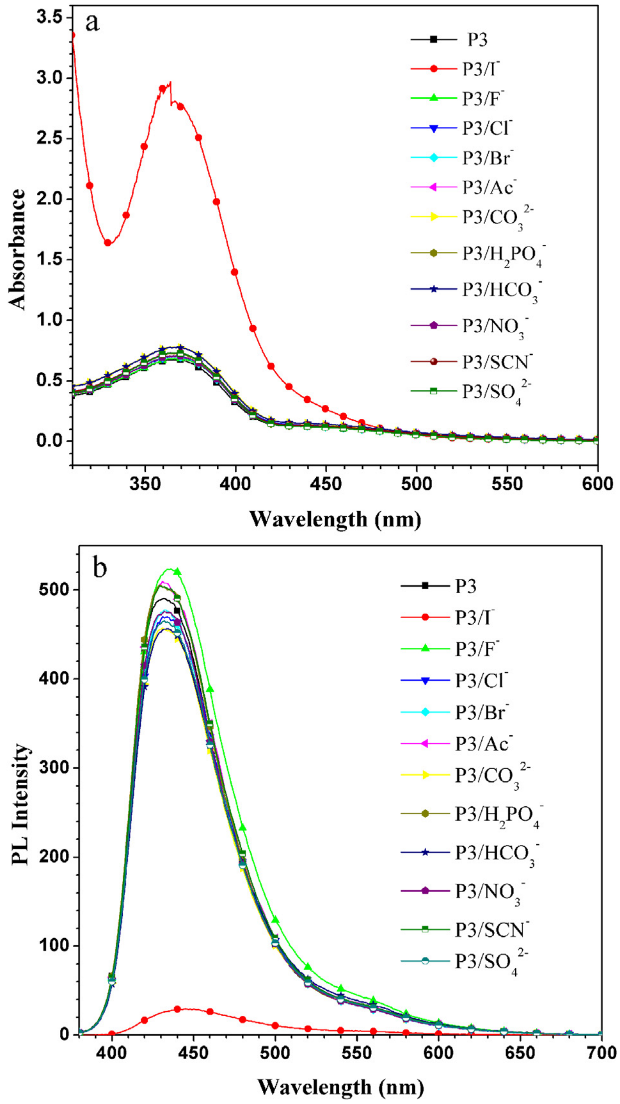


Fig. 3. The UV–*vis* absorption (**a**) and fluorescence response (**b**) of **P3** (with the concentration of 1.0×10^{-5} M) in the presence of common anions (with concentration of 3.5×10^{-4} M for each ion).

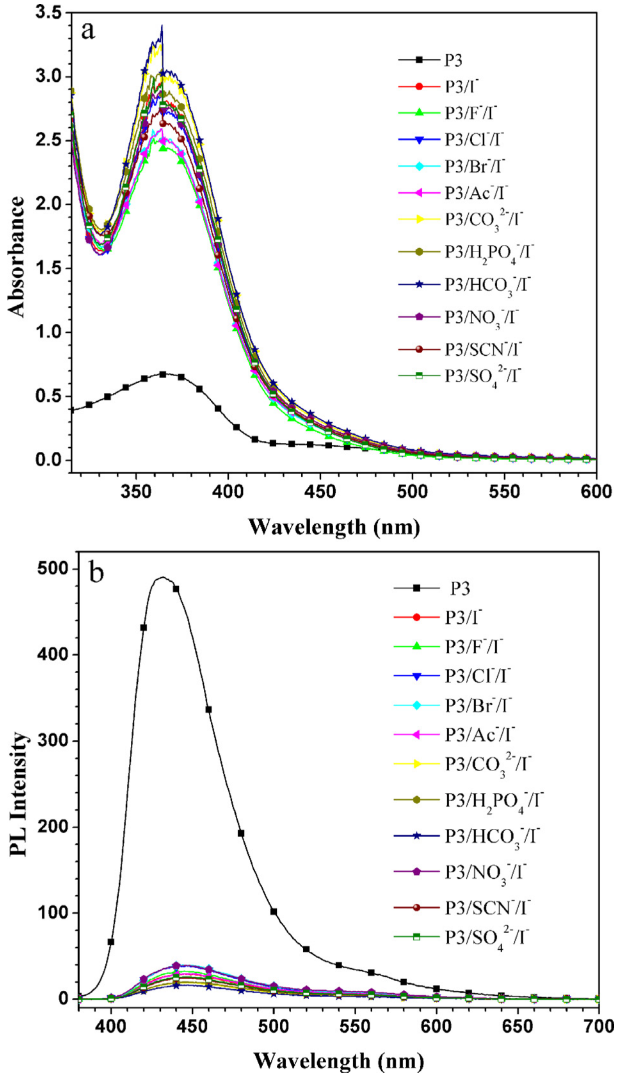


Fig. 4. UV–*vis* absorption (**a**) and fluorescence (**b**) alteration of **P3** in THF (with concentration of ~1.0×10^{-5} M) in the presence of various background anions and with sequential addition of I$^-$ (with concentration of ~3.5×10^{-4} M).

the redox activities of the polymers and estimate their energy levels. For **P1** and **P2**, we just obtained their oxidation curves and the corresponding reduction process was not recorded after several trials. The oxidation onset potentials (E_{oxonset}) of **P1** and **P2** appear at ~1.10 V and 1.06 V (Fig. S3), respectively, and the corresponding the highest occupied molecular orbital (HOMO) levels are ~−5.50 and ~−5.46 eV, respectively, according to an empirical formula, $E_{\text{HOMO}} = -e(E_{\text{oxonset}} + 4.4)$ (eV) [36]. In contrast, the TCNE adducted polymer **P3** exhibits both anodic and cathodic profiles under the same measurement condition (Fig. 2), which might be ascribed to the coexistence of triphenylamine donor and tetracyanobuta-1,3-dienyl acceptor moieties. The E_{oxonset} of **P3** appears at ~0.90 V, which is lower than that of **P1** and **P2**. This is consistent with previous report that donor–acceptor type CPs generally possess narrower band gaps with an elevated HOMO level and a lowered the lowest occupied molecular orbital (LUMO) level, as compared to the neutral or donor-type polymers [28]. During the cathodic scanning, there are two-step reduction processes of **P3** and with the first reduction onset potential (E_{redonset}) at ~−1.02 V. The HOMO level of **P3** is ~−5.30 eV and the LUMO level of **P3** can be calculated according to $E_{\text{LUMO}} = -e(E_{\text{reonset}} + 4.4)$ (eV), to be ~−3.38 eV [36]. The corresponding bandgap of **P3** can be obtained by the subtraction of its HOMO and LUMO levels, to be ~1.92 eV.

3.4. *Optical response of **P3** toward I*$^-$

According to previous investigation, carbazole or triphenylamine-based conjugated systems can be applied as sensitive and selective I^- optical probe [22,23,37,38]. Spectral response of **P3** (with the concentration of ~1.0×10^{-5} M in THF) toward I^- was thus investigated. Various anionic ions were introduced into solution of **P3**, and corresponding UV–*vis* spectra are illustrated in Fig. 3a. From Fig. 3a one can note that the distinct enhancement in absorbance was detected exclusively with the addition of I^-, and other anions just brought slight influence. Fig. 3b exhibits fluorescence spectra of **P3** toward various anions. In consistent with our previous results about triphenylamine or carbazole-containing CPs [22,23], the addition of I^- led to tremendous fluorescence quenching while other anions brought inconspicuous influence toward fluorescence intensity of **P3**.

Fig. S4 displays detailed fluorescent response of **P3** toward I^-. Upon addition of increasing amount of I^-, fluorescence intensity of **P3** decreased gradually, accompanied by the alteration of its apparent color (Fig. S5). The detection limit of I^- by **P3** reaches ~9.7×10^{-8} M (according to 3σ rule) [39] as is reflected by its PL spectra (Fig. S4). The mechanism of fluorescence quenching in this case might *via* "heavy-atom" effect [22,23,37,38]. Here, the "heavy-atom" interaction exists between the excited state of triphenylamine-containing polymer and I^-, which lead to an enhancement of the spin-orbit coupling [22,23,37,38].

To evaluate the selectivity of **P3** toward I^-, competition experiments were carried out. As is shown in Fig. 4, the background anions brought slight influence for **P3**'s optical response toward I^-. It suggests that this polymer possess excellent selectivity and anti-interference toward I^-.

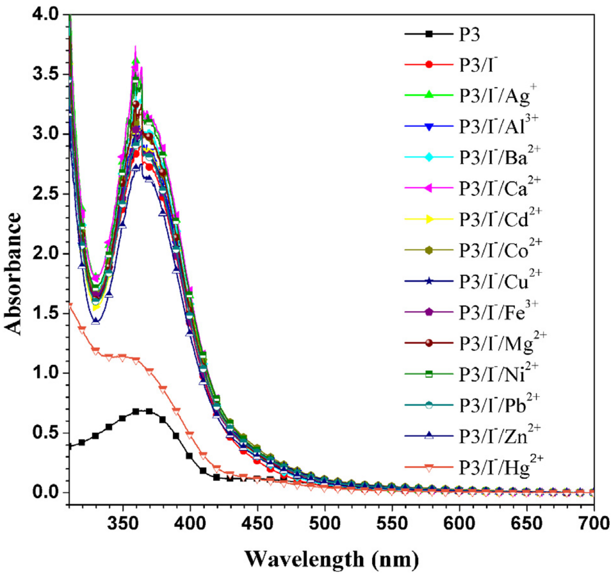


Fig. 5. UV–*vis* absorption changes of **P3**/I^- in THF (concentrations of **P3** and I^- were 1.0×10^{-5} and 3.5×10^{-4} M, respectively) in the presence of various metal ions (~7.5×10^{-5} M).

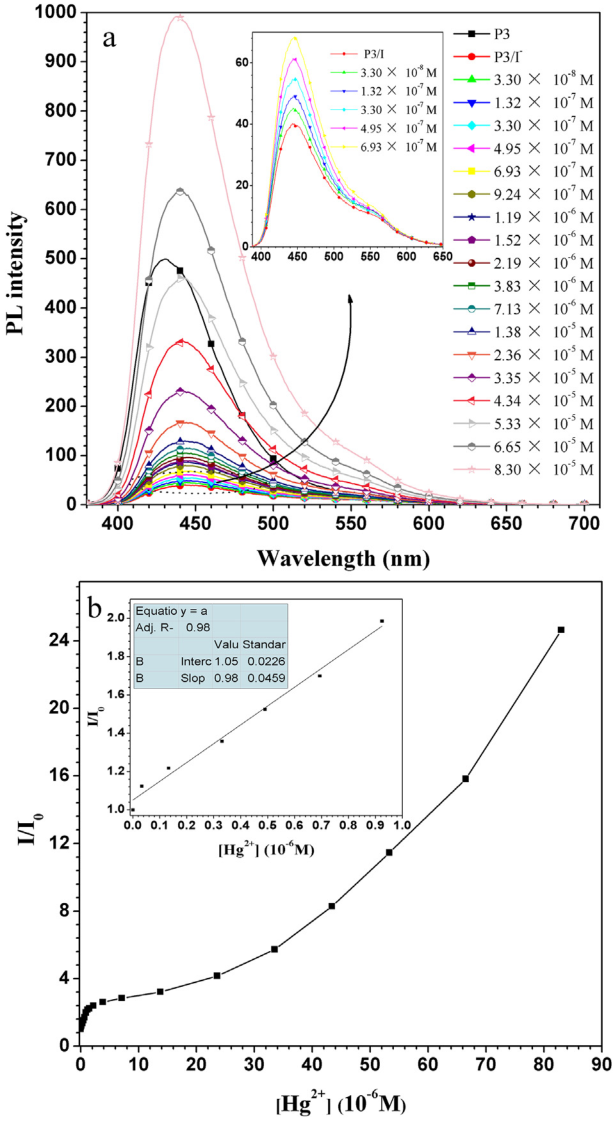


Fig. 6. Fluorescence intensity changes of **P3**/I^- in THF (concentrations of **P3** and I^- were 1.0×10^{-5} and 3.5×10^{-4} M, respectively) in the presence of incremental Hg^{2+} (**a**) (inset is the enlarged region of spectrum with low concentration of Hg^{2+}) and relationship between I/I_0 and Hg^{2+} (**b**) (inset is the fitting curve with concentration of Hg^{2+} lower than 9.24×10^{-7} M).

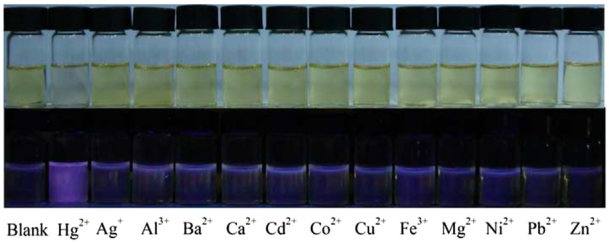


Fig. 7. Photograph of **P3**/I^- in THF (concentrations of **P3** and I^- were 1.0×10^{-5} and 3.5×10^{-4} M, respectively) under natural light (**upper**) and ultraviolet light (365 nm) (**bottom**) with the addition of various metal ions ($\sim 7.5 \times 10^{-5}$ M).

3.5. *Optical response of **P3**/I^- complex toward Hg^{2+}*

We further find that the quenched fluorescence of **P3**/I^- complex restored in the presence of Hg^{2+}. In order to confirm whether **P3**/I^- complex can be used as a selective, sensitive and anti-interferential optical Hg^{2+} probe, the corresponding investigation was carried out.

As can be seen from Fig. 5, with the addition of Hg^{2+}, obvious decrease of **P3**/I^- complex's absorption at $\sim$365 nm takes place, while the curves with other metal ions altered slightly as compared to that of Hg^{2+}. Similar recovery trend can be observed in the investigation of **P3**/I^-'s fluorescence within the Hg^{2+} titration process (Fig. 6). As can be seen from Fig. 6, with the incremental addition of Hg^{2+}, fluorescence intensity of **P3**/I^- increased gradually, accompanied by the alteration of its apparent color (turned back to slight brown, Fig. 7), suggesting the distraction of I^- from **P3**/I^- complex due to the stronger association between I^- and Hg^{2+} [22,23,40]. The heavy atom effect brought by I^- is thus removed and the fluorescence recovered accordingly [22,23]. It is interesting to find that the fluorescence of **P3**/I^-/Hg^{2+} system has restored even higher than **P3**'s initial intense when the concentration of Hg^{2+} reaches $\sim 6.65 \times 10^{-5}$ M, and further remarkable enhancement of the fluorescence of this system can be detected with more Hg^{2+} ($\sim 8.30 \times 10^{-5}$ M) (Fig. 6). Detection limit of Hg^{2+} reaches $\sim$6.9 nM (according to 3σ rule) [39] by this probing system. This value is superior to our recent reports regarding triphenylamine or carbazole-derivated CPs without the TCNE adduct (has improved by two orders of magnitude) [22,23], and is comparable or little better than reported CPs-based turn-on type Hg^{2+} probes [21,41,42].

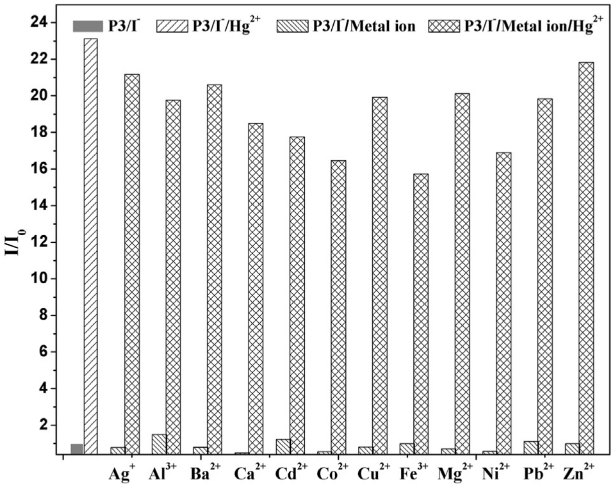


Fig. 8. Fluorescence alterations of **P3**/I^- in THF (concentrations of **P3** and I^- were 1.0×10^{-5} and 3.5×10^{-4} M, respectively) in the presence of various background metal ions (with concentration of 7.5×10^{-5} M for each ion) and with sequential addition of Hg^{2+} (7.5×10^{-5} M).

In order to propose the possible reason for such impressive fluorescence enhancement of **P3**/I^- toward Hg^{2+}, the corresponding control experiments were carried out to use **P1**/I^- and **P2**/I^- as probing substrates. From Fig. S6, with the addition of I^-, one can also find the obvious fluorescence quenching for both **P1** and **P2** solutions. This result is reasonable due to the presence of triphenylamine segment in these two polymers [22]. With the following addition of Hg^{2+} (1.5×10^{-4} M), fluorescence of **P1** and **P2**-involved systems recovered to $\sim$90% and 81% of their initial values, and the fluorescence intensity of both systems altered slightly with the further addition of Hg^{2+}.

Interestingly, **P3**/I^- displays different performance from **P1** and **P2**. When the concentration of Hg^{2+} reaches $\sim 6.65 \times 10^{-5}$ M, the fluorescence intensity of **P3**/I^- system has exceeded the corresponding value of pristine **P3** (Fig. S6c). When the concentration of Hg^{2+} came up to $\sim 8.30 \times 10^{-5}$ M, the fluorescence intensity of **P3**/I^-/Hg^{2+} system even as high as two folds of the initial value of **P3** (Fig. S6c) (the fluorescence with more Hg^{2+} could not be recorded due to the corresponding value has surpassed the equipment's measurement range with the fixed slit width). Given the same maintain structures of these three polymers, such difference in their fluorescence recovery might be attributed to their different tethered substituents.

To get more insight about such speculation, the fluorescence response of bare **P3** toward Hg^{2+} was investigated and the result is shown in Fig. S7. As shown in Fig. S7, the fluorescence of **P3** decreased monotonously with the addition of Hg^{2+} (which might be due to the interaction between Hg^{2+} and dicyano-linked carbon atoms in pendent TCNE) [24]. As combined with the fact that the fluorescence of **P3** also has been quenched monotonously by I^- (Fig. S4), one can deduce that the further fluorescence enhancement of **P3**/I^- with Hg^{2+}'s concentration above $\sim 6.65 \times 10^{-5}$ M is not stem from the presence of isolated Hg^{2+} or I^- (not participate into the mutual association). Such results indicate that the extraordinary fluorescence enhancement of **P3**/I^- is stem from the synergic effect of I^- abstraction (by the strong association between Hg^{2+} and I^-) and the further interaction between Hg^{2+}/I^- complex with the pendent TCNE, although the exact mechanism is not clear at this stage.

To evaluate the selectivity of **P3**/I^- toward Hg^{2+}, responses of a number of common metal ions (Ag^+, Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}) were investigated in competition experiments. Fig. 8 illustrates the interference of these metal ions for **P3** against Hg^{2+}. From it we can find that the addition of Hg^{2+} brought considerable fluorescence enhancement with the existence of background cations, and all of background metal ions just brought tiny influence for the detection of Hg^{2+}. Considering that these spectra were recorded in a short time interval without long-time standing at room temperature (20 s later with the addition of each ion) and its anti-interference and sensitivity, **P3** might be act as a promising immediacy turn-on optical probe for Hg^{2+}.

4. Conclusion

A TCNE-decorated triphenylamine-based conjugated polymer, **P3**, was successfully prepared *via* efficient click postfunctional addition reaction between alkynes in side chain of **P2** and TCNE. Due to the presence of triphenylamine segment in polymer backbone, **P3** can be utilized as efficient turn-off fluorescence probe for I^- by "heavy-atom" mechanism. We further find that the probing performance for **P3**/I^- complex to realize turn-on detection of Hg^{2+} is modified with the introduction of electron-withdrawing, cyano-containing TCNE adduct. Results support that **P3**/I^- complex can act as potential anti-interferential, selective and sensitive Hg^{2+} optical probe.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.12.016.

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