



# Benzylidenecyclohexanone-triazole-based conjugated polymer: Click synthesis, Staudinger end-capping and application as optical probe scaffold



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## ARTICLE INFO

### Article history:

Received 29 April 2016

Received in revised form

15 June 2016

Accepted 18 June 2016

Available online 18 June 2016

### Keywords:

Conjugated polymer

Benzylidenecyclohexanone

Phosphinimine

Optical probe

Ratiometric

## ABSTRACT

A type of benzylidenecyclohexanone-triazole based conjugated polymer (**P5**) was successfully synthesized by Cu<sup>+</sup>-catalyzed Click reaction. The THF solution of **P5** exhibited specific optical response (increase in absorption and decrease in fluorescence) toward I<sup>-</sup>. With the further addition of Hg<sup>2+</sup> into the assembly of **P5**-I<sup>-</sup>, distinctive recovery of optical properties was detected, suggests that **P5**-I<sup>-</sup> adduct can act as fluorescence turn-on probing platform for Hg<sup>2+</sup>. Post-polymerization of **P5** was implemented by catalyst-free Staudinger reaction between **P5** and triphenylphosphine to afford phosphinimine-endcapped polymer (**P5**-TPP). Different from the blue-greenish emission (~490 nm) of **P5**, **P5**-TPP emitted yellow light (~550 nm) in THF-water mixture (V<sub>THF</sub>/V<sub>water</sub> = 2/8). **P5**-TPP displayed specific fluorescence ratiometric alteration toward hypochlorite ion in THF-water mixture (V<sub>THF</sub>/V<sub>water</sub> = 2/8, pH = 7.4), which might be due to the hypochlorite-induced hydrolysis of phosphinimine energy-transfer acceptors in **P5**-TPP. The results suggest that **P5** can act as structure scaffold for the construction of optical probe for triple analytes (I<sup>-</sup>, Hg<sup>2+</sup> and ClO<sup>-</sup>).

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## 1. Introduction

Thanks to high selectivity, good sensitivity, low toxicity, and the specific signal-amplification characteristic, conjugated polymer (CP)-based optical probes have attracted great attention in recent years [1–4]. In spite of the great advance achieved about the single-analyte-targeting CPs probes, the design and preparation of CPs-based scaffolds for multiple-analytes detection purpose is still a desirable and challenging task and have been limitedly reported so far [5,6].

In recent reports by our lab and others, a series of aromatic nitrogen-atom-containing agents (triphenylamine [7,8], carbazole [9–13] and thiazole [14,15], etc.) derivativated oligomer and CPs displayed specific optical response toward I<sup>-</sup> among various anions. The so-called ‘heavy-atom effect’ [16,17] of I<sup>-</sup> was activated by the

weak and transient interaction between I<sup>-</sup> and N-atoms, which is the plausible reason for the optical alteration (enhancement in absorption and decrease in fluorescence) of these probes. With the further introduction of strong I<sup>-</sup>-binding agent, the Hg<sup>2+</sup>, quenched fluorescence of these probes recovered accordingly due to the broken of I<sup>-</sup>-N interaction [7–10,13–15]. These reports represent the successful example of consecutive detection of I<sup>-</sup> and Hg<sup>2+</sup> by single organic detection scaffolds thus.

Besides the above-mentioned interaction between I<sup>-</sup>-N, the presence of specific interaction between the C–H site on triazole ring and I<sup>-</sup> has been proven by recent literature [13,18,19]. Along with this line, Wang et al. have made attempt to introduce triazole groups into carbazole-based CP to modify the interrelation between resultant polymer and I<sup>-</sup> by the coexistence of I<sup>-</sup>-N and CH...I<sup>-</sup> interaction [13]. Inspired by these findings, our research interest has been aroused to explore that if the interaction between triazole-I<sup>-</sup> alone is sufficient enough to render the alteration of optical properties of CP, which with no triphenylamine, carbazole or thiazole segments in its structure. As well documented, triazole can be facily introduced into CPs by high-efficiency, practical-

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simple Click reaction [20–24]; this provides the convenience for the preparation of triazole-containing CPs from the synthetic viewpoint.

According to previous reports, benzylidenecyclohexanone could act as bridge for the construction of conjugated scaffolds [25,26]. In our recent research, we reported a type of yellow fluorescent phosphinimine derivative based on benzylidenecyclohexanone, 2,6-bis(4-triphenylphosphiniminebenzylidene)-4-methyl-cyclohexanone (**M1**) [27]. Results illustrated that the phosphinimine (P=N) segments in the structure of **M1** participated in the whole electron delocalization system [27–29]. On the other hand, previous literature reported that like phosphorus ylides, phosphinimines could also react with carbonyl compounds to afford a novel method (nitrogen analogue Wittig reaction) for the construction of C=N double bonds [30–34]. The oxygen atoms were abstracted from carbonyl compounds and directly linked to phosphine to form phosphine oxide (P=O) derivatives [30–34], and the P=N linkage of phosphinimine was broken accordingly. Besides this, some phosphinimines could be hydrolyzed to yield corresponding amines and phosphine oxide (Staudinger reaction) [35–38]. These findings imply that phosphinimines might be susceptible to oxidative environment. To the best of our knowledge, the optical responding behaviors of fluorescent phosphinimines toward oxidation agents have not been reported by now.

Herein, we select a type of commercialized diazido-containing aromatic derivative, 2,6-bis(4-azido-benzylidene-yl)-4-methylcyclohexanone as starting material, to synthesize a type of benzylidenecyclohexanone-triazole-based CP (**P5**) by Cu<sup>+</sup>-catalyzed Click reaction. The azido (–N<sub>3</sub>) residuals at the chain ends of **P5** were further end-capped by triphenylphosphine via catalyst-free Staudinger reaction under mild condition to afford novel phosphinimine-containing CP (**P5-TPP**). Further optical investigation illustrates that **P5** displayed specific optical response to I<sup>–</sup> in THF, and the optical alteration trend could be reversed by the further introduction of Hg<sup>2+</sup> into the assembly of **P5-I<sup>–</sup>**. Besides this, different from the green-bluish emission of **P5** (~490 nm), **P5-TPP** emitted yellow light (~550 nm) in aqueous media with relative high-water-fraction ( $V_{\text{THF}}/V_{\text{water}} = 2/8$ , pH = 7.4). We further found that **P5-TPP** can act as ratiometric fluorescence probe for hypochlorite (ClO<sup>–</sup>) in aforementioned aqueous medium.

## 2. Experimental section

### 2.1. Materials and apparatus

Tetrahydrofuran (THF) and toluene were distilled from sodium at the presence of benzophenone and degassed before use. Other materials used for synthesis were obtained from Adamas-beta Chemical Co. and used without further purification. Aqueous solutions of metal ions, with the exception of Hg(OAc)<sub>2</sub>, were prepared from their nitrate salts. Hydroxyl radical ( $\cdot\text{OH}$ ) was generated by Fenton reaction on mixing Fe(SO<sub>4</sub>)<sub>2</sub> with 10 equiv. of H<sub>2</sub>O<sub>2</sub>; the concentration of  $\cdot\text{OH}$  was estimated from the concentration of Fe<sup>2+</sup>. Singlet oxygen ( $[^1\text{O}_2]$ ) was generated by the addition of NaClO and H<sub>2</sub>O<sub>2</sub> [39]. *tert*-Butyl peroxy radical (TBO $\cdot$ ) was generated in situ by addition of ferrous sulfate in the presence of 20 equiv. of *tert*-Butyl hydroperoxide (TBHP). Concentrations of H<sub>2</sub>O<sub>2</sub> and NaClO were determined by measuring their UV absorbance immediately before use. [O<sub>2</sub><sup>–</sup>], [NO] and [ONOO<sup>–</sup>] were prepared by the reported methods [40].

IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets. <sup>1</sup>H NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating at 400 MHz in deuterated chloroform solution with tetramethylsilane as reference. UV–visible absorption spectra were recorded on a SHIMADZU UV-2450

UV–vis spectrophotometer. PL spectra were recorded on SHIMADZU RF-5301-PC spectrophotometer.

### 2.2. Synthesis

Synthetic route of target polymers is outlined in Scheme 1. 2,6-bis(4-triphenylphosphiniminebenzylidene)-4-methyl-cyclohexanone (**M1**) [27] and 1,4-bis-dodecyloxy-2,5-diethynyl-benzene (**5**) were synthesized with the method reported by our group [34].

#### 2.2.1. Synthesis of Poly[(2,5-bis-dodecyloxy-phenyl)-(4-methyl-2,6-bis-(4-[1,2,3]triazol-1-yl-benzylidene)-cyclohexanone)] (**P5**)

1,4-bis-dodecyloxy-2,5-diethynyl-benzene (**5**, 247.4 mg, 0.5 mmol), 2,6-bis(4-azido benzylidene-yl)-4-methylcyclohexanone (**6**, 203.7 mg, 0.55 mmol), CuBr (7.2 mg, 0.05 mmol) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDTA, 17.3 mg, 0.10 mmol) were dissolved in 20 mL of dry toluene. The mixture was degassed with nitrogen and reacted under room temperature for 3 days. The crude product was concentrated under reduced pressure, and then precipitated into methanol. The formed precipitate was purified by flash column chromatography using toluene as eluent. The target polymer was obtained by reprecipitation in methanol and dried in vacuum at 45 °C for 24 h as yellow powder (238.1 mg). Yield: 57%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.69–8.52 (m, triazole H), 8.13–8.00 (m), 7.86–7.50 (m), 7.09–6.91 (m), 4.29–3.97 (m, –OCH<sub>2</sub>–), 3.10 (m), 2.57 (m), 1.87 (m), 1.21–0.74 (m, alkyl H).

#### 2.2.2. Synthesis of **P5-TPP**

Poly[(2,5-bis-dodecyloxy-phenyl)-(4-methyl-2,6-bis-(4-[1,2,3]triazol-1-yl-benzylidene)-cyclohexanone)] (**P5**) (100 mg) and triphenylphosphine (131.1 mg, 0.5 mmol) were added in Schlenk tube. After purged with nitrogen, THF (10 mL) was injected subsequently. The mixture was reacted under 60 °C for 24 h. After being cooled to room temperature, the solvent was removed under reduced pressure. The crude product was precipitated into methanol to get the target polymer (**P5-TPP**) (65.3 mg). Yield: ~65%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.63–8.59 (m, triazole H), 8.13–8.01 (m), 7.91–7.47 (m), 7.16–6.93 (m), 4.34–3.82 (m, –OCH<sub>2</sub>–), 3.11 (m), 2.57 (m), 1.86 (m), 1.20–0.76 (m, alkyl H).

### 2.3. Comparison experiment

Benzylidenecyclohexanone and phosphinimine containing small molecule, 2,6-bis(4-triphenylphosphiniminebenzylidene)-4-methyl-cyclohexanone (**M1**) was selected as the control agent to explain the recognition mechanism of **P5-TPP** to ClO<sup>–</sup>. The mixture of THF (4 mL) and buffer solution (Phosphate Buffer (PB), 0.005 M, pH = 7.4, 16 mL) was prepared in a two necked flask. Under the protection of N<sub>2</sub>, **M1** (167.8 mg, 0.2 mmol) and 0.5 mL of NaClO aqueous solution (1.0 M) were added into the flask respectively. The reaction was carried out at room temperature for 1 h. The mixture was extracted by dichloromethane and washed by deionized water for 3 times to get rid of the inorganic salt. The product (**M1-OX**) was obtained by removing the solvent.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The synthetic route of relevant polymers is outlined in Scheme 1. Cu<sup>+</sup>-catalyzed Click reaction between 1,4-bis-dodecyloxy-2,5-diethynyl-benzene (**5**) and commercial-available diazido-containing compound, 2,6-bis(4-azido benzylidene-yl)-4-methylcyclohexanone (**6**) was carried out to afford target

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