



A type of novel fluorescent phosphinimine derivative: Catalyst-free simple synthesis and optical properties



Linxian Xu, Fan Yue, Wei Shi*, Yonghai Hui, Hongyu Mi, Fudong Ma, Yong Tian, Zhengfeng Xie*

Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education, College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi 830046, Xinjiang, PR China

ARTICLE INFO

Article history:

Received 3 June 2013

Received in revised form

2 July 2013

Accepted 11 July 2013

Available online 20 July 2013

Keywords:

Staudinger reaction

Catalyst-free synthesis

Phosphinimine

Benzylidene cyclohexanone

Fluorescent indicator

pH sensitive

ABSTRACT

A type of fluorescent benzylidene cyclohexanone-containing phosphinimine derivative, 2,6-bis(4-triphenylphosphiniminebenzylidene)-4-methyl-cyclohexanone, has been synthesized by catalyst-free Staudinger reaction. Chemical structure of this compound was verified by Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance and Electrospray Ionization analyses. Optical properties of this compound in different solvents were investigated by Ultraviolet–visible spectroscopy and fluorescence analyses. Pale-yellow color of the dimethyl sulfoxide solution of this compound subsequently took off with the presence of incremental H^+ , accompanied by the quenching of its fluorescence. Furthermore, the color and fluorescence of this compound recovered gradually when H^+ in the solution being neutralized, indicating that it could be applied as reversible optical pH indicator.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Phosphinimines are important intermediates of Staudinger reaction [1–6] (the reaction between azides and phosphines), and were widely used in organic synthesis [7–10], polymer preparation [11–14], coordination chemistry [8,15–22], etc. Recently, a type of phosphinimine-bridged Donor-Acceptor type polymer was successfully prepared with high molecular weight by employing diphosphane and diazido-substituted ferrocene and 11,11,12,12-tetracyanoanthraquinomethane derivatives as copolymerization monomers under mild reaction condition [23]. The P=N bond in backbone of this polymer has been proven to be a good bridge for intramolecular charge transfer [23]. Thanks to the high efficiency and no requirement for any catalyst in Staudinger reaction, the contamination of obtained polymer by residual catalyst can be readily overcome. This report presents a new approach for the synthesis of novel conjugated compound with interesting properties and without the involvement of catalyst.

For phosphinimines, there are lone pair electrons on the nitrogen atoms (involved in the P=N bonds) and they will be protonated

in acidic environment [8,18,24–26]. This implies that phosphinimine derivatives have the potential to act as effective pH indicators if they are integrated with some easily-detectable signals, such as UV–vis absorption and fluorescence properties. To the best of our knowledge, most of reported phosphinimine derivatives are nonfluorescent and their application as optical probe was scarcely investigated [27].

On the basis of these studies, in this effort we select a commercial conjugated bridge component, benzylidene cyclohexanone [28,29] to act as reaction primitive to obtain a type of fluorescent phosphinimine derivative (**M1**) by non-catalyst Staudinger synthesis. We find that **M1** can act as an optical pH indicator with fluorescence quenching and color change in acidic environment. In addition, protonated **M1** (**M1-H⁺**) can be reverted to its pristine state by adjusting the pH value.

2. Experimental section

2.1. Materials and apparatus

Toluene was distilled from sodium at the presence of benzophenone. Other materials used for synthesis were obtained from commercial suppliers and used without further purification. HNO_3 aqueous solution was used to act as protonation agent. Aqueous solutions of metal ions, with the exception of $HgAc_2$, were prepared

* Corresponding authors. Tel.: +86 0991 8583575; fax: +86 0991 8582809.

E-mail addresses: xjuwshi@gmail.com, shiwei@xju.edu.cn (W. Shi), xiezhf72@gmail.com (Z. Xie).

from their nitrate salts. Flash chromatography was carried out on silica gel.

IR spectra were recorded on an EQUINOX 55 FT-IR spectrometer with KBr pellets. ^1H NMR and ^{13}C NMR spectra were collected on a VARIAN INOVA-400 spectrometer operating respectively at 400 MHz (for ^1H) and 100 MHz (for ^{13}C) in deuterated chloroform solution with tetramethylsilane as reference. ESI mass analyses were operated on an HP1100 LC/MSD. UV–visible absorption spectra were recorded on an SHIMADZU UV-2450 UV–vis spectrophotometer. PL spectra were recorded on HITACHIF-4500 spectrophotometer. Cyclic voltammogram was carried out on a CHI660D electrochemical workstation with platinum electrodes at scan rate of 50 mV/s against a saturated calomel reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) in CH_2Cl_2 .

2.2. Synthesis of compound **M1**

Triphenylphosphine (**1**, 332.2 mg, 1.2 mmol) and 2,6-bis(4-azido benzylidene-yl)-4-methylcyclohexanone (**2**, 185.2 mg, 0.5 mmol) were dissolved in 20 mL of dry toluene. The mixture was degassed with nitrogen and then heated under 60 °C for 24 h. After being cooled to room temperature, the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel with CH_2Cl_2 /acetone (10/1, v/v) as eluent to afford **M1** as orange powder (215.2 mg, yield 51.3%). HRMS (ESI) m/z : calcd for $\text{C}_{57}\text{H}_{48}\text{N}_2\text{OP}_2$ [**M1** + H^+] 839.95; found 840.0. ^1H NMR (400 MHz, CDCl_3) δ 7.82–7.71 (m, 12H), 7.64–7.71 (m, 2H), 7.59–7.51 (m, 6H), 7.51–7.43 (m, 12H), 7.23 (d, $J = 8.2$ Hz, 4H), 6.80 (d, $J = 8.3$ Hz, 4H), 3.04 (dd, $J = 15.7, 3.5$ Hz, 2H), 2.52–2.28 (m, 2H), 1.89–1.74 (m, 1H), 1.06 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 189.77, 152.86, 132.59, 132.04, 131.99, 131.29, 130.89, 129.91, 128.61, 123.12, 36.89, 29.45, 21.94. IR (KBr, cm^{-1}): 3052, 2949, 1655, 1583, 1499, 1435, 833, 719, 692.

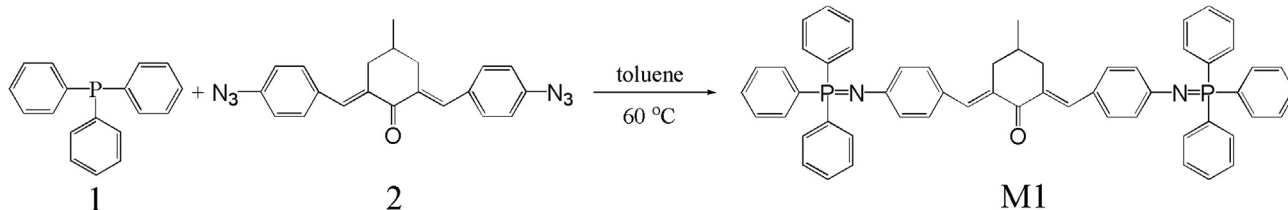
2.3. Comparison experiment

DMSO solutions (with concentration of 1.0×10^{-2} M) of triphenylphosphine (**1**), tricyclohexylphosphine (**3**) and 2,6-bis(4-azido benzylidene-yl)-4-methylcyclohexanone (**2**) were prepared in 10 mL of volumetric flasks, respectively. Two portions of **2** (with the volume of 30 μL) were introduced into separate cuvettes containing 60 μL of **1** and **3**, respectively. DMSO was supplied into these two cuvettes to keep the total volume as 3 mL. UV and fluorescence alteration measurements along with the elongation of reaction time were carried out subsequently at room temperature (as shown in Scheme 1 and Scheme S1).

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route of **M1** is outlined in Scheme 1. **M1** was obtained by the reaction between commercialized triphenylphosphine



Scheme 1. Synthetic route of **M1**.

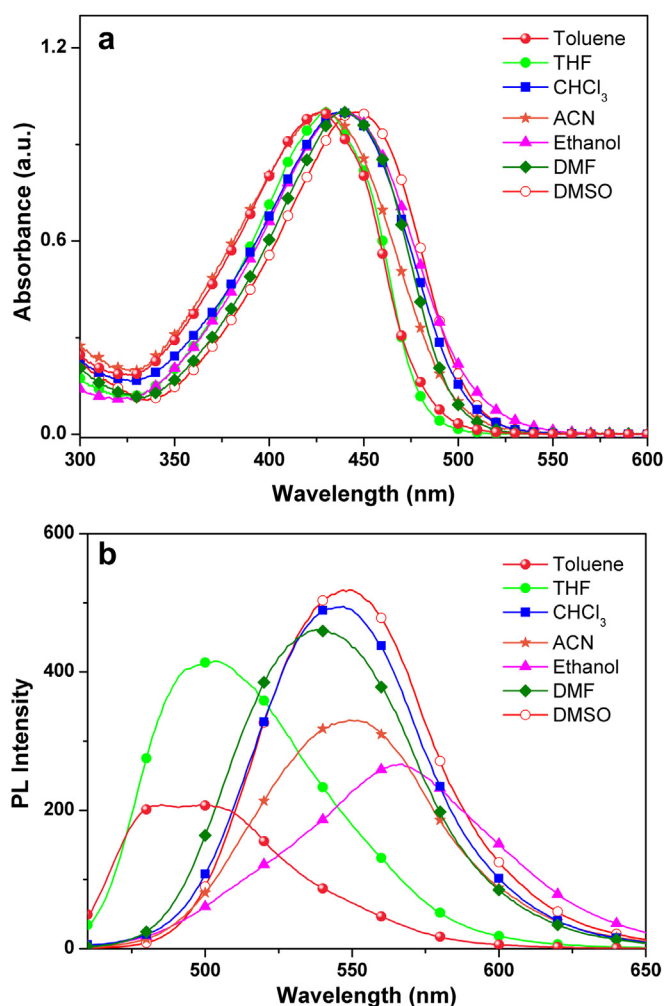


Fig. 1. UV–vis absorption (a) and fluorescence (b) spectra of **M1** in different solvents ($[\text{M1}] = 2.5 \times 10^{-5}$ M, excitation was 440 nm for PL investigation).

(**1**) and diazido-containing benzylidene cyclohexanone derivative (**2**). The reaction was carried out in toluene under 60 °C without the addition of any external catalyst. Nitrogen generated during the reaction and the careful exclusion of water prevents the further possible hydrolysis of **M1** in our case. **M1** is soluble in common organic solvents, such as THF, toluene, chloroform, DMSO, DMF and ethanol, etc.

The chemical structure of **M1** was characterized by FT-IR, NMR and ESI mass analyses. Fig. S1 shows the FT-IR spectrum of **M1**, the absorption signal peak at $\sim 1654.82\text{ cm}^{-1}$ corresponds to the stretching vibration absorption of carbonyl ($\text{C}=\text{O}$) on cyclohexanone in **M1**. As compared to those of common carbonyl-containing compounds, this absorption signal of carbonyl group moves to lower wavenumber and with relatively weak intensity, which might be stem from the formation of ketene style with resonant

Download English Version:

<https://daneshyari.com/en/article/176371>

Download Persian Version:

<https://daneshyari.com/article/176371>

[Daneshyari.com](https://daneshyari.com)