

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Triazole-based highly selective supramolecular sensor for the detection of diclofenac in real samples



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ARTICLE INFO

Article history: Received 17 December 2015 Received in revised form 10 March 2016 Accepted 14 March 2016 Available online 19 March 2016

Keywords: Supramolecular chemistry Human blood's plasma Chemosensors Diclofenac UV-visible spectrophotometery Tap water

ABSTRACT

A triazole-based supramolecular chemosensor **6** for the selective spectrophotometric detection of diclofenac in human plasma and tap water was developed. The **6** was synthesized through click approach and characterized *via* UV–vis spectroscopy, FT-IR, Mass and NMR spectroscopy. The supramolecular interaction of compound **6** with commonly used drugs has been investigated with the help of UV–vis spectral titrations, FT-IR and ¹H, ¹³C NMR spectroscopy. The UV–visible spectral changes upon addition of various commonly used drugs showed that compound **6** is highly selective for diclofenac over other drugs. The supramolecule **6** exhibited a selective enhancement in the absorbance intensity after mixing with diclofenac in human plasma and water samples in the presence of other drugs at pH 6–7, with a linear range of 0.938 (R^2 =0.938) and a limit of detection 10 µM. The relative standard deviation (RSD) for 100 µM diclofenac was found to be 0.462. The Job's plot analysis revealed that diclofenac bind to compound **6** in 1:1 stoichiometry.

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1. Introduction

Supramolecular chemosensor are molecular devices that bind with particular analyte through non-bonding interaction and produce significant changes in the optical properties of chemosensor. (Bell and Hext, 2004). Since the introduction of click chemistry by K.B. sharpless in 2001 the 1,4-disubstituted triazole has attracted the attention of chemists(Thakur et al., 2012). Triazoles generated through Click chemistry are mainly used as ligand and have gained popularity as chemosensor due to its potential to interact with both cation and anions (Lau et al., 2011). 1, 2, 3 triazole based chemosensor can interact with neutral species through non-bonding interactions (Khan et al., 2015).

The wide spread occurrence of antibiotic in the surface water of Karachi became an incipient environmental contaminants and have gained our attention recently. Our nontarget chemical analyses of the drinking water of Karachi, Pakistan, showed the presence of various pharmaceuticals in alarmingly high concentration in different compartment. (Surface water, drainage, effluent) (Selke et al., 2010). Especially the non-steroidal anti-inflammatory drug diclofenac (2-[2,6-dichlorophenylamino] phenylethanoic acid) was found in

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http://dx.doi.org/10.1016/j.ecoenv.2016.03.017 0147-6513/© 2016 Elsevier Inc. All rights reserved. alarmingly high concentration in the drinking water resources and in effluent samples of Karachi, Pakistan (Scheurell et al., 2009). The outcome of these results motivated us to stress on sustainable approaches to improve the drinking water situation of Karachi. The diclofenac is extensively used for relief of pain in humans as well as veterinary medicine (Oaks et al., 2004). Diclofenac distributes in large quantities in the environment in Pakistan compared to the other countries mainly due to unrestricted and non-regulated mixing of pharmaceutical and sewerage waste into water. In one of our earlier study we discovered alarming concentration of diclofenac in water resources (Scheurell et al., 2009).

Similarly the presence of diclofenace in a number of environmental samples such as waste water, surface water and drinking water (Halling-Sørensen et al., 1998; Ternes, 1998; Heberer, 2002), (Vieno and Sillanpää, 2014; Stülten et al., 2008) is reported by a number of other groups. Several methods are reported in literature for the quantitative and qualitative analysis of diclofenac which includes spectrophotometery (Agatonović-Kuštrin et al., 1991; Kamath and Shivram, 1993) spectrofluorimetry (Kramancheva et al., 1997), voltammetry (Ensafi et al., 2013; Sanati, Karimi-Maleh et al., 2014; Mokhtari et al., 2012; Blanco-López et al., 2003) high performance liquid chromatography (HPLC) (González et al., 1999) and high-performance liquid chromatography-mass spectrometry (HPLC-MS) (Abdel-Hamid et al., 2001). All the aforementioned methods have certain drawbacks usually they are slow, laborious and require sophisticated instrumentations. Therefore the development of new cost effective, rapid, highly selective and sensitive methods for the precise determination of diclofenac in the pharmaceutical sample is badly needed. The development of safe and reliable methods is a very important means for the quality control of pharmaceutical products and raw material. Here we are reporting a highly selective and sensitive method for the detection and determination of diclofenac in the water resources of Karachi and in biological matrices via click generated 1, 2,3 triazole based chemosensor 6. Diclofenac bear two benzene rings in its skeleton which can interact with other aromatic system through π - π interaction. The secondary amine and carboxylic functional group of diclofenac can take part in hydrogen bond formation. The compound **6** was designed in such a way that one part of it facilitate hydrogen bonding with neighbouring molecule while other part is capable to interact through π - π stacking. The geometrical shape of 1, 2, 3, triazole, amide, and thiazole function group can promote clip conformation which is ideal host for diclofenac. The compound 6 selectively recognize diclofenac in DMSO/water (1:1). The compound 6 showed high selectivity, stability, quick response for diclofenac over a wide range of concentration.

2. Materials and methods

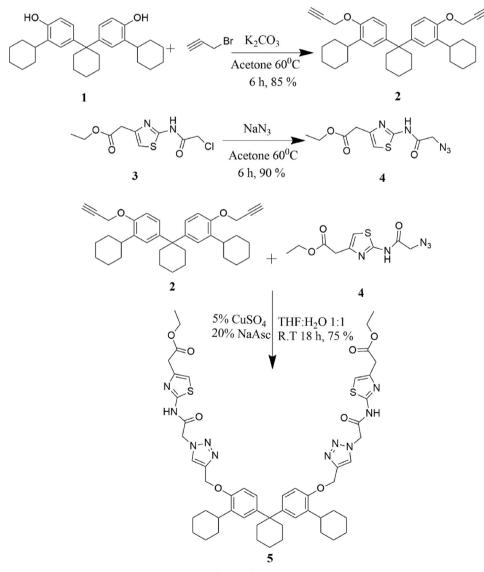
2.1. Materials and instruments

All solvents and reagents were purchased from sigma Aldrich (St. Louis, USA) and used as received without further purification. UV– Visible spectra were recorded on UV-1800 Shimadzu spectrophotometer (Tokyo, Japan). Mass spectra were recorded on EI-MS, FAB (Fast Atomic Bombardment). ¹H NMR spectra were recorded at 300 MHz and ¹³C NMR 125 MHz on Bruker NMR spectrometer (Switzerland). Chemical shifts (δ) are given in ppm and coupling constants J are given in Hz, and the multiplicities are expressed as follows: s=singlet, d=doublet, t=triplet, m=multiplet.

The authors of the manuscript strictly adhered to all national and institutional guidelines for the protection of human subjects and animal welfare.

2.2. Synthesis and characterization of supramolecule 6

The supramolecular chemosensor **6** was synthesized by the reaction of terminyl alkyne **3** with azide **5** under click condition as shown in Scheme 1. The alkynes **3** were obtained by the reactions of



Scheme 1. Synthesis of highly functionalized supramolecule 6.

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