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Benzimidazole: A solid state colorimetric chemosensor for fluoride and acetate

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ABSTRACT

A new benzimadazole based solid state chemosensor 5, 6-Dimethyl-2, 2′-bis-1*H*-benzimidazole (here after **R-1**) was reported. Sensor **R-1** showed high selectivity and sensitivity towards fluoride and acetate anions over the series of tested anions in solid state as well as in CH_3CN medium. A distinct colour change of **R-1** from yellow to deep green and finally brown, was observed through a –NH deprotonation mechanism. Photophysics, ^1H NMR, Cyclic voltametry and DFT based computation justified this colour change with profound support of extraction of –NH proton from **R-1**.

1. Introduction

In recent years, anion sensing by a synthesized receptor is of major interest in analytical chemistry and also in environmental aspect as anions known to play a momentous role in a wide range of environmental, chemical and biological process. Fluoride having the smallest ionic radius, highest charge density and hard Lewis basic character, has emerged as significant target in the field of supramolecular chemistry as excess intake or chronic ingestion of lower doses F^- can result kidney and gastric troubles, urolithiasis in humans [1,2], dental and skeletal flourosis. It is well known that fluoride ion also plays a role for dental care and has potential use for the treatment of osteoporosis [3,4]. Thus the importance of fluoride ion has led to develop fluoride sensor over the past 2–3 decades [5–23]. Fluoride ion has the highest affinity towards the proton among the various anions and this property reveals the deprotonation from the hydrogen containing polar groups like –NH, –OH groups etc. via strong hydrogen bonding interaction. Therefore fluoride sensor containing –NH groups such as sulphonamide [24,25], urea [26], imidazole [27–41] have been designed to detect fluoride ion. However, in most of the cases sensing mechanism depends on spectroscopic changes at a particular wavelength. But direct or immediate colour change in solid state reaction is rare [42]. So it is a challenge to employ a solid state fluoride sensor among the various competitive anions. Here, we report a highly selective and sensitive solid state fluoride and acetate ion sensor, R-1 based on benzimadazole (Fig. 1) [43]. R-1 showed a very remarkable colour change in solid state reaction as well as in CH_3CN medium.

2. Experimental

2.1. General procedure for synthesis of R-1: 5, 6-Dimethyl-2, 2′-bis-1H-benzimidazole (R-1): A mixture of 4,5-dimethylbenzene-1,2-diamine (1 mmol), benzene-1,2-diamine (1 mmol) and Oxalic acid (1 mmol) were heated at 150 °C with 0.1 mL of HBF_4 (45% in water) for 2.5 h under solvent free condition. After cooling to room temp, the reaction mixture solidified and was taken out of oil bath. After that saturated aqueous $NaHCO_3$ (8 mL) solution was added, stirred for 10 min to remove the acid catalyst and filtered to separate the solid product, washed with brine and dried. The product was finally recrystalized from methanol/ethylacetate (1:3; v/v).

m.p. >250 °C [DMSO/H_2O (1:1; v/v)]; ^1H NMR (DMSO-d_6) δ 2.29 (s, 6H, C_5-CH_3 and C_6– CH_3), 7.24 (br s, 3H, C_7-H, $C_{5'}$-H, and $C_{6'}$-H), 7.44 7.68 (m, 3H, C_4—H, $C_{4'}$-H and C_7—H), 13.17 (brs, 1H, N_1—H) and 13.17–13.37 (brs, 1H, N_1'-H); ^{13}C NMR (DMSO-d_6) δ 20.1 (C_5-CH_3 and C_6-CH_3), 112.0 (C_7 and $C_{7'}$), 119.0 (C_4 and $C_{4''}$), 122.3 ($C_{5''}$), 123.7 ($C_{6'}$), 130.8 (C_6), 132.4 (C_5), 133.4 ($C_{3'a}$), 142.3 (C_{3a}), 143.0 ($C_{7'a}$), 143.3 ($C_{2'}$), 143.9 (C_{7a}) and 144.2 (C_2); IR (KBr): 2920, 2664, 1584, 1395, 1327, 1001, 953, 847 and 737 cm^{-1}; MS: *m/z* (%): 262.1 (M^+, 100), 263.1 (M + 1, 20), 264.1 (M + 2, 2); Anal. calcd. for $C_{16}H_{14}N_4$; C: 73.26, H: 5.38, N: 21.36. Found; C: 73.44, H: 5.23, N: 21.50%.

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