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Epoxy-based oligomer bearing naphthalene units: fluorescent sensor for 4-nitrophenol

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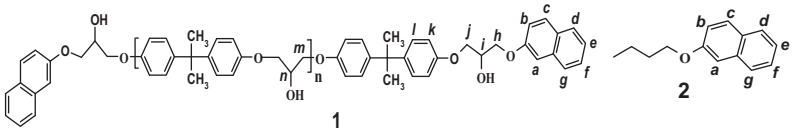
ABSTRACT

A simple epoxy-based oligomer **1** bearing naphthalene units at the chain-ends is shown to be ON–OFF type fluorescent sensor for 4-nitrophenol with high sensitivity and selectivity. The recognition mechanism can be attributed to the possibilities of fluorescence resonance energy transfer (FRET) and also photo induced electron transfer (PET) between naphthalene moiety and 4-nitrophenol. In the sensing process, diverse nitroaromatics such as 3-nitrophenol, 2-nitrophenol 1,3-dinitrobenzene, 2-chloronitrobenzene, 2-nitropthalic acid and non-nitroaromatics such as 2-chlorobenzoic acid, 4-hydroxybenzoic acid did not interfere.

The fluorescent chemosensors for the detection of 4-nitrophenol (4-NP) have attracted considerable attention.[1,2] The toxicity, carcinogenicity and high persistence in the environment make such compound danger to human health and the environment.[3–5] It has become a common pollutant in natural and wastewater. Letter, we present, for the first time, the synthesis of a new epoxy-based oligomeric probe **1** having naphthalene moieties at the chain-ends. In relation to this, 2-butoxynaphthalene **2** was prepared as model compound. The designed probe **1** was found to be an efficient fluorosensor for 4-NP.



1 **2**

4-NP originating from pesticide degradation products, car exhausts, dyes, plastics and industrial wastes is cited in the Environmental Protection Agency List of Priority Pollutants.[6] Hence, the detection of 4-NP is of paramount importance for the environment and health protection. Epoxy-based framework has attracted our attention in the design of macromolecular probes for sensing application[7] because of its fascinating properties like easy processibility, good chemical resistance, dimensional stability and potentiality for reuse. In addition, the ease of linking of a variety of chromophores utilizing reactive epoxy groups of such framework is considered to be an effective route to develop macromolecular probes. Hence epoxy-based macromolecules with appropriately appended fluorophores would provide new opportunities for 4-NP sensing studies. In this context, naphthalene fluorophore[7a,b,8] is one of the attractive functional subunits used in the design of a variety of probes for recognition and sensing studies. In this

The designed oligomer **1** was prepared[9] through the reaction of diglycidyl ether of bisphenol-A (DGEBA)[10] and 2-naphthol as outlined in Scheme 1. The structure of **1** was identified by FT-IR, UV–vis, NMR (^{1}H and ^{13}C), elemental and GPC analyses[9] (ESI, Figs. S1–S3). At the same time, its structurally simplified small molecular analogue **2** as model compound was synthesized[11] in good yield using the method shown in Scheme 2. The ^{1}H NMR spectrum of **1** reveals the appearance of naphthalene protons in the region 7.78–7.10 ppm. Oligomer **1** has good solubility in common organic solvents such as THF, 1,4-dioxane, DMF and DMSO. The structure of **2** was identified by FT-IR, ^{1}H NMR and elemental analysis[11] (ESI, Fig. S4).

The spectroscopic properties of **1** were evaluated in CH_3CN ([**1**] = 3.37×10^{-5} M with respect to repeat unit). As shown in Figure 1, the probe **1** exhibits distinct absorption band in the region 304–339 nm typical of naphthalene moiety. Fluorescence spectrum of

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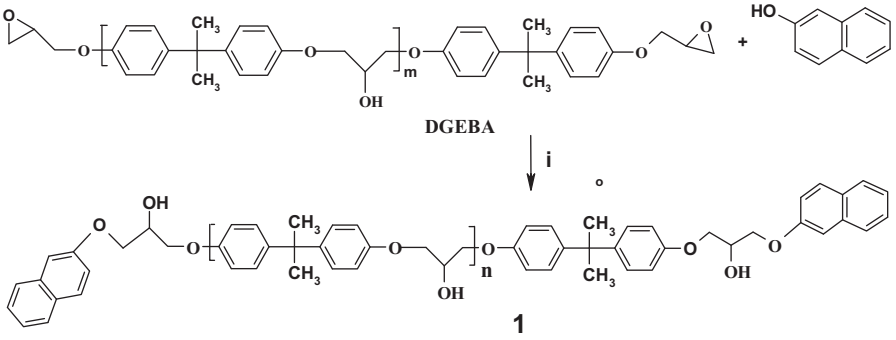
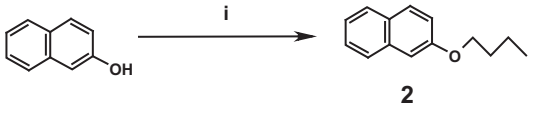


Scheme 1. (i) NaOH, 85–90 °C, 4 h.



Scheme 2. (i) 1-Butylbromide, K_2CO_3, KI, acetone (dry), reflux, 10 h.

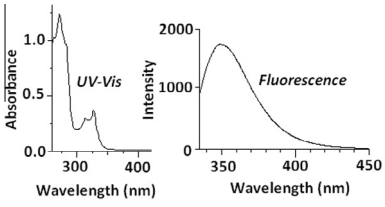


Figure 1. UV–vis and fluorescence spectra of **1** ($c = 3.37 \times 10^{-5}$ M) in CH_3CN ($\lambda_{exc} = 325$ nm).

1 shows the maximum at 350 nm typical of naphthalene monomeric emission when excited at 325 nm. We evaluated the fluorescence response of **1** towards diverse aromatics such as

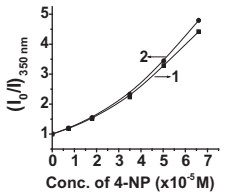


Table 1. Fluorescence quenching of 4-NP (6×10^{-5} M) in CH_3CN for **1** and **2**.

Compound	Concentration	λ_{exc}	Quenching Efficiency (%)
1	3.37×10^{-5} M	325 nm	77.36
2	2.48×10^{-4} M	325 nm	79.14

Figure 4. Stern–Volmer plot for **1** and **2** upon addition of 4-NP (up to $c \sim 6.6 \times 10^{-5}$ M in CH_3CN, $\lambda_{exc} = 325$ nm, [**1**] = 3.37×10^{-5} M, [**2**] = 2.48×10^{-4} M).

4-nitrophenol (4-NP), 3-nitrophenol (3-NP), 2-nitrophenol (2-NP), 1,3-dinitrobenzene (1,3-DNB), 2-chloronitrobenzene (2-CNB), 2-chlorobenzoic acid (2-CBA), 4-hydroxybenzoic acid (4-HBA) and 2-nitropthalic acid (2-NPA).

Gradual addition of 4-NP to a solution of **1** leads to drastic quenching in fluorescence intensity (ON–OFF) at 350 nm ($\lambda_{exc} = 325$ nm). Figure 2a shows the fluorescence quenching of **1** upon incremental addition of 4-NP. The sensing property of **1** was also investigated in CH_3CN–water (4/1, v/v) (Fig. 2b). Figure 2c, in this regard, shows better sensitivity of **1** in aqueous-CH_3CN over pure CH_3CN solvent demonstrating its practical relevance. The

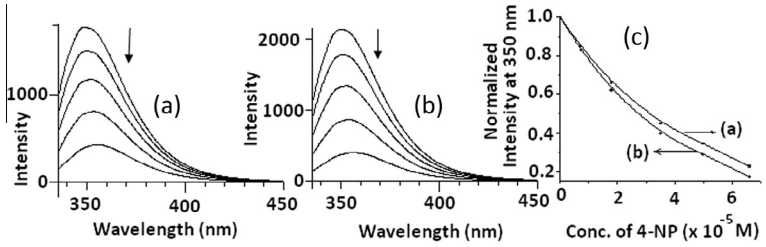


Figure 2. Fluorescence spectral changes of **1** ($c = 3.37 \times 10^{-5}$ M) with different concentrations of 4-NP (up to 6.6×10^{-5} M) in (a) CH_3CN ($\lambda_{exc} = 325$ nm) (b) CH_3CN–water (4:1) ($\lambda_{exc} = 325$ nm) (c) plot of normalized fluorescence intensity of **1** at 350 nm versus concn of 4-NP for (a) and (b).

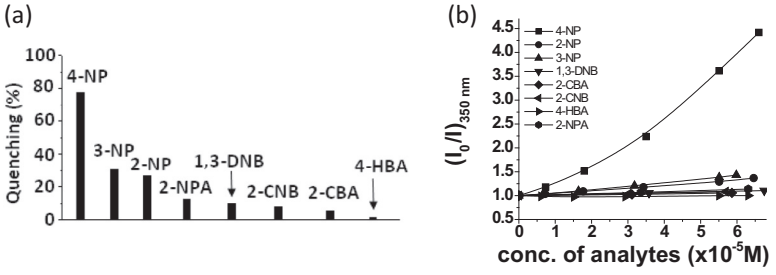


Figure 3. (a) Bar diagram showing quenching efficiency (%) of **1** ($c = 3.37 \times 10^{-5}$ M; $\lambda_{exc} = 325$ nm) at 350 nm in CH_3CN after the addition of different aromatics ($\sim 6 \times 10^{-5}$ M) (b) Stern–Volmer plot with different aromatics in CH_3CN ($\lambda_{exc} = 325$ nm; [**1**] = 3.37×10^{-5} M).