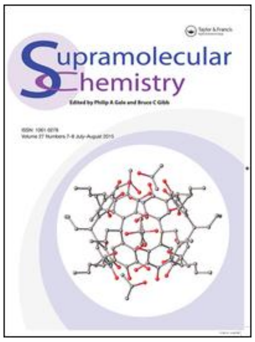

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Epoxy-based oligomeric probe bearing naphthalene units for selective turn-OFF fluorescent sensing of fluoride anion

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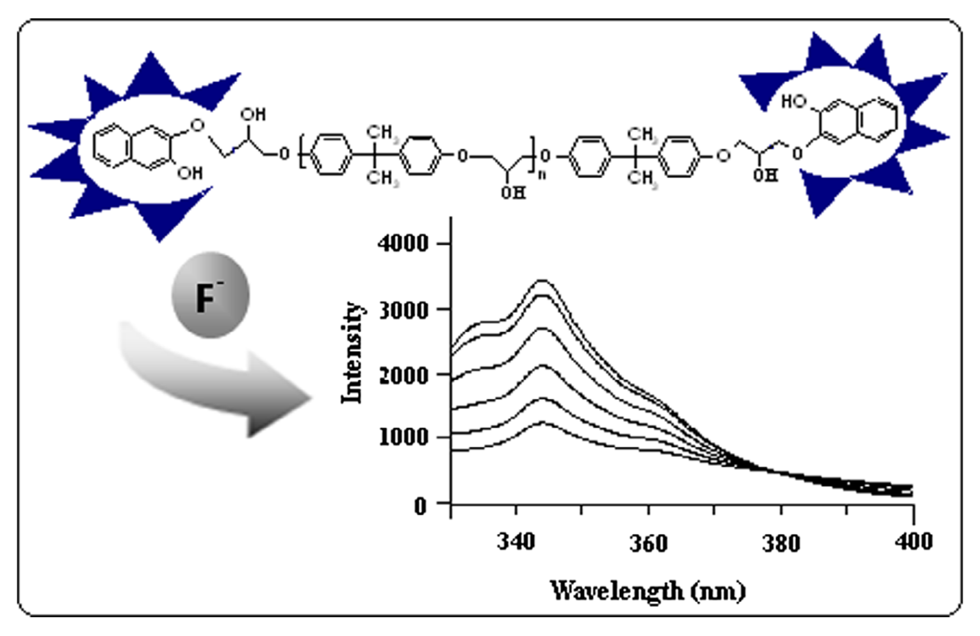
ABSTRACT

A simple epoxy-based oligomer **1** bearing naphthalene unit at the chain-ends is reported to be highly selective ON–OFF type fluorescent probe for fluoride anion. The titled oligomer displayed fluorescence quenching upon addition of F^-, resulting in selective detection of fluoride anion over other anions, such as AcO^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^- and $H_2PO_4^-$ in CH_3CN. Fluorescence experiments suggest the significant influence of the oligomer chain on the sensitivity and selectivity of **1** towards fluoride anion.



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KEYWORDS
Epoxy-based oligomer; fluorescent sensor; fluoride anion detection

Introduction

The development of fluorescent chemosensors capable of selective recognition and sensing of anions is an area of significant importance in a wide range of chemical, biological and environmental processes (*1*). Of the different anionic species, fluoride ion draws attention. A high intake of fluoride is associated with the skeletal and dental fluorosis, osteoporosis, neurological and metabolic dysfunctions, and kidney failure (*2–4*). Accordingly, the sensitive and selective detection of F^- is of great concern in the context of both human health and environment. A number of molecular probes for the detection of F^- have been reported in recent years (*5, 6*). However, the design of macromolecular chemosensors (*5, 7*) for the detection of F^- is a challenge. On account of the reactive epoxy groups capable of incorporating a variety chromophores and fascinating properties such as easy processibility, good chemical resistance, dimensional stability and potentiality for reuse, epoxy-based frameworks have led us to explore macromolecular probes for sensing application

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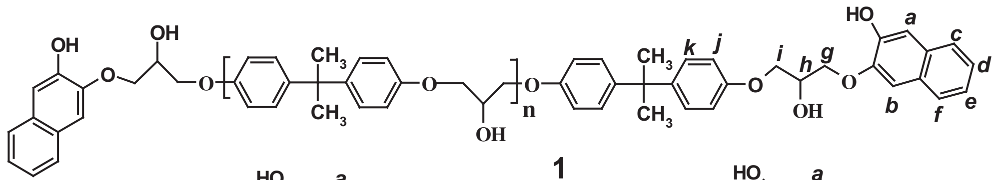
(*8*). Hence, as further advance, epoxy-based macromolecules with appropriately appended fluorophores would be good candidates for F$^-$ sensing studies. In this context, naphthalene and its derivatives are attractive fluorophores (*8, 9*) employed in the design of many unique probes for recognition and sensing studies. In this article, we present the synthesis of a new epoxy-based oligomeric probe **1** in which naphthalene-2,3-diol fluorophores are facilely attached at the chain-ends. In relation to this, 3- butoxy-2-naphthol **2** and 3-(2-hydroxyethoxy)-2-naphthol **3** have been prepared as model compounds. The designed probe 1 was found to be an efficient fluorosensor for fluoride ion in CH$_3$CN.



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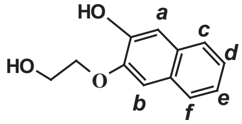

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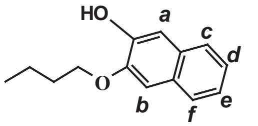

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Results and discussion

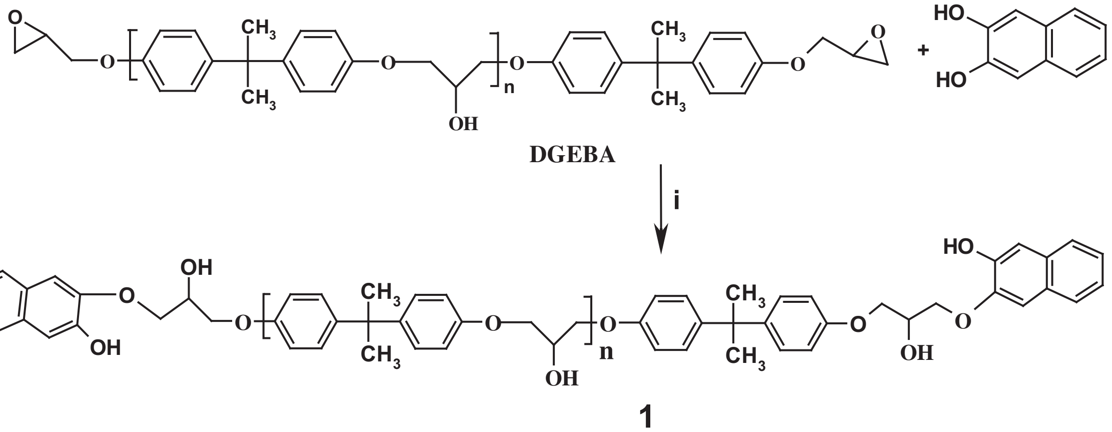
Synthesis and characterisation

The titled oligomer **1** was easily synthesised through the reaction of diglycidyl ether of bisphenol-A (DGEBA) with naphthalene-2,3-diol according to the Scheme 1 and was unambiguously characterised by FT-IR, UV–vis and NMR (^{1}H and ^{13}C), elemental and GPC analyses (Figures S1, S2, and S3).

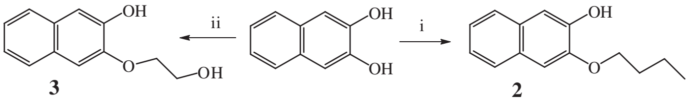
At the same time, structurally simplified small molecular analogues **2** and **3** as model compounds were synthesised in good yield using the method shown in Scheme 2. Oligomer **1** is soluble in common organic solvents such as THF, 1,4-dioxane, DMF, DMSO and CH$_3$CN. The structures of **2** and **3** were identified by ^{1}H NMR and elemental analyses (Figure S4).

Chemosensing behaviour

The spectroscopic properties of **1** were evaluated in CH$_3$CN ([**1**] = 1.48 x 10^{-4} M with respect to repeat unit). As shown in Figure 1, the probe **1** exhibits well-resolved absorption bands in the range of λ = 306 to 324 nm attributed to the naphthalene units. Titled oligomer **1** displayed an intense fluorescence emission at 344 nm, typical of naphthalene



Scheme 1. Synthesis of oligomer 1: (i) NaOH, 85–90 °C, N$_2$ atmosphere, 5 h.



Scheme 2. Synthesis of model compounds **2** and **3**: (i) 1-Butylbromide, K$_2$CO$_3$, KI, acetone (dry), reflux, 14 h; (ii) 2-Chloro ethanol, K$_2$CO$_3$, acetone (dry), reflux, 30 h.

monomeric emission when excited at 320 nm (Figure 1). We evaluated the fluorescence response of **1** to various anions such as F^-, AcO^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^- and $H_2PO_4^-$ [as the tetrabutylammonium (TBA^+) salts] in CH_3CN. A drastic quenching in fluorescence intensity (ON-OFF) of **1** at 344 nm (λ_{exc}= 320 nm) was observed upon progressive addition of F^- anion. Figure 2(a), in this regard, gives the distinct change in fluorescence intensity of **1** upon gradual addition of F^- anion. Under similar conditions, the corresponding UV-vis spectral variation of **1** indicates groundstate interaction with F^- anion. Titration of **1** as a function of [F^-] gave a small decrease in intensity of the peaks in the region of 306 nm to 324 nm with the formation of new band in the region 339 – 366 nm (Figure 2b).

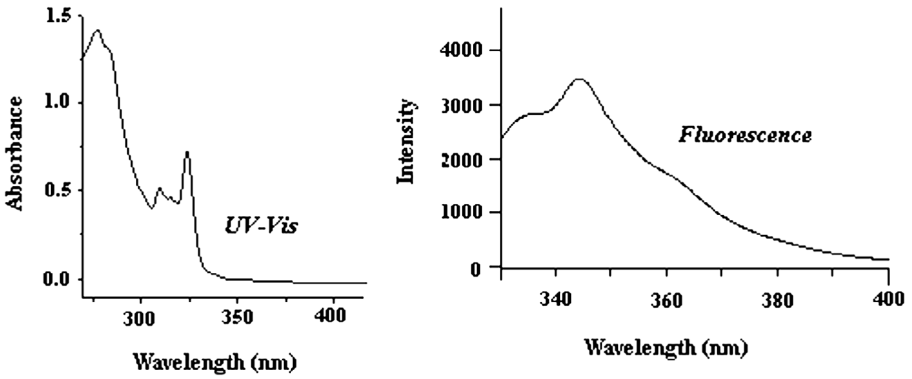


Figure 1. UV–vis and fluorescence spectra of 1 ($c = 1.48 \times 10^{-4}$ M) in CH_3CN.

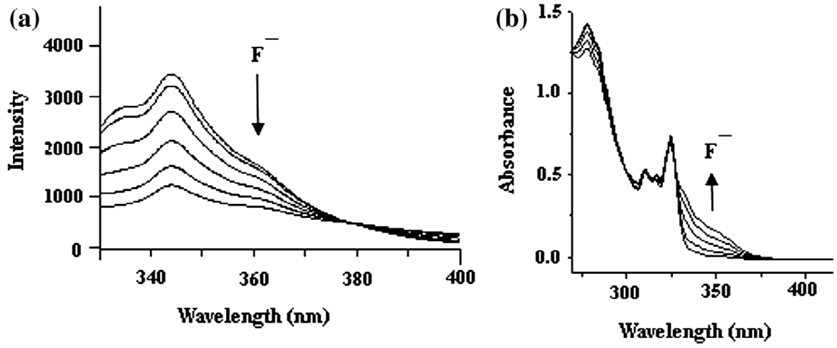


Figure 2. (a) Fluorescence response of **1** ($c = 1.48 \times 10^{-4}$ M) to different concentrations of F^- ($c = 0 – 5.4 \times 10^{-4}$ M) in CH_3CN (λ_{exc} = 320 nm) (b) UV-vis spectral changes upon addition of F^- ($c = 0 – 5.4 \times 10^{-4}$ M)

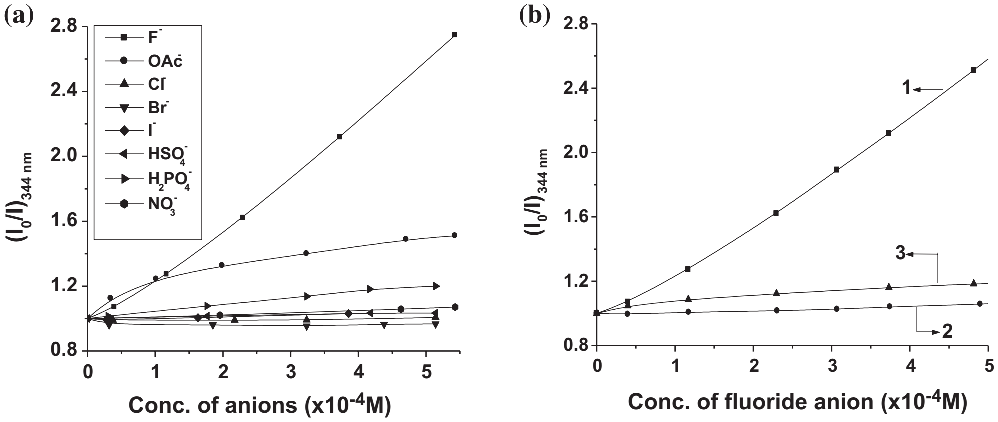


Figure 3. Stern-Volmer plots for (a) **1** with (TBA^+) salts of different anions in CH_3CN (b) **1**, **2** and **3** upon addition of TBAF in CH_3CN (λ_{exc}= 320 nm, [**1**] = 1.48×10^{-4} M, [**2**] = 1×10^{-4} M, [**3**] = 1.36×10^{-4} M)

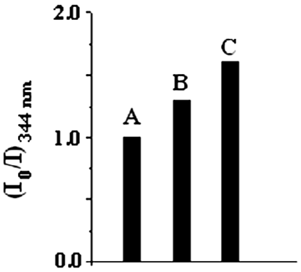


Figure 4. Fluoride anion selectivity of **1** ($c = 1.48 \times 10^{-4}$ M) in CH_3CN in the presence of various anions: (A) **1** only; (B) **1** + X (X = AcO^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^- and $H_2PO_4^-$; $c = \sim 10^{-4}$ M); (C) **1** + X + Y (Y = F^-, $c = \sim 10^{-4}$ M ($\lambda_{exc} = 320$ nm).

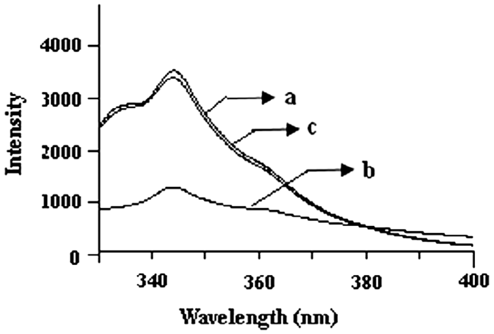


Figure 5. Change in emission spectra of **1** by the addition of $Ca(NO_3)_2$ to **1** + F^- in CH_3CN: (a) Free **1**($c = 1.48 \times 10^{-4}$ M) (b) **1** + F^- ($[F^-] = \sim 5.4 \times 10^{-4}$ M) (c) **1** + F^- + Ca^{2+} ($[Ca^{2+}] = 6.2 \times 10^{-4}$ M) ($\lambda_{exc} = 320$ nm).

This is attributed to the hydrogen bonding of –OH and F^- followed by deprotonation.

In contrast, AcO^- ion being less basic than F^- showed weak response in fluorescence quenching. The rest of the anions in the study showed only negligible quenching (Figure S5). The result of Stern–Volmer plot as illustrated in Figure 3(a) indicates that **1** is enough sensitive for detecting F^- ion in CH_3CN.

Interestingly, as we move from oligomer **1** to model compounds **2** and **3** without and with aliphatic –OH group in the backbone, respectively, mere change in the emission spectra upon interaction with TBAF was observed (Figure S6). Figure 3(b), in this regard, shows a comparison of Stern–Volmer plots for **1**, **2** and **3** with TBAF in CH_3CN. The comparison of emission intensities at 344 nm in Stern–Volmer plot is significant, since excitation has been performed at the same wavelength on solutions having the same absorbance. In the study, the F^--induced greater quenching in emission of **1** than **2** and **3** suggested a favourable impact of oligomer backbone. The backbone structure of oligomer in combination with aliphatic –OH groups are believed to bind F^- effectively inducing greater quenching in emission. The ability to detect fluoride anion with high selectivity is an important aspect for an excellent probe. To utilise oligomer **1** as F^--selective fluorescent sensor, experiment was also carried out in the presence of F^- mixed with a series of potentially competing anions. As shown in Figure 4, F^--induced ON–OFF type fluorescence response of **1** was unaffected in the background of coexistent anions demonstrating its ability to discriminate F^- ion.

To gain insight into the reversibility in binding process, $Ca(NO_3)_2$ was added to the solution of **1** containing F^- anion. The addition of $Ca(NO_3)_2$ resulted in revival of the original F^--free spectrum, which demonstrated the reversibility in the binding (Figure 5). Similar but smaller fluorescence quenching was observed in CH_3CN mixed with a protic solvent such as water ($CH_3CN:H_2O = 4:1$, v/v) (Figure S7). It was also noted that the addition of 10% water to the CH_3CN solution of **1**-F^- results in almost revival of the original emission spectrum of **1** (Figure S8).

These observations suggested that the interaction of **1** and F^- is due to hydrogen bonding followed by deprotonation (Table 1). In an experiment, initial addition of same equivalent of strong base OH^- (as TBA^+ salt), which definitely leads to deprotonation, induced drastic quenching of emission (~71%) than that caused by F^- anion (~38%) (Figure 6).

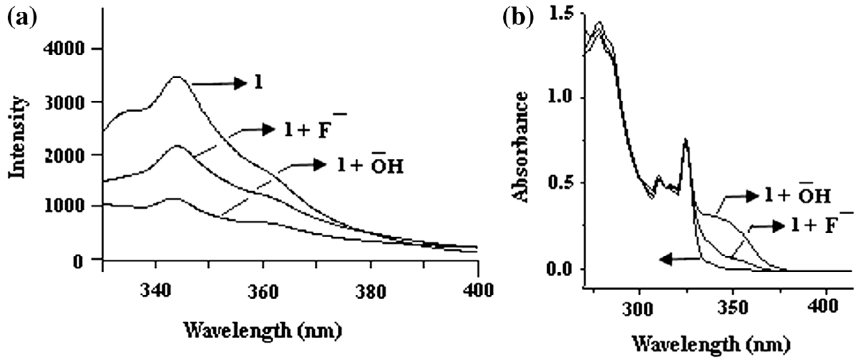


Figure 6. (a) Fluorescence emission changes of **1** ($c = 1.48 \times 10^{-4}$ M) upon the addition of F^- ($c = 2.3 \times 10^{-4}$ M) and OH^- ($c = 2.3 \times 10^{-4}$ M) in CH_3CN ($\lambda_{exc} = 320$ nm) (b) UV–vis spectral changes upon addition of F^- ($c = \sim 1.8 \times 10^{-4}$ M) and OH^- ($c = \sim 1.8 \times 10^{-4}$ M) in CH_3CN.

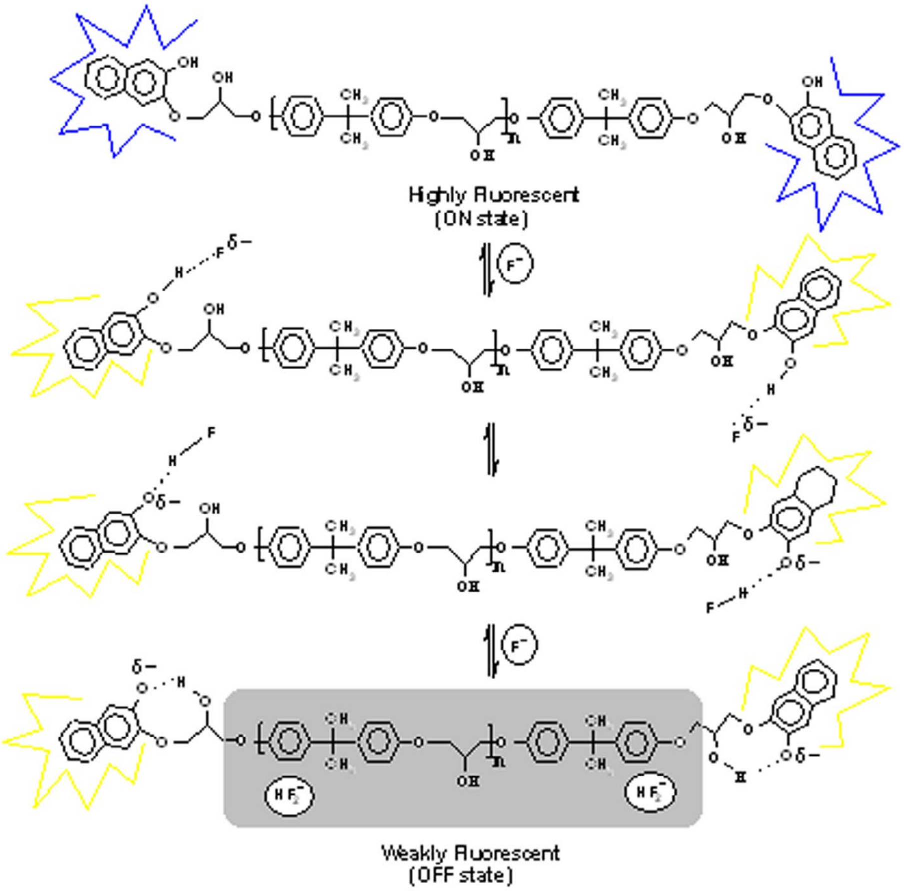
Table 1. Fluorescence quenching degrees $[(I_0-I)/I]$ of **1** by F^- in different solvents ($[\mathbf{1}] = 1.48\times10^{-4}$ M; $[F^-] = 5.4\times10^{-4}$ M; $\lambda_{exc} = 320$ nm).

Solvent	Fluorescence quenching degrees
CH_3CN	1.746
CH_3CN-H_2O (4:1, v/v)	0.067

Concurrently, the absorption spectrum of **1** was affected to a large extent by the addition of OH^- ion. However, further addition of F^- caused quenching by about 64%. These features clearly suggest that the naphthalene $^-$OH groups are initially involved in the formation of hydrogen-bonded complex (*10*) with more basic F^- ion and then undergo deprotonation (*11*) upon further increase of F^- concentration as illustrated in Scheme 3. This is in accordance with the findings reported in the literature (*6, 12*).

In order to understand the interaction of F^- with the oligomeric species **1** and also the case of deprotonation, we investigated the change in ^{1}H NMR of **1** in presence of TBAF in $CDCl_3$. Upon addition of F^- the signals for the naphthalene ring protons of types 'c', 'd', 'e' and 'f' moved to the upfield directions. The protons of types 'd' and 'e' suffered more upfield chemical shifts ($\Delta\delta = 0.17$ ppm) than protons of 'c' and 'f' types and merged together with the ring protons of type 'k'. This indicated the deprotonation of the naphthalene $^-$OH group for which the naphthalene rings became electron rich and showed upfield chemical shifts. The naphthalene –OH which appeared as broad singlet at 7.99 ppm became invisible (Figure S8). In this aspect, it is to note that no peak at ~16 ppm for HF_2^- that results in from deprotonation was observed. This is due to broadening of the peak that presumably occurs through extensive hydrogen bonding effect from the interference of the aliphatic –OH groups in the oligomer backbone.

The quenching of emission in the presence of F^- in the present case might be attributed to the intramolecular charge transfer (ICT) mechanism (*13*) occurring between negative charge density of naphthol oxygen atom and naphthalene ring. It is noteworthy to mention that the presence of oligomer backbone of **1**, which possesses alcoholic $^-$OH groups, competently increases the F^- binding potential (*14*) and modulates the ICT process as evidenced from profound fluorescence quenching than observed for **2** and **3**. It might be expected further that the favourable interaction of deprotonated O^- anion with the appropriately positioned OH groups of oligomer framework strengthens its sensitivity (Scheme 3). Negligible fluorescence change of **1** with Cl^-, Br^- or I^- rules out the quenching by heavy atom effect.



Scheme 3. (Colour online) Suggested sensing mechanism of 1 for F^-.

Conclusion

A new and simple epoxy-based oligomer **1** bearing naphthalene unit at the chain-ends has been synthesised. Oligomer **1** exhibits selective ON–OFF type fluorescence response to F^- in CH_3CN. In particular, we find the impact of oligomer chain of **1** on the F^- induced perturbation of naphthalene electronics through hydrogen bonding/deprotonation dualism as compared to small molecular analogues **2** and **3**. To our opinion, processing ability and blending nature would also demonstrate the value of **1** in the fabrication of environmental application-oriented F^--sensing devices. Further study in this direction is under progress in our laboratory.

Experimental

Synthesis of oligomer 1

A mixture of DGEBA (0.2 g, 0.67 mmol), naphthalene-2,3-diol (0.64 g, 4.0 mmol) and sodium hydroxide (0.06 g, 1.0 mmol) was allowed to stir at 85–90 °C for 5 h under nitrogen atmosphere. Then, the reaction mixture was washed with water, dissolved in N,N-dimethylformamide. To the resulting solution, water was added and extracted with dichloromethane. The organic layer was separated, washed, respectively, with 5% aqueous NaOH solution, dil HCl and aqueous $NaHCO_3$ solution. Organic layer was dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo* to yield gummy product. ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.99 (br *s*, Ar-OH), 7.66–7.62 (*m*, $H^{c,f}$), 7.32–7.27 (*m*, $H^{d,e}$), 7.25 (*s*, H^b), 7.15–7.09 (*m*, $H^{a,k}$), 6.84 (*d*, H^j, *J* = 8 Hz), 6.0 (*s*, Ar-OH), 4.5 (br *m*, H^g), 4.32 (br *m*, H^i), 4.19–4.15 (br *m*, H^h), 4.04 –3.75 (br *m*, oligomer chain $–CH_2–$), 3.50–3.34 (br *m*, oligomer chain –CH–), 2.89 (*m*, –OH), 2.74 (*m*, ^-OH), 1.62 (*s*, $^-CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 156.15 (unresolved), 146.0, 144.0, 143.21, 128.80, 127.91, 127.77, 126.31, 124.61, 123.88, 113.94, 68.86, 68.73, 68.65, 50.22, 44.80, 41.74, 31.01; FTIR (KBr): v_{max} = 3345, 2964, 2928, 1655, 1606, 1509, 1485, 1459, 1416, 1385, 1262, 1180, 1108, 1042, 947, 860, 829, 747, 478 cm^{-1}; GPC (using polystyrene and THF): $M_w = 1120$, PDI = 1.234; Anal. Calcd for $(C_{39}H_{46}O_7)_n\ C_{20}H_{14}O_4$: C, 75.0; H, 6.35%. Found: C, 74.97; H, 6.30%.

Synthesis of model compound 2

To a nitrogen flushed (20 min) stirred mixture of naphthalene-2,3-diol (0.1 g, 0.625 mmol), dry acetone (1 ml), and anhydrous K_2CO_3 (0.2 g, 1.27 mmol), 1-butylbromide (0.086 g, 0.625 mmol) was added. To this solution was added potassium iodide (catalytic amount). The mixture was stirred for 15 min, and then heated to reflux for 14 h. After evaporation of the solvent, water was added and the mixture was extracted with CH_2Cl_2 and dried over *anhyd.* Na_2SO_4. The product was purified by column chromatography (silica gel 60–120, eluent petroleum ether/EtOAc 5:0.3) and obtained as yellowish semisolid (90%), ^1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (m, 2H, $H^{c,f}$), 7.32 (*m*, 2H, $H^{d,e}$), 7.25 (*s*, 1H^b, marged with solvent peak), 7.11 (*s*, 1H, H^a), 5.94 (*s*, Ar-OH), 4.18 (*t*, 2H, *J* = 6.4 Hz, $^-OCH_2^-$), 1.88 (*m*, 2H, $^-OCH_2CH_2^-$), 1.56 (*m*, 2H, $^-OCH_2CH_2CH_2^-$), 1.02 (*t*, 3H, *J* = 7 Hz, $^-CH_3$); FTIR (KBr): v_{max} = 3453, 2966, 2945, 2872, 1635, 1485, 1262, 1459, 1416, 1385, 1160, 1096, 840 cm^{-1}; Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.77; H, 7.40%. Found: C, 77.75; H, 7.37%.

Synthesis of model compound 3

To a stirred solution of naphthalene-2,3-diol (0.1 g, 0.625 mmol) in dry acetone, anhydrous K_2CO_3 (0.2 g, 1.27 mmol) was added, and the mixture was stirred for 30 min at room temperature. Then 2-chloroethanol (0.05 g, 0.625 mmol) was added. The reaction mixture was heated to reflux for 30 h. After evaporation of the solvent, water was added and the mixture was extracted with CH_2Cl_2 and dried over *anhyd.* Na_2SO_4. The crude was purified by column chromatography (silica gel 60–120, eluent petroleum ether/EtOAc (10:1) to obtain the desired product as yellowish solid (yield 70%), ^1H NMR ($CDCl_3$, 400 MHz) δ 7.64 (*m*, 2H, $H^{c,f}$), 7.31–7.26 (*m*, 3H, $H^{d,e,b}$, merged with solvent peak), 7.15 (*s*, 1H, H^a), 6.56 (br s, Ar-OH), 4.30 (*m*, 2H, $^-OCH_2^-$), 4.10 (*m*, 2H, $^-OCH_2CH_2OH$), 1.69 (*s*, 2H, CH_2OH); FTIR (KBr): $\boldsymbol{v}_{max}$ = 3401, 2925, 2870, 1637, 1512, 1487, 1454, 1353, 1268, 1179, 1166, 1115, 1069, 1043, 928, 904, 847, 739 cm^{-1}; Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.88%. Found: C, 70.56; H, 5.87%.

Supplemental material

Figures showing NMR, GPC data, fluorescence titrations with various anions and partial ^1H NMR of **1** with F^- are available online here: http://dx.doi.org/10.1080/10610278.2016.1139113.

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References

(1) Gale, P.A.; Busschaert, N.; Haynes, C.J.E.; Karagiannidis, L.E.; Kirby, I.L. *Chem. Soc. Rev.* **2014**, *43*, 205–241.; Duke, R.M.; Veale, E.B.; Pfeffer, F.M.; Kruger, P.E.; Gunnlaugsson, T. *Chem. Soc. Rev.* **2010**, *39*, 3936–3953.; Kim, S.K.; Kim, H.N.; Xiaoru, Z.; Lee, H.N.; Lee, H.N.; Soh, J.H.; Swamy, K.M.K.; Yoon, J. *Supramol. Chem.* **2007**, *19*, 221–227.; Fang, L.; Chan, W.-H.; He, Y.-B.; Kwong, D.W.J.; Lee, A.W.M.

J. Org. Chem. **2005**, *70*, 7640–7646.; Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103*, 4419–4476.

(2) Ayoob, S.; Gupta, A.K. *Crit. Rev. Environ. Sci. Technol.* **2006**, *36*, 433–487.; Kirk, K.L. *Biochemistry of the Halogens and Inorganic Halides*; Plenum Press: New York, **1991**; p 58.

(3) Sandhu, R.; Lal, H.; Kundu, Z.S.; Kharb, S. *Bio. Trace Elem. Res.* **2011**, *144*, 1–5.; Wiseman, A. Handbook of Experimental Pharmacology XX/2; Springer-Verlag: Berlin. **1970**, Part *2*; pp. 48–97; Dreisbuch, R.H. *Handbook of Poisoning*; Lange Medical: Los Altos, CA, **1980**.

(4) Gazzano, E.; Bergandi, L.; Riganti, C.; Aldieri, E.; Doublier, S.; Costamagna, C.; Bosia, A.; Ghigo, D. *Curr. Med. Chem.* **2010**, *17*, 2431–2441.

(5) Zhou, Y.; Zhang, J.F.; Yoon, J. *Chem. Rev.* **2014**, *114*, 5511–5571 and references therein .; Ghosh, K.; Kar, D.; Frohlich, R.; Chattopadhyay, P.; Sammader, A.; Khuda-Bukhsh, A.R. *Analyst* **2013**, *138*, 3038–3045.; Rajamalli, P.; Prasad, E. *Org. Lett.* **2011**, *13*, 3714–3717.; Zhang, J.F.; Lim, C.S.; Bhniya, S.; Cho, B.R.; Kim, J.S. *Org. Lett.* **2011**, *13*, 1190–1193.; Qu, Y.; Hua, J.; Tian, H. *Org. Lett.* **2010**, *12*, 3320–3323.; Mashraqui, S.H.; Betkar, R.; Chandiramani, M.; Quinonero, D.; Frontera, A. *Tetrahedron Lett.* **2010**, *51*, 596–599.; Hu, R.; Feng, J.; Hu, D.; Wang, S.; Li, S.; Li, Y.; Yang, G. *Angew. Chem. Int. Ed.* **2010**, *49*, 4915–4918.; Kim, S.Y.; Hong, J.-I. *Org. Lett.* **2007**, *9*, 3109–3112.; Swamy, K.M.K.; Lee, Y.J.; Lee, H.N.; Chun, J.; Kim, Y.; Kim, S.-J.; Yoon, J. *J. Org. Chem.* **2006**, *71*, 8626–8628.; Fillaut, J.-L.; Andries, J.; Toupet, L.; Desvergne, J.-P. *Chem. Commun.* **2005**, 2924–2926.; Kim, S.K.; Bok, J.H.; Bartsch, R.A.; Lee, J.Y.; Kim, J.S. *Org. Lett.* **2005**, *7*, 4839–4842.; Salman, H.; Abraham, Y.; Tal, S.; Meltzman, S.; Kapon, M.; Tessler, N.; Speiser, S.; Eichen, Y. *Euro. J. Org. Chem.* **2005**, 2207–2212.; Cho, E.J.; Moon, J.W.; Ko, S.W.; Lee, J.Y.; Kim, S.K.; Yoon, J.; Nam, K.C. *J. Am. Chem. Soc.* **2003**, *125*, 12376–12377.; Mizuno, T.; Wei, W.-H.; Eller, L.R.; Sessler, J.L. *J. Am. Chem. Soc.* **2002**, *124*, 1134–1135.; Yamaguchi, S.; Akiyama, S.; Tamo, K. *J. Am. Chem. Soc.* **2000**, *122*, 6793–6794; Miyaji, H.; Sato, W.; Sessler, J.L. *Angew. Chem. Int. Ed.* **2000**, *39*, 1777–1780.

(6) Chawla, H.M.; Gupta, T. *Tetrahedron Lett.* **2013**, *54*, 1794–1797.; Zhang, X.; Fu, J.; Zhan, T.-G.; Dai, L.; Chen, Y.; Zhao, X. *Tetrahedron Lett.* **2013**, *54*, 5039–5042.; Kim, H.J.; Kim, S.K.; Lee, J.Y.; Kim, J.S. *J. Org. Chem.* **2006**, *71*, 6611–6614.; Lee, S.H.; Kim, H.J.; Lee, Y.O.; Vicens, J.; Kim, J.S. *Tetrahedron Lett.* **2006**, *47*, 4373–4376.; Xu, G.; Tarr, M.A. Chem. Commun. **2004**, 1050–1051.

(7) Jiang, Y.; Hu, X.; Hu, J.; Liu, H.; Zhong, H.; Liu, S. *Macromolecules* **2011**, *44*, 8780–8790.; Ding, J.; Day, M. *Macromolecules* **2006**, *39*, 6054–6062.; Tong, H.; Wang, L.; Jing, X.; Wang, F. *Macromolecules* **2003**, *36*, 2584–2586.

(8) Ghosh, S.; Dey, C.K.; Manna, R. *Tetrahedron Lett.* **2010**, *51*, 3177–3180.; Ghosh, S.; Manna, R. *Supramol. Chem.* **2011**, *23*, 558–562.; Ghosh, S.; Dey, C. K. *J. Macromol. Sci. Pure & Appl. Chem. Part-A* **2014**, *51*, 217–222; Ghosh, S.; Manna, R. *RSC Adv.* **2014**, *4*, 5798–5802 and references therein.

(9) de Castro, C.S.; de Melo, J.S.S.; Fernández-Lodeiro, A.; Núñez, C.; Lodeiro, C. *Inorg. Chem. Commun.* **2014**, *47*, 27–30.; Singh, N.; Kaur, N.; Choitir, C.N.; Callan, J.F. *Tetrahedron Lett.* **2009**, *50*, 4201–4204.; Cho, E.J.; Moon, J.W.; Ko, S.W.; Lee, J.Y.; Kim, S.K.; Yoon, J.; Nam, K.C. *J. Am. Chem. Soc.* **2003**, *125*, 1237612377.

(10) Miyaji, H.; Sessler, J.L. *Angew. Chem., Int. Ed.* **2001**, *40*, 154–157.

(11) Lee, K.H.; Lee, H.-Y.; Lee, D.H.; Hong, J.-I. *Tetrahedron Lett.* **2001**, *42*, 5447–5449.

(12) Zhang, X.; Shiraishi, Y.; Hirai, T. *Tetrahedron Lett.* **2007**, *48*, 8803–8806.

(13) Ma, J.; Li, Z.; Zong, Y.; Men, Y.; Xing, G. *Tetrahedron Lett.* **2013**, *54*, 1348–1351.; Wen, Z.C.; Jiang, Y.B. *Tetrahedron* **2004**, *60*, 11109–11115.

(14) Winstanley, K.J.; Smith, D.K. *J. Org. Chem.* **2007**, *72*, 2803–2815 and references therein.; Lee, D.H.; Lee, K.H.; Hong, J.-I. *Org. Lett.* **2001**, *3*, 5–8.