



# A new insight into fluoride anion in electron transfer reactions



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## ABSTRACT

Recently, scientists have developed fluoride anion recognition synthetic macromolecules for potential applications in environmental monitoring. However, the actual role of fluoride anion remains highly debated in the reaction of anion-induced electron transfer (ET) to  $\pi$ -electron-deficient naphthalenediimides. The present study demonstrates that the ET reaction is induced by the complexation of  $F^-$  with the cation radical formed with the assistance of polar aprotic solvent. The results present an alternative mechanism of the actual role of  $F^-$  in ET reactions in polar aprotic solvents that could provide novel implications for anion-mediated ET reactions.

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## 1. Introduction

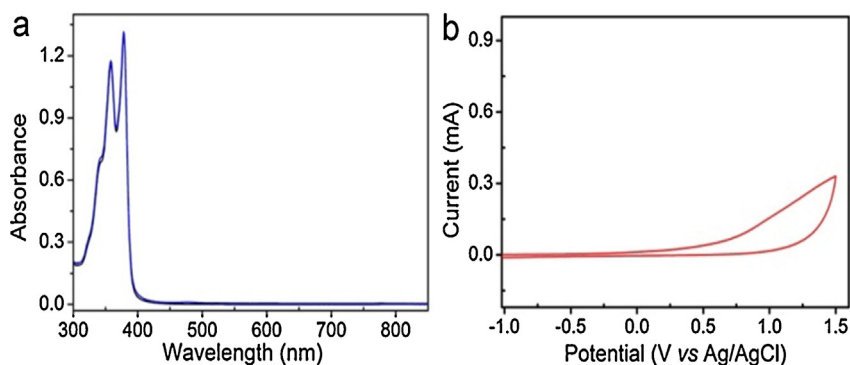
Anion recognition and transport play a critical role in many key chemical and biochemical processes [1–5]. However, the actual mechanisms of anion induced electron transfer (ET) remain highly debated. Recently, thorough studies have been conducted by Saha's group, and they found that  $F^-$  acted as a strong electron donor to reduce weakly oxidising naphthalenediimides [6–8] (NDI). Similar results were reported by Ballester et al. between  $F^-$  and 1,4,5,8,9,12-hexaazatriphenylene [9] (HAT(CN)<sub>6</sub>) in aprotic solvents. It was also proposed that the weak solvation of  $F^-$  in aprotic solvents render higher its Lewis basicity and, in turn, higher electron-donating abilities, whereas protic solvents (H<sub>2</sub>O, MeOH) can better solvate  $F^-$  and thus diminish its electron-donating ability.

Although  $F^-$  induced the thermal ET to form NDI radicals in aprotic solvents, there is still some concern about the involvement of one electron transfer from  $F^-$  to NDI to yield fluoride radicals ( $F^\bullet$ ), which includes: (1) the ESR spectrum of the radicals (assigned to  $NDI^{\bullet-}$ ) [6–8] obtained in  $F^-$ /NDI systems is not consistent with that of  $NDI^{\bullet-}$  with the characteristic superhyperfine structure reported in the literature [10]; (2) the good stability of the radicals under ambient conditions (last for an extended time) [6–8] is elusive given that strong reductive  $NDI^{\bullet-}$  (ca. –0.4 eV for  $E_{ox}$ ) can readily reduce oxygen to afford neutral NDI and superoxide ( $O_2^{\bullet-}$ ) [11]; (3) there is no evidence to prove that the weak solvation of  $F^-$  by aprotic

solvents can increase the electron-donating ability sufficiently to reduce NDI (ca. –0.4 eV for  $E_{red}$  [8,12]), though an aprotic solvent such as acetonitrile can negatively shift the oxidation potential of anions when compared to water [11]. Our observations herein (as revealed in Fig. 1a), where no electron transfer took place from  $F^-$  to NDI when dichloromethane, chloroform or toluene was used as aprotic solvent, further put the statement of  $F^-$  acting as the strong electron donor in aprotic organic solvents in doubt. Furthermore, the cyclic voltammogram displayed no oxidation reaction of  $F^-$  at the range of –1 to 1.5 V using acetonitrile as solvent (as shown in Fig. 1b), suggesting that the solvation of  $F^-$  by aprotic solvents did not result in a dramatic negative shift of the oxidation potential of  $F^-$ .

These elusive observations raise questions about the actual role of  $F^-$  in the ET reaction in aprotic solvents. In the present work, we demonstrate that the ET reaction in the NDI/ $F^-$  system is induced by the complexation of  $NDI^{\bullet+}$  and  $F^-$  (Scheme 1) combined with the solvation of polar aprotic solvents, not direct  $F^-$ -reduced NDI to afford  $NDI^{\bullet-}$ . The simultaneous formation of  $NDI^{\bullet-}$  with characteristic superhyperfine coupling lines and  $NDI^{\bullet+}$ - $F^-$  complex radical in deaerated solvents was confirmed by ESR measurements. In contrast, only the  $NDI^{\bullet+}$ - $F^-$  complex radical was observed under ambient conditions because  $NDI^{\bullet-}$  was readily oxidised by oxygen. We also conducted similar experiments for aperylenediimide (PDI), which has a larger conjugated backbone compared to NDI. An ET reaction induced by the  $PDI^{\bullet+}$ - $F^-$  complex in polar aprotic solvents took place, giving rise to  $PDI^{\bullet-}$  and  $PDI^{\bullet+}$ - $F^-$  complex radicals in the absence of oxygen, as confirmed by the ESR spectra. Our findings here provide a clear picture for the actual role of the Lewis base (e.g.,  $F^-$ ) in ET reactions in aprotic solvents.

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**Fig. 1.** (a) UV-vis absorption spectral changes of NDI (50  $\mu\text{M}$ ) (black) in dichloromethane upon the addition of 20 equiv.  $\text{F}^-$  (blue). Identical results observed when chloroform and toluene were used as the solvents. (b) Cyclic voltammogram of  $\text{F}^-$  (2 mM) in deaerated acetonitrile using  $\text{Bu}_4\text{N}^+\text{PF}_6^-$  (0.1 M) as the supporting electrolyte,  $\text{Ag}/\text{AgCl}$  as the reference electrode, platinum wire as the counter electrode, platinum as the working electrode, and a scan rate of 100 mV/s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

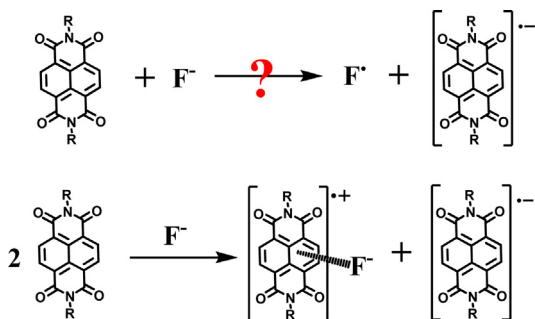
## 2. Experimental

### 2.1. General

Unless otherwise noted, all commercial solvents were HPLC grade and used as received. The tetra-*n*-butylammonium (TBA) salt of  $\text{F}^-$  (1 M solution in THF, containing ca. 5%  $\text{H}_2\text{O}$ ) was purchased from Sigma–Aldrich, Shanghai, China, and protected from moisture.

### 2.2. Measurements

UV-vis absorption spectra were measured on a PerkinElmer Lambda 35 spectrophotometer. Experiments were carried out in Teflon-stoppered 1 cm path length quartz cuvettes. Electron spin resonance (ESR) measurements were performed on a Bruker model E-500 electron paramagnetic resonance spectrometer at room temperature. The deaerated samples for the ESR measurements were prepared as follows. The DMF solutions of NDI (50  $\mu\text{M}$ ) or PDI (10  $\mu\text{M}$ ) and  $n\text{-Bu}_4\text{N}^+\text{F}^-$  with different equivalents were deaerated in a glove-box before mixing. The mixed solution was then loaded into a quartz capillary that was encapsulated into an NMR tube in the glove-box for ESR measurements. By simply removing the tube cap to expose the sample to air, the ESR spectral changes can be in situ observed. The settings were a centre field of 3482.00 G, a microwave frequency of 9.78 GHz and power of 6.39 mW. Cyclic voltammetry measurements of  $\text{F}^-$  (2 mM) were performed on a CHI760D electrochemical analyser in the deaerated DMF or acetonitrile containing 0.10 M  $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$  as a supporting electrolyte at room temperature. The platinum working electrode was rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an  $\text{Ag}/\text{AgCl}$  (0.01 M) reference electrode.



**Scheme 1.** Proposed mechanism for fluoride-induced ET to naphthalenediimide.

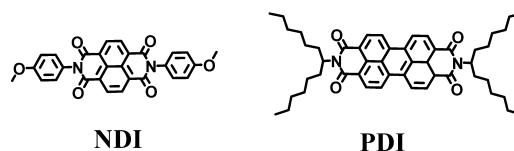
### 2.3. Synthesis

The NDI [7,13] and PDI [14] molecules used in this work were synthesised following the reported procedure and confirmed by  $^1\text{H}$  NMR and MOLDI-MASS.

## 3. Results and discussion

### 3.1. The stability of the radical species against oxygen

The typical NDI and PDI molecules we chose in this work are shown in Scheme 2 and were synthesised following the previously reported procedure. Our experiments were similar to those described in previous literature [7,8]. Upon the addition of 4 equiv.  $\text{F}^-$  into the DMF solution of NDI ( $\lambda = 340\text{--}390\text{ nm}$ ) (the blue line in Fig. 2a), the absorption features identical to those of  $\text{NDI}^{\bullet-}$  ( $\lambda_{\text{max}} = 473\text{ nm}$ ) appeared [7,8]. Likewise, the absorption spectrum generated upon the addition of 20 equiv.  $\text{F}^-$  into the DMF solution of PDI ( $\lambda = 490\text{--}530\text{ nm}$ ) was the same as the featured absorption of  $\text{PDI}^{\bullet-}$  ( $\lambda_{\text{max}} = 702\text{ nm}$ ) [15] (as shown in Fig. 2b). On the basis of the spectra features, it seems reasonable to presume the generation of  $\text{NDI}^{\bullet-}$  or  $\text{PDI}^{\bullet-}$  via  $\text{F}^-$ -induced ET reaction. However, the formed radical anions were relatively stable under ambient conditions (lasting over tens of minutes), which is not consistent with the fact that  $\text{NDI}^{\bullet-}$  or  $\text{PDI}^{\bullet-}$  can readily be oxidised by oxygen [15]. This observation motivated us to investigate the stability of these radical species against oxygen. We first performed the  $\text{F}^-$ -induced ET reaction in the deaerated DMF solution of an NDI/ $\text{F}^-$  or PDI/ $\text{F}^-$  system and then exposed the resulting system to air. As shown in Fig. 2a or b, the featured absorption (red line) in the absence of oxygen was greatly enhanced compared to that generated under ambient conditions. When exposed to air, the featured absorption quickly decreased in the beginning until it reached the value observed under ambient conditions (Fig. S1). These observations led us to consider if the observed radicals in the absence or presence of oxygen belong to different type of radicals rather than only radical anions as previously reported [7,8].



**Scheme 2.** NDI and PDI molecules studied in this work.

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