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Antioxidant-substituted tetrapyrazinoporphyrazine as a fluorescent sensor for basic anions†‡§

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Tetrapyrazinoporphyrazine substituted at its periphery with eight antioxidant 3,5-di-*t*-butyl-4-hydroxyphenyl groups behaves as a turn-on fluorescent sensor for fluoride anions. Conversely, the precursor antioxidant-substituted 1,2-phthalonitrile was found to act in turn-off mode suggesting that the origin of the phenomenon lies at the phenolate-substituted 1,4-pyrazinyl moiety.

Chromophoric molecular systems for sensing of analyte species are receiving increasing attention[1] due to their ease of preparation, high sensitivities and tunable specificities as well as for their simple implementation. Several dye species have been developed for this purpose especially the oligo-pyrromethanes[2] and porphyrinogens.[3] Phthalocyanines, although possessing several of the requirements of facile syntheses, well-defined electrochemistry and intense optical absorptions, which might be strongly perturbed by analyte species, have been less well developed for use as sensing elements despite the phthalocyanines being one of the best studied classes of organic compounds.[4] On the other hand, fluoride and other anions are important analytes for a variety of reasons including potential toxicities. Detection of fluoride anions may be facilitated due to its differing reactivity from the other halides and several promising chemical sensors of fluoride anions have been reported.[5] Usually their sensing capabilities are based on variation of electronic absorption (or fluorescence) spectra in the presence of fluoride anions or modulation of electrochemical potentials.[6] Additionally, substantial changes in colour can be used as a qualitative indicator of the presence of fluoride (or other) anions in analyte solutions.[7]

In this work we have prepared a tetrapyrazinoporphyrazine[8] substituted with antioxidant 2,6-di-*t*-butylphenol groups with the initial aim of investigating any structural changes that might be promoted by oxidation of the compound in a way analogous with other similarly substituted molecules.[9] Unexpectedly, our new tetrapyrazinoporphyrazine derivative was found to operate as a fluorescent sensor especially for fluoride anions due to the phenolic substituents whose acidity is such that deprotonation occurs in the presence of basic anions.[10] That is, the compound 2,3,9,10,16,17,23,24-*octakis*(3,5-di-*t*-butyl-4-hydroxyphenyl) tetrapyrazinoporphyrazine, **1** (Fig. 1), operates as a chromogenic and fluorogenic indicator for the presence of fluoride anions (and other basic anions) in solutions. **1** precursor **2**[11,12] was also found to be sensitive to the presence of basic anions. Control analogues of **1** and **2** bearing no phenol substituents were also prepared.[12]

Compound **1** was synthesized according to methods reported by Makhseed, McKeown and coworkers.[12,13] McKeown and coworkers have previously prepared phthalocyanines peripherally substituted with up to four 3,5-di-*t*-butyl-4-hydroxyphenyl groups.[14] A subphthalocyanine analogue of **1** was also recently reported.[15] Although metal complexes (*e.g.* Co^{II}) of **1** can be obtained with good purity,[16] samples of the free base tetrapyrazinoporphyrazine **1** always contained ~5% of a singly hexyloxy-substituted molecule due to the *in situ* substitution of a 3,5-di-*t*-butyl-4-hydroxyphenyl group during the macrocyclisation (Li/hexanol; reflux) as reported previously.[13]

Fig. 1(a,b) respectively show the chemical structure and a scanning tunneling microscopy image of **1** while Fig. 1(c,d) respectively show the structure of **1** precursor **2** as well as a

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‡ Electronic Supplementary Information (ESI) available: Details of syntheses, additional experimental procedures and cif files for **2** and its semi-substituted precursor 5-chloro-6-(3,5-di-*t*-butyl-4-hydroxyphenyl) pyrazine-2,3-dicarbonitrile, **3**. See DOI: 10.1039/c2cc30712j

§ X-ray Crystallography data for **2**: $C_{34}H_{42}N_4O_2$, M = 538.72 g mol^{-1}, space group P 43 21 2, a = 15.9922(12), b = 15.9922(12), c = 12.4393(19) Å, α = 90.00°, U = 3181.36(59) Å^3, Z = 4, ρ_{calcd} = 1.125 mg m^{-3}, μ(Mo-Kα) = 0.070 mm^{-1}, 25867 reflections measured, 1997 were unique (Rint. 0.0271); refinement against F2 to $wR2$: 0.1360, R_1 = 0.0491 (1855 reflections with $I > 2\sigma(I)$), 193 parameters.

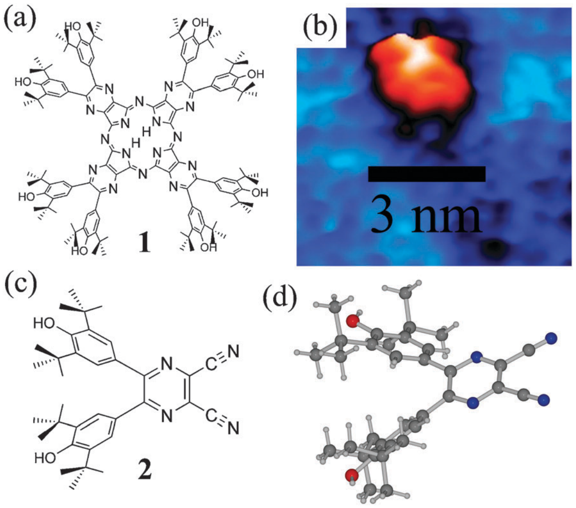

Fig. 1 (a) Chemical structure of **1**. (b) Scanning tunneling microscopy (STM) image of **1** (sample bias = 1.5 V). (c) Chemical structure of **2** and (d) its X-ray crystal structure.

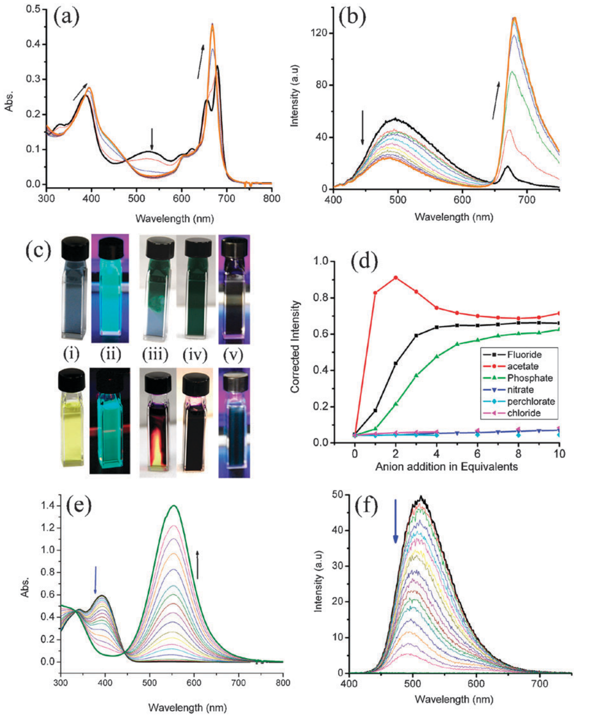

Fig. 2 Electronic absorption spectra (UV-vis) and fluorescence emission (Fl) spectra of **1** and **2** in the presence of increasing quantities of fluoride anions in benzonitrile solution. (a) **1**; UV-vis. (b) **1**; Fl. ($c = 5 \times 10^{-6}$ M) (c) Photographs of solutions of **1** (upper) and **2** (lower) in benzonitrile: (i) No anions present; (ii) no anions present with irradiation (365 nm UV); (iii) just following addition of a drop of a solution of tetrabutyl-ammonium fluoride; (iv) mixed with an excess of F^- anions; (v) with F^- under 365 nm UV. (d) Change in fluorescence emission intensity from **1** in the presence of increasing quantities of the noted anions. (e) **2**; UV-vis. (f) **2**; Fl. ($c = 8 \times 10^{-6}$ M).

view of the X-ray crystal structure of the latter. The STM image clearly shows the lobes of the molecule and a two-tier arrangement of the bulky *t*-butyl groups[12] caused by their twisting due to steric requirements and surface interactions. The molecular structure of **2** reveals the twisting of phenyl substituents and an angle of 39.8° is subtended between the 1,4-pyrazinyl ring and phenyl rings of the phenol substituents. Such an arrangement may persist in tetramerised **2**.

1 responds to the presence of fluoride anions by changing colour of its solutions in organic solvents from gray-blue to green. Variation of its UV/vis spectrum upon addition of fluoride anions is shown in Fig. 2(a). Essentially, bands around 700 nm coalesce while the broad band at 540 nm disappears. Additionally, a large fluorescence response was found (Fig. 2b) with a very substantial increase in emission intensity at 680 nm with a decrease in intensity of the fluorescence emission band at 500 nm.[17] Phthalonitrile precursor **2** also responds to the presence of fluoride anions. A new intense absorbance band appears at 550 nm in its UV/vis spectrum with concurrent attenuation of the band at 400 nm (Fig. 2e). Also, in contrast to **1**, fluorescence emission intensity of **2** is completely attenuated by addition of fluoride anions (Fig. 2f). Analogues of **1** and **2** containing no phenol groups[12] underwent no similar variation in their electronic absorption or fluorescence spectra indicating strongly that the phenol groups of **1** and **2** are interacting with fluoride anions, most likely through deprotonation.[10]

To assess the degree of deprotonation of **1** necessary for anion detection the dependency of the fluorescence emission intensity on the amount of fluoride or other anions present was investigated (see Fig. 2d). This data suggests that approximately 4 equivs of the respective anions suffice to saturate the fluorescence response of **1**. Photographs of solutions of **1** and **2** in benzonitrile[18] in the absence and presence of F^- anions (Fig. 2c) show its colour variations suggesting use of **1** as a sensor for F^- anions. **1** and **2** exhibit a similar yellow-green fluorescence [around 500 nm; Fig. 2c(ii)], which originates at their substituted pyrazinyl moieties. In **2**, addition of F^- anions causes formation of a deep purple almost non-emissive solution [Fig. 2c(v); $\lambda_{max} = 550$ nm].[19] In contrast, **1** contains bands at 500 nm and a weak fluorescence band at 680 nm.[12,17] When F^- anions are added emission at 500 nm is attenuated while emission at 680 nm due to deprotonated species is enhanced. We are currently investigating these phenomena from experimental and theoretical viewpoints.

Fig. 3 shows the cyclic voltammograms of **1** and **2** measured in benzonitrile solution. **1** exhibits two reversible and three quasi-reversible reduction processes and, interestingly, these reduction waves of **1** are anodically shifted by up to 100 mV depending on the quantity of fluoride anions added. On the other hand, **2** does not undergo well-defined redox processes in its reduction wave. The redox behaviour of **1** is due to the conversion of phenolate groups to easily reducable hemiquinonoid groups, a feature which is observed in other similarly substituted compounds including porphyrins[20] and several other species.[9c,d,e] **1** appears not to be significantly affected by addition of F^- anions in terms of UV/vis (*i.e.* it still exhibits a typical phthalocyanine-like spectrum) so that it is not surprising that only observable shifts in reduction potentials can be observed. On the other hand, **2** is strongly affected apparently experiencing strong delocalization of its electron system upon deprotonation. This results in a new UV/Vis band[19] and also to two reversible oxidations presumably due to oxidation to a quinonoid state.[12]

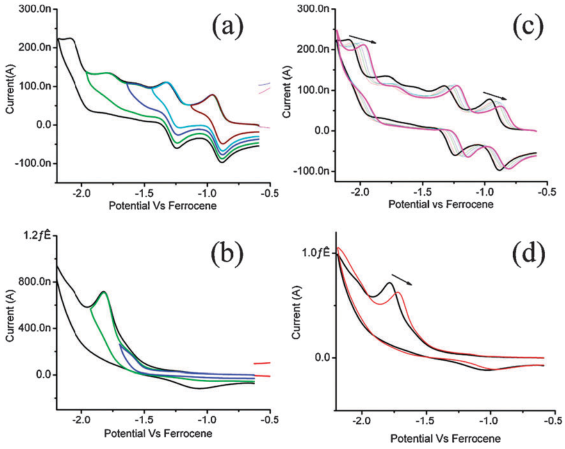

Fig. 3 Cyclic voltammograms in benzonitrile/(0.1 M n-Bu$_4$N ClO$_4$). (a) **1**. (b) **2**. (c) **1** in the presence of increasing amounts of fluoride anions (up to 10 eq.). (d) **2** in the presence of increasing amounts of F$^-$ (up to 10 eq.).

In conclusion, we have synthesized for the first time a phthalocyanine-type molecule, **1**, symmetrically substituted at its periphery with eight antioxidant 3,5-di-*t*-butyl-4-hydroxyphenyl groups. The phenol groups of **1** confer on it sensing abilities in terms of its increased fluorescence emission when it is deprotonated by basic anions especially fluoride, acetate or phosphate. In addition, **1** precursor **2** is also active as a fluorescent sensor for basic anions although it contrasts with **1** in that its fluorescence is attenuated. **1** and **2** also exhibit electrochemical responses which are modified in the presence of fluoride anions making these compounds also interesting as potential redox anion sensing elements. Apart from these features, **1** is an unusual molecule bearing multiple phenol groups that can exist in several stable forms including as phenoxyl radicals. This implies potential applications for **1** as a molecular memory element since it can in principle possess many redox states although these may be subject to delocalization. We are currently investigating the redox properties of **1** and some unsymmetrically substituted derivatives and metal complexes at the single molecule level.

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