A subtle change in substituent enabled multi-ways fluoride signals including paper-strip colorimetric detection using urea receptor functionalized 1,1,4,4-tetracyanobuta-1,3-diene-based push-pull chromophore

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Supporting information is available

Abstract: A simple color change detection by the naked-eye using untreated paper for a biologically relevant fluoride (F^-) anion in water is a challenge. New non-planar push-pull chromophore involving intramolecular charge-transfer (ICT) from urea donor in 2,3-disubstituted-1,1,4,4-tetracyanobuta-1,3-diene (TCBD) turns out to be an efficient system for detecting F^- ion giving various output signals. But, replacing phenyl (Ph) at C_3 -position with 4-(dimethylamino)phenyl (DMA) led to the absence of colorimetric and fluorometric detections due to the masking and quenching, nature of strong ICT by the DMA. NMR and electrochemical studies revealed that the sensing mechanism is governed by H-bonding as well as the deprotonation of N–H attached with TCBD moiety which reduces the HOMO–LUMO gap and causes the dramatic color change. Coupled with excellent sensitivity (3 ppm) and specificity towards F^- , a successful demonstration of cheap tissue paper-based visual strip-detection in aqueous is presented.

Introduction

Human health is very much dependent on drinking water. Naturally, micronutrient fluoride (F^-) is present in the ground-water and the level of F^- contamination is ranging from 1 to 30 ppm based on geology.^[1] According to the world health organization, the maximum permissible limit of F^- in drinking water is 1.5 ppm and at this level, it prevents dental caries and bone disorder issues.^[2] The environmental protection agency fixed the maximum contaminant level for F^- in drinking water as 4 ppm.^[3] Consuming ≥ 4 ppm for a long time may lead to dental and

skeletal fluorosis, and disease may cause teeth mottling and calcinations of ligaments, bone deformities, and other physiological disorders, and that can ultimately, lead to death.^[4] As a whole, F^- is one of the most beneficial micronutrients for our body but not in optimum level can harm us in many ways. Therefore to get beneficial effects of F^- , it is important to detect and quantify the F^- content before consuming drinking water especially countries like Brazil, China, India, and throughout Africa, where F^- content and dental fluorosis is more prevalent.^[5] Simple, equipment-free, easy to perform detection kit with high sensitivity and specificity over other common anions is the need of the hour as the main demands are remote place checking, periodic testing to maintain the optimum level, and sense of satisfaction to those living in the F^- rich areas.

Significant interests have been devoted to the development of colorimetric chemosensors (F^- reversibly bind to the receptor motif) due to the promising possibility for the low cost and equipment free selective F^- ion detection kit.^[6] Although other approaches like coordination of F^- to trivalent boron^[7] and luminescent lanthanide complexes^[8] have been investigated for colorimetric indicators, the major approach used for this purpose is to adopt H-bond donors such as urea, N–H, or imine moieties which have been proven to bind with high electronegative atom like F^- ion selectively while conjugated with a chromophore unit for detection output.^[9]

Though a vast number of reports are available for chromogenic and chromo-fluorogenic receptors in solution,^[4b,10] in this article, we focus mainly on the limited number of reports which studied solid-phase detection (see Table S3, Section F, in the

Supporting Information). Colorimetric and ratiometric fluorescent chemosensors for F^- have been prepared, which are based on a combination of desilylation reaction and excited-state proton transfer from the desilylation product to F^- .^[11] In 2014, Rurack et al reported strip and solution F^- detection in dimethylsulphoxide (DMSO)/ H_2O system but with the help of lateral-flow fluorescence reader.^[12] Duan and Bai et al. have developed a chromogenic and fluorogenic dual signal responding F^- sensor, comprising of a photoactive $Ru(bipy)_3$ moiety ($bipy=2,2'$ -bipyridine) derivatives and a 2,4-dinitrophenylhydrazone chromophore, which can detect F^- in aqueous media at a low limit about 10 ppm using an easy-to-prepare F^- test-paper.^[13] There are a couple of other examples also reported using Schiff base derivatives, though they show the promising colorimetric change in test-strip kit. In general, they generally do not exhibit high selectivity towards F^- as other anions such as acetate, phosphate, and in some case chloride also show the color change.^[14] S. Ghosh et al. have shown that colorimetric test-strip-based F^- sensing with good selectivity using Schiff base derivative, however, this receptor works only in acetonitrile (CH_3CN).^[15] All these receptors suffer some drawbacks such as, they generally exhibit color change only in organic-medium and in organic F^- source, competing-affinity towards acetate and phosphate ions, relatively high minimum detection limit of 10–30 ppm, work only with conc. HCl, use of metal, delayed response, etc while some work only with UV-lamp and chemically treated paper. One of the challenges in H-bonding mediated F^- recognition is its reversibility in water (H_2O).^[16] Hence, no single receptor works under environmentally relevant aqueous conditions and without any of the above limitations. To overcome this challenge, our approach is to combine the urea moiety with a strong chromophore whose charge-transfer (CT) properties can be greatly altered upon binding with F^- ion. Thus, enabling to exhibit enhanced colorimetric color change.

Various electron-donating group (EDG)-substituted TCBDs were known as strong chromophores due to their push-pull nature with remarkable intramolecular charge-transfer (ICT) process.^[17] These push-pull TCBDs are very colorful and they generally do not exhibit emission property due to photoinduced electron transfer (PET) process.^[18] Recently, we demonstrated a methodology for the synthesis of mono (C_2)-substituted 1,1,4,4-tetracyano-1,3-butadienes (TCBDs) including compound mono-TCBD with urea moiety as EDG, which exhibited unusual luminescence property with white-light emission (Figure 1).^[19] However, its use in sensing of F^- ion in combination with urea moiety has not been reported before.

Figure 1. Molecular structure of mono-substituted TCBD.^[19]

Hence, upon testing they failed to exhibit F^- sensing ability based on UV/Vis, fluorescence, and more importantly naked-eye detection in both solution as well as in solid-phase (Figure S16, Supporting Information). Failure to sense F^- can be attributed to the aggregation phenomenon between intermolecular urea

moieties leading to unavailability H-donors for fluoride.^[19,20] We envisaged that substitution of **mono-TCBD** at the C_3 -position with phenyl (Ph) and 4-(dimethylamino)phenyl (DMA) would retain the single molecular integrity of resulting 2,3-disubstituted 1,1,4,4-tetracyano-1,3-dienes **1** and **2**, respectively due to the absence of relatively unstable free dicyanovinyl (DCV) moiety (Figure 1, Scheme 1).^[19] Herein, we show that how the judicious choice of substituents at the C_3 -position in non-planar push-pull chromophores **1** and **2** led to multi-ways F^- detection including non-chemical treated paper-strip based colorimetric sensing under aqueous medium.

Results and Discussion

The first time synthesis of 2,3-disubstituted non-planar push-pull chromophores **1** and **2** conjugated with urea receptor moiety is shown in Scheme 1. A two-steps synthesis involving the preparation of urea-functionalized unsymmetrical alkynes **5** and **6** with $-H$ and $-NMe_2$ as R, respectively, followed by [2+2] cycloaddition-retroelectrocyclization (CA-RE) reactions with tetracyanoethene (TCNE) to provide the corresponding **1** and **2** chemosensor molecules is described. The synthesis of alkyne precursors **5** and **6** was accomplished by the corresponding NH_2 -functionalized unsymmetrical alkynes **3** and **4** reactions with benzyliocyanate, respectively. It was found that the alkyne **6** with two donor moieties (urea and $-NMe_2$) underwent smooth reaction at 25 °C providing **2** in 79% yield. Whereas, alkyne **5** with only one donor moiety (urea) requires to be heated at 70 °C and the presence of Lewis-acid ($LiClO_4$)^[21] has improved the yield by up to 83% isolated yield for compound **1**. All new compounds were characterized by IR, NMR, and ESI-MS spectral techniques (see Section A, Supporting Information).

Scheme 1. Synthetic pathway for compounds **1** and **2**: i) CH_2Cl_2 , 25 °C, 24 h, 75% (**5**), 70% (**6**); ii) $ClCH_2CH_2Cl$, $LiClO_4$, 70 °C, 1 h, 83% (**1**); CH_2Cl_2 , 25 °C, 1 h, 79% (**2**).

The unambiguous structural identity for receptor **1** was obtained by a single-crystal diffraction study (CCDC number: 2016856; Figure 2, for details, see Section C in the Supporting Information). Unlike mono-substituted TCBDs,^[19] the di-substituted TCBDs such as phenyl-TCBD **1** and DMA-TCBD **2** did not exhibit self-assembly behavior driven by the H-bonded network in solution. However, in solid-state, as revealed by the crystal structure that urea exhibits, its characteristics one-dimensional H-bonded α -networks with a repeat distance of about 4.62 Å (Figures 2b,c, Figure S15).^[20a,b] Very interestingly, the crystal packing in the unit cell has revealed that arrangement between the molecules has adopted an entropically unfavorable D–A segregated structure which is difficult to develop by self-assembly (Figure 2c).^[20c,d] We infer that the segregated structure

is stabilized due to the strong-H-bonding of α -networks such kind of arrangement has not been observed for other TCBDs reported so far.^[18] Similar to other EDG-substituted TCBDs,^[18] the chromophore **1** also exhibited non-planarity at the single bond of TCBD part with a dihedral angle (θ) of 132°. To understand the nature and extent of the CT, the quinoid character (δr (Å)) parameter was calculated based on the bond lengths alternation in the benzene ring substituted by donor group (for a formula see caption to Figure 2a, for bond lengths, see Figure S15 in the Supporting Information). It has been used previously for other TCBDs in excellent agreement with other structural characterization.^[22] In benzene, the δr value equals 0, whereas values between 0.08 and 0.1 are found in fully quinoid rings. The calculated δr value for compound **1** was found to be 0.031 Å which is a good indication for the partial CT from the urea donor to the DCV-acceptor moiety. This is quite comparable with similar TCBDs with aniline as donor.^[23,18]

Figure 2. a) ORTEP plot of **1** with vibrational ellipsoids shown at the 50% probability level (H-atoms are omitted for clarity). Arbitrary numbering. For selected bond lengths (Å) and angles (°), see Figure S15. Quinoid character: $\delta r = \{[(a + a') - (b + b')]/2 + [(c + c') - (b + b')]/2\}/2$.^[22] b) Arrangement of neighboring molecules in the crystal packings within the unit cell of **1**. c) selected part of a one-dimensional H-bond network showing segregated donor and acceptor units in the crystal packing along the c-axis.

The obtained chromophores **1** and **2** have yellow and maroon colors, respectively in solution due to ICT bands arise from urea to the π -conjugated DCV moiety in **1**. Whereas in compound **2**, in addition to this CT, the additional lower-energy CT arise from NMe_2 to the π -conjugated DCV moiety is responsible for the more intense maroon color. This delicate balance in the CT property of **1** and **2** prompted us to investigate their ability to detect F^- ion colorimetrically. Visual detection and UV/Vis absorption spectroscopy were carried out to check the visible color change that occurs when receptors **1** and **2** are titrated with tetrabutylammonium (TBA) salts of the various anions in DMSO solution. A yellow solution of TCBD **1** (1.0×10^{-5} M) turned into a maroon color when treated with one equivalent (eq) of F^- ion, whereas no color change was detected when treated with other anions up to 15 eq such as Cl^- , Br^- , I^- , OAc^- , ClO_4^- , PO_4^- , N_3^- , NO_2^- , and NO_3^- (Figure 3a). Although at 1 ppm we could see the color change, quite distinguishable color of maroon

with the minimum level of detection was found to be at 3 ppm in $\text{H}_2\text{O}/\text{DMSO}$ 1:1. The intense color change was observed even with 1 ppm in DMSO alone. These results indicate that receptor **1** acts as an efficient and specific colorimetric sensor for F^- ion. Similarly, the UV/Vis spectra of these solutions showed no significant shift in the λ_{max} of TCBD **1** at 410 nm for various anions, except for F^- ion which showed a greater bathochromic shift of 78 nm (Figure 3b) suggesting the CT band energy between the urea to the acceptor moiety has been reduced because of F^- ion interaction. Interestingly, though similar CT also exist in TCBD **2**, however, TCBD **2** having additional CT due to NMe_2 substitution at the C_3 -position did not exhibit any color change even up to 30 eq addition of F^- ion (Figure S22). This is because the newly generated CT upon F^- binding probably overlaps with the existing CT of the NMe_2 group.^[18]

Figure 3. a) Color changes and b) changes in absorbance of **1** (1.0×10^{-5} M in DMSO) after the addition of 15 eq of various anions in the DMSO solution.

UV/Vis titration experiments were performed to investigate the quantitative analysis of receptor Ph-TCBD **1** for F^- ion (Figure 4a). In the absence of anions, the spectrum of **1** showed maximum absorbance bands λ_{max} at 338 and 410 nm which are assigned to CT-transitions from urea to acceptor (DCV) moiety in the receptor. It is well known that acidic proton from urea tends to bind with electronegative F^- ion via H-bonding interactions.^[9,24] The band at 410 nm for **1** disappear gradually with the formation of a new peak centered at 488 nm, resulting in a clear isosbestic point that was observed at 450 nm on the incremental addition of F^- ion (2.0 eq). A significant bathochromic shift of $\Delta\lambda_{\text{max}}$ of 78 nm can be attributed to enhanced CT interaction between the urea and the acceptor moiety.

Ph-TCBD **1** can also act as a fluorometric sensor as demonstrated by the fluorescence titration experiment in DMSO (Figure 4b). In the absence of anion, **1** exhibited emission at 441 nm upon exciting the solution at 375 nm. The gradual addition of F^- (2 to 6 eq) increases the emission intensity at 475 nm for up to ~1.8 times than its original intensity. Further increment of F^- (6 to 30 eq) quenches the emission significantly up to ~60% of its original increased intensity. This indicates that fluorescence gets enhanced due to H-bonding interaction of F^- with N–H at lower

concentration and gets quenched due to deprotonation of more acidic N–H proton. This observation was supported by the NMR study (*vide infra*). Similarly, fluorescence titration experiment has been carried out with DMA-TCBD **2**, but there is no noticeable emission in the spectra with or without F[−]. It is well known that generally, DMA-TCBDs do not exhibit emission property due to the PET process.^[18]

Figure 4. a) UV/Vis spectral changes of chromophore **1** (1.0×10^{-5} M) upon titration of TBAF (0–22 eq) in DMSO. b) Fluorescence titration spectra of chromophore **1** (1.0×10^{-6} M) with the addition of different equivalents of TBAF in DMSO ($\lambda_{\text{ex}} = 375$ nm). c) Job's plot at 490 nm in the DMSO solution. d) B-H plot for the titration of **1** with F[−] ion.

Continuous variation methods were applied to determine the stoichiometric ratio of the chromophore **1** with F[−] using UV/Vis spectroscopy. A Job-plot of receptor **1** with F[−] in DMSO shows maxima at 0.5 of $[F^-]/([F^-] + [1])$ (Figure 4c). This phenomenon confirmed that the TCBD **1** associated with F[−] is 1:1 ratio during the initial stage of the reaction. The binding stoichiometry of TCBD **1** with F[−] ion also calculated by the Benesi-Hildebrand (B-H) equation: A_0 is the absorbance of neat **1**, A_∞ is the absorbance treated with the excess amount of F[−], A is the absorbance treated with a certain concentration of F[−] ion, K is the binding constant (M^{-1}) and $[F^-]_0$ is the concentration of F[−] ion (M). The plot of $1/(A - A_0)$ against $1/[F^-]_0$ showed linear relationship ($R = 0.9998$), indicating that TCBD **1** bound to F[−] ion in 1:1 stoichiometry (Figure 4d). The association constant K between **1** and F[−] ion was determined from the ratio of intercept/slope to be $1325 M^{-1}$.

Figure 5. a) Schematic representation of H-bonding and deprotonation mechanism involved in the chemosensor of **1** by F[−] ion. b) ¹H-NMR titration spectra of **1** (2×10^{-3} M) with various equivalents of F[−] ion in DMSO- d_6 (inset: chemosensor **1** with and without F[−] ion in DMSO- d_6).

¹H-NMR titration experiments were carried out in DMSO- d_6 to establish the actual interaction between the F[−] as TBA salt and chemosensor **1** (Figure 5). The two N–H protons of urea moiety having distinct acidity as indicated by chemical shift values of 9.5 and 7.0 ppm of which N–H attached to TCBD part is more acidic. When 1 eq of F[−] is added, both N–H of urea signals completely disappear while other peaks broadened. Further, the gradual addition of F[−] until 5 eq showed the reappearance of N–H attached to TCBD moiety, but not the N–H attached to TCBD moiety, also other broad peaks turn into sharpened. Meanwhile, when ≥ 5 eq of F[−] addition, a new peak characteristic of $[HF_2]^-$, started to appear at 15.7 ppm (triplet). This indicates that F[−] interacts with Ph-TCBD **1** through H-bonding at lower concentration (0 to 2 eq), but at higher concentration (> 2 eq), it induces the deprotonation of N–H proton attached to the TCBD moiety.^[9d] After deprotonation, the anion generated at the N-atom in **1**–H would tend to delocalize to DCV moiety through Ph linker (Figure 5a). This explains the enhanced CT which resulted in contrast color change from yellow to maroon color (Figure 5 inset). Similarly, various equivalents of the TBAF titration experiment by ¹H-NMR has been carried out for DMA-TCBD **2** in DMSO- d_6 and found a similar change in the NMR signals (Figure S14). However, no colorimetric change has been observed presumably due to CT overlaps by the DMA to DCV moiety (*vide infra*).

Figure 6. Cyclic voltammetry of **1** (1.0×10^{-5} M) upon titration of TBAF (0.1–2 mM) in DMF.

The electrochemical properties of chromophores **1** and **2** were analyzed by cyclic voltammetry (CV) technique, containing 0.1M Bu₄NClO₄ in DMF at 25 °C (see Table S2). Further, the redox properties of receptors **1** and **2** alone and in the presence of various concentrations of F[−] were studied (see Section E, Supporting Information). Both the receptors have exhibited two reversible well-resolved reduction peaks, centered at $E_0 \approx -0.72$; -1.16 V vs Fc/Fc⁺ and $E_0 \approx -0.90$; -1.25 V vs Fc/Fc⁺ for Ph-TCBD **1** and DMA-TCBD **2**, respectively. The two reversible peaks are ascribed to the stepwise formation of the anionic radical and dianionic-species. The reverse scan indicates the corresponding

oxidation as shown in Figure S23. The electron-deficient DCV moiety is responsible for reversible peaks and the reduction potentials of DCV can be tuned by properly choosing EDG.^[18] At positive potentials, the urea donor of Ph-TCBD **1** oxidizes irreversibly, indicated by the steep rise in the anodic current around 1 V. The anodic current for the oxidation of the DMA-TCBD **2** appears at ~ 0.7 V which is approximately 300 mV more negative than the Ph-TCBD **1**. The easy oxidation of the DMA-TCBD **2** may be attributed to the presence of electron-rich DMA moiety. The oxidations of the donor on both compounds are irreversible due to the chemical reactions after the electron transfer. The DMA-TCBD **2** exhibits a lower HOMO to LUMO (H-L) band-gap of ~ 1.52 eV than **1** which shows ~ 1.67 eV (Table S2). Figure 6 shows the titration of F^- ion (as TBAF) to the DMF solution of receptor **1**. On the gradual increment of F^- (0.1–2 mM), the negative shift in the first reversible reduction wave is observed as shown in the inset. There is no change in the peak potential observed after the concentration of F^- equivalent to the concentration of compound **1**, indicated by the parallel line to the x-axis. A similar titration experiment was carried out with receptor **2**, and the 90 mV negative shift in the first reduction wave at -0.90 V was observed (Figure S24).

To get further insights into the electronic and molecular structural properties and to interpret the interaction between the F^- and receptors **1** and **2**, theoretical calculations based on density functional theory (DFT) were carried out. The geometries of all the compounds were first optimized using the B3LYP/def2-TZVP method.^[25] The electronic absorption spectra were computed by the means of time-dependent DFT (TD-DFT)^[25,26] calculations by computing the singlet vertical excitation energies and their oscillator strengths employing the CAMB3LYP^[27] functional. Complete details of the computational methods are given in Section G, Supporting Information.

Figure 7. Calculated UV/Vis electronic spectra of a) **1** and b) **2** and corresponding deprotonated species **1-H** and **2-H**, respectively obtained from CAM-B3LYP/def2-TZVP level. The molecular orbitals associated with the lowest energy transition at 414 nm and 513 nm for **1** and **1-H**, respectively reveal ICT from urea-phenyl to DCV. For **2** and **2-H**, overlapping ICT bands are observed at 469 nm and 497 nm, respectively.

As illustrated in Figure 7, the calculated electronic spectrum of **1** reveals the lowest-energy absorption at 414 nm arising due to the electronic transition from HOMO to LUMO. Frontier molecular orbitals sketch indicates that the orbital transition from H-L involves ICT from urea-phenyl to DCV. However, the CT band arising from the H-L transition for the deprotonated species by the F^- ion (**1-H**), got significantly shifted to 513 nm with $\Delta\lambda = 99$ nm as observed in the UV/Vis study (Figure 4a). The orbital contributions for the other dominant peaks of **1** and **1-H** are tabulated in Table S7. Similarly, the TD-DFT electronic spectrum of chromophore **2** is shown in Table S8 and Figure S27) reveals two ICT bands at 382 and 469 nm corresponding to transitions from urea to DCV (H-1 $\rightarrow$ L) and DMA to DCV (H $\rightarrow$ L). Whereas, for the deprotonated species of **2-H**, a new CT band is observed at 497 nm, which overlaps closely with the existing CT at 469 nm of **2** by the DMA moiety. This explains the absence of colorimetric detection for receptor **2**.

Figure 8. a) Wet-agarose gel prepared with no fluoride followed by the addition of **1** (10 μ L, 1 mM), b) wet-Agarose gel prepared with F^- (3 eq ratio concerning the **1**) water followed by the addition of **1** (10 μ L, 1 mM), c) agarose gel (dried 15 h at the ambient condition) prepared with no F^- followed by the addition of **1** (10 μ L, 1 mM), d) agarose gel (dried 15 h at the ambient condition) prepared with F^- (3 eq ratio concerning the **1**) water followed by the addition of **1** (10 μ L, 1 mM).

A comparison table is provided in Table S3, in Section F, Supporting Information, for the chromo-fluorogenic receptors reported in the literature that deal with strip detection. It is noteworthy that Ph-TCBD **1** has shown multi-ways responses, as so far the reported receptors have limitations of at least any one aspect including aqueous detection. Though Ph-TCBD **1** has shown positive responses in almost every analytical techniques such as UV/Vis, fluorescence, NMR, and CV, these methods are inconvenient and expensive to be applied in the real-time application. Even liquid phase colorimetric detection is inconvenient to handle on-site detection due to multiple reasons like requiring more quantity of receptor, the requirement of apparatus, etc. Thus, colorimetric test-strip based assay was desired to achieve the detection of F^- in the mixture of an aqueous medium. Preliminary investigations were failed to exhibit color change during the initial testing for paper-strip detection using Whatman filter papers and commercial notebook papers, as the paper-strip detection is hard to obtain especially in an aqueous system (Table S3). To overcome this, instead of cellulose-paper, acid-treated hydrophobic paper nitrocellulose has been used.^[12] Other than the paper support, we also tried using the polymeric

system as support, for example, agarose gel was prepared with and without F^- ion separately followed by the treatment of TCBD **1** solution. However, these studies did not yield the desired color change (Figures 8a,b). We infer that the presence of water in the gel prevents the F^- binding reaction, to overcome this challenge, we have carried out the same study after drying the gel at ambient conditions for overnight and found that clear color change was observed from yellow to maroon (Figures 8c,d). Though the color change was achieved, this method is not practical due to the need to prepare the gel using fluoride-containing water.

Nevertheless, after several attempts with various papers as the solid support, we discovered that simple low cost commercially available tissue-paper has shown remarkable sensing ability for test-strip detection of F^- ion (Figure 9). The following procedure was used to achieve solid-phase sensing using a tissue-paper strip. A drop of an acetone solution of **1** ($10\ \mu\text{L}$, $10^{-3}\ \text{M}$) has been placed on porous tissue paper and dried for a minute. The color of TCBD **1** on paper is shown yellow. Upon adding various concentrations (ppm) of both organic- (TBAF) and inorganic- (CaF_2) fluorides were shown clear color change to maroon in a mixture of $\text{H}_2\text{O}/\text{DMSO}$ 1:1 on the TCBD spot up to 3 ppm minimum detection limit (Figure 9a,b). 3 ppm is the minimum concentration to learn whether the drinking water is safer or not. Whereas no color change was observed for a safer range of 1–2 ppm. However, 1 ppm F^- in DMSO solution has shown clear maroon color change (Figure 9c). These results can be regarded as the presence and absence of F^- ion both qualitatively as well as quantitatively depending on the color change and intensity calibration using the software, respectively. The free color processing software (e.g. ImageJ) can be used to quantify the color histograms of Figure 9a-c as shown in Figure S27, Supporting Information, which can be compared with the control sample without fluoride. We infer that the successful paper-strip detection could be attributed to the high sensitivity of the chromophore **1** as well as the porous nature of the paper which helps to absorb the water away from the dye molecule which facilitates the F^- binding reaction.

Figure 9. Colorimetric solid-phase sensing of chemosensor **1** showing no maroon color change when treated with a) 1 ppm of CaF_2 in $\text{H}_2\text{O}/\text{DMSO}$ 1:1 (the contrast color is due to the solvent wet nature). Whereas showing the clear color change to maroon when treated with b) 3 ppm in $\text{H}_2\text{O}/\text{DMSO}$ 1:1. c) Also, the color change was observed with 1 ppm in DMSO.

The right balance between the charge-transfer (CT) efficiency and urea-receptor binding efficacy with F^- and its effect on the generated new CT species was fallen right at the required detection sensitivity. This sensitivity is retained for both solutions as well as in solid-phase sensing. Though it can be quantified using mobile phone app-based color intensity quantification, the present detection kit is not limited to any electronic items (minor or major) or consumables like strong acid and toxic chemicals, apparatus, etc. The only component required for simple strip-detection is a sensor-coated paper and a drop of a testing water sample and a drop DMSO.

Conclusion

In this study, we explored the synthesis of Ph- and DMA-substitution at the C_3 -position of C_2 -urea-functionalized mono-TCBD push-pull chromophore and its successful utilization for the detection of fluoride ion. Compared with mono-substituted TCBDs, the present di-substituted TCBDs exhibited the absence of the H-bonded network in the solution that facilitated easy purification coupled with elegant synthesis. The structural identity was confirmed by IR, NMR, and ESI-MS including an unambiguous single-crystal structure for receptor **1**. Interestingly, we showed how a subtle change in the substitution of **1** and **2** with H or NMe_2 groups, respectively on the urea-functionalized 2-(1-benzyl-3-phen-4'-yl-carbonyl)-3-phenyl-1,1,4,4-tetracyanobuta-1,3-diene led to a remarkable F^- sensing ability with multi-ways F^- detection including paper-strip. ^1H -NMR and other studies confirm that the sensing mechanism involves H-bonding followed by deprotonation at the N-H connected to TCBD moiety which is crucial for colorimetric detection. Spectroscopic studies including TD-DFT study reveal that the unsuccessful colorimetric detection for compound **2** with additional CT is due to a clear overlap of the newly generated CT corresponding to fluoride-induced deprotonation species. Lastly, we presented a simple, easy to perform paper-strip F^- detection based on naked-eye colorimetric sensing in an aqueous condition which uses simple tissue paper with promising features like multi-ways detection, specific over other anions (especially acetate and phosphate ions which are the common hindering ions in other reported systems), instant detection in few seconds, and high-sensitivity up to 3 ppm which is still high enough at the level of drinking water standard. We believe that the findings here would open up new windows for the search of better receptor systems not only for F^- but for other analytes as well.

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Supporting Information

A subtle change in substituent enabled multi-ways fluoride signals including paper-strip colorimetric detection using urea receptor functionalized 1,1,4,4-tetracyanobuta-1,3-diene-based push-pull chromophore

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A Experimental Section.

A1 General Procedure and Materials.

All starting materials and chemicals were purchased from Aldrich and TCI-India and used as received. Dimethylformamide (DMF), CH₃CN, CH₂Cl₂ was freshly distilled from P₂O₅ under the nitrogen (N₂) atmosphere. THF was dried in sodium. Column chromatography (CC) was carried out with SiO₂ (particle size 60–120 mesh). TLC was performed on precoated plastic sheets of silica gel G/UV-254 of 0.2 mm thickness (Macherey Nagel, Germany) using appropriate solvents and visualized with UV light ($\lambda = 254$ nm). The synthesis of **mono-TCBD** was achieved as per the literature.^[1] Alkynes **3** and **4** were synthesized as per literature.^[2] Melting points (M.p.) were measured in open capillaries with a Stuart (automatic melting point SMP50) apparatus and are uncorrected. “Decomp.” refers to decomposition. ¹H- and ¹³C-NMR spectra were measured on Bruker Avance II 400 MHz instrument at 25 °C in (CD₃)₂CO, CDCl₃ or DMSO-*d*₆. Residual solvent signals in the ¹H and ¹³C NMR spectra were used as an internal reference. Chemical shifts (δ) are reported in ppm downfield from SiMe₄, with the residual solvent signal. Coupling constants (*J*) are given in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), and m (multiplet). Transmission Spectra were measured using ATR-FT-IR Bruker Vertex 70; signal designations: s (strong), m (medium), and w (weak). Selected absorption bands are reported in wavenumbers (cm⁻¹). UV/Vis spectra were recorded on a Shimadzu UV/Vis spectrophotometer. The spectra were measured in a quartz cuvette of 1 cm at 298 K. The absorption maxima (λ_{max}) is reported in nm with the extinction coefficient (ϵ) in dm³ mol⁻¹ cm⁻¹ in brackets. Shoulders are indicated as sh. Fluorescence spectra were measured on an Edinburgh FS5 spectrophotometer in 1 cm quartz cuvette. ESI-MS spectra were measured on a Bruker maXis ESI-Q-TOF spectrometer. The most important signals are reported in *m/z* units with *M*⁺ as the molecular ion.

Electrochemistry

The redox properties were measured by cyclic voltammetry. *N,N'*-dimethylformamide (DMF) (HPLC grade, spectrochem, India) was distilled over anhydrous calcium hydride protected by 4 Å molecular sieves under argon atmosphere before each experiment. Tetrabutylammonium perchlorate ([Bu₄NClO₄], TBAP) (Sigma-Aldrich, electrochemical grade) was used as supporting electrolyte without further purifications. 1 mM solutions of the compounds in distilled DMF was used for all studies.

The voltammetric experiments were carried out in a single compartment electrochemical cell using the three-electrode potentiostat (CH Instruments 660A). The working electrode (Glassy

Carbon (GC) electrode of 3 mm dia, CH Instruments, USA) was polished with 0.05 micron alumina slurry to mirror finish and sonicated to remove the abrasive particles before each experiment. The Ag/Ag⁺(0.01M) electrode is used as a quasi-reference electrode prepared from the same supporting electrolyte in acetonitrile (*caution: preparation of the Ag/Ag⁺ reference electrode in DMF/TBAP leads to the formation of Ag nanoparticles*). A platinum wire was used as a counter electrode. Later, the potential scale is corrected with the ferrocene/ferrocenium-ion using the ferrocene as an internal standard. Cyclic voltammetry experiments were performed with a CH Instruments three-electrode potentiostat.

A2 Synthetic Procedures and Characterization Data for Urea Functionalized Alkynes 5-6

1-benzyl-3-[4',1-(ethyne-1,2-yl)diphenyl]urea **5**:

A solution of benzyl isocyanate (0.1 g, 0.75 mmol) in CH₂Cl₂ (3 mL) under N₂ was treated with 4-(2-phenylethynyl)aniline^[2] **3** (0.174 g, 0.90 mmol) and stirred at 25 °C for 24 h. The white precipitate formed was collected by filtration, washed with CH₂Cl₂, Et₂O and dried in *vacuo*. The white solid **5** (0.24 g, 98%) obtained is air stable, and well soluble in DMF. M.p. 350–360 °C (decomp.); ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ = 4.35–4.25 (m, 2 H), 6.76–6.64 (m, 1 H), 7.57–7.21 (m, 14 H), 8.83 ppm (s, 1 H); ¹³C NMR (100 MHz, DMSO-*d*₆, 298 K): δ = 42.7, 87.9, 89.9, 114.3, 117.5, 120.0, 122.8, 126.7, 127.1, 128.30, 128.33, 128.7, 131.1, 132.1, 137.2, 140.2, 141.1, ppm 154.9; IR (KBr) $\tilde{\nu}$ = 3303 (m), 2931 (w), 2875 (w), 1631 (s), 1557 (s), 1533 (s), 1241 (s), 857 (w), 752 (s), 690 (s), 647 (s), 529 cm⁻¹ (m); HRMS (ESI): *m/z* (%) calcd for C₂₂H₁₉N₂O⁺: [M+H]⁺ 327.1497; found: 327.1503.

1-benzyl-3-{4-[2-(4-N,N-dimethylaminophenyl)ethynyl]phenyl}urea **6**:

A solution of benzyl isocyanate (0.034 g, 0.25 mmol) in CH₂Cl₂ (3 mL) under N₂ was treated with 4-{{2-(4-aminophenyl)ethynyl}}*N,N'*-dimethylaniline^[2] (0.072 g, 0.31 mmol) and stirred at 25 °C for 24 h. The white precipitate formed was collected by filtration, washed with CH₂Cl₂, Et₂O and dried *in vacuo*. The white solid **6** (0.048 g, 89%) obtained is air stable, and well soluble in CH₂Cl₂. M.p. 354–358 °C (decomp.); ¹H NMR (400 MHz, DMSO-*d*₆, 298 K): δ = 2.93 (s, 6 H), 4.32 (d, *J* = 5.9 Hz, 2 H), 6.72–6.66 (m, 3 H), 7.27–7.22 (m, 1 H), 7.38–7.29 (m, 8 H), 7.46–7.41 (m, 2 H), 8.75 ppm (s, 1 H); ¹³C NMR (100 MHz, DMSO-*d*₆, 298 K): δ = 40.2, 42.7, 87.5, 89.2, 109.0, 111.9, 115.4, 117.5, 126.7, 127.1, 128.3, 131.6, 132.1, 140.2, 140.3, 149.9, ppm 155.0; IR (KBr) $\tilde{\nu}$ = 3328 (w), 2913 (w), 2813 (w), 1644 (s), 1581 (s), 1514 (s), 1365 (m), 1296 (m), 1229 (m), 801 (s), 691 (m), 634 (m) and 529 cm⁻¹ (m); HRMS (ESI): *m/z* (%) calcd for C₂₄H₂₄N₃O⁺: [M+H]⁺ 370.1919; found: 370.1924.

A3 Synthetic Procedures and Characterisation Data for Urea Functionalized TCBDs 1-2

1-benzyl-3[4(1,1,4,4-tetracyano-3-phenyl)buta-1,3-dien-2-yl]phenyl]urea **1**:

TCNE (35 mg, 0.28 mmol) and LiClO₄ (39 mg, 0.37 mmol) were added to a solution of 1-benzyl-3-{4-[2-(4-*N,N'*-dimethylaminophenyl)ethynyl]phenyl}urea **5** (60 mg, 0.18 mmol) in 1,2-dichloroethane (ClCH₂CH₂Cl) (2 mL) in a round bottomed flask under N₂ atmosphere and heated at 70 °C for 1 h. After completion of the reaction, the reaction mixture was directly passed through silica gel column chromatography eluted with hexane/EtOAc 80:20. The solid orange colored compound **1** was isolated and dried *in vacuo*. The compound **1** (70 mg, 83%) obtained is well soluble in acetone, DMF, DMSO, MeOH and less soluble in CH₂Cl₂, *R*_f = 0.3 (SiO₂; hexane/EtOAc 8:2); M.p. 288–290 °C; ¹H NMR (400 MHz, DMSO-*d*₆, 298 K) : δ = 4.30 (d, *J* = 4.7 Hz, 2 H), 6.96 (t, *J* = 4.8 Hz, 1 H), 7.35–7.21 (m, 5 H), 7.68–7.57 (m, 5 H), 7.90–7.85 (m, 4 H), 9.36 ppm (s, 1 H); ¹³C NMR (100 MHz, acetone-*d*₆, 298 K): δ = 44.0, 112.7, 113.0, 113.6, 113.8, 118.66, 118.73, 123.7, 127.7, 128.1, 129.1, 130.3, 130.6, 132.3, 132.4, 134.9, 140.6, 148.1, 155.1, 165.6, ppm 167.8; IR (KBr) $\tilde{\nu}$ = 3332 (m), 2232 (m), 1673

(s), 1551 (s), 1507 (s), 1324 (s), 1237 (s), 1175 (s), 844 (m), 687 (s), 495 cm^{-1} (w); HRMS (ESI, positive mode); m/z (%): calcd for $\text{C}_{28}\text{H}_{19}\text{N}_6\text{O}$ $[\text{M}+\text{H}]^+$: 455.1620, Found: 455.1631.

1-benzyl-3-{4[1,1,4,4-tetracyano-3(4-N,N-dimethylaminophenyl)buta-1,3-dien-2-yl]phenyl}urea **2:**

TCNE (26 mg, 0.2 mmol) was added to a solution of 1-benzyl-3-{4-[2-(4-N,N'-dimethylaminophenyl)ethynyl]phenyl}urea **6** (50 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) in a round bottomed flask under N_2 atmosphere and stirred at 25 $^\circ\text{C}$ for 1 h. After completion of the reaction, the reaction mixture was directly passed through silica gel column chromatography eluted with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 8:2. The solid marooned colored compound was isolated and dried *in vacuo*. The compound **2** (52 mg, 79%) obtained is well soluble in CH_2Cl_2 , acetone, DMF, MeOH, R_f = 0.3 (SiO_2 ; $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 95:5); M.p. 294–297 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3 , 298 K): δ = 3.14 (s, 6 H), 4.33 (d, J = 4.6 Hz, 2 H), 5.91 (t, J = 4.6 Hz, 1 H), 6.68 (d, J = 7.2 Hz, 2 H), 7.28–7.18 (m, 5 H), 7.39 (d, J = 6.9 Hz, 2 H), 7.63 (d, J = 6.8 Hz, 2 H); 7.75 (d, J = 7.3 Hz, 2 H), 7.97 ppm (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3 , 298 K): δ = 40.3, 44.1, 112.2, 112.3, 112.4, 113.3, 114.1, 114.7, 118.3, 118.5, 125.0, 127.3, 127.7, 128.9, 131.6, 132.83, 132.8, 133.0, 138.3, 145.9, 154.7, 154.9, 164.1, ppm 167.8; IR (KBr) $\tilde{\nu}$ = 3350 (m), 2930 (w), 2197 (m), 1639 (m), 1604 (s), 1490 (s), 1385 (m), 1158 (m), 949 (w), 817 (m), 548 (m) cm^{-1} (m); HRMS (ESI): m/z (%) calcd for $\text{C}_{30}\text{H}_{24}\text{N}_7\text{O}^+$: $[\text{M}+\text{H}]^+$ 498.2042; found: 498.2046.

B Spectra of Newly Synthesized Compounds

B1 NMR (^1H and ^{13}C) Spectra

Figure S1. 400 MHz ^1H NMR spectrum of **5** recorded at 298 K in $\text{DMSO}-d_6$.

Figure S2. 100 MHz ^{13}C NMR spectrum of **5** recorded at 298 K in $\text{DMSO}-d_6$.

Figure S3. 400 MHz ¹H NMR spectrum of **6** recorded at 298 K in DMSO-*d*₆.

Figure S4. 100 MHz ¹³C NMR spectrum of **6** recorded at 298 K in DMSO-*d*₆.

Figure S5. 400 MHz ¹H NMR spectrum of **1** recorded at 298 K in DMSO-*d*₆.

Figure S6. 100 MHz ¹³C NMR spectrum of **1** recorded at 298 K in acetone-*d*₆.

Figure S7. 400 MHz ¹H NMR spectrum of **2** recorded at 298 K in CDCl₃

Figure S8. 100 MHz ¹³C NMR spectrum of **2** recorded at 298 K in CDCl₃.

B2 ESI-MS Spectra of synthesized compounds

030519-G-50 18 (0.183) AM (Cen,4, 85.00, Ar,10000.0,0.00,0.00); Sm (SG, 1x3.00); Cm (18:24)

1: TOF MS ES+
3.88e+007

Figure S9. High-resolution ESI-MS spectrum of **5**.

030519-G-64 19 (0.203) AM (Cen,4, 85.00, Ar,10000.0,0.00,0.00); Sm (SG, 1x3.00); Cm (19:28)

1: TOF MS ES+
4.70e+007

Figure S10. High-resolution ESI-MS spectrum of **6**.

Figure S11. High-resolution ESI-MS spectrum of 1.

Figure S12. High-resolution ESI-MS spectrum of 2.

B3 Fluoride titration spectra

Figure S13. Partial ^1H NMR spectra of receptor **1** (2×10^{-3} M) on the addition of TBAF in DMSO-d_6 .

Figure S14. Partial ^1H NMR spectra of receptor **2** (2×10^{-3} M) on the addition of TBAF in DMSO-d_6 . Inset shows the deprotonated species **2-H** structure.

C X-ray Data

C1 X-Ray Crystal Structure of 1 (CCDC 2016856, 298 K). A dark Maroon crystal (cubic dimensions ca. $0.356 \times 0.319 \times 0.278$ mm) was obtained from CH_2Cl_2 /hexane solution at 20 °C. Crystal data for $\text{C}_{28}\text{H}_{18}\text{N}_6\text{O}$, $M_r = 454.48$, Monoclinic, space group $P 2_1/c$ (14), $D_{\text{calc}} = 1.276 \text{ g cm}^{-3}$, $Z = 4$, $a = 17.1219(6) \text{ \AA}$, $b = 15.3831(6) \text{ \AA}$, $c = 9.0207(4) \text{ \AA}$, $V = 2364.94(16) \text{ \AA}^3$; $m = 0.082 \text{ mm}^{-1}$. Numbers of measured and unique reflections were 17916 and 5116, respectively ($R_{\text{int}} = 0.0462$, $R_{\text{sigma}} = 0.0503$). Final $R(F) = 0.0597$, $wR(F_2) = 0.1263$ for 3477 parameters and 5116 reflections with $I > 2\sigma(I)$ and $5.466^\circ < 2\theta < 54.308^\circ$.

Single crystal X-ray structural data of compound **1** were collected on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC micro-focus source with graphite monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 30 mA. The SAINT program was used for integration of diffraction profiles and absorption correction was made with SADABS program. The structures were solved by SIR 92 and refined by full-matrix least square method using SHELXL-2013^[3] and WinGX system, Ver 2014.7. The structure was refined using TWIN and BASF instructions of WinGX system. The non-hydrogen atoms in all the structures were located from the difference Fourier map and refined anisotropically. All the hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using riding model with isotropic thermal parameters. The potential solvent accessible area or void space was calculated using the PLATON software. The crystallographic information file is deposited with the CCDC number 2016856. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(1223)-336-033; e-mail: deposit@ccdc.cam.ac.uk), or via www.ccdc.cam.ac.uk/data_request/cif

b)

c)

Figure S15. a) a) ORTEP plot of **1** (arbitrary numbering, H-atoms are omitted for clarity). Atomic displacement parameters are drawn at 50% probability level. Selected bond lengths [Å], angles [°], and torsional angles [°]: C1–C2: 1.321(2), C2–C3: 1.378(2), C3–C4: 1.358(2), C4–C5: 1.490(2), C4–C17: 1.367(2), C17–C18: 1.397(2), C1–C18: 1.337(2), C7–C8: 1.401(2), C8–C9: 1.364(2), C9–C10: 1.390(2), C10–C11: 1.464(2), C11–C12: 1.498(2), C11–C24: 1.350(2), C12–C13: 1.468(2), C13–C14: 1.389(2), C14–C15: 1.371(2), C15–C16: 1.370(2), C16–C22: 1.345(2), C22–C23: 1.373(2), C24–C26: 1.444(2), C12–C19: 1.345(2), C19–C21: 1.429(2), C19–C20: 1.446(2), C10–C27: 1.406(2), C27–C28: 1.366(2), C7–C28: 1.397(2), C5–N1–C6: 2.468(2), C6–N2–C7: 2.491(2), C20–N3: 1.129(2), C20–N4: 1.140(2), C25–N5: 1.134(2), C26–N6: 1.136(2), C19–C12–C11–C24: 131.9 (2), C27–C10–C11–C24: 44.6 (2),

C19–C12–C13–C14: 44.8 (2), C9–C10–C11–C12: 42.2 (2), C8–C7–N2–C6: –7.54 (2), O1–N1: 2.876 (2), O1–N2: 2.882 (2), O1–H2: 2.088 (2), O1–H1: 2.072. b) Arrangement of neighboring molecules in the crystal packing of **1** (H-atoms except in the urea moieties are omitted for clarity). c) one-dimensional hydrogen-bonded α -networks with a repeat distance of about 4.6 Å.^[4]

C2 Quinoid Character

To understand the nature and extent of the charge transfer, the quinoid character (δr (Å)) parameter was calculated. It has been used previously for other TCBDs in excellent agreement with other structural characterization.^[5] The quinoid character (δr) was calculated based on the bond lengths alternation in the benzene ring substituted by the donor group [Eq. (1)].^[6] In benzene, the δr value equals 0, whereas values between 0.08 and 0.1 are found in fully quinoid rings (see Figure S15a for the definition of bonds a, a', b, b', c, and c').

$$\delta r = \{[(a + a') - (b + b')]/2 + [(c + c') - (b + b')]/2\}/2 \quad (1)$$

The calculated δr values for **1** is $\delta r = 0.031$ Å which is comparable with other aniline and DMA-TCBDs^[7] indicating CT characteristics.

D Spectroscopic Data

D1 Mono-TCBD sensing studies

Figure S16. a) UV/Vis absorption spectra of **mono-TCBD** (6×10^{-5} M) in the absence (**A**) and presence (**B**) of excess TBAF in CH₃CN. b) Fluorescence spectra of **mono-TCBD** (6×10^{-5} M) in the absence (**A**) and presence (**B**) of excess TBAF in CH₃CN upon excitation at λ_{ex}

= 365 nm. c) visual color solution of **mono-TCBD** (6×10^{-5} M) in the absence (**A**) and presence (**B**) of excess TBAF in CH_3CN . d) **mono-TCBD** (6×10^{-5} M) solution drop-casted in the tissue-paper in the absence (**A**) and presence (**B**) of excess TBAF in CH_3CN .

D2 UV/Vis

Figure S17. UV/Vis absorption spectra of **1** and **2** in MeCN (1×10^{-5} M) at 298 K.

Figure S18. UV/Vis absorption spectra of **1** in MeCN (1×10^{-5} M) at 298 K recorded a) neat, b) after acidification with TFA, and c) neutralization with Et_3N .

Figure S19. UV/Vis absorption spectra of **2** in MeCN (1×10^{-5} M) at 298 K recorded a) neat, b) after acidification with TFA, and c) neutralization with Et₃N.

Figure S20. UV/Vis absorption spectra of **1** in a mixture of solvents (1×10^{-5} M) at 298 K.

Figure S21. UV/Vis absorption spectra of **2** in a mixture of solvents (1×10^{-5} M) at 298 K.

Figure S22. UV/Vis absorption spectra of **2** (2×10^{-5} M) in the presence of TBAF (9.8×10^{-4} M) in DMSO.

Table S1. UV/Vis spectroscopic data for chromophores **1** and **2** in CH₃CN at 298 K and a summary of electrochemical gaps.

compound	ICT Bands	
	$\lambda_{\max}$ [nm (eV)]	λ_{end} [nm (eV)]
1	284 (4.37)	544 (2.28)
	332 (3.73)	
	410 (3.02)	
2	407 (3.05)	614 (2.02)
	476 (2.60)	

D3. Fluorescence data

Quantum yield for **1** was determined by comparing the integrated PL intensities (excited at 375 nm) and the absorbance values (at 375 nm) of **1** using quinine sulphate ($\Phi_F = 0.54$) as a reference.^[8] Quantum yield for **1** calculated (in CH₃CN) : 2.3%. Quantum yield for **2** was not calculated as no significant emission was observed.

E Electrochemistry Data

Table S2. Electrochemical data of **1** and **2** observed by cyclic voltammetry (CV) (Scan Rate $v = 0.1 \text{ V s}^{-1}$) in DMF (in the presence of 0.1M Bu₄NClO₄).

Receptors	Peak parameters				
	E° [V] ^a	ΔE_p [mV] ^b	E_{onset} [V] ^c	DPV [V] ^d	HOMO–LOMO (H–L) [V] ^e
1			+0.96		
	–0.72	67		–0.71	1.67
	–1.16	65		–1.14	
2			+0.65		
	–0.90	65		–0.87	1.52
	–1.25	66		–1.23	

^a $E^\circ = (E_{\text{pc}} + E_{\text{pa}})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively; Values reported versus F_c/F_c^+ . ^b $\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$. ^c E_{onset} = Onset potential of the irreversible oxidation of compounds while applying positive potentials. ^d DPV: differential pulse voltammetry. ^e $H-L = |E_1^0| + |E_{\text{onset}}|$, where E_1^0 is the first standard reduction potential of the compound.

Figure S23. Cyclic voltammograms of **1** and **2** on GC electrode in DMF containing 0.1M Bu₄NClO₄ as a supporting electrolyte. Scan rate is 100 mV/s.

Figure S24. Cyclic voltammetry of **2** with the titration of 0.1 mM TBAF. The inset shows the variation of the peak potential with the concentration of TBAF.

F Literature receptors that deal with strip detection for fluoride

Table S3. Comparison of chromo-fluorogenic receptors that deal with solution and solid phase sensing of fluoride with this work.^a

ent ry	Chromophore	Solution		Test-strip				Selective for	Multi-mode responses	Mode of detection	referen ces
		Fluoride source	solvent	Contrast Color change	Fluoride source	solvent	Sensit ivity (ppm)				
1.	Ru-bipy based quinonehydrazone	TBAF	CH ₃ CN	yes	TBAF	aqueous	10	F ^{-c}	no	Naked-eye	[a]
2.	Ru-bipy 2,4- dinitrophenylhydraz one	TBAF	CH ₃ CN	no	TBAF	aqueous	10	F ⁻ , PO ₄ ^{-d}	no	Naked-eye	[b]
3.	N-(3- (benzo[d]thiazol-2- yl)-4-(hydroxy- phenyl) benzamide	NaF	CTAB/ water	no	NaF	aqueous micelle	3.8	F ⁻	no	Hand-held UV lamp	[c]
4.	Reduced Schiff base	TBAF	CH ₃ CN	Colorless to yellow	TBAF	aqueous	N.D ^b	F ⁻ , OAc ⁻	no	Naked-eye	[d]
5.	bis(5-nitro- salicylidene)hydrazi ne	TBAF	CH ₃ CN /water	Colorless to yellow	TBAF	aqueous	5.0	F ⁻ , OAc ⁻ , PO ₄ ⁻	no	Naked-eye	[e]
6.	Fluorene & triazolium	TBAF	DMSO	no	TBAF	aqueous	1.9	F ⁻	no	Hand-held UV lamp	[f]
7.	2-thio- hydantoin	TBAF	CH ₃ CN	Colorless to purple	TBAF	aqueous	1.9	F ^{-c}	no	Naked-eye	[g]
8.	graphene oxide and silver nanoparticles	KF	water	no	KF	aqueous	0.1 ^e	F ⁻	no	Hand-held UV lamp	[h]

9.	BODIPY– amidothiourea	NaF	DMSO/ water 1:1	no	NaF	aqueous	0.2	F [−] , OAc [−] , PO ₄ [−]	no	Lateral flow reader	[i]
10.	benzohydrazide and –NO ₂ benzaldehyde	TBAF	CH ₃ CN	Colorless to yellow	TBAF	aqueous	N.D. ^b	F [−]	no	Naked-eye	[j]
11.	Rhodamine derivative	TBAF	CH ₃ CN /water 3:7	Colorless to pink	NaF	aqueous	10	F [−]	no	Naked-eye	[k]
12.	Dimeric azulene boronate ester	TBAF	THF	Light green to yellow	TBAF	THF	1.5	F [−] , PO ₄ ^{−d}	no	Naked-eye	[l]
13.	4-nitro benzylidene hydrazono	TBAF	DMSO/ water 9:1	Light brown to purple	TBAF	DMSO	0.29	F [−] , OAc [−] , PO ₄ [−]	no	Naked-eye	[m]
14.	Urea-functionalized 1,1,4,4- tetracyanobuta-1,3- diene	TBAF	DMSO/ water 1:1	Yellow to maroon	CaF ₂	aqueous DMSO	3.0 1.0	F [−] F [−]	 Yes	Naked-eye	[n]

^a limitations are highlighted with grey color, ^b Not determined, ^c acetate and phosphate ions are not tested. ^d acetate ion is not tested. ^e clear visualization only at 1000 ppm.

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- [n] this work.

G Computational Details

Geometry optimizations were performed at DFT level using B3LYP method within restricted formalism.^[9] For all the atoms, we employed def2-TZVP basis set. The calculations were accelerated by employing the Resolution of Identity (RI) approximation with the large grid 5. To compute the exchange terms effectively ‘Chain of Spheres Exchange’ (COSX) is used. All the electronic structure calculations were performed with ORCA program. The general features of B3LYP/def2-TZVP optimized frontier molecular orbitals of **1** and **2** are illustrated in **Table S4**. The deprotonated species are obtained by removing H-atom from the NH adjacent to TCBD moiety.

Table S4. Frontier molecular orbitals of **1** and **2** as obtained at B3LYP/def2-TZVP level of electronic structure theory. The MOs are plotted with isosurface value of 0.02 a.u.

	1	2

LUMO+2
LUMO+1

Table S5. Frontier molecular orbitals of **1-H** and **2-H** calculated at B3LYP/def2-TZVP level with isosurface value of 0.02 a.u.

LUMO+2

LUMO+1

LUMO

HOMO

HOMO-1

HOMO-2

Figure S25. DFT energy level diagram presenting the energies of frontier molecular orbitals calculated at B3LYP/def2-TZVP level for **1** and **2** (marked with black) and deprotonated forms **1-H** and **2-H** (marked with red). The decrease in HOMO–LUMO gap upon deprotonation is evident for both **1** and **2**.

UV/Vis Spectra Calculations

The electronic spectra (UV/Vis) were calculated with time-dependent DFT (TD-DFT).^[10] A total of 50 excited states are accounted considering only singlet-singlet excitations. Owing to a better performance for predicting spectral properties, CAM-B3LYP was chosen as a functional for all the electronic spectra calculations.^[11] As the experimental data were acquired in CH₃CN solvents, the implicit solvent effects were also incorporated in the calculations (CH₃CN, $\epsilon = 36.6$) adopting the Conductor like Polarizable Continuum Model (CPCM) as implemented in *ORCA*.^[12]

Table S6. UV/Vis spectrum: Excitation wavelengths, oscillator strengths (f) and dominant electronic transitions of **1** in CH₃CN.

S.No	λ (nm)	f	Main Transitions
1	414	0.373	H $\rightarrow$ L (91.9%)
2	332	0.172	H-3 $\rightarrow$ L (88.0%)
3	316	0.620	H $\rightarrow$ L+1 (78.2%)
4	270	0.300	H-3 $\rightarrow$ L+1 (79.1%)
5	253	0.098	H-8 $\rightarrow$ L (42.5%)
6	229	0.104	H-9 $\rightarrow$ L (62.5%)
7	207	0.194	H $\rightarrow$ L+4 (28.6%), H $\rightarrow$ L+9 (18.1%)
8	184	0.330	H $\rightarrow$ L+8 (29.6%), H $\rightarrow$ L+6 (10.9%)
8	182	0.437	H $\rightarrow$ L+9 (43%) H $\rightarrow$ L+8 (18.2%), H $\rightarrow$ L+13 (13.3%)

Table S7. UV/Vis spectrum: Excitation wavelengths, oscillator strengths (f) and dominant electronic transitions of **1-H** in CH₃CN.

S.No	λ (nm)	f	Main Transitions
1	513	0.054	H $\rightarrow$ L (69.1%)
2	379	1.540	H $\rightarrow$ L+1 (67.1%), H $\rightarrow$ L (25.4%)
3	291	0.264	H-4 $\rightarrow$ L (53.9%), H-4 $\rightarrow$ L+1 (11.5%)

4	230	0.162	H-8 $\rightarrow$ L+1 (22.6%), H $\rightarrow$ L+3 (31.0%)
5	210	0.133	H-10 $\rightarrow$ L (23.9%), H-4 $\rightarrow$ L+2 (13.3%)
6	193	0.105	H $\rightarrow$ L+12 (40.1%)

Table S8. UV/Vis spectrum: Excitation wavelengths, oscillator strengths (f) and dominant electronic transitions of **2** in CH₃CN.

S.No	λ (nm)	f	Main Transitions
1	469	0.246	H $\rightarrow$ L (94.3%)
2	382	0.426	H-1 $\rightarrow$ L (90.4%)
3	361	0.632	H $\rightarrow$ L+1 (92.7%)
4	320	0.381	H-1 $\rightarrow$ L+1 (88.3%)
5	260	0.130	H-7 $\rightarrow$ L (58.5%)
6	229	0.101	H-5 $\rightarrow$ L+1 (30.1%), H-1 $\rightarrow$ L+2 (30.9%)
7	213	0.162	H $\rightarrow$ L+4 (11.0%), H $\rightarrow$ L+7 (26.8%)
8	186	0.651	H-1 $\rightarrow$ L+7 (17.6%), H-1 $\rightarrow$ L+5 (16.3%)

Table S9. UV/Vis spectrum: Excitation wavelengths, oscillator strengths (f) and dominant electronic transitions of **2-H** in CH₃CN.

S.No	λ (nm)	f	Main Transitions
1	497	0.200	H $\rightarrow$ L (81.6%)
2	385	0.912	H-1 $\rightarrow$ L (46.9%), H $\rightarrow$ L+1 (40.7%)

3	373	0.963	H-1 $\rightarrow$ L (45.8%), H $\rightarrow$ L+1 (38.5%)
4	239	0.132	H-9 $\rightarrow$ L (28.4%), H-6 $\rightarrow$ L+1 (20.3%)
5	222	0.233	H $\rightarrow$ L+8 (27.8%), H $\rightarrow$ L+9 (20.1%)
6	212	0.105	H-1 $\rightarrow$ L+8 (44.4%)

Figure S26. UV/Vis electronic spectra of **1** and the deprotonated species **1-H** in CH₃CN obtained from TD-DFT.

Figure S27. Calculated UV/Vis electronic spectra of **2** and the deprotonated species **2-H** in CH₃CN from TD-DFT calculations at CAM-B3LYP/def2-TZVP level.

Table S10. Cartesian coordinates from the optimized structure of **1**.

Atomic Type	Coordinates {Å}		
	x	y	z
C	14.56091	5.70842	0.80653
C	14.39722	4.33397	0.65355
C	13.4662	6.56175	0.65955
H	15.54404	6.11877	1.0228
C	13.14007	3.81272	0.35266
H	15.25229	3.67061	0.75381
C	12.1926	6.05071	0.36292
H	13.61958	7.63506	0.75496
C	12.04453	4.66597	0.20117
H	13.01641	2.74152	0.21582
H	11.07819	4.24589	-0.07032
C	11.05558	7.00081	0.09296
N	9.78659	6.57537	0.64938
H	10.96146	7.13351	-0.99138
H	11.26845	7.98395	0.53048
C	8.64716	7.20766	0.19614
H	9.79908	6.23142	1.59562
O	8.68776	8.00021	-0.73786
N	7.51847	6.83895	0.89986
C	6.19969	7.26514	0.61627

H	7.66448	6.33479	1.75974
C	5.83947	7.83791	-0.6027
C	5.20988	7.09873	1.59418
C	4.53447	8.27617	-0.83038
H	6.5516	7.94484	-1.41594
C	3.55514	8.17118	0.16824
H	4.30764	8.7041	-1.80551
C	3.89864	7.56094	1.38037
H	5.45121	6.63553	2.54783
H	3.16584	7.44339	2.17523
C	2.17782	8.69473	-0.1082
C	2.079761	0.04972	-0.27367
C	0.99336	7.75466	-0.14416
C	1.04761	6.45024	-0.54765
C	0.903091	0.7153	-0.72912
C	3.179641	0.93606	-0.03227
C	-0.06773	5.56042	-0.41772
C	2.1945	5.84984	-1.14463
N	-0.018461	1.28722	-1.14196
N	4.054021	1.66879	0.17987
N	-0.96137	4.82785	-0.31099
N	3.10013	5.33096	-1.65165
C	-0.33315	8.23096	0.3694
C	-0.48871	8.59514	1.7138
C	-1.42259	8.37685	-0.50848
C	-1.70927	9.10378	2.16598
H	0.33186	8.50117	2.42071
C	-2.78157	9.24557	1.28574
H	-1.82675	9.39946	3.2059
C	-2.64046	8.87835	-0.04948
H	-1.33307	8.12949	-1.56483
H	-3.72762	9.65081	1.63726
H	-3.47281	8.99929	-0.7391

Table S11. Cartesian coordinates from the optimized structure of **1-H**.

Atomic Type	Coordinates {Å}		
	x	y	z
C	12.70508	5.96931	3.001254
C	12.41469	4.674085	2.589209
C	11.93202	7.036469	2.550812
H	13.5277	6.150602	3.683031
C	11.3513	4.457563	1.716405
H	13.00652	3.84087	2.948677
C	10.8573	6.830315	1.684877
H	12.16063	8.042172	2.888428

C	10.58302	5.525281	1.269394
H	11.11229	3.45368	1.384968
H	9.745852	5.350913	0.60513
C	10.00035	7.9888	1.206724
N	8.596588	7.672572	1.163552
H	10.2745	8.280218	0.188526
H	10.19813	8.858752	1.845946
C	7.807703	7.808989	0.029699
H	8.172453	7.170793	1.925585
O	8.258487	8.335918	-0.98915
N	6.569041	7.250343	0.256216
C	5.507103	7.509325	-0.49457
C	5.38264	8.476514	-1.55779
C	4.309642	6.77413	-0.1904
C	4.178783	8.741305	-2.14527
H	6.270554	8.998886	-1.87828
C	2.972361	8.061706	-1.78226
H	4.152355	9.489447	-2.92344
C	3.120763	7.031106	-0.79891
H	4.385912	6.009025	0.571909
H	2.256788	6.451793	-0.50049
C	1.687978	8.396952	-2.27899
C	1.302343	9.474884	-3.09397
C	0.51889	7.563738	-1.81441
C	0.239013	6.39653	-2.47366
C	-0.04994	9.608062	-3.51294
C	2.13233	10.53739	-3.53406
C	-0.75505	5.458864	-2.05152
C	0.958537	5.992581	-3.64185
N	-1.1504	9.731624	-3.85146
N	2.741767	11.44484	-3.91442
N	-1.52809	4.664677	-1.72934
N	1.492612	5.622917	-4.59501
C	-0.25385	8.080617	-0.68788
C	0.372989	8.846979	0.309685
C	-1.64107	7.896505	-0.57062
C	-0.32384	9.350854	1.387075
H	1.43687	9.030456	0.251202
C	-1.71498	9.149806	1.51107
H	0.219379	9.909431	2.134427
C	-2.35493	8.416301	0.489074
H	-2.1846	7.382923	-1.3498
H	-3.42497	8.271982	0.505121
N	-2.41664	9.663411	2.575052
C	-1.764	10.55535	3.514422
H	-1.01305	10.03226	4.117619

H	-2.5082	10.97259	4.1895
H	-1.26829	11.38761	3.003993
C	-3.8433	9.436584	2.685465
H	-4.0819	8.37009	2.640244
H	-4.40973	9.942082	1.893795
H	-4.19276	9.814809	3.643958

Table S12. Cartesian coordinates from the optimized structure of **2**.

Atomic Type	Coordinates {Å}		
	x	y	z
C	14.45837	5.9784	0.49894
C	14.3751	4.59393	0.39486
C	13.29436	6.74806	0.4654
H	15.42775	6.46191	0.59138
C	13.12944	3.98352	0.25255
H	15.28075	3.99282	0.41035
C	12.0275	6.14922	0.32907
H	13.38238	7.83186	0.52512
C	11.96218	4.75542	0.21027
H	13.06966	2.90223	0.15564
H	11.00912	4.2549	0.0603
C	10.82742	7.05618	0.20135
N	9.53582	6.45928	0.48963
H	10.81312	7.46786	-0.81467
H	10.9362	7.89226	0.90415
C	8.41424	7.21028	0.17385
H	9.48672	5.88489	1.31532
O	8.50052	8.25337	-0.46379
N	7.24974	6.6569	0.66675
C	5.93961	7.17267	0.50557
H	7.34872	5.83934	1.24785
C	5.61024	8.17296	-0.40716
C	4.91398	6.6489	1.29997
C	4.28509	8.61383	-0.55091
H	6.35951	8.61827	-1.05586
C	3.24866	8.09929	0.24468
H	4.09834	9.37224	-1.30918
C	3.59591	7.14	1.20623
H	5.12418	5.86128	2.01992
H	2.85265	6.72802	1.88492
C	1.83978	8.62066	0.05654
C	1.708951	0.09314	-0.06717
C	0.59087	7.75957	0.11949
C	0.55258	6.40151	-0.02687
C	1.142861	0.65442	-1.23963
C	2.197691	0.92625	0.97656

C	-0.61396	5.63159	0.29321
C	1.62895	5.62372	-0.54387
N	0.685451	1.09734	-2.21098
N	2.584831	1.58798	1.84449
N	-1.5421	4.99457	0.57522
N	2.46789	4.95833	-0.99093
C	-0.75983	8.42938	0.25401
C	-1.10904	9.2376	1.33924
C	-1.71013	8.26296	-0.7706
C	-2.39103	9.81529	1.40989
H	-0.41506	9.4249	2.15509
C	-3.37297	9.57503	0.43327
H	-2.647491	0.42556	2.27446
C	-2.99957	8.79806	-0.66489
H	-1.48162	7.68102	-1.66239
H	-3.70284	8.59278	-1.46706
N	-4.669541	0.0826	0.61271
C	-4.761201	1.53159	0.41533
H	-4.035011	2.07793	1.02572
H	-5.756101	1.88482	0.71167
H	-4.611511	1.79566	-0.63811
C	-5.76962	9.3275	0.00716
H	-5.69848	8.26064	0.24834
H	-5.80073	9.45184	-1.08129
H	-6.72689	9.67959	0.40831

Table S13. Cartesian coordinates from the optimized structure of **2-H**.

Atomic Type	Coordinates {Å}		
	x	y	z
C	12.70508	5.96931	3.001254
C	12.41469	4.674085	2.589209
C	11.93202	7.036469	2.550812
H	13.5277	6.150602	3.683031
C	11.3513	4.457563	1.716405
H	13.00652	3.84087	2.948677
C	10.8573	6.830315	1.684877
H	12.16063	8.042172	2.888428
C	10.58302	5.525281	1.269394
H	11.11229	3.45368	1.384968
H	9.745852	5.350913	0.60513
C	10.00035	7.9888	1.206724
N	8.596588	7.672572	1.163552
H	10.2745	8.280218	0.188526
H	10.19813	8.858752	1.845946

C	7.807703	7.808989	0.029699
H	8.172453	7.170793	1.925585
O	8.258487	8.335918	-0.98915
N	6.569041	7.250343	0.256216
C	5.507103	7.509325	-0.49457
C	5.38264	8.476514	-1.55779
C	4.309642	6.77413	-0.1904
C	4.178783	8.741305	-2.14527
H	6.270554	8.998886	-1.87828
C	2.972361	8.061706	-1.78226
H	4.152355	9.489447	-2.92344
C	3.120763	7.031106	-0.79891
H	4.385912	6.009025	0.571909
H	2.256788	6.451793	-0.50049
C	1.687978	8.396952	-2.27899
C	1.302343	9.474884	-3.09397
C	0.51889	7.563738	-1.81441
C	0.239013	6.39653	-2.47366
C	-0.04994	9.608062	-3.51294
C	2.13233	10.53739	-3.53406
C	-0.75505	5.458864	-2.05152
C	0.958537	5.992581	-3.64185
N	-1.1504	9.731624	-3.85146
N	2.741767	11.44484	-3.91442
N	-1.52809	4.664677	-1.72934
N	1.492612	5.622917	-4.59501
C	-0.25385	8.080617	-0.68788
C	0.372989	8.846979	0.309685
C	-1.64107	7.896505	-0.57062
C	-0.32384	9.350854	1.387075
H	1.43687	9.030456	0.251202
C	-1.71498	9.149806	1.51107
H	0.219379	9.909431	2.134427
C	-2.35493	8.416301	0.489074
H	-2.1846	7.382923	-1.3498
H	-3.42497	8.271982	0.505121
N	-2.41664	9.663411	2.575052
C	-1.764	10.55535	3.514422
H	-1.01305	10.03226	4.117619
H	-2.5082	10.97259	4.1895
H	-1.26829	11.38761	3.003993
C	-3.8433	9.436584	2.685465
H	-4.0819	8.37009	2.640244
H	-4.40973	9.942082	1.893795
H	-4.19276	9.814809	3.643958

H Solid-phase sensing of fluoride detection

The following procedure was used to achieve solid-phase sensing using an agarose-gel strip. Agarose gel preparation: 20 mg of agarose in 2 mL of deionized water added in a glass vial and put for stirring at 98 °C for 20 min. Then the agarose solution was kept overnight to dry at room temperature.

Agarose gel + fluoride: 20 mg of agarose in 0.002 mL of F^- ion and 1.998 mL of distilled water added in a glass vial and put for stirring at 98 °C for 20 min. then the agarose solution was kept overnight to dry at room temperature.

Agarose gel + TCBD **1** preparation: 2.2 mg of TCBD initially dissolved in 0.1 mL of acetone then 10 mg agarose is added into the TCBD solution. A 0.9 mL of H_2O is added to that vial and put for stirring at 98 °C for 20 min. Then the TCBD **1** containing agarose solution was kept overnight to dry at room temperature.

Figure S28. Mean grey values obtained using ImageJ software for the sensing of chromophore **1** showing no maroon color change when treated with a) 1 ppm of CaF_2 in $H_2O/DMSO$ 1:1 (the contrast color is due to the solvent wet nature). Whereas showing the clear color change to maroon when treated with b) 3 ppm in $H_2O/DMSO$ 1:1. c) Also, the color change was observed with 1 ppm in DMSO.

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