Electronic Supplementary Information for

Through Bond Energy Transfer (TBET)-operated fluoride ion sensing *via* spirolactam ring opening of a coumarin-fluorescein bichromophoric dyad

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1. Materials

All reagents and solvents (analytical grade and spectroscopic grade) were obtained from Merck (India) and Spectrochem Pvt. Limited (India) and were used without further purification. The required starting materials, 8-formyl-7-hydroxy-4-methyl coumarin,[1] coumarin hydrazide[2] (**1**) and fluorescein hydrazide[3] (**2**) were prepared according to the literature procedures published earlier. The dyad **R3** was synthesized by condensation reaction of 8-formyl-7-hydroxy-4-methyl coumarin with fluorescein hydrazide (**2**) according to Scheme S1. Anions such as F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^- and AcO^- were used in the form of their tetrabutylammonium (TBA) salts whereas CN^- and S^{2-}were used as KCN and Na_2S salt respectively to study the anion binding properties of dyad **R3**. All the binding studies were carried out in acetonitrile (AcN) solvent medium at 10 μM concentration of **R3**. The various equivalents of guest anions were added from their respective stock solutions varying from 1.0 to 0.1 mM prepared in AcN medium. For CN^- and S^{2-} ions, the stock solutions were prepared in UV-grade DMSO.

2. General methods

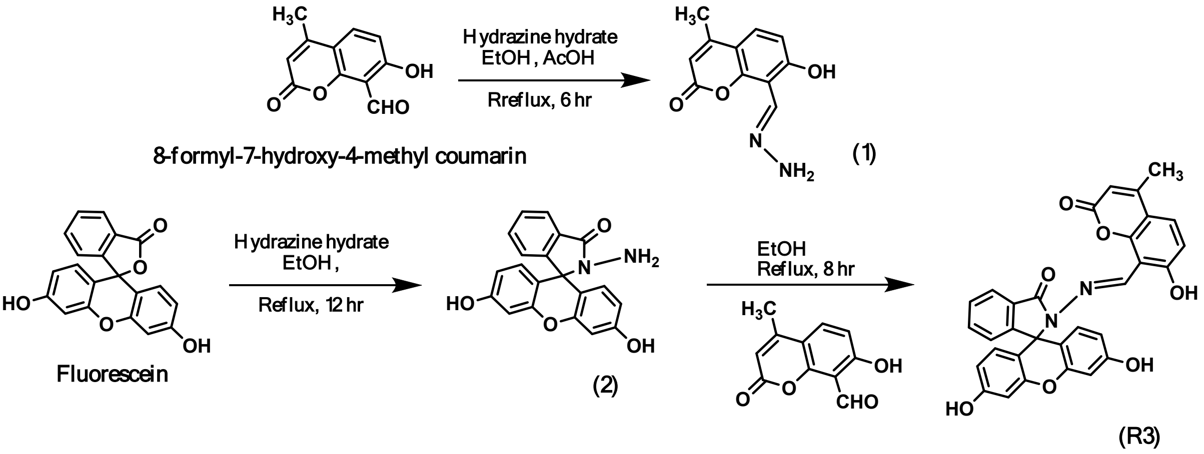
^{1}H NMR was recorded on an Avance III–400 MHz Bruker spectrometer. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane with the solvent (DMSO-d_6: 2.5 ppm) resonance as the internal standard. Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (*J* in Hz).^{13}C NMR (100 MHz) spectra were recorded on an Avance III–400 MHz Bruker spectrometer in proton decoupling mode. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (DMSO-d_6: 39.51 ppm). UV–visible absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence emission spectra were recorded on a Hitachi F-7000 fluorescence spectrophotometer. FTIR spectra were recorded on Eco-ATR, Alpha, Bruker Optik GmbH, Ettlingen, Germany. Mass spectrum was measured on Xevo G2S QTof Mass analyser (Waters). Elemental analysis was carried out by using Elementar Vario EL III CHNS. Chromatographic purification was done using 60–120 mesh silica gels (Merck). For reaction monitoring, manually coated silica gel-60 TLC plates were used.

3. Experimental method for UV–Visible and Fluorescence studies of dyad R3 with anions

For UV–visible experiments, 10 μM concentration of **R3** was prepared from its stock solution (1 mM) in acetonitrile (AcN) medium. Anion selectivity study was conducted by addition of 10.0 equivalents of various anions individually to a 10 μM solution of **R3**. The spectrophotometry titrations were carried by gradual addition of various equivalents of fluoride ion through a micro pipette to a 2 mL (10 μM in AcN medium) solution of **R3** taken in a cuvette and the absorption and emission spectra were recorded.

4. Experimental method for ^{1}H NMR titration experiments

A 5.0 mM solution of dyad **R3** was prepared in DMSO-d_6. Various equivalents of tetrabutylammonium fluoride (from a stock solution of 10 mM in DMSO-d_6) were added to 0.5 mL of dyad solution in an NMR tube through a micro pipette and the ^{1}H NMR spectra were recorded after each addition.



Scheme S1. Synthesis protocol for compounds **1**, **2**, and **R3**.

5. General procedure for synthesis of dyad R3

The dyad **R3** was synthesised as per the synthetic protocol given in Scheme S1. A solution of fluorescein hydrazide (**2**) (0.38 g, 1.0 mmol) in 20 mL of absolute ethanol was taken in a 50 mL round bottom flask. To this solution, 1.5 mmol of 8-formyl-7-hydroxy-4-methyl coumarin (0.306 g) dissolved in 10 mL of absolute ethanol was added slowly in drop wise manner under stirring condition at room temperature. Then the reaction mixture was refluxed in an oil bath for 8 hours till completion of the starting materials as monitored by thin layer chromatography. After cooling of the reaction mixture, the precipitate thus obtain was filtered under vacuum and subsequently washed for three times with 20 mL ethanol to remove any remaining unreacted starting materials. Then the product was dried under reduced pressure and further purified by recrystallization from acetonitrile solvent to afford **R3** in more than 80% yields.

6. Characterization data for dyad R3

White Powder (Yield: 81%) MP: 338°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 2.39 (3H, s, -CH_3), 6.26 (s, 1H, Coumarin ring-H), 6.52 (d, J = 8Hz, 2H, Xanthene-H), 6.61 (d, J = 8Hz, 2H, Xanthene-H), 6.71 (s, 2H, Xanthene-H), 6.85 (d, J = 8Hz, 1H, Ar-H), 7.22 (d, J = 8Hz, 1H, Ar-H), 7.69 (m, 3H, Ar-H), 8.02 (d, J = 8Hz, 1H, Ar-H), 9.70 (s, 1H, -N=CH), 10.05 (s, broad, 2H, Xanthene-OH), 11.57 (s, broad, 1H, Coumarin -OH). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 18.2, 55.7, 114.9, 123.9, 126.8, 127.1, 128.6, 128.9, 129.1, 129.1, 130.2, 130.4, 131.5, 144.4, 147.0, 159.6, 165.1. FTIR (KBr) υ(cm^{-1}) 3400-2700 broad (-OH), 1721 (>C=N), 1620, 1575, 1487, 1448, 1273, 1203, 1111, 1031, 979, 896, 755, 680, 561, 459. ESI-MS *m/z*: calcd for $C_{31}H_{20}N_2O_7$ $[M+H]^+$: 533.12; found, 533.02. Elemental analysis: $C_{31}H_{20}N_2O_7$: calcd. C 69.92, H 3.79, N 5.26; found: C 69.80, H 3.91, N 5.15%.

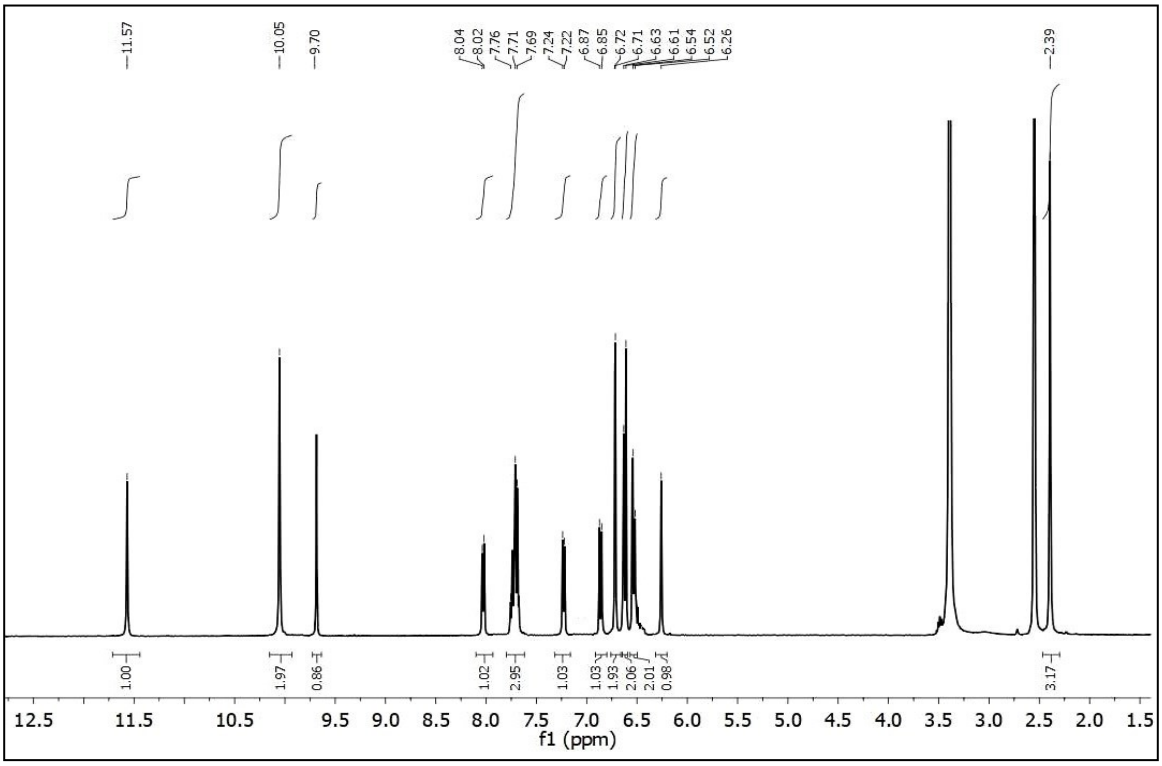


Fig. S1. ^{1}H NMR spectrum of **R3** in DMSO-d_6.

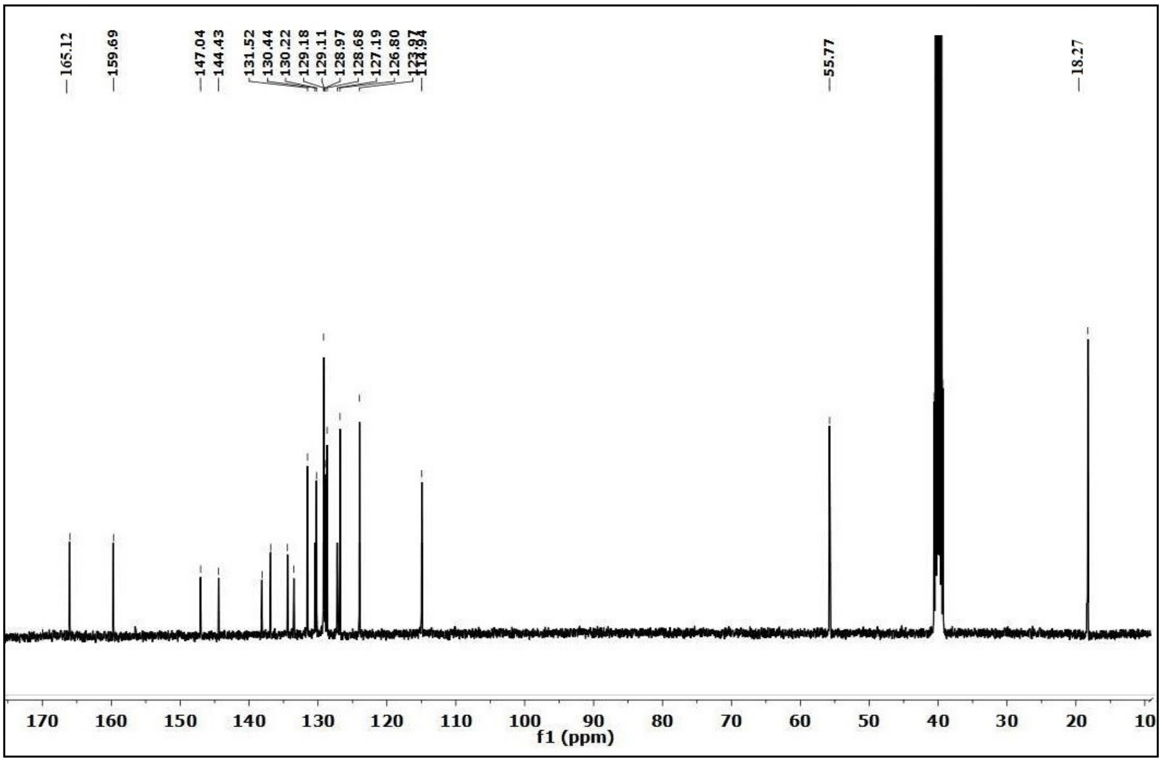


Fig. S2. ^{13}C NMR spectrum of **R3** in DMSO-d_6.

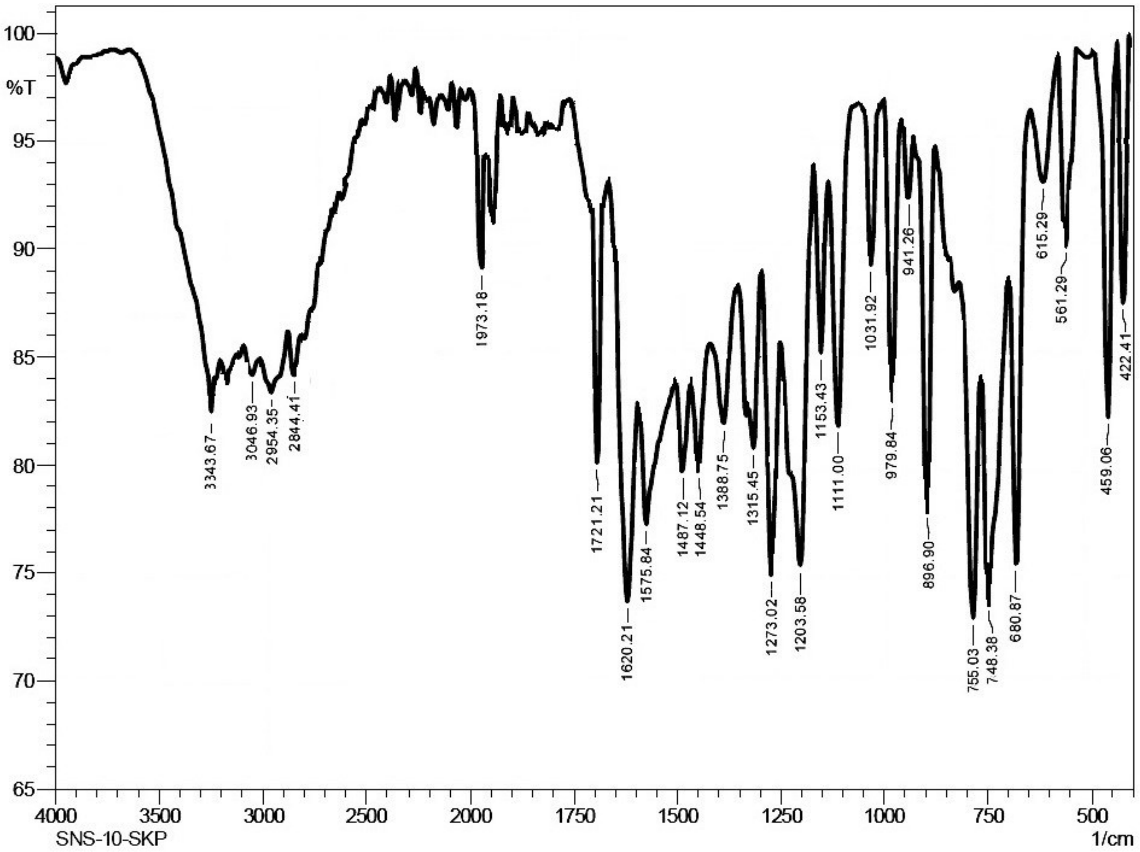


Fig. S3. FTIR spectrum (in KBr) of **R3**.

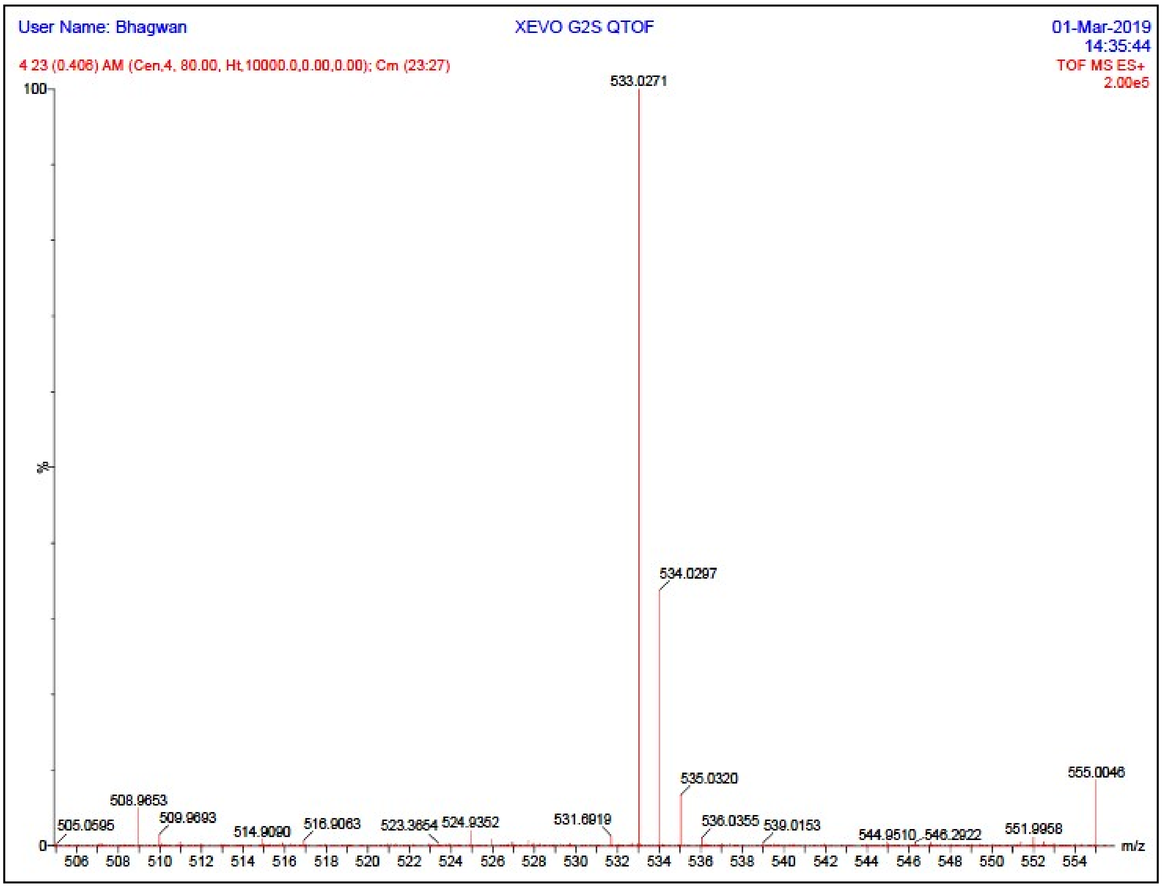


Fig. S4. ESI mass spectrum of **R3**.

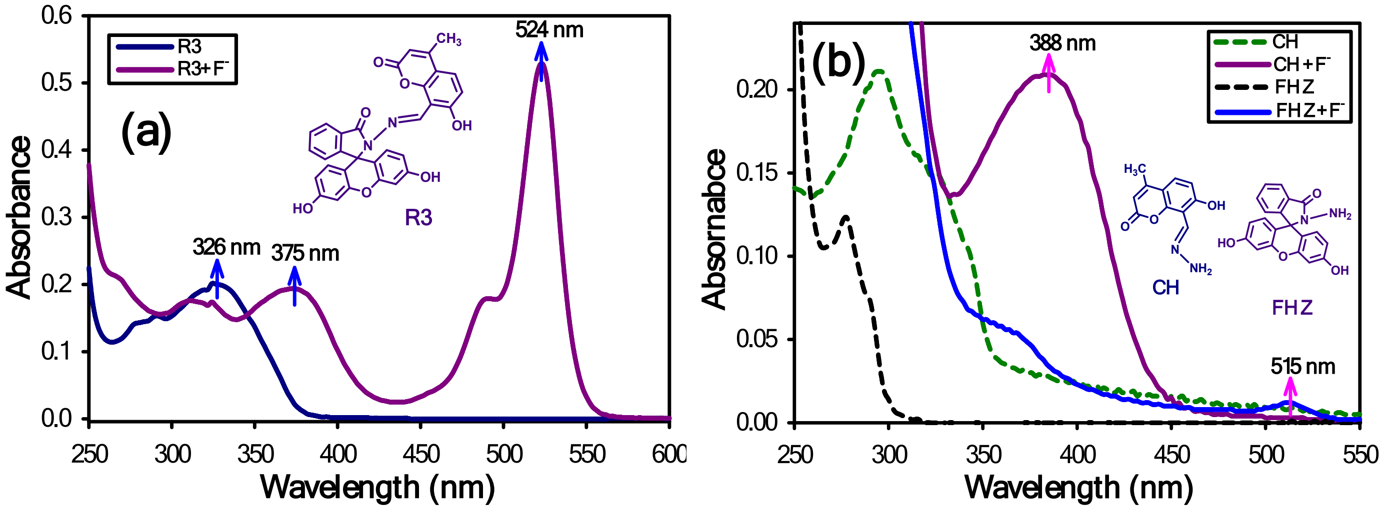


Fig. S5. (a) Absorption spectra of 10 μM solution of dyad **R3** with excess of F⁻ ions (10 equiv.) (b) Absorption spectra of 10 μM solution of coumarin component (**1**, CH) and fluorescein component (**2**, FHZ) with excess of F⁻ ions (10 equiv.).

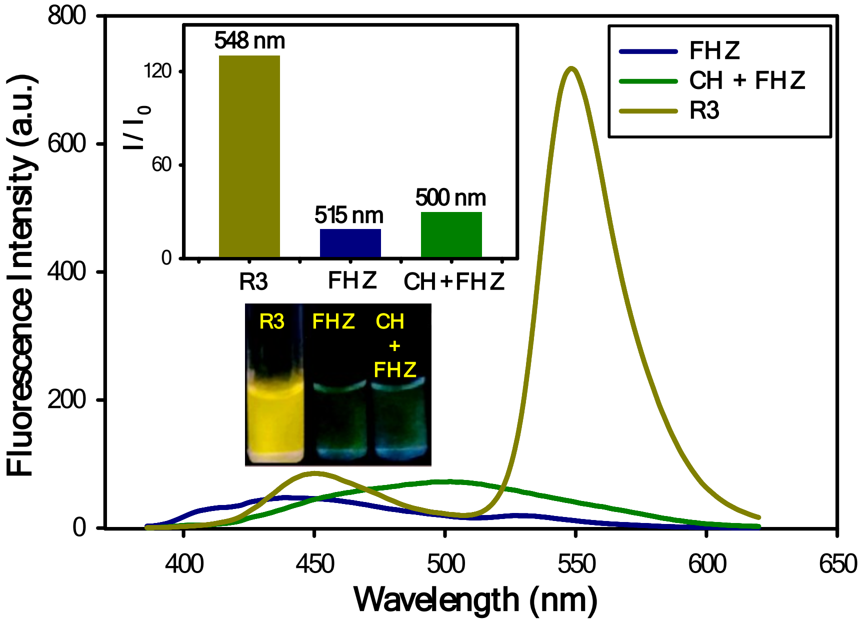


Fig. S6. Emission spectra of 10 μM solution of dyad **R3** (yellow colour), Fluorescein component (**2**, FHZ) (blue colour) and equimolar (10 μM each) mixture of coumarin component (**1**, CH) and fluorescein component (**2**, FHZ) (green colour) in the presence of F⁻ ions (10 equiv.). Inset shows I/I_0 at their respective I_{max} in absence (I_0) and presence (I) of F⁻ ions. Inset also shows a visual fluorescence colour change in dyad **R3**, component **2** and equimolar mixture (**1**+**2**) with fluoride ion under UV-light at 365 nm. λ_{ex} = 376 nm.

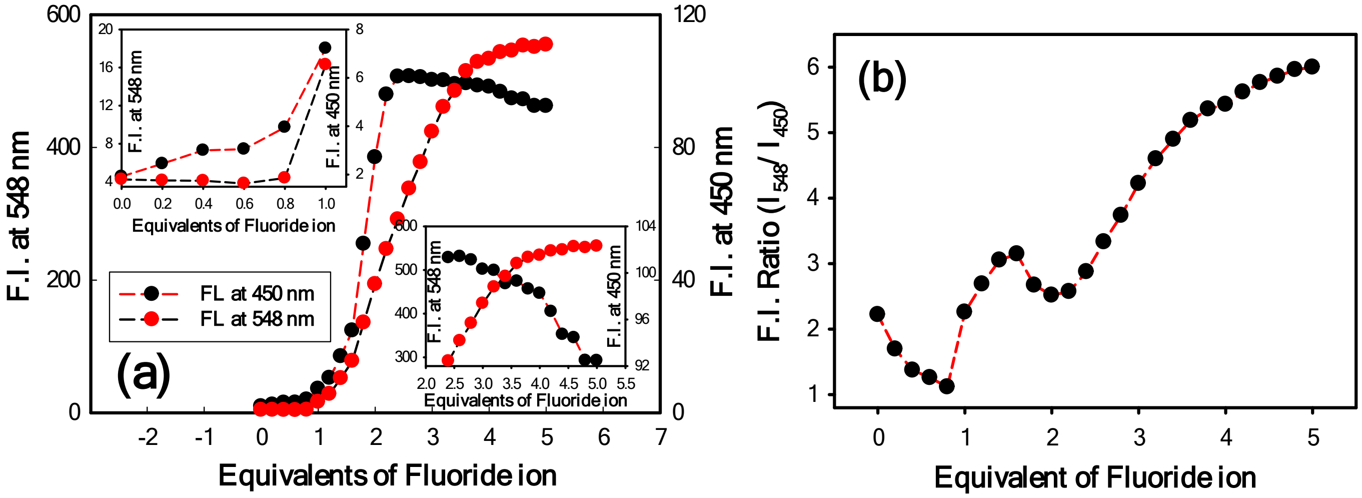


Fig. S7. (a) Change in fluorescence intensity at 548 nm and 450 nm in dyad **R3** (10 µM) against various equivalents of fluoride ion. Insets show the change in fluorescence intensity at 548 nm and 450 nm in dyad **R3** between 0.0-1.0 equivalent and 2.0-5.0 equivalents of fluoride ions. (b) Ratio of fluorescence intensity (I_{548}/I_{450}) against various equivalents of fluoride ion.

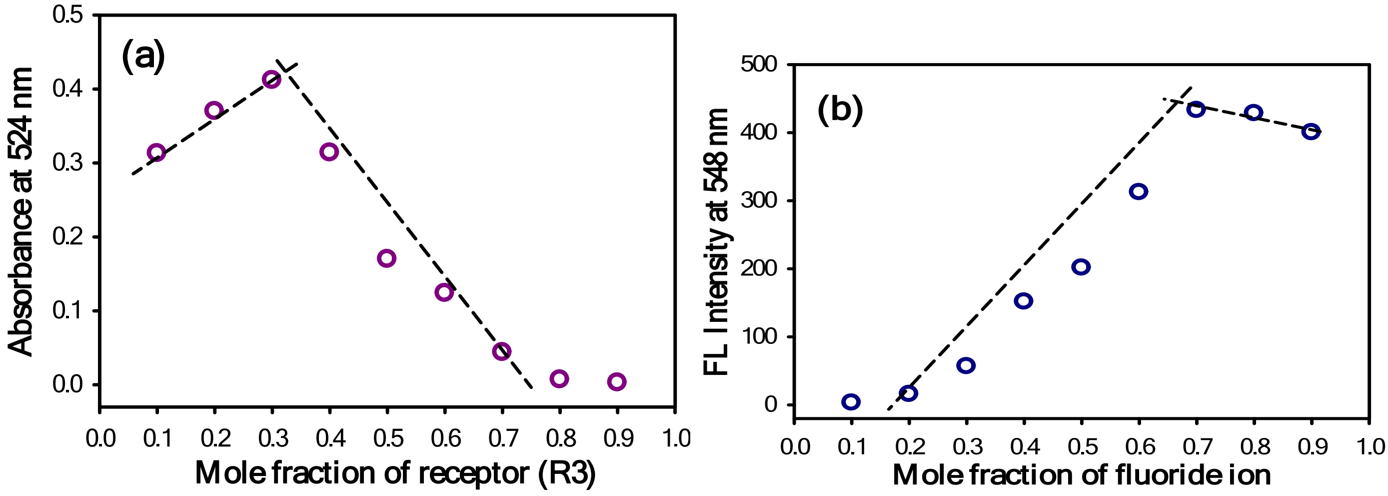


Fig. S8. Job's plot of **R3** with F^- ions determined from UV-visible (λ_{max} = 524 nm) and fluorescence (λ_{em} = 548 nm; λ_{ex} = 376 nm) experiments at 298 K.

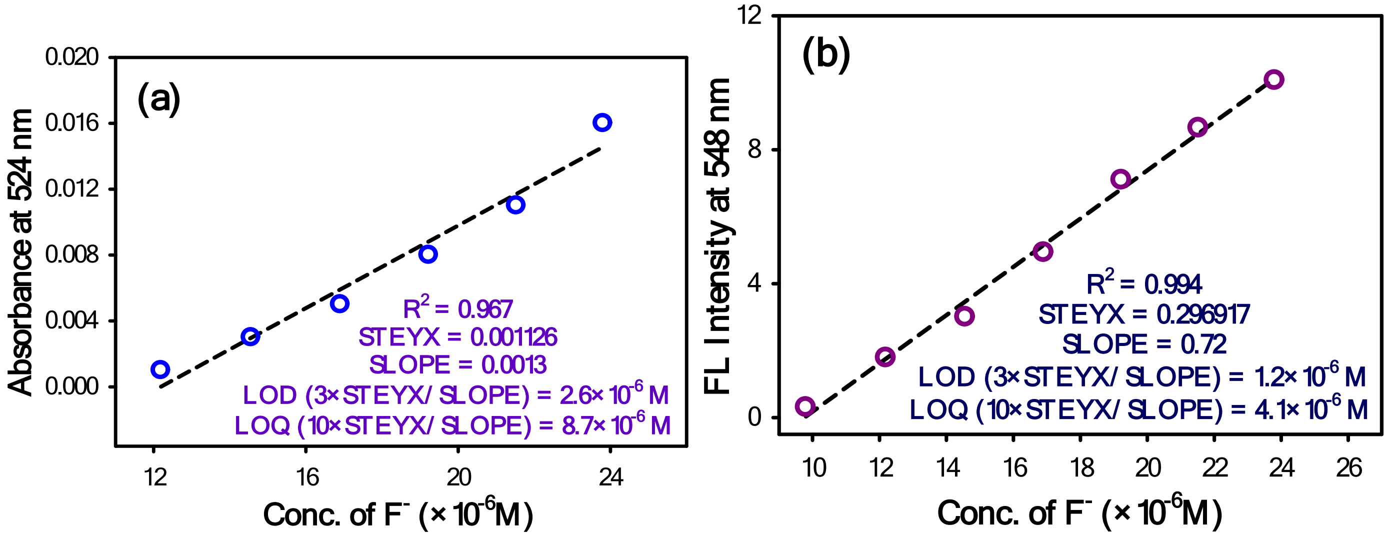


Fig. S9. Calculation of limit of detection (LOD) of **R3** for F^- ion from (a) UV-visible method, (b) Fluorescence method.

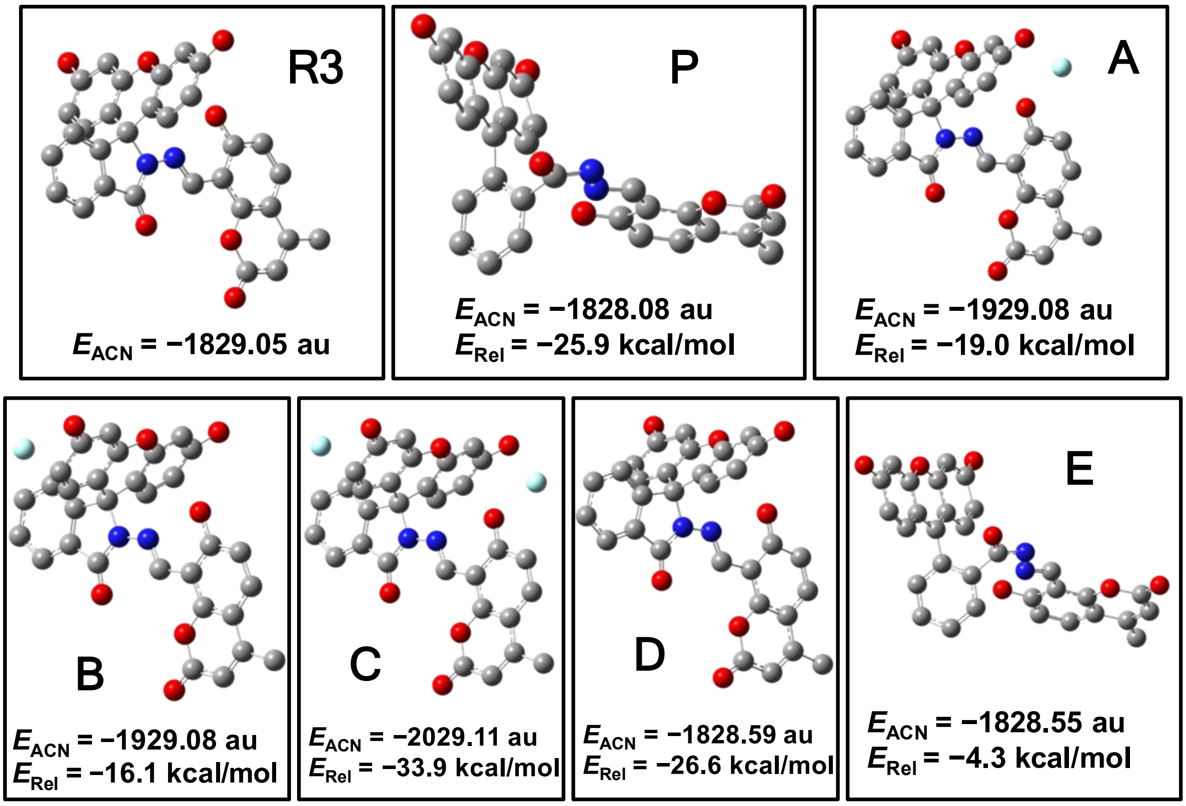


Fig. S10. Optimized structures of dyad **R3**, various **R3**-fluoride intermediates (A, B, C, D, E) and deprotonated product P (colour key: grey = carbon; blue = nitrogen; red = oxygen; cyan = fluorine). E_{ACN} indicates the calculated total energy in acetonitrile solvent. E_{Rel} indicates the relative energy of the species calculated (from Table S1) with respect to dyad **R3** in acetonitrile solvent.

Table S1. Calculated relative energy of species A, B, C, D, E and P (refer Scheme 2 of main article) with respect to the energy of dyad **R3**.

Species	DFT Energy (in atomic unit)	Relative energy with respect to R3 (kcal/mol)	Remarks (method of calculation of relative energy)
R3	-1829.05873084	0	Reference
A	-1929.08908962	-19.0	(Energy of A) − (Energy of F^-)
B	-1929.08444269	-16.1	(Energy of B) − (Energy of F^-)
C	-2029.11273075	-33.9	(Energy of C) − (2×Energy of F^-)
D	-1828.59389167	-26.6	(Energy of D) + (Energy of HF_2^-) − (2×Energy of F^-)
E	-1828.55845112	-4.3	(Energy of E) + (Energy of HF_2^-) − (2×Energy of F^-)
Product P	-1828.08558067	-25.9	(Energy of product P) + (2×Energy of HF_2^-) − (4×Energy of F^-)
Fluoride ion (F^-)	-99.99997769		
Bifluoride ion (HF_2^-)	-200.50716628		

Table S2. Comparison of experimental and computed absorption bands of dyad **R3** and product P.

Complex	Experimental Wavelength (nm)	Calculated Wavelength (nm)	Oscillator strength (*f*)	Orbital Contribution
Product P	524	491	0.02	H-2 →L, H→L
Product P	375	370	0.49	H-8→L, H-5→L, H-4→L, H→L+2, H→L+7
Product P		326	0.61	H-5→ L, H→L+2, H→L+2, H→L+5
R3	326	297	0.73	H-3→L, H-3→L+1, H→L
R3	271	284	0.30	H-3→L, H-3→ L+1, H -2→L, H-2→L+1, H→L
R3		280	0.18	H-9→L, H-2→L, H-2→L+1, H-2→L+2, H-2→L+4, H→L

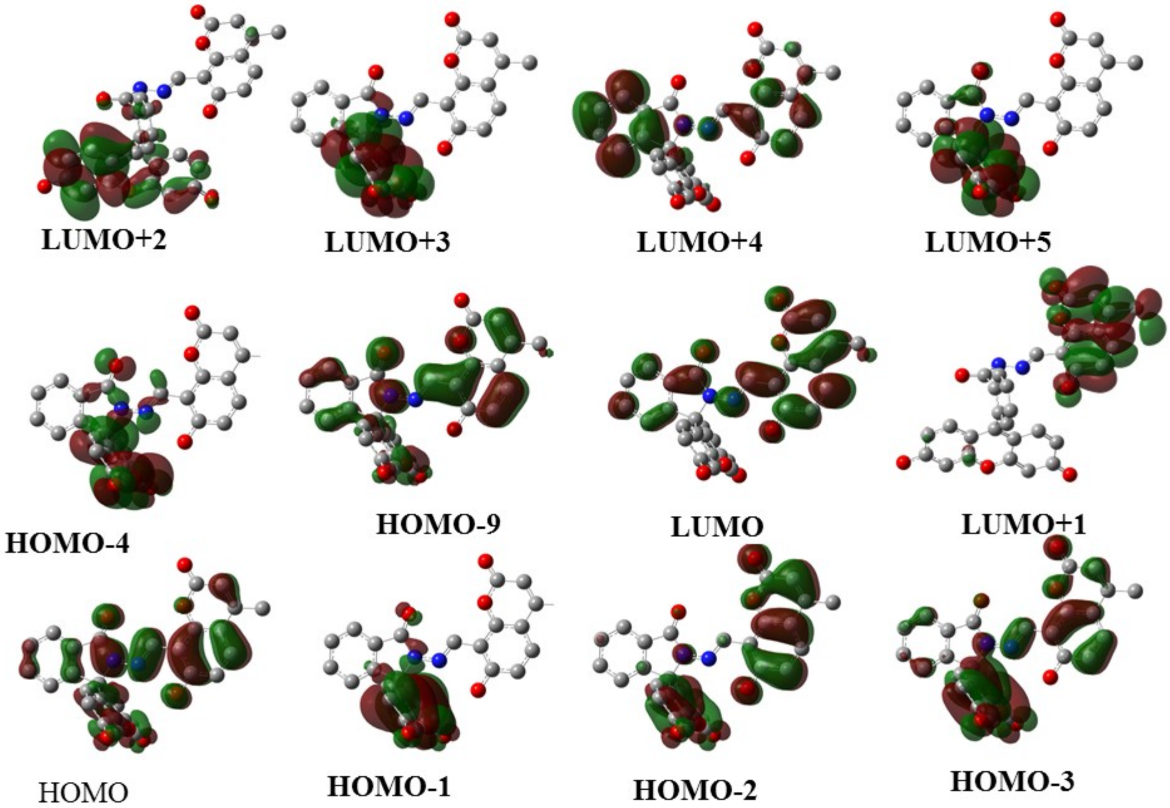


Fig. S11. Frontier molecular orbitals of dyad **R3**.

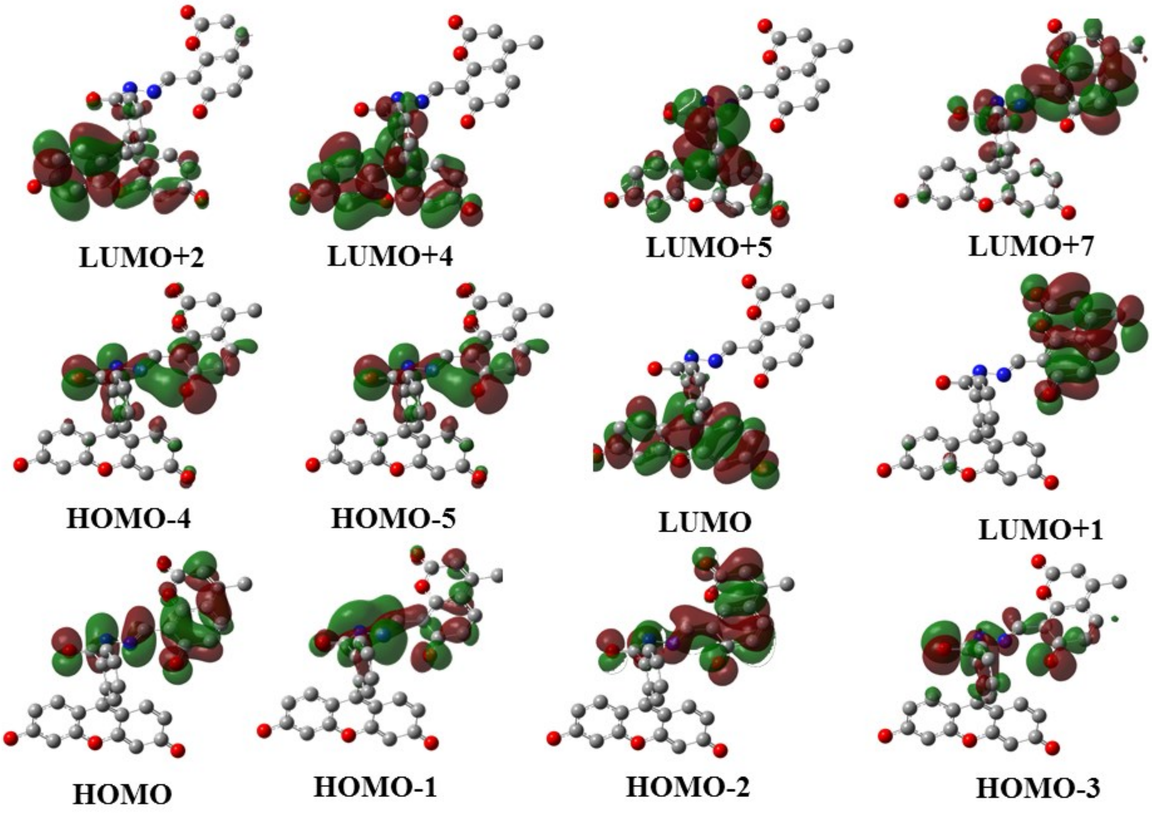


Fig. S12. Frontier molecular orbitals of product P (refer Scheme 2 of main article).

References

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