

CHEMISTRY A European Journal



Accepted Article Title: Phenothiazine based Donor - Acceptor Compounds with Solid-State Emission in the Yellow to NIR Region and their Highly Selective and Sensitive Detection of Cyanide Ion in ppb Level Authors: Raghavachari Dhamodharan, Ramachandran Elumalai, Anbu Anjugam Vandarkuzhali Somasundaram, and Sivaraman Gandhi This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201800216 Link to VoR: http://dx.doi.org/10.1002/chem.201800216

Supported by ACES



FULL PAPER

Phenothiazine based Donor - Acceptor Compounds with Solid-State Emission in the Yellow to NIR Region and their Highly Selective and Sensitive Detection of Cyanide Ion in ppb Level

Elumalai Ramachandran^[a], Somasundaram Anbu Anjugam Vandarkuzhali^[b], Gandhi Sivaraman^[c] and Raghavachari Dhamodharan^{*[a]}

Dedication ((optional))

Abstract: Four new novel donor-acceptor (A- π -D-A, A-D- π -D-A) compounds (1a, 1b, 2a and 2b) based on ethylenedioxythiophene (EDOT) and phenothiazine (PTz) have been rationally designed and synthesized towards solid state emission ranging from yellow to near infrared (NIR). The compounds 1b and 2b, in thin film form showed emission maximum at 713 nm and 696 nm, respectively with the corresponding absolute solid-state quantum yield of 3.3 % and 9.0 %. The fluorophores showed high emission in the doped state as well when dispersed in polystyrene (PS) matrix with emission maximum ranging from 536 nm to 648 nm with quantum yield in the range 12.4 % - 64.4 %. The presence of dicyanovinyl (DCV) group in both the fluorophores was exploited towards cyanide sensing in DMSO leading to turn-on fluorescence emission with high selectivity and sensitivity for cyanide ion with a detection limit of as low as 0.32 μ M (8 ppb) for 1b and 0.57 µM (14 ppb) for 2b. DFT and TTDFT calculations suggested that the addition of cyanide ion prevented the intramolecular charge transfer (ICT) from the donor (PTz or EDOT) to acceptor (DCV), thereby turning the fluorescence "On". Using fluorescent spectral and colour switching we have explored logic gates with single and two input signal amplification by applying chemical and light inputs in the form of CN⁻ ion and UV.

Introduction

Solid state emitting fluorophores have attracted a great deal of attention^[1-3] owing to their widespread applications such as organic light emitting diodes^[4-6], organic solid state lasers^[7], flat panel displays^[8], fluorescent sensors^[9-11], etc., Although a number

[a]	E. Ramachandran, Prof. R. Dhamodharan
	Department of Chemistry
	Indian Institute of Technology Madras
	Chennai – 600 036
	E-mail: damo@iitm.ac.in
[b]	Dr. S. A. A. Vandarkuzhali
	National Centre for Catalysis Research
	Department of Chemistry
	Indian Institute of Technology Madras
	Chennai – 600 036.
[C]	Dr. G. Sivaraman
	Institute for Stem Cell Biology and Regenerative Medicine
	(INSTEM),
	National Centre for Biological Sciences
	Bangalore – 560 065.
	Supporting information for this article is given via a link at the end of
	the document.

of organic fluorophores, emitting in the entire visible region have been developed, those emitting in the near infrared (NIR) are still rare.^[12] On the contrary, solution state red and NIR emitting organic fluorophores are very common. The fluorophores with NIR emission are of immense importance since they find numerous applications in various fields, especially in bio-imaging, heat absorbers, optical disks, plasma panel and laser printers.[13] One common method applied to make low band-gap emitters is to use organic molecules with planar architecture containing extended π -conjugation as a core structure. This method yields fluorophores emitting in the long wavelength regimes but severely suffers from concentration or aggregation caused quenching (ACQ) owing to the planar architecture. This detrimental phenomenon prevents these fluorophores from real world applications, which primarily require high emission in the solid state. The limitations of ACQ can be overcome in two ways: (i) use of propeller type molecule as a core structure, with D-A type fluorophores attached to the core^[14] and (ii) use of non-planar (π-breaker) with chromophore strong donor-acceptor substitution.^[12] With this strategy in mind, we have designed and synthesized four new fluorophores based on phenothiazine (PTz) and ethylenedioxythiophene (EDOT) (Scheme 1). To the best of our knowledge, there are only very few examples of small donoracceptor molecules based on phenothiazine, which exhibit solid state emission in the deep red and NIR regions.[12,18]

PTz is a highly electron rich molecule and its butterfly-like structure provides steric hindrance, which should prevent self-aggregation in the solid state.^[12-15,18] EDOT, on the other hand is known for its high molar absorptivity and bathochromic shift of absorption when π -linked to other chromophores. Recently we reported PTz and EDOT based fluorophores that exhibited emission in the red and NIR region in solid state^[12]. In this work, we have designed and synthesized four fluorophores **1a**, **1b**, **2a** and **2b** (two *A*- π -*D*-*A* and two *A*-*D*- π -*D*-*A*) by varying, i) the ratio of the phenothiazine [(Donor and a Stacking Breaker (SB)] to ethylenedioxythiophene (π -linker) and ii) the strength of acceptor (aldehyde or DCV). The non-planar structure of the resulting fluorophores prevented the molecules from close packing and resulted in moderate to high quantum yield in solution, thin film and polystyrene matrix.

Cyanide ions find widespread industrial use in gold mining, electroplating, metallurgy, synthetic fibers, herbicides and resins.^[19-21] Salts with cyanide as the anion are used in the production of organic chemicals.^[22] The global production of cyanides is about 1.1 MMT.^[23] The extensive use of cyanide mandates that the environment is monitored for its release in view



Scheme 1. Synthesis of DCV compounds 1b and 2b. a) Malononitrile, Al₂O₃, DCM, RT, 4 h

of its serious threat to aquatic and human life even at low concentrations. The World Health Organization's (WHO) maximum permissible limit of cyanide in drinking water is lower than 1.9 µM.^[24] The permissible limit of cyanide in drinking water as suggested by the Environment Protection Agency (EPA) is 200 ppb.^[19,25] A number of methods have been developed to detect cyanide ion.^[26] But all these require sophisticated instruments as well as time consuming procedures. This calls for the development of a low cost, on-site optical probe to monitor the presence of cyanide ion through mere color change and/or fluorescence intensity (or emission wavelength).^[26] Many probes with reversible sensing nature for cyanide ion have been reported in literature.^[27-38] It may be more advantageous if cyanide can be detected and scavenged in an irreversible manner through covalent bond formation between cyanide ion and the sensor.[39-^{70]} The DCV group, present in **1b** and **2b** was exploited for selective and sensitive detection of aqueous cyanide in DMSO solution of the probes.

Results and Discussion

The aldehydes, **1a** and **2a**, were synthesized through Sonogashira coupling reaction from the corresponding alkyne and aryl halides of PTz and EDOT (given in the supporting information); the DCV derivatives, **1b** and **2b**, were obtained by a simple condensation of the aldehydes with malononitrile.^[12] All the compounds (**1-2**) were thoroughly characterized by ¹H and ¹³C NMR spectroscopy, mass spectrometry (Figures S1-S16 in the supporting information), IR spectroscopy and elemental analysis.

Photophysical properties

The UV-Visible absorption and fluorescence ($\lambda_{exc} = \lambda_{max}$, longest wavelength) spectra of the aldehydes **1a** and **2a** and their corresponding DCV derivatives, **1b** and **2b**, in toluene, are given in Figure S17 in the supporting information). The aldehydes showed two absorption maxima. Similarly, the DCV derivative **1b** showed two absorption maxima along with a shoulder both in toluene and DCM. Compound **2b** also showed two absorption

maxima along with a shoulder band. The details of the absorption and emission maxima are given in Table S1 in supporting informatio. The emission maxima of the aldehydes in toluene, range from 513 nm to 519 nm (greenish yellow) while those of the DCV derivatives from 616 nm to 622 nm (red). The red shifted absorption and emission of the DCV derivatives 1b and 2b can be attributed to the stronger electron acceptor nature of the DCV group, compared to that of the aldehydes. The emission spectra recorded in more polar solvent, such as CH₂Cl₂, showed red shifted emission maxima (compared to those measured in toluene), which suggest strong ICT (Figure S17 in the supporting information). The emission maxima of the aldehydes appeared in the region ranging from 534 nm to 536 nm. Similarly, the emission maxima of the DCV compounds ranged from 629 nm to 637 nm. The fluorescence quantum yield of 1a and 2a in toluene was found to be 17 % and 27 %, respectively against fluorescein as standard.

The DCV compounds **1b** and **2b** in toluene exhibited quantum vield of 19 % and 18 %, respectively against rhodamine 6G as standard. The emission spectra of both aldehydes and DCV derivatives had very little overlap with their corresponding absorption spectra, intimating that there would be a decreased energy transfer leading to self-quenching (detrimental phenomenon in many technological applications) via Förster mechanism.^[1] The aldehyde **1a** exhibited three absorption bands in thin film whereas the aldehyde 2a showed two absorption maxima. The emission maxima of the aldehydes 1a and 2a are observed in the yellow region. The DCV compounds, 1b and 2b showed two absorption maxima. The emission maxima of the DCV compounds 1b and 2b appeared in the NIR and deep red regions, respectively (Figure 1 and Table 1). The emission maxima of the aldehvdes in thin film form was red shifted to the extent of 4 to 22 nm when compared to those in DCM. Similar red shift was observed for the DCV compounds though the range was between 38 and 57 nm. The fluorescence guantum yield of the aldehydes and the DCV compounds in thin film ranged from 3.3 % to 13.4 %.

The higher shift in the emission maximum of the DCV compounds in the solid state can be attributed to the stronger dipole–dipole interaction, which is due to the stronger electron withdrawing nature of the two DCV group. Moreover all the molecules (1-2) showed large Stokes shift, both in solution and in



Figure 1. Absorption and emission spectra of the aldehydes (left) and DCV compounds (right) in thin film form. The inset of figure on the left shows the aldehydes 1a (1 and 2) and 2a (3 and 4) in thin film and powder forms. The inset of figure on the right shows the DCV compounds 1b (5 and 6) and 2b (7 and 8) in thin film and powder forms under UV light (excited at 365 nm).

Table 1. Photophysical properties of the aldehydes	1a and 2a) and DCV com	pounds (1b and 2b) in solution
powder and PS film.		

			100			
Compound		$\lambda_{abs} \left[nm \right]^{[a,b]} (\epsilon)^{[c]}$			$\lambda_{\text{em}} [\text{nm}]^{[d]} (\Phi_{\text{f}} \%)^{[e]}$	
	Solution ^[a]	Thin film	PS film ^[f]	Solution ^[a]	Thin film	PS film ^[f]
1a	332 (π-π*) 411 (29942) (ICT)	294 (π-π [*]) 347 (π-π [*]) 446 (ICT)	330 (π-π [*]) 416 (ICT)	519 (17)	570 (5.5)	534 (12.4)
1b	366 (π-π [*]) 419 (50726) (ICT)	295(π-π [*]) 444 (ICT)	366 (π-π [*]) 420 (ICT)	513 (27)	541 (13.4)	517 (31.5)
2a	366 (π-π [*]) 401 (π-π [*]) 488 (46913) (ICT)	427 (π-π [•]) 550 (ICT)	311 (π-π ^ˆ) 403 (π-π ^ˆ) 495 (ICT)	616 (19)	713 (3.3)	609 (47.7)
2b	326 (π-π [*]) 482 (52928) (ICT)	402 (π-π [*]) 503 (ICT)	327 (π-π [*]) 384 (π-π [*]) 491 (ICT)	622 (18)	696 (9.0)	624 (65.4)

[a] 1x10⁻⁵ M toluene. Fluorescein and rhodamine 6G were used as quantum yield standards for the aldehydes and DCV compounds, respectively. [b] Absorption maximum at the longest wavelength. [c] Molar absorption coefficient [M⁻¹cm⁻¹] calculated for the longest absorption maximum. [d] Emission maximum upon photoexcitation. [e] Absolute quantum yield determined with a calibrated integrating sphere. [f] Polystyrene film doped with **1-2**.

the solid state. The Stokes shift in solution ranged from 128 to 168 and in the thin film form it was found to be in the range of 97 - 155 nm (aldehydes) and 163 - 206 nm (DCV) (Table 1)

The compounds (1-2) showed similar trend in absorption and emission behavior in PS film. The fluorescence maxima of all the compounds in polystyrene (Figure 2 and Figure S18 in the supporting information) were blue shifted when compared to those in the neat film and red shifted compared to solution (except 1b). The absolute quantum yield of the compounds 1-2 in PS film ranged from 12.4 % to 65.4 %. The quantum yields of 1-2 in PS matrix were higher than those in the neat solid form. The higher quantum yield observed in the PS thin film can be attributed to the lower probability of the interaction between the chromophores and the consequent lowering of self-quenching. Surprisingly the quantum yield in solution was also lower than that in the PS thin film form (except for **1a**). This might be due to the inability to obtain absolute quantum yield in solution where a standard is always used. All the compounds, when analysed by cyclic voltammetry exhibited reversible anodic waves whereas the cathodic waves were featureless (Figure S19 in the supporting inforamtion). For

FULL PAPER

WILEY-VCH



Figure 2. Absorption and emission spectra of 1a and 1b in thin film form dispersed in polystyrene (0.1 mg/ml of PS solution of concentration 250 mg/ml in benzene).

the aldehydes **1a** and **2a** and their DCV derivatives, the first oxidation peak was found to be reversible while the second oxidation peak was quasi-reversible, suggesting that the monocation of phenothiazine is stable while the dication is unstable. However, aldehyde **2a** showed only one reversible oxidation peak while its DCV derivative **2b** exhibited two anodic waves, of which the first one was found to be reversible whereas the second one was irriversible suggesting that the dication is either unstable or its formation is not feasible.^[23] The HOMO – LUMO energy gap and the energy level of the compounds **1-2** were determined by optical and electrochemical methods

The powder XRD analysis of the aldehydes **1a** and **2a** showed very sharp peaks with narrow peak width suggesting that they are all crystalline in nature. On the contrary, the DCV derivatives **1b** and **2b** exhibited high degree of amorphous nature (Figure S20 in the supporting information). It is well known that amorphous organic light emitting materials have advantage over crystalline compounds, when light emitting diodes are fabricated since they have better light emitting properties compared to their crystalline counterparts, in general.^[71] All the compounds showed very high thermal stability with a decomposition temperature ranging from 345 °C to 370 °C at 5 % weight loss. The thermal properties of the compounds are presented in the supporting information (Figures S21 and S22).

Gas-phase density functional theory (DFT) calculations (B3LYP/6-31G^{*} level) were carried out in order to get a clear insight into the intramolecular charge transfer character of **1-2** at the molecular level and time-dependent DFT (TDDFT) was employed to investigate ground to excited-state transitions. The pertinent results are provided in the Tables S2-S5 in the supporting information. In all these energy optimized structures (Figures S23 and S24 in the supporting information), phenothiazine adopted a puckered butterfly structure. In the case of compound **1a**, the HOMO is primarily localized on phenothiazine ring and the ethynyl bond while the LUMO spreads over the aldehyde attached to the EDOT and ethynyl bond. In case of **2a** the HOMO is spread on EDOT and partly over phenothiazine rings through the ethynyl bond. The LUMO of **2a** has more density in the center of the molecule and spreads

across the ethynyl bond. In the same manner, the HOMO of **1b** is manly located on phenothiazine and ethynyl bond whereas LUMO is spread over EDOT and DCV unit. In the case of **2b**, the HOMO is distributed mainly on EDOT and partly over phenothiazine rings while the LUMO is situated on the DCV attached phenothiazine. Thus, HOMO \rightarrow LUMO transition, which corresponds to the absorption edge in all the compounds, involves considerable intramolecular charge transition (ICT).^[72]

Naked eye sensing of cyanide ion

The two DCV probes (**1b** and **2b**) in DMSO were employed in naked eye sensing of cyanide ion from aqueous solution. Since the probes were insoluble either in water or any water/organic mixed solvents owing to the presence of long hydrophobic alkyl group, we carried out the sensing experiments in DMSO. A rapid decolorization was observed, within a minute, when an aqueous solution of cyanide was added. In both the cases, the solution of the probe with no or little emissive property was found to exhibit enhanced emission upon the addition of cyanide ions.

In the case of probe 1b, a very weak yellowish fluorescence turned into a bright green fluorescence and for probe 2b the solution with weak yellow orange fluorescence exhibited bright yellow fluorescence upon the addition of cyanide. This clearly shows that the compounds 1b and 2b operate as "turn-on" fluorescent probes towards CN⁻ ion. The sensitivity, as estimated from the emission spectral changes, has been found to be 8 and 14 ppb for compounds 1b and 2b, respectively. These values are much lower than the limit set by EPA for drinking water.^[7, 19, 24, 25] The probes were found to be highly selective to cyanide ion. The color of the probes in DMSO solution remained unaltered upon the addition of other ions such as F⁻, Cl⁻, Br⁻, l⁻, HCO₃⁻, NO₂⁻, N₃⁻, AcO⁻, H₂PO₄⁻, and their mixture under day and UV light whereas an enhanced fluorescence was observed in the presence of aqueous CN⁻ ion. The above experiments suggest that the probes can sense CN⁻ ion very efficiently even in the presence of other interfering ions (Figure 3).

FULL PAPER



Figure 3. Color change observed for probes 1b and 2b (10 μ M, DMSO) upon addition of aqueous CN⁻ and other ion (20 equivalents). (In each case, top row: under day light and bottom row: UV light, 365 nm).

UV-visible and fluorescence spectroscopy studies for selectivity and sensitivity

In order to evaluate the selectivity of these probes towards cyanide ion, UV-Visible and fluorescence measurements were carried out in the presence of other ions (Figure S25 in the supporting information). The probes were dissolved in DMSO and aqueous solution of various ions was added before recording the absorption and emission spectra. Both the probes (1b and 2b) exhibited very high selectivity for cyanide ion while showing virtually no change in both the UV and fluorescence spectra in the presence of other ions such as F⁻, Cl⁻, Br⁻, l⁻, HCO₃⁻, NO₂⁻, N₃⁻, OAc⁻, and H₂PO₄⁻. The probe **1b** showed two absorbance maxima, one centered around 406 nm and the other around 494 nm; the former peak corresponds to π - π^* transition and the latter is ascribed to the charge transfer transition ^[43]. Upon addition of other ions these two peaks were found to be intact whereas the addition of cyanide resulted in the vanishing of the peaks with a concomitant appearance of two new peaks at 377 nm and 322 nm (Figure 4). The compound 2b showed similar results (Figure S26 in the supporting information).

The emission behavior was also similar; the compound **1b** showed a very weak emission at 539 nm, which was turned on by

the addition of cyanide ion into a bright green emission at 510 nm. Similarly, a weak emission of **2b** at 544 nm was turned on into a bright yellow emission at 548 nm upon the addition of cyanide ion. It is well known that the DCV group, present in these fluorophores, is prone to nucleophilic attack specifically by cyanide ion.^[39,44,45,54]

The strong electronic coupling between the donors (phenothiazine and EDOT) and acceptor DCV groups, formed through the donor-acceptor interaction is eliminated when cyanide ion attacks the double bond of the DCV group; this causes the disappearance of the charge transfer peak originally present at 494 nm. The emission spectrum of probes **1b** and **2b** also showed similar high selectivity towards cyanide ion as opposed to other ions. The emission spectra of probe **1b** upon addition of other ions showed literally no change. However, the emission intensity increased sharply upon the addition of cyanide with an associated blue shift in the emission maximum to 510 nm, which showed green fluorescence (Figure 5). For both the probes the absorption and emission spectra showed a clear change even in the presence of other ions.

The effect of cyanide ion on the absorption and the emission spectra of 2b is found to be similar to that of 1b. That is, three absorption maxima were observed (327 nm, 385 nm and 493 nm). These peaks were also unaffected in the presence of other ions, whereas the addition of cyanide led to the formation of two new peaks at 409 nm and 346 nm (Figure S26 in the supporting information). The emission characteristics of the probes 1b and 2b were also changed only by the presence of cyanide ion. The emission spectra remained unaltered upon the addition of other ions, while a sharp increase in fluorescence was observed when cyanide ion was added. The probe 1b exhibited a green fluorescence with an emission maximum at 510 nm whereas probe 2b showed yellow emission with an emission maximum at 550 nm (Figure 5 and Figure S26 in the supporting information, respectively). These studies suggested, clearly, that the designed probes are highly selective for cyanide ion and are able to sense cyanide even in the presence of other competing ions. Therefore, these probes could be potentially used in order to test the presence of cyanide ion and could be possibly scavenged easily.



10.1002/chem.201800216

WILEY-VCH

FULL PAPER



Figure 5. Emission spectra of 1b (10 µM) in presence of cyanide and other ions (a) and increasing concentration of cyanide ion (b), respectively.

The sensitivity of these probes towards cyanide ion detection was deduced by treating the DMSO solution of the fluorophores with varying concentrations of cyanide ion in water. The concentration of cyanide and its limit of detection were calculated from the emission spectral changes (Figure S28 in the supporting information). The fluorescence detection limits for **1b** and **2b** were estimated to be 0.32 μ M (8 ppb) and 0.57 μ M (14 ppb) at S/N = $3^{[39]}$. Wang *et al* have reported a polymer-based cyanide sensor with a detection limit of 14 ppb and in the same work the monomer was also used for sensing cyanide with a detection limit of 70 ppb.⁷³ Sulfonium boranes-based sensors have been reported, by Gabbai *et al* for the selective capture of cyanide ion, with a detection limit of 50 ppb.⁷⁴ The results of our work are comparable to those of literature with cyanide detection limits well below EPA suggested value, 200 ppb and WHO permissible level, 50 ppb.

Mechanism of cyanide addition onto the DCV group – NMR titration

In order to get insight into the nature of interaction between the probes and cvanide ion. ¹H NMR titration was performed in CDCl₃ using tetrabutylammonium cyanide as the cyanide source. In the ¹H NMR spectrum of probe **1b**, the two different vinyl protons, designated as H_a and H_b appeared at δ = 7.83 ppm and 7.5 ppm, respectively before cyanide addition. Upon the addition of cyanide, the vinyl carbon attached to Ha (or Hb) undergoes nucleophilic attack; this converts the double bond into a single bond and the vinyl protons are no longer in the deshielding region and hence they start to appear in the up-field portion of the NMR spectrum. The newly formed protons, represented as Ha' and Hb' appear at δ = 4.52 ppm and 4.2 ppm, respectively. As the concentration of cyanide ion is increased, the intensity of peaks at δ = 7.83 ppm and 7.5 ppm decreases with a concomitant increase in the intensity of the peaks at δ = 4.52 ppm and 4.2 ppm (Figure 6). In a similar way, for probe **2b**, a chemical shift from δ = 7.48 ppm to δ = 4.26 was observed upon addition of cyanide ion (Figure S29 in the supporting information). These studies clearly imply that the nucleophilic addition of cyanide ion onto the vinyl carbon leads to a new redistributed electronic configuration.

Computational analysis of the cyanide addition to the DCV group.

The nucleophilic attack of cyanide ion onto the DCV group, as established by the UV-Visible, fluorescence and NMR analyses was further supported by the DFT analyses of the flurophores before and after the addition of cyanide. The gas phase density functional theory (DFT) analysis performed using B3LYP/6-31G* basis set shows, for probe 1b, that the highest occupied molecular orbital (HOMO) is primarily located on the phenothiazine ring while the lowest unoccupied molecular orbital (LUMO) is concentrated on the DCV part of the molecule.[44] Upon the addition of cyanide ion, the HOMO is still located on phenothiazine ring as before, but the LUMO is now localized mainly on the ethynyl bond and EDOT molecule, leaving no distribution of LUMO on the cyano groups. The energy levels of the HOMO (-5.5941 eV and -5.4118 eV) are not altered much before and after the addition of cyanide ion but those of LUMO (-3.0583 eV and -2.0378 eV) differ very much after cyanide ions were added, which is consistent with the experimental results.



Figure 6. ¹H NMR (partial) spectral changes seen upon the addition of increasing concentration of cyanide ion as its tetrabutylammonium salt to probe 1b (20 mM) in CDCl₃.

FULL PAPER



Figure 7. Schematic representation of logic gate for probe 1b and 2b. a) NOT, b) YES and c) AND gate, d) truth table of logic gate with single input and e) truth table of logic gate with two inputs.

Similar results were obtained for probes **2b** as well (Figures S30 and S31 in the supporting information).

In the case of 1b, the two DCV groups are attached to two different aromatic rings, namely EDOT and phenothiazine. Hence, we analyzed their reactivity difference using Mulliken charge analysis. The electrostatic potential surfaces of 1b and its cyanide adduct are shown in Figure S30 in the supporting information. The Mulliken charge on the β -carbon of the DCV group attached to the phenothiazine ring has been estimated to be +0.276 while that attached to EDOT is +0.201. This implies that the reactivity of the β -carbons towards the nucleophilic cyanide is nearly the same, which was supported by the ¹H NMR analysis as well. The intensities of the peaks corresponding to the vinyl protons of the DCV groups at δ = 7.83 and 7.5 ppm started to diminish simultaneously with a concurrent appearance of two new peaks at δ = 4.5 and δ = 4.2 ppm. These studies clearly show that the addition of cyanide to the two different DCV groups is rather simultaneous than stepwise. On the other hand, the probe 2b has only one kind of DCV group and so the addition of cyanide is indistinguishable.

Design of molecular logic gate

Generally, molecular logic gates mimic the electronic circuits *via* physicochemical changes. These types of logic gates can be designed using the changes in the fluorescence response of the probe with the analyte. Based on the fluorescent spectral and color switching in our system, we have explored individual logic gate with single and two input signal amplification using various

combinations of chemical and light inputs in the form CN⁻ and UV. The input and output signals were coded in binary units "0" and "1" for "OFF" and "ON" states, respectively. The interaction of CNwith the probes **1b** and **2b** creates NOT and YES or IDENTITY function; the absorption and fluorescence spectra exhibit NOT function for the inputs A₄₀₉, A₄₉₄ and F₅₂₇, whereas appearance of new peaks exhibits YES function with respect to the outputs A₃₇₄, A₃₂₁ and F₅₁₀ (Figure 7a-c).

Interpretation of logic gate with single input:

In single input operation, probes **1b** and **2b** act as gate and CN⁻ as chemical input. Boolean operations "1" and "0" represent the presence and absence of the analyte. Emission intensity at 527 and 510 nm was considered as the output signal for analyzing the "ON" and "OFF" states, respectively. Chemical inputs with two different combinations (1,0; 0,1) were analyzed. Upon addition of the analyte CN⁻, the emission maxima corresponding to the probe blue shifts to 17 nm and thereby exhibits NOT and YES functions with respect to F_{527} and F_{510} , respectively. This is due to the formation of new cyano complex as confirmed from the blue shifted emission, which correlates with the "YES" gate i.e. "ON" state (Figure 7d).

Interpretation of logic gate with two inputs:

Since the emission of probes **1b** and **2b** can be stimulated by UV light, a combinatorial logic circuit was constructed using analyte (CN^{-}) and UV as chemical and light input. The emission maxima

Accepted Manuscrip

WILEY-VCH

FULL PAPER

of probe 1b at 527 nm were considered as initial value. The truth table was generated by the combination of Boolean values '0' and '1', and the switching behavior ("off-on" state) was observed with different possibilities of inputs. Since UV is the main trigger for the fluorescence, absence of all inputs (0,0) and presence of CN-, (0,1) as single input shows an "off" state, i.e. no fluorescence is observed. Combination of UV+ CN⁻ (1,1) doesn't seem to show any fluorescence, which indicates that system is in "off" state. The presence of UV (1,0) alone favors the fluorescence in the system i.e. "on' state. Thus, an IMP function has been observed with respect to the emission of the probe at 527 nm i.e., F₅₂₇. Whereas, combination of UV+ CN⁻ (1,1) favors "on" state in the system, due to the formation of the DCV compound as evidenced from the blue shift in the emission spectra. Thus, AND function is obtained from the truth table with respect to the emission of the probe at 510 nm i.e. F₅₁₀. The truth table confirms the switching behavior of the system in the presence of light and analyte (Figure 7e).

Conclusions

In conclusion, we have designed and synthesized four new phenothiazine based donor-acceptor molecules. They exhibit solid-state emission in thin film and in PS matrix. The emission in the solid state range from yellow to NIR whereas the PS films exhibit green to orange emission. The fluorophores (1-2) may be applied to fabricate OLEDs owing to their high solid-state emission. The two DCV derivatives, 1b and 2b in DMSO were employed as probes in sensing the presence of cyanide ion in aqueous solution. A very rapid response was observed for both the probes with a vivid colour change upon the addition of aqueous cyanide solution to the DMSO solution of the dyes. The limit of detection through fluorescence results has been found to be 8 and 14 ppb, for the probes 1b and 2b, respectively. Since the probes react with the cyanide ion and form a permanent covalent bond, the toxic cyanide ions are removed from the cyanide containing solution, which is an advantage. These molecules may serve as a simple probe in order to detect and scavenge cyanide ions from the medium suspected to have been contaminated with cyanide. Though the present probes can be used to detect cyanide ion, they have limitation since they cannot be used for bio-sensing owing to the presence of long alkyl chain, which impedes their water solubility. The mechanism of cyanide addition was confirmed by ¹H NMR analysis. Theoretical calculations furnish insight into the electronic energy levels and the band gap of the probes before and after the cyanide addition. Finally, using fluorescent spectral and color switching we have explored logic gates with single and two input signal amplification by applying chemical and light inputs in the form of CN⁻ ion and UV.

Acknowledgements

The authors gratefully acknowledge Prof. A. K. Mishra, Dr. P. Venkatakrishnan, Dr. John Prakash and Mr. Sudhakar Maddala of Department of Chemistry IIT Madras for fluorescence

measurements. We sincerely thank Prof. Ajayghosh, NIIST Trivandrum for solid state quantum yield measurements. Dr. Deepan Chakravarthy, Dr. Ananthakrishan and Mr. Ravindran are sincerely acknowledged for their valuable comments and useful discussions. The authors acknowledge IIT Madras for the infrastructure and high-performance computing facility.

Conflicts of interest

There are no conflicts to declare.

Keywords: cyanide sensing • fluorophores • logic gates • phenothiazine • solid state emission

- [1] M. Shimizu, T. Hiyama, *Chem. Asian. J.*, 2010, **5**, 1516-1531.
- [2] Z. Zhang, B. Xu, J. Su, L. Shen, Y. Xie, H. Tian, Angew. Chem., Int. Ed., 2011, 50, 11654-11657.
- [3] H.-L. Liu, X.-L. Hou, L. Pu, Angew. Chem., Int. Ed., 2009, 48, 382-385.
- [4] A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.*, 2004, 16, 4556-4573.
- [5] M. A. Wolak, J. Delcamp, C. A. Landis, P. A. Lane, J. Anthony, Z. Kafafi, Adv. *Func. Mater.*, **2006**, *16*, 1943-1949.
- [6] Introduction to Organic Electronics and Optoelectronic Materials and Devices Vol. 2 (Eds: S.-S. Sun, L. R. Dalton), TAYLOR & FRANCIS, New York, 2008, pp. 130-167)
- [7] I. D. W. Samuel, G. A. Turnbull, Chem. Rev., 2007, 107, 1272-1295.
- [8] A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, A. Salleo, Chem. Rev., 2010, 110, 3-24.
- [9] S.-W. Zhang, T. M. Swager, J. Am. Chem. Soc., 2003, 125, 3420-3421.
- [10] J.-S. Yang, T. M. Swager, J. Am. Chem. Soc., **1998**, 120, 5321-5322.
- [11] J.-S. Yang, T. M. Swager, J. Am. Chem. Soc. **1998**, *120*, 11864-11873.
- [12] E. Ramachandran, R. Dhamodharan, J. Mater. Chem. C., 2015, 3, 8642-8648.
- [13] C. S. Kramer, T. J. J. Muller, *Eur. J. Org. Chem.*, **2003**, 3534-3548.
- [14] C. S. Kramer, K. Zeitler, T. J. J. Muller, Org. Lett., 2000, 2, 3723-3726.
 [15] C. S. Barkschat, S. Stoycheva, M. Himmelhaus, T. J. J. Muller, Chem. Mater. 2010, 22, 52-63.
- [16] G. Qian, Z. U. Wang, Chem. Asian J., 2010, 5, 1006-1029.
- [17] B.R. Gao, H-Y. Wang, Y-W. Hao, L-M. Fu, H-H. Fang, Y. Jiang, L. Wang, Q-D. Chen, H. Xia, L-Y. Pan, Y-G. Ma, H-B. Sun, *J. Phys. Chem. B.*, **2010**, *114*, 128–134.
- [18] C. Arivazhagan, A. Maity, K. Bakthavachalam, A. Jana, S. K. Panigrahi, E. Suresh, A. Das, S. Ghosh, *Chemistry-A European Journal.*, 2017, 29, 7046-7051.
- [19] Z. Xu, X. Chen, H.N. Kim, J. Yoon, Chem. Soc. Rev. 2010, 39, 127-137.
- [20] C.L. Chen, Y.-H. Chen, C.-Y. Chen, S.-S. Sun, Org. Lett. 2006, 8, 5053-5056.
- S. Saha, A. Ghosh, P. Mahato, S. Mishra, S.K. Mishra, E. Suresh, S. Das, A, Org. Lett. 2010, 10, 3406-3409.
- [22] L. Peng, M. Wang, G. Zhang, D. Zhang, D. A. Zhu, Org. Lett., 2009, 11, 1943-1946.
- [23] E.P. Randviir, C.E. Banks, *Trends Anal. Chem.*, **2015**, 64, 75-85.
- [24] Guidelines for drinking water quality, world health organization, Geneva 1996.
- [25] J.V. Ros-Lis, R. Martinez-Manez, J. Soto, Chem. Commun., 2005, 5260-5262.
- [26] J. Ma, P.K. Dasgupta, Anal. Chim. Acta., 2010, 673, 117 125.
- [27] H.-T. Niu, X. Jiang, J. He, J.-P. Cheng, *Tetrahedron Lett.*, 2008, 49, 6521-6524.
- [28] J. Isaad, A.E.A. Achari, Anal. Chim. Acta., 2011, 694, 120-127.

FULL PAPER

- [29] H.-T. Niu,D. Su, X. Jiang, W. Yang, Z. Yin, J. He, J.-P. Cheng, Org. Biomol. Chem., 2008, 6, 3038-3040.
- [30] H. Li, B. Li, L.-Y.Jin, Y. Khan, B. Yin, *Tetrahedron*, 2011, 67, 7348-7353.
- [31] T. Agou, M. Sekine, J. Kobayashi, T. Kawashima, J. Organomet. Chem., 2009, 694, 3833-3836.
- [32] H. Yu, Q. Zhao, Z. Jiang, J. Qin, Z. Li, Sensors and Actuators B, 2010, 148, 110-116.
- [33] H. Li, F. Jakle, Angew. Chem., Int. Ed., 2009, 48, 2313-2316.
- [34] H. Xia, J. Li, G. Zou, Q. Zhang, C. Jia, J. Mater. Chem. A., 2013, 1, 10713-10719.
- [35] M.V. Ramakrishnam Raju, H.-C. Lin, J. Mater. Chem. A., 2015, 3, 6414-6422.
- [36] R. Badugu, J.R. Lakowicz, C.D. Geddes, J. Am. Chem. Soc., 2005, 127, 3635-3641.
- [37] M. Jamkratoke, V. Ruangpornvisuti, G. Tumcharern, T. Tuntulani, B. Tomapatanaget, J. Org. Chem., 2009, 74, 3919-3922.
- [38] T. Liu, F. Huo, J. Li, F. Cheng, C. Yin, Sensors and Actuators B, 2017, 239, 526-535.
- [39] P. Kaur, D. Sareen, K. Singh, *Dalton Trans.*, **2012**, *41*, 9607-9610.
- [40] Z. Liu, X. Wang, Z. Yang, W. He, J. Org. Chem., 2011, 76, 10286-10290.
- [41] Y. Zhang, D. Li, J. Yu, Chem. Sci., 2014, 5, 2710-2716.
- [42] X. Cheng, Y. Zhou, J. Qin, Z. Li, ACS Appl. Mater. Interfaces, 2012, 4, 2133-2138.
- [43] M.R. Ajayakumar, K. Mandal, K. Rawat, D. Asthana, R. Pandey, A. Sharma, S. Yadav, S. Ghosh, P. Mukhopadhyay, ACS Appl. Mater. Interfaces, 2013, 5, 6996-7000.
- [44] L. Yang, X. Li, J. Yang, Y. Qu, J. Hua, ACS Appl. Mater. Interfaces, 2013, 5, 1317-1326.
- [45] J. Yoshino, N. Kano, T. Kawashima, J. Org. Chem., 2009, 74, 7496-7503.
- [46] D.-G. Cho, J.H. Kim, J.L. Sessler, J. Am. Chem. Soc., 2008, 130, 12163-12167.
- [47] J.L. Sessler, D.-G. Cho, Org. Lett., 2008, 10, 73-75.
- [48] K.-S. Lee, H.-J. Kim, G.-H. Kim, I. Shin, J.-I. Hong, Org. Lett., 2008, 10, 49-51.
- [49] S. Vallejos, P. Estvez, F.C. Garcia, F. Serna, J.L De la Pena, J.M. Garcia, Chem. Commun., 2010, 46, 7951-7953.
- [50] Y.-D. Lin, Y.-S. Peng, W. Su, C.-H. Tu, C.-H. Sun, T.J. Chow, *Tetrahedron*, **2012**, 68, 2523-2526.
- [51] G. Qian, X. Li, Z.Y. Wang, J. Mater. Chem., 2009, 19, 522-530.
- [52] S.-H. Kim, S.-J. Hong, J. Yoo, S.K. Kim, J.L. Sessler, C.H. Lee, Org. Lett. 2009, 11, 3626-3629.

- [53] M. Tomasulo, F.M. Raymo, *Org. Lett.*, **2005**, 7, 4633-4636.
- [54] Y. Ding, T. Li, W. Zhu, Y. Xie, *Org. Biomol. Chem.*, **2012**, *10*, 4201-4207.
 [55] S. Madhu, S.K. Basu, S. Jadhav, M. Ravikanth, *Analyst*, **2013**, *138*, 299-
- 306. [56] X. Huang, X. Gu, G. Zhang, D. Zhang, *Chem. Commun.*, **2012**, *48*,
- [20] 12195-12197.
 [57] J.H. Lee, A.R. Jeong, I.-S. Šhi, H.-J. Kim, J.-I. Hong, Org. Lett., 2010,
- 12, 764-767.
- [58] P. Kaur, D. Sareen, S. Kaur, K. Singh, *Inorg. Chem. Commun.*, 2009, 12, 272-275.
- [59] Y.-W. Liu, M.X. Kao, A.-T. Wu, Sensors and Actuators B, 2015, 208, 429-435.
- [60] X. Wu, B. Xu, H. Tong, L. Wang, *Macromolecules*, **2011**, *44*, 4241-4248.
 [61] J. Chao, Z. Li, Y. Zhang, F. Huo, C. Yin, H. Tong, Y. Liu, *Sensors and*
- Actuators B, **2016**, 228, 192-199. [62] S. Park, H.-J. Kim, Sensors and Actuators B, **2012**, 161, 317-321.
- [63] F. Huo, J. Kang, C. Yin, J. Chao, Y. Zhang, Sensors and Actuators B, 2015, 215, 93-98.
- [64] F. Huo, Y. Zhang, Y. Yue, J. Chao, Y. Zhang, C. Yin, Sensors and Actuators B. 2017, 143, 270-275.
- [65] C. Yin, F. huo, M. Xu, C. L. Barnes, T. E. Glass, Sensors and Actuators B, 2017, 252, 592-599.
- [66] F.-J. huo, J. Su, Y.-Q. Sun, C.-X. Yin, J.-B. Chao, Chem. Lett., 2010, 39, 738-740.
- [67] G. R. Kumar, S. K. Sarkar, P. Thilagar, *Chem. Eur. J.*, 2016, 22, 17215– 17225.
- [68] N. Gimeno, X. Li, J. R. Durrant, R. Vilar, Chem. Eur. J, 2008, 14, 3006-3012.
- [69] C. Wang, J. Jia, W.-N. Zhang, H.-Y. Zhang, C.-H. Zhao, Chem. Eur. J, 2014, 20, 16590-16601.
- [70] Y. Yang, C. Yin, F. Huo, J. Chao, Y. Zhang, F. Cheng, Sensors and Actuators B, 2014, 193, 220-224.
- [71] D. Yokoyama, A. Sakaguchi, M. Suzuki, C. Adachi, Org. Electron., 2009, 10, 127-137.
- [72] W.-W. Zhang, W.-L. Mao, Y.-X Hu, Z.-Q. Tian, Z.-L. Wang, Q.-J. Meng. J. Phys. Chem. A., 2009, 113, 9997-10004.
- [73] X. Wu, B. Xu, H. Tong, L. Wang, Macromolecules, **2011**, *44*, 4241-4248.
 [74] Y. Kim, H. Zhao, F. P. Gabbai, *Angew. Chem., Int. Ed.*, **2009**, *48*, 4957-
- 4960.

FULL PAPER

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Four new D-A type fluorophores based on phenothiazine are reported. The fluorophores exhibit solid state emission in the yellow to NIR region. Two of the fluorophores, **1b** and **2b** have been exploited for highly selective and sensitive detection of cyanide ion in ppb level. Elumalai Ramachandran, Somasundaram Anbu Anjugam Vandarkuzhali, Gandhi Sivaraman and Raghavachari Dhamodharan*



Title

This article is protected by copyright. All rights reserved.