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# Aggregation-Induced Emission and Sensing Characteristics of Triarylborane–Oligothiophene–Dicyanovinyl Triads

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**Abstract:** The design, synthesis and aggregation-induced emission properties of a new series of triarylborane–oligothiophene–dicyanovinyl (DCV) conjugates 4-6 (A–D–A' type molecular configuration) are reported. The optical properties of 4-6 can be modulated by judiciously varying the number of thiophene units between electron deficient boryl and dicyanovinyl units. Compound **6** with terthiophene spacer showed highly red-shifted absorption and emission compared to **5** and **4** with bithiophene and monothiophene

## Introduction

The design and synthesis of functional luminescent materials have attracted a lot of attention due to their potential applications in the field of OLEDs (organic light-emitting diodes), biological and chemical diagnostic agents, security markers, among others.<sup>[1]</sup> In the last two decades, several molecular systems with intriguing optical properties have been developed by elegantly modulating the molecular conformations and inter/intramolecular interactions.<sup>[2,3]</sup> Owing to their large Stokes shifted luminescence characteristics, molecular systems with donor-acceptor (D-A) architecture have been well exploited for developing several functional materials.<sup>[4]</sup> However, often luminescence of D-A systems in the solid state is quenched due to intermolecular dipole-dipole interactions induced molecular aggregation. In the last decade molecule with donor-acceptor-donor' and acceptor-donor-acceptor' (D-A-D' and A-D-A') architectures have been employed to circumvent the dipole-dipole interactions induced PL quenching and subsequently to enhance the luminescence in the solid state.<sup>[5]</sup>

In recent years, aggregation-induced emission enhancement (AIEE) has been the subject of several investigations, as most of the optoelectronic applications require the luminogens to be emissive in the solid state.<sup>[6]</sup> The concept of AIEE has opened up new opportunities and perspectives for developing functional luminescence materials that could find applications in areas such as chemo-sensing, bio-imaging and optoelectron-

spacers, respectively. Compounds **5** and **6** show aggregation-induced emission enhancement in water/THF mixtures. Compounds **5** and **6** also showed solvent viscosity dependent emission characteristics. All the three compounds show distinct optical responses for small anions such as fluoride and cyanide. Filter paper strips coated with compounds **5** and **6** can detect  $F^-$  and  $CN^-$  in aqueous media with different colorimetric responses.

ics.<sup>[7]</sup> In this regard, seminal work has been carried out by Tang and Parker.<sup>[6a-c]</sup> Recently, chemical modifications of AIE luminogens with other functional units such as triarylborane, polymers, crown ethers, peptides and metal complexes have also been studied actively.<sup>[8]</sup> As a versatile fluorophore, triarylboranes (TAB) have gained special attention for various purposes for the last two decades.<sup>[9]</sup> Very recently, Chujo et al. and others have developed tri- and tetra-coordinated boron based AIE luminogens and utilized them for optoelectronic applications.<sup>[10]</sup>

Recently, we become interested in studying the structureproperty relationships of boron-containing luminogens.<sup>[11]</sup> As part of the on-going program, we have studied the AIE properties of series of dyads composed of boron dipyrromethenenaphthalimide (BODIPY-NPI) moieties.<sup>[12b,c]</sup> Initial studies involving systematic alterations of the NPI based molecules revealed that a balance of intermolecular forces and molecular environment can be an effective recipe to impart AIE features in NPIs. Later on, incorporation of NPI with boron containing dyes resulted in broad emissive AIES-active (aggregation-induced emission switching) materials and it was unveiled that,  $\pi$ - $\pi$  interactions can be either detrimental or beneficial depending on the relative arrangements of neighbouring luminescent units.<sup>[12]</sup> It occurred to us that incorporation of oligothiophene between two different electron deficient receptors will result in A-D-A' types of luminogen. In addition, thiophene has a lower resonance stabilization energy (29 kcal mol<sup>-1</sup>) compared to benzene (36 kcal mol<sup>-1</sup>) and induce better electronic communication between two receptor sites. Moreover, if the receptors have different affinities for different anions, the resulting A-D-A' system can be utilised for selective detection of more than one anion. Accordingly, we designed and synthesised a series of boryl- $\pi$ -spacer-DCV-based (DCV: dicyanovinyl and  $\pi$ -spacer: oligothiophene) luminogens (4, 5, and 6) pos-

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sessing typical A–D–A' architecture. The  $\pi$ -spacer length in triads **4**, **5**, and **6** has been judiciously fine-tuned to impart flexibility and effective electronic communication between the two acceptors. Compounds **5** and **6** with longer spacers show interesting AIE properties. Moreover, TAB and DCV units are well known for their sensing abilities of fluoride and cyanide ions.<sup>[13]</sup> Thus, the anion-sensing ability of the new triads **4**, **5**, and **6** has also been evaluated.

## **Results and Discussion**

#### Synthesis and characterisation

Compounds 1 and 2 were synthesized by selective borylation of the respective bromoacetals (a for 1 and b for 2) and subsequent deprotection of aldehyde functional with 2N hydrochloric acid (Scheme 1). Compound 3 was obtained by a metalmediated (Pd(PPh<sub>3</sub>)<sub>4</sub>) cross-coupling reaction between "c" and 5-bromo-2-thiophenecarboxaldehyde in toluene.<sup>[14]</sup> Condensation of aldehydes (1-3) with malanonitrile in ethanol in the presence of a catalytic amount of piperidine gave corresponding compounds 4-6 (Scheme 2). All the compounds are characterized by NMR, high-resolution mass spectrometric techniques and CHN analysis. The appearance of a new singlet peak (7.92 ppm for 4; 7.76 ppm for 5; 7.75 ppm for 6) confirms the transformation of aldehyde functional groups into dicyanovinyl moieties. Due to the fast relaxation of the boron nucleus, the peaks corresponding to the carbon attached to boron are not observed in the <sup>13</sup>C NMR spectra of compounds 4-6. From HRMS analysis, it is clear that the molecular ion peaks correspond to the respective sodium ion (Na<sup>+</sup>) adducts.



Scheme 1. Synthesis of compounds 1–3.



Scheme 2. Synthesis of compounds 4-6.

**Optical properties** 

Hexane solutions of compounds **4**, **5**, and **6** showed absorption maxima at 382, 434, and 468 nm, respectively (Figure 1). These absorption peaks can be attributed to the combined intramolecular charge transfer (ICT) transitions (thiophene to DCV and thiophene to BMes<sub>2</sub>), and thiophene-based  $\pi \rightarrow \pi^*$  transitions. Compounds **5** and **6** exhibit distinct boryl-based  $\pi \rightarrow p_{\pi}^*$  transitions at around 350 nm; the same for **4** is merged with the lower energy band. Compound **6** (468 nm) shows the most red-shifted absorption band followed by **5** (434 nm) and compound **4** (382 nm). This trend in the absorption features of **4**, **5**, and **6** clearly indicate that the bandgap is highly depend on the length of the donor oligothiophene unit.



**Figure 1.** UV/Vis absorption (left) and photoluminescence (right) spectra of **4–6** in hexane under ambient conditions. Conc.  $1 \times 10^{-5}$  M,  $\lambda_{ex} = 382$ , 434 and 468 nm for **4**, **5**, and **6**, respectively.

The molecular geometries of 4-6 are optimized using DFT computational method. The aim is to understand their molecular and electronic structures (Figure 2). In all the cases, the dicyanovinyl unit and the neighbouring thiophene ring are in coplanar arrangement. The boron centre in all the three compounds adopts a perfect trigonal planar geometry. The boroncarbon (mesothiophene) bond lengths in 5 (1.555 Å), and 6 (1.551 Å) are slightly shorter than the value noted for 4 (1.561 Å). The dihedral angle between the planes of boron (BC2) unit and DCV moiety gradually decreases as the thiophene chain length increases (for 4,  $25.6^{\circ}$ ; for 5,  $11.4^{\circ}$  and for 6, 7°). The dihedral angle between the mesothiophene and BC2 unit in 5 (18.5°), or 6 (18.0°) is significantly lower than the value calculated for 4 (20.8°). These results clearly indicate that an increase in number of thiophenyl moiety between TAB and DCV enhances the electronic communication between these two acceptor units.

Upon photo-excitation at corresponding absorption maxima, compound **4** showed a single emission peak with maxima at around 461 nm, whereas structured emission bands were observed for **5** and **6** ( $\lambda_{max}$ ; 481 nm for **5** and 527 nm for **6**, respectively; Figure 1). The energy of the emission peaks of **4**, **5**, and **6** followed a similar trend as observed for absorption spectra of these compounds. Compound **6** showed the most red-shifted emission band followed by **5** and **4**. Absolute fluorescence quantum yield values clearly indicate that compound **6** ( $\Phi_{\rm f}$  = 10.1%) is a better luminophore than **5** ( $\Phi_{\rm f}$  = 1.0%)

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Figure 2. Energy minimized geometries of 4 (top left), 5 (top right) and 6 (bottom) obtained from DFT (B3LYP as hybrid functional and 6-31G as basis set) computational methods. Colour code; black = boron, grey = sulfur, light grey = nitrogen.

**4** ( $\Phi_f = 0.9\%$ ; Table 1). Time-resolved fluorescence studies were carried out and radiative/non-radiative decay constant values calculated using the following relationships.  $k_r$  (radiative decay constant) =  $\Phi_f/\tau$ ;  $k_{nr}$  (non-radiative decay constant) =  $(1 - \Phi_f)/\tau$ . For **4** and **5**, radiative and non-radiative decay pathways are comparable whereas for **6**, the radiative decay pathway is preferred. Thus, a higher fluorescence quantum yield is observed for **6** compared to **4** and **5**. The observed fluorescence quantum yields of compounds **4**–**6** are significantly lower than the values observed for TAB-amine–DCV systems reported independently by Zhao et al.<sup>[15]</sup> and Thilagar and co-workers.<sup>[11g]</sup>

<b>Table 1.</b> Optical properties of <b>4–6</b> in hexane $(1 \times 10^{-5} \text{ M})$ .						
Cmpd	$\lambda_{abs}$	λ <sub>em</sub> [nm]	$arPsi_{f}$ [%] <sup>[a]</sup>	τ [λ <sub>max</sub> ns]	k <sub>r</sub> [1×10 <sup>6</sup> s <sup>−1</sup> ] <sup>[b]</sup>	$k_{\rm nr}$ [1×10 <sup>8</sup> s <sup>-1</sup> ] <sup>[b]</sup>
4	382	461	0.9	3.8	2.4	2.6
5	434	481	1.0	4.4	2.3	2.2
6	468	527	10.1	4.1	24.6	2.1
[a] Absolute guantum yields are measured using integrating sphere.						

[b]  $k_r$ -radiative decay constant,  $k_{nr}$ -non-radiative decay constant [calculated using the relationship,  $k_r = \Phi/\tau$  and  $k_{nr} = (1-\Phi)/\tau$ ].

#### Solvent polarity-dependent photophysical studies

To gain further insight into their optical features, the UV/Vis absorption and fluorescence of **4**, **5**, and **6** were recorded in solvents with different polarity (Figures 3 and 4). As the solvent polarity was increased from hexane to DMSO, both absorption and emission peaks of compounds **4**, **5**, and **6** were red-shifted (Table 2). The bathochromic shift observed in the emission

Table 2. Photophysical properties of 4–6 in solvents of various polarities.					
Cmpd	Hexane ( $\lambda_{abs}/\lambda_{em}$ ) [nm]	Toluene ( $\lambda_{abs}/\lambda_{em}$ ) [nm]	$CH_2CI_2$ ( $\lambda_{abs}/\lambda_{em}$ ) [nm]	DMSO $(\lambda_{abs}/\lambda_{em})$ [nm]	
4 5 6	382/461 434/481 468/527	387/494 443/495 478/555	388/535 447/508 486/586	394/– 448/516 487/606	

spectra of compounds **4**, **5**, and **6** in polar solvents is significantly higher compared to their respective absorption bands. Thus, the excited state of these compounds is more polarized than their corresponding ground state. As the polarity of the solvent medium increases, fluorescence intensity of compound **4** gradually decreased with bathochromic shift. Compound **5** also showed significant Stokes shift in polar solvents, but the intensity of the luminescence did not change with solvent polarity. Interestingly, as solvent polarity increased, the fluorescence intensity of **6** progressively increased with significant bathochromic shift (Table 3).

Quantum yields of **4** and **5** were not measurable in polar solvents.

Table 3. Quantum yields of 6 in solvents of different polarities.					
	Hexane	Toluene	$CH_2CI_2$	DMSO	
$arPsi_{ extsf{F}}$ [%]	10	11	16	18	

#### Calculation of the excited-state dipole moment

Further, the change in dipole moment was calculated using the Lippert–Mataga relationships from Stokes shift values observed in various solvents for **4**, **5**, and **6** (Figure 5).<sup>[17]</sup> Changes



Figure 3. UV/Vis absorption spectra of 4 (left), 5 (middle), and 6 (right) in solvents  $(1 \times 10^{-5} \text{ M})$  of different polarity.

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Figure 4. Photoluminescence spectra of 4 (left), 5 (middle), and 6 (right) in solvents  $(1 \times 10^{-5} \text{ M})$  of different polarity.



Figure 5. Lippert–Mataga plots for compounds 4–6. A linear relationship is noted between Stokes shift and the solvent polarity parameter.

in dipole moments were calculated using the relationship described in Equation (1):

$$\Delta f = \frac{D-1}{2D+1} + \frac{n^2 - 1}{2n^2 + 1} \Delta v = \frac{2\Delta \mu^2}{hca^3} + \text{constant}$$
 1

in which *D* and *n* represent the dielectric constant and refractive index of the solvent, respectively. The term  $\Delta \mu$  is change in dipole moment [ $\Delta \mu = \mu g - \mu_e$ ;  $\mu g$  and  $\mu_e$  are the dipole moments in the ground and excited states, respectively], *h* is Plank's constant, *c* is velocity of light and *a* is the Onsagar radius (Supporting Information, Table S1), which was obtained from the optimized molecular structures in all the cases in the absence of crystal structures. Compounds **4–6** show a linear relationship between  $\Delta \nu$  and  $\Delta f$  and from the slope of the plot, the changes in dipole moments ( $\Delta \mu$ ) were calculated to be  $\approx 19.7$ ,  $\approx 13.4$ , and  $\approx 19.4$  D for **4**, **5**, and **6**, respectively. The  $\Delta \mu$  for **4** and **6** is significantly larger than the value calculated for **5**. Hence, larger Stokes shifts are observed for **4** and **6** compared to **5** in polar solvents.

#### Aggregation-induced emission studies

Fluorescence of **4**, **5**, and **6** in various fractions of  $\text{THF/H}_2\text{O}$  mixtures were studied (Figure 6). Compounds **5** and **6** show aggregation-induced emission but not **4**. In the case of **5**, no fluorescence change is observed until the water fraction ( $f_w$ %)

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increased to 50 volume%. A sudden rise in emission maxima (481 nm) was noted when the water fraction becomes 70%. At  $f_w \% = 90\%$ , 5 showed a 14-fold increase in its emission intensity. These preliminary observations suggest that formation of aggregated particles may be responsible for the observed fluorescence enhancement. Under similar conditions, compound 6 behaves in a different way. The emission maximum at 567 nm is red-shifted to 590 nm and no significant emission enhancement was noted until the water fraction reached 60%. Emission enhancement was observed when the water fraction reaches 70 volume%. A further increase in the water fraction led to a decrease in emission intensity ( $f_w$ %; 0%: 567 nm and 90%: 615 nm) with a red-shift. These results are slightly contradictory with the previously reported TAB-TPE-based (TPE: tetraphenylethylene) AIE luminogens, for which only emission enhancement was observed.<sup>[10]</sup> The presence of the larger planar terthiophene unit in 6 may impart more hydrophobic nature and induce the formation of larger aggregates. As a result, the emission intensity of 6 in higher water fractions decreases with a red-shift. Compounds 5 and 6 are more flexible (structurally) than 4. As a result, upon aggregation, rotational/vibrational motions are minimized to a greater extent in 5 and 6 which result in AIE enhancement. Being a poor luminescent material with less possibilities of restricted structural reorganisation, the probability of 4 to show AIE enhancement is much lower.



Figure 6. Fluorescence spectra of 5 (left) and 6 (right) in various fractions of THF/water mixtures.

To further elucidate the emission enhancement of **5** and **6** in THF solution containing higher water fractions, time resolved fluorescence studies of **5** and **6** are carried out (Figure 7 and Table S2, Supporting Information). Compound **5** exhibits a single exponential fluorescence decay ( $\tau$  = 5.9 ns) profile in

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THF solution and a bi-exponential fluorescence decay ( $\tau_1 =$ 6.8 ns,  $\tau_2$ =37.7 ns and  $\tau_{av}$ =14.5 ns, see the Supporting Information for more details) in THF containing 90% water by volume. The mean fluorescence lifetime of 5 at  $f_w = 90\%$  is significantly higher than the fluorescence lifetime at  $f_w = 0\%$ . In the aggregated state, due to the restricted intramolecular rotations of the thiophene units, a large number of molecules prefer the radiative decay pathway. Thus, the average fluorescence lifetime is significantly increased with enhanced fluorescence intensity. As in the case of 5, 6 also exhibits a single exponential fluorescence decay profile in THF solution ( $\tau = 4.4$ ). When the water fraction reached 70%, bi-exponential fluorescence decay ( $\tau_1$  = 3.3 ns,  $\tau_2$  = 14.2 ns and  $\tau_{av}$  = 4.06 ns) was observed. The relative amplitude of  $\tau_2$  (14.2 ns) is very small (see the Supporting Information for details). When the water fraction reached 90%, the bi-exponential decay was mostly dominated by  $\tau_2$  ( $\tau_{av}$  = 36.5 ns) and contribution from  $\tau_1$  decreased. As discussed vide-supra, at higher water fractions (beyond 70%), aggregates increase in size and more of them are formed. Upon aggregation, non-radiative decay pathways of 5 and 6 are significantly reduced. In true solution, structural reorganisations facilitate rapid relaxation of the excited fluorophores to the ground state via non-radiative pathways. Since the structural reorganisation is prevented in aggregated form, greater numbers of molecules prefers to relax from the excited state via a radiative decay pathway and consequently fluorescence lifetime is increased. This is further supported by the values of absolute quantum yields (Table 4). Both 5 and 6 show higher quantum yields in aggregated forms as compared to their true solutions. The red-shift of the emission band in 6 during aggregation may be due to  $\pi$ - $\pi$  stacking facilitated by planar terthiophene-DCV unit.



Figure 7. Fluorescence decay profiles of compounds 5 (left) and 6 (right) in THF and THF/water mixtures.

Table 4. Quantum yields of 5 and 6 in THF/water mixtures.				
THF:H <sub>2</sub> O [%]	5 [ $arPhi_{ m F}\%$ ]	$6 \; [\varPhi_{\mathrm{F}}\%]$		
10:90 90:10	9 1.5	17 5.6		

To understand the aggregation process, size-distribution of aggregated particles formed is measured using dynamic light scattering (Figures S21 and S22 in the Supporting Information). The results showed that compounds **5** and **6** form nano-aggre-

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gates in the presence of large fractions of water. In the case of **5**, at  $f_w = 90\%$ , 458 nm sized particles are formed. In the case of **6**, the aggregated particles grow bigger as the water fraction increases ( $f_w$ : 70%; 712 nm,  $f_w$ : 80%; 825 nm). At 90% water fraction, aggregated particle size becomes 955 nm. It is evident that the reduced luminescence intensity of **6** in THF solutions containing 80 and 90% water can be due to the formation of bigger particles which may facilitate  $\pi$ - $\pi$  stacking between neighbouring molecules.

#### Solvent viscosity-dependent fluorescence studies

It is important to note that compounds 5 and 6 showed significant increase in the luminescence intensity in highly viscous solvents. To gain further insight into the solvent viscosity-dependent optical features of 4, 5, and 6, their optical signatures were recorded in a highly viscous polar solvent, ethylene glycol. Upon increasing the ethylene glycol fractions in methanol solutions of 4, 5, and 6, the fluorescence intensity of 5 and 6 increased progressively (Figure 8), but no changes were observed for 4. Compound 5 showed a three-fold increase of the fluorescence intensity in viscous solvents, whereas 6 showed a 1.4-fold increase. This type of viscosity-dependent fluorescence enhancement is well known for compounds with flexible structures.<sup>[16]</sup> Since compounds **5** and **6** have long spacer they may undergo structural reorganization in the excited state which may partly deactivate the radiative decay of 5 and 6. In viscous solvents, such structural reorganizations are restricted due to the rigid environment and consequently the radiative decay of 5 and 6 is facilitated.



Figure 8. Fluorescence spectra of 5 (left) and 6 (right) in various fractions of methanol/glycerol mixtures.

To determine whether the viscosity or solvent polarity controls the optical dynamics of **5** and **6**, their PL features were recorded in nonpolar viscous paraffin oil (Figure 9). As the paraffin oil fractions increase in hexane solutions of **4**, **5**, and **6**, the fluorescence intensity of **5** and **6** increased gradually (2.3 times for **5** and 1.4 times for **6**) as observed in ethylene glycol. Compound **4** showed no changes. Based on these results we conclude that viscosity plays a major role in determining the emission intensity of **5** and **6** could be controlled by increasing the viscosity of the solvent medium. These observations confirm the

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Figure 9. Fluorescence spectra of 5 (left) and 6 (right) in various fractions of hexane/paraffin mixtures.

involvement of restricted intramolecular motion in the process of emission enhancement.

#### Solid-state emission characteristics

Although 5 and 6 show AIE characteristics, they are not fluorescent in the solid state. To check whether a polymeric rigid matrix can activate luminescence in the solid state, thin films of 5 and 6 are made along with polymethylmethacrylate (PMMA). PMMA and 5/6 were dissolved in THF and thin films were made over a quartz plate by a drop-casting method (Figure 10). Both the compounds showed intense luminescence with considerable absolute quantum yields (5:  $\lambda_{max} =$ 517 nm,  $\Phi = 4.4\%$  and **6**:  $\lambda_{max} = 567$  nm,  $\Phi = 11.4\%$ ). As observed in solution state, compound 6 exhibits higher quantum yield in PMMA matrix also. The rigid environment provided by PMMA significantly reduces non-radiative decay channels and enhances the emission efficiency. Maximum emission intensity was observed when the weight percentage of compounds 5 and 6 are around 20%. Upon increasing the weight percentage of fluorophores beyond 20%, the fluorescence intensity started to decrease. Probably at higher concentrations, 5 and 6 form short contacts between neighbouring molecules. As a result, fluorescence decreases at higher weight percentages.



**Figure 10.** Photoluminescence spectra of thin films made up of **5** (left) and **6** (right) in PMMA (20% w/w). Inset shows photographic images taken under the UV lamp (colour images are given in Supporting Information).

On the other hand, compound **4** does not show any fluorescence in the solid state even after mixing with PMMA. The observed solid-state quantum yields are lower than the values noted for TAB-TPE derivatives.<sup>[10]</sup>

#### Density functional theory studies

To understand the electronic structures of compounds **4–6**, DFT computational studies were performed using the B3LYP functional and 6-31G(d) as basis set (Figure 11). The number of thienyl units has a considerable impact on their molecular orbital localizations and electronic conjugation. In the case of **4**, the HOMO is localized on the  $\pi$ -orbital of the mesityl rings whereas in the case of **5** and **6**, it is delocalized over the bithiophene and terthiophene rings, respectively, with a small contribution from dicyanovinyl unit. In all the cases, LUMO is delocalized over the dicyanovinyl unit, spacer (mono-, bi- and terthiophene) and the empty orbital of the boron centre. The energy of HOMO of **4**, **5**, and **6** steadily increase with increasing donor oligothiophene length. Thus, HOMO–LUMO gap decreases effectively in **5** and **6**. These observations corroborate well with the experimental results.



**Figure 11.** Calculated frontier molecular orbitals of 4-6 and the corresponding energy levels by DFT method (B3LYP/6-31G, isovalue = 0.04).

#### Anion binding studies

To evaluate the anion sensing abilities of **4–6**, their photophysical properties were examined in the presence of variety of anions such cyanide, fluoride, chloride, bromide, iodide, nitrate, and perchlorate (Figure S24, Supporting Information). The results indicate that compounds **4**, **5**, and **6** can selectively sense small anions such as fluoride and cyanide.

Upon fluoride binding, the intensity of the respective absorption bands of **4**, **5**, and **6** decrease and concomitantly a new absorption band appears in the longer wavelength region (Figure 12). The new absorption band observed for **5**·F<sup>-</sup> (526 nm) and **6**·F<sup>-</sup> (572 nm) are significantly red-shifted compared to the band observed for **4**·F<sup>-</sup> (424 nm). Since the new absorption bands observed for **5**·F<sup>-</sup> (526 nm) and **6**·F<sup>-</sup> (572 nm) fall in the visible region of the electromagnetic spectrum, a distinct colour change could be observed by the naked eye. Thus, compounds **5** and **6** are potential colorimetric sensor for selective detection of fluoride ions.

The fluoride-binding event was also monitored by <sup>1</sup>H and <sup>19</sup>F NMR titrations (Figure S25, Supporting Information). The

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Figure 12. Changes in UV/Vis absorption spectra of 4 (top left), 5 (top right), and 6 (bottom; conc.  $1\!\times\!10^{-5}\,\text{m})$  in the presence of TBAF (2  $\mu\text{L}\!=\!0.1$  equiv) in THF.

CDCl<sub>3</sub> solution 5 was mixed with 10 equivalents of tetrabutylammonium fluoride (TBAF) and changes in <sup>1</sup>H and <sup>19</sup>F resonances were monitored. In <sup>1</sup>H NMR, the proton region corresponding to the mesityl proton showed a complex NMR pattern but no changes in the DCV proton signal was observed. Only, <sup>19</sup>F signal corresponding to the  $Ar_3B\cdot F^-$  moiety was observed in <sup>19</sup>F NMR. Based on these results one can conclude that the fluoride binds only to the boron centre and does not interact with the DCV unit. These results are in-line with the previous reports on similar molecules.<sup>[11f,g]</sup> Having confirmed the formation of monofluoride complexes of 4 and 5 and 6, computational studies<sup>[18-20]</sup> were carried out with the objective of understanding the origin of new absorption bands for 4.F<sup>-</sup>, 5.F<sup>-</sup> and 6-F<sup>-</sup> (Figure S27, Supporting Information). The HOMO of 4·F<sup>-</sup>is localized on one of the two mesityl moieties of Ar<sub>3</sub>B·F<sup>-</sup> fragment. In contrast, the HOMO of 5.F<sup>-</sup> and 6.F<sup>-</sup> is delocalized over the entire  $Ar_3B \cdot F^-$  fragment in both the complexes. The LUMOs of  $4 \cdot F^-$ ,  $5 \cdot F^-$ , and  $6 \cdot F^-$  are delocalized over the DCV and thiophenyl spacers. Furthermore, the HOMO --- LUMO bandgap of fluoride complexes decreased significantly compared to their respective free Lewis acids 4, 5, and 6. From these results we conclude that the new absorption band observed for fluoride complexes  $4 \cdot F^-$ ,  $5 \cdot F^-$  and  $6 \cdot F^-$  arises from intramolecular charge transfer from in situ generated electronrich borate donor  $(Ar_3B\cdot F^-)$  to the electron-deficient DCV acceptor. These results are in line with our earlier report on fluoride binding studies of TAB-BTH-BODIPY triad.<sup>[11b]</sup>

The fluoride-binding event was also studied using fluorescence spectrometry (Figure 13). When excited at 380 nm, the fluorescence intensity of compound **4** decreases steadily as the concentration of TBAF increases. Under similar conditions, upon excitation at 430 nm the intensity of emission peak at 501 nm for **5** gradually decrease and a new emission peak progressively appears at 608 nm. In the case of **6**, the fluoride binding considerably increases the intensity of the fluorescence with 17 nm bathochromic shift. These results clearly indicate that the fluoride complexes **5**·F<sup>-</sup> and **6**·F<sup>-</sup> are better luminophores than their corresponding free Lewis acids **5** and **6**.



**Figure 13.** Changes in photoluminescence spectra of **4** (top left,  $\lambda_{ex} = 380 \text{ nm}$ ), **5** (top right,  $\lambda_{ex} = 430 \text{ nm}$ ) and **6** (bottom,  $\lambda_{ex} = 460 \text{ nm}$ ; conc.  $1 \times 10^{-5} \text{ M}$ ) in the presence of TBAF (2  $\mu$ L=0.1 equiv) in THF.

Since compound **5** exhibits ratiometric fluorescence response (the peak at 501 nm decreases and the peak at 608 nm increases) for fluoride binding, this molecule can be used as selfcalibrating fluorescence probe for fluoride ions. The change in absorption and fluorescence features of **4**, **5**, and **6** stops after the addition of one equivalent of fluoride ions confirming the formation of 1:1 fluoride adducts.

Upon addition of tetrabutyl ammonium cyanide ions, the absorption of **4** gradually decreases with 31 nm bathochromic shift. In the presence of 1 equivalent of cyanide, the absorption peaks of **5** and **6** decrease and a new absorption band appears in the longer wavelength region (Figure 14). Upon addition of second equivalent of cyanide, the newly formed absorption peaks at longer wavelength region disappear; subsequently the solution of **5** and **6** become colourless. These colour changes can be seen by the naked eye. Hence, compounds **5** and **6** can be used as a colorimetric sensor for cyanide ions.

To rationalize the cyanide binding process, NMR titrations were carried out (Figure S26, Supporting Information). In gen-



**Figure 14.** Changes in UV/Vis absorption spectra of **4** (top left), **5** (top right), and **6** (bottom;  $1 \times 10^{-5}$ M) in presence of TBACN (2  $\mu$ L = 0.1 equiv) in THF.

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eral, the hydrogen atom attached to the electrophilic carbon centre of dicyanovinyl group resonates at around 7-8 ppm in the <sup>1</sup>H NMR spectrum and upon cyanide coordination undergoes an upfield shift to around 4-5 ppm.<sup>[21]</sup> Compounds 5 and 6 exhibit a singlet peak at 7.75 ppm corresponding to the dicyanovinyl unit. The addition of one equivalent of cyanide ions to 5 resulted in the formation of complex multiple peaks at aromatic region and two singlet peaks at 4.4 and 4.5 ppm. The formation of these peaks along with the coexistence of another singlet at 7.75 ppm indicates that cyanide ions bind with both the receptor sites simultaneously (Scheme 3). After the addition of two equivalents of cyanide ions, the spectrum shows only one singlet peak at around 4.4 ppm indicating that both the receptor sites are completely saturated. Thus, the complex NMR pattern observed for a 1:1 mixture of cyanide and probe 5 can be attributed to the presence of multiple species at this stage of titrations. These results are in accordance with our previous reports on TAB-DCV based cyanide receptors.

As observed for fluoride binding, the cyanide binding also quenches the luminescence of compound 4 at 382 nm. In the case of 5 and 6, the cyanide binding exhibited complex luminescence characteristics (Figure 15). In the presence of one equivalent of cyanide, the fluorescence intensity of both 5 and 6 increased with significant red-shift. When an additional equivalent of cyanide was added, the intensity of the luminescence decreased with considerable blue-shift. The spectral changes observed for 4, 5, and 6 stop upon addition of two equivalents of cyanide. These results clearly indicate that two equivalents of cyanide saturate both the receptors in 4, 5, and 6 and generate [4·(CN)<sub>2</sub>]<sup>2-</sup>, [5·(CN)<sub>2</sub>]<sup>2-</sup>, and [6·(CN)<sub>2</sub>]<sup>2-</sup>, respectively. Significant residual fluorescence observed for cyanide complexes  $[5 \cdot (CN)_2]^{2-}$  and  $[6 \cdot (CN)_2]^{2-}$  suggest that these complexes are better luminophores than the corresponding compounds 5 and 6.

#### **Binding constants**

The fluoride and cyanide binding constants of **4**, **5**, and **6** were calculated using the absorption titration data. Stock solutions  $(1.0 \times 10^{-5} \text{ M})$  of receptors (**4–6**) and TBAF/TBACN  $(1 \times 10^{-3} \text{ M})$  in tetrahydrofuran (THF) were prepared. A stock solution (2 mL) of receptor was placed in a screw-capped quartz cell of 1 cm width and fluoride/cyanide was added in an incremental fashion. After a constant interval of time, their corresponding absorption spectra were recorded at 298 K. Each titration was repeated at least three times to get consistent values. Absorp-





Figure 15. Changes in photoluminescence spectra of 4 (top left), 5 (top right) and 6 (bottom;  $1 \times 10^{-5}$  M) in the presence of TBACN (2  $\mu$ L = 0.1 equiv) in THF.

Table 5. Binding constants. <sup>[a]</sup>				
	4	5	6	
К (F <sup>-</sup> ) [10 <sup>5</sup> м <sup>-1</sup> ]	0.21	0.53	3.58	
К (CN <sup>-</sup> ) [10 <sup>5</sup> м <sup>-1</sup> ]	1.33	0.86	0.10	
[a] Binding constants are plotting $(1 - l/l_0)/[Anion]$ at the values correspond to sites.	calculated from	UV/Vis absorption t	itrations by	
	against //I <sub>0</sub> .For <b>4</b> , <u>5</u>	5, and <b>6</b> . In the case	of <i>K</i> (CN <sup>-</sup> ),	
	o average for bin	ding at two differe	nt receptor	

tion wavelengths of 381, 434, and 468 nm are chosen for **4**, **5**, and **6**, respectively for calculating the binding constants (Table 5).

Linear relationships were noted between  $(1-I/I_0)/[X^-]$  and  $I/I_0$ in which  $I_0$ , I and  $[X^-]$  are initial absorbance value, absorbance value after each addition of anion source, and concentration of fluoride/cyanide, respectively (Figures S13–S15, Supporting Information). The slope obtained from the fitted linear line directly gave the value of the binding constants. Compound **6** exhibited the highest binding affinity towards fluoride ions, whereas **4** exhibits highest binding affinity towards cyanide ions. Anion binding constant values for **4–6** are comparable to those obtained for TAB–amine–DCV<sup>[11f]</sup> based probes.

To find out the sensitivity of the probes **4–6** towards fluoride and cyanide ions, detection limits are calculated by adopting the procedures reported elsewhere<sup>[22]</sup> using the formula  $3\sigma/k$ ,  $\sigma$ ; standard deviations, k; slope of the linear fitting (emission



Scheme 3. Possible species formed during the cyanide titration of 5; predicted using <sup>1</sup>H NMR studies.

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intensity vs. [X<sup>-</sup>], Supporting Information). The fluoride detection limits for compounds **4**, **5**, and **6** were found to be 2.02, 1.52, and 2.82 ppm, respectively. In the case of cyanide ion, the detection limits were found to be 2.0, 0.2 and 0.16 ppm for **4**, **5**, and **6**, respectively. Detection limit values indicate that the reported probes are able to sense  $F^-/CN^-$  from the medium even in ppm range indicating higher sensitivity. Compound **5** exhibits lowest detection limit for fluoride ions whereas **6** exhibits lowest detection for cyanide ions (see the Supporting Information for more details).

Reversible anion binding behaviour is an essential characteristic for the probes to be utilized in multiple numbers of times. Hence, the reversibility of fluoride binding in **4**, **5**, and **6** were examined by using an external reagent (BF<sub>3</sub>·OEt<sub>2</sub>) to remove fluoride ions from the fluoride bound species (**4**·F<sup>-</sup>, **5**·F<sup>-</sup>, and **6**·F<sup>-</sup>). Addition of BF<sub>3</sub>·OEt<sub>2</sub> (4×10<sup>-2</sup> M, 2 mL) to solutions of fluoride bound species resulted in nearly complete restoration of the luminescence probes **4**, **5**, and **6** (Supporting Information) indicating that **4–6** can be regenerated after utilizing for fluoride ion detection.

### Test-strip method for aqueous fluoride and cyanide ion detection

The selective and visual colorimetric responses of **5** and **6** towards fluoride and cyanide provided an opportunity to develop low-cost test strips for practical applications. These test strips are made by coating the solutions of **5** and **6** on filter paper strips. When these strips were dipped into water contaminated with fluoride and cyanide ions (0.1  $\times$  solution), the colour changed completely (Figure 16). These results clearly demonstrate the potential practical applications of **5** and **6** to detect fluoride and cyanide in water by a simple test-dip method.



**Figure 16.** Photographs of THF solutions of **5** and **6** in presence/absence of fluoride and cyanide under day light (top). Test strips coated with probes **5** and **6** and their colorimetric response towards  $F^-$  and  $CN^-$  in water (0.1 m).

# Conclusions

A new series of TAB-thiophene-DCV (A-D-A') conjugates 4, 5, and 6 was synthesized. It was found that, increasing the number of thiophene rings between the two acceptor sites can facilitate increased electronic conjugation between the two acceptors with significant reduction of band gap between frontier molecular orbitals. Interestingly, compounds 5 and 6 with longer  $\pi$ -spacers showed higher fluorescence in polar solvents, which is quite rarely observed for fluorophores with donor-acceptor configurations. The fluorescence quantum yield of 5 and 6 can be modulated by viscosity of the solvent medium. Compounds 5 and 6 exhibit aggregation-induced emission and strong luminescence in the solid state in a polymeric matrix. DLS measurement confirms formation of aggregated particles is responsible for the enhanced luminescence of 5 and 6 in poor solvents. Since reorganisation of the molecular structure is restricted in a rigid environment, non-radiative decay channels are minimized to a significant extent. Compounds 4-6 exhibit selective response towards fluoride and cyanide ions. Importantly, 5 and 6 show different colorimetric response towards the interfering anions fluoride and cyanide ions. Compound 5 showed fluorescence ratiometric response towards fluoride ions and can be used as a self-calibrating fluoride indicator. Test strips made up of probes 5 and 6 have potential application in identifying fluoride and cyanide ions in aqueous medium with different colorimetric responses.

### **Experimental Section**

#### Materials and methods

All moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. THF was distilled over sodium prior to use. HPLC grade solvents were used for absorption and emission spectroscopic measurements. All the UV/Vis absorption, fluorescence and NMR titrations were carried out at room temperature in freshly distilled solvents. Electronic absorption spectra were recorded on a PerkinElmer LAMBDA 750 UV/visible spectrophotometer. Fluorescence emission and excitation spectra were recorded on a Horiba JOBIN YVON Fluoromax-4 spectrometer. DFT calculations were performed using standard computational methods and basis sets as incorporated in the Gaussian 09 software package. Dimesitylborylbithiophene aldehyde (2) was synthesized following previously reported methods.<sup>[11b]</sup>

#### Synthetic procedures

**Synthesis of 1**: 5-Bromo-2-thiophenecarboxaldehyde (1.25 mL, 10.47 mmol) and triethylorthoformate (1.9 mL, 12.56 mmol) were dissolved in ethanol (30 mL). A catalytic amount of dil. HCl was added and the reaction mixture was heated under reflux for 6 h. Evaporation of all the volatiles gave the protected aldehyde "a" (2.6 g; 93.86% yield) which was used for next step without any further purification. To a solution of "a" (2 g, 7.54 mmol) in THF, *n*BuLi (1.6 M in hexane, 5.19 mL, 8.30 mmol) was added dropwise under a N<sub>2</sub> atmosphere at -78 °C and the reaction mixture was stirred at this temperature for 60 min. BFMes<sub>2</sub> (2.43 g, 9.05 mmol) was added. The reaction mixture allowed to attain room temperature and stirring was continued for another 12 h. The reaction was

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quenched with 2 N HCl. The reaction mixture was extracted with ethyl acetate. The combined organic layer was washed with water, dried under Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to afford a crude product. Analytically pure product was obtained by column chromatography over silica gel using 5% ethyl acetate in hexane as eluent. Yield: 1.5 g (55.14%) as an off-white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$ =9.99 (s, 1H), 7.81 (d, *J*=4 Hz, 2H), 7.45 (d, *J*=4 Hz, 2H), 6.84 (s, 4H), 2.31 (s, 6H), 2.07 ppm (s, 12 H).

**Synthesis of 3**: 5-Bromo-2-thiophenecarboxaldehyde (0.21 mL, 1.73 mmol) and **c** (1 g, 1.73 mmol) were taken in a two-necked flask under nitrogen atmosphere in toluene. The resultant solution was degassed for 30 min to remove all the dissolved oxygen, subsequently a catalytic amount of Pd(PPh<sub>3</sub>)<sub>4</sub> (0.09 g, 0.05 mmol) was added. The reaction mixture was heated under reflux condition for 12 h. All the volatiles are evaporated completely and the product was extracted with ethyl acetate and purified by column chromatography over silica gel using 50% ethyl acetate in hexane eluent. Yield: 0.8 g (88%; straw-yellow solid). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =9.86 (s, 1H), 7.67 (d, *J*=4 Hz, 1H), 7.37 (d, *J*=4 Hz, 1H), 7.34 (d, *J*=4 Hz, 1H), 7.27 (d, *J*=4 Hz, 1H), 7.23 (d, *J*=4 Hz, 1H), 7.21 (d, *J*=4 Hz, 1H), 6.85 (s, 4H), 2.32 (s, 6H), 2.15 ppm (s, 12H).

**Synthesis of 4**: Malanonitrile (19 μL, 0.191 mmol), **1** (0.1 g, 0.277 mmol) and a catalytic amount of piperidine were dissolved in ethanol (25 mL) under stirring. The progress of the reaction was monitored by TLC. After complete consumption of compound **1**, all the volatiles were removed and the resultant crude product was purified by column chromatography over silica gel (eluent: hexane/ethyl acetate 96:4) to obtain the analytically pure compound. Yield: 15 mg (13%), off-white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.92 (d, *J* = 4 Hz, 1 H), 7.82 (s, 1 H), 7.44 (d, *J* = 4 Hz, 1 H), 6.84 (s, 4 H), 2.31 (s, 6 H), 2.06 ppm (s, 12 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 156.11, 152.82, 141.73, 140.11, 139.65, 129.03, 115.48, 114.40, 23.89, 21.77 ppm; ESI-MS calcd: C<sub>26</sub>H<sub>25</sub>BN<sub>2</sub>S (*M*+Na<sup>+</sup>) 431.1724; found 431.1767; elemental analysis calcd (%) for C<sub>26</sub>H<sub>25</sub>BN<sub>2</sub>S: C, 76.47; H, 6.17; N, 2.65; found: C, 76.82; H, 6.08; N, 2.48.

**Synthesis of 5**: Compound **5** was synthesized following a similar procedure as that for **4**. The quantities involved and characterization data are as follows. **2** (0.1 g, 0.226 mmol), malanonitrile (15 μL, 0.226 mmol), piperidine (catalytic amount), Yield: 0.035 g in 31.5% as a reddish-black powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.76 (s, 1H), 7.62 (d, *J*=4 Hz, 1H), 7.51 (d, *J*=4 Hz, 1H), 7.39 (d, *J*=4 Hz, 1H), 7.33 (d, *J*=4 Hz, 1H), 6.84 (s, 4H), 2.31 (s, 6H), 2.12 ppm (s, 12 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =153.67, 150.60, 149.23, 146.63, 141.49, 141.34, 140.29, 139.65, 134.91, 129.28, 128.83, 126.18, 114.51, 113.70, 23.91, 21.71 ppm; ESI-MS calcd: C<sub>30</sub>H<sub>27</sub>BN<sub>2</sub>S<sub>2</sub> (*M*+Na<sup>+</sup>) 513.1601; found 513.1604; elemental analysis calcd (%) for C<sub>30</sub>H<sub>27</sub>BN<sub>2</sub>S<sub>2</sub>: C, 73.46; H, 5.55; N, 5.71; found: C, 73.31; H, 5.75; N, 5.78.

**Synthesis of 6**: Compound **6** was synthesized following a similar procedure as that for **4** and **5**. The quantities involved and characterization data are as follows. **3** (0.1 g, 0.191 mmol), malanonitrile (12  $\mu$ L, 0.191 mmol), piperidine (catalytic amount), yield: 80 mg in 73% as reddish-black powder. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =7.75 (s, 1H), 7.62 (d, *J*=4 Hz, 1H), 7.37 (d, *J*=4 Hz, 1H), 7.35 (m, 2H), 7.24 (m, *J*=4 Hz, 2H), 6.84 (s, 4H), 2.31 (s, 6H), 2.14 ppm (s, 12H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =150.40, 149.10, 148.39, 141.81, 141.31, 140.73, 140.51, 139.30, 135.20, 134.13, 128.72, 128.65, 127.20, 126.62, 125.08, 115.65, 113.85 ppm; ESI-MS calcd: C<sub>34</sub>H<sub>29</sub>BN<sub>2</sub>S<sub>3</sub> (*M*+Na<sup>+</sup>) 595.1478; found 595.1812; elemental analysis calcd (%) for C<sub>34</sub>H<sub>29</sub>BN<sub>2</sub>S<sub>3</sub>: C, 71.32; H, 5.10; N, 4.89; found: C, 71.20; H, 5.13; N, 4.75.

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- a) J. H. Schön, H. Meng, Z. Bao, *Nature* 2001, *413*, 713–716; b) J. Kido, Y. Okamoto, *Chem. Rev.* 2002, *102*, 2357–2368; c) Y. L. Tung, P. C. Wu, C. S. Liu, Y. Chi, K. K. Yu, Y. H. Hu, P. T. Chou, S. M. Peng, G. H. Lee, Y. Tao, A. J. Carty, C. F. Shu, F. I. Wu, *Organometallics* 2004, *23*, 3745–3748; d) S. C. Lo, P. L. Burn, *Chem. Rev.* 2007, *107*, 1097–1116; e) Q. Zhao, C. Huanga, F. Li, *Chem. Soc. Rev.* 2011, *40*, 2508–2524; f) G. Crivat, J. W. Taraska, *Trend. Biotechnol.* 2012, *30*, 8–16; g) F. Steiner, S. Bange, J. Vogelsang, J. M. Lupton, *J. Phys. Chem. Lett.* 2015, *6*, 999–1004; h) Y. Chen, R. Guan, C. Zhang, J. Huang, L. Ji, H. Chao, *Coord. Chem. Rev.* 2016, *310*, 16–40.
- [2] a) G. Zhang, J. Lu, M. Sabat, C. L. Fraser, J. Am. Chem. Soc. 2010, 132, 2160–2162; b) O. Bolton, K. Lee, H. J. Kim, K. Y. Lin, J. K. Kim, Nat. Chem. 2011, 3, 205–207; c) P. Galer, R. C. Korošec, M. V. Vidmar, B. J. Šket, J. Am. Chem. Soc. 2014, 136, 7383–7394; d) Y. Gong, Y. Zhang, W. Z. Yuan, J. Z. Sun, Y. Zhang, J. Phys. Chem. C 2014, 118, 10998–11005; e) S. Mu-kherjee, P. Thilagar, Chem. Commun. 2015, 51, 10988–11003; f) C. Botta, S. Benedini, L. Carlucci, A. Forni, D. Marinotto, A. Nitti, D. Pasini, S. Righettoce, E. Cariati, J. Mater. Chem. C. 2016, 4, 2979–2989.
- [3] a) Y. Li, G. Vamvounis, S. Holdcroft, *Chem. Mater.* 2002, *14*, 1424–1429;
   b) Y. Yamaguchi, Y. Matsubara, T. Ochi, T. Wakamiya, Z. Yoshida, *J. Am. Chem. Soc.* 2008, *130*, 13867–13869; c) Y. Niko, S. Kawauchi, S. Otsu, K. Tokumaru, G. Konishi, *J. Org. Chem.* 2013, *78*, 3196–3207.
- [4] a) S. Priyadarshy, M. J. Therien, D. N. Beratan, J. Am. Chem. Soc. 1996, 118, 1504–1510; b) S. A. Jenekhe, L. Lu, M. M. Alam, Macromolecules 2001, 34, 7315–7324; c) J. S. Yang, S. Y. Chiou, K. L. Liau, J. Am. Chem. Soc. 2002, 124, 2518–2527; d) X. Sun, Y. Liu, X. Xu, C. Yang, G. Yu, S. Chen, Z. Zhao, W. Qiu, Y. Li, D. Zhu, J. Phys. Chem. B 2005, 109, 10786–10792; e) H. Meier, Angew. Chem. Int. Ed. 2005, 44, 2482–2506; Angew. Chem. 2005, 117, 2536–2561; f) S. Haid, M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J. E. Moser, R. H. Baker, S. M. Zakeeruddin, M. Grätzel, P. Bäuerle, Adv. Funct. Mater. 2012, 22, 1291–1302; g) D. Su, J. Oh, S. C. Lee, J. M. Lim, S. Sahu, X. Yu, D. Kim, Y. T. Chang, Chem. Sci. 2014, 5, 4812–4818; h) H. Chen, W. Lin, W. Jiang, B. Dong, H. Cuia, Y. Tang, Chem. Commun. 2015, 51, 6968–6971; J. S. Sasaki, G. P. C. Drummen, G. Konishi, J. Mater. Chem. C 2016, 4, 2731–2743.
- [5] a) K. R. Justin Thomas, J. T. Lin, M. Velusamy, Y. T. Tao, C. H. Chuen, *Adv. Funct. Mater.* 2004, *14*, 83–90; b) G. Qian, B. Dai, M. Luo, D. Yu, J. Zhan, Z. Zhang, D. Ma, Z. Y. Wang, *Chem. Mater.* 2008, *20*, 6208–6216; c) E. Ramachandran, R. Dhamodharan, *J. Mater. Chem. C* 2015, *3*, 8642–8648.
- [6] a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, Chem. Commun. 2001, 1740-1741; b) B. K. An, S. K. Kwon, S. D. Jung, S. Y. Park, J. Am. Chem. Soc. 2002, 124, 14410-144154; c) J. Chen, C. C. W. Law, J. W. Y. Lam, Y. Dong, S. M. F. Lo, I. D. Williams, D. Zhu, B. Z. Tang, Chem. Mater. 2003, 15, 1535-1546; d) S. J. Lim, B. K. An, S. D. Jung, M. A. Chung, S. Y. Park, Angew. Chem. Int. Ed. 2004, 43, 6346-6350; Angew. Chem. 2004, 116, 6506-6510; e) S. J. Lim, B. K. An, S. Y. Park, Macromolecules 2005, 38, 6236-6239; f) Q. Zeng, Z. Li, Y. Dong, C. Di, A. Qin, Y. Hong, L. Ji, Z. Zhu, C. K. W. Jim, G. Yu, Q. Li, Z. Li, Y. Liu, J. Qin, B. Z. Tang, Chem. Commun. 2007, 70-72; g) Y. Hong, J. W. Y. Lam, B. Z. Tang, Chem. Commun. 2009, 4332-4353; h) R. Hu, E. Lager, A. A. Aguilar, J. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, Y. Zhong, K. S. Wong, E. P. Cabrera, B. Z. Tang, J. Phys. Chem. C 2009, 113, 15845-15853; i) Z. Zhao, B. Hea, B. Z. Tang, Chem. Sci. 2015, 6, 5347-5364; j) F. Bu, R. Duan, Y. Xie, Y. Yi, Q. Peng, R. Hu, A. Qin, Z. Zhao, B. Z. Tang, Angew. Chem. Int. Ed. 2015, 54, 14492-14497; Angew. Chem. 2015, 127, 14700-14705; k) J. Freudenberg, F. Rominger, U. H. F. Bunz, Chem. Eur. J. 2015, 21, 16749-16753; I) M. Han, Y. Takeoka, T. Seki, J. Mater. Chem. C 2015, 3, 4093-4098; m) M. Huang, R. Yu, K. Xu, S. Ye,

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S. Kuang, X. Zhu, Y. Wan, *Chem. Sci.* **2016**, *7*, 4485–4491; n) B. Xu, W. Li, J. He, S. Wu, Q. Zhu, Z. Yang, Y. C. Wu, Y. Zhang, C. Jin, P. Y. Lu, Z. Chi, S. Liu, J. Xua, M. R. Bryce, *Chem. Sci.* **2016**, *7*, 5307–5312.

- [7] a) D. Ding, K. Li, B. Liu, B. Z. Tang, Acc. Chem. Res. 2013, 46, 2441–2453;
  b) C. T. Leung, Y. Hong, S. Chen, E. Zhao, J. W. Y. Lam, B. Z. Tang, J. Am. Chem. Soc. 2013, 135, 62–65; c) C. Zhang, S. Jin, S. Li, X. Xue, J. Liu, Y. Huang, Y. Jiang, W. Chen, G. Zou, X. J. Liang, ACS Appl. Mater. Interfaces 2014, 6, 5212–5220; d) X. J. Feng, J. Peng, Z. Xu, R. Fang, H. Zhang, X. Xu, L. Li, J. Gao, M. S. Wong, ACS Appl. Mater. Interfaces 2015, 7, 28156–28165; e) E. Zhao, Y. Chen, H. Wang, S. Chen, J. W. Y. Lam, C. W. T. Leung, Y. Hong, B. Z. Tang, ACS Appl. Mater. Interfaces 2015, 7, 7180–7188; f) J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, Chem. Rev. 2015, 11718–11940; g) L. Hu, Y. Duan, Z. Xu, J. Yuan, Y. Dong, T. Han, J. Mater. Chem. C 2016, 4, 5334–5341.
- [8] a) D. Chen, J. Zhan, M. Zhang, J. Zhang, J. Tao, D. Tang, A. Shen, H. Qiua, S. Yin, *Polym. Chem.* **2015**, *6*, 25–29; b) A. Han, H. Wang, R. T. K. Kwok, S. Ji, J. Li, D. Kong, B. Z. Tang, B. Liu, Z. Yang, D. Ding, *Anal. Chem.* **2016**, *88*, 3872–3878; c) Y. X. Zhu, Z. W. Wei, M. Pan, H. P. Wang, J. Y. Zhanga, C. Y. Su, *Dalton Trans.* **2016**, *45*, 943–950.
- [9] a) T. Noda, Y. Shirota, J. Am. Chem. Soc. 1998, 120, 9714-9715; b) S. Yamaguchi, T. Shirasaka, T. Tamao, Org. Lett. 2000, 2, 4129-4132; c) C. D. Entwistle, T. B. Marder, Angew. Chem. Int. Ed. 2002, 41, 2927-2931; Angew. Chem. 2002, 114, 3051-3056; d) A. Sundararaman, K. Venkatasubbaiah, M. Victor, L. N. Zakharov, A. L. Rheingold, F. Jakle, J. Am. Chem. Soc. 2006, 128, 16554-16565; e) T. Agou, J. Kobayashi, T. Kawashima, Chem. Eur. J. 2007, 13, 8051-8060; f) U. Megerle, F. Selmaier, C. Lambert, E. Riedlea, S. Lochbrunnerc, Phys. Chem. Chem. Phys. 2008, 10, 6245-6251; g) Z. M. Hudson, S. Wang, Acc. Chem. Res. 2009, 42, 1584-1596; h) G. L. Fu, H. Y. Zhang, Y. Q. Yan, C. H. Zhao, J. Org. Chem. 2012, 77, 1983 - 1990; i) M. Steeger, C. Lambert, Chem. Eur. J. 2012, 18, 11937 -11948; i) L. Chen, Y. Jiang, H. Nie, R. Hu, H. S. Kwok, F. Huang, A. Oin, Z. Zhao, B. Z. Tang, ACS Appl. Mater. Interfaces 2014, 6, 17215-17225; k) C. Reus, F. Guo, A. John, M. Winhold, H. W. Lerner, F. Jäkle, M. Wagner, Macromolecules 2014, 47, 3727-3235; I) T. Kushida, A. Shuto, M. Yoshio, T. Kato, S. Yamaguchi, Angew. Chem. Int. Ed. 2015, 54, 6922-6925; Angew. Chem. 2015, 127, 7026-7029; m) L. Ji, R. M. Edkins, L. J. Sewell, A. Beeby, A. S. Batsanov, K. Fucke, M. Drafz, J. A. K. Howard, O. Moutounet, F. Ibersiene, A. Boucekkine, E. Furet, Z. Liu, J. F. Halet, C. Katan, T. B. Marder, Chem. Eur. J. 2014, 20, 13618-13635; n) X. Yin, J. Chen, R. A. Lalancette, T. B. Marder, F. Jakle, Angew. Chem. Int. Ed. 2014, 53, 9761-9765; Angew. Chem. 2014, 126, 9919-9923; o) A. G. Bonn, O. S. Wenger, J. Org. Chem. 2015, 80, 4097-4107; p) Z. Zhang, R. Edkins, J. Nitsch, K. Fucke, A. Eichhorn, A. Steffen, Y. Wang, T. B. Marder, Chem. Eur. J. 2015, 21, 177-190; q) K. Schickedanz, T. Trageser, M. Bolte, H. W. Lerner, M. Wagner, Chem. Commun. 2015, 51, 15808-15810; r) V. M. Hertz, H. W. Lerner, M. Wagner, Org. Lett. 2015, 17, 5240-5243; s) P. Joshi, R. Vedarajan, N. Matsumi, Chem. Commun. 2015, 51, 15035-15038; t) X. Yin, F. Guo, R. A. Lalancette, F. Jäkle, Macromolecules 2016, 49, 537-546; u) Y. Ren, F. Jäkle, Dalton Trans. 2016, 45, 13996-14007.
- [10] a) W. Z. Yuan, S. Chen, J. W. Y. Lam, C. Deng, P. Lu, H. H. Y. Sung, I. D. Williams, H. S. Kwok, Y. Zhang, B. Z. Tang, *Chem. Commun.* 2011, *47*, 11216–11218; b) R. Yoshii, A. Hirose, K. Tanaka, Y. Chujo, *Chem. Eur. J.* 2014, *20*, 8320–8324; c) R. Yoshii, A. Hirose, K. Tanaka, Y. Chujo, *J. Am. Chem. Soc.* 2014, *136*, 18131–18139; d) M. Tominaga, H. Naito, Y. Morisaki, Y. Chujo, *New J. Chem.* 2014, *38*, 5686–56980; e) R. Yoshii, K. Tanaka, Y. Chujo, *New J. Chem.* 2014, *47*, 2268–2278; f) K. Tanaka, Y. Chujo, *NPG Asia Materials* 2015, *7*, e223; g) L. Chen, G. Lin, H. Peng, H. Nie, Z. Zhuang, P. Shen, S. Ding, D. Huang, R. Hu, S. Chen, F. Huang, A. Qin, Z. Zhao, B. Z. Tang, *J. Mater. Chem. C* 2016, *4*, 5241–5247; h) S. Li, Y. Shang, L. Wang, R. T. K. Kwokb, B. Z. Tang, *J. Mater. Chem. G* 2016, *4*, 5363–5369; i) H. Shi, D. Xin, X. Gu, P. Zhang, H. Peng, S. Chen, G. Lin, Z. Zhao, B. Z. Tang, *J. Mater. Chem. C* 2016, *4*, 1228–1237; j) T. Butler, W. A. Morris, J. S. Kosicka, C. L. Fraser, *ACS Appl. Mater. Interfaces* 2016, *8*, 1242–1251.

- [11] a) C. A. Swamy, P. S. Mukherjee, P. Thilagar, J. Mater. Chem. C 2013, 1, 4691–4698; b) S. K. Sarkar, P. Thilagar, Chem. Commun. 2013, 49, 8558–8560; c) P. C. A. Swamy, S. Mukherjee, P. Thilagar, Chem. Commun. 2013, 49, 993–995; d) P. Sudhakar, S. Mukherjee, P. Thilagar, Organometallics 2013, 32, 3129–3133; e) C. A. Swamy, P. S. Mukherjee, P. Thilagar, Inorg. Chem. 2014, 53, 4813–4823; f) G. R. Kumar, P. Thilagar, Dalton Trans. 2014, 43, 7200–7207; g) G. R. Kumar, S. K. Sarkar, P. Thilagar, Phys. Chem. Chem. Phys. 2015, 17, 30424–30432; h) S. K. Sarkar, G. R. Kumar, P. Thilagar, Chem. Commun. 2016, 52, 4175–4178.
- [12] a) S. Mukherjee, P. Thilagar, Chem. Commun. 2013, 49, 7292-7294; b) S. Mukherjee, P. Thilagar, Chem. Eur. J. 2014, 20, 8012-8023; c) S. Mukherjee, P. Thilagar, Chem. Eur. J. 2014, 20, 9052-9062; d) S. Mukherjee, P. Thilagar, Phys. Chem. Chem. Phys. 2014, 16, 20866-20877.
- [13] a) S. Yamaguchi, S. Akiyama, K. Tamao, J. Am. Chem. Soc. 2001, 123, 11372 - 11375; b) T. W. Hudnall, Y. M. Kim, M. W. P. Bebbington, D. Bourissou, F. Gabbai, J. Am. Chem. Soc. 2008, 130, 10890-10891; c) G. Zhou, C. L. Ho, W. Y. Wong, Q. Wang, D. Ma, L. Wang, Z. Lin, T. B. Marder, A. Beeby, Adv. Funct. Mater. 2008, 18, 499-511; d) T. W. Hudnall, C. W. Chiu, F. P. Gabbaï, Acc. Chem. Res. 2009, 42, 388-397; e) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbai, Chem. Rev. 2010, 110, 3958-3984; f) Z. M. Hudson, C. Sun, M. G. Helander, H. Amarne, Z. H. Lu, S. Wang, Adv. Funct. Mater. 2010, 20, 3426-3439; g) Y. Kim, H. S. Huh, M. Lee, I. L. Lenov, H. Zhao, F. P. Gabbai, Chem. Eur. J. 2011, 17, 2057-2062; h) C. Sun, Z. M. Hudson, M. G. Helander, Z. H. Lu, S. Wang, Organometallics 2011, 30, 5552-5555; i) Z. M. Hudson, C. Sun, M. G. Helander, Y. L. Chang, Z. H. Lu, S. Wang, J. Am. Chem. Soc. 2012, 134, 13930-13933; j) B. Chen, Y. Ding, X. Li, W. Zhu, J. P. Hill, K. Ariga, Y. Xie, Chem. Commun. 2013, 49, 10136-10138; k) W. Lin, Q. Tan, H. Liang, K.Y. Zhang, S. Liu, R. Jiang, R. Hu, W. Xu, Q. Zhao, W. Huang, J. Mater. Chem. C 2015, 3, 1883-1887; I) K. Suzuki, S. Kubo, K. Shizu, T. Fukushima, A. Wakamiya, Y. Murata, C. Adachi, H. Kaji, Angew. Chem. Int. Ed. 2015, 54, 15231-15235; Angew. Chem. 2015, 127, 15446-15450; m) P. Puneet, R. Vedarajan, N. Matsumi, Polym. Chem. 2016, 7, 4182-4187.
- [14] S. Ma, H. Zhang, N. Zhao, Y. Cheng, M. Wang, Y. Shena, G. Tu, J. Mater. Chem. A 2015, 3, 12139–12144.
- [15] C. Wang, J. Jia, W. N. Zhang, H. Y. Zhang, C. H. Zhao, Chem. Eur. J. 2014, 20, 16590–16601.
- [16] a) G. Oster, Y. Nishijlx, J. Am. Chem. Soc. 1956, 78, 1581-1584; b) S. Sharafy, K. A. Muszkat, J. Am. Chem. Soc. 1971, 93, 4119-4125.
- [17] E. Sakuda, Y. Ando, A. Ito, N. Kitamura, J. Phys. Chem. A 2010, 114, 9144-9150.
- [18] a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648–5652; b) Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [19] A. D. Becke, Phys. Rev. A 1988, 38, 3098-3100.
- [20] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
- [21] W. C. Lin, S. K. Fang, J. W. Hu, H. Y. Tsai, K. Y. Chen, Anal. Chem. 2014, 86, 4648–4652.
- [22] A. Shrivastava, V. B. Gupta, Chron. Young Sci. 2011, 2, 21-25.

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# **FULL PAPER**



# Fluorescent Sensors

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Sensing Characteristics of Triarylborane-Oligothiophene-Dicyanovinyl Triads



**Hazard detectors**: The design and synthesis of a series of triarylborane–oligothiophene–dicyanovinyl triads **4–6** (A– D–A') is reported (see figure). The optical properties of **4–6** were elegantly modulated by judiciously varying the number of thiophenyl spacer between the acceptors. Compounds **5** and **6** are AIE active and also exhibit significant luminescence in a PMMA matrix. Filter paper strips coated with compounds **5** and **6** can detect F<sup>-</sup> and CN<sup>-</sup> in aqueous media with different colorimetric responses.