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Triphenylethylenyl–Based Donor–Acceptor–Donor Molecules: Structural and Optical Properties Studies, and AIE Properties for Cyanide Detection

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Six novel molecules with donor-acceptor-donor (D-A-D) configurations were synthesized with a middle acceptor flanked by two electron-rich triphenylthylenyl- moieties. The first set of three molecules (**TPE-FLN**, **TPE-AQN** and **TPE-BZQ**) consists of fluorenone, anthraquinone and benzophenone as acceptors, respectively, which then underwent Knoevenagel condensation with malononitrile to give the second set of 1,1-dicyanomethylidene – containing molecules **CS1**, **CS2** and **CS3**. Compounds **CS1**, **CS2** and **CS3** were found to be selective to nucleophilic attack by cyanide ion and hence their potential as optical cyanide sensors was investigated. It was found that the main cyanated products of **CS1** and **CS3** were aggregation-induced emission (AIE) active, and they were successfully isolated and fully characterized. Finally, paper probes were fabricated from the three compounds, of which **CS1**-coated paper probe gave a remarkable turn-on of fluorescence in the presence of cyanide, revealing potential for use as cyanide sensors.

Introduction

The discovery of aggregation-induced emission (AIE) phenomenon in 2001 has led to immense research interest globally in this class of compounds.¹ The usefulness of AIEactive luminogens (AIE-gens) in combating deadlock faced by conventional aggregation-caused quenching (ACQ) luminogens has led to the emergence of a myriad of reports of AIE-gens for a wide range of applications, ranging from organic light emitting diodes, chemosensors and bioimaging.^{1,2} In the aspect of molecular structure design, functionalizing conjugated molecules and conventional ACQ luminogens with rotor-like AIE-active moieties such as triphenvlethylene and tetraphenylethylene (TPE) may confer the highly sought-after AIE properties via the prevention of π - π stacking and the introduction of restriction-of-intramolecular rotation (RIR) on aggregation.³ Also, the strategy of introducing electron donating (D) and withdrawing (A) groups in appropriate arrangements was commonly adopted to tune optical bandgaps of AIE-gens, particularly to red-shift emission wavelengths, and hence generating AIE-gens with different absorption and emission wavelengths to cater for its various application needs.4

Development of optical chemosensors can provide spontaneous and convenient detection of harmful materials, bypassing the time-consuming and inconvenient route of performing instrumental analysis. Particularly, the detection of cyanide received considerable attention with numerous reports of novel optical and fluorescent sensors being developed, with the potential for sensing in environmental and biological samples.⁵ Cyanide is one of the deadliest toxic species present with a lethal dose of 1.5 mg/kg of body weight. Unfortunately for us, exposure to cyanide remains a possible threat to us through industrial contamination of the environment.⁶ Designs of novel cyanide chemosensors often utilize mechanisms of coordination and nucleophilic addition reactions.⁵ However, the development of fluorescent cyanide sensors is often faced with challenges of low selectivity and low reactivity with CN⁻ in aqueous media. More importantly, the problem of ACQ characteristics further limits their practicability. Notably, there were only few reports of AIEactive cyanide sensors to date.⁷

Similar to TPE, triphenylethylene is an AIE-active moiety useful in the structural design of novel AIE-gens.⁸ We synthesized six simple triphenylethylenyl-based molecules with donoracceptor-donor (D-A-D) configurations as potential AIE-gens, which contain acceptors with different electron-withdrawing abilities and slight structural variations. The effects of these differences on the structural and photophysical properties of this D-A-D system were investigated. To begin with, triphenylethylenyl- functionalized fluorenone (**TPE-FLN**), anthraquinone (**TPE-AQN**) and benzophenone (**TPE-BZP**), were synthesized. To enhance the strength of the middle acceptors, Knoevenagel condensation reactions with malononitrile were

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Electronic Supplementary Information (ESI) available: UV-Vis and fluorescence spectra; crystallographic data; DFT calculations, relevant data for cyanide detection, NMR spectra, mass spectra and FTIR spectra. See DOI: 10.1039/x0xx00000x

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using silica gel grade 60 (0.040 – 0.063 mm).

NC `CN Knoe (d)

TPE-BZP

(a) K₂CO₃, Pd(PPh₃)₄, Toluene, H₂O, Ethanol, 100°C for 18 hours. (b) Piperidine, DMF, 100°C for 1hr. (c) TiCl₄, Pyridine, DCM, reflux for 3 days. (d) Pyridine, reflux for overnight.

The ^1H and ^{13}C NMR spectra of products and intermediates were recorded using Bruker 400 MHz NMR Spectrometer. Electron ionization (EI) mass spectra were obtained using Finnigan TSQ 7000 mass spectrometer and atmospheric pressure chemical ionization (APCI) mass spectra were recorded on a Bruker MicrOTOF-QII mass spectrometer coupled to an Dionex Ultimate 3000 RSLC system. Single crystal XRD analysis of products was performed with Bruker D8 Venture Single Crystal X-ray Diffractometer and refined using Bruker SHELXTL Software Package. FTIR spectra of compounds were recorded using Perkin Elmer Spectrum 2000 FT-IR Spectrometer using KBr pellets. UV-Vis absorption spectra recorded using Shimadzu UV3600 UV-Vis-NIR were spectrophotometer and photoluminescence (fluorescence) obtained Shimadzu RF501 spectra were using spectrofluorometer.

Synthetic Procedures and Characterization Data

The pinacolato- boronic esters intermediates were synthesised via Miyaura borylation in accordance to the reported synthetic procedures and their ¹H NMR and mass spectral data were consistent with reported findings.¹⁰

2,7-Bis(1,2,2-triphenylvinyl)-9H-fluoren-9-one (TPE-FLN). A flamedried Schlenk tube is charged with 9H-fluoren-9-one-2,7bis(boronic acid pinacol ester) (645 mg, 1.49 mmol), 2-bromo-1,2,2-triphenylethene (1.1 g, 3.28 mmol) and potassium carbonate (2.1 g, 15 mmol). Toluene (30mL), ethanol (5 mL) and deionised water (5 mL) were then added. The mixture was thoroughly degassed before adding Pd(PPh₃)₄ catalyst (173 mg, 0.15 mmol). The reaction was allowed to stir at 100 °C for 18 hours under inert argon gas atmosphere, then cooled to room

Scheme 1. Synthesis and molecular structures of triphenylethylenyl-functionalized carbonyl compounds TPE – FLN, TPE – AQN and TPE – BZP, and subsequent Knoevenagel condensation to cyanocarbons CS1, CS2 and CS3. intermediates were achieved via column chromatography

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CS1

CS2

Journal Name



cyanocarbons and cyanide. We further managed to isolate and characterize the cyanated species of CS1 and CS3 (CS1-CN and CS3-CN, respectively) which were confirmed to be AIE-active. Finally, paper probes were fabricated to demonstrate cyanide detection using AIE properties, of which we found the fluorescence turn-on effect of CS1 to be the most ideal of all three compounds.

performed to convert the keto group to dicyanomethylidene

group. The reactions were found to proceed at a different level

of ease for each carbonyl intermediate, requiring different

reagents and conditions. The resultant compounds, CS1, CS2 and CS3, yielded interesting emission and structural changes

compared to their carbonyl precursors.

Experimental Section

General Methods and Analytical Instruments

All reagents and starting materials used in synthesis and analytical procedures were purchased from commercial suppliers (Sigma Aldrich, TEDIA and TCI) and used without further purification, unless otherwise stated. Anhydrous toluene and THF solvents for synthesis were purified via distillation with sodium-benzophenone immediately before use. ¹H and ¹³C NMR spectra of compounds and intermediates were recorded in deuterated solvents (CDCl₃ and THF- d_8) purchased from commercial supplier (Cambridge Isotope Laboratories, Inc.) with tetramethylsilane (TMS) as internal standards. Preparative separation of compounds and



Reagents and Conditions

functionalization

of

potential

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temperature and quenched by the addition of saturated aqueous sodium hydrogen carbonate. The mixture was then extracted with dichloromethane (DCM) and the combined organic layer was washed with brine solution then dried with magnesium sulphate. The mixture was filtered and the solvent removed via a rotary evaporator. The crude product was purified via column chromatography using DCM/hexane mixture (2:3 v/v) as eluent to yield the product as a bright yellow solid (0.65 g, 63% yield). ¹H NMR (400 MHz, CDCl₃, δ): 6.99 – 7.02 (m, 6H), 7.05 – 7.15 (m, 28H), 7.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 119.58, 126.66, 126.80, 127.07, 127.90, 127.93, 131.23, 134.32, 137.67, 139.84, 141.98, 142.19, 142.83, 143.23, 145.06, 193.62. IR(KBr): v = 1720 (s; v(C=O)). HRMS (APCI, m/z): [M]⁺ calcd for C₅₃H₃₇O, 689.2839; found, 689.2831.

2,6-Bis(1,2,2-triphenylvinyl)anthracene-9,10-dione (TPE-AQN): TPE-AQN was synthesized via Suzuki coupling of the same procedure as described above in **TPE-FLN** synthesis, with 9,10-anthraquinone-2,6-bis(boronic acid pinacol ester) (600 mg, 1.3 mmol), 2-bromo-1,2,2-triphenylethene (872 mg, 2.6 mmol) potassium carbonate (1.8 g, 13 mmol) and Pd(PPh₃)₄ catalyst (150 mg, 0.13 mmol). The crude product was purified via column chromatography using ethyl acetate (EA)/ hexane mixture (1:19 v/v - 3:17 v/v) as eluent to yield the product as a bright yellow solid (650 mg, 70% yield). ¹H NMR (400 MHz, $CDCl_3$, δ): 7.00 – 7,12 (m, 30H), 7.39 (dd, ${}^{3}J$ = 8 Hz, ${}^{4}J$ = 1.3 Hz, 2H), 7.83 – 7.95 (m, 4H). ¹³C NMR (100 MHz, CDCl₃, δ): 126.77, 126.99, 127.04, 127.22, 127.76, 128.03, 129.80, 131.7, 131.24, 131.28, 131.38, 133.19, 136.65, 139.30, 142.39, 142.67, 142.83, 143.67, 150.42, 182.75. IR(KBr): v = 1675 (s; v(C=O)). HRMS (APCI, m/z): $[M]^+$ calcd for C₅₄H₃₇O₂, 717.2782; found, 717.2788.

Bis(4-(1,2,2-triphenylvinyl)phenyl)methanone (TPE-BZQ): TPE-BZP was synthesized via the same procedure as described above in TPE-FLN synthesis, with benzophenone-4,4bis(boronic acid pinacol ester) (500 mg, 1.2 mmol), 2-bromo-1,2,2-triphenylethene (850 mg, 2.5 mmol), potassium carbonate (1.6 g, 11.5 mmol) and Pd(PPh₃)₄ catalyst (133 mg, 0.12 mmol). The crude product was purified via column chromatography using EA/ hexane mixture (1:4 v/v) as eluent and then washed with hexane to yield the product as a white solid (670mg, 84% yield). ¹H NMR (400 MHz, CDCl₃, δ): 7.02 – 7.12 (m, 34H), 7.50 (d, J = 8 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃, δ): 126.72, 127.84, 129.51, 131.12, 131.28, 135.36, 139.96, 142.50, 143.11, 143.16, 143.25, 148.21, 195.91. IR(KBr): v = 1655 (s; v(C=O)). HRMS (APCI, m/z): [M]⁺ calcd for $C_{53}H_{38}O$, 691.2995; found, 691.3007.

2-(2,7-Bis(1,2,2-triphenylvinyl)-9H-fluoren-9-

ylidene)malononitrile (CS1): TPE–FLN (50 mg, 0.073 mmol) and malononitrile (48 mg, 0.73 mmol) were dissolved in 5 mL DMF solvent under inert argon gas atmosphere in a flamedried Schlenk tube. 0.5mL of piperidine was added and the mixture was allowed to stir at 100°C and monitored via TLC. The reaction mixture was observed to turn deep purple after 5 minutes and completion was indicated via TLC after an hour. The DMF solvent was then removed under reduced pressure and the crude product was purified via column chromatography using EA/ hexane mixture (1:3 v/v) as eluent and then washed with hexane to yield the product as a greyish purple solid (38 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃, δ): 7.01 – 7.04 (m, 8H), 7.08 – 7.20 (m, 26H), 7.99 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 75.60, 112.95, 119.87, 126.75, 126.89, 127.89, 127.66, 127.99, 128.06, 129.76, 131.14, 131.35, 134.13, 137.37, 139.44, 139.97, 142.50, 142.69, 142.94, 143.03, 145.22, 160.87. IR(KBr): v = 2224 (m; v(C=N)). HRMS (EI, m/z): [M]⁺ calcd for C₅₆H₃₆N₂, 736.28785; found, 738.28630.

2,2'-(2,6-Bis(1,2,2-triphenylvinyl)anthracene-9,10-diylidene)

dimalononitrile (CS2): A flame-dried Schlenk tube was charged with TPE-AQN (50 mg, 0.07 mmol) and malononitrile (12.6 mg, 0.19 mmol), then evacuated and backfilled with argon gas three times. 3 mL of anhydrous DCM was added to dissolved the reactants and the reaction mixture cooled with an icewater bath. 0.4mL of 1M titanium(IV) chloride solution (0.4 mmol) was added slowly where the reaction mixture turned dark green. The reaction mixture was then allowed to stir for 20 minutes at 0°C before pyridine (0.13 mL) was added. The reaction mixture was then warmed to room temperature and then heated to reflux for 16 hours. Another loading of malononitrile (12.6 mg, 0.19 mmol), titanium(IV) chloride (0.4 mmol) and pyridine (0.13 mL) were added and the reaction. The reaction mixture was allowed to continue stirring under reflux condition for another 24 hours. The reaction was constantly monitored by TLC over 3 days with addition of malononitrile (12.6 mg, 0.19 mmol), titanium(IV) chloride (0.4 mmol) and pyridine (0.13 mL) every day until TLC showed complete consumption of TPE-AQN and formation of product. The mixture was added to 0.1 M HCl solution to quench the reaction and extracted with chloroform. The combined organic layer was then dried over magnesium sulphate, filtered and the solvent was removed via a rotary evaporator. The crude product was purified via column chromatography with chloroform/hexane (1:1 v/v to 3:1 v/v) as eluent. The product was then further washed with hexane and dried, to afford the pure orangey-red solid product (42mg, 74% yield) ¹H NMR (400 MHz, CDCl₃, δ): 7.00 – 7.18 (m, 30H), 7.32 (dd, ³J = 8 Hz, ³J = 1.3 Hz, 2H), 7.80 – 7.82 (m, 4H). 13 C NMR (100 MHz, CDCl₃, δ): 81.93, 112.78, 126.38, 126.98, 127.22, 127.47, 127.89, 128.09, 129.48, 129.86, 130.77, 130.83, 130.91, 134.52, 137.73, 141.32, 141.90, 141.95, 144.75, 148.54, 159.27. IR(KBr): v = 2226 (m; $v(C \equiv N)$). HRMS (APCI, m/z): [M]⁺ calcd for $C_{60}H_{37}N_4$, 813.3013; found, 813.3033.

2-(Bis(4-(1,2,2-triphenylvinyl)phenyl)methylene)

malononitrile (CS3): **TPE–BZQ** (100 mg, 0.14 mmol) and malononitrile (96 mg, 1.45 mmol) were dissolved in 5 mL of pyridine in a 1-neck RBF with a magnetic stirrer and allowed to stir under reflux condition overnight. The pyridine solvent was then removed under reduced pressure and the crude product

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Figure 1. Single crystal X-ray structures of TPE-FLN, TPE-AQN, TPE-BZP, CS1, CS2 and CS3.

purified via column chromatography using DCM/hexane (1:1 v/v) as eluent to afford a bright yellow solid product (98 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃, δ): 7.02 – 7.03 (m, 10H), 7.10 – 7.11 (m, 28H). ¹³C NMR (100 MHz, CDCl₃, δ): 79.90, 114.17, 126.91, 127.74, 127.88, 127.97, 129.52, 131.29, 131.52, 133.82, 139.52, 142.67, 142.95, 143.32, 148.76, 173.85. IR(KBr): v = 2220 (m; v(C=N)). HRMS (APCI, m/z): [M]⁺ calcd for C₅₆H₃₉N₂, 739.3108; found, 739.3103.

2-(9-Cyano-2,7-bis(1,2,2-triphenylvinyl)-9H-fluoren-9-

yl)malononitrile (CS1-CN): CS1 (15 mg, 0.02 mmol) was dissolved in 2mL THF in a glass vial and added tetrabutylammonium cyanide pre-dissolved in water (0.024mmol). The reaction mixture was allowed to stand for a few minutes and then purified via column chromatography using EA/hexane mixture (1:19 v/v - 1:6 v/v) as eluent to afford a white solid (14mg, 90% yield). ¹H NMR (400 MHz, $CDCI_3$, δ): 3.58 (s, 1H), 7.05 – 7.18 (m, 30H), 7.22 (d, J = 4 Hz, 2H), 7.39 (s, 2H), 7.45 (d, J = 4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃, δ): 33.10, 47.44, 108.38, 115.55, 120.79, 126.90, 126.97, 127.23, 127.77, 127.99, 128.40, 131.23, 131.34, 134.78, 136.45, 139.41, 142.74, 142.94, 143.16, 145.46. HRMS (APCI, m/z): $[M]^+$ calcd for $C_{57}H_{38}N_3$, 764.3060; found, 764.3046.

2,2-Bis(4-(1,2,2-triphenylvinyl)phenyl)ethane-1,1,2-tricarbonitrile

(**CS3-CN**): The reaction follows the same procedure and scale (15mg) as CS1+CN. Purification via column chromatography using EA/hexane mixture (1:5 v/v) as eluent affords a white solid (6mg, 39% Yield). ¹H NMR (400 MHz, CDCl₃, δ): 4.55 (s, 1H), 6.95 (m, 4H), 7.01 – 7.11 (m, 34H). ¹³C NMR (100 MHz, CDCl₃, δ): 34.05, 53.11, 109.35, 117.52, 126.30, 126.86, 127.74, 127.83, 127.94, 131.23, 132.38, 139.12, 142.64, 142.94, 146.08. HRMS (APCI, m/z): [M]⁺ calcd for C₅₇H₃₉N₃, 765.3138; found, 765.3133.

Results and Discussion

Structures and Synthesis of Compounds

The synthesis and chemical structures of the six compounds with a general D-A-D configuration, in which a middle electronwithdrawing carbonyl- or 1,1-dicyanomethylidene- containing acceptor was flanked by two electron-rich triphenylethylenylmoieties, are as shown in Scheme 1. Palladium catalysed Suzuki coupling was used to attach triphenylethylenylmoieties to 9-fluorenone, 9,10-anthraquinone and benzophenone at the 2,7-, 2,6- and 4,4- positions respectively to afford TPE-FLN, TPE-AQN and TPE-BZP. Knoevenagel condensation with malononitrile was then performed on TPE-FLN, TPE-AQN and TPE-BZP to convert the carbonyl groups to 1,1-dicyanomethylidene groups in a bid to increase the electron-withdrawing strength of the acceptor moiety. The reaction proceeded under different sets of reagents and conditions. TPE-FLN underwent condensation with malononitrile readily in the presence of piperidine base in dimethylformamide (DMF) solvent under reflux condition. The reaction mixture turned dark purple within 5 minutes indicating the formation of CS1. However, no reaction was observed for TPE-AQN and TPE-BZP under the same conditions. TPE-BZP is required to reflux with malononitrile in pyridine, functioning as both a base and solvent, for at least 16 hours for complete conversion to CS3. The conversion of TPE-AQN to CS2 was even more challenging and required the use of titanium tetrachloride (TiCl₄) as catalyst, with addition of pyridine and malononitrile multiple times over the span of three days. The low reactivity of TPE-AQN towards Knoevenagel condensation is consistent with early report on the synthesis of tetracyanoanthraquinodimethane (TCNAQ), which stated excessive overcrowding of a severely deformed TCNAQ as the reason for the need of excess TiCl₄ catalyst to push the reaction equilibrium forward.¹¹

Single Crystal X-Ray Structures and Packing

The structures of the six compounds were confirmed by singlecrystal X-ray diffraction (XRD) characterization and as shown in **Figure 1**. The single crystals of the six compounds were grown *via* slow vapour diffusion method. In general, the introduction of triphenylethylenyl- groups brought about sufficient steric hindrance which resulted in highly twisted structures.

To study the effect of triphenylethylenyl- functionalization on overall structure of the molecules, the single-crystal X-ray structures of **TPE-FLN**, **TPE-AQN**, **TPE-BZP** and **CS2** were compared with the reported structures of their respective unsubstituted analogues (ESI Fig. S10). Triphenylethylenyl-functionalization of a relatively planar 9-fluorenone resulted in slight bending of the acceptor moiety in **TPE-FLN**.¹² It is also noted that the conversion of carbonyl- group of **TPE-FLN** into 1,1-dicyanomethylidene- group of **CS1** led to greater planarity of the fluorene moiety. Likewise, the twisted butterfly-like structure of TCNAQ moiety experienced greater distortion on functionalization with triphenylethylenyl- moieties in **CS2**.¹⁵

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Figure 2. (a) Normalized UV-Vis absorption spectra of TPE-FLN, TPE-AQN, TPE-BZP, CS1, CS2 and CS3 measured in dilute THF solutions. (b) Normalized fluorescence spectra of TPE-FLN, TPE-AQN, TPE-BZP and CS3 measured in dilute THF solutions. (c) Fluorescence intensity of emission peaks of TPE-FLN, TPE-AQN, TPE-BZP and CS3 measured in different proportions of THF and water solutions at fixed concentration of 10µM. Insert are photos of the respective series of solutions taken under UV irradiation at 365nm. Fluorescence spectra are available in ESI.

The planarity of the centre 9,10-anthraquinone moiety was however retained in **TPE-AQN**.¹³ Also, an already non-planar benzophenone moiety experience minimum structural distortion on functionalization for **TPE-BZP**.¹⁴

An analysis of the packing structures of the six compounds revealed similarities in terms of intermolecular interactions involved (ESI Fig. S11 - S12). The oxygen atoms on the carbonyl groups of TPE-AQN and TPE-BZP participate in hydrogen bonding with a phenyl ring proton of an adjacent molecule, whereas the oxygen atoms on TPE-FLN's carbonyl group participate in hydrogen bonding with an ethanol solvent molecule which serves as a bridge between adjacent TPE-FLN molecules. Likewise, the 1,1-dicyanomethylidene- groups of CS1, CS2 and CS3 also participate in supramolecular interactions crucial for molecular packing. Nitrogen atoms of the 1,1-dicyanomethylidene groups are involved in hydrogen bonding with phenyl protons of adjacent molecules. Other intermolecular weak interactions were also observed to contribute to molecular packing, which include interactions between carbonyl and 1,1-dicyanomethylidene carbons with phenyl ring protons, as well as CH- π interactions between phenyl rings of adjacent molecules. By and large, the steric crowdedness caused by triphenylethylenyl- moieties prevents close π - π stacking of the centre acceptors, hence giving rise to AIE properties observed in the compounds.

Optical Properties and Aggregation Induced Emission

The optical properties of the six compounds were measured and their absorption and emission spectra are shown in **Figure 2**. The optical data are summarised in **Table 1**. Of the three carbonyl groups containing compounds, **TPE-FLN**'s absorption profile was the most red-shifted followed by **TPE-AQN**, then **TPE-BZP**. Interestingly, the molar extinction coefficient value, ε , was the lowest for **TPE-FLN** followed by **TPE-AQN** then **TPE-BZP**. The nature of the absorption peaks will be further discussed later with the aid of time-dependent density functional theory (TD-DFT) studies performed.

The conversion of the carbonyl group in TPE-FLN, TPE-AQN and TPE-BZP into 1,1-dicyanomethylidene groups in CS1, CS2

and **CS3** respectively gave a stronger acceptor group which, in a typical push-pull-push system, will result in lowering of the LUMO, narrowing of the HOMO-LUMO energy gap and hence a red-shifting of the respective absorption shown in **Figure 2a**. The absorption maxima of **TPE-FLN** red-shifted from 452 to 562nm upon undergoing Knoevenagel condensation into **CS1**. Likewise, for the conversion of **TPE-AQN** and **TPE-BZP** into **CS2** and **CS3**, absorption maxima were red-shifted from 395 and 338 to 443 and 386nm respectively. The molar extinction coefficient values for the **CS1**, **CS2** and **CS3** were found to be correspondingly lower than their carbonyl- containing precursors.

Table 1. Summary of photo-physical properties measurements for TPE-FLN, TPE-AQN, TPE-BZP, CS1, CS2 and CS3.

	$\lambda_{abs} (nm)^{a}$	ε (cm⁻¹M⁻¹) ^d	$\lambda_{em} \left(nm \right)^{b}$	$\mathbf{\Phi}^{\mathrm{e}}$	Δv (nm) ^c
TPE-FLN	<u>452</u> , 353	2171	546 (559 ^f)	0.12	94
TPE-AQN	<u>395</u> , 304	10 700	573 (562 ^f)	0.02	178
TPE-BZP	<u>338</u>	25,997	467 (487 ^f)	0.004	129
CS1	<u>562</u> , 333	993	-	-	-
CS2	<u>443</u> , 335	9863	(653 ^f)	-	-
CS3	<u>386</u>	22 325	573 (543 ^f)	0.004	187

^a Absorption maxima wavelength; ^b Fluorescence maxima wavelength; ^c Stoke's shift; ^d molar extinction coefficient with respect to absorption wavelength underlined; ^e Relative quantum yield measured in reference to Quinine Sulphate in 0.5M H₂SO₄ (Φ = 0.54), excitation wavelengths as underlined in λ_{absr} , measurements subjected to ±10% error; ^f fluorescence maxima in thin film state.

TPE-FLN and TPE-AQN dissolved in pure organic solvent were emissive with emission maxima of 546 and 573 nm, respectively. Interestingly, the emission maximum appears more red-shifted for TPE-AQN when its absorption maximum was in fact at a lower wavelength compared to TPE-FLN. TPE-AQN thus, also has a larger Stokes shift. TPE-BZP and CS3 were weakly emissive in organic solvent, with emission maxima at 467 and 561 nm, respectively, whereas CS1 and CS2 were totally non-emissive. The normalized fluorescence spectra were shown in Figure 2b. All compounds except CS1 exhibit solid state (thin film) fluorescence (ESI Fig. S2).

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CS3

 $\begin{array}{c} \hline 2.167 \\ \hline 2.602 \\ \hline \hline 1.852 \\ \hline \hline 3.013 \\ \hline \hline 3.545 \\ \hline \hline \hline 1.5516 \\ \hline \hline 1.5516 \\ \hline \hline 1.5516 \\ \hline \hline 1.6543 \\ \hline \hline 1.5519 \\ \hline \hline 1.5563 \\ \hline 1.5563 \\$

Figure 3. DFT Calculated energy levels and molecular orbital amplitude plots of frontier molecular orbitals of TPE-FLN, TPE-AQN, TPE-BZP, CS1, CS2 and CS3. The calculated optimised structures of the six compounds can be found in the ESI.

TPE - BZF

CS1

TPE - FLN

TPE - AQN

The HOMO and LUMO molecular orbital amplitude plots of the six compounds yielded interesting comparisons. In general, the HOMOs of all six compounds are localised mostly over the electron rich triphenylethylenyl- moieties on both sides of the molecules, leaving the centre electron-withdrawing 1,1-dicyanomethylidene and carbonyl groups bare. On the other hand, the corresponding LUMOs are localised over the centre acceptor moieties while barely reaching towards the electron-rich triphenylethylenyl- groups. Slight anomaly was observed for **CS3** however where its HOMO extended throughout the whole molecule covering also the 1,1-dicyanomethylidene group.

The TD-DFT calculated absorption spectra (ESI Table S4, S6, S8) largely agree with that measured except for the non-existence of a 702 nm peak for **CS1** and 705 nm peak for **CS2**. These absorption bands were calculated to correspond to HOMO \rightarrow LUMO and HOMO–1 \rightarrow LUMO transitions for **CS1** and **CS2** respectively. Interestingly, HOMO \rightarrow LUMO transition was calculated to be forbidden (oscillator strength, *f* = 0) for **CS2**. The weak 562 nm absorption band measured for **CS1** was calculated to correspond to a HOMO–1 \rightarrow LUMO+1 transition whereas the 452nm absorption band corresponds to a HOMO \rightarrow LUMO+1 transition. The 386 nm absorption band measured for **CS3** was calculated to correspond to a combination of HOMO–1 \rightarrow LUMO and HOMO \rightarrow LUMO transitions.

Reaction with Cyanide and Resulting Optical Properties

The 1,1-dicyanovinyl group is often employed in the development of fluorescent cyanide chemosensors. ^{8c,10} The structural similarity of the 1,1-dicyanomethylidene functional groups in **CS1**, **CS2** and **CS3** prompted us to investigate if they also can react with cyanide to bring about possible optical and fluorescent changes. The (2-)carbon vicinal of the two cyanogroups 1,1-dicyanomethylidene moiety is electrophilic, and thus susceptible to nucleophile's attacks. A simple visual

using THF (good solvent) and water (poor solvent) in different proportions. The results were summarised in Figure 2c. TPE-FLN and TPE-AQN were emissive in pure THF solvent with a relative quantum yield of 0.12 and 0.02, respectively. Their emission intensities, however, drop drastically when proportion of water was increased slightly from 0% to 10%. This is attributed to twisted intramolecular charge transfer (TICT), where free TPE-FLN and TPE-AQN molecules adopted an even more twisted structure to acclimatize to the slight increase in solvent polarity, hence effectively quenching fluorescence. Such TICT phenomena is rather typical for many reported donor-acceptor based AIE and aggregationenhanced emission (AEE) luminogens.¹⁶ Aggregation occurred when the proportion of water was increased beyond 70% where the enhancement of fluorescence intensities prevailed and AIE effect attributed to triphenylethylenylfunctionalization prevailed. The fluorescence intensities of **TPE-FLN** and **TPE-AQN**, were however, lower in the aggregated state as compared to in pure THF solutions, with relative quantum yields of 0.024 and 0.011 (in 90% water) respectively.

The AIE properties of the six compounds were investigated

Unlike TPE-FLN and TPE-AQN, TPE-BZP and CS3 are AIE active as shown in Figure 2c. Their solutions were non-emissive at a low water concentration but fluorescence intensified as proportion of water increased beyond 70%. The relative quantum yields of TPE-BZP and CS3 at the aggregated states (90% water) were 0.11 and 0.03, respectively. The lack of TICT properties for the two compounds is attributed to the absence of a centre planar acceptor moiety, which is otherwise present for TPE-FLN and TPE-AQN. AIE active CS2 remains nonemissive until in the aggregated state (90% water), a very weak emission band peaking around 629 nm emerged. (ESI Fig. S6) The quantum yield, however, is too low to meaningfully determine. Like TPE-FLN, TPE-AQN, TPE-BZP and CS3, CS2 exhibit fluorescence in thin film solid state (ESI Fig. S2). On the other hand. CS1 is non-emissive in solution, aggregated and solid thin film state.

Density Functional Theory (DFT) Calculations

Time-dependent density functional theory (TD-DFT) calculations (Gaussian 09, at B3LYP/6-31G(d,p) level)¹⁷ were performed on the six compounds synthesized and the HOMO and LUMO energy levels are charted in Figure 3 together with the respective molecular orbital amplitude plots. Of the three carbonyl-group containing compounds, TPE-AQN has the lowest LUMO energy level of -2.602 eV while TPE-BZP has the highest LUMO energy level of -1.852 eV, well reflecting the electron withdrawing strength of the centre acceptor groups. The conversion of the carbonyl groups of TPE-FLN, TPE-AQN and TPE-BZP into 1,1-dicyanomethylidene groups resulted in a slight lowering of HOMO and a larger extent lowering of LUMO energy levels across the board for CS1, CS2 and CS3, and hence a narrowing of HOMO-LUMO gap, which is consistent with the increase in electron withdrawing ability of the acceptors.

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Figure 4. Absorption profiles of (a) CS1, (b) CS2 and (c) CS3 solutions (in THF) in incremental addition of cyanide. Insert are photos depicting colour changes of CS1, CS2 and CS3 solutions (0.5mM) after addition of the stipulated amount of cyanide shown.

selectivity test with common anions OH⁻, F⁻, Cl⁻, Br⁻, I⁻, S²⁻, SO₃²⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻ and CN⁻ shows that all three compounds **CS1**, **CS2** and **CS3** are generally responsive towards CN⁻, bringing about spontaneous colour changes in the respective solutions (ESI Fig. S16). Interestingly, of the three compounds, **CS2** shows reactivity towards OH⁻, F⁻, S²⁻ and PO₄³⁻ anions, whereas **CS1** shows reactivity towards S²⁻. The relatively poor selectivity of **CS2** towards CN⁻ could be due to the steric hindrance about the C=C bond in the twisted butterfly structure of TCNAQ moiety upon undergoing nucleophilic reaction. **CS3** appears to exhibit the best selectivity towards CN⁻ as evidenced by the fact that it is non-unreactive towards other anions.

Spectrophotometric titrations of CS1, CS2 and CS3 solutions in THF with cyanide were performed. The changes in absorption profile of the three compounds were as shown in Figure 4. Reaction with cyanide anions resulted in the weak charge transfer absorption band of CS1 at 562 nm to gradually decrease, as well as the slight decrease and red-shifting of the 333 nm absorption band. Subsequently, a decolourisation of the purple CS1 solution was observed. Likewise, the reaction between cyanide anions and CS3 resulted in gradual collapse of the 386nm absorption band and the emergence of two more defined absorption bands peaking at 242 and 311 nm. Decolourisation of the yellow CS3 solution was observed (Figure 4c). As CS2 contains two 1,1-dicyanomethylidene groups, it is expected that it reacts with two molar equivalence of cyanide anions. The addition of cyanide caused a gradual collapse of the 443 and 335 nm absorption peaks and an emergence of new absorption bands peaking at 308, 387 nm and more interestingly, 599 nm. This 599nm absorption band was calculated by TD-DFT to correspond to both the HOMO \rightarrow LUMO and HOMO-1 \rightarrow LUMO transitions of the mono-cyanated species (ESI Table S7). The colour of CS2 solution changed from orange to light green on reaction with cyanide but on standing for approximately 10 minutes, changed to a lighter shade of orange, indicating the instability and possible decomposition of the cyanated species. The findings from TD-DFT calculations (B3LYP/6-31G(d,p))¹⁶ performed on both cyanated and un-cyanated form of CS1, CS2 and CS3 supports the experimental results (ESI Fig. S15).

Monitoring the changes in absorption intensities at 562, 599 and 385 nm for **CS1**, **CS2** and **CS3**, the limit of detection was determined to be 24.5, 1.70 and 5.07 μ M respectively (ESI Fig. S18).

AIE Properties of Cyanated Solutions

The presence of AIE-active TPE units pushed us to examine the AIE properties of cyanated **CS1** – **CS3** solutions. The respective fluorescence spectra were measured by diluting 0.1 mM cyanated **CS1** – **CS3** solutions tenfold with water and THF. (ESI Fig. S19 – S21). More than one fluorescent compounds were present for each of the cyanated **CS1** – **CS3** solutions which was confirmed by TLC analysis. Both cyanated solutions of **CS1** and **CS3** appear to contain an orange-emitting species with ACQ nature, and an AIE-active blue-emitting species with emission maxima at 484 and 480 nm, respectively (ESI Fig S19, S21). TLC analysis of cyanated solutions of **CS2** showed the presence of multiple fluorescent species. The red fluorescence emitted by dilute cyanated **CS2** in THF was gradually quenched upon addition of water, but it emerged weakly again when water approached to 80%.

Next, 0.1 mM solutions of **CS1** – **CS3** in THF were reacted with an incremental amount of cyanide before diluting tenfold with water and the corresponding changes to the emission profile were monitored (ESI Fig. S23). Emissions at 485 and 480 nm were observed to intensify for **CS1** and **CS3** solutions, respectively, on being exposed to an increasing concentration of cyanide, due to the formation of AIE-active cyanated species. Monitoring the increase of these emission peaks, the limit of cyanide detection for **CS1** and **CS3** determined from this spectrofluorometric titration studies were 9.27 and 8.81 μ M, respectively. Cyanated species of **CS2** were previously shown to be weakly fluorescent in the aggregated state with no distinctive emission peaks formed (ESI Fig. 20). Hence, it would not be meaningful to derive the LOD from the spectrofluorometric studies performed.

Mechanism of Sensing and Isolation of Cyanated Products

As previously mentioned, the 1,1-dicyanomethylidene groups in compounds CS1 - CS3 are susceptible to be attacked by

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Scheme 2. Proposed mechanism of cyanide sensing by CS1, CS2 and CS3 via nucleophilic addition, and structures of the corresponding cyanated species.



Figure 5. (a) Normalised absorption and emission spectra of CS1-CN and CS3-CN; (b) Fluorescence intensity of emission peaks (480 and 475 nm, respectively) of CS1-CN and CS3-CN solutions measured in different proportions of THF and water (10 μ M). Insert are photos of the solutions taken under UV irradiation (365nm).

nucleophiles, such as cyanide. The nucleophilic addition of cyanide onto the three compounds, as shown in **Scheme 2** would effectively break off direct conjugation between the two electron-withdrawing cyano- groups and the electron-richer rest of the molecules, hence resulting in corresponding changes to the optical properties observed. This explained how charge transfer absorption bands of the three compounds collapsed on the addition of cyanide as shown in **Figure 4**.

It was thus proposed that nucleophilic addition of cyanide at the 1,1-dicyanomethylidene groups of the three compounds resulted in the formation of anionic species as shown in **Scheme 2**. However, it appears that these anionic species readily undergo protonation. The protonated species **CS1-CN** and **CS3-CN** could be detected on TLC and they were even isolated by column chromatography from freshly cyanated solutions of **CS1** and **CS3** at 90% and 39% yield, respectively. However, **CS2-CN** was not isolatable *via* column chromatography but its presence was detectable by high resolution mass spectrometry (HR-APCI-MS) (ESI, Fig. S22). Dicyanated **CS2-2CN** may exist theoretically, but it could not be detected by HR-APCI-MS, hence raising the doubt if a second cyanation would have taken place.

The identity of isolated cyanated species CS1-CN and CS3-CN were confirmed by ¹H and ¹³C NMR, as well as high-resolution mass spectrometry characterization. The singlet peak at 3.58 and 4.55 ppm on the ¹H NMR spectra of CS1-CN and CS3-CN, respectively, indicates the protonation on the anionic cyanated species. Optical properties of the two isolated compounds were measured and their AIE properties was investigated. The results were shown in Figure 5. The absorption peaks for compounds CS1-CN and CS3-CN were 365 and 313 nm, with molar extinction coefficient values of 29,040 and 24,560 cm ¹M⁻¹, respectively. The comparatively red-shifted absorption wavelength for CS1-CN was due to greater extent of conjugation within the triphenylethylenyl- functionalised fluorene moiety, whereas CS3-CN can be regarded as two separate TPE units. Absorption profiles of these two compounds were consistent with findings from Figure 4. The two compounds were very weakly emissive in pure THF with relative quantum yield of 0.003 and 0.0031, respectively.

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However, on aggregation at high proportions of water in THF/water mixtures, the two compounds emit blue bright fluorescence. The relative quantum yield for CS1-CN and CS3-CN aggregates in 90% water were 0.22 and 0.21, respectively. The orange emissions with ACQ nature observed for CS3-CN solutions from 0% to 60% water could arise from the slight decomposition of the product. It is however, not conclusive to determine if the orange-emitting ACQ species observed in the cyanated solutions of CS1-CN and CS3-CN. There were no previous reports of isolation and AIE investigations of similar anionic species, and neither were there previous reports of isolation and characterization of protonated species similar to CS1-CN and CS3-CN, to the best of our knowledge.

Cyanide Detection in Solution and via Paper Probes

Paper probes were developed to demonstrate the possibilities of cyanide detection by compounds **CS1** – **CS3** in the solid state. 4 cm-sized Whatman[®] filter paper was separately soaked in 1mM solutions of compounds **CS1** – **CS3** for a minute and then air-dried. When observed under UV irradiation at a wavelength of 365 nm, **CS1**-coated paper probes appeared non-emissive, **CS2**-coated paper probe emits weak red fluorescence, and **CS3**-coated paper probe bright yellow fluorescence. Aqueous cyanide solutions with different concentrations were then applied onto the paper probes *via* capillary tubes, and water blank was used as reference for comparison. The paper probes were briefly air-dried before visually observing under the UV lamp (365 nm), as shown in **Figure 6**.

The probes were all reactive to cyanide given fluorescence changes were observed for all three paper probes on application of cyanide. No significant fluorescence changes were observed when water was applied as a blank. For the CS1-coated paper probe, fluorescence turn-on was observed, which is attributed to the formation of AIE species CS1-CN as discussed in the previous section. The turn-on emission colour (of yellow, instead of blue), could have been influenced by the formation of orange-emitting side product. Likewise, applying cyanide onto the CS2-coated paper probe caused it to emit yellow fluorescence but weakly. Interestingly, application of cvanide onto the CS3-coated paper probe mainly led to a "turn-off" of fluorescence, accompanying with very weak blue emission caused by the formation of AIE species CS3-CN. Overall, the CS3-coated paper probe exhibited delicate detection of cyanide.

Conclusions

Six triphenylethylenyl-based donor–acceptor–donor (D-A-D) molecules **TPE-FLN**, **TPE-AQN** and **TPE-BZP** containing 9-fluorenone, 9,10-anthraquinone and benzophenone moieties as acceptors, respectively, and their derivatives **CS1**, **CS2** and

CS3, with 1,1-dicyanomethylidene functional groups converted through Knoevenagel condensation from their respective ketones were synthesized. We've demonstrated that slight modifications in molecular structures resulted in vast differences in absorption, emission and AIF properties in such a push-pull-push system. In addition, single crystal X-ray structures of the six compounds provide information on how structural and functional group differences affect the overall chemical structure and packing, as well as in turn affect their optical properties. DFT calculations were also performed to support these experimental findings. CS1 - CS3 were found to be reactive and selective to cyanide. The anionic cyanated form of CS1 and CS3 were found to undergo protonation readily, and cyanated species CS1-CN and CS3-CN, respectively, could even be isolated and were confirmed to be AIE-active. Paper probes developed from the three dicyanomethylidene-modified compounds CS1 - CS3 provide fast and convenient detection of cyanide in aqueous samples in terms of visible fluorescence changes, of which fluorescence turn-on effect of CS1 was the most desirable, although the detection limit still needs further improvement. The results derived from this work particularly on the mechanism of the formation of cyanated intermediates, protonation of these intermediates as well as their optical behaviours and AIE properties at the aggregate state would be useful for us to design better and more sensitive TPE-based AIE-active materials for detection of toxic substances such as cyanide.

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Notes and references

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Figure 6. Photos of paper probes with aqueous cyanide solutions of different concentrations (indicated above the spot of application) applied, taken under UV irradiation (365nm). Due to non-fluorescence of CS1, white dotted lines were added to mark out the circumference of CS1-coated paper probe. Water was used as a blank.

- Crystallographic data and CCDC Number: Compound TPE-FLN (CCDC No.: 1573521)
 Compound TPE-AQN (CCDC No.: 1573522)
 Compound TPE-BZP (CCDC No.: 1573523)
 Compound CS1 (CCDC No.: 1573518)
 Compound CS2 (CCDC No.: 1573519)
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Triphenylethylenyl–Based Donor–Acceptor–Donor Molecules: Structural and Optical Properties Studies, and AIE Properties for Cyanide Detection

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Triphenylethylenyl–based donor–acceptor–donor molecules are synthesized and they exhibit strong response to cyanide ions.