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Graphical Abstract

Triptycene scaffolds: Synthesis and properties of triptycene-derived Schiff base compounds for the selective and sensitive detection of CN^- and Cu^{2+}

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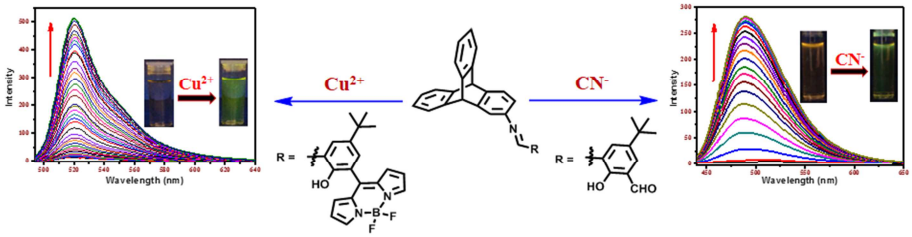

Manuscript for *Tetrahedron*

Triptycene scaffolds: Synthesis and properties of triptycene-derived Schiff base compounds for the selective and sensitive detection of CN^- and Cu^{2+}

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A series of triptycene-derived Schiff bases were synthesized by condensation between amino triptycenes with an appropriate aldehyde and were isolated in good to excellent (85-90 %) yields. Amongst these, a triptycene-hydroxybenzaldehyde Schiff base compound proved to be a selective sensor for cyanide. It exhibited a "turn-on" fluorescence response at 490 nm to CN^- facilitated by the nucleophilic addition of CN^- to the aldehyde group, accompanied by a visible color change from orange to yellow. Likewise, a triptycene salicylaldehyde adduct was shown to be highly sensitive towards the detection of the CN^- ion with a detection limit of 0.9 µM. On the other hand a triptycene-BODIPY Schiff base compound could be used for the detection of Cu^{2+} ions over other competing, biologically relevant metal ions in acetonitrile. Photophysical studies revealed a 1:1 binding model for the triptycene-BODIPY compound.

Key words: Triptycene; Schiff base; Sensor; Cyanide; Copper ions

1. Introduction

Triptycene **1**, as the first representative of the iptycene family,[1] has been known since the early 1940s[2] and is the parent compound in this unique family of homoconjugated aromatic compounds with D_{3h} symmetry. The three-dimensional rigid framework offers a void space in the clefts between the rings to create a well-defined spatial arrangement and substantial internal free volume (IFV).[3] The arene subunits of triptycene are amenable to further functionalization and it has found use in a wide range of applications such as in electron transfer systems,[4] anti-cancer,[5] sensing,[6] molecular machines,[7] material and polymer science,[6a,7c,8] in host–guest chemistry[6,9] or as building blocks for functional and supramolecular systems.[10]

Our long term interest in this area is to use the triptycene scaffold for the presentation of multiple and different functional units to prepare multi-modal systems which may find use in sensing and theranostics. After reporting on triptycene dye systems[4b,9d,10b] and recently on organometallic hexafunctionalization reactions for triptycene[10c] we have now turned our attention to simple sensing systems prior to the investigation of unsymmetrical triptycenes with multiple and diverse binding and reporting units (Fig. 1).

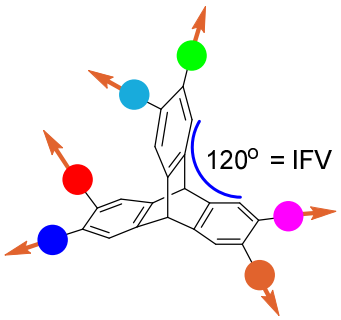


Figure 1. Illustration of unsymmetrically substituted triptycenes with different effector units.

We were interested in Schiff-base derivatives, which have been used for a long time for the formation of various (metal) complexes or as bidendate ligands.[11,12] For initial studies we chose mono- and trifunctionalized Schiff base targets of triptycene as these might be more easily accessible from available triptycene amino precursor compounds. As coupling partner we used commercially available salicylaldehyde/salicyldialdehyde and fluorescent molecules having hydroxyl groups suitable for sensing applications.

As possible analytes for sensing evaluations we chose cyanide and copper(II). Cyanide is one of the most toxic anions deleterious to human health and the environment and has both natural and anthropogenic origin. It still finds use in many products and processes. Examples are resins, fibers, dyes, gold extraction and precious metal mining and plating, plastics and fertilizer plants. It is also used as a chelating ligand for pharmaceuticals and new sensors thereof are actively sought after.[13] Copper is an essential metal ion for humans and is involved in various physiological reactions such as the formation of hemoglobin and iron utilization. Copper deficiency can increase the risk of developing coronary heart disease, while excess copper can promote the production of

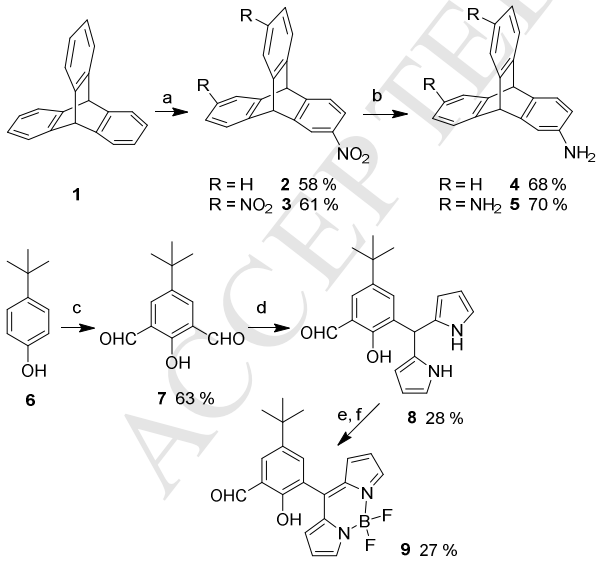
harmful reactive oxygen species and is implicated in oxidative stress and neurodegenerative disorders.[14]

Although many CN^- and Cu^{2+}[15] selective sensors have been reported only a few studies describe "turn-on" fluorescent sensors,[16,17] rather than those quenching fluorescence. In the following we outline that a combination of salicylaldehyde or salicyldialdehyde[18] or BODIPY[19] (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) units with the triptycene scaffold gives triptycene-derived Schiff base compounds which selectively turn on fluorescence as sensors towards cyanide and copper(II) ions. Analyte binding was accompanied by changes in the NMR and absorption spectra and visual color changes, too.

2. Results and Discussion

2.1. Synthesis of triptycene Schiff bases

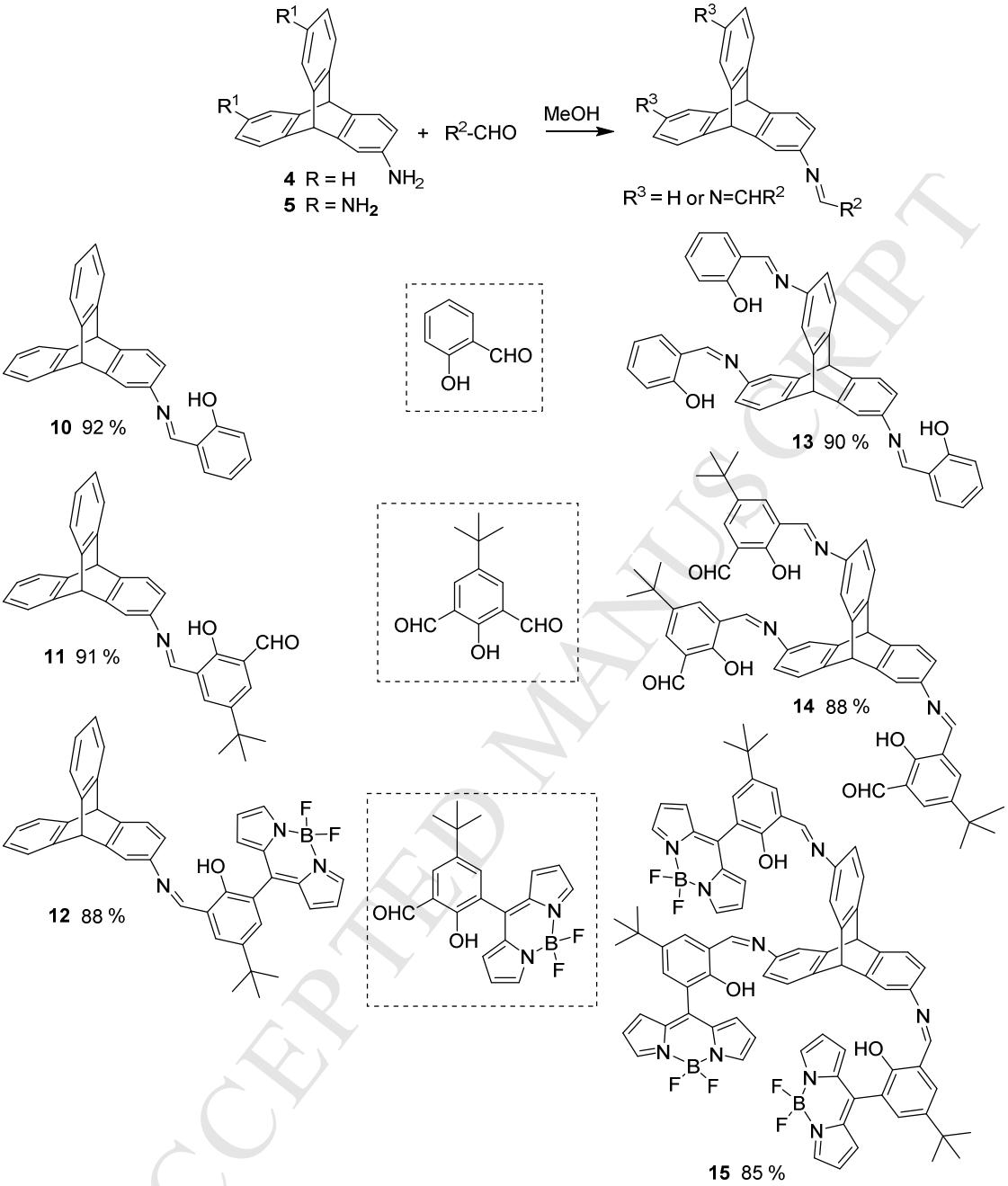
The essential starting materials of 2-aminotriptycene **4**,[20] 2,6,14-triaminotriptycene **5**[21] and meso-salicylaldehyde substituted BODIPY **9**,[22] were synthesized over a series of sequential steps from commercially available triptycene **1** and 4-*tert*-butylphenol **6** according to procedures previously reported (Scheme 1). First, triptycene was treated with a mixture of nitric acid and glacial acetic acid under reflux conditions to give mononitrotriptycene **2** in 58 % yield, while longer reaction times afforded the three-fold functionalized 2,6,14-trinitrotriptycene **3** in 61 % yield. The mononitro **2** and trinitro **3** derivatives were reduced by Raney-Ni in the presence of hydrazine to yield the corresponding monoaminotriptycene **4** and triaminotriptycene **5** in 68 % and 70 % yields, respectively.



Scheme 1. Synthesis of triptycene and BODIPY monomers **7**-**13**. Reagents and conditions: a) Conc. HNO_3, CH_3COOH, 75 °C, 24h; b) Raney-Ni, $NH_2NH_2{\bullet}H_2O$, THF, rt; c) hexamine, TFA, rt; d) pyrrole, $BF_3{\bullet}OEt_2$, rt; e) DDQ, CH_2Cl_2; f) Et_3N, $BF_3{\bullet}OEt_2$, rt.

On the other hand, treatment of 4-*tert*-butylphenol **6** with hexamine in the presence of trifluoroacetic acid gave 5-*tert*-butyl-2-hydroxyisophthalaldehyde **7** in good yield. Subsequently, 5-salicylaldehyde substituted BODIPY **9** was prepared by reaction of 5-*tert*-butyl-2-hydroxyisophthalaldehyde **7** with an excess of pyrrole in the presence of catalytic amounts of BF_3•OEt_2 in dichloromethane to afford dipyrromethane **8**. This in turn was further oxidized with DDQ and neutralized with triethylamine, followed by complexation with BF_3•OEt_2 to yield the salicylaldehyde substituted BODIPY **9** as an orange solid in 27 % yield.

Afterwards, two series of target compounds were prepared (Scheme 2). The synthesis of the triptycene-derived Schiff base compounds **10**-**15** was achieved by using aminotriptycene (**4**/**5**) with an appropriate aldehyde in methanol. The reaction of amino triptycene (**4**/**5**) with salicylaldehyde was performed at room temperature for 12 h to give a precipitate of the required compounds **10** and **13** in 92 % and 90 % yields, respectively. Under the same reaction conditions, treatment of aminotriptycene (**4**/**5**) with either 5-*tert*-butyl-2-hydroxyisophthalaldehyde **7** or *meso*-salicylaldehyde substituted BODIPY **9** gave no products. However, addition of 3 mol-% TFA and heating the reaction mixture for 12 h resulted in product precipitation from the reaction medium and the target compounds **10**-**15** were isolated in yields of 85-91 %.



Scheme 2. Synthesis of triptycene-derived Schiff base compounds **10**-**15**.

The identity and purity of the new compounds was established by FT-IR, ^{1}H, ^{1}H-^{1}H COSY and ^{13}C NMR spectroscopy as well as high resolution mass spectrometry analysis. In the FT-IR spectra, characteristic stretching bands between 1603 to 1610 cm^{-1} were identified for the imine bond of the triptycene Schiff base compounds **10**-**15** and a band around 1680 cm^{-1} corresponded to the salicylaldehyde moiety of compounds **11**, **14** and was not observed for the other compounds. Similarly, the ^{1}H NMR gave characteristic signals. Taking the ^{1}H NMR spectrum of compound **12** as an example (Fig. S10 in

Supporting Information (SI)), a broad signal of the hydroxyl proton appears at 13.80 ppm and the imine (-CH=N) proton appears as a singlet at 8.68 ppm. The BODIPY unit in compound **12** containing six pyrrole protons appears as three sets of signals at δ = 7.91 (s), 6.91(d) and 6.50 (dd) ppm. The other signals at δ = 7.51 to 7.01 ppm can be assigned as the aromatic protons of the triptycene and BODIPY units and the bridgehead protons of triptycene appear as two singlet resonances at 5.45 and 5.44 ppm while the *tert*-butyl group could be identified as a singlet at 1.37 ppm. In the ^{13}C NMR spectrum of compound **12**, the resonance of the imine carbon nucleus signal is located at 162.6 ppm and the bridgehead carbon nuclei give signals at 54.3 and 53.8 ppm. In addition, compound **12** with a BODIPY unit exhibited two sets of octets at -143 and -147 ppm in the ^{19}F NMR spectrum (Fig. S14 in SI). This can be attributed to the presence of two non-equivalent fluorine atoms in the BODIPY moiety, each fluorine coupled with boron to give a quartet, which is further coupled with non-equivalent fluorine[23] and appeared as an octet. The ^{11}B NMR spectrum of compound **12** showed a typical triplet at 0.3 ppm (Fig. S13 in SI).

2.2. Photophysical and electrochemical properties

The target compounds **10**-**15** were characterized further by absorption and emission spectroscopy. For compounds **12** and **13** data were obtained in six different solvents of varying polarity (see Fig. S43-S46 in SI), while a comparison of normalized absorption and emission spectra of compounds **12**, **13**, **14** and **15** is presented in Figure 2. The absorption spectra of compounds **13** and **15**, which contain BODIPY units, show a characteristic strong absorption band corresponding to the $S_0 \rightarrow S_1$ transition at 500 nm along with one vibronic component on the lower wavelength side as a shoulder at 475 nm. Furthermore, an ill-defined band in the 300-400 nm range corresponding to an $S_0 \rightarrow S_2$ transition is also observed, similar to other meso-aryl BODIPYs. Both compounds exhibit very weak fluorescence compared to the individual BODIPY unit **9** (Φ=0.136) with a quantum yield of Φ=0.004 for compound **13** and Φ=0.003 for compound **15**. This is due to a photo-induced electron transfer (PET) from the triptycene moiety to the BODIPY unit causing an effective quenching of fluorescence.

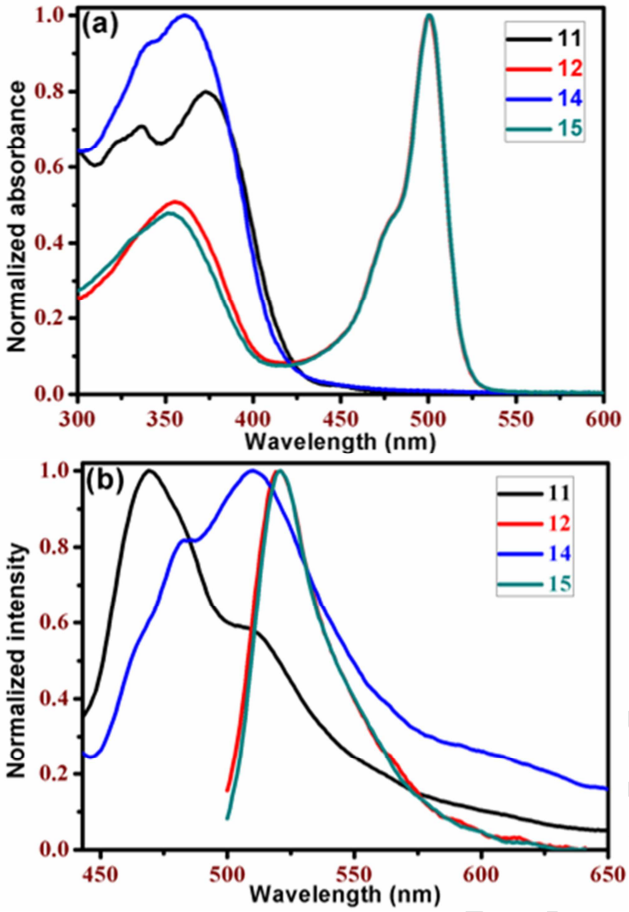


Figure 2. Comparison of normalized absorption (a) and emission (b) spectra of compounds **11**, **12**, **14** and **15** recorded (λ_{ex}=380 nm for **11**, **14** and λ_{ex}=488 nm for **12**, **15**) in $CHCl_3$.

The redox potentials of compounds **12** and **15** were measured in chloroform by using cyclic voltammetry at a scan rate of 100 mV s^{-1} with tetrabutylammonium perchlorate as the supporting electrolyte. The electrochemical redox behavior of compounds **3** and **6** was similar to that observed for salicylaldehyde substituted BODIPY **13**. Thus, the cyclic voltammograms of the salicylaldehyde substituted BODIPY **9**[22b] showed one reversible reduction at -0.58 V, whereas the triptycene Schiff base compounds **12** and **15** exhibited one reversible reduction at -0.846 V and -0.843 V, respectively. The reduction peak of both triptycene Schiff base compounds **12** and **15** occurred at more negative potentials relative to that found for meso-aryl BODIPY derivatives. The anodic shift in reduction potential was more pronounced (270 mV) than for BODIPY **13**. This indicates that the triptycene Schiff base compounds **3** and **6** are more difficult to reduce compared to salicylaldehyde substituted BODIPY **13** (see Fig. S47-S48).

2.3. Anion sensing studies

The chemodosimetric approach[22b] involves the use of a specific chemical reaction initiated by the analyte coupled to a color or spectral variation. In our case, the aldehyde

group can be converted irreversibly into a cyanohydrin group *via* nucleophilic addition of cyanide. Therefore, compounds **11** and **14** are potential chemodosimetric sensors for the presence of CN^- by monitoring the absorption, emission and/or NMR spectral changes. First, we investigated color changes of compound **11** upon addition of different anions. Compound **11** was weakly fluorescent under UV light, however, upon addition of cyanide its fluorescence (UV lamp) was enhanced significantly to green and a color change from orange to yellow was observable by naked eye, too (Fig. 3). In contrast, addition of various other anions, such as F^-, Cl^-, Br^-, I^-, AcO^-, ClO_4^-, $H_2PO_4^-$, HSO_4^- (used as their tetrabutylammonium salts) did not result in a color change. This indicated that compound **11** has the potential to act as a selective turn-on chemodosimeter for CN^- ions.

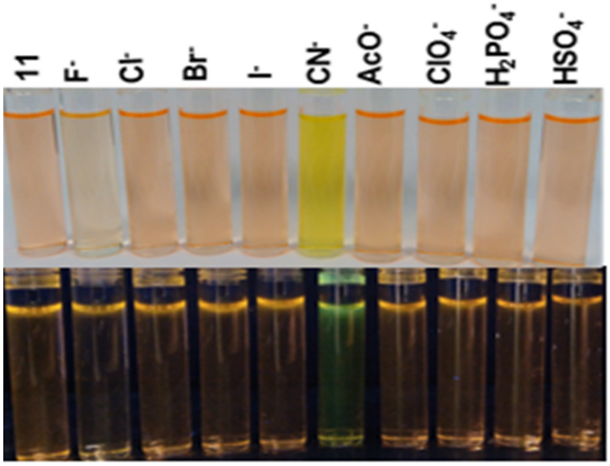


Figure 3. Changes in the color of **11**(10 µM) upon addition of 10 equiv. of different anions in acetonitrile. Top: naked-eye; bottom: excitation at 360 nm.

This prompted further investigations into the selectivity of compound **11** for CN^- using various spectrophotometric techniques. Fig. 4a shows the absorption spectra of **11** (10 µM) upon addition of different anions in CH_3CN. Only in the presence of CN^- is a red shift of about 100 nm compared to the original compound **11** observed. Additionally, the fluorescence emission spectrum of compound **11** was found to be considerably altered in the presence of CN^- (Fig. 4b). Note, that the emission maxima remained unchanged in the presence of other anions.

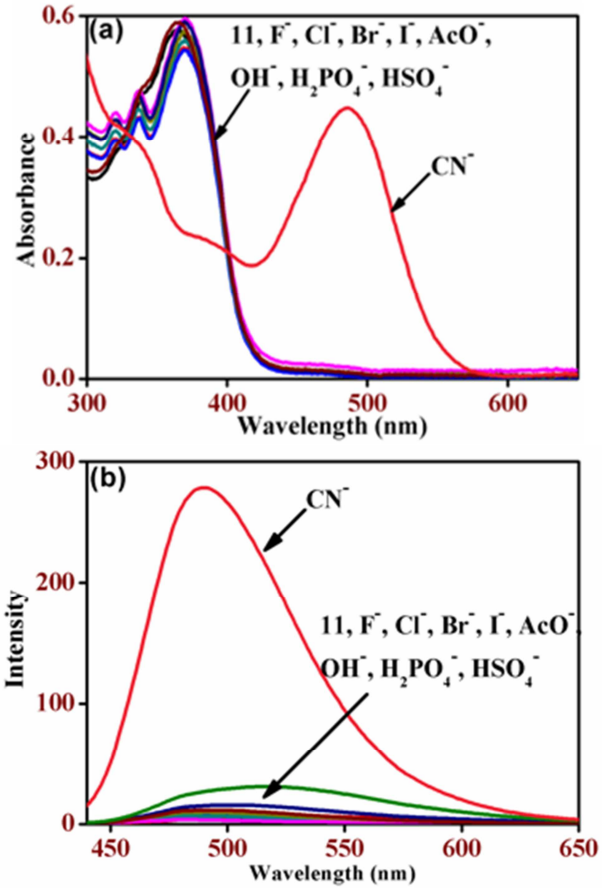


Figure 4. Changes in (a) absorption and (b) emission of compound **11** (10 μM) upon addition of various anions (20 equiv.) in acetonitrile (λ_{ex}=380 nm).

Next, we studied the specific detection of CN^- by compound **11** by following the concentration dependent changes in the absorption and fluorescence spectra (Fig. 5). Changes in the absorption spectra of compound **11** upon addition of increasing amounts of CN^- ion in CH_3CN are shown in Fig. 5a. With increasing amounts of cyanide, the intensity of the absorption band at 374 nm decreased accompanied by the appearance and concomitant increase of a new absorption band at 480 nm with a clear isosbestic point at 407 nm indicating the binding of CN^- ion to compound **11**. Further evidence is derived from the ratiometric plot, which shows the changes in the absorption bands at 374 nm and 485 nm *versus* the concentration of cyanide. The sigmoidal nature clearly indicates analyte binding (inset in Fig. 5a).

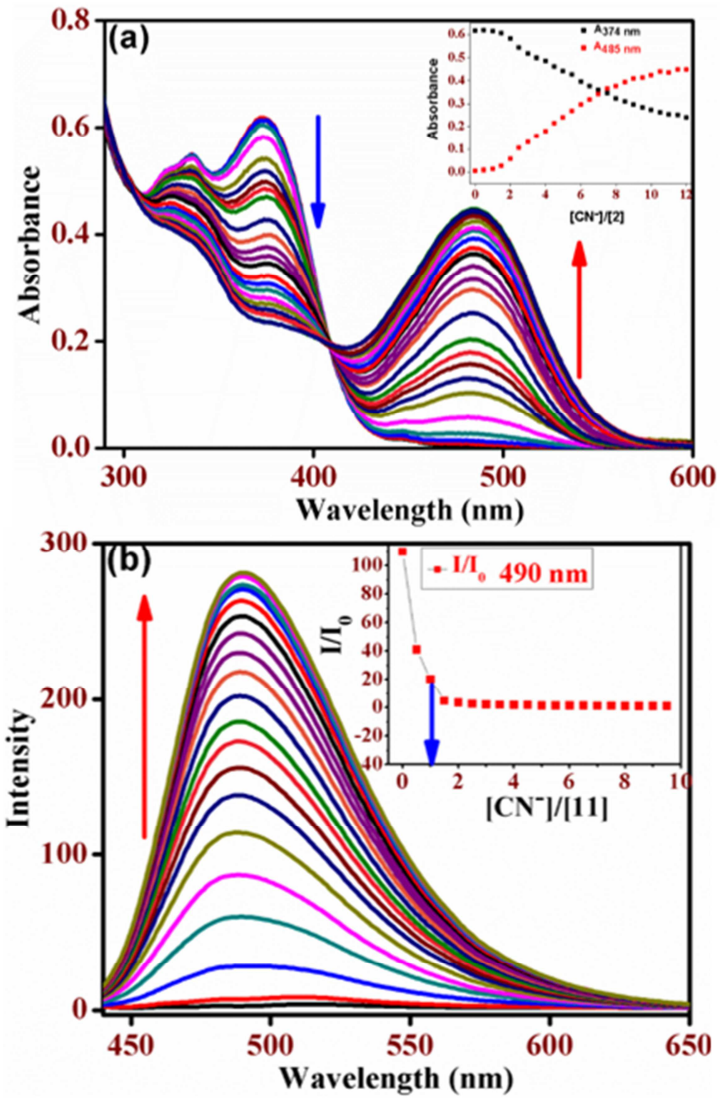


Figure 5. Changes in (a) absorption, (b) fluorescence spectra of compound **11** (10 µM) upon titration with CN^- (0 to 12 equiv.) in acetonitrile (λ_{ex}=380 nm). Insets show: (a) plot of absorbance *vs* [CN^-]/[**11**] molar ratio for absorbance at 374 and 485 nm, respectively; (b) plot of relative intensity maxima at 490 nm as a function of [CN^-]/[**11**] molar ratio.

Cyanide sensing was investigated using fluorescence studies (Fig 5b). With increasing amounts of CN^- ions the fluorescence spectra of the sensor displayed a continuous enhancement of the emission intensity of the band at 490 nm. Based on the Stern-Volmer equation,[24] the binding constant (K) for the binding of cyanide to compound **11** was determined as 7.41 (±0.32) × 10^5 M^{-1} (Fig. S51). The Job's plot analysis of the CN^- ion titration with compound **11** also corroborated a 1:1 binding stoichiometry (Fig. S52). The sensitivity of compound **11** for the CN^- ion was further evaluated in fluorescence titration profiles, which demonstrated that compound **11** has a detection limit of 0.9 × 10^{-6} M for the CN^- anion, which is lower than the WHO guideline of 1.9 µM cyanide (Fig. S53).[25]

To further explore the utility of compound **11** towards CN^-, we carried out competition experiments. Compound **11** (10 µM) was treated with 12 equiv. CN^- in the presence of different background anions (50 equiv.). All tested background anions showed small or no interference with the detection of cyanide (Figure S64 in SI) indicating that **11** could be used as a potential CN^- selective turn-on fluorescent sensor. Similar observations were made in the case of the three-fold functionalized triptycene **14**; full details are given in the supporting information (Fig. S54-S55).

To gain further insight into the structural aspects of compound **11** upon binding with CN^- a ^1H NMR titration in CD_3CN was performed (Fig. 6). In native form compound **11** exhibited three singlet signals (a, b, c) at 10.57, 8.65 and 13.80 ppm, respectively. Upon addition of one equiv. of CN^- ion to the solution the signal corresponding to the aldehyde proton at 10.57 ppm disappeared and a new signal appeared at 4.49 ppm. This signal corresponds to the formation of the cyanohydrin which was further confirmed by LC-mass spectrometry. Here, a molecular ion peak was found at *m/z* = 483.3128 which corresponds to the cyanohydrin form {**11**.CN^-} (Fig. S56).

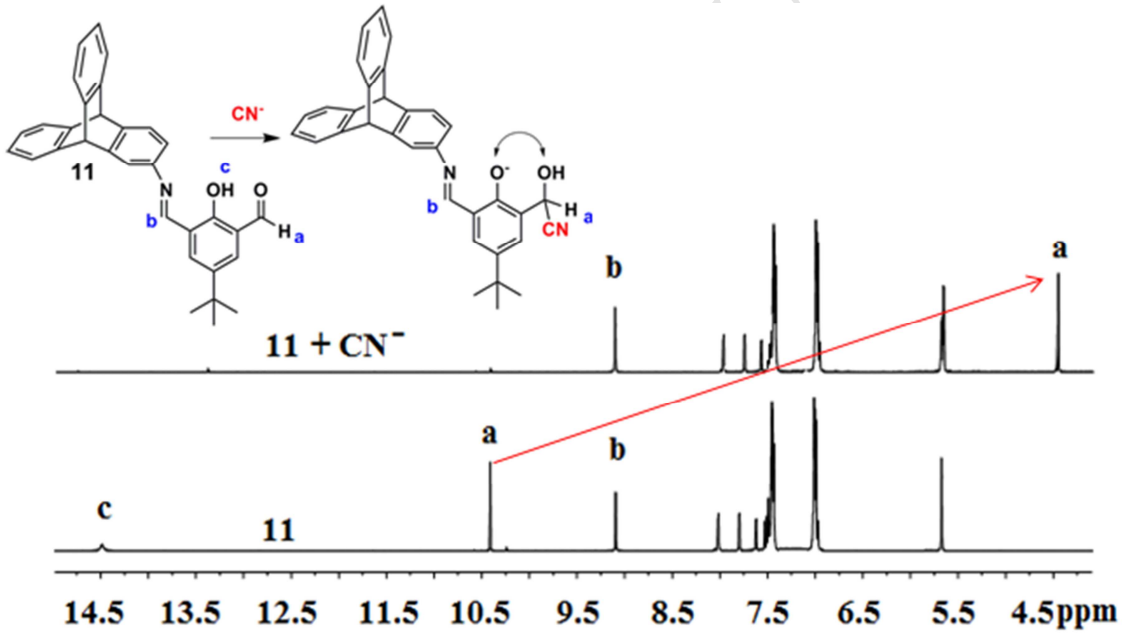


Figure 6. Partial ^1H NMR spectra of compound **11** (3.64×10^{-2} M) alone and with one equivalent of cyanide in CD_3CN.

2.4. Metal ion sensing studies

Compounds **12** and **15** contain different binding sites and can easily form the complexes with different metal ions, which can be monitored by absorption and fluorescence techniques. To test the metal ion sensing property of compound **12** spectroscopic studies with different metal ions such as Na^+, K^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} (as their perchlorate salts) in CH_3CN were conducted. In all experiments using compound **12** (10 µM) with these metal ions, only Cu^{2+} affected the absorption and fluorescence spectra in a significant manner (Fig 7a and

7b). As evidenced in Fig. 7c increasing the concentrations of Cu^{2+} (0 to 10 equiv.) is accompanied by an increase in the absorbance at 415 nm and a decrease in the 350 nm and 500 nm bands with four clear isosbestic points at 313, 375, 487 and 510 nm. This clearly indicates conversion of free compound **12** to its Cu^{2+} bound species with nitrogen and oxygen donor atoms.

In order to further investigate the selective binding of Cu^{2+} ions to compound **12** fluorescence spectra (10 µM) in the presence of the above mentioned metal perchlorates were recorded (Fig 7d). Here incremental addition of Cu^{2+} ion to a solution of compound **12** (10 µM) led to significantly enhanced fluorescence at 520 nm, whereas addition of the other metal ions under identical conditions resulted in either no or significantly weaker changes in either fluorescence band or intensity. In order to establish the selectivity of compound **12** as a selective fluorescence probe for Cu^{2+} ion competitive fluorescence binding titration studies with other competing metal ions were performed. The initial fluorescence intensity of compound **12** did not change significantly upon mixing with excess equivalents of alternative metal cations (Figure S65 in SI). Taken together these data confirm that compound **12** acts as a selective chemodosimeter for detection of Cu^{2+} over other biologically relevant metal ions.

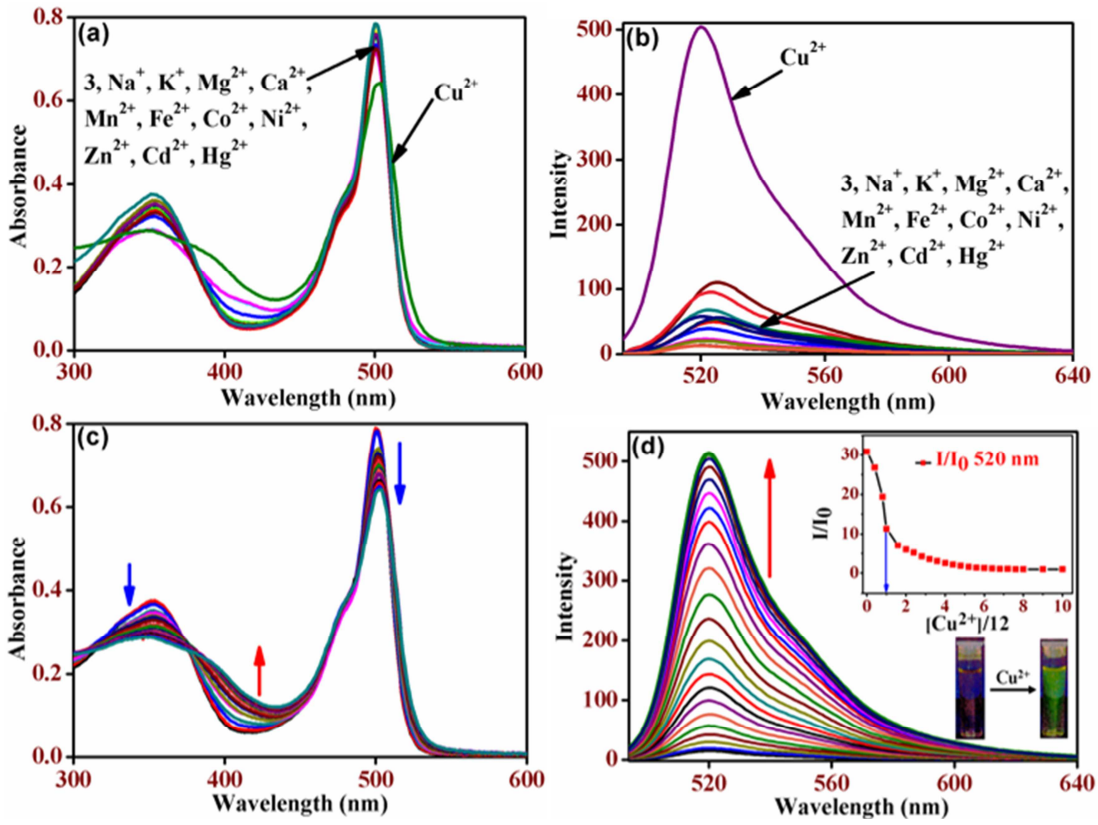


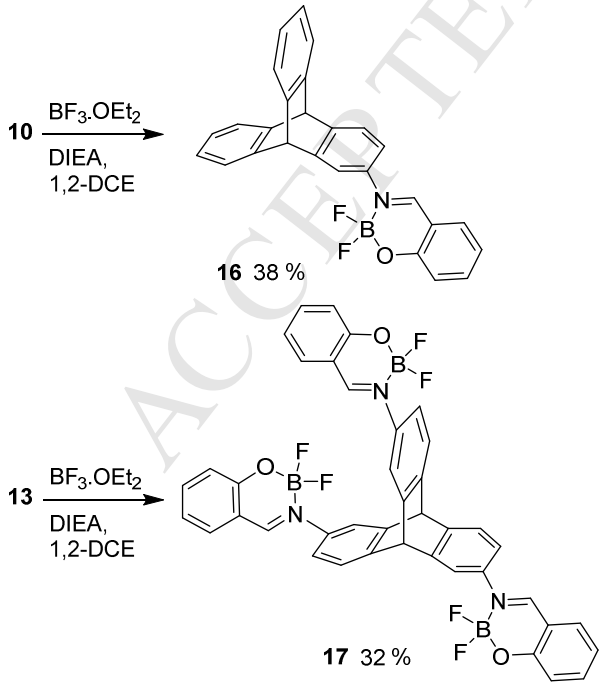
Figure 7. Changes in (a) absorption and (b) emission of compound **12** (10 µM) upon addition of various cations (50 equiv.) in acetonitrile. Systematic titration of compound **12** (10 µM) with Cu^{2+} (0 to 10 equiv.) in acetonitrile: (c) absorption spectra, (d) fluorescence spectra (λ_{ex}=488 nm). Inset (d) shows plot of relative intensity maxima at

520 nm as a function of [Cu^{2+}]/[**12**] molar ratio and the color change of compound **12** solution upon addition of Cu^{2+}.

A Job's plot based on the fluorescence data agrees well with a 1:1 complex (Fig. S58) and based on the Stern-Volmer equation, the binding constant (K) for the binding of Cu^{2+} to compound **12** was determined as 3.07 (±0.62) × 10^4 M^{-1} (Fig. S59). This value was within the range (10^3–10^{12}) of reported Cu^{2+} chemosensors. The sensing of Cu^{2+} by compound **12** is further demonstrated by observing the visual fluorescence under UV lamp illumination in the presence of different metal ions (Fig. S60). Similar results were obtained with compound **15** and are given in the supporting information (Fig. S62-S63).

2.5. Triptycene boranil complexes

Boron complexes of Schiff base compounds are yet another type of four-coordinate boron complex that has gained interest due to their greater stability than tri-coordinate boron compounds. E.g., Ziessel and co-workers reported the first synthesis and photophysical properties of boranil complexes.[12b] Later, Lee and co-workers reported boron complexes of stackable pseudo triphenylenes, which showed interesting enhanced fluorescence upon aggregation in solution.[12d] In view of the potential applications of these boranil complexes, we synthesized the triptycene-derived boranil complexes **16** and **17**. Compounds **10** and **13** were deprotonated by using base (DIEA) in dry 1,2-dichloroethane in an argon atmosphere, followed by reaction with excess amount of BF_3•OEt_2 to afford the boranil complexes **16** and **17** in moderate yields (Scheme 3). Boranil formation was evidenced by the disappearance of the signal for the phenolic proton at 13.80 ppm in the ^{1}H NMR spectrum of **16**. This was supported by the required signals in the ^{11}B (triplet at 0.8 ppm) and ^{19}F NMR (quartet at -133.9 ppm) spectra. Further evidence is provided in the Supporting Information as are data for compound **16**.



Scheme 3. Synthesis of boranil complexes **16** and **17**.

The absorption and emission profiles of both boranil complexes (**16** and **17**) were recorded in chloroform and are shown in Fig 8. Compounds **16** and **17** exhibit absorption maxima at 395 and 399 nm, respectively while the maximum absorption of the molecules showed fluorescence emission at 468 and 469 nm, respectively.

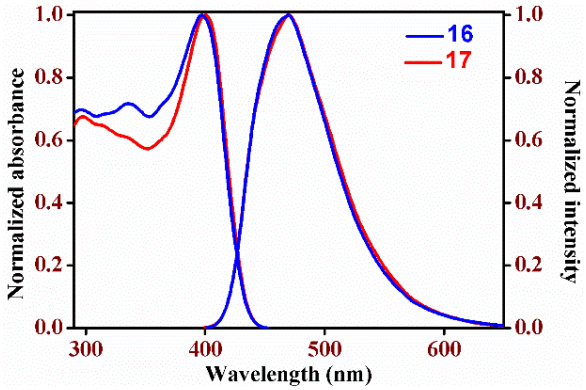


Figure 8. Comparison of normalized absorption and emission spectra of **16** (blue line) and **17** (red line) recorded in chloroform. The excitation wavelength was 400 nm.

3. Conclusions

In conclusion, we have synthesized a series of new triptycene-derived Schiff base compounds (**10-15**) by condensation of either mono- or triaminotriptycene with an appropriate aldehyde in methanol. The nucleophilic addition of CN^- to triptycene-hydroxybenzaldehyde Schiff-base compound **11** was monitored by absorption and emission spectral changes as well as "naked-eye" detection. Additionally, ^1H NMR studies clearly indicated the formation of the cyanohydrin confirming its utility as a fluorescence "turn-on" cyanide sensor. The triptycene-BODIPY Schiff base compound **12** can be used for detection of Cu^{2+} over other metal ions. Furthermore, to test the reactivity of these triptycene-derived Schiff base compounds, we synthesized triptycene boranil complexes and studied their properties. Overall, these novel triptycene scaffolds have been used for the detection of CN^- and Cu^{2+} ions illustrating that the triptycene scaffold is a convenient scaffold system for dyes and analytical residues.

4. Experimental

4.1. General methods

Chemicals, such as triptycene, boron trifluoride diethyl etherate, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were used as obtained from Aldrich. All other chemicals used for the synthesis were reagent grade and solvents were dried by routine procedures immediately before use. Thin layer chromatography was performed with silica gel 60 (fluorescence indicator F254; Merck) or pre-coated aluminium sheets and visualized with UV irradiation. Column chromatography was performed on silica gel (60 Å, 230-400 mesh). ^1H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded with an Agilent 400 MHz (400 MHz for ^1H; 100.6 MHz for ^{13}C) and Bruker Advance 400 and 600 spectrometers (400 MHz for ^1H; 100.6 or 150 MHz for ^{13}C; 128.4 MHz for ^{11}B and 376.5

MHz for ^{19}F). NMR spectra were recorded at room temperature with the deuterated solvent indicated in each case. UV-Vis absorption measurements were performed with a Specord 250 spectrophotometer. Fluorescence spectra were obtained using a Varian Cary-Eclipse instrument. Infrared spectra were recorded on a Mattson Genesis II FTIR spectrophotometer equipped with a Gateway 2000 4DX2-66 workstation. HRMS spectra were measured with a MALDI-Q-TOF Premier Micromass and Micromass/WatersCorp. USA liquid chromatography time-of-flight spectrometer equipped with an electrospray ionization source (ESI). Melting points were acquired with a Stuart SMP-10 melting point apparatus.

4.2. Binding studies

The binding constant of the complexes formed in solution were estimated by using the standard Stern-Volmer equation, viz., $I_0/I = 1 + K [A]$; where I_0 is the intensity of the compounds **11** and **12** before addition of anion/cation, I is the intensity in the presence of anion/cation [A] and K is the association constant of the complex formed. Solutions of Bu_4N salts and metal perchlorates were prepared in CH_3CN (1×10^{-2} M). The solution containing compounds **11** and **12** was placed in a quartz cell (1 cm width), and Bu_4NCN or $Cu(ClO_4)_2$ solutions were added in an incremental fashion. The corresponding UV-Vis and fluorescence spectra were recorded at 298 K. For ^1H NMR titration experiments, the spectra were measured on a Bruker Advance 400 MHz NMR spectrometer. A solution of **11** in CD_3CN was prepared (3.64×10^{-2} M), and a 0.4 mL portion of this solution was transferred to a 5 mm NMR tube. Small aliquots of Bu_4NCN in CD_3CN were added in an incremental fashion, and the corresponding spectra were recorded.

4.3. Electrochemistry

All electrochemical experiments were undertaken in a standard three-electrode cell using a high performance digital potentiostat (CH model 1760 D Bi-potentiostat system monitored using CH1760D electrochemical workstation beta software). The working electrodes consisted of a glassy carbon electrode; a Pt wire was employed as a counter-electrode and a saturated calomel electrode (SCE) was used as reference standard. Electrochemical measurements were taken at a constant temperature of 25 °C, using a thermal bath with the temperature maintained by a thermostat. All solutions were degassed with N_2 for 10 minutes before commencing any analysis to eliminate any dissolved oxygen present in the electrolyte. Cyclic voltammetry (CV) experiments were conducted in chloroform with 0.1 M TBAP electrolyte at 100 mV s^{-1} between the limits of 0 V and 1.2 V vs. SCE. Differential Pulse Voltammetry (DPV) was measured between the limits of 1.5 V and -1.5 V vs. SCE.

4.4. Syntheses

4.4.1. General procedure I for the synthesis of triptycene-Schiff bases. The corresponding aldehydes were added to a stirred solution of aminotriptycene (50 mg) in dry methanol. The reaction mixture was stirred for 12 h at room temperature and the

resulting precipitate was collected by suction filtration, washed several times with methanol and dried *in vacuo* to give the desired product.

4.4.2. General procedure II for the synthesis of triptycene-Schiff bases. The corresponding aldehydes were added to a stirred solution of aminotriptycene (50 mg) in dry methanol, followed by addition of TFA (3 mol-% in CH_2Cl_2). The reaction mixture was stirred for 12 h under heating to reflux and the resulting precipitate was collected by suction filtration, washed several times with methanol and dried in vacuum to give the desired product.

4.4.3. General procedure III for the synthesis of triptycene boranil complexes. Samples of triptycene-derived Schiff base compound (50 mg) and *N*,*N*-diisopropylethylamine (DIEA) were dissolved in anhydrous dichloroethane (5 mL) in a 50 mL Schlenk flask under argon atmosphere and refluxed for 10 min. To this reaction mixture BF_3•OEt_2 was added and heating under reflux continued for 3 h while monitoring the reaction by TLC analysis. After cooling to rt, the reaction mixture was washed with a saturated solution of $NaHCO_3$ and extracted with dichloromethane. Organic layers were dried over $MgSO_4$ and the solvent evaporated under vacuum. The product was purified by silica gel column chromatography by using ethyl acetate and hexane as an eluent.

*4.4.4. 2-(((9,10-Dihydro-9,10-[1,2]benzenoanthracen-2-yl)imino)methyl)phenol (**10**).* Following general procedure I, monoaminotriptycene **4** (50 mg, 0.186 mmol) and salicylaldehyde (23 mg, 20 µL, 0.186 mmol) were dissolved in methanol (10 mL). After 12 h, compound **10** was obtained as a pale yellow solid (63 mg, 0.169 mmol, 92 %). Mp: 242 °C; R_f=0.67 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=13.27 (bs, 1H, O<u>H</u>), 8.56 (s, 1H, C<u>H</u>, imine), 7.45-7.41 (m, 5H, Ar-<u>H</u>), 7.37-7.35 (m, 3H, Ar-<u>H</u>), 7.06-7.02 (m, 5H, Ar-<u>H</u>), 6.92-6.90 (m, 2H, Ar-<u>H</u>), 5.47 (s, 1H, bridgehead-<u>H</u>), 5.46 ppm (s, 1H, bridgehead-<u>H</u>); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=162.2, 161.2, 146.9, 145.9, 145.1, 145.0, 144.4, 133.1, 132.3, 125.6, 125.5, 124.5, 123.9, 123.8, 119.4, 119.1, 118.1, 117.4, 116.9, 54.3, 53.8 ppm; IR (ATR): ν_{max} (cm^{-1})- 3320, 1604, 1570, 1469, 1412, 1278, 1188, 1150, 1087, 1047, 970, 945, 880, 748; HRMS (ESI): *m/z* calcd. for $[C_{27}H_{20}NO]$ $(M+H)^+$ 374.1545; found 374.1550.

*4.4.5. 5-(tert-Butyl)-3-(((9,10-dihydro-9,10-[1,2]benzenoanthracen-2-yl)imino)methyl)-2-hydroxybenzaldehyde (**11**).* Prepared following general procedure II, monoaminotriptycene **4** (50 mg, 0.186 mmol) and 5-*tert*-butyl-2-hydroxyisophthalaldehyde **7** (38 mg, 0.186 mmol) were dissolved in methanol (10 mL). After 12 h, the title compound **11** was obtained as a light orange solid (77 mg, 0.168 mmol, 91 %). Mp: 258 °C; R_f=54 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=13.80 (bs, 1H, O<u>H</u>), 10.57 (s, 1H, C<u>H</u>O), 8.65 (s, 1H, C<u>H</u> imine), 7.95 (d, *J*=6.5 Hz, 1H, Ar-<u>H</u>), 7.62 (s, 1H, Ar-<u>H</u>), 7.46-7.40 (m, 6H, Ar-<u>H</u>), 7.08-7.01 (m, 5H, Ar-<u>H</u>), 5.47 (s, 1H, bridgehead-<u>H</u>), 5.46 (s, 1H, bridgehead-<u>H</u>), 1.34 ppm (s, 9H, C<u>H</u>$_3$); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=196.7, 145.0, 144.9, 144.3, 141.9, 135.3, 130.3, 125.6, 125.5, 124.4, 123.9, 123.8, 118.2, 116.6, 113.1, 54.3, 54.2, 31.4 ppm; IR (ATR): ν_{max} (cm^{-1})- 3340, 1670, 1610, 1468, 1277, 1186, 1150, 1087, 1047, 946, 881, 743; UV-Vis ($CHCl_3$): λ_{max} (lg ε)=374 nm (4.3); fluorescence: λ_{em}=470 nm with excitation at 380 nm; HRMS (ESI): *m/z* calcd. for $[C_{32}H_{28}NO_2]$ $(M+H)^+$ 458.2120; found 458.2119.

*4.4.6. 4-(tert-Butyl)-2-(((9,10-dihydro-9,10-[1,2]benzenoanthracen-2-yl)imino)methyl)-6-(BODIPY)-phenol (**12**).* Following general procedure II, monoaminotriptycene **4** (50 mg, 0.185 mmol) and *meso*-salicylaldehyde substituted BODIPY **9** (68 mg, 0.185 mmol) were dissolved in methanol (20 mL). After 12 h, the title compound **12** was obtained as an orange solid (101 mg, 0.163 mmol, 88 %). Mp: 233 °C; R_f=0.62 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=13.82 (bs, 1H, OH), 8.68 (s, 1H, CH imine), 7.91 (s, 2H, Py-H), 7.51 (d, *J*=6.3 Hz, 1H, Ar-H), 7.45 (d, *J*=6.8 Hz, 1H, Ar-H), 7.42-7.39 (m, 5H, Ar-H), 7.36 (d, *J*=7.1 Hz, 1H, Ar-H), 7.05-7.00 (m, 5H, Ar-H), 6.91 (d, *J*=4.6 Hz, 2H, Py-H), 6.50 (dd, *J*=4.5, 2.8 Hz, 2H, Py-H), 5.47 (s, 1H, bridgehead-H), 5.46 (s, 1H, bridgehead-H), 1.35 ppm (s, 9H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=161.6, 156.9, 147.0, 145.0, 144.9, 144.1, 141.4, 132.7, 131.5, 130.9, 125.6, 125.5, 124.6, 123.9, 123.8, 121.7, 119.1, 118.4, 116.8, 54.3, 53.8, 31.4 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ_B=0.31 ppm (t, $^1J_{B-F}$=28.9 MHz, 1B); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ_F=−143.17 and -147.27 ppm (octate, $^1J_{F-B}$=28.6 MHz, 2F); IR (ATR): ν_{max} (cm^{-1})- 3340, 1608, 1458, 1411, 1383, 1257, 1088, 1047, 971, 879, 742; UV-Vis ($CHCl_3$): λ_{max} (lg ε)=500 nm (4.9); fluorescence: λ_{em}=520 nm with excitation at 490 nm; HRMS (MALDI): *m/z* calcd. for [$C_{40}H_{32}BN_3OF_2$] M^+ 619.2606; found 619.2625.

*4.4.7. 2,2',2''-(((9,10-Dihydro-9,10-[1,2]benzenoanthracene-2,6,14-triyl)tris(azaneylylidene))tris(methaneylylidene)) triphenol (**13**).* Synthesized following general procedure I, triaminotriptycene **5** (50 mg, 0.167 mmol) and salicylaldehyde (68 mg, 59 µL, 0.552 mmol) were dissolved in methanol (20 mL). After 12 h, compound **13** was obtained as a yellow solid (92 mg, 0.150 mmol, 90%). Mp: 248 °C; R_f=0.52 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=13.20 (bs, 3H, OH), 8.57 (s, 3H, CH imine), 7.46 (dd, *J*=7.7, 3.9 Hz, 3H, Ar-H), 7.39-7.34 (m, 9H, Ar-H), 7.02 (d, *J*=8.5 Hz, 3H, Ar-H), 6.97-6.91 (m, 6H, Ar-H), 5.53 (s, 1H, bridgehead-H), 5.52 ppm (s, 1H, bridgehead-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=162.3, 161.0, 146.2, 146.1, 146.0, 143.3, 133.0, 132.1, 124.5, 124.4, 119.1, 119.0, 118.2, 118.0, 117.2, 116.9, 53.7, 53.2 ppm; IR (ATR): ν_{max} (cm^{-1})- 3330, 1603, 1468, 1276, 1187, 1150, 1089, 1047, 946, 881, 749; LR-MS: calcd. for [$C_{41}H_{30}N_3O_3$] 612.22; found 612.21; HRMS (ESI): *m/z* calcd. for [$C_{41}H_{30}N_3O_3$] $(M+H)^+$ 612.2287; found 612.2284.

*4.4.8. 3,3',3''-(((9,10-Dihydro-9,10-[1,2]benzenoanthracene-2,6,14-triyl)tris(azaneylylidene))tris(methaneylylidene))tris(5-(tert-butyl)-2-hydroxybenzaldehyde) (**14**).* Prepared following general procedure II using triaminotriptycene **5** (50 mg, 0.167 mmol) and 5-*tert*-butyl-2 hydroxyisophthalaldehyde **7** (114 mg, 0.552 mmol) dissolved in methanol (20 mL). After 12 h, compound **14** was obtained as a light orange solid (127 mg, 0.146 mmol, 88 %). Mp: 262 °C; R_f=0.45 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=13.48 (bs, 3H, OH), 10.63 (s, 3H, CHO), 8.69 (s, 3H, CH imine), 7.92 (d, *J*=6.9 Hz, 2H, Ar-H), 7.67 (d, *J*=7.3 Hz, 3H, Ar-H), 7.43-7.39 (m, 5H, Ar-H), 7.03-6.97 (m, 5H, Ar-H), 5.53 (s, 1H, bridgehead-H), 5.52 (s, 1H, bridgehead-H), 1.36 ppm (s, 27H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=196.5, 162.5, 162.4, 162.0, 157.0, 156.6, 146.0, 142.3, 141.8, 141.2, 135.2, 132.3, 130.1, 129.0, 128.2, 125.7, 125.1, 124.5, 123.6, 120.1, 118.3, 116.9, 99.4, 98.9, 54.1, 54.0, 31.2 ppm; IR (ATR): ν_{max} (cm^{-1})- 3302, 2961, 1467, 1363, 1269, 1207, 1109, 1052, 978, 946, 887, 799, 726; UV-Vis ($CHCl_3$): λ_{max} (lg ε)=361 nm (4.5); fluorescence:

λ_{em}=510 nm with excitation at 380 nm; HRMS (ESI): *m/z* calcd. for [$C_{56}H_{54}N_3O_6$] $(M+H)^+$ 864.4013; found 864.4042.

*4.4.9. 2,2',2''-(((9,10-Dihydro-9,10-[1,2]benzenoanthracene-2,6,14-triyl)tris(azaneylylidene))tris(methaneylylidene))tris(5-(tert-butyl))-tris(6-(BODIPY))triphenol (**15**).* Following general procedure II, triaminotriptycene **5** (50 mg, 0.167 mmol) and meso-salicylaldehyde substituted BODIPY **9** (203 mg, 0.552 mmol) were dissolved in methanol (20 mL). After 12 h, compound **15** was obtained as an orange solid (192 mg, 0.142 mmol, 85 %). Mp: 245 °C; R_f=0.53 (CH_2Cl_2/C_6H_{14}, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=13.70 (bs, 3H, OH), 8.69 (s, 3H, CH imine), 7.92 (s, 6H, Py-H), 7.53 (d, *J*=6.9 Hz, 3H, Ar-H), 7.47 (d, *J*=6.7 Hz, 5H, Ar-H), 7.44 (d, *J*=7.2 Hz, 2H, Ar-H), 7.39 (d, *J*=7.1 Hz, 3H, Ar-H), 6.98 (d, *J*=6.9, 2H, Ar-H), 6.91 (d, *J*=4.4 Hz, 6H, Py-H), 6.51 (d, *J*=4.1 Hz, 6H, Py-H), 5.50 (s, 1H, bridgehead-H), 5.49 (s, 1H, bridgehead-H), 1.35 ppm (s, 27H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=162.0, 156.8, 146.3, 146.1, 145.6, 145.5, 144.2, 144.0, 143.8, 143.7, 141.5, 135.7, 132.9, 132.8, 131.5, 131.0, 124.8, 121.8, 119.1, 119.0, 118.5, 118.4, 117.2, 53.6, 53.4, 31.5 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ_B=0.31 ppm (t, $^1J_{B-F}$=28.7 MHz, 1B); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ_F=−143.42 and −147.04 ppm (octate, $^1J_{F-B}$=28.6 MHz, 2F); IR (ATR): ν_{max} (cm^{-1})- 3342, 1607, 1465, 1385, 1259, 1167, 1072, 1046, 970, 880, 772; UV-Vis ($CHCl_3$): λ_{max} (lg ε)=501 nm (4.8); fluorescence: λ_{em}=520 nm with excitation at 490 nm; HRMS (MALDI): *m/z* calcd. for [$C_{80}H_{68}B_3N_9O_3F_6$] M^+ 1349.5628; found 1349.5643.

*4.4.10. 3-(9,10-Dihydro-9,10-[1,2]benzenoanthracen-2-yl)-2,2-difluoro-benzo[e][1,3,2]oxazaborinine (**16**).* Compound **10** (50 mg, 0.133 mmol), *N*,*N*-diisopropylethylamine (43 mg, 58 µL, 0.330 mmol) and $BF_3{\cdot}OEt_2$ (47 mg, 41 µL, 0.330 mmol) were dissolved in dry dichloroethane (5 mL) and heated to reflux following general procedure III to obtain compound **16** as a pale yellow solid in 38 % (21 mg, 0.045 mmol) yield. Mp: 220 °C; R_f=0.72 ($C_4H_8O_2/C_6H_{14}$, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=8.25 (s, 1H, CH imine), 7.64-7.58 (m, 2H, Ar-H), 7.44-7.39 (m, 6H, Ar-H), 7.13-7.08 (m, 2H, Ar-H), 7.05-7.02 (m, 4H, Ar-H), 6.98-6.96 (m, 1H, Ar-H), 5.51 (s, 1H, bridgehead-H), 5.50 ppm (s, 1H, bridgehead-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=163.4, 159.7, 147.2, 146.9, 144.6, 144.5, 139.4, 139.2, 132.2, 125.7, 125.6, 124.5, 124.0, 123.9, 120.5, 120.2, 119.6, 119.3, 53.9, 53.7 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ_B=0.77 ppm (t, $^1J_{B-F}$=27.5 MHz, 1B); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ_F=−133.8 ppm (quartet, $^1J_{F-B}$=27.6 MHz, 2F); IR (ATR): ν_{max} (cm^{-1})- 1609, 1560, 1468, 1411, 1385, 1259, 1169, 1110, 1071, 1033, 947, 882, 828, 747; UV-Vis ($CHCl_3$): λ_{max} (lg ε)=395 nm (4.1); flurorescence: λ_{em}=468 nm with excitation at 400 nm; HRMS (ESI): *m/z* calcd. for [$C_{27}H_{18}BNOF_2K$] $(M+K)^+$ 460.1087; found 460.1078.

*4.4.11. 3,3',3''-(9,10-Dihydro-9,10-[1,2]benzenoanthracene-2,6,14-triyl)tris(2,2-difluoro-benzo[e][1,3,2]oxazaborinine) (**17**).* Following general procedure III, compound **13** (50 mg, 0.08 mmol), *N*,*N*-diisopropylethylamine (79 mg, 107 µL, 0.6 mmol) and $BF_3{\cdot}OEt_2$ (87 mg, 76 µL, 0.6 mmol) in dry dichloroethane (5 mL) were used to obtain compound **17** as a yellow solid in 32 % (20 mg, 0.025 mmol) yield. Mp: 226 °C; R_f=0.64 ($C_4H_8O_2/C_6H_{14}$, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H=8.38 (s, 3H, CH imine), 7.69-7.64 (m, 6H, Ar-H), 7.52-7.46 (m, 6H, Ar-H), 7.19-7.17 (m, 2H, Ar-H), 7.15-7.12 (m, 4H, Ar-H), 7.06-7.02 (m, 3H, Ar-H), 5.63 (s, 1H, bridgehead-H), 5.62 ppm (s, 1H,

bridgehead-H); ^{13}C NMR (150 MHz, $CDCl_3$): δ_C=162.4, 1621.2, 146.3, 146.2, 143.5, 143.3, 133.2, 132.3, 124.7, 124.6, 119.3, 119.2, 118.4, 118.2, 117.3, 117.1, 53.9, 53.4 ppm; ^{11}B NMR (128.4 MHz, $CDCl_3$): δ_B=0.93 ppm (t, J=27.9 MHz, 1B); ^{19}F NMR (376.5 MHz, $CDCl_3$): δ_F=−133.59 ppm (bs, J=28.3 MHz, 2F); IR (ATR): ν_{max} (cm^{-1})-1606, 1561, 1468, 1385, 1253, 1166, 1109, 1071, 1032, 973, 947, 890, 829, 746; UV-Vis ($CHCl_3$) λ_{max} (lg ε): 399 nm (4.3); fluorescence: λ_{em}=469 nm with excitation at 400 nm; HRMS (MALDI): *m/z* calcd. for $[C_{41}H_{26}B_3N_3O_3F_6Na]$ $(M+Na)^+$ 778.2055; found 778.2090.

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Supplementary Material

Analytical spectra and photophysical characterizations for all compounds.

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