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Boranil dyes bearing tetraphenylethene: synthesis, AIE/AIEE effect properties, pH sensitive properties and application in live cell imaging

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ABSTRACT

A serial of novel fluorescent boranil dyes (**7, 8, 9, 10**) bearing tetraphenylethene were prepared through an efficient process. These dyes exhibited large stokes shifts (more than 5000 cm^{-1}) and moderate fluorescent quantum yield from 0.22 to 0.53. Dye **9** exhibited AIE/AIEE and exhibited weak fluorescence in pure MeCN or the MeCN/water mixture with a water fraction below 80%, in which a significant AIEE effect was observed in the mixture with 80% of water fraction and a sharp increasement in fluorescence intensity was also observed. And dye **8** and **10** showed moderate solvatochromism with the solvent changed from toluene to DMSO, and they displayed sensitivities to pH change in MeCN/water solution. Interestingly, dyes **8** and **10** obtained by column chromatography and slow solvent evaporation showed different X-ray diffraction properties. Moreover, compound **8** and **10** could be applied to cell imaging.

Introduction

Recently organic luminophores have attracted much attention in several lines of research due to their exciting potential applications such as laser dyes[1, 2], bioimaging[3-5], sensitizer[6-8] as well as chemosensors[9-14] . Among fluorescent organoboron complexes such as pyrromethene[15-18], diketone[19-22], subphthalocyanine[23-25], subporphyrin[26-28], borylazobenzene[29-31] and others[32-34] , boron dipyrromethene (BODIPY) is well-known to show excellent optical properties such as high fluorescent quantum yield, sharp absorption and fluorescent emission spectra, and chemical stability[35] .

However, since most BODIPY dyes have a rigid structure with minimal differences between the ground-state and excited-state structures[36, 37] , in most case, they exhibit small stokes shifts[38-40](400-600 cm^{-1}) , which makes it difficult for optical filters to cut the excitation light, much less to read the fluorescent signal over the noise in a bioassay[36].

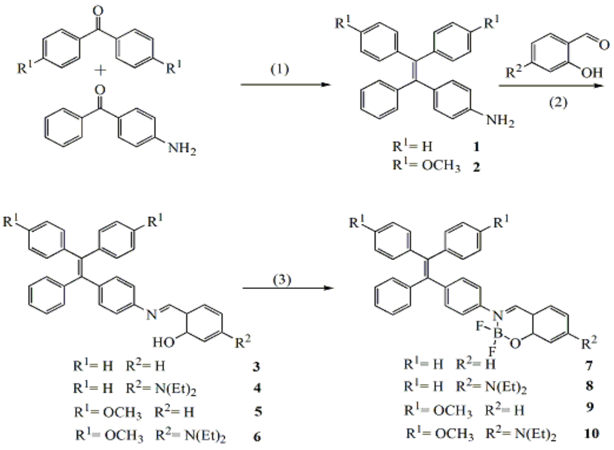
Another disadvantage of BODIPY dyes is that many of those dyes suffer from notorious aggregation-caused quenching (ACQ) effect in aggregate state[41-43], which severely limits their application in optoelectronic devices[44]. To overcome the ACQ obstacle, an effective and universal strategy is to design those dyes in combination with some special chromophores such as tetraphenylethene[45-47] , siloles[48-50] and diphenyldibenzofulvenes[51, 52] , in which their aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) effects are employed. And dyes containing the binding site groups such as hydroxyl subunits[53-55] , amino groups[54, 56-60] and others[61-64] can also be used as pH indicators.

Therefore, a promising direction for new organoboronic compound is to increase stokes shifts while keeping their attractive qualities. Based on this reason, recent efforts have been made to develop new fluoroborate structures presenting features to correct some of the weaknesses of BODIPY dyes[65-69]. And we designed and synthesized dyes based on the structure of boranil[70-73], which were named by Ziessel based on the NBO atomic sequence and were combined with tetraphenylethene and diethylamino group. Herein, we reported the synthesis and optical properties of boranil dyes bearing tetraphenylethene, which showed large stokes shifts and attractive properties for live cell imaging.

Results and discussion

1. Synthesis

All new tetraphenylethene-salicylaldhyde ligands (**3, 4, 5, 6**) and their corresponding boron complexes (**7, 8, 9, 10**) were fully characterized by various spectroscopic techniques and their synthetic routes were shown in **Scheme 1**. Details of the experimental procedures and data for structural characterization were described in *the Supporting Information*. The key precursors, tetraphenylethene-salicyaldheyde derivatives **3-6**, showed a distinctively downfield 13 ppm (-OH) shifted ^{1}H-NMR signal for the H-bonded enol proton in comparison to 8~9 ppm (-N=CH-) of dyes **7-10**, which was consistent with the previous reports of boranil precursors [74].



Scheme 1. Synthetic routes of teteaphenylethene-salicyaldhyde ligands (**3, 4, 5, 6**) and their corresponding boron complexes (**7, 8, 9, 10**); Reaction condition (1) Zn, $TiCl_4$, THF, reflux, 68℃ 14 h; (2) p-TsOH, CH_2Cl_2, 40℃,10h ;(3) BF_3-Et_2O, DIPEA, CH_2Cl_2, Room Temperature, 24h.

2. Photo-physical properties

The optical properties of the boranil dyes were first studied in dilute MeCN and CH_2Cl_2 solution by UV-vis absorption and fluorescence spectroscopy and the results were summarized in **Table 1**.

Table1: Photo-physical Properties of dyes **7-10** (1×10^{-5}mol/L) in MeCN and CH_2Cl_2 at room temperature.

Dye	λ_{abs}/nm	λ_{em}/nm	ε_{max} ($M^{-1}.cm^{-1}$)	Stoke shifts(cm^{-1})	Φ_F
7	383	640	N^a	10485	N^a
8	413	525	53800^b	5165	0.35^b
9	392	515	12400^b	6093	0.22^b
10	411	610	37810^b	7937	0.53^b
8+H$^{+\,c}$	409	528	N^a	5510	N^a
10+H$^{+\,c}$	412	613	N^a	7958	N^a

[a] Not tested; [b] Fluorescent quantum yield was obtained by using perylene (Φ_F = 0.94 in cyclohexane λ_{ex} = 400nm) as a reference compound for **8** ,**9** and **10** in CH_2Cl_2; [c] pH = 6.5.; λ_{ex} = 400nm.

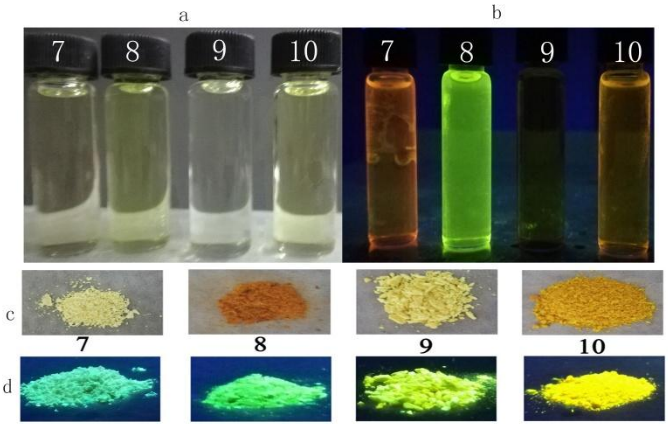


Figure 1. Photographs of dye **7-10** in solution (1×10^{-5} mol/L): a (under daylight), b (λ = 365 nm) ; Photographs of dye **7-10** powder: c (under daylight); d (λ = 365 nm).

As shown in **Table 1**, compound **7** had a maximum absorption peak at 383 nm in MeCN solution. Compounds **8-10** exhibited red-shift which might be due to the increasing electron-donating ability of diethyl amino and methoxy groups in comparison to the H atom in compound **7**. Moreover, larger bathochromic shifts of absorption maxima were observed for the dyes **8** (413nm) and **10** (411nm). The molar absorption coefficient (ε) of **8** (53800) and **10** (37810) were higher than that of **9** (12400). The longest wavelength emission maximum (640 nm) was observed for the dye **7**, while emission maximum of 515-610 nm was observed for the dyes **8-10**. More importantly, all the dyes exhibited large stokes shifts (more than 5000 cm^{-1}) in comparison to BODIPY dyes. All the dyes exhibited solid fluorescence at wavelength of 365nm (**Figure 1**).

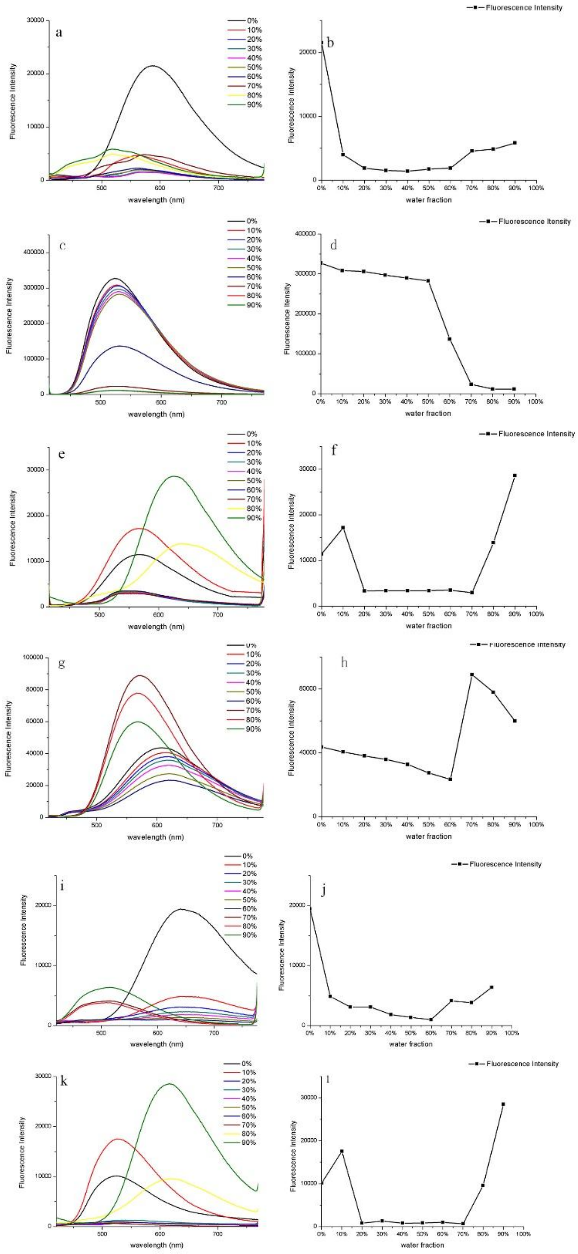


Figure 2. Fluorescence spectra of a (**7**), c (**8**), e (**9**), g (**10**) in MeCN/water solution with different fractions of water. Luminogen concentration：1×10^{-5} mol/L ； The dependence of intensity on water fraction in the solution: b (**7**), d (**8**), f (**9**), h (**10**);

λ ex =400 nm.;Fluorescence spectra i（7）, k（9） and the dependence of intensity on water spectra, j（7）, l（9）in partly aggregated state .

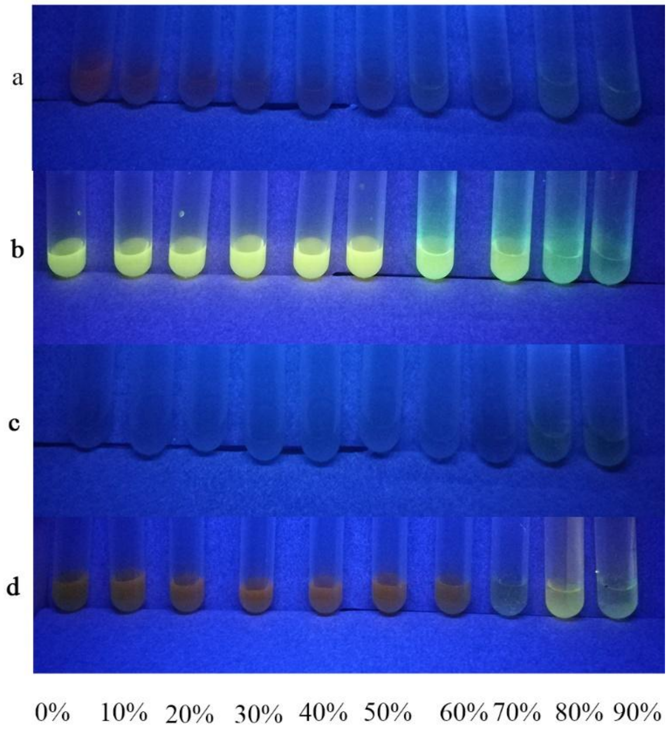


Figure 3. Photographic images of the dyes (1×10-4 mol/L) in MeCN/water solution (water fraction from 0% to 90%) at the wavelength of 365 nm: a (7), b (8), c (9), d (10)

To explore the different photo-physical properties of dye **7-10**, especially bearing tetraphenylethene, we utilized the general method to investigate the fluorescence spectra of the complexes in MeCN/water solution with different water fractions. The photographs and fluorescence spectra were shown in **Figure 2** and **Figure 3**. When the dyes in the mixture formed some aggregates, the dyes were gradually dissolved in the solution by shaking the mixture for about 10min and letting the mixture stand for 1 day.

When **7** was dissolved in MeCN (1×10^{-4} mol/L), the pure MeCN solution emitted red light (**Figure 3a**.). With an increasing content of water from 0 to 10%, the fluorescence spectra showed obvious fluorescence decreasement. While the water fraction was increased to 60%, the intensity of fluorescence decreased but the rate of decreasement was not like before. With the water fraction was increased to 90%, the fluorescence increased modestly. Meanwhile, the color of the solution changed from red to light-yellow, which could be attributed to aggregation-caused quenching effect (ACQ effect). More interestingly, the florescence spectra showed obvious blue shift (about 85 nm) (**Figure 2a**), which might be attributed to intramolecular charge transfer (ICT) from tetraphenylethene to boron complex. In comparison to the fluorescence spectra of the dye **7** dissolved in the solution, the fluorescence spectra **i** exhibited more distinct blue-shift (about 100 nm), which might be attributed to the aggregated state that released energy of transition state.

As for dye **8**, it emitted strong yellow light when dissolved in pure MeCN solution (**Figure 3b**). With an increasing water fraction, the fluorescence intensity decreased gradually. And when the water fraction was increased to 60%, the solution showed a distinct color change from yellow to light green. The fluorescence spectra also showed a moderate red-shift (about 6 nm) (**Figure 2c**)

When the dye **9** was dissolved in the pure MeCN solution, it was non-luminescent (**Figure 3c**)，which could be attributed to that the free rotation of methoxy group effectively consumed the energy of the excitations via nonradiative relaxation channels. As for the fluorescence spectra of dye **9**, when the water fraction was increased to 10%, a modest fluorescence enhancement behavior was observed as shown in **Figure 2e**. However, with more water was induced to the solution, the fluorescence spectra showed sharp decreasement and the solution still seemed non-luminescent. While the water fraction was increased to 80%, a light-yellow fluorescence was observed (**Figure 3c**), which might result from aggregation-induced emission(AIE) effect. Meanwhile, as to the fluorescence spectra of dye **9**, a dramatic fluorescence enhancement was observed, which could be attributed to AIEE effect, namely that the enhancement of the fluorescence was related to the formation of the aggregates of dye **9**, which prevented the intramolecular rotation and boosted the fluorescence. More importantly, it was similar to the previous reports of AIE/AIEE-based luminophores, and was in contrast to the aggregation–caused quenching (ACQ) of classical luminophores, which were non-luminescent or weakly luminescent in dilute solutions and became modestly or highly emissive in the aggregate state[75]. More interestingly, the fluorescence spectra exhibited a distinct bathochromic shift (more than 53 nm). According to the reported literature[76, 77], dyes with twisted intramolecular charge transfer (TICT) effect usually exhibited red-shift properties, especially dyes with donor-acceptor or donor-acceptor-donor structures. As for dye **9**, the methoxy-substituted tetraphenylethene acted as donor, while the difluoroboron complex acted as acceptor, which also led to its bathochromism. More interestingly, the fluorescence spectra of dye **9** in the solution (**Figure 2e**) or in the aggregated state (**Figure 2k**) did not show much difference.

Similar to dye **7**, the pure MeCN solution of **10** emitted red light. With the increasement of water fraction to 60%, the fluorescence spectra of **10** showed a decrease and the color of the solution became faint. And the color of the solution became yellow with the water fraction up to 70%, and the fluorescence spectra showed a dramatical enhancement. The fluorescence spectra showed distinct decreasement when the water fraction was increased to 90%, and the color of the solution also became faint. And the fluorescence spectra also exhibited a blue-shift (more than 50 nm). The reason why dye **10** did not show the AIE or AIEE effect, in comparison to dye **9** was that the diethylamino group might consume the excited-stated energy by rotation and hinder the planarity of dye **10**.

Based on the absorption and fluorescence spectra studies of dyes **7-10**, **8** and **10** were chosen for further study. The photo-physical properties of **8** and **10** in various organic solvents were investigated (as shown in **Figure 2**.), and detailed data were summarized in **Table S1** (*in supporting information*)

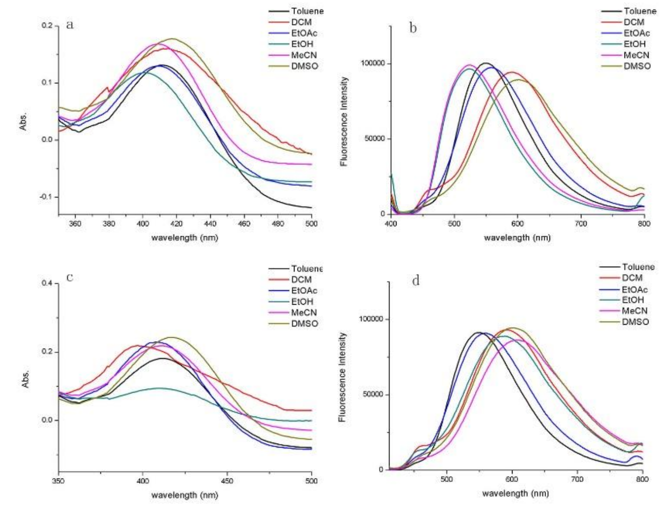


Figure 4: UV-vis spectra of dye 8 (a) and **10** (c) in the solution toluene, DCM, EtOAc, EtOH, MeCN, DMSO; The fluorescence spectra of **8** (b) and **10** (d) in the solution toluene, DCM, EtOAc, EtOH, MeCN, DMSO. λ_{ex} = 400nm

The maximum absorption of **8** red-shifted about 16 nm when the solvent was changed from toluene to DMSO. Meanwhile, the fluorescence spectra exhibited more obvious solvatochromic behaviour and the maximum emission peak red-shifted about 80 nm when the solvent was changed from toluene to DMSO. Similar to dye **8**, the absorption of maximum of **10** red-shifted about 9 nm when the solvent was changed from toluene to DMSO. Also, the fluorescence spectra exhibited obvious solvatochromic behaviour in which the maximum emission peak red-shifted about 52 nm when the solvent was changed from toluene to DMSO.

3. pH sensitivity studies

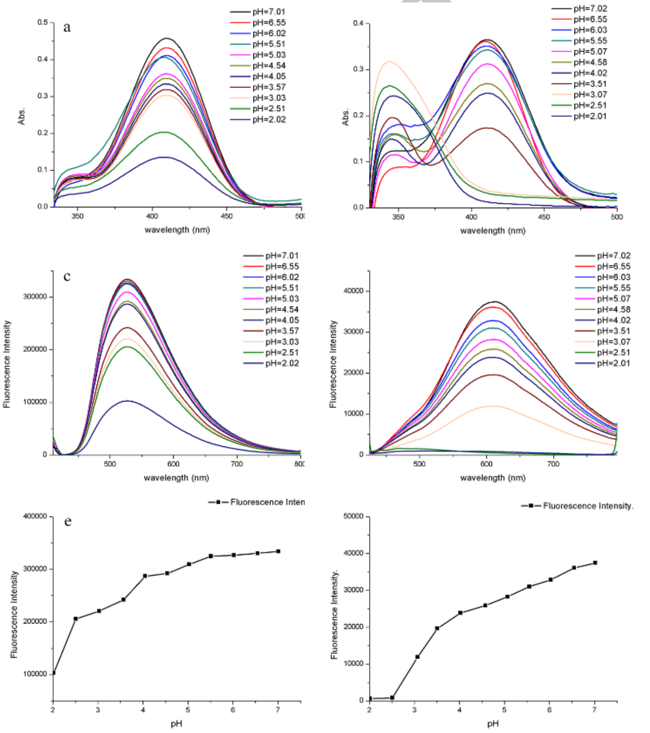


Figure 5. UV-vis spectra of dyes (1×10^{-5} mol/L) dissolved in MeCN /water(v:v =19:1) solution with pH value range from about 7.0 to 2.0 : a (**8**) ,b (**10**) ;The fluorescence spectra of dyes dissolved in MeCN/water /buffer()solution with pH value range from about 7.0 to 2.0: c (**8**) ,d (**10**) ; The PH-dependence fluorescence spectra ： e (**8**), f (**10**); λ_{ex} = 400nm ； pH buffer ： Citric acid buffer.

To explore the pH-dependent photophysical properties of **8** and **10**, pH titration experiments were carried out in MeCN/water (v/v=19:1) by the sequential addition of HCl （0.1 mol/L）. As shown in **Figure 5a** ,by the addition of the HCl solution to decrease pH value from 7.01 to 2.02 , the UV-vis spectra showed gradual decreasement. Akin to the UV-vis spectra, the fluorescence spectra also exhibited gradual decreasement (**Figure 5c**), with the pH value was changed from 7.01 to 2.02.

More interestingly, with the pH value decreased from 7.02 to 2.01, the absorbance at 411nm decreased while the absorbance at 351 nm increased gradually (**Figure 5b**). And the absoption band diminshes while the pH value was less than 2.5. The fluoresence spectra of dye **10** also displayed gradual decreasement with the pH value decreased. The dyes **8** and **10** possessed a potential H^+ binding position, namely the diethylamino group, which might be responsible for their sensitivities to pH change.

4. X-ray diffraction studies

When compounds **8** and **10** were obtained with the method of chromatography and slow solution evaporation, they showed different color in solid state. The compound **8** obtained by slow solvent evaporation became darker while the compound **10** brightened in color. X-ray diffraction measurements (XRD) showed that different methods to obtain **8** and **10** led to intensity changes and slightly shift of the peak

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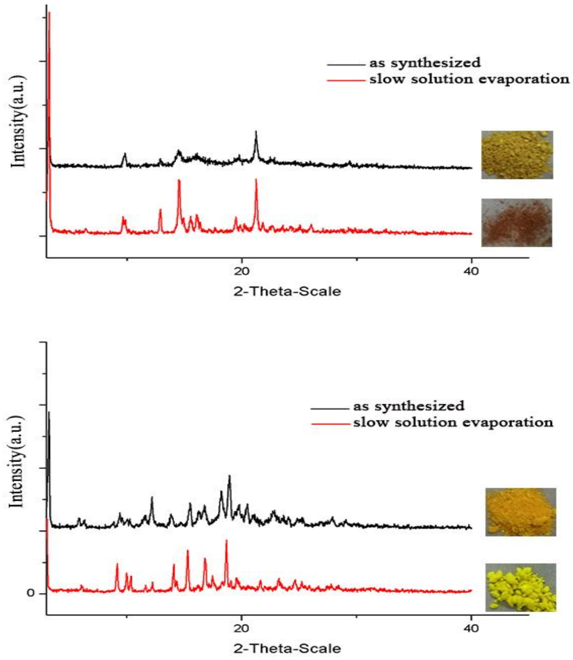

Figure 6. X-ray diffraction (XRD) patterns of dyes **8** and **10** obtained by silica column chromatography (as synthesized) and slow solution evaporation (the solution petroleum ether: CH_2Cl_2 =2:1); Insert photographic images of the powdered compounds **8** (top) and **10** (bottom) obtained by silica column chromatography (as synthesized) and slow solution evaporation

5. Cytotoxicity and bioimaging studies

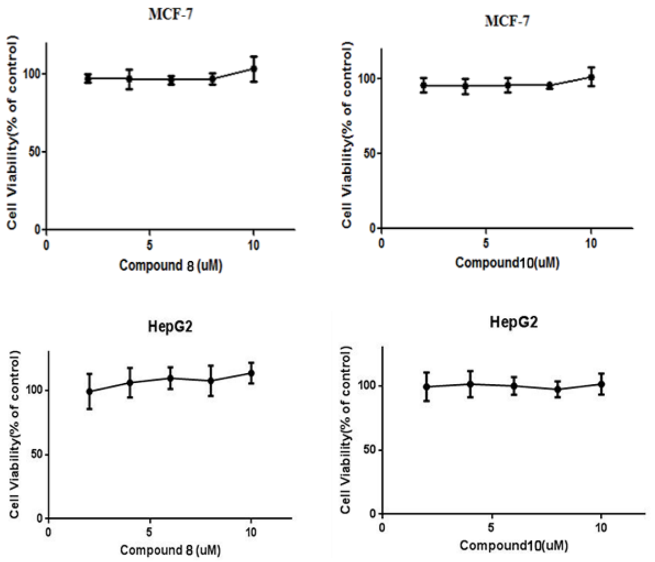

Figure 7. Cell viability of MCF-7 and HepG2 cells incubated with **8** and **10** for 24h.

Dye **8** and **10** were chosen for biological evaluation in human HepG2 cells and MCF-7 cells and the biocompatibility of **8** and **10** were evaluated via MTT assays and were shown in **Figure 7**. The detailed procedures were summarized in *supporting information* and DMSO was chosen as the solvent. As shown in **Figure 7**, there was no evident cell death even at a high concentration of 10 μM of **8** and **10**, indicating nontoxicity of the compounds to cells under the present condition. Dye **8** and **10** were readily taken up by the human HePG2 cells and MCF-7 cells respectively, and the images taken by a fluorescence microscope were shown in **Figure 8**.

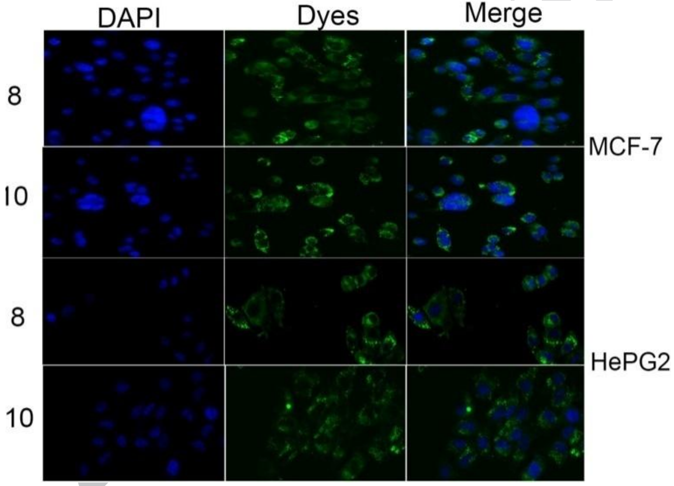

Figure 8. Fluorescence images of MCF-7 cells stained with **8** or **10** (5.0 μM) and DAPI (1.67 μg/mL) (top); Fluorescence images of HepG2 cells stained with **8** or **10** (5.0 μM) and DAPI (1.67 μg/mL) (bottom).

After the incubation of the HePG2 cells and MCF-7 with **8** and **10** for 8 hours respectively, these dyes were proven to be membrane permeable, and a strong green fluorescence was observed in the cytoplasm (**Figure 8**). The fluorescence of **8** and **10** in cells showed an attractive cell imaging property, which was potentially useful for the further application in in vitro and in vivo.

Conclusion

In summary, we have developed a new family of boranil dyes (**7-10**) obtained by efficient three-step reaction, and their ACQ effect and AIE/AIEE properties have been investigated. All dyes exhibited large stokes shifts (more than 5000 cm^{-1}) in MeCN. Dye **9** exhibited AIE/AIEE effect in MeCN/water solution when the water fraction was increased to 80%. Dye **8** and **10** showed moderate solvatochromism when the solvent was changed from toluene to DMSO, and more importantly, they displayed distinct pH sensitive properties in MeCN/water (19:1) solution when the pH was changed from about 7.0 to 2.0. And the color of **8** and **10** powders showed obvious changes when the compounds were obtained by different methods. More importantly, compound **8** and **10** were proven to be membrane permeable, which might hold great potential for application in vitro and in vivo.

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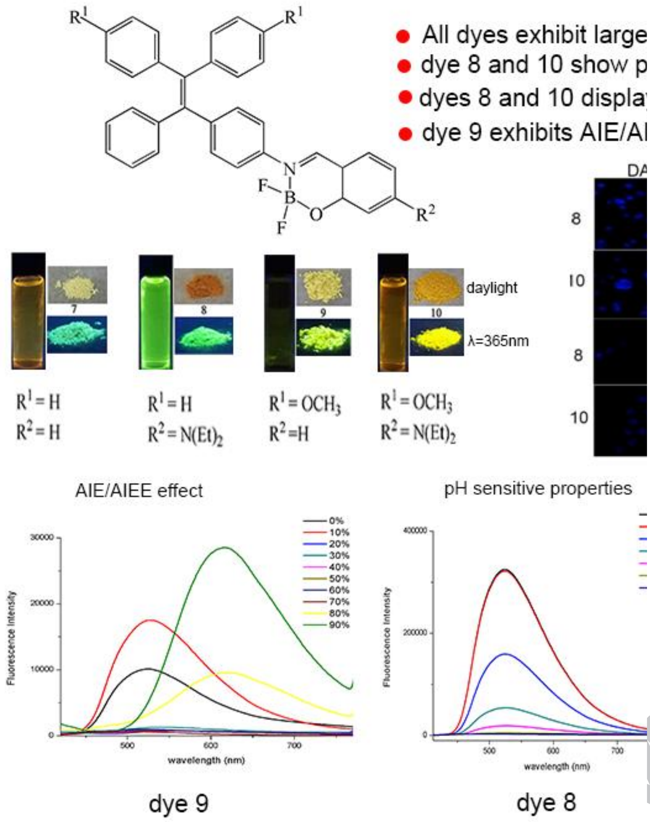
The highlights of our manuscript:

1. Novel sensors **7-10** were synthesized and characterized.
2. The sensors exhibited large stokes shifts.
3. The sensors could be applied as fluorescent imaging probes.

8

Graphic abstract



A family of new boranil dyes was prepared by three-step procedures

All the dyes exhibit large stokes shift (more than 5000 cm^{-1})

Dye 9 exhibits AIE/AIEE effect in MeCN/water solution when the water fraction increases to 80%

Dye 8 and 10 show pH sensitive properties and can be used for cell imaging.