# A multi-sensing fluorescent compound derived from cyanoacrylic acid

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A new cyanoacrylic acid derivative of carbazole-triphenylethylene as a fluorescent probe has been synthesized and characterized. The derivative exhibits not only aggregation-induced effect (AIE) properties, but also interesting fluorescence multi-responses to solvents, water, ethanol and metal ions due to its chemical structure. Responses of the compound solution in DMF to water can be explained in terms of H-bond, multimer and AIE effects. In addition, the derivative was found to be highly sensitive to potassium ions. It is suggested that the compound has potential applications in chemosensors.

# Introduction

Fluorescent chemosensors are of great value to pharmaceutics, physiology, chemistry and environmental sciences due to their selectivity and sensitivity for some chemical materials, which is a fundamental goal for chemists.<sup>1</sup> Very recently, aggregation-induced emission (AIE) materials were used as fluorescent chemosensors to detect DNA and proteins.<sup>2</sup> AIE materials were first reported by Tang *et al.* in 2001,<sup>3</sup> which are contrary to common fluorescent materials and are weakly fluorescent in solution; however, they exhibit strong fluorescence upon aggregation. Considering the introduction of the AIE effect to fluorescent chemosensors, we synthesized an interesting cyanoacrylic acid derivative that exhibits not only AIE properties but also multi-sensing properties to many chemicals.

# **Results and discussion**

## Synthesis

This new cyanoacrylic acid derivative  $Cz_2P_4CA$  (3-(4'-(2,2-bis(4-(9*H*-carbazole-9-yl)phenyl)vinyl)biphenyl-4-yl)-2-cyano acrylic acid) was prepared by a Pd-catalyzed Suzuki coupling reaction of an intermediate compound 9,9'-(4,4'-(2-(4- bromophenyl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9*H*-carbazole) (2)<sup>4</sup> with 4-formyl phenylboronic acid followed by Knoevenagel condensation with cyanoacetic acid. As a reference compound,  $Cz_2P_4CE$  (3-(4'-(2,2-bis(4-(9*H*-carbazol-9-yl)phenyl)) vinyl) biphenyl- 4-yl)-2-cyanoacrylate), with an ethyl carboxylic group instead of a carboxylic group in  $Cz_2P_4CA$ , was also synthesized. The chemical structure and the synthetic routes to the two cyanoacrylic acid derivatives are depicted in Scheme 1.

#### Responses to water and ethanol

The Cz<sub>2</sub>P<sub>4</sub>CA in dimethylformamide (DMF) showed interesting response sensitivities when water was added. Photoluminescence (PL) emission wavelength and intensity of the solutions with different water fractions (V<sub>H<sub>2</sub>O%) are shown in Fig. 1(*a*). As V<sub>H<sub>2</sub>O%</sub> increased, the change of PL emission wavelength exhibited a 4-step process: first, a blue shift (V<sub>H<sub>2</sub>O</sub>% < 2%), then a red shift (V<sub>H<sub>2</sub>O%</sub> = 2–40%), followed by another blue shift (V<sub>H<sub>2</sub>O%</sub> = 40–50%), and finally another red shift (V<sub>H<sub>2</sub>O%</sub> > 50%). A corresponding change in wavelength was also observed for PL emission intensity: first enhanced (V<sub>H<sub>2</sub>O%</sub> < 8%), then reduced (V<sub>H<sub>2</sub>O%</sub> = 8–40%) again enhanced (V<sub>H<sub>2</sub>O%</sub> = 40–50%), and at last reduced (V<sub>H<sub>2</sub>O%</sub> > 50%).</sub>

To investigate whether the carboxyl group is a major contributor to the above responses in Step 1 and 2, similar experiments were done by using  $Cz_2P_4CE$ . As shown in Fig. 1(*b*), with an increase of water fraction, the fluorescence emission wavelength and intensity of  $Cz_2P_4CE$  exhibits a large difference in comparison to  $Cz_2P_4CA$ . The fluorescence emission intensity of  $Cz_2P_4CE$  in solution was very weak until the water fraction increased to more than 25%. In the 25–50% water fraction region, fluorescence emission intensity increased sharply by about 250-fold, reflecting a notable AIE effect. Photoluminescence photos of  $Cz_2P_4CA$  and  $Cz_2P_4CE$  solutions in DMF with varying water fractions under 365 nm UV irradiation are shown in Fig. 2.

A schematic graph proposed for the 4-step changes is shown in Fig. 3. In Step I, as it is known, DMF is an extremely good H-bond acceptor and its electron donor capacity is even higher than that of water. In other words, the H-bond between  $Cz_2P_4CA$  and DMF is more stable. As the  $V_{H_2O}$ % increased, the strength of the H-bond between  $Cz_2P_4CA$  and DMF would decrease because of competition with water, thus resulting in an increase of the energy level of excitation and the occurrence of a blue shift with enhanced intensity. This is typical intramolecular charge transfer (ICT) fluorescent probe character: more stable H-bond complexes were formed to lower the energy level upon excitation, which resulted in a red shift with reduced intensity when returning to ground state.<sup>5</sup> The effect in this step

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Fig. 1 PL wavelength and intensity of (a)  $Cz_2P_4CA$  and (b)  $Cz_2P_4CE$  (50 $\mu$ M) in DMF with varying amounts of water (% fraction of volume).

(a)  $\bigcup_{0\%} \bigcup_{2\%} \bigcup_{40\%} \bigcup_{50\%} \bigcup_{60\%} \bigcup_{90\%} \bigcup_{90\%}$ (b)  $\bigcup_{0\%} \bigcup_{2\%} \bigcup_{2\%} \bigcup_{2\%} \bigcup_{50\%} \bigcup_{90\%} \bigcup_{90\%}$ 

Fig. 2 Photoluminescence of  $Cz_2P_4CA$  (*a*) and  $Cz_2P_4CE$  (*b*) in DMF solutions with water fractions under UV irradiation (excited at 365 nm).

may be called the H-bond effect. Obviously, it was difficult to find traces of H-bond interactions associated with  $Cz_2P_4CE$ .

In Step II, with an increase of water fraction, the solubility of  $Cz_2P_4CA$  in mixed solvents decreased and led to an increase of  $Cz_2P_4CA$  concentration in DMF, and resulted in the formation of dimers or multimers of  $Cz_2P_4CA$ . The formation of dimers or multimers is the possible reason for the red shift with reduced intensity.



Fig. 3 Schematic graph for the 4-step changes in PL wavelength and intensity during water addition.

From Fig. 1(a), we see that when the water fraction was increased from 2%, the wavelength has a red shift. Yet, PL intensity did not decrease until the water fraction was more than 8%. It was suggested that the change in wavelength was more sensitive than that of intensity. Further evidence was obtained from the excitation spectrum (Fig. 4a): when the water fraction was at or below 4%, there was no 450 nm peak; as the water fraction reached 6%, the 450 nm peak likely reflected dimer formation appeared in the excitation spectrum. The peaks appeared at ~475 nm probably reflected multimer formation in high water fraction (24% and 36%). In comparison, there are no new peaks appeared in the excitation spectra of  $Cz_2P_4CE$  as the increase of water fraction. <sup>1</sup>H NMR spectra of the two compounds in CDCl<sub>3</sub> with varying concentrations (c = 5, 0.5 and 0.05 mM) were carried out to prove the existence of molecular association of carboxylic acid. As the concentration increased, fine <sup>1</sup>H-NMR structures of  $Cz_2P_4CE$  could be still observed. However, the 5 mM solution of Cz<sub>2</sub>P<sub>4</sub>CA did not present a fine <sup>1</sup>H-NMR spectrum (Fig. 5). These different <sup>1</sup>H-NMR behaviors are thought to be related to the different chemical structures of the compounds, because the carboxylic group in  $Cz_2P_4CA$  can form intermolecular hydrogen bonds. Therefore, it is possible that the intermolecular interactions promote molecular association through intermolecular hydrogen bonding to form multimers. It is well known that the existence of multimer (a mixture of dimer, trimer, tetramer,..., etc.) will often result in the disappearance of the fine structures of NMR spectra. The effect of this step may be called the multimer effect.

In Step III, a blue shift with enhanced intensity of PL emission was the consequence of AIE effect. In this region of water fraction,  $Cz_2P_4CA$  would aggregate into suspension as crystal particles, which led to a blue shift of PL emission at 470–490 nm. The suspension was unstable and would form precipitates after several minutes.

In comparison to Step III, the suspension formed in Step IV is transparent and remained stable for months. This formation of a suspension caused a red shift and a reduction in intensity. The suspension was indeed composed of amorphous particles, which was also observed for several AIE compounds in THF–water mixtures.<sup>6</sup> The wide angle X-ray diffraction patterns of the two kinds of particles also showed to be different in some diffraction bands as well as in crystallinity (Fig. 6), and need further detailed identification.



**Fig. 4** Excitation spectrum changes of (*a*)  $Cz_2P_4CA$  and (*b*)  $Cz_2P_4CE$  (50  $\mu$ M) in DMF with varying amounts of H<sub>2</sub>O (% fraction of volume).

400

320 <del>\_</del>i

740 intensity/a.u

Ц

160



Fig. 5 <sup>1</sup>H NMR spectra of CDCl<sub>3</sub> solutions of  $Cz_2P_4CA$  and  $Cz_2P_4CE$  at different concentrations.

The Cz<sub>2</sub>P<sub>4</sub>CA compound in DMF solution can also exhibit a response to ethanol, but is quite different from that for water (Fig. 7). By increasing ethanol fraction (V<sub>ethanol</sub>%), the fluorescence emission wavelength of Cz<sub>2</sub>P<sub>4</sub>CA exhibited a blue shift (V<sub>ethanol</sub>% < 8%) and then a red shift (V<sub>ethanol</sub>% > 8%), while the fluorescence intensity was enhanced the entire time under experimental conditions.



#### **Concentration effect**

Fig. 9 shows the relationship between fluorescence emission and concentration of  $Cz_2P_4CA$  in DMF solution. While fluorescence intensity enhanced sharply by  $\sim 10$  times as the concentration

Wavelenath

516

510

504

498

492

-10 0 10 20 30 40 50 60

μM) in DMF with different ethanol fraction.

Wavelength/nm

PL Intensity

70

V(EtOH) / %

Fig. 7 Fluorescence emission wavelength and intensity of  $Cz_2P_4CA$  (50

80

90

100



Fig. 6 WXRD patterns of the crystal and amorphous particles of  $Cz_2P_4CA$  obtained from the Step III (*a*) and Step IV (*b*).



Fig. 8 Fluorescence emission spectra of  $Cz_2P_4CA$  (50  $\mu$ M) in different solvents.

Table 1 Fluorescence properties of Cz<sub>2</sub>P<sub>4</sub>CA in different solvents

solvent		DMF	DMSO	THF	Dio	HAc	CH <sub>2</sub> Cl <sub>2</sub>
$\lambda_{max}^{em}$ (nm)	a b	489 523	489 504	495 525	506 506	544 549	547 555
$\Phi_{\mathrm{FL}}{}^c$		0.017	0.027	0.053	0.11	0.0027	0.066
and the	50					. 0.10	

 $^{a}$  0.5  $\mu$ M.  $^{o}$  50  $\mu$ M.  $^{c}$  Fluorescence quantum yields, using 9,10-diphenylanthracene as standard.

increased from 0.001 to 0.1 mM, there was a large red shift of  $\sim 50$  nm of the maximum emission wavelength (from 472 nm to 526 nm). It was clear that the compound had a sensitive response to its concentration in the solution in this region. The maximum emission wavelength had a slight red shift, and intensity decreased after enhancing slowly to the maximum of  $\sim 0.6$  mM.

The cyanoacrylic acid moiety must play an important role in these phenomena due to the carboxyl group being capable of forming hydrogen bonds (H-bonds) with solvent molecules. These H-bonds between  $Cz_2P_4CA$  and solvent molecules change the energy level of the ground and excited states of the  $Cz_2P_4CA$  molecule quite similarly to those of typical ICT fluorescent probes.<sup>5b</sup> Meanwhile, the AIE moiety of the  $Cz_2P_4CA$  molecule plays a unique role in these energy level changes. Therefore, there are variations in both fluorescence maximum emission wavelength and fluorescence intensity of the spectra of  $Cz_2P_4CA$  in different solvents and concentrations.

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## Responses to metal ions

Responses of  $Cz_2P_4CA$  to various metal ions (M) were also investigated. Here, the ions are provided from their acetates (M(OAc)<sub>x</sub>, where x = 1 for monovalent metal ion, and 2 for divalent metal ion). As shown in Fig. 10(*a*), a blue shift was observed upon addition of  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$  and  $K^+$ , while a red shift of about 21 nm on addition of  $Zn^{2+}$ . Among these metal ions, the response for  $Zn^{2+}$  is an exceptional case probably due to its d<sup>10</sup> atomic orbital configuration. From Fig. 10(*a*), it can be seen that the compound is particularly sensitive to K<sup>+</sup> with large slope. The  $Cz_2P_4CA$  and  $Cz_2P_4CE$  also showed remarkably different responses for metal ion K<sup>+</sup>: there was a blue shift of 43 nm for  $Cz_2P_4CA$  while only a blue shift of 4 nm for  $Cz_2P_4CE$ when adding 10 equivalent K<sup>+</sup> (Fig. 10(*b*)).

As shown in Fig. 10(*a*), fluorescence quenching was observed for  $Cz_2P_4CA$  upon addition of the above metal ions. The following equation has often been used to describe the static quenching mechanism with good linearity: <sup>7</sup>

$$\log[(I_0 - I)/I] = \log K_a + n\log C$$

where log is the common logarithm, C is the concentration of metal ion in the mixture system,  $I_0$  is the PL intensity of the  $Cz_2P_4CA$  in DMF solution without metal ion, I is the PL intensity of the system while the concentration of metal ion is C,  $K_a$  is the association constant and n is the association ratio.

As seen in Fig. 11, a good linearity between  $\log[(I_0-I)/I]$  and the logC was constructed (linear correlation coefficient



Fig. 10 PL wavelength changes of (*a*)  $Cz_2P_4CA$  (50  $\mu$ M) in DMF with increasing concentrations of metal ions (M(OAc)<sub>x</sub>); and (*b*)  $Cz_2P_4CA$  and  $Cz_2P_4CE$  (50  $\mu$ M) in DMF upon adding KOAc.



**Fig. 9** (*a*) PL emission spectra and (*b*) PL peak wavelength and intensity with varying concentration of  $Cz_2P_4CA$  in DMF solution.



Fig. 11 Plot of  $\log[(I_0-I)/I]$  vs. logC for different metal ions added into  $Cz_2P_4CA$  (50 µM) in DMF.

Table 2 Data of  $K_a$ , n and  $R^2$  of different metal ions for  $Cz_2P_4CA$ 

Ion	$K_a/M^{-1}$	Ν	<b>R</b> <sup>2</sup>
Zn <sup>2+</sup>	51	0.51	0.995
Cu <sup>2+</sup>	148	0.66	0.998
Ni <sup>2+</sup>	117	0.51	0.987
Co <sup>2+</sup>	224	0.56	0.998
Mn <sup>2+</sup>	123	0.49	0.996
K <sup>+</sup>	$1.82 \times 10^{4}$	0.90	0.997

R<sup>2</sup>: 0.995–0.998, see Table 2). According to the above equation, the association ratio (n) of  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$  and  $Mn^{2+}$  with Cz<sub>2</sub>P<sub>4</sub>CA was obtained from 0.49 to 0.66 and thus the stoichiometric ratio between  $Cz_2P_4CA$  and these metal ions was 1 : 2. However, for K<sup>+</sup> n was 0.9, giving a 1 : 1 stoichiometric ratio between  $Cz_2P_4CA$  and K<sup>+</sup>. The association constant, K<sub>a</sub>, for K<sup>+</sup> was  $1.82 \times 10^4 \ \mathrm{M^{-1}}$ , the highest amongst all the metal ions studied here.

## Conclusions

A fluorescent compound Cz<sub>2</sub>P<sub>4</sub>CA with AIE effect and interesting fluorescence responses to water, ethanol and metal ions has been synthesized and characterized. The special response of the compound solution in DMF to water can be explained in terms of H-bond, multimer and AIE effects. It was found that the compound exhibits high sensitivity to K<sup>+</sup> and a different response to Zn<sup>2+</sup>. It is suggested that Cz<sub>2</sub>P<sub>4</sub>CA may be a promising fluorescent probe or chemosensor to investigate the interactions between fluorescent molecules and various media.

## Experimental

#### Materials and Measurements

All reagents and chemicals were purchased from Alfa-Aesar company and used as received. Analytical grade DMF was purified by distillation under an inert nitrogen atmosphere. Ultra-pure water was used in the experiments. All other solvents as analytical grade were purchased from Guangzhou Dongzheng Company and used without further purification.

<sup>1</sup>H-NMR was measured on a Mercury-Plus 300 spectrometer with chemical shifts reported as ppm (in CDCl<sub>3</sub> or DMSO-d<sub>6</sub>, TMS as internal standard). Mass spectra were measured on a Thermo MAT95XP-HRMS spectrometer or a Thermo DSQ-MS spectrometer. Elemental analyses were performed with an Elementar Vario EL Elemental Analyzer. Fluorescence spectra were determined on Shimadzu RF-5301PC spectrometer and the slit width was 3 nm for both excitation and emission. The fluorescent compounds and the metal ions of acetate were all dissolved in DMF in proper proportion.

#### Synthesis of 1

To a stirred carbazole (25.0 g, 0.149 mol) in anhydrous DMF (200 mL), t-BuOK (20.0 g, 0.178 mol) was added and heated to 60 °C, followed by the addition of bis(4-fluorophenyl) methanone (14.8 g, 0.0678 mol). The reaction mixture was then heated to 110 °C for 12 h. The resulting mixture was poured into water (500 mL) and filtered. Washed with water for 3 times and dissolved in CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>. The crude product was recrystallized with acetone to give 1 (32.0 g, 92% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δppm: 7.36 (t, 4 H), 7.48 (t, 4 H), 7.58 (d, 4 H), 7.82 (d, 4 H), 8.19 (d, 8 H). MS (EI) calcd for C<sub>52</sub>H<sub>36</sub>N<sub>2</sub>, 512; found, 512. Anal. Calc. for C52H36N2: C 86.69, H 4.72, N 5.46; Found: C 86.75, H 4.81, N 5.39.

## Synthesis of 2

To a stirred solution of 1 (10.4 g, 0.0203 mol) and diethyl (4-bromophenyl) methylphosphonate (6.20 g, 0.0203 mol) in anhydrous THF (200 mL) at room temperature, t-BuOK (2.20 g, 0.0200 mol) was added under Ar gas. After stirred for 12 h at room temperature, the resulting mixture was poured into ethanol (400 mL) and filtered, washed with ethanol for 3 times and dried to give 2 (12.6 g, 95% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δppm: 7.05 (d, 2H), 7.11 (s, 1H), 7.27-7.57 (m, 16H), 7.58-7.71 (m, 6H), 8.10-8.24 (m, 4H) MS (EI) calcd. for C<sub>44</sub>H<sub>29</sub>N<sub>2</sub>Br 666, found 666. Anal. Calc. for C44H29N2Br: C 79.40, H 4.39, Br 12.00, N 4.21; Found: C 79.31, H 4.42, Br 11.95, N 4.18.

#### Synthesis of 3

2 (3.30 g, 4.96  $\times$  10<sup>-3</sup> mol) and 4-formylphenylboronic acid (0.750 g, 5.00  $\times$  10<sup>-3</sup> mol) were dissolved in the mixture of toluene (20.0 mL), TBAB (1.00 g) and 2M potassium carbonate aqueous solution (5 mL). The mixture was stirred at room temperature for 0.5 h under Ar gas followed adding tetrakis(triphenylphosphine)palladium (0.0100 g,  $8.70 \times 10^{-6}$  mol) and then heated to 90 °C for 24 h. After that the mixture was poured into water and extracted three times with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto silica gel column with n-hexane– $CH_2Cl_2$  (1 : 1, v/v) as eluent to give 3 (1.90 g, 55% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δppm: 7.24 (s, 1H), 7.26–7.37 (m, 6H), 7.42–7.79 (m, 20H), 7.95 (d, 2H), 8.13-8.22 (m, 4H), 10.05 (s, 1H) MS (EI) calcd. for  $C_{51}H_{34}N_2O$  690, found 690. Anal. Calc. for C<sub>51</sub>H<sub>34</sub>N<sub>2</sub>O: C 88.67, H 4.96, N 4.06; Found: C 88.61, H 4.92, N 4.03.

## Synthesis of Cz<sub>2</sub>P<sub>4</sub>CA

**3** (0.330 g,  $4.78 \times 10^{-4}$  mol), cyanoacetic acid (0.0800 g,  $9.41 \times 10^{-4}$  mol), and piperidine (20 drops) were added to 100 mL acetonitrile. The mixture was refluxed for 20 h. Then the solvent was removed and the residue was purified by column chromatography with CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (10 : 1, v/v) as eluent to give **4** (0.330 g, 91% yield). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ ppm: 7.26–7.35 (m, 4H), 7.40–7.91 (m, 22H), 7.92–8.03 (m, 4H), 8.21–8.31 (m, 4H); MS (FAB) calc. for C<sub>54</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub> 758, found 758; Anal. Calc. for C<sub>54</sub>H<sub>35</sub>N<sub>3</sub>O<sub>2</sub>: C 85.58, H 4.65, N 5.54. Found: C 85.62, H 4.41, N 5.67.

## Synthesis of Cz<sub>2</sub>P<sub>4</sub>CE

**3** (0.100 g,  $1.45 \times 10^{-4}$  mol), ethyl cyanoacetate (0.0400 g,  $3.54 \times 10^{-4}$  mol), and piperidine (10 drops) were added to 40.0 mL acetonitrile. The mixture was refluxed for 20 h. Then the solvent was removed and the residue was purified by column chromatography with n-hexane–CH<sub>2</sub>Cl<sub>2</sub> (1 : 2, v/v) as eluent to give **5** (0.100 g, 88% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 1.42 (t, 3H), 4.41 (d, 2H), 7.23 (s, 1H), 7.27–7.37 (m, 6H), 7.41–7.79 (m, 20H), 8.08 (d, 2H), 8.17 (d, 4H), 8.27 (s, 1H) MS (EI) calcd. for C<sub>56</sub>H<sub>39</sub>N<sub>3</sub>O<sub>2</sub> 786, found 786. Anal. Calc. for C<sub>56</sub>H<sub>39</sub>N<sub>3</sub>O<sub>2</sub>: C 85.58, H 5.00, N 5.35; found C 85.61, H 4.98, N 5.31.

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