

Comparison of Responsive Behaviors of Two Cinnamic Acid Derivatives Containing Carbazolyl Triphenylethylene

Xi-qi Zhang · Zhen-guo Chi · Bing-jia Xu · Hai-yin Li ·
Wei Zhou · Xiao-fang Li · Yi Zhang · Si-wei Liu ·
Jia-rui Xu

Received: 8 April 2010 / Accepted: 22 June 2010 / Published online: 1 July 2010
© Springer Science+Business Media, LLC 2010

Abstract Two cinnamic acid derivatives (**CPA** and **CPC**) containing carbazolyl triphenylethylene moiety have been synthesized and characterized. The two derivatives possessed aggregation-induced emission property. They exhibited different and interesting responsive behaviors to solvents, water and metal ions. Considering the structural differences between the two derivatives resulting in different interactions between their molecules and the various media was proposed as a possible explanation for these observations. The intermolecular interactions of **CPC** were much stronger than those of **CPA**, which promoted molecular association through intermolecular hydrogen bonding to form multimers. It was found that **CPC** and **CPA** exhibited high sensitivity to K^+ and Mn^{2+} , respectively. It is suggested that the derivatives have potential technological applications in chemosensor fields.

Keywords Cinnamic acid derivative · Responsive behavior · Chemosensor · Carbazolyl triphenylethylene · Aggregation-induced emission

Electronic supplementary material The online version of this article (doi:10.1007/s10895-010-0697-y) contains supplementary material, which is available to authorized users.

X.-q. Zhang · Z.-g. Chi (✉) · B.-j. Xu · H.-y. Li · W. Zhou ·
X.-f. Li · Y. Zhang · S.-w. Liu · J.-r. Xu (✉)
PCFM Lab, DSAPM Lab, FCM Institute, State Key Laboratory of
Optoelectronic Materials and Technologies, School of Chemistry
and Chemical Engineering, Sun Yat-sen University,
Guangzhou 510275, China
e-mail: chizhg@mail.sysu.edu.cn
e-mail: xjr@mail.sysu.edu.cn

Introduction

Fluorescent chemosensors are receiving increasing attention due to their potential applications in analytical chemistry, the life sciences, medical analysis, and environmental monitoring [1–7]. As a new class of fluorescent materials, aggregation-induced emission (AIE) materials that are highly luminescent in their aggregation states have attracted much interest owing to their unique properties [8]. Tang et al. have very recently employed a hexaphenylsilole derivative to detect DNA and proteins by making use of the AIE phenomenon [9, 10].

Recently, a series of compounds containing triphenylethylene moiety with AIE properties and favorable thermal stabilities have been developed in our laboratory [11, 12]. In order to improve the responsibility of the compounds to better use as a chemosensor, we introduced the cinnamic acid unit to the compounds and obtained cinnamic acid derivatives. In our previous study, we have found that a cinnamic acid derivative, **CPC**, exhibited interesting fluorescence multi-responses to solvents, water and metal ions [13]. In this paper, we will further report the different responsive behaviors resulting from their special chemical structures between **CPC** and the other derivative, **CPA**.

Experimental

Materials and methods

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 were analytical grade and purchased

from Guangzhou Dongzheng Company and used without further purification. Intermediates **1** and **2** were synthesized according to our previous procedure [11–13].

¹H-NMR was measured on a Mercury-Plus 300 spectrometer and ¹³C-NMR spectra were recorded on a Varian INOVA500NB spectrometer with chemical shifts reported as ppm (in CDCl₃ or DMSO-d₆, 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. UV-Vis spectra were obtained using a Shimadzu UV-Vis-NIR Spectrophotometer UV-3150. Fluorescence spectra were determined on a Shimadzu RF-5301PC spectrometer with a slit width of 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 compound **3**

2 (3.3 g, 5 mmol) and 4-formylphenylboronic acid (0.75 g, 5 mmol) were dissolved in the mixture of toluene (20 mL), TBAB (1 g) and 2 M potassium carbonate aqueous solution (5 mL). The mixture was stirred at room temperature for 0.5 h under Ar gas, followed by addition of tetrakis(triphenylphosphine)palladium (0.01 g) and then heated to 90 °C for 24 h. After this, 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 a silica gel column with n-hexane/CH₂Cl₂ (1:1, v/v) as eluent to give **3** (1.9 g, 55% yield). ¹H NMR (300 MHz, CDCl₃) 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 C₅₁H₃₄N₂O 690, found 690. Anal. Calc. for C₅₁H₃₄N₂O: C 88.67, H 4.96, N 4.06. Found: C 88.63, H 4.91, N 4.10.

Synthesis of the compound **CPA**

To a stirred solution of **3** (0.45 g, 0.65 mmol) and ethyl 2-(diethoxyphosphoryl) acetate (0.16 g, 0.71 mmol) in anhydrous THF (10 mL) at room temperature, t-BuOK (0.24 g, 2.14 mmol) was added under Ar gas. After stirred for 12 h at room temperature, the resulting mixture was acidified by 5 mL concentrated HCl and poured into 50 mL water. And then, the mixture was extracted three times with methylene chloride. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was loaded onto a silica gel column with CH₂Cl₂/methanol (20:1, v/v) as eluent to give 0.25 g yellow solid **CPA** (52% yield). ¹H NMR (300 MHz, DMSO-d₆) δ ppm: 7.24–7.35 (m, 6H),

7.41–7.78 (m, 24H), 7.98 (d, 1H), 8.25 (q, 4H); ¹³C NMR (125 MHz, DMSO-d₆) δ ppm: 167.47, 143.27, 140.95, 140.82, 140.41, 140.02, 139.94, 138.82, 137.70, 136.34, 133.38, 131.64, 130.09, 129.87, 128.78, 128.63, 128.50, 127.36, 126.76, 126.51, 126.26, 122.77, 120.50, 120.10, 119.10, 109.65; IR (KBr) ν: 3044, 1682, 1623, 1599, 1513, 1477, 1451, 1421, 1361, 1334, 1315, 1229, 1170, 835, 816, 748, 723 cm⁻¹; MS (FAB) calcd. for C₅₃H₃₆N₂O₂ 733, found 733; Anal. Calc. for C₅₃H₃₆N₂O₂: C 86.86, H 4.95, N 3.82. Found: C 86.81, H 4.92, N 3.79.

Synthesis of the compound **CPC**

3 (0.33 g, 0.48 mmol), cyanoacetic acid (0.08 g, 0.94 mmol), and piperidine (20 drops) were added to 100 mL acetonitrile. The mixture was refluxed for 20 h. The solvent was then removed and the residue was purified by column chromatography with CH₂Cl₂/CH₃OH (10:1, v/v) as eluent to give **CPC** (0.33 g, 91% yield). ¹H NMR (300 MHz, DMSO-d₆) δppm: 7.26–7.35 (m, 4H), 7.40–7.91 (m, 22H), 7.92–8.03 (m, 4H), 8.21–8.31 (m, 4H); ¹³C NMR (125 MHz, DMSO-d₆) δppm: 163.19, 148.02, 141.67, 140.95, 140.56, 140.02, 139.94, 138.79, 137.39, 136.63, 136.36, 132.00, 131.64, 130.18, 130.12, 128.65, 128.47, 127.39, 126.81, 126.52, 126.42, 126.27, 122.78, 120.51, 120.11, 118.64, 109.66; IR (KBr) ν: 3424, 3049, 2217, 1624, 1597, 1513, 1478, 1451, 1391, 1363, 1334, 1314, 1228, 1191, 1171, 835, 817, 750, 723 cm⁻¹; MS (FAB) calc. for C₅₄H₃₅N₃O₂ 758, found 758; Anal. Calc. for C₅₄H₃₅N₃O₂: C 85.58, H 4.65, N 5.54. Found: C 85.62, H 4.41, N 5.67.

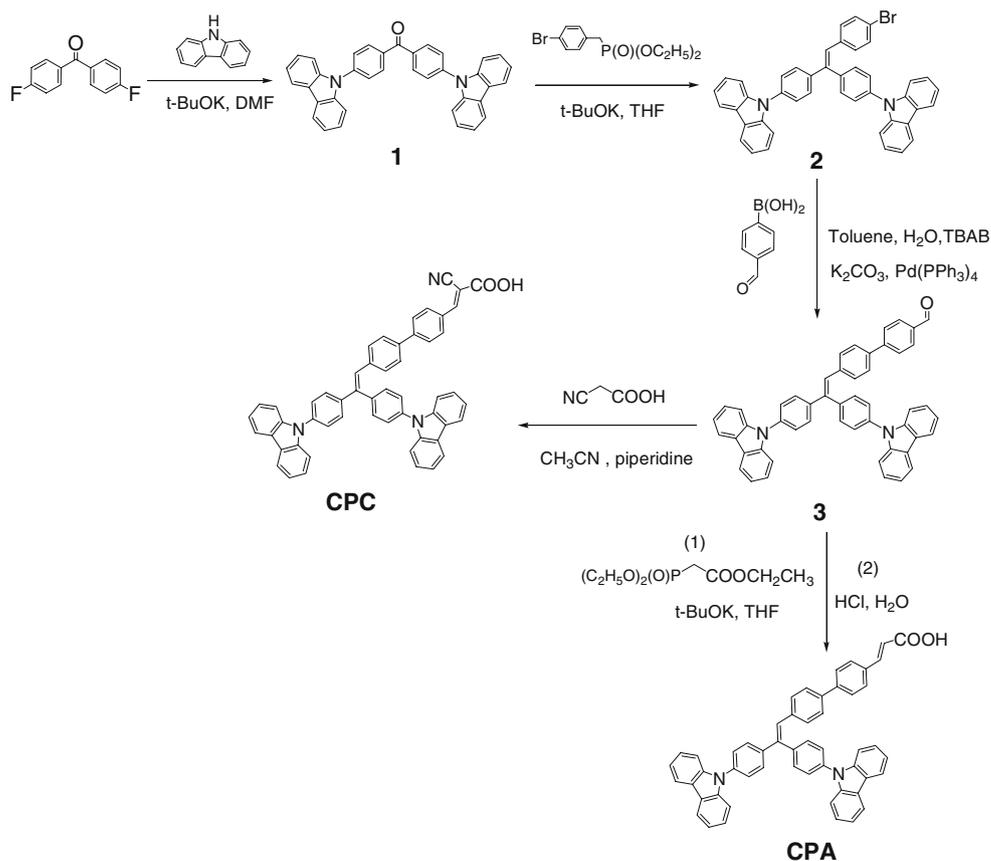
Results and discussion

Synthesis

The two cinnamic acid derivatives were prepared according to the synthesis route shown in Scheme 1. **CPC** was synthesized according to our previous procedure [13]. The new compound, **CPA**, was prepared with **3** and ethyl 2-(diethoxyphosphoryl)acetate by Wittig-Horner reaction. From Scheme 1, we can see that **CPA** has a similar chemical structure to **CPC**, except that the H in **CPA** is replaced by a cyano group in **CPC**. Both structures include the dicarbazol-triphenylethylene moiety, which provides the unique AIE feature [11].

Responses to solvents

To study the responses of **CPA** and **CPC** to solvents, the UV and photoluminescence (PL) spectra (Fig. 1S, 2S, in the Supplementary Information) of the compounds were measured in five common solvents at the same concentration (10⁻⁵ M), as summarized in Table 1. Table 1 shows that the

Scheme 1 Synthetic routes of **CPC** and **CPA**

optical properties of both **CPA** and **CPC** did not monotonically change with increasing solvent polarity (polarity order: methylene chloride (MC) < tetrahydrofuran (THF) < dioxane (DX) < N,N-dimethyl formamide (DMF) < dimethyl sulfoxide (DMSO)) due to the existence of H-bond interactions between the compounds and the solvents, except MC. The maximum emission wavelengths for **CPA** and **CPC** shifted from 463 nm (in DX) to 486 nm (in MC) and from 474 nm (in DMF) to 547 nm (in MC), respectively. The carboxylic acid moiety must play an important role in these phenomena due to the carboxyl groups being capable of forming hydrogen bonds (H-bonds) with solvent molecules. Although the solvent responses were quite different, both of the compounds exhibited the strongest emission in DX and the most red-shifted emission in MC. It is known that MC

cannot form hydrogen bonds with carboxylic acids, thus, it is possible that the carboxylic acid moieties form molecular associations through intermolecular hydrogen bonding interactions and may be responsible for the red-shift in emission wavelength.

Responses to water

CPA and **CPC** showed interesting responsive sensitivities when water was added into their solutions in DMF (Fig. 3S, in the Supplementary Information). PL emission wavelengths and fluorescence images of the solutions with different water fractions ($V_{\text{H}_2\text{O}}\%$) are shown in Figs. 1 and 2, respectively. As $V_{\text{H}_2\text{O}}\%$ increased, the changes in PL emission wavelength exhibited a 3-step (redshift-blueshift-

Table 1 Optical properties of **CPA/CPC** in different solvents

	$\lambda_{\text{max}}^{\text{abs}}$ (nm)		$\lambda_{\text{max}}^{\text{em}}$ (nm)		PL(a.u.)		$\lambda_{\text{max}}^{\text{ex}}$ (nm)		$\Phi_{\text{FL}}^{\text{a}}$	
	CPA	CPC	CPA	CPC	CPA	CPC	CPA	CPC	CPA	CPC
MC	343	373	486	547	90	292	377	397	2.1	6.6
THF	342	367	466	495	78	297	376	382	1.6	5.3
DX	340	370	463	506	164	954	377	398	2.9	11
DMF	344	361	478	474	125	44	377	383	2.1	1.1
DMSO	344	364	471	489	136	133	378	383	3.1	2.7

^a Quantum yields (Φ_{FL}) were calculated on the basis of 9,10-diphenylanthracene as standard

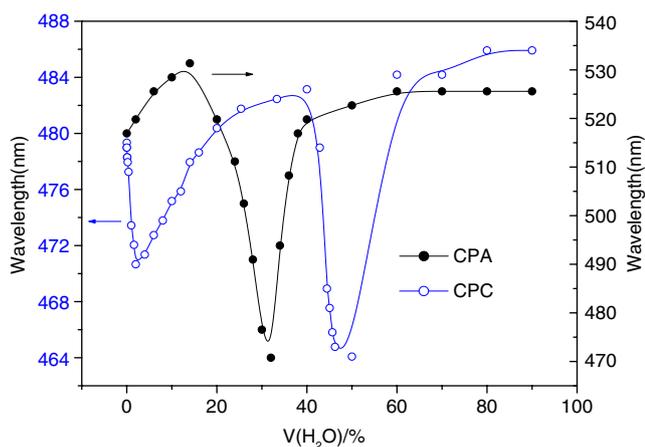


Fig. 1 PL emission wavelength of **CPA** and **CPC** (50 μ M) in DMF with different H_2O fractions

redshift) or a 4-step (blueshift-redshift-blueshift-redshift) process for **CPA** and **CPC**, respectively. The fluorescent responsive behaviors of **CPA** and **CPC**, with rich color changes in DMF and water mixtures, were probably caused by the synergistic interaction between the compound molecules and the media, such as the H-bond effect, the effect of molecular associations with carboxylic acids and the AIE effect. These results suggest that the compounds are potential materials for use as probes to detect intermolecular interactions.

Responses to concentrations

It is well known that two carboxylic groups can be connected by hydrogen bonds to form dimers, trimers and so on, up to multimers (commonly called a molecular

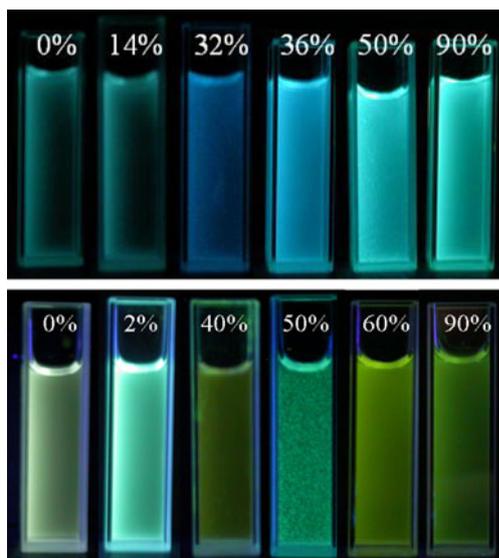


Fig. 2 Photographs of **CPA** (top) and **CPC** (bottom) (50 μ M) in DMF with different H_2O fractions

association). To experimentally verify the existence of molecular associations with carboxylic acid, absorption, emission and excitation spectra of **CPA** and **CPC** were recorded at a wide range of concentrations in DMF solutions.

When investigating concentration responses on the fluorescence emission of **CPA** and **CPC** in DMF solutions, a remarkable modification in the fluorescence spectra was observed as the concentration increased (Fig. 3 and Fig. 4S, 5S in the Supplementary Information), while the wavelength of UV absorption (Fig. 6S, in the Supplementary Information) changed very little. As the concentration of **CPC** increased from 0.001 mM to 0.1 mM, there was larger red shift (~ 50 nm, from 472 nm to 526 nm) in the maxima emission wavelength than that of **CPA** (~ 13 nm, from 468 nm to 481 nm). It is clear that both compounds gave a sensitive response to concentration in this concentration range and that **CPC** is more sensitive than **CPA**. The emission wavelength showed almost no change for **CPA** when the concentration was higher than 0.1 mM. However, for **CPC**, the wavelength gradually increased with concen-

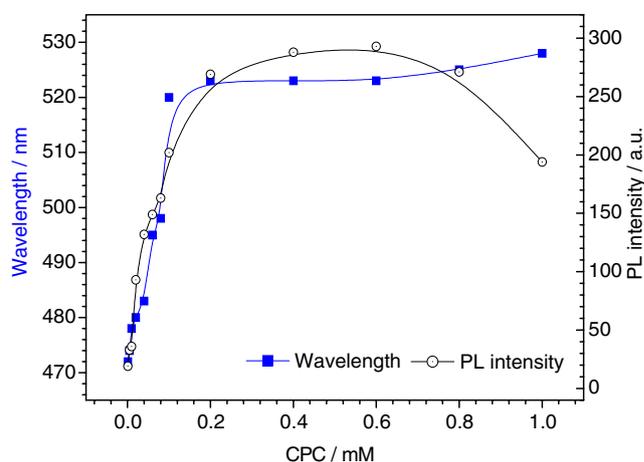
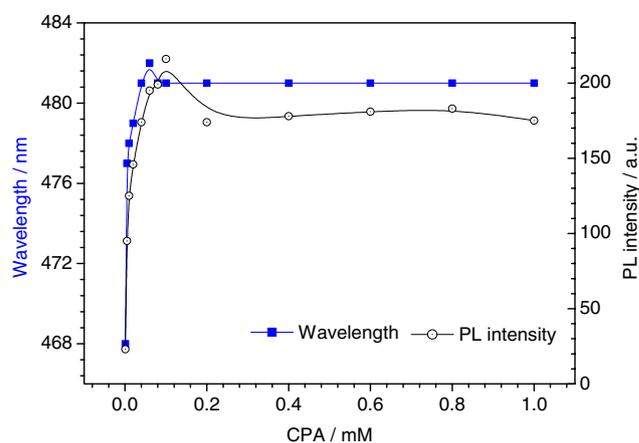


Fig. 3 PL emission spectra of **CPA** (top) and **CPC** (bottom) in DMF at different concentrations

tration over the entire concentration range. From the excitation spectra (Fig. 4), it can be clearly seen that new peaks appeared around 450–500 nm when the concentration of **CPC** was increased above 0.06 mM. However, no new peaks appeared for **CPA**. These results imply that the cyano group or the cyanoacrylic acid moiety in **CPC** plays an important role.

It is well known that the emission wavelength of a fluorescent molecule is independent of excitation wavelength. Thus, it can be used for component qualitative analysis according to the emission spectra obtained at different excitation wavelengths. Figure 5 shows the excitation spectra and fluorescence emission spectra of **CPA** and **CPC** in DMF solution excited at different wavelengths. The 0.1 mM solutions were excited by 398 nm, 410 nm and 435 nm and the 0.08 mM solutions were excited by 402 nm, 410 nm and 435 nm, respectively.

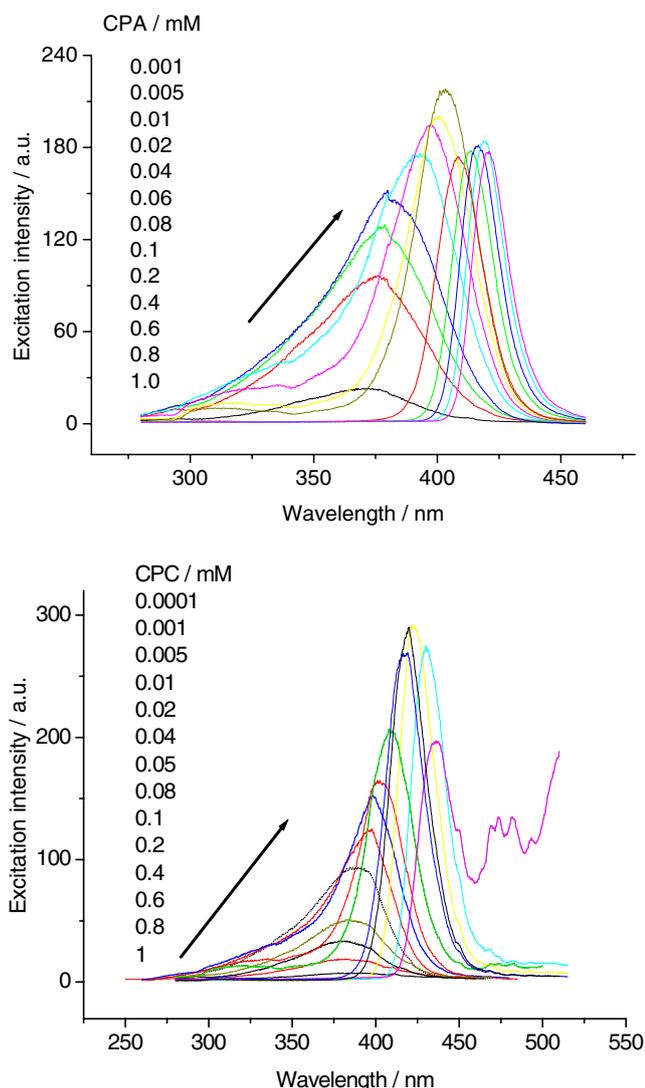


Fig. 4 Excitation spectra of **CPA** and **CPC** in DMF at different concentrations

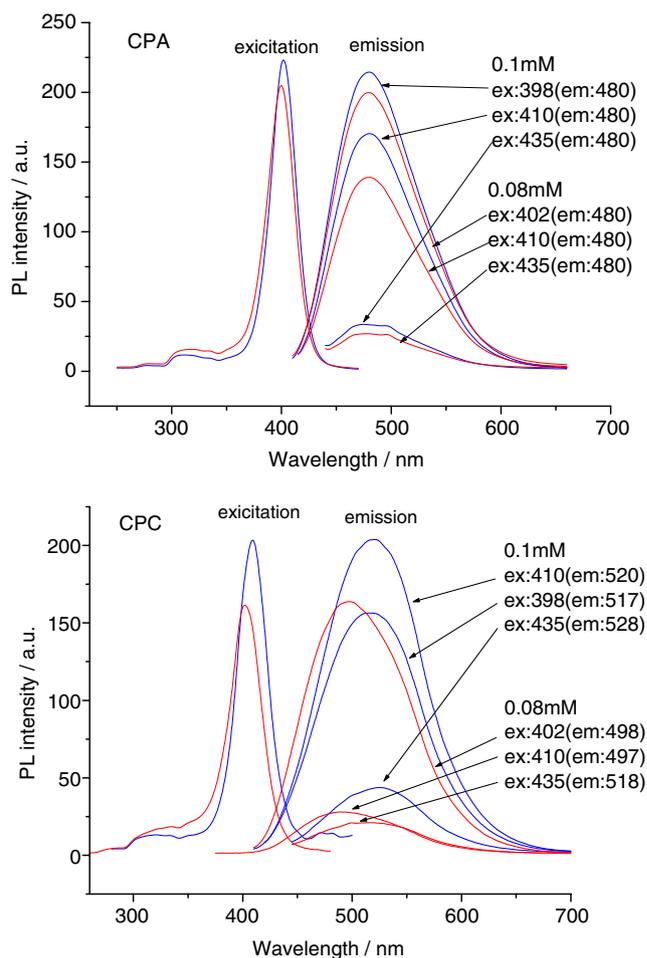


Fig. 5 PL excitation and emission spectra of **CPA** and **CPC** in DMF ($c=0.1$ mM and 0.08 mM) by different excited wavelengths

Although the **CPA** solutions were excited by different wavelengths, the maximum emission wavelengths were the same, 480 nm, which indicated that a single fluorescent-emitting component was present at concentrations of either 0.1 mM or 0.08 mM. It can be also seen that the shapes of the two excitation spectra were identical. However, for **CPC** solutions, the maximum emission wavelengths obtained under different excited wavelengths were different. For 0.1 mM solution, under excitation at 398 nm, 410 nm and 435 nm, the maximum emission wavelengths obtained were 517 nm, 520 nm and 528 nm. For 0.08 mM solutions, under excitation at 402 nm, 410 nm and 435 nm, they were 498 nm, 497 nm and 518 nm, respectively. On the other hand, the shapes of the two excitation spectra were different. It can be seen that new weak peaks at ~ 480 nm appeared in the excitation spectrum of the 0.1 mM solution. The results indicate that the fluorescent-emitting component was not unique and it was thought that there existed various molecular associations of carboxylic acids (dimers, trimers, ..., multimers or mixtures) in the solution.

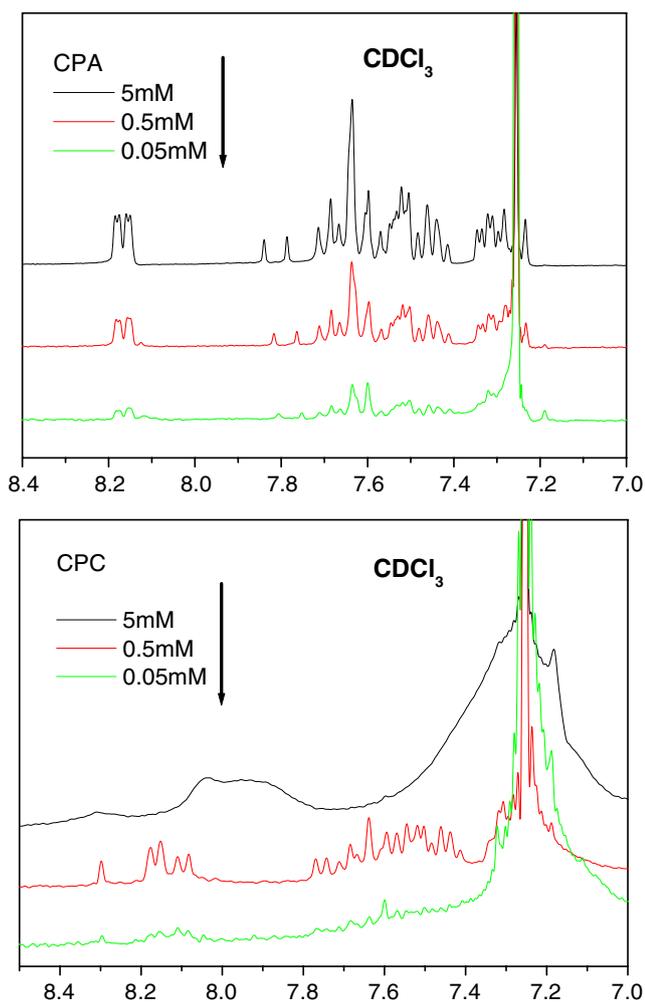


Fig. 6 $^1\text{H-NMR}$ of CPA and CPC in CDCl_3 at different concentrations

Figure 6 shows the $^1\text{H-NMR}$ spectra of the compounds in CDCl_3 at different concentrations ($c=5, 0.5$ and 0.05 mM). As the concentration increased, fine $^1\text{H-NMR}$ structures of CPA could still be observed. However, the 5 mM solution of CPC did not present a fine $^1\text{H-NMR}$

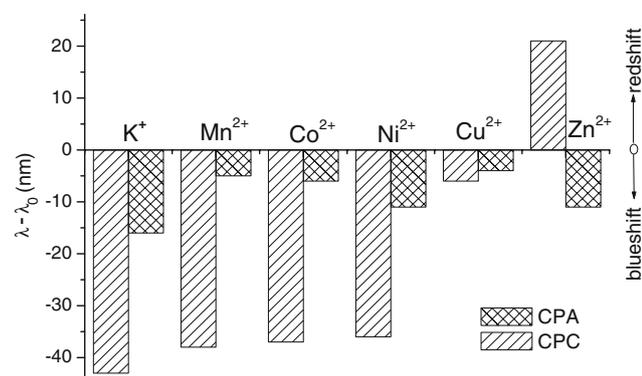


Fig. 7 PL wavelength changes of CPA and CPC in DMF ($50\ \mu\text{M}$) with metal ions 0.5 mM

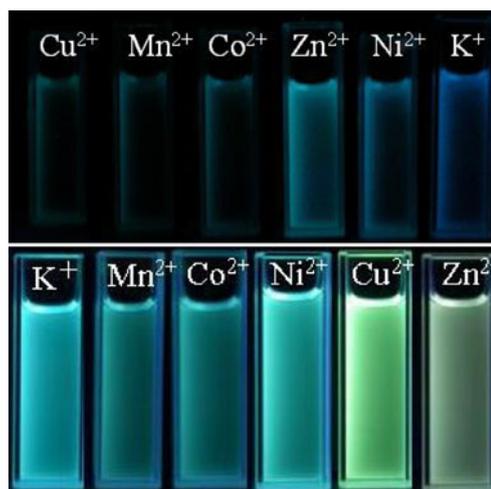


Fig. 8 Photographs of CPA (top) and CPC (bottom) ($50\ \mu\text{M}$) in DMF with 0.5 mM metal ions

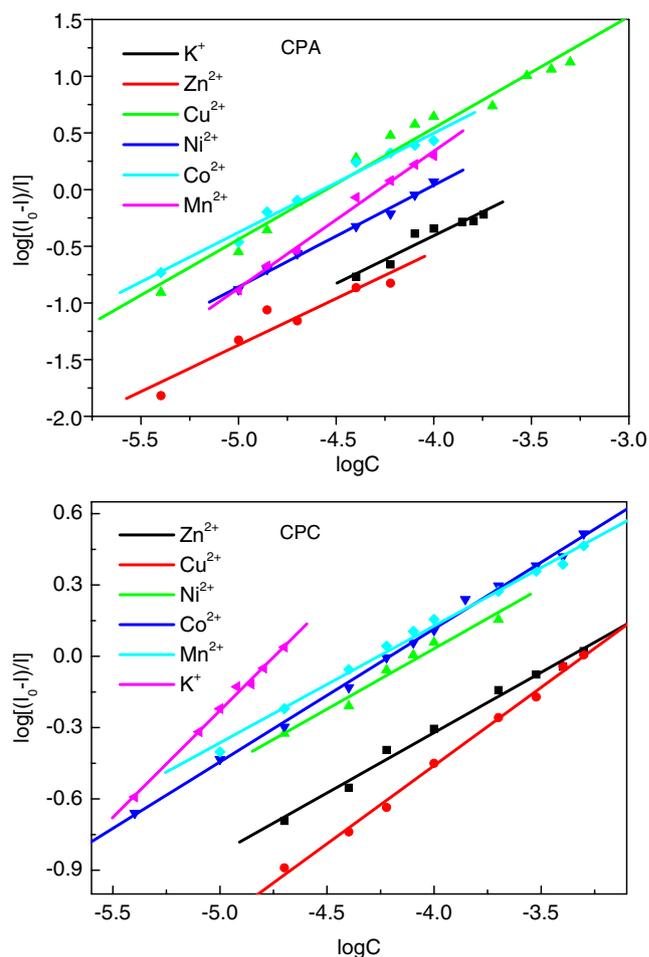


Fig. 9 Plot of $\log[(I_0 - I)/I]$ vs $\log C$ for different metal ions added into CPA and CPC ($50\ \mu\text{M}$) in DMF

Table 2 The parameters of **CPA/CPC** with different metal ions obtained from the fluorescent static quenching mechanism

Ion	$K_a(M^{-1})$		n		R^2	
	CPA	CPC	CPA	CPC	CPA	CPC
Zn ²⁺	5.39×10^2	51	0.82	0.51	0.952	0.995
Cu ²⁺	2.97×10^4	148	0.98	0.66	0.988	0.998
Ni ²⁺	4.21×10^3	117	0.90	0.51	0.996	0.987
Co ²⁺	9.90×10^3	224	0.87	0.56	0.991	0.998
Mn ²⁺	1.47×10^5	123	1.21	0.49	0.996	0.996
K ⁺	9.22×10^2	1.82×10^4	0.84	0.90	0.958	0.997

spectrum. These different ¹H-NMR behaviors are thought to be related to the different chemical structures of the compounds in solution. It is well known that the introduction of a cyano group can significantly increase intermolecular interactions because of its high polarity and ability of form hydrogen bonds. Therefore, it is possible that the intermolecular interactions of **CPC** are much stronger than those of **CPA**, which promotes molecular association through intermolecular hydrogen bonding to form multimers.

Responses to metal ions

We also investigated the response behaviors of **CPA** and **CPC** towards various metal ions in acetate form. As shown in Figs. 7 and 7S (in the Supplementary Information), a blue shift with **CPA** was observed upon addition of Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺ and K⁺. However, for **CPC**, a red shift of about 21 nm occurred on addition of Zn²⁺. Clearly,

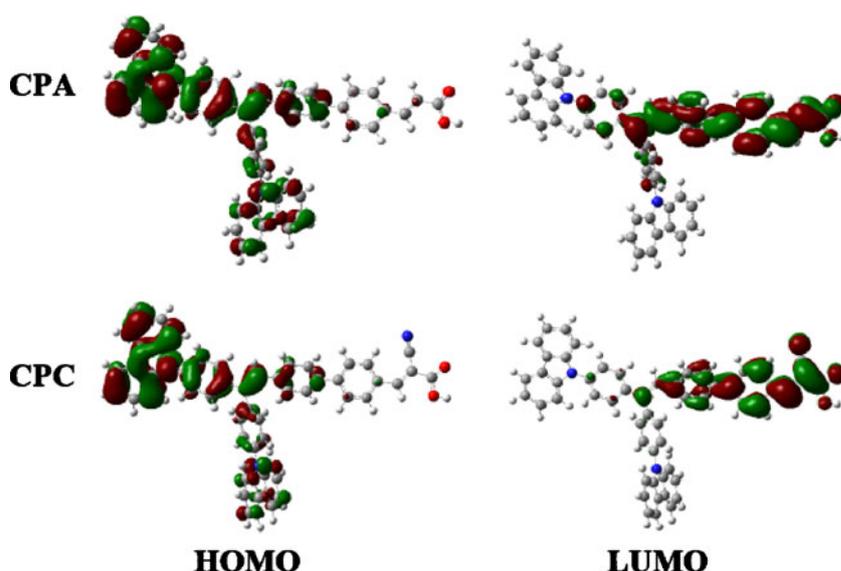
among these metal ions, the responsive behavior of **CPC** for Zn²⁺ is an exceptional case, probably due to its atomic orbital configuration. It can be seen clearly that **CPC** and **CPA** are particularly sensitive to K⁺ and Mn²⁺, respectively. It is very clear that simple modification of the substituent groups of the cinnamic acid derivatives containing carbazoyl triphenylethylene can dramatically influence their response behaviors. Figure 8 shows photographs of the solution of **CPA**-metal ion or **CPC**-metal ion under irradiation at 365 nm.

As shown in Fig. 8S (in the Supplementary Information), fluorescence quenching was observed for **CPA** and **CPC** upon addition of the above metal ions. The following equation has often been used to describe the static quenching mechanism, with good linearity [14]:

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

Where log is the common logarithm, C is the concentration of metal ion in the mixture system, I₀ is the PL intensity of the **CPC** 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. 9, a good linearity between $\log[(I_0 - I)/I]$ and the logarithm of the concentration of metal ion (C) (linear correlation coefficient R²: 0.995–0.998 for **CPC**, and 0.952–0.996 for **CPA**, respectively) was constructed. The parameters were listed in Table 2. According to the above equation, the association ratio (n) of Zn²⁺, Cu²⁺, Ni²⁺, Co²⁺ and Mn²⁺ with **CPC** was obtained from 0.49 to 0.66 and thus the stoichiometric ratio between **CPC** and these metal ions was 1:2. However, for K⁺ n was 0.9, giving a 1:1 stoichiometric ratio between **CPC** and K⁺. The association constant, K_a, for K⁺ was $1.82 \times 10^4 M^{-1}$, the highest amongst

Fig. 10 Calculated spatial distributions of LUMO and HOMO of **CPA** and **CPC**

all the metal ions studied here. In contrast, for **CPA**, n was in the range 0.82–1.21, thus the stoichiometric ratio between **CPA** and these metal ions was 1:1. K_a for Mn^{2+} was the highest amongst the metal ions.

Molecular energy levels of the compounds

To better understand the structure-property relationships of the two derivatives, it would be very helpful to study their molecular energy levels and electronic structures. The lowest unoccupied molecular orbital/highest occupied molecular orbital (LUMO/HOMO) energy gaps (ΔE_g) for **CPA** and **CPC** were estimated from the onset absorption wavelengths of UV absorption spectra and were 2.98 eV and 2.75 eV, respectively. The HOMO energy levels of the two derivatives were obtained using the onset oxidation potentials from cyclic voltammetry (CV) curves and the HOMO values of **CPA** and **CPC** were 5.59 eV and 5.52 eV, respectively. Thus, the LUMO energy levels of **CPA** and **CPC** were 2.61 eV and 2.77 eV, respectively. From the energy levels, it could be seen that **CPC** exhibited lower band gap and higher LUMO than **CPA**, which might result in essential differences in responsive behaviors to solvents, water and metal ions between the two derivatives. To gain insight as to why the two derivatives exhibited the differences in energy levels, we obtained their HOMOs and LUMOs based on B3LYP/6-31G(d) calculations [15] (Fig. 10). The calculation results showed that the majority of the electron distribution of the HOMO was located on the carbazolyl triphenylethylene moiety, and the LUMO distribution resided on the cinnamic acid moiety. The electron distribution of the HOMOs of the two compounds were very similar to each other. However, due to the effect of cyano group (CN), the electron of the LUMO of **CPC** distributed much more concentrated on the cinnamic acid moiety. From Fig. 10, we could also see that there existed antibonding repulsion between p-orbitals in CN and C = C, which caused **CPC** to be high LUMO energy level.

Conclusions

Two fluorescent compounds, **CPA** and **CPC**, were synthesized, possessing AIE effects and interesting fluorescence responses to solvents, water, and metal ions. The response behaviors of the compounds are different due to the difference of their chemical structures. It was found that **CPC** exhibits high sensitivity to K^+ and a different response to Zn^{2+} . It is therefore clear that simple modification of the substituent group of the cinnamic acid derivatives containing carbazolyl triphenylethylene can dramatically influence their response behaviors.

Acknowledgements The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant numbers: 50773096, 50473020), the Start-up Fund for Recruiting Professionals from “985 Project” of SYSU, the Science and Technology Planning Project of Guangdong Province, China (Grant numbers: 2007A010500001-2), Construction Project for University-Industry cooperation platform for Flat Panel Display from The Commission of Economy and Informatization of Guangdong Province (Grant numbers: 20081203), and the Open Research Fund of State Key Laboratory of Optoelectronic Materials and Technologies.

References

- Amendola V, Fabbrizzi L, Licchelli M, Mangano C, Pallavicini P, Parodi L, Poggi A (1999) Molecular events switched by transition metals. *Coord Chem Rev* 190–192:649–669
- De Silva AP, Gunaratne HQN, Gunnlaugsson T, Huxley AJM, McCoy CP, Rademacher JT, Rice TE (1997) Signaling recognition events with fluorescent sensors and switches. *Chem Rev* 97:1515–1566
- Wiegmann TB, Welling LW, Beatty DM, Howard DE, Vamos S, Morris JA (1993) Simultaneous imaging of intracellular $[Ca^{2+}]$ and pH in single MDCK and glomerular epithelial cells. *J Physiol* 265:C1184–C1190
- Salvador JM, Inesi G, Rigaud JL, Mata AM (1998) Ca^{2+} transport by reconstituted synaptosomal ATPase is associated with H^+ countertransport and net charge displacement. *J Biol Chem* 273:18230–18234
- Vo-Dinh T, Viallet P, Ramirez L, Pal A, Vigo J (1994) Detection of cadmium ion using the fluorescence probe Indo-1. *Anal Chim Acta* 295:67–72
- Hirshfeld KM, Toptygin D, Grandhige G, Packard BZ, Brand L (1998) A nanosecond fluorescence study of the simultaneous influx of Ca^{2+} and Cd^{2+} into liposomes. *Biophys Chem* 71:63–72
- Yuasa J, Fukuzumi S (2006) An Off-On fluorescence sensor for metal ions in stepwise complex formation of 2, 3, 5, 6-tetrakis(2-pyridyl)pyrazine with metal ions. *J Am Chem Soc* 128:15976–15977
- Liu JZ, Lam JWY, Tang BZ (2009) Aggregation-induced emission of silole molecules and polymers: fundamental and applications. *J Inorg Organomet Polym* 19:249–285
- Dong Y, Lam JWY, Qin A, Li Z, Liu J, Sun J, Dong Y, Tang B (2007) Endowing hexaphenylsilole with chemical sensory and biological probing properties by attaching amino pendants to the silolyl core. *Chem Phys Lett* 446:124–127
- Wang M, Zhang D, Zhang G, Tang Y, Wang S, Zhu D (2008) Fluorescence turn-on detection of DNA and label-free fluorescence nuclease assay based on the aggregation-induced emission of silole. *Anal Chem* 80:6443–6448
- Yang Z, Chi Z, Yu T, Zhang X, Chen M, Xu B, Liu S, Zhang Y, Xu J (2009) Triphenylethylene carbazole derivatives as a new class of AIE materials with strong blue light emission and high glass transition temperature. *J Mater Chem* 19:5541–5546
- Xu B, Chi Z, Yang Z, Chen J, Deng S, Li H, Li X, Zhang Y, Xu N, Xu J (2010) Facile synthesis of a new class of aggregation-induced emission materials derived from triphenylethylene. *J Mater Chem*. doi:10.1039/C0JM00229A
- Zhang X, Yang Z, Chi Z, Chen M, Xu B, Wang C, Liu S, Zhang Y, Xu J (2010) A multi-sensing fluorescent compound derived from cyanoacrylic acid. *J Mater Chem* 20:292–298
- Feng X, Bai C, Lin Z, Wang N, Wang C (1998) The interaction between acridine orange and bovine serum albumin. *Chin J Anal Chem* 26:154–157
- Frisch MJ, Trucks GW, Schlegel HB et al (2004) Gaussian 03. Revision D.01. Gaussian, Inc, Wallingford