Determination Limit of Fluorescence Turn-On Probes for the Acetate Anion

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Three fluorescent turn-on probes containing 3,6-dichloro-9*H*-carbazole as carbazyl part have been designed and synthesized. Among studied anions F^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^- and I^-, AcO^- showed the strongest binding ability with all probes. The strong basic anions, such as AcO^-, $H_2PO_4^-$, and F^-, induced a significant red-shift in absorption and a concomitant increase in fluorescent emission of the probes caused by photoinduced electron transfer (PET). The determination limit of probe **3** (*Scheme 1*) toward AcO^- is 3.0×10^{-7} M. ^{1}H-NMR Titration experiments shed light on the nature of the interaction between the probes and the anions. Theoretical investigation further illustrated the possible binding mode in these host–guest interactions and the roles of molecular frontier orbitals in molecular interplay.

Introduction. – Selective anion sensing by artificial receptors are particularly attractive due to its important role in a wide range of environmental, clinical, chemical, and biological applications [1–10]. Among biologically important anions, AcO^- has attracted growing attention for its established role in enzymes and antibodies. Moreover, AcO^- is also a significant component of numerous metabolic processes. Therefore, the recognition and sensing of AcO^- becomes increasingly important in comparison to other biologically functional anions [11–13].

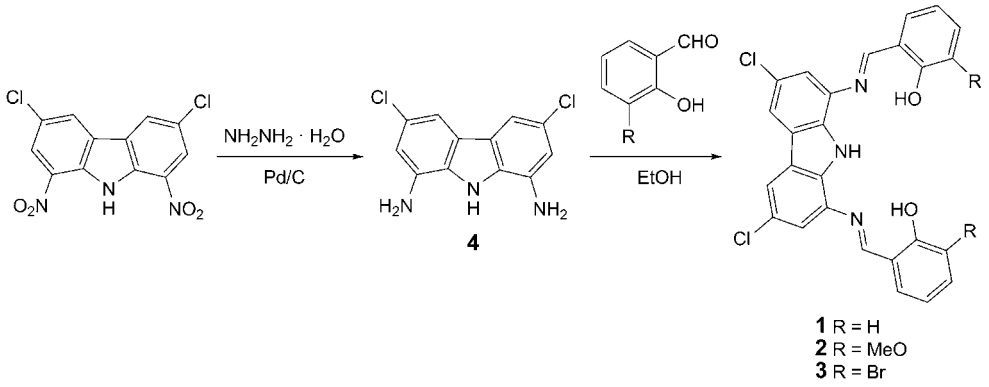
Currently, a fluorescence probe has attracted increased attention being constructed according to the receptor-chromophore principle, which involves binding sites and a fluorophore, and which can translate the receptor–anion binding into an optical signal [14][15]. Among these signaling mechanisms [16–19], the photoinduced electron transfer (PET) mechanism is often exploited for probes, showing the fluorescence response to the guest binding. Such fluorescent host molecules based on PET are mostly structurally simple [20].

Various types of artificial receptors have been developed, which employ H-bonding due to specific binding sites, such as those of urea or thiourea [21], amides [22], thioamides [23], pyrroles [24][25], or of azamacrocycles [26] heading for binding of anions with size and shape selectivity in various media. Phenol groups are among the most frequently used fragments to design neutral receptors for anion recognition by directional H-bonding interaction of anions even in aqueous solutions [27][28]. Although anion receptors containing phenol groups as binding sites have been investigated, recognition mechanism based on the synergism of phenol and 9*H*-carbazole is scarcely reported [29][30].

Despite the high sensitivity of modern analytical instruments and methods, some components of detection such as the level of trace concentration have been left aside (no signal). The minimum concentration in environment and organisms is essential for the judgment of the pollutant content of anions and the causes of disease. Therefore, research on the determination limit of anion recognition is still important. However, literature on the determination limit of anion recognition is rather scarce.

Herein, we report the synthesis of three fluorescent anion probes, **1**–**3**, based on 3,6-dichloro-9*H*-carbazole derivatives (*Scheme 1*) providing phenol OH and carbazole NH groups as binding sites, and together with the PET signaling mechanism and the determination limit with their three ligands. We reason that the OH and NH groups incorporated in the conjugated system with the carbazole moiety (fluorophore) will render the probes capable of sensing anions optically in organic media. As expected, the probes **1**–**3** showed fluorescence turn-on upon the addition of anions in organic solvents.

Scheme 1. *General Synthetic Route to the Target Compounds* **1**–**3**



Results and Discussion. – *UV/VIS Titration.* The anion-binding ability of **1**–**3** were investigated in detail by UV/VIS spectroscopy in DMSO. *Fig. 1*, *a*, shows the changes in UV/VIS spectra of **1** (2.0×10^{-5} M) upon the titration with AcO^- in DMSO solution. The absorption spectrum of free **1** exhibited two broad absorption bands centered at 330 and 400 nm, which could be assigned to the excitation of π electrons in the carbazole system and the intramolecular charge-transfer (ICT) transitions within the whole structure of **1**, respectively [19]. With the stepwise addition of AcO^- ion to the solution of **1** (2.6×10^{-5} M), the absorbance values at 330 and 400 nm were reduced in intensity, and a new absorbance band at 500 nm developed gradually. The red-shift phenomenon occurred, induced by the addition of AcO^-, in the absorption spectrum of **1**. The reason could be the enhancement of the conjugative host–guest effect after H-bonding between **1** and AcO^- [31][32]. However, a clear isosbestic point at 430 nm was observed, indicating stable complex formation between **1** and AcO^- [33]. Particularly, the presence of F^- and $H_2PO_4^-$ induced changes in the UV/VIS spectra of **1** similar to those of AcO^-. However, the additions of excess equiv. of Cl^-, Br^-, and I^- resulted only in slight changes in the UV/VIS spectra of **1** (*Fig. 2*, *a*), which indicated

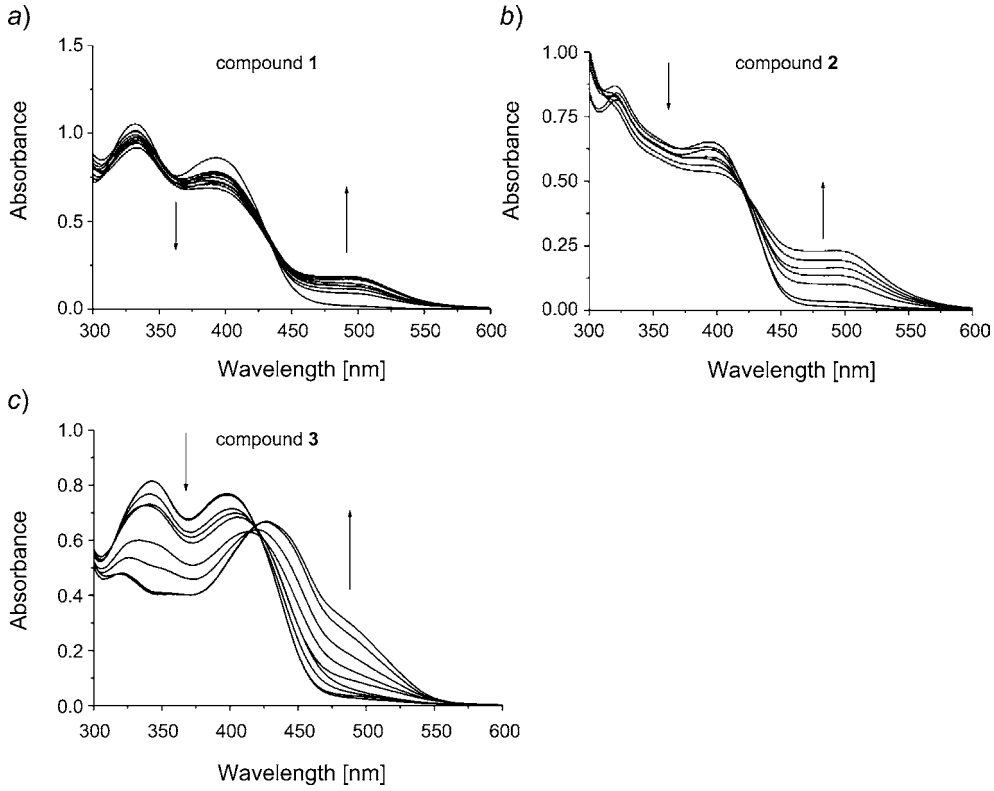


Fig. 1. *Changes in the absorption spectra of probes* **1**–**3** (20 μM) *in absence and presence of* AcO^- *in DMSO.* Arrows indicate the increase of anion concentration.

that **1** showed different binding ability with F^-, $H_2PO_4^-$, and almost no or very weak binding ability with Cl^-, Br^-, and I^-.

Similar effects are observed with **2**. As the concentration of AcO^- increased, the absorption intensity at 315 and 390 nm decreased. At the same time, a new absorbance at 500 nm formed, and the intensity increased gradually. The appearance of an isosbestic point at 425 nm indicated formation of a stable complex between **2** and anions. Moreover, addition of F^- or $H_2PO_4^-$ induced similar changes in the spectra of **2**, in comparison to AcO^- (*Fig. 2,b*). However, the additions of Cl^-, Br^-, and I^- to **2** virtually led to almost no spectral changes, indicating that the interaction between **2**, and Cl^-, Br^-, and I^- was very weak and could be neglected.

For free **3**, strong absorptions at 340 and 400 nm appeared. With the addition of AcO^- ion, the absorption intensity decreased, and a new absorption peak at 430 nm developed gradually (*Fig. 1,c*). A clear red-shift phenomenon occurred with **3** and AcO^-. In addition, one isosbestic point at 425 nm appeared, indicating formation of a stable complex [31]. The presence of $H_2PO_4^-$ and F^- induced similar changes in UV/VIS spectra of **3**, but the additions of excess equiv. of Cl^-, Br^-, and I^- resulted only in

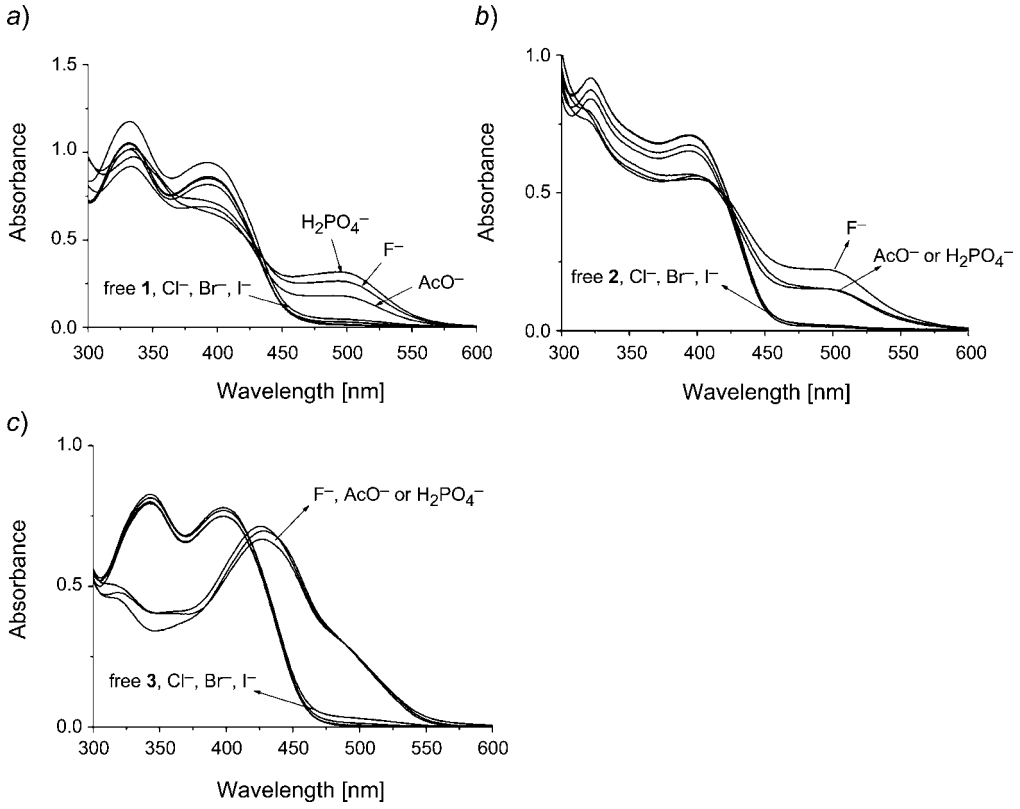


Fig. 2. *Changes in the absoprtion spectra of probes* **1**–**3** (20 μM) *induced by addition of 20 equiv. of tested anions*

slight changes in the UV/VIS spectra of **3**, which indicated very weak interactions which could be neglected (*Fig. 2*,*c*).

Fluorescence Titration. The photophysical responses of **1**–**3** toward the addition of the anions mentioned above were also investigated. As shown in *Fig. 3*,*a*, the fluorescence (FL) spectra of **1** exhibited very weak response. Upon the addition of AcO^- (0–10 equiv.) to the solution of **1**, the fluorescence centered at 471 nm (excited at 427 nm) became enhanced. To account for such FL enhancement, the PET mechanism was exploited. For **1**, the excited state of the fluorophore was not, or only to a minor extent, enhanced by electron transfer (ET) from the receptor to the fluorophore and the receptor–anion interaction. The addition of F^- induced a similar fluorescence enhancement. Nevertheless, FL emission of **1** was insensitive to the additions of excess equiv. of $H_2PO_4^-$, Cl^-, Br^-, and I^- ions (*Fig. 4*,*a*), indicating very weak, hence negligible interactions.

In the FL titration spectra of **2**, the intensity centered at 500 nm enhanced significantly with the increase of AcO^- concentration (*Fig. 3*,*b*), which indicated that **2** interacted with AcO^-. The addition of F^- induced similar FL enhancement. However,

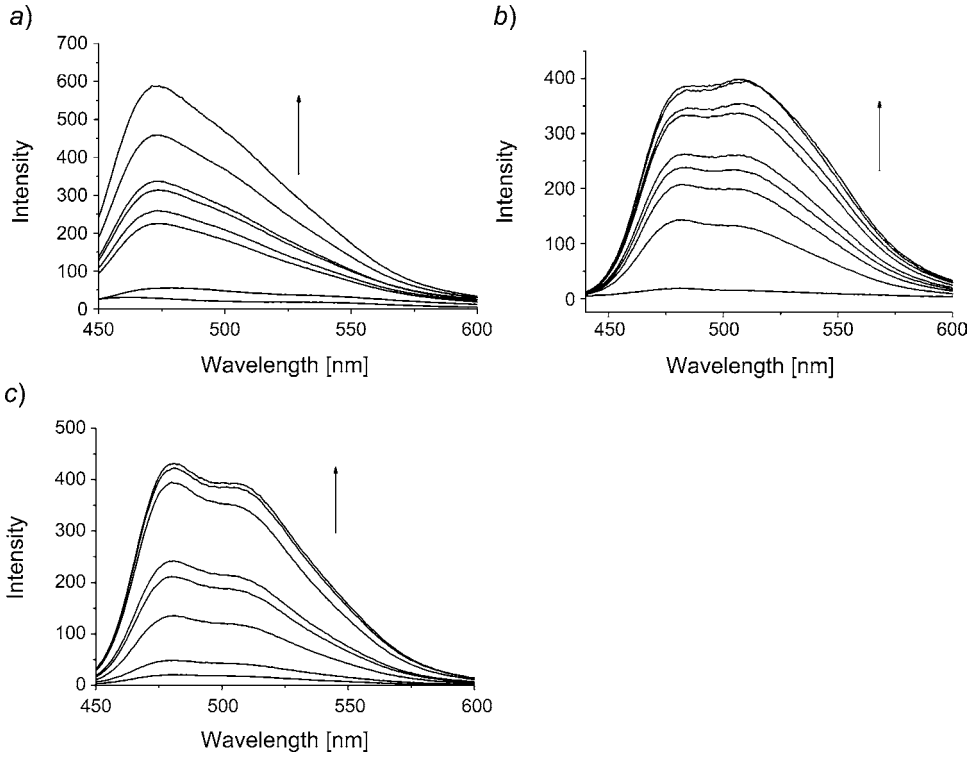


Fig. 3. *Changes in the emission spectra of probes* **1**–**3** (26 μM) *in absence and presence of* AcO^- *in DMSO. a*) **1**; λ_{ex} 427 nm; *b*) **2**; λ_{ex} 422 nm; *c*) **3**; λ_{ex} 435 nm.

the additions of $H_2PO_4^-$, Cl^-, Br^-, and I^- caused very weak FL enhancements, so that these host–guest interactions could be neglected (*Fig. 4*,*b*). As for **3**, the additions of AcO^-, F^-, $H_2PO_4^-$ induced strong FL enhancements. With the addition of anions, the intensity of emission band at 480 nm with a shoulder centered at 520 nm gradually enhanced. There were almost no changes upon the additions of Cl^-, as well as Br^- and I^- (*Fig. 4*,*c*), suggesting very weak, hence ignorable interactions.

Binding Constants. The above analyses indicated that the spectral changes could be ascribed to the formation of 1:1 host–guest complexes. The binding constants obtained by using the method of nonlinear least-squares calculation according to the UV/VIS and FL data are compiled in the *Table* [34–36]. The trend of binding of **1**–**3** to anions are as follows: $AcO^- > F^- > H_2PO_4^- >> Cl^- \approx Br^- \approx I^-$. The selectivity for specific anions could be rationalized on the basis of the anion basicity, and the interactions between the host and the anionic guests. However, multiple H-bonding interactions are also necessary in high-affinity anion-binding sites [37]. As expected from their basicity, AcO^-, F^-, and $H_2PO_4^-$ bound more strongly than the other anions studied; in addition, the triangle structure of AcO^- may well match with **1**–**3** in terms of shape and could form multiple H-bonding interactions. Consequently, AcO^- can be selectively differentiated from other anions based on affinity constant. Especially, the selectivity was

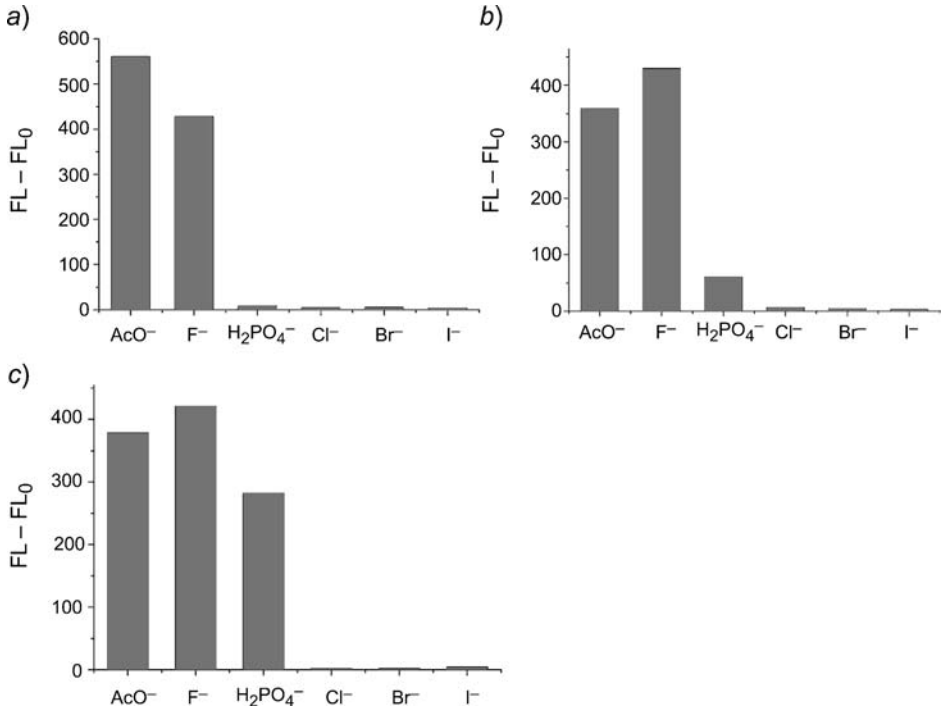


Fig. 4. *Changes in intensity of the emission band in the presence of 10 equiv. of tested anions. a*) **1**; 471 nm; *b*) **2**; 490 nm; *c*) **3**; 480 nm.

Table. *Binding Constants of Compounds* **1**–**3** *with Various Anions*

Anion[a])		Binding constant (K_s)		
		1	**2**	**3**
AcO^-	Absorption	$(1.25 \pm 0.71) \times 10^5$	$(1.38 \pm 0.31) \times 10^4$	$(2.12 \pm 0.49) \times 10^5$
	Emission	$(3.81 \pm 0.13) \times 10^5$	$(3.51 \pm 0.73) \times 10^4$	$(5.08 \pm 0.81) \times 10^5$
F^-	Absorption	$(2.36 \pm 0.54) \times 10^4$	$(6.63 \pm 0.17) \times 10^3$	$(8.65 \pm 0.32) \times 10^3$
	Emission	$(9.04 \pm 0.25) \times 10^3$	$(5.04 \pm 0.26) \times 10^3$	$(9.18 \pm 0.24) \times 10^3$
$H_2PO_4^-$	Absorption	< 10	< 10	$(1.41 \pm 0.52) \times 10^3$
	Emission	< 10	78 ± 16	$(7.42 \pm 0.06) \times 10^3$
Cl^- (Br^- or I^-)		ND[b])	ND	ND

[a]) All anions were added in form of Bu_4N^+ salts. [b]) The binding constant could not be determined.

more apparent for **3**. For the same anion, the binding ability is: **3** > **1** > **2**. The reason may be that the electron-withdrawing groups in the phenolic part could enhance the acidity of the probe, and the binding ability increased. As a result, the anion-binding ability of **3** was higher than that of **2**, whereas that of **1** was medium. Moreover, the binding constants obtained by UV/VIS data were in the same order of magnitude with

fluorescence data, which indicated that the results of binding constants obtained by UV/VIS data were confirmed by fluorescence.

Determination Limit. For cation recognition, determination limits were sufficiently reported [38][39], whereas reports on the determination limits for anions are almost nonexistent. Thus, the determination limit in case of **3** with AcO^- was studied (*Fig. 5*). The interaction of **3** with AcO^- could be detected down to a concentration of 3.0×10^{-7} M; at this point $[AcO^-]$ is 4.7×10^{-7} M, with a 1.3 times enhanced absorption intensity. Under optimal conditions, the FL intensity of **3** and the concentration of added AcO^- displayed a good linear relationship (0–2 μM), indicating the quantitative detection of AcO^- in the above concentration range. These results revealed that **3** could potentially be used as a probe for monitoring AcO^- levels in physiological and environmental systems.

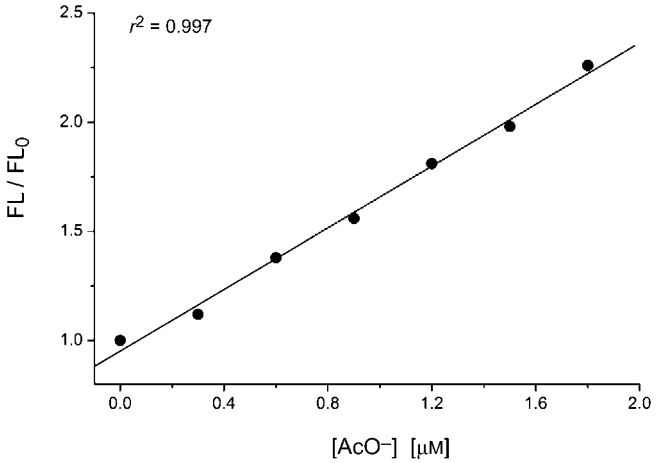
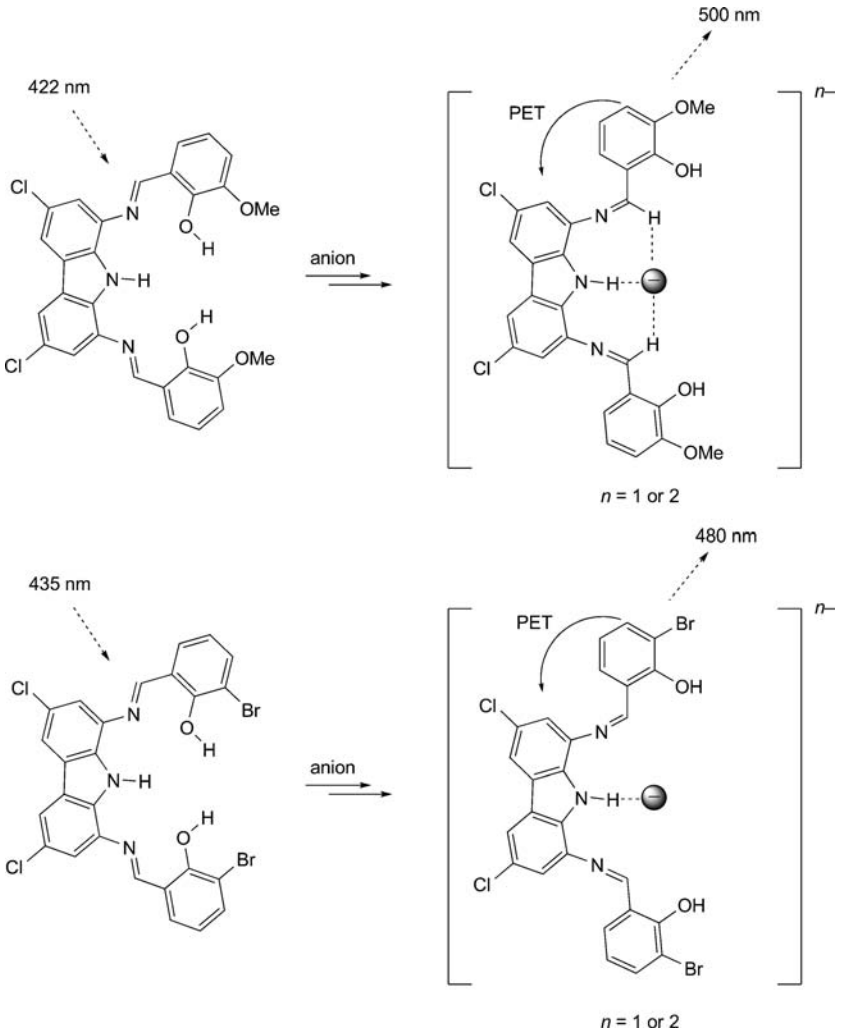


Fig. 5. *Fluorescence intensity* (482 nm) *of* **3** (0.30 μM) *in DMSO as a function of concentrations of* AcO^- (0–1.8 μM) *with an excitation wavelength of 435 nm*

^{1}H-NMR Titration. To further shed light on the nature of the interactions of **1**–**3** and anions, ^{1}H-NMR spectral changes upon addition of AcO^- with Bu_4N^+ as counterion to the (D_6)DMSO solution of **2** and **3** (1×10^{-2} M) were investigated. As shown in *Fig. 6*, the signal at δ(H) 11.84 (NH), which was assigned to the NH H-atom, broadened and exhibited a downfield shift to δ(H) 12.28 upon addition of increasing equiv. of AcO^-, thus indicating strong H-bonding interactions [40]. The OH H-signal at δ(H) 12.24 became weaker and finally disappeared with the increase of AcO^-, which indicated deprotonation of the OH groups. At the same time, the signal at δ(H) 9.05 (CH in the *Schiff* base parts) was shifted downfield, indicating a potential H-bonding. The signals of the H-atoms of the carbazole part (δ(H) 7.47 (H_d), 8.25 (H_e)) and the phenol parts (δ(H) 7.35 (H_c), 7.17 (H_a), 6.94 (H_b)) exhibited slight upfield shifts, evidencing the increase of the electron density on there moieties due to through-bond effects. The reason may be as follows: in compound **2**, the OH groups form intramolecular H-bonds with NH, a finding established by theoretical investigations. With the addition of AcO^-, intramolecular H-bonds are cleaved, and H-bonds are

formed between the interacting sites (NH and OH) and AcO^-. With further addition of AcO^-, OH moieties are deprotonated, and the potential CH···OAc bonds develop [41]. The proposed binding mode of **2** with anions in solution is outlined in *Scheme 2*.

Scheme 2. *Proposed Host–Guest Binding Modes in Solution*



For **3**, the signals of OH (δ(H) 11.95) and NH (δ(H) 11.93) overlapped. The signal of OH disappeared, and the signal of NH was shifted downfield after addition of AcO^-, which indicates that the H-bonds between carbazole NH in **3** and AcO^- were formed and deprotonation took place in the OH moieties. The carbazole H-signals (δ(H) 8.04 (H_d) and 8.25 (H_e)) and the H-signals of the phenol part (δ(H) 7.44 (H_b), 7.58 (H_c), and 7.00 (H_a)) exhibited slight upfield shifts, evidencing the increase of the electron density

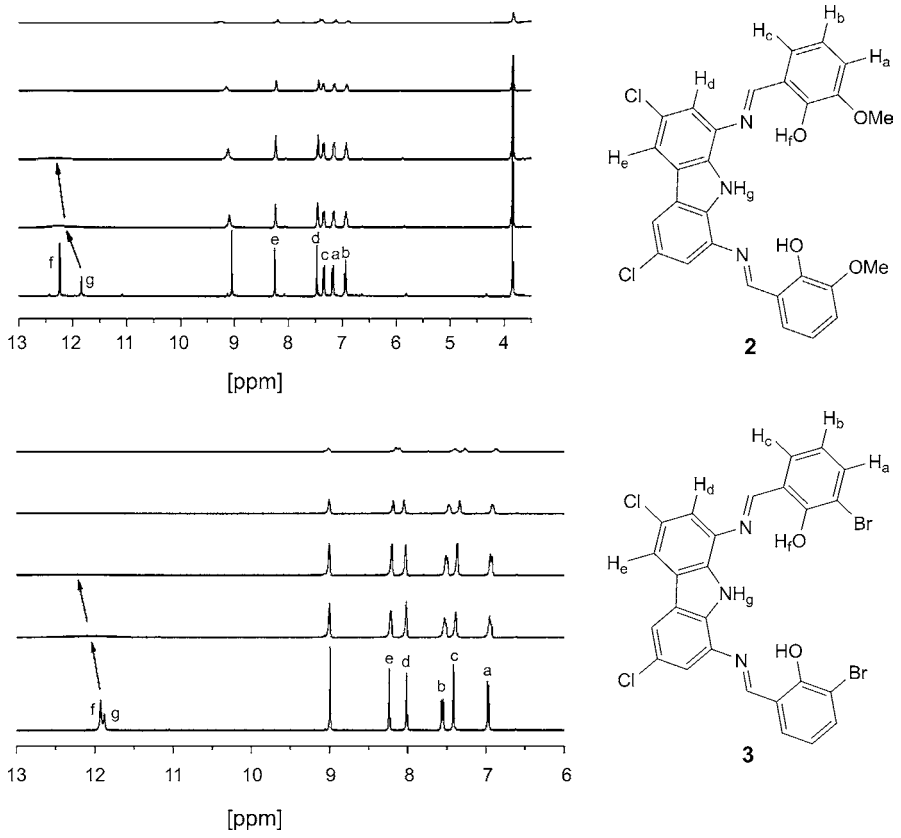


Fig. 6. *^{1}H-NMR Spectra of compounds* **2** *and* **3** *in (D$_6$)DMSO* (10 mM) *upon the addition of molar equiv. of AcO$^-$*. From bottom to top: addition of 0, 0.5, 1, 2, and 5 equiv. of AcO$^-$.

on these moieties due to through-bond effects. However, the signal at δ(H) 9.02 (CH in *Schiff* base part) almost did not change, evidencing that the corresponding H-atom does not participate the host–guest interaction. The proposed binding mode of host–guest in solution is depicted in *Scheme 2*.

According to the results from UV/VIS, FL, and ^{1}H-NMR titrations, the proposed host–guest binding modes in solution can be seen as shown in *Scheme 2*. In the complex structure, an anion interacts with **1**–**3** *via* N–H and O–H H-bonds. With further anion addition, OH undergoes deprotonation, and the H-bonding still exists between the NH of carbazole and the anion.

Theoretical Investigations. The geometries of **1**–**3** were optimized (*Fig. 7*) using density functional theory at B3LYP/3–21G level with Gaussian03 program [42]. *Fig. 7* shows that the intramolecular H-bonds are indeed possible between NH of carbazole and OH of the benzene ring of compounds **1**–**3**. In compound **1**, one OH group underwent a prototropic 1,5-shift to the *Schiff* base N-atom. Compounds **2** and **3** both exist in their bis-phenolic form. In view of geometry, the anion-binding ability of compound **2** was weaker than that of compounds **1** and **3** due to specific hinderance of

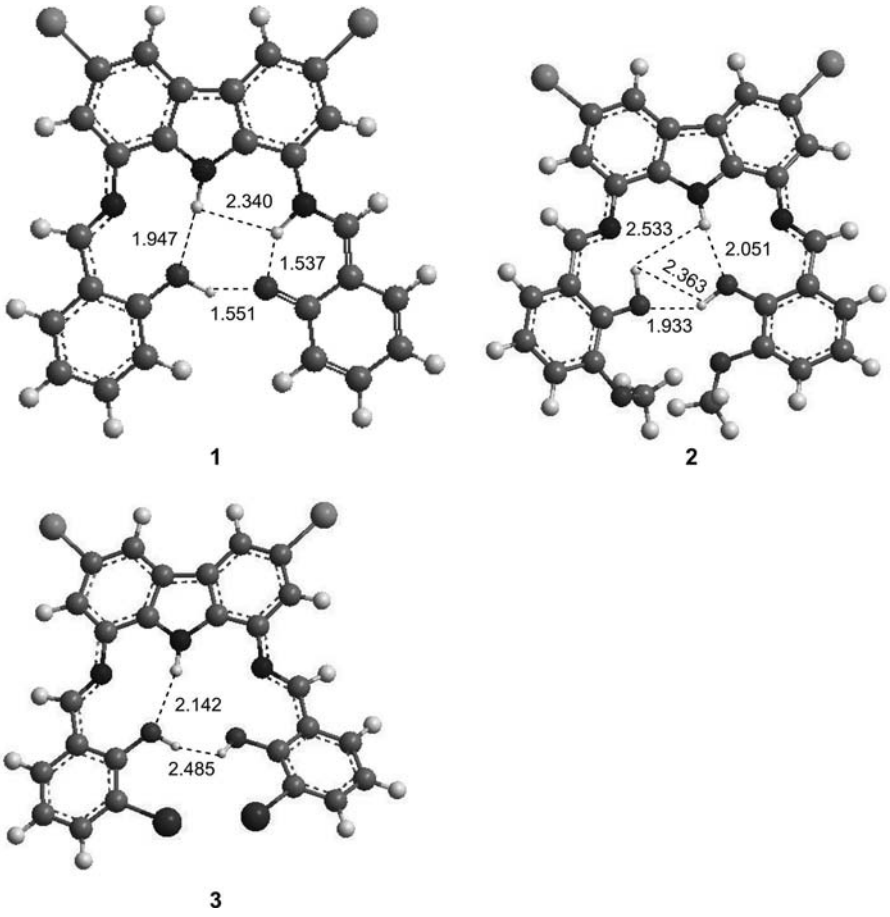


Fig. 7. *Optimized geometries of compounds* **1**–**3**

the MeO group. The distance of the two H-atoms of the OH groups in compound **3** was 2.485 Å, which was close to the distance of the two O-atoms in AcO^- (2.309 Å). Therefore, compound **3** showed the strongest binding ability for AcO^- among the anions tested.

Selected frontier orbitals for **1**–**3** are shown in *Fig. 8*. We looked at the molecular frontier orbitals to explain the UV/VIS absorption spectra for the host–guest interaction by electron transition of frontier orbitals. The highest HOMO density in **1**–**3** was mainly localized on the carbazole and phenol moieties. In contrast, the highest LUMO density was mainly localized on one of the phenol moieties, indicating that the electron transition of the highest LUMO causes the red shift phenomenon in the UV/VIS spectra of the ligand (**1**–**3**)–anion complexes.

Conclusions. – In conclusion, three fluorescent anion probes have been designed and synthesized. The probes are based on PET FL enhancement (turn-on), which

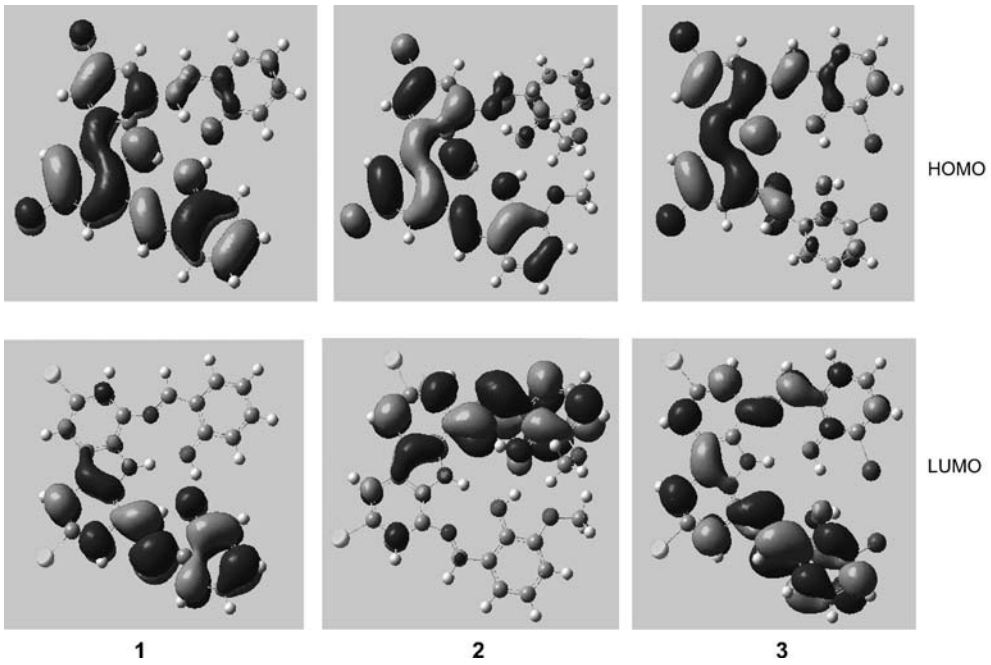


Fig. 8. *Molecular orbital levels of compounds* **1**–**3**

offers the potential for high sensitivity. The results indicate that these probes show the strongest binding ability for AcO^- among the anions tested. Theoretical investigation indicates that it is the electron transition of the highest LUMO that causes the red-shift phenomenon in UV/VIS spectra of probe–anion complexes. The determination limit of **3** for AcO^- is 3.0×10^{-7} M, whereby the concentration of AcO^- is 4.7×10^{-7} M. Under optimal conditions, the FL intensity of **3** and the concentration of added AcO^- display a good linear relationship (0–2 μM) indicating the quantitative detection of AcO^- in the above concentration range.

Experimental Part

General. Most of the starting materials were obtained commercially, and all reagents and solvents used were of anal. grade. All anions, in the form of Bu_4N^+ salts such as Bu_4NF, Bu_4NCl, Bu_4NBr, Bu_4NI, Bu_4NOAc, and $Bu_4NH_2PO_4$ were purchased from *Sigma-Aldrich Chemical Co.*, stored in a desiccator under vacuum, and used without any further purification. The Bu_4N salts were dried for 24 h *in vacuo* with P_2O_5 at 333 K. DMSO was distilled *in vacuo* after drying on CaH_2. UV/VIS Titration experiments were conducted on a *Shimadzu UV2550* spectrophotometer at 298 K. The affinity constant, K_s, was obtained by nonlinear least-squares calculation method for data fitting. ^{1}H-NMR Spectra were recorded on a *Varian UNITY Plus-400-MHz* spectrometer; δ in ppm rel. to Me_4Si as internal standard, J in Hz. ESI-MS was performed with a *MARINER* apparatus; in m/z. Elemental analyses (C, H, N) were performed on a *Vanio-EL* instrument. Compounds **1**–**3** were synthesized according to the route outlined in *Scheme 1*.

3,6-Dichloro-1,8-dinitro-9*H*-carbazole was synthesized as described in [43]. Yield: 86%. M.p. 282–283° ([43]: 284°). ^{1}H-NMR ((D$_6$)DMSO): 11.30 (*s*, NH); 8.98 (*s*, 2 H); 8.48 (*d*, $J = 4.0$, 2 H). ESI-MS:

324.30 ([$M-H$]$^-$). Anal. for $C_{12}H_5Cl_2N_3O_4$ (326.09): C 44.20, H 1.55, N 12.89; found: C 44.36, H 1.61, N 12.85.

*3,6-Dichloro-9*H*-carbazole-1,8-diamine* (**4**). In a three-neck, 250-ml round-bottomed flask, 3,6-dichloro-1,8-dinitro-9*H*-carbazole (5 mmol) and Pd/C were suspended in EtOH (100 ml). The soln. was heated at reflux, and $NH_2NH_2 \cdot H_2O$ (10 ml) dissolved in EtOH (30 ml) was added dropwise. After the addition was completed, the mixture was heated at reflux for 12 h until the soln. became colorless. Then, the hot suspension was filtered, and the filter was washed with EtOH. The EtOH was removed in a rotary evaporator, resulting in a gray-white solid which was recrystallized from EtOH. Yield: 59%. ^{1}H-NMR ((D$_6$)DMSO): 10.67 (*s*, NH); 8.91 (*s*, 2 H); 8.36 (*s*, 2 H); 5.42 (*s*, 2 NH$_2$). Anal. for $C_{12}H_9Cl_2N_3$ (266.13): C 54.16, H 3.41, N 15.79; found: C 54.28, H 3.66, N 15.65.

*2,2′-[(3,6-Dichloro-9*H*-carbazole-1,8-diyl)bis(nitrilomethylylidene)]diphenol* (**1**). Diamine **4** (1 mmol, 265 mg) and salicylaldehyde (=2-hydroxybenzaldehyde; 2 mmol, 122 mg) were suspended in 35 ml of EtOH. The mixture was heated under reflux for 4 h. The yellow precipitate was separated by filtration. The solid was washed with Et_2O and dried under vacuum. ^{1}H-NMR ((D$_6$)DMSO): 12.17 (*s*, 2 OH); 11.88 (*s*, NH); 9.07 (*s*, 2 H); 8.26 (*d*, J = 4.0, 2 H); 7.77 (*d*, J = 4.0, 2 H); 7.47 (*d*, J = 4.0, 4 H); 7.01 (*d*, J = 8.0, 4 H). ESI-MS: 472.2 ([$M-H$]$^-$). Anal. for $C_{26}H_{17}Cl_2N_3O_2$ (474.34): C 65.83, H 3.61, N 8.86; found: C 65.65, H 3.12, N 8.59.

*2,2′-[(3,6-Dichloro-9*H*-carbazole-1,8-diyl)bis(nitrilomethylylidene)]bis(6-methoxyphenol)* (**2**). The synthesis procedure was similar to that of compound **1**. ^{1}H-NMR ((D$_6$)DMSO): 12.24 (*s*, 2 OH); 11.84 (*s*, NH); 9.05 (*s*, 2 H); 8.25 (*s*, 2 H); 7.46 (*d*, J = 4.0, 2 H); 7.33 (*d*, J = 8.0, 2 H); 7.16 (*d*, J = 8.0, 2 H); 6.94 (*t*, J = 16.0, 2 H); 3.84 (*s*, 6 H). ESI-MS: 532.3 ([$M-H$]$^-$). Anal. for $C_{28}H_{21}Cl_2N_3O_4$ (534.39): C 62.93, H 3.96, N 13.27; found: C 63.03, H 3.94, N 13.67.

*2,2′-[(3,6-Dichloro-9*H*-carbazole-1,8-diyl)bis(nitrilomethylylidene)]bis(6-bromophenol)* (**3**). The synthesis procedure was similar to that of compound **1**. ^{1}H-NMR ((D$_6$)DMSO): 11.91 (*d*, J = 16.0, 2 H); 9.02 (*s*, 2 CH); 8.26 (*d*, J = 4.0, 2 H); 8.03 (*d*, J = 4.0, 2 H); 7.58 (*dd*, J = 12.0, 2 H); 7.43 (*d*, J = 4.0, 2 H); 6.98 (*d*, J = 8.0, 2 H). ESI-MS: 627.7 ([$M-H$]$^-$). Anal. for $C_{26}H_{15}Br_2Cl_2N_3O_2$ (632.13): C 49.40, H 2.39, N 6.65; found: C 49.77, H 2.36, N 6.82.

This work was supported by the *Natural Science Fund of Henan Province* (2010B150024, 112300410104), the *Young Teacher Fund of Henan Province* (2011GGJS-126), and the *Doctorial Starting Fund of Xinxiang Medical University.*

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Received May 30, 2012