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Electronic Supplementary Information

Different sensing modes of fluoride and acetate based on a calix[4]arene with 25,27-bistriazolylmethylpyrenylacetamides

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Figure No	Contents	Page
Figures S1 & S2.	¹ H and ¹³ C NMR spectra of compound 4 .	S2
Figure S3.	UV/vis and Fluorescence titration spectra ($\lambda_{ex} = 326$ nm) of 4	
	(10 μ M) with various amount of HO ⁻ in CH ₃ CN at 298 K.	S 3
Figures S4 & S5.	¹ H and ¹³ C NMR spectra of compound 6 .	S 4
Figure S6.	UV/vis and Fluorescence titration spectra ($\lambda_{ex} = 326$ nm) of 6	S5
	(10 μ M) with various amount of OH ⁻ in CH ₃ CN at 298 K.	
Figure S7.	Fluorescence titration spectra ($\lambda_{ex} = 326$ nm) of 6 (a) 1 μ M and	S5
	(b) 10 μ M with various amount of F ⁻ in CH ₃ CN at 298 K.	
Figure S8.	The oscillator strengths of neutral (black square) and anion	
	(red circle) species of 6 predicted using TTDFT method at the	
	B3LYP/6-31G(d) level.	S 6
Figure S9–S10.	The molecular orbital of neutral-6 under B3LYP/6-31G*	
	calculation.	S 7
Figure S11.	¹ H NMR titration spectra of 4 upon addition of various amount	
	of F ⁻ in CD ₃ CN at 298 K	S 8
Figure S12.	¹ H NMR titration spectra of 4 upon addition of various amount	
	of H ₂ PO ₄ ⁻ in CD ₃ CN at 298 K	S 9
Figure S13.	¹ H NMR titration spectra of 4 upon addition of various amount	
	of AcO ⁻ in CD ₃ CN at 298 K	S 10
Figure S14.	¹ H NMR titration spectra of 6 upon addition of various amount	
	of F [−] in CD ₃ CN at 298 K	S 11



Figure S1. ¹H NMR (CD₃CN, 500 MHz) spectrum of 25,27-Bis{1'-*N*-(1-pyrenyl)-amino-carbonylmethyl-1*H*-[1',2',3']triazolyl-4'-methoxy}-26,28-dihydroxy calix[4]arene **4**.



Figure S2. ¹³C NMR (DMSO- d_6 , 125 MHz) spectrum of 25,27-Bis-{1'-*N*-(1-pyrenyl)-amino-carbonylmethyl-1*H*-[1',2',3']triazolyl-4'-methoxy}-26,28-dihydroxy calix[4]arene **4**.



Figure S3. (a) UV/vis and (b) Fluorescence titration spectra ($\lambda_{ex} = 326$ nm) of **4** (10 μ M) with various amount of OH⁻ in CH₃CN at 298 K.



Figure S4. ¹H NMR (CDCl₃, 500 MHz) spectrum of 2-{4'-[(4"-tert-butylphenoxy)methyl]-1*H*-[1',2',3']-1-triazolyl}-*N*-(1-pyrenyl)-acetamide **6**.



Figure S5. ¹³C NMR (CDCl₃, 125 MHz) spectrum of 2-{4'-[(4''-tert-butylphenoxy)-methyl]-1*H*-[1',2',3']-1-triazolyl}-*N*(1-pyrenyl)-acetamide **6**.

Total 11 pages, page S4



Figure S6. (a) UV/vis and (b) Fluorescence titration spectra ($\lambda_{ex} = 326 \text{ nm}$) of **6** (10 µM) with various amount of OH⁻ in CH₃CN at 298 K.



Figure S7. Fluorescence titration spectra ($\lambda_{ex} = 326$ nm) of **6** (a) 1 μ M and (b) 10 μ M with various amount of F⁻ in CH₃CN at 298 K.



Figure S8. The oscillator strengths of neutral (black square) and anionic (red circle) species of **6** predicted using TDDFT method at the B3LYP/6-31G(d) level.

Hung, H.-C. 20130924



Figure S9. The molecular orbital of neutral-6 under B3LYP/6-31G* calculation.



Figure S10. The molecular orbitals of anion-6 under B3LYP/6-31G* calculation.



Figure S11. The ¹H NMR (300 MHz) titration spectra of (a) **4** (5.0 mM) in CD₃CN at 25° C with the addition of various equiv of F⁻: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, (h) 3.0, (i) 4.0, and (j) 5.0 equiv. Where signals denoted with @ came from external standard CHCl₃. The counter cation for fluoride is tetrabuthyammonium ion.



Figure S12. The ¹H NMR (300 MHz) titration spectra of (a) **4** (5.0 mM) in CD₃CN at 25° C with the addition of various equiv of H₂PO₄⁻: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, (h) 3.0, (i) 4.0, (j) 5.0 and (k) 10.0 equiv. Where signals denoted with @ came from external standard CHCl₃. The counter cation is tetrabuthylammonium ion.



Figure S13. The ¹H NMR (300 MHz) titration spectra of (a) **4** (5.0 mM) in CD₃CN at 25° C with the addition of various equiv of OAc⁻: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, (h) 3.0, (i) 4.0, (j) 5.0, and (k) 10.0 equiv. Where signals denoted with @ came from external standard CHCl₃. The counter cation for acetate is tetrabuthylammonium ion.



Figure S14. The ¹H NMR (300 MHz) titration spectra of (a) **6** (5.0 mM) in CD₃CN at 25° C with the addition of various equiv of F⁻: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, and (h) 3.0 equiv. Where signals denoted with @ came from external standard CHCl₃. The counter cation for fluoride is tetrabuthyammonium ion.