Electronic Supplementary Information

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

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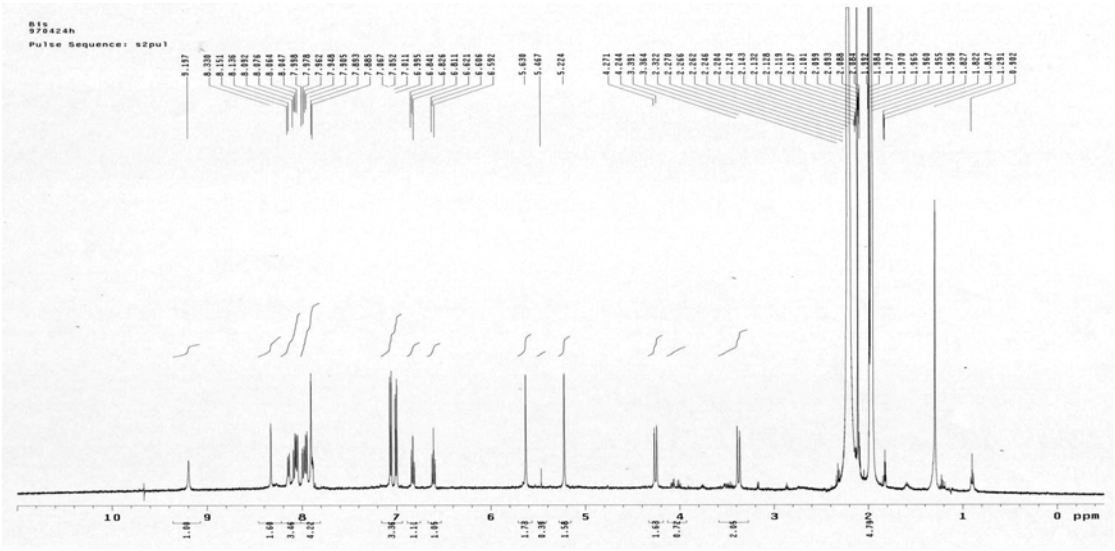


Figure S1. ^{1}H NMR (CD_3CN, 500 MHz) spectrum of 25,27-Bis{1'-*N*-(1-pyrenyl)-amino-carbonylmethyl-1*H*-[1',2',3']triazolyl-4'-methoxy}-26,28-dihydroxy calix[4]arene **4**.

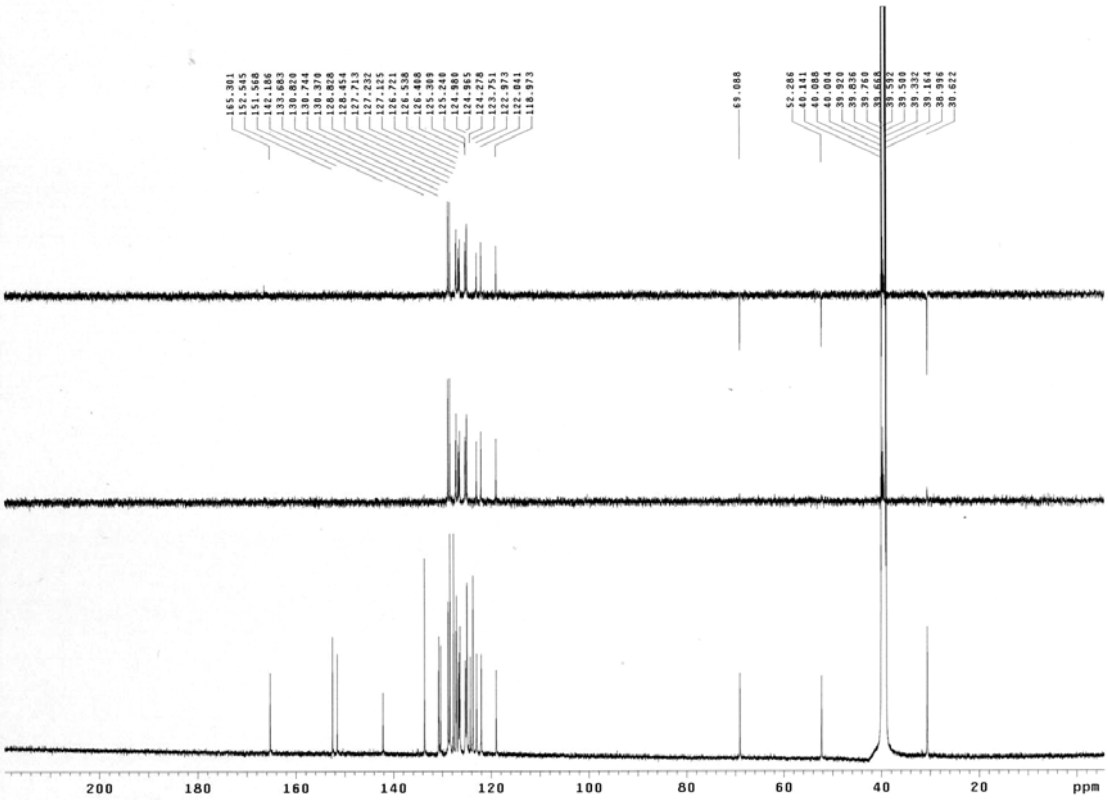


Figure S2. ^{13}C NMR (DMSO-d_6, 125 MHz) spectrum of 25,27-Bis-{1'-*N*-(1-pyrenyl)-amino-carbonylmethyl-1*H*-[1',2',3']triazolyl-4'-methoxy}-26,28-dihydroxy calix[4]arene **4**.

(a) (b)

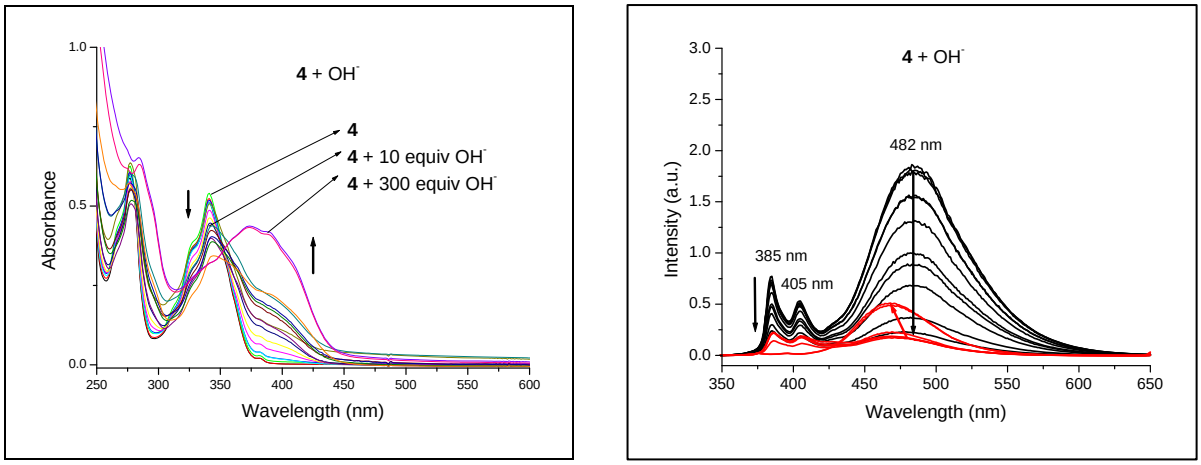


Figure S3. (a) UV/vis and (b) Fluorescence titration spectra (λ_{ex} = 326 nm) of **4** (10 μM) with various amount of OH^- in CH_3CN at 298 K.

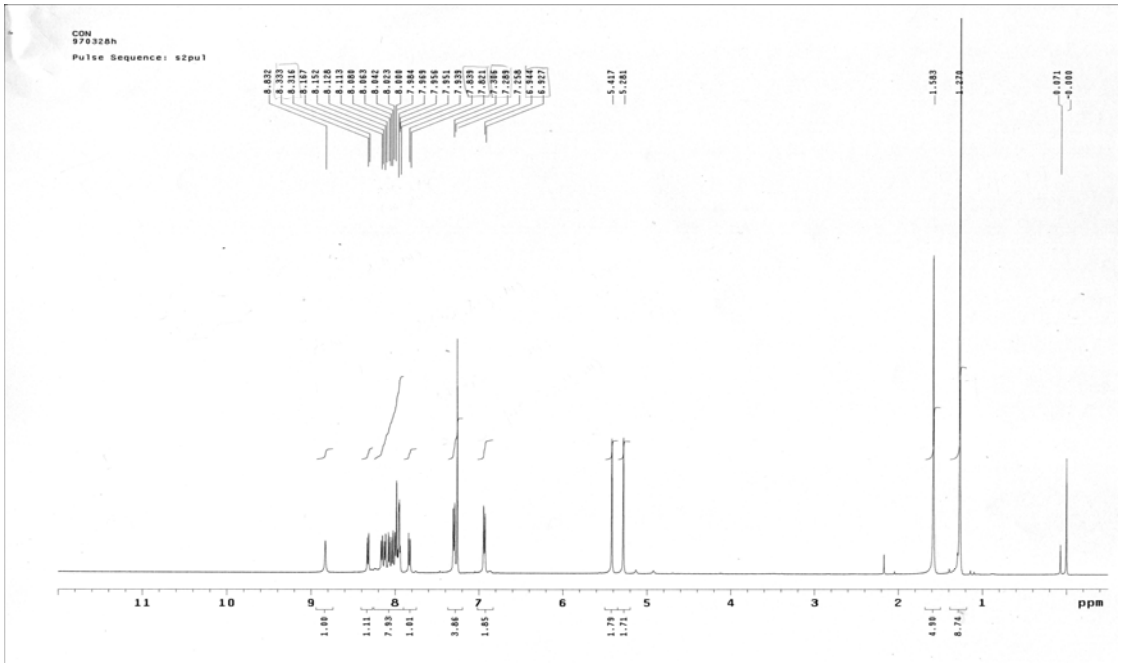


Figure S4. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of 2-{4'-[(4''-tert-butylphenoxy)-methyl]-1*H*-[1',2',3']-1-triazolyl}-*N*-(1-pyrenyl)-acetamide **6**.

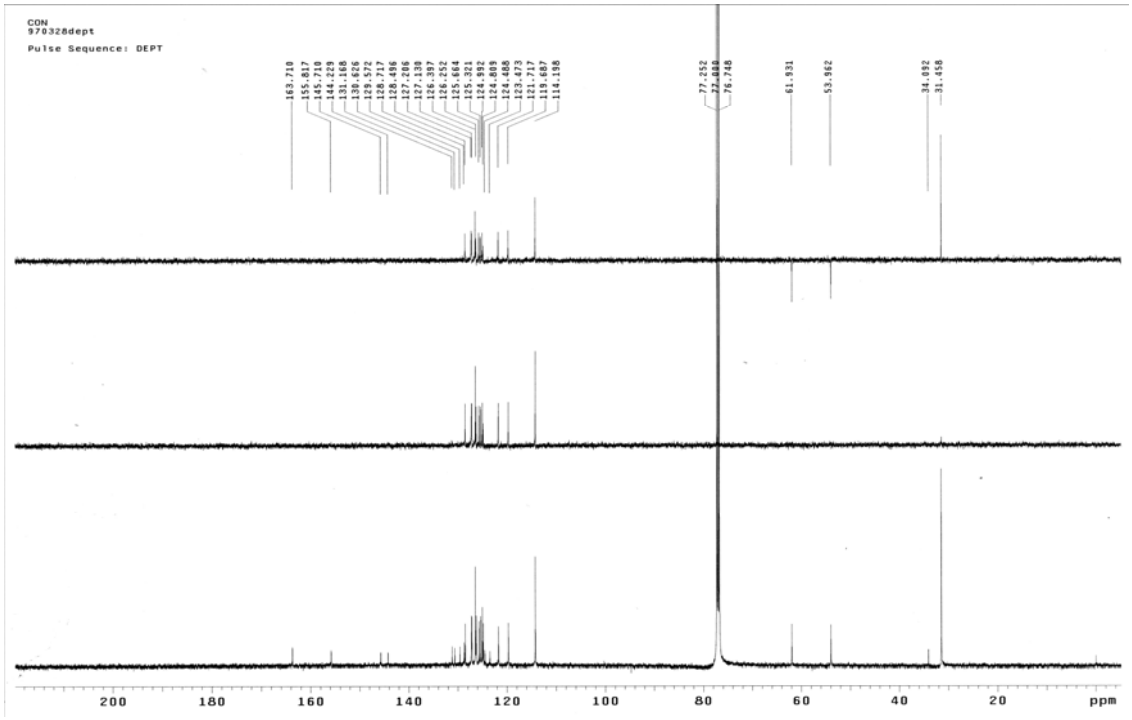


Figure S5. ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of 2-{4'-[(4''-tert-butylphenoxy)-methyl]-1*H*-[1',2',3']-1-triazolyl}-*N*(1-pyrenyl)-acetamide **6**.

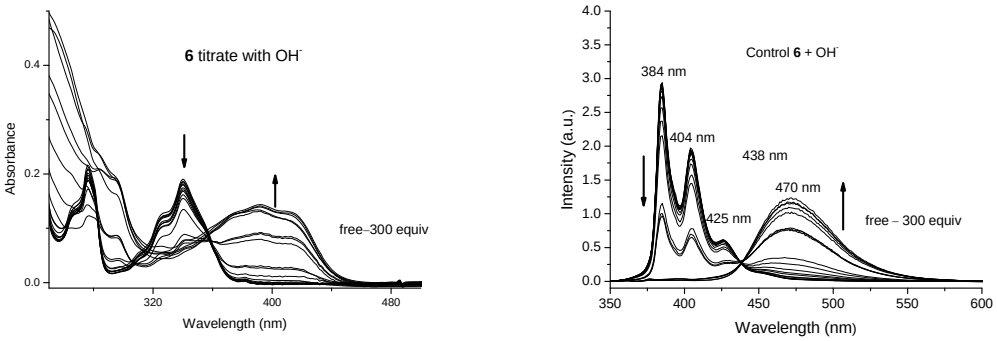


Figure S6. (a) UV/vis and (b) Fluorescence titration spectra (λ_{ex} = 326 nm) of **6** (10 μM) with various amount of OH^- in CH_3CN at 298 K.

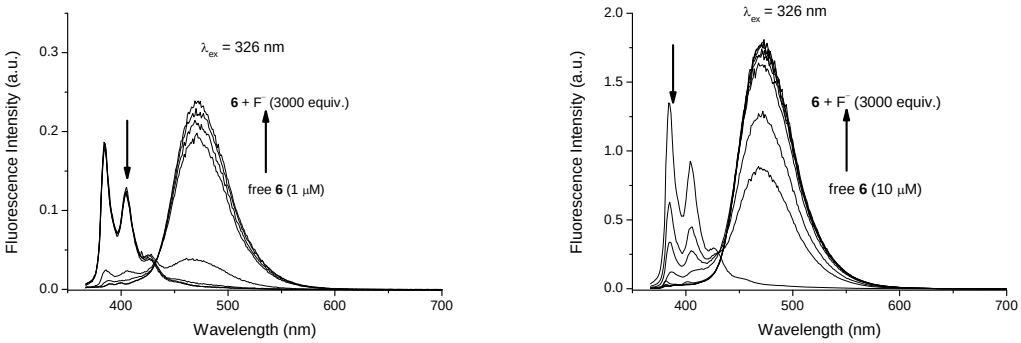


Figure S7. Fluorescence titration spectra (λ_{ex} = 326 nm) of **6** (a) 1 μM and (b) 10 μM with various amount of F^- in CH_3CN at 298 K.

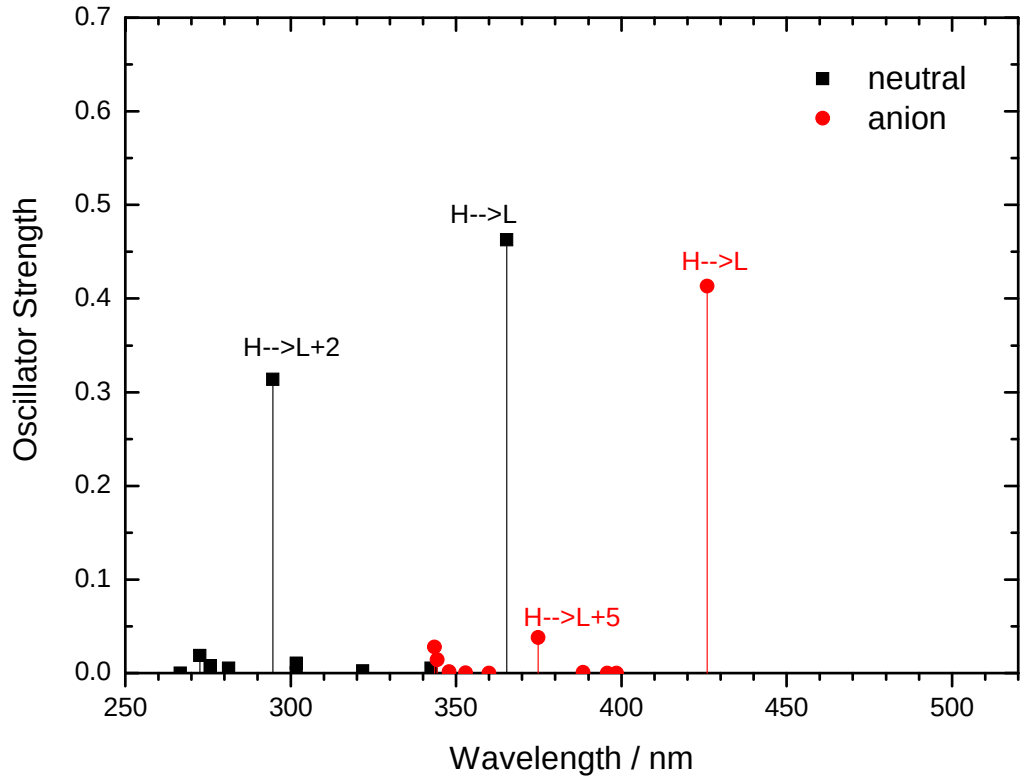


Figure S8. The oscillator strengths of neutral (black square) and anionic (red circle) species of **6** predicted using TDDFT method at the B3LYP/6-31G(d) level.

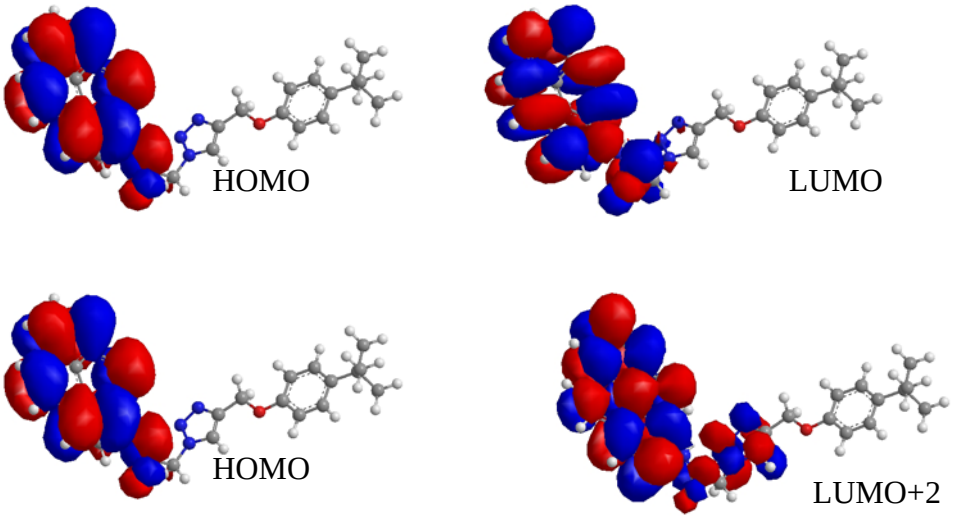


Figure S9. The molecular orbital of neutral-**6** under B3LYP/6-31G* calculation.

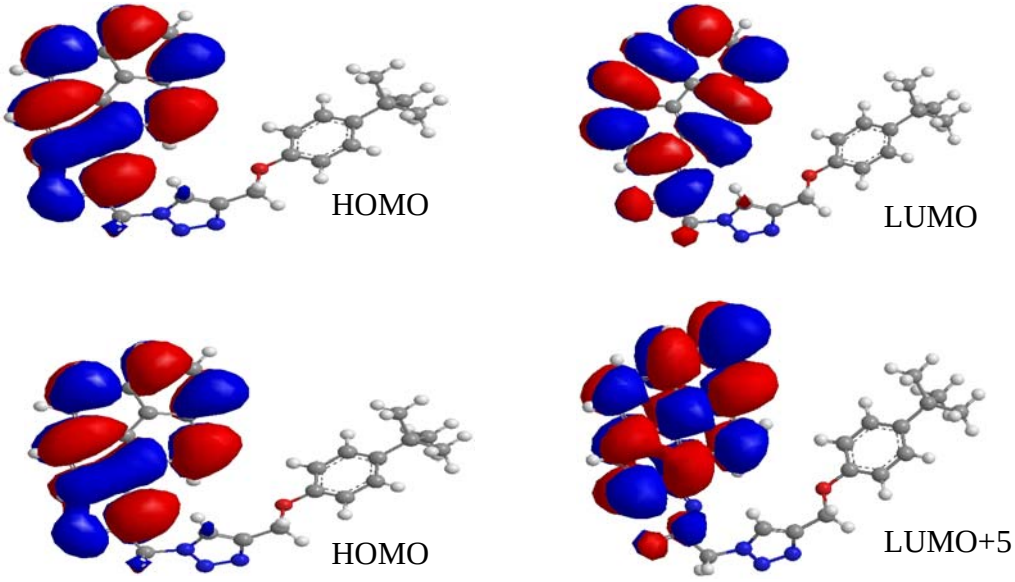


Figure S10. The molecular orbitals of anion-**6** under B3LYP/6-31G* calculation.

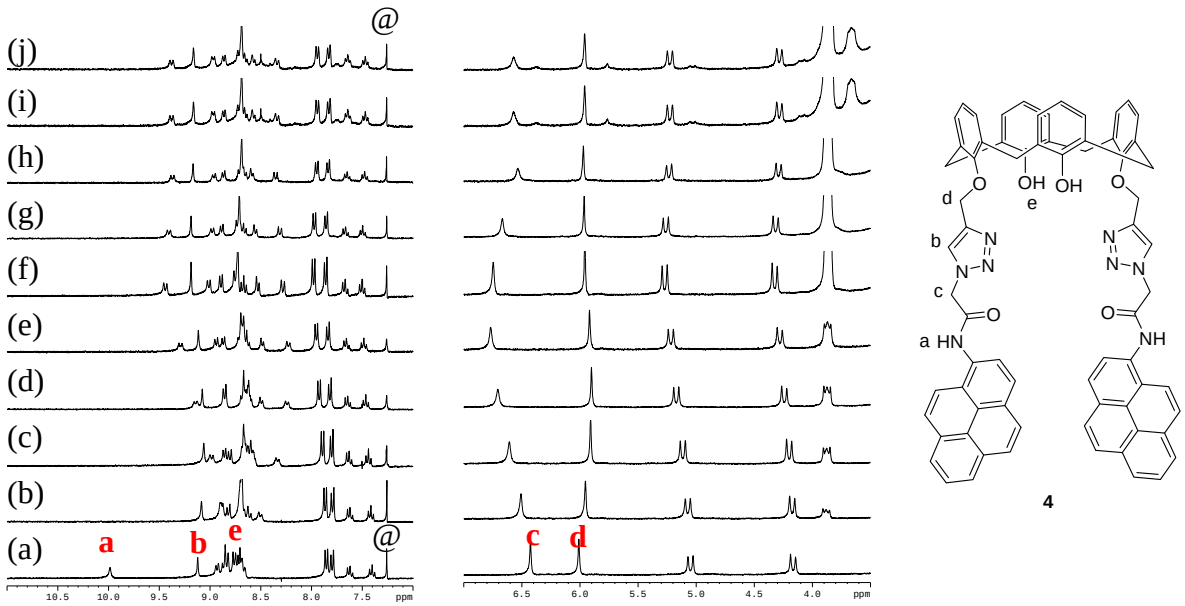
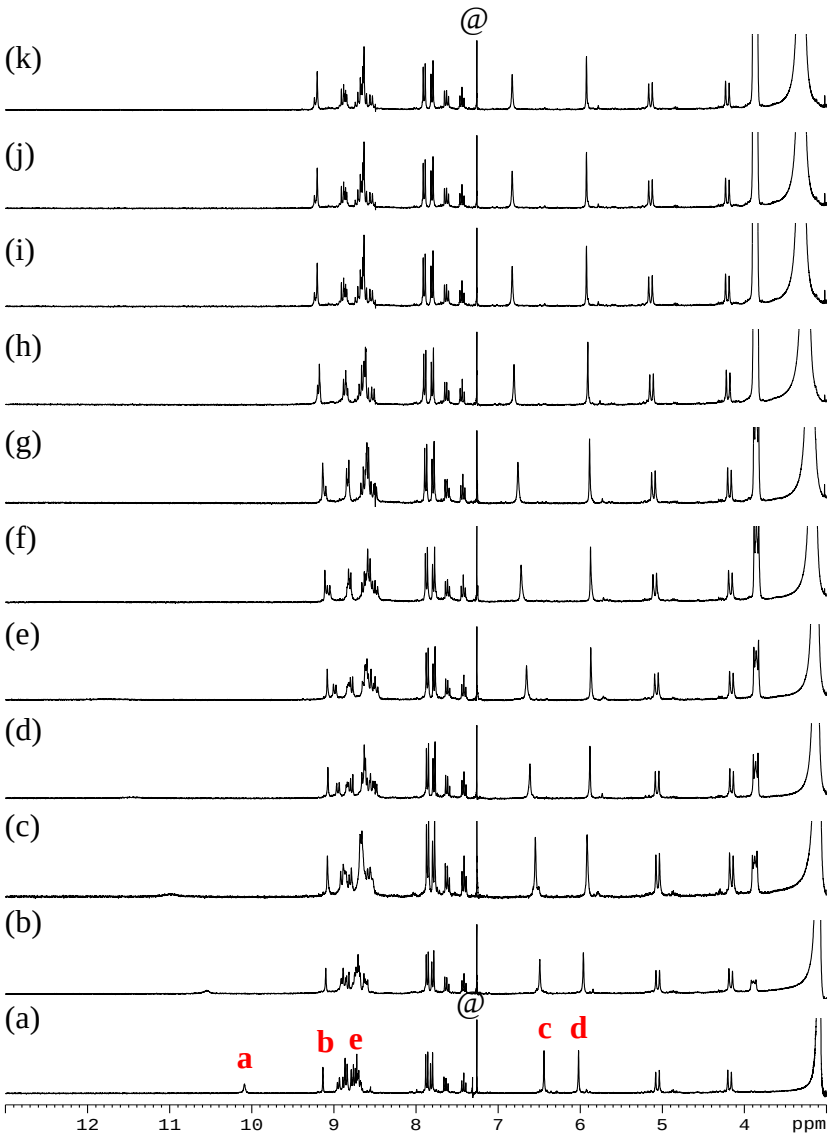


Figure S11. The ^{1}H NMR (300 MHz) titration spectra of (a) **4** (5.0 mM) in CD_3CN at 25^{o}C with the addition of various equiv of F^{-}: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, (h) 3.0, (i) 4.0, and (j) 5.0 equiv. Where signals denoted with @ came from external standard $CHCl_3$. The counter cation for fluoride is tetrabuthyammonium ion.



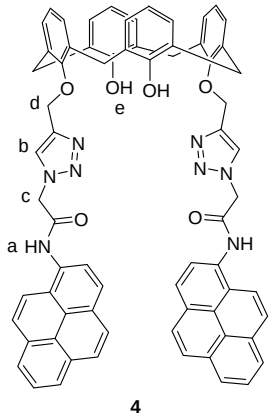


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Figure S12. The ^{1}H NMR (300 MHz) titration spectra of (a) **4** (5.0 mM) in CD_3CN at 25^{o}C with the addition of various equiv of $H_2PO_4^-$: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, (h) 3.0, (i) 4.0, (j) 5.0 and (k) 10.0 equiv. Where signals denoted with @ came from external standard $CHCl_3$. The counter cation is tetrabuthylammonium ion.

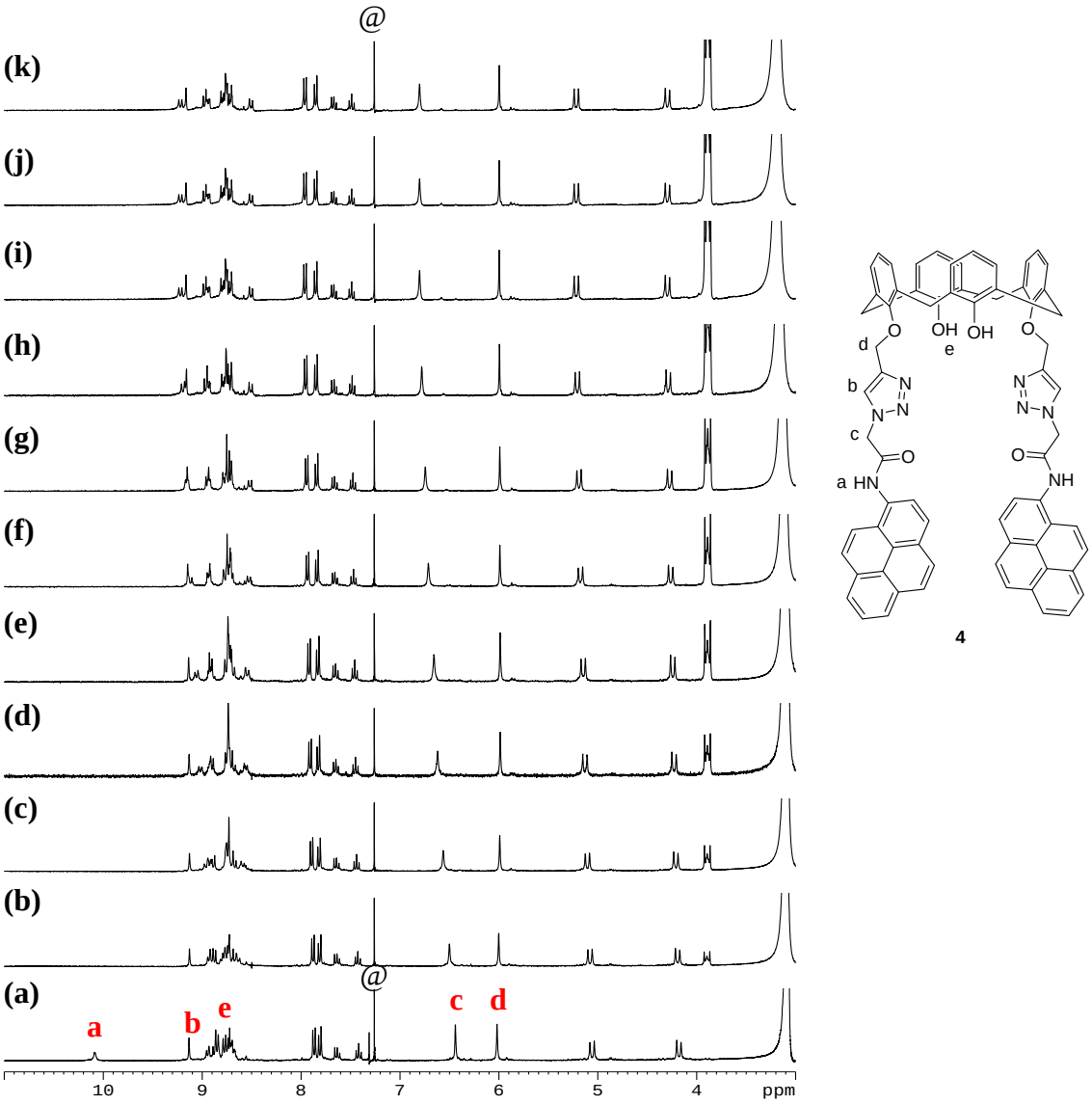

Figure S13. The ^{1}H NMR (300 MHz) titration spectra of (a) **4** (5.0 mM) in CD_3CN at 25^{o}C with the addition of various equiv of OAc^{-}: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, (h) 3.0, (i) 4.0, (j) 5.0, and (k) 10.0 equiv. Where signals denoted with @ came from external standard $CHCl_3$. The counter cation for acetate is tetrabuthylammonium ion.

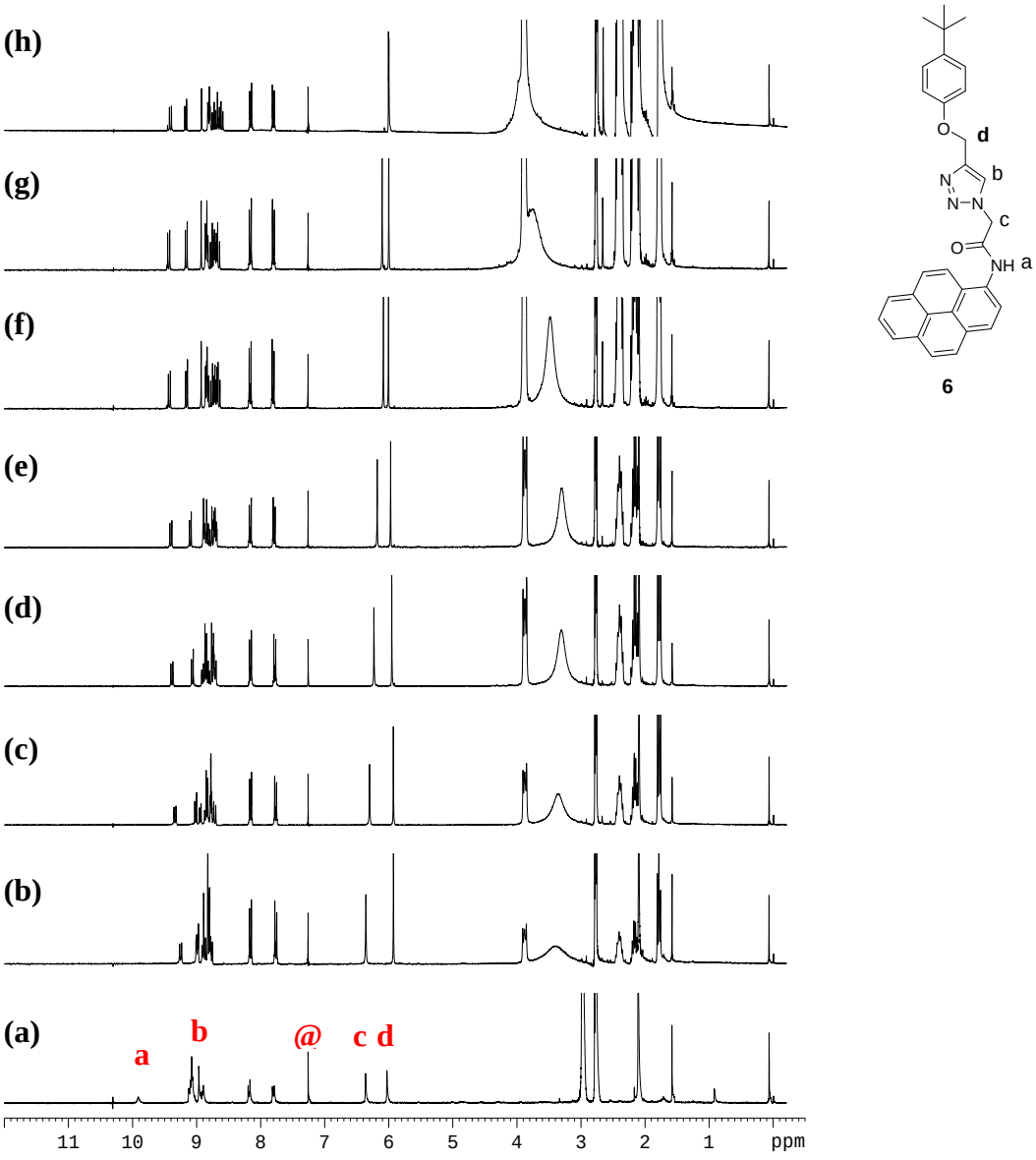

Figure S14. The ^{1}H NMR (300 MHz) titration spectra of (a) **6** (5.0 mM) in CD_3CN at 25^{o}C with the addition of various equiv of F^-: (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.5, (g) 2.0, and (h) 3.0 equiv. Where signals denoted with @ came from external standard $CHCl_3$. The counter cation for fluoride is tetrabuthyammonium ion.