Stable Core-modified Calixsmaragdyrins:
Synthesis, Structure and Specific Sensing of Hydrogen Sulfate Ion
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Compound 2a
Mol. Wt. = 544.22
Peak at [M+1]$^+$ = 545.23

Figure S1. HR-MS spectrum of compound 2a
Figure S2. HR-MS spectrum of compound 2b
Figure S3. HR-MS spectrum of compound 3
Figure S4. $^1$H NMR spectrum of compound 2a recorded in CDCl$_3$ at room temperature.
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Figure S14. Partial $^1$H NMR spectrum of compound 2a.2H$^{2+}$ recorded in CDCl$_3$ (★ residual solvent peak) at room temperature.
**Figure S15.** Partial $^1$H-$^1$H COSY NMR spectrum of compound 2a.2H$^{2+}$ showing the cross-peak connectivities between inner NH protons and $\beta$-pyrrole and $\beta$-furan protons recorded in CDCl$_3$ at room temperature.
Figure S16. Change in absorption spectra of compound 2b (1x10^{-5} M) upon systematic addition of TFA solution (0-2 equiv.) in CHCl\textsubscript{3} solution.
**Figure S17.** Absorption spectra of compound 2b.2H⁺² (1x10⁻⁵ M) in the presence of various anions such as F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, CH₃COO⁻, H₂PO₄⁻, HPO₄⁻², HSO₄⁻, SO₄⁻, SCN⁻, S₂O₃⁻, NO₃⁻ and N₃⁻ (excess of equivalents) recorded in CHCl₃ solution.
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Figure S19. Absorption spectra of compound 3.2H⁺² (1x10⁻⁵ M) in the presence of various anions F⁻, Cl⁻, Br⁻, I⁻, ClO₄⁻, CH₃COO⁻, H₂PO₄⁻, HPO₄⁻², HSO₄⁻, SO₄⁻², SCN⁻, S₂O₃⁻, NO₃⁻ and N₃⁻ (excess of equivalents) recorded in CHCl₃ solution.
Figure S20. Variable temperature $^1$H NMR spectra of compound 2b recorded in the temperature range 20°C to -20°C in CDCl$_3$ (* CDCl$_3$ peak).
**Figure S21.** Square Wave Voltamogram of compound 2b (1.2x10^{-2} M) upon titration with HSO_{4}^{-} ion (0-20 equiv.) recorded in CH_{2}Cl_{2} containing 0.1 M TBAP as supporting electrolyte at scan rates of 50 mVs^{-1}. 
**Figure S22.** Job’s plot for evolution of binding stoichiometry between Compound 2b and HSO₄⁻ in CHCl₃ solution. Where \( n_A \) is mole fraction of the anion added and \( A \) is absorbance of compound 2b in the presence of anion and \( A_0 \) is the absorbance of compound 2b in the absence of anion which forms 1:1 complex.
Figure S23. HR-MS spectrum of compound 2b+ HSO₄⁻ ion complex
Table S1. Selected bond lengths [Å] and angles [˚] for compound 2a.

<table>
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<th>Bond length[Å]</th>
<th>Parameters</th>
<th>Bond angle[˚]</th>
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Table S2. Hydrogen bonding parameter for compound 2a [Å and °].

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<th>D-H...A</th>
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<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
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<td>N(3)-H(3N)...O(2)</td>
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