Supporting Information


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General Procedure: Proton NMR spectra (400 MHz, Bruker DPX-400) were recorded using TMS as the internal standard. High resolution mass spectra were obtained on Voyager-DE STR MALDI-TOF mass spectrometer. Column chromatography was performed over silica gel (Merck, 230-400 mesh). Pyrrole was distilled at atmospheric pressure from CaH₂. All other reagents were obtained from Aldrich and used as received unless noted otherwise.

Synthetic Experimental

β - Dicyanovinyl calix[4]pyrrole (1): Compound 2 (85 mg, 0.19 mmol) and malononitrile (15 µL, 0.24 mmol) were dissolved in 3 mL of toluene, then piperidine (25 µL, 0.27 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 6h. The mixture was extracted with CHCl₃, and dried over anhydrous sodium sulfate. After the drying agent was filtered off, the organic solutions were combined and evaporated under reduced pressure. The residue was purified by column chromatography on silica (from CH₂Cl₂ / EtOAc = 95 / 5) to give compound 1 (54 mg, 58%) as yellowish solid; ¹H NMR (400 MHz, CDCl₃) δ 1.50 (s, 3H), 1.53 (s, 3H), 1.55 (s, 3H), 1.68 (s, 3H), 5.84-5.86 (m, 1H), 5.91-5.92 (m, 1H), 5.96-6.02 (m, 4H), 6.85 (brs, 1H), 6.95 (d, 1H, J = 2.7 Hz), 7.17 (brs, 1H), 7.23 (brs, 1H), 7.39 (brs, 1H), 7.94 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 28.44, 28.50, 28.95, 29.79, 35.11, 35.16, 35.22, 37.79, 72.35, 101.20, 102.83, 103.43, 104.11, 104.70, 104.88, 114.46, 114.82, 116.03, 135.28, 136.03, 137.11, 138.39, 139.36, 140.11, 140.23, 148.12, 151.78; MALDI-TOF MS calcd for C₃₂H₃₆N₆ 504.30, found 504.31.
Figure S1. $^1$H NMR spectrum of compound 1.
Figure S2. $^{13}$C NMR spectrum of compound 1.
Figure S3. MALDI-TOF MS spectrum of compound 1.

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Figure S4. Job plot analysis of compound 1 (4.12 x 10^{-5} M) with various anions in CH$_3$CN / 3% DMSO.
Figure S5. UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of F^- as a tetrabutylammonium salt in CH_3CN / 3% DMSO.
**Figure S6.** UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of Cl⁻ as a tetrabutylammonium salt in CH₃CN / 3% DMSO.
Figure S7. UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of Br⁻ as a tetrabutylammonium salt in CH₃CN / 3% DMSO.
Figure S8. UV-Visible spectral changes of I (4.12 x 10^{-5} M) upon addition of AcO^- as a tetrabutylammonium salt in CH$_3$CN / 3% DMSO.
Figure S9. UV-Visible spectral changes of I (4.12 x 10^{-5} M) upon addition of H_2PO_4^- as a tetrabutylammonium salt in CH_3CN / 3% DMSO.
Figure S10. UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of NO$_3^-$ as a tetrabutylammonium salt in CH$_3$CN / 3% DMSO.

Figure S11. UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of SCN$^{-}$ as a tetrabutylammonium salt in CH$_3$CN / 3% DMSO.
**Figure S12.** UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of HP_2O_7^{3-} as a tetrabutylammonium salt in CH_3CN / 3% DMSO.

a)

![Graph showing UV-Visible spectral changes](image)

b) biphasic behavior.

c) isotherm of first process.
**Figure S13.** UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of CN⁻ as a tetrabutylammonium salt in CH₃CN / 3% DMSO.

a)

![UV-Visible spectral changes](image)

b) Profile of [CN⁻] versus absorbance changes at 350 nm in the absence and the presence of Cl⁻ (as a tetrabutylammonium salt in CH₃CN / 3% DMSO). (1 = [4.12 x 10^{-5} M])

![Profile of [CN⁻] versus absorbance changes](image)
**Figure S14.** UV-Visible spectra changes and time-dependent absorbance changes (403 nm) of I (4.12 x 10^{-5} M) upon addition of CN\(^-\) (8.22 x 10^{-4} M) as a tetrabutylammonium salt in CH\(_3\)CN / 3% DMSO.

a)
**Figure S15.** UV-Visible spectra changes and time-dependent absorbance changes of 3-dicyanoethenylpyrrole (6.71 x 10^{-5} M) upon addition of CN\(^-\) as a tetrabutylammonium salt in CH\(_3\)CN / 3% DMSO.

a)

![UV-Visible spectra](image1)

b) Profile of [CN\(^-\)] versus absorbance changes at 338 nm.

![Profile of [CN\(^-\)]](image2)
Figure S16. $^1$H NMR spectral changes of 1 in CD$_3$CN / 3% DMSO-d$_6$ (1.0 x 10$^{-2}$ M) upon addition of Cl$^-$ added as a tetrabutylammonium salt.

Figure S17. $^1$H NMR spectral changes of 1 in CD$_3$CN / 3% DMSO-d$_6$ (1.0 x 10$^{-2}$ M) upon addition of CN$^-$ added as a tetrabutylammonium salt.
**Figure S18.** UV-Visible spectral changes of 1 (4.12 x 10^{-5} M) upon addition of CN\(^-\) in the presence of 20 equiv. of Cl\(^-\) as tetrabutylammonium salts in CH\(_3\)CN / 3% DMSO.

![UV-Visible spectral changes](image)

**Figure S19.** \(^1\)H NMR spectral changes of 1 in CD\(_3\)CN / 3% DMSO-d\(_6\) (1.0 x 10\(^{-2}\) M) upon addition of CN\(^-\) in the presence of Cl\(^-\) added as tetrabutylammonium salts.

![\(^1\)H NMR spectral changes](image)
Kinetic experiments of compound 1

**Figure S20.** Time-dependent absorbance changes upon addition of cyanide to 1 in CH$_3$CN / 3% DMSO (4.12 x 10$^{-5}$ M) where blue curve (compound 1 with 8.20 x 10$^{-4}$ M of CN$^-$) at 374 nm, red curve (compound 1 with 8.18 x 10$^{-4}$ M of CN$^-$ in the presence of 8.38 x 10$^{-4}$ M of Cl$^-$) at 336 nm and green curve (compound 1 with 8.37 x 10$^{-4}$ M of CN$^-$ in the presence of 8.30 x 10$^{-4}$ M of F$, Cl^-$, AcO$^-$, and H$_2$PO$_4^-$, respectively, as form of tetrabutylammonium salts) at 336 nm.

<table>
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<td>3$^c$</td>
<td>1.63</td>
<td>2.45</td>
<td>0.9995</td>
</tr>
</tbody>
</table>

$a$ compound 1 with CN$^-$ (20 equiv)

$b$ compound 1 with CN$^-$ (20 equiv) in the presence of Cl$^-$ (20 equiv)

$c$ compound 1 with CN$^-$ (20 equiv) in the presence of F$, Cl^-$, AcO$^-$, and H$_2$PO$_4^-$ (20 equiv, respectively)

**Table S1.** Pseudo-first order rate constants $k$ and $k_{obs}$ values of compound 1 with CN$^-$ in CH$_3$CN / 3% DMSO (4.12 X 10$^{-5}$ M) at 25 $^\circ$C.
Figure S21. Time-dependent absorbance changes upon addition of cyanide to 1 in CH$_3$CN / 3% DMSO (4.12 x 10$^{-5}$ M) where black curve (compound 1 with 4.23 x 10$^{-5}$ M of CN$^-$), green curve (compound 1 with 8.45 x 10$^{-4}$ M of CN$^-$), blue curve (compound 1 with 2.11 x 10$^{-4}$ M of CN$^-$), orange curve (compound 1 with 4.19 x 10$^{-4}$ M of CN$^-$), and red curve (compound 1 with 8.20 x 10$^{-4}$ M of CN$^-$) at 374 nm as form of tetrabutylammonium salts.)
Figure S22. UV-Visible spectra of 1 (4.12 X 10^{-5} M) with various anions where [F\textsuperscript{-}] = 3.80 X 10^{-4} M, [Cl\textsuperscript{-}] = 9.19 X 10^{-4} M, [Br\textsuperscript{-}] = 3.72 X 10^{-4} M, [AcO\textsuperscript{-}] = 6.77 X 10^{-4} M, [NO_3\textsuperscript{-}] = 6.83 X 10^{-4} M, [H_2PO_4\textsuperscript{-}] = 6.76 X 10^{-4} M, [SCN\textsuperscript{-}] = 3.85 X 10^{-4} M, [HP_2O_7\textsuperscript{3-}] = 4.46 X 10^{-4} M, and [CN\textsuperscript{-}] = 6.63 X 10^{-4} M in CH_3CN / 3% DMSO.

Figure S23. Color changes of 1 (1.03 X 10^{-3} M) in the presence of anions (20 equiv, respectively) in CH_3CN / 3% DMSO.