Supporting Information for

Anion binding modes in cis/trans-isomers of binding site–fluorophore–π-extended system

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1. General methods.

Unless otherwise noted, solvents and reagents were analytical grade and used without further purification. THF were distilled from Na prior to use. Flash chromatography was carried out on silica gel (200–300 mesh). UV-vis absorption spectra were obtained on a SHIMADZU UV-1800 spectrophotometer. Fluorescence emission spectra were obtained on a Hitach F-4600 Fluorescence spectrophotometer. IR were recorded on NICOLET 6700 FT-IR. $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AVANCE III 500 MHz and 400 MHz (operating at 500 MHz for $^1$H NMR and 100 MHz for $^{13}$C NMR), and chemical shifts were reported in parts per million (ppm, $\delta$ ) downfield from internal standard Me$_4$Si (TMS). HRMS were recorded on solan X 70 FT-MS spectrometer with methanol and water (v/v = 1:1) as solvent. Melting points were determined using melting point apparatus (WRS-2A) and uncorrected. Multiplicities of signals are described as follows: s --- singlet, br. s --- broad singlet, d --- doublet, t --- triplet, m --- multiplet.
2. Synthesis routes of dosimeter 3 (cis, trans) and its ketone derivatives 4 (cis, trans).

**Description:** The compounds cis-3 and trans-3 were synthesized using the following methods:\textsuperscript{1-6}: 4-bromo-1,8-naphthalenedicarboxylic anhydride (1) reacted with $o$-phenylenediamine to give the isomers cis-2 and trans-2, which was further condensed with phenylacetonitrile to afford the mixture of cis-3 and trans-3. The mixture of isomers was purified by column chromatography on silica gel, affording pure unreactive starting material cis-2, target compounds cis-3 and trans-3. The separated component, cis-2, was further transformed to isomer cis-3 by the similar workup. Moreover, the oxidative decyanation of isomers cis-3 and trans-3 with TBAF afforded the corresponding isomers cis-4 and trans-4, respectively.

**Synthesis of bromo-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-ones (trans-2 and cis-2):** To an acetic acid solution (25 mL) of 4-bromo-1,8-naphthalenedicarboxylic anhydride (1, 2.76 g, 10 mmol) was added o-phenylenediamine (1.10 g, 10 mmol), and the mixture was refluxed for 3 h. After the reaction was completed by TLC analysis, the mixture was poured into ice water (50 mL). The resulting precipitate was filtered and purified by recrystallization from toluene. The residues were dried 6 h at 80 °C to afford the pure mixtures of cis-2 and trans-2 (3.00 g, 85.6 %).
and isolation of single isomer (cis-2): Sodium hydride (60 w % in oil, 0.42 g, 10.5 mmol) was added to a solution of phenylacetonitrile (0.30 g, 2.56 mmol) under N₂ in tetrahydrofuran (30 mL), and the mixture was stirred at room temperature for 45 min. The reaction mixture was added with the mixture of trans-2 and cis-2 (0.62 g, 1.61 mmol), stirred at room temperature for another 12 h. The reaction mixture was poured into the ice water (50 mL), subsequently dropped the hydrochloric acid until pH = 2~3, then extracted with dichloromethane (20 mL × 3), finally the organic layer was washed with brine, dried with Na₂SO₄ and filtered. After concentration of solvent, the residue was purified by chromatography with silica gel to obtain the unreactive cis-2 (0.18 g, recrystallization twice from toluene), the target compounds trans-3 (0.25 g, 38 %) and cis-3 (0.12 g, 19 %). Moreover, the product cis-3 (0.52 g, 44 %) was further synthesized by the pure cis-2 (1.05 g, 3.02 mmol) with phenylacetonitrile (0.53 g, 4.53 mmol) based on the above-mentioned procedures.

3-bromo-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-ones (cis-2): ¹H NMR (500 MHz, CDCl₃) δ 7.47-7.49 (m, 2H), 7.85-7.91 (m, 2H), 8.06 (d, J = 8.0 Hz, 1H), 8.50-8.52 (m, 1H), 8.64 (d, J = 8.0 Hz, 1H), 8.65 (dd, J₁ = 8.0 Hz, J₂ = 1.0 Hz, 1H), 8.81 (dd, J₁ = 7.0 Hz, J₂ = 1.0 Hz, 1H).

4-(2-phenylacetonitrile)-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one (trans-3): mp 254.4-256.8 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 6.90 (s, 1H, C-H), 7.36-7.43 (m, 1H), 7.45 (dd, J₁ = 7.5 Hz, J₂ = 8.0 Hz, 2H), 7.49-7.51 (m, 4H, Ar-H), 7.87-7.89 (m, 1H), 7.96 (dd, J₁ = 7.5 Hz, J₂ = 8.5 Hz, 1H), 8.15 (d, J = 7.5 Hz, 1H), 8.42-8.44 (m, 1H), 8.50 (d, J = 8.5 Hz, 1H), 8.77 (d, J = 7.0 Hz, 1H), 8.80 (d, J = 7.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 149.0, 143.9, 138.8, 134.2, 131.8, 131.3, 129.6, 129.6, 129.0, 128.3, 127.9, 127.8, 127.3, 127.0, 126.1, 125.8, 124.2, 121.8, 120.2, 118.7, 115.9, 40.3; IR (KBr, cm⁻¹): νmax = 3058 (C-H), 2244 (C≡N), 1703 (C=O), 1610, 1596, 1548, 1449, 1359, 1322, 1231, 938, 778, 765, 755, 702 cm⁻¹; HRMS-ESI (m/z): [M + H]+ Calcd for C₂₂H₁₇N₅O 386.12934, Found 386.13333.

3-(2-phenylacetonitrile)-7H-benz[de]benzimidazo[2,1-a]isoquinoline-7-one (cis-3): mp 258.7 - 258.9 °C; ¹H NMR (500 MHz, DMSO-d₆), δ 6.86 (s, 1H, C-H), 7.35-7.38 (m, H), 7.44(t, J = 7.0 Hz, 2H), 7.49-7.50 (m, 4H, Ar-H), 7.89 (s, 1H), 8.00 (dd, J₁ = 7.5 Hz, J₂ = 8.0 Hz, 1H), 8.08 (d, J = 7.5 Hz, 1H), 8.42 (s, 1H), 8.65 (d, J = 8.5 Hz, 1H), 8.71 (d, J = 6.5 Hz, 1H), 8.85 (d, J = 7.5 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆), δ 160.5, 149.2, 143.9, 136.8, 136.0, 132.0, 131.8, 131.5, 129.9, 129.5, 128.9, 128.4, 128.3, 128.2, 127.9, 127.0, 126.1, 125.8, 124.3, 121.5, 120.4, 115.7, 115.1, 114.8; HRMS-ESI (m/z): [M + H]+ Calcd for C₂₂H₁₇N₅O 386.12934, Found 386.13333.
55.4, 38.9; IR (KBr, cm\(^{-1}\)): \(v_{\text{max}} = 2878\) (C-H), 2242 (C≡N), 1701 (C=O), 1586, 1609, 1596, 1548, 1448, 1359, 1322, 1231, 926, 769, 755, 742, 696 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^+\) Calcd for C\(_{26}\)H\(_{16}\)N\(_3\)O\(_3\) 386.12934, Found 386.13342.

**Synthesis of 4-benzoyl-7H-benz[d]benzimidazo[2,1-a]isoquinoline-7-one (trans-4):** The tetrabutylammonium fluoride (98 %, 0.08 g, 0.3 mmol) was added into the mixture of compound trans-3 (0.06 g, 0.15 mmol) and dichloromethane (20 mL), and stirred at room temperature. After the completion of reaction monitored by TLC, the reaction liquid was evaporated to dryness under reduced pressure. The residue was purified by chromatography with silica gel to obtain the target compound trans-4 (0.05 g, 87 %). mp. 235.4-235.6 \(^\circ\)C; \(^1\)H NMR (500 MHz, DMSO-\(d_6\)), \(\delta\) 7.53 (m, 2H), 7.62 (dd, \(J_1 = 7.0\) Hz, \(J_2 = 8.0\) Hz, 2H), 7.77 (t, \(J = 7.0\) Hz, 1H), 7.85 (d, \(J = 7.5\) Hz, 2H), 7.93 (dd, \(J_1 = 7.5\) Hz, \(J_2 = 8.0\) Hz, 2H), 8.04 (d, \(J = 7.0\) Hz, 1H), 8.15 (d, \(J = 8.5\) Hz, 1H), 8.47 (m, 1H), 8.80 (d, \(J = 7.5\) Hz, 1H), 8.83 (d, \(J = 7.0\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)), \(\delta\) 196.4, 160.1, 149.1, 143.9, 143.4, 134.3, 130.5, 130.3, 129.7, 128.9, 128.4, 127.6, 127.0, 126.1, 125.7, 121.0, 120.1, 115.9; IR (KBr, cm\(^{-1}\)): \(v_{\text{max}} = 3057, 1702(\text{C}=\text{O}), 1655, 1613, 1595, 1579, 1552, 1448, 1366, 1348, 1269, 1127, 1160, 908, 884, 779, 762, 748 cm\(^{-1}\); HRMS-ESI (m/z): [M+H]\(^+\) Calcd for C\(_{25}\)H\(_{15}\)N\(_2\)O\(_2\) 375.11335, Found 375.11549.
Synthesis of 3-benzoyl-7H-benzo[de]benzimidazo[2,1-a]isoquinoline-7-one (cis-4): The tetrabutylammonium fluoride (98 %, 0.08 g, 0.3 mmol) was added into the mixture of compound cis-3 (0.06 g, 0.15 mmol) and dichloromethane (20 mL), and stirred at room temperature. After the completion of reaction monitored by TLC, the reaction liquid was evaporated to dryness under reduced pressure. The residue was purified by chromatography with silica gel to obtain the target compound cis-4 (0.04 g, 70 %). mp 258.3-259 °C; \(^1\)H NMR (500 MHz, DMSO-d\(_6\)) , 7.54 (m, 2H), 7.61 (t, \(J = 7.5\) Hz, 2H), 7.77 (dd, \(J_1 = 6.0\) Hz, \(J_2 = 7.5\) Hz, 2H), 7.87 (d, \(J = 8.0\) Hz, 2H), 7.94 (d, \(J = 7.5\) Hz, 2H), 7.98 (dd, \(J_1 = 7.5\) Hz, \(J_2 = 8.0\) Hz, 1H), 8.01 (d, \(J = 7.5\) Hz, 1H), 8.42 (d, \(J = 8.5\) Hz, 1H), 8.48 (d, \(J = 7.5\) Hz, 1H), 8.78 (d, \(J = 7.0\) Hz, 1H), 8.85 (d, \(J = 7.5\) Hz, 1H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)) , \(\delta\) 196.5, 160.5, 149.1, 144.0, 139.6, 137.5, 134.7, 133.1, 132.1, 130.6, 129.8, 129.5, 128.9, 127.4, 126.2, 126.1, 125.9, 123.9, 123.0, 120.6, 115.8; IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) = 3057, 1699 (C=O), 1655, 1608, 1596, 1580, 1546, 1505, 1449, 1389, 1355, 1307, 1273, 1230, 1099, 930, 919, 882, 857, 802, 768, 761, 710, 692, 670 cm\(^{-1}\); HRMS-ESI (m/z): [M + H]\(^+\) Calcd for C\(_{25}\)H\(_{15}\)N\(_3\)O\(_2\) 375.11335, Found 375.11564.

Reference:


4. $^1$H-NMR spectrum of the compound cis-2 and the mixture of trans-2 and cis-2.

**Figure S1.** $^1$H-NMR (CDCl$_3$, 500 MHz) spectrum of the mixture of trans-2 and cis-2.

**Figure S2.** $^1$H-NMR (CDCl$_3$, 500 MHz) spectrum of compound cis-2
5. $^1$H-NMR, $^{13}$C-NMR, IR and HRMS-ESI spectrum of the compound trans-3.

**Figure S3.** $^1$H-NMR (DMSO-$d_6$, 500 MHz) spectrum of compound trans-3

**Figure S4.** $^{13}$C-NMR (CDCl$_3$, 400 MHz) spectrum of compound trans-3
Figure S5. IR spectrum of compound *trans*-3

Figure S6. HRMS-ESI mass spectrum of compound *trans*-3
6. $^1$H-NMR, $^{13}$C-NMR, IR and HRMS-ESI spectrum of the compound \textit{trans-4}.

\textbf{Figure S7}. $^1$H-NMR (DMSO-$d_6$, 500 MHz) spectrum of compound \textit{trans-4}

\textbf{Figure S8}. $^{13}$C-NMR (CDCl$_3$, 400 MHz) spectrum of compound \textit{trans-4}
Figure S9. IR spectrum of compound *trans*-4

Figure S10. HRMS-ESI mass spectrum of compound *trans*-4
7. $^1$H-NMR, $^{13}$C-NMR, IR and HRMS-ESI spectrum of the compound cis-3.

Figure S11. $^1$H-NMR (DMSO-$d_6$, $500$ MHz) spectrum of compound cis-3

Figure S12. $^{13}$H-NMR (DMSO-$d_6$, $400$ MHz) spectrum of compound cis-3
Figure S13. IR spectrum of compound cis-3.

Figure S14. HRMS-ESI mass spectrum of compound cis-3.
8. $^1$H-NMR, $^{13}$C-NMR, IR and HRMS-ESI spectrum of the compound cis-4.

![Figure S15. $^1$H-NMR (DMSO-$d_6$, 400 MHz) spectrum of compound cis-4](image)

![Figure S16. $^{13}$C-NMR (DMSO-$d_6$, 400 MHz) spectrum of compound cis-4](image)
Figure S17. IR spectrum of compound cis-4

Figure S18. HRMS-ESI mass spectrum of compound cis-4
9. The absorbance detection limit of cis-3 and trans-3 with CN⁻ in CH₃CN

Figure S19. Absorbance intensity ratio (A_{717}/A_{383}) of cis-3 (20 μM) as a function of CN⁻ concentration from 0 – 20 μM (0–1.0 equivalents)

Linear Regression for Book1_B:

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<tr>
<td>R</td>
<td>SD</td>
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<tr>
<td>0.98822</td>
<td>0.02423</td>
</tr>
</tbody>
</table>

Linear Equation: Y = 0.02291 * X, R = 0.99289

S = 2.143 * 10⁴, K = 3, δ = 0.02423

LOD = K * δ / S = 0.81 μM
Figure S20. Absorbance intensity ratio \((A_{620}/A_{352})\) of trans-3 (20 μM) as a function of CN\(^{-}\) concentration from 0–32 μM (0–1.6 equivalents)

Linear Regression for Book1_B:

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<th>Equation</th>
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<td>(0.99848)</td>
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</table>

The result of the analysis as follows:

Linear Equation: \(Y = -0.27198 + 0.09365 \times X\), \(R = 0.99848\)

\(S = 9.365 \times 10^4\), \(K = 3\), \(\delta = 0.05466\)

\(\text{LOD} = K \times \delta / S = 1.75 \mu M\)
10. UV-vis titration of cis-3 and trans-3 with CN⁻ in CH₃CN.

Figure S21. UV-visible spectral changes of 20 µM solution of cis-3 upon titration with CN⁻ (as its TBA salts) in CH₃CN;

Figure S22. UV-visible spectral changes of 20 µM solution of trans-3 upon titration with CN⁻ (as its TBA salts) in CH₃CN;
11. UV-vis interference experiments of trans-3 and cis-3 toward CN⁻ ions.

**Figure S23.** UV-visible spectral changes ($A_{717}$) of cis-3 (20 μM in CH₃CN) upon addition of 1.6 equiv of CN⁻ and 1.6 equiv of various interference anions. (the light gray bars represent the change in $A_{717}$ from 0 to 10 : cis-3 only, F⁻, AcO⁻, H₂PO₄⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, HSO₄⁻, BF₄⁻, ClO₄⁻; the red bars represent the addition of corresponding equiv of CN⁻ ions)

**Figure S24.** UV-visible spectral changes ($A_{620}$) of trans-3 (20 μM in CH₃CN) upon addition of 2.0 equiv of CN⁻ and 2.0 equiv of various interference anions. (the light gray bars represent the change in $A_{620}$ from 0 to 10 : trans-3 only, F⁻, AcO⁻, H₂PO₄⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, HSO₄⁻, BF₄⁻, ClO₄⁻; the red bars represent the addition of corresponding equiv of CN⁻ ions);
12. UV-vis titration of \textit{trans}-3 with \textit{CN}^{-} in CH$_3$CN-H$_2$O solution.

**Figure S25.** UV-visible spectral changes of 20 \mu{M} solution of \textit{trans}-3 upon titration with \textit{CN}^{-} (as its TBA salts) in CH$_3$CN-H$_2$O (95:5, v/v) solution;

**Figure S26.** Time-dependence of UV-visible spectral changes of 20 \mu{M} solution of \textit{trans}-3 upon titration with \textit{CN}^{-} (56 equiv) in CH$_3$CN-H$_2$O (9:5, v/v) solution;
13. UV-vis titration of compounds cis-3 and trans-3 with OH\textsuperscript{–} in CH\textsubscript{3}CN.

**Figure S27.** UV-visible titration of cis-3 (20 \(\mu\)M) with Bu\textsubscript{4}N\textsuperscript{+}OH\textsuperscript{−} (25% aq.) in CH\textsubscript{3}CN. Arrows show changes due to increasing concentration of OH\textsuperscript{−} (500 \(\mu\)M). The inset shows the absorbance at 717 nm as a function of [OH\textsuperscript{−}].

**Figure S28.** UV-visible titration of trans-3 (20 \(\mu\)M) with Bu\textsubscript{4}N\textsuperscript{+}OH\textsuperscript{−} (25% aq.) in CH\textsubscript{3}CN. Arrows show changes due to increasing concentration of OH\textsuperscript{−} (500 \(\mu\)M). The inset shows the absorbance at 620 nm as a function of [OH\textsuperscript{−}].
14. UV-vis spectrum of selectivity of \textit{trans}-3 with anion in CH$_3$CN-H$_2$O solution.

\textbf{Figure S29.} UV-visible spectra of 20 \textmu M solution of \textit{trans}-3 in CH$_3$CN-H$_2$O (95:5, v/v) solution in the presence of 56 equiv of different anions.
15. Emission spectra of selectivity and titration of cis-3 and trans-3 with CN$^{-}$ in CH$_3$CN.

Figure S30. Emission spectra of 20 μM solution of (a) cis-3 and (c) trans-3 in CH$_3$CN in the presence of different anions (4.0 equiv for cis-3 and 2.0 equiv for trans-3), Inset: from left to right: cis-3/trans-3 only, CN$^{-}$, F$^{-}$, AcO$^{-}$, H$_2$PO$_4^-$, Cl$^{-}$, Br$^{-}$, HSO$_4^-$, I$^{-}$, NO$_3^-$, BF$_4^-$, ClO$_4^-$ (as its TBA salts); Emission spectra taken upon titration of (b) cis-3 and (d) trans-3 (20 μM, λ$_{ex}$ = 414 nm) in CH$_3$CN with CN$^{-}$, Inset: Plot of relative emission intensity versus TBACN concentration.
16. The fluorescence detection limit of tran-3 and cis-3 with CN⁻ in CH₃CN.

Figure S31. Emission intensity ratio \((F_{504})\) of cis-3 (20 μM) as a function of CN⁻ concentration from 0–68 μM (0–3.40 equiv).

Linear Regression for Book1_B:

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<th>Equation</th>
<th>(Y = A + B \times X)</th>
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The result of the analysis as follows:

Linear Equation: \(Y = 4.41667 + 0.82699 \times X, R = 0.99096\)

\(S = 82.699 \times 10^4, K = 3, \delta = 0.03996\)

\(\text{LOD} = K \times \delta / S = 0.145 \mu M\)
Figure S32. Emission intensity ratio \((F_{515})\) of *trans*-3 (20 \(\mu\)M) as a function of CN\(^-\) concentration from 0-32 \(\mu\)M (0–1.6 equiv).

Linear Regression for Book1_B:

<table>
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<th>Parameter</th>
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<th>Error</th>
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<td>B</td>
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<tr>
<td>0.97981</td>
<td>0.07157</td>
<td>8</td>
</tr>
</tbody>
</table>

The result of the analysis as follows:

Linear Equation: \(Y = 5.82316 + 1.06292 \times X\), \(R = 0.97981\)

\(S = 106.292 \times 10^4\), \(K = 3\), \(\delta = 0.07157\)

\(LOD = K \times \delta / S = 0.202 \mu\)M
17. The $^1$H NMR titration of *trans*-3 with F$^-$ ions.

Figure S33. $^1$H NMR titration spectra of *trans*-3 in DMSO-$d_6$ ($1.09 \times 10^{-2}$ mol/L) upon addition of F$^-$ ions (as tetrabutylammonium salts in DMSO-$d_6$) at 298 K, from the bottom to top: 0, 0.5, 1.0, 1.5, 2.5, 4.5, 6.5 equiv.
18. The DFT calculations of \textit{trans}-3 with CN$^-$ ions.

\textbf{Figure S34.} HOMO-LUMO energy levels and the interfacial plots of the orbitals for \textit{trans}-3 and the \textit{trans}-3 + CN$^-$ complex.