Supporting Information

Anion Sensing by Novel Triarylboranes Containing Boraanthracene: DFT Functional Assessment, Selective Interactions, and Mechanism Demonstration

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Table S1: Calculated geometrical parameters: bond lengths (in Å) and bond angles (in °) for the fully optimized structures of 1CN at CAM-B3LYP/6-31G(d) level; the corresponding X-ray data\textsuperscript{1} (in parentheses).

| Parameter          | 1CN\textsuperscript{a} | 1CN\textsuperscript{b} |
|--------------------|-------------------------|--------------------------|
| B1 – C2            | 1.650 (1.647)           | 1.646                    |
| B1 – C41           | 1.637 (1.627)           | 1.617                    |
| B1 – C31           | 1.638 (1.625)           | 1.616                    |
| N18 – C7           | 1.502                   | 1.501                    |
| C2 – B1 – C41      | 111.3 (111.7)           | 110.7                    |
| C2 – B1 – C31      | 110.6 (109.1)           | 110.2                    |
| C31 – B1 – C41     | 112.3 (112.7)           | 115.4                    |
| C7 – N18 – C19     | 112.7                   | 112.7                    |
| C7 – N18 – C23     | 109.8                   | 109.8                    |
| C7 – N18 – C27     | 109.5                   | 109.6                    |
| C4 – C2 – B1       | 117.9                   | 117.7                    |
| C3 – C2 – B1       | 125.8                   | 125.8                    |
| C32 – C31 – B1     | 121.9                   | 121.4                    |
Table S2: Calculated geometrical parameters: bond lengths (in Å) and bond angles (in °) for the fully optimized structures of 2 and 2F at CAM-B3LYP/6-31G(d) level

| Parameter             | 2<sup>a</sup> | 2<sup>b</sup> | 2F<sup>a</sup> | 2F<sup>b</sup> |
|-----------------------|---------------|---------------|---------------|---------------|
| B1 – C2               | 1.584         | 1.588         | 1.680         | 1.656         |
| B1 – C41              | 1.541         | 1.542         | 1.639         | 1.615         |
| B1 – C31              | 1.541         | 1.542         | 1.626         | 1.612         |
| P18 – C7              | 1.795         | 1.791         | 1.785         | 1.733         |
| C2 – B1 – C41         | 119.7         | 119.8         | 112.1         | 102.5         |
| C2 – B1 – C31         | 119.7         | 119.8         | 116.8         | 113.3         |
| C31 – B1 – C41        | 120.6         | 120.5         | 104.4         | 114.1         |
| C7 – P18 – C19        | 110.1         | 110.1         | 110.9         | 111.6         |
| C7 – P18 – C23        | 110.5         | 110.8         | 110.5         | 111.2         |

<sup>a</sup>Implies ground state (S<sub>0</sub>); <sup>b</sup>Implies excited state (S<sub>1</sub>)
| Bond                              | 2CN<sup>a</sup> | 2CN<sup>b</sup> |
|----------------------------------|-----------------|-----------------|
| B1 – C2                          | 1.675           | 1.645           |
| B1 – C41                         | 1.635           | 1.621           |
| B1 – C31                         | 1.630           | 1.634           |
| P18 – C7                         | 1.785           | 1.730           |
| C2 – B1 – C41                    | 113.2           | 110.8           |
| C2 – B1 – C31                    | 114.6           | 106.6           |
| C31 – B1 – C41                   | 103.2           | 104.3           |
| C7 – P18 – C19                   | 110.8           | 111.1           |

<sup>a</sup> Implies ground state (S<sub>0</sub>); <sup>b</sup> Implies excited state (S<sub>1</sub>)

Table S3: Calculated geometrical parameters: bond lengths (in Å) and bond angles (in °) for the fully optimized structures of 2CN at CAM-B3LYP/6-31G(d) level.
C7 – P18 – C23  110.4  116.0
C7 – P18 – C27  110.4  112.1
C4 – C2 – B1   120.7  124.8
C3 – C2 – B1   122.9  120.5
C32 – C31 – B1 125.0  128.1
C33 – C31 – B1 118.7  116.2
C42 – C41 – B1 118.7  116.9
C43 – C41 – B1 125.2  127.2
C14 – C4 – C2  123.5  121.9
C10 – C3 – C2  123.9  121.0
C31 – C33 – S51 119.5  118.2
C41 – C42 – S51 119.4  118.0
C36 – C33 – S51 118.2  118.0
C44 – C42 – S51 118.2  118.4
C5 – C7 – P18  119.8  121.6
C6 – C7 – P18  121.7  122.4
C2 – B1 – C52  105.7  113.1
C31 – B1 – C52 110.1  111.0
C41 – B1 – C52 110.1  110.5
B1 – C52   1.603  1.600
C52 – N53   1.161  1.161

a Implies ground state (S₀); b Implies excited state (S₁)

Table S4: Calculated geometrical parameters: bond lengths (in Å) and bond angles (in °) for the fully optimized structures of 3 and 3F at CAM-B3LYP/6-31G(d) level

| Parameter     | 3ᵃ | 3ᵇ | 3Fᵃ | 3Fᵇ |
|---------------|----|----|-----|-----|
| B1 – C2       | 1.579 | 1.579 | 1.650 | 1.658 |
| B1 – C41      | 1.531 | 1.538 | 1.621 | 1.589 |
| B1 – C31      | 1.531 | 1.538 | 1.621 | 1.605 |
| N18 – C7      | 1.501 | 1.502 | 1.503 | 1.492 |
| C2 – B1 – C41 | 122.6 | 122.8 | 112.8 | 119.1 |
| C2 – B1 – C31 | 122.5 | 122.7 | 112.8 | 86.0 |
| Parameter | $3\text{CN}^a$ | $3\text{CN}^b$ |
|-----------|----------------|----------------|
| B1 – C2   | 1.651          | 1.654          |
| B1 – C41  | 1.626          | 1.609          |
| B1 – C31  | 1.626          | 1.602          |
| N18 – C7  | 1.501          | 1.494          |
| C2 – B1 – C41 | 112.6 | 114.6         |

$^a$Implies ground state ($S_0$); $^b$Implies excited state ($S_1$)
| Parameter | 4a | 4b | 4F<sup>a</sup> | 4F<sup>b</sup> |
|-----------|----|----|---------------|---------------|
| B1 – C2   | 1.579 | 1.578 | 1.651 | 1.725 |
| B1 – C41  | 1.531 | 1.539 | 1.621 | 1.606 |
| B1 – C31  | 1.531 | 1.539 | 1.620 | 1.584 |
| P18 – C7  | 1.795 | 1.790 | 1.784 | 1.732 |

<sup>a</sup> Implies ground state (S<sub>0</sub>);  <sup>b</sup> Implies excited state (S<sub>1</sub>)

Table S6: Calculated geometrical parameters: bond lengths (in Å) and bond angles (in °) for the fully optimized structures of 4 and 4F at CAM-B3LYP/6-31G(d) level
| Bond                  | "\(\text{C2-B1-C41}\)" | "\(\text{C2-B1-C31}\)" | "\(\text{C31-B1-C41}\)" | "\(\text{C7-P18-C19}\)" | "\(\text{C7-P18-C23}\)" | "\(\text{C7-P18-C27}\)" | "\(\text{C4-C2-B1}\)" | "\(\text{C3-C2-B1}\)" | "\(\text{C32-C31-B1}\)" | "\(\text{C33-C31-B1}\)" | "\(\text{C42-C41-B1}\)" | "\(\text{C43-C41-B1}\)" | "\(\text{C14-C4-C2}\)" | "\(\text{C10-C3-C2}\)" | "\(\text{C31-C33-O51}\)" | "\(\text{C41-C42-O51}\)" | "\(\text{C36-C33-O51}\)" | "\(\text{C44-C42-O51}\)" | "\(\text{C5-C7-P18}\)" | "\(\text{C6-C7-P18}\)" | "\(\text{C31-C33-O52}\)" | "\(\text{C41-C42-O52}\)" | "\(\text{C36-C33-O52}\)" | "\(\text{C44-C42-O52}\)" | "\(\text{C2-B1-F51}\)" | "\(\text{C31-B1-F51}\)" | "\(\text{C41-B1-F51}\)" | "\(\text{B1-F51}\)" |
|----------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
|                      | 122.5                    | 122.7                    | 112.3                    | 94.29                    |                          |                          | 120.3                    | 120.2                    | 124.7                    | 118.5                    | 118.5                    | 124.7                    | 120.4                    | 120.4                    | 122.8                    | 121.4                    | 114.9                    | 114.3                    | 114.9                    | 114.3                    | 120.5                    | 121.3                    | 119.6                    | 120.4                    | 119.8                    | 119.3                    | 121.6                    | 121.6                    | 122.8                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 123.3                    | 122.2                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 123.3                    | 123.4                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 113.9                    | 114.7                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 114.0                    | 113.9                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 109.7                    | 110.0                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 106.8                    | 110.3                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 106.9                    | 115.6                    |
|                      |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          |                          | 1.450                    | 1.405                     |

* Implies ground state (\(S_0\));  * Implies excited state (\(S_1\))

Table S7: Calculated geometrical parameters: bond lengths (in Å) and bond angles
(in °) for the fully optimized structures of 4CN at CAM-B3LYP/6-31G(d) level

| Parameter                  | 4CN\(^a\) | 4CN\(^b\) |
|----------------------------|-----------|-----------|
| B1 – C2                    | 1.650     | 1.653     |
| B1 – C41                   | 1.626     | 1.609     |
| B1 – C31                   | 1.626     | 1.607     |
| P18 – C7                   | 1.786     | 1.729     |
| C2 – B1 – C41              | 111.5     | 105.1     |
| C2 – B1 – C31              | 112.7     | 113.9     |
| C31 – B1 – C41             | 108.1     | 109.5     |
| C7 – P18 – C19             | 110.8     | 111.4     |
| C7 – P18 – C23             | 110.6     | 114.1     |
| C7 – P18 – C27             | 110.2     | 113.3     |
| C4 – C2 – B1               | 125.2     | 122.6     |
| C3 – C2 – B1               | 118.0     | 121.3     |
| C32 – C31 – B1             | 123.3     | 123.7     |
| C33 – C31 – B1             | 120.5     | 120.7     |
| C42 – C41 – B1             | 120.5     | 120.2     |
| C43 – C41 – B1             | 123.3     | 124.9     |
| C14 – C4 – C2              | 123.7     | 123.5     |
| C10 – C3 – C2              | 123.1     | 122.9     |
| C31 – C33 – O53            | 123.3     | 122.1     |
| C41 – C42 – O53            | 123.3     | 122.0     |
| C36 – C33 – O53            | 114.2     | 114.3     |
| C44 – C42 – O53            | 114.2     | 114.2     |
| C5 – C7 – P18              | 119.8     | 120.7     |
| C6 – C7 – N18              | 121.6     | 123.1     |
| C2 – B1 – C51              | 116.1     | 116.1     |
| C31 – B1 – C51             | 102.7     | 102.7     |
| C41 – B1 – C51             | 104.9     | 109.5     |
| B1 – C51                   | 1.614     | 1.605     |
| C51 – N52                  | 1.161     | 1.160     |

\(^a\) Implies ground state (S\(_0\)); \(^b\) Implies excited state (S\(_1\))
Table S8: Calculated geometrical parameters: bond lengths (in Å) and bond angles (in °) for the fully optimized structures of 1F at CAM-B3LYP/6-31G(d) level; available corresponding X-ray data\textsuperscript{1} are given in parentheses along with the values of CAM-B3LYP.

| Parameter | B3PW 91 | M06-2X | CAMB3LYP | HCTH | LSDA | PBEPBE |
|-----------|---------|--------|----------|------|------|--------|
| B1 – C2   | 1.691   | 1.693  | 1.678 (1.640) | 1.910 | 1.699 | 1.687  |
| B1 – C41  | 1.656   | 1.641  | 1.625 (1.617) | 1.637 | 1.652 | 1.644  |
| B1 – C31  | 1.653   | 1.651  | 1.639 (1.630) | 1.611 | 1.647 | 1.655  |
| C2 – B1 – C41 | 116.9 | 117.1  | 116.7 (114.5) | 117.0 | 118.2 | 117.6  |
| C2 – B1 – C31 | 114.8  | 115.3  | 112.0 (113.1) | 111.3 | 115.0 | 115.2  |
| C31 – B1 – C41 | 101.2 | 102.9  | 104.4 (111.1) | 102.1 | 101.7 | 103.0  |
| C2 – B1 – F52 | 104.1  | 104.5  | 106.8 (109.6) | 105.2 | 103.7 | 103.8  |
| C31 – B1 – F52 | 110.1  | 111.3  | 109.1 (105.2) | 112.4 | 109.9 | 110.7  |
| C41 – B1 – F52 | 108.3  | 109.2  | 107.6 (102.4) | 109.7 | 108.7 | 108.9  |
| B1 – F52  | 1.529   | 1.531  | 1.448 (1.479) | 1.585 | 1.601 | 1.623  |
| S51 – C43 | 1.871   | 1.886  | 1.791 (1.765) | 1.901 | 1.972 | 1.986  |
| S51 – C33 | 1.889   | 1.902  | 1.790 (1.768) | 1.961 | 1.972 | 1.872  |

Table S9: Calculated electronic excitation energies and corresponding oscillator strengths of singlet excited states of 1-4, 1F-4F and 1CN-4CN at DFT/CAM-B3LYP/6-31G(d) level of theory.

| Receptor /complex | Electronic transition\textsuperscript{a} | Energy (nm/eV) | f\textsuperscript{b} | Contrib.\textsuperscript{c} | CI\textsuperscript{d} |
|-------------------|------------------------------------------|----------------|-----------------|-----------------|-----------------|
| S\textsubscript{0} → S\textsubscript{1} | 371 (3.34) | 0.1657 | HOMO→LUMO | 0.692 |
| S\textsubscript{0} → S\textsubscript{2} | 323 (3.83) | 0.0047 | HOMO-1→LUMO | 0.517 |
| S\textsubscript{0} → S\textsubscript{3} | 262 (4.73) | 0.0007 | HOMO-2→LUMO | 0.581 |
| S\textsubscript{0} → S\textsubscript{4} | 249 (4.97) | 0.0093 | HOMO-4→LUMO | 0.463 |
| S\textsubscript{0} → S\textsubscript{5} | 248 (4.99) | 0.0090 | HOMO-3→LUMO+1 | 0.482 |
| S\textsubscript{0} → S\textsubscript{6} | 230 (5.39) | 0.0081 | HOMO→LUMO+2 | 0.519 |
| S\textsubscript{0} → S\textsubscript{7} | 229 (5.41) | 0.0029 | HOMO-3→LUMO | 0.578 |
| S\textsubscript{0} → S\textsubscript{8} | 224 (5.53) | 0.0018 | HOMO-5→LUMO | 0.491 |
| S\textsubscript{0} → S\textsubscript{9} | 215 (5.76) | 0.0003 | HOMO→LUMO+1 | 0.674 |
| S\textsubscript{0} → S\textsubscript{10} | 211 (5.85) | 0.0038 | HOMO→LUMO+4 | 0.507 |
| S\textsubscript{0} → S\textsubscript{11} | 209 (5.93) | 0.0004 | HOMO→LUMO+5 | 0.527 |
| S\textsubscript{0} → S\textsubscript{12} | 208 (5.96) | 0.0001 | HOMO→LUMO+6 | 0.645 |
| S\textsubscript{0} → S\textsubscript{13} | 206 (6.02) | 0.0043 | HOMO-6→LUMO | 0.640 |
| S\textsubscript{0} → S\textsubscript{14} | 204 (6.08) | 0.0031 | HOMO-2→LUMO+1 | 0.434 |
| S\textsubscript{0} → S\textsubscript{15} | 199 (6.23) | 0.0001 | HOMO-7→LUMO | 0.658 |
| Transition | Energy (eV) | Oscillator Strength | Orbital Change | Energy Gap (eV) |
|------------|-------------|---------------------|----------------|----------------|
| $S_0 \rightarrow S_1$ | 245 (5.06) | 0.0018 | HOMO→LUMO | 0.473 |
| $S_0 \rightarrow S_2$ | 238 (5.20) | 0.0184 | HOMO→LUMO+4 | 0.497 |
| $S_0 \rightarrow S_3$ | 233 (5.32) | 0.0022 | HOMO-1→LUMO+3 | 0.341 |
| $S_0 \rightarrow S_4$ | 232 (5.33) | 0.0041 | HOMO-4→LUMO | 0.435 |
| $S_0 \rightarrow S_5$ | 227 (5.46) | 0.0029 | HOMO→LUMO+3 | 0.449 |
| $S_0 \rightarrow S_6$ | 222 (5.58) | 0.0023 | HOMO→LUMO+3 | 0.406 |
| $S_0 \rightarrow S_7$ | 219 (5.66) | 0.0051 | HOMO-1→LUMO | 0.409 |
| $S_0 \rightarrow S_8$ | 215 (5.76) | 0.0024 | HOMO-3→LUMO | 0.330 |
| $S_0 \rightarrow S_9$ | 212 (5.84) | 0.0048 | HOMO→LUMO+1 | 0.548 |
| $S_0 \rightarrow S_{10}$ | 208 (5.96) | 0.0016 | HOMO-2→LUMO | 0.356 |
| $S_0 \rightarrow S_{11}$ | 205 (6.04) | 0.0006 | HOMO-1→LUMO | 0.322 |
| $S_0 \rightarrow S_{12}$ | 202 (6.14) | 0.0001 | HOMO→LUMO+7 | 0.367 |
| $S_0 \rightarrow S_{13}$ | 201 (6.17) | 0.0014 | HOMO→LUMO+2 | 0.275 |
| $S_0 \rightarrow S_{14}$ | 198 (6.26) | 0.0004 | HOMO-1→LUMO+3 | 0.306 |
| $S_0 \rightarrow S_{15}$ | 195 (6.36) | 0.0011 | HOMO-1→LUMO+4 | 0.281 |

| Transition | Energy (eV) | Oscillator Strength | Orbital Change | Energy Gap (eV) |
|------------|-------------|---------------------|----------------|----------------|
| $S_0 \rightarrow S_1$ | 253 (4.90) | 0.0014 | HOMO→LUMO+3 | 0.475 |
| $S_0 \rightarrow S_2$ | 248 (4.99) | 0.0011 | HOMO→LUMO+2 | 0.576 |
| $S_0 \rightarrow S_3$ | 242 (5.12) | 0.0294 | HOMO→LUMO+4 | 0.521 |
| $S_0 \rightarrow S_4$ | 232 (5.34) | 0.0012 | HOMO-5→LUMO | 0.497 |
| $S_0 \rightarrow S_5$ | 226 (5.47) | 0.0028 | HOMO→LUMO | 0.635 |
| $S_0 \rightarrow S_6$ | 218 (5.69) | 0.0017 | HOMO→LUMO+5 | 0.637 |
| $S_0 \rightarrow S_7$ | 214 (5.79) | 0.0010 | HOMO-3→LUMO | 0.431 |
| $S_0 \rightarrow S_8$ | 213 (5.82) | 0.0031 | HOMO→LUMO+7 | 0.557 |
| $S_0 \rightarrow S_9$ | 208 (5.96) | 0.0016 | HOMO→LUMO+1 | 0.436 |
| $S_0 \rightarrow S_{10}$ | 202 (6.14) | 0.0025 | HOMO→LUMO+4 | 0.423 |
| $S_0 \rightarrow S_{11}$ | 201 (6.17) | 0.0010 | HOMO-1→LUMO+1 | 0.285 |
| $S_0 \rightarrow S_{12}$ | 196 (6.32) | 0.0002 | HOMO-1→LUMO+2 | 0.406 |
| $S_0 \rightarrow S_{13}$ | 195 (6.36) | 0.0001 | HOMO-2→LUMO+2 | 0.254 |
| $S_0 \rightarrow S_{14}$ | 194 (6.39) | 0.0011 | HOMO-2→LUMO | 0.379 |
| $S_0 \rightarrow S_{15}$ | 192 (6.46) | 0.0013 | HOMO-3→LUMO+1 | 0.327 |

| Transition | Energy (eV) | Oscillator Strength | Orbital Change | Energy Gap (eV) |
|------------|-------------|---------------------|----------------|----------------|
| $S_0 \rightarrow S_1$ | 410 (3.02) | 0.1750 | HOMO→LUMO | 0.691 |
| $S_0 \rightarrow S_2$ | 351 (3.53) | 0.0037 | HOMO-1→LUMO | 0.508 |
| $S_0 \rightarrow S_3$ | 303 (4.09) | 0.0021 | HOMO-4→LUMO | 0.462 |
| $S_0 \rightarrow S_4$ | 248 (4.99) | 0.0002 | HOMO-3→LUMO | 0.665 |
| $S_0 \rightarrow S_5$ | 239 (5.19) | 0.0003 | HOMO-2→LUMO+1 | 0.583 |
| $S_0 \rightarrow S_6$ | 229 (5.41) | 0.0005 | HOMO→LUMO+1 | 0.687 |
| $S_0 \rightarrow S_7$ | 228 (5.44) | 0.0021 | HOMO→LUMO+2 | 0.514 |
| $S_0 \rightarrow S_8$ | 226 (5.48) | 0.0016 | HOMO-2→LUMO | 0.680 |
| $S_0 \rightarrow S_9$ | 224 (5.53) | 0.0023 | HOMO-5→LUMO | 0.481 |
| $S_0 \rightarrow S_i$ | Energy (eV) | $\Delta E$ (eV) | $\Delta E_{HOMO\rightarrow LUMO}$ (eV) | $\Delta E_{HOMO\rightarrow LUMO+1}$ (eV) |
|---------------------|-------------|----------------|----------------------------------|----------------------------------|
| $S_0 \rightarrow S_{10}$ | 218 (5.69) | 0.0007 | HOMO-3→LUMO+1 | 0.530 |
| $S_0 \rightarrow S_{11}$ | 210 (5.90) | 0.0017 | HOMO-5→LUMO | 0.463 |
| $S_0 \rightarrow S_{12}$ | 209 (5.93) | 0.0006 | HOMO→LUMO+5 | 0.529 |
| $S_0 \rightarrow S_{13}$ | 207 (5.99) | 0.0001 | HOMO→LUMO+6 | 0.673 |
| $S_0 \rightarrow S_{14}$ | 205 (6.05) | 0.0009 | HOMO-6→LUMO+3 | 0.664 |
| $S_0 \rightarrow S_{15}$ | 203 (6.11) | 0.0001 | HOMO-7→LUMO | 0.657 |
| $S_0 \rightarrow S_1$ | 254 (4.88) | 0.0016 | HOMO→LUMO | 0.589 |
| $S_0 \rightarrow S_2$ | 244 (5.08) | 0.0021 | HOMO-4→LUMO | 0.518 |
| $S_0 \rightarrow S_3$ | 240 (5.17) | 0.0006 | HOMO→LUMO+2 | 0.420 |
| $S_0 \rightarrow S_4$ | 237 (5.23) | 0.0211 | HOMO→LUMO+4 | 0.434 |
| $S_0 \rightarrow S_5$ | 233 (5.32) | 0.0020 | HOMO→LUMO+5 | 0.298 |
| $S_0 \rightarrow S_6$ | 230 (5.39) | 0.0004 | HOMO-3→LUMO | 0.446 |
| $S_0 \rightarrow S_7$ | 225 (5.51) | 0.0025 | HOMO→LUMO+3 | 0.456 |
| $S_0 \rightarrow S_8$ | 223 (5.56) | 0.0005 | HOMO-1→LUMO | 0.472 |
| $S_0 \rightarrow S_9$ | 221 (5.61) | 0.0013 | HOMO→LUMO+3 | 0.371 |
| $S_0 \rightarrow S_{10}$ | 211 (5.87) | 0.0023 | HOMO-1→LUMO+2 | 0.410 |
| $S_0 \rightarrow S_{11}$ | 210 (5.90) | 0.0013 | HOMO→LUMO+1 | 0.455 |
| $S_0 \rightarrow S_{12}$ | 203 (6.11) | 0.0016 | HOMO-1→LUMO+4 | 0.384 |
| $S_0 \rightarrow S_{13}$ | 202 (6.14) | 0.0021 | HOMO→LUMO+9 | 0.458 |
| $S_0 \rightarrow S_{14}$ | 200 (6.20) | 0.0012 | HOMO-1→LUMO+3 | 0.371 |
| $S_0 \rightarrow S_{15}$ | 197 (6.29) | 0.0032 | HOMO-2→LUMO+3 | 0.325 |

**2F**

| $S_0 \rightarrow S_1$ | 256 (4.84) | 0.0005 | HOMO-4→LUMO | 0.621 |
| $S_0 \rightarrow S_2$ | 244 (5.08) | 0.0002 | HOMO-4→LUMO | 0.491 |
| $S_0 \rightarrow S_3$ | 238 (5.20) | 0.0020 | HOMO→LUMO+2 | 0.360 |
| $S_0 \rightarrow S_4$ | 237 (5.23) | 0.0003 | HOMO→LUMO+4 | 0.500 |
| $S_0 \rightarrow S_5$ | 232 (5.34) | 0.0198 | HOMO→LUMO+3 | 0.350 |
| $S_0 \rightarrow S_6$ | 228 (5.44) | 0.0003 | HOMO-1→LUMO+3 | 0.422 |
| $S_0 \rightarrow S_7$ | 225 (5.51) | 0.0008 | HOMO→LUMO+3 | 0.313 |
| $S_0 \rightarrow S_8$ | 222 (5.58) | 0.0011 | HOMO-1→LUMO | 0.573 |
| $S_0 \rightarrow S_9$ | 219 (5.66) | 0.0005 | HOMO-2→LUMO | 0.461 |
| $S_0 \rightarrow S_{10}$ | 212 (5.84) | 0.0002 | HOMO-1→LUMO+2 | 0.406 |
| $S_0 \rightarrow S_{11}$ | 209 (5.93) | 0.0006 | HOMO→LUMO+1 | 0.528 |
| $S_0 \rightarrow S_{12}$ | 203 (6.11) | 0.0004 | HOMO-1→LUMO+4 | 0.353 |
| $S_0 \rightarrow S_{13}$ | 202 (6.14) | 0.0009 | HOMO→LUMO+7 | 0.420 |
| $S_0 \rightarrow S_{14}$ | 197 (6.29) | 0.0005 | HOMO-1→LUMO+3 | 0.409 |
| $S_0 \rightarrow S_{15}$ | 194 (6.39) | 0.0006 | HOMO-1→LUMO+5 | 0.324 |
| Transition  | E (eV)  | Oscillator Strength | Type of Transition | Emissions (eV) |
|------------|---------|---------------------|--------------------|---------------|
| $S_0 \rightarrow S_1$ | 0.1561 | 0.682 | HOMO$\rightarrow$LUMO$+1$ | 24.5 |
| $S_0 \rightarrow S_2$ | 0.0001 | 0.597 | HOMO$-1$$\rightarrow$LUMO | 25.8 |
| $S_0 \rightarrow S_3$ | 0.0003 | 0.585 | HOMO$-2$$\rightarrow$LUMO | 26.0 |
| $S_0 \rightarrow S_4$ | 0.0005 | 0.549 | HOMO$-4$$\rightarrow$LUMO | 26.2 |
| $S_0 \rightarrow S_5$ | 0.0032 | 0.487 | HOMO$-3$$\rightarrow$LUMO$+1$ | 26.5 |
| $S_0 \rightarrow S_6$ | 0.0007 | 0.598 | HOMO$-2$$\rightarrow$LUMO | 26.8 |
| $S_0 \rightarrow S_7$ | 0.0018 | 0.601 | HOMO$-5$$\rightarrow$LUMO | 27.1 |
| $S_0 \rightarrow S_8$ | 0.0012 | 0.535 | HOMO$\rightarrow$LUMO$+3$ | 27.4 |
| $S_0 \rightarrow S_9$ | 0.0029 | 0.439 | HOMO$-2$$\rightarrow$LUMO$+1$ | 27.7 |
| $S_0 \rightarrow S_{10}$ | 0.0013 | 0.586 | HOMO$-6$$\rightarrow$LUMO | 28.0 |
| $S_0 \rightarrow S_{11}$ | 0.0004 | 0.696 | HOMO$-4$$\rightarrow$LUMO$+1$ | 28.3 |
| $S_0 \rightarrow S_{12}$ | 0.0036 | 0.541 | HOMO$-6$$\rightarrow$LUMO$+4$ | 28.6 |
| $S_0 \rightarrow S_{13}$ | 0.0021 | 0.332 | HOMO$-1$$\rightarrow$LUMO$+3$ | 28.9 |
| $S_0 \rightarrow S_{14}$ | 0.0001 | 0.661 | HOMO$-7$$\rightarrow$LUMO | 29.2 |
| $S_0 \rightarrow S_{15}$ | 0.0016 | 0.538 | HOMO$\rightarrow$LUMO$+5$ | 29.5 |

### 3F

| Transition  | E (eV)  | Oscillator Strength | Type of Transition | Emissions (eV) |
|------------|---------|---------------------|--------------------|---------------|
| $S_0 \rightarrow S_1$ | 0.0001 | 0.616 | HOMO$\rightarrow$LUMO$+2$ | 29.8 |
| $S_0 \rightarrow S_2$ | 0.0015 | 0.445 | HOMO$\rightarrow$LUMO$+3$ | 30.1 |
| $S_0 \rightarrow S_3$ | 0.0161 | 0.452 | HOMO$\rightarrow$LUMO$+4$ | 30.4 |
| $S_0 \rightarrow S_4$ | 0.0002 | 0.447 | HOMO$\rightarrow$LUMO$+5$ | 30.7 |
| $S_0 \rightarrow S_5$ | 0.0013 | 0.410 | HOMO$\rightarrow$LUMO$+2$ | 31.0 |
| $S_0 \rightarrow S_6$ | 0.0011 | 0.467 | HOMO$-2$$\rightarrow$LUMO | 31.3 |
| $S_0 \rightarrow S_7$ | 0.0017 | 0.464 | HOMO$-6$$\rightarrow$LUMO$+2$ | 31.6 |
| $S_0 \rightarrow S_8$ | 0.0009 | 0.476 | HOMO$-2$$\rightarrow$LUMO$+3$ | 31.9 |
| $S_0 \rightarrow S_9$ | 0.0024 | 0.477 | HOMO$-2$$\rightarrow$LUMO$+5$ | 32.2 |
| $S_0 \rightarrow S_{10}$ | 0.0014 | 0.406 | HOMO$-1$$\rightarrow$LUMO$+3$ | 32.5 |
| $S_0 \rightarrow S_{11}$ | 0.0012 | 0.258 | HOMO$-1$$\rightarrow$LUMO$+5$ | 32.8 |
| $S_0 \rightarrow S_{12}$ | 0.0003 | 0.540 | HOMO$-2$$\rightarrow$LUMO$+1$ | 33.1 |
| $S_0 \rightarrow S_{13}$ | 0.0025 | 0.324 | HOMO$-2$$\rightarrow$LUMO$+1$ | 33.4 |
| $S_0 \rightarrow S_{14}$ | 0.0011 | 0.470 | HOMO$-1$$\rightarrow$LUMO$+2$ | 33.7 |
| $S_0 \rightarrow S_{15}$ | 0.0013 | 0.293 | HOMO$-6$$\rightarrow$LUMO$+2$ | 34.0 |
| State Transition | E (eV) | ΔE (eV) | Excitation Type | Transition Energy (eV) |
|------------------|--------|---------|-----------------|-----------------------|
| $S_0 \rightarrow S_1$ | 247 (5.02) | 0.0001 | HOMO→LUMO+2 | 0.616 |
| $S_0 \rightarrow S_2$ | 241 (5.15) | 0.0005 | HOMO→LUMO | 0.417 |
| $S_0 \rightarrow S_3$ | 234 (5.29) | 0.0151 | HOMO→LUMO+3 | 0.512 |
| $S_0 \rightarrow S_4$ | 232 (5.34) | 0.0001 | HOMO→LUMO | 0.478 |
| $S_0 \rightarrow S_5$ | 229 (5.41) | 0.0006 | HOMO→LUMO | 0.521 |
| $S_0 \rightarrow S_6$ | 217 (5.71) | 0.0003 | HOMO→LUMO | 0.463 |
| $S_0 \rightarrow S_7$ | 211 (5.87) | 0.0011 | HOMO→LUMO+1 | 0.512 |
| $S_0 \rightarrow S_8$ | 201 (6.17) | 0.0007 | HOMO→LUMO+2 | 0.439 |
| $S_0 \rightarrow S_9$ | 198 (6.26) | 0.0001 | HOMO→LUMO | 0.507 |
| $S_0 \rightarrow S_{10}$ | 196 (6.32) | 0.0003 | HOMO→LUMO+2 | 0.511 |
| $S_0 \rightarrow S_{11}$ | 195 (6.36) | 0.0001 | HOMO→LUMO+1 | 0.261 |
| $S_0 \rightarrow S_{12}$ | 192 (6.46) | 0.0002 | HOMO→LUMO+1 | 0.317 |
| $S_0 \rightarrow S_{13}$ | 191 (6.49) | 0.0007 | HOMO→LUMO | 0.336 |
| $S_0 \rightarrow S_{14}$ | 190 (6.52) | 0.0003 | HOMO→LUMO+2 | 0.357 |
| $S_0 \rightarrow S_{15}$ | 189 (6.56) | 0.0017 | HOMO→LUMO | 0.287 |
| $S_0 \rightarrow S_{1}$ | 316 (3.92) | 0.1674 | HOMO→LUMO | 0.681 |
| $S_0 \rightarrow S_{2}$ | 255 (4.86) | 0.0002 | HOMO→LUMO+2 | 0.591 |
| $S_0 \rightarrow S_{3}$ | 241 (5.14) | 0.0008 | HOMO→LUMO+3 | 0.661 |
| $S_0 \rightarrow S_{4}$ | 240 (5.17) | 0.0003 | HOMO→LUMO+1 | 0.582 |
| $S_0 \rightarrow S_{5}$ | 239 (5.19) | 0.0011 | HOMO→LUMO+1 | 0.539 |
| $S_0 \rightarrow S_{6}$ | 221 (5.61) | 0.0005 | HOMO→LUMO+2 | 0.608 |
| $S_0 \rightarrow S_{7}$ | 220 (5.63) | 0.0007 | HOMO→LUMO+1 | 0.679 |
| $S_0 \rightarrow S_{8}$ | 217 (5.71) | 0.0002 | HOMO→LUMO+1 | 0.696 |
| $S_0 \rightarrow S_{9}$ | 212 (5.84) | 0.0021 | HOMO→LUMO+2 | 0.514 |
| $S_0 \rightarrow S_{10}$ | 211 (5.85) | 0.0006 | HOMO→LUMO+3 | 0.601 |
| $S_0 \rightarrow S_{11}$ | 208 (5.96) | 0.0004 | HOMO→LUMO+4 | 0.669 |
| $S_0 \rightarrow S_{12}$ | 199 (6.23) | 0.0006 | HOMO→LUMO+4 | 0.542 |
| $S_0 \rightarrow S_{13}$ | 197 (6.29) | 0.0012 | HOMO→LUMO+2 | 0.308 |
| $S_0 \rightarrow S_{14}$ | 194 (6.39) | 0.0003 | HOMO→LUMO+1 | 0.658 |
| $S_0 \rightarrow S_{15}$ | 193 (6.42) | 0.0006 | HOMO→LUMO+2 | 0.676 |
| Excited State Transition | Energy (eV) | Oscillator Strength | Configuration | Oscillator Strength |
|--------------------------|------------|---------------------|---------------|---------------------|
| $S_0 \rightarrow S_1$    | 248 (4.99) | 0.0001              | HOMO→LUMO     | 0.616               |
| $S_0 \rightarrow S_2$    | 245 (5.06) | 0.0002              | HOMO→LUMO+2   | 0.600               |
| $S_0 \rightarrow S_3$    | 241 (5.14) | 0.0001              | HOMO→LUMO     | 0.467               |
| $S_0 \rightarrow S_4$    | 234 (5.29) | 0.0162              | HOMO→LUMO+4   | 0.491               |
| $S_0 \rightarrow S_5$    | 231 (5.37) | 0.0001              | HOMO→LUMO     | 0.456               |
| $S_0 \rightarrow S_6$    | 224 (5.53) | 0.0002              | HOMO→LUMO+3   | 0.466               |
| $S_0 \rightarrow S_7$    | 221 (5.61) | 0.0004              | HOMO→LUMO     | 0.451               |
| $S_0 \rightarrow S_8$    | 207 (5.99) | 0.0008              | HOMO→LUMO+1   | 0.527               |
| $S_0 \rightarrow S_9$    | 206 (6.02) | 0.0011              | HOMO→LUMO     | 0.505               |
| $S_0 \rightarrow S_{10}$ | 202 (6.14) | 0.0006              | HOMO→LUMO+2   | 0.517               |
| $S_0 \rightarrow S_{11}$ | 199 (6.23) | 0.0023              | HOMO→LUMO+2   | 0.387               |
| $S_0 \rightarrow S_{12}$ | 196 (6.33) | 0.0012              | HOMO→LUMO     | 0.576               |
| $S_0 \rightarrow S_{13}$ | 195 (6.36) | 0.0003              | HOMO→LUMO+2   | 0.383               |
| $S_0 \rightarrow S_{14}$ | 194 (6.39) | 0.0001              | HOMO→LUMO+2   | 0.303               |
| $S_0 \rightarrow S_{15}$ | 192 (6.46) | 0.0011              | HOMO→LUMO+1   | 0.514               |

| Excited State Transition | Energy (eV) | Oscillator Strength | Configuration | Oscillator Strength |
|--------------------------|------------|---------------------|---------------|---------------------|
| $S_0 \rightarrow S_1$    | 253 (4.90) | 0.0001              | HOMO→LUMO     | 0.638               |
| $S_0 \rightarrow S_2$    | 247 (5.02) | 0.0003              | HOMO→LUMO+2   | 0.610               |
| $S_0 \rightarrow S_3$    | 242 (5.12) | 0.0002              | HOMO→LUMO+3   | 0.424               |
| $S_0 \rightarrow S_4$    | 236 (5.25) | 0.0003              | HOMO→LUMO     | 0.534               |
| $S_0 \rightarrow S_5$    | 234 (5.29) | 0.0161              | HOMO→LUMO+4   | 0.371               |
| $S_0 \rightarrow S_6$    | 231 (5.37) | 0.0003              | HOMO→LUMO+5   | 0.474               |
| $S_0 \rightarrow S_7$    | 211 (5.87) | 0.0005              | HOMO→LUMO+2   | 0.513               |
| $S_0 \rightarrow S_8$    | 209 (5.93) | 0.0001              | HOMO→LUMO+1   | 0.525               |
| $S_0 \rightarrow S_9$    | 203 (6.11) | 0.0002              | HOMO→LUMO+3   | 0.444               |
| $S_0 \rightarrow S_{10}$ | 201 (6.17) | 0.0004              | HOMO→LUMO     | 0.412               |
| $S_0 \rightarrow S_{11}$ | 197 (6.29) | 0.0006              | HOMO→LUMO+4   | 0.495               |
| $S_0 \rightarrow S_{12}$ | 195 (6.36) | 0.0011              | HOMO→LUMO+2   | 0.491               |
| $S_0 \rightarrow S_{13}$ | 194 (6.39) | 0.0002              | HOMO→LUMO+1   | 0.390               |
| $S_0 \rightarrow S_{14}$ | 193 (6.42) | 0.0003              | HOMO→LUMO     | 0.303               |
| $S_0 \rightarrow S_{15}$ | 192 (6.46) | 0.0006              | HOMO→LUMO+3   | 0.345               |

\(^{a}\) Only the selected low-lying excited states are presented. \(^{b}\) Oscillator strengths. \(^{c}\) Only the main configurations are presented. \(^{d}\) The CI coefficients are in absolute values.

Table S10: Calculated electronic excitation energies and corresponding oscillator strengths of the singlet excited state transitions of 1, 1F and 1CN by employing different functionals.
| Functional | Receptor/complex | Electronic transition<sup>a</sup> | Energy (nm/eV) |<sup>b</sup> | Contrib.<sup>c</sup> | CI<sup>d</sup> |
|------------|-----------------|---------------------------------|--------------|--------|-----------------|--------|
| M06-2X     | 1               | $S_0 \rightarrow S_1$          | 327 (3.79)   | 0.1684 | HOMO→LUMO       | 0.694  |
|            |                 | $S_0 \rightarrow S_2$          | 260 (4.76)   | 0.0109 | HOMO-1→LUMO     | 0.479  |
|            |                 | $S_0 \rightarrow S_3$          | 253 (4.90)   | 0.0004 | HOMO-2→LUMO     | 0.603  |
|            |                 | $S_0 \rightarrow S_4$          | 246 (5.04)   | 0.0038 | HOMO-4→LUMO     | 0.429  |
|            |                 | $S_0 \rightarrow S_5$          | 231 (5.36)   | 0.0063 | HOMO→LUMO+2     | 0.491  |
|            |                 | $S_0 \rightarrow S_6$          | 228 (5.44)   | 0.0092 | HOMO-3→LUMO+1   | 0.489  |
| M06-2X     | 1F              | $S_0 \rightarrow S_1$          | 290 (4.28)   | 0.0021 | HOMO→LUMO       | 0.544  |
|            |                 | $S_0 \rightarrow S_2$          | 271 (4.57)   | 0.0107 | HOMO→LUMO+4     | 0.516  |
|            |                 | $S_0 \rightarrow S_3$          | 234 (5.29)   | 0.0026 | HOMO-1→LUMO+3   | 0.325  |
|            |                 | $S_0 \rightarrow S_4$          | 232 (5.34)   | 0.0035 | HOMO-4→LUMO     | 0.371  |
|            |                 | $S_0 \rightarrow S_5$          | 230 (5.39)   | 0.0021 | HOMO-2→LUMO     | 0.317  |
|            |                 | $S_0 \rightarrow S_6$          | 226 (5.48)   | 0.0013 | HOMO→LUMO+3     | 0.530  |
| M06-2X     | 1CN             | $S_0 \rightarrow S_1$          | 275 (4.51)   | 0.0033 | HOMO→LUMO+3     | 0.493  |
|            |                 | $S_0 \rightarrow S_2$          | 268 (4.63)   | 0.0012 | HOMO→LUMO+2     | 0.603  |
|            |                 | $S_0 \rightarrow S_3$          | 263 (4.71)   | 0.0151 | HOMO→LUMO+4     | 0.507  |
|            |                 | $S_0 \rightarrow S_4$          | 233 (5.32)   | 0.0005 | HOMO→LUMO       | 0.605  |
|            |                 | $S_0 \rightarrow S_5$          | 231 (5.37)   | 0.0002 | HOMO-5→LUMO     | 0.480  |
|            |                 | $S_0 \rightarrow S_6$          | 220 (5.63)   | 0.0023 | HOMO→LUMO+5     | 0.633  |
| B3PW91     | 1               | $S_0 \rightarrow S_1$          | 355 (3.49)   | 0.1210 | HOMO→LUMO       | 0.698  |
|            |                 | $S_0 \rightarrow S_2$          | 290 (4.27)   | 0.0002 | HOMO-2→LUMO     | 0.621  |
|            |                 | $S_0 \rightarrow S_3$          | 285 (4.35)   | 0.0021 | HOMO-1→LUMO     | 0.544  |
|            |                 | $S_0 \rightarrow S_4$          | 278 (4.46)   | 0.0006 | HOMO-3→LUMO     | 0.584  |
|            |                 | $S_0 \rightarrow S_5$          | 277 (4.47)   | 0.0012 | HOMO→LUMO+1     | 0.648  |
|            |                 | $S_0 \rightarrow S_6$          | 267 (4.64)   | 0.0029 | HOMO-4→LUMO     | 0.619  |
| Method  | State  | E (eV)  | δ (eV)  | Transition          | Envelope (eV) |
|---------|--------|---------|---------|---------------------|---------------|
| **B3PW91 1F** | $S_0 \rightarrow S_1$ | 296 (4.19) | 0.0016 | HOMO→LUMO          | 0.699         |
|         | $S_0 \rightarrow S_2$ | 270 (4.59) | 0.0134 | HOMO→LUMO+4        | 0.697         |
|         | $S_0 \rightarrow S_3$ | 264 (4.69) | 0.0032 | HOMO→LUMO+2        | 0.525         |
|         | $S_0 \rightarrow S_4$ | 261 (4.75) | 0.0013 | HOMO-1→LUMO        | 0.544         |
|         | $S_0 \rightarrow S_5$ | 257 (4.82) | 0.0019 | HOMO→LUMO+4        | 0.629         |
|         | $S_0 \rightarrow S_6$ | 252 (4.92) | 0.0025 | HOMO→LUMO+3        | 0.620         |
| **B3PW91 1CN** | $S_0 \rightarrow S_1$ | 302 (4.10) | 0.0027 | HOMO→LUMO          | 0.703         |
|         | $S_0 \rightarrow S_2$ | 288 (4.30) | 0.0011 | HOMO→LUMO+1        | 0.667         |
|         | $S_0 \rightarrow S_3$ | 278 (4.46) | 0.0147 | HOMO→LUMO+4        | 0.681         |
|         | $S_0 \rightarrow S_4$ | 271 (4.57) | 0.0004 | HOMO→LUMO+3        | 0.649         |
|         | $S_0 \rightarrow S_5$ | 260 (4.77) | 0.0006 | HOMO→LUMO+4        | 0.652         |
|         | $S_0 \rightarrow S_6$ | 244 (5.08) | 0.0013 | HOMO→LUMO+5        | 0.660         |
| **HCTH 1** | $S_0 \rightarrow S_1$ | 404 (3.07) | 0.1613 | HOMO→LUMO          | 0.695         |
|         | $S_0 \rightarrow S_2$ | 340 (3.64) | 0.0001 | HOMO→LUMO+1        | 0.706         |
|         | $S_0 \rightarrow S_3$ | 330 (3.76) | 0.0003 | HOMO-1→LUMO        | 0.592         |
|         | $S_0 \rightarrow S_4$ | 325 (3.81) | 0.0006 | HOMO-3→LUMO        | 0.594         |
|         | $S_0 \rightarrow S_5$ | 314 (3.94) | 0.0001 | HOMO→LUMO+2        | 0.468         |
|         | $S_0 \rightarrow S_6$ | 311 (3.98) | 0.0026 | HOMO→LUMO+3        | 0.594         |
| **HCTH 1F** | $S_0 \rightarrow S_1$ | 310 (3.99) | 0.0023 | HOMO→LUMO          | 0.704         |
|         | $S_0 \rightarrow S_2$ | 301 (4.12) | 0.0157 | HOMO→LUMO+4        | 0.705         |
|         | $S_0 \rightarrow S_3$ | 295 (4.20) | 0.0001 | HOMO-1→LUMO        | 0.701         |
|         | $S_0 \rightarrow S_4$ | 288 (4.30) | 0.0014 | HOMO→LUMO+2        | 0.668         |
|         | $S_0 \rightarrow S_5$ | 275 (4.51) | 0.0019 | HOMO-1→LUMO+1      | 0.693         |
|         | $S_0 \rightarrow S_6$ | 267 (4.64) | 0.0011 | HOMO-2→LUMO        | 0.637         |
| Method | 1CN |  |
|--------|-----|--|
| S0 → S1 | 393 (3.15) | 0.0015 | HOMO→LUMO | 0.704 |
| S0 → S2 | 382 (3.26) | 0.0002 | HOMO→LUMO+1 | 0.686 |
| S0 → S3 | 375 (3.31) | 0.0158 | HOMO→LUMO+4 | 0.683 |
| S0 → S4 | 371 (3.34) | 0.0016 | HOMO→LUMO+3 | 0.661 |
| S0 → S5 | 365 (3.39) | 0.0021 | HOMO→LUMO+4 | 0.645 |
| S0 → S6 | 332 (3.73) | 0.0002 | HOMO-1→LUMO | 0.676 |
| S0 → S1 | 420 (2.95) | 0.1883 | HOMO→LUMO | 0.694 |
| S0 → S2 | 346 (3.58) | 0.0048 | HOMO-1→LUMO | 0.690 |
| S0 → S3 | 340 (3.64) | 0.0015 | HOMO-2→LUMO | 0.625 |
| S0 → S4 | 338 (3.66) | 0.0004 | HOMO→LUMO+1 | 0.702 |
| S0 → S5 | 318 (3.89) | 0.0033 | HOMO-3→LUMO | 0.460 |
| S0 → S6 | 314 (3.95) | 0.0019 | HOMO→LUMO+3 | 0.658 |
| S0 → S1 | 375 (3.31) | 0.0029 | HOMO→LUMO | 0.704 |
| S0 → S2 | 341 (3.64) | 0.0146 | HOMO→LUMO+4 | 0.705 |
| S0 → S3 | 324 (3.82) | 0.0006 | HOMO-1→LUMO | 0.696 |
| S0 → S4 | 307 (4.03) | 0.0017 | HOMO→LUMO+2 | 0.675 |
| S0 → S5 | 300 (4.13) | 0.0027 | HOMO-1→LUMO+1 | 0.690 |
| S0 → S6 | 299 (4.15) | 0.0002 | HOMO-2→LUMO | 0.567 |
| S0 → S1 | 393 (3.15) | 0.0004 | HOMO→LUMO | 0.706 |
| S0 → S2 | 360 (3.44) | 0.0018 | HOMO→LUMO+1 | 0.692 |
| S0 → S3 | 323 (3.84) | 0.0166 | HOMO→LUMO+4 | 0.672 |
| S0 → S4 | 316 (3.92) | 0.0009 | HOMO→LUMO+3 | 0.653 |
| S0 → S5 | 299 (4.15) | 0.0003 | HOMO→LUMO+4 | 0.662 |
| S0 → S6 | 293 (4.23) | 0.0029 | HOMO-1→LUMO | 0.517 |
Table S11: Calculated electronic de-excitation energies and corresponding oscillator strengths of the low-lying singlet excited states of 1, 1F and 1CN by Employing Different Functionals

| Function | Receptor/complex | Electronic de-excitation | Energy (nm/eV) | ƒ  | Contrib. | CI  |
|----------|------------------|--------------------------|---------------|----|----------|----|
| PBEPBE   | 1                | S₀ → S₁                  | 380 (3.26)    | 0.1635 | HOMO↔LUMO | 0.695 |
|          |                  | S₀ → S₂                  | 351 (3.53)    | 0.0004 | HOMO↔LUMO | 0.658 |
|          |                  | S₀ → S₃                  | 297 (4.17)    | 0.0003 | HOMO↔LUMO | 0.601 |
|          |                  | S₀ → S₄                  | 398 (3.11)    | 0.1177 | HOMO↔LUMO | 0.701 |
| M06-2X   | 1F               | S₀ → S₁                  | 346 (3.58)    | 0.0002 | HOMO↔LUMO | 0.705 |
|          | 1CN              | S₀ → S₁                  | 359 (3.46)    | 0.0001 | HOMO↔LUMO | 0.705 |

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Table S12: Calculated electronic de-excitation energies and corresponding oscillator strengths of the higher singlet excited states of $1F$-$4F$ and $1CN$-$4CN$ at DFT/CAM-B3LYP/631G(d) level of theory

| Receptor/complex | Electronic de-excitation $^a$ | Energy (eV) | $f^b$ | Contrib. $^c$ | CI $^d$ |
|------------------|-------------------------------|-------------|-------|---------------|---------|
| $1F$             | $S_1 \leftarrow S_2$         | 1.44        | 0.0001| HOMO$\rightarrow$LUMO | 0.667   |
|                  | $S_2 \leftarrow S_3$         | 0.38        | 0.0002| HOMO$\rightarrow$LUMO | 0.682   |
|                  | $S_3 \leftarrow S_4$         | 0.44        | 0.0004| HOMO-2$\rightarrow$LUMO | 0.494   |
|                  | $S_4 \leftarrow S_5$         | 0.32        | 0.0001| HOMO-5$\rightarrow$LUMO | 0.468   |
| $1CN$            | $S_1 \leftarrow S_2$         | 0.41        | 0.0001| HOMO$\rightarrow$LUMO+1 | 0.492   |
|                  | $S_2 \leftarrow S_3$         | 0.34        | 0.0003| HOMO$\rightarrow$LUMO+2 | 0.643   |
|                  | $S_3 \leftarrow S_4$         | 0.55        | 0.0001| HOMO$\rightarrow$LUMO | 0.684   |
|                  | $S_4 \leftarrow S_5$         | 0.33        | 0.0005| HOMO-2$\rightarrow$LUMO | 0.517   |
|                  | $S_5 \leftarrow S_6$         | 0.41        | 0.0003| HOMO-1$\rightarrow$LUMO | 0.527   |
|                  | $S_6 \leftarrow S_7$         | 0.22        | 0.0002| HOMO$\rightarrow$LUMO+1 | 0.411   |

$^a$ Only the selected low-lying excited states are presented. $^b$ Oscillator strength. $^c$ Only the main configurations are presented. $^d$ The CI coefficients are in absolute values.
|    | $S_1 \leftarrow S_2$ | $S_2 \leftarrow S_3$ | $S_3 \leftarrow S_4$ | $S_4 \leftarrow S_5$ | $S_5 \leftarrow S_6$ | $S_6 \leftarrow S_7$ |
|----|----------------------|----------------------|---------------------|----------------------|----------------------|----------------------|
| 3F | 0.79                 | 0.0001               | HOMO$\leftarrow$LUMO+1 | 0.632                |
|    | 0.62                 | 0.0002               | HOMO-1$\leftarrow$LUMO | 0.403                |
| 3CN| 0.79                 | 0.0003               | HOMO$\leftarrow$LUMO+2 | 0.629                |
|    | 0.66                 | 0.0001               | HOMO$\leftarrow$LUMO   | 0.393                |
| 4F | 0.49                 | 0.0005               | HOMO$\leftarrow$LUMO   | 0.637                |
|    | 0.55                 | 0.0001               | HOMO$\leftarrow$LUMO+1 | 0.484                |
|    | 0.33                 | 0.0004               | HOMO$\leftarrow$LUMO+2 | 0.453                |
| 4CN| 0.22                 | 0.0001               | HOMO$\leftarrow$LUMO   | 0.547                |
|    | 0.54                 | 0.0004               | HOMO$\leftarrow$LUMO+3 | 0.454                |
|    | 0.11                 | 0.0002               | HOMO$\leftarrow$LUMO+4 | 0.551                |
|    | 0.20                 | 0.0001               | HOMO-5$\leftarrow$LUMO | 0.601                |

\(^a\) Only the selected low-lying excited states are presented. \(^b\) Oscillator strength. \(^c\) Only the main configurations are presented. \(^d\) The CI coefficients are in absolute values.
Figure S1: Ground state (S₀) optimized structures of 1F-4F and 1CN-4CN calculated at CAM-B3LYP/6-31G(d) level with the CPCM solvation model. Hydrogen atoms are omitted for clarity. Geometry at the boron center (B1) in 1F-4F and 1CN-4CN is tetrahedral.
Figure S2: Potential energy curves of corresponding $S_0$ states of (I) 1F and (III) 2CN; and corresponding $S_1$ states of (II) 1F and (IV) 2CN calculated at the CAM-B3LYP/6-31G(d) level with the CPCM solvation model as functions of the angles mentioned.
Figure S3: Molecular orbital diagrams of (I) 1 and (II) CN−

Figure S4: Calculated FMO energies for (I) 2 in the ground state and excited state (2^*) (II) 2F in ground state and excited state (2F^*) and (III) 2CN in ground state and excited state (2CN^−) at CAM-B3LYP/6-31G(d) level using CPCM solvation model.
Figure S5: Calculated FMO energies for (I) 3 in the ground state and excited state ($3^*$) (II) 3F in ground state and excited state ($3F^*$) and (III) 3CN in ground state and excited state ($3CN^*$) at CAM-B3LYP/6-31G(d) level using CPCM solvation model.
Figure S6: Calculated FMO energies for (I) 4 in the ground state and excited state ($4^*$) (II) 4F in ground state and excited state ($4F^*$) and (III) 4CN in ground state and excited state ($4CN^*$) at CAM-B3LYP/6-31G(d) level using CPCM solvation model.

Figure S7: Excited state ($S_1$) optimized structures of 1-4, 1F-4F, and 1CN-4CN calculated at CAM-B3LYP/6-31G(d) level with the CPCM solvation model. Hydrogen atoms are omitted for
clarity. Geometry at boron centers in 1-4 is trigonal planar while as geometry at boron centers in 1F-4F and 1CN-4CN is tetrahedral.

Figure S8: Excited state optimized structures of 1F (S₂), 1CN (S₃), 2F (fourth excited state, S₄), 2CN (S₅), 3F (S₃), 3CN (S₃), 4F (S₄) and 4CN (S₅) calculated at CAM-B3LYP/6-31G(d) level with the CPCM solvation model. Hydrogen atoms are omitted for clarity.
Figure S9: Scheme of the different mechanisms of fluorescence emission for 2, 2F and 2CN.
Figure S10: Scheme of the different mechanisms of fluorescence emission for 3, 3F and 3CN
Figure S11: Scheme of the different mechanisms of fluorescence emission for 4, 4F and 4CN

References

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