*Supporting Information*

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| **Scheme S1:** The sixteen possible stereoisomers, the structures with the same color are enantiomer and those in a framework are equivalent. |
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| 1. **Optimized structures and relative energy of TCPs-F-** | 1. **Optimized structures and relative energy of TCPs-Cl-** |
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| 1. **Optimized structures and relative energy of TCPs-Br-** | 1. **Optimized structures and relative energy of TCPs-Li+** |
|  |  |
| 1. **Optimized structures and relative energy of TCPs-Na+** | 1. **Optimized structures and relative energy of TCPs-K+** |
| **Figure S1:** Optimized structures and relative energy of TCPs-ions complexes calculated at the M06-2X level of theory in the gas phase. | |

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| 1. **Optimized structures and relative energy of TCPs-F-** | 1. **Optimized structures and relative energy of TCPs-Cl-** |
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| 1. **Optimized structures and relative energy of TCPs-Br-** | 1. **Optimized structures and relative energy of TCPs-Li+** |
|  |  |
| 1. **Optimized structures and relative energy of TCPs-Na+** | 1. **Optimized structures and relative energy of TCPs-K+** |
| **Figure S2:** Optimized structures and relative energy of TCPs-ions complexes calculated at the M06-2X level of theory in aqueous phase. | |

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| **TCP-F-** | **TCP-Cl-** |
| **TCP-Li+** | **TCP-Br-** |
| **TCP-Na+** | **TCP-K+** |
| **Figure S3**. Relative energy of TCPs-ions complexes calculated at the M06-2X level of theory in gas-phase (red line) and aqueous-phase (blue line). | |

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|  | **F-** | **Cl-** | **Br-** | **Li+** | **Na+** | **K+** |
| **TCP1** |  |  |  |  |  |  |
| **TCP2** |  |  |  |  |  |  |
| **TCP3** |  |  |  |  |  |  |
| **TCP4** |  |  |  |  |  |  |
| **TCP5** |  |  |  |  |  |  |
| **TCP6** |  |  |  |  |  |  |
| **TCP7** |  |  |  |  |  |  |
| **TCP8** |  |  |  |  |  |  |
| **TCP9** |  |  |  |  |  |  |
| **TCP10** |  |  |  |  |  |  |
| **Scheme S2: Intramolecular interaction in TCP-ions in the gas phase.** | | | | | | |

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| **Table S1:** Calculated NBO partial charges of the selected atoms of TCP-ion complexes at M06-2X level of theory in the gas phase. | | | | | | | | | |
| **TCP1,2** | **before** | **Li+** | **Na+** | **K+** | **TCP1,2** | **before** | **F-** | **Cl-** | **Br-** |
| S5 | 0.087 | 0.153 | 0.043 | 0.003 | H10 | 0.244 | 0.210 | 0.244 | 0.279 |
| S24 | 0.087 | 0.153 | 0.043 | 0.003 | H11 | 0.234 | 0.324 | 0.215 | 0.256 |
| N14 | -0.661 | -0.731 | -0.667 | -0.667 | H13 | 0.248 | 0.311 | 0.241 | 0.252 |
| O8 | -0.623 | -0.567 | -0.542 | -0.654 | H16 | 0.406 | 0.409 | 0.469 | 0.409 |
| O27 | -0.623 | -0.567 | -0.542 | -0.654 | H29 | 0.244 | 0.210 | 0.244 | 0.280 |
| N33 | -0.661 | -0.731 | -0.667 | -0.667 | H30 | 0.234 | 0.324 | 0.215 | 0.255 |
| ion | 1.000 | 0.256 | 0.658 | 0.850 | H32 | 0.248 | 0.311 | 0.241 | 0.252 |
| H35 | 0.406 | 0.409 | 0.469 | 0.409 |
| ion | -1.000 | -0.887 | -0.85 | -0.943 |
| **TCP4,10** |  |  |  |  | **TCP4,10** |  |  |  |  |
| S5 | 0.097 | 0.154 | 0.142 | 0.121 | H10 | 0.244 | 0.26762 | 0.308 | 0.299 |
| S23 | 0.128 | 0.196 | 0.182 | 0.036 | H16 | 0.410 | 0.55568 | 0.412 | 0.417 |
| S24 | 0.074 | 0.128 | 0.026 | 0.115 | H17 | 0.259 | 0.19445 | 0.297 | 0.288 |
| O8 | -0.612 | -0.508 | -0.783 | -0.741 | H29 | 0.228 | 0.20748 | 0.264 | 0.255 |
| O27 | -0.615 | -0.567 | -0.772 | -0.734 | ion | -1.000 | -0.65936 | -0.91 | -0.911 |
| N14 | -0.674 | -0.738 | -0.630 | -0.661 |
| N34 | -0.669 | -0.745 | -0.664 | -0.628 |
| ion | 1.000 | 0.332 | 0.943 | 0.927 |
| **TCP5,9** |  |  |  |  | **TCP5,9** |  |  |  |  |
| S5 | 0.098 | 0.118 | 0.084 | 0.111 | H10 | 0.261 | 0.316 | 0.252 | 0.252 |
| O8 | -0.633 | -0.751 | -0.747 | -0.761 | H17 | 0.229 | 0.321 | 0.305 | 0.295 |
| O27 | -0.633 | -0.522 | -0.543 | -0.752 | H28 | 0.214 | 0.308 | 0.300 | 0.293 |
| N15 | -0.678 | -0.782 | -0.759 | -0.649 | H36 | 0.212 | 0.331 | 0.298 | 0.285 |
| ion | 1.000 | 0.733 | 0.859 | 0.966 | ion | -1.000 | -0.892 | -0.900 | -0.905 |
| **TCP6** |  |  |  |  | **TCP6** |  |  |  |  |
| S24 | 0.098 | 0.103 | 0.098 | 0.099 | H10 | 0.267 | 0.258 | 0.226 | 0.268 |
| O8 | -0.621 | -0.533 | -0.756 | -0.743 | H17 | 0.223 | 0.335 | 0.293 | 0.291 |
| O27 | -0.629 | -0.535 | -0.763 | -0.748 | H28 | 0.235 | 0.306 | 0.310 | 0.286 |
| N34 | -0.685 | -0.772 | -0.630 | -0.636 | H32 | 0.267 | 0.313 | 0.252 | 0.252 |
| ion | 1.000 | 0.582 | 0.944 | 0.965 | ion | -1.000 | -0.886 | -0.910 | -0.910 |
| **TCP7,8** |  |  |  |  | **TCP7,8** |  |  |  |  |
| S5 | 0.058 | 0.151 | 0.087 | 0.083 | H9 | 0.245 | 0.289 | 0.290 | 0.288 |
| S24 | 0.058 | 0.151 | 0.087 | 0.084 | H13 | 0.250 | 0.315 | 0.299 | 0.258 |
| O8 | -0.614 | -0.566 | -0.767 | -0.750 | H28 | 0.245 | 0.289 | 0.294 | 0.281 |
| O27 | -0.614 | -0.566 | -0.767 | -0.750 | H32 | 0.250 | 0.315 | 0.271 | 0.294 |
| N14 | -0.673 | -0.739 | -0.685 | -0.685 | ion | -1.000 | -0.900 | -0.890 | -0.895 |
| N33 | -0.673 | -0.739 | -0.685 | -0.685 |
| ion | 1.000 | 0.250 | 0.934 | 0.958 |

| **Table S2:** The bond length, RHB, and bond angle of hydrogen bonds in TCP-anion complexes at the level of M06-2X in the gas phase. | | | | | | | | | |
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|  |  | **Geometry parameters** | |  | **Geometry parameters** | |  | **Geometry parameters** | |
| **Complex** | **H-bond** | **RHB/A˚** | **θ (˚)** | **H-bond** | **RHB/A˚** | **θ (˚)** | **H-bond** | **RHB/A˚** | **θ (˚)** |
| **TCP1, 2** | C3-H11…F- | 1.8 | 166.4 | N15-H16…Cl- | 2.2 | 152.4 | N15-H16…Br- | 2.5 | 151.3 |
| C6-H13…F- | 1.8 | 166.8 |
| C22-H30…F- | 1.8 | 166.4 | N34-H35…Cl- | 2.2 | 152.4 | N34-H35…Br- | 2.5 | 151.0 |
| C25-H32…F- | 1.8 | 166.8 |  |  |  |
| **TCP3** | C1- H9…F- | 1.7 | 158.5 | C1-H9…Cl- | 2.3 | 147.3 | C1-H9…Br- | 2.5 | 145.2 |
| C7- H17…F- | 1.9 | 150.6 | C7-H17…Cl- | 2.5 | 161.2 | C7-H17…Br- | 2.7 | 163.9 |
| C22- H30…F- | 1.8 | 171.0 | C22-H30…Cl- | 2.5 | 167.7 | C22-H30…Br- | 2.7 | 161.5 |
| C25- H32…F- | 1.9 | 164.4 | C25-H32…Cl- | 2.5 | 161.9 | C25-H32…Br- | 2.7 | 160.5 |
| **TCP4, 10** | F--H16…N15- | 1.6 | 175.6 | C3-H10…Cl- | 2.4 | 160.7 | C3-H10…Br- | 2.6 | 168.9 |
| C7-H17…Cl- | 2.4 | 136.4 | C7-H17…Br- | 2.6 | 134.1 |
| C22-H29…Cl- | 2.7 | 114.6 | C22-H29…Br- | 2.9 | 111.8 |
| **TCP5, 9** | C3-H10…F- | 1.9 | 156.5 | C7-H17…Cl- | 2.5 | 145.8 | C7-H17…Br- | 2.7 | 144.8 |
| C7-H17…F- | 1.9 | 152.2 | C20-H28…Cl- | 2.4 | 151.1 | C20-H28…Br- | 2.5 | 149.3 |
| C20-H28…F- | 1.9 | 145.3 | C26-H36…Cl- | 2.4 | 156.9 | C26-H36…Br-- | 2.6 | 149.8 |
| C26-H36…F- | 1.8 | 153.0 |
| **TCP6** | C3- H10…F- | 1.9 | 123.9 | C3- H10…Cl- | 2.8 | 109.1 | C3-H10…Br- | 2.8 | 152.3 |
| C7- H17…F- | 1.8 | 156.4 | C7- H17…Cl- | 2.5 | 152.5 | C7-H17…Br- | 2.6 | 160.7 |
| C20- H28…F- | 1.9 | 146.9 | C20- H28…Cl- | 2.3 | 162.2 | C20-H28…Br- | 2.7 | 154.3 |
| C3-25H32…F- | 1.8 | 133.0 | C25- H32…Cl- | 2.6 | 133.5 | C25-H31…Br- | 2.8 | 127.7 |
| **TCP7, 8** | C1- H9…F- | 1.8 | 131.8 | C1- H10…Cl- | 2.5 | 141.4 | C1-H9…Br- | 2.6 | 155.9 |
| C6- H13…F- | 1.8 | 142.6 | C6- H13…Cl- | 2.4 | 161.0 | C6-H13…Br- | 2.7 | 138.0 |
| C20- H28…F- | 1.8 | 131.8 | C20- H28…Cl- | 2.4 | 153.2 | C20-H28…Br- | 2.7 | 138.9 |
| C25- H32…F- | 1.8 | 142.6 | C25- H32…Cl- | 2.5 | 146.7 | C25-H32…Br- | 2.5 | 164.2 |