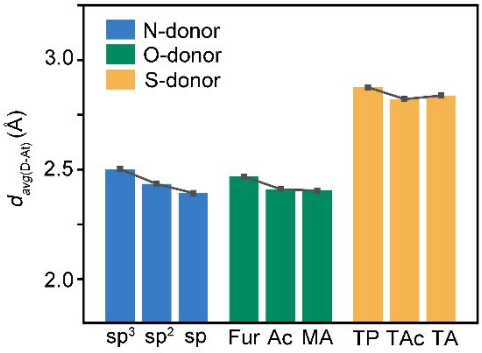

Figure S1. The bond lengths ($d_{avg(D-At)}$) of different $[D\cdots At\cdots D]^+$ complexes at the SO-DFT/B3LYP-D3 level. The horizontal axis represents different donors. The hybridization type of the nitrogen atom in N-donor groups are labelled by sp^3, sp^2 and sp, respectively.

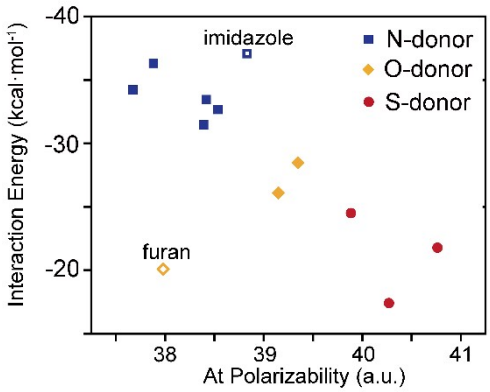

Figure S2. The interaction energy ΔE_{int}(SO-CC) and the polarizability α of At in $[D\cdots At\cdots D]^+$ complexes with different donor types. The $[IA\cdots At\cdots IA]^+$ and $[Fur\cdots At\cdots Fur]^+$ complexes are labeled using hollow patterns.

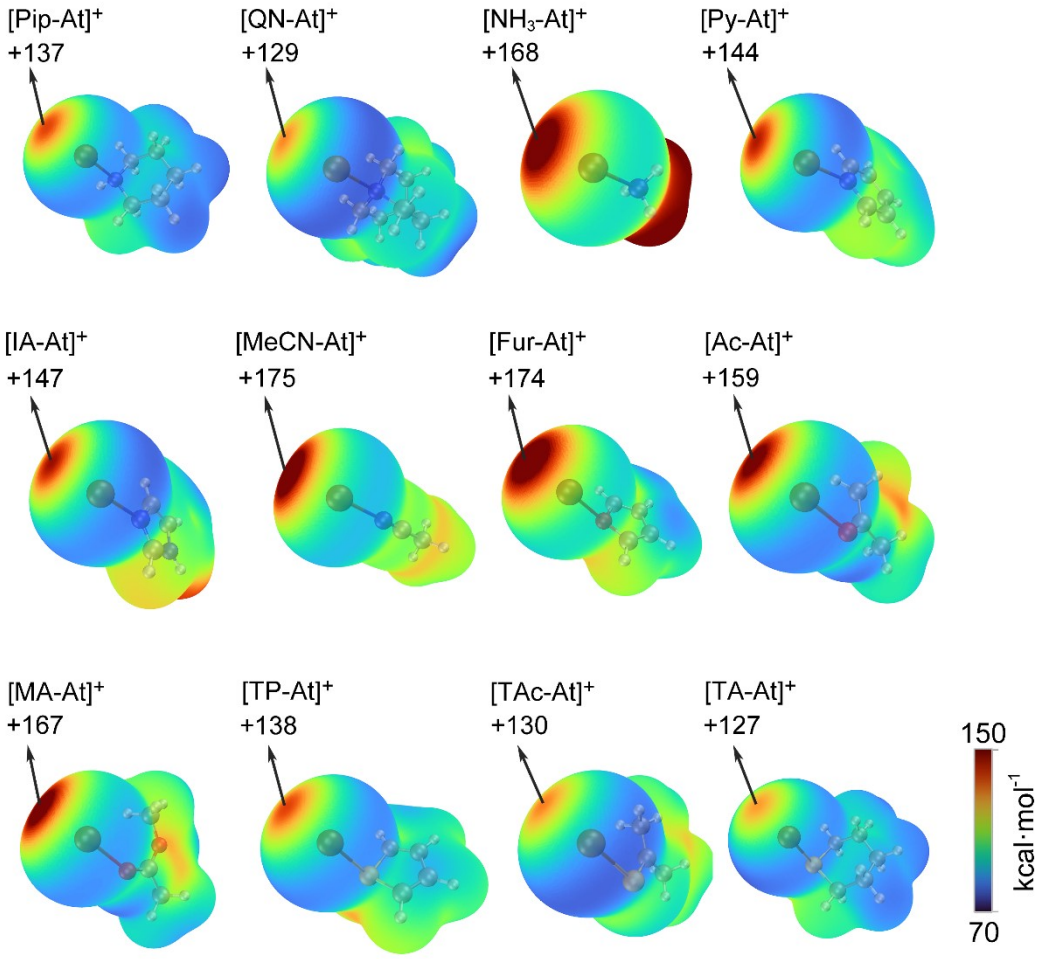

Figure S3. SR-DFT/B3LYP-D3 calculated MEP maps for $[D\cdots At]^+$ cations at the SO-DFT/B3LYP-D3 optimized geometries of $[D\cdots At]^+$ cations. Energies are given in kcal·mol^{-1}. Blue and red colors indicate the least and most positive MEP values, respectively.

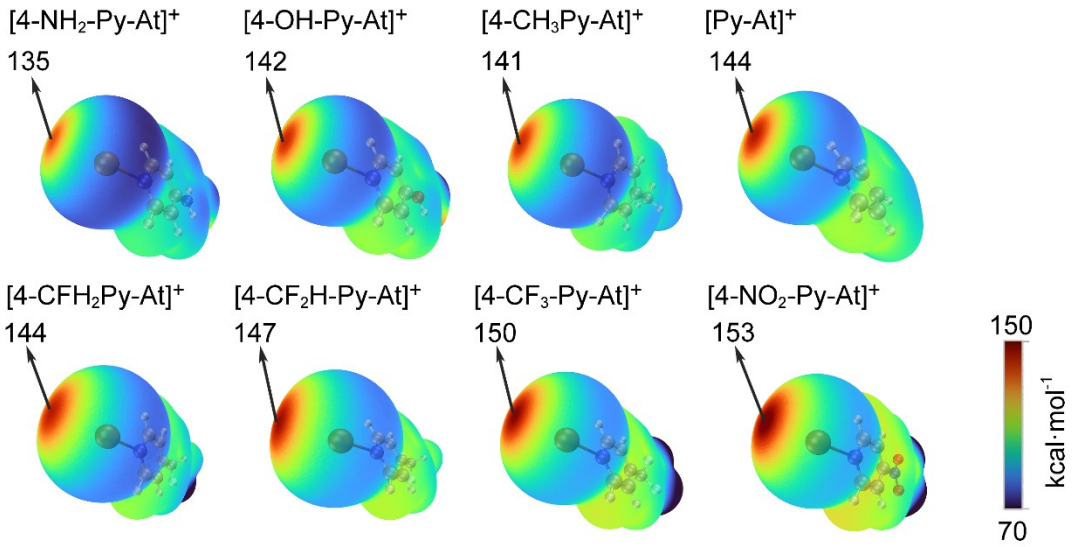

Figure S4. SR-DFT/B3LYP-D3 calculated MEP maps for [4-R-py···At]$^+$ cations at the SO-DFT/B3LYP-D3 optimized geometries of [4-R-py···At]$^+$ cations. Energies are given in kcal·mol^{-1}. Blue and red colors indicate the least and most positive MEP values, respectively.

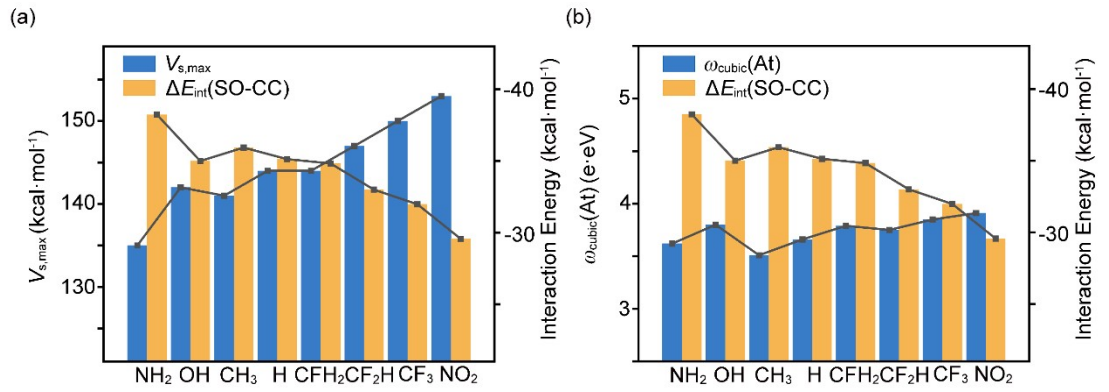

Figure S5. (a) The SR-DFT/B3LYP-D3 calculated $V_{s,max}$ values of [4-R-Py···At]$^+$ cations and SO-CCSD(T) calculated interaction energies (ΔE_{int}(SO-CC)) in different [4-R-Py···At···4-R-Py]$^+$ complexes. (b) The SR-DFT/B3LYP-D3 calculated ω_{cubic}(At) values and SO-CCSD(T) calculated interaction energies (ΔE_{int}(SO-CC)) in different [4-R-Py···At···4-R-Py]$^+$ complexes. The horizontal axis represents different R substituents.

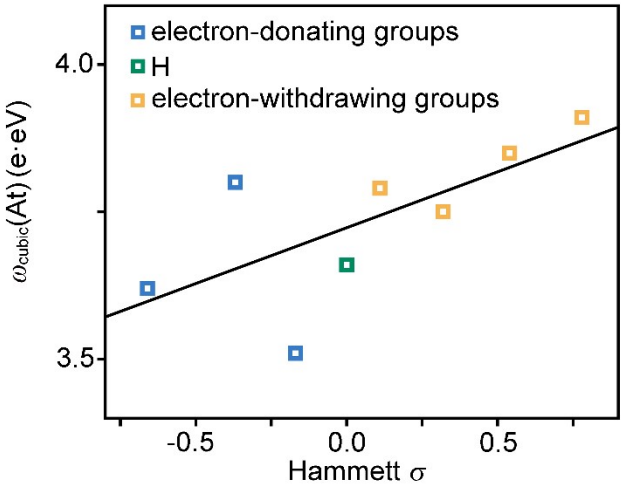

Figure S6. Dependence on the Hammett σ parameter of the local electrophilicity index $\omega_{cubic}(At)$ ($\omega_{cubic}(At) = 0.19 \cdot \sigma + 3.72$, $R^2 = 0.47$).