Polaron formation in potassium poly(heptazine imide) —— an ab initio molecular dynamics simulation study

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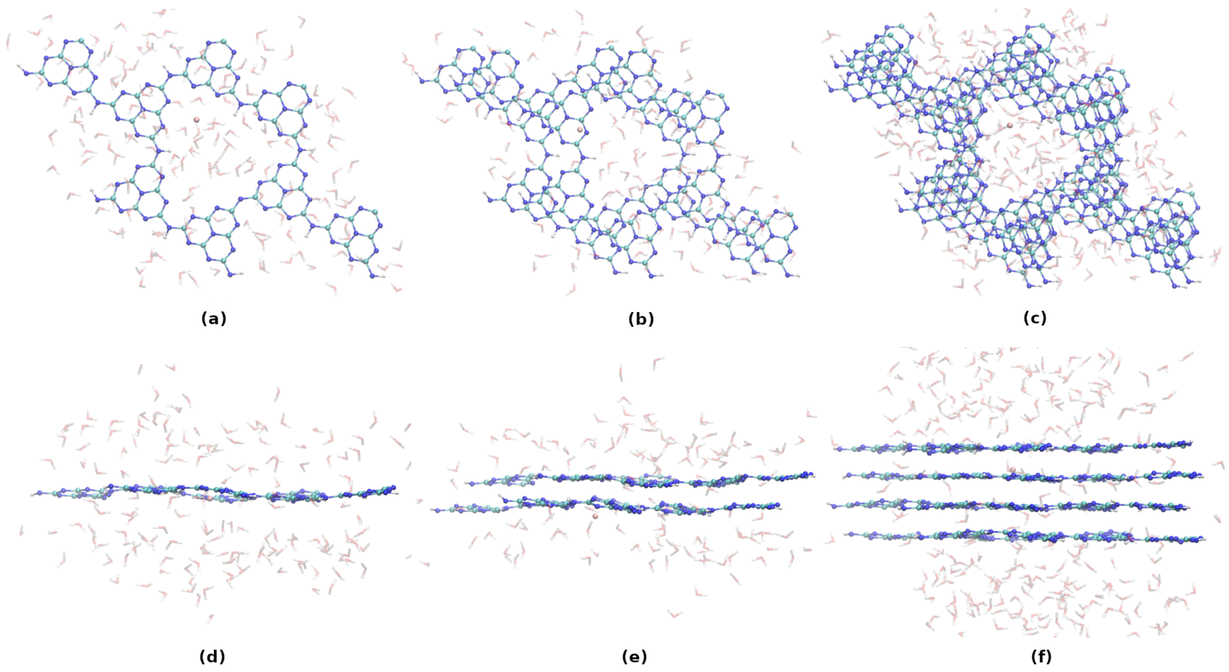
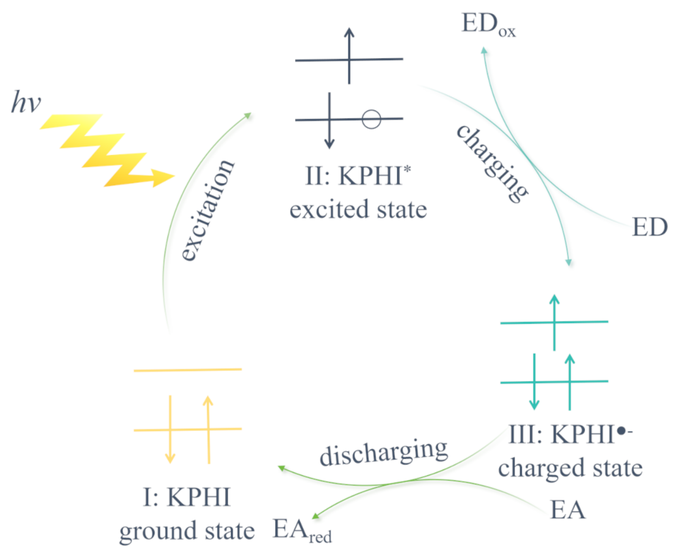
Introduction

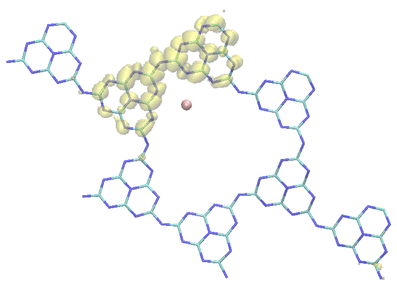
We conducted hybrid functional-based ab initio molecular dynamics (AIMD) simulations to investigate polaron formation in potassium poly(heptazine)-imide (KPHI) systems with varying structural complexities. Our simulation results demonstrate that three critical factors - potassium ion positioning, interlayer aromatic interactions, and hydration environment - collectively govern polaron formation and stabilization dynamics. The flexibility of the imide linker facilitates lattice distortions, enabling the relatively rigid heptazine units to accommodate excess electron while effectively confining polarons within the ring structures, preventing electron leakage into the surrounding aqueous medium. These findings provide insights into the electronic and structural dynamics of KPHI, offering perspectives for understanding its catalytic capabilities at the atomic level.

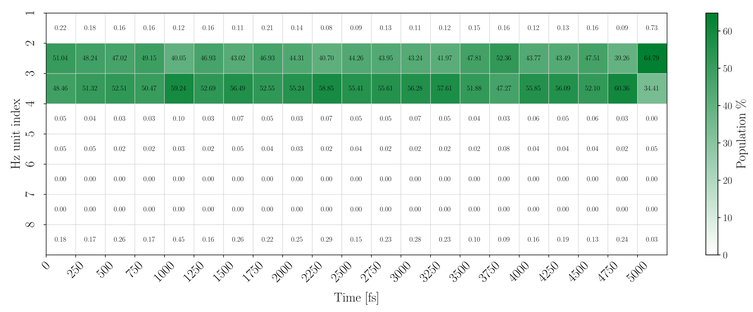
AIMD Models

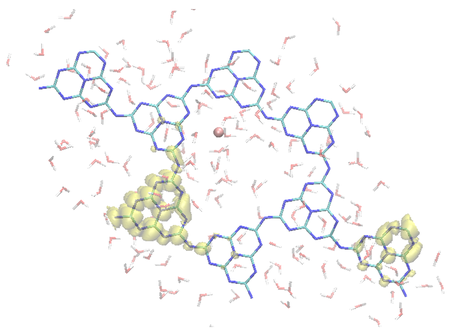


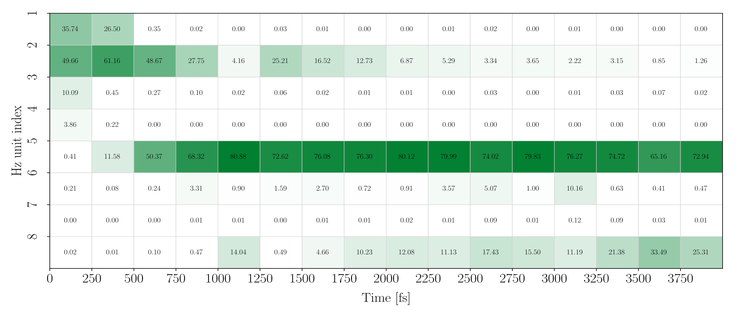
	isolated monolayer	monolayer	bilayer	quadruple-layer
No. H_2O	0	161	128	265
No. atom in PHI	127	127	255	511
No. K^+	1	1	1	1
total atoms	128	611	640	1307

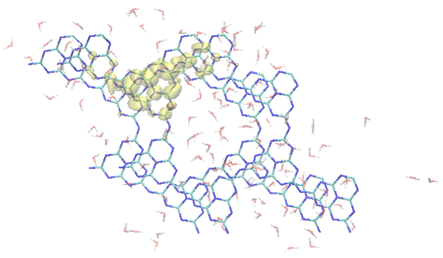


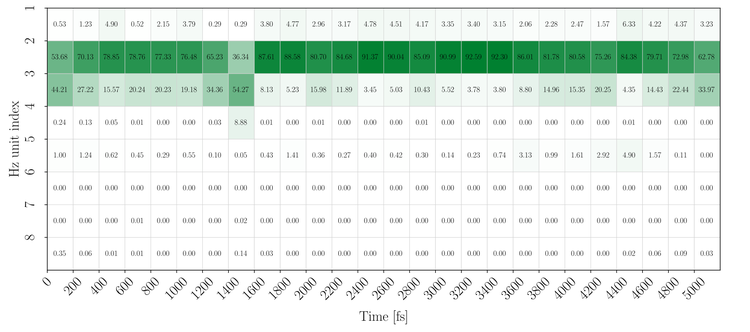


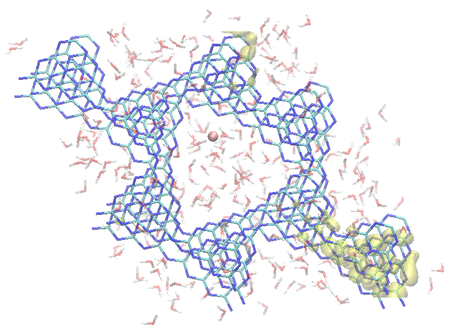


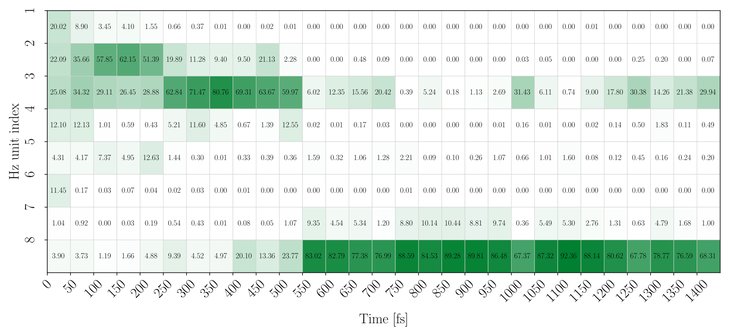












Discussion

We modeled four KPHI systems (isolated monolayer KPHI, solvated monolayer KPHI, solvated bilayer KPHI, and solvated quadruple-layer KPHI) and employed hybrid functional based AIMD with 40\% hfx to study the formation and dynamics of polaron in these systems. In all our simulations, localized polaronic solutions were yielded with varying collapse time and localization positions. In all cases except the isolated system, the majority of the excess charge was accommodated by a single heptazine unit. Notably, the excess electron remained confined to heptazine units without leakage into the bulk water. This observation supports the heptazine-centered nature of polaron formation in KPHI. The polaron in KPHI is medium-sized, spanning the dimensions of a heptazine ring, and adopts a plate-like shape.

	isolated monolayer	monolayer	bilayer	quadruple-layer
mean radius of gyration of localizaed polaronic solution (Å)	4.19	3.83	3.37	4.55
main localized heptazine unit(s)	two, three	five	two	eight
localized layer (relative to potassium ion)	same	same	different	same

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