SUPPLEMENTARY INFORMATION
Size scalability of Monte Carlo simulations applied to oxidized polypyrrole systems

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1. SI.1 Size and composition of the computational boxes modeling the oxidized PPy systems in condensed phases.

In order to scale up the size of the initial computational boxes containing N_{py} oligomers and N_{dop} dopants, an equilibrated sample of the small system with 64 oligomers and 256 dopants that is previously equilibrated at 600 K is denoted a 1×4×4 supercell. Larger systems are obtained by stacking replicas of this almost cubic box to yield supercells n×4n×4n, with n = 2, 3, 4, 5 and indicated in Table SI.1.

Table SI.1: Size of the oxidized PPy systems containing N_{py} oligomers and N_{dop} dopants, for a total of $N_{particles}$.

n	Supercell	N_{py}	N_{dop}	$N_{particles}$
1	1×4×4	64	256	1024
2	2×8×8	512	2048	8192
3	3×12×12	1728	6912	27648
4	4×16×16	4096	16384	65536
5	5×20×20	8000	32000	128000

2. SI.2 Approximation by piecewise polynomial interpolation to compute the pair additive interactions in the force field

The adopted numerical approximation for the calculation of the coarse grained force field (CGFF) pairwise additive terms U_{py-py}, U_{py-dop}, $U_{dop-dop}$, main manuscript Eqs. A.2, A.3, A.4, yields small errors. The overall RMSD that the polynomial approximation produces on each of these terms is reported in Table SI.2. Figure SI.1 illustrates visually the dependence of the three above mentioned terms as function of the distance between particles (full line) compared with multiple scattered points calculated using the numerical polynomial approximation. The CGFF parameters in these calculations

are from Abere, Y., Helmick, G., Blaisten-Barojas, E., J. Phys.: Condens. Matter 34 (2022) 185701.

Table SI.2: RMSE of three different polynomial approximations compared to the analytical solver solution of the U_{py-py}, U_{py-dop}, $U_{dop-dop}$ terms of the CGFF described in main manuscript. Units are Ha.

	U_{py-py}	U_{py-dop}	$U_{dop-dop}$
Cubic Spline	6.55E-11	1.71E-15	2.5E-12
3^{th} Order physicist's Hermite Polynomial	1.19E-09	3.45E-12	4.79E-09
6^{rd} Order physicist's Hermite Polynomial	1.30E-12	3.69E-15	5.66E-12

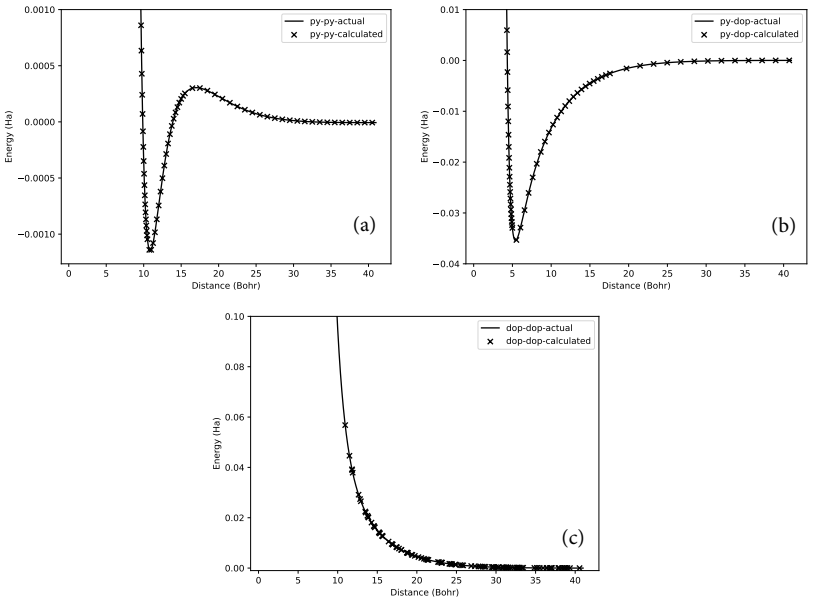

Figure SI.1: Comparison of the (a) U_{py-py} (Eq. A.2), (b) U_{py-dop} (Eq. A.3), and (c) $U_{dop-dop}$ (Eq. A.4) analytical dependence on distance (full line) with a set of points from the functional domain calculated with the polynomial approximation (depicted with "x").

Additionally, for the oxidized PPy large system size, the MMC simulation using several piecewise polynomial approximations yielded the density, enthalpy and potential energy values listed in Table SI.3.

Table SI.3: Properties of the Cl-oxidized PPy system with 27648 particles at 300 K and 1 atm compared between MMC simulations using the direct solver and three different approximation methods. Averages and s.d are from the last 10^6 MMC passages over all the particles of the NPT pre-equilibrated system.

Property/Solver type	Cubic Spline	3rd order Hermite Polynomial	6th order Hermite Polynomial	Direct solver
U_{total}/particle (eV)	-3.383 ±0.001	-3.385 ± 0.001	-3.383 ±0.001	-3.383 ±0.001
U_{inter}/particle (eV)	-1.676 ±0.001	-1.677 ±0.001	-1.673 ±0.001	-1.674 ±0.001
U_{intra}/particle (eV)	-1.708 ±0.001	-1.708 ±0.001	-1.710 ±0.001	-1.708 ±0.001
Enthalpy/particle (eV)	-3.345 ±0.001	-3.346 ±0.001	-3.344 ±0.001	-3.344 ±0.001
Density (kg/m^3)	1376.2 ±2.0	1379.3 ±2.5	1375.8 ±3.3	1373.3 ±2.0
Volume (nm^3)	71.41 ±0.10	71.25 ±0.13	71.43 ±0.17	71.56 ±0.11

3. SI.3 Thermal behavior and structural properties of the oxidized PPy systems.

Concerning the thermal behavior of these systems, an isobaric cooling process from 600 K to 300 K was undertaken along the 1 atm isobar. The density as a function of temperature is depicted in Fig. SI.2 for the large size systems containing 27648 particles of oxidized PPy with F, Br, I dopants. Each point corresponds to a previousy equilibrated MMC simulation with 5×10^5 passages over all the system particles.These points are fitted with two lines, one on points at temperatures close to 300 and the other on points closer to 600 K. This process permits the identification of a temperature range where the glass transition temperature T_g is estimated to occur.

Concerning structural properties, as evidenced in Table SI.4, the 12-Py oligomers maintain very similar structural properties. These properties indicate a strong chain stacking, which is predicted experimentally.

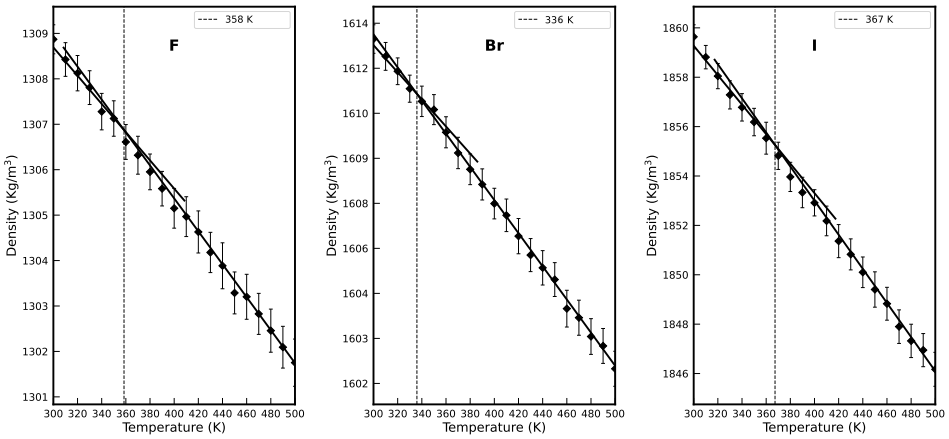

Figure SI.2: Density of the oxidized PPy large size systems with F, Br, and I dopants along an isobaric cooling process at 1 atm. Averages and s.d. are from MMC simulations with 10^6 MMC passages over the particles in each system that were started from the final configuration of the higher temperature simulation. Full lines are fits to the simulated values; their crossing point is marked with a vertical dotted line.

Table SI.4: Structural properties of the 12-Py oligomers in the small, mid and large size oxidized PPy systems with F, Br, and I dopants at 300 K and 1 atm. The ± identifies one time the standard deviation.

	Small size	**Mid size**	**Large size**
Fluorine dopants			
Vector Order Parameter (S)	0.995876 ± 0.00001	0.992737±0.00005	0.993244 ± 0.00005
Orientation Order Parameter (Z)	0.641692 ± 0.0012	0.669669±0.0021	0.667526 ± 0.002
12-Py Radius of Gyration (nm)	1.19 ± 0.0004	1.2±0.0003	1.2 ± 0.00029
12-Py End-to-end Distance (nm)	3.763 ± 0.003	3.78765±0.0022	3.783 ± 0.002
Bromine dopants			
Vector Order (S)	0.99457 ± 0.0001	0.962558 ± 0.000065	0.985392± 0.00004
Orientation Order (Z)	0.661155 ± 0.0011	0.700149 ± 0.00165	0.687277± 0.0021
12-Py Radius of Gyration (nm)	1.185 ± 0.00045	1.17437 ± 0.00036	1.174 ± 0.0002
12-Py End-to-end Distance (nm)	3.784 ± 0.0004	3.83523 ± 0.0034	3.81263 ± 0.0025
Iodine dopants			
Vector Order (S)	0.996577 ± 0.00002	0.968676 ± 0.00004	0.978475± 0.0006
Orientation Order (Z)	0.69734 ± 0.0015	0.713749 ± 0.0015	0.691431± 0.0022
12-Py Radius of Gyration (nm)	1.12456 ± 0.0005	1.14034 ± 0.00031	1.181 ± 0.0004
12-Py End-to-end Distance (nm)	3.842 ± 0.002	3.86129 ± 0.0021	3.83 ± 0.003