## Supporting Information:

## Benchmarking Electronic Structure Methods for Accurate Fixed-Charge Electrostatic Models

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**Figure S1.** Calculated gas phase dipole moments vs. experimental gas phase dipole moments for B3LYP/aug-cc-pV(T+d)Z. The black dotted line indicates perfect agreement with experiment (i.e., no under- or overpolarization).



**Figure S2.** Exact residuals for robust linear regression fits to experimental gas phase dipole moments for (a)  $HF/6-31G^*$ , (b) HF/aug-cc-pV(T+d)Z, (c) B3LYP/aug-cc-pV(T+d)Z with PCM benzene, and (d) B3LYP/aug-cc-pV(T+d)Z with PCM water. A residual of zero indicates a prediction with no deviation from the regression line, or in other words, a prediction that is perfectly consistent with a linear model for overpolarization. All molecules with zero dipole moment are excluded from this analysis.



**Figure S3.** Calculated dipole moments vs. experimental gas phase dipole moments for PW6B95/def2-TZVPD with (a) PCM benzene and (b) PCM water. The black dotted line indicates perfect agreement with experiment (i.e., no under- or overpolarization).



**Figure S4.** Weighted residuals for robust linear regression fits to experimental gas phase dipole moments for PW6B95/def2-TZVPD with (a) PCM benzene and (b) PCM water. A weighted residual of zero indicates a prediction with no deviation from the regression line, or in other words, a prediction that is perfectly consistent with a linear model for overpolarization. All molecules with zero dipole moment are excluded from this analysis.



**Figure S5.** Fractional dipole enhancement relative to experimental gas phase data for PW6B95/def2-TZVPD with (a) PCM benzene and (b) PCM water. The solid gray line indicates perfect agreement with experiment; the black dashed line indicates the median for each method/basis set combination. All molecules with zero dipole moment are excluded from this analysis.

## METHODS: COMPARISON TO GAS PHASE "REFERENCE THEORY" DIPOLE MOMENTS

For the gas phase reference theory calculations, all molecular structures were built from SMILES strings using Open Babel 2.4.1.<sup>1</sup> In the case of acetic acid, the structure was modified to the *syn* conformer (the preferred conformer in gas phase) using Avogadro 1.2.0.<sup>2</sup> The resulting geometries were optimized with Gaussian 16<sup>3</sup> in a three-step process: the initial structure was first optimized using HF/6-31G\*<sup>4-6</sup>, then with B3LYP<sup>7-10</sup>/cc-pV(T+d)Z<sup>11-13</sup>, and finally with B3LYP/cc-pV(Q+d)Z. Geometry optimization was stopped when the maximum force was below 0.0045 Hartree/Bohr and the maximum displacement was smaller than 0.0018 Bohr. The SCF convergence criterion was set to 10<sup>-8</sup> Hartree. A single point calculation on the final optimized structure was performed using the DSD-PBEP86-D3BJ<sup>14,15</sup> functional in combination with aug-cc-pV(Q+d)Z basis set. We chose DSD-PBEP86-D3BJ as our standard because it is a close relative of DSD-PBEPBE-D3BJ<sup>14</sup> (which is available in Psi4, but one-electron properties for double hybrid functionals are currently not implemented correctly), which offers performance on par with CCSD<sup>16</sup> for reproducing dipoles and polarizabilities from reference CCSD(T)<sup>17/</sup>CBS calculations at a fraction of the computational cost.<sup>18,19</sup>



**Figure S6.** Calculated dipole moments vs. "reference theory" DSD-PBEP86-D3BJ/aug-cc-pV(Q+d)Z gas phase dipole moments for (a) HF/6-31G\*, (b) HF/aug-cc-pV(T+d)Z, (c) B3LYP/aug-cc-pV(T+d)Z with PCM benzene, and (d) P B3LYP/aug-cc-pV(T+d)Z with PCM water. The black dotted line indicates perfect agreement with experiment (i.e., no under- or overpolarization).



**Figure S7.** Weighted residuals for robust linear regression fits to "reference theory" DSD-PBEP86-D3BJ/aug-cc-pV(Q+d)Z gas phase dipole moments for (a) HF/6-31G\*, (b) HF/aug-ccpV(T+d)Z, (c) B3LYP/aug-cc-pV(T+d)Z with PCM benzene, and (d) B3LYP/aug-cc-pV(T+d)Z with PCM water. A residual of zero indicates a prediction with no deviation from the regression line, or in other words, a prediction that is perfectly consistent with a linear model for overpolarization. All molecules with zero dipole moment are excluded from this analysis.

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