# ELECTRONIC SUPPLEMENTARY INFORMATION:

# Self-interaction error in DFT-based modelling of ionic liquids

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Table S 1: Dependence of interaction energy (kJ $mol^{-1}$) on the basis set. Calculations were performed using revPBE density functional with the Grimme's dispersion correction and without BSSE correction

| Ionic Pair | DZ | DZP | TZP | TZ2P | QZ4P |
|---|---|---|---|---|---|
| [BMIm]Cl | −418.02 | −425.89 | −407.02 | −408.23 | −396.18 |
| [BMIm]I | −378.74 | −381.75 | −373.30 | −379.66 | −361.54 |
| [BMIm]SCN | −363.63 | −374.01 | −366.69 | −366.02 | −365.51 |
| [BMIm][$BF_4$] | −353.80 | −370.58 | −362.25 | −361.00 | −359.82 |
| [BMIm][$N(CN)_2$] | −355.68 | −364.59 | −356.85 | −355.93 | −355.81 |
| [BMIm][$PF_6$] | −325.31 | −349.41 | −343.00 | −341.41 | −341.79 |
| [BMIm][TFSI] | −379.74 | −352.13 | −340.12 | −340.33 | −339.62 |
| [BMIm][FEP] | −312.25 | −320.20 | −310.66 | −304.18 | −312.54 |
| [BPy]Cl | −434.97 | −441.87 | −415.51 | −416.89 | −403.38 |
| [BPy]I | −389.78 | −392.92 | −377.40 | −383.63 | −366.02 |
| [BPy]SCN | −385.35 | −387.27 | −367.65 | −368.11 | −367.10 |
| [BPy][$BF_4$] | −358.07 | −365.26 | −349.91 | −349.91 | −350.24 |
| [BPy][$N(CN)_2$] | −366.64 | −373.30 | −359.95 | −359.57 | −359.36 |
| [BPy][$PF_6$] | −325.26 | −337.15 | −326.06 | −326.14 | −327.82 |
| [BPy][TFSI] | −368.48 | −347.98 | −334.68 | −335.14 | −334.22 |
| [BPy][FEP] | −297.90 | −296.81 | −275.01 | −304.05 | −277.52 |
| [BMPyr]Cl | −402.12 | −411.75 | −397.31 | −397.69 | −387.19 |
| [BMPyr]I | −359.03 | −362.25 | −360.41 | −366.31 | −349.57 |
| [BMPyr]SCN | −355.64 | −365.18 | −358.65 | −358.19 | −358.02 |
| [BMPyr][$BF_4$] | −347.65 | −364.18 | −358.15 | −358.82 | −355.68 |
| [BMPyr][$N(CN)_2$] | −347.48 | −356.77 | −352.08 | −351.08 | −351.20 |
| [BMPyr][$PF_6$] | −314.89 | −336.02 | −331.83 | −330.54 | −331.04 |
| [BMPyr][TFSI] | −353.80 | −370.58 | −362.25 | −361.00 | −359.82 |
| [BMPyr][FEP] | −267.99 | −281.54 | −273.30 | −272.59 | −275.39 |

Table S 2: Basis set superposition error (kJ $mol^{-1}$) dependence on the basis set. Calculations were performed using revPBE density functional with the Grimme's dispersion correction and according to the counterpoise method

| Ionic Pair | DZ | DZP | TZP | TZ2P | QZ4P |
|---|---|---|---|---|---|
| [BMIm]Cl | −15.40 | −14.90 | −9.58 | −9.62 | −3.05 |
| [BMIm]I | −14.35 | −14.39 | −14.23 | −10.92 | −0.75 |
| [BMIm]SCN | −11.84 | −7.95 | −3.10 | −2.93 | −2.18 |
| [BMIm][$BF_4$] | −6.49 | −6.95 | −5.06 | −3.97 | −2.68 |
| [BMIm][$N(CN)_2$] | −19.12 | −12.59 | −3.85 | −3.56 | −2.18 |
| [BMIm][$PF_6$] | −7.03 | −5.56 | −2.89 | −1.88 | −1.51 |
| [BMIm][TFSI] | −43.47 | −14.27 | −5.44 | −4.60 | −2.43 |
| [BMIm][FEP] | −18.66 | −9.50 | −4.73 | −3.56 | −4.60 |
| [BPy]Cl | −35.90 | −30.67 | −15.94 | −15.86 | −4.69 |
| [BPy]I | −13.43 | −14.85 | −13.68 | −16.61 | −0.84 |
| [BPy]SCN | −19.87 | −14.48 | −3.56 | −3.26 | −2.26 |
| [BPy][$BF_4$] | −17.82 | −15.27 | −4.94 | −3.93 | −2.09 |
| [BPy][$N(CN)_2$] | −27.45 | −18.79 | −4.69 | −4.31 | −2.18 |
| [BPy][$PF_6$] | −40.21 | −24.52 | −6.53 | −4.02 | −2.30 |
| [BPy][TFSI] | −32.64 | −14.23 | −3.68 | −3.10 | −1.80 |
| [BPy][FEP] | −26.07 | −17.07 | −4.48 | −3.56 | −2.59 |
| [BMPyr]Cl | −19.71 | −20.84 | −13.68 | −13.77 | −4.06 |
| [BMPyr]I | −12.05 | −11.97 | −13.72 | −16.86 | −1.00 |
| [BMPyr]SCN | −12.93 | −8.41 | −2.59 | −2.38 | −1.76 |
| [BMPyr][$BF_4$] | −7.70 | −6.90 | −4.81 | −3.93 | −2.68 |
| [BMPyr][$N(CN)_2$] | −16.48 | −10.42 | −3.43 | −3.14 | −1.84 |
| [BMPyr][$PF_6$] | −6.82 | −4.44 | −2.51 | −1.63 | −1.00 |
| [BMPyr][TFSI] | −40.79 | −10.84 | −4.77 | −4.02 | −1.88 |
| [BMPyr][FEP] | −16.15 | −7.61 | −4.48 | −3.60 | −3.72 |

Table S 3: Dependence of dipole moment (D) on the basis set. Calculations were performed using revPBE density functional in comparison to the MP2/6-311+G(3df) result

| Ionic Pair | DZ | DZP | TZP | TZ2P | QZ4P | MP2 |
|---|---|---|---|---|---|---|
| [BMIm]Cl | 7.7 | 8.1 | 7.4 | 8.1 | 8.1 | 9.2 |
| [BMIm]SCN | 13.1 | 12.5 | 12.4 | 12.4 | 12.1 | 12.7 |
| [BMIm][$N(CN)_2$] | 11.6 | 10.9 | 10.7 | 10.7 | 10.5 | 10.8 |
| [BMIm][$BF_4$] | 13.4 | 12.7 | 12.9 | 12.9 | 12.7 | 13.0 |
| [BMIm][$PF_6$] | 15.2 | 14.3 | 14.5 | 14.5 | 14.2 | 14.5 |
| [BMIm][TFSI] | 12.1 | 11.5 | 11.6 | 11.6 | 11.3 | 11.5 |
| [BMIm][FEP] | 15.5 | 15.2 | 15.3 | 15.6 | 15.1 | 15.6 |
| [BPy]Cl | 6.7 | 6.4 | 6.7 | 6.7 | 7.0 | 8.2 |
| [BPy]SCN | 10.2 | 9.9 | 10.1 | 10.1 | 10.2 | 11.9 |
| [BPy][$N(CN)_2$] | 10.6 | 9.9 | 10.0 | 10.0 | 9.7 | 10.9 |
| [BPy][$BF_4$] | 13.1 | 12.3 | 12.7 | 12.7 | 12.3 | 12.6 |
| [BPy][$PF_6$] | 15.2 | 14.4 | 14.6 | 14.6 | 14.2 | 14.5 |
| [BPy][TFSI] | 13.6 | 13.0 | 13.3 | 13.2 | 12.7 | 13.1 |
| [BPy][FEP] | 14.9 | 14.8 | 15.1 | 15.3 | 14.6 | 15.4 |
| [BMPyr]Cl | 13.0 | 12.4 | 12.6 | 12.6 | 12.6 | 13.8 |
| [BMPyr]SCN | 14.2 | 13.5 | 13.4 | 13.4 | 13.1 | 13.4 |
| [BMPyr][$N(CN)_2$] | 13.5 | 12.7 | 12.3 | 12.3 | 12.0 | 12.8 |
| [BMPyr][$BF_4$] | 14.9 | 14.1 | 14.2 | 14.3 | 14.1 | 14.6 |
| [BMPyr][$PF_6$] | 17.1 | 16.2 | 16.2 | 16.2 | 16.0 | 16.5 |
| [BMPyr][TFSI] | 15.2 | 14.6 | 14.7 | 15.2 | 14.4 | 15.2 |
| [BMPyr][FEP] | 18.1 | 17.8 | 17.8 | 17.8 | 17.6 | 18.3 |

Table S 4: BSSE corrected interaction energy (kJ $mol^{-1}$) calculated with TZ2P and ATZ2P basis sets at revPBE level in comparison to the BSSE corrected MP2/6-311+G(3df) result

| Ionic Pair | revPBE+DB/ATZ2P | revPBE+DB/TZ2P | MP2 |
|---|---|---|---|
| [BMIm]Cl | −396.60 | −398.61 | −378.23 |
| [BMIm]SCN | −378.78 | −363.09 | −366.82 |
| [BMIm][$N(CN)_2$] | −354.22 | −357.02 | −366.87 |
| [BMIm][$BF_4$] | −355.85 | −352.38 | −365.23 |
| [BMIm][$PF_6$] | −349.95 | −339.53 | −347.25 |
| [BMIm][TFSI] | −354.93 | −335.72 | −363.44 |
| [BMIm][FEP] | −313.55 | −300.62 | −349.75 |
| [BPy]Cl | −399.15 | −401.04 | −371.77 |
| [BPy]SCN | −363.25 | −364.84 | −348.67 |
| [BPy][$N(CN)_2$] | −344.18 | −345.97 | −349.72 |
| [BPy][$BF_4$] | −355.18 | −355.26 | −343.35 |
| [BPy][$PF_6$] | −323.34 | −322.13 | −325.56 |
| [BPy][TFSI] | −329.20 | −332.04 | −330.87 |
| [BPy][FEP] | −298.82 | −300.49 | −326.78 |
| [BMPyr]Cl | −386.52 | −383.92 | −375.99 |
| [BMPyr]SCN | −375.60 | −355.81 | −353.02 |
| [BMPyr][$N(CN)_2$] | −349.82 | −354.89 | −350.22 |
| [BMPyr][$BF_4$] | −355.51 | −347.94 | −347.49 |
| [BMPyr][$PF_6$] | −343.21 | −328.90 | −321.83 |
| [BMPyr][TFSI] | −338.23 | −314.43 | −310.35 |
| [BMPyr][FEP] | −279.45 | −268.99 | −284.14 |

Table S 5: Dipole moment (D) calculated with TZ2P and ATZ2P basis sets at revPBE level in comparison to the MP2/6-311+G(3df) result

| Ionic Pair | revPBE+DB/ATZ2P | revPBE+DB/TZ2P | MP2 |
|---|---|---|---|
| [BMIm]Cl | 8.2 | 8.1 | 9.2 |
| [BMIm]SCN | 12.3 | 12.4 | 12.7 |
| [BMIm][$N(CN)_2$] | 10.5 | 10.7 | 10.8 |
| [BMIm][$BF_4$] | 13.0 | 12.9 | 13.0 |
| [BMIm][$PF_6$] | 14.6 | 14.5 | 14.5 |
| [BMIm][TFSI] | 11.9 | 11.6 | 11.5 |
| [BMIm][FEP] | 15.6 | 15.6 | 15.6 |
| [BPy]Cl | 6.8 | 6.7 | 8.2 |
| [BPy]SCN | 10.2 | 10.2 | 11.9 |
| [BPy][$N(CN)_2$] | 9.6 | 10.0 | 10.9 |
| [BPy][$BF_4$] | 12.5 | 12.7 | 12.6 |
| [BPy][$PF_6$] | 14.5 | 14.6 | 14.5 |
| [BPy][TFSI] | 13.2 | 13.2 | 13.1 |
| [BPy][FEP] | 15.2 | 15.3 | 15.4 |
| [BMPyr]SCN | 13.1 | 13.4 | 13.8 |
| [BMPyr]Cl | 12.7 | 12.6 | 13.4 |
| [BMPyr][$N(CN)_2$] | 12.1 | 12.3 | 12.8 |
| [BMPyr][$BF_4$] | 14.2 | 14.3 | 14.6 |
| [BMPyr][$PF_6$] | 16.2 | 16.6 | 16.5 |
| [BMPyr][TFSI] | 15.2 | 15.2 | 15.2 |
| [BMPyr][FEP] | 18.2 | 17.8 | 18.3 |

Table S 6: Interaction energy (kJ $mol^{-1}$) calculated at revPBE/TZ2P level including full Perdew–Zunger (PZ) and scaled Perdew–Zunger (sPZ) corrections in comparison to the BSSE corrected MP2/6-311+G(3df) result

| Ionic Pair | revPBE+PZ | revPBE+sPZ | MP2 |
|---|---|---|---|
| [BMIm]Cl | −247.79 | −368.45 | −378.23 |
| [BMIm]I | −188.36 | −332.66 | −324.63 |
| [BMIm]SCN | −304.65 | −351.40 | −348.52 |
| [BMIm][$BF_4$] | −347.31 | −355.08 | −354.63 |
| [BMIm][$N(CN)_2$] | −331.54 | −348.21 | −355.14 |
| [BMIm][$PF_6$] | −326.85 | −337.00 | −340.68 |
| [BMIm][TFSI] | −295.97 | −327.77 | −336.82 |
| [BMIm][FEP] | −324.07 | −305.31 | −331.84 |
| [BPy]Cl | −206.37 | −362.10 | −371.77 |
| [BPy]I | −154.67 | −324.55 | −316.74 |
| [BPy]SCN | −301.08 | −352.09 | −348.67 |
| [BPy][$BF_4$] | −337.60 | −344.30 | −349.72 |
| [BPy][$N(CN)_2$] | −324.79 | −349.17 | −353.03 |
| [BPy][$PF_6$] | −303.60 | −318.42 | −325.56 |
| [BPy][TFSI] | −370.33 | −339.70 | −330.87 |
| [BPy][FEP] | −321.43 | −304.68 | −326.78 |
| [BMPyr]Cl | −232.76 | −353.69 | −375.99 |
| [BMPyr]I | −209.80 | −321.52 | −326.97 |
| [BMPyr]SCN | −335.23 | −351.69 | −353.02 |
| [BMPyr][$BF_4$] | −293.08 | −342.52 | −350.22 |
| [BMPyr][$N(CN)_2$] | −322.98 | −342.95 | −347.49 |
| [BMPyr][$PF_6$] | −307.90 | −324.70 | −321.83 |
| [BMPyr][TFSI] | −321.32 | −315.81 | −310.35 |
| [BMPyr][FEP] | −263.45 | −267.88 | −283.28 |