Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Ethylene glycol energetically disfavours oligomerization of pseudoisocyanine dyestuffs at crowded concentrations

Satyendra Rajput[a], Roland Pollak[b], Klaus Huber[c], Simon Ebbinghaus[b], Divya Nayar[a,*]

[a] Department of Materials Science and Engineering, Indian Institute of Technology Delhi, New Delhi-110016, India

[b] Institute of Physical and Theoretical Chemistry, TU Braunschweig, 38196 Braunschweig, Germany

[c] Department of Chemistry, University of Paderborn, 33098 Paderborn, Germany

[*]e-mail: divyanayar@mse.iitd.ac.in

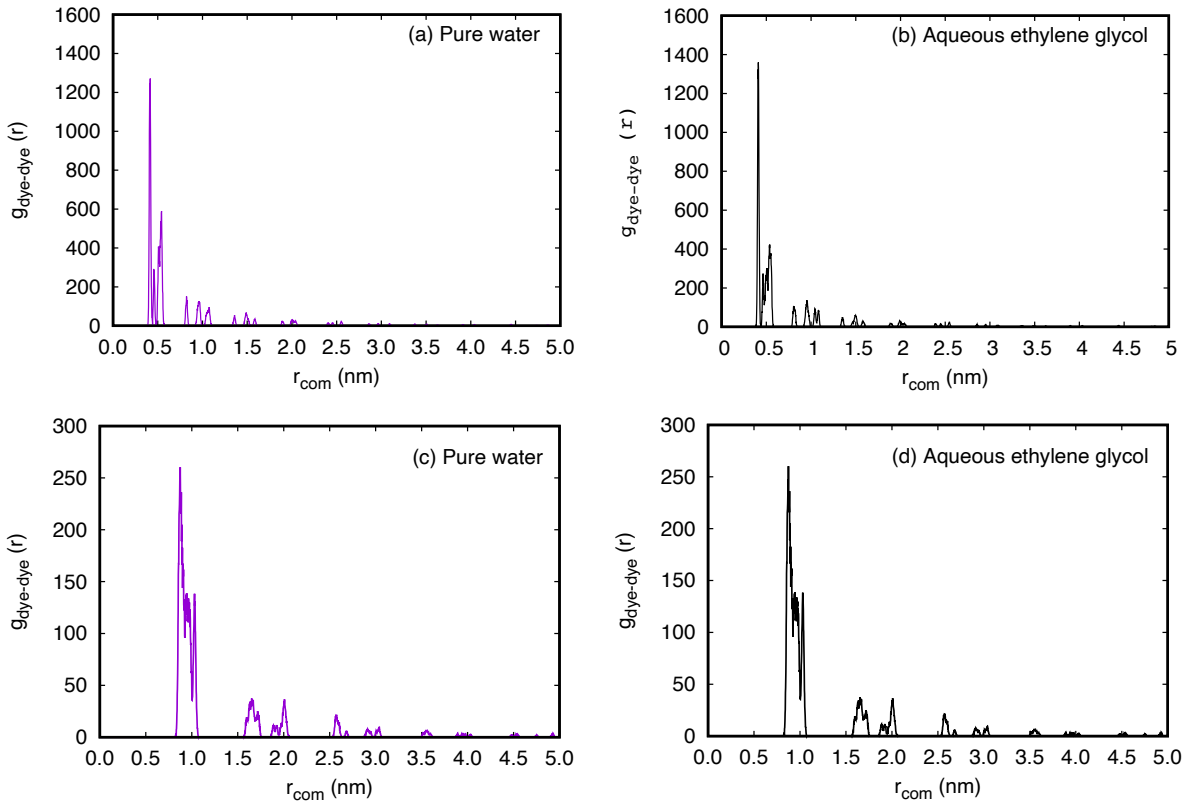

Figure S1: Radial distribution function (rdf) of center of mass of dye-dye interaction in H-aggregate in (a) pure water and (b) aqueous ethylene glycol and in J-aggregate in (c) pure water and (d) aqueous ethylene glycol.

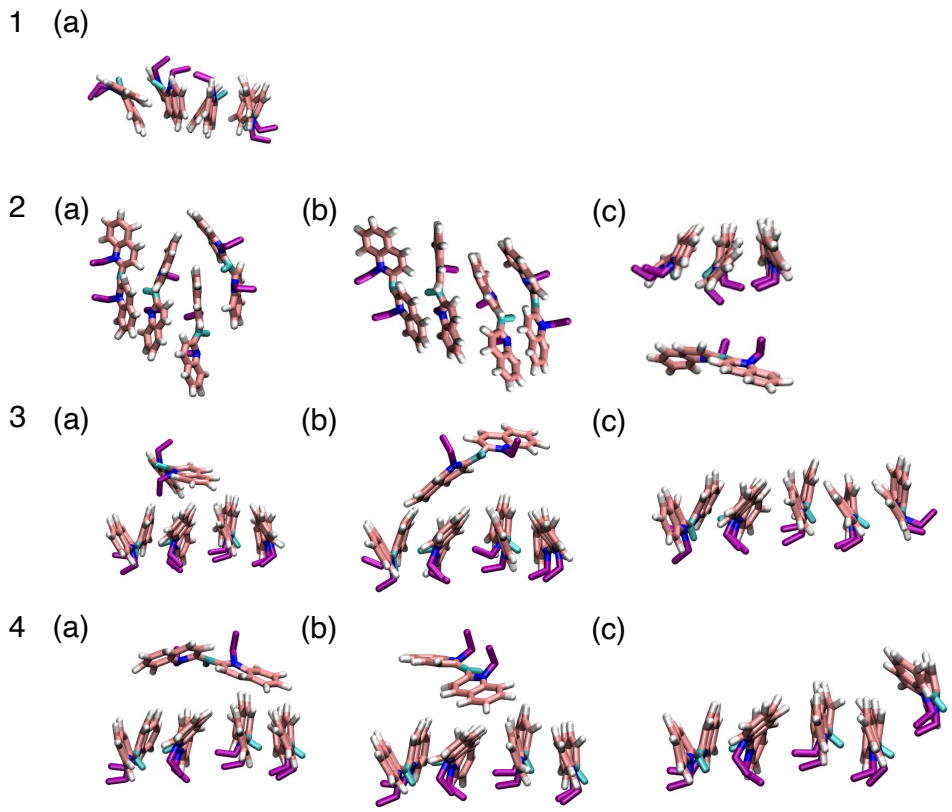

Figure S2: Snapshots of PIC H-oligomers: 1(a) tetramer in pure water in global minimum at 0.82 nm. 2.) Tetramer in aqueous ethylene glycol at (a) first local minimum at 0.72 nm, (b) global minimum at 0.82 nm (c) second local minimum at 0.92 nm. 3.) Pentamer in pure water at (a) first local minimum at 0.62 nm, (b) second local minimum at 0.74 nm and (c) global minima at 1.05 nm. 4.) Pentamer in aqueous ethylene glycol at (a) first local minimum at 0.62 nm, (b) second local minimum at 0.74 nm and (c) global minimum at 1.05 nm

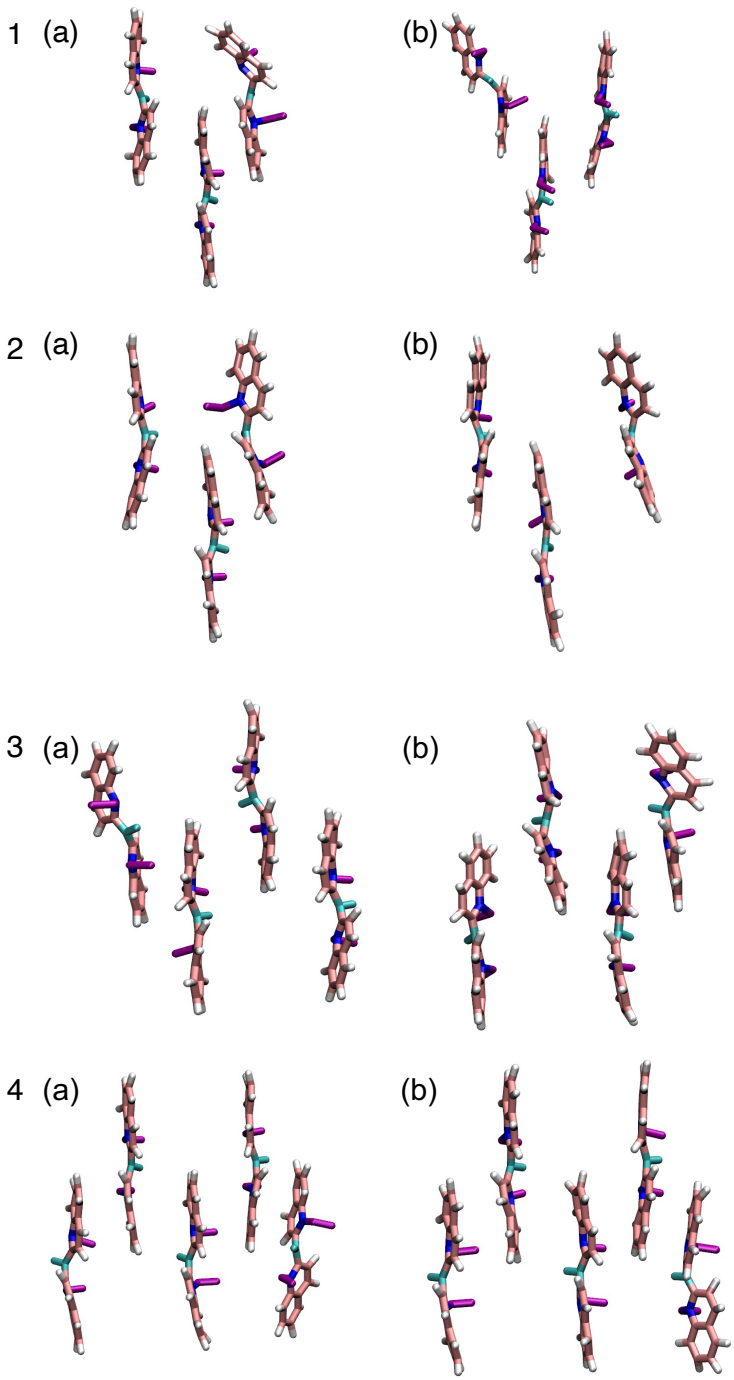

Figure S3: Snapshots of PIC J-oligomers: 1.) trimer in pure water at (a) local minimum at 0.72 nm, (b) global minimum at 1.05 nm. 2.) Trimer in aqueous ethylene glycol at (a) local minimum at 0.82 nm, (b) global minimum at 1.02 nm. 3.) Tetramer in pure water at global minima at 1.05 nm and (b) Tetramer in aqueous ethylene glycol at global minimum of 1.05 nm. 4.) Pentamer in (a) pure water at global minimum of 1.12 nm, (b) aqueous ethylene glycol at global minimum at 1.12 nm.

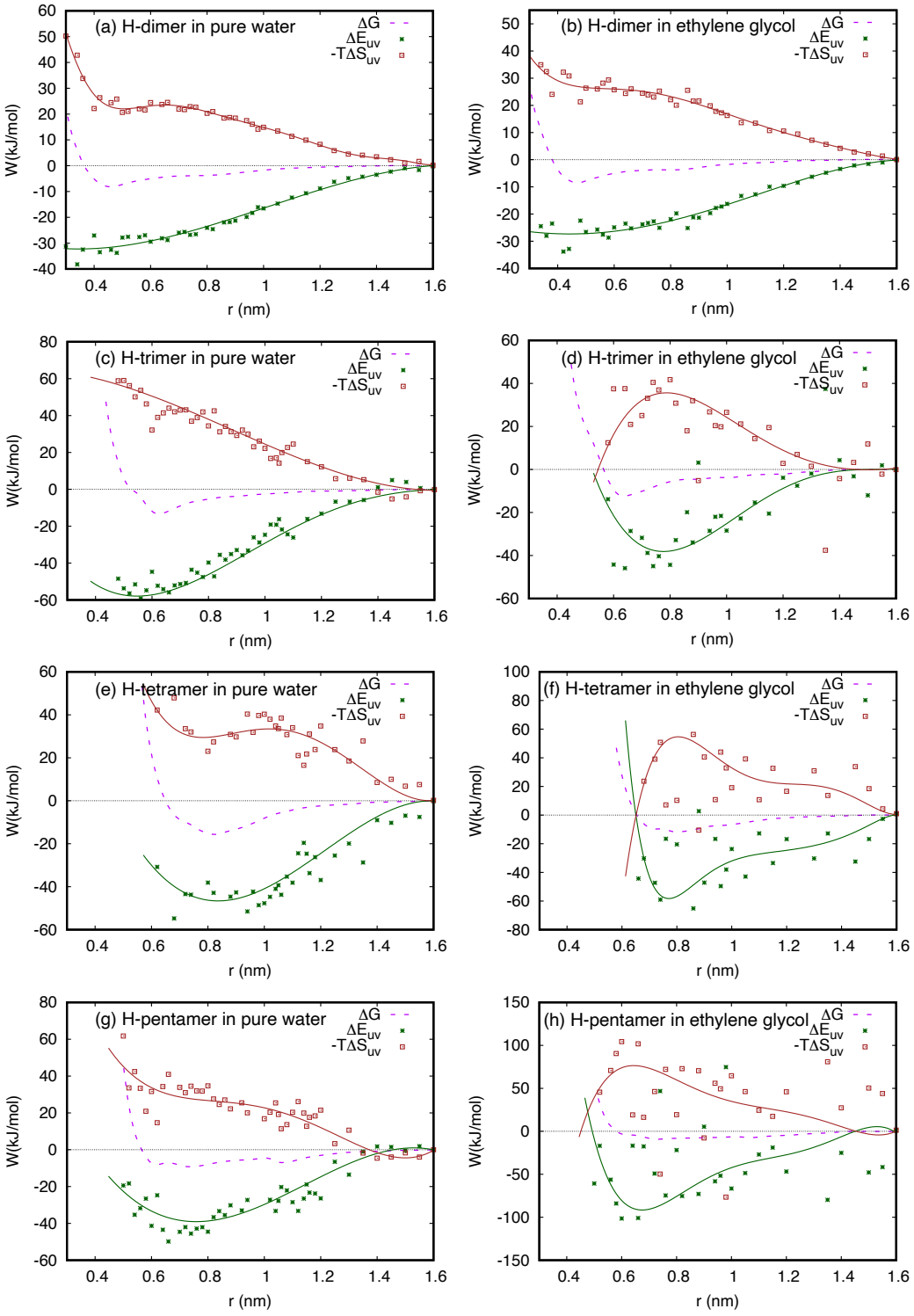

Figure S4: The profiles for the bindng free energy ($\Delta G^{u\to b}$), change in dye-solvent energy ($\Delta E_{dv}^{u\to b}$) and change in dye-solvent entropy ($\Delta E_{dv}^{u\to b}$) on dye association into H-oligomers. The left column represents for pure water solutions and right column repesents for aqueous ethylene glycol solution.

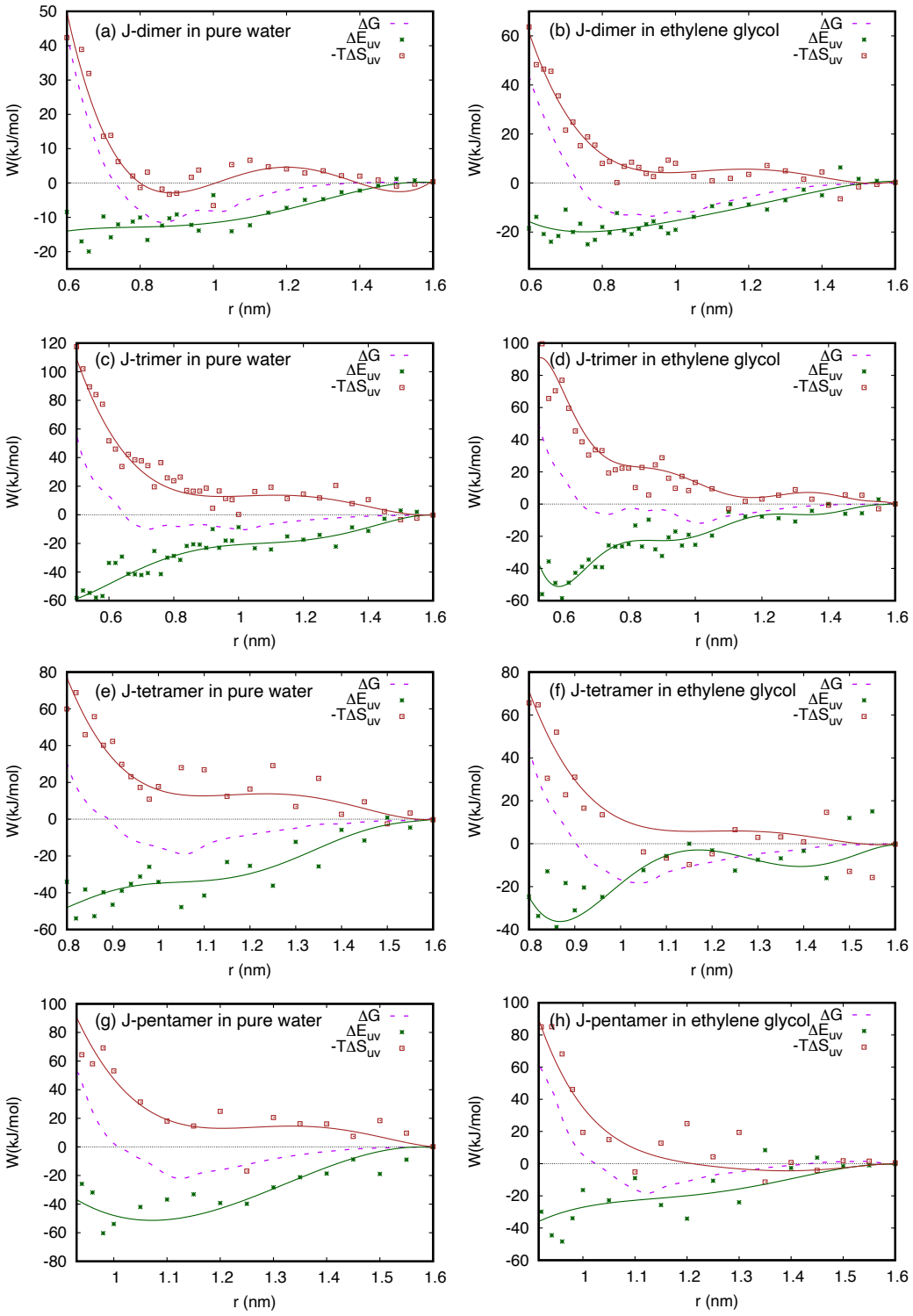

Figure S5: The profiles for the bindng free energy ($\Delta G^{u\to b}$), change in dye-solvent energy ($\Delta E_{dv}^{u\to b}$) and change in dye-solvent entropy ($\Delta E_{dv}^{u\to b}$) on dye association into J-oligomers. The left column represents for pure water solutions and right column repesents for aqueous ethylene glycol solution.

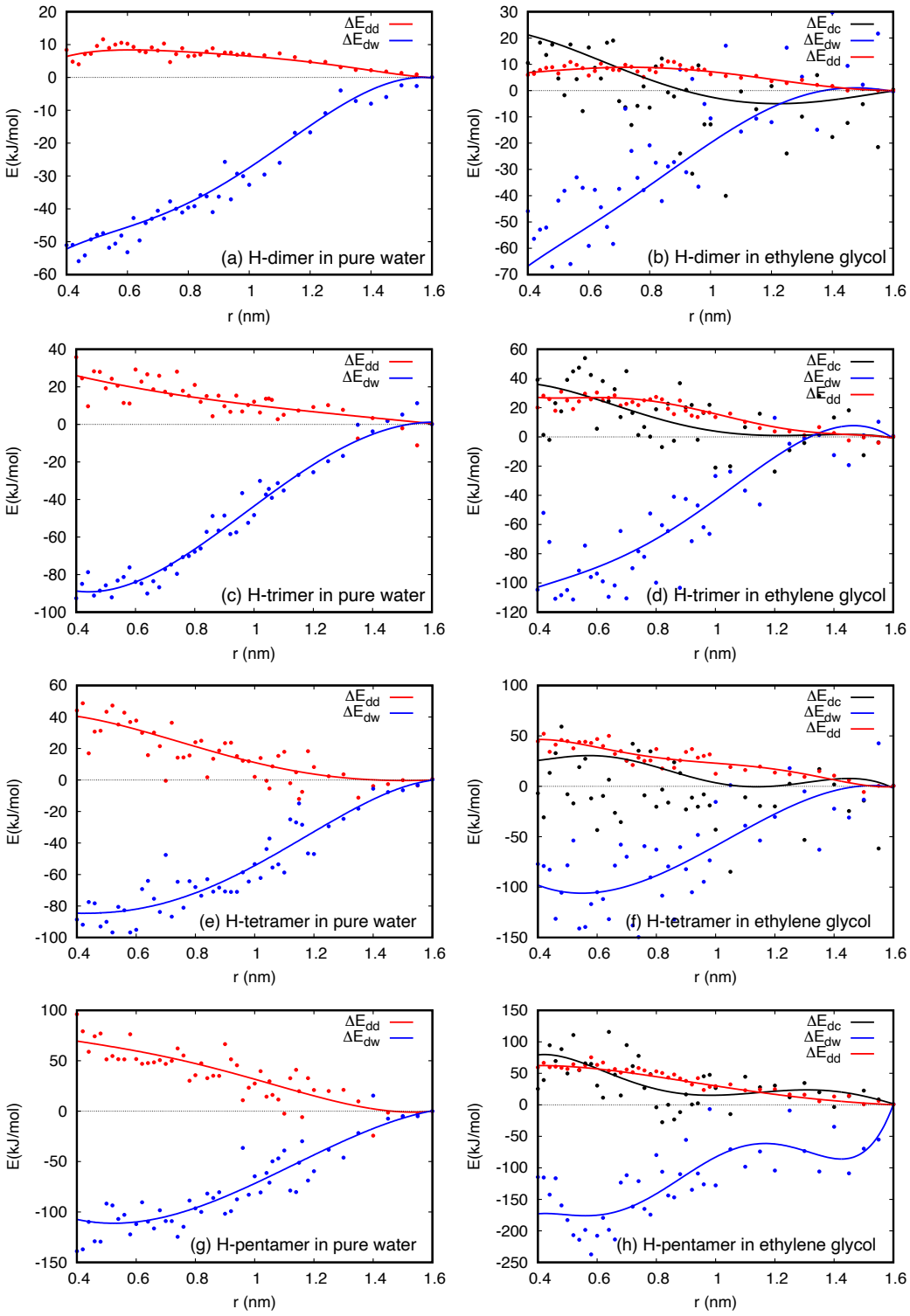

Figure S6: Profiles of components of total dye-solvent energy change ($\Delta E_{dv}^{u\to b}$) for H-oligomers arising from the change in dye-water energy ($\Delta E_{dw}^{u\to b}$), dye-dye energy ($\Delta E_{dd}^{u\to b}$) that includes dye-ion energy and dye-crowder energy ($\Delta E_{dc}^{u\to b}$). The left column represents for pure water solutions and right column repesents for aqueous ethylene glycol solution.

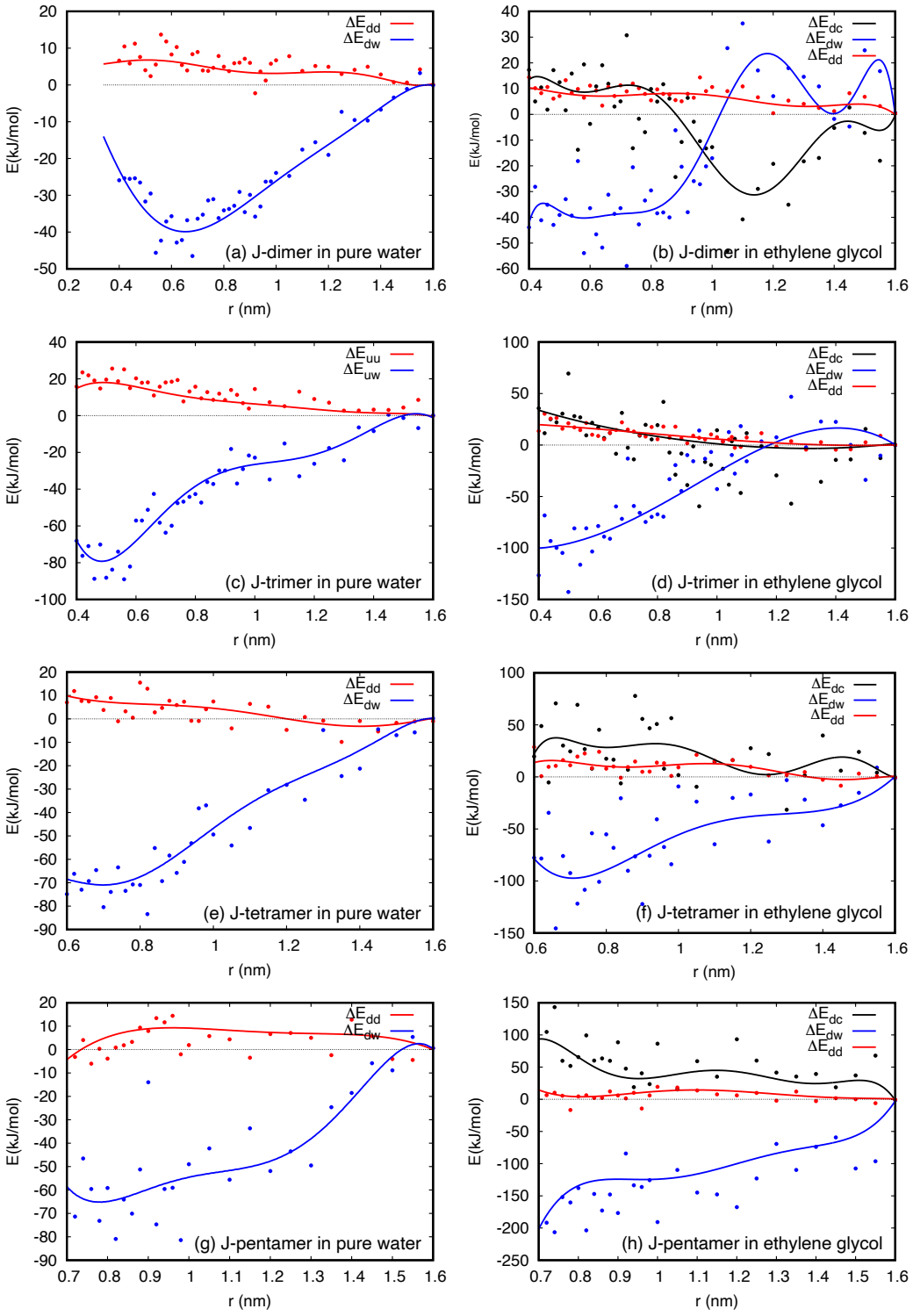

Figure S7: Profiles of components of total dye-solvent energy change ($\Delta E_{dv}^{u\to b}$) for J-oligomers arising from the change in dye-water energy ($\Delta E_{dw}^{u\to b}$), dye-dye energy ($\Delta E_{dd}^{u\to b}$) that includes dye-ion energy and dye-crowder energy ($\Delta E_{dc}^{u\to b}$). The left column represents for pure water solutions and right column repesents for aqueous ethylene glycol solution.

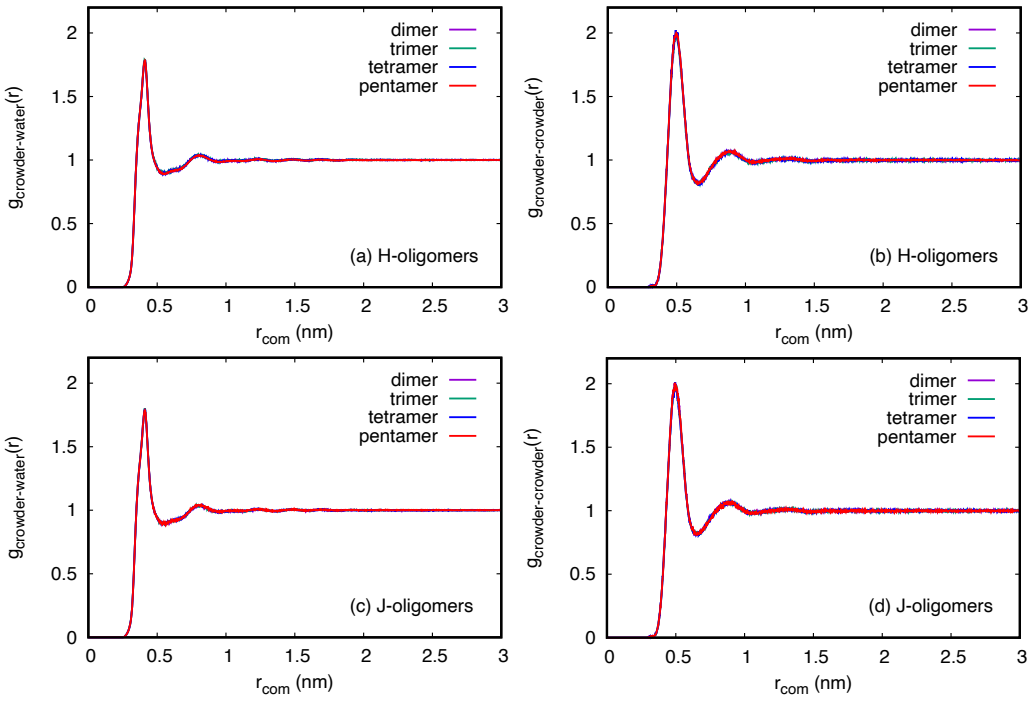

Figure S8: Radial distribution functions of crowder-water and crowder-crowder interactions in solutions of (a), (b) H-oligomers and (c), (d) J-oligomers.

Table S1: The interaction energies between different components in aquoeous solutions of dispersed PIC dye molecules in aqueous crowded solution of ethylene glycol. Here, E_{dw} is dye-water, E_{dc} is dye-crowder, E_{dd} is dye-dye, E_{di} dye-ion, E_{ww} is water-water, E_{cc} is crowder-crowder, E_{cw} is crowder-water interaction energy in kJ/mol. To compute this data, separate MD simulations were performed with one to five PIC monomers dispersed in aqueous ethylene glycol with no oligomers in solution. The simulation parameters used remain the same as described in the Methods section of the main manuscript.

No. of dye molecules	E_{dw}	E_{dc}	E_{dd}	E_{di}	E_{ww}	E_{cc}	E_{cw}
1	-168.56	-112.08	174.18	-0.66	-178341	-196034	-122945
2	-335.71	-222.76	347.89	-2.36	-176181	-196094	-122537
3	-504.37	-329.55	525.85	-3.73	-175719	-195814	-121631
4	-672.95	-438.29	697.75	-4.88	-173698	-196183	-121781
5	-836.54	-548.74	872.28	-6.12	-174280	-196000	-121784