Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Effect of substituents in sulfoxides on the enhancement of thermoelectric properties of PEDOT:PSS: experimental and modelling evidences

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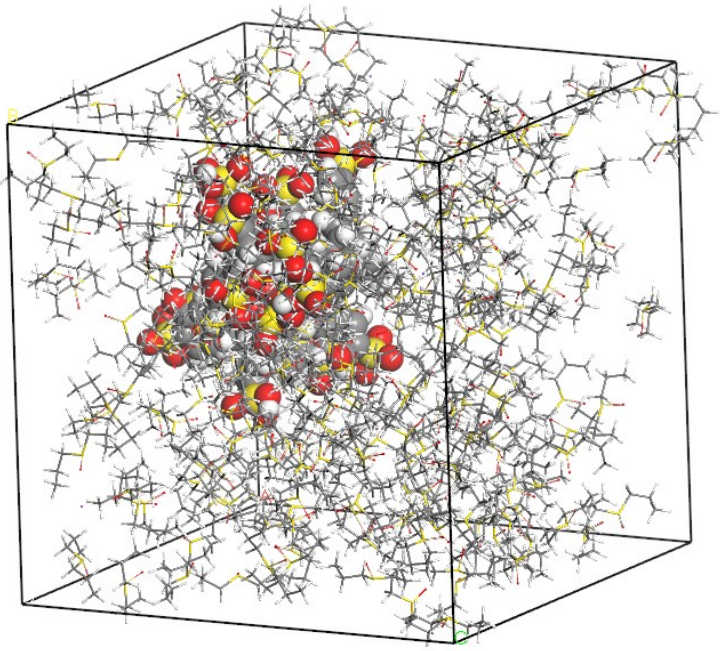

Figure S1. Initial cell structure with one chain of PSS_{18}^{-6}, six Na^{+} cation and 232 Sulfoxide **1** molecules corresponding to 90% weight fraction of additive at 1 g/cm^3 density.

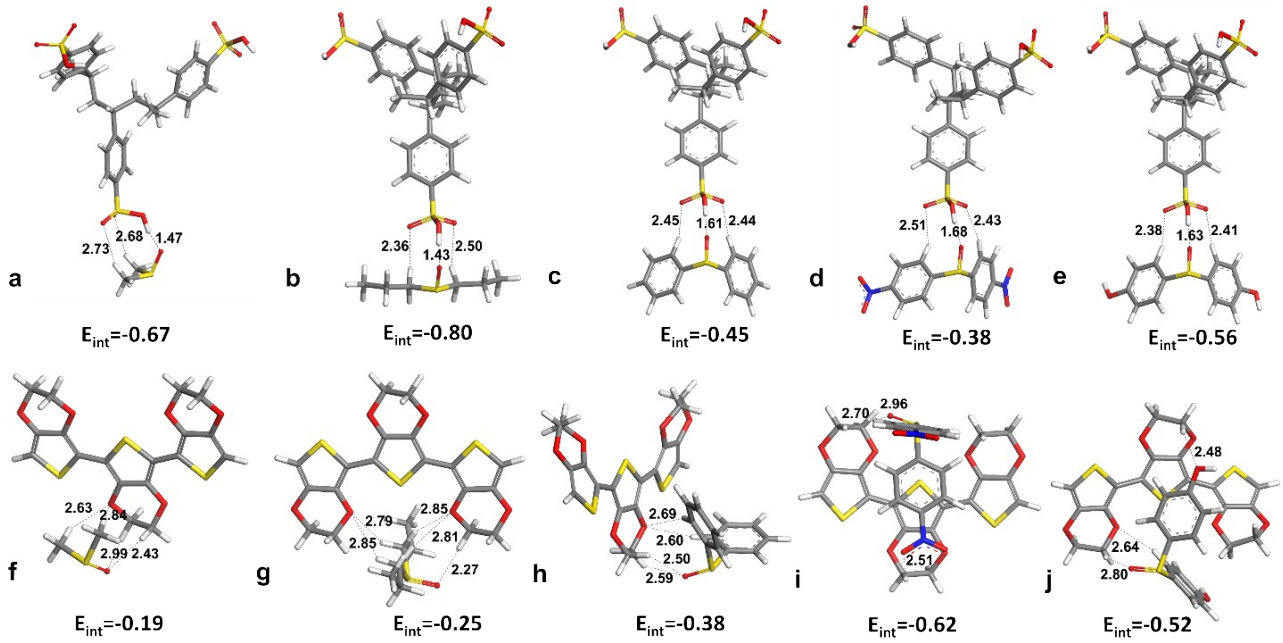

Figure S2. Second lowest energy optimized structures and the pairwise interaction energies for a-e) PSS trimer with DMSO and new sulfoxides, f-j) PEDOT trimer with DMSO and new sulfoxides by B3LYP/DNP method.

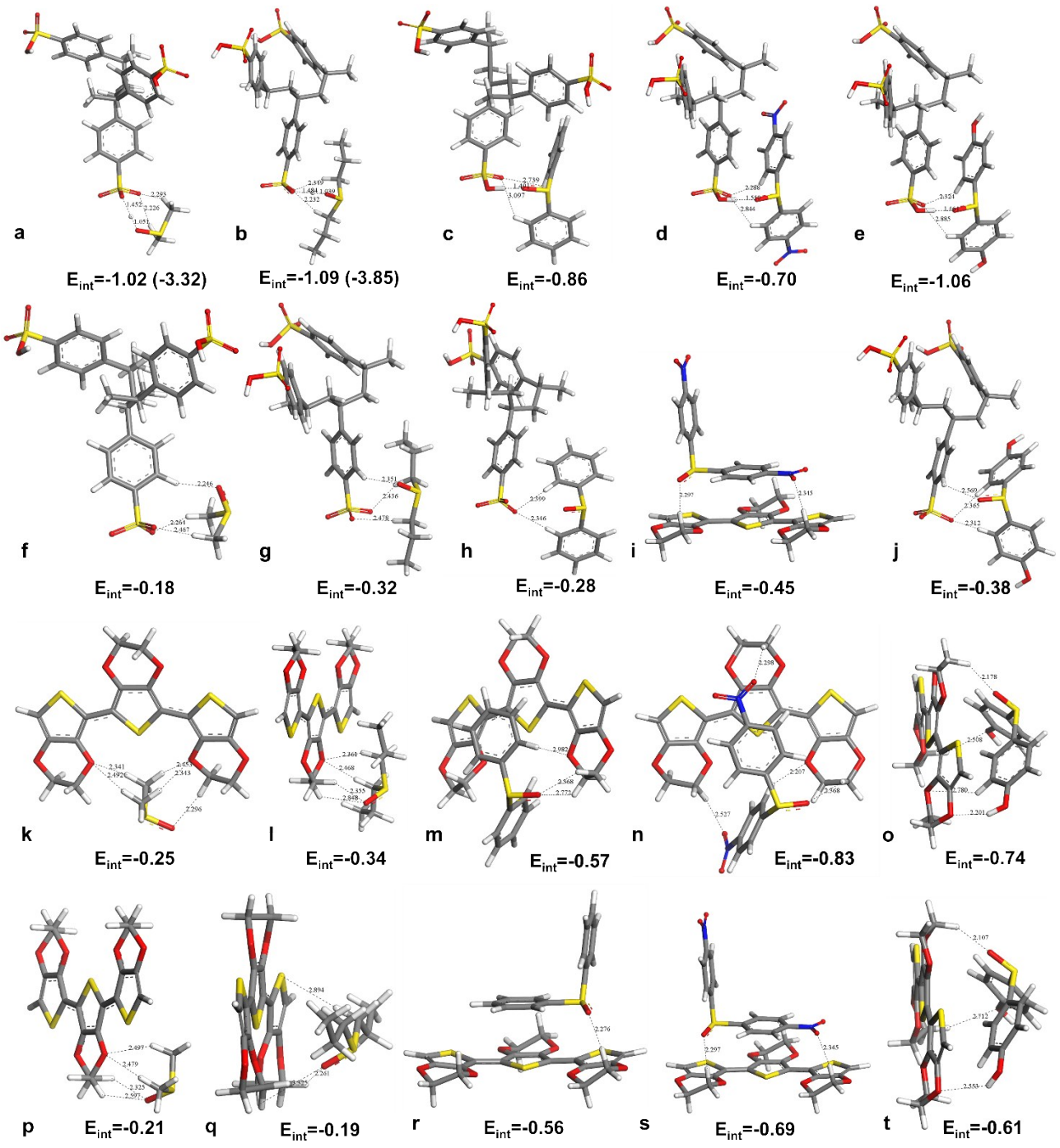

Figure S3. Lowest energy optimized structures and the pairwise interaction energies for a-e) PSS trimer, f-j) PSS^- anionic trimer k-o) PEDOT trimer, p-t) $PEDOT^+$ cation trimer polaron with DMSO and 4 new sulfoxides calculated by M06-2X/6-31+g(d) method.

Two types of calculations were performed to calculate octanol/water partition coefficient (logP) values which are related to the hydrophobic character of the solvents. Calculation method for logP by using Molinspiration software[1] is based on group contributions. This method is developed by fitting theoretical logP values with experimental logP values for a training set including twelve thousand organic molecules. Second is an atom-type-based logP method based on the set of parameters[2] Hydrophobicity is calculated by classification of atoms and their contributions to octanol-water partition coefficient followed by the summation of the number of atoms multiplied by an optimized coefficient.

Table S1. Hydrophobicity of DMSO and additives in terms of octanol/water partition coefficient, LogP.

	DMSO	**Sulfoxide 1**	**Sulfoxide 2**	**Sulfoxide 3**	**Sulfoxide 4**
LogP[1]	-0.69	0.06	3.34	3.26	2.38
LogP[2]	-0.32	0.38	2.84	2.62	2.35

Table S2. Solubility parameters in terms of electrostatic and van der Waals components calculated for the sulfoxide derivatives. Solubility parameters were calculated by for the 100 different amorphous cells at the experimental densities with 150 sulfoxide molecules in each cell.

Sulfoxide	**Electrostatic solubility parameter ($MPa^{1/2}$)**	**vdW solubility parameter ($MPa^{1/2}$)**	**Total solubility parameter ($MPa^{1/2}$)**
DMSO	12.391 ± 0.014	22.058 ± 0.018	25.300 ± 0.020*
1	8.654 ± 0.004	21.006 ± 0.008	22.720 ± 0.014
2	6.315 ± 0.038	19.576 ± 0.079	20.582 ± 0.077
3	10.711 ± 0.142	16.008 ± 0.024	19.423 ± 0.021
4	14.153 ± 0.043	17.231 ± 0.167	22.486 ± 0.036
water	53.418 ± 0.012	NA**	53.418 ± 0.012***

* Experimental solubility parameter for DMSO was reported as 26.4 $MPa^{1/2}$. [3]

** vdW contribution to the cohesive energy density of water is close to zero and vdW solubility parameter could not be calculated in the calculated error range.

*** Experimental solubility parameter for water was reported as 48 $MPa^{1/2}$. [3]

Table S3. Detailed results for the calculation of of mixing energy (E_{mix}) and its components including pairwise binding energies (E_{i-i}, E_{i-j}, E_{j-j}) and coordination numbers (Z) calculated for PEDOT and PSS with DMSO and alternative new sulfoxides.

i	j	E_{mix} (kcal/mol)	E_{i-i} (kcal/mol)	E_{i-j} (kcal/mol)	E_{j-j} (kcal/mol)	Z_{i-i}	Z_{i-j}	Z_{j-i}	Z_{j-j}
PSS	DMSO	-37.32	-2.92	-8.33	-2.22	5.41	9.16	3.18	5.54
	1	-39.26	-2.92	-9.37	-2.64	5.41	7.82	3.81	5.54
	2	-27.57	-2.92	-7.72	-3.10	5.41	7.38	4.06	5.59
	3	-29.51	-2.92	-8.57	-5.71	5.41	9.32	4.38	5.61
	4	-51.41	-2.92	-12.62	-4.47	5.41	7.21	4.17	5.59
PEDOT	DMSO	13.94	-10.05	-2.90	-2.22	4.82	7.97	3.37	5.54
	1	10.10	-10.05	-4.02	-2.64	4.82	6.62	4.06	5.54
	2	6.35	-10.05	-5.03	-3.11	4.82	6.22	4.34	5.59
	3	1.46	-10.05	-7.08	-5.10	4.82	5.81	4.67	5.60
	4	7.93	-10.05	-5.47	-4.47	4.82	6.07	4.45	5.59

Table S4. Components of free energy of solvation (ΔE_{sol}) calculated for PEDOT and PSS with DMSO and 4 alternative new sulfoxides.

Solute	Solvent	Ideal free energy (kcal/mol)	vdW free energy (kcal/mol)	Electrostatic free energy (kcal/mol)	Total solvation free energy (kcal/mol)
PSS	DMSO	257.86	-70.72	-503.31	-316.17
	1	248.08	-62.61	-425.10	-239.63
	2	257.29	-60.58	-371.21	-174.50
	3	269.31	-61.88	-338.90	-131.47
	4	282.31	-50.96	-458.38	-227.03
PEDOT	DMSO	-34.82	-41.01	21.38	-54.45
	1	-34.73	-35.32	26.89	-43.16
	2	-34.76	-21.75	27.03	-29.48
	3	-34.74	-25.00	20.93	-38.81
	4	-34.71	-11.50	29.40	-16.81

References

1. https://www.molinspiration.com/cgi-bin/properties
2. A. K. Ghose, V. N. Viswanadhan and J. J. Wendoloski, *J. Phys. Chem.*, 1998, 102, 3762-3772.
3. A.F.M. Barton, CRC Handbook of Solubility Parameters and Other Cohesion Parameters, 2nd edition, CRC Press, Boca Raton, FL, 1991.