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Supplementary Information: Molecular-Scale Understanding of Diluent Effects for Metal Ion Separations

Derrick Poe,*,† Soenke Seifert,‡ and Michael J. Servis*,†

†*Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA*

‡*X-ray Science Division, Argonne National Laboratory, Lemont, IL 60439, USA*

E-mail: dpoe@anl.gov; mservis@anl.gov

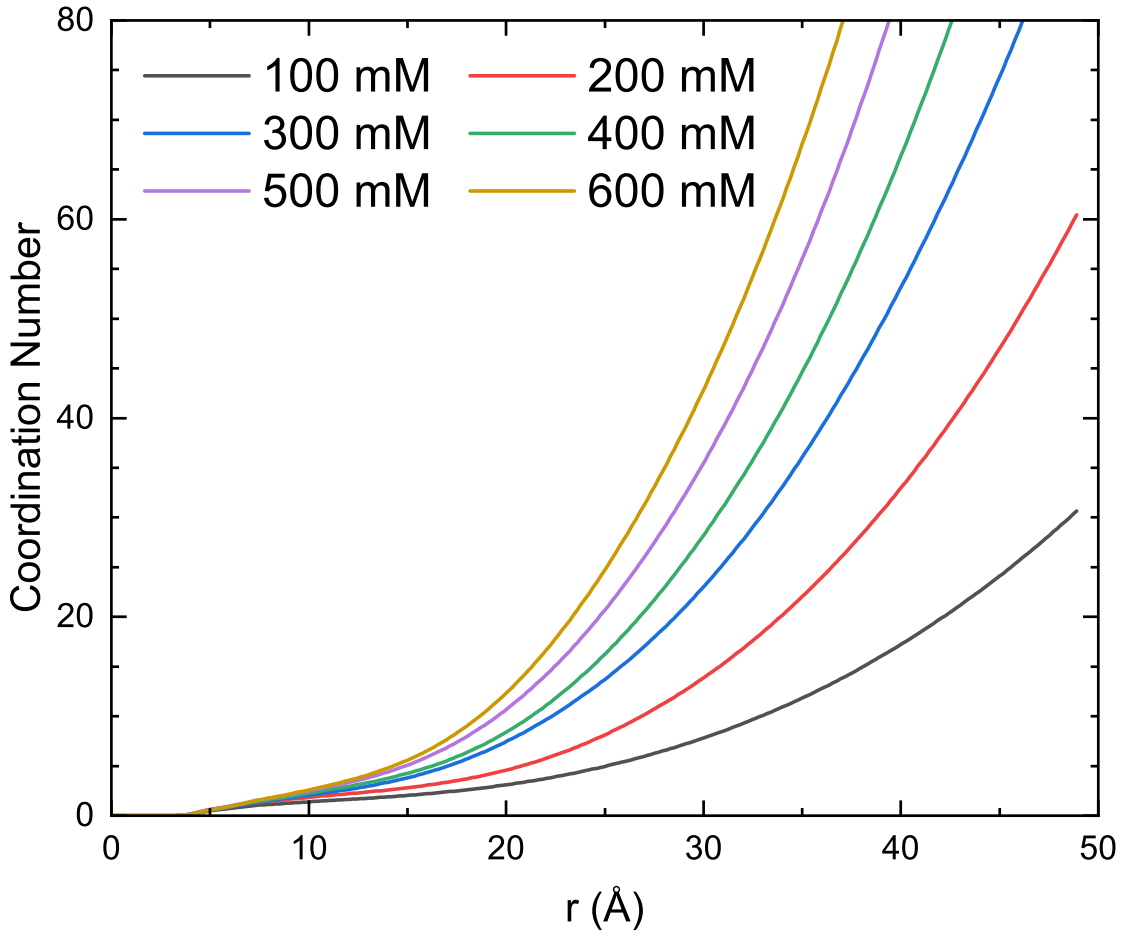


Figure S1: Zoomed out coordination numbers between ether oxygens of TODGA molecules in n-dodecane at various concentrations of TODGA demonstrating appropriate long-range concentration trends.

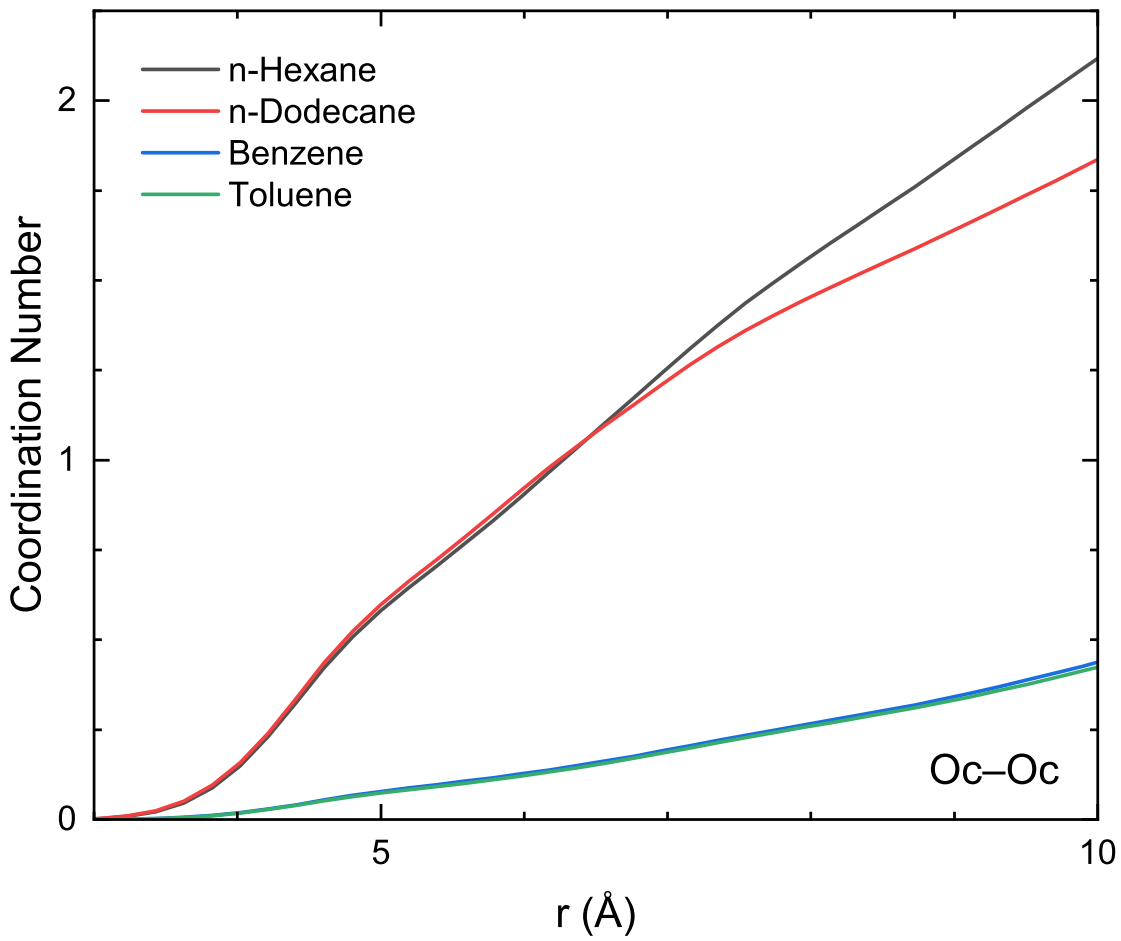


Figure S2: Coordination number plot of TODGA etheric-oxygen O–O at 200 mM TODGA in various solvents.

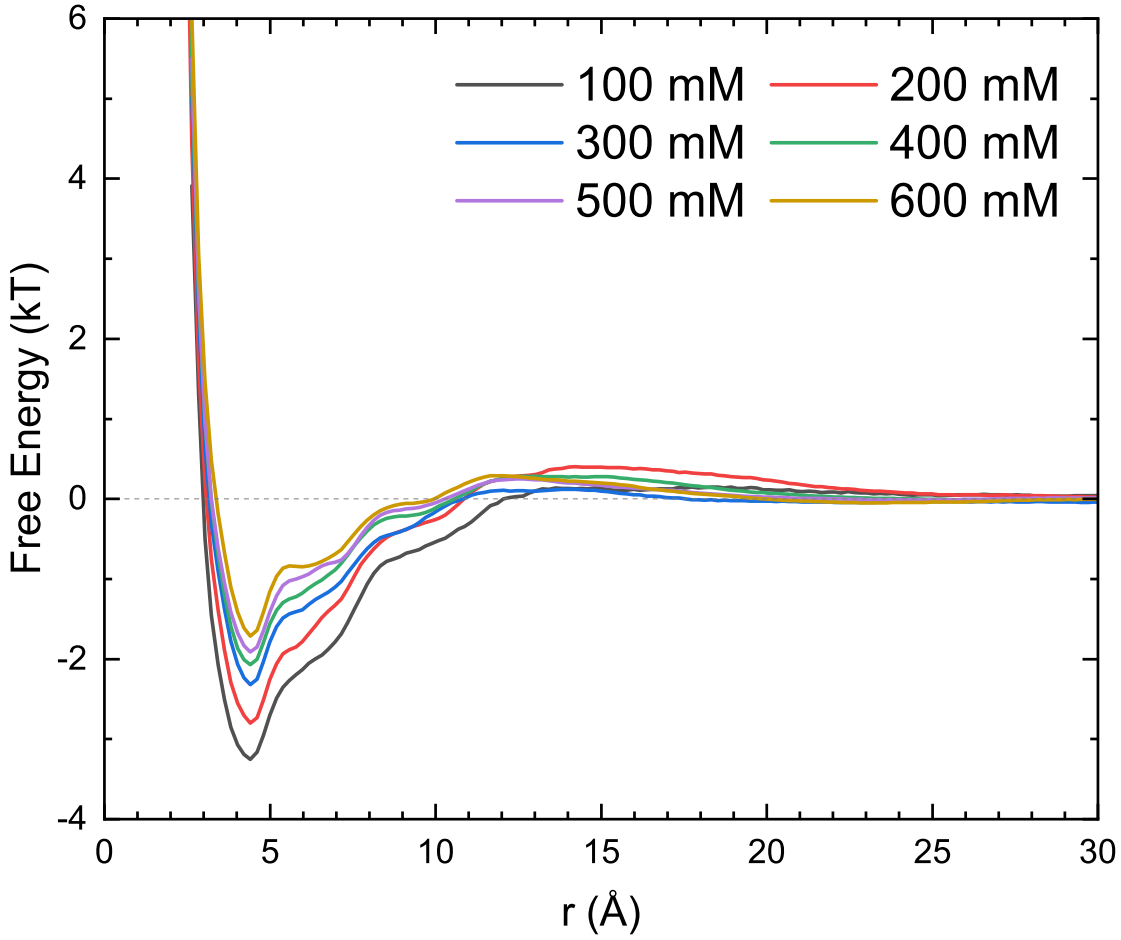


Figure S3: Pairwise free energy of TODGA ether oxygens in n-dodecane at various TODGA concentrations calculated via $w(r) = -kT \ln[g(r)]$.

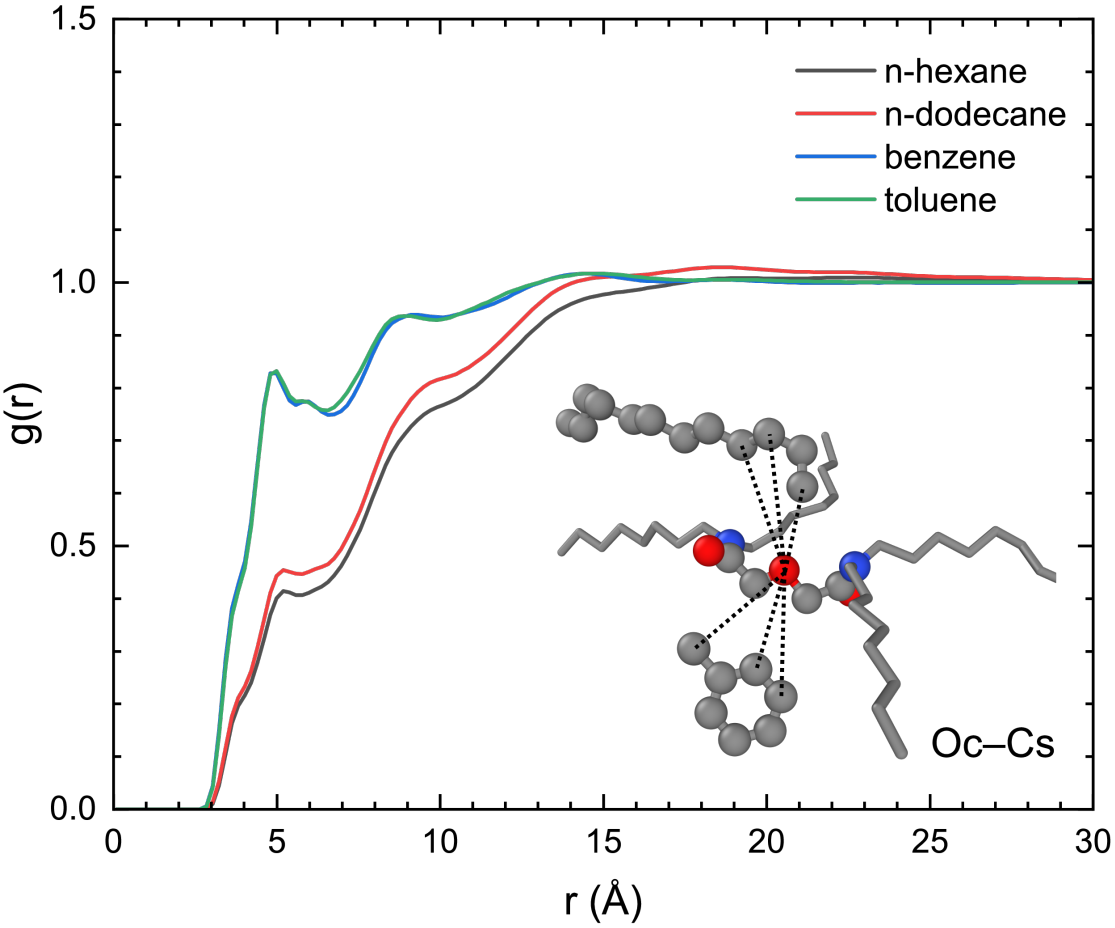


Figure S4: Radial distribution function of TODGA etheric oxygen to solvent carbons. An example of TODGA, n-dodecane, and toluene with some example O–C pairs are included for reference.

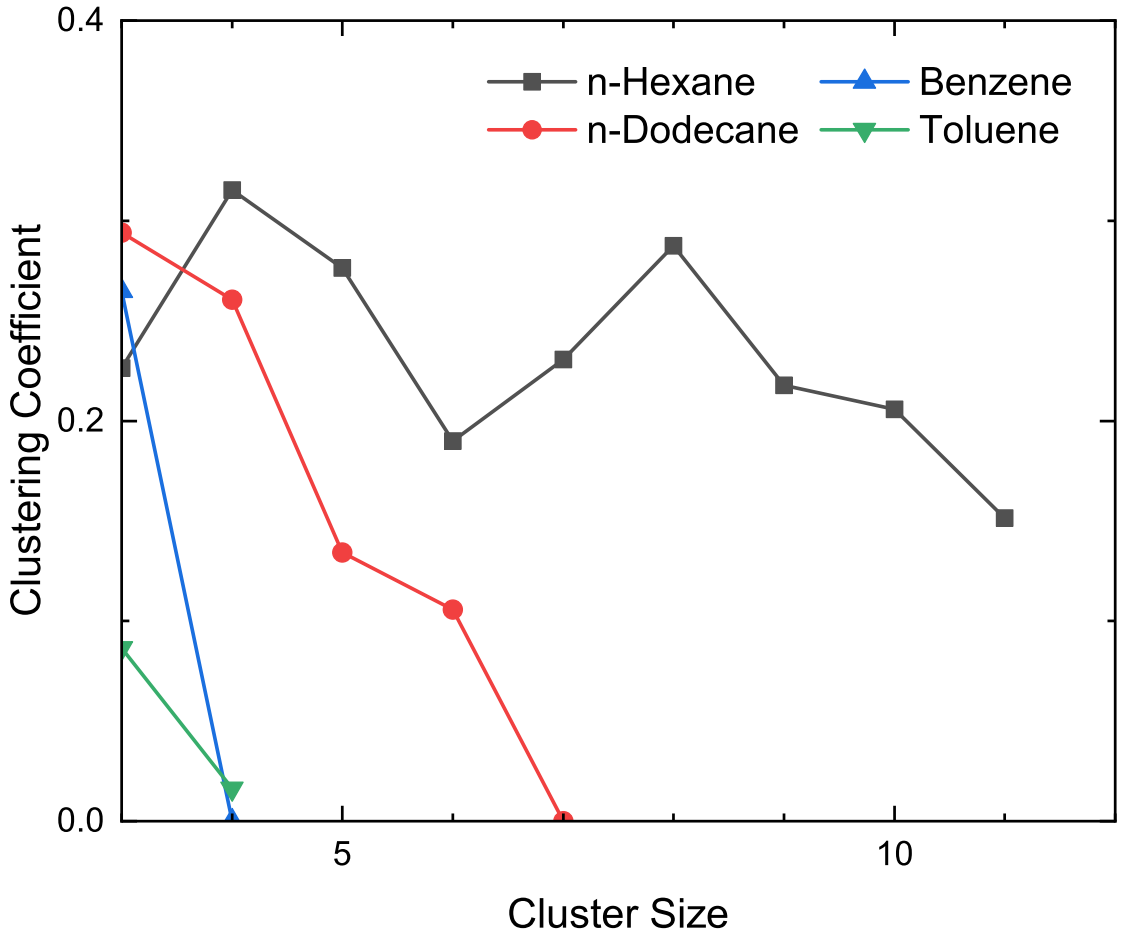


Figure S5: Clustering coefficient distribution of 200 mM TODGA in various solvents with a 6 Å cutoff.

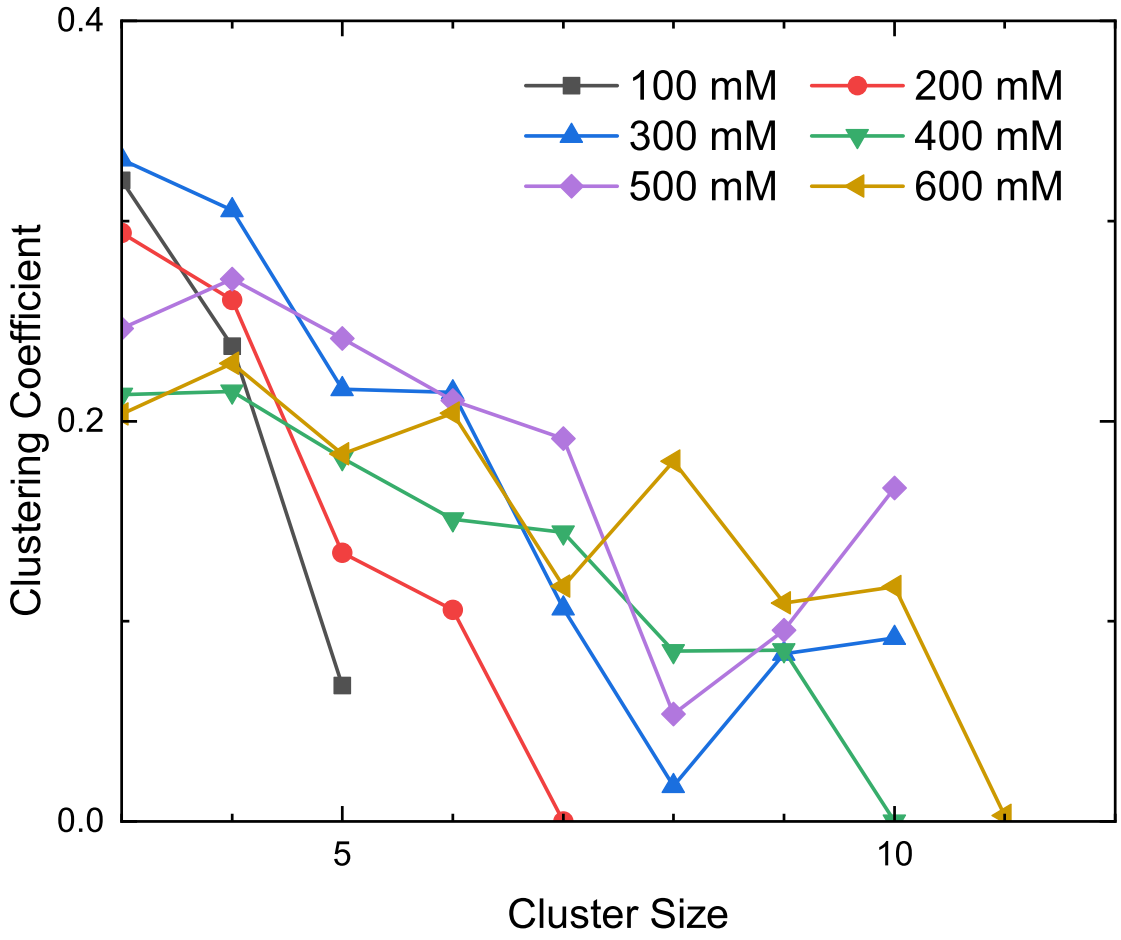


Figure S6: Clustering coefficient distribution of various concentrations of TODGA in n-dodecane with a 6 Å cutoff.

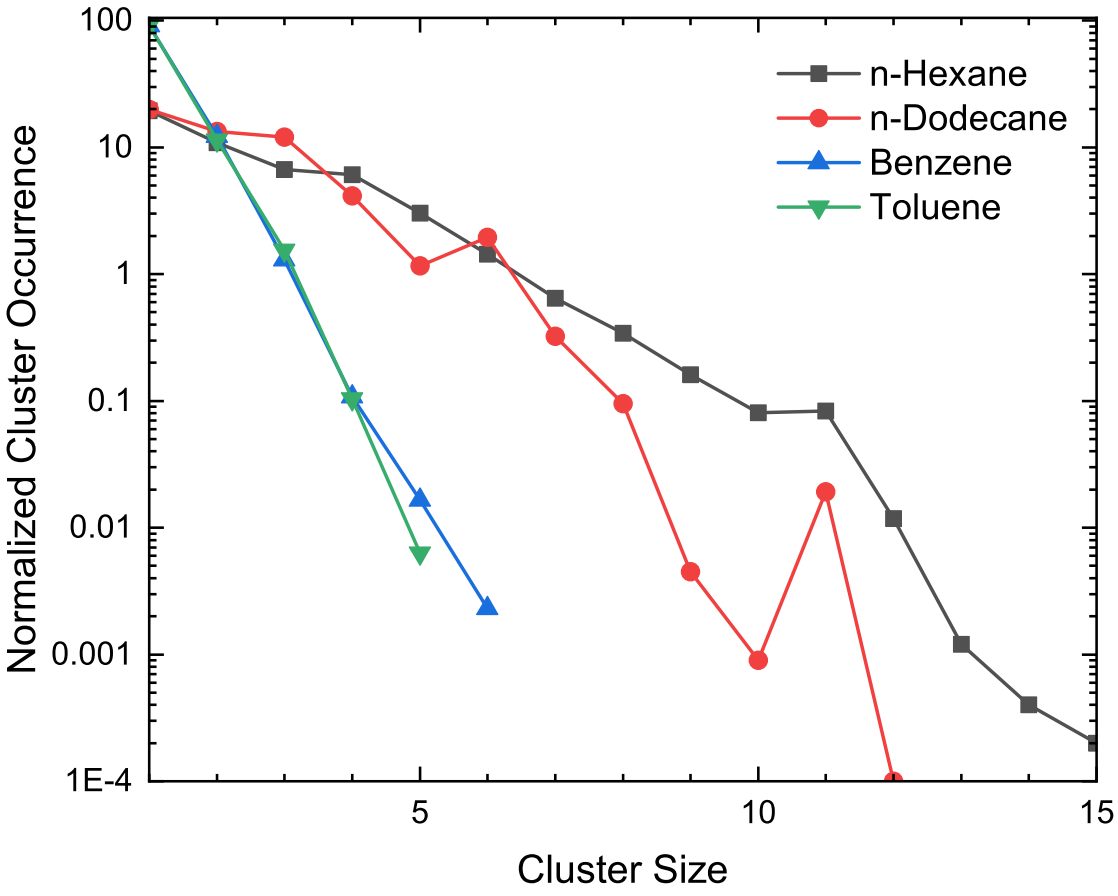


Figure S7: Cluster size distribution in various solvents with an 8 Å cutoff.

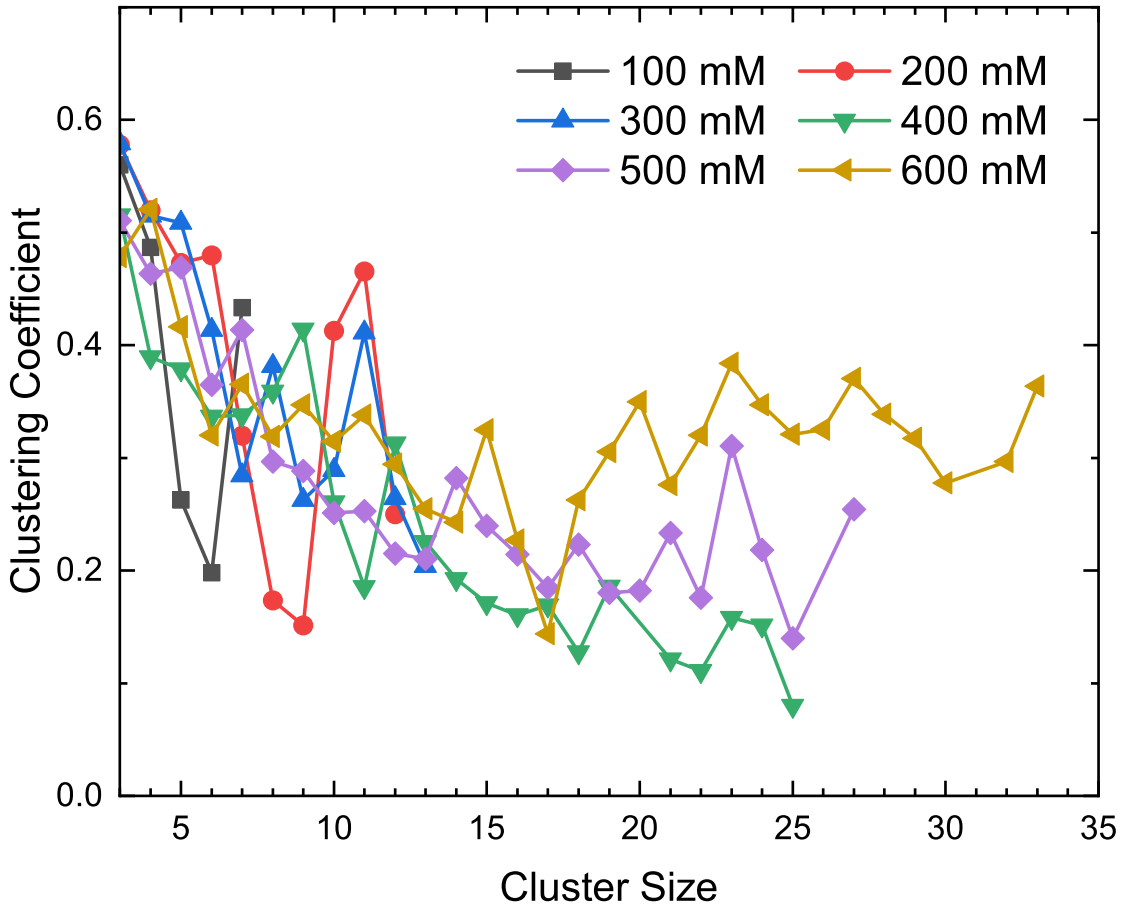


Figure S8: Clustering coefficient distribution of various concentrations of TODGA in n-dodecane with an 8 Å cutoff.

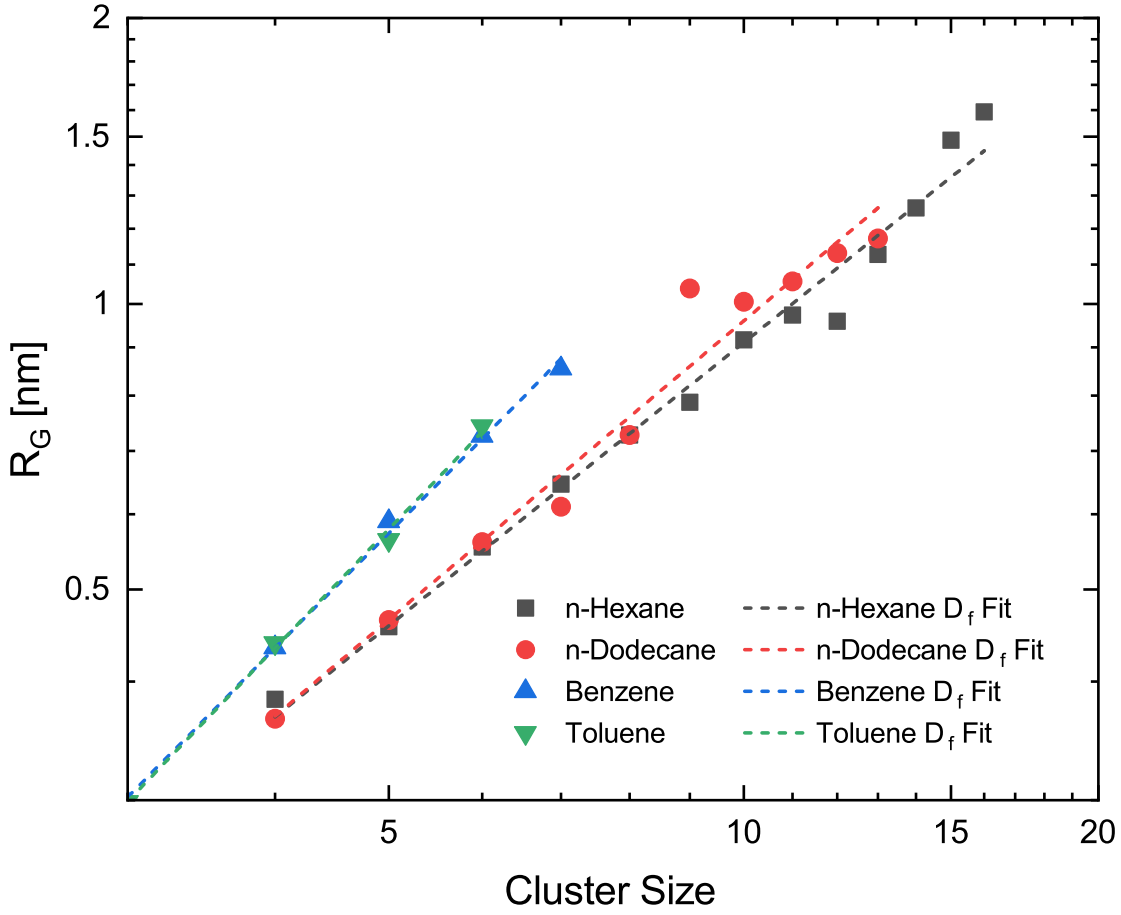


Figure S9: Radius of gyration distribution with fractal fits in various solvents with an 8 Å cutoff.

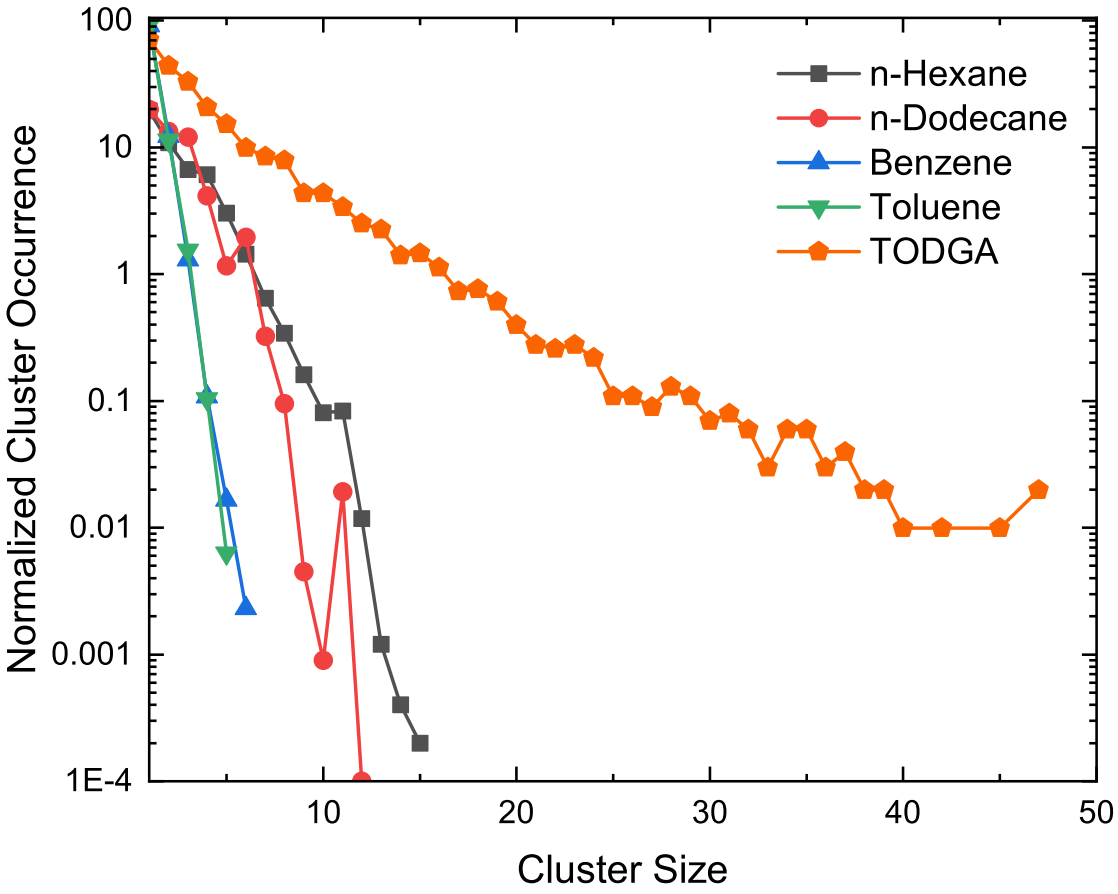


Figure S10: Cluster size distributions of TODGA clusters in various solvents at 200 mM TODGA as well as pure TODGA with 8 Å cutoff.

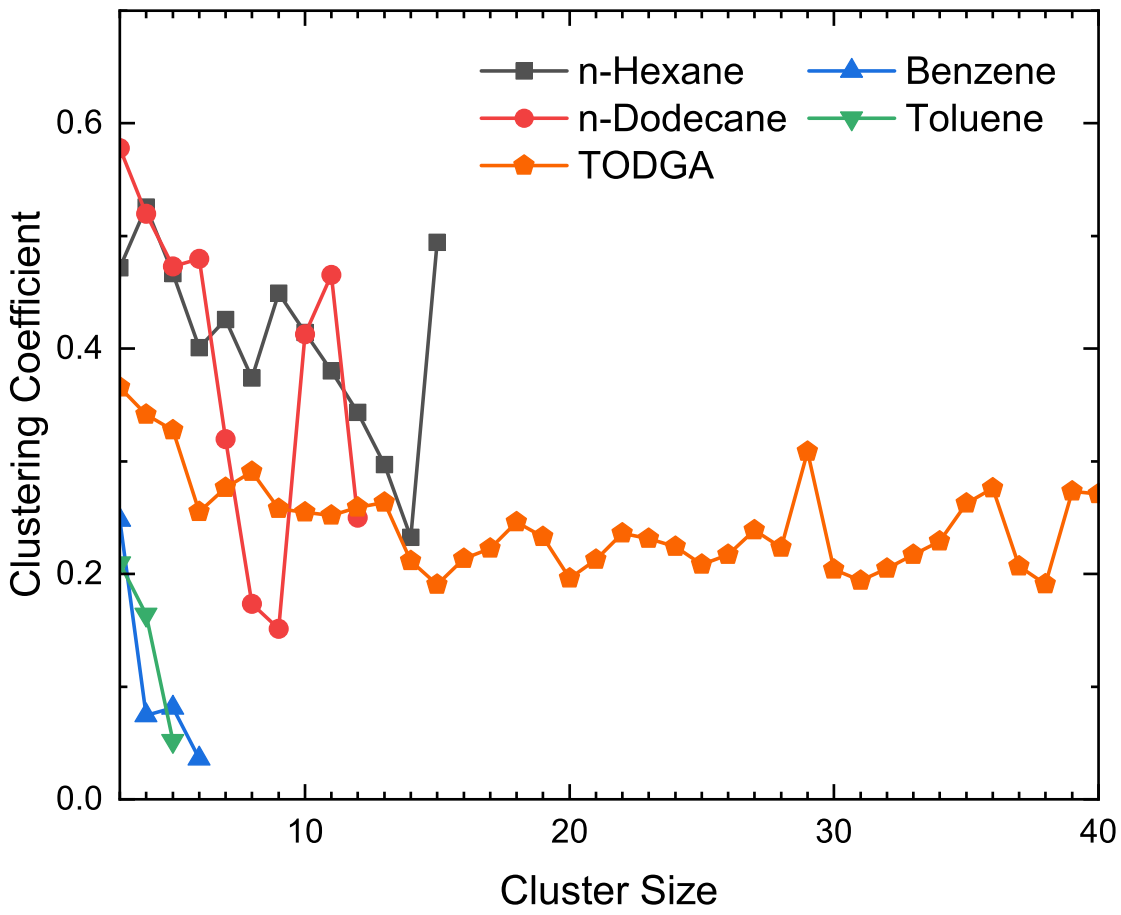
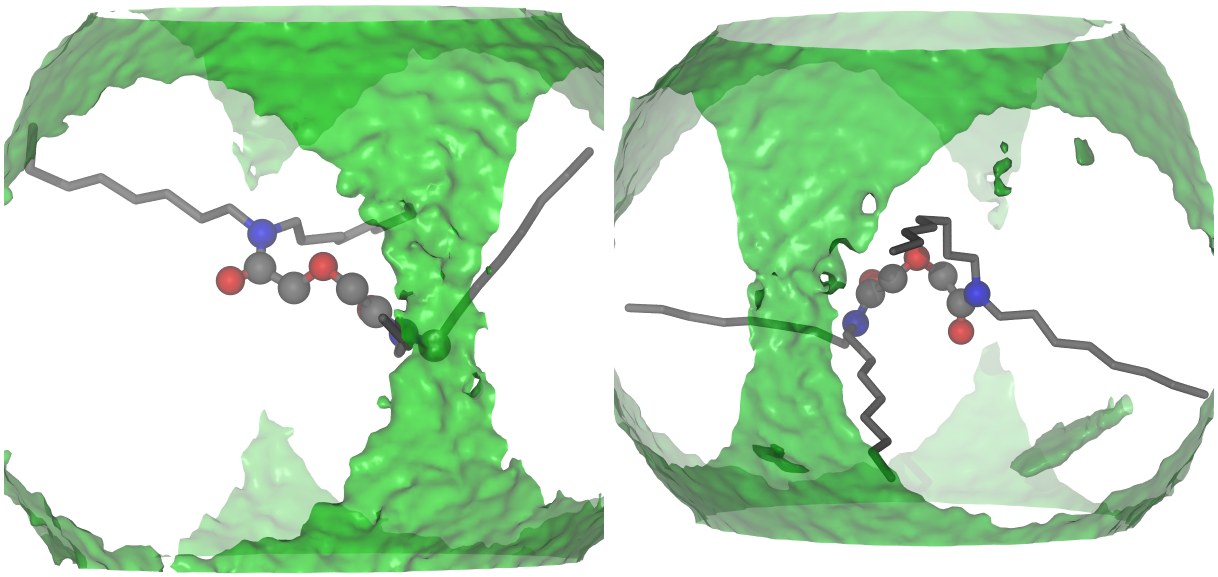


Figure S11: Cluster coefficient distributions of TODGA clusters in various solvents at 200 mM TODGA as well as pure TODGA with 8 Å cutoff.



(a) (b)

Figure S12: Spatial distribution functions (SDFs) of solvent structuring around the central TODGA ether group in n-hexane (a) and n-dodecane (b). The solvent center of mass is use for the observed pair. The green isosurface represents 60% and 90% of the max isodensity for the oxygen – solvent pair in that particular solvent for n-hexane and n-dodecane respectively. n-Dodecane uses an 90% value for clarity.

Table S1: Summary of SDF displayed isodensity value, percent of maximum, and maximum isodensity values for Figures 6, 7, and S12 in counts per nm^3.

Solvent	O–O Displayed Isodensity	O–O Maximum Isodensity	O–C Displayed Isodensity	O–C Maximum Isodensity
n-Hexane	1.496 (25%)	5.984	3.797 (90%)	4.219
n-Dodecane	1.800 (18%)	10.00	2.290 (90%)	2.544
Benzene	0.289 (35%)	0.826	9.500 (65%)	15.83
Toluene	0.254 (35%)	0.726	7.160 (65%)	11.93

Fractal Dimension

A clustering coefficient, given its assessment of triplets, is inherently a local descriptor of clustering behavior. Another descriptor of clusters describes how size relates to mass distribution is the fractal dimension, which is often applied to colloid and aerosol systems.[1–4]

What is useful is that, as the name would suggest, these descriptors are invariant to the scale of the cluster and can feasibly describe small and large-scale clustering shape simultaneously. This fractal dimension, D_f, is a scalar from zero to three ranging from entirely linear to perfectly spherical in shape. Fractal dimension values provide some indication of cluster assembly, though their application to molecular-level systems is less well-defined and under-explored.

The mathematical formula for determining the fractal dimension of clusters in each system is simple, defined as $N = k_0 \left(\frac{R_g}{a}\right)^{D_f}$ where N is the cluster size, k_0 is a proportionality constant of order 1, R_g is the cluster radius of gyration, a is the monomer radius, and D_f is the fractal dimension. Using the graph theoretic approach from earlier to identify clusters, plots of radius of gyration as a function of cluster size can be generated and fit to a linearized version of the previous equation:

$$\log(R_g) = \log(a) + \left(\frac{1}{D_f}\right) \log\left(\frac{N}{k_0}\right) \tag{1}$$

with k_0 set to unity and both D_f and a set as variables for fitting. While a has explicit meaning for colloidal systems, a "monomer radius" of the O_c site analog is less easily assigned. With these given parameters, the fit D_f values of each system is shown in Figure S16 and the fits on a plot of R_g and N in Figures S14 and S13. Looking at Figure S16a, it seems that the linear alkanes and aromatics again fall into two regimes, with hexane and dodecane having a higher fractal dimension than toluene and benzene. Values for all four TODGA in solvent systems are quite low compared to more standard colloidal systems[2] being between 0.95 and 1.3. It is also apparent that with a maximum achieved D_f of roughly 1.4, in 9b these systems are still far away from the percolation threshold value of at least 2.53 for 3D space, something that is also evident from the lack of percolation behavior in Figure 9b.

While these fractal dimension fits appear less applicable than the graph theoretic approach, it is of general interest that TODGA clusters at this low concentration can be

somewhat fit to a power law relationship. Fractal dimension studies of molecular systems typically focus on concentrations of monomer at or near the percolation threshold,[5,6] resulting in study of much higher D_f values. Previous fractal dimension studies have noted that that a power law relationship was not observed until a sufficient monomer concentration was achieved,[7] and similar behavior was seen in these systems where lower cluster sizes had a steeper slope before following a less steep power law for larger cluster sizes, most noticeable for pure TODGA in Figure S15. The extremely low and sub-one dimensionality of the aromatics implies similar issues with reliably fitting a fractal dimension at this concentration in these particular solvents.

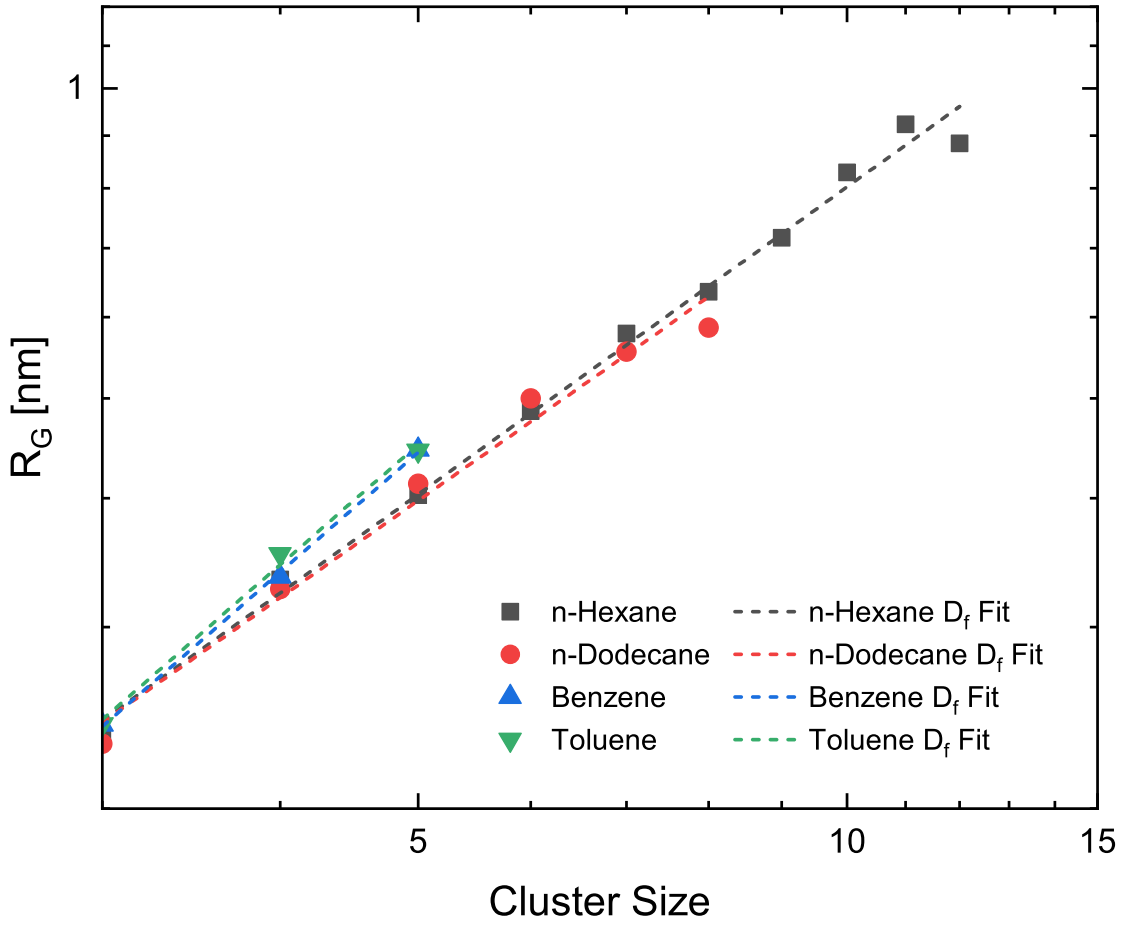


Figure S13: Fractal dimension fitting of TODGA clusters at 200 mM TODGA in various solvents.

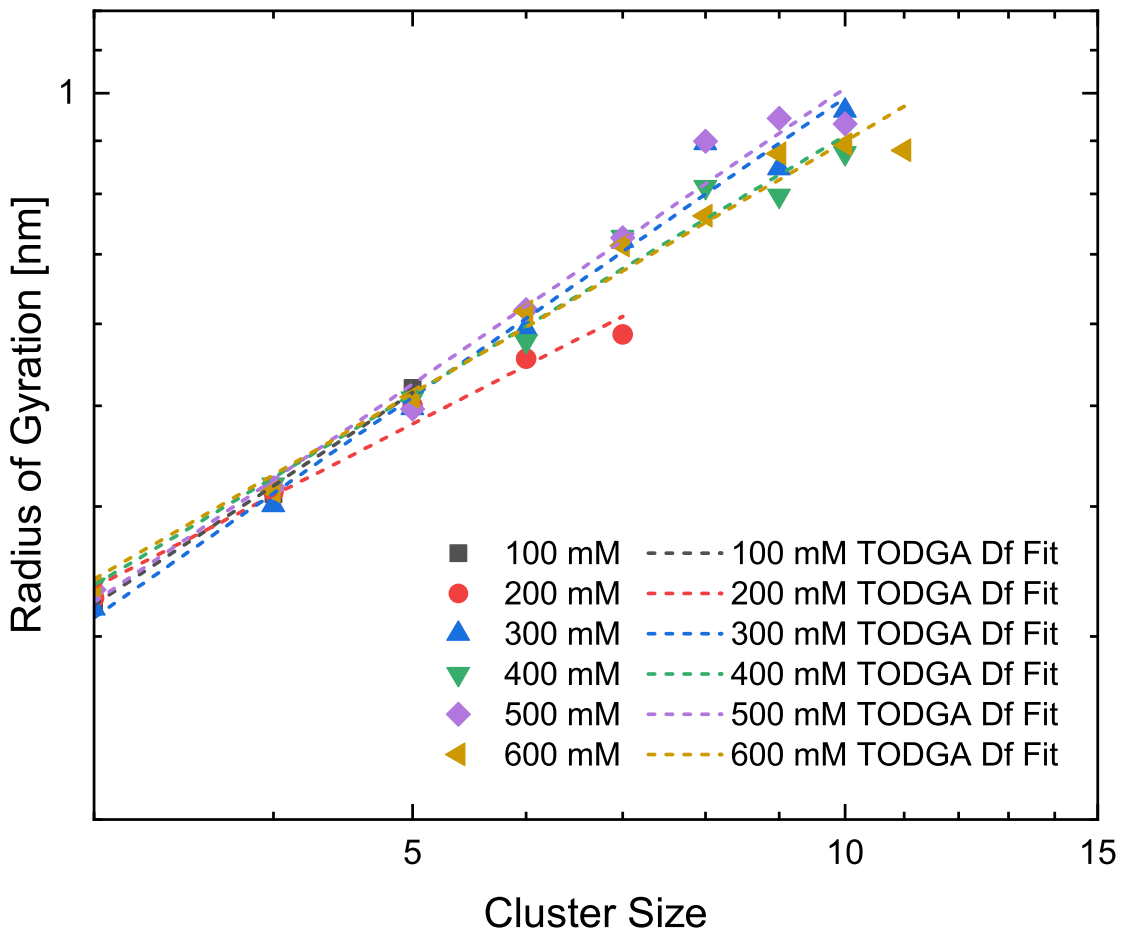


Figure S14: Fractal dimension fitting of TODGA clusters in n-dodecane at various concentrations of TODGA.

The D_f values found for solvent, concentration, and pure TODGA studies show alack of spanning or percolating clusters with a maximum D_f of 1.4 seen in Figures 9b and S10 as well as the tabulated values in Tables S2 and S3. In the limit of pure TODGA, a fit D_f of 1.53, which while larger than all other systems, is still not near the percolation threshold of 2.53, let alone the *lattice animal* threshold of 2 for large, finite clusters.[8,9] This may seem somewhat unintuitive given that the system is pure monomers, but the separation of octyl tails and DGA head group sheds insight on the lack of percolation in pure TODGA. Given a random distribution, of 937 spheres (the number of TODGA molecules) of radius 4 Å (half of the full edge cutoff connecting two points) in a 100 Å box, results in a volume fraction of 0.251. This, at the limit of no overlap, is still less than the approximately 0.29

needed for a percolating system based on overlapping 3D continuum percolation theory.[10–12] Pure TODGA can be understood as DGA solute clusters in an n-octane solvent with a 0.25 molar ratio limit, preventing any percolation with this cluster size definition. Ultimately, the fractal dimension of this system is somewhat unique and difficult to apply as it does not involve monomers on the order of nanometers, but it also is somewhat of an atypical molecular monomer due to the DGA functional group being hindered by the tetraoctyl tails requiring a non-clustering volume. It implies that a certain degree of intelligent descriptor selection is needed to represent this ligand–solvent system, and not just any cluster descriptor methodology can be applied.

Table S2: Fractal dimension fitting and weighted average clustering coefficients (CC) of varied concentrations of TODGA in n-dodecane.

mM TODGA in n-Dodecane	D_f	D_f Fit R^2	ACC
100	1.1363	0.9921	0.415
200	1.0456	0.9623	0.3799
300	0.8349	0.9961	0.3299
400	0.8322	0.9965	0.2651
500	0.8819	0.9951	0.2672
600	0.7557	0.9942	0.DATA

Table S3: Average clustering coefficients and fit fractal dimension of 200 mM TODGA clusters in solvents as well as pure TODGA.

Solvent	D_f	D_f Fit R^2	ACC
n-Hexane	0.9901	0.9810	0.49383
n-Dodecane	1.0456	0.9623	0.50706
Benzene	1.2540	0.9969	0.17991
Toluene	1.2939	0.9963	0.23817
Pure TODGA	0.7295	0.9810	0.31055

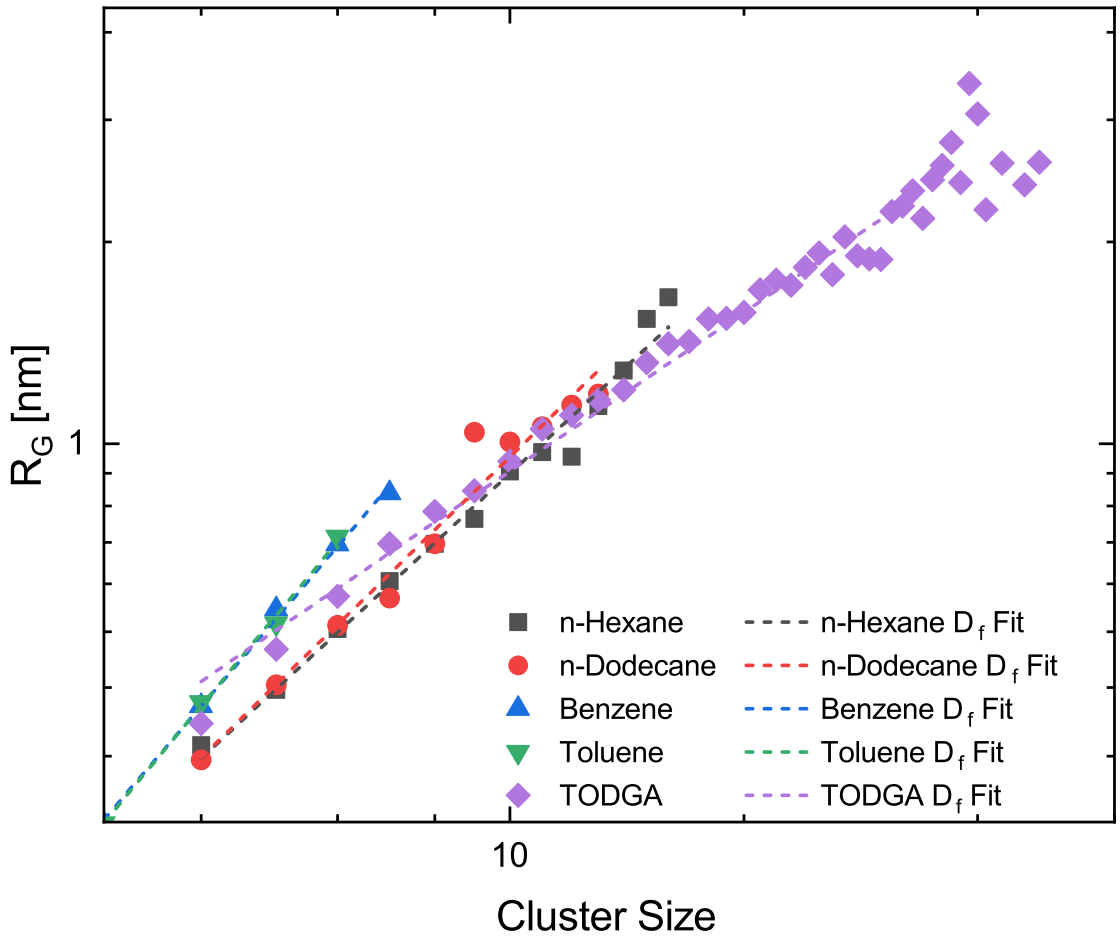
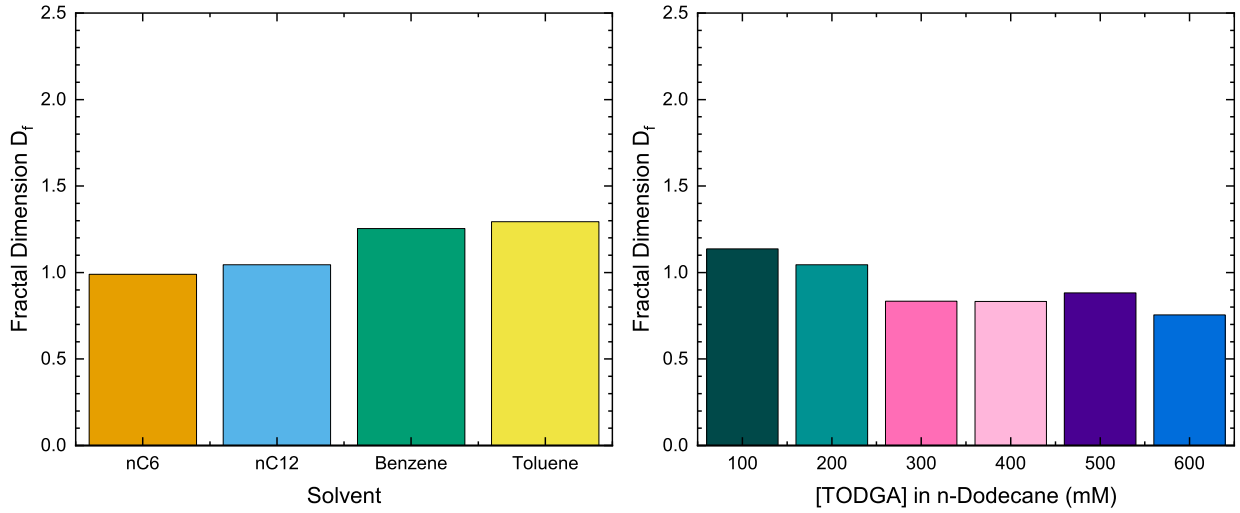


Figure S15: Fractal dimension fitting of TODGA clusters in various solvents at 200 mM TODGA as well as pure TODGA (with an 8 Å cutoff).



(a) (b)

Figure S16: Fit fractal dimensions of TODGA clusters as a solvent effect at 200 mM TODGA (a) and a concentration effect of TODGA in pure n-dodecane (b).

References

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