Supporting Information

Competitive Self-Assembly Driven as a Route To Control the Morphology of Poly(Tannic Acid) Assemblies

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Ⅰ. Results and Discussion

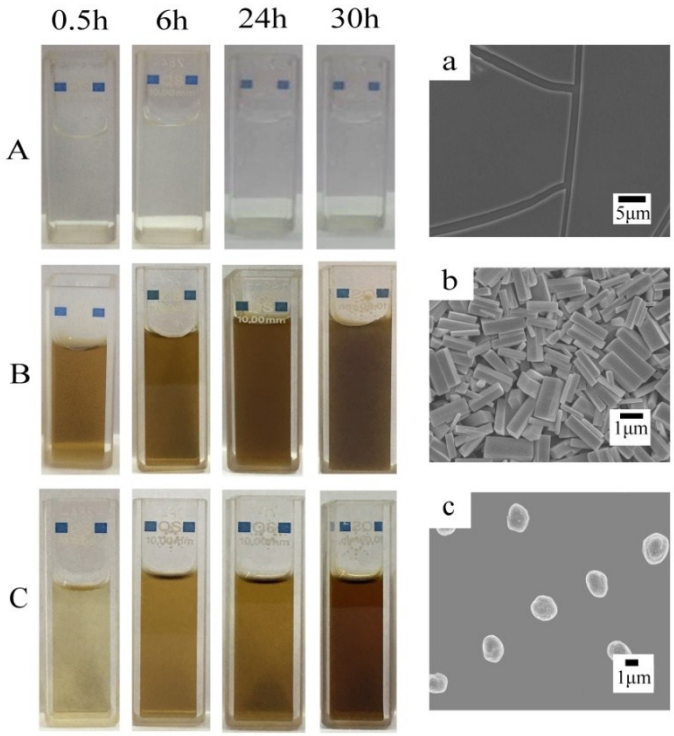

Figure S1. The SEM images of PTA assemblies solution at different reaction conditions. (A, a) 10% V_{IPA}:$V_{IPA+H2O}$, 0 mL NH_4OH (B, b) 10% V_{IPA}:$V_{IPA+H2O}$, 0.75 mL NH_4OH (C, c) 40% V_{IPA}:$V_{IPA+H2O}$, 0.75 mL NH_4OH

Compared Figure S1A, S1B and S1C, when NH_4OH was added into the aqueous IPA solution, the color of TA solutions became dark green from colorless. A readily observable, variable color change emerged for all TA after 0.5 hours of incubation, with further colors intensifying over 6 hours, resulting in light brown coloration of the transparent solutions, beige coloration of the milky PTA suspension, suggesting the different extents of polymerization. Compared SEM images (Figure S1a, S1b and S1c) obtained in different conditions, cuboids and spheres were easily observed after adding NH_4OH. We propose the following mechanism for PTA assembly proceeded: Initially, the self-polymerization of TA species aggregate to higher molecular oligomer species via covalent bond. Over time, the oligomer species began to self-assemble and form cuboids or spheres. (As shown in Scheme 1)

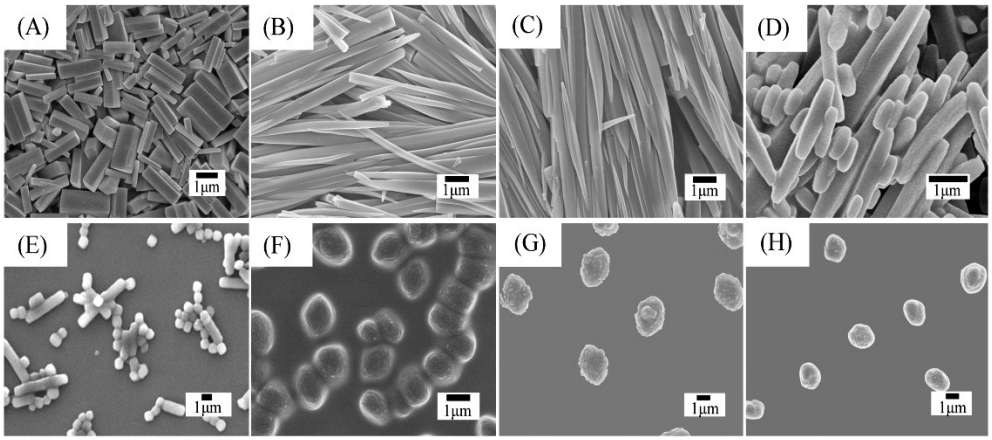

Figure S2. SEM images showing the morphological evolution of PTA assemblies constructed from the reactions of IPA in the presence of various ratios of IPA and H_2O. A: 10% $V_{IPA}/V_{IPA+H2O}$; B:15% $V_{IPA}/V_{IPA+H2O}$; C: 20% $V_{IPA}/V_{IPA+H2O}$ D: 25% $V_{IPA}/V_{IPA+H2O}$; E: 26% $V_{IPA}/V_{IPA+H2O}$; F: 30% $V_{IPA}/V_{IPA+H2O}$; G: 35% $V_{IPA}/V_{IPA+H2O}$; H: 40% $V_{IPA}/V_{IPA+H2O}$.

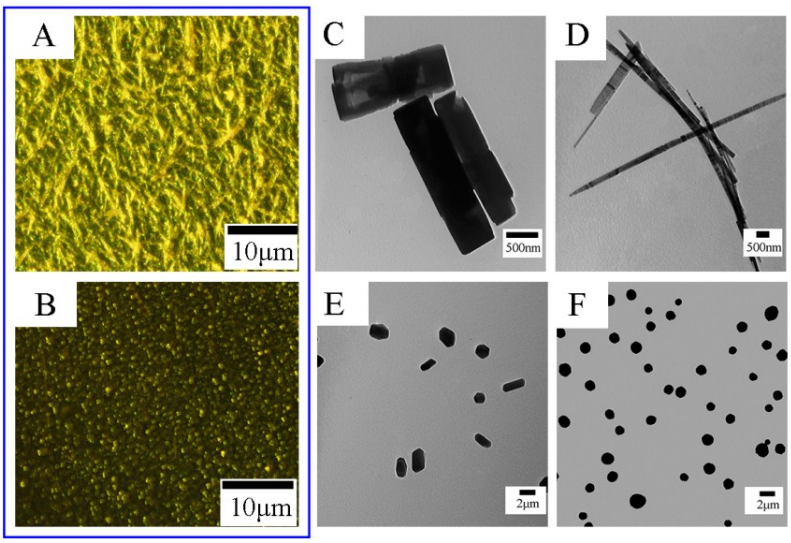

Figure S3. Microscopy images and TEM images showing the morphological evolution of PTA assemblies constructed from the reactions of IPA in the presence of various ratios of IPA and H_2O; (A, C): 10% $V_{IPA}/V_{IPA+H2O}$; D:15% $V_{IPA}/V_{IPA+H2O}$; E: 26% $V_{IPA}/V_{IPA+H2O}$; (B,F): 40% $V_{IPA}/V_{IPA+H2O}$.

Table S1 Hydrogen bond and π-π stacking population for PTA

Sample	Morphology	H-bond population (f1693, C=O, %)	π-π population (f1587, C=C, %)
PTA (10%V_{IPA}:$V_{IPA+H2O}$)	cuboids	0.17	0.49
PTA (26%V_{IPA}:$V_{IPA+H2O}$)	mixed	0.31	0.21
PTA (40%V_{IPA}:$V_{IPA+H2O}$)	spheres	0.33	0.10

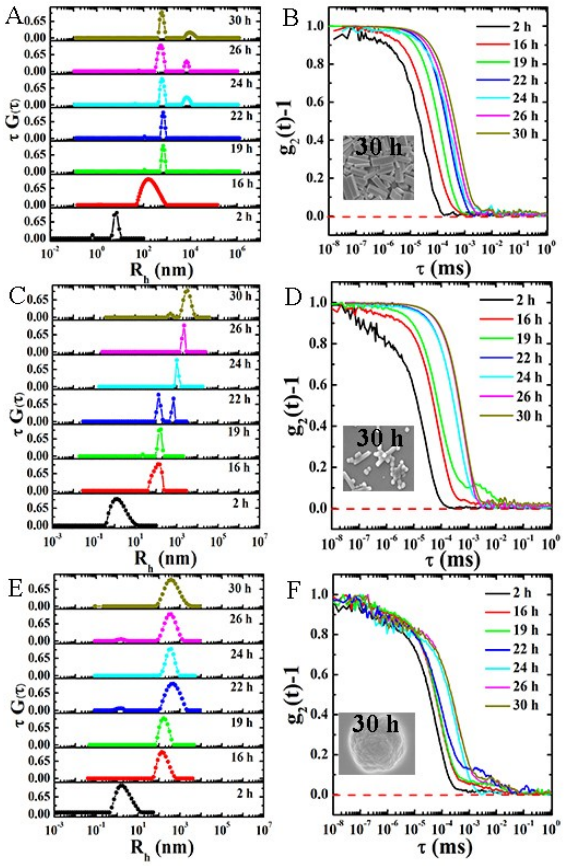

Figure S4. (A, C, E) Size distribution of PTA obtained from DLS measurements at different reaction time; (B, D, F) Time correlation functions of scattering intensity, g2(τ)−1, measured at a different time; The temperature is fixed at T =25 °C; (A, B) 10% (C, D) 26% (E, F) 40% $V_{IPA}/V_{IPA+H2O}$;

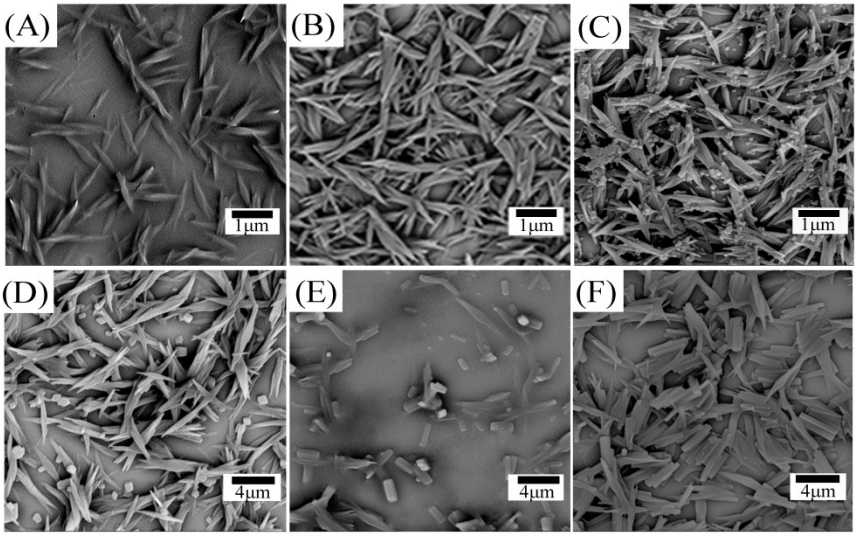

Figure S5. The SEM images of the morphological evolution of PTA (10% V_{IPA}:$V_{IPA+H2O}$) assemblies at different reaction time; A: 16 h, B: 19 h, C: 22 h, D: 24 h, E: 26 h, F: 30 h.

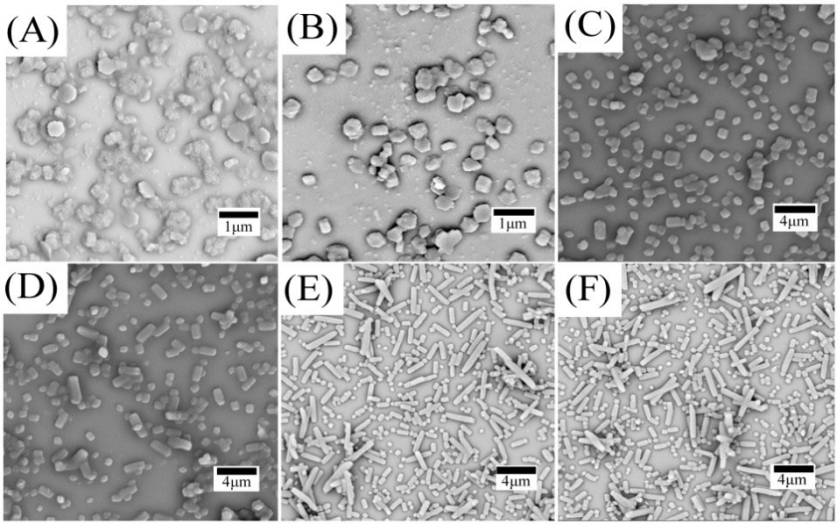

Figure S6. The SEM images of the morphological evolution of PTA assemblies (V_{IPA}:$V_{IPA+H2O}$ = 26%) at different reaction time; A: 16 h, B: 19 h, C: 22 h, D: 24 h, E: 26 h, F: 30 h.

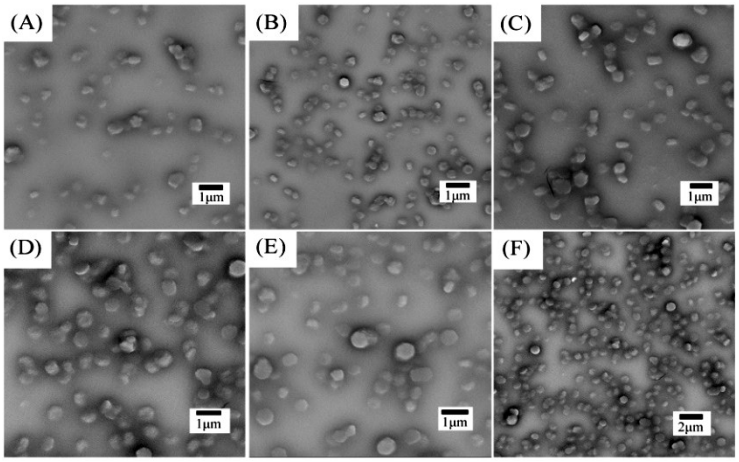

Figure S7. The SEM images of the morphological evolution of PTA assemblies (40% V_{IPA}:$V_{IPA+H2O)}$ at different reaction periods; A: 16 h, B: 19 h, C: 22 h, D: 24 h, E: 26 h, F: 30 h.

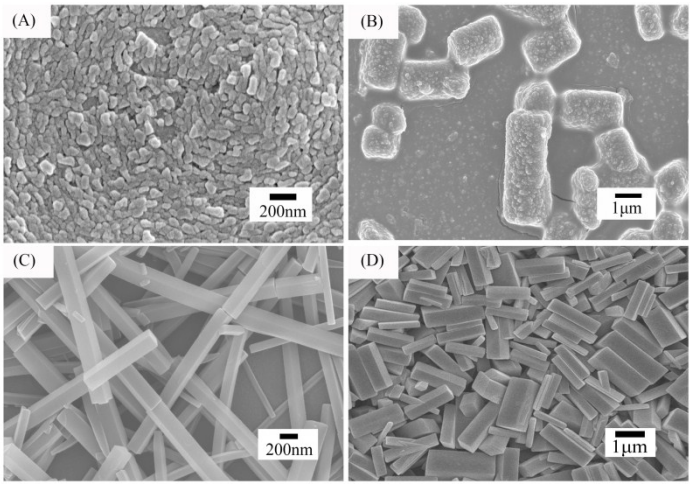

Figure S8. The SEM images of PTA assemblies under various conditions:10% V_{IPA}:$V_{IPA+H2O}$ (A) 1.3 mg mL-1 TA (B) 2 mg mL^{-1} TA (C) 2.7 mg mL-1 TA (D) 3 mg mL^{-1} TA.

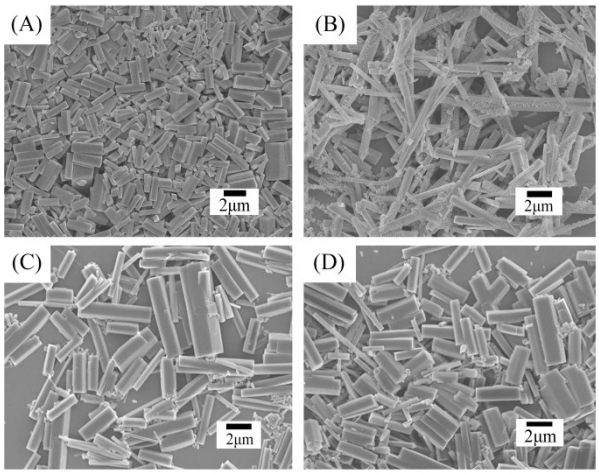

Figure S9. The SEM images of PTA assemblies under various conditions: 10% V_{IPA}: $V_{IPA+H2O}$ (A) pH= 9.8 (B) pH= 9.4 (C) pH= 8.9 (D) pH= 8.0.

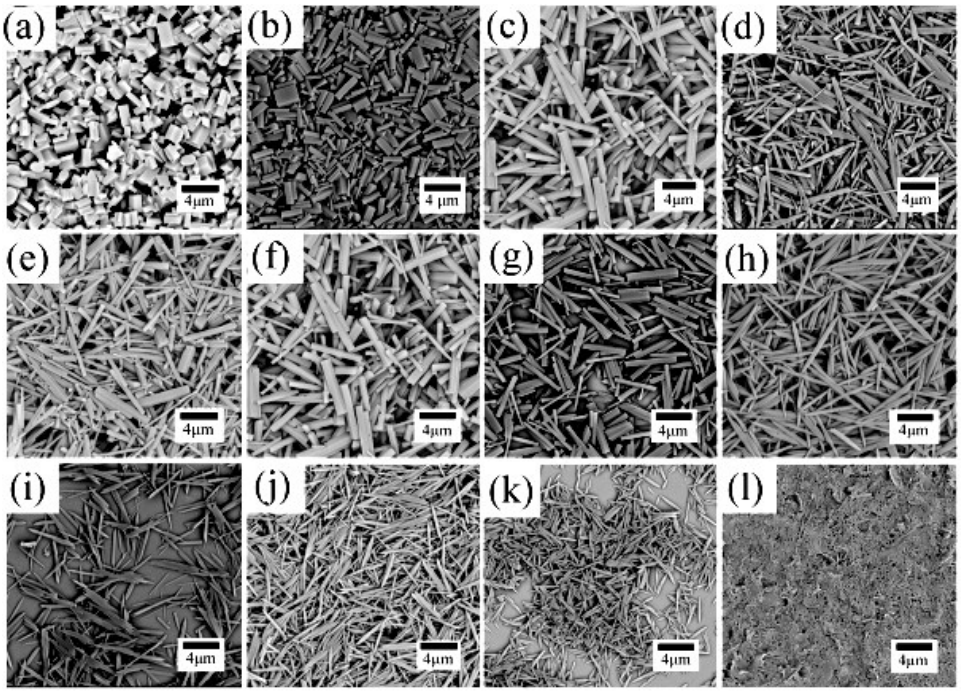

Figure S10. The SEM images of the morphological evolution of PTA assemblies under various conditions; a: 10% V_{MeOH}:$V_{MeOH+H2O}$, b: 15% V_{MeOH}:$V_{MeOH+H2O}$, c: 20% V_{MeOH}:$V_{MeOH+H2O}$, d: 25% V_{MeOH}:$V_{MeOH+H2O}$, e: 30% V_{MeOH}:$V_{MeOH+H2O}$, f: 35% V_{MeOH}:$V_{MeOH+H2O}$, g: 40% V_{MeOH}:$V_{MeOH+H2O}$, h: 45% V_{MeOH}:$V_{MeOH+H2O}$, i: 50% V_{MeOH}:$V_{MeOH+H2O}$, j: 60% V_{MeOH}:$V_{MeOH+H2O}$, k: 70% V_{MeOH}:$V_{MeOH+H2O}$, l: 80% V_{MeOH}:$V_{MeOH+H2O}$.

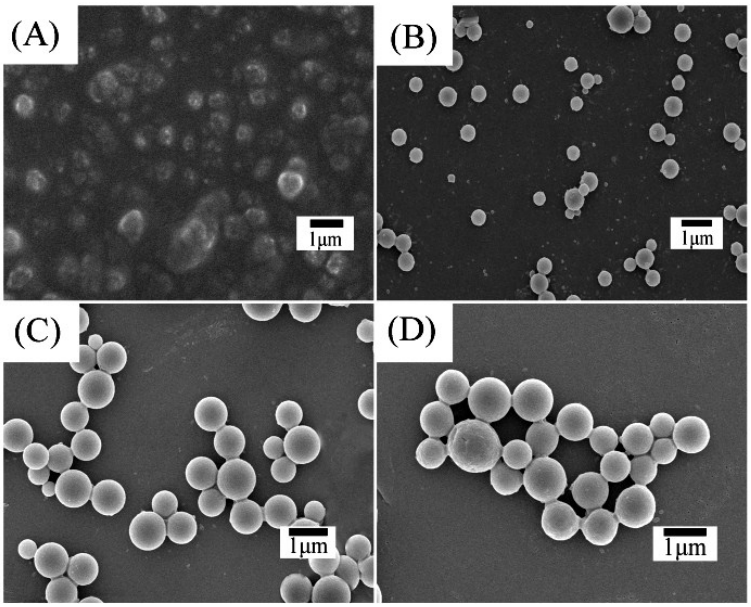

Figure S11. The SEM images of the morphological evolution of PTA assemblies under various conditions; A: 10% $V_{Pyridine}$:$V_{Pyridine+H2O}$, B: 15% $V_{Pyridine}$:$V_{Pyridine+H2O}$, C: 20% $V_{Pyridine}$:$V_{Pyridine+H2O}$, D: 25% $V_{Pyridine}$:$V_{Pyridine+H2O}$.

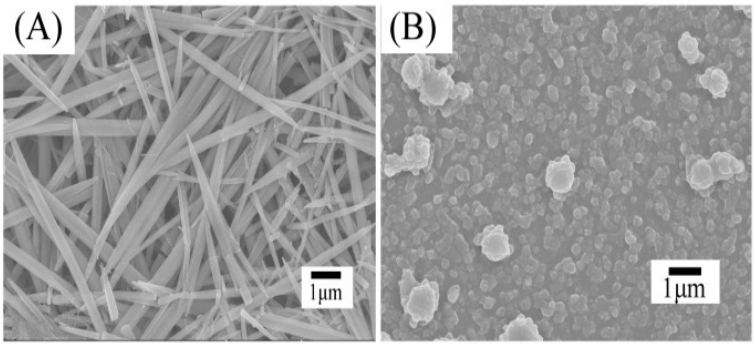

Figure S12. The SEM images of the morphological evolution of PTA assemblies under various conditions; A: 10% V_{THF}:$V_{THF+H2O}$, B: 15% V_{THF}:$V_{THF+H2O}$.

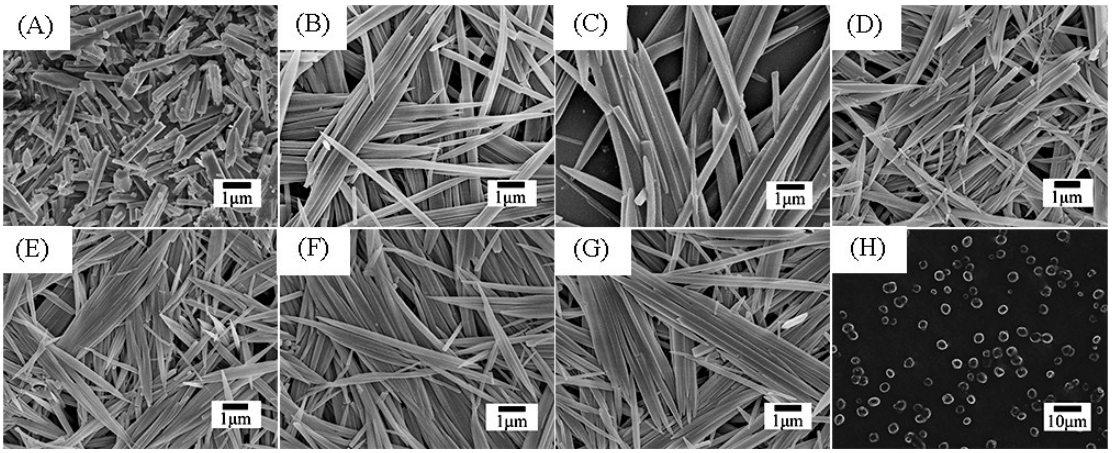

Figure S13. The SEM images of the morphological evolution of PTA assemblies under various conditions: A: 0% V_{EA}:V_{EA+H2O}; B:10% V_{EA}:V_{EA+H2O}; C: 15% V_{EA}:V_{EA+H2O}; D: 20% V_{EA}:V_{EA+H2O}; E: 25% V_{EA}:V_{EA+H2O}; F: 30% V_{EA}:V_{EA+H2O}; G: 35% V_{EA}:V_{EA+H2O}; H:40% V_{EA}:V_{EA+H2O}.

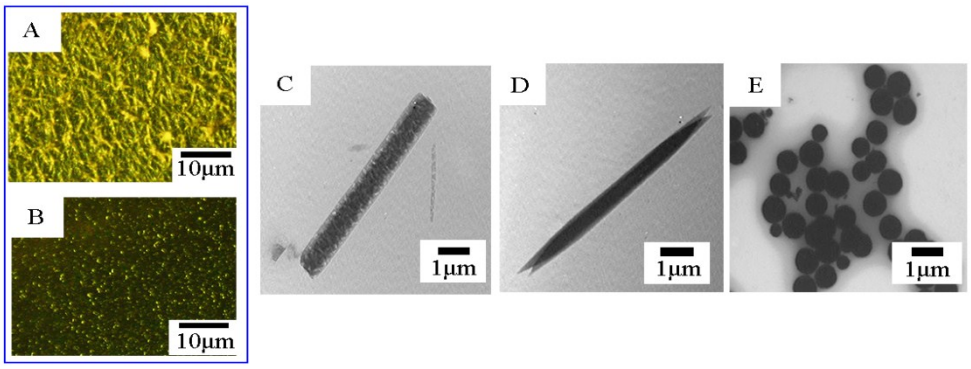

Figure S14. Microscopy images and TEM images showing the morphological evolution of PTA assemblies constructed from the reactions of IPA in the presence of various ratios of IPA and H_2O; (A, C): 10% V_{EA}/V_{EA+H2O}; D:15% V_{EA}/V_{EA+H2O}; (B, E): 40% V_{EA}/V_{EA+H2O};

Apart from IPA, the morphologies of the PTA assemblies can also be easily controlled by the ethanol concentration. Figure S13 and Figure S14 depict the SEM images, microscopy images and TEM of PTA assemblies synthesized by EA. The PTA assemblies fabricated by EA are similar to the one synthesized by IPA. While the volume ratio of ethanol is from 0% to 40%, and the morphologies of the PTA assemblies changed from quadrilateral cuboids to angulated cuboids and finally almost spheres with the ethanol concentration increasing.

Table S2. The thermodynamic parameters for the systems made of water and co-solvents.

Dimers	Δ(*E*+ZPE) / (kJ / mol)	Δ*H* / (kJ / mol)	Δ*G* / (kJ / mol)	*d*(O…H) / Å	*d*(N…H) / Å	Water*
MeOH-H_2O	-13.1	-13.5	12.6	1.91449		A
EtOH-H_2O	-13.4	-13.4	12.7	1.91554		A
IPA-H_2O	-17.7	-16.6	9.3	1.92818		A
Pyr-H_2O	-18.9	-20.3	14.1		1.97904	D
THF-H_2O	-34.4	-32.1	8.8	1.90411		D

* D = proton donor; A = proton acceptor.

As shown in Table S2， the value of ΔG in Table S2 shows an order of THF-H_2O < IPA-H_2O < EtOH-H_2O ≈ MeOH-H_2O < Pyr-H_2O. Based on our argument here, this order should be the order of the co-solvent concentration at which the phase change from cuboid to spherical morphology occurs. Within this frame of rationalization, Pyr-H_2O syste m and MeOH-H_2O systems exhibit exceptions. In the case of Pyr-H_2O system, there are two factors that may lead to the exception. First, compare with other solvents, pyridine has a pK_b of 8.75, which has the strongest ability to alter the pH value of solution. In a way, the concentration dependence in Pyr-H_2O system is at a different pH range from other systems. It, therefore, makes it incomparable with other systems. Second, pyridine itself has potential to form a π-π stacking interaction with the oligomers and consequently interfere with the π-π stacking among oligomers. On the other hand, while the ΔG values for MeOH-H_2O and EA-H_2O are similar, the aggregation is characterized as the cuboid shaped morphology in the entire concentration range in MeOH-H_2O system. Evidently, the solvent-solvent interaction only is inadequate to explain the morphology difference of the aggregates. Moreover, other than the different size, water, MeOH and EA have very different values of dielectric constant (ε_{water} = 78.5, $\varepsilon_{methanol}$ = 32.6, $\varepsilon_{ethanol}$ = 25.3).

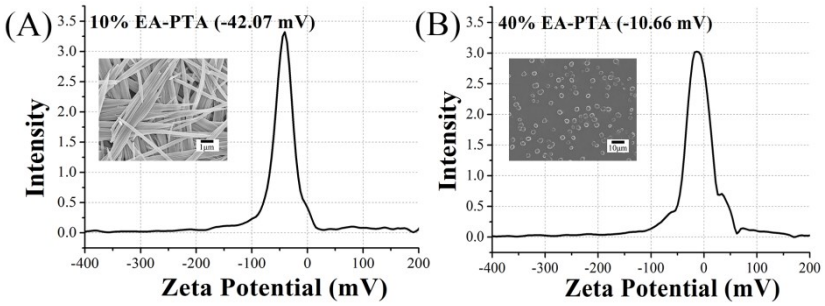

Figure S15. Zeta potential (A-B) of PTA assemblies under different conditions. The zeta potential were tested in aqueous solution; A: 10% V_{EA}: V_{EA+H2O}, B: 40% VEA: V_{EA+H2O}.

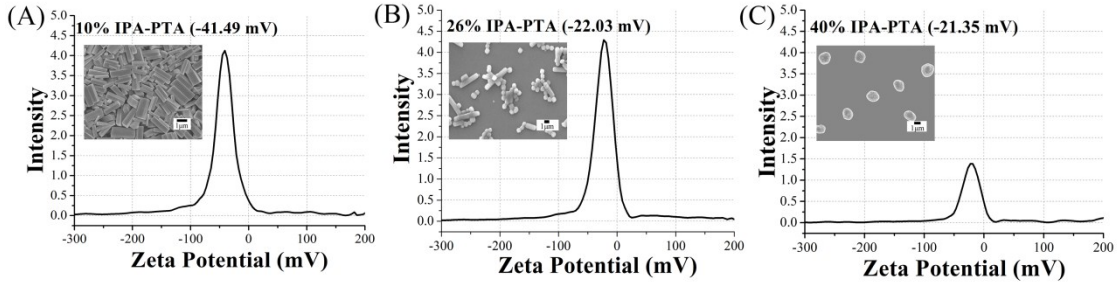

Figure S16. Zeta potential (A-C) of PTA assemblies under different conditions. The zeta potential were tested in aqueous solution; A: 10% V_{IPA}:$V_{IPA+H2O}$, B: 26% V_{IPA}:$V_{IPA+H2O}$, C: 40% V_{IPA}:$V_{IPA+H2O}$.

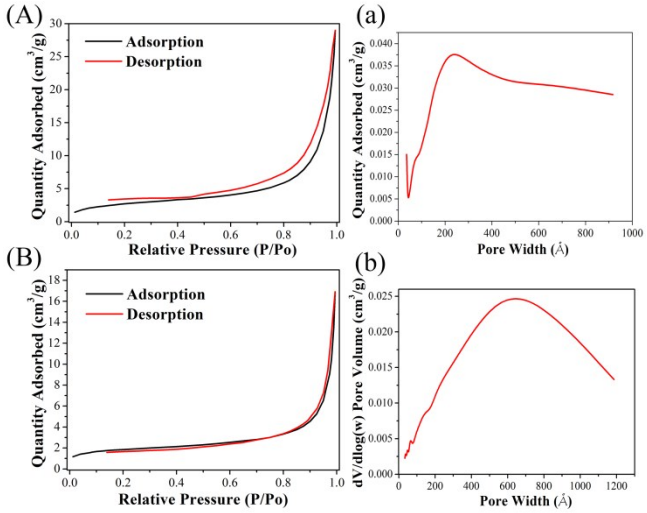

Figure S17. The BET measurement and corresponding surface area for different assemblies; (A, a): 10% V_{EA}:V_{EA+H2O}, BET Surface Area: 9.8247 ± 0.0561 m²/g, BJH Desorption average pore width (4V/A): 186.030 Å. (B, b): 40% V_{EA}:V_{EA+H2O}, BET Surface Area: 6.3047 ± 0.1218 m²/g, BJH Desorption average pore width (4V/A): 283.202 Å.

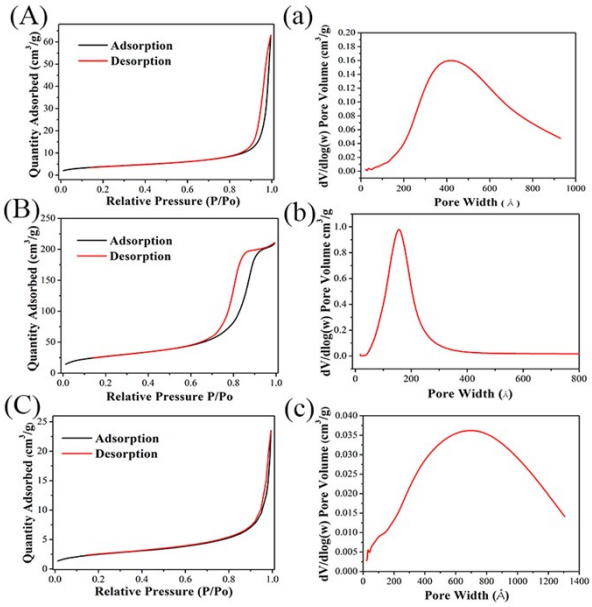

Figure S18. The BET measurement and corresponding surface area for different assemblies; A: 10% V_{IPA}:$V_{IPA+H2O}$, BET Surface Area: 13.9706 ± 0.1665 m²/g, BJH Desorption average pore width (4V/A): 306.964 Å. B: 26% V_{IPA}:$V_{IPA+H2O}$, BET Surface Area: 97.8109 ± 0.6057 m²/g, BJH Desorption average pore width (4V/A): 100.614 Å. C: 40% V_{IPA}:$V_{IPA+H2O}$, BET Surface Area: 9.0074 ± 0.0793 m²/g, BJH Desorption average pore width (4V/A): 219.784 Å.

DGE carries multiple hydroxyl groups, and it is therefore necessary to know the level of deprotonation of DGE. Experiments were carried out to obtain Zeta potential (Figure S15, S16) and BET surface area (Figure S17, S18). Thanks to a simple theoretical model, the derivation of the amount of charge carried by each DGE molecule distributed on the surface was possible. This value

is -1.59 10^{-16} *e* (10% EA-PTA) and -2.30 10^{-16} *e* (10% IPA-PTA) for cuboid morphology and -1.44 10^{-17} *e* (40% EA-PTA) and -4.63 10^{-17} *e* (40% IPA-PTA) for the spherical one. Hence, the TA molecules participating in the self-assembly are likely fully protonated.

We investigated the interaction between fully protonated DGE and solvent. The structure of DGE is strongly affected by the polarity of the solvent; in specific, the more polar the solvent, the greater the dihedral angle between the two moieties. This implies a large contribution to the internal organization energy upon the solvation process. Since DGE contains many functional groups that likely interact with water molecules (*viz.* -OH and C=O), the molecule was found more stable in aqueous solution rather than in any other binary mixture of solvents at different composition. The energetic results prepare the ground for the calculations of dimers. Meanwhile it is essential to confirm that DGE is a good representative of PTA, as shown by the comparison computed and experimental IR spectra (Figure S19).

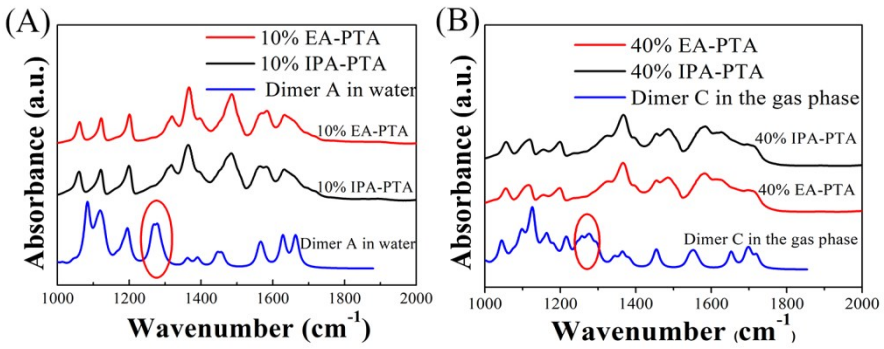

Figure S19. Comparison of IR absorbance in the wavenumber range from 1000 cm^{-1} to 2000 cm^{-1}. (A): The calculated IR spectrum for dimer A in water and FT-IR spectrum where a typical cuboid morphology was observed; (B): The calculated IR spectrum for dimer C in the gas phase and FT-IR spectrum where a typical spherical morphology was observed;

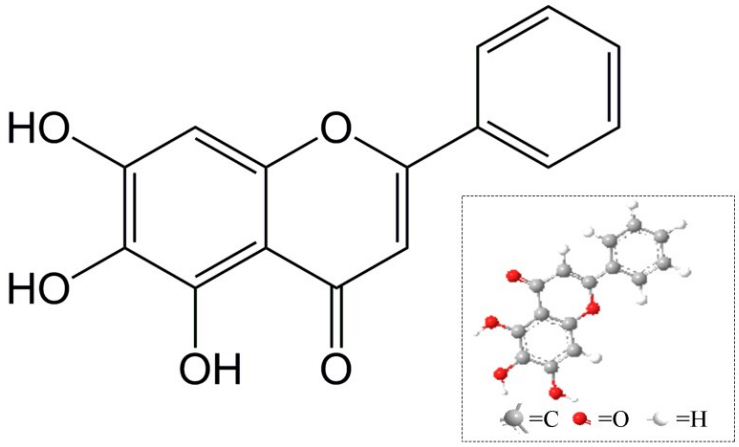

Figure S20. The molecular structure of Baicalein

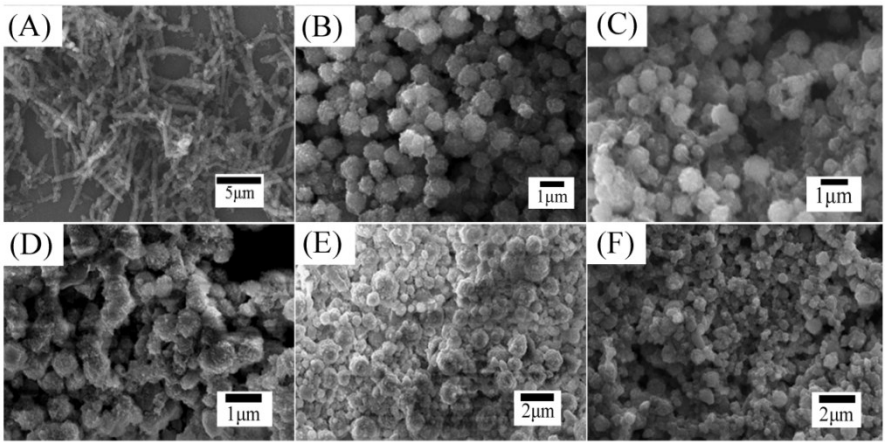

Figure S21. The SEM images of the morphological evolution of Poly(Baicalein) assemblies under various conditions; A: 10% V_{IPA}:$V_{IPA+H2O}$; B: 15% V_{IPA}:$V_{IPA+H2O}$; C: 20% V_{IPA}:$V_{IPA+H2O}$; D: 25% V_{IPA}:$V_{IPA+H2O}$; E: 30% V_{IPA}:$V_{IPA+H2O}$; F: 40% V_{IPA}:$V_{IPA+H2O}$.

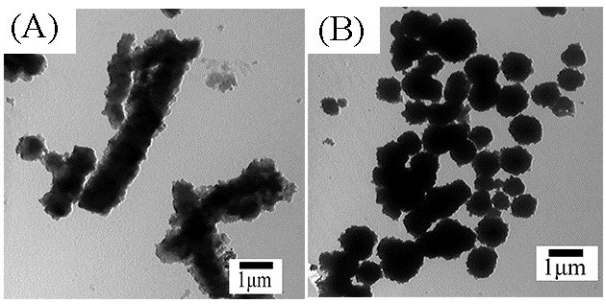

Figure S22. The TEM images of the morphological evolution of Poly(Baicalein) assemblies under various conditions; A: 10% V_{IPA}:$V_{IPA+H2O}$; B: 15% V_{IPA}:V_{IPA}.

II. Theory and Computation

A Surface Charge Density and Molecular Deprotonation Degree

The nonlinear homogeneous Poisson-Boltzmann equation (PBE) can be written in polar coordinates as follows:

$$\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2}\right)\Psi+\frac{4\pi qnN}{\varepsilon}e^{-\frac{q\Psi}{kT}}=0 \quad . \qquad \textbf{(A.1)}$$

where $n\equiv\int_\Omega d\tau e^{-q\Psi/kT}$ indicates the normalization factor, wherein the integration is over the volume of the electrolyte under consideration Ω, N indicates the number of free ions with charge q per unit axial length. In order to make it easier to solve, we may introduce auxiliary variables:

$$\lambda_D\equiv q^2/kT\,, \qquad f_D\equiv\sqrt{\frac{4\pi nN}{\varepsilon}\lambda_D}\,,$$

$$\text{‰}\equiv\rho f_D\,, \qquad \xi\equiv\ln\text{‰}, \qquad \Psi\text{‰}\equiv-\frac{q\Psi}{kT}+2\xi\,. \qquad \textbf{(A.2)}$$

Now eq. (A.1) reads:

$$\frac{\partial^2\Psi\text{‰}}{\partial\xi^2}+\frac{\partial^2\Psi\text{‰}}{\partial\varphi^2}=e^{\Psi\text{‰}} \quad . \qquad \textbf{(A.3)}$$

Using Bäcklund's transformation, the solutions of eq. **(A.3)** may be expressed through arbitrary harmonic functions, $Y(x,\varphi)$:

$$\Psi\text{‰}=\ln\left[2\frac{\left(\frac{\partial Y}{\partial\xi}\right)^2+\left(\frac{\partial Y}{\partial\varphi}\right)^2}{Y^2}\right], \qquad \textbf{(A.4)}$$

and thus for the electric potential solution of the PBE we get:

$$\Psi=-\frac{kT}{q}\ln\left[2\frac{\left(\rho\text{‰}\frac{\partial Y}{\partial\text{‰}}\right)^2+\left(\frac{\partial Y}{\partial\varphi}\right)^2}{\rho\text{‰}Y^2}\right]. \qquad \textbf{(A.5)}$$

Assuming the thermal and chemical equilibria are reached, we can easily demonstrate that the surface charge density, σ, is related to the charge density difference of each ion, $\Delta\varrho_i\equiv\varrho_{0i}-\varrho_{\infty i}$:

$$\sigma^2=2\varepsilon_0\varepsilon k_BT\sum_i\Delta\varrho_i \quad , \qquad \textbf{(A.6)}$$

where ε_0 indicates the vacuum permittivity, ε the absolute permittivity of the medium (solution, in our case), k_B the Boltzmann constant, and T the absolute temperature. By using the conditions of electroneutrality for the system, σ can be related to the zero-potential, ψ_0:

$$\sigma=\sqrt{8c_0\varepsilon_0\varepsilon k_BT}\sinh\left(\frac{ze\psi_0}{2k_BT}\right), \qquad \textbf{(A.7)}$$

where c_0 indicates the concentration per unit volume, and ze the charge. In Table SA1, we show the values of σ computed for 10% and 40% solutions (EA and IPA as co-solvents). The value of absolute permittivity of the solvents' mixtures, ε_m, was computed by means of the

parameterization described in ref.[1] (Table SA2 and Figure SA1). We observe that the value of surface charge density is about the same for the two co-solvents (EA and IPA) when the rod-shape aggregation (10% co-solvent) occurs and that (in absolute value) it is larger than the corresponding values for the sphere-shape aggregation (40% co-solvent). In the latter cases, the value of σ is different for the two co-solvents (the value measured in EA is about one half of the value measured in IPA).

In order to estimate the amount of charge carried by each DGE molecule located on the surface of the aggregate (and thus to know the level of de-protonation), we used two approaches. By using the experimental average values for the size of the aggregate particles (as obtained from SEM images), we may readily estimate the value of the surface of the particle, S_{part}, and its volume, V_{part}. On the other hand, the BET volume was also experimentally measured, S_{BET}. We observe that S_{BET} is smaller than the geometrical values.

The volume occupied by a single DGE molecule was estimated from the QM calculations, $V_{mol} \sim 2.85 \times 10^{-28}$ m^3. Assuming that each DGE molecule is inserted in a sphere and that these spheres are arranged in hcp packing to form the particle, we can estimate the number of DGE molecules forming each particle and the number of DGE molecules laying on the surface of the particle. Since each PTA molecule is formed of four DGE units, we can estimate the number of PTA molecules on the surface of the particle.

Combining these values with the previous, we can readily calculate the total charge carried by each particle (Q_{tot}) and per molecule (q). From the computed values we conclude that the degree of deprotonation of PTA is practically null.

From the zero-potential it is also possible to calculate the interaction constant:

$$Z = 64\pi\varepsilon_0\varepsilon(k_BT/e)^2 tanh^2\left(\frac{ze\psi_0}{4k_BT}\right). \quad \textbf{(A.8)}$$

This can be used to estimate the classical interaction energy, E, between two macroscopic objects close in distance to each other. For example, for two spheres of radii R_1 and R_2 whose surfaces are distant d,

$$E = (\frac{1}{R_1} + \frac{1}{R_2})^{-1} Ze^{-d/\lambda_D}, \quad \textbf{(A.9)}$$

where λ_D indicates the Debye length; for two cylinders of radii R_1 and R_2 (values per unit length) whose surfaces are distant d,

$$E = [2\pi\lambda_D(\frac{1}{R_1} + \frac{1}{R_2})]^{-1/2} Ze^{-d/\lambda_D}, \quad \textbf{(A.10 a)}$$ or

$$E = \sqrt{R_1R_2}Ze^{-d/\lambda_D}, \quad \textbf{(A.10 b)}$$

in the case the two cylinders have parallel or perpendicular axes, respectively.

Table SA1. Values of dielectric constant of the solvents' mixtures (ε_m), experimental zero-point potential (ψ_0), interaction constant (Z), surface charge density (σ), surface of the particle calculated using elementary geometry (S_{part}) and measured by BET (S_{BET}), volume of the particle (V_{part}), number of DGE and PTA molecules, total charge (Q_{tot}), and charge per molecule (q).

Component	-	Unit	EA		IPA	
-	-	-	10%	40%	10%	40%
-	-	-	Rod	Sphere	Rod	Sphere
ε_m			56.0840	21.1719	59.3728	25.6672
ψ_0		eV	-4.21E-02	-1.07E-02	-4.15E-02	-2.14E-02
Z		N	9.93E-12	2.66E-13	1.03E-11	1.27E-12
σ		C/m^2	-3.68E-15	-5.18E-16	-3.72E-15	-1.17E-15
S_{part}		m^2	1.19E-10	7.07E-12	1.19E-10	7.07E-12
S_{BET}		m^2/g	9.80	6.30	14.0	9.00
		m^2	3.71E-12	1.43E-13	5.30E-12	2.04E-13
V_{part}		m^3	2.95E-17	1.77E-18	2.95E-17	1.77E-18
#(DGE)			7.65E+10	4.59E+09	7.65E+10	4.59E+09
#(DGE)@Surf			5.36E+08	3.21E+07	5.36E+08	3.21E+07
#(PTA)@Surf			1.34E+08	8.04E+06	1.34E+08	8.04E+06
Q_{tot}	using S_{part}	*e*	-2.74E-06	-2.29E-08	-2.78E-06	-5.15E-08
q per molecule		*e*	-5.12E-15	-7.11E-16	-5.18E-15	-1.60E-15
Q_{tot}	using S_{BET}	*e*	-8.52E-08	-4.63E-10	-1.23E-07	-1.49E-09
q per molecule		*e*	-1.59E-16	-1.44E-17	-2.30E-16	-4.63E-17

Table SA2. Values of mean dielectric constant, ε_m, for different ratios of co-solvent : water = x : (1 – x) mixtures, at T = 298.15 K.

	x	0.00	0.10	0.15	0.20	0.25	0.30
water +	THF	78.300	55.1254	46.3549	39.1218	33.1840	28.3239
	i-PrOH	78.300	59.3728	51.0181	43.7910	37.7320	32.7737
	EA	78.300	56.0840	47.3173	39.9542	33.8277	28.7636
	MeOH	78.300	56.7341	48.1068	40.7536	34.5289	29.2859
	x	0.35	0.40	0.45	0.50	0.75	1.00
water +	THF	24.3521	21.1079	18.4570	16.2888	10.0481	7.5200
	i-PrOH	28.7970	25.6672	23.2545	21.4442	18.56822	20.1800
	EA	24.5952	21.1719	18.3621	16.0535	9.254846	6.0814
	MeOH	24.8845	21.1970	18.1095	15.5232	7.569782	3.9000

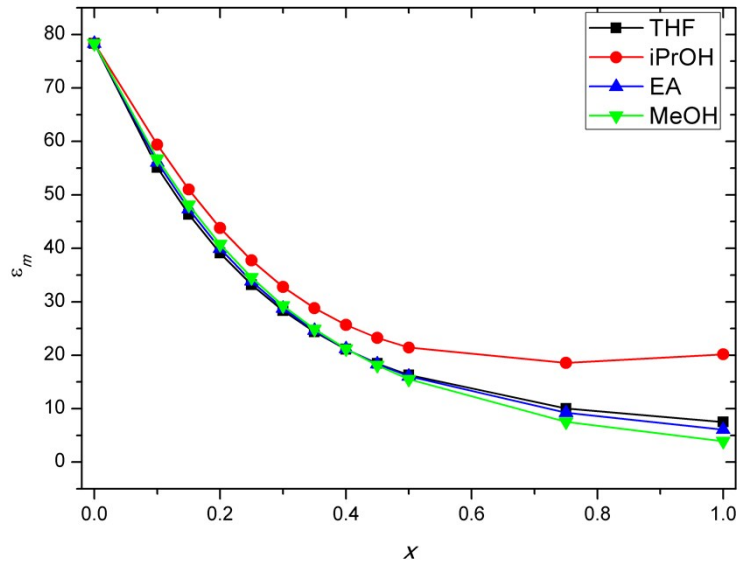

Figure SA1. Plot of values of mean dielectric constant, εm, as a function of the co-solvent's molar fraction x in water mixtures, at T = 298.15 K.

B Quantum Mechanical Calculations

In this Session we shall describe the computational details about the quantum mechanical (QM) calculations performed for this work. As hinted in the main text, PTA is too big and flexible to allow the performance of high level QM calculations. We therefore considered DGE as a valid model to describe it, assuming that the central moiety of sugar in PTA works just as a linker for the four DGE sub-units.

This Session is organized in five sub-parts, concerning the description of methods used for co-solvents and their dimers with water (B.1), DGE (and its interaction with water; B.2), DGE dimers (B.3), and some other technical detail and the codes used (B.4), followed by the collection of the most meaningful results (B.5).

B.1 Co-Solvents and Their Dimers with Water

The ground state optimized geometry and thermochemicals of single molecules of water and co-solvents (*viz.*, methanol, ethanol, iso-propanol, formaldehyde, tetrahydrofuran, and pyridine) were computed at Gaussian-4[2] level of theory. For each co-solvent, different possible dimers with a molecule of water, wherein water may play the role of proton donor or acceptor, were built and optimized at the same level of theory. Thermochemicals for dimers were computed as well.

In order to investigate the type of intermolecular interactions existing between dimers, we performed two types of analysis, by mean of the Bader Atoms in Molecules (AIM) theory of bonding, based on electron density[3], and the Non-Covalent Interaction (NCI) Index[4, 5], as a more general description of intramolecular interactions based on density changes.

B.2 DGE

DGE may undergo both rotameric and deprotonation equilibria. In this study we shall limit ourselves accounting for only one of the four stable rotamers. Moreover, it will be considered in its fully protonated (neutral) form; the latter choice is justified on the basis of results shown in Session A. Concerning the choice of the rotamer, an extensive investigation has been carried out and will be object of a dedicated work.

The molecular geometry of DGE was fully optimised both in the gas phase and in solution at Density Functional Theory (DFT) level. The vibrational frequencies and thermochemicals were computed in harmonic approximation at T = 298.15 K and p = 1 atm, and no imaginary frequencies were found.

The calculations were performed by using B3LYP[6] and M06-2X[7] DFT functionals. In the case of B3LYP, the D3 version of Grimme's dispersion with Becke-Johnson damping was included[8]. Two types of basis sets were employed in combination with each method, *viz.* 6-31++G** and 6-311++G**[9-12].

For both water and all co-solvents, solvent effects were taken into account via the implicit polarizable continuum model in its integral equation formalism (IEF-PCM)[13]. In case of water, in order to include the specific effects of H-bonding, an explicit micro solvation with 11 molecules of solvent surrounding DGE, additionally embedded by the continuum model, was also considered. The PCM molecular cavity was built according to the SMD parameterization[14] radii within the value used in the last implementation of the PCM (based on a continuum surface charge formalism). The standard values for dielectric constants and refractive indexes were always assumed in case of calculations in pure solvents. Calculations were also run considering water/co-solvent mixtures; in these cases, the values reported in Table SA2 were used for the dielectric constant of the medium.

B.3 DGE Dimers

In order to evaluate the importance of inter-molecular interactions (*viz.* H-bonding and π-π stacking), four different models of DGE dimers were built (see main text). The optimized geometries of DGE dimers was computed at the same levels of theory used for DGE single molecules. The vibrational frequencies and thermochemicals were computed in harmonic approximation at T = 298.15 K and p = 1 atm, and no imaginary frequencies were found. Calculations were performed in the gas phase and in implicit IEF-PCM (SMD) water solution. The topological AIM and NIC analyses were also performed for DGE dimers.

B.4 Other Details and Used Codes

Integration grid for the electronic density topological and RDG analyses was set to 150 radial shells and 974 angular points. In other cases, integration grid was set as 99 radial shells and 590 angular points. Convergence criteria of Self-Consistent Field were set to 10^{-12} for root mean square (RMS) change in density matrix and 10^{-10} for maximum change in density matrix. Convergence criteria for optimizations were set to 2×10^{-6} a.u. for maximum force, 1×10^{-6} a.u. for RMS force, 6×10^{-6} a.u. for maximum displacement and 4×10^{-6} a.u. for RMS displacement.

All calculations were performed using GAUSSIAN G09.D01 package[15]. The topological AIM analysis with the location of BCPs and subsequent calculation of SF values were performed using a modified version of the PROAIMV program[16]. The Non-Covalent Interactions analysis was performed using a homemade code.

B.5 QM Results

B.5.1 Optimised geometries

water

8	-0.021743	0.000000	-0.015367
1	0.026700	0.000000	0.945286
1	0.899979	0.000000	-0.290374

methanol

8	-0.010735	0.050838	-0.011927
1	-0.013461	-0.059466	0.942993
6	1.334365	0.008393	-0.449789
1	1.320084	0.135425	-1.535741
1	1.946985	0.816086	-0.021872
1	1.824435	-0.951276	-0.226997

ethanol

8	0.100132	0.433785	0.034075
1	0.076342	0.249285	0.977414
6	1.314687	-0.085790	-0.488595
1	2.186966	0.375378	0.002314
1	1.385576	-1.172672	-0.320822
6	1.345860	0.209300	-1.979250
1	1.293884	1.287647	-2.155449
1	2.266843	-0.173877	-2.428857
1	0.492662	-0.259122	-2.478476

i-propanol

6	0.008126	0.014100	-0.014472
1	0.005447	0.009721	1.085460
6	1.456771	-0.015810	-0.500245
1	1.968612	-0.908926	-0.130289
1	1.484090	-0.038930	-1.594626
1	2.007557	0.867134	-0.159464
6	-0.742186	1.253543	-0.500541
1	-0.775643	1.265509	-1.594930
1	-1.771644	1.250145	-0.130798
1	-0.253132	2.172120	-0.159766
8	-0.665355	-1.152721	-0.503494
1	-0.964469	-1.670689	0.246194

pyridine

7	0.036090	0.000000	-0.008863
6	0.033030	0.000000	1.327106

6	1.189145	0.000000	2.103709
6	2.421278	0.000000	1.457628
6	1.226780	0.000000	-0.614536
6	2.441761	0.000000	0.066664
1	3.345556	0.000000	2.026200
1	-0.945645	0.000000	1.801951
1	1.120349	0.000000	3.185985
1	1.208992	0.000000	-1.702151
1	3.376729	0.000000	-0.482804

formaldehyde

6	-0.067517	0.000000	0.032018
8	-0.017851	0.000000	1.240227
1	0.833846	0.000000	-0.614956
7	-1.211887	0.000000	-0.702723
1	-2.101019	0.000000	-0.228648
1	-1.194122	0.000000	-1.707518

[methanol+water] – dimer A

8	0.337135	0.144397	0.483706
1	0.753613	-0.277707	1.240071
6	1.236788	0.097022	-0.620854
1	0.649809	0.356381	-1.503751
1	2.060151	0.814105	-0.504492
1	1.655647	-0.906172	-0.770836
1	-1.329145	-0.313516	-0.359738
8	-1.955425	-0.380117	-1.096855
1	-2.415173	0.464197	-1.078780

[methanol+water] – dimer B

8	0.006826	-0.066648	0.002738
1	0.013958	-0.116300	0.970591
6	1.343149	0.009240	-0.436584
1	1.330801	0.064257	-1.530050
1	1.868905	0.902941	-0.063308
1	1.940099	-0.872763	-0.153458
8	-0.218147	-0.221844	2.868026
1	-0.822770	0.510092	3.032504
1	-0.767604	-1.008575	2.954670

[methanol+water] – dimer C

8	-0.003851	0.037584	0.023539
1	0.017595	-0.023766	0.982433
6	1.334033	0.012636	-0.467630

1	1.281552	0.326060	-1.511804
1	1.984883	0.715089	0.068359
1	1.769183	-0.993739	-0.408333
8	-0.866279	1.988228	-1.843452
1	-1.442625	1.479299	-2.420857
1	-0.779419	1.427146	-1.057545

[methanol+water] – dimer D

8	0.005235	0.058258	-0.003988
1	0.008589	0.121646	0.963092
6	1.343681	-0.010869	-0.437893
1	1.335546	-0.081835	-1.530483
1	1.931062	0.880949	-0.165692
1	1.876882	-0.893870	-0.050003
8	-0.232982	0.254337	2.857584
1	-0.786406	1.039782	2.929251
1	-0.835365	-0.477825	3.029097

[ethanol+water] – dimer A

8	0.391141	0.484895	0.192757
1	0.604135	0.202151	1.087506
6	1.354733	-0.082931	-0.703909
1	2.358915	0.291681	-0.458038
1	1.371147	-1.177574	-0.604380
6	0.963794	0.308290	-2.118452
1	0.975735	1.396420	-2.232966
1	1.663973	-0.124149	-2.839069
1	-0.043490	-0.057764	-2.334361
1	-1.336861	-0.157405	-0.371153
8	-2.094871	-0.528044	-0.851834
1	-2.592007	0.248621	-1.124645

[ethanol+water] – dimer B

8	0.103135	0.436913	-0.181189
1	0.213009	0.204539	0.753428
6	1.176062	-0.127293	-0.907052
1	2.148610	0.247604	-0.544533
1	1.201653	-1.225280	-0.799405
6	1.006752	0.235559	-2.374937
1	1.004058	1.322597	-2.500600
1	1.819700	-0.182999	-2.976560
1	0.056519	-0.151207	-2.755621
8	0.235744	-0.136281	2.638269

1	-0.638716	-0.513453	2.784338
1	0.175743	0.753236	3.003557

[ethanol+water] – dimer C

8	0.878387	0.840888	-0.440976
1	1.612302	1.137023	0.118712
6	1.409729	0.059649	-1.491540
1	2.128507	0.636563	-2.098478
1	1.956641	-0.817134	-1.104327
6	0.260245	-0.406912	-2.372486
1	-0.277357	0.452787	-2.784022
1	0.628146	-1.018084	-3.202630
1	-0.449244	-1.001827	-1.789265
8	2.905918	1.842270	1.342735
1	2.561165	1.551430	2.194101
1	2.709605	2.785142	1.315584

[ethanol+water] – dimer D

8	0.060536	-1.019265	-0.094653
1	0.199890	-1.216395	0.836066
6	0.980143	-0.002602	-0.472786
1	0.831665	0.908568	0.128761
1	2.019848	-0.329938	-0.311547
6	0.761278	0.310296	-1.943387
1	1.452171	1.091406	-2.275835
1	0.920849	-0.587763	-2.548681
1	-0.266314	0.649536	-2.108701
8	2.907811	2.847405	-3.288901
1	3.131679	2.228060	-3.991078
1	2.116012	3.287144	-3.615153

[i-propanol+water] – dimer A

6	0.491429	-0.044036	-0.022623
1	0.918377	-0.028316	0.996565
6	1.609106	0.267726	-1.012297
1	2.389711	-0.496171	-0.956191
1	1.216438	0.277610	-2.034640
1	2.058962	1.243047	-0.802430
6	-0.640280	0.986447	-0.080894
1	-1.075000	1.014618	-1.086078
1	-1.433119	0.726212	0.628499
1	-0.278390	1.989777	0.169232
8	0.019220	-1.346339	-0.330524

1	-0.712348	-1.547172	0.273094
8	-2.194263	-2.015930	1.414403
1	-1.898783	-2.798492	1.892124
1	-2.848268	-2.346823	0.789342

[i-propanol+water] – dimer B

6	0.000364	0.000166	0.000790
1	-0.000247	-0.003114	1.101650
6	1.440786	0.003718	-0.509138
1	1.993905	-0.867467	-0.137510
1	1.439342	-0.020049	-1.602771
1	1.972090	0.899810	-0.173082
6	-0.800659	1.196570	-0.495914
1	-0.807443	1.216315	-1.589591
1	-1.832936	1.138974	-0.140343
1	-0.358382	2.127842	-0.130336
8	-0.697880	-1.175138	-0.455605
1	-0.214309	-1.946825	-0.142313
1	-0.666553	-1.065880	-2.399978
8	-0.462963	-0.785657	-3.307433
1	0.155729	-1.447771	-3.628774

[i-propanol+water] – dimer C

6	0.679047	0.438292	-0.113056
1	1.195421	1.172171	0.531971
6	1.568482	0.154965	-1.319074
1	2.518011	-0.281165	-0.996248
1	1.078293	-0.557797	-1.990755
1	1.777419	1.072730	-1.877393
6	-0.675622	1.028595	-0.516179
1	-1.209086	0.335635	-1.176021
1	-1.295854	1.205407	0.369033
1	-0.553941	1.982952	-1.040196
8	0.520616	-0.789751	0.580170
1	-0.067113	-0.630956	1.334650
8	-1.252773	-0.408711	2.838878
1	-0.721666	-0.641687	3.608020
1	-1.866011	-1.144520	2.736696

[formaldehyde+water] – dimer A

6	-0.349410	-0.034446	0.140833
8	-0.656272	-0.135043	1.315643
1	0.702751	-0.023462	-0.191174

7	-1.237189	0.077350	-0.872285
1	-2.224464	0.058687	-0.670834
1	-0.935757	0.134089	-1.829379
1	1.105638	-0.338506	2.065809
8	2.076065	-0.301829	2.017683
1	2.286053	0.564915	2.377301

[formaldehyde+water] – dimer B

6	0.150829	0.042578	-0.173818
8	0.600425	-0.038279	0.960351
1	0.811271	0.160020	-1.052924
7	-1.158328	0.006740	-0.487702
1	-1.825696	-0.113846	0.273130
1	-1.461944	0.050028	-1.444576
1	-0.913283	-0.297709	2.104146
8	-1.878515	-0.321173	2.255525
1	-2.065286	0.509884	2.703391

[formaldehyde+water] – dimer C

6	-0.667052	-0.708292	0.000000
8	0.515601	-1.014400	-0.000359
1	-1.464526	-1.474636	0.000007
7	-1.145062	0.551411	0.000404
1	-0.488622	1.326468	-0.000185
1	-2.134897	0.724046	-0.000097
8	1.469810	1.589459	0.000948
1	2.373653	1.911330	-0.001030
1	1.511026	0.615848	0.000312

[formaldehyde+water] – dimer D

6	-0.421911	0.176036	-0.002093
8	-0.832936	0.628825	1.056664
1	0.645969	-0.067714	-0.153531
7	-1.188596	-0.080025	-1.079274
1	-2.183152	0.133816	-1.014942
1	-0.784539	-0.427189	-1.931283
8	-3.521617	0.854212	0.272644
1	-2.703006	0.944050	0.799219
1	-4.008171	0.151847	0.715618

[formaldehyde+water] – dimer E

6	0.000387	-0.003512	0.007855
8	-0.011388	0.008739	1.219959
1	0.941269	-0.019226	-0.583781

7	-1.086673	-0.000347	-0.798644
1	-2.000651	0.013842	-0.374565
1	-0.997091	-0.010684	-1.808336
8	-0.554703	-0.034942	-3.741572
1	-0.013818	-0.804382	-3.948090
1	-0.000128	0.719349	-3.966793

[formaldehyde+water] – dimer F

6	-0.020581	-0.158270	-0.091140
8	0.004353	-0.152347	1.120833
1	0.869527	-0.405528	-0.709228
7	-1.093606	0.124214	-0.866369
1	-1.962960	0.363214	-0.416356
1	-1.038039	0.097099	-1.878195
8	-0.672140	-0.029193	-3.823257
1	-0.352092	-0.910592	-4.042215
1	0.050610	0.558998	-4.065923

[pyridin+water] – dimer A

8	0.639367	-0.276198	0.181869
1	0.558296	0.364131	0.894732
1	1.451900	-0.001229	-0.278783
7	2.447464	1.018956	-1.658833
6	1.418313	1.457854	-2.392461
6	3.681792	1.324644	-2.066900
6	1.577528	2.213638	-3.549708
1	0.435128	1.180935	-2.022264
6	3.943291	2.075017	-3.209433
1	4.496890	0.951990	-1.451723
6	2.867122	2.528727	-3.965927
1	0.709319	2.544139	-4.108528
1	4.965937	2.294596	-3.494570
1	3.031347	3.115940	-4.863435

[pyridin+water] – dimer B

8	-0.643312	-0.287005	-0.136377
1	-0.932417	0.615710	0.025765
1	0.298819	-0.272038	0.109566
7	2.231124	-0.082824	-0.273846
6	2.189061	-0.031645	-1.609974
6	3.429755	-0.068706	0.315287
6	3.329274	0.039325	-2.404236

1	1.192596	-0.052499	-2.042501
6	4.626081	0.000514	-0.392140
1	3.431276	-0.114964	1.401346
6	4.573205	0.056222	-1.781605
1	3.239556	0.078569	-3.483909
1	5.572099	0.009281	0.137315
1	5.485036	0.110234	-2.367214

[THF+water] – dimer A

6	0.000000	1.207079	-0.254017
8	0.000000	0.039628	-1.069865
6	0.000000	-1.165865	-0.307203
6	0.000000	-0.786328	1.187416
6	0.000000	0.761307	1.222494
1	0.886039	1.806485	-0.498760
1	-0.886039	1.806485	-0.498760
1	-0.885521	-1.751762	-0.581506
1	0.885521	-1.751762	-0.581506
1	-0.878270	-1.193438	1.693157
1	0.878270	-1.193438	1.693157
1	-0.878273	1.145694	1.745733
1	0.878273	1.145694	1.745733
1	0.000000	-0.012821	-3.017008
8	0.000000	-0.039979	-3.985557
1	0.000000	0.886683	-4.240312

[THF+water] – dimer B

6	-0.626310	0.954589	-0.396992
8	-0.730804	-0.325439	-1.041851
6	-0.284788	-1.363863	-0.153718
6	0.002125	-0.691007	1.195483
6	0.332655	0.749813	0.775495
1	-0.265769	1.667239	-1.142657
1	-1.620861	1.269681	-0.049135
1	-1.061840	-2.133460	-0.091644
1	0.618543	-1.822560	-0.575922
1	-0.891039	-0.706517	1.829018
1	0.810201	-1.182401	1.742063
1	0.185737	1.479563	1.575050
1	1.369307	0.822216	0.430593
1	0.270132	0.028377	-2.622536
8	0.805503	0.520133	-3.266791

1	0.182275	0.731883	-3.967685

DGE (in the gas phase)

6	-2.531601	-1.203797	-0.919241
6	-1.252859	-1.094267	-0.389797
6	-0.969944	-0.060591	0.499758
6	-1.946131	0.868421	0.864896
6	-3.215638	0.748469	0.330795
6	-3.512579	-0.282962	-0.557772
1	-0.496074	-1.805202	-0.691074
1	-1.693971	1.664814	1.555748
6	0.374326	0.115596	1.101932
8	0.702095	1.019643	1.810793
8	1.217857	-0.907795	0.754994
6	2.530319	-0.880968	1.211156
6	2.939231	-2.030887	1.873865
6	3.405442	0.162470	0.975215
6	4.258016	-2.143792	2.320946
6	4.715929	0.040595	1.427887
1	3.087370	1.060861	0.463828
6	5.145677	-1.105057	2.099478
1	6.165224	-1.196984	2.448333
8	-2.822116	-2.200828	-1.786109
1	-3.743304	-2.118195	-2.060530
8	-4.746140	-0.432949	-1.104175
1	-5.322543	0.271549	-0.783822
8	-4.264102	1.582194	0.600083
1	-3.993589	2.286551	1.195230
8	2.110536	-3.079443	2.116297
1	1.249903	-2.901842	1.719181
8	4.663009	-3.264442	2.965986
1	3.919616	-3.875800	3.025081
6	5.637437	1.179004	1.161082
8	5.329392	2.178755	0.566177
8	6.866428	0.972446	1.657297
6	7.799267	2.029636	1.432241
1	7.442482	2.952202	1.890485
1	8.728547	1.705532	1.892864
1	7.934920	2.192723	0.362895

DGE (implicit water solution - IEFPCM)

6	-2.460238	-0.944950	-1.139134

6	-1.202442	-0.936822	-0.556636
6	-0.986642	-0.159776	0.581151
6	-2.014403	0.602177	1.140679
6	-3.265505	0.583820	0.549963
6	-3.495219	-0.186724	-0.592080
1	-0.413334	-1.529487	-0.999640
1	-1.843492	1.203275	2.025964
6	0.333389	-0.106921	1.239926
8	0.605535	0.552125	2.211565
8	1.251492	-0.907669	0.627153
6	2.544533	-0.899937	1.141767
6	2.918603	-1.992229	1.915567
6	3.424529	0.124579	0.852831
6	4.227477	-2.054921	2.408723
6	4.721464	0.051020	1.353864
1	3.097765	0.962104	0.249153
6	5.123850	-1.038973	2.130259
1	6.129718	-1.108015	2.523678
8	-2.674913	-1.700321	-2.256316
1	-3.591301	-1.597260	-2.548152
8	-4.705237	-0.230477	-1.208564
1	-5.330518	0.348521	-0.749560
8	-4.342083	1.287285	1.008790
1	-4.094738	1.811633	1.781668
8	2.084509	-3.011780	2.227638
1	1.209518	-2.865903	1.839397
8	4.625287	-3.116071	3.167360
1	3.883102	-3.723882	3.294280
6	5.654742	1.160612	1.033971
8	5.351600	2.132026	0.372403
8	6.870985	0.984417	1.545787
6	7.836068	2.009841	1.260355
1	7.995776	2.081072	0.184873
1	7.493895	2.966398	1.653734
1	8.748658	1.696874	1.759585

DGE (explicit microsolvation + IEFPCM)

6	-3.783505	-0.882939	1.406529
6	-2.419056	-0.681060	1.247809

6	-1.909826	-0.443009	-0.029182
6	-2.747296	-0.443613	-1.146428
6	-4.110969	-0.650679	-0.984008
6	-4.643695	-0.869632	0.297663
1	-1.783039	-0.665268	2.126159
1	-2.343982	-0.285568	-2.139709
6	-0.500940	-0.077643	-0.229295
8	-0.036239	0.359828	-1.270992
8	0.260068	-0.259663	0.873318
6	1.611327	0.069503	0.779893
6	2.026643	1.261346	1.371710
6	2.500739	-0.796545	0.166281
6	3.397186	1.577075	1.326929
6	3.854764	-0.464738	0.139639
1	2.132139	-1.714850	-0.277907
6	4.307354	0.727001	0.723270
1	5.356568	1.000776	0.707363
8	-4.260208	-1.036705	2.676771
1	-5.243830	-1.130126	2.725797
8	-5.964159	-1.057851	0.521365
1	-6.518076	-0.985412	-0.297001
8	-4.982542	-0.640100	-2.030915
1	-4.564198	-0.175299	-2.806498
8	1.218123	2.143358	1.983296
8	3.834676	2.742576	1.889286
1	3.077089	3.233828	2.250012
6	4.791752	-1.405592	-0.516612
8	4.440778	-2.431066	-1.086011
8	6.065562	-1.039827	-0.428857
6	7.023851	-1.923606	-1.037711
1	6.841448	-1.985707	-2.112388
1	7.995458	-1.475488	-0.842175
1	6.958012	-2.913309	-0.582330
1	5.256327	2.307604	3.119592
8	5.986365	1.916481	3.627072
1	6.026273	2.426594	4.445544
1	1.273112	3.638750	0.581139
8	1.383748	4.038667	-0.294445
1	1.718108	3.314432	-0.859190
1	0.222977	2.024904	1.806018
8	-1.288523	2.239000	1.524774

1	-1.420473	3.197867	1.510564
1	-1.888523	1.901709	2.227374
1	-1.054817	1.492114	-2.482032
8	-1.552631	2.042280	-3.111589
1	-1.768904	2.849613	-2.625917
1	1.574691	1.282086	-1.698726
8	2.247387	1.929089	-1.976576
1	3.081057	1.595095	-1.615769
1	-3.528276	0.618272	3.425507
8	-2.964178	1.394418	3.588968
1	-3.567844	2.099576	3.857405
1	-7.246263	-1.417209	2.291849
8	-6.908394	-1.299863	3.191715
1	-7.074202	-2.139864	3.641107
1	-7.122668	-0.863495	-2.234654
8	-7.747981	-0.871919	-1.494361
1	-8.252014	-1.691417	-1.589833
8	-3.885398	0.778596	-3.997401
1	-3.631846	0.254955	-4.769399
1	-3.061755	1.216878	-3.691352
1	2.848487	-3.176366	-1.895374
8	2.338118	-3.806137	-2.432778
1	1.881855	-3.267107	-3.091943
1	5.305782	-3.818694	-2.347628
8	5.091388	-4.504697	-2.998548
1	4.119835	-4.475090	-3.027009

DGE dimer A (in the gas phase)

6	3.786685	0.123448	-1.022230
6	2.426114	-0.014840	-0.766825
6	2.004836	-0.907833	0.219087
6	2.918864	-1.704627	0.915367
6	4.269272	-1.574290	0.636762
6	4.707262	-0.645636	-0.308609
1	1.722793	0.593650	-1.322139
1	2.561034	-2.386773	1.680659
6	0.585961	-1.016643	0.639578
8	0.219184	-1.575467	1.641754
8	-0.261354	-0.400945	-0.236355
6	-1.639997	-0.499484	-0.065061
6	-2.341117	0.657620	-0.398585

6	-2.299865	-1.650663	0.335966
6	-3.736934	0.679062	-0.292004
6	-3.690064	-1.616198	0.430395
1	-1.767082	-2.553069	0.604083
6	-4.412887	-0.459582	0.124738
1	-5.491110	-0.425944	0.230611
8	4.212814	1.024027	-1.938775
1	5.179532	1.053402	-1.927335
8	6.031500	-0.410601	-0.524485
1	6.547233	-0.906115	0.130754
8	5.270175	-2.269112	1.260850
1	4.941830	-2.701476	2.059185
8	-1.733004	1.804312	-0.806483
1	-0.773743	1.701935	-0.737825
8	-4.425725	1.815554	-0.560999
1	-3.820724	2.574134	-0.563777
6	-4.356411	-2.859636	0.904449
8	-3.793909	-3.915395	1.077259
8	-5.675160	-2.691837	1.123231
6	-6.349929	-3.851104	1.614332
1	-5.925428	-4.151131	2.575505
1	-7.394237	-3.560908	1.723286
1	-6.251303	-4.676493	0.906614
6	4.656364	1.280950	2.092185
6	3.295006	1.400545	2.349968
6	2.704777	0.597237	3.325199
6	3.460082	-0.326766	4.052706
6	4.811449	-0.452050	3.771319
6	5.413885	0.345053	2.798905
1	2.717447	2.093222	1.750919
1	2.970361	-0.949870	4.795430
6	1.245117	0.632336	3.611597
8	0.721949	0.150320	4.578709
8	0.566522	1.279212	2.618489
6	-0.815153	1.437973	2.664804
6	-1.234759	2.620805	2.059732
6	-1.731929	0.506026	3.135870
6	-2.596934	2.896930	1.932400
6	-3.088589	0.816862	3.030591
1	-1.417306	-0.442488	3.550991
6	-3.526350	2.012039	2.451569

1	-4.583042	2.222168	2.335116
8	5.229948	2.044930	1.132586
1	6.139232	1.745249	0.986207
8	6.724905	0.203331	2.458242
1	7.128108	-0.458726	3.038952
8	5.644336	-1.384354	4.343557
1	5.282497	-1.693705	5.182572
8	-0.365706	3.514595	1.508446
1	0.537136	3.268126	1.750852
8	-3.006667	3.995644	1.238615
1	-2.227370	4.501297	0.966868
6	-4.072755	-0.211316	3.473102
8	-3.787257	-1.336400	3.815458
8	-5.334541	0.248938	3.442517
6	-6.337300	-0.692574	3.826579
1	-6.138317	-1.067508	4.832735
1	-7.278587	-0.146250	3.796609
1	-6.349772	-1.525716	3.121263

DGE dimer A (implicit water solution - IEFPCM)

6	4.216385	-0.937337	-1.191525
6	2.856436	-0.898758	-0.915889
6	2.397589	-1.402171	0.305333
6	3.278181	-1.953543	1.240150
6	4.635264	-1.967884	0.956986
6	5.112109	-1.458427	-0.254671
1	2.182158	-0.458178	-1.640854
1	2.918195	-2.325171	2.194604
6	0.978198	-1.286372	0.699026
8	0.511402	-1.650397	1.756890
8	0.229152	-0.689253	-0.269261
6	-1.133871	-0.508399	-0.070371
6	-1.587579	0.800753	-0.217462
6	-2.004318	-1.556073	0.176794
6	-2.962550	1.060819	-0.128958
6	-3.367376	-1.278529	0.283678
1	-1.628674	-2.566999	0.286081
6	-3.849901	0.025899	0.123878
1	-4.907512	0.250648	0.211159
8	4.677778	-0.426324	-2.372269
1	5.642784	-0.517557	-2.413122

8	6.437493	-1.431497	-0.563639
1	6.960227	-1.743759	0.192816
8	5.594248	-2.419054	1.818490
1	5.203167	-2.618523	2.682909
8	-0.757568	1.851512	-0.426630
1	0.167620	1.552481	-0.417420
8	-3.435275	2.332396	-0.281981
1	-2.694723	2.958547	-0.327145
6	-4.276628	-2.413495	0.579269
8	-3.905631	-3.571535	0.686703
8	-5.554370	-2.051991	0.710281
6	-6.485965	-3.123876	0.932237
1	-6.217946	-3.676175	1.835063
1	-7.457481	-2.646991	1.046021
1	-6.488157	-3.795536	0.071561
6	4.028588	1.432784	1.409894
6	2.693264	1.457376	1.792914
6	2.327192	0.883328	3.013596
6	3.280354	0.300405	3.856164
6	4.609639	0.285467	3.462193
6	4.988165	0.841464	2.235585
1	1.960125	1.905523	1.129955
1	2.989461	-0.148279	4.800835
6	0.919074	0.851332	3.458104
8	0.536040	0.486062	4.548924
8	0.066207	1.288918	2.492898
6	-1.280825	1.419872	2.799830
6	-1.795399	2.704766	2.642039
6	-2.087845	0.342192	3.126567
6	-3.165631	2.918430	2.844458
6	-3.449826	0.572031	3.315852
1	-1.666262	-0.653797	3.207288
6	-3.989471	1.857839	3.183609
1	-5.050321	2.038436	3.315416
8	4.394160	1.981526	0.213654
1	5.326295	1.779776	0.032099
8	6.271863	0.808346	1.789884
1	6.817134	0.273290	2.389801
8	5.624824	-0.268432	4.191189
1	5.278956	-0.673233	5.000736
8	-1.035597	3.769653	2.283269

1	-0.117266	3.488512	2.133376
8	-3.701423	4.163731	2.682860
1	-3.004502	4.797179	2.450215
6	-4.324514	-0.595797	3.589866
8	-3.955904	-1.758252	3.528112
8	-5.572029	-0.247895	3.909692
6	-6.476989	-1.322639	4.207762
1	-6.105805	-1.897918	5.057763
1	-7.423350	-0.845001	4.452777
1	-6.589345	-1.968845	3.336726

DGE dimer B (in the gas phase)

6	4.678686	-4.760323	3.933427
6	4.383254	-6.073987	3.608211
6	5.265394	-6.765950	2.770938
6	6.418836	-6.153490	2.274745
6	6.689989	-4.827725	2.590724
6	5.829617	-4.131479	3.446051
1	3.467467	-6.527900	3.968281
1	7.081173	-6.703355	1.613171
6	4.991775	-8.144469	2.310335
8	5.662784	-8.764698	1.526476
8	3.845267	-8.655537	2.868004
6	3.369409	-9.864207	2.371878
6	3.200816	-10.875081	3.314681
6	3.024348	-10.030093	1.040865
6	2.662907	-12.104412	2.896460
6	2.501394	-11.253611	0.638981
1	3.165378	-9.232119	0.321299
6	2.319189	-12.288432	1.565269
1	1.906933	-13.237205	1.235844
8	3.780432	-4.012595	4.648394
1	4.191742	-3.150788	4.825204
8	5.993828	-2.839683	3.791570
1	6.581058	-2.355313	3.173217
8	7.732419	-4.126159	2.068897
1	7.856154	-4.391914	1.140689
8	3.532713	-10.715740	4.611403
1	3.866296	-9.816390	4.737103
8	2.516117	-13.053505	3.856673
1	2.150182	-13.856183	3.468336

6	2.153956	-11.412553	-0.797031
8	2.314678	-10.556730	-1.638553
8	1.635263	-12.621182	-1.074755
6	1.284206	-12.830179	-2.444003
1	2.166234	-12.729123	-3.079504
1	0.885521	-13.841683	-2.494231
1	0.533587	-12.101544	-2.756634
6	6.940194	3.592769	0.497145
6	6.443429	2.298670	0.604878
6	7.093062	1.390233	1.441679
6	8.229208	1.752801	2.173562
6	8.712571	3.045058	2.055075
6	8.074113	3.964481	1.221329
1	5.561454	2.017447	0.042973
1	8.709505	1.020883	2.815644
6	6.611207	-0.000371	1.596324
8	7.123349	-0.821183	2.327303
8	5.538929	-0.266324	0.817227
6	4.990349	-1.539857	0.875272
6	3.825453	-1.719099	1.622347
6	5.566606	-2.595121	0.193254
6	3.219992	-2.984581	1.639707
6	4.937612	-3.841671	0.197861
1	6.502837	-2.454736	-0.337067
6	3.741068	-4.030926	0.895158
1	3.257722	-5.002095	0.916723
8	6.325228	4.490925	-0.308582
1	6.796399	5.334637	-0.261078
8	8.518685	5.240716	1.079922
1	9.302869	5.369541	1.632337
8	9.809977	3.539492	2.705582
1	10.208960	2.864794	3.266417
8	3.319726	-0.697848	2.336144
1	2.495057	-1.010077	2.741628
8	2.095818	-3.104248	2.427379
1	2.332911	-3.606159	3.227343
6	5.654215	-4.976358	-0.435965
8	6.859017	-4.977705	-0.630484
8	4.861942	-6.000174	-0.739377
6	5.510138	-7.152242	-1.302928
1	6.178065	-7.600704	-0.565249

1	4.707380	-7.842692	-1.555016
1	6.070275	-6.862974	-2.193409

DGE dimer B (implicit water solution - IEFPCM)

6	4.562219	-4.615176	4.150844
6	4.307978	-5.928537	3.785112
6	5.258259	-6.599706	3.011488
6	6.448692	-5.979280	2.620873
6	6.684874	-4.662622	2.995174
6	5.740545	-3.972319	3.764060
1	3.368344	-6.389432	4.066413
1	7.171737	-6.504068	2.002344
6	5.008699	-7.964091	2.504570
8	5.789422	-8.628004	1.858465
8	3.763868	-8.420288	2.830154
6	3.377587	-9.636859	2.273419
6	3.410699	-10.755353	3.101532
6	2.932586	-9.699252	0.964448
6	2.980790	-11.986762	2.581303
6	2.515613	-10.929343	0.460894
1	2.914314	-8.799862	0.357495
6	2.539335	-12.073010	1.269469
1	2.212497	-13.034165	0.886116
8	3.603232	-3.907586	4.827031
1	3.930660	-3.005417	4.985915
8	5.900406	-2.679020	4.152073
1	6.412813	-2.173005	3.484569
8	7.791768	-3.956421	2.626226
1	8.331726	-4.478125	2.012888
8	3.839248	-10.710142	4.385674
1	4.055932	-9.795052	4.628761
8	3.031458	-13.051842	3.433012
1	2.710266	-13.847762	2.982911
6	2.054377	-10.982348	-0.948647
8	2.040012	-10.017307	-1.695962
8	1.655365	-12.197016	-1.327596
6	1.201881	-12.318847	-2.686126
1	2.007154	-12.053972	-3.373272
1	0.925040	-13.364048	-2.806134
1	0.338455	-11.672117	-2.850747

6	6.932597	3.281634	0.174562
6	6.444586	1.999878	0.389475
6	7.065612	1.189765	1.344434
6	8.162144	1.647498	2.083635
6	8.637035	2.930319	1.857826
6	8.027665	3.751591	0.903514
1	5.595266	1.652820	-0.187018
1	8.638506	1.014618	2.825332
6	6.589614	-0.181243	1.610511
8	7.113207	-0.951486	2.396004
8	5.500030	-0.507294	0.882846
6	4.978904	-1.795907	0.983859
6	3.806212	-1.961991	1.724250
6	5.556136	-2.849658	0.302170
6	3.186081	-3.218937	1.726959
6	4.927550	-4.098721	0.319748
1	6.483051	-2.696358	-0.241200
6	3.725828	-4.275846	1.011162
1	3.226890	-5.238867	1.037979
8	6.334214	4.080588	-0.758758
1	6.782889	4.940212	-0.790027
8	8.460807	5.015144	0.647039
1	9.214163	5.231948	1.219953
8	9.695044	3.490385	2.516960
1	10.073146	2.861238	3.149442
8	3.306875	-0.916630	2.418484
1	2.477993	-1.193881	2.845828
8	2.016812	-3.354230	2.453904
1	2.248904	-3.584743	3.374812
6	5.612680	-5.226590	-0.357522
8	6.720619	-5.136248	-0.863484
8	4.909704	-6.360069	-0.357536
6	5.522829	-7.473590	-1.031292
1	6.483067	-7.709574	-0.570225
1	4.829326	-8.304825	-0.917713
1	5.660491	-7.232826	-2.087192

DGE dimer C (in the gas phase)

6	5.054209	1.577558	-1.350399
6	3.726637	1.717970	-0.966618

6	3.290252	1.105169	0.211462
6	4.159439	0.353344	1.014999
6	5.486259	0.231017	0.626053
6	5.927620	0.837581	-0.554859
1	3.051663	2.284233	-1.596011
1	3.790962	-0.125052	1.917512
6	1.882525	1.212865	0.646049
8	1.374636	0.612937	1.562492
8	1.175429	2.104117	-0.116643
6	-0.187676	2.253672	0.104099
6	-0.609519	3.575583	0.237095
6	-1.074164	1.188890	0.114715
6	-1.983032	3.835831	0.387456
6	-2.430452	1.461278	0.273947
1	-0.708071	0.174414	0.017230
6	-2.883072	2.782405	0.405330
1	-3.944146	2.977846	0.523957
8	5.498132	2.158629	-2.491992
1	6.435352	1.947897	-2.607715
8	7.216823	0.730754	-0.966728
1	7.700340	0.188144	-0.325825
8	6.457568	-0.455149	1.283142
1	6.202502	-0.742963	2.177805
8	0.249559	4.610873	0.221435
1	1.145620	4.270677	0.086709
8	-2.336117	5.140677	0.509065
1	-3.291519	5.213575	0.613781
6	-3.379654	0.324508	0.308353
8	-3.063459	-0.853722	0.316148
8	-4.658795	0.708203	0.328378
6	-5.623203	-0.348451	0.377828
1	-5.478382	-0.947420	1.278712
1	-6.593362	0.143839	0.391523
1	-5.524328	-0.988070	-0.500894
6	5.917492	-2.441036	4.467041
6	4.807718	-3.070449	3.924378
6	4.374595	-4.270091	4.489934
6	5.032411	-4.843218	5.580709
6	6.151014	-4.207148	6.095967
6	6.597035	-3.005090	5.542801
1	4.262206	-2.624228	3.099477

1	4.652679	-5.766132	6.009658
6	3.133125	-4.920484	3.989379
8	2.494286	-5.748297	4.585560
8	2.814787	-4.435998	2.764403
6	1.504718	-4.426230	2.320290
6	1.036286	-3.155525	1.986107
6	0.722651	-5.558831	2.160998
6	-0.260170	-3.025125	1.466161
6	-0.568605	-5.407346	1.653638
1	1.094567	-6.538983	2.432330
6	-1.062844	-4.144017	1.302720
1	-2.065921	-4.040404	0.902207
8	6.347668	-1.247628	3.952202
1	7.119499	-0.942731	4.452028
8	7.680919	-2.339018	6.025102
1	8.047829	-2.827924	6.775510
8	6.898993	-4.653637	7.150895
1	6.536324	-5.473665	7.504574
8	1.837268	-2.089176	2.169466
1	1.371437	-1.262207	1.943703
8	-0.612960	-1.751574	1.158767
1	-1.543757	-1.659043	0.881402
6	-1.389836	-6.634038	1.491814
8	-1.013018	-7.755651	1.747533
8	-2.625190	-6.374194	1.019693
6	-3.455708	-7.520880	0.842865
1	-3.599727	-8.035423	1.795301
1	-4.402783	-7.142918	0.461347
1	-3.000617	-8.213062	0.131216

DGE dimer C (implicit water solution - IEFPCM)

6	3.472381	-2.335642	-0.878845
6	2.637224	-1.315716	-0.444952
6	3.050791	-0.502811	0.614318
6	4.301175	-0.675404	1.216227
6	5.133784	-1.688483	0.763057
6	4.719239	-2.528280	-0.276345
1	1.664298	-1.195349	-0.909157
1	4.616736	-0.043257	2.040612
6	2.160202	0.528995	1.180923

8	2.356934	1.132137	2.214929
8	1.060371	0.750359	0.408659
6	0.106333	1.644415	0.883466
6	-0.019221	2.840647	0.181024
6	-0.711753	1.332481	1.956861
6	-1.015361	3.749970	0.570504
6	-1.689691	2.249772	2.336675
1	-0.581339	0.394586	2.486720
6	-1.843953	3.457207	1.642870
1	-2.606139	4.173470	1.931476
8	3.050925	-3.163454	-1.880211
1	3.721000	-3.844990	-2.047516
8	5.493088	-3.553312	-0.726997
1	6.299662	-3.609175	-0.188256
8	6.369206	-1.962966	1.281927
1	6.466290	-1.586749	2.177067
8	0.776729	3.170495	-0.863934
1	1.426311	2.465998	-1.020407
8	-1.095655	4.900554	-0.159104
1	-1.811348	5.458666	0.180279
6	-2.557119	1.904914	3.490699
8	-2.469138	0.864561	4.122996
8	-3.452986	2.850898	3.775997
6	-4.326042	2.583072	4.885740
1	-3.741845	2.463458	5.799698
1	-4.976227	3.452235	4.958730
1	-4.910488	1.682146	4.691722
6	5.046418	-1.642725	4.601894
6	4.151421	-2.411346	3.873183
6	2.818764	-2.476927	4.279408
6	2.381240	-1.818217	5.432810
6	3.292136	-1.069279	6.163913
6	4.625656	-0.966310	5.747973
1	4.500830	-2.937026	2.992920
1	1.342631	-1.867769	5.744792
6	1.820127	-3.189842	3.456079
8	0.699478	-3.494144	3.805842
8	2.299191	-3.455092	2.213151
6	1.428682	-3.957549	1.257634
6	0.379187	-3.150839	0.817813
6	1.694041	-5.187370	0.682366

6	-0.418649	-3.606938	-0.241338
6	0.883078	-5.630008	-0.363757
1	2.526988	-5.781257	1.042408
6	-0.173769	-4.838925	-0.829009
1	-0.805008	-5.170972	-1.646600
8	6.338950	-1.542456	4.161788
1	6.849170	-0.951945	4.738675
8	5.543250	-0.221475	6.421883
1	5.127605	0.196191	7.193444
8	2.982413	-0.375271	7.300241
1	2.044423	-0.483980	7.518323
8	0.177569	-1.951338	1.401417
1	-0.523289	-1.468453	0.932113
8	-1.409917	-2.750066	-0.628606
1	-1.895095	-3.109413	-1.386648
6	1.183314	-6.951651	-0.967663
8	2.098907	-7.674233	-0.607444
8	0.348060	-7.281225	-1.954349
6	0.581749	-8.551637	-2.583781
1	0.486157	-9.354401	-1.850620
1	-0.185340	-8.640781	-3.350103
1	1.576208	-8.568522	-3.032835

DGE dimer D (in the gas phase)

6	3.591904	2.390443	-0.300055
6	2.339763	1.800207	-0.425096
6	2.172200	0.464752	-0.055198
6	3.246787	-0.294068	0.423989
6	4.493219	0.302355	0.530821
6	4.668609	1.641497	0.178408
1	1.519712	2.392702	-0.811381
1	3.087725	-1.329812	0.707568
6	0.847399	-0.197810	-0.084853
8	0.628567	-1.310809	0.335135
8	-0.115164	0.599273	-0.624606
6	-1.455802	0.261564	-0.452728
6	-2.253936	1.325201	-0.031789
6	-1.983191	-0.996067	-0.682191
6	-3.602133	1.098401	0.285463
6	-3.336450	-1.198360	-0.410916

1	-1.368898	-1.813359	-1.034741
6	-4.139824	-0.169246	0.089858
1	-5.178882	-0.344077	0.343519
8	3.765595	3.686927	-0.644830
1	4.684447	3.940577	-0.477787
8	5.869894	2.264326	0.277545
1	6.526808	1.645285	0.627050
8	5.625778	-0.316514	0.984194
1	5.461573	-1.249525	1.162916
8	-1.768812	2.578721	0.125785
1	-0.802598	2.552692	0.071157
8	-4.371893	2.088100	0.785014
1	-3.828614	2.780308	1.209280
6	-3.852891	-2.571753	-0.620830
8	-3.176889	-3.480437	-1.075977
8	-5.124886	-2.729761	-0.260408
6	-5.661017	-4.049311	-0.427696
1	-5.100057	-4.769590	0.172439
1	-6.692857	-3.985793	-0.088322
1	-5.614797	-4.339767	-1.479023
6	-2.980245	-4.689809	1.836217
6	-2.440817	-3.431563	2.111648
6	-2.876938	-2.722444	3.233929
6	-3.839864	-3.258262	4.094332
6	-4.360251	-4.509885	3.819769
6	-3.944953	-5.233121	2.695666
1	-1.688228	-3.011091	1.450014
1	-4.161025	-2.684248	4.958390
6	-2.357081	-1.383411	3.590399
8	-2.747603	-0.710873	4.509217
8	-1.348173	-0.979129	2.753198
6	-0.821685	0.288547	2.921847
6	0.569079	0.363325	2.977329
6	-1.599503	1.435582	2.946948
6	1.196110	1.617826	3.032803
6	-0.964977	2.674354	3.006201
1	-2.681207	1.371397	2.911661
6	0.430158	2.775822	3.052501
1	0.922774	3.740553	3.083380
8	-2.610114	-5.449618	0.777147
1	-2.486556	-4.878346	-0.000609

8	-4.477880	-6.441571	2.412585
1	-5.112550	-6.666520	3.107910
8	-5.310929	-5.140491	4.578304
1	-5.567430	-4.591608	5.327586
8	1.371200	-0.733087	2.989900
1	0.931894	-1.449965	2.503363
8	2.548698	1.693970	3.060249
1	2.906835	0.803240	2.926457
6	-1.826222	3.881451	2.913978
8	-3.000353	3.863933	2.596057
8	-1.176656	5.013226	3.199562
6	-1.950544	6.211719	3.086443
1	-2.794356	6.179782	3.777957
1	-1.271038	7.022514	3.340894
1	-2.324970	6.322151	2.066996

DGE dimer D (implicit water solution - IEFPCM)

6	3.433386	2.401078	-0.249702
6	2.193856	1.784208	-0.359435
6	2.080162	0.427197	-0.042996
6	3.191324	-0.314856	0.374052
6	4.425267	0.311264	0.464765
6	4.552508	1.669817	0.156978
1	1.341626	2.372723	-0.678803
1	3.095973	-1.366600	0.624995
6	0.774224	-0.263401	-0.058281
8	0.566201	-1.360412	0.411649
8	-0.203981	0.478287	-0.658871
6	-1.534126	0.160918	-0.403046
6	-2.302097	1.237717	0.042768
6	-2.086746	-1.096402	-0.584257
6	-3.627120	1.013590	0.440879
6	-3.420280	-1.293231	-0.222055
1	-1.491466	-1.912233	-0.974458
6	-4.183303	-0.251813	0.318625
1	-5.208268	-0.410119	0.635584
8	3.546581	3.731117	-0.542691
1	4.458269	4.025798	-0.391621
8	5.742512	2.323477	0.241297
1	6.439808	1.704932	0.513644

8	5.580623	-0.306926	0.853987
1	5.418307	-1.242033	1.049938
8	-1.822385	2.498715	0.135960
1	-0.856970	2.496424	0.027814
8	-4.368610	2.039838	0.954109
1	-3.782677	2.737546	1.309076
6	-3.989155	-2.651039	-0.413509
8	-3.470601	-3.512717	-1.105672
8	-5.135694	-2.839401	0.241149
6	-5.797698	-4.096071	0.018124
1	-5.102433	-4.925653	0.150454
1	-6.596738	-4.141326	0.756309
1	-6.209329	-4.114308	-0.993451
6	-2.632960	-4.691270	1.801529
6	-2.170000	-3.425145	2.140548
6	-2.885258	-2.662023	3.069345
6	-4.059016	-3.147835	3.652420
6	-4.507899	-4.413736	3.305784
6	-3.797115	-5.196894	2.389829
1	-1.263913	-3.047501	1.675958
1	-4.614270	-2.550454	4.368625
6	-2.431061	-1.315413	3.474683
8	-2.968775	-0.618587	4.308496
8	-1.309933	-0.935268	2.807916
6	-0.770354	0.327241	2.990622
6	0.622212	0.367119	3.080086
6	-1.523330	1.489877	2.974703
6	1.269070	1.611701	3.112932
6	-0.865280	2.717401	3.017872
1	-2.603484	1.445173	2.910935
6	0.530887	2.785674	3.082323
1	1.051803	3.736594	3.089823
8	-2.009172	-5.506528	0.901655
1	-1.257324	-5.042517	0.503103
8	-4.215940	-6.440583	2.038363
1	-5.050658	-6.640309	2.492603
8	-5.640846	-4.990644	3.807186
1	-6.074996	-4.391474	4.432538
8	1.400075	-0.740981	3.137578
1	0.891480	-1.524278	2.867796
8	2.630210	1.672389	3.169804

1	3.002549	0.782219	3.055968
6	-1.698567	3.938790	2.893567
8	-2.895001	3.927010	2.636952
8	-1.016511	5.065871	3.078782
6	-1.759541	6.289191	2.937741
1	-2.559112	6.326643	3.679254
1	-1.039332	7.085875	3.110374
1	-2.174604	6.358189	1.930939

B.5.2 Stability of DGE in Different Media

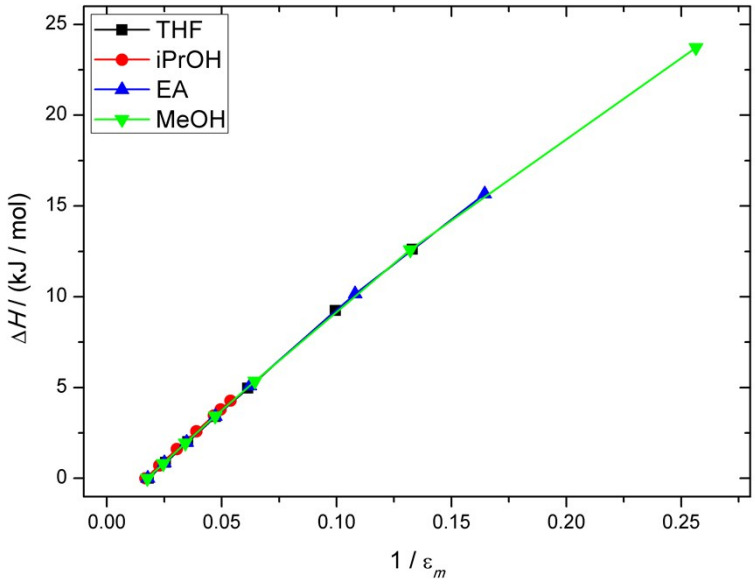

Figure SB1. Variation of Enthalpy of DGE Computed at 298.15 K and 1.00 atm as a Function of the Dielectric Constant of the Medium (Mixtures Co-Solvent / Water).

C Classical Models for Aggregates

C.1 General Theory

Our aim is to derive a simple, analytical model to describe the interaction energy of a molecular system with the surrounding environment. In particular, this model will be developed within the framework of the Classical Electrodynamic theory. The analytical models are convenient means for reducing the dimensionality (and the computational cost) of theoretical treatments of molecules in the condensed phase. From this perspective, a molecular (or super-molecular) system in the gas phase may be modeled as a collection of *N* point charges $\{q_k(\mathbf{r}_k)\}_{k=1,\ldots N}$, located in a region of an evacuated, three dimensional Cartesian space. We can identify the position of the *k*th charge with respect to a prefixed Cartesian system of coordinates by mean of a vector, $\mathbf{r}_k \equiv (x_k \quad y_k \quad z_k)$, defining the position of the charge with respect to the origin of the Cartesian system of coordinates. This may be a simplified but reasonable electrostatic picture of a molecule in the gas phase.

The set of electric charges can be now supposed to be bounded within a closed cavity of surface Σ_0, obtained within a homogeneous, isotropic, continuum, dielectric medium, characterised by a dielectric constant, ε_B (where the subscript *B* stands for "bulk"). Such a medium can represent an electrostatic picture of a solvent (or environment), interacting with a solute molecule by mean of electrostatic interaction only; any specific interaction (for instance, hydrogen bonding) is excluded. Dependently of the chemico-physical system to describe, this "bulk" region may be partitioned in imbedded, "onion like" shells, separated by surfaces (Σ_1, Σ_2, Σ_3, etc.), each of those shells may have a different dielectric constant and include an ionic atmosphere. Concerning the internal region (cavity), we shall account for the general case for which the cavity is filled by a homogeneous, isotropic, continuum, dielectric medium, characterised by a dielectric constant, ε_C (where the subscript *C* stands for "cavity"). (Commonly, the cavity is considered evacuated, so $\varepsilon_C = \varepsilon_0$).

In order to compute the Helmholtz free energy of polarisation of an arbitrary distribution of charges imbedded in concentric dielectric shells, we have to solve the Laplace equation (LE):

$$\nabla^2 \Phi = 0 \,, \tag{C.1a}$$

for the regions without ionic atmosphere, and the linearised Poisson-Boltzmann equation (PBE):

$$\left(\nabla^2 - \kappa^2\right)\Phi = 0 \,, \tag{C.1b}$$

for the regions including ionic atmosphere, where Φ indicates the electrostatic potential and κ the Debye inverse length parameter, which is proportional to the square root of ionic strength:

$$\kappa^2 = \frac{\pi N_A e^2}{125 \varepsilon k_B T} I \,. \tag{C.2}$$

General solutions of (C.1a) and (C.1b) read

$$\Phi_{\mathrm{LE}} = \sum_k \frac{B_k}{|\mathbf{r} - \mathbf{r}_k|} \,, \tag{C.3a}$$

$$\Phi_{\mathrm{PBE}} = \sum_k \left(\frac{A_k}{|\mathbf{r} - \mathbf{r}_k|} \mathrm{e}^{-\kappa|\mathbf{r}-\mathbf{r}_k|} + \frac{B_k}{|\mathbf{r} - \mathbf{r}_k|} \mathrm{e}^{\kappa|\mathbf{r}-\mathbf{r}_k|} \right) \,, \tag{C.3b}$$

respectively, where the sums run over all charges, and the constants A_k and B_k are obtained when appropriate boundary conditions are imposed. The boundary conditions needed to solve the problem are: (1) continuity of the electric potential across the boundary surfaces Σ_i, and (2) continuity of the normal component of the dielectric displacement vector across the boundary surface Σ_i. Once solved LE

and/or PBE for the bounded problem, we are able to determine the potentials within the cavity, Φ_C the bulk, Φ_B, and (in case) the sub-shells. The charges within the cavity induce a polarisation in the dielectric, giving rise to a reaction potential, $\Phi_{\mathrm{R}}\left(\mathbf{r}_k\right)$, which acts back on the dissolved charges. Once determined the analytical expression for $\Phi_{\mathrm{R}}\left(\mathbf{r}_k\right)$, the Helmholtz free energy of this interaction is just the difference between the reversible work of assembling the charge distribution in the presence of the dielectric and under *vacuum*, and simply reads:

$$A_{el} = \frac{1}{2}\sum_k q_k\left(\mathbf{r}_k\right)\Phi_{\mathrm{R}}\left(\mathbf{r}_k\right) \quad \textbf{(C.4)}$$

In the followings we will show the solution of the problem for some cavities with special symmetry.

The solution of the problem is analytical and in a closed-form if special symmetry conditions are verified for the shape of the cavity (and concentric shells). The simplest case is the spherical shape, which was solved by Kirkwood in 1934[17]. This is a case of our interest, since the PTA aggregates were determined to show two shapes, *viz.* sphere- and rod-like. In the following we shall derive a possible model for the latter aggregation geometry. We consider the shape of the cavity *C* as a cylinder of radius *a* and length *L*. In order to keep the problem rather general, we consider *C* as surrounded by another region, still cylindrical, of radius *b*, representing a local solvation, with a homogeneous, isotropic, continuum, dielectric shell, without ionic atmosphere, characterised by a dielectric constant, ε_{shell}. The bulk region is the one containing ionic atmosphere. In cylindrical coordinates, the position of charges is described by the vector $\mathbf{r}_k \equiv \left(\rho_k \quad \theta_k \quad z_k\right)$. After some elementary calculus, we find that for the cylindrical cavity eq. (C.4) reads:

$$A_{el} = \frac{1}{\varepsilon_C L}\sum_{kl} q_k q_l\left(\Phi_0 + \Phi_1 + \Phi_2 + \Phi_4\right), \quad \textbf{(C.5)}$$

where:

$$\Phi_0 \equiv \left(\frac{1}{\varepsilon_a} - 1\right)\left[\frac{1}{\varepsilon_b}\frac{K_0\left(\kappa b\right)}{\left(\kappa b\right)K_1\left(\kappa b\right)} + \ln\frac{b}{a}\right] + \left[\frac{1}{\varepsilon_b}\frac{K_0\left(\kappa b\right)}{\left(\kappa b\right)K_1\left(\kappa b\right)} + \ln b\right], \quad \textbf{(C.6a)}$$

$$\Phi_1 \equiv \sum_{m=1}^{\infty}\frac{\cos\left[m\left(\theta_l - \theta_k\right)\right]}{m}\rho_l^m\rho_k^m\left[\left(\frac{1}{\varepsilon_a} - 1\right)\left(\frac{1}{a^{2m}} + \frac{\beta_m}{b^{2m}}\right) + \frac{\beta_m}{b^{2m}}\right], \quad \textbf{(C.6b)}$$

$$\Phi_2 \equiv 2\sum_{n=1}^{\infty}\cos\left[\lambda_n\left(z_l - z_k\right)\right]I_0\left(\lambda_n\rho_l\right)I_0\left(\lambda_n\rho_k\right)\left[\left(1-\varepsilon_a''\right)\frac{K_1\left(\lambda_n a\right)}{I_1\left(\lambda_n a\right)} + \varepsilon_a''\Psi_n^0\right], \quad \textbf{(C.6c)}$$

$$\Phi_4 \equiv 4\sum_{m=1}^{\infty}\cos\left[m\left(\theta_l - \theta_k\right)\right]\times \times\sum_{n=1}^{\infty}\left\{\cos\left[\lambda_n\left(z_l - z_k\right)\right]I_m\left(\lambda_n\rho_l\right)I_m\left(\lambda_n\rho_k\right)\left[-\left(1-\varepsilon_a'\right)\frac{K_m'\left(\lambda_n a\right)}{I_m'\left(\lambda_n a\right)} + \varepsilon'\Psi_n^m\right]\right\} \quad \textbf{(C.6d)}$$

In these equations, the functions $K_m\left(\xi\right)$ and $I_m\left(\xi\right)$ are the modified Bessel functions of *m*th order, and $K_m'\left(\xi\right)$ and $I_m'\left(\xi\right)$ their derivatives, computed as:

$$K_m'\left(\xi\right) = \frac{m}{\xi}K_m\left(\xi\right) - K_{m+1}\left(\xi\right) = -\left[\frac{m}{\xi}K_m\left(\xi\right) + K_{m-1}\left(\xi\right)\right], \quad \textbf{(C.7a)}$$

$$I'_m(\xi) = \frac{m}{\xi} I_m(\xi) + I_{m+1}(\xi) = -\left[\frac{m}{\xi} I_m(\xi) - I_{m-1}(\xi)\right]. \quad \textbf{(C.7b)}$$

In equations (C.6b) to (C.6d), the convergence of series was defined by a threshold value on energy 0.1 kJ/mol. The meaning of the other auxiliary variables and functions is explained hereafter.

$$\lambda_n \equiv 2\pi n / L, \quad \textbf{(C.8a)}$$

$$\mu_n \equiv \sqrt{\lambda_n^2 + \kappa^2}, \quad \textbf{(C.8b)}$$

$$\varepsilon_a \equiv \varepsilon_{shell} / \varepsilon_C, \quad \textbf{(C.8c)}$$

$$\varepsilon_b \equiv \varepsilon_B / \varepsilon_{shell}, \quad \textbf{(C.8d)}$$

$$\beta_m \equiv \frac{mK_m(\kappa b) + \varepsilon_b(\kappa b) K'_m(\kappa b)}{mK_m(\kappa b) - \varepsilon_b(\kappa b) K'_m(\kappa b)}, \quad \textbf{(C.8e)}$$

$$\Psi_n^0 \equiv \frac{-\varepsilon_b \mu_n K_1(\mu_n b) K_0(\lambda_n b) + \lambda_n K_0(\mu_n b) K_1(\lambda_n b)}{\varepsilon_b \mu_n K_1(\mu_n b) I_0(\lambda_n b) + \lambda_n K_0(\mu_n b) I_1(\lambda_n b)}, \quad \textbf{(C.8f)}$$

$$\Psi_n^m \equiv \frac{\varepsilon_b \mu_n K'_m(\mu_n b) K_m(\lambda_n b) - \lambda_n K_m(\mu_n b) K'_m(\lambda_n b)}{-\varepsilon_b \mu_n K'_m(\mu_n b) I_m(\lambda_n b) + \lambda_n K_m(\mu_n b) I'_m(\lambda_n b)}, \quad \textbf{(C.8g)}$$

$$\varepsilon'_a \equiv \left\{\frac{\lambda_n a}{\varepsilon_a}\left[(1-\varepsilon_a)\Psi_n^m I_m(\lambda_n a) I'_m(\lambda_n a) + K_m(\lambda_n a) I'_m(\lambda_n a) - \varepsilon_a K'_m(\lambda_n a) I_m(\lambda_n a)\right]\right\}^{-1}, \quad \textbf{(C.8h)}$$

$$\varepsilon''_a \equiv \left\{\frac{\lambda_n a}{\varepsilon_a}\left[(1-\varepsilon_a)\Psi_n^0 I_0(\lambda_n a) I_1(\lambda_n a) + K_0(\lambda_n a) I_1(\lambda_n a) + \varepsilon_a K_1(\lambda_n a) I_1(\lambda_n a)\right]\right\}^{-1}. \quad \textbf{(C.8i)}$$

C.2 Modelling Self-Assembled PTA Aggregates

C.2.1 Shape and Size

From the experiments, we know that we have two types of PTA aggregates, which we shall consider of spherical and cylindrical shape. From SEM pictures, we can estimate the average radius of the spherical aggregates r ~ (0.75 ÷ 1.00) × 10^{-6} m, and the dimensions of the cylindrical aggregates a ~ 0.5 × 10^{-6} m (radius) and L ~ 40 × 10^{-6} m (length). Concerning the intermediate shell, its thickness was computed as the 20 % of the radius of the aggregate.

In the model we exposed in Paragraph C.1, the molecular system is defined by the position and amount of atomic charges. The geometry of the aggregate is not available, either experimentally or computationally. To circumvent this lack we modelled the aggregate as constituted of close-packed spheres, each containing a randomly oriented molecule of DGE, whose optimised geometry and atomic charges are known by QM calculations. The radius of these spheres was taken so that their volume reproduces the same molecular volume of DGE.

C.2.2 Dielectric properties

The dielectric constant of the solution ("bulk") was calculated as a function of the water/co-solvent ratio by means of the parameterization described in ref.[1] (Table SA2). The ionic strength of this region was varied (I = 0.0, 0.1, and 1.0 M).

In order to estimate the dielectric constant inside the cavity, we made the assumption that the cavity is filled of a dielectric material having the same dielectric constant of DGE. From the quantum mechanical calculations performed for DGE, we obtained the static

isotropic molecular electric polarizability, α_0. From α_0, it is possible to calculate the dielectric constant using the Mossotti-Clausius equation ($\varepsilon_C \sim 5.5$).

Concerning the intermediate shell, two values of dielectric constant were considered, $\varepsilon_{shell} = \varepsilon_B$ and $\varepsilon_{shell} = (\varepsilon_C + \varepsilon_B) / 2$.

The reference state is defined by the gas phase ($\varepsilon_B = 1$ and $\varepsilon_{shell} = 1$; $I = 0.0$ M).

C.3 Results

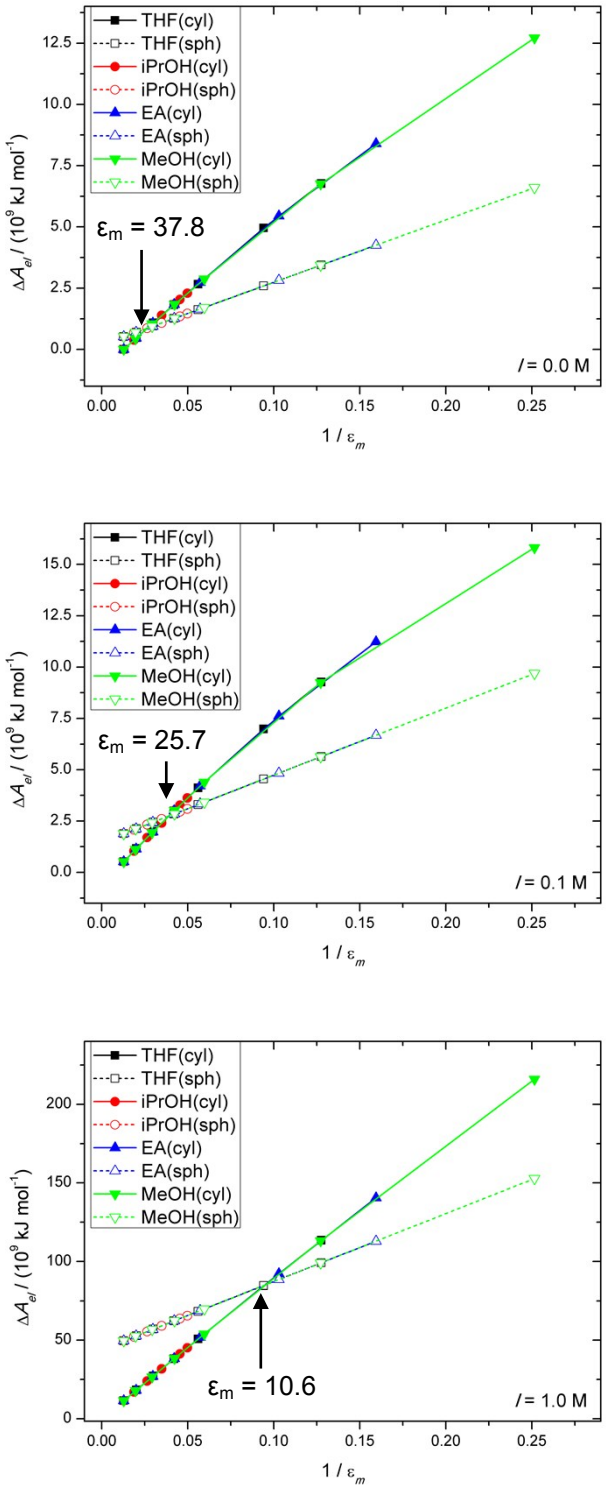

Figure SC.1. Energy of spherical (unfilled symbols) and cylindrical (filled symbols) aggregates as a function of the dielectric constant and ionic strength of the environment.

References

1 A. Jouyban and S. Soltanpour, *J. Chem. Eng. Date* 2010, **55**, 2951-2963.
2 L. A. Curtiss, P. C. Redfern and K. Raghavachari, *J. Chem. Phys.*, 2007, **126**, 084108.
3 R. F. W. Bader, *Chem. Rev.* , 1991, **91**, 893-928.
4 R. A. Boto, J. Contreras-García, J. Tierny and J.-P. Piquemal, *Mol. Phys.*, 2016, **114**, 1406-1414.
5 Y. Zhang, H. He, K. Dong, M. Fan and S. Zhang, *RSC Adv.*, 2017, **7**, 12670-12681.
6 A. D. Becke, *J. Chem. Phys.* , 1993, **98**, 5648-5652.
7 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
8 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem.*, 2011, **32**, 1456-1465.
9 A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639-5648.
10 R. C. Binning and L. A. Curtiss, *J. Comp. Chem*, 1990, **11**, 1206-1216.
11 M. P. McGrath and L. Radom, *The Journal of Chemical Physics*, 1991, **94**, 511-516.
12 L. A. Curtiss, M. P. McGrath, J. P. Blaudeau, N. E. Davis, R. C. Binning and L. Radom, *J. Chem. Phys.*, 1995, **103**, 6104-6113.
13 J. Tomasi, B. Mennucci and E. Cancès, *J. Mol. Struct: Theochem.*, 1999, **464**, 211-226.
14 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378-6396.
15 T. G. W. Frisch M J, Schlegel H B, et al., *Gaussian 09, Revision D.01, Gaussian, Inc.: Wallingford, CT,*, 2009.
16 W. Biegler‐könig Friedrich, F. W. Bader Richard and T. H. Tang, *J. Comput. Chem.*, 1982, **3**, 317-328.
17 J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351-361.