Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information for:

3D-RISM-KH Molecular Theory of Solvation and Density Functional Theory Investigation of the Role of Water in the Aggregation of Model Asphaltenes

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Table S1: DFT method exploration: Gas phase ^{1}H NMR shifts for benzene, pyridine and pyrene relative to TMS in $CHCl_3$

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Basis	Proton	EXP	B3LYP-D	Error (%)	WB97XD	Error (%)	B97D	Error (%)
					Benzene			
6-31G(d)	H	7.34	6.91	-5.86	7.12	-3.00	6.75	-8.04
6-31G(d,p)	H		7.12	-3.00	7.30	-0.54	6.99	-4.77
6-31+G(d)	H		7.09	-3.41	7.29	-0.68	6.89	-6.13
6-31+G(d,p)	H		7.08	-3.54	7.45	1.50	7.14	-2.72
					Pyridine			
6-31G(d)	H_1	7.23	6.69	-7.47	6.89	-4.70	6.53	-9.68
	H_2	8.59	8.34	-2.91	8.52	-0.81	8.17	-4.89
	H_3	7.62	7.07	-7.22	7.31	-4.07	6.88	-9.71
6-31G(d,p)	H_1		6.93	-4.15	7.10	-1.80	6.79	-6.09
	H_2		8.52	-0.81	8.67	0.93	8.40	-2.21
	H_3		7.28	-4.46	7.49	-1.71	7.12	-6.56
6-31+G(d)	H_1		6.87	-4.98	7.04	-2.63	6.67	-7.75
	H_2		8.50	-1.05	8.62	0.35	8.31	-3.26
	H_3		7.28	-4.46	7.48	-1.84	7.05	-7.48
6-31+G(d,p)	H_1		7.10	-1.80	7.23	-0.01	6.93	-4.15
	H_2		8.64	0.58	8.75	1.86	8.51	-0.93
	H_3		7.48	-1.84	7.65	0.39	7.23	-5.12
					Pyrene			
6-31G(d)	H_1	7.99	7.60	-4.88	7.74	-3.13	7.46	-6.63
	H_2	8.16	7.72	-5.39	7.91	-3.06	7.55	-7.48
	H_3	8.05	7.71	-4.22	7.89	-1.99	7.55	-6.21
6-31G(d,p)	H_1		7.79	-2.50	7.92	-0.88	7.66	-4.13
	H_2		7.91	-3.06	8.09	-0.86	7.77	-4.78
	H_3		7.89	-1.99	8.06	0.12	7.75	-3.73
6-31+G(d)	H_1		7.87	-1.50	7.79	-2.50	7.62	-4.63
	H_2		7.93	-2.82	8.60	5.39	7.69	-5.76
	H_3		7.89	-1.99	7.94	-1.37	7.63	-5.22
6-31+G(d,p)	H_1		8.04	0.63	7.91	-1.00	7.90	-1.13
	H_2		8.14	-0.25	8.64	5.88	7.94	-2.70
	H_3		8.06	0.12	8.11	0.75	7.91	-1.74

Table S2: DFT method exploration: CPCM ^{1}H NMR shifts for benzene, pyridine and pyrene relative to TMS in $CHCl_3$.

Basis	Proton	EXP	B3LYP-D	Error (%)	WB97XD	Error (%)	B97D	Error (%)
					Benzene			
6-31G(d)	H	7.34	7.17	-2.32	7.25	-1.23	6.86	-6.54
6-31G(d,p)	H		7.35	0.14	7.44	1.36	7.10	-3.27
6-31+G(d)	H		7.37	0.41	7.43	1.23	7.02	-4.36
6-31+G(d,p)	H		7.57	3.13	7.59	3.41	7.27	-0.95
					Pyridine			
6-31G(d)	H_1	7.23	7.08	-2.07	7.10	-1.80	6.73	-6.92
	H_2	8.59	8.47	-1.40	8.52	-0.81	8.16	-5.01
	H_3	7.62	7.48	-1.84	7.55	-0.92	7.09	-6.96
6-31G(d,p)	H_1		7.31	1.11	7.32	1.24	6.99	-3.32
	H_2		8.64	0.58	8.67	0.93	8.39	-2.33
	H_3		7.67	0.66	7.72	1.31	7.33	-3.81
6-31+G(d)	H_1		7.29	0.83	7.28	0.69	6.90	-4.56
	H_2		8.63	0.47	8.62	0.35	8.31	-3.26
	H_3		7.72	1.31	7.74	1.57	7.29	-4.33
6-31+G(d,p)	H_1		7.52	4.01	7.47	3.32	7.15	-1.11
	H_2		8.78	2.21	8.75	1.86	8.50	-1.05
	H_3		7.92	3.94	7.91	3.81	7.53	-1.18
					Pyrene			
6-31G(d)	H_1	7.99	7.91	-1.00	7.90	-1.13	7.60	-4.88
	H_2	8.16	8.02	-1.72	8.08	-0.98	7.70	-5.64
	H_3	8.05	8.01	-0.50	8.04	-0.12	7.69	-4.47
6-31G(d,p)	H_1		7.96	-0.38	8.08	1.13	7.81	-2.25
	H_2		8.09	-0.86	8.26	1.23	7.92	-2.94
	H_3		8.05	-0.05	8.10	0.62	7.89	-1.99
6-31+G(d)	H_1		8.06	0.88	7.96	-0.38	7.79	-2.50
	H_2		8.12	-0.49	8.79	7.72	7.84	-3.92
	H_3		8.06	0.12	8.13	0.99	7.79	-3.23
6-31+G(d,p)	H_1		8.19	2.50	8.07	1.00	8.07	1.00
	H_2		8.30	1.72	8.83	8.21	8.09	-0.86
	H_3		8.19	1.74	8.29	2.98	8.08	0.37

Table S3: DFT method exploration: PCM ^{1}H NMR shifts for benzene, pyridine and pyrene relative to TMS in $CHCl_3$.

Basis	Proton	EXP	B3LYP-D	Error (%)	WB97XD	Error (%)	B97D	Error (%)
				Benzene				
6-31G(d)	H	7.34	7.14	-2.72	7.23	-1.50	6.85	-6.68
6-31+G(d)	H		7.33	-0.14	7.41	0.95	7.03	-4.22
6-31+G(d,p)	H		7.51	2.32	7.56	3.00	7.27	-0.95
				Pyridine				
6-31G(d)	H_1	7.23	7.04	-2.63	7.08	-2.07	6.71	-7.19
	H_2	8.59	8.45	-1.63	8.51	-0.93	8.16	-5.01
	H_3	7.62	7.44	-2.36	7.52	-1.31	7.07	-7.22
6-31+G(d)	H_1		7.24	0.14	7.25	0.28	6.88	-4.84
	H_2		8.61	0.23	8.61	0.23	8.31	-3.26
	H_3		7.67	0.66	7.71	1.18	7.27	-4.59
6-31+G(d,p)	H_1		7.47	3.32	7.44	2.90	7.13	-1.38
	H_2		8.75	1.86	8.74	1.75	8.50	-1.05
	H_3		7.87	3.28	7.88	3.41	7.51	-1.44
				Pyrene				
6-31G(d)	H_1	7.99	7.75	-3.00	7.87	-1.50	7.58	-5.08
	H_2	8.16	7.86	-3.68	8.05	-1.35	7.68	-5.93
	H_3	8.05	7.86	-2.36	8.01	-0.50	7.67	-4.80
6-31+G(d)	H_1		8.01	0.25	7.90	-1.13	7.78	-2.76
	H_2		8.06	-1.23	8.26	1.23	7.77	-4.79
	H_3		8.01	-0.50	8.09	0.50	7.82	-2.93
6-31+G(d,p)	H_1		8.17	2.25	8.05	0.75	8.04	-0.69
	H_2		8.27	1.35	8.30	1.72	8.07	-1.16
	H_3		8.17	1.49	8.26	2.61	8.05	-0.03

Table S4: Interaction energies, enthalpies, and Gibbs free energies (kcal.mol^{-1}) defined in eq. 6 for the dimers of 2,2'-bipyridine with alternative N atom configuration presented in Figure S2 calculated with the WB97Xd(B3LYP-DCP)/6-31G(d,p) methods and PCM solvation model.

Structure	ΔE	ΔH	ΔG^{298}	d_{BIP}	d_{PYR}
4	-9.2(-8.3)	-8.7(-8.5)	1.7(4.7)	3.39(3.39)	-
5	-49.0(-41.6)	-51.5(-44.1)	2.4(10.0)	3.33(3.23)	-
6	-64.8(-55.2)	-68.2(-58.8)	3.8(15.1)	3.31(3.21)	-
8	-43.1(-37.5)	-43.4(-37.7)	-23.4(-14.1)	3.32(3.28)	3.60(3.49)
9	-67.63(56.9)	-69.24(-59.5)	-25.12(-10.0)	3.29(3.26)	3.62(3.52)
10	-88.2(-72.2)	-90.1(-75.7)	-26.7(-7.9)	3.33(3.35)	3.75(3.48)
11	-107.3(-84.8)	-112.4(-90.1)	-27.1(-0.6)	3.31(3.33)	3.70(3.69)
12	-129.1(-103.4)	-135.5(-109.1)	-26.8(3.1)	3.38(3.40)	3.31(3.35)

Table S5: Interaction energies, enthalpies, and Gibbs free energies (kcal.mol^{-1}) defined in eq. 6 for the PBP dimers calculated with the WB97Xd(B3LYP-DCP)/6-31G(d,p) methods in gas phase.

Structure	ΔE	ΔH	ΔG^{298}
8	-47.7(-39.0)	-47.7(-39.2)	-28.9(-15.2)
9	-76.5(-62.1)	-78.0(-64.0)	-36.8(-18.3)
10	-101.7(-83.7)	-104.7(-87.5)	-41.9(-21.1)
11	-125.9(-103.4)	-130.6(-108.4)	-45.7(-22.0)
12	-153.0(-125.8)	-159.8(-132.7)	-52.7(-25.0)

Figure S1: DFSE of PBP in water-saturated chloroform solvent (left) and water in water (right).

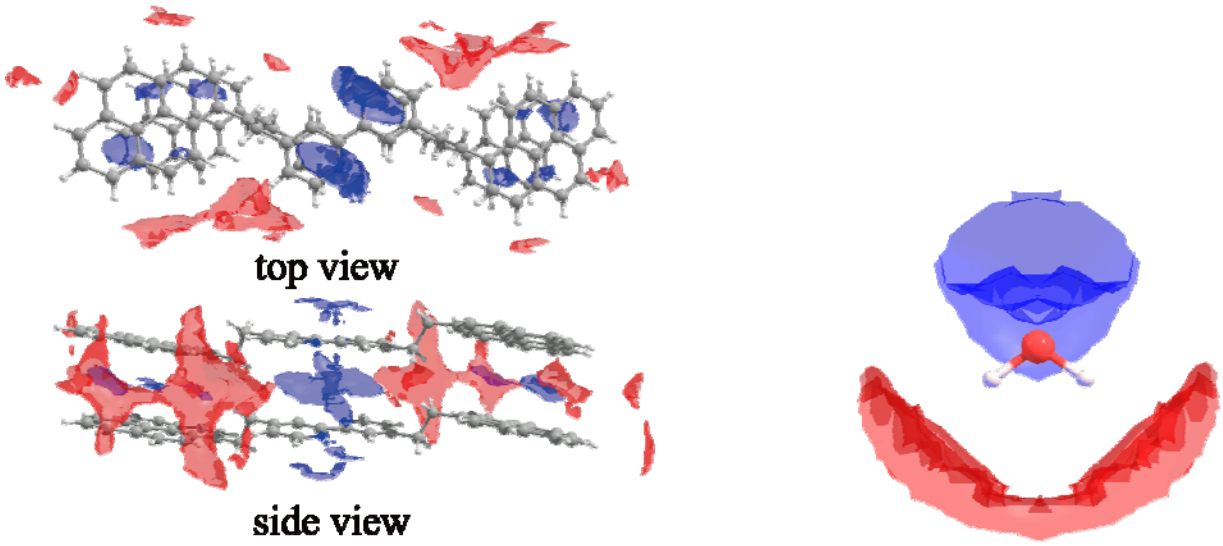

Figure S2: Optimized structures of aggregates, in an alternative N atom configuration, containing 2,2‘-bipyridine, PBP, and water.