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Electronic Supplementary Information for

Energetics and molecular structure of an ion-paired supramolecular system in water

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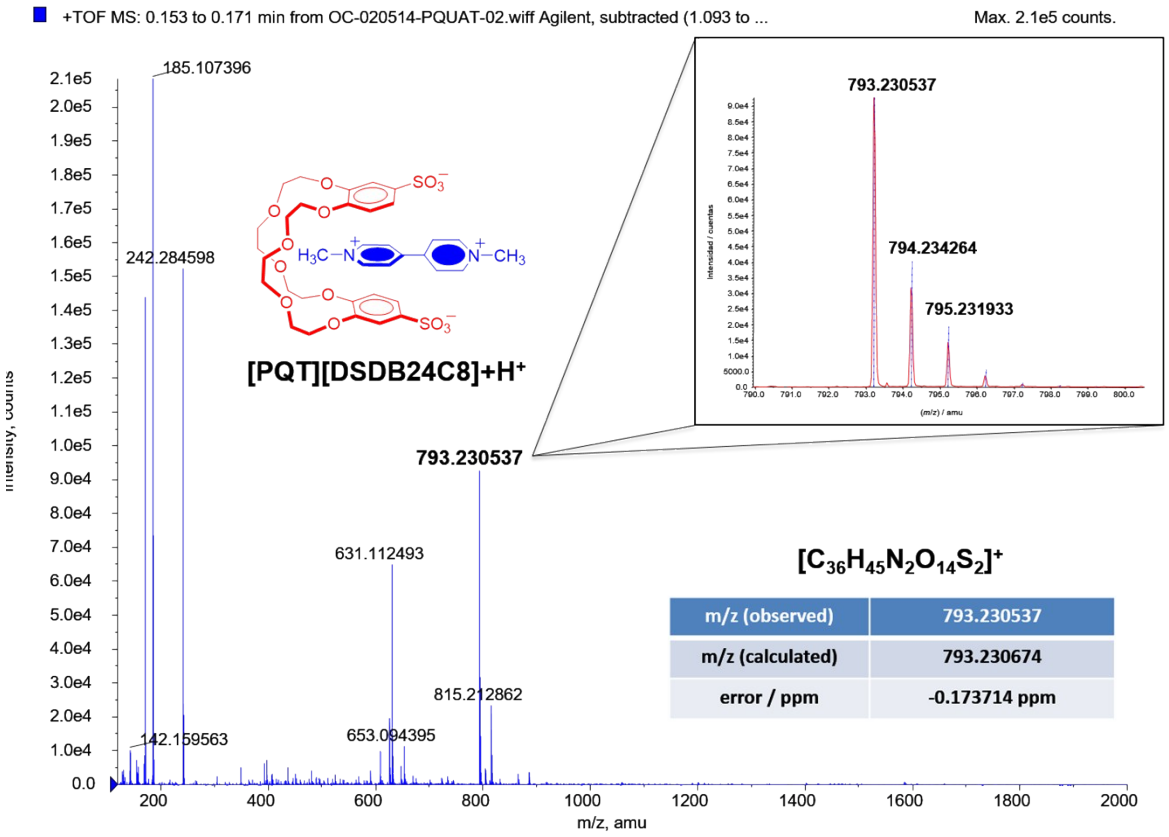

Figure S1. Representative TOF MS spectrum of the supramolecular ion pair [PQT][DSDB24C8].

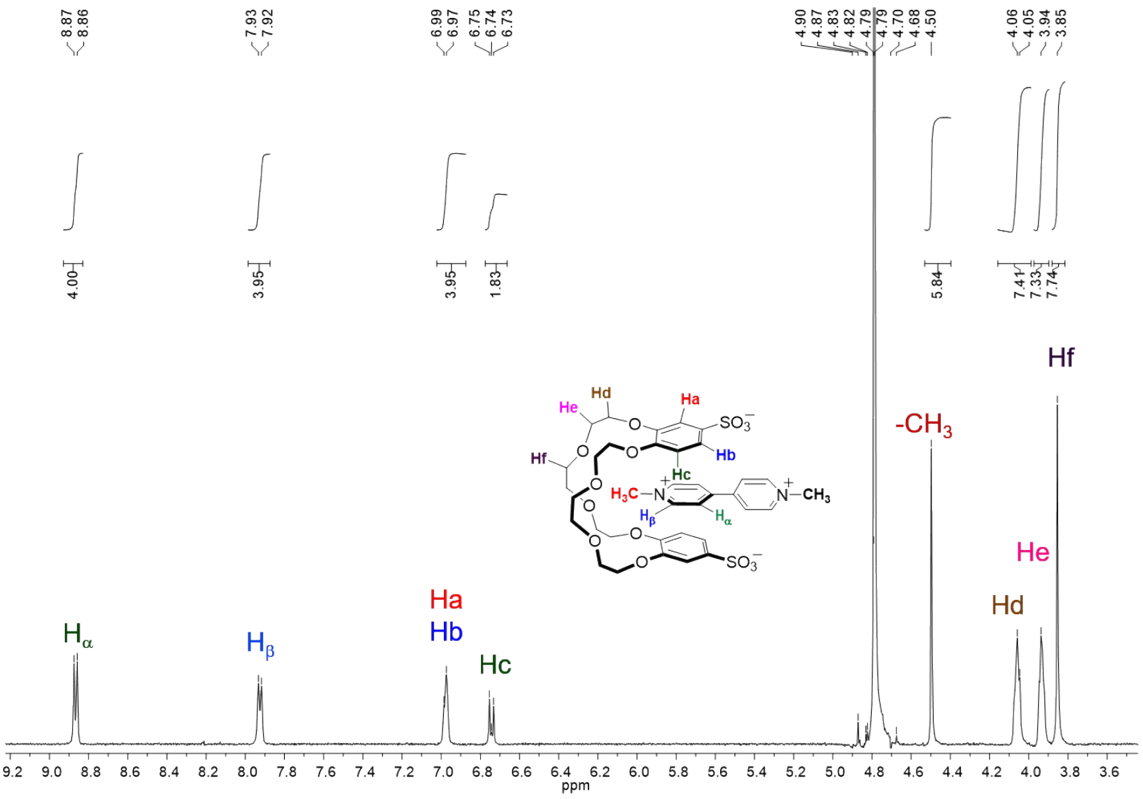

Figure S2. Representative H^1 NMR spectrum of the supramolecular ion pair [PQT][DSDB24C8].

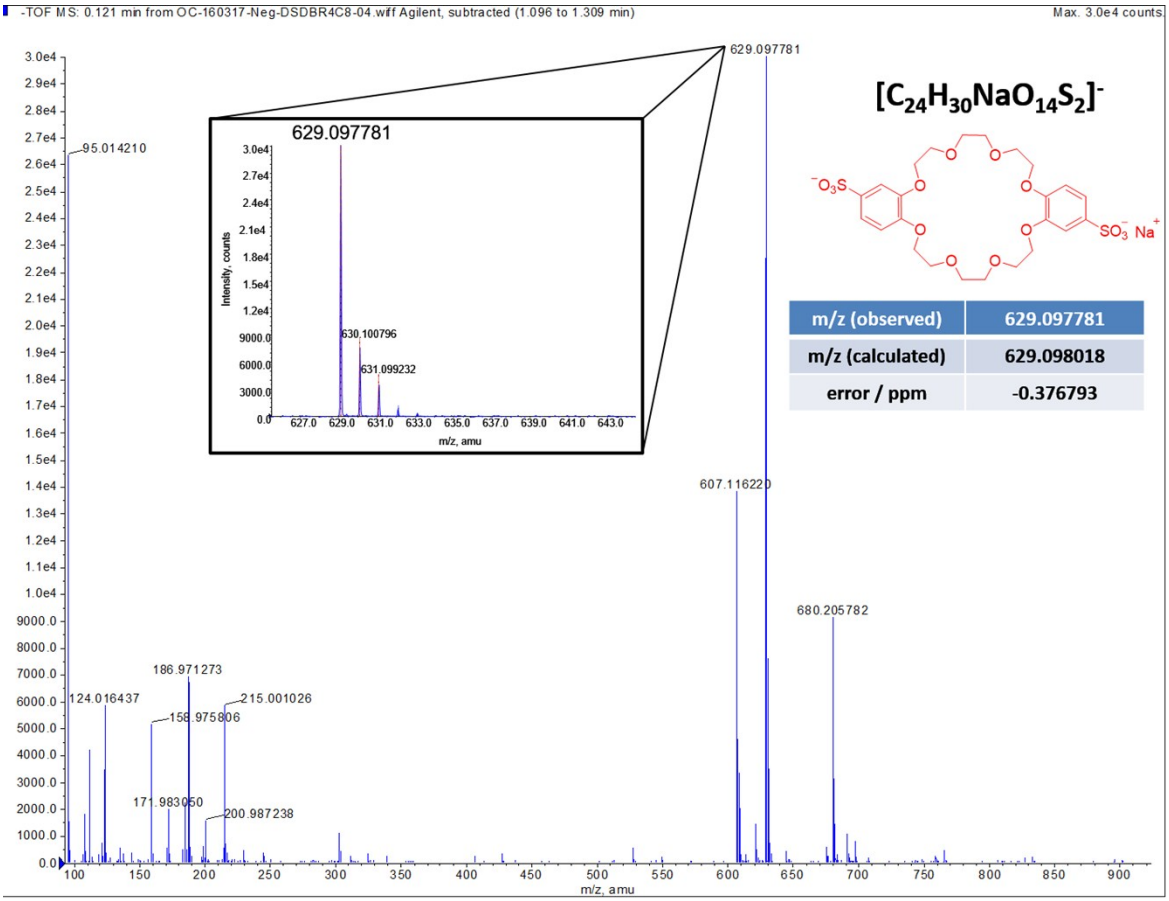

Figure S3. Representative -TOF MS spectrum of the disulfonated crown ether $[N(CH_3)_4]_2$[DSDB24C8].

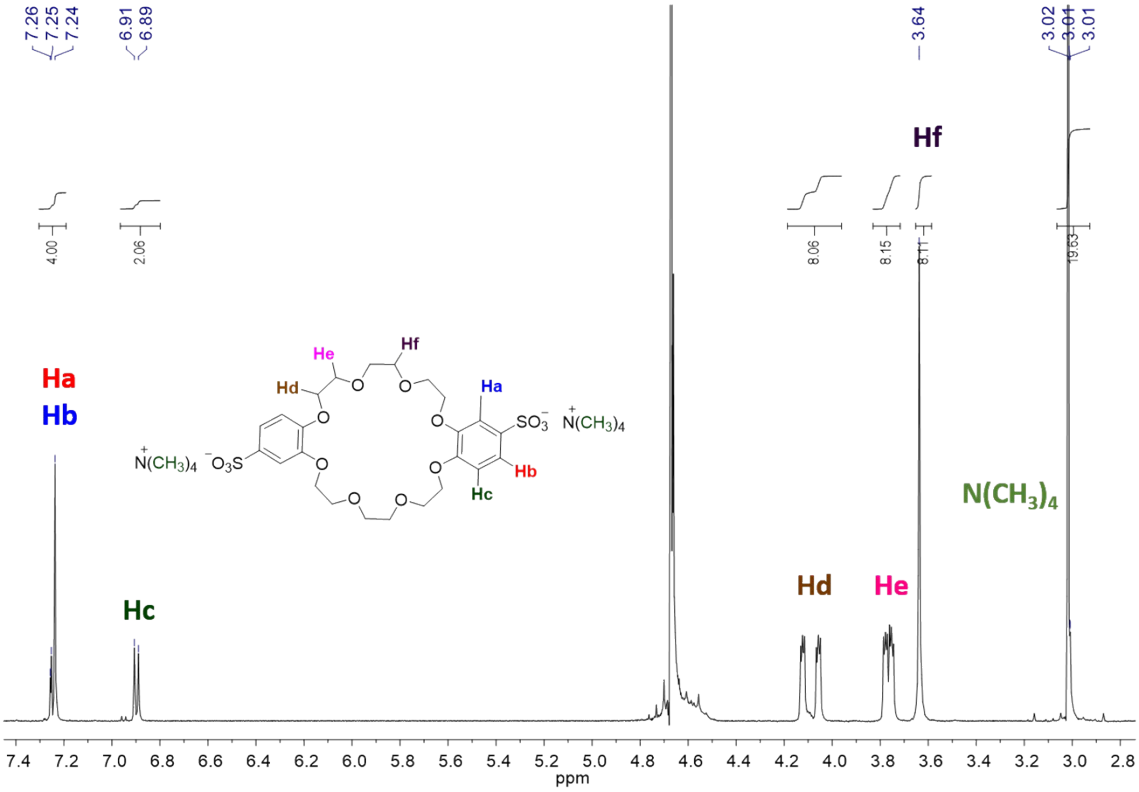

Figure S4. Representative H^1 NMR spectrum of the disulfonated crown ether $[N(CH_3)_4]_2$[DSDB24C8].

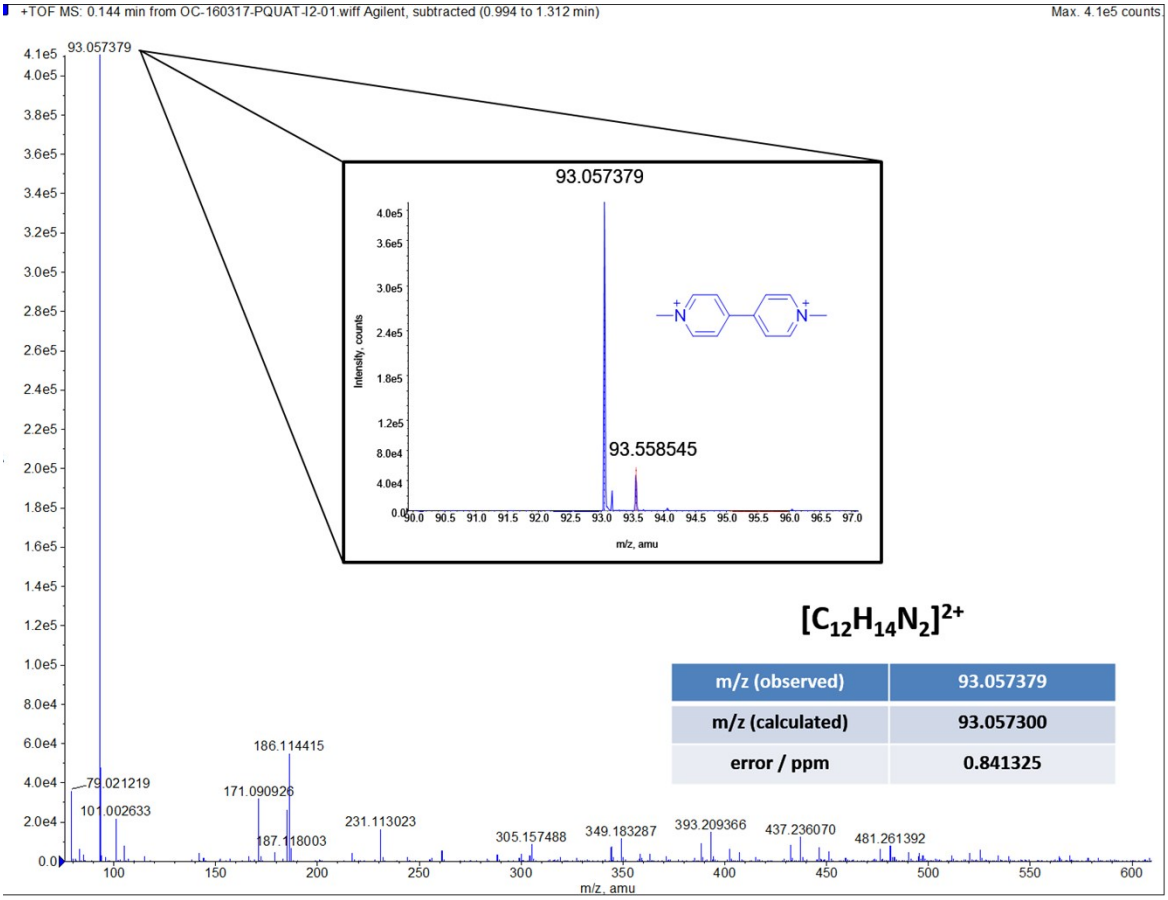

Figure S5. Representative TOF MS spectrum of the salt $[PQT][I]_2$

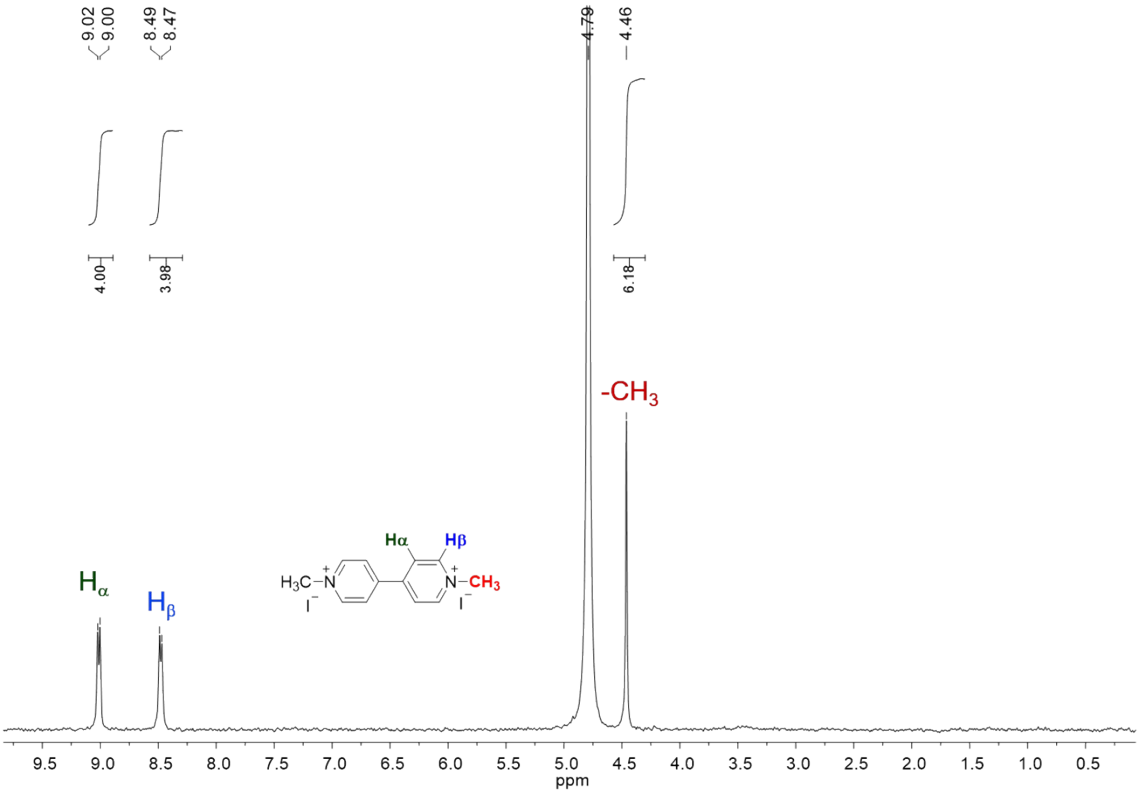

Figure S6. Representative ^{1}H NMR spectrum of the salt $[PQT][I]_2$.

Experimental procedure for NMR titrations: A volume of 0.5 mL of a 2 mM $[PQT][I]_2$ ($1.0x10^{-6}$ mol) solution, was sequentially added with 2 μL of a 0.1 M solution containing the anionic crown ether $[N(CH_3)_4]_2[DSDB24C8]$ ($2x10^{-7}$ mol). Both solutions were prepared using deuterated water as the solvent. After each addition, the corresponding ^1H NMR spectrum of the mixture was recorded on a Bruker 300 MHz spectrophotometer at 298.15 K. The chemical shifts of hydrogen atoms H_α, H_β and those belonging to $-CH_3$ in the dication $[PQT]^{2+}$ were monitored as the concentration of $[N(CH_3)_4]_2[DSDB24C8]$ increased, and their values were plotted against the anionic crown ether concentration to obtain three different association constants (see Table S1) by a least-squares nonlinear fitting by means of the software WinEQNMR.[1] In figure S7, the variation of the chemical shifts of the hydrogen atoms belonging to $[PQT]^{2+}$ with different equivalent amounts of $[DSDB24C8]^{2-}$ added is shown.

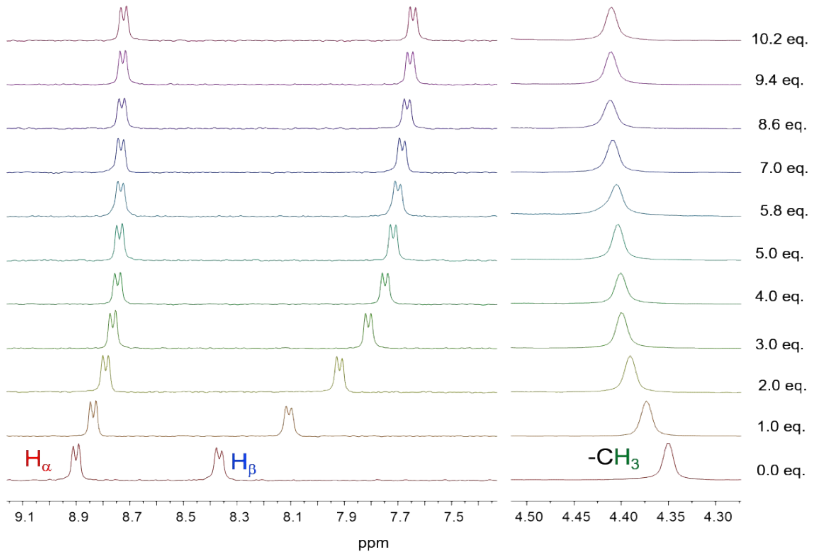

Figure S7. Variation of the chemical shifts of protons H_α, H_β and $-CH_3$ upon the addition of different equivalent values of $[DSDB24C8]^{2-}$.

Table S1. $K_{as}(M^{-1})$ values determined by least-square fitting analysis from the ^1H NMR titration of $[PQT][I]_2$ with $[N(CH_3)_4]_2[DSDB24C8]$ in D_2O at 298 K.		
$-CH_3$	H_α	H_β
$(5.3\pm0.2)x10^2$	$(4.3\pm0.2)x10^2$	$(4.4\pm0.2)x10^2$
Average Value	K_{as}/M^{-1}	$(4.7\pm0.2)x10^2$

[1] Hynes, M. J. EQNMR: a computer program for the calculation of stability constant from nuclear magnetic resonance chemical shift data *J. Chem. Soc., Dalton Trans.* **1993**, 311–312

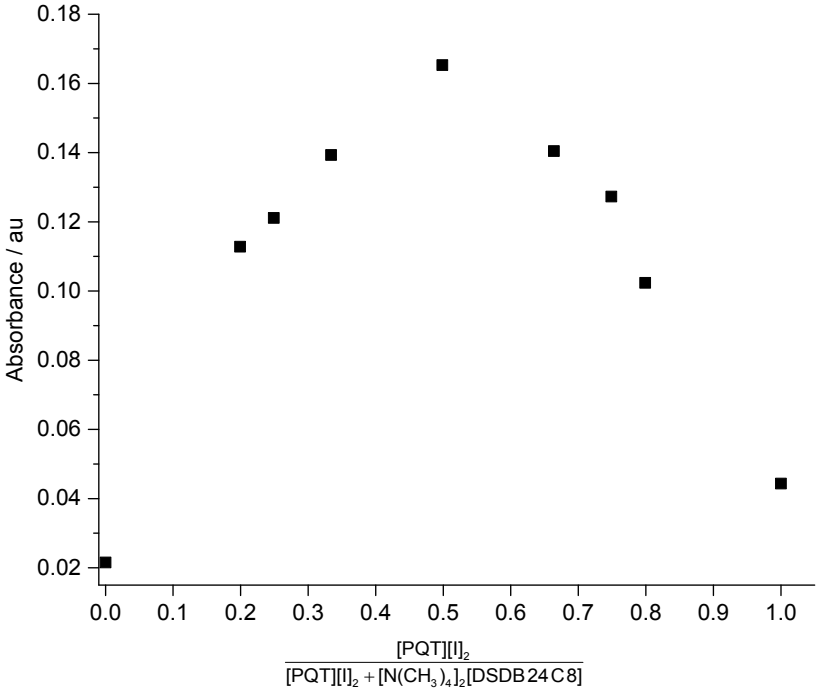

Figure S8. Job plot for the complex [PQT][DSDB24C8] ($\lambda = 370$ nm) in water at 298.15 K.

Table S2. Experimental data and results of the solution enthalpy of the tetramethyl ammonium anti-disulfodibenzo-24-crown-8 ether ($[N(CH_3)_4]_2$[DSDB24C8]), paraquat iodide $[PQT][I]_2$, the association complex [PQT][DSDB24C8] and tetramethyl ammonium iodide $N(CH_3)_4I$.

Exp.	m_{solute}/ mg	$n_{solute}\cdot10^5$/ mol	m_{H2O}/ mg	$n_{H2O}\cdot10^2$/ mol	n_{H2O}/n_{solute}	Q_{sol}/ J	**b**/ mol·kg^{-1}	$\Delta_{sol}H^o_m$/ kJ·mol^{-1}
				$[N(CH_3)_4]_2$ [DSDB24C8]				
1	13.242	1.754	3025.91	16.797	9576	0.3271	0.0058	18.65
2	17.212	2.280	3019.02	16.758	7350	0.4033	0.0076	17.69
3	22.038	2.919	3026.90	16.802	5756	0.5142	0.0096	17.61
4	14.780	1.958	2014.82	11.184	5712	0.3261	0.0097	16.66
5	7.246	0.960	800.13	4.442	4627	0.1703	0.0120	17.74
6	10.054	1.332	999.41	5.548	4165	0.2319	0.0133	17.41
7	33.072	4.381	3025.87	1.680	3834	0.7070	0.0145	16.14
8	12.628	1.673	1009.02	5.601	3348	0.2830	0.0166	16.92
9	9.703	1.285	558.88	3.102	2414	0.1954	0.0230	15.20
10	15.023	1.990	800.02	4.441	2232	0.3007	0.0249	15.11
$\Delta_{sol}H^o_m$/(kJ·mol^{-1})=-164.5·**b**+19.2				r^2=0.8116	σ_y=0.4	$\Delta_{sol}H^o_{m(\infty)}$=(19.2±0.4) kJ·mol^{-1}		
				$[PQT][I]_2$				
1	7.913	1.798	3038.17	16.865	9379	1.1348	0.0059	63.11
2	10.241	2.327	3040.22	16.876	7252	1.4561	0.0077	62.57
3	10.779	2.449	3003.62	16.673	6807	1.5139	0.0082	61.81
4	12.890	2.929	3026.90	16.802	5736	1.8221	0.0097	62.21
5	13.043	2.964	3060.55	16.989	5732	1.8557	0.0097	62.61
6	12.872	2.925	3008.30	16.699	5709	1.8630	0.0097	63.69
7	12.927	2.938	3014.47	16.733	5696	1.8756	0.0097	63.85
8	19.215	4.366	3002.68	16.668	3817	2.7767	0.0145	63.59
9	13.246	3.010	1022.82	5.678	1886	1.8432	0.0294	61.24
10	21.999	4.999	1007.76	5.594	1119	3.0722	0.0496	61.46
11	38.646	8.782	1042.57	5.787	659	5.2738	0.0842	60.05
12	47.641	10.826	1026.97	5.701	527	6.5771	0.1054	60.75
13	48.401	10.999	1003.28	5.569	506	6.6616	0.1096	60.57
14	60.068	13.650	1024.01	5.684	416	8.0314	0.1333	58.84
15	44.033	10.006	504.10	2.798	280	5.7902	0.1985	57.87
$\Delta_{sol}H^o_m$/(kJ·mol^{-1})=-27.1·**b**+63.0				r^2=0.8431	σ_y=0.3	$\Delta_{sol}H^o_{m(\infty)}$=(63.0±0.3) kJ·mol^{-1}		
				[PQT][DSDB24C8]				
1	3.990	0.503	1000.82	5.555	11039	0.2184	0.0050	43.40
2	6.655	0.839	1001.20	5.558	6621	0.3485	0.0084	41.52
3	10.005	1.262	1206.12	6.695	5306	0.4817	0.0105	38.17
4	9.998	1.261	1004.17	5.574	4420	0.5023	0.0126	39.83
5	15.940	2.010	1001.21	5.558	2764	0.7708	0.0201	38.34
6	20.002	2.523	1001.08	5.557	2203	0.8387	0.0252	33.24
$\Delta_{sol}H^o_m$/(kJ·mol^{-1})=-416.8·**b**+44.4				r^2=0.8275	σ_y=1.5	$\Delta_{sol}H^o_{m(\infty)}$=(44.4±1.5) kJ·mol^{-1}		
				$N(CH_3)_4I$				
1	10.343	5.145	1516.01	8.415	1636	2.0564	0.0339	39.97
2	12.404	6.170	1513.25	8.400	1361	2.4515	0.0408	39.73
3	10.050	4.999	1016.85	5.645	1129	1.9914	0.0492	39.84
4	20.008	9.952	1022.20	5.674	570	4.0146	0.0974	40.34
5	29.991	14.917	1026.64	5.699	382	6.0523	0.1453	40.57
6	40.053	19.922	1007.09	5.590	281	8.1148	0.1978	40.73
7	49.884	24.812	1025.07	5.690	229	9.9706	0.2421	40.18
8	60.142	29.914	1030.62	5.721	191	11.8887	0.2903	39.74
$\Delta_{sol}H^o_m$/(kJ·mol^{-1})=-53.0·**b**^{2}+17.2·**b**+39.2				r^2=0.8843	σ_y=0.2	$\Delta_{sol}H^o_{m(\infty)}$=(39.2±0.2) kJ·mol^{-1}		

Q_{sol}, is the heat evolved in each dissolution experiment calculated from the calorimetric curve; **b**, is the molality of the resulting solution. The uncertainty of the enthalpy of solution at infinite dilution $u\left[\Delta_{sol}H^o_m(\infty),\text{compound}\right]$ is the standard deviation of the intercept calculated

from the least-square fit of the data to a linear or a polynomial second-order equation.

Table S3. Detailed experimental data and results of the enthalpy of association between the dianionic host $[DSDB24C8]^{2-}$ and the dicationic guest $[PQT]^{2+}$. The enthalpy of association was computed from equation $\Delta_{as\text{-}dil}H^{o}_{m} = \Delta_{dil}H^{o}_{m}[N(CH_3)_4]_2[DSDB24C8] + \Delta_{dil}H^{o}_{m}[PQT][I]_2 + \Delta_{as}H^{o}_{m}$ derived from the path II of Scheme 2 of the article.

$m_{DSDB24C8}$ / mg	$n_{DSDB24C8}$ / 10^{-5} mol	$m_{H_2O\ solution\ DSDB24C8}$ / mg	$b_{initial\ DSDB24C8}$ / mol/kg	m_{PQT} / mg	n_{PQT} / 10^{-5} mol	$m_{H_2O\ solution\ PQT}$ / mg	$b_{initial\ PQT}$ / mol/kg	n_{PQT} / $n_{DSDB24C8}$	$m_{H_2O\ solution\ after\ mixing}$ / mg	$b_{final\ DSDB24C8}$ / mol/kg	$\Delta_{dil}H^{o}_{m\ DSDB24C8}$ / kJ/mol	$b_{final\ PQT}$ / mol/kg	$\Delta_{dil}H^{o}_{m\ PQT}$ / kJ/mol	$Q_{as\text{-}dil}$ / J	$\Delta_{as\ -\ dil}H^{o}_{m}$ / kJ/mol	$b_{final\ complex}$ / mol/kg	$\Delta_{as}H^{o}_{m}$ / kJ/mol
7.504	0.994	1001.716	0.0099	4.43	1.007	1001.21	0.0101	1.013	2002.93	0.0050	0.8	0.0050	0.1	-0.2840	-28.6	0.0050	-29.5
9.410	1.247	1000.381	0.0125	5.54	1.259	1001.72	0.0126	1.010	2002.10	0.0062	1.0	0.0063	0.2	-0.3341	-26.8	0.0062	-28.0
11.330	1.501	1000.668	0.0150	6.66	1.513	1000.65	0.0151	1.008	2001.32	0.0075	1.2	0.0076	0.2	-0.3826	-25.5	0.0075	-26.9
12.806	1.696	1000.980	0.0170	7.51	1.707	1000.84	0.0171	1.006	2001.82	0.0085	1.4	0.0085	0.2	-0.4268	-25.2	0.0085	-26.8
15.111	2.002	1002.150	0.0200	8.89	2.020	1009.21	0.0200	1.009	2011.36	0.0100	1.6	0.0100	0.3	-0.5096	-25.5	0.0100	-27.4
16.591	2.198	1000.320	0.0220	9.75	2.216	1000.68	0.0221	1.008	2001.00	0.0110	1.8	0.0111	0.3	-0.5724	-26.0	0.0110	-28.2
16.613	2.201	1001.004	0.0220	9.75	2.216	1000.90	0.0221	1.007	2001.90	0.0110	1.8	0.0111	0.3	-0.6150	-27.9	0.0110	-30.1
18.103	2.398	1000.280	0.0240	10.64	2.415	1001.38	0.0242	1.008	2001.66	0.0120	2.0	0.0121	0.3	-0.6259	-26.1	0.0120	-28.4
18.901	2.504	1000.552	0.0250	11.01	2.502	1003.36	0.0249	0.999	2003.91	0.0125	2.1	0.0125	0.3	-0.7243	-28.9	0.0125	-31.3
22.610	2.995	1000.420	0.0299	13.72	3.118	1001.24	0.0311	1.041	2001.66	0.0150	2.5	0.0156	0.4	-0.8753	-29.2	0.0150	-32.1

$\Delta_{as}H^{o}_{m}$/(kJ·mol^{-1})=-114911.2·b^2 + 1894.8·b - 35.4 r^2=0.7135 σ_y=3.6 $\Delta_{as}H^{o}_{m}(\infty)$/(kJ·mol^{-1})=-35.4±3.7

DSDB24C8 refers to anti-disulfodibenzo[24]crown-8 tetramethyl ammonium; PQT refers to paraquat iodide; $m_{H_2O\ solution}$ is the mass of water in the respective solution; $\mathbf{b}_{initial}$ is the initial molal concentration of the solution of the respective reactant;

$\mathbf{b}_{final}$ is the final molal concentration of the solution of the respective reactant; dilution enthalpy for DSDB24C8 was calculated as $^{\Delta_{dil}H^{o}_{m}(DSDB24C8)}$=-164.5·($b^2_{final}$-$b^2_{initial}$); dilution enthalpy for [PQT][I]$_2$ was calculated as $^{\Delta_{dil}H^{o}_{m}(PQT)}$=-27.1·($b^2_{final}$-$b^2_{initial}$). Uncertainty associated to each result of enthalpy of dilution was computed as $u\left[\Delta_{dil}H^{o}_{m}(DSDB24C8)\right] = \sqrt{2\left\{u\left[\Delta_{sol}H^{o}_{m}(\infty), DSDB24C8\right]\right\}^2}$ = ±0.6 kJ·mol^{-1} and $u[\Delta_{dil}H^{o}_{m}(PQT)] = \sqrt{2\{u\left[\Delta_{sol}H^{o}_{m}(\infty), PQT\right]\}^2}$ =±0.4 kJ·mol^{-1}. Uncertainty of the result of enthalpy of association-dilution at infinite dilution, $u\left[\Delta_{aso\text{-}dil}H^{o}_{m}(\infty)\right]$, was calculated as ±3.6 kJ·mol^{-1} and is the standard deviation of the intercept calculated from the least squares fitting of data $^{\Delta_{aso\text{-}dil}H^{o}_{m}}$ vs **b** to a second-order function. Uncertainty of the enthalpy of association at infinite dilution represents the overall uncertainty calculated as $u^{[\Delta_{aso}H^{o}_{m}(\infty)]} = \sqrt{\{u\left[\Delta_{aso\text{-}dil}H^{o}_{m}(\infty)\right]\}^2 + \left\{u\left[\Delta_{dil}H^{o}_{m}(\infty), DSDB24C8\right]\right\}^2 + \{u\left[\Delta_{dil}H^{o}_{m}(\infty), PQT\right]\}^2}$ = ±3.7 kJ·mol^{-1}.

Table S4. Detailed experimental data and results of the enthalpy of association between the dianionic host $[DSDB24C8]^{2-}$ and the dicationic guest $[PQT]^{2+}$. The enthalpy of association was computed from equation $\Delta_{as\text{-}dil}H^{o}_{m} = \Delta_{as}H^{o}_{m} + \Delta_{dil}H^{o}_{m}[PQT][DSDB24C8] + \Delta_{dil}H^{o}_{m}\left[N(CH_3)_4I\right]$ derived from the path III of Scheme 2 of the article.

$m_{complex}$ / mg	$n_{complex}$ / 10^{-5} mol	$m_{H_2O\ solution\ complex}$ / mg	$\mathbf{b}_{initial\ complex}$ / mol/kg	$m_{N(CH3)4I2}$ / mg	$n_{N(CH_3)_4I_2}$ / 10^{-5} mol	$m_{H_2O\ solution\ N(CH_3)_4I_2}$ / mg	$\mathbf{b}_{initial\ N(CH_3)_4I_2}$ / mol/kg	$n_{N(CH_3)_4I_2}$ / $n_{complex}$	$m_{H_2O\ solution\ after\ mixing}$ / mg	$\mathbf{b}_{final\ complex}$ / mol/kg	$\Delta_{dil}H^{o}_{m\ complex}$ / kJ/mol	$\mathbf{b}_{final\ N(CH_3)_4I_2}$ / mol/kg	$\Delta_{dil}H^{o}_{m\ N(CH_3)_4I_2}$ / kJ/mol	$Q_{as\text{-}dil}$ / J	$\Delta_{as\text{-}dil}H^{o}_{m}$ / kJ/mol	$\mathbf{b}_{final\ complex}$ / mol/kg	$\Delta_{as}H^{o}_{m}$ / kJ/mol
7.881	0.994	1001.716	0.0099	1.998	0.994	1001.21	0.0099	1.0000	2002.926	0.0050	2.1	0.0050	-0.1	-0.2840	-28.6	0.0050	-30.5
9.883	1.247	1000.381	0.0125	2.506	1.247	1001.72	0.0124	1.0000	2002.101	0.0062	2.6	0.0062	-0.1	-0.3341	-26.8	0.0062	-29.3
11.900	1.501	1000.668	0.0150	3.017	1.501	1000.65	0.0150	1.0000	2001.318	0.0075	3.1	0.0075	-0.1	-0.3826	-25.5	0.0075	-28.5
13.450	1.696	1000.980	0.0169	3.411	1.696	1000.84	0.0169	1.0000	2001.820	0.0085	3.5	0.0085	-0.2	-0.4268	-25.2	0.0085	-28.5
15.87	2.002	1002.15	0.020	4.024	2.002	1009.21	0.019	1.0000	2011.360	0.0100	4.2	0.010	-0.2	-	-25.5	0.010	-29.5

1		0	0				8					0		0.5096		0	
17.425	2.198	1000.320	0.0220	4.419	2.198	1000.68	0.0220	1.0000	2001.000	0.0110	4.6	0.0110	-0.2	-0.5724	-26.0	0.0110	-30.4
17.448	2.201	1001.004	0.0220	4.424	2.201	1000.90	0.0220	1.0000	2001.904	0.0110	4.6	0.0110	-0.2	-0.6150	-27.9	0.0110	-32.3
19.013	2.398	1000.280	0.0240	4.821	2.398	1001.38	0.0239	1.0000	2001.660	0.0120	5.0	0.0120	-0.2	-0.6259	-26.1	0.0120	-30.9
19.851	2.504	1000.552	0.0250	5.034	2.504	1003.36	0.0250	1.0000	2003.912	0.0125	5.2	0.0125	-0.2	-0.7243	-28.9	0.0125	-33.9
23.747	2.995	1000.420	0.0299	6.022	2.995	1001.24	0.0299	1.0000	2001.660	0.0150	6.2	0.0150	-0.3	-0.8753	-29.2	0.0150	-35.2

$\Delta_{as}H^{o}_{m}$/(kJ·mol^{-1})= -115503.0·b^2 + 1699.9·b - 35.4 r^2=0.8178 σ_y=3.6 $\Delta_{as}H^{o}_{m}(\infty)$/(kJ·mol^{-1})=-35.4±4.2

Complex refers to the supramolecular complex [PQT][DSDB24C8]; $N(CH_3)_4I$ refers to tetramethyl ammonium iodide; $m$$H_2O$ solution is the mass of water in the respective solution; $\mathbf{b}_{initial}$ is the initial molal concentration of the solution of the respective

reactant; $\mathbf{b}_{final}$ is the final molal concentration of the solution of the respective reactant; dilution enthalpy for the complex [PQT][DSDB24C8] was calculated as $\Delta_{dil}H^{o}_{m}(complex)$ =-416.8·(b^2_{final}-$b^2_{initial}$); dilution enthalpy for $N(CH_3)_4I$ was calculated as $\Delta_{dil}H^{o}_{m}(N(CH3)4I)$=-53.0·($b^2_{final}$-$b^2_{initial}$)+17.2·($b^2_{final}$-$b^2_{initial}$). Uncertainty associated to each result of enthalpy of dilution was computed as $u\left[\Delta_{dil}H^{o}_{m}(complex)\right] = \sqrt{2\left\{u\left[\Delta_{sol}H^{o}_{m}(\infty), complex\right]\right\}^2}$ = ±2.1 kJ·mol^{-1} and $u^{[\Delta_{dil}H^{o}_{m}(N(CH3)4I)]} = \sqrt{2\{u\left[\Delta_{sol}H^{o}_{m}(\infty), N(CH3)4I\right]\}^2}$ =±0.3 kJ·mol^{-1}. Uncertainty of the result of enthalpy of association-dilution at infinite dilution, $u\left[\Delta_{aso\text{ - }dil}H^{o}_{m}(\infty)\right]$, was calculated as ±3.6 kJ·mol^{-1} and is the standard deviation of the intercept calculated from the least squares fitting of data $\Delta_{aso\text{ - }dil}H^{o}_{m}$ vs **b** to a second-order function. Uncertainty of the enthalpy of association at infinite dilution represents the overall uncertainty calculated as $u^{[\Delta_{aso}H^{o}_{m}(\infty)]} = \sqrt{\{u\left[\Delta_{aso\text{ - }dil}H^{o}_{m}(\infty)\right]\}^2 + \left\{u\left[\Delta_{dil}H^{o}_{m}(\infty), complex\right]\right\}^2 + \{u\left[\Delta_{dil}H^{o}_{m}(\infty), N(CH3)4I\right]\}^2}$ = ±4.2 kJ·mol^{-1}.