SUPPLEMENTARY MATERIAL

Acid-Base Properties of Sulfur-Bridged Calix[4]arenes

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1. 1. 1 Summary of the experimental parameters

Temperature/K	298
p[H] range	2.85-12.08
Total number of datum points	75
Solution conditions	
Initial volume/dm^3	55.0
Amount of the compound/mmol	0.2211
Ionic strength/mol dm^{-3}, electrolyte	0.2, NaCl
Titrant	0.1038 mol dm^{-3} NaOH

1. 1. 2 Calculation of the first acid dissociation constant

1. 1. 2. 1 Summary of the calcuration parameters

Method	linear regression analysis of eqn. (6), setting allowable error to be 0.1%
p[H] range for calculation	2.85-3.88
Number of datum points	21

1. 1. 2. 2 Results

pK_{a1} ± error	$3.09_9 \pm 0.00_3$
correlation coefficient	0.99921

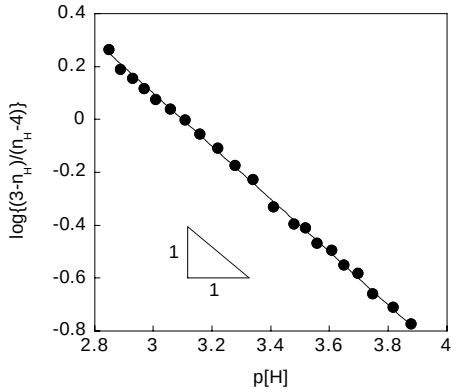

Figure S-1. 1. 1 Evaluation of the pK_{a1} value for the calixarene **3**; plots of eqn. (6)

Table S-1. 1 Raw data

p[H]	V_{NaOH}/ml	$C_{calixarene}$/M	C_{NaOH}/M	F	$\bar{n}_H$	$\log\{(3-\bar{n}_H)/(\bar{n}_H-4)\}$
2.849	0.000	0.004020	0.000	0.000	3.648	0.2648
2.889	0.1500	0.004009	0.0002823	0.07042	3.608	0.1898
2.929	0.2500	0.004002	0.0004697	0.1174	3.588	0.1552
2.969	0.3500	0.003994	0.0006564	0.1643	3.567	0.1168
3.009	0.4500	0.003987	0.0008424	0.2113	3.543	0.07510
3.059	0.5500	0.003980	0.001028	0.2582	3.522	0.03909
3.109	0.6500	0.003973	0.001212	0.3052	3.499	-0.001674
3.159	0.7600	0.003965	0.001415	0.3568	3.468	-0.05507
3.219	0.8700	0.003957	0.001616	0.4085	3.439	-0.1066
3.279	0.9900	0.003949	0.001835	0.4648	3.402	-0.1724
3.339	1.090	0.003942	0.002017	0.5117	3.372	-0.2273
3.409	1.240	0.003931	0.002289	0.5822	3.319	-0.3300
3.479	1.340	0.003924	0.002469	0.6291	3.286	-0.3966
3.519	1.370	0.003922	0.002523	0.6432	3.280	-0.4109
3.559	1.440	0.003917	0.002648	0.6761	3.253	-0.4691
3.609	1.480	0.003915	0.002720	0.6948	3.242	-0.4951
3.649	1.540	0.003910	0.002827	0.7230	3.220	-0.5506
3.699	1.580	0.003908	0.002899	0.7418	3.207	-0.5832
3.749	1.650	0.003903	0.003023	0.7746	3.180	-0.6595
3.819	1.700	0.003899	0.003112	0.7981	3.163	-0.7106
3.879	1.750	0.003896	0.003201	0.8216	3.144	-0.7724
3.959	1.790	0.003893	0.003272	0.8404	3.131	-0.8202
4.039	1.850	0.003889	0.003378	0.8685	3.108	-0.9171
4.149	1.900	0.003886	0.003466	0.8920	3.090	-1.006
4.279	1.950	0.003882	0.003554	0.9155	3.071	-1.117
4.449	2.030	0.003877	0.003695	0.9531	3.038	-1.406
4.739	2.060	0.003875	0.003747	0.9671	3.028	-1.538
5.459	2.100	0.003872	0.003818	0.9859	3.013	-1.874
9.089	2.170	0.003867	0.003940	1.019	2.987	3.400e+38
9.669	2.250	0.003862	0.004079	1.056	2.965	3.400e+38
9.949	2.300	0.003859	0.004166	1.080	2.961	3.400e+38
10.11	2.350	0.003855	0.004253	1.103	2.956	3.400e+38
10.23	2.400	0.003852	0.004340	1.127	2.951	3.400e+38
10.32	2.450	0.003848	0.004427	1.150	2.946	3.400e+38
10.40	2.490	0.003846	0.004496	1.169	2.947	3.400e+38

Table S-1. 1 Raw data (continued)

10.46	2.550	0.003842	0.004599	1.197	2.936	3.400e+38
10.52	2.610	0.003838	0.004703	1.225	2.928	3.400e+38
10.57	2.660	0.003834	0.004789	1.249	2.923	3.400e+38
10.62	2.720	0.003830	0.004891	1.277	2.916	3.400e+38
10.66	2.760	0.003828	0.004960	1.296	2.916	3.400e+38
10.73	2.870	0.003821	0.005148	1.347	2.902	3.400e+38
10.79	2.990	0.003813	0.005352	1.404	2.883	3.400e+38
10.84	3.100	0.003805	0.005538	1.455	2.867	3.400e+38
10.89	3.210	0.003798	0.005724	1.507	2.856	3.400e+38
10.93	3.310	0.003792	0.005892	1.554	2.844	3.400e+38
10.97	3.440	0.003783	0.006110	1.615	2.823	3.400e+38
11.03	3.580	0.003774	0.006344	1.681	2.823	3.400e+38
11.07	3.750	0.003763	0.006626	1.761	2.793	3.400e+38
11.11	3.950	0.003751	0.006955	1.854	2.755	3.400e+38
11.16	4.150	0.003738	0.007283	1.948	2.738	3.400e+38
11.20	4.350	0.003725	0.007608	2.042	2.713	3.400e+38
11.25	4.700	0.003703	0.008172	2.207	2.645	3.400e+38
11.30	4.860	0.003694	0.008427	2.282	2.677	3.400e+38
11.35	5.200	0.003673	0.008966	2.441	2.640	3.400e+38
11.40	5.650	0.003645	0.009670	2.653	2.570	3.400e+38
11.45	6.050	0.003622	0.01029	2.840	2.541	3.400e+38
11.50	6.550	0.003592	0.01105	3.075	2.487	3.400e+38
11.54	6.950	0.003569	0.01165	3.263	2.461	3.400e+38
11.62	7.550	0.003535	0.01253	3.545	2.548	3.400e+38
11.67	8.400	0.003487	0.01375	3.944	2.436	3.400e+38
11.70	9.250	0.003441	0.01494	4.343	2.242	3.400e+38
11.73	10.55	0.003373	0.01671	4.953	1.872	3.400e+38
11.76	11.20	0.003340	0.01756	5.258	1.799	3.400e+38
11.79	12.05	0.003297	0.01865	5.657	1.661	3.400e+38
11.83	13.05	0.003249	0.01991	6.127	1.566	3.400e+38
11.86	14.10	0.003200	0.02118	6.620	1.398	3.400e+38
11.90	15.05	0.003156	0.02230	7.066	1.400	3.400e+38
11.92	16.05	0.003112	0.02345	7.535	1.208	3.400e+38
11.95	17.05	0.003069	0.02456	8.005	1.149	3.400e+38
11.98	18.03	0.003027	0.02563	8.465	1.133	3.400e+38
12.00	19.05	0.002986	0.02670	8.944	0.9996	3.400e+38

Table S-1. 1 Raw data (continued)

12.01	20.05	0.002946	0.02773	9.413	0.7507	3.400e+38
12.03	21.02	0.002908	0.02870	9.869	0.6692	3.400e+38
12.07	22.00	0.002871	0.02966	10.33	0.9323	3.400e+38
12.08	23.03	0.002833	0.03064	10.81	0.7172	3.400e+38

1. 2 Thiacalix[4]arenetetrasulfonate (4)

1. 2. 1 Summary of the experimental parameters

Temperature/K	298
p[H] range	2.57-12.04
Total number of datum points	98
Solution conditions	
Initial volume/dm^3	55.0
Amount of the compound/mmol	0.2045
Ionic strength/mol dm^{-3}, electrolyte	0.2, NaCl
Titrant	0.1038 mol dm^{-3} NaOH

1. 2. 2 Calculation of the first acid dissociation constant

1. 2. 2. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (6), setting allowable error to be 0.1%
p[H] range for calculation	2.57-3.27
Number of datum points	9

1. 2. 2. 2 Results

pK_{a1} ± error	$2.17_1 \pm 0.00_7$
correlation coefficient	0.99548

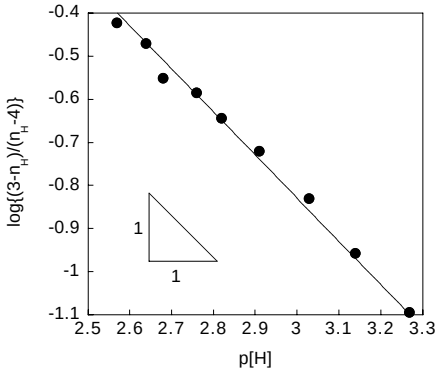

Figure S-1. 2. 1 Evaluation of the pK_{a1} value for the calixarene **4**; plots of eqn. (6)

1. 2. 3. Calculation of the second acid dissociation constant

1. 2. 3. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (8), setting allowable error to be 0.1%
p[H] range for calculation	7.75-8.67
Number of datum points	17

1. 2. 3. 2 Results

pK_{a2} ± error	$8.41_3 \pm 0.00_2$
correlation coefficient	0.99944

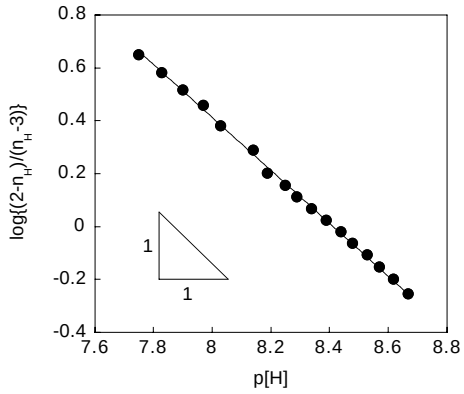

Figure S-1. 2. 2 Evaluation of the pK_{a2} value for the calixarene **4**; plots of eqn. (8)

Table S-1. 2 Raw data

p[H]	V_{NaOH}/ml	$C_{calixarene}$/M	C_{NaOH}/M	F	$\bar{n}_H$	log{(3-$\bar{n}_H$)/($\bar{n}_H$-4)}	log{(2-$\bar{n}_H$)/($\bar{n}_H$-3)}
2.569	0.000	0.003718	0.000	0.000	3.275	-0.4220	3.400e+38
2.639	0.2500	0.003701	0.0004697	0.1269	3.253	-0.4706	3.400e+38
2.679	0.4200	0.003690	0.0007866	0.2132	3.219	-0.5513	3.400e+38
2.759	0.6300	0.003676	0.001176	0.3198	3.206	-0.5848	3.400e+38
2.819	0.7900	0.003665	0.001470	0.4010	3.185	-0.6435	3.400e+38
2.909	0.9900	0.003652	0.001835	0.5025	3.160	-0.7205	3.400e+38
3.029	1.210	0.003638	0.002234	0.6142	3.129	-0.8306	3.400e+38
3.139	1.380	0.003627	0.002541	0.7005	3.099	-0.9575	3.400e+38
3.269	1.530	0.003617	0.002809	0.7767	3.075	-1.094	3.400e+38
3.399	1.630	0.003611	0.002988	0.8274	3.062	-1.179	3.400e+38
3.479	1.710	0.003606	0.003130	0.8680	3.040	-1.381	3.400e+38

Table S-1. 2 Raw data (continued)

3.679	1.810	0.003599	0.003307	0.9188	3.023	-1.627	3.400e+38
3.829	1.850	0.003597	0.003378	0.9391	3.020	-1.697	3.400e+38
4.049	1.910	0.003593	0.003484	0.9695	3.006	-2.249	3.400e+38
4.539	1.940	0.003591	0.003537	0.9848	3.007	-2.141	3.400e+38
6.249	2.010	0.003587	0.003660	1.020	2.980	3.400e+38	1.680
6.939	2.050	0.003584	0.003730	1.041	2.959	3.400e+38	1.373
7.219	2.120	0.003580	0.003853	1.076	2.924	3.400e+38	1.084
7.409	2.180	0.003576	0.003957	1.107	2.894	3.400e+38	0.9238
7.549	2.230	0.003573	0.004045	1.132	2.868	3.400e+38	0.8187
7.659	2.280	0.003570	0.004132	1.157	2.843	3.400e+38	0.7295
7.749	2.330	0.003567	0.004219	1.183	2.818	3.400e+38	0.6513
7.829	2.380	0.003564	0.004305	1.208	2.792	3.400e+38	0.5812
7.899	2.430	0.003561	0.004392	1.234	2.767	3.400e+38	0.5172
7.969	2.480	0.003558	0.004478	1.259	2.742	3.400e+38	0.4578
8.029	2.550	0.003553	0.004599	1.294	2.706	3.400e+38	0.3807
8.139	2.640	0.003548	0.004754	1.340	2.661	3.400e+38	0.2892
8.189	2.730	0.003542	0.004909	1.386	2.615	3.400e+38	0.2034
8.249	2.780	0.003539	0.004994	1.411	2.590	3.400e+38	0.1576
8.289	2.830	0.003536	0.005080	1.437	2.564	3.400e+38	0.1126
8.339	2.880	0.003533	0.005165	1.462	2.539	3.400e+38	0.06818
8.389	2.930	0.003530	0.005250	1.487	2.514	3.400e+38	0.02419
8.439	2.980	0.003527	0.005335	1.513	2.489	3.400e+38	-0.01964
8.479	3.030	0.003524	0.005420	1.538	2.463	3.400e+38	-0.06361
8.529	3.080	0.003521	0.005505	1.563	2.438	3.400e+38	-0.1078
8.569	3.130	0.003518	0.005589	1.589	2.413	3.400e+38	-0.1526
8.619	3.180	0.003515	0.005673	1.614	2.388	3.400e+38	-0.1981
8.669	3.240	0.003511	0.005775	1.645	2.358	3.400e+38	-0.2542
8.719	3.320	0.003506	0.005909	1.685	2.317	3.400e+38	-0.3326
8.759	3.380	0.003503	0.006010	1.716	2.287	3.400e+38	-0.3948
8.809	3.430	0.003500	0.006093	1.741	2.262	3.400e+38	-0.4494
8.869	3.480	0.003497	0.006177	1.766	2.237	3.400e+38	-0.5071
8.919	3.530	0.003494	0.006260	1.792	2.212	3.400e+38	-0.5693
8.979	3.580	0.003491	0.006344	1.817	2.188	3.400e+38	-0.6365
9.039	3.630	0.003488	0.006427	1.843	2.163	3.400e+38	-0.7107
9.109	3.680	0.003485	0.006510	1.868	2.139	3.400e+38	-0.7937
9.179	3.730	0.003482	0.006592	1.893	2.114	3.400e+38	-0.8892

Table S-1. 2 Raw data (continued)

9.259	3.780	0.003479	0.006675	1.919	2.091	3.400e+38	-1.002
9.339	3.830	0.003476	0.006758	1.944	2.067	3.400e+38	-1.144
9.439	3.930	0.003470	0.006922	1.995	2.019	3.400e+38	-1.709
9.539	3.980	0.003467	0.007004	2.020	1.997	3.400e+38	3.400e+38
9.659	4.030	0.003464	0.007086	2.046	1.978	3.400e+38	3.400e+38
9.769	4.070	0.003462	0.007152	2.066	1.964	3.400e+38	3.400e+38
9.889	4.130	0.003458	0.007250	2.096	1.943	3.400e+38	3.400e+38
10.01	4.180	0.003455	0.007332	2.122	1.931	3.400e+38	3.400e+38
10.12	4.230	0.003452	0.007413	2.147	1.921	3.400e+38	3.400e+38
10.21	4.280	0.003449	0.007494	2.173	1.911	3.400e+38	3.400e+38
10.29	4.330	0.003447	0.007575	2.198	1.902	3.400e+38	3.400e+38
10.36	4.390	0.003443	0.007673	2.228	1.890	3.400e+38	3.400e+38
10.42	4.430	0.003441	0.007737	2.249	1.887	3.400e+38	3.400e+38
10.47	4.530	0.003435	0.007899	2.299	1.853	3.400e+38	3.400e+38
10.53	4.580	0.003432	0.007979	2.325	1.850	3.400e+38	3.400e+38
10.57	4.630	0.003429	0.008060	2.350	1.842	3.400e+38	3.400e+38
10.62	4.680	0.003426	0.008140	2.376	1.840	3.400e+38	3.400e+38
10.66	4.730	0.003424	0.008220	2.401	1.836	3.400e+38	3.400e+38
10.69	4.780	0.003421	0.008300	2.426	1.828	3.400e+38	3.400e+38
10.75	4.880	0.003415	0.008459	2.477	1.815	3.400e+38	3.400e+38
10.81	4.980	0.003409	0.008618	2.528	1.808	3.400e+38	3.400e+38
10.86	5.110	0.003402	0.008824	2.594	1.784	3.400e+38	3.400e+38
10.90	5.230	0.003395	0.009013	2.655	1.760	3.400e+38	3.400e+38
10.96	5.380	0.003387	0.009249	2.731	1.747	3.400e+38	3.400e+38
11.02	5.540	0.003378	0.009499	2.812	1.738	3.400e+38	3.400e+38
11.06	5.730	0.003367	0.009794	2.909	1.696	3.400e+38	3.400e+38
11.12	5.930	0.003356	0.01010	3.010	1.687	3.400e+38	3.400e+38
11.17	6.130	0.003345	0.01041	3.112	1.673	3.400e+38	3.400e+38
11.21	6.340	0.003334	0.01073	3.218	1.645	3.400e+38	3.400e+38
11.26	6.630	0.003318	0.01117	3.365	1.608	3.400e+38	3.400e+38
11.30	6.900	0.003303	0.01157	3.503	1.569	3.400e+38	3.400e+38
11.36	7.330	0.003281	0.01221	3.721	1.518	3.400e+38	3.400e+38
11.41	7.780	0.003257	0.01286	3.949	1.451	3.400e+38	3.400e+38
11.47	8.310	0.003230	0.01362	4.218	1.403	3.400e+38	3.400e+38
11.52	8.830	0.003204	0.01436	4.482	1.352	3.400e+38	3.400e+38
11.56	9.310	0.003180	0.01503	4.726	1.300	3.400e+38	3.400e+38

Table S-1. 2 Raw data (continued)

11.59	9.830	0.003154	0.01574	4.990	1.199	3.400e+38	3.400e+38
11.63	10.33	0.003130	0.01641	5.244	1.175	3.400e+38	3.400e+38
11.69	11.38	0.003081	0.01780	5.777	1.045	3.400e+38	3.400e+38
11.74	12.33	0.003037	0.01901	6.259	0.9520	3.400e+38	3.400e+38
11.78	13.33	0.002993	0.02025	6.766	0.8064	3.400e+38	3.400e+38
11.82	14.33	0.002949	0.02145	7.274	0.7009	3.400e+38	3.400e+38
11.85	15.28	0.002910	0.02257	7.756	0.5613	3.400e+38	3.400e+38
11.88	16.33	0.002867	0.02376	8.289	0.4062	3.400e+38	3.400e+38
11.91	17.33	0.002827	0.02487	8.797	0.3050	3.400e+38	3.400e+38
11.94	18.33	0.002789	0.02595	9.305	0.2378	3.400e+38	3.400e+38
11.96	19.33	0.002751	0.02699	9.812	0.07054	3.400e+38	3.400e+38
11.98	20.33	0.002715	0.02801	10.32	-0.07695	3.400e+38	3.400e+38
12.00	21.33	0.002679	0.02901	10.83	-0.2036	3.400e+38	3.400e+38
12.02	22.33	0.002644	0.02997	11.34	-0.3081	3.400e+38	3.400e+38
12.04	23.33	0.002611	0.03092	11.84	-0.3894	3.400e+38	3.400e+38

1. 3 Sulfonylcalix[4]arenetetrasulfonate (5)

1. 3. 1 Summary of the experimental parameters

Temperature/K	298
p[H] range	2.11-11.98
Total number of datum points	95
Solution conditions	
Initial volume/dm^3	55.0
Amount of the compound/mmol	0.2560
Amount of HCl/mmol	0.2501
Ionic strength/mol dm^{-3}, electrolyte	0.2, NaCl
Titrant	0.1038 mol dm^{-3} NaOH

1. 3. 2 Calculation of the third and fourth acid dissociation constant

1. 3. 2. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (9), setting allowable error to be 0.1%
p[H] range for calculation	3.90-5.41
Number of datum points	26

1. 3. 2. 2 Results

pK_{a3} ± error	$4.71_6 \pm 0.02_1$
pK_{a4} ± error	$4.39_2 \pm 0.02_1$
correlation coefficient	0.99966

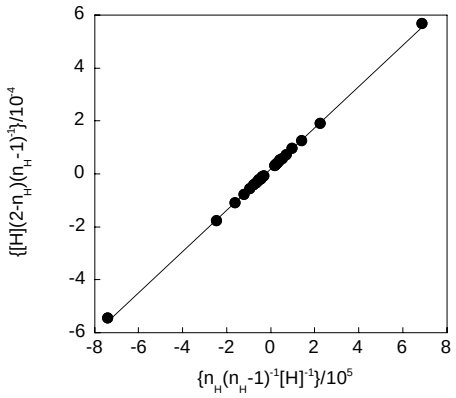

Figure S-1. 3. 1 Evaluation of the pK_{a3} and pKa$_4$ value for the calixarene **5**; plots of eqn. (9)

Table S-1. 3 Raw data

p[H]	V_{NaOH}/ml	C_L/M	C_{HCl}/M	C_{NaOH}/M	F	$\bar{n}_H$	$\bar{n}_H(\bar{n}_H-1)^{-1}[H]^{-1}$	$(2-\bar{n}_H)[H](\bar{n}_H-1)^{-1}$
2.109	0.000	0.004655	0.004547	0.000	0.000	2.306	227.0	-0.001822
2.139	0.3200	0.004628	0.004521	0.0006004	0.1297	2.279	245.5	-0.001582
2.169	0.6000	0.004605	0.004498	0.001120	0.2432	2.262	264.5	-0.001408
2.209	1.000	0.004572	0.004466	0.001854	0.4054	2.220	294.5	-0.001114
2.269	1.400	0.004540	0.004434	0.002577	0.5676	2.224	337.7	-0.0009840
2.319	1.750	0.004512	0.004407	0.003201	0.7095	2.204	381.6	-0.0008134
2.399	2.280	0.004470	0.004366	0.004132	0.9243	2.160	466.7	-0.0005502
2.459	2.580	0.004447	0.004344	0.004651	1.046	2.149	538.2	-0.0004517
2.519	2.850	0.004426	0.004323	0.005114	1.155	2.138	620.9	-0.0003661
2.599	3.200	0.004399	0.004297	0.005707	1.297	2.107	756.0	-0.0002440
2.659	3.420	0.004383	0.004281	0.006077	1.386	2.090	874.5	-0.0001812
2.729	3.610	0.004369	0.004267	0.006393	1.464	2.086	1029	-0.0001480
2.809	3.820	0.004353	0.004252	0.006741	1.549	2.072	1246	-0.0001037
2.909	4.050	0.004336	0.004235	0.007119	1.642	2.051	1583	-5.935e-05
2.989	4.200	0.004325	0.004225	0.007364	1.703	2.037	1916	-3.658e-05
3.059	4.300	0.004318	0.004218	0.007527	1.743	2.031	2257	-2.658e-05
3.139	4.400	0.004310	0.004210	0.007689	1.784	2.025	2722	-1.743e-05

Table S-1. 3 Raw data (continued)

3.179	4.500	0.004303	0.004203	0.007850	1.824	1.999	3023	9.190e-07
3.229	4.550	0.004300	0.004200	0.007931	1.845	1.995	3398	2.989e-06
3.269	4.600	0.004296	0.004196	0.008011	1.865	1.987	3741	7.275e-06
3.329	4.650	0.004292	0.004193	0.008092	1.885	1.982	4305	8.366e-06
3.379	4.700	0.004289	0.004189	0.008172	1.905	1.974	4851	1.116e-05
3.489	4.800	0.004282	0.004182	0.008332	1.946	1.955	6312	1.524e-05
3.539	4.850	0.004278	0.004179	0.008412	1.966	1.943	7129	1.746e-05
3.649	4.950	0.004271	0.004172	0.008571	2.007	1.918	9315	2.017e-05
3.699	5.000	0.004267	0.004168	0.008650	2.027	1.903	1.054e+04	2.150e-05
3.749	5.050	0.004264	0.004165	0.008729	2.047	1.888	1.193e+04	2.254e-05
3.789	5.110	0.004260	0.004161	0.008824	2.072	1.867	1.325e+04	2.493e-05
3.829	5.150	0.004257	0.004158	0.008887	2.088	1.854	1.465e+04	2.531e-05
3.899	5.300	0.004246	0.004148	0.009123	2.149	1.798	1.785e+04	3.185e-05
3.969	5.400	0.004239	0.004141	0.009280	2.189	1.762	2.153e+04	3.349e-05
4.019	5.500	0.004232	0.004134	0.009436	2.230	1.724	2.487e+04	3.640e-05
4.069	5.610	0.004224	0.004126	0.009608	2.274	1.682	2.891e+04	3.972e-05
4.139	5.800	0.004211	0.004113	0.009902	2.351	1.608	3.642e+04	4.677e-05
4.189	5.950	0.004201	0.004103	0.01013	2.412	1.549	4.360e+04	5.310e-05
4.249	6.100	0.004191	0.004093	0.01036	2.473	1.490	5.393e+04	5.856e-05
4.309	6.320	0.004175	0.004079	0.01070	2.562	1.403	7.094e+04	7.274e-05
4.359	6.550	0.004160	0.004063	0.01105	2.655	1.311	9.639e+04	9.697e-05
4.419	6.750	0.004146	0.004050	0.01135	2.736	1.231	1.398e+05	0.0001267
4.469	6.950	0.004133	0.004037	0.01165	2.818	1.151	2.245e+05	0.0001909
4.519	7.200	0.004116	0.004021	0.01202	2.919	1.051	6.870e+05	0.0005687
4.589	7.450	0.004100	0.004005	0.01238	3.020	0.9502	-7.415e+05	-0.0005435
4.639	7.700	0.004084	0.003989	0.01275	3.122	0.8496	-2.460e+05	-0.0001756
4.689	7.900	0.004071	0.003976	0.01304	3.203	0.7691	-1.628e+05	-0.0001091
4.739	8.100	0.004058	0.003964	0.01332	3.284	0.6885	-1.212e+05	-7.678e-05
4.799	8.320	0.004044	0.003950	0.01364	3.373	0.5999	-9.440e+04	-5.558e-05
4.869	8.530	0.004030	0.003937	0.01394	3.458	0.5153	-7.866e+04	-4.141e-05
4.919	8.700	0.004019	0.003926	0.01418	3.527	0.4468	-6.703e+04	-3.383e-05
4.999	8.900	0.004007	0.003914	0.01446	3.608	0.3662	-5.765e+04	-2.583e-05
5.049	9.000	0.004001	0.003908	0.01460	3.649	0.3259	-5.413e+04	-2.218e-05
5.109	9.150	0.003991	0.003899	0.01481	3.709	0.2654	-4.644e+04	-1.837e-05
5.169	9.250	0.003985	0.003893	0.01494	3.750	0.2251	-4.288e+04	-1.552e-05
5.249	9.350	0.003979	0.003887	0.01508	3.791	0.1848	-4.024e+04	-1.255e-05

Table S-1. 3 Raw data (continued)

5.349	9.450	0.003973	0.003881	0.01522	3.831	0.1446	-3.776e+04	-9.709e-06
5.409	9.550	0.003967	0.003875	0.01536	3.872	0.1042	-2.983e+04	-8.251e-06
5.489	9.600	0.003963	0.003872	0.01543	3.892	0.08409	-2.831e+04	-6.783e-06
5.589	9.650	0.003960	0.003869	0.01549	3.912	0.06399	-2.654e+04	-5.328e-06
5.719	9.700	0.003957	0.003866	0.01556	3.932	0.04389	-2.404e+04	-3.907e-06
5.909	9.750	0.003954	0.003863	0.01563	3.953	0.02379	-1.977e+04	-2.496e-06
6.289	9.800	0.003951	0.003860	0.01570	3.973	0.003706	-7238	-1.030e-06
8.319	9.830	0.003949	0.003858	0.01574	3.985	-0.007397	1.531e+06	-9.558e-09
9.579	9.900	0.003945	0.003854	0.01583	4.014	-0.01961	7.297e+07	-5.221e-10
9.919	9.950	0.003942	0.003851	0.01590	4.034	-0.01954	1.591e+08	-2.387e-10
10.12	10.00	0.003939	0.003848	0.01597	4.054	-0.01787	2.309e+08	-1.507e-10
10.25	10.05	0.003936	0.003845	0.01604	4.074	-0.01735	3.027e+08	-1.117e-10
10.36	10.11	0.003932	0.003841	0.01612	4.099	-0.01847	4.146e+08	-8.670e-11
10.44	10.15	0.003930	0.003839	0.01617	4.115	-0.01370	3.715e+08	-7.228e-11
10.51	10.20	0.003927	0.003836	0.01624	4.135	-0.01211	3.864e+08	-6.157e-11
10.58	10.30	0.003921	0.003830	0.01637	4.176	-0.02681	9.907e+08	-5.203e-11
10.62	10.32	0.003920	0.003829	0.01640	4.184	-0.01826	7.461e+08	-4.765e-11
10.68	10.40	0.003915	0.003824	0.01651	4.216	-0.02247	1.050e+09	-4.141e-11
10.72	10.45	0.003912	0.003821	0.01657	4.236	-0.02163	1.109e+09	-3.779e-11
10.79	10.55	0.003906	0.003815	0.01671	4.277	-0.02011	1.213e+09	-3.218e-11
10.89	10.71	0.003897	0.003806	0.01692	4.342	-0.01158	8.868e+08	-2.567e-11
10.96	10.90	0.003885	0.003795	0.01717	4.419	-0.02558	2.270e+09	-2.170e-11
11.04	11.10	0.003874	0.003784	0.01743	4.500	-0.02089	2.239e+09	-1.809e-11
11.11	11.30	0.003862	0.003772	0.01769	4.581	-0.01233	1.566e+09	-1.546e-11
11.19	11.60	0.003844	0.003755	0.01808	4.703	-0.01100	1.682e+09	-1.287e-11
11.26	11.90	0.003827	0.003738	0.01846	4.824	-0.003807	6.886e+08	-1.099e-11
11.34	12.30	0.003804	0.003716	0.01897	4.986	0.01075	-2.372e+09	-9.211e-12
11.40	12.70	0.003782	0.003694	0.01947	5.149	0.006730	-1.698e+09	-8.006e-12
11.46	13.20	0.003754	0.003667	0.02009	5.351	-0.01137	3.235e+09	-6.910e-12
11.52	13.70	0.003727	0.003640	0.02070	5.554	-0.0006332	2.091e+08	-6.051e-12
11.57	14.30	0.003695	0.003609	0.02142	5.797	-0.03605	1.290e+10	-5.301e-12
11.62	14.80	0.003668	0.003583	0.02201	6.000	-0.006573	2.716e+09	-4.792e-12
11.65	15.35	0.003640	0.003555	0.02265	6.223	-0.06829	2.849e+10	-4.344e-12
11.68	15.80	0.003616	0.003532	0.02316	6.405	-0.08003	3.539e+10	-4.032e-12
11.72	16.45	0.003583	0.003500	0.02390	6.669	-0.09332	4.470e+10	-3.656e-12
11.76	17.25	0.003544	0.003462	0.02478	6.993	-0.1350	6.830e+10	-3.276e-12

11.81	18.25	0.003495	0.003414	0.02586	7.399	-0.1441	8.114e+10	-2.909e-12
11.85	19.30	0.003446	0.003366	0.02696	7.824	-0.2020	1.187e+11	-2.593e-12
11.89	20.30	0.003400	0.003321	0.02798	8.230	-0.2019	1.301e+11	-2.365e-12
11.92	21.30	0.003356	0.003278	0.02898	8.635	-0.2599	1.712e+11	-2.161e-12
11.95	22.30	0.003312	0.003235	0.02994	9.041	-0.2890	1.994e+11	-1.997e-12
11.98	23.30	0.003270	0.003194	0.03089	9.446	-0.2867	2.124e+11	-1.865e-12

2. Spectrophotometric titration for the evaluation of the acid dissociation constants

2. 1 Calix[4]arenetetrasulfonate (3)

2. 1. 1 Summary of the experimental parameters

Temperature/K	298
p[H] range	1.00-12.88
Total number of datum points	49
Solution conditions	
Concentration of the compound/μmol dm^{-3}	44.22
Ionic strength/mol dm^{-3}, electrolyte	0.2, NaCl

2. 1. 2 Calculation of the first acid dissociation constant

2. 1. 2. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (11), setting allowable error to be 0.1%		
Wavelength/nm	260	280	300
p[H] range for calculation	1.68-4.45	1.68-4.45	1.68-4.45
Number of datum points	14	14	14
Inputted A_{H4L}	0.09442	0.21911	0.00092
Inputted A_{H3L}	0.32200	0.34500	0.15200

2. 1. 2. 2 Results

Wavelength/nm	260	280	300
pK_{a1} ± error	$3.08_7 \pm 0.00_6$	$3.05_2 \pm 0.00_4$	$3.07_8 \pm 0.00_5$
Correlation coefficient	0.99968	0.99981	0.99974

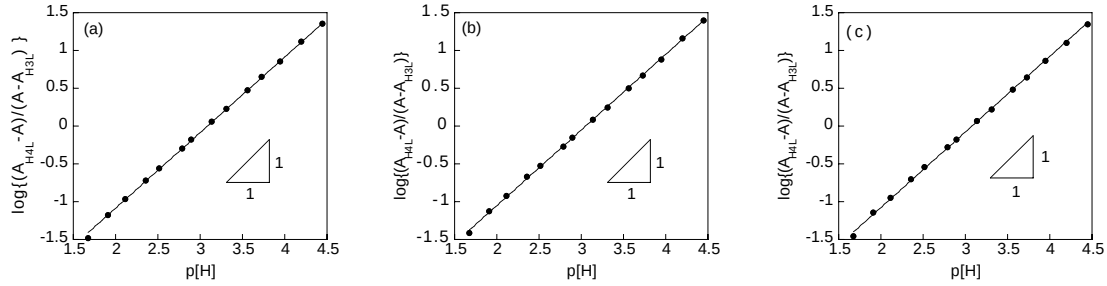

Figure S-2. 1. 1 Evaluation of the pK_{a1} value for the calixarene **3**; plots of eqn. (11).
(a) λ = 260 nm, (b) λ = 280 nm, (a) λ = 300 nm.

2. 1. 3 Estimation of the A_{H2L} values

2. 1. 3. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (27), setting allowable error to be 0.1%		
Wavelength/nm	260	280	300
p[H] range for calculation	10.90-12.88	11.32-12.88	11.32-12.88
Number of datum points	11	9	9
Inputted A_{H3L}	0.3220	0.3450	0.1520

2. 1. 3. 2 Results

wavelength/nm	260	280	300
A_{H2L}± error	$0.7916_7 \pm 0.0027_0$	$0.5959_0 \pm 0.0016_4$	$0.4396_1 \pm 0.0010_4$
pK_{a2} ± error	$12.01_0 \pm 0.00_4$	$12.01_3 \pm 0.00_6$	$12.01_9 \pm 0.00_3$
Correlation coefficient	0.99960	0.99981	0.99983

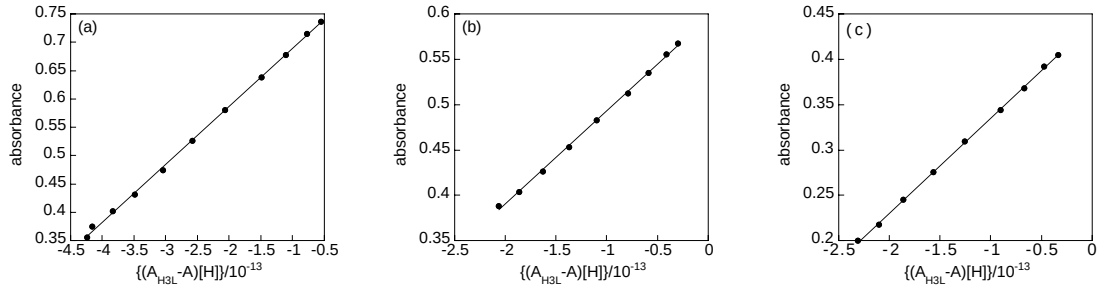

Figure S-2. 1. 1 Estimation of the A_{H2L} values for the calixarene **3**; plots of eqn. (27). (a) λ = 260 nm, (b) λ = 280 nm, (a) λ = 300 nm.

2. 1. 4 Calculation of the second acid dissociation constant

2. 1. 4. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (12), setting allowable error to be 0.1%		
Wavelength/nm	260	280	300
p[H] range for calculation	10.73-12.82	10.90-12.88	10.90-12.88
Number of datum points	12	11	11
Inputted A_{H3L}	0.32200	0.34500	0.15200
Inputted A_{H2L}	0.79157	0.59590	0.43961

2. 1. 4. 2 Results

Wavelength/nm	260	280	300
pK_{a2} ± error	$12.00_5 \pm 0.00_4$	$12.00_9 \pm 0.00_4$	$12.01_9 \pm 0.00_2$
Correlation coefficient	0.99984	0.99984	0.99992

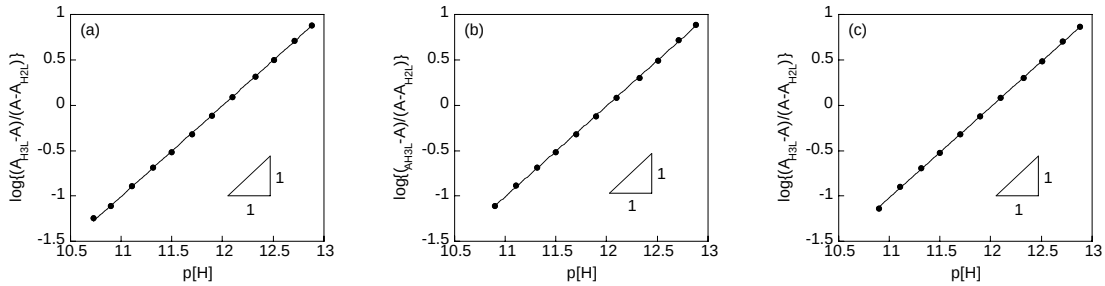

Figure S-2. 1. 3 Evaluation of the pK_{a2} value for the calixarene **3**; plots of eqn. (12).
(a) λ = 260 nm, (b) λ = 280 nm, (a) λ = 300 nm.

Table S-2. 1 Raw data

(a) at 260 nm

p[H]	absorbance	log{(A_{H_4L}-A)/(A- A_{H_3L})}	(A_{H_3L}-A)[H]	log{(A_{H_3L}-A)/(A- A_{H_2L})}
0.9991	0.094420	-8.398	0.02281	3.400e+38
1.239	0.096010	-2.153	0.01303	3.400e+38
1.449	0.098030	-1.793	0.007964	3.400e+38
1.679	0.10166	-1.483	0.004613	3.400e+38
1.909	0.10866	-1.176	0.002630	3.400e+38
2.119	0.11676	-0.9632	0.001560	3.400e+38
2.359	0.13079	-0.7208	0.0008364	3.400e+38
2.519	0.14363	-0.5593	0.0005398	3.400e+38
2.789	0.17128	-0.2925	0.0002450	3.400e+38
2.899	0.18526	-0.1776	0.0001725	3.400e+38
3.139	0.21606	0.06002	7.691e-05	3.400e+38
3.309	0.23785	0.2316	4.130e-05	3.400e+38
3.559	0.26536	0.4797	1.563e-05	3.400e+38
3.729	0.28071	0.6543	7.705e-06	3.400e+38
3.949	0.29443	0.8606	3.100e-06	3.400e+38
4.199	0.30589	1.118	1.019e-06	3.400e+38
4.449	0.31237	1.355	3.424e-07	3.400e+38
4.709	0.31640	1.598	1.094e-07	3.400e+38

Table S-2. 1 Raw data (continued)

5.099	0.31982	2.014	1.735e-08	3.400e+38
5.469	0.32069	2.237	4.448e-09	3.400e+38
5.919	0.32161	2.765	4.699e-10	3.400e+38
6.289	0.32201	3.400e+38	-5.145e-12	-4.671
6.699	0.32203	3.400e+38	-6.000e-12	-4.194
6.969	0.32196	3.755	4.295e-12	3.400e+38
7.199	0.32177	2.995	1.454e-11	3.400e+38
7.539	0.32181	3.078	5.491e-12	3.400e+38
7.839	0.32196	3.755	5.794e-13	3.400e+38
7.969	0.32352	3.400e+38	-1.632e-11	-2.488
8.259	0.32348	3.400e+38	-8.151e-12	-2.500
8.669	0.32367	3.400e+38	-3.578e-12	-2.447
8.909	0.32376	3.400e+38	-2.170e-12	-2.425
9.209	0.32465	3.400e+38	-1.637e-12	-2.246
9.499	0.32480	3.400e+38	-8.873e-13	-2.222
9.819	0.32714	3.400e+38	-7.796e-13	-1.956
10.10	0.33020	3.400e+38	-6.527e-13	-1.750
10.32	0.33389	3.400e+38	-5.703e-13	-1.585
10.50	0.33791	3.400e+38	-5.042e-13	-1.455
10.73	0.34738	3.400e+38	-4.736e-13	-1.243
10.90	0.35559	3.400e+38	-4.238e-13	-1.113
11.11	0.37542	3.400e+38	-4.156e-13	-0.8915
11.32	0.40188	3.400e+38	-3.831e-13	-0.6883
11.50	0.43190	3.400e+38	-3.483e-13	-0.5149
11.70	0.47423	3.400e+38	-3.044e-13	-0.3190
11.90	0.52597	3.400e+38	-2.573e-13	-0.1147
12.10	0.58108	3.400e+38	-2.062e-13	0.09020
12.33	0.63846	3.400e+38	-1.483e-13	0.3153
12.51	0.67848	3.400e+38	-1.104e-13	0.4986
12.71	0.71568	3.400e+38	-7.692e-14	0.7150
12.88	0.73705	3.400e+38	-5.483e-14	0.8815

(b) at 280 nm

p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$	$(A_{H_3L}-A)[H]$	$\log\{(A_{H_3L}-A)/(A-A_{H_2L})\}$
0.9991	0.21636	3.400e+38	0.01289	3.400e+38
1.239	0.21911	3.400e+38	0.007260	3.400e+38

Table S-2. 1 Raw data (continued)

1.449	0.22094	-1.831	0.004411	3.400e+38
1.679	0.22375	-1.417	0.002539	3.400e+38
1.909	0.22784	-1.128	0.001444	3.400e+38
2.119	0.23261	-0.9204	0.0008544	3.400e+38
2.359	0.24130	-0.6696	0.0004536	3.400e+38
2.519	0.24797	-0.5266	0.0002936	3.400e+38
2.789	0.26338	-0.2657	0.0001327	3.400e+38
2.899	0.27104	-0.1536	9.331e-05	3.400e+38
3.139	0.28813	0.08409	4.129e-05	3.400e+38
3.309	0.29953	0.2476	2.232e-05	3.400e+38
3.559	0.31491	0.5029	8.305e-06	3.400e+38
3.729	0.32290	0.6718	4.124e-06	3.400e+38
3.949	0.33043	0.8831	1.638e-06	3.400e+38
4.199	0.33696	1.166	5.084e-07	3.400e+38
4.449	0.34017	1.399	1.717e-07	3.400e+38
4.709	0.34258	1.708	4.729e-08	3.400e+38
5.099	0.34406	2.124	7.483e-09	3.400e+38
5.469	0.34478	2.757	7.470e-10	3.400e+38
5.919	0.34536	3.400e+38	-4.337e-10	-2.843
6.289	0.34512	3.400e+38	-6.168e-11	-3.320
6.699	0.34531	3.400e+38	-6.199e-11	-2.908
6.969	0.34511	3.400e+38	-1.181e-11	-3.358
7.199	0.34539	3.400e+38	-2.466e-11	-2.808
7.539	0.34497	3.623	8.674e-13	3.400e+38
7.839	0.34548	3.400e+38	-6.953e-12	-2.717
7.969	0.34786	3.400e+38	-3.071e-11	-1.938
8.259	0.34855	3.400e+38	-1.955e-11	-1.843
8.669	0.34848	3.400e+38	-7.456e-12	-1.852
8.909	0.34818	3.400e+38	-3.921e-12	-1.892
9.209	0.34819	3.400e+38	-1.971e-12	-1.890
9.499	0.34871	3.400e+38	-1.176e-12	-1.824
9.819	0.34952	3.400e+38	-6.856e-13	-1.736
10.10	0.35159	3.400e+38	-5.246e-13	-1.569
10.32	0.35317	3.400e+38	-3.919e-13	-1.473
10.50	0.35525	3.400e+38	-3.248e-13	-1.371
10.73	0.35961	3.400e+38	-2.726e-13	-1.209

Table S-2. 1 Raw data (continued)

10.90	0.36302	3.400e+38	-2.273e-13	-1.111
11.11	0.37390	3.400e+38	-2.248e-13	-0.8855
11.32	0.38798	3.400e+38	-2.062e-13	-0.6846
11.50	0.40364	3.400e+38	-1.858e-13	-0.5157
11.70	0.42625	3.400e+38	-1.625e-13	-0.3197
11.90	0.45342	3.400e+38	-1.368e-13	-0.1186
12.10	0.48285	3.400e+38	-1.097e-13	0.08614
12.33	0.51285	3.400e+38	-7.868e-14	0.3056
12.51	0.53487	3.400e+38	-5.880e-14	0.4929
12.71	0.55536	3.400e+38	-4.110e-14	0.7151
12.88	0.56735	3.400e+38	-2.937e-14	0.8914

(c) at 300 nm

p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$	$(A_{H_3L}-A)[H]$	$\log\{(A_{H_3L}-A)/(A-A_{H_2L})\}$
0.9991	0.00092000	-9.869	0.01514	3.400e+38
1.239	0.0019700	-2.155	0.008652	3.400e+38
1.449	0.0033500	-1.787	0.005286	3.400e+38
1.679	0.0060600	-1.453	0.003056	3.400e+38
1.909	0.011030	-1.144	0.001738	3.400e+38
2.119	0.016370	-0.9434	0.001031	3.400e+38
2.359	0.025950	-0.7021	0.0005514	3.400e+38
2.519	0.034530	-0.5435	0.0003555	3.400e+38
2.789	0.052850	-0.2809	0.0001611	3.400e+38
2.899	0.061610	-0.1730	0.0001140	3.400e+38
3.139	0.082300	0.06728	5.060e-05	3.400e+38
3.309	0.095450	0.2231	2.776e-05	3.400e+38
3.559	0.11457	0.4823	1.033e-05	3.400e+38
3.729	0.12433	0.6493	5.163e-06	3.400e+38
3.949	0.13406	0.8705	2.017e-06	3.400e+38
4.199	0.14100	1.105	6.955e-07	3.400e+38
4.449	0.14557	1.352	2.286e-07	3.400e+38
4.709	0.14811	1.578	7.601e-08	3.400e+38
5.099	0.15032	1.949	1.337e-08	3.400e+38
5.469	0.15114	2.242	2.920e-09	3.400e+38
5.919	0.15182	2.923	2.169e-10	3.400e+38
6.289	0.15195	3.480	2.570e-11	3.400e+38

Table S-2. 1 Raw data (continued)

6.699	0.15218	3.400e+38	-3.599e-11	-3.203
6.969	0.15210	3.400e+38	-1.074e-11	-3.459
7.199	0.15209	3.400e+38	-5.691e-12	-3.504
7.539	0.15214	3.400e+38	-4.046e-12	-3.312
7.839	0.15197	3.702	4.346e-13	3.400e+38
7.969	0.15150	2.479	5.369e-12	3.400e+38
8.259	0.15232	3.400e+38	-1.762e-12	-2.953
8.669	0.15228	3.400e+38	-5.999e-13	-3.011
8.909	0.15211	3.400e+38	-1.356e-13	-3.417
9.209	0.15269	3.400e+38	-4.264e-13	-2.619
9.499	0.15284	3.400e+38	-2.662e-13	-2.533
9.819	0.15496	3.400e+38	-4.490e-13	-1.983
10.10	0.15695	3.400e+38	-3.940e-13	-1.757
10.32	0.15932	3.400e+38	-3.511e-13	-1.583
10.50	0.16129	3.400e+38	-2.944e-13	-1.477
10.73	0.16723	3.400e+38	-2.842e-13	-1.252
10.90	0.17161	3.400e+38	-2.474e-13	-1.136
11.11	0.18421	3.400e+38	-2.506e-13	-0.8992
11.32	0.20014	3.400e+38	-2.309e-13	-0.6967
11.50	0.21820	3.400e+38	-2.098e-13	-0.5243
11.70	0.24504	3.400e+38	-1.860e-13	-0.3204
11.90	0.27586	3.400e+38	-1.563e-13	-0.1213
12.10	0.30960	3.400e+38	-1.255e-13	0.08358
12.33	0.34394	3.400e+38	-8.997e-14	0.3024
12.51	0.36841	3.400e+38	-6.702e-14	0.4828
12.71	0.39192	3.400e+38	-4.688e-14	0.7016
12.88	0.40514	3.400e+38	-3.344e-14	0.8659

2. 2 Thiacalix[4]areretetrasulfonate (4)

2. 2. 1 Summary of the experimental parameters

Temperature/K	298
p[H] range	0.97-12.83
Total number of datum points	60
Solution conditions	
Concentration of the compound/μmol dm^{-3}	20.45
Ionic strength/mol dm^{-3}, electrolyte	0.2, NaCl

2. 2. 2 Calculation of the first acid dissociation constant

2. 2. 2. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (11), setting allowable error to be 0.1%		
Wavelength/nm	300	310	320
p[H] range for calculation	0.97-3.14	1.37-3.35	0.97-3.35
Number of datum points	8	11	13
Inputted A_{H4L}	0.28300	0.16560	0.03707
Inputted A_{H3L}	0.36850	0.29350	0.14500

2. 2. 2. 2 Results

Wavelength/nm	300	310	320
pK_{a1} ± error	$2.10_7 \pm 0.01_3$	$2.18_9 \pm 0.00_9$	$2.20_0 \pm 0.01_0$
Correlation coefficient	0.99815	0.99897	0.99878

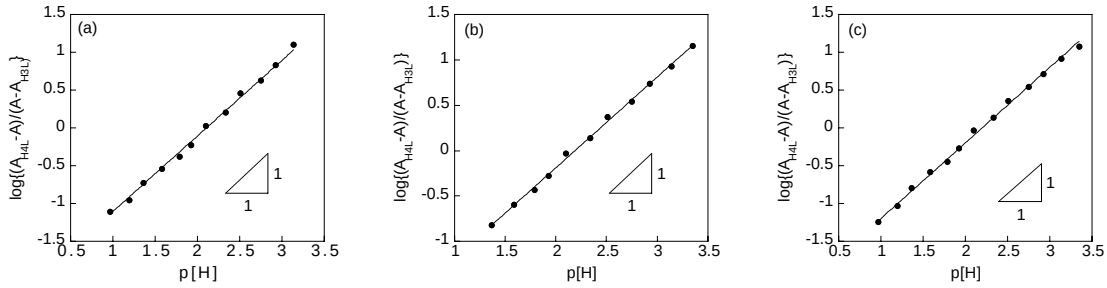

Figure S-2. 2. 1 Evaluation of the pK_{a1} value for the calixarene **4**; plots of eqn. (11). (a) λ = 300 nm, (b) λ = 310 nm, (a) λ = 320 nm.

2. 2. 3 Estimation of the A_{H2L} values

2. 2. 3. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (27), setting allowable error to be 0.1%		
Wavelength/nm	330	340	350
p[H] range for calculation	7.37-9.35	7.54-9.35	7.37-9.35
Number of datum points	13	12	13
Inputted A_{H3L}	0.07760	0.02000	0.00270

2. 2. 3 .2 Results

Wavelength/nm	330	340	350
A_{H2L}± error	$0.2548_9 \pm 0.0035_2$	$0.1733_5 \pm 0.0041_1$	$0.1108_3 \pm 0.0032_3$
pK_{a2} ± error	$8.55_2 \pm 0.01_5$	$8.50_2 \pm 0.02_0$	$8.49_5 \pm 0.02_2$
Correlation coefficient	0.99403	0.98953	0.98722

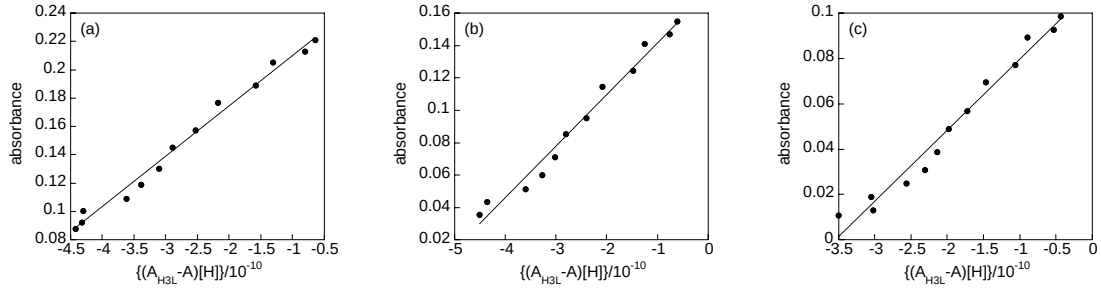

Figure S-2. 2. 2 Estimation of the A_{H2L} values for the calixarene **4**; plots of eqn. (27).
(a) λ = 330 nm, (b) λ = 340 nm, (a) λ = 350 nm.

2. 2. 4 Calculation of the second acid dissociation constant

2. 2. 4. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (12), setting allowable error to be 0.1%		
Wavelength/nm	330	340	350
p[H] range for calculation	7.37-9.35	7.54-9.35	7.37-9.35
Number of datum points	13	12	13
Inputted A_{H3L}	0.07760	0.02000	0.00270
Inputted A_{H2L}	0.24589	0.17335	0.11083

2. 2. 4. 2 Results

Wavelength/nm	330	340	350
pK_{a2} ± error	$8.55_4 \pm 0.00_9$	$8.49_9 \pm 0.01_1$	$8.49_0 \pm 0.01_2$
Correlation coefficient	0.99859	0.99779	0.99771

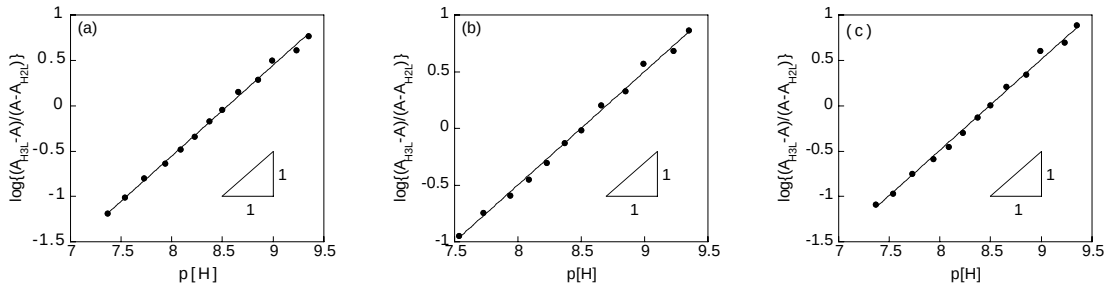

Figure S-2. 2. 3 Evaluation of the pK_{a2} value for the calixarene **4**; plots of eqn. (12).
(a) λ = 330 nm, (b) λ = 340 nm, (a) λ = 350 nm.

2. 2. 5 Calculation of the third and fourth acid dissociation constant

2. 2. 5. 1 Summary of the calculation parameters

Method	curve-fitting regression analysis of eqn. (13), setting allowable error to be 0.1%		
Wavelength/nm	330	340	350
p[H] range for calculation	10.56-12.83	10.56-12.83	10.56-12.83
Number of datum points	16	16	16
Inputted A_{H2L}	0.24589	0.17335	0.11083

2. 2. 5. 2 Results

Wavelength/nm	330	340	350
pK_{a3} ± error	$11.94_1 \pm 0.28_3$	$12.17_8 \pm 0.32_6$	$12.16_3 \pm 0.30_5$
pK_{a4} ± error	$11.72_8 \pm 0.10_8$	$11.73_0 \pm 0.14_9$	$11.71_4 \pm 0.14_9$
A_{HL} ± error	$0.4174_9 \pm 0.1657_0$	$0.4114_3 \pm 0.2492_9$	$0.2712_9 \pm 0.1455_6$
A_L ± error	$0.6219_7 \pm 0.0172_5$	$0.5576_7 \pm 0.0241_5$	$0.3433_9 \pm 0.0145_6$
Correlation coefficient	0.99791	0.99740	0.99741

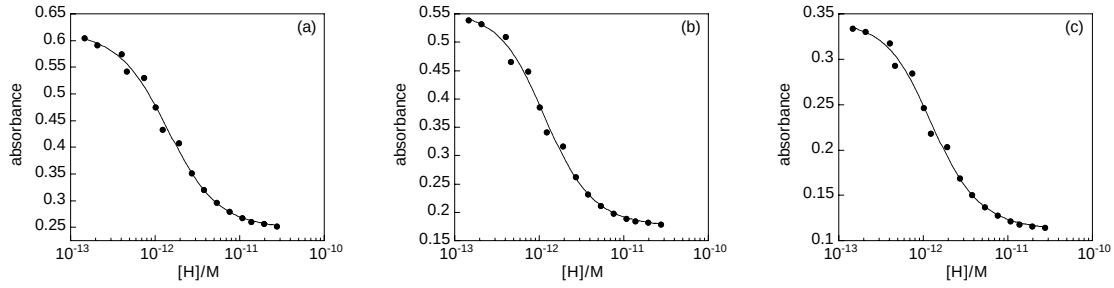

Figure S-2. 2. 4 Evaluation of the pK_{a3} and pK_{a4} values for the calixarene **4**; curve-fittings of eqn. (13). Solid lines, simulated curves. (a) λ = 330 nm, (b) λ = 340 nm, (a) λ = 350 nm.

Table S-2. 2 Raw data

(a) at 300 nm

p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$	p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$
(1 M HCl)	0.28300	-1.536	8.369	0.34296	0.3706
0.9691	0.28922	-1.105	8.499	0.33817	0.2598
1.199	0.29149	-0.9576	8.659	0.33104	0.1080
1.369	0.29661	-0.7228	8.849	0.32707	0.02683
1.589	0.30227	-0.5362	8.989	0.32074	-0.1023
1.789	0.30816	-0.3799	9.229	0.31838	-0.1513
1.929	0.31497	-0.2239	9.349	0.31534	-0.2158
2.099	0.32701	0.02561	9.539	0.31361	-0.2536
2.339	0.33556	0.2029	9.679	0.31174	-0.2956
2.509	0.34641	0.4580	9.819	0.31106	-0.3111
2.749	0.35218	0.6273	9.969	0.31006	-0.3344
2.929	0.35747	0.8294	10.13	0.30913	-0.3564
3.139	0.36229	1.106	10.25	0.30737	-0.3994
3.349	0.36576	1.480	10.43	0.30658	-0.4193
3.599	0.36711	1.782	10.56	0.30504	-0.4593
3.729	0.36762	1.983	10.71	0.30460	-0.4710
3.939	0.36923	3.400e+38	10.86	0.30293	-0.5172
4.359	0.36940	3.400e+38	10.97	0.30073	-0.5823
4.719	0.36963	3.400e+38	11.12	0.29736	-0.6950
5.169	0.36853	3.400e+38	11.27	0.29314	-0.8711
5.639	0.36859	3.400e+38	11.42	0.28833	-1.177
5.939	0.36842	3.028	11.57	0.28100	3.400e+38
6.339	0.36814	2.374	11.72	0.27114	3.400e+38
6.529	0.36756	1.954	11.91	0.26624	3.400e+38
6.919	0.36539	1.423	11.99	0.25977	3.400e+38
7.369	0.36461	1.322	12.13	0.25194	3.400e+38
7.539	0.36236	1.111	12.33	0.25103	3.400e+38
7.729	0.35899	0.9026	12.39	0.24838	3.400e+38
7.939	0.35658	0.7905	12.68	0.24588	3.400e+38
8.089	0.35190	0.6181	12.83	0.24552	3.400e+38
8.229	0.34813	0.5048			

Table S-2. 2 Raw data (continued)

(b) at 310 nm

p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$	p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$
(1 M HCl)	0.16560	-2.433	8.369	0.32050	3.400e+38
0.9691	0.17153	-1.313	8.499	0.32472	3.400e+38
1.199	0.17479	-1.111	8.659	0.33203	3.400e+38
1.369	0.18234	-0.8222	8.849	0.33635	3.400e+38
1.589	0.19148	-0.5957	8.989	0.34268	3.400e+38
1.789	0.19985	-0.4368	9.229	0.34593	3.400e+38
1.929	0.20957	-0.2808	9.349	0.34838	3.400e+38
2.099	0.22716	-0.03248	9.539	0.34993	3.400e+38
2.339	0.23991	0.1420	9.679	0.35158	3.400e+38
2.509	0.25535	0.3715	9.819	0.35210	3.400e+38
2.749	0.26492	0.5410	9.969	0.35286	3.400e+38
2.929	0.27381	0.7400	10.13	0.35313	3.400e+38
3.139	0.28001	0.9285	10.25	0.35349	3.400e+38
3.349	0.28511	1.154	10.43	0.35333	3.400e+38
3.599	0.28655	1.241	10.56	0.35324	3.400e+38
3.729	0.28900	1.438	10.71	0.35210	3.400e+38
3.939	0.29129	1.755	10.86	0.35073	3.400e+38
4.359	0.29214	1.969	10.97	0.34846	3.400e+38
4.719	0.29197	1.917	11.12	0.34535	3.400e+38
5.169	0.29274	2.223	11.27	0.34036	3.400e+38
5.639	0.29338	3.027	11.42	0.33386	3.400e+38
5.939	0.29373	3.400e+38	11.57	0.32418	3.400e+38
6.339	0.29431	3.400e+38	11.72	0.30710	3.400e+38
6.529	0.29595	3.400e+38	11.91	0.30018	3.400e+38
6.919	0.29638	3.400e+38	11.99	0.28716	1.283
7.369	0.29817	3.400e+38	12.13	0.27015	0.6510
7.539	0.30001	3.400e+38	12.33	0.26682	0.5791
7.729	0.30325	3.400e+38	12.39	0.25666	0.3930
7.939	0.30655	3.400e+38	12.68	0.25102	0.3034
8.089	0.31066	3.400e+38	12.83	0.25364	0.3441
8.229	0.31438	3.400e+38			

Table S-2. 2 Raw data (continued)

(c) at 320 nm

p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$	p[H]	absorbance	$\log\{(A_{H_4L}-A)/(A-A_{H_3L})\}$
(1 M HCl)	0.037070	-1.630	8.369	0.22459	3.400e+38
0.9691	0.042890	-1.244	8.499	0.23815	3.400e+38
1.199	0.046270	-1.031	8.659	0.26040	3.400e+38
1.369	0.052070	-0.7921	8.849	0.27323	3.400e+38
1.589	0.059290	-0.5863	8.989	0.29196	3.400e+38
1.789	0.065670	-0.4431	9.229	0.30097	3.400e+38
1.929	0.074760	-0.2704	9.349	0.31013	3.400e+38
2.099	0.088910	-0.03422	9.539	0.31579	3.400e+38
2.339	0.099610	0.1392	9.679	0.32016	3.400e+38
2.509	0.11223	0.3605	9.819	0.32283	3.400e+38
2.749	0.12107	0.5453	9.969	0.32692	3.400e+38
2.929	0.12742	0.7109	10.13	0.32940	3.400e+38
3.139	0.13339	0.9189	10.25	0.33170	3.400e+38
3.349	0.13674	1.082	10.43	0.33377	3.400e+38
3.599	0.13860	1.200	10.56	0.33699	3.400e+38
3.729	0.14072	1.384	10.71	0.33860	3.400e+38
3.939	0.14216	1.568	10.86	0.34017	3.400e+38
4.359	0.14353	1.860	10.97	0.34311	3.400e+38
4.719	0.14453	2.359	11.12	0.34687	3.400e+38
5.169	0.14510	3.400e+38	11.27	0.35139	3.400e+38
5.639	0.14517	3.400e+38	11.42	0.35675	3.400e+38
5.939	0.14637	3.400e+38	11.57	0.36241	3.400e+38
6.339	0.14754	3.400e+38	11.72	0.37221	3.400e+38
6.529	0.15034	3.400e+38	11.91	0.37572	3.400e+38
6.919	0.15535	3.400e+38	11.99	0.38007	3.400e+38
7.369	0.15859	3.400e+38	12.13	0.38316	3.400e+38
7.539	0.16559	3.400e+38	12.33	0.38453	3.400e+38
7.729	0.17376	3.400e+38	12.39	0.38430	3.400e+38
7.939	0.18395	3.400e+38	12.68	0.38302	3.400e+38
8.089	0.19527	3.400e+38	12.83	0.39271	3.400e+38
8.229	0.20801	3.400e+38			

Table S-2. 2 Raw data (continued)

(d) at 330 nm

p[H]	absorbance	(A_{H_3L}-A)[H]	log{(A_{H_3L}-A)/(A-A_{H_2L})}
(1 M HCl)	0.0054800		3.400e+38
0.9691	0.0077600	0.007499	3.400e+38
1.199	0.0093400	0.004316	3.400e+38
1.369	0.013460	0.002742	3.400e+38
1.589	0.018420	0.001524	3.400e+38
1.789	0.022990	0.0008876	3.400e+38
1.929	0.029020	0.0005720	3.400e+38
2.099	0.037770	0.0003171	3.400e+38
2.339	0.044690	0.0001507	3.400e+38
2.509	0.052920	7.643e-05	3.400e+38
2.749	0.058630	3.381e-05	3.400e+38
2.929	0.063530	1.657e-05	3.400e+38
3.139	0.066740	7.884e-06	3.400e+38
3.349	0.069150	3.782e-06	3.400e+38
3.599	0.070390	1.815e-06	3.400e+38
3.729	0.072040	1.038e-06	3.400e+38
3.939	0.072960	5.339e-07	3.400e+38
4.359	0.073850	1.640e-07	3.400e+38
4.719	0.074200	6.492e-08	3.400e+38
5.169	0.075230	1.606e-08	3.400e+38
5.639	0.075950	3.788e-09	3.400e+38
5.939	0.077600	-2.634e-15	-7.866
6.339	0.077620	-9.161e-12	-3.925
6.529	0.080100	-7.394e-10	-1.822
6.919	0.084150	-7.892e-10	-1.393
7.369	0.087920	-4.412e-10	-1.185
7.539	0.092540	-4.318e-10	-1.011
7.729	0.10064	-4.299e-10	-0.7996
7.939	0.10907	-3.621e-10	-0.6383
8.089	0.11920	-3.389e-10	-0.4836
8.229	0.13015	-3.101e-10	-0.3429
8.369	0.14522	-2.891e-10	-0.1728
8.499	0.15724	-2.524e-10	-0.04655
8.659	0.17659	-2.170e-10	0.1549

Table S-2. 2 Raw data (continued)

8.849	0.18886	-1.575e-10	0.2902
8.989	0.20533	-1.310e-10	0.4982
9.229	0.21283	-7.980e-11	0.6118
9.349	0.22130	-6.432e-11	0.7667
9.539	0.22628	-4.297e-11	0.8798
9.679	0.23133	-3.219e-11	1.024
9.819	0.23381	-2.369e-11	1.112
9.969	0.23735	-1.715e-11	1.272
10.13	0.24007	-1.207e-11	1.446
10.25	0.24367	-9.359e-12	1.874
10.43	0.24629	-6.281e-12	3.400e+38
10.56	0.25128	-4.794e-12	3.400e+38
10.71	0.25623	-3.490e-12	3.400e+38
10.86	0.26068	-2.533e-12	3.400e+38
10.97	0.26782	-2.043e-12	3.400e+38
11.12	0.27961	-1.536e-12	3.400e+38
11.27	0.29639	-1.177e-12	3.400e+38
11.42	0.31983	-9.229e-13	3.400e+38
11.57	0.35101	-7.375e-13	3.400e+38
11.72	0.40767	-6.303e-13	3.400e+38
11.91	0.43265	-4.377e-13	3.400e+38
11.99	0.47497	-4.075e-13	3.400e+38
12.13	0.52966	-3.358e-13	3.400e+38
12.33	0.54253	-2.179e-13	3.400e+38
12.39	0.57510	-2.031e-13	3.400e+38
12.68	0.59190	-1.077e-13	3.400e+38
12.83	0.60444	-7.809e-14	3.400e+38

(e) at 340 nm

p[H]	absorbance	$(A_{H_3L}-A)[H]$	$\log\{(A_{H_3L}-A)/(A-A_{H_2L})\}$
(1 M HCl)	0.00087000		3.400e+38
0.9691	0.0015000	0.001987	3.400e+38
1.199	0.0024400	0.001110	3.400e+38
1.369	0.0031400	0.0007207	3.400e+38
1.589	0.0053900	0.0003763	3.400e+38
1.789	0.0056400	0.0002334	3.400e+38

Table S-2. 2 Raw data (continued)

1.929	0.0068200	0.0001552	3.400e+38
2.099	0.0094800	8.374e-05	3.400e+38
2.339	0.011510	3.889e-05	3.400e+38
2.509	0.012440	2.341e-05	3.400e+38
2.749	0.014280	1.019e-05	3.400e+38
2.929	0.015850	4.886e-06	3.400e+38
3.139	0.015070	3.579e-06	3.400e+38
3.349	0.017300	1.209e-06	3.400e+38
3.599	0.016570	8.634e-07	3.400e+38
3.729	0.016710	6.139e-07	3.400e+38
3.939	0.017010	3.440e-07	3.400e+38
4.359	0.017600	1.050e-07	3.400e+38
4.719	0.019470	1.012e-08	3.400e+38
5.169	0.019720	1.897e-09	3.400e+38
5.639	0.020370	-8.494e-10	-2.616
5.939	0.020120	-1.381e-10	-3.106
6.339	0.022640	-1.209e-09	-1.757
6.529	0.024300	-1.272e-09	-1.540
6.919	0.027260	-8.747e-10	-1.304
7.369	0.029530	-4.074e-10	-1.179
7.539	0.035600	-4.509e-10	-0.9460
7.729	0.043310	-4.350e-10	-0.7465
7.939	0.051270	-3.598e-10	-0.5915
8.089	0.060050	-3.262e-10	-0.4516
8.229	0.071100	-3.015e-10	-0.3012
8.369	0.085490	-2.800e-10	-0.1276
8.499	0.095410	-2.390e-10	-0.01433
8.659	0.11460	-2.074e-10	0.2069
8.849	0.12451	-1.479e-10	0.3304
8.989	0.14107	-1.242e-10	0.5741
9.229	0.14706	-7.498e-11	0.6842
9.349	0.15505	-6.045e-11	0.8680
9.539	0.15952	-4.032e-11	1.004
9.679	0.16389	-3.013e-11	1.182
9.819	0.16689	-2.228e-11	1.357
9.969	0.16907	-1.601e-11	1.542

Table S-2. 2 Raw data (continued)

10.13	0.17065	-1.119e-11	1.747
10.25	0.17410	-8.684e-12	3.400e+38
10.43	0.17500	-5.771e-12	3.400e+38
10.56	0.17870	-4.380e-12	3.400e+38
10.71	0.18215	-3.168e-12	3.400e+38
10.86	0.18465	-2.278e-12	3.400e+38
10.97	0.18887	-1.813e-12	3.400e+38
11.12	0.19733	-1.348e-12	3.400e+38
11.27	0.21108	-1.028e-12	3.400e+38
11.42	0.23145	-8.056e-13	3.400e+38
11.57	0.26209	-6.530e-13	3.400e+38
11.72	0.31599	-5.652e-13	3.400e+38
11.91	0.34088	-3.956e-13	3.400e+38
11.99	0.38529	-3.746e-13	3.400e+38
12.13	0.44902	-3.187e-13	3.400e+38
12.33	0.46567	-2.089e-13	3.400e+38
12.39	0.50938	-1.998e-13	3.400e+38
12.68	0.53240	-1.073e-13	3.400e+38
12.83	0.53902	-7.693e-14	3.400e+38

(f) at 350 nm

p[H]	absorbance	$(A_{H_3L}-A)[H]$	$\log\{(A_{H_3L}-A)/(A-A_{H_2L})\}$
(1 M HCl)	-0.00095000		3.400e+38
0.9691	-0.00037000	0.0003297	3.400e+38
1.199	8.0000e-05	0.0001657	3.400e+38
1.369	0.00021000	0.0001064	3.400e+38
1.589	6.0000e-05	6.800e-05	3.400e+38
1.789	0.00095000	2.844e-05	3.400e+38
1.929	0.00046000	2.637e-05	3.400e+38
2.099	0.00095000	1.393e-05	3.400e+38
2.339	0.0017900	4.168e-06	3.400e+38
2.509	0.0016400	3.283e-06	3.400e+38
2.749	0.0026200	1.426e-07	3.400e+38
2.929	0.0019600	8.713e-07	3.400e+38
3.139	0.0025300	1.234e-07	3.400e+38
3.349	0.0023800	1.432e-07	3.400e+38

Table S-2. 2 Raw data (continued)

3.599	0.0026600	1.007e-08	3.400e+38
3.729	0.0022300	8.770e-08	3.400e+38
3.939	0.0024500	2.876e-08	3.400e+38
4.359	0.0021400	2.450e-08	3.400e+38
4.719	0.0025200	3.437e-09	3.400e+38
5.169	0.0027800	-5.420e-10	-3.131
5.639	0.0025400	3.673e-10	3.400e+38
5.939	0.0044500	-2.014e-09	-1.784
6.339	0.0041600	-6.688e-10	-1.864
6.529	0.0054100	-8.015e-10	-1.590
6.919	0.0084500	-6.928e-10	-1.251
7.369	0.010880	-3.497e-10	-1.087
7.539	0.013150	-3.020e-10	-0.9707
7.729	0.019040	-3.049e-10	-0.7495
7.939	0.024930	-2.558e-10	-0.5871
8.089	0.030950	-2.301e-10	-0.4514
8.229	0.038830	-2.132e-10	-0.2995
8.369	0.048860	-1.973e-10	-0.1279
8.499	0.056930	-1.719e-10	0.002651
8.659	0.069520	-1.465e-10	0.2089
8.849	0.077290	-1.056e-10	0.3471
8.989	0.089260	-8.876e-11	0.6035
9.229	0.092650	-5.308e-11	0.6944
9.349	0.098520	-4.289e-11	0.8912
9.539	0.10121	-2.847e-11	1.010
9.679	0.10429	-2.127e-11	1.191
9.819	0.10657	-1.575e-11	1.387
9.969	0.10829	-1.134e-11	1.619
10.13	0.10906	-7.901e-12	1.779
10.25	0.11101	-6.104e-12	3.400e+38
10.43	0.11238	-4.084e-12	3.400e+38
10.56	0.11431	-3.081e-12	3.400e+38
10.71	0.11578	-2.210e-12	3.400e+38
10.86	0.11801	-1.595e-12	3.400e+38
10.97	0.12158	-1.277e-12	3.400e+38
11.12	0.12797	-9.523e-13	3.400e+38

Table S-2. 2 Raw data (continued)

11.27	0.13705	-7.230e-13	3.400e+38
11.42	0.15053	-5.632e-13	3.400e+38
11.57	0.16898	-4.485e-13	3.400e+38
11.72	0.20349	-3.834e-13	3.400e+38
11.91	0.21825	-2.657e-13	3.400e+38
11.99	0.24618	-2.497e-13	3.400e+38
12.13	0.28457	-2.094e-13	3.400e+38
12.33	0.29315	-1.361e-13	3.400e+38
12.39	0.31751	-1.285e-13	3.400e+38
12.68	0.33062	-6.866e-14	3.400e+38
12.83	0.33359	-4.905e-14	3.400e+38

2. 3 Sulfonylcalix[4]areretetrasulfonate (5) in the absence of electrolyte

2. 3. 1 Summary of the experimental parameters

Temperature/K	298
p[H] range	4.38-10.02
Total number of datum points	30
Solution conditions	
Concentration of the compound/μmol dm^{-3}	20.45
Ionic strength/mol dm^{-3}, electrolyte	< 0.0008, none

2. 3. 2 Calculation of the third and fourth acid dissociation constant

2. 3. 2. 1 Summary of the calculation parameters

Method	curve-fitting regression analysis of eqn. (13), setting allowable error to be 0.1%		
Wavelength/nm	340	345	350
p[H] range for calculation	4.38-10.02	4.38-10.02	4.38-10.02
Number of datum points	30	30	30
Inputted A_{H2L}	0.27900	0.30700	0.30300
Inputted A_L	0.66000	0.72500	0.63270

2. 3. 2. 2 Results

Wavelength/nm	340	345	350
pK_{a3} ± error	$6.84_7 \pm 0.03_9$	$6.72_2 \pm 0.06_3$	$6.69_1 \pm 0.07_8$
pK_{a4} ± error	$6.73_5 \pm 0.03_7$	$6.73_6 \pm 0.02_9$	$6.78_4 \pm 0.03_6$
A_{HL} ± error	$0.4568_1 \pm 0.0296_7$	$0.4041_1 \pm 0.0314_8$	$0.3874_6 \pm 0.0296_7$
Correlation coefficient	0.99987	0.99983	0.99978

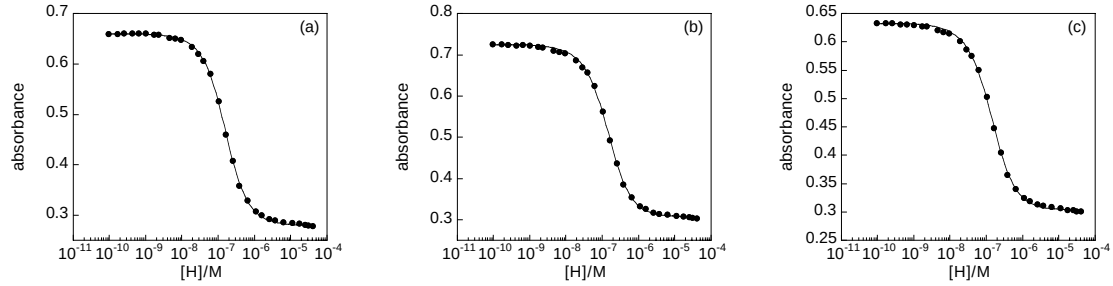

Figure S-2. 3. 1 Evaluation of the pK_{a3} and pK_{a4} values for the calixarene **5**; curve-fittings of eqn. (13). Solid lines, simulated curves. (a) λ = 340 nm, (b) λ = 345 nm, (a) λ = 350 nm.

Table S-2. 3 Raw data

p[H]	absorbance at 340 nm	absorbance at 345 nm	absorbance at 350 nm
4.380	0.27872	0.30268	0.30062
4.500	0.27911	0.30468	0.30131
4.590	0.28055	0.30643	0.30316
4.750	0.28386	0.30779	0.30338
4.950	0.28489	0.31013	0.30693
5.200	0.28654	0.31218	0.30906
5.420	0.28962	0.31414	0.31116
5.580	0.29269	0.31785	0.31377
5.800	0.29964	0.32567	0.31975
5.950	0.30748	0.33329	0.32485
6.190	0.32870	0.35399	0.34076
6.420	0.35899	0.38522	0.36523
6.590	0.40743	0.43628	0.40463
6.780	0.46031	0.49287	0.44847
6.980	0.52608	0.56205	0.50309
7.210	0.58057	0.62465	0.55083
7.400	0.60670	0.65705	0.57565

Table S-2. 3 Raw data (continued)

7.540	0.61973	0.66974	0.58664
7.730	0.63360	0.68759	0.60113
8.030	0.64794	0.70434	0.61509
8.180	0.65027	0.70719	0.61758
8.350	0.65141	0.71030	0.62048
8.640	0.65789	0.71847	0.62802
8.760	0.65798	0.71992	0.62812
8.990	0.66082	0.72256	0.63012
9.200	0.66106	0.72352	0.63086
9.370	0.66082	0.72317	0.63127
9.590	0.66127	0.72407	0.63294
9.780	0.65991	0.72537	0.63278
10.02	0.65980	0.72521	0.63281

2. 4 Sulfonylcalix[4]areretetrasulfonate (5) at the ionic strength of 0.2 mol dm^{-3}

2. 4. 1 Summary of the experimental parameters

Temperature/K	298
p[H] range	0.97-12.51
Total number of datum points	52
Solution conditions	
Concentration of the compound/μmol dm^{-3}	20.45
Ionic strength/mol dm^{-3}, electrolyte	0.2, NaCl

2. 4. 2 Estimation of the A_{H3L} values

2. 4. 2. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (28), setting allowable error to be 0.1%		
Wavelength/nm	340	345	350
p[H] range for calculation	0.97-1.88	0.97-1.88	0.97-1.72
Number of datum points	6	6	5
Inputted A_{H2L}	0.27900	0.30700	0.30300

2. 4. 2. 2 Results

Wavelength/nm	340	345	350
A_{H3L}± error	$0.1182_5 \pm 0.0028_6$	$0.1249_5 \pm 0.0028_6$	$0.1177_3 \pm 0.0015_0$
pK_{a2} ± error	$1.30_3 \pm 0.01_3$	$1.30_3 \pm 0.01_2$	$1.26_8 \pm 0.00_6$
Correlation coefficient	0.99812	0.99854	0.99967

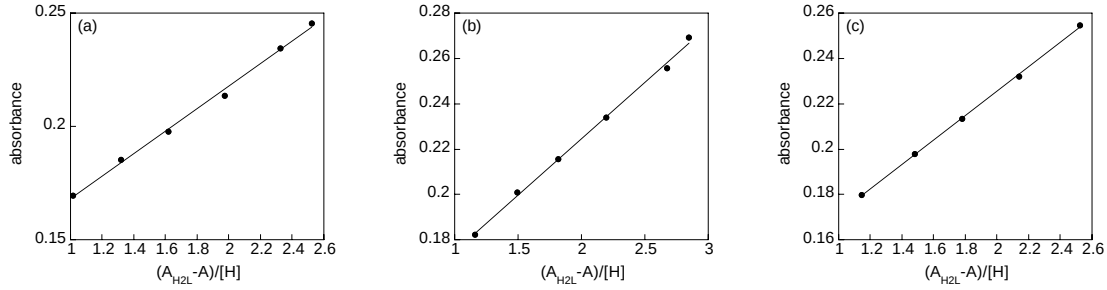

Figure S-2. 4. 1 Estimation of the A_{H3L} values for the calixarene **5**; plots of eqn. (28). (a) λ = 340 nm, (b) λ = 345 nm, (a) λ = 350 nm.

2. 4. 3 Calculation of the second acid dissociation constant

2. 4. 3. 1 Summary of the calculation parameters

Method	linear regression analysis of eqn. (12), setting allowable error to be 0.1%		
Wavelength/nm	340	340	350
p[H] range for calculation	0.97-2.03	0.97-2.03	0.97-1.88
Number of datum points	7	7	6
Inputted A_{H3L}	0.11825	0.12495	0.11773
Inputted A_{H2L}	0.27900	0.30700	0.30300

2. 4. 3. 2 Results

Wavelength/nm	340	340	350
pK_{a2} ± error	$1.30_0 \pm 0.00_4$	$1.29_6 \pm 0.00_7$	$1.23_8 \pm 0.00_4$
Correlation coefficient	0.99965	0.99897	0.99956

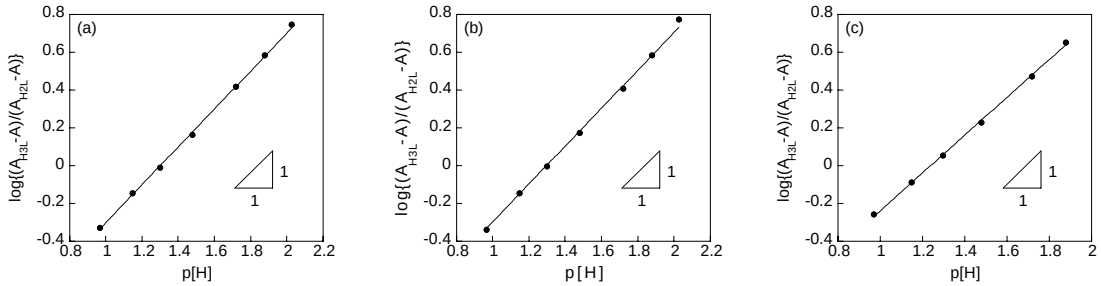

Figure S-2. 4. 2 Evaluation of the pK_{a2} value for the calixarene **5**; plots of eqn. (12). (a) λ = 340 nm, (b) λ = 345 nm, (a) λ = 350 nm.

2. 4. 4 Calculation of the third and fourth acid dissociation constant

2. 4. 4. 1 Summary of the calculation parameters

Method	curve-fitting regression analysis of eqn. (13), setting allowable error to be 0.1%		
Wavelength/nm	340	345	350
p[H] range for calculation	3.41-7.77	3.41-7.77	3.41-7.77
Number of datum points	26	26	26
Inputted A_{H2L}	0.27900	0.30700	0.30300
Inputted A_L	0.66000	0.72500	0.63270

2. 4. 4. 2 Results

Wavelength/nm	340	345	350
pK_{a3} ± error	$4.68_0 \pm 0.01_7$	$4.55_2 \pm 0.01_5$	$4.72_5 \pm 0.01_8$
pK_{a4} ± error	$4.56_0 \pm 0.03_3$	$4.39_2 \pm 0.01_0$	$4.53_6 \pm 0.02_6$
A_{HL} ± error	$0.5585_7 \pm 0.0176_3$	$0.4844_7 \pm 0.0094_2$	$0.5681_9 \pm 0.0111_8$
Correlation coefficient	0.99990	0.99998	0.99994

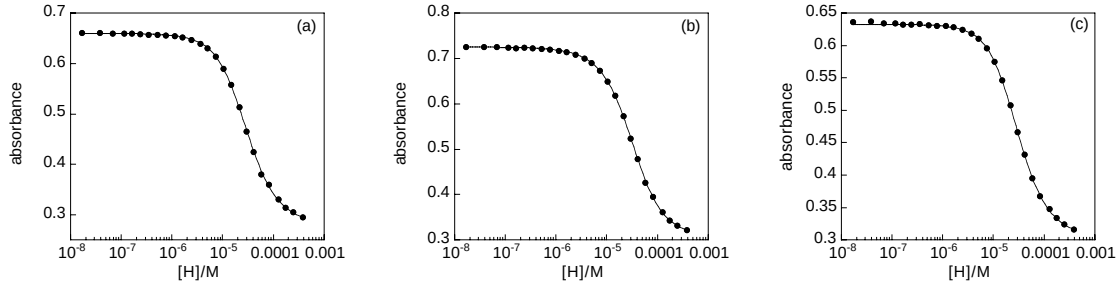

Figure S-2. 4. 3 Evaluation of the pK_{a3} and pK_{a4} values for the calixarene **5**; curve-fittings of eqn. (13). Solid lines, simulated curves. (a) λ = 340 nm, (b) λ = 345 nm, (a) λ = 350 nm.

Table S-2. 4 Raw data

(a) at 340 nm

p[H]	absorbance	$(A_{H_2L}-A)/[H]$	$\log\{(A_{H_3L}-A)/(A-A_{H_2L})\}$
0.9691	0.16968	1.018	-0.3275
1.149	0.18526	1.321	-0.1458
1.299	0.19766	1.620	-0.01043
1.479	0.21349	1.974	0.1625
1.719	0.23455	2.328	0.4177
1.879	0.24565	2.524	0.5821
2.029	0.25447	2.623	0.7445
2.159	0.26174	2.490	0.9198
2.369	0.26912	2.311	1.184
2.509	0.27278	2.008	1.395
2.709	0.27812	0.4504	2.259
2.869	0.28267	-2.715	3.400e+38
3.029	0.28586	-7.335	3.400e+38
3.199	0.28807	-14.34	3.400e+38
3.409	0.29500	-41.04	3.400e+38
3.599	0.30554	-105.4	3.400e+38
3.749	0.31372	-194.8	3.400e+38
3.899	0.33090	-411.4	3.400e+38
4.079	0.36016	-973.7	3.400e+38
4.229	0.37980	-1708	3.400e+38
4.389	0.42385	-3548	3.400e+38
4.519	0.46511	-6150	3.400e+38
4.669	0.51310	-1.093e+04	3.400e+38
4.829	0.55788	-1.881e+04	3.400e+38
4.979	0.59021	-2.966e+04	3.400e+38
5.129	0.61324	-4.499e+04	3.400e+38
5.299	0.63047	-6.998e+04	3.400e+38
5.439	0.63969	-9.913e+04	3.400e+38
5.609	0.64699	-1.496e+05	3.400e+38
5.789	0.65177	-2.294e+05	3.400e+38
5.939	0.65433	-3.262e+05	3.400e+38
6.119	0.65634	-4.964e+05	3.400e+38
6.279	0.65666	-7.181e+05	3.400e+38
6.459	0.65697	-1.088e+06	3.400e+38

Table S-2. 4 Raw data (continued)

6.619	0.65811	-1.577e+06	3.400e+38
6.779	0.65902	-2.285e+06	3.400e+38
6.939	0.66014	-3.313e+06	3.400e+38
7.169	0.65977	-5.620e+06	3.400e+38
7.409	0.66108	-9.800e+06	3.400e+38
7.769	0.66041	-2.241e+07	3.400e+38
8.139	0.66131	-5.266e+07	3.400e+38
8.589	0.66113	-1.484e+08	3.400e+38
8.929	0.66100	-3.244e+08	3.400e+38
9.299	0.66048	-7.595e+08	3.400e+38
9.709	0.66067	-1.953e+09	3.400e+38
10.13	0.66065	-5.137e+09	3.400e+38
10.50	0.66107	-1.206e+10	3.400e+38
10.94	0.66170	-3.326e+10	3.400e+38
11.32	0.66107	-7.966e+10	3.400e+38
11.70	0.66028	-1.907e+11	3.400e+38
12.12	0.66030	-5.016e+11	3.400e+38
12.51	0.66019	-1.231e+12	3.400e+38

(b) at 345 nm

p[H]	absorbance	$(A_{H_2L}-A)/[H]$	$\log\{(A_{H_3L}-A)/(A-A_{H_2L})\}$
0.9691	0.18229	1.161	-0.3374
1.149	0.20085	1.496	-0.1457
1.299	0.21555	1.821	-0.004055
1.479	0.23401	2.200	0.1744
1.719	0.25582	2.680	0.4077
1.879	0.26938	2.848	0.5842
2.029	0.28068	2.814	0.7721
2.159	0.28756	2.804	0.9225
2.369	0.29693	2.356	1.232
2.509	0.30098	1.944	1.466
2.709	0.30706	-0.03071	3.400e+38
2.869	0.30982	-2.086	3.400e+38
3.029	0.31348	-6.929	3.400e+38
3.199	0.31580	-13.92	3.400e+38
3.409	0.32170	-37.72	3.400e+38

Table S-2. 4 Raw data (continued)

3.599	0.33144	-97.11	3.400e+38
3.749	0.34298	-201.9	3.400e+38
3.899	0.36083	-426.7	3.400e+38
4.079	0.39503	-1056	3.400e+38
4.229	0.42669	-2028	3.400e+38
4.389	0.47807	-4190	3.400e+38
4.519	0.52330	-7147	3.400e+38
4.669	0.57307	-1.242e+04	3.400e+38
4.829	0.61765	-2.096e+04	3.400e+38
4.979	0.64949	-3.264e+04	3.400e+38
5.129	0.67253	-4.920e+04	3.400e+38
5.299	0.69041	-7.634e+04	3.400e+38
5.439	0.70043	-1.081e+05	3.400e+38
5.609	0.70871	-1.633e+05	3.400e+38
5.789	0.71441	-2.507e+05	3.400e+38
5.939	0.71758	-3.568e+05	3.400e+38
6.119	0.72014	-5.435e+05	3.400e+38
6.279	0.72166	-7.884e+05	3.400e+38
6.459	0.72256	-1.196e+06	3.400e+38
6.619	0.72352	-1.733e+06	3.400e+38
6.779	0.72317	-2.502e+06	3.400e+38
6.939	0.72407	-3.625e+06	3.400e+38
7.169	0.72537	-6.175e+06	3.400e+38
7.409	0.72521	-1.073e+07	3.400e+38
7.769	0.72556	-2.459e+07	3.400e+38
8.139	0.72555	-5.765e+07	3.400e+38
8.589	0.72605	-1.627e+08	3.400e+38
8.929	0.72554	-3.555e+08	3.400e+38
9.299	0.72540	-8.330e+08	3.400e+38
9.709	0.72540	-2.141e+09	3.400e+38
10.13	0.72546	-5.633e+09	3.400e+38
10.50	0.72553	-1.321e+10	3.400e+38
10.94	0.72663	-3.647e+10	3.400e+38
11.32	0.72546	-8.724e+10	3.400e+38
11.70	0.72555	-2.093e+11	3.400e+38
12.12	0.72605	-5.512e+11	3.400e+38

Table S-2. 4 Raw data (continued)

12.51	0.72554	-1.351e+12	3.400e+38

(C) data at 350 nm

p[H]	absorbance	$(A_{H_2L}-A)/[H]$	$\log\{(A_{H_3L}-A)/(A-A_{H_2L})\}$
0.9691	0.17995	1.146	-0.2564
1.149	0.19780	1.483	-0.08738
1.299	0.21348	1.782	0.05543
1.479	0.23203	2.139	0.2290
1.719	0.25479	2.525	0.4723
1.879	0.26810	2.642	0.6512
2.029	0.27914	2.551	0.8460
2.159	0.28611	2.436	1.014
2.369	0.29130	2.738	1.186
2.509	0.29558	2.395	1.394
2.709	0.30029	1.385	1.843
2.869	0.30341	-0.3011	3.400e+38
3.029	0.30648	-3.723	3.400e+38
3.199	0.31000	-11.07	3.400e+38
3.409	0.31629	-34.08	3.400e+38
3.599	0.32378	-82.57	3.400e+38
3.749	0.33356	-171.5	3.400e+38
3.899	0.34738	-351.8	3.400e+38
4.079	0.36764	-775.6	3.400e+38
4.229	0.39497	-1559	3.400e+38
4.389	0.43202	-3160	3.400e+38
4.519	0.46654	-5404	3.400e+38
4.669	0.50736	-9538	3.400e+38
4.829	0.54648	-1.643e+04	3.400e+38
4.979	0.57531	-2.595e+04	3.400e+38
5.129	0.59583	-3.942e+04	3.400e+38
5.299	0.61080	-6.128e+04	3.400e+38
5.439	0.61846	-8.670e+04	3.400e+38
5.609	0.62415	-1.306e+05	3.400e+38
5.789	0.62812	-2.000e+05	3.400e+38
5.939	0.63012	-2.843e+05	3.400e+38
6.119	0.63086	-4.313e+05	3.400e+38

Table S-2. 4 Raw data (continued)

6.279	0.63127	-6.242e+05	3.400e+38
6.459	0.63294	-9.495e+05	3.400e+38
6.619	0.63278	-1.372e+06	3.400e+38
6.779	0.63281	-1.983e+06	3.400e+38
6.939	0.63417	-2.878e+06	3.400e+38
7.169	0.63441	-4.892e+06	3.400e+38
7.409	0.63699	-8.567e+06	3.400e+38
7.769	0.63614	-1.958e+07	3.400e+38
8.139	0.63778	-4.611e+07	3.400e+38
8.589	0.63748	-1.299e+08	3.400e+38
8.929	0.63801	-2.845e+08	3.400e+38
9.299	0.63744	-6.659e+08	3.400e+38
9.709	0.63722	-1.710e+09	3.400e+38
10.13	0.63830	-4.513e+09	3.400e+38
10.50	0.63778	-1.056e+10	3.400e+38
10.94	0.63748	-2.907e+10	3.400e+38
11.32	0.63801	-6.985e+10	3.400e+38
11.70	0.63744	-1.673e+11	3.400e+38
12.12	0.63722	-4.397e+11	3.400e+38
12.51	0.63830	-1.083e+12	3.400e+38

3. A-, AD-, and ADQ-diagram of calix[4]areretetrasulfonate (3)

3. 1 A-diagram

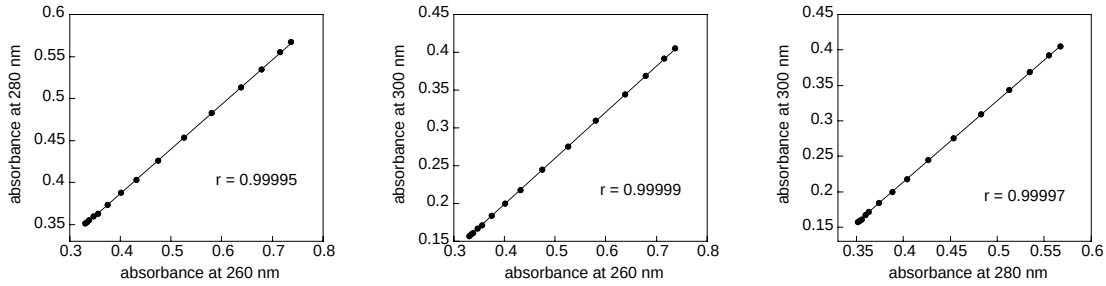

Figure S-3.1 A-diagram for the calixarene **3** in the region of 10.10 < p[H] <12.88.
[calixarene **3**]$_T$ = 44.2 µmol dm^{-3}, I = 0.2 mol dm^{-3}, optical path-length = 1 cm.

3. 2 AD-diagram

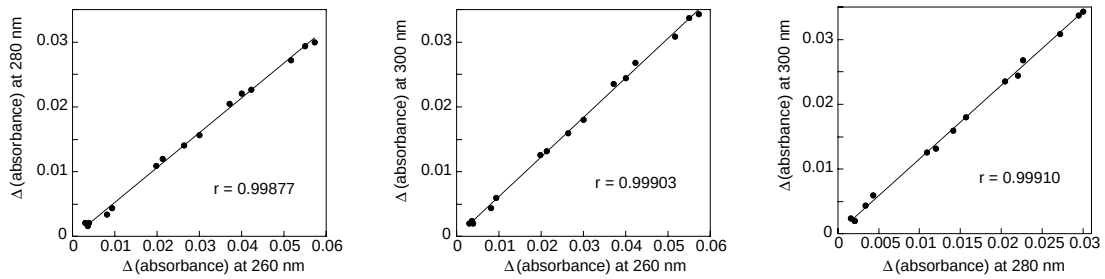

Figure S-3.2 AD-diagram for the calixarene **3** in the region of 10.10 < p[H] <12.88.
[calixarene **3**]$_T$ = 44.2 µmol dm^{-3}, I = 0.2 mol dm^{-3}, optical path-length = 1 cm.

3. 2 ADQ-diagram

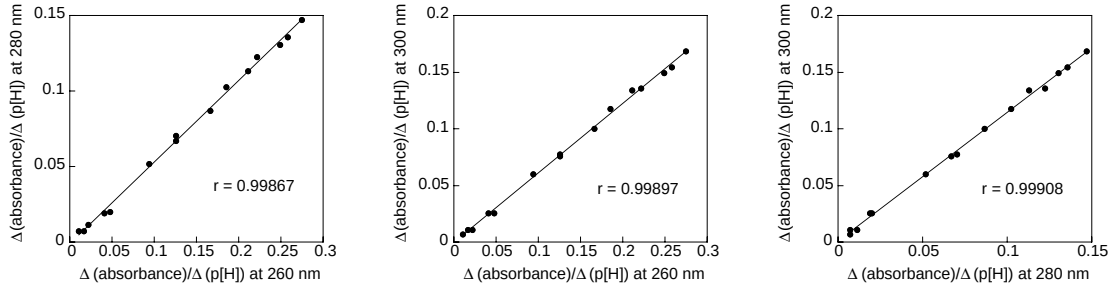

Figure S-3.3 ADQ-diagram for the calixarene **3** in the region of 10.10 < p[H] <12.88.
[calixarene **3**]$_T$ = 44.2 µmol dm^{-3}, I = 0.2 mol dm^{-3}, optical path-length = 1 cm.