Supplementary information

Sulfate anion templation of a neutral pseudorotaxane assembly using an indolocarbazole threading component

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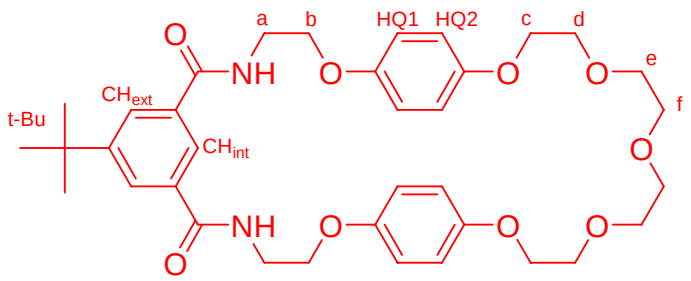
I) ^{1}H NMR spectra of macrocycle 2 in $(CD_3)_2SO$ and CD_3CN:



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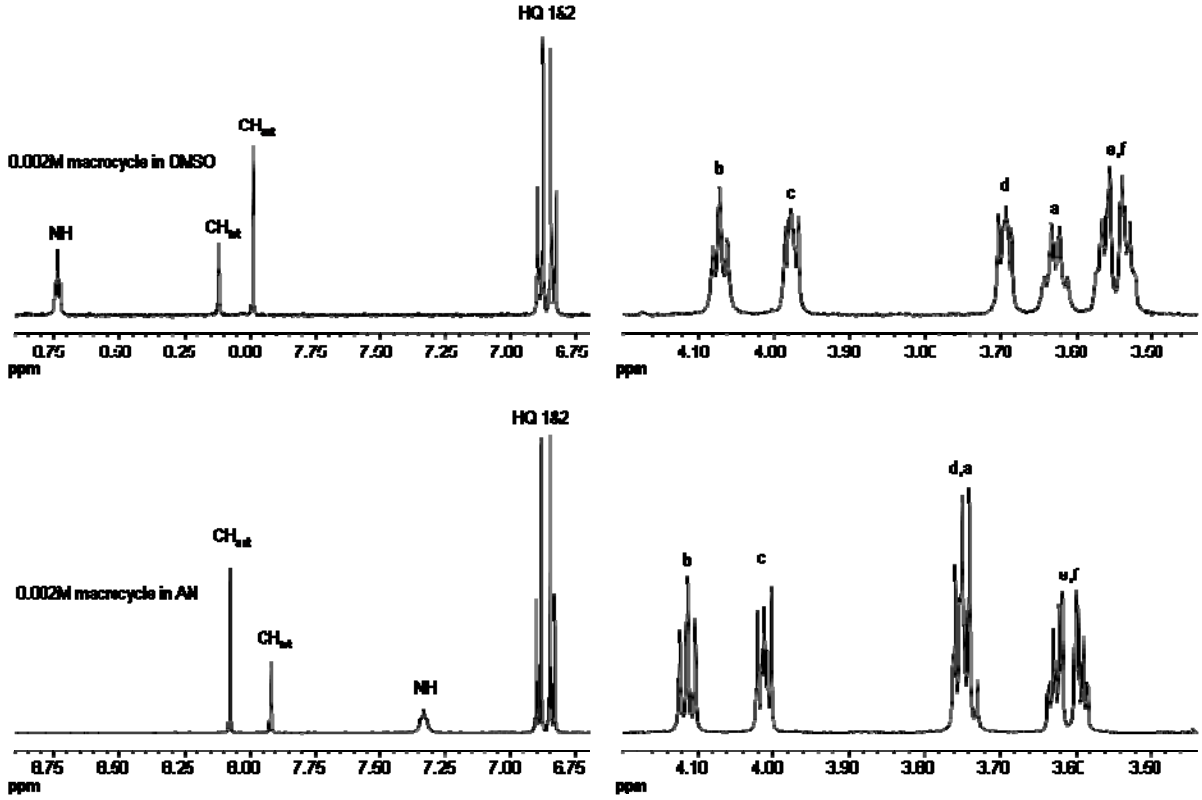
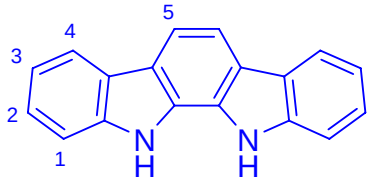


^{1}H NMR spectra of indolocarbazole **1** in $(CD_3)_2SO$ and CD_3CN**:**



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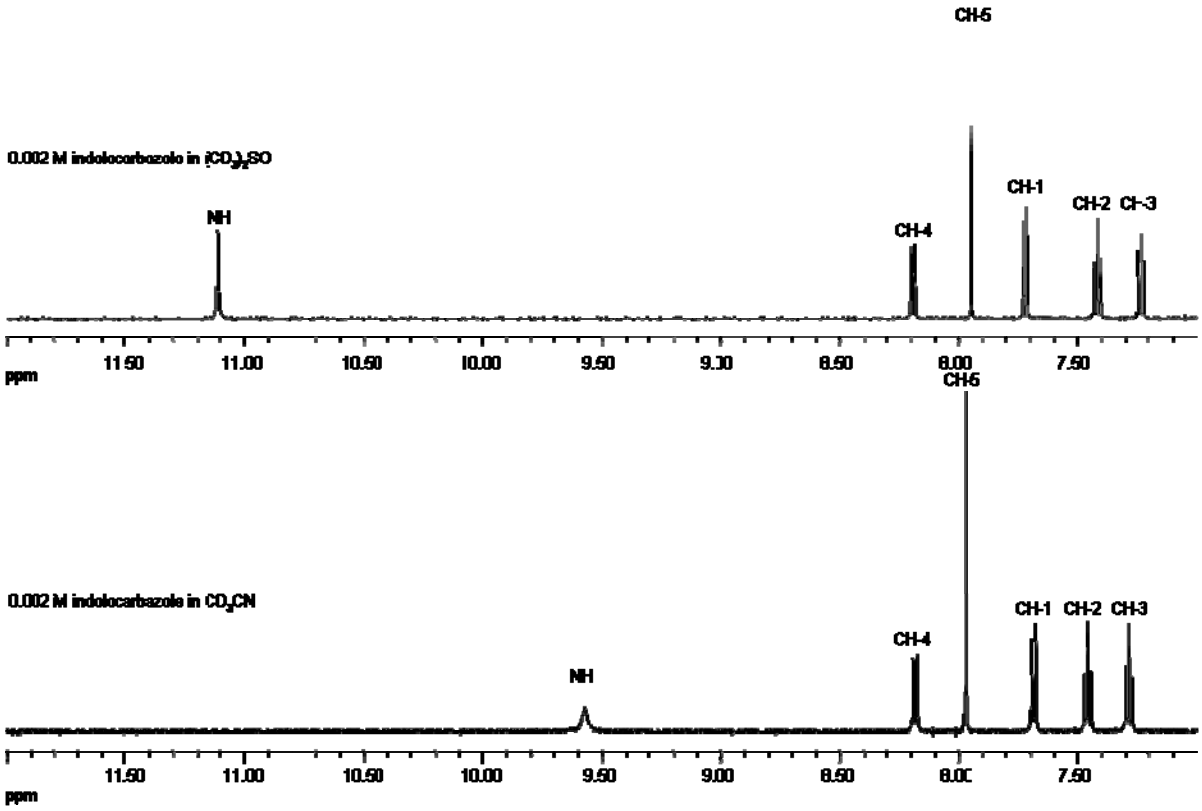
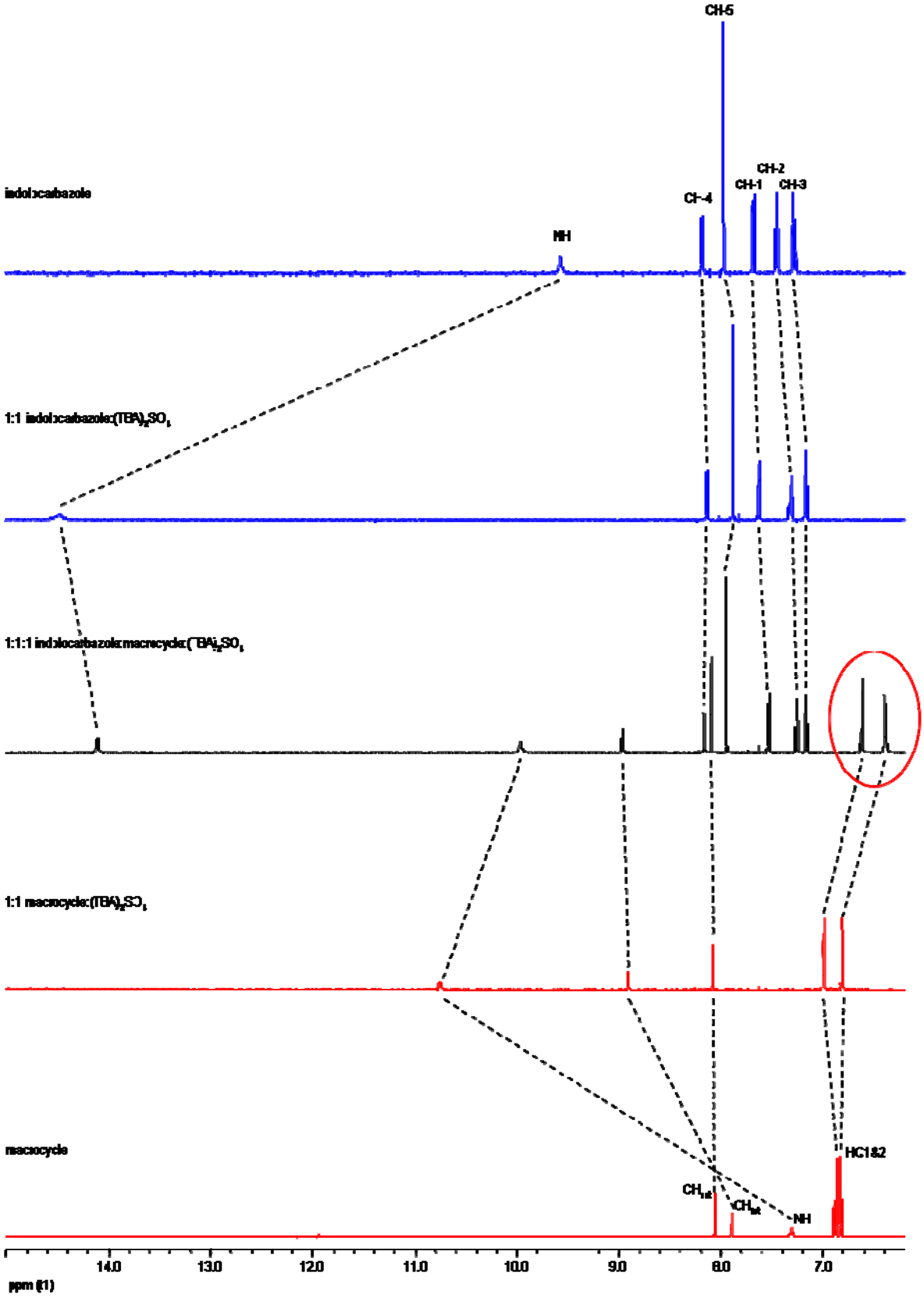


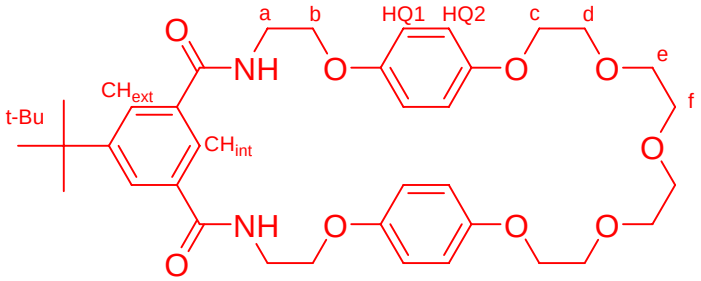
II) ^{1}H NMR spectra of pseudorotaxane [2×SO_4×1]$^{2-}$

Qualitative ^{1}H NMR studies of pseudorotaxane formation in CD_3CN - comparison of spectra of the free ligands, their sulfate complexes and ternary 1:1:1 complex between indolocarbazole, sulfate and macrocycle, i.e. the pseudorotaxane. The concentration of each component is 0.002M.



III) Summary of 1D NOE experiments on pseudorotaxane $[2\times SO_4\times 1]^{2-}$ in CD_3CN

1D NOE experiments were performed at 20°C on 1:1:1 mixture of macrocycle **2**, indolocarbazole **1** and $(TBA)_2SO_4$ (0.006M each) in CD_3CN.



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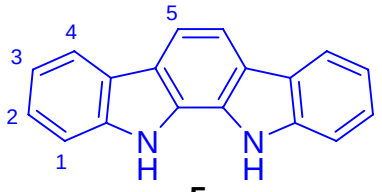

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Table S1.

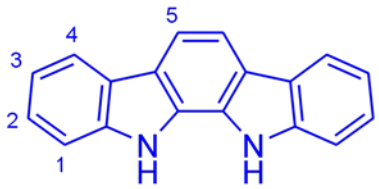
Irradiated proton (chemical shift [ppm])	**Observed NOE [%]**															
	NH 14.15	NH_{amide} 10.30	CH_{int} 9.04	CH-4 8.17	CH_{ext} 8.10	CH-5 7.94	CH-1 7.54	CH-2 7.27	CH-3 7.16	HQ1 6.65	HQ2 6.41	B 4.13	c 3.82	d,e,f 3.67	a 3.62	t-Bu 1.36
NH (14.15)	-100						6.5			**1.3**		**0.6**				
CH-4 (8.17)				-100		3.9			9.8							
CH-5 (7.94)				2.5		-100										
CH-1 (7.54)	3.2						-100	7.5								
CH-2 (7.27)							6.9	-100	1.92	**-1.7**	**-1.0**					
CH-3 (7.16)				10.6			0.7		-100	**-2.7**	**-1.5**					
HQ1 (6.65)	**1.2**		0.2	**0.2**			**0.2**		**-0.6**	-100	1.6	3.8				
HQ2 (6.41)				**0.2**	0.2	**0.4**	**0.3**			3.6	-100		5.4			
b (4.13)	**1.4**	1.6					**0.4**			10.4		-100			3.0	
c (3.82)		0.5		**0.3**		**0.5**					10.2					
d,e,f (3.67)	**1.5**	1.5		**0.3**	0.2	**0.4**	**0.4**	**0.2**	**0.3**	0.4	0.8	1.6				

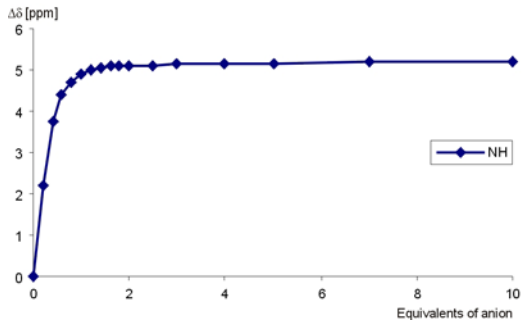
IV) ^{1}H NMR titrations.

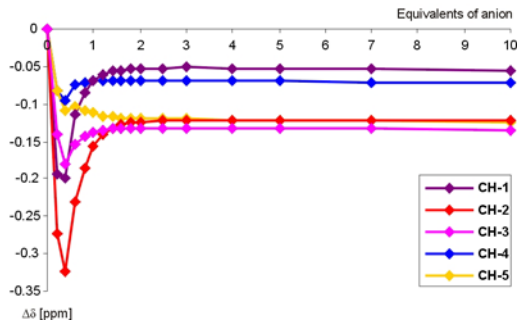
1. **Typical ^{1}H NMR Titration Procedure.** To a solution of host (0.002M, 600µl) in an NMR tube appropriate aliquots of titrant (0.0600 M; 0.2, 0.4, …, 1.8, 2.0, 2.5, 3.0, 4.0, 5.0, 7.0, and 10.0 equiv) were added with a 25 µl microsyringe. In case of competitive titrations a 1:1 mixture of two hosts (macrocycle and indolocarbazole) was used, 0.002M each.
2. ^{1}H NMR titration of 0.002M solution of indolocarbazole **1** in CD_3CN with 0.06M $(TBA)_2SO_4$.
2a. Raw data. Chemical shifts of indolocarbazole protons during titration.

Equivalents of $(TBA)_2SO_4$	NH	CH-1	CH-2	CH-3	CH-4	CH-5
0	9.5930	7.7041	7.4744	7.3041	8.2019	7.9920
0.2	11.7779	7.5096	7.2019	7.1645	8.1190	7.9107
0.4	13.3637	7.5046	7.1508	7.1234	8.1058	7.8832
0.6	14.0088	7.5898	7.2425	7.1513	8.1272	7.8887
0.8	14.2890	7.61895	7.2887	7.1612	8.1316	7.8843
1.0	14.4813	7.6349	7.3173	7.1667	8.1338	7.8799
1.2	14.5967	7.64425	7.3349	7.1700	8.1338	7.8755
1.4	14.6462	7.64755	7.3426	7.1711	8.1338	7.8744
1.6	14.6682	7.6497	7.3469	7.1711	8.1338	7.8733
1.8	14.6879	7.6508	7.3491	7.1711	8.1338	7.8733
2	14.6989	7.6519	7.3502	7.1722	8.1338	7.8733
2.5	14.7176	7.6519	7.3524	7.1722	8.1338	7.8722
3	14.7319	7.6530	7.3535	7.1722	8.1338	7.8722
4	14.7495	7.6519	7.3535	7.1722	8.1327	7.8711
5	14.7594	7.6519	7.3535	7.1711	8.1327	7.8700
7	14.7737	7.6508	7.3535	7.1711	8.1316	7.8689
10	14.7879	7.64865	7.3535	7.1700	8.1305	7.8678

2b. Titration curves.





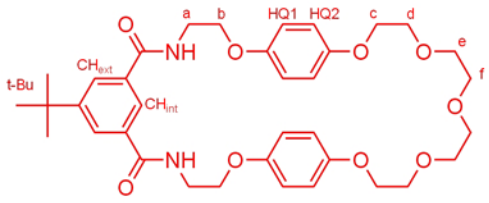


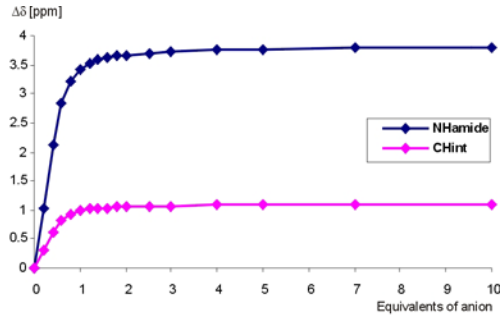
3. ^{1}H NMR titration of 0.002M solution of macrocycle **2** in CD_3CN with 0.06M $(TBA)_2SO_4$.

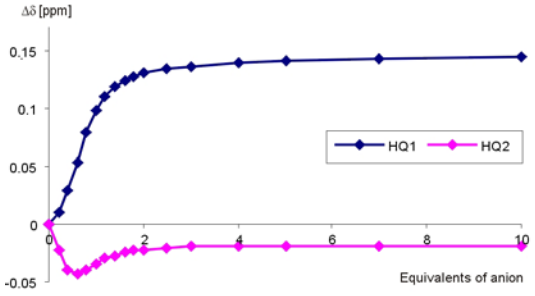
3a. Raw data:

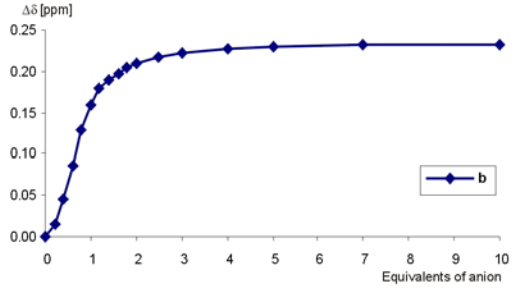
Equivalents of $(TBA)_2SO_4$	NH	CHint	CHext	HQ1	HQ2	a	b	c	d	e,f	t-Bu
0	7.3349	7.9228	8.08265	6.8920	6.8590	3.7380	4.1061	4.0046	3.7416	3.6019	1.3665
0.2	8.3723	8.2250	8.0782	6.9030	6.8370	3.6871	4.1225	3.9942	3.7308	3.6005	1.3544
0.4	9.4525	8.5371	8.0756	6.9217	6.8195	3.6442	4.1518	3.9862	3.7207	3.5999	1.3445
0.6	10.1778	8.7459	8.0761	6.9458	6.8151	3.6329	4.1919	3.9842	3.7151	3.5993	1.3412
0.8	10.5608	8.8547	8.0782	6.9711	6.8195	3.6452	4.2340	3.9865	3.7130	3.5983	1.3434
1	10.7504	8.9075	8.0799	6.9898	6.8249	3.6600	4.2646	3.9892	3.7124	3.5977	1.3456
1.2	10.8526	8.9360	8.0810	7.0019	6.8293	3.6708	4.2843	3.9911	3.7123	3.5979	1.3467
1.4	10.9119	8.9525	8.0821	7.0096	6.8315	3.6785	4.2964	3.9923	3.7122	3.5975	1.3478
1.6	10.9482	8.9635	8.0838	7.0151	6.8348	3.6827	4.3042	3.9931	3.7120	3.5969	1.3500
1.8	10.9779	8.9712	8.0838	7.0195	6.8359	3.6863	4.3105	3.9937	3.7119	3.5967	1.3500
2	10.9999	8.9778	8.0843	7.0228	6.8370	3.6891	4.3152	3.9942	3.7119	3.5971	1.3500
2.5	11.0350	8.9866	8.0838	7.0261	6.8381	3.6935	4.3227	3.9948	3.7116	3.5965	1.3500
3	11.0570	8.9932	8.0838	7.0283	6.8392	3.6961	4.3272	3.9951	3.7115	3.5960	1.3500
4	11.0845	9.0009	8.0838	7.0315	6.8403	3.6987	4.3322	3.9953	3.7110	3.5954	1.3500
5	11.1010	9.0053	8.0838	7.0326	6.8403	3.6999	4.3349	3.9952	3.7105	3.5948	1.3500
7	11.1229	9.0119	8.0838	7.0348	6.8403	3.7008	4.3376	3.9948	3.7097	3.5938	1.3500
10	11.1383	9.0163	8.0832	7.0359	6.8403	3.7010	4.3391	3.9941	3.7085	3.5927	overlap

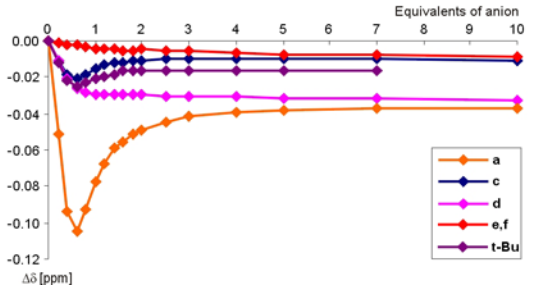
3b. Titration curves.

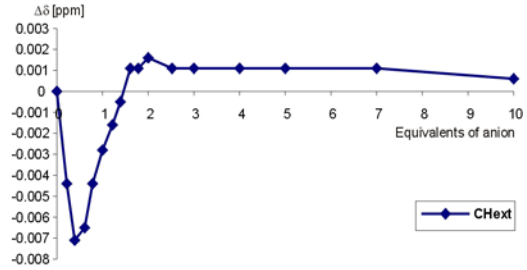










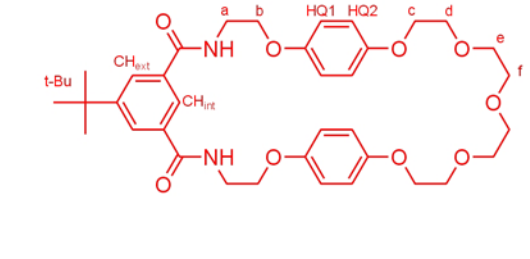


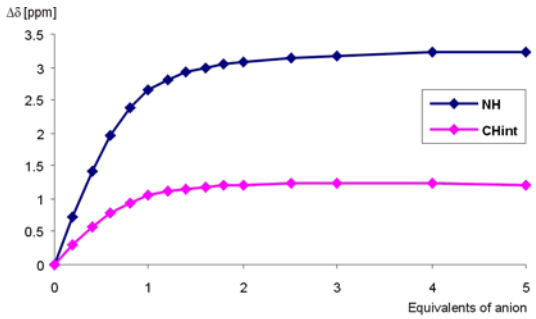
4. ^{1}H NMR titration of 0.002M solution of macrocycle **2** in CD_3CN with a 1:1 mixture of $(TBA)_2SO_4$ and indolocarbazole **1** (0.06M each)

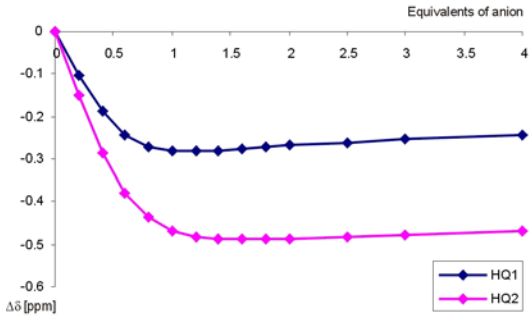
4a. Raw data. Chemical shifts of macrocycle protons during titration.

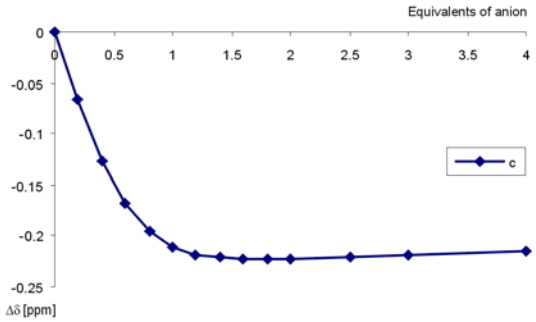
Equivalents of [2× $(TBA)_2SO_4$]	NH	CH_{int}	CH_{ext}	HQ1	HQ2	a	b	c	d	e,f	t-Bu
0	7.3183	7.9043	8.0634	6.8769	6.8440	3.7424	4.1092	4.0078	3.7456	3.6060	1.3682
0.2	8.0411	8.1937	8.0634	6.7744	6.6926	3.6971	4.0884	3.9413	3.7234	3.6270	1.3621
0.4	8.7443	8.4708	8.0655	6.6883	6.5583	overlap	4.0774	3.8815	3.7014	overlap	1.3579
0.6	9.2919	8.6887	8.07065	6.6346	6.4655	overlap	4.0792	3.8399	3.6849	overlap	1.3579
0.8	9.6929	8.8462	8.07735	6.6065	6.4081	3.6263	4.0884	3.8131	overlap	overlap	1.3597
1	9.9695	8.9543	8.0832	6.5955	6.3764	3.6235	4.1006	3.7972	overlap	overlap	1.3627
1.2	10.1361	9.0178	8.08775	6.5943	6.3623	3.6248	4.1122	3.7899	overlap	overlap	1.3652
1.4	10.2381	9.0550	8.0908	6.5967	6.3568	3.6266	4.1214	3.7868	overlap	overlap	1.3670
1.6	10.3089	9.0800	8.0926	6.5998	6.3556	3.6290	4.1287	3.7856	overlap	overlap	1.3682
1.8	10.3595	9.0971	8.0944	6.6041	6.3556	3.6312	4.1348	3.7856	overlap	overlap	1.3695
2	10.3968	9.1099	8.0957	6.6077	6.3568	3.6333	4.1403	3.7856	overlap	overlap	1.3701
2.5	10.4603	9.1283	8.0975	6.6163	6.3617	3.6376	4.1494	3.7874	overlap	overlap	1.3713
3	10.4975	9.1386	8.0984	6.6236	6.3660	3.6416	4.1562	3.7887	overlap	overlap	1.3719
4	10.5408	9.1490	8.1000	6.6340	6.3751	3.6446	4.1653	3.7923	overlap	overlap	1.3731
5	10.5325	9.1256	8.07665	6.6241	6.3648	3.6400	4.1628	3.7881	overlap	overlap	1.3758

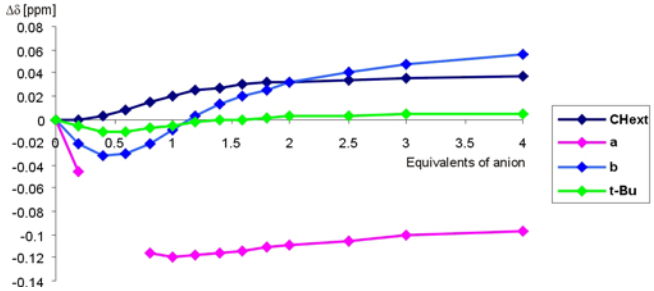
4b. Titration curves. Large upfield shifts of both hydroquinone protons HQ1 and HQ2 are indicative of pseudorotaxane formation.









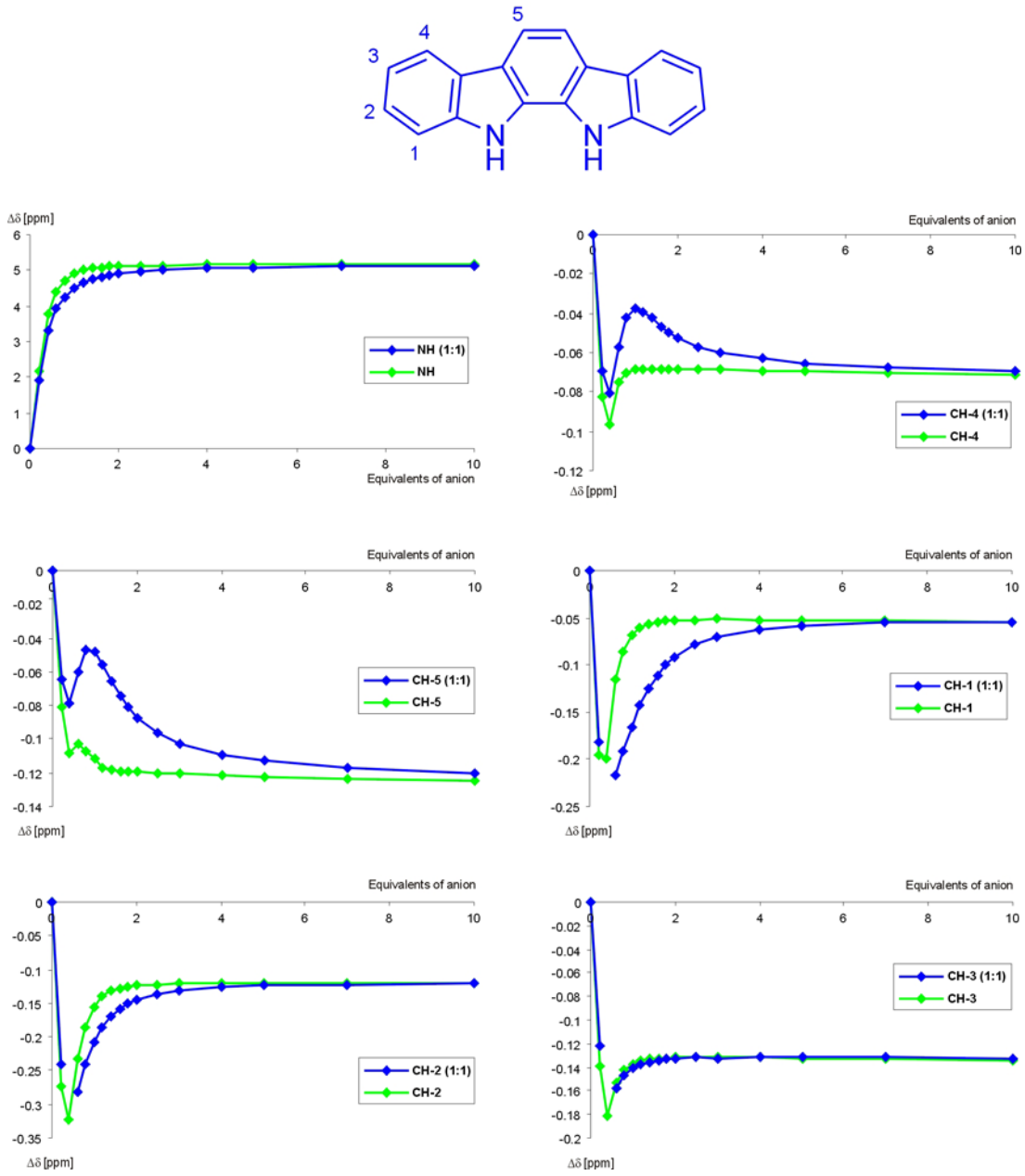


5. ^{1}H NMR titration of 1:1 mixture of macrocycle **2** and indolocarbazole **1** (0.002M each) in CD_3CN with $(TBA)_2SO_4$ (0.06M).

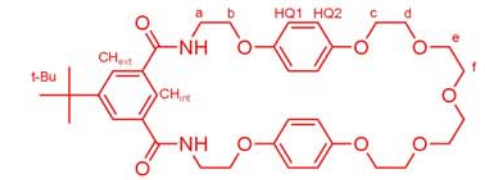
5a. Raw data. Chemical shifts of indolocarbazole and macrocycle protons during titration.

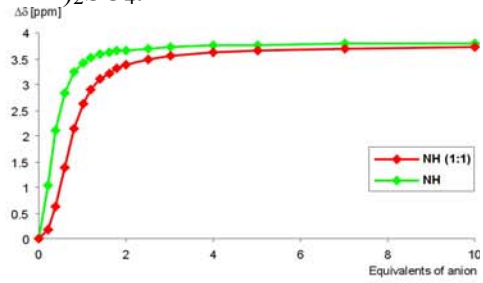
Equivalents of $(TBA)_2SO_4$	NH	CH-1	CH-2	CH-3	CH-4	CH-5	NH	CHint	CHext	HQ1	HQ2	a	b	c	d	e,f	t-Bu
0	9.6108	7.7014	7.4733	7.3036	8.2024	7.9920	7.3360	7.9239	8.0838	6.8887	6.8546	3.7487	4.1138	4.0105	3.7493	3.6105	1.3643
0.2	11.5197	7.5195	7.2327	7.1821	8.1332	7.9272	7.5184	8.0151	8.0750	6.8436	6.7953	3.7330	4.1039	3.9853	3.7412	3.6194	1.3577
0.4	12.9065	overlap	overlap	overlap	8.1217	7.9129	7.9660	8.2228	8.0652	6.7513	6.6689	3.7009	4.0864	3.9314	3.7249	3.6390	1.3478
0.6	13.5384	7.4838	7.1904	7.1458	8.1454	7.9316	8.7200	8.5371	8.0696	6.6414	6.5030	overlap	4.0688	3.8589	3.7001	overlap	1.3445
0.8	13.8769	7.5102	7.2327	7.1562	8.1602	7.9448	9.4679	8.8107	8.0887	6.5931	6.4029	3.6340	4.0776	3.8116	overlap	overlap	1.3533
1	14.1011	7.5354	7.2656	7.1623	8.1652	7.9437	9.9630	8.9624	8.1019	6.6150	6.3975	3.6304	4.1072	3.8061	overlap	overlap	1.3599
1.2	14.2495	7.5580	7.2876	7.1656	8.1635	7.936	10.2482	9.0206	8.1052	6.6667	6.4425	3.6364	4.1413	3.8259	overlap	overlap	1.3621
1.4	14.3539	7.5760	7.3030	7.1678	8.1602	7.9261	10.4330	9.0382	8.1046	6.7238	6.5019	3.6440	4.1732	3.8512	3.6820	overlap	1.3610
1.6	14.4258	7.5904	7.3140	7.1689	8.1558	7.9173	10.5554	9.0404	8.1024	6.7744	6.5557	overlap	4.2007	3.8754	3.6878	overlap	1.3599
1.8	14.4835	7.60135	7.3217	7.1700	8.1525	7.9107	10.6482	9.0371	8.10025	6.8162	6.6019	3.6628	4.2226	3.8962	3.693	3.6406	1.3588
2	14.5242	7.6102	7.3272	7.1706	8.1503	7.9041	10.7163	9.0338	8.0980	6.8491	6.6370	3.6700	4.2413	3.9127	3.6972	3.6354	1.3577
2.5	14.5923	7.62335	7.3371	7.1716	8.1454	7.8953	10.8255	9.0250	8.0948	6.9030	6.6975	3.6828	4.2721	3.9402	3.7042	3.6266	1.3566
3	14.6324	7.6310	7.3415	7.1711	8.1426	7.8887	10.8900	9.0195	8.0926	6.9370	6.7337	3.6900	4.2908	3.9556	3.7084	3.6212	1.3555
4	14.6780	7.6393	7.3469	7.1722	8.1393	7.8821	10.9614	9.0141	8.0904	6.9722	6.7733	3.6997	4.3105	3.9743	3.7128	3.6156	overlap
5	14.7022	7.6432	7.3491	7.1722	8.1371	7.8788	10.9966	9.0119	8.0892	6.9898	6.7920	3.7031	4.3215	3.9820	3.7146	3.6120	1.3533
7	14.7286	7.6459	7.3513	7.1716	8.1349	7.8755	11.0339	9.0086	8.0876	7.0074	6.8107	3.7085	4.3303	3.9908	3.7157	3.60885	1.3522
10	14.7462	7.6476	7.3519	7.1711	8.1327	7.8722	11.0548	9.0075	8.0860	7.0173	6.8216	3.7102	4.3358	3.9951	3.7167	3.6060	overlap

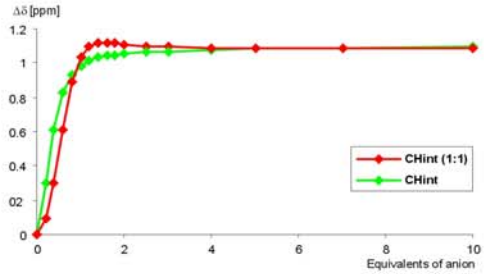
5b. Titration curves from indolocarbazole protons. Comparison of chemical shifts of indolocarbazole protons from the titration of 1:1 mixture of indolocarbazole and macrocycle with $(TBA)_2SO_4$ versus indolocarbazole alone with $(TBA)_2SO_4$.

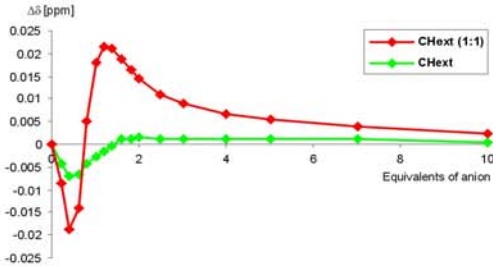


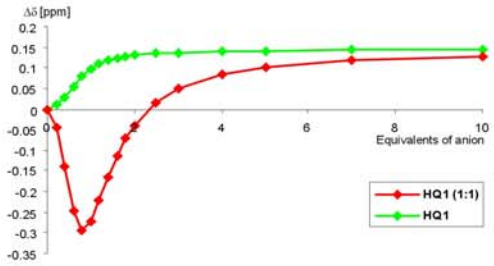
5c. Titration curves from macrocycle protons. Comparison of chemical shifts of macrocycle protons from the titration of 1:1 mixture of indolocarbazole and macrocycle with $(TBA)_2SO_4$ versus indolocarbazole alone with $(TBA)_2SO_4$.

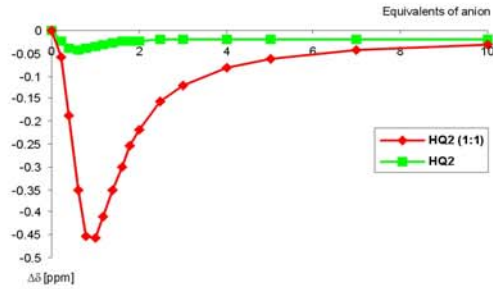


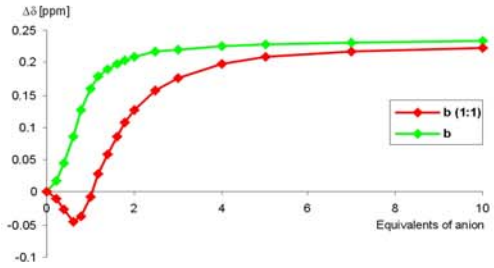


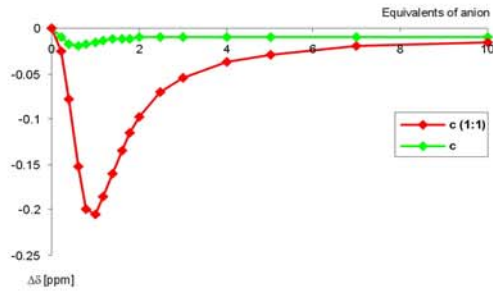


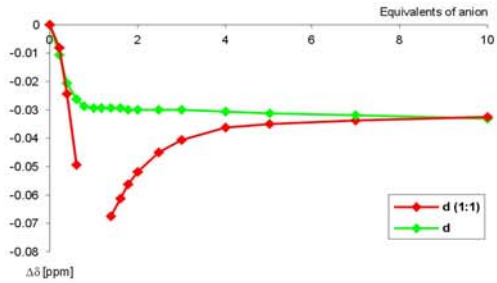


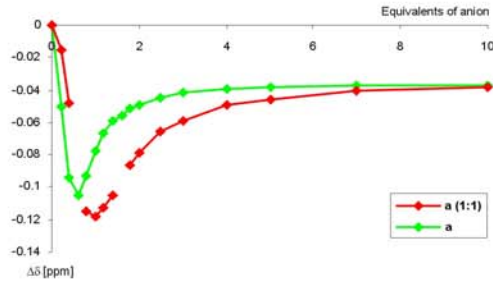


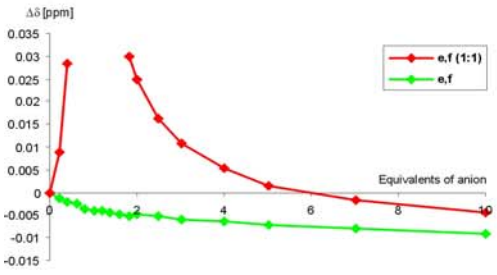


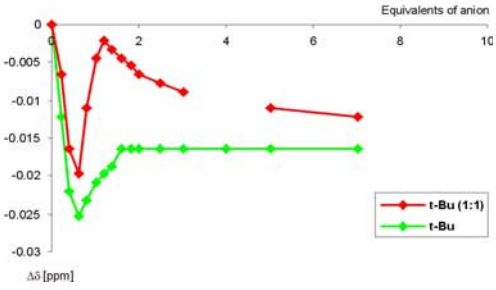








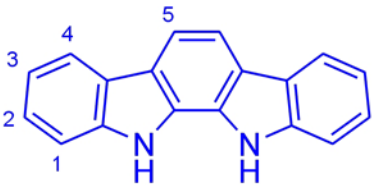


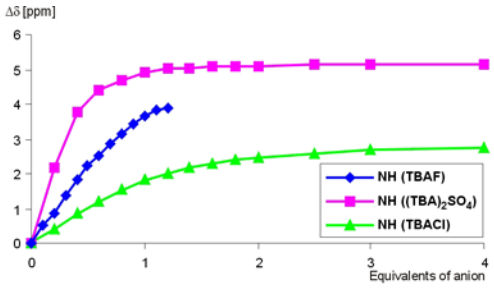


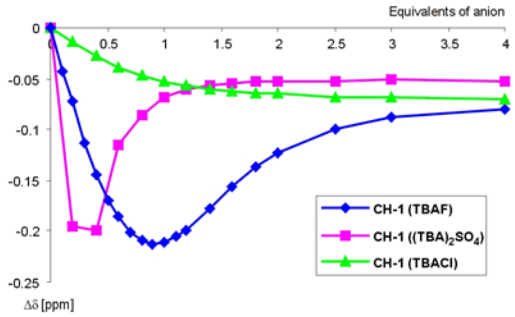
6. ^{1}H NMR titration of indolocarbazole **1** (0.002M) in CD_3CN with TBAF (0.06M).
6a. Raw data. Chemical shifts of indolocarbazole protons during titration.

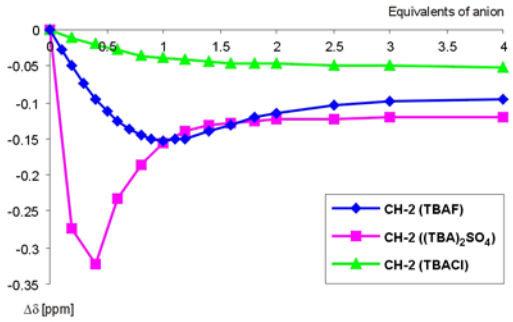
Equivalents of TBAF	NH	CH-1	CH-2	CH-3	CH-4	CH-5
0	9.5714	7.6606	7.4320	7.2623	8.1572	7.9478
0.1	10.0671	7.6179	7.4051	7.2458	8.1514	7.9386
0.2	10.4499	7.5884	7.3837	7.2330	8.1462	7.9307
0.3	10.9639	7.5470	7.3575	7.2165	8.1396	7.9203
0.4	11.3912	7.5162	7.3359	7.2030	8.1345	7.9118
0.5	11.8098	7.4904	7.3191	7.1935	8.1301	7.9041
0.6	12.1141	7.4746	7.3070	7.1855	8.1267	7.8973
0.7	12.4196	7.4602	7.2963	7.1768	8.1229	7.8906
0.8	12.7272	7.4514	7.2876	7.1694	8.1200	7.8839
0.9	12.9764	7.4472	7.2822	7.1633	8.1173	7.8772
1	13.2148	7.4494	7.2802	7.1593	8.1153	7.8711
1.1	13.3793	7.4561	7.2810	7.1573	8.1139	7.8664
1.2	13.4814	7.4622	7.2829	7.1559	8.1133	7.8631
1.4	13.7889	7.4824	7.2914	7.1533	8.1113	7.8523
1.6	-	7.5045	7.3010	7.1526	8.1102	7.8436
1.8	-	7.5236	7.3104	7.1526	8.1096	7.8376
2	-	7.5381	7.3164	7.1526	8.1086	7.8335
2.5	-	7.5616	7.3279	7.1539	8.1086	7.8275
3	-	7.5723	7.3326	7.1546	8.1086	7.8255
4	-	7.5804	7.3359	7.1546	8.1079	7.8235

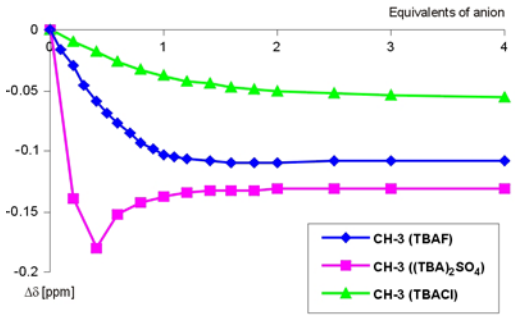
6b. Titration curves. Comparison of chemical shifts of indolocarbazole protons during titration with TBAF versus $(TBA)_2SO_4$ and TBACl.

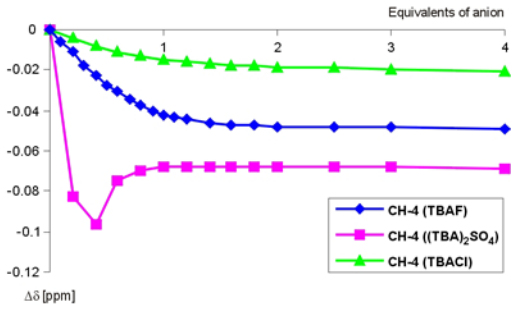


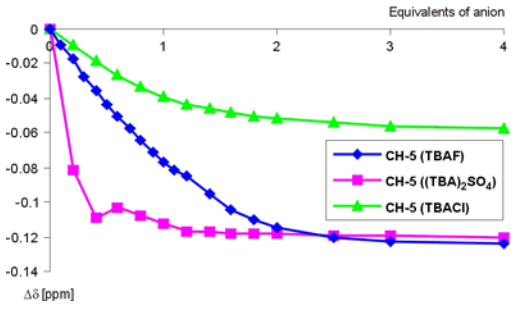










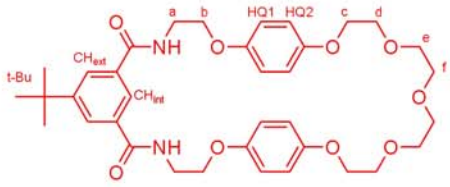


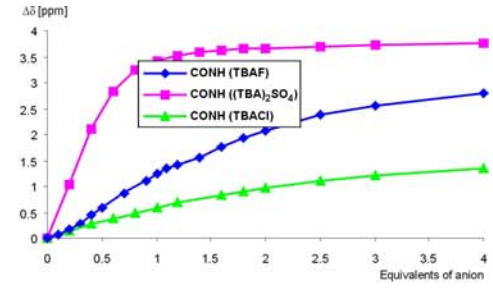
7. ^{1}H NMR titration of macrocycle **2** (0.002M) in CD_3CN with TBAF (0.06M).

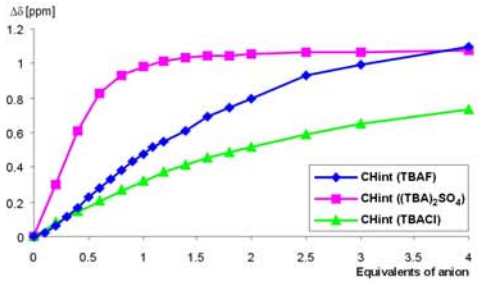
7a. Raw data. Chemical shifts of macrocycle protons during titration.

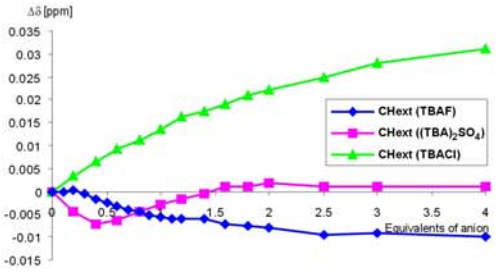
Equivalents of TBAF	CONH	CHint	CHext	HQ1	HQ2	a	b	c	d	e,f	t-Bu
0	7.2980	7.8814	8.0391	6.8572	6.8242	3.7350	4.1008	3.9999	3.7389	3.5996	1.3708
0.1	7.3628	7.9057	8.0391	6.8576	6.8232	3.7260	4.1004	3.9993	3.7385	3.5995	1.3704
0.2	7.4593	7.9424	8.0392	6.8585	6.8221	3.7219	4.1001	3.9987	3.7382	3.5997	1.3699
0.3	7.5900	7.9930	8.0387	6.8594	6.8207	3.7159	4.0989	3.9980	3.7380	3.5998	1.3691
0.4	7.7403	8.0511	8.0375	6.8604	6.8190	3.7091	4.0971	3.9972	3.7376	3.6000	1.3683
0.5	7.8961	8.1126	8.0366	6.8616	6.8174	3.7027	4.0954	3.9963	3.7372	3.6001	1.3674
0.6	overlap	8.1655	8.0358	6.8629	6.8160	3.6975	4.0945	3.9956	3.7370	3.6002	1.3666
0.7	8.1632	8.2175	8.0351	6.8644	6.8148	3.6925	4.0941	3.9950	3.7366	3.6004	1.3660
0.8	overlap	8.2658	8.0346	6.8660	6.8137	3.6884	4.0940	3.9945	3.7364	3.6006	1.3654
0.9	8.4042	8.3109	8.0340	6.8677	6.8127	3.6846	4.0943	3.9940	3.7361	3.6006	1.3649
1	8.5298	8.3602	8.0335	6.8696	6.8116	3.6808	4.0946	3.9934	3.7357	3.6007	1.3643
1.1	8.6287	8.3974	8.0332	6.8713	6.8109	3.6788	4.0954	3.9930	3.7355	3.6007	1.3639
1.2	8.7228	8.4344	8.0329	6.8730	6.8102	3.6768	4.0962	3.9927	3.7353	3.6008	1.3635
1.4	8.8628	8.4876	8.0329	6.8759	6.8092	3.6753	4.0985	3.9921	3.7348	3.6008	1.3630
1.6	9.0696	8.5696	8.0318	6.8798	6.8078	3.6716	4.1000	3.9915	3.7344	3.6010	1.3622
1.8	9.2132	8.6250	8.0316	6.8831	6.8071	3.6705	4.1025	3.9912	3.7341	3.6011	1.3618
2	9.3614	8.6816	8.0311	6.8864	6.8063	3.6696	4.1045	3.9907	3.7337	3.6010	1.3613
2.5	9.6780	8.8074	8.0296	6.8943	6.8050	3.6691	4.1098	3.9902	3.7331	3.6012	1.3604
3	9.8432	8.8718	8.0298	6.8992	6.8045	3.6715	4.1145	3.9898	3.7327	3.6012	1.3600
4	10.1026	8.9754	8.0290	6.9072	6.8039	3.6753	4.1211	3.9895	3.7320	3.6010	1.3593

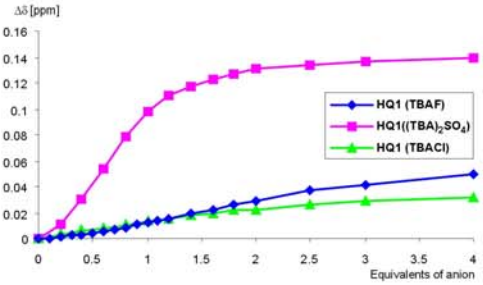
7b. Titration curves. Comparison of chemical shifts of macrocycle protons during titration with TBAF versus $(TBA)_2SO_4$ and TBACl.

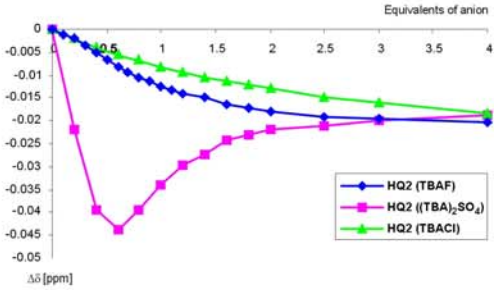


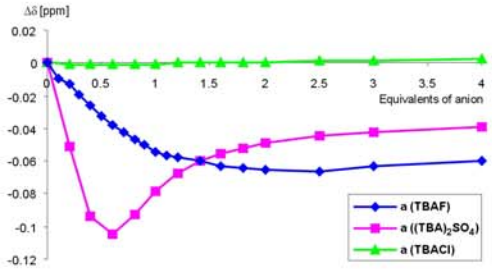


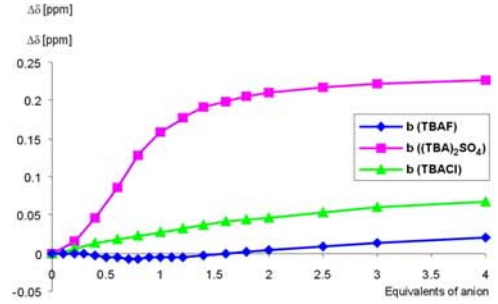


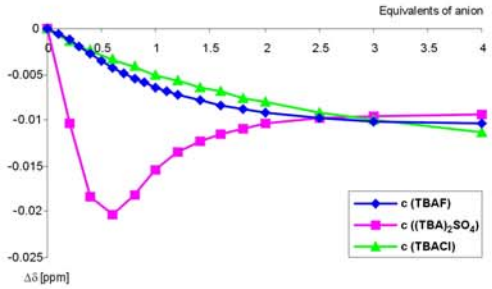


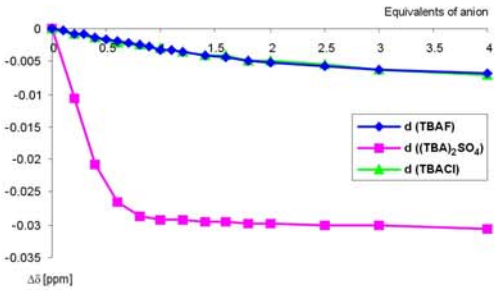


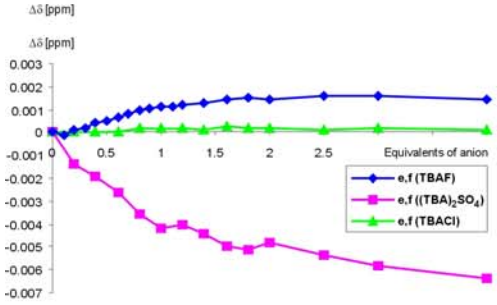


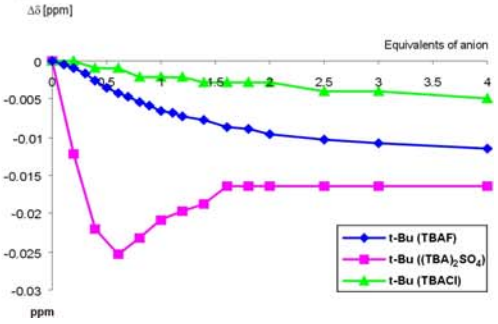










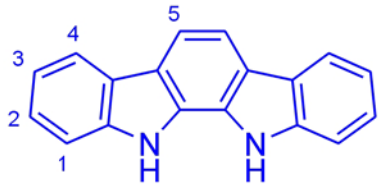


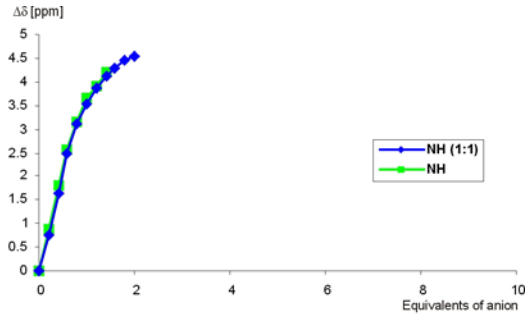
8. ^{1}H NMR titration of 1:1 mixture of macrocycle **2** and indolocarbazole **1** (0.002M each) in CD_3CN with TBAF (0.06M).

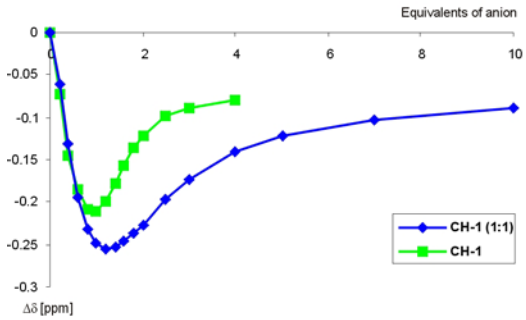
8a. Raw data. Chemical shifts of indolocarbazole and macrocycle protons during titration.

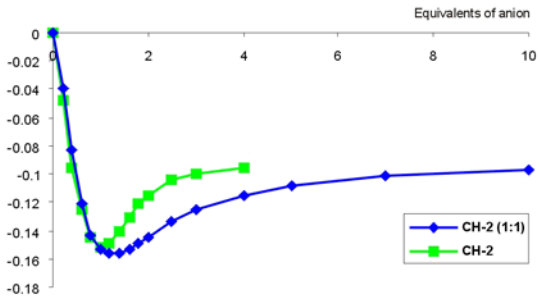
Equivalents of TBAF	NH	CH-1	CH-2	CH-3	CH-4	CH-5	CONH	CHint	CHext	HQ1	HQ2	a	b	c	d	e,f	t-Bu
0	9.5733	7.6589	7.4329	7.2645	8.1567	7.9479	7.2982	7.8818	8.0397	6.8530	6.8196	3.7347	4.0983	3.9957	3.7360	3.5982	1.3688
0.2	10.3441	7.5971	7.3932	7.2399	8.1467	7.9320	7.3276	7.8967	8.0407	6.8499	6.8161	3.7325	4.0965	3.9944	3.7356	3.5988	1.3694
0.4	11.1999	7.5276	7.3499	7.2131	8.1362	7.9148	7.3754	7.9228	8.0424	6.8444	6.8095	3.7293	4.0934	3.9922	3.7350	3.5998	1.3703
0.6	12.0552	7.4645	7.3115	7.1880	8.1267	7.8972	overlap	7.9699	8.0456	6.8345	6.7977	3.7239	4.0882	3.9883	3.7340	3.6019	1.3717
0.8	12.6881	7.4267	7.2888	7.1717	8.1204	7.8834	7.5920	8.0346	8.0504	6.8211	6.7816	3.7111	4.0815	3.9830	3.7326	3.6048	1.3735
1	13.1083	7.4098	7.2791	7.1627	8.1168	7.8730	7.7345	overlap	8.0553	6.8071	6.7641	3.7038	4.0746	3.9772	3.7312	3.6081	1.3752
1.2	13.4211	7.4043	7.2763	7.1575	8.1147	7.8646	7.8908	8.1835	8.0601	6.7938	6.7471	3.6950	4.0679	3.9715	3.7297	3.6113	1.3768
1.4	13.6761	7.4058	7.2771	7.1542	8.1136	7.8570	overlap	8.2633	8.0644	6.7820	6.7312	3.6856	4.0619	3.9661	3.7283	3.6143	1.3781
1.6	13.8584	7.4120	7.2801	7.1523	8.1123	7.8507	8.2259	8.3399	8.0671	6.7740	6.7191	3.6768	4.0575	3.9620	3.7272	3.6166	1.3788
1.8	14.0190	7.4214	7.2842	7.1513	8.1117	7.8457	-	8.4137	8.0681	6.7705	6.7115	3.6690	4.0550	3.9593	3.7264	3.6180	1.3788
2	14.1060	7.4322	7.2887	7.1509	8.1112	7.8419	-	8.4837	8.0676	6.7715	6.7083	3.6624	4.0543	3.9580	3.7260	3.6186	1.3782
2.5	-	7.4613	7.2994	7.1511	8.1105	7.8356	-	8.6527	8.0622	6.7869	6.7129	3.6514	4.0590	3.9592	3.7259	3.6178	1.3752
3	-	7.4856	7.3075	7.1518	8.1099	7.8324	-	8.7715	8.0560	6.8065	6.7238	3.6493	4.0676	3.9624	3.7263	3.6157	1.3722
4	-	7.5180	7.3182	7.1531	8.1092	7.8291	-	8.9140	8.0474	6.8379	6.7433	3.6544	4.0840	3.9687	3.7272	3.6119	1.3680
5	-	7.5365	7.3244	7.1542	8.1089	7.8280	-	8.9806	8.0430	6.8571	6.7559	3.6611	4.0953	3.9726	3.7277	3.6093	1.3657
7	-	7.5566	7.3313	7.1559	8.1087	7.8274	-	9.0404	8.0388	6.8783	6.7701	3.6707	4.1084	3.9771	3.7281	3.6063	1.3632
10	-	7.5710	7.3364	7.1574	8.1084	7.8278	-	9.0672	8.0366	6.8926	6.7800	3.6786	4.1178	3.9801	3.7282	3.6039	1.3614

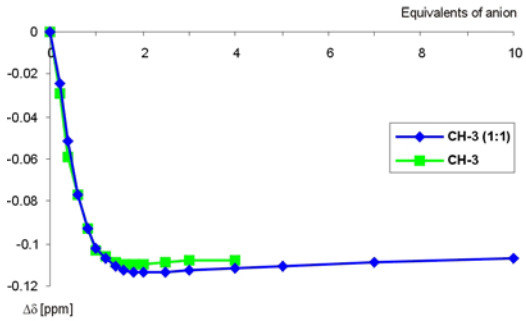
8b. Titration curves from indolocarbazole protons. Comparison of chemical shifts of indolocarbazole protons during titration of 1:1 indolocarbazole:macrocycle mixture with TBAF versus indolocarbazole alone with TBAF.

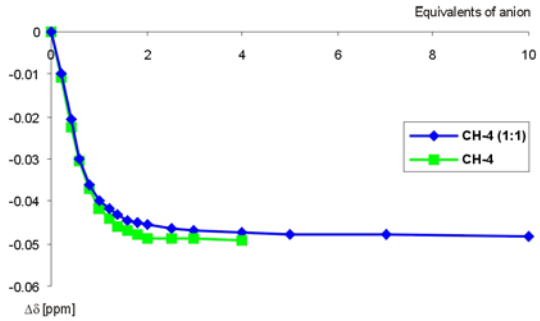


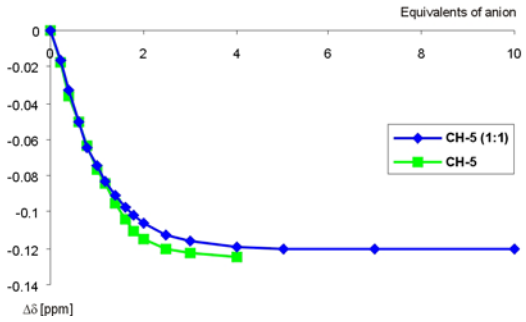




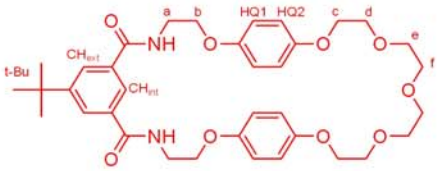


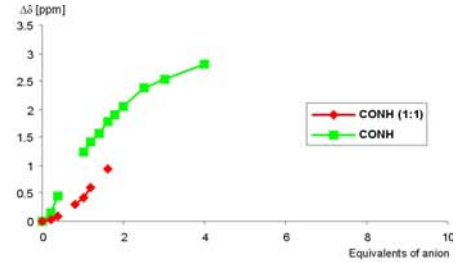


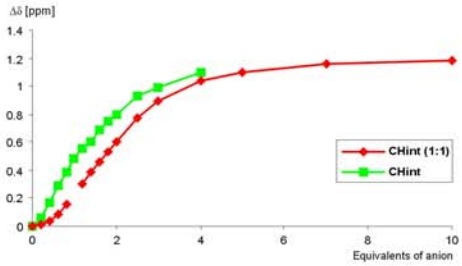


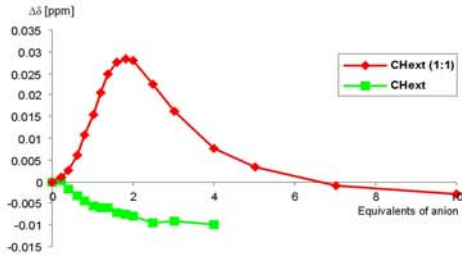


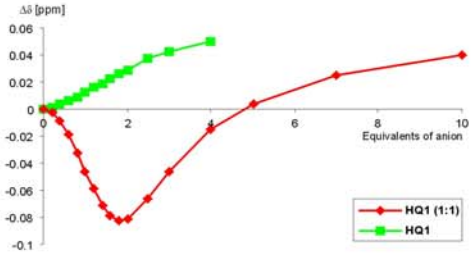
8c. Titration curves from macrocycle protons. Comparison of chemical shifts of macrocycle protons during titration of 1:1 indolocarbazole:macrocycle mixture with TBAF versus imacrocycle alone with TBAF.

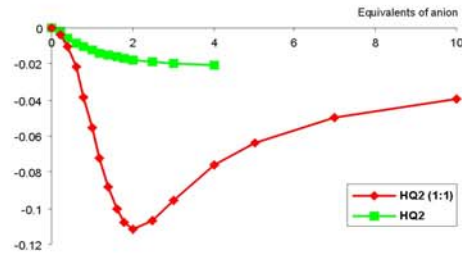


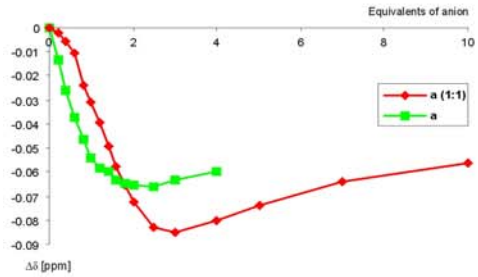


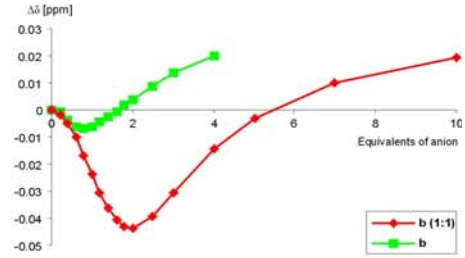


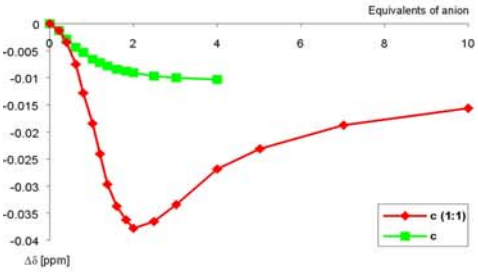


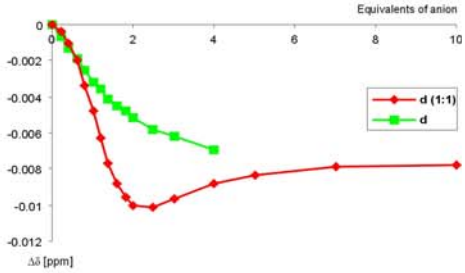


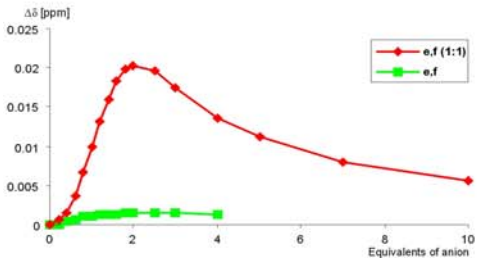


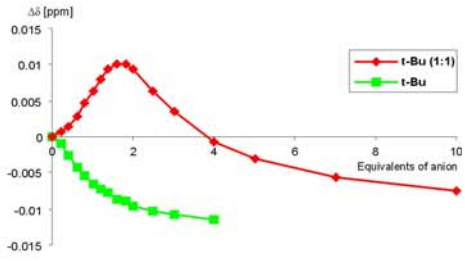








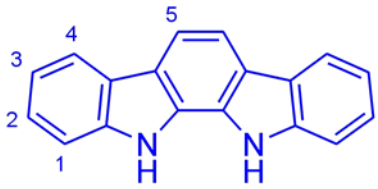


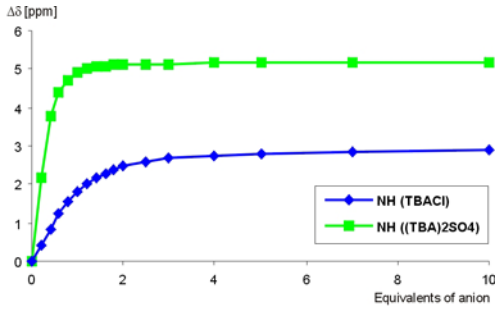


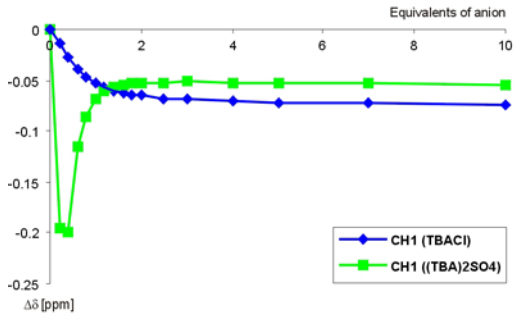
9. ^{1}H NMR titration of indolocarbazole **1** (0.002M) in CD_3CN with TBACl (0.06M).
9a. Raw data.

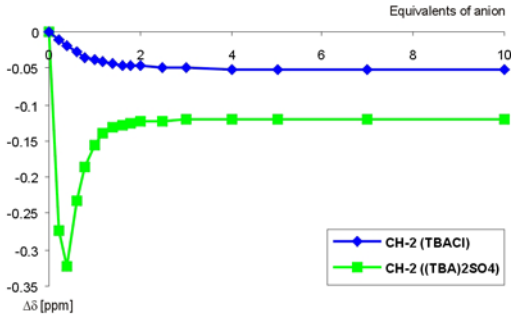
Equivalents of TBACl	NH	CH-1	CH-2	CH-3	CH-4	CH-5
0	9.5950	7.6994	7.4702	7.3000	8.1972	7.9871
0.2	10.0218	7.6848	7.4594	7.2903	8.1933	7.9777
0.4	10.4291	7.6720	7.4500	7.2812	8.1898	7.9687
0.6	10.8142	7.6612	7.4419	7.2731	8.1865	7.9605
0.8	11.1341	7.6530	7.4360	7.2667	8.1843	7.9538
1	11.4001	7.6468	7.4315	7.2616	8.1824	7.9483
1.2	11.6093	7.6422	7.4282	7.2576	8.1811	7.9440
1.4	11.7745	7.6392	7.4262	7.2550	8.1804	7.9410
1.6	11.8865	7.6372	7.4247	7.2529	8.1798	7.9389
1.8	11.9826	7.6354	7.4235	7.2512	8.1792	7.937
2	12.0556	7.6340	7.4226	7.2499	8.1788	7.9355
2.5	12.1851	7.6316	7.4211	7.2476	8.1781	7.9329
3	12.2657	7.6302	7.4202	7.2463	8.1776	7.9313
4	12.3524	7.6286	7.4193	7.2448	8.1770	7.9295
5	12.4007	7.6276	7.4188	7.2440	8.1766	7.9285
7	12.4472	7.6264	7.4183	7.2431	8.1762	7.9274
10	12.4816	7.6253	7.4179	7.2426	8.1756	7.9266

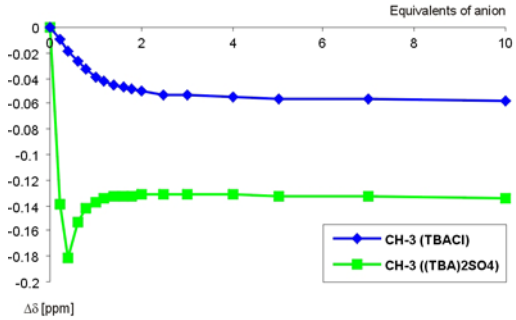
9c. Comparison of chemical shifts of indolocarbazole protons during titration with TBACl vs. with $(TBA)_2SO_4$.

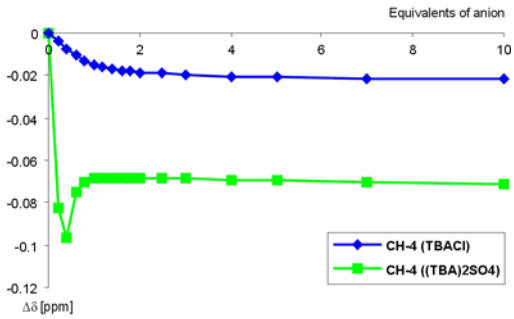


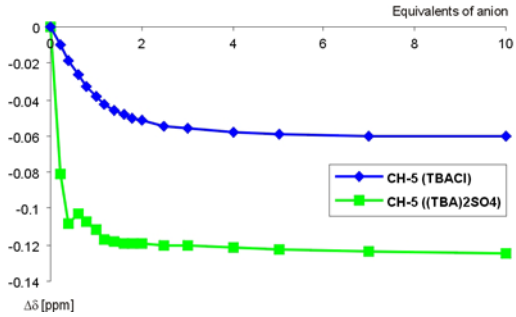










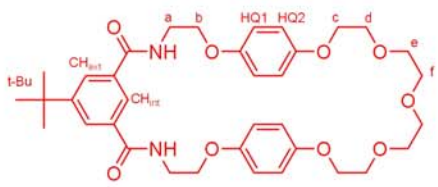


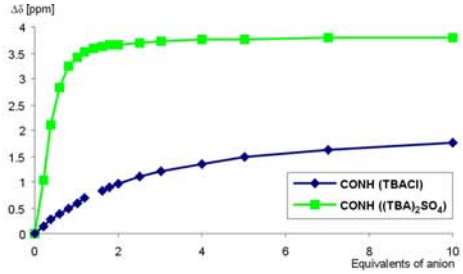
10. ^{1}H NMR titration of macrocycle **2** (0.002M) in CD_3CN with TBACl (0.06M).

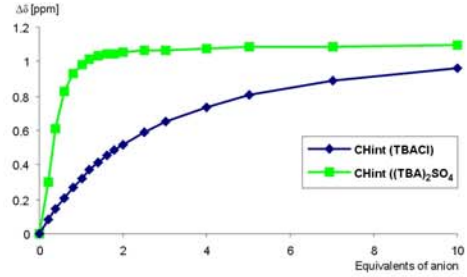
10a. Raw data. Chemical shifts of macrocycle protons during titration.

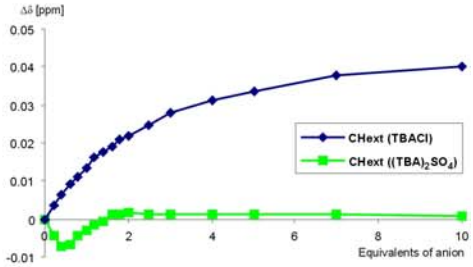
Equivalents of TBACl	NH	CH_{int}	CH_{ext}	HQ1	HQ2	a	b	c	d	e,f	t-Bu
0	7.3338	7.9197	8.0781	6.8884	6.8551	3.7465	4.1144	4.0128	3.7502	3.6100	1.3669
0.2	7.4774	7.9973	8.0816	6.8923	6.8531	3.7462	4.1211	4.0115	3.7493	3.6100	1.3669
0.4	7.6044	8.0662	8.0844	6.8953	6.8513	3.7460	4.1272	4.0105	3.7487	3.6100	1.3659
0.6	7.7226	8.1306	8.0874	6.8972	6.8497	3.7460	4.1329	4.0095	3.7481	3.6100	1.3659
0.8	7.8261	8.1865	8.0894	6.9001	6.8483	3.7462	4.1382	4.0087	3.7477	3.6102	1.3649
1	7.9238	8.2395	8.0918	6.9021	6.8470	3.7462	4.1428	4.0078	3.7471	3.6102	1.3649
1.2	8.0146	8.2889	8.0942	6.9041	6.8458	3.7464	4.1475	4.0071	3.7466	3.6102	1.3649
1.4	overlap	8.3312	8.0956	6.9060	6.8447	3.7466	4.1514	4.0064	3.7462	3.6101	1.3640
1.6	8.1631	8.3701	8.0972	6.908	6.8438	3.7469	4.1551	4.0059	3.7460	3.6102	1.3640
1.8	8.2295	8.4060	8.0991	6.9099	6.8428	3.7470	4.1583	4.0052	3.7454	3.6102	1.3640
2	8.2891	8.4383	8.1000	6.9109	6.8421	3.7472	4.1615	4.0048	3.7453	3.6102	1.3640
2.5	8.4219	8.5106	8.1030	6.9148	6.8403	3.7476	4.1683	4.0036	3.7446	3.6101	1.3630
3	8.5294	8.5690	8.1060	6.9167	6.8389	3.7482	4.1740	4.0028	3.7440	3.6102	1.3630
4	8.6944	8.6587	8.1094	6.9207	6.8367	3.7491	4.1826	4.0014	3.7430	3.6101	1.3620
5	8.8107	8.7226	8.1118	6.9236	6.8351	3.7498	4.1889	4.0003	3.7424	3.6099	1.3620
7	8.9650	8.8066	8.1157	6.9275	6.8328	3.7507	4.1970	3.9987	3.7413	3.6096	1.3610
10	9.0968	8.8783	8.1182	6.9314	6.8308	3.7514	4.2039	3.9972	3.7401	3.6090	1.3600

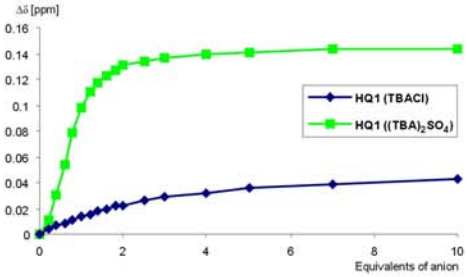
10d. Comparison of chemical shifts of macrocycle protons during titration with TBACl vs. with $(TBA)_2SO_4$.

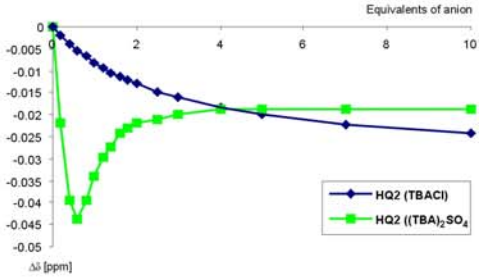


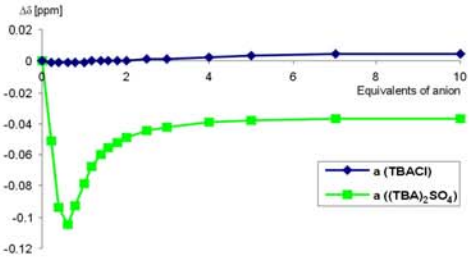


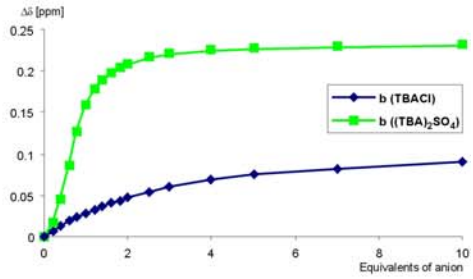


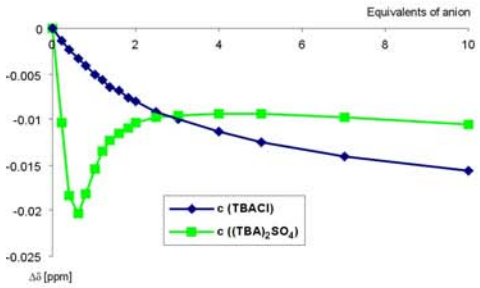


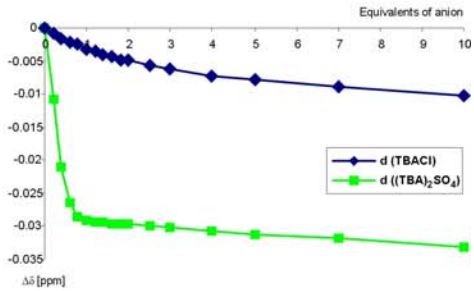


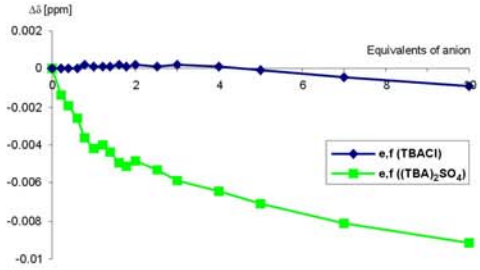


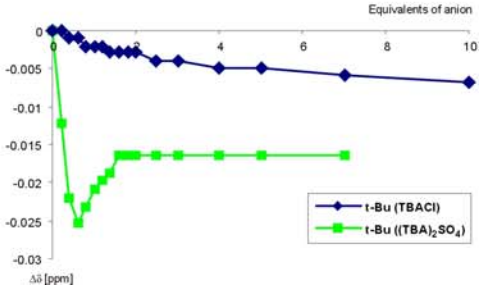










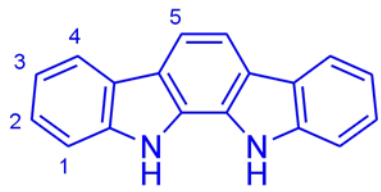


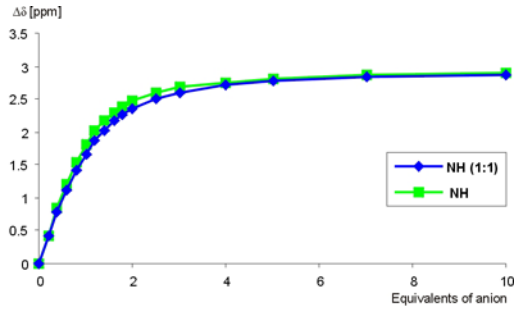
11. ^{1}H NMR titration of 1:1 mixture of macrocycle **2** and indolocarbazole **1** (0.002M each) in CD_3CN with TBACl (0.06M).

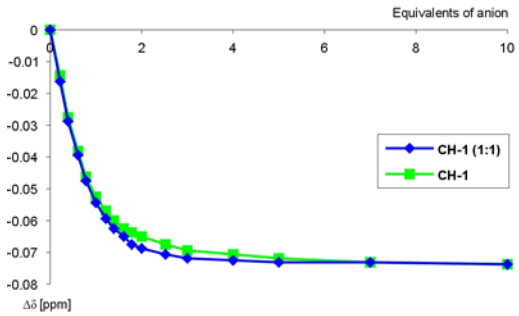
11a. Raw data. Chemical shifts of indolocarbazole and macrocycle protons during titration.

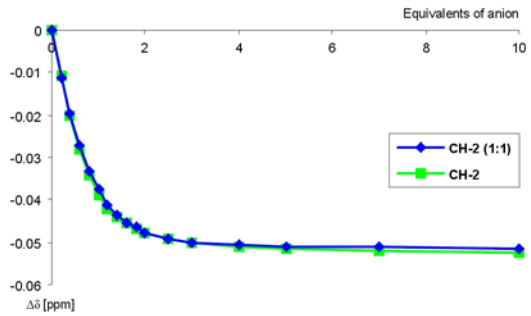
Equivalents of TBACl	NH	CH-1	CH-2	CH-3	CH-4	CH-5	CONH	CHint	CHext	HQ1	HQ2	a	b	c	d	e,f	t-Bu
0	9.6054	7.6959	7.4684	7.2990	8.1966	7.9867	7.3304	7.9192	8.0788	6.8844	6.8507	3.7461	4.1119	4.0087	3.7475	3.6090	1.3651
0.2	10.0356	7.6796	7.4570	7.2891	8.1926	7.9773	7.3732	7.9428	8.0799	6.8841	6.8487	3.7454	4.1133	4.0078	3.7472	3.6092	1.3651
0.4	10.3928	7.6673	7.4485	7.2811	8.1895	7.9695	7.4182	7.9674	8.0810	6.8841	6.8469	3.7447	4.1147	4.0069	3.7470	3.6093	1.3652
0.6	10.7269	7.6567	7.4410	7.2739	8.1867	7.9623	7.4723	7.9966	8.0823	6.8845	6.8451	3.7441	4.1167	4.0060	3.7466	3.6095	1.3651
0.8	11.0169	7.6483	7.4353	7.2680	8.1846	7.9563	7.5329	8.0296	8.0837	6.8852	6.8435	3.7437	4.1192	4.0052	3.7463	3.6097	1.3650
1	11.2670	7.6418	7.4307	7.2631	8.1830	7.9511	7.6006	8.0665	8.0854	6.8863	6.8421	3.7434	4.1222	4.0044	3.7460	3.6097	1.3649
1.2	11.4746	7.6367	7.4273	7.2591	8.1817	7.9469	7.6754	8.1075	8.0869	6.8878	6.8408	3.7433	4.1257	4.0038	3.7457	3.6099	1.3648
1.4	11.6367	7.6332	7.4249	7.2561	8.1807	7.9436	7.7500	8.1478	8.0887	6.8895	6.8397	3.7432	4.1293	4.0032	3.7454	3.6100	1.3647
1.6	11.7641	7.6306	7.4231	7.2538	8.1798	7.9410	7.8235	8.1877	8.0904	6.8913	6.8387	3.7433	4.1330	4.0027	3.7451	3.6101	1.3645
1.8	11.8711	7.6287	7.4218	7.2519	8.1793	7.9389	7.8998	8.2290	8.0921	6.8933	6.8378	3.7435	4.1369	4.0022	3.7448	3.6101	1.3643
2	11.9530	7.6273	7.4208	7.2505	8.1788	7.9373	7.9690	8.2667	8.0937	6.8951	6.8372	3.7436	4.1405	4.0018	3.7445	3.6102	1.3641
2.5	12.1027	7.6252	7.4192	7.2480	8.1781	7.9343	8.1354	8.3570	8.0974	6.8998	6.8356	3.7443	4.1493	4.0009	3.7439	3.6102	1.3638
3	12.2008	7.6241	7.4184	7.2465	8.1776	7.9324	8.2815	8.4362	8.1007	6.9041	6.8344	3.7451	4.1572	4.0001	3.7435	3.6103	1.3634
4	12.3103	7.6232	7.4176	7.2448	8.1770	7.9302	8.5037	8.5568	8.1057	6.9106	6.8328	3.7464	4.1694	3.9990	3.7425	3.6102	1.3628
5	12.3698	7.6228	7.4173	7.2439	8.1766	7.9290	8.6631	8.6437	8.1092	6.9155	6.8316	3.7476	4.1784	3.9982	3.7420	3.6100	1.3623
7	12.4316	7.6225	7.4171	7.2430	8.1762	7.9276	8.8689	8.7554	8.1136	6.9219	6.8302	3.7492	4.1900	3.9971	3.7410	3.6097	1.3615
10	12.4729	7.6222	7.4169	7.2424	8.1757	7.9266	9.0382	8.8476	8.1171	6.9270	6.8288	3.7506	4.1995	3.9960	3.7398	3.6092	1.3607

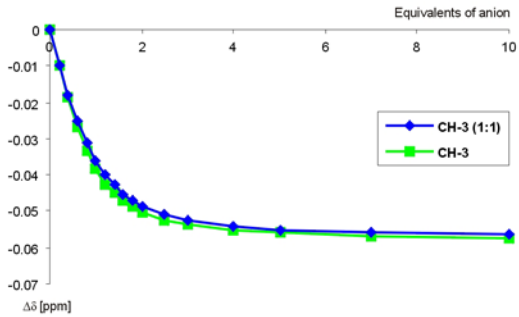
11b. Comparison of chemical shifts of indolocarbazole protons from the titration of 1:1 mixture of **2** and **1** versus **1** alone with TBACl.

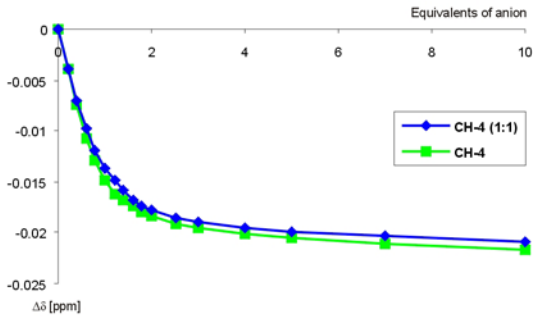


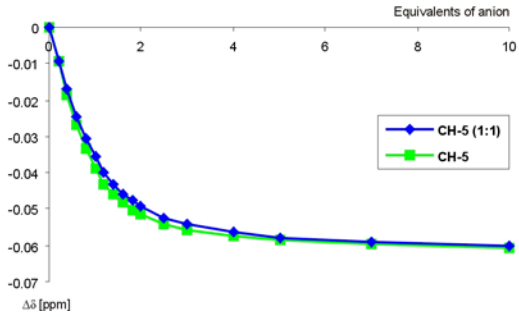




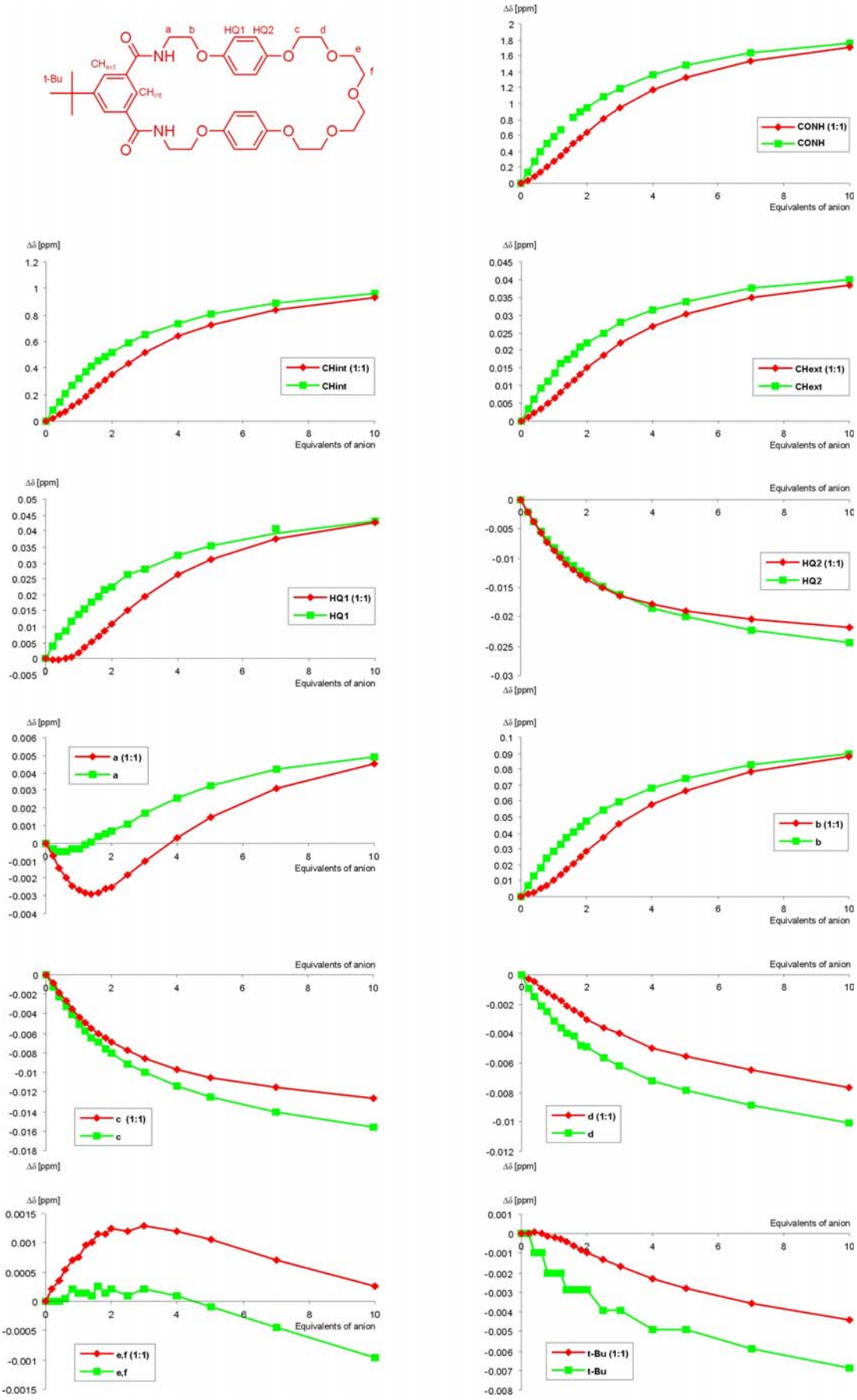








11c. Comparison of chemical shifts of macrocycle protons from the titration of 1:1 mixture of **2** and **1** versus **2** alone with TBACl.

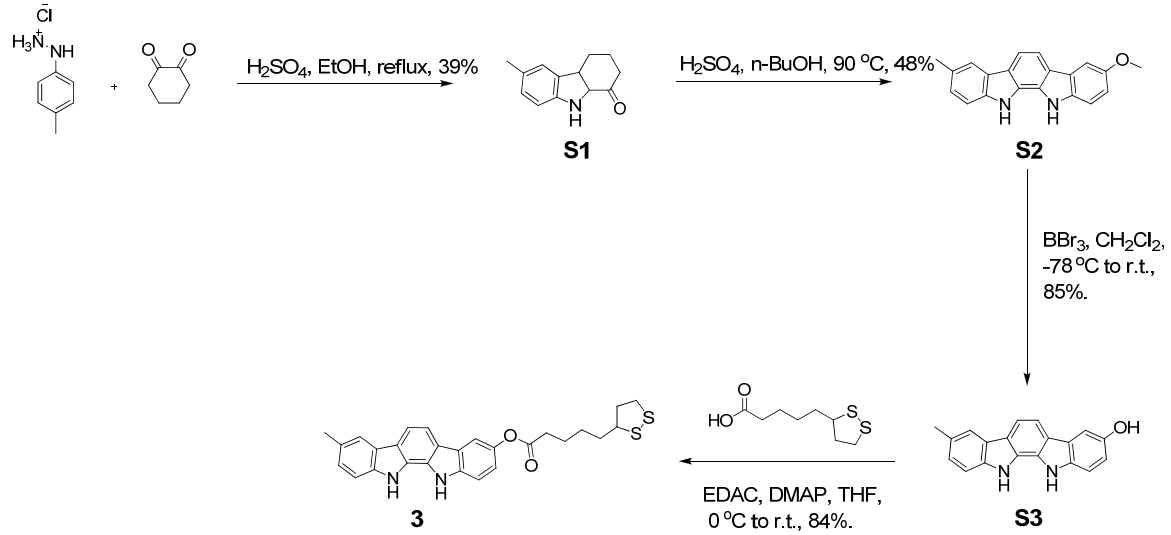


V) Experimental details on surface confined pseudorotaxane

1. Synthesis of disulfide-tethered indolocarbazole **3**

Dry solvents were obtained by purging with nitrogen and then passing through a column of activated alumina using Grubbs apparatus. H_2O was de-ionised and microfiltered using a Milli-Q ® Millipore machine. A 50% aqueous solution of TBA_2SO_4 was obtained from Sigma-Aldrich and dehydrated by evaporating most of the water on a rotary evaporator followed by prolonged drying *in vacuo* over P_4O_{10}. All other solvents and commercial grade reagents were used without further purification.

^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-VX 300, a Varian Unity Plus 500 or a Bruker AVII500 with cryoprobe at 293 K. Chemical shifts are quoted in parts per million relative to the residual solvent peak. Mass spectra were obtained using a Micromass GCT (EI) instrument. Melting points were recorded on a Gallenkamp capillary melting point apparatus and are uncorrected.



Scheme S1. Synthesis of disulfide-functionalised indolocarbazole **3**.

6-Methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one (S1). To a solution of 1,2-cyclohexanedione (1.68 mg, 15 mmol) and *p*-tolylhydrazine hydrochloride (1.59 g, 10 mmol) in absolute ethanol (150 ml) was added concentrated H_2SO_4 (1 ml). The mixture was heated to reflux for 16 hours and then poured onto water (600 ml). The resultant precipitate was collected by filtration through a plug of Celite. The Celite was washed thoroughly with water and then with dichloromethane to elute the product. The dichloromethane solution was evaporated to dryness and the residual solid was redissolved in dichloromethane, dry-loaded onto 5 g of silica and purified by column chromatography (hexane:ethyl acetate 9:1) on 20 g of silica to yield the product (0.778 g, 39%) as a white solid. δ_H(500 MHz; DMSO-d_6): δ 11.51 (1 H, s, N*H*), 7.46 (1 H, s, Ar*H*), 7.31 (1 H, d, J = 8.4 Hz, 1H), 7.16 (1 H, dd, ^3J = 8.4 Hz, ^4J = 1.7 Hz, Ar*H*) 2.92 (2 H, t, J = 6.1 Hz, CH_2), 2.54 (2 H, t, J = 6.4 Hz, 2H), 2.37 (3 H, s, CH_3), 2.13 (2 H, m, CH_2) (as lit.[1]).

3-Methoxy-8-methyl-11,12-dihydroindolo[2,3-a]carbazole (S2).
4-Methoxyphenylhydrazine hydrochloride (0.52 g, 3.0 mmol) and 6-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one **S1** (0.40 g, 2.0 mmol) were dissolved in n-butanol (10 ml) and concentrated H_2SO_4 (0.2 ml) was added dropwise via syringe. The solution was heated under reflux for 24 hours, during which time it became dark brown in colour. The reaction mixture was cooled to room temperature and allowed to stand for 24 hours. The resultant precipitate was collected by filtration and washed successively with methanol (2 x 10 ml), water (5 x 30 ml), methanol (4 x 20 ml) and ice-cold dichloromethane (2 x 5 ml). The solid was dried under high vacuum to yield 3-methoxy-8-methyl-11,12-dihydroindolo[2,3-a]carbazole **S2** (0.283 g, 48%) as an off-white solid. Mp > 310 ºC (decomp.); δ_H(300 MHz; DMSO-d_6) 10.88 (1 H, s, N*H*), 10.79 (1 H, s, N*H*), 7.92 (1 H, s, Ar*H*), 7.86 (1 H, d, ^3J = 8.5 Hz, Ar*H*), 7.81 (1 H, d, ^3J = 8.5 Hz, Ar*H*), 7.69 (1 H, d, ^3J = 2.4 Hz, Ar*H*), 7.58 (1 H, d, ^3J = 8.8 Hz, Ar*H*), 7.55 (1 H, d, ^3J = 8.2 Hz, Ar*H*), 7.20 (1 H, d, ^3J = 8.2 Hz, Ar*H*), 7.01 (1 H, dd, ^3J = 8.8 Hz, ^4J = 2.4 Hz, Ar*H*), 2.49 (3 H, s, CH_3, coincident with DMSO); δ_C(125 MHz, DMSO-d_6) 153.29, 137.19, 133.81, 127.46, 126.43, 125.94, 125.76, 124.26, 123.98, 120.00, 119.68, 119.41, 113.69, 112.21, 111.51, 111.22, 111.10, 102.36, 55.57, 21.21; *m/z* (EI) 300.1260 (M^+. $C_{20}H_{16}N_2O$ requires 300.1263).

8-Methyl-11,12-dihydroindolo[2,3-a]carbazol-3-ol (S3).
3-Methoxy-8-methyl-11,12-dihydroindolo[2,3-a]carbazole **S2** (0.20 g, 0.67 mmol) was suspended in dry dichloromethane (15 ml) under nitrogen. The suspension was cooled to -78 ºC and BBr_3 (0.8 ml of a 1 M solution in dichloromethane, 0.8 mmol) was added. After stirring at -78 ºC for 60 minutes, the reaction mixture was allowed to warm to room temperature and stirred for a further 16 hours. Methanol (10 ml) was added and the mixture was allowed to stir at room temperature for 30 minutes. The solvent was removed *in vacuo* and the residual white solid was suspended in dichloromethane:methanol 9:1 (10 ml). After removal of the solvent *in vacuo* the residual solid was suspended in dichloromethane:methanol 9:1 (5 ml), filtered, washed with dichloromethane (3 x 20 ml) and dried under high vacuum to the yield the product (0.162 g, 85%) as a white solid. Mp > 220 ºC (decomp.); δ_H(300 MHz; DMSO-d_6) 10.85 (1 H, s, N*H*), 10.66 (1 H, s, N*H*), 8.94 (1 H, s, O*H*), 7.92 1 H, s, Ar*H*), 7.79 (1 H, d, ^3J = 8.5 Hz, Ar*H*), 7.74 (1 H, d, ^3J = 8.5 Hz, Ar*H*), 7.56 (1 H, d, ^3J = 8.2 Hz, Ar*H*), 7.48 (1 H, d, ^3J = 8.7 Hz, Ar*H*), 7.45 (1 H, d, ^3J = 2.4 Hz, Ar*H*), 7.20 (1 H, d, ^3J = 8.2 Hz, Ar*H*), 6.88 (1 H, dd, ^3J = 8.7 Hz, ^4J = 2.4 Hz, Ar*H*); δ_C(75 MHz; DMSO-d_6) 150.74, 137.18, 133.09, 127.43, 126.45, 125.95, 125.71, 124.57, 124.02, 119.81, 119.59, 119.41, 113.97, 111.93, 111.43, 111.21, 110.97, 104.32, 21.22; *m/z* (EI) 286.1096 (M^+. $C_{19}H_{14}N_2O$ requires 286.1106).

8-Methyl-11,12-dihydroindolo[2,3-a]carbazol-3-yl 5-(1,2-dithiolan-3-yl)pentanoate (3)
8-Methyl-11,12-dihydroindolo[2,3-a]carbazol-3-ol **S3** (0.10 g, 0.35 mmol) and DL-6,8-thioctic acid (0.14 g, 0.70 mmol) were dissolved in dry tetrahydrofuran (15 ml) under an atmosphere of nitrogen. The solution was cooled to 0 ºC and *N*-Ethyl-*N*′-(3-dimethylaminopropyl)carbodiimide hydrochloride (0.089 g, 0.46 mmol) and 4-(dimethylamino)pyridine (0.010 g, 0.082 mmol) were added as solids. The reaction mixture was allowed to warm slowly to room temperature and stirred overnight. It was then poured into water (100 ml) and the resultant precipitate was collected by filtration. The solid was washed with water (3 x 15 ml) followed by methanol (3 x 15 ml) and dried under high vacuum to yield the title compound (0.14 g, 84%) as a white solid. Mp > 290 ºC (decomp.); δ_H(500 MHz; DMSO-d_6) 11.18 (1 H,s, N*H*), 11.03 (1 H, s, N*H*), 7.98 (1 H, s, Ar*H*), 7.91 (1 H, d, ^4J = 2.4 Hz, Ar*H*), 7.89 (2 H, s, Ar*H*), 7.71 (1 H, d, ^3J = 8.3 Hz, Ar*H*), 7.61 (1 H, d, ^3J = 8.3 Hz, Ar*H*), 7.25 (1 H, d, ^3J = 8.3 Hz, Ar*H*), 7.14 (1 H, dd, ^3J = 8.3 Hz, ^4J = 2.4 Hz), 3.73–3.68 (1 H, m) 3.26–3.21 (1 H, m), 3.18–3.13 (1 H, m), 2.65 (2 H, t, ^3J = 7.3 Hz, CH_2), 2.50 (3 H, s, CH_3), 2.48–2.43 (1 H, m), 1.95-1.89 (1 H, m), 1.80–1.60 (4 H, m), 1.58–1.47 (2 H, m); δ_C(125 MHz;

DMSO-d_6) 172.50, 143.46, 137.27, 136 59, 127.59, 126.59, 125.99, 125.79, 124.04, 123.87, 120.12, 119.72, 119.50, 118.45, 112.29, 111.82, 111.68, 111.50, 111.32, 56.11, 39.96, 38.15, 34.10, 33.45, 28.15, 24.30, 21.20; *m/z* (EI) 474.1441 (M^+. $C_{20}H_{16}N_2O$ requires 474.1436).

2. Formation of SAM of **3** on gold

Gold was treated with piranha solution (concentrated H_2SO_4 and 33% aqueous H_2O_2 in a 3:1 ratio) pirior to its monolayer formation in direct immersing in 1mM solution of **3** in DMF for 18 h. ***(Caution: Piranha solution should be handled with caution: it has been reported to detonate unexpectedly).*** After that, the substrate was sonicated in DMF for 1 min, followed by flushing with DMF, ethanol for 1 min respectively, and blow drying with nitrogen afterwards.

3. FTIR analyses

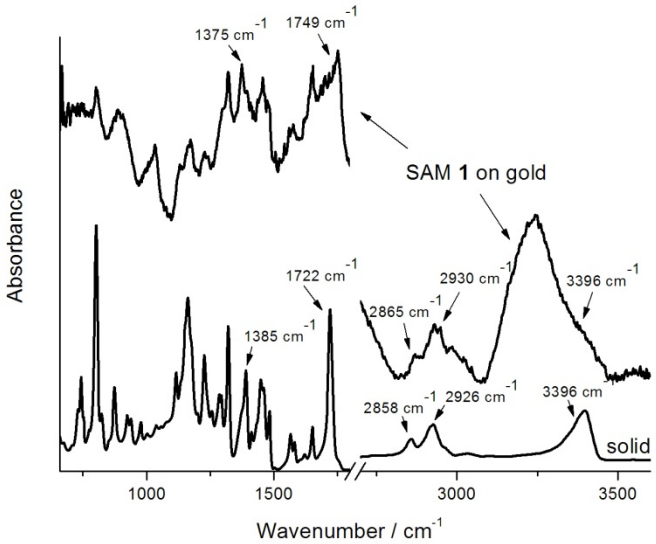


Figure S1. FTIR spectra of indolocarbazole axle **1** SAM on gold and the solid, respectively.

FTIR spectra were recorded using a Varian Digilab FTS 7000 series FTIR spectrometer, with a liquid nitrogen cooled MCT detector. For reflectance measurements, a Pike Veemax Specular reflectance accessory was used, with the sample inverted on top of this accessory, supported on a mask with an aperture diameter of 16 mm. An angle of incidence of 75º was used for all reflectance measurements in order to give as large a signal-noise ratio as possible. Prior to measurements, the instrument and the reflectance accessory were purged with CO_2 and H_2O free air from a FTIR Purge Gas Generator (Whatman). Background scans were recorded using a clean, bare gold substrate. Data were averaged over 2000 scans using a resolution of 4 cm^{-1} for each measurement. Spectra of solid samples were recorded using a DurasamplIR II diamond attenuated total reflectance (ATR) accessory.
Figure 1 shows the reflectance FTIR spectra of the SAM on gold substrate compared to the solid sample. It can be clearly seen that the spectrum of the axle monolayer is similar to that of its solid, with the peaks at 2930 cm^{-1} corresponding to asymmetric CH_2, 2860 cm^{-1} to symmetric CH_2, 1725 cm^{-1} to COO and 1380 cm^{-1} to CH_3, respectively, which confirms the attachment of the axle to the surface. The little difference in peak positions and intensities for

the monolayer and the solid is due to the different recording modes of the spectra and the different tilt mode of the chain in monolayer on surface and in solids.

4. Redox probe and reductive strip analyses

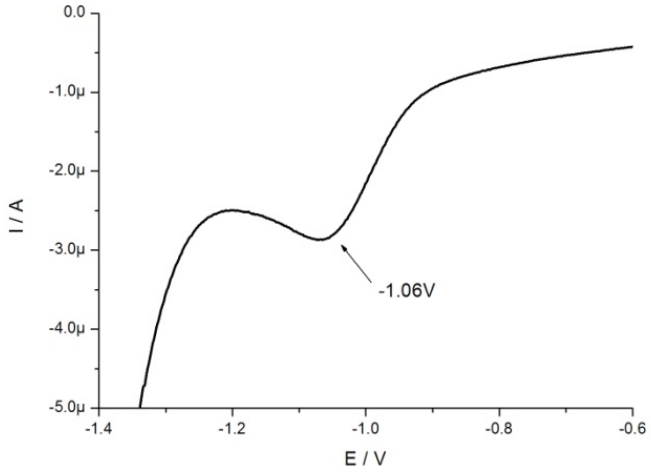


Figure S2. Reductive desorption of SAM **3** on a polycrystalline gold electrode in an electrolyte solution of 0.1 M NaOH in CH_3OH:H_2O (95:5 v/v) after 20 min degrassing with nitrogen; scan rate 0.1 V s^{-1}.

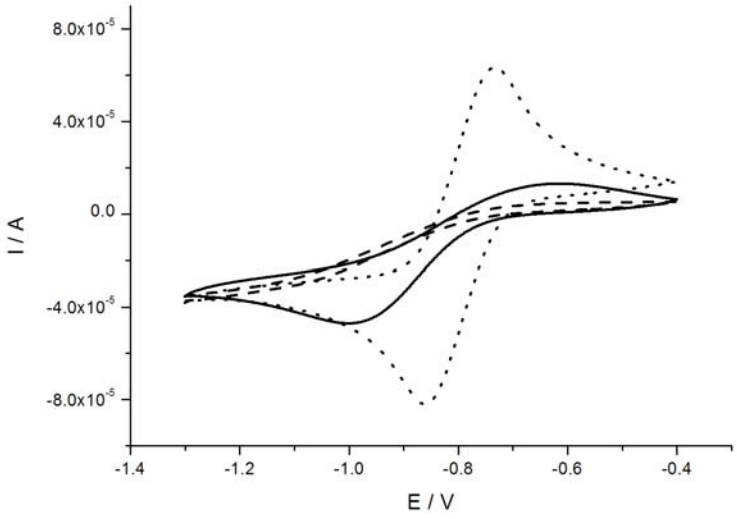


Figure S3. Cyclic voltammetry of 0.01 M benzoquinone recorded with a polycrystalline gold electrode (dotted curve), gold electrode modified with SAM of **3**(solid curve) and gold electrode modified with mixed SAMs of **3** and thiotic acid (dashed curve), respectively, in 0.1 M $TBAPF_6$ / acetonitrile; scan rate 0.1 V s^{-1}.

Figure **S3** shows comparative CVs recorded with a diffusive benzoquinone redox probe. The axle SAM does not completely inhibit Faradaic activity, indicating the presence of appreciable

pinhole/spatial defects in the monolayer. This equates with the comparatively large footprint of **3** as calculated from reductive stripping. Though such spatial defects, which we ascribe the steric bulk of **3**, can be blocked by subsequent chemisorption on an alkyl thiol, they are likely to be advantageous in providing space for subsequent template macrocycle threading.

5. SPR analyses

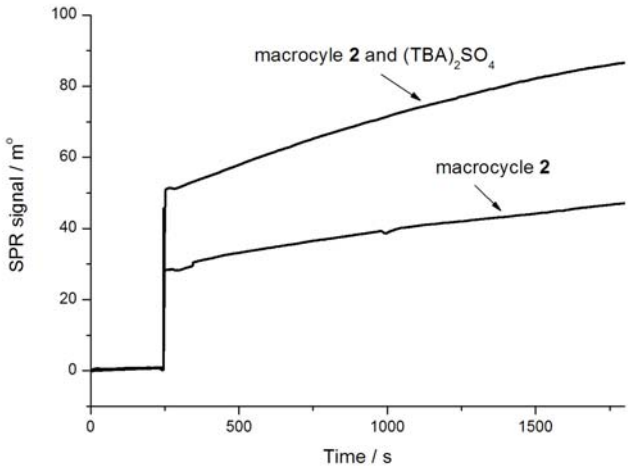


Figure S4. SPR sensorgram showing the comparison between addition of **2** over surface-confined **3** SAM in the presence and absence of $(TBA)_2SO_4$, respectively.

VI) Molecular modeling

a)

b)

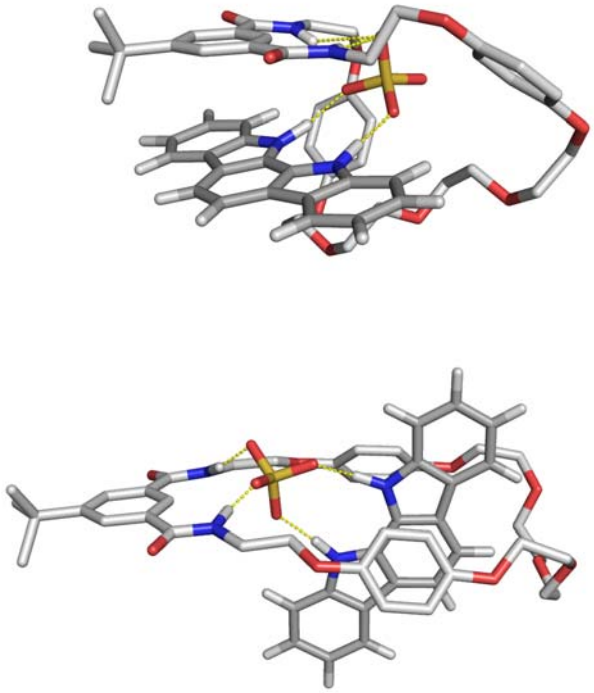


Figure S5. Co-conformations of $[\mathbf{2}\times SO_4\times\mathbf{1}]^{2-}$ in *a)* gas-phase and *b)* CH_3CN (solvent molecules have been omitted for clarity). Co-conformation *b)* corresponds to the average structure obtained from a 5ns trajectory.

Experimental section

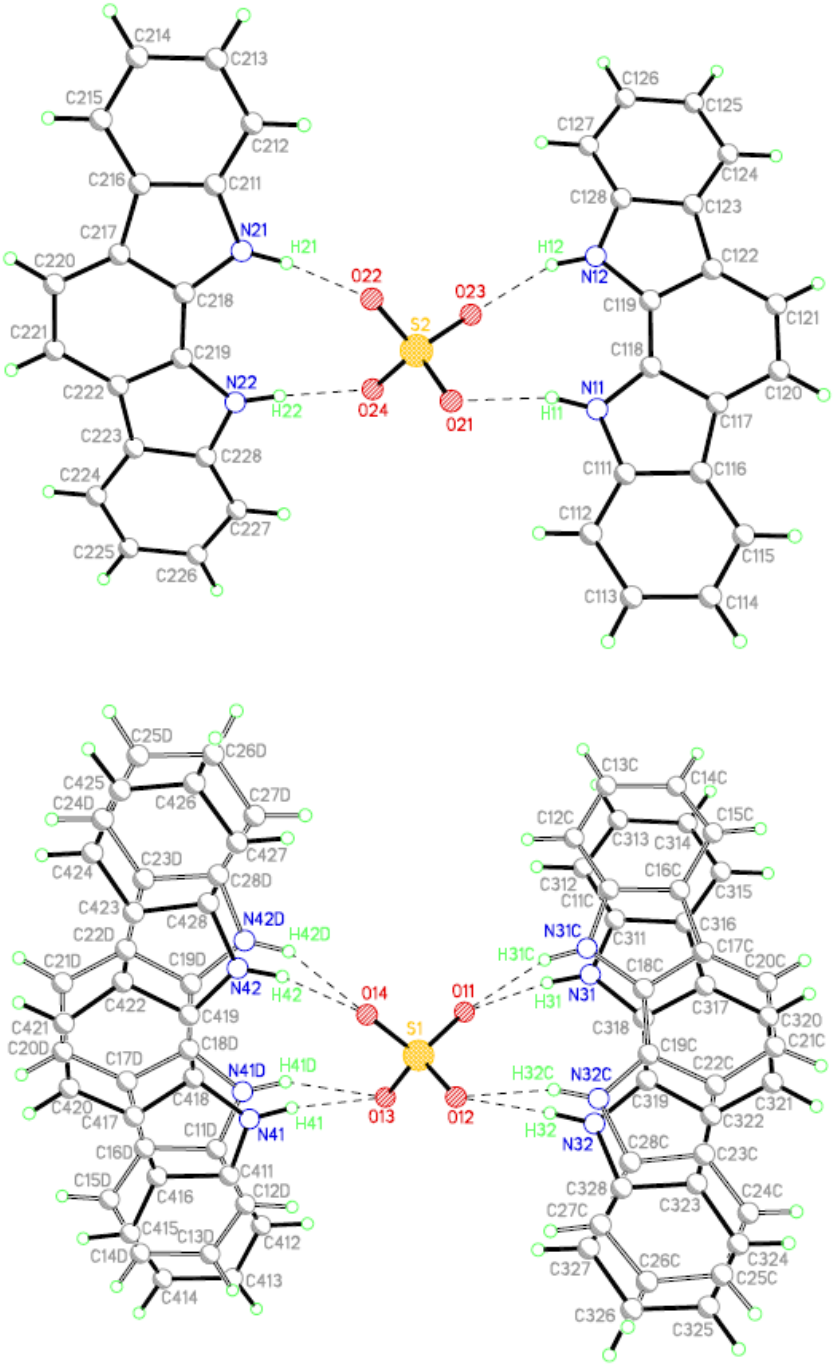
Conventional Molecular Dynamic (MD) simulations were carried out with the AMBER9[2] software package. Parameters for **2**, **5** and SO_4^{2-} were taken from GAFF;[3] acetonitrile was described using a full atoms model with parameters taken from ref.4. Partial RESP3[5] fitted charges for **2**, **5** and SO_4^{2-} were obtained from HF/6-31G* level calculations using Gaussian03.[6]

Starting models for [**2**×SO_4×**5**]$^{2-}$ were obtained through assembly of the adequate individual moieties, which were then submitted to gas phase simulated annealing, consisting on the heating of the structures up to 1000K followed by slow cooling to 0 K, thus yielding its lowest energy conformations. No bond or angle parameters between SO_4^{2-} and the N-H binding sites of **2** and **5** were applied, for what the attractive interactions were primarily electrostatic. For both systems, two lowest energy binding arrangements were then immersed in separated cubic boxes (typically *ca*. 50 Å in size after equilibration) containing approximately 1200 molecules of acetonitrile. MD simulations of the several systems started with an initial solvent and solute relaxation, followed by 50 ps NVT heating to 300 K and 500 ps NPT equilibration periods. The final densities of the equilibrated boxes were in close agreement with the experimental density of the pure solvent, and remained constant during, at least, the final 300 ps of the NPT equilibration period. The SHAKE[7] algorithm was employed in all condensed phase simulations to constrain all hydrogen involving bonds, thus allowing the usage of 2 fs time steps. Non-bonded van der Waals interactions were restrained to a 12 Å cutoff, while the particle mesh Ewald method was used to describe the long range electrostatic interactions. The double negative charge was balanced assuming uniform neutralizing plasma. The temperature of the systems was controlled by the Langevin thermostat, using a collision frequency of 1.0 ps^{-1}. The MM-PBSA (Molecular Mechanics-Poisson Boltzmann Surface Area) methodology[8] and Normal Mode Analysis[9] were used to determine the entalphic and entropic contributions to the solvation process at 300 K, respectively, using the modules provided by the AMBER9 suite. Dielectric constants of 1.0 and 36.64 were used for the pseudorotaxane and CH_3CN, respectively. The calculations were based on 2500 independent structures, extracted from 5ns long trajectories with a 10 frame frequency.

VII) X-Ray structure of $(TBA)_2[1_2 \times SO_4]$.

Experimental Section

Crystals were grown by slow diffusion of pentane or ether into a solution of a 2:1 mixture of indolocarbazole and $(TBA)_2SO_4$ in dichloromethane. Single crystal X-ray diffraction data were collected using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius KappaCCD diffractometer. The diffractometer was equipped with a Cryostream N2 open-flow cooling device,[10] and the data were collected at 150(2) K. Series of ω-scans were performed in such a way as to cover a sphere of data to a maximum resolution of 0.78 Å. Cell parameters and intensity data were processed using the DENZO-SMN package.[11] The was solved by direct F^2 using the SHELXTL software.[12] Intensities were corrected for absorption effects by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections (using the SORTAV software.[13] The structure was found to be very badly disordered and a complete anisotropic refinement was not possible. The disorder was modelled using principally using a large number of same distance and vibrational restraints and it was necessary to refine some parts of the structure using isotropic displacement parameters. For further details see the supplementary information. *Single Crystal X-ray Diffraction Data*: Chemical formula moiety 2(C18 H12 N2), 2(C16 H36 N), S O4, 0.5(H2 O), 0.25 (C H2 Cl2), empirical formula C68.25 H97.50 Cl0.50 N6 O4.50 S, Mr = 1123.81, triclinic (P-1), a = 13.3572(2) Å, b = 17.5978(3) Å, c = 28.2466(5) Å, α = 88.0490(10)º, β = 87.7290(10)º, γ = 84.2600(10)º, V = 6598.07(19) $Å^3$, Z = 4, μ = 0.120 mm^{-1} D_{calc} = 1.131 Mg/m3, T = 150(2) K, 57686 reflections collected, 10110 independent [R(int) = 0.0989], R1 = 0.1411, wR2 = 0.3693 [I>2sigma(I)]. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre, CCDC 683020. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +44 (1223) 336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).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N11
H11
C120
C117
C111
C116
C112
C115
C113
C114
C25D
C26D
C425
C24D
C426
C27D
C424
C23D
C427
C28D
C423
C428
N42D
H42D
C22D
C21D
C19D
N42
H42
C422
C419
C421
C20D
C18D
C17D
N41D
H41D
C420
C417
C418
C11D
N41
H41
C16D
C411
C15D
C416
C12D
C415
C13D
C412
C14D
C413
C414
O14
O11
S1
O13
O12
C13C
C14C
C12C
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C313
C314
C16C
C312
C315
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C316
N31C
C311
C17C
H31C
C18C
C20C
H31
N31
C317
C320
C318
C21C
C19C
C22C
H32C
N32C
C319
C321
C322
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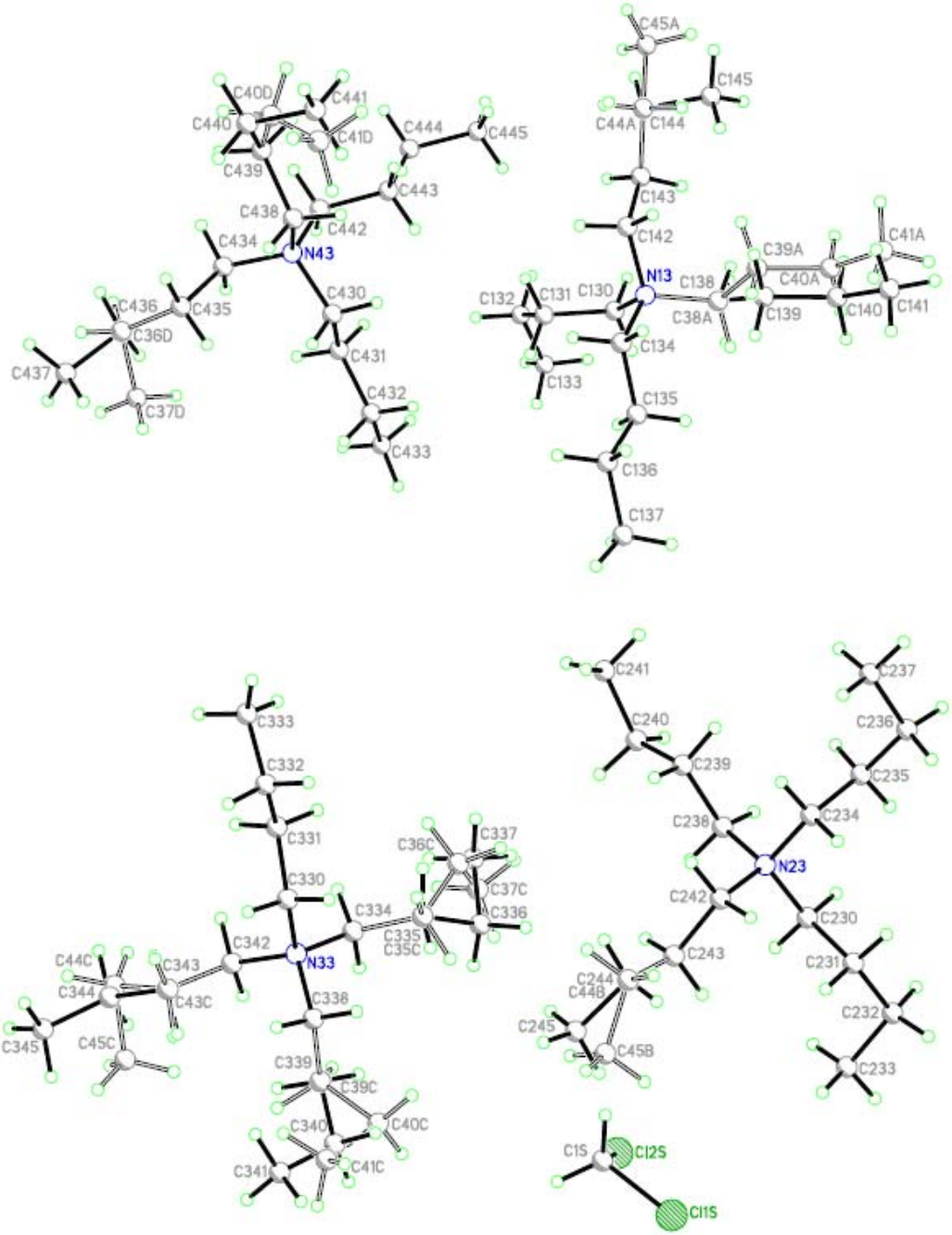
C328
C24C
C27C
C323
C26C
C324
C327
C25C
C326
C325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C135
C136
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C40D
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C439
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C234
N23
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C243
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C244
C44B
C232
C245
C45B
C233
C1S
Cl2S
Cl1S

Table 1. Crystal data and structure refinement for Indolocarbazole Sulfate

Identification code	Indolocarbazole Sulfate
Chemical formula moiety	2(C18 H12 N2), 2(C16 H36 N), S O4, 0.5(H2 O), 0.25 (C H2 Cl2)
Empirical formula	C68.25 H97.50 C10.50 N6 O4.50 S
Formula weight	1123.81
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 13.3572(2) Å α= 88.0490(10)˚. b = 17.5978(3) Å β= 87.7290(10)˚. c = 28.2466(5) Å γ= 84.2600(10)˚.
Volume	6598.07(19) $Å^3$
Z	4
Density (calculated)	1.131 Mg/m^3
Absorption coefficient	0.120 mm^{-1}
F(000)	2438
Crystal size	1.00 x 0.02 x 0.02 mm^3
Theta range for data collection	5.09 to 25.33˚.
Index ranges	-16<=h<=16, -21<=k<=21, -28<=l<=33
Reflections collected	57686
Independent reflections	22832 [R(int) = 0.0989]
Completeness to theta = 25.33˚	94.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.046 and 0.969
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	22832 / 2100 / 153
Goodness-of-fit on F^2	1.302
Final R indices [I>2sigma(I)]	R1 = 0.1411, wR2 = 0.3693
R indices (all data)	R1 = 0.2635, wR2 = 0.4323
Extinction coefficient	0
Largest diff. peak and hole	2.366 and -0.631 e.$Å^{-3}$

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