Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Introducing a static receptor to compete with a dynamic combinatorial library in template binding

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Supplementary Information

Procedures for library preparations and analysis.

Synthesis of $\mathbf{1_n}$ and preparation of its stock solution was described previously.[S1]

All DCL experiments were conducted in DMSO + 0.5% H_2O on 100 μL scale with a total concentration of monomer: 0.005 mol/dm^3. The mixture of DCL, static receptor and/or TBA benzoate salt was stirred for 4 h. After that time, TFA in MeCN (0.1 mol/dm^3, 400 μL) was added to freeze the equilibrium. The samples were then subjected to HPLC analysis: ACE-Phenyl 5 μm, I.D.= 4.6 mm, l=25 cm, column. Flow: 1.5mL/min, gradient indicated in Table S1. Retention time of all compounds are presented in Table S2.

Table S1. Gradient composition in HPLC analyses.

Time [min]	MeCN (%)	H_2O (%)	1% TFA in MeCN (%)
0	39	60	1
12	59	40	1
14	89	10	1
16	89	10	1

Table S2. HPLC peaks assignments.

Time [min]	Compound
3.62	BzOH
4.43	$\mathbf{M_2}$
5.21	Host **5**
7.51	$\mathbf{M_3}$
8.77	Host **4**
9.21	$\mathbf{M_4}$
10.68	$\mathbf{M_5}$
12.17	Host **1**
15.78	Host **3**
16.74	Host **2**

Fitting procedure using DCL-fit

Equilibrium constants of formation of library components (K_n) and association constants ($K_{n\text{-}T}$) of complexes of receptors $\mathbf{1_n}$ with benzoate were determined previously.[S1]

DCL-fit software (availabe form Otto, http://www.otto-lab.com/software.htm) was applied as depicted in Fig S1.

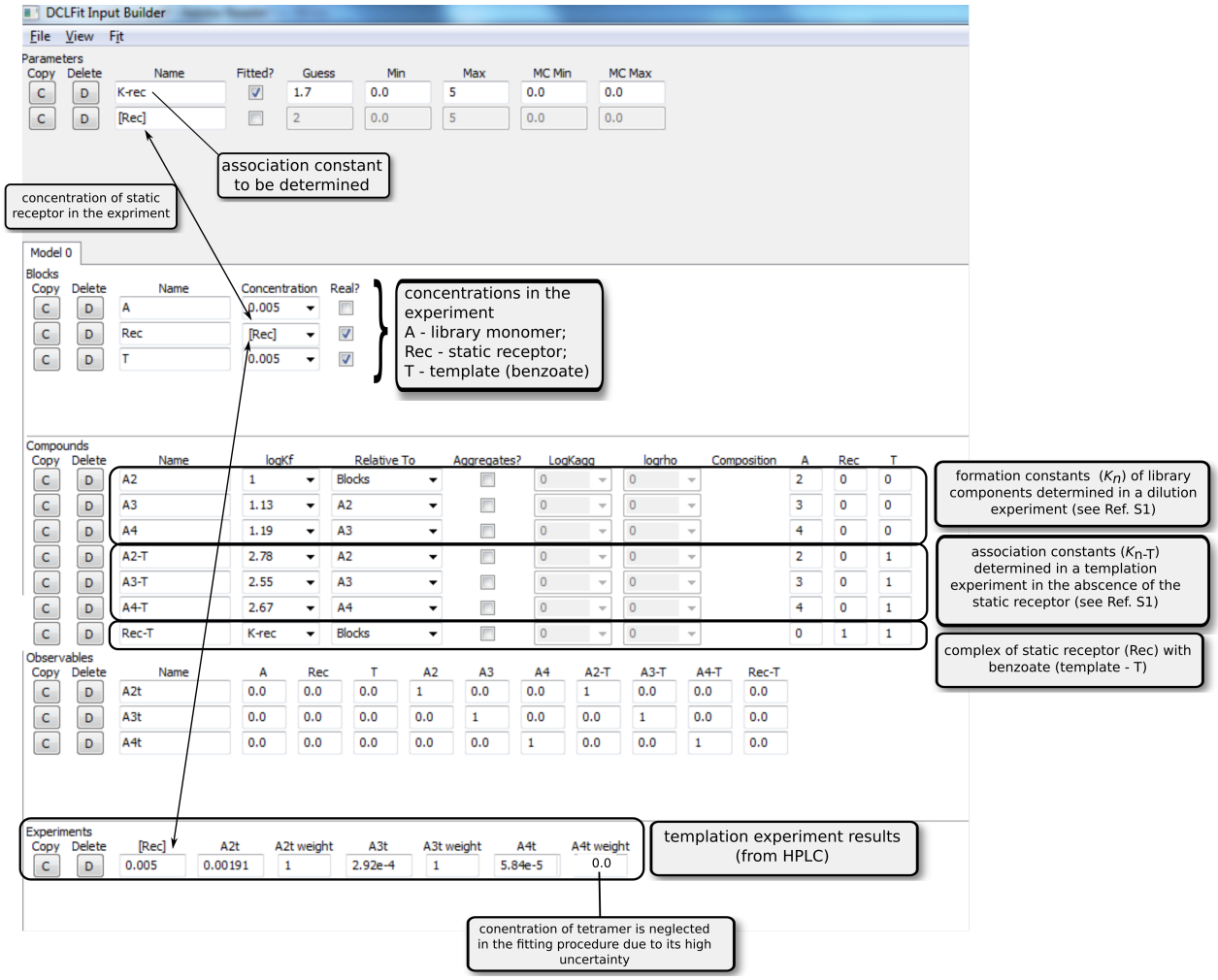

Figure S1 Input data in DCL-fit for the experiment with a static receptor and benzoate.

Table S3. DCLfit results for receptors **1,2,4,5**.

	concentrations in DCL					
host	$\mathbf{M_2}$	$\mathbf{M_3}$	$\mathbf{M_4}$	**z=[M$_2$]/[M$_3$]**	log(K_{Rec}) by DCLfit	log(K_{Rec}) by titraion
1	2.02E-3	2.44E-4	4.52E-5	8.27	1.74	1.78
2	1.91E-3	2.92E-4	5.87E-5	6.53	3.24	3.11
4	1.91E-3	2.92E-4	5.84E-5	6.53	3.23	3.20
5	1.96E-3	2.78E-4	5.03E-5	7.04	2.75	2.77

Templation effects of host 3

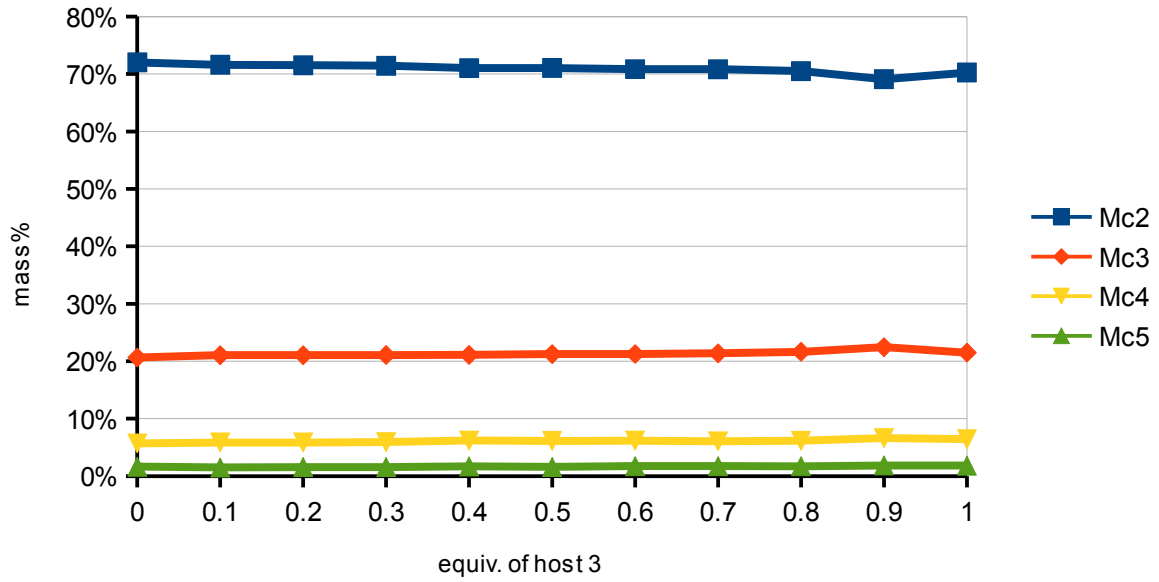

Figure S2 Templation of library $\mathbf{M_n}$ with receptor **3** induces a slight reduction in the abundance of dimer, while trimer and tetramer are amplified.

Dilution experiments – check for thermodynamic control of the system

We conducted a set of dilution experiments in which the composition of DCL was evaluated at different total concentrations of monomer. Experiments were run with pure DCL and with static receptor **1** added (c=0.005M in all experiments). Our system can be treated with a modified Jacobson-Stockmayer theory with monomer as a virtual component and no linear oligomers. The linear correlations between the concentrations of a given macrocylce ($\mathbf{M_n}$) and the total concentration of a monomer in a double log plot prove the reversibility of the system (Fig. S3). The data were also nicely fitted (Fig. S4) with DCLfit software utilising the model expressed in Scheme 1. The conformity between results obtained for pure DCL and DCL with static host indicates that addition of static host does not influence the reversiblity of the disulfide bond exchange.

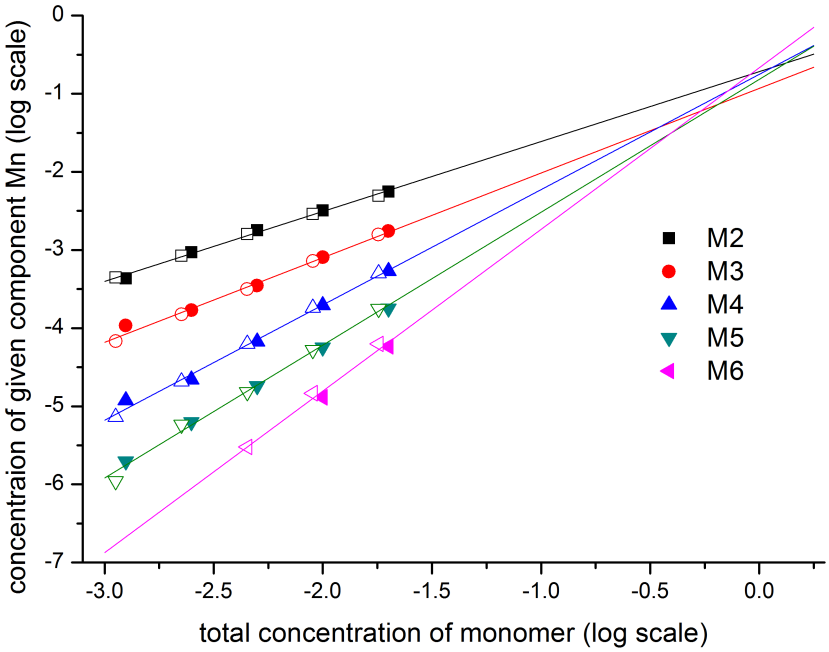

Figure S3 A plot in logarithm scale depicting the concentrations of macrocycles in a series of DCLs set with various total concentration of monomer. Full symbols correspond to solutions of pure DCL, open symbols correspond to DCLs containing static receptor **1** (c=0.005M in all solutions).

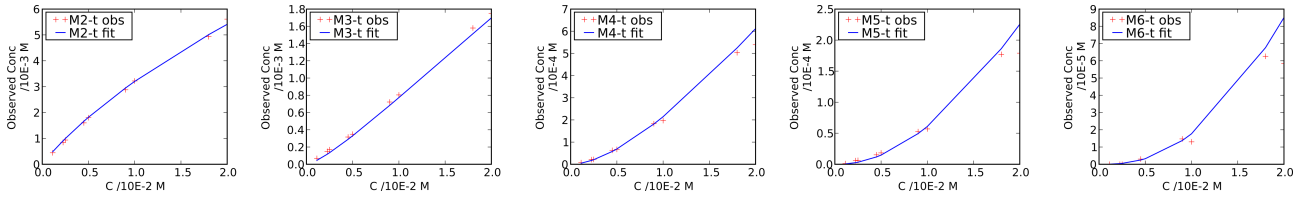

Figure S4 Concentrations of macrocycles in dilution experiments fitted with DLCfit.

Reference:

S1 F. Ulatowski, A. Sadowska-Kuzioła and J. Jurczak, *J. Org. Chem.*, 2014, **79**, 9762–9770.