Electronic supplementary information

Factors driving the self-assembling of water-soluble calix[4]arene and gemini guests: a combined solution, computational and solid-state study

Carmela Bonaccorso,*[a] Giovanna Brancatelli,[b] Giuseppe Forte,[c] Giuseppe Arena,[a] Silvano Geremia,[b] Domenico Sciotto[a] and Carmelo Sgarlata*[a,d]

[a] Dipartimento di Scienze Chimiche, Università degli Studi di Catania, Viale A. Doria 6, 95125, Catania, Italy

[b] Centro di Eccellenza di Biocristallografia, Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, 34127, Trieste, Italy

[c] Dipartimento di Scienze del Farmaco, Università degli Studi di Catania, Viale A. Doria 6, 95125, Catania, Italy

[d] Consorzio I.N.B.B., Viale delle Medaglie d'Oro 305, 00136, Roma, Italy

email: sgarlata@unict.it, bonaccorsoc@gmail.com

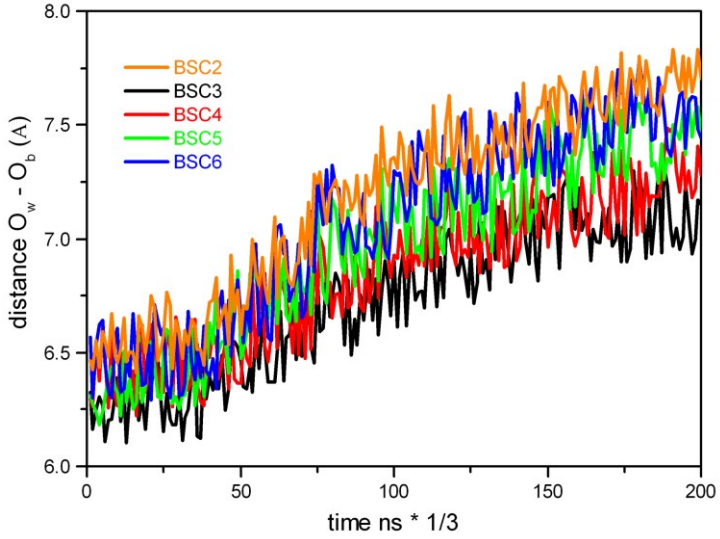

Fig. S1 Fluctuation of the distances $O_w - O_b$.

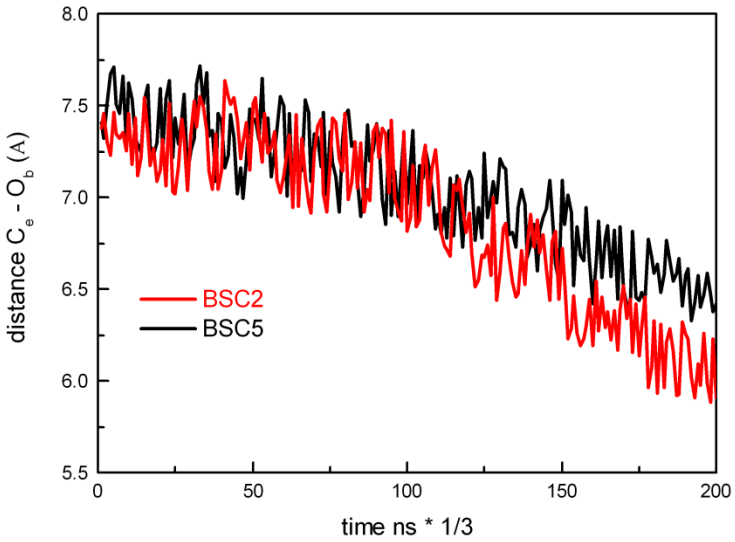

Fig. S2 Fluctuation of the distances $C_e - O_b$; only the distances of guests with n = 2 and 5 are reported.

Table S1. Crystal data and structure refinement for **TAC4** and complexes **1, 2** and **3**.

	TAC4	**1**	**2**	**3**
Formula	$C_{40}H_{56}N_4O_4$, 4 Cl, 5 H_2O	$C_{40}H_{56}N_4O_4$, 1.5 ($C_{16}H_{16}O_8S_2$), Cl, 4 H_2O	2 ($C_{40}H_{56}N_4O_4$), 2 ($C_{16}H_{16}O_8S_2$), 4 Cl, 12 H_2O	3 ($C_{40}H_{56}N_4O_4$), 3 ($C_{16}H_{16}O_8S_2$), 6 Cl, 10 H_2O
Formula weight (Da)	878.68	1356.95	2576.37	3544.24
T (K)	100	100	100	100
λ (Å)	0.700	0.800	0.700	0.700
Crystal system	Monoclinic	Triclinic	Triclinic	Trigonal
Space group	*C*2/c	*P* -1	*P* -1	*P* 3_2
Unit cell dimensions (Å, °)	a = 14.290(1), α = 90 b = 30.628(2), β = 90.29(3) c = 10.624(2), γ = 90	a = 14.69(1), α = 113.62(2) b = 16.86(1), β = 101.51(4) c = 17.36(1), γ = 102.11(1)	a = 15.4765(2), α = 100.475(4) b = 18.1323(3), β = 98.972(3) c = 23.5934(1), γ = 98.56(1)	a = 35.50(2), α = 90 b = 35.50(2), β = 90 c = 14.80(1), γ = 120
V (Å^3)	4649.8(10)	3654(4)	63223.0(2)	16153(21)
Z	8	2	2	3
ρ_{calc} (g/mm^3)	1.255	1.233	1.352	1.093
μ (mm^{-1})	0.291	0.281	0.234	0.194
F(000)	1856	1434	2708.0	5621
Resolution (Å)	15.33-0.90	9.95-0.79	22.79-0.73	11.62-0.74
Reflections collected	10506	41705	67794	134131
Independent reflections	3275	12823	29989	38600
Data / restraints / parameters	3275 / 0 / 282	10061 / 0 / 983	21692 / 12 / 1681	38600 / 86 / 2213
R_1, wR_2 [I>2σ(I)]	0.0798, 0.2089	0.1119, 0.2909	0.0872, 0.2211	0.0811, 0.2098
R_1, wR_2 (all data)	0.1207, 0.2436	0.1168, 0.2949	0.0910, 0.2235	0.0855, 0.2174
GooF	1.018	1.016	1.074	1.038
CCDC code number	1005754	1002190	1002197	1002465

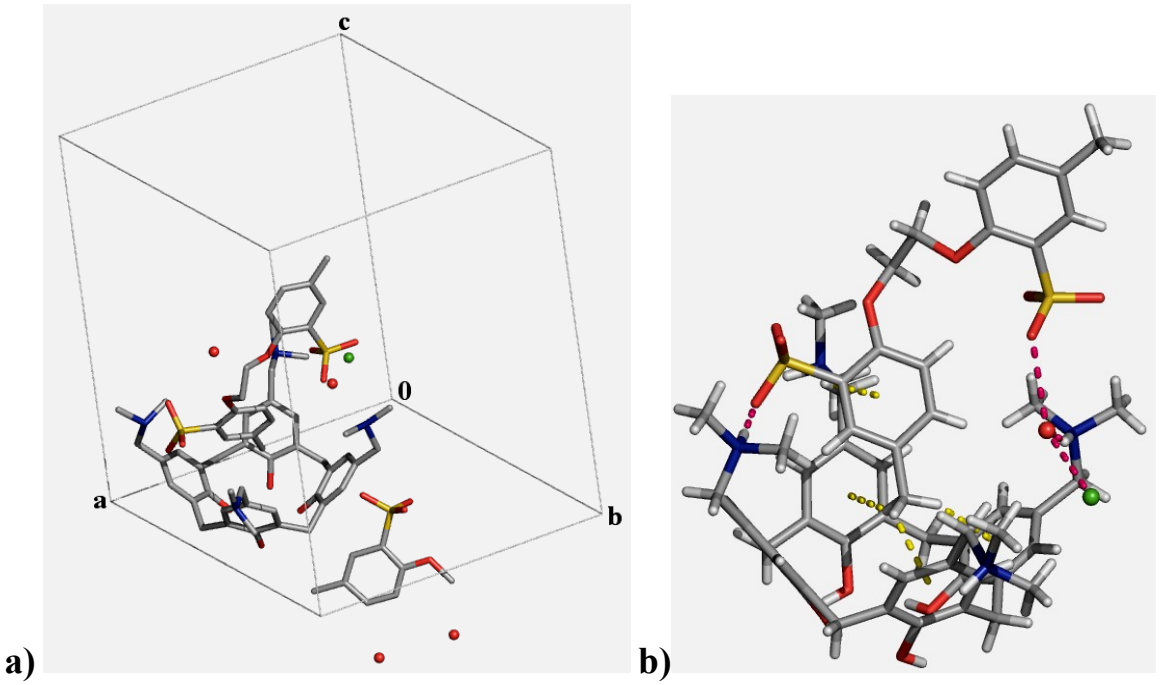

Fig. S3 a) Asymmetric unit of crystal **1**. Green and red spheres represent chloride anions and water molecules, respectively. Hydrogen atoms were omitted for clarity. b) Detail of the intermolecular interactions between host, guest and water molecule. Green and red spheres represent the chloride anion and the water molecule, respectively.

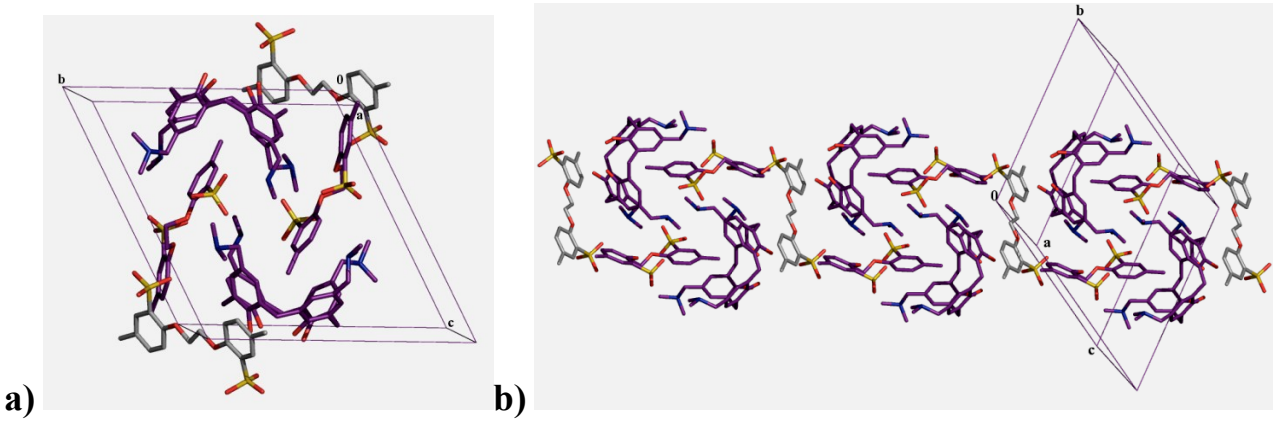

Fig. S4 Crystal packing of **1**: a) self-assembly of two complexes in an antiparallel fashion, sandwiched by two external **BSC2** anions; b) propagation of the complex pairs along the *bc* plane, alternating with the **BSC2** anions. Water molecules and chloride anions were omitted for clarity.

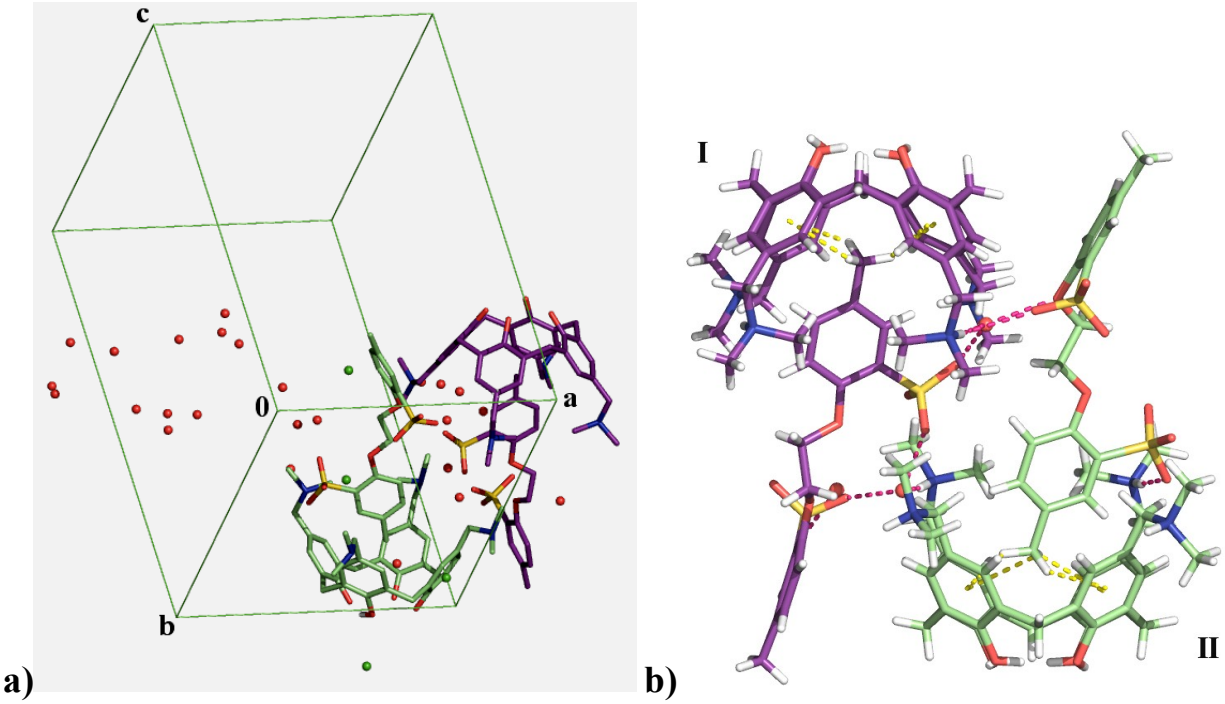

Fig. S5 a) The asymmetric unit of crystal **2** showing the two independent complexes **I** and **II** depicted in violet and green, respectively. Green and red spheres represent chloride anions and water molecules, respectively. Hydrogen atoms were omitted for clarity. b) Detail of the intermolecular interactions between the two complexes and involving water molecules.

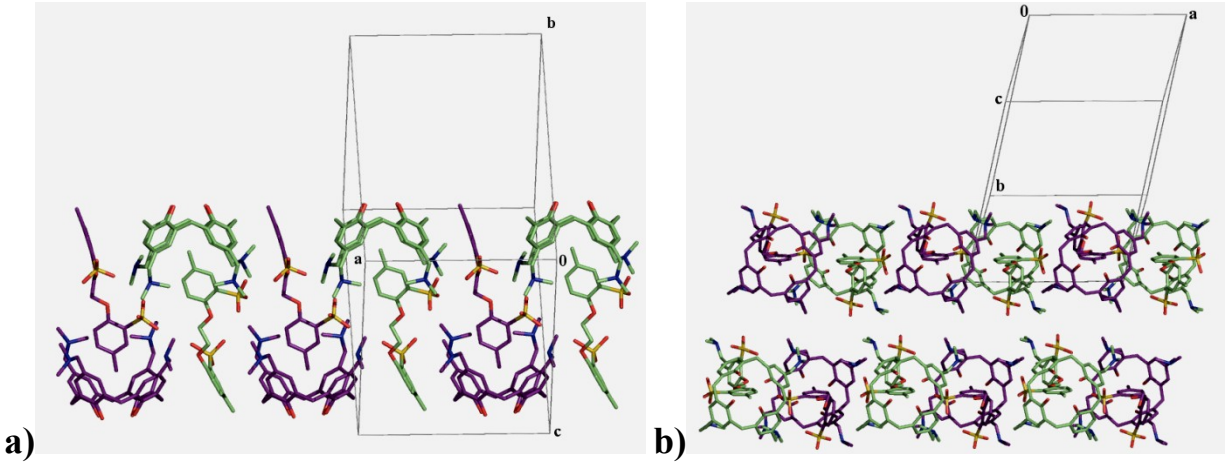

Fig. S6 Crystal packing of **2**: infinite chains of host-guest complexes head-to-tail oriented, extending along the *a* axis a) and b) view of parallel chains. Water molecules and chloride anions were omitted for clarity.

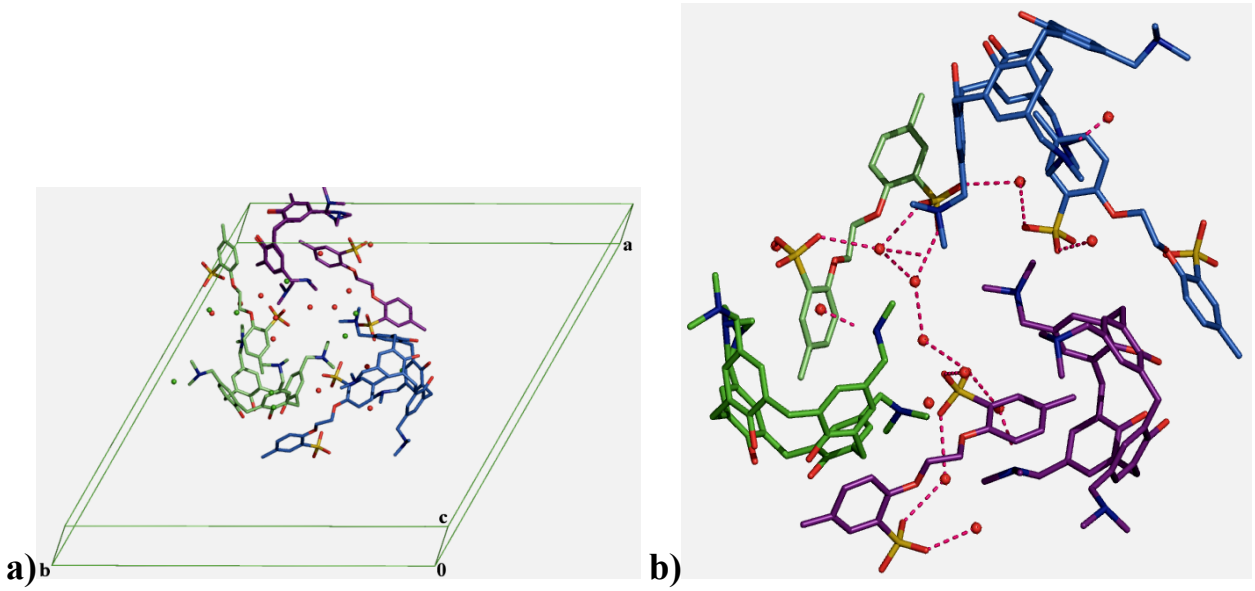

Fig. S7 a) The asymmetric unit of **3** showing the three independent complexes **I, II** and **III**, depicted in blue, green and violet, respectively, arranged in a trimeric supramolecular assembly. Green and red spheres represent chloride anions and water molecules, respectively. Hydrogen atoms were omitted for clarity. b) Dense network of hydrogen bonding interactions stabilizing the trimeric assembly and involving sulfonate groups from guests, dimethylammonim groups from hosts and several solvating water molecules.

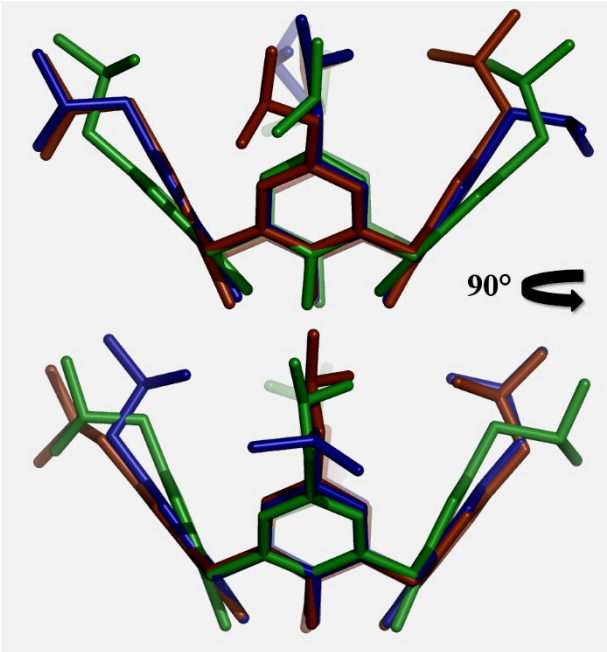

Fig. S8 Overlay of the **TAC4** host in **1** (green), **2** (brown) and **3** (blue) crystal structures, highlighting the different cavity conformations adopted by the calixarene.

Table S2. Non-covalent interactions C–H···π in the crystal structure of **1, 2** and **3** complexes (distances in Å).

1		**2**		**3**	
C−H···π		**C−H···π**		**C−H···π**	
		I		**I**	
C(5h)···Cg(A)	3.65(2)	C(5h)···Cg(A)	3.53(5)	C(5i)···Cg(A)	3.61(2)
C(5h)···Cg(B)	3.43(2)	C(5h)···Cg(B)	3.73(6)	C(5i)···Cg(B)	3.78(2)
C(5h)···Cg(C)	3.75(2)	C(5h)···Cg(C)	3.53(4)	C(5i)···Cg(C)	3.79(2)
C(4h)···Cg_{BS2}	3.50(2)	C(5h)···Cg(D)	3.80(5)	C(5i)···Cg(D)	3.76(3)
		II		**II**	
		C(11h)···Cg(A)	3.53(4)	C(11i)···Cg(A)	3.57(2)
		C(11h)···Cg(B)	3.59(5)	C(11i)···Cg(B)	3.82(2)
		C(11h)···Cg(C)	3.65(6)	C(11i)···Cg(C)	3.84(3)
		C(11h)···Cg(D)	3.77(5)	C(11i)···Cg(D)	3.86(4)
				III	
				C(18i)···Cg(A)	3.53(2)
				C(18i)···Cg(B)	3.72(3)
				C(18i)···Cg(C)	3.82(3)
				C(18i)···Cg(D)	3.77(2)

Table S3. Comparison of the relevant conformational parameters of **1**, **2** and **3**: dihedral angles (°) between the lower calixarene mean plane[a] and the aromatic planes of **TAC4** (θ_A θ_B θ_C θ_D), and between the lower calixarene mean plane[a] and the mean plane of the *endo*-**BSC2** guest[b] (θ_{BS2}).

θ_A	θ_B	θ_C	θ_D	θ_{BS2}
1				
135.6(1)	115.9(2)	136.0(1)	113.1(1)	68.3(1)
2				
I				
116.7(1)	124.9(2)	120.9(1)	131.4(1)	69.2(1)
II				
125.3(1)	120.5(2)	123.0(1)	121.5(1)	69.4(1)
3				
I				
122.61(2)	122.28(2)	128.05(2)	121.35(2)	88.47(2)
II				
127.90(2)	122.41(2)	127.36(2)	118.74(2)	82.06(2)
III				
122.28(2)	126.92(2)	121.63(2)	124.43(2)	88.10(2)

[a] The "lower" calixarene mean plane is defined by the four methylene bridging carbon atoms.
[b] The guest mean plane is defined by the six aromatic and the methyl carbon atoms of the guest end inserted into the calixarene cavity.

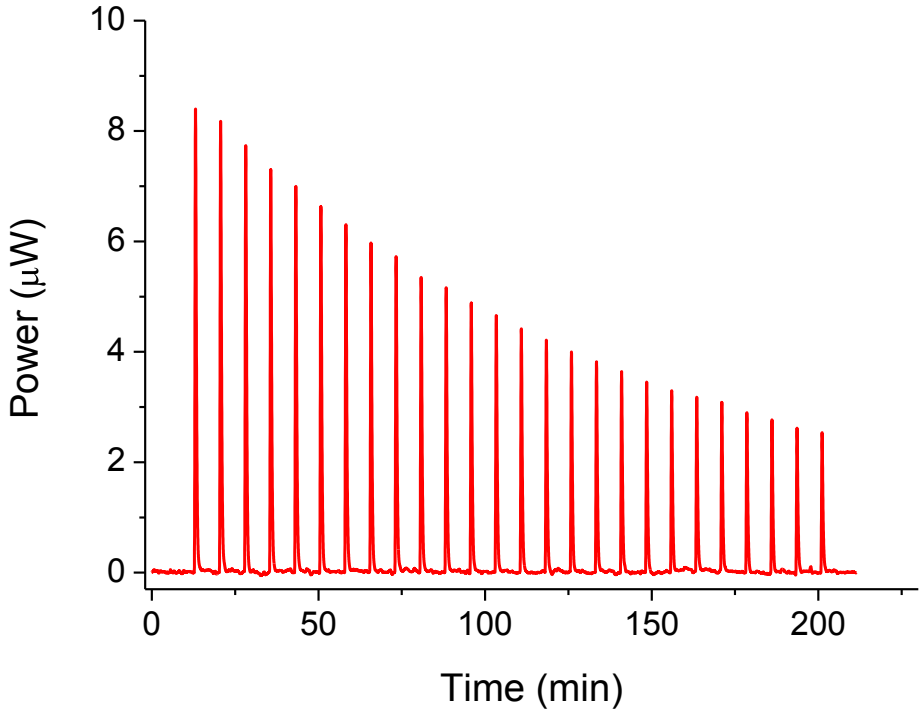

Figure S9 Typical ITC titration of **BSC2** into **TAC4** in buffered aqueous solution (pH 6.8; 25 °C).

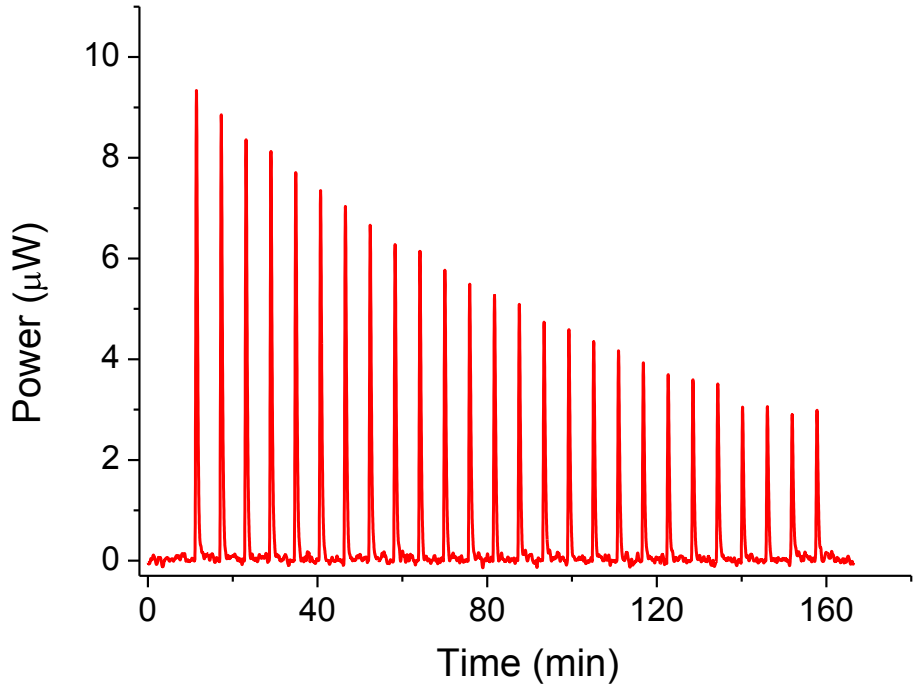

Figure S10 Typical ITC titration of **BSC3** into **TAC4** in buffered aqueous solution (pH 6.8; 25 °C).

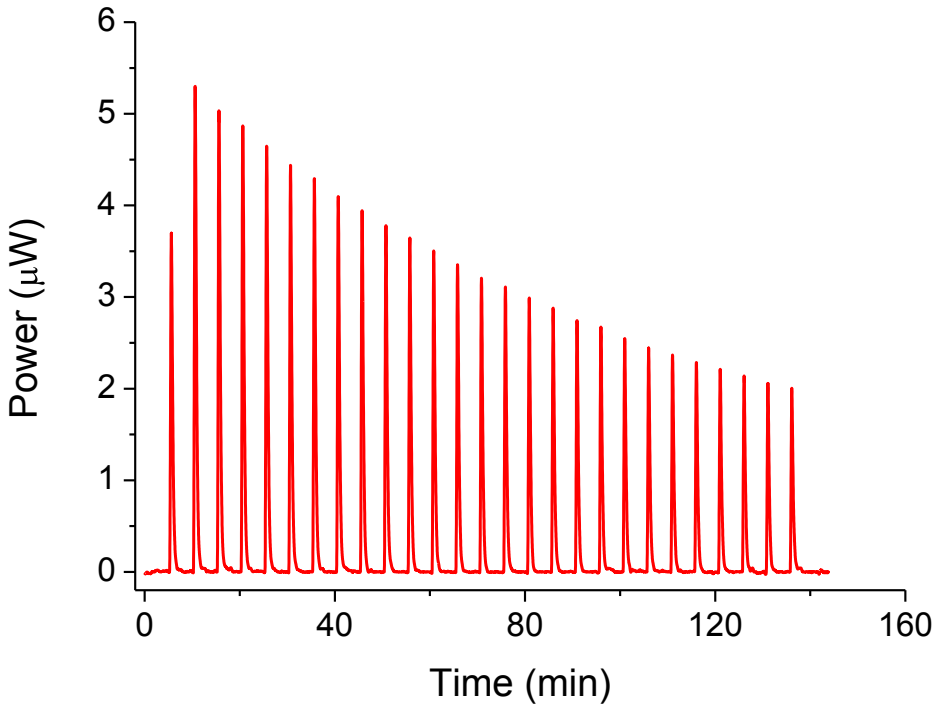

Figure S11 Typical ITC titration of **BSC5** into **TAC4** in buffered aqueous solution (pH 6.8; 25 °C).

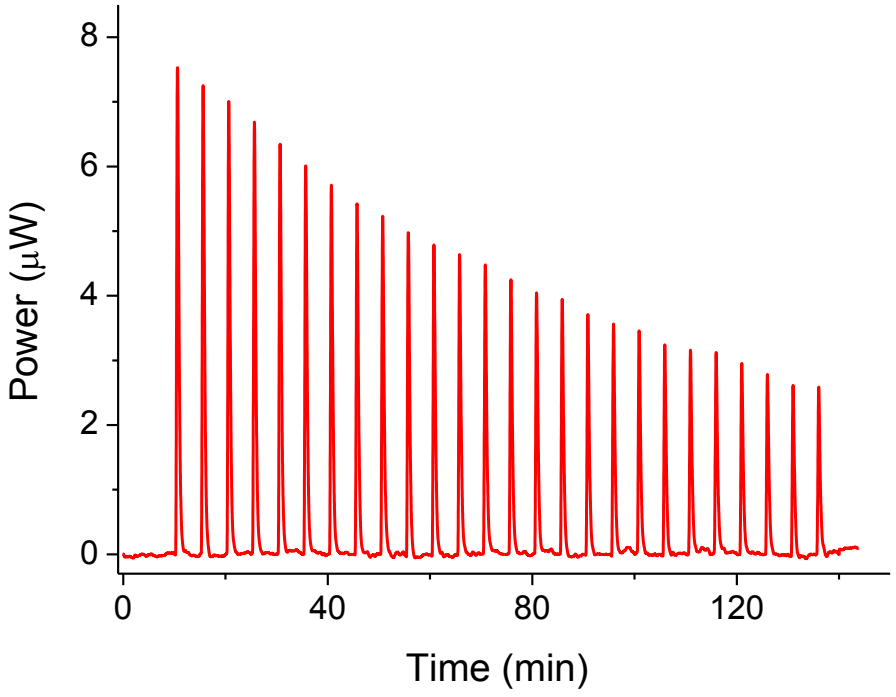

Figure S12 Typical ITC titration of **BSC6** into **TAC4** in buffered aqueous solution (pH 6.8; 25 °C).