Role of free space and conformational control on photoproduct selectivity of optically pure  $\alpha$ -alkyldeoxybenzoins within a water-soluble organic capsule

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**Figure S1**: HPLC traces of racemic (red) and chiral (blue) of  $\alpha$ -alkyl deoxybenzoin. (i)  $\alpha$ -methyl deoxybenzoin (**1a**), (ii)  $\alpha$ -propyl deoxybenzoin (**1b**), (iii)  $\alpha$ -hexyl deoxybenzoin (**1c**) and (i)  $\alpha$ -octyl deoxybenzoin (**1d**).

## <sup>1</sup>H NMR titration spectra of host-guest complexes:



**Figure S2**: <sup>1</sup>H NMR titration spectra (500 MHz) of  $1a@OA_2$  capsular assembly. (i) OA (1 mM in 10 mM borate buffer, (ii) OA: 1a (1:0.25), (iii) OA: 1a (1:0.5), (iv) OA: 1a (1:0.75) and (v) 1a (1mM in CDCl<sub>3</sub>). Solvent peak is marked as • and residual water peak is marked as•.



**Figure S3**: <sup>1</sup>H NMR titration spectra (500 MHz) of  $1b@OA_2$  capsular assembly. (i) OA (1 mM in 10 mM borate buffer, (ii) OA: 1b (1:0.25), (iii) OA: 1b (1:0.5), (iv) OA: 1b (1:0.75) and (v) 1b (1mM in CDCl<sub>3</sub>). Solvent peak is marked as • and residual water peak is marked as•.



**Figure S4**: <sup>1</sup>H NMR titration spectra (500 MHz) of  $1c@OA_2$  capsular assembly. (i) OA (1 mM in 10 mM borate buffer, (ii) OA: 1c (1:0.25), (iii) OA: 1c (1:0.5), (iv) OA: 1c (1:0.75) and (v) 1c (1mM in CDCl<sub>3</sub>). Solvent peak is marked as • and residual water peak is marked as•.



**Figure S5**: <sup>1</sup>H NMR titration spectra (500 MHz) of  $1d@OA_2$  capsular assembly. (i) OA (1 mM in 10 mM borate buffer, (ii) OA: 1d (1:0.25), (iii) OA: 1d (1:0.5), (iv) OA: 1d (1:0.75) and (v) 1d (1mM in CDCl<sub>3</sub>). Solvent peak is marked as • and residual water peak is marked as•.

Complex	Diffusion Constant $(10^{-10} \text{m}^2 \text{s}^{-1})$
OA	1.88
1a@OA <sub>2</sub>	1.23
1 <b>b</b> @OA <sub>2</sub>	1.25
1c@OA <sub>2</sub>	1.19
1d@OA <sub>2</sub>	1.17

Table S1. Diffusion coefficients of complexes of octa acid and guests 1a- d calculated by DOSY NMR analysis.



Figure S6. 2D COSY spectrum of  $1a@OA_2$  (5mM of OA, 50mM sodium tetraborate in  $D_2O$ ). Aliphatic signals of the guest are labeled with numbers and host signals are labeled from **a-j** as shown above. Aromatic signals of the guest marked with \*.



Figure S7. 2D COSY spectrum of  $1b@OA_2$  (5mM of OA, 50mM sodium tetraborate in D<sub>2</sub>O). Aliphatic signals of the guest are labeled with numbers and host signals are labeled from **a-j** as shown above. Aromatic signals of the guest marked with \*.



Figure S8. (Top) Partial 2D NOESY spectrum of  $1b@OA_2$  (5mM of OA, 50mM sodium tetraborate in D<sub>2</sub>O). Aliphatic signals of the guest are labeled with numbers and host signals are labeled from **a-h** as shown above. Aromatic signals of the guest marked with \*. (Bottom) NOESY interactions of the host- guest complex.



Figure S9. 2D COSY spectrum of  $1c@OA_2$  (5mM of OA, 50mM sodium tetraborate in D<sub>2</sub>O). Aliphatic signals of the guest are labeled with numbers and host signals are labeled from **a-j** as shown above. Aromatic signals of the guest marked with \*.



Figure S10. (Top) Partial 2D NOESY spectrum of  $1c@OA_2$  (5mM of OA, 50mM sodium tetraborate in  $D_2O$ ). Aliphatic signals of the guest are labeled with numbers and host signals are labeled from **a-h** as shown above. Aromatic signals of the guest marked with \*. (Bottom) NOESY interactions of the host- guest complex.



Figure S11. 2D COSY spectrum of  $1d@OA_2$  (5mM of OA, 50mM sodium tetraborate in D<sub>2</sub>O). Aliphatic signals of the guest are labeled with numbers and host signals are labeled from **a**-**j** as shown above. Aromatic signals of the guest marked with \*.