Accessory Materials

Scheme S1 describes the template-directed assembly of four equivalents of alkenyl porphyrin **1** simultaneously coordinated to free base porphyrin **10**, which arranges the components in the desired square geometry and organizes them for metathesis conditions.



Scheme S1

Figure S1 illustrates the time-averaged ¹H NMR spectroscopic changes upon addition of four equivalents of **1** to a CDCl₃ solution of tetrapyridylporphyrin **10**. Upon cooling, even more significant complexation induced chemical shifts were observed for the templating porphyrin due to the close proximity of the alkenyl porphyrins anisotropy (spectra not shown). In particular, at 228 K, the α pyridyl and β -pyridyl protons are shifted upfield by 6.5 and 2.5 ppm, respectively, which is characteristic of the magnitude of complexation induced shifts with zinc(II) porphyrins. Also at these low temperatures, the β -pyrrolic protons of **10** split into two resonances reflecting the slowing of the inner peripheral proton exchange and the resultant two tautomeric forms of **10**.



Fig. S1. ¹H NMR spectra of (*a*) zinc(II) porphyrin monomer **1**, (*b*) solution containing zinc(II) porphyrin **1** and template **10** in a ratio of 4 : 1, and (*c*) free template porphyrin **10**. All spectra were acquired in CDCl₃ at 303 K. The significant magnitude of complexation induced chemical shift for the proton resonances of **10** are highlighted by the dashed lines.