Electronic Supplementary Information

Scavenger templates: a systems chemistry approach to the synthesis of porphyrin-based molecular wires

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General Procedures

Unless stated otherwise, all reagents were obtained from commercial sources and used as received without further purification. Chloroform and toluene were dried by passing over activated alumina. Diisopropylamine was dried by distillation over CaH_2. Linear porphyrin hexamer **P6$_{Si2}$** and hexakis-(4-[4-pyridy]phenyl)benzene **T6** were synthesized using published procedures.[1–3] The linear porphyrin dodecamer **P12$_{Si2}$** synthesized in this study has been prepared previously by another route; material from both routes gave identical NMR spectra, mass spectra and GPC traces.[4]

NMR spectra were recorded on a Bruker AVII400, Bruker AVIII400 (400 MHz) or Bruker DRX500 (500 MHz) spectrometer. The residual solvent peak was used as internal reference (chloroform, ^{1}H δ = 7.26 ppm, ^{13}C δ = 77 ppm).

Preparative recycling GPC was performed on a JAIGEL H-P pre-column, a JAIGEL 3H (20 mm × 600 mm) and a JAIGEL 4H column (20 mm × 600 mm) in series with toluene/pyridine 100/1 as eluent.

Partial deprotection of P6$_{Si2}$

To a solution of **P6$_{Si2}$** (10 mg, 0.9 μmol) in CD_2Cl_2 (0.4 mL) and pyridine-d_5 (20 μL) in an NMR tube was added TBAF (2 μL of 1.0 M solution in THF, 2 μmol). The contents of the tube were mixed thoroughly and the reaction was monitored by ^{1}H NMR. The conversion was estimated by the ratio of the integrals for the β-protons adjacent to the outer alkynes (~9.8 ppm, Ha/Hb and ~9.0 ppm Hc/Hd) and the free alkyne CH (~4.4 ppm, 1H @ 50% conversion). A typical NMR spectrum is shown in Figure S1. When optimal conversion was observed, acetic acid (20 μL) was added to quench the reaction. The reaction mixture was passed through a small silica plug (100:1 CH_2Cl_2:pyridine) and concentrated to yield a mixture of **P6$_{Si2}$**, **P6$_{Si}$** and **P6** as a black solid.

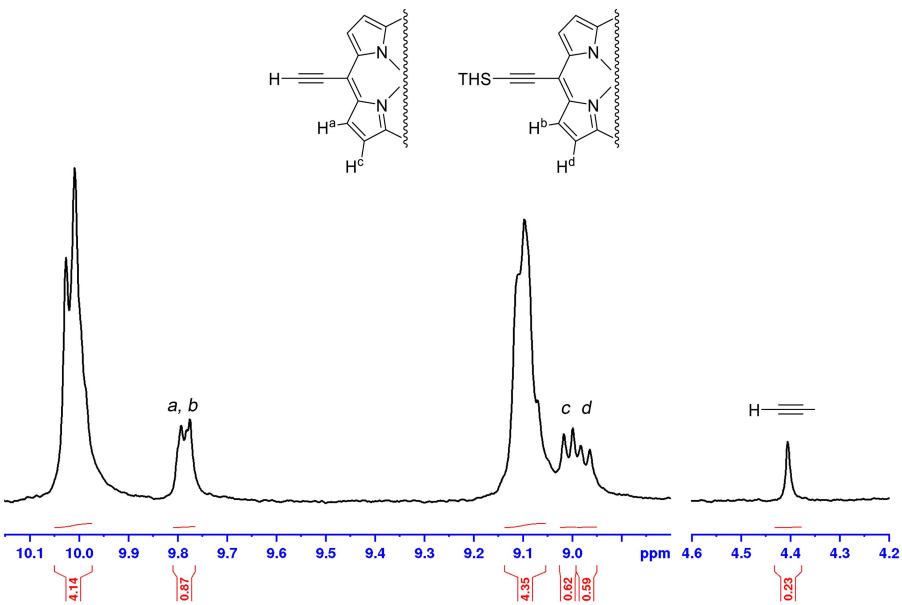


Figure S1. Partial ^{1}H NMR spectrum of a statistical mixture of $\mathbf{P6_{Si2}}$, $\mathbf{P6_{Si}}$ and **P6** (250 MHz, $CDCl_3$ at 25 °C).

General procedure for scavenger template reactions

To a solution of a mixture of $\mathbf{P6_{Si2}}$, $\mathbf{P6_{Si}}$ and **P6** in $CHCl_3$ was added **T6** (2 eq.). The mixture was sonicated for 15 min and stirred at 20 °C for 1 h before addition of $Pd(PPh_3)_2Cl_2$ (50 mol%, added as a solution in $CHCl_3$), CuI (50 mol%, added as a solution in 1:1 $CHCl_3$: *i*-Pr_2NH) and 1,4-benzoquinone (2 eq., added as a solution in $CHCl_3$). The reaction mixture was stirred for 4 h at 20 °C and then an aliquot was taken and analyzed by GPC (*vide infra*). If the reaction was not complete, an additional portion of catalyst was added and stirring was continued.

Determination of binding constants

UV/vis/NIR spectra were recorded on a Perkin-Elmer Lambda 20 photospectrometer at 25 °C. To assess the stability of the complexes between the **T6** template and protected and deprotected hexamer, respectively, a solution of a 1:1 complex in $CHCl_3$ was titrated with pyridine (Figure S2). Denaturation constants K_{dn} were obtained by fitting the data to a binding model:[5]

$$\frac{A - A_0}{A_\infty - A_0} = \frac{-K_{dn}\,[\mathrm{Py}]^6 + \sqrt{{K_{dn}}^2\,[\mathrm{Py}]^{12} + 4\,K_{dn}\,[\mathrm{Py}]^6\,[\mathrm{P}]_0}}{2\,[\mathrm{P}]_0}$$

where A is the absorption at a given point in the titration, A_0 is the initial absorption at [Py] = 0, A_∞ is the asymptotic final absorption at [Py] = ∞, and $[P]_0$ is the total concentration of 1:1 porphyrin oligomer template complex at the start of the titration. The final values are obtained by averaging of at least two runs.

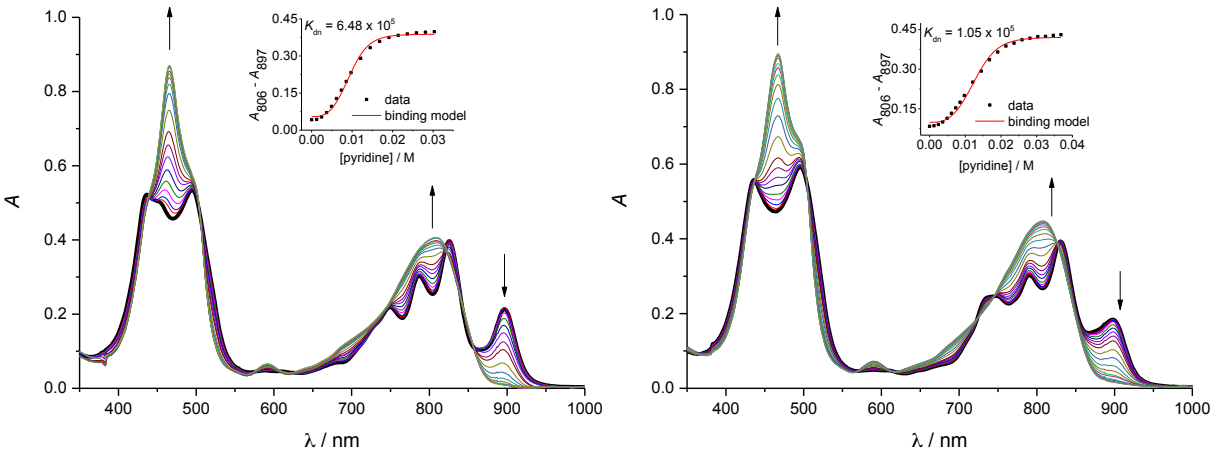


Figure S2. Representative UV/vis/NIR titration of **P6$_{Si2}$·T6** (left) and **P6·T6** (right) in $CHCl_3$ with pyridine. Inset: fit of the data to the binding model. In each titration, the initial concentration of 1:1 porphyrin oligomer template complex was $[P]_0$ = 1.3 μM.

The formation constants K_f for the complexes could be determined using:

$$K_f = \frac{{K_{Py}}^6}{K_{dn}}$$

where K_{Py} is the binding constant of a single molecule of pyridine to a molecule of hexamer. K_{Py} can be approximated by the binding constant of pyridine to porphyrin monomer **P1$_{Si2}$**, which was determined by titration to be 8.92×10^3 M^{-1} (Figure S3).

Table 1. Summary of equilibrium constants (in $CHCl_3$ at 25 °C)

Complex	K_{dn}	K_f
P6$_{Si2}$·T6	$4.19 \pm 2.16 \times 10^5$ M^{-5}	$1.20 \pm 0.74 \times 10^{18}$ M^{-1}
P6·T6	$1.63 \pm 0.58 \times 10^5$ M^{-5}	$3.09 \pm 1.5 \times 10^{18}$ M^{-1}
P1$_{Si2}$·Py		$8.92 \pm 0.49 \times 10^3$ M^{-1}

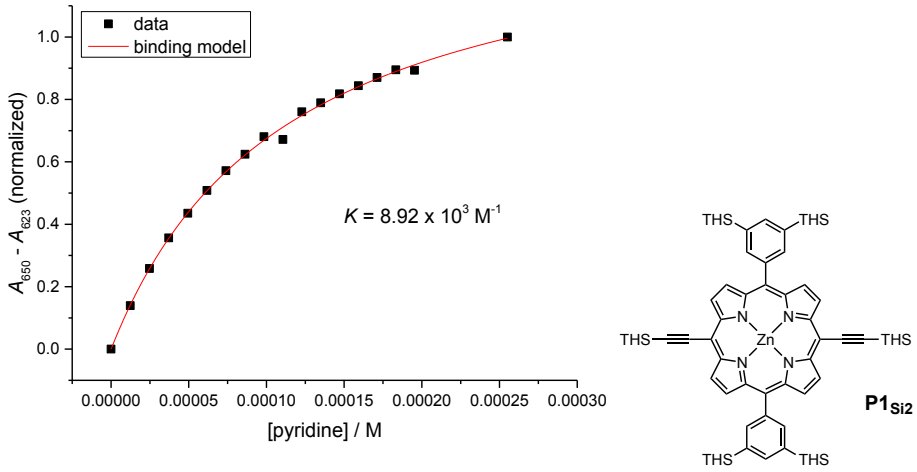


Figure S3. Determination of the binding constant of porphyrin monomer **P1$_{Si2}$** with pyridine in $CHCl_3$ at 25 °C.

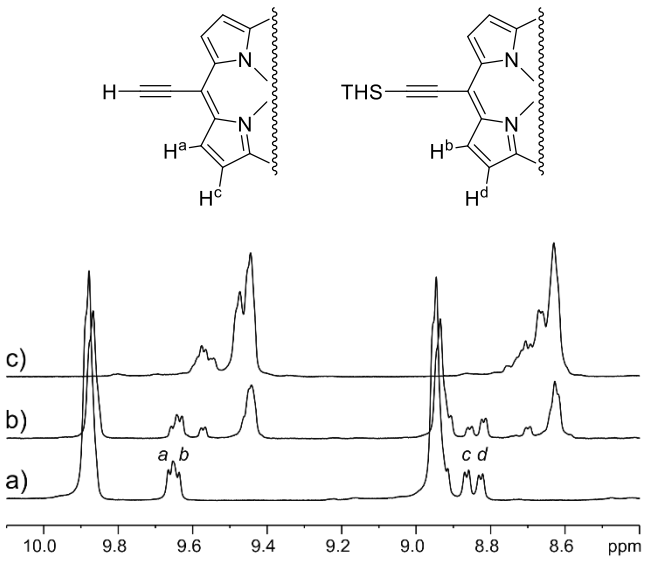
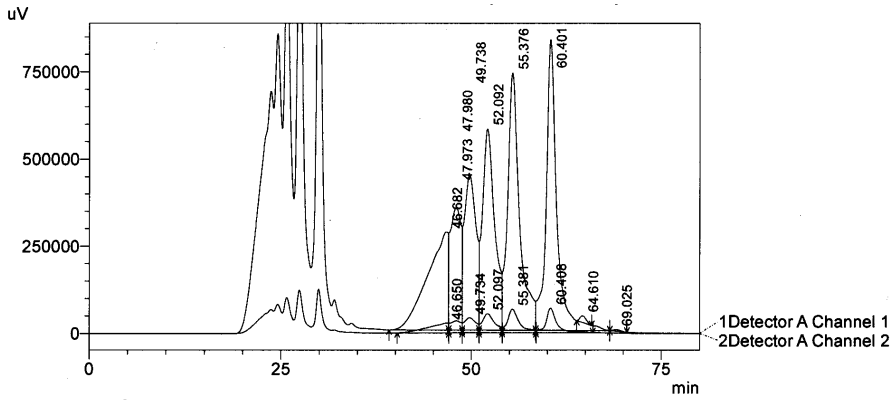


Figure S4. a) Partial ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of a 1:1 mixture of $\mathbf{P6_{Si2}}$ and **P6**. b) The same mixture after addition of 1 equivalent of **T6**. c) The same mixture after addition of a second equivalent of **T6**.

GPC analysis

Analytical gel permeation chromatography (GPC) was performed on a JAIGEL H-P pre-column, a JAIGEL 3H-A (8 mm × 500 mm) and a JAIGEL 4H-A column (8 mm × 500 mm) in series with toluene/pyridine 100/1 as eluent. Samples were passed through a short size-exclusion column (Bio-Beads S-X1, $CHCl_3$) before analysis to remove any traces of low molecular weight compounds and insoluble material. The sample was cycled for two runs to ensure maximum separation of the peaks. Chromatograms were analyzed by absorption at 591 nm. Peak areas were then corrected for differences in molar absorption coefficients between species at this wavelength (**P6$_{Si2}$**: 5.6×10^4 M^{-1} cm^{-1}, ***c*-P6·T6**: 8.3×10^4 M^{-1} cm^{-1}) to obtain the final GPC yield. The molar absorption coefficient for longer oligomers was estimated by extrapolation of the molar absorption coefficients of a series of linear oligomers according to the equation $\varepsilon_{591} = 6562 + 8118N$, where N is the number of porphyrin units. The template totally dissociates from all the linear porphyrin oligomers under the conditions of the GPC analysis (1% pyridine in toluene) to form pyridine complexes, whereas it does not dissociate from the cyclic hexamer.

Chromatograms



1 Detector A Channel 1 / 464nm
2 Detector A Channel 2 / 591nm

PeakTable

Detector A Channel 1 464nm

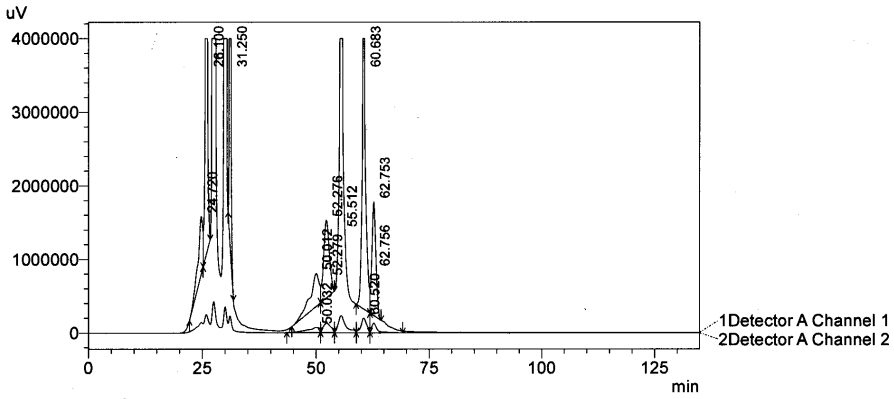
Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.682	53326503	281420	14.611	8.653
2	47.973	34095115	352255	9.342	10.831
3	49.738	47504195	446623	13.015	13.733
4	52.092	65056515	577127	17.825	17.745
5	55.376	80990912	737797	22.190	22.686
6	60.401	82623550	833648	22.638	25.633
7	64.610	1107223	18987	0.303	0.584
8	69.025	279084	4389	0.076	0.135
Total		364983098	3252247	100.000	100.000

PeakTable

Detector A Channel 2 591nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.650	5166567	27313	15.534	9.256
2	47.980	3273312	34043	9.841	11.537
3	49.734	4553425	42720	13.690	14.477
4	52.097	6134404	54229	18.443	18.378
5	55.381	7393777	66984	22.230	22.700
6	60.408	6739205	69792	20.262	23.652
Total		33260689	295080	100.000	100.000

Figure S5. GPC chromatogram of the coupling of a mixture of **P6$_{Si2}$**, **P6$_{Si}$** and **P6** (2 mM) in the absence of template.



PeakTable

Detector A Channel 1 464nm

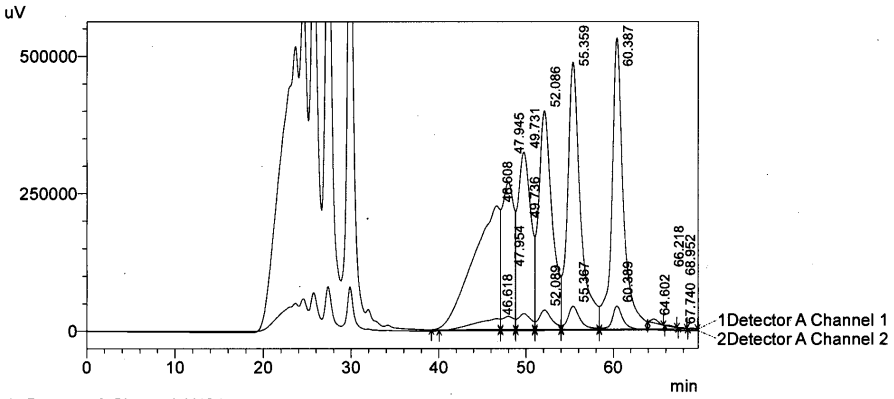
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.720	55090385	793168	7.334	5.923
2	26.100	140175114	2872773	18.661	21.453
3	31.250	94226878	2992041	12.544	22.343
4	50.012	63180657	446352	8.411	3.333
5	52.276	93287165	1056545	12.419	7.890
6	60.683	209363733	3681963	27.872	27.495
7	62.753	95833425	1548323	12.758	11.562
Total		751157358	13391166	100.000	100.000

PeakTable

Detector A Channel 2 591nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.032	13415345	70550	15.729	9.281
2	52.279	15832162	130170	18.563	17.123
3	55.512	27246331	232481	31.946	30.582
4	60.520	17762118	197877	20.826	26.030
5	62.756	11033076	129112	12.936	16.984
Total		85289030	760190	100.000	100.000

Figure S6. GPC chromatogram of the coupling of a mixture of **P6$_{Si2}$**, **P6$_{Si}$** and **P6** (2 mM) in the presence of template.



PeakTable

Detector A Channel 1 464nm

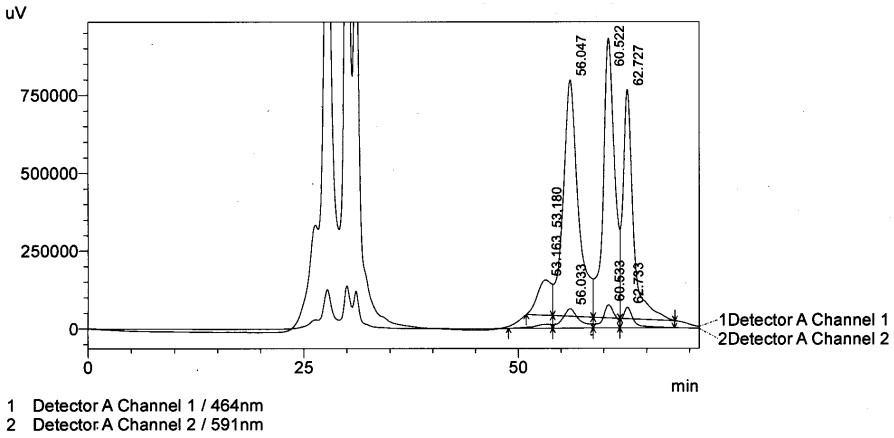
Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.608	47794590	224449	19.074	10.031
2	47.945	25153843	267747	10.038	11.966
3	49.731	33637853	322649	13.424	14.420
4	52.086	42798056	397063	17.080	17.746
5	55.359	50290594	486078	20.070	21.724
6	60.387	50385881	529797	20.108	23.678
7	64.602	399302	7215	0.159	0.322
8	66.218	68783	1258	0.027	0.056
9	67.740	19112	595	0.008	0.027
10	68.952	26512	669	0.011	0.030
Total		250574525	2237521	100.000	100.000

PeakTable

Detector A Channel 2 591nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.618	4532882	21531	20.265	10.657
2	47.954	2422052	25582	10.828	12.663
3	49.736	3157503	30515	14.116	15.104
4	52.089	3950212	36895	17.660	18.262
5	55.367	4453390	43694	19.909	21.628
6	60.389	3852174	43813	17.222	21.686
Total		22368212	202029	100.000	100.000

Figure S7. GPC chromatogram of the coupling of a mixture of **P6$_{Si2}$**, **P6$_{Si}$** and **P6** (0.2 mM) in the absence of template.



PeakTable

Detector A Channel 1 464nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.163	12865593	113207	5.094	4.515
2	56.047	94297065	759019	37.333	30.273
3	60.522	83287641	898815	32.974	35.849
4	62.727	62134355	736197	24.599	29.363
Total		252584654	2507238	100.000	100.000

PeakTable

Detector A Channel 2 591nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.180	1811596	12536	7.872	5.826
2	56.033	8359865	62279	36.324	28.945
3	60.533	7120019	74165	30.937	34.469
4	62.733	5723050	66185	24.867	30.760
Total		23014530	215164	100.000	100.000

Figure S8. GPC chromatogram of the coupling of a mixture of $\mathbf{P6_{Si2}}$, $\mathbf{P6_{Si}}$ and **P6** (0.2 mM) in the presence of template.

References

1 F. C. Grozema, C. Houarner-Rassin, P. Prins, L. D. A. Siebbeles and H. L. Anderson, *J. Am. Chem. Soc.*, 2007, **129**, 13370–13371.

2 C. E. Tait, P. Neuhaus, M. D. Peeks, H. L. Anderson and C. R. Timmel, *J. Am. Chem. Soc.*, 2015, **137**, 8284–8293.

3 M. Hoffmann, J. Kärnbratt, M. H. Chang, L. M. Herz, B. Albinsson and H. L. Anderson, *Angew. Chem. Int. Ed.*, 2008, **47**, 4993–4996.

4 N. Kamonsutthipaijit and H. L. Anderson, *Chem. Sci.,* 2017, **8**, 2729–2740.

5 H. J. Hogben, J. K. Sprafke, M. Hoffmann, M. Pawlicki and H. L. Anderson, *J. Am. Chem. Soc.*, 2011, **133**, 20962–20969.