# Novel porphyrin–viologen rotaxanes

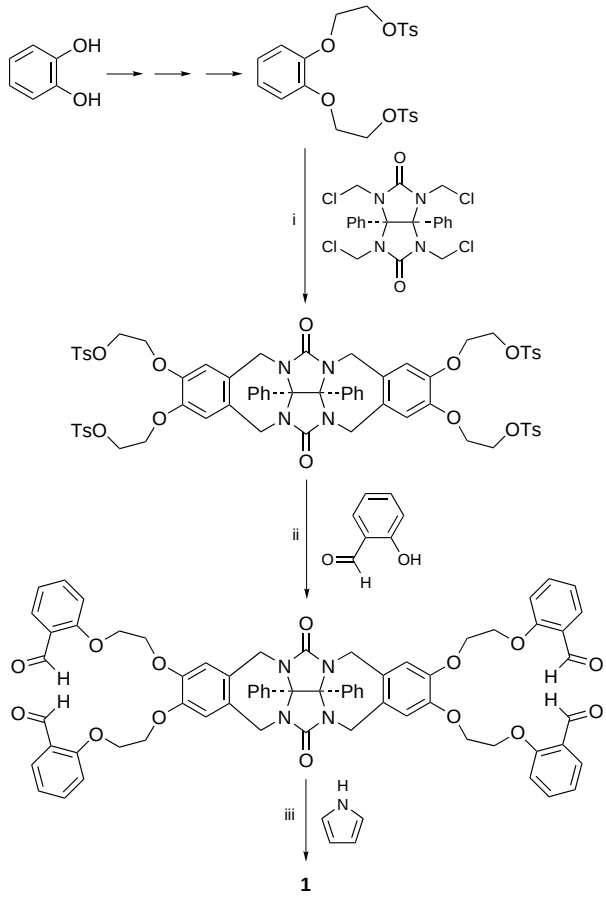
**Alan E. Rowan,*† Patrick P. M. Aarts and Koen W. M. Koutstaal**

*Department of Organic Chemistry, NSR Center, University of Nijmegen, Toernooiveld 6525 ED Nijmegen, The Netherlands*

**A new porphyrin-containing host has an exceptionally high affinity for viologen guests, with binding constants as high as $K_{ass}$ = 7 × $10^6$ $M^{-1}$ in organic solvents, allowing the construction of porphyrin–viologen rotaxanes.**

The design and construction of rotaxanes and catenanes using a 'self-assembling' approach is now regularly reported in literature.[1] In general, however, few systems have been assembled which possess addressable cyclic components, with an eye toward the construction of functional devices.[2] An interesting functional species for incorporation in a rotaxane is a porphyrin. Somewhat surprisingly the inclusion of a porphyrin in such a system has only been preliminarily explored and mainly only as a photoactive endgroup.[3,4] Reported here is a new porphyrin-clip macrocycle **1** which binds methyl viologen (*N*,*N*′-dimethyl-4,4′-bipyridinium) and a variety of *N*-substituted derivatives with the highest binding constants reported to date and is an ideal basic building block for rotaxane synthesis.

Compound **1** was synthesized as depicted in Scheme 1.[5] Catechol was converted in three steps into 1,2-bis(2-*p*-tolylsulfonylethoxy)benzene (in 57% yield) which was then coupled with tetrachloromethyldiphenylglycoluril,[6] to generate the tetratosylate molecular clip. This U-shaped molecule was converted to the tetraaldehyde derivative and subsequently cyclized with pyrrole to give the porphyrin clip **1** (6%). NOESY and COSY 2D spectra revealed that the porphyrin moiety is situated rigidly and symmetrically, directly above the cavity.[5]




**Scheme 1** *Reagents and conditions*: i, $SnCl_4$, $ClCH_2CH_2Cl$, 72%; ii, MeCN, $K_2CO_3$, 59%; iii, $BF_3{\cdot}Et_2O$, $CH_2Cl_2$, *p*-chloranil, 6%

The affinity of this new host for complexation with *N*,*N*′-derivatized 4,4-bipyridinium guests was investigated by UV–VIS spectroscopy. Host–guest titrations in MeCN–$CHCl_3$ (1 : 1, v/v) revealed the formation of exceptionally strong 1 : 1 charge-transfer complexes with all the viologen guests **2**. The strength and geometry of binding is strongly dependent upon the N-functionality of the guest. In the case of the methyl derivative **2a** the association constant, $K_{ass}$ = (6.0 ± 0.9) × $10^5$ $M^{-1}$, is several orders of magnitude higher than previously reported association constants for similar complexes.[3,7] Complexation of porphyrin clip **1** with *N*,*N*′-bis(2-hydroxyethyl)-4,4′-bipyridinium **2b**,[8] resulted in one of the strongest host–guest complexes in organic solvents reported to date [$K_{ass}$ = (7.4 ± 0.8) × $10^6$ $M^{-1}$]. The complex between **1** and the propylamine derivative **2c** displayed an association constant, $K_{ass}$ = (9.0 ± 1) × $10^5$ $M^{-1}$, which is more similar to that of the complex between **1** and **2a**.

$^1$H NMR studies on an equimolar solution of **1** and **2b** in $CD_3CN$–$CDCl_3$ (1 : 1, v/v) revealed large complexation shifts (see structure **1**). In the case of the porphyrin host, the central NH resonance was shifted significantly upfield by 1.16 ppm (from $\delta$ −2.79 to −3.95) implying that this proton is situated over the centre of an aromatic ring of the guest. Both sets of $CH_2$ protons, which link the porphyrin with the aromatic side-walls of the cavity, (ArOC$H_aH_b$ and PorOC$H_aH_b$) were shifted downfield by identical amounts (+0.4 and +0.7 ppm), suggesting that these protons are at the side of an aromatic ring which is situated symmetrically between the two sets of protons. In the case of the resonances for the bipyridinium guest **2b** even larger shifts were observed, with the value of the shift diminishing as one goes from the centre of the bipyridinium ring to the end of the hydroxyethyl functions (see structure **2b** for $\Delta\delta$s). The exceptionally large upfield shifts for the β and α protons (−3.51 and −1.99 ppm) confirm that the guest sits in the cavity parallel to the porphyrin ring.

The $^1$H NMR spectra (500 MHz) of an equimolar solution of **2a** and porphyrin clip **1** in contrast showed three broad resonances at $\delta$ 6.20, 4.13 and 3.35 for the α, β and methyl protons of the guest, respectively. The complexation shifts are even larger than those for the complex with **2b**: $\Delta\delta_\alpha$ = −2.66, $\Delta\delta_\beta$ = −4.24 and $\Delta\delta_{methyl}$ = −1.05 ppm. In contrast to the complex of **1** with **2b**, upon the addition of **2a** to the host only a very small upfield shift of the central NH proton (−0.17 ppm) was observed. The host protons ArOC$H_2$ of the complex with **2a** were now shifted upfield (−0.16 and −0.69 ppm) with the protons PorOC$H_2$ being unaffected by the complexation of the guest. The geometry of complexation of **2a** is such that the bipyridinium rings sit between the two aromatic walls of **1**, perpendicular with respect to the porphyrin. This binding geometry is different from that of **2b** but the same as that observed for complexation of this guest in a molecular basket derived from diphenylglycoluril.[7]

The difference in binding geometry of the two guests is also reflected in the UV–VIS spectra of the complexes. Upon

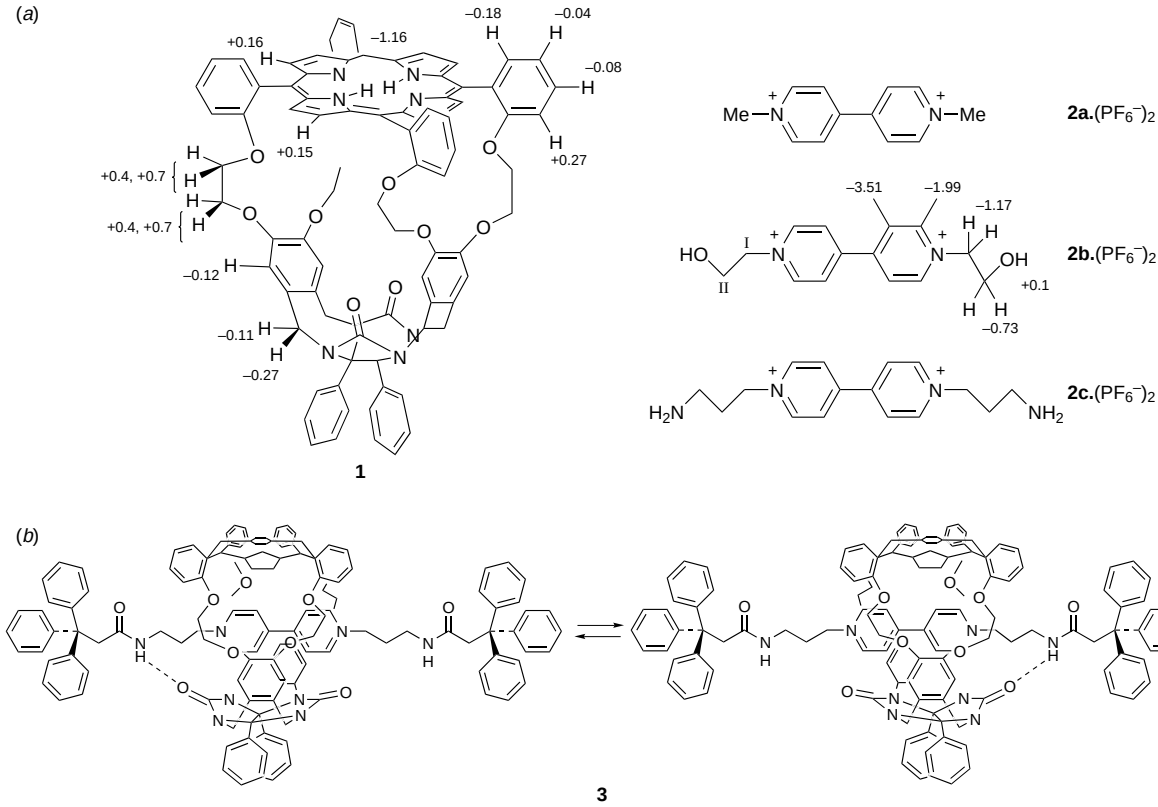



**Fig. 1** (*a*) Porphyrin clip **1** and viologen guests **2**. The observed $^1$H NMR complexation shifts for the 1 : 1 complex of **1** and **2b** ($CDCl_3$–$CD_3CN$) are indicated. (*b*) Rotaxane **3** assembled by the condensation reaction of 3,3,3-triphenylpropionyl chloride and the pseudo-rotaxane complex of **1** and **2c**.

addition of excess guest, the porphyrin Soret band in the UV–VIS spectrum was shifted to the red by 5 nm in the case of **2b** and only by 2 nm in the case of **2a**. The Q-bands remained unaffected. The addition of 10 equiv. of guest **2b** or 100 equiv. of the methyl derivative **2a** to the porphyrin clip caused an almost complete quenching of the porphyrin fluorescence {$I/I_0$ at 645 nm (excitation 418 nm) = 0.02; [Host] = $2.9 \times 10^{-6}$ mol $l^{-1}$, $CH_3CN$–$CHCl_3$ (1 : 1, v/v)}, confirming the close proximity of the guest to the porphyrin.

Toward the construction of [*n*]rotaxanes assemblies it was decided to use the 1 : 1 complex of bis(aminopropyl)bipyridinium **2c** and porphyrin clip **1** as the basic building block. NMR studies showed that guest **2c** forms a pseudo-rotaxane complex with the $NH_2$ functions sticking outside the cavity. Simple condensation reactions of this 1 : 1 complex with acid chloride derivatives should enable a variety of amide rotaxanes to be formed.[9] Using the bulky stopper 3,3,3-triphenylpropionyl chloride a condensation reaction was carried out with the 1 : 1 complex of **1** and **2c**, to give molecule **3·(PF$_6$)$_2$** in 30% yield after column chromatography and counter-ion exchange. The resulting rotaxane was, surprisingly, very soluble in $CHCl_3$. $^1$H NMR studies confirmed that the viologen is bound in the cavity, in an asymmetric geometry, rapidly exchanging between two equivalent sites in which the amide function of the thread hydrogen bonds to the carbonyl of the porphyrin clip (see structure **3**).[5]

As shown here the strong complexation between porphyrin clip **1** and bipyridinium guests **2** generates stable pseudo-rotaxane complexes. The cyclic porphyrin component allows the system to be potentially addressed by a variety of means: chemically,[3] electrochemically or photochemically.[4] Current studies are directed towards the construction of larger [*n*]rotaxane systems and arrays of porphyrin–viologens and the study of their properties.

We thank Professor R. J. M. Nolte and Professor J. F. Stoddart for discussions and their interest in this work.

## Footnotes and References

† E-mail: rowan@sci.kun.nl

1 D. Philip and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154; F. Vögtle, M. Handel, S. Meier, S. Ottens-Hildebrandt, F. Ott and T. Schmidt, *Liebigs. Ann.*, 1995, 739.
2 P. R. Aston, R. Ballardini, V. Balzani, S. E. Boyd, A. Credi, M. T. Gandolfi, M. Gomez-Lopez, S. Iqbal, D. Philip, J. A. Preece, L. Prodi, H. G. Ricketts, J. F. Stoddart, M. S. Tolley, M. Venturi, A. J. P. White and D. J. Williams, *Chem. Eur. J.*, 1997, **3**, 152.
3 M. J. Gunter and M. R. Johnston, *J. Chem. Soc., Perkin Trans. 1*, 1994, 995; M. J. Gunter, D. C. R. Hockless, M. R. Johnston, B. W. Skelton and A. H. White, *ibid.*, 1994, 1008; M. J. Gunter, D. C. R. Hockless, M. R. Johnston, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.*, 1994, **116**, 4810.
4 Porphyrins in rotaxanes; D. B. Amabillino and J.-P. Sauvage, *Chem. Commun.*, 1996, 2441; F. Vögtle, F. Ahuiis, S. Baumann and J. L. Sessler, *Liebigs, Ann.*, 1996, 921; M. C. Feiters, M. C. T. Fyfe, M.-V. Martinez-Diaz, S. Menzer, R. J. M. Nolte, J. F. Fraser, P. J. M. van Kan and D. J. Williams, *J. Am. Chem. Soc.*, 1997, **119**, 8119; R. B. Hannak, G. Farber, R. Konrat and B. Krautler, *J. Am. Chem. Soc.*, 1997, **119**, 2313.
5 The full synthesis and characterization of all compounds will be reported in full in a forthcoming paper.
6 J. N. H. Reek, J. A. A. W. Elemans and R. J. M. Nolte, *J. Org. Chem.*, 1997, **62**, 2234.
7 A. P. H. J. Schenning, B. de Bruin, A. E. Rowan, H. Kooijman, A. L. Spek and R. J. M. Nolte, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2132.
8 P. R. Aston, D. Philip, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 1680.
9 A. G. Johnston, D. A. Leigh, A. Murphy, J. P. Smart and M. D. Deegan, *J. Am. Chem. Soc.*, 1966, **118**, 10 662; F. Vögtle, T. Duennwald, M. Haendel, R. Jaeger, S. Meier and G. Harder, *Chem. Eur. J.*, 1996, **2**, 640.

*Received in Cambridge, UK, 20th November 1997; 7/08373D*