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Porphyrinic supramolecular daisy chains incorporating pillar[5]arene-viologen host-guest interactions

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A porphyrin functionalised with pillar[5]arene and a viologen at its 5- and 15-meso positions assembles in a head-to-tail manner, producing linear supramolecular daisy chains in dichloromethane. At high concentrations, it forms an organogel which has been investigated by electron microscopy and rheological measurements, paving the way for the preparation of other functional supramolecular assemblies which harness viologenCpillararene host-guest interactions.

The exploitation of supramolecular chemistry to assemble functional porphyrin arrays¹ has attracted the interest of numerous researchers over the past few decades. During the early days, hydrogen bonding² and metal coordination³ motifs played a major role in creating simple, as well as sophisticated porphyrin-containing assemblies. Recently, self-assembly initiated by host-guest interactions has emerged as a potential strategy⁴ to build a wide range of porphyrin architectures, ranging from dimers to oligomers. Owing to their well-established chemistry, cyclodextrins⁵ have been utilised widely as hosts in assembling supramolecular porphyrin architectures. Additionally, synthetic hosts such as calixarenes⁶ and cucurbiturils⁷ have also been employed to assemble new supramolecular porphyrin architectures.

A relatively new family of cyclic hosts, namely the pillar[*n*]arenes,⁸ which are composed of hydroquinone units linked between their 2- and 5-positions by methylene bridges, have been reported^{8a} to display a high affinity towards the encapsulation of π -electron-poor guests. The increasing interest in pillar[*n*]arene-containing functional materials⁹ has prompted us to harness the unique interactions of pillar[5]arene with

viologens to assemble (Fig. 1) a porphyrin-containing supramolecular daisy chain.¹⁰ One advantage of using

Fig. 1 Structural formula and proposed self-assembly of porphyrin 1^{2+} to form linear supramolecular daisy chains.

pillar[5]arene as a host is that it enables the synthesis of supramolecular porphyrin assemblies containing viologens as electron acceptors which will provide insight into the photo-induced electron transfer processes¹¹ between a porphyrin (donor) to viologen (acceptor) within the noncovalently bonded assemblies.

Scheme 1 Synthesis of the porphyrins **1·2PF₆** and **5·2PF₆** using CuAAC (See ESI†).

Polymeric supramolecular daisy chain are composed of monomers with both guest and host components.¹⁰ Herein, we report the synthesis of a porphyrin **1**²⁺ functionalised with both a pillar[5]arene (host) and a viologen (guest) at its 5- and 15-meso positions. The formation of either cyclic or linear daisy chains (Fig. 1), held together by donor-acceptor and charge transfer interactions, is anticipated.

The synthesis of the porphyrin **1·2PF₆** is outlined in Scheme 1. Briefly, **1·2PF₆** was obtained in 45% yield via a copper-catalysed azide-alkyne cycloaddition¹² (CuAAC) between the 5,15-dialkyne derivative of the Zn-containing porphyrin **2** with two mono-azide components – namely, the azide-containing pillar[5]arene **3** and the viologen **4·2PF₆**.^{8c} Additionally, another porphyrin conjugate **5·2PF₆** was designed and synthesised in which the viologen component **6·2PF₆** was linked covalently to a 3,5-di-*tert*-butyl phenyl stopper in order to prevent host-guest complexation. Both **1·2PF₆** and **5·2PF₆** were characterised fully by ¹H and ¹³C NMR spectroscopies, as well as by high-resolution mass spectrometry (See the ESI†).

UV-Vis spectroscopy of **1·2PF₆** in CH₂Cl₂ indicates that ground-state interactions between porphyrin and viologen within **1**²⁺ are absent since the spectrum matches closely that of the dialkyne porphyrin **2**. Excitation of a solution of porphyrin **1·2PF₆** in CH₂Cl₂ (λ_{ex} = 555 nm), however, resulted in the quenching of the emission of the porphyrin in **1**²⁺ (See Fig. S1 in

the ESI†) through a photo-induced electron transfer mechanism¹¹ to the viologen acceptor.

It has been established^{8a} that viologens and pillar[5]arenes form stable 1:1 inclusion complexes in polar organic solvents with association constants (K_a) ranging from 10² to 10⁴ M⁻¹. This host-guest system has been harnessed by a number of groups¹³ in building supramolecular assemblies. In order to explore the probability of daisy chain formation as a result of these noncovalent bonding interactions, porphyrin **1**²⁺ was dissolved in CH₂Cl₂ and the resulting assembly was investigated by scanning tunneling microscopy (STM). The STM image (Fig. 2A) indicates the formation of unidirectional nanowires which are hundreds of nanometers in length. Enlarged STM images and STM measurements (Fig. 2B and C) reveal that the resulting assembly consists of a chain of bright protrusions with a periodicity of ~1.7 nm and a height of ~0.8 nm. These dimensions are in good agreement with a model proposed for the linear daisy chain (See Fig. S2 in the ESI†), in which the bright protrusions correspond to alternating porphyrin moieties and 1:1 inclusion complexes between viologen and P5A within the daisy chain.

The superstructures of the daisy chain polymers formed from **1·2PF₆** in CH₂Cl₂ were also investigated by transmission electron microscopy (TEM). The TEM image (Fig. 3A) of the supramolecular assembly indicates the presence of unidirectional fibres which are hundreds of nanometers in length and tens of nanometers in width. Larger bundles of the daisy chain polymers, which are also observed by TEM, are most likely formed as discrete fibres. They undergo further aggregation as a result of the π - π stacking of porphyrin macrocycles at high concentrations.

The dimensions of the supramolecular daisy chains in solution were also measured by dynamic light scattering (DLS). The DLS of three solutions (1, 5, 10 μ M) of **1·2PF₆** in CH₂Cl₂ (See Fig. S3 in the ESI†) indicate the formation of various polymeric species with hydrodynamic radii which are dependent on the sample concentration. At a 1 μ M concentration of **1·2PF₆** in CH₂Cl₂, three different species with hydrodynamic radii of 3 nm, and 1.2 and 4 μ m are observed by DLS. The 3 nm species is most likely the porphyrin monomer **1**²⁺ while the 1.2 and 4 μ m species are believed to arise from discrete fibres and large bundles of daisy chain polymer, respectively. Furthermore,

Fig. 2 Constant current STM images of porphyrin daisy chains of **1**²⁺ after drop-casting **1·2PF₆** onto an HOPG support. Image sizes are 81 × 22 nm² (A) and 7 × 4 nm² (B); Tunneling conditions: V_{sample} and I_{tunnel} for (A) and (B) are +2.6 V and 0.3 nA, and +2.3 V and 0.3 nA, respectively. The coloured line indicates the position where the line profile was taken.

Fig. 3 (A) TEM Image of daisy chains formed from 1·2PF₆, (B) image of the reversible formation of an organogel from 1·2PF₆ and (C) SEM of the gel formed from high concentrations of 1·2PF₆.

larger aggregates were observed for the 5 and 10 μM concentrations of 1·2PF₆ in line with the disappearance of the DLS signals that can be assigned to the monomeric porphyrin 1²⁺. The 10 μM sample contains even larger hydrodynamic radii peaks (~ 600 nm) corresponding to discrete fibres which, upon further aggregation, form larger bundles with dimensions (6 μm) higher than the detection limit of the DLS instrument.

The ability of 1·2PF₆ to form large aggregates at micromolar concentrations in CH₂Cl₂ prompted us to examine the self-assembly of 1·2PF₆ at millimolar concentrations in order to discern the nature of the resulting assembly. Increasing the concentration of 1·2PF₆ to 7 mM in CH₂Cl₂ results in the formation of an organogel. The organogel can be returned to the solution phase reversibly (Fig. 3B) through heating and cooling.

The morphology of the resulting gel (Fig. 3C) was investigated by scanning electron microscopy (SEM). The SEM image reveals a series of entangled fibres of porphyrin 1·2PF₆. We have proposed a mechanism (see the ESI†) for the formation of the organogel from 1²⁺ which involves (1) the formation of a daisy chain-type polymer through noncovalent interactions between P5A and the viologen moieties of adjacent units of 1²⁺, followed by (2) individual daisy chains assembling with one another to form discrete fibres at higher concentrations, and (3) the formation of larger bundles which comprise an organogel.

In an effort to isolate the function of the noncovalent bonding interactions between the viologens and pillar[5]arenes in the formation of the daisy chains and the organogel, a control porphyrin conjugate 6²⁺ in which the viologen is tethered to a 3,5-di-*tert*-butyl phenyl group was prepared (Scheme 1). The bulky stopper in 6²⁺ serves to block the encapsulation of viologen by pillar[5]arene. A solution of 6·2PF₆ in CH₂Cl₂ does not produce daisy chain polymers at lower concentrations as confirmed by TEM investigations. High concentrations of 6·2PF₆ in CH₂Cl₂ do not result in the formation of an organogel. These experiments indicate the essential role of the charge-transfer interactions between pillar[5]arene and viologen units in the formation of the supramolecular assemblies.

The mechanical properties of the organogels were investigated through rheology experiments. The dynamic storage modulus (G') and loss modulus (G'') were measured as a function of angular frequency (ω) at a strain amplitude (γ) of 0.1. The rheology measurements (Fig. 4) were carried out with a gel created from a 10 mM CH₂Cl₂ solution of 1·2PF₆. The organogel

exhibits a plateau region as the angular frequency was varied from 100 to 0.1 rad s^{-1} . The G'' value was lower than G' over the entire frequency range, signifying that the gel has a substantial elastic response, and consequently it retains its gel-like nature over a wide range of strain amplitudes.

Fig. 4 Angular frequency (ω) dependencies of dynamic storage (G') and loss (G'') moduli of the organogel of 1·2PF₆ at 10 mM at 25 $^{\circ}\text{C}$ at a strain amplitude (γ) of 0.1.

In conclusion, we have harnessed the noncovalent bonding interactions between pillar[5]arene and viologen units to assemble a porphyrin-containing supramolecular daisy chain which forms discrete fibres as well as larger bundles at high concentrations. Furthermore, the entanglement of these bundles results in the formation of an elastic organogel. Given the potential photo-induced electron transfer processes between porphyrin and viologen, the reported synthetic approach could be used to synthesise porphyrin supramolecular assemblies having potential application in the fields of sensing and organic solar cells.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures and characterizations; additional TEM and SEM images; UV-Vis and steady state fluorescence spectra. See DOI: 10.1039/c5cc00000x/.

- 1 (a) J. Tanihara, K. Ogawa, Y. Kobuke, *J. Photochem. Photobiol., A*, 2006, **178**, 140; (b) Y. Gao, X. Zhang, C. Ma, X. Li and J. Jiang, *J. Am. Chem. Soc.*, 2008, **130**, 17044; (c) C. J. Medforth, Z. Wang, K. E. Martin, Y. Song, J. L. Jacobsen and J. A. Shelnutt, *Chem. Commun.*, 2009, **47**, 7261; (d) Y. Qiu, Y., P. Chen and M. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 9644; (e) M. Vizuete, M. J. Gomez-Escalonilla, J. G. Fierro, A. S. D. Sandanayaka, T. Hasobe, M. Yudasaka, S. Iijima, O. Ito and F. Langa, *Chem. Eur. J.*, 2010, **16**, 10752; (f) A. Satake, S. Azuma, Y. Kuramochi, S. Hirota and Y. Kobuke, *Chem. Eur. J.*, 2011, **17**, 855; (g) Q. Wang, Y. Chen, P. Ma, J. Lu, X. Zhang and J. Jiang, *J. Mater. Chem.*, 2011, **21**, 8057; (h) C. J. Medforth and J. A. Shelnutt, *Handbook of Porphyrin Science*, 2011, **11**, 181; (i) S. Fruehbeisser and F. Groehn, *J. Am. Chem. Soc.*, 2012, **134**, 14267; (j) G. Bottari, O. Trukhina, M. Ince and T. Torres, *Coord. Chem. Rev.*, 2012, **256**, 2453.
- 2 (a) C. M. Drain, K. C. Russell and J.-M. Lehn, *Chem. Commun.*, **1996**, 337; (b) X. Shi, K. M. Barkigia, J. Fajer and C. M. Drain, *J. Org. Chem.*, 2001, **66**, 6513; (c) S. George and I. Goldberg, *Cryst. Growth Des.*, 2006, **6**, 755; (d) I. Radivojevic, I. Likhtina, X. Shi, S. Singh and C. M. Drain, *Chem. Commun.*, **2010**, 46, 1643.
- 3 (a) J.-C. Chambron, J.-P. Collin, J.-O. Dalbavie, C. O. Dietrich-Buchecker, V. Heitz, F. Odobel, N. Solladie and J.-P. Sauvage, *Coord. Chem. Rev.*, 1998, **178**, 1299; (b) M. Ayabe, K. Yamashita, K. Sada, S. Shinkai, A. Ikeda, S. Sakamoto and K. Yamaguchi, *J. Org. Chem.*, 2003, **68**, 1059; (c) Y. Kobuke, *Eur. J. Inorg. Chem.*, **2006**, 2333; (d) M. C. Lensen, J. A. A. W. Elemans, S. J. T. Dingenen, J. W. Gerritsen, S. Speller, A. E. Rowan and R. J. M. Nolte, *Chem. Eur. J.*, 2007, **13**, 7948; (e) J. K. Sprafke, B. Odell, T. D. W. Claridge and H. L. Anderson, *Angew. Chem. Int. Ed.*, 2011, **50**, 5572.
- 4 (a) M. Bonchio, T. Carofiglio, M. Carraro, R. Fornasier and U. Tonellato, *Org. Lett.*, 2002, **4**, 4635; (b) G. Moschetto, R. Lauceri, F. G. Gulino, D. Sciutto and R. Purrello, *J. Am. Chem. Soc.*, 2002, **124**, 14536; (c) L. Baldini, P. Ballester, A. Casnati, R. M. Gomila, C. A. Hunter, F. Sansone and R. Ungaro, *J. Am. Chem. Soc.*, 2003, **125**, 14181; (d) G. de Miguel, M. Perez-Morales, M. T. Martin-Romero, E. Munoz, T. H. Richardson and L. Camacho, *Langmuir*, 2007, **23**, 3794; (e) Y. Liu, C.-F. Ke, H.-Y. Zhang, J. Cui and F. Ding, *J. Am. Chem. Soc.*, 2008, **130**, 600; (f) P. Kubat, K. Lang, P. Lhotak, P. Janda, J. Sykora, P. Matejcek, M. Hof, K. Prochazka and Z. Zelinger, *J. Photochem. Photobiol., A*, 2008, **198**, 18; (g) J. Mohanty, A. C. Bhasikuttan, S. D. Choudhury and H. Pal, *J. Phy. Chem. B*, 2008, **112**, 10782; (h) Z.-Y. Gu, D.-S. Guo, M. Sun and Y. Liu, *J. Org. Chem.*, 2010, **75**, 3600; (i) M. Fathalla, A. Neuberger, S.-C. Li, R. Schmehl, U. Diebold and J. Jayawickramarajah, *J. Am. Chem. Soc.*, 2010, **132**, 9966; (j) A. D'Urso, P. F. Nicotra, G. Centonze, M. E. Fragala, G. Gattuso, A. Notti, A. Pappalardo, S. Pappalardo, M. F. Parisi and R. Purrello, *Chem. Commun.*, 2012, **48**, 4046; (k) L. Baldini, P. Ballester, A. Casnati, R. M. Gomila, C.A. Hunter, F. Sansone and R. Ungaro, *J. Phy. Chem. C*, 2013, **117**, 3069.
- 5 (a) F. Cramer, *Einschlussverbindungen*; Springer-Verlag:Berlin, 1954; (b) D. French, *Adv. Carbohydr. Chem.*, 1957, **12**, 189; (c) A. Harada, *Acc. Chem. Res.*, 2001, **34**, 456.
- 6 (a) C. D. Gutsche, *Calixarenes*; Royal Society of Chemistry: Cambridge, U.K., 1989; (b) L. Baldini, A. Casnati, F. Sansone and R. Ungaro, *Chem. Soc. Rev.*, 2007, **36**, 254.
- 7 (a) W. A. Freeman, W. L. Mock and N. Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367; (b) K. Kim, *Chem. Soc. Rev.*, 2002, **31**, 96.
- 8 (a) T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.*, 2008, **130**, 5022; (b) C. Li, Q. Xu, J. Li, F. Yao and X. Jia, *Org. Biomol. Chem.*, 2010, **8**, 1568; (c) Y. Kou, H. Tao, D. Cao, Z. Fu, D. Schollmeyer and H. Meier, *Eur. J. Org. Chem.*, 2010, 6464; (d) Z. Zhang, Y. Luo, J. Chen, S. Dong, Y. Yu, Z. Ma and F. Huang, *Angew. Chem. Int. Ed.*, 2011, **50**, 1397; (e) N. L. Strutt, R. S. Forgan, J. S. Spruell, Y. Y. Botros and J. F. Stoddart, *J. Am. Chem. Soc.*, 2011, **133**, 5668; (f) P. J. Cragg and K. Sharma, *Chem. Soc. Rev.*, 2012, **41**, 597; (g) M. Xue, Y. Yang, X. Chi, Z. Zhang and F. Huang, *Acc. Chem. Res.*, 2012, **45**, 1294; (h) X.-B. Hu, Z. Chen, L. Chen, L. Zhang, J.-L. Hou and Z.-T. Li, *Chem. Commun.*, 2012, **48**, 10999; (i) X. Shu, S. Chen, J. Li, Z. Chen, L. Weng, X. Jia and C. Li, *Chem. Commun.*, 2012, **48**, 2967; (j) T. Ogoshi and T.-a. Yamagishi, *Eur. J. Org. Chem.*, 2013, 2961; (k) H. Zhang and Y. Zhao, *Chem. Eur. J.*, 2013, **19**, 16862; (l) Z. Li, J. Yang, G. Yu, J. He, Z. Abliz and F. Huang, *Chem. Commun.*, 2014, **50**, 2841.
- 9 (a) T. Ogoshi, Y. Nishida, T.-a. Yamagishi and Y. Nakamoto, *Macromolecules*, 2010, **43**, 7068; (b) T. Ogoshi, M. Hashizume, T.-a. Yamagishi and Y. Nakamoto, *Chem. Commun.*, 2010, **46**, 3708; (c) D.-X. Chen, Y.-L. Sun, Y. Zhang, J.-Y. Cui, F.-Z. Shen and Y.-W. Yang, *RSC Adv.*, 2013, **3**, 5765; (d) C. Li, K. Han, J. Li, Y. Zhang, W. Chen, Y. Yu and X. Jia, *Chem. Eur. J.*, 2013, **19**, 11892; (e) X. Wang, K. Han, J. Li, X. Jia and C. Li, *Polym. Chem.*, 2013, **4**, 3998 (f) Z.-Y. Li, Y. Zhang, C.-W. Zhang, L.-J. Chen, C. Wang, H. Tan, Y. Yu, X., Li and H.-B. Yang, *J. Am. Chem. Soc.*, 2014, **136**, 8577; (g) Q. Wang, M. Cheng, Y. Zhao, L. Wu, J. Jiang, L. Wang and Y. Pan, *Chem. Commun.*, 2015, **51**, 3623; (h) L.-B. Meng, D. Li, S. Xiong, X.-Y. Hu, L. Wang and G. Li, *Chem. Commun.*, 2015, **51**, 4643; (i) N. Song, D.-X. Chen, M.-C. Xia, X.-L. Qiu, K. Ma, B. Xu, W. Tian and Y.-W. Yang, *Chem. Commun.*, 2015, **51**, 5526.
- 10 (a) P. R. Ashton, I. Baxter, S. J. Cantrill, M. C. T. Fyfe, P. T. Glink, J. F. Stoddart, A. J. P. White and D. J. Williams, *Angew. Chem. Int. Ed.*, 1998, **37**, 1294; (b) S. Cantrill, G. J. Youn, J. F. Stoddart, D. J. Williams, *J. Org. Chem.*, 2001, **66**, 6857; (c) M. Miyauchi, A. Harada, *J. Am. Chem. Soc.*, 2004, **126**, 11418; (d) K. D. Johnstone, K. Yamaguchi and M. J. Gunter, *Org. & Biomol. Chem.*, 2005, **3**, 3008; (e) R. Nally and L. Isaacs, *Tetrahedron*, 2009, **65**, 7249; (f) J. Rotzler and M. Mayor, *Chem. Soc. Rev.*, 2013, **42**, 44.
- 11 For examples on the photo-induced electron transfer in porphyrin-viologen conjugates see: (a) R. Laudien, I. Yoshida and T. Nagamura, *J. Chem. Soc., Perkin Trans 2*, 2002, 1772; (b) J. Petersson, M. Eklund, J. Davidsson and L. Hammarstrom, *J. Am. Chem. Soc.*, 2009, **131**, 7940; (c) T. Yui, Y. Kobayashi, Y. Yamada, K. Yano, Y. Fukushima, T. Torimoto and K. Takagi, *ACS Appl. Mater. Interfaces*, 2011, **3**, 931; (d) H. Tahara, H. Yonemura, S. Harada, A. Nakashima and S. Yamada, *Chem. Phys. Lett.*, 2012, **524**, 42.
- 12 (a) R. Huisgen, R. Knorr, L. Mobius and G. Szeimies, *Chem. Ber.*, 1965, **98**, 4014; (b) V. V. Rostovtsev, L. G. Green, V. V. Folkin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.
- 13 (a) H. Zhang, X. Ma, K. T. Nguyen and Y. Zhao, *ACS Nano*, 2013, **7**, 7853; (b) H. Zhang, K. T. Nguyen, X. Ma, H. Yan, J. Guo, L. Zhu and Y. Zhao, *Org. Biomol. Chem.*, 2013, **11**, 2070; (c) X.-Y. Hu, X. Wu, S. Wang, D. Chen, W. Xia, C. Lin, Y. Pan and L. Wang, *Polym. Chem.*, 2013, **4**, 4292; (d) Y. Zhou, Z. Li, Z. Chi, C. Thompson and Y. Yao, *Chem. Commun.*, 2014, **50**, 10482.