A New Class of Giant Tetrads for Studying Aspects of Long-Range Intramolecular Electron Transfer Processes: Synthesis and Computational Studies**

Katrina A. Jolliffe, Steven J. Langford, Anna M. Oliver, Michael J. Shephard, and Michael N. Paddon-Row*[a]

Abstract: A modular approach for synthesising the giant multichromophoric systems **19**, **20** and **5**·2PF$_6$ is presented which involves the sequential Diels–Alder reactions of tetraene **7** with the chromophore-based dienophiles **6**, **8** and **23**. The π-facial stereoselectivity of the Diels–Alder reactions between such building blocks enables the isolation of two major stereoisomers, namely *syn*,*syn*-**5**·2PF$_6$ and *anti*,*syn*-**5**·2PF$_6$, which differ substantially in their shape. This geometrical difference offers a unique opportunity for the delineation of two mechanisms of photoinduced electron transfer (ET): solvent-mediated ET and through-bridge-mediated ET. The stereochemical assignments of *syn*,*syn*-**5**·2PF$_6$ and *anti*,*syn*-**5**·2PF$_6$ were secured on the basis of ^{1}H NMR and photophysical studies, namely the observation of NOE effects and strong upfield chemical shifts of the bipyridine proton resonances in *syn*,*syn*-**19**, and the observation of photoinduced ET in *syn*,*syn*-**5**·2PF$_6$, but not in *anti*,*syn*-**5**·2PF$_6$. The results of gas-phase semi-empirical (AM1) and ab initio (HF/3-21G) MO calculations also lend support to the interpretation of the NMR studies and to the stereochemical assignments for the two isolated stereoisomers of **5**·2PF$_6$. Importantly, **19** and **5**$^{2+}$ are not as rigid as might be expected and give rise to the existence of two conformers for *syn*,*syn*-**19**, and the formation of a closed form for *syn*,*syn*-**5**$^{2+}$ in which the terminal chromophores are separated by a distance of only ≈4 Å in the gas phase.

Keywords: computational chemistry · cycloadditions · electron transfer · multichromophores · stereochemistry

Introduction

Molecular systems constructed from the covalent attachment of donor and acceptor chromophores to rigid saturated hydrocarbon bridges continue to provide important and fundamental insights into the characteristics of long-range intramolecular electron transfer (ET) processes. Experimental studies on these systems have revealed that the bridges not only serve as a scaffolding that fixes the chromophores at well-defined separations and orientations with respect to each other, but they also play a crucial role in the mediation of the ET process by a superexchange, or through-bond (TB) coupling, mechanism.[1]

Many different hydrocarbon bridges have been employed[2] in ET studies, including steroid-based systems,[1a, 3] cyclohexane and decalin,[4] oligobicyclo[2.2.2]octanes,[5] triptycenes,[6] polyspirocyclobutanes,[7] and norbornylogous bridge systems comprising linearly fused norbornane and bicyclo[2.2.0]hexane units,[8] such as **1** and **2**. Our studies over the past decade on norbornylogous bichromophoric systems have provided unprecedented insight into the dependence of ET dynamics on such factors as interchromophore distance and orientation, bridge configuration, orbital symmetry and solvent, particularly in solvent-mediated ET processes.[1b, 8] The norbornylogous bridge has two important advantages over most of the other types of hydrocarbon bridges that have been used for ET studies. Firstly, TB coupling is quite good in our systems, although not optimal.[9] This coupling enables ET processes to occur over very large interchromophore separations (>12 Å) on a nanosecond time-scale. The second advantage is synthetic versatility. A wide range of different chromophores may be easily attached to the termini of the norbornylogous bridge, for example naphthalene[10] and anthracene rings,[11] pyridazines,[12] pyridines,[13] quinones,[14] tetracyanonaphthoquinones,[15] porphyrins,[14, 16] diones,[17] dipyridyls,[18] and even the C_{60} cage.[19]

Our work on ET has recently been extended to the synthesis of the trichromophoric systems, such as **3** and homologues that possess longer bridges (Scheme 1).[20] These systems exist in two supposedly rigid, non-interconverting

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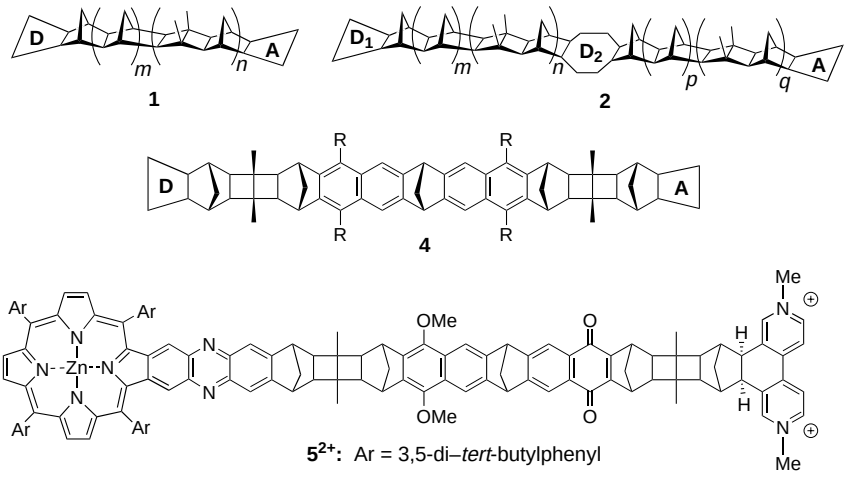


diastereomeric *syn* and *anti* forms. Interestingly, the charge recombination dynamics for the giant charge-separated states of these triads, generated by photoinduced ET, are noticeably different for the *syn* and *anti* stereoisomers; charge recombination in the former system occurs much faster than in the latter system.[21] This behaviour might be the consequence of the fact that the *syn* diastereomer possesses a U-shaped geometry with the terminal chromophores facing each other. This orientation of terminal chromophores in the *syn* diastereomer might be conducive to a facile solvent-mediated charge recombination process, that is not available to the *anti* diastereomer.

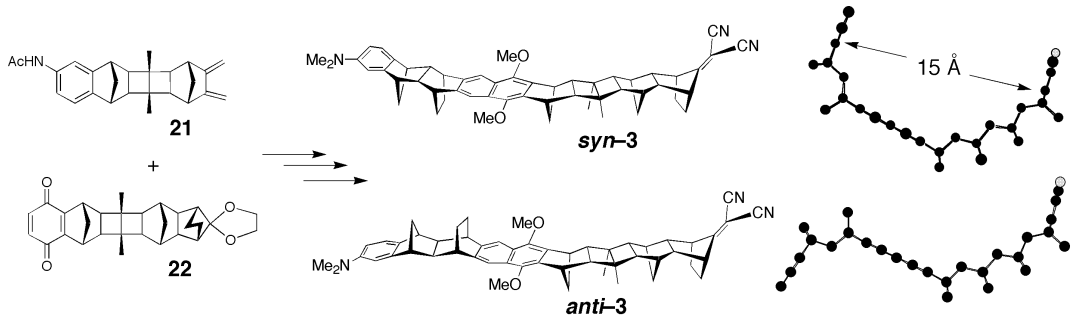
In order to extend our studies on ET dynamics in systems possessing U-shaped cavities, we[22] and others[23] are currently designing and synthesising rigid systems that possess U-shaped cavities of various sizes. Tetrads of the type **4** are illustrative of one class of systems that we wish to study. Herein, we describe in detail the synthesis of the first member of this class of tetrads, namely $\mathbf{5}\cdot 2PF_6$. The chromophores in these systems are tetraarylporphyrin, dimethoxynaphthalene, naphthoquinone and methyl viologen (MV^{2+}). This system can exist in four diastereomeric forms that are distinguished by the relative disposition of the *methano* groups of the norbornane rings fused to the naphthalene and naphthoquinone groups (see Figure 1). If the pair of *methano* groups lie on the same side of the aromatic ring they are said to be *syn* related, and if they are on opposite sides of the aromatic ring, they are said to be *anti* related.

The AM1-optimised shapes of the four diastereomers of **27**, a less substituted relative of $\mathbf{5}^{2+}$, are shown in Figure 1. Although these structures are discussed in detail in the computational section below, it is apparent from Figure 1 that the *syn*,*syn* stereoisomer possess a remarkable U-shaped geometry in which the terminal porphyrin and bipyridyl chromophores are facing each other and are separated by a relatively short distance. We have managed to synthesise and isolate two of the four stereoisomers of $\mathbf{5}^{2+}$, namely *syn*,*syn*-$\mathbf{5}\cdot PF_6$ and *anti*,*syn*-$\mathbf{5}\cdot PF_6$. In particular, the geometry of *syn*,*syn*-$\mathbf{5}\cdot 2PF_6$, the major stereoisomer formed, is discussed in light of NMR spectral data and molecular orbital calculations. The tetrad *syn*,*syn*-$\mathbf{5}\cdot 2PF_6$ is endowed with several features which make it suitable for the investigation of ET processes.[22a] Such features include:

1) The porphyrin donor and methyl viologen acceptor groups serve as acceptable mimics of redox chromophores that participate in biological ET processes.
2) The internal naphthalene ring units serve not only to sculpture the U-shaped cavity, but they also might participate in superexchange-mediated ET between the photoexcited porphyrin donor and the MV^{2+} acceptor.
3) The AM1-optimised structure for *syn*,*syn*-$\mathbf{5}\cdot 2PF_6$ reveals that the porphyrin and MV^{2+} chromophores face each other and are separated by a distance of ≈ 5 Å. The near cofacial alignment of the two chromophores provides an excellent opportunity to explore the role (if any) of solvent-mediated ET processes.

Results and Discussion

Synthetic strategy: The most reasonable retrosynthetic strategy for $\mathbf{5}\cdot 2PF_6$ is depicted in Scheme 2. It involves disconnections through the central naphthalene moieties to produce three subunits, **6**, **7** and **8**. These subunits may be united by sequential Diels–Alder reactions to form the two naphtha-



Scheme 1. Diene **21** reacts with the dienophile **22** to yield the stereomeric mix **3** of which the *syn* isomer is the major component. The AM1 structures (right) show the geometries of both isomers.

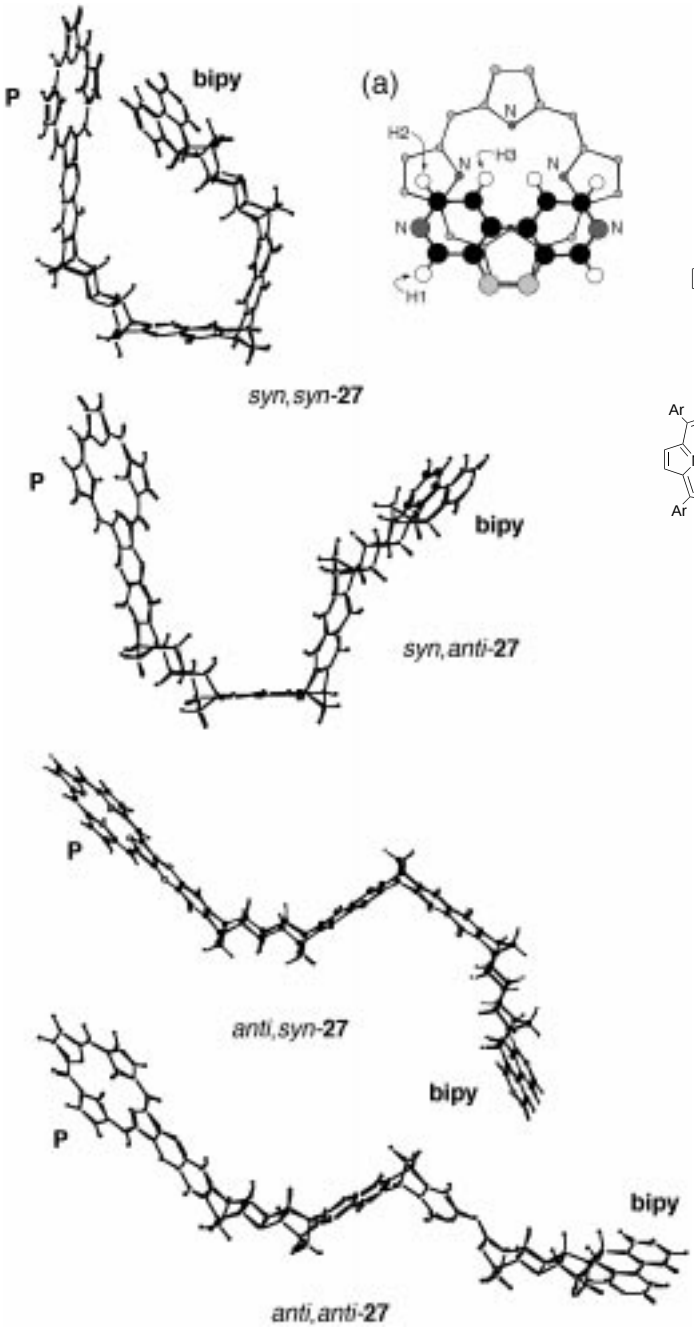
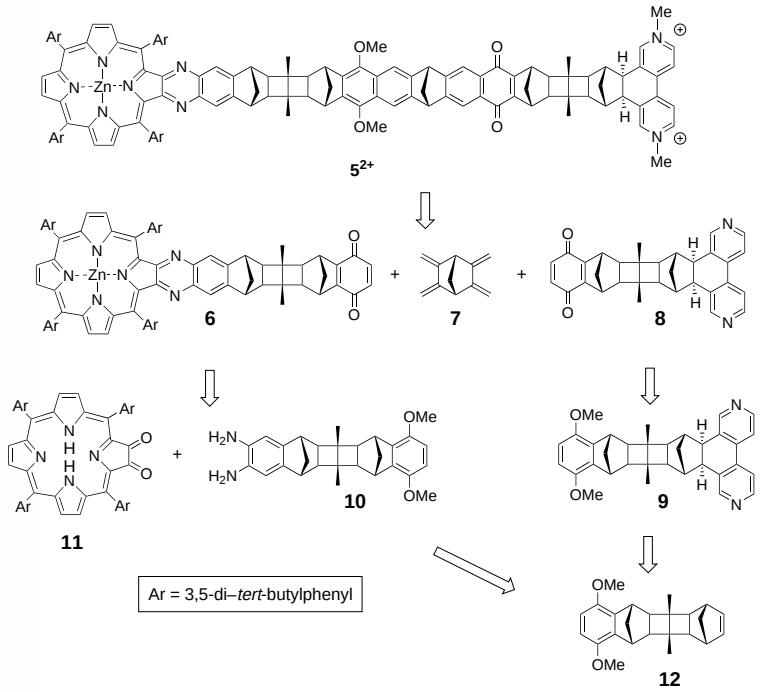


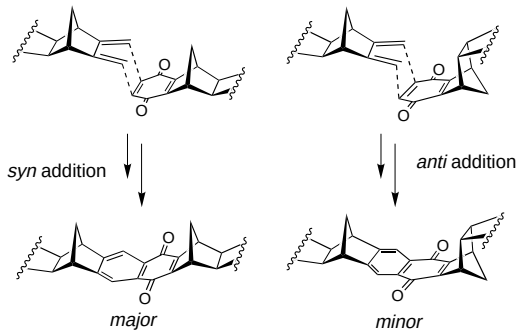
Figure 1. AM1-optimised structures of the four diastereoisomers of **27**. (a): A view of the spatial relationship between the porphyrin (P) and bpy rings in the *syn*,*syn* diastereoisomer showing the positions of the H1, H2 and H3 bpy protons relative to the porphyrin ring.



Scheme 2. Retrosynthetic analysis for the tetrad *syn*,*syn*-**5**·2PF$_6$.

lene rings in the centre of **5**·2PF$_6$. The synthesis of the tetraene **7** have been described previously.[24] The preparation of the porphyrin-containing bridge unit **6** relies upon well-developed procedures[14, 16a] (see Scheme 4), and the quinone **8** should be easily prepared from **9** (see Scheme 5)—the synthesis of which has been recently reported.[18]

There is, of course, a stereochemical ambiguity in the Diels–Alder reactions between the tetraene **7**, and either of the benzoquinones **6** and **8**, which ultimately gives rise to the *syn*,*syn* and *anti*,*syn* stereoisomers of **5**·2PF$_6$ (see Scheme 6).[20b, 25–29] The ambiguity arises because both the benzo quinone and diene fragments contain two diastereotopic π faces, which are differentiated by the neighbouring methano bridges (Scheme 6) of the norbornane skeleton.[20b, 22b] The nature of the π-facial diastereoselectivity of cycloaddition reactions of the type discussed here has been investigated both computationally and experimentally.[25–29] In brief, norbornane-fused *p*-benzoquinones and exocyclic 1,3-dienes exhibit fairly strong *exo*- and *endo*-facial selectivities, respectively.[25, 29] In light of these earlier studies, it would be reasonable to expect, after aromatisation, a preponderance of the *syn* stereoisomer for the cycloaddition between **7** and **6** as well as between **7** and **8** (Scheme 3).[20b]



Scheme 3. The two possible stereochemical consequences of a Diels–Alder reaction which involves a norbornylogous diene and dienophile units.

The tetraene **7** is ideal for the synthesis of **5**·2PF$_6$ by means of sequential Diels–Alder reactions, since the rate of the first Diels–Alder reaction of **7** has been found to be much faster than the rate of the second Diels–Alder reaction.[24a, 30] Thus, it should be possible to sequentially react **7** with the dieneophiles **6** and **8** to produce the backbone of **5**·2PF$_6$ in good yield (Scheme 2).

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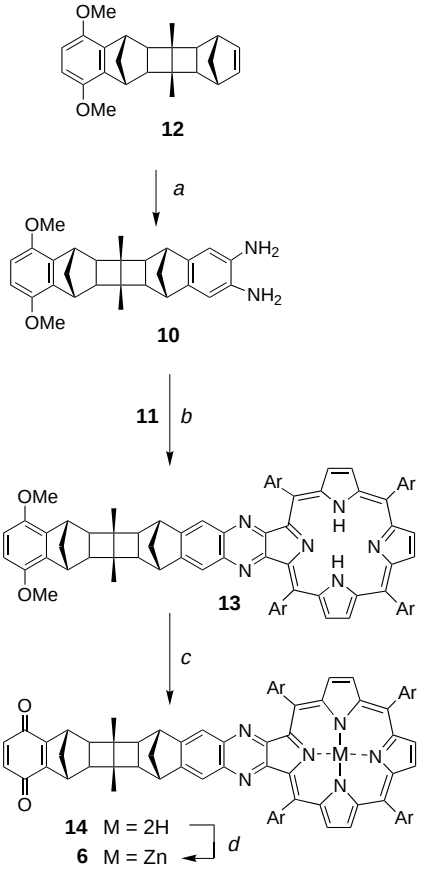
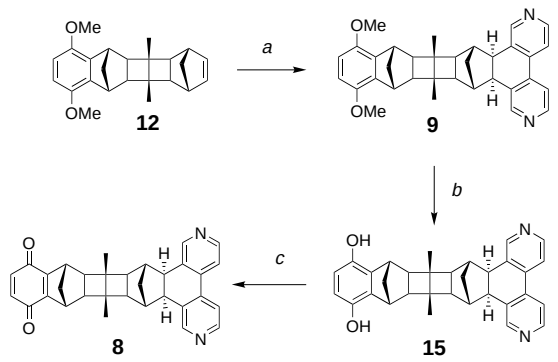
Synthesis: The synthesis of **6** (Scheme 4) was achieved by using the procedures reported by Antolovich et al:[14] condensation of the diamine **10**,[14] prepared from **12** in 10 steps, with the porphyrin-dione **11**[31] in CH_2Cl_2 resulted in the formation of the porphyrin **13** as a red solid in excellent yield. Treatment of **13** with BBr_3 gave the hydroquinone in 85% yield. Oxidation of the hydroquinone (DDQ, CH_2Cl_2) gave the porphyrin{bridge}quinone **14** which was readily converted to **6** with zinc(II) acetate.



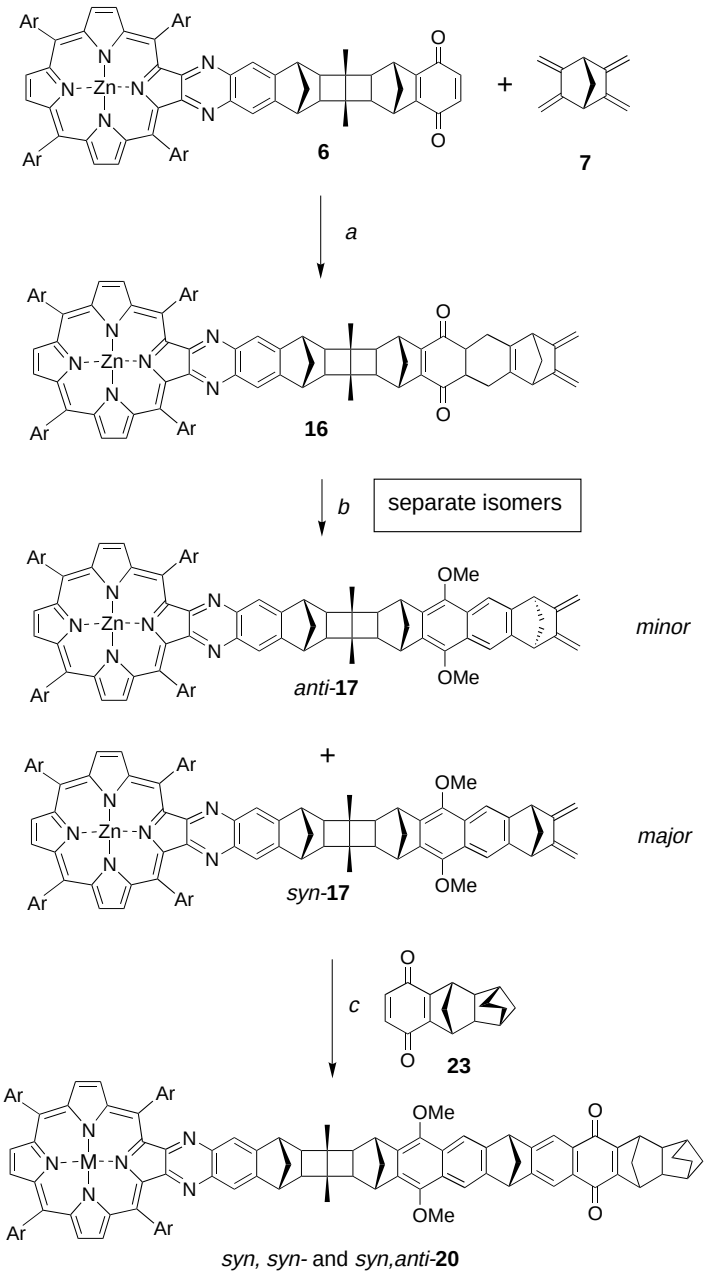
Scheme 4. Synthesis of the porphyrin-quinone **6**. a) Ref. [14], 10 steps; b) CH_2Cl_2, dark, 2 h, 75%; c) BBr_3, CH_2Cl_2, dark, Ar, 85%; d) DDQ, CH_2Cl_2, 95%; e) $Zn(OAc)_2 \cdot 2H_2O$, MeOH, CH_2Cl_2, 96%.

The bipyridyl-quinone derivative **8** was synthesised from the known dimethoxybenzene derivative **9**[18] in two steps (Scheme 5). Treatment of **9** with BBr_3 led to the formation of the corresponding hydroquinone **15** which was oxidised to quinone **8** with a mixture of AgO and Ag_2O.[32] The addition of small amounts of the stronger oxidant AgO to the oxidation reaction resulted in higher yields of the quinone **8**.

The final stages of the synthesis (Schemes 6 and 7) involved sequential Diels–Alder reactions between the bridge units **6**, **7** and **8**. The first of these reactions was carried out with the quinone **6** and the tetraene **7** to yield a stereomeric mixture of adduct **16** (Scheme 6). This mixture was not separated; it was directly converted into the mixture of dimethoxynaphthalene stereoisomers **17** by treatment with K_2CO_3 and MeI, followed



Scheme 5. Synthesis of **8**. a) Ref. [18]; b) BBr_3, CH_2Cl_2, 83%; c) AgO, Ag_2O, $MgSO_4 \cdot 3H_2O$, CH_2Cl_2, 85%.

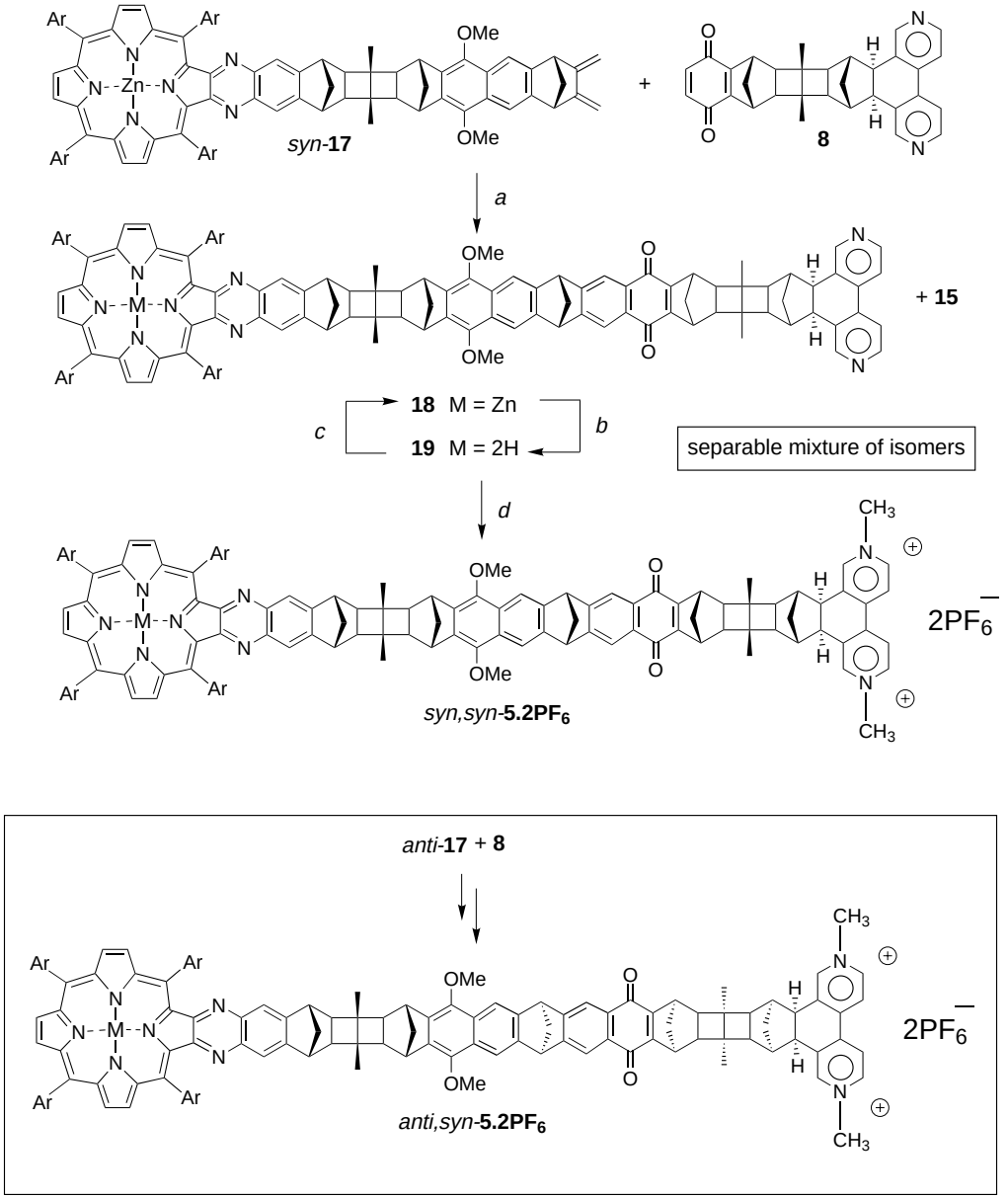


Scheme 6. Synthesis of triads **20**. a) toluene, 80°C, Ar, 99%; b) K_2CO_3, Me_2CO, MeI, 86%; c) DDQ, CH_2Cl_2, 83%, separate isomers; d) **23** (4 equiv), 40 h, reflux, $CH_3C_6H_5$, 60%.

by oxidation with DDQ. ^{1}H NMR analysis of the crude mixture of **17** showed it to comprise a 70:30 mixture of two diastereomeric dimethoxynaphthalene derivatives, presumed to be *syn*-**17** and *anti*-**17**, respectively. The mixture was separated by preparative thin-layer chromatography; the major stereoisomer had the higher R_f value. The MALDI mass spectra of both compounds gave molecular ion peaks at m/z 1690 $[M+2]^+$ and 1689 $[M+1]^+$ for the higher and lower R_f fractions, respectively. These values suggest that the two fractions are indeed the diastereomers *syn*-**17** and *anti*-**17**. The ^{1}H and ^{13}C spectra of the two fractions are very similar, although several proton signals of the stereoisomer with the lower R_f exhibit small downfield shifts. Previous investigations, based on model studies of the Diels–Alder reaction of the diene **21** with the quinone **22** (Scheme 1)[20b] strongly suggest that the major stereoisomer obtained from this series of reactions should be *syn*-**17**. Further support for this assertion is provided by the facial selectivity observed in the reaction between **21** and **22** (*syn*:*anti* = 72:28) which is virtually identical to that observed in the reaction between **6** and **7** (*syn*:*anti* = 70:30).

The model trichromophore **20**, which was required for photophysical studies, was prepared in 60% yield by the treatment of *syn*-**17** with excess quinone **23** in toluene. Excess **23** was used in order to oxidise the cycloadduct directly to the corresponding naphthoquinone. No attempt was made to separate the two diastereoisomers in this case, since the orientation of the methano bridges that flank the naphthoquinone group of **20** will have no bearing on its use as a model trichromophore for electron transfer studies.

Following the successful preparation of **20**, a second series of Diels–Alder reactions were performed with the diene *syn*-**17** and the quinone **8** (Scheme 7). This set of reactions illustrates how a building block approach to the preparation



Scheme 7. Synthesis of tetrad *syn*,*syn*-**5**·2PF$_6$. a) **8** (7 equiv), 40 h, reflux, $CH_3C_6H_5$; b) HCl (2M), CH_2Cl_2, 60% (2 steps), separate isomers; c) $Zn(OAc)_2 \cdot 2H_2O$, MeOH, $CHCl_3$; d) MeI, MeCN, reflux; e) NH_4PF_6, H_2O, Me_2CO, 72% (3 steps).

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of a range of multichromophoric systems might be accomplished. A large excess of quinone **8** was employed in this reaction, leading directly to the formation of the diastereomeric quinones *syn*,*syn*-**18** and *anti*,*syn*-**18**. Again, the excess quinone was used to oxidise the initially formed cycloadduct to the naphthoquinone **18**. The hydroquinone by-product **15** was readily separated from the desired products by chromatography. Separation of the diastereoisomers of **18** was unsuccessful; however, demetallation (2 M HCl) allowed the easy separation of the diastereomers of the free-base analogue **19**. MALDI mass spectra of both fractions obtained from column chromatography gave molecular ion peaks at *m*/*z* 2097 $[M+2]^+$, suggesting that the two fractions were the diastereomers *syn*,*syn*-**19** and *anti*,*syn*-**19**. On the basis of previous studies,[20] the major stereoisomer (which has the higher R_f value) should be *syn*,*syn*-**19**. Attempts to grow single crystals of X-ray quality from various solvent mixtures by vapour diffusion methods have been unsuccessful to date. Unfortunately, the minor fraction containing the putative *anti*,*syn*-**19** diastereomer could not be purified completely by either preparative thin-layer chromatography or recrystallisation. Observations supporting the proposed assignment of *syn*,*syn* stereochemistry to the major stereoisomer **19** are discussed below.

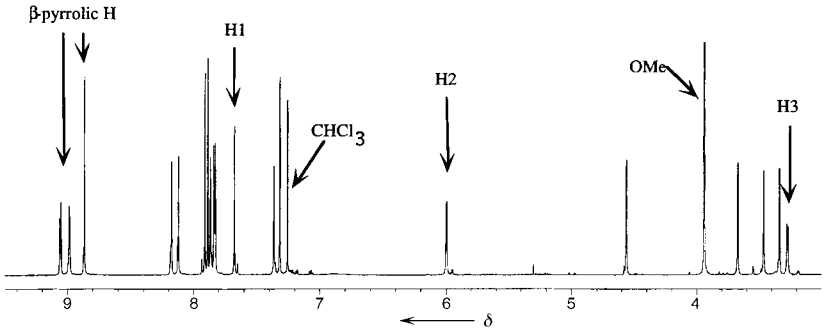
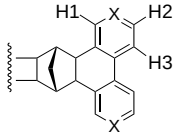


Figure 2. ^{1}H NMR spectrum of *syn*,*syn*-**19** (in $CDCl_3$) showing the relative positions of the dipyridyl protons H1, H2 and H3 as defined in Table 1.

Table 1. Chemical shifts (δ) of selected protons from **24**, **19**, *syn*,*syn*-**5**·$2PF_6$ and **25**.



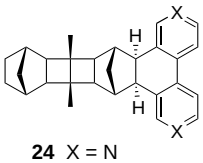
Compound	H1 (δ)	H2 (δ)	H3 (δ)
24 (X = N)[a]	8.48	8.42	7.58
syn,*syn*-**19**[a]	7.67	6.01	3.31
anti, *syn*-**19**[a]	8.25	8.25	7.48
syn,*syn*-**5**·$2PF_6$ [b]	8.90	8.10	7.60
25 (X = $^+$NMe, BF_4^-)[c]	8.79	8.58	8.49

[a] $CDCl_3$. [b] CD_3COCD_3. [c] CD_3CN.

Metallation of the free-base porphyrin *syn*,*syn*-**19** with $Zn(OAc)_2 \cdot 2H_2O$ followed by methylation of the ring-fused bipyridyl unit (MeI/MeCN/heat) and counterion exchange (NH_4PF_6, aq. Me_2CO) gave the desired tetrad *syn*,*syn*-**5**·$2PF_6$ in 72% yield after recrystallisation from CH_2Cl_2/CH_3OH (Scheme 7). A MALDI mass spectrum of *syn*,*syn*-**5**·$2PF_6$ showed a parent ion at *m*/*z* 2188, which corresponds to the molecular mass of $[\mathbf{5} \cdot 2PF_6]^+$. In a similar reaction sequence (Scheme 7), *anti*-**17** was converted to *anti*,*syn*-**5**·$2PF_6$ in slightly lower yields. As in the previous case, the minor stereoisomer *anti*,*anti*-**5**·$2PF_6$ was obtained in small amounts and could not be fully purified from small amounts of *anti*,*syn*-**5**·$2PF_6$ for subsequent characterisation.

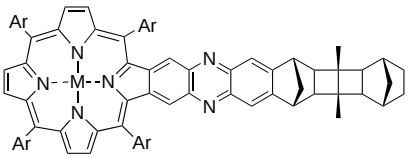
Stereochemistry: To confirm the stereochemistry of the putative *syn*,*syn*-**5**·$2PF_6$, a number of NMR experiments were performed on this material and its progenitor, *syn*,*syn*-**19**. The results of these studies, taken in conjunction with MO calculations (next Section) confirm the stereochemistry of these molecules. The ^{1}H NMR spectrum of *syn*,*syn*-**19** in $CDCl_3$ was well resolved and indicated the presence of a single diastereomer (Figure 2). Interestingly, the resonances of the protons of the bipyridyl (bpy) unit in the model compound **24**[18] (at $\delta = 8.48$, 8.42 and 7.58, respectively, Table 1) were not present in the ^{1}H NMR spectrum of *syn*,*syn*-**19**. Instead, the ^{1}H NMR spectrum of *syn*,*syn*-**19** exhibits a pair of AX doublets at $\delta = 3.31$ and 6.01 (Table 1), each with a coupling constant of 5.1 Hz. A combination of 2D NMR techniques (COSY, TOCSY and NOESY experiments) revealed that these signals, together with a singlet at $\delta = 7.67$ are caused by the aromatic protons of the bpy unit. In particular, the NOESY experiments (mixing time of 200 ms) indicate that a range of NOE interactions exist between the protons of the bpy group, which give signals at $\delta = 6.01$ and 3.31, and the inner peripheral porphyrin protons, several of the β-pyrrolic protons and several of the protons of the *meso* substituents. These observations clearly reveal that the bpy and porphyrin rings lie in close proximity to each other and that the large upfield shifts of the bpy proton signals are the result of the porphyrin ring current. The spatial relationship between the bpy and porphyrin rings in the *syn*,*syn* stereoisomer is shown in Figure 1, from which it can be seen that the protons H2 and H3 of the bpy group lie over the centre of the porphyrin ring, whereas H1 lies outside the porphyrin perimeter. Thus, the resonances of both H2 and H3, but not H1, should experience strong upfield shifts, and this is in agreement with the experimental results. Similar upfield shifts have been observed for systems containing both MV^{2+} and porphyrin units in which the interchromophore distance is between 3.25 and 3.84 Å,[32] although, in these cases the affected protons are associated with the MV^{2+} group, rather than with the bpy unit.

While the origin of the proximity between the bpy and porphyrin rings in *syn*,*syn*-**19** is best explained in terms of the *syn*,*syn* stereochemistry (Figure 1), it is necessary to eliminate the possibility that the upfield chemical shifts of the bpy protons and the NOE data are caused by intermolecular association. Such an association would be observed for all



24 X = N

25^{2+} X = $^{+}$NMe BF_4^-



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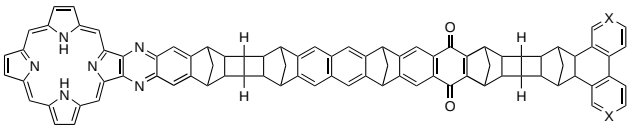
M = 2H; Ar = 3,5-di–*tert*-butylphenyl



27 X = N

28^{2+} X = $^{+}$NMe

stereoisomers of **19**, not just the *syn*,*syn* system. However, the chemical shifts of the bpy protons in the *anti*,*syn* stereoisomer of **19** (Table 1) are similar to those of the model compound **24** (to within 0.2 ppm) and show no evidence of any shielding by the porphyrin ring current. In addition, ^{1}H NMR and UV/Vis dilution studies were also carried out on the *syn*,*syn* stereoisomer of **19**, together with ^{1}H NMR titration studies of the model compounds **24** and **26**.[14] Dilution experiments (10^{-2} to 10^{-5} M, $CDCl_3$) resulted in no observable changes in the ^{1}H NMR spectrum of *syn*,*syn*-**19**, nor did its electronic spectrum (in $CHCl_3$) show any deviation from the Beer–Lambert law. Mixtures of the model systems **24** and **26** in ratios varying from 1:10 to 10:1 resulted in no observable upfield shifts of the bpy protons of **24**. The results of these experiments indicate that both the observed upfield chemical shifts of the bpy protons of *syn*,*syn*-**19** and the NOE interactions must be intramolecular in origin. Therefore, the assigned *syn*,*syn* stereochemistry of this isomer is correct, since only this stereochemistry is able to bring the bpy and porphyrin groups close together.

Interestingly, the ^{1}H NMR spectrum of *syn*,*syn*-**5**$\cdot 2PF_6$ ([D_6]acetone, Table 1) showed only moderate shielding of the MV^{2+} protons which occur at $\delta = 8.90, 8.10, 7.60$, compared to $\delta = 8.79, 8.58, 8.49$ for the model viologen **25**$^{2+}$ (Table 1). Therefore, the shielding of the MV^{2+} protons H2 and H3 in *syn*,*syn*-**5**$\cdot 2PF_6$ amounts to 0.5 and 0.9 ppm, respectively. The fairly small effect of the porphyrin ring current on the MV^{2+} proton resonances in *syn*,*syn*-**5**$\cdot 2PF_6$ contrasts with the strong shielding observed for the bpy protons in *syn*,*syn*-**19**. This puzzling observation may be the consequence of subtle solvent-induced changes in the molecular geometry upon changing the solvent from $CDCl_3$ (used for *syn*,*syn*-**19**) to acetone (used for *syn*,*syn*-**5**$\cdot 2PF_6$). Unfortunately, this proposal could not be verified because *syn*,*syn*-**5**$\cdot 2PF_6$ is not soluble in $CDCl_3$ and attempts to obtain ^{1}H NMR spectra of *syn*,*syn*-**19** in [D_6]acetone gave only very broad peaks attributable to porphyrin aggregation. The connection between molecular geometry and chemical shifts in the *syn*,*syn* stereoisomers of **5**$\cdot 2PF_6$ and **19** will be discussed in detail in the computational section below.

Computational studies: In the absence of X-ray structural data and in light of the unusual upfield chemical shifts of the bpy protons observed in *syn*,*syn*-**19**, the structural features of **5**$^{2+}$ and **19** were investigated with the AM1[33] and HF/3-21G[34] theoretical models as incorporated in the SPARTAN[35a] and GAUSSIAN[35b] programs, respectively. Both theoretical models are known to reproduce reliable experimental geometries for multichromophoric systems based on the polynorbornane bridge.[19c, 22b, 36]

Because of the large sizes of **19** and **5**$^{2+}$, calculations were performed on the less substituted analogues, **27** and **28**$^{2+}$, respectively. The AM1 geometry optimisations were carried out with no symmetry constraints (i.e. C_1 symmetry). The structures were also optimised under a C_s symmetry constraint; however, this only led to minor geometrical changes relative to the respective C_1 forms of lower energy. For reasons of limited computing resources, the HF/3-21G geometry optimisations were performed with a C_s symmetry constraint. Profiles of the AM1-optimised structures for the *syn*,*anti*, *anti*,*syn*, *anti*,*anti* and *syn*,*syn* bpy systems **27**, and the *syn*,*syn* viologen system **28**$^{2+}$ are given in Figures 1 and 3, respectively. Selected energies and structural details are given in Table 2. Full structural and energetic details of all optimised systems are available on request.[37]

As to be expected, only one optimised structure was located for each of the three *anti* diastereomers of the tetrad **27**. Their structures are unexceptional; the centre-to-centre separation

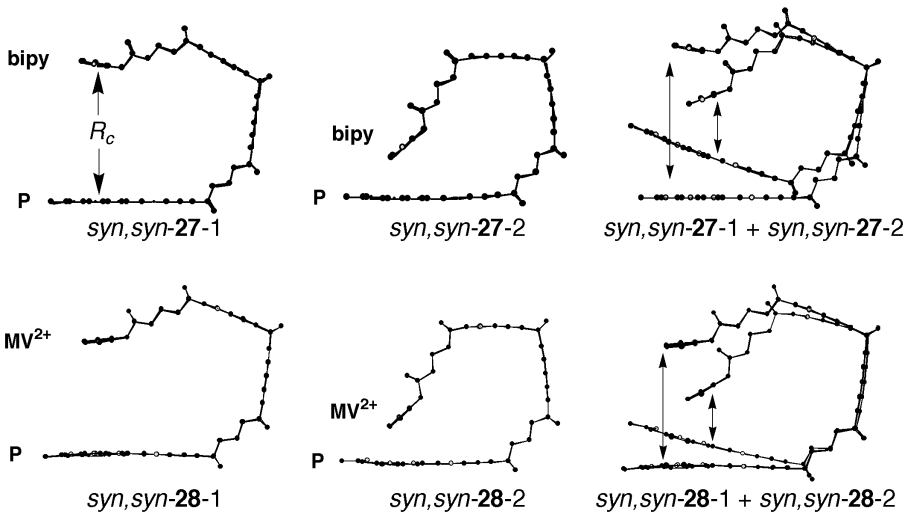


Figure 3. Profiles of the AM1-optimised geometries for the *syn*,*syn* diastereomers of **27** and **28**$^{2+}$.

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Table 2. AM1 Heats of formation, ΔH_f [kcal mol^{-1}], HF/3–21G energies [Hartrees], and terminal chromophore centre-to-centre separations R_c [Å] calculated for the stereoisomers of the tetrads **27** and **28**$^{2+}$.[a]

Method		*syn*,*syn*-**27**-1	*syn*,*syn*-**27**-2	*anti*,*syn*-**27**	*syn*,*anti*-**27**	*anti*,*anti*-**27**	*syn*,*syn*-[**28**-1]$^{2+}$	*syn*,*syn*-[**28**-2]$^{2+}$	*anti*,*syn*-**28**$^{2+}$	*syn*,*anti*-**28**$^{2+}$	*anti*,*anti*-**28**$^{2+}$
AM1	ΔH_f	587.14 (0.02)	588.21 (1.09)	587.12 (0.0)	587.16 (0.04)	587.14 (0.02)	943.16 (11.9)	931.23 (0.0)	945.55 (14.3)	945.52 (14.3)	945.45 (14.2)
	R_c	13.83	6.15	32.19	24.42	34.86	9.98	5.26	32.87	23.68	35.00
HF[b]	energy	−3817.544 (0.42)	−3817.545 (0.0)					−3895.914			
	R_c	12.86	4.41					4.08			

[a] Relative energies (in kcal mol^{-1}) are in parentheses. [b] HF refers to H/3–21G.

R_c between the two terminal chromophores ranges from 24 Å to 35 Å. Of greater interest is the discovery of two energetically stable conformations for the *syn*,*syn* diastereomer, *syn*,*syn*-**27**-1 and *syn*,*syn*-**27**-2. The main distinguishing feature between the two conformations is the inter-terminal chromophore separation R_c. For *syn*,*syn*-**27**-1, R_c is 13.8 Å and 12.9 Å at the AM1 and HF/3-21G levels, respectively. In marked contrast, R_c for *syn*,*syn*-**27**-2 is only 6.2 Å at the AM1 level and 4.4 Å at the HF/3-21G level.

The *syn*,*syn*-**27-**1 structure comprises an unstrained bridge and non-interacting terminal porphyrin and bpy chromophores. Thus, the geometries of the naphthalene, naphthoquinone and saturated hydrocarbon bridge segments in *syn*,*syn*-**27-**1 are identical to those of the corresponding units in the *anti* isomers.

In contrast, the naphthoquinone and naphthalene groups in *syn*,*syn*-**27-**2 are slightly bowed. The HF/3-21G out-of-plane bending angles associated with the naphthoquinone and naphthalene rings are about 6° and 12°, respectively. This effect may be seen in the superposition of the profiles of *syn*,*syn*-**27-**1 and *syn*,*syn*-**27-**2 shown in Figure 3. From the results of HF/3-21G calculations on model naphthalene and naphthoquinone systems, it is estimated that the bending of the naphthalene and naphthoquinone units by the amounts found in *syn*,*syn*-**27-**2 incurs an energy penalty of only $\approx$1.5 kcal mol^{-1}. This slightly unfavourable situation is apparently compensated by electrostatic stabilisation[38] between the proximal porphyrin and bpy groups.

It is noteworthy that only a moderate amount of combined bending of the aromatic rings (totalling 18°) in *syn*,*syn*-**27** results in a massive change in the porphyrin-to-bpy separation, namely, as much as 7.7 Å! Although this is largely caused by the long arms of the hydrocarbon bridges, it is important to note that aromatic rings do have fairly soft bending potentials and that extended systems based on aromatic rings fused to rigid saturated bridges may not be as rigid as is generally thought. At the AM1 level, the open structure, *syn*,*syn*-**27-**1 is 1.1 kcal mol^{-1} more stable than the closed structure *syn*,*syn*-**27-**2, whereas at the HF/3-21G level it is less stable than *syn*,*syn*-**27-**2 by 0.4 kcal mol^{-1}.

It is important to ascertain the effect of solvent on the geometries and relative energies of *syn*,*syn*-**27-**1 and *syn*,*syn*-**27-**2 since it is expected that the presence of the solvent will lead to an increase in the value of R_c for the closed structure *syn*,*syn*-**27-**2, and that the magnitude of this increment should increase with increasing solvent polarity. Unfortunately, solvation continuum calculations on *syn*,*syn*-**27-**1 and *syn*,*syn*-**27-**2 have so far resulted in convergence failures. Assuming that the geometry of the tetrad *syn*,*syn*-**19** in chloroform (a low polarity solvent[39]) resembles the HF/3-21G closed structure *syn*,*syn*-**27-**2, then the NOE results and the observed upfield chemical shifts of the bpy protons in *syn*,*syn*-**19** are readily explained.

As found for the bpy system *syn*,*syn*-**27**, the viologen tetrad *syn*,*syn*-**28**$^{2+}$ was also predicted to exist in open and closed conformations at the AM1 level. The R_c value is 10.0 Å for the open structure *syn*,*syn*-[**28-**1]$^{2+}$ and 5.3 Å for the closed structure *syn*,*syn*-[**28**-2]$^{2+}$. The closed structure is 11.9 kcal mol^{-1} more stable than the open structure. From the comparison of the results given in Table 2 for the bpy tetrad *syn*,*syn*-**27** with those for the viologen tetrad *syn*,*syn*-**28**$^{2+}$, we note that the replacement of the bpy group by the viologen unit leads to a significant increase in the stabilisation of the closed structure over the open structure, and to a decrease in the R_c value in the closed structure. These effects are explained in terms of increased electrostatic stabilising interactions involving the viologen dication compared to its bpy precursor.

At the HF/3-21G level, only the closed structure *syn*,*syn*-[**28-**2]$^{2+}$ could be located, in which R_c is found to be only 4.1 Å. As for *syn*,*syn*-**27-**2, the solvent is expected to modify the geometry of *syn*,*syn*-[**28-**2]$^{2+}$ primarily through an increase of the R_c value. So far solvent continuum calculations on *syn*,*syn*-[**28-**2]$^{2+}$ have been unsuccessful. Interestingly, only moderate upfield shifts of the viologen proton resonances were observed in the ^{1}H NMR spectrum of *syn*,*syn*-**5**$\cdot$2PF$_6$ in [D$_6$]acetone (vide supra and Table 1). It would appear, therefore, that acetone is sufficiently polar to cause R_c to increase beyond 5 Å, at which distance the ring current effects of the porphyrin unit on the viologen proton resonances would be small. Chloroform is much less polar than acetone[39] and so the observation of anomalous upfield shifts of the bpy proton resonances in *syn*,*syn*-**19** in this solvent is reasonable.[40]

The close proximity of the porphyrin to the bpy and MV^{2+} groups in *syn*,*syn*-**27**-2 and *syn*,*syn*-[**28**-2]$^{2+}$, respectively, is perhaps surprising. However, the four bulky 3,5-di-*tert*-butylphenyl *meso* substituents on the porphyrin ring in **19** and **5**$^{2+}$ might sterically hinder close approach of the bpy or MV^{2+} group to the porphyrin ring in these molecules. This point was tested by model HF/3-21G calculations on the complex between a norbornane-viologen molecule and a tetrakis(3,5-di-*tert*-butylphenyl)porphyrin molecule, which possesses the same geometry as that calculated between the

MV^{2+} and porphyrin groups within *syn*,*syn*-[**28**-2]$^{2+}$. This complex is calculated to be $\approx$35 kcal mol^{-1} more stable than the isolated components, thereby demonstrating that the aryl substituents pose no steric impediment to the close approach of the viologen moiety[41] (the closest distance between the aryl substituents and the MV^{2+} group in the complex is 3.3 Å).

Comments on photophysical studies of 5·2PF$_6$: Recently, we reported that flash photolysis of the putative *syn*,*syn* stereoisomer of **5**·2PF$_6$ in acetonitrile resulted in a rapid and efficient electron transfer (ET) from the locally excited porphyrin (P) to the viologen group to yield the giant charge-separated species $^{\cdot+}$P-DMN-NQ-MV$^{\cdot+}$.[22a] It has subsequently been determined that photoinduced ET does *not* occur in the alleged *anti*,*syn* stereoisomer of **5**·2PF$_6$.[42] These observations immediately lead to two important conclusions:

1) The stereochemical assignment of *syn*,*syn*-**5**·2PF$_6$ is correct since it is extremely unlikely that photoinduced ET should occur in *anti*,*syn*-**5**·2PF$_6$ and not in *syn*,*syn*-**5**·2PF$_6$.
2) Photoinduced ET in *syn*,*syn*-**5**·2PF$_6$ occurs *directly* from the locally excited porphyrin to the viologen chromophore, either through space or through intervening solvent molecule(s), and does *not* occur through the bridge, by a through-bond or superexchange mechanism. If photoinduced ET in *syn*,*syn*-**5**·2PF$_6$ were to occur by a through-bridge mechanism, then it is difficult to explain why it does not also occur in *anti*,*syn*-**5**·2PF$_6$ which has the same bridge composition as *syn*,*syn*-**5**·2PF$_6$.

The second conclusion immediately implies that the terminal porphyrin and viologen chromophores in *syn*,*syn*-**5**·2PF$_6$ are proximate to each other, almost certainly less than 10 Å apart.[43] Our calculated HF/3-21G gas-phase geometry for *syn*,*syn*-**28**-2^{2+} is consistent with the photophysical data for *syn*,*syn*-**5**·2PF$_6$, although we expect R_c for this system in polar solvents (such as acetonitrile) to be larger than the gas-phase value of 4 Å.

Conclusions

1) We have demonstrated a modular approach for synthesising giant multichromophoric systems, such as **19**, **20** and **5**$^{2+}$, which involves the sequential Diels–Alder reactions of a tetraene, such as **7**, with a range of chromophore-based dienophiles, such as **6**, **8** and **23**. The π-facial stereoselectivity of the Diels–Alder reactions enabled the isolation of two stereoisomers, *syn*,*syn*-**5**·2PF$_6$ and *anti*,*syn*-**5**·2PF$_6$.
2) The stereoisomers *syn*,*syn*-**5**·2PF$_6$ and *anti*,*syn*-**5**·2PF$_6$ offer a unique opportunity for delineating two mechanisms of photoinduced ET: solvent-mediated ET and through-bridge-mediated ET. The *syn*,*syn* stereoisomer, possessing a U-shaped geometry with proximal terminal chromophores, might be able to support through-solvent-mediated ET, whereas the *anti*,*syn* stereoisomer, possessing an extended geometry, is unable to do so.
3) The stereochemical assignments of *syn*,*syn*-**5**·2PF$_6$ and *anti*,*syn*-**5**·2PF$_6$ were secured on the basis of ^{1}H NMR and photophysical studies, namely the observation of NOE effects and strong upfield chemical shifts of the bpy proton resonances in *syn*,*syn*-**19**, and the observation of photoinduced ET in *syn*,*syn*-**5**·2PF$_6$, which did not occur in *anti*,*syn*-**5**·2PF$_6$.
4) The results of gas-phase semi-empirical (AM1) and ab initio (HF/3-21G) MO calculations also lend support to the interpretation of the NMR studies and to the stereochemical assignments given to the two isolated stereoisomers of **5**·2PF$_6$. Importantly, **19** and **5** are not as rigid as might have been expected; bending of the dimethoxynaphthalene and naphthoquinone rings allows the existence of two conformers of *syn*,*syn*-**19** and the formation of a closed form for *syn*,*syn*-**5** in which the terminal chromophores are separated by only 4–5 Å (in the gas phase).
5) We have partly achieved our major objective in this work, namely we have successfully synthesised the U-shaped tetrad *syn*,*syn*-**5**·2PF$_6$ and we have shown that solvent-mediated ET appears to take place in this molecule (in acetonitrile).[22a] We say partly because we would also like to determine the magnitude of the electronic coupling term for ET from the rate data for *syn*,*syn*-**5**·2PF$_6$ and to investigate how the strength of the coupling depends on solvent properties (such as electron affinity and polarisability). Unfortunately, an evaluation of the coupling by means of the ET rate data, in conjunction with semi-classical ET theory,[44] will be quite difficult because of the variability of the interchromophore separation in *syn*,*syn*-**5**·2PF$_6$. This variability gives rise to two problems: i) The interchromophore separation will be associated with one or more low frequency skeletal breathing modes which should be incorporated into the semi-classical treatment, either explicitly, by using a multi-quantised mode model, or through adjustment of the low-frequency solvent reorganisation energy term. ii) Both solvent reorganisation energy and driving force terms are strongly dependent on the interchromophore separation, and knowledge of these two quantities is necessary for the evaluation of the electronic coupling.[23c] In principle, it is possible to overcome these problems by ab initio MO calculation of how the interchromophore separation changes with the solvent. The calculations would need to include both specific solvent effects and solvent continuum methods. This approach is currently underway.
6) A significant outcome of our studies, that has general implications for several areas, is that aromatic rings appear to have fairly soft bending potentials and that, consequently, extended systems based on aromatic rings fused to rigid saturated bridges may not be as rigid as is generally thought.

Experimental Section

General: Chemicals were purchased from Aldrich and used as received. Solvents were dried and reagents were purified where necessary by the use of literature methods.[45] Thin-layer chromatography (TLC) was performed

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on aluminium sheets precoated with Merck 5735 Kieselgel 60F. Column chromatography was carried out with Kieselgel 60 (0.040–0.063 mm mesh, Merck 9385). Melting points are uncorrected. Low-resolution mass spectra (MS) were obtained by either electron impact (EI-MS) or matrix-assisted laser desorption ionization (MALDI) mass spectrometry in conjunction with a 3,5-dihydrobenzoic acid matrix and were recorded in the negative ion mode with relatively low laser power. NMR spectra were recorded at 300 MHz (^{1}H) and 75 MHz (^{13}C) with the DEPT pulse sequence.

Quinone 8: A solution of BBr_3 (1.0 M, 17 mL) was added dropwise to a solution of **9**[18] (1.4 g, 2.8 mmol) in anhydrous CH_2Cl_2 (100 mL) at 0 °C under an argon atmosphere. The solution was then warmed to room temperature and stirring was continued for a further 18 h. A saturated solution of sodium bicarbonate (150 mL) was added dropwise to the solution until the mixture reached pH 8. The mixture was then heated at reflux for 10 min and the CH_2Cl_2 was removed under reduced pressure. The resulting aqueous solution was cooled to 0 °C and the beige precipitate which formed was collected by filtration and washed well with ice-cold H_2O to yield the hydroquinone **15** (1.1 g), which was used without further purification. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 0.82$ (s, 6H, CH_3), 1.35 (m, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.92 (s, 2H, CH), 2.34 (s, 2H, CH), 2.47 (s, 2H, CH), 3.36 (s, 2H, CH), 3.40 (s, 2H, CH), 3.81 (br s, 2H, O*H*), 6.33 (s, 2H, phenyl-H), 8.43 (d, $J = 5.6$ Hz, 2H, phenyl-H), 8.71 (d, $J = 5.6$ Hz, 2H, phenyl-H), 8.86 (s, 2H, phenyl-H). To a suspension of the hydroquinone **15** (0.6 g, 1.3 mmol) in CH_2Cl_2 (20 mL) was added Ag_2O (1.5 g, 6.5 mmol), AgO (0.5 g, 4.0 mmol) and $MgSO_4 \cdot 3H_2O$ (1.5 g, 8.6 mmol). The resulting mixture was stirred vigorously for 2 h under an argon atmosphere in the dark and then filtered through a pad of silica and the silica was then extracted with ethyl acetate/triethylamine (99:1, 300 mL). The organic solutions were combined and the solvent was removed under reduced pressure to yield quinone **8** as a yellow solid which slowly decomposed on standing at room temperature. Yield: 0.51 g (85%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$ (s, 6H, CH_3), 1.41 (d, $J = 10.8$ Hz, 1H, CH_2), 1.46 (d, $J = 9.8$ Hz, 1H, CH_2), 1.50 (d, $J = 10.8$ Hz, 1H, CH_2), 1.60 (d, $J = 9.8$ Hz, 1H, CH_2), 2.07 (s, 2H, CH), 2.34 (s, 2H, CH), 2.46 (s, 2H, CH), 3.18 (s, 2H, CH), 3.46 (s, 2H, CH), 6.60 (s, 2H, quinone-H), 7.62 (d, $J = 5.1$ Hz, 2H, phenyl-H), 8.47 (d, $J = 5.1$ Hz, 2H, phenyl-H), 8.52 (s, 2H, phenyl-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 9.3$, 30.0, 41.0, 41.5, 43.8, 48.5, 49.5, 52.7, 108.1, 116.1, 132.5, 136.2, 147.9, 151.4, 152.4, 184.0 (C=O); MS (EI): *m*/*z* (%): 472 [M^+, (5)], 326 (30), 181 (100).

Porphyrin 13: To a solution of **10**[14] (0.8 g, 1.86 mmol) in CH_2Cl_2 (80 mL) was added a solution of **11**[31] (2.03 g, 1.86 mmol) in CH_2Cl_2 (100 mL) and the resulting solution was stirred in the dark for 2 h. The solvent was removed under reduced pressure to give a purple solid which was purified by column chromatography (CH_2Cl_2/light petroleum, 1:1) to give **13** as a purple solid. Yield: 2.07 g (75%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.51$ (br s, 2H, NH), 1.11 (s, 6H, CH_3), 1.48 (s, 18H, *t*Bu-H), 1.51 (s, 18H, *t*Bu-H), 1.54 (s, 36H, *t*Bu-H), 1.62 (m, 1H, CH_2), 1.84 (m, 2H, CH_2), 1.96 (s, 2H, CH), 2.04 (s, 2H, CH), 2.06 (m, 1H, CH_2), 3.50 (s, 2H, CH_2), 3.56 (s, 2H, CH_2), 3.78 (s, 6H, OCH_3), 6.55 (s, 2H, phenyl-H), 7.42 (s, 2H, phenyl-H), 7.80 (t, $J = 1.8$ Hz, 2H, phenyl-H), 7.92 (m, 2H, phenyl-H), 7.95 (s, 2H, phenyl-H), 7.99 (s, 2H, phenyl-H), 8.11 (s, 4H, phenyl-H), 8.79 (s, 2H, β-pyrrolic-H), 9.01 (ABq, $J = 4.6$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 9.5$, 31.7, 31.9, 35.0, 35.0, 40.3, 43.0, 43.6, 43.8, 49.7, 50.5, 56.0, 108.9, 118.0, 120.5, 120.6, 121.0, 122.5, 127.8, 128.1, 128.4, 129.6, 134.0, 136.5, 137.9, 139.6, 140.6, 141.0, 141.2, 146.5, 147.7, 148.7, 150.3, 151.8, 154.6; MALDI MS: *m*/*z*: 1486 [M^+].

Porphyrin 14: A solution of BBr_3 (1.7 mL, 1.86 mmol, 2 M) was added dropwise to a solution of **13** (1.0 g, 0.67 mmol) in anhydrous CH_2Cl_2 (150 mL) under an argon atmosphere at −5 °C in the dark. The mixture was then slowly warmed to room temperature and stirring was continued for a further 18 h. The solvent was removed under reduced pressure and the residue was dissolved in the minimum amount of anhydrous CH_2Cl_2 and loaded onto a silica column. The column was eluted with CH_2Cl_2/CH_3OH (99:1) and the bright red fraction was collected. The solvent was removed under reduced pressure to give the corresponding hydroquinone as a purple solid. Yield: 0.83 g (85%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.37$ (br s, 2H, NH), 1.09 (s, 6H, CH_3), 1.61 (s, 18H, *t*Bu-H), 1.64 (s, 18H, *t*Bu-H), 1.66 (s, 36H, *t*Bu-H), 1.76 (m, 1H, CH_2), 1.88 (m, 2H, CH_2), 2.00 (s, 2H, CH), 2.07 (s, 2H, CH), 2.08 (m, 1H, CH_2), 3.48 (s, 2H, CH), 3.50 (s, 2H, CH), 4.33 (br s, 2H, OH), 6.31 (s, 2H, phenyl-H), 7.57 (s, 2H, phenyl-H), 7.93 (t, $J = 1.5$ Hz, 2H, phenyl-H), 8.05 (t, $J = 1.5$ Hz, 2H, phenyl-H), 8.09 (s, 2H, phenyl-H), 8.14 (s, 2H, phenyl-H), 8.24 (d, $J = 2.0$ Hz, 4H, phenyl-H), 8.94 (s, 2H, β-pyrrolic-H), 9.15 (ABq, $J = 5.1$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 9.4$, 31.8, 31.9, 35.0, 35.1, 39.9, 42.9, 43.4, 43.8, 49.6, 50.5, 13.7, 118.1, 120.6, 120.7, 121.1, 122.5, 127.9, 128.2, 128.6, 129.6, 133.9, 135.1, 137.9, 139.7, 140.6, 141.0, 141.2, 142.9, 146.4, 148.8, 150.3, 151.8, 154.7. To a solution of the hydroquinone (0.85 g, 0.58 mmol) in CH_2Cl_2 (100 cm^3) was added DDQ (0.15 g, 0.66 mmol) and the resulting mixture was stirred in the dark for 1 h. The solvent was removed under reduced pressure to give a purple solid which was purified by column chromatography (CH_2Cl_2/light petroleum, 1:1) to yield the quinone **14** as a purple solid. Yield: 0.81 g (95%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.52$ (br s, 2H, NH), 1.07 (s, 6H, CH_3), 1.47 (s, 18H, *t*Bu-H), 1.50 (s, 18H, *t*Bu-H), 1.53 (s, 36H, *t*Bu-H), 1.72 (m, 1H, CH_2), 1.78 (m, 1H, CH_2), 1.87 (m, 1H, CH_2), 1.94 (s, 2H, CH), 2.02 (m, 1H, CH_2), 2.04 (s, 2H, CH), 3.48 (s, 2H, CH), 3.53 (s, 2H, CH), 6.53 (s, 2H, quinone-H), 7.44 (s, 2H, phenyl-H), 7.79 (t, $J = 1.8$ Hz, 2H, phenyl-H), 7.92 (m, 4H, phenyl-H), 7.98 (s, 2H, phenyl-H), 8.09 (d, $J = 2.0$ Hz, 4H, phenyl-H), 8.87 (s, 2H, β-pyrrolic-H), 9.01 (ABq, $J = 4.6$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 9.3$, 31.7, 31.9, 35.0, 35.0, 41.1, 41.6, 42.8, 43.0, 43.8, 48.5, 50.6, 118.0, 120.7, 120.7, 121.0, 122.5, 127.8, 128.1, 128.4, 128.5, 129.5, 134.0, 136.1, 137.9, 139.6, 140.6, 140.9, 141.1, 146.3, 148.7, 149.8, 151.5, 151.8, 154.6, 184.1 (C=O); MALDI MS: *m*/*z*: 1457 [M+H]$^+$.

Zinc(II) porphyrin 6: To a solution of **14** (0.64 g, 0.44 mmol) in CH_2Cl_2 (65 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.29 g, 1.32 mmol) in CH_3OH (20 mL) and the resulting solution was stirred in the dark for 1 h. The solvent was removed under reduced pressure to give a purple solid which was purified by column chromatography (CH_2Cl_2/light petroleum, 1:1) to give **6** as a deep purple solid. Yield: 0.64 g (96%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.08$ (s, 6H, CH_3), 1.48 (s, 18H, *t*Bu-H), 1.49 (s, 18H, *t*Bu-H), 1.52 (s, 36H, *t*Bu-H), 1.74 (m, 2H, CH_2), 1.90 (d, $J = 8.7$ Hz, 1H, CH_2), 1.94 (s, 2H, CH), 2.05 (s, 2H, CH), 2.06 (m, 1H, CH_2), 3.48 (s, 2H, CH), 3.56 (s, 2H, CH), 6.52 (s, 2H, quinone-H), 7.50 (s, 2H, phenyl-H), 7.79 (t, $J = 1.8$ Hz, 2H, phenyl-H), 7.79 (s, 4H, phenyl-H), 7.96 (s, 2H, phenyl-H), 8.09 (d, $J = 1.6$ Hz, 4H, phenyl-H), 8.90 (s, 2H, β-pyrrolic-H), 9.01 (ABq, $J = 4.62$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 9.4$, 31.7, 31.9, 34.9, 35.0, 41.1, 41.6, 42.8, 43.1, 43.8, 48.5, 50.7, 118.8, 120.4, 120.6, 120.8, 124.5, 128.2, 128.2, 129.3, 131.5, 131.5, 132.2, 136.1, 140.9, 141.5, 141.7, 142.2, 148.6, 148.6, 149.0, 149.6, 149.8, 150.0, 151.5, 152.5, 184.1 (C=O); MALDI MS: *m*/*z*: 1520 [M^+].

***syn*-17 and *anti*-17**: A mixture of **7** (0.20 g, 1.4 mmol) and **6** (0.48 g, 0.3 mmol) was placed in a Schlenk tube and the tube was then flushed with argon and evacuated. This procedure was repeated three times. Deoxygenated toluene (1 mL) was added and the mixture was deoxygenated further by freeze-thaw techniques. The deoxygenated solution was warmed to 80 °C for 24 h under an argon atmosphere in the dark, then cooled to room temperature. The solvent was removed under reduced pressure to give **16** as a purple solid which was used without further purification. Yield: 0.51 g; m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.19$ (s, 6H, CH_3), 1.51 (s, 18H, *t*Bu-H), 1.54 (s, 18H, *t*Bu-H), 1.56 (s, 36H, *t*Bu-H), 1.65–2.35 (m, 12H), 2.65 (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 3.09 (s, 2H, CH), 3.43 (2H, s, CH), 3.59 (s, 2H, CH), 3.74 (s, 2H, CH), 4.89 (s, 2H, CH), 5.10 (s, 2H, CH), 7.54 (s, 2H, phenyl-H), 7.82 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.96 (d, $J = 1.5$ Hz, 4H, phenyl-H), 8.02 (t, $J = 1.5$ Hz, 2H, phenyl-H), 8.13 (d, $J = 1.5$ Hz, 4H, phenyl-H), 8.93 (s, 2H, β-pyrrolic-H), 9.05 (ABq, $J = 4.6$ Hz, 4H, β-pyrrolic-H). To a solution of **16** (0.51 g, 0.31 mmol) in anhydrous acetone (6.0 mL) was added anhydrous potassium carbonate (0.33 g, 2.4 mmol) and the resulting mixture was deoxygenated by freeze–thaw techniques. The deoxygenated mixture was heated at reflux for 30 min under an argon atmosphere in the dark and then cooled to room temperature. Deoxygenated MeI (0.5 g, 8.0 mmol) was added and the mixture was then heated at reflux for 18 h. After cooling to room temperature, the mixture was poured onto ice (40 g) and the resulting mixture was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic extracts were washed with an aqueous saturated solution of ammonium chloride (3 × 30 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure to yield a purple solid (0.45 g) which was used without further purification. M.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (s, 6H, CH_3), 1.47 (s, 18H, *t*Bu-H), 1.52 (s, 18H, *t*Bu-H), 1.55 (s, 36H, *t*Bu-H), 1.87 (m, 2H, CH_2), 2.00–2.13 (m, 4H), 2.15 (s, 4H, CH), 3.17 (br s, 2H, CH), 3.39 (t, $J = 1.5$ Hz, 4H, CH), 3.53 (s, 2H, CH), 3.56 (s, 2H, CH), 3.81 (s, 6H, OCH_3), 4.86 (s, 2H, CH), 4.97 (s, 2H, CH), 7.48 (s, 2H, phenyl-H),

7.78 (t, $J = 2.0$ Hz, 2H, phenyl-H), 7.90 (m, 4H, phenyl-H), 7.97 (t, $J = 2.0$ Hz, 2H, phenyl-H), 8.08 (s, 2H, β-pyrrolic-H), 8.09 (s, 2H, β-pyrrolic-H). To a solution of this purple solid (400 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) was added DDQ (65 mg, 0.29 mmol) and the resulting solution was stirred for 20 min at room temperature in the dark. The mixture was passed through a silica pad which was then eluted with CH_2Cl_2 (20 mL). The organic solutions were combined and the solvent was removed under reduced pressure to yield a purple solid. The products were separated by preparative thin-layer chromatography (silica, light petroleum/CH_2Cl_2, 70:30) (5 developments) to yield *syn*-**17** and *anti*-**17**.

syn-***17***: Yield: 0.23 g (58%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.15$ (s, 6H, CH_3), 1.45 (s, 18H, *t*Bu-H), 1.50 (s, 18H, *t*Bu-H), 1.52 (s, 18H, *t*Bu-H), 1.53 (s, 18H, *t*Bu-H), 1.72 (m, 1H, CH_2), 1.87 (m, 1H, CH_2), 1.96 (m, 2H, CH_2), 2.02 (s, 2H, CH), 2.03 (s, 2H, CH), 2.09 (m, 2H, CH_2), 3.54 (s, 2H, CH), 3.64 (s, 2H, CH), 3.90 (s, 6H, OCH_3), 3.91 (s, 2H, CH), 5.00 (s, 2H, CH), 5.08 (s, 2H, CH), 7.49 (s, 2H, phenyl-H), 7.77 (s, 2H, phenyl-H), 7.79 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.90 (s, 2H, phenyl-H), 7.91 (s, 2H, Ar-H), 7.97 (t, $J = 1.5$ Hz, 2H, phenyl-H), 8.09 (brs, 4H, phenyl-H), 8.90 (s, 2H, β-pyrrolic-H), 8.99 (ABq, $J = 5.0$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 9.6$, 31.7, 31.8, 31.9, 34.9, 35.0, 40.6, 42.9, 43.5, 43.8, 50.6, 52.3, 61.9, 102.2, 113.2, 118.7, 120.3, 120.5, 120.8, 124.4, 126.9, 128.2, 128.4, 129.4, 131.4, 132.2, 134.5, 141.0, 141.6, 141.8, 142.2, 144.0, 144.6, 148.5, 148.6, 148.9, 149.6, 149.7, 150.3, 152.5; MALDI MS: *m*/*z*: 1690 $[M+2H]^+$.

anti-***17***: Yield: 0.10 g (25%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (s, 6H, CH_3), 1.45 (s, 18H, *t*Bu-H), 1.50 (s, 8H, *t*Bu-H), 1.52 (s, 36H, *t*Bu-H), 1.73 (m, 1H, CH_2), 1.83 (m, 1H, CH_2), 1.99 (m, 2H, CH_2), 2.05 (s, 2H, CH), 2.09 (m, 2H, CH_2), 2.13 (s, 2H, CH), 3.55 (s, 2H, CH), 3.70 (s, 2H, CH), 3.92 (s, 2H, CH), 3.96 (s, 6H, OCH_3), 5.07 (s, 2H, CH), 5.18 (s, 2H, CH), 7.49 (s, 2H, phenyl-H), 7.78 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.83 (s, 2H, Ar-H), 7.90 (brs, 4H, phenyl-H), 7.97 (t, $J = 1.5$ Hz, 2H, phenyl-H), 8.08 (s, 2H, phenyl-H), 8.09 (s, 2H, phenyl-H), 8.89 (s, 2H, β-pyrrolic-H), 8.99 (ABq, $J = 5.0$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 9.6, 31.7, 31.9, 34.9, 35.0, 40.6, 43.0, 43.6, 43.8, 50.7, 52.4, 62.0, 102.3, 113.3, 118.7, 120.3, 120.5, 120.8, 124.4, 127.0, 128.3, 129.3, 131.4, 132.2, 134.7, 141.0, 141.6, 141.7, 142.2, 144.0, 144.6, 148.5, 148.9, 149.7, 150.3, 152.5; MALDI MS: *m*/*z*: 1689 $[M+H]^+$.

***syn*,*syn*-19**: A solution of *syn*-**17** (0.19 g, 0.11 mmol) and **8** (0.37 g, 0.77 mmol) in toluene (1 mL) was deoxygenated by freeze–thaw techniques, then heated at reflux under an argon atmosphere in the dark for 40 h. The resulting mixture was cooled to room temperature and the solvent was removed under reduced pressure to give a green solid which was redissolved in CH_2Cl_2 (50 mL). This green solution was washed with hydrochloric acid (2M, 3 × 20 mL) then shaken with a saturated aqueous solution of sodium bicarbonate for 5 min. The resulting red solution was dried ($MgSO_4$) and the solvent was removed under reduced pressure to give a purple solid which was purified by column chromatography (CH_2Cl_2/CH_3OH, 97:3). Recrystallisation of this solid from CH_2Cl_2/CH_3OH gave *syn*,*syn*-**19** as a purple solid. Yield: 0.34 g (60%); m.p. > 300 °C; ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = -2.64$ (brs, 2H, NH), 0.45 (m, 1H, CH_2), 0.52 (s, 6H, CH_3), 0.92 (m, 1H, CH_2), 1.11 (s, 6H, CH_3), 1.34 (m, 1H, CH_2), 1.41 (s, 18H, *t*Bu-H), 1.46 (s, 18H, *t*Bu-H), 1.54 (s, 36H, *t*Bu-H), 1.60 (s, 2H, CH), 1.63 (m, 1H, CH_2), 1.70 (s, 2H, CH), 1.75 (m, 1H, CH_2), 1.79 (m, 1H, CH_2), 1.83 (s, 2H, CH), 1.90 (s, 4H, CH), 1.97 (m, 1H, CH_2), 2.03 (m, 1H, CH_2), 2.28 (s, 2H, CH), 2.66 (ABq, $J = 10.8$ Hz, 2H, CH_2), 3.30 (d, $J = 5.1$ Hz, 2H, phenyl-H), 3.34 (s, 2H, CH), 3.46 (s, 2H, CH), 3.67 (s, 2H, CH), 3.94 (s, 6H, OCH_3), 4.56 (s, 2H, CH), 6.01 (d, $J = 5.1$ Hz, 2H, phenyl-H), 7.32 (s, 2H, phenyl-H), 7.36 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.67 (s, 2H, phenyl-H), 7.82 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.83 (t, $J = 1.8$ Hz, 2H, phenyl-H), 7.86 (m, 2H, phenyl-H), 7.89 (s, 2H, Ar-H), 7.91 (s, 2H, Ar-H), 8.12 (t, $J = 1.8$ Hz, 2H, phenyl-H), 8.18 (t, $J = 1.8$ Hz, 2H, phenyl-H), 8.86 (s, 2H, β-pyrrolic-H), 9.03 (ABq, $J = 4.8$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 8.8, 9.5, 31.8, 31.9, 34.9, 35.1, 40.0, 40.7, 40.8, 41.0, 42.8, 43.0, 43.5, 43.8, 48.4, 48.6, 50.5, 50.6, 51.0, 52.6, 62.0, 63.2, 113.4, 115.0, 118.1, 119.2, 120.6, 121.2, 122.4, 126.4, 126.8, 128.0, 128.1, 128.6, 129.4, 129.5, 130.5, 131.7, 133.8, 134.1, 135.4, 137.6, 139.6, 140.3, 140.6, 141.2 144.7, 144.8, 145.7, 146.0, 148.4, 148.6, 148.8, 150.0, 150.7, 151.6, 152.6, 154.7, 155.8, 181.8 (C=O); MS (MALDI): *m*/*z*: 2097 $[M+2]^+$. Column chromatography of the mixture of products obtained gave a lower R_f fraction, presumed to be *syn*,*anti*-**19** (0.05 g, 21%) which could not be purified: MS (MALDI): *m*/*z*: 2097 $[M+2]^+$.

***syn*,*syn*-5 · 2 PF$_6$**: To a solution of *syn*,*syn*-**19** (63 mg, 0.03 mmol) in chloroform (2 mL) was added a solution of zinc(II) acetate dihydrate (11 mg, 0.05 mmol) in CH_3OH (2 mL). The resulting solution was stirred at 25 °C for 2 h, then passed through a silica pad. The filtrate was collected and the solvent was removed under reduced pressure to give *syn*,*syn*-**18** as a purple solid which was dissolved in CH_2Cl_2 (1 mL). Acetonitrile (1 mL) and methyl iodide (1.0 mL, 16 mmol) were added and the mixture was heated at reflux for 18 h. The solvent was removed under reduced pressure to give a dark purple solid which was redissolved in acetone (20 mL). An aqueous solution of ammonium hexafluorophosphate (0.5 g in 3 mL) was added to this solution and the acetone was removed under reduced pressure. The resulting green precipitate was filtered and dried over phosphorus pentoxide. Recrystallisation of this solid from CH_2Cl_2/CH_3OH gave *syn*,*syn*-**5** · 2 PF_6 as dark purple needles. Yield: 45 mg (72%); m.p. > 300 °C; ^{1}H NMR (500 MHz, [D$_6$]Me_2CO): $\delta = 0.68$ (s, 6H, CH_3), 0.92 (m, 1H, CH_2), 1.09 (m, 1H, CH_2), 1.17 (s, 6H, CH_3), 1.40 (s, 18H, *t*Bu-H), 1.48 (s, 18H, *t*Bu-H), 1.54 (s, 36H, *t*Bu-H), 1.70 (m, 2H, CH_2), 1.92 (m, 3H, CH_2, CH), 2.19 (m, 3H, CH_2, CH), 2.30 (s, 2H, CH), 2.58 (ABq, $J = 10.8$ Hz, 2H, CH_2), 3.09 (s, 2H, CH), 3.32 (s, 2H, CH), 3.60 (s, 2H, CH), 3.75 (s, 2H, CH), 3.92 (s, 6H, OCH_3), 4.15 (s, 6H, NCH_3), 4.69 (s, 2H, CH), 7.55 (m, 4H, phenyl-H), 7.73 (m, 2H, phenyl-H), 7.89 (s, 2H, ArH), 7.90 (m, 2H, phenyl-H), 7.93 (m, 2H, phenyl-H), 7.96 (s, 2H, Ar-H), 7.97 (m, 2H, phenyl-H), 8.07 (m, 6H), 8.86 (ABq, $J = 4.6$ Hz, 4H, β-pyrrolic-H), 8.90 (brs, 2H, phenyl-H); ^{13}C NMR (75.5 MHz, [D$_6$]Me_2CO): $\delta = 8.4$, 8.8, 31.1, 31.3, 34.6, 34.7, 34.8, 40.7, 40.8, 40.9, 41.0, 42.8, 43.0, 43.6, 43.8, 47.9, 48.3, 49.6, 50.8, 50.9, 52.4, 61.1, 114.8, 118.0, 118.6, 120.3, 120.5, 121.1, 122.0, 123.7, 126.3, 127.7, 128.4, 128.9, 129.3, 131.1, 131.2, 131.5, 131.7, 135.0, 138.7, 139.6, 140.5, 141.5, 142.1, 142.3, 142.5, 144.6, 145.2, 147.9, 148.4, 148.6, 148.7, 148.8, 149.7, 149.8, 150.9, 152.1, 152.9, 156.3, 181.1 (C=O); MS (MALDI): *m*/*z*: 2188 $[M - 2PF_6]^+$.

***syn*,*syn*-20 and *anti*,*syn*-20**: A solution of *syn*-**17** (50.1 mg, 0.03 mmol) and **23** (26.0 mg, 0.12 mmol) in toluene (1 mL) was deoxygenated by freeze-thaw techniques. The mixture was heated at reflux under an argon atmosphere in the dark for 40 h. The resulting mixture was cooled to room temperature and the solvent was removed under reduced pressure to give a green solid which was purified by column chromatography (CH_2Cl_2) to give the inseparable mixture of stereoisomers *syn*,*syn*-**20** and *anti*,*syn*-**20** as a purple solid. Yield: 33 mg (60%); m.p. > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (m, 2H, CH_2), 1.12 (s, 6H, CH_3), 1.31 (m, 2H, CH_2), 1.42 (s, 18H, *t*Bu-H), 1.46 (s, 18H, *t*Bu-H), 1.53 (s, 36H, *t*Bu-H), 1.67 (2H, m, CH_2), 1.80 (m, 3H, CH_2, CH), 1.95 (s, 4H, CH), 1.96 (s, 2H, CH), 2.06 (m, 1H, CH_2), 2.57 (s, 2H, CH), 3.11 (s, 2H, CH), 3.51 (s, 2H, CH), 3.61 (s, 2H, CH), 3.86 (s, 6H, OCH_3), 4.47 (2H, s, CH), 7.46 (s, 2H, phenyl-H), 7.78 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.81, (s, 2H, phenyl-H), 7.82 (s, 2H, Ar-H), 7.87 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.88 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.95 (t, $J = 1.5$ Hz, 2H, phenyl-H), 8.08 (m, 4H, phenyl-H), 8.88 (s, 2H, β-pyrrolic-H), 8.97 (ABq, $J = 4.5$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 9.6$, 23.9, 31.8, 31.9, 32.0, 34.9, 35.0, 35.1, 39.3, 40.6, 40.7, 40.8, 42.9, 43.5, 43.9, 45.3, 46.6, 50.7, 51.0, 61.9, 64.0, 114.9, 118.8, 119.0, 120.4, 120.5, 120.9, 124.5, 126.2, 128.3, 128.4, 129.4, 129.5, 131.3, 131.4, 131.5, 132.2, 135.3, 141.0, 141.6, 141.8, 142.2, 144.6, 144.7, 148.6, 148.7, 149.0, 149.6, 149.8, 150.3, 152.6, 155.7, 158.7, 181.9 (C=O); MS (MALDI-TOF): *m*/*z*: 1928 $[M+H]^+$.

***anti*,*syn*-19**: This compound was prepared from *anti*-**17** (90.4 mg, 0.05 mmol) and **8** (200 mg, 0.41 mmol) in an identical manner to that described for *syn*,*syn*-**19**. Yield: 58 mg (52%); m.p. > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = -2.51$ (s, 2H, NH), 0.70 (m, 1H, CH_2), 0.79 (s, 6H, CH_3), 1.13 (m, 8H, CH_2, CH_3), 1.33 (m, 1H, CH_2), 1.46 (s, 18H, *t*Bu-H), 1.50 (s, 18H, *t*Bu-H), 1.52 (s, 36H, *t*Bu-H), 1.85 (m, 1H, CH_2), 1.79 (s, 2H, CH), 2.05 (s, 2H, CH), 2.11 (s, 2H, CH), 2.17 (m, 1H, CH_2), 2.32 (s, 2H, CH), 2.60 (ABq, $J = 8.1$ Hz, 2H, CH_2), 3.49 (s, 2H, CH), 3.52 (s, 2H, CH), 3.67 (s, 2H, CH), 3.94 (s, 6H, OCH_3), 3.98 (s, 2H, CH), 4.53 (s, 2H, CH), 7.43 (s, 2H, phenyl-H), 7.48 (brm, 2H, phenyl-H), 7.79 (t, $J = 1.5$ Hz, 2H, phenyl-H), 7.92 (m, 6H, phenyl-H), 7.96 (s, 2H, Ar-H), 7.98 (t, $J = 1.5$ Hz, 2H, phenyl-H), 8.09 (d, $J = 1.5$ Hz, 2H, phenyl-H), 8.25 (brm, 4H, phenyl-H), 8.77 (s, 2H, β-pyrrolic-H), 9.00 (ABq, $J = 4.6$ Hz, 4H, β-pyrrolic-H); ^{13}C NMR (75.5 MHz, $CDCl_3$) $\delta = 9.28$, 9.63, 29.7, 29.9, 31.7, 31.8, 31.9, 35.0, 35.1, 40.7, 41.3, 41.6, 41.7, 43.6, 43.9, 43.9, 48.5, 49.4, 50.6, 50.7, 51.1, 52.7, 61.9, 62.0, 114.9, 116.0, 118.1, 119.3, 120.6, 120.7, 121.0, 122.5, 126.3, 127.9, 128.1, 128.5, 128.6, 129.6, 131.6, 132.5, 134.0, 135.5, 136.2, 137.9, 139.7, 140.6, 141.0, 141.2, 144.7, 146.4, 148.7, 148.8, 150.1, 150.2, 151.8, 151.9, 153.4, 153.5, 154.7, 155.9, 181.9 (C=O); MS (MALDI-TOF): *m*/*z*: 1928 $[M+H]^+$. Column chroma-

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tography of the mixture of products obtained gave a lower R_f fraction, presumed to be *anti*,*anti*-**19** (20 mg) which could not be purified.

***Anti*,*syn*-5·2PF$_6$**: This compound was prepared from *anti*,*syn*-**19** (42 mg, 0.02 mmol) in an identical manner to that described for *syn*,*syn*-**5**·2PF$_6$. Yield: 28 mg (61 %); m.p. > 300 °C; ^{1}H NMR (300 MHz, [D$_6$]Me$_2$CO): δ = 0.85 (m, 7H, CH$_2$, CH$_3$), 1.18 (m, 7H, CH$_2$, CH$_3$), 1.49 (s, 18H, *t*Bu-H), 1.51 (s, 18H, *t*Bu-H), 1.54 (s, 36H, *t*Bu-H), 1.91 (m, 3H, CH$_2$, CH$_3$), 2.04 (s, 2H, CH), 2.12 (s, 2H, CH), 2.30 (m, 1H, CH$_2$), 2.43 (m, 1H, CH$_2$), 3.59 (m, 4H, CH), 3.65 (s, 2H, CH), 3.74 (s, 2H, CH), 3.86 (s, 6H, OCH$_3$), 3.91 (s, 2H, CH), 4.56 (s, 2H, CH), 4.57 (s, 6H, OCH$_3$), 7.60 (s, 2H, phenyl-H), 7.81 (m, 2H, phenyl-H), 7.86–7.99 (m, 12H, phenyl-H), 8.08 (d, J = 1.5 Hz, 4H, phenyl-H), 8.76 (s, 2H, β-pyrrolic-H), 8.85 (br s, 4H, β-pyrrolic-H), 8.99 (br m, 2H, phenyl-H), 9.26 (br m, 2H, phenyl-H); ^{13}C NMR (75.5 MHz, [D$_6$]Me$_2$CO): δ = 8.4, 8.7, 30.9, 31.0, 31.3, 31.6, 34.5, 34.6, 40.5, 40.7, 41.4, 43.2, 43.3, 43.6, 43.7, 48.3, 49.7, 50.6, 50.8, 52.5, 54.4, 60.9, 117.9, 118.5, 120.2, 120.7, 123.0, 123.5, 126.1, 128.0, 128.1, 128.2, 128.3, 129.0, 129.1, 130.8, 131.3, 131.5, 139.2, 140.5, 140.7, 141.2, 142.1, 142.2, 142.3, 143.5, 144.4, 144.9, 148.3, 148.4, 148.8, 149.5, 149.8, 150.4, 152.1, 152.7, 155.9, 180.8; MS (MALDI): m/z: 2188 [M – 2PF$_6$]$^+$.

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[37] See footnotes on the first page of this article for details of how to obtain the supporting information (10 pages).
[38] The precise origin of the stabilising interaction between the porphyrin and bpy groups is unknown, although it is clearly not caused by dispersive forces. Presumably, the stabilisation involves multipole–multipole and multipole-induced-multipole interactions which we simply call electrostatic interactions.
[39] The dielectric constants of chloroform, acetone and acetonitrile are 4.8, 21 and 37.5, respectively.
[40] The situation is complicated by the observation that the addition of small amounts of [D_6]acetone to a $CDCl_3$ solution of *syn*,*syn*-**19** did not noticeably influence the chemical shifts of the bpy protons. It was expected that the chemical shifts of these protons should move progressively downfield with as the solvent polarity increased, as a consequence of the increase in R_c with the decrease in electrostatic stabilising interactions between the porphyrin and bpy groups. However, the low solubility of both *syn*,*syn*-**19** and *syn*,*syn*-**5**$\cdot 2PF_6$ in most solvents has so far thwarted a comprehensive ^{1}H NMR study of solvent effects on chemical shifts in these molecules.
[41] a) The magnitude of the stabilisation energy is exaggerated by basis set superposition errors (BSSE) which, according to the counterpoise method,[41b] amount to ≈ 8 kcal mol^{-1}. The BSSE-corrected stabilisation energy of 27 kcal mol^{-1} is still significant; b) S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, *19*, 553.
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